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Chemical Analysis of Soil and Leachate from Experimental Wetland Mesocosms Lined with Coal Combustion Products

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ABSTRACT

Small-scale (1 m²) wetland mesocosm experiments were conducted over two consecutive growing seasons to investigate the effects on soil and leachate chemistry of using a recycled coal combustion product as a liner. The coal combustion product used as a liner consisted of flue gas desulfurization (FGD) by-products and fly ash. This paper provides the chemical characteristics of mesocosm soil and leachate after 2 yr of experimentation. Arsenic, Ca, and pH were higher in FGD-lined mesocosm surface soil relative to unlined mesocosms. Aluminum was higher in the soils of unlined mesocosms relative to FGD-lined mesocosms. No significant difference of potentially phytotoxic B was observed between lined and unlined mesocosms in the soil. Higher pH, conductivity, and concentrations of Al, B, Ca, K, and S (SO₄-S) were observed in leachate from lined mesocosms compared with unlined controls while Fe, Mg, and Mn were higher in leachate from unlined mesocosms. Concentrations of most elements analyzed in the leachate were below national primary and secondary drinking water standards after 2 yr of experimentation. Initially high pH and soluble salt concentrations measured in the leachate from the lined mesocosms may indicate the reason for early effects noted on the development of wetland vegetation in the mesocosms.

LINERS are important to the success of constructed wetlands in areas where ground water levels are

typically close to the ground surface or where native soils are too permeable (Kadlec and Knight, 1996; Kadlec et al., 2000). Liners not only protect ground water resources but also ensure that there is adequate water in the wetlands to support appropriate aquatic life, particularly wetland vegetation. The most frequently used liners for constructed wetlands are clays, clay bentonite mixtures, and synthetic materials such as polyvinylchloride (PVC) and high-density polyethylene (HDPE) (Kadlec and Knight, 1996). However, synthetic liners are potentially expensive and are prone to more damage than are clay or clay-bentonite liners (Kadlec and Knight, 1996). In addition, natural clays are not always available where wetlands are to be constructed.

Flue gas desulfurization (FGD) materials are produced by lime-scrubbing sulfur oxides from flue gases of coal-fired electrical generating stations. Four to 6 million tons of these materials are produced annually in Ohio alone (Bigham et al., 1993). Flue gas desulfurization materials are generally treated as waste products and landfilled. The disposal of the enormous volume of this waste generated by every power plant with sulfur scrubbers, however, has become increasingly difficult as landfill costs increase, landfill space decreases, and sulfur scrubbers are deployed in increasing numbers

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Published in *J. Environ. Qual.* 30:1457–1463 (2001).

Abbreviations: FGD, flue gas desulfurization; ICP, inductively coupled plasma.

(American Coal Ash Association Survey, 1997). Several studies have been carried out on the reuse of FGD by-products for land application, agricultural liming, highway and civil engineering applications, and waste-storage pond liners (Bigham et al., 1993; Stehouwer et al., 1995a,b, 1996; Crews and Dick, 1998; Butalia and Wolfe, 1999), but no studies that we are aware of have investigated the use of this material as potential liners in constructed wetlands. The idea of using FGD by-products as liners for constructed wetlands has three possible advantages. First, the FGD material, when properly applied, can have a very low permeability (Butalia and Wolfe, 1999). Second, FGD by-products, which are high in calcium content, can lead to increased calcium-phosphate precipitation in the wetlands, thereby enhancing the water quality function of the constructed wetlands. Third, the FGD material can be obtained in many regions at an economically attractive price.

Coal combustion products in general and FGD materials in particular need to be studied carefully to determine their potentially deleterious effects on soil and water quality since they can leach significant amounts of soluble salts and a variety of trace elements of environmental concern (Stehouwer et al., 1996; Crews and Dick, 1998). For example, one element of concern for plants grown on soils amended with FGD by-products is boron (B), since coal combustion products often contain high levels of B (Crews and Dick, 1998; Sloan et al., 1999). Although no serious phytotoxicity has been reported in previous studies (Stehouwer et al., 1995a; Stehouwer et al., 1996; Crews and Dick, 1998; Clark et al., 1999; Sloan et al., 1999), little is known about the effects of FGD by-products on rooted wetland macrophytes.

The purpose of this paper was to identify potential chemical contamination of soil and ground water from constructed wetland systems that might use coal combustion products as liner material. In a companion paper (Ahn et al., 2001), the effects of using FGD material on surface water quality and vegetation production were examined from the same experiment.

MATERIALS AND METHODS

Stabilized Flue Gas Desulfurization By-Product

Flue gas desulfurization (FGD) material may be dry or wet depending on the desulfurization process. The wet scrubbing process commonly used by large electric utilities in Ohio involves the injection of a reagent, typically quicklime composed of calcium carbonate (CaCO_3) and portlandite [$\text{Ca}(\text{OH})_2$], into the flue gases. The wet product generated (referred to as FGD filter cake) is a dewatered mixture of sulfites and sulfates of the reagent, unreacted reagent, and some water. The filter cake was mixed with dry fly ash and lime (CaO) to produce the stabilized FGD material. Stabilized FGD material used as a liner in this study was imported from the American Electric Power's Conesville Power Plant in Coshocton County, Ohio. The stabilized FGD used in this study consisted of a fly ash to filter cake ratio of 1.25:1 plus 5% (w/w) CaO.

Experimental Design

The experiment was carried out over two growing seasons (1997 and 1998) under field conditions. A set of 20 flow-

through mesocosms ($1\text{-m}^2 \times 0.6\text{-m}$ polyethylene tubs; Fig. 1a) were positioned at the Olentangy River Wetland Research Park (ORWRP), a 12-ha research site located on the Columbus campus of The Ohio State University (Mitsch et al., 1998). Stabilized FGD waste was randomly assigned to half of the mesocosms; the other half with no FGD in the tubs served as controls. Mesocosms were buried in the ground to insulate roots against freezing and received 10 cm of noncalcareous river pea gravel, completely covering the drain to the standpipe (Fig. 1b). Ten of the 20 mesocosms were then overlain by 10 to 15 cm of FGD material. Fifteen to 20 cm of topsoil obtained during the excavation of the mesocosm site were then added to the mesocosms as "surface soil." The FGD material was layered and compacted manually. Mechanical compaction (Goldman, 1988; Butalia and Wolfe, 1999) was not used. The FGD material was smoothed to obtain a uniform and solid surface, and boulders that could not be easily worked into the layer were removed. This type of light compaction allowed some portion of water in the mesocosms to seep through the FGD layer and to rise up in the standpipe connected to the bottom of the mesocosms as leachate (Fig. 1b), thus representing a worst-case scenario of FGD by-product effects on water and soil.

Three rhizomes of softstem bulrush [*Schoenoplectus tabernaemontani* (K.C. Gmel.) Palla, formerly *Scirpus validus* Vahl.] were planted in each of 20 mesocosms in May 1997, 2 mo before the first-year experiment began. This macrophyte is a common wetland plant recommended for constructed wetlands (Kusler and Kentula, 1990; Thunhorst, 1993). Rhizomes were equally spaced lengthwise in the mesocosm, pressed just below the surface of moist soil and buried to 3 cm depth. Plants were well established by the beginning of the first growing season experiment (Fig. 1a).

A water delivery system was constructed to simulate flow-through conditions of full-scale constructed wetlands for treating wastewater. This was accomplished through a series of manifolds and valves that distributed similar volumes of water from the Olentangy River to each of the 20 mesocosms. The river water, moderate in nutrient concentrations ($\sim 0.1 \text{ mg P L}^{-1}$) was first stored in two 1600-L tanks, then fed by gravity to each mesocosm (Fig. 1). A continuous inflow rate of 70 mL min^{-1} to each mesocosm was chosen as a target inflow during the experiments. Steady flow rates at this scale were difficult to maintain, so a pulse system was used to deliver a similar volume of water for 1 h per day to each mesocosm in the second year of study. Hydraulic loading rates (HLR) were maintained between 5 and 7 cm d^{-1} in both years of the experiments with an average of 10 cm of mean standing water in each mesocosm.

In the second-year study, we added P as super phosphate (P_2O_5 , 46%) to 10 mesocosms (five lined and five unlined) to simulate high-P loading typical of secondarily treated wastewater ($2\text{--}3 \text{ mg P L}^{-1}$). Therefore, the experimental design of the second-year study included four different treatment schemes: liner plus riverwater (L + R), no liner plus riverwater (N + R), liner plus P-spiked water (L + P), and no liner plus P-spiked water (N + P).

Coal Combustion Product and Soil Analysis

Chemical analysis of the stabilized FGD material and surface soil was conducted at the Ohio Agricultural Research and Development Center (OARDC) Star lab in Wooster, OH. Surface soil samples were collected from approximately the top 5 to 10 cm in each mesocosm at the end of second growing season after plants were harvested. This soil layer (top 5 cm of the wetland sediment) is most important in a wetland in

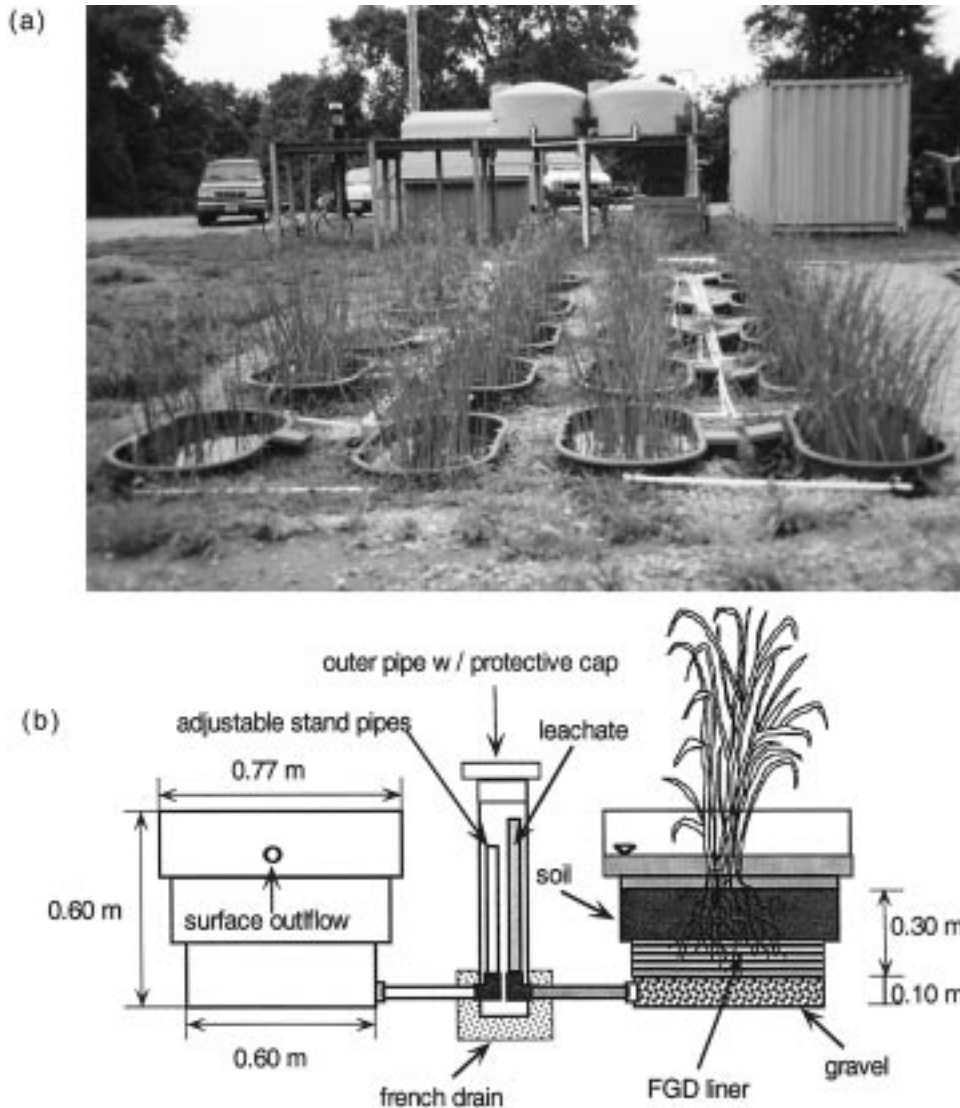


Fig. 1. Experimental wetland mesocosms used in this study. (a) Layout of 20 mesocosms at the Olentangy River Wetland Research Park, Columbus, OH. (b) Details of mesocosm drain system and flue gas desulfurization (FGD) by-product placement in 10 of the 20 mesocosms. Reprinted from *Water Research*, Vol. 35, Ahn et al., "Effects of recycled FGD liner material on water quality and macrophytes of constructed wetlands: A mesocosm experiment", p. 633–642, 2001, with permission from Elsevier Science.

water–soil exchange processes and in nutrition for wetland plants (Johnston, 1991). Three subsamples were taken from each mesocosm, combined into one composite sample to represent each of the 20 mesocosms, air-dried, ground using a mortar and pestle to pass a 2-mm screen, and extracted with the Mehlich 3 procedure (Council on Soil Testing and Plant Analysis, 1974). Elemental analyses for the soil and FGD samples were conducted by inductively coupled plasma (ICP) emission spectroscopy for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, V, and Zn using USEPA Method PB 84-128677 (USEPA, 1983). Boron was extracted using hot water (extracted by refluxing 1:2, sample to water for 10 min) and analyzed by ICP (Sah and Brown, 1997).

Leachate Analysis

Leachate samples were obtained from standpipes (Fig. 1b) connected to the bottom layer of each mesocosm. Leachate was analyzed three times per week in situ for pH and conduc-

tivity with a YSI (Yellow Springs, OH) data sonde. Four randomly chosen lined mesocosms and two unlined mesocosms were used for leachate collection at the end of the second year of the study. Leachate samples were analyzed for major and trace elements by ICP emission spectroscopy, and for Cl^- , NO_3^- , and SO_4^{2-} by ion chromatography, all by the Ohio Agricultural Research and Development Center (OARDC) Star Lab in Wooster, OH.

Vegetation Response

Total number of stems, number of stems bearing flowers, and stem lengths were recorded weekly in each mesocosm for two growing seasons to measure the effects of FGD material on plant growth during the experiments. For stem length measurements, 20 randomly chosen stems were measured for each mesocosm with a ruler. Plant biomass production and elemental analysis of plant tissue for this study are reported by Ahn et al. (2001).

Data Analysis

Statistical analyses for the effects of treatments (FGD material and P addition) on soil and leachate were conducted as a two-way analysis of variance using the General Linear Model (GLM) (SAS Institute, 1988). Duncan's multiple tests were used to test pairwise contrasts of means for significance at $P < 0.05$ (Steel et al., 1997). In the analysis of leachate, the data were divided only by the FGD treatment because no effect of P addition was detected for the elements analyzed. The averages of the parameters measured in both liner and no-liner mesocosms were calculated and compared via two-sample unpaired *t*-tests assuming unequal variance.

RESULTS AND DISCUSSION

Chemical Analysis of Starting Media

Chemical analyses of the three media used in this experiment—stabilized FGD, original topsoil, and Olentangy River water—are given in Table 1. The FGD material is quite alkaline, and has much higher concentrations than the surface soil for the following chemicals: Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, P, Pb, S, Sr, V, and Zn. The soil had higher concentrations of Mn and Si. The Olentangy River has relatively high concentrations of S (as sulfate), Na, and Cl compared with most rivers (Livingston, 1963) but was otherwise dilute in almost all metals.

Soil Chemistry after the Experiment

A variety of important biogeochemical processes in wetlands occur through the contact between standing

Table 1. Chemical properties of the flue gas desulfurization (FGD) by-product, topsoil, and Olentangy River water used in mesocosm wetland FGD liner study.

Parameter	FGD†	Topsoil†	Olentangy River water†
pH	10.6	7.8	7.6
EC‡ (µS cm ⁻¹)	na§	1000	510
	g kg ⁻¹		mg L ⁻¹
Al	25.5	0.42	0.05
Ca	146	2.4	62
Fe	85	0.17	0.08
K	2.7	0.06	3.0
Mg	3.7	0.45	16
S	85	0.03	22
	µg g ⁻¹		
As	107	<0.45	0.07
B	356¶	2.1	0.05
Ba	140	40	0.04
Cd	<0.2	0.3	<0.002
Co	20	1.7	<0.01
Cr	51	0.5	<0.005
Cu	49	5.0	<0.01
Mn	130	146	<0.002
Mo	15	<0.1	<0.01
Na	722	225	20
Ni	48	3.3	<0.01
P	573	8.4	0.13
Pb	15	5.0	<0.02
Si	342	650	1.8
Sr	254	8.1	0.63
V	74	0.6	<0.01
Zn	133	5.2	0.01
Cl ⁻	na	na	38
NO ₃ ⁻	na	na	2.0
SO ₄ ²⁻	na	na	65

† Average of two or three randomly-taken samples.

‡ Electrical conductivity.

§ na, not available.

¶ Total amount of B in FGD; plant-available B extracted out of the material by hot water was 29.4 µg g⁻¹.

water and the top surface soil layer. Morris and Bowen (1986), based on their sediment model calculations, showed that large changes in nutrients occur in the top 2 cm of the sediment layer. Furthermore, their results suggested that organic matter decomposes quickly within the top 5 cm of sediment compared with deeper sediment in wetlands and, because wetland plants are generally shallow-rooted, the chemistry of this surface soil will explain plant vitality. For these reasons, we wanted to see the effects, if any, of the FGD material on the surface soil in the mesocosms.

The pH of soil was greater in mesocosms with stabilized FGD liner materials ($P < 0.05$) than in mesocosms with no liners even after two growing seasons (Table 2). However, the pH of surface soils in both FGD and control mesocosms remained circumneutral, so effects on plants and microbes in the topsoil were probably minimal for this parameter. No statistical differences in conductivity of topsoil were observed between lined mesocosms and unlined mesocosms (Table 2). Only Al, As, and Ca of the 22 elemental concentrations were significantly different between lined and unlined mesocosms ($P < 0.05$) (Table 2). Arsenic and Ca were greater in the FGD treatment than in the controls; Al was lower in the FGD treatment soils than in the controls. Lower Al may be attributed to factors such as leaching from the FGD and immobilization as Al precipitation. Wendell and Ritchey (1996) also observed lower Al concentrations in soils amended with high-calcium FGD by-products relative to unamended controls and attributed this to both leaching of Al and precipitation as soil Al sulfates. Higher Ca concentrations of the surface soil in lined mesocosms probably contributed to the immobilization of additional P as Ca-P precipitates such as apatite [Ca₅(Cl, F)(PO₄)₃] and hydroxylapatite [Ca(PO₄)₆(OH)₂] (Sposito, 1989), lowering the P concentrations in the surface outflow. Increased phosphorus retention was observed in the lined mesocosms fed by P-spiked riverwater in the second year (Ahn et al., 2001), probably a result of the greater Ca in the surface soil.

Boron should be closely observed in studies with FGD because fly ash, one of the main components of stabilized FGD material, usually contains high B concentrations and can cause phytotoxicity (Carlson and Adriano, 1993; Crew and Dick, 1998; Sloan et al., 1999; Clark et al., 1999). No significant difference was found in soil B concentrations between lined and unlined mesocosms ($P < 0.05$) (Table 2).

Leachate Chemistry

Conductivity, pH, and concentrations of most elements analyzed in leachate were significantly different in lined mesocosms compared with unlined mesocosms ($P < 0.05$; Table 3). The pH of leachate was greater in lined mesocosms compared with unlined mesocosms after two growing seasons, reflecting high alkalinity produced by the liner material. The pH of leachate initially increased to 10, and then stabilized over time at slightly alkaline levels (7.0 to 8.0) in lined mesocosms. Initially high pH and alkalinity can be detrimental to plant

Table 2. Chemical properties of mesocosm wetland soils (mean \pm standard error) after two growing seasons.

	Treatment†			
	L + R	N + R	L + P	N + P
pH	6.73 \pm 0.13a*	6.38 \pm 0.04b	6.70 \pm 0.15ab	6.57 \pm 0.10ab
EC‡ ($\mu\text{S cm}^{-1}$)	862 \pm 142a	748 \pm 100a	1,080 \pm 326a	988 \pm 198a
	$\mu\text{g g}^{-1}$ soil			
Al	484 \pm 17b	525 \pm 12a	480 \pm 28b	524 \pm 16a
As	0.21§	nd¶	0.40 \pm 0.10a	0.22 \pm 0.07b
B	1.5 \pm 0.2a	1.4 \pm 0.1a	1.3 \pm 0.1a	1.3 \pm 0.1a
Ba	17.2 \pm 3.1a	21.9 \pm 3.9a	17.0 \pm 3.8a	17.8 \pm 4.5a
Ca	2858 \pm 203ab	2169 \pm 45c	3251 \pm 545a	2745 \pm 263ab
Cd	0.26 \pm 0.04a	0.26 \pm 0.03a	0.23 \pm 0.05a	0.28 \pm 0.04a
Co	1.44 \pm 0.07a	1.54 \pm 0.09a	1.45 \pm 0.13a	1.56 \pm 0.11a
Cr	0.21 \pm 0.02a	0.21 \pm 0.05a	0.23 \pm 0.01a	0.25 \pm 0.04a
Cu	5.4 \pm 0.7a	5.1 \pm 0.8a	5.1 \pm 0.9a	5.2 \pm 0.8a
Fe	416 \pm 18a	414 \pm 31a	422 \pm 30a	421 \pm 23a
K	77 \pm 8a	93 \pm 11a	78 \pm 5a	87 \pm 11a
Mg	362 \pm 8ab	369 \pm 10a	342 \pm 6b	351 \pm 7b
Mn	128 \pm 13a	110 \pm 8a	126 \pm 15a	102 \pm 14a
Mo	0.06§	0.17 \pm 0.07a	0.06§	0.15 \pm 0.04a
Na	74 \pm 3a	73 \pm 4a	72 \pm 4a	74 \pm 1a
Ni	3.12 \pm 0.1b	3.41 \pm 0.1ab	3.41 \pm 0.1ab	3.56 \pm 0.1a
P	7.1 \pm 0.3b	8.5 \pm 0.5b	9.2 \pm 1.0ab	11.5 \pm 1.3a
Pb	3.85 \pm 1.3a	3.76 \pm 1.1a	3.02 \pm 1.3a	3.40 \pm 1.2a
S	322 \pm 51a	221 \pm 41a	396 \pm 132a	372 \pm 88a
Si	182 \pm 7a	189 \pm 4a	189 \pm 8a	192 \pm 4a
Sr	23.1 \pm 1.7a	21.2 \pm 1.2a	26.3 \pm 3.7a	26.0 \pm 2.3a
Zn	7.74 \pm 0.88a	7.27 \pm 0.33a	6.98 \pm 0.40a	7.40 \pm 0.46a

* Different letters indicate significant differences between treatments within each row ($P < 0.05$).

† L + R, flue gas desulfurization (FGD) liner + river water; N + R, no liner + river water; L + P, FGD liner + phosphorus-spiked water; N + P, no liner + phosphorus-spiked water.

‡ Electrical conductivity.

§ Indicates the number of samples used was one since other samples were below the detection limit.

¶ nd, the concentration of the element was below the detection limit of Inductively Coupled Plasma (ICP) emission spectroscopy.

growth (see Effects on Early Vegetation Development, below).

High conductivity of the leachate was observed in lined mesocosms relative to unlined mesocosms ($p < 0.05$). Conductivity of leachate continued to increase in lined mesocosms over time (Ahn et al., 2001) and stabilized at almost 2000 $\mu\text{S cm}^{-1}$ at the end of two growing seasons (Table 3). Conductivity, however, did not reach levels considered potentially detrimental to salt-sensitive plants ($\sim 4000 \mu\text{S cm}^{-1}$) (Sposito, 1989).

Concentrations of Al, B, Ca, Fe, K, Mg, Mn, and $\text{SO}_4\text{-S}$ in leachate differed between lined and unlined mesocosms ($P < 0.05$). Higher concentrations of Al, B, Ca, K, and $\text{SO}_4\text{-S}$ were observed in leachates from lined mesocosms (Table 3), but the concentrations of most elements analyzed in leachates were less than primary drinking water standards (Table 3). Calcium and $\text{SO}_4\text{-S}$ increased in the leachate by 6 and 20 times, respectively, in lined mesocosms over unlined controls; the dramatic increase was expected because liner material used in this experiment consisted of varying amounts of sulfates and/or sulfites of calcium ($\text{CaSO}_4/\text{CaSO}_3$) with unreacted lime and fly ash (Bigham et al., 1993). The $\text{SO}_4\text{-S}$ concentrations of leachate in our study were the same as total S content. Apparently the conditions present in the wetland mesocosms were not anaerobic enough to produce hydrogen sulfide. Stehouwer et al. (1996) found that more than 90% of leachate S was present as $\text{SO}_4\text{-S}$ from fields where FGD by-products were applied. Average leachate concentration of $\text{SO}_4\text{-S}$ from lined mesocosms was 394 mg L^{-1} and was greater than the secondary drinking water standard of 250 mg L^{-1} (Table 3). High concentrations of $\text{SO}_4\text{-S}$ in leachate from lined mesocosms after 2 yr of experimentation suggest that

this element should be carefully monitored in any large-scale application of FGD material as a liner. Potassium was also higher in leachates from lined mesocosms com-

Table 3. pH, conductivity, and elemental concentrations of leachates (mean \pm standard error) from mesocosm wetlands after two growing seasons.

	Treatment		NPDWR†	NSDWR‡
	FGD§ liner	No liner		
pH	* 7.30 \pm 0.14	6.62 \pm 0.01		
	* (9.79 \pm 0.23)¶	(7.85 \pm 0.1)¶		
EC# ($\mu\text{S cm}^{-1}$)	* 1746 \pm 346	848 \pm 86		
	mg L^{-1}			
Al	* 0.11 \pm 0.03	0.04 \pm 0.00		0.2
As	0.06 \pm 0.02	<0.035	0.05	
B	* 1.44 \pm 0.3	0.08 \pm 0.0		
Ca	* 452 \pm 124	75 \pm 3		
Cd	<0.001	<0.001	0.005	
Cr	0.002 \pm 0.001	<0.002	0.1	
Cu	0.004††	<0.002	1.3	
Fe	* 15.5 \pm 1.6	22.0 \pm 2.7		
K	* 14.4 \pm 6.4	0.48 \pm 0.14		
Mg	* 15.6 \pm 2.2	21.6 \pm 1.2		
Mn	* 1.10 \pm 0.4	3.52 \pm 0.1		0.05
Na	21.8 \pm 4.2	14.9 \pm 0.3		
Ni	<0.005	<0.005		
Pb	<0.02	<0.02	0.015	
Zn	0.003 \pm 0.00	<0.001	5.0	
Cl ⁻	69 \pm 1.3	62 \pm 11		250
SO_4^{2-}	* 394 \pm 126	20.0 \pm 0.4		250

* Significant difference at the 0.05 probability level between lined and unlined mesocosms.

† National Primary Drinking Water Regulations (USEPA, 1995).

‡ National Secondary Drinking Water Regulations (USEPA, 1995).

§ Flue gas desulfurization.

¶ Values in parentheses are the pH of leachate in the first year experiment (from Ahn et al., 2001).

Electrical conductivity.

†† No standard error available because the other samples were analyzed below the detection limit of inductively coupled plasma (ICP) emission spectroscopy.

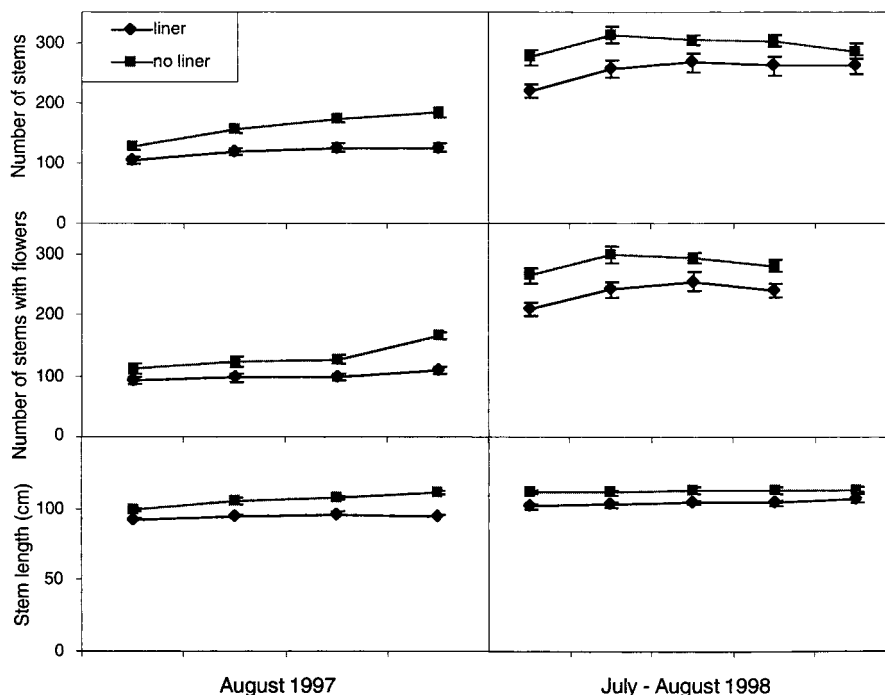


Fig. 2. Morphometric measurements of plant growth including number of stems, number of stems with flowers, and average stem length during the first two growing seasons in the mesocosm flue gas desulfurization (FGD) liner study. Error bars indicate ± 1 SE, $n = 10$.

pared with unlined mesocosms, clearly a result of high amounts of potassium provided by stabilized FGD materials (Table 1).

Iron, Mg, and Mn were lower in leachates from lined mesocosms compared with unlined mesocosms. This may have resulted from immobilization of these elements due to increased pH of the soil and leachate by the alkaline FGD material. Concentrations of Mn exceeded secondary drinking water standards in both lined and unlined mesocosms. Of the trace elements reported (Table 3), Cd, Ni, and Pb were below ICP detection limits ($\text{Cd} < 0.001 \text{ mg L}^{-1}$, $\text{Ni} < 0.005 \text{ mg L}^{-1}$, $\text{Pb} < 0.02 \text{ mg L}^{-1}$), suggesting no contributions of the elements from the liner materials. Arsenic in some of the leachate samples from lined mesocosms was slightly higher than primary drinking water standards (Table 3).

Effects on Early Vegetation Development

Figure 2 shows morphometric measurements of vegetation during the first two growing seasons of the experiment. Significantly fewer stems, fewer stems bearing flowers, and lower stem length were observed in the lined mesocosms compared with unlined mesocosms during the first growing season. We believe that this effect was due to the extremely high pH (up to 10) observed in the leachate water soon after the experiment began as found in Stehouwer et al. (1995a). A similar pattern was continually monitored in the second growing season, but the difference between lined and unlined mesocosms seemed to become less over time.

It is also possible that early leaching of boron had a phytotoxic effect on the early wetland vegetation. Boron is known to have the greatest effects during the initial 2 to 3 yr after the land application of fly ash materials (Adriano et al., 1980). Phytotoxic effects of B may disap-

pear or be mitigated with time by immobilization, leaching, and plant uptake (Sposito, 1988). Ransome and Dowdy (1987) reported that B concentrations in soil solutions decreased to background levels 3 yr after application of FGD by-products to soybean fields. Sloan et al. (1999) reported that $>97\%$ of soluble B existed as H_3BO_3 , a form readily taken up by plants in FGD by-product-treated soils. In this experiment, higher B concentrations were observed in belowground tissues of plants grown in lined mesocosms than in unlined mesocosms (Ahn et al., 2001), although biomass production was not negatively affected. The amount of plant-available B in the FGD by-product was low ($29 \mu\text{g g}^{-1}$) (Table 1), and the concentrations in the surface soil considerably lower ($\sim 2 \mu\text{g g}^{-1}$). Generally, B above 50 to $100 \mu\text{g g}^{-1}$ in soil is considered high for many plants (Clark et al., 1999). Potentially phytotoxic B concentrations in leachates averaged 1.44 mg L^{-1} (Table 3). Boron in excess of 2 mg L^{-1} in irrigation water is usually considered deleterious to certain plants (American Public Health Association, 1992); therefore, it seems that B concentrations in the leachate were safe for plants, but only after the initial period of growth. Boron content of soil and water, however, should be monitored continually from the beginning of the application of the FGD materials because the difference between toxicity and deficiency for B is narrower than for most mineral elements (Sposito, 1988; Crews and Dick, 1998).

CONCLUSIONS

The study was conducted to identify potential soil and ground water contamination from constructed wetlands that might utilize coal combustion products as liner materials. We have identified the major limitations of FGD

material to be used as liners for constructed wetlands—relatively high B and $\text{SO}_4\text{-S}$ concentrations in leachate, and early retardation of plant growth. Attention should also be paid to the early release of other chemicals from the liner material. High concentrations of B and $\text{SO}_4\text{-S}$ in leachate from lined mesocosms after 2 yr of experimentation suggest that this element should be carefully monitored in any large-scale application of FGD material as a liner. Our study suggests that it may be desirable to delay planting a wetland for approximately 3 to 4 mo if coal combustion products are used as liners to avoid the early effects of high pH and possibly phytotoxic chemicals such as B on vegetation.

The study shows that stabilized FGD by-products may have the potential to be used as liners in constructed wetlands, but only if the material is machine-compacted to achieve a certain impermeability as a liner so that leaching is minimal to nonexistent. The susceptibility of other components of a wetland ecosystem, such as benthic invertebrates (especially burrowing invertebrates) and amphibians, to the effects of FGD material was not investigated in this study and are currently unknown. Furthermore, long-term chronic effects of FGD material on wetland soils and water quality cannot be ascertained through this relatively short 2-yr study. The relevance of our mesocosm study to field application of FGD by-products as liners in constructed wetlands may be limited because some mesocosm-scale artifacts were also found during the experiments, such as “pot-bound” plants after 2 yr and the inability to machine-compact the liner material. Therefore, a larger-scale, longer-term wetland experiment closer to full-scale should be conducted to better predict the effects, both positive and negative, of using FGD by-products to seal constructed wetlands before a full-scale application is attempted.

ACKNOWLEDGMENTS

The principal sponsor of this research project is the Ohio Coal Development Office within the Ohio Department of Development (OCDO Grant CDO/D-95-10), Jackie Bird, Director. American Electric Power kindly provided the FGD material. Some salaries were provided by the Ohio Agricultural Research and Development Center and the Environmental Science Graduate Program, both at The Ohio State University. We want to particularly thank Bill Wolfe and Tarunjit Butalia for getting us involved in these FGD studies and Bill Acton for the installation of mesocosms. We also appreciate the time of editor Warren Dick and three anonymous reviewers for a number of valuable suggestions. Publication 01-003 of the Olentangy River Wetland Research Park.

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