A soil column study to evaluate treatment of trace elements from saline industrial wastewater

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ABSTRACT

Industrial wastewater from the flue gas desulfurization (FGD) process is characterized by the presence of trace elements of concern, such as selenium (Se) and boron (B) and relatively high salinity. To simulate treatment that FGD wastewater undergoes during transport through soils in subsurface treatment systems, a column study (140-d duration) was conducted with native Kansas soil and saline FGD wastewater, containing high Se and B concentrations (170 μg/L Se and 5.3 mg/L B) and negligible arsenic (As) concentration (∼1.2 μg/L As). Se, B, and As, and dissolved organic carbon concentrations and organic matter spectroscopic properties were measured in the influent and outflow. Influent Se concentrations were reduced by only ~half in all treatments, and results suggest that Se sorption was inhibited by high salinity of the FGD wastewater. By contrast, relative concentrations (C/Co) of B in the outflow were typically <10%, suggesting that B sequestration may have been enhanced by higher salinity. Unexpected elevated As concentrations in the outflow (at >150 μg/L in the treatment with labile organic carbon addition) suggest that soils not previously known to be geogenic arsenic sources have the potential to release As to groundwater in the presence of high salinity wastewater and under reducing conditions.

Key words | arsenic, boron, constructed wetlands, flue gas desulfurization, fluorescence, selenium

INTRODUCTION

Flue gas desulfurization (FGD) wastewater from coal-fired power plants is known to contain potentially harmful pollutants, such as arsenic (As), boron (B), cadmium (Cd), chromium (Cr), copper (Cu), chlorine (Cl), lead (Pb), mercury (Hg), nitrate (NO3), selenium (Se), sulfate (SO42−), and zinc (Zn) (Miezewski 1991; Eggert et al. 2008). In addition, the high salinity of FGD wastewater, ranging from as low as ~5 parts per thousand (ppt) in this study to as high as 20 ppt in Mooney & Murray-Gulde 2008, and high total dissolved solids (TDS) concentrations, ranging from 1,400 to 50,000 mg/L (EPRI 2006), may negatively affect chemical and biological processes designed to treat wastewater (e.g. Koenig & Liu 2004).

Constructed wetland treatment systems (CWTSs) have been used to treat municipal and industrial wastewater, including FGD wastewater, urban and agricultural runoff, and acid-mine drainage through both soil filtration and phytoremediation processes (Vymazal 2009, 2014; El-Sheikh et al. 2010). Constructed wetlands have been shown to effectively remove some toxic trace elements, such as Se, via sorption and precipitation reactions occurring in the soils (Masscheleyn & Patrick 1995; Gambrell 1994; Kadlec & Knight 1996; Marshand et al. 2010). Microbial processes, such as sulfate reduction, which can lead to the formation of As-sulfides and Se-sulfides under reducing conditions, also act to transform and immobilize toxic trace elements (Moore et al. 1988; Plant et al. 2005).

Subsurface flow constructed wetland treatment systems (SSF CWTSs) are particularly effective at promoting such reactions under reducing conditions. For the treatment of
FGD wastewater, the use of CWS has relied mostly on free water surface constructed wetland treatment systems (FWS CWTSs) (Eggert et al. 2008; Mooney & Murray-Gulde 2008). Experiments with pilot FWS wetland cells shows that these can achieve highly reducing conditions, on the order of \(-400\) mV (Sundberg-Jones & Hassan 2007). The fate of Se and B has been experimentally evaluated in the field and laboratory, using FWS CWTSs (Kropfelova et al. 2009). However, our knowledge of the behavior and transport characteristics of Se and B through SSF CWTSs under saline and reducing conditions is limited. Moreover, studies evaluating the removal of trace elements from FGD wastewater, which tends to have high concentrations of multiple trace elements as well as high salinity, are few (Ye et al. 2005; Türker et al. 2014).

Further, the presence of dissolved organic matter (DOM) in groundwater and soil pore water can be an important control on the speciation, solubility, mobility, and bioavailability of trace elements. DOM contains both labile and recalcitrant moieties that have important biogeochemical roles in subsurface environments. Biologically recalcitrant DOM compounds, including dissolved humic substances, are typically chemically reactive and undergo complexation and electron transfer reactions with free metal ions and metal (hydro)oxide surfaces (Lovley et al. 1996; Kaiser & Guggenberger 2000). By contrast, labile DOM compounds serve as a carbon source and electron donor for microbes (e.g. Hery et al. 2010). Whereas there may be sufficient supply of microorganisms and electron acceptors to promote redox reactions in many subsurface environments, the availability of labile DOM is typically the limiting factor in bioremediation (Sposito 2008). It is common practice to add a labile DOM source, such as methanol, to contaminated subsurface environments and industrial wastewaters that may be otherwise low in C to promote degradation processes and reducing conditions. In reducing subsurface environments, labile DOM fuels microbial redox reactions, such as denitrification, sulfate reduction, iron reduction, and methanogenesis (Bethke et al. 2011). However, these reactions can have contrasting effects on the mobility of trace elements. For example, iron (Fe) reductive dissolution leads to the release of As from sediments (Wang & Mulligan 2006), but sulfate reduction can lead to the sequestration of both As (Hery et al. 2010; Lizama et al. 2011) and Se (Uhrig et al. 1996). Given the juxtaposition of reactions that may occur under reducing conditions and the contrasting influence of those reactions on the mobility of trace elements, more needs to learned about the role that both humic and labile DOM play in driving redox reactions in soils and sediments receiving FGD wastewater.

An effective and widely used technique to track the chemical quality of DOM in diverse environments is optical spectroscopy. Ultraviolet-visible (UV-vis) absorbance spectroscopy has been used to provide information about the aromaticity of DOM compounds (Weishaar et al. 2003). Fluorescence characterization of DOM is a highly sensitive technique that provides rapid and reliable information about DOM sources, transformations, and biological reactivity (Fellman et al. 2010). The excitation and emission wavelengths at which fluorescence occurs are related to specific molecular structures or interactions (Fellman et al. 2010). For example, fluorescence at low excitation and high emissions wavelengths reflect the presence of humic structures, and a humification index (HIX) has been described to track the presence of humic DOM (Zsolnay et al. 1999).

In this study, we aimed to advance the understanding of the fate of Se and B from saline (4.88 ppt; Table 1) FGD wastewater during transport through a native Kansas soil, which represents the type of treatment that would occur in subsurface flow CWTS. To simulate subsurface flow through soils under reducing conditions, we used a laboratory-based column experiment, for which columns were continuously supplied with FGD wastewater, containing negligible As concentration and elevated sulfate-S, Se, and B concentrations (Table 1). We evaluated influent and outflow concentrations of sulfate-S, Se, As, and B and applied fluorescence spectroscopy to track the change in DOM quality over the course of the experiment. The effects of labile organic carbon (OC) addition on the retention capacity of these constituents were also investigated.

**MATERIALS AND METHODS**

**Soil and FGD wastewater**

Soil and FGD wastewater used in the column experiment were collected from the Jeffrey Energy Center (JEC), a coal-fired power plant located in Emmett Township, Pottawatomie County, approximately 160 km northwest of Kansas City, Kansas, USA (39°17′10″N, 96°07′01″W). The JEC is the largest coal-fired power plant in Kansas, using up to 36,000 tons of low-sulfur coal per day or 9 to 10 million tons per year (Westar Energy 2014). The JEC is equipped with a limestone forced-oxidation wet FGD scrubber to reduce sulfur dioxide and other emissions (Westar Energy 2014). To reduce high concentrations of these constituents, the JEC treats the
FGD wastewater with a proprietary process to remove Hg and As and then passes wastewater through a SSF CWTS.

Approximately 0.1 m³ of topsoil (soil) located <500 m from the existing SSF CWTS at the JEC was collected on 8 August 2013. The soil was hand-homogenized, gently ground using a ceramic mortar and pestle, sieved through 2-mm screen, and air-dried. Soil characteristics are described in the supplementary information (Supplementary Methods and Table S1, available with the online version of this paper).

Approximately 40 L of FGD wastewater was collected from an effluent sampling line at JEC on the same date that soil was collected. FGD wastewater used for the column experiment was kept unfiltered and unacidified. FGD wastewater was bubbled with N₂ gas (to reach an Eh of ∼100 mV as measured with an Orion Ag/AgCl₂ ORP (redox) combination electrode) prior to pumping onto columns.

**Experimental setup**

The experimental setup is shown in Figure 1. The air-dried soil was wetted to a known water content of 0.27 g/g and packed into acrylic columns (30.5 cm length, 5.08 cm i.d.; 50 cm height).

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**Table 1** | Chemical composition (mean concentrations ± standard deviations) of flue gas desulfurization wastewater (FGD WW), OC-amended FGD wastewater, and Kansas Department of Health and Environment Standards (KDHE STDs) (KDHE 2004)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FGD WW</th>
<th>OC-amended FGD WW</th>
<th>KDHE STDs</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total alkalinity</td>
<td>840</td>
<td>NM</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Arsenic, Total</td>
<td>1.2 ± 0.70</td>
<td>1.2 ± 0.70</td>
<td>340</td>
<td>150</td>
</tr>
<tr>
<td>Boron, Total</td>
<td>5.3 ± 0.28</td>
<td>5.78 ± 0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>22.0 ± 0.10</td>
<td>22.2 ± 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>610 ± 26.9</td>
<td>667 ± 48.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>952 ± 51.2</td>
<td>976 ± 25.7</td>
<td>860</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>9.3 ± 0.11</td>
<td>9.7 ± 0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Hardness</td>
<td>380</td>
<td>NM</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>UD</td>
<td>UD</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>770 ± 29.4</td>
<td>849 ± 72.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>3.2</td>
<td>NM</td>
<td></td>
<td>μg/L</td>
</tr>
<tr>
<td>Nitrate-Nitrogen</td>
<td>48.3 ± 1.66</td>
<td>42.7 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>18.8</td>
<td>NM</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Nitrogen, Total</td>
<td>97.3 ± 0.50</td>
<td>100 ± 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>116 ± 4.09</td>
<td>120 ± 6.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.20 ± 0.13</td>
<td>6.95 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>4.88</td>
<td>NM</td>
<td></td>
<td>ppt</td>
</tr>
<tr>
<td>Selenium</td>
<td>170 ± 7.1</td>
<td>181 ± 15</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Sodium</td>
<td>727 ± 34.3</td>
<td>988 ± 70.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate-Sulfur</td>
<td>1,340 ± 45.5</td>
<td>1,380 ± 22.5</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfur, Total</td>
<td>1,780 ± 72.5</td>
<td>1,970 ± 156</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>31.0 ± 0.43</td>
<td>291 ± 4.80</td>
<td></td>
<td>mg/L</td>
</tr>
<tr>
<td>SUVA</td>
<td>2.40 ± 0.08</td>
<td>0.268 ± 0.008</td>
<td>(L/mg-m)</td>
<td></td>
</tr>
<tr>
<td>HIX</td>
<td>9.4 ± 0.10</td>
<td>5.6 ± 0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FI</td>
<td>1.65 ± 0.02</td>
<td>1.64 ± 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freshness index</td>
<td>0.74 ± 0.002</td>
<td>0.75 ± 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>3,650</td>
<td>NM</td>
<td></td>
<td>mg/L</td>
</tr>
</tbody>
</table>

UD = undetectable (<0.1); NM = not measured; ppt = parts per thousand.

Source: Galkaduwa et al. (2017).
To evaluate the addition of labile OC to stimulate microbial processes in CWTSs, 2 L of raw undiluted FGD wastewater was amended with 1.92 g sodium lactate (Figure 1). The dissolved organic carbon (DOC) concentration of this solution was ~295 mg C/L. Two controls (columns 1 and 2) were prepared without inoculum or labile OC amendment.

Upward flow was used for all columns to facilitate and maintain saturated conditions and to simulate the wetland design recommended to JEC. Upward flow also minimizes the potential for density- and viscosity-driven mixing of influent solution with the resident solution in columns. The columns were saturated from below with tap water that had been exposed to air to lessen the chlorine residual. Saturation was achieved in ~48 h and steady-state conditions were established after 12 days of pumping with tap water. The flow rate used for column 1 was 1.42 mL/h (hereafter referred to as the 2× flow rate), which is equivalent to a volumetric flux of 1.68 cm/d and is representative of the effluent flow rate at JEC at the time of sampling. Due to equipment constraints, the 2× flow rate could not be applied for all treatments. The flow rate used for all other columns (columns 2–6) was 0.71 mL/h (hereafter referred to as the 1× flow rate), which is equivalent to a volumetric flux of 0.84 cm/d. After steady-state was achieved, deoxygenated (bubbled with N2) FGD wastewater was passed through the columns for 140 days at the same flow rates used to achieve steady state.

Column effluent that accumulated in vials placed at the outflow was collected every 48 h. Approximately 15 mL of each sample was immediately filtered using 0.45 μm syringe filters (Environmental Express Inc., SC, USA) and acidified by adding 2–3 drops of 6M HCl prepared from trace metal-grade concentrated HCl acid (weight of 35–38%). Additional filtered (0.20 μm syringe filters) samples were kept unacidified for optical spectroscopic analyzes. All unfiltered/unacidified, filtered-only, and filtered/acidified samples were stored at 4 °C until analysis.

At the end of the experiment, columns were sectioned into six segments (5.1 cm per segment) with a hand saw. After each segment was removed, it was immediately wrapped with a plastic wrapper, weighed, and temporarily stored in a glove box (<1% oxygen). Soil was separated from each column segment in the glove box to reduce oxygen diffusion. The remainder of the soil was stored in a zip-lock bag at 4 °C until analysis.

Solution chemical properties

Raw unfiltered FGD wastewater was analyzed for total alkalinity using Phenolphthalein and Brom cresol Green-Methyl Red indicators and for total hardness with EDTA (ethylene diamine tetra-acetic acid) titrant (Rice et al. 2012). The unfiltered/unacidified samples were measured for conductivity (EC) and salinity with a Fisher Scientific AR20 pH/Conductivity meter. The pH was measured with a Fisher Scientific Education pH meter, and TDS concentration was measured gravimetrically (Rice et al. 2012). It
was not possible to measure redox couples, such as nitrate/nitrite and Fe(III)/Fe(II) to determine redox state. All samples for further analyses were stored at 4°C until analysis.

Unacidified samples were analyzed on an ion chromato-
graph (ICS-1000, Dionex Corporation) for the determination of anions (F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, and SO₄²⁻). Appropriate dilutions were used to minimize instrument damage caused by FGD wastewater and to maintain concentrations within the calibration range. Recoveries of replicates, spikes and blanks for quality control of all analyses are reported in the Supplementary Methods.

Subsamples for elemental analysis (described below) were filtered through 0.45 μm nylon syringe filters (Environmental Express Inc., SC, USA) and acidified with 2–3 drops of 6M HCl. Filtered and acidified samples were measured for total elemental analysis (B, Na, Mg, Ca, S, Fe, and K) using a Varian 720-ES inductively coupled plasma-optical emission spectrometer (ICP-OES). The ICP-OES was calibrated with six multi-element standards, and it was re-calibrated after every 30 samples. A subset of samples was sent to the Veterinary Diagnostic Laboratory at Kansas State University for analysis of Se using an Agilent Technologies, Santa Clara, CA, USA) ICP-MS coupled with a dynamic reaction cell (ICP-MS-DRC). Environmental Calibration Standard 5183-4688 (Agilent Technologies, Santa Clara, CA, USA) and multi-element Calibration Standard 8500-6942 (Agilent Technologies, Santa Clara, CA, USA) were used for calibration. Due to cost considerations, samples containing the inoculum-amended soils were not analyzed for Se. Arsenic concentrations were measured using a Graphite Furnace Atomic Absorption Spectrometer (GF-AAS; Varian Inc., Foster City, CA, USA) with a standard addition method to minimize matrix effects. Three micro-liters of 2,000 mg/L Palladium (Pd) were used as the modifier to enhance the signal (absorbance) of As in GF-AAS.

The filtered/acidified samples were also measured for total organic carbon (TOC) and total nitrogen (TN) using a Shimadzu TOC-L TOC/TN analyzer calibrated with a TC standard solution prepared from reagent grade potassium hydrogen phthalate and a TN standard solution prepared from reagent grade potassium nitrate. The samples were sparged for 5 min with ultra-high purity air to remove inorganic carbon.

Filtered unacidified samples were analyzed with UV-vis absorbance and fluorescence spectroscopy to track the sources and transformations of DOM. Excitation emission matrix (EEM) fluorescence spectra were collected at excitation wavelength increments of 3 nm over a 250 to 400 nm range and at emission wavelength increments of 10 nm over a 350 to 600 nm range using a Horiba Aqualog Fluorometer. UV-vis absorbance was measured simultaneously with fluorescence over the same range of excitation wavelengths. The UV absorbance at 254 nm (abs254) was normalized to DOC concentration to determine the specific UV absorbance (SUVA). The EEMs were corrected for the inner filter effect, normalized to the area under the Raman peak (excitation ≈ 397 nm), and blank-subtracted for each sample EEM.

The EEMs contain three-dimensional information about the optical spectroscopic character of fluorescent DOM (FDOM). Some fluorescent peaks are ubiquitous and have been reported in a wide range of aquatic environments. For example, amino acid-like fluorescence is typically visible in region T (excitation (ex) 275 nm, emission (em) 370–430 nm) where tryptophan fluoroses and region B (ex 370 nm, em 304–312 nm) where tyrosine fluoroses. Peaks A (ex < 260 nm, em 448–480 nm) and C (ex 320–360 nm, em 420–460 nm) are both associated with humic FDOM that is aromatic, highly conjugated, of high molecular weight (Fellman et al. 2010), but peak A has been shown to be more resistant to degradation than peak C (Coble 1996).

The fluorescence index (FI) provides information about the relative amounts of terrestrial and microbial fluorescence of DOM (McKnight et al. 2001) and was calculated as the ratio of intensities at 470/520 nm emission and 370 nm excitation (Cory & McKnight 2005). The HIX, calculated as the ratio of peak area under the emission spectra at 435–480 nm to peak area from 300 to 345 nm obtained at an excitation wavelength of 254 nm (Zsolnay et al. 1999), provides information about the degree of humification of soil organic matter. The freshness index (β/α index), calculated as the ratio of emission intensity at 380 nm to the maximum intensity between 420 and 435 nm obtained at an excitation wavelength of 254 nm (Parlanti et al. 2000), provides information about the age and freshness of DOM. Variations in these three indices were recorded over the course of the experiment to quantify variations in DOM quality of column outflow over time. All corrections and calculations were performed using MATLAB R2013a.

**Soil chemical properties**

Soil was analyzed prior to packing the columns and at the end of the column experiment. First, air-dried soil samples were finely ground using an agate mortar and pestle. Then,
elemental concentrations were determined using microwave-assisted acid digestion USEPA method SW846-3051 (USEPA 2007). Soil samples were digested according to the procedure described by Attanayake et al. (2014), which is described in greater detail in the Supplementary Methods. The solution was then analyzed for Fe, S, Mn, Al, B, and Si using the ICP-OES. The concentrations of As and Se were measured using the GF-AAA. The Pd modifier was used to enhance the absorbance signal. To analyze soil total C and N a LECO TruSpec CN carbon/nitrogen combustion analyzer was used.

Statistical analyses

Statistical analysis, one-way analysis of variance (ANOVA) using PROC MIXED, was performed to evaluate Type 3 tests of fixed effects (treatment type and time) on concentrations of solutes using SAS 9.4 software. We used a split-plot arrangement with a completely-randomized design, where the main plot factor was the OC treatment and the split-plot factor was time (pore volume).

RESULTS

Characterization of wastewater

Compared to untreated FGD wastewaters reported in other studies (EPRI 2006), the treated FGD wastewater (referred to as influent in this study) had lower concentrations of most water chemistry parameters (Table 1). Dissolved As concentration (1.21 μg/L) of the influent was below the US EPA maximum contaminant level for drinking water of 10 μg/L and was much lower than the range observed in various FGD wastewaters (EPRI 2006; Eggert et al. 2008). However, Se and chloride concentrations of the influent (at 170 μg/L for Se and 952 mg/L for chloride) exceeded the Kansas Department of Health and the Environment (KDHE) limits (20 μg/L for Se and 860 mg/L for chloride) for acute toxicity of surface water (Table 1). Hg analysis of the influent was done in a concurrent study (Galkaduwa et al. 2017), which reported a Hg concentration of 3.2 μg/L. Other dissolved trace element concentrations of influent, reported by Westar Energy (unpublished), were 94.6 μg/L Cr, 15.7 μg/L Cu, and 8 μg/L Pb. The addition of OC (sodium lactate) into the influent (for columns 5 and 6) caused only DOC and sodium concentrations to be elevated compared to the original FGD wastewater (Table 1).

Inorganic constituents in column outflows

Inorganic constituents, such as conductivity, and anion and cation concentrations, were variable over the course of the experiment, whereas pH remained fairly constant, between 7.4 and 8.0. The electrical conductivity increased from ~2.5 mS/cm in the influent to >8 mS/cm in the outflow of all treatments (Tables S2–S7, available with the online version of this paper). Sodium and chloride concentrations were initially low, but increased to >900 mg/L and >1,100 mg/L, respectively by the last pore volume (Tables S2–S7), which means that all columns reached relative concentrations of ~1.0 or greater for these two constituents. Concentrations of K and Fe remained low (except for early pulses of Fe) during the course of the experiment (Tables S2–S7). Nitrate-N was high in the influent (Table 1) and decreased to only ~12 mg NO₃-N/L (Tables S2–S7).

Initial sulfate-S concentrations in the outflow of all columns were low but still >0 mg/L. Sulfate-S concentrations in the outflow gradually increased over time (Figure 2(a)), and by the end of the experiment, relative sulfate-S concentrations in all columns were >1.0 (Figure 2(b)), supporting that SO₄²⁻ was released from the soils. Sulfate-S concentrations were lowest in the outflow of columns with OC-amended FGD wastewater. Statistical analyses to evaluate the influence of treatment type and time on key constituents of the column effluent (Tables S8–S13, available online) indicate that both treatment type (OC addition) and time had a significant (p < 0.0001) effect on sulfate-S and total S concentration in the outflow (Tables S8 and S9).

Boron, selenium, and arsenic in column outflows

Contrasting results were observed for the main constituents of concern, B, Se, and As. In the case of B, concentrations remained low in the outflow, with relative concentrations at <0.1 for most of the experiment (Figure 2(c) and 2(d)), signifying strong B retention. Well over 90% of B was retained in the control column with 1 x flow rate and in columns with inoculum and OC amended FGD wastewater. However, in the control column with the 2 x flow rate, B concentrations did eventually increase after the eighth pore volume and reached a relative concentration of 1.0 after 14 pore volumes (Figure 2(d)).

A smaller dataset of Se measurements was available only for outflows of the controls and OC amended columns. For these treatments, Se relative concentrations remained at <50% throughout the experiment (Figure 2(e) and 2(f)). Outflow Se concentrations of the first pore volume were quite variable, and subsequent pore volumes had Se concentrations
ranging from ~40 to 80 μg/L, with no evident difference between columns (Figure 2(f)). Also, S and Se masses accumulated in some of the soil sections during the experiment but were negligible or desorbed in others (Tables S14 and S15, available online). Although a portion of dissolved Se was retained, the outflow concentration did not meet KDHE acute (20 μg/L) and chronic (5 μg/L) limits.

Soil As concentration (3.8 mg/kg; Table S1) was at the low range when compared to the background concentration (mean of >77,000 data points was ~8.5 mg/kg) for As in US soils (USGS 2004). Nevertheless, elevated As concentrations were observed in the outflow of all columns within the first pore volume, and concentrations generally increased over the course of the experiment at the 1× flow rate (Figure 2). The column with the 2× flow rate had the lowest outflow As concentrations compared to columns with the 1× flow rate. The columns with OC amended solution had the highest outflow As concentrations, which were substantially higher than in the control column with the 1× flow rate (Figure 2(g) and 2(h)). Arsenic concentration peaked at approximately four pore volumes at a value of 161 μg/L (Figure 2(g)), which is greater than the KDHE limits for chronic toxicity (150 μg/L) (Table 1). Statistical analyses indicate that both treatment type (flow rate and OC addition) and time had significant ($p < 0.0001$) effects on As concentration in the outflow (Table S11).

Figure 2 | Temporal variation in concentration (left panels) and relative concentration (C/Co; right panels) of sulfate (a and b), boron (c and d), selenium (e and f), and arsenic (g and h) in column outflow, where X is the column flow rate (0.71 mL/h). Results of each duplicate experiment with inoculum added (red squares) and lactate added (green circles) are shown individually (rather than as averages). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wst.2017.413.
Organic constituents in column outflows

Both concentrations and chemical character of DOM changed over the course of the experiments. In controls (i.e. at both 1× and 2× flow rates) and in columns with inoculum added, the outflow DOC concentration was several times greater than influent DOC concentration (relative DOC concentration was always >1.0; Tables S2–S7). By contrast, in the ‘OC added’ columns, relative DOC concentrations were <1.0 and decreased over the course of the experiment. For all columns, statistical analyses indicated that these changes in DOC concentration over time were statistically significant (Table S12). In the first 3–4 pore volumes, outflow of all columns had a spike in DOC concentration (Figure 3(a) and 3(b)), which corresponded to changes in fluorescence and UV-vis absorbance indices. For example, in the first three pore volumes, DOM had a low HIX (Figure 3(c)) and low SUVA (Figure 3(e)). The EEMs for this period had pronounced fluorescence in region T associated with amino acid-like FDOM (Figure 4), which indicate that less humified and less aromatic DOM was released initially.

After the initial pulse of less humic DOM in all columns, the FDOM quality became more humic. All columns, irrespective of treatment, showed the same changes in fluorescence and absorbance indices. Indeed, statistical analyses indicate that changes in fluorescence indices (FI, β/α index, and HIX) were not influenced by treatment type. Only time had a significant (p < 0.0001) effect on fluorescence indices in the outflow (Table S13). By the end of the experiment, the HIX doubled from 6 to ~12, and SUVA increased from ~1.5 to 3 L/mg-m (Figure 3). The FI remained at ~1.6, which was lower than the influent FI (Figure 3). The EEMs acquired in the later pore volumes (e.g. day 56 and day 122 in Figure 4) also showed reduction in peak T and a much broader humic peak A.

DISCUSSION

Retention of selenium

It was anticipated that reducing conditions would result in removal of Se from solution due to microbial Se reduction.
to insoluble elemental Se and/or concurrent sulfate reduction and subsequent formation of Se sulfides (Siddique et al. 2007). However, observed Se retention was lower than expected (at 20% to 50%), with Se concentrations in the outflow reaching >50 μg/L (Figure 2), which exceeds KDHE acute and chronic limits (Table 1). After sectioning the columns, we did find accumulation of S and Se (Tables S14 and S15), which represents the portion of Se that was retained in the soil. Concurrent research on Se retention using diluted (1:1 with Kansas River water) FGD wastewater from JEC demonstrated that similar soils loaded with the more dilute influent solution were able to retain 100% of Se (Galkaduwa et al. 2017), due to microbial reduction of Se(VI) and Se(IV) to insoluble and immobile Se(0) (Siddique et al. 2007).

We hypothesize that the lower retention of Se observed in our study than in Galkaduwa et al. (2017) was due to the higher salinity of the undiluted wastewater, which may have adversely affected the microbial communities involved in Se reduction. Most Se reduction has been reported for freshwater systems, and several studies suggest that Se reduction is retarded under saline conditions. Deverel & Fujii (1998) found that the concentration of Se in groundwater increased as salinity increased in the shallow groundwaters near Kesterson Reservoir, CA, USA. Smedley et al. (2002) found similar results in La Pampa, Argentina, where the highest Se concentrations were found in the highest salinity shallow groundwater.

Galkaduwa et al. (2017) also found that high nitrate-N concentrations in their dilute FGD influent, similar to those of our study (~48 mg/L), were reduced to ~4 mg/L. By contrast, the hindered denitrification (outflow nitrate-N concentrations of ~12 mg/L) in our study may further support the negative impact of salinity on redox reactions. Evaluation of the changes in microbial community composition over time, which were not possible in this study, would be needed to demonstrate how increased salinity or ionic strength influences microbial processes that sequester trace elements under reducing conditions.

Sequestration of boron

Substantial B sequestration also occurred in all columns, although the control treatment with 2x flow rate did have breakthrough after longer operation of the column. Both Evans (1987) and Ye et al. (2003) suggested B removal can increase due to co-precipitation with calcium. However, in our study, Ca concentration in the outflow samples was observed to be up to three times greater than in the influent (Supplementary Tables S2–S6); therefore co-precipitation with Ca appears to be unlikely.

Generally, below pH 9.2, B mainly exists in soil solution as uncharged B(OH)3 with a small amount of borate anion. Due to this behavior, borate will have much stronger affinity towards soil particles compared to most other anions including sulfate. Sulfate ions are less strongly held and relatively more exchangeable compared to borate, selenite, and phosphate (Sposito 2008; Essington 2015). Indeed, in our study, the gradually increasing sulfate-S concentrations in the outflow support the higher mobility of sulfate compared to B. This behavior was also observed by Galkaduwa et al. (2017).

In addition, the high salinity of the FGD wastewater may have influenced B sequestration. Studies have shown that when the ionic strength of a solution increases, an increase of B adsorption occurs (Kister & Helvaci 1994; Türker et al. 2014). Sartaj & Fernandes (2005) explained this phenomenon with electrical double layer theory. The thickness of the charged layer on a soil surface decreases with increasing ionic strength of the solution (Türker et al. 2014) and promotes adsorption of B to soil particles. In experiments using diluted FGD wastewater with 50% lower salinity, Galkaduwa et al. (2017) found that the removal of B was indeed lower (from 68% to 82% of B was removed compared to >90% in our study). Therefore, high salinity may be an important factor in the retention of B in our study.

The control treatment with 2x flow rate did show breakthrough after ~13 PV. Boron concentrations for columns with the 1x flow rate are expected to follow similar trends to the control column with the 2x flow rate and reach a
relative concentration ~1.0 if the experiment continued. The results suggest that although sequestration of B was enhanced under saline conditions, high concentrations of sorbable anions will ultimately diminish B retention through saturation of adsorption/exchange sites.

**Mobilization of arsenic**

Another important finding was that the low-As native Kansas soils used to pack the columns were a source of arsenic to water under reducing conditions. Although the As concentration in the FGD wastewater was negligible (1.21 μg/L; Table 1) and soil As concentration was low compared to global averages, elevated As concentrations were observed in the outflow of all columns, including those with and without labile OC addition. The highest As concentrations, observed in columns with OC-amended FGD solution, exceeded the 150 μg/L chronic aquatic life limit for As set by KDHE. This finding suggests that reducing conditions are able to mobilize As even in soils with low As content. Arsenic mobilization has been observed from other reducing environments that were not previously known to leach As, such as wetland sediments under reducing conditions (Fox & Doner 2003; Eggert et al. 2008; Kropfelova et al. 2009).

The lowest overall As concentrations were observed in the outflow of column 1 (Figure 2(a)), which used a 2x flow rate, and reflect the shorter reaction time between constituents in the FGD wastewater and soil under higher flow rate conditions. By contrast, the slower 1x flow rate experiments allowed more time for reactions between labile OC, microbes, and soil, ultimately resulting in the release more As.

The highest As concentrations (up to 161 μg/L) in columns with OC-amended FGD wastewater are consistent with many other studies in which microorganisms oxidize labile OC as an electron donor and drive reactions that mobilize As under reducing conditions. For example, microorganisms can directly reduce As(V) to the more mobile As(III) form or indirectly mobilize As via the reductive dissolution of As-bearing minerals, such as poorly soluble Fe (hydr)oxides (Borch et al. 2010). Our solids analysis of column segments at the end of the study indicated that loss of As (Table S17) was accompanied by loss of Fe (Table S16). (Tables S16 and S17 are available with the online version of this paper.) Therefore, Fe reductive dissolution may be a mechanism for As release in this study.

Other ways in which As may have been released into solution are through (1) the microbial reduction of manganese minerals and subsequent liberation of As that may have been sorbed to those minerals or (2) direct microbial reduction of As(V) to the more mobile As(III) phase (Borch et al. 2010). Indeed, the high salinity of FGD wastewater may be beneficial to As-reducing microorganisms, which can survive under high salinity environments (Kulp et al. 2007). For future investigations, we recommend metal speciation analyses to better constrain the reasons for As mobilization from these native soils used for wetland construction.

**DOM optical properties and mobility**

The higher DOC concentration in column outflow than inflow of both control soil columns indicates DOC was leached from the soils. In columns with lactate amended FGD wastewater, low relative DOC concentrations <1.0 (Figure 3) suggest that, most likely, the labile OC was rapidly utilized by microorganisms in the sediments. The mineralization of OC is consistent with our interpretation of OC fueling Fe- or As-reducing bacteria and contributing to the mobilization of As from these soils.

Whereas labile DOM in column influent was removed, results from UV-vis absorbance and fluorescence analyses indicate that the chemical quality of DOM in the outflow was different than that of the influent DOM. The more humic and aromatic DOM of the outflow (compared to influent), which also contained lower amino acid-like fluorescence (peak T; Tables S2–S7) and a broader humic-like peak A, suggests that humic DOM was brought into solution from the soils. The increasingly humic (higher HIX) and aromatic (higher SUVA values) DOM character is consistent with the release of more aromatic and humified organic molecules from soils (Zsolnay et al. 1999).

One important observation is that column outflow of all treatments exhibited very similar changes in SUVA and fluorescence indices, even for those with and without addition of labile OC. This suggests that influent may already contain sufficient labile DOM to stimulate bacterial processes. The release of humic, sediment-derived DOM would then proceed as a result of microbially driven reductive dissolution, such as the reductive dissolution of Fe(III)- or Mn(IV)-containing minerals. Similar fluorescence characteristics to those in our study were previously observed in incubation experiments with As-containing sediments in Bangladesh, when sediment-derived DOM was released during reductive dissolution of Fe minerals (Mladenov et al. 2010).

**CONCLUSION**

Our results indicate that, although slow filtration through soils under reducing conditions enhanced the removal of
Se present in FGD wastewater, the retention was only half that of columns treating more dilute wastewater. Column outflow concentrations of Se did not meet KDHE standards for surface water quality. We hypothesize that the high salinity of FGD wastewater may inhibit biological Se reduction. By contrast, under the high salinity conditions of this study, B was almost completely retained in the soils. For treatment of FGD wastewater with SSF constructed wetland systems, we recommend dilution to eliminate or minimize the negative impacts of high salinity.

Our results also showed that both As and humic DOM were mobilized from the soil in all columns, suggesting that soil with low As content placed under reducing conditions represent an environment where the mobilization of As is possible. The occurrence of unexpected and extremely elevated outflow As concentrations in this study has important implications for treatment of high salinity wastewater with subsurface systems. In particular, the influence of the labile OC amendment on As mobilization from the soils is an important consideration for subsurface environments at risk of groundwater contamination by saline and OC-rich wastewater, such as FGD wastewater or production flowback water in hydraulic fracturing operations. Moreover, the unexpectedly high As concentrations that we observed in column outflow suggest that even soils containing background levels of As may represent As sources under reducing and high salinity and OC conditions.

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