



## Performance of a pilot-scale constructed wetland system for treating simulated ash basin water

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### ABSTRACT

A pilot-scale constructed wetland treatment system (CWTS) was designed and built to decrease the concentration and toxicity of constituents of concern in ash basin water from coal-burning power plants. The CWTS was designed to promote the following treatment processes for metals and metalloids: precipitation as non-bioavailable sulfides, co-precipitation with iron oxyhydroxides, and adsorption onto iron oxides. Concentrations of Zn, Cr, Hg, As, and Se in simulated ash basin water were reduced by the CWTS to less than USEPA-recommended water quality criteria. The removal efficiency (defined as the percent concentration decrease from influent to effluent) was dependent on the influent concentration of the constituent, while the extent of removal (defined as the concentration of a constituent of concern in the CWTS effluent) was independent of the influent concentration. Results from toxicity experiments illustrated that the CWTS eliminated influent toxicity with regard to survival and reduced influent toxicity with regard to reproduction. Reduction in potential for scale formation and biofouling was achieved through treatment of the simulated ash basin water by the pilot-scale CWTS.

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### 1. Introduction

Coal combustion wastes generated at thermoelectric power plants contain numerous trace elements such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, selenium, and zinc (Cherry and Guthrie, 1977; Walia and Mehra, 1998; Smith, 2003). These elements may cause severe physiological effects on organisms exposed to certain forms or species above tolerable concentrations (Chang, 1996). Coal combustion wastes include slag and bottom ash, fly ash, and flue gas desulfurization (FGD) scrubber sludge (Dvorak et al., 1978). Fly ash is fine grained and usually collected by a particulate control device. Bottom ash is coarser grained and falls from the combustion chamber into an ash hopper (Shorney, 1983). Disposal techniques for fly and bottom ash include hydraulic transportation (sluicing) to a receiving basin followed by settling and subsequent disposal in a landfill or removal for reuse. Toxic elements in ash may be transferred to the aqueous phase and subsequently introduced to aquatic receiving systems (Walia and Mehra, 1998). Power companies are encountering increased disposal costs and growing environmental concerns regarding ash and associated water. Conventional treatment methods, such as transportation to a water treatment facility, are often unattractive because of high capital costs and continuing high

costs associated with operation and maintenance (Bhamidimarri et al., 1991).

The purpose of this investigation was to assess specifically designed pilot-scale constructed wetland systems for treating ash basin water. These systems are self-maintaining and provide a cost-effective alternative to traditional remediation approaches for many industrial waters (LeDuc and Terry, 2005; Mooney and Murray-Gulde, 2008; Nelson and Gladden, 2008). Constructed wetland treatment systems (CWTSs) have successfully treated a wide range of impaired waters, including stormwater runoff, municipal wastewater, agricultural runoff, flue gas desulfurization water, acid mine drainage, and other waters containing various inorganics and organics (Cronk, 1996; Hawkins et al., 1997; Barton and Karathanasis, 1998; Knight et al., 1999; Gillespie et al., 2000; Murray-Gulde et al., 2005a, 2008; Eggert et al., 2008; Huddleston and Rodgers, 2008; Johnson et al., 2008; Kanagy et al., 2008a).

Specific objectives of this research were to measure performance of CWTSs for: (1) decreasing the concentration of constituents of concern (COCs) in simulated ash basin water; (2) reducing toxicity associated with COCs in simulated ash basin water; and (3) reducing reuse-limiting parameters of simulated ash basin water. Analytical techniques were used to assess concentrations of COCs in CWTS influent and effluent (untreated and treated simulated ash basin water, respectively). Toxicity testing of CWTS effluent identified unanticipated deleterious constituents and provided data concerning bioavailability of COCs.

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## 2. Materials and methods

### 2.1. Identification of constituents of concern and design of CWTS

To design a CWTS capable of decreasing concentration and toxicity of COCs in simulated ash basin water, COCs were identified by the risk quotient (RQ) method, which uses a sentinel species (e.g. *Ceriodaphnia dubia*) to assess risks to receiving system biota (USEPA, 2004). The CWTS was designed based on biogeochemical treatment processes that transfer or transform the identified COCs by promoting conditions that produce these processes (Rodgers and Castle, 2008), thus decreasing aqueous concentrations of COCs. To incorporate desired biogeochemical processes, two specifically designed pilot-scale wetland reactor series were built. Each reactor series (A and B) consisted of an initial 150-gallon (568 L) reactor (Rubbermaid® Utility Tank) (i.e. reactor 1), followed by two 70-gallon (265 L) reactors (reactors 2 and 3), and a final 150-gallon (568 L) reactor (reactor 4; Fig. 1). Reactor 4 of series A and B included a rock cascade near the influent position. The nominal hydraulic retention time (HRT) of reactor 1 in each series was 48 h, and the nominal HRT of reactors 2, 3, and 4 in each series was 24 h per reactor. Total system HRT was 120 h (5 d).

Simulated ash basin water was formulated for use in the pilot-scale reactors by addition of high purity salts (Fisher Scientific Inc., Fair Lawn, NJ) of COCs to municipal water in a 1000-gallon (3785 L) detention basin (polypropylene tank). Simulated ash basin water was transferred from the detention basin to the CWTS via Fluid Metering Inc. (FMI®) piston pumps. Use of simulated water rather than actual ash basin water provided a savings in transport and storage costs. In addition, inputs to the system could be controlled more precisely than if using actual ash basin water.

Hydrosoil in the reactors was formulated using quartz sand collected from a nearby creek (18 Mile Creek, near Clemson, South Carolina). Kanagy et al. (2008b) described particle size distribution, organic matter content, pH, Eh, and acid volatile sulfide concentration in hydrosoil formulated using sand from the same location. Hydrosoil was amended with organic matter because organic matter is a carbon and energy source for microbial activity (Dvorak et al., 1992; Murray-Gulde et al., 2005b), contributes to ambient dissolved oxygen concentrations (Kadlec and Knight, 1996), decreases hydrosoil oxidation-reduction potential (Eh) (Sobolewski, 1999), and provides sorption and/or exchange sites for COCs (Sobolewski, 1999). The target hydrosoil Eh range for each reactor was based on Eh–pH diagrams of the S–H–O system, COC–S–O–H system, and Fe–O–H<sub>2</sub>O system (Brookins, 1988; Drever, 1988).

Reactors 1, 2, and 3 in series A and B were designed to promote dissimilatory sulfate reduction. Based on equilibrium biogeochemistry, dissimilatory sulfate reduction is promoted by Eh less than

–50 mV (Brookins, 1988). Therefore, the target Eh range for reactors 1, 2, and 3 in series A and B was –250 to –50 mV (i.e. reducing reactors). Sulfide ions produced during dissimilatory sulfate reduction may combine with cations, including arsenic, chromium, mercury, selenium, and zinc, to precipitate non-bioavailable metal/metalloid-sulfide minerals (Murray-Gulde et al., 2005b). Reducing reactors were planted with *Schoenoplectus californicus*. The *Schoenoplectus* genus (viz. *Schoenoplectus robustus*) can phytovolatilize selenium (Lin and Terry, 2003), and previous studies have shown that *S. californicus* C. promotes reducing hydrosoil conditions (Hawkins et al., 1997; Gillespie et al., 1999, 2000) required for dissimilatory sulfate reduction.

Reactor 4 in series A and B was designed to promote oxidizing conditions for the formation of ferric oxides and ferric hydroxides. The reactors were planted with *Typha angustifolia* L. because the *Typha* genus (viz. *Typha latifolia*) readily transfers oxygen to the water column (Hammer, 1989) and root horizons (Moshiri, 1993), potentially increasing hydrosoil Eh (Jacob and Otte, 2003). Target hydrosoil Eh of –50 to 250 mV was selected to promote co-precipitation of COCs with iron oxyhydroxides and sorption of COCs onto iron oxides (Drever, 1988). Iron oxides have a strong affinity for cations that are of similar size to ferric and ferrous cations (Sinicrope et al., 1992). Physical dimensions of zinc, cadmium, copper, and nickel cations, all of which occur in ash basin water, are similar to dimensions of ferric and ferrous cations (Kabata-Pendias and Pendias, 1984). Therefore, zinc, cadmium, copper, and nickel may combine with iron in the CWTS forming metal-oxide complexes (Benjamin and Leckie, 1981). Arsenic, also present in ash basin water, may be removed from the water column by adsorbing onto amorphous iron hydroxides (Pierce and Moore, 1980) or by co-precipitating with iron oxyhydroxides (Manning et al., 1998; Raven et al., 1998; Johnson and Hallberg, 2005). Ferric oxides and hydroxides have been reported as adsorbents for selenate (Se(vi)) (Peak and Sparks, 2002) and selenite (Se(iv)) (Zhang and Sparks, 1990).

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

### 2.2. Water chemistry – sampling and analysis

To determine the ability of CWTSs to decrease concentrations of COCs in simulated ash basin water, aqueous samples were collected from multiple locations within the CWTS and analyzed for general water chemistry parameters and for concentrations of COCs. General water chemistry parameters were measured following methods of Clesceri et al. (1999) and Kanagy et al. (2008a) and included temperature, dissolved oxygen, conductivity, pH, alkalinity, and hardness. The sampling period for COCs included active growth (i.e. spring/summer) and dormant (i.e. winter) stages of macrophyte development.

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

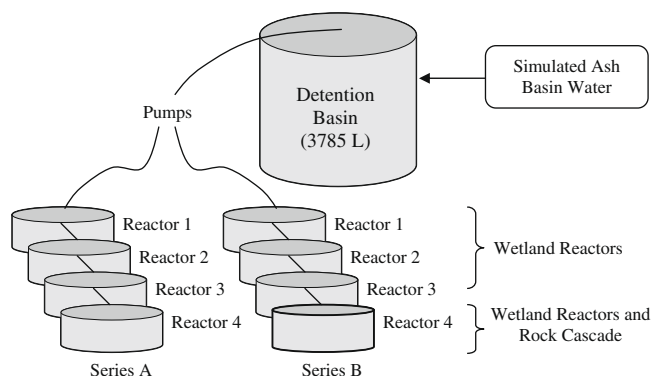


Fig. 1. Schematic diagram of pilot-scale constructed wetland system designed for treatment of ash basin water. Two reactor series (A and B) were used.

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