

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). Selenium, B, and As, and dissolved organic carbon concentrations and organic matter spectroscopic properties were measured in 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/C_o) 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 (NO_3^-), selenium (Se), sulfate (SO_4^{2-}), and zinc (Zn) (Miezejewski, 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 and Murray-Gilde (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 et al., 2004).

Constructed wetland treatment systems (CWTs) 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; El-Sheikh et al., 2010; Vymazal, 2014). 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 and Patrick, 1993; Gambrell, 1994; Kadlec and 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 (Plant et al., 2003; Moore et al., 1988).

Subsurface flow constructed wetland treatment systems (SSF CWTs) 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 CWTs) (Eggert et al., 2008; Mooney and Murray-Gilde, 2008). Experiments with pilot FWS wetland cells shows that these can achieve highly reducing conditions, on the order of -400 mV (Sundberg-Jones and Hassan, 2007). The fate of Se and B has been experimentally evaluated in the field and laboratory, using FWS CWTs (Kropfelova et al., 2009). However, our knowledge of the behavior and transport characteristics of Se and B through SSF CWTs 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., 2003; 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 (Kaiser and Guggenberger, 2000; Lovley et al., 1996). 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 and Mulligan, 2006), but sulfate reduction can lead to the sequestration of both As (Hery et al., 2010; Lizama et al., 2011) and Se (Uhrie 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 be 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., 2001). 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 reflects 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 (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).

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.; column setup described in Supplementary Methods and shown in Figure 1) using the wet packing procedure described by Klute (1986). All columns were packed to a target bulk density of 1.17 g/cm³, and packing was done in eight 3.8-cm “lifts” to minimize variation in bulk density with depth. Prior to packing, soil in Treatment 1 (columns 3 and 4) was inoculated at ~0.5g for each 100 g of soil with soil slurry (Ivan, Kennebec, and Kahola silt loam), known to be rich in microbial consortia including sulfate reducing organisms (Karna et al., 2016). The soil slurry was obtained from creek sediments, located at the North Agronomy Farm at Kansas State University. The rationale for adding a soil slurry inoculum was that microbial limitation, if any, would be counteracted and enhanced biological processes would improve retention capacity of the columns.

To evaluate the addition of labile OC to stimulate microbial processes in CWTSSs, 2 L of raw undiluted FGD wastewater in Treatment 2 (columns 5 and 6) was amended with 1.92 g sodium lactate (Figure 1). The 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 hours 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 2X 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 2X 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 1X 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 hours. 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 analyses. All unfiltered/unacidified, filtered-only, and filtered/acidified samples were stored at 4°C until analysis.

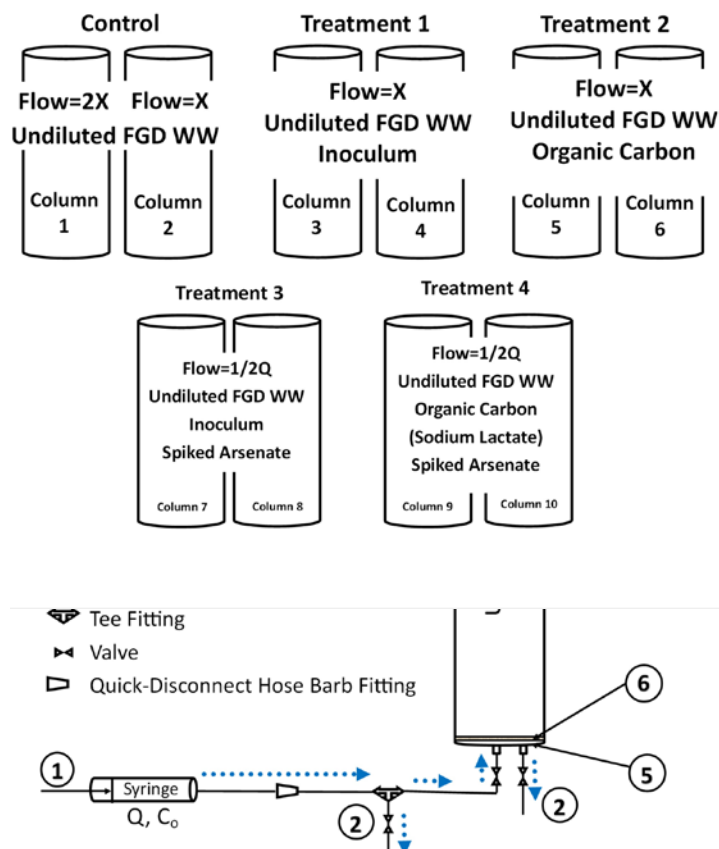


Figure 1. Schematic of column setup and 6 column treatments showing controls (columns 1 and 2) and treatments with microbial consortia inoculum (columns 3 and 4) and labile organic carbon addition (columns 5 and 6).

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 Bromocresol Green-Methyl Red indicators and for total hardness with EDTA (ethylenediaminetetraacetic 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 total dissolved solids (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 chromatograph (ICS-1000, Dionex Corporation) for the determination of anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , and SO_4^{2-}). 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 7500 series (Agilent Technologies, Santa Clara, CA) ICP-MS coupled with a dynamic reaction cell (ICP-MS-DRC). Environmental Calibration Standard 5183-4688 (Agilent Technologies, Santa Clara, CA) and multi-element Calibration Standard 8500-6942 (Agilent Technologies, Santa Clara, CA) 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) with a standard addition method to minimize matrix effects. Three micro-liters of 2000 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 minutes 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 $\approx$ 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 fluoresces and region B (ex 370 nm, em 304-312 nm) where tyrosine fluoresces. 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 and McKnight, 2005). The humification index (HIX), calculated as the ratio of peak area under the emission spectra at 435-480 nm to peak area from 300-345 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 420-435 nm obtained at an excitation wavelength of 310 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 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 $\mu\text{g/L}$) of the influent was below the US EPA maximum contaminant level for drinking water of 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ for Se and 952 mg/L for chloride) exceeded the Kansas Department of Health and the Environment (KDHE) limits (20 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. Other dissolved trace element concentrations of influent, reported by Westar Energy (unpublished), were 94.6 $\mu\text{g/L}$ Cr, 15.7 $\mu\text{g/L}$ Cu, and 8 $\mu\text{g/L}$ 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).

Table 1. Chemical composition (mean concentrations $\pm$ standard deviations) of flue gas desulfurization wastewater (FGD WW), organic carbon-amended FGD wastewater, and Kansas Department of Health and Environment Standards (KDHE STDs).

Parameter	Concentration		KDHE STDs		Units
	FGD WW	OC-amended FGD WW	Acute	Chronic	
Total alkalinity	840	NM			mg/L
Arsenic, Total	1.2 $\pm$ 0.70	1.2 $\pm$ 0.70	340	150	μ g/L
Boron, Total	5.3 $\pm$ 0.28	5.78 $\pm$ 0.33			mg/L
Bromide	22.0 $\pm$ 0.10	22.2 $\pm$ 0.10			mg/L
Calcium	610 $\pm$ 26.9	667 $\pm$ 48.8			mg/L
Chloride	952 $\pm$ 51.2	976 $\pm$ 25.7	860		mg/L
Conductivity	9.3 $\pm$ 0.11	9.7 $\pm$ 0.18			mS/cm
Total Hardness	380	NM			mg/L
Iron	UD	UD			mg/L
Magnesium	770 $\pm$ 29.4	849 $\pm$ 72.4			mg/L
Mercury [§]	3.2	NM			μ g/L
Nitrate-Nitrogen	48.3 $\pm$ 1.66	42.7 $\pm$ 0.7			mg/L
Nitrite	18.8	NM			mg/L
Nitrogen, Total	97.3 $\pm$ 0.50	100 $\pm$ 2.0			mg/L
Potassium	116 $\pm$ 4.09	120 $\pm$ 6.36			mg/L
pH	6.20 $\pm$ 0.13	6.95 $\pm$ 0.02			pH
Salinity	4.88	NM			ppt
Selenium	170 $\pm$ 7.1	181 $\pm$ 15	20	5	μ g/L
Sodium	727 $\pm$ 34.3	988 $\pm$ 70.0			mg/L
Sulfate-Sulfur	1340 $\pm$ 45.5	1380 $\pm$ 22.5			mg/L
Sulfur, Total	1780 $\pm$ 72.5	1970 $\pm$ 156			mg/L
Dissolve organic carbon	31.0 $\pm$ 0.43	291 $\pm$ 4.80			mg/L
Specific UV absorbance	2.40 $\pm$ 0.08	0.268 $\pm$ 0.008			(L/mg-m)
Humification index	9.4 $\pm$ 0.10	5.6 $\pm$ 0.41			dimensionless
Fluorescence index	1.63 $\pm$ 0.02	1.64 $\pm$ 0.001			dimensionless
Freshness index	0.74 $\pm$ 0.002	0.75 $\pm$ 0.001			dimensionless
Total dissolved solids	3650	NM			mg/L

UD = Undetectable (< 0.1); NM = Not Measured; ppt = parts per thousand

[§]Source: Galkaduwa, et al. (2017).

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 $\sim$ 2.5 mS/cm in the influent to $>$ 8 mS/cm in the outflow of all treatments (Tables S2 – S7). Sodium and chloride concentrations were initially low, but increased to $>$ 900 mg/L and $>$ 1100 mg/L, respectively by the last pore volume (Tables S2 – S7), which means that all columns reached relative concentrations of $\sim$ 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 2a), and by the end of the experiment, relative sulfate-S concentrations in all columns were > 1.0 (Figure 2b), supporting that SO₄ 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) 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 (Figures 2c and 2d), signifying strong B retention. Well over 90% of B was retained in the control column with 1X flow rate and in columns with inoculum and OC amended FGD wastewater. However, in the control column with the 2X 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 2d).

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 (Figures 2e and 2f). 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 2f). 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). 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 U.S. 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 1X flowrate (Figure 2). The column with the 2X flow rate had the lowest outflow As concentrations compared to columns with the 1X 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 1X flow rate (Figures 2g and 2h). Arsenic concentration peaked at approximately 4 pore volumes at a value of 161 µg/L (Figure 2g), 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).

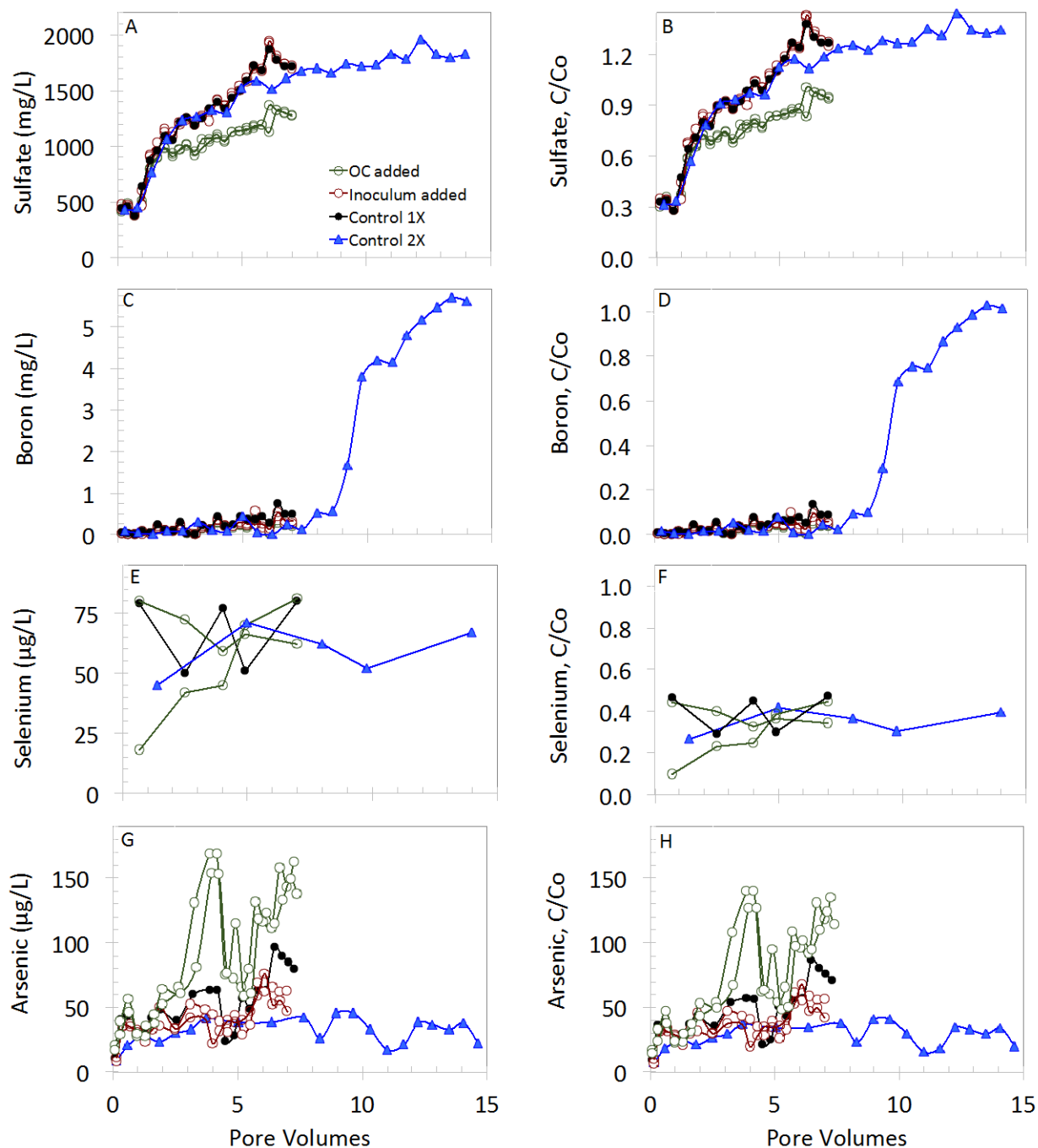


Figure 2. Temporal variation in concentration (left panels) and relative concentration (C/Co; right panels) of sulfate (A and B), boron (C and D), selenium (E and F), and arsenic (G and H) in column outflow, where X is the column flowrate (0.71 mL/h). Results of each duplicate experiment with inoculum added (red) and organic carbon added (dark green) are shown individually (rather than as averages).

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 1X and 2X 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 (Figures 3a and 3b), 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 3c) and low SUVA (Figure 3e). 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.

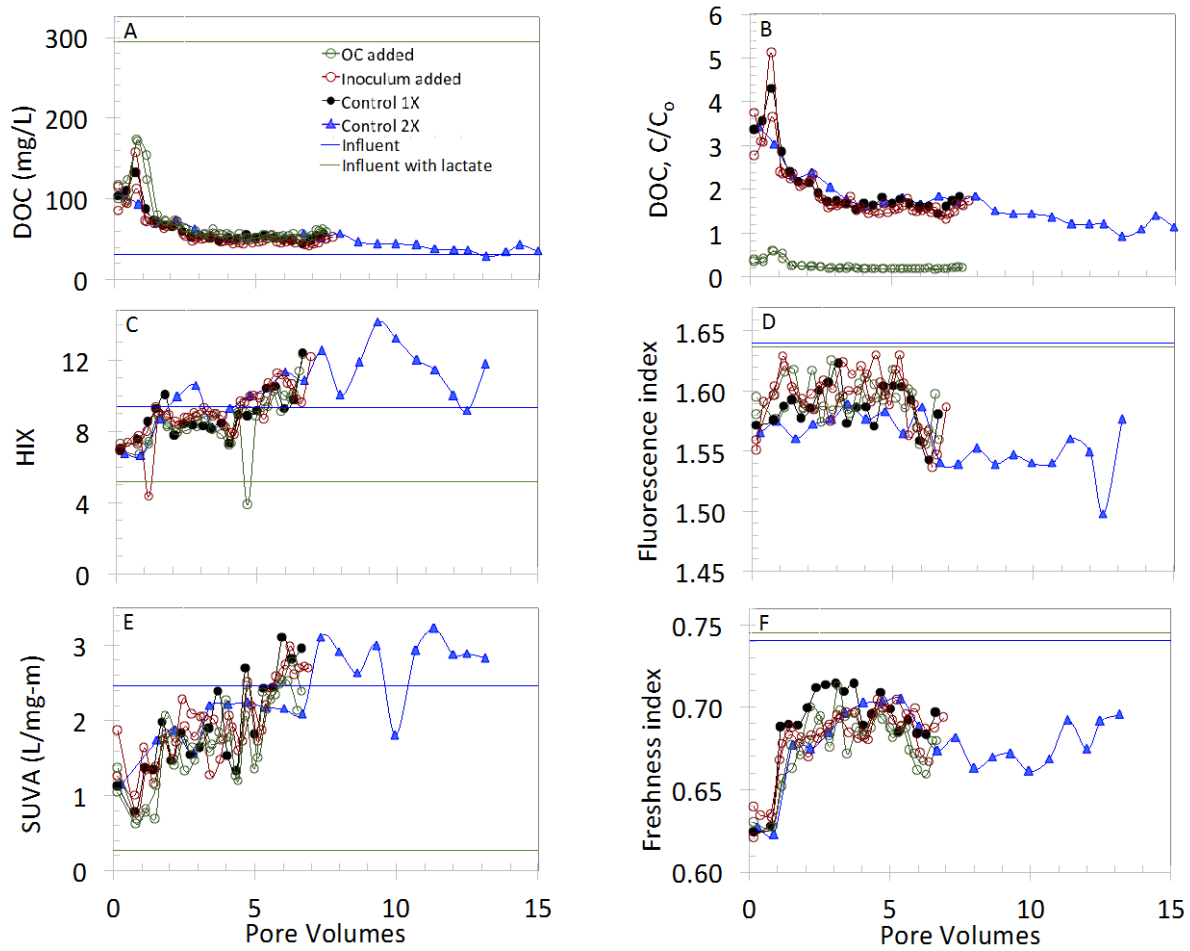


Figure 3. Temporal variation of dissolved organic carbon (DOC) concentration (A) and relative concentration (B), humification index (HIX) (C), freshness index (D), SUVA (E), and freshness index (F) in outflow of columns 1-6. Characteristics of the unamended (blue) and organic carbon-amended (green) influent are given with solid lines. Results of each duplicate experiment with inoculum added (red) and organic carbon added (dark green) are shown individually (rather than as averages).

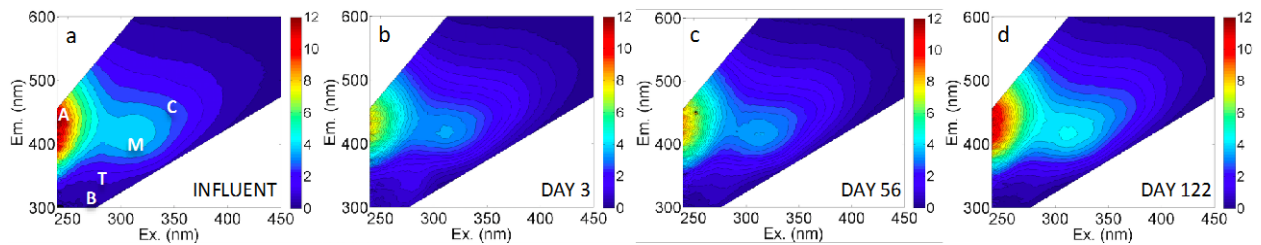


Figure 4. Representative excitation emission matrix spectra (EEMs) of influent (a) and outflow on day 3 (b), day 56 (c), and day 122 (d) from column 2 (control at the Q flowrate). The location of ubiquitous fluorescent dissolved organic matter peaks A, B, T, M, and C, described in the methods, are shown in panel (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 $> 50 \mu\text{g/L}$ (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 and Fujii (1998) found that the concentration of Se in groundwater increased as salinity increased in the shallow groundwaters near Kesterson Reservoir, CA. 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 ($\sim 48 \text{ mg/L}$), were reduced to $\sim 4 \text{ mg/L}$. By contrast, the hindered denitrification (outflow nitrate-N concentrations of $\sim 12 \text{ mg/L}$) 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 3 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)_3^0 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 (Essington, 2015; Sposito, 2008). 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 (Türker et al., 2014; Kistler and Helvacı, 1994). Sartaj and

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 and Doner, 2003; Eggert et al. 2008, Kropfelova et al., 2009).

The lowest overall As concentrations were observed in the outflow of column 1 (Figure 2a), 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). 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 dissolved organic matter 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 or 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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Supplementary Information

Supplementary Methods: Soil characteristics, column setup, quality control for dissolved constituents, sediment digestion.

Table S1: Chemical composition of soil samples utilized in the column experiment.

Tables S2–S7: Water quality results for columns 1–6.

Tables S8–S13: Statistical analysis to evaluate treatment type and time effects on total S, sulfate-S, B, As, DOC, and fluorescence indices.

Tables S14–S19: Soil analysis for elements S, Se, Fe, As, Mn, and Al for six sections in each of the columns 1–6.

Supplementary Methods

Soil characteristics. The soil was composed of 23% sand, 45% silt, and 32% clay and it was Clime (fine, mixed, active, mesic Udorthentic Haplustolls)-Sogn (Loamy, mixed, superactive, mesic Lithic Haplustolls) complex clay loam. The measured soil pH was 6.73 (1:1 soil:water). Total N and total C content in soil, measured using a Leco CN analyzer, were 0.28% and 3.98%, respectively.

Column setup. A precision constant-volume syringe pump (Legato 210 Syringe pump, KD Scientific Inc., USA) was used to deliver solution to each column at a constant flow rate (Figure 1). At the column entrance (Figure 1), a plate and filter (10 μ m) were fitted to help distribute inflowing wastewater solution over the entire soil surface. An end cap held the plate and filter in place and connected the columns to the syringe pump. Two sealable openings in the end cap were used to bleed entrapped air and solution at the column entrance. The column exit also was fitted with an end cap, plate, and filter. An opening in the end cap funneled column outflow freely to a vial where the effluent was collected.

Quality control for analyses of dissolved constituents. For ICP-OES, the repeatability of duplicate analysis of randomly selected samples ranged from 96.3% to 108.8%. Blanks (acidified Milli-Q water only), spikes with the multi-element standard, and NIST 1643e “Trace Elements in Water” SRM were analyzed. Recovery was between 84.0% and 99.4% for the NIST sample and between 87.2% and 123.5% for the spike. For ICP-MS-DRC, an internal standard solution 5188-6525 (Agilent Technologies, Santa Clara, CA, USA) was analyzed for quality control.

Quality control for GF-AAS consisted of running blanks, spikes, and a NIST standard for trace elements in waters (SRM 1643e). Between 99% and 112% As recovery was achieved for the NIST sample. The spiked recoveries were in the range of 97–108%. For IC analyses, recoveries were 88.1–101.3% for spikes and (81.8–108.6%) for duplicates. For DOC and TDN analyses, measurements were made in triplicate for each sample and coefficients of variation did not exceed 2%. Random duplicate samples were included in each run for quality control.

Sediment digestion. For digestion of soils, 10 mL of trace metal-grade concentrated HNO₃ acid was added to 0.5 g of soil and digested in a microwave digestion unit (MARSPress, CEM Corp.). A standard reference soil (NIST 2711a-Montana II) and a blank (concentrated HNO₃ acid) were included for QA/QC. All soil samples were digested in duplicate. In the first stage of the temperature program, the temperature in the soil-acid mixture was increased to 165°C within 5.5 min. In the second stage, the temperature was raised to 175°C in 4.5 min and then maintained at that temperature for an additional 5 min. The digest (soil-acid mixture) was filtered using Whatman No. 42 filter papers.

Table S2. Chemical composition of soil samples utilized in the column experiment

Constituent	Concentration (mg/kg)
Arsenic	3.8
Aluminum	24,000
Boron	UD
Iron	21,500
Manganese	419
Silicon	UD
Selenium	0.327
Sulfur	1,340
UD = Undetectable (< 0.1 mg/kg).	

Table S2. Water quality results* for Column 1: Control at flowrate, 2X

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.3	7.81	2.77	0.083	17.33	5.59	29.24	944.49	509.23	4.36	14.39	427.75	8.37	104.70	14.31	1.64	0.74	9.34	14.90	1.22	2.31	6.22	9.11
8	0.9	-	3.31	0.034	16.82	0.77	118.69	951.18	511.02	1.77	14.77	453.48	20.46	92.48	24.52	1.57	0.63	6.76	10.88	1.99	2.76	5.05	6.77
14	1.5	7.61	6.20	0.009	25.15	0.51	27.79	1698.39	1126.42	940.84	13.71	766.46	27.89	70.20	61.48	1.57	0.62	6.63	11.51	2.31	2.87	5.11	7.14
20	2.2	-	7.81	0.087	24.27	0.36	535.28	1783.27	1582.93	977.58	82.19	1065.99	23.36	72.38	71.68	1.56	0.68	8.67	13.88	1.77	2.49	7.24	8.64
26	2.8	7.48	8.38	0.08	24.43	0.24	732.54	1498.91	1521.84	1039.57	12.40	1236.23	29.89	62.84	84.72	1.57	0.67	9.95	16.46	1.74	2.50	7.30	9.74
32	3.4	-	8.25	0.303	24.98	0.24	628.76	889.58	991.33	1045.40	48.80	1263.07	32.88	53.96	76.78	1.58	0.68	10.55	18.16	1.69	2.64	7.79	10.65
38	4.1	7.45	8.36	0.112	27.17	0.25	766.05	1132.08	1263.30	1064.00	49.00	1319.80	41.38	49.86	80.48	1.59	0.70	8.21	20.72	2.86	3.76	9.39	12.63
44	4.7	-	7.03	0.084	28.37	0.18	995.87	1641.00	1731.16	964.00	48.20	1306.20		51.76	80.68	1.58	0.70	9.25	23.32	2.42	3.81	10.29	13.85
50	5.4	7.48	8.65	0.436	26.27	0.18	751.19	922.97	1289.65	1067.00	49.37	1526.01	38.20	55.62	91.64	1.58	0.70	9.96	18.24	1.75	2.91	8.13	10.92
56	6.0	-	9.18	0.052	28.36	0.04	632.24	803.99	1266.33	1122.64	48.20	1589.87		50.72	84.46	1.56	0.71	10.47	14.21	1.32	2.05	6.37	8.26
62	6.7	7.76	9.17	0.004	26.72	0.13	816.50	1125.25	1891.95	1006.17	47.95	1516.56	38.49	55.82	86.52	1.59	0.69	11.30	14.78	1.15	1.94	6.23	8.46
68	7.3	-	9.31	0.236	27.08	0.07	768.93	910.62	1760.58	1062.26	45.73	1607.69		52.80	78.98	1.54	0.67	10.87	21.65	1.70	2.80	8.73	11.63
74	8.0	7.61	9.26	0.13	26.73	0.07	771.45	799.54	1737.83	1089.63	47.54	1678.88	42.30	56.18	74.08	1.54	0.68	12.51	24.15	1.54	2.97	9.93	13.02
80	8.6	7.73	9.49	0.52	31	0	760.04	795.00	1853.73	1143.60	59.20	1700.93	25.68	45.93	68.80	1.55	0.66	10.02	34.15	2.72	4.54	13.33	18.75
86	9.3	7.76	9.63	0.555	32.59	0	787.23	795.96	2005.48	1102.40	52.40	1660.00	45.42	44.07	72.00	1.54	0.67	11.87	20.01	1.32	2.50	8.81	10.41
92	10.0	7.92	9.32	1.656	34.93	0	828.29	818.98	2144.78	1157.20	38.00	1739.73	45.51	43.83	79.52	1.55	0.67	14.13	21.40	1.41	2.47	9.38	10.70
98	10.7	-	9.17	3.809	34.66	0	787.93	757.82	1956.25	1148.90	42.41	1717.55	33.00	42.19	84.77	1.54	0.66	13.18	11.91	0.76	1.32	4.75	6.34
104	11.3	-	9.29	4.189	33.8	0.00	783.29	753.11	1983.09	1146.38	53.58	1727.51	17.13	36.85	89.48	1.54	0.67	12.00	20.71	1.52	2.66	8.51	11.22
110	12.0	-	9.32	4.151	32.65	0	777.70	740.04	1981.08	1189.23	38.08	1830.50	20.88	36.66	92.88	1.56	0.69	11.43	14.40	1.06	1.92	6.04	7.91
116	12.5	-	9.79	4.80	36.16	0.75	845.96	808.62	2101.31	1166.56	40.26	1780.88	38.32	36.59	87.63	1.55	0.67	10.00	13.66	1.03	1.90	5.23	7.48
122	13.2	-	9.49	5.17	38.63	3.21	925.32	828.65	2206.91	1259.92	23.52	1955.31	36.70	28.28	90.87	1.50	0.69	9.11	14.34	1.11	2.21	5.53	8.04
128	13.8	-	9.70	5.46	35.55	5.22	872.75	801.68	2142.60	1152.50	34.99	1824.47	32.62	33.07	83.98	1.58	0.70	11.75	11.29	0.79	1.42	4.84	6.22
134	14.3	-	9.85	5.70	38.65	0.00	865.37	805.47	2127.01	1119.31	56.91	1797.93	37.87	42.43	74.06	-	-	-	-	-	-	-	-
140	15.0	7.45	9.17	5.62	40.07	0	904.86	835.04	2226.80	1147.37	35.95	1825.62	21.94	34.39	75.26	-	-	-	-	-	-	-	-

*All units in mg/L except As (µg/L), EC (mS/cm), and all peaks (Raman units, R.U.). Values for FI, FRI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Table S3. Water quality results* for Column 2: Control at flowrate, X

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	7.61	2.66	0.046	17.11	7.39	27.93	875.85	500.53	4.07	13.95	444.73	10.50	103.14	14.90	1.57	0.62	6.97	11.23	2.13	2.57	4.97	6.92
8	0.4	-	2.22	0.015	16.37	8.17	35.57	681.33	363.81	4.17	14.82	458.35	40.76	108.98	14.60	-	-	-	-	-	-	-	-
14	0.8	7.66	3.06	0.005	16.61	1.15	17.97	901.34	467.34	249.14	13.43	375.09	43.36	132.08	30.96	1.58	0.63	7.55	12.33	2.05	2.48	5.46	7.61
20	1.1	-	5.35	0.093	23.23	0.37	17.05	1800.89	1025.11	764.34	14.98	638.73	28.50	87.16	55.16	1.59	0.69	8.51	13.49	1.82	2.43	6.32	8.29
26	1.4	7.72	6.07	0.05	22.87	0.29	91.06	1869.32	1169.22	950.96	13.49	866.89	33.24	73.30	69.66	1.59	0.69	9.22	18.16	2.36	3.18	8.13	11.26
32	1.7	-	7.31	0.241	24.6	0.14	238.97	1287.90	915.26	1026.00	46.80	961.00	41.63	66.00	70.98	1.58	0.69	10.04	21.71	2.08	3.43	9.64	12.79
38	2.1	7.37	7.63	0.106	26.71	0.15	450.03	1528.71	1190.58	1053.40	100.2	1085.00	48.48	65.14	91.60	1.59	0.70	7.78	18.91	2.58	3.41	8.61	10.85
44	2.4	-	7.18	0.088	27.59	0.14	585.04	1638.72	1412.28	994.00	57.60	1052.13	-	58.30	78.30	1.60	0.71	8.38	16.62	2.04	2.90	7.58	10.15
50	2.7	7.75	7.55	0.304	23.59	0.14	689.11	1349.41	1265.78	1105.30	52.44	1212.54	40.09	52.28	82.04	1.61	0.71	8.35	9.36	1.22	1.65	4.33	5.77
56	3.1	-	7.83	0.033	24.82	0.01	629.72	1384.17	1253.56	1126.34	51.64	1253.33	-	53.24	80.86	1.62	0.71	8.30	11.77	1.39	2.06	5.26	7.16
62	3.4	7.67	7.89	0	18.77	0.02	771.12	1311.81	1259.86	1053.90	50.75	1186.07	60.10	51.48	82.88	1.57	0.71	8.15	17.43	2.01	2.86	7.61	10.23
68	3.7	-	6.62	0.21	27.5	0	813.48	1562.71	1443.09	1068.91	51.04	1250.25	-	47.08	73.70	1.59	0.71	8.44	13.55	1.59	2.37	6.00	8.17
74	4.0	7.54	8.31	0.134	28.46	0.03	774.93	1559.23	1402.16	1096.46	47.04	1337.62	63.75	51.14	56.84	1.59	0.69	7.32	17.23	2.18	3.15	7.56	10.19
80	4.4	7.56	7.78	0.435	31.5	0	750.61	862.76	823.17	1140.80	49.20	1395.33	63.62	49.55	30.87	1.57	0.70	8.91	10.16	1.07	1.69	4.43	5.97
86	4.7	7.67	6.89	0.206	32.38	0	771.33	986.27	968.44	984.40	49.20	1334.80	23.81	55.08	31.37	1.60	0.71	8.87	19.57	2.35	3.38	8.61	11.57
92	5.0	7.67	6.88	0.239	33.05	0	753.60	966.53	1095.39	1141.60	36.40	1433.87	28.38	51.37	31.48	1.60	0.70	9.14	13.50	1.44	2.11	5.77	7.75
98	5.3	-	8.73	0.423	32.97	0	784.23	860.77	1067.81	1138.60	40.62	1495.90	57.06	53.99	32.26	1.60	0.69	10.37	20.97	2.05	3.23	8.89	11.98
104	5.7	-	8.73	0.359	31.31	0	783.78	856.13	1181.81	1149.91	48.14	1587.76	48.92	51.19	33.47	1.59	0.69	10.52	18.07	1.64	2.61	7.59	10.12
110	6.0	-	8.85	0.36	32.21	0	773.40	1480.18	1829.56	1170.49	43.64	1720.49	63.72	49.21	38.60	1.56	0.68	9.22	18.11	1.33	2.70	7.05	9.90
116	6.3	-	9.39	0.437	33.60	0	719.80	743.90	1261.72	1127.27	36.04	1684.73	63.72	48.91	43.76	1.54	0.68	9.78	18.62	1.37	2.66	7.00	10.13
122	6.6	-	9.23	0.290	34.77	0	903.42	717.77	1508.27	1251.34	25.06	1867.69	96.58	43.74	44.28	1.58	0.70	12.39	17.15	1.23	1.99	7.00	9.15
128	6.9	-	9.32	0.765	34.21	0	686.36	694.37	1347.86	1146.68	25.06	1771.88	90.10	49.29	47.31	-	-	-	-	-	-	-	-
134	7.2	-	8.96	0.491	37.49	0	874.91	1000.58	1816.28	1117.18	44.50	1715.43	85.12	53.35	46.37	-	-	-	-	-	-	-	-
140	7.4	7.77	8.74	0.501	39.93	0	841.29	947.89	1873.23	1169.86	58.43	1717.82	79.78	55.83	48.98	-	-	-	-	-	-	-	-

*All units in mg/L except As (µg/L), EC (mS/cm), and all peaks (Raman units, R.U.). Values for FI, FRI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Table S4. Water quality results* for Column 3: Inoculum-amended soil

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	7.61	2.80	0.028	17.17	6.85	40.13	749.99	442.69	3.81	13.82	475.09	7.62	114.70	14.28	1.56	0.62	7.02	11.93	2.00	2.45	5.23	7.14
8	0.5	-	2.25	0.01	15.8	6.2	21.34	692.53	357.96	4.93	13.03	458.67	35.41	94.22	14.34	-	-	-	-	-	-	-	-
14	0.8	7.70	2.93	0.003	16.72	1.32	24.12	927.50	460.99	258.67	13.09	381.33	37.28	111.92	26.98	1.60	0.63	7.69	13.40	2.28	2.62	6.06	8.56
20	1.2	-	5.37	0.005	18.96	0.33	13.02	1610.26	1008.93	901.66	14.19	603.32	30.55	71.58	60.04	1.62	0.68	4.31	13.72	5.77	3.40	6.36	8.69
26	1.5	7.72	5.55	0.03	25.29	0.26	41.86	1758.59	1174.78	1037.50	13.09	908.17	23.07	71.98	69.62	1.60	0.69	9.03	16.11	2.11	2.70	7.29	10.09
32	1.9	-	7.36	0.201	24.41	0.17	260.71	1526.15	1084.20	981.20	46.00	948.40	36.15	64.52	75.40	1.59	0.68	8.91	20.79	2.54	3.49	9.27	12.76
38	2.2	7.49	7.74	0.102	26.78	0.17	513.96	1592.67	1310.62	1047.00	94.80	1126.27	35.59	71.36	86.30	1.58	0.68	8.35	22.14	2.56	3.78	10.40	13.42
44	2.5	-	7.75	0.089	27.76	0.17	668.14	1638.47	1451.57	991.80	54.00	1087.80		53.94	78.76	1.61	0.68	8.73	20.77	2.42	3.43	9.40	12.73
50	2.9	7.81	7.44	0.239	24.84	0.17	716.55	1358.34	1262.76	1078.79	51.98	1190.92	32.90	49.76	84.64	1.60	0.69	8.79	12.68	1.47	2.14	5.73	7.86
56	3.2	-	6.71	0.049	27.56	0.03	793.24	1654.96	1515.49	1100.40	49.36	1240.45		50.88	76.82	1.62	0.69	9.12	15.27	1.82	2.48	6.87	9.46
62	3.6	7.59	7.47	0	25.88	0.03	837.86	1363.20	1316.86	1069.76	56.18	1188.46	52.06	56.12	87.20	1.61	0.68	8.96	13.66	1.61	2.16	5.81	8.15
68	3.9	-	7.26	0.195	28.31	0.03	804.41	1527.05	1406.25	1105.03	49.81	1257.00		47.98	80.72	1.62	0.68	8.20	10.82	1.25	1.87	4.75	6.58
74	4.2	7.55	8.24	0.133	27.51	0.04	698.13	1455.51	1300.71	1134.63	54.93	1321.00	48.27	43.86	71.12	1.59	0.68	7.80	21.24	2.67	3.63	9.37	12.93
80	4.6	7.62	8.28	0.373	29.73	0	755.04	1290.39	1159.54	1141.60	36.40	1411.60	45.08	43.64	44.83	1.61	0.70	9.61	11.24	1.14	1.78	4.92	6.75
86	4.9	7.51	7.92	0.214	30.52	0	600.64	1166.17	1017.76	1111.20	54.80	1365.07	38.89	44.89	29.19	1.59	0.70	9.97	17.47	2.00	2.72	7.70	10.30
92	5.3	7.61	6.94	0.203	32.4	0	808.32	1197.00	1275.10	1147.20	56.00	1450.00	31.06	47.42	28.09	1.63	0.70	8.66	11.66	1.23	1.87	4.98	6.79
98	5.6	-	8.54	0.302	30.46	0	781.81	854.85	1043.81	1141.38	58.02	1499.07	44.05	54.89	31.29	1.56	0.70	10.50	19.84	1.73	2.90	8.43	11.16
104	5.9	-	8.62	0.254	31.39	0	775.24	1002.66	1280.11	1144.84	45.21	1575.57	28.82	45.12	30.15	1.57	0.70	11.16	16.77	1.37	2.29	7.08	9.39
110	6.2	-	8.90	0.243	32.54	0	760.79	910.66	1330.81	1164.12	43.07	1698.66	36.70	47.89	38.13	1.57	0.69	10.64	17.39	1.20	2.46	6.67	9.53
116	6.6	-	7.73	0.254	34.35	0	877.61	746.90	1384.16	1121.73	35.29	1691.66	68.82	48.27	38.88	1.55	0.69	9.57	17.35	1.21	2.52	6.55	9.51
122	6.9	-	9.29	0.144	35.55	0	945.02	735.46	1516.60	1242.20	23.93	1944.58	62.06	40.64	35.69	1.59	0.69	12.19	15.78	1.07	1.87	6.47	8.39
128	7.2	-	9.09	0.532	36.45	0	838.18	759.11	1530.39	1130.77	39.98	1781.13	65.78	45.29	41.55	-	-	-	-	-	-	-	-
134	7.5	-	9.09	0.332	39.64	0	845.61	855.41	1651.45	1000.40	37.21	1740.43	62.21	50.26	44.79	-	-	-	-	-	-	-	-
140	7.7	7.73	8.42	0.331	41.04	0	818.71	1031.76	1773.98	1131.95	38.74	1697.93	63.07	52.97	48.81	-	-	-	-	-	-	-	-

*All units in mg/L except As (µg/L), EC (mS/cm), and all peaks (Raman units, R.U.). Values for FI, FRI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Table S5. Water quality results* for Column 4: Inoculum-amended soil

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	7.75	2.52	0.021	17.36	5.97	30.99	781.58	442.70	3.54	15.15	432.62	11.06	84.84	14.07	1.55	0.64	6.91	12.27	2.23	2.91	5.46	7.27
8	0.4	-	2.54	0.011	16.18	5.52	20.62	702.86	381.47	3.58	13.70	471.18	35.20	94.80	14.31	1.59	0.63	7.34	11.68	2.16	2.66	5.31	7.21
14	0.8	7.75	2.72	0.005	16.17	2.42	14.56	912.57	444.14	193.50	13.18	395.72	34.96	156.90	21.30	1.60	0.64	7.26	13.70	2.45	2.87	6.29	8.47
20	1.1	-	5.06	0.081	18.26	0.31	9.84	1370.36	812.19	893.61	13.67	467.71	32.00	72.98	58.20	1.63	0.67	7.97	11.86	1.90	2.24	5.59	7.65
26	1.4	7.74	5.41	0.02	24.62	0.23	14.51	2055.99	1366.93	1044.03	13.31	920.52	30.25	68.32	69.02	1.60	0.68	9.38	18.25	2.23	3.07	8.27	11.63
32	1.8	-	7.59	0.174	23.89	0.18	211.87	1562.00	1124.70	1050.40	46.20	1030.13	33.06	63.04	73.40	1.59	0.68	8.86	20.97	2.53	3.45	9.39	12.91
38	2.1	7.41	7.46	0.099	25.94	0.19	498.10	1442.51	1126.58	1049.20	117.20	1150.53	50.49	66.54	92.14	1.60	0.67	8.49	24.14	2.99	3.96	10.65	14.65
44	2.4	-	6.80	0.087	27.21	0.13	647.53	1641.48	1488.67	991.20	56.80	1124.73	-	55.36	79.84	1.60	0.68	8.75	18.01	2.15	2.96	8.24	11.25
50	2.8	7.66	7.77	0.19	25.19	0.13	717.59	1221.43	1169.69	1084.37	53.95	1212.91	33.50	47.92	86.00	1.57	0.69	9.03	10.67	1.28	1.74	4.82	6.66
56	3.1	-	6.70	0.043	27.18	0.02	792.41	1268.17	1241.65	1129.66	50.50	1251.80	-	49.40	86.98	1.59	0.69	9.29	19.27	2.00	3.11	8.51	11.64
62	3.4	7.57	8.01	0	26.46	0.07	710.23	1307.42	1259.26	1023.15	48.56	1193.43	41.95	51.42	91.90	1.60	0.70	8.85	11.96	1.23	2.05	5.28	7.32
68	3.8	-	6.82	0.175	26.81	0.02	635.40	1337.42	1221.47	1088.50	49.44	1270.14	-	46.30	87.64	1.60	0.70	8.85	11.96	1.23	2.05	5.28	7.32
74	4.1	7.56	8.53	0.129	28.17	0.04	714.72	1528.90	1380.11	1075.73	54.95	1226.33	41.05	47.00	74.80	1.61	0.68	7.90	20.76	2.57	3.71	9.15	12.61
80	4.4	7.62	8.55	0.34	30.32	0	757.26	1069.64	1007.06	1142.00	35.60	1420.40	22.01	45.50	55.56	1.63	0.70	9.64	12.85	1.37	2.10	5.72	7.90
86	4.8	7.61	7.03	0.201	31.36	0	782.78	1312.83	1224.82	1104.80	56.40	1368.93	31.23	51.00	39.07	1.60	0.70	9.92	17.09	1.90	2.68	7.57	10.24
92	5.1	7.60	6.99	0.194	32.27	0	787.94	1143.74	1241.05	1149.60	62.40	1471.87	39.59	46.65	32.78	1.62	0.69	9.85	12.77	1.28	1.89	5.40	7.44
98	5.4	-	8.66	0.265	31.65	0	785.44	878.90	1072.44	1142.41	40.58	1536.24	38.34	49.45	31.49	1.61	0.69	10.70	20.26	1.72	2.90	8.58	11.61
104	5.7	-	8.53	0.216	30.1	0	817.53	889.31	1254.48	1137.51	38.69	1613.62	40.16	46.34	32.98	1.59	0.69	11.24	17.76	1.53	2.37	7.52	10.10
110	6.1	-	8.97	0.571	31.8	0	768.09	919.44	1334.29	1153.10	42.98	1711.84	46.61	46.04	34.32	1.56	0.67	10.68	18.51	1.13	2.50	7.03	10.08
116	6.4	-	9.42	0.169	32.31	0	876.43	763.03	1444.96	1124.72	41.54	1675.88	59.05	44.54	37.00	1.54	0.67	9.74	16.12	1.09	2.27	5.89	8.65
122	6.7	-	9.33	0.088	33.61	0	916.35	748.29	1545.33	1262.62	22.17	1927.26	76.08	42.61	34.88	1.57	0.68	12.92	15.74	1.02	1.73	6.36	8.43
128	7.0	-	9.28	0.428	38.52	0	855.52	1010.65	1775.96	1150.32	38.54	1809.61	52.08	44.13	39.89	-	-	-	-	-	-	-	-
134	7.3	-	9.12	0.268	36.12	0	847.77	843.78	1696.74	1125.38	47.79	1741.69	55.46	50.83	41.81	-	-	-	-	-	-	-	-
140	7.5	7.77	8.81	0.261	36.52	0	857.00	990.17	1893.67	1144.16	48.10	1726.55	46.85	49.67	42.22	-	-	-	-	-	-	-	-

**All units in mg/L except As ($\mu\text{g/L}$), EC (mS/cm), and all peaks (Raman units, R.U.). Values for FI, FrI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	7.62	2.66	0.02	17.24	9.6	27.80	732.71	435.91	3.73	13.63	429.30	20.56	99.76	14.34	1.58	0.63	7.30	12.14	2.09	2.48	5.36	7.30
8	0.5	-	2.55	0.008	15.93	3.82	23.72	813.88	413.85	3.72	13.63	456.11	39.47	97.60	13.73	-	-	-	-	-	-	-	-
14	0.8	7.62	3.05	0.005	16.45	0.95	15.29	930.03	441.25	226.83	12.97	382.21	56.28	173.38	23.12	1.60	0.63	7.34	14.35	2.53	2.97	6.40	8.94
20	1.2	-	5.18	0.076	17.89	0.28	13.25	1376.98	753.02	936.10	13.32	477.01	27.56	122.92	59.90	1.62	0.65	7.41	11.98	2.21	2.46	5.49	7.71
26	1.5	7.80	5.84	0.02	20.86	0.41	18.86	1625.52	991.12	998.44	13.85	798.65	27.68	71.40	66.44	1.62	0.68	8.98	14.86	1.92	2.70	6.81	9.65
32	1.8	-	7.24	0.156	24.29	0.17	259.04	1802.79	1195.66	1093.00	46.40	905.87	38.12	73.10	70.32	1.59	0.67	8.20	24.13	3.34	4.30	10.70	15.04
38	2.2	7.43	7.21	0.099	25.55	0.17	604.55	1595.97	1220.31	1098.60	108.60	979.73	52.50	67.46	89.14	1.62	0.68	8.05	25.84	3.42	4.49	11.54	15.77
44	2.5	-	7.38	0.087	26.55	0.18	785.92	1369.83	1213.91	983.60	54.00	907.80	-	64.30	76.26	1.57	0.69	8.42	14.11	1.76	2.44	6.31	8.65
50	2.8	7.72	7.07	0.158	26.19	0.18	868.32	1220.34	1167.16	1079.22	49.05	975.14	65.34	55.22	78.24	1.63	0.68	8.83	9.75	1.24	1.68	4.37	6.12
56	3.2	-	6.37	0.043	28.82	0.04	982.34	1369.36	1270.43	1115.92	51.23	1012.52	-	55.04	70.40	1.59	0.71	8.70	13.68	1.74	2.31	6.15	8.49
62	3.4	7.86	5.86	0	21.89	0.05	1020.20	1369.32	1250.30	1019.02	47.18	951.41	130.84	54.32	58.92	1.58	0.69	8.13	17.26	2.10	3.03	7.59	10.66
68	3.7	-	6.67	0.164	29.08	0.04	916.43	1229.53	1061.36	1065.58	47.18	1065.35	-	56.00	34.80	1.59	0.70	7.79	13.81	1.64	2.46	6.10	8.54
74	4.0	7.60	7.75	0.125	28.33	0.08	976.20	1306.05	1123.63	1098.81	46.58	1066.76	168.83	55.68	29.22	1.61	0.68	7.18	22.78	2.95	4.11	10.00	14.04
80	4.3	7.59	6.42	0.312	33.73	0	984.85	1241.89	1040.84	1154.40	50.80	1106.53	168.87	50.60	31.50	1.61	0.69	9.00	10.84	1.34	1.93	4.79	6.72
86	4.7	7.65	6.14	0.199	33.43	0	746.00	1169.84	988.22	1074.80	36.00	1040.13	75.49	24.64	18.37	1.59	0.70	3.85	17.06	8.44	4.43	7.73	10.66
92	5.0	7.61	6.32	0.185	34.02	0	951.42	1086.72	1097.88	1119.20	36.00	1127.87	72.46	51.30	34.38	1.62	0.69	8.84	12.86	1.42	2.09	5.67	8.01
98	5.3	-	6.60	0.24	32.31	0	963.45	1228.36	1194.17	1115.95	53.42	1139.62	65.28	54.65	35.88	1.61	0.68	9.62	20.08	2.05	3.16	8.68	11.90
104	5.6	-	6.40	0.194	33.03	0	955.49	1065.49	1154.55	999.90	38.97	1145.72	79.16	53.52	36.02	1.60	0.69	10.23	19.23	1.91	2.75	8.27	11.45
110	5.9	-	6.44	0.447	32.16	0	919.58	1093.99	1186.12	1012.17	38.97	1185.64	131.52	52.87	33.51	1.57	0.67	9.07	17.05	1.57	2.63	6.81	10.08
116	6.2	-	8.87	0.114	34.17	0	1068.47	1349.67	1435.23	1113.75	38.96	1194.66	116.19	53.54	35.54	1.56	0.67	9.86	20.31	1.41	2.93	7.86	11.53
122	6.5	-	8.22	0.049	32.87	0	1139.96	1323.71	1560.89	1246.39	22.42	1369.67	111.64	48.47	35.00	1.60	0.68	11.35	16.05	1.37	2.14	6.88	9.29
128	6.9	-	8.40	0.341	31.12	0	1042.47	1078.28	1428.98	1014.04	36.68	1323.71	157.99	51.84	37.20	-	-	-	-	-	-	-	-
134	7.1	-	8.42	0.234	34.25	0	1047.12	987.82	1507.29	1118.81	55.65	1306.57	143.24	61.10	38.30	-	-	-	-	-	-	-	-
140	7.4	7.81	8.72	0.228	34.01	0	1039.96	919.87	1436.81	1009.69	55.65	1269.52	163.04	62.99	38.05	-	-	-	-	-	-	-	-

Table S6. Water quality results* for Column 5: Organic carbon-amended wastewater

*All units in mg/L except As ($\mu\text{g/L}$), EC (mS/cm), and all peaks (Raman units, R.U.). Values for FI, FRI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Table S7. Water quality results* for Column 6: Organic carbon-amended wastewater

Day	PV	pH	EC	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate-S	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	7.58	2.81	0.019	17.3	7.69	27.13	775.14	445.43	3.90	12.70	409.07	17.04	116.50	15.61	1.60	0.62	6.90	11.13	2.12	2.67	4.97	6.77
8	0.5	-	2.90	0.007	16.01	9.7	12.38	463.89	242.31	3.79	12.70	482.01	28.77	123.54	15.45	-	-	-	-	-	-	-	-
14	0.8	7.68	2.90	0.001	16.7	1.41	16.07	936.50	439.29	218.36	12.70	386.04	45.79	171.24	24.62	1.58	0.63	6.66	12.87	2.62	3.04	5.59	7.75
20	1.2	-	5.17	0.074	19.71	0.32	44.37	1216.09	595.49	904.12	12.70	505.77	29.12	153.22	59.68	1.59	0.66	7.23	14.01	2.60	3.04	6.39	8.88
26	1.5	7.62	5.92	0.02	20.36	0.24	17.71	1505.53	909.88	1045.50	12.70	789.92	36.00	80.72	61.43	1.59	0.66	8.83	11.07	1.54	1.95	4.93	6.88
32	1.8	-	7.22	0.148	24.06	0.17	261.04	1476.88	1015.65	1061.20	46.00	894.73	44.59	71.36	68.84	1.59	0.68	8.31	22.26	3.11	4.03	9.98	13.76
38	2.2	7.53	7.02	0.095	26.16	0.19	632.26	1533.78	1233.75	1089.40	114.60	988.27	64.10	72.86	85.02	1.58	0.70	7.91	19.68	2.58	3.54	8.82	12.00
44	2.5	-	6.39	0.086	27.28	0.17	821.94	1390.17	1266.21	1041.40	64.40	935.07	-	62.94	80.57	1.59	0.69	8.08	17.50	2.30	3.16	7.87	10.86
50	2.9	7.52	7.42	0.122	23.24	0.17	904.50	1237.12	1211.06	1075.80	52.18	965.96	60.4-2	59.74	83.54	1.58	0.68	8.21	11.94	1.54	2.10	5.45	7.59
56	3.2	-	6.32	0.024	26.92	0.04	972.74	1318.50	1270.60	1131.40	52.99	1003.51	-	56.72	80.65	1.60	0.70	8.54	13.96	1.68	2.37	6.28	8.72
62	3.5	7.52	6.35	0	21.32	0.05	1038.88	1592.68	1307.18	1022.07	47.33	919.66	80.94	62.76	74.00	1.58	0.67	8.94	18.95	2.26	3.12	8.23	11.66
68	3.8	-	6.35	0.161	28.27	0.06	970.67	1284.28	1142.52	1069.60	47.97	985.07	-	55.42	54.91	1.61	0.69	8.35	13.13	1.63	2.41	5.90	8.32
74	4.1	7.63	7.72	0.121	27.92	0.07	889.40	1193.69	1009.47	1104.87	54.07	1042.00	153.64	53.44	30.72	1.59	0.68	7.32	25.52	3.42	4.69	11.51	16.23
80	4.4	7.50	7.90	0.285	31.6	0	945.46	1179.88	997.63	1136.00	51.60	1079.73	152.86	55.82	28.23	1.59	0.70	9.41	11.30	1.29	1.82	5.10	7.01
86	4.8	7.43	6.61	0.192	30.98	0	973.28	1408.05	1222.84	1100.00	53.60	1051.47	76.86	51.71	30.13	1.60	0.69	9.13	16.30	1.88	2.66	7.36	10.22
92	5.1	7.48	6.46	0.18	31.04	0	1017.75	1100.80	1085.65	1132.00	51.20	1127.73	114.92	50.73	29.29	1.59	0.68	9.06	11.70	1.28	1.81	5.04	7.06
98	5.4	-	6.42	0.219	31.05	0	906.32	1113.27	1087.31	1128.84	46.84	1138.04	58.41	51.20	29.75	1.59	0.69	9.37	20.69	2.20	3.42	9.06	12.54
104	5.7	-	6.50	0.181	30.14	0	958.14	984.49	1099.23	1123.56	41.95	1157.79	60.68	52.52	29.97	1.60	0.67	10.35	17.81	1.76	2.57	7.54	10.26
110	6.0	-	6.32	0.361	29.73	0	927.52	1072.87	1194.38	1127.70	41.98	1164.64	118.30	53.44	29.56	1.56	0.66	9.97	17.39	1.34	2.50	6.71	9.93
116	6.3	-	8.77	0.078	34.63	0	1085.41	1309.94	1454.44	1122.83	45.55	1194.12	123.30	56.41	32.77	1.57	0.66	10.11	20.69	1.52	3.02	8.05	11.91
122	6.6	-	8.69	0.031	33.66	0	1099.92	1128.40	1435.19	1036.56	27.69	1126.16	114.58	55.67	31.61	1.56	0.68	12.29	16.65	1.11	2.02	6.92	9.26
128	7.0	-	8.43	0.272	30.81	0	1043.48	1072.39	1477.04	1145.06	55.36	1322.12	133.13	53.72	33.84	-	-	-	-	-	-	-	-
134	7.3	-	8.03	0.211	33.75	0	1067.27	977.43	1547.57	1137.52	54.51	1299.09	149.56	59.56	34.07	-	-	-	-	-	-	-	-
140	7.5	7.69	8.22	0.199	32.24	0	1024.05	599.58	1439.32	1137.94	42.78	1283.99	138.06	58.34	34.19	-	-	-	-	-	-	-	-

*All units in mg/L except As (µg/L), EC (electrical conductivity, mS/cm), and all peaks (Raman units, R.U.). Values for FI, FRI, HIX, and pH are dimensionless. Dash indicates that measurements were not performed.

Table S8. Type 3 Tests of fixed effects on total sulfur

Effect	Num DF	Den DF	F Value	Pr > F
Treatment	1	48	380.17	<.0001
Time	23	48	72.69	<.0001
Time*Treatment	23	48	3.67	<.0001

Table S9. Type 3 Tests of fixed effects on sulfate-S

Effect	Num DF	Den DF	F Value	Pr > F
Treatment	1	2	1343.68	0.0007
Time	23	46	448.04	<.0001
Time*Treatment	23	46	28.43	<.0001

Table S10. Type 3 Tests of fixed effects on boron

Effect	Num DF	Den DF	F Value	Pr > F
Treatment	1	2	12.47	0.0717
Time	23	46	30.39	<.0001
Time*Treatment	23	46	1.22	0.2806

Table S11. Type 3 Tests of fixed effects on arsenic

Effect	Num DF	Den DF	F Value	Pr > F
Treatment	1	2	289.30	0.0034
Time	20	40	30.66	<.0001
Time*Treatment	20	40	14.37	<.0001

Table S12. Type 3 Tests of fixed effects on DOC

Effect	Num DF	Den DF	F Value	Pr > F
Treatment	1	2	22.53	0.0416
Time	20	40	50.44	<.0001
Time*Treatment	20	40	3.49	0.0004

Table S13. Type 3 Tests of fixed effects on fluorescence indices

			Fluorescence index		Freshness index		Humification index	
Effect	Num DF	Den DF	F Value	Pr > F	F Value	Pr > F	F Value	Pr > F
Treatment	1	2	0.02	0.9041	6.78	0.1212	5.20	0.1501
Time	19	38	4.26	<.0001	20.89	<.0001	11.92	<.0001
Time*Treatment	19	38	1.32	0.2262	1.45	0.1624	1.26	0.2664

Table S14. Mass of dry soil in each section, sulfur concentration of dry soil (Cs), and mass of sulfur retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (mg/kg)	Ms Retained (mg)
1 (2x control)	1	126.79	3574.65	283.97
	2	116.30	4002.55	310.22
	3	119.28	3362.90	241.89
	4	118.13	1914.48	68.45
	5	117.04	1331.70	-0.39
	6	122.77	1309.97	-3.07
2 (1x control)	1	121.74	3527.72	266.95
	2	124.37	3091.21	218.41
	3	118.18	2671.38	157.94
	4	120.55	2365.29	124.20
	5	113.87	1909.56	65.43
	6	125.15	1254.84	-10.03
3 (soil inoculum)	1	123.50	3817.68	306.60
	2	118.09	2799.54	172.94
	3	119.99	2269.41	112.12
	4	118.23	2313.56	115.69
	5	47.49	2000.42	31.60
	6	125.97	1100.23	-29.58
4 (soil inoculum)	1	120.46	3271.10	233.22
	2	118.77	2567.26	146.35
	3	116.39	2207.43	101.54
	4	116.62	2194.69	100.26
	5	120.39	1755.28	50.60
	6	125.58	1107.18	-28.61
5 (OC amended WW)	1	122.51	2533.74	146.86
	2	115.12	2405.19	123.20
	3	119.48	2057.67	86.34
	4	120.41	2031.10	83.82
	5	118.31	2385.69	124.31
	6	128.97	4430.75	399.27
6 (OC amended WW)	1	119.06	2735.66	166.76
	2	121.65	2771.61	174.76
	3	120.38	2353.65	122.62
	4	119.39	2143.97	96.58
	5	119.42	5412.73	486.97
	6	125.20	2623.12	161.28

Table S15. Mass of dry soil in each section, Se concentration of dry soil (Cs), and mass of Se retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (µg/kg)	Ms Retained (µg)
1 (2x control)	1	126.79	609.60	35.86
	2	116.30	537.20	24.47
	3	119.28	515.20	22.47
	4	118.13	631.60	36.01
	5	117.04	1369.60	122.05
	6	122.77	3561.20	397.08
2 (1x control)	1	121.74	568.00	29.36
	2	124.37	357.20	3.78
	3	118.18	286.00	-4.82
	4	120.55	242.80	-10.13
	5	113.87	523.60	22.41
	6	125.15	272.00	-6.86
3 (soil inoculum)	1	123.50	335.20	1.04
	2	118.09	114.00	-25.13
	3	119.99	227.20	-11.95
	4	118.23	857.20	62.71
	5	47.49	2137.60	86.00
	6	125.97	526.00	25.09
4 (soil inoculum)	1	120.46	425.20	11.85
	2	118.77	254.40	-8.60
	3	116.39	408.40	9.50
	4	116.62	552.40	26.31
	5	120.39	1746.80	170.95
	6	125.58	328.80	0.25
5 (OC amended WW)	1	122.51	324.00	-0.34
	2	115.12	268.80	-6.68
	3	119.48	726.80	47.79
	4	120.41	772.80	53.70
	5	118.31	1471.20	135.39
	6	128.97	314.40	-1.60
6 (OC amended WW)	1	119.06	324.80	-0.24
	2	121.65	354.00	3.31
	3	120.38	257.20	-8.38
	4	119.39	1987.60	198.28
	5	119.42	272.40	-6.50
	6	125.20	281.20	-5.71

Table S16. Mass of dry soil in each section, Fe concentration of dry soil (Cs), and mass of Fe retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (mg/kg)	Ms Retained (mg)
1 (2x control)	1	126.79	18390.68	-394.29
	2	116.30	18264.47	-376.33
	3	119.28	17505.94	-476.46
	4	118.13	17338.53	-491.64
	5	117.04	17170.68	-506.74
	6	122.77	18793.44	-332.33
2 (1x control)	1	121.74	18797.14	-329.11
	2	124.37	18303.67	-397.57
	3	118.18	18031.30	-409.99
	4	120.55	15423.11	-732.64
	5	113.87	14895.55	-752.11
	6	125.15	16009.32	-687.20
3 (soil inoculum)	1	123.50	16119.25	-664.56
	2	118.09	16390.52	-603.42
	3	119.99	15413.20	-730.43
	4	118.23	16098.52	-638.66
	5	47.49	16711.22	-227.45
	6	125.97	17024.29	-563.88
4 (soil inoculum)	1	120.46	17882.39	-435.82
	2	118.77	18991.32	-298.00
	3	116.39	18504.74	-348.67
	4	116.62	20090.00	-164.48
	5	120.39	20022.53	-177.93
	6	125.58	21415.87	-10.62
5 (OC amended WW)	1	122.51	19499.89	-245.09
	2	115.12	17735.39	-433.45
	3	119.48	14683.32	-814.52
	4	120.41	16232.63	-634.31
	5	118.31	15691.64	-687.23
	6	128.97	16219.37	-681.13
6 (OC amended WW)	1	119.06	15775.47	-681.63
	2	121.65	18647.50	-347.06
	3	120.38	15711.08	-696.91
	4	119.39	16067.38	-648.66
	5	119.42	18072.97	-409.32
	6	125.20	17614.22	-486.57

Table S17. Mass of dry soil in each section, As concentration of dry soil (Cs), and mass of As retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (µg/kg)	Ms Retained (µg)
1 (2x control)	1	126.79	4335.20	69.89
	2	116.30	4178.40	45.87
	3	119.28	3952.40	20.09
	4	118.13	4341.20	65.82
	5	117.04	3933.20	17.46
	6	122.77	4967.60	145.31
2 (1x control)	1	121.74	3754.80	-3.55
	2	124.37	3530.40	-31.54
	3	118.18	3519.60	-31.25
	4	120.55	3304.00	-57.87
	5	113.87	3190.00	-67.64
	6	125.15	3204.80	-72.49
3 (soil inoculum)	1	123.50	3388.80	-48.81
	2	118.09	3092.80	-81.62
	3	119.99	3207.20	-69.21
	4	118.23	3304.40	-56.70
	5	47.49	3582.80	-9.56
	6	125.97	3666.40	-14.81
4 (soil inoculum)	1	120.46	3750.00	-4.10
	2	118.77	3774.40	-1.14
	3	116.39	3973.60	22.07
	4	116.62	3817.20	3.87
	5	120.39	3325.60	-55.19
	6	125.58	3451.20	-41.79
5 (OC amended WW)	1	122.51	3522.80	-32.00
	2	115.12	3390.00	-45.36
	3	119.48	3403.20	-45.50
	4	120.41	3305.20	-57.65
	5	118.31	4587.60	95.07
	6	128.97	1837.20	-251.09
6 (OC amended WW)	1	119.06	3908.40	14.81
	2	121.65	3996.00	25.79
	3	120.38	3990.40	24.85
	4	119.39	3957.60	20.73
	5	119.42	2191.20	-190.22
	6	125.20	5526.40	218.16

Table S18. Mass of dry soil in each section, Mn concentration of dry soil (Cs), and mass of Mn retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (µg/kg)	Ms Retained (mg)
1 (2x control)	1	126.79	285.62	-16.94
	2	116.30	319.97	-11.54
	3	119.28	358.21	-7.28
	4	118.13	500.86	9.65
	5	117.04	575.77	18.32
	6	122.77	680.87	32.12
2 (1x control)	1	121.74	416.61	-0.32
	2	124.37	385.53	-4.19
	3	118.18	332.98	-10.19
	4	120.55	340.09	-9.54
	5	113.87	442.86	2.69
	6	125.15	583.57	20.57
3 (soil inoculum)	1	123.50	480.63	7.59
	2	118.09	346.05	-8.64
	3	119.99	290.24	-15.48
	4	118.23	331.20	-10.41
	5	47.49	416.06	-0.15
	6	125.97	582.96	20.63
4 (soil inoculum)	1	120.46	478.98	7.20
	2	118.77	362.78	-6.70
	3	116.39	292.11	-14.79
	4	116.62	337.12	-9.57
	5	120.39	477.76	7.05
	6	125.58	613.08	24.35
5 (OC amended WW)	1	122.51	478.72	7.29
	2	115.12	461.18	4.83
	3	119.48	382.35	-4.40
	4	120.41	285.54	-16.09
	5	118.31	332.81	-10.22
	6	128.97	717.90	38.52
6 (OC amended WW)	1	119.06	500.38	9.66
	2	121.65	505.54	10.50
	3	120.38	380.65	-4.64
	4	119.39	847.03	51.08
	5	119.42	354.23	-7.76
	6	125.20	437.96	2.35

Table S19. Mass of dry soil in each section, Al concentration of dry soil (Cs), and mass of Al retained in each section of the column (Ms retained)

Column	Section	Dry Soil (g)	C _s (µg/kg)	Ms Retained (mg)
1 (2x control)	1	126.79	18890.13	-653.88
	2	116.30	18344.02	-663.27
	3	119.28	18075.84	-712.28
	4	118.13	20553.75	-412.69
	5	117.04	19059.75	-583.73
	6	122.77	20570.68	-426.82
2 (1x control)	1	121.74	19062.26	-606.89
	2	124.37	18697.21	-665.37
	3	118.18	17833.41	-734.38
	4	120.55	13710.48	-1246.13
	5	113.87	14872.29	-1044.78
	6	125.15	15977.24	-1009.95
3 (soil inoculum)	1	123.50	13758.48	-1270.63
	2	118.09	15081.65	-1058.74
	3	119.99	13565.28	-1257.77
	4	118.23	14276.86	-1155.14
	5	47.49	17804.95	-296.47
	6	125.97	17910.68	-773.06
4 (soil inoculum)	1	120.46	17371.05	-804.20
	2	118.77	17767.05	-745.89
	3	116.39	15715.05	-969.79
	4	116.62	18320.84	-667.81
	5	120.39	19950.83	-493.18
	6	125.58	21261.55	-349.85
5 (OC amended WW)	1	122.51	18839.76	-638.00
	2	115.12	17867.91	-711.40
	3	119.48	12977.49	-1322.64
	4	120.41	14554.73	-1143.03
	5	118.31	15175.42	-1049.63
	6	128.97	15985.20	-1039.81
6 (OC amended WW)	1	119.06	13731.67	-1228.20
	2	121.65	15572.11	-1031.02
	3	120.38	13934.81	-1217.32
	4	119.39	14846.84	-1098.45
	5	119.42	19288.89	-568.27
	6	125.20	17572.01	-810.74