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Prescribed Fire-Induced Changes in Soil Properties of the Southeastern Forests of the United States: Sorption Behavior of Polar and Nonpolar Compounds

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PRESCRIBED FIRE-INDUCED CHANGES IN SOIL PROPERTIES OF THE SOUTHEASTERN FORESTS OF THE UNITED STATES: SORPTION BEHAVIOR OF POLAR AND NONPOLAR COMPOUNDS

A Thesis
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by
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ABSTRACT

Due to an increase in wildfires across the US and world, prescribed fires are implemented to reduce fuel loads. Obvious changes occur in the total organic matter by visual observations made after a fire, however, events lead to a production of hydrophobic substances due to the incomplete combustion of organic matter that have the potential to alter soil sorption capabilities. The objective of this research is to determine the sorption capabilities of field collected soil profiles subjected to various levels of prescribed burning using polar and nonpolar compounds. Laboratory controlled soil heating was also conducted to compare the sorption capabilities of the burned soil to that of the collected bulk soil. Soil from Frances Marion National Forest in Cordesville, South Carolina was collected from three locations. WS80 serves as a control, which has never been exposed to prescribed burning, WS77 has been managed with prescribed burns for over 15 years, and WSAA was collected following a low-intensity prescribed burn the day prior to sampling. Field samples were collected at 2.5 cm incremental depths up to a total depth of 25 cm. Using nonpolar 1,3,5 trichlorobenzene and polar 1,3,5 trinitrobenzene, batch sorption experiments were conducted to compare the sorption capabilities of the soil at the surface and lower depths. This study demonstrated a long term prescribed burning has an impact on soil physical and chemical properties. Additionally, a gradient in sorption properties as a function of depth of burned soil. Key findings of this study include increased sorption capability of top layer soil from prescribed burned watershed WS77 increased for polar and nonpolar compounds compared to control site, WS80 (increase of 34% for TCB and 64% for TNB).

Keywords

Fire, soil, sorption, polar compounds, nonpolar compounds, 1,3,5 trichlorobenzene, 1,3,5-trinitrobenzene

DEDICATION

This thesis is dedicated to my mother, Jennifer Schilling, and my sister, Megan Vanderloop for their continued support.

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BC	Black Carbon
CEC	Cation Exchange Capacity
ECD	Electron Capture Detector
GC	Gas Chromatograph
HPLC	High Performance Liquid Chromatograph
SOM	Soil Organic Matter
TCB	1,3,5 Trichlorobenzene
TNB	1,3,5 Trinitrobenzene
UV	Ultraviolet
WS80	Watershed 80, control site
WS77	Watershed 77, experimental burned site
WSAA	Watershed AA, experimental burned site

INTRODUCTION

The increase of intensity and frequency of wildfires in recent decades has altered ecosystems to which they are present has led to a lack of understanding of the relationship between kilometer-scale high-impact watershed processes and pore-scale soil physiochemical properties as they relate to human health. Fire exposure results in 13 deaths per year, and smoke related exposure can cause harmful health effects due to the chemicals emitted (Thomas et al., 2017). Along with the potential direct losses of human life, the economic costs has resulted in significant property damage and billions of dollars in losses (Thomas et al., 2017). An additional cost includes the funds required to suppress and prevent uncontrollable wildfires with the use of prescribed burns. Reviews of the costs and losses of forest fires has been extensively studied in previous research (Liu et al., 2010; Mitchell et al., 2014; Thomas et al., 2017).

Observed effects are experienced worldwide in not only human safety and economic costs but also enhanced hydrogeological and geomorphological activity. Wildfires alter watershed processes due to the direct and indirect effects they have on soil and water resources such as, water quality, physicochemical soil properties, and hydrogeological processes. Previous research has aimed to summarize the effects experienced on the soil properties, watershed processes, and water quality following a forest fire (Hohner et al., 2019; Ice et al., 2004; Shakesby and Doerr, 2006; Shakesby, 2011). The negative effects of wildfires on soil and water resources has led to an increased understanding in the processes altered. However, wildfires are influential at natural levels in the ecosystems they serve and offer many positive benefits to forest restoration (Pausas et al., 2019).

While their increase warrants concern, wildfires are a natural phenomenon, providing redistribution of open habitats for wildlife, reduced water consumption of vegetation by eliminating woody plants, and enhanced long-term carbon fixation (Pausas and Keeley, 2019). Wildfires also regulate biogeochemical cycles by maintaining the mobility, transport, and plant uptake of micro- and macro-nutrients in the soil (Pausas and Keeley, 2019). Their positive benefits are apparent at natural levels. In an effort to minimize the uncontrollable wildfires by reducing carbon emissions as well as mimic the positive benefits of natural forest fires, prescribed fires are commonly used as a land management practice (Alcañiz et al., 2018).

History of Prescribed Fires in United States

A prescribed fire is a low-intensity fire under specific weather and fuel load conditions practiced around the United States, with 70% of prescribed burns occurring in the Southeast United States (Chiodi et al., 2018). South Carolina employs prescribed burning for forest understory management, forestry site preparation, wildlife management, and agriculture adaptability (South Carolina Forestry Commision, 2018). Prescribed burning was first introduced by Native Americans and early Europeans during heavy logging era for forest regeneration (Robert J. Mitchell et al., 2014). The National

Park Service allowed natural fires and prescribed burning to suppress wildfires around 1967 after their introduction in Sequoia and Kings Canyon (Kilgore, 1976).

In the 1970s, research was conducted on the effect prescribed fires have on water repellency. Water repellency was discovered following a prescribed burn (Zwolinski, 1971), but other studies were not in agreement in that they did not observe the same increased water repellency following prescribed burns (Agee, 1979). Evidence points out that research on the Santee Experimental Forest in Cordesville, South Carolina began to explore the effects of prescribed burns prior to 1984 (Richter and Gilliam, 1984). Honing in on the relationship between prescribed burns and soil properties, specific studies have begun to investigate soil aggregate stability (Zavala et al., 2010), mineral soil chemical properties (Coates et al., 2018), and organic matter changes (Waldrop et al., 1987). Various studies have been conducted on the sorption capabilities of burned forest soils and their implications on overall watershed processes after a fire (Peng et al., 2017; Yang and Sheng, 2003). Extensive reviews on the physio-chemical property changes have been published (Alcaniz et al., 2018; DeBano, 1981; Neary et al., 1999). Large-scale studies have been conducted in order to determine the overall implications changes in soil physicochemical properties following prescribed burning has on overall watershed processes (Cawson et al., 2016; Ice et al., 2004; Moody et al., 2008).

Soil Heating During Prescribed Fires

Although they produce much lower temperatures, prescribed fires are highly variable and unique to which the ecosystem they are administered. Prescribed fires generate a mosaic of severities, duration, and combustion type (Shakesby, 2011). The impact of a prescribed fire is related to the fire intensity, frequency, and duration, along with specific properties of the forest, such as vegetation and climate (Shakesby and Doerr, 2006). Fire intensity, frequency, and duration have been used as measures of the impact a fire can have on the below ground sustainability (Moody et al., 2013). Fire burn severity is the term used to characterize the results of the burn, while fire intensity is used to describe the rate of burning (Ice et al., 2004). The classes of soil-burn severity are unburned to very low, low, moderate, and high. Low includes light ground char, mineral soil is unchanged, and very little changes in watershed processes expected (Ice et al., 2004). A low intensity fire has a rate of heat transfer of less than 500 kW m^{-1} (Shakesby and Doerr, 2006). Moderate soil heating includes moderate ground char, decreased infiltration capacity due to alterations in soil structure, and a shallow light-colored ash layer present (Ice et al., 2004) with a rate of heat transfer of 501-3000 kW m^{-1} (Shakesby and Doerr, 2006). High burn severity and soil heating include deep ground chars, soil structure is destroyed, and watershed processes and water quality effects are expected (Ice et al., 2004). The heat transferred of a high intensity fire can be 3001-7000 kWm^{-1} (Shakesby and Doerr, 2006). The intensity of the fire is a result of the combustion process, which results in quantitative and qualitative measures to predict the soil heating, such as combustion temperatures of soil and soil constituents as well as depth of burn and visual indicators (e.g., ash presence, litter cover changes) (Parsons et al., 2010; Vega et al., 2013).

Combustion and Heat Transfer

The combustion process is an incorporation of a chemical energy source, thermal energy, and presence of oxygen (Neary et al., 1999). In addition to combustion, phases to consider when understanding a fire include pre-ignition, flaming combustion, smoldering combustion, glowing combustion, and extinction (DeBano, 2000). The most changes experienced in the soil are from the heat transfer due to radiation and convection during the combustion phases (Chandler et al., 1983). Another important process in alterations of soil physiochemical properties following a forest fire is the vaporization and condensation of water in the pores that can cause structural and chemical changes (Neary et al., 1999). The complex nature of fire has resulted in modeling efforts that aim to predict the combustion process using experimentally defined variables such as fuel characteristics, vegetation, percent moisture, humidity, and weather conditions (Valette et al., 1994); (Udell, 1983); (Celia et al., 1990); (Massman, 2012).

Soil Temperatures

Temperature can be an indicator of physio-chemical and biological changes in the soil. Temperatures in a forest fire (wildfire or prescribed) can range from 50 ˚C to over 1500 ˚C, and heat release in the form of radiation into the soil can reach as high as 2.1 million J/kg (Neary et al., 1999). The smoldering phase, although much lower temperatures reached, can have lasting impacts on soil due to the longer duration it occurs (Neary et al., 1999). Soil and its constituents are highly variable depending on the region to which they serve. Temperature ranges can be used to predict the effects experienced following a prescribed burn (Cawson et al., 2016).

Although a small portion of heat generated during a fire is actually radiated to the soil, loss of organic carbon in soil begins at 100 to 200 ˚C (González-Pérez et al., 2004). The charring process begins around 200 ˚C. Smoldering combustion takes place around 250-450˚C. Heating above 460 ˚C eliminates hydroxyl (OH) groups from the clay percentage of the soil that form bonds with surrounding water molecules, (Shakesby and Doerr, 2006). The production of mineral ash is produced when complete combustion of organic matter takes place. However, in most circumstances, incomplete combustion occurs under most forest fire conditions due to the oxygen availability, which is where pyrogenic organic matter is produced (Bodí et al., 2014). Pyrogenic organic matter is a fire derived substance due to incomplete combustion, which is responsible for the hydrophobic nature of the soil following a forest fire (DeBano, 1981). These processes take place on a heightened and much faster scale during uncontrollable wildfires, but also can reach damaging levels in certain areas during a prescribed burn as well.

Soil temperatures during a prescribed burn can range from 50 - 1000 ˚C (Cawson et al., 2016). The temperature to which the soil reaches is dependent on the surface fuel and water content (Massman, 2012). The soil temperature is also a function of depth. During three prescribed burns administered in a dry Ecalyptus forest in Australia with silty clay loam and sandy loam dominant soils, the peak surface soil temperatures were a maximum of 622 ˚C and an average of 238 ˚C (Cawson et al., 2016). In a prescribed burn in Montana, soil temperatures were between 69 - 612 ˚C (Rochichaud, 2000). However, at a depth of 10 mm, the soil temperatures dropped below 300 ˚C in Australia (Cawson et al., 2016) and below 50 ˚C in Montana (Robichaud et al., 2016). Furthermore, where the heating is reaching the boiling point of water throughout the soil core, the temperature of the soil will remain stable until it is almost completely dry. After the soil has dried out, a rapid temperature increase is expected, and hence the large drop in temperature as a function of depth in the soil (Robichaud and Hungerford, 2000). In addition to depth, the soil temperatures are affected by the duration of time heat is being transferred (Cawson et al., 2016). Although prescribed fires reach much lower temperatures, the smoldering phase of combustion can have lasting impacts on the soil at lower temperatures due to their slow movement.

Impacts of Prescribed Fires on Physiochemical Soil Properties

Prescribed burning is often described as a mosaic of high, medium, and low intensity fire in an area (Shakesby, 2011). The resulting fire produced is highly variable depending on the ecosystem properties that make an area unique, such as the vegetation, moisture content, humidity, air temperature, and the physiochemical properties that govern the overall watershed processes. The amount of heat generated during a forest fire that radiates into the soil is insignificant, but the production of fire derived substances that remain incorporated in the soil can have lasting impacts (González-Pérez et al., 2004). Soil is considered an important resource (Alcañiz et al., 2018). Understanding the physiochemical soil properties affected by forest fires is essential in predicting the kilometer scale changes to occur in a fire-prone ecosystem. Although many variables affect the changes experienced in post-fire hydrogeological settings, the alterations of prominent physiochemical properties for the research discussed here includes soil organic matter, soil aggregate stability, soil hydrophobicity, and soil sorption capabilities.

Soil Organic Matter

Soil organic matter (SOM) is an essential measure of overall soil health by protecting soil cover and minimizing erosion as well as regulating soil temperature (Neary et al., 1999). SOM is an essential measure of forest productivity (Hatten et al., 2008). SOM is composed of fresh plant residues and small living soil organisms, active organic matter (detritus), and stable organic matter (humus) (USDA, 2010). Humic substances are formed due to diagenesis or the reactions of partial degradation, rearrangement, and recombination of molecules formed in biogenesis, which is the production of new living organisms (Schwarzenbach et al., 2003). SOM includes a wide array of sites that have reactivity. Some examples may include hydroxyls, carboxylic, and amino groups as well as aromatics and aliphatics (Aaron et al., 2012). Soil organic carbon (SOC) is a component of SOM, and it refers to the carbon component of organic compounds in SOM. Soil is the largest carbon pool of which 70 percent is organic (González-Pérez et al., 2004).

In addition to the main components of SOM, fire produces combustion byproducts, which include pyrogenic matter. The carbon within the pyrogenic matter is known as pyrogenic carbon or black carbon (Hobley et al., 2017). Black carbon involves the residues that form from incomplete combustion (Hobley et al., 2017; Schwarzenbach et al., 2003). BC is broadly known as charcoal, soot, or elemental carbon. BC is almost unalterable in terms of decomposition time (González-Pérez et al., 2004). Black carbon has been observed to be present in surface waters following a forest fire (Hohner et al., 2019). BC contributes roughly one to ten percent of the fraction of organic carbon present in sediments and soils (Gustafsson and Gschwend, 1998). The inorganic portion of black carbon produced following a fire is typically referred to as ash. However, in low intensity forest fires especially, there is an organic fraction of ash, which contributes to the overall pyrogenic carbon produced (Bodí et al., 2014). Ash is highly mobile and transported downstream, which can also effect water quality (Hohner et al., 2019).

A major contributor to the visual differences in SOM after a fire is the distribution and incorporation of ash. The organic portion of ash is incorporated into the pyrogenic carbon (Bodí et al., 2014), which is transformed through charring vegetation in the duff layer. The inorganic component of ash is considered “mineral ash” (Bodí et al., 2014). Mineral ash tends to be light in color, whereas organic compounds tend to be darker in color when charred (Bodí et al., 2014). The presence of both black and white ash has been shown to alter the reactivity of the soil (Wang et al., 2016). The soil layers are composed of a litter layer atop of a duff layer. The duff layer is the between the litter layer and soil mineral surface. The incomplete combustion of litter and duff layers produce unburned or partially burned fragments, which contribute to ash composition and overall carbon reservoirs following a prescribed burn. Plant residue and waxy material found in the duff layer contain natural aromatic compounds, and, during combustion, the aromatic compounds can deposit on the soil surface and increase soil surface hydrophobicity (DeBano, 1981). Together, ash presence and waxy-substance combustion contribute to the overall soil organic matter (SOM). Ash is incorporated into soil through downward migration from erosion and soil organisms that transport them to deeper depths (Hohner et al., 2019). Further investigation of the fraction of organic matter has been done to understand the transport of DOM following wildfires into water supplies (Wang et al., 2016). In this study, it was concluded the increase in intensity of fire can increase the aromaticity and reactivity of organic matter (Wang et al., 2016).

With the incorporation of ash and unburned or partially burned slash fragments, it is expected to find a change in SOM after a prescribed fire due to the incomplete combustion of organic matter during low temperatures (Alcañiz et al., 2018). In an extensive review, a sample of studies were conducted following prescribed burns across the world (Alcañiz et al., 2018). It was found after prescribed burns there can be an increase, decrease, or no change detected in SOM due to the high variability and susceptibility of SOM on several factors including vegetation, climate, fire severity, fire intensity, and fire duration (Alcañiz et al., 2018). An increase in SOM of up to 30 percent was detected following a prescribed fire (Chandler et al., 1983). More specifically, there is an increase in the carbon pool due to the incorporation of the fire-derived substances previously discussed and introduction of pyrogenic aromatic structures (Alexis et al., 2012) (Neary et al., 1999). However, decreased SOM is possible due to the combustion of the litter layer that acts to protect the soil (Swanson, 1981). A 21 to 80 percent decrease in surface organic matter has been observed (Pase and Lindenmuth, 1971). At temperatures above 450 ˚C, a complete loss of SOM is observed, which has been observed during prescribed burns (Granged et al., 2011). The variable changes in soil organic matter are associated with altered nutrient cycling and other essential ecosystem function that result in forest health.

Soil Aggregate Stability

SOM is an important indicator of soil health and an essential measure to consider when predicting effects experienced after a forest fire. It is also the main driver in soil structure and aggregate stability, which is needed for optimal plant growth and water storage (Oades, 1984). Soil aggregate stability (SAS) refers to the ability of a soil to retain its structure when exposed to different environmental disturbances (Amézketa, 1999). It is another indicator of soil health and quality along with forest productivity (Arshad and Coen, 1992).

Soil aggregates are formed by organic and inorganic materials holding them together (Arshad and Coen, 1992). Aggregates are a variety of sized characterized by macroaggregates (>250 μm) and microaggregates (<250 μm) (Bronick and Lal, 2005).

Organic materials binding to clay particles form microaggregates. Microaggregates can join to form macroaggregates (Tisdall et al., 1978). Macroaggregates can also form through the formation of particulate organic matter (POM), which is SOM that is 0.05–2 mm in size (Bronick and Lal, 2005). Other processes of aggregate formation include roots and hyphae that release organic compounds to form with clay particles as well as precipitations of hydroxides, phosphates, and carbonates (Bronick and Lal, 2005). Extensive reviews have been done on the processes involved in the formation of soil aggregates (Bronick and Lal, 2005; Manirakiza and Seker, 2018; Tisdall et al., 1978).

The formation of soil aggregates due to organic materials aids in understanding the effects experienced on SAS following a prescribed burn. The aromatic compounds produced during a fire that increase the SOM can coat soil aggregates and alter their overall function, water retention capacities, and infiltration ability (DeBano, 1981). In addition, ash incorporated into the soil was found to effect SAS using scanning electron microscopy six months after a fire in Spain (Mataix-Solera et al., 2002). The combustion of SOM can also break down soil aggregates and alter soil structure that may lead to altered infiltration, erosion, and flash flooding (Moody et al., 2008). SAS was shown to decrease following a prescribed burn due to the combustion of SOM and binding agents when fires reached above 170 ˚C (Benito and Diaz-Fierros, 1992). Heating above 500 ˚C resulted in complete loss of SOM and almost complete loss of clay particles (Badía and Martí, 2003). In addition, a decrease in the soil structure is expected when the temperature is held above 100 ˚C for a sufficient amount of time and the soil becomes dry and susceptible to minor stresses (Robichaud and Hungerford, 2000). However, an increase in SAS was observed in some cases when fire was heated below 170 ˚C (Benito and Diaz-Fierros, 1992).

SOM has shown to increase following a prescribed burn due to mechanisms in described above. The increase in SOM has been shown to increase the SAS due the presence of more cementing agents to bind the aggregates together (Granged et al., 2011). In addition to overall SOM increase, the increased hydrophobic or water repellent nature of the materials coating the aggregates (aromatic pyrogenic matter) could help maintain the structure and increase SAS due to the attractive force between water and soil particles being reduced (DeBano, 1981; Zavala et al., 2010). This pattern was observed under laboratory conditions by heating the soils at 170-220 ˚C. (García-Corona et al., 2004).

Soil Hydrophobicity

The previous sections have eluded to the introduction of water repellency and hydrophobicity following a prescribed burn. The hydrophobic organic compounds produced during a fire coat the soil aggregates and minerals to create a water repellent nature and layer (DeBano et al., 1970). Extensive reviews have been conducted on the increased water repellency following a forest fire (Alcañiz et al., 2018; DeBano, 2000, 1981; Doerr et al., 2000). The overall response to wettability and water repellency following a prescribed burn are variable due to the degree of intensity and duration achieved during a burning event along with vegetation and duff layer thickness.

However, as the effects experienced on SOM and SAS, the water repellency has been proven a function of temperature. Under laboratory conditions, soil temperatures above 176 °C, water repellency is formed and destroyed at temperatures above 288 °C (DeBano, 1981; Robichaud and Hungerford, 2000; Zavala et al., 2010). However, other field studies have found an increase in water repellency even when the temperature exceeded 288 °C (Cawson et al., 2016; Granged et al., 2011). The discrepancy between lab and field has been predicted to be due to the variation in the durations of burning in the field and constant temperatures during lab studies (Cawson et al., 2016). Another explanation could be the moisture content in the samples during the burning. When exposed to temperatures below 200 °C, the water repellency decreased as a function of depth, which is predicted to be due to the dry surface layers exhibiting more water repellency (Zavala et al., 2010).

The top surface of the soil is protected by a duff layer composed of litter and plant residues, which is consumed by the fire and creates an ash layer and increases organic compounds at the surface (Doerr et al., 2000). The negative effects of wildfires originate due to the combustion of the substances on the top layer that go on to generate an ash layer that induces water repellency (American Forest Foundation, 2015). The increase in the water repellent zone decreases the wettable soil layer that infiltrates, filters, and stores water for plant uptake, mobility, and transport (Hohner et al., 2019). In a flat terrain, the effects of water repellency may only be at the location and not have broad scale watershed effects, but on a sloped surface, the potential increase of water repellency can increase erosion, flash flooding, and surface sealing (Cawson et al., 2016). Surface sealing and pore clogging can occur as a result of water repellency and the increase in ash layer thickness (Woods and Balfour, 2010). This phenomenon could not only effect erosion and flooding but also decrease the infiltration flux into the soil.

Soil Sorption Capabilities

The presence and distribution of fire derived hydrophobic aromatic substances is expected to alter soil sorption capabilities (González-Pérez et al., 2004). Soil sorption capabilities are important to overall infiltration, flow, and contaminant transport (Xing and Pignatello, 1996). Sorption refers to the process in which compounds becomes associated with solid phases (Schwarzenbach et al., 2003). Adsorption refers to the compound attaching to the two-dimensional surface, whereas absorption refers to the molecules penetrating the three-dimensional matrix (Schwarzenbach et al., 2003). For the purpose of this research, the term sorption was used to encompass the underlying processes occurring. In general, the compound or chemical (sorbate) will associate with the solids (sorbent) through a combination of interactions (Schwarzenbach et al., 2003). Solutes in the liquid phase that have the potential to sorb are referred to as sorptives (Aaron et al., 2012). The main drivers of sorbents in soils are SOM and clay particles (Aaron et al., 2012). A common measure of the sorption capabilities of the soil and therefore contaminant transport calculations is the partition coefficient, K_D, a solid-water distribution ratio (Schwarzenbach et al., 2003).

The importance of SOM in the sorption capabilities of soil has been extensively studied (Ahangar, 2010; Chefetz and Xing, 2009; Delle Site, 2001). Inorganic constituents are generally not as effective sorbents in nature due to their ability to form hydrogen bonds with water molecules (Schwarzenbach et al., 2003). This makes it difficult for sorptives to overcome the energy investment needed to displace the water molecules on the inorganic surfaces (Schwarzenbach et al., 2003). The organic component of soil does not require the displacement of these water molecules, and therefore, is more energetically favorable to compounds that are introduced into the system (Schwarzenbach et al., 2003). The sorption capabilities of SOM are more specifically due to the amount of carbon, hydrogen, nitrogen, oxygen present within the solid phase. In general, natural organic matter is made up of about half carbon, so the f_{oc} can be estimated by dividing the fraction of organic matter (f_{om}) in half (Schwarzenbach et al., 2003). The SOM and therefore f_{oc} decrease as a function of depth within the soil (Schwarzenbach et al., 2003).

SOM is naturally polar due to the proposed humic structures consisting of macromolecules with numerous oxygen-containing functional groups (carboxy-, phenoxy-, hydroxy, and carbonyl) (Schwarzenbach et al., 2003). Extensive reviews have been done on the proposed structure of SOM (Hayes and Wilson, 1997; Schulten, 1997). Humic acids consisting of high aromatic content and low polarity showed stronger sorption affinity than high polarity substances due to hydrophobic partitioning (Sun et al., 2008). Hydrophobic partitioning refers to the segregation of non-polar compounds from water in the presence of a non-polar sorbent, which reduces the overall surface area and is therefore energetically favorable (Aaron et al., 2012). BC has a high percent aromaticity due to the non-polar surface they exhibit (Goldberg, 1985; Schwarzenbach et al., 2003). The amount and type of BC produced is a function of the degree and severity of the burn, which include the fuel type, fuel load, fuel condition, and weather conditions (Schmidt and Noack, 2000). Compared to activated carbon, BC has a low surface area but high surface acidity contributing to a low isoelectric point (Qiu et al., 2008). This means the pH at which BC has no charge is lower. A rise in the pH can enhance the sorption capabilities of BC due to the dissociation of acidic functional groups (Qiu et al., 2008). In an extensive review of the effects of soil properties after a prescribed burn, the pH was shown to either increase or remain unchanged following a variety of prescribed burns due to the loss of hydroxyl groups during combustion (Alcaniz et al., 2018). Similar results were found following a high severity, medium severity, and low severity burn, which they attributed to either the increase in SOM contributing to the release of basic cations as well as the accumulation of ash, which naturally has a high pH (Heydari et al., 2017).

With an increase in pH, an increase of the cation exchange capacity (CEC) is expected (Brady and Weil, 2010). CEC is the sum of the cations that can be exchanged into the solution from the solid phase when the soil is at equilibrium with a salt solution (Aaron et al., 2012). The expected increase in pH following a forest fire allows the negative charges on soil particles to become greater, which increases the CEC in the organic fraction of the soil (Brady and Weil, 2010).

In addition to the presence of BC within the SOM, clay content may be altered following a fire due to the irreversible removal of hydroxyl groups and potential destruction of the crystalline structure (Heydari et al., 2017). The clay content present in the soil can give rise to different sorption capabilities of the soil (Brady and Weil, 2010). Clay particles are smaller than 0.002 mm and therefore have very large specific surface areas, which allows them to readily adsorb water and other compounds (Brady and Weil, 2010). Although sorption of non-polar compounds is assumed highly correlated with SOM, clay particles play a dominant role in the sorption of polar compounds (Charles et al., 2006). Sorption of non-polar organic compounds were seen to be 9 to 13 times higher in soil clay-sized fractions compared to that of SOM (Charles et al., 2006). However, the temperatures during a low intensity prescribed fire are unlikely to irreversibly alter clay content due to the high temperatures input required (Heydari et al., 2017). Additionally, BC was shown to exceed the humic acid and active clay minerals in sorption capabilities by more than two orders of magnitude (Shi et al., 2010).

Sorption of Polar and Nonpolar Compounds

The comparison between sorption capacity of polar and nonpolar compounds have been compared in previous literature (Liu et al., 2008; Shi et al., 2010). Polarity in this research is due to the relative solubility in the polar compound of water. Chlorobenzenes, such as 1,3,5 trichlorobenzenes, are considered nonpolar in water, whereas nitrobenzenes, such as 1,3,5 trinitrobenzene, are considered highly polar (Shi et al., 2010). The soil and its components have different affinities to organic chemicals due to the soil mineral composition and soil organic matter present as well as the structure of the chemicals themselves (Liu et al., 2008). It has been hypothesized that the role of nonpolar organic chemical sorption is heavily reliant on the soil organic matter (Shi et al., 2010). Polar compounds, however, have been shown to be more reliant on the surface minerals and charged clays present in the soil (Shi et al., 2010).

When considering the sorption of polar and nonpolar compounds, it is important to determine the interactions between the molecule and soil constituents to understand the sorption capacity of a soil sample. The nonpolar compound, 1,3,5 trichlorobenzene (TCB) has a chlorine functional group at the 1,3, and 5 position on the ring structure. Chlorine is an electronegative element, and therefore, will not want to share electrons with water molecules to form hydrogen bonds. In addition, the polar compound, 1,3,5 trinitrobenzene (TNB) with the nitro functional groups at the 1,3, and 5 position have two oxygens, which will want to share electrons with hydrogen to form hydrogen bonds with water molecules.

A comparison of the specific interactions and forces present in the bonding of the nonpolar, TCB, and polar, TNB, can be described using the π-π electron donor-acceptor interactions and hydrophobic partitioning (Zhu and Pignatello, 2005). The interactions taking place, in brief, are between the chemicals, TCB or TNB, and soil organic matter or soil mineral components (clays). The organic mater is composed of humic acid substances that are made up of a variety of functional groups that can alter reactivity (Schwarzenbach et al., 2003). Black carbon is proposed to be composed of aromatic sheets, which also alter the reactivity (Schwarzenbach et al., 2003; Zhu and Pignatello, 2005). The fused aromatic rings in soil humus structures and black carbon interact with organic chemicals by π-electron-donor-acceptors (Shi et al., 2010). For the polar, TNB, the nitro groups will draw electrons away from the humic acid and black carbon present to be effective electron acceptors. Nonpolar, TCB, may also form the π-π electron donor- acceptor interactions. However, the interactions governing the sorption of nonpolar organic chemicals like TCB has been hypothesized to be hydrophobic partitioning between the organic chemical and humic acid structures or black carbon within the soil organic matter (Liu et al., 2008; Shi et al., 2010).

Rationale

The increase of wildfires worldwide gives rise to more frequent and intense catastrophic conditions for human health and safety. To combat this crisis, the implementation of prescribed fires as a land management practice to reduce impacts of wildfire and mimic positive benefits has inflated. However, knowledge of the alterations in burned soil physiochemical properties is scarce. Understanding the changes in the physico-chemical properties of burned soils and their associated impacts on hydrogeologic processes and contaminant transport is critical for sustainable forest management, assessing, and mitigating their influences on soil and water resources. The sorption properties and capabilities of the soil give rise to the fate and transport of organic pollutants as well as offer insight to overall infiltration capabilities. By quantitatively assessing the changes in soil sorption properties, a link can be made between other physio-chemical soil properties and overall watershed processes.

Hypotheses

The hypotheses of this research are (1) soil samples collected from site where prescribed burning is heavily practiced will have a higher sorption capacity than that of unburned control soil, (2) the top layers of soils will have a greater sorption capacity than that of the bottom layer counterparts, and (3) soil subjected to high-intensity will be less reactive than soils subjected to low-intensity or unburned.

Objectives

The objectives of this research are to (1) measure the sorption of polar and non-polar compounds on forest soils subject to prescribed burns, (2) assess the influence of soil depth and burned temperatures on the sorption behaviors of these polar and non-polar compounds, and (3) Compare sorption of laboratory controlled low- and high-intensity burned soils. Batch sorption experiments were employed using a polar and non-polar compound to quantifiy the amount sorbed to each field collected soil subject to various prescribed burning practices at varying depths along with a control consisting of burned soil at a low-intensity (200˚C) and a high-intensity (500˚C).

2 MATERIALS AND METHODS

Site Characterization

Samples (0-30 cm) were collected from the Francis Marion National Forest located in Cordesville, South Carolina, United States (Figure 2.1). on March 20, 2018. Figure 2.2 shows exact locations of sampling. Samples were collected from three different locations within the forest denoted in Figure 2.2. The control site (WS80) is in the Santee Experimental Forest within the Frances Marion National Forest. WS80 has never been exposed to burning practices. Also shown in Figure 2.2 is another sampling location in the Santee Experimental Forest (WS77), which has been exposed to prescribed burning for over 20 years. The most recent burning occurred three months prior to sampling. The dominant soil type in this area is a Wahee loam soil (Figure 2.3). An additional sample was taken that experienced burning two weeks prior to sampling. Soil at this site belonged to a site (WSAA) within the Frances Marion Forest outside of the Santee Experimental Forest. Figure 2.4 depicts the landscape and visual representation of the sites. Qualitative site assessments were done using visual interpretation of the landscape prior to sampling. WS80 was composed of a thick underbrush and dense vegetation with a thick top layer. WS77 had approximately 4-6 feet of scorching evidence up the trunks of trees, but the underbrush had regrown since the last burning event. WSAA was obviously just recently burned with ash particles present on the topmost layer of soil, which were included in sampling. Samples were collected from the top surface to a depth of 25 cm in 2.5 cm incremental depths using a shovel (Figure 2.4). Prior to collection, the uppermost layer of the soil (duff layer) was removed to exclude unwanted non-soil materials. Each soil layer collection was brought to the lab, air-dried, passed through a 2 mm sieve, and stored at room temperature prior to experimentation.

Figure 2.1. Map of South Carolina, United States, with Francis Marion National Forest including the Santee Experimental Forest.

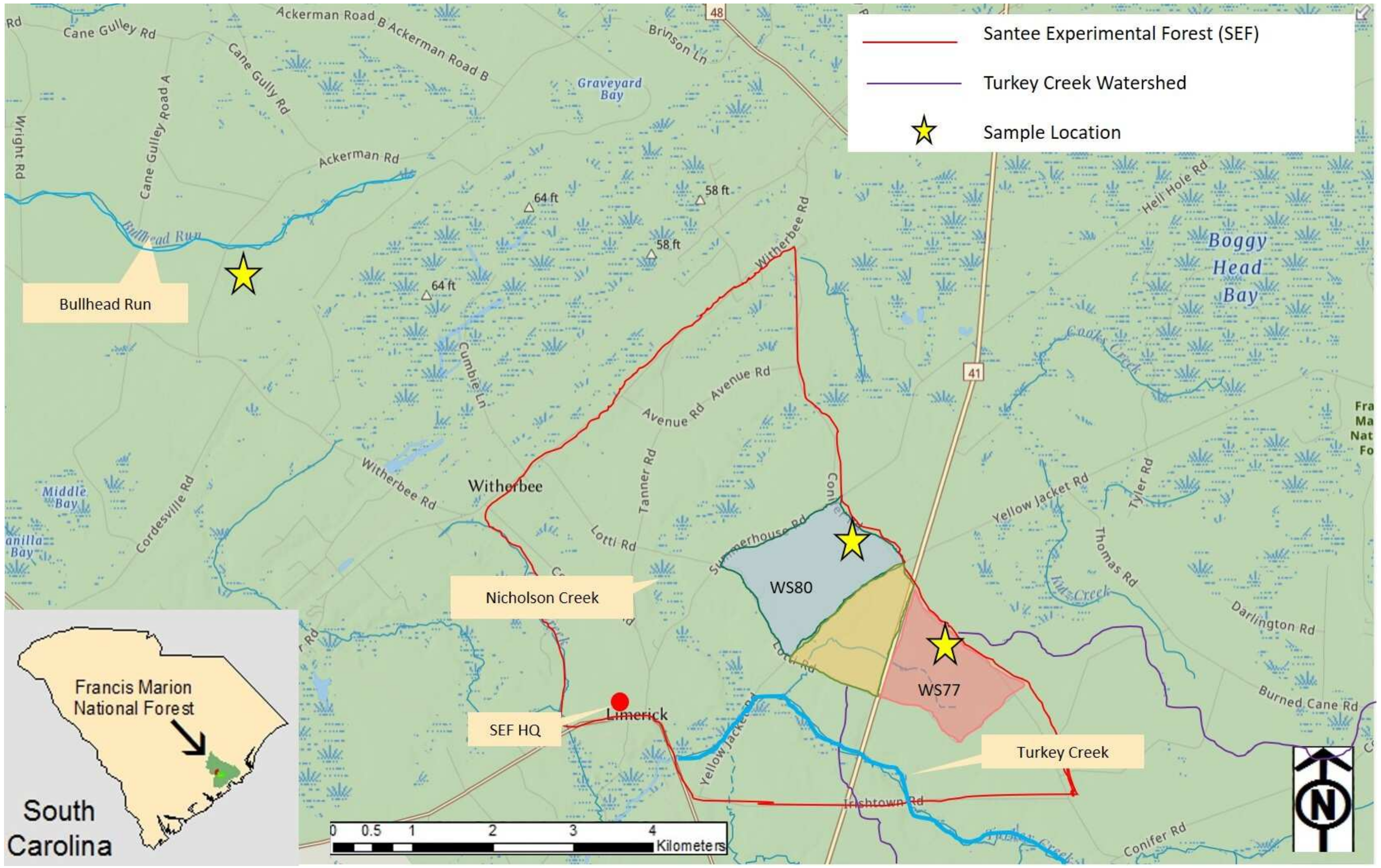


Figure 2.2. Specific sampling locations within Santee Experimental Forest and the Francis Marion National Forest. WS80 sampled site served as the control site with no previous burning activity taking place. WS77 within the Santee Experimental Forest also has been subject to prescribed burning for over 20 years. The site in the Northeast corner of this map was located off Ackerman road and was within a watershed outside of the Santee but within the Francis Marion National Forest. It was labelled WSAA and was burned two weeks prior to sampling.

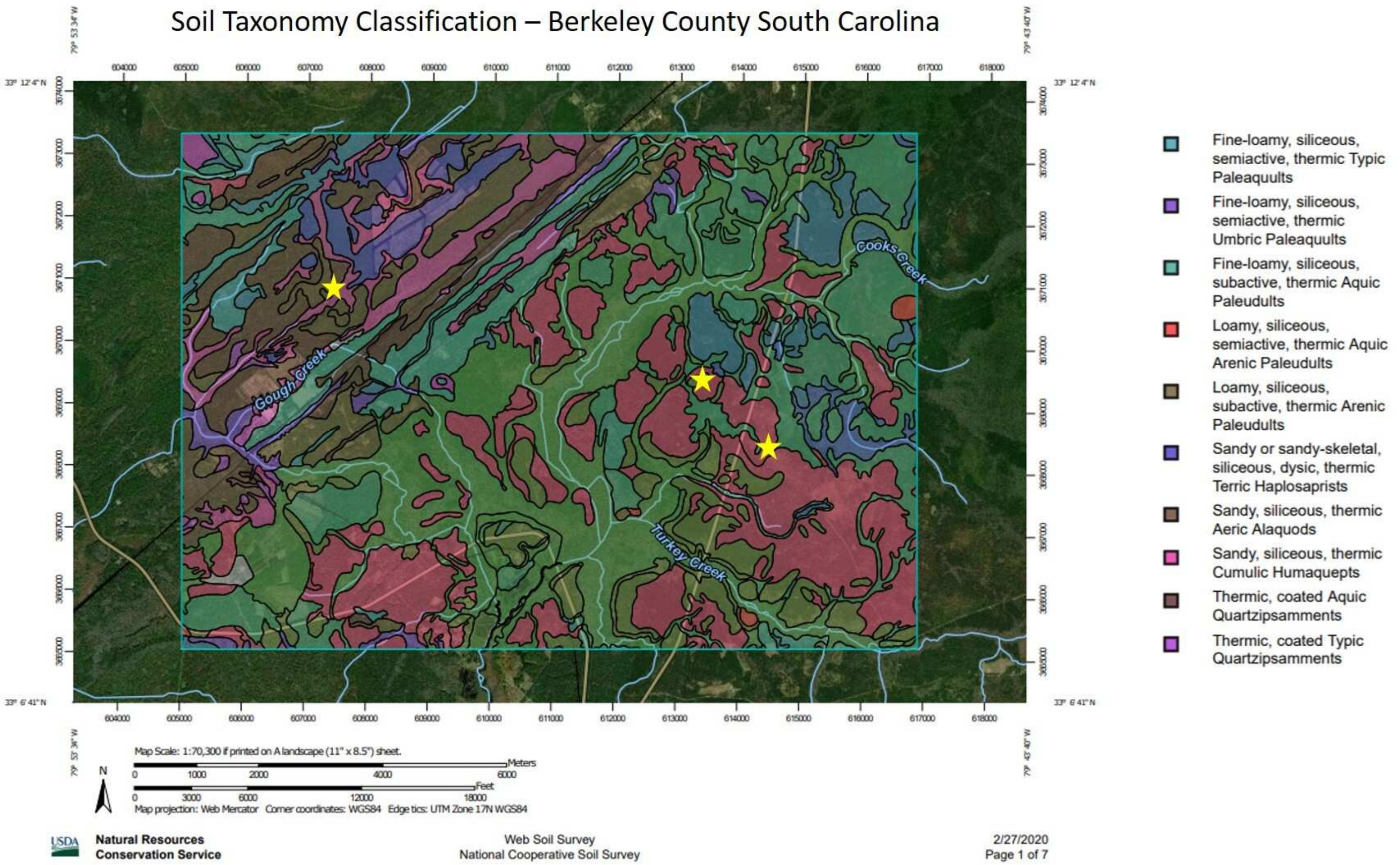


Figure 2.3. Soil taxonomy classification for Berkeley County in South Carolina. Sample locations are denoted by yellow stars, where sample locations were of the same dominant soil type in that area. Wahee loam was the dominant soil type, which is a sandy, sileous, thermic soil with consistent properties.

0

WS80 - Control

WS77 – Prescribed Burning (+20 yrs)

WSAA – Prescribed Burning

WS80 - Control

WS77 – Prescribed Burning (+20 yrs)

WSAA – Prescribed Burning

Figure 2.4. Qualitative site assessment of WS80, WS77, and WSAA on the day of sampling. WS80 had a thick underbrush with a darker soil color throughout the sampled depth of 25 cm. WS77 had scorch marks present on the trees with a less thick underbrush with a discoloration in the soil as depth increased. WSAA had higher scorch marks and an ash layer present atop the soil when sampled.

Soil Characterization

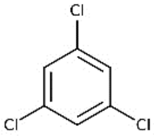
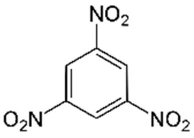
Bulk soil was sent to University of Georgia Laboratory for Environmental Analysis and Center for Applied Isotope Studies for fine-grained particle size distribution using sedimentation rate of particles in water as described by Stokes Law. Metals analysis and speciation using a Perkin Elmer Elan 9000 inductively coupled {argon} plasma (ICP) equipped with a mass spectrometer (MS) detector system was performed by the Laboratory for Environmental Analysis and Center for Applied Isotope Studies at the University of Georgia. Nutrient availability testing was performed at the Clemson University Agricultural Service Labs. Cation Exchange Capacity (CEC) was calculated using the milliequivalents of the basic and acidic cations H, K, Ca, and Mg per 100 grams of soil. The percent base saturation uses the basic cations in meq/100 g of soil to determine what percentage of exchange sites are occupied by basic cations (Mg^{+2}, Ca^{+2}, K^{+1}, and Na^{+1}). The acidity in meq/100 g of soil represents the amount of total CEC occupied by acidic ions (H^+ and Al^{3+}). Organic matter was determined based on weight percentages of each layer. Total soil organic matter (SOM) was determined based on loss of ignition by heating sample at 500 degrees C for six hours in muffle furnace model 126 (Fisher Scientific, Waltham, MA).

Chemicals

Two sorbate compounds were chosen with properties listed in Table 2.1 nonpolar 1,3,5 trichlorobenzene (TCB, Fisher Scientific ®, Waltham, MA) and polar 1,3,5-

trinitrobenzene (TNB, Fischer Scientific ®, Waltham, MA) were chosen based on differences in K_{ow} values and polarity (Table 2.1). Water solubilities are listed in Table 2.1 in mol/L and mg/L. Octanol-water partition coefficients are a sufficient measure of the level of hydrophobicity due to the affinity of the chemical to be in the organic (octanol) phase compared to that of the water phase. If the K_{ow} value is high, like that of TCB, the molecule will partition more strongly to the organic phase than that of the water phase.

Table 2.1. Chemical properties of sorbates 1,3,5 trichlorobenzene and 1,3,5 trinitrobenzene.

	1,3,5 trichlorobenzene	1,3,5 trinitrobenzene
Abbreviation	TCB	TNB
MW (g/mol)	181.45	213.15
Solubility (S_W) (mmol/L)	2.95E-05[a]	1.55E-03[a]
Solubility (S_W) (mg/L)	5.35E-03	3.30E-01
K_{OW} (L/L)	15,488[a]	15.1[a]
K_{HW} (L/L)	30,200[b]	1.00[b]
Molecular Structure		

[a] Schwarzenbach et al. (2003)

[b] Abraham et al. (1996)

Batch Sorption Experiments

Sorption experiments were conducted to quantify the sorption of 1,3,5-trichlorobenzene and 1,3,5-trinitrobenzene under oxic conditions like those experienced in the top layer of the vadose zone. These sorption experiments were performed in 160 mL glass serum bottles with septa plugs and aluminum crimp caps. Stock solutions of sorbates at 0.02 M dissolved in methanol (VWR ®, Radnor, PA) were prepared in chemical laboratory fume hood and stored in the dark at 4 ^{0}C for the duration of experimentation. The volume percentage of stock solution added was kept below 0.1% to minimize competition between the methanol and NaCl solvents. Soil (air dried and sieved < 2 mm) was added to ten bottles ranging from 0.1 g to 10 g followed by enough background solution (10 mM NaCl) to minimize headspace (157 mL). Exact suspended solids concentrations and soil:solution ratios can be found in Table 2.2. Stock solution of sorbates were added to each bottle at a volume of 160 µL followed by pH adjustment to 5.5 using 0.1 M NaOH and HCl. The pH of 5.5 allowed for all adjustments to be made with NaOH only, while remaining at low enough volume to not be concerned with overflowing the serum bottle to accurately adjust pH. The value selected is also similar to value used in previous studies (Liu et al., 2008; Shi et al., 2010). The working solution was then capped and placed on tumbler at 25 ^{0}C and 20 rpm rotator speed for 7 days for both TCB and TNB. The sorption kinetics results indicate this is sufficient time for compounds to reach equilibrium under working conditions (see Appendix).

Table 2.2. Experimental procedure for each sample container and soil:solution ratios used.

C_e	SS (kg/L)	Soil (mg)	Soil (g)	Solution (mL)	Ratio
1	6.97E-04	100	0.1	157	6.25E-04
2	1.59E-03	250	0.25	157	1.56E-03
3	3.26E-03	500	0.5	157	3.13E-03
4	6.36E-03	1000	1	157	6.25E-03
5	1.27E-02	2000	2	157	1.25E-02
6	7.80E-03	3000	3	157	1.88E-02
7	7.44E-03	4000	4	157	2.50E-02
8	3.69E-02	5000	5	157	3.13E-02
9	1.82E-02	7500	7.5	157	4.69E-02
10	4.86E-02	10000	10	157	6.25E-02

All Ce values were calculated using analytical detection methods

Solution (mL) was target solution and actual solution volumes were recorded gravimetrically

At each sampling event for TCB, 15 mL aliquots of the working solution was extracted from each (160 mL) serum bottle using a pipette (Eppendorf, Fisher Scientific, Waltham, MA), placed in 15 mL screw cap centrifuge vials, and centrifuged using an Eppendorf 5810 (Fisher Scientific, Waltham, MA) at 4000 RPM for 20 minutes to separate suspended solids from the solution. Following centrifugation, 10 mL aliquot of aqueous phase was transferred to a 25 mL glass vial using a syringe (VWR, Radnor, PA), needle (VWR, Radnor, PA), and passed through a 0.2 µm nylon syringe filter (VWR, Radnor, PA). A hexane extraction was performed to quantify TCB. Table 2.3 shows the octanol-water partition coefficient (K_{OW}) and hexane-water partition coefficient (K_{HW}) for TCB. Hexane (1 mL; Fisher Scientific, Waltham, MA) was placed into the glass vial atop of the 10 mL sample in tall glass vial and hand turned end over end. Extraction of TCB from hexanes at 0.5 mL was placed in 1.5 mL septa lined amber glass detection vial (VWR, Radnor, PA).

At each sampling event for TNB, 1.5 mL aliquots of the working solution was extracted from each serum bottle using pipett, placed in 2 mL centrifuge vials, and centrifuged at 12500 RPM for 20 min using an Eppendorf MiniSpin (Fisher Scientific, Waltham, MA) to separate suspended solids from the solution. Following centrifugation, one mL from aqueous phase was extracted using syringe, needle, and passed through 0.2 µm nylon syringe filter (VWR, Radnor, PA). Solution was placed in screw cap 1.5 mL septa-lined amber glass detection vial for analytical detection.

An additional laboratory batch sorption experiment was done in addition to the field soil batch sorption experiments to further understanding of the effect soil temperatures have on soil sorption capabilities. WS80 bulk soil was placed in a muffle furnace at a low-intensity temperature (200 ˚C) and a high intensity temperature (500 ˚C) for 12 hours to determine the impact of soil temperature on the sorption of TCB and TNB. Each heated soil was placed in a suite of five different soil masses (100, 500, 1000, 2000, 4000, 5000 mg), into serum bottles and followed exact experimentation procedure as field soil in batch sorption experiments.

Analyses

TCB was analyzed using gas a chromatograph (GC) equipped with an electron capture detector (ECD) (5890 GC System, Agilent, Santa Clara, CA) using a 30 m x 250 µm x 1.00 µm DB-5 column (Agilent 122-5033). The initial oven temperature was set at 75 °C and ramped to 250 °C at a rate of 15 °C/min. The detector temperature was set at 350 °C, carrier gas flow was 0.6 mL/min, and pressure was 4.62 psi. The retention time of TCB was approximately 5.86 min. Calibration included five standards over concentration range (3.0E-06 – 1.5E-02 mmol/L for TCB and 7E-04 – 1.5E-02 mmol/L for TNB) and a linear response was detected ($R^2 = 0.9992$). Minimum detection limit was $< 1 \times 10^{-6}$ mmol L^{-1}.

TNB was analyzed by high-performance liquid chromatography (HPLC) (110 Series, G1311A quat pump. Agilent, Santa Clara, CA) using 4.6 × 100 mm C18 column (Acclaim ®, Fisher Scientific, Waltham, MA) with a pore size of 3 µm. Quantification was performed with an ultraviolet detector (UV) under the following conditions: 55% water, 45% methanol at a wavelength of 250 nm. Calibration included five standards over concentration range expected, and a linear response was observed ($R^2 = 0.9942$). To assess the impact on standards due to environmental samples, standard addition analyses were performed to calculate a percent recovery, Rsf, on bulk soil using equation (2.1).

$$Rsf = \frac{A-0.5B}{C} \times 100 \qquad 2.1$$

where A is the concentration in the sample + standard (50:50 mixture by volume), B is the concentration of sorbate in the sample, and C is the concentration of sorbate after mixing 50:50 with 10 mM NaCl (background solution) (see Appendix).

Based on the calibration standards generated for each compound, the aqueous phase concentration was calculated. Sorption controls were performed for both TCB and TNB to determine the amount sorbed to the glass during experimentation. Results of these analyses showed negligible sorption for TCB and TNB. To account for the adsorption of sorbate to the glass container in future calculations, a control bottle was carried through the same experimentation procedure and analyzed for aqueous phase TCB. Calculations below consider sorbate adsorbing to glass. The concentration sorbed was calculated by subtracting the mass in the aqueous phase from the total concentration initially added. The initial concentration added, C_{0added}, found using equation 2.2, where V_{stock} is the amount of the stock solution added, and V_{NaCl} is the amount of background solution added. This value was divided by the molecular weight, which was used in equation 2.3 to find the initial concentration, C_0. The amount sorbed to the glass was considered by subtracting the initial amount added, C_{0added}, to the control bottle from the aqueous concentration measured in the control bottle, $C_{control\ aq.}$

The peak area computed by analytical detection methods and calibration curves computed a response factor, which was multiplied by the peak area to compute the equilibrium aqueous phase concentration, C_e. After the equilibrium concentration was measured, the solid phase concentration, C_s, was calculated using equation 2.5, where M_{soil} is the amount of soil added in kg. The solid phase concentration sorbed and the measured equilibrium aqueous concentration were used to determine a solid-water ratio or distribution coefficient known as the K_D value.

$$C_{0_{added}}\left[\frac{mg}{L}\right] = \frac{C_{stock}\left[\frac{mg}{L}\right] \times V_{stock}[L]}{V_{NaCl}[L]} \tag{2.2}$$

$$C_0\left[\frac{mmol}{L}\right] = C_{0_{added}} - (C_{control_{added}} - C_{control_{aqueous}}) \tag{2.3}$$

$$C_e\left[\frac{mmol}{L}\right] = Peak\ Area\ \times Response\ Factor \tag{2.4}$$

$$C_s\left[\frac{mmol\ sorbate}{kg\ soil}\right] = \frac{(C_0 - C_{aq})\ [\frac{mmol\ sorbate}{L}] \times V_{NaCl}[L]}{M_{soil}[kg\ soil]} \tag{2.5}$$

Due to the isotherm shape generated, it was determined there is multi-phase sorption competition occurring at higher concentrations. Because of the nature of the isotherm shape and measures taken during batch sorption experimentation (pH adjustment, background solution, soil:solution ratios, methanol co-solvent effects), the higher aqueous phase concentrations did not produce feasible measurements to be modelled in the objectives to compare sorption to the soil samples. To accommodate the trend generated, the low aqueous phase concentrations applicable was used to determine a linear K_D value using equation (2.6). A linear regression on the aqueous phase versus the sorbed phase concentrations was performed using a minimum of four low concentrations to a maximum of six concentrations determined by the combinations with the R^2 closest to one. For TNB, some of the aqueous phase measurements were below the minimum detection level of the analytical detection equipment, so the linear portion of the lowest applicable concentrations were used.

$$K_D \left[\frac{L}{kg}\right] = \frac{C_S}{C_e} \tag{2.6}$$

The low-intensity and high-intensity laboratory-controlled experiments were conducted at the higher concentrations due to the minimum detection limit of the HPLC, so temperature experiments did not generate a K_D value.

Statistical Analyses

Sites, depth, sorbate, and temperature were all compared at each calculated K_D, and aqueous concentration at each suspended solid concentration using an ANOVA with repeated measures in JMP software. ANOVA tables for each parameter and variable can be found in the appendices. The percent difference for a combination of samples were calculated to compare the effects seen on the burned and unburned soils at different depths and sorption capabilities of each sorbate (eq. 2.7).

$$\%\,Change = 100\ \times \frac{|A-B|}{\frac{A+B}{2}} \tag{2.7}$$

RESULTS

Burn Characteristics and Soil Physical and Chemical Properties

Burn characteristics of each site exposed to burning, WS77 and WSAA, can be found in Table 3.1. The live woody percentage refers to the amount of moisture present in woody plants (live needles, twigs, etc.) that persist all year and can easily ignite. The 100-hour fuels percentage refers to the stick and/or branches that are 1 to 3 inches in diameter, which can be used to predict what happened in the last 24 hours. The prescribed burning that occurred on the WS77 site three months prior to sampling, and the fire that occurred on WSAA site days prior to sampling were performed under similar environmental conditions (temperature, humidity, and wind speed).

Soil physical and chemical properties can be found in Figures 3.1-3.4. The particle size distribution results of weight percentage of sand/silt/clay content correspond with WS80 (72/16/1), WS77 (70/22/8); WSAA (90/7/4) corresponds to sandy loam, sandy loam, and loamy sand, respectively. Between sites, the pH was similar between WS80 and WS77 (4.3±0.1). WSAA had an average pH of 5.26, which was 1 pH unit higher than WS80 and WS77 averages. The pH varied between ±0.1 pH unit between the depths of WS80 and WS77. WSAA varied more with depth (±0.5 pH unit). The organic matter content was higher in all top layers compared to that of the bulk and bottom layered soil, which was expected (Figure 3.1). Cation Exchange Capacity (CEC) was also higher in all top layers of WS80, WS77, and WSAA (10.6, 10.6, and 7.1 (meq/100 g)^2). Like pH and organic matter, the CEC was similar between WS80 and WS77, but varied slightly more between WSAA (Figure 3.2). Metals content was analyzed on bulk soils only, and the resulting trends were similar in all three sites except for WSAA (Figure 3.3). Alkaline earth metals showed similar trends between sites with a significantly higher concentration of calcium in each sample (Figure 3.4). The temperature-controlled experiments produced a higher pH at 200 ˚C (pH=4.1) and a lower pH at 500 ˚C (pH=5). The organic matter was lower in the high intensity 500 ˚C compared to all other soils (0.17%) (Table 3.2). Additionally, the CEC decreased from WS80 bulk soil of 8.5 meq/100 g to 4.7 meq/100 g in the high intensity burning (Table 3.3). Metals such as calcium and manganese decreased in the burning experiments compared to that of the unburned WS80 bulk soil. However, most alkaline earth metal compositions remained the same (Table 3.3).

Table 3.1. Burn information at each site collected from WS77, which has been burned for over 20+ years and WSAA, which had been burned weeks before sampling.

	Exp WS77	**Ash WSAA**
Date Burned	3/10/18	3/3/19
Date Sampled	3/20/19	3/20/19
Temperature (°C)	20.5	22.7
Relative Humidity (%)	32	27
Winds (mph)	2	1
100-hr Fuels (%)	14	17
Live Woody (%)	126	148
Critical Live Woody (%)	130%	130%
Fire Classification	Prescribed, mixed intensity	Prescribed, mixed intensity

*Live woody refers to the amount of moisture present in woody plants (live needles, twigs, etc.) that persist all year and can easily ignite

*Critical values include those if achieved putting forest at risk for large uncontrollable fire

*100-hr fuels refers to stick and/or branches that are 1-3 inches in diameter; used to determine what happened in last 24 hours.

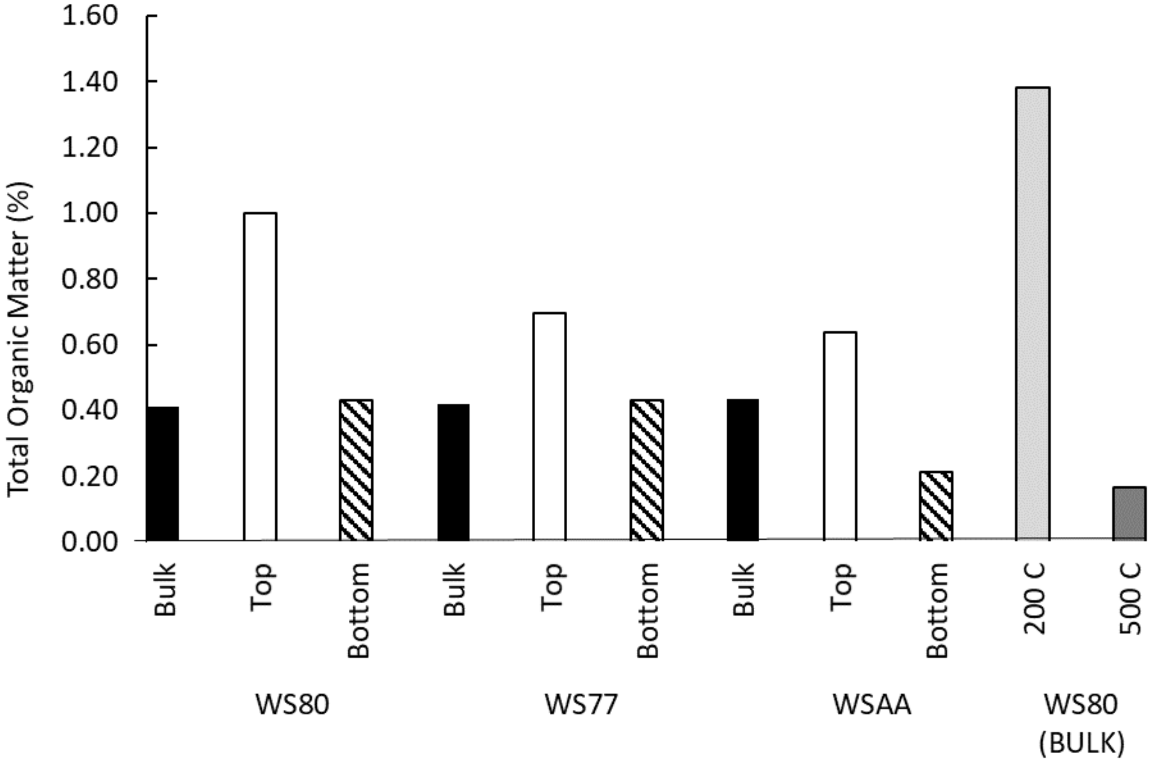


Figure 3.1. Organic matter percentages based on Loss on Ignition (LOI) at 500 ˚C for 6 hours.

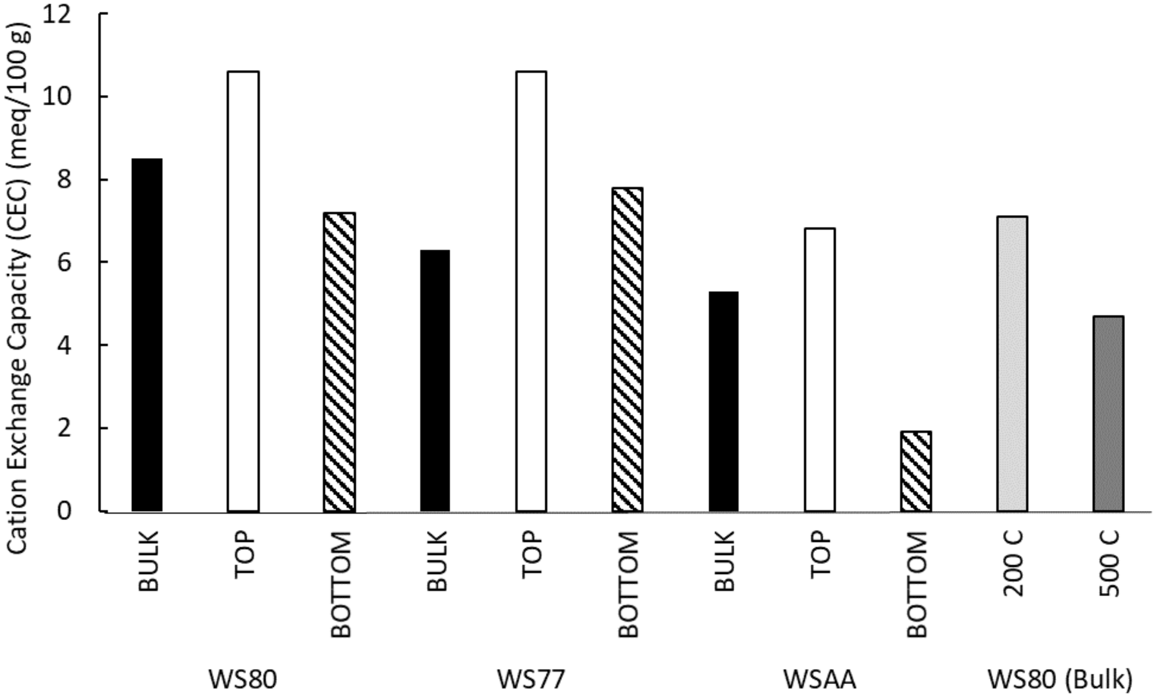


Figure 3.2. Cation Exchange Capacity (CEC) (meq/100 g soil) performed by Clemson University Agricultural Service Laboratory – Standard soil test.

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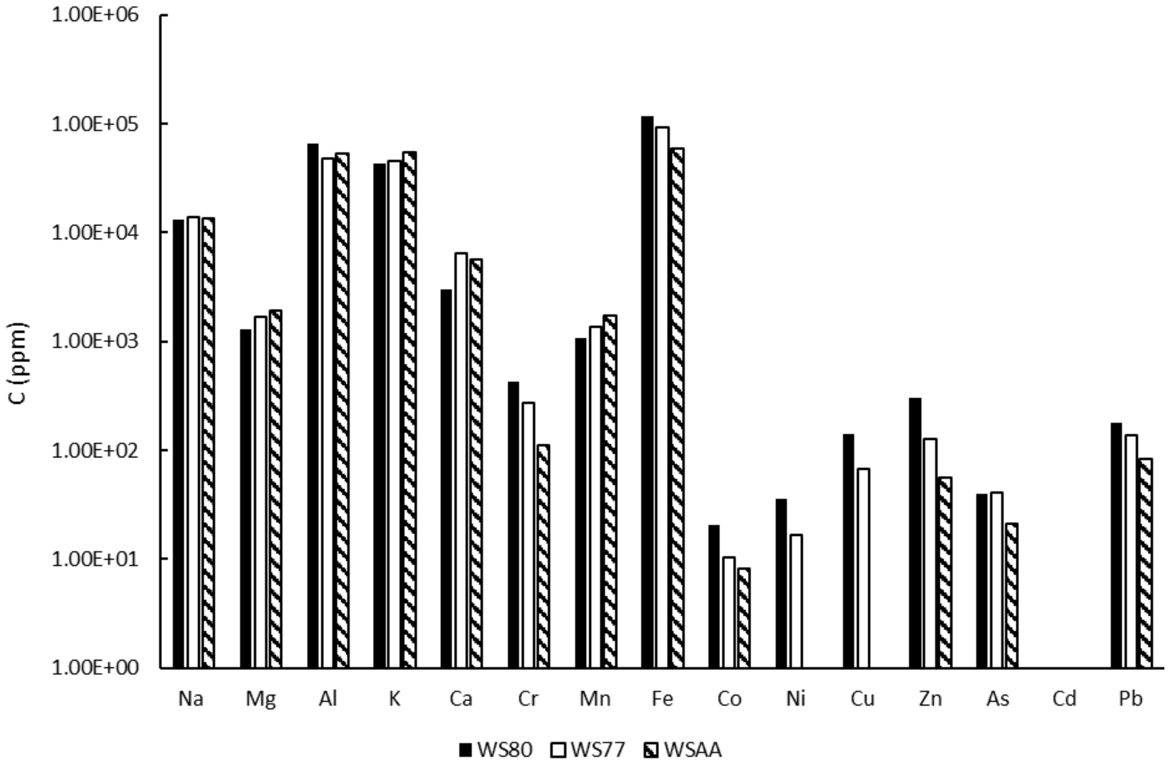


Figure 3.3. Metals analysis performed by the University of Georgia Soil Testing Lab using an ICP-MS.

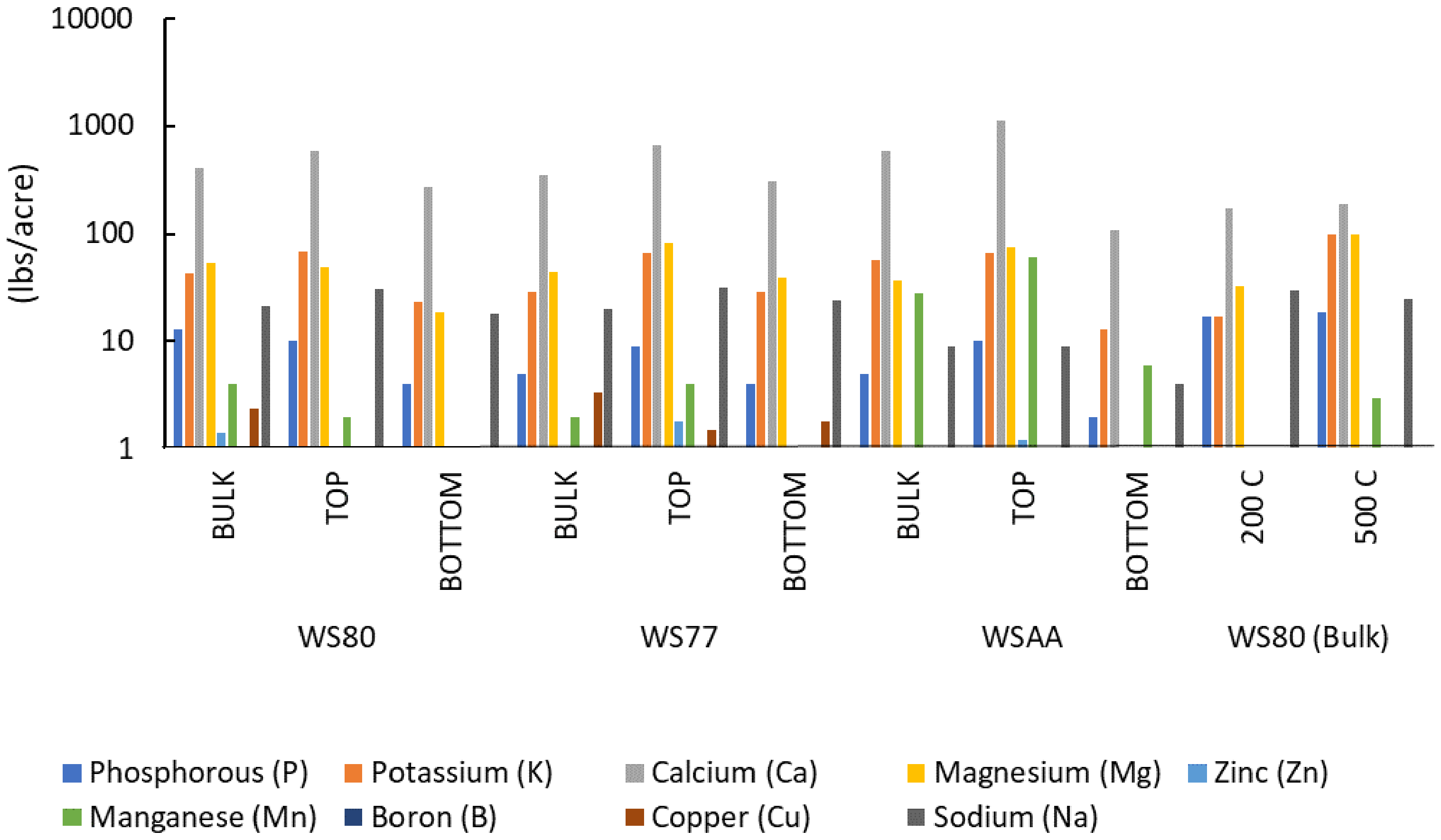


Figure 3.4. Alkaline Earth Metals composition in each sample performed by Clemson Agricultural lab – Standard Soil Tests.

2

Sorption of TCB and TNB

Overall data for all measured aqueous phase concentrations at the ten suspended solids concentrations can be found in Table 3.3. Sorption isotherms of TCB and TNB at low aqueous phase concentrations were fit to a linear sorption isotherm (Figures 3.5). K_D values were calculated using equation (2.5), and the sorption data agree with the linear K_D reasonably for most samples (R^2 in Table 3.4). The K_D values for TCB range between 89.9 – 487 L/kg (Table 3.4) with an average of 251 L/kg (Table 3.5). K_D values calculated for TNB concentrations range between 14.8 – 286 L/kg (Table 3.4) with an average of 102 (Table 3.5). Table 3.5 indicates significant difference between the sorption of TCB and the sorption of TNB for the K_D and all suspended solids concentrations used with corresponding aqueous phase measured concentrations (p-value=0.013). The percent differences were calculated for each sorbate in each soil sample (Table 3.6). The results show a range of 18% - 161% change between TCB and TNB using the linear K_D values calculated. The most significant change was seen between the WSAA Bulk soil (161% difference), whereas the least change was seen between the WSAA top layer (18.1%).

Table 3.2. C_e-(1-10) (mg/L) are corresponding aqueous equilibrium measured concentrations at each of the suspended solids concentrations used during experimentation. K_D (L/kg) are based on the low concentration linear fit. Values not listed were below minimum detection limit.

	Sites	Depth	K_D (L/kg)	Ce-1 (mg/L)	Ce-2 (mg/L)	Ce-3 (mg/L)	Ce-4 (mg/L)	Ce-5 (mg/L)	Ce-6 (mg/L)	Ce-7 (mg/L)	Ce-8 (mg/L)	Ce-9 (mg/L)	Ce-10 (mg/L)
TCB	**80**	**Bulk**	3.25E+02	1.24E-03	1.19E-03	1.11E-03	9.20E-04	6.38E-04	7.37E-04	6.46E-04	5.93E-04	4.96E-04	4.81E-04
	80	**Top**	3.48E+02	1.82E-03	1.73E-03	1.36E-03	1.04E-03	7.34E-04	5.06E-04	4.26E-04	3.17E-04	2.37E-04	2.46E-04
	80	**Bottom**	8.62E+01	2.05E-03	2.13E-03	2.16E-03	1.75E-03	1.36E-03	1.29E-03	1.11E-03	1.18E-03	7.53E-04	5.76E-04
	77	**Bulk**	2.22E+02	1.43E-03	1.41E-03	1.24E-03	1.09E-03	7.24E-04	5.43E-04	5.51E-04	3.48E-04	6.82E-05	
	77	**Top**	4.51E+02	1.64E-03	1.77E-03	1.28E-03	9.77E-04	5.17E-04	3.05E-04	3.35E-04	2.33E-04		1.18E-04
	77	**Bottom**	8.99E+01	2.08E-03	2.40E-03	2.33E-03	1.81E-03	1.59E-03	1.38E-03	1.36E-03	1.21E-03	9.88E-04	7.46E-04
	AA	**Bulk**	4.87E+02	1.31E-03	1.37E-03	1.29E-03	1.17E-03	1.09E-03	1.00E-03	8.41E-04	6.72E-04	5.85E-04	3.78E-04
	AA	**Top**	1.23E+02	2.29E-03	1.93E-03	1.52E-03	1.49E-03	8.72E-04	8.60E-04	8.94E-04	6.48E-04	4.20E-04	2.63E-04
	AA	**Bottom**	1.25E+02	1.86E-03	1.87E-03	1.95E-03	1.89E-03	1.79E-03	1.39E-03	1.57E-03	1.65E-03	1.41E-03	1.42E-03
	80	**Bulk (200 C)**		1.14E-03	1.23E-03	1.10E-03	8.00E-04	6.17E-04					
	80	**Bulk (500 C)**		1.10E-03	1.17E-03	1.29E-03	1.23E-03	1.19E-03					
TNB	**80**	**Bulk**	4.93E+01	1.13E-02	1.09E-02	1.03E-02	8.86E-03	6.92E-03	5.01E-03	2.88E-03	1.90E-03	4.71E-04	
	80	**Top**	1.74E+02	1.11E-02	1.11E-02	6.70E-03	3.89E-03	1.82E-03					
	80	**Bottom**	3.23E+01	1.36E-02	1.34E-02	1.39E-02	1.23E-02	8.65E-03	8.31E-03	5.05E-03	4.81E-03	4.35E-03	
	77	**Bulk**	1.10E+02	1.11E-02	1.08E-02	1.03E-02	6.78E-03	3.90E-03	1.96E-03	7.71E-04			
	77	**Top**	2.86E+02	1.34E-02	9.33E-03	4.67E-03	1.11E-03	8.07E-04					
	77	**Bottom**	1.48E+01	1.52E-02	1.43E-02	1.30E-02	1.01E-02	5.10E-03	2.81E-03	6.93E-04			
	AA	**Bulk**	5.20E+01	1.56E-02	1.33E-02	1.32E-02	1.12E-02	5.67E-03	5.64E-03	4.28E-03	2.97E-03	1.16E-03	
	AA	**Top**	1.47E+02	1.46E-02	1.27E-02	8.69E-03	6.02E-03	2.66E-03	8.97E-04				
	AA	**Bottom**	5.21E+01	1.38E-02	1.30E-02	1.51E-02	1.17E-02	1.00E-02	8.63E-03	9.70E-03	9.00E-03	5.80E-03	6.99E-03
	80	**Bulk (200 C)**		1.37E-02	9.44E-03	8.21E-03	7.18E-03	7.33E-03					
	80	**Bulk (500 C)**		1.76E-02	1.45E-02	1.21E-02	2.46E-03	1.60E-03					

Concentrations without corresponding values were below minimum detection limit

K_D values not listed were not able to be calculated

Table 3.3. Partition coefficient**,** $K_{D,}$ values approximated at low concentrations of suspended solids added using a linear regression (R^2).

			K_D (L/kg)	**R^2**
TCB	**WS80**	*Bulk*	325	0.91
	WS80	*Top*	348	0.94
	WS80	*Bottom*	86	0.77
	WS77	*Bulk*	222	0.78
	WS77	*Top*	451	0.94
	WS77	*Bottom*	90	0.87
	WSAA	*Bulk*	487	0.75
	WSAA	*Top*	123	0.82
	WSAA	*Bottom*	125	0.54
TNB	**WS80**	*Bulk*	49	0.96
	WS80	*Top*	174	0.79
	WS80	*Bottom*	32	0.56
	WS77	*Bulk*	110	0.98
	WS77	*Top*	286	0.85
	WS77	*Bottom*	15	0.50
	WSAA	*Bulk*	52	0.82
	WSAA	*Top*	147	0.86
	WSAA	*Bottom*	52	0.59

Values are based on the low-aqueous phase concentrations measured

0
1

Table 3.4. ANOVA Statistical Analysis for parameters sorbate, site, and depth for each linear K_D (L/kg) value and aqueous measured concentrations at equilibrium (mmol/L).

	Sorbate					**Sites**							**Depth**						
	Least Squares Mean				**p-value**	**Least Squares Mean**						**p-value**	**Least Squares Mean**						**p-value**
	TCB		**TNB**			**WS80**		**WS77**		**WSAA**			**Bulk**		**Top**		**Bottom**		
K_D (L/kg)	2.51E+02	^{A}	1.02E+02	^{B}	0.013 *	1.69E+02	^{AB}	1.96E+02	^{A}	1.64E+02	^{B}	0.865	2.08E+02	^{A}	2.55E+02	^{A}	6.68E+01	^{B}	0.027*
C_{aq}-1	1.69E-03	^{A}	1.38E-02	^{B}	0.000 *	7.49E-03	^{A}	7.47E-03	^{A}	8.25E-03	^{A}	0.606	7.65E-03	^{A}	7.47E-03	^{A}	8.10E-03	^{A}	0.776
C_{aq}-2	1.75E-03	^{A}	1.22E-02	^{B}	0.000 *	6.82E-03	^{A}	6.68E-03	^{A}	7.37E-03	^{A}	0.610	6.59E-03	^{A}	6.43E-03	^{B}	7.85E-03	^{A}	0.124
C_{aq}-3	1.56E-03	^{A}	1.06E-02	^{B}	0.000 *	5.80E-03	^{A}	5.47E-03	^{A}	6.97E-03	^{A}	0.328	6.12E-03	^{AB}	4.04E-03	^{B}	8.07E-03	^{A}	0.004 *
C_{aq}-4	1.37E-03	^{A}	7.49E-03	^{B}	0.000 *	4.09E-03	^{A}	3.64E-03	^{A}	5.57E-03	^{A}	0.315	4.30E-03	^{AB}	2.42E-03	^{B}	6.57E-03	^{A}	0.019 *
C_{aq}-5	9.95E-04	^{A}	4.93E-03	^{B}	0.000 *	3.11E-03	^{A}	2.11E-03	^{A}	3.68E-03	^{A}	0.324	2.91E-03	^{AB}	1.23E-03	^{B}	4.75E-03	^{A}	0.013 *
C_{aq}-6	8.92E-04	^{A}	4.34E-03	^{B}	0.004 *	3.27E-03	^{A}	1.50E-03	^{A}	3.07E-03	^{A}	0.269	2.48E-03	^{A}	1.39E-03	^{A}	3.97E-03	^{A}	0.1307
C_{aq}-7	8.60E-04	^{A}	3.74E-03	^{B}	0.025 *	2.25E-03	^{B}	9.68E-04	^{B}	3.68E-03	^{A}	0.123	1.66E-03	^{A}	1.99E-03	^{A}	3.25E-03	^{A}	0.3586
C_{aq}-8	7.62E-04	^{A}	4.41E-03	^{B}	0.007 *	2.05E-03	^{A}	2.42E-03	^{A}	3.28E-03	^{A}	0.418	1.63E-03	^{A}	2.22E-03	^{A}	3.90E-03	^{A}	0.0916
C_{aq}-9	5.55E-04	^{A}	2.69E-03	^{B}	0.043 *	1.41E-03	^{A}	1.44E-03	^{A}	2.02E-03	^{A}	0.703	7.32E-04	^{B}	1.30E-03	^{AB}	2.84E-03	^{A}	0.0765
C_{aq}-10	4.96E-04	^{A}	6.38E-03	^{B}	0.001 *	3.38E-03	^{A}	3.31E-03	^{A}	3.63E-03	^{A}	0.524	3.31E-03	^{A}	3.15E-03	^{A}	3.86E-03	^{A}	0.1278

Levels not connected by the same letter are significantly different

* Indicates p-value of less than 0.05 and therefore is statistically different

2

Table 3.5. Percent differences of K_D (L/kg) values based on low-concentration linear range values found in Table 3.3.

		WS80	**WS77**	**Percent Difference**
TCB	*Bulk*	325	222	37%
	Top	348	451	26%
	Bottom	86	90	4%
TNB	*Bulk*	49	110	76%
	Top	174	286	49%
	Bottom	32	15	74%

		Top	**Bottom**	**Percent Difference**
TCB	*WS80*	348	86	121%
	WS77	451	90	134%
	WSAA	123	125	2%
TNB	*WS80*	174	32	137%
	WS77	286	15	180%
	WSAA	147	52	95%

		TCB	**TNB**	**Percent Difference**
WS80	*Bulk*	325	49	147%
	Top	348	174	67%
	Bottom	86	32	91%
WS77	*Bulk*	222	110	68%
	Top	451	286	45%
	Bottom	90	15	143%
WSAA	*Bulk*	487	52	161%
	Top	123	147	18%
	Bottom	125	52	83%

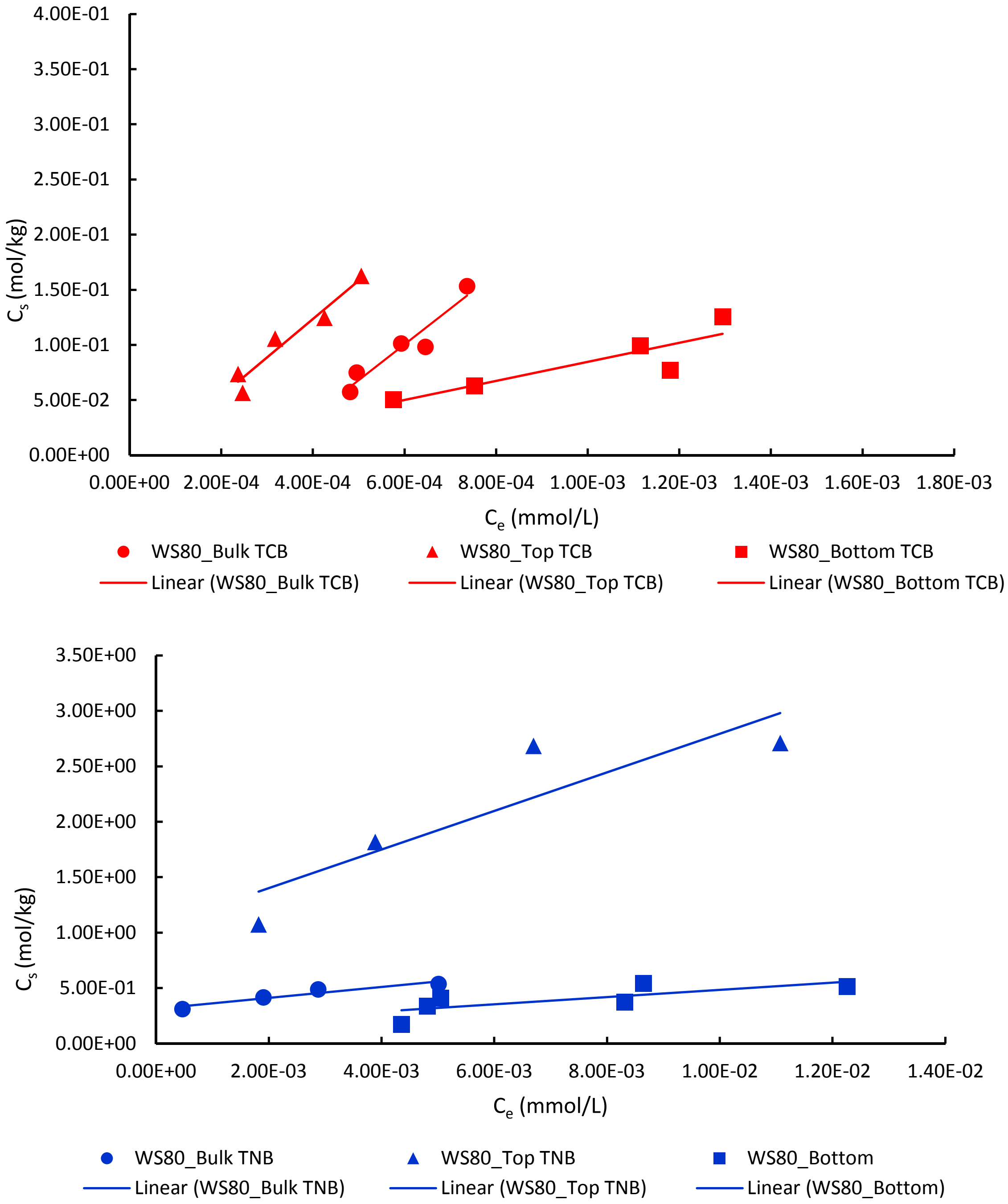


Figure 3.5. WS80 control (unburned) soil isotherms depicting Ce vs. Cs for the TCB (red) and TNB (blue). The slope of the linear regression lines are the fitted K_D values found in Table 3.3

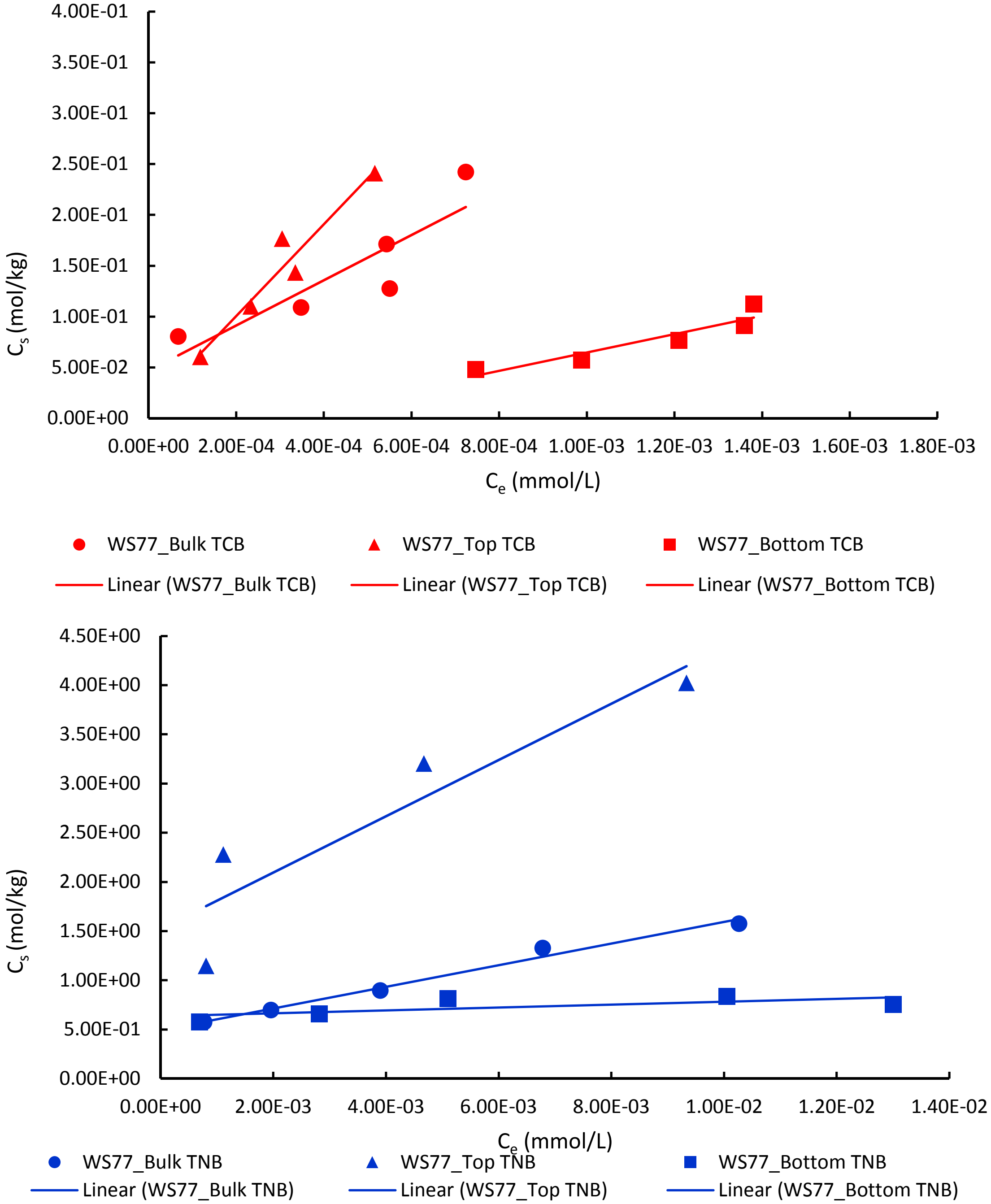


Figure 3.6. WS77 experimental site burned for 20+ years soil isotherms depicting Ce vs. Cs for the TCB (red) and TNB (blue). The slope of the linear regression lines are the fitted K_D values found in Table 3.3.

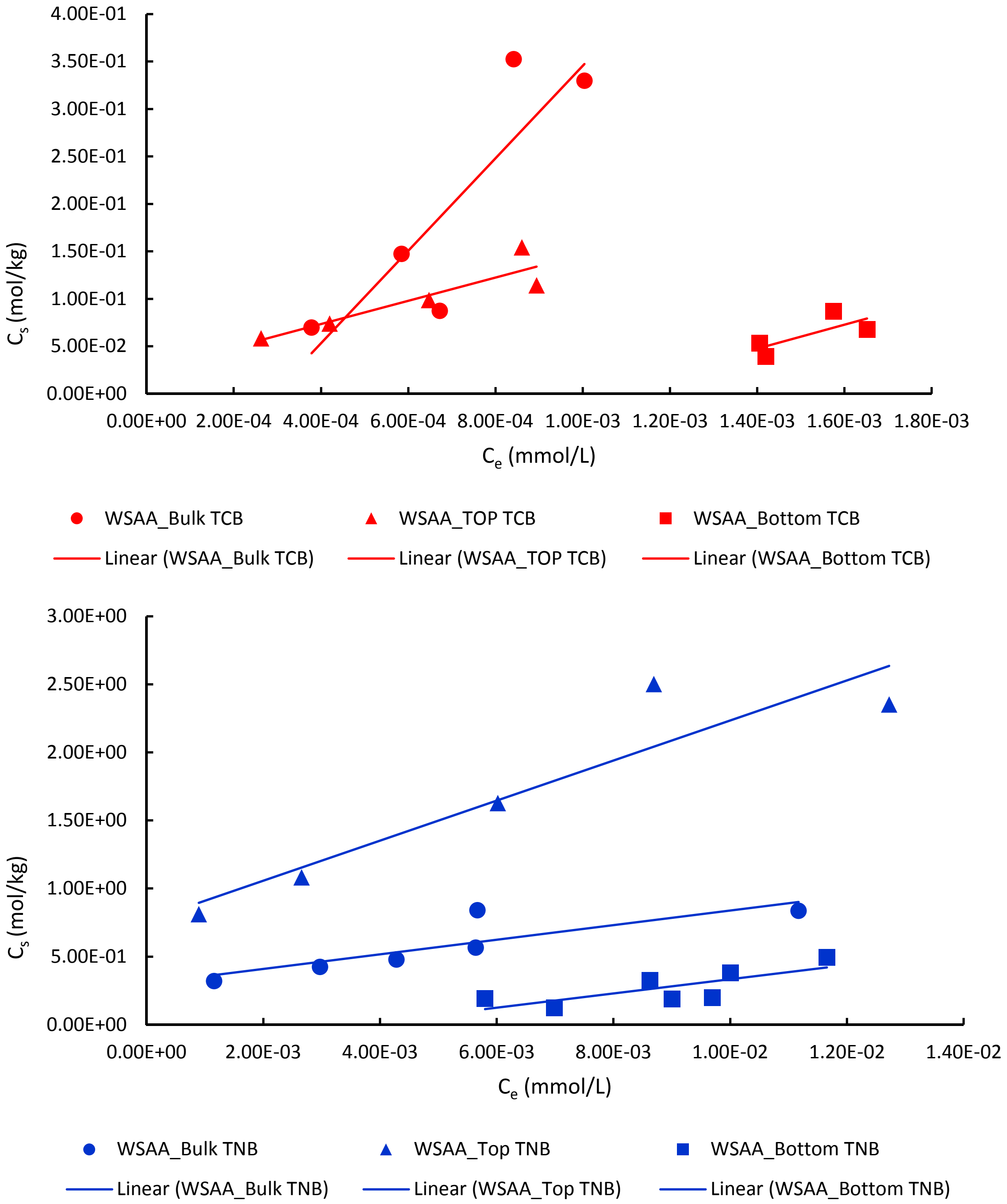


Figure 3.7. WSAA experimental msot site most recetnly burned soil isotherms depicting Ce vs. Cs for the TCB (red) and TNB (blue). The slope of the linear regression lines are the fitted K_D values found in Table 3.3.

Site effects on Sorption

Figure 3.5 indicates the linear sorption trend at low aqueous concentrations of TCB and TNB at WS80, WS77, and WSAA. K_D values can be found in Table 3.4. with resulting R^2 values for the low concentration linear isotherm fit. Overall numerical data used for statistical analyses can be found in Table 3.3. Figure 3.5 indicates the linear sorption activity of bulk, top, and bottom soil at WS80, where no burning activity took place. Figure 3.6 indicates sorption activity at low concentration of isotherm resulting from data corresponding to WS77, experimental site subjected to 20+ years of burning. WS77 was shown to be more reactive with a higher K_D value and higher percent sorbed than that of WS80 for the top and bottom layers (Table 3.6). WS77 exhibited top and bottom layer K_D values of 451 and 89.9 (L/kg), respectively, whereas WS80 exhibited K_D values of 348 and 86.2 (L/kg) (Table 3.4). However, when comparing the aqueous phase equilibrium concentrations measured at each suspended solid concentration, significant difference was found (Table 3.7). The results indicate percent differences due to sites, which indicate an alteration in sorption properties following a fire.

Figure 3.7 denotes the same information for WSAA, experimental site burned days prior to sampling. The slope of these lines is the K_D values listed in Table 3.4 with resulting R^2 values. WSAA varied from WS80 and WS77 overall when comparing linear K_D values (L/kg) (student t-test, Table 3.5). WSAA also exhibited less change between the top and bottom layer (1.94% , TCB and 95.4%, TNB) compared to the changes experienced in WS80 (121%, TCB and 137%, TNB) and WS77 (133%, TCB and 180%, TNB) top and bottom layers, respectively (Table 3.6).

Table 3.6. ANOVA statistical analyses for the comparison of WS80 and WS77 based on site and depth for both sorbates TCB and TNB.

		Sites					**Depth**						
		Least Squares Mean					**Least Squares Mean**						
		WS80		**WS77**		**p-value**	**Bulk**		**Top**		**Bottom**		**p-value**
TCB	**K_D (L/kg)**	2.53E+02	A	2.55E+02	A	0.98	2.74E+02	A	4.00E+02	A	8.81E+01	A	0.10
	C_{aq}-1 (mmol/L)	1.70E-03	A	1.71E-03	A	0.95	1.33E-03	B	1.73E-03	AB	2.06E-03	A	0.06
	C_{aq}-2 (mmol/L)	1.69E-03	A	1.86E-03	A	0.14	1.30E-03	C	1.75E-03	B	2.27E-03	A	0.02*
	C_{aq}-3 (mmol/L)	1.54E-03	A	1.62E-03	A	0.43	1.17E-03	B	1.32E-03	B	2.25E-03	A	0.01*
	C_{aq}-4 (mmol/L)	1.24E-03	A	1.29E-03	A	0.52	1.01E-03	B	1.01E-03	B	1.78E-03	A	0.02*
	C_{aq}-5 (mmol/L)	9.12E-04	A	9.42E-04	A	0.84	6.81E-04	B	6.25E-04	B	1.47E-03	A	0.05*
	C_{aq}-6 (mmol/L)	8.46E-04	A	7.43E-04	A	0.39	6.40E-04	B	4.05E-04	B	1.34E-03	A	0.03*
	C_{aq}-7 (mmol/L)	7.29E-04	A	7.48E-04	A	0.88	5.98E-04	B	3.80E-04	B	1.24E-03	A	0.04*
	C_{aq}-8 (mmol/L)	6.97E-04	A	5.97E-04	A	0.34	4.71E-04	B	2.75E-04	B	1.20E-03	A	0.02*
	C_{aq}-9 (mmol/L)	4.95E-04	A	3.99E-04	A	0.82	2.82E-04	A	1.88E-04	A	8.70E-04	A	0.44
	C_{aq}-10 (mmol/L)	4.35E-04	A	4.56E-04	A	0.91	4.92E-04	A	1.82E-04	A	6.61E-04	A	0.30
TNB	**K_D (L/kg)**	8.52E+01	A	1.37E+02	A	0.30	7.96E+01	B	2.30E+02	AB	2.36E+01	A	0.09
	C_{aq}-1 (mmol/L)	1.20E-02	A	1.32E-02	A	0.24	1.12E-02	A	1.22E-02	A	1.44E-02	A	0.13
	C_{aq}-2 (mmol/L)	1.18E-02	A	1.15E-02	A	0.75	1.09E-02	A	1.02E-02	A	1.38E-02	A	0.11
	C_{aq}-3 (mmol/L)	1.03E-02	A	9.32E-03	A	0.25	1.03E-02	C	5.69E-03	B	1.34E-02	A	0.02*
	C_{aq}-4 (mmol/L)	8.33E-03	A	5.98E-03	B	0.01	7.82E-03	C	2.50E-03	B	1.12E-02	A	0.00*
	C_{aq}-5 (mmol/L)	5.80E-03	A	3.27E-03	A	0.08	5.41E-03	A	1.31E-03	B	6.87E-03	A	0.05*
	C_{aq}-6 (mmol/L)	4.44E-03	A	1.59E-03	A	0.21	3.48E-03	A	1.63E-19	A	5.56E-03	A	0.19
	C_{aq}-7 (mmol/L)	2.64E-03	A	4.88E-04	A	0.23	1.82E-03	A	0.00E+00	A	2.87E-03	A	0.36
	C_{aq}-8 (mmol/L)	2.24E-03	A	0.00E+00	A	0.25	9.52E-04	A	5.42E-20	A	2.40E-03	A	0.50
	C_{aq}-9 (mmol/L)	1.61E-03	A	1.08E-19	A	0.36	2.35E-04	A	0.00E+00	A	2.18E-03	A	0.50
	C_{aq}-10 (mmol/L)	0.00E+00	A	0.00E+00	A		0.00E+00	A	0.00E+00	A	0.00E+00	A	

Levels not connected by the same letter are significantly different

* Indicates p-value of less than 0.05 and therefore is statistically different

3

Depth Effects on Sorption

In Figure 3.5-3.7, sites are graphed at each depth (bulk, top, and bottom layers). The bulk soil was comprised of 0-25 cm sampled depth. The top layer consisted of 0-2.54 cm, and the bottom layer was below 20 cm in depth. The resulting graphs indicate differences in the top and bottom layers of all soil samples at each site when measuring TCB as the sorbate (WS80, WS77, and WSAA). The most change was experienced in the WS77 soil, where the percent difference was 134%. The least change was observed in WSAA top and bottom layers at 1.94% for TCB. For TNB, the most change was experienced in WS77 as well with a percent difference of 180%, and the least at WSAA again with a percent difference of 95.5% (Table 3.6). In all soil samples and sites, the top layer sorbed more sorbate (TCB/TNB) than the bottom layers with the exception of WSAA TCB top (123 L/kg) and bottom (125 L/kg), where the bottom K_D value was slightly higher than that of the top layer (Table 3.6). When using all the K_D value and concentration data calculated and measured (Table 3.3), a significant difference was found between the top, bottom, and bulk K_D values as well as the suspended solids concentrations 3.26E-03, 6.36E-03, and 1.27E-02 kg/L (Table 3.5). The aqueous phase equilibrium concentrations were less in the top layer than that in the bottom layer for WS80, WS77, WSAA TCB and TNB, which indicates less sorbate in the aqueous phase of the top layer and therefore more sorbate in the solid phase of the top layer compared to that of the bottom layer (Table 3.3).

Temperature Effects on Sorption

Figure 3.6 shows the linear sorption trends of TCB and TNB at WS80 Bulk and the soil burned under low-intensity conditions (200˚ C) and high-intensity (500˚ C). The trends for TCB (Figure 3.8) are very similar with the high intensity having slightly lower sorption activity. The trends for TNB, indicate slightly more variation between the top and bulk layered soil. However, trends are difficult to indicate at the suspended solids concentration for these three samples due to the multi-phase sorption occurring.

Statistical analyses on the concentrations and Kd values are provided in Table 3.8. Differences in TCB and TNB were observed at the lowest possible suspended solids concentrations, but as the suspended solids increased, the differences between aqueous phase measured concentrations diminished generating p-values less than 0.05. There were no significant differences observed for the control, high-intensity, and low-intensity soils. However, TNB equilibrium aqueous phase measurements were higher than that of the TCB equilibrium aqueous phase measurements, which indicates a higher sorption concentration for TCB compared to that of TNB when going from 200 ˚C to 500 ˚C (Table 3.3).

Table 3.7. Statistical analyses on values of KD (L/kg) and aqueous phase concentrations at suspended solids concentrations (1-10) for site WS80 Bulk soil at control temperature, low-intensity (200 C), and high-intensity (500 C).

	Sorbate					**Temperature**						
	Least Squares Mean				**p-value**	**Least Squares Mean**						**p-value**
	TCB		**TNB**			**Control**		**200 C**		**500 C**		
C_{aq}-1 (mmol/L)	1.16E-03	A	1.42E-02	B	0.020 *	6.26E-03	A	7.42E-03	A	9.35E-03	A	0.521694
C_{aq}-2 (mmol/L)	1.20E-03	A	1.16E-02	B	0.020 *	6.05E-03	A	5.34E-03	A	7.84E-03	A	0.510902
C_{aq}-3 (mmol/L)	1.17E-03	A	1.02E-02	B	0.013 *	5.68E-03	A	4.66E-03	A	6.70E-03	A	0.45213
C_{aq}-4 (mmol/L)	9.83E-04	A	6.17E-03	A	0.124	4.89E-03	A	3.99E-03	A	1.85E-03	A	0.557504
C_{aq}-5 (mmol/L)	8.15E-04	A	5.28E-03	A	0.159	3.78E-03	A	3.97E-03	A	1.40E-03	A	0.60063

Levels (A,B) not connected by the same letter are significantly different

* Indicates p-value of less than 0.05 and therefore is statistically different

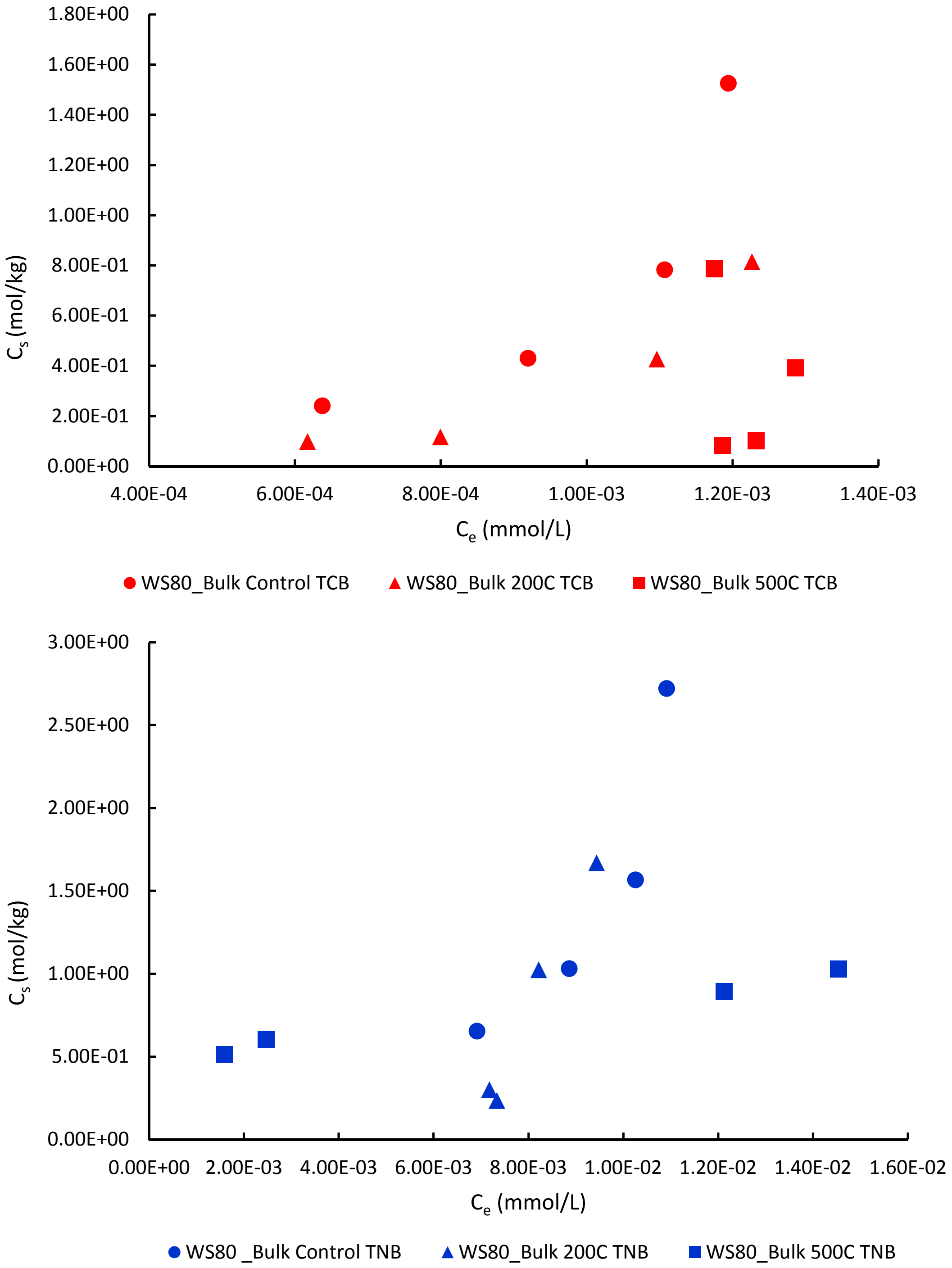


Figure 3.8. WS80 bulk soil temperature-controlled experiment isotherms. Control WS80 unburned soil (circles), low intensity 200 ˚C (triangles), and high intensity 500 ˚C (squares) for TCB (red) and TNB (blue).

DISCUSSION

Physical and Chemical Properties of Burned Soil

The soil physical and chemical properties were similar between WS80 and WS77. WS80 and WS77 had similar properties, which made them comparable throughout the study when comparing sorption capabilities. WSAA had a slightly higher sand content and pH value, which altered other properties, which made drawing conclusions in the data challenging. The differences in the metal composition and cations present in the soils are not assumed to be due to any burning activity. Instead these differences are assumed to be due to natural differences due to their environmental locations within the Francis Marion National Forest and Santee Experimental Forest.

The trends in organic matter, pH, and CEC were expected and similar to other studies found (Alcañiz et al., 2018; Sherman et al., 2005) when comparing the top and bottom layers of soil. K_D values were higher for top layers than bottom layers, which supports more sorption to the solid phase. This is due to the nature and chemistry of organic matter. Natural organic matter is slightly polar because of the functional groups it possesses that are able to interact and bind with water molecules, but the actual structure of organic matter is not always consistent within complex heterogeneous mixtures like soil (Schwarzenbach et al., 2003). Further information on the specific characteristics of the organic matter present within each soil would be needed to fully understand the nature of the sorption behavior occurring. Studies also correlate with the change in CEC and pH at top and bottom layers. The CEC was also higher for all top layers, which is an indication for surface hydrophobicity. The CEC is a property of the surface tension and surface area of the soil, which in turn, can alter the overall charge on the soil. When a soil has a net positive charge, negatively charged particles or pollutants may want to bind to the soil, which may suggest an increase in contaminant transport. However, the findings of this study do not suggest such variations to be of concern. The pH was slightly increased at the WSAA sight, which could be due to the increase of ash content and BC due to the prescribed fire since ash has a naturally high pH (Heydari et al., 2017). It could also be due to the higher sand content initially present in the soil, which might alter the chemical composition and therefore increase the pH as well. In previous studies where ash content was present, they reported an increase in pH and increase in CEC following a fire (Alcañiz et al., 2018).

The laboratory-controlled temperature experiments produced a much lower organic matter when the soil was burned above 500˚C (high intensity) compared to all other soil samples. The soil burned at a low intensity of 200 ˚C. These results were expected due to the loss of organic matter occurring above 500 ˚C. The pH was also increased following the high intensity burning, which is supported by previous literature and the theory that the hydroxyl groups are driven off during burning or heating, which may raise the pH of the soil (Sherman et al., 2005).

Sorption of Nonpolar and Polar Compounds

The nonpolar TCB sorbed stronger in most cases than the polar TNB, which was expected due to their octanol-water partition coefficients and previous literature (Liu et al., 2008; Shi et al., 2010). The K_D values for TCB in previous studies showed greater affinity to the soil than TNB (Liu et al., 2008; Lv et al., 2012), which is consistent with these findings. Previous studies indicate K_D values estimated using Freundlich parameters and untreated soil at 22 ($mmol^{1-n}L^{n}kg^{-1}$) for TCB and 3.0 ($mmol^{1-n}L^{n}kg^{-1}$) for TNB (Shi et al., 2010). When comparing sorption to maize burn residue, previous studies indicated higher K_D values as well with 16,000 ($mmol^{1-n}L^{n}kg^{-1}$) and 820 ($mmol^{1-n}L^{n}kg^{-1}$) for TCB and TNB, respectively (Qiu et al., 2008). Previous studies were not in agreement on isotherm derivation and K_D values generated. Interestingly, the lowest percent change was experienced in the WSAA top layer soil between TCB and TNB K_D values (Table 3.6.). The TNB sorbed much more strongly to the top layer of WSAA than it did to the bottom layer, which may be due to the more reactive BC material present. Black carbon (BC) is a potent sorbent and it involves the residues from incomplete combustion (Schwarzenbach et al., 2003). BC also has a high affinity for organic pollutants due to the hypothesized aromatic structure (Schwarzenbach et al., 2003). Of the total organic matter (TOM) calculated, it is natural to find 1 to 10% of the fraction of organic carbon within the TOM to be BC (Schwarzenbach et al., 2003). WSAA would have had a higher fraction of BC within the TOM even though the calculated TOM values based on LOI were relatively low. That means the percentage of BC within the TOM was higher for WSAA than the other soils present, which would indicate different sorption capabilities of WSAA and support the findings presented here. Because of the presence of black carbon and other reactive sorptive materials that are produced following a fire, the potential for contaminant transport of organics could increase. Previous studies suggest BC plays a role in the sorption of nonpolar compounds (TCB). However, previous studies indicate the sorption behavior of TNB is not due to the presence of BC but is more influenced by the clay particles present (Shi et al., 2010).

The sorption behavior of the temperature-controlled experiments was difficult to determine due to the nature of the isotherms generated at the higher concentrations. However, the unburned bulk WS80 soil sorbed slightly more in TCB and TNB according to the trends in Figure 3.6. The high intensity 500 ˚C sorbed less in the case of TNB and much less in the case of TCB. The theory presented in (Shi et al., 2010) supports this behavior in that the presence of organic matter is playing a stronger role in the sorption of TCB than that of TNB.

Sorption Capabilities and Hydrophobicity

The method employed to determine the level of hydrophobicity and quantify the amount sorbed produced notable differences in the sorption of polar and nonpolar compounds. Previous literature is in agreement on the sorption of nonpolar is dominanted by hydrophobic partitioning (Sun et al., 2008). When comparing the sorption capabilities of the soil to TCB versus TNB, the results were as expected with TNB sorbing less to the soil. However, when comparing the effects of the burning on the level of hydrophobicity, the burned site, WS77, had more sorption in both TCB (increase of 30% sorbed, Table 3.6) and TNB (increase of 64% sorbed, Table 3.6). Therefore, it is difficult to draw conclusions on the level of hydrophobicity of the burned site compared to that of the non-burned site. Burned site WS77 was more effective at sorbing both TCB and TNB. The WSAA soil with an ash presence did sorb more to the top layer than that of the bottom layer for both TCB and TNB. In addition, the bulk soil was more influenced by the nonpolar compound TCB compared to that of TNB, where the sorption of the bulk soil was more like bottom layers, where ash and BC may not be present. This finding is consistent with previous studies on BC and pyrogenic carbon (Liu et al., 2008; Lv et al., 2012). The presence of BC is shown to more heavily influence nonpolar sorbates due to the polarity of the compounds and aromatic ring structures present, whereas the influence of TNB sorption has been hypothesized to be due more the specific functional groups and polarity of the soil organic matter and humic acid structures present instead (Shi et al., 2010).

Multiphase Sorption

The complete data sets for the sorption isotherms of each site and sorbate can be found in the appendices. Two trends were exhibited in the isotherm plots of the soil samples. The lower concentrations exhibited a traditional linear isotherm. However, as the concentration increased, the isotherm trend indicated multiphase sorption occurring. The upper data points were omitted in calculation of K_D values due to the indication for precipitation occurring. Upper solubility limits for each compound in pure water are provided in Table 2.1 (Schwarzenbach et al., 2003), and measured concentrations were an order of magnitude below solubility limits. However, the background solution was NaCl at 10 mmol, which would increase the ionic strength of the solution, which was performed to simulate the aqueous phase materials more accurately in the subsurface. The ionic strength increases the solubility of a compound (Schwarzenbach et al., 2003), which does not support why the precipitation could be occurring. However, by altering the suspended solids concentration or soil:solution ratios, the ionic strength can also be affected, which could be the cause of the multi-phase sorption (Roy et al., 1991). Table 4.1 provides conditional solubilities for TCB and TNB for the experimental conditions used in this study (0.1% methanol, 99.9% 10 mM NaCl), which were found by calculating the average of the upper concentration data points. The solubility values listed may need to be taken into consideration in future studies. Another factor to consider, is the sorption to the container. The kinetics of the sorption would most likely indicate the soil is a stronger sorbent than that of the glass container. In calculations, the amount sorbed was assumed constant due to an inability to determine the partitioning of the two sorbents.

Table 4.1. Conditional solubilities of TCB and TNB given experimental conditions of 99% NaCl and 0.1% Methanol cosolvents at pH of 5.5

		TCB S_w (mmol/L)	TNB S_w (mmol/L)
WS80	**Bulk**	1.12E-03	1.03E-02
	Top	1.49E-03	8.18E-03
	Bottom	2.02E-03	1.33E-02
WS77	**Bulk**	1.29E-03	9.74E-03
	Top	1.42E-03	7.12E-03
	Bottom	2.15E-03	1.31E-02
WSAA	**Bulk**	1.28E-03	1.33E-02
	Top	1.81E-03	1.05E-02
	Bottom	1.89E-03	1.27E-02

CONCLUSIONS

The results of this study indicate changes in burned forest soils compared to that of unburned soils. The following conclusions were made based on the data generated for this research.

- Long term prescribed burning has an impact on soil physical and chemical properties.
- The sorption capability of top layer soil from the prescribed burned watershed WS77 were increased for polar compounds and non-polar compounds compared to non-burned soil from watershed WS80 (increase of 34% for TCB and 64% for TNB).
- All top layer soils behaved differently than bottom layer soils in that they sorbed each sorbate more strongly due to the increase in soil organic matter on all top layers compared to that of bottom layers
- Nonpolar, TCB, and polar, TNB, exhibited notable differences in sorption behavior due to their polarity and affinity to the sorbents used.
- Method demonstrate the ability to use this method to draw conclusions on the hydrophobic nature of the soil.

Conclusions of this research include the observations of sorption capacities of unburned and burned soils varied on the top layers due to the higher soil organic matter content on top layers. In addition, the burned site, WS77, was more reactive for both polar and nonpolar compounds compared to that of the unburned WS80. The ash presence of WSAA produced inconsistent results compared to WS80 and WS77 that may give rise to a further investigation of how ash and BC play a role in the sorption capabilities of polar and nonpolar compounds on burned forest soils.

Future work is needed to produce a more comprehensive review of the sorption capabilities of burned forest soils. The soil organic matter played a dominant role in the sorption capacity of the soil due to the reactive nature and chemical composition including many functional groups present. Organic matter speciation is needed to fully understand the mechanisms responsible for the sorption interactions occurring between the top layers with the highest sorption capabilities. Previous studies have differentiated total organic matter from dissolved organic matter (DOM) using extraction methods (Wang et al., 2016). DOM would give insights on the effects that can be seen on water quality, which have been proven to be enhanced following a wildfire (Hobley et al., 2017; Wang et al., 2016). Black carbon contents are able to be quantified, and a more specific comparison can be made between black carbon content and sorption capacity (Qiu et al., 2008).

APPENDICES

APPENDIX A.1: GC RESPONSE FACTORS AND STANDARD CURVES

Table A.1. TCB response factor and retention time on GC/ECD.

Compound	GC RT (min)	RF (mmol/L/peak area unit)	R^2
1,3,5 trichlorobenzene	5.8	6E-08	0.9992

*Based on 158 mL background solution volume in 160 mL serum bottle

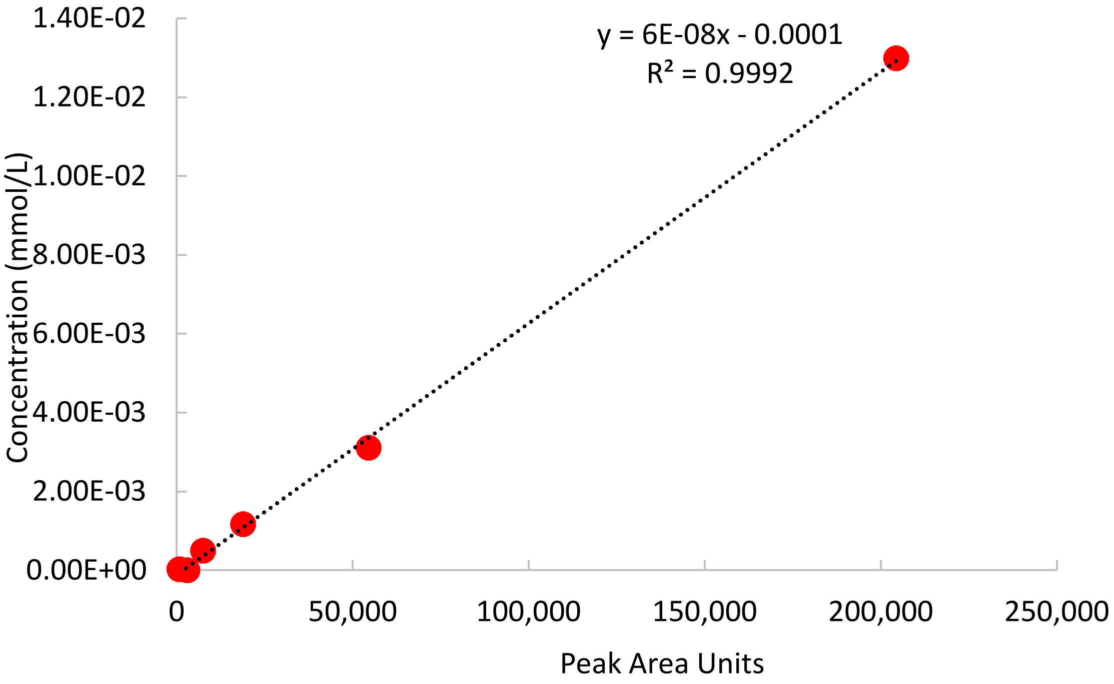


Figure A.1. TCB Calibration curve.

APPENDIX A.2: TCB STANDARD ADDITION ANALYSIS

Table A.2. GC Standard Addition Analysis for Bulk Soil Samples.

Sample	GC Vial		Area (Peak Area Units)	TCB in the sample (mmol/L)	Std. Recovery
WS80 Bulk	A	1 mmol/L std + sample	18288.7	1.10E-03	119.7%
	B	Sample	15328.7	9.20E-04	
	C	1 mmol/L std + NaCl	8872.9	5.32E-04	
WS77 Bulk	A	1 mmol/L std + sample	24452.1	1.47E-03	113.80%
	B	Sample	21685	1.30E-03	
	C	1 mmol/L std + NaCl	11962	7.18E-04	
WSAA Bulk	A	1 mmol/L std + sample	27162.4	1.63E-03	112.30%
	B	Sample	27449.7	1.65E-03	
	C	1 mmol/L std + NaCl	11962	7.18E-04	

*Standard recovery of sorbate= ((B-0.5*A)/C)*100; where A=mmol/L of sorbate in experimental sample; B=mmol/L of sorbate with 50% of experimental sample + 50% of 1 mmol/L standard, C=mmol/L of sorbate with 50% of DDI + 50% of 1000 mmol/L standard

APPENDIX B.1: HPLC RESPONSE FACTORS AND STANDARD CURVES

Table B.1. TNB response factor and retention time on HPLC/UV.

Compound	GC RT (min)	RF (mmol/L/peak area unit)	R^2
1,3,5 trinitrobenzene	12.1	3E-05	0.995

*Based on 158 mL background solution volume in 160 mL serum bottle

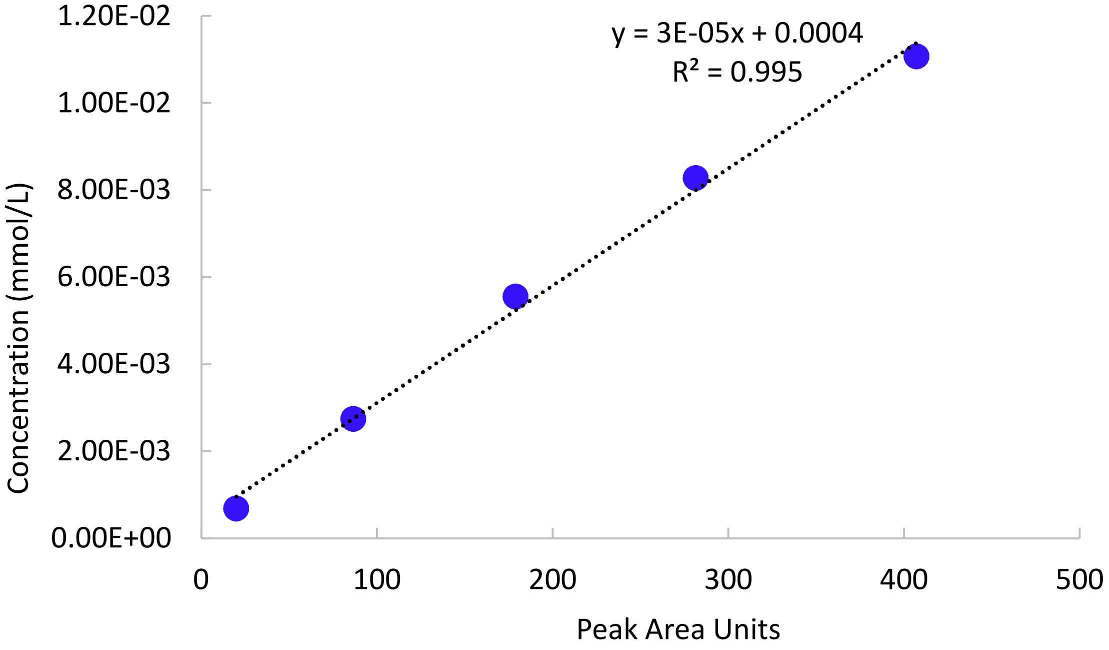


Figure B.1. TNB Calibration Curve.

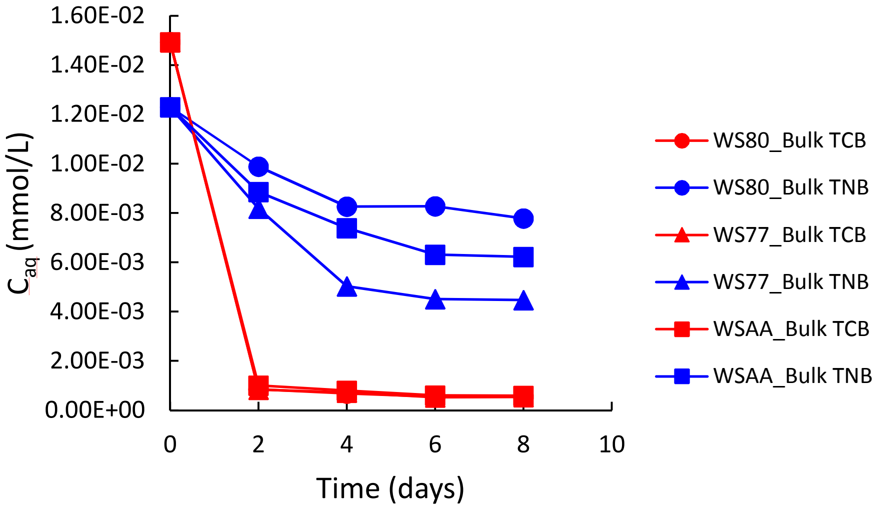
APPENDIX B.2: TNB STANDARD ADDITION ANALYSIS

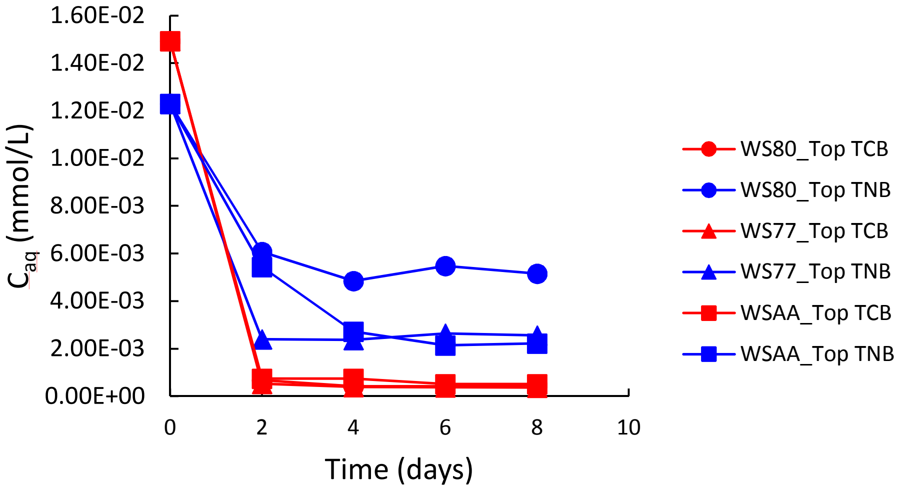
Table B.2. HPLC Standard Addition Analysis.

Sample	GC Vial		Area (Peak Area Units)	TNB in the sample (mmol/L)	Std. Recovery
WS80 Bulk	A	1 mmol/L std + sample	114.3	3.43E-03	114.9%
	B	Sample	56.2	1.69E-03	
	C	1 mmol/L std + NaCl	75	2.25E-03	
WS77 Bulk	A	1 mmol/L std + sample	126.1	3.78E-03	116.20%
	B	Sample	86.3	2.59E-03	
	C	1 mmol/L std + NaCl	71.4	2.14E-03	
WSAA Bulk	A	1 mmol/L std + sample	124.6	3.74E-03	82.30%
	B	Sample	131.77	3.95E-03	
	C	1 mmol/L std + NaCl	71.4	2.14E-03	

*Standard recovery of sorbate= ((B-0.5*A)/C)*100; where A=mmol/L of sorbate in experimental sample; B=mmol/L of sorbate with 50% of experimental sample + 50% of 1 mmol/L standard, C=mmol/L of sorbate with 50% of DDI + 50% of 1000 mmol/L standard

APPENDIX C.1: KINETIC SORPTION





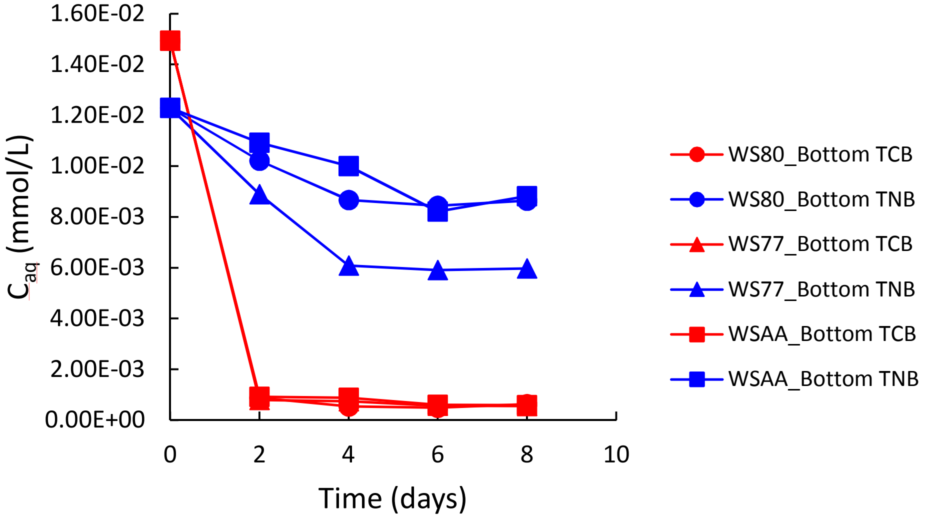
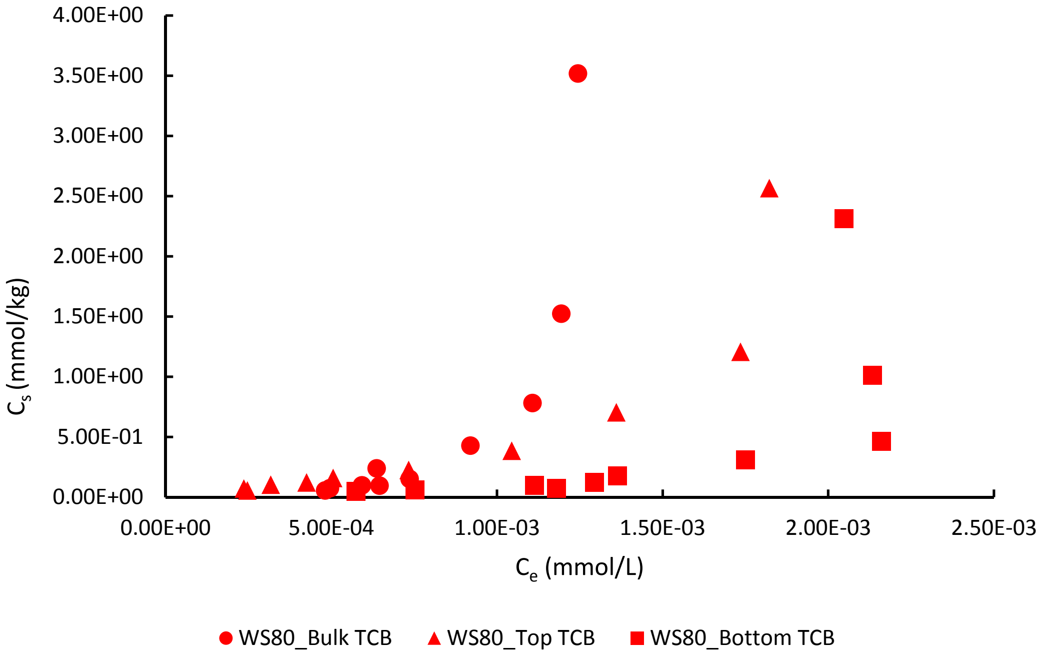


Figure C.1. Kinetic sorption results at each soil layer for WS80, WS77, and WSAA. Kinetic sorption was performed using 250 mL Teflon glass vials with a septa plug to minimize sorption to the container. For TCB, at each sampling event, 12 mL aliquouts were extracted from each sample, centrifuged, and analytical detection methods employed to obtain aqueous concentration. For TNB, at each sampling event, 2 mL aliquouts were extracted, centrifuged, and analytical detection methods were employed to obtain aqueous phase concentrations.

APPENDIX D.1: FULL SORPTION DATA SETS



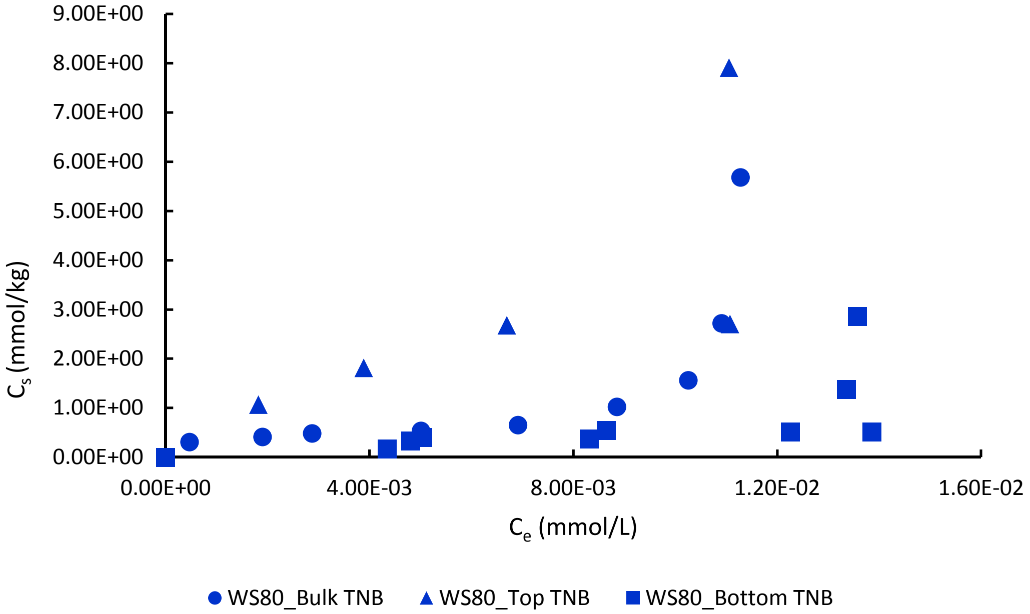


Figure D.1. Full data sets for WS80 bulk (circles), top (triangles), and bottom (squares) for TCB (top, red) and TNB (bottom, blue).

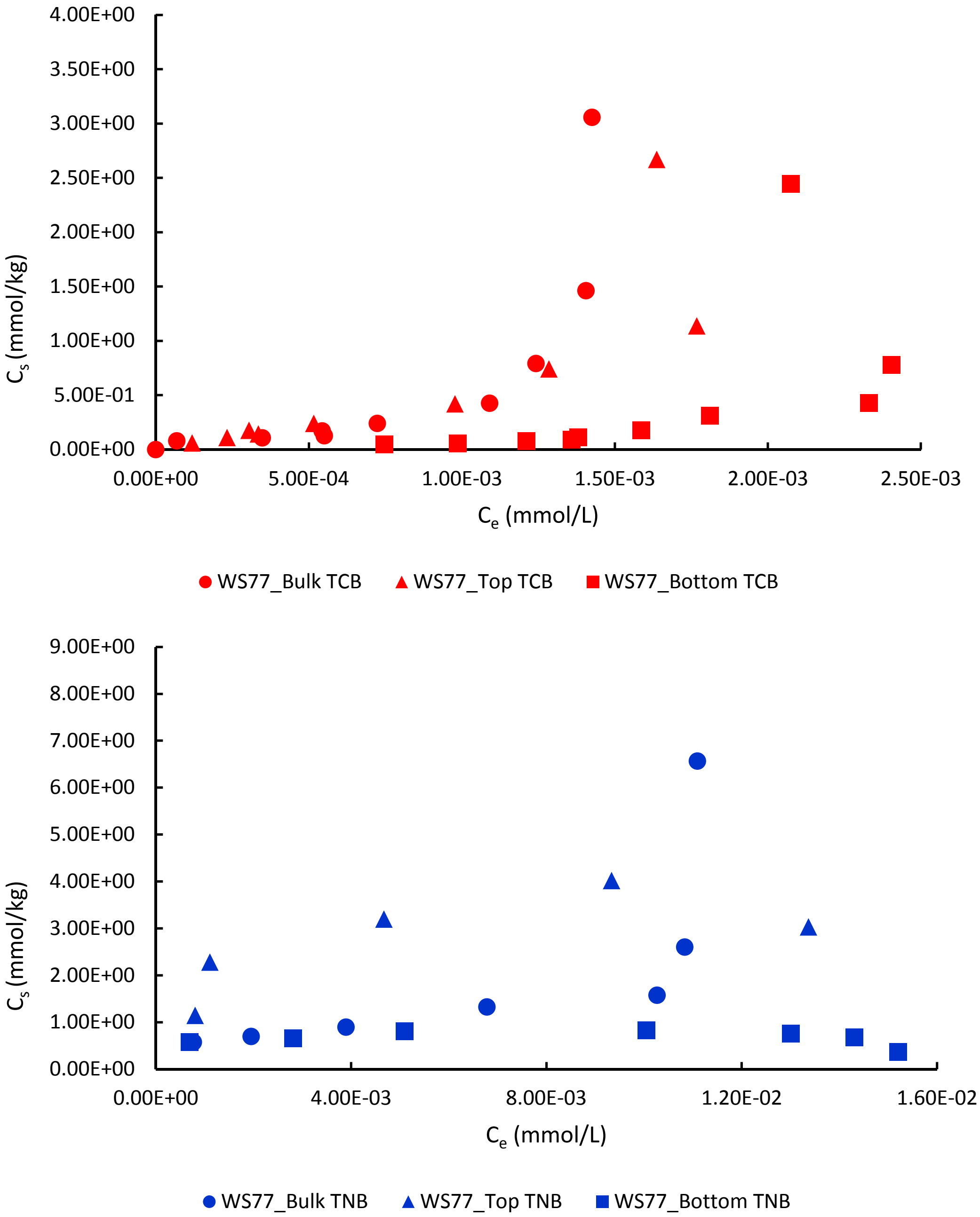


Figure D.2. Full data sets for WS77 bulk (circles), top (triangles), and bottom (squares) for TCB (top, red) and TNB (bottom, blue).

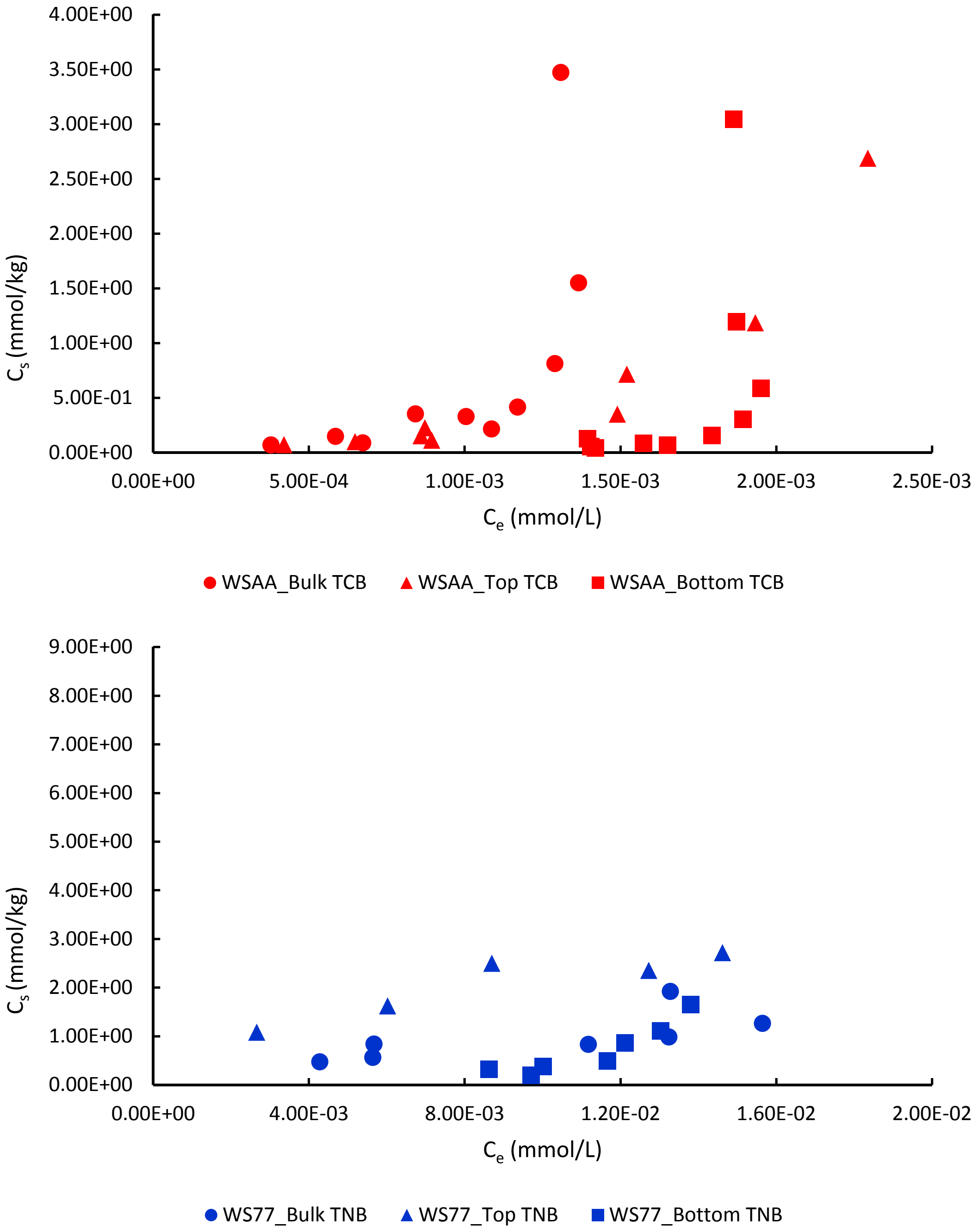


Figure D.3. Full data sets for WSAA bulk (circles), top (triangles), and bottom (squares) for TCB (top, red) and TNB (bottom, blue).

APPENDIX E.1. SOIL PHYSICAL AND CHEMICAL PROPERTIES

Table E.1. Physical and chemical properties of soil samples used in experimentation.

	WS80			**WS77**			**WSAA**			**WS80 (Bulk)**	
	BULK	**TOP**	**BOTTOM**	**BULK**	**TOP**	**BOTTOM**	**BULK**	**TOP**	**BOTTOM**	**200 C**	**500 C**
Sand/Silt/Clay (wt%)[1]	72/16/1			70/22/8			90/7/4				
pH[2]	4.4	4.3	4.4	4.4	4.2	4.3	5.3	5	5.5	4.1	5
TOM (%) - LOI	0.41	1.00	0.43	0.42	0.70	0.43	0.44	0.64	0.22	1.38	0.17
CEC (meq/100 g) [2]	8.5	10.6	7.2	6.3	10.6	7.8	5.3	6.8	1.9	7.1	4.7
Sodium (Na) (ppm) [3]	13,305.81			13,851.28			13,579.15				
Magnesium (Mg) (ppm) [3]	1,289.20			1,670.30			1,915.71				
Aluminum (Al) (ppm) [3]	65,701.54			48,434.22			53,230.72				
Potassium (K) (ppm) [3]	42,824.68			45,186.41			54,933.83				
Calcium (Ca) (ppm) [3]	3,040.08			6,505.80			5,699.13				
Chromium (Cr) (ppm) [3]	430.21			270.46			111.81				
Manganese (Mn) (ppm) [3]	1,087.33			1,377.21			1,717.97				
Iron (Fe) (ppm) [3]	117,596.39			93,586.68			59,711.68				
Cobalt (Co) (ppm) [3]	20.69			10.41			8.12				
Nickel (Ni) (ppm) [3]	35.51			16.65			<0.04				
Copper (Cu) (ppm) [3]	139.26			67.43			<0.04				
Zinc (Zn) (ppm) [3]	305.21			127.08			55.94				
Arsenic (As) (ppm) [3]	40.11			40.64			21.04				
Cadmium (Cd) (ppm) [3]	0.00			0.00			0.00				
Lead (Pb) (ppm) [3]	177.05			138.63			82.37				

Phosphorous (P) (lbs/acre) ²	13	10	4	5	9	4	5	10	2	17	19
Potassium (K) (lbs/acre) ²	43	69	23	29	66	29	57	67	13	17	98
Calcium (Ca) (lbs/acre) ²	402	595	269	349	671	306	585	1104	109	173	191
Magnesium (Mg) (lbs/acre) ²	53	49	19	45	82	39	37	74	1	33	100
Zinc (Zn) (lbs/acre) ²	1.4	0.6	0	0.9	1.8	0	0.5	1.2	0.1	0.2	0.6
Manganese (Mn) (lbs/acre) ²	4	2	1	2	4	1	28	60	6	1	3
Boron (B) (lbs/acre) ²	0.1	0.2	0	0	0.1	0	0	0.2	0	0.1	0.6
Copper (Cu) (lbs/acre) ²	2.4	0.9	1	3.4	1.5	1.8	0.4	0.5	0.3	0.3	0.2
Sodium (Na) (lbs/acre) ²	21	31	18	20	32	24	9	9	4	30	25
Acidity ² (%)	7.2	8.8	6.4	5.2	8.4	6.8	3.6	3.6	1.6	6.4	3.6
Ca ² (%)	12	14	9	14	16	10	28	41	14	6	10
Mg ² (%)	3	2	1	3	3	2	3	5	0	2	9
K ² (%)	1	1	0	1	1	0	1	1	1	0	3
Na ² (%)	1	1	1	1	1	1	0	0	0	1	1
Total ²	16	17	11	18	21	13	32	47	16	9	23

[1] UGA Research Laboratory- Particle Size Distribution (Stokes Law)

[2] Clemson Agricultural Service Laboratory- Standard Soil Test

[3] UGA Metals Analysis (ICP-MS)

LOI - Loss on Ignition at 500˚ C for 6 hours

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