An Innovative System for the Efficient and Effective Treatment of Non-traditional Waters for Reuse in Thermoelectric Power Generation

Final Technical Report

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Abstract

This study assessed opportunities for improving water quality associated with coal-fired power generation including the use of non-traditional waters for cooling, innovative technology for recovering and reusing water within power plants, novel approaches for the removal of trace inorganic compounds from ash pond effluents, and novel approaches for removing biocides from cooling tower blowdown. This research evaluated specifically designed pilot-scale constructed wetland systems for treatment of targeted constituents in non-traditional waters for reuse in thermoelectric power generation and other purposes. The overall objective of this project was to decrease targeted constituents in non-traditional waters to achieve reuse criteria or discharge limitations established by the National Pollutant Discharge Elimination System (NPDES) and Clean Water Act (CWA). The six original project objectives were completed, and results are presented in this final technical report. These objectives included identification of targeted constituents for treatment in four non-traditional water sources, determination of reuse or discharge criteria for treatment, design of constructed wetland treatment systems for these non-traditional waters, and measurement of treatment of targeted constituents in non-traditional waters, as well as determination of the suitability of the treated non-traditional waters for reuse or discharge to receiving aquatic systems. The four non-traditional waters used to accomplish these objectives were ash basin water, cooling water, flue gas desulfurization (FGD) water, and produced water. The contaminants of concern identified in ash basin waters were arsenic, chromium, copper, mercury, selenium, and zinc. Contaminants of concern in cooling waters included free oxidants (chlorine, bromine, and peroxides), copper, lead, zinc, pH, and total dissolved solids. FGD waters contained contaminants of concern including arsenic, boron, chlorides, selenium, mercury, chemical oxygen demand (COD), and zinc. Similar to FGD waters, produced waters contained contaminants of concern that are predominantly inorganic (arsenic, cadmium, chlorides, chromium, copper, lead, mercury, nickel, sulfide, zinc, total dissolved solids), but also contained some organics (benzene, PAHs, toluene, total organic carbon, total suspended solids, and oil and grease). Constituents of concern that may cause chemical scaling, biofouling and corrosion, such as pH, hardness and ionic strength, and nutrients (P, K, and N) may also be found in all four non-traditional waters. NPDES permits were obtained for these non-traditional waters and these permit limits are summarized in tabular format within this report. These limits were used to establish treatment goals for this research along with toxicity values for *Ceriodaphnia dubia*, water quality criteria established by the US EPA, irrigation standards established by the United States Department of Agriculture (USDA), and reuse standards focused on minimization of damage to the power plant by treated waters. Constructed wetland treatment systems were designed for each non-traditional water source based on published literature reviews regarding remediation of the constituents of concern, biogeochemistry of the specific contaminants, and previous research. During this study, four non-traditional waters, which included ash basin water, cooling water, FGD water and produced water (PW) were obtained or simulated to measure constructed wetland treatment system performance. Based on data collected from FGD experiments, pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (As, B, Hg, N, and Se). Percent removal was specific for each element, including ranges of 40.1% to 77.7% for As, 77.6% to 97.8% for Hg, 43.9% to 88.8% for N, and no measureable removal to 84.6% for Se. Other constituents of interest in final outflow samples should have aqueous characteristics sufficient for discharge, with the exception of chlorides (<2000 mg/L). Based on total dissolved

solids, co-management or ion reduction (e.g. reverse osmosis, nanofiltration, ultrafiltration, etc.) techniques will be needed for discharge or reuse of high ionic strength waters. Data collected from produced water experiments indicate that hybrid pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (Zn, Cd, Pb, and Cu). Percent removal was specific for each element, including ranges of 38.4% to 99.6% for Cd, 90.6% to 99.8% for Cu, 93.1% to 99.3% for Pb, and 40.0% to 99.8% for Zn. Reuse of these waters will likely depend on the chloride concentration of the outflow samples, but with use of reverse osmosis technology, chloride concentrations can be decreased sufficiently for reuse as service water. Concentrations of arsenic, selenium, chromium, and zinc were decreased in ash basin waters by pilot-scale constructed wetland treatment systems. Average removal for arsenic, selenium, chromium, zinc, and mercury was 88, 21, 71, 68, and 94%, respectively. Pilot-scale constructed wetland treatment systems were also successful in reducing the potential for scale formation and biofouling in the ash basin water. Toxicity significantly decreased in the pilot-scale constructed wetland treatment systems' effluent as compared to inflow. Pilot-scale constructed wetland treatment systems decreased aqueous concentrations of chlorine, copper, zinc and lead in cooling waters. Average percent removals for each element were 97% for Cu, 88% for Pb, and 30% for Zn. The relatively low percent removals for zinc and lead are a result of minimal initial elemental concentration. Pilot-scale constructed wetland treatment systems were successful in reducing potential for corrosion and biofouling in cooling waters and for treating cooling water for internal reuse. Data from pilot-scale studies clearly indicate that constructed wetland treatment systems can remediate FGD waters, ash basin waters, cooling waters and produced waters for reuse or discharge.

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Executive Summary

This research evaluated specifically designed pilot-scale constructed wetland systems for treatment of targeted constituents in non-traditional waters for reuse in thermoelectric power generation or other purposes. Non-traditional waters used in this study include ash basin waters, cooling waters, flue gas desulfurization waters, and produced waters. Although the targeted constituents in non-traditional waters may vary from site to site, metals, organics, and biocides are among the more difficult to treat and tend to limit the utility of these waters for reuse or other purposes. The overall objective of this project is to decrease targeted constituents in non-traditional waters to achieve reuse for power generation and discharge criteria established by the National Pollutant Discharge Elimination System (NPDES) and Clean Water Act (CWA). Specific objectives of this research include: 1) identify the targeted constituents for treatment in four non-traditional water sources; 2) determine reuse or discharge criteria (performance criteria for treatment); 3) configure appropriate pilot-scale constructed wetland treatment systems for each of the four non-traditional waters; 4) measure performance of pilot-scale constructed wetland treatment systems and removal rate coefficients for targeted constituents using both analytical and toxicological techniques; 5) determine the suitability of the treated non-traditional waters for reuse or discharge to receiving aquatic systems; and 6) develop a decision support system for using this approach to renovate non-traditional waters for reuse or other purposes. Ash basin waters are generally low ionic strength waters contaminated with elements or compounds associated with combustion by-products (i.e. bottom ash) from coal burning. Cooling waters characteristically use additives such as free oxidants (e.g. ClO_2, HOCl, NaBr, etc.) for control of biofouling in once-through cooling systems. Constituents such as copper, zinc, lead and other metals contained in the cooling pipes or towers can be leached due to biocide reactivity resulting in elevated concentrations in the cooling water. These constituents can cause potential problems for receiving systems, specifically in low hardness waters (e.g. southeastern U.S.). Flue gas desulfurization (FGD) waters and produced waters (PW) that contain chloride concentrations that can be tolerated by salt- or fresh-water plants can be treated in CWTS. Alternatively, remediation of chlorides can be achieved using techniques such as reverse osmosis or low chloride service water. FGD waters typically contain potentially toxic elements such as mercury, selenium, arsenic, and zinc. PW often contain not only elements of concern such as arsenic, zinc, lead, copper, and cadmium but also organics associated with production of natural gas, oil refining, coal-bed methane, and other sources. Constituents that would prohibit or interfere with reuse of these waters in electric power production (corrosive, biofouling and scaling potential) and potentially toxic contaminants that are associated with these waters must be treated before discharge.

Introduction

During thermoelectric power generation, water is used for a variety of purposes, including: once-through condenser cooling, flue-gas scrubbing, ash sluicing, coal washing, natural gas storage produced water. In addition to these servicing waters (direct usage for thermoelectric operations), produced waters are obtained during oil and gas extraction from storage fields, which can include coal bed methane and natural gas (Veil *et al.*, 2004). These types of waters are referred to as “non-traditional” waters. Although the chemical composition of non-traditional waters may vary from site to site, these waters typically include inorganics (transitional metals, halogens and metalloids), organics, and biocides that limit reuse or discharge. Discharge limitations to aquatic systems are established by the National Pollutant Discharge Elimination System (NPDES) and Clean Water Act (CWA). Options for use and reuse of non-traditional waters are site specific. Power plants can choose to partially or fully reuse the water for power generation, discharge the water to receiving systems, or sell the water for non-site applications (irrigation, aquaculture, drinking water, etc.). Those decisions would logically be affected by economics and local availability of water as well as the character or quality of that water.

As the demand for water resources increases, the need to conserve water increases. Water is required for power production and may limit existing or future power plant sites. Reuse of water becomes a viable strategy for water conservation. Water can be reused within a plant before or after treatment, co-managed with other water resources, or used as irrigation water and other off-site applications. Discharging water for either irrigation or to surface or sub-surface water sources is regulated by the USEPA through NPDES permits. NPDES permit limits are influenced by USEPA water quality criteria and USDA criteria for irrigation. The degree of treatment required to meet NPDES permits is often greater for waters that are discharged in comparison to waters that are reused within power plants, making reuse an ideal strategy for decreasing water use.

Coal-fired power plants require water for FGD processes, cooling, and removal of ash materials. These processes produce waters that require different forms of treatment based on their intended use. Reuse of these by-product waters in power generation will be limited by chemical composition, and more specifically by constituents that prohibit the water serving a specific function (e.g. decrease the transfer of heat) or cause damage to system components (e.g. corrosion). Increases in ionic strength, or dissolved solids, pH, suspended solids and organics such as oil and grease can potentially intensify scaling, biofilm growth and corrosion in condensing/transfer pipes.

Although water reused within a plant is not subject to permits enforced by the USEPA, some treatment may be required before the water can be recirculated. Reuse criteria can be described as the concentrations of constituents of concern in non-traditional waters required in order to accomplish potential reuse within power plants. Due to differences between coal-fired power plants throughout the United States and various waters used at each site, detailed reuse criteria would consequently need to be defined case specifically. Treatment goals for reuse target the mitigation of risk to the physical components of the plant, such as piping, as well as the efficiency of the plant. For recirculated waters, chemical scaling, biofilm accretion and corrosion can cause detrimental effects to both the physical components and the efficiency of the plant.

Therefore, these three criteria will be targeted treatment goals for in-plant reuse. Increases in ionic strength, or dissolved solids, pH, suspended solids and organics such as oil and grease, or organic biocides can potentially intensify chemical scaling, biofilm growth and corrosion.

Reuse criteria for off-site applications (discharging water for non-power generation) are often established by the specific water resource usage such as irrigation, aquaculture, drinking water, and other types of water usages. For thermoelectric companies to meet regulatory compliance requirements for discharging waters (NPDES), non-traditional waters must be treated in order to decrease contaminants of concern. NPDES permits are site specific, require monitoring and reporting of identified contaminants, and can include toxicity testing of discharged effluents. Current treatment strategies for non-traditional 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 non-traditional 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), flue gas desulfurization water (FGD; pilot-scale), acid mine drainage (Sobolewski 1996), municipal water (Ansola *et al.* 2003), agricultural runoff (Moore *et al.* 2000), and other waters containing elevated concentrations of inorganics and organics. These 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 stable solids within the treatment systems. Organics may be retained and chemically altered by abiotic and biodegradation processes that can occur throughout the different reactors in specifically designed constructed wetlands. Since these systems are robust, most variations of inflows and concentrations of contaminants do not require rigorous alterations or additions to the system during treatment. Thus, the constructed wetland treatment systems must be poised to make the appropriate reactions possible and likely. The design of CWTS is based in sound biogeochemical theory and modeling, as well as in published literature. Predictions of rate coefficients, speciation, and extent of transfers and transformations guide the design of the pilot-scale constructed wetland treatment systems.

For accurate assessment of potential performance and determination of potential cost-effectiveness of the specifically constructed wetland treatment systems, pilot-scale studies are required. Pilot-scale studies can provide crucial information and important benefits such as: 1) rigorous testing of hypotheses embodied in replicated physical model constructed wetland treatment systems as well as measurements of performance under varied conditions; 2) instill confidence in potential owners regarding the robust seasonal performance of these systems; 3) ensure regulatory approval and decrease time from permit-to-construction of full-scale systems; and 4) provide refined rate coefficients and extents of removal to improve full-scale designs. This research addresses the following areas for improving water quality associated with thermoelectric power generation: 1) use of non-traditional waters for cooling; 2) innovative technology for recovering and reusing water from power plants; 3) novel approaches for the removal of trace inorganics from ash pond effluents; and 4) unique approaches for removing biocides from cooling tower blowdown. The results from this research have obvious and significant financial implications for water reuse in thermoelectric power generation and compliance with the CWA (NPDES permits). Existing technologies or "concrete and steel" treatment systems for non-traditional waters are very costly and are often unable to achieve the new, rigorous water quality standards.

Experimental Methods

For this final technical report, research objectives included: 1) identification of targeted constituents for treatment of four non-traditional water sources; 2) determination of reuse or discharge criteria (performance criteria for treatment) for four non-traditional waters produced as by-products of thermoelectric power generation; 3) configure appropriate pilot-scale constructed wetland treatment systems for each of the four non-traditional waters; 4) measure performance of pilot-scale constructed wetland treatment systems and removal rate coefficients for targeted constituents using both analytical and toxicological techniques; 5) determine the suitability of the treated non-traditional waters for reuse or discharge to receiving aquatic systems; and 6) develop a decision support system for using this approach to renovate non-traditional waters for reuse or other purposes. These waters include ash basin waters, cooling tower blowdown, flue gas desulfurization waters, and produced waters.

Objective One: Characterize the four non-traditional waters and identify targeted constituents for treatment

To specifically address these non-traditional waters, a detailed description and classification was produced for each type or category of non-traditional water. Data on the composition of each non-traditional water were obtained from published journal articles, review of product labels, and chemical analyses of non-traditional water samples. Constituents measured in non-traditional waters included water chemistry parameters and measurable trace inorganic and organic compounds. Water chemistry parameters measured for this study included pH, alkalinity, hardness, dissolved oxygen, conductivity, biochemical oxygen demand, and chemical oxygen demand. The results of chemical composition for each non-traditional water were organized into concentration ranges [i.e. minimum and maximum concentrations (mg/L)] and classified into sub-groups based on variables that affect treatment strategies and NPDES permit compliance (e.g. chloride concentration).

Objective Two: Determination of reuse or discharge criteria for each non-traditional water

1. Determine in-plant reuse criteria for elements or compounds present in non-traditional waters.
2. Determine off-site reuse criteria.
    A. National Pollutant Discharge Elimination System (NPDES) permitted constituents and their concentration ranges for each non-traditional water.

B. Determine toxicity measurements (NOEC, LOEC, and LC_{50} values) for *Ceriodaphnia dubia* for elements or compounds observed in non-traditional waters.
C. Determine and identify constituents of concern for each non-traditional water based on chemical composition (i.e. contaminants), contaminant concentration, NPDES permits, water quality criteria, and toxicity evaluations (published literature).

For non-traditional waters with low chloride concentrations (< 500 mg/L), reuse of these waters was based on published data, predictive estimators, and measurements (Objective Four) of scaling, biofilm accretion, and corrosion of pre- and post-treatment non-traditional waters. For non-traditional waters with chloride concentrations greater than 500 mg/L, reuse of these waters in power generation was limited to assessment for applicability as sluicing water or reuse as cooling water after co-management with make-up water (treatment via reverse osmosis). Non-traditional waters with chloride concentrations exceeding 500 mg/L and not co-managed with make-up water were assessed for discharge criteria and other reuse options (e.g. sold off-site).

Other water usages can include discharge to receiving systems and off-site application (irrigation, recreation, and drinking water for human consumption). Irrigation water standards or permitted limits of contaminants are established by the United States Department of Agriculture (USDA). Recreational water (i.e. water quality criteria) and drinking water standards are proposed by the United States Environmental Protection Agency (USEPA). Discharge permits for non-traditional waters are established and regulated by the National Pollutant Discharge Elimination System (NPDES; USEPA 2004). For analyses of NPDES permits, data were collected from USEPA websites and permit number, site location, total maximum concentration (TMC) limits, monthly average contaminant discharge limits, and toxicity test requirements (USEPA 2004) were recorded. Results for reuse and discharge criteria for each non-traditional water were organized into NPDES permit limits and are presented as ranges [i.e. minimum and maximum concentrations (mg/L)] due to the variability and site-specific nature of these values.

Reuse Criteria

In-plant Reuse

Water reuse criteria for power plants are established based on constituents in water that may decrease the efficiency of heat transfer by impairing the physical structure of the cooling system. Impairment could be caused by chemical scaling, biofouling and corrosion. Chemical scaling is caused by deposition of solids on the inner-walls of cooling or condenser pipes and results mainly from constituents with low solubility at high temperatures (> 50°C) such as calcium carbonate. Waters containing high total dissolved solids (TDS) can exhibit chemical scaling of cooling pipes; specifically attributed to divalent cations such as Ca^{2+} and Mg^{2+} that can readily form solids. Biofouling is caused by both the presence of organisms in the system as well as biofilm. Biofilm is a gelatinous slime deposited by algae, fungi and bacteria for structure (growth substrate) and energy assimilation (food resources). These deposits also trap suspended solids that accumulate and decrease the internal diameter of cooling or condenser pipes (Strauss and Puckorious 1984). The potential for biofouling increases when nutrients (e.g. potassium, nitrogen and phosphorous) are found in cooling waters at high concentrations. Corrosion is the oxidation of metals in cooling pipes. Corrosion can be caused by low pH levels or high concentrations of oxidants, such as free chlorine. Reuse criteria are commonly established by these three water characteristics and may be site specific, due to the capacity of individual power plants (e. g. type of metal alloys used in cooling or condenser pipes) to withstand various levels of chemical scaling, corrosion and biofouling. Reuse criteria for on-site reuse of power plant waters were established based on experiments that test for the rate and extent of biofouling, scaling, and corrosion in pre- and post-treatment non-traditional waters. These data were collected during objective four of this research.

Off-Site Reuse

For water that is discharged from the plant, reuse criteria are based on three categories of exposure: acute and chronic exposure of animals, and exposure of agricultural crops. Table 1 shows elements selected by the USEPA and the USDA that are of potential importance due to toxicity.

Table 1. National Recommended Water Quality Criteria from the United States Environmental Protection Agency (USEPA) and United States Department of Agriculture (USDA).

Element	**FW Acute (mg/L)**	**FW Chronic (mg/L)**	**SW Acute (mg/L)**	**SW Chronic (mg/L)**	**Irrigation (mg/L)**
Aluminum					**5.0**
Arsenic	**0.340**	**0.150**	**0.069**	**0.036**	**0.100**
Boron					**0.500**
Cadmium	**0.020**	**0.00025**	**0.040**	**0.0088**	**0.010**
Chromium (III)	**0.570**	**0.074**			**0.100**
Chromium (VI)	**0.016**	**0.011**	**1.1**	**0.050**	
Copper	**0.013**	**0.009**	**0.0048**	**0.0031**	**0.200**
Lead	**0.065**	**0.0025**	**0.210**	**0.0081**	
Manganese					**0.200**
Mercury	**0.0014**	**0.00077**	**0.0018**	**0.00094**	
Nickel	**0.470**	**0.052**	**0.074**	**0.0082**	**0.200**
Selenium		**0.005**	**0.290**	**0.071**	
Zinc	**0.120**	**0.120**	**0.090**	**0.081**	**2.0**

FW Freshwater
SW Salt water

Toxicity Measurements for Elements or Compounds in Non-traditional Waters

Since most NPDES permits require toxicity testing with *Ceriodaphnia dubia,* the responses of this species to exposures of elements or compounds can help estimate maximum concentrations at which no adverse effect (i.e. no-observable effect concentration; NOEC) should be observed during an aqueous exposure. The NOECs for particular elements or compounds are affected by the duration of exposure (i.e. acute/chronic), water chemistry (i.e. pH, conductivity, etc), form of the element or compound, and mixture effects (antagonism, addition, and synergism). For this assessment, NOEC, lowest observable effect concentration (LOEC), and lethal mean concentration (LC_{50}) values for 7-day static/renewal *C. dubia* toxicity experiments were tabulated (Table 3).

Of the elements or compounds present in non-traditional waters that may pose potential toxicity to *C. dubia*, only cadmium and copper had reported NOEC and LOEC values. The lack of data for elements such as arsenic, mercury, chloride, chlorine, chromium, lead, selenium, and zinc indicates that research is needed to answer these questions. To accurately understand the rate and extent of treatment (i.e. removal of elements or compounds) that a system must provide for a single contaminant, the concentration of an element or compound that causes no adverse effect to *C. dubia* (in this case 7d static/renewal experiments) must be known to establish treatment goals for a system. Since these values are not available from literature reviews, this study provided toxicity measurements (NOEC and LOEC) for 7d static/renewal experiments with *C. dubia* for contaminants found in non-traditional waters that may pose potential toxicity to these organisms. Lethal mean concentrations (LC_{50}) values are reported in this technical report for elements or compounds observed in non-traditional waters; however, these values are less informative as an interpretative values to discern treatment goals since they only provide estimates of concentrations that cause an estimated 50% mortality to an experimental population. Toxicity measurements from *D. magna* experiments are listed in Table 3 to summarize the most current data on toxicity for each given element or compound.

Determination of Constituents of Concern

Constituents of concern (COCs) were identified as elements or compounds observed in a particular non-traditional water at sufficient concentrations to cause significant adverse effects to organisms in receiving systems, or to toxicity testing species used for NPDES permitting. When toxicity measurements (NOEC and LOEC for 7d static/renewal *C. dubia* experiments) for an element or compound were not available from literature reviews, water quality criteria established by the United States Environmental Protection Agency (USEPA) were used to identify an element or compound as a COC. COCs for each non-traditional water were also identified as compounds that may potentially cause biofouling, scaling, or corrosion based on chemical concentrations.

Objective Three: Configure appropriate pilot-scale constructed wetland treatment systems for each of the four non-traditional waters

The third objective of this project was to design constructed wetland treatment systems to effectively and consistently treat constituents of concern in non-traditional waters. Each CWTS was designed to efficiently and effectively remediate identified constituents of concern in the four non-traditional waters through chemical, physical, and biological (i.e. microbial) pathways by decreasing the constituent's concentration, reducing potential to cause scaling, corrosion, biofouling, bioavailability, and decreasing toxicity from inflow to outflow of the CWTS. Published literature and previous research conducted with constituents of concern in these waters were utilized in the design process. These data included Eh-pH diagrams, chemical modeling programs (Minteq), complexation reactions, solubility products (k_{sp}), oxidation/reduction reactions, and data from pilot- and full-scale constructed wetland treatment systems.

Biogeochemistry of Constituents of Concern

Constructed wetland treatment systems have been used extensively for risk mitigation or treatment of elements or compounds present in solution that cause adverse effects when aquatic organisms are exposed. To successfully remediate these constituents of concern, biogeochemical cycling of these contaminants must be considered. Adequately designed treatment systems can transform and/or transfer specific constituents of concern to stable chemical forms that limit the mobility, bioavailability, and re-distribution (solubilization over time) of constituents that limit the reuse of these waters. Each constituent of concern was investigated for chemical reaction pathways that provided adequate transformation and transfer mechanisms (i.e. stable chemical forms) and these constituents are discussed separately below.

Acidity

Acidity, or low water pH, can be neutralized in a wetland. Submerged soils such as those found in wetlands have a tendency to neutralize acidity. The buffering capacity of the soils and water can also influence the acidity of the water. Increased alkalinity, or availability of carbonate forms, increases the buffering capacity of soils and water.

Arsenic

Arsenic biogeochemistry in aquatic systems is strongly linked to pH, electrochemical potential (Eh), oxidation state and molecular form. Like selenium, arsenic is commonly found as an oxyanion in oxic and suboxic environments that include inorganic forms [arsine (-III), elemental (As^0), arsenite (III) and arsenate (V)] and organic forms (monomethyl and dimethyl arsenites). The mobility of arsenic under low dissolved oxygen concentrations (suboxic to anaerobic) can be decreased by co-precipitation reactions with sulfide-bearing minerals (Moore et al., 1988). In reducing wetland environments, dissimilatory sulfate reduction can occur, thus providing sulfides and mineral-bearing sulfides useful for removing arsenic from impacted waters. Other minerals such as manganese and iron oxyhydroxides can influence the biogeochemistry of arsenic (Edenborn et al., 1986). Under high dissolved oxygen concentrations (oxidizing environments), dissolved iron is commonly transformed into solid forms (oxyhydroxides) that can co-precipitate arsenic species by inter and outer sphere complexation reactions (Kirk 2004).

Boron

Boron is generally present as borate [$B(OH)_3$] in natural waters and sediments. At higher pH levels, boron can dissociate into mono- and di-protic acid forms (HBO_3^{2-} and $H_2BO_3^-$) (pK_a=9.0 and 11.0), which can co-precipitate with magnesium, calcium, and iron to form insoluble salts. These forms of salts are both insoluble and soluble and can occur at the same time (Kirk, 2004).

Cadmium

Cadmium is normally present as the Cd (II) oxidation state in naturally occurring water and sediments. This transitional metal can form strong covalent bonds with reduced forms of sulfur (pK CdS = 27.0) and partition to organic matter by weak non-specific sorption reactions. In reducing conditions, CdS minerals are relatively stable indicated by its pK value and require strongly acidic or oxidizing conditions to release Cd from this mineral formation (Kirk, 2004).

Chlorine

Active chlorine (Cl^+) is a toxic form of chlorine present in some power plant waters. As an oxidant, active chlorine can be transformed into the less toxic Cl^-, or other chlorine containing compounds, through reductive pathways. Active chlorine is readily reduced by sulfites, reduced sulfur, organic matter or zero-valent iron (MacCrehan *et al.* 2005).

Chromium

Chromium as Cr (III) is relatively immobile and often occurs as a precipitant; however, the fully oxidized form of Cr [chromate, Cr (VI)], is more bioavailable due to its higher solubility and reactivity with biota. At higher pH levels Cr (III) can precipitate as a hydroxide, $Cr(OH)_3$. Chromate forms can be converted to the less toxic Cr (III) species through microbial-mediated reactions, in which chromate is an electron acceptor or reduced by electron donors [i.e. oxidation of Fe(II)]. Other forms of iron can serve as an electron donor, such as zero-valent iron (Fe^0) that reduce chromate species and thus reduce its toxicity. Reducing wetland systems can transform potentially toxic forms of chromium by providing “available” electrons for the reduction of chromate, sites for sorption reactions, and microbial remediation. These reactions favor the dissolution of chromium species and thus decrease the biotic exposure (bioavailability).

$$2Fe^{2+} + HCrO_4^- + 8H_20 \rightarrow 3Fe(OH)_3 + Cr(OH)_3 + 5H^+$$

Copper

Copper is normally present as the Cu (II) oxidation state in naturally occurring waters and sediments, but can be reduced to the monovalent oxidation state (Cu I) in the presence reactive electron donors (e.g. halides) and reducing environments ($Eh < -50$ mV and $pH > 7$) . Insoluble copper sulfides (CuS, CuS_2, and Cu_2S_2) can be formed in reducing conditions. If sediments remain saturated, the mobility of hydrated copper ions (Cu^{2+}) can decrease over time and copper can accumulate in sediments by sorption reactions with organic matter, co-precipitate as hydroxides forms (e.g. $CuOH_2$), and sulfur-copper complexations. Accumulation of copper in sediments has been shown to be greater in high organic environments. Higher pH environments can facilitate increased copper-sediment sorption reactions; however, the solubility of most copper forms is the lowest under semi-neutral pH values (Kirk 2004; Murray-Gulde *et al* 2003).

Hardness

Divalent cations such as Mg^{2+} and Ca^{2+} are the cause of water hardness. The primary route of transformation for such cations is co-precipitation with divalent cations of similar radii. $CaCO_3$ precipitates with Mn^{2+}, Fe^{2+} and Cd^{2+}, however the presence of organic ligands can inhibit calcite precipitation. Magnesium co-precipitates with Zn^{2+}, Fe^{2+} and Al^{2+} (Kirk, 2004).

Lead

Lead is typically found as the Pb (II) form in aqueous systems, but can also exist as a fully oxidized species, Pb (IV). Lead is commonly found at low aqueous concentrations (> 1 mg/L) due to its reactivity with carbonates and hydroxides, but can be potently toxic to aquatic life. In aerobic soils, lead can form attractions onto clay surfaces and oxide formations or complexes with organic matter and reduced sulfur compounds. Lead can also form insoluble hydroxides, carbonates and phosphate complexes. Consequently, the solubility of lead tends to increase at low pH conditions when ligands such as sulfide are not present or availability is low (e.g. mineral formations). In anaerobic soils, galena (PbS) is formed as a highly insoluble precipitate (pK =27.5). Galena is often formed in systems designed to promote dissimilatory sulfate reduction (Kirk 2004).

Mercury

Mercury is typically found in low concentrations in non-impacted aqueous systems with the higher concentrations occurring in the sediments (40 to 200 ng/g). Mercury can exist as inorganic ions [mercurous (I), mercuric (II) and elemental (Hg^0) inorganic salts (e.g. $HgCl_2$)], and as an organic species (e.g. mono and dimethyl mercury). The fate of mercury in an aqueous system is affected by pH, redox potential, and other chemical species present in the system. Under sediment conditions in which iron oxyhydroxides are present, sorption reactions between these iron species and mercury can result in the loss of mercury from the water column. In wetland hydrosoils, surface reactions such as sorption or ion exchange on mineral surfaces such as montmorillonite can occur. Complexation and sorption reactions with organic material and sulfur-species have been documented in suboxic and anoxic environments, thus providing a relatively stable species of mercury that is less mobile (Wang and Driscoll, 1995 and Davis et al., 1997). Given an adequate source of reduced sulfur (S^{2-}), mercury may convert to a stable mercuric sulfide (HgS), which will limit its bioavailability to aquatic plants and animals (Fagerstrom and Jernelov, 1972).

Nutrients

Submerged soils, and therefore wetlands, are ideal sinks for nutrients such as phosphorous, nitrogen and potassium. In wet soils, the rate of nitrogen uptake is very high. Inorganic forms of nitrogen are readily transformed into organic nutrient forms. These organic forms of nitrogen and other nutrients are readily used by plants and other organisms in the wetland system. In anaerobic soils dissimilatory reduction occurs readily;

$$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+,$$

whereas in aerobic soils denitrification is the primary pathway of nitrogen transformation (Kirk 2004).

Selenium

Not unlike other constituents, alterations in the form of selenium affect solubility and influence mobility, transport, and fate in wetland environments (Jayaweera and Biggar, 1996; Masscheleyn et al., 1990; Masscheleyn and Patrick, 1993). At semi-neutral pH and oxidation-reduction (redox) conditions occurring in many aqueous and sedimentary environments, selenium exists as a soluble oxyanion. In reducing environments, selenium can exist in elemental (Se^0), selenide forms (e.g. H_2Se) and as insoluble metal selenides (Masscheleyn and Patrick, 1993). Under reducing conditions in wetlands, elemental selenium and metal selenides can form from both chemical and microbial reduction processes. These selenium species are typically less mobile and bioavailable. Reduction of selenate (VI) to selenite (IV) and selenite (IV) to insoluble Se^0 has been documented to occur under reducing aqueous environments (Zhang et al. 2003).

Zinc

Based on pH and redox conditions normally established in reducing wetlands, zinc is dominantly present in the Zn (II) oxidation state in soils, sediment, and water column. The only other oxidation state for zinc is the elemental form (Zn^0), but is characteristically limited to solid forms (low solubility). Under reducing conditions in which sulfur is present, zinc can be reduced to an insoluble sulfide form (ZnS, pK=24.7). Under higher pe and pH conditions FeS and FeS_2 are preferred to ZnS, however zinc will still form solids with oxides and clays present in the soil. In aerobic conditions, zinc is mostly immobile, but under acidic oxidizing conditions, zinc can form soluble and mobile species of Zn. In higher pH ranges (pH 8-11), Zn (II) combines with calcium and magnesium carbonates to form co-precipitants (hydroxyl-carbonates) that can removed by settling. To avoid the preferential formation of iron sulfides, maintaining neutral pH levels will allow zinc sulfides to form as the major pathway of removal in a reducing wetland environment (Kirk 2004).

Pilot-Scale Constructed Wetland Treatment Systems (CWTS)

Pilot constructed wetland treatment systems (CWTS) were designed and constructed for each of the four non-traditional waters at Clemson University in Clemson, SC. Each system was designed to efficiently and effectively remediate identified constituents of concern in the four non-traditional waters through chemical, physical, and biological (i.e. microbial) pathways by decreasing the concentration of constituents, their bioavailability, and their toxicity from inflow to outflow of the CWTS. Published literature and previous research with the identified constituents of concern were utilized in the design process. These data included eh-pH diagrams, chemical modeling programs (Minteq), complexation reactions, solubility products, reduction/oxidation reactions, and data from pilot- and full-scale constructed wetland treatment systems.

Reducing Wetland Reactors

Reducing wetland reactors which contain sediments with a bulk reducing environment were amended with gypsum to provide a sulfur ligand source. Sulfur ligands effectively decrease concentrations of the targeted constituents through complexation reactions with reduced sulfur. Hydrosoil redox ranging from -50 to -250 mV in reducing wetland reactors and semi-neutral aqueous pH concentrations (6-9 SU) indicate that the environmental conditions are favorable for dissimilatory sulfate reduction, which provides reduced sulfide for precipitating available cationic metals such as mercury, copper, lead, zinc, cadmium, chromium, selenium, and arsenic (Brookins, 1988; Morse, 1995; Carbonell et al., 1999). Precipitated metal-sulfide minerals are largely stable in aqueous systems, significantly limiting metal bioavailability (Morse, 1995). Reducing environments will also reduce active chlorine.

Oxidizing Wetland Reactors

Oxidizing wetland reactors are designed as bulk oxidizing environments (Eh -50 to 200 mV) that aid in the removal of constituents of concern (COC) by providing environments that favor co-precipitation of oxyhydroxides and COC. These wetland reactors also enable re-oxygenation of the water column to meets water quality standards set forth by NPDES.

Objective Four: Assessment of pilot-scale CWTS for non-traditional waters by measuring reuse potential, removal of constituents of concern and toxicity of post-treatment samples

Each non-traditional water was loaded into a specifically designed CWTS. Pre- and post-treatment waters was assessed for potential reuse by measuring biofilm accretion, corrosion, and scaling, constituents of concern (i.e. total concentrations), aqueous toxicity, and general water chemistry parameters. Chemical scaling, biofouling and corrosion was measured using glass and metal coupons suspended in each water. Accretion of non-ashable and ashable (organic matter) matter on glass coupons was used to determine chemical scaling and biofouling, respectively. Loss of mass of the metal coupon determined corrosion potential of the waters.

For elemental analysis of non-traditional waters, an aliquot of 100-ml was preserved with trace metal nitric acid (10% v/v; Fisher Scientific Inc.) and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-AES; Spectro) according to EPA Method 200.7 and EPA Method 200.8 (USEPA 1994) using a Sciex Elan 9000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Perkin-Elmer, Norwalk, CT). Total arsenic, mercury, and selenium analysis was conducted by cold vapor hydride atomic fluorescence (Aurora Instruments; AFS 3200). Additional constituents and properties (Table 2) 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 for the Examination of Water and Wastewater* (APHA 1998).

Percent removal of constituents of concern was calculated for pilot-scale constructed wetland treatment systems used in this study. Removal rate coefficients were calculated by the following equation,

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

where $[A]_o$ is the concentration of the constituent in the equalization basin prior to treatment, $[A]_t$ is the concentration of the constituent in the final outflow, t is the total time of treatment, and k is the first-order removal rate coefficient.

Redox Potential

Oxidation-reduction (redox) potential of wetland hydrosoil was monitored monthly by placing platinum-tipped electrodes *in situ* and measuring using an Accumet® calomel reference electrode (Faulkner et al., 1989). Dissolved oxygen and pH of surface waters were measured using YSI® and Orion® field instruments, respectively.

Toxicity Test

Since constituents of concern may pose risks for sensitive, sentinel aquatic species such as microcrustaceans, *Ceriodaphnia dubia* were selected as the assessment species for this study and are routinely used in toxicity testing required by NPDES permits (Murray-Gulde et al., 2005, USEPA, 1995). Initial 7-day static/renewal toxicity tests were performed on pre- and post-treatment non-traditional waters to determine the magnitude of toxicity (i.e. dilution series), following the U.S. EPA protocol for chronic toxicity of effluents and receiving waters to freshwater organisms (EPA/600/4-91/002) for toxicity identification. Toxicity was evaluated by comparing survival and reproduction of test organisms to responses of control organisms to determine exposures that statistically affect these parameters. *C. dubia* survival was evaluated by comparing control and treatment organisms using chi-square analysis. Reproductive toxicity was evaluated using the analysis of variance procedure (ANOVA; Statistical Software Analysis, Version 8.1), in which the reproductive efficiency (average neonates per surviving adult) for each testing concentration were compared to the reproductive efficiency of control organisms. The alpha or significance level was set at 0.05 for all experimental tests. Lethal mean concentration, LC_{50} (the concentration at which 50% mortality is estimated to occur), lowest observable effect concentration (LOEC), and no observable effect concentration (NOEC) was estimated for testing dilutions using the spearman-karber method and ANOVA (LOEC and NOEC).

Reuse criteria established in Objective Two (on- and off-site reuse) was compared to data on treatment performance of pilot-scale CWTS for each non-traditional water.

Table 2. Analytical methods for parameters monitored each treatment week from pilot constructed wetland system experiments.

Parameter	Method	Method Detection Limit
Temperature	Direct Instrumentation: YSI Model 52	0.5°C
pH	Direct Instrumentation: Orion Model 420A	0.01
Conductivity	Direct Instrumentation: YSI 30	0.1 µS/cm
Alkalinity	Standard Methods: 2320 B	2 mg/L as $CaCO_3$
Hardness	Standard Methods: 2340 C	2 mg/L as $CaCO_3$
DO[1]	Direct Instrumentation: YSI Model 52	0.1 mg/L
COD[2]	Closed reflux colorimetry (HACH - modified from Standard Methods: 5220D)	3 mg/L
BOD_5 [4]	Standard Methods: 5210 B	0.1 mg/L
TSS[5]	Standard Methods: 2540 D	0.1 mg/L
TDS[6]	Standard Methods: 2540 C	0.1 mg/L
Selenium	Inductively Coupled Plasma with Mass Spectrometry (ICP-MS): EPA 200.8	0.0001 mg/L
Mercury	Inductively Coupled Plasma with Mass Spectrometry (ICP-MS): EPA 200.8	0.00009 mg/L
Arsenic	Inductively Coupled Plasma with Mass Spectrometry (ICP-MS): EPA 200.8	0.0001 mg/L
Chloride	HACH Colorimetric Method 8207	25 mg/L
Sulfate	Standard Methods: 4500 E	1 mg/L
Nitrate	HACH Cadium Reduction Method	0.01 mg/L
Nitrite	HACH Diazotization Method	0.01 mg/L
Ammonia	Ion Selective Electrode: EPA Method 350.3	0.0001 mg/L
Total Nitrogen	HACH Persulfate Digestion Method	0.01 mg/L

[1] Dissolved Oxygen
[2] Chemical Oxygen Demand
[3] Non-purgable Organic Carbon
[4] Five-day Biological Oxygen Demand
[5] Total Suspended Solids
[6] Total Dissolved Solids

Table 3. Summary of toxicity measurements (NOEC, LOEC, and LC50) to *Ceriodaphnia dubia* and *Daphnia magna* for elements or compounds present in non-traditional waters.

Constituent	*Form*	*Species*	*Experiment*	*Effect*	*NOEC (mg/L)*	*LOEC (mg/L)*	*LC_{50} (mg/L)*	*Reference*
Arsenic	Na_2AsO_4	C. dubia	8d Renewal	Mort	1.14			1
Arsenic	Na_2AsO_4	D. magna	48 h Static	Repro		1.02		1
Cadmium	$CdCl_2$	C. dubia	7d Static /Renewal	Mort	0.01	0.013	0.0116	2
Cadmium	$CdCl_2$	C.dubia	7d Static/Renewal	Repro	0.001	0.004	0.0116	2
Cadmium	$CdCl_2$	C.dubia	48h Static	Mort			0.0542	3
Cadmium	$CdCl_2$	C.dubia	10d Static	Mort			0.0106	2
Cadmium	$CdCl_2$	C.dubia	10d Static	Mort			0.0195	4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Repro	0.0016	0.003		4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Repro	0.0057	0.0085		4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Repro	0.0028	0.004		4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Mort	0.0055		0.011	4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Mort	0.0085		0.0109	4
Cadmium	$CdCl_2$	C.dubia	8d Static/Renewal	Mort	0.008		0.009	4
Chloride	NaCl	C.dubia	7d Static/Renewal	Mort			1042	5
Chlorine	Cl_2	D. magna	48 h Static	Mort			0.130	6
Chromium	$CrCl_3$	D. magna	24 Static	Mort			22.0	22
Copper	$CuCl_2$	C. dubia	96d Static	Mort			0.095	7
Copper	$CuCl_2$	C. dubia	7d Static/Renewal	Mort	0.012	0.032		7
Copper	$CuCl_2$	C.dubia	7d Static/Renewal	Repro	0.012	0.032		7
Lead	$PbCl_2$	D. magna	48h Static	Mort			9.5	8
Lead	$PbCl_2$	D. magna	48h Static	Mort			4.2	8
Lead	$PbCl_2$	D. magna	120h Static	Mort			0.330	8
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.002	9
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.005	10
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.0032	11
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.0015	11
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.0022	11
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.0044	12
Mercury	$HgCl_2$	D. magna	48 h Static	Mort			0.0044	12

Selenium	Na_2SeO_3	C. dubia	Flow	Mort	0.44	13
Selenium	Na_2SeO_3	D. magna	48 h Static	Mort	0.43	14
Selenium	Na_2SeO_3	D. magna	Static	Mort	0.215	15
Selenium	Na_2SeO_3	D. magna	Static	Mort	0.87	16
Selenium	Na_2SeO_3	D. magna	Static	Mort	2.37	16
Selenium	Na_2SeO_3	D. magna	Renewal	Mort	0.55	17
Selenium	Na_2SeO_4	D. magna	48 h Static	Mort	0.55	18
Selenium	Na_2SeO_4	D. magna	48 h Static	Mort	0.71	19
Selenium	Na_2SeO_4	D. magna	48 h Static	Mort	1.01	20
Selenium	Na_2SeO_4	C. dubia	48 h Static	Mort	1.96	21
Selenium	Na_2SeO_4	C. dubia	48 h Static	Mort	1.86	21
Selenium	Na_2SeO_4	D. magna	48 h Static	Mort	0.57	21
Selenium	Na_2SeO_4	D. magna	48 h Static	Mort	5.30	21
Zinc	$ZnCl_2$	C. dubia	7d Static/Renewal	Mort	0.18	7
Zinc	$ZnCl_2$	C. dubia	7d Static/Renewal	Mort	0.164	7
Zinc	$ZnCl_2$	C. dubia	7d Static/Renewal	Mort	0.149	7
Zinc	$ZnCl_2$	C. dubia	48h Static	Mort	0.163	7

1. Naddy et al. 1995
2. Suedel et al. 1997
3. Bitton et al. 1995
4. Southwest Texas State University 2000
5. DeGraeve et al. 1992
6. Fort and Stover. 1995
7. Carlson et al. 1986
8. Cabejszek et al. 1960a b or both ?
9. Guilhermino et al. 2000
10. Biesinger and Christensen 1972
11. Canton and Adema 1978
12. Barera and Adams 1983
13. GLEC 1999
14. Leblanc 1980
15. Adams and Heidolph 1985
16. Mayer and Ellerieck 1986
17. Maier et al. 1993
18. Johnson 1987
19. Halter 1980
20. Brooke 1985
21. Brix et al. 2001
22. Kuhn 1988

RESULTS

ASH BASIN WATERS

Objective I: Chemical Composition

Ash basin waters consist largely of ash-contacted water (e.g. sluice) used in coal-fired power production and may include surface water runoff from precipitation events. These waters are usually held for a period of time in a depression known as an ash basin, and can contain dissolved and particulate inorganics, organics, and total suspended solids. Currently, ash basins provide minimal treatment for inorganics and organics, and their primarily utilization is for settling of solids. Constituents of concern or contaminants that may require treatment before discharge include mercury, copper, zinc, arsenic, selenium, cadmium, and chromium (Cherry and Guthrie 1977; Cherry and Guthrie 1978; Cherry *et al*. 1984). The contaminants of concern contained in ash basin water from Savannah River Site, SC, were reported as total aqueous concentrations of mercury (0.0267 mg/L (± 0.007 mg/L)), copper (1.003 mg/L (± 0.901 mg/L)), zinc (3.27 mg/L (± 2.839 mg/L)), arsenic (4.08 mg/L (± 9.70 mg/L)), selenium (0.79 mg/L (± 1.52 mg/L)), cadmium (0.1083 mg/L (± 0.061)), and chromium (0.324 mg/L (± 0.382 mg/L)) (Cherry and Guthrie 1977; Cherry and Guthrie 1978; and Babcock *et al*. 1983). Similar to Cherry and Guthrie (1978), Larrick *et al.* (1981), examined ash basin water from a site in Virginia and measured total aqueous concentrations of mercury (0.025 ± 0.007 mg/L), zinc (2.67 mg/L; n=1), arsenic (0.450 ± 0.424 mg/L), and cadmium (0.17 mg/L; n=1), but did not measure copper, selenium, or chromium concentrations. Analysis of ash basin waters from a site in New Mexico indicated elevated total aqueous concentrations of zinc (0.510 ± 0.098 mg/L), arsenic (0.030 ± 0.004 mg/L), and selenium (0.058 ± 0.002 mg/L), but concentrations were not elevated for copper (0.0025 ± 0.0007 mg/L), cadmium (0.001 mg/L), or chromium (0.0025 ± 0.0007 mg/L) (Dreesen *et al.* 1977). Total aqueous mercury concentrations were not reported in this study. Recent analyses of ash basin waters (n=13) for constituents of possible concern by Clemson University, SC indicated concentrations of zinc (0.030 ± 0.023 mg/L), arsenic (0.039 ± 0.061 mg/L), and selenium (0.0158 ± 0.0167 mg/L) for a North Carolina ash basin.

Objective II: Determination of Reuse and Constituents of Concern

For ash basin waters, the majority of constituents of concern requiring NPDES discharge limits are inorganics commonly associated with coal combustion such as aluminum (monitor-and-report) arsenic (0.293 µg/L), boron (9.0 to 11.0 mg/L), cadmium (monitor-and-report), chromium (monitor and report), copper (0.4 to 1.0 mg/L), mercury (monitor-and-report), nickel (monitor-and-report), selenium (monitor-and-report), and zinc (monitor-and-report). Other constituents listed on NPDES permits include pH (6-9 SU), total suspended solids [30 to 100 mg/L as total maximum concentration], and oil and grease (15 to 20 mg/L as TMC). Toxicity requirements range from ≥50% to ≥80% survival of *P. promelas* or *C. dubia* in non-diluted ash basin water.

Constituents of Concern

Constituents of concern in ash basin waters were determined based on the concentrations of chemical elements and compounds in ash basin waters, NPDES permits, USEPA water quality criteria (USEPA WQC), and published literature. Using these criteria and sources, constituents of concern in ash basin waters include arsenic, cadmium, chromium, copper, mercury, selenium, and zinc. Total arsenic concentrations ranged from 0.013 to 23.9 mg/L, which exceed NPDES permits and recommended water quality criteria. According to NPDES permits, the TMC limit for arsenic is 0.293 mg/L, and the USEPA WQC recommends that arsenic concentrations should not exceed 340 µg/L. Aqueous cadmium concentrations representative of ash basin waters ranged from as low as 0.001 mg/L to concentrations as high as 1.72 mg/L. Although there is not a specified TMC limit for cadmium, NPDES permits require this element to be monitored and reported. The recommendation for cadmium by the USEPA WQC is 20 µg/L, which is lower than some of the documented concentrations in ash basin waters. Total chromium concentrations in ash basin waters ranged from 0.002 mg/L to 11.4 mg/L. According to an NPDES permit, the TMC must be no more than 0.2 mg/L for chromium. The USEPA WQC recommends that trivalent chromium remain below a concentration of 570 µg/L, while the recommended hexavalent chromium concentration should be less than 16 µg/L. Concentrations of copper found within ash basin waters are as low as 0.002 mg/L and as high as 19.5 mg/L. NPDES permits indicate that copper has a TMC limit of 0.04 to 1.0 mg/L. The recommended concentration for copper according to the USEPA WQC is 13 µg/L. Both the permits and WQC are lower than most of the observed concentrations in ash basin waters. Mercury concentrations in ash basin waters are between 0.0003 and 0.041 mg/L, and the USEPA WQC recommends that the concentration remain at or below 1.4 µg/L. Mercury concentrations in some ash basins waters exceed the lowest observable effect concentration (LOEC), requiring this element to be identified as a constituent of concern. Literature values for selenium concentrations in ash basin waters are between 0.007 and 3.9 mg/L. The USEPA WQC for chronic exposure of selenium is 5 µg/L, while the NPDES permits have established a TMC at 56 µg/L. Zinc concentrations found in ash basin waters have a minimum concentration of 0.011 mg/L and maximum concentration of 8.1 mg/L. The NPDES permits usually include monitoring concentrations of zinc as well as one specific permit indicating a TMC of 1.0 mg/L, and the USEPA WQC recommend that concentrations of zinc not exceed 120 µg/L. Due to the low ionic strength of ash basin water, formation of chemical scale is of little concern. Biofouling is also of minimal concern due to the source of ash basin water, and the other constituents that may pose risk to living organisms (i.e. mercury, arsenic, zinc). Corrosion potential is the main concern when considering reuse of ash basin waters.

Table 4. Composition of ash basin waters based upon published literature and analyses of waters

CONSTITUENTS	CONCENTRATIONS	UNITS
pH	6.4 - 7.9	SU
DISSOLVED OXYGEN	6.9 - 9.5	mg/L
SULFATE, TOTAL	16 – 60	mg/L
ARSENIC, TOTAL	0.013 - 23.9	mg/L
BERYLLIUM, TOTAL	< 0.0002	mg/L
BORON, TOTAL	11.0 – 12.0	mg/L
CADMIUM, TOTAL	0.001 – 1.72	mg/L
CALCIUM, TOTAL	13.7 - 37.6	mg/L
CHLORIDE, TOTAL	3.8 – 156	mg/L
CHROMIUM, TOTAL	0.002 - 11.4	mg/L
COPPER, TOTAL	0.002 - 19.5	mg/L
FLUORIDE, TOTAL	16.0	mg/L
IRON, TOTAL	0.05 – 4679	mg/L
LEAD, TOTAL	0.0026 – 0.12	mg/L
MAGNESIUM, TOTAL	0.01 – 7.0	mg/L
MANGANESE, TOTAL	0.08 - 117	mg/L
MERCURY, TOTAL	0.0003 – 0.41	mg/L
MOLYBDENUM	0.16 - 14.5	mg/L
NICKEL, TOTAL	0.35 – 2.26	mg/L
SELENIUM, TOTAL	0.007 - 3.9	mg/L
SODIUM, TOTAL	14 – 20	mg/L
VANADIUM, TOTAL	0.013 - 14.7	mg/L
ZINC, TOTAL	0.011 - 8.1	mg/L

Table 5. NPDES permit limits for ash basin waters reported as minimum and maximum ranges.

CONSTITUENTS	TOTAL MAX. CONC. LIMIT	MONTHLY AVG. LIMIT	UNITS
pH	6.0-9.0		SU
Flow	monitor/report		
Nitrite and Nitrate	monitor/report		mg/l
Phosphorus, Total	Monitor		mg/l
Oil & Grease	20-15	15-9	mg/l
Total suspended solids	100-30	100-15	mg/L
TOTAL INORGANICS			
Arsenic	0.293 or monitor		mg/l
Boron	9.9-1.8		mg/l
Cadmium	Monitor		mg/l
Chromium	Monitor		mg/l
Copper	1.0-.04		mg/l
Mercury	Monitor		µg/l
Nickel	Monitor		mg/l
Selenium	Monitor		mg/l
Silver	Monitor		mg/l
Zinc	Monitor		mg/l
TOXICITY REQUIREMENTS			
Ceriodaphnia dubia	50%/pass	Minimum	
Pimephales promelas	50%/pass	Minimum	

Objective III: Construction of Pilot-Scale CWTS

One system was configured consisting of two wetland treatment series each. Treatment series consist of two 70-gallon wetland reactors (Rubbermaid® Utility Tanks) for a reducing environment (Eh < -150 mV), one 150-gallon wetland reactor for a moderately reducing environment (Eh -100 to 100 mV), and two 150-gallon wetland reactor for an oxidizing environment (Eh -100 to 250 mV). The dimensions of the 70-gallon Rubbermaid® tubs are 102.9 cm (40.5 in) long by 81.3 cm (32 in) wide by 60.9 cm (24 in) deep, 265 L (70 gal). The dimensions of the 100-gallon Rubbermaid® tub are 121.9 cm (48 in) long by 77.5 cm (30.5 in) wide by 63.5 cm (25 in) deep, 378 L (100 gal). The dimensions of the 150-gallon Rubbermaid® tubs are 147.3 cm (58 in) long by 99.0 cm (39 in) wide by 63.5 cm (25 in) deep, 568 L (150 gal). Simulated ash basin water was formulated in a 1000-gallon equalization basin (polypropylene container) with the addition of high-purity salts of mercury, arsenic, selenium, chromium, and zinc. Simulated ash basin water was transferred into the CWTS via Fluid Metering, Inc. (FMI)® piston pumps at a calibrated flow rate to establish a 36-hr hydraulic retention time (HRT) per wetland reactor. The sequential ordering (first to last wetland reactor) of the CWTS included a moderately reducing wetland reactor, two reducing wetland reactors, and one oxidizing wetland reactor. Flow through this system was gravity assisted after inflow from the equalization basin. The moderately reducing and reducing wetland reactors of each treatment series contained approximately 30-cm of river sand hydrosoil and *Schoenoplectus californicus* C. A. Meyer planted at realistic field densities. The first half of each fourth wetland reactor consists of a rock cascade constructed using medium-sized granite rocks, and 30-cm of river sand hydrosoil planted with *Typha angustifolia* L. The reactors were connected by PVC pipe fittings and approximately 30 cm long segments of ¾" PVC tubing. The PVC pipe fittings were designed to maintain surface flow and were placed 6 cm below the top of each Rubbermaid® tub.

Objective IV: Treatment Performance of Pilot Scale Constructed Wetland

Readiness for Treatment Performance

Before a CWTS is used for treatment, the readiness of the system must be determined to ensure successful treatment, a step that is very important when using newly constructed wetland treatment systems. In this case, the system readiness is quantified by field plant density, appropriate sediment bulk redox conditions (Eh) and sediment organic matter percentage. The first reactor in each series was designed for moderately bulk reducing environments as indicated with measured redox values of -76 and -67 mV. The measured redox values of reactors 2 and 3 ranged from -182 to -67mV, indicating a bulk reducing environment. The measured redox values for reactor 4 ranged from -17 to 189 mV, indicating a bulk oxidizing environment. The average plant density for the bulk reducing reactors (1-3) was 367 plants (*S. californicus*) per meter squared. The average plant density for the bulk oxidizing reactors (4) was 136 plants (*T. angustifolia*) per meter squared. The sediment for treatment series A ranged from 0.12 to 0.25 % organic matter. The sediment for treatment series B ranged from 0.10 to 0.42 % organic matter. To maintain a bulk reducing condition, a higher organic matter percentage is required; therefore the reactors 1, 2 and 3 of both series were subsequently amended with more organic matter.

These systems are therefore poised and ready for testing the removal of the identified constituents of concern.

Table 6. Parameters indicating readiness for treatment of ash basin waters

Series	**A**				**B**			
Reactor	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Eh (mV)	-76	-172	-182	189	-67	-174	-167	-17
Sediment % Organic Matter	0.10	0.42	0.36	0.19	0.12	0.24	0.25	0.18
Plant density (shoots or leaflets/m^2)	272	340	336	152	436	432	384	120

Methods for the evaluation of treatment performance

Formulation of simulated water

Simulated cooling water was formulated in a 1000 gallon detention basin using municipal water at Clemson University, Clemson, SC. Appropriate salts were added to the municipal water to create water with the prescribed metal concentrations, alkalinity, hardness and sulfate concentrations. The salts were mixed for 24 hours in the detention basin by a submersible pump.

Hydraulic Retention Time (HRT)

The hydraulic retention time, regulated by calibrated metering pumps (FMI^{TM}), transferred water from the detention basin to the first wetland reactor. Two pumps were used, one for each series of reactors. The pumps were adjusted to a flow rate of 90mL per minute. This flow rate allows a hydraulic retention time of approximately 5 days for the reactor systems.

Sampling

Samples were collected every two weeks. Sampling from a new batch of water was initiated only after seven days of inflow from the detention basin in order to ensure a complete hydraulic retention time had been met. Samples were collected in HDPE Nalgene bottles from the outflow of each reactor as well as the outflow of the detention basin. Sample analysis included fundamental water characteristics such as: pH, temperature, dissolved oxygen, hardness, alkalinity and conductivity. The redox potential of each sample was also measured *in situ* every month. Water samples were preserved with trace metal grade nitric acid for metal analysis with ICP-AES. Any remaining water was stored at 4^{0}C in nalgene bottles.

Every four weeks, additional water was sampled from the detention basin outflow and the final reactor outflow to conduct toxicity testing using *Ceriodaphnia dubia*. Toxicity tests measured the survival and reproductive effects of the water. Dilutions of the outflow of reactor four (100, 50, 25 and 10%) allowed the relative toxicity of outflow water to be assessed. These 4 week samples were also analyzed for sulfates, chlorides, total dissolved solids and total dissolved solids (TDS/TSS).

Every six weeks, scaling, biofouling and corrosion were measured by removing glass and copper coupons from the system and measuring the loss or accretion of mass on each coupon. New coupons are introduced to each system at this time.

Table 7. Sampling locations and measured parameters

Sampling Location	**Measured Parameters**
Detention Basin	Corrosion, biofouling and scaling
Inflow from detention basin	Metal analysis, water chemistry, toxicity testing
Center Reactor 1	Redox measurements
Outflow reactor 1	Metal analysis and water chemistry
Center Reactor 2	Redox measurements
Outflow reactor 2	Metal analysis and water chemistry
Center Reactor 3	Redox measurements
Outflow Reactor 3	Metal analysis and water chemistry
Center Reactor 4	Redox measurements
Outflow reactor 4	Metal analysis, water chemistry, toxicity testing, corrosion, biofouling and scaling

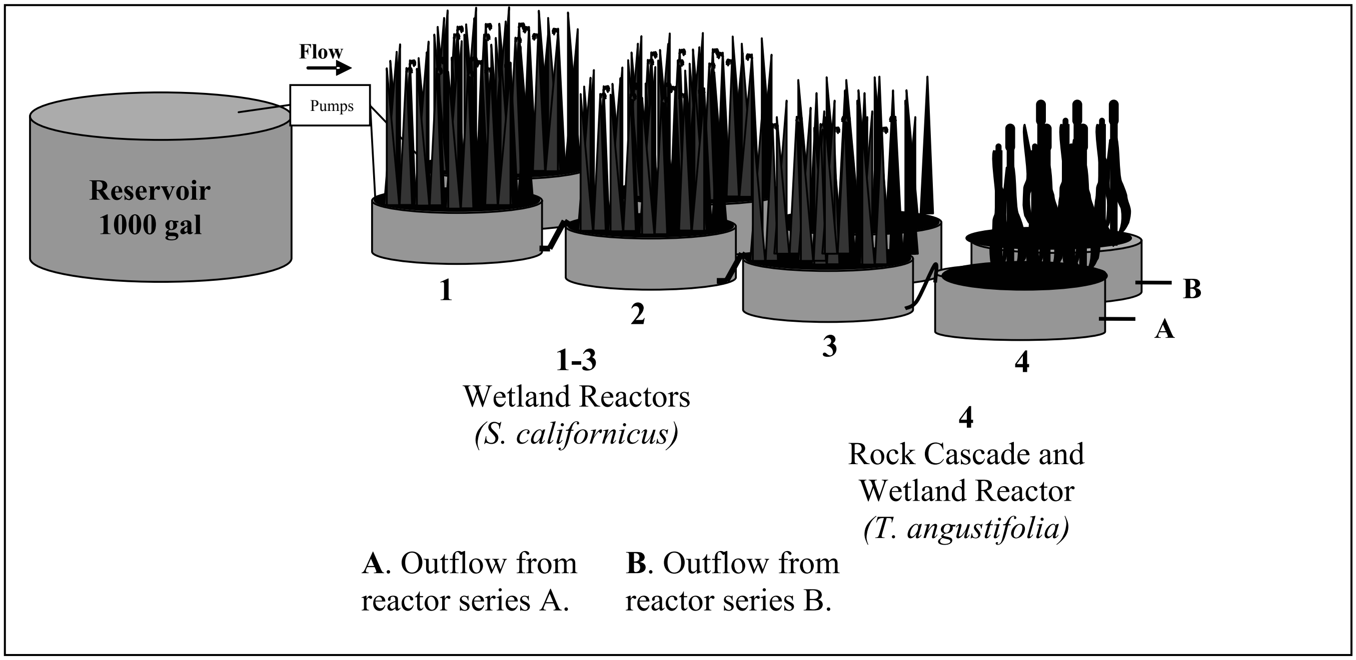


Figure 1. Schematic of the design of the CWTS for ash basin water.

Figure 2. The detention basin, pump house, and pilot-scale CWTS designed for ash basin waters.

Results

The results below show the water chemistry parameters for the CWTS designed to treat ash basin water, the decrease in concentration of constituents of concern, toxicity testing data, scaling potential data, biofouling potential data, and corrosion potential data. The general water chemistry data are given as the average for the treatment weeks 11/28/06-4/26/07. The decrease in concentration of constituents of concern (Figures 3-7) is shown graphically as the average concentration of each constituent in the inflow (influent) and effluent (reactor 1,2,3,4 by series A or B) of individual reactors. The error bars represent one standard deviation. Series A error bars are shown with extended caps. Toxicity data show the survival and reproduction for toxicity tests performed on CWTS inflow and effluent. Reuse limitations assessed include scaling, biofouling, and corrosion. Initial results show a decrease in the potential of these limiting parameters.

Table 8. Average water chemistry for ash basin treatment weeks 11/28/06-4/26/07.

Reactor	Temperature	Dissoved Oxygen	Conductivity	pH	Alkalinity	Hardness
Influent	22.2	8.8	671.4	6.6	14.2	189.1
A-1	21.79	8.7	668.7	6.2	11.2	194.7
A-2	21.6	8.4	674.3	6.4	17.0	203.0
A-3	21.4	8.4	682.1	6.0	13.6	199.0
A-4	21.6	8.6	678.7	6.2	12.8	196.5
B-1	21.1	8.3	670.9	6.4	15.0	199.7
B-2	20.8	8.6	674.3	6.1	14.5	202.6
B-3	21.1	8.4	691.3	6.3	14.5	213.4
B-4	22.0	8.6	696.6	6.7	19.7	207.6

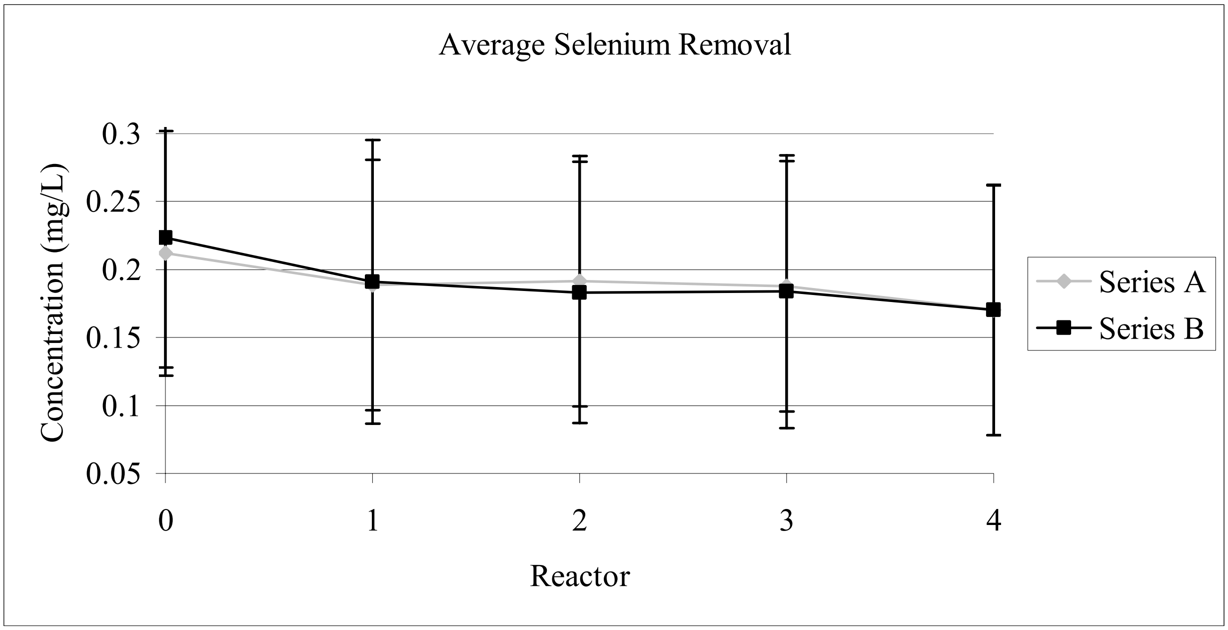


Figure 3. Removal of selenium from simulated ash basin water by CWTS

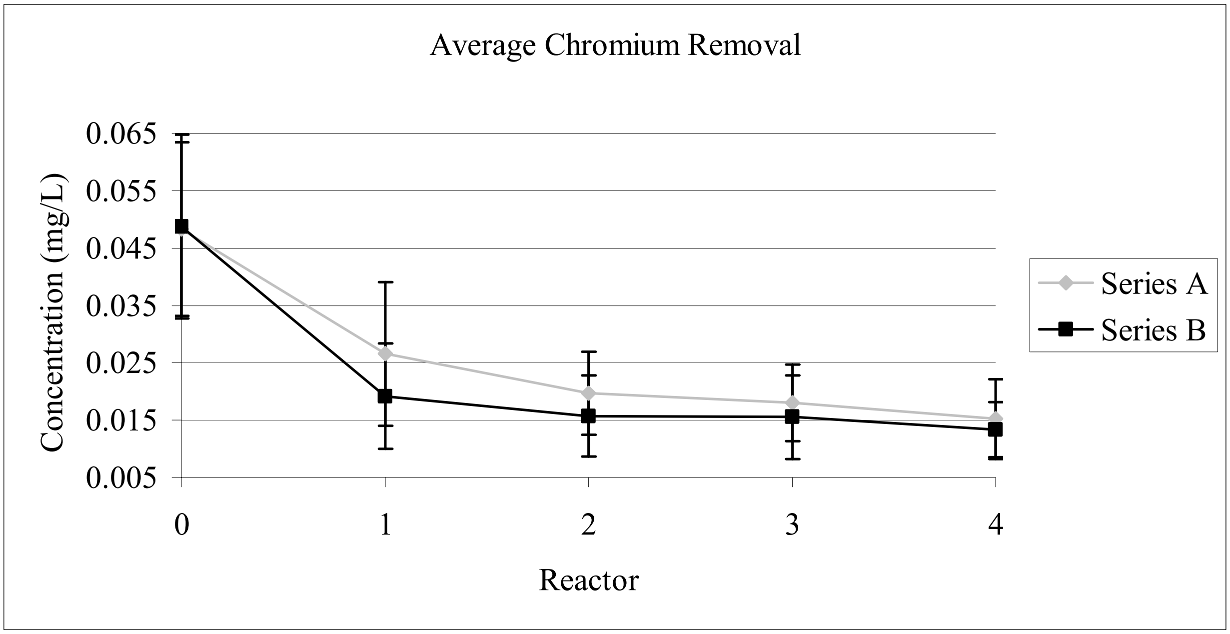


Figure 4. Removal of chromium from simulated ash basin water by CWTS

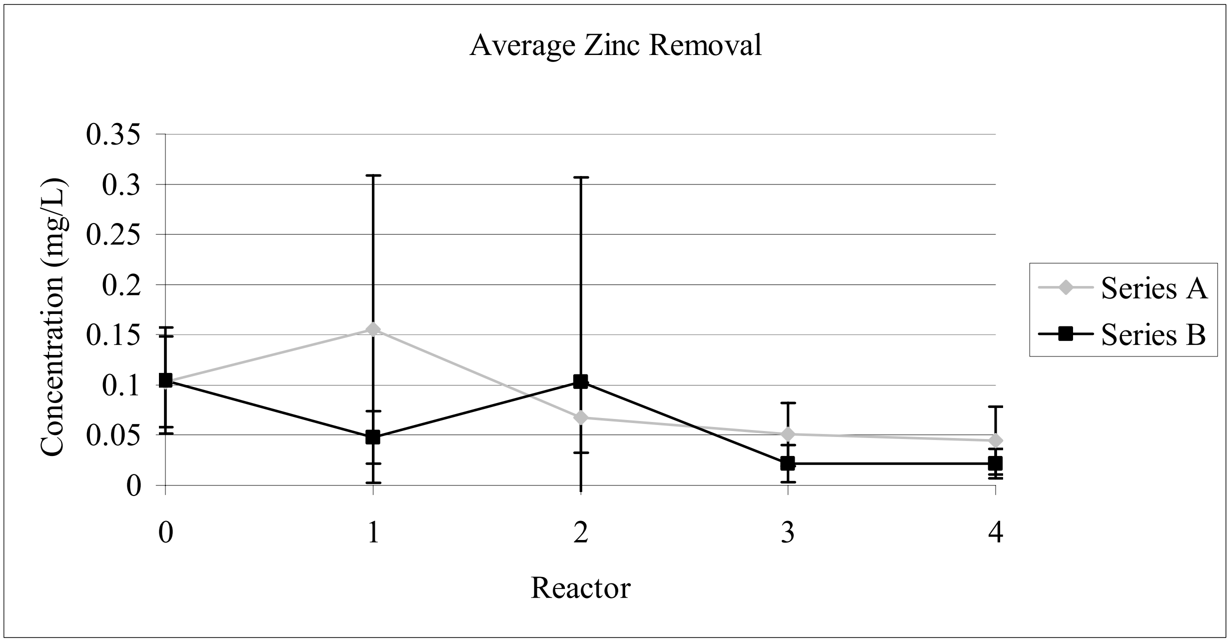


Figure 5. Removal of zinc from simulated ash basin water by CWTS

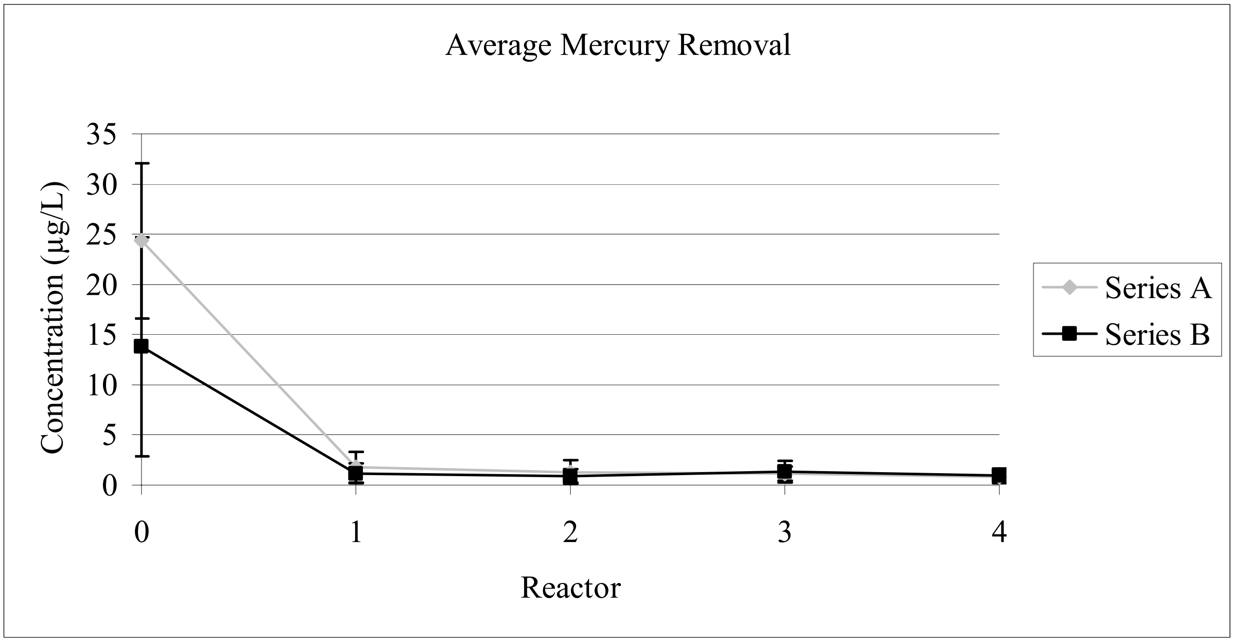


Figure 6. Removal of mercury from simulated ash basin water by CWTS

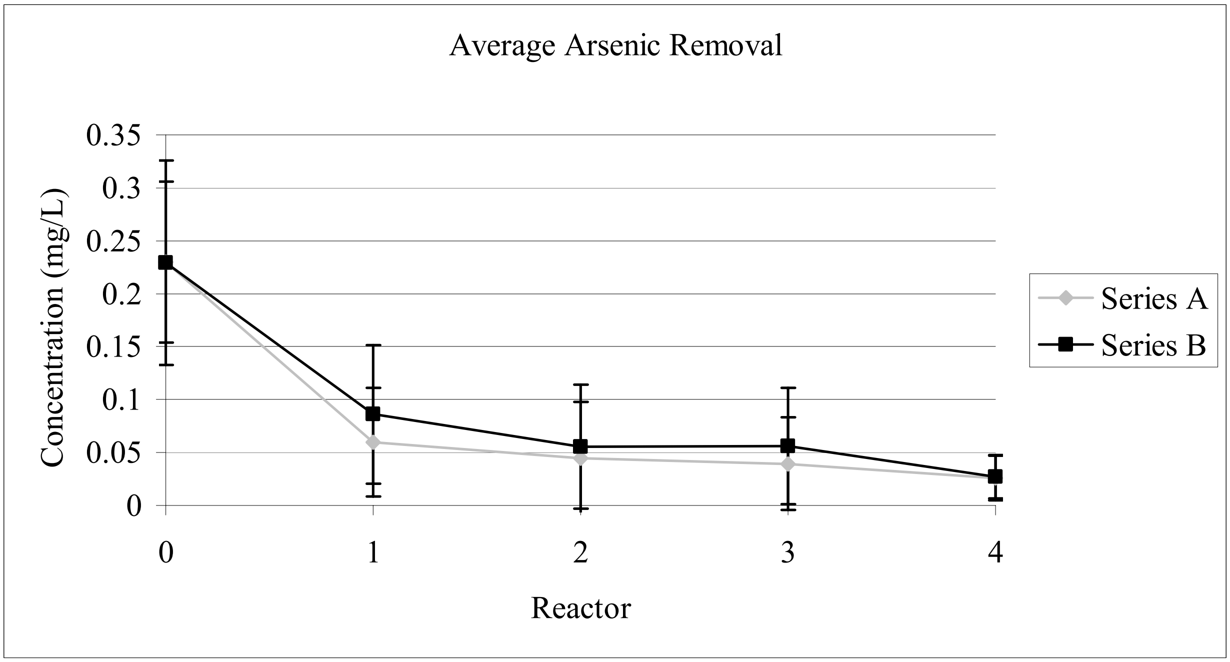


Figure 7. Removal of arsenic from simulated ash basin water by CWTS

Toxicity

Toxicity experiments conducted with *Ceriodaphnia dubia* were used to evaluate treatment of toxicity of ash basin waters. 7-day static renewal experiments measuring survival and reproduction compared to control organism were conducted. The results of toxicity tests performed on the inflow and outflow of the CWTS designed to treat ash basin water (Figures 8-

9) show a decrease in the toxicity imposed by simulated ash basin waters. Figure 8 displays the average adult *C. dubia* mortality for all toxicity experiments. Figure 9 displays the average total number of neonates per parthenogenic female produced over the course of the 7 day exposure.

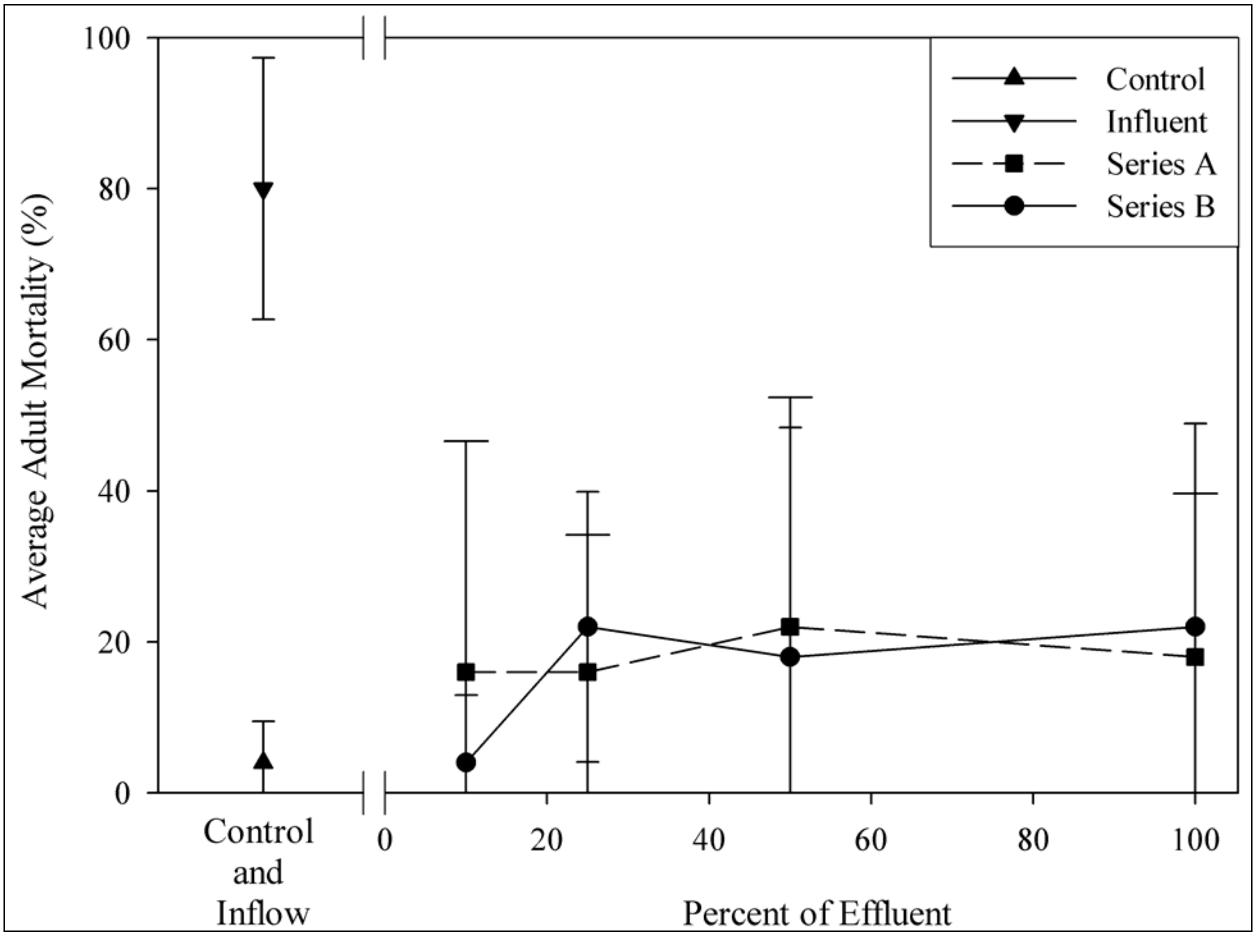


Figure 8. Average (n = 5) percent mortality of *C. dubia*. Error bars represent one standard deviation; Series A error bars are displayed with extended end caps.

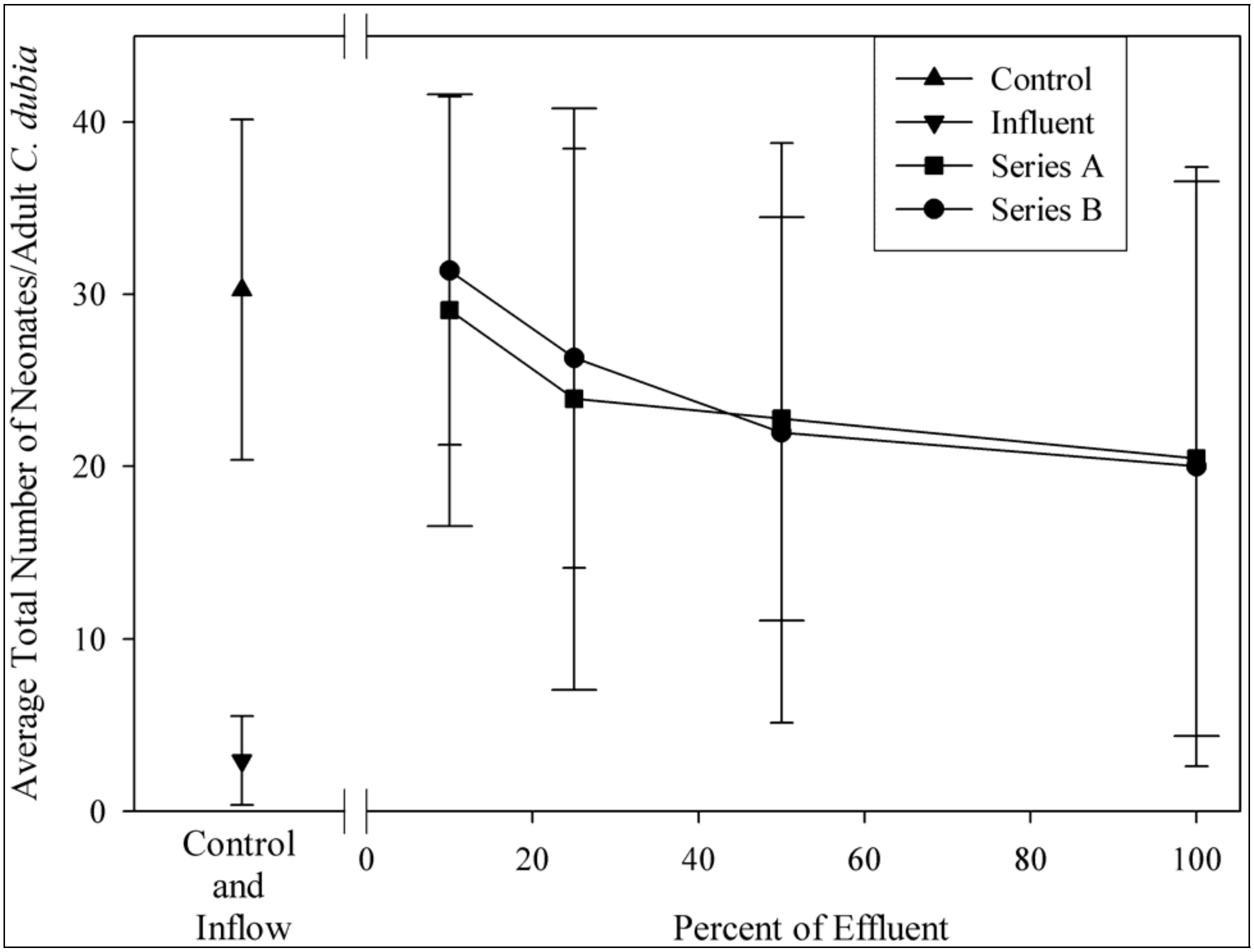


Figure 9. Average (n = 5) reproduction of *C. dubia*. Error bars represent one standard deviation; Series A error bars are displayed with extended end caps.

Scaling, Corrosion, and Biofouling

The potential for the reduction in scaling, corrosion, and biofouling by CWTS was assessed by comparing the change in mass of glass and copper coupons placed in the detention basin and in the effluent of the CWTS. Scaling and biofouling potential decreased as water moved through the CWTS reactor series. However, corrosion potential increased as water moved through the CWTS reactor series (Figure 10). While evidence is provided supporting the reduction in the potential for scale and biofouling formation in CWTS effluent, further study will be required to assess the effect(s) of CWTS on corrosion.

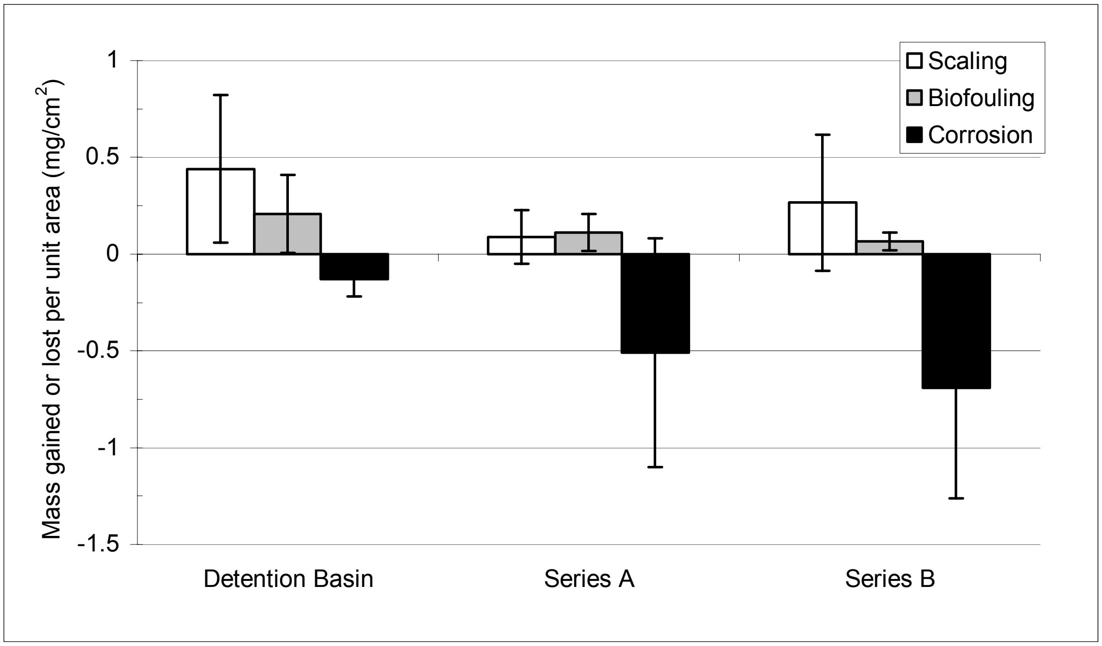


Figure 10. Scaling, biofouling, and corrosion potential of CWTS effluent and inflow

Discussion & Conclusion

The removal data show decreases in the concentration of all the constituents of concern. Method detection limits (MDL) for the following elements using the ICP-AES method employed in the analysis of effluent are: selenium (0.05), arsenic (0.05), zinc (0.01), chromium (0.06), mg/L (ppm). Mercury analyses were conducted on ICP-MS. The method detection limit for mercury was 0.05 µg/L.

Toxicity testing data show decreased toxicity in the effluents of the CWTS treating simulated ash basin waters. Survival and reproduction increased in the effluents of the CWTS compared to inflow waters.

The reuse potential of ash basin water was improved after treatment with the CWTS. A decrease in the scaling and biofouling potential of simulated ash basin water was observed in the effluents of the CWTS as compared to the inflow water. The corrosion potential of the simulated ash basin water increased in CWTS effluents.

COOLING WATERS

Objective I: Characterization

The source of intake water is a primary controlling factor for characteristics of cooling waters. Cooling water is used as a heat exchanger to dissipate heat produced from production of useable energy in thermoelectric power plants. To reduce the temperature of cooling water most thermoelectric power plants use cooling towers. In this structure, hot cooling water is first indirectly cooled [heat passes through non-contacting water (condensers and heat exchangers)] or directly cooled by contact with lower temperature water. The heated water is supplied to the cooling tower by spraying into fill material. This increases heat transfer to the atmosphere due to increased surface area of the fill material. Some water and volatile compounds are evaporated during this process, increasing the concentrations of non-volatile constituents such as some transitional elements and inorganic compounds (e.g. chlorides, sulfates, calcium, copper, zinc, lead). Since cooling water is passed through pipes, heat exchangers and condensing coils, chemical additives may be needed to inhibit corrosion and fouling of these pipes. The use of chemical additives such as biocides, anti-foulants, corrosion inhibitors, and surfactants or water dispersants is based on site-specific requirements. For this study, only data concerning once-through cooling water was used. Literature reviews for cooling waters indicate that commonly utilized biocides or biological growth inhibitors are free oxidants. A variety of chemical forms are used as free oxidants including chlorine dioxide (ClO_2), sodium hypochlorite (NaOCl), sodium bromide (NaBr), and hydrogen peroxide (H_2O_2) (Brady *et al.* 1998). Of these chemical additives, chlorine dioxide is the most commonly utilized due to its concentration requirement for toxicity to target species and neutralization capacity (e.g. sodium bisulfite). Inorganics such as copper, zinc, and lead were present in analyses of cooling water effluents obtained from literature reviews. Some of these constituents may not be present in once-flow through cooling water initially or derive from chemical additions, but were most likely introduced through leaching of metal pipes (i.e. corrosion). Some organic additives are used in cooling waters, but applications of these compounds are site-specific and these data are limited in the literature obtained to date.

Table 9. **Composition of cooling waters based upon published literature and analyses.**

Constituents	Concentrations	Units
pH	6.5 - 10.5	SU
AMMONIA	0-2.0	mg/L
ALKALINITY (as CaCO3)	0-180.0	mg/L
CONDUCTIVITY	150-540	μS/cm^2
DISSOLVED OXYGEN	6.9 - 16.0	mg/L
HARDNESS (as $CaCO_3$)	64.0-254	mg/L
NITRATE	3.0-14.0	mg/L
SULFATE	4.0-18.0	mg/L
TOTAL SUSPENDED SOLIDS	0-19.0	mg/L
TURBIDITY	0-15.3	
INORGANIC ELEMENTS		
ARSENIC, TOTAL	ND-0.016	mg/L
CADMIUM, TOTAL	ND-0.00032	mg/L
CALCIUM, TOTAL	40-153	mg/L
CHROMIUM, TOTAL	ND-0.00365	mg/L
CHLORIDE, TOTAL	4.0-18.0	mg/L
COPPER, TOTAL	0.1-4.0	mg/L
LEAD, TOTAL	ND-0.00032	mg/L
IRON, TOTAL	0.1-1.2	mg/L
MAGNESIUM, TOTAL	24-92.0	mg/L
MERCURY, TOTAL	ND-0.00064	mg/L
NICKEL, TOTAL	ND-0.00635	mg/L
SELENIUM, TOTAL	ND-0.0064	mg/L
ZINC, TOTAL	ND-0.03175	mg/L
FREE CHLORINE	0.5-1.2	mg/L
CHLORINE DIOXIDE	0.1-47.6	mg/L
BROMINE	0.1-3.0	mg/L
HYDROGEN PEROXIDE	0-86.0	mg/L
SODIUM BISULFITE (Free oxidant neutralizer)	2.5-8.4	mg/L
SODIUM HYPOCHLORITE	0.2-1.0	mg/L
ADDITIONAL ADDITIVES		
GLUTARALDEHYDE	0-100	mg/L
POLYQUATERNARY AMMONIUM	2.0-20.0	mg/L
POTASSIUM	1.7-400	mg/L
n-ALKYLDIMETHYLBENZYL NH_4Cl (CT1)	6.0-120	mg/L
n-ALKYLDIMETHYLBENZYL NH_4Cl(CT2)	2.0-20.0	mg/L

Objective II: Determination of Reuse and Constituents of Concern

NPDES Permits

For cooling waters, the majority of constituents of concern requiring NPDES discharge limits are inorganics including aluminum (monitor and report to 0.0015 mg/L), arsenic (monitor and report to 0.05 mg/L), boron (1 mg/L), cadmium (0.002 to 0.2 mg/L), chromium (0.1 to 0.2 mg/L), copper (0.0037 to 1.2 mg/L), cyanide (0.002 mg/L), lead (0.0056 to 0.015 mg/L), mercury (0.000025 to 0.002 mg/L), phosphorous (1.0 mg/L), selenium (0.020 to 0.071 mg/L), and zinc (0.086 to 1.0 mg/L) as TMCs. NPDES permits for organic constituents are similar to other non-traditional waters in regards to oil and grease (10 to 25 mg/L as TMC), but additional constituents of concern derive from chemical treatment strategies for purification of cooling water (Table 9). These constituents must meet a variety of discharge concentrations and mainly include antifoaming agents and surfactants. Free oxidants used as biocides must meet discharge limits between 0.01 to 0.5 mg/L as a TMC and 0.05 to 0.2 mg/L as a monthly average concentration in effluent samples. Toxicity requirements at site-specific locations can range from monthly monitoring to pass/fail tests for *P. promelas* or *C. dubia* exposed to non-diluted cooling waters. Pass/fail toxicity tests require ≥ 80% survival of *P. promelas* or *C. dubia* and statistically similar reproduction between non-diluted cooling water and control organisms.

Constituents of Concern

For cooling waters, constituents of concern were identified based on concentrations of elements and chemical compounds in cooling waters, NPDES permit values, USEPA water quality criteria and USEPA water reuse guidelines. The identified constituents of concern include copper, chlorine (as a free oxidant), phosphorus, nitrogen containing compounds, organic compounds used as biocides, antifoaming agents or surfactants, hardness (specifically due to magnesium and calcium concentrations), pH, total suspended solids (TSS) and total dissolved solids (TDS). Copper concentrations in cooling waters have been found at 4.0 mg/L, which exceeds NPDES permit levels of 1.2 mg/L as a TMC. Chlorine concentrations (as free chlorine) have been found as high as 1.2 mg/L which exceeds NPDES permit levels of 0.5mg/L. For reuse of treated water as cooling water the main constituents of concern are hardness (calcium and magnesium concentrations), TSS, TDS, and nutrients such as phosphorus and nitrogen containing compounds (USEPA WQC). The NPDES limits concerning organic compounds such as biocides and surfactants vary according to specific sites and compounds that are being used at that site. NPDES permits for Naphthenic oil (an antifoam agent) and some nonionic alkyl polyglycosides and polymers (biodetergents and biodispersants) have limits of non-detect. In some cooling waters, organic compounds such as these have been observed at levels as high as 100 mg/L. Magnesium and calcium concentrations, to which hardness can be attributed, have been measured in cooling waters at concentrations of 92.0 and 153 mg/L respectively. Calcium and magnesium are major contributors to scaling of cooling systems; therefore, low hardness is targeted for waters reused as cooling waters. By keeping TDS at low concentrations, the number of reuse cycles for cooling water can be increased according to the method of calculating cycles of concentration, which is the ratio of [TDS] in inflow waters versus [TDS] in reuse waters.

Table 10. NPDES permit limits for cooling waters reported as minimum and maximum concentration ranges.

CONSTITUENTS	TOTAL MAX. CONC. LIMIT	MONTHLY AVG. LIMIT	UNIT
pH	6-9	---	SU
Flow	Monitor	---	
Oil & Grease	25-10	20-10	mg/L
Sulfides		0.05	mg/L
Temp	121.2-86.0	102.0-81.0	deg. F
Total Phosphorus	5	5	mg/L
Total Suspended Solids	100-30	30-15	mg/L
TOTAL INORGANIC			
Aluminum	0.0015/monitor	---	mg/L
Arsenic	0.2-0.05/ monitor	---	mg/L
Beryllium	0.002	0.002	mg/L
Boron	1	1	mg/L
Cadmium	0.2-0.002	0.2-0.002	mg/L
Chromium	0.2-0.1	0.2-0.1	mg/L
Copper	1.2-0.0037	0.811-0.024	mg/L
Cyanide	0.002	0.002	mg/L
Iron	0.3	---	mg/L
Lead	0.015-0.0056	0.0038	mg/L
Phosphorus	1	1	mg/L
Mercury	0.002-0.000025	0.002	mg/L
Selenium	0.071-0.02	0.02-0.016	mg/L
Silver	0.002	0.002	mg/L
Zinc	1-0.086	1-0.106	mg/L

Table 10. (Cont'd)

TOTAL ORGANIC	TOTAL MAX. CONC. LIMIT (mg/L)	MONTHLY AVG. LIMIT	UNITS
Antifoam (mg/l)			
Naphthenic Oil		Non-Detect	mg/L
Petroleum Distillate, Silica		1.0-2.0	mg/L
Biocide (free oxidants)			mg/L
Addition of Cl_2	120	---	min/unit/day
Chlorine	0.5-0.019	0.5-0.011	mg/L
Free oxidants	0.5-0.01	0.2-0.05	mg/L
Sodium Chlorite / Chlorine Dioxide		Non-Detect	mg/L
Sodium Hypochlorite 12.5 %		Non-Detect	mg/L
Sodium Bromide		Non-Detect	mg/L
Sodium Bisulfite (free oxidant neutralizer)		2.0-5.0	mg/L
Polyethylene Dichloride		<0.5	mg/L
Biodetergent/Biodispersant Surfactant			mg/L
Alcohols/ethoxylated propylated		Non-Detect	mg/L
Nonionic Alkyl Polyglycoside		Non-Detect	mg/L
Polymer		Non-Detect	mg/L
Surfactant in Aqueous Solution		1.00	mg/L
Water based deposit control		Non-Detect	mg/L

TOXICITY REQUIREMENTS	
Ceriodaphnia dubia	Monitor/report pass/fail
Pimephales promelas	Monitor/report pass/fail

Objective III: Construction of Pilot-Scale CWTS

One system was configured consisting of two wetland treatment series. Treatment series consist of two 100-gallon wetland reactors (Rubbermaid® Utility Tanks) for a reducing environment (Eh < -150 mV) and one 100-gallon wetland reactor for an oxidizing environment (Eh -100 to 250 mV). The dimensions of the 100-gallon Rubbermaid® tub are 121.9 cm (48 in) long by 77.5 cm (30.5 in) wide by 63.5 cm (25 in) deep, 378 L (100 gal). Simulated cooling water is formulated in a 1000-gallon equalization basin (polypropylene container) with the addition of high-purity salts (copper, lead and zinc), chlorine, and biocide. Simulated cooling water is transferred into the CWTS via Fluid Metering, Inc. (FMI)® piston pumps at a calibrated flow rate to establish a 24-hr hydraulic retention time (HRT) per wetland reactor. The sequential ordering (first to last wetland reactor) of the CWTS includes two reducing wetland reactors and one oxidizing wetland reactor. Flow through this system is gravity assisted after inflow from the equalization basin. The reducing wetland reactors of each treatment series contains approximately 30-cm of river sand hydrosoil and *Schoenoplectus californicus* C. A. Meyer planted at realistic field densities. The first half of each third wetland reactor consists of a rock cascade constructed using medium-sized granite rocks, and 30-cm of river sand hydrosoil planted with *Typha angustifolia* L. The final oxidizing wetland reactors of each treatment series contains approximately 30-cm of river sand hydrosoil and is planted with *T. angustifolia.* The reactors were connected by PVC pipe fittings and approximately 30 cm long segments of ¾" PVC tubing. The PVC pipe fittings were designed to maintain surface flow and were placed 6 cm below the top of each Rubbermaid® tub.

Objective IV: Treatment Performance of Pilot-Scale Constructed Wetlands

Readiness for Treatment Performance

Before a CWTS can be used for treatment, readiness of the system must be determined to ensure successful treatment, a step that is very important when using newly constructed treatment systems. For this CWTS, system readiness is quantified by field plant density, appropriate sediment bulk redox conditions (Eh) and sediment organic matter percentage. The average plant density of reactors 1 and 2 in both series was 211 plants (*S. californicus*) per meter squared. The average plant density in the third reactors of both series was 80 plants (*T. angustifolia*) per meter squared. The organic matter content of sediment for treatment series A ranged from 0.11 to 0.14 %. The sediment for treatment series B ranged from 0.16 to 0.25 % organic matter. To maintain a bulk reducing condition, a higher organic matter percentage is required; therefore reactors 1 and 2 of both series have been amended with more organic matter. With this addition, the system for cooling water treatment is poised for the removal of chlorine, copper, lead and zinc through reductive pathways.

Formulation of simulated water

Simulated cooling water was formulated in a 1500 gallon detention basin using municipal water from Clemson University, Clemson, SC. Appropriate salts were added to the detention basin to create water with specified metal concentrations, alkalinity, hardness and sulfate concentrations. The salts and water were mixed for 24 hours in the detention basin by a submersible pump prior to treatment.

Hydraulic Retention Time (HRT)

The hydraulic retention time was regulated by calibrated metering pumps from Fluid Metering Inc®. These pumps were adjusted to a flow rate of approximately 97mL per minute to insure a hydraulic retention time of 24 hours for each reactor. Two pumps were used, one for each series of reactors.

Sampling

Samples were collected every two weeks and at least five days after a new batch of simulated water was formulated. This was to ensure that the new batch of water had passed completely through the entire series, based on a 24 hour retention time. Samples were collected in HDPE Nalgene bottles from the outflow of each reactor as well as the outflow of the detention basin. At every sampling event, fundamental water characteristics including pH, temperature, dissolved oxygen, hardness, alkalinity and conductivity were measured. From the water samples, 50mL were preserved with trace metal grade nitric acid for metal analysis by ICP-AES. Any remaining water was stored at 4^0C in nalgene bottles.

Every four weeks, additional water was sampled from the detention basin outflow and the final reactor outflow to conduct toxicity testing using *Ceriodaphnia dubia*. Toxicity tests measured the survival and reproductive effects of dilutions (100, 50, 25 and 10%) of treatment water. These 4 week samples were also analyzed for sulfates, chlorides, total dissolved solids and total suspended solids (TDS/TSS). The redox potential of each reactor was measured *in situ* every four weeks.

Every six weeks scaling, biofouling and corrosion were measured by removing glass and copper coupons from the system and measuring the loss or accretion of mass on each coupon. New coupons were introduced to each system at this time.

Table 11. Sampling locations and measured parameters

Sampling Location	**Measured Parameters**
Detention Basin	Corrosion, biofouling and scaling
Inflow from detention basin	Metal analysis, water chemistry, toxicity testing
Center Reactor 1	Redox measurements
Outflow reactor 1	Metal analysis and water chemistry
Center Reactor 2	Redox measurements
Outflow reactor 2	Metal analysis and water chemistry
Center Reactor 3	Redox measurements
Outflow reactor 3	Metal analysis, water chemistry, toxicity testing, corrosion, biofouling and scaling

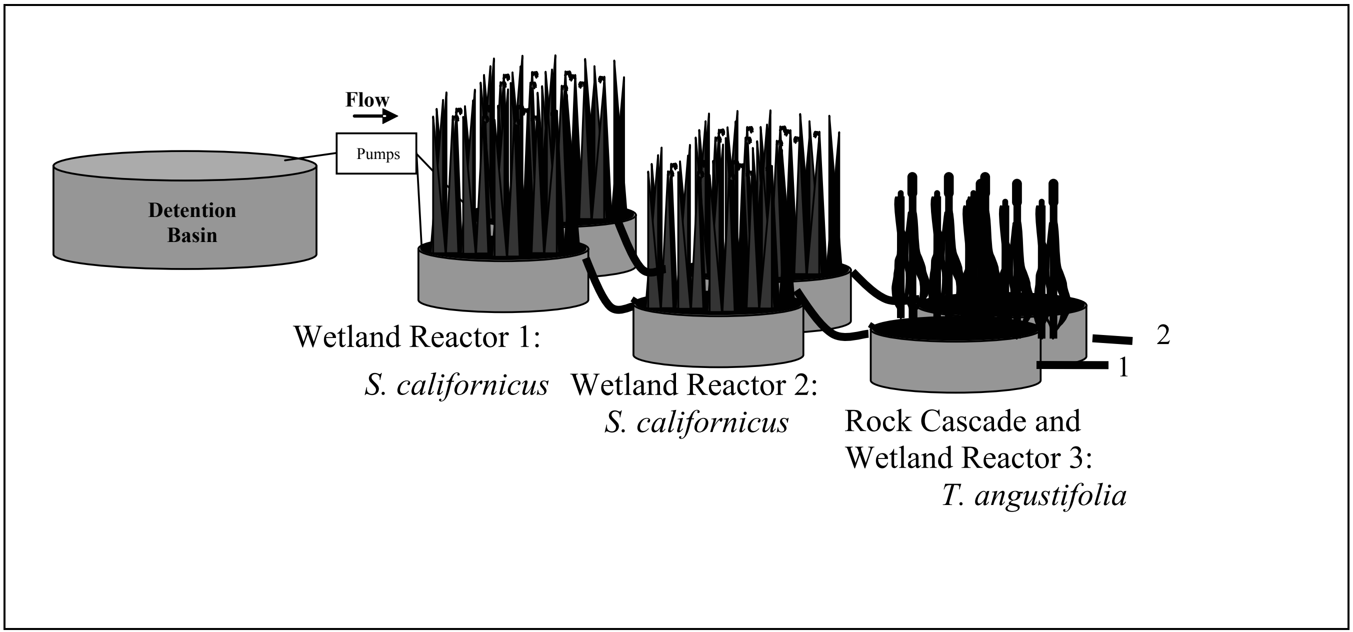


Figure 11. CWTS design and configuration for treatment of cooling waters

Figure 12. Pilot-scale CWTS for treatment of cooling waters

Results

Table 12. Fundamental water chemistry ranges for cooling water treatment

Wetland	Temperature	pH	Dissolved Oxygen	Conductivity	Alkalinity	Hardness
Reactor	(°C)		(mg/L)	(μmhos/cm)	(mg/L as CaCO3)	(mg/L as CaCO3)
Inflow	15.9-21.4	6.45-6.94	8.76-10.30	25-4863	14-18	68-680
1	16.0-23.2	6.24-6.94	16.0-10.52	143-707	12-16	60-300
2	16.3-22.7	6.10-7.09	9.04-10.40	146-696	10-14	80-300
3	16.1-22.0	6.28-7.20	8.85-10.00	141-684	10-18	56-360

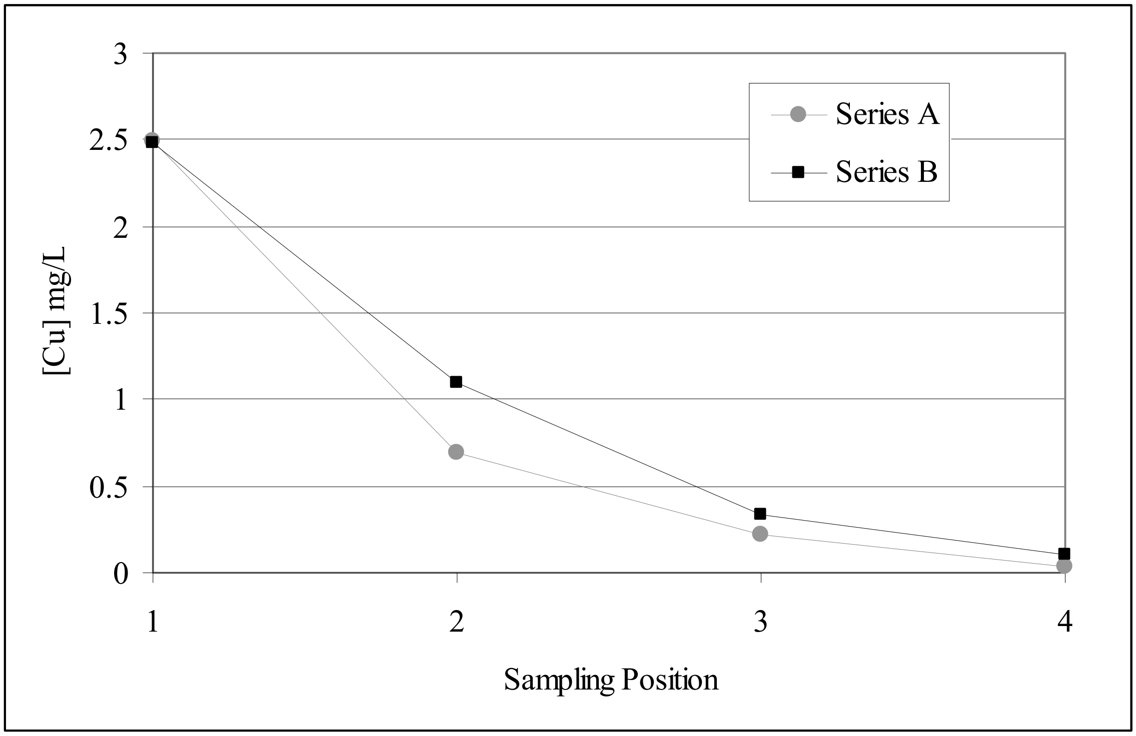


Figure 13. Total copper removal from simulated cooling water by CWTS

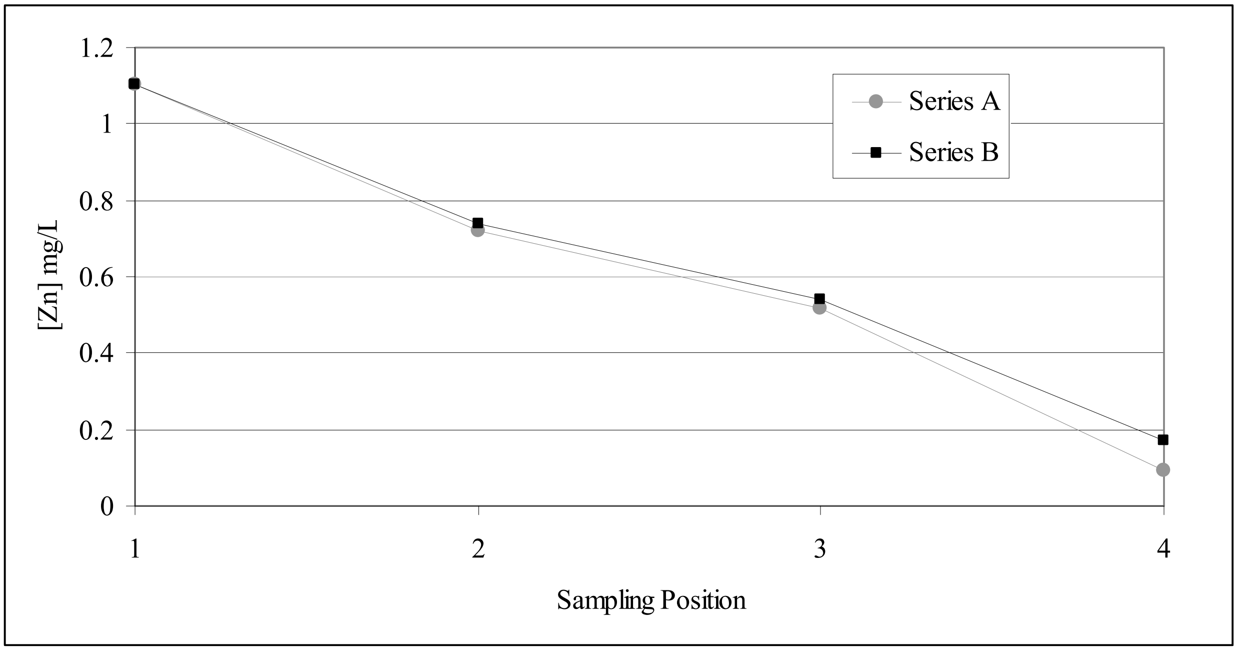


Figure 14. Total zinc removal from simulated cooling water by CWTS

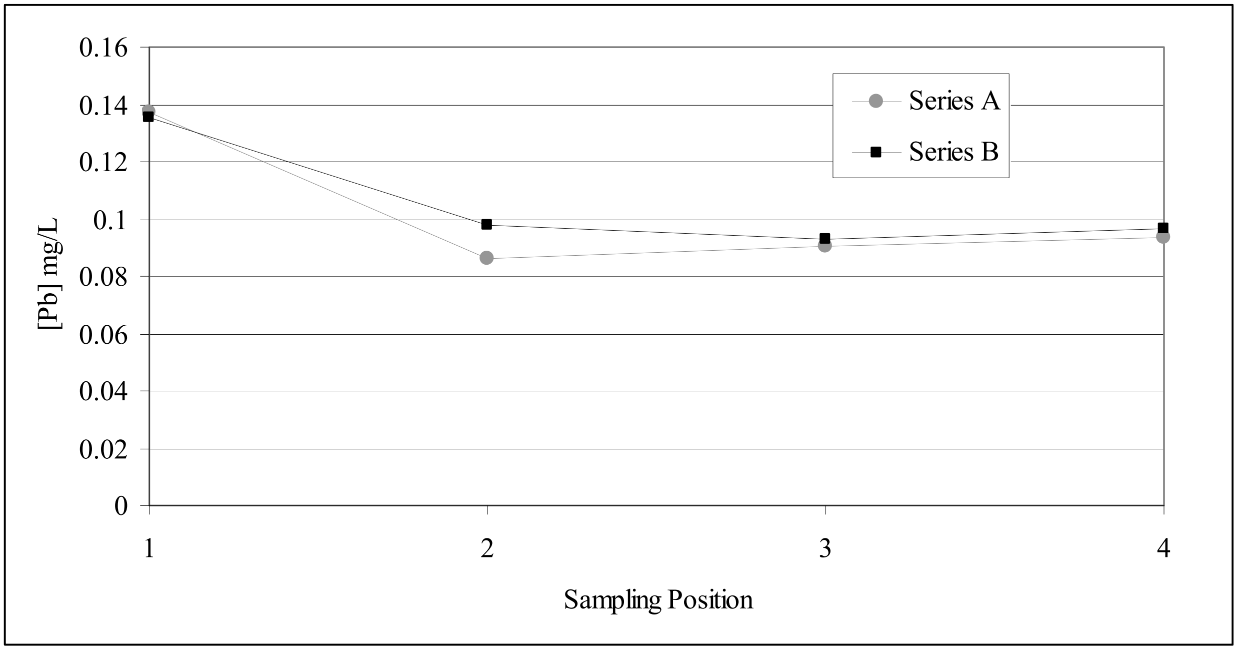


Figure 15.Total lead removal from simulated cooling water by CWTS

Table 13. Percent removal of copper, lead and zinc via treatment by pilot-scale constructed wetlands and reaction rate coefficients by CWTS reactor.

		Removal Rate Coefficient (k) by Reactor (d^{-1})		
	% Removal	**1**	**2**	**3**
Copper	97	0.042	0.049	0.059
Lead	88	0.0016	0.001	0.001
Zinc	30	0.017	0.013	0.058

Scaling, Corrosion and Biofouling

Using corrosion and scaling coupons, the potential for chemical scale formation, corrosion and biofouling was measured before treatment (inflow) and after treatment by a constructed wetland (outflow). Biofouling potential significantly decreased from inflow to outflow, averaging 81% reduction of biofouling potential for CWTS series A and B. For cooling waters, potential for scaling decreased 74% (0.086 mg/cm^2 to 0.065mg/cm^2).

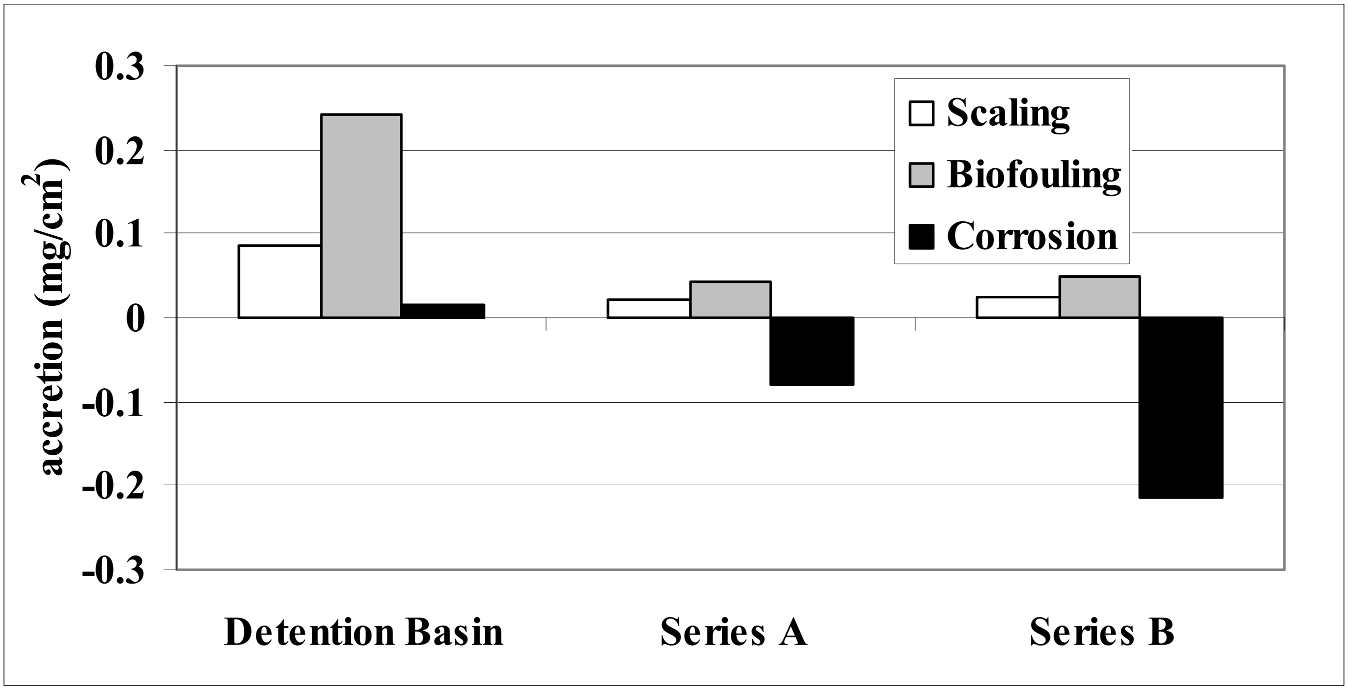


Figure 16. Scaling, corrosion and biofouling potential of cooling waters.

Practical Scaling Index (PSI)

Using the Puckorious (Practical) Scaling Index and measured water chemistry parameters, the calculated PSI value for cooling water entering the CWTS is 9.10, or “corrosion intolerable.” After treatment in the wetland, the PSI status was decreased to “heavy corrosion” a PSI value of 8.53, indicating the corrosion potential increased in the CWTS.

Discussion & Conclusion

Zinc, copper and lead were essentially eliminated from the water column through treatment in the CWTS. Lead had a low removal percentage of less than 60%, however this is a consequence of the low lead concentration in the inflow. Elements with low initial concentrations have lower apparent removal rates, due to the thermodynamic minimums of the system. Significant decrease of biofouling potential was measured.

FLUE GAS DESULFURIZATION WATERS

Objective I: Characterization

Flue gas desulfurization (FGD) water is the blowdown product of flue gas that has been scrubbed with a slurry containing lime (calcium carbonate) and chemical enhancers for sulfur oxidation or co-precipitation as calcium sulfite or sulfate. Dewatering steps are conducted to remove solids and extracted water is collected for treatment. The chemical composition of FGD waters can vary significantly from site to site due to factors such as coal type, boiler requirements, reactor/burner type, scrubber design, fly ash cyclones, and chemical additives (Mierzejewski, 1991). Data collected from literature reviews and analysis of FGD waters indicate that the constituents of concern include chloride, selenium, mercury, boron, arsenic, biochemical oxygen demand, and chemical oxygen demand. Chloride concentrations in these waters can range from mid-freshwater to saline (1,000 mg/L < [Cl] < 20,000 mg/L) ultimately dictating the treatment requirements. The elemental composition of FGD waters indicated that the waters could be generally classified based on chloride concentrations (Table 15). This classification of FGD waters included low-chloride (<2000 mg/L as Cl^-), mid-chloride (2000 to 8000 mg/L), and high-chloride (>8000 to 25,000 mg/L). For the low-chloride FGD waters, constituents of concern include chlorides (1640 and 1496 mg/L), chemical oxygen demand (1845 mg/L; FGD w 1), selenium (0.76 and 0.051 mg/L), mercury (0.77 and 1.2 μg/L), zinc (16.0 and 0.13 mg/L), arsenic (0.13 and 0.0105 mg/L), and boron (32.5 mg/L; FGD w 2). For the mid-chloride FGD waters, constituents of concern include chlorides (mean =4345 mg/L), chemical oxygen demand (268, 610, 693, and 388 mg/L), selenium (0.610, 2.97, 2.09, and 0.649 mg/L), mercury (0.89, 43.2, 47.0, and 0.39 μg/L), and arsenic (0.004, 0.101, 0.036, and 0.035 mg/L). For high-chloride FGD waters, constituents of concern include chlorides (mean =14,940 mg/L), chemical oxygen demand (938, 1239, 1337, and 3000 mg/L), selenium (0.15, 2.3, 17.2, and 5.4 mg/L), mercury (<0.2, 1.80, 58.0, and 1.70 μg/L), copper (0.025, 0.12, 3.2, 0.031), zinc (0.82, 0.62, 6.2, and 2.3 mg/L), arsenic (0.006, <0.05, 4.1, and 0.028 mg/L), chromium (0.014, <0.05, 4.4, and 0.44 mg/L), and boron (463 mg/L FGD w 4). Current treatment strategies for chlorides in FGD waters are costly and require routine maintenance or monitoring to be effective. These methods include reverse osmosis (RO), crystallization techniques, and dilution with low ionic strength water. Elevated concentrations of chlorides can be accompanied by higher concentrations of certain inorganics making chlorides a distinguishing characteristic of FGD waters.

Table 14. Composition of flue gas desulfurization (FGD) waters based upon published literature and analyses.

CONSTITUENTS	CONCENTRATIONS	UNITS
pH	5.9 - 7.9	SU
[1]BOD_5	0.5 - 11.71	mg/L
[2]COD	4 - 3000	mg/L
DISSOLVED OXYGEN	0.5 - 11.7	mg/L
SOLIDS, TOTAL DISSOLVED	4799 - 51,565	mg/L
SOLIDS, TOTAL SUSPENDED	8 - 40,950	mg/L
NITROGEN, TOTAL	12	mg/L
PHOSPHORUS, TOTAL	45 - 166	mg/L
SULFATE, TOTAL	1200 - 3160	mg/L
ALUMINUM, TOTAL	1.6 - 323	mg/L
ARSENIC, TOTAL	0.006 - 4.1	mg/L
BARIUM, TOTAL	0.15 - 1.1	mg/L
BERYLLIUM, TOTAL	0.0019	mg/L
BORON, TOTAL	33 - 460	mg/L
CADMIUM, TOTAL	0.002 - 0.28	mg/L
CALCIUM, TOTAL	3830	mg/L
CHLORIDE, TOTAL	1640 - 20,163	mg/L
CHROMIUM, TOTAL	0.002 - 4.4	mg/L
COPPER, TOTAL	0.008 - 3.2	mg/L
FLUORIDE, TOTAL	40 - 85	mg/L
IRON, TOTAL	0.17 - 2550	mg/L
LEAD, TOTAL	0.005 - 0.11	mg/L
MAGNESIUM, TOTAL	3650	mg/L
MANGANESE, TOTAL	1.3 - 330	mg/L
MERCURY, TOTAL	<0.0002 - 0.06	mg/L
NICKEL, TOTAL	0.07 - 4.5	mg/L
SELENIUM, TOTAL	0.05 - 17.2	mg/L
SILVER, TOTAL	< 0.005 - < 0.25	mg/L
SODIUM, TOTAL	128 - 2240	mg/L
VANADIUM, TOTAL	0.047 - 1.7	mg/L
ZINC, TOTAL	0.13 - 16.0	mg/L

[1] BOD_5: 5-d biochemical oxygen demand.

[2] COD: chemical oxygen demand.

Table 15. Composition (elements expressed as mg/L) and classification of flue gas desulfurization (FGD) waters categories based on chloride concentrations.

FGD Water Type[1]	**pH**	**TSS**	**TDS**	**COD**	**Hard[2]**	**ALK[2]**	**SO_4^{2-}**	**Cl**	**As**	**Hg[3]**	**Se**	**B**	**Cd**	**Cr**	**Cu**	**Zn**
Low-Chloride																
FGD water 1	5.95	1331	48031	1845	20040	328	1350	1640	0.13	0.77	0.76	n/a	0.21	<0.05	<0.10	16.0
FGD water 2	7.33	8.84	4892	32.6	2875	58	1767	1496	0.0105	1.20	0.051	32.53	0.068	0.006	0.008	0.13
Mid-Chloride																
[4]Pilot Scrubber W 1	7.16	14	10600	268	4200	46	1780	4250	0.004	4.7	0.610	n/a	<0.001	0.007	n/a	n/a
[4]Pilot Scrubber W 2	6.23	48	11100	610	9800	26	1280	3880	0.101	43.2	2.97	n/a	0.002	0.199	n/a	n/a
[4]Pilot Scrubber W 3	6.9	46	10400	693	6400	31	1200	4500	0.035	47.0	2.09	n/a	0.002	0.187	n/a	n/a
[4]Pilot Scrubber W 4	6.8	55	10600	388	6400	24	1210	4750	0.035	0.39	0.649	n/a	0.006	0.002	n/a	n/a
High-Chloride																
FGD water 1	6.38	25	23875	938	10400	152	1645	9300	0.0064	<0.2	0.15	n/a	0.046	0.014	0.025	0.82
FGD water 2	6.32	1297	39646	1239	19467	480	3160	14400	<.05	1.80	2.3	n/a	0.027	<0.05	0.12	0.62
FGD water 3	6.46	40950	44858	1337	24800	600	2080	15900	4.1	58.0	17.2	n/a	0.28	4.4	3.2	6.2
FGD water 4	5.89	375	51656	3000	27000	531	3360	20163	0.028	1.70	5.4	463	0.24	0.44	0.031	2.3

[1] FGD water type: Low-Chloride (<2000 mg/L as Cl^-), Mid-Chloride (2000 mg/L to 8000 mg/L), and High-Chloride (>8000 mg/L to 25,000 mg/L).

[2] Alkalinity and hardness are expressed as mg/L as $CaCO_3$.

[3] Mercury concentrations are expressed in μg/L.

[4] Pilot-scrubber waters were collected from a pilot-scale FGD scrubber unit and are described independently due to differences in the source of flue gas (i.e. coal type burn)

Objective II: Determination of Reuse and Constituents of Concern

NPDES Permits

The majority of elements or compounds in FGD effluents that require NPDES discharge criteria are inorganics including arsenic, cadmium, chlorides, chromium, copper, lead, mercury, nitrogen (reported as total), nickel, phosphorous, selenium, and zinc. For the inorganics listed above, only copper and iron have discharge limits (only exception of selenium at a historically contaminated site; 26 µg/L) of 1 mg/L. All other listed inorganics are classified as monitor and report. FGD effluents are typically co-mingled with other service waters (cooling water, runoff water, ash basin water) before discharge into a settling basin or ash pond. For this report, coal-fired power plants that practice co-mingling of FGD effluents with service waters were assigned NPDES permits based on NPDES permits for ash pond discharge. Of these elements or compounds in FGD effluents, chlorides may be the most potentially toxic constituent due to typical chloride concentrations in the FGD effluents, in comparison to adverse effects caused by this ion in receiving systems. Other constituents that require NPDES discharge limits are pH (6-9 SU), oil and grease (15 to 20 mg/L), and total suspended solids (20-100 mg/L). For the collected NPDES permits, most coal-fired power plants with FGD scrubbers (with only one exception) must conduct quarterly 7-d static/renewal toxicity test of effluents with *Ceriodaphnia dubia*. Waters used in these experiments range between 1.9 and 19% as discharge effluent and require no significant inhibition of reproduction throughout the testing period. One power plant is required to conduct 24-hr static toxicity experiments with *Pimephales promelas* for 90% of the effluent discharged from the co-mingled ash basin.

Constituents of Concern

Constituents of concern (COCs) in FGD waters were identified based on the chemical composition of FGD waters, element or compound concentrations, NPDES permits, USEPA water quality criteria (USEPA WQC), and published literature. Initial analysis of these data indicated three distinct classes of FGD waters based on chloride concentrations (low, mid, and high-chloride FGD waters). For the low-chloride FGD waters, arsenic, boron, chemical oxygen demand (COD), chloride, mercury, selenium, total suspended solids, and zinc were identified as COCs for this water. Total arsenic concentrations ranged from 10.5 to 130 µg/L, which are below NPDES permits, estimated NOEC, or USEPA water quality criteria; however, synergistic effects may be observed when this element is present with other potentially toxic elements (i.e. mercury and selenium). Chloride, COD, mercury, selenium, total suspended solids, and zinc concentrations have ranges that exceeded individual NOECs or USEPA water quality criteria, identifying them as COCs for this water. For the mid-chloride FGD waters, arsenic, COD, chloride, mercury, selenium, total suspended solids, and zinc met the COC criteria for this research. Chemical concentrations of COCs ranged from 268 to 693 mg/L as COD, 3880 to 4750 mg/L as chloride (15.5 to 19 times greater than USEPA WQC), 0.39 to 47.0 µg/L as mercury (less than to 21 times greater than the estimated NOEC; USEPA), 0.61 to 2.97 mg/L as selenium (122 to 594 times greater than USEPA WQC), and 14 to 55 mg/L as total suspended solids (less than 2.75 times greater than NPDES permit limits). For the high-chloride FGD waters, identified COCs include arsenic, COD, chlorides, mercury, selenium, total suspended solids, and zinc. Chemical concentrations of COCs ranged from 0.006 to 4.1 mg/L as arsenic (below to 27 times greater than USEPA WQC), 938 to 3000 mg/L as COD, 9300 to 20163 mg/L as chloride (37 to 80 times greater than USEPA WQC), <0.02 to 58 µg/L as mercury (below to 26 times greater than the estimated NOEC; USEPA), 0.150 to 17.2 mg/L as selenium (30 to 3440 times greater than USEPA WQC), 25 to 40,950 mg/L as total suspended solids (1.25 to 2040 times greater than USEPA WQC), and 0.62 to 6.2 mg/L (5 to 50 times greater than USEPA WQC). Chemical oxygen demand (COD) is listed as a constituent of concern for these waters due to the potential for these compounds to deplete dissolved oxygen when introduced into a receiving system.

Table 16. NPDES permit limits for flue gas desulfurization (FGD) reported as minimum and maximum concentration ranges.

CONSTITUENTS	TOTAL LIMIT	MONTHLY AVG. LIMIT	UNITS
pH	6.0-9.0		SU
Flow	monitor/report		
Nitrite and Nitrate, Total N	monitor/report		mg/l
Phosphorus, Total	monitor/report		mg/l
Oil & Grease	20-15	20	mg/l
Sulfate	monitor/report		mg/l
Total suspended solids	100-30	100-65	mg/l
TOTAL INORGANICS			
Arsenic	monitor/report		mg/l
Beryllium	monitor/report		mg/l
Cadmium	monitor/report		mg/l
Chloride	monitor/report		mg/l
Chromium	monitor/report		mg/l
Copper	1.0 - monitor/report	1.0	mg/l
Fluoride	monitor/report		mg/l
Iron	1.0 - monitor/report	1.0	mg/l
Mercury	0.63 - monitor/report		µg/l
Nickel	monitor/report		mg/l
Selenium	0.026 - monitor/report		mg/l
Silver	monitor/report		mg/l
Zinc	monitor/report		mg/l
TOXICITY REQUIREMENTS			
Ceriodaphnia dubia	1.9 - 19%/dilution	No reproduction inhibition	
Pimephales promelas	90%/pass	No growth inhibition	

Objective III: Construction of Pilot-Scale CWTS

The pilot-scale constructed wetland systems were configured with two wetland treatment series each (Figure 23-24). Treatment series consisted of three 150-gallon and two 70-gallon wetland reactors (Rubbermaid® Utility Tanks) in series. Wetland reactors one, four, and five were constructed with the 150-gallon wetland reactors due to the targeted constituents and hydraulic retention times needed for treatment. The first, second, and third wetland reactors of each treatment series contain approximately 30-cm of hydrosoil and are planted with *Schoenoplectus californicus* C. A. Meyer planted at realistic field densities. The first half of each fourth wetland reactor consists of a rock cascade constructed using medium-sized granite rocks, followed by *Typha angustifolia* L. For this pilot system, the fifth wetland reactors of each treatment series contain approximately 30-cm of hydrosoil and are 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 compatible with the target hydraulic retention time (HRT). FGD water supplying the pilot-scale system was renewed at the beginning of each treatment period (i.e. treatment week) from a 1000-gallon polyethylene reservoir (i.e. equalization basin).

Additional Treatment System

In review of the results from the first four treatment weeks, an additional pilot-scale constructed wetland treatment system was monitored for removal rates, extents, and other constituents of FGD water. This system was constructed in the same manner as described above with only one minor change, in that six wetland reactors were constructed with 100-gallon wetland reactors, but total hydraulic retention time was identical between these two treatment systems. Osmocote (nitrogen, phosphorus, and potassium supplement) was amended prior to FGD water treatment and therefore nutrient removal rates were less than observed for the initial treatment system (i.e. treatment weeks 1-4, 6, and 8).

Objective IV: Treatment Performance of Pilot-Scale Constructed Wetlands

FGD Water Treatments

Treatment FGD water used to obtain all results discussed in the latter sections of this report was received from operating coal fired power plant in the southeastern United States. FGD water was shipped in storage tanker and analyzed for elemental composition upon arrival. Dilutions were not needed for treatment with these systems (< 4000 mg/L as Cl^-), therefore FGD water was directly introduced into pilot-scale constructed wetland treatment systems after an appropriate equalization period of 24-h.

Sampling and Analysis

Physical and chemical characteristics of the FGD water, as presented in Tables 15-17 , were analyzed at the following stages of (or locations in) the pilot constructed wetland treatment systems:

Initial Pilot-Scale Constructed Wetland Treatment System

1. Equalization Basin
2. Inflow to the first wetland reactor of each series
3. Outflow from the first wetland reactor of each series
4. Outflow from the second wetland reactor of each series
5. Outflow from the third wetland reactor of each series
6. Outflow from the fourth wetland reactor of each series
7. Outflow from the fifth wetland reactor of each series (Final Outflow Sample)

Additional Pilot-Scale Constructed Wetland Treatment System

1. Equalization Basin
2. Inflow to the first wetland reactor of each series
3. Outflow from the first wetland reactor of each series
4. Outflow from the second wetland reactor of each series
5. Outflow from the third wetland reactor of each series
6. Outflow from the fourth wetland reactor of each series
7. Outflow from the fifth wetland reactor of each series
8. Outflow from the sixth wetland reactor of each series (Final Outflow Sample)

Hydraulic Retention Time (HRT)

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 carefully measuring overlying water volume in each wetland reactor coupled with accurate and precise measurement of inflow volume (ml/min). HRT was calculated by the ratio of volume to inflow rate. Flow rate to each series was confirmed weekly. The hydraulic retention times used for all treatment weeks were 24-hr for each wetland reactors.

Table 17. System components of the pilot-scale constructed wetlands utilized for treatment of FGD water.

Treatment Type	Wetland Series	Wetland Reactor	Reactor Volume	Flow Rate (mL/min)	Hydraulic Retention Time
FGD Water	Initial	Reactor 1	244 L	90	24 hr
	System	Reactor 2, 3 , 4 and 5	130 L	90	24 hr
FGD Water	Additional System	Reactor 1, 2, 3, 4	183L	128	24 hr
		Reactor 5, 6	244L	128	24 hr

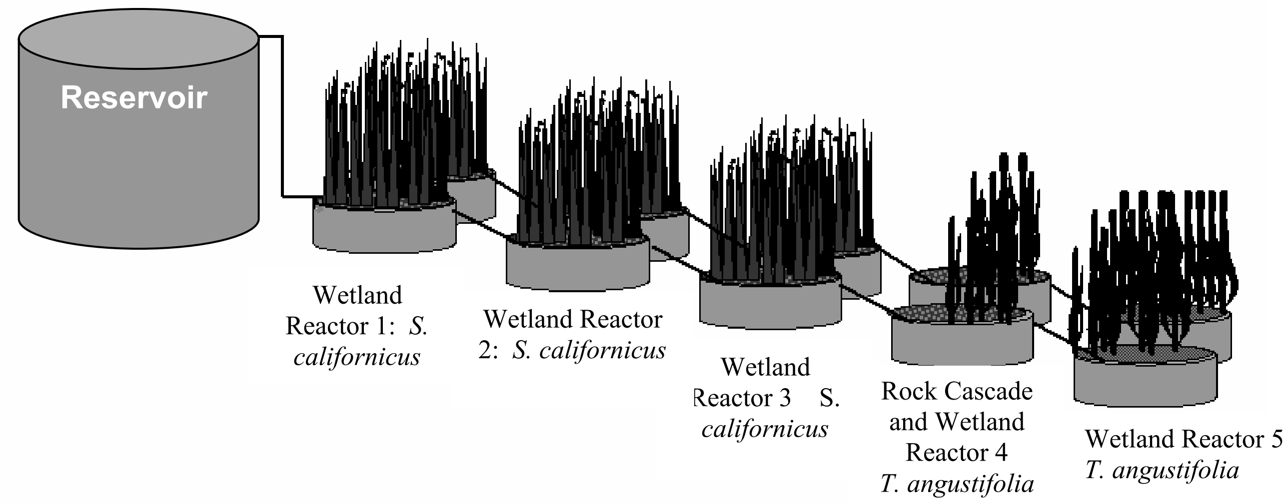


Figure 17. Initial pilot-scale constructed wetland systems used for evaluating treatment of FGD water. Wetland reactors 1, 4, and 5 were planted in 250-gallon containers and wetland reactors 3 and 4 were planted in 70-gallon containers. All hydraulic retention times were established as 24-hr per wetland reactor.

Figure 18. Initial pilot-scale CWTS.

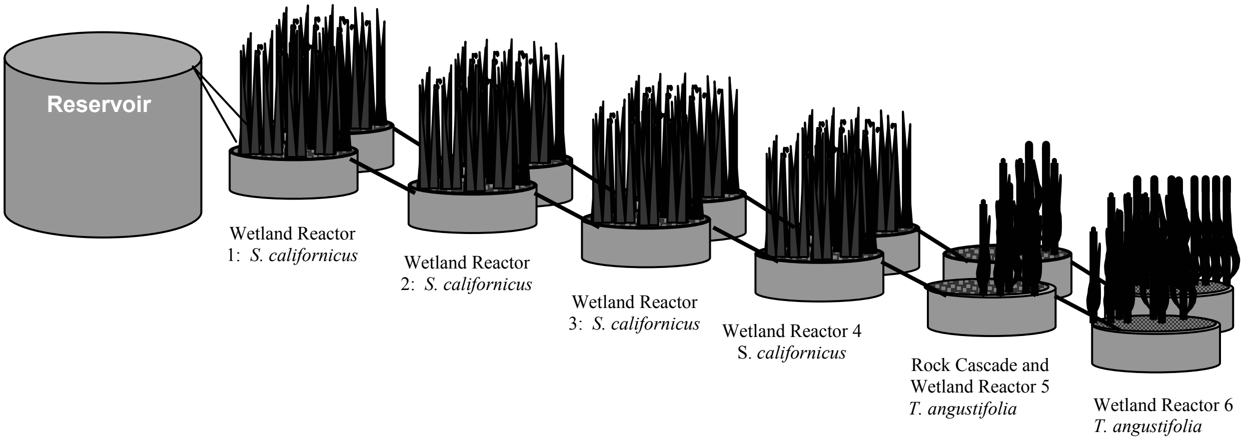


Figure 19. Schematic of the additional pilot-scale constructed wetland systems used for evaluating treatment of FGD water. All wetland reactors were planted in 100-gallon containers with a hydraulic retention time of 24-hr per wetland reactor.

Figure 20. Additional CWTS for FGD treatment.

Table 18. Initial elemental analysis of three subsamples of actual FGD water from shipping tanker. Concentrations are listed as mg/L.

Element	Top of Tanker	1st Purge from Rear Valve	2nd Purge from Rear Valve
B	**30.592**	**28.574**	**27.639**
C	9.978	7.937	7.575
Na	17.709	15.368	16.195
Mg	171.289	151.963	161.976
Al	0.840	0.142	0.112
Si	4.773	4.330	4.855
P	0.005	0.003	0.002
K	30.589	26.947	27.53
Ca	228.667	210.684	207.420
Cr	0.009	0.005	0.005
Mn	1.444	1.17	1.251
Fe	5.509	0.452	0.268
Co	0.020	0.014	0.015
Ni	0.131	0.095	0.099
Cu	0.010	0.006	0.007
Zn	0.184	0.111	0.107
As	**0.010**	**0.010**	**0.011**
Se	**0.049**	**0.057**	**0.046**
Br	1.479	1.434	1.569
Mo	0.911	0.912	0.974
Ag	ND	ND	0.017
Cd	0.017	0.016	0.171
Ba	0.156	0.143	0.003
Hg	**0.003**	**0.003**	**0.028**
Pb	0.004	0.002	0.002

Primary and other targeted constituents are presented in Tables 20-28. Removal rate coefficients and percent removals for arsenic, mercury and selenium by the pilot constructed wetland treatment systems are presented in Tables 29-36.

Removal of Constituents of Concern

Mercury Analysis

For the second week of treatment, the total mercury concentration in the equalization basin was 0.002794 mg/L, with inflow concentrations to the first wetland reactor averaging 0.002781 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.000091 mg/L for the second week of treatment. Removal of total mercury by CWTS was 96.74% at the final outflow (Figure 27) with a removal rate coefficient of 0.5749 d^{-1}.

For the third week of treatment, the total mercury concentration in the equalization basin was 0.000553 mg/L, with inflow concentrations to the first wetland reactor averaging 0.000517 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.000124 mg/L for the second week of treatment. Removal of total mercury by CWTS was 77.58% in the final outflow (Figure 28) with a removal rate coefficient of 0.2495 d^{-1}.

For the fourth week of treatment, the total mercury concentration in the equalization basin was 0.00079 mg/L, with inflow concentrations to the first wetland reactor averaging 0.000544 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.000104 mg/L for the second week of treatment. Removal of total mercury by CWTS was 86.93% in the final outflow (Figure 29) with a removal rate of 0.3394 d^{-1}.

For the sixth week of treatment, the total mercury concentration in the equalization basin was 0.00282 mg/L, with inflow concentrations to the first wetland reactor averaging 0.00132 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.00006 mg/L for the second week of treatment. Removal of total mercury by CWTS was 97.78% in the final outflow (Figure 31) with a removal rate coefficient of 0.6515 d^{-1}.

Additional CWTS

For the fifth week of treatment, the total mercury concentration in the equalization basin was 0.00157 mg/L, with inflow concentrations to the first wetland reactor averaging 0.00182 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.000168 mg/L for the second week of treatment. Removal of total mercury by CWTS was 89.28% in the final outflow (Figure 30) with a removal rate coefficient of 0.3730 d^{-1}.

For the seventh week of treatment, the total mercury concentration for the inflow samples to the first wetland reactor averaged 0.001632 mg/L. The mercury concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.000056 mg/L for the second week of treatment. Removal of total mercury by CWTS was 96.77% in the final outflow (Figure 32) with a removal rate coefficient of 0.5941 d^{-1}.

Selenium Analysis

For the second week of treatment, the total selenium concentration in the equalization basin was 0.0562 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0548 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.1725 mg/L for the second week of treatment. Percent removal and removal rate coefficient of total selenium by CWTS was not calculated due to evaluated selenium concentrations in final outflow samples (see discussion and conclusion section for explanatory hypothesis of this phenomenon).

For the third week of treatment, the total selenium concentration in the equalization basin was 0.0584 mg/L, with inflow concentrations to the first wetland reactor averaging 0.04987 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.1397 mg/L for the second week of treatment. Percent removal and removal rate coefficient of total selenium by CWTS was not calculated due to evaluated selenium concentrations in final outflow samples (see discussion and conclusion section for explanatory hypothesis of this phenomenon).

For the fourth week of treatment, the total selenium concentration in the equalization basin was 0.0522 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0502 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.08934 mg/L for the second week of treatment. Percent removal and removal rate coefficient of total selenium by CWTS was not calculated due to evaluated selenium concentrations in final outflow samples (see discussion and conclusion section for explanatory hypothesis of this phenomenon).

For the sixth week of treatment, the total selenium concentration in the equalization basin was 0.0531 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0520 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0473 mg/L for the second week of treatment. Removal of total selenium by CWTS was 28.97% in the final outflow with a removal rate coefficient of 0.07221 d^{-1}. Both series did not have similar percent removals or removal rate coefficients for total selenium. Series 2 had a percent removal of 57.95% in the final outflow with a removal rate coefficient of 0.1444 d^{-1}; however, series 1 did not have selenium removal greater than the inflow concentration to the CWTS (see discussion and conclusions section).

For the eighth week of treatment, the total selenium concentration in the equalization basin was 0.0458 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0428 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0293 mg/L for the second week of treatment. Removal of total selenium by CWTS was 39.45% in the final outflow (Figure 33) with a removal rate coefficient of 0.0743 d^{-1}.

Additional CWTS

For the fifth week of treatment, the total selenium concentration in the equalization basin was 0.0501 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0501 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0146 mg/L for the second week of treatment. Removal of total selenium by CWTS was 70.81% in the final outflow (Figure 30) with a removal rate coefficient of 0.2081 d^{-1}.

For the seventh week of treatment, the total selenium concentration for the inflow samples to the first wetland reactor averaging 0.0522 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0191 mg/L for the seventh week of treatment. Removal of total selenium by CWTS was 65.69% in the final outflow (Figure 32) with a removal rate coefficient of 0.1783 d^{-1}.

For the ninth week of treatment, the total selenium concentration in the equalization basin was 0.0435 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0423 mg/L. The selenium concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0066 mg/L for the second week of treatment. Removal of total selenium by CWTS was 84.6% in the final outflow (Figure10) with a removal rate coefficient of 0.3187 d^{-1}.

Arsenic Analysis

For the second week of treatment, the total arsenic concentration in the equalization basin was 0.0138 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0141 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.003 mg/L for the second week of treatment. Removal of total selenium by CWTS was 77.68% in the final outflow (Figure 27) with a removal rate coefficient of 0.2510 d^{-1}.

For the third week of treatment, the total arsenic concentration in the equalization basin was 0.0133 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0118 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0079 mg/L for the second week of treatment. Removal of total selenium by CWTS was 40.10% in the final outflow (Figure 28) with a removal rate coefficient of 0.0861 d^{-1}.

For the fourth week of treatment, the total arsenic concentration in the equalization basin was 0.0174 mg/L, with inflow concentrations to the first wetland reactor averaging 0.022 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0041 mg/L for the second week of treatment. Removal of total selenium by CWTS was 76.44% in the final outflow (Figure 29) with a removal rate coefficient of 0.2409 d^{-1}.

For the sixth week of treatment, the total arsenic concentration in the equalization basin was 0.0131mg/L, with inflow concentrations to the first wetland reactor averaging 0.0083 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.004 mg/L for the second week of treatment. Removal of total selenium by CWTS was 69.21% in the final outflow (Figure 31) with a removal rate coefficient of 0.1970 d^{-1}.

For the eighth week of treatment, the total arsenic concentration in the equalization basin was 0.00167 mg/L, with inflow concentrations to the first wetland reactor averaging 0.00165 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.00141 mg/L for the second week of treatment. Removal of total selenium by CWTS was 14.97% in the final outflow (Figure 33) with a removal rate coefficient of 0.0270 d^{-1}.

Additional CWTS

For the fifth week of treatment, the total arsenic concentration in the equalization basin was 0.0120 mg/L, with inflow concentrations to the first wetland reactor averaging 0.0177 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0067 mg/L for the second week of treatment. Removal of total arsenic by CWTS was 43.85% in the final outflow (Figure 30) with a removal rate coefficient of 0.0999 d^{-1}.

For the seventh week of treatment, the total arsenic concentration for the inflow samples to the first wetland reactor averaged 0.0098 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.0034 mg/L for the second week of treatment. Removal of total arsenic by CWTS was 66.77% in the final outflow (Figure 32) with a removal rate coefficient of 0.1838 d^{-1}.

For the ninth week of treatment, the total arsenic concentration in the equalization basin was 0.00158 mg/L, with inflow concentrations to the first wetland reactor averaging 0.00148 mg/L. The arsenic concentrations in the outflows of the pilot-scale constructed wetland system averaged 0.00058 mg/L for the second week of treatment. Removal of total arsenic by CWTS was 62.97% in the final outflow (Figure 34) with a removal rate coefficient of 0.1725 d^{-1}.

Total Nitrogen Analysis

For the second week of treatment, the total nitrogen concentration in the equalization basin was 11.91 mg/L, with inflow concentrations to the first wetland reactor averaging 12.47 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 1.59 mg/L for the second week of treatment. Removal of total selenium by CWTS was 86.65% in the final outflow (Figure 27) with a removal rate coefficient of 0.3356 d^{-1}.

For the third week of treatment, the total nitrogen concentration in the equalization basin was 12.12 mg/L, with inflow concentrations to the first wetland reactor averaging 12.55 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 1.36 mg/L for the second week of treatment. Removal of total selenium by CWTS was 88.78% in the final outflow (Figure 28) with a removal rate coefficient of 0.3655 d^{-1}.

For the fourth week of treatment, the total nitrogen concentration in the equalization basin was 13.01 mg/L, with inflow concentrations to the first wetland reactor averaging 11.80 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 5.72 mg/L for the second week of treatment. Removal of total selenium by CWTS was 56.02% in the final outflow (Figure 29) with a removal rate coefficient of 0.1378 d^{-1}.

For the sixth week of treatment, the total nitrogen concentration in the equalization basin was 9.772 mg/L, with inflow concentrations to the first wetland reactor averaging 9.50 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 1.83 mg/L for the second week of treatment. Removal of total selenium by CWTS was 69.21% in the final outflow (Figure 31) with a removal rate coefficient of 0.2792 d^{-1}.

For the eighth week of treatment, the total nitrogen concentration in the equalization basin was 13.20 mg/L, with inflow concentrations to the first wetland reactor averaging 13.35 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 1.36 mg/L for the second week of treatment. Removal of total selenium by CWTS was 89.69% in the final outflow (Figure 33) with a removal rate coefficient of 0.3784 d^{-1}.

Additional CWTS

For the fifth week of treatment, the total nitrogen concentration in the equalization basin was 13.98 mg/L, with inflow concentrations to the first wetland reactor averaging 13.32 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 6.61 mg/L for the second week of treatment. Removal of total nitrogen by CWTS was 43.85% in the final outflow (Figure 30) with a removal rate coefficient of 0.1268 d^{-1}.

For the seventh week of treatment, the total nitrogen concentration for the inflow samples to the first wetland reactor averaged 10.45 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 2.99 mg/L for the second week of treatment. Removal of total nitrogen by CWTS was 71.42% in the final outflow (Figure 32) with a removal rate coefficient of 0.2091 d^{-1}.

For the ninth week of treatment, the total nitrogen concentration in the equalization basin was 11.36 mg/L, with inflow concentrations to the first wetland reactor averaging 11.23 mg/L. The nitrogen concentrations in the outflows of the pilot-scale constructed wetland system averaged 2.09 mg/L for the second week of treatment. Removal of total nitrogen by CWTS was 81.53% in the final outflow (Figure 34) with a removal rate coefficient of 0.2837 d^{-1}.

Alkalinity, Hardness, pH, and Dissolved Oxygen

In review of general water characteristics for FGD water, such as pH, alkalinity, hardness, and dissolved oxygen, results were within ideal discharge limits (except hardness due to an elevated salinity of this water) after treatment with constructed wetland treatment systems.

Conductivity

Conductivity in the equalization basin for the first nine weeks of treatment was 4.34, 4.21, 4.15, 4.19, 4.11, 4.15, 4.34, and 4.17 mS/cm, respectively. Conductivity in the outflows of reactors 1, 2, 3, and 4 for the first four treatment weeks did not significantly vary from the equalization basin and changes can be attributed to two factors: evapo-transpiration (increased conductivity) and precipitation (decreased conductivity).

Biochemical Oxygen and Chemical Oxygen Demand

All observed 5-d biochemical oxygen demand values were less than 10 mg/L as O_2 consumption and should not pose a risk to receiving systems. Chemical oxygen demand values were greatest during treatment week one to three with a range of 13 to 151 mg/L as O_2 consumption, but significantly decreased to values less than 15 mg/L after treatment week three.

Solids

Total suspended solids (TSS) in the equalization basin for the first four weeks of treatment were 3.20 mg/L, 26.05 mg/L, 10.50 mg/L, and 3.40 mg/L, 2.10 mg/L, 2.30 mg/L, 3.10 mg/L, and 10.6 respectively. Outflow concentrations of TSS were relatively consistent, and were generally less than 15 mg/L. Total dissolved solids (TDS) in the equalization basin for the first four weeks of treatment were 4722 mg/L, 4814 mg/L, 4845 mg/L, 4817 mg/L, 4702 mg/L, 4948 mg/L, 4895 mg/L, and 4792 mg/L, respectively. TDS concentrations did not significantly differ from inflow to final outflow with only slight changes occurring due to climatic variations.

Chlorides

Chloride concentrations in the equalization basin for the first seven weeks of treatment were 1225 mg/L, 1250 mg/L, 1700 mg/L, 1600 mg/L, 1600 mg/L, 1700 mg/L, 1550 mg/L, and 1575 mg/L, respectively. Chloride concentrations in the outflows of reactors 1, 2, 3, 4, and 5 for the first seven treatment weeks did not significantly vary from the equalization basin.

Sulfates

Sulfate concentrations in the equalization basin for the first seven weeks of treatment were 1897 mg/L, 1539 mg/L, 1797 mg/L, 1701 mg/L, 1982 mg/L, and 1935 mg/L, 1572 mg/L, 1919 mg/L, respectively. Sulfate concentrations in the outflows of reactors 1, 2, 3, 4, and 5 for the first seven treatment weeks did not significantly vary from the equalization basin.

Hydrosoil Oxidation-Reduction Potential (Redox)

Redox potential of the hydrosoil in each wetland reactor of the pilot constructed wetland treatment system was recorded monthly. Redox potentials for the months of July, August, and September are illustrated in Figures 11-15.

Table 19. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week One

Week of 5-5-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
TVA Inflow	20.3	8.55	7.52	64	2000	3.94	1.04	69.0	11.80	5552	1475	1773	7.72	0.750	n/a	12.880	0.004669	0.0668	0.0055	29.37
TVA Train 1 Cell 1 Outflow	22.2	7.16	8.49	78	1900	4.51	4.97	81.9	12.50	5971	1425	1407	5.22	0.357	n/a	8.742	0.014185	0.2944	0.0406	25.59
TVA Train 2 Cell 1 Outflow	22.5	7.08	8.10	80	2100	4.6	4.32	69.0	17.80	6055	1550	1503	5.91	0.213	n/a	6.312	0.014583	0.2275	0.0361	35.80
TVA Train 1 Cell 2 Outflow	22.4	7.04	8.30	88	1900	4.69	3.86	77.6	12.30	5155	1550	1638	4.01	0.232	n/a	4.013	0.002197	0.3692	0.0485	35.14
TVA Train 2 Cell 2 Outflow	22.4	6.88	7.29	88	1800	4.63	3.44	68.4	21.40	5977	1750	1471	4.65	0.121	n/a	4.275	0.008954	0.2730	0.0501	32.30
TVA Train 1 Cell 3 Outflow	22.2	9.15	8.44	94	1600	4.88	4.3	60.4	10.70	6074	1600	1439	3.02	0.024	n/a	2.436	0.002348	0.2946	0.0492	37.19
TVA Train 2 Cell 3 Outflow	22.0	8.94	8.41	96	1500	4.73	4.43	62.6	28.10	5887	1725	1355	2.67	0.035	n/a	2.371	0.029379	0.2455	0.0407	28.76
TVA Train 1 Cell 4 Outflow	20.7	8.73	8.07	94	1600	5.1	1.9	34.7	12.00	6491	1775	1580	1.96	0.005	n/a	1.845	0.005275	0.2790	0.0328	31.34
TVA Train 2 Cell 4 Outflow	20.6	7.68	7.91	94	1600	4.97	1.83	39.0	24.30	6774	1850	1587	1.92	0.004	n/a	1.779	0.002829	0.2718	0.0225	23.90
TVA Train 1 Cell 5 Outflow	22.9	8.57	7.61	102	1200	4.22	5.37	30.4	3.70	5076	1675	1028	0.88	0.004	n/a	1.188	0.001559	0.1926	0.0172	21.99
TVA Train 2 Cell 5 Outflow	22.8	9.02	7.55	106	1300	4.46	3.3	30.4	1.20	5674	1725	1047	0.80	0.004	n/a	1.254	0.000985	0.2047	0.0134	17.69

Table 20. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Two

Week of 5-17-05	Temp ^{o}C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl$^-$ mg/L	NO$_3^-$ mg/L	NO$_2^-$ mg/L	NH$_3$ mg/L	Total N	SO$_4$ mg/L	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	24.1	7.5	7.49	60	3600	4.34	4.94	151	3.20	4722	1225	6.73	0.623	0.054	11.91	1897	0.002794	0.0562	0.0138	35.015
TVA Train 1 Inflow	25.1	8.7	7.44	58	3800	4.1	3.37	93	6.10	4425	1250	6.17	0.619	0.004	11.97	1811	0.002936	0.0539	0.0147	34.213
TVA Train 2 Inflow	24.8	8.87	7.43	60	3400	4.1	2.82	89	6.90	4739	1350	7.07	0.623	0.019	12.96	1998	0.002625	0.0558	0.0136	35.191
TVA Train 1 Cell 1 Outflow	22.4	8.4	7.45	60	3000	3.5	3.06	98	0.30	4123	1075	5.00	0.249	0.034	7.16	1674				
TVA Train 2 Cell 1 Outflow	22.2	8.7	7.75	64	2600	3.7	3.64	131	2.00	4279	1250	5.04	0.307	0.011	7.69	1607				
TVA Train 1 Cell 2 Outflow	22.6	8.52	7.77	72	2800	3.85	3.98	122	0.70	4275	1100	4.78	0.099	0.068	4.85	1646				
TVA Train 2 Cell 2 Outflow	22.6	9.55	8.08	70	3000	3.82	3.26	93	1.80	4394	1200	5.43	0.298	0.027	6.57	1717				
TVA Train 1 Cell 3 Outflow	22.4	7.97	7.68	82	2800	3.94	2.94	107	2.90	3731	1150	4.35	0.119	0.070	3.80	1763				
TVA Train 2 Cell 3 Outflow	22.4	8.09	7.63	84	2600	3.88	3.56	112	2.60	4476	1350	3.10	0.058	0.086	3.34	1843				
TVA Train 1 Cell 4 Outflow	22.5	7.84	7.67	84	3000	4.2	2.96	126	2.90	4914	1250	1.63	0.008	0.067	1.62	1833	0.000349	0.1617	0.0050	32.693
TVA Train 2 Cell 4 Outflow	22.6	7.92	7.81	82	2600	4.1	2.95	122	4.70	4810	1450	1.58	0.002	0.084	1.75	1747	0.000228	0.1456	0.0038	28.461
TVA Train 1 Cell 5 Outflow	22.5	8.28	7.64	76	2800	4.25	3.47	108	N/A	5010	1350	1.07	ND	0.049	1.62	1827	0.000111	0.1821	0.0034	20.344
TVA Train 2 Cell 5 Outflow	21.7	8.67	7.78	80	3000	4.08	2.26	122	0.10	4947	1400	2.36	0.001	0.038	1.56	1824	0.000071	0.1629	0.0027	29.303

Table 21. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Three

Week of 7-1-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	Total N	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	SO_4 mg/L	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	22.8	9.25	7.36	60	3000	4.21	4.13	27	26.05	4814	1250	6.73	0.218	12.12	N/A	1539	0.000553	0.0584	0.0133	34.157
TVA Train 1 Inflow	22.5	9.23	7.63	66	3600	4.22	3.54	20	7.85	4775	1300	6.17	0.087	11.26	N/A	1730	0.000470	0.0494	0.0117	32.371
TVA Train 2 Inflow	22.7	9.30	7.66	60	3200	4.18	4.12	20	8.45	4847	1225	7.07	0.094	13.83	N/A	1436	0.000563	0.0504	0.0121	34.278
TVA Train 1 Cell 1 Outflow	22.7	9.73	7.56	66	2600	3.85	1.81	23	4.05	4339	1275	5.00	0.018	7.77	N/A	1544	0.000346	0.0941	0.0098	29.212
TVA Train 2 Cell 1 Outflow	22.4	9.45	7.58	62	2800	3.73	2.17	17	1.45	4179	1300	5.04	0.021	7.49	N/A	1489	0.000272	0.0665	0.0103	28.389
TVA Train 1 Cell 2 Outflow	22.2	9.94	7.67	72	2400	3.91	2.63	13	1.85	4547	1400	4.78	0.014	7.35	N/A	1486				
TVA Train 2 Cell 2 Outflow	22.7	9.65	7.66	64	2800	3.86	2.55	20	1.05	4392	1375	5.43	0.010	9.27	N/A	1478				
TVA Train 1 Cell 3 Outflow	23.7	8.76	8.05	84	2800	4.14	3.07	30	2.95	4779	1500	4.35	0.012	4.71	N/A	1634	0.000361	0.1157	0.0131	31.314
TVA Train 2 Cell 3 Outflow	23.0	8.6	8.15	72	2800	3.75	3.4	17	4.45	4168	1325	3.10	0.024	5.71	N/A	1465	0.000368	0.1070	0.0119	30.122
TVA Train 1 Cell 4 Outflow	23.0	8.68	8.10	92	3000	4.61	3.08	27	2.05	5299	1425	1.63	0.218	3.85	N/A	1677	0.000373	0.1284	0.0107	32.111
TVA Train 2 Cell 4 Outflow	22.2	9.56	8.32	82	2600	4.1	3.86	34	3.25	4580	1450	1.58	0.218	3.36	N/A	1277	0.000227	0.1259	0.0098	30.989
TVA Train 1 Cell 5 Outflow	27.6	7.7	8.02	86	3000	4.82	8.24	23	3.15	5562	1475	1.07	0.002	1.22	N/A	1645	0.000132	0.1470	0.0087	21.913
TVA Train 2 Cell 5 Outflow	28.2	7.91	8.19	80	3000	4.11	5.03	23	6.45	4625	1525	2.36	0.002	1.50	N/A	1317	0.000116	0.1326	0.0072	18.059

Table 22. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Four

Week of 6-7-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	23.2	9.03	7.42	60	3000	4.15	1.45	3.0	10.50	4845	1700	1797	9.79	0.073	0.039	13.01	0.00079	0.0522	0.0174	35.528
TVA Train 1 Inflow	21.9	8.95	7.37	54	3000	4.17	1.06	6.0	4.60	4761	1725	1729	11.14	0.045	0.023	11.80	0.00061	0.0501	0.0229	33.341
TVA Train 2 Inflow	23.4	9.66	7.44	60	3600	4.08	1.19	15.0	5.20	4754	1625	1769	10.73	0.063	0.022	11.80	0.00047	0.0504	0.0211	33.891
TVA Train 1 Cell 1 Outflow	21.9	8.71	7.34	72	2800	4.11	1.21	0.0	8.10	4925	1700	1523	4.76	0.020	0.039	8.54	0.00047	0.1183	0.0096	31.334
TVA Train 2 Cell 1 Outflow	22.04	9.05	7.33	70	3600	4.11	1.38	9.0	10.50	4919	1550	1795	6.46	0.025	0.039	10.32	0.00038	0.0802	0.0140	34.236
TVA Train 1 Cell 2 Outflow																				
TVA Train 2 Cell 2 Outflow																				
TVA Train 1 Cell 3 Outflow	22.2	8.29	7.28	64	3800	3.15	2.6	3.0	9.50	3585	1500	1304	4.59	0.039	0.039	9.51	0.00025	0.0747	0.0145	24.071
TVA Train 2 Cell 3 Outflow	22.5	9.48	7.45	56	3600	3.11	2.09	3.0	6.00	3506	1450	1304	3.71	0.023	0.039	8.70	0.00031	0.0614	0.0125	24.995
TVA Train 1 Cell 4 Outflow	23.3	7.93	7.42	82	2200	3.54	1.99	6.0	13.80	4468	1400	1455	2.43	0.010	0.039	5.85	0.00025	0.0768	0.0152	27.839
TVA Train 2 Cell 4 Outflow	22.9	8.23	7.43	82	2200	3.54	2.56	9.0	7.00	4209	1425	1471	1.72	0.009	0.039	5.65	0.00026	0.0761	0.0186	28.286
TVA Train 1 Cell 5 Outflow	23	8.51	7.64	72	2400	3.56	1.85	6.0	5.80	4513	1525	1309	1.61	0.002	0.039	5.14	0.00010	0.0964	0.0041	17.077
TVA Train 2 Cell 5 Outflow	22.2	8.36	7.69	72	2200	3.42	3.04	9.0	7.30	4005	1675	1259	1.20	0.006	0.039	6.31	0.00011	0.0834	0.0041	27.878

Table 23. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Four

Week of 6-8-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	21.8	9.8	7.27	58	3000	4.19	1.66	6.0	3.40	4817	1600	1701	9.79	0.044	0.168	13.98	0.00157	0.0501	0.0120	31.383
CWTS Train 1 Inflow	21.7	13.84	8.03	62	2600	4.09	2.48	9.0	6.20	4961	1625	1633	7.86	0.038	0.052	13.42	0.00221	0.0496	0.0199	32.820
CWTS Train 2 Inflow	21.7	13.69	7.92	60	2800	4.09	2.62	9.0	2.80	4868	1625	1633	7.45	0.029	0.062	13.22	0.00143	0.0506	0.0157	31.241
CWTS Train 1 Cell 1 Outflow	21.8	7.54	7.19	68	2600	4.08	2.54	9.0	3.20	4805	1525	1533	4.12	0.137	0.341	8.85				
CWTS Train 2 Cell 1 Outflow	21.7	8.11	7.24	74	2600	3.93	2.61	12.0	5.70	4545	1600	1484	3.83	0.110	0.243	9.10				
CWTS Train 1 Cell 2 Outflow	21.7	8.68	7.01	88	2200	3.49	4.58	18.0	37.40	3988	1625	1152	3.30	0.040	0.770	6.26	0.00053	0.0298	0.0110	23.250
CWTS Train 2 Cell 2 Outflow	21.6	7.43	7.23	82	2200	3.28	3.04	9.0	9.10	3742	1650	1157	2.07	0.055	0.297	6.10	0.00099	0.0241	0.0092	22.261
CWTS Train 1 Cell 3 Outflow	22.2	8.44	7.13	66	1800	2.99	3.13	6.0	8.10	3505	1475	1058	3.42	0.091	0.471	5.60				
CWTS Train 2 Cell 3 Outflow	22.3	8.09	7.19	82	2000	3.1	3.23	9.0	7.00	3587	1450	1100	3.13	0.053	0.102	5.60				
CWTS Train 1 Cell 4 Outflow	21.9	8.69	7.33	92	1800	2.93	3.75	15.0	17.20	3269	1300	953	2.66	0.009	0.107	6.41	0.00053	0.0118	0.0100	18.389
CWTS Train 2 Cell 4 Outflow	21.9	7.45	7.19	82	2000	3.19	3.49	21.0	17.80	3524	1625	1089	1.61	0.004	0.047	6.36	0.00173	0.0115	0.0113	18.844
CWTS Train 1 Cell 5 Outflow	22.2	7.45	7.34	110	1800	3.11	5.85	15.0	21.90	3273	1500	833	3.89	0.017	0.082	6.41	0.00055	0.0113	0.0067	15.250
CWTS Train 2 Cell 5 Outflow	22.1	7.18	7.42	90	2000	3.63	4.5	24.0	7.70	3240	1700	791	2.25	0.013	0.220	6.36	0.00052	0.0148	0.0068	13.938
CWTS Train 1 Cell 6 Outflow	22	6.62	7.20	98	2000	3.14	6.48	27.0	19.90	3046	1700	726	3.36	0.020	0.021	5.60	0.00019	0.0119	0.0053	12.610
CWTS Train 2 Cell 6 Outflow	21.8	7.08	7.59	96	2400	4.39	7.05	27.0	15.80	4343	1725	747	2.07	0.015	0.033	7.63	0.00015	0.0173	0.0081	11.766

Table 24. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Six

Week of 6-17-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	22..2	8.23	7.26	56	2600	4.11	1.39	3.3	2.10	4702	1600	1982	11.91	0.000	0.0073	9.7725	0.00282	0.0531	0.0131	32.680
TVA Train 1 Inflow	22	8.46	7.53	56	3000	4.09	2.66	3.3	1.50	4728	1400	1626	10.32	0.044	0.0073	9.8227	0.00153	0.0525	0.0089	33.104
TVA Train 2 Inflow	21.9	8.57	7.45	54	2600	4.1	1.47	2.0	3.50	4586	1525	1969	10.58	0.045	0.0073	9.1693	0.00112	0.0517	0.0078	32.002
TVA Train 1 Cell 1 Outflow	22.9	8.91	7.48	64	4000	4.17	1.41	2.0	16.30	4886	1750	1923	4.20	0.007	0.0073	3.2379	0.00059	0.1156	0.0086	32.391
TVA Train 2 Cell 1 Outflow	23	9.18	7.48	82	3800	4.11	1.43	2.0	3.30	4888	1600	1892	3.94	0.008	0.0005	3.0871	0.00055	0.0844	0.0083	32.431
TVA Train 1 Cell 2 Outflow	22.8	8.88	7.72	82	4000	4.43	1.74	3.3	5.00	5163	1700	2043	3.18	0.018	0.0013	4.6956				
TVA Train 2 Cell 2 Outflow	22.8	9.27	7.71	86	4000	4.36	2.09	3.9	4.80	5373	1750	2034	3.63	0.015	0.0006	5.2988				
TVA Train 1 Cell 3 Outflow	22.1	8.44	7.57	110	4000	4.43	3.76	2.6	9.70	5435	1600	1873	1.46	0.020	0.0017	2.9865	0.00068	0.0799	0.0104	36.698
TVA Train 2 Cell 3 Outflow	22.3	8.2	7.60	114	4000	4.4	3.23	3.9	6.90	5529	1725	1746	0.88	0.012	0.0212	2.9363	0.00043	0.0721	0.0080	35.437
TVA Train 1 Cell 4 Outflow	21.9	8.05	7.68	112	4200	4.67	2.64	3.3	6.40	5835	1850	1907	0.44	0.003	0.0242	2.8357	0.00026	0.0935	0.0068	41.465
TVA Train 2 Cell 4 Outflow	22.1	8.25	7.67	112	4200	4.67	3.83	4.6	6.80	5653	1875	1907	0.82	0.002	0.0195	2.9363	0.00029	0.0838	0.0070	39.773
TVA Train 1 Cell 5 Outflow	23.3	6.98	7.40	98	4400	4.71	2.13	3.3	6.40	6017	1775	1941	0.12	0.003	0.0074	1.8304	0.00004	0.0723	0.0037	22.599
TVA Train 2 Cell 5 Outflow	23.4	7.07	7.45	100	4000	4.59	3.29	3.3	8.00	5597	1800	1879	0.37	0.004	0.0046	1.8304	0.00009	0.0223	0.0044	23.032

Table 25. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Seven

Week of 6-21-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
CWTS Train 1 Inflow	22.0	11.71	7.94	62	4000	4.15	1.45	3.3	2.30	4948	1700	1935	10.26	0.006	0.0013	9.47	0.00173	0.0559	0.0105	33.783
CWTS Train 2 Inflow	21.9	11.82	7.94	56	3800	4.12	1.23	3.3	3.30	5203	1750	1920	10.77	0.004	0.0010	11.43	0.00153	0.0487	0.0087	31.012
CWTS Train 1 Cell 1 Outflow	22.7	9.12	7.35	66	3800	4.09	1.26	2.0	6.40	4938	1700	1830	7.52	0.042	0.0007	9.02				
CWTS Train 2 Cell 1 Outflow	21.8	8.93	7.49	66	3800	4.06	1.42	7.9	13.30	5067	1675	1749	7.58	0.025	0.0017	8.52				
CWTS Train 1 Cell 2 Outflow	22.2	8.9	7.32	76	3800	4.07	2.43	9.2	5.30	4785	1800	1601	5.16	0.040	0.0015	4.70	0.00073	0.0414	0.0074	32.349
CWTS Train 2 Cell 2 Outflow	21.9	7.73	7.25	76	4000	3.99	1.55	3.3	6.00	4640	1800	1514	3.94	0.068	0.0017	3.84	0.00091	0.0354	0.0069	29.327
CWTS Train 1 Cell 3 Outflow	22.2	7.95	7.30	80	3800	4.04	1.76	2.6	7.00	4800	1775	1752	1.27	0.021	0.0018	2.48				
CWTS Train 2 Cell 3 Outflow	21.9	7.56	7.23	94	3800	4.18	1.97	4.6	11.30	5060	1725	1530	2.22	0.024	0.0023	3.39				
CWTS Train 1 Cell 4 Outflow	22.2	8.23	7.36	96	4000	4.22	2.09	3.3	18.40	5085	1650	1718	1.65	0.013	0.0005	2.89	0.00029	0.0157	0.0087	34.097
CWTS Train 2 Cell 4 Outflow	22.4	7.43	7.22	102	4000	4.21	3.11	3.3	12.60	5483	1650	1836	2.10	0.006	0.0010	4.19	0.00089	0.0123	0.0098	32.882
CWTS Train 1 Cell 5 Outflow	22.4	8.01	7.70	104	4000	4.59	6.55	4.6	15.50	5609	1875	1851	1.84	0.014	0.0007	1.73	0.00020	0.0201	0.0058	22.477
CWTS Train 2 Cell 5 Outflow	22.6	8.22	7.60	104	4200	4.69	3.8	3.3	39.10	5838	1900	1799	1.52	0.008	0.0016	2.48	0.00026	0.0182	0.0060	36.636
CWTS Train 1 Cell 6 Outflow	22.9	8.19	7.44	108	4200	4.96	6.86	5.2	17.30	5994	1975	1845	3.24	0.022	0.0019	3.19	0.00008	0.0194	0.0036	21.843
CWTS Train 2 Cell 6 Outflow	22.7	7.57	7.49	100	4200	4.92	5.64	4.6	11.10	5860	2025	1876	1.97	0.007	0.0016	2.79	0.00003	0.0189	0.0033	22.233

Table 26. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Eight

Week of 7-1-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	21.1	7.57	7.06	60	2800	4.34	8.4	0.0	3.10	4895	1550	1572	10.40	1.485	0.0348	13.2028		0.0458	0.00167	
TVA Train 1 Inflow	21.9	9.88	7.50	44	3000	4.23	1.11	0.7	3.10	4860	1725	1577	13.50	0.035	0.0395	13.2773		0.0433	0.00162	
TVA Train 2 Inflow	22.1	10.16	7.41	40	2800	4.22	5.02	0.7	2.80	4798	1600	1691	13.10	0.039	0.0348	13.4262		0.0424	0.00169	
TVA Train 1 Cell 1 Outflow	21.7	10.44	7.44	60	2800	4.31	5.29	3.3	4.20	5024	1525	1590	8.10	0.005	0.0240	7.9914		0.0644	0.00367	
TVA Train 2 Cell 1 Outflow	21.8	9.9	7.40	60	2800	4.34	1.08	1.3	4.60	4932	1700	1737	6.40	0.003	0.0529	8.0658		0.0562	0.00284	
TVA Train 1 Cell 2 Outflow	21.5	9.78	7.52	70	2800	4.32	6.64	2.0	3.20	4999	1775	1643	6.10	0.006	0.0186	7.0236		0.0743	0.00464	
TVA Train 2 Cell 2 Outflow	21.1	10.07	7.44	72	1800	4.3	2.37	2.6	4.10	5075	1650	1714	5.60	0.009	0.0306	5.9813		0.0562		
TVA Train 1 Cell 3 Outflow	21.1	9.54	7.35	36	1600	2.72	2.58	1.3	5.20	2853	1800	1043	3.80	0.010	0.1287	3.8967		0.0584	0.00172	
TVA Train 2 Cell 3 Outflow	21.0	9.15	7.36	44	1000	2.76	3.71	0.0	3.60	2982	1550	1070	2.50	0.013	0.0812	2.7055		0.0339	0.00140	
TVA Train 1 Cell 4 Outflow	21.5	9.43	7.45	36	1000	2.27	1.83	0.0	3.20	2352	1750	972	2.90	0.008	0.0390	2.5566		0.0278	0.00178	
TVA Train 2 Cell 4 Outflow	21.8	9.31	7.47	52	2000	2.78	2.89	1.3	3.40	3115	1650	1136	1.00	0.009	0.0388	1.9610		0.0303	0.00152	
TVA Train 1 Cell 5 Outflow	21.9	9.54	7.73	50	1600	2.69	4.16	1.3	3.80	3047	1825	1040	0.50	0.005	0.0476	1.4399		0.0286	0.00144	
TVA Train 2 Cell 5 Outflow	22.0	8.93	7.60	58	1600	2.95	7.64	2.0	4.40	3238	1525	1179	0.30	0.002	0.0497	1.2910		0.0301	0.00140	

Table 27. Analytical results of FGD water constituents and parameters monitored in the pilot-scale constructed wetland system for Treatment Week Nine

Week of 7-9-05	Temp °C	DO mg/L	pH	Alk mg/L	Hard mg/L	Cond mS/cm	BOD mg/L	COD mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	SO_4 mg/L	NO_3^- mg/L	NO_2^- mg/L	NH_3 mg/L	Total N	Hg mg/L	Se mg/L	As mg/L	B mg/L
Equalization Basin	22.3	9.04	7.45	52	3000	4.17	1.01	1.3	10.6	4792	1575	1919	10.70	0.010	0.0255	11.3625		0.04351	0.00158	
CWTS Train 1 Inflow	22.2	8.98	7.27	44	2600	4.23	1.13	1.5	n/a	4727	1550	2100	10.60	0.031	0.0182	11.5472		0.04233	0.00148	
CWTS Train 2 Inflow	22.1	8.94	7.54	68	2600	4.23	1.15	1.3	0.3	4684	1750	2042	10.90	0.023	0.0155	10.9317		0.04225	0.00149	
CWTS Train 1 Cell 1 Outflow	22.1	8.67	7.46	64	2000	2.98	1.88	0.0	3.6	3176	1500	1396	5.00	0.017	0.0129	5.8230		0.02341	0.00032	
CWTS Train 2 Cell 1 Outflow	22.1	9.07	7.37	78	2400	4.00	1.94	1.3	5.9	3793	1825	1955	8.60	0.034	0.0174	8.4081		0.03125	0.00054	
CWTS Train 1 Cell 2 Outflow	22.1	8.40	7.49	62	2200	3.34	1.54	0.0	6.9	3557	1775	1661	4.20	0.023	0.0131	4.0380		0.02559	0.00086	
CWTS Train 2 Cell 2 Outflow	22.2	9.01	7.57	80	2400	3.62	1.77	0.0	2.1	4040	1625	1668	2.90	0.017	0.0132	3.0532		0.02618	0.00087	
CWTS Train 1 Cell 3 Outflow	22.3	8.36	7.45	38	2200	3.36	2.83	3.8	12.8	3584	1625	1266	1.80	0.007	0.0205	2.1914				
CWTS Train 2 Cell 3 Outflow	22.3	8.76	7.49	60	2400	3.94	2.79	1.3	8.2	4558	1850	1773	0.72	0.008	0.0127	2.5608				
CWTS Train 1 Cell 4 Outflow	22.2	8.28	7.36	108	2000	3.08	1.31	1.3	3.3	2830	1550	1360	1.70	0.003	0.0165	1.6990		0.01014	0.00109	
CWTS Train 2 Cell 4 Outflow	22.0	7.94	7.37	58	2400	3.86	1.17	1.3	3.5	4737	1825	1799	0.80	0.003	0.0215	3.3609		0.01644	0.00172	
CWTS Train 1 Cell 5 Outflow	21.8	8.03	7.37	42	1800	2.98	1.54	0.0	n/a	3110	1675	1077	0.76	0.001	0.0185	3.4840		0.00652	0.00058	
CWTS Train 2 Cell 5 Outflow	21.3	8.61	7.52	52	2200	3.65	3.45	1.3	2.4	4103	1775	1436	0.99	0.003	0.0172	2.2530		0.0080	0.00088	
CWTS Train 1 Cell 6 Outflow	21.7	7.80	7.50	42	1800	2.91	1.93	1.3	4.6	3236	1600	1026	0.25	0.004	0.0188	1.7606		0.00484	0.00042	
CWTS Train 2 Cell 6 Outflow	21.7	8.29	7.49	46	2000	3.65	3.39	1.3	7.7	4094	1900	1454	0.63	0.004	0.0279	2.4377		0.00848	0.00075	

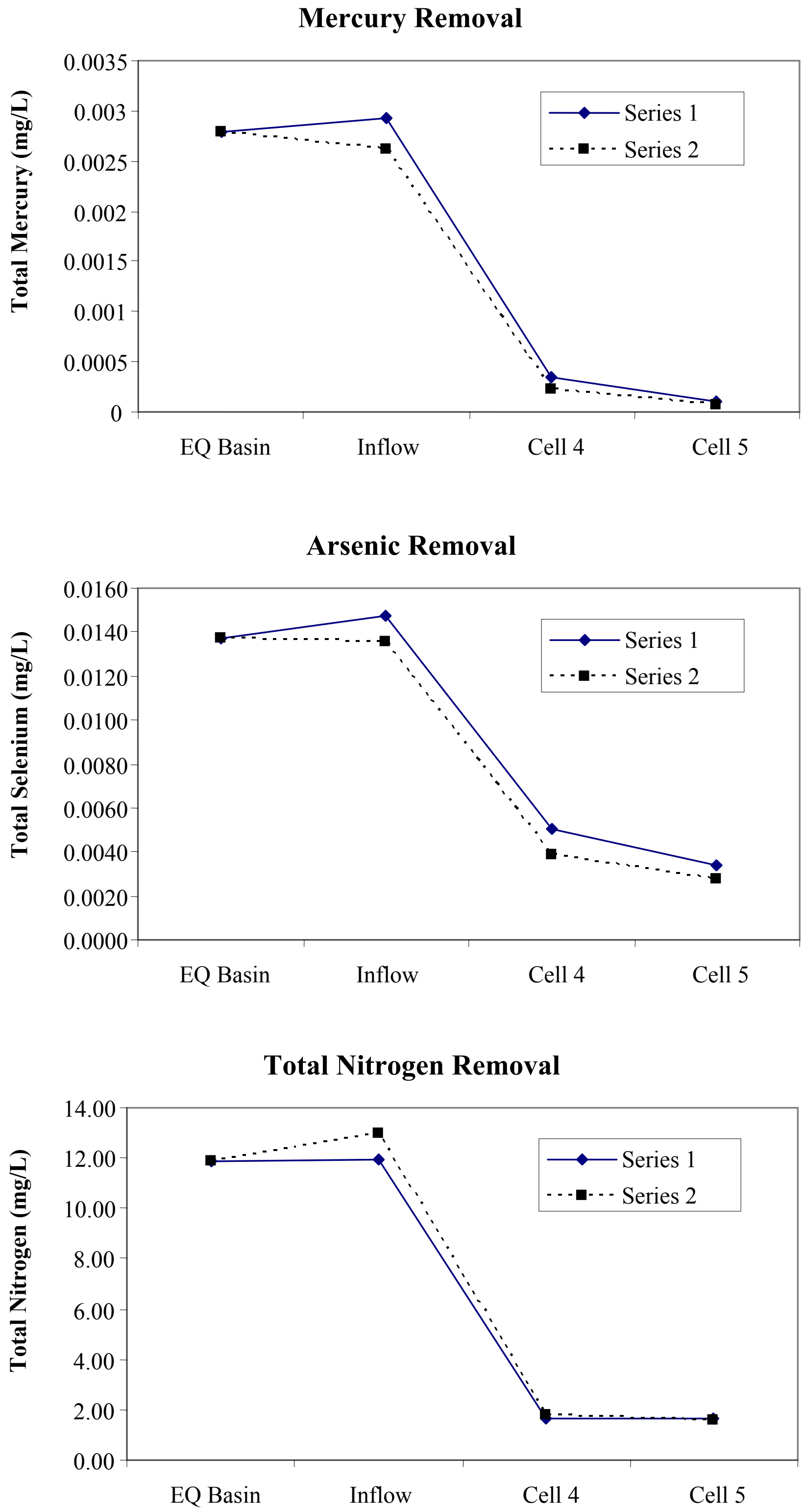
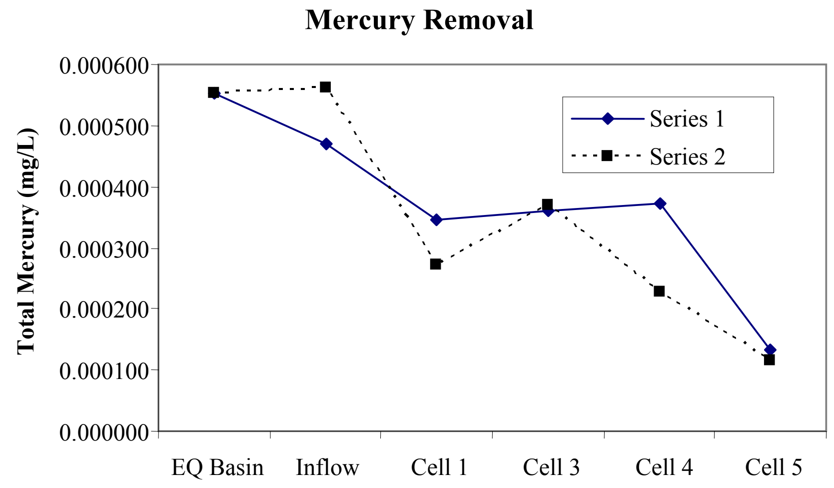
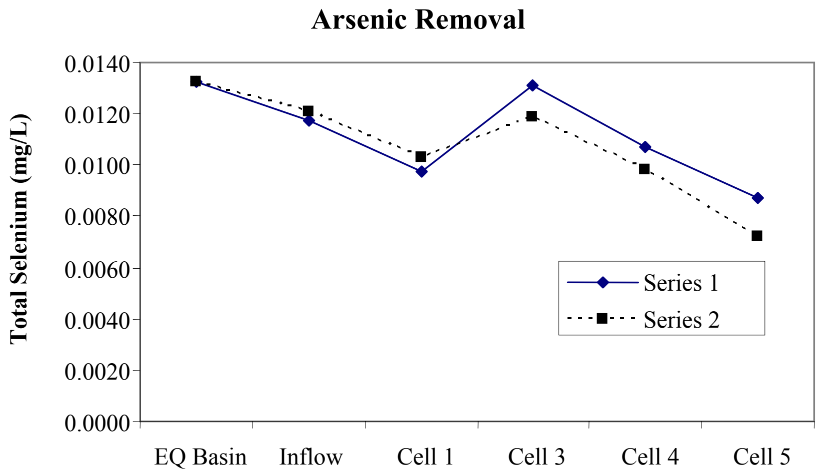


Figure 21. Average total mercury, arsenic, and nitrogen removal for Treatment Week Two by the initial pilot-scale constructed wetland treatment system





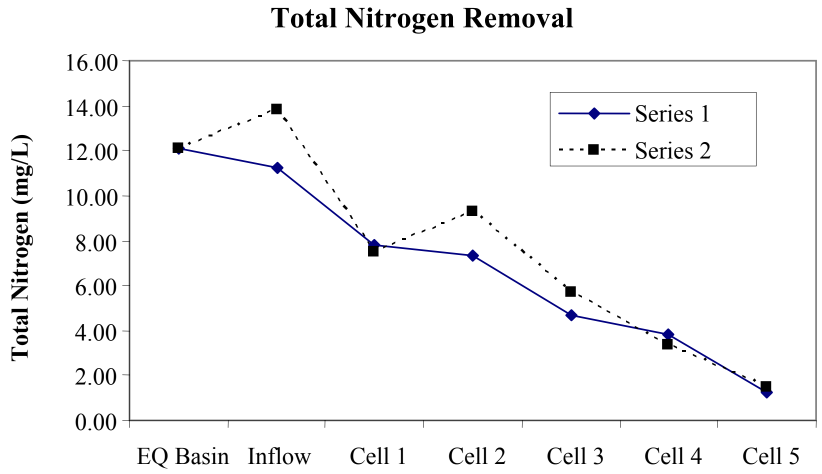
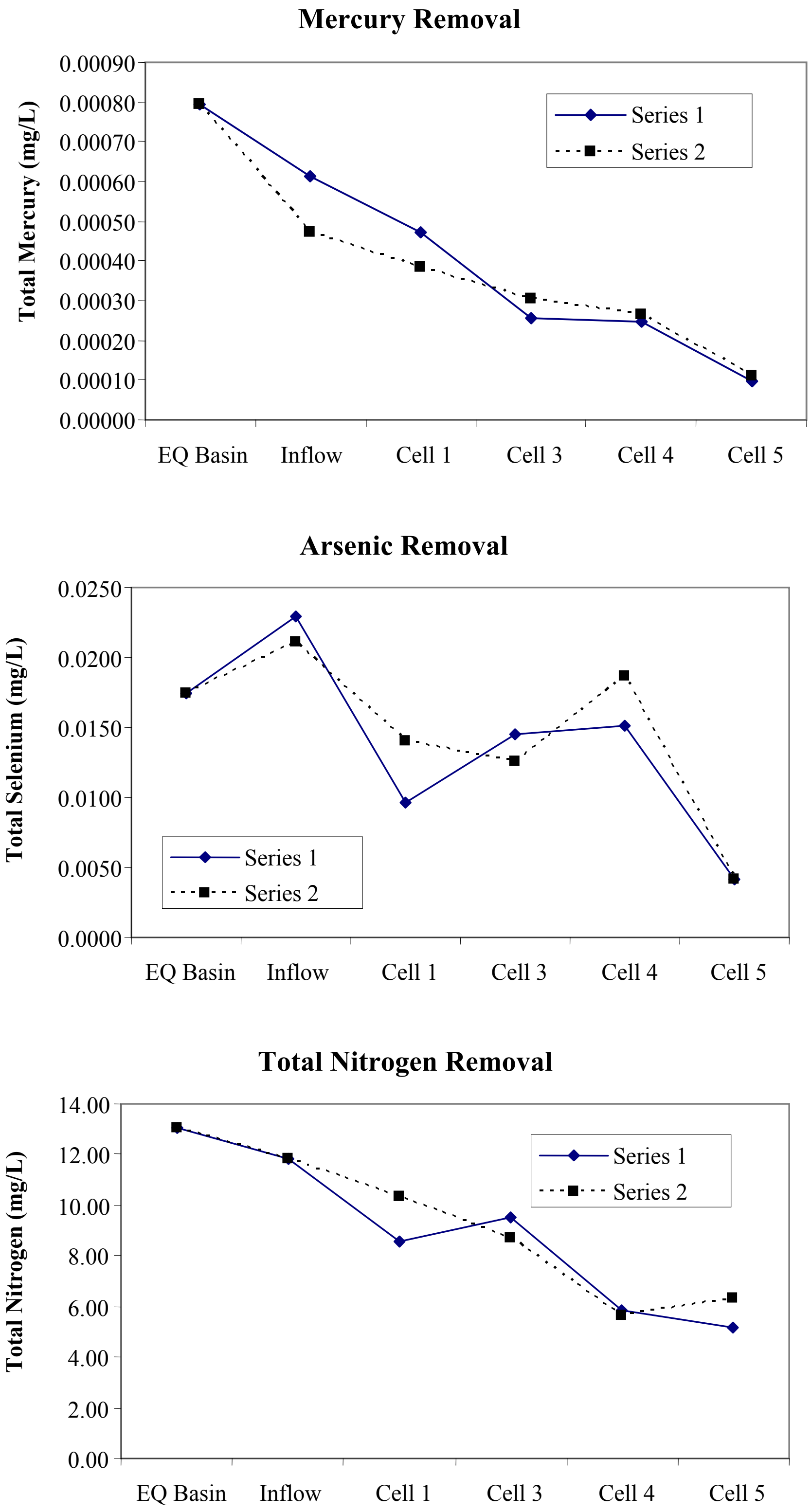


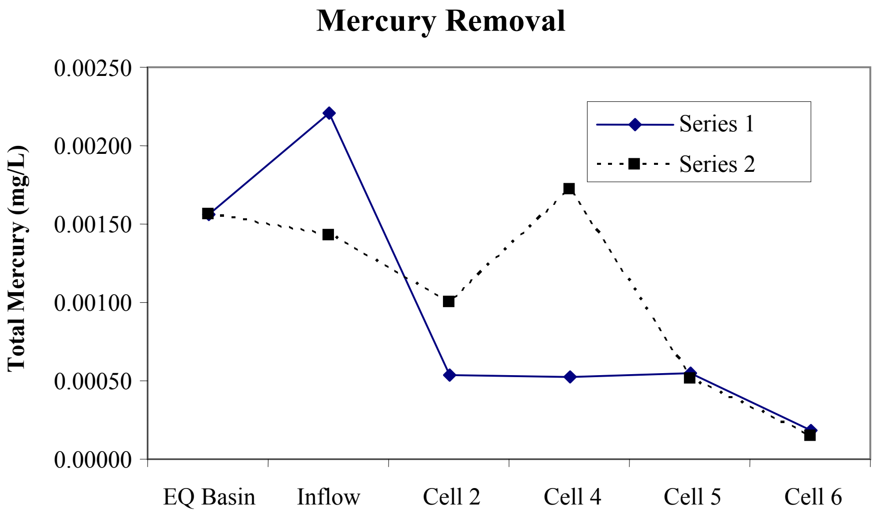
Figure 22. Average total mercury, arsenic, and nitrogen removal for Treatment Week Three by the initial pilot-scale constructed wetland treatment system

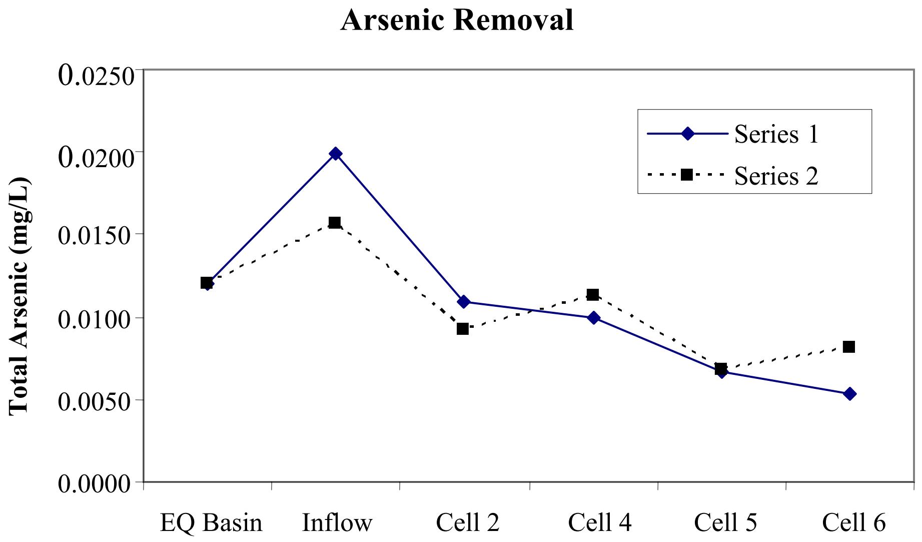

Mercury Removal

Arsenic Removal

Total Nitrogen Removal

Figure 23. Average total mercury, arsenic, and nitrogen removal for Treatment Week Four by the initial pilot-scale constructed wetland treatment system


Mercury Removal
Total Mercury (mg/L)
0.00250
0.00200
0.00150
0.00100
0.00050
0.00000
EQ Basin
Inflow
Cell 2
Cell 4
Cell 5
Cell 6
Series 1
Series 2


Arsenic Removal
Total Arsenic (mg/L)
0.0250
0.0200
0.0150
0.0100
0.0050
0.0000
EQ Basin
Inflow
Cell 2
Cell 4
Cell 5
Cell 6
Series 1
Series 2

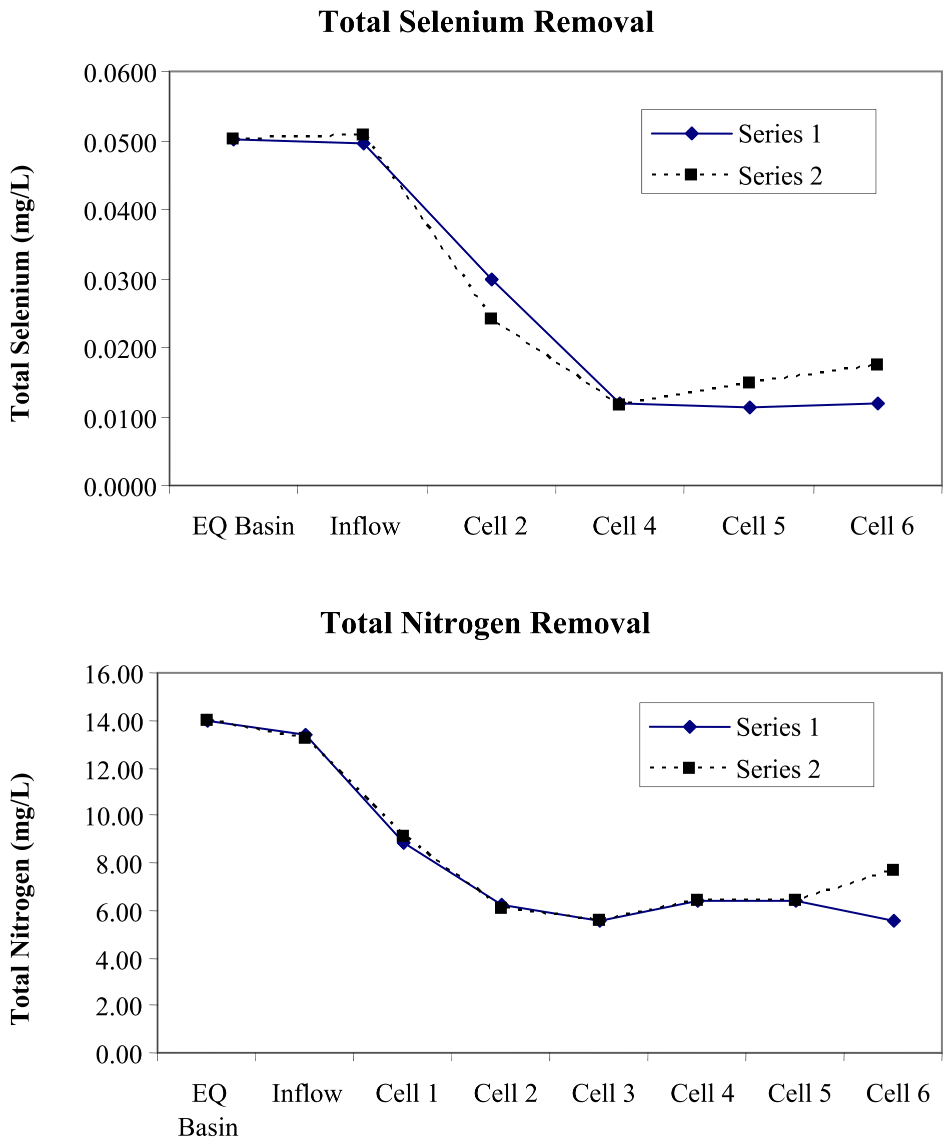


Figure 24. Average total mercury, arsenic, selenium and nitrogen removal for Treatment Week Five by the initial pilot-scale constructed wetland treatment system

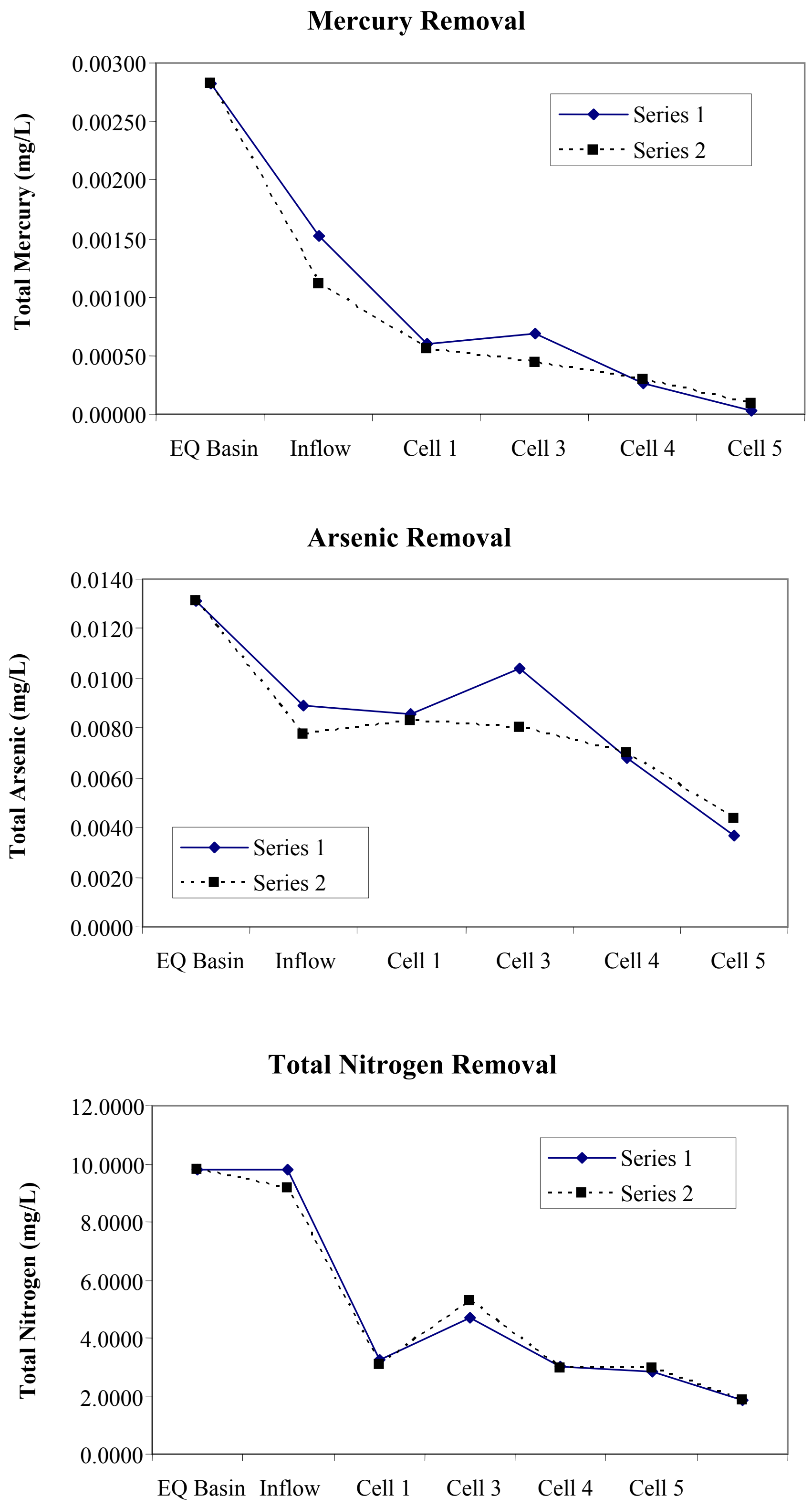
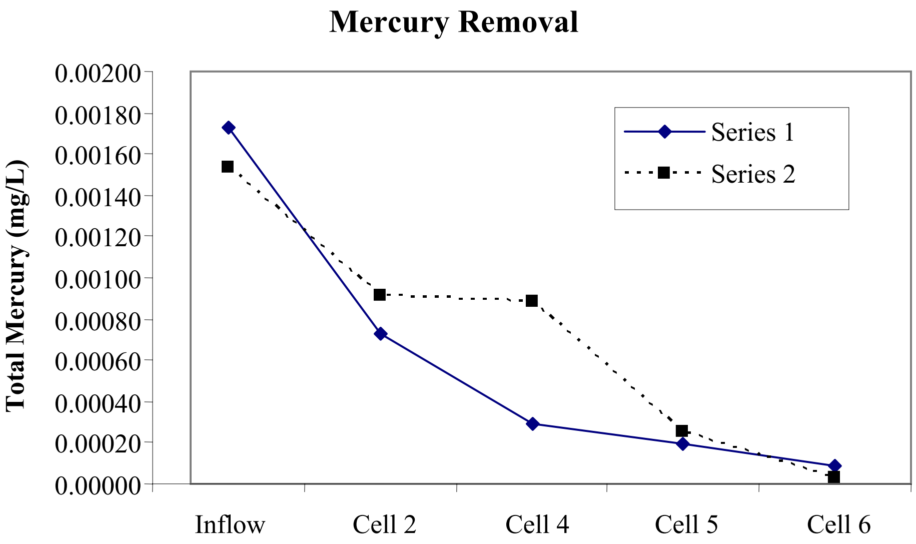
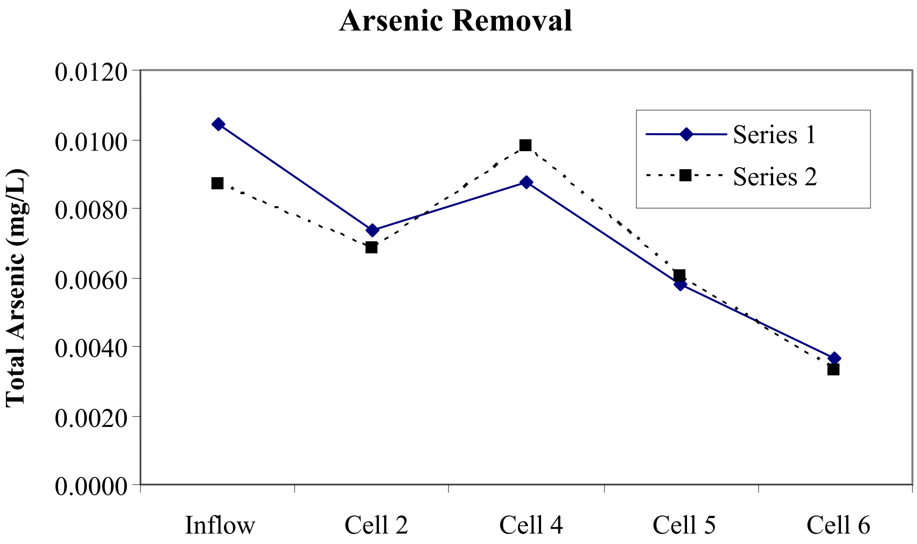
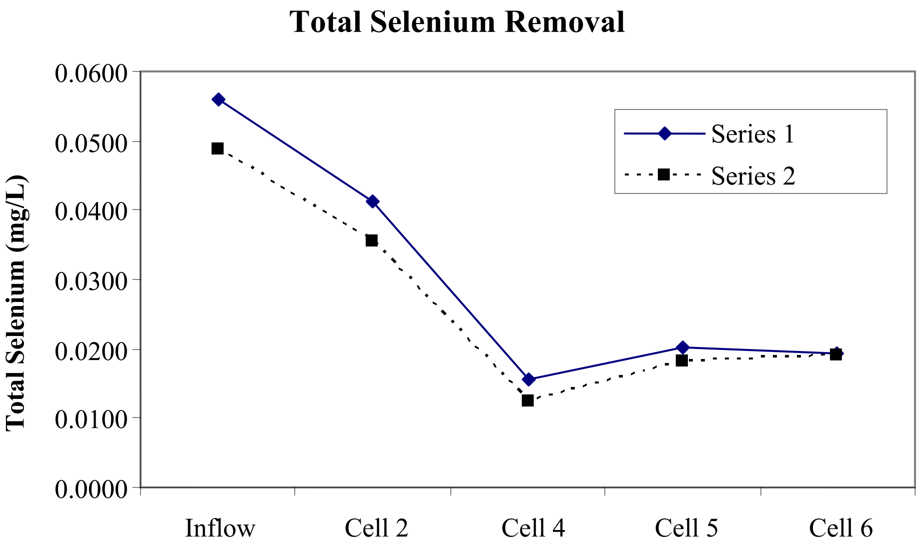


Figure 25. Average total mercury, arsenic, and nitrogen removal for Treatment Week Six by the initial pilot-scale constructed wetland treatment system


Mercury Removal
Total Mercury (mg/L)
0.00200
0.00180
0.00160
0.00140
0.00120
0.00100
0.00080
0.00060
0.00040
0.00020
0.00000
Inflow
Cell 2
Cell 4
Cell 5
Cell 6
Series 1
Series 2


Arsenic Removal
Total Arsenic (mg/L)
0.0120
0.0100
0.0080
0.0060
0.0040
0.0020
0.0000
Inflow
Cell 2
Cell 4
Cell 5
Cell 6
Series 1
Series 2



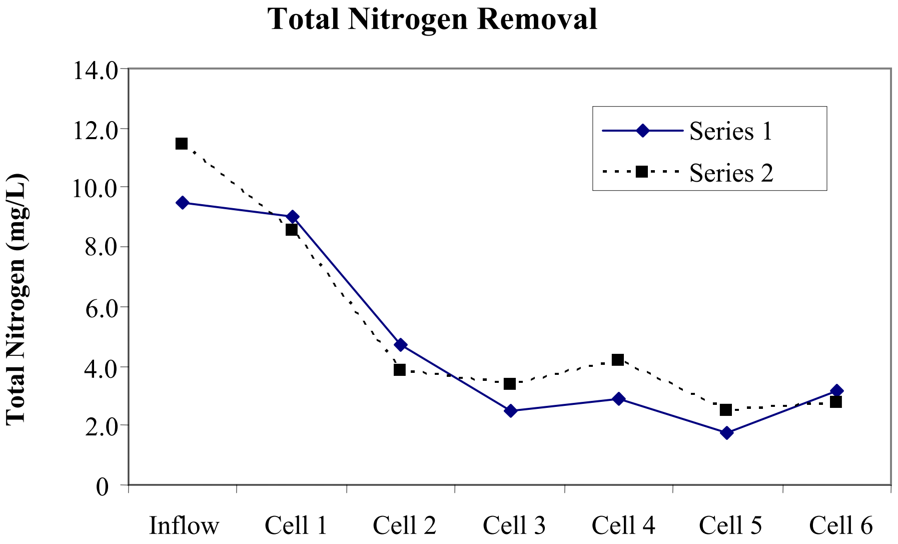
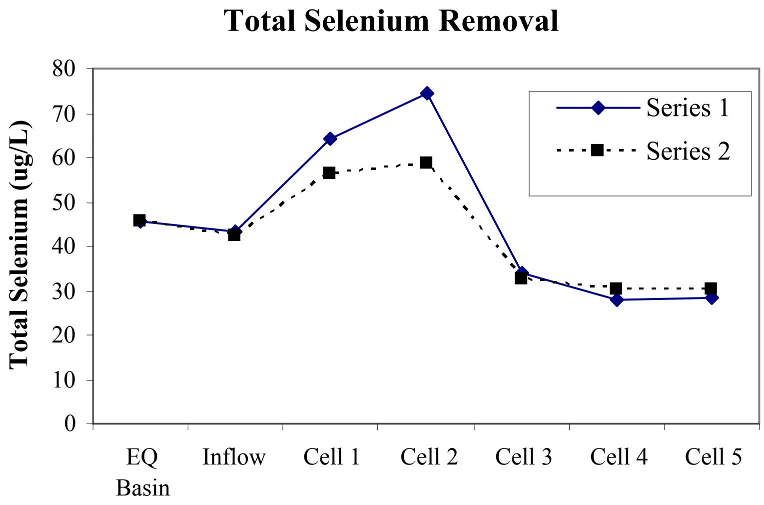
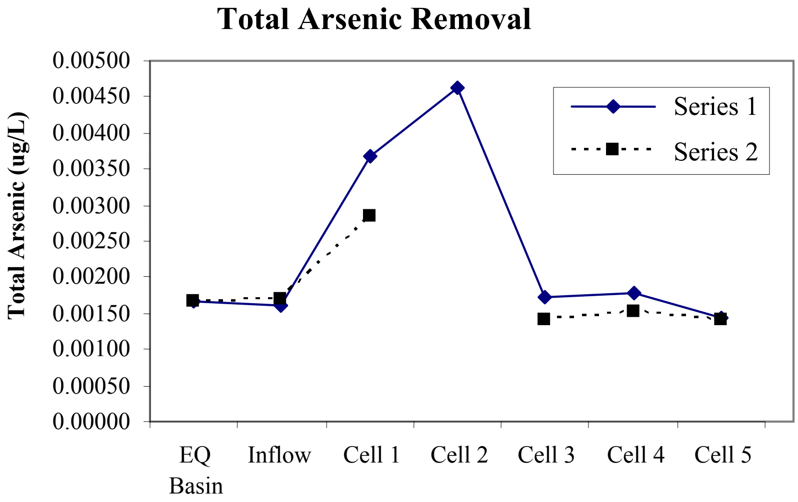


Figure 26. Average total mercury, arsenic, selenium and nitrogen removal for Treatment Week Seven by the initial pilot-scale constructed wetland treatment system





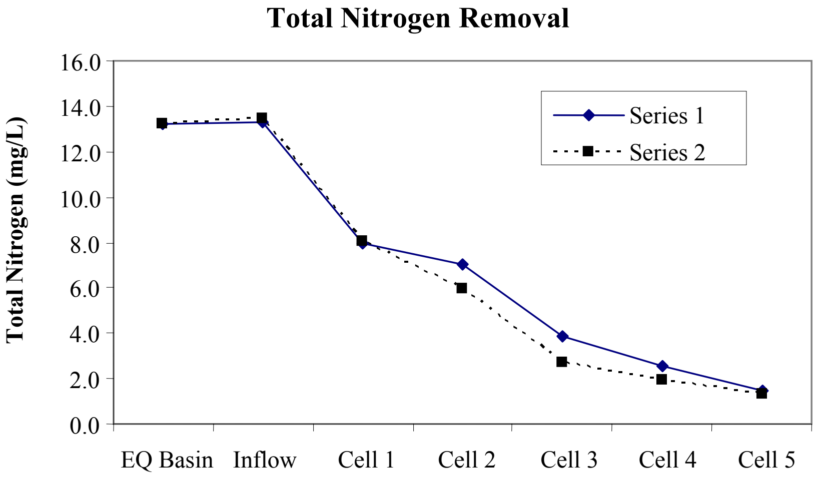


Figure 27. Average total selenium, arsenic, and nitrogen removal for Treatment Week Eight by the initial pilot-scale constructed wetland treatment system

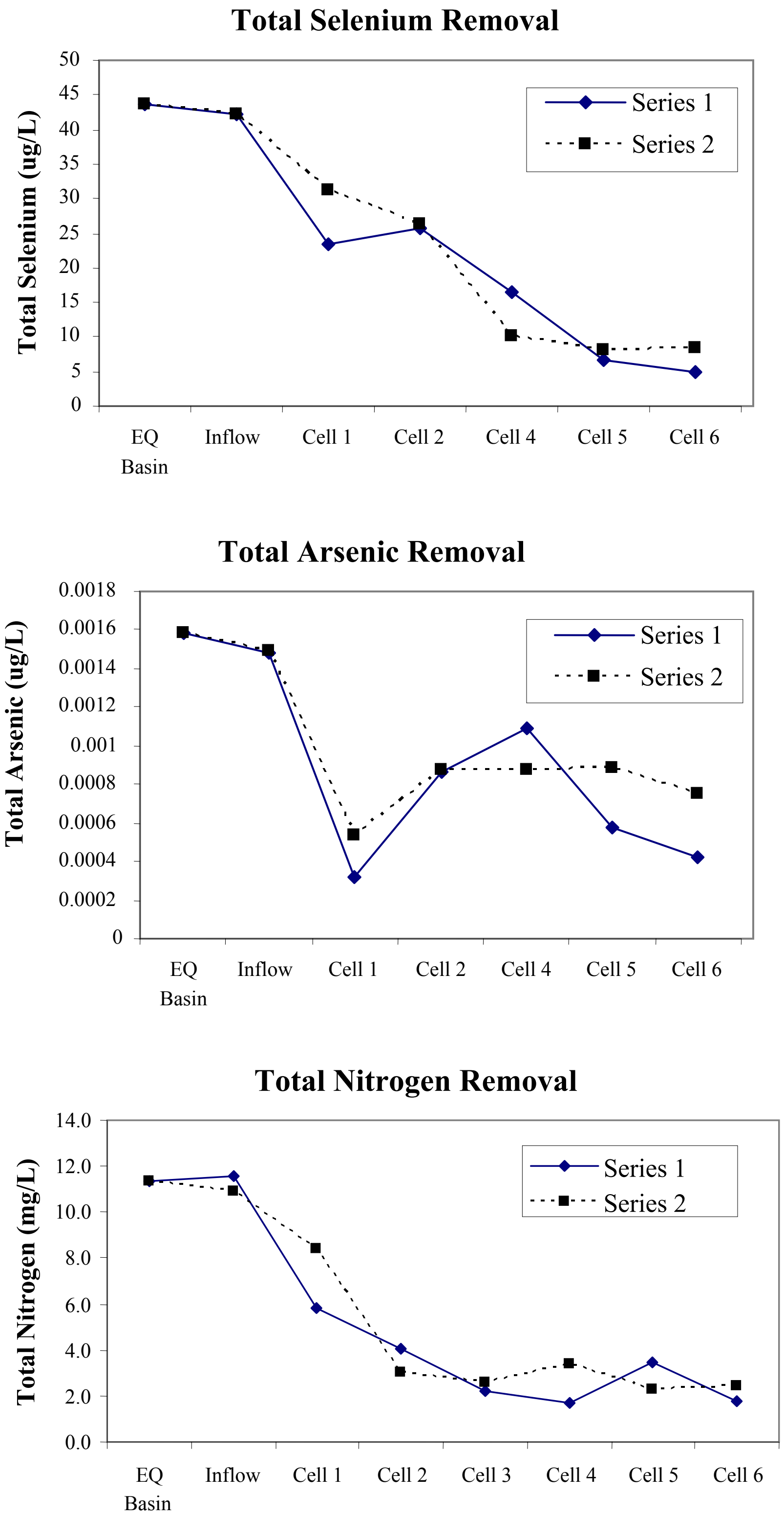


Figure 28. Average total selenium, arsenic, and nitrogen removal for Treatment Week Nine by the initial pilot-scale constructed wetland treatment system

Table 28. Percent removals and rate coefficients of removal of arsenic, mercury and selenium in the FGD water. Results were from Treatment Week Two

Week Two	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se[b]**	**As**	**Hg**	**Se**	**As**
Series 1	96.03%	NR	75.24%	0.5376	NR	0.2327
Series 2	97.46%	NR	80.12%	0.6121	NR	0.2693
CWTS Average	**96.74%**	**NR**	**77.68%**	**0.5749**	**NR**	**0.2510**

[a] First order rate of removal.

[b] No removal observed.

Table 29. Percent removals and rate coefficients of removal of arsenic, mercury and selenium in the FGD water. Results were from Treatment Week Three.

Week Three	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se[b]**	**As**	**Hg**	**Se**	**As**
Series 1	76.13%	NR	34.47%	0.2388	NR	0.0704
Series 2	79.02%	NR	45.73%	0.2603	NR	0.1019
CWTS Average	**77.58%**	**NR**	**40.10%**	**0.2495**	**NR**	**0.0861**

[a] First order rate of removal.

[b] No removal observed.

Table 30. Percent removals and rate coefficients of removal of arsenic, mercury and selenium in the FGD water. Results were from Treatment Week Four

Week Four	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se[b]**	**As**	**Hg**	**Se**	**As**
Series 1	87.63%	NR	76.45%	0.3483	NR	0.2410
Series 2	86.24%	NR	76.43%	0.3305	NR	0.2409
CWTS Average	**86.93%**	**NR**	**76.44%**	**0.3394**	**NR**	**0.2409**

[a] First order rate of removal.

[b] No removal observed.

Table 31. Percent removals and rate coefficients of removal of arsenic, mercury and selenium in the FGD water. Results were from Treatment Week Five

Week Five	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se[b]**	**As**	**Hg**	**Se**	**As**
Series 1	88.19%	76.19%	55.65%	0.3561	0.2392	0.1355
Series 2	90.36%	65.43%	32.05%	0.3899	0.1770	0.0644
CWTS Average	**89.28%**	**70.81%**	**43.85%**	**0.3730**	**0.2081**	**0.0999**

[a] First order rate of removal.

Table 32. Percent removals and rate coefficients of removal of arsenic, mercury and selenium in the FGD water. Results were from Treatment Week Six

Week Six	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se**	**As**	**Hg**	**Se**	**As**
Series 1	98.72%	NR	71.83%	0.7269	NR	0.2112
Series 2	96.85%	57.95%	66.60%	0.5760	0.1444	0.1828
CWTS Average	**97.78%**	**28.97%**	**69.21%**	**0.6515**	**0.0722**	**0.1970**

[a] First order rate of removal.

Table 33. Percent removals and rate coefficients of removal of arsenic, mercury, and selenium in the FGD water. Results were from Treatment Week Seven

Week Seven	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Hg	**Se**	**As**	**Hg**	**Se**	**As**
Series 1	95.21%	65.23%	65.32%	0.5065	0.1761	0.1765
Series 2	98.33%	66.15%	68.21%	0.6817	0.1806	0.1910
CWTS Average	**96.77%**	**65.69%**	**66.77%**	**0.5941**	**0.1783**	**0.1838**

[a] First order rate of removal.

Table 34. Percent removals and rate coefficients of removal of arsenic, nitrogen, and selenium in the FGD water. Results were from Treatment Week Eight

Week Eight	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Se	**As**	**N**	**Se**	**As**	**N**
Series 1	37.63%	13.77%	89.09%	0.0787	0.0247	0.3693
Series 2	34.26%	16.17%	90.22%	0.0699	0.0294	0.3875
CWTS Average	**35.94%**	**14.97%**	**89.66%**	**0.0743**	**0.0270**	**0.3784**

[a] First order rate of removal.

Table 35. Percent removals and rate coefficients of removal of arsenic, nitrogen, and selenium in the FGD water. Results were from Treatment Week Nine

Week Nine	**% Removal**			**Rate of Removal[a] (d^{-1})**		
	Se	**As**	**N**	**Se**	**As**	**N**
Series 1	88.83%	73.42%	84.51%	0.3653	0.2208	0.3108
Series 2	80.45%	52.53%	78.55%	0.2720	0.1242	0.2565
CWTS Average	**84.64%**	**62.97%**	**81.53%**	**0.3187**	**0.1725**	**0.2837**

[a] First order rate of removal.

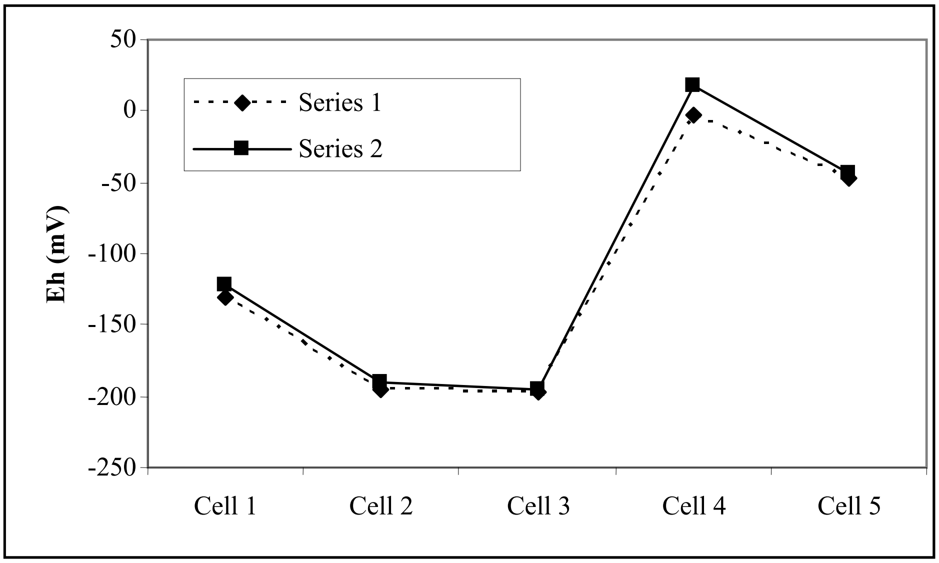


Figure 29. Oxidation-reduction potential of the initial pilot-scale constructed wetland treatment system hydrosoil in the five wetland reactors for the month of July 2006

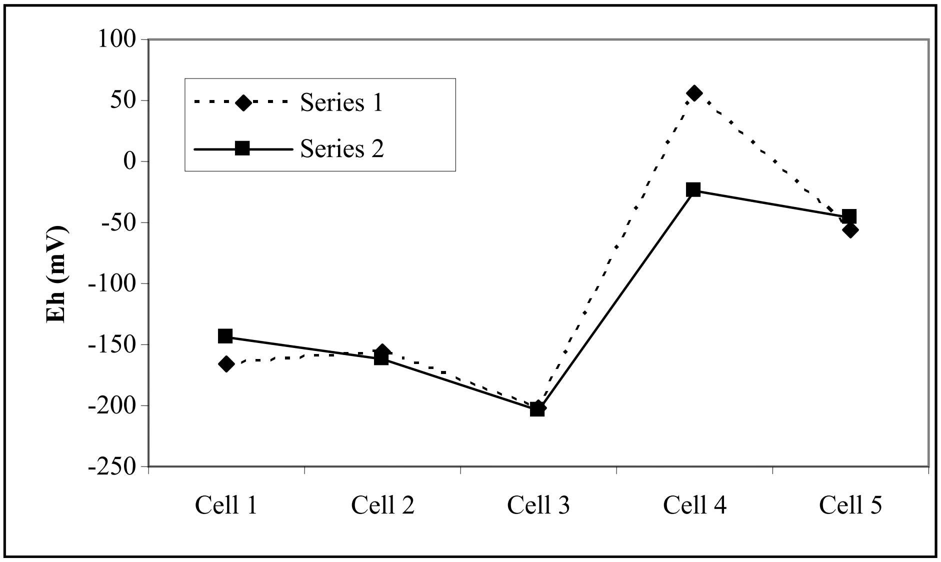


Figure 30. Oxidation-reduction potential of the initial pilot-scale constructed wetland treatment system hydrosoil in the five wetland reactors for the month of August 2006

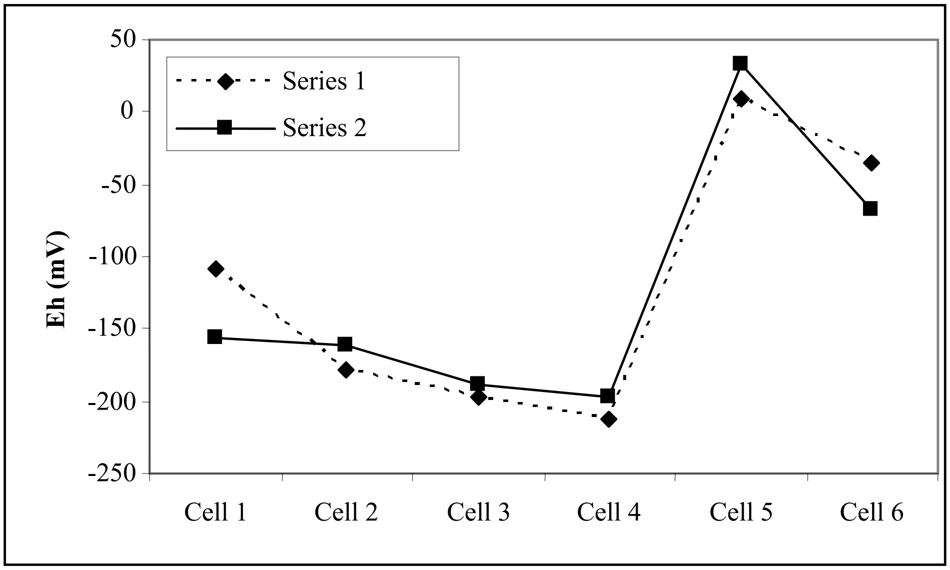


Figure 31. Oxidation-reduction potential of the additional pilot-scale constructed wetland treatment system hydrosoil in the six wetland reactors for the month of August 2006

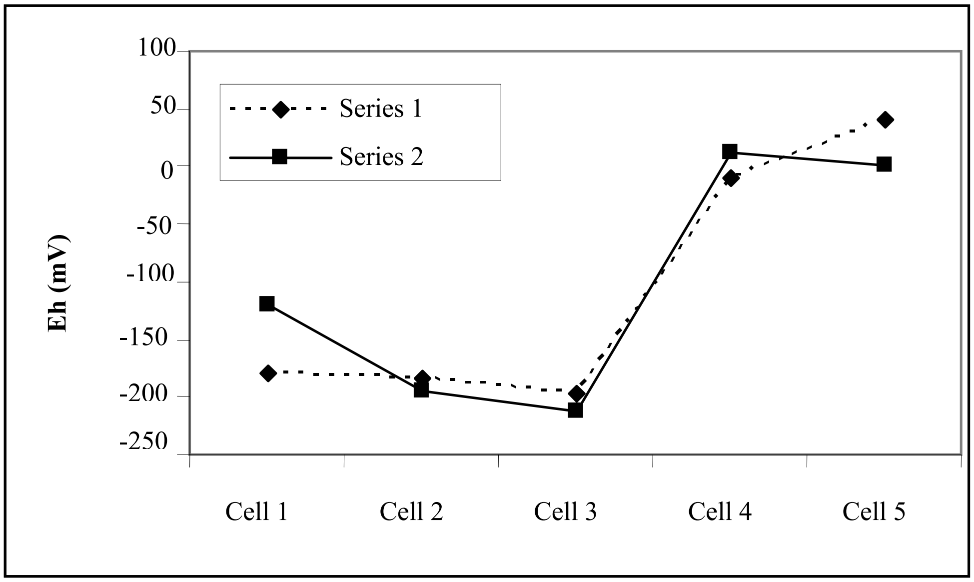


Figure 32. Oxidation-reduction potential of the initial pilot-scale constructed wetland treatment system hydrosoil in the five wetland reactors for the month of September 2006

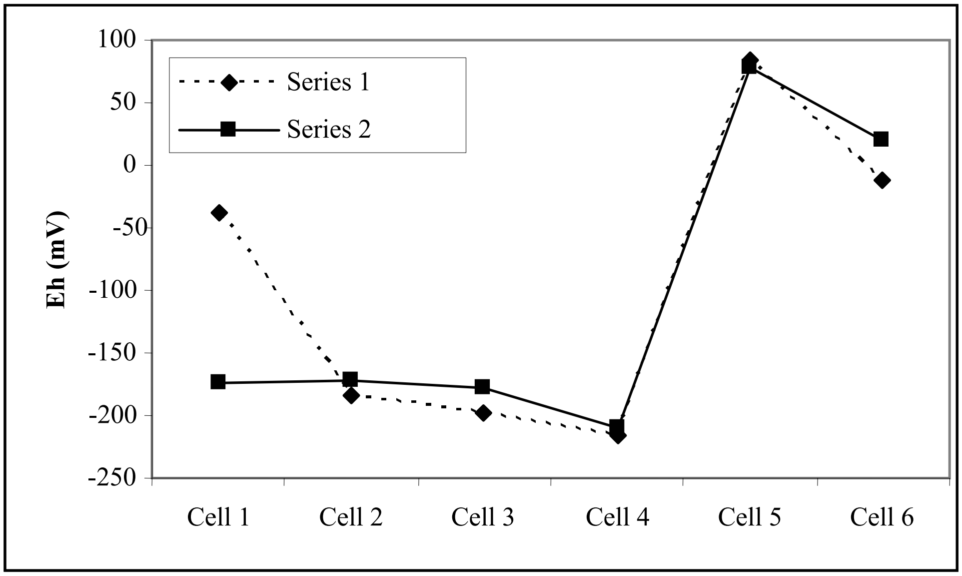


Figure 33. Oxidation-reduction potential of the additional pilot-scale constructed wetland treatment system hydrosoil in the six wetland reactors for the month of September 2006.

FGD Water containing Dibasic Acid

Dibasic acid is an amendment used to stabilize the pH of the scrubbing solution (calcium carbonate or limestone waters) for the specific purpose of increasing the removal extent of sulfur dioxide in the flue gas. Dibasic acid forms can be inorganic, but most commonly are in the form of a di-carboxylic organic alkane used in for this process. This amendment, however, may affect the treatment system's ability to decrease constituents of concern and can cause undesirable characteristics in the FGD water such as biological oxygen demand, chemical oxygen demand, and low pH. To test the treatment efficiency of pilot-scale constructed wetland treatment systems for FGD water affected by amendments within an operating scrubber system, FGD waters with dibasic acid amendments were collected, analyzed, and introduced into these treatment systems. In order to better understand the effect of dibasic acid and other potentially problematic constituents such as boron (phytotoxicity to aquatic plants), three dilutions of FGD water were used in this study. The objective of this study was to determine the treatment efficiency of pilot-scale constructed wetland treatment systems for FGD waters containing dibasic acid amendments.

Pilot-scale CWTS Experimental Approach

FGD water (FGD blowdown from a facility in Florida) was delivered to Clemson University. Samples were collected from a transporting tanker for chemical analysis for constituents of interest (Table 18). Based on the analytical results, initial chloride concentrations in the water were 18,600 mg/L. To maintain the health of the vegetation, the chloride concentration should not exceed 4,000 mg/L. Given this dilution, the concentration of dibasic acid was approximately 710 mg/L, and a boron concentration of 58 mg/L was present in this FGD water. This was a dilution of approximately one part FGD water and 4.5 parts municipal city water from Clemson, SC. For this study, this FGD water was referred to as "dilution one." For the next dilution (dilution two), the tanker FGD water was diluted by 86% (1 part FGD water: 7 parts city water) and included 460 mg/L as dibasic acid and 37 mg/L as boron. For the final dilution (dilution three), the FGD tanker water was diluted 89% (one part FGD water: 9 parts city water) and included 355 mg/L as dibasic acid and 26 mg/L as boron.

Following the dilutions described, selenium concentrations in the FGD wastewater were at concentrations of interest (1.4 mg/L, 0.89 mg/L and 0.68 mg/L for dilutions of 77% (1:4.5), 86% (1:7), and 89% (1:9), respectively). To achieve concentrations discernable for treatment efficiency studies, the concentrations of mercury and arsenic in the diluted FGD waters were amended to 0.01 mg/L and 0.05 mg/L in the 77% diluted wastewater. The concentrations decrease as expected in the 86% and 89 % diluted water. The treatment efficiency of these systems were monitored by collecting aqueous samples from the equalization basin, inflow to the CWTS, outflows from wetland cells 1, 2, 3, and 4 (final outflow of the system). Measurements on these samples were conducted for pH, alkalinity, hardness, chlorides, 5-d biological oxygen demand (BOD_5), chemical oxygen demand (COD), sulfates, total suspended solids (TSS), total dissolved solids (TDS), and total inorganic analysis of constituents of concern (Arsenic, Boron, Mercury, and Selenium) (Table 36).

Table 36. Chemical analyses of tanker FGD water and estimated concentrations of constituents in dilution treatments for experiments two and three. Concentrations in mg/L except where noted.

Constituents	Tanker FGD W.W	Dilution 1 (1:4.5)	Dilution 2 (1:7)	Dilution 3 (1:9)
Arsenic*	0.043	0.050	0.035	0.025
Boron	260	60	40	30
Mercury*	BDL	0.010	0.007	0.005
Selenium	6.2	1.4	0.89	0.68
5-d BOD	1700	377.8	242	189
COD	4000	888.9	571	444
DBA	3200	711.1	461	355
pH (SU)	8.00	TBD	TBD	TBD
TSS	19	4.2	2.7	2.1
TDS	41,000	9,000	5,800	4,500

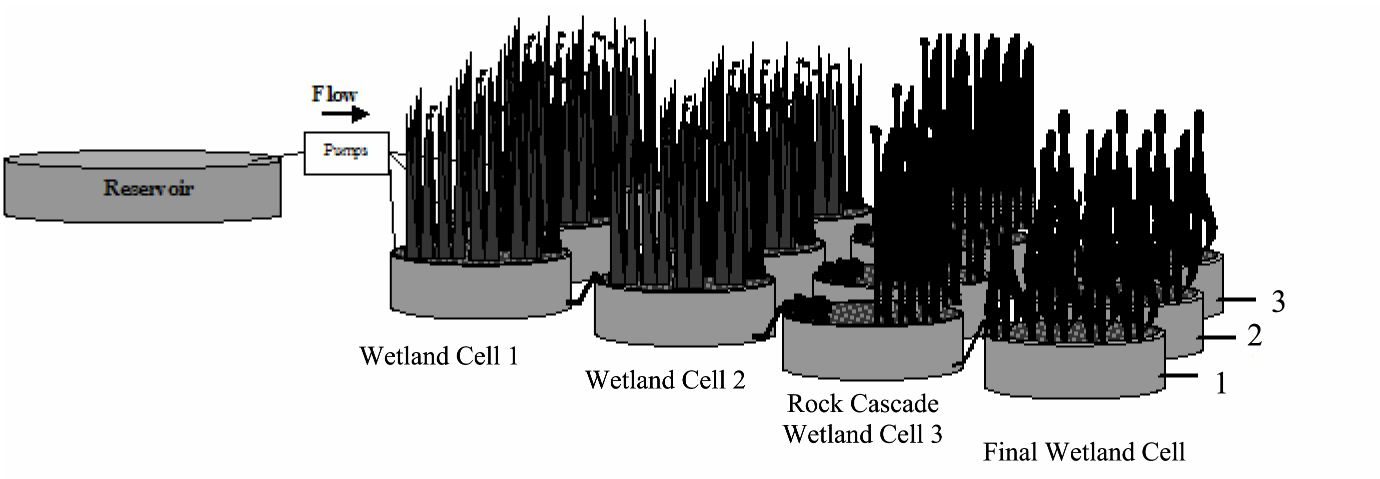
* Amended in the equalization basin before introduction into CWTS

Pilot-scale Constructed Wetland Treatment Systems

Pilot-scale constructed wetland 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® utility tank. All reducing reactors contained approximately 30-cm of river sand hydrosoil, 3-5% organic matter by volume, 1% gypsum by volume, and *S. californicus*. The modified rock basin was equally divided with the inflow-half consisting of 12.7 to 17.8-cm granite rocks and the latter half consisting of 30-cm of river sand hydrosoil and *T. angustifolia*. Oxidizing reactors contained approximately 30-cm of river sand hydrosoil, and were planted with *T. angustifolia*. Total hydraulic retention time (HRT) for the CWTS was established as 168-hr or 36-hr per reducing reactor and 24-hr per modified rock basin and oxidizing reactor.

Sampling sites from the constructed wetland treatment systems

1. Equalization Basin
2. Inflow to the first wetland cell of each train
3. Outflow from the first wetland cell of each train
4. Outflow from the second wetland cell of each train
5. Outflow from the third wetland cell of each train
6. Outflow from the fourth wetland cell of each train (Final Outflow)



CWTS 1: Dilution FGD wastewater 1 - 77% dilution
CWTS 2: Dilution FGD wastewater 2 - 86% dilution
CWTS 3: Dilution FGD wastewater 3 - 89% dilution

Figure 34. Schematic of the pilot-scale constructed wetland system for evaluating treatment efficiency of dilution inflows of 77, 86, and 89% tanker FGD wastewater for experiments Two and Three.

The systems were allowed to stabilize and acclimate to a chloride concentration of 4000 mg/L using simulated FGD water for approximately two months. The actual diluted FGD waters described previously were introduced to these treatment systems and monitored weekly.
An analysis of the results for constituents of interest provided useful information on potential impacts from DBA. Throughout the 10 weeks of running the DBA wastewater through the pilot units, mercury removal was greater than 90% for Dilution 1, 2 and 3. The range of mercury concentrations for each of the dilutions were as follows:

- Dilution 1 (1:4.5) = 9 -11 ug/L inflow, 0.29 - 0.91 ug/L outflow
- Dilution 2 (1:7) = 6-8 ug/L inflow, <0.01 - 0.97 ug/L outflow
- Dilution 3 (1:9) = 3-6 ug/L inflow, <0.01 – 0.56 ug/L outflow.

The overall selenium removal for the 10 weeks of the DBA FGD water study was 27% for Dilution 1, 30% for Dilution 2 and 46% for Dilution 3. Differences in the FGD water (as a result of dilution) that may have contributed to the decreased selenium removal observed in Dilution 1 vs. Dilution 3 such as BOD concentrations (average inflow concentration 556 mg/L vs. 399 mg/L) or COD concentrations (average inflow 532 mg/L vs. 297 mg/L). Other constituents that may have contributed to the observed differences in the dilutions are dissolved oxygen, chlorides, boron or other constituents not measured as part of this investigation. Over the course of the 10 week pilot study with DBA FGD water, a measurable difference in the ability of the CWTS to decrease COD concentrations was observed. The most significant impacts of DBA were observed in the Dilution 1 treatment system. At the study initiation, the constructed wetland increased dissolved oxygen (DO) concentrations from 0.76 to 7.32 mg/L (week 1). During this same period, 53% of BOD was removed and 35% of COD was removed. Some of the removal efficiency observed during the first week may have been due to mixing/dilution of the FGD water containing DBA with the simulated water that was used during the acclimation period for the treatment systems. During the following several weeks (week 2 – week 4), DO continued to increase from inflow to outflow through the system (average increase from 2.0 mg/L to 4.8 mg/L). During this same period, BOD concentrations decreased an average of 34% and COD decreased 22% on average.

Following approximately one month of DBA addition to the treatment systems at an influent COD concentration of 532 mg/L (DBA concentration of approximately 425mg/L), the system reached capacity for degrading DBA. At this point (weeks 5-7), there was no significant increase in DO, and no significant change in BOD or COD concentrations from inflow to outflow (i.e. concentration in is approximately equal to concentration out). Over the next three weeks of the study (weeks 7 – 10), the capacity of the system to degrade DBA was exceeded and the oxygen demand of the system increased. During this period, influent dissolved oxygen concentrations remained at an average of 2 mg/L but effluent concentrations were 0.76 mg/L on average. During previous weeks, the DO increased from inflow to outflow. Influent COD concentrations remained at an average of 520 mg/L during weeks 7-10 but effluent COD concentrations increased by an average of 32% during this period. Changes in BOD from inflow to outflow remained consistent with previous weeks. Also observed during weeks 7-10 was a film on the vegetation and surface of the water as a result of the continued DBA additions.

An analysis of the COD and BOD from the wetland treatment systems receiving Dilution 2 (DBA concentration approximately 313 mg/L) and Dilution 3 (DBA concentration of approximately 237 mg/L) indicates similar shifts from an oxidizing constructed wetland system to an anoxic constructed wetland system were observed over the 10 week study; however, the shift from the systems decreasing COD to increasing COD were delayed approximately 2 weeks, and the extent of COD production was not as severe as observed in the Dilution 1 constructed wetland treatment system. During weeks 6-10, the average increase in COD concentrations for the Dilution 2 train was 36% (average inflow COD concentration = 420 mg/L and average outflow COD concentration 570 mg/L). For constructed wetland treatment system for Dilution 3, a 31% increase in COD concentrations was observed during weeks 6-10 (average inflow COD concentration = 320 mg/L and average outflow COD concentration 420 mg/L).

Results from these DBA experiments indicate that FGD water containing DBA concentrations may negatively impact the functional performance of the constructed wetland treatment systems, especially for selenium and arsenic removal, as well as increase the COD and BOD of the FGD water.

Since FGD waters can vary in constituent concentrations and forms, which affect the ability of the treatment system to efficiently treat these constituents of concern, an additional FGD water without dibasic acid amendments was collected and introduced into the same pilot-scale constructed wetland treatment system used for dibasic studies. An FGD water was collected from an Asheville, North Carolina Facility to use as a control for the DBA/FGD wastewater experiments. The water was collected following the clarifier. Upon arrival at Clemson University, the water was diluted with municipal water to a chloride concentration of approximately 4000 mg/L (range 3900 – 4250 mg/L). Selenium concentrations in the diluted Asheville water ranged from 0.65 mg/L to 0.7 mg/L. Mercury concentrations ranged from 0.018 to 0.022 mg/L, and boron ranged from 13 to 18 mg/L. Experiments were conducted with the

Asheville water using the pilot scale constructed wetlands for a period of 4 weeks. During this period, average mercury removal from inflow to outflow was 90% and average selenium removal was 16%.

Selenium Speciation

To assist in determining the factor contributing to decreased inhibiting selenium removal in some FGD waters, selenium speciation of the non-DBA and DBA FGD waters was conducted. Results of the selenium speciation indicate that selenate ranged from 53% to 77% of the total selenium and only 1% of the total selenium was selenite in the non-DBA water. Other known species of selenium also made up only 1% of the total selenium. The remaining 23-47% of selenium was unidentified species. In comparison, in the DBA containing FGD wastewater, less than 1% of the total selenium was selenate. Ten percent of the total selenium was selenite and approximately 10% was other readily identified forms of selenium (i.e. selenocyanate, methylselenic acid, and selenomethionine). Therefore, in the FGD water containing DBA, approximately 80% of the selenium was in unidentified forms (likely complexed forms that are difficult to treat).

Based on the selenium speciation of these FGD waters, as well as speciation of other FGD waters, it was concluded that FGD waters are very complex in character. The forms of selenium (and other constituents) are influenced by multiple parameters and processes including source of coal, burner rate and process, scrubbing processes and post scrubbing processes. From the ongoing pilot-scale studies conducted at Clemson University, we have confirmed that while each constructed treatment system for FGD waters is similar in appearance, the internal functions that drive the wetland removal mechanisms and processes are site and FGD water specific. Since FGD waters are relatively high in salinity and most likely unsuitable for re-use within a power plant, the current focus of this research is to develop a robust and reliable treatment system for FGD waters in order to meet discharge criteria (NPDES permits). Continued research on identifying amendments and adjustments to constructed wetland treatment systems is warranted to optimize the removal of constituents of concern and toxicity of FGD waters.

Scaling, Corrosion and Biofouling

Using corrosion and scaling coupons the potential for chemical scale formation, corrosion and biofouling was measured before treatment (inflow) and after treatment by a constructed wetland (outflow). Biofouling potential significantly decreased from inflow to outflow, averaging 20% reduction of biofouling potential for CWTS series A and B. The potential for chemical scale formation was essentially unchanged by treatment in the CWTS, while the potential for corrosion was enhanced.

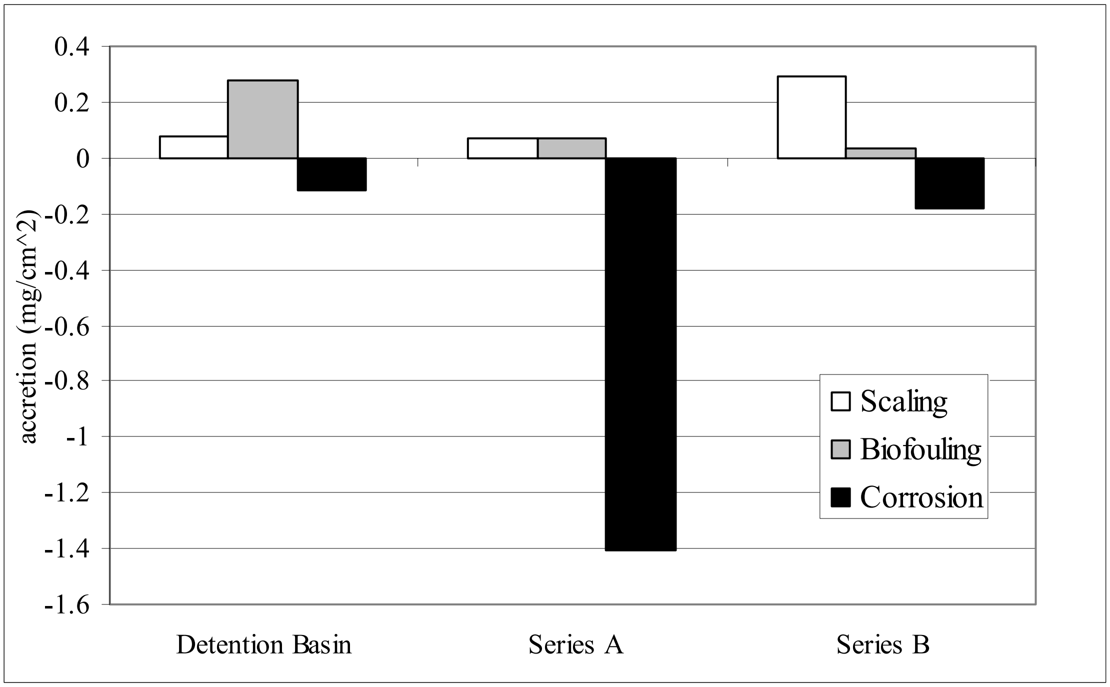


Figure 35. Corrosion, scaling and biofouling potential for FGD waters

Discussion and Conclusions

Analytical results and observations indicate that this constructed wetland system design has application for decreasing aqueous levels of arsenic, mercury, nitrogen, and selenium associated with FGD water. The initial CWTS used in this study was loaded with high concentrations of arsenic, mercury, and selenium in simulated FGD water for the intent of system acclimation. This concept was based on previous research for FGD water treatment (1 month acclimation period); however, due to differences in acclimation FGD water versus actual FGD water (ionic strength of ~9.2 vs. 4.4 mS/cm^2), leaching of selenium occurred during treatment weeks one to four. Due to this phenomenon, FGD water was loaded into a similar CWTS designed for FGD water, and percent removals for selenium ranged from 66 to 85%. With this additional CWTS, removal of arsenic, mercury, and nitrogen occurred at similar rates in comparison to the initial CWTS. Total nitrogen removal was lower for the first treatment period (44%) with the additional CWTS; however, removal percentages increased for the final two treatment weeks to percentages greater than 70%. Mercury removal percentages ranged from 78 to 98% with a mean of 91%, and arsenic removal percentages ranged from 14 to 78% with a mean of 57%. Overall analyses of these data indicate that constructed wetland treatment systems can decrease aqueous concentrations of As, Hg, N, and Se. These elements are normally of concern due to NPDES permits, toxic effects to organisms associated with receiving systems, and nutrient loading that can alter ecosystem health. Based on this pilot-scale study and previous research, CWTS are a robust and viable treatment strategy for FGD waters.

PRODUCED WATERS

Objective I: Characterization

Produced waters (PWs) are those waters contaminated by contact with coal, oil and gas during production and extraction from underground fields. These waters contain many potentially toxic inorganics including chlorides, lead, cadmium, zinc, copper, arsenic, selenium, mercury, and nickel. Other constituents of concern include organics such as polyaromatic hydrocarbons (e.g. benzene, toluene, xylene, ethylated compounds, alkanes, alkenes, etc.), grease, and other components of oil. Analyses of twenty-four waters by Clemson University, SC provided chloride ranges of 576 to 100,000 mg/L indicating that this element must be considered as the primary toxicant due to its concentration and toxicity. For this study, produced waters were classified by chloride concentrations: freshwater, brackish, saline, and hyper-saline produced waters (Table 38). Elemental constituents of concern in fresh PWs include arsenic (mean =0.204 ± 0.28 mg/L), selenium (mean =0.051 ± 0.02 mg/L), zinc (mean=0.289 ± 0.15 mg/L), and mercury (mean =0.3 ± 0.3 μg/L). For brackish PWs, elemental constituents of concern include chlorides (mean =7,778 ± 4040 mg/L), arsenic (mean =2.99 ± 0.83 mg/L), zinc (mean =0.147 ± 0.09 mg/L), and mercury (mean =0.5 ± 0.5 μg/L). For saline PWs, elemental constituents of concern include chlorides (mean =23,701 ± 5,764 mg/L), arsenic (mean =7.27 ± 13.2 mg/L), zinc (mean =0.156 ± 0.077 mg/L), boron (X=5.10 ± 9.37 mg/L), selenium (X=0.026 ± 0.037 mg/L), and mercury (X=1.0 ± 2.0 μg/L). For hyper-saline PWs, elemental constituents of concern include chlorides (mean =73,327 ± 24,916 mg/L), mercury (24.0 ± 42.0 μg/L), arsenic (mean =3.48 ± 3.03 mg/L), zinc (mean =0.173 ± 0.100), copper (mean =0.038 ± 0.016 mg/L), selenium (mean =0.050 ± 0.034 mg/L), and boron (mean =1.75 ± 3.37 mg/L).

Objective II: Determination of Reuse and Constituents of Concern

NPDES Permits

Produced waters can contain many constituents of concern that require NPDES discharge permits including such elements (total elemental analysis) such as barium (154 mg/L), chlorides (5,000 mg/L), chlorine (0.038 mg/L), chromium (0.0001 to 0.1 mg/L), copper (0.37 to 1.0 mg/L), lead (0.0026 to 0.4 mg/L), mercury (0.004 mg/L), nickel (2.0 mg/L), sulfide (0.21 to 1.0 mg/L), and zinc (0.4 to 5.0 mg/L). Organic constituents of concern that require NPDES discharge permits include oil and grease (15 mg/L), total organic carbon (5 mg/L), benzene (0.06 to 2.88 μg/L), toluene (0.028 to 5.0 μg/L), ethylbenzene (0.142 to 5.0 μg/L), ortho-xylene (5 μg/L), xylene (meta and para: 0.01 to 100 μg/L), BTEX (<5.0 μg/L), naphthalene (0.2 mg/L), 1,1,1 trichloroethane (0.05 mg/L), 1,2 dichloropropane (0.196 μg/L), ethylene glycol (50 μg/L), and polyaromatic hydrocarbons (2.8 to 12.2 mg/L). NPDES permit limits for water chemistry of these waters, such as biochemical and chemical oxygen demand [BOD (29 to 57 mg/L) and COD (170 to 292 mg/L)], total dissolved solids (500 mg/L), and total suspended solids (30 to 70 mg/L) require treatment of these constituents thus influencing the treatment system design. Of the constituents, however, chloride concentrations must be considered due to the difficult and costly procedures required for removal of this ion from solution. Concentrations of chlorides in PWs can exceed saltwater concentrations (i.e. 23,800 mg/L as Cl^-), and have been measured greater than 100,000 mg/L.

Constituents of Concern

Constituents of concern (COCs) for produced waters were identified utilizing information such as the concentrations of elements and chemical compounds in produced water, USEPA water quality criteria (WQC), NPDES permit values, and published literature. Initial analysis of these data indicated four produced water classifications based on chloride content (Fresh, Brackish, Saline, and Hyper-Saline produced waters). Produced waters can vary greatly in composition due to the constituents in the formation water and extraction methods; therefore, constituents of concern can vary between produced waters from different regions or production sites. Produced waters can have many elemental constituents of concern that require NPDES discharge permits including chlorides (5,000 mg/L), chlorine (0.038 mg/L), chromium (0.0001 to 0.1 mg/L), copper (0.37 to 1.0 mg/L), lead (0.0026 to 0.4 mg/L), mercury (0.004 mg/L), nickel (2.0 mg/L), sulfide (0.21 to 1.0 mg/L), arsenic (340 µg/L), and zinc (0.4 to 5.0 mg/L). Organic constituents of concern that require NPDES discharge permits include oil and grease (15 mg/L), total organic carbon (5 mg/L), benzene (0.06 to 2.88 µg/L), toluene (0.028 to 5.0 µg/L), BTEX (<5.0 µg/L), naphthalene (0.2 mg/L), and polycyclic aromatic hydrocarbons (2.8 to 12.2 mg/L). NPDES permit limits for chemical constituents of these waters include biochemical and chemical oxygen demand [BOD (29 to 57 mg/L) and COD (170 to 292 mg/L)], total dissolved solids (500 mg/L), and total suspended solids (30 to 70 mg/L). Total chloride concentrations in produced waters can range from < 400 mg/L to > 300,000 mg/L, which may exceed NPDES permit limits ranging from 2,500 to 5,000 mg/L. The chloride concentrations greater than 640 mg/L (as Cl^-) can cause toxicity to *C. dubia* indicating that this element is a COC. The remaining COCs can vary regardless of chloride concentrations**.** Cadmium concentrations can range from non-detect to 0.098 mg/L, which may exceed USEPA WQC for both acute and chronic exposures (40 and 8.8 µg/L respectively). Total chromium concentrations have been observed as high as 0.39 mg/L, which is greater than NPDES permit limit of 0.1mg/L. Copper has been measured as high as 1.45 mg/L in these waters, exceeding both NPDES permitted limits (0.37-1.0 mg/L) and USEPA WQC acute and chronic exposures (4.8 and 3.1 µg/L respectively). Lead concentrations can range from 3 to 38 µg/L which is lower than the NPDES permit limit (2.6-400 µg/L), but exceeds USEPA WQC for chronic exposure (2.5 µg/L) [USEPA & USDA]. Mercury can range in concentration from non-detect to 0.086 mg/L, thus exceeding the NDPES permit limit of 0.004 mg/L. Nickel can range in concentration from non-detect to 1.7 mg/L which meets NPDES permit limits but is greater than the USEPA WQC for acute and chronic concentration exposures of 74 and 8.2 µg/L respectively. Sulfide concentrations can range from < 10 to > 1000 mg/L, which is greater than NPDES permit limits of 1.0 mg/L. Arsenic concentrations can range from non-detect to approximately 51 mg/L exceeding NPDES permit limits and USEPA WQC for acute and chronic exposures of 69 and 36 µg/L respectively. Zinc concentrations range from 0.017-1.6 mg/L, which meets NPDES discharge limits (0.4-5.0 mg/L) but exceeds USEPA WQC criteria for both acute and chronic exposures (90 & 91 µg/L respectively). Oil and grease concentrations in produced waters can range from non-detect to 78 mg/L, indicating that some produced waters exceed the NPDES permit limit of 15 mg/L. Total organic carbon (TOC) can range from 3.9-1077 mg/L exceeding the NPDES permit limit of 5 mg/L. Organic compounds such as benzene (non-detect to 12.1 mg/L) and toluene (non-detect to 19.8 mg/L) are reported to have concentrations in produced waters which exceed NPDES permits, identifying these compounds as COCs. Polycyclic aromatic hydrocarbons (non-detect to 0.11 mg/L) have been reported at concentrations less than NPDES permit criteria, excluding these compounds as COC. BOD and COD, are not included as COC since the concentrations of these constituents are less than the NPDES permit limits, (29 to 57 mg/L and 170 to 292 mg/L respectively). Total suspended solids [TSS] (24 to 101 mg/L) and total dissolved solids [TDS] (668 to 38,938 mg/L) concentrations have been reported to exceed NPDES permit limits of 30 to 70 mg/L and 500 mg/L thus identifying them as COCs.

Table 37. Constituents and their concentration ranges collected from literature reviews and analyses of produced waters (PWs).

CONSTITUENT	CONCENTRATIONS	UNITS	CONSTITUENT	CONCENTRATIONS	UNITS
pH	7.84 - 9.56	SU	COBALT, TOTAL	0.0009 - 0.058	mg/L
COD	11.2 - 45.8	mg/L	COPPER, TOTAL	0 - 1.45	mg/L
SOLIDS, TOTAL DISSOLVED	668 - 38,938	mg/L	GALLIUM	0 - 0.003	mg/L
SOLIDS, TOTAL SUSPENDED	24 - 101	mg/L	GOLD, TOTAL	0 - 0.095	mg/L
CARBON, TOTAL	3.9 - 1077	mg/L	IODINE, TOTAL	0 - 3.91	mg/L
PHOSPHORUS, TOTAL	0 - 0.763	mg/L	IRON, TOTAL	1.6 - 768	mg/L
SULFATE, TOTAL	< 10 - 1, 100	mg/L	LITHIUM, TOTAL	0 - 64	mg/L
			MAGNESIUM, TOTAL	0.6 - 3,671	mg/L
ORGANIC CONSTITUENT			MANGANESE, TOTAL	0 - 15	mg/L
PAH	0 - 0.11	mg/L	MERCURY, TOTAL	0 - 0.086	mg/L
NAPTHALENES	0 -1.18	mg/L	MOLYBDENUM	0 - 0.003	mg/L
PHENOLS	0.15 - 21.5	mg/L	NIOBIUM, TOTAL	0 - 0.002	mg/L
BENZENE	0.683 - 12.1	mg/L	NICKEL, TOTAL	0 - 1.7	mg/L
TOLUENE	1.01 - 19.8	mg/L	POTASSIUM, TOTAL	0.67 - 669	mg/L
C2- BENZENE	0.05 - 3.7	mg/L	RUBIDIUM, TOTAL	0 - 1.59	mg/L
OIL AND GREASE	0 - 78	mg/L	RUTHENIUM, TOTAL	0 - 0.018	mg/L
			SELENIUM, TOTAL	0 - 0.14	mg/L
INORGANIC CONSTITUENT			SILICON, TOTAL	0.05 - 2.9	mg/L
ALUMINUM, TOTAL	.0015 - 0.473	mg/L	SILVER, TOTAL	0.012 - 0.15	mg/L
ARSENIC, TOTAL	0 - 51	mg/L	SODIUM, TOTAL	7 - 13,704	mg/L
BARIUM, TOTAL	0.23 - 17	mg/L	STRONTIUM, TOTAL	0.65 - 917	mg/L
BERYLLIUM, TOTAL	0 - 0.001	mg/L	SULFUR, TOTAL	0 - 1,556	mg/L
BORON, TOTAL	0.019 - 28	mg/L	TELLURIUM, TOTAL	0 - 0.004	mg/L
BROMINE, TOTAL	0.7 - 350	mg/L	TIN, TOTAL	0 - 0.001	mg/L
CADMIUM, TOTAL	0 - 0.098	mg/L	TITANIUM, TOTAL	0 - 4,402	mg/L
CALCIUM, TOTAL	1 - 818	mg/L	URANIUM, TOTAL	0 - 0.018	mg/L
CHLORIDE, TOTAL	133 - 108,968	mg/L	VANADIUM, TOTAL	0 - 1.1	mg/L
CHROMIUM, TOTAL	0 - 0.39	mg/L	ZINC, TOTAL	0.017 - 1.6	mg/L

[1] COD = chemical oxygen demand.

[2] PAH = polyaromatic hydrocarbons.

Table 38. Elements (expressed in mg/L and µg/L) associated with produced waters and categories based on chloride concentrations.

PW Type[1]	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	B (mg/L)	Cl (mg/L)	As (mg/L)	Cd (µg/L)	Cu (µg/L)	Hg (µg/L)	Pb (µg/L)	Se (µg/L)	Zn (mg/L)
Fresh													
Mean	2.93	2.20	3.46	45.6	0.05	448	0.204	16.0	18.0	0.3	30.0	51.0	0.289
SD[2]	±1.30	±1.12	±2.68	±47.7	±0.019	±364	±0.28	±28.0	±27.0	±0.3	±59.0	±20.0	±0.15
Brackish													
Mean	150	148	223	8,319	1.123	7,778	2.99	0.6	17.0	0.5	3.0	6.0	0.147
SD[2]	±121	±128	±273	±7029	±1.09	±4040	± 0.83	±0.1	±11.0	±0.5	±3.0	±10.0	±0.09
Saline													
Mean	211	239	286	2,592	5.10	23,701	7.27	6.0	20.0	1.0	18.0	26.0	0.156
SD[2]	±145	±224	±200	±3701	±9.37	±5764	±13.2	±14.0	±10.0	±2.0	±37.0	±37.0	±0.077
Hyper-Saline													
Mean	464	154	1,256	366	1.75	73,327	3.48	1.0	38.0	24.0	6.0	50.0	0.173
SD[2]	±270	±99	±1610	±322	±3.37	±24916	±3.03	±0.9	±16.0	±42.0	±10.0	±34.0	±0.100

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[1] Produced water type: Fresh (<400-2,500 mg/L), Brackish (2,500-15,000mg/L), Saline (15,000-40,000mg/L), Hyper Saline water(>40,000 mg/L).

[2] SD = Standard deviation.

Table 39. NPDES permit limits for produced waters reported as minimum and maximum concentration ranges

CONSTITUENT	LIMITS	UNITS	CONSTITUENT	LIMITS	UNITS
PH	6-9	SU	TIN, TOTAL	50	µg/L
BOD_5(20*C)	29-57	mg/L	ZINC, TOTAL	0.4-5.0	mg/L
$CBOD_5$	25	mg/L			
COD	170-292	mg/L	OIL & GREASE	15	mg/L
SOLIDS, TOTAL DISSOLVED	500	mg/L	CARBON, (TOC)	5	mg/L
SOLIDS, TOTAL SUSPENDED	30-70	mg/L			
ALKALINITY/ACIDITY	alkalinity<acidity		BENZENE	0.06-2.88	µg/L
			TOLUENE	0.028-5.0	µg/L
BARIUM	154	mg/L	ETHYLBENZENE	0.142-5.0	µg/L
CHLORIDES	5,000	mg/L	ORTHO-XYLENE	5	µg/L
CHLORINE, TOTAL RESIDUAL	0.038	mg/L	XYLENE, META & PARA	0.01-100	µg/L
CHROMIUM, TOTAL	0.1-100	mg/L	BTEX	< 5.0	µg/L
COPPER, TOTAL	0.37-1.0	mg/L	NAPTHALENE	0.2	mg/L
CYANIDE, TOTAL	0.4	mg/L	1,1,1-TRICHLORO-	0.05	mg/L
FLUORIDE, TOTAL	30	mg/L	1,2-DICHLOROPROPANE	0.196	µg/L
IRON, TOTAL	0.6-9.4	mg/L	ETHYLENE GLYCOL	50	µg/L
LEAD, TOTAL	2.6-400	mg/L	PAHs	2.8-12.2	mg/L
MANGANESE, TOTAL	1-4.4	mg/L			
MERCURY, TOTAL	0.004	mg/L	TOXICITY	Zero discharge of water containing toxic in concentrations that are toxic to human, animal or aquatic life	
NICKEL, TOTAL	2	mg/L			
NITROGEN, AMMONIA TOTAL	1.5-6.6	mg/L			
PHOSPHOROUS, TOTAL	1	mg/L			
SULFIDE, TOTAL	0.21-1.0	mg/L			

Objective III: Construction of Pilot-Scale CWTS

A hybrid pilot-scale CWTS was designed for produced waters based on chloride concentrations. For simulated produced waters in which chloride concentrations exceed 4000 mg/L, a reverse osmosis system (RO) and *Spartina alterniflora* treatment wetlands were utilized. For these produced waters, the treatment system consisted of a 3780 L (1000 gallon) retention basin, allowing time for some solids to settle. Water was pumped from the retention basin by a Fluid Metering, Inc.® (FMI) piston pump to an oil/water separator based on American Petroleum Institute (API) specifications at a rate to achieve a 24-hr hydraulic retention time per treatment system component (i.e. equalization basin, oil/water separator, RO permeate, and wetland reactor). For this pilot study, the oil/water separator was 116.8 cm (46 in) long by 55.9 cm (22 in) wide by 30.4 cm (12 in) deep. The body of the separator was fiberglass with a skimmer and baffle of Plexiglas. The water leaving the oil/water separator enters a saltwater wetland treatment system (two reactors in series). These reactors were planted with both tall and short forms of *Spartina alterniflora* in a river sand hydrosoil. The purpose of these reactors was to remove any residual oil and grease from the produced water in order to prevent fouling of the RO membrane. These reactors provided an opportunity for retained organics to be oxidized and for precipitation of various inorganic compounds. The water leaving the pilot-scale saltwater wetland reactors drains into a detention basin prior to treatment by the RO system. The use of RO enables conservative ions such as salt (ion pairs; i.e. Na and Cl) to be removed from the produced water. RO systems can decrease chloride concentration and total dissolved solids (TDS) concentration in saline waters to tolerable levels for freshwater wetland and aquatic life. After treatment of the produced water by RO, a pilot-scale freshwater CWTS was designed to remove residual metals and organic compounds that remain after passing through the API oil/water separator, the saltwater wetland reactors, and the RO system. The freshwater system may also be used independently (i.e., bypassing the *Spartina* reactors and RO) for treatment of waters with less than 4,000 mg/L chloride concentrations. Its primary purpose is to ensure that the post-treatment water is non-toxic. In the pilot-scale freshwater wetland system, there were two parallel series consisting of four reactors. Each reactor was contained within a 121.9 cm (48 in) long by 77.5 cm (30.5 in) wide by 63.5 cm (25 in) deep, 378 L (100 gal) Rubbermaid® tub. The four reactors in series provided adequate sampling locations and prevented "short circuiting" (water passing through without adequate treatment). The reactors were connected by PVC pipe fittings and approximately 30 cm long segments of ¾" poly-tubing. The PVC pipe fittings were designed to maintain surface flow and were placed 6 cm below the top of each Rubbermaid® tub.

Each of the freshwater wetland reactors consists of three macrofeatures: hydrosoil, macrophytes, and a hydroperiod. The first two reactors in each series contained reducing hydrosoil (river sand hydrosoil and organic matter as pine mulch) and were planted with *Schoenoplectus californicus* C.A. Meyer (California bulrush) with the exception of the ash basin system, which contained three reactors containing reducing hydrosoil. The final two reactors in each series contained oxidizing hydrosoil (quartz sand) and were planted with *Typha latifolia* L. (broadleaf cattail). By maintaining a calibrated flow rate, the hydroperiod or hydraulic retention time (HRT) of the CWTS was maintained at 24 hours per reactor or 96 hours for the entire freshwater system.

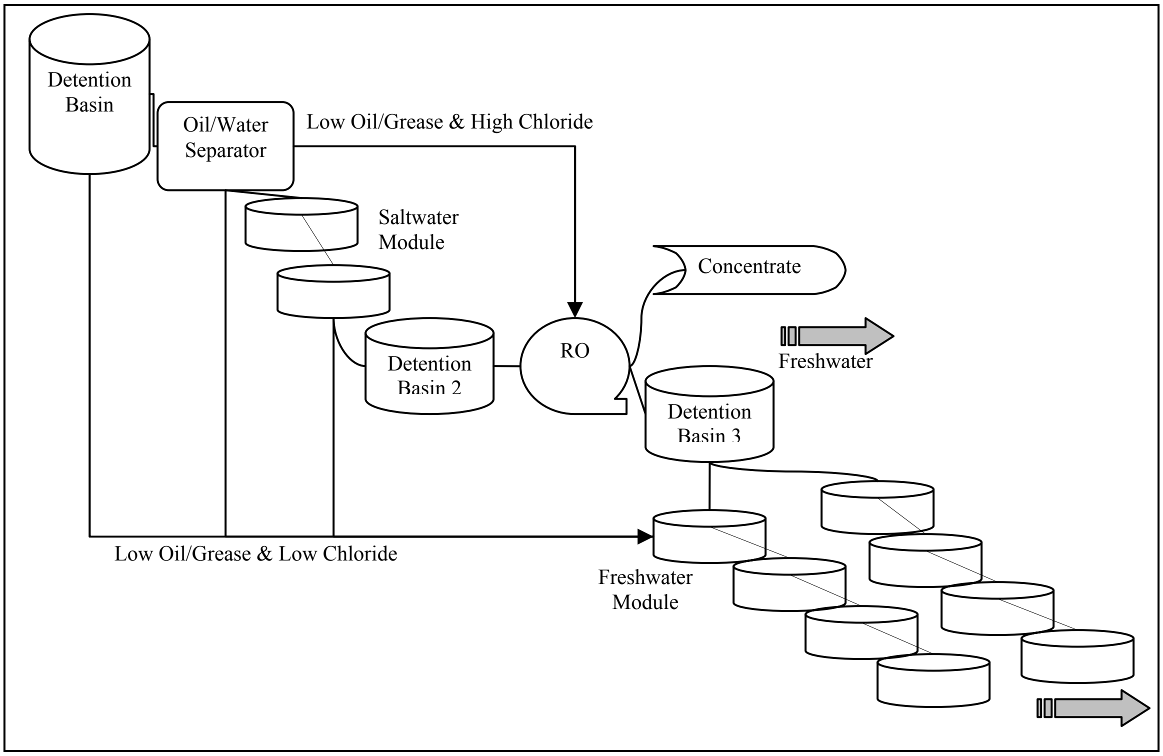

Figure 36. Schematic for the pilot-scale hybrid constructed wetland treatment system for treatment of constituents in produced waters

Simulated Produced Waters

Produced waters vary significantly in composition because of geologic formation of the source water, contact with hydrocarbons, and other production processes (Ray and Engelhardt, 1992; Veil et al., 2004). Produced waters were statistically grouped into four general categories (fresh, brackish, saline, and hyper-saline) using primarily the median and quartiles of chloride concentrations found in the characterization of produced waters (PWs). Based on their presence in concentrations that pose potential risks for receiving aquatic system biota, six targeted constituents (chlorides, cadmium, copper, lead, zinc, and oil/grease) were chosen to represent produced water composition for the purpose of evaluating treatment effectiveness. The constituents chosen (Cl, Cd, Cu, Pb, Zn, and oil/grease) were used to formulate simulated waters for treatment in this study. The target inflow concentrations for simulated PWs are shown in Table 40. Simulated waters were formulated to represent categories of produced water: freshwater, brackish water, saline water, and hyper-saline water (Table 40). Treatment effectiveness and performance were evaluated from the samples of inflow and outflow waters. Samples were collected from the initial detention basin and at intervals throughout the system (at the outflow of each module) with consideration of the hydraulic retention time. Sampling and analyzing the outflow from each module allowed us to discern the time and location of removal of constituents of concern from the water column.

Table 40. Composition of Fresh, Brackish, Saline, and Hyper-saline simulated PWs.

Constituent	Chemical Source	Fresh Target Inflow (mg/L)	Brackish Target Inflow (mg/L)	Saline Target Inflow (mg/L)	Hyper-Saline Target Inflow (mg/L)
Chlorides	$CaCl_2$, NaCl, $MgCl_2 \cdot 6H_2O$	<400-2,500	2,500-15,000	15,000-40,000	>40,000
Cadmium	$CdCl_2$	0.4	0.4	0.8	1.2
Copper	$CuCl_2 \cdot 2H_2O$	0.8	1.7	3.3	5.0
Lead	$PbCl_2$	1.0	5.5	6.8	10.2
Zinc	$ZnCl_2$	5.0	23.0	45.9	69.0
Oil/Grease	Motor Oil	20.0	19.0	49.0	78.0

Objective IV: Treatment Performance of Pilot-Scale Constructed Wetlands

System performance was measured by decrease in concentrations of constituents of concern and toxicity from the inflow simulated PWs to the outflow from the CWTS. Each constituent of concern (Cd, Cu, Pb, Zn and organics) was removed effectively from the water column by the pilot-scale hybrid CWTS. Percent removal and removal rate coefficients for Cd ranged from 38.4 to 99.6% and 0.121 to 0.745 days^{-1} respectively, for these waters. Percent removal and removal rate coefficients for Cu ranged from 90.6 to greater than 99.8% and 0.555 to 0.953 days^{-1}, respectively. Results from this pilot-scale study show greater removal of Cu than results from the Hawkins et al. (1997) pilot-scale study with inflow and outflow concentrations of 22.4 and 12 ug/L, respectively, resulting in 33% removal. Murray-Gulde et al. (2003) found comparable removal of copper in a full-scale CWTS with 78% removal of total-recoverable Cu, where average inflow and outflow Cu concentrations were 25(±10) ug/L and 6(±3) ug/L, respectively. Percent removal and removal rate coefficients for Pb ranged from 93.1 to greater than 99.3% and 0.474 to 0.964 days^{-1}, respectively. The removal of Pb in this pilot-scale study is greater than removal found by Hawkins et al. (1997) who found 79% removal of Pb with 10.5 inflow concentration and 2.2 ug/L outflow concentration. Percent removal and removal rate coefficients for Zn ranged from 40.0 to 99.8% and 0.128 to 0.758 days^{-1}, respectively. Removal of Zn from the simulated PW was comparable to removal observed in microcosm and pilot-scale wetland studies performed by Gillespie et al. (1999) and Hawkins et al. (1997) who reported removal percentages ranging from 38 to 85%. Performance of the CWTS was least for the metals in the treatment of simulated brackish water; however, 0.157 mg Cd/L, 0.953 mg Cu/L, 2.539 mg Pb/L, and 8.655 mg Zn/L was removed from the water column.

Table 41. System inflow concentration (mg/L), outflow concentration (mg/L), percent removal, and rate coefficients (days-1) for cadmium, copper, lead and zinc in simulated PWs.

Water Category	Cadmium (as $CdCl_2$)			
	Inflow	Final Outflow	% removal	K ($days^{-1}$)
Fresh	0.312	0.008	97.6%	0.745
Brackish	0.409	0.252	38.4%	0.121
Saline	1.008	0.004	99.6%	0.705
Hypersaline	1.976	0.008	99.6%	0.686
	Copper (as $CuCl_2$)			
	Inflow	Final Outflow	% removal	K ($days^{-1}$)
Fresh	0.703	Non-Detect	>99.1%	0.953
Brackish	1.052	0.099	90.6%	0.592
Saline	5.314	0.063	98.8%	0.555
Hypersaline	3.498	Non-Detect	>99.8%	0.796
	Lead (as $PbCl_2$)			
	Inflow	Final Outflow	% removal	K ($days^{-1}$)
Fresh	0.744	Non-Detect	>99.1%	0.964
Brackish	2.557	0.176**	93.1%	0.669
Saline	6.012	0.136	97.7%	0.474
Hypersaline	13.170	0.095	99.3%	0.616
	Zinc (as $ZnCl_2$)			
	Inflow	Final Outflow	% removal	K ($days^{-1}$)
Fresh	5.180	0.367	92.9%	0.530
Brackish	21.630	12.985	40.0%	0.128
Saline	48.634	0.374	99.2%	0.608
Hypersaline	79.400	0.185	99.8%	0.758

k = rate coefficient

**Indicates a non-detect value was present (ND values were not included in average calculations)

- Detection limit for each element was 0.002 mg as Cd/L, 0.006 mg as Cu/L, 0.006 mg as Pb/L, and 0.005 mg as Zn/L.

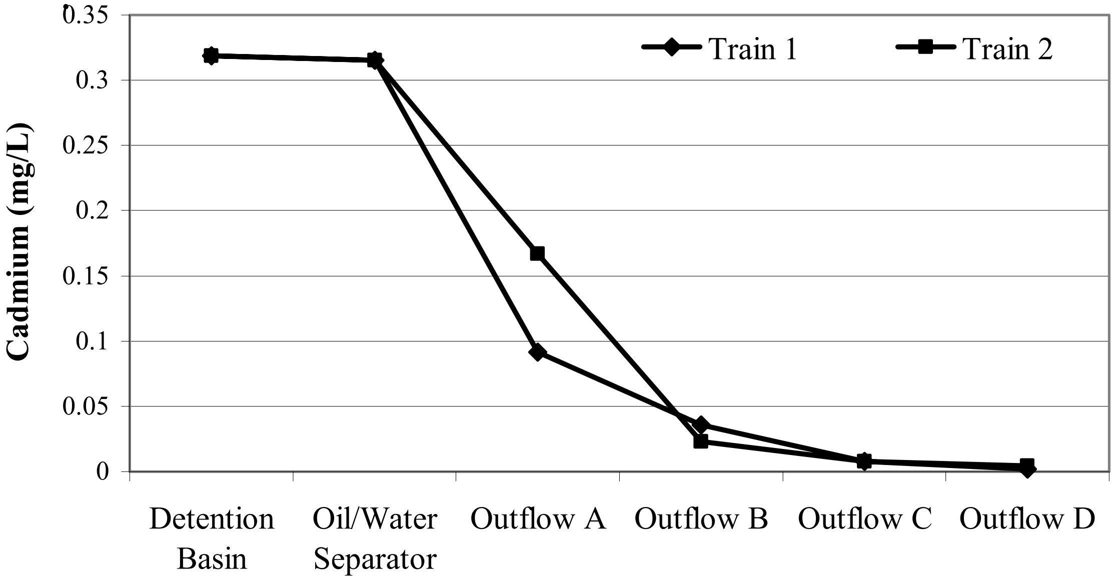

Figure 37. Total cadmium removal from simulated fresh PW by the pilot-scale CWTS

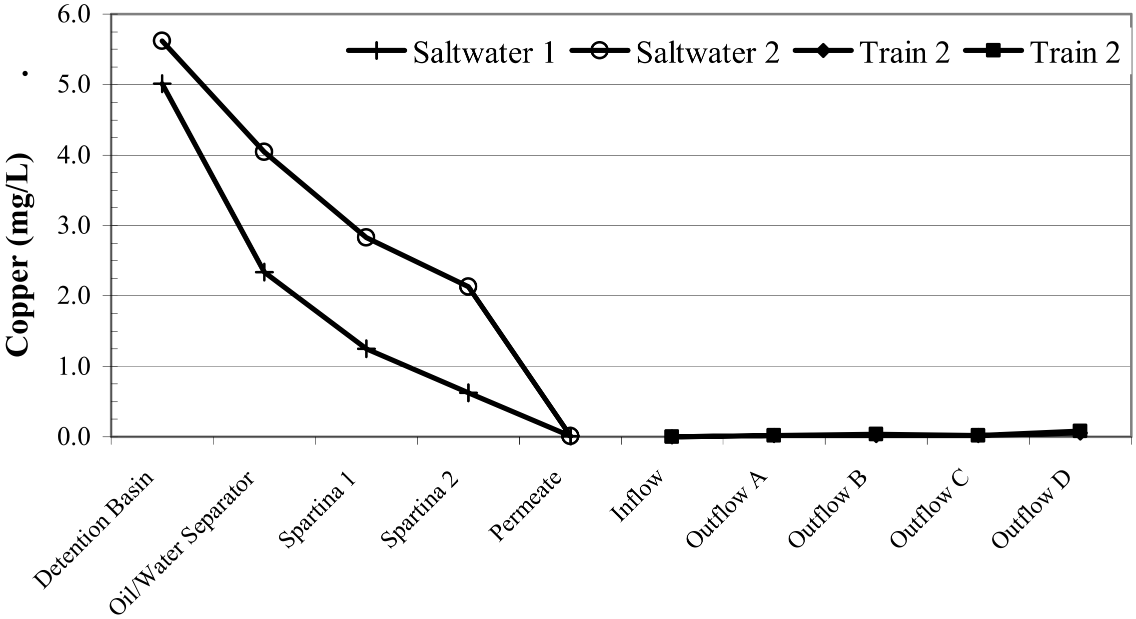

Figure 38. Total copper removal from simulated saline PW by the pilot-scale CWTS

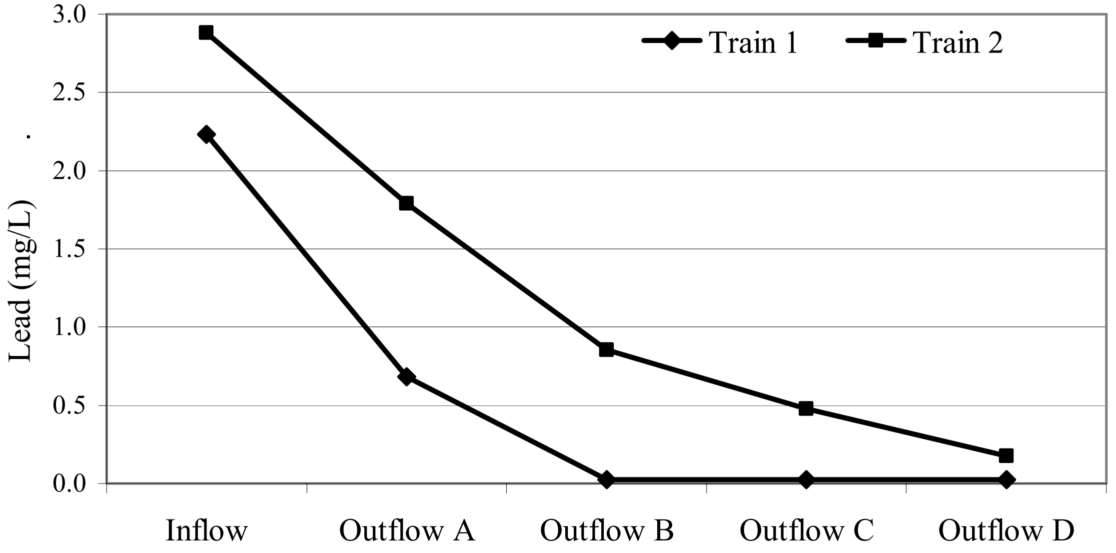

Figure 39. Total lead removal from simulated brackish PW by the pilot-scale CWTS

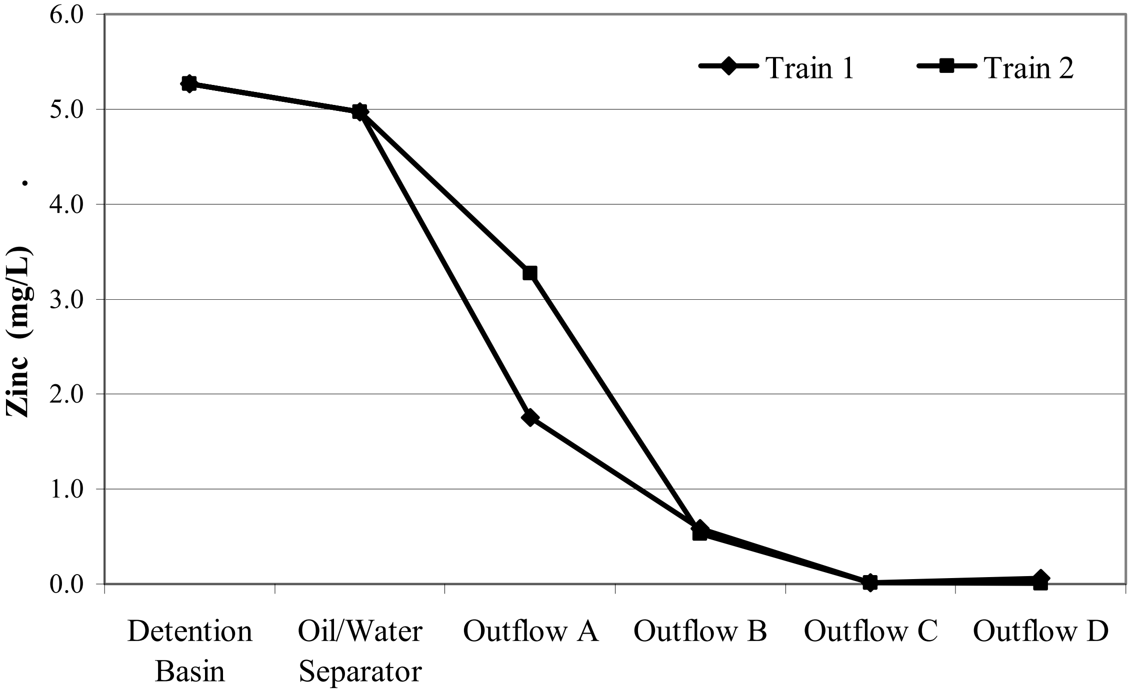

Figure 40. Total zinc removal from simulated fresh PW by the pilot-scale CWTS

Figures 17-20 illustrate removal of Cd, Cu, Pb, and Zn from the water column by the pilot-scale CWTS. For the experiments, Cd, Pb, and Zn were extensively removed in the initial two reactors of the CWTS. Figure 18 illustrates Cu removal from the simulated Saline PW using the saltwater portion of the CWTS. Though the primary purpose of the saltwater wetland module was removal of residual organics post-oil/water separator treatment, the saltwater system was also effective for removal of metals from the water column.

Oil/grease was measured as total petroleum hydrocarbons (TPH) in the inflow and outflow for simulated fresh PW. The inflow water contained 1.5 mg/L TPH as diesel fuel. The oil/water separator outflow and final outflows were non-detect (<1 mg/L TPH as diesel fuel).

Toxicity

Toxicity experiments were used to assess performance of the pilot-scale CWTS using *C. dubia* in 7-day static renewal toxicity tests for each simulated PW. *C. dubia* were exposed to inflow and outflow waters from the pilot-scale CWTS. Chloride concentrations for Brackish, Saline and Hyper-saline simulated produced waters would contribute directly to the toxicity of the sample, and thus conceal or confound other potential toxicants (Sauer et al., 1997). Samples were diluted to chloride concentrations less than 400 mg Cl/L.

Fresh PW inflow water to the CWTS was toxic; exposures of 5% resulted in 90% mortality of *C. dubia*. A 1% dilution of inflow water caused no mortality of *C. dubia*, however statistically decreased reproduction was observed. No mortality or reproductive effects were observed for *C. dubia* exposed to undiluted (100%) outflow from the CWTS. These results indicate mitigation of risk (i.e. decrease in toxicity) to *C. dubia* from fresh PWs by the pilot-scale CWTS.

For the Brackish PW, both the inflow and outflow waters were toxic; however, the outflow water was less toxic than the inflow water. Exposures of 2.5% Brackish PW inflow water resulted in complete mortality of *C. dubia.* Inflow waters diluted to 1.2% caused no mortality but statistically decreased reproduction. Outflow waters diluted to 2.5% caused no mortality but reproduction impairment was observed. Outflow waters diluted to 1.2% caused no measured toxicological effects. Poor performance in terms of removal of toxicity may be the result of the lack of maturity of the system and relatively high initial loading of constituents of concern. The Brackish PW was the first water introduced to the system. Upon analysis of samples, noting that there was not efficient removal, the system was given more time to mature before continuing experiments with the simulated fresh, saline, and hyper saline PWs.

For both Saline and Hyper-saline PW inflow waters resulted in complete mortality of *C. dubia* while outflow waters resulted in no mortality or reproductive effects. Saline and Hyper-saline inflow waters were diluted to 3% and 1.2%, respectively, in order to eliminate toxicity from chlorides. Outflow waters were not diluted because the RO unit removed chlorides.

Toxicity to *C. dubia* was reduced from inflow to outflow for each of the four waters. Though the outflow brackish waters were still toxic, the toxicity was still decreased from inflow to outflow. Toxicity was removed completely by the pilot-scale CWTS for Fresh, Saline, and Hyper-saline PWs.

Scaling, Corrosion and Biofouling

Using corrosion and scaling coupons the potential for chemical scale formation, corrosion and biofouling was measured before treatment (inflow) and after treatment by a constructed wetland (outflow). Biofouling potential significantly decreased from inflow to outflow, averaging 92% reduction of biofouling potential for CWTS series A and B. Potential for scaling was not significantly impacted by the CWTS. However, corrosion potential increased.

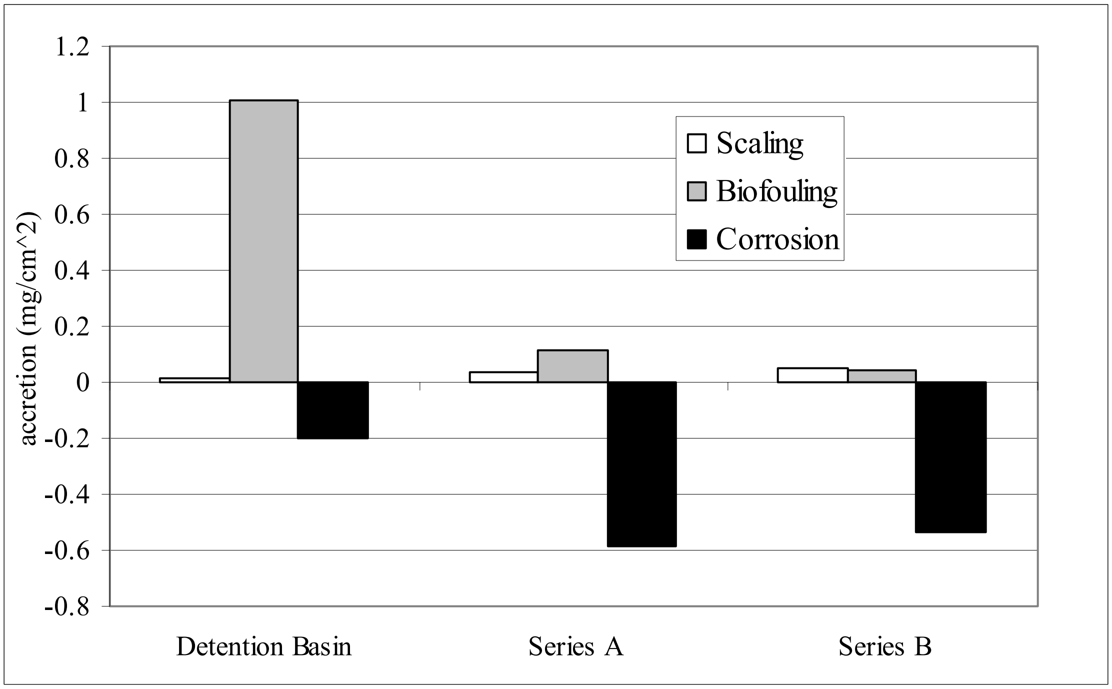

Figure 41. Corrosion, scaling and biofouling in PW

Discussion and Conclusions

CWTS in this pilot-scale study were capable of removing constituents of concern and consequently toxicity from simulated PWs. This pilot-scale system utilized a modular design, which allowed for flexibility in treatment of waters that varied widely in composition. Fresh and some brackish PWs may be readily treated with freshwater CWTS. PWs with chloride concentrations greater than the tolerance of *S. californicus* and *T. latifolia* require either comanagement with lower chloride waters or additional treatment. Chloride concentration is a dominating factor in choosing a risk mitigation strategy for treating PWs. RO systems, as used in this study, provided adequate chloride removal. Further research is needed to investigate alternative and cost effective chloride removal processes. The use of hybrid CWTS for mitigation of risks posed by PWs is a readily implemented approach with the potential to reduce the costs of handling water produced from a variety of sources.

Using the Puckorious Scaling Index (PSI) and formula ($PSI=2pH_s - pH_e$), the relative potential for each water to form chemical scale or cause corrosion was calculated. The specific parameters in this study were measurements of temperature, total dissolved solids, alkalinity and hardness. The variable that did change for practical purposes throughout treatment was water temperature. However, for temperatures that the CWTS experience (~0 to 37^0C) there were no significant changes in the calculated outcome. Using these measurements and calculations, all waters with the exception of ash basin water were identified prior to treatment as having "Intolerable Corrosion" on the PSI, with calculated PSI values ranging from 9 to 10.1. Ash basin water had a calculated PSI between 8 and 8.2 prior to treatment. All four non-traditional waters in this study had lower calculated PSI after treatment. And all four waters were identified as having "Heavy Corrosion" and little chemical scale forming potential after treatment in the CWTS.

DECISION SUPPORT SYSTEM FOR NON-TRADITIONAL WATERS AT THERMOELECTRIC POWER PLANTS

The purpose of this section of this report is to present a decision support system for constructed wetland treatment systems for non-traditional waters associated with thermoelectric power generation. For this study, these waters include cooling waters, ash basin waters, flue gas desulfurization waters and produced waters. However, this decision support system can apply to other waters at other sites and other industries.

The decision support system is intended to guide a manager or potential owner to arrive at an informed decision regarding pursuing a constructed wetland treatment system for a water or wastestream at a specific site. The decision support system is outlined below and is accompanied by explanatory information to aid in use of the system.

Decision Support System for Thermoelectric Power Plant Waters

The purpose of this Decision Support System is to provide guidance for managers or potential owners in order to determine whether or not a constructed wetland treatment system would be an appropriate strategy for renovation of their non-traditional water for reuse (Table 1). In this case, non-traditional waters are cooling waters, ash basin waters, flue gas desulfurization waters and produced waters. For the purpose of this study, reuse refers to renovation of non-traditional waters for internal (within the thermoelectric power plant) reuse or for external reuse (for propagation of fish and wildlife or for irrigation). Renovation or treatment criteria for non-traditional waters for internal reuse include standards for corrosion, biofouling and scaling. Renovation or treatment criteria for non-traditional waters for external reuse may include water quality criteria designed to be protective of aquatic life as well as irrigation standards for specific food or non-food plants.

1. Targeted Constituents – Concentrations, Forms

The first consideration in selection of a constructed wetland treatment system for a non-traditional water at a thermoelectric power plant is based on the applicability of this approach to the targeted constituent(s) in the water that requires treatment. For example, typical constituents of concern in cooling waters include antibiofouling agents (e.g. chlorine) and metals such as copper. Constituents of concern in ash basin waters include divalent metals such as copper, mercury and zinc and other metals and metaloids such as iron and selenium. In flue gas desulfurization waters, constituents of concern can include selenium, mercury and arsenic that are relatively readily treatable in constructed wetland treatment systems, as well as chlorides and boron that are not treatable in constructed wetland treatment systems, but must be treated using "hybrid" systems (Rodgers and Castle 2008) or co-managed with other site waters. Constituents in produced waters range widely (Johnson et al. 2008) as do constituents of concern in those waters. Produced waters may contain organics and metals that are amenable to treatment in constructed wetland treatment systems. They may also contain chlorides and other conservative or recalcitrant constituents that are treatable by methods involving reverse osmosis or other engineered techniques.

Important in this initial step in the decision process is identification of potential pathways that can treat (transfer or transform) the constituents of concern into sequestered, non-bioavailable forms in constructed wetland treatment systems (Rodgers and Castle 2008). Then you would want to determine if the rate of removal and extent of removal of the constituents of concern are sufficient to achieve the requisite performance goals. Those performance goals (or design criteria) arise from the internal reuse criteria (for corrosion, biofouling and scaling) or external reuse criteria (e.g. water quality criteria, NPDES criteria, irrigation criteria, etc.).

2. Land Availability (Related to Volume and Flow)

Since constructed wetland treatment systems are essentially solar driven systems, they require sufficient land or "footprint" to retain the water for a duration that is adequate to accomplish the transfers or transformations of the targeted constituents. The land requirement is related to the flow of the non-traditional water to be treated as well as the periodicity (magnitude, frequency, etc.) of the flow. Typically, for non-traditional waters such as flue gas desulfurization waters, about one acre per 250,000 gallons per day is a satisfactory initial estimate. Land that is unsuitable for other uses (e.g. land under power or transmission lines) is satisfactory for constructed wetland treatment systems. For some situations, treatment systems can be housed in a greenhouse to maximize efficiency year-round.

3. Latitude / Altitude – weather, climate

As noted above, the climate and growing season can affect the sustained performance of constructed wetland treatment systems. These effects are generally due to weather associated with latitude and altitude, although longitude (desert, seashore, etc.) can also play a role. As long as water can be maintained as a liquid, the constructed wetland treatment systems can continue to function. Other approaches for dealing with weather (especially cold) include utilization of "waste" heat and incorporation of sub-surface flow insulated by the earth. If wetlands exist in the vicinity of the source of the water to be treated, it is probable that a constructed wetland treatment system can be specifically designed for that site.

4. Regulatory Acceptance

One consideration in selection of a constructed wetland treatment system for non-traditional waters at thermoelectric power plants is regulatory acceptance. Regulatory authorities should be engaged as soon as practical in the decision making process. They are usually involved in the feasibility study or after that study has produced a positive recommendation. Pilot-scale studies are often used in site-specific situations to provide performance data and to provide additional information in support of the feasibility study. The pilot-scale studies are also useful for providing information that can be used for efficient design of the full scale treatment system.

5. Cost

A final, major consideration regarding the feasibility of a constructed wetland treatment system for a specific site is cost. In general, capital costs for constructed wetland treatment systems are 10-50% of the cost for conventional treatment systems. Land is usually a major portion of the cost if it must be acquired. Operation and maintenance costs are usually minimal (a small fraction of conventional treatment systems).

Outline of Example of a Decision Regarding Implementation of a Constructed Wetland Treatment System

The initial consideration involves the type of non-traditional water and the targeted constituent. If the targeted constituent can be treated (transferred or transformed) in a constructed wetland treatment system, then the feasibility process can proceed. The next decision criterion that must be answered affirmatively involves the rate and extent of treatment achievable in comparison with the performance criteria for internal or external reuse. The data to support an informed decision regarding rate and extent of treatment achievable may be derived from a previous study (i.e. published literature) or from a pilot-scale study (Rodgers and Castle 2008). The decision criterion regarding land availability requires an initial estimate of the land required. This estimate can also be obtained from published literature or a pilot study. If the requisite land is available or can be acquired for an acceptable price, the next portion of the decision process involves site-specific consideration of weather parameters such as degree days and evapotranspiration rate. The final part of a feasibility decision or study is concerned with regulatory acceptance. If regulatory authorities with responsibility for the site are receptive to constructed wetland treatment systems by virtue of education or positive past experiences, they can support and facilitate the implementation. A final, major consideration is cost. In general, costs for constructed wetland treatment systems are 10-50% of the cost for conventional treatment systems.

TARGETED CONSTITUENTS

- -Water to be treated
    - -cooling water
    - -ash basin water
    - -flue gas desulfurization water
    - -produced water
- -Constituents of concern
    - -concentrations
    - -forms
- -Performance goals
    - -internal
        - -biofouling
        - -scaling
        - -corrosion
    - -external
        - -water quality criteria
        - -NPDES discharge limits
        - -irrigation criteria
- -Potential pathways for treatment
- -Rate and extent of removal

LAND AVAILABILITY

- -Volume
- -Flow
- -Area required

LATITUDE / ALTITUDE - WEATHER, CLIMATE

- -Climate
- -Growing season
- -Degree days

REGULATORY ACCEPTANCE

- -Experience

COST

- -~10-50% of cost of conventional treatment systems
- -O&M costs minimal

OVERALL DISCUSSION AND CONCLUSIONS

To efficiently design treatment systems for remediation of a variety of waters, specific information was needed for this task such as chemical composition, variability in constituents, toxicity effects of single and multiple constituents, and discharge limits. For the four non-traditional waters addressed in this study, constituents of concern were identified from data collected through literature reviews and analyses of the waters. Certain inorganics such as arsenic, cadmium, chloride, copper, mercury, selenium, and zinc were observed at concentrations requiring monitoring or permitting limits for most non-traditional waters assessed in this study. Chlorides are a primary concern, in particular for FGD water and produced waters in which concentrations can range from as low as 130 mg/L to greater than 100,000 mg/L. Chloride concentrations in excess of 800 mg/L can cause toxic effects to *Ceriodaphnia dubia* (NPDES testing species), requiring remediation of this ion. Organic constituents such as benzene, toluene, total organic carbon, and PAHs were observed as contaminants of concern in PWs. Other water characteristics requiring monitoring and treatment can include pH, hardness, alkalinity, dissolved oxygen, biochemical oxygen demand, and chemical oxygen demand to ensure that discharge effluents do not negatively impact receiving system organisms. Characterizations of these non-traditional waters, along with treatment system requirements, establish criteria to design CWTS and monitor treatment system performance. Assessments of innovative treatment processes can provide results that have obvious and significant financial implications for water reuse in thermoelectric power generation and compliance with CWA (NPDES permits). Existing technologies or "concrete and steel" treatment systems for non-traditional waters are very costly and are often unable to achieve rigorous water-quality standards.

Based on data collected from FGD experiments, pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (As, B, Hg, N, and Se). Percent removal was specific for each element, including ranges of 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. Other constituents of interest (as listed above) in final outflow samples should have aqueous characteristics sufficient for discharge, with the exception of chlorides (<2000 mg/L). Biofouling potential was successfully treated by the CWTS, however no alteration could be determined for potential for chemical scale formation and corrosion potential was enhanced in these CWTS. However, based on total dissolved solids, co-management techniques will be needed for discharge or reuse. Based on data collected from PW experiments, hybrid pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (Zn, Cd, Pb, and Cu). Percent removal was specific for each element, including ranges of 38.4% to 99.6% for Cd, 90.6% to 99.8% for Cu, 93.1% to 99.3% for Pb, and 40.0% to 99.8% for Zn. Potential for biofouling and chemical scale formation were treated in the CWTS, however, reuse of these waters will likely depend on chloride concentration of the outflow. With use of reverse osmosis technology, chloride concentrations may be decreased sufficiently for reuse as service water. Concentrations of arsenic, selenium, chromium, and zinc were decreased in ash basin waters by CWTS. Average removal for arsenic, selenium, chromium, zinc, and mercury was 88, 21, 71, 68, and 94% respectively. CWTS were successful in reducing the potential for scale formation and biofouling in the ash basin water. Toxicity was successfully decreased in the pilot-scale CWTS effluent as compared to inflow. Pilot-scale CWTS can decrease aqueous concentrations of copper, zinc and lead in cooling waters. Average percent removal for each element was 97% for Cu, 88% for lead, and 30 % for zinc. The low percent removal for zinc is a result of minimal initial elemental concentration. CWTS were successful in reducing potential for biofouling in cooling waters. Toxicity of cooling waters was decreased by treatment with pilot-scale CWTS. Pilot-scale CWTS were successful for treating cooling water for internal reuse. Overall, pilot-scale constructed wetland treatment systems decreased constituents of concern in FGD waters, ash basin waters, cooling waters and produced waters, and could be used for treating biofouling, scaling and corrosion potential.

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