COAL-FIRED POWER PLANT FLUE GAS DESULFURIZATION WASTEWATER
TREATMENT USING CONSTRUCTED WETLANDS

by

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Abstract

In the United States approximately 37% of the 4 trillion kWh of electricity is generated annually by combusting coal (USEPA, 2013). The abundance of coal, ease of storage, and transportation makes it affordable at a global scale (Ghose, 2009). However, the flue gas produced by combusting coal affects human health and the environment (USEPA, 2013). To comply with federal regulations coal-fired power plants have been implementing sulfur dioxide scrubbing systems such as flue gas desulfurization (FGD) systems (Alvarez-Ayuso et al., 2006). Although FGD systems have proven to reduce atmospheric emissions they create wastewater containing harmful pollutants. Constructed wetlands are increasingly being employed for the removal of these toxic trace elements from FGD wastewater.

In this study the effectiveness of using a constructed wetland treatment system was explored as a possible remediation technology to treat FGD wastewater from a coal-fired power plant in Kansas. To simulate constructed wetlands, a continuous flow-through column experiment was conducted with undiluted FGD wastewater and surface sediment from a power plant in Kansas. To optimize the performance of a CWTS the following hypotheses were tested: 1) decreasing the flow rate improves the performance of the treatment wetlands due to an increase in reaction time, 2) the introduction of microbial cultures (inoculum) will increase the retention capacity of the columns since constructed wetlands improve water quality through biological process, 3) the introduction of a labile carbon source will improve the retention capacity of the columns since microorganisms require an electron donor to perform life functions such as cell maintenance and synthesis. Although the FGD wastewater collected possessed a negligible concentration of arsenic, the mobilization of arsenic has been observed in reducing

sediments of wetland environments. Therefore, constructed wetlands may also represent an environment where the mobilization of arsenic is possible. This led us to test the following hypothesis: 4) Reducing environments will cause arsenic desorption and dissolution causing the mobilization of arsenic.

As far as removal of the constituents of concern (arsenic, selenium, nitrate, and sulfate) in the column experiments, only sulfate removal increased as a result of decreasing the flow rate by half (1/2Q). In addition, sulfate-S exhibited greater removal as a result of adding organic carbon to the FGD solution when compared to the control (at 1/2Q). Moderate selenium removal was observed; over 60% of selenium in the influent was found to accumulate in the soil.

By contrast, arsenic concentrations increased in the effluent of the 1/2Q columns, most likely by dissolution and release of sorbed arsenic. When compared to the control (at 1/2Q), arsenic dissolution decreased as a result of adding inoculum to the columns. Dissolved arsenic concentrations in the effluent of columns with FGD solution amended with organic carbon reached 168 mg/L. These results suggest that native Kansas soils placed in a constructed wetland configuration and amended with labile carbon do possess an environment where the mobilization of arsenic is possible

Table of Contents

List of Figures

List of Tables

Acknowledgements

Dedication

To Papanesh, mi abuelito.

Chapter 1 - Introduction

Coal-Fired Power Plants

In the United States approximately 37% of the 4 trillion kWh of electricity is generated annually by combusting coal (USEPA, 2013). In fact, one pound of coal yields enough electricity to power ten 100-watt light bulbs for one hour (USEPA, 2013). Its abundance, ease of storage, and transportation makes it affordable at a global scale (Ghose, 2009). Coal is a sedimentary rock composed of carbon and hydrocarbons and is the most abundant fossil fuel produced in the United States (USEPA, 2013). As of 2012 there are over 550 electrical power plants (from all sectors), which use coal as an energy source (USEPA, 2013). Figure 1-1 shows the location of coal-fired power plants in the continental United States. The majority of the coal-fired power plants are concentrated east of the Mississippi.
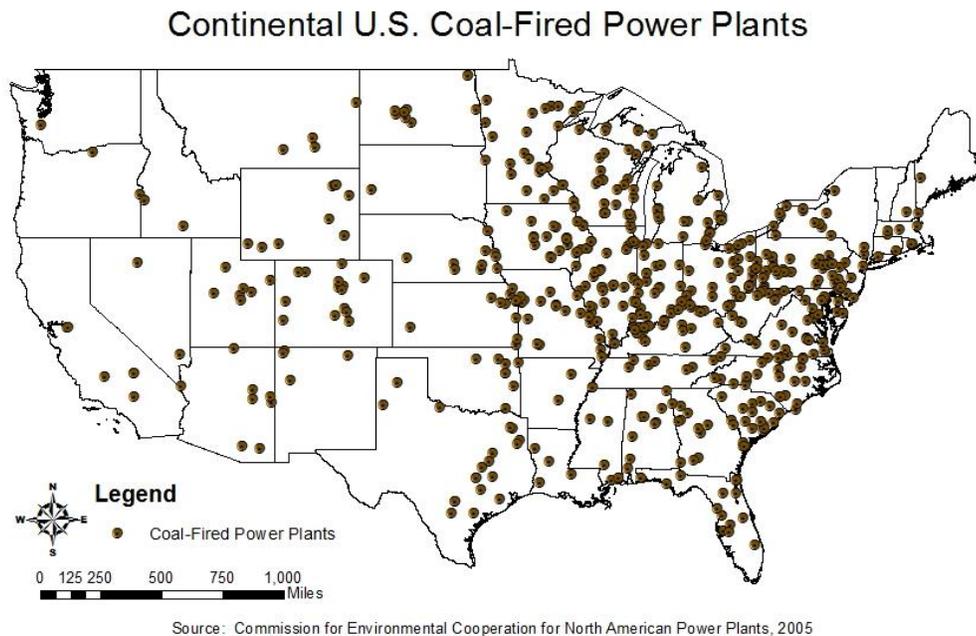
Figure 1-1. Location of Coal-Fired Power Plants in the Continental U.S.

Electricity in power plants is generated by feeding fuels (coal, petroleum coke, oil, gas, or nuclear fuel) to boilers to generate steam (USEPA, 2009). The high-pressure and high-temperature steam is used to drive turbine blades as it moves from high-pressure to low-pressure stages within the turbine generator (USEPA, 2009). The spinning turbine blades drive the generator, which produces electricity. The hot gases produced from combusting fuels, known as flue gas, pass through particulate collection, sulfur dioxide scrubbing system (if present), and are then emitted into the atmosphere through smoke stacks (USEPA, 2009).

Although coal is an important component for keeping electricity cost down it does bring many environmental disadvantages. The flue gas produced by combusting coal effect human health and the environment (USEPA, 2013). The principal emissions present in flue gas include sulfur dioxide (SO_2), nitrogen oxides (NOx), and carbon dioxide (CO_2), which contribute to acid rain, respiratory illness, and greenhouse effects (USEPA, 2013).

To combat these harmful emissions the U.S. Congress introduced a series of legislative actions which include the Clean Air Act Amendments of 1963, 1966, 1970, 1977, and 1990. Much of the basic structure of the Clean Air Act was established in the 1970 amendment. The 1970 amendment requires the U.S. Environmental Protection Agency (USEPA) to establish *National Ambient Air Quality Standards* (NAAQS) and requires states to submit *State Implementation Plans* (SIPs), which show how they would meet those standards (USEPA, 2013). NAAQS were established "to protect public health and welfare nationwide for certain common and widespread pollutants based on the latest science" (USEPA, 2013). There are six "criteria pollutants" set by the USEPA, including carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO_2), ozone (O^3), sulfur dioxide (SO_2), and particulate matter (USEPA, 2013). The Clean Air

Act identifies two types of NAAQS, primary and secondary standards. Primary standards provide health protection for the sensitive population such as asthmatics, children, and elderly (USEPA, 2013). Secondary standards provide welfare protection against decreased visibility and damage to animals, crops, vegetation, and buildings (USEPA, 2013). Table 1-1 shows the primary standards in NAAQS. From Table 1-1 nitrogen dioxide and sulfur dioxide is of concern to coal-fired power plants.

Over the last 20 years, total emissions of the six criteria pollutants have decreased by more than 41% (USEPA, 2013). The decrease is in part due to coal-fired power plants switching from high- to low- sulfur coal and/or implementing sulfur dioxide scrubbing systems such as flue gas desulfurization (FGD) systems (Alvarez-Ayuso et al., 2006). Power plants use FGD systems to reduce sulfur dioxide emissions from the flue gas generated in the boiler (USEPA, 2009).

Table 1-1. Primary National Ambient Air Quality Standards (NAAQS)

Pollutant		Averaging Times	Level	Form
Carbon Monoxide		8-hour	9 ppm	Not to be exceeded more than once per year
		1-hour	35 ppm	
Lead		3 months	$0.15 \ \mu g/m^3$	Not to be exceeded
Nitrogen Dioxide		1-hour	100 ppb	98th percentile, averaged over 3 years
		Annual	53 ppb	Annual Mean
Ozone		8-hour	75 ppb	Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years
Particulate Matter	$PM_{2.5}$	Annual	$12 \ \mu g/m^3$	Annual mean, averaged over 3 years
		24-hour	$35 \ \mu g/m^3$	Annual mean, averaged over 3 years
	PM_{10}	24-hours	$150 \ \mu g/m^3$	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide		1-hour	75 ppb	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years

Several categories of FGD systems have been developed. The different types can be classified into two major groups, wet and dry FGD process (Alvarez-Ayuso et al., 2006). They are further subdivided depending on the chemical reactions taking place and flow conditions (Alvarez-Ayuso et al., 2006).

A dry FGD system uses a spray dryer absorption process (USEPA, 2009). A dry FGD system is typically used when the power plant's coal contains less than 2% sulfur, as it typically does in the western United States (Heimbigber, 2007). Wet lime slurry, which ranges from 18-25% solids, is atomized and sprayed to a spray dryer (USEPA, 2009). The percentage of solids in the lime slurry is precisely calculated so that sulfur dioxide is removed and all water within the spay dryer is evaporated (USEPA, 2009). The flue gas enters the system through a dispenser which allows for maximum contact with the atomized droplets (USEPA, 2009). The sulfur dioxide in the flue gas is absorbed by the spray droplets and reacts with the lime in the slurry and produces calcium sulfite (USEPA, 2013). The reactions occur in the aqueous phase of the spray droplets. The heat from the flue gas causes the water from the spray droplets to evaporate. Consequently, a dry FGD system does not produce wastewater.

The most commonly used sulfur dioxide scrubbing systems is the wet FGD system, representing over 90% of the installed desulfurization systems in the world (USEPA, 2009; Eggert et al, 2008; Alvarez-Ayuso et al., 2006; Liu et al. 2008). This is due to its high desulphurization performance, reliability, and low utility consumption (Kikkawa et al, 2002). Wet FGD systems are preferred when coal contains higher sulfur concentrations (Heimbigber, 2007). A model for a limestone forced oxidation wet FGD system is shown in **Error! Not a valid bookmark self-reference.**. In a wet FGD system a liquid stream is released through scrubbers containing a sorbent, typically lime ($Ca(OH)_2$) or limestone ($CaCO_3$) (USEPA, 2009).

The flue gas enters the system near the bottom just above the water level of the reaction tank. As the liquid stream is released through the scrubbers it comes into contact with the rising flue gas. Sulfur dioxide is removed from the flue gas after the limestone (or lime) saturated liquid solubilizes gaseous SO_2 and oxidizes and precipitates sulfur compounds as calcium sulfite ($CaSO_3$) (Eggert et al, 2008). The following chemical reaction shows the reaction that occurs between limestone and sulfur dioxide which produces calcium sulfite (Alvarez-Ayuso et al., 2006; USEPA, 2009):

$$CaCO_{3(s)} + SO_{2(g)} + \frac{1}{2}H_2O \rightarrow CaSO_3 * \frac{1}{2}H_2O_{(s)} + CO_{2(g)}$$
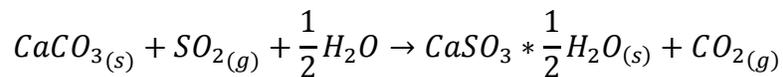
Some coal-fired plants will further oxidize the calcium sulfite ($CaSO_3$) to calcium sulfate ($CaSO_4$) or gypsum in a process called forced oxidation. This is accomplished by injecting air into the calcium sulfite slurry which is collected and ponded in a reaction tank at the bottom of the FGD system and vigorously mixed. The chemical reaction which describes the reaction that produces gypsum ($CaSO_3*2H_2O$) from calcium sulfite ($CaSO_3$) is (Alvarez-Ayuso et al., 2006; USEPA, 2009):

$$CaSO_3 \bullet \frac{1}{2}H_2O_{(s)} + \frac{1}{2}O_{2(g)} + \frac{3}{2}H_2O \rightarrow CaSO_3 * \frac{1}{2}H_2O_{(s)} + CO_{2(g)}$$
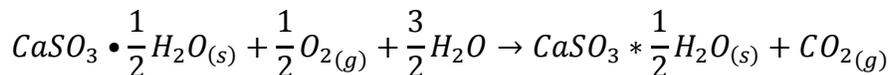
The slurry mixture is continuously recirculated from the reaction tank to various levels in the FGD system (USEPA, 2009). When the percent of solids or the chloride concentration in the slurry exceeds a set high point in the reaction tank a scrubber blowdown pump removes some of the slurry (USEPA, 2009). The partial removal of the slurry will decrease levels of solids and chloride concentration. The power plant will then shut-off the blowdown pumps until the percent solids and chloride concentration builds up again to the set high point (USEPA, 2009). Plants control the percent solids because they can affect the operation of the FGD system and they must also limit the amount of fines in the gypsum by-product (USEPA, 2009). High chloride

5

concentrations, in the range of 12,000-20,000 ppm, can be corrosive to the components in the

FGD system, which is why the chloride concentration is decreased (USEPA, 2009).

The gypsum-rich blowdown stream is transferred to a solid separation process. The dried

gypsum by-product is removed from the dewatering process, stored, and then transferred off site,

for beneficial use or disposal at a landfill (USEPA, 2009; Changwoo & Mitsch, 2002). The low-

solid stream from the solids separation process is typically transferred to a purge tank, sent to a

wastewater treatment system, and discharged (USEPA, 2009). Most FGD wastewater treatment

systems currently in operation in
power plants do not significantly
affect the concentration of chlorides
in the wastewater; hence, the treated
wastewater is not recycled back to
the FGD scrubber (USEPA, 2009).
However, there are plants capable of
purging sufficient chlorides along
with the solids to allow reuse of FGD
water. These plants typically don't
market their dried gypsum by-
product for beneficial use;
consequently, they don't need to
meet gypsum chloride and fines
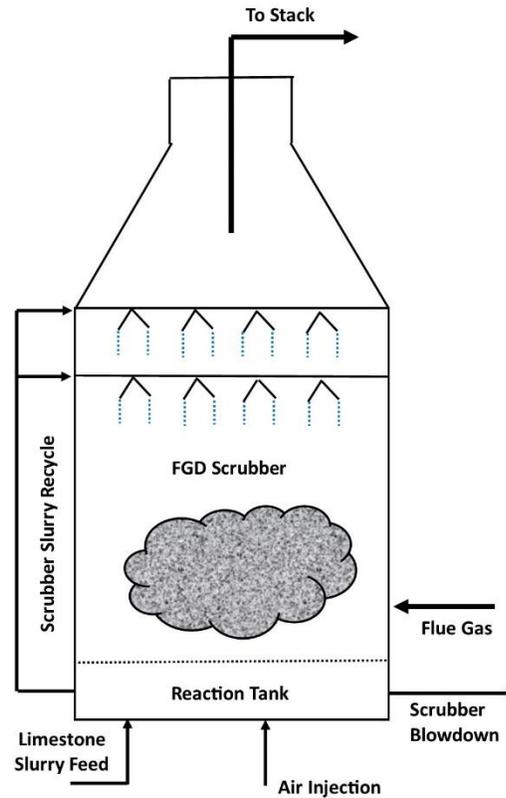
**Figure 1-2. Model for Limestone Forced Oxidation
System. Derived from USEPA, 2009**

specifications (USEPA, 2009). They are able to purge enough chlorides with the FGD solids so that the low-solid stream from the solid separation process is recycled back to the FGD scrubbers. (USEPA, 2009).

There is no argument against the effectiveness of using FGD systems to reduce harmful air pollutants from being emitted into the atmosphere. Issues do arise, however, with the low-solid blowdown stream from the dewatering process that gets discharged into aquatic systems. As much as 0.5 to 3.0 million gallons per day (MGD) of FGD blowdown (wastewater) can be generated from an FGD system in a coal-fired power plant (Mooney & Murray-Gulde, 2008). The FGD wastewater contains problematic constituents of environmental concern such as arsenic, chemical and biological oxygen demand, boron, cadmium, chromium, copper, chloride, lead, mercury, nitrate, selenium, sulfate, and zinc (USEPA, 2009; Eggert et al, 2008; Alvarez-Ayuso et al., 2006; Liu et al. 2008; Miezejewski, 1991). Now the challenge remains to design treatment systems for the sequestration of toxic trace elements that are released in the FGD wastewater stream.

Typical Wastewater Composition

The FGD wastewater produced by coal-fired power plants can vary widely in chemical composition. They may contain polluants of concentrations and forms that are toxic to the receiving aquatic environment (Eggert et al, 2008). The composition of FGD wastewater is a function of several physical and chemical variables (Eggert et al, 2008). Factors that can affect the composition and flow rate of FGD wastewater include type of coal, scrubber design, operating practices, solid separation process, and solids dewatering process (USEPA, 2009). All things considered, most of the constituents present in the FGD wastewater originate from either the coal or type of the sorbent used (EPRI, 2006; USEPA, 2009).

The pollutants present in the coal are most likely present in the FGD wastewater. In the Electrical Power Research Institute's *EPRI Technical Manual: Guidance for Assessing Wastewater Impacts of FGD Scrubbers* the partitioning of metals from coal to FGD wastewater from two plants was determined. Their results are duplicated in Table 1-2, which show the ratio of metals present in FGD wastewater to the metals present in the coals. The FGD wastewater composition is largely determined by coal composition (Table 1-2). The ratio of metals from coal to metals from FGD wastewater also vary significantly between sites (Table 1-2).

Table 1-2. Partitioning From Coal to FGD Wastewater in Two FGD Systems.

Duplicated from (EPRI, 2006)

Parameters	Site 1 (Ratio: Liquid Out/Coal In)	Site 2 (Ratio: Liquid Out/Coal In)
Aluminum	0%	1%
Arsenic	1%	19%
Copper	3%	<2%
Iron	1%	5%
Mercury	13%	74%
Selenium	Not Detected	<99%

The type of coal can also have a significant impact on the FGD wastewater flow rate. High-sulfur coals produce more sulfur dioxide which increases the amount of sulfur dioxide that needs to be removed in the FGD system (USEPA, 2009). As the amount of sulfur dioxide removed increases the solids generated in the scrubber also increase, which results in the increase in blowdown volumes (USEPA, 2009). A high-chloride coal can also increase the volume and frequency of the FGD scrubber blowdown (USEPA, 2009). High concentrations of chloride in the FGD scrubber can be corrosive to components in the system. A power plant

operating with high-sulfur and/or high-chloride coal will rapidly reach the maximum allowable percent solids and/or chloride concentration in the FGD scrubber, which will trigger more frequent blowdowns (USEPA, 2009).

The type of sorbent used can also effect the FGD wastewater composition. For example, if limestone is used as a sorbent it may contain clay impurities (EPRI, 2006). These clay impurities in limestone can contribute aluminum, silicon, nickel, and zinc to the FGD wastewater.

EPRI (2006) evaluated the composition of FGD wastewater at eight coal-fired power plants across the United States. The results are reproduced on Table 1-3. The table shows the significant variations of FGD wastewater constituents between sites. For example total arsenic ranged from 10 to 380 μg/L, total selenium from 86-2,600 μg/L, and total mercury from 8.2 to 99 μg/L. The significant variations make it difficult to design treatment systems. Treatment systems should be designed for a specific wastewater and for a specific site (Mooney & Murray-Gulde, 2008).

Table 1-3. FGD Wastewater Characteristics from Eight Power Plants. Reproduced from (EPRI, 2006).

| Parameter | Units | EPRI Screening Study | | | |
| | | Dissolved | | Total | |
		Median	Range	Median	Range
Aluminum	µg/L	1000	260-18,000	39,000	9,700-170,00
Antimony	µg/L	50	100-50	280	12-500
Arsenic	µg/L	16	4.1-110	260	10-380
Barium	µg/L	250	97-840	2,000	180-3,000
Beryllium	µg/L	40	5.2-40	220	3.2-400
Boron	µg/L	260	15-480	200	3.2-400
Cadmium	µg/L	50	13-83	280	9.3-500
Calcium	µg/L	750	670-4,000	2,900	700-33,000
Chromium	µg/L	100	14-100	600	30-1,000
Cobalt	µg/L	78	22-100	1,000	22-1,000
Copper	µg/L	100	63-270	650	100-3,300
Iron	µg/L	1,000	130-1,000	62,000	1,500-280,000
Lead	µg/L	50	6.5-50	280	6.8-500
Magnesium	µg/L	1,100	390-4,400	1,500	440-4,300
Manganese	µg/L	6,400	1,700-52,000	11,000	1,900-52,000
Mercury	µg/L	0.6	0.1-8.5	61	8.2-99
Molybdenum	µg/L	170	40-700	2,500	52-2,500
Nickel	µg/L	260	120-1,200	1,700	86-2,600
Potassium	µg/L	115	21-880	99	27-577
Selenium	µg/L	1,100	70-1,800	1,700	86-2,600
Selenium IV	µg/L	410	110-430		
Selenium VI	µg/L	6.0	4.2-1,207		
Silver	µg/L	100	13-100	550	4-1,000
Sodium	µg/L	670	72-4,800	320	66-45,00
Thallium	µg/L	100	13-100	550	5.6-1,000
Vanadium	µg/L	150	31-250	2,500	33-2,200
Zinc	µg/L	1,000	100-2,800	1,700	180-7,100
Acidity	mg CaCO$_3$/L	270	46-11,000	370	53-10,000
Alkalinity	mg CaCO$_3$/L	180	23-520	250	26-4,500
Conductivity	µhos/cm	10,000	4,300-6300	9,500	4,200
Fluoride	mg/L	15	6.5-51		
Hardness as CaCO3	mg/L	4,100	3,000-5,300	4,300	3,000-5,600
pH	pH units	7.3	6.2-7.3	6.9	6.1-7.3
Sulfate	mg/L	3,200	1,700-5,700	9,500	9,500-9,500
TDS	mg/L	14,000	6,000-50,000	14,000	1,400-45,000
TSS	mg/L	4.2	2.2-7.6	13,000	33-140,000
Flow	Mgd	0.19	0.17-0.21	0.19	0.17-0.21

Arsenic

The most increasingly regulated constituent of concern shown in Table 1-3 is arsenic. Historically, it has been the perfect poison. Arsenic was cheap, tasteless, odorless, and small amounts would mimic death from natural causes (Henke & Atwood, 2009). Typically, murder victims were given small concentration over several months to mimic the appearance of a natural disease (Henke & Atwood, 2009). Once the victim was weak, the murder would administer the final fatal dosage (Henke & Atwood, 2009). As techniques to detect trace amounts became available its use as a poison quickly diminished (Weir, 2002). These techniques permitted investigators to identify low concentrations of arsenic in autopsies, which consequently increased the number of murder convictions (Henke & Atwood, 2009). Today, arsenic continues to affect the lives of millions of people. Although it is no longer frequently used as poison, arsenic contamination of drinking water is a serious and widespread problem.

Long-term exposure to arsenic can result in a variety of health issues including various forms of cancer, cardiovascular and peripheral vascular disease, and diabetes (Henke & Atwood, 2009). The World Health Organization (WHO) guideline for arsenic concentration in drinking water is 10 μgL^{-1}. Communities across the globe obtain drinking water from a variety of sources depending on availability. Drinking water sources include surface water (such as rivers, lakes, reservoirs, and ponds), groundwater, and rain water. High concentrations of arsenic are mainly found in groundwater (Smedley & Kinniburgh, 2002). Numerous aquifers around the world have been identified with arsenic concentrations significantly above the WHO limit. The aquifers can be found in parts of Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam, and the United States (Nriagu et al., 2007; Smedley & Kinniburgh, 2002).

Arsenic is a naturally occurring constituent and ranks 20th in abundance in relation to other elements (Henke & Hutchison, 2009; Nriagu et al., 2007). Arsenic exists in four oxidation states (-III, 0, +III, and +V) as both inorganic and organometallic species (Henke & Hutchison, 2009; Smedley & Kinniburgh, 2002; Wang & Mulligan, 2006) but in natural waters it is mostly found in the inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] (Henke & Hutchison, 2009; Nriagu et al., 2007; Smedley & Kinniburgh, 2002). Arsenite is the more mobile and toxic form for living organisms (Nriagu et al., 2007). Organic arsenic may be produced by biological activity in surface waters but its quantities are rarely of importance (Smedley & Kinniburgh, 2002).

The speciation of dissolved arsenic in water depends on pH, redox conditions, biological activity, and other aqueous chemistry (Henke & Hutchison, 2009), where redox potential and pH are the most important factors (Smedley & Kinniburgh, 2002). The distribution of arsenic species as a function of pH is shown in Figure 1-3. Under reducing conditions arsenite is the dominant species, where H_3AsO_3 is dominant at pH below 9.2 and $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{-3} are dominant under more alkaline conditions (Henke & Hutchison, 2009; Smedley & Kinniburgh, 2002). Under oxidizing conditions arsenate is the dominant species where $H_3AsO_4^0$ is dominant at pH less than 2, $H_2AsO_4^-$ is dominant at pH less than 6.9, and $HAsO_4^-$ becomes dominant at higher pH. AsO_4^{3-} dominates in extreme alkaline waters (Henke & Hutchison, 2009; Smedley & Kinniburgh, 2002).
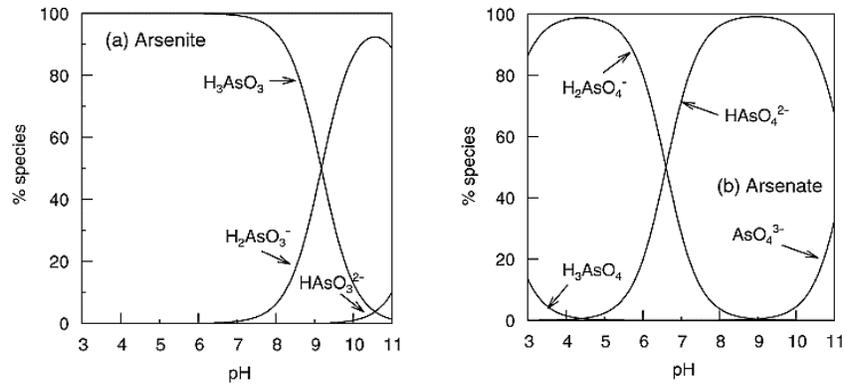
Figure 1-3. Arsenite (left) and arsenate (right) speciation as a function of pH. Taken from (Smedley & Kinniburgh, 2002)

Often, when groundwater arsenic concentrations are elevated, arsenic originates from geologic sources (Barringer & Pamela, 2013; Smedley & Kinniburgh, 2002), but it may also occur as a byproduct of mining activities. Arsenic can be found as a major constituent in more than 200 minerals (Nriagu et al., 2007; Smedley & Kinniburgh, 2002). Of those 200 minerals, approximately 24 arsenic bearing minerals are frequently found in hydrothermal veins, ore deposits, and rocks (Barringer & Pamela, 2013). Some of these minerals include elemental As, arsenides, sulphides, oxides, arsenates, and arsenites (Smedley & Kinniburgh, 2002).

Arsenic is also found in coals. All coals contain some arsenic (USGS, 2006). Southwestern China has some of the highest arsenic content in coals reported, between 826-2,578 mg/kg (Nriagu et al., 2007). The U.S Geological Survey (USGS) maintains a database of over 7,000 analyses of American coals. The mean arsenic content of the 7,000 samples is about 24 mg/kg. The highest reported was 2,200 mg/kg (Barringer & Pamela, 2013). Pyrite is the main source of arsenic in coals with high arsenic content (Barringer & Pamela, 2013; Smedley & Kinniburgh, 2002; USGS, 2006), whereas the main source of arsenic in low arsenic coals is organic material (Barringer & Pamela, 2013). Pyrite, for example, is the largest fraction of

arsenic in bituminous coals, whereas in lower rank coals (lignite and subbituminous) the larger

portion of their arsenic in the organic portion (USGS, 2006).

Arsenic may arise from anthropogenic activates as well. These activities include mining

and processing of ores, nonferrous metal mining and smelting, fossil fuel (coal or peat)

processing and combustion, wood preserving, pesticide production and application, and disposal

and incineration of municipal and industrial waste (Nriagu et al., 2007; Wang & Mulligan,

2006). Elevated concentrations of arsenic due to anthropogenic activities in soils occur only

locally (Bhattacharya et al., 2007). These anthropogenic sources of arsenic can negatively affect

surface and groundwater through discharge and runoff.

The threat to human health from arsenic contamination has motivated many studies on

variables controlling the distribution of arsenic and conditions contributing to the mobilization of

arsenic from sediment into groundwater. Studies reveal that arsenic concentrations in

groundwater are controlled by many complex sets of conditions and biogeochemical processes

(Smedley & Kinniburgh, 2002). Of those sets of complex conditions redox potential and pH are

the most important factors controlling arsenic speciation. High arsenic waters can occur under

both reducing and oxidizing conditions. Furthermore, the mobility of As(III) and As(V) is

controlled by adsorption onto (and redox reactions with) metal oxides and clay minerals (Sharma

et al., 2011).

In anoxic environments microbes survive by capturing some of the energy released when

they catalyze the transfer of electrons from a reduced species (acetate, lactate, dihydrogen) to an

oxidized species (dioxygen, nitrate, ferric iron, or sulfate) (Bethke et al., 2011). The energy

captured by the microbes is used to perform life functions such as cell maintenance (Bethke et

al., 2011) and synthesis (Metcalf & Eddy, 2003). As the microbes transfer electrons they oxidize

the donor species and reduce the acceptor. This process controls the redox state, quality, and chemical properties of the subsurface environment they reside in (Bethke et al., 2011).

An important factor in any groundwater, and critical for arsenic, is the gradual exhaustion of oxygen sources. Although the redox potential can be measured in an aquatic environment, the redox state is best predicted from the dissolved species present (dioxygen, nitrate, ferric iron, or sulfate) (Ravenscroft, et al., 2009). This is best described using a concept known as the thermodynamic ladder in geomicrobiology, which illustrates the distribution of microbial activity in groundwater flow. The thermodynamic ladder describes how microorganisms use the most energetically favorable electorn accetors. The most favorable electron acceptors, listed in decreasing order, are nitrate (NO_3^-), Fe(III), sulfate (SO_4^{2-}), and methane (CH_4). For example, near recharge areas in an aquifer, atmospheric oxygen will dissolve in the groundwater as the aquifer is recharged. As the groundwater flows away from the recharge area nitrate is reduced to nitrogen gas. As the oxygen and nitrate is exhausted manganese and iron are reduced. Further increasing reduction will cause sulfate to reduce to sulfide. If iron is present in the solution as sulfate is reduced to sulfide, pyrite will precipitate (Ravenscroft, et al., 2009).

This is a critical factor for arsenic since reducing conditions, sufficient to allow Fe(III) and SO_4 reduction to occur, can trigger the release of arsenic (Smedley & Kinniburgh, 2002). The presence of organic carbon in the sediment largely controls the rate at which these reducing conditions are established (Smedley & Kinniburgh, 2002) since organic carbon consumes all available sources of oxygen (Ravenscroft et al., 2009). In near neutral, reducing water, the mechanism believed to mobilize arsenic is reductive-dissolution. As microbes decompose natural organic matter (such as labile organic carbon) they transfer the liberated electron to ferric iron, which drives the reductive-dissolution of metal oxides and hydroxides (Langner et al., 2013).

The consumption of organic matter is known to generate high concentrations of bicarbonate and an increase in concentration of reduced species such as As(III), manganese, ferrous iron, ammonium, and DOC (Ravenscroft et al., 2009). The absence of oxidized species such as dissolved oxygen and nitrate are observed as well (Ravenscroft, et al., 2009). Under such conditions, sulfate concentrations are typically low or signs of sulfate reduction exist (Ravenscroft et al., 2009).

<center>*Selenium*</center>

Selenium, along with arsenic, has become increasingly significant in the environment because of its importance to human health (Plant et al., 2003). Contrary to arsenic, trace concentrations of selenium are esential for human, plant, and animal health (Plant et al., 2003; Simmons & Wallschlager, 2005; Wang et al., 2007). At times it has been called an "essential toxin" as it is required for certain cell process and enzynes (Stolz et al., 2006). Selenium deficiency has been linked to cancer, AIDS, heart disease, muscular dystrophy, multiple sclerosis, osteoarthropathy, immune system and reproductive disorders in humans and white muscle disease in animals (Plant et al., 2003). However, at higher doses it becomes toxic. The range of intake between selenium deficiency (<40 μg/d) and selenosis (poisoning due to excessive intake of selenium) (<400 μg/d) is narrow in humans (WHO, 1996). Selenosis can cause hair and nail loss and disruption of the nervous and digestive system in humans and to alkali disease in animals (Plant, et al., 2003).

One of the best documented cases of selenosis in animals occurred at Kesterson Reservoir, CA (Jacobs, 1989; Wu et al., 2000). During the 1970s, inflow to the reservoir was primarily surface water, however, between 1981 and 1986 the majority of the inflow was from shallow agricultural drainage in which the reservoir acted as evaporation ponds (Plant et al.,

<center>16</center>

2003). The agricultural drainage inflow contained between 250 to 350 µg/L of selenium (Plant, et al., 2003). The high concentration of selenium resulted in negative health effects of fish and wildlife (Plant et al., 2003). Twenty-two percent of eggs contained dead or deformed embryos (Tokunaga et al., 1994). The deformities encompassed missing or absormal eyes, beaks, wings, legs, and feet (Plant et al., 2003).

Selenium is a naturally occurring trace element found in the earth's crust, soils, and minerals (Simmons & Wallschlager, 2005). It can occurs in four oxidation states, selenate (Se(VI)), selenite (Se(IV)), elemental selenium (Se(0)), and selenide (Se(-II)) (Stolz et al., 2006; Plant et al., 2003; Simmons & Wallschlager, 2005) and as organic compounds (Herbel et al., 2002). In aquatic environments selenium primarily exist in two soluble forms, selenate (Se(VI)) and selenite (Se(IV)), (Plant et al., 2003; Zawislanski et al., 2001). In contrast, elemental selenium (Se(0)) and selenide (Se(-II)) are insoluble in water (Plant et al., 2003). The difference species distribution of selenium vary with the environent, however, soluble selenate and selenite are typically found in oxic environments whereas insoluble elemental selenium is largely found in anoxic environemnets (Stolz et al., 2006). In aquatic environments selenium has three fates: 1) it can be taken up by organisms; 2) it can be complexed with particulate/colloidal matter and sediments; 3) or it can be dissolved in solution (Simmons & Wallschlager, 2005).

Selenium can be immobilized by chemical and microbial reduction of Se(VI) and Se(IV) to Se(0), adsorption of selenite to clay, minerals (such as iron minerals), and dissolved organic carbon (Simmons & Wallschlager 2005; Siddique et al., 2007), methylation, and colatilization (Siddique et al., 2007). Microbially mediated oxidation-reduction reactions has been directly linked to the production of Se(0) in many anoxic sediments (Stolz et al., 2006). This common link leads many researchers to believe selenium speciation in nature is strongly dependent on

microbial actibity (Stolz et al., 2006). Since selenium respiring bacteria are mostly heterotrohic, an organic carbon source is required to fuel selenium reduction.

Selenium content in coal can be high and typically range from 1 mg/kg to 20 mg/kg (Plant et al., 2003). In the United States the average selenium concentration in coal is 4.1 mg/kg (Plant et al., 2003). Similar to arsenic, the high selenium content is often linked the abudance of free iron oxides and other sorbents (Plant et al., 2003).

Effectiveness of Using Constructed Wetlands

The USEPA has identified a variety of FGD wastewater treatment technologies operated by coal-fired power plants for treating FGD blowdown wastewater in ***Steam Electric Power Generating Point Source Category: Final Detailed Study Report***. These technologies include settling ponds, chemical precipitation, biological treatment, constructed wetlands, vapor-compression evaporation system, and the design/operation of zero discharge. According to the report most power plants use settling ponds to treat FGD wastewater. However, the uses of more advanced wastewater treatment systems are increasing due to the implementation of stringent requirements imposed by some states. Potential FGD wastewater treatment systems that will aid plants meet these requirements are constructed wetland treatment systems (CWTS). CWTS can be designed to transform targeted constituents to stable chemical forms, which may decrease their mobility, bioavailability, and dissolution (Eggert et al., 2008). They offer an effective and economical alternative to improving effluent water quality through biological and physical means.

CWTS are engineered systems designed to use the natural biological process involving vegetation, soils, and microbial activity to reduce metal, nutrient, biochemical oxygen demand (BOD) and TSS concentration in wastewater (Vymazal, 2010; USEPA, 2009). CWTS are

18

designed to capitalize on the same process occuring in a natural wetland but within a more controlled environment (Vymazal, 2010). CWTS can be classified according to their hydrology: free water surface (FWS) are those wetlands with the water surface open to the atmosphere, and subsurface flow systems (SSF), which have the water table elevation that is beneath the soil surface (Vymazal, 2010). SSF are further classified according to the flow direction: horizontal and vertical (Vymazal, 2010).

A FWS wetland typically consist of four major components: a basin or a channel, a barrier to prevent seepage, soil to support vegetation roots, and water at a shallow depth flowing through the system. The water surface in a FWS wetland is exposed to the athmosphere and the flow path through the sytem is horizontal (USEPA, 1993). A SSF wetland also consist of a basin or channel with a seepage prevention barrier, but the bed of soil contains porous media of a suitable depth (USEPA, 1993). The water level and flow path through the system remain below the top of the porous media. The flow path through the system can either be horizontal or vertical. The use of a SSF wetland can be advantageous over FWS wetlands. Maintaining the water level below the media surface reduces the risk of odors, exposure to the enviroment, and insects vectors (USEPA, 1993). The media also provides greater available surface area for treatment which will expedite the treatment process and decrease the overall area of the system.

CWTSs require low to zero energy input (Vymazal, 2010) and are widely prefered due to their low technology characteristics (Reagin, 2002). The capitol costs of CWTSs are generally slightly lower than alternative treatment systems and require much lower operational cost (Reagin, 2002). This is due to CWTS's use of naturally occurring processes, which require less skilled operators compared to alternatives methods that use mechanical process (Reagin, 2002) or expensive chemicals.

Traditionally CWTSs have been utilized to reduce nitrogen and phosphorus concentration and lower (BOD) in municipal wastewaters. However, the use of CWTSs to treat urban runoff and industrial wastewater by removing metals has increased in the last two decades. Today, CWTSs are considered a sustainable method for treating wastewater such as urban, agriculture runoff, municipal, industrial wastewater, and acid mine drainage (El-Sheikh et al., 2010). Although CWTSs has been proven to successfully treat many wastewaters, few studies have been published that evaluate the potential for the treatment of FGD wastewater. A notable study was conducted at Clemson University, which evaluated the performance of a pilot scale constructed wetland treatment system for FGD wastewaters (Eggert et al., 2008).

In Eggert et al. (2008) a pilot scale CWTSs were designed to remediate constituents of concern (arsenic, mercury, and selenium) by evaluating their biogeochemical cycling. Three different types of FGD wastewater were fed through two types of pilot-scale CWTS to determine their performance. The three types of FGD wastewater included formulated FGD water, actual FGD water, and pilot-scale scrubber FGD water. Both systems contained an equalization (EQ) basin in common. The EQ basin was utilized to control the contaminant loading entering the treatment system.

To evaluate the performance of the pilot scale CWTS with formulated and actual FGD a treatment system comprised of three replicated series of reactors per system with each system having four treatment reactors in series. The reactors included two reducing reactors, a rock basin, and an oxidizing reactor. The main objective of the reducing reactors was to immobilize selenium. Under reducing conditions Se (VI) is reduced to a less mobile Se (IV). The oxidizing reactor was designed to decrease the nutrient loading in the effluent.

To evaluate the performance of the pilot-scale CWTS fed with pilot-scrubber FGD wastewater two treatment systems each with two replicates were utilized. Each system was defined as either Ash CWTS or No-Ash CWTS. Each system contained four reactors in series which included two reducing reactors, a modified rock basin, and an oxidizing reactor. The most significant difference between the two systems lied in the modified rock basin. The system defined as Ash CWTS contained bottom ash whereas the rest of the reactors contained river sand hydrosoil.

For each experiment aqueous samples were collected from the EQ basin, inflows to the pilot scale –CWTS, and outflows from each reactor in series. The extent of removal and removal rates were calculated for each constituent of concern. The extent of removal for actual, formulated, and all for pilot-scale scrubber water is summarized in Table 1-4 .

Table 1-4. Mean extent of removal calculated by Eggert, et al. (2008).

FGD WW Type	Mean Extent of Removal		
	Mercury	Selenium	Arsenic
Actual	96.1%	80.1%	No removal
Formulated	93.2%	84.6%	64.4%
Pilot-Scale Scrubber	66.6%[a]	58.5%[a]	No removal

[a]Mean removal rates from the four scrubber water produced

The study determined that the pilot-scale CWTSs can decrease environmental risk by FGD wastewaters to a receiving stream. It was concluded that CWTs are viable treatment strategy for FGD waters specifically cadmium, COD, chloride, copper, mercury, selenium, and zinc. Eggert does warn the results from the study are site specific and results may differ for other sites because of factors such as the state regulatory criteria and wet scrubber operation (coal composition, chemical additives, and source of water).

21

Based on the information obtained from the pilot-scale studies at Clemson University, CWTSs were designed and constructed at power plants in North Carolina to specifically target selenium and mercury. Their results are summarized in ***Constructed treatment wetlands for flue gas desulfurization waters: Full-scale design, construction issues, and performance*** by Douglas Mooney and Cynthia Murray-Gulde. The FGD wastewater constituents of concern for the CWTS were primary mercury and selenium. The system consisted of four stages in series, which also included two wetland cells planted with bulrush, a rock cascade, and another with cattails. Performance evaluation was conducted from December 2006 to June 2007. The results showed variable performance, which ranged from 0-25% removal for selenium and 88-91% for mercury. It was concluded that the performance of the full scale CWTS was reasonable. The full-scale CWTS did achieved mercury and selenium levels established for the discharge into the facility's ash basin which has been in compliance with NPDES limits. At the time of the study, no numerical NPDES limit for selenium and mercury immediately following the CWTS existed, the requirement was only for monitoring and reporting. However, the facility has consistently been in compliance with the NPDES limits at the monitoring stations downstream of the CWTS and ash basin.

In the Eggert et al. (2008) study no measured removal extents were observed for arsenic in actual FGD wastewater. In the Mooney (2008) study only selenium and mercury were of concern. In Eggert et al. (2008) an interesting phenomenon occurred, the total arsenic concentration in the effluent (173 µg/L) was approximately 2.5 times greater than in the EQ basin (73µg/L) during the first sampling period. This indicates that leaching of insoluble forms of arsenic occurred during these sampling periods. Although it was not documented in Eggert et

al. (2008) experiment, it was concluded that insoluble forms of arsenic in FGD waters would occur in reducing reactors with Eh less than -200 mV and a pH of 7.

A similar situation was documented in Fox et al. (2003), a study that focused on the distribution of As, Mo, and V in the sediments of a constructed wetland flooded with drain water that contained elevated levels of As, Mo, and V. The study showed total arsenic concentrations in the sediments decreased significantly with depth. In other words, arsenic retention or accumulation in soil decreased with depth. In fact, a net loss of arsenic was observed in the sediments. To understand the reasons for the decrease of arsenic concentration Fox et al. (2003) focused on the different geochemical conditions present at different depths. The redox potentials were lowest at the sediment surface and increased with depth. The redox potentials of approximately -200 mV in the top 5 cm of soil were observed compared to 300 mV at a depth below 15 cm. This trend was due to high levels of organic matter and microbial activity at the surface and the presence of an underlying unsaturated zone at depths greater than 10-20 cm. Fox et al. (2003) concluded that under moderately reducing conditions arsenic may be mobilized, while under strongly reducing conditions arsenic is accumulated or retained in the sediment. Under moderately reducing conditions dissolution of adsorbing phases, such as Fe oxides and oxyhydroxides, occurs. Evidence of this is shown by higher water-soluble Fe and Mn concentrations at depth than at the surface. Near the surface, where strongly reducing conditions exist, precipitated Fe and Mn sulfides may have retained some trace elements such as arsenic. Most likely, there were several competing reactions including both dissolution or desorption and precipitation or adsorption occurring simultaneously. This study highlights the complexity of arsenic redox behavior.

Kansas Water Quality Standards

The Kansas Department of Health and Environment regulates surface water standards in the state of Kansas. Water quality levels in surface water are maintained to protect the existing uses of the surface water (KDHE, 2004). In the event a body of surface water is below the water quality criteria established in the regulation, the existing water quality will be fully maintained and protected (KDHE, 2004). The KDHE surface water standards for the constituents presented in this report are listed in Table 1-5. The standards are divided into three categories, aquatic life, agriculture, and public health. Aquatic life is further categorized into acute and chronic conditions. Agriculture is also further categorized into livestock and irrigation. Empty values in Table 1-5 mean there are no numeric criteria available for those substances.

Table 1-5. Kansas Surface Water Quality Standards: Tables of Numeric Criteria

Kansas Department of Health and Environment: Surface Water Standards					
Substance	Aquatic Life (µg/L)		Agriculture (µg/L)		Public Health (µg/L)
	Acute	Chronic	Livestock	Irrigation	Water Supply
Arsenic, Total	340	150	200	100	10
Boron, Total			5,000	750	
Calcium					
Iron					
Magnesium					
Nitrate (as N)					10,000
Potassium					
Selenium, Total	20	5	50	20	170
Sodium					
Sulfate			1,000,000		250,000
Sulfur					

Background on fluorescence spectroscopy to characterize Natural Organic Matter (NOM)

Natural organic matter (NOM) is a complex mixture of polyfunctional organic acids derived from the decomposition of terrestrial and aquatic animals and plants (Wang & Mulligan, 2006; Kordel et al., 1997) and is one of the largest sources of biologically available organic carbon in aquatic ecosystems (Fellman et al., 2010). NOM plays an important role in governing the speciation, solubility, mobility, and bioavailability of both organic and inogranic contaminants (Wang & Mulligan, 2006). This is due to NOM's high reactivity with soluble metals and metal (hydro)oxide surfaces (Wang & Mulligan, 2006).

NOM can be characterized into two categories: dissolved organic matter (DOM) and particulate organic matter (POM). DOM includes true dissolved matter along with colloidal material that passes through a 0.45 µm membrane filter. POM is compromised of material having a diameter greater than 0.45 µm. DOM includes chemically defined compounds such as carbohydrates and proteins, and humic substances (Lapworth et al., 2008). Of the major fractions of DOM, humic substances are most commonly studied. Humic substances are divided into three groups according to their solubility in aqueous solution at different pH values (Kordel, et al., 1997). These groups include humic acids, fulvic acids and humins. Humic acids are acid compounds that are soluble in bases but precipitate in acids (Kordel et al., 1997). Fulvic acids are acid compounds that are soluble in both bases and acids (Kordel et al., 1997). Humin is a component of humic substances that are not soluble in either bases or acids (Kordel et al., 1997).

Characterization of DOM has traditionally involved techniques such as stable isotope analysis (e.g ^{13}C and ^{15}N), bulk properies (e.g. C:N ratio), and amino acid, carbohydrate, and lingnin phenol measurements (Fellman, et al., 2010). More recently the light absorbing

characteristics of DOM have made it possible to characterize DOM using spectroscopic analysis. For example, fluorescence spectroscopy has been used in many studies to understand the source and composition of DOM in marine, wastewater, surface water, groundwater, and terrestrial ecosystems (Coble, 1996; Sierra et al.,2001; McKnight et al., 2001; Reynolds and Ahmad, 1997; Holbrook et al., 2006; Baker, 2001; Baker and Curry, 2004; Cannavo et al., 2004). Spectroscopic analysis is a fast and relatively inexpensive alternative technique to characterize DOM compared to traditional techniques. Fluorescence characterization of DOM provides reliable information about source, redox state, and biological reactivity (Fellman et al., 2010). The rapid collection of high resolution flourescence data at multiple excitation-emission wavelengths (Lapworth et al., 2008) has led to the use of excitation-emission matrices (EEMs). EEMs represent a 3-dimensional fluorescence landscape of a particular sample. DOM optical spectroscopic properties can provide important information on the quality of organic mater being consumed in an environment.

Fluorescence occurs when a molecule absorbs energy and causes an electron to be excited to a higher energy level (Fellman et al., 2010). As the electron returns to the original ground state, energy is lost as light or fluorescence (Fellman et al., 2010). Consequently, the excitation and emission wavelength at which the fluorescence occurs is related to specific molecular structures (Fellman et al., 2010). Several studies have identified common fluorophores (organic matter that fluoresces upon excitation) such as protein-like and humic-like, and indices used to quantify DOM fluorescence properties (Coble, 1996; McKnight et al., 2001; Ohno 2002; Wilson and Xenopolous, 2008: Cory and McKnight, 2005; Stedmon et al., 2003; Parlanti et al., 2000).

Three important indices used to quantify differences in fluorescence properties are defined in Table 1-6. One of the simplest and widely used is the fluoresence index (FI). It provides information about the source. It reflects the relative contribution of aromatic versus nonaromatic DOM (Coble 1996; McKnight et al., 2001). The freshness index estimates biological activity and stage of production. It will identify freshly transformed DOM or more decomposed DOM. The humification index is an indicator of humification or degree of DOM degradation.

Table 1-6. Ecological definitions for fluorescence indices. Derived from (Fellman, et al., 2010).

Parameter	Excitation (nm)	Calculated	Description
Fluorescence Index (FI)	370	$$\frac{470\ nm}{520\ nm}$$	Determines source of DOM: Microbial: high FI~1.8 Terrestrial: low FI~1.2
Freshness Index (β:α)	310	$$\frac{380\ nm}{\max 420 - 435\ nm}$$	Indicator of the contribution of recently produced DOM. β represents more recently derived DOM α represents more decomposed DOM.
Humification Index (HIX)	254	$$\frac{Area\ under\ 435 - 480nm}{Area\ under\ 300 - 445}$$	Indicator of humic substance content or extent of humification. Higher values indicate an increasing degree of humification.

Visual inspection of fluorescence peaks in EEMs is commonly used to analyze EEMs (Coble, 1996). Individual peaks can be compared across a wide range of samples. Although there are several fluorophores identified in the literature to date, Coble (1996) has identified the most prominent peaks as shown in Figure 1-4. Peaks A, C, and M represent humic-like substances while Peaks B and T represent protein-like substances (Fellman et al., 2010). Peaks A and C are derived from vascular plant sources, are aromatic, highly conjugated, and represent the highest

molecular weight fraction of DOM (Coble et al., 1998). Peak M is less aromatic and contributes a lower molecular weight DOM fraction to the DOM pool (Fellman et al., 2010).
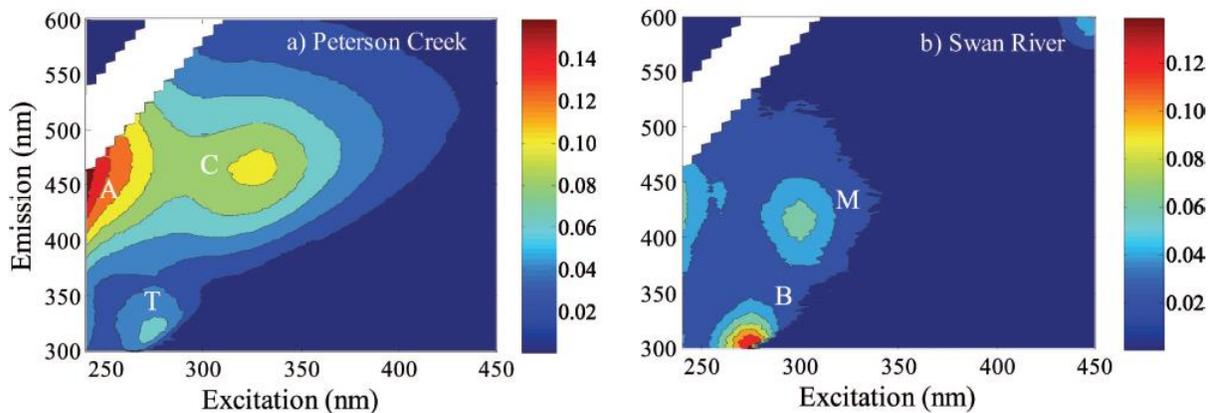
Figure 1-4. Example of EEMs showing the position of the five primary fluorescence peaks. Duplicated from (Fellman, et al., 2010).

Background on Solute Transport

To understand the theoretical backgrounds on solute transport assume a column packed with sediment is being supplied with water containing no solute at a constant flow-rate, Q (Skaggs & Leij, 2002). After some time, solute is suddenly introduced with a solute concentration (C_o) at a constant flow-rate (Q) (Skaggs & Leij, 2002). As the effluent concentration (C) is monitored over time the sharp increase in solute concentration introduced at the influent does appear in the effluent (Skaggs & Leij, 2002). Rather, the effluent concentration increases gradually over time (Skaggs & Leij, 2002). This is due to the fact that many of these solutes interact with the soil phase during transport (adsorption and desorption). Furthermore, these solutes may also experience chemical reactions and microbial transformations.

The results of the situation described above can be plotted in what is known as a breakthrough curve (Figure 1-5). The relative concentration (ratio of effluent and influent

28

concentration) is plotted as a function of pore volume (a dimensionless time variable that corresponds physically to the number of volumes eluted).

Three components distinctly represent different transport process, which include advection, diffusion, and hydrodynamic dispersion. Advection represents the mass flow of solute due to the motion of the soil water. In the absence of diffusion and hydrodynamic dispersion, solute molecules would be transported at the same rate as the average velocity of the soil water. If the breakthrough curve were to be plotted, in the situation where solute is influence by advection alone, a sharp concentration front at which the relative concentration changes from $C/C_o=0$ to $C/C_o=1$ would be observed (Figure 1-5). Diffusion is another process, which is the movement of solute molecules in response to a concentration gradient. Dispersion occurs because of the variations in magnitude and direction in velocity at the pore scale. The net result of the effects of advection, diffusion and dispersion causes spreading of the solute front (Figure 1-5). A gradual increase in concentration in observed rather than a sharp front (Figure 1-5). This is because some particles arrive prematurely while others arrive later (Figure 1-5).
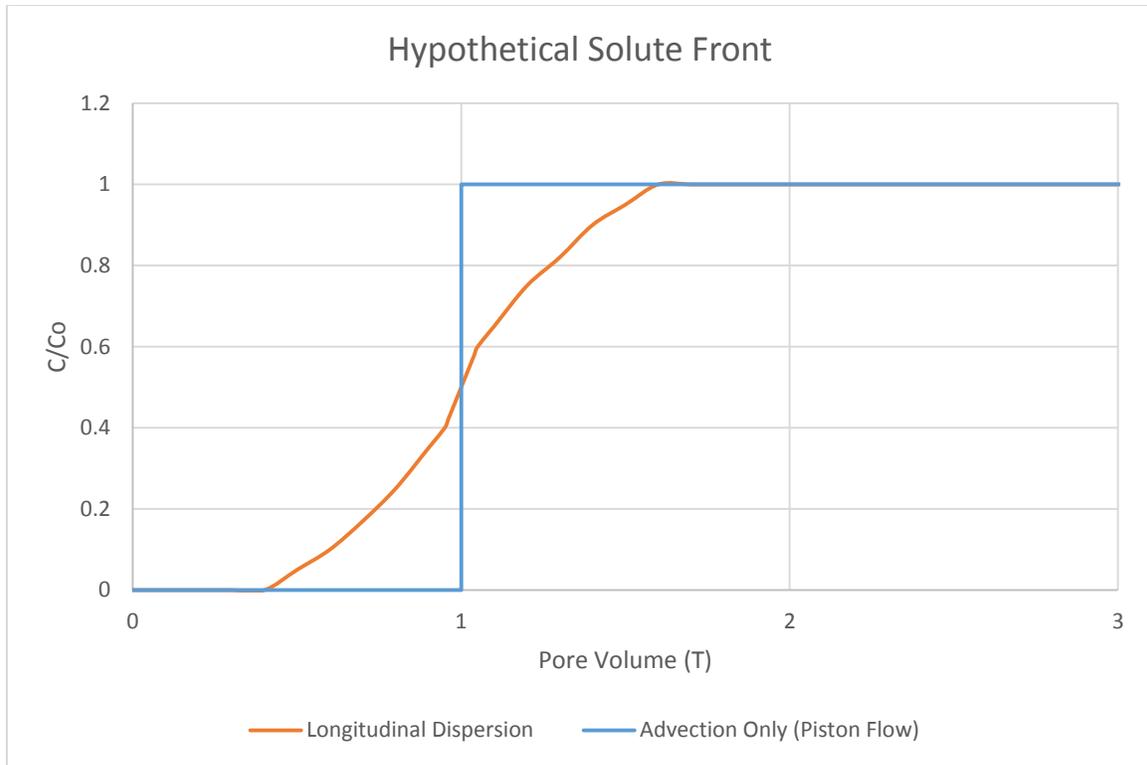
Figure 1-5. Breakthrough Curves for a hypothetical solute experiencing Advection, Diffusion, Dispersion.

Research Objectives

There is no question regarding FGD systems' effectiveness to reduce sulfur dioxide and other harmful atmospheric emissions. Data show that the increasing number of FGD systems has greatly decreased emissions of Clean Air Act criteria pollutants emissions. However, the decrease in air pollution has resulted in an increase in water pollution. This dilemma was made clear, more recently, by the media. In 2009, New York Times journalist Charles Duhigg shed light on the impacts of utilizing FGD systems in a newspaper article titled ***Cleansing the Air at the Expense of Waterways***. Duhigg (2009) discusses the tens of thousands of gallons of FGD wastewater discarded into southwest Pennsylvania's Monongahela River, which is a source of potable water for 350,000 people. A resident in the area was quoted saying "it's like they

decided to spare us having to breathe in these poisons, but now we have to drink them instead…we can't escape." Consequently, research is needed to develop and implement a sustainable remediation plan to minimize the environmental effects resulting from FGD wastewater.

In this study the effectiveness of using constructed wetlands is explored as a possible remediation technology to treat FGD wastewater from a coal-fired power plant in Kansas. The USEPA and other studies (Eggert, et al., 2008; Mooney & Murray-Gulde, 2008) have developed strong evidence for its effectiveness. To simulate constructed wetlands a continuous flow-through column experiment was conducted with undiluted FGD wastewater and surface sediment from a power plant in Kansas. To optimize the performance of a CWTS the following hypothesis were tested:

1. Decreasing the flow rate improves the performance of the treatment wetlands due to an increase in reaction time between FGD wastewater and sediments.

2. The introduction of microbial cultures will increase the retention capacity of the columns since constructed wetlands improve water quality through biological processes.

3. The introduction of a labile carbon source will improve the retention capacity of the columns since microorganisms require an electron donor to perform life functions such as cell maintenance and synthesis.

The FGD wastewater collected from the Jeffrey Energy Center possessed negligible concentration of arsenic (0.72 μg/L, Table 3-1). However, EPRI (2006) found a concentration of arsenic that ranged from 10 to 380 μg/L in eight power plants across the United States. Thus, the arsenic concentration has been spiked in the FGD solution of some columns to evaluate the

performance of the treatment wetlands with respect to the removal of arsenic as well as selenium in Hypotheses 1 – 3.

In the Clemson University study (Eggert et al., 2008) no arsenic removal was observed for actual FGD water in their constructed wetland systems. Instead, approximately 2.5 times the initial concentration of arsenic was observed in the effluent. This leads us to believe constructed wetlands may be promoting the leaching of naturally occurring arsenic in the soils. Constructed wetlands induce reducing conditions, which can potentially potentially promote the reductive dissolution arsenic. This led me to test the following additional hypothesis:

4. Reducing environments will cause arsenic desorption and dissolution resulting in the mobilization of arsenic.

FGD technology has great potential for reducing harmful air pollutants from being emitted. Now the challenge remains to design treatment systems for the sequestration of toxic trace elements that are released in the FGD wastewater stream. Therefore, evaluation of the sustainability and most effective process parameters of constructed wetland systems is important for power providers.

Chapter 2 - Methods and Materials

To determine the effectiveness of utilizing a constructed wetland as a remediation technology to treat FGD wastewater and to test the aforementioned hypotheses, a laboratory based continuous flow-through column outflow experiment (column experiment) was performed. Disturbed surface sediment and FGD wastewater were initially collected from Jeffery Energy Center in St. Mary's, Kansas. The surface soil, FGD wastewater, and columns were then prepared. The column experiment consisted of establishing steady-state upward flow conditions in a soil column and then introducing the FGD wastewater at the inlet while maintaining the same flow rate. Outflow samples were collected periodically and analyzed for constituents of concern. The methods and materials used to perform the column experiment are presented in this chapter.

Site Description

The Jeffrey Energy Center (JEC) is a coal-fired power plant located in Emmett Township, Pottawatomie County, approximately 100 miles northwest of Kansas City, Kansas ($39°17'10"$N, $96°07'01"$W) as shown in Figure 2-1. JEC is jointly owned by Westar Energy (92%) and Great Plain, Inc. (8%) (Westar Energy, 2014). Westar Energy is the largest electric utility company in the state of Kansas (Westar Energy, 2014). It provides nearly 700,000 residential, commercial, and industrial customers with electric utility using wind, coal, nuclear energy, natural gas, and landfill gas generation (Westar Energy, 2014). JEC is the largest plant in Kansas using up to 36,000 tons of low-sulfur coal per day or 9 to 10 million tons per year and generates 175 million megawatt-hours annually (Westar Energy, 2014).
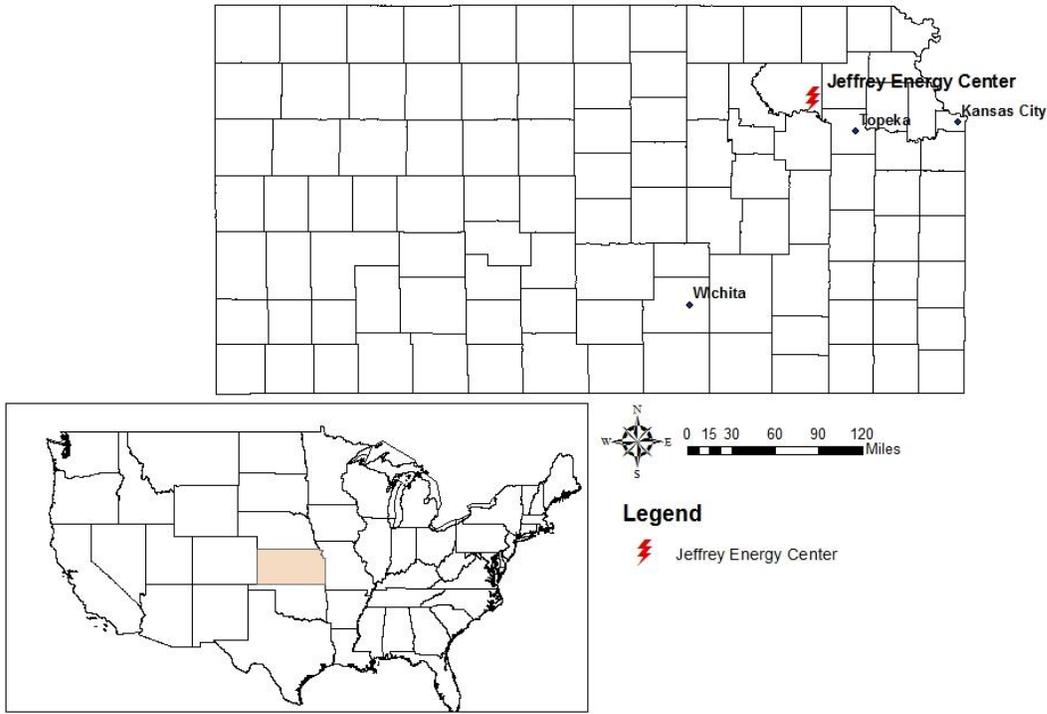
Figure 2-1. Location of Jeffrey Energy Center
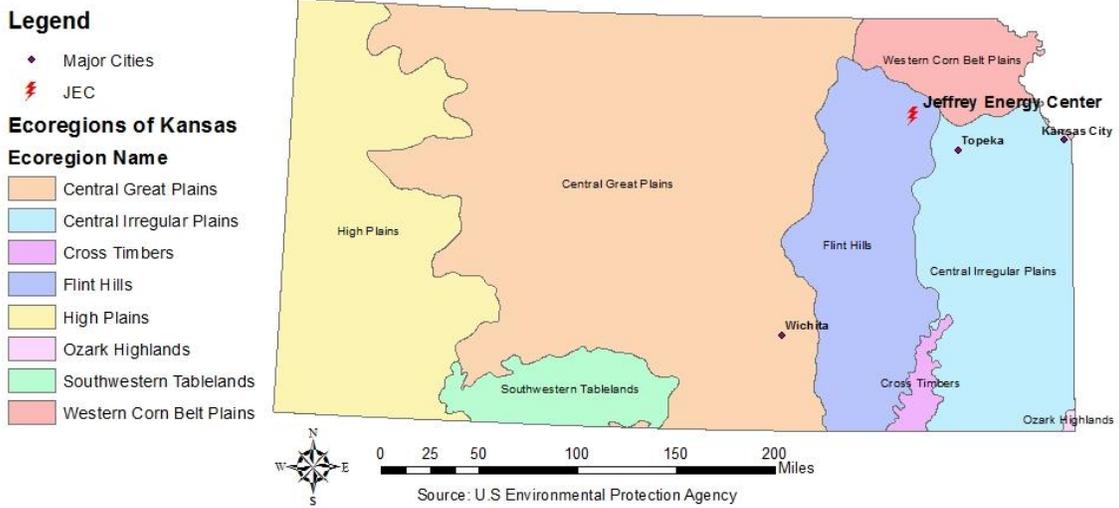
Figure 2-2. Ecoregions of Kansas. JEC is located in the northwest region of the Flint Hills ecoregion.

Jeffery Energy Center is located in the Flint Hills ecoregion (USEPA Level III ecoregions) as shown in Figure 2-2. The Flint Hills ecoregion marks the western edge of the tall grass prairie and is the largest remaining tall grass prairie in the Great Plains (Chapman et al., 2001). It is characterized by rolling hills composed of shale and cherty limestone, rocky soils, and by humid, wet summers (Chapman et al., 2001). Average annual precipitation in the area ranges from 28 to 35 inches (Chapman et al., 2001). JEC is located in an area that contains three types of soils, a Tully silty clay loam, a Benfield silty clay loam, and Clime-Sogn complex (**Error! Reference source not found.**).

Figure 2-3. Soil unit map overlaid on the aerial photograph of JEC.

To reduce emissions JEC is equipped with sulfur dioxide scrubbers. The sulfur dioxide scrubbers were recently upgraded from a system capable of removing 60% to a system capable

of removing over 95% of SO_2 emissions (Westar Energy, 2014). It is also capable of reducing

mercury emissions by more than 25% and particulate matter emissions by over 20% (Westar

Energy, 2014). JEC uses a limestone forced-oxidation wet flue gas desulfurization process to

meet or exceed their emission rate expectation (Westar Energy, 2014). Consequently, the plant

utilizes 24,000 gallons of water per minute (Westar Energy, 2014).

JEC's scrubber blowdown from the limestone forced-oxidation wet FGD process is sent

to an onsite physical/chemical wastewater treatment facility and discharged into Lost Creek,

which eventually discharges into the Kansas River. However, the Kansas Department of Health

and Environment (KDHE) will begin enforcing stricter pollutant concentration limitation

entering the Kansas River. The current wastewater treatment facility is not capable of meeting

the stricter limitations. Due to that fact, JEC will construct and operate a constructed wetland

onsite to meet these limitations.

The CWTS being constructed at JEC is classified as a subsurface flow system (SSF). SSF

are systems which have a water table elevation beneath the soil surface. The CWTS will also

have an upward vertical flow direction.

Field Sampling

Disturbed surface sediment and FGD wastewater were collected from JEC in St. Mary's,

Kansas. Approximately 0.1 m^3 of surface soil and 40 L of FGD wastewater were collected. The

surface sediment was collected from a site adjacent to the constructed wetland construction site.

FGD wastewater was collected from JEC's physical/chemical wastewater treatment facility

effluent. Both the surface soil and FGD wastewater were transported by vehicle to Kansas State

University. FGD wastewater was stored at Throckmorton Plant Sciences Center at 4°C. Surface

soil was stored in the greenhouse located in the Throckmorton Plant Sciences Center. The sludge

used as inoculum was collected from a creek located at Kansas State University's North Farm (39°12'44.36"N, 96°35'36.96").

Treatments to Optimize CWTS Performance and Test Hypothesis

To optimize the performance of a CWTS and to test the hypothesis in this study four treatments and a control were developed. The treatments are shown in Figure 2-4. The control was composed of two columns which are fed with undiluted FGD WW. Column 1 had a flow rate of Q=1.42 mL/h (q=1.68 cm/d) and column 2 had a flow rate of 0.71 mL/h (q=0.84 cm/d). The flow rate, Q, was determined by the consulting engineers responsible for designing the full scale CWTS at JEC. The control in this experiment will serve two purposes. It served as a control for evaluating effects of the four treatments and it was used to test hypothesis 1.
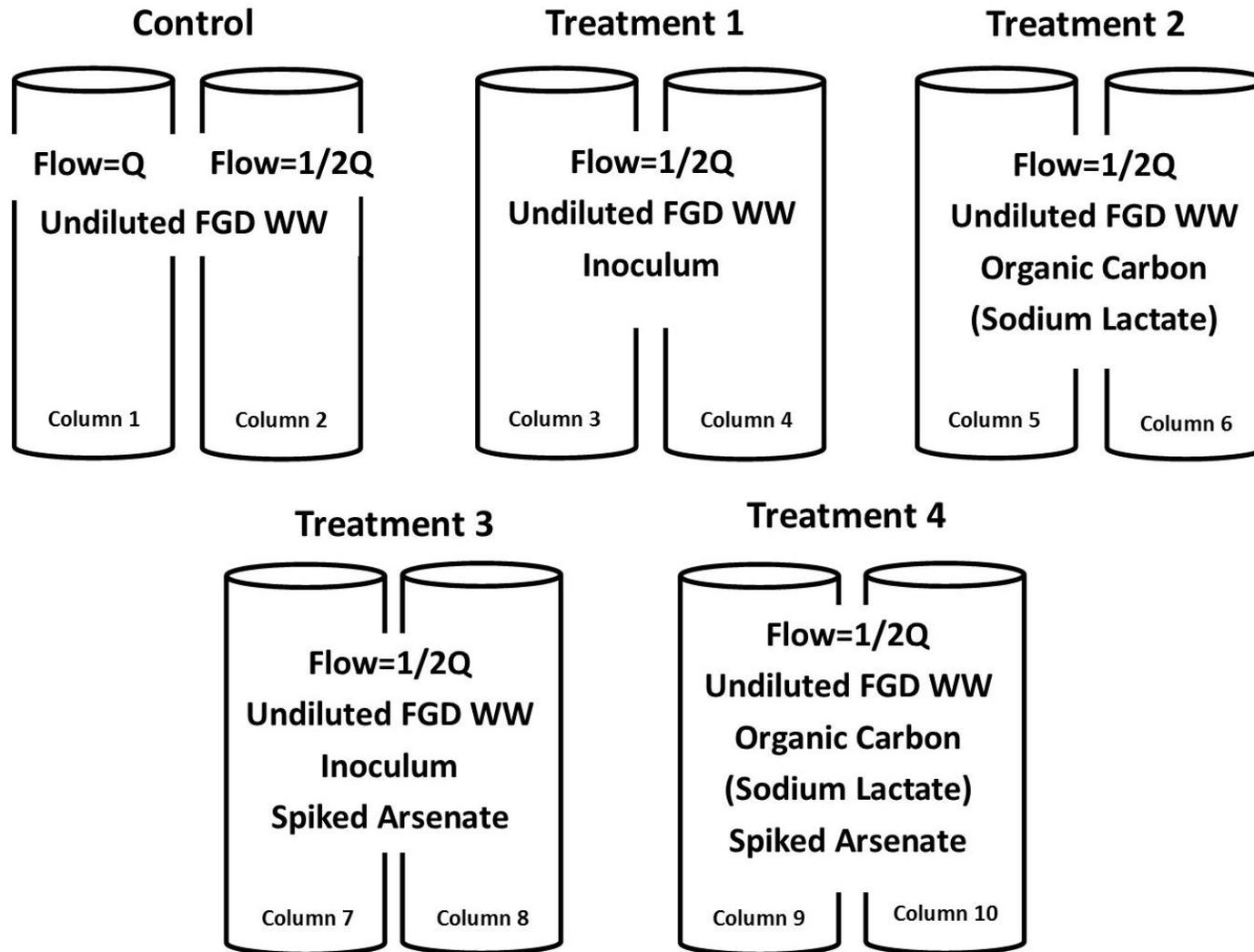
Figure 2-4. Treatments developed to optimize the performance of a CWTS and to test the hypotheses, where Q=1.42 mL/h (q=1.68 cm/d)

Treatment 1 was supplied with undiluted FGD wastewater at a 1/2Q flow rate, and the soil was inoculated with sludge obtained from the North Farm at Kansas State University. The treatment was replicated twice, utilizing columns 3 and 4 (Figure 2-4). This treatment was used to test hypothesis 2, which states the introduction of microbial cultures will increase the retention capacity of the columns because constructed wetlands improve water quality through biological process.

In Treatment 2 duplicate columns 5 and 6 were fed with undiluted FGD wastewater amended with labile organic carbon (sodium lactate) at 1/2Q flow rate (Figure 2-4). Treatment 2 was used to test hypothesis 3, which states the introduction of a labile carbon source will improve the retention capacity of the columns because microorganisms require an electron donor to perform life functions such as cell maintenance and synthesis.

Since the concentration of arsenic was negligible in the FGD wastewater collected at JEC, the FGD wastewater solution supplied in columns 7 through 8 was amended with arsenate (As(V)). Hypothesis 2 and hypothesis 3 were tested using these columns. To determine the possibility of arsenic dissolution and mobilization, the columns with negligible quantities of arsenic were used (columns 1-6)

Column Packing

The disturbed surface sediment was air dried, ground, and passed through a 2 mm sieve. The columns (L=30.5 cm I.D= 5 cm) were then packed using a wet procedure described by Klute (1986). In preparation for column packing the sieved soil was separated into 10 batches (for the 10 columns) having a mass of 1000 g each. To make the soil slightly cohesive 230 ml of water was added to each batch of sieved soil. The gravimetric water content of each batch was then

determined. Results for the gravimetric water content can be found in Appendix A. To determine

the gravimetric water content the following equation was used:

$$\theta_g = \frac{M_t - M_d}{M_d - M_p}$$

Where,

M_p= mass of pan.

M_t= total mass of the representative soil sample and pan.

M_d= Mass of dry soil sample and pan (dried at T=104°F)

The mass required to pack each column was then calculated using the equation below. The soil

mass used for each column can be found in Appendix A.

$$M_c = (1 - \theta_g)\rho_B V_c$$

Where,

M_c= Mass of soil required to pack each column

θ_g= Gravimetric water content

ρ_B= Bulk Density

V_c=Volume of column

For columns inoculated with sludge from the north farm, 0.8 g of wet sludge was added to every

100 g of soil. Approximately 0.8% of the column was composed of wet sludge.

Given the long length of each column (30.5 cm), the columns were packed in layers to a

target bulk density of 1.15 g/cm^3. The column walls were marked and divided into eight sections

(1.5 inches per section). The mass required to pack each column (M_c) was divided by 8 (M_c/8) to

determine the mass required to pack each section (M_s). The calculated mass of soil (M_s) was

weighed and packed into the column uniformly with a piston. The top of each layer was lightly

raked before packing the next layer to help assure uniform contact between layers.

Continuous Flow-through Column Outflow Experiment Apparatus

The experiment used a vertical column (L=30.5 cm, I.D=5 cm) (Figure 2-5) and upward flow to facilitate and maintain saturated conditions. A precision constant-volume syringe pump (KD Scientific) was used to apply the FGD solution into the columns at a constant flow rate. At the column entrance, a plate and filter (10 μm) were fitted to help distribute inflowing FGD solution over the entire soil surface. An end cap held the plate, filter, and O-ring (to prevent leaks) in place and connected the columns to the syringe pump. Two sealable (with valves) openings were used to bleed entrapped air and solution at the column entrance. The column exit was fitted with an end cap, plate, filter, and O-ring. An opening in the end cap funneled column outflow freely to a vial where the effluent is collected.
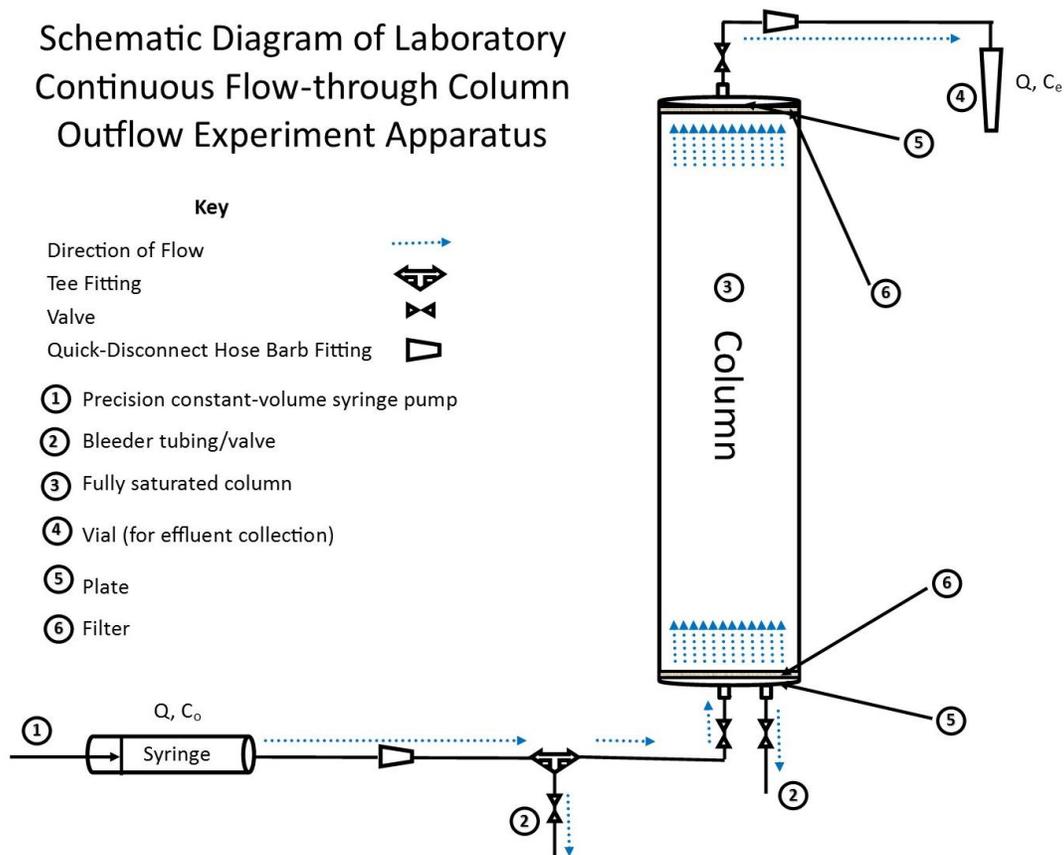
Figure 2-5. Schematic Diagram of Laboratory Continuous Flow-through Column Outflow Experiment Apparatus

Column Saturation and Reaching Steady-State Conditions

Columns were initially saturated with tap water, exposed to air for 7 days to lessen the chlorine residual, using a precision constant-volume syringe pump (KD Scientific) at a constant flow rate of 3.42 mL/h (q=4.04 cm/d). To determine the flow rate, the volume of air-filled pores was first determined using the following equation:

$$V_f = V_c(f - \theta_v)$$

Where,

V_f= Volume of air filled pores

f= porosity

θ_v= volumetric water content

To saturate the columns in 48 hours V_f was divided by 48 hours. That resulted in a flow rate of 3.42 mL/h (q=4.04 cm/d).

After saturating the columns, steady-state conditions were established by supplying each column with tap water. Tap water was supplied at a constant flow rate, Q=1.42 mL/h (q=1.68 cm/d) for column 1 and Q=0.71 mL/h (q=0.84 cm/d) for columns 2-10. Steady-state conditions were achieved when the volume being supplied into the columns was approximately equal to the volume exiting the columns. This process took 12 days.

FGD Wastewater Solution Preparation

Depending on the column, raw FGD wastewater was amended with arsenate and/or organic carbon. For columns 1-4 raw undiluted FGD wastewater was supplied into the columns. The FGD wastewater solutions in columns 5 and 6 were amended with labile organic carbon as sodium lactate. The solution was prepared by adding 1.92 g of sodium lactate to 2 L of raw undiluted FGD wastewater. The approximate DOC concentration of this solution was 310 mg

C/L(Table 2-1). The FGD wastewater solution in columns 7 and 8 were amended with arsenate

at a concentration of 56.25 mg As/L. To prepare the solution a standard solution containing 1000

ppm of arsenate was first prepared. Then 0.112 mL of the arsenate standard solution was added

to 2 L of raw undiluted FGD wastewater. FGD solution in columns 9 and 10 were amended with

both arsenate and organic carbon. The solution was prepared by adding 1.92 g of sodium lactate

and 0.112 mL of the arsenate standard solution to 2 L of raw undiluted FGD wastewater. The

concentrations of sodium lactate and arsenate added to each column are summarized in Table

2-1. The solutions were stored at 4°C until they were utilized in the column experiment.

Before introducing the respective FGD wastewater solution to the columns the solution

was purged with nitrogen gas for approximately 5-10 minutes. This was done to ensure that

deoxygenated FGD wastewater was introduced to each column.

Table 2-1. Concentration of sodium lactate, DOC, and arsenate added to each column

Column	Concentration of amended Sodium Lactate (mg/L)	Concentration of amended DOC (mgC/L)	Concentration of amended Arsenate (μg/L)
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	960	310	0
6	960	310	0
7	0	0	56.25
8	0	0	56.25
9	960	310	56.25
10	960	310	56.25

Column Sampling

The laboratory based continuous flow-through column outflow experiment (column

experiment) was conducted from January 21, 2014 to June 5, 2014 (140 days). Samples were

collected manually from vials every 48 hours. The mass of each sample was recorded (data can

be found in Appendix B). Approximately 15 mL of each sample was immediately filtered using a

0.45μm syringe filters (Environmental Express) and acidified by adding 2-3 drops of 6M HCl

prepared from trace metal-grade concentrated HCl acid (weight of 35-38%). Both unfiltered/non-

acidified and filtered/acidified samples were stored at 4°C until they were analyzed. Starting with

day 3, samples were analyzed for constituents of concern (if not otherwise stated) every 6th day.

For example, day 3, 8, 14, 20…128, 134, 140 were analyzed.

Column Sectioning

At the conclusion of the column experiment, columns were sectioned into six segments (2

inches 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. A

portion of the soil was placed in a container and immediately stored in a freezer (-17.7°C) until

analysis. The remainder of the soil was stored in a zip-lock bag at 4°C until analyzed. Before

storage, a representative soil sample was obtained from each section and the gravimetric water

content was determined.

Water Analyses

Total Dissolved Ion Analysis

The filtered and acidified samples were measured for total elemental analysis (B, Na, Mg, Ca, S,

Fe, and K) using a Varian 720-ES ICP-optical emission spectrometry (ICP-OES). Calibration

plots of each element were developed using six multi-element standards. Re-calibration was

performed after 30 samples and a duplicate of a sample was analyzed to check the repeatability

of the analytical method. Appropriate dilutions of samples were carried out to maintain

concentrations within the calibration range. A blank (acidified Milli-Q water only) and NIST 1643e "Trace Elements in Water" SRM were analyzed as quality assurance/quality control. In addition, spiked recoveries were assessed by adding a known amount of multi-element standard to selected water samples.

Arsenic concentrations of effluent samples were measure using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS; Varian Inc., Foster City, CA) with standard addition method to minimize matrix effect. Three micro-liters of 2000 mg/L Palladium (Pd) were used as the modifier to enhance the signal (absorbance) of As in GF-AAS. For quality control/assurance, a blank and a NIST standard for trace elements in waters (SRM 1643e) were used and 99-112% As recovery was achieved for the NIST sample. The spiked recoveries were in the range of 97-108%.

Acidified samples were filtered through 0.20 µm syringe filters for the determination of anions. Anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) were analyzed on an ion chromatograph (ICS-1000, Dionex Corporation). Appropriate dilutions were used to minimize instrument damage caused by FGD wastewater and maintain concentrations within the calibration range. Spiked recoveries and duplicates were used as a quality assurance/quality control to assess the analytical procedure.

Total Organic Carbon and Total Nitrogen

The filtered/acidified samples were measured for total organic carbon (TOC) and total nitrogen (TN) using a Shimadzu TOC-L TOC/TN analyzer. The instrument was calibrated using 1, 2, 5, 10, 20, and 50 mg C/L of TC standard solution prepared from reagent grade potassium hydrogen phthalate and 1, 2, 5, 10, 20 mg N/L of 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.

Conductivity and pH

The unfiltered/non-acidified samples were measured for conductivity (EC) and pH. EC was measured with a Fisher Scientific AR20 pH/Conductivity meter calibrated using LabChem Inc. (Pittsburg, PA) conductivity standard solution of 1409 μmho/cm @ 25°C. pH was measured with a Fisher Scientific Education pH meter calibrated with Fisher Scientific pH 4, 7, and 10 buffer solution.

Fluorescence Spectroscopy

EEM spectra were collected at increments of 3 nm excitation wavelengths over a 250 to 400 nm range and increments of 10 nm emission wavelengths over 350 to 600 nm range using a Horiba Aqualog Fluorometer. To correct for instrument specific biases spectra were collected in signal to reference (S:R) mode. EEMs were corrected for the inner filter effect using a modified Matlab correction function for the Aqualog Fluorometer. Intensities were normalized to the area under the Raman peak (excitation≈397 nm) for every new batch of samples that were analyzed. Ultra-pure blank water samples were subtracted from each sample EEM. Fluorescence indices, such as the FI, HIX, and BIX (Table 1-6), were calculated to quantify variations in DOM fluorescence properties and plotted over time.

Sediment Analysis

Sediment was analyzed prior to packing the columns and at the conclusion 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). In summary, 10 mL of trace metal-grade concentrated HNO_3 was added to 0.5 g of soil and digested in a microwave digestion unit (MARSXpress, CEM Corp.). A standard reference soil (NIST 2711a-Montana II) and a blank (concentrated HNO_3 acid) were included in every batch of test samples for quality assurance and control. All soil samples were digested in duplicate. In the first stage of the temperature program in the microwave digestion unit, the temperature in the soil-acid mixture increases to 165°C in 5.5 minutes. In the second stage, the temperature rose to 175°C in 4.5 minutes and was maintained at that temperature for an additional 5 minutes. The soil-acid mixture was then filtered using Whatman No. 42 filter papers. The solution was then analyzed for Fe, S, Mn, Al, B, and Si using ICP-OES and for As and Se using a graphite furnace.

Extent of Removal

To determine the total mass retained of each solute, the difference between the total mass of the solute introduced in the influent and total mass of solute measured in the effluent was calculated.

$$[C_o]_m - [C]_m = R_m$$

Where,

$[C_o]_m$ = Total mass of solute introduced in influent

$[C]_m$ = Total mass of solute measured in effluent

R_m = Total mass of solute retained

The extent of removal was calculated based on the following (variables are defined above):

47

$$1 - \left(\frac{[C_o]_m}{[C]_m}\right) * 100\%$$

Breakthrough Curves

Temporal variations for each solute are presented as breakthrough curves (Figure 2-6).

Relative concentration was plotted as a function of pore volume. Relative concentration is

defined as the ratio between the effluent concentration (C) and influent concentration (C_o). A

pore volume, a dimensions volume or time, is used in the place of time. The dimensionless

volume (T) is defined as the ratio between the cumulative volume of effluent collected at time (t)

and the total volume of water-filled pore spaces in the column. Thus, at T=1, the cumulative

volume of effluent collected equals the total volume of water filled pore space in the column.
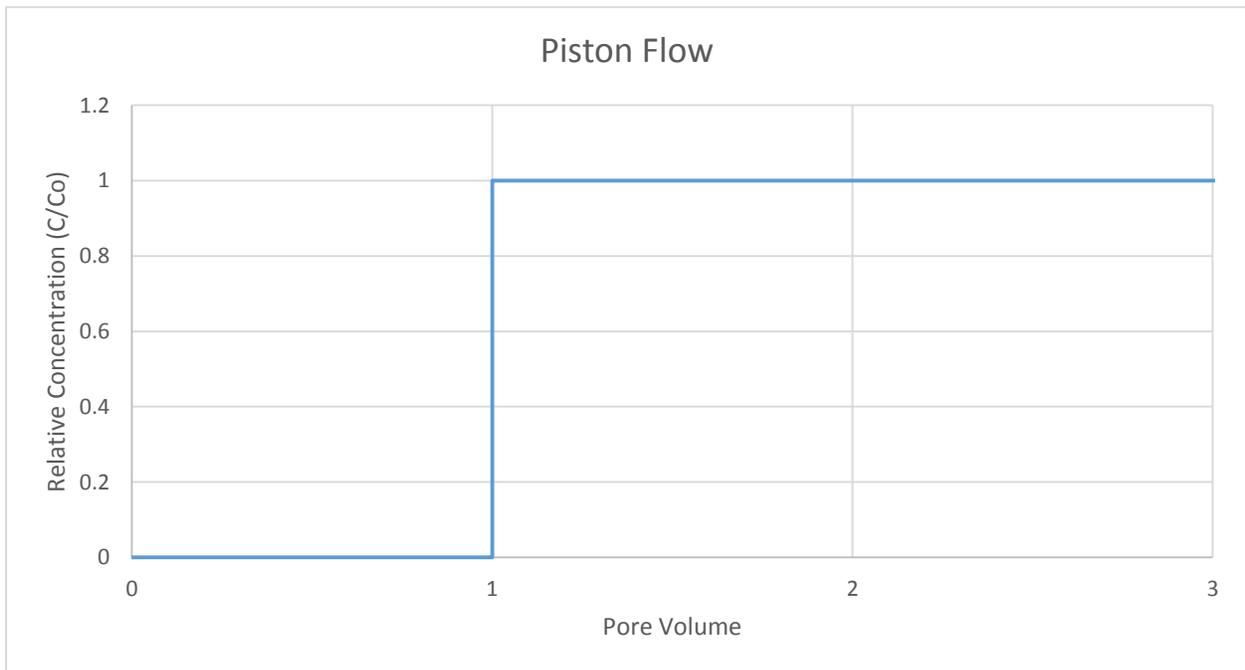
Figure 2-6. Example of breakthrough curve.

Chapter 3 - Results

Chemical Composition of Flue Gas Desulfurization Wastewater

FGD wastewater collected from JEC was analyzed for water chemistry parameters and total elemental composition (Table 3-1). The chemical composition of FGD wastewater from JEC has values that are at the lower range of the EPRI study. This is likely due to the fact that wastewater collected from JEC was from the plant's wastewater facility effluent and not directly from the FGD system effluent. Selenium concentration was at the lower range of the EPRI study at 170 μg/L. Additionally, arsenic concentration in the FGD wastewater collected at JEC was negligible (0.72 μg/L) compared to the range of FGD wastewater from the EPRI study of eight power plants.

Table 3-1. Chemical Composition of FGD wastewaters collected from JEC in St. Mary's, KS

Constituent	Concentration	EPRI Study Range	KDHE STDs		Units
			Acute	Chronic	
Total Alkalinity	840	26-4,500			mg/L
Arsenic, Total	1.21	10-380	340	150	µg/L
Boron, Total	5.55	16-450			mg/L
Bromide	22.1				mg/L
Calcium	575	700-33,000			mg/L
Chloride	965	460-25,00	860		mg/L
Conductivity	9.34	4.2-67			mS/cm
Dissolved Organic Carbon	31.0				mg/L
Total Hardness	380	3,000-5,600			mg/L
Iron	0.03	15-280			mg/L
Magnesium	703	1.9-52			mg/L
Nitrate (as N)	186				mg/L
Nitrite	18.8				mg/L
Nitrogen, Total	99.0				mg/L
Potassium	118	27-577			mg/L
pH	6.29	6.1-7.3			pH
Selenium	175	70-1,800	20	5	µg/L
Sodium	703	66-45,000			mg/L
Sulfate	1355	9,500-9,500			mg/L
Sulfur	1870				mg/L
Salinity	4.88				ppt
TDS	3650	1,400-45,000			mg/L

To test the effectiveness of different treatments, FGD wastewater was amended with labile organic carbon (sodium lactate) and/or arsenate. The addition of these constituents changed the chemical composition of the FGD wastewater (Table 3-2). Columns 1 through 4 were supplied with undiluted FGD wastewater. Columns 5 and 6 were supplied with FGD wastewater solution amended with organic carbon (sodium lactate), columns 7 and 8 with arsenate, and columns 9-10 with both organic carbon and sodium lactate. The chemical composition for the FGD wastewater solution supplied into columns 5, 6, 9, and 10 was similar

to that of the original FGD wastewater solution, except that DOC and sodium concentration was much higher due to addition of sodium lactate (Table 3-2). Columns 9-10 have higher arsenic concentrations than the original FGD wastewater because arsenate was added to these duplicate columns (Table 3-2).

Table 3-2. Chemical Composition of FGD Wastewater solution supplied to columns (C_o).

Constituent	Concentration				Units
	Columns 1-4	Columns 5-6	Column 7-8	Columns 9-10	
Arsenic, Total	1.21	1.21	54.6	57.0	µg/L
Boron, Total	5.55	5.55	5.55	5.55	mg/L
Bromide	22.1	22.1	22.1	22.1	mg/L
Calcium	575	702	630	633	mg/L
Chloride	965	965	965	965	mg/L
Conductivity	9.34	9.53	9.19	9.79	mS/cm
DOC	31.0	291	31.0	291	mg/L
Nitrate (as N)	186	186	186	186	mg/L
Nitrite	18.8	18.8	18.8	18.8	mg/L
Nitrogen, Total	99.0	99.0	99.0	99.0	mg/L
Potassium	118	118	118	118	mg/L
pH	6.29	6.93	6.11	6.96	pH
Selenium	175	175	NA	NA	µg/L
Sodium	703	1040	751	938	mg/L
Sulfate-S	1355	1355	1355	1355	mg/L
Sulfur	1870	1870	1870	1870	mg/L

Chemical Composition of Sediment

The chemical composition of the sediment initially collected at JEC had high content of aluminum and iron (Table 3-3). Arsenic content (3.8 mg/kg; Table 3-3) was in the lower range in continental unconsolidated sediments, which varies between 3 and 10 mg/kg (Smedley and Kinniburgh, 2002).

Table 3-3. Sediment Chemical Composition

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

Breakthrough Curves and Percent Retained

Breakthrough curves and the percent retained in columns were developed for each constituent to determine the effectiveness of each treatment. The solution concentration in breakthrough curves were plotted so that they coincide with the mid-point of the volume increments collected.

Arsenic

Over the course of the experiment, extremely poor retention was observed for arsenic (Table 3-4). In fact, more arsenic was detected in the effluent than was introduced in the influent. In the control (1/2Q), for example, over 35x the mass introduced in the influent was detected in the effluent. In contrast, columns amended with inoculum and FGD solution amended with organic carbon retained the most arsenic, an average of 36% (Table 3-4).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain arsenic, $t(40) = -3.97$, $p = 0.0003$, Q flow rate leached less arsenic than 1/2Q ($Q_{mean} = 31.3$ µg/L, $1/2Q_{mean} = 52.9$ µg/L). The effectiveness of inoculum to retain arsenic was evaluated, $t(40) = 1.99$, $p = 0.05$, columns amended with inoculum leached less arsenic than control (1/2Q) ($Inoculum_{mean} = 41.3$ µg/L, $Control(1/2Q)_{mean} = 52.9$ µg/L). The effectiveness of organic carbon to

retain arsenic was evaluated, t(40)=-3.08, p=0.003, columns with FGD solution amended with organic carbon leached more arsenic than control (1/2Q) (Organic Carbon$_{mean}$=88.4 µg/L, Control(1/2Q)$_{mean}$=52.9 µg/L). The effectiveness of inoculum in As amended FGD solution to retain arsenic was evaluated, t(40)=-1.04, p=0.30, columns amended inoculum leached more arsenic than control (1/2Q) (Inoculum$_{mean}$=60.5 µg/L, Control(1/2Q)$_{mean}$=52.9 µg/L). The effectiveness of organic carbon in As amended FGD solution to retain arsenic was evaluated, t(40)=3.37, p=0.002, columns with FGD solution amended with organic carbon leached less arsenic than control (1/2Q) (Organic Carbon$_{mean}$=35.22 µg/L, Control(1/2Q)$_{mean}$=52.9 µg/L). The effectiveness of organic carbon and inoculum to retain arsenic was evaluated, t(40)=-4.35, p<0.001, columns with FGD solution amended with organic carbon leached more arsenic than columns amended with inoculum (Organic Carbon$_{mean}$=88.4 µg/L, Inoculum$_{mean}$=41.3 µg/L).

The control (1/2Q) produced the highest relative concentration over the life of the experiment of C/C$_o$=135 at T=6.6 (Figure 3-1). The control (Q) has the least variation over time compared to the other treatments where relative concentration falls and rises periodically over time (Figure 3-1). With the exception of the control (Q), overall, arsenic concentrations appear to increase over time (Figure 3-1). Although the highest relative concentration was produced by the control (1/2), the highest effluent concentration, C, was produced by the columns with organic carbon as shown in Figure C-1 and Figure C-2 in the Appendix C. The maximum effluent concentration for columns with inoculum was 168 µg/L and occurred between 4 and 4.3 pore volumes. The column with the lowest effluent concentration over time was the control (Q), which averaged 30 µg/L over the life of the experiment.

With the exception of columns with FGD solution amended with organic carbon, all columns met KDHE aquatic life acute and chronic standards of 340 µg/L and 150 µg/L,

respectively (Figure C-1and Figure C-2) Columns with organic carbon exceeded 150 µg/L on

two occasions over the life of the experiment for an average of 8 days (~0.3 pore volumes;

Figure C-1).

Table 3-4 Arsenic Extent of Removal

Treatment	Total Influent (µg)	Total Effluent (µg)	Mass Retained (µg)	Percent Retained
Control (Q)	5.77	150	-144	-2500%
Control (1/2Q)	2.89	110	-107[a]	-3710%
With Inoculum	2.89	89	-86[bc]	-2980%
With Organic Carbon	2.89	182	-179[bc]	-6220%
With Inoculum & As	130	83	47[b]	36%
With Organic Carbon & As	136	140	-4[b]	-3%

[a] significant difference between control (Q)
[b] significant difference between control (1/2Q)
[c] significant difference between inoculum/organic carbon
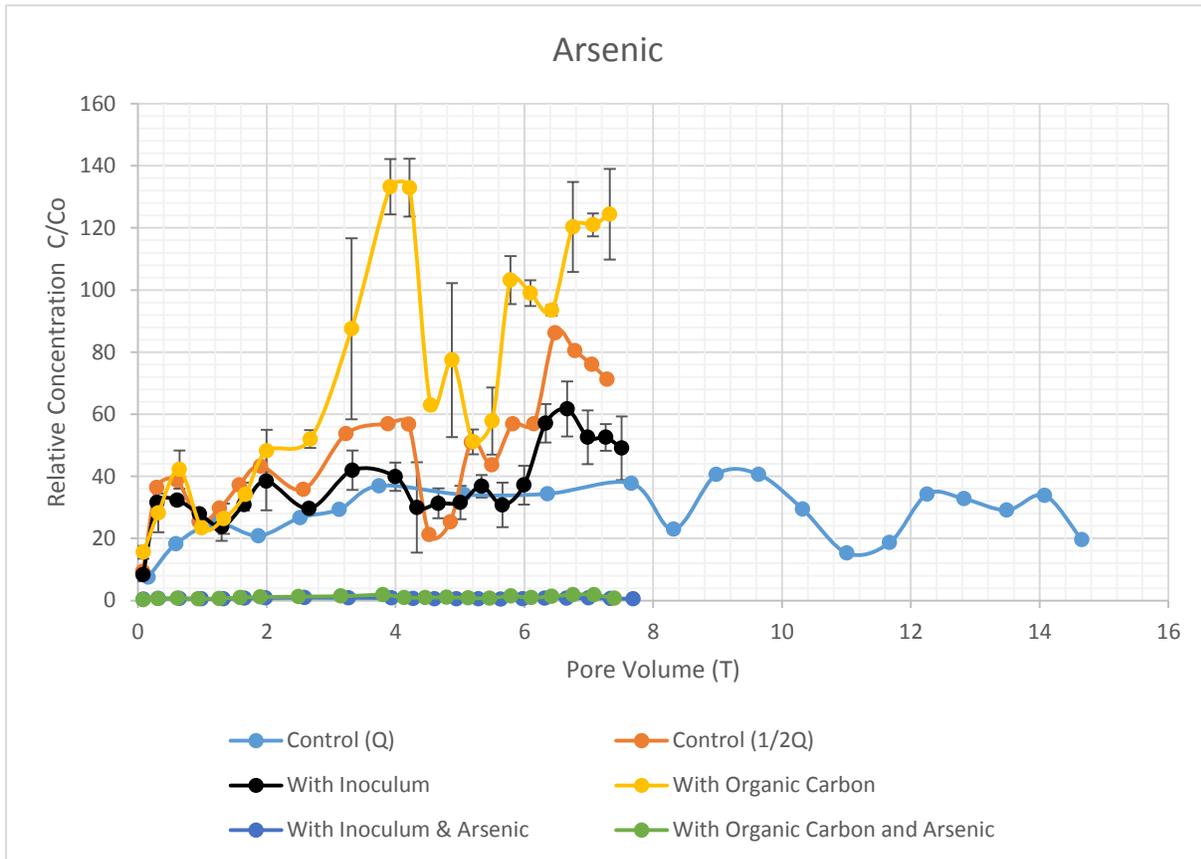
Figure 3-1 Arsenic breakthrough curves.

Boron

All columns, except the control (Q), retained over 90% of boron whereas the control (Q) only retained 72% as shown in Table 3-5. The data show that the addition of inoculum and organic carbon did improve boron retention in the columns when compared to the control. An average of 98% of boron was retained in columns with FGD solution amended with organic carbon and an average of 96% was retained in columns amended with inoculum compared to the control (1/2Q) where only 94% was retained. There is also a significant difference in boron retention when flow rates are compared. The control with the lower flow rate (1/2Q) retained 96% of boron compared to the higher flow rate (Q) where 72% was retained.

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain boron, $t(46)=3.35$, $p=0.002$, Q flow rate retained less boron than 1/2Q ($Q_{mean}=1.80$ mg/L, $1/2Q_{mean}=0.24$ mg/L). The effectiveness of inoculum to retain boron was evaluated, $t(46)=1.43$, $p=0.15$, but no significant difference was found ($Inoculum_{mean}=0.17$ mg/L, Control $(1/2Q)_{mean}=0.24$ mg/L). The effectiveness of organic carbon to retain boron was evaluated, $t(46)=2.30$, $p=0.03$, columns with FGD solution amended with organic carbon retained more boron than control (1/2Q) (Organic $Carbon_{mean}=0.14$ mg/L, $Control(1/2Q)_{mean}=0.24$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain boron was evaluated, $t(46)=2.61$, $p=0.01$, columns with inoculum retained more boron than control (1/2Q) ($Inoculum_{mean}=0.13$ mg/L, $Control(1/2Q)_{mean}=0.24$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain boron was evaluated, $t(46)=2.40$, $p=0.02$, columns with FGD solution amended with organic carbon retained more boron than control (1/2Q) (Organic $Carbon_{mean}=0.13$ mg/L, $Control(1/2Q)_{mean}=0.25$ mg/L). The effectiveness of organic carbon and

inoculum to retain boron was evaluated, $t(40)=1.01$, $p=0.31$, but no significant difference was found (Organic Carbon$_{mean}$=0.17 mg/L, Inoculum$_{mean}$=0.13 mg/L).

The breakthrough curves show no significant change over time for all columns except for the control (Q) (Figure 3-2). Relative concentration remained low as time progressed signifying strong boron retention (Figure 3-2). Concentration for boron in the control (Q) began to increase at 8 pore volumes (74 days) and broke through at approximately 13.2 pore volumes (122 days). Some spreading is observed as the control (Q) broke through indicating some dispersion is occuring (Figure 3-2)..

There is no KDHE acute or chronic aquatic criterion currently available for boron concentration as shown in Table 1-5. Thus, the concentration of boron will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-5. Boron Extent of Removal.

Treatment	Total Influent (µg)	Total Effluent (µg)	Mass Retained (µg)	Percent Retained
Control (Q)	26.5	7.55	18.9	72%
Control (1/2Q)	13.2	0.50	12.7[a]	96%
With Inoculum	13.2	0.37	12.9[b]	97%
With Organic Carbon	13.2	0.29	13.0[b]	98%
With Inoculum & As	13.2	0.31	12.9[b]	98%
With Organic Carbon & As	13.2	0.28	13.0[b]	98%

[a] significant difference between control (Q)
[b] significant difference between control (1/2Q)
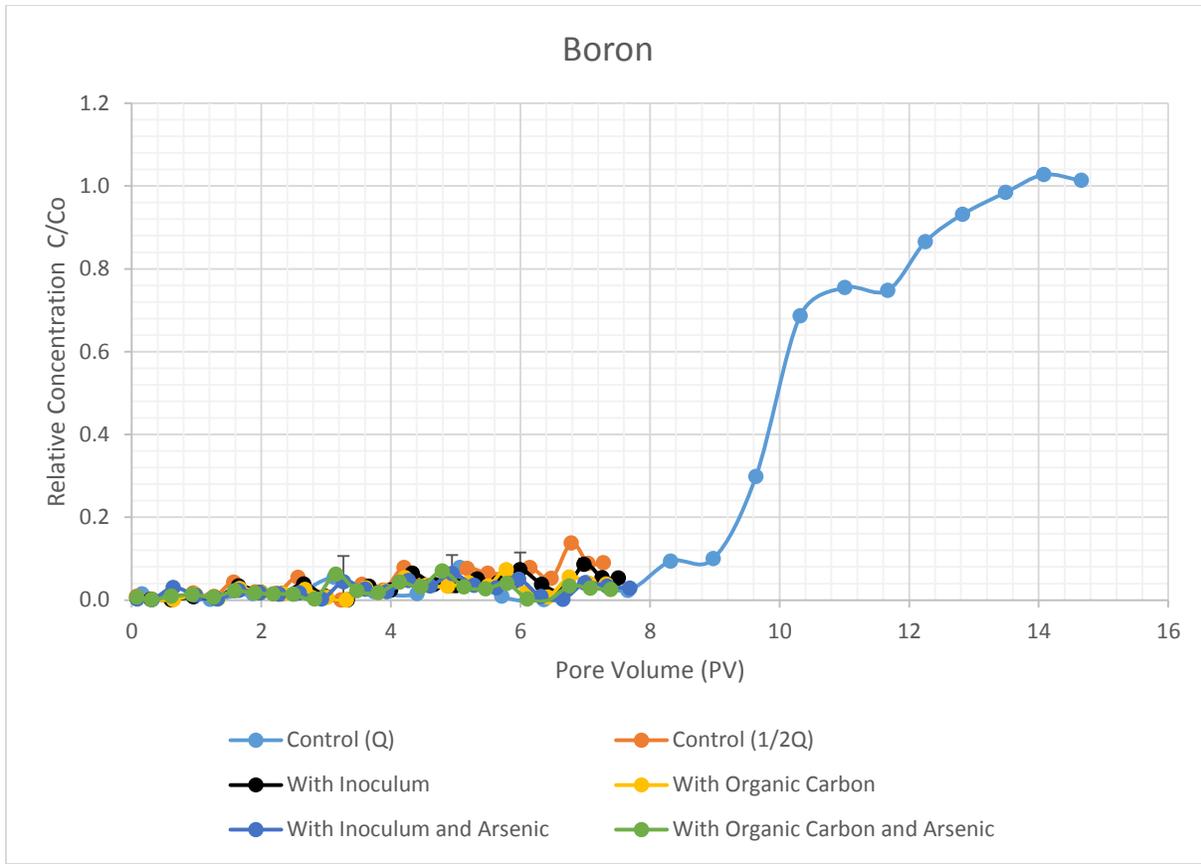
Figure 3-2. Boron breakthrough curves.

Calcium

The data show absolutely no retention of calcium occurred in any columns (Table 3-6). In

fact, more calcium was detected in the effluent than was introduced in the influent. For example,

in columns amended with inoculum, 1370 mg of calcium was introduced in the influent;

however, 2630 mg of calcium was detected in the effluent (Table 3-6). That means nearly 2

times the influent concentration of calcium was detected in the effluent of column 3. The data

also show flow rate influenced the amount of calcium that was leached. At the higher flow rate

(Q), approximately two times the influent concentration was detected in the effluent compared to

the lower flow rate (1/2Q) where nearly three times the influent concentration was detected (Table 3-6).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain calcium, $t(46)=-1.67$, $p=0.1$, but no significant difference was found (Q_{mean}=993 mg/L, $1/2Q_{mean}$=1160 mg/L). The effectiveness of inoculum to retain calcium was evaluated, $t(46)=-0.08$, $p=0.94$, but no significant difference was found ($Inoculum_{mean}$=1170 mg/L, Control $(1/2Q)_{mean}$=1160 mg/L). The effectiveness of organic carbon to retain calcium was evaluated, $t(46)=-0.32$, $p=0.75$, but no significant difference was found ($Organic\ Carbon_{mean}$=1190 mg/L, Control$(1/2Q)_{mean}$=1160 mg/L). The effectiveness of inoculum in As amended FGD solution to retain calcium was evaluated, $t(46)=-0.21$, $p=0.82$, but no significant difference was found) ($Inoculum_{mean}$=1180 mg/L, Control$(1/2Q)_{mean}$=1162 mg/L). The effectiveness of organic carbon in As amended FGD solution to retain calcium was evaluated, $t(46)=-0.52$, $p=0.60$, but no significant difference was found ($Organic\ Carbon_{mean}$=1212 mg/L, Control$(1/2Q)_{mean}$=1160 mg/L). The effectiveness of organic carbon and inoculum to retain calcium was evaluated, $t(46)=-0.25$, $p=0.80$, but no significant difference was found ($Organic\ Carbon_{mean}$=1190 mg/L, $Inoculum_{mean}$=1170 mg/L).

Immediately following the start of the experiment effluent calcium concentration exceeded the influent concentration ($C/C_o \geq 1$) in all columns (Figure **3**-**3**). In less than one pore volume a sharp increase in calcium is observed (Figure **3**-**3**). After the sharp increase in concentration a downward trend is observed in the all curves signifying calcium is decreasing over time (Figure **3**-**3**). The relative concentration in the control (1/2Q) reached steady-state at approximately 8 pore volumes thereafter maintaining a C/C_o of approximately 1.35 or a concentration of approximately 800 mg/L.

There is no KDHE acute or chronic aquatic criterion currently available for calcium concentration (Table 1-5). Thus, the concentration of calcium will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-6. Calcium Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	2740	4580	-1840	-67%
Control (1/2Q)	1370	2550	-1180	-86%
With Inoculum	1370	2630	-1260	-92%
With Organic Carbon	1680	2590	-917	-55%
With Inoculum & As	1500	2730	-1230	-82%
With Organic Carbon & As	1510	2700	-1190	-79%
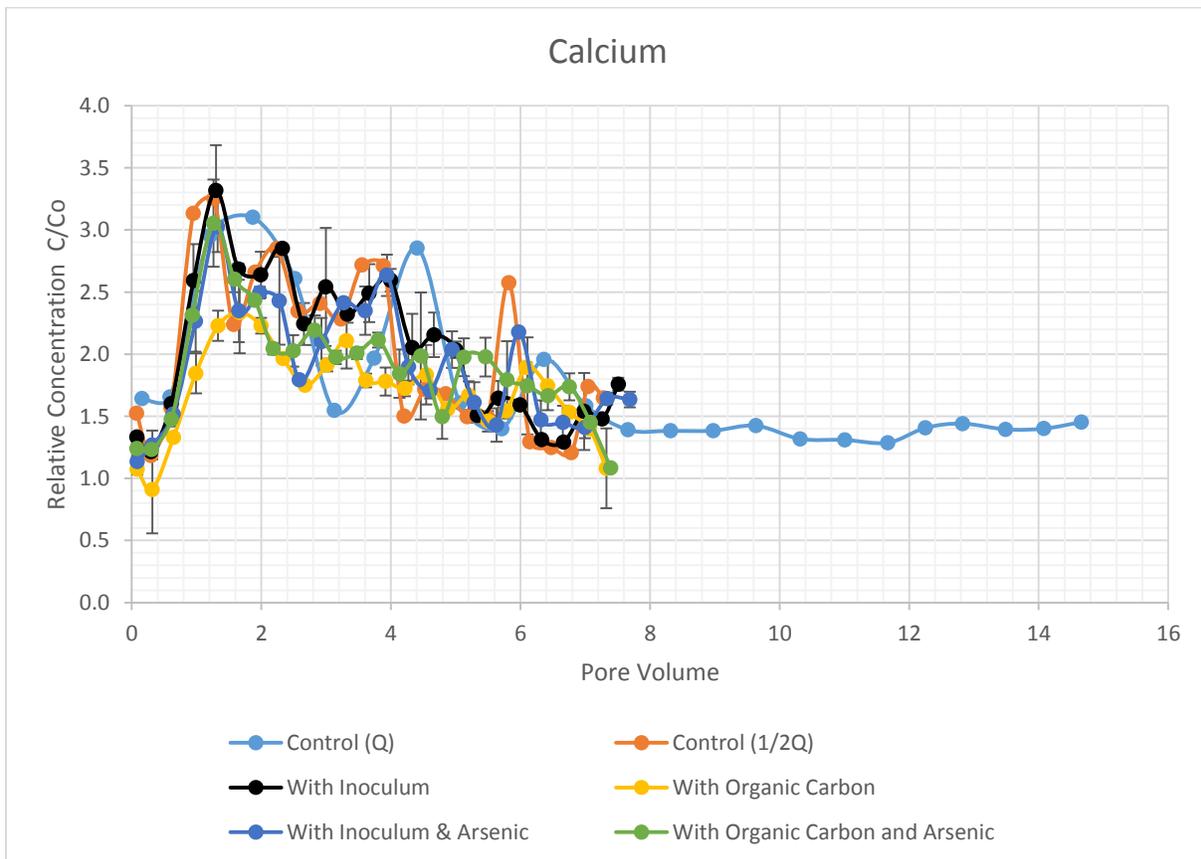
Figure 3-3. Calcium breakthrough curves

Chloride

Minimal chloride retention was observed in any of the columns (Table 3-7). Less chloride was observed in the column with the higher flow rate (Q) than the column with the lower flow rate (1/2Q). No significant differences was observed for the other treatments.

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain chloride, $t(46)=0.46$, $p=0.64$, but no significant difference was found ($Q_{mean}=1000$ mg/L, $1/2Q_{mean}=960$ mg/L). The effectiveness of inoculum to retain chloride was evaluated, $t(46)=-0.08$, $p=0.93$, but no significant difference was found ($Inoculum_{mean}=968$ mg/L, Control $(1/2Q)_{mean}=860$ mg/L). The effectiveness of organic carbon to retain chloride was evaluated, $t(46)=0.05$, $p=0.95$, but no significant difference was found ($Organic\ Carbon_{mean}=954$ mg/L, Control$(1/2Q)_{mean}=960$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain chloride was evaluated, $t(46)=0.05$, $p=0.96$, but no significant difference was found ($Inoculum_{mean}=965$ mg/L, Control$(1/2Q)_{mean}=960$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain chloride was evaluated, $t(46)=-0.07$, $p=0.94$, but no significant difference was found ($Organic\ Carbon_{mean}=966$ mg/L, Control$(1/2Q)_{mean}=960$ mg/L). The effectiveness of organic carbon and inoculum to retain chloride was evaluated, $t(46)=0.13$, $p=0.90$, but no significant difference was found ($Organic\ Carbon_{mean}=954$ mg/L, $Inoculum_{mean}=967$ mg/L).

All columns were similar in terms of the temporal trends in chloride relative concentration (Figure 3-4). The curves begin with no chloride concentration. An extremely sharp increase in concentration is observed as chloride breaks through at approximately 1.0 pore volumes. After chloride breaks through, concentrations remained relatively constant (with the exception of some noise) until the experiment concluded.

None of the columns met the KDHE acute aquatic life standard of 860 mg/L. After breaking through all columns exceeded 860 mg/L until the experiment concluded.

Table 3-7. Chloride Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	4600	4580	29	1%
Control (1/2Q)	2300	2060	243	11%
With Inoculum	2300	2130	170	7%
With Organic Carbon	2300	2020	285	12%
With Inoculum & As	2300	2160	139	6%
With Organic Carbon & As	2300	2150	153	7%
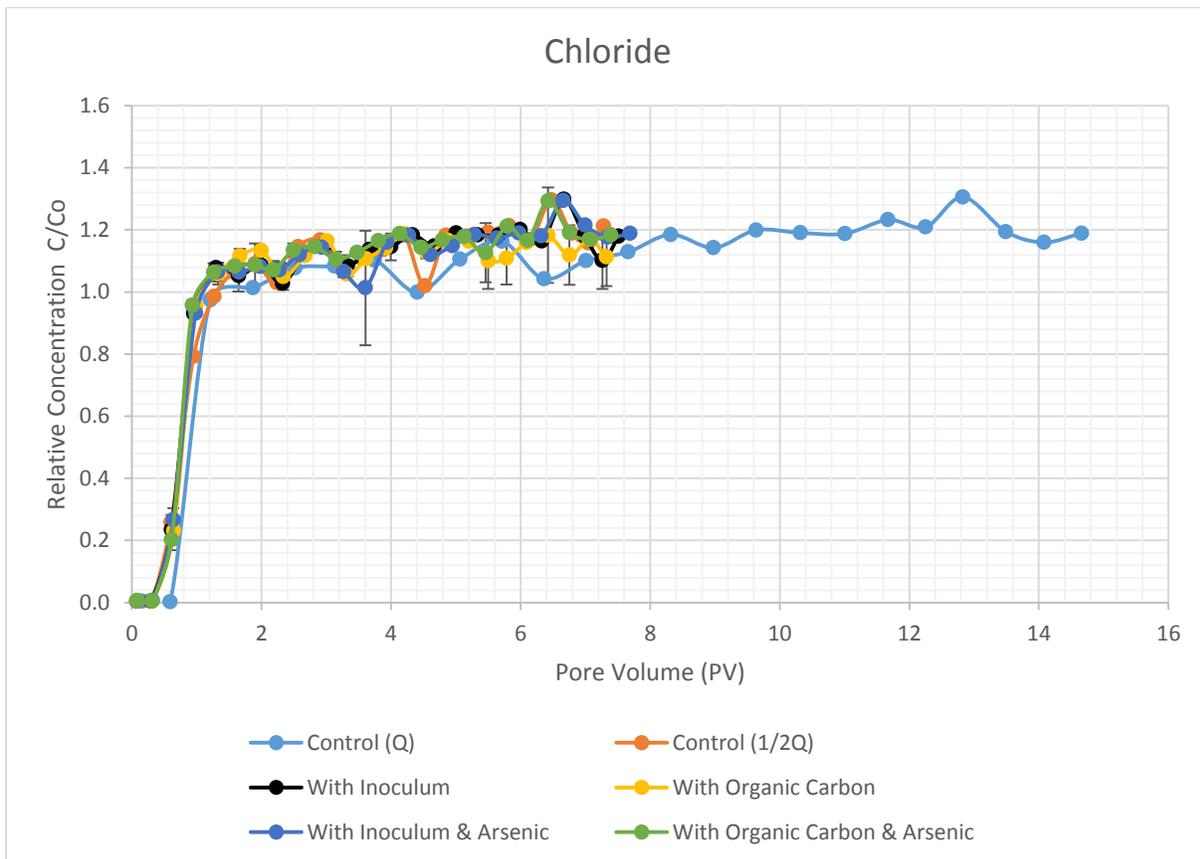
Figure 3-4. Chloride breakthrough curves.

Iron

No detectable amounts of iron were found in the influent (Table 3-2). For that reason an extent of removal is not presented. The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain iron, $t(46)=-0.01$, $p=0.99$, but no significant difference was found ($Q_{mean}=0.74$ mg/L, $1/2Q_{mean}=0.75$ mg/L). The effectiveness of inoculum to retain iron was evaluated, $t(46)=0.18$, $p=0.85$, but no significant difference was found ($Inoculum_{mean}=0.64$ mg/L, Control $(1/2Q)_{mean}=0.75$ mg/L). The effectiveness of organic carbon to retain iron was evaluated, $t(46)=-0.008$, $p=0.99$, but no significant difference was found ($Organic\ Carbon_{mean}=0.76$ mg/L, Control$(1/2Q)_{mean}=0.75$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain iron was evaluated, $t(46)=0.06$, $p=0.95$, but no significant difference was found ($Inoculum_{mean}=0.71$ mg/L, Control$(1/2Q)_{mean}=0.75$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain iron was evaluated, $t(46)=0.19$, $p=0.84$, but no significant difference was found ($Organic\ Carbon_{mean}=0.63$ mg/L, Control$(1/2Q)_{mean}=0.75$ mg/L). The effectiveness of organic carbon and inoculum to retain iron was evaluated, $t(46)=0.20$, $p=0.84$, but no significant difference was found ($Organic\ Carbon_{mean}=0.63$ mg/L, $Inoculum_{mean}=0.75$ mg/L).

Since no detectable amount of iron was measured in the influent breakthrough curves are presented with concentration instead of C/C_o (Figure 3-5). All curves follow a similar trend. The experiment begins with a relatively high concentration of iron, between 5.5 mg/L and 10.0 mg/L. The concentration of iron rapidly decreases to extremely low to undetectable amounts within 1.5 pore volumes. At approximately 12 pore volumes iron concentration in the control (1/2Q) increases to approximately 5 mg/L and then rapidly decreases to undetectable amount.

There is no KDHE acute or chronic aquatic criterion currently available for iron concentration (Table 1-5). Thus, the concentration of iron will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).
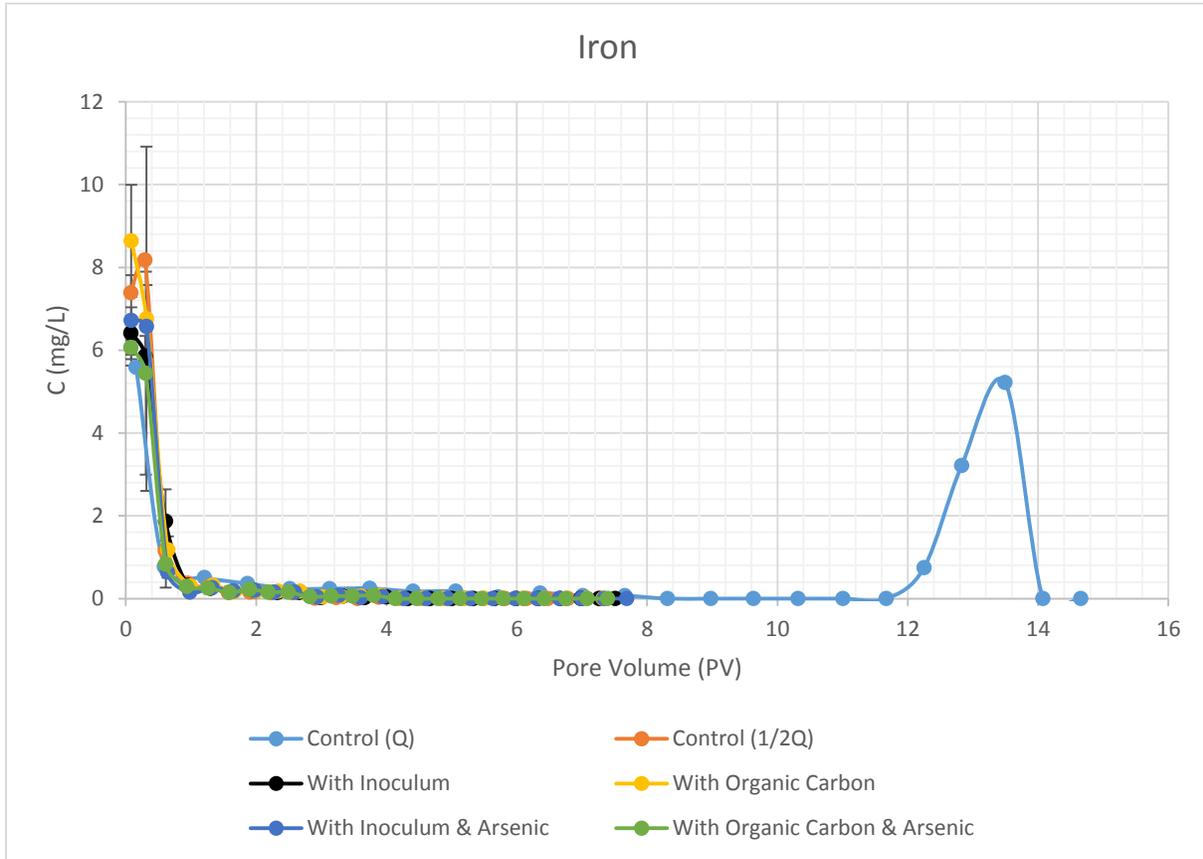
Figure 3-5. Iron breakthrough curves

Nitrate

A substantial amount of nitrate was retained within each column, with an average of 80% (Table 3-8). Retention in each column ranged from 78% to 80% (Table 3-8). The data show no significant difference between each column and treatment.

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain nitrate, $t(46)=0.10$, $p=0.91$, but no significant difference was found ($Q_{mean}=41.5$ mg/L,

63

$1/2Q_{mean}$=41.0 mg/L). The effectiveness of inoculum to retain nitrate was evaluated, t(46)=-0.16, p=0.87, but no significant difference was found (Inoculum$_{mean}$=42.0 mg/L, Control $(1/2Q)_{mean}$=41.0 mg/L). The effectiveness of organic carbon to retain nitrate was evaluated, t(46)=-0.24, p=0.81, but no significant difference was found (Organic Carbon$_{mean}$=42.4 mg/L, Control$(1/2Q)_{mean}$=41.0 mg/L). The effectiveness of inoculum in As amended FGD solution to retain nitrate was evaluated, t(46)=-0.53, p=0.59, but no significant difference was found (Inoculum$_{mean}$=44.1 mg/L, Control$(1/2Q)_{mean}$=41.0 mg/L). The effectiveness of organic carbon in As amended FGD solution to retain nitrate was evaluated, t(46)=0.10, p=0.91, but no significant difference was found (Organic Carbon$_{mean}$=41.7 mg/L, Control$(1/2Q)_{mean}$=41.0 mg/L). The effectiveness of organic carbon and inoculum to retain nitrate was evaluated, t(46)=-0.08, p=0.93, but no significant difference was found (Organic Carbon$_{mean}$=42.4 mg/L, Inoculum$_{mean}$=41.0 mg/L).

At the start of the nitrate breakthrough curves, concentration is relatively low and is then followed by a sharp increase in concentration at approximately 1.5 pore volumes. Between 2 and 2.5 pore volumes nitrate concentration decreases and remains relatively constant (with the exception of some noise) for the remainder of the experiment. Nitrate does not breakthrough in any of the columns.

There is no KDHE acute or chronic aquatic criterion currently available for nitrate concentration (Table 1-5). Thus, the concentration of nitrate will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-8. Nitrate Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	887	193	695	78%
Control (1/2Q)	444	89	355	80%
With Inoculum	444	93	351	79%
With Organic Carbon	444	90	354	80%
With Inoculum & As	444	93	351	79%
With Organic Carbon & As	444	94	350	79%
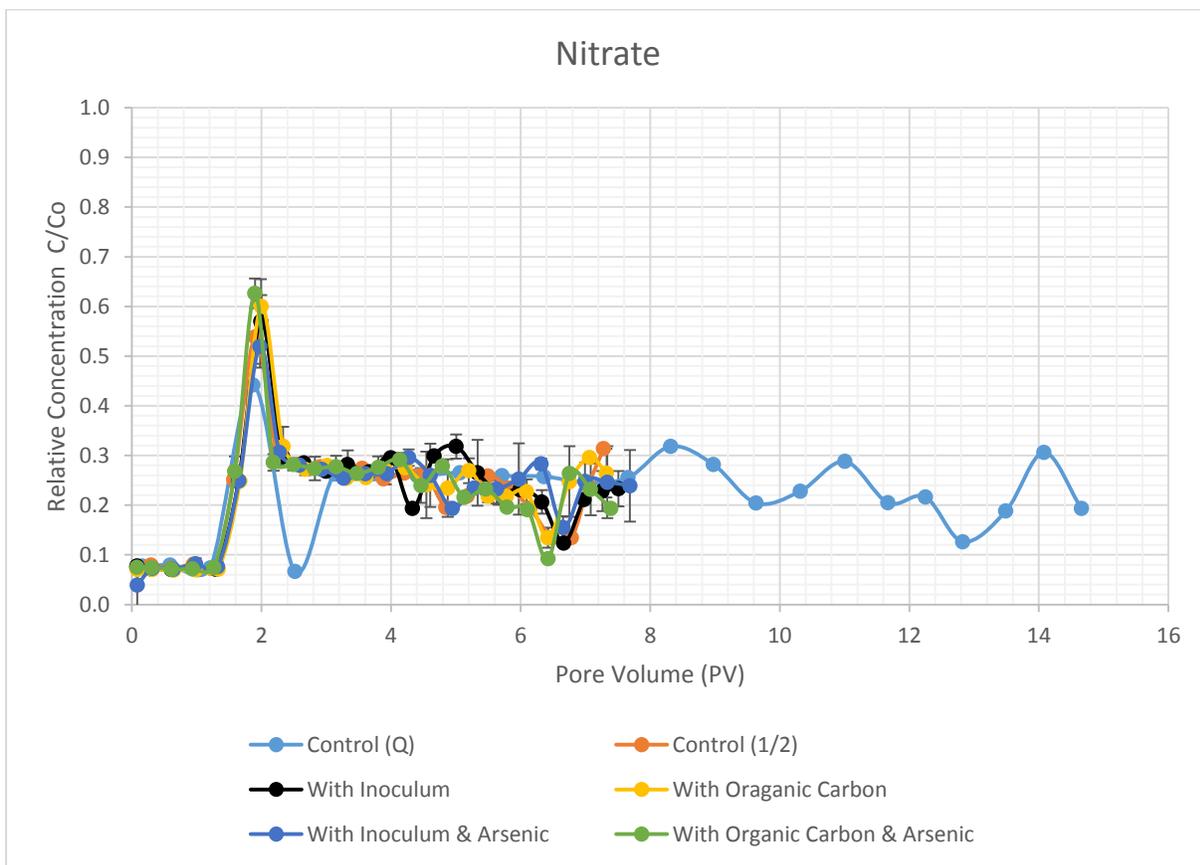
Figure 3-6. Nitrate breakthrough curves.

Total Nitrogen

Minimal total nitrogen (TN), the sum of total kjeldahl nitrogen (ammonia, organic and reduced nitrogen, and nitrate-nitrite (USEPA, 2013) was retained within each column (Table 3-9). The highest TN retention occurs in columns with FGD solution amended with only organic carbon with an average of 50% retained (Table 3-9). The control (1/2Q) retained more TN than all columns with inoculum and columns with FGD solution amended with both arsenic and organic carbon (Table 3-9). The control with the lower flow (1/2Q) rate also retained more nitrogen than the control with the higher flow rate (Q) (Table 3-9).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain TN, $t(46)=4.00$, $p=0.0002$, Q flow rate retained less nitrogen than 1/2Q ($Q_{mean}=75.4$ mg/L, $1/2Q_{mean}=51.3$ mg/L). The effectiveness of inoculum to retain TN was evaluated, $t(46)=-0.14$, $p=0.88$, but no significant difference was found ($Inoculum_{mean}=52.2$ mg/L, Control $(1/2Q)_{mean}=51.3$ mg/L). The effectiveness of organic carbon to retain TN was evaluated, $t(46)=1.05$, $p=0.30$, but no significant difference was found ($Organic\ Carbon_{mean}=44.5$ mg/L, Control$(1/2Q)_{mean}=51.3$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain TN was evaluated, $t(46)=-2.47$, $p=0.017$, columns with inoculum retained less TN than control (1/2Q) ($Inoculum_{mean}=66.8$ mg/L, Control$(1/2Q)_{mean}=51.3$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain TN was evaluated, but no significant difference was found $t(46)=-0.24$, $p=0.81$, ($Organic\ Carbon_{mean}=51.8$ mg/L, Control$(1/2Q)_{mean}=51.3$ mg/L). The effectiveness of organic carbon and inoculum to retain TN was evaluated, $t(46)=1.14$, $p=0.26$, but no significant difference was found ($Organic\ Carbon_{mean}=44.5$ mg/L, $Inoculum_{mean}=51.3$ mg/L).

Except for the control (Q), all columns followed a similar trend in the breakthrough curves (Figure **3**-**7**). A sharp increase in concentration is initially observed but never breaks through (Figure **3**-**7**). Concentration remained relatively constant (with the exception of some noise) from approximately pore volume 2 through 4. A sharp decrease in concentration in concentration is then observed. After the sharp decrease, concentration gradually increases. The control (Q) also experiences a sharp increase in concentration early in the experiment. In contrast, the control (Q) does not inhibit a sharp decrease in concentration but rather remained relatively constant (with the exception of some noise) until the experiment concluded.

Table 3-9. Total Nitrogen Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	472	344	128	27%
Control (1/2Q)	236	112	124[a]	53%
With Inoculum	236	118	119	50%
With Organic Carbon	236	97	140	59%
With Inoculum & As	236	150	86.4[b]	37%
With Organic Carbon & As	236	116	120	51%

[a] significant difference between control (Q)
[b] significant difference between control (1/2Q)
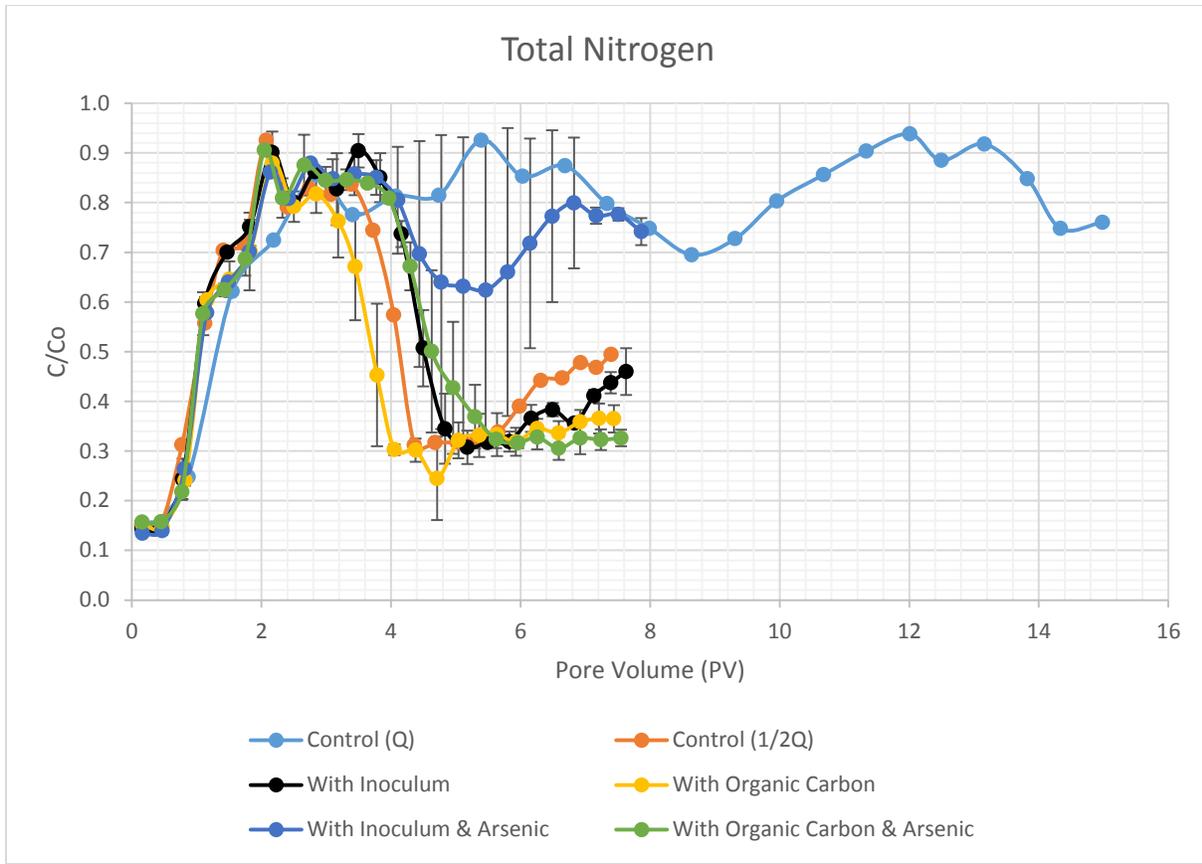
Figure 3**-**7**. Total Nitrogen breakthrough curves**

Potassium

A sizeable amount of potassium was retained in each column; with retention exceeding 75% (Table 3-10).The data show no significant differences between columns and treatments. The percent retained for all columns ranged from 77% to 80% or a 3% difference (Table 3-10).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain potassium, $t(46)=0.91$, $p=0.36$, but no significant difference was found ($Q_{mean}=29.68$ mg/L, $1/2Q_{mean}=28.0$ mg/L). The effectiveness of inoculum to retain potassium was evaluated, $t(46)=-0.06$, $p=0.94$, but no significant difference was found ($Inoculum_{mean}=28.1$ mg/L, Control $(1/2Q)_{mean}=28.0$ mg/L). The effectiveness of organic carbon to retain potassium was evaluated,

t(46)=0.39, p=070, but no significant difference was found (Organic Carbon$_{mean}$=27.3 mg/L, Control(1/2Q)$_{mean}$=28.0 mg/L). The effectiveness of inoculum in As amended FGD solution to retain potassium was evaluated, t(46)=0.23, p=0.82, but no significant difference was found (Inoculum$_{mean}$=27.5 mg/L, Control(1/2Q)$_{mean}$=28.0 mg/L). The effectiveness of organic carbon in As amended FGD solution to retain potassium was evaluated, t(46)=0.46, p=0.64, but no significant difference was found (Organic Carbon$_{mean}$=27.1 mg/L, Control(1/2Q)$_{mean}$=28.0mg/L). The effectiveness of organic carbon and inoculum to retain potassium was evaluated, t(46)=0.64, p=0.65, but no significant difference was found (Organic Carbon$_{mean}$=27.3 mg/L, Inoculum$_{mean}$=28.0 mg/L).

Potassium did not break through during the experiment (Figure 3-8). The concentration in the effluent for all columns increased linearly at approximately 2 mg/L per pore volume, which is relatively gradual (Figure 3-8).

There is no KDHE acute or chronic aquatic criterion currently available for potassium concentration (Table 1-5). Thus, the concentration of potassium will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-10. Potassium Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	563	132	431	77%
Control (1/2Q)	282	58.8	223	79%
With Inoculum	282	60.1	221	79%
With Organic Carbon	282	56.8	225	80%
With Inoculum & As	282	59.7	222	79%
With Organic Carbon & As	282	58.7	223	79%
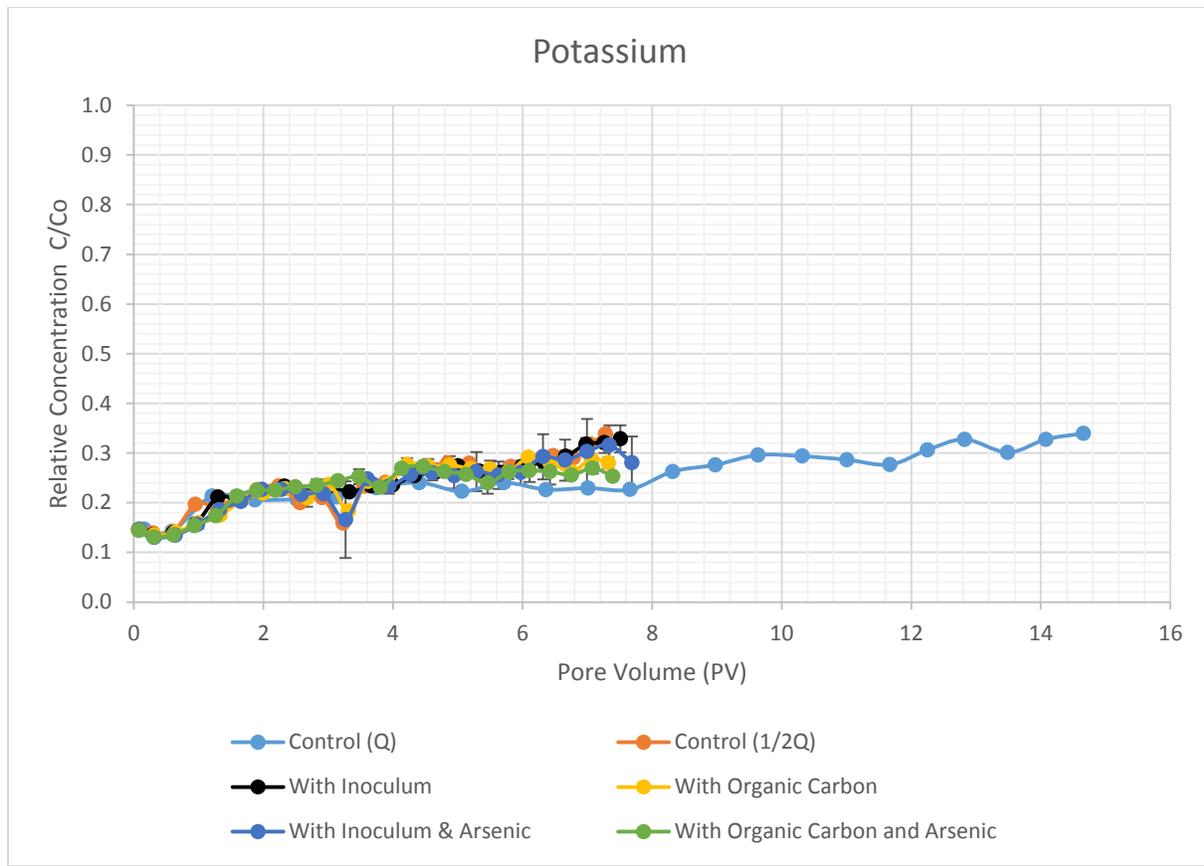
Figure 3-8. Potassium breakthrough curves.

Sodium

There was minimal retention of sodium in the columns (Table 3-11). From the data, the control (Q) retained the least sodium whereas columns with FGD solution amended with organic carbon retained the most.

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain sodium, $t(46)=1.45$, $p=0.15$, $p=0.15$, but no significant difference was found ($Q_{mean}=696$ mg/L, $1/2Q_{mean}=574$ mg/L). The effectiveness of inoculum to retain sodium was evaluated, $t(46)=-0.16$, $p=0.86$, but no significant difference was found (Inoculum$_{mean}=589$ mg/L, Control $(1/2Q)_{mean}=574$ mg/L). The effectiveness of organic carbon to retain sodium was evaluated, $t(46)=-1.47$, $p=0.14$, but no significant difference was found (Organic Carbon$_{mean}=729$ mg/L,

Control(1/2Q)$_{mean}$=574 mg/L). The effectiveness of inoculum in As amended FGD solution to retain sodium was evaluated, $t(46)$=-0.88, p=0.38, but no significant difference was found (Inoculum$_{mean}$=661 mg/L, Control(1/2Q)$_{mean}$=574 mg/L). The effectiveness of organic carbon in As amended FGD solution to retain sodium was evaluated, $t(46)$=-0.09, p=0.92, but no significant difference was found (Organic Carbon$_{mean}$=583 mg/L, Control(1/2Q)$_{mean}$=574 mg/L). The effectiveness of organic carbon and inoculum to retain sodium was evaluated, $t(46)$=-1.31, p=0.20, but no significant difference was found (Organic Carbon$_{mean}$=729 mg/L, Inoculum$_{mean}$=589 mg/L).

All columns were similar in terms of the temporal trends in sodium relative concentration (Figure 3-9). All curves consist of a relatively sharp front as they breakthrough signifying little longitudinal dispersion (Figure 3-9). After sodium breaks through the concentration is relatively constant with the exception of some noise (Figure 3-9).

There is no KDHE acute or chronic aquatic criterion currently available for sodium concentration (Table 1-5). Thus, the concentration of sodium will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-11. Sodium Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	3350	2930	419	13%
Control (1/2Q)	1680	1120	561	34%
With Inoculum	1680	1170	510	30%
With Organic Carbon	2470	1370	1100	44%
With Inoculum & As	1790	1190	598	33%
With Organic Carbon & As	2240	1490	745	33%
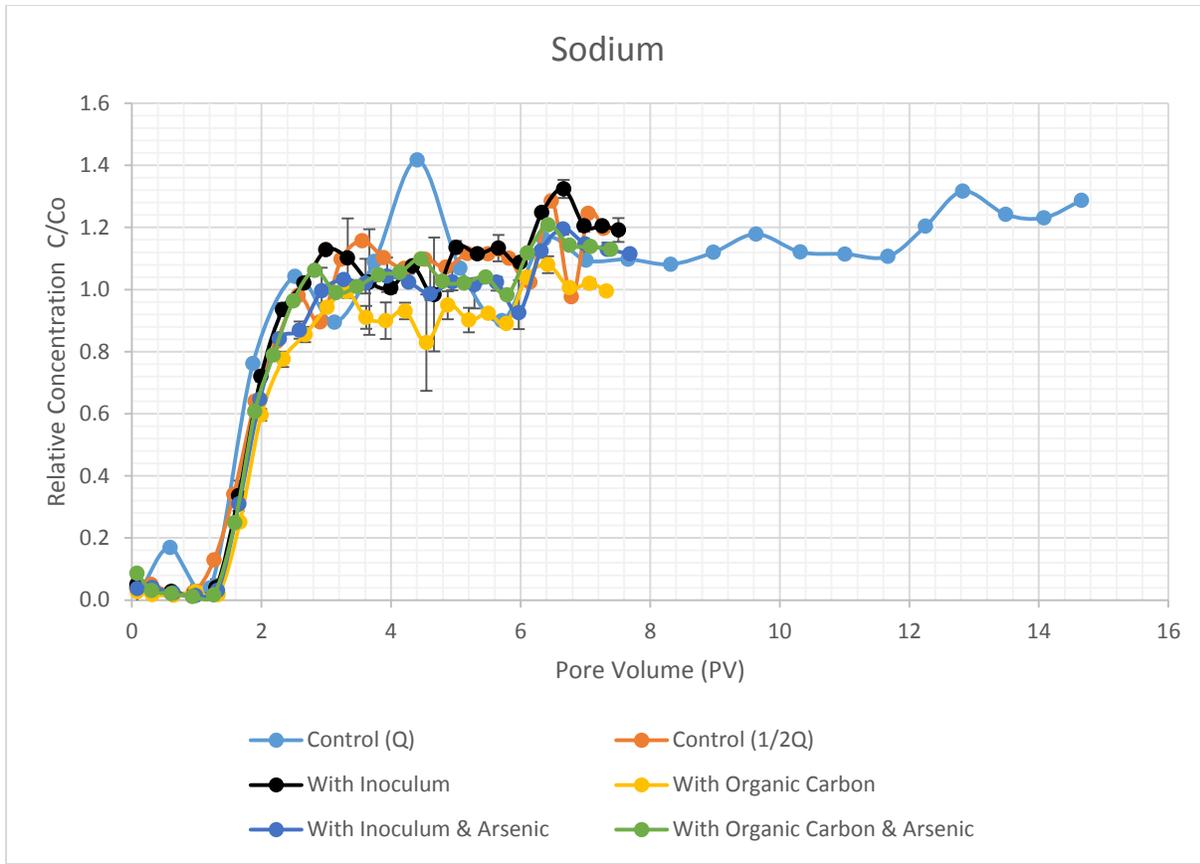
Figure 3-9. Sodium breakthrough curves.

Selenium

Limited data for total selenium analysis is available (Figure 3-10). Only five points from columns 1(Q), 2 (1/2Q), 5, and 6 (with organic carbon) were analyzed (Figure 3-10). Selenium did not breakthrough (Figure 3-10). A lot of variation in relative concentration is observed for the control (1/2Q) as it falls and rises over time (Figure 3-10). The maximum was $C/C_o=0.74$ and minimum was observed at $C/C_o=0.30$ (Figure 3-10). Variation is also observed for the control (Q) initially but not enough data is available to determine the trends after PV=8 (Figure 3-10). The control does reach a maximum $C/C_o=0.54$ at the conclusion of the experiment (Figure

3-10). The columns amended with organic carbon are fairly constant up until PV=4.4 where a slight increase is observed (Figure 3-10).

On average, columns retained 60%, 60%, and 70% of selenium in the control (Q), (1/2Q), and columns with organic carbon, respectively over time (Figure 3-10). Although on average the columns amended with organic carbon retained 10% more selenium than the controls (Q and 1/2Q) there is no significant difference between the three after applying the t-test for independent samples.

Although the majority of selenium was retained in the column, effluent concentration did not meet the KDHE acute (20 µg/L) and chronic (5 µg/L) limits (Figure 3-10). From the start of the column experiment concentration in the effluent ranged between 45 µg/L and 90 µg/L in columns.
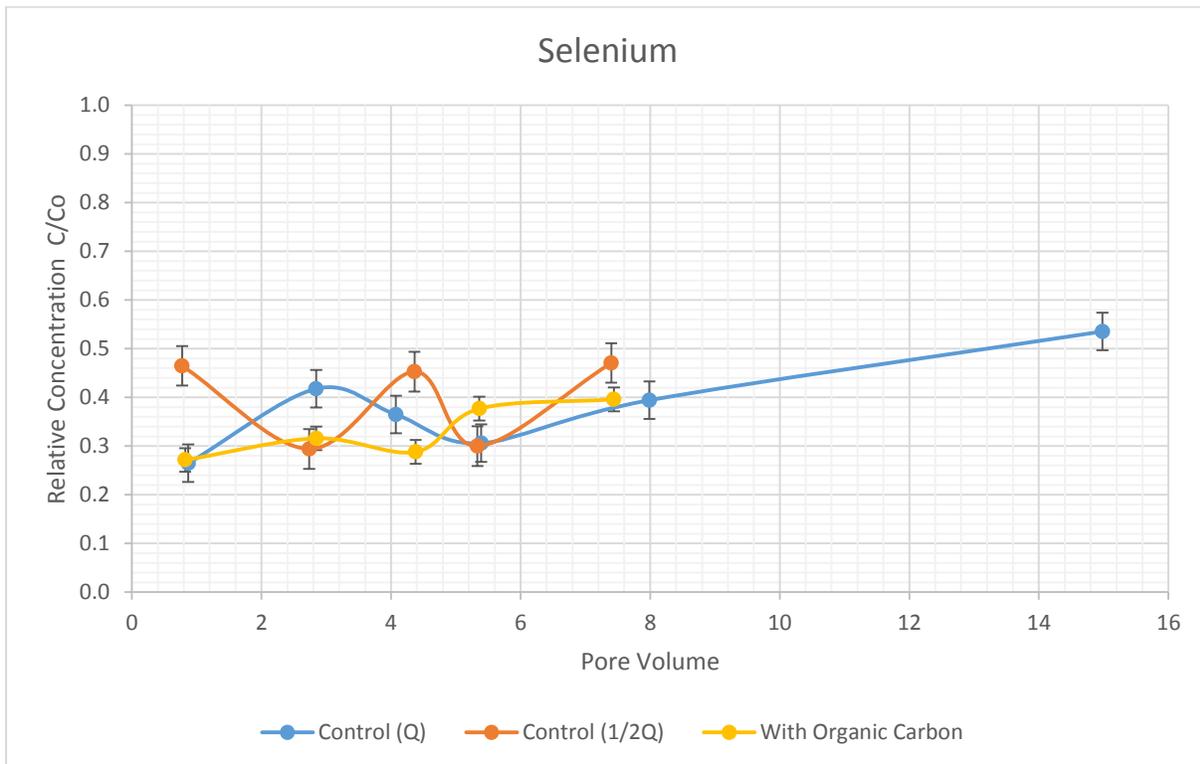
Figure 3-10. Selenium breakthrough curves

Sulfate

There is little to no retention of sulfate in each column (Table 3-12). In fact, more sulfates was measured in the effluent than was introduced in the influent in the control (Q). The control (Q) retained no sulfate (Table 3-12); in fact, 3 percent more sulfate was detected in the effluent than was introduced in the influent. Columns with FGD solution amended with organic carbon performed the best, retaining an average of 37% of sulfate (Table 3-12).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain sulfate, $t(46)=1.83$, $p=0.074$, but no significant difference was found ($Q_{mean}=1470$ mg/L, $1/2Q_{mean}=1240$ mg/L). The effectiveness of inoculum to retain sulfate was evaluated, $t(46)=-0.08$, $p=0.93$, but no significant difference was found ($Inoculum_{mean}=1254$ mg/L, Control $(1/2Q)_{mean}=1243$ mg/L). The effectiveness of organic carbon to retain sulfate was evaluated, $t(46)=2.51$, $p=0.02$, columns with FGD solution amended with organic carbon retained more sulfate than the control $(1/2Q)$ (Organic Carbon$_{mean}=976$ mg/L, Control$(1/2Q)_{mean}=1243$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain sulfate was evaluated, $t(46)=1.17$, $p=0.25$, but no significant difference was found $(1/2Q)$ ($Inoculum_{mean}=1109$ mg/L, Control$(1/2Q)_{mean}=1243$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain sulfate was evaluated, $t(46)=2.50$, $p=0.017$, columns with FGD solution amended with organic carbon retained more sulfate than the control (Organic Carbon$_{mean}=970$ mg/L, Control$(1/2Q)_{mean}=1243$ mg/L). The effectiveness of organic carbon and inoculum to retain sulfate was evaluated, $t(46)=2.57$, $p=0.013$, columns with FGD solution amended with organic carbon retained more sulfate than columns with inoculum (Organic Carbon$_{mean}=976$ mg/L, Inoculum$_{mean}=254$ mg/L).

In the breakthrough curves all columns follow a similar trend (Figure 3-11). Sulfate concentration begins low and then follows a relatively sharp increase in concentration between pore volumes one and two (Figure 3-11). The sharp front between pore volumes one and two signifies very little longitudinal dispersion. After the sharp front, the rate at which sulfate leaves the column decreases (Figure 3-11). The rate at which sulfate exits the columns is lower in columns with organic carbon than the other columns (Figure 3-11). The controls and columns with inoculum broke through at approximately 4 pore volumes. Columns with organic carbon broke through at approximately 6.5 pore volumes (Figure 3-11).

There is no KDHE acute or chronic aquatic criterion currently available for sulfate concentration as shown in Table 1-5. Thus, the concentration of sulfate will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-12. Sulfate Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	6460	6680	-216	-3%
Control (1/2Q)	3230	2640	592[a]	18%
With Inoculum	3230	2720	514[c]	16%
With Organic Carbon	3230	2050	1180[bc]	37%
With Inoculum & As	3230	2720	517	16%
With Organic Carbon & As	3230	2220	1020[b]	31%

[a] significant difference between control (Q)
[b] significant difference between control (1/2Q)
[c] significant difference between inoculum/organic carbon
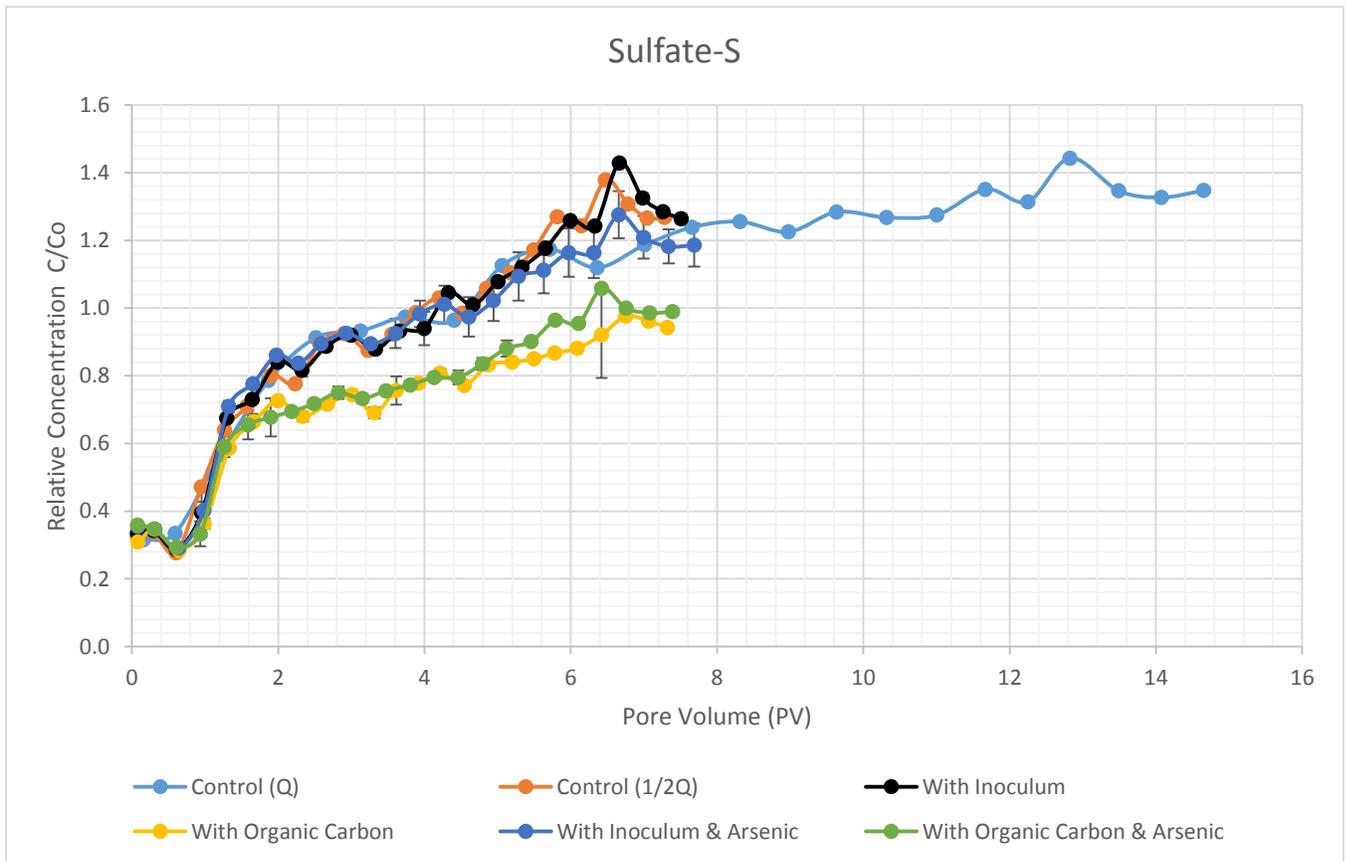
Figure 3-11. Sulfate breakthrough curves.

Sulfur

There was minimal retention for sulfur (Table 3-13). The control (Q) retained sulfur the least; in fact, approximately 3% more sulfur was detected in the effluent than was introduced in the influent (Table 3-13). There is no significant difference between the control (1/2Q) and columns with inoculum (Table 3-13). Conversely, a significant difference is observed between the control (1/2Q) and the columns with organic carbon (Table 3-13). An average of 25% was retained in columns with organic carbon and 17% in columns with FGD wastewater amended

with both organic carbon and arsenic (Table 3-13), which is substantial when compared to the control with 13% (Table 3-13).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain sulfur, $t(46)=3.65$, $p<0.001$, Q flow rate retained less sulfur than 1/2Q ($Q_{mean}=1663$ mg/L, $1/2Q_{mean}=1185$ mg/L). The effectiveness of inoculum to retain sulfur was evaluated, $t(46)=-0.21$, $p=0.83$, but no significant difference was found ($Inoculum_{mean}=1208$ mg/L, Control $(1/2Q)_{mean}=1185$ mg/L). The effectiveness of organic carbon to retain sulfur was evaluated, $t(46)=083$, $p=0.41$, but no significant difference was found ($Organic\ Carbon_{mean}=1100$ mg/L, Control$(1/2Q)_{mean}=1185$ mg/L). The effectiveness of inoculum in As amended FGD solution to retain sulfur was evaluated, $t(46)=0.14$, $p=0.88$, but no significant difference was found (1/2Q) ($Inoculum_{mean}=1170$ mg/L, Control$(1/2Q)_{mean}=1185$ mg/L). The effectiveness of organic carbon in As amended FGD solution to retain sulfur was evaluated, $t(46)=-0.60$, $p=0.55$, columns with FGD solution amended with organic carbon retained more sulfur than control (1/2Q) ($Organic\ Carbon_{mean}=1254$ mg/L, Control$(1/2Q)_{mean}=1185$ mg/L). The effectiveness of organic carbon and inoculum to retain sulfur was evaluated, $t(46)=1.1$, $p=0.28$, but no significant difference was found ($Organic\ Carbon_{mean}=1097$ mg/L, $Inoculum_{mean}=1208$ mg/L).

In the breakthrough curves all columns broke through except the columns with organic carbon (columns 5, 6, 9, and 10) (Figure 3-12). All columns begin at approximately $C/C_o=0.2$ and experience a sharp increase in concentration in less than one pore volume after commencing (Figure 3-12). However, at that sharp front none of the columns break through (Figure 3-12). After the sharp increase, the concentration of each column stays fairly constant (with the exception of some noise) then begins to gradually increase after approximately 5 pore volumes. During the gradual increase columns 1, 2, 3, 4, 7, and 8 break through.

There is no KDHE acute or chronic aquatic criterion currently available for sulfur concentration as shown in Table 1-5. Thus, the concentration of sulfur will not be regulated as it discharges into Lost Creek (which eventually discharges into the Kansas River).

Table 3-13. Sulfur Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	8920	7530	1400	16%
Control (1/2Q)	4460	2490	1970[a]	44%
With Inoculum	4460	2610	1850	41%
With Organic Carbon	4460	2300	2160	48%
With Inoculum & As	4460	2780	1680	38%
With Organic Carbon & As	4460	2530	1930	43%

[a] significant difference between control (Q)
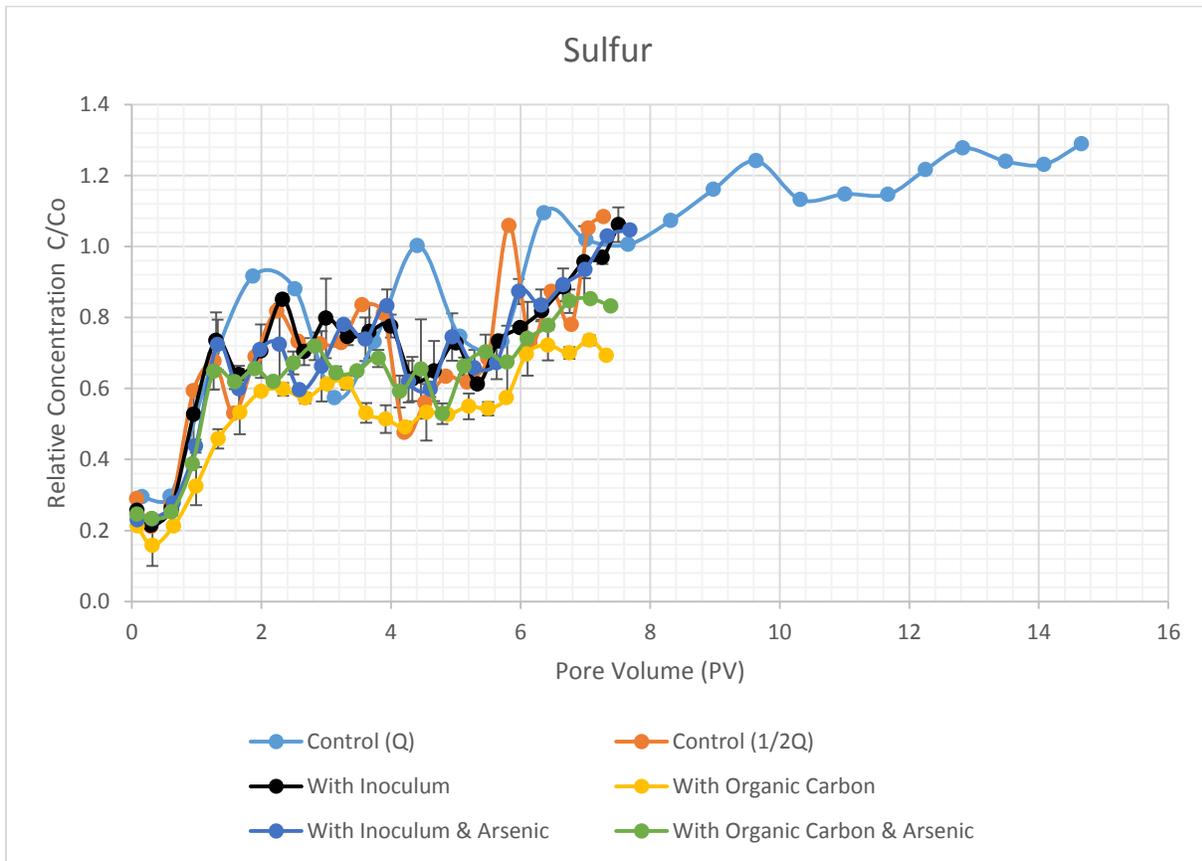
Figure 3-12. Sulfur breakthrough curves.

Dissolved Organic Carbon

Except for the column with organic carbon, no DOC retention was observed (Table 3-14). An effluent concentration of 1.5 to 2 times greater than the concentration introduced in the influent was observed (Table 3-14). Columns with FGD solution amended with organic carbon retained an average of 78% of DOC (Table 3-14).

The independent-sample t-test was used to check the effectiveness of decreasing the flow to retain DOC, t(46)=-1.81, p=0.07, but no significant difference was found (Q_{mean}=52.2 mg/L, $1/2Q_{mean}$=63.0 mg/L). The effectiveness of inoculum to retain DOC was evaluated, t(46)=0.57, p=0.57, but no significant difference was found ($Inoculum_{mean}$=59.2 mg/L, Control $(1/2Q)_{mean}$=63.0 mg/L). The effectiveness of organic carbon to retain DOC was evaluated, t(46)=-0.86, p=0.40, but no significant difference was found (1/2Q) (Organic $Carbon_{mean}$=69.8 mg/L, Control$(1/2Q)_{mean}$=63.0 mg/L). The effectiveness of inoculum in As amended FGD solution to retain DOC was evaluated, t(46)=-0.39, p=0.70, but no significant difference was found ($Inoculum_{mean}$=66.0 mg/L, Control$(1/2Q)_{mean}$=63.0 mg/L). The effectiveness of organic carbon in As amended FGD solution to retain DOC was evaluated, t(46)=0.67, p=0.5, but no significant difference was found (Organic $Carbon_{mean}$=58.6 mg/L, Control$(1/2Q)_{mean}$=63.0 mg/L). The effectiveness of organic carbon and inoculum to retain DOC was evaluated, t(46)=-1.34, p=0.19, but no significant difference was found (Organic $Carbon_{mean}$=69.8 mg/L, $Inoculum_{mean}$=59.2 mg/L).

All columns with inoculum and the control (1/2Q) were similar in terms of the temporal trends in DOC relative concentration (Figure 3-13). The initial DOC concentration at pore volume 1 was approximately 3-3.5x greater than the influent concentration (Figure 3-13). A sharp concentration increase was then observed within one pore volume. After the sharp increase

a sharp decrease is observed followed by a steady decrease until the experiment concludes (Figure 3-13). All columns with organic carbon followed a similar trend as well. An apparent sharp increase in concentration was observed between 0.5 and 1.5 pore volumes (Figure 3-13). Concentration then decreases and remains relatively constant until the conclusion of the experiment (Figure 3-13).

Table 3-14. DOC Extent of Removal

Treatment	Total Influent (mg)	Total Effluent (mg)	Mass Retained (mg)	Percent Retained
Control (Q)	148	246	-98	-66%
Control (1/2Q)	74.0	139	-65	-88%
With Inoculum	74.0	133	-59	-80%
With Organic Carbon	694	153	541	78%
With Inoculum & As	74.0	134	-60	-81%
With Organic Carbon & As	694	154	540	78%
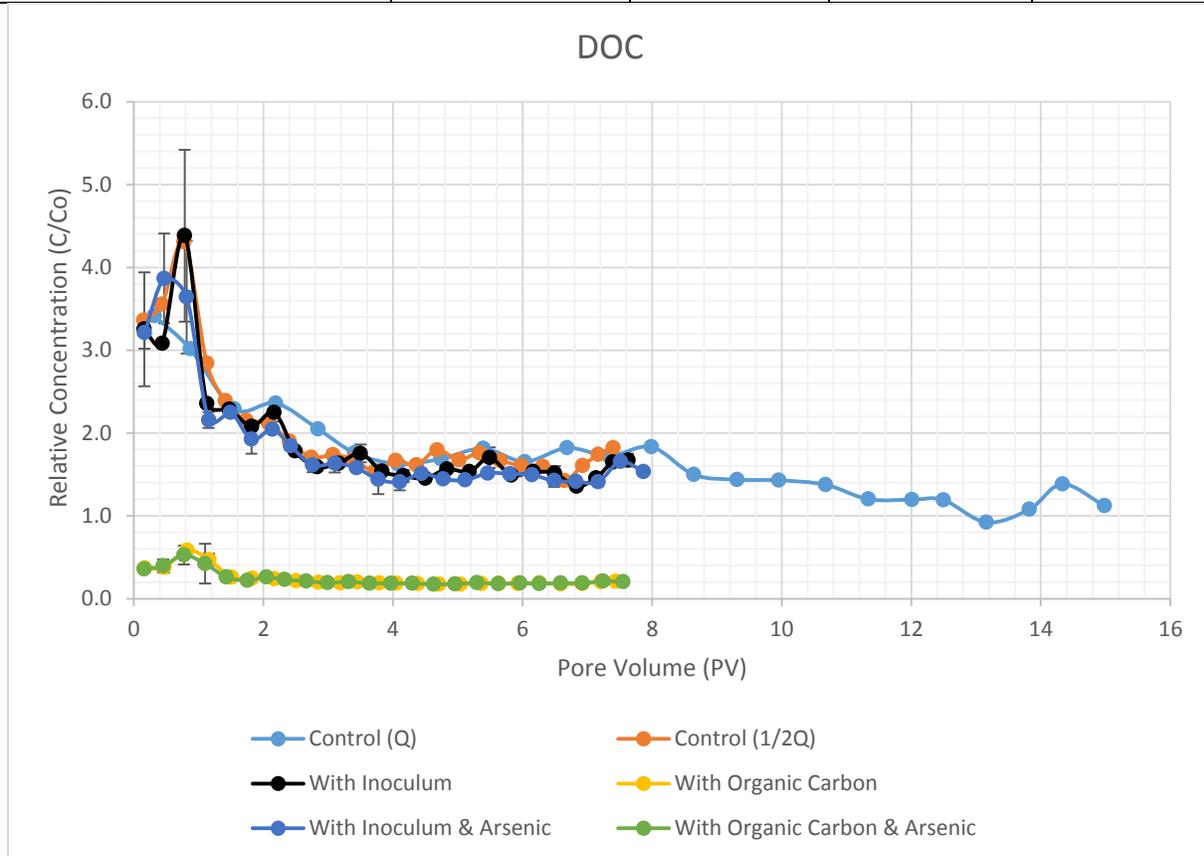
Figure 3-13. DOC breakthrough curves.

Conductivity and pH

Results showed that pH does not change significantly over time; in fact, pH ranged from 7.3 to 7.9 for all columns over the life of the experiment (Figure 3-14). All columns were also similar in terms of the temporal trends for conductivity (Figure 3-15). Conductivity begins at approximately 3 mS/cm and is followed by a rapid increase in conductivity between 1 and 2 pore volumes. After the rapid increase, conductivity gradually increases (with the exception of some noise) until the conclusion of the experiment (Figure 3-15).
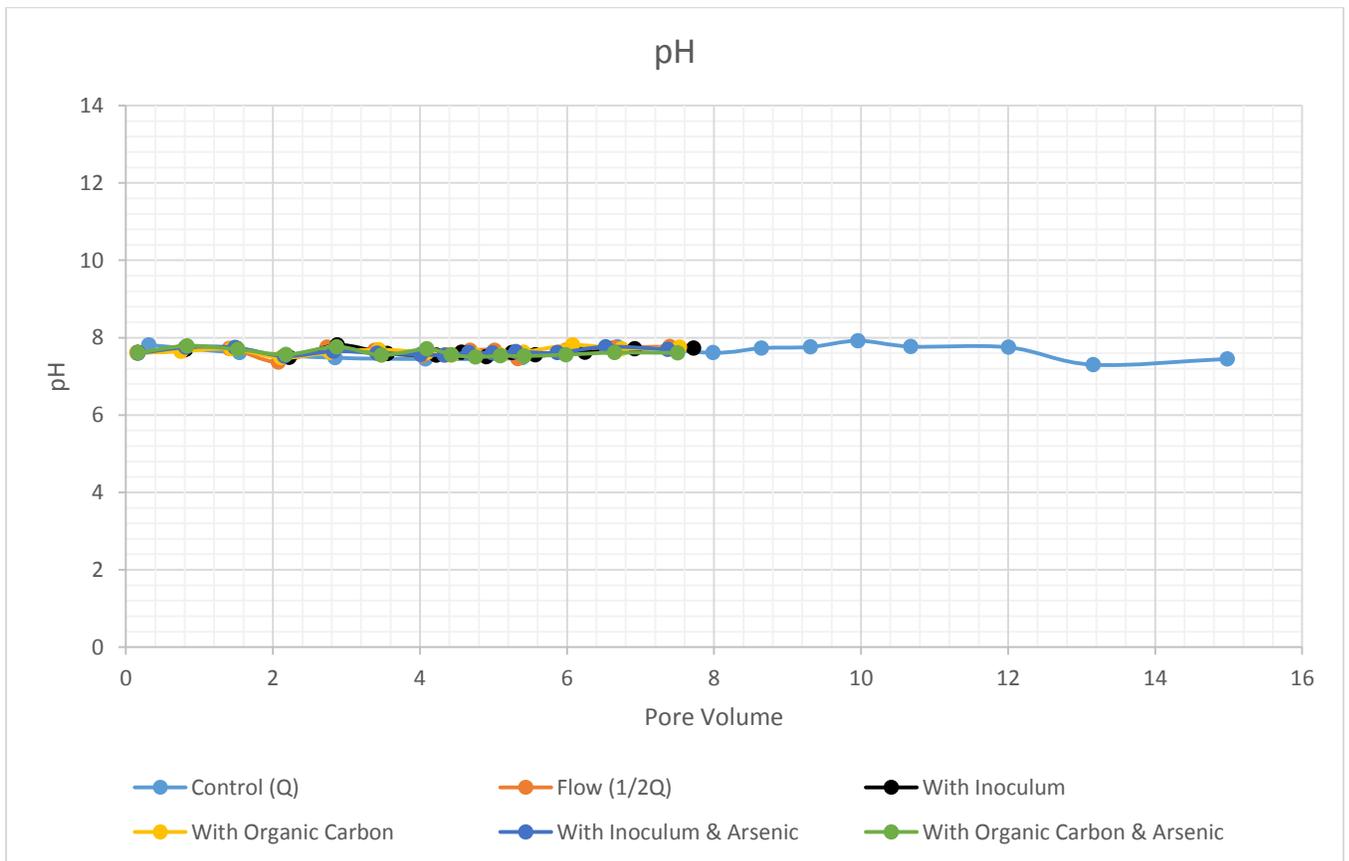
Figure 3-14. pH Breakthrough Curves
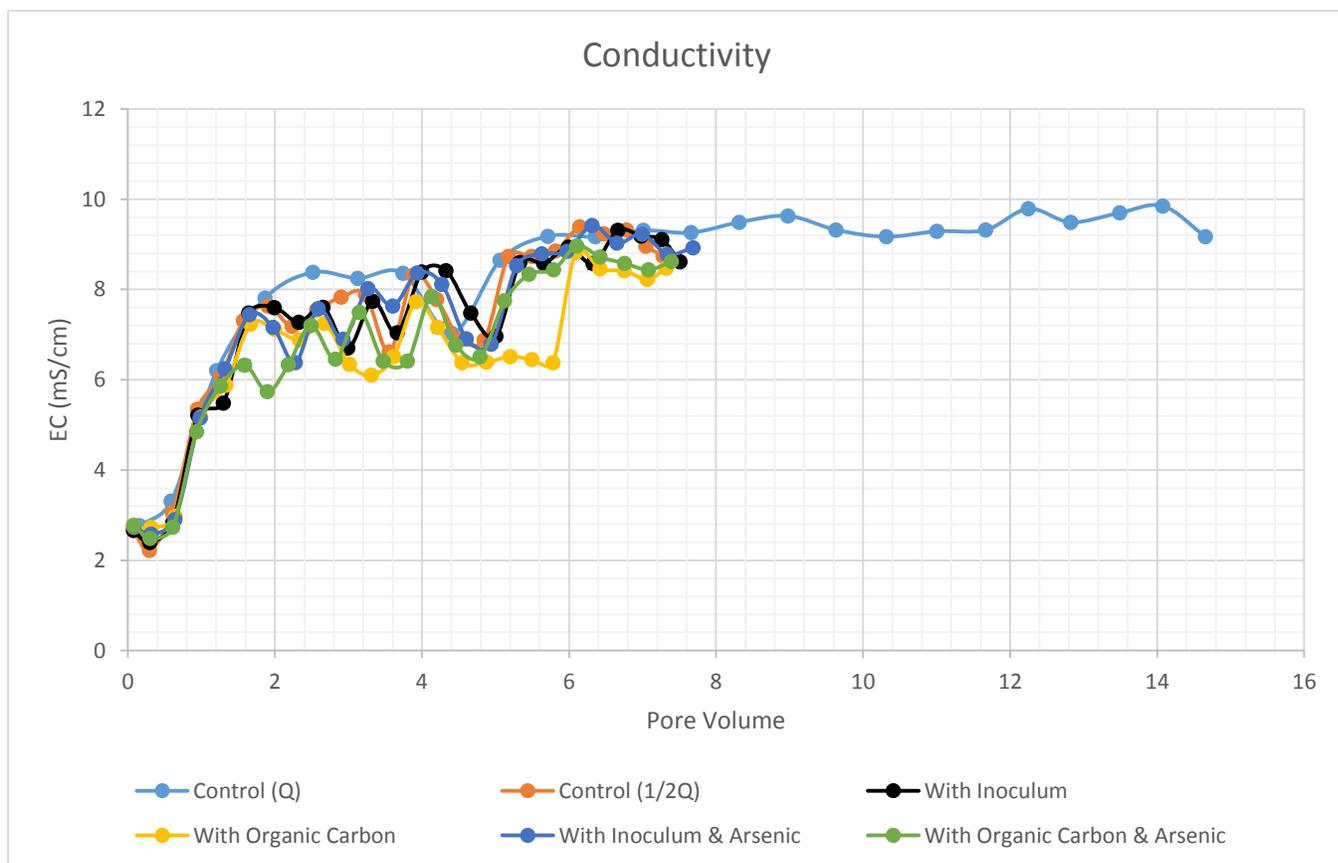
Figure 3-15. Conductivity Breakthrough Curves

Fluorescence Indices

Florescence index did not change significantly over time and ranged between 1.5 and 1.6 (Figure 3-16). Freshness index did not significantly change over time for any columns (Figure 3-17), ranging from approximately 0.6 to 0.7 (Figure 3-17). All columns were also similar in terms of the temporal trends for the Humification index (Figure 3-18) and $SUVA_{254}$ (Figure 3-19). HIX begins at approximately 7 and gradually increases to approximately 12.5-13 (Figure 3-18). Variation is observed in $SUVA_{254}$ rising and falling several times over the course of the experiment. However, overall $SUVA_{254}$ did increase from approximately 1.5 to 3 L/mg-m.
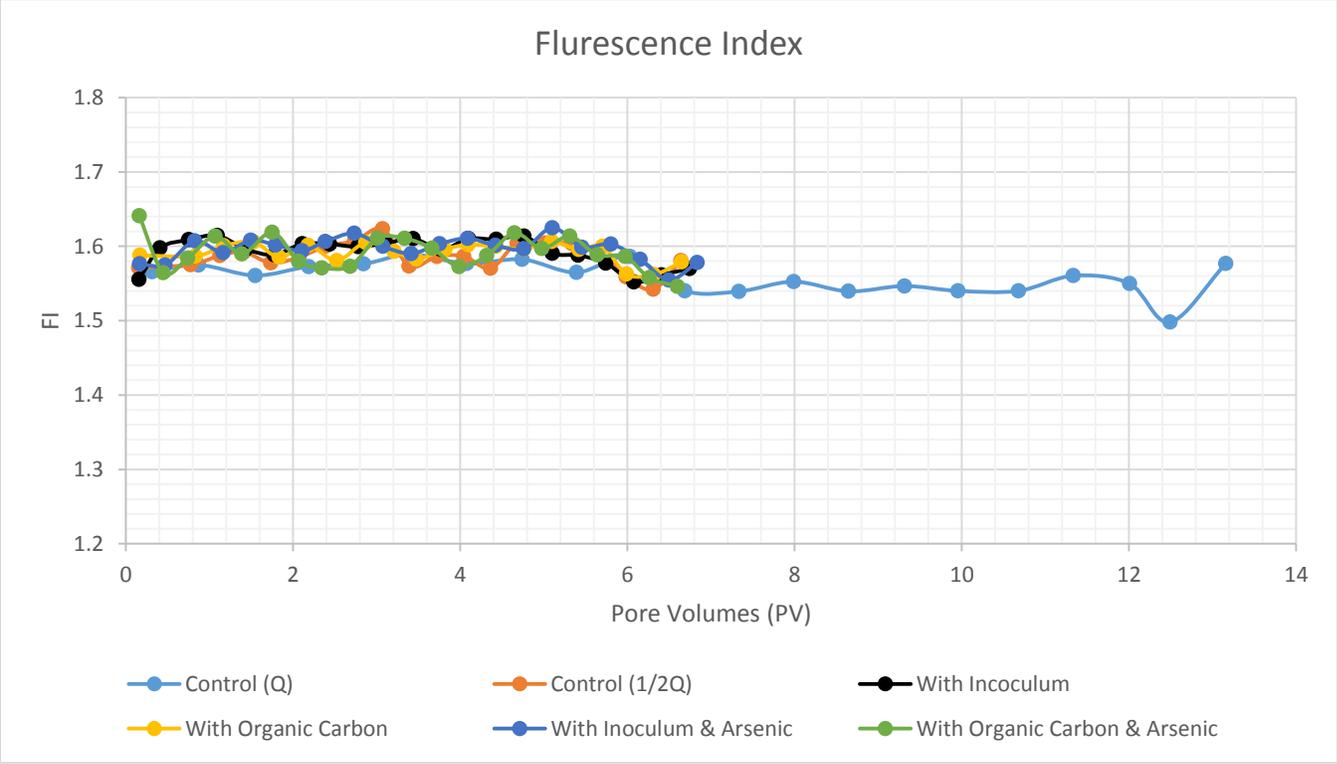
Figure 3-16. Fluorescence Index
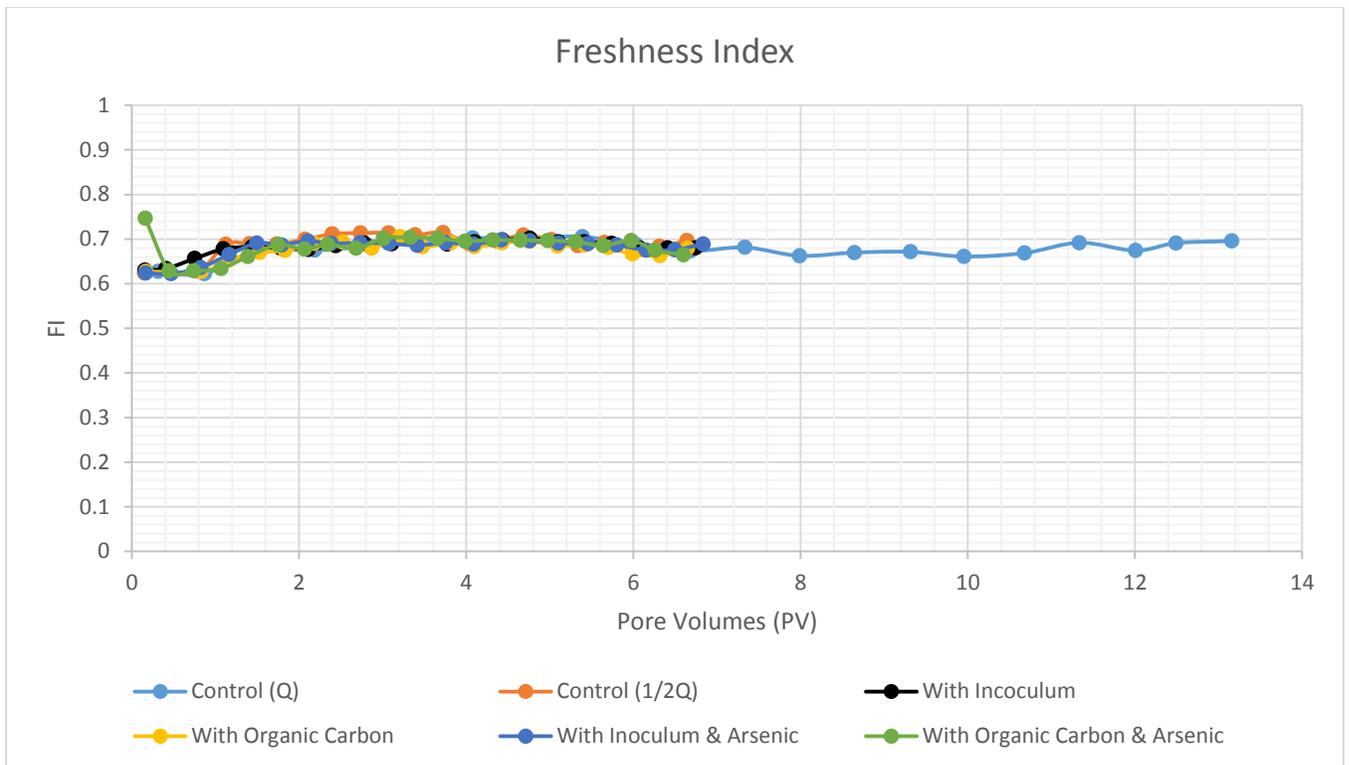
Figure 3-17. Freshness Index
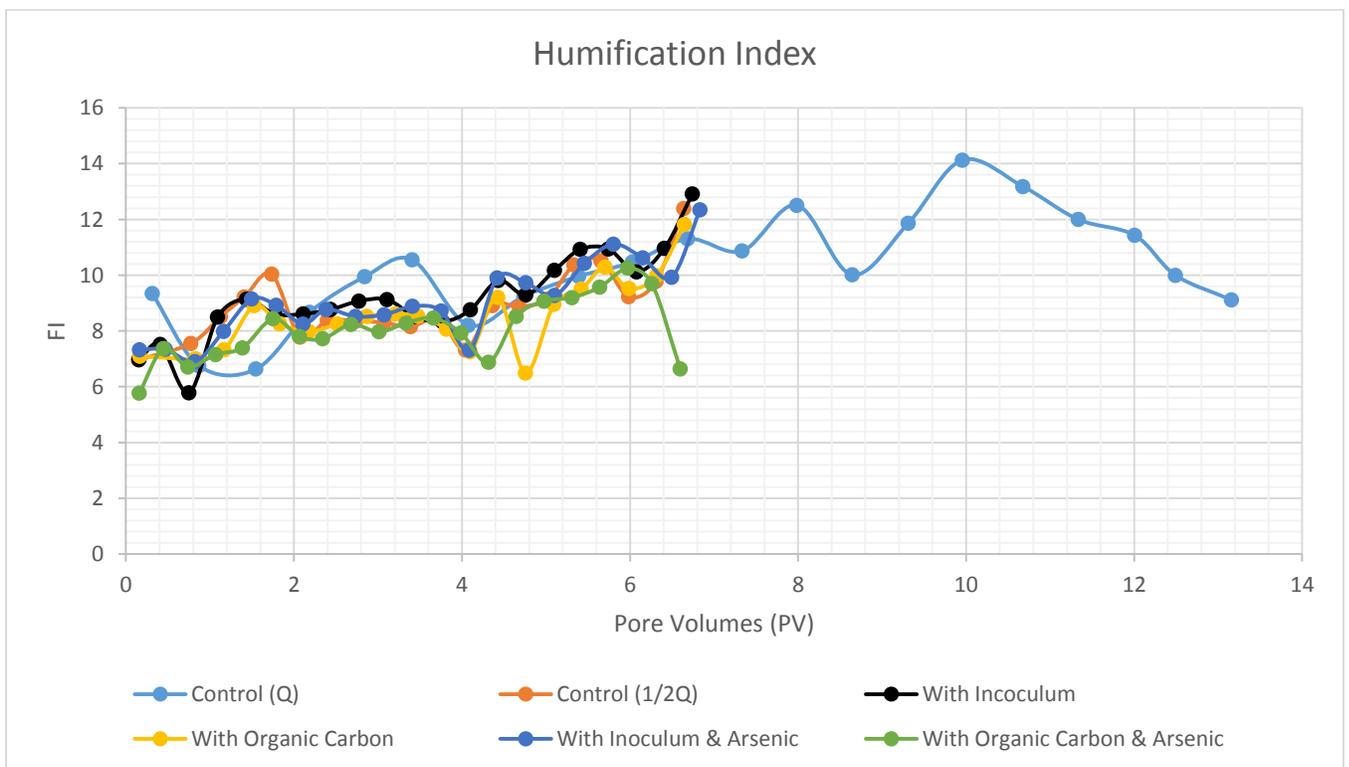
Figure 3-18. Humification Index
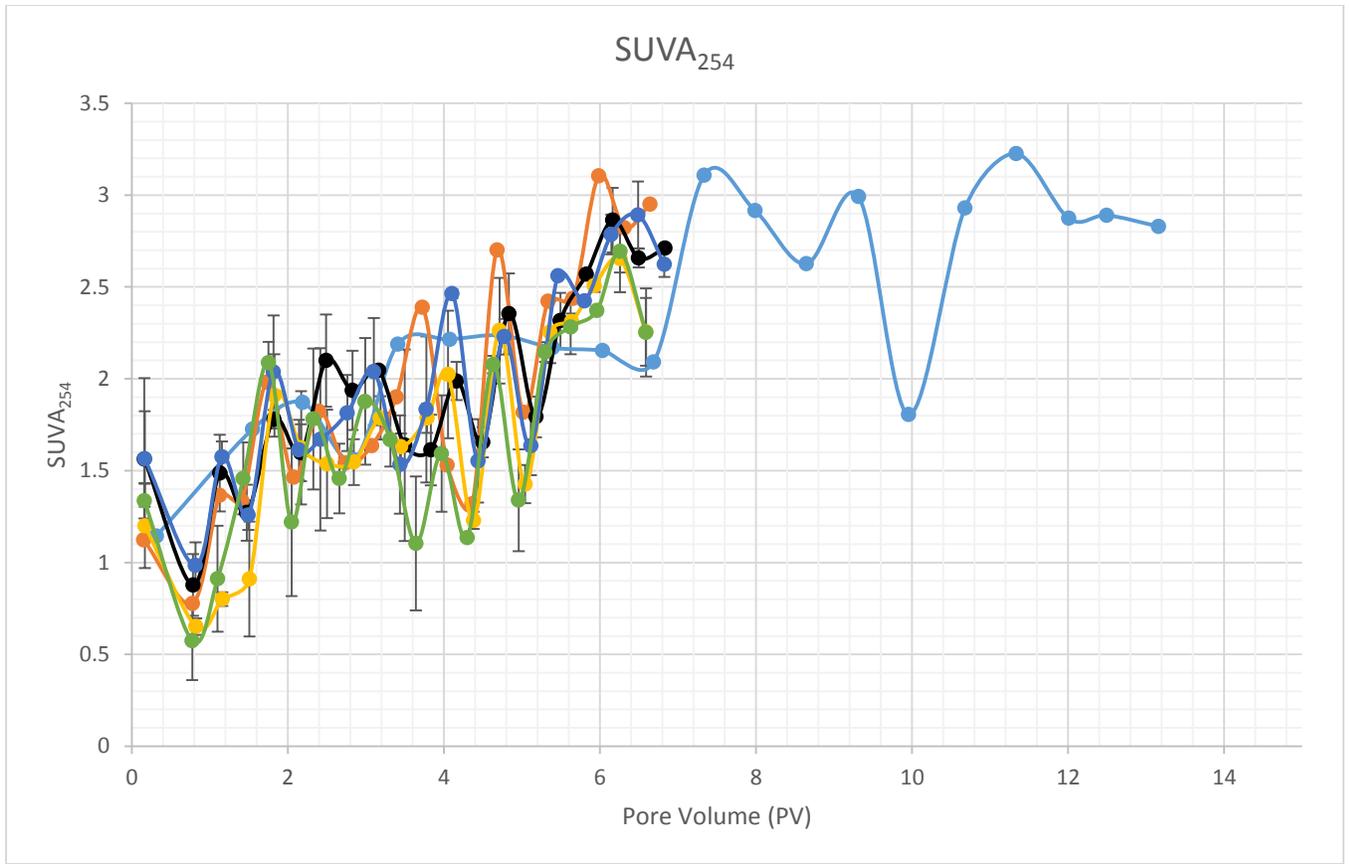
Figure 3-19. SUVA$_{254}$ Breakthrough Curves (include units, L mg-1 m-1)

Sediment Analysis Results

The results for the sediment analysis are presented in Appendix D. At the conclusion of the experiment columns were sectioned into 6 segments. Section 1 represents the effluent and section 6 represents the influent. The purpose of the sediment analysis was to determine the location in the column where constituents were retained or leached. Unfortunately, the difference between the duplicated data was not consistent enough to make definite conclusions. For example, the duplicate columns containing organic carbon (columns 3 and 4) showed conflicting results for arsenic leaching. The majority of arsenic leashing occurred in sections 1-4 for column 3 whereas the majority of the leaching occurred in sections 5-6 for column 4.

Chapter 4 - Discussion

To understand the trends occurring in the breakthrough curves presented in the previous chapter we must first understand the theoretical background of solute transport in soils. The columns were initially supplied with tap water, a solution which contains little to no solutes (or contaminants) compared to the FGD wastewater solution. After 12 days of supplying tap water, FGD wastewater was introduced into the columns all at once, and the influent had a solute concentration of C_o, for each chemical constituent (Table 3-2). Solutes then flowed into the column and were transported through the soil and eventually exited the soil and column in the column's effluent as shown in Figure 2-5. A sharp front is not observed in the effluent, as shown by the piston flow curve in Figure 1-5, because many of these solutes may experience advection, diffusion and dispersion. Additionally, many of these solutes are subject to chemical reactions and microbial transformations.

The retardation of these solutes due to the interactions with the soil, chemical reactions, and microbial transformation is what causes the reduction of solutes in the effluent. One of the advantages of a constructed wetland treatment system is that we can manipulate the conditions in the system to enhance these interactions and reactions to further retard the transport of solute. Our four hypotheses reflect this theory. Decreasing the flow rate will allow more time for these chemical reactions and microbial transformations to occur, which in theory will reduce solute effluent. The addition of inoculum and labile organic carbon are meant to enhance microbial transformation. Finally, under certain conditions the opposite can occur where we can increase the transport of a solute as we hypothesized with arsenic. In this chapter we review our results and discuss the effectiveness of the claims made in the hypotheses.

Solute Transport

Theoretically, a conservative non-interacting solute that does not interact with the soil solid phase and does not undergo chemical reactions will appear similar to the longitudinal dispersion curve in Figure 1-5. Chloride is an example of a conservative non-interacting solute. Chloride appears in the effluent at approximately T=0.5 and breaks through at approximately T=1.5 similarly to Figure 1-5 (Figure 3-4). Once chloride breaks through, a relative concentration of 1.0 is maintained until the conclusion of the experiment. We can conclude, in this study, that chloride does not experience chemical reactions or microbial transformations. Chloride is described as a conservative tracer by Siemens, et al (2010) in a similar column experiment, which investigated the transport of pharmaceuticals.

Sodium is another solute that has similar characteristics to Figure 1-5. The major difference between chloride and sodium is that it took 1.3 pore volumes for sodium to reach the effluent. This is an indication of a chemical reaction, which caused sodium to appear at the column effluent later in the experiment. Skaggs & Leij (2002) suggest that a solute that appears at the column effluent later in the experiment is typically due to sorption or exchange reactions.

Although most constituents experience the initial surge of concentration in the effluent, many did not reach equilibrium or breakthrough as chloride and sodium did. These constituents are believed to have experienced a chemical reaction and/or microbial transformation which retarded or prevented them from reaching equilibrium.

Biological denitrification is the most probable reason for nitrate and TN not reaching equilibrium or breaking through. It has been estimated that denitrification in wetlands account for as much as 90% of overall nitrogen removal (Gruyer et al., 2013; Lin et al., 2002). Biological denitrification involves the biological oxidation of organic matter using nitrate or nitrite as the

electron acceptor instead of oxygen. The nitrate reduction reaction involves nitrate being reduced to nitrite, nitrite to nitric oxide, nitric oxide to nitrous oxide, and nitrous oxide to nitrogen gas (Metcalf & Eddy, 2003). Denitrification typically occurs under the absence of or limited amount of dissolved oxygen (Metcalf & Eddy, 2003), which are the conditions present in the columns. The data show no significant difference between treatments. This is contrary to Gruyer et al. (2013) where a significant difference was obserbed in a constructed wetland amended with an external carbon source treating greenhouse wastewater.

The data also show complete denitrification did not occur. Microorganisms that favor nitrate as an electron acceptor did not utilize all the nitrate that was made available in the FGD wastewater solution. Approximately 30% of the nitrate in the influent was detected in the effluent (Table 3-8). It is hypothesized the high concentration of salinity in the FGD wastewater solution may have affected microorganisms from transforming nitrogen. Indeed, Rysgaard (1999) showed that higher salinity significantly influence nitrification and denitrification rates.

Biological sulfate reduction is the most probable cause for sulfate and total sulfur not breaking through immediately after the initial surge of concentration. Sulfate reduction, in which sulfate acts as a source of oxygen or electron acceptor and is converted to sulfide, is mediated by a group of microorganism known as sulfate reducing bacteria (SRB) (Liamleam, & Annachhatre, 2007). Sulfate reduction usually occurs in the absence of dissolved oxygen and nitrate. The data show sulfate does eventually break through but it takes approximately 4 pore volumes in columns with FGD solution not amended with organic carbon (Figure 3-11) and 6 pore volumes in columns with FGD solution amended with organic carbon (Figure 3-11). Since sulfate broke through complete sulfate reduction was not achieved (Figure 3-11).

An essential component for treating sulfate contaminated wastewater by biological sulfate reduction is an electron donor (Liamleam, & Annachhatre, 2007). Electron donors that are oxidized by SRB are usually low-molecular-weight organic compounds (Liamleam, & Annachhatre, 2007). The carbon source is closely related to the redox potential (Gruyer et al., 2013). To enhance biological sulfate reduction a carbon source (sodium lactate) was added to columns 5, 6, 9, and 10. The results show the addition of a labile carbon source in the FGD solution (Figure 3-11) did retard sulfate from breaking through. The lower sulfate mass in the effluent compared to the influent, as calculated in the mass balance (Table 3-12), for columns with FGD solution amended with organic carbon is evidence that the addition of sodium lactate retarded sulfate from breaking through. This agrees with Gruyer et al. (2013) where a significant difference was obserbed in sulfate reduction due to the addition of an external carbon source to a constructed wetland treating greenhouse wastewater.

Evidence that microbes were consuming sodium lactate can be assessed by viewing the DOC results (Table 3-14). The lower DOC mass in the effluent compared to the influent, as calculated in the mass retained (Figure 3-11), is most likely the result of degradation of labile DOM. Furthermore, the effluent concentration, C, of columns with FGD solution amended with organic carbon are approximately equal to the columns with FGD solution not amended with organic carbon (Figure C-9 and Figure C-10). This holds true even though influent concentration for columns with FGD solution amended with organic carbon were 9x greater than the columns with FGD solution not amended with organic carbon (Table 3-2). Since the effluent concentrations are approximately equal in all columns, this indicates that microorganisms are consuming the sodium lactate completely and leaving behind the less favorable DOC.

A strong correlation between DOC and sulfate was found (R^2=0.62). This agrees with our hypothesis: as DOC concentration increases, more labile organic carbon is available to reduce sulfate because SRB require an electron donor to perform life functions. However, sulfate reduction did cease in the column experiment indicating that a limiting factor influenced SRB from reducing sulfate. These factors can include the presence of more energetically favorable elements, redox conditions, but most importantly the availability of carbon (Gruyer et al., 2013). The fact that approximately 30% of energetically favorable nitrate was still present in the effluent might have influenced SRB. However, carbon availability was most likely the limiting factor. The DOC/SO_4^{2-} ratio can be an indicator of carbon availability for sulfate reduction (Gruyer et al., 2013). Neculita et al. (2007) estimated the optimal ratio for biological treatment of sulfate in acid mine drainage was between 0.32 to 0.38. DOC/SO_4^{2-} ratios in this study ranged from 0.05 to 0.1, where the highest ratios were associated with columns with FGD solution amended with organic carbon (Table B-11). The low DOC/SO_4^{2-} ratios indicate carbon availability may have limited sulfate reduction.

Sulfate reduction is a critical process that can control the fate of other constituents present in FGD wastewater, especially arsenic and selenium. In reducing waters sulfate-reduction provides the sulfides and mineral-bearing sulfides necessary for coprecipitation reactions to occur (Eggert et al., 2008). The sulfides produced precipitate with arsenic and selenium ions to remove them from solution. Higher sulfate reduction rates may have increased the immobilization of the more critical constituents, such as arsenic, as documented by Moore et al. (1988) and Rittle et al. (1995)

Several constituents not only reached equilibrium but also reached a relative concentration greater than 1.0. The only other source of these constituents in the columns was

the soil. This leads to the conclusion that these constituents were leaching from the soil and increasing in concentration in the effluent. For example, DOC concentration initially started at a relative concentration of approximately 3 for the columns with FGD solution not amended with organic carbon (Figure 3-13). This would indicate organic carbon is leaching from the sediment. The fluorescence indices, especially the humification index and $SUVA_{254}$, which indicate more condensed, aromatic, and higher molecular weight polymers converted from lower molecular weight compounds by microorganisms (Weishaar et al., 2003; Fellman et al., 2010), support this claim. Both humification index and $SUVA_{254}$ increase over time (Figure 3-18 and Figure 3-19). This suggests that over time sediment dissolution may have occurred and more humic DOM was released from those sediments during dissolution.

Iron was not detected in the influent solution (Table 3-1), however, leaching from the sediment was observed initially (Figure 3-5). Concentrations of over 8 mg Fe/L were observed and then gradually decreased to undetectable levels (Figure 3-5). The soil analysis (Table D-2) indicates a small percentage of the total iron present in the soil leached. This would indicate that the decrease in iron concentration was not due to the exhaustion of iron from the soil. Rather, the mechanism driving the mobilization of iron initially was possibly the reductive dissolution of iron minerals, which may have been inhibited later in the experiment as Fe-reducing microbes became influenced by high salinity. In anoxic sediments, microorganisms use Fe(III) as electron acceptors (Heiberg et al., 2012). Columns were initially submerged in tap water before FGD solution was introduced to the columns. There was enough organic matter and microbes in the soil to start the reductive dissolution process. Alternatively, the decrease of iron concentration to undetectable levels in the effluent might have been due to precipitation reactions. Iron is known to coprecipitate with many constituents in FGD wastewater or byproducts produced in the

wetlands. These include ferrous phosphates (Heiberg et al., 2012), ferrous sulfide (Ravenscroft, et al., 2009), and ferrous arsenate (Johnston & Singer, 2007).

For columns with FGD wastewater amended with arsenic, poor arsenic removal was observed. This observation agrees with Eggert et al. (2008) where little arsenic removal was documented in constructed wetlands treating FGD wastewater. However, a significant difference was observed between the control (1/2) and columns with FGD wastewater amended with arsenic. More arsenic was accumulated in columns with FGD wastewater amended with arsenic than in the control (1/2Q) (where As dissolution from soils is observed). One possible explanation is that arsenate, the As^{+5} state of arsenic, was added to the FGD solution. Arsenate is more strongly adsorbed than arsenite and moves slower in soil water especially in near neutral conditions (Plant et al., 2003). The arsenic soil analysis (Table D-3) shows excess As accumulation (most likely from the arsenate introduced in the influent) accumulating in the soil. The arsenate being supplied was most likely being adsorbed or precipitating and accumulating in the sediment.

Moderate selenium retention was observed in the columns. On average columns retained 60%, 60%, and 70% of selenium in the control (Q), (1/2Q), and columns amended with organic carbon, respectively over time (Figure 3-10). Selenium immobilization was likely caused by a combination of mechanisms; microbial mediated oxidation-reduction reactions and the adsorption of selenite in sediments and minerals. Bacteria can use Se(VI) and Se(IV) as a terminal electron acceptor in energy metabolism (Siddique, et al. 2007). Se(VI) and Se(IV) are then reduced to insoluble Se(0). The soil analysis indicates a large amount of selenium was retained in the soil (Table D-4), which could be an indication of insoluble Se(0) accumulating in the soil. Alternatively, selenite, which has a strong adsorption tendency to clay and minerals

(Plant, et al., 2003), may have also accumulated in the soil. A combination of these two mechanisms is the likely cause of selenium retention.

Although selenium retention was moderate, effluent concentration in the columns did not meet KDHE limits. Between 30% and 40% of selenium introduced in the influent was detected in the effluent. This could have been due to the high salinity in FGD wastewater. Deverel, et al. (2010) found concentration of selenium in groundwater increased as salinity increased in the shallow groundwaters near Kesterson Resovoir, CA. Smedley, et al. (2002) found similar results in La Pampa, Argentina. In the La Pampa study, selenium concentration in the groundwater ranged from <2-40 µg/L with the highest concentration located in high salinity shallow groundwaters.

Dissolution and Mobilization of Arsenic

It was hypothesized that under reducing environments, such as a subsurface flow CWTS, the dissolution and mobilization of arsenic could occur. Examples of such incidents were documented by Eggert et al. (2008) and Fox et al. (2003). Both studies observed the leaching of arsenic in wetland sediments. The arsenic concentration in the FGD wastewater of this study was negligible (0.72 µg/L); however, between 8.0 µg/L and 168 µg/L of arsenic was observed in the effluent (Figure C-1). This suggests that mobilization of arsenic occurred from these native Kansas soils under the conditions of this experiment. Since we are concerned with the dissolution and mobilization of arsenic this discussion will focus on the columns that were supplied with negligible arsenic concentration (columns 1 through 6).

The mobility, bioavailability, toxicity, and environmental fate of arsenic are controlled directly and indirectly by microbial transformations (Borch et al., 2010). Microorganisms can directly modify the redox state and chemical speciation of arsenic or they can indirectly mobilize

arsenic by destroying arsenic bearing carrier phases (Borch et al., 2010). Dissolved arsenic in groundwater is closely related to poorly soluble iron (hydr)oxides that strongly sorb both As(III) and As(V) (Borch et al., 2010). Microorganisms can reduce Fe(III) on sediment surfaces to Fe(II), which then gets released into the water along with the sorbed arsenic. Typically, when As is mobilized by reductive dissolution of Fe minerals, high dissolved As and Fe(II) concentrations would be observed simultaneously under controlled experimental conditions (Borch et al., 2010). By contrast, our data do not show a simultaneous increase in As and Fe concentrations. High iron concentration, as shown in Figure 3-5, occurs early in the experiment without a concurrent increase in arsenic and decreases to undetectable levels over time. However, Fe (II) is known to coprecipitate with many constituents in FGD wastewater or byproducts produced in the wetlands, which may have decreased total iron concentration in the effluent. Other ways in which arsenic may have been mobilized in these columns 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).

The high salinity in the FGD wastewater may have also influenced microbial communities. Kulp et al. (2007) observed dissimilatory As(V) reduction in active anaerobic slurries from two California soda lakes at all salinity levels, including salt saturation. Since microorganisms directly reducing As(V) to a more mobile As(III) can survive under high salinity environments they may have outcompeted other cultures in the columns, enducing As(V) reduction.

Arsenic may also be mobilized under a variety of other circumstances related to high pH and oxidizing conditions, neither of which were representative of this column study. To evaluate

94

manganese reduction or direct arsenate reduction, additional measurements of Mn concentrations and As speciation would be needed, but are not available in the current study.

Nevertheless, the chemical data available for this study do shed some light on the mechanisms for arsenic release from native Kansas sediments. We do know that the columns had reducing conditions, sufficient to allow for Fe(III) and SO_4 reduction, which can trigger the release of arsenic (Smedley & Kinniburgh, 2002). The presence of organic carbon largely controlled the rate at which reducing conditions were established in the column. Furthermore, the columns with organic carbon had the highest concentrations of arsenic, up to 168 μg/L, suggesting that the DOM addition served to fuel bacteria in the respiration of electron acceptors.

Flow rate was also a controlling factor of arsenic dissolution. The column with the higher flow rate (Q) leached less arsenic from the sediments than the lower flow rate (1/2Q). This is possibly due lower reaction time associated with the higher flow rate. By contrast, the ½ Q flow rate allows more time for reactions to occur because FGD wastewater is in contact with the sediment for a longer period of time.

Chapter 5 - Conclusion and Recommendations

In the United States approximately 37% of the 4 trillion kWh of electricity is generated by combusting coal (USEPA, 2013). In fact, one pound of coal supplies enough electricity to power ten 100-watt light bulbs for one hour (USEPA, 2013). Its abundance, ease of storage, and transportation makes it affordable at a global scale (Ghose, 2009). Although coal is an important component for keeping electricity cost down, it does bring many environmental disadvantages. The flue gasses produced by combusting coal affect human health and the environment (USEPA, 2013). To combat these harmful emissions the U.S. Congress introduced a series of legislative actions regulating air emissions. Coal-fired power plants have since implemented sulfur dioxide scrubbing systems such as flue gas desulfurization (FGD) systems. In FGD systems, a limestone slurry is typically misted simultaneously as flue gas raises through the smoke stacks to absorb sulfur dioxide and other pollutants to the slurry. This process prevents many harmful pollutants from being emitted into the atmosphere; however, it also produces toxic wastewaters that contain problematic constituents of environmental concern.

Concerns expressed by the media and public, in addition to increased environmental regulations, have intensified the need to find a remediation technology to treat FGD wastewater. In this study, constructed wetland treatment systems (CWTS) were investigated as a possible remediation technology. To simulate constructed wetlands, a continuous flow-through column experiment was conducted with undiluted FGD wastewater and surface sediment from a power plant in Kansas. To optimize the performance of a CWTS the following hypotheses were tested: 1) decreasing the flow rate improves the performance of the treatment wetlands due to an increase in reaction time between solutes and sediments, 2) the introduction of microbial cultures

will increase the retention capacity of the columns because constructed wetlands improve water quality through biological process, and 3) the introduction of a labile carbon source will improve the retention capacity of the columns because microorganisms require an electron donor to perform life functions such as cell maintenance and synthesis. Although the FGD wastewater collected possessed a negligible concentration of arsenic, mobilization of arsenic has been observed in reducing sediments of wetland environments. Therefore, constructed wetlands may also represent an environment where the mobilization of arsenic is possible. This led to testing of a fourth hypothesis: 4) Reducing environments will cause arsenic desorption and dissolution causing the mobilization of arsenic.

Of the constituents of concern (arsenic, selenium, nitrate, and sulfate) sulfate removal increased as a result of decreasing the flow rate. In addition, sulfate-S exhibited greater removal as a result of adding organic carbon to the FGD solution when compared to the control (1/2Q). Also, moderate selenium removal was observed, over 60% of selenium was accumulated in the soil.

By contrast, arsenic mobilization was observed in all columns with the lower flow rate treatment. Dissolved arsenic concentrations in the effluent of columns with FGD solution amended with organic carbon reached 168 mg/L, suggesting that native Kansas soils placed in a constructed wetland configuration and amended with labile carbon do possess an environment where the mobilization of arsenic is possible. When compared to the control, arsenic dissolution decreased as a result of adding inoculum to the columns.

From the number of constituents monitored in this study arsenic, selenium, and chloride are the only pollutants regulated by the Kansas Department of Health and Environment (KDHE). Chloride effluent concentrations in columns surpassed the 860 mg/L acute aquatic life limit set

by KDHE. Selenium effluent concentration also surpassed the KDHE limits for both acute and chronic. Arsenic concentration limits were met by all columns except the columns with organic carbon. Columns with organic carbon exceed the 150 μg/L chronic aquatic life limit set by KDHE for an average of 0.3 pore volumes. In this small scale laboratory experiment that is the equivalent of approximately 8-10 days, which by definition would not be chronic and, in turn, lethal to aquatic life. However, in a full scale CWTS, 0.3 pore volumes can equate to weeks or longer, which by definition would be lethal to aquatic life.

Although an attempt was made to simulate field conditions at the CWTS in JEC, the sediment packed in the laboratory column experiment was air dried, grounded, sieved, and homogenized, a process not normally applied in the field. This process might have enhanced the leaching of some constituents from the sediment. For example, grinding produces smaller grains with higher surface area and, in turn, more reaction sites that may increase mobility of constituents, such as DOM and arsenic. For that reason, actual field concentrations of some constituents may be lower than what we observed in this study.

Recommendations

From the conclusions made in this study, it is highly recommended FGD wastewater is diluted before it is supplied into a CWTS as recommended by the USEPA (2009). This would decrease the salinity concentration in the influent. Using undiluted FGD wastewater resulted in poor retention of the majority of constituents measured in this study. High salt concentrations can be bioenergetically demanding to some organisms (Kulp, et al., 2007). Organisms must uphold an osmotic balance between their cytoplasm and the surrounding media while preventing sodium ions from entering the cell interior (Kulp, et al., 2007).

Although the removal of sulfate improved by the addition of organic carbon and the reduction of flow rate, it was also responsible for producing the highest concentration of arsenic. Furthermore, because there are uncertainties regarding the overall mechanism driving arsenic release in the columns, it is recommended that the concentration of arsenic and low-molecular-weight organic compounds (such as organic carbon) be monitored over time in CWTS. The results of this study provide significant evidence that organic carbon will increase the rate at which arsenic is released.

These uncertainties warrant further research to determine the overall mechanism that is driving the release of arsenic. This result also has important implications for Kansas groundwater should aquifers receive labile carbon addition. One scenario in which this may occur is the introduction of labile carbon into groundwater from landfill leachate. Environmental accidents in which landfill leachate breached landfill liner systems have been shown to result in arsenic mobilization and elevated groundwater arsenic concentrations down gradient from landfills (Mayo, 2006). Another scenario that should be investigated is the leaching of saline and organic carbon-laden production water from hydraulic fracturing operations into groundwater aquifers. Production and flowback waters, high in organic carbon and conductivity, are often stored in lined pits near hydraulic fracturing operations, and studies have documented accidental leaching of these waters into adjacent, shallow groundwater (Entrekin, et al., 2011; Hammer & VanBriesen, 2012).

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Appendix A - Soil Physical Data

Initial Water Content

Table A-1. Water content calculation for each column

Column	Sample ID	Empty Pan (g)	Pan w/ Soil (g)	Pan w/ dry soil (g)	θg (%)	Mean θg (%)
1	1	1.097	5.043	4.226	26%	26%
	2	1.11	8.089	6.643	26%	
2	1	1.059	6.592	5.428	27%	27%
	2	1.058	8.757	7.139	27%	
3	1	1.066	5.326	4.428	27%	27%
	2	1.056	6.452	5.31	27%	
4	1	1.061	6.627	5.446	27%	27%
	2	1.056	5.222	4.345	27%	
5	1	1.1	5.47	4.535	27%	27%
	2	1.06	5.09	4.237	27%	
6	1	1.083	7.26	5.935	27%	27%
	2	1.069	6.341	5.22	27%	
7	1	1.075	5.696	4.665	29%	29%
	2	1.073	7.258	5.876	29%	
8	1	1.086	4.9	4.09	27%	27%
	2	1.077	5.872	4.847	27%	
9	1	1.062	6.341	5.226	27%	26%
	2	1.115	6.707	5.557	26%	
10	1	1.083	7.673	6.269	27%	27%
	2	1.121	8.208	6.698	27%	

Calculation of Required Soil Mass in Each Column

Table A-2. Calculation of Required Soil Mass in Each Column

Column	Mean θg (%)	Required Soil Mass (g)	Required soil mass per section (g)
1	26%	896	112
2	27%	900	112
3	27%	901	113
4	27%	901	113
5	27%	903	113
6	27%	904	113
7	29%	915	114
8	27%	903	113
9	26%	898	112
10	27%	903	113
ρ_B (g/cm^3)	1.15		
V (cm^3)	618.03		

Volume of Effluent Collected

Table A-3. Volume of effluent (mL) collected per day from each column

Column	Day							
	3	6	8	10	12	14	16	18
1	96	101	69	71	68	69	69	66
2	45	49	34	35	30	35	35	33
3	47	50	36	34	32	35	34	32
4	46	39	36	34	32	35	35	31
5	48	51	35	36	31	35	34	29
6	48	51	36	36	32	36	32	32
7	47	51	36	33	31	35	35	31
8	47	52	35	32	33	35	32	33
9	47	51	36	36	32	36	32	32
10	47	50	35	20	33	33	34	31

Column	Day							
	20	22	24	26	28	30	32	34
1	61	67	69	65	64	40	69	70
2	35	36	29	19	32.5	29	34	35
3	33	36	32	33	35	34	34	35
4	35	35	31	35	34	31	35	36
5	35	32	32	33	32.5	31	34	34
6	33	36	31	36	33.5	21	33	36
7	32	34	34	31	34	34	33	34
8	32	36	24	35	33	18	33	35
9	31	34	30	35	35	16	34	33
10	32	35	31	29	37.5	33	36	33

Column	Day							
	36	38	40	42	44	46	48	50
1	66	68	67	68	68	65	68	67
2	32.5	32.5	32.5	33	30	32.5	35	32
3	32	35	32.5	35	24.5	32.5	32.5	32
4	31	32.5	32.5	35	29	32.5	35	32.5
5	31	32.5	32.5	35	27.5	32.5	35	31
6	32	32.5	34	34	30	32.5	35	32
7	32.5	30	15	33	32	32	36	30
8	22.5	32.5	15	34	30	32.5	34	32.5
9	22.5	25	17.5	32.5	32	32.5	35	30
10	30	30	17.5	32.5	32.5	35	32.5	32

Column	Day							
	52	54	56	58	60	62	64	66
1	68	61	67	69	65	67	66	68
2	33	33	33	30	32	31	32	32.5
3	32	33	33	32.5	33	32	31	32.5

Column	4	5	6	7	8	9	10	
4	32.5	35	31	33	31	33	32	32.5
5	32.5	34	32	30	16	28	30	32.5
6	32	35	31	32	15	30	32.5	32.5
7	31	34	32.5	31	32	33	30	32.5
8	31	34	32.5	32	32.5	32	30	32.5
9	32	34	32.5	30	32.5	32	32	32
10	31	34	32.5	31	32	32.5	31	32.5

Column	Day							
	68	70	72	74	76	78	80	82
1	64	67	67	66	65	69	67	69
2	34	34	26	34	34	27	33	34
3	33	33	30	32.5	34	30	34	34
4	34	35	28	34	35	29	34	32.5
5	34	21	22	33	33	27	33	33
6	33	22	25	33	32.5	29	34	33
7	34	32.5	30	32.5	35	29	33	32.5
8	34	32.5	30	33	32.5	29	33	34
9	33	34	30	34	34	30	32.5	32.5
10	32.5	34	31	31	35	29	34	32

Column	Day							
	84	86	88	90	92	94	96	98
1	67	69	65	69	63	71	83	67
2	33	27	34	34	31	28	31	34
3	34	30	35	35	31	28	29	34
4	34	31	33	35	32.5	28	29	34
5	32.5	31	32.5	32.5	28	34	33	26
6	32	30	32	34	31	34	33	26
7	33	30	32.5	33	31	32	33	34
8	33	30	33	34	31	34	32.5	34
9	34	31	32.5	34	31	34	33	34
10	34	31	34	32	31	34	32.5	32.5

Column	Day							
	100	102	104	106	108	110	112	114
1	67	70	64	69	68	69	30	50
2	27.5	35	32	31	34	32	34	29
3	29	35	33	32	33	32.5	34	30
4	29	37	32.5	33	33	33	34	31
5	27.5	27	22.5	31	29	27	33	29
6	29	30	22.5	32	29	21	32.5	29
7	29	35	32.5	30	34	34	34	30
8	29	37	32.5	32.5	33	34	34	30
9	28	35	33	32	34	34	32	24
10	29	35	33	31	33	35	29	22.5

Column	Day							
	116	118	120	122	124	126	128	130
1	69	70	65	69	65	69	69	70

2	33	33	32	32.5	27.5	32	24.5	20
3	32.5	33	32	32.5	27.5	31	29	20
4	33	33	32.5	33	27.5	31	30	19
5	33	33	31	32	33	33	30	34
6	33	32.5	31	32	33	32.5	31	34
7	34	33	31	33	33	33	32	34
8	34	32.5	31	33	33	34	31	34
9	34	33	32	32.5	33	32.5	31	34
10	33	34	32.5	33	34	33	32	33

Column	**Day**				
	132	**134**	**136**	**138**	**140**
1	17	69	69	68	62
2	23	27.5	22.5	20	26
3	24	30	23	20	27
4	25	32	22.5	20	26
5	22	27.5	10	22	34
6	22	28	10	22.5	34
7	34	32	34	32	35
8	34	30	34	32.5	35
9	34	25	34	22.5	32.5
10	35	27	34	27.5	32.5

Final Water Content Calculation

Table A-4. Water content calculation at the conclusion of experiment.

Column	Section	Empty Pan (g)	Pan w/ Soil (g)	Pan w/ dry soil (g)	θg (%)	Mean θg (%)	θv (%)	Mean θv (%)
1	1	1.08	4.634	3.561	43%	43%	51%	50%
	2	1.07	7.245	5.391	43%		50%	
	3	1.072	4.959	3.819	41%		49%	
	4	1.046	4.85	3.697	43%		51%	
	5	1.043	5.271	4.004	43%		50%	
	6	1.083	6.26	4.671	44%		52%	
2	1	1.093	5.555	4.253	41%	41%	48%	48%
	2	1.068	4.635	3.602	41%		48%	
	3	1.071	7.155	5.382	41%		48%	
	4	1.062	7.392	5.542	41%		48%	
	5	1.062	5.762	4.38	42%		49%	
	6	1.063	6.813	5.099	42%		50%	
3	1	1.081	6.339	4.821	41%	40%	47%	47%
	2	1.078	7.228	5.437	41%		48%	
	3	1.091	5.025	3.882	41%		48%	
	4	1.05	6.394	4.835	41%		48%	
	5	1.058	5.169	4.008	39%		46%	
	6	1.053	5.124	3.965	40%		47%	
4	1	1.055	3.909	3.067	42%	42%	49%	48%
	2	1.088	7.877	5.843	43%		50%	
	3	1.086	5.898	4.465	42%		49%	
	4	1.09	4.701	3.652	41%		47%	
	5	1.091	3.528	2.822	41%		47%	
	6	1.075	4.818	3.737	41%		47%	
5	1	1.079	5.076	3.899	42%	41%	49%	48%
	2	1.086	5.033	3.886	41%		48%	
	3	1.061	5.785	4.421	41%		47%	
	4	1.066	5.074	3.912	41%		48%	
	5	1.091	4.605	3.587	41%		48%	
	6	1.08	4.872	3.785	40%		47%	
6	1	1.08	6.331	4.799	41%	40%	48%	47%
	2	1.115	5.296	4.081	41%		48%	
	3	1.07	4.504	3.521	40%		47%	
	4	1.071	4.804	3.728	40%		47%	
	5	1.089	5.611	4.315	40%		47%	

	6	1.083	4.495	3.524	40%		47%	
7	1	1.071	6.402	4.849	41%	41%	48%	48%
	2	1.038	7.075	5.305	41%		49%	
	3	1.112	5.476	4.202	41%		48%	
	4	1.065	5.339	4.12	40%		47%	
	5	1.054	5.58	4.291	40%		47%	
	6	1.078	5.345	4.12	40%		47%	
8	1	1.069	4.966	3.832	41%	40%	48%	47%
	2	1.076	6.958	5.256	41%		48%	
	3	1.085	4.997	3.877	40%		47%	
	4	1.082	4.687	3.648	40%		47%	
	5	1.081	6.488	4.966	39%		46%	
	6	1.085	6.262	4.812	39%		46%	
9	1	1.066	5.872	4.416	43%	41%	50%	48%
	2	1.059	7.038	5.256	42%		49%	
	3	1.08	6.377	4.811	42%		49%	
	4	1.057	5.454	4.178	41%		47%	
	5	1.069	6.908	5.245	40%		46%	
	6	1.067	4.925	3.816	40%		47%	
10	1	1.061	4.788	3.674	43%	42%	50%	49%
	2	1.064	5.976	4.537	41%		48%	
	3	1.082	4.82	3.747	40%		47%	
	4	1.079	5.819	4.429	41%		49%	
	5	1.072	5.384	4.112	42%		49%	
	6	1.082	6.603	4.983	42%		49%	

Dry Soil and Bulk Density

Table A-5. Dry soil and bulk density calculation

Column	Sample ID	Mass (g)				θg (%)	ρ_b (g/cm³)
		Soil & Cylinder	Cylinder	Soil	Dry Soil		
1	1	242.772	61.146	181.626	126.791	0.43	1.17
	2	226.865	60.671	166.194	116.295	0.43	
	3	232.032	63.251	168.781	119.280	0.41	
	4	232.759	63.252	169.507	118.129	0.43	
	5	228.043	60.926	167.117	117.037	0.43	
	6	240.102	62.965	177.137	122.768	0.44	
2	1	235.431	63.528	171.903	121.742	0.41	1.17
	2	243.678	68.614	175.064	124.366	0.41	
	3	233.024	66.236	166.788	118.183	0.41	
	4	237.124	66.790	170.334	120.552	0.41	
	5	226.236	64.934	161.302	113.872	0.42	
	6	247.883	69.589	178.294	125.147	0.42	
3	1	241.284	67.663	173.621	123.496	0.41	1.17
	2	233.192	66.585	166.607	118.088	0.41	
	3	236.637	67.503	169.134	119.993	0.41	
	4	235.195	68.271	166.924	118.227	0.41	
	5	232.835	66.651	166.184	119.251	0.39	
	6	244.616	68.503	176.113	125.974	0.40	
4	1	236.994	66.127	170.867	120.457	0.42	1.16
	2	237.704	68.132	169.572	118.768	0.43	
	3	229.856	64.106	165.750	116.390	0.42	
	4	230.653	66.286	164.367	116.618	0.41	
	5	236.707	67.214	169.493	120.391	0.41	
	6	243.591	67.008	176.583	125.585	0.41	
5	1	240.976	67.328	173.648	122.514	0.42	1.17
	2	228.374	66.090	162.284	115.124	0.41	
	3	235.538	67.553	167.985	119.481	0.41	
	4	238.868	69.291	169.577	120.413	0.41	
	5	233.251	66.689	166.562	118.309	0.41	
	6	251.431	70.628	180.803	128.975	0.40	
6	1	235.568	67.460	168.108	119.062	0.41	1.17
	2	237.871	66.386	171.485	121.651	0.41	
	3	235.715	67.059	168.656	120.377	0.40	
	4	234.293	66.553	167.740	119.391	0.40	
	5	235.247	67.848	167.399	119.423	0.40	

	6	242.839	67.830	175.009	125.204	0.40	
7	1	242.590	66.742	175.848	124.621	0.41	1.17
	2	228.157	64.804	163.353	115.459	0.41	
	3	235.165	66.280	168.885	119.582	0.41	
	4	237.072	66.806	170.266	121.704	0.40	
	5	229.326	65.071	164.255	117.475	0.40	
	6	241.218	67.819	173.399	123.618	0.40	
8	1	243.121	70.304	172.817	122.528	0.41	1.17
	2	230.451	66.846	163.605	116.265	0.41	
	3	238.796	69.229	169.567	121.020	0.40	
	4	235.161	67.955	167.206	119.015	0.40	
	5	233.264	67.010	166.254	119.456	0.39	
	6	238.518	66.700	171.818	123.694	0.39	
9	1	244.429	68.218	176.211	122.827	0.43	1.16
	2	230.423	66.928	163.495	114.766	0.42	
	3	237.932	68.568	169.364	119.293	0.42	
	4	235.868	67.354	168.514	119.612	0.41	
	5	235.556	67.285	168.271	120.346	0.40	
	6	236.227	68.709	167.518	119.364	0.40	
10	1	239.573	66.644	172.929	121.241	0.43	1.17
	2	233.687	65.803	167.884	118.701	0.41	
	3	233.729	65.068	168.661	120.247	0.40	
	4	243.028	68.178	174.850	123.575	0.41	
	5	232.841	65.781	167.060	117.779	0.42	
	6	237.998	65.694	172.304	121.746	0.42	

Pore Volume Calculation

Pore Volumes were calculated using the following equation:

$$T = \frac{V(t)}{V_o}$$

Where,

V(t)=Cumulative Total Volume (from Table A-3.)

Vo=$V_c\theta_v$ (V_c=618.03, θ_v from Table A-4.)

Table A-6. Results for pore volume calculation

Column	Day							
	3	6	8	10	12	14	16	18
1	0.3	0.6	0.9	1.1	1.3	1.5	1.8	2.0
2	0.2	0.3	0.4	0.6	0.7	0.8	0.9	1.0
3	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.0
4	0.2	0.3	0.4	0.5	0.6	0.8	0.9	1.0
5	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.0
6	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.1
7	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.0
8	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.0
9	0.2	0.3	0.5	0.6	0.7	0.8	0.9	1.0
10	0.2	0.3	0.4	0.5	0.6	0.7	0.9	1.0
Column	Day							
	20	22	24	26	28	30	32	34
1	2.2	2.4	2.6	2.8	3.1	3.2	3.4	3.6
2	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.9
3	1.2	1.3	1.4	1.5	1.6	1.7	1.9	2.0
4	1.1	1.2	1.3	1.4	1.6	1.7	1.8	1.9
5	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
6	1.2	1.3	1.4	1.5	1.6	1.7	1.8	2.0
7	1.1	1.3	1.4	1.5	1.6	1.7	1.8	2.0
8	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
9	1.1	1.2	1.3	1.5	1.6	1.6	1.8	1.9
10	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.9
Column	Day							
	36	38	40	42	44	46	48	50
1	3.9	4.1	4.3	4.5	4.7	5.0	5.2	5.4
2	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7

3	2.1	2.2	2.3	2.5	2.5	2.7	2.8	2.9
4	2.0	2.1	2.2	2.3	2.4	2.5	2.7	2.8
5	2.0	2.2	2.3	2.4	2.5	2.6	2.7	2.8
6	2.1	2.2	2.3	2.4	2.5	2.6	2.8	2.9
7	2.1	2.2	2.2	2.3	2.4	2.6	2.7	2.8
8	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7
9	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6
10	2.0	2.1	2.1	2.2	2.3	2.5	2.6	2.7

Column	Day							
	52	54	56	58	60	62	64	66
1	5.6	5.8	6.0	6.3	6.5	6.7	6.9	7.1
2	2.8	3.0	3.1	3.2	3.3	3.4	3.5	3.6
3	3.0	3.1	3.2	3.3	3.4	3.6	3.7	3.8
4	2.9	3.0	3.1	3.2	3.3	3.4	3.5	3.7
5	2.9	3.1	3.2	3.3	3.3	3.4	3.5	3.6
6	3.0	3.1	3.2	3.3	3.4	3.5	3.6	3.7
7	2.9	3.0	3.1	3.2	3.3	3.5	3.6	3.7
8	2.8	3.0	3.1	3.2	3.3	3.4	3.5	3.6
9	2.7	2.9	3.0	3.1	3.2	3.3	3.4	3.5
10	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.6

Column	Day							
	68	70	72	74	76	78	80	82
1	7.3	7.6	7.8	8.0	8.2	8.4	8.6	8.9
2	3.7	3.8	3.9	4.0	4.2	4.2	4.4	4.5
3	3.9	4.0	4.1	4.2	4.3	4.4	4.6	4.7
4	3.8	3.9	4.0	4.1	4.2	4.3	4.4	4.5
5	3.7	3.8	3.9	4.0	4.1	4.2	4.3	4.4
6	3.8	3.9	4.0	4.1	4.2	4.3	4.4	4.5
7	3.8	3.9	4.0	4.1	4.2	4.3	4.5	4.6
8	3.8	3.9	4.0	4.1	4.2	4.3	4.4	4.5
9	3.6	3.7	3.8	4.0	4.1	4.2	4.3	4.4
10	3.7	3.8	3.9	4.0	4.1	4.2	4.3	4.4

Column	Day							
	84	86	88	90	92	94	96	98
1	9.1	9.3	9.5	9.8	10.0	10.2	10.5	10.7
2	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3
3	4.8	4.9	5.0	5.1	5.3	5.4	5.5	5.6
4	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.4
5	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3
6	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.4
7	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.5
8	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.5
9	4.5	4.6	4.7	4.8	4.9	5.1	5.2	5.3
10	4.5	4.6	4.8	4.9	5.0	5.1	5.2	5.3

Column	Day							
	100	**102**	**104**	**106**	**108**	**110**	**112**	**114**
1	10.9	11.1	11.3	11.6	11.8	12.0	12.1	12.3
2	5.4	5.5	5.7	5.8	5.9	6.0	6.1	6.2
3	5.7	5.8	5.9	6.0	6.1	6.2	6.4	6.5
4	5.5	5.6	5.7	5.9	6.0	6.1	6.2	6.3
5	5.4	5.5	5.6	5.7	5.8	5.9	6.0	6.1
6	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.2
7	5.6	5.7	5.8	5.9	6.0	6.1	6.3	6.4
8	5.6	5.7	5.8	5.9	6.0	6.2	6.3	6.4
9	5.4	5.5	5.6	5.7	5.8	5.9	6.1	6.1
10	5.4	5.5	5.6	5.7	5.9	6.0	6.1	6.1

Column	Day							
	116	**118**	**120**	**122**	**124**	**126**	**128**	**130**
1	12.5	12.7	12.9	13.2	13.4	13.6	13.8	14.1
2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0
3	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3
4	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1
5	6.2	6.3	6.4	6.5	6.6	6.8	6.9	7.0
6	6.3	6.4	6.5	6.6	6.8	6.9	7.0	7.1
7	6.5	6.6	6.7	6.8	6.9	7.0	7.2	7.3
8	6.5	6.6	6.7	6.8	6.9	7.1	7.2	7.3
9	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0
10	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0

Column	Day				
	132	**134**	**136**	**138**	**140**
1	14.1	14.3	14.6	14.8	15.0
2	7.1	7.2	7.2	7.3	7.4
3	7.4	7.5	7.6	7.6	7.7
4	7.2	7.3	7.4	7.4	7.5
5	7.1	7.1	7.2	7.3	7.4
6	7.2	7.3	7.3	7.4	7.5
7	7.4	7.5	7.6	7.7	7.8
8	7.4	7.5	7.6	7.8	7.9
9	7.1	7.2	7.3	7.4	7.5
10	7.2	7.3	7.4	7.5	7.6

Appendix B - Water Analysis Data

All units in mg/L except As(µg/L), pH, EC (mS/cm), FI, FRI, HIX, and all Peaks

Column 1

Table B-1. Column 1: Water Analysis Data (Control Q)

Day	PV	Boron (mg)	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.3	0.083	17.33	5.59	29.24	944.49	509.23	4.36	14.39	427.75	7.81	2.77	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	0.034	16.82	0.77	118.69	951.18	511.02	1.77	14.77	453.48		3.31	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	0.009	25.15	0.51	27.79	1698.39	1126.42	940.84	13.71	766.46	7.61	6.20	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	0.087	24.27	0.36	535.28	1783.27	1582.93	977.58	82.19	1065.99		7.81	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	0.08	24.43	0.24	732.54	1498.91	1521.84	1039.57	12.40	1236.23	7.48	8.38	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	0.303	24.98	0.24	628.76	889.58	991.33	1045.40	48.80	1263.07		8.25	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	0.112	27.17	0.25	766.05	1132.08	1263.30	1064.00	49.00	1319.80	7.45	8.36	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	0.084	28.37	0.18	995.87	1641.00	1731.16	964.00	48.20	1306.20		7.03		51.76	80.68	1.58	0.70	9.25	23.32	2.42	3.81	10.29	13.85
50	5.4	0.436	26.27	0.18	751.19	922.97	1289.65	1067.00	49.37	1526.01	7.48	8.65	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	0.052	28.36	0.04	632.24	803.99	1266.33	1122.64	48.20	1589.87		9.18		50.72	84.46	1.56	0.71	10.47	14.21	1.32	2.05	6.37	8.26
62	6.7	0.004	26.72	0.13	816.50	1125.25	1891.95	1006.17	47.95	1516.56	7.76	9.17	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	0.236	27.08	0.07	768.93	910.62	1760.58	1062.26	45.73	1607.69		9.31		52.80	78.98	1.54	0.67	10.87	21.65	1.70	2.80	8.73	11.63
74	8.0	0.13	26.73	0.07	771.45	799.54	1737.83	1089.63	47.54	1678.88	7.61	9.26	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	0.52	31	0	760.04	795.00	1853.73	1143.60	59.20	1700.93	7.73	9.49	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	0.555	32.59	0	787.23	795.96	2005.48	1102.40	52.40	1660.00	7.76	9.63	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	1.656	34.93	0	828.29	818.98	2144.78	1157.20	38.00	1739.73	7.92	9.32	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	3.809	34.66	0	787.93	757.82	1956.25	1148.90	42.41	1717.55		9.17	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	4.189	33.8	0.00	783.29	753.11	1983.09	1146.38	53.58	1727.51		9.29	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	4.151	32.65	0	777.70	740.04	1981.08	1189.23	38.08	1830.50		9.32	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	4.80	36.16	0.75	845.96	808.62	2101.31	1166.56	40.26	1780.88		9.79	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	5.17	38.63	3.21	925.32	828.65	2206.91	1259.92	23.52	1955.31		9.49	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	5.46	35.55	5.22	872.75	801.68	2142.60	1152.50	34.99	1824.47		9.70	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	5.70	38.65	0.00	865.37	805.47	2127.01	1119.31	56.91	1797.93		9.85	37.87	42.43	74.06								
140	15.0	5.62	40.07	0	904.86	835.04	2226.80	1147.37	35.95	1825.62	7.45	9.17	21.94	34.39	75.26								

Column 2

Table B-2. Column 2: Water Analysis Data (Control 1/2Q)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.046	17.11	7.39	27.93	875.85	500.53	4.07	13.95	444.73	7.61	2.66	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	0.015	16.37	8.17	35.57	681.33	363.81	4.17	14.82	458.35		2.22	40.76	108.98	14.60								
14	0.8	0.005	16.61	1.15	17.97	901.34	467.34	249.14	13.43	375.09	7.66	3.06	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	0.093	23.23	0.37	17.05	1800.89	1025.11	764.34	14.98	638.73		5.35	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	0.05	22.87	0.29	91.06	1869.32	1169.22	950.96	13.49	866.89	7.72	6.07	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	0.241	24.6	0.14	238.97	1287.90	915.26	1026.00	46.80	961.00		7.31	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	0.106	26.71	0.15	450.03	1528.71	1190.58	1053.40	100.20	1085.00	7.37	7.63	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	0.088	27.59	0.14	585.04	1638.72	1412.28	994.00	57.60	1052.13		7.18		58.30	78.30	1.60	0.71	8.38	16.62	2.04	2.90	7.58	10.15
50	2.7	0.304	23.59	0.14	689.11	1349.41	1265.78	1105.30	52.44	1212.54	7.75	7.55	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	0.033	24.82	0.01	629.72	1384.17	1253.56	1126.34	51.64	1253.33		7.83		53.24	80.86	1.62	0.71	8.30	11.77	1.39	2.06	5.26	7.16
62	3.4	0	18.77	0.02	771.12	1311.81	1259.86	1053.90	50.75	1186.07	7.67	7.89	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	0.21	27.5	0	813.48	1562.71	1443.09	1068.91	51.04	1250.25		6.62		47.08	73.70	1.59	0.71	8.44	13.55	1.59	2.37	6.00	8.17
74	4.0	0.134	28.46	0.03	774.93	1559.23	1402.16	1096.46	47.04	1337.62	7.54	8.31	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	0.435	31.5	0	750.61	862.76	823.17	1140.80	49.20	1395.33	7.56	7.78	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	0.206	32.38	0	771.33	986.27	968.44	984.40	49.20	1334.80	7.67	6.89	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	0.239	33.05	0	753.60	966.53	1095.39	1141.60	36.40	1433.87	7.67	6.88	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	0.423	32.97	0	784.23	860.77	1067.81	1138.60	40.62	1495.90		8.73	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	0.359	31.31	0	783.78	856.13	1181.81	1149.91	48.14	1587.76		8.73	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	0.36	32.21	0	773.40	1480.18	1829.56	1170.49	43.64	1720.49		8.85	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	0.437	33.60	0	719.80	743.90	1261.72	1127.27	36.04	1684.73		9.39	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	0.290	34.77	0	903.42	717.77	1508.27	1251.34	25.06	1867.69		9.23	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	0.765	34.21	0	686.36	694.37	1347.86	1146.68	25.06	1771.88		9.32	90.10	49.29	47.31								
134	7.2	0.491	37.49	0	874.91	1000.58	1816.28	1117.18	44.50	1715.43		8.96	85.12	53.35	46.37								
140	7.4	0.501	39.93	0	841.29	947.89	1873.23	1169.86	58.43	1717.82	7.77	8.74	79.78	55.83	48.98								

Column 3

Table B-3. Column 3: Water Analysis Data (with inoculum)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.028	17.17	6.85	40.13	749.99	442.69	3.81	13.82	475.09	7.61	2.80	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	0.01	15.8	6.2	21.34	692.53	357.96	4.93	13.03	458.67		2.25	35.41	94.22	14.34								
14	0.8	0.003	16.72	1.32	24.12	927.50	460.99	258.67	13.09	381.33	7.70	2.93	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	0.005	18.96	0.33	13.02	1610.26	1008.93	901.66	14.19	603.32		5.37	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	0.03	25.29	0.26	41.86	1758.59	1174.78	1037.50	13.09	908.17	7.72	5.55	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	0.201	24.41	0.17	260.71	1526.15	1084.20	981.20	46.00	948.40		7.36	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	0.102	26.78	0.17	513.96	1592.67	1310.62	1047.00	94.80	1126.27	7.49	7.74	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	0.089	27.76	0.17	668.14	1638.47	1451.57	991.80	54.00	1087.80		7.75		53.94	78.76	1.61	0.68	8.73	20.77	2.42	3.43	9.40	12.73
50	2.9	0.239	24.84	0.17	716.55	1358.34	1262.76	1078.79	51.98	1190.92	7.81	7.44	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	0.049	27.56	0.03	793.24	1654.96	1515.49	1100.40	49.36	1240.45		6.71		50.88	76.82	1.62	0.69	9.12	15.27	1.82	2.48	6.87	9.46
62	3.6	0	25.88	0.03	837.86	1363.20	1316.86	1069.76	56.18	1188.46	7.59	7.47	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	0.195	28.31	0.03	804.41	1527.05	1406.25	1105.03	49.81	1257.00		7.26		47.98	80.72	1.62	0.68	8.20	10.82	1.25	1.87	4.75	6.58
74	4.2	0.133	27.51	0.04	698.13	1455.51	1300.71	1134.63	54.93	1321.00	7.55	8.24	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	0.373	29.73	0	755.04	1290.39	1159.54	1141.60	36.40	1411.60	7.62	8.28	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	0.214	30.52	0	600.64	1166.17	1017.76	1111.20	54.80	1365.07	7.51	7.92	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	0.203	32.4	0	808.32	1197.00	1275.10	1147.20	56.00	1450.00	7.61	6.94	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	0.302	30.46	0	781.81	854.85	1043.81	1141.38	58.02	1499.07		8.54	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	0.254	31.39	0	775.24	1002.66	1280.11	1144.84	45.21	1575.57		8.62	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	0.243	32.54	0	760.79	910.66	1330.81	1164.12	43.07	1698.66		8.90	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	0.254	34.35	0	877.61	746.90	1384.16	1121.73	35.29	1691.66		7.73	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	0.144	35.55	0	945.02	735.46	1516.60	1242.20	23.93	1944.58		9.29	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	0.532	36.45	0	838.18	759.11	1530.39	1130.77	39.98	1781.13		9.09	65.78	45.29	41.55								
134	7.5	0.332	39.64	0	845.61	855.41	1651.45	1000.40	37.21	1740.43		9.09	62.21	50.26	44.79								
140	7.7	0.331	41.04	0	818.71	1031.76	1773.98	1131.95	38.74	1697.93	7.73	8.42	63.07	52.97	48.81								

Column 4

Table B-4. Column 4: Water Analysis Data (with inoculum)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.021	17.36	5.97	30.99	781.58	442.70	3.54	15.15	432.62	7.75	2.52	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	0.011	16.18	5.52	20.62	702.86	381.47	3.58	13.70	471.18		2.54	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	0.005	16.17	2.42	14.56	912.57	444.14	193.50	13.18	395.72	7.75	2.72	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	0.081	18.26	0.31	9.84	1370.36	812.19	893.61	13.67	467.71		5.06	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	0.02	24.62	0.23	14.51	2055.99	1366.93	1044.03	13.31	920.52	7.74	5.41	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	0.174	23.89	0.18	211.87	1562.00	1124.70	1050.40	46.20	1030.13		7.59	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	0.099	25.94	0.19	498.10	1442.51	1126.58	1049.20	117.20	1150.53	7.41	7.46	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	0.087	27.21	0.13	647.53	1641.48	1488.67	991.20	56.80	1124.73		6.80		55.36	79.84	1.60	0.68	8.75	18.01	2.15	2.96	8.24	11.25
50	2.8	0.19	25.19	0.13	717.59	1221.43	1169.69	1084.37	53.95	1212.91	7.66	7.77	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	0.043	27.18	0.02	792.41	1268.17	1241.65	1129.66	50.50	1251.80		6.70		49.40	86.98	1.59	0.69	9.29	19.27	2.00	3.11	8.51	11.64
62	3.4	0	26.46	0.07	710.23	1307.42	1259.26	1023.15	48.56	1193.43	7.57	8.01	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	0.175	26.81	0.02	635.40	1337.42	1221.47	1088.50	49.44	1270.14		6.82		46.30	87.64	1.60	0.70	8.85	11.96	1.23	2.05	5.28	7.32
74	4.1	0.129	28.17	0.04	714.72	1528.90	1380.11	1075.73	54.95	1226.33	7.56	8.53	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	0.34	30.32	0	757.26	1069.64	1007.06	1142.00	35.60	1420.40	7.62	8.55	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	0.201	31.36	0	782.78	1312.83	1224.82	1104.80	56.40	1368.93	7.61	7.03	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	0.194	32.27	0	787.94	1143.74	1241.05	1149.60	62.40	1471.87	7.60	6.99	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	0.265	31.65	0	785.44	878.90	1072.44	1142.41	40.58	1536.24		8.66	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	0.216	30.1	0	817.53	889.31	1254.48	1137.51	38.69	1613.62		8.53	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	0.571	31.8	0	768.09	919.44	1334.29	1153.10	42.98	1711.84		8.97	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	0.169	32.31	0	876.43	763.03	1444.96	1124.72	41.54	1675.88		9.42	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	0.088	33.61	0	916.35	748.29	1545.33	1262.62	22.17	1927.26		9.33	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	0.428	38.52	0	855.52	1010.65	1775.96	1150.32	38.54	1809.61		9.28	52.08	44.13	39.89								
134	7.3	0.268	36.12	0	847.77	843.78	1696.74	1125.38	47.79	1741.69		9.12	55.46	50.83	41.81								
140	7.5	0.261	36.52	0	857.00	990.17	1893.67	1144.16	48.10	1726.55	7.77	8.81	46.85	49.67	42.22								

121

Column 5

Table B-5. Column 5: Water Analysis Data (with organic carbon)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	DOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.02	17.24	9.6	27.80	732.71	435.91	3.73	13.63	429.30	7.62	2.66	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	0.008	15.93	3.82	23.72	813.88	413.85	3.72	13.63	456.11		2.55	39.47	97.60	13.73								
14	0.8	0.005	16.45	0.95	15.29	930.03	441.25	226.83	12.97	382.21	7.62	3.05	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	0.076	17.89	0.28	13.25	1376.98	753.02	936.10	13.32	477.01		5.18	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	0.02	20.86	0.41	18.86	1625.52	991.12	998.44	13.85	798.65	7.80	5.84	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	0.156	24.29	0.17	259.04	1802.79	1195.66	1093.00	46.40	905.87		7.24	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	0.099	25.55	0.17	604.55	1595.97	1220.31	1098.60	108.60	979.73	7.43	7.21	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	0.087	26.55	0.18	785.92	1369.83	1213.91	983.60	54.00	907.80		7.38		64.30	76.26	1.57	0.69	8.42	14.11	1.76	2.44	6.31	8.65
50	2.8	0.158	26.19	0.18	868.32	1220.34	1167.16	1079.22	49.05	975.14	7.72	7.07	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	0.043	28.82	0.04	982.34	1369.36	1270.43	1115.92	51.23	1012.52		6.37		55.04	70.40	1.59	0.71	8.70	13.68	1.74	2.31	6.15	8.49
62	3.4	0	21.89	0.05	1020.20	1369.32	1250.30	1019.02	47.18	951.41	7.86	5.86	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	0.164	29.08	0.04	916.43	1229.53	1061.36	1065.58	47.18	1065.35		6.67		56.00	34.80	1.59	0.70	7.79	13.81	1.64	2.46	6.10	8.54
74	4.0	0.125	28.33	0.08	976.20	1306.05	1123.63	1098.81	46.58	1066.76	7.60	7.75	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	0.312	33.73	0	984.85	1241.89	1040.84	1154.40	50.80	1106.53	7.59	6.42	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	0.199	33.43	0	746.00	1169.84	988.22	1074.80	36.00	1040.13	7.65	6.14	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	0.185	34.02	0	951.42	1086.72	1097.88	1119.20	36.00	1127.87	7.61	6.32	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	0.24	32.31	0	963.45	1228.36	1194.17	1115.95	53.42	1139.62		6.60	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	0.194	33.03	0	955.49	1065.49	1154.55	999.90	38.97	1145.72		6.40	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	0.447	32.16	0	919.58	1093.99	1186.12	1012.17	38.97	1185.64		6.44	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	0.114	34.17	0	1068.47	1349.67	1435.23	1113.75	38.96	1194.66		8.87	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	0.049	32.87	0	1139.96	1323.71	1560.89	1246.39	22.42	1369.67		8.22	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	0.341	31.12	0	1042.47	1078.28	1428.98	1014.04	36.68	1323.71		8.40	157.99	51.84	37.20								
134	7.1	0.234	34.25	0	1047.12	987.82	1507.29	1118.81	55.65	1306.57		8.42	143.24	61.10	38.30								
140	7.4	0.228	34.01	0	1039.96	919.87	1436.81	1009.69	55.65	1269.52	7.81	8.72	163.04	62.99	38.05								

122

Column 6

Table B-6. Column 6: Water Analysis Data (with organic carbon)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.019	17.3	7.69	27.13	775.14	445.43	3.90	12.70	409.07	7.58	2.81	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	0.007	16.01	9.7	12.38	463.89	242.31	3.79	12.70	482.01		2.90	28.77	123.54	15.45								
14	0.8	0.001	16.7	1.41	16.07	936.50	439.29	218.36	12.70	386.04	7.68	2.90	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	0.074	19.71	0.32	44.37	1216.09	595.49	904.12	12.70	505.77		5.17	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	0.02	20.36	0.24	17.71	1505.53	909.88	1045.50	12.70	789.92	7.62	5.92	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	0.148	24.06	0.17	261.04	1476.88	1015.65	1061.20	46.00	894.73		7.22	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	0.095	26.16	0.19	632.26	1533.78	1233.75	1089.40	114.60	988.27	7.53	7.02	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	0.086	27.28	0.17	821.94	1390.17	1266.21	1041.40	64.40	935.07		6.39		62.94	80.57	1.59	0.69	8.08	17.50	2.30	3.16	7.87	10.86
50	2.9	0.122	23.24	0.17	904.50	1237.12	1211.06	1075.80	52.18	965.96	7.52	7.42	60.42	59.74	83.54	1.58	0.68	8.21	11.94	1.54	2.10	5.45	7.59
56	3.2	0.024	26.92	0.04	972.74	1318.50	1270.60	1131.40	52.99	1003.51		6.32		56.72	80.65	1.60	0.70	8.54	13.96	1.68	2.37	6.28	8.72
62	3.5	0	21.32	0.05	1038.88	1592.68	1307.18	1022.07	47.33	919.66	7.52	6.35	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	0.161	28.27	0.06	970.67	1284.28	1142.52	1069.60	47.97	985.07		6.35		55.42	54.91	1.61	0.69	8.35	13.13	1.63	2.41	5.90	8.32
74	4.1	0.121	27.92	0.07	889.40	1193.69	1009.47	1104.87	54.07	1042.00	7.63	7.72	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	0.285	31.6	0	945.46	1179.88	997.63	1136.00	51.60	1079.73	7.50	7.90	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	0.192	30.98	0	973.28	1408.05	1222.84	1100.00	53.60	1051.47	7.43	6.61	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	0.18	31.04	0	1017.75	1100.80	1085.65	1132.00	51.20	1127.73	7.48	6.46	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	0.219	31.05	0	906.32	1113.27	1087.31	1128.84	46.84	1138.04		6.42	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	0.181	30.14	0	958.14	984.49	1099.23	1123.56	41.95	1157.79		6.50	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	0.361	29.73	0	927.52	1072.87	1194.38	1127.70	41.98	1164.64		6.32	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	0.078	34.63	0	1085.41	1309.94	1454.44	1122.83	45.55	1194.12		8.77	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	0.031	33.66	0	1099.92	1128.40	1435.19	1036.56	27.69	1126.16		8.69	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	0.272	30.81	0	1043.48	1072.39	1477.04	1145.06	55.36	1322.12		8.43	133.13	53.72	33.84								
134	7.3	0.211	33.75	0	1067.27	977.43	1547.57	1137.52	54.51	1299.09		8.03	149.56	59.56	34.07								
140	7.5	0.199	32.24	0	1024.05	599.58	1439.32	1137.94	42.78	1283.99	7.69	8.22	138.06	58.34	34.19								

Column 7

Table B-7. Column 7: Water Analysis Data (with inoculum and arsenic)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.015	16.93	5.95	27.79	735.64	438.76	5.36	13.66	468.91	7.62	2.61	26.22	96.16	13.51	1.58	0.62	7.48	13.81	2.21	2.73	6.04	8.32
8	0.5	0.006	14.78	5.86	31.27	746.91	412.30	7.74	14.10	460.79		2.62	33.65	108.96	13.26	1.57	0.62	7.51	12.64	2.17	2.57	5.50	7.83
14	0.8	0.197	15.78	0.54	16.08	910.58	481.44	231.76	13.23	390.73	7.78	2.86	35.09	128.90	25.28	1.61	0.64	6.89	13.63	2.58	2.99	6.08	8.53
20	1.1	0.077	18.75	0.31	10.90	1317.43	776.81	904.85	16.74	519.90		5.03	25.27	65.32	57.16	1.60	0.67	7.88	12.41	1.91	2.40	5.82	7.92
26	1.5	0.01	22.96	0.22	21.60	1814.37	1232.69	1007.58	15.41	976.45	7.75	6.35	27.67	70.30	63.51	1.61	0.69	9.12	16.43	2.12	2.85	7.39	10.29
32	1.8	0.131	23.7	0.16	230.81	1590.38	1179.99	994.60	46.60	1053.67		7.66	35.73	63.96	74.94	1.59	0.68	8.91	21.11	2.67	3.53	9.39	12.84
38	2.2	0.095	26.74	0.19	481.64	1592.54	1310.20	1040.40	102.20	1170.73	7.47	7.06	45.83	64.52	84.70	1.60	0.70	8.19	19.80	2.44	3.42	8.91	12.12
44	2.4	0.08	26.56	0.14	626.13	1686.30	1474.48	1016.80	53.60	1143.73		6.38		56.58	79.51	1.60	0.69	8.68	19.86	2.46	3.43	8.88	12.25
50	2.8	0.101	24.62	0.14	637.26	1124.23	1083.84	1081.31	53.19	1223.24	7.66	7.40	45.06	48.54	87.28	1.64	0.70	8.52	11.87	1.48	2.04	5.42	7.50
56	3.1	0.016	25.66	0.03	708.68	1237.74	1085.04	1109.34	49.99	1266.26		6.97		53.50	81.17	1.60	0.69	8.80	13.19	1.46	2.15	5.82	8.18
62	3.5	0	13.16	0.12	771.17	1508.35	1422.92	1016.15	47.78	1213.46	7.58	8.01	40.64	49.02	81.92	1.60	0.68	8.89	16.17	1.82	2.73	7.20	10.03
68	3.8	0.154	29.66	0	808.24	1566.77	1431.62	1103.66	50.33	1295.09		8.19		49.00	81.75	1.60	0.69	8.58	11.77	1.29	1.97	5.17	7.30
74	4.1	0.11	28.74	0.05	815.34	1733.06	1583.50	1116.99	49.22	1369.12	7.57	8.36	40.65	46.30	72.16	1.59	0.69	7.01	21.17	2.63	3.87	9.24	12.99
80	4.5	0.265	30.71	0	754.93	1131.55	1057.53	1134.80	57.20	1422.27	7.56	7.97	34.68	48.17	53.02	1.59	0.70	10.23	11.25	1.08	1.84	4.87	6.70
86	4.8	0.19	31.96	0	796.14	1101.43	1121.29	1084.00	56.80	1375.20	7.62	6.90	33.63	45.56	42.65	1.60	0.70	9.61	16.60	1.73	2.76	7.39	10.30
92	5.1	0.179	32.15	0	799.47	1347.93	1450.45	1104.40	36.00	1442.93	7.68	6.70	31.03	44.60	41.52	1.63	0.68	8.97	11.89	1.23	1.87	5.12	7.12
98	5.5	0.206	34.27	0	752.04	942.22	1139.98	1138.62	42.77	1550.45		8.67	26.58	47.19	40.87	1.61	0.69	10.41	20.42	1.76	3.06	8.65	11.78
104	5.8	0.168	32.45	0	760.04	839.79	1171.46	1124.82	47.14	1571.35		8.80	26.91	46.25	45.11	1.61	0.69	11.19	17.29	1.43	2.33	7.28	9.92
110	6.1	0.296	32.75	0	751.05	1368.44	1643.88	1148.85	56.46	1645.73		8.93	31.30	47.43	56.30	1.56	0.67	10.63	18.55	1.07	2.26	6.31	9.17
116	6.5	0.055	38.31	0	848.66	855.73	1469.04	1138.84	54.06	1648.98		9.49	45.96	46.16	64.39	1.55	0.67	9.96	18.22	1.21	2.59	6.80	10.04
122	6.8	0.016	37.13	0	892.82	851.43	1573.15	1241.30	25.96	1795.08		9.15	32.11	44.41	69.92	1.57	0.69	11.82	16.28	1.11	1.97	6.57	8.86
128	7.2	0.243	41.24	0	859.07	848.50	1679.82	1183.22	51.03	1698.14		9.35	51.67	45.27	75.43								
134	7.5	0.191	40.60	0	860.46	1013.25	1880.89	1123.86	55.32	1649.74		9.10	39.12	50.70	75.97								
140	7.8	0.179	37.48	0	834.46	1001.56	1910.50	1142.00	53.95	1667.59	7.71	8.94	33.20	47.92	75.30								

Column 8

Table B-8. Column 8: Water Analysis Data (with inoculum)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.012	17.53	7.49	27.42	694.82	401.87	3.91	0.98	491.61	7.57	2.89	17.04	104.68	13.08	1.58	0.63	7.17	12.55	2.12	2.64	5.60	7.60
8	0.5	0.006	15.93	7.28	29.56	850.62	439.09	3.80	12.99	477.70		2.54	33.36	132.90	14.36	1.58	0.62	7.18	11.60	2.12	2.38	5.11	7.21
14	0.8	0.136	16.03	0.73	17.54	997.76	531.70	282.46	13.32	397.52	7.72	2.95	37.24	98.86	26.98	1.60	0.63	6.91	12.59	2.35	2.56	5.73	7.98
20	1.2	0.054	18.1	0	10.14	1535.04	825.03	892.87	13.85	569.40		5.28	33.71	69.62	57.30	1.59	0.66	8.10	12.63	1.98	2.42	5.85	8.02
26	1.5	0.01	20.96	0.3	25.30	1994.11	1415.95	1048.24	13.00	944.86	7.74	6.14	32.00	70.44	63.21	1.61	0.69	9.17	17.52	2.22	2.94	7.90	11.05
32	1.8	0.124	24.02	0.21	234.01	1366.10	1012.09	1057.60	46.20	1049.67		7.22	39.86	56.38	63.98	1.62	0.69	8.92	22.20	2.62	3.70	9.96	13.46
38	2.1	0.09	26.8	0.21	490.67	1549.89	1284.80	1048.60	91.00	1162.67	7.58	7.26	44.58	63.32	85.82	1.59	0.69	8.30	21.25	2.57	3.56	9.38	12.81
44	2.4	0.078	26.91	0.17	637.87	1372.04	1178.83	1050.40	60.20	1124.13		6.38		58.82	80.53	1.61	0.69	8.86	12.82	1.56	2.23	5.79	7.93
50	2.7	0.091	26.44	0.17	667.82	1133.98	1098.36	1080.97	51.26	1200.36	7.64	7.75	51.79	52.34	86.78	1.60	0.69	8.52	10.81	1.30	1.84	4.87	6.68
56	3.1	0.011	25.77	0.04	787.89	1407.98	1341.51	1098.72	51.32	1242.41		6.83		48.70	86.69	1.59	0.69	8.36	15.37	1.80	2.79	7.00	9.51
62	3.4	0.49	26.04	0.05	779.06	1529.79	1433.12	1041.13	46.71	1212.03	7.62	8.03	54.82	49.68	87.90	1.58	0.69	8.87	12.54	1.32	1.99	5.52	7.56
68	3.8	0.136	28.79	0.05	724.98	1392.47	1273.27	851.88	47.52	1004.88		7.07		41.08	86.67	1.60	0.69	8.84	14.54	1.65	2.53	6.45	8.98
74	4.1	0.111	26.24	0.04	751.80	1584.69	1463.94	1121.50	48.71	1294.96	7.56	8.37	46.84	41.82	87.20	1.63	0.69	7.62	24.16	2.84	4.20	10.58	14.86
80	4.4	0.252	29.72	0	783.71	1258.25	1209.85	1148.40	52.80	1317.20	7.54	8.26	34.85	46.41	84.88	1.61	0.70	9.57	12.75	1.29	2.06	5.55	7.65
86	4.8	0.184	29.43	0	685.58	1046.51	1066.42	1077.60	40.00	1263.60	7.60	6.92	21.37	44.81	84.09	1.59	0.69	9.84	17.15	1.74	2.59	7.49	10.31
92	5.1	0.53	27.85	0	740.90	1216.04	1277.77	1112.80	36.00	1326.80	7.53	6.87	30.47	44.96	83.52	1.62	0.70	9.58	11.01	1.06	1.64	4.76	6.61
98	5.5	0.191	27.67	0	773.53	1087.14	1269.70	1148.12	44.35	1412.88		8.38	27.16	47.58	82.66	1.59	0.69	10.44	20.87	1.81	3.06	8.86	11.98
104	5.8	0.159	27.84	0	777.98	959.47	1289.87	1139.54	39.48	1441.33		8.78	22.48	48.07	85.68	1.60	0.68	11.03	17.54	1.44	2.27	7.25	9.93
110	6.2	0.261	28.76	0	639.42	1372.20	1552.19	1147.98	37.54	1508.33		8.76	30.05	46.00	85.86	1.60	0.68	10.61	17.77	1.30	2.37	6.86	9.82
116	6.5	0.037	30.72	0	840.81	996.20	1585.03	1139.76	51.32	1504.54		9.35	36.89	42.94	88.60	1.56	0.68	9.90	18.35	1.28	2.68	7.00	10.11
122	6.8	0.006	30.24	0	902.76	972.75	1692.73	1255.72	31.82	1661.85		8.91	47.68	43.96	88.35	1.58	0.69	12.87	16.38	1.05	1.86	6.75	8.82
128	7.2	0.210	30.27	0	864.54	926.40	1744.25	1162.09	41.23	1577.87		9.10	34.88	42.98	77.74								
134	7.5	0.175	33.99	0	837.00	1054.40	1885.64	1145.68	36.27	1553.68		8.47	31.59	52.81	77.71								
140	7.9	0.137	28.70	0	840.47	1056.86	1920.82	1152.56	35.02	1546.20	7.60	8.91	28.79	48.06	71.49								

Column 9

Table B-9. Column 9: Water Analysis Data (with organic carbon and arsenic)

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.008	16.58	5.94	28.40	776.27	453.98	3.66	13.11	485.97	7.60	2.80	15.72	104.36	15.76	1.57	0.63	7.28	12.37	2.14	2.70	5.51	7.49
8	0.5	0.005	14.81	3.71	28.05	787.87	422.09	3.70	13.89	473.20		2.33	31.34	129.52	16.00	1.58	0.63	6.25	10.47	2.28	2.66	4.69	6.55
14	0.8	0.1	15.69	0.43	16.88	953.40	481.00	217.20	13.13	386.64	7.79	2.81	35.96	174.02	22.74	1.62	0.64	6.90	8.83	1.67	1.97	3.95	5.72
20	1.1	0.075	18.54	0.3	8.02	1437.62	705.55	935.08	13.13	485.80		4.94	25.19	170.66	60.08	1.58	0.67	7.03	14.23	2.71	3.05	6.58	9.13
26	1.5	0.01	20.69	0.22	16.38	1777.46	1134.26	1046.55	13.82	829.11	7.67	6.01	28.39	73.92	60.93	1.62	0.69	8.48	18.50	2.56	3.41	8.31	11.75
32	1.8	0.123	24.33	0.16	240.05	1602.24	1120.99	1042.60	53.80	928.27		5.56	40.40	61.74	65.60	1.58	0.68	7.94	23.26	3.19	4.17	10.52	14.59
38	2.0	0.093	26.1	0.28	572.82	1551.03	1215.29	1096.20	120.40	971.53	7.57	5.50	56.65	78.94	89.34	1.58	0.67	7.63	14.59	1.96	2.79	6.46	8.94
44	2.3	0.082	26.25	0.15	744.67	1315.17	1165.34	1053.00	51.00	935.73		6.33		67.52	77.33	1.60	0.67	8.20	17.12	2.42	3.08	7.64	10.88
50	2.6	0.08	26.95	0.15	886.73	1226.39	1203.59	1079.56	50.92	959.66	7.75	7.09	68.85	59.84	82.38	1.62	0.69	8.08	11.48	1.61	2.14	5.32	7.33
56	3.0	0.017	26.73	0.05	969.47	1335.53	1281.90	1102.61	47.80	998.04		6.47		56.58	81.77	1.61	0.69	8.09	14.49	1.92	2.71	6.58	9.11
62	3.3	0.37	28.48	0.05	953.12	1274.58	1218.06	1083.73	54.48	980.13	7.52	7.30	79.40	61.58	85.20	1.59	0.70	8.64	18.78	2.44	3.32	8.63	11.59
68	3.6	0.123	28.54	0.07	969.12	1293.14	1215.09	1078.83	48.96	1014.53		6.52		53.34	83.05	1.57	0.69	8.26	11.56	1.45	2.20	5.21	7.19
74	4.0	0.101	27.23	0.09	1016.08	1366.26	1301.94	1124.79	54.29	1036.30	7.77	6.35	67.90	55.22	80.40	1.59	0.69	6.87	15.34	2.27	2.99	6.94	9.72
80	4.3	0.244	32.46	0	995.56	1254.55	1156.12	1156.40	52.40	1081.87	7.58	7.68	40.42	53.70	63.14	1.60	0.69	8.08	9.91	1.26	1.78	4.37	6.13
86	4.6	0.179	31.69	0	1043.95	1486.80	1397.58	1100.40	40.00	1097.73	7.59	6.56	41.68	50.30	38.12	1.60	0.69	8.97	16.05	1.91	2.62	7.20	9.89
92	4.9	0.424	30.23	0	981.79	868.65	942.97	1125.20	52.40	1148.80	7.53	6.56	52.98	52.76	32.96	1.60	0.69	9.64	12.54	1.31	1.99	5.55	7.70
98	5.3	0.183	30.6	0	1008.97	1183.34	1195.81	1143.78	40.34	1216.48		8.20	43.25	57.92	32.06	1.59	0.67	10.07	20.15	2.10	3.22	8.64	11.82
104	5.6	0.15	26.47	0	994.69	1322.47	1367.26	1021.91	42.00	1219.85		8.24	43.91	51.45	30.77	1.58	0.69	10.30	16.87	1.73	2.45	7.33	9.93
110	5.9	0.233	30.21	0	957.45	1275.20	1384.81	1176.01	37.19	1314.75		8.49	79.10	53.65	30.57	1.55	0.68	9.58	17.53	1.51	2.63	7.04	10.19
116	6.3	0.019	29.32	0	1063.60	1280.60	1508.81	1133.58	35.28	1291.93		9.03	63.29	51.42	30.73	1.54	0.66	3.85	18.09	9.98	4.34	7.04	10.40
122	6.6	0.004	28.85	0	1145.60	1057.93	1451.69	1250.51	17.26	1432.52		8.74	70.18	55.96	28.64	1.58	0.67	11.84	16.82	1.25	2.12	6.96	9.47
128	6.9	0.199	29.89	0	1053.48	1051.55	1525.82	1155.59	48.08	1357.06		8.50	108.82	53.07	30.02								
134	7.2	0.165	30.91	0	1066.17	918.25	1577.34	1131.07	36.26	1337.79		8.44	107.62	61.17	30.49								
140	7.5	0.141	30.14	0	1061.29	690.06	1543.71	1134.41	36.26	1330.67	7.60	8.53	33.10	58.61	31.12								

Column 10

Table B-10. Column 10: Water Analysis Data (with organic carbon and arsenic

Day	PV	Boron	Potassium	Iron	Sodium	Calcium	Sulfur	Chloride	Nitrate	Sulfate	pH	EC	Arsenic	TOC	TN	FI	FrI	HIX	Peak A	Peak B	Peak T	Peak C	Peak M
3	0.2	0.072	17.44	6.19	132.97	795.26	458.87	7.48	14.68	487.39	7.62	2.75	14.15	102.04	15.30	1.56	0.63	7.46	12.49	2.08	2.65	5.60	7.56
8	0.4	0	16.1	7.18	29.19	771.94	441.52	3.81	13.86	467.96		2.64	35.56	98.38	15.21	1.59	0.63	7.16	12.11	2.19	2.85	5.37	7.36
14	0.7	0	16.27	1.24	21.44	917.45	453.47	172.09	13.36	406.79	7.79	2.65	44.78	128.14	20.42	1.61	0.63	7.41	10.51	1.84	2.25	4.69	6.55
20	1.1	0.07	17.76	0.27	13.66	1492.14	731.21	911.79	13.47	415.63		4.76	39.19	72.62	54.04	1.60	0.65	7.76	9.65	1.50	1.80	4.40	6.17
26	1.4	0.07	20.21	0.29	14.02	2091.86	1269.63	1005.97	13.89	770.04	7.72	5.72	47.35	76.14	62.77	1.62	0.69	8.39	18.67	2.56	3.40	8.41	11.72
32	1.7	0.121	25.98	0.14	227.79	1696.02	1173.17	1047.60	46.00	846.73		7.08	69.20	64.42	70.30	1.58	0.68	7.66	23.18	3.06	4.11	10.45	14.31
38	2.1	0.094	26.93	0.17	566.87	1532.82	1215.84	1003.00	112.60	863.67	7.56	5.97	69.29	70.72	89.92	1.57	0.70	7.82	21.24	2.81	3.89	9.62	12.82
44	2.3	0.083	26.84	0.16	736.93	1274.19	1133.48	1013.20	55.40	947.00		6.34		64.16	82.89	1.55	0.69	8.27	20.28	2.66	3.70	9.13	12.42
50	2.7	0.074	27.83	0.16	921.83	1340.45	1288.29	1109.73	54.04	984.62	7.78	7.32	75.37	62.54	90.94	1.60	0.71	7.86	9.66	1.46	1.82	4.49	6.07
56	3.0	0.012	28.71	0.04	1022.51	1442.32	1384.82	1107.76	54.04	1033.23		6.44		53.60	85.53	1.61	0.71	8.48	16.34	2.03	2.88	7.57	10.33
62	3.3	0.32	29.11	0.07	904.12	1226.40	1171.41	1050.01	48.71	1005.97	7.58	7.69	79.55	55.84	82.32	1.61	0.71	8.30	17.79	2.39	3.20	8.16	11.10
68	3.7	0.124	31.01	0.06	925.39	1251.15	1191.86	1097.56	49.32	1034.06		6.30		53.70	83.09	1.57	0.70	7.59	8.26	1.07	1.55	3.77	5.19
74	4.0	0.094	27.39	0.07	949.69	1311.39	1237.95	1123.35	48.46	1057.60	7.65	6.47	138.43	51.38	79.80	1.58	0.70	6.88	21.64	3.16	4.37	9.95	13.72
80	4.3	0.231	31.06	0	985.86	1079.87	1038.74	1136.40	56.00	1071.33	7.54	8.01	70.53	52.67	69.87	1.63	0.70	8.97	9.61	1.13	1.78	4.36	6.08
86	4.6	0.179	32.7	0	1018.50	1029.01	1030.90	1106.80	49.20	1057.73	7.41	6.97	65.38	49.09	60.99	1.59	0.70	9.16	16.52	1.97	2.82	7.55	10.44
92	5.0	0.349	31.7	0	944.85	1028.34	1019.70	1128.00	51.20	1114.13	7.53	6.46	61.07	49.68	51.57	1.63	0.70	8.76	9.08	1.02	1.58	4.01	5.56
98	5.3	0.17	30.07	0	907.50	1319.94	1261.50	1129.66	39.97	1170.49		7.30	50.81	52.72	41.05	1.58	0.70	9.08	19.36	2.23	3.25	8.49	11.82
104	5.6	0.148	30.05	0	958.28	1182.06	1239.39	1152.36	44.61	1221.85		8.43	41.51	51.70	33.26	1.59	0.70	10.21	18.20	1.83	2.64	7.94	10.65
110	6.0	0.209	31.68	0	887.24	996.46	1117.46	1161.76	35.85	1297.89		8.39	82.21	53.82	32.11	1.56	0.67	9.81	17.16	1.31	2.54	6.83	9.83
116	6.3	0.009	33.11	0	1034.41	930.57	1236.78	1117.91	35.85	1295.66		8.90	39.30	53.22	34.16	1.55	0.67	9.43	19.45	1.61	3.01	7.77	11.35
122	6.6	0.000	33.16	0	1121.52	1050.61	1430.39	1245.58	17.00	1434.62		8.70	78.50	53.02	31.91	1.57	0.69	11.99	16.88	1.36	2.12	7.11	9.38
128	6.9	0.178	30.48	0	1091.20	1149.34	1612.63	1142.83	50.01	1352.13		8.66	107.08	54.66	34.50								
134	7.3	0.154	32.75	0	1070.60	917.96	1586.94	1125.26	50.01	1333.57		8.44	109.44	60.01	33.41								
140	7.6	0.137	29.59	0	1058.20	681.77	1543.79	1149.63	35.66	1350.51	7.61	8.71	48.20	58.28	33.46								

DOC/Sulfate Ratios

Table B-11. DOC/Sulfate Ratios

Treatment	DOC/SO$_4$$^{-2}$
Control (Q)	0.05
Control (1/2Q)	0.07
With Inoculum	0.07
With Organic Carbon	0.10
With Inoculum & As	0.07
With Organic Carbon & As	0.09

Appendix C - Breakthrough Curves In Terms of Concentration

Arsenic

Figure C-1. Arsenic BTC for columns with FGD solution not amended with arsenic
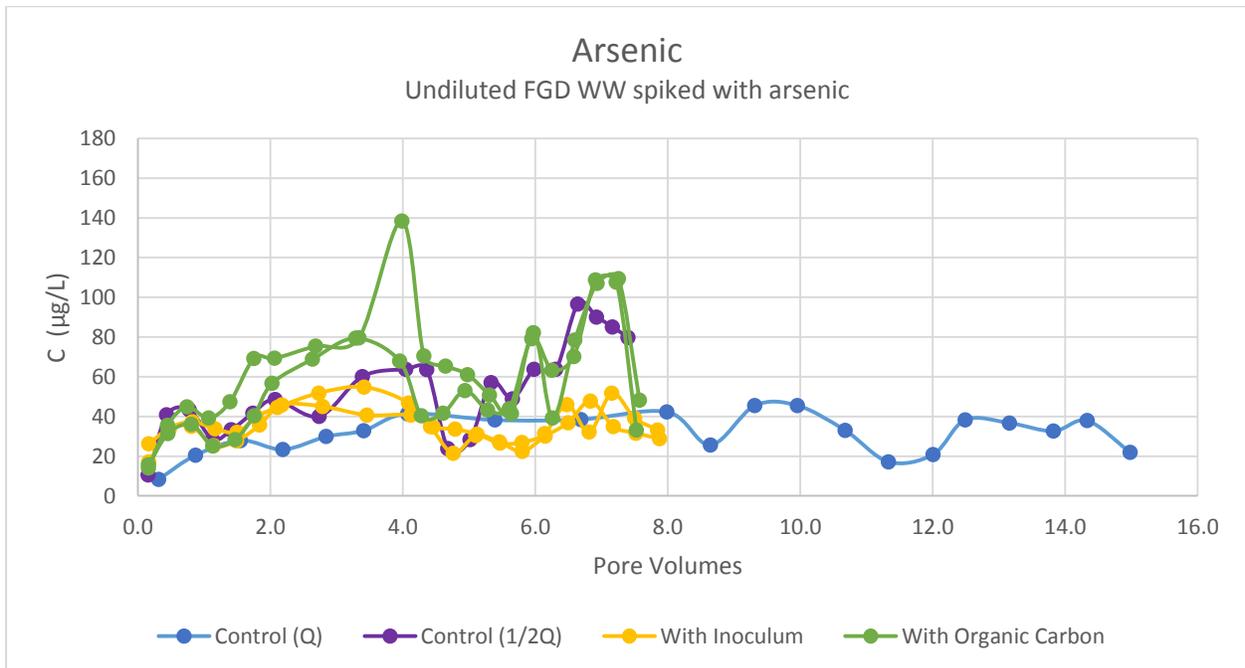
Figure C-2. Arsenic BTC for columns with FGD solution amended with arsenic

Boron

Figure C-3. Boron BTC for columns with FGD solution not amended with arsenic

Figure C-4. Boron BTC for columns with FGD solution amended with arsenic

Calcium

Figure C-5. Calcium BTC for columns with FGD solution not amended with arsenic

Figure C-6. Calcium BTC for columns with FGD solution amended with arsenic

Chloride

Figure C-7 Chloride BTC for columns with FGD solution not amended with arsenic

Figure C-8 Chloride BT BTC for columns with FGD solution amended with arsenic

Dissolved Organic Carbon
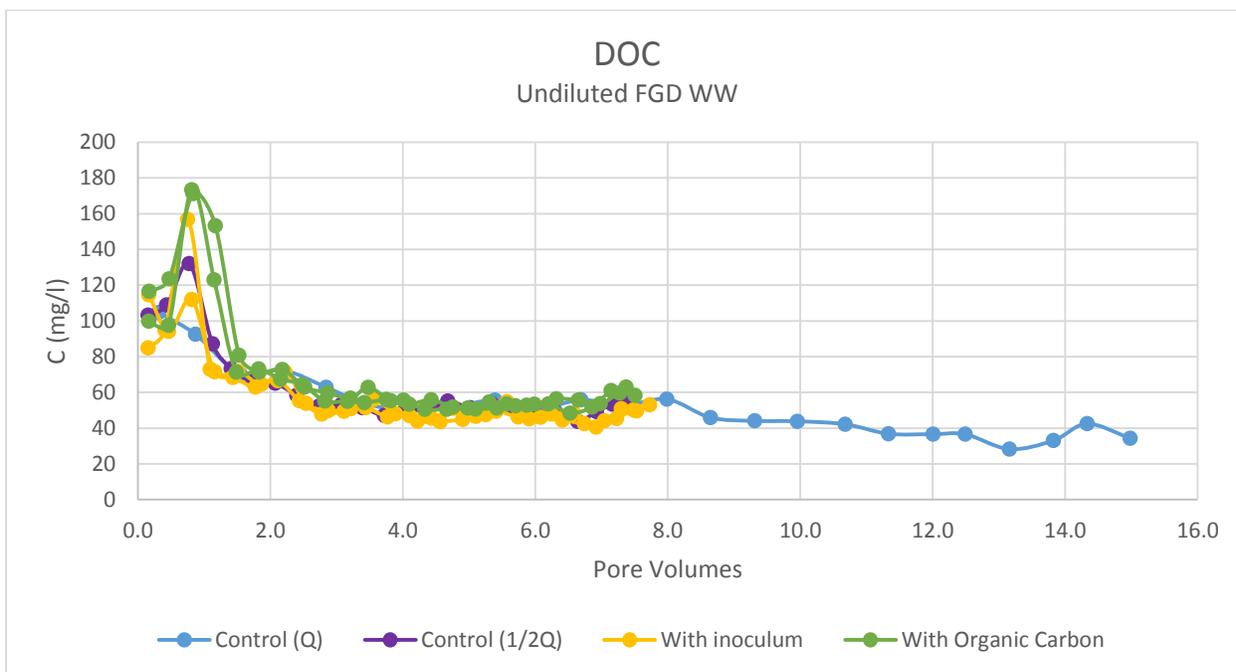
Figure C-9. DOC BTC for columns with FGD solution not amended with arsenic
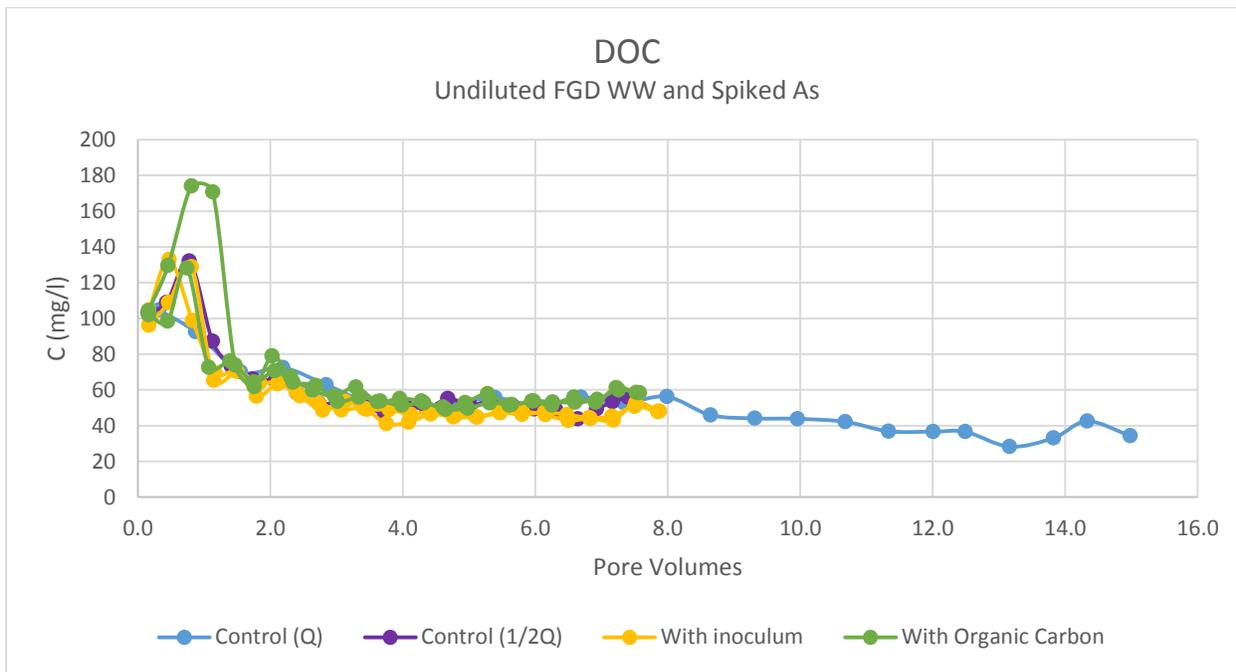
Figure C-10. DOC BTC for columns with FGD solution amended with arsenic

Nitrate
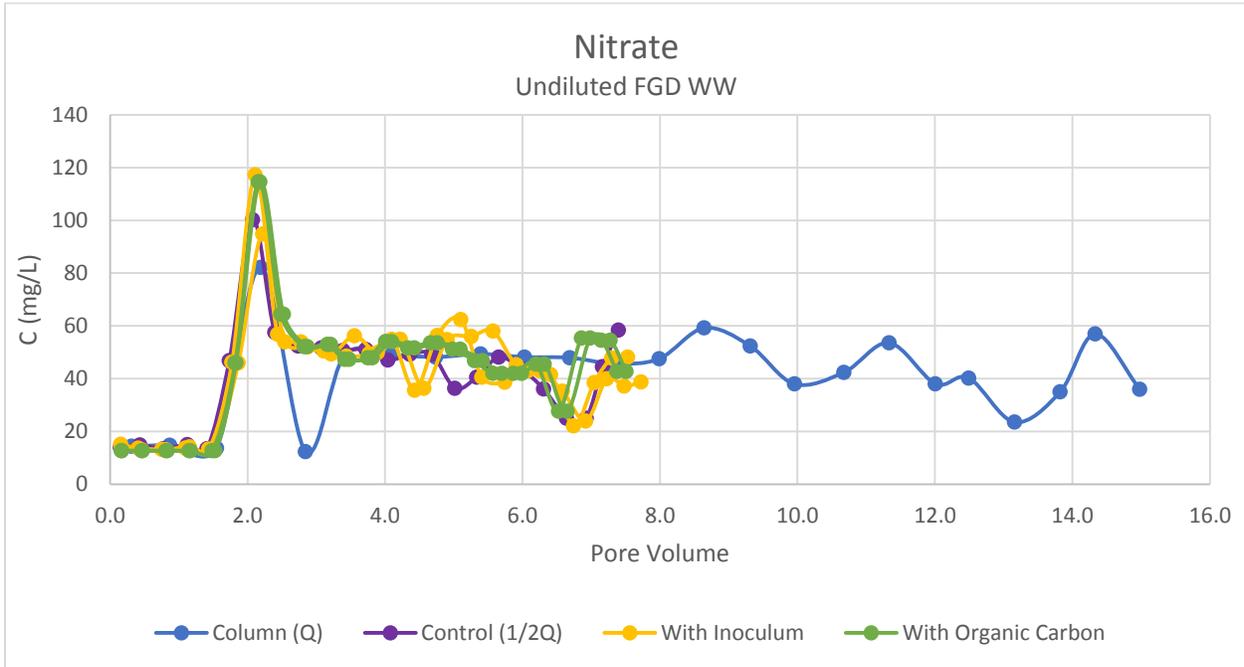
Figure C-11. Nitrate BTC for columns with FGD solution not amended with arsenic
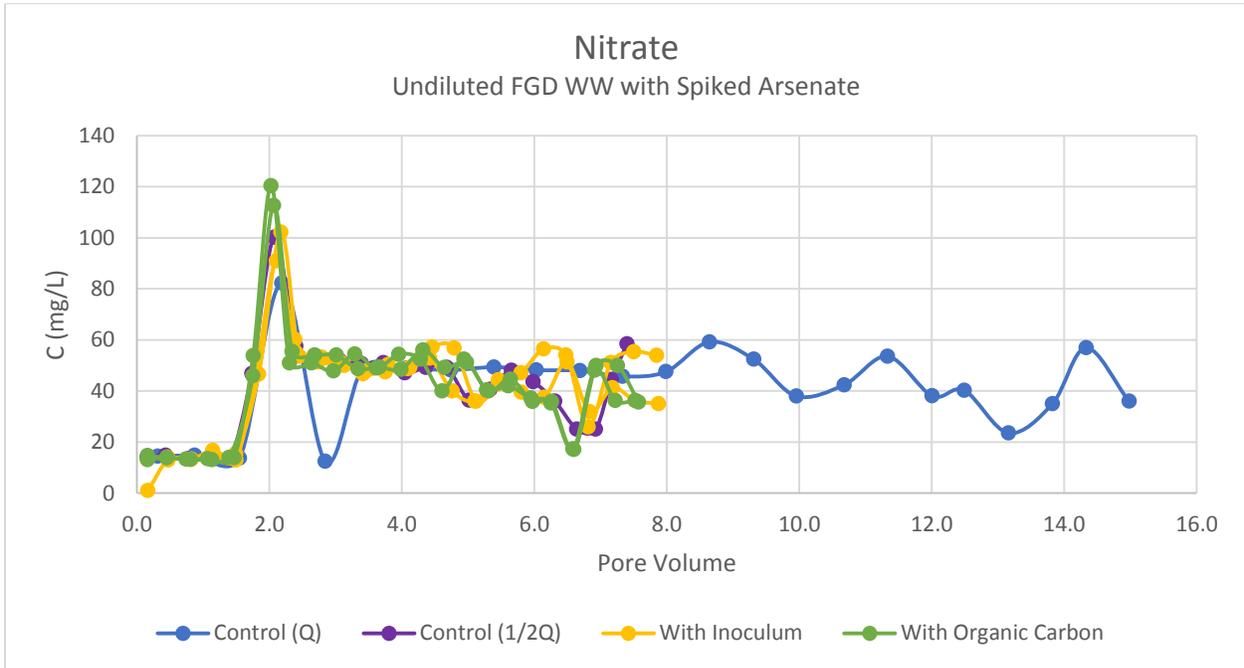
Figure C-12. Nitrate BTC for columns with FGD solution amended with arsenic

Total Nitrogen
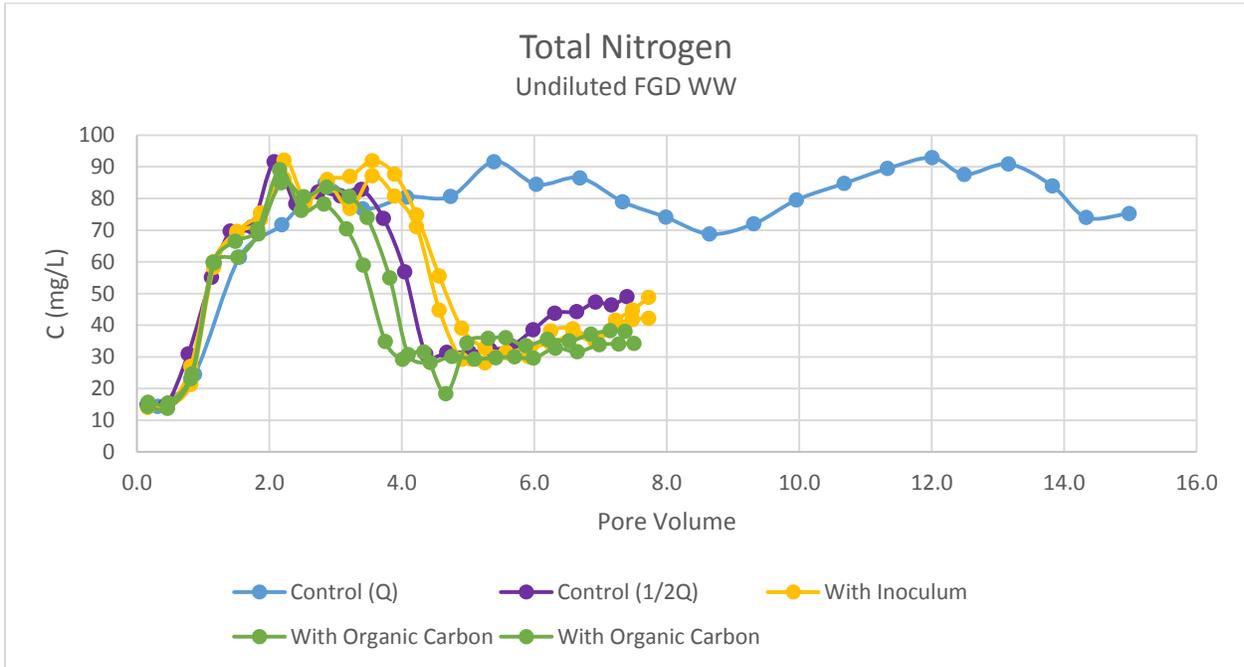
Figure C-13 Total Nitrogen BTC for columns with FGD solution not amended with arsenic
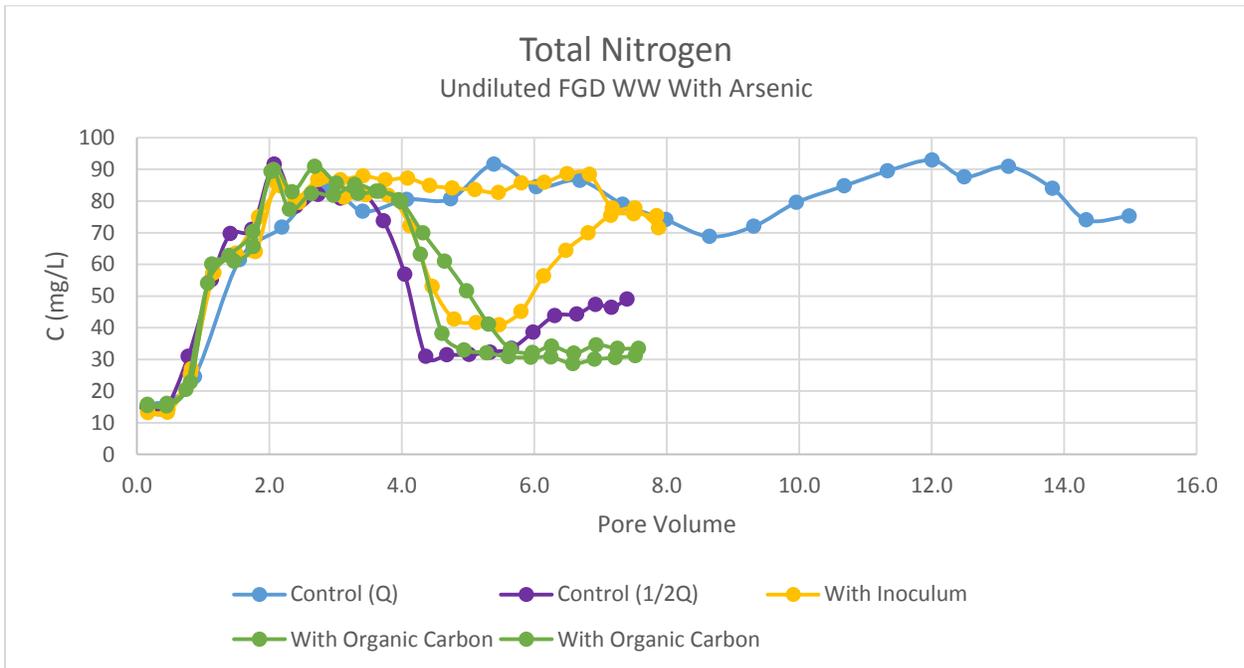
Figure C-14. Total Nitrogen BTC for columns with FGD solution amended with arsenic
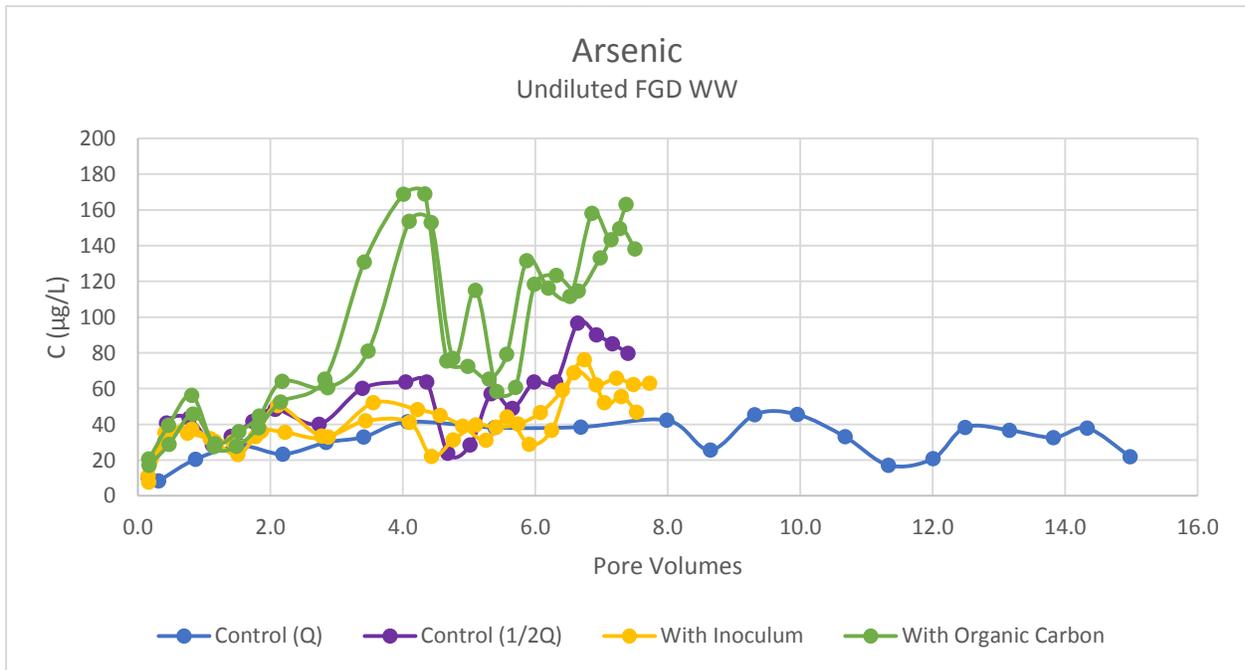
Sodium
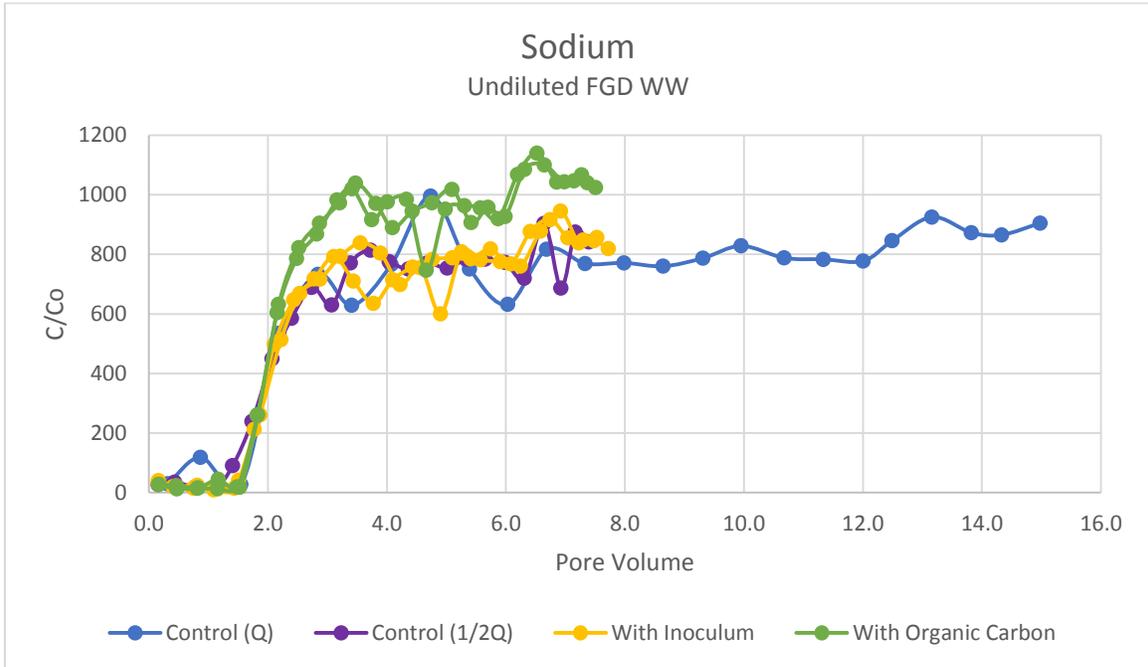
Figure C-15. Sodium BTC for columns with FGD solution not amended with arsenic
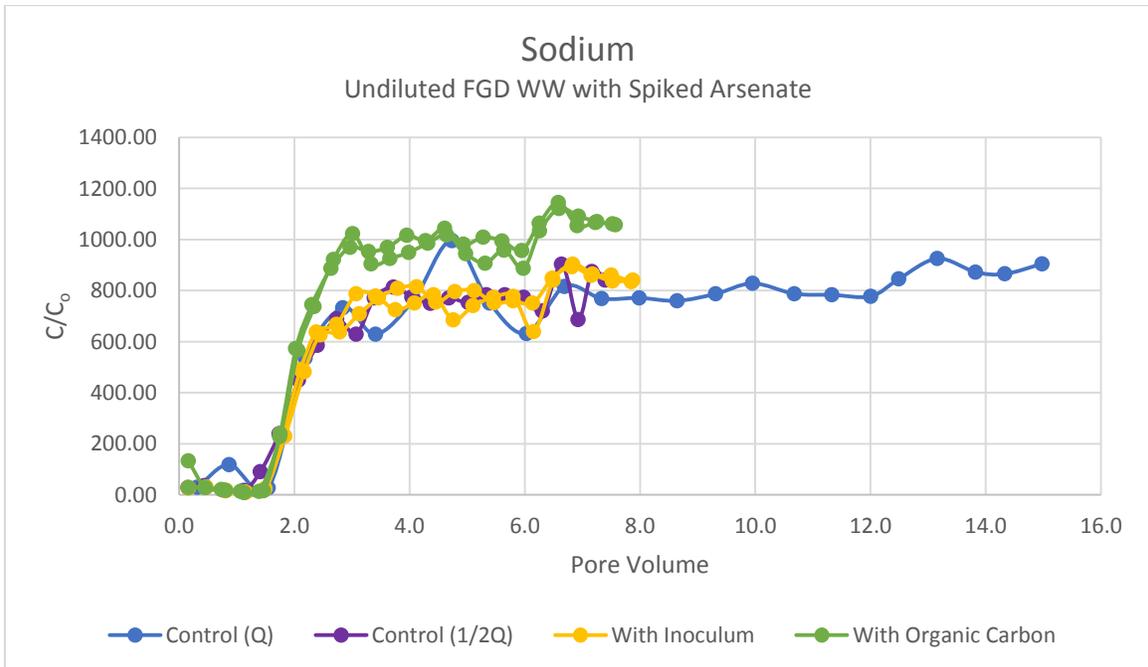
Figure C-16. Sodium BTC for columns with FGD solution amended with arsenic

Selenium
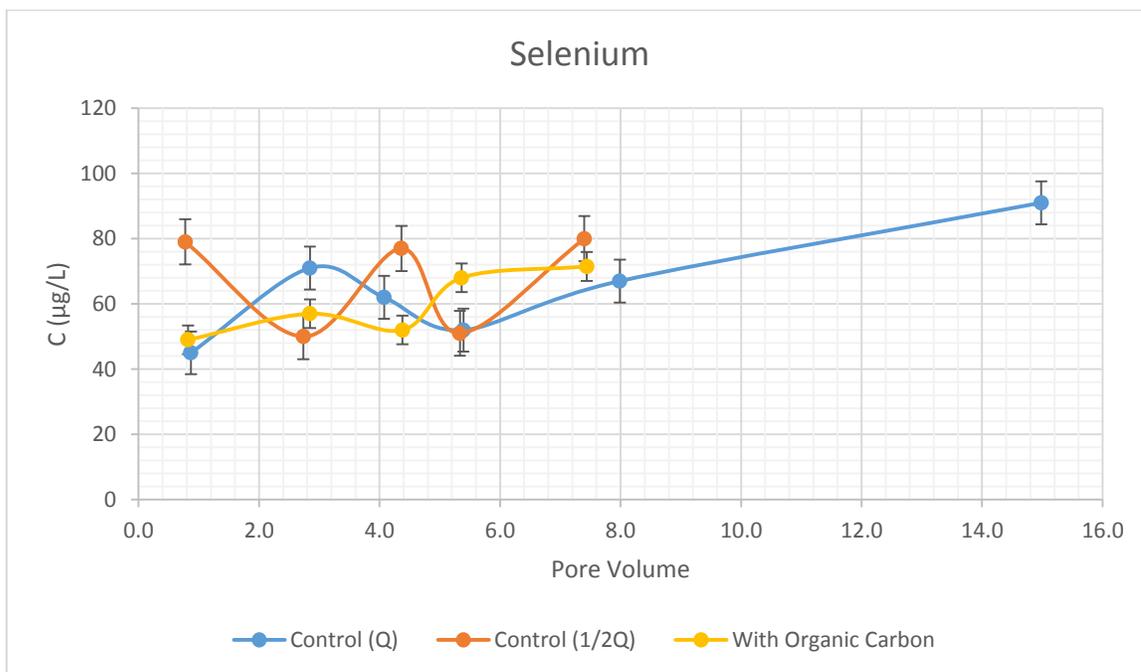
Figure C-17. Selenium BTC

Sulfate-S
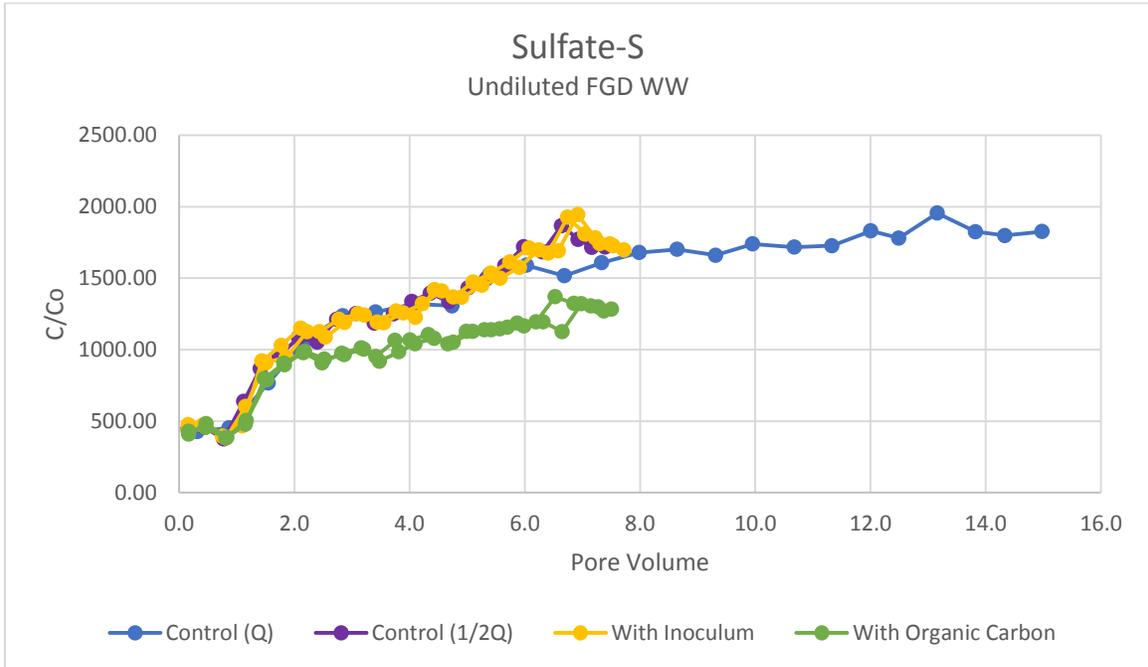
Figure C-18. Sulfate-S BTC for columns with FGD solution not amended with arsenic
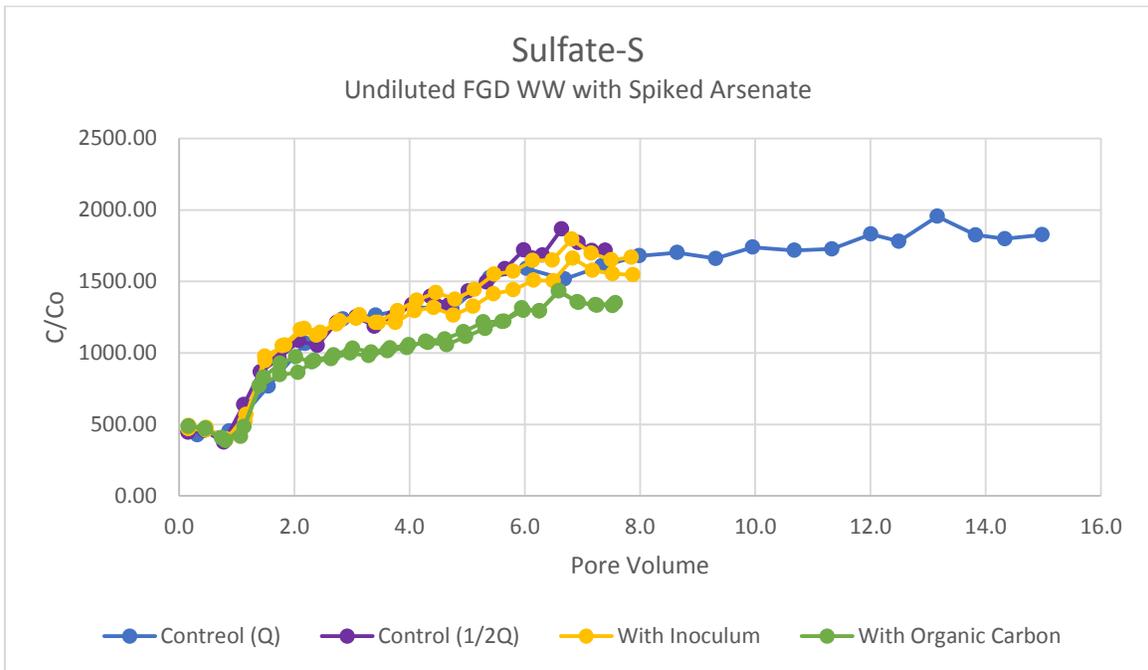
Figure C-19 Sulfate-S BTC for columns with FGD solution amended with arsenic
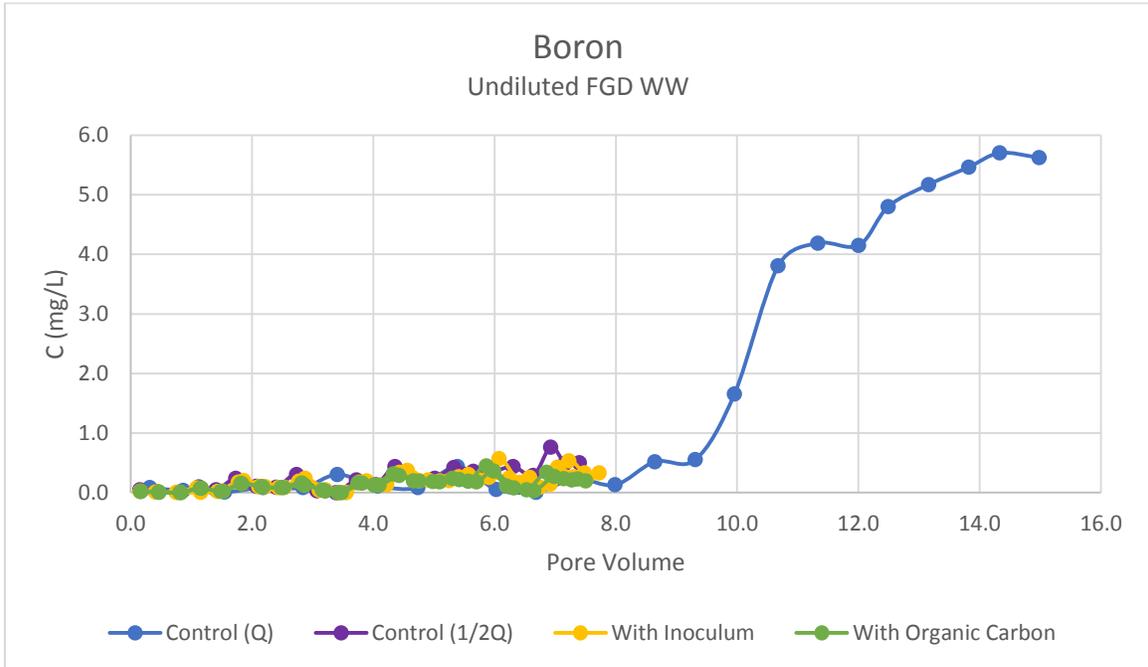
138
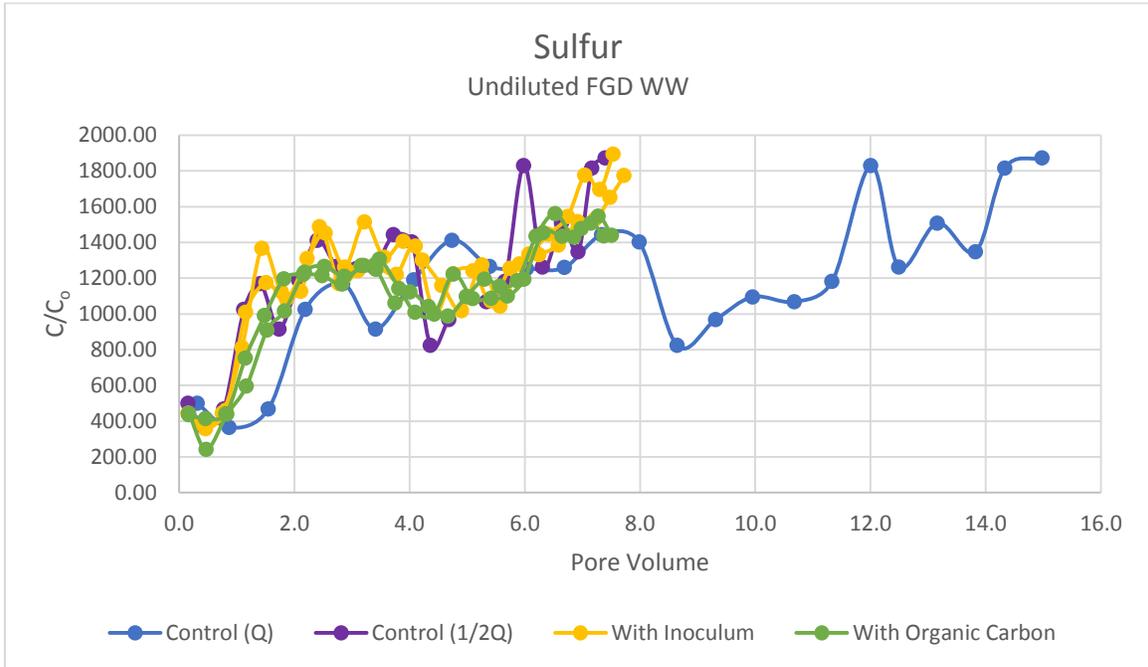
Sulfur

Figure C-20 Sulfur BT BTC for columns with FGD solution not amended with arsenic

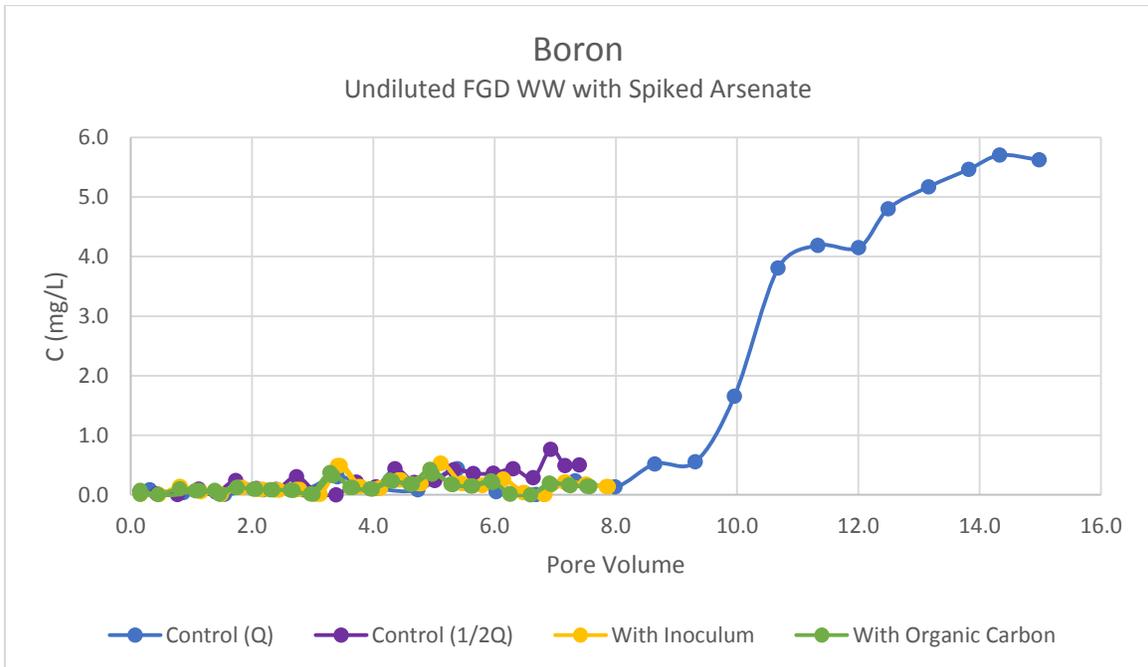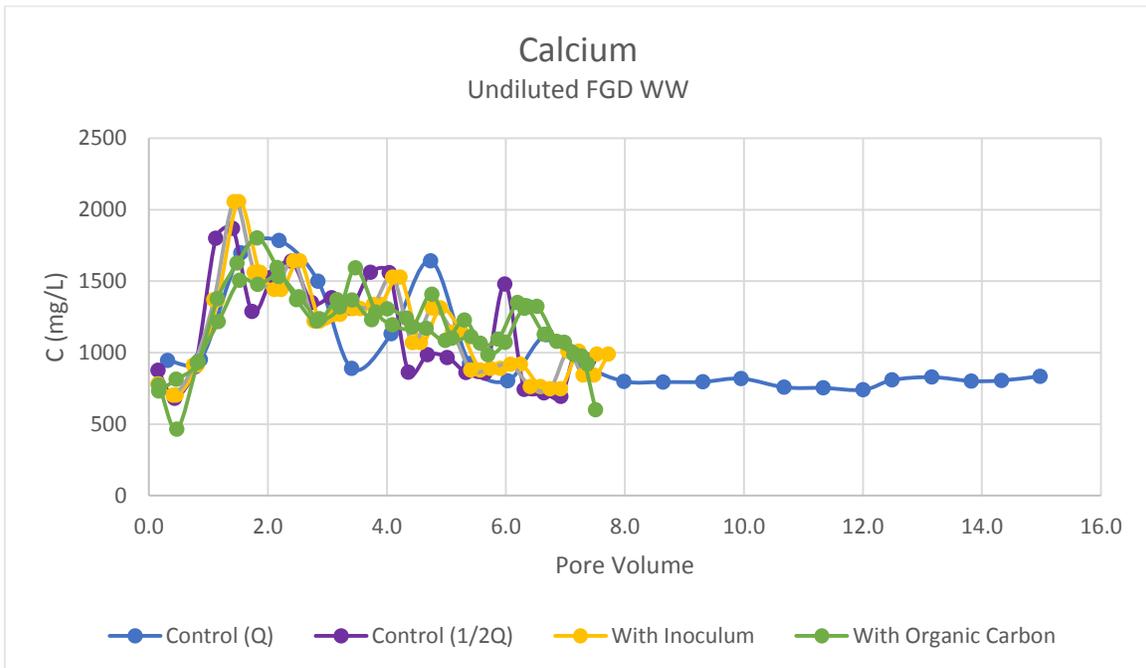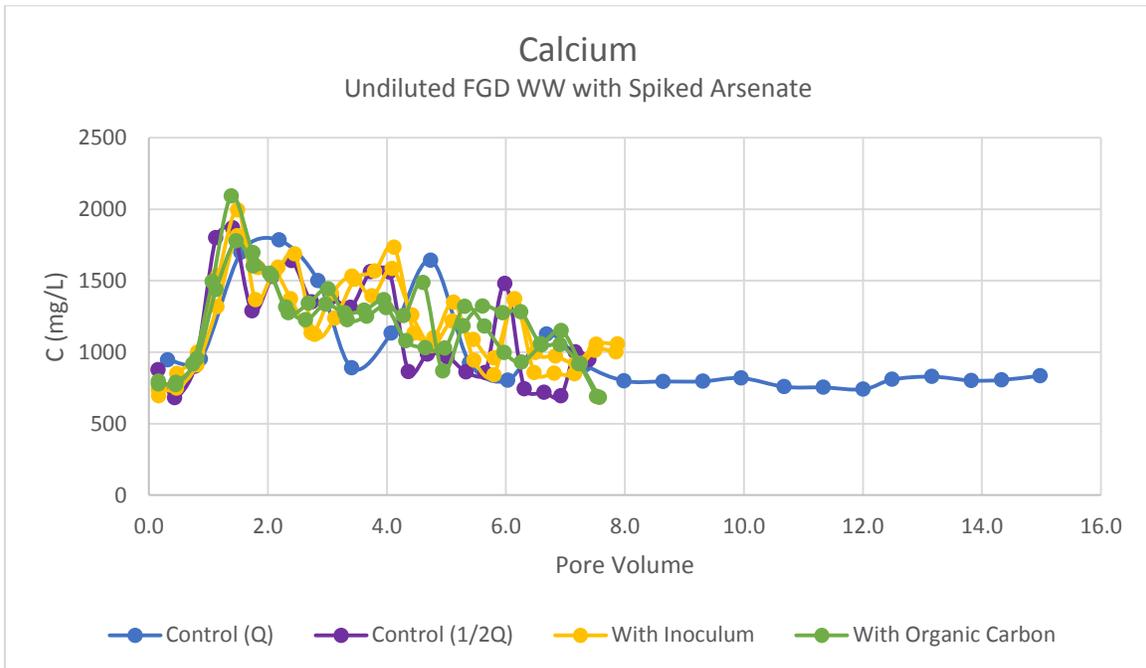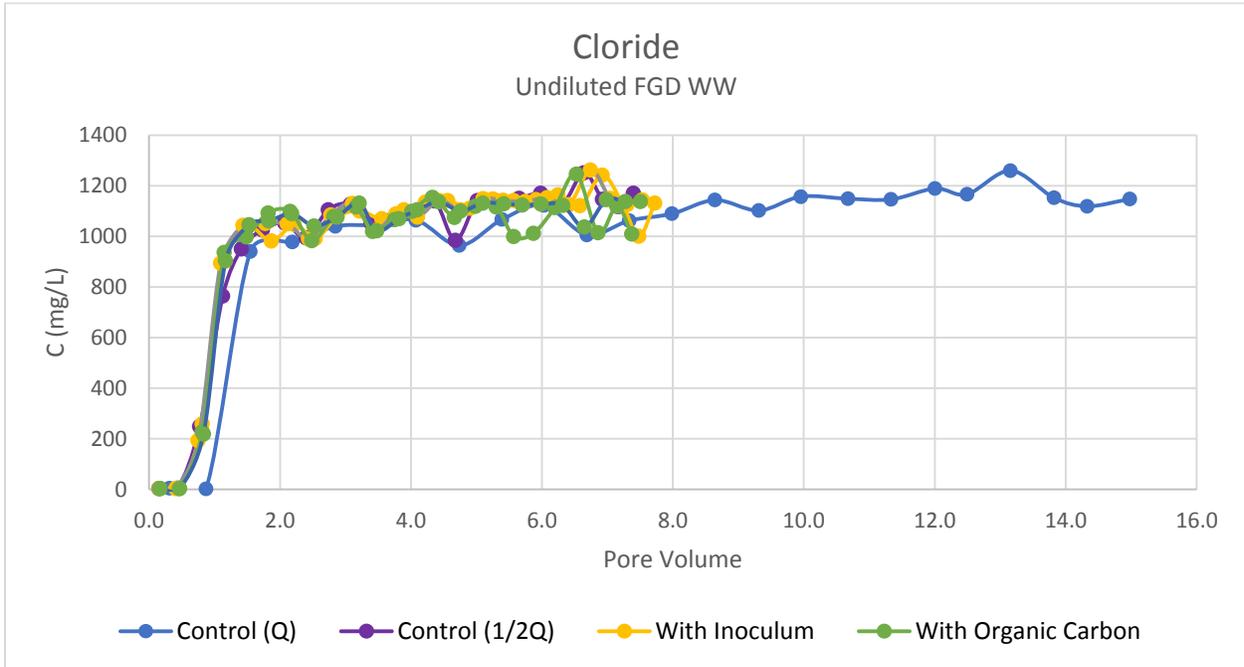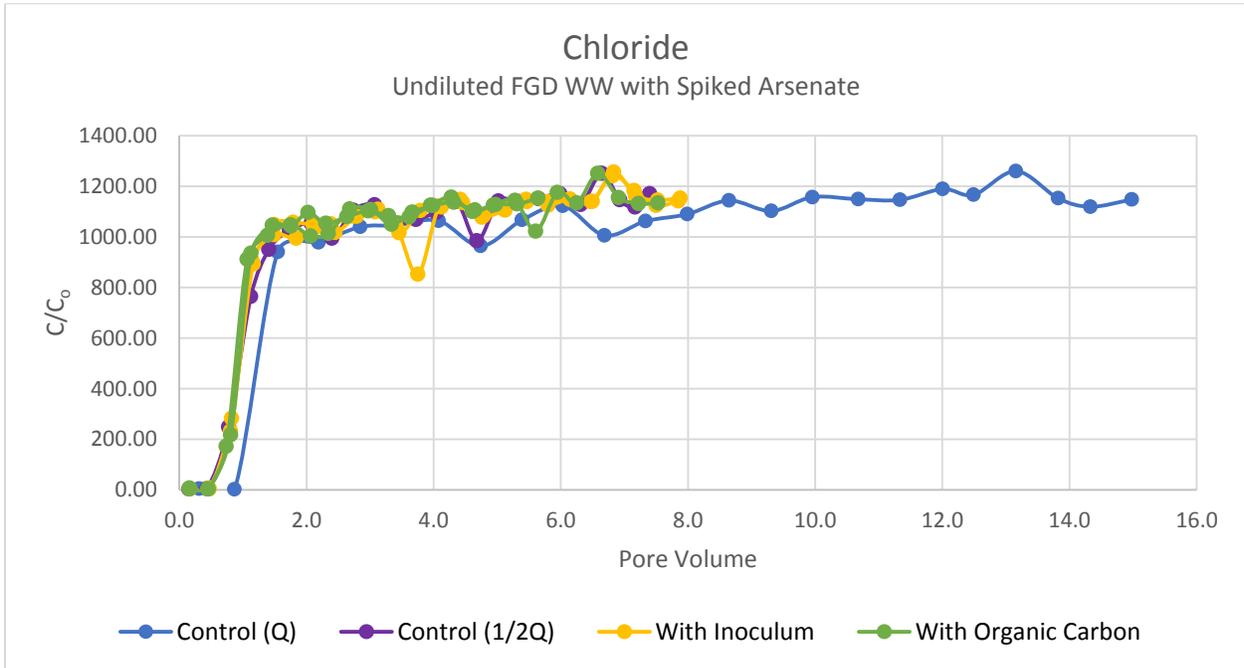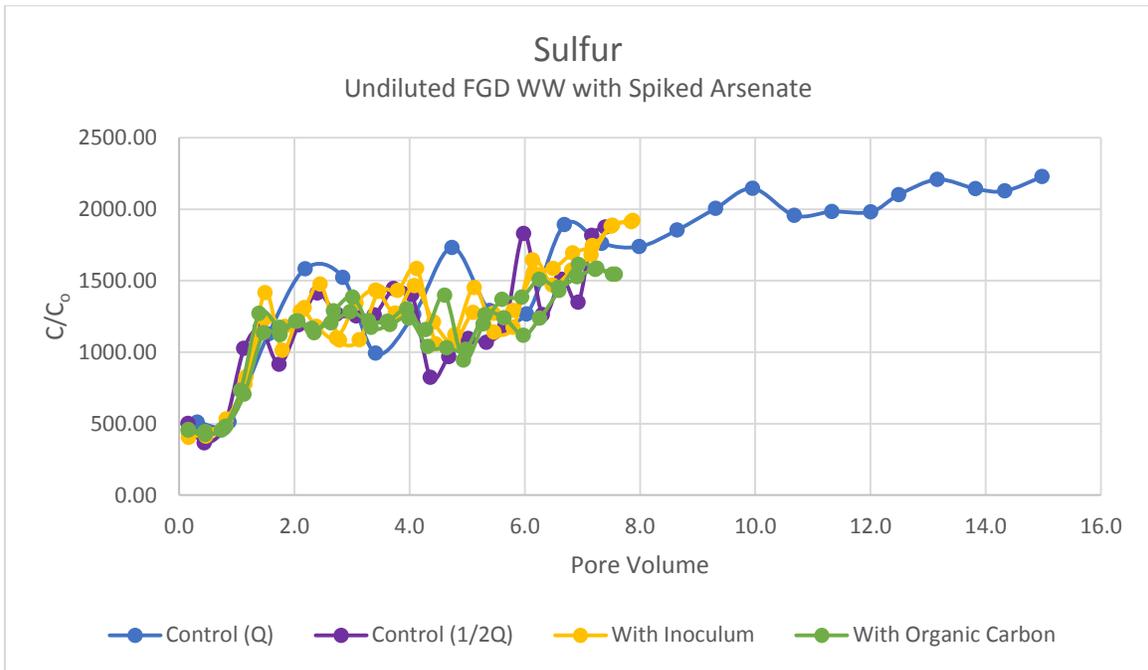**Figure C-21. Sulfur BTC for columns with FGD solution amended with arsenic**

139

Appendix D - Soil Analysis Data

Soil Analysis Data for Sulfur

Table D-1. Soil Analysis Data for Sulfur

Column	Section	Dry Soil (g)	C_s (mg/kg)	Ms Retained (mg)	Ms (mg)
1	1	126.79	3574.65	283.97	4532.32
	2	116.30	4002.55	310.22	4654.79
	3	119.28	3362.90	241.89	4011.27
	4	118.13	1914.48	68.45	2261.56
	5	117.04	1331.70	-0.39	1558.59
	6	122.77	1309.97	-3.07	1608.22
2	1	121.74	3527.72	266.95	4294.72
	2	124.37	3091.21	218.41	3844.40
	3	118.18	2671.38	157.94	3157.10
	4	120.55	2365.29	124.20	2851.41
	5	113.87	1909.56	65.43	2174.46
	6	125.15	1254.84	-10.03	1570.39
3	1	123.50	3817.68	306.60	4714.68
	2	118.09	2799.54	172.94	3305.91
	3	119.99	2269.41	112.12	2723.14
	4	118.23	2313.56	115.69	2735.26
	5	47.49	2000.42	31.60	950.06
	6	125.97	1100.23	-29.58	1386.01
4	1	120.46	3271.10	233.22	3940.27
	2	118.77	2567.26	146.35	3049.08
	3	116.39	2207.43	101.54	2569.23
	4	116.62	2194.69	100.26	2559.41
	5	120.39	1755.28	50.60	2113.20
	6	125.58	1107.18	-28.61	1390.44
5	1	122.51	2533.74	146.86	3104.18
	2	115.12	2405.19	123.20	2768.96
	3	119.48	2057.67	86.34	2458.53
	4	120.41	2031.10	83.82	2445.72
	5	118.31	2385.69	124.31	2822.50

	6	128.97	4430.75	399.27	5714.54
6	1	119.06	2735.66	166.76	3257.13
	2	121.65	2771.61	174.76	3371.70
	3	120.38	2353.65	122.62	2833.26
	4	119.39	2143.97	96.58	2559.70
	5	119.42	5412.73	486.97	6464.02
	6	125.20	2623.12	161.28	3284.25
7	1	124.62	3342.36	250.16	4165.27
	2	115.46	2401.16	123.10	2772.36
	3	119.58	2133.58	95.49	2551.37
	4	121.70	2090.93	92.00	2544.74
	5	117.48	1784.18	52.77	2095.97
	6	123.62	1197.13	-17.04	1479.87
8	1	122.53	2975.63	201.02	3646.00
	2	116.26	2475.27	132.57	2877.87
	3	121.02	2182.00	102.50	2640.67
	4	119.02	2128.57	94.45	2533.33
	5	119.46	1848.85	61.38	2208.56
	6	123.69	1146.65	-23.30	1418.35
9	1	122.83	2744.81	173.16	3371.37
	2	114.77	2379.63	119.89	2731.01
	3	119.29	2014.11	81.01	2402.69
	4	119.61	2076.40	88.68	2483.62
	5	120.35	2651.83	158.47	3191.36
	6	119.36	5463.52	492.80	6521.49
10	1	121.24	2658.09	160.41	3222.68
	2	118.70	2595.16	149.58	3080.49
	3	120.25	2112.22	93.46	2539.87
	4	123.58	2135.99	98.98	2639.56
	5	117.78	2372.83	122.23	2794.69
	6	121.75	4637.73	402.09	5646.24

Iron

Table D-2. Soil Analysis Data for Iron

Column	Section	Dry Soil (g)	C_s (mg/kg)	Ms Retained (mg)	Ms (mg)
1	1	126.79	18390.68	-394.29	2331.77
	2	116.30	18264.47	-376.33	2124.07
	3	119.28	17505.94	-476.46	2088.11
	4	118.13	17338.53	-491.64	2048.19
	5	117.04	17170.68	-506.74	2009.61
	6	122.77	18793.44	-332.33	2307.22
2	1	121.74	18797.14	-329.11	2288.40
	2	124.37	18303.67	-397.57	2276.35
	3	118.18	18031.30	-409.99	2130.99
	4	120.55	15423.11	-732.64	1859.29
	5	113.87	14895.55	-752.11	1696.19
	6	125.15	16009.32	-687.20	2003.52
3	1	123.50	16119.25	-664.56	1990.67
	2	118.09	16390.52	-603.42	1935.52
	3	119.99	15413.20	-730.43	1849.48
	4	118.23	16098.52	-638.66	1903.29
	5	47.49	16711.22	-227.45	793.66
	6	125.97	17024.29	-563.88	2144.62
4	1	120.46	17882.39	-435.82	2154.06
	2	118.77	18991.32	-298.00	2255.56
	3	116.39	18504.74	-348.67	2153.77
	4	116.62	20090.00	-164.48	2342.86
	5	120.39	20022.53	-177.93	2410.53
	6	125.58	21415.87	-10.62	2689.51
5	1	122.51	19499.89	-245.09	2389.00
	2	115.12	17735.39	-433.45	2041.77
	3	119.48	14683.32	-814.52	1754.38
	4	120.41	16232.63	-634.31	1954.62
	5	118.31	15691.64	-687.23	1856.47
	6	128.97	16219.37	-681.13	2091.89
6	1	119.06	15775.47	-681.63	1878.26
	2	121.65	18647.50	-347.06	2268.49
	3	120.38	15711.08	-696.91	1891.26

	4	119.39	16067.38	-648.66	1918.29
	5	119.42	18072.97	-409.32	2158.32
	6	125.20	17614.22	-486.57	2205.38
7	1	124.62	18189.61	-412.60	2266.81
	2	115.46	17708.03	-437.87	2044.56
	3	119.58	17978.15	-421.20	2149.86
	4	121.70	18452.92	-370.89	2245.79
	5	117.48	17200.66	-505.12	2020.65
	6	123.62	17480.29	-496.96	2160.89
8	1	122.53	17031.95	-547.52	2086.90
	2	116.26	15558.03	-690.89	1808.85
	3	121.02	14886.39	-800.43	1801.55
	4	119.02	15582.72	-704.30	1854.58
	5	119.46	14398.23	-848.40	1719.95
	6	123.69	15468.49	-746.12	1913.37
9	1	122.83	16784.26	-579.27	2061.56
	2	114.77	15127.02	-731.46	1736.07
	3	119.29	19196.12	-274.89	2289.97
	4	119.61	22262.72	91.18	2662.88
	5	120.35	18563.36	-353.47	2234.02
	6	119.36	37685.10	1931.87	4498.25
10	1	121.24	20214.89	-155.86	2450.86
	2	118.70	20418.92	-128.38	2423.75
	3	120.25	19882.85	-194.51	2390.84
	4	123.58	20775.47	-89.59	2567.34
	5	117.78	20014.04	-175.07	2357.23
	6	121.75	21188.96	-37.92	2579.66

Arsenic

Table D-3. Soil Analysis Data for Arsenic

Column	Section	Dry Soil (g)	C_s (µg/kg)	Ms Retained (µg)	Ms (µg)
1	1	126.79	4335.20	69.89	549.66
	2	116.30	4178.40	45.87	485.93
	3	119.28	3952.40	20.09	471.44
	4	118.13	4341.20	65.82	512.82
	5	117.04	3933.20	17.46	460.33
	6	122.77	4967.60	145.31	609.86
2	1	121.74	3754.80	-3.55	457.12
	2	124.37	3530.40	-31.54	439.06
	3	118.18	3519.60	-31.25	415.96
	4	120.55	3304.00	-57.87	398.30
	5	113.87	3190.00	-67.64	363.25
	6	125.15	3204.80	-72.49	401.07
3	1	123.50	3388.80	-48.81	418.50
	2	118.09	3092.80	-81.62	365.22
	3	119.99	3207.20	-69.21	384.84
	4	118.23	3304.40	-56.70	390.67
	5	47.49	3582.80	-9.56	170.16
	6	125.97	3666.40	-14.81	461.87
4	1	120.46	3750.00	-4.10	451.71
	2	118.77	3774.40	-1.14	448.28
	3	116.39	3973.60	22.07	462.49
	4	116.62	3817.20	3.87	445.15
	5	120.39	3325.60	-55.19	400.37
	6	125.58	3451.20	-41.79	433.42
5	1	122.51	3522.80	-32.00	431.59
	2	115.12	3390.00	-45.36	390.27
	3	119.48	3403.20	-45.50	406.62
	4	120.41	3305.20	-57.65	397.99
	5	118.31	4587.60	95.07	542.76
	6	128.97	1837.20	-251.09	236.95
6	1	119.06	3908.40	14.81	465.34
	2	121.65	3996.00	25.79	486.12
	3	120.38	3990.40	24.85	480.35

	4	119.39	3957.60	20.73	472.50
	5	119.42	2191.20	-190.22	261.68
	6	125.20	5526.40	218.16	691.93
7	1	124.62	4407.20	77.66	549.23
	2	115.46	4325.60	62.53	499.43
	3	119.58	4500.00	85.62	538.12
	4	121.70	4500.00	87.14	547.67
	5	117.48	4110.40	38.34	482.87
	6	123.62	5129.20	166.29	634.06
8	1	122.53	4256.00	57.83	521.48
	2	116.26	4674.40	103.52	543.47
	3	121.02	4214.40	52.09	510.03
	4	119.02	4072.00	34.28	484.63
	5	119.46	4184.80	47.88	499.90
	6	123.69	4946.00	143.73	611.79
9	1	122.83	4747.20	118.31	583.08
	2	114.77	3353.20	-49.44	384.83
	3	119.29	4132.80	41.61	493.02
	4	119.61	4889.20	132.19	584.81
	5	120.35	4272.40	58.78	514.17
	6	119.36	3030.40	-89.95	361.72
10	1	121.24	4759.20	118.23	577.01
	2	118.70	4797.20	120.27	569.43
	3	120.25	5165.20	166.08	621.10
	4	123.58	4601.20	100.99	568.60
	5	117.78	5392.40	189.44	635.11
	6	121.75	2249.60	-186.81	273.88

Selenium

Table D-4. Soil Analysis Data for Selenium

Column	Section	Dry Soil (g)	C_s (µg/kg)	Ms Retained (µg)	Ms (µg)
1	1	126.79	609.60	35.86	77.29
	2	116.30	537.20	24.47	62.47
	3	119.28	515.20	22.47	61.45
	4	118.13	631.60	36.01	74.61
	5	117.04	1369.60	122.05	160.29
	6	122.77	3561.20	397.08	437.20
2	1	121.74	568.00	29.36	69.15
	2	124.37	357.20	3.78	44.42
	3	118.18	286.00	-4.82	33.80
	4	120.55	242.80	-10.13	29.27
	5	113.87	523.60	22.41	59.62
	6	125.15	272.00	-6.86	34.04
3	1	123.50	335.20	1.04	41.40
	2	118.09	114.00	-25.13	13.46
	3	119.99	227.20	-11.95	27.26
	4	118.23	857.20	62.71	101.34
	5	47.49	2137.60	86.00	101.52
	6	125.97	526.00	25.09	66.26
4	1	120.46	425.20	11.85	51.22
	2	118.77	254.40	-8.60	30.21
	3	116.39	408.40	9.50	47.53
	4	116.62	552.40	26.31	64.42
	5	120.39	1746.80	170.95	210.30
	6	125.58	328.80	0.25	41.29
5	1	122.51	324.00	-0.34	39.69
	2	115.12	268.80	-6.68	30.95
	3	119.48	726.80	47.79	86.84
	4	120.41	772.80	53.70	93.06
	5	118.31	1471.20	135.39	174.06
	6	128.97	314.40	-1.60	40.55
6	1	119.06	324.80	-0.24	38.67
	2	121.65	354.00	3.31	43.06
	3	120.38	257.20	-8.38	30.96

	4	119.39	1987.60	198.28	237.30
	5	119.42	272.40	-6.50	32.53
	6	125.20	281.20	-5.71	35.21
7	1	124.62	226.40	-12.51	28.21
	2	115.46	164.80	-18.70	19.03
	3	119.58	473.20	17.51	56.59
	4	121.70	958.00	76.82	116.59
	5	117.48	1734.80	165.41	203.80
	6	123.62	340.40	1.68	42.08
8	1	122.53	400.80	9.07	49.11
	2	116.26	475.20	17.25	55.25
	3	121.02	522.80	23.72	63.27
	4	119.02	803.60	56.75	95.64
	5	119.46	1674.40	160.98	200.02
	6	123.69	432.00	13.01	53.44
9	1	122.83	567.20	29.53	69.67
	2	114.77	282.00	-5.14	32.36
	3	119.29	460.80	15.99	54.97
	4	119.61	498.80	20.57	59.66
	5	120.35	1439.20	133.87	173.20
	6	119.36	496.00	20.20	59.20
10	1	121.24	774.80	54.32	93.94
	2	118.70	608.00	33.38	72.17
	3	120.25	615.20	34.68	73.98
	4	123.58	928.80	74.39	114.78
	5	117.78	1753.60	168.05	206.54
	6	121.75	2249.60	234.09	273.88

Manganese

Table D-5. Soil Analysis Data for Manganese

Column	Section	Dry Soil (g)	C_s (µg/kg)	Ms Retained (mg)	Ms (µg)
1	1	126.79	285.62	-16.94	36.21
	2	116.30	319.97	-11.54	37.21
	3	119.28	358.21	-7.28	42.73
	4	118.13	500.86	9.65	59.17
	5	117.04	575.77	18.32	67.39
	6	122.77	680.87	32.12	83.59
2	1	121.74	416.61	-0.32	50.72
	2	124.37	385.53	-4.19	47.95
	3	118.18	332.98	-10.19	39.35
	4	120.55	340.09	-9.54	41.00
	5	113.87	442.86	2.69	50.43
	6	125.15	583.57	20.57	73.03
3	1	123.50	480.63	7.59	59.36
	2	118.09	346.05	-8.64	40.86
	3	119.99	290.24	-15.48	34.83
	4	118.23	331.20	-10.41	39.16
	5	47.49	416.06	-0.15	19.76
	6	125.97	582.96	20.63	73.44
4	1	120.46	478.98	7.20	57.70
	2	118.77	362.78	-6.70	43.09
	3	116.39	292.11	-14.79	34.00
	4	116.62	337.12	-9.57	39.31
	5	120.39	477.76	7.05	57.52
	6	125.58	613.08	24.35	76.99
5	1	122.51	478.72	7.29	58.65
	2	115.12	461.18	4.83	53.09
	3	119.48	382.35	-4.40	45.68
	4	120.41	285.54	-16.09	34.38
	5	118.31	332.81	-10.22	39.37
	6	128.97	717.90	38.52	92.59
6	1	119.06	500.38	9.66	59.58
	2	121.65	505.54	10.50	61.50
	3	120.38	380.65	-4.64	45.82

	4	119.39	847.03	51.08	101.13
	5	119.42	354.23	-7.76	42.30
	6	125.20	437.96	2.35	54.83
7	1	124.62	366.84	-6.53	45.72
	2	115.46	331.93	-10.08	38.32
	3	119.58	346.18	-8.73	41.40
	4	121.70	493.21	9.01	60.03
	5	117.48	623.27	23.97	73.22
	6	123.62	461.61	5.24	57.06
8	1	122.53	368.39	-6.23	45.14
	2	116.26	303.38	-13.47	35.27
	3	121.02	339.43	-9.65	41.08
	4	119.02	498.38	9.42	59.32
	5	119.46	598.53	21.42	71.50
	6	123.69	444.83	3.17	55.02
9	1	122.83	415.90	-0.41	51.08
	2	114.77	393.06	-3.00	45.11
	3	119.29	345.56	-8.79	41.22
	4	119.61	467.40	5.76	55.91
	5	120.35	771.03	42.34	92.79
	6	119.36	528.79	13.08	63.12
10	1	121.24	486.69	8.18	59.01
	2	118.70	389.57	-3.52	46.24
	3	120.25	325.18	-11.31	39.10
	4	123.58	357.23	-7.66	44.15
	5	117.78	767.67	41.04	90.42
	6	121.75	2249.60	222.84	273.88

Aluminum

Table D-6. Soil Analysis Data for Aluminum

Column	Section	Dry Soil (g)	C_s (µg/kg)	Ms Retained (mg)	Ms (µg)
1	1	126.79	18890.13	-653.88	2395.09
	2	116.30	18344.02	-663.27	2133.33
	3	119.28	18075.84	-712.28	2156.09
	4	118.13	20553.75	-412.69	2428.00
	5	117.04	19059.75	-583.73	2230.70
	6	122.77	20570.68	-426.82	2525.41
2	1	121.74	19062.26	-606.89	2320.68
	2	124.37	18697.21	-665.37	2325.29
	3	118.18	17833.41	-734.38	2107.60
	4	120.55	13710.48	-1246.13	1652.83
	5	113.87	14872.29	-1044.78	1693.54
	6	125.15	15977.24	-1009.95	1999.50
3	1	123.50	13758.48	-1270.63	1699.12
	2	118.09	15081.65	-1058.74	1780.96
	3	119.99	13565.28	-1257.77	1627.74
	4	118.23	14276.86	-1155.14	1687.92
	5	47.49	17804.95	-296.47	845.61
	6	125.97	17910.68	-773.06	2256.28
4	1	120.46	17371.05	-804.20	2092.46
	2	118.77	17767.05	-745.89	2110.15
	3	116.39	15715.05	-969.79	1829.08
	4	116.62	18320.84	-667.81	2136.54
	5	120.39	19950.83	-493.18	2401.90
	6	125.58	21261.55	-349.85	2670.13
5	1	122.51	18839.76	-638.00	2308.13
	2	115.12	17867.91	-711.40	2057.03
	3	119.48	12977.49	-1322.64	1550.57
	4	120.41	14554.73	-1143.03	1752.58
	5	118.31	15175.42	-1049.63	1795.39
	6	128.97	15985.20	-1039.81	2061.69
6	1	119.06	13731.67	-1228.20	1634.92
	2	121.65	15572.11	-1031.02	1894.37
	3	120.38	13934.81	-1217.32	1677.44

	4	119.39	14846.84	-1098.45	1772.57
	5	119.42	19288.89	-568.27	2303.53
	6	125.20	17572.01	-810.74	2200.09
7	1	124.62	17200.16	-853.30	2143.50
	2	115.46	17563.56	-748.61	2027.87
	3	119.58	17667.84	-762.87	2112.75
	4	121.70	18578.11	-665.63	2261.03
	5	117.48	19036.75	-588.62	2236.35
	6	123.62	17842.03	-767.09	2205.60
8	1	122.53	15903.51	-997.85	1948.63
	2	116.26	13179.18	-1263.58	1532.27
	3	121.02	13201.84	-1312.52	1597.69
	4	119.02	14032.40	-1191.93	1670.07
	5	119.46	14225.69	-1173.25	1699.34
	6	123.69	13721.85	-1277.20	1697.32
9	1	122.83	15434.08	-1057.94	1895.72
	2	114.77	13335.15	-1229.40	1530.43
	3	119.29	20639.94	-406.48	2462.21
	4	119.61	23920.62	-15.15	2861.18
	5	120.35	20092.45	-475.95	2418.04
	6	119.36	42488.69	2201.24	5071.63
10	1	121.24	21156.41	-350.50	2565.01
	2	118.70	21102.81	-349.52	2504.93
	3	120.25	20854.99	-383.87	2507.74
	4	123.58	21531.11	-310.94	2660.72
	5	117.78	22582.14	-172.57	2659.70
	6	121.75	26334.70	278.48	3206.14