Performance of pilot-scale constructed wetland treatment systems for flue gas desulfurization waters

Derek A. Eggert, John H. Rodgers Jr., George M. Huddleston, and Carl E. Hensman

ABSTRACT

Federal laws regarding ambient air quality are currently requiring industries to reduce emissions of sulfur and nitrous oxides. Coal-fired power plants have therefore begun implementing flue gas desulfurization (FGD) scrubbers that use a highly oxygenated water stream (calcium-carbonate-saturated water) to transform sulfur gases into soluble anion species (sulfite and sulfate). The chemical compositions of FGD waters are dependent on the FGD scrubber design, coal types burned, chemical additives, and scrubbing solution source. The FGD waters contain potentially toxic elements including arsenic, cadmium, chemical oxygen demand (COD), copper, mercury, selenium, chloride, sulfates, and zinc. Therefore, these waters must be treated before discharge into a receiving system because of constituents that can elicit toxicity. The specific objectives of this research were to (1) characterize FGD waters in terms of chemical composition and constituents of concern, (2) design constructed wetland treatment systems (CWTSs) for the remediation of constituents of concern in FGD waters, and (3) measure the performance of CWTSs for formulated and actual FGD waters based on discharge criteria established by the United States Environmental Protection Agency and regulated by National Pollutant Discharge Elimination System permits. The FGD waters are characteristically high in total dissolved solids (calcium, chloride, magnesium, and sulfate), are semineutral in pH, contain high concentrations of total suspended solids, and contain several potentially toxic constituents. Constituents of concern were identified as cadmium, COD, chloride, copper, mercury, selenium, and zinc. Pilot-scale CWTSs were designed based on biogeochemical data, and each system contained an equalization basin and two reducing and oxidizing wetland reactors in series. Three FGD waters were introduced in the pilot-scale

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CWTS, and the performance was assessed by measuring targeted constituents of concern (mercury and selenium) and the toxicity of pre- and posttreatment waters. Results from these studies indicate that mercury and selenium concentrations in FGD waters can be decreased using CWTSs, and, with an appropriate comanagement of low-ionic strength water for chloride concentrations, toxicity of posttreatment samples is decreased to acceptable discharge limits.

INTRODUCTION

Coal-burning power plants are significantly decreasing air emissions of sulfur dioxides (SO_2) by installing flue gas desulfurization (FGD) scrubbers (United States Department of Energy [U.S. DOE], 2000). As the demand for electrical energy increases, a concomitant increased production of FGD scrubber waters is observed. According to the U.S. DOE, the United States burned 1039 million short tons of coal (Freme, 2005), and the amount of this by-product water can exceed 0.1 million gallons per day at large facilities (>1000 MW). The most commonly used FGD scrubber is referred to as a "wet scrubber," which uses lime- or limestone- (calcium carbonate) saturated water to solubilize gaseous SO_2 and oxidize and precipitate sulfur compounds as calcium sulfite ($CaSO_3$) or calcium sulfate ($CaSO_4$). This scrubbing process occurs by directly contacting the flue gas that remains after the oxidization of coal with the scrubbing solution and is oxygenated by forced air injection in the collection basin. The resulting by-product water is typically referred to as FGD water. At each coal-fired power plant, the composition of FGD water is a function of several chemical and physical variables that include the coal source and composition, burner and FGD scrubber design and operation, postscrubber treatment processes, and initial constituents in the local water supply (Mierzejewski, 1991). Because coals can differ drastically in chemical composition (Gluskoter et al., 1977; PECH, 1980; Devito et al., 1994; Yudovich and Ketris, 2005a, 2005b), FGD waters can be influenced by the type of coal burned as well as the burner capacity and environment (i.e., oxygen content and heat). The FGD scrubber design and operation can influence the composition of FGD waters caused by physical mechanisms (e.g., area of the gas-water interface, salinity capacity of the reactor, and loss of water vapor) and chemical mechanisms such as pH buffers (i.e., organic dibasic acids). Postscrubber treatment processes typically target the removal of suspended solids and the reclamation of FGD water using gravitational settling basins (e.g., clarifier), hydrocyclones, and dewatering devices (e.g., sludge belt press). Some coal-fired power plants also employ charge-neutralizing and chelating compounds (e.g., iron salts, flocculants, and metal precipitants) for the removal of solids and specific contaminants.

The FGD waters pose several environmental challenges. The FGD waters are produced in large volumes, can vary widely in chemical composition, and may contain constituents in concentrations and forms that are toxic to the receiving aquatic system biota. Constituents of environmental concern in FGD waters may include arsenic, chemical and biological oxygen demand, boron, cadmium, chromium, copper, chloride, lead, mercury, nitrate, selenium, sulfate, and zinc (Mierzejewski, 1991). The FGD waters are typically not suitable for reuse within a power plant as make-up or cooling water because of corrosion, scaling, and the biofouling effects of these waters. Therefore, the treatment and discharge of these waters are required, and releases to aquatic systems are regulated by the United States Environmental Protection Agency (USEPA) under the Clean Water Act through National Pollutant Discharge Elimination System (NPDES) permits. The treatment criteria for FGD waters are site specific and can include limits for contaminant concentrations (i.e., maximum daily limit), speciation of contaminants (e.g., selenite or selenate), and toxicity measurements (e.g., 7-day static or renewal toxicity experiments with *Ceriodaphnia dubia*). The *C. dubia* is a sentinel aquatic invertebrate species widely used for toxicity testing in NPDES programs (Spehar and Fiandt, 1986; Mount et al., 1997; Brix et al., 2001).

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

One potential remediation strategy for FGD waters is constructed wetland treatment systems (CWTSs). By understanding and manipulating the biogeochemical cycles of constituents of concern, constructed wetlands can be designed to transform or transfer targeted constituents to stable chemical forms thereby decreasing their mobility, bioavailability, and redistribution (i.e., dissolution). A successful remediation of diverse waters has been achieved with this treatment strategy including storm water runoff (Murray-Gulde et al., 2005a, b), nutrient-enriched waters (Huett et al., 2005), acid mine drainage (Sobolewski, 1996), municipal waters (Ansola et al., 2003), and agricultural runoff (Moore et al., 2000). These systems have been used extensively for risk mitigation of many elements or compounds present in FGD waters; however, no studies have been published to date on CWTSs for FGD waters.

This study was initiated to evaluate the potential for CWTSs to mitigate the risks of constituents of concern in FGD waters. Each identified constituent of concern in FGD waters was investigated for chemical reaction pathways that provided adequate transformation and transfer mechanisms (i.e., stable chemical forms) in aquatic environments (i.e., wetland reactors). After pilot-scale CWTSs were designed to treat constituents of concern in FGD waters, we measured the ability of these systems to decrease the targeted constituents of concern. To thoroughly evaluate the ability of CWTSs to mitigate risks in diverse FGD waters, formulated FGD water, actual FGD waters, and pilot-scale scrubber FGD waters were used in these experiments. Formulated FGD waters were used to initially assess the potential treatment and design of CWTSs for synthesized FGD waters, whereas actual FGD waters were used to assess the performance and design of CWTSs for FGD waters that varied in chemical composition. Pilot-scrubber FGD waters were actual FGD waters produced in small volumes (operated for 1 week) at a coal-fired power plant to assess the influence of four coal types on the chemical composition of FGD waters and measure the treatment performance of pilot-scale CWTSs. The specific objectives of this research were to (1) characterize FGD waters in terms of chemical composition and constituents of concern, (2) design CWTSs for the remediation of constituents of concern in FGD waters, and (3) measure the performance of CWTSs for formulated and actual FGD waters based on the discharge criteria established by the USEPA and regulated by NPDES permits.

MATERIALS AND METHODS

Characterization of Flue Gas Desulfurization Waters

Four actual FGD waters were collected from operating scrubber systems, shipped on ice, and measured for chemical composition using total elemental and water chemistry analyses. For elemental composition measurements, a 100-mL aliquot of FGD water was preserved with trace metal nitric acid (10% v/v; Fisher Scientific Inc.) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Elan 9000, Perkin-Elmer Inc.). Total mercury analyses were conducted by cold vapor hydride generation atomic absorption (Perkin-Elmer FIMS-400) and ICP-MS. Other water chemistry parameters were analyzed according to standard methods (American Public Health Association, 1998). The constituents of concern were identified based on comparisons between the criteria in NPDES permits and the mean concentrations of each constituent in four actual FGD waters. The NPDES permit criteria included the maximum discharge limit (MDL) and toxicity reference values. The MDLs for each constituent were obtained from the USEPA's NPDES permit database for operating FGD scrubber coal-fired power plants. Toxicity reference values were obtained from the EPA's toxicity database (ECOTOX Release 4.0) and analyzed for the lowest observable effect concentration (LOEC) or lethal mean concentration values, if LOEC values could not be obtained from this database or literature reviews. When the concentration of a constituent in FGD waters exceeded the MDL or the toxicity reference value, the constituent was classified as a constituent of concern.

Design Pilot-Scale Constructed Wetland Treatment Systems

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

Assembly of Constructed Wetland Treatment Systems

The initial component of the CWTS, the equalization (EQ) basin, consisted of a polypropylene cylindrical container ranging in volume from 3780 to 6800 L. Inflow FGD waters were loaded into the treatment systems using piston-driven pumps (Fluid Metering Inc.) calibrated at flow rates (mL/min) to establish a specific hydraulic retention time (HRT) in each system component. A sequential flow through these systems was established using gravity.

To evaluate the performance of pilot-scale CWTSs, three replicated series of reactors were used for each system (Figure 1A). Each system consisted of four treatment reactors in series that included two reducing reactors, a rock basin, and an oxidizing reactor. Each reactor was contained in a 378-L Rubbermaid® utility tank. Reducing reactors contained approximately 30 cm (11.8 in.) of river sand as hydrosoil (3–5% organic matter by volume, 1% gypsum by volume, and 200 lb/ac of zero-valent iron) planted with *Schoenoplectus californicus* C. A. Meyer. The rock basin was 50 cm (19.6 in.) of pea gravel, and the oxidizing reactor contained approximately 30 cm (11.8 in.) of river sand hydrosoil planted with *Typha angustifolia* L.

To evaluate the treatment performance of pilot-scale CWTSs for pilot-scrubber FGD waters, the experimental pilot-scale CWTS consisted of two treatment systems each with two replicates (Figure 1B). Treatment systems were defined as Ash CWTS and No-Ash CWTS. Both treatment systems were established with four reactors in series that included two reducing reactors, a modified rock basin, and an oxidizing reactor. Each reactor was contained in a 265-L Rubbermaid® utility tank. All reducing reactors contained approximately 30 cm (11.8 in.) of river sand hydrosoil (3–5% organic matter by volume and 1% gypsum by volume) planted with *S. californicus*. The modified rock basin was equally divided with the inflow half consisting of 12.7–17.8-cm (5–7-in.) granite rocks and the latter half consisting of 30 cm (11.8 in.) of hydrosoil and *T. angustifolia*. Oxidizing reactors contained approximately 30 cm (11.8 in.) of hydrosoil and were planted with *T. angustifolia*. The Ash CWTS differed from the No-Ash CWTS in that the modified rock basins and oxidizing reactor contained bottom ash as a substitute for river sand hydrosoil. The total HRT for the CWTS was 168 or 36 hr per reducing reactor and 48 hr each for the modified rock basin and oxidizing reactor.

Performance Measurement of Constructed Wetland Treatment Systems for Flue Gas Desulfurization Waters

Flue Gas Desulfurization Waters

To understand the remediation potential of CWTSs for constituents of concern in FGD waters, three different FGD water types were selected for this study as described below. These waters were used to assess the removal of constituents of concern from formulated and actual FGD waters that range widely in chemical composition. Because of the adverse effects of FGD waters on the wetland plants, chloride concentrations were decreased to less than 5000 mg/L for all experimental

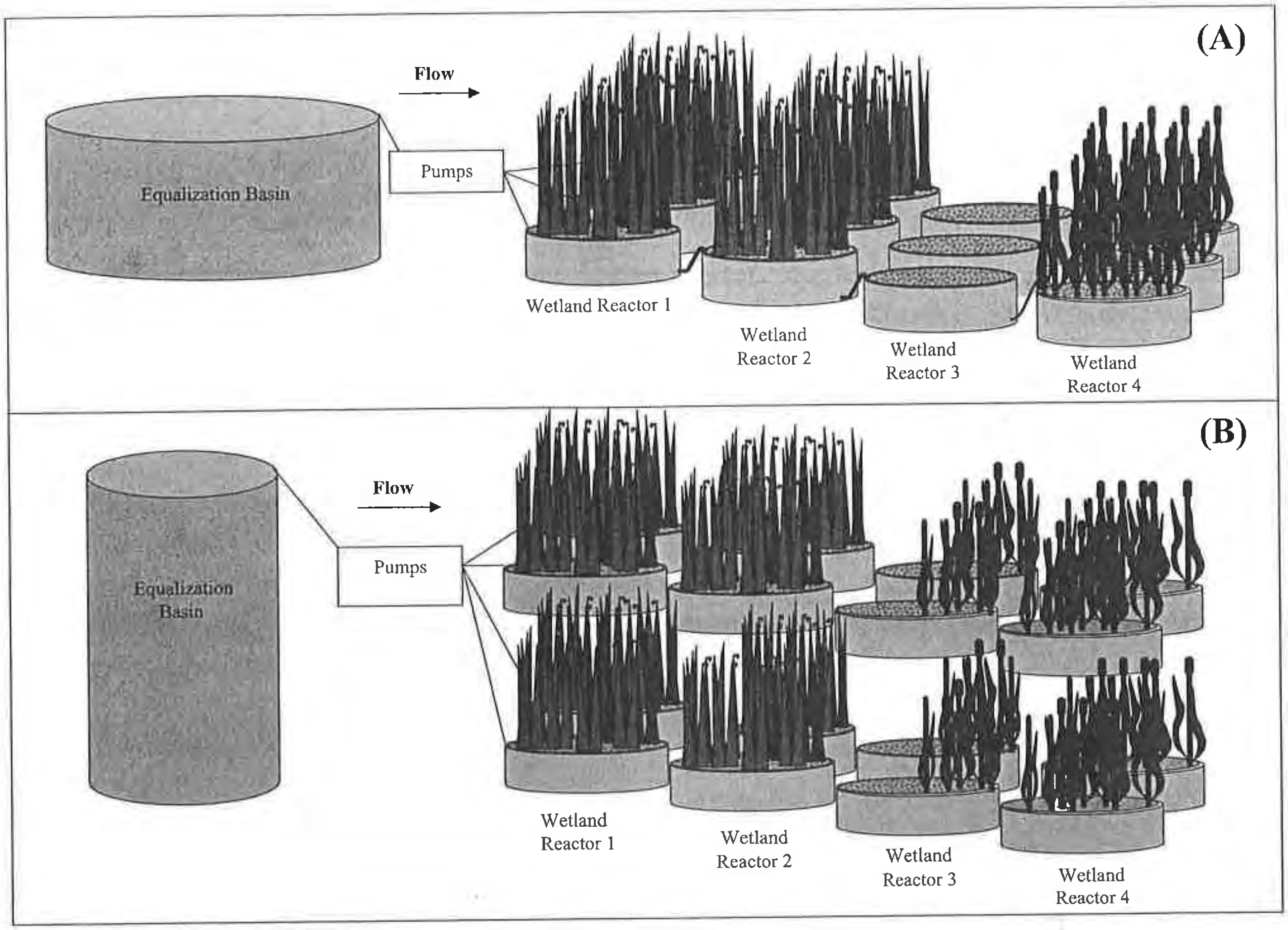

Figure 1. Systematic diagram of the pilot-scale constructed wetland treatment systems used to determine the performance criteria for (A) formulated and actual-amended FGD waters and (B) pilot-scrubber FGD waters.

waters described in this article by comanagement with waters containing low chloride concentrations.

Formulated FGD water was synthesized based on data from chemical analyses of actual FGD waters. This formulation process included amending municipal water with (1) high-purity salts (Fisher Scientific Inc.) of targeted constituents of concern (Hg, Se, and As), (2) technical grade salts for chloride and sulfate, (3) fly ash at 1000 mg/L, and (4) dibasic acid at an equivalent COD concentration of 250 mg/L. For this initial research, additional constituents such as nitrate, boron, copper, chromium, zinc, and other elements or compounds were not amended. Formulated FGD waters were loaded into the pilot-scale CWTS for 20 weeks (June to November), and samples were collected and analyzed bimonthly ($n = 10$) for treatment performance criteria. Because formulated FGD waters omit some constituents that may influence performance, actual FGD waters were also evaluated in this study.

Actual FGD water from an operating coal-fired facility was transported to Clemson University in an 18,900-L tanker. Because of low concentrations of selenium and mercury measured in this FGD water after the dilution for chlorides, amendments were initiated so the removal rates and extents of these constituents could be measured. Selenium was amended using sodium selenate and sodium selenite (2:1, respectively) to achieve a total selenium concentration of approximately 2 mg/L. Mercuric nitrate was added to achieve a target total mercury concentration of approximately 0.2 mg/L. Actual FGD water was tested in addition to formulated FGD waters to assess any effects of other normally occurring elements and compounds in FGD waters on the removal of mercury, selenium, and arsenic in pilot-scale CWTSs.

Four pilot-scrubber FGD waters were produced using a pilot-scale scrubber (URS Corp., Austin, Texas) in conjunction with a full-scale coal-fired burner. These

FGD waters were transported to Clemson University via two 18,900-L tankers. Comanagement water from this specific location was also shipped to decrease the chloride concentrations for treatment with pilot-scale CWTSs. Pilot-scrubber FGD waters were used to test the treatment efficiency of pilot-scale CWTSs for four distinct FGD waters originating from four different coal sources. The FGD waters were diluted to approximately 4000 mg/L as chloride using the site water before loading into the pilot-scale CWTS.

Analytical Procedures

For each experiment conducted in this study, aqueous samples were collected from the EQ basin, inflows to the pilot-scale CWTS, and outflows from each reactor in series. Aqueous samples were collected in 1000-mL Nalgene® containers, preserved, and analyzed as previously described. The extent of removal was calculated based on

$$\text{Extent of removal} = (1 - ([A]_t/[A]_0)) * 100 \qquad (1)$$

where $[A]_t$ is the concentration of the constituent in the EQ basin (pretreatment) and $[A]_0$ is the concentration of the constituent in the outflow sample of reactor four (posttreatment). Removal rates for mercury and selenium were calculated using the first-order rate equation

$$\text{Removal rate} = \ln([A]_t/[A]_0) = kt \qquad (2)$$

where $[A]_t$ and $[A]_0$ are the same as described for the extent of removal, t is the total time of treatment, and k is the first-order rate coefficient. Oxidation-reduction (redox) potentials of wetland hydrosoils were measured using a millivolt meter connected to in-situ platinum-tipped electrodes and an Accumet® calomel reference electrode (Faulkner et al., 1989). All measurements were adjusted based on hydrogen ion potential.

Toxicity Evaluations

Toxicity evaluations were performed on pre- and posttreatment samples diluted to less than or equal to 500 mg/L as chloride to remove the toxicity solely caused by chloride concentrations (reproductive no observable effect concentration [NOEC] = 640 mg/L as Cl^-; unpublished data). These evaluations were conducted with C. *dubia* following the U.S. EPA protocol for measuring chronic toxicity of effluents and receiving waters to freshwater organisms (Lewis et al., 1994). Toxicity measurements were evaluated by comparing the responses of C. *dubia*, in terms of survival and reproduction, exposed to pre- and posttreatment samples of FGD and control water (moderately hard water). Survival data were statistically compared using chi-square analysis (PROC FREQ; SAS Institute Inc., 1989), and reproduction data were compared using a one-way analysis of variance with Dunnett's means separation (PROC GLM; SAS Institute Inc., 1989). All alpha levels were set at 0.05. Water quality parameters including hardness, alkalinity, pH, dissolved oxygen, conductivity, and water temperature were measured initially (day 0) and daily throughout the duration of the toxicity experiment (days 1–7) according to standard methods (American Public Health Association, 1998).

RESULTS

Characterization of Flue Gas Desulfurization Waters

Four actual FGD waters were analyzed for water chemistry parameters and total elemental composition (Table 1). The constituents of concern were identified as cadmium, chemical oxygen demand (COD), chloride, copper, mercury, selenium, and zinc (Table 2). All constituents of concern were identified based on toxicity values, except COD, which was identified as a potential constituent of concern because of high concentrations measured in FGD waters (1339.3 ± 377.3 mg/L) and the relationship of COD to 5-day biochemical oxygen demand (BOD_5) (NPDES maximum daily limit of 30 mg/L as BOD_5). Boron was not assessed for potential toxicity effects because elemental analyses were not conducted, but it may be identified as a constituent of concern if total concentrations exceed 18 mg/L in effluent samples (Hickey, 1989). Current available NPDES permits for the discharge of FGD waters analyzed in this study have maximum daily limits for copper (≥1 mg/L), iron (≥1 mg/L), mercury (≥0.63 μg/L), total suspended solids (≥65 mg/L), BOD_5 (≥45 mg/L), oil and grease (≥12 mg/L), pH (6–9), and toxicity evaluations using 7-day static or renewal experiments with C. *dubia* for exposures of greater than or equal to 1.9% as FGD water. Based on a review of available information, all other NPDES permits require the monitoring and reporting for constituents in FGD water other than the listed constituents above. Apparently, only one discharge site is required to meet a maximum daily limit for selenium (≤26 μg/L as Se). Some NPDES permits also have tissue monitoring in

Table 1. Chemical Composition of Actual, Formulated, Actual-Amended, and Pilot-Scrubber FGD Waters for Elemental and Water Chemistry Parameters Presented as Means and Standard Deviation Values (Mean ± Standard Deviation) in Milligrams per Liter (mg/L)

Parameter	Actual FGD Waters	Formulated FGD Waters*		Actual-Amended FGD Waters		Pilot-Scrubber FGD Waters			
		Nominal	Measured	Pre-Amended	Post-Amended	PS1	PS2	PS3	PS4
Mercury, total**	15.2 ± 28.5	2.0	2.57 ± 1.2	<0.2	160.0	43.2	4.7	0.39	47.0
Selenium, total	5.10 ± 8.12	4.00	4.22 ± 0.319	0.15	1.80	2.97	0.61	0.649	2.09
Selenite (Se IV)†	NM‡	NM	NM	NM	NM	95.0%	50.2%	34.8%	86.3%
Selenate (Se VI)†	NM	NM	NM	NM	NM	<1.0%	6.0%	3.6%	<1.0%
Arsenic, total	1.07 ± 2.02	0.17	0.171 ± 0.023	0.014	0.072 ± 0.001	0.101	0.004	0.035	0.035
Boron, total††	NM	NM	NM	NM	NM	60	32	100	110
Chloride, total	10,310 ± 6433	4000	3678 ± 288	9300	4675 ± 742	3550	3150	4050	4225
Calcium, total	2308 ± 1103	900	NM	2880	NM	NM	NM	NM	NM
Magnesium, total	2960 ± 1156	1150	NM	1360	NM	NM	NM	NM	NM
Sodium, total	708 ± 472	NA‡‡	NM	624	NM	NM	NM	NM	NM
Sulfate	2059 ± 793	800	828 ± 181	1645	432 ± 35	1522	1611	1245	1364
pH	6.28 ± 0.23	7.00	7.00 ± 0.26	6.38	6.72 ± 0.23	6.79	6.99	7.11	7.10
Alkalinity as $CaCO_3$	390 ± 194	150	103.4 ± 10.5	152	63 ± 7.1	26	46	24	32
Hardness as $CaCO_3$	18,677 ± 6013	7250	6540 ± 2480	10,400	6600 ± 282	9800	4200	6400	6400
Conductivity	28.86 ± 8.31	11.00	9.21 ± 0.60	23.11	11.16 ± 2.44	10.88	10.05	11.65	11.96
Dissolved oxygen	7.23 ± 1.22	8.00	7.75 ± 1.55	9.03	8.48 ± 0.16	9.09	8.66	8.66	8.96
Chemical oxygen demand	1339.9 ± 377.3	250	227.4 ± 44.9	938	238.5 ± 3.5	183	81	155	208
Nonpurgable organic carbon	81.94 ± 40.29	100	91.96 ± 58.73	64.49	161.3 ± 95.1	NM	NM	NM	NM
Total suspended solids	10,901 ± 20,042	200	207.0 ± 136.6	25	66.4 ± 1.9	5.80	10.35	159.6	356
Total dissolved solids	39,103 ± 10,724	8000	6183.8 ± 2965.8	23,875	12,267 ± 380	11,674	10,921	13,851	19,025

*Formulated FGD waters were synthesized based on a chloride concentration of approximately 4000 mg/L.
**Reported as micrograms per liter (μg/L).
†Analyzed by ion chromatography inductively coupled plasma dynamic reaction cell mass spectrometry (IC-ICP-DRC-MS).
††Measured before dilution for chloride concentrations.
‡NM = not measured.
‡‡NA = not amended.

fish species for mercury and selenium, speciation of selenium in the effluent samples, and toxicity evaluations using *Pimephales promelas*, but these criteria on NPDES permits were not common and therefore not used as performance criteria in this study.

Design Constructed Wetland Treatment Systems for Flue Gas Desulfurization Waters

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

- Equalization basins were designed as the initial component in each experimental system to remove suspended solids and homogenize (equalize) concentrations of contaminants before the introduction into the treatment system. The Scale and dimensions of this component simulated an actual full-scale EQ

Table 2. Identified Constituents of Concern from Four Actual FGD Waters Based on Toxicity Effects After Comanagement for Chlorides

Constituent*	Species	Experiment	FGD waters** (mg/L)	Toxicity Value† (mg/L)	Reference
Cadmium	*C. dubia*	7 days static or renewal	0.037	0.004	Suedel et al., 1997
Chloride	*C. dubia*	7 days static or renewal	4000	**1042**	DeGraeve et al., 1992
Copper	*C. dubia*	7 days static or renewal	0.283	0.032	Carlson et al., 1986
Mercury	*D. magna*	48 hr static	0.0051	**0.0044**	Barera and Adams, 1983
Selenium	*D. magna*	48 hr static	1.30	**0.55**	Maier et al., 1993
Zinc	*C. dubia*	7 days static or renewal	1.50	**0.149**	Carlson et al., 1986

*Amendment source for toxicity tests included $CdCl_2$, NaCl, $CuCl_2$, $HgCl_2$, Na_2SeO_3, and $ZnCl_2$.
**Estimated mean concentration of constituents in actual FGD waters after dilution to 4000 mg/L.
†Toxicity values in bold are estimated as lethal mean concentration values (LC_{50}).

basin that has been designed based on settling rates of particulates and ambient heat transfer rates for cooling of actual FGD waters.

- Treatment reactors were designed based on the environmental criteria that established conditions favorable for either the reductive or oxidative transformation of constituents of concern. For this study, two treatment reactor types were used and are operationally defined as reducing and oxidizing reactors.
- Reducing reactors were designed to have redox conditions of −250 to −100 mV and pH values between 5 and 7 standard units in the bulk hydrosoil. Hydrosoil was planted with a giant bulrush (*S. californicus* C. A. Meyer); a plant that has little radial oxygen loss that aids in maintaining low redox conditions (Murray-Gulde et al., 2005b). An organic matter as 5% (v/v) double chip pine mulch was used as the electron donor for microbial activity (e.g., dissimilatory sulfate reduction) and regulation of dissolved oxygen within sediments. These systems were designed based on studies that indicated that the mobility of arsenic, cadmium, copper, mercury, and zinc under low dissolved oxygen concentrations (suboxic to anaerobic) can be decreased by coprecipitation reactions with sulfide-bearing minerals (Moore et al., 1988; Kirk, 2004; Murray-Gulde et al., 2005a). In these reducing reactors, dissimilatory sulfate reduction provides sulfides and mineral-bearing sulfides for removing many constituents of concern from FGD waters. Based on studies by Masscheleyn and Patrick (1993) and Johnson and Bullen (2003), elemental selenium and metal selenides can form from both chemical and microbial reduction processes. Reduced selenium species are typically less mobile and reduction of Se (VI) to Se (IV) and further reduction of selenite to insoluble Se° have been documented within reducing aqueous environments (Zhang and Frankenberger, 2003).
- Oxidizing reactors were designed to establish an oxidizing wetland environment with bulk sediment redox potentials of −50 to +200 mV. This was accomplished by selecting a porous hydrosoil with low organic carbon and wetland plants with a high rate of radial oxygen loss (*T. angustifolia*). These design characteristics were chosen based on studies by Kirk (2004) and on biogeochemical modeling (Brookens, 1988), which indicate that, under high dissolved oxygen concentrations, dissolved iron species can be transformed into solid forms (oxyhydroxides) that enable coprecipitation with arsenic and selenium oxyanions. Oxidizing reactors enable the reoxygenation of the ambient water and can decrease nutrient concentrations, thus limiting the environmental risks these waters pose to aquatic receiving systems.

Flue Gas Desulfurization Waters: Chemical Composition

The chemical compositions of FGD waters are listed in Table 1. For formulated FGD waters, the targeted constituents of concern (Hg and Se) were amended as the mean concentrations found in undiluted actual FGD waters and arsenic concentrations were amended at concentrations of 0.17 mg/L instead of the mean of undiluted actual FGD waters because of the effect of an outlier in the data set (4.10 mg/L as As). Mean COD concentrations were greater for actual FGD waters because of amendments of organic acids used in the scrubbing process. All other water chemistry parameters tested were constant between formulated and actual FGD waters.

Actual-amended FGD waters (n = 2) were similar in composition to actual FGD waters after the amendments for the targeted constituents of concern (As, Hg, and Se). The second actual-amended FGD water received less dilution water than the first actual-amended FGD water and resulted in an increase in chloride concentrations (5200 vs. 4150 mg/L) between sampling periods. Nonamended constituents in the actual FGD waters may have differed by approximately 13%, but selenium and mercury concentrations had no measurable deviation (Table 1).

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

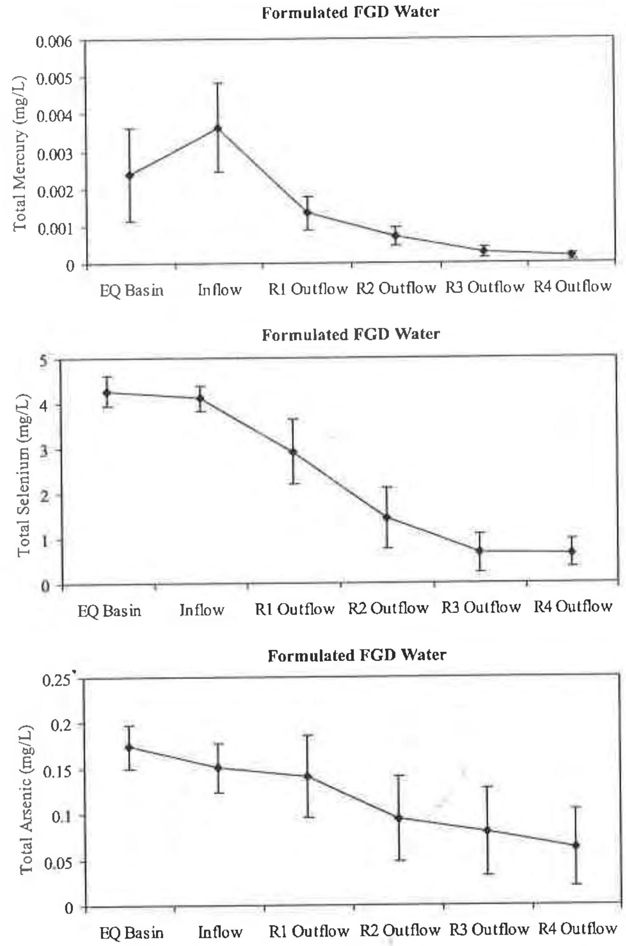

Figure 2. Total aqueous concentration of arsenic, selenium, and mercury from each reactor component of the constructed wetland treatment system exposed to formulated FGD waters.

Performance Measurement of Constructed Wetland Treatment Systems

Based on the NPDES permit criteria identified in this study, the performance of pilot-scale CWTSs was determine by monitoring the removal extents and rates of mercury to meet a discharge criteria of less than or equal to 0.63 μg/L, the removal extents and rates of selenium, and the pre- and posttreatment toxicity of FGD waters from the pilot-scale CWTS. No statistical differences were measured for constituent removal extents or rates between ash and no-ash pilot-scale CWTSs ($P < 0.001$), and these data are presented as mean values.

Mean removal extents and rates of mercury from EQ basin samples (pretreatment) to outflow samples (posttreatment) from the pilot-scale CWTS were 93.2% and 0.677 d^{-1} for formulated FGD waters ($n = 10$); 96.1 % and 0.2370 d^{-1} for actual-amended FGD waters ($n = 2$); and 99.0% and 0.687 d^{-1} ($n = 2$), 68.7% and 0.168 d^{-1} ($n = 2$), no removal ($n = 2$), and 98.7% and 0.621 d^{-1} for the first, second, third, and fourth pilot-scrubber FGD waters (Figures 2–4). Based on an NPDES permit criterion of less than or equal to 0.63 μg/L of total mercury in effluent samples, 87% of the posttreatment FGD waters (13 of 15) achieved the targeted treatment performance using pilot-scale CWTSs. Only the posttreatment samples from pilot-scale CWTSs with the loading of actual-amended FGD waters (6.2 μg/L; $n = 2$) and one effluent sample from the third pilot-scrubber FGD waters (1.2 μg/L; $n = 1$) exceeded this maximum daily loading concentration. Actual-amended FGD waters contained mercury concentrations of 160 μg/L and may not be representative of currently produced actual FGD waters because the highest concentration measured in actual FGD waters was only 47 μg/L. Dissolved concentrations of mercury in FGD waters may increase if air emission criteria for mercury are established because forms of mercury such as elemental mercury (Hg^0) are relatively insoluble in

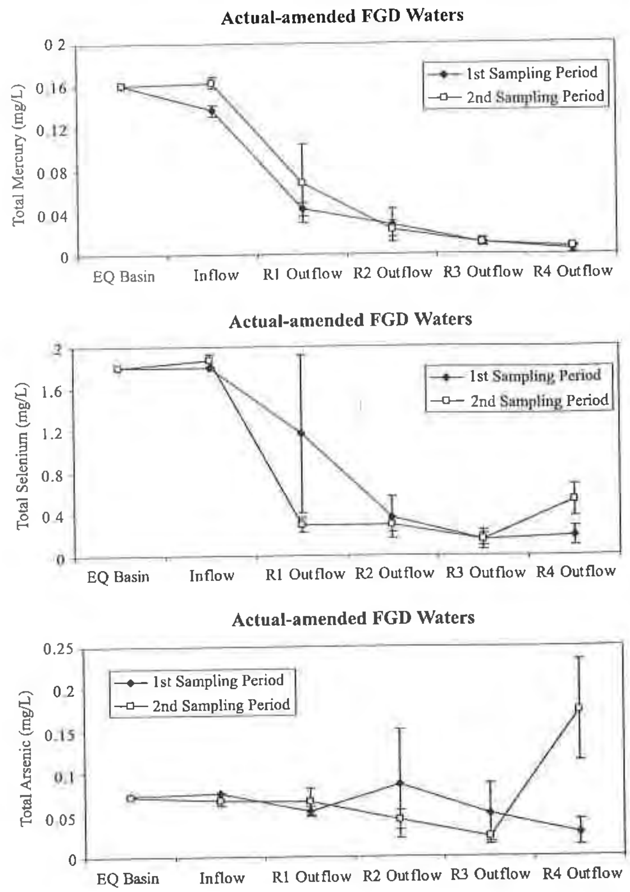

Figure 3. Total aqueous concentration of arsenic, selenium, and mercury from each reactor component of the constructed wetland treatment system exposed to actual-amended FGD waters.

FGD waters compared to mercuric chloride ($HgCl_2$) (Diaz-Somoano et al., 2005). Mercury removal (>98%) was greater for FGD waters, in which inflow concentrations exceeded 36 μg/L, but apparently less effective for FGD waters containing less than 0.9 μg/L as mercury (no removal to 68.5%). As constituent concentrations decrease, the formation of insoluble complexes becomes more thermodynamically unfavorable (Stumm and Morgan, 1995). This concentration-dependent response may explain the differences in mercury removal for these experiments; however, the effects of prior loading, biological activity, and differences in constituent speciation cannot be eliminated as influencing factors.

Mean removal extents and rates of selenium from EQ basin samples (pretreatment) to outflow samples (posttreatment) from pilot-scale CWTSs were 84.6 % and 0.468 d^{-1} for formulated FGD waters (n = 10); 80.1 % and 0.404 d^{-1} for actual amended FGD waters (n = 2); and 89.7% and 0.327 d^{-1} (n = 2), 63.6 % and 0.145 d^{-1} (n = 2), 51.2% and 0.103 d^{-1} (n = 2), and 29.5% and 0.050 d^{-1} (n = 2) for the first, second, third, and fourth pilot-scrubber FGD waters (Figures 2 –4). To date, available NPDES permits for FGD water discharge do not contain a maximum daily limit for elemental constituent concentrations other than copper, iron, and mercury. Performance criteria for pilot-scale CWTSs or maximum daily limit could not be established for selenium (or arsenic, cadmium, and zinc) and therefore must be determined using toxicity evaluations. For the pilot-scrubber FGD water experiments, selenium removal declined with each sequentially loaded FGD water (Table 3). This trend indicates that removal mechanisms were possibly inhibited by constituents in these FGD waters, subject to decreasing binding sites or reactants, or were less efficient because of differences in forms of selenium. Based on selenium biogeochemistry and selenium speciation results, it is likely that the microbial activity (i.e., selenium or iron reduction) or products of these reactions (i.e., ferrous ions) were being inhibited because the reduction of selenium to elemental forms and complexation reactions with ferrous iron can decrease the solubility of selenium oxyanions (Francisco et al., 1992; Losi and Frankenberger, 1997; Oremland et al., 1999; Zhang et al., 2005). Based on potential in-situ selenate reduction rates within sediments (Steinberg and Oremland, 1990; Oremland et al., 1991; Lortie et al., 1992; Herbel et al., 2003) coupled with electron donor concentrations in these pilot-scale CWTSs, we suggest that the microbial reduction of selenium species to elemental forms does not account for the removal extents and rates measured in these experiments. Reduction reactions of selenium forms in FGD waters with ferrous or zero-valent iron species (Zhang et al., 2005) and coprecipitation with ferrihydrite or goethite (Balistrieri and Chao, 1987, 1990) may have accounted for the relatively high removal extents measured for the first pilot-scrubber FGD water and may have decreased for the latter pilot-scrubber FGD waters because of the decrease of reactive iron species. Zero-valent iron was amended to all pilot-scale CWTSs at concentrations of 22 g per reducing reactor and therefore could have served as a reducing and complexing agent for selenium species. Zingaro et al. (1997) suggested that Se (VI) can be reduced to Se (IV) in the presence of ferrous iron, and after the transformation to Se (IV), rapid complexation with iron oxyhydroxides (Fe_{OH}) can occur. Zhang et al. (2005) suggested that Se (VI) may directly adsorb to Fe_{OH} and further react to produce an insoluble selenium-iron species. Microbial transformations of selenium species maybe important reaction pathways in these systems and may aid in the

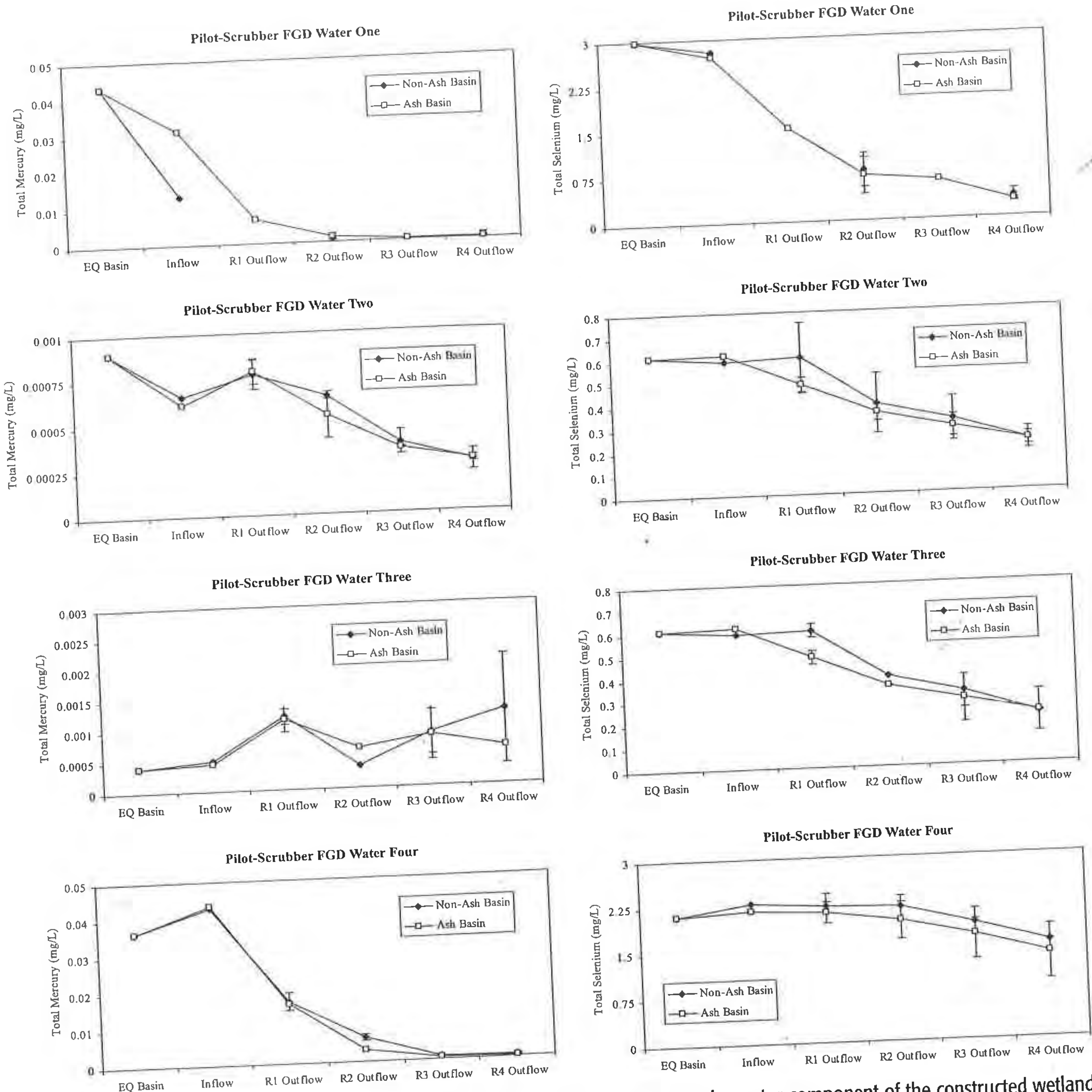

Figure 4. Total aqueous concentration of arsenic, selenium, and mercury from each reactor component of the constructed wetland treatment system exposed to pilot-scrubber FGD waters.

sequestering and limit dissolution of selenium by further reductive transformations such as Se (IV) to Se^0 and Se (−II) in the sedimentary environment (Masscheleyn and Patrick, 1993).

Mean removal extents and rates for arsenic were 64.4% and 0.258 d^{-1} for formulated FGD waters, but no removal was measured for actual FGD waters. For the actual-amended FGD waters, the total arsenic concentration in the EQ basin after 4 weeks of loading was 0.074 mg/L, and the mean outflow concentration was 0.028 ± 0.383 mg/L, indicating a removal extent of 61.6%. However, during the first sampling period, the total arsenic concentrations in the outflow samples (0.173 ± 0.06 mg/L) were approximately 2.5 times greater than the EQ basin (0.073 mg/L). For both sampling periods with the actual-amended FGD water experiments, the total selenium removal was greatest in outflow samples of the rock basins (91.7%) versus the

Table 3. Total Aqueous Concentrations of Mercury (μg/L) and Selenium (mg/L) Measured in Samples from Constructed Wetland Treatment System Components by FGD Water Type

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

*Hg = total aqueous mercury; Se = total aqueous selenium.
**NR = no measured removal.

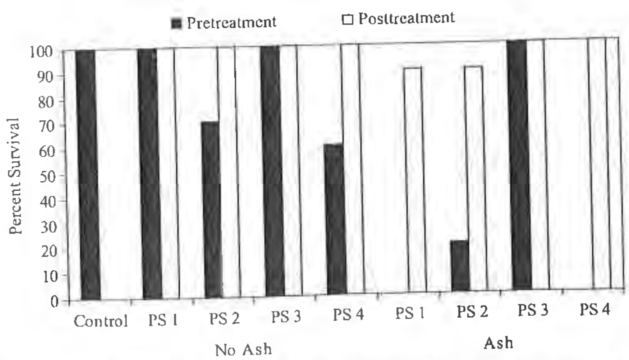

Figure 5. Percent survival of *Ceriodaphnia dubia* exposed to pre- and posttreatment samples of four pilot-scrubber FGD waters treated by no-ash and ash pilot-scale constructed wetland treatment systems.

oxidation reactor (80.1%). These data indicate that the leaching of insoluble forms of arsenic and selenium occurred during these sampling periods. Based on elemental analyses from each treatment reactor, we hypothesize that the final wetland reactor was the site of resuspension of the arsenic and selenium forms. Arsenic removal did not occur in either pilot-scale CWTSs for pilot-scrubber FGD waters receiving inflow concentrations ranging from 0.005 to 0.101 mg/L. Biogeochemical modeling of arsenic in FGD waters indicated that insoluble forms would occur in reducing reactors with an Eh less than −200 mV and a pH of 7 (Brookens, 1988), but it was not documented in these experiments.

Toxicity evaluations using C. *dubia* were used to determine the treatment performance of pilot-scale CWTSs for the three types of FGD waters used in this study. These evaluations are routinely used for the NPDES monitoring of discharge effluents and can indicate the treatment efficiency of a system (i.e., transfer or transformation) for constituents of concern contrasting results from the testing of pre- and posttreatment samples. For the actual-amended FGD waters, pre- and posttreatment samples were diluted for chloride toxicity (unpublished data) by 93.75% or approximately 260 (1st sampling period) and 330 mg/L (2nd sampling period) as chloride. Because blowdown FGD waters typically contain approximately 16,000 mg/L as chloride, the concentrations used in these experiments are similar to the NDPES permit criteria of grater than or equal to 1.9% as FGD water or approximately 300 mg/L as Cl^-. For both posttreatment samples (1st and 2nd sampling periods), there was a significant decrease in toxicity from the inflow to outflow of pilot-scale CWTSs. The C. *dubia* survival increased from 20 to 80% for the first sampling period. Reproduction was statistically greater for post- versus pretreatment samples, and reproduction in posttreatment samples did not differ from laboratory organisms (controls; $P < 0.001$). For the first and fourth pilot-scrubber FGD waters, significant C. *dubia* mortality occurred in the exposures of all pretreatment samples (both treatment systems); however, no differences were observed for any posttreatment samples (Figure 5). Additionally, for both pilot-scrubber FGD waters, no statistical differences in reproduction occurred for posttreatment samples of either treatment system; however, both pretreatment samples statistically inhibited reproduction (Figure 6). For the second pilot-scrubber FGD water, significant C. *dubia* mortality occurred for the pretreatment samples but no differences were measured for either posttreatment sample (Figure 6). A significant increase in C. *dubia* reproduction was measured between the pre- and posttreatment samples of both systems. For the third pilot-scrubber FGD water, no significant mortality effects were caused by C. *dubia* for any pre- or posttreatment samples of either treatment system. Reproduction was not affected in the pretreatment samples for the no-ash or ash systems, but a significant decrease was measured in the exposures of the posttreatment sample from the no-ash system. This effect is believed to be caused by a handling error because the initial introduction of C. *dubia* resulted in the complete mortality and retesting of the sample resulting in complete survival. Lower reproduction may have been a result of an inadequate feeding of the C. *dubia* population used in the retesting of the sample. These data indicate that pilot-scale CWTSs can decrease the environmental risks FGD waters may pose to receiving systems, thus enabling the discharge of posttreatment waters in compliance with NPDES permits.

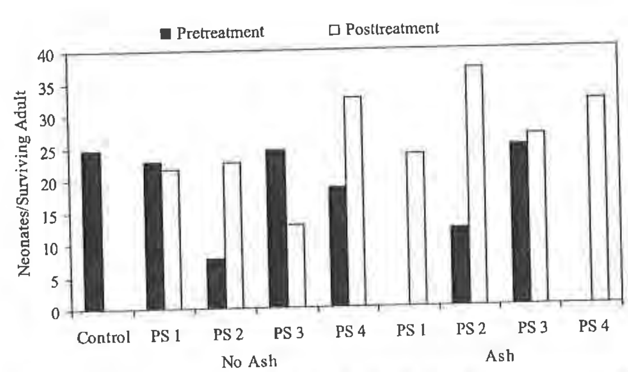

Figure 6. Reproduction of *Ceriodaphnia dubia* exposed to pre- and posttreatment samples of four pilot-scrubber FGD waters treated by no-ash and ash pilot-scale constructed wetland treatment systems.

CONCLUSIONS

For this study, a risk characterization was conducted by comparing the mean concentration of elements or compounds measured in four actual FGD waters to the NPDES permit criteria obtained from the USEPA databases. The results of this risk-based characterization indicate that cadmium, COD, chloride, copper, mercury, selenium, and zinc are constituents of concern in these FGD waters that require treatment before discharge. Because FGD waters must meet the discharge criteria established by the USEPA through NPDES permits, we designed a series of reactors or CWTSs that would alter the chemical solubility of the targeted constituents. This was accomplished by assessing the biogeochemical cycling of the constituents of concern through literature reviews and proposed biogeochemical models. Each treatment system contained an EQ basin and two reducing and oxidizing reactor types. The treatment performance of these systems was monitored for three FGD water types (formulated, actual-amended, and pilot-scrubber FGD waters) by measuring removal extents and rates and toxicity evaluations. The results from these studies indicated that targeted constituents of concern in FGD waters can be decreased in CWTSs, and with an appropriate comanagement of low-ionic strength water for chloride concentrations, toxicity is decreased to acceptable discharge limits. These studies indicate that CWTSs can be a viable treatment strategy for FGD waters, but a continued research is needed to thoroughly understand the biogeochemical cycling (i.e., fate and transport) of constituents of concern in these systems thereby enhancing the sequestration of these contaminants. The experiments presented in this article are part of an ongoing research project to compare and contrast the treatment performance of pilot- and full-scale constructed wetland treatments systems for FGD waters. An additional research is underway to determine the dominant removal pathways (chemical and microbial) for selenium and mercury in full-scale CWTSs for FGD waters to discern the toxicity sources in FGD waters based on C. *dubia* responses and to measure the binding strength of sequestered constituents of concern from the hydrosoil of full-scale CWTSs. The results presented in this article are specific to the FGD waters used in this study and may differ for other site-specific FGD waters because of factors such as the state regulatory criteria (i.e., toxicity testing protocols and MDLs) and wet scrubber operation (i.e., coal composition, chemical additions, and source water).

REFERENCES CITED

American Public Health Association, 1998, Standard methods for examination of water and wastewater, 20th ed.: Washington, D.C., American Public Health Association, p. 1325.

Ansola, G., J. M. González, R. Cortijo, and E. de Luis, 2003, Experimental and full-scale pilot plant constructed wetlands for municipal wastewaters treatment: Ecological Engineering, v. 21, p. 43–52.

Balistrieri, L. S., and T. T. Chao, 1987, Selenium adsorption by goethite: Soil Science Society of America Journal, v. 51, p. 1145–1151.

Balistrieri, L. S., and T. T. Chao, 1990, Adsorption of selenium by amorphous iron oxyhydroxides and manganese dioxide: Geochimica et Cosmochimica Acta, v. 54, p. 739–751.

Barera, Y., and W. J. Adams, 1983, Resolving some practical questions about *Daphnia* acute toxicity tests, *in* W. E. Bisnop et al., eds., Aquatic toxicology and hazard assessment: Sixth Symposium. ASTM STP 802: American Society for Testing and Materials, Philadelphia, Pennsylvania, p. 509.

Brix, K. V., D. G. Henderson, W. J. Adams, R. J. Reash, R. G. Carlton, and D. O. McIntyre, 2001, Acute toxicity of sodium selenate to two daphnids and three amphipods: Environmental Toxicology, v. 16, p. 142–50.

Brookens, D. G., 1988, EH, pH diagram for geochemistry: Berlin, Springer, p. 1–14.

Carlson A. R., H. Nelson, and D. Hammermeister, 1986, Development and validation of site-specific water quality criteria for copper: Environmental Toxicology and Chemistry v. 5, p. 997–1012.

DeGraeve, G. M., J. D. Cooney, B. H. Marsh, T. L. Pollock, and N. G. Reichenbach, 1992, Variability in the performance of the 7-D Ceriodaphnia dubia survival and reproduction test: An intra- and interlaboratory study: Environmental Toxicology and Chemistry, v. 11, p. 851–866.

Devito, M., L. Rosendale, V. Conrad, and B. Jackson, 1994, Trace elements in coals and their emissions: Proceeding of the American Power Conference, v. 56-1, p. 438.

Díaz-Somoano, M., S. Unterberger, and K. R. G. Hein, 2005, Using wet-FGD systems for mercury removal: Journal of Environmental Monitoring, v. 7, p. 906–909.

Faulkner, S. P., W. H. Patrick Jr., and R. P. Gambrell, 1989, Field techniques for measuring wetland soil parameters: Soil Science Society of America Journal, v. 53, p. 883–890.

Francisco, A. T., L. L. Barton, C. L. Lemanski, and T. G. Zocco, 1992, Reduction of selenate and selenite to elemental selenium by *Wolinella succinogenes*: Canadian Journal of Microbiology, v. 38, p. 1328–1333.

Freme, F., 2005, U.S. coal supply and demand: 2005 review: Washington, D.C., U.S. Energy Information Administration, p. 175.

Gluskoter, H. J., R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn, 1977, Trace elements in coal: Occurrence and distribution: Illinois State Geological Survey Circular 499, Urbana IL, 154 p.

Herbel, M. J., J. Switzer Blum, S. E. Borglin, and R. S. Oremland, 2003, Reduction of elemental selenium to selenide: Experiments with anoxic sediments and bacteria that respire Se-oxyanions: Geomicrobiology Journal, v. 20, p. 587–602.

Hickey, C. W., 1989, Sensitivity of four New Zealand cladoceran species and *Daphnia magna* to aquatic toxicants: New Zealand Journal of Marine and Freshwater Research, v. 23, p. 131–137.

Huett, D. O., S. G. Morris, G. Smith, and N. Hunt, 2005, Nitrogen and phosphorus removal from plant nursery runoff in vegetated and unvegetated subsurface flow wetlands: Water Research, v. 39, p. 3259–3272

Johnson, T. M., and T. D. Bullen, 2003, Selenium isotope fractionation during reduction of Se oxyanions by Fe(II) + Fe(III) hydroxide-sulfate (green rust): Geochimica et Cosmochimica Acta, v. 67, p. 413–419.

Kirk, G., 2004, Biogeochemistry of submerged soils: New York, John Wiley, p. 304.

Lewis, P. A., D. J. Klemm, J. M. Lazorchak, T. J. Norberg-King, W. H. Peltier, and M. A. Heber, 1994, Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms, 4th ed.: Cincinnati, Ohio, U.S. Environmental Protection Agency EPA/600/4-91/002, p. 334.

Lortie, L., W. D. Gould, S. Rajan, R. G. L. McCready, and K. J. Cheng, 1992, Reduction of selenate and selenite to elemental selenium by a *Pseudomonas stutzeri* isolate: Applied and Environmental Microbiology, v. 58, p. 4042–4044.

Losi, M. E., and W. T. Frankenberger Jr., 1997, Reduction of selenium oxyanions by *Enterobacter cloacae* strain SLDaa-1: Isolation and growth of the bacterium and its expulsion of selenium particles: Applied and Environmental Microbiology, v. 63, p. 3079–3084.

Maier, K. J., C. G. Foe, and A. W. Knight, 1993, Comparative toxicity of selenate, selenite, seleno-dl-methionine and seleno-dl-cystine to *Daphnia magna*: Environmental Toxicology and Chemistry, v. 124, p. 755–763.

Masscheleyn, P. H., and W. H. J. Patrick, 1993, Biogeochemical processes affecting selenium cycling in wetlands: Environmental Toxicology and Chemistry, v. 12, p. 2235–2243.

Miezejewski, M. K., 1991, The elimination of pollutants from FGD waste waters, *in* 1991 SO_2 control symposium: Electric Power Research Institute, v. 3, p. 421–440.

Moore, J. N., W. H. Ficklin, and C. Johns, 1988, Partitioning of arsenic and metals in reducing sulfidic sediments: Environmental Science and Technology, v. 22, p. 432–437.

Moore, M. T., J. H. Rodgers Jr., C. M. Cooper, and S. Smith Jr., 2000, Constructed wetlands for mitigation of atrazine-associated agricultural runoff: Environmental Pollution, v. 110, p. 393–399.

Mount, D. R., D. D. Gulley, J. R. Hockett, T. D. Garrison, and J. M. Evans, 1997, Statistical models to predict the toxicity of major ions to *Ceriodaphnia dubia, Daphnia magna* and *Pimephales promelas* (Fathead Minnows): Environmental Toxicology and Chemistry, v. 16, p. 2009–2019.

Murray-Gulde, C. L., J. Bearr, and J. H. Rodgers, 2005a, Evaluation of a constructed wetland treatment system specifically designed to decrease bioavailable copper in a waste stream: Ecotoxicology and Environmental Safety, v. 61, p. 60–73.

Murray-Gulde, C. L., G. M. Huddleston, K. V. Garber, and J. H. Rodgers Jr., 2005b, Contribution of *Schoenoplectus californicus* in a constructed wetland system receiving copper contaminated wastewater: Water, Air and Soil Pollution, v. 163, p. 355–378.

National Research Council, Panel on Trace Element Geochemistry of Coal Resource Development Related to Health (PECH), 1980, Trace-element geochemistry of coal resource development related to environmental quality and health: Washington, D.C., National Academy Press, p. 1–153.

Oremland, R. S., N. A. Steinberg, T. S. Presser, and L. G. Miller, 1991, In situ bacterial selenate reduction in the agricultural drainage systems of western Nevada: Applied and Environmental Microbiology, v. 57, p. 615–617.

Oremland, R. S., J. S. Blum, A. Burns Bindi, P. R. Dowdle, M. Herbel, and J. F. Stolz, 1999, Simultaneous reduction of nitrate and selenate by cell suspensions of Selenium-respiring bacteria: Applied and Environmental Microbiology, v. 65, p. 4385–4392.

SAS Institute Inc., 1989, SAS/STAT user's guide, version 6, 4th ed.: Cary, North Carolina, SAS Institute, p. 846.

Sobolewski, A., 1996, Metal species indicate the potential of constructed wetlands for long-term treatment of metal mine drainage: Ecological Engineering, v. 6, p. 259–271.

Spehar, R. L., and J. T. Fiandt, 1986, Acute and chronic effects of water quality criteria-based mixtures on three aquatic species: Environmental Toxicology and Chemistry, v. 5, p. 17–93.

Steinberg, N. A., and R. S. Oremland, 1990, Dissimilatory selenate reduction potentials in a diversity of sediment types: Applied and Environmental Microbiology, v. 56, p. 3550–3557.

Stumm, W., and J. J. Morgan, 1995, Aquatic chemistry: Chemical equilibria and rates in natural waters: New York, John Wiley, p. 1022.

Suedel, B. C., J. H. Rodgers Jr., and E. Deaver, 1997, Experimental factors that may affect toxicity of cadmium to freshwater organisms: Archives of Environmental Contamination and Toxicology, v. 33, p. 188–193.

U.S. DOE, 2000, Analysis of strategies for reducing multiple air emissions from power plants: Sulfur dioxide, nitrous oxides, and carbon dioxide: Washington, D.C., U.S. Energy Information Administration, p. 299.

Yudovich, Y. E., and M. P. Ketris, 2005a, Arsenic in coal: International Journal of Coal Geology, v. 61, p. 141–196.

Yudovich, Y. E., and M. P. Ketris, 2005b, Mercury in coal: International Journal of Coal Geology, v. 62, p. 107–134.

Zhang, Y. Q., and W. T. Frankenberger Jr., 2003, Characterization of selenate removal from drainage water using rice straw: Journal of Environmental Quality, v. 32, p. 441–446.

Zhang, Y. Q., J. Wang, C. Amrhein, and W. T. Frankenberger Jr., 2005, Removal of selenate from water using zero-valent iron: Journal of Environmental Quality, v. 34, p. 487–495.

Zingaro, R. A., D. C. Dufner, A. P. Murphy, and C. D. Moody, 1997, Reduction of oxoselenium anions by iron (II) hydroxide: Environment International, v. 23, p. 299–304.