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Trichloroethylene (TCE) adsorption using sustainable organic mulch

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A Thesis

entitled

Trichloroethylene (TCE) Adsorption Using Sustainable Organic Mulch

by

Zongsu Wei

Submitted to the Graduate Faculty as partial fulfillment of

the requirements for Masters of Science degree in Civil Engineering

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August 2010

An Abstract of

Trichloroethylene (TCE) Adsorption Using Sustainable Organic Mulch

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Soluble substrates (electron donors) have been commonly injected into chlorinated solvent contaminated plume to stimulate reductive dechlorination. Recently, different types of organic mulches possessing economic advantages and sustainable benefits have received much attention as new supporting materials that can provide long term sources as electron donors for chlorinated solvent bioremediation in engineered biowall systems. However, sorption capacities of organic mulches for chlorinated solvents have not yet been studied. In this study, the physiochemical properties of organic mulches (pine, hardwood and cypress mulches) were measured and their adsorption capacity as a potential media was elucidated. Single, binary and quaternary isotherm tests were conducted with trichloroethylene (TCE), tetrachloroethylene (PCE), trans-

dichloroethylene (trans-DCE) and cis-dichloroethylene (cis-DCE). Among the three tested mulches, pine mulch showed the highest sorption capacity for the majority of the tested chemicals in single isotherm test. In binary or quaternary isotherm tests, competition among chemicals appears to diminish the differences in Qe for tested mulches. However, pine mulch also showed higher adsorption capacity for most chemicals when compared to hardwood and cypress mulches in the two isotherm tests. Based upon physicochemical properties of the three mulches, higher sorption capacity of pine mulch over hardwood and cypress mulches appears to be attributed to a higher organic carbon content and the lower polarity.

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List of Abbreviation

APHA……… American Public Health Association

ATSDR…….. Agency for Toxic Substances and Disease Registry

BC…………. Biomaterial Content

BET……….. Brunaeur, Emmett and Teller

CEC……….. Cation Exchange Capacity

CNS……….. Central Nervous System

CWA………. Clean Water Act

cis-DCE …… cis-dichloroethylene

DBP……….. Disinfection Byproduct

GAC……….. Granular Activated Carbon

MCL……….. Maximum Contamination Level

MMO……... Monooxygenase

MSD……… Mass Selective Detector

NIOSH…… National Institute for Occupational Safety and Health

O&M……… Operation and Maintenance

OSHA…….. Occupational Safety and Health Administration

PAC………. Powdered Activated Carbon

PCE ……… tetrachloroethylene

ppb……….. Parts-per-billion

ppm………   Parts-per-million

RCRA……   Resource Conservation and Recovery Act

SDWA……   Safe Drinking Water Act

SOCs……..   Synthetic Organic Chemicals

TCE ………   trichloroethylene

trans-DCE ..   trans-dichloroethylene

VC………..   Vinyl Chloride

WC……….   Water Content

Chapter 1

Introduction

1.1 Contamination of TCE

Trichloroethylene (TCE) is a manufactured, volatile organic chemical. It is a nonflammable, colorless liquid with a sweet aroma and a burning taste as reported by EPA. Chemical and physical properties of TCE are available in table 1.1. TCE is an industrial product used commonly as a solvent to remove grease from metal parts. However, it is also an ingredient in adhesives, paint removers, typewriter correction fluids, and spot removers (DeLuca et al., 1983). As a synthetic chemical, TCE is considered not to be natural in the environment. However, as a result of the manufacture, use, and disposal of TCE, this chemical has been found in many underground water systems and many surface waters.

Since TCE was first detected in groundwater in late 1970s, it has been identified as one of the most common contaminants in U.S. Superfund sites (Schaumburg, 1990). The agency for the Toxic Substances and Disease Registry has reported that TCE was present in 852 of 1430 National Priority List sites in 1997 (Doherty, 2000). The EPA has set a 5 ppb limit for the maximum contamination level (MCL) of TCE. TCE contamination has

been a great concern due to its high solubility in water (1100 mg L^{-1} at 25°C) and resistance to biological degradation. TCE will degrade in the atmosphere within one week, but requires considerably more time for degradation in surface water. Thus, a small amount of TCE can contaminate a large amount of ground water for a long time (Aggarwal et al., 2006). Both atmosphere and surface water transport TCE primarily through soil where it passes to groundwater bodies (EPA, 2005). As a result, there is a need to develop efficient treatment techniques for TCE removal in the groundwater systems. Although much research has been completed studying the chemical in the last 30 years, TCE contamination is still a significant problem today (Schaumburg, 1990; Shen and Wilson, 2007).

In regards to various exposure vectors for humans, TCE has a known affect on the central nervous system (CNS), the liver, the kidneys, the reproductive system, and invitro organism development according to a large amount of human and animal data. Available epidemiologic studies provide evidence for a positive association between occupational TCE exposure and several types of cancer in humans (New York State Department of Health, 2006). In industries related to TCE, workers also suffer from exposure to the chemical. The most significant source of TCE in the environment is the evaporation from factories that use it to remove grease from metals (U.S. Department of Health and Human Services, 1997). TCE as well as other contaminants in groundwater affect human health via transportation to drinking water sources. Nausea, liver damage, unconsciousness, impaired heart function, or death might occur if large amounts of water contaminated with TCE are consumed. Furthermore, liver and kidney damage, impaired immune system function, and impaired fetal development in pregnant women may be caused by

drinking small amounts of water contaminated with TCE for long periods, although the extent of some of these effects is not yet clear (U.S. Department of Health and Human Services, 2003). TCE is a great threat to individuals working in those TCE exposure sites, as well as individuals using improperly treated water.

TCE was listed as a priority pollutant under the Clean Water Act (CWA) and a MCL was set under the Safe Drinking Water Act (SDWA). Under the Resource Conservation and Recovery Act (RCRA), it was regulated as a characteristically toxic waste and as a spent solvent process waste (EPA, 2005).

Federal organizations, such as the Agency for Toxic Substances and Disease Registry (ATSDR) and the National Institute for Occupational Safety and Health (NIOSH), developed regulations and recommendations for TCE. The MCL standard of TCE by the EPA (0.005 mg L^{-1}) has been put into effect since January 9 in 1989 and is applied to community water systems and those that serve the same 25 or more persons for at least 6 months. The EPA has also developed regulations for the handling and disposal of TCE. Spills of 1,000 pounds or more of TCE must be reported by industries in the past, and this number has been proposed for reduction to 100 pounds nowadays. TCE levels in the workplace are regulated by the Occupational Safety and Health Administration (OSHA). The occupational exposure limit is an average concentration of 100 ppm in air for an 8-hour workday, 40-hour workweek. The 15-minute average exposure in air is 300 ppm, which should not be exceeded at any time during a workday. Preventing central nervous system effects after TCE exposure is a critical component in determination and application of the OSHA standards (U.S. Department of Health and Human Services, 1997).

1.2 Conventional Treatment Technology of TCE

There are two options for TCE removal in the environment: abiotic and biotic. The abiotic method is to reduce or oxidize TCE by means of adding chemical materials. For example, using zero-valent metals to reduce TCE is a promising technology (Gotpagar et al., 2007). The biotic removal method, on the other hand, emphasizes the impacts of microorganisms on chloroethene contaminants in groundwater. After largely unsuccessful pump-and-treat attempts, subsequent research reveals that TCE is biodegradable under certain conditions (Bradley et al., 1998). For example, enhanced in situ anaerobic bioremediation can be an effective method of degrading TCE due to its advantages, including its low impact on infrastructure and its relatively low cost (Air Force, 2004). Usually, dechlorination ends with at Dichloroethylene (DCE) or vinyl chloride (VC) as products in the majority of groundwater systems. Moreover, a single bioremediation process cannot achieve the goal of total hazardous waste removal. The combination of reductive dechloriation of TCE and microbial oxidation of DCE and VC may be a possible method for complete degradation (Bradley et al., 1998).

Anaerobic reductive dechlorination is a process during which microorganisms use a carbon source as the electron donor to degrade chlorinated solvents without oxygen. This is one of the most common and most efficient ways to solve the TCE problem thus far. Various substrates are used for the anaerobic reductive dechlorination process. Simply, they can be divided and classified according to their existing phase as either solid-phase substrates or liquid-phase substrates. The solid-phase substrates, such as mulch and compost, are used less frequently. The mulch and compost are often a byproduct of the timber industry. However, since organic mulches are plentiful, inexpensive and readily

available, mulch is gaining much attention as a simple, effective and economical means of treatment at Superfund sites (Henry et al., 2005). Typically, mulch or peat moss has been installed in trenches as biowall (Shen and Wilson, 2007, Seo and Bishop, 2008), or biological filter media for volatile organic compounds (Ergas et al., 1995). Previous field studies also demonstrated that the application of mulches in permeable reactive barrier enhanced anaerobic bioremediation of chlorinated solvents in groundwater (Air Force et al., 2005).

Wood mulches are composed of many biopolymers, and their chemical composition of the cell wall mainly determined the biological properties. Cellulose, hemicelluloses and lignin are the primarily three polymeric components of wood cell walls: (Mackay and Gschwend, 2000). It was reported that lignin was known to have a high affinity and sorption capacity for nonionic organic compounds (Garbarini and Lion, 1986). Moreover, mulch is rich in carbon and can provide an alternative carbon source for microorganisms to degrade chlorinated solvents anaerobically (Air Force, 2004). However, while organic mulch has shown its potential for anaerobic bioremediation of chlorinated solvents, the adsorption capacity of mulch for chlorinated solvents has not been studied yet.

1.3 Experimental Strategy

1.3.1 Experimental Objectives

The overall objective of this research was to study the adsorption capacity of pine mulch, hardwood mulch and cypress mulch for chlorinated solvents. Besides these considerations, other objectives are the following:

(1) Study the physicochemical properties of three commercially available mulches (hardwood mulch, pine mulch, and cypress mulch).

(2) Investigate sorption capacities of mulches in binary and quaternary isotherm tests with TCE, PCE, trans-DCE and cis-DCE, additionally considering the coexistence of the four chemicals in chlorinated solvent contaminated groundwater or soil.

(3) Compare the adsorption data of different adsorbents to determine which one best remediates organic components.

(4) Compare organic mulches with commercially available adsorbents.

(5) Economic advantages of organic mulches.

1.3.2 Experimental Strategy

This study aims to explore the adsorption capacity of organic mulches (hardwood, pine and cypress mulches) for TCE removal. These mulches are by-products of wood and lumber industries and are the most common mulches used in the United States. These mulches were selected as potential supporting materials for the biowall where anaerobic reductive dechlorination takes place. Sorption capacities of mulches were tested with four chemicals: TCE, PCE, trans-DCE and cis-DCE. First, single isotherm tests for each type of mulch were conducted to obtain its adsorption capacity. Then, binary and quaternary isotherm experiments were conducted and results were compared to those from the single isotherm test.

Table 1.1 Chemical and physical properties of TCE

Empirical formula	C_2HCl_3
Rel. molecular mass	131.4 g
Density	1.46 g/cm^3 at 20°C
Relative gas density	4.54
Boiling point	86.7°C
Melting point	-73 to -87°C
Vapor pressure	77 hPa at 20°C
Ignition temperature	410°C
Explosion limits	7.9 - 41 Vol%
Odor threshold	50 ppm in air
Solvolysis/solubility	in water: 1.1 g L^{-1} at 20°C; readily soluble in organic solvents
Conversion factors	1 ppm = 5.46 mg/m^3 1 mg/m^3 = 0.18 ppm

Note: source is from http://ces.iisc.ernet.in/energy/HC270799/HDL/ENV/enven/vol366.htm

Chapter 2

Background

2.1 TCE Degradation

2.1.1 TCE Degradation Mechanisms

Because of its potential harmful health effects and its widespread occurrence in groundwater and soil systems, TCE removal technology needs to be investigated. At present, several TCE degradation mechanisms have been identified in groundwater:

(1) Oxidation

Chemicals such as potassium ferrate at a 30ppm concentration can completely oxidize 100 ppb TCE in less than fifty minutes (after an initial 5 to 20 minute delay) at 23 degrees Celsius and a pH of 8.3. Another process, ozonation, has also been approved as an efficient way to remove TCE in water treatment (DeLuca et al., 1983).

(2) Reduction

TCE, as a highly oxidized chemical, is susceptible to reduction. Anaerobic reductive dechlorination is an attractive process for engineers in practice. There are two reactions in the anaerobic reductive bioremediation process: direct anaerobic reductive dechlorination and cometabolic anaerobic reductive dechlorination. Besides these two bioremediation

processes, chemical reductive dechlorination also provides significant advantages. In this kind of reaction, a chlorinated hydrocarbon is reduced by a reactive compound, such as metal sulfides, that can degrade TCE (Butler and Hayes, 1999; Lee and Batchelor). In this case, an anaerobic environment may be created and the substrate addition may indirectly cause and sustain abiotic reductive dechlorination.

(3) Dehalohydrolysis

Natural dehalohydrolysis of TCE is possible even if the mechanism of it is not significantly efficient. The process involves the removal of a chlorine atom from one carbon coincides with removal of a hydrogen atom from the adjacent carbon, with the subsequent production of an alcohol. Usually, catalysts, ultraviolet light for instance, are developed to enhance the rate of this reaction (Russell et al., 1992).

In practice, methods for TCE removal include surface treatment technologies and subsurface remediation technologies. Examples of surface treatment are air stripping or combination of air stripping and carbon adsorption. GAC is usually used for TCE adsorption. Subsurface treatments include soil venting, in-well aeration, bioremediation, bioremediation of extracted ground waters/subsurface air streams, and in situ bioremediation (Russell et al., 1992).

2.1.2 TCE Bioremediation

Bioremediation technology remains attractive because it can completely mineralize TCE to CO_2, water, and chlorine instead of simply a transfer from one medium to another. Meanwhile, enzymes and cofactors are produced by bacteria to enhance the reaction rate in this process.

Anaerobic reductive dechlorination is more likely to occur due to the oxidized state of TCE. This process has been studied for many years (Bouwer and McCarty, 1983; Bouwer et al., 1981). The obligate anaerobic methanogenic bacteria was first reported in reduced dechlorination, with volatile fatty acids and toluene as oxidizable substrates (electron donors) (Sewell et al., 1990). Wackett and Gibson (1988) reported three pure cultures (strain G4, Pseudomonas putida Fl, and P. putida B5) that catabolize toluene were able to degrade TCE. Dehalococcoides ethenogenes was a single species that can complete sequential dechlorination of PCE (perchloroethylene) to ethane (Air Force et al., 2004). Freedman et al. (1989) and Vogel and McCarty (1985) found the conversion of PCE and TCE in groundwater system under anaerobic conditions. Degradation of PCE to ethane by the step-wise process including TCE, DCE isomers (1, 1-DCE or cis-DCE or trans-DCE), and VC is illustrated in Figure 2.1 (Air Force, 2004). In this pathway, chloride icons are sequentially removed.

Aerobic degradation of TCE can be fulfilled by a number of monooxygenases, where an aromatic compound such as toluene or phenol is required (Nelson et al., 1987). Pseudomonas cepacia G4 was reported to cometabolically degrade TCE to CO_2 (Krumme et al., 1993). Methylotrophic bacteria can also produce the enzyme methane monooxygenase (MMO) that epoxidates TCE with methane in the presence of oxygen.

In addition, mixed consortia of bacteria provide an efficient approach to degrade TCE (Henson et al., 1993). Under proper conditions, aerobic oxidation and anaerobic reductive dechlorination can occur naturally. The addition of electron donors, electron acceptors, or nutrients helps aerobic oxidation or anaerobic reductive dechlorination occur. Typically, mechanisms occurring during bioremediation of TCE include cometabolic aerobic

oxidation, direct anaerobic reductive dechlorination, cometabolic anaerobic reductive dechlorination and the combination of direct and cometabolic anaerobic reductive dechlorination (USEPA, 2000a). Table 2.1 shows the selected information on the TCE degradation mechanisms.

2.1.3 Substrates for Anaerobic Reductive Bioremediation of TCE

Many substrates may be used for the anaerobic reductive dechlorination process (table 2.1). Moreover, they can be divided into types according to their existing phase: solid-phase substrate, liquid-phase substrate and gas-phase substrate. Selection of substrate is often based on the application environment, commercial market, and the experience of engineers. As the carbon source, most substrates can be fermented or degraded to produce hydrogen that will reduce the chlorinated pollutant (Air Force, 2004).

Liquid phase substrates are the most commonly used materials for bioremediation, especially the soluble substrates including lactate, molasses and so on. The solubility of liquid phase substrates make it possible for them to travel with advective groundwater flow, and their typical function is to maintain a specified reactive treatment zone if applied in a continuous or periodic (pulsed) mode.

Used less frequently are the solid phase substrates that include mulch and compost. Mulch, which is primarily composed of cellulose and lignin, is generally obtained from shredding and chipping of tree and shrub trimmings. It provides a source of nitrogen for microbial growth and also offers a source of readily degraded organic carbon. Secondary fermentable substrates, such as metabolic and humic acids, are generated by degradation of the substrate in microbial processes and may accept electrons by oxidizing cis-DCE in

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anaerobic condition (Bradley et al., 1998). Although solid phase substrates have many limitations, they still receive great attention because of their valuable advantages that will be discussed later.

Typically, solid substrates are placed in trenches or in excavations as backfill in a one-time event using conventional construction techniques. Surface amendment infiltration plots (Hass et al., 2000; GSI, 2001) and recirculation of contaminated groundwater through mulch bioreactors (Parsons, 2003) are two other variations. Usually, biowalls are installed to capture the chlorinated pollutant in the trenches that is perpendicular to the groundwater flow. Available examples are projects at Building 301, Offutt Air Force Base (AFB), Nebraska and OU1, Altus AFB, Oklahoma (Henry et al., 2005). At the Building 301 site, the mean percent removal of TCE was calculated to be approximately 75 percent with the full-scale biowall application; at OU1 site, concentrations of TCE had been reduced from 8000 μg L^{-1} to below the MCL (5.0 μg L^{-1}) within the biowall in 9 months. Figure 2.2 is the schematic diagram showing the proposed biawall system.

In general, the most attractive advantage of solid phase substrates is their low-cost. Besides this advantage, solid phase substrates possess many other benefits. Below are the advantages of permeable mulch and compost biowalls:

(1) They perform well for shallow groundwater flumes in very low to moderate permeability or highly heterogeneous formations. The trenches have excellent capacity to intercept contaminants because preferential flow paths for pollutants are generated.

(2) Mulch is inexpensive and easy to generate — often manufactured as waste product.

(3)　Little reduction in performance over a long operation time (Robertson, 2000) and require no operation and maintenance (O&M) other than periodic performance monitoring.

(4)　Mulch is rich in carbon, nitrogen and offers essential energy for bioremediation.

(5)　When carbon loading is necessary, liquid substrates can be easily introduced to biowall trenches via injection wells or perforated pipe.

Limitations are:

(1)　Depth of placed mulch is limited, only for relatively shallow groundwater plumes (approximately 30 to 35 feet), and trenching may interfere with underground utilities or other site infrastructure.

(2)　Long-term effectiveness is unknown.

(3)　When concentrations of chlorinated solvents are in excess of 10 to 100 milligrams per liter (mg L^{-1}), the contaminant retention time in the trench and substrate loading capacity (i.e., the rate at which organic carbon is added to the groundwater passing through the trench) may be insufficient.

Although it has some limitations, mulch and compost can absorb TCE and at the same time provide carbon source for cultures in an anaerobic process. The economic advantage of mulch also makes it a preferred choice in engineering projects.

2.2 TCE Adsorption

2.2.1 Adsorption Process

Adsorption is a mass transfer process during which chemicals are adsorbed or accumulated from a liquid phase onto a solid phase. Adsorption processes are developed in drinking water treatment to remove taste- and odor-causing compounds, synthetic organic chemicals (SOCs), color-forming organics, and disinfection byproduct (DBP) precursors. It can also remove hazardous inorganic substances, such as perchlorate, arsenic, and some heavy metals. The most common adsorbents are GAC and powdered activated carbon (PAC). GAC can be efficiently used to dechlorinate drinking water efficiently.

Adsorbates can be captured by a chemical reaction (chemisorption) or physical attraction (physical adsorption) onto the surface of adsorbents. Physical adsorption and chemisorption mechanisms are listed in Table 2.1. The surface area and pore size are two important factors that determine the adsorption capacities of adsorbents. Usually, a smaller the pore size for a given pore volume holds a larger the surface area. Adsorption isotherms are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and at a constant temperature. An isotherm is a function of the aqueous-phase concentration and the amount of adsorbate adsorbed (Crittenden et al., 2005). Different procedures, protocols, and problems associated with performing adsorption equilibrium isotherms have been presented in previous studies (Crittenden et al., 1987b; Luft, 1984; Randtke and Snoeyink, 1983; Summers, 1986)

2.2.2 Adsorption of TCE and Available Adsorbents

For TCE contaminated soil and groundwater remediation, biotic and abiotic methods have been employed. The biotic removal of TCE utilizes microorganisms to dechlorinate PCE and TCE into less chlorinated by-products such as DCE and VC in aerobic or anaerobic environments. The abiotic removal methods for TCE include the chemical oxidation/reduction of TCE (Gotpagar et al., 1997) or the physical adsorption using various adsorbents.

Among available treatment methods, the adsorption process is one of the most commonly used techniques for the purification of TCE contaminated groundwater. Generally, various adsorbents have been employed to mitigate the migration of TCE in subsurface aquifers. The most popular media for TCE adsorption has been activated carbon in both granular and powered forms. However, even though the activated carbon shows the highest sorption capacity for TCE, it has been reported that the activated carbon cannot enhance the decomposition of adsorbed TCE into harmless substances (Yoichi et al., 2000; Kilduff and Karanfil, 2002). Many researchers reported that the strong sorption of organic chemicals by the activated carbon decreased their bioavailability (Alexander, 1995). Also, the activated carbon cannot provide an alternative carbon source for microorganisms to degrade TCE even if it has high organic carbon content (Zytner, 1992; Yoichi et al., 2000). It is also expensive for field application.

Other available adsorbents for TCE are soils, peat moss (Zytner, 1992; Steinberg et al., 1996), organo-clays (Sheng et al., 1998; Zhao and Vance, 1998), polymeric adsorbent (Fei et al., 2004; Liu et al., 2009), zeolites (Kleineidam et al., 2002; Farrell et al., 2003)

and other carbon-based materials (Langer et al., 1999; Yu and Chou, 2000). Among them,

wood materials have recently received much attention (see 1.2).

Cl Cl
 C=C   PCE
Cl Cl

Cl Cl
 C=C   TCE
Cl H

Cl H   Cl Cl   H Cl
 C=C   C=C   C=C
Cl H   H H   Cl H
1,1 DCE   1,2 cis-DCE   1,2 trans-DCE

H Cl
 C=C   VC
H H

H H
 C=C   Ethylene
H H

CO_2 H_2O
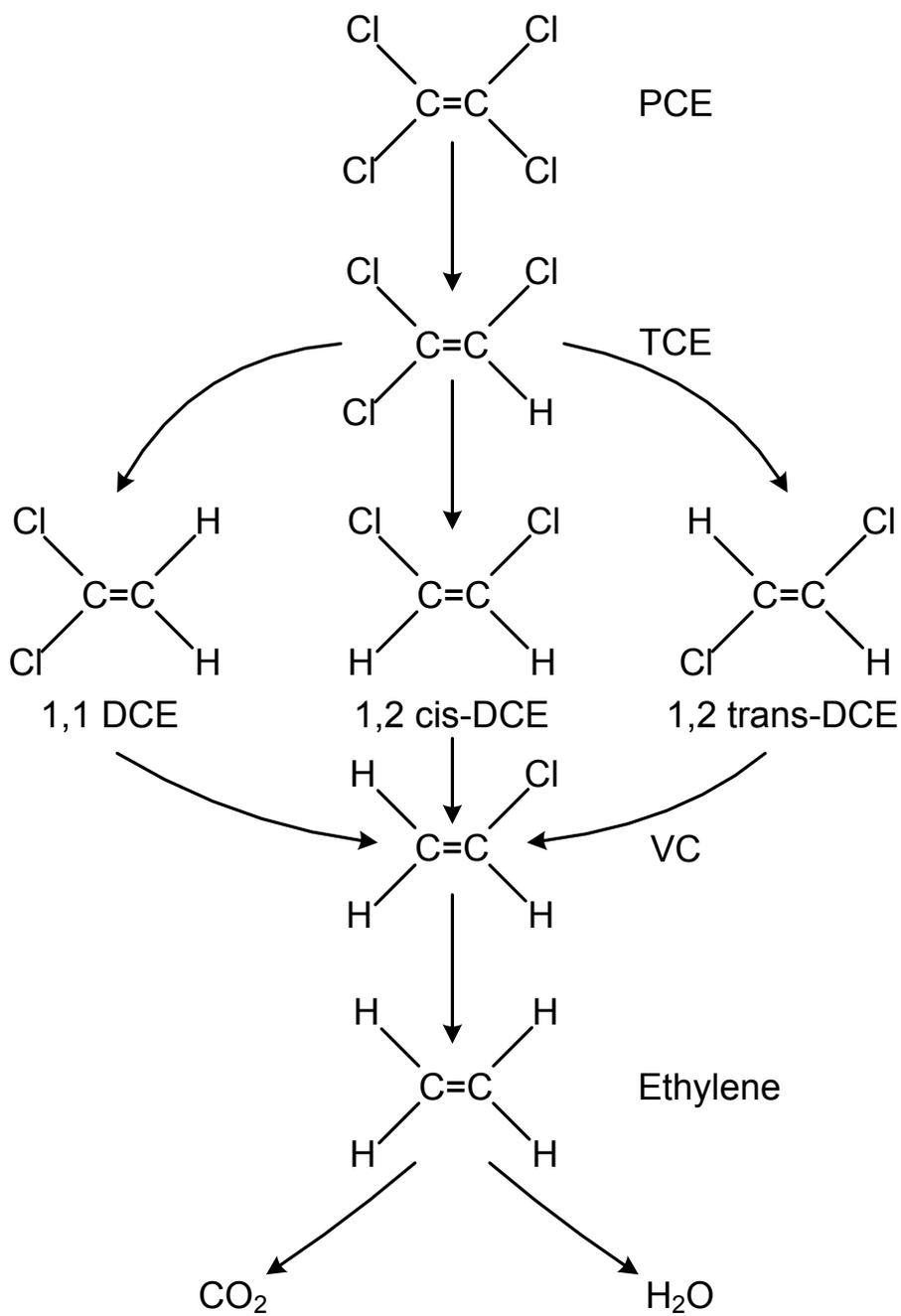
Figure 2.1 Sequential reduction of PCE to ethene by anaerobic reductive dechlorination

Ground Surface   Barrier System

Water Table

PCE/TCE

Bacteria

Biological Active
Zone

Mulch

Bacteria

Groundwater Flow Direction ——————→
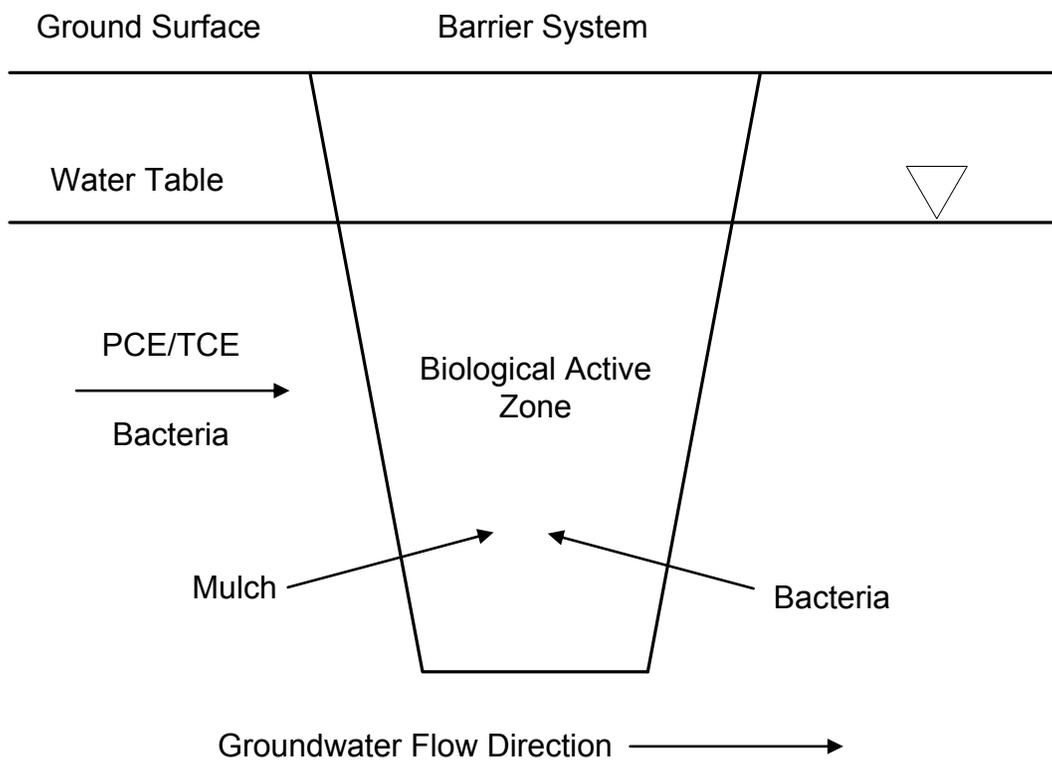
Figure 2.2 Schematic diagram showing the proposed biawall system

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Table 2.1 Selected information on TCE degradation

Degradation Mechanisms	Conditions	Reported Bacteria	Product
Cometabolic aerobic oxidation	Aerobic, electron donor (phenol, toluene, benzene)	Burkholderia cepacia G4, PR1	CO_2
	Aerobic, electron donor (toluene)	Not reported	Not reported
Direct anaerobic reductive dechlorination	Anaerobic, electron donor (lactate, methanol butyrate, glutamate 1,2-propanediol, toluene)	Alcaligenes	Ethene
	Anaerobic, electron donor (Hydrogen, propionate or lactate)	Not reported	Not reported
Cometabolic anaerobic reductive dechlorination	Anaerobic, electron acceptor (nitrate, sulfate), electron donor (hydrogen)	Methanosarcina barkeri, Desulfomonile tiedjei	Ethene, ethane
	Anaerobic, electron acceptor (nitrate, sulfate), electron donor (hydrogen)	Methanogens, denitrifiers, sulfate reducers	Ethene, ethane

Table 2.2 Comparison of adsorption mechanisms

between physical adsorption and chemisorption

Parameter	Physical Adsorption	Chemisorption
Use for water treatment	Most common type of adsorption mechanism	Rare in water treatment
Process speed	Limited by mass transfer	Variable
Type of bonding	Nonspecific binding mechanisms such as van der Waals forces, vapor condensation	Specific exchange of electrons, chemical bond at surface
Type of reaction	Reversible, exothermic	Typically nonreversible, exothermic
Heat of adsorption	4–40 kJ M^{-1}	> 200 kJ M^{-1}

Note: source is from book of ―Water Treatment - Principles and Design (2nd Edition)".

Chapter 3

Materials and Methods

3.1 Absorbents and Absorbates

The adsorbents (pine, hardwood and cypress mulches) used in this experiment were purchased from Ohio Mulch (Cincinnati, OH, USA). The selected mulches are by-products of the paper and lumber industries. The preparation of mulches followed the method reported by Seo et al. (2007). The mulches were first washed with deionized water so that sand, fine debris and easily leachable materials were removed. Then, the rinsed mulches were autoclaved twice at 135 ℃ for 10 min to eliminate all bacterial and fungal spores. The mulches were dried at 60 °C in the oven. A mechanical blender was used to grind the dried mulches to a fine consistency. The mulches were autoclaved again after sieving with #10 mesh (2 mm) and #16 mesh (1.18 mm) sieves. Finally, homogenized mulches were obtained and were used to characterize physicochemical properties and for isotherm testing (Seo, 2008).

An Elemental Analyzer equipped with an inductive furnace analyzer (Perkin Elmer 2400) was used to test the carbon, hydrogen and nitrogen contents. The Brunaeur,

Emmett and Teller (BET) surface area, porosity, and pore size distribution of the three mulches were measured using nitrogen adsorption and desorption isotherms. The pore sizes of mulches were determined by a Tristar 3000 (Micromeritics, GA, USA) pore size analyzer, and all samples were purged with nitrogen gas for 2 hours at 150 ^{o}C using a Flow Prep 060 (Micromeritics, GA, USA) before analyses. Surface area was measured according to the multi point BET method (Seo, 2008). Huang et al. (2006) measured the total pore volume of chosen mulch at P/P_o=0.95 and calculated the meso-pore volume as the difference between total pore volume and micro pore volume. The data of pH, water content (WC), and biomaterial content (BC) for the mulches was from APHA (1998). Ciesielski and Sterckeman (1997) measured the cation exchange capacity (CEC) using the ammonium acetate method. Considering their coexistence in contaminated soil and groundwater, four chemicals (TCE, PCE, trans-DCE and cis-DCE; Sigma Aldrich Co.) were selected for adsorption tests.

3.2 Single Solute Adsorption Isotherm Test

Batch isotherm tests were conducted with Teflon-lined screw cap bottles to evaluate the adsorption capacity of organic mulches for all four tested chemicals. To minimize volatilization loss of tested chemicals, all bottles were filled up with adsorbate solution to remove head space and 3 to 6 blank samples were also added at each sampling point.

To obtain an adsorption equilibrium time for each chemical on the mulches, preliminary isotherm tests were conducted with each chemical. Sample bottles were placed in a rotary tumbler at 12 rpm. Then samples were harvested at 1d, 2d, 3d, 5d, 7d, and 10d and liquid phase concentrations of the tested chemicals were monitored.

For the single isotherm tests for each chemical (PCE, TCE, cis-DCE and trans-DCE), samples with varied amounts of mulch mass were prepared. All chemical solutions were prepared with deionized water (18.2 MΩ) and the initial concentration was 50 mg L^{-1}. All isotherm tests were conducted in room temperature (20°C). After samples reached adsorption equilibrium time, liquid phase chemical concentrations were monitored and the adsorbed amount of chemicals on different mulches was calculated.

3.3 Binary and Quaternary Solutes Adsorption Isotherm Test

In TCE contaminated groundwater or soil, chemicals from the anaerobic reductive dechlorination pathway coexist with TCE and the mixed condition may have competitive adsorption on adsorbents. Therefore, after obtaining single solute isotherm results, both binary isotherm tests (combination of TCE and PCE; TCE and cis-DCE) and quaternary isotherm tests were conducted with three different mulches. Test conditions were identical to those of the single isotherm test.

3.4 Analytical Methods

A Hewlett-Packard model 6890 gas chromatograph (GC) equipped with a mass selective detector (MSD) was used to measure the concentration of TCE, PCE, cis-DCE and trans-DCE solutions. The HP-624 column for volatile organic compounds (30.0 m × 250 μm × 0.25 μm nominal; Restek RTX-5) was used. The total flow was 6.7 mL min^{-1}. The set point temperature of the heater was 260°C and pressure was 2.82 psi. Detector and injector temperatures were held at 250°C and 220°C, respectively. To monitor liquid phase chemical concentration, 2 ml of samples were collected from each bottle and

chemicals were extracted by methylene chloride for GC analysis. GC/MS analysis methods are shown in Table 3.1.

3.5 Adsorption models

The mass balance expression used to determine the amount of adsorbates retained by adsorbents was calculated using aqueous phase concentration of adsorbates.

$$Q_e = \frac{V}{M}(C_o - C_e) \tag{1}$$

where Q_e is equilibrium adsorbent-phase concentration of adsorbate, mg g^{-1}; C_e is the aqueous phase concentration of adsorbate at equilibrium, mg L^{-1}; C_o is the initial adsorbate concentration, mg L^{-1}; V is volume of aqueous-phase adsorbate solution, L; M is mass of adsorbent, g.

In order to quantify the adsorption capacity of the mulches, obtained experimental data were fitted according to the Freundlich and Langmuir Isotherm equations.

$$\text{Freundlich isotherm: } Q_e = K_f C_e^{\frac{1}{n_f}} \tag{2}$$

$$\text{Langmuir isotherm: } Q_e = \frac{S_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where K_f is the Freundlich constant indicative of adsorptive capacity, $(\text{mg kg}^{-1})(\text{mg L}^{-1})^{\frac{-1}{n_f}}$; n_f is the Freundlich constant related to adsorption intensity; K_L (mg^{-1}) is the Langmuir isotherm constant related to the equilibrium constant or

binding energy; S_m (mg g^{-1}) is the amount of sorption corresponding to complete surface

coverage.

Table 3.1 GC/MS analysis methods

Chemical	TCE	PCE	trans-DCE	cis-DCE
Initial Temperature (°C)	80	130	40	50
Hold Time at the beginning (min)	5.5	5.5	5.5	4.5
Ramp (°C min^{-1})	20	20	40	40
End Temperature (°C)	190	190	190	190
Hold Time in the end (min)	2.0	2.0	2.0	2.0
Solvent Delay Time (min)	3.5	3.2	4.75	4.9
Carry Gas (Helium)Flow Rate(mL min^{-1})	0.4	0.4	0.4	0.4

Note: in cis-DCE program, detector is off during 4min to 8 min.

Chapter 4

Results and Discussion

4.1 Physicochemical properties of the experimental mulches

Physicochemical properties of the three types of organic mulches (cypress, hardwood, and pine mulches) were measured and summarized in These three mulches showed surface areas between 0.62 and 1.37 m^2 g^{-1}, which are slightly higher than aspen wood bark (0.62 m^2 g^{-1}, Huang et al., 2006). Among the three mulches, cypress mulch showed the relatively highest surface area (1.3725 m^2 g^{-1}), followed by hardwood mulch (1.0972 m^2 g^{-1}) and pine mulch (0.6195 m^2 g^{-1}). The fact that the experimental cypress mulch has more surface area under the same unit mass might be related to its fibrous character (Seo, 2008).

Among the three mulches, pine mulch had the highest carbon content while cypress mulch had the lowest. Xing et al. (1994), calculated the atomic ratios [(N+O)/C, (O/C)] in order to measure the polarity of the three mulches based on the results of elemental composition analysis. It was reported that polarity was one of the most important compositional factors governing sorption of hydrophobic organic compounds in soil (Boving and Zhang, 2004; Chen et al., 2005; Huang et al., 2006). Xing et al. (2006) also

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reported that the lowest polarity [(O+N)/C or (O/C)] represented the highest K_{oc} values (the soil-water partition coefficient, determining the mobility of organic chemicals in soil) as well as the highest sorption capacity with chemically treated wood. The pine mulch showed the lowest polarity [(N+O)/C, (O/C)] while cypress mulch showed the highest polarity based on the mass atomic ratio. For cation exchange capacities of tested mulches, the hardwood mulch showed the highest CEC (around 40 meq/100 g) among the three adsorbents (Seo, 2008). The physicochemical properties of the selected mulches were summarized in Table 4.1.

4.2 Single Adsorption Isotherm

For all selected chemicals (PCE, TCE, trans-DCE and cis-DCE), preliminary isotherm tests were conducted with different mulches to elucidate equilibrium time. Based on the preliminary adsorption results (data not shown), approximately all the equilibriums were reached after 1 day for all tested chemicals with all three mulches. However, a 2 day equilibrium time was selected to ensure enough equilibrium time for all isotherm tests.

To assess the adsorption capacity of different mulches, a single solute adsorption isotherm experiment was conducted with varied mulch dosages from 0.2 g per vial to 5 g per bottle. The collected data were correlated to the linearized Freundlich and Langmuir Isotherm models to obtain adsorption kinetics. The rearranged equations are shown as follows.

$$\text{Linearized Freundlich Isotherm:} \log (Q_e) = \log (K_f) + \frac{1}{n_f} \log(C_e) \tag{4}$$

Linearized Langmuir Isotherm: $\dfrac{C_e}{Q_e} = \dfrac{1}{K_L S_m} + \dfrac{C_e}{S_m}$ (5)

Figures 4.1-4.4 show the linear relation between Q_e and C_e with linearized Freundlich Isotherm model and compares the adsorption capacity of different mulches. Among the three mulches, overall, pine mulch showed higher adsorption capacity than hardwood and cypress mulches. Table 4.2 shows the Freundlich and Langmuir isotherm coefficients of single solute adsorption on different mulches. Both models adequately described the adsorption data (over 0.9 regression coefficients) and also showed pine mulch had better adsorption capacity. A detailed analysis of both Freundlich and Langmuir isotherm coefficients suggested that PCE and TCE had a higher affinity to all three mulches than trans-DCE and cis-DCE. Among the four tested chemicals, trans-DCE was the most difficult to be absorbed by all three mulches. Table 4.3 shows the Q_e and removal efficiency for different mulches. In single isotherm test, pine mulch showed the highest Q_e (2181.52 µg g^{-1}) followed by cypress mulch (1511.4 µg g^{-1}) and hardwood mulch (1300.6 µg g^{-1}) for PCE; for TCE, the Q_e decreases in the following order: pine mulch (1076.0 µg g^{-1}), cypress mulch (942.7 µg g^{-1}), and hardwood mulch (540.9 µg g^{-1}); for trans-DCE, the Q_e decreases in the following order: hardwood mulch (510.4 µg g^{-1}), cypress mulch (451.3 µg g^{-1}), and pine mulch (369.1 µg g^{-1}); and for cis-DCE, the Q_e decreases in the following order: pine mulch (696.3 µg g^{-1}), hardwood mulch (574.3 µg g^{-1}), and cypress mulch (337.4 µg g^{-1}). Under the same initial conditions, pine mulch adsorbed the largest amount of PCE, TCE and cis-DCE according to the above results.

Zytner (1992) reported that there is a corresponding increase in the adsorption capacity of adsorbent as its organic carbon content, CEC and surface area increase. Among three

mulches, pine mulch has the highest organic carbon content (51.62%), while hardwood mulch and cypress mulch had 43.23% and 19.05% of organic carbon content, respectively (Zytner, 1992). All three mulches showed small surface areas (between 0.62 and 1.37 m^2 g^{-1}) that would not make a significant difference in adsorption capacity. Furthermore, CEC, which is important for metal ion adsorption, appears not to be important. Therefore, the high organic carbon content of pine mulch affected the adsorption capacity for chlorinated solvents. Polarity [(O+N)/C or (O/C)] has also been considered an influencing parameter on the adsorption of organic chemicals. It was reported that lower polarity presented the higher sorption capacity with chemically treated wood (Huang et al., 2006). Among three mulches, pine mulch showed the lowest polarity (0.84 or 0.83) followed by hardwood mulch (1.19 or 1.17) and cypress mulch (4.14 or 4.12). Higher sorption capacity of pine mulch over hardwood mulch and cypress mulch appears to be attributed to a higher organic carbon content and the lowest polarity.

4.3 Binary and Quaternary Solutes Adsorption Isotherm

Figures 4.5-4.8 show the binary and quaternary tests of adsorption under linearized Freundlich Isotherm model, respectively. In the binary isotherm tests, similar to the isotherm results of single solute isotherm tests, pine mulch had higher adsorption capacity for most chemicals than those of hardwood and cypress mulches. Figures 4.5-4.7 show that the amount of adsorbed chemicals on mulches is in direct proportion to the y axis intersection. According to the results, PCE is most likely to be adsorbed by all three mulches followed by TCE. Trans-DCE and cis-DCE showed little affinity to the tested mulches.

The removal efficiencies, percent mass of chemicals removed by mulch, are shown in Table 4.3. Among the tested mulches, pine mulch had the highest removal efficiency for most tested chemicals in all isotherm tests, followed by hardwood mulch and cypress mulch. The removal efficiencies of tested chemicals in binary and quaternary isotherm results were lower than those of single isotherm tests for all mulches. The slight decrease in removal efficiencies of binary and quaternary isotherm tests suggests that there was adsorption competition among adsorbates onto adsorbent surfaces. The multi-components adsorption is complicated process because of the solute–surface interactions. Mixture of adsorbates has to compete to be adsorbed onto media in the binary or quaternary system, while a single component can reach saturation in the same solution. However, compared to the single solute isotherm test results, there was not a significant difference in both the adsorption capacity of three mulches and the chemical removal efficiency in binary and quaternary isotherm tests. None of the tested chemicals showed any significant mixture effects on adsorption capacity and affinity changes. Affinity of each chemical to the tested mulches showed the same trend with that of single solute isotherm tests. Larger molecular weight chemicals (PCE, TCE) appear to be more adsorbed on mulch surfaces compared to trans-DCE or cis-DCE which have smaller molecular weights.

4.4 Comparison of Sorption Capacity of Mulches to Other Adsorbents

For its high efficiency to remove various organic contaminants, activated carbon has been widely used. Zytner (1992) tested granular activated carbon (GAC), peat moss, organic top soil, and sandy loam soil for TCE adsorption. The results reported that GAC

had the highest sorption capacity followed by peat moss, organic top soil and sandy loam soil. The organic carbon content of GAC was reported to be much higher (74.1%) than those of organic mulches (pine, 51.6%; hardwood, 43.2%; cypress, 19.1%). GAC is also reported to possess a much higher surface area, 1300 m^2 g^{-1}, than that of the tested mulches in this study (between 0.62 m^2 g^{-1} and 1.37m^2 g^{-1}). The Freundlich adsorption coefficients K_f is 81076 for GAC while the adsorption coefficients for tested mulches are below 10 as shown in table 3. However, activated carbon can only physically adsorb chlorinated solvents from liquid or gas phase into solid phase. The high content of organic carbon cannot provide an electron donor for microorganisms to anaerobically degrade TCE (Yoichi et al., 2000). In addition, many researchers reported that strong adsorption of organic compounds on adsorbents significantly decreases biological availability of adsorbed compounds (Alexander, 1995). Therefore, the adsorption capacity of GAC implemented to biowall systems may not be regenerated by enhanced biological activity and exhausted activated carbon would need to be replenished.

A slight difference in adsorption capacity was reported for peat moss as compared to tested mulches. The K_f of both tested mulches and peat moss was less than 0.5% of that of GAC. The physiochemical properties of peat moss (organic carbon content 49.4% and surface area 0.4 m^2 g^{-1}; Zytner, 1992) were similar to those of tested mulches in this study.

Aggarwal et al., (2006) demonstrated clay minerals and especially smectites as potential sorbents of organic compounds because they are abundant in soils and aquifer materials and have large surface areas. Zhao and Vance (1998) illustrated that organo-clays had roughly 20% organic carbon content, and 15 to 87 m^2 g^{-1} surface areas. Based

on the properties of clays and adsorbed phase TCE on it, mulches have a higher capacity of adsorption than clays.

As a cost-effective substrate, mulches only cost from \$0 – \$0.55 per kilogram, while the price of GAC is \$2.0 – \$4.0 per kilogram (Air Force et al., 2004; Jang et al., 2005). Being both plentiful and in-expensive, mulches showed a high potential to provide adsorption and sequential degradation of TCE from contaminated soil and groundwater.

Figure 4.1 Log-Log PCE Adsorption Isotherm for Different Mulches (●—Pine; ○—Hardwood; ▼—Cypress)

Figure 4.2 Log-Log TCE Adsorption Isotherm for Different Mulches (●—Pine; ○—Hardwood; ▼—Cypress)

Figure 4.3 Log-Log trans-DCE Adsorption Isotherm for Different Mulches (●—Pine;
○—Hardwood; ▼—Cypress)

Figure 4.4 Log-Log cis-DCE Adsorption Isotherm for Different Mulches (●—Pine; ○—Hardwood; ▼—Cypress)

Figure 4.5 Log-Log TCE and PCE Binary Adsorption Isotherm for Different Mulches
(●—Pine; ○—Hardwood; ▼—Cypress)
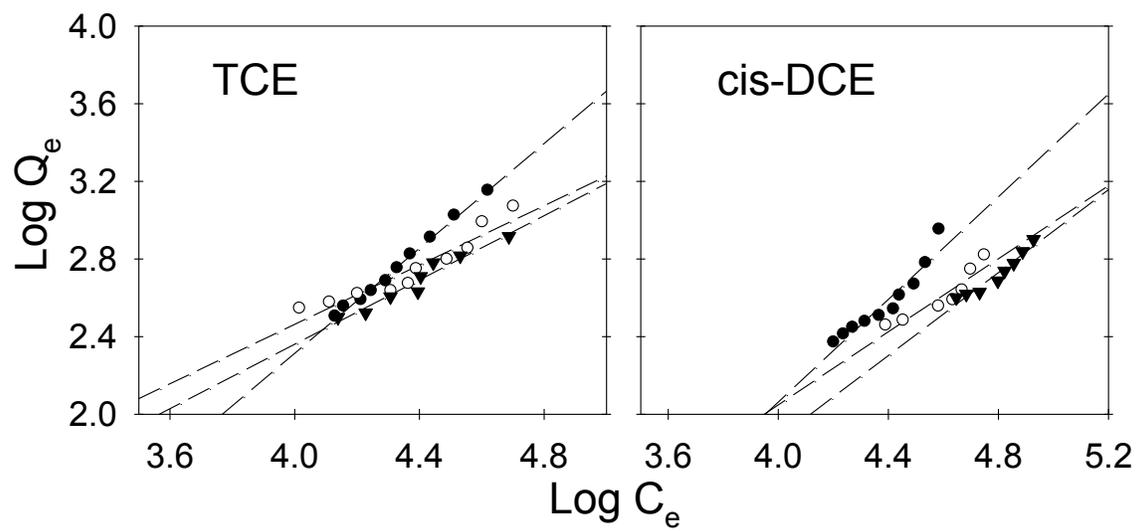
Figure 4.6 Log-Log TCE and cis-DCE Binary Adsorption Isotherm for Different Mulches
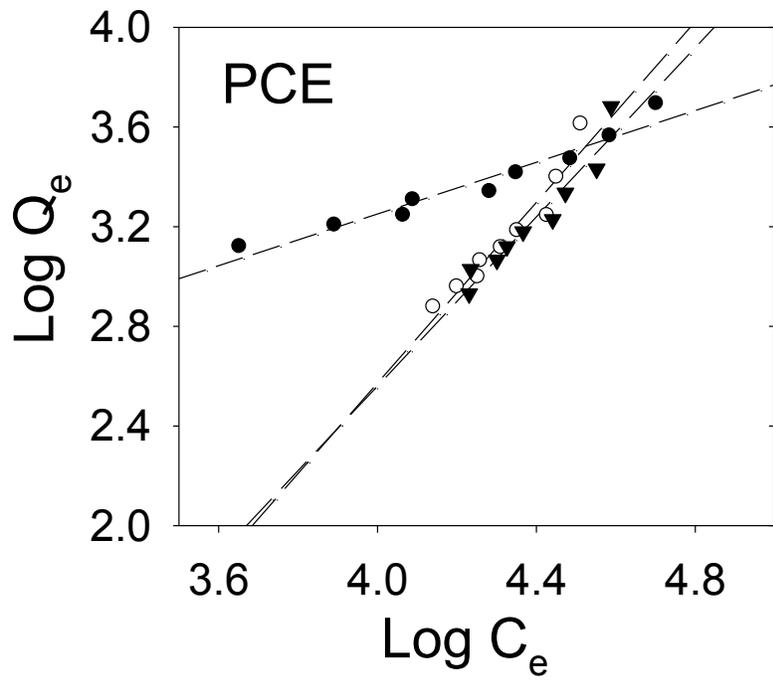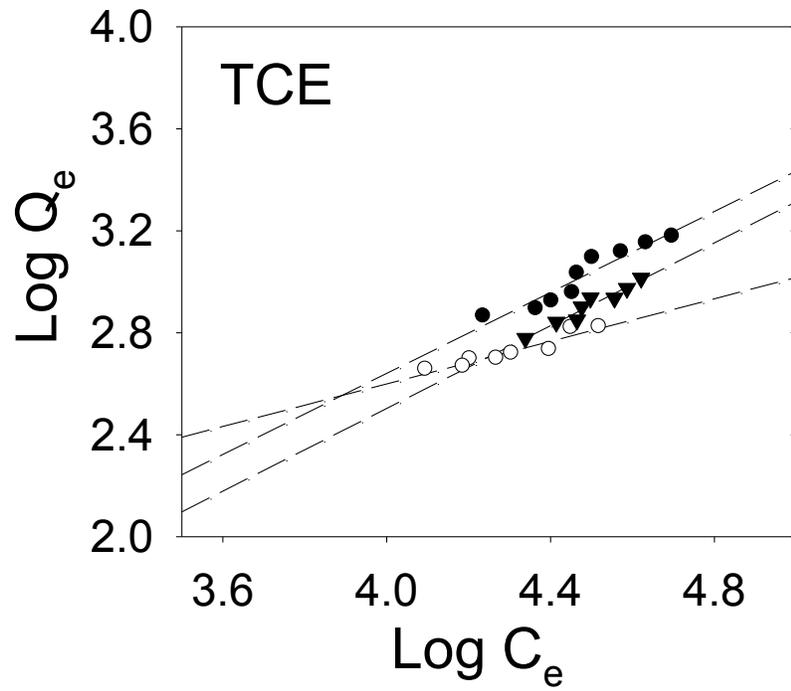(●—Pine; ○—Hardwood; ▼—Cypress)
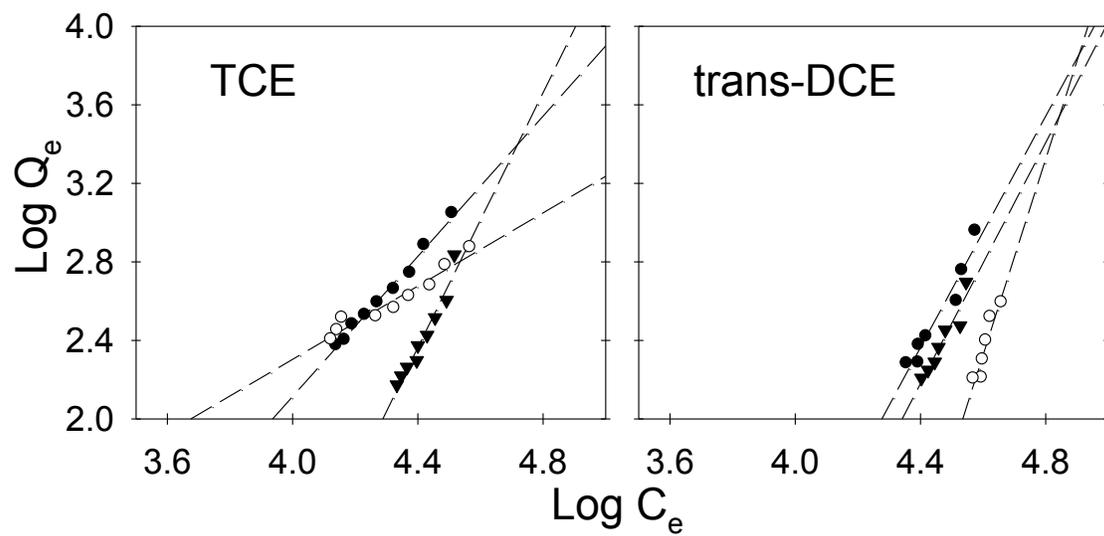
Figure 4.7 Log-Log TCE and trans-DCE Binary Adsorption Isotherm for Different Mulches (●—Pine; ○—Hardwood; ▼—Cypress)
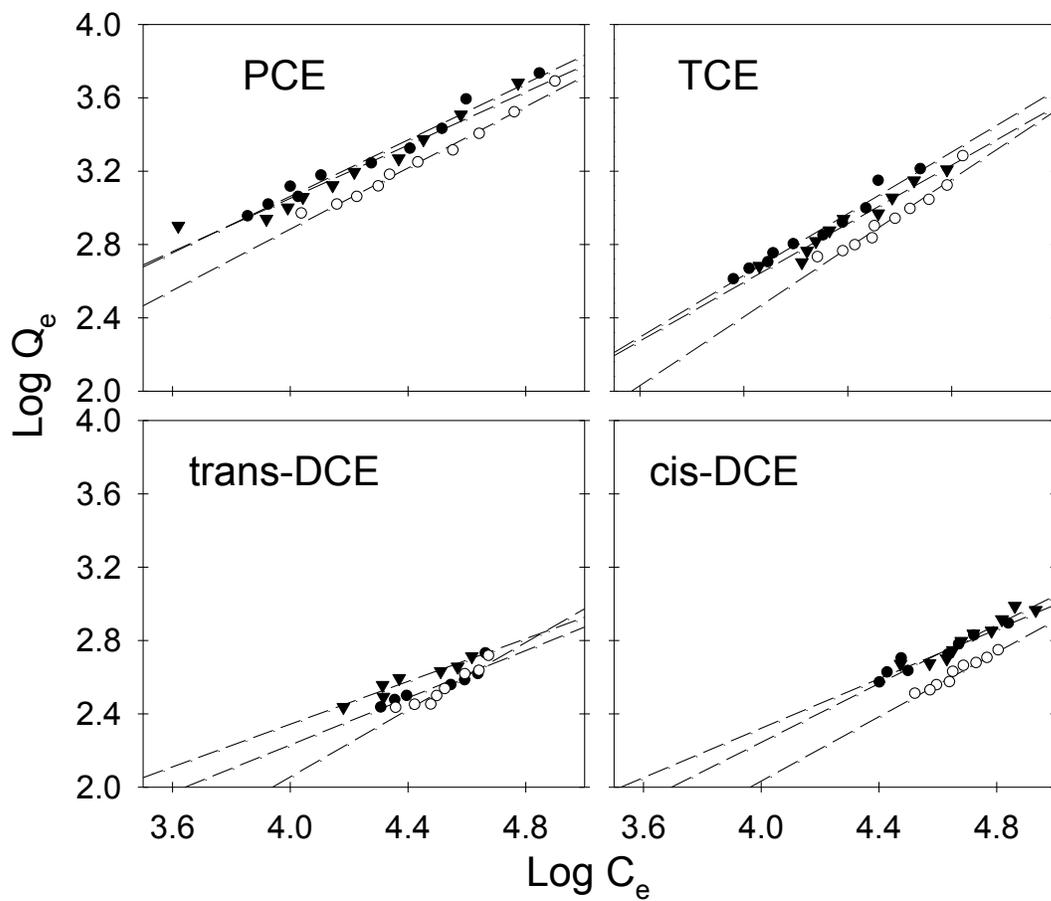
Figure 4.8 Log-Log Quaternary Adsorption Isotherm for Different Mulches (●—Pine;
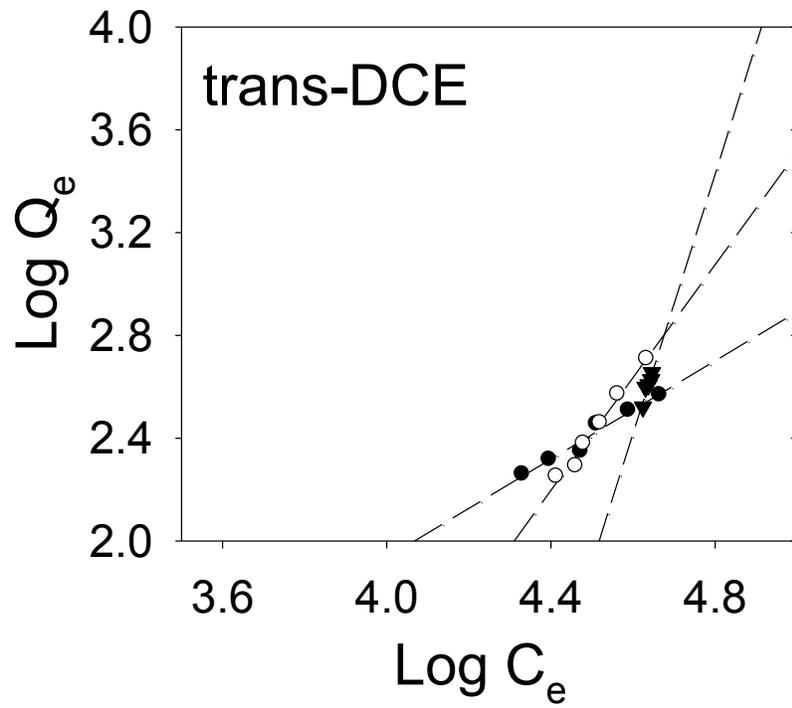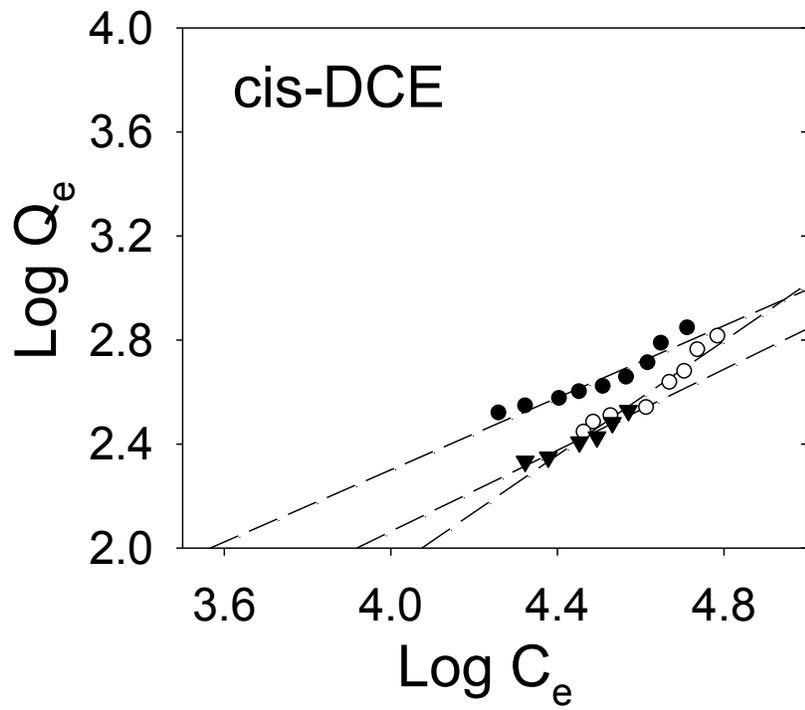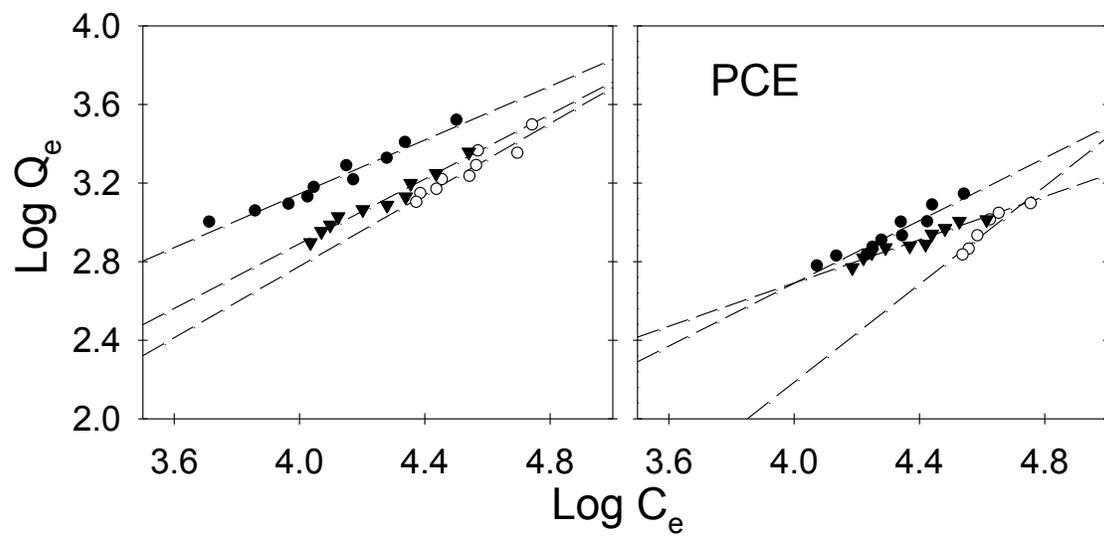○—Hardwood; ▼—Cypress)

Table 4.1 Physicochemical properties of the organic mulches used in this study

Elements	Type of Mulch		
	Pine	Hardwood	Cypress
Carbon (%)	51.62	43.23	19.05
Hydrogen (%)	4.99	5.44	1.98
Nitrogen (%)	0.68	0.31	0.36
Oxygen (%)	43.09	50.65	78.60
Atomic ratio $[(N+O) C^{-1}]$	0.84	1.19	4.14
Atomic ratio $[O C^{-1}]$	0.83	1.17	4.12
BET surface area $(m^2 g^{-1})$	0.6195	1.0972	1.3725
Total pore volume $(cm^3 g^{-1})$	0.0012	0.0078	0.0121
Micro pore volume $(cm^3 g^{-1})$	0.00006	0.00016	0.00008
Meso pore volume $(cm^3 g^{-1})$	0.001119	0.007581	0.011801
Water content (%)	49.4±9.5	55.9±6	36.9±4.6
Biomaterial content (%)	11.2±0.8	14.7±0.4	5.3±0.4
Cation Exchange Capacity (meq $100^{-1}g^{-1}$)	10.8±2.5	42.3±3.4	20.5±2.5
Conductivity (mS cm^{-1}), at 25°C	0.17±0.06	0.36±0.01	0.25±0.01
pH	4.26±0.08	7.43±0.28	5.15±0.06

Note: the data is from Dr. Youngwoo Seo's Ph.D thesis ―Application of Nonionic Surfactant for the Bioremediation of Polycyclic Aromatic Hydrocarbons"

Table 4.2 Langmuir and Freundlich isothem constants and correction coefficients (r^2 values) for single solute adsorption on different mulches. (a. Freundlich isotherm coefficients; b. Langmuir isotherm coefficients)

(a)

Chemical	Pine			Hardwood			Cypress		
	K_f	$1/n_f$	r^2	K_f	$1/n_f$	r^2	K_f	$1/n_f$	r^2
PCE	14.93	0.518	0.943	2.1×10^{-5}	1.813	0.934	5.9×10^{-5}	1.697	0.924
TCE	0.292	0.793	0.907	8.453	0.417	0.900	0.189	0.811	0.944
trans-DCE	0.013	0.956	0.963	3.4×10^{-8}	2.195	0.984	1.6×10^{-21}	5.046	0.889
cis-DCE	0.339	0.647	0.913	0.003	1.098	0.947	0.089	0.692	0.911

(b)

Chemical	Pine			Hardwood			Cypress		
	S_M	K_L	r^2	S_M	K_L	r^2	S_M	K_L	r^2
PCE	1.931	7.8×10^{-5}	0.979	0.552	-0.00013	0.911	0.589	-0.000141	0.971
TCE	1.261	0.00012	0.914	2.398	3.6×10^{-5}	0.914	1.233	-0.000701	0.959
trans-DCE	1.046	0.0006	0.967	0.456	-5.4×10^{-5}	0.985	0.198	-2.9×10^{-5}	0.899
cis-DCE	1.546	9.8×10^{-5}	0.930	0.911	-0.000163	0.946	1.445	0.000146	0.957

Table 4.3 Comparison of Q_e and removal efficiency for different mulches

in single, binary and quaternary experiment

Adsorbates	Mixture Type	Pine		Hardwood		Cypress	
		Q_e ($\mu g\ g^{-1}$)	RE (%)	Q_e ($\mu g\ g^{-1}$)	RE (%)	Q_e ($\mu g\ g^{-1}$)	RE (%)
TCE	Single	1076.0	49.3	540.9	32.5	942.7	39.3
	[a] Binary	999.3	48.5	1104.3	37.4	930.0	43.5
	[b] Binary	1053.3	54.0	974.0	39.1	830.1	41.1
	[c] Binary	768.0	43.6	606.6	33.7	401.2	25.4
	Quaternary	1394.8	51.3	1314.5	34.4	1407.1	43.5
PCE	Single	2181.5	74.1	1300.6	67.7	1511.4	74.5
	[a] Binary	2104.2	73.5	2292.5	60.0	1577.0	70.6
	Quaternary	3879.1	70.9	3295.0	58.0	3215.2	67.7
cis-DCE	Single	696.3	26.2	574.3	21.2	337.4	19.3
	[b] Binary	599.3	30.4	555.0	22.6	688.1	18.0
	Quaternary	916.2	29.0	553.9	17.4	972.0	24.9
trans-DCE	Single	369.1	16.3	510.4	22.1	451.3	28.6
	[c] Binary	571.9	30.7	330.2	16.82	298.1	19.0
	Quaternary	533.5	22.4	516.4	20.9	516.4	23.6

Note: a—binary of TCE and PCE; b—binary of TCE and cis-DCE; c—binary of TCE and trans-DCE; Mulch weight is 1.0g; Initial concentration is 50mg L^{-1}; RE stands for removal efficiency, calculated using equation: $RE = \dfrac{C_o - C_e}{C_o} \times 100\%$.

Chapter 5

Conclusion and Future Work

5.1 Conclusion

Adsorption capacity of pine, hardwood and cypress mulches for PCE, TCE, tran-DCE, and cis-DCE were measured using single, binary and quaternary isotherm tests. According to the isotherm experiment results, PCE showed the highest affinity to all tested mulches, followed by TCE and cis-DCE/trans-DCE. Among the three mulches, pine mulch showed better adsorption capacity for most tested chemicals compared to hardwood mulch and cypress mulch in single solute isotherm tests. High organic carbon content and low polarity of pine mulch may explain its higher effectiveness for chlorinated solvents adsorption over other two tested mulches. Other physicochemical properties of the three tested mulches, such as surface area and total pore volume, were similar and appear to have little effect on the adsorption capacity. In binary and quaternary isotherm tests, adsorption capacity of all tested mulches showed slight differences from single solute tests due to adsorption competition among adsorbates onto adsorbent surfaces. Both Freundlich and Langmuir Isotherm models fit all adsorption isotherm data well. Overall, compared to other adsorbents for the removal of chlorinated

solvents, organic mulches show promising adsorption capacity, economic advantages, and sustainable benefits for TCE bioremediation.

5.1 Future Work

1,1-DCE and VC are also generated during the process of TCE degradation. The adsorption isotherms of both chemicals will be a valuable supplement for this research. After adsorption work, the batch experiments for anaerobic bioremediation of TCE will be conducted using organic mulches as substrates. Dechlorination rates of different batches will be investigated to compare the performance of pine mulch, hardwood mulch, and cypress mulch. Finally, soluble substrates (lactate and vegetable oil) will be used as electron donors to conduct the batch TCE biodegradation experiments. The performance of organic mulches as substrates for TCE removal with these two soluble substrates will ultimately be compared to explore the difference among them.

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Appendix

Appendix A: Experimental procedure for preliminary isotherm

1. 50 mg L^{-1} adsorbate solution was prepared.

2. Six groups of 40 mL vials were prepared. Each group had 3 vials numbered from 1 to 3. Each vial contained 1.0 g mulch inside.

3. Another group of three vials without mulch were prepared as the blank sample.

4. All vials were filled with prepared adsorbate solution to remove gas-phase headspace and sealed with Teflon-lined screw caps.

5. The vials containing adsorbent and adsorbate were placed into the tumbler for mixing at 12 rpm.

6. The samples were harvested at 1day, 2 day, 3 day, 5 day, 7 day and 10 day. 2 mL solution was taken out from each vial and transferred into a 4 mL vial. 2 mL methylene chloride was added into the 4 mL vial for extraction. Then the 4 mL vials were shaken for 5 min.

7. A pipette was used to transfer the methylene chloride solution into the GC vial, and then the liquid phase concentration of adsorbate was measured using a GC/MS.

Appendix B: Experimental procedure for isotherm test

1. 50 mg L^{-1} adsorbate solution was prepared.

2. Ten groups of 40 mL vials were prepared. Each group contained 3 vials numbered from 1 to 3. Each group had a mulch dosage of 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g, 3.0 g, 3.5 g, 4.0 g, 4.5 g, or 5.0 g, respectively.

3. All vials were filled with prepared adsorbate solution to remove gas-phase headspace and sealed with Teflon-lined screw caps.

4. Another group of three vials without mulch were prepared as the blank sample.

5. The vials with adsorbent and adsorbate were placed into the tumbler for mixing at 12 rpm.

6. After all samples reached equilibrium, 2 mL solution was taken out from each vial and transferred into a 4 mL vial. 2 mL methylene chloride was added into the 4 mL vial for extraction. The 4 mL vials were shaken for 5 min.

7. A pipette was used to transfer the methylene chloride solution into the GC vial, and then the liquid concentration of adsorbate was measured using a GC/MS.