BIO-SEPARATOR DESIGN IMPROVEMENTS FOR REMOVAL OF PETROLEUM HYDROCARBONS FROM RUNOFF

By

MICHELLE ANN MELONE

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Thesis Approved:

Dr. Jason R. Vogel

Thesis Adviser

Dr. Glenn O. Brown

Dr. Todd Halihan

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FOREWORD

In the fall of 2013, the Oklahoma State University (OSU) Fire Service Training Center reached out to a senior design team from the Department of Biosystems and Agricultural Engineering at OSU to find a treatment for their runoff that contains liquid fuel. The Fire Service Training Center is an outreach unit of OSU that has a legislative mandate to train emergency responders in proper safety procedures for a wide variety of fire extinguishing scenarios. Aviation grade fire training fuel with low flash point and low emissions is used to train emergency responders to put out liquid fuel fires. Currently, the water and unburned fuel runoff has limited treatment before it enters a retention pond and it overflows on occasion. Thus, an alternative treatment method is critical to lessen the impact of petroleum hydrocarbons on receiving water bodies. The senior design team created the bio-separator, an innovative design utilizing horizontal flow through layers of wood mulch and aggregate that, after limited prototype testing, showed the potential to passively decrease the level of petroleum hydrocarbons in runoff from fire training centers. This thesis 1) completes a comprehensive literature review on treatment options for removing petroleum hydrocarbons from runoff and the performance of wood mulch for stormwater pollutant removal, 2) elucidates on the removal processes of the bio-separator, and 3) investigates design options for enhanced performance of the bio-separator for a defined range of operating conditions.

This thesis follows a traditional format, with an introduction of the bio-separator and justification and objectives for this thesis in Chapter I. Chapter II is a literature review of current fuel contaminated water treatment options and the governing principles of the bio-separator.

Chapter III is the material and methods for improving the bio-separator design. The results and discussion is in Chapter IV. Conclusions and future work recommendations are located in Chapter V.

Name: MICHELLE ANN MELONE

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Abstract: A number of methods exist for removing petroleum hydrocarbons from water to lower the risk to the environment. Firefighting training generates a unique case of immiscible-phase hydrocarbons with intermittent flow, high total petroleum hydrocarbon (TPH) concentrations, and strict regulations. The available treatment options for this contaminated water have a number of disadvantages that include: expense, waste disposal, fluctuating effectiveness, and intensive manual maintenance that make it unsuitable for firefighting training centers. Thus, a bio-separator was designed for remediating the impacts of immiscible-phase hydrocarbon using horizontal flow through a layer of mulch and a layer of aggregate in series. Free-phase hydrocarbon is retained in a fuel storage reservoir while remediated water flows out of an inverted siphon. This research 1) completes a comprehensive literature review on methods for removing petroleum hydrocarbons from runoff and the performance of wood mulch for stormwater pollutant removal, 2) elucidates on the physical and biological removal processes of the bio-separator, and 3) investigates and tests design options for the bio-separator. Using the results from the tests, multiple regression analysis was performed and predictive equations for immiscible-phase hydrocarbon breakthrough time and concentration reduction were found. A case study bio-separator was designed for the Oklahoma State University (OSU) Fire Service Training Center. The results suggest that further work testing the bio-separator at a larger scale is needed before widespread implementation.

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CHAPTER I

INTRODUCTION AND JUSTIFICATION

In an ever urbanizing society, pollution is becoming more and more of a concern for our health and the health of the environment. There are many water contaminants associated with urbanization: nutrients, heavy metals, eroded sediment, petroleum hydrocarbons, etc. Petroleum hydrocarbons, such as fuel and used motor oil, from vehicles are susceptible to washing off roads and entering waterways. It is a reasonable assumption that water polluted with petroleum hydrocarbons can be found adjacent to fueling stations, high traffic roadways, parking lots, and industrial areas. However, surprising to many, live-firefighting training facilities also are associated with petroleum contaminated water. Live-firefighting training facilities are uniquely positioned in that they have strict regulations for runoff that leave the facility, high total petroleum hydrocarbon (TPH) concentrations, and intermittent flow. A biological material passive separator was designed by a senior design team in the Biosystems and Agricultural Engineering Department at Oklahoma State University in 2014 with the intent of treating the unique runoff from live-firefighting training facilities. Hereafter referred to as the bio-separator, it treats immiscible-phase fuel contaminated water through horizontal flow through a layer of mulch and a layer of aggregate in series. The mixture is separated through the mulch and aggregate and fuel is retained in the fuel storage reservoir while remediated water flows out the inverted siphon. Figure 1.1 presents a schematic of the bio-separator design.

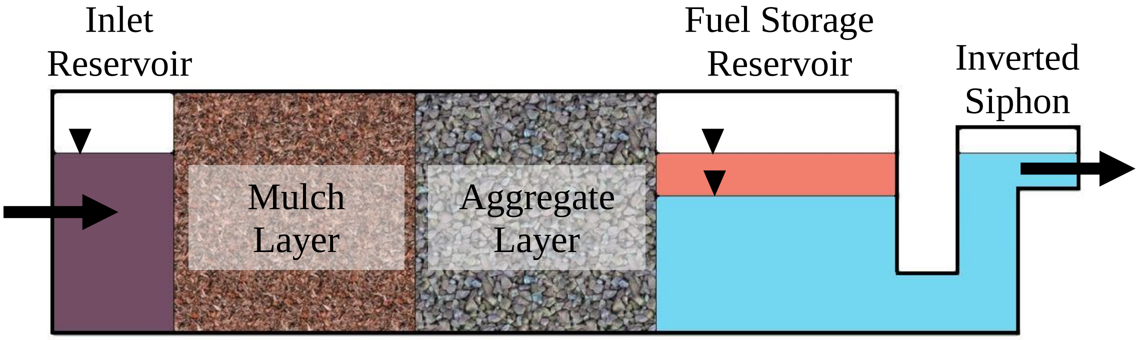

Figure 1.1: Side view schematic of the bio-separator. Arrows indicate flow direction and triangles indicate free surface.

1.1 BACKGROUND AND JUSTIFICATION

1.1.1 Petroleum Hydrocarbons

Total petroleum hydrocarbons is a term used to describe a broad family of chemical compounds associated with crude oil (ATSDR, 1999). Many petroleum hydrocarbons are aliphatic, consisting of simple carbon-hydrogen (hydrocarbon) linear or branched chains. Aliphatic hydrocarbons can be alkanes (single carbon-carbon bonds), alkenes (double carbon-carbon bonds), or alkynes (triple carbon-carbon bonds). Non-aliphatic hydrocarbons, or aromatic hydrocarbons, are included in the TPH category; they can be polycyclic aromatic hydrocarbons (PAH) or monocyclic aromatic hydrocarbons (MAH). These too can contain alkane, alkene, and alkyne bonds. Whether the hydrocarbon is aliphatic or aromatic, they are all considered environmental pollutants. Certain petroleum hydrocarbons pose a higher health risk than others (ATSDR, 1999).

1.1.2 Toxicity of Petroleum Hydrocarbons

1.1.2.1 Exposure to Humans

The Agency for Toxic Substances and Disease Registry states that petroleum hydrocarbons can effect developmental, hematological, immunological, hepatic, and renal organ systems in humans (ATSDR, 2011). Based on human and lab animal studies, benzene and benzo[a]pyrene are human carcinogens whether inhaled or ingested (IARC, 2016). Toluene is a probable human carcinogenic (IARC, 2016). Naphthalene is classified as reasonably anticipated human carcinogen (IARC, 2016).

1.1.2.2 Exposure to Aquatic Organisms

Aquatic organisms accumulate petroleum hydrocarbons in their lipid-rich tissue, which can be detrimental to their health. The bioconcentration factor of lipophilic compounds is the ratio of the concentration in the aquatic organism’s body to that in the surrounding water. The bioconcentration factor of a particular hydrocarbon in the lipid-rich tissue can be estimated by that hydrocarbon’s octanol-water partition coefficient, K_{ow} (Connell and Hawker, 1988; Di Toro et al., 2000). Many studies have researched the lethal concentration required to cause mortality to 50% of test organisms (LC_{50}) for aquatic species for individual petroleum hydrocarbons; EPA’s ECOTOX (ecotoxicology database) contains these references as well as indexes of the organisms tested for LC_{50}.

1.1.3 Petroleum Hydrocarbons Impacted Runoff

Petroleum hydrocarbon impacted water is most likely found near highly urbanized areas such as airports, high traffic roadways and parking lots, live-fire training facilities, and industrial areas. Table 1.1 contains the minimum and maximum TPH concentrations found in impacted runoff from the literature. The highest TPH concentrations in Table 1.1 were found at a municipal maintenance garage and an airport commuter terminal with concentrations of 14 and 28 $mg·L^{-1}$ respectively. Oil and Grease (O&G) concentrations reported from a live-fire training facility had even higher values, 4.4 $mg·L^{-1}$ at the lowest and 730 $mg·L^{-1}$ at the highest (Hylton and Walker, 1989). Though O&G is similar to TPH, the values are not equivalent and O&G cannot be directly compared to TPH.

Table 1.1: Summary of minimum (min) and maximum (max) total petroleum hydrocarbon (TPH) concentrations measured in runoff water in the literature for different runoff sources. ND = Non detected.

Source	**TPH ($mg\cdot L^{-1}$)** **Min Sampled**	**Max Sampled**	**Detection Limit**	**Reference**
Municipal Maintenance Garage	0.026[1]	14[1]	0.026[1]	Thurston, 1999
Urban Area (75% Residential, 12% Open Land, 9% Commercial, 3% Public, 1% Industrial)	0.16	8	Not Specified	Hunter et al., 1979
Airport Runway	0.4	8.8	0.4	USEPA, 2000
Airport Terminal	1.0	3.9	0.4	USEPA, 2000
Airport Commuter Terminal	ND	28	Not Specified	USEPA, 2000
Airport Main Terminal Area	ND	ND	Not Specified	USEPA, 2000
Commercial Area	0.059	5.7	Not Specified	Hoffman et al., 1982
Retention Pond at Live Fire Training Facility	<2.0[2]	44[2]	2.0[2]	Hylton and Walker, 1989
Fuel/Water Separator at Live Fire Training Facility	4.4[2]	730[2]	2.0[2]	Hylton and Walker, 1989

[1] Calculated with the density of Diesel #2: 850 $kg\cdot m^{-3}$

[2] Reported as Oil and Grease, not TPH

1.1.4 Live-Fire Training Centers

Removing petroleum hydrocarbons from water has been researched in the chemical, petroleum, and environmental fields. Research done in the chemical field is usually aimed at separating low concentrations and/or emulsions (Simmons et al., 2002), while the petroleum field is more interested in separating out high concentrations of hydrocarbons from produced water, a byproduct of oil and gas production (Li and Gu, 2005; Frising et al., 2006; Ahmadun et al., 2009). The environmental field has a broad range of goals from cleaning oil spills to improving greywater, which has much lower concentrations of hydrocarbons (El-Masry et al., 2004; Schlieper et at., 2004; Hsieh and Davis, 2005; Hong et al., 2006; Zuma et al., 2008; Avellaneda et al., 2010; Dalahmeh et al., 2011). Firefighting training does not entirely fall into one of the previous mentioned fields since they fill a very specific niche. Their unique characteristics include intermittent flow, high TPH concentrations, and strict regulations.

There are over a hundred live-fire training facilities across the United States (based on a Google® search conducted on July 22, 2016), and these facilities utilize a number of different types of fuel to practice extinguishing fires. A majority of these fuels are specifically composed for training, meaning they will have varying behaviors such as lower emissions, a lower flash point, or a higher resistance to extinguishing. Regardless of the particular composition, all fuels used are hazardous to human health. As an example, some firefighting training centers use kerosene-type jet fuels for liquid-fuel-fire training. They are predominantly composed of aliphatic hydrocarbons in the carbon number range of C_9-C_{16}, containing less than 0.02% of MAHs and no PAHs (ATSDR, 1999). According to the Agency for Toxic Substances and Disease Registry (1999), specific toxicity of jet fuel for humans include eye and skin irritation for acute direct contact and respiratory, neurotoxic, and gastrointestinal effects from acute ingestion as indicated by results from animal studies. The water used to extinguish the fire and unburned fuel will then have a chance to mix and may lead to environment contamination issues that must be addressed.

Currently, there are no published values of TPH concentration in runoff waters from any live-fire training centers. A Biosystems and Agricultural Engineering senior design team from Oklahoma State University (OSU) took several soil and water samples in and around a retention pond which liquid-fuel runoff from a live-fire training center is held. The water samples were taken a day before a scheduled liquid-fuel fire burn and on three burn days: October 15, 2013; October 21, 2013; November 18, 2013; and April 7, 2014. Two or three retention pond water samples were taken on each sampling day. Two water samples were also collected from an adjacent well. Table 1.2 contains the results from the water samples. All water samples were below the TPH detection limit of 10 $mg \cdot L^{-1}$ using Wilks InfraCal TOG/TPH Analyzer Model HATR-T2 and CH User’s Guide. Soil samples were also collected around the retention pond on April 7, 2014. The soil TPH results are reported in Table 1.3 as mg TPH per kg dry soil using Wilks InfraCal TOG/TPH Analyzer Model HATR-T2 and CH User's Guide. The soil sample by the inlet pipe has the highest TPH concentration of 26,849.45 mg·kg^{-1}. The other two samples were taken at the retention pond berm's lowest elevation where water can escape if the retention pond were to overflow. The soil in the shallows had a higher TPH concentration than the soil on the berm, 4505.36 and 1294.30 mg·kg^{-1} respectively. The data have not previously been published.

Table 1.2: Total petroleum hydrocarbon (TPH) concentrations from a retention pond for a liquid-fuel live-fire training center in Stillwater, OK with sampling location and date.

Location Description	**Date Sampled**	**TPH Concentration** (mg·L^{-1})
East of inlet before burn	10/15/2013	<10
West of inlet before burn	10/15/2013	<10
Southeast shallows before burn	10/15/2013	<10
East of inlet after burn	10/21/2013	<10
West of inlet after burn	10/21/2013	<10
Southeast shallows after burn	10/21/2013	<10
East of inlet after burns	11/18/2013	<10
West of inlet after burns	11/18/2013	<10
Southeast shallows after burns	11/18/2013	<10
East of inlet after burn	4/7/2014	<10
Southeast shallows after burn	4/7/2014	<10

Table 1.3: Total petroleum hydrocarbon (TPH) concentration in soil from a retention pond for a liquid-fuel live-fire training center in Stillwater, OK with sampling location and day.

Description	**Date Sampled**	**TPH Concentration** (mg·kg^{-1})
By inlet pipe	4/7/2014	26,849.45
Southeast shore of pond	4/7/2014	1,294.30
Southeast shallows	4/8/2014	4,505.36

The research in removing petroleum hydrocarbons from firefighting training runoff has been little investigated. The answers found in such research could be a valuable addition to what has already been investigated in removing petroleum hydrocarbons from water.

1.1.4.1 Regulations

There are regulations for O&G, though these standards do not apply to petroleum hydrocarbons since the standard test methods quantify triglyceride concentrations (Hoffman et al., 1982). For live-fire training centers, petroleum hydrocarbons are treated as a hazardous material. Oklahoma Department of Environmental Quality Title 252 Chapter 205 Hazardous Waste Management requires renewing permits periodically to lessen the impacts of hazardous waste on the environment (ODEQ, 2015). This is a case by case approach. Live-fire training centers may be required to capture all concentrations of fuel before runoff leaves the facility from storm and burn events.

1.1.5 Objectives

The objectives for this thesis are to

1. complete a comprehensive literature review on treatment options for removing petroleum hydrocarbons from runoff and the performance of wood mulch for stormwater pollutant removal,
2. elucidate on the removal processes of the bio-separator, and
3. investigate design options for enhanced performance of the bio-separator for a defined range of operating conditions.

Enhanced performance is defined by increased fuel removal efficiency and increased breakthrough time, while maintaining a saturated hydraulic conductivity greater than 45 $\mathrm{cm \cdot min^{-1}}$. This is considered a threshold parameter to ensure proper flow through the bio-separator and to prevent unwanted overflow in the inlet reservoir. Fuel breakthrough time is the time that it takes for a continuous flow of free-phase fuel to penetrate the bio-separator’s fuel storage reservoir.

CHAPTER II

LITERATURE REVIEW

There are currently many types of commercially available treatment options for immiscible-phase petroleum hydrocarbons contaminated water on the market. Most of the immiscible-phase treatments can be placed into four different categories; physical, chemical, biological, and membrane treatment. Physical treatment options include oil/water separators, absorbent materials, and skimmers. Chemical treatment options include oxidizers, surfactants, and combustion. Biological treatment options include biostimulation and bioaugmentation. Some of these treatment options are multi-process based, containing aspects from two or more of the categories. Physical and biological treatment are the focus for this review because chemical treatment, in general, is too labor-intensive and membrane treatment is expensive for live-fire training facilities. This sections describe examples of treatment options within the physical treatment and biological treatment categories. Currently available treatment options have a number of disadvantages for live-fire service training facilities including expense, waste disposal, fluctuating effectiveness, intensive manual maintenance. The advantages and disadvantages for each option will be explored.

There are several governing principles that dictate the removal of fuel from water. This literature review will touch on only four: flow through porous media, multiphase flow through porous media, microbial activity, and physical properties of wood mulch.

2.1 PHYSICAL TREATMENT OPTIONS

Physical treatment options for free-phase petroleum hydrocarbons use the difference in fluid properties to treat immiscible-phase petroleum hydrocarbons contaminated water. Gravity settling tanks, adsorptive materials, centrifuges, and electrostatic coalescence treatment are the treatment option examples expounded on in this section.

2.1.1 Gravity Settling Tanks

The most straight forward type of physical separator is a gravity settling tank (Simmons et al., 2002; Frising et al., 2006; Ahmadun et al., 2009). These oil-water separators use the differences in densities between the fluids to its advantage. The fuel coalesces and rises to the top of the gravity settling tank while water escapes through plumbing in the bottom of the tank, trapping the fuel in the apparatus. The holding tanks can be outfitted with additional coalescing technologies such as microwave (Chan and Chen, 2002), ultrasonic (Stack et al., 2005), electrostatic (Eow et al., 2001a; Eow et al., 2001b; Rincón and Motta, 2014), ozonation (Morrow et al., 1999; Hong and Xiao, 2013), fibrous beds (Speth et al., 2002; Li and Gu, 2005), plates (Meon, 1993; Schlieper et at., 2004), baffles (Ni et al., 2002), and thermal treatment. Figure 2.1 is an example of a gravity settling tank with parallel plates. The advantages in using a settling tank are that it can handle water with high concentrations of oil, the oil can be reused, and it is a passive treatment design. Passive designs do not require additional energy to function if there are no additional coalescers or the additions are also passive (fibrous beds, baffles, plates, etc.). Disadvantages are inherent bulkiness, high installation costs, and if the oil is not going to be reused, it must be disposed of which can also be an expense.

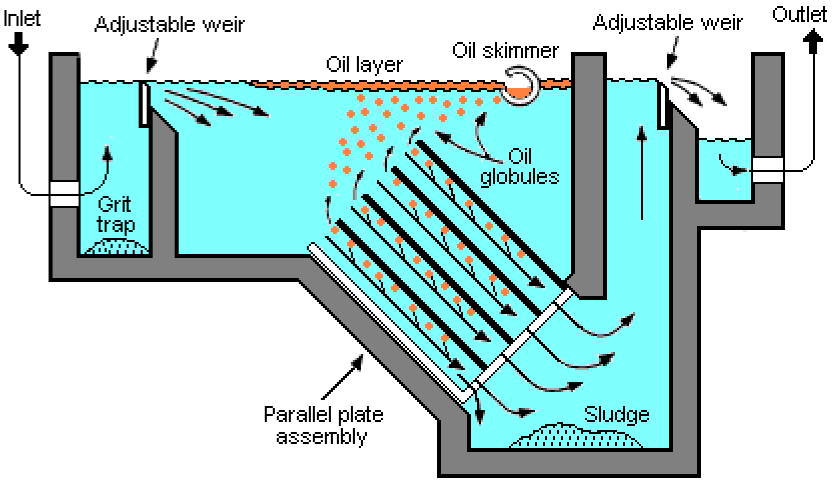

Figure 2.1: Cross-section schematic of a gravity settling tank with tilted parallel plate assembly and weir system to enhance oil removal performance (Milton, 2007).

2.1.2 Adsorptive Materials

Absorptive materials are another common physical treatment. Absorptive materials are used to preserve the physical and chemical characteristics of the oil (Dave and Ghaly, 2011). Typically, the materials are highly hydrophobic and oleophilic. They can come in several different forms: absorptive booms and mats (Dave and Ghaly, 2011), activated carbon and organoclay (Doyle and Brown, 2000), copolymers (Sokker et al., 2011), and resins (Mitchell et al., 1992). The advantages of using absorptive materials are convenience, simple installation, and simple maintenance. The disadvantages are limitations in absorbance, replacement and disposal once the material is saturated, and reoccurring expense from disposal and replacement.

2.1.3 Centrifuges

Centrifuges can be used to separate fluids with different inertias. Hydrocyclones, designed for the separation of water and oil, are growing in popularity in the petroleum industry to treat produced water (Young et al., 1994; Delfos et al., 2004; Huang, 2005). Figure 2.2 is an example of the 1981 double-cone Colman's design, in which the oil-water influent enters through the feed (bottom left) and the oil discharges from the overflow outlet on the left while the water discharges from the underflow outlet on the right. The advantages include their small space requirements and quick results. The disadvantages are that they require energy to pump the influent and the inability to handle oil droplets that have a diameter less than 50 µm (Cumming et al., 1999).

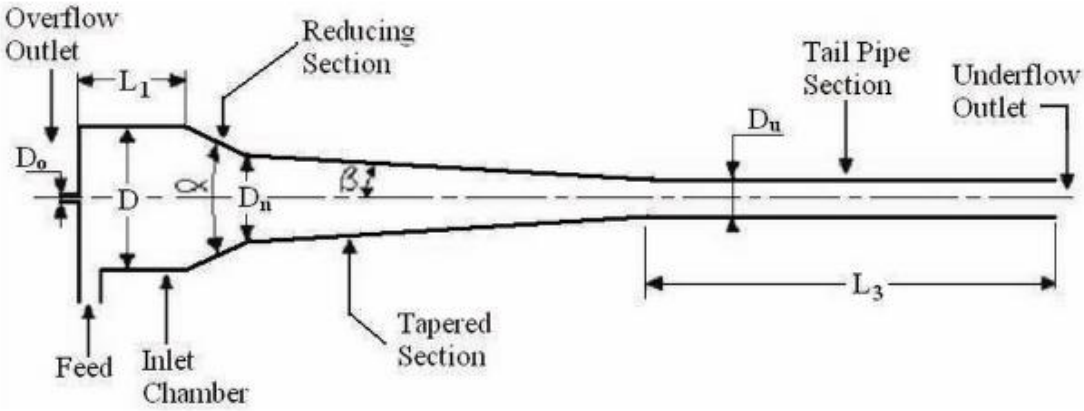

Figure 2.2: Example of a hydrocyclone for separation of oil and water. This particular cross-section is the double-cone Colman's design (Huang, 2005).

2.1.4 Electrostatic Coalescence

Electrostatic coalescence is an emerging technology for the environmental field to encourage oil and water emulsions to coagulate and then be separated. This technology has been utilized in the petroleum industry to remove water droplets from oil (Eow and Ghadiri, 2002); more recently, the research in this technology has shifted to the environmental field to decontaminate water (Vigo and Ristenpart, 2010; Hosseini and Shahavi, 2012). It works by applying an electrostatic field to an emulsion in which the droplets undergo drop charging, agglomeration and then coalescence (Eow et al., 2001a). The advantages for using electrostatic coagulation include high coalescing performance for emulsions, small space requirements, and it is better suited than chemical or other physical treatment options for oil droplet sizes in the nanometer range (Hosseini and Shahavi, 2012). The disadvantages relative to removing oil from water runoff are the relatively high energy required to create the electrostatic field and most of the research has been done on water-in-oil separation rather than oil-in-water separation (Eow et al., 2001a; Eow et al., 2001b; Eow and Ghadiri, 2002; Vigo and Langmuir, 2010; Hosseini and Shahavi, 2012).

2.2 BIOLOGICAL TREATMENT OPTIONS

Biological treatment is appealing for removal of petroleum hydrocarbons from water because it is typically applied to a passive design and is inexpensive. It speeds up natural degradation; given enough time, any contaminant will be effectively decomposed (Dave and Ghaly, 2011).

Biostimulation and bioaugmentation are typical biological treatment methods for fuel contaminated soils (Bento et al., 2005). Biostimulation is the supplementation of a natural system with nutrients to stimulate the resident microbial communities. Bioaugmentation is the supplementation of a natural system with microbial communities to amend the water or soil. The advantages for employing biostimulation or bioaugmentation are in-situ treatment and little maintenance. The disadvantages are performance fluctuations with season, bioavailable nutrients, time, and impracticality for flowing water.

2.3 MULTIPLE PROCESS TREATMENT OPTIONS

Some treatment options for immiscible-phase petroleum hydrocarbons contaminated water use a combination of processes. This section expounds on treatments that contain both aspects of biological and physical treatments. The example treatment options are sand filters, bioretention cells, permeable reactive barriers, and air sparging.

2.3.1 Sand Filters

Sand filters are commonly used to treat polluted water. Sand filters are not only a physical treatment, but they can also be used for biological treatment. For water that is polluted with petroleum hydrocarbons, typically other amendments are added to the sand such as activated carbon (Kalmykova et al., 2014), ozone (Hong and Xiao, 2013), or air to encourage microorganisms' metabolism processes. The advantages for using sand filters are their convenience, simple installation, and little maintenance. The disadvantages are that hydraulic conductivity decreases over time, causing longer hydraulic retention times and decreasing performance with time.

2.3.2 Bioretention Cells

Bioretention cells are an application of low impact development, the practice of restoring an urban environment's hydrology to the natural pre-development hydrology. Bioretention cells collect the stormwater in a depressed area that is filled with high infiltration soils and, in some cases, have an underlying drain. Their purposes are to prolong and lower the peak discharge, encourage infiltration to reduce runoff, and remove contaminants from inflowing water. Figure 2.3 is an illustration of a general bioretention cell design. Petroleum hydrocarbons may be one of many contaminants being targeted for removal (Hsieh and Davis, 2005; Hong et al., 2006; LeFevre et al., 2012). The advantages for using bioretention cells are aesthetic value, relatively minimal maintenance, and passive treatment design. The disadvantages are relatively low hydraulic conductivity and the fact that treatment performance decreases over time and may fluctuate with season and bioavailable nutrients.

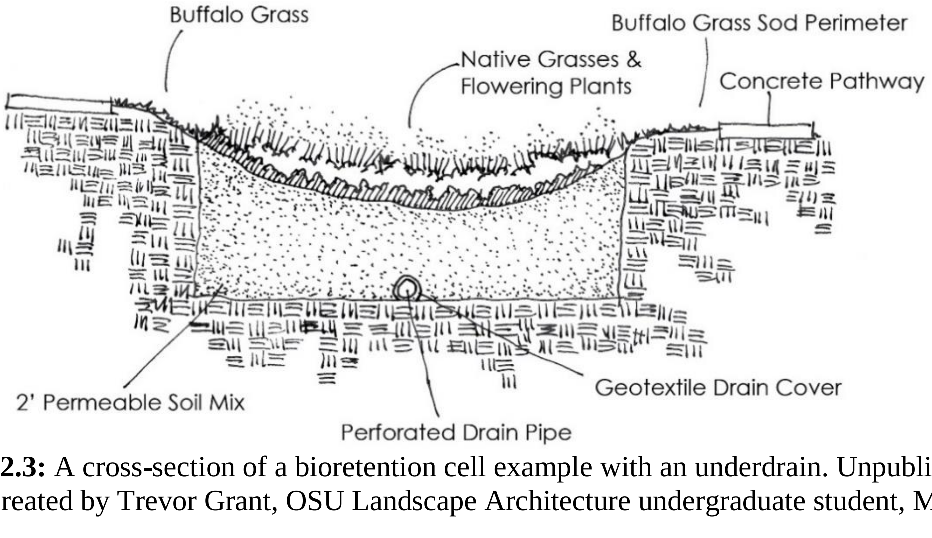

Figure 2.3: A cross-section of a bioretention cell example with an underdrain. Unpublished image created by Trevor Grant, OSU Landscape Architecture undergraduate student, March 2016.

2.3.3 Permeable Reactive Barriers

Permeable reactive barriers (also known as biowalls) are a passive in-situ bioremediation technique used for groundwater; an example diagram is shown in Figure 2.4. The materials used in permeable reactive barriers utilize one or more of the following processes to target specific pollutants in groundwater: sorption and precipitation, chemical reactions, and biologically mediated reactions (Scherer et al., 2000). This technology has effectively treated petroleum hydrocarbons (Guerin et al., 2002; McGovern et al., 2002; Seo et al, 2009; Zhang et al., 2013). Their advantages include cost effectiveness, little maintenance, and passive treatment design. The disadvantages are hydraulic conductivity decreases over time, inherent bulkiness, and it is a defensive treatment rather than an offensive treatment.

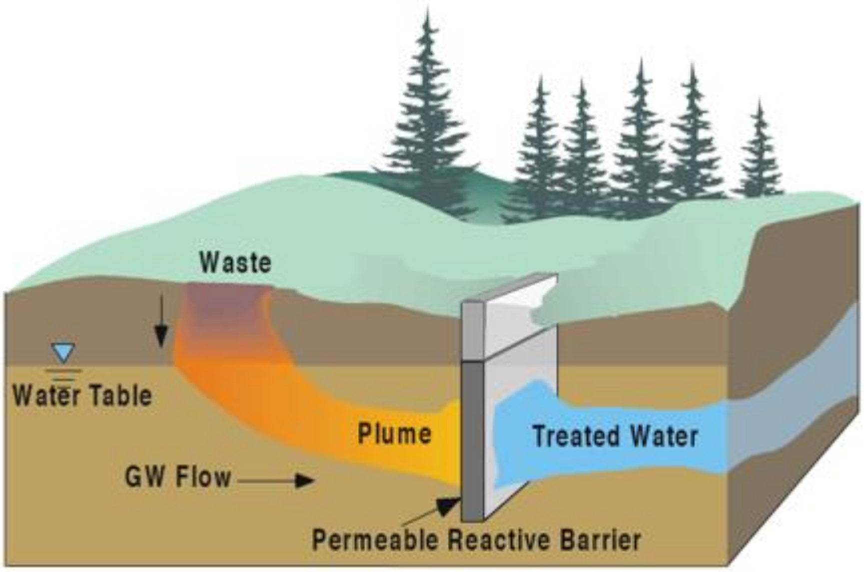

Figure 2.4: Permeable reactive barrier diagram remediating a contaminant plume within a water table (Powell, 2014). GW=Groundwater.

2.3.4 Air Sparging

Air sparging is an in-situ bioremediation technique used for soil and groundwater. Air is pumped into the ground to encourage volatilization and aerobic microbial degradation of immiscible-phase petroleum hydrocarbons. Air-sparging systems typically include an air injection well, air compressor, air extraction well, and vacuum pump (Johnson et al., 1993). Their advantages include simple implementation and fastest treatment of groundwater remediation if the system is properly designed and installed (Marley et al., 1992). Disadvantages include that it is not a passive treatment and it is a defensive treatment rather than an offensive treatment.

2.4 GOVERNING PRINCIPLES

There are several governing principles that dictate the removal of fuel from water. This literature review will discuss four that are primarily applicable to this research: single-phase flow through porous media, multiphase flow through porous media, microbial activity, and physical properties of wood mulch.

2.4.1 Single-phase Flow through Porous Media

The general approach to quantifying single-phase flow through porous media is by Darcy's law. This assumes complete saturation of the porous media; the pore space between the particles making up the medium is completely filled with the wetting phase, typically water. Figure 2.5 is a diagram of Darcy's tube with the parameters for the Darcy-Buckingham equation labeled. The Darcy-Buckingham equation for single-phase flow is,

$$Q = -k_{Sat}\frac{h_a - h_b}{L} * A \tag{2.1}$$

where Q is the flowrate of the phase, k_{Sat} is saturated hydraulic conductivity of the medium, A is cross-sectional area, h_a-h_b is pressure head loss, and L is the length of the media (Brown, 2002).

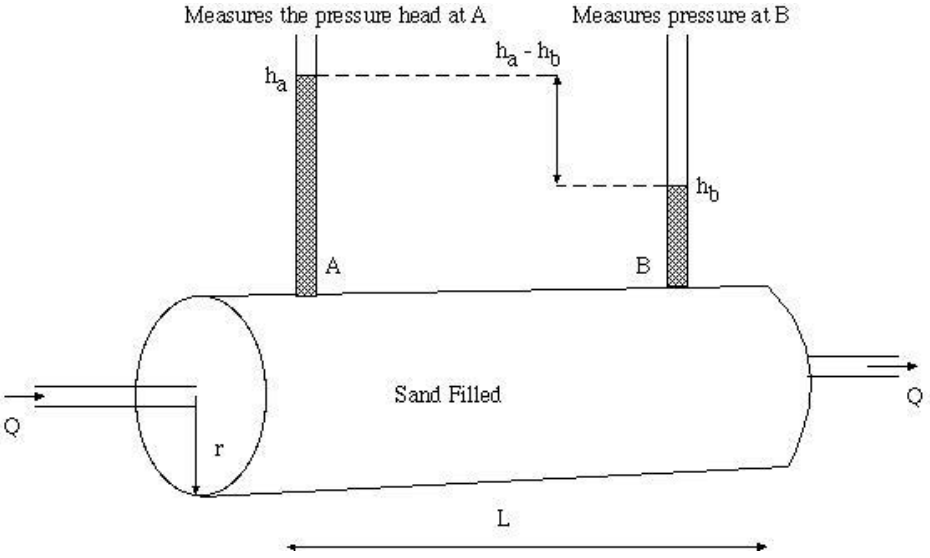

Figure 2.5: Darcy's tube diagram for single-phase flow through porous media. A and B are location points, r is radius, Q is volumetric flowrate, L is length, and h_a and h_b are the pressure heads at points A and B. (Lecture 9: Darcy's Law).

2.4.2 Multi-phase Flow through Porous Media

2.4.2.1 Modified Darcy-Buckingham for Multi-phase Flow

In single-phase flow, the absolute permeability (k) is the ability of the porous media to be penetrated and is only a function of the geometry of the media, not the characteristics of the fluid. Brooks and Corey (1964) define the effective permeability (k_{ei}) as the permeability of a particular fluid (phase i) when the porous media is occupied by more than one phase. The modified version of the Darcy-Buckingham equation for multi-phase flow is,

$$q_i = -k\frac{k_{ri}(S_i)}{\mu_i}\left(\frac{dP_i}{dz} + \rho_i g\right) \tag{2.2}$$

where q_i is the velocity of the phase, S_i is the phase saturation of pore volume, μ_i is the phase viscosity, dP_i/dz is the pressure gradient within the phase, ρ_i is the phase density, and g is the gravity constant (Dehghanpour and DiCarlo, 2013). It is assumed that the movement of the phase is dependent on the pressure gradient within the phase and gravitational forces (if the flow being observed is in the vertical direction).

The multi-phase Darcy equation is the most straight forward approach to finding the relative permeability of oil, but is not the most accurate. Many other flow models are extensions of Darcy's law in which they model each phase separately and assume the pressure gradients between the two phases are related by capillary pressure.

2.4.2.2 Stone's Model I and II

Stone's Models I and II are used regularly in the oil and gas field. Stone started the trend of extrapolating two-phase models into three-phase models. His models assume that the relative permeability of a phase is only a function of its own saturation (Stone, 1973). The most common version to calculate residual oil saturation (S_{ro}) is Stone's Model I with a normalization proposed by Aziz and Settari (1979) given in,

$$S_{ro} = \frac{S_{oe} k_{row} k_{rog}}{k_{rowi}(1-S_{we})(1-S_{ge})} \tag{2.3}$$

Where S_{oe} is the effective oil saturation, k_{row} is the two-phase oil relative permeability after water flooding, k_{rog} is the two-phase oil relative permeability after air is allowed to enter, and k_{rowi} is the two-phase oil relative permeability with irreducible water. The i phase effective saturation (S_{ie}) is given by Equations (2.4), (2.5), and (2.6) for oil, water, and gas respectively,

$$S_{oe} = \frac{S_o - S_{om}}{1 - S_{wi} - S_{om}} \tag{2.4}$$

$$S_{we} = \frac{S_w - S_{wi}}{1 - S_{wi} - S_{om}} \tag{2.5}$$

$$S_{ge} = \frac{S_g}{1 - S_{wi} - S_{om}} \tag{2.6}$$

where S_{wi} is the initial water saturation and S_{om} is the residual oil saturation in three-phase flow. This model assumes that the water saturation and initial water saturation are the same.

2.4.2.3 Baker's Model

Another three-phase model that is modified from extrapolating two-phase data is Baker's model, which is based on saturation weighted interpolation between two-phase values (Blunt, 2000). Baker's solution to finding oil relative permeability is,

$$k_{ro} = \frac{(S_w - S_{wi})k_{row} + (S_g - S_{gr})k_{rog}}{(S_w - S_{wi}) + (S_g - S_{gr})} \tag{2.7}$$

where S_{gr} is the residual gas saturation.

2.4.2.4 Flow Coupling

The previously mentioned models are all Darcy-derived, but do not take into account the interactions between fluids. Flow coupling is the viscous interaction between the two liquids. It is also called layer drainage, double drainage, and viscous flow in the literature. The term encompasses the dragging forces between the fluids. Flow coupling is not critical when the oil saturation is high, but becomes the dominating factor when oil saturation is low and water saturation is significant (Dehghanpour and DiCarlo, 2013). Figure 2.6 illustrates the types of drag that the water exerts on the oil, friction drag and form drag. Friction drag is due to the velocity and surface differences between the water and oil. Form drag is due to the wake from the water towing the oil behind it.

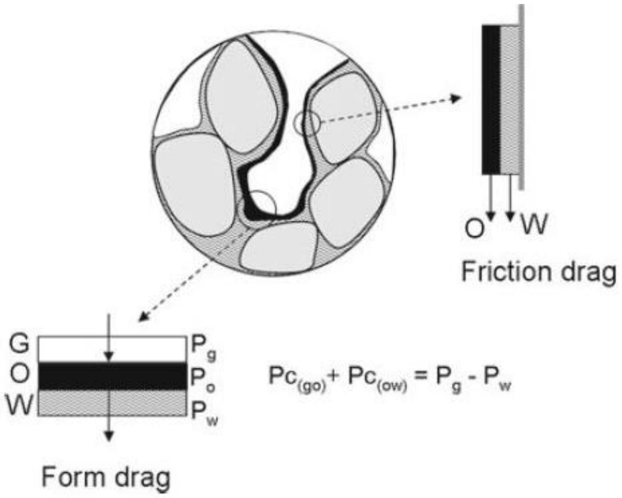

Figure 2.6: Schematic of oil/water flow coupling in porous media (Dehghanpour et al., 2013). G = gas, O = oil, W = water, P_g = gas pressure, P_o = oil pressure, P_w = water pressure, $Pc_{(go)}$ = capillary pressure between gas and oil phases, and $Pc_{(ow)}$ = capillary pressure between oil and water phases.

Layer drainage has only recently been introduced to relative permeability modeling. Blunt (2000) was the first to include this phenomenon in his empirically derived three-phase relative permeability model which was a modification of Baker's model. He suggested that layer drainage is best suited for media that has oil spreading and is water-wet which might imply low oil saturations. Long periods of time or high capillary pressure are needed to reach low saturations of oil in pores. As there was no previous experimental research involving high capillary pressures for oil permeability, there was little data for low oil saturations. In Blunt's research, the method used to quantify layer drainage was to extrapolate experimentally found oil permeability curves to lower saturation levels. The extrapolation took into account gas permeability and saturation because Blunt assumed gas was the main factor for layer drainage.

Blunt further modified Baker's model by including trapping of oil/gas and miscible/near-miscible flows. To solve Blunt's equations for oil relative permeability, three two-phase experiments need to be completed to find each of the six relative permeabilities. One experiment to solve oil-water with residual gas saturation (to find k_{row} and k_{rwo}), one experiment to solve oil-gas with residual water saturation (to find k_{rog} and k_{rgo}), and one experiment to solve water-gas with residual oil saturation (to find k_{rgw} and k_{rwg}). Once these parameters are found, oil relative permeability, along with water and gas, can be calculated using the method that Blunt laid out in detail in his paper (2000).

2.4.3 Microbial Activity

Over time, material will naturally propagate microorganisms that use the carbon in petroleum products as their electron donor (energy source) and/or carbon source. Some aerobic and anaerobic microorganisms use *n*-alkanes found in petroleum products as their sole energy and carbon source (Jones and Edington, 1968; Coates et al., 1997; Hamamura and Arp, 2000; Prenafeta-Boldú et al., 2001; Jung et al., 2002; Balachandran et al., 2012). The relative ease for microorganisms to degrade a petroleum hydrocarbon compound depends on the type of hydrocarbon. Aromatic compounds are generally harder to degrade than aliphatic (Evans et al., 1996). Branched aliphatic are generally harder to degrade than alkanes of a similar molecular weight (Aelion and Bradley, 1991). Higher *n*-alkanes are generally harder to degrade than lower *n*-alkanes (Jung et al., 2002). The rate a compound is degraded also depends on nutrient availability and the environment’s electron acceptor, be it aerobic, anoxic, or anaerobic.

2.4.4 Wood’s Water Pollutant Removal Capabilities

Wood has been investigated as an inexpensive treatment medium for many classes of pollutants. A list of pollutants that mulch or woody material has been shown to effectively remove from water is given in Table 2.1.

For heavy metal removal, mulch and wood products have proven effective (Bailey et al., 1999; Jang et al., 2005; Ray et al., 2006; Seelsaen et al., 2006; Edwards et al., 2009). Wood mulches have also been used to treat water with excess nutrients, mainly nitrate but also sulphate, ammonia, ammonium, nitrite, and orthophosphorus (Robertson et al., 2000; Kim et al., 2003; Savage and Tyrrl, 2005; Gibert et al., 2008; Edwards et al., 2009; Xuan et al., 2010; Saeed and Sun, 2011; Camilo et al., 2013; Frank et al., 2015). Several studies have investigated the use of wood mulch to remove pesticides (Bras et al., 1999; Trapp et al., 2001; Huang et al., 2006; Camilo et al., 2013). Other pollutants that wood mulch can treat include: explosives such as Trinitrotoluene (TNT), Rapid Detonating Explosive (RDX), and octogen (HMX) (Ahmad et al., 2007); surfactants (Seo et al., 2009); and other halocarbons (Trapp et al., 2001; Boving and Zhang, 2004; Ray et al., 2006; Shenl et al., 2010).

Table 2.1: Literature summary of pollutant removal from water by wood mulch. TPH = total petroleum hydrocarbons, PAH = polycyclic aromatic hydrocarbon, MAH = monocyclic aromatic hydrocarbon, Cd = Cadmium, Cr = chromium, Hg = mercury, Pb = lead, Mn = manganese, Cu = copper, Zn = zinc, WQ = water quality, BOD = biochemical oxygen demand, COD = chemical oxygen demand, SS = suspended solids, and TSS = total suspended solids.

	Target Pollutant	**Wood Type(s)**	**Research Focus**	**Reference**
TPH	PAH (anthracene), MAH (naphthalene and pyrene)	Aspen wood fibers	Wood Sorption Capacity	Boving and Zhang, 2004
	MAH (benzene, toluene, and o-xylene)	Douglas fir and Ponderosa pine	Wood Sorption Capacity	MacKay and Gschwend, 2000
	MAH (naphthalene and benzopyrene)	Hardwood mulch (combination of Silver Maple, Norway Maple, Red Oak, and Cherry)	Heavy metal and organic removal	Ray et al., 2006
	PAH (phenanthrene and pyrene)	Hardwood bark mulch	Biofilm Barrier for groundwater	Seo et al., 2009
	MAH (benzene, phenol, xylene, and naphthalene)	Willow branches, oak branches	Wood Sorption Capacity	Trapp et al., 2001
Heavy Metals	Cd, Cr(III), Cr(VI), Hg, Pb	Multiple (review paper)	potentially low-cost sorbents for heavy metals	Bailey et al., 1999
	Mn	Chipped wood mulch	Bioreactor for mine drainage	Edwards et al., 2009
	Cu, Pb, Zn	Cypress bark, hardwood bark, pine bark nugget	Urban runoff	Jang et al., 2005
	Cu, Cd, Cr, Pb, Zn	Hardwood mulch	Heavy metal and organic removal	Ray et al., 2006
	Cu, Zn, Pb	Packing wood	Urban runoff	Seelsaen et al., 2006
WQ Indicators	BOD, COD, SS	Multiple types (review paper)	Greywater treatment	Dalahmeh et al., 2011
	BOD	Eucalypt wood mulch	Constructed wetland	Saeed and Sun, 2011
	BOD	Wood mulch	Biofiltration for compost liquor	Savage and Tyrrl, 2005
	BOD, COD, TSS	Wood mulch	Greywater treatment	Zuma et al., 2009

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	Target Pollutant	Wood Type(s)	Research Focus	Reference
Nutrients	Ammonia, nitrate, nitrite, orthophosphorus	Wood chips and fibers	Septic tank leachate	Xuan et al., 2010
	Ammonia, Ammonium	Wood mulch	Biofiltration for compost liquor	Savage and Tyrrl, 2005
	Nitrate	Pine wood mulch and wheat straw	Bioreactors	Camilo et al., 2013
		Pine bark mulch	Landfill leachate	Frank et al., 2015
		Softwood (branches and bark), hardwood chips & branches, coniferous twigs and leaves, mulch (wood chips, shredded bark, and topsoil), willow wood chips, compost, and beech leaves	Permeable Reactive Barrier for groundwater	Gibert et al, 2008
		Wood chips	Bioretention for urban runoff	Kim et al., 2003
		wood mulch, sawdust, leaf compost	Permeable Reactive Barrier for groundwater	Robertson et al., 2000
		Eucalypt wood mulch	Constructed wetland	Saeed and Sun, 2011
	Sulphate	Chipped wood mulch	Bioreactor for mine drainage	Edwards et al., 2009
Pesticides	heptachlor, aldrin, endrin, dieldrin, DDD, DDT, DDE	Pine bark	Halocarbon pesticide removal	Bras et al., 1999
	atrazine, bentazone	Pine wood mulch and wheat straw	Bioreactors	Camilo et al., 2013
	diuron, isoxaben, oryzalin, clopyralid	Shredded cedar mulch	Herbicide removal	Huang et al., 2006
	DDT	Willow branches, oak branches	Wood Sorption Capacity	Trapp et al., 2001

Table continued on next page

	Target Pollutant	Wood Type(s)	Research Focus	Reference
Other Halocarbons	Fluorene	Aspen wood fibers	Wood Sorption Capacity	Boving and Zhang, 2004
	1,3-Dichlorobenzene, butylbenzylphthalate, and fluoranthene	Hardwood mulch (combination of Silver Maple, Norway Maple, Red Oak, and Cherry)	Heavy metal and organic removal	Ray et al., 2006
	Surfactant	Hardwood bark mulch	Biofilm Barrier for groundwater	Seo et al., 2009
	Trichloroethylene	Shredded tree mulch and cotton gin trash	Permeable Reactive Barrier for groundwater	Shenl et al., 2010
	1,2-Dichlorobenzene, 1,3,5-Trichlorobenzene, and chlorobenzene	Willow branches, oak branches	Sorption of lipophilic organic compounds	Trapp et al., 2001
Explosives	TNT, RDX, HMX	Pine bark, pine mulch	Permeable Reactive Barrier for groundwater	Ahmad et al., 2007

2.4.4.1 Wood's Sorption Capacity for Petroleum Hydrocarbons

Wood's sorption capacity can be expressed by capillary flow, which is the movement of liquid by capillary action. Washburn (1921) defined capillary action for straight cylindrical tubing as,

$$l^2 = \frac{\gamma\ D\ cos(\theta)}{4\eta} t = Kt \tag{2.13}$$

where l is the length the fluid traveled, γ is the surface tension, D is the tube diameter, t is time, θ is the contact angle, η is the dynamic viscosity, and K is referred to as the Washburn slope. The Washburn equation, that assumes straight capillary tubes, can be adapted for use in porous media that have tortuous connecting pores. In fibrous materials, such as wood mulch, the pore spaces are irregular. This can cause variations in the effective pore diameter and contact angle. Wålinder and Gardner (1999) examine the factors influencing effective pore radius and contact angle in spruce chips with several different wetting fluids. They used fluids that have low surface tensions, methanol and hexane, with an effective contact angle of zero. From those experiments, the effective pore diameter for the spruce chips was found. For diiodomethane, ethylene glycol, and hexane, there is an initial delay of capillary rise and then capillary rise occurs at a constant rate. This behavior may be due to the initial disturbances caused by the immersion of the column in the liquid (van Oss et al., 1992).

Staples and Shaffer (2002) present an equation that was catered to capillary rise in porous media rather than using the Washburn equation that was intended for straight cylindrical tubing. This was done by testing the wetting front of saline in uniform glass bead beds to find the simplistic flow front model,

$$\ln\left(l - \frac{l}{l_{eq}}\right) + \frac{l}{l_{eq}} = -\frac{D_{vis}^2\ \rho g}{32\eta l_{eq}} t \tag{2.14}$$

where D_{vis} is the diameter at the throat that limits viscous drag, ρ is the fluid density, g is the gravity constant, t is the time, and l_{eq} is the equilibrium length which is a function of surface tension, contact angle, throat diameter, density, and gravity given by,

$$l_{eq} = \frac{4\gamma cos\theta}{D_{cap}\rho g} \tag{2.15}$$

where D_{cap} is the diameter at the largest portion of the tube that limits capillary pressure.

Wood has been found to be effective at removing petroleum hydrocarbons from water. Column and batch studies for petroleum hydrocarbons, specifically PAH and MAH, removal by sorption to wood products from contaminated water has been investigated by MacKay and Gschwend (2000), Trapp et al. (2001), Boving and Zhang (2004), Hong et al. (2006), Ray et al. (2006), and Seo et al. (2009).

Trees can be categorized as either softwoods and hardwoods. Softwoods are coniferous trees that produce their seeds in cones. Examples of softwoods are cedar, redwoods, and pine. Hardwoods are flowering trees that produce their seeds in fruit. Some hardwoods are denser than others and are further separated as soft hardwoods and hard hardwoods. Examples of soft hardwoods include cottonwoods, balsa, and willows. Examples of hard hardwoods include oak, hickory, and mahogany. Softwoods generally have higher amounts of lignin than hardwoods. Lignin is lipophilic making it important in the woody product's role of sorbing hydrocarbons. MacKay and Gschwend (2000) found that two different softwoods, Douglas fir and Ponderosa pine, had a high equilibrium sorption capacity for benzene, o-xylene, and toluene. They also combined the work of Stamm and Millet (1941), Garbarini and Lion (1986), Xing et al. (1994), and Severtson and Banerjee (1996) to determine a relationship between the lignin-water partition coefficient of the wood (K_{lignin}) and octanol-water partition coefficient of the chemical (K_{ow}). The additional chemicals include other petroleum hydrocarbons and chlorocarbons such as phenol, trichloroethylene, dichlorophenol, and trichlorophenol. The best fit regression for K_{lignin} and K_{ow} of the data that MacKay and Gschwend (2000) compiled is,

$$\log K_{lignin} = 0.74(\pm 0.09)\log K_{ow} - 0.04(\pm 0.25) \quad (2.8)$$

where K_{lignin} is in $(\text{mol}\cdot\text{g}_{\text{lignin}}^{-1})\cdot(\text{mol}\cdot\text{mL}_{\text{water}}^{-1})^{-1}$ and K_{ow} is in $\text{mL}\cdot\text{g}^{-1}$. Trapp et al. (2001) expanded on MacKay and Gschwend's (2000) work by analyzing the sorption capacity of common oak (hard hardwood) and basket willow (soft hardwood) for more petroleum hydrocarbons and halocarbons: phenol, benzene, chlorobenzene, naphthalene, 1,2-Dichlorobenzene, lindane, 1,3,5-Trichlorobenzene, dieldrin, and dichlorodiphenyltrichloroethane (DDT). To compare the regression lines, Equation 2.7 was adjusted to represent the lignin content of softwood with the assumption that 30% of softwood is made up of lignin (Equation 2.9). Equation 2.10 and 2.11 are the best fit regression for K_{lignin} and K_{ow} of oak and willow respectively (Trapp et al., 2001). Boving and Zhang (2004) did a similar study with aspen wood fibers and PAHs – pyrene, anthracene, fluorine, and naphthalene (Equation 2.12).

Softwood: $$\log K_{wood} = 0.74\log K_{ow} - 0.56 \quad (2.9)$$

Oak: $$\log K_{wood} = 0.632(\pm 0.063)\log K_{ow} - 0.27(\pm 0.25) \quad (2.10)$$

Willow: $$\log K_{wood} = 0.668(\pm 0.103)\log K_{ow} - 0.28(\pm 0.40) \quad (2.11)$$

Aspen fibers: $$\log K_{wood} = 0.59(\pm 0.08)\log K_{ow} - 0.23(\pm 0.20) \quad (2.12)$$

where K_{wood} is the wood-water partition coefficient $((\text{mol}/\text{g}_{\text{wood}})(\text{mol}/\text{mL}_{\text{water}})^{-1})$. Trapp et al. (2001) found that, statistically, the softwood, oak, and willow equations are not significantly different.

2.4.4.2 Shape of Wood Particle on Petroleum Hydrocarbon Removal

The shape and size of the wood particles can also contribute to the effective sorbing capacities. Time of sorptive equilibrium increased with particle size for toluene (MacKay and Gschwend, 2000). Ponderosa pine and Douglas fir shavings exhibited fastest uptake times followed by sticks and then chips (MacKay and Gschwend, 2000).

2.4.4.3 Unanswered Questions in the Literature

There are still some unanswered questions in the literature regarding wood's pollutant removal capabilities. Some questions include:

- What is the effect of moisture content on wood's ability to remove contaminants?
- What is the effect of temperature, humidity, solar radiation, and wind speed wood's ability to remove contaminants?
- How well can wood remove other pollutants such as pathogens and arsenic that have not been previously investigated?
- How well can wood remove aliphatic petroleum hydrocarbons?

Several studies have researched mulch's capacity to remove PAHs and MAHs, but limited research has been conducted on removal of petroleum hydrocarbons that are aliphatic hydrocarbons. This research fills that literary gap by testing the removal efficiency of red cedar mulch for a kerosene-type jet fuel.

CHAPTER III

MATERIALS AND METHODS

The bio-separator has been tested for a variety of parameters and using a laboratory-scale prototype for single events and back-to-back events. Specific analyses that were completed include E-III™ Aviation Grade Fire Training Fluid concentration analysis, mulch water-content determination, saturated hydraulic conductivity determination, and mulch liquid-uptake.

3.1 BIO-SEPARATOR

The bio-separator uses filtration and adsorption in a passive system to treat free-phase fuel contaminated water. It achieves this from horizontal flow through a layer of mulch and a layer of aggregate in series (Figure 3.1). Polluted water flows through the inlet reservoir (left side of the image) and then into the biomaterial. The filtered water exits the apparatus via an inverted siphon (right side of the image), while the lighter density fuel is stored in the storage reservoir for recovery. The reservoirs, aggregate layer, and mulch layer are separated by screens. Two lab-scale prototype bio-separators were used: a small bio-separator and a large bio-separator (shown in Figure 3.1). The total dimensions and section length dimensions for the small and large bio-separator are located in Table 3.1.

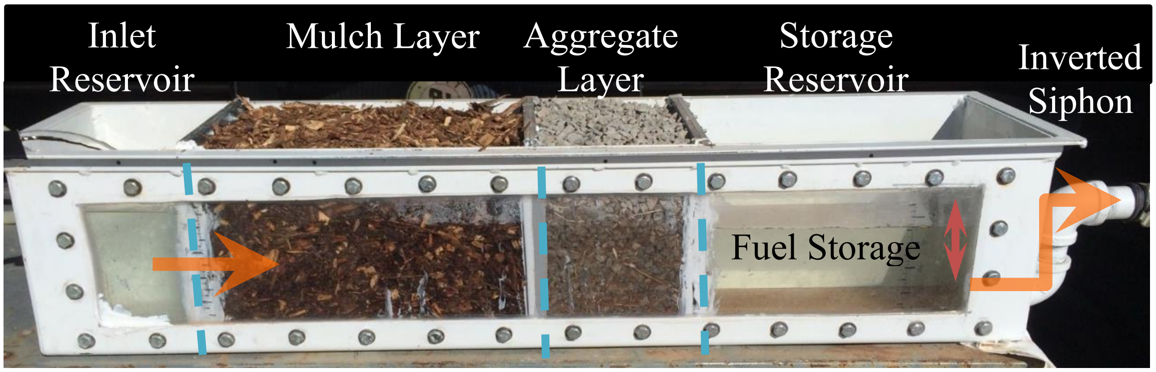

Figure 3.1: Side view of the large bio-separator with a mulch layer length of 31 cm containing chipped eastern red cedar mulch and aggregate layer length of 15 cm containing crushed limestone (size #8). The orange arrows show direction of flow, the double-sided red arrow indicates the fuel storage and the blue dotted lines are the locations of the screens.

Table 3.1: Total dimensions and section length dimensions of the two lab-scale prototype bio-separators. The small bio-separator was used for single material tests and the large bio-separator was used for dual-material length-proportion tests.

	Total Dimensions			**Length of Sections**		
Testing Prototype	**Height**, m (in)	**Width**, m (in)	**Length**, m (in)	**Inlet Reservoir**, m (in)	**Material**, m (in)	**Storage Reservoir**, m (in)
Small Bio-separator	0.20 (8)	0.20 (8)	0.61 (24)	0.15 (6)	0.31 (12)	0.15 (6)
Large Bio-separator	0.20 (8)	0.20 (8)	0.91 (36)	0.15 (6)	0.46 (18)	0.31 (12)

3.2 TESTING PARAMETERS

Enhanced performance is defined as increased fuel removal efficiency and breakthrough time, while maintaining a saturated hydraulic conductivity greater than 45 cm·min^{-1}. This is to ensure proper flow through the bio-separator to prevent unwanted overflow in the inlet reservoir. Removal efficiency (Γ) is calculated by,

$$\Gamma = \frac{C_{in} - C_{out}}{C_{in}} * 100 \tag{3.1}$$

where C_{in} is the influent fuel concentration, and C_{out} is the maximum effluent fuel concentration. Concentration reduction of fuel was also used to compare results. It is in log base 10 scale is calculated by,

$$\delta = \log\left(\frac{C_{in}}{C_{out}}\right) \tag{3.2}$$

where δ is the concentration reduction. The fuel breakthrough time is the time that it takes for a continuous flow of free-phase fuel to penetrate the bio-separator’s fuel storage reservoir (Figure 3.2).

Figure 3.2: Images of fuel breakthrough into the bio-separator’s fuel storage reservoir. Bio-separator tests were concluded at time of breakthrough. Both images are of shredded mulch replicate B test.

To improve the bio-separator operation, two design parameters were investigated to increase removal efficiency and breakthrough time:

1. mulch and aggregate types individually, and
2. length-proportion of mulch and aggregate.

Individual materials were tested separately in the small bio-separator and dual-material tests were conducted in the large bio-separator.

3.2.1 Materials

For each of the materials listed, at least one individual single-material bio-separator test was run. One mulch and one aggregate was selected for dual-material length-proportion testing.

3.2.1.1 Petroleum Hydrocarbon Source

The petroleum hydrocarbon source used was E-III™ Aviation Grade Fire Training Fluid (E-III fuel) by Chevron Phillips. It is a kerosene-type jet fuel used by fire-training centers. It consists of chain and branched *n*-alkanes with *n* ranging from nine to thirteen carbons. Appendix A contains the Material Safety Data Sheet for E-III.

3.2.1.2 Mulch

All mulch tested was eastern red cedar (*Juniperus virginiana*). It was selected because it is a widespread species in Oklahoma that is easy and inexpensive to attain. All chipped cedar mulch was collected from Nate's Tree Service, LLC (Stillwater, OK). The particle sizes within a single sample were mixed and ranged from 2.5 cm chips to particles less than 0.25 cm. There were three levels of decays for the chipped mulch: low degradation, medium degradation, and high degradation (Figure 3.3). Low degradation was mulch that was chipped three months prior to being used in the experiments and still contained green foliage. Medium degradation was chipped between three and eight months prior to use. Highly degraded mulch had been left in the elements for over eight months and looked similar to compost. All chipped mulch was stored outside exposed to the elements. Timberline brand shredded chipped cedar mulch was purchased from Lowe's Home Improvement in Stillwater, OK. It consisted of long fibrous strands, ranging from 5 to 15 cm in length. Figure 3.3 shows images of shredded, high degradation, medium degradation chipped, and low degradation chipped eastern red cedar mulch.

Figure 3.3: Image of the mulch used in single material testing. From left to right: a) shredded, b) high degradation chipped, c) medium degradation chipped, and d) low degradation chipped eastern red cedar mulch.

3.2.1.3 Aggregate

The aggregates used were concrete sand, large crushed limestone (size #4), pea gravel, and small crushed limestone (size #8) (Figure 3.4). All of the aggregates with the exception of the pea gravel were purchased from Stillwater Sand & Gravel Co (Stillwater, OK). The EarthEssentials pea gravel by Quikrete was purchased from Lowe's Home Improvement in Stillwater, OK. Table 3.3 contains information on approximate aggregate size for each.

Figure 3.4: Image of the aggregate materials used for single material testing. From left to right: a) concrete sand, b) pea gravel, c) small crushed limestone (size #8), and d) large crushed limestone (size #4).

Table 3.2: Approximate particle diameter for concrete sand, pea gravel, small crushed limestone (size #8), and large crushed limestone (size #4).

Aggregate Type	**Approximate Particle Diameter** cm
Concrete Sand	<0.095
Pea Gravel	2.54 to 0.25
Small Crushed Limestone (size #8)	0.95 to 0.24
Large Crushed Limestone (size #4)	3.75 to 1.9

3.2.2 Length Proportions

The second design parameter that was tested was mulch to aggregate length proportions for the mulch and aggregate types with the best results. Four length proportions were tested: 2:3, 5:4, 2:1, and 3:1. The corresponding lengths for the mulch and aggregate layers are located in Table 3.3.

Table 3.3: Length of mulch and aggregate layer for each dual-material length-proportion test. Length proportion is a mulch to aggregate ratio.

Length Proportion	**Mulch Length**, m (in)	**Aggregate Length**, m (in)
2:3	0.18 (7.2)	0.27 (10.8)
5:4	0.25 (10.0)	0.20 (8.0)
2:1	0.31 (12.0)	0.15 (6.0)
3:1	0.34 (13.5)	0.11 (4.5)

3.2.3 Test Selection

Two single-material tests were completed for shredded mulch and medium-degraded chipped mulch. Once fuel-effluent concentrations were analyzed for these tests, single-material tests for low degradation and high degradation chipped mulch were completed. One single-material test was completed for large crushed limestone, concrete sand, and pea gravel, and two tests were completed for small crushed limestone.

Medium degradation chipped mulch and small crushed limestone were chosen to move forward with dual-material length-proportion testing. The length proportions that were tested were 2:3, 5:4, 2:1, and 3:1 mulch to aggregate. Table 3.4 contains the number of replicates completed for every bio-separator test.

Table 3.4: List of bio-separator tests ran and number of replicates completed for each bio-separator test. Med. = medium, Deg. = degradation.

Single Material	**Number of Replicates**
Shredded Mulch	2
Med. Deg. Chipped Mulch	3
High Deg. Chipped Mulch	1
Low Deg. Chipped Mulch	1
#4 Large Crushed Limestone	1
Pea Gravel	1
#8 Small Crushed Limestone	2
Concrete Sand	1
Dual-Material Length-Proportion	**Number of Replicates**
2:3	2
5:4	3
2:1	3
3:1	4

3.3 LABORATORY METHODS

This section describes the laboratory methods used. Experimental setup, sample collection, fuel concentration analysis, mulch water content, saturated hydraulic conductivity, and mulch liquid uptake are the laboratory methods used.

3.3.1 Experimental Setup

A 200 L cylindrical tank was the water reservoir from which a peristaltic pump drew from. The water was pumped to a 2000 mL Griffin beaker where mixing occurred via magnetic stir plate. The fuel was stored in a 1000 mL Erlenmeyer flask with a spout that fit the peristaltic pump tubing which transferred the fuel to the mixing beaker. The magnetic stir plate was fast enough so that the vortex reached the stir rod, otherwise the fuel would not be entrained with the water. A 1.59 cm (5/8-in) inside diameter clear vinyl tube siphoned the fuel/water mixture into the first reservoir of the bio-separator; the height between the mixing container fluid level and the siphons free jet was 0.31 m (12-in). This coresponded to flowrate of 3.94 $L \cdot min^{-1}$ (1.04 $gal \cdot min^{-1}$). The mixture then traveled through the bio-separator and water exited the inverted siphon into a

5.08 cm (2-in) hose to the sewage drain. For tests that required half the normal flowrate, the bio-separator was placed on 15.2 cm (6-in) tall cinder blocks. The expiremental setup is portrayed in Figure 3.5. The concentration of fuel was ajusted by increasing or decreasing the fuel pump's flowrate. The water pump remained at a constant rate since the flowrate leaving the mixing beaker was at steady state.

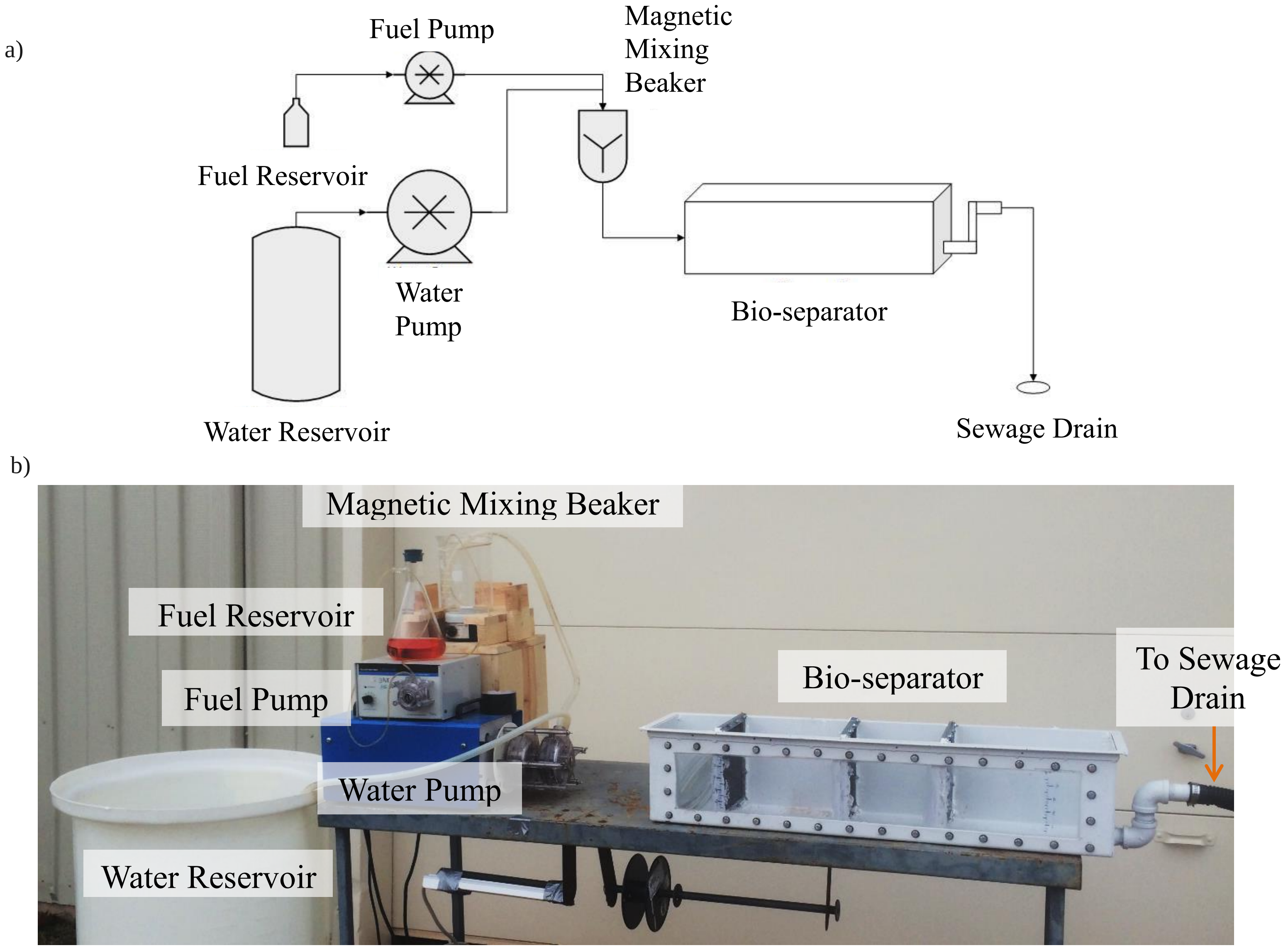

Figure 3.5: The bio-separator experimental setup a) schematic and b) picture. Both depict the transfer of water and fuel to the magnetic mixing beaker and bio-separator.

3.3.2 Sample Collection

Water samples were taken periodically during bio-separator tests for fuel concentration analysis. The flowrate was measured with a stopwatch and graduated container. The inlet reservoir fluid height, storage reservoir fluid height, temperature, and humidity directly after each water sample was recorded. Water samples were taken periodically at the inverted siphon: 15-minute intervals for single material tests, 30-minutes to 1-hour intervals for dual-material tests that lasted less than six hours, and 2-4 hour intervals for dual-material tests that lasted longer than six hours. A test was ended once free-phase fuel covered a majority of the surface of the water in the storage reservoir. A 40 mL clear EPA vial (27.5 x 95 mm) with silicone/PTFE septum and cap was used to collect and store the sample until analysis. The entire set of samples were transported to a laboratory and stored under a vent hood until analysis. Samples were analyzed prior to the seventh day after collection.

3.3.3 E-III Fuel Concentration Analysis Procedure

To determine concentration of E-III fuel in effluent water, head-space analysis was performed with a Hewlett Packard 5890 Series II gas chromatographer (GC) with a Flame Ionization Detector (FID) and a DB-1 capillary column (30m x 0.53mm). GC Inlet temperature was 250°C, and detector temperature was 340°C. The carrier gas was helium with a flowrate of 43 $mL \cdot min^{-1}$ and a column pressure head of 200 kPa. Makeup gases for the FID were hydrogen and air, flowing at 25 $mL \cdot min^{-1}$ and 308 $mL \cdot min^{-1}$ respectively. Samples were injected manually with 250 μL gas tight syringes. Table 3.5 presents the oven-operating program.

Table 3.5: Gas chromatography oven program for E-III™ Aviation Grade Fire Training Fluid concentration head-space analysis.

Oven Program
Initial temp.: 105°C
Ramp One: 105 to 120, at $25^{o}C \cdot min^{-1}$
Ramp Two: 120 to 225, at $35^{o}C \cdot min^{-1}$
Oven run time: 3.60 min
Cool down time: 3 min

Using Agilent ChemStation, each chromatograph was integrated from time 0.47 to 1.42 minute, correlating to the 9-alkane through 13-alkane peaks, for a total count. An example chromatograph of E-III fuel is shown in Figure 3.6. Three samples of each standard mixture of deionized water and fuel at concentrations of 1, 10, 50, 75, and 100 mg·L^{-1} were used to create a fitted calibration regression. Figure 3.7 is the mean count results for the standard in log scale with error bars. Figure 3.8 is the fitted calibration regression for the standards. The lower limit and upper detection limit for this study are 1 and 100 mg·L^{-1}, respectively.

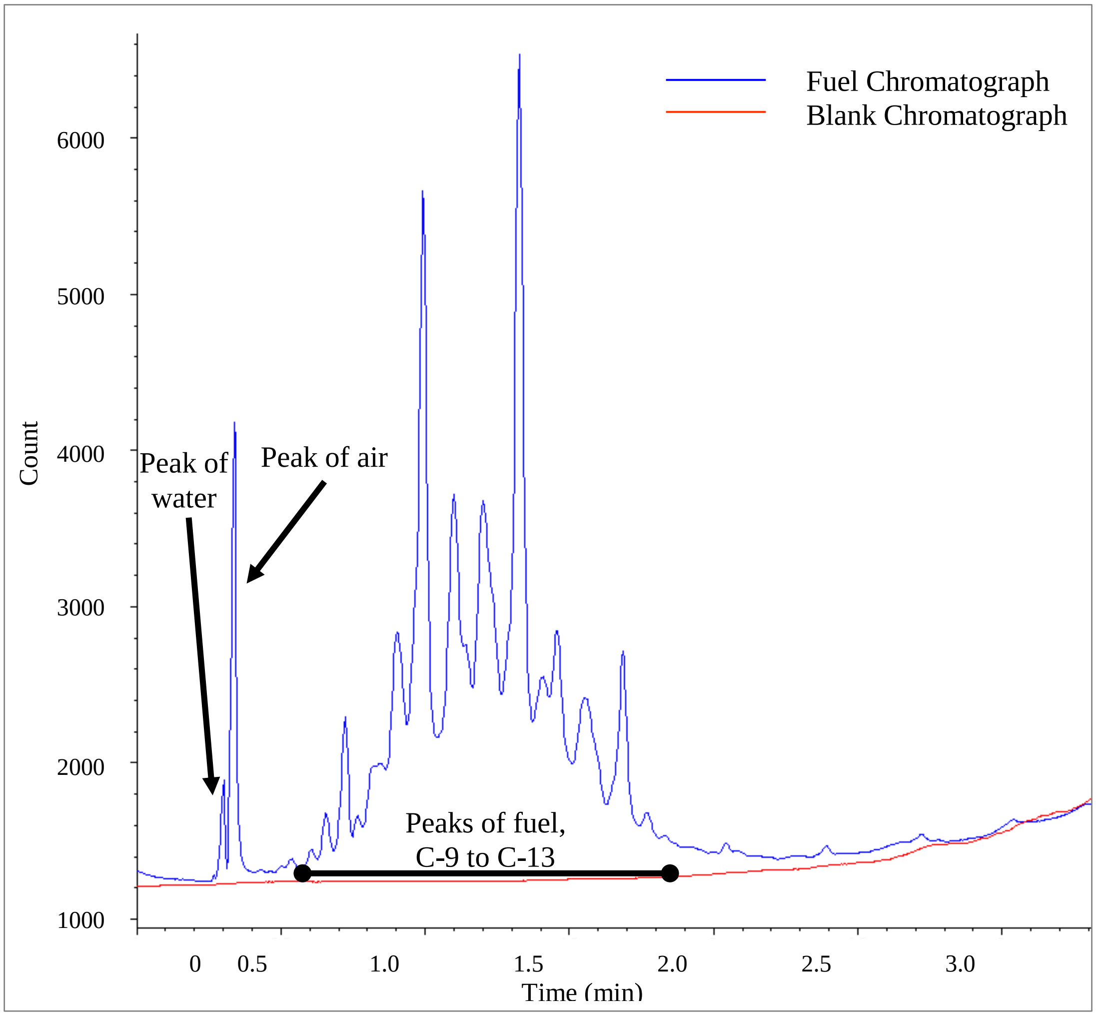

Figure 3.6: Example chromatograph of the Chevron Phillips' E-III™ Aviation Grade Fire Training Fluid for headspace analysis (Agilent ChemStation software). The red line is a blank run and the blue line is the fuel. Time in minutes is on the x-axis and count is on the y-axis.

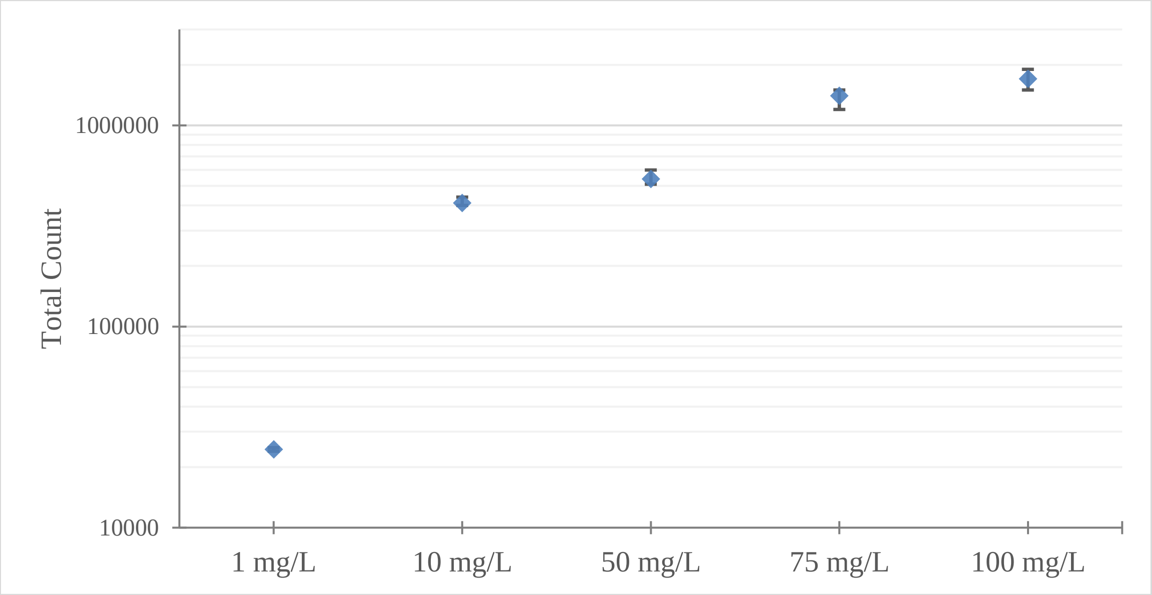

Figure 3.7: The mean count for each E-III fuel concentration standard with error bars. Total count is the value for the integrated fuel peaks from the chromatograph from time 0.47 minute to 1.42 minute.

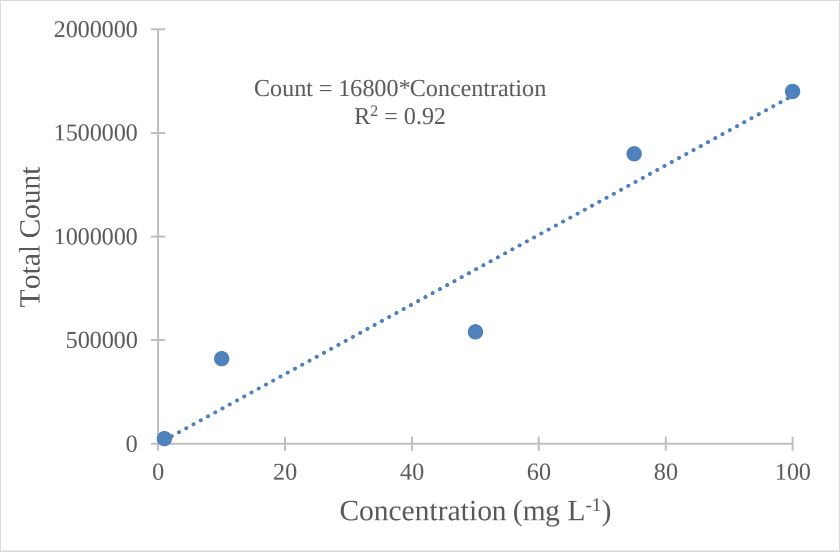

Figure 3.8: Linear calibration equation fitted onto standards. Total count is the value for the integrated fuel peaks from the chromatograph from time 0.47 minute to 1.42 minute.

3.3.4 Mulch Water Content

Metal tins were weighed before mulch samples were placed in the tin. The samples were dried in an oven for at least three days at 105ºC. The tin and mulch were then weighed. Gravimetric water content for mulch was calculated on a total weight basis given by,

$$\theta = \frac{W_{wet} - W_{dry}}{W_{wet} - W_{tin}} \tag{3.3}$$

where θ is the gravimetric moisture content ($g \cdot g^{-1}$), W_{wet} is the weight of the tin plus the weight of the wet mulch (g), W_{dry} is the weight of the tin plus the weight of the dry mulch, and W_{tin} is the weight of the tin (g).

3.3.5 Saturated Hydraulic Conductivity

Saturated hydraulic conductivity was measured for all the aggregates and medium-degraded chipped and shredded mulch in the small bio-separator. The flowrate was measured at the inverted siphon with a stopwatch and graduated cylinder. The height of the water was measured in the inlet and storage reservoir. Saturated hydraulic conductivity was calculated from the Darcy-Buckingham Equation,

$$Q = -k_{Sat} \frac{h_a - h_b}{L} * A \tag{3.4}$$

where Q is the flowrate of the phase, k_{Sat} is saturated hydraulic conductivity of the medium, A is cross-sectional area, h_a-h_b is pressure head loss, and L is the length of the media (Brown, 2002). Five measurements were taken for each media and then averaged. The acceptable saturated hydraulic conductivity for the small bio-separator was calculated to be at least 45 $cm \cdot min^{-1}$ based on the testing flowrate of 3.85 $L \cdot min^{-1}$ and the vertical distance of 10 cm (4-in) between the highest fluid level in the inlet reservoir and the inverted siphon. The testing flowrate was chosen based on scientific judgement such that there was a low enough linear velocity to keep from disturbing the mulch and aggregate in the bio-separator.

3.3.6 Mulch Liquid-Uptake Experimental Setup

A mulch liquid mass-uptake experiment was performed to quantify the amount of free-phase fuel and water adsorbed to mulch partially submerged in fluid and partially suspended in air. This experiment was used to investigate the rate of uptake of fluid to the mulch particles. The uptake of only water, only fuel, and fuel and water with a concentration of 800 mg·L^{-1} were tested.

Before the test, the mulch was evenly distributed over trays and dried overnight to obtain a consistent moisture content throughout. Three samples of the mulch were taken to determine moisture content as described in the mulch water content section. A 105-g sample of air-dried mulch was packed to a uniform bulk density into the vegetable steamer strainer compartment. Figure 3.9b is an example image of the strainer compartment filled with medium-degraded shredded mulch during an experiment. The vegetable steamer reservoir was filled with 350 mL of the appropriate liquid, either deionized water, E-III fuel, or 800 mg·L^{-1} E-III fuel mixture; Figure 3.9a is an example image of the vegetable steamer reservoir filled with water. This allowed for the bottom of the strainer compartment to be submerged in 2.54 cm (1-in) of liquid. For each experiment, a predetermined number of samples, strainer compartments filled with packed mulch, were lowered into the reservoir simultaneously. A range of 7 to 11 individual samples were used for each experiment (Table 3.6). Lids and lead weights were placed on top of the vegetable steamer assemblies to minimize fuel vaporization under a vent hood. At predetermined times for each sample (Table 3.6), the strainer compartments were weighed after allowing the mulch to drain until there was no longer free-flowing liquid. Once a sample was weighed, it was not reused in the experiment.

Figure 3.9: Example images of mulch liquid-uptake experiments. a) shows the vegetable steamer reservoir with water and loose soil after an experiment and b) shows the strainer compartment filled with medium-degraded shredded mulch during an experiment.

Table 3.6: Parameters for mulch liquid-uptake experiment with water and E-III™ Aviation Grade Fire Training Fluid (E-III fuel).

Experiment Name	**Liquid Used**	**Number of Samples**	**Sampling Times,** minutes
Water	Deionized water	10	15, 30, 60, 120, 180, 240, 300, 360, 420, and 480
Fuel-Water A	800 mg·L^{-1} E-III fuel and deionized water	10	15, 30, 60, 120, 180, 240, 300, 360, 420, and 480
Fuel-Water B	800 mg·L^{-1} E-III fuel and deionized water	11	5, 10, 15, 25, 35, 50, 70, 100, 240, and 1440
Fuel-Water C	800 mg·L^{-1} E-III fuel and deionized water	8	1, 5, 15, 30, 60, 90, 150, and 240
Fuel	E-III fuel	7	1, 5, 15, 30, 60, 150, and 240

3.3.7 Consecutive Flow-Event Tests

Consecutive flow-event simulations were completed on 2:1 and 3:1 length proportion of chipped mulch and small crushed limestone. The flowrate for the first flow-event was half the testing flowrate used for the single-media tests: 1.96 L·min^{-1} (0.52 gal·min^{-1}). Once the test concluded, when breakthrough of fuel occurred, the bio-separator was left undisturbed for three days outside. The second storm simulation was completed at the average flowrate used for the single-media of 3.94 $L \cdot min^{-1}$ (1.04 $gal \cdot min^{-1}$) for the 2:1 length proportion test. For the 3:1 length proportion test, a slower flowrate of 1.74 $L \cdot min^{-1}$ (0.46 $gal \cdot min^{-1}$) was used for the second flow-event. Since there was already fuel in the storage reservoir, the test was concluded after two hours instead of at time of breakthrough. Water samples were taken at time of first flow, 5, 10, 20, 30, 45, 60, 90, and 120 minutes. At the time of each sample, depth of fuel in storage reservoir was recorded and a picture was taken of the storage reservoir to determine fuel surface coverage.

3.4 STATISTICAL ANALYSIS

For single material tests, statistical difference between means for both removal efficiencies and breakthrough times was found by running a two-sample t-test with a confidence interval of 95%. P-values less than 0.05 were considered significantly different, and p-values greater than 0.05 were not considered significantly different. For dual-material tests, a one-way ANOVA with Tukey comparison with a 95% confidence interval was run to identify statistical differences between the means of length proportion tests for removal efficiencies and breakthrough times. P-values less than 0.05 were considered significantly different, and p-values greater than 0.05 were not considered significantly different. Not significantly different Tukey groups have the same assigned group letter. The modified Thompson τ technic was used to find outliers in the data.

Multiple regressions were analyzed using Minitab® 17 statistical software. A best-subsets regression was completed and then regression models were fit and analyzed. Regressions were considered acceptable when the following criteria were met: parameters were significant at a 90% confidence interval (p-value < 0.10), R^2 values greater than or equal to 0.70, R^2-adjusted values greater than or equal to 0.60, and standard error of regression (S) that were less than or equal to 20% of the total range of observed data. Regressions were plotted with the observed values on the y-axis and predicted values on the x-axis (Piñeiro et al., 2008). Regression slope and intercept for predicted versus observed data was considered statistically significant within the 95% confidence interval if the p-values were less than 0.05 using the Microsoft Excel 2013 Analysis Toolpac Add-in regression tool. The upper and lower 95% confidence interval limit was used to determine whether the slope was significantly different from one and the intercept was significantly different from zero. Correlations between parameters was done using Microsoft Excel 2013 Analysis Toolpac Add-in correlation tool. Parameters with a correlation value (C) greater than 0.75 or less than -0.75 were considered to be correlated and are presented in the Regression Analysis Results section.

CHAPTER IV

RESULTS AND DISCUSSION

The bio-separator for removing petroleum hydrocarbons has been tested for varying materials, proportions, flowrates, and number of flow-events. These results have been utilized to develop a design procedure and operation and maintenance recommendations, with a case study completed for the OSU Fire Service Training Center near Stillwater, Oklahoma.

4.1 SATURATED HYDRAULIC CONDUCTIVITY

Saturated hydraulic conductivity results for each material are shown in Table 4.1. Concrete sand had a low saturated hydraulic conductivity of 4 cm·min^{-1}. Chipped red cedar mulch had the second lowest saturated hydraulic conductivity at 250 cm·min^{-1} and large crushed limestone has the highest saturated hydraulic conductivity at 990 cm·min^{-1}.

Table 4.1: Saturated hydraulic conductivity (K_{sat}) test results for shredded and chipped eastern red cedar mulch, concrete sand, pea gravel, small crushed limestone, and large crushed limestone.

Material	K_{sat}, cm·min^{-1}
Shredded Eastern Red Cedar	270
Chipped Eastern Red Cedar	250
Concrete Sand	4
Pea Gravel	330
Small Crushed Limestone (size #8)	390
Large Crushed Limestone (size #4)	990

These results were used as a threshold parameter to ensure proper flow through the bio-separator to prevent unwanted overflow in the inlet reservoir. The minimum saturated hydraulic conductivity considered acceptable for this application is 45 cm·min^{-1}, as this rate is too low to maintain the testing flowrate. Sand was excluded from dual-materiel testing as its saturated hydraulic conductivity was less than this rate. The remaining materials had satisfactory saturated hydraulic conductivities and moved forward with single material testing.

4.2 SINGLE MATERIAL TESTS

4.2.1 Mulch

Single material test results for the mulches are shown in Table 4.2. High and low degradation chipped mulch had the lowest removal efficiencies, 94.3% and 85.9% respectively, and higher maximum effluent fuel concentrations, with values greater than 15 $mg \cdot L^{-1}$. Statistical tests could not be completed to determine if the removal efficiencies and breakthrough times were significantly different for high and low degradation mulches since only one test was completed for each material. Figure 4.1 shows the individual removal efficiencies for two medium-degraded shredded-mulch tests and the three medium-degraded chipped-mulch tests. Breakthrough times for shredded mulch had a smaller range than chipped mulch, chipped mulch contained both the greatest and the least observed removal efficiency values. However, the mean values for removal efficiencies were not found to be significantly different from a two-sample t-test (p-value = 0.36). Figure 4.2 shows the fuel breakthrough time for the two shredded mulch tests and two of the three chipped mulch tests. Breakthrough time for chipped mulch replicate B test was excluded from the figure and statistical testing since the test was interrupted due to time constraints and restarted the following day. The mean breakthrough time for shredded mulch was less than that of the chipped mulch, but not significantly different according to a two-sample t-test (p-value = 0.47).

Table 4.2: Single material test parameters and results for mulch. Med. = medium, Deg. = degradation, Conc. = concentration, Max = maximum, and NA = not available.

Mulch Type	**Replicate**	**Pack Density** (kg·m^{-3})	**Moisture Content** (g·g^{-1})	**Influent Conc.** (mg·L^{-1})	**Break-through Time** (min)	**Max Fuel Conc.** (mg·L^{-1})	**Removal Efficiency** (%)
Shredded Mulch	A	270	0.18	977	38	5.8	99.4
Shredded Mulch	B	318	0.18	643	71	6.0	99.1
Chipped Mulch (Med. Deg.)	A	254	0.35	821	63	< 1.0	> 99.9
Chipped Mulch (Med. Deg.)	B	254	0.35	373	363*	8.8	97.7
Chipped Mulch (Med. Deg.)	C	159	NA	255	210	8.9	96.5
Chipped Mulch (High Deg.)	A	302	0.44	641	120	36.3	94.3
Chipped Mulch (Low Deg.)	A	286	0.51	593	51	83.4	85.9

*Test interrupted due to time constraints, breakthrough time may not be representative.

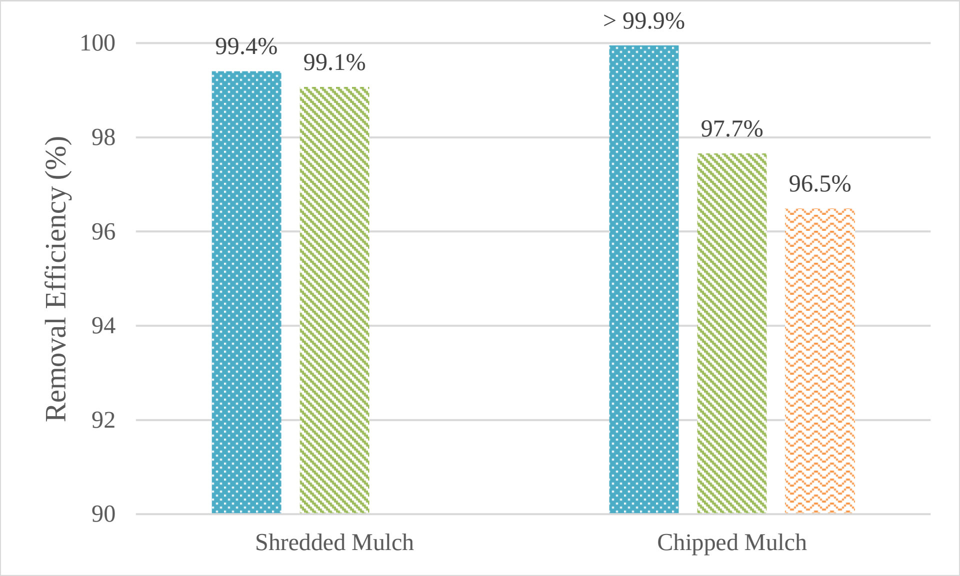

Figure 4.1: Removal efficiencies for mulch tests. The different colored patterns represent each replicate: spotted blue pattern for A, stripped green pattern for B, and chevron orange pattern for C. Reduction is located above the bars.

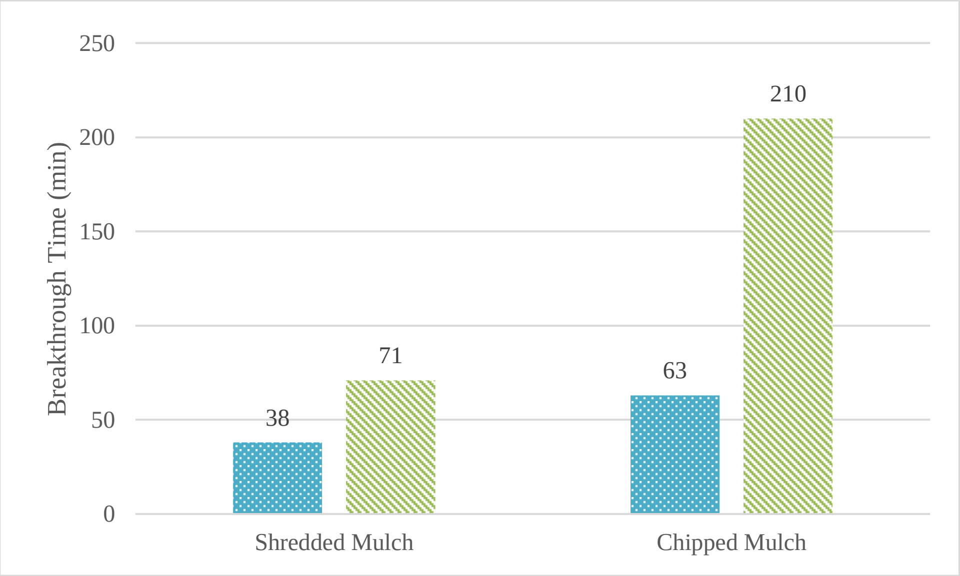

Figure 4.2: Breakthrough times for mulch tests. The different colored patterns represent each replicate: spotted blue pattern for A and stripped green pattern for B. Times are located above the bars.

Both high degradation and low degradation chipped mulch had the lowest removal efficiencies and the highest moisture contents. These parameters may be correlated; further testing with a wider range of moisture contents would clarify any correlations. Because high and low degradation chipped mulch had the lowest removal efficiencies, they were not chosen to progress to dual-material length-proportion testing. Either medium-degraded chipped or shredded mulch could be used for dual-material testing since, based on this limited testing, both the removal efficiency and the breakthrough times were not significantly different between the mulches. Medium-degraded chipped mulch was chosen for dual-material testing because it is readily available, often sold in bulk, and usually less expensive than shredded mulch.

4.2.2 Aggregate

Pea gravel, small crushed limestone, and large crushed limestone single material test results are in Table 4.3. Concrete sand was tested, but results were not included in Table 4.3 due to its low saturated hydraulic conductivity. Fuel-effluent concentrations for pea gravel, one of two tests for small crushed limestone, and large crushed limestone was detectable but, because of skewed chromatographs, fuel-effluent concentrations could not be quantified. The fuel concentrations in the large limestone and pea gravel effluent were detectable by odor, while the small crushed limestone was not. Figure 4.3 shows the breakthrough times of the aggregates. Small limestone had the highest and lowest breakthrough times, 104 and 42 minutes respectively. Pea gravel had the second highest breakthrough time at 69 minutes and large limestone was the second lowest at 44 minutes. The statistical difference in breakthrough times could not be determined since there were not enough data points for pea gravel and large crushed limestone.

Table 4.3: Single material length-proportion test parameters and results for aggregate. NA = not available, and are tests with gas chromatography errors.

Aggregate	**Replicate**	**Pack Density,** $kg\cdot m^{-3}$	**Influent Conc.,** $mg\cdot L^{-1}$	**Break-through Time,** min	**Max Fuel Conc.,** $mg\cdot L^{-1}$	**Removal Efficiency,** %
#4 Large Limestone	A	1335	688	44	NA	NA
Pea Gravel	A	1430	638	69	NA	NA
#8 Small Limestone	A	1143	868	104	NA	NA
#8 Small Limestone	B	1287	862	42	16.1	98.1

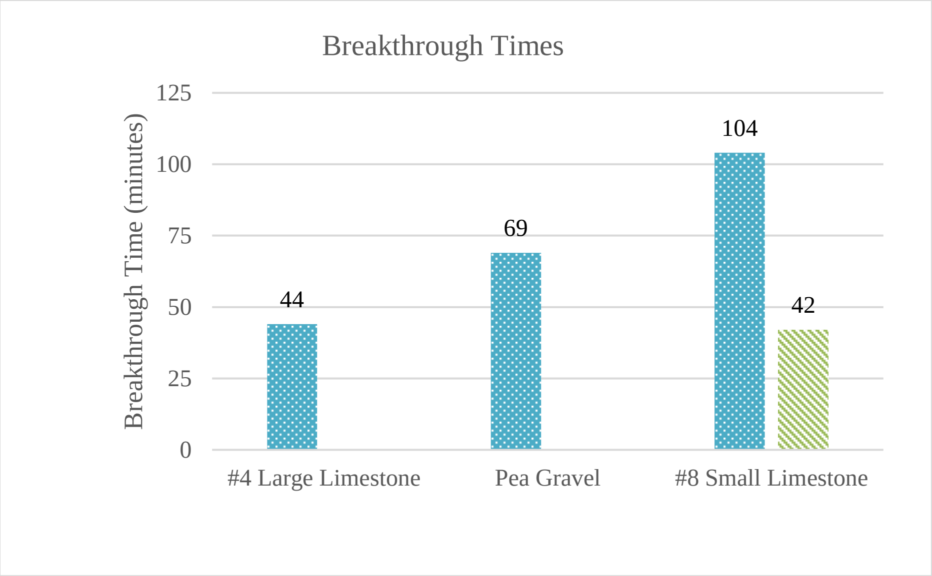

Figure 4.3: Breakthrough times for single aggregate tests. The different colored patterns represent each replicate: spotted blue pattern for A and stripped green pattern for B. The values are located above the bars.

All of the effluent samples collected for concrete sand were below the fuel detection limit of 1 mg·L^{-1}. It is speculated that concrete sand would perform better for low flow or high head systems compared to the other aggregates because none of the effluent tested was above the EIII fuel detection limit (Appendix B). Even though removal efficiencies could not be quantified for all of the aggregates, the small crushed limestone had the lowest fuel-effluent concentrations from odor comparisons. Crushed limestone was selected to use for dual-material testing.

4.3 DUAL-MATERIAL LENGTH-PROPORTION TESTS

Based on single material testing and availability, medium-degraded chipped mulch and small crushed limestone were paired together for dual-material length-proportion testing. Four length proportions of medium-degraded mulch and small crushed limestone were tested: 2:3, 5:4, 2:1, and 3:1. Table 4.4 contains the test parameters and results. The length proportion with the largest breakthrough time and largest removal efficiency was the 3:1 mulch to aggregate (Figures 4.4 and 4.5). There was no statistical difference between the means of the breakthrough times for the different length proportions according to the ANOVA test (p-value = 0.61) and all length proportions were in the same Tukey comparison group. Means for removal efficiency was also not statistical different for the different length proportions (p-value = 0.962) and all length proportions were in the same Tukey comparison group.

Table 4.4: Dual-material test parameters and results. Conc. = Concentration and NA = not available.

Mulch Length in	**Limestone Length** in	**Replicate**	**Length Ratio** Mulch:Aggregate	**Mulch Pack Density** kg·m^{-3}	**Moisture Content** g·g^{-1}	**Dry Bulk Density** kg·m^{-3}	**Limestone Pack Density** kg·m^{-3}	**Influent Conc.** mg·L^{-1}	**Break-through Time** min	**Removal Efficiency** %
7.2	10.8	A	2:3	265	0.40	160	1360	1271	94	96.0
7.2	10.8	B	2:3	238	0.38	148	1395	1239	62	98.9
10	8	A	5:4	191	0.25	143	1335	695	248	98.5
10	8	B	5:4	229	0.26	170	1287	445	227	97.7
10	8	C	5:4	286	0.40	171	1406	429	303	97.3
12	6	A	2:1	191	0.35	124	1271	600	433	95.4
12	6	B	2:1	286	0.47	152	1303	509	158	97.9
12	6	C	2:1	222	0.30	155	1367	281	1458	97.7
13.5	4.5	A	3:1	NA	0.43	NA	1229	538	450	96.8
13.5	4.5	B	3:1	268	0.25	202	1271	120	1632	92.1
13.5	4.5	C	3:1	283	0.43	161	1271	937	120	99.4
13.5	4.5	D	3:1	311	0.45	170	1271	466	85	99.6

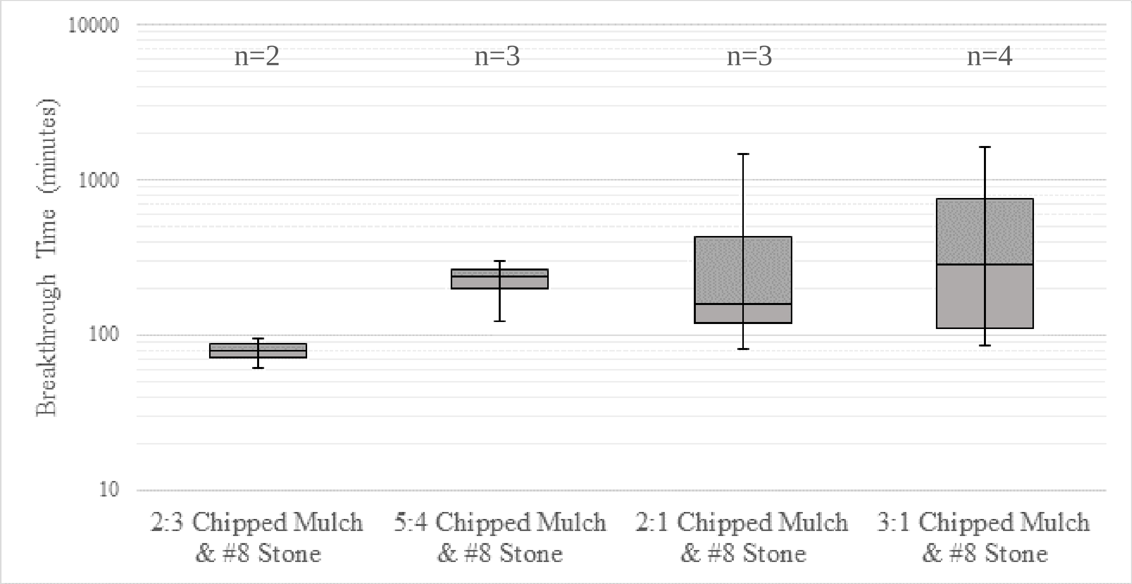

Figure 4.4: Boxplot for bio-separator dual-material length-proportion tests using varying proportions of medium-degraded chipped eastern red cedar mulch and #8 crushed limestone. n = sample size.

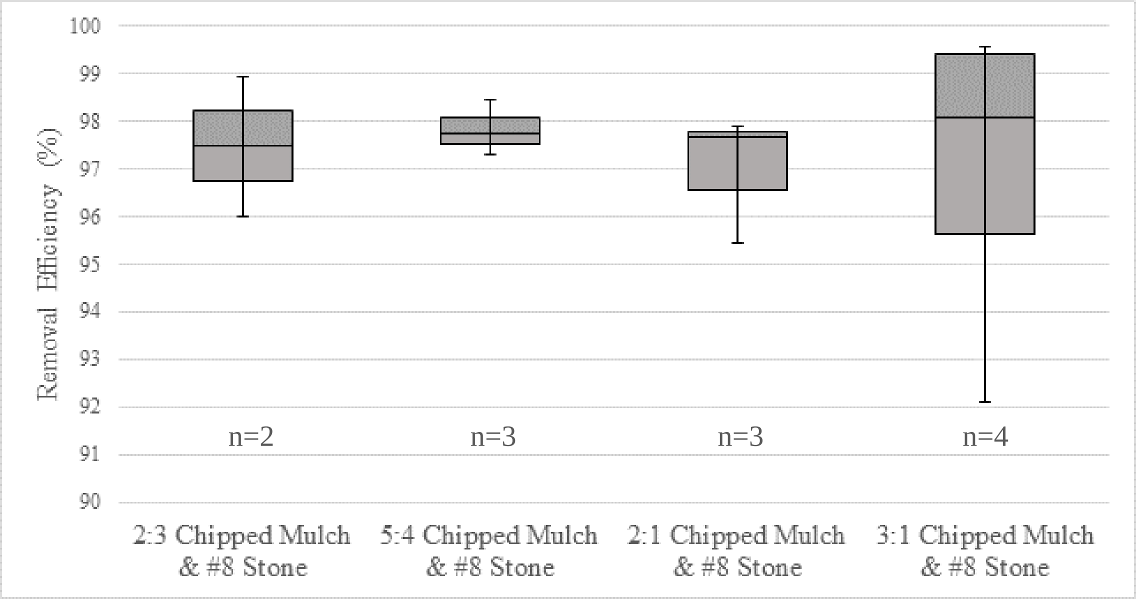

Figure 4.5: Boxplot of removal efficiencies for dual-material length-proportion tests. n = sample size.

Seven out of twelve of the dual-material tests had higher breakthrough times than an equivalent length of individual material. These results provide initial evidence that mulch and crushed limestone may remove fuel from runoff water better when together than separate, potentially because of the multiple modes of removal and flow regulation provided by using the materials together. The length proportion with the highest breakthrough time and highest removal efficiency was the 3:1 mulch to aggregate. The high ratio of mulch was expected to be the best length proportion since mulch out performed small crushed limestone in single material testing. Higher proportions, such as 4:1 or 10:1, may have better performance. However, 3:1 length proportion is recommended for full-scale bio-separators since it has been tested.

4.4 MULCH LIQUID-UPTAKE EXPERIMENT

The mulch mass-uptake of only water, fuel and water with a concentration of 800 $mg{\cdot}L^{-1}$, and only fuel were tested. As shown in Figure 4.6, the fuel only experiment has a slightly lower maximum liquid content than the water only experiment, although without replicates of the experiment it cannot be known if this is just an artifact of the experiment or an actual difference.

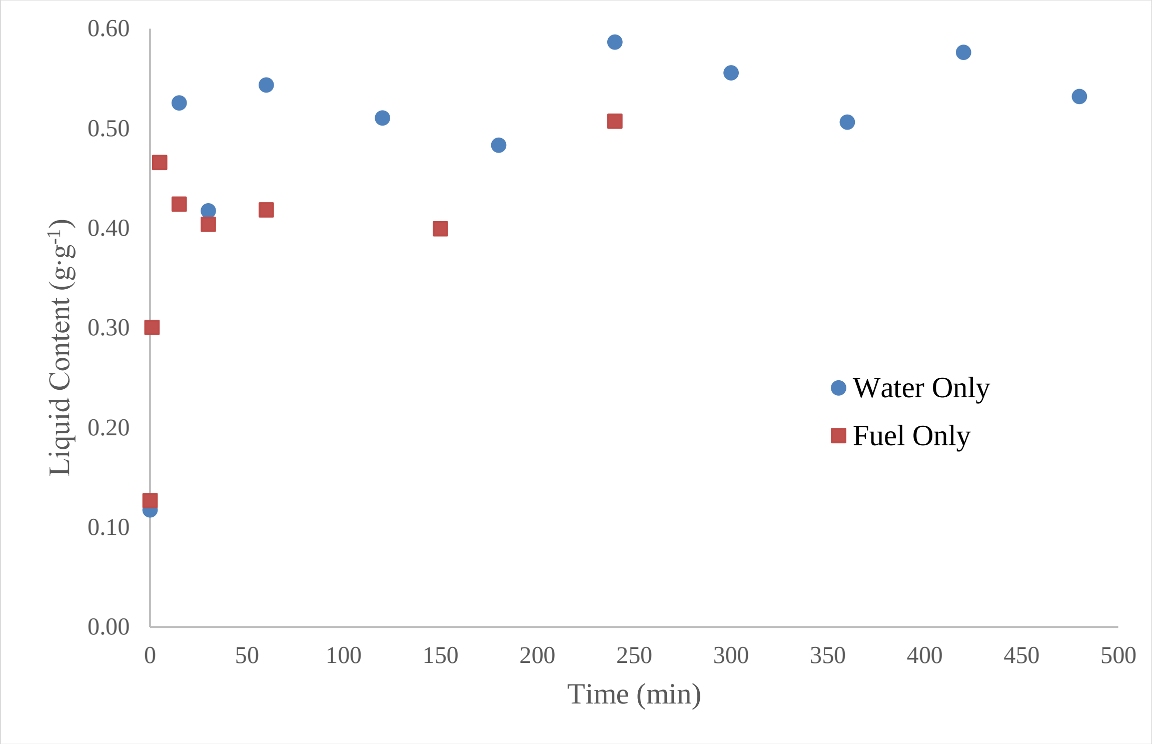

Figure 4.6: Mulch liquid-uptake experiments for water only and fuel only. Liquid content in mulch on the y-axis and time in minutes on the x-axis. The blue circles are water only and red squares are fuel only.

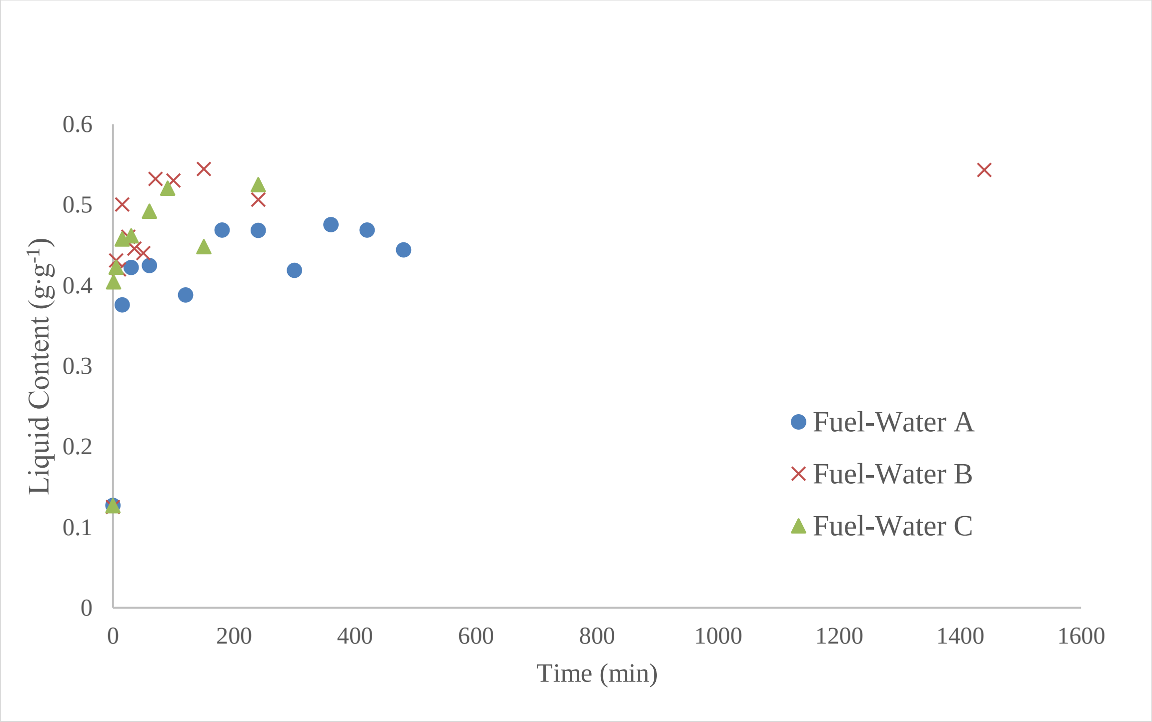

Figure 4.7: Mulch liquid-uptake experiments for three replicates of EIII fuel and water at 800 $mg{\cdot}L^{-1}$. Liquid content in mulch on the y-axis and time in minutes on the x-axis. The blue circles are replicate A, red squares are replicate B, and green triangles replicate C.

Figure 4.7 indicates that in all experiments, uptake of over 80% of the total liquid that was taken up into the mulch occurred within the first five minutes after the experiment. There was some variability of moisture content within each experiment, which was expected since there were 7 to 11 different samples for each experiment. Though it was not measured, it is probable that there was a slight variability in moisture content and packing of each tray. The mulch liquid-uptake experiment proved that mulch can easily adsorb both fuel and water. Although numerically the results appear similar, the fuel-only experiment exhibited a noticeable fuel sheen on the mulch, while the rest of the uptake experiments did not. Not only can mulch absorb fuel and water, it absorbs a majority of its fluid capacity in under five minutes. This demonstrates that the height of mulch above saturation is important to the amount of fuel that the bio-separator can remove before fuel breakthrough. It also supports the design hydraulic retention times through the mulch of five minutes for both the lab-scale bio-separators and pilot-scale bio-separator. More liquid uptake experiments may shed more light on the role of the mulch in removing fuel, such as by varying initial moisture contents of the mulch.

4.5 REGRESSION ANALYSIS

Fuel breakthrough times were variable for tests that contain chipped mulch; the standard deviation was 485 minutes for all tests containing medium-degraded chipped mulch. To attempt to explain this variability, a multiple regression was applied to all tests with chipped mulch using Minitab® 17 statistical software. One data point was removed from the regression analysis using the modified Thomspon τ technic; this sample had a mulch pack density that was much different that the rest of the samples. Fuel mass flowrate ($C_{in} \cdot Q$), total hydraulic retention time (HRT), hydraulic retention time through the mulch (MRT), and mulch moisture content (θ) were the significant parameters found to predict the variation in breakthrough time (t_b). HRT is the time it takes for water to travel through the whole system, while MRT is the time it takes for water to travel through the mulch layer. The multiple regression that fit the parameters is,

$$t_b = -0.30(C_{in} \cdot Q) + 18860\left(\frac{MRT}{HRT}\right) + 3789\left(\frac{\theta}{\frac{MRT}{HRT}}\right) - 14450(\theta) - 4128 \qquad (4.1)$$

where t_b in minutes, Q is the volumetric flowrate in L·min^{-1}, C_{in} influent fuel concentration in mg·L^{-1}, MRT in minutes, HRT in minutes, and θ in g·g^{-1} is shown in Figure 4.8. The multiple regression accurately predicted the breakthrough time ($R^2 = 0.90$, R^2-adjusted = 0.85, and S = 193 min). The S value was approximately 12% of the total range in observed breakthrough time. For the observed versus predicted regression, the slope was statistically significant (p-value < 0.001) and not significantly different from one within the 95% confidence interval (0.788 to 1.21). The intercept was not significant (p-value = 1), making it not significantly different from zero within the 95% confidence interval (-130 to 130). The parameter $\theta/(MRT/HRT)$ is positive correlated with mass flowrate (C = 0.72) and negatively correlated with the hydraulic retention time ratio (C = -0.70). Equation 4.1 was applied to observed breakthrough times less than 500 minute (Figure 4.9) for validation of the lower range. The R^2 value was 0.63, R^2-adjusted value was 0.60, and the S was 91 minutes, approximately 23% of the total range in observed breakthrough time. For the observed versus predicted regression, the slope was statistically significant (p-value = 0.002) and not significantly different from one within the 95% confidence interval (0.263 to 0.883). The intercept was not significant (p-value = 0.097), making it not significantly different from zero within the 95% confidence interval (-17 to 170). By the criteria listed in the criteria listed in the Methods, Equation 4.1 was not an acceptable regression for breakthrough times under 500 minutes. Another multiple regression for the lower range was determined,

$$t_b = -1.56(\rho_m) - 0.080(C_{in} \cdot Q) + 809 \qquad (4.2)$$

where ρ_m is the mulch pack density in kg·m^{-3} is shown in Figure 4.10. All parameters were significant in the 95% confidence interval with a R^2 value of 0.70, R^2-adjusted value of 0.67, and S value of 74, approximately 20% of the total range in observed breakthrough time. For the observed versus predicted regression, the slope was statistically significant (p-value = 0.0013) and not significantly different from one within the 95% confidence interval (0.51 to 1.5). The intercept was not significant (p-value = 0.99), making it not significantly different from zero within the 95% confidence interval (-108 to 109).

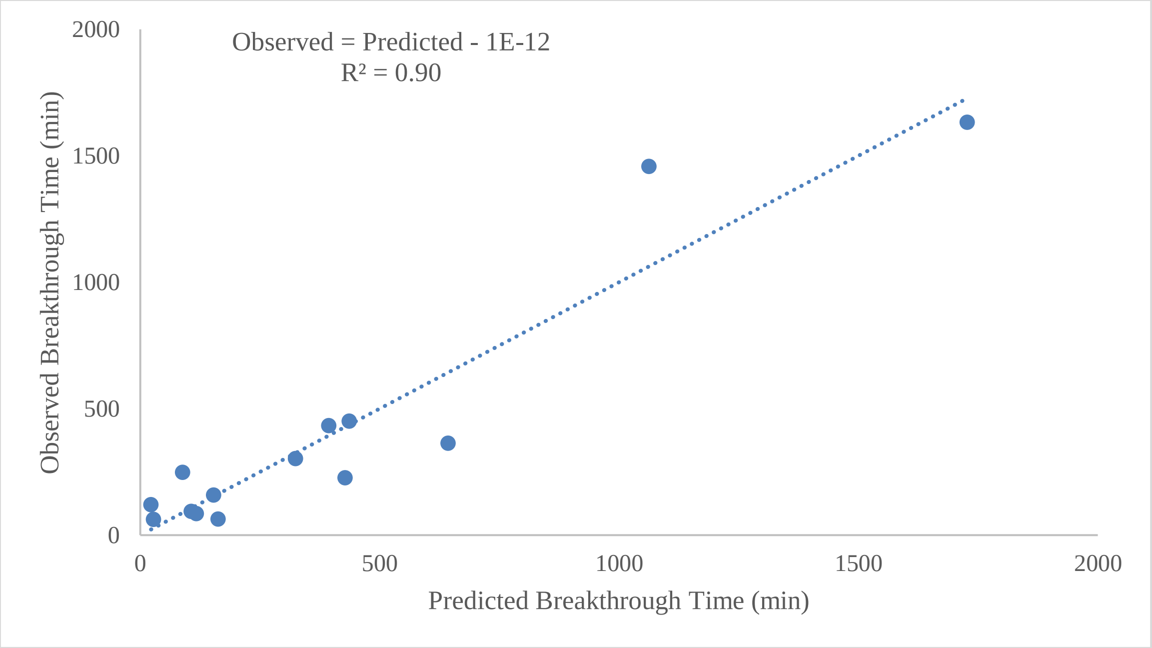

Figure 4.8: Observed breakthrough time versus predicted breakthrough time. Predicted values were calculated by multiple regression analysis results (Equation 4.1) for all tests containing medium-degraded mulch. The dotted line is the linear trendline.

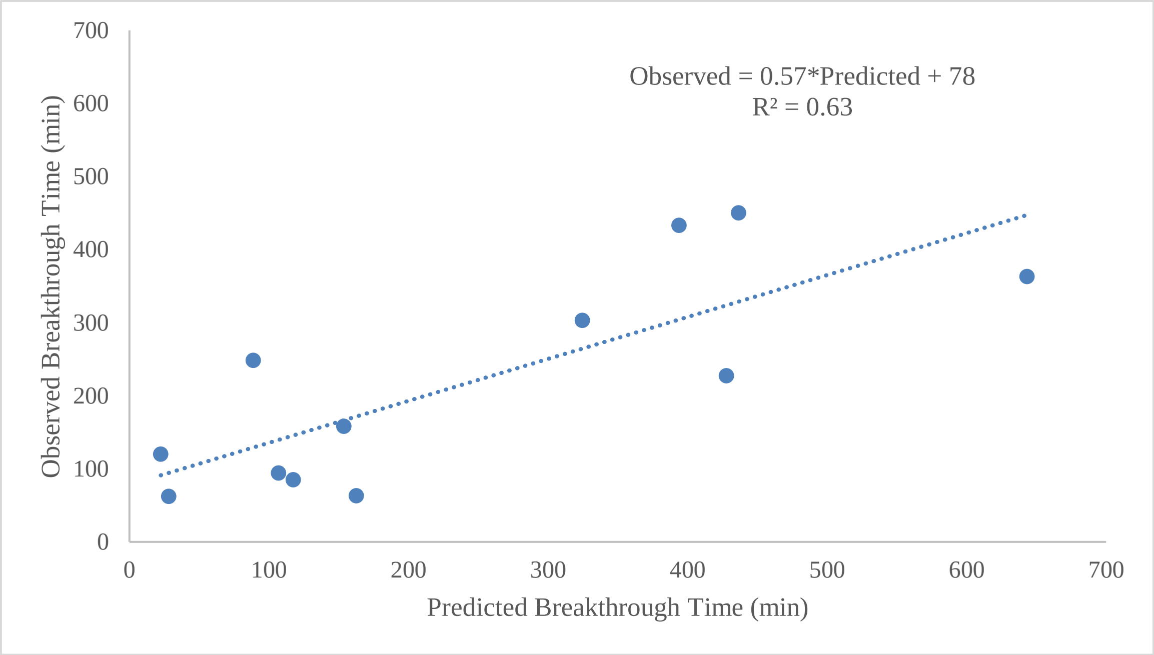

Figure 4.9: Observed breakthrough time for all tests under 500 minutes versus predicted breakthrough time. Predicted values were calculated by multiple regression analysis results (Equation 4.1) for all tests containing medium-degraded mulch. The dotted line is the linear trendline.

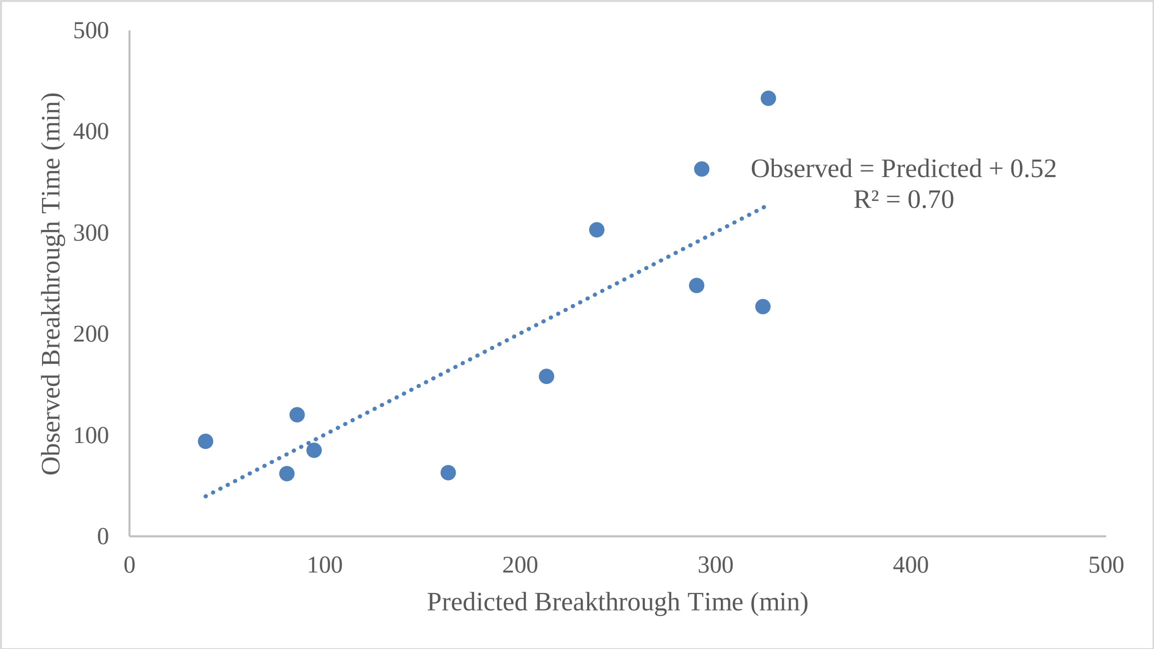

Figure 4.10: Observed breakthrough time for all tests under 500 minutes versus predicted breakthrough time. Predicted values were calculated by multiple regression analysis results (Equation 4.2) for all tests containing medium-degraded mulch with breakthrough times under 500 minutes. The dotted line is the linear trendline.

A multiple regression analysis was also completed for the concentration reduction of all the tests that contained medium-degraded chipped mulch and small crushed limestone. The best regression was considered the regression where all the variables were significant at a 90% confidence interval (p-value < 0.10). Significant parameters found to describe concentration reduction were t_b, MRT, C_{in}, and Q. The multiple regression equation that fit the acceptable regression criteria is,

$$\delta = -0.709 * \ln(t_b) + 0.532(MRT) + 0.000503(C_{in} * Q) - 0.00235(C_{in}) + 4.67 \qquad (4.3)$$

where δ is concentration reduction, shown in Figure 4.11. The multiple regression predicted the concentration reduction ($R^2 = 0.79$, R^2- adjusted = 0.70, and S = 0.25). The S-value was approximately 12% of the total range in observed breakthrough time. For the observed versus predicted regression, the slope was statistically significant (p-value < 0.001) and not significantly different from one within the 95% confidence interval (0.68 to 1.3). The intercept was not significant (p-value = 1), making it not significantly different from zero within the 95% confidence interval (-0.60 to 0.60). The $\ln(t_b)$ parameter was negatively correlated with mass flowrate (C = -0.86) and influent fuel concentration (C = -0.80). Mass flowrate was positively correlated with influent concentration (C = 0.84).

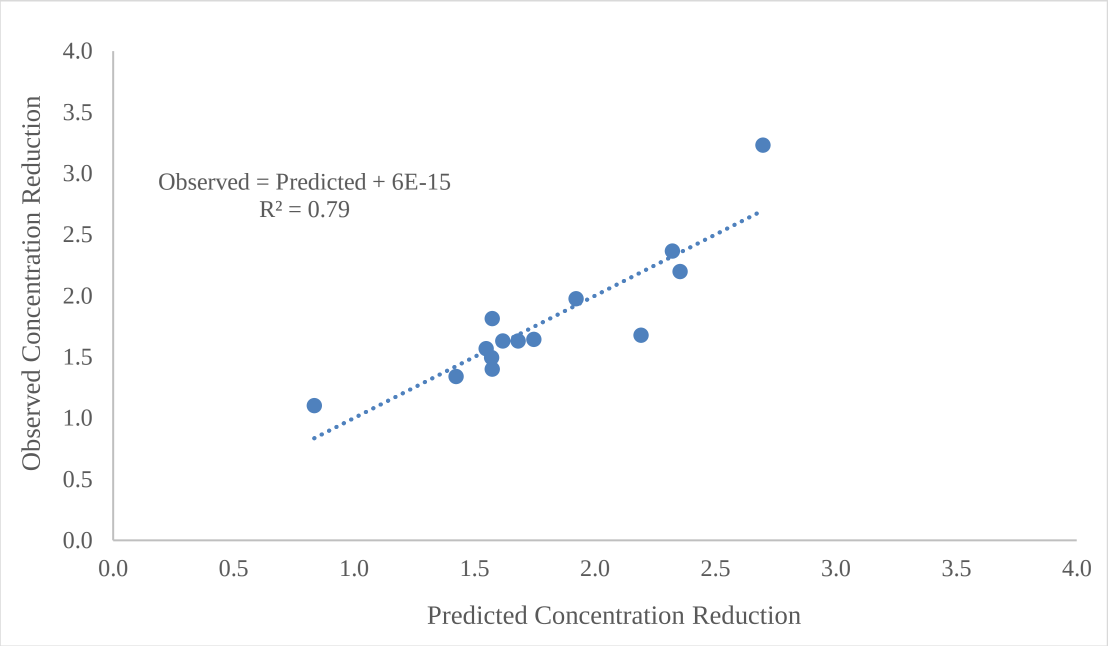

Figure 4.11: Observed concentration reductions versus concentration reductions. Predicted values were calculated by multiple regression analysis results (Equation 4.3) for all tests containing medium-degraded mulch. The dotted line is the linear trendline.

Multiple regression analysis provided predictive equations for breakthrough time and concentration reduction. These regression equations should be considered predictive equations rather than an explanation of the specific parameters that contribute to breakthrough time and concentration reduction. For traditional regression analysis, none of the parameters are allowed to be correlated. For this application, however, the equations are only used as predictive tools to approximate breakthrough time and concentration reduction. These equations can be applied to pilot-scale bio-separator designs if the conditions are within the lab-scale operating condition ranges.

4.6 CONSECUTIVE FLOW-EVENT TESTS

Consecutive flow-event tests were completed on 2:1 and 3:1 length proportion of chipped mulch and small crushed limestone (Figure 4.12). The maximum fuel-effluent concentration for each of the second simulated flow-event was similar to the first event. For the 2:1 test, the maximum fuel-effluent concentration was 6.6 mg·L^{-1} for the first event, and 7.1 mg·L^{-1} for the second event. Likewise, for the 3:1 test, maximum fuel-effluent concentration for the first event was 7.1 mg·L^{-1}, and 6.0 mg·L^{-1} for the second event.

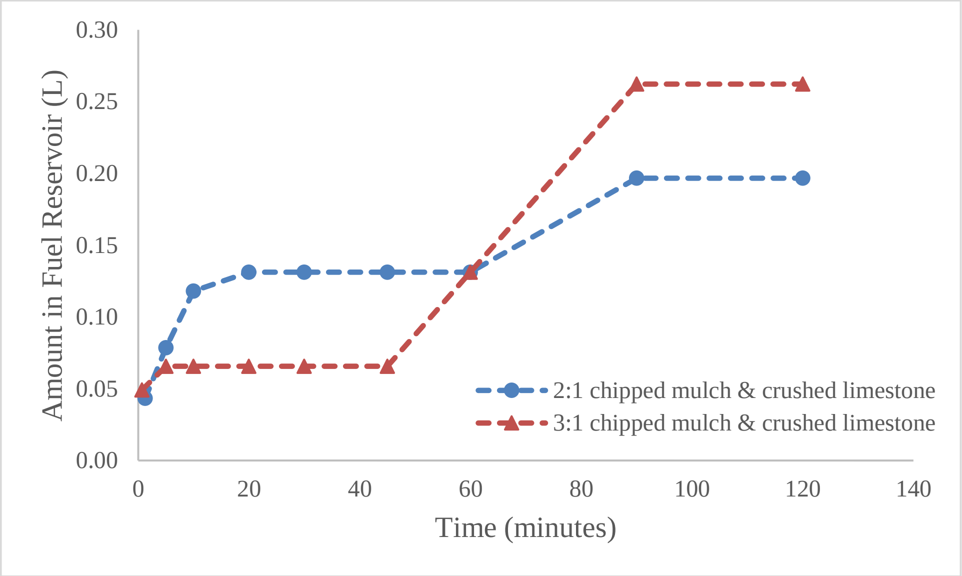

Figure 4.12: Amount of fuel accumulated in fuel storage reservoir over time during a second simulated flow-event. The 2:1 proportion test is blue dashed line with circle points, and the 3:1 proportion test is red dashed line with triangle points.

The results suggest that EIII fuel does not dissolve in solution, even after a period of days. This is significant, because in the field the bio-separator will experience stagnant, saturated conditions a majority of the time but EIII fuel is not expected to dissolve in the water and leave the system. This also indicates that removal efficiencies may be uniform after the second flow-event. More testing is required to conclude that the removal efficiencies will stay uniform over time.

4.7 GOVERNING PRINCIPLES

Several governing principles dictate how the bio-separator operates. The governing principles discussed in this section are flow through porous media, microbial activity, and water quality benefits from mulch and limestone.

4.7.1 Flow through Porous Media

The general approach to quantifying single-phase flow through porous media is by Darcy's law. This assumes complete saturation of the porous media; the pore space between the particles making up the medium is completely filled with the wetting phase. In the case of the bio-separator, there are multiple phases: water, fuel, and air. The multi-phase Darcy equation is the most straight forward approach to finding the relative permeability of oil (or fuel), but is not the most accurate. Many other flow models are extensions of Darcy's law in which they model each phase separately and assume the pressure gradients between the two phases are related by capillary pressure. Oil saturation is low and water saturation is significant in the bio-separator, which are characteristics that allow flow coupling to be the dominating forces considered in three-phase flow modeling.

4.7.2 Expected Benefits from Microbial Activity

For media exposed to petroleum products, the media will naturally accumulate microorganisms that use the carbon in petroleum products as their electron donor (energy source) and/or carbon source over time. Some aerobic and anaerobic microorganisms, petrophilic microbes, use n-alkanes found in petroleum products as their sole energy and carbon source (Jones and Edington, 1968; Coates et al., 1997; Hamamura and Arp, 2000; Prenafeta-Boldú et al., 2001; Jung et al., 2002; Balachandran et al., 2012). The relative ease for microorganisms to degrade a compound depends on the type of petroleum hydrocarbon. Aromatic compounds are generally harder to degrade than aliphatic (Evans et al., 1996). Branched aliphatic are generally harder to degrade than alkanes of a similar molecular weight (Aelion and Bradley, 1991). Higher n-alkanes are generally harder to degrade than lower n-alkanes (Jung et al., 2002). How well a compound is degraded also depends on nutrient availability and the environment's electron acceptor, aerobic, anoxic, or anaerobic. E-III fuel is composed of strait and branched alkanes with a *n* range from nine to thirteen carbons (Appendix A). This makes E-III fuel microbial degradation easier than most other petroleum products.

Some studies have shown that specific juniper trees species, Greek juniper and white cedar, contain oils that are anti-microbial (Khoury et al., 2014 and Poaty et al., 2015). Currently, no papers in the literature have investigated the effect on more than three bacteria strains or have specifically tested eastern red cedar for anti-microbial properties. This may or may not have an effect on the bio-separator's ability to accumulate petrophilic microbial communities.

4.7.3 Expected Benefits from Mulch

Wood products have proven effective for the removal of heavy metals (Bailey et al., 1999; Jang et al., 2005; Ray et al., 2006; Seelsaen et al., 2006; Edwards et al., 2009). Jang et al. (2005) found that mulch could remove 654 $mg \cdot kg^{-1}$ of Cu, 8,589 $mg \cdot kg^{-1}$ of Pb, and 3,124 $mg \cdot kg^{-1}$ of Zn. Not only would the bio-separator remove petroleum hydrocarbons, it will effective remove heavy metals.

Wood mulches have also been used to treat water with excess nutrients, mainly nitrate but also sulphate, ammonia, ammonium, nitrite, and orthophosphorus (Robertson et al., 2000; Kim et al., 2003; Savage and Tyrrl, 2005; Gibert et al., 2008; Edwards et al., 2009; Xuan et al., 2010; Saeed and Sun, 2011; Camilo et al., 2013; Frank et al., 2015). Many of these systems are anoxic and the mulch acts as the substrate and carbon source for anaerobic microbial communities. While the bio-separator may never reach complete anoxic conditions, after long periods of no water flow it would be possible for the bio-separator to harbor anaerobic microbial communities that use nitrate, sulphate, ammonia, ammonium, nitrite, and orthophosphorus as their electron donor.

Like petroleum hydrocarbons, pesticides pose a threat to marine biology in receiving waterbodies. Several studies have investigated the use of wood material to remove pesticides (Bras et al., 1999; Trapp et al., 2001; Huang et al., 2006; Camilo et al., 2013) and other halocarbons (Trapp et al., 2001; Boving and Zhang, 2004; Ray et al., 2006; Shenl et al., 2010).

Huang et al. (2006) specifically looked at the removal of diuron, isoxaben, oryzalin, and clopyralid with red cedar and found from model sensitivity analysis that over 80% removal efficiency of herbicide for detention times greater than eight minutes and less than 100 minutes. The bio-separator has the potential to treat pesticides and other halocarbons.

Typical wastewater pollutants such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS) can be reduced by woody products (Savage and Tyrrl, 2005; Zuma et al., 2008; Dalahmeh et al., 2011; Saeed and Sun, 2011). Dalahmeh et al. (2011) concludes that mulches can achieve higher organic matter removal than ordinary septic tanks. The bio-separator could potential lower the concentrations of BOD, COD, and TSS from runoff water.

Explosives such as TNT, RDX, and HMX can be removed by pine bark and mulch (Ahmad et al., 2007). One study for removing explosives in groundwater is under aerobic conditions (Ahmad et al., 2007). The bio-separator operates at mostly aerobic conditions and would most likely have similar results even though the mulch is red cedar instead of pine since they are both softwoods.

Wood is made up of cellulose, hemicellulose, and lignin. Lignin is lipophilic making it important in the woody product’s role of sorbing hydrocarbons. Softwoods, such as pines and cedars, generally have higher amounts of lignin than hardwoods. This makes softwoods better at sorbing petroleum hydrocarbons than hardwoods. The bio-separator employs a softwood, red cedar mulch, thus the petroleum hydrocarbons removal capacity is better than technologies that employ hardwoods such as bioretention cells.

4.7.4 Expected Benefits from Crushed Limestone Aggregate

Limestone is a rock that is mostly different forms of calcium carbonate. Calcium carbonate is known for its pH buffering capacity. The addition of limestone to water, in a powdered or crushed form, can help with the removal of heavy metals (Dean et al., 1972; Aziz et al., 2007; Cravotta et al., 2008). The addition of crushed limestone to the bio-separator increases the water quality of the runoff by increasing the pH buffer and removing heavy metals.

4.8 BIO-SEPARATOR APPLICATION

An initial operation and maintenance plan for the bio-separator is given. A recommended design procedure is described, followed by a case study using the design procedure for OSU Fire Service Training Center.

4.8.1 Operation and Maintenance

An important aspect of bio-separator implementation is the expected operation and maintenance of a bio-separator at live-firefighting training facilities. Since there is little data for operation and maintenance for the bio-separator at this time, these are recommendations and are subject to change after further testing.

Before other operation and maintenance practices can be discussed, being permitted for treating petroleum hydrocarbon contaminated water through the state environmental protection department is necessary. The permitting process varies from state to state, and from site to site. Most permits will have a yearly renewal process in which proof of completing proper maintenance may be required.

From preliminary testing of successive runoff events, the bio-separator does not decrease in removal efficiencies over two runoff events. During the live-firefighting training off-season, the bio-separator will still be operating during storm events. How well the bio-separator will perform during the off-season cannot be inferred from the lab-scale tests performed. Since the bio-separator’s main separation mechanisms are physical rather than biological, the bio-separator is expected to perform in hot and cold weather. The lab-scale bio-separator performed at temperatures ranging from 5^{o}C to 36^{o}C. It is speculated that the warmer the weather, the more active petrophilic microbes will become and microbial degradation rates will increase, but this has not been tested.

Proposed maintenance for each component and frequency of inspection is shown in Table 4.5. The facility area should be cleared of trash and debris every inspection. Concrete walls and baffles, limestone section, and inverted siphon should be checked for cracks and clogging annually. The mulch section should be checked for clogging and degrading at least biannually. Water levels in the bio-separator should also be checked quarterly. Letting a bio-separator run dry would lead to fuel escaping out of the inverted siphon and should be avoided by keeping the water levels at the height of the inverted siphon. Levels that are two low may also lead to faster degradation of the mulch. However, if water levels get too high, the water will flow over the material and short-circuit the system. Quarterly or after storm events larger than the design storm, inspection of the inlet reservoir, screens, and fuel storage reservoir should take place.

Table 4.5: Table of the maintenance for each component of a bio-separator at live-firefighting training facilities. Includes inspection frequency, conditions for maintenance, and action needed. A = annual, Bi = biannual, Q = quarterly, Storm = storm events over 64 mm, HB = high burn period.

Component	Inspection Frequency	Condition when Maintenance is Needed	Action Needed
Facility Area	During every inspection	Trash and debris present	Clean out trash and debris
Concrete Walls and Baffles	A	Cracks or failure	Repair/seal cracks Replace if repair is insufficient
Inlet Reservoir	Q or Storm	Build-up of sediment	Remove sediment
Screens	Q or Storm	Clogging and rips/tears	Power was screens Patch rips and tears
Mulch Section	Bi	Clogging or degrading	Replace mulch, dry and burn the waste
Limestone Section	A	Clogging	Remove, wash, and return to section
Fuel Storage Reservoir	Q or HB	Excess fuel	Skim or siphon the fuel for reuse
Inverted Siphon	A	Cracking or clogging	Repair/seal cracks Replace if repair is insufficient Remove clog
Water Level	Q	Lower than inverted siphon level Higher than inverted siphon level	Add water Check for clogging and remove clog

4.8.2 Bio-separator Design Procedure

This section provides a suggested procedure for designing a bio-separator. This procedure is used in the Case Study section. Steps 1-5 are procedures for finding a total volume based upon the runoff area and peak flow of a design storm event. Steps 6-10 are procedures for finding the dimensions of the material section of the bio-separator. Steps 11-16 are procedures for finding the dimensions of the inlet reservoir of the bio-separator with baffles for settling particles to prevent clogging in the material. Steps 17 and 18 are procedures for calculating the dimensions of the fuel storage reservoir.

1. *Delineate runoff area for the bio-separator.*
2. *Select design storm event.* Stormwater detention facilities use a 2-year 6-hour frequency storm as the design storm event (Clark County Regional Flood Control District, 2014), but other frequency storms can be selected since there are no design storm regulations for stormwater facilities.
3. *Calculate peak discharge.* There are several methods to calculate peak flow from a storm event; this section uses the Rational Method to calculate the peak discharge,

   $$Q = CiA \tag{4.3}$$

   where Q is the peak discharge in $ft^3 \cdot s^{-1}$, C is the runoff coefficient, i is the rainfall intensity $in \cdot hr^{-1}$, and A is the area in acres.
4. *Select a total hydraulic retention time (*HRT*) for the system.* To stay within the range of hydraulic retention times that was tested for the lab-scale bio-separator, a hydraulic retention time of 8 to 20 minutes is recommended. This concurs with the results of the mulch liquid-uptake experiments that verify over a majority of the mulch is saturated in under five minutes.
5. *Calculate total volume.* Total volume is calculated using the design *Q*, *HRT,* and following equation,

   $$V = Q * HRT \tag{4.4}$$

where V is the volume in m^3, Q is the peak discharge in $m^3 \cdot s^{-1}$, and HRT is the hydraulic retention time in seconds.

6. *Determine volume of material section.* The suggested percentage of the volume for the material section is between 20% and 40% of the total volume of the bio-separator. This is based upon the lab-scale conditions that were tested.
7. *Determine a linear velocity.* From length-proportion lab-scale testing, a linear velocity of near 0.126 $m \cdot min^{-1}$ (223 $in \cdot hr^{-1}$) is suggested for the bio-separator design. The linear velocity through the 3:1 mulch to crushed limestone bio-separator tests was calculated by,

$$v = \frac{Q}{A_c} \tag{4.5}$$

   where Q is the discharge in $m^3 \cdot s^{-1}$, v is the linear velocity in $m \cdot s^{-1}$, and A_c is the cross-sectional area of the bio-separator in m^2.
8. *Calculate cross-sectional area.* By rearranging Equation 4.5, the A_c can be calculated with design Q and v.
9. *Select height, width, and length.* The height and width must multiple to equal the A_c. It is suggested to keep in mind the periodic replacement of the mulch at this step; for example, a mulch layer with a height of 0.1 m and width of 2-m would be easier to clean than a mulch layer with reversed height and width. The length can then be calculated from the design material volume, height, and width. At this step, it is recommended that the *MRT* be checked. If the MRT is less than 5 minutes, the volume of the material section can be adjusted and steps eight and nine be re-done.
10. *Calculate chipped red cedar mulch and small crushed limestone (size #8) layer length.* Based upon the lab-scale testing, a length proportion ratio of 3:1 is recommended for best performance. If the goal of the design is to minimize maintenance then a lower length proportion can be used since crushed limestone will not need to be replaced.
11. *Select material section's width as the width for the inlet reservoir.*

12. *Determine a volume of inlet reservoir.* The suggested percentage of the volume for the inlet reservoir is between 15% and 30% of the total volume of the bio-separator. This is based upon the lab-scale conditions that were tested.
13. *Determine a target particle size to settle out in the inlet reservoir.* A particle size in the sand particle range (0.05-2 mm) is recommended so that the inlet reservoir does not dwarf the rest of the bio-separator.
14. *Calculate settling velocity of particle size.* The particle settling velocity can be calculated using an adapted Navier-Stokes equation,

$$v_s = \frac{g\, d_p^2(\rho_p - \rho_f)}{18\mu} \tag{4.6}$$

where v_s is the settling velocity in m·s^{-1}, g is the gravity constant in m·s^{-2}, d_p is the particle diameter in m, ρ_p is the particle density in kg·m^{-3}, ρ_f is the fluid density in kg·m^{-3}, μ is the fluid dynamic viscosity in N·s·m^{-2}.

15. *Select number of baffles.* The recommendations for baffle numbers is two baffles for a runoff area less than 0.25 acres, and as many as five baffles for runoff areas greater than 1 acre. This is to increase the flow-path length and allow longer time for particle settling.
16. *Determine height and flow-path length.* The flow-path length can be solved by comparing the flow and settling velocity ratio with the flow-path length and depth ratio,

$$\frac{v}{v_s} \leq \frac{L}{D} \tag{4.7}$$

where L is length in m and D is depth in m. Using a software with a solver function is recommended for this step to adjust the target particle size and number of baffles to find a reasonable height and flow-path length. A flow-path length to depth ratio greater than or equal to two is recommended.

17. *Calculate volume for fuel storage reservoir to maintain the design* HRT.
18. *Select material section's width as the width for the fuel storage reservoir.*
19. *Select the height and length for the fuel storage reservoir with the design volume.*

4.8.3 Case Study at Oklahoma State University Fire Service Training Center

A pilot scale bio-separator has been designed for the OSU Fire Service Training Center to replace their limited treated liquid-fuel and water runoff. Flow from storm events are larger than from live-fire training burns; thus, a design storm event was selected for the pilot scale bio-separator design.

1. *Delineate runoff area for the bio-separator.* For the Fire Service Training Center, the runoff area to be treated by the bio-separator is 0.42 acres.
2. *Select design storm event.* A 2-year 6-hour frequency storm was selected as the design storm (Clark County Regional Flood Control District, 2014). For Stillwater, Oklahoma, that corresponds to 7.21 cm (2.84-in) of rainfall with a rainfall intensity (*i*) of 1.21 cm·hr^{-1} (0.475 in·hr^{-1}) (National Oceanic and Atmospheric Administration, 2014).
3. *Calculate peak discharge.* The area is impervious which correlates to a runoff coefficient of 0.95. Using the Rational Method to calculate the peak discharge,

   $$Q = 0.95 * 0.475\,\frac{\text{in}}{\text{hr}} * 0.42\ \text{acres} \tag{4.3}$$

   Q is 0.19 ft^3·s^{-1} (0.32 m^3·min^{-1}).
4. *Select a total hydraulic retention time (*HRT*) for the system.* A hydraulic retention time of 15 minutes was chosen because it falls between the recommended range of 8 to 20 minutes.
5. *Calculate total volume.* Total volume was calculated with the design *Q*, *HRT*, and

   $$V = 0.32\,\frac{\text{m}^3}{\text{min}} * 15\ \text{min} \tag{4.4}$$

   V is 4.8 m^3.
6. *Determine volume of material section.* The volume of the material section was selected to be 40% of the total volume of the bio-separator. This allows for a 5 minute *MRT*, correlating a mulch layer volume that is 33% of the total volume.
7. *Determine a linear velocity.* From length-proportion lab-scale testing, a linear velocity of 0.126 m·min^{-1} (223 in·hr^{-1}) was selected.

8. *Calculate cross-sectional area.* By rearranging Equation 4.5, the A_c was calculated with design Q and v,

$$A_c = 0.32 \frac{\mathrm{m}^3}{\mathrm{min}} / 0.126 \frac{\mathrm{m}}{\mathrm{min}} \tag{4.5}$$

   A_c is 2.54 m^2.

9. *Select height, width, and length.* An initial height of 1.68 m (5.5 ft), width of 1.68 m (5.5 ft), and length of 0.69 m (2.25 ft) was chosen.

10. *Calculate chipped red cedar mulch and small crushed limestone (size #8) layer length.* Based upon the lab-scale testing, a length proportion ratio of 3:1 is recommended for best performance. This correlates to a mulch layer length of 0.52 m (1.7 ft) and a limestone layer of 0.18 m (0.6 ft). The *MRT* is 4.5 minutes, correlating to a mulch layer volume that is 30% of the total volume.

11. Select material section's width as the width for the inlet reservoir. An initial width of 1.68 m (5.5 ft) was selected.

12. *Determine a volume of inlet reservoir.* A percent volume of 35% was selected. This is correlates to a volume of 1.71 m^3.

13. Determine a target particle size to settle out in the inlet reservoir. A particle size in the sand particle range was selected, 0.05 mm.

14. *Calculate settling velocity of particle size.* The particle settling velocity was calculated using an adapted Navier-Stokes equation,

$$v_s = \frac{g\, d_p^2(\rho_p - \rho_f)}{18\mu} \tag{4.6}$$

   v is 0.00224 $\mathrm{m \cdot s^{-1}}$.

15. Select number of baffles. Three baffles were selected.

16. *Determine height and flow-path length.* An equation to correlate the flow length and width was developed using Figure 4.13. The flow length is 3 2/3 times the width.

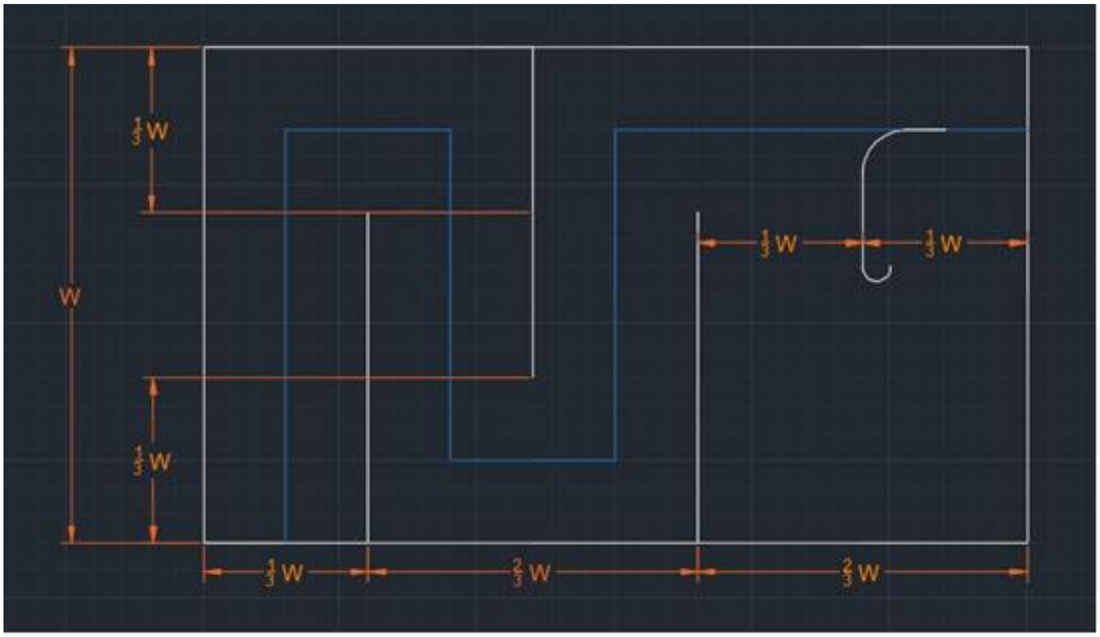

Figure 4.13: A schematic of the inlet reservoir design. The white lines are the walls and baffles of the inlet reservoir, the blue line is the flow length, and the orange lines are the dimension delineators.

The flow-path length can be solved by comparing the flow and settling velocity ratio with the flow-path length and depth ratio,

$$\frac{v}{v_s} \leq \frac{L}{D} \tag{4.7}$$

where L is length in m and D is depth in m. Both equations were put into the solver add-in function in Microsoft Excel 2013 Analysis ToolPac. A final width of 1.52 m (5 ft) was able to maintain the correct velocity to satisfy Equation 4.7. The total length of the inlet reservoir is 2.53 m (8.3 ft).

17. *Calculate volume for fuel storage reservoir to maintain the design* HRT. The volume to maintain the design HRT is 1.13 m^3.
18. *Select material section's width as the width for the fuel storage reservoir.* To maintain both a height and width similar to the material section, a width of 1.22 m (4 ft) was selected.
19. *Select the height and length for the fuel storage reservoir with the design volume*. A height of 1.52 m (5 ft) and a length of 0.61 m (2 ft) was selected.

The final design dimensions of the bio-separator are located in Table 4.6.

Table 4.6: Design dimensions for a pilot scale bio-separator at the Oklahoma State University Fire Service Training Center.

	Initial/Settling Reservoir	Material Layers		Fuel Storage Reservoir	Total Dimensions
		Mulch	**Aggregate**		
Length, m (ft)	2.53 (8.3)	0.52 (1.7)	0.18 (0.6)	0.61 (2)	3.84 (12.6)
Width, m (ft)	1.52 (5)	1.68 (5.5)	1.68 (5.5)	1.22 (4)	-
Height, m (ft)	0.46 (1.5)*	1.68 (5.5)*	1.68 (5.5)*	1.52 (5.0)*	-
Volume, m^3 (ft^3)	1.77 (62)	1.47 (51)	0.51 (18)	1.13 (40)	4.88 (172)
Percent of Volume, %	36%	30%	10%	23%	
Hydraulic Retention Time, min	5.44	4.50	1.59	3.50	15.02

*Freeboard of 0.3 m (1 ft) not included in height

The dimensions of the pilot-scale bio-separator and the multiple-regression analysis were used to calculate the approximate breakthrough time and removal efficiency. For some of the variables needed in the regressions, the average value of all the dual-material tests was used. The values used are located in Table 4.7. For this pilot-scale bio-separator, the breakthrough time was estimated to be approximately 340 minutes and the removal efficiency was found to be 99.8%. These values are consistent with the observed values from lab testing.

Table 4.7: Input values for breakthrough time and removal efficiency regression equation. C_{in} = influent fuel concentration, Q = total flowrate, HRT = total hydraulic retention time, MRT = mulch hydraulic retention time, and θ = mulch moisture content.

$C_{in}\cdot Q$ $mg\cdot min^{-1}$	MRT/HRT $min\cdot min^{-1}$	θ/(MRT/HRT)	MRT min	θ $g\cdot g^{-1}$	C_{in} $mg\cdot L^{-1}$
2390*	0.34	1.07*	3.61	0.36*	708

*Average values used from dual-material tests

CHAPTER V

CONCLUSIONS AND FUTURE WORK

A biological material passive separator (bio-separator) was designed with the intent of treating free-phase petroleum hydrocarbons from runoff waters at live-firefighting training facilities. The bio-separator treats free-phase liquid-fuel contaminated water through horizontal flow through a layer of mulch and a layer of aggregate in series. The mixture is separated through the mulch and aggregate and fuel is retained in the fuel storage reservoir while water flows out the inverted siphon.

This thesis 1) completes a comprehensive literature review on methods for removing petroleum hydrocarbons from runoff and the performance of wood mulch for stormwater pollutant removal, 2) elucidates on the removal processes of the bio-separator, and 3) investigates design options for enhanced performance of the bio-separator.

The final objective of investigating bio-separator design options for increased fuel removal efficiency and increased fuel breakthrough time was reached by running several lab-scale tests in two prototype bio-separators. Removal efficiency was determined by the incoming concentration and maximum observed concentration of the effluent. The fuel breakthrough time was the time that it takes for a continuous flow of fuel to penetrate the bio-separator’s fuel storage reservoir. To improve the bio-separator design, two design parameters were investigated,

1) determine the best mulch and aggregate individually and 2) determine the best length proportion of mulch and aggregate. The best individual mulch and aggregate is medium-degraded chipped red cedar mulch and small crushed limestone size #8, respectively. The best performing length proportion is 3:1 mulch to aggregate.

Using the results from the tests runs, multiple regression analysis was performed and relationships for breakthrough time and concentration reduction were found. Breakthrough time was correlated to fuel mass flowrate, moisture content of mulch by mass, and length of mulch; while concentration reduction was correlated to length of mulch, moisture content of mulch by mass, breakthrough time, total volumetric flowrate, and aggregate pack density.

An initial operation and maintenance plan was provided as well as a recommended design procedure. Given the design procedure and enhanced design of the bio-separator through lab-scale tests, a pilot-scale case study bio-separator was designed for the OSU Fire Service Training Center.

In conclusion, originally designed for a live-fire training center, the bio-separator can effectively remove free-phase petroleum hydrocarbons from runoff water through horizontal flow through a layer of chipped red cedar mulch and a layer of small crushed limestone (size #8) in series. The bio-separator is an innovative and sustainable design that effectively treats water impacted by free-phase light density petroleum hydrocarbons, while minimizing the disadvantages other commercially available treatment options possess such as waste disposal, fluctuating effectiveness, and intensive manual maintenance. The potential for petroleum hydrocarbons to contaminate water is ever expanding in our ever urbanizing society.

5.1 FUTURE WORK RECOMMENDATIONS

There are several work recommendations to further improve the design and expand on the governing principles of the bio-separator. They are organized by steps to take before a pilot study, steps to take before construction at different locations, and general design improvements.

5.1.1 Proceeding Pilot Study

Before a pilot-scale bio-separator can be constructed, there are two recommended actions:

- Completion of a comprehensive Operation and Maintenance plan, and
- Research effects of upscaling on performance.

The operation and maintenance plan presented in the Chapter IV is preliminary and needs to be expanded on. Suggested expansion includes a step-by-step permitting process, detailed off-season and seasonal performance, and detailed maintenance of mulch. Upscaling will affect the performance of the bio-separator. Researching the effects of upscaling the design is highly recommended before the final design and construction of the OSU Fire Service Training pilot-scale bio-separator. Once the pilot-scale bio-separator is completed, it should be monitored for performance.

5.1.2 Proceeding Construction at Other Locations

There are two recommended actions before a bio-separator can be constructed at other locations:

- Test the removal of different petroleum hydrocarbons, and
- Apply knowledge from the pilot-scale study to design recommendations.

Knowing how well the bio-separator performs at removing different petroleum hydrocarbon, such as gasoline, diesel, and used motor oil, is important for improving the bio-separator design for different locations, be it gas stations, airports, or parking lots. The conclusions from the pilot-scale study will also be important for improving the bio-separator design.

5.1.3 Expanding on Governing Principles and Further Design Improvements

Other recommendations for general design improvements and expanding on governing principles are:

- Quantify effects of biological processes on performance,

- Quantify effects of mulch height on breakthrough time,
- Quantify effects of environmental factors on performance,
- Test other biological materials, and
- Develop a theoretical equation for performance.

Further understanding the effects of biological processes and quantifying the time it takes for petroleum products to degrade in the bio-separator's system via microbial activity are important expansions on understanding the governing principles of the bio-separator. Because mulch can uptake water and fuel, the effect of mulch height is important for design improvements. Environmental factors, such as temperature, humidity, solar radiation, and wind speed, effects on the bio-separator's performance will contribute to the design modifications for different locations. The testing of pine needle, coconut fiber, and other various biological materials that are cheap and locally available in other regions (preferable products that would otherwise be considered waste) will also contribute to the design modifications for different regions. And, finally, having a theoretical equation for performance will make it possible to optimize the bio-separator.

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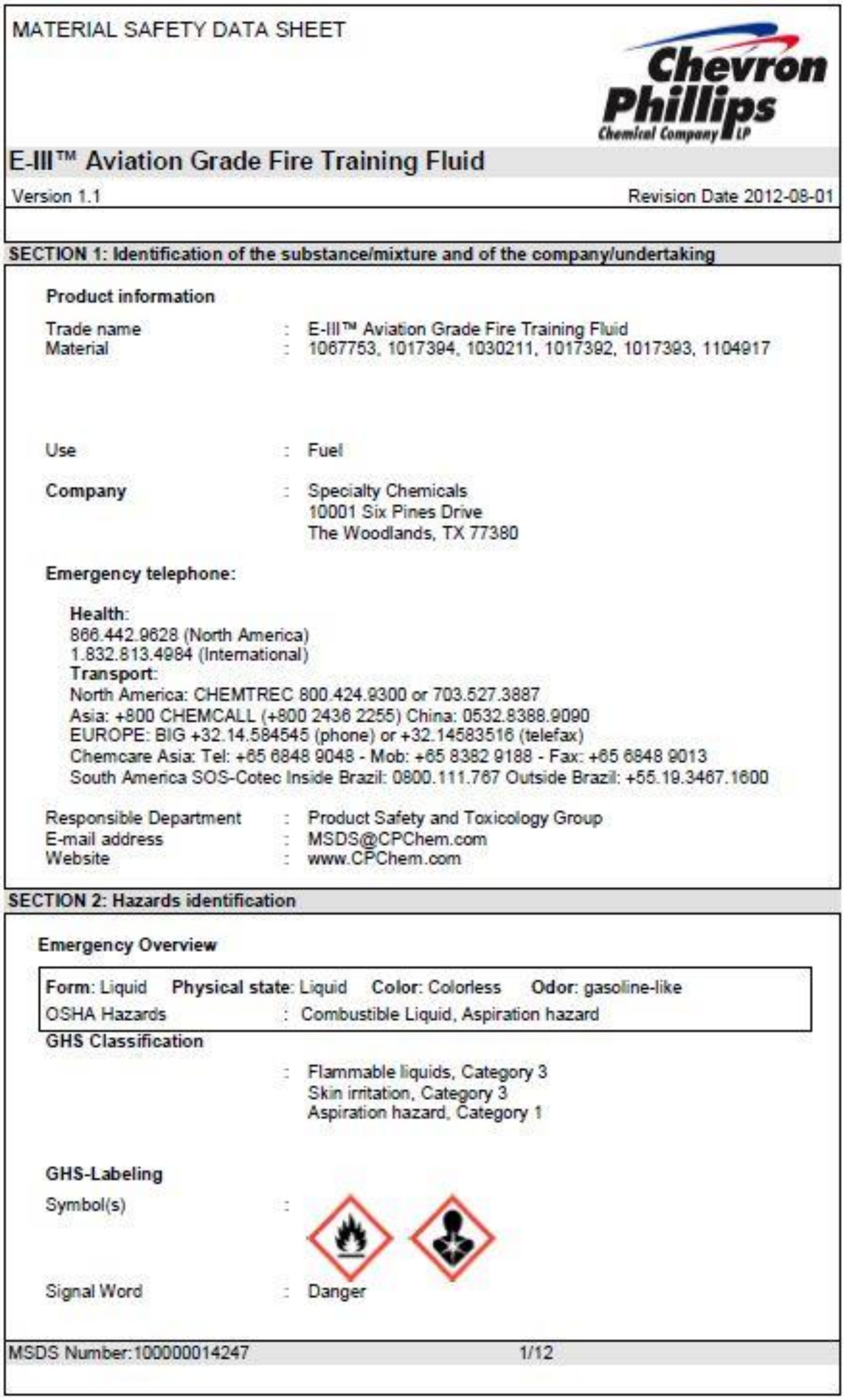
APPENDICES

APPENDIX A: E-III™ Aviation Grade Fire Training Fluid MSDS



MATERIAL SAFETY DATA SHEET

E-III™ Aviation Grade Fire Training Fluid

Version 1.1

Revision Date 2012-08-01

SECTION 1: Identification of the substance/mixture and of the company/undertaking

Product information

Trade name : E-III™ Aviation Grade Fire Training Fluid
Material : 1067753, 1017394, 1030211, 1017392, 1017393, 1104917

Use : Fuel

Company : Specialty Chemicals
10001 Six Pines Drive
The Woodlands, TX 77380

Emergency telephone:

Health:
866.442.9628 (North America)
1.832.813.4984 (International)
Transport:
North America: CHEMTREC 800.424.9300 or 703.527.3887
Asia: +800 CHEMCALL (+800 2436 2255) China: 0532.8388.9090
EUROPE: BIG +32.14.584545 (phone) or +32.14583516 (telefax)
Chemcare Asia: Tel: +65 6848 9048 - Mob: +65 8382 9188 - Fax: +65 6848 9013
South America SOS-Cotec Inside Brazil: 0800.111.767 Outside Brazil: +55.19.3467.1600

Responsible Department : Product Safety and Toxicology Group
E-mail address : MSDS@CPChem.com
Website : www.CPChem.com

SECTION 2: Hazards identification

Emergency Overview

Form: Liquid **Physical state**: Liquid **Color**: Colorless **Odor**: gasoline-like
OSHA Hazards : Combustible Liquid, Aspiration hazard

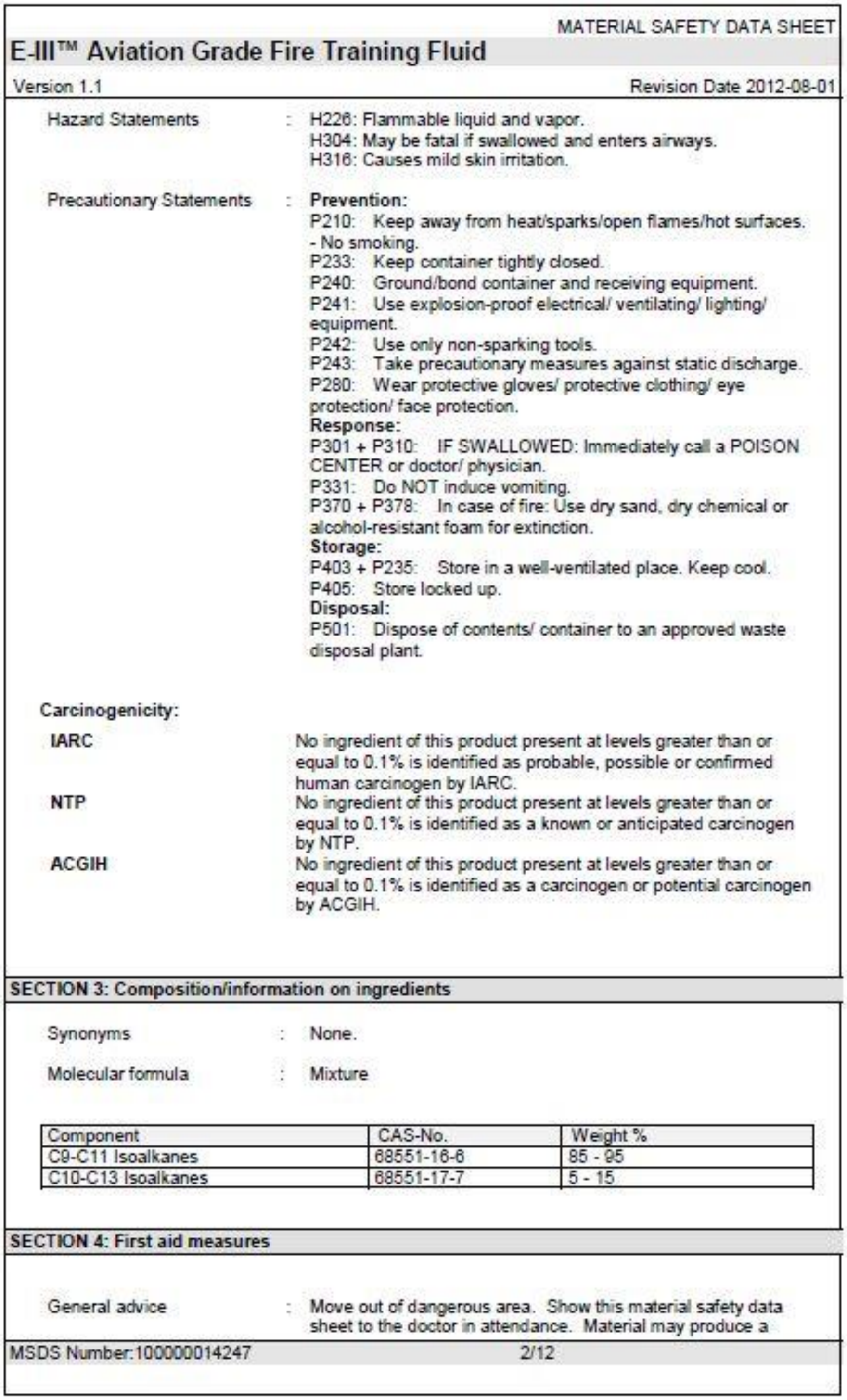
GHS Classification

: Flammable liquids, Category 3
Skin irritation, Category 3
Aspiration hazard, Category 1

GHS-Labeling

Symbol(s) :

Signal Word : Danger



MATERIAL SAFETY DATA SHEET

E-III™ Aviation Grade Fire Training Fluid

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Hazard Statements : H226: Flammable liquid and vapor.
H304: May be fatal if swallowed and enters airways.
H316: Causes mild skin irritation.

Precautionary Statements : **Prevention:**
P210: Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
P233: Keep container tightly closed.
P240: Ground/bond container and receiving equipment.
P241: Use explosion-proof electrical/ ventilating/ lighting/ equipment.
P242: Use only non-sparking tools.
P243: Take precautionary measures against static discharge.
P280: Wear protective gloves/ protective clothing/ eye protection/ face protection.
Response:
P301 + P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/ physician.
P331: Do NOT induce vomiting.
P370 + P378: In case of fire: Use dry sand, dry chemical or alcohol-resistant foam for extinction.
Storage:
P403 + P235: Store in a well-ventilated place. Keep cool.
P405: Store locked up.
Disposal:
P501: Dispose of contents/ container to an approved waste disposal plant.

Carcinogenicity:

IARC No ingredient of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

NTP No ingredient of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

ACGIH No ingredient of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

SECTION 3: Composition/information on ingredients

Synonyms : None.

Molecular formula : Mixture

Component	CAS-No.	Weight %
C9-C11 Isoalkanes	68551-16-6	85 - 95
C10-C13 Isoalkanes	68551-17-7	5 - 15

SECTION 4: First aid measures

General advice : Move out of dangerous area. Show this material safety data sheet to the doctor in attendance. Material may produce a

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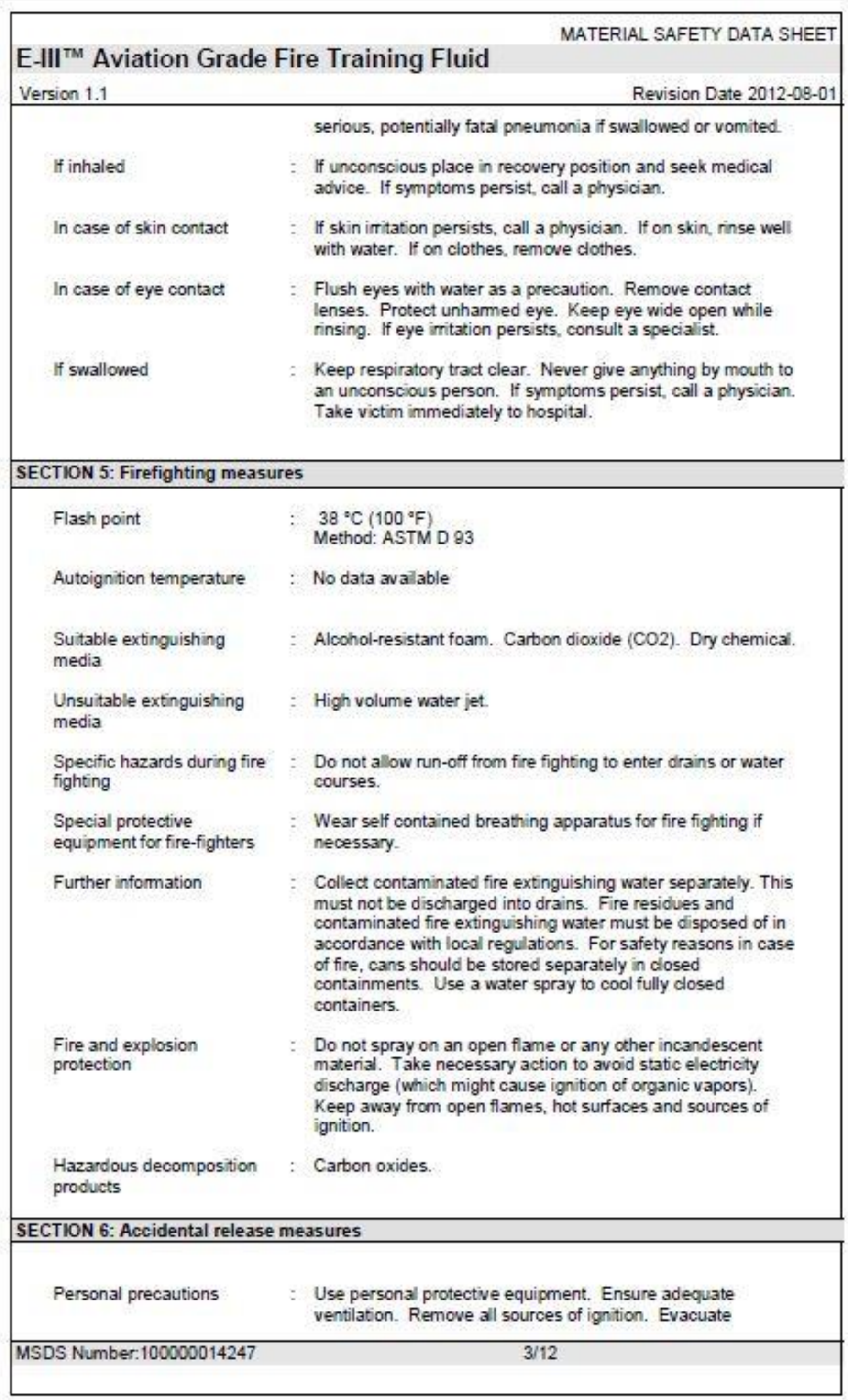

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	serious, potentially fatal pneumonia if swallowed or vomited.
If inhaled	: If unconscious place in recovery position and seek medical advice. If symptoms persist, call a physician.
In case of skin contact	: If skin irritation persists, call a physician. If on skin, rinse well with water. If on clothes, remove clothes.
In case of eye contact	: Flush eyes with water as a precaution. Remove contact lenses. Protect unharmed eye. Keep eye wide open while rinsing. If eye irritation persists, consult a specialist.
If swallowed	: Keep respiratory tract clear. Never give anything by mouth to an unconscious person. If symptoms persist, call a physician. Take victim immediately to hospital.

SECTION 5: Firefighting measures

Flash point	: 38 °C (100 °F) Method: ASTM D 93
Autoignition temperature	: No data available
Suitable extinguishing media	: Alcohol-resistant foam. Carbon dioxide (CO2). Dry chemical.
Unsuitable extinguishing media	: High volume water jet.
Specific hazards during fire fighting	: Do not allow run-off from fire fighting to enter drains or water courses.
Special protective equipment for fire-fighters	: Wear self contained breathing apparatus for fire fighting if necessary.
Further information	: Collect contaminated fire extinguishing water separately. This must not be discharged into drains. Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations. For safety reasons in case of fire, cans should be stored separately in closed containments. Use a water spray to cool fully closed containers.
Fire and explosion protection	: Do not spray on an open flame or any other incandescent material. Take necessary action to avoid static electricity discharge (which might cause ignition of organic vapors). Keep away from open flames, hot surfaces and sources of ignition.
Hazardous decomposition products	: Carbon oxides.

SECTION 6: Accidental release measures

Personal precautions	: Use personal protective equipment. Ensure adequate ventilation. Remove all sources of ignition. Evacuate

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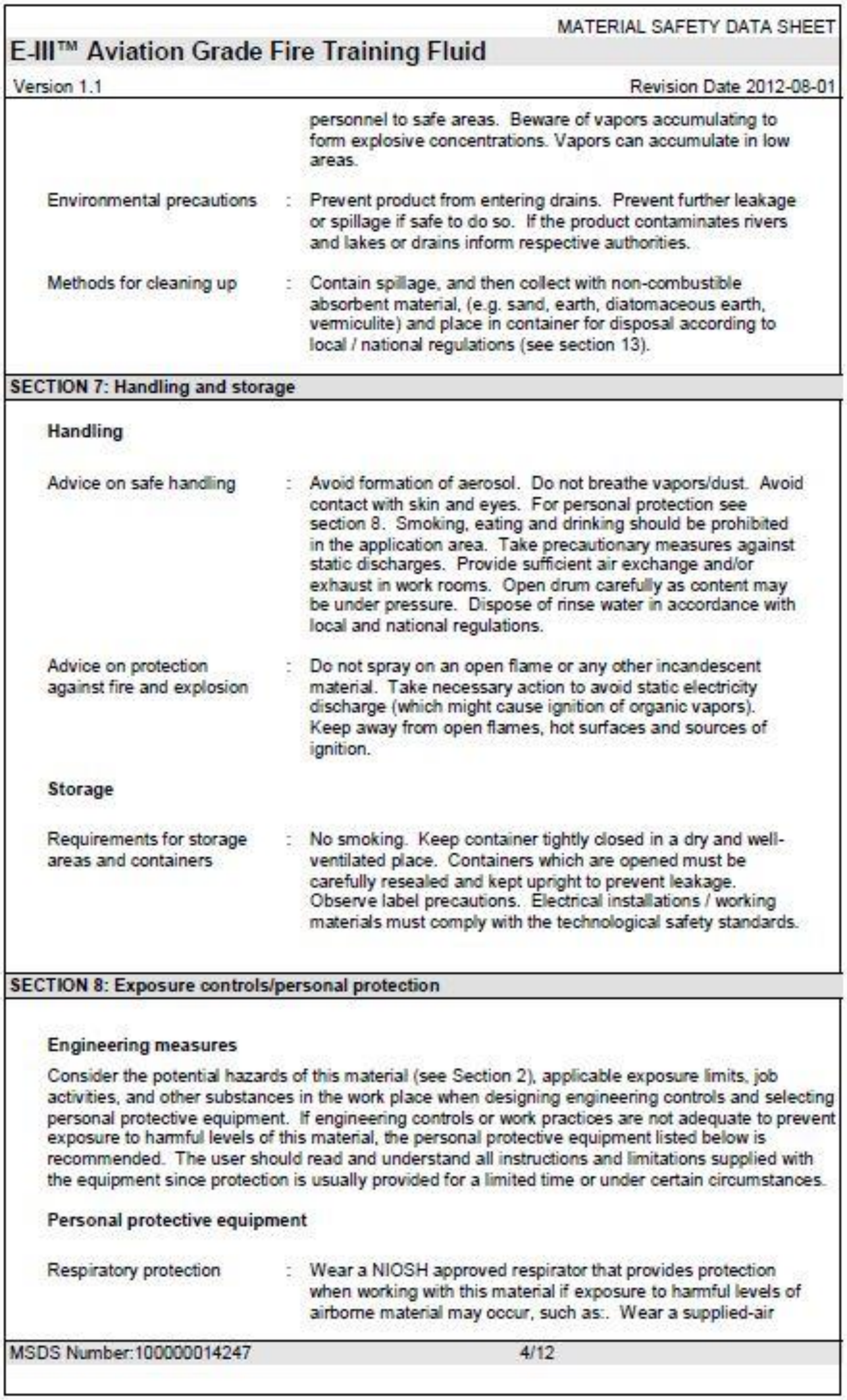

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	personnel to safe areas. Beware of vapors accumulating to form explosive concentrations. Vapors can accumulate in low areas.
Environmental precautions	: Prevent product from entering drains. Prevent further leakage or spillage if safe to do so. If the product contaminates rivers and lakes or drains inform respective authorities.
Methods for cleaning up	: Contain spillage, and then collect with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and place in container for disposal according to local / national regulations (see section 13).

SECTION 7: Handling and storage

Handling

Advice on safe handling	: Avoid formation of aerosol. Do not breathe vapors/dust. Avoid contact with skin and eyes. For personal protection see section 8. Smoking, eating and drinking should be prohibited in the application area. Take precautionary measures against static discharges. Provide sufficient air exchange and/or exhaust in work rooms. Open drum carefully as content may be under pressure. Dispose of rinse water in accordance with local and national regulations.
Advice on protection against fire and explosion	: Do not spray on an open flame or any other incandescent material. Take necessary action to avoid static electricity discharge (which might cause ignition of organic vapors). Keep away from open flames, hot surfaces and sources of ignition.

Storage

Requirements for storage areas and containers	: No smoking. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. Observe label precautions. Electrical installations / working materials must comply with the technological safety standards.

SECTION 8: Exposure controls/personal protection

Engineering measures

Consider the potential hazards of this material (see Section 2), applicable exposure limits, job activities, and other substances in the work place when designing engineering controls and selecting personal protective equipment. If engineering controls or work practices are not adequate to prevent exposure to harmful levels of this material, the personal protective equipment listed below is recommended. The user should read and understand all instructions and limitations supplied with the equipment since protection is usually provided for a limited time or under certain circumstances.

Personal protective equipment

Respiratory protection	: Wear a NIOSH approved respirator that provides protection when working with this material if exposure to harmful levels of airborne material may occur, such as:. Wear a supplied-air

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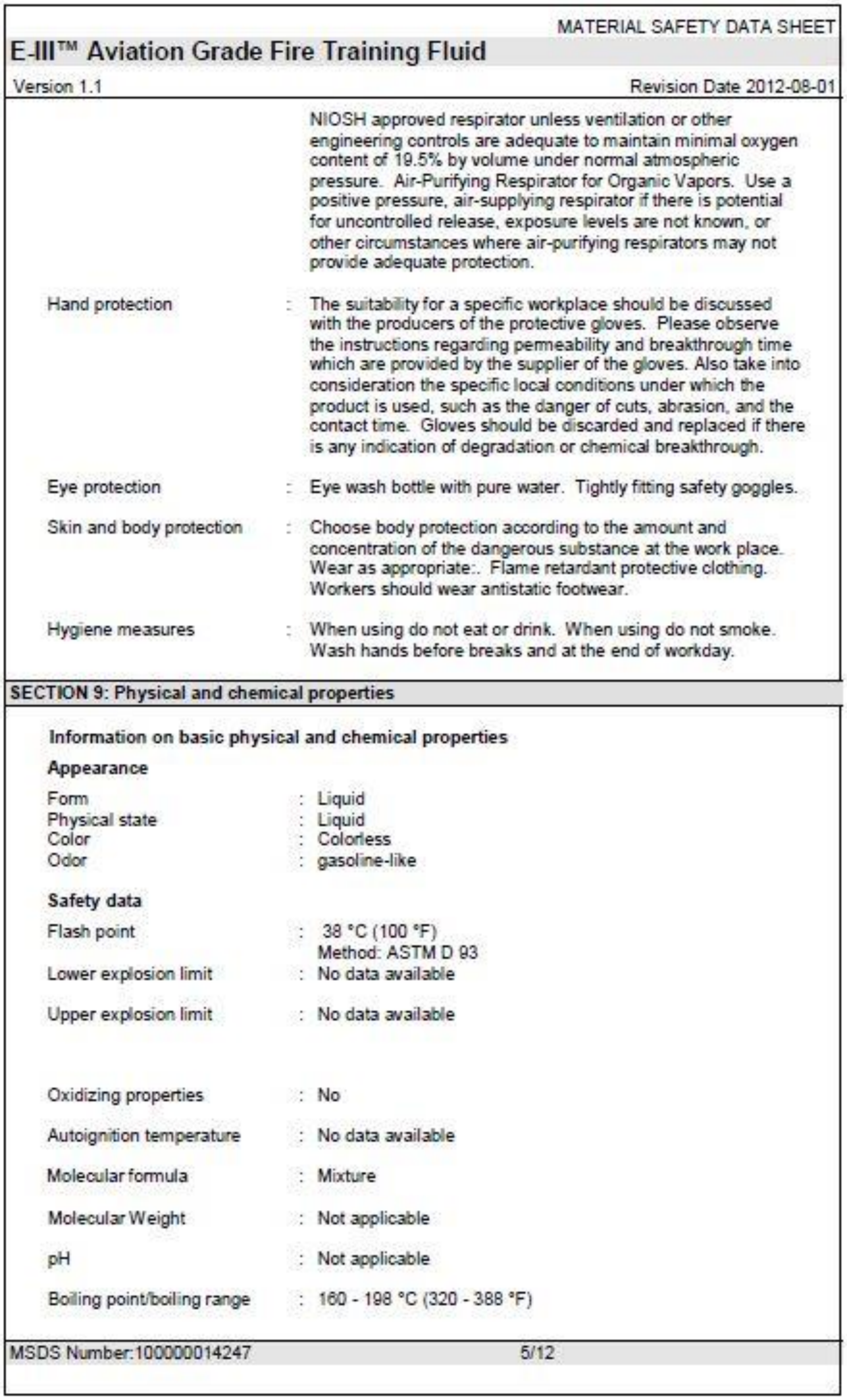

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NIOSH approved respirator unless ventilation or other engineering controls are adequate to maintain minimal oxygen content of 19.5% by volume under normal atmospheric pressure. Air-Purifying Respirator for Organic Vapors. Use a positive pressure, air-supplying respirator if there is potential for uncontrolled release, exposure levels are not known, or other circumstances where air-purifying respirators may not provide adequate protection.

Hand protection : The suitability for a specific workplace should be discussed with the producers of the protective gloves. Please observe the instructions regarding permeability and breakthrough time which are provided by the supplier of the gloves. Also take into consideration the specific local conditions under which the product is used, such as the danger of cuts, abrasion, and the contact time. Gloves should be discarded and replaced if there is any indication of degradation or chemical breakthrough.

Eye protection : Eye wash bottle with pure water. Tightly fitting safety goggles.

Skin and body protection : Choose body protection according to the amount and concentration of the dangerous substance at the work place. Wear as appropriate:. Flame retardant protective clothing. Workers should wear antistatic footwear.

Hygiene measures : When using do not eat or drink. When using do not smoke. Wash hands before breaks and at the end of workday.

SECTION 9: Physical and chemical properties

Information on basic physical and chemical properties

Appearance

Form : Liquid
Physical state : Liquid
Color : Colorless
Odor : gasoline-like

Safety data

Flash point : 38 °C (100 °F)
Method: ASTM D 93

Lower explosion limit : No data available

Upper explosion limit : No data available

Oxidizing properties : No

Autoignition temperature : No data available

Molecular formula : Mixture

Molecular Weight : Not applicable

pH : Not applicable

Boiling point/boiling range : 160 - 198 °C (320 - 388 °F)

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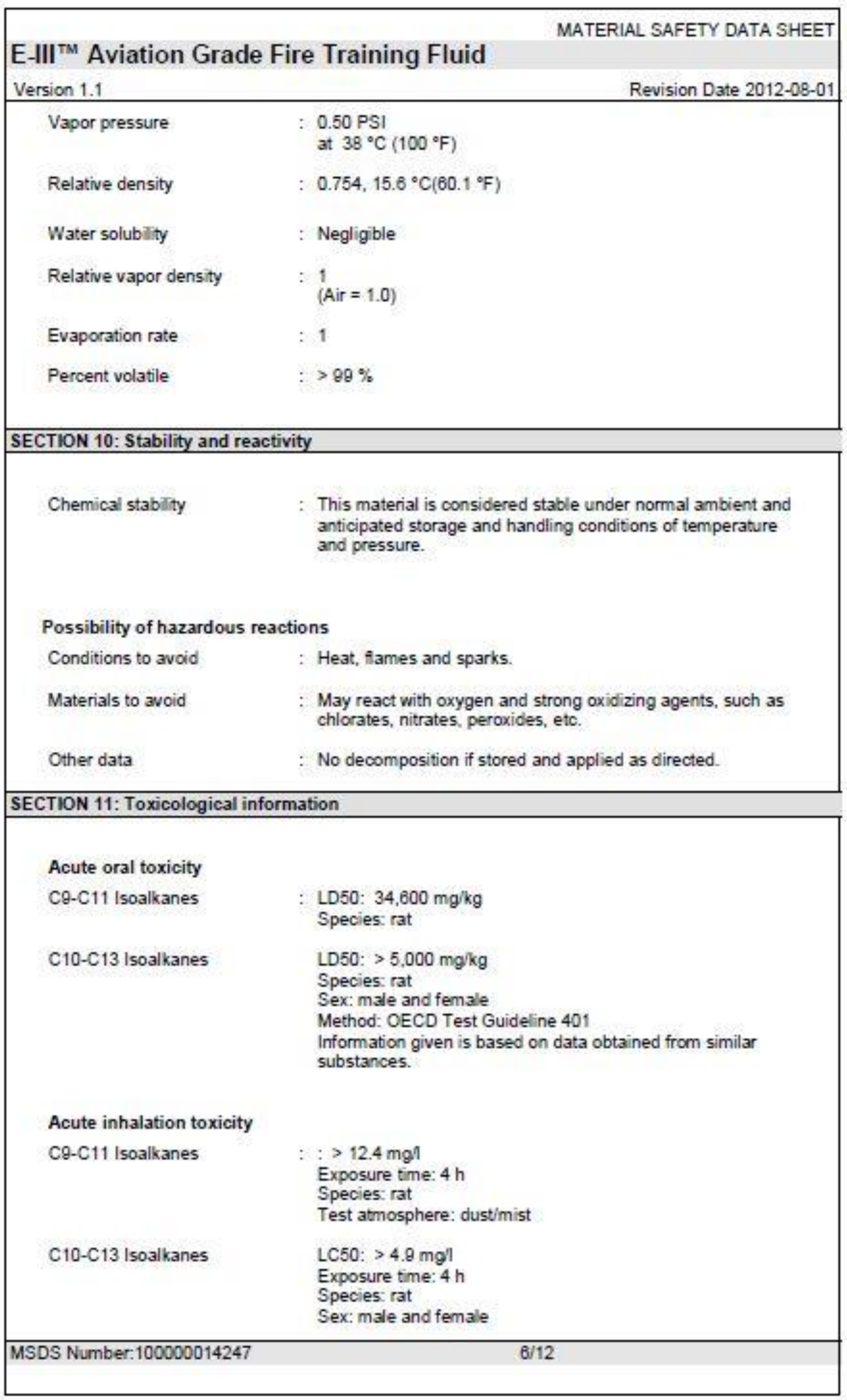

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Vapor pressure	: 0.50 PSI at 38 °C (100 °F)
Relative density	: 0.754, 15.6 °C(60.1 °F)
Water solubility	: Negligible
Relative vapor density	: 1 (Air = 1.0)
Evaporation rate	: 1
Percent volatile	: > 99 %

SECTION 10: Stability and reactivity

Chemical stability	: This material is considered stable under normal ambient and anticipated storage and handling conditions of temperature and pressure.

Possibility of hazardous reactions

Conditions to avoid	: Heat, flames and sparks.
Materials to avoid	: May react with oxygen and strong oxidizing agents, such as chlorates, nitrates, peroxides, etc.
Other data	: No decomposition if stored and applied as directed.

SECTION 11: Toxicological information

Acute oral toxicity

C9-C11 Isoalkanes	: LD50: 34,600 mg/kg Species: rat
C10-C13 Isoalkanes	LD50: > 5,000 mg/kg Species: rat Sex: male and female Method: OECD Test Guideline 401 Information given is based on data obtained from similar substances.

Acute inhalation toxicity

C9-C11 Isoalkanes	: : > 12.4 mg/l Exposure time: 4 h Species: rat Test atmosphere: dust/mist
C10-C13 Isoalkanes	LC50: > 4.9 mg/l Exposure time: 4 h Species: rat Sex: male and female

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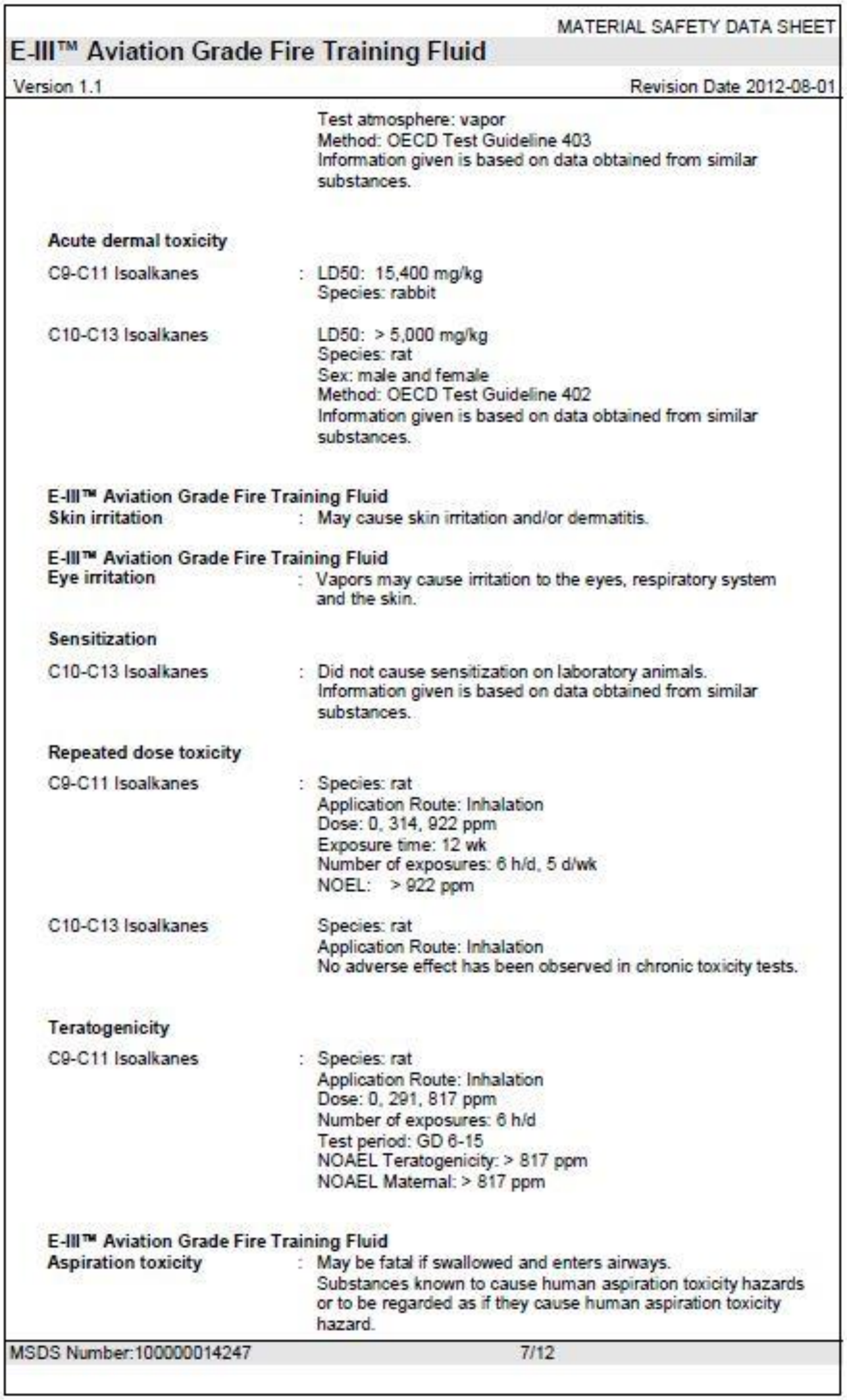

Test atmosphere: vapor
Method: OECD Test Guideline 403
Information given is based on data obtained from similar substances.

Acute dermal toxicity

C9-C11 Isoalkanes	: LD50: 15,400 mg/kg Species: rabbit
C10-C13 Isoalkanes	LD50: > 5,000 mg/kg Species: rat Sex: male and female Method: OECD Test Guideline 402 Information given is based on data obtained from similar substances.

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Skin irritation : May cause skin irritation and/or dermatitis.

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Eye irritation : Vapors may cause irritation to the eyes, respiratory system and the skin.

Sensitization

C10-C13 Isoalkanes	: Did not cause sensitization on laboratory animals. Information given is based on data obtained from similar substances.

Repeated dose toxicity

C9-C11 Isoalkanes	: Species: rat Application Route: Inhalation Dose: 0, 314, 922 ppm Exposure time: 12 wk Number of exposures: 6 h/d, 5 d/wk NOEL: > 922 ppm
C10-C13 Isoalkanes	Species: rat Application Route: Inhalation No adverse effect has been observed in chronic toxicity tests.

Teratogenicity

C9-C11 Isoalkanes	: Species: rat Application Route: Inhalation Dose: 0, 291, 817 ppm Number of exposures: 6 h/d Test period: GD 6-15 NOAEL Teratogenicity: > 817 ppm NOAEL Maternal: > 817 ppm

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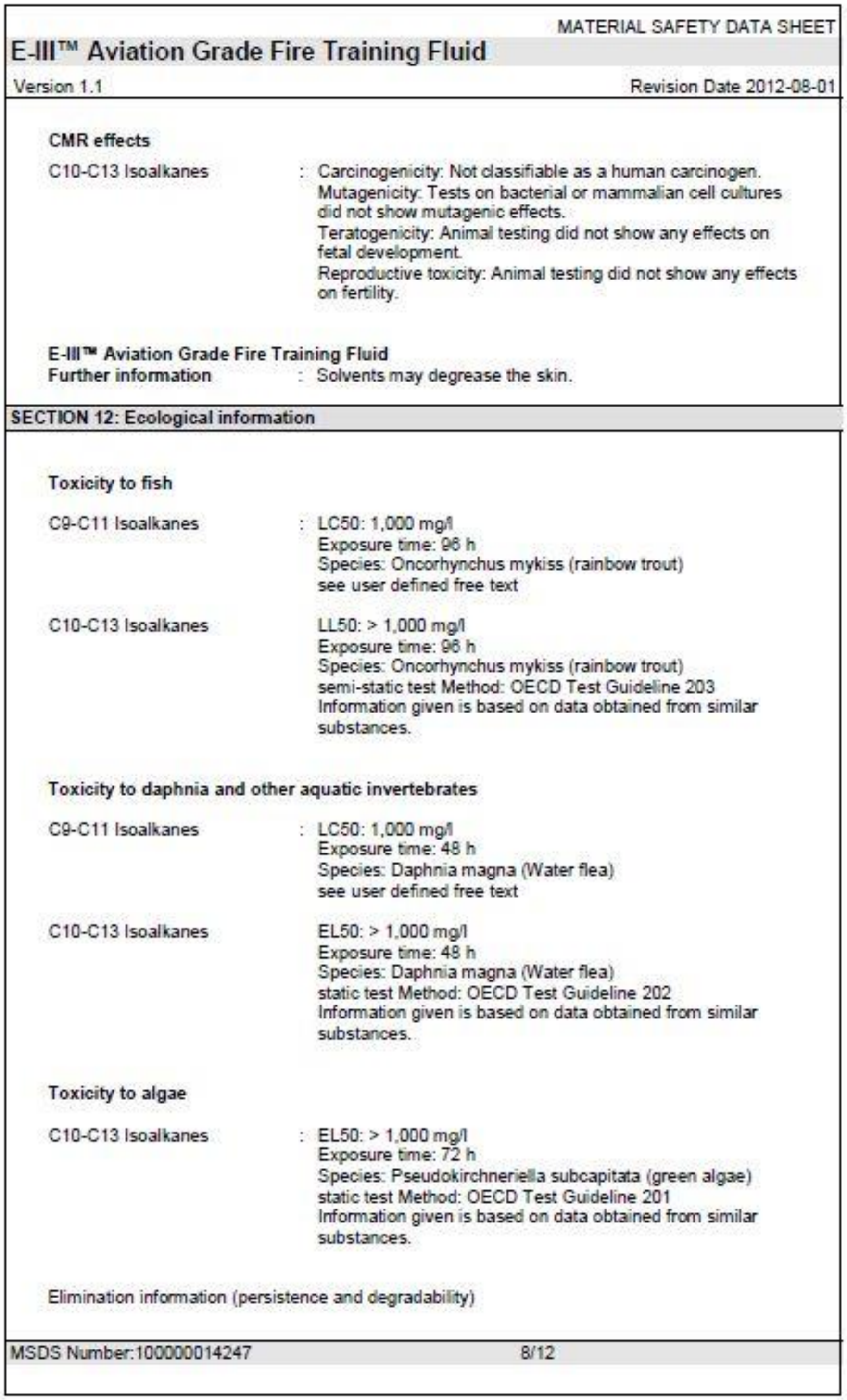
Aspiration toxicity : May be fatal if swallowed and enters airways.
Substances known to cause human aspiration toxicity hazards or to be regarded as if they cause human aspiration toxicity hazard.



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CMR effects

C10-C13 Isoalkanes : Carcinogenicity: Not classifiable as a human carcinogen.
Mutagenicity: Tests on bacterial or mammalian cell cultures did not show mutagenic effects.
Teratogenicity: Animal testing did not show any effects on fetal development.
Reproductive toxicity: Animal testing did not show any effects on fertility.

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Further information : Solvents may degrease the skin.

SECTION 12: Ecological information

Toxicity to fish

C9-C11 Isoalkanes : LC50: 1,000 mg/l
Exposure time: 96 h
Species: Oncorhynchus mykiss (rainbow trout)
see user defined free text

C10-C13 Isoalkanes LL50: > 1,000 mg/l
Exposure time: 96 h
Species: Oncorhynchus mykiss (rainbow trout)
semi-static test Method: OECD Test Guideline 203
Information given is based on data obtained from similar substances.

Toxicity to daphnia and other aquatic invertebrates

C9-C11 Isoalkanes : LC50: 1,000 mg/l
Exposure time: 48 h
Species: Daphnia magna (Water flea)
see user defined free text

C10-C13 Isoalkanes EL50: > 1,000 mg/l
Exposure time: 48 h
Species: Daphnia magna (Water flea)
static test Method: OECD Test Guideline 202
Information given is based on data obtained from similar substances.

Toxicity to algae

C10-C13 Isoalkanes : EL50: > 1,000 mg/l
Exposure time: 72 h
Species: Pseudokirchneriella subcapitata (green algae)
static test Method: OECD Test Guideline 201
Information given is based on data obtained from similar substances.

Elimination information (persistence and degradability)

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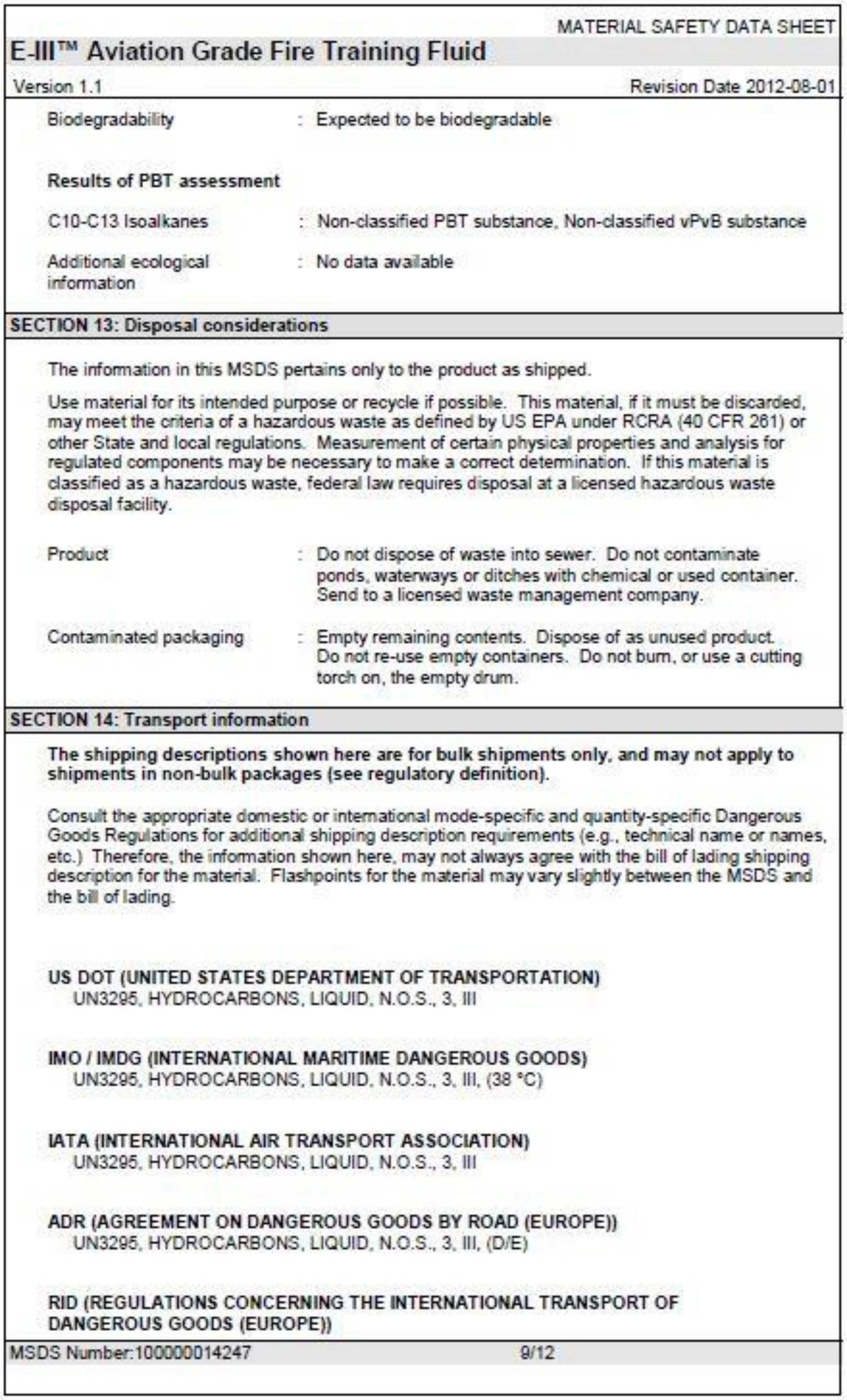

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Biodegradability	: Expected to be biodegradable

Results of PBT assessment

C10-C13 Isoalkanes	: Non-classified PBT substance, Non-classified vPvB substance
Additional ecological information	: No data available

SECTION 13: Disposal considerations

The information in this MSDS pertains only to the product as shipped.

Use material for its intended purpose or recycle if possible. This material, if it must be discarded, may meet the criteria of a hazardous waste as defined by US EPA under RCRA (40 CFR 261) or other State and local regulations. Measurement of certain physical properties and analysis for regulated components may be necessary to make a correct determination. If this material is classified as a hazardous waste, federal law requires disposal at a licensed hazardous waste disposal facility.

Product	: Do not dispose of waste into sewer. Do not contaminate ponds, waterways or ditches with chemical or used container. Send to a licensed waste management company.
Contaminated packaging	: Empty remaining contents. Dispose of as unused product. Do not re-use empty containers. Do not burn, or use a cutting torch on, the empty drum.

SECTION 14: Transport information

The shipping descriptions shown here are for bulk shipments only, and may not apply to shipments in non-bulk packages (see regulatory definition).

Consult the appropriate domestic or international mode-specific and quantity-specific Dangerous Goods Regulations for additional shipping description requirements (e.g., technical name or names, etc.) Therefore, the information shown here, may not always agree with the bill of lading shipping description for the material. Flashpoints for the material may vary slightly between the MSDS and the bill of lading.

US DOT (UNITED STATES DEPARTMENT OF TRANSPORTATION)
UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III

IMO / IMDG (INTERNATIONAL MARITIME DANGEROUS GOODS)
UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III, (38 °C)

IATA (INTERNATIONAL AIR TRANSPORT ASSOCIATION)
UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III

ADR (AGREEMENT ON DANGEROUS GOODS BY ROAD (EUROPE))
UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III, (D/E)

RID (REGULATIONS CONCERNING THE INTERNATIONAL TRANSPORT OF DANGEROUS GOODS (EUROPE))

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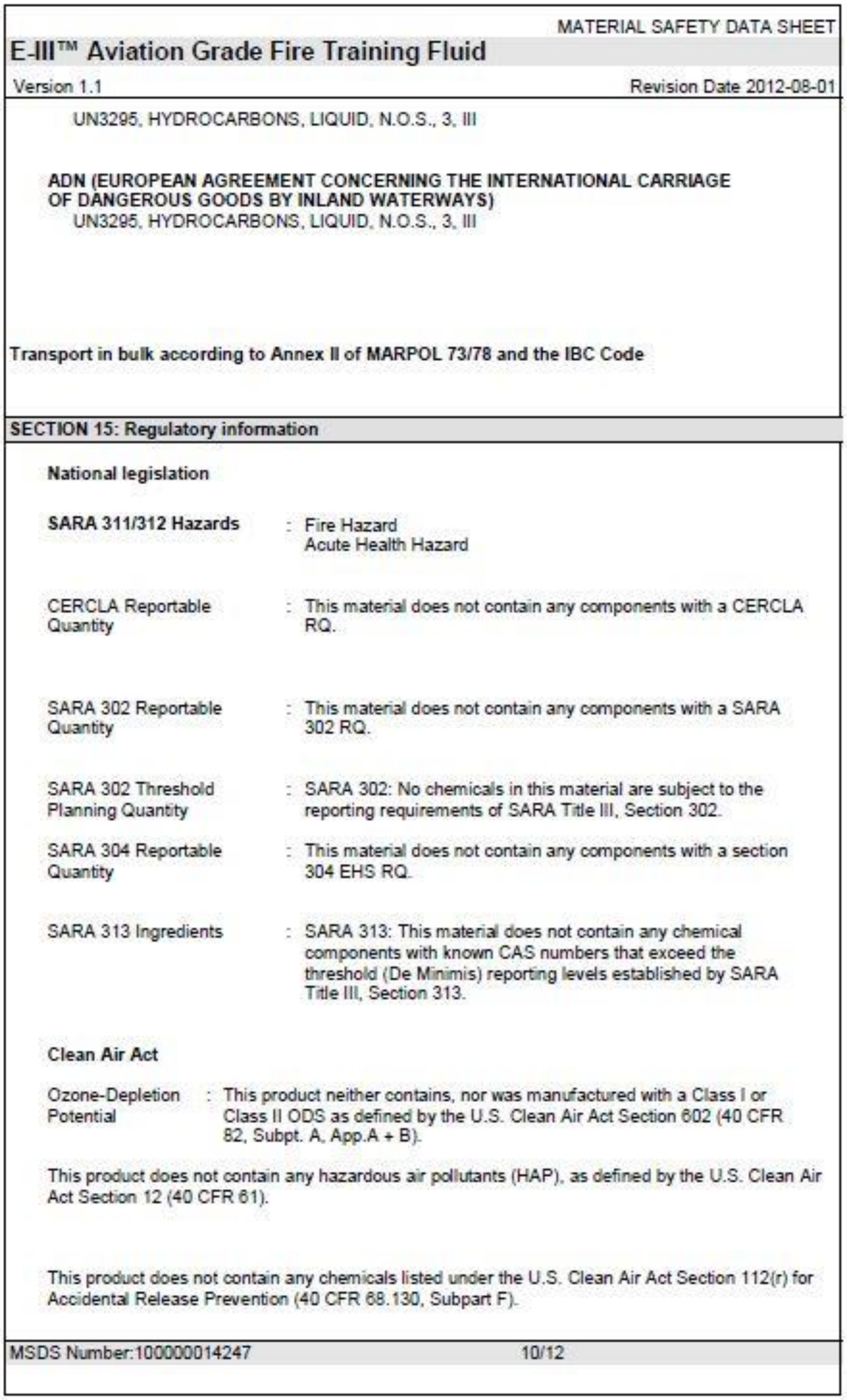


UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III

ADN (EUROPEAN AGREEMENT CONCERNING THE INTERNATIONAL CARRIAGE OF DANGEROUS GOODS BY INLAND WATERWAYS)
UN3295, HYDROCARBONS, LIQUID, N.O.S., 3, III

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code

SECTION 15: Regulatory information

National legislation

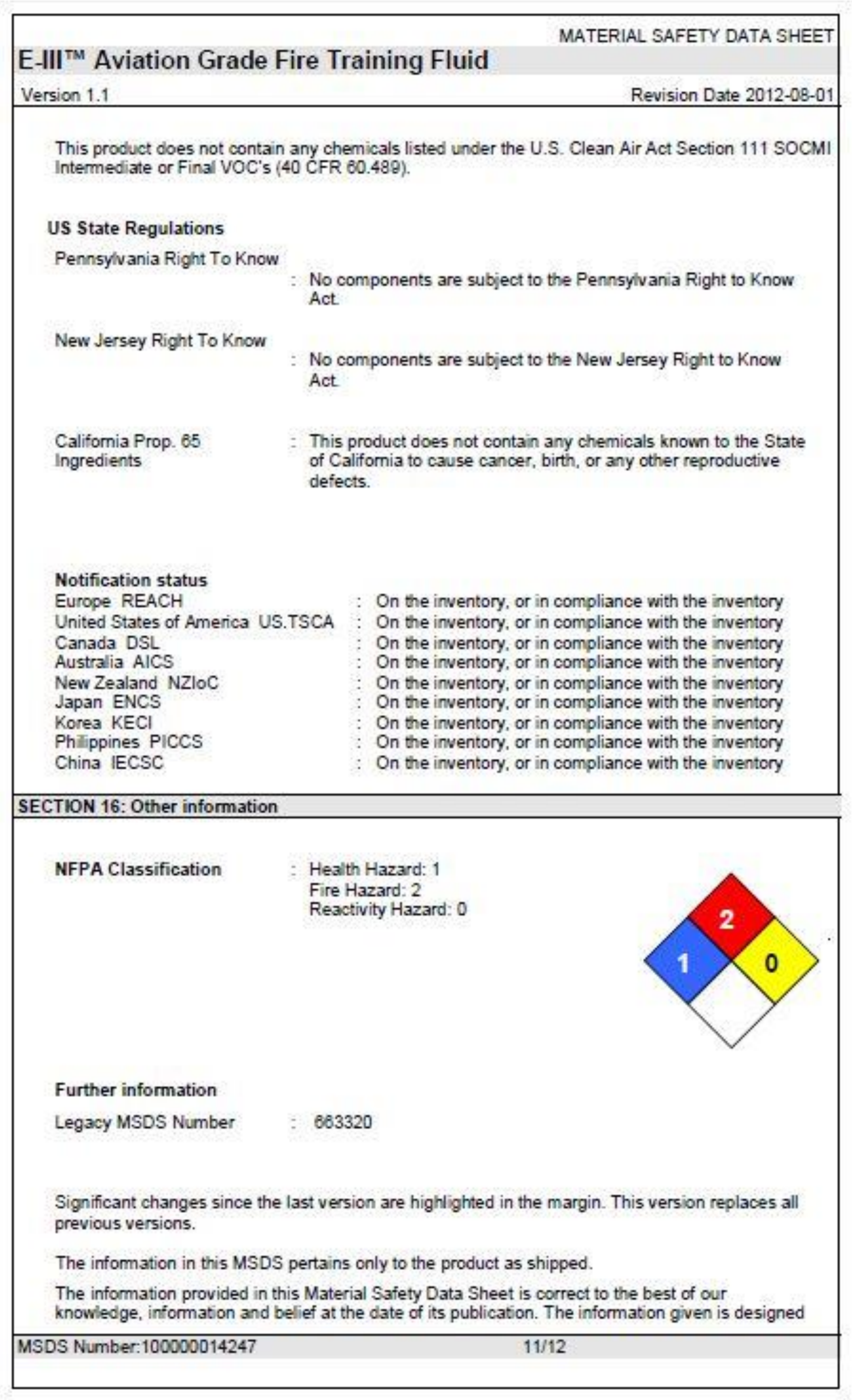
SARA 311/312 Hazards	: Fire Hazard Acute Health Hazard
CERCLA Reportable Quantity	: This material does not contain any components with a CERCLA RQ.
SARA 302 Reportable Quantity	: This material does not contain any components with a SARA 302 RQ.
SARA 302 Threshold Planning Quantity	: SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.
SARA 304 Reportable Quantity	: This material does not contain any components with a section 304 EHS RQ.
SARA 313 Ingredients	: SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

Clean Air Act

Ozone-Depletion Potential	: This product neither contains, nor was manufactured with a Class I or Class II ODS as defined by the U.S. Clean Air Act Section 602 (40 CFR 82, Subpt. A, App.A + B).

This product does not contain any hazardous air pollutants (HAP), as defined by the U.S. Clean Air Act Section 12 (40 CFR 61).

This product does not contain any chemicals listed under the U.S. Clean Air Act Section 112(r) for Accidental Release Prevention (40 CFR 68.130, Subpart F).



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This product does not contain any chemicals listed under the U.S. Clean Air Act Section 111 SOCMI Intermediate or Final VOC's (40 CFR 60.489).

US State Regulations

Pennsylvania Right To Know : No components are subject to the Pennsylvania Right to Know Act.

New Jersey Right To Know : No components are subject to the New Jersey Right to Know Act.

California Prop. 65 Ingredients : This product does not contain any chemicals known to the State of California to cause cancer, birth, or any other reproductive defects.

Notification status

Europe REACH	: On the inventory, or in compliance with the inventory
United States of America US.TSCA	: On the inventory, or in compliance with the inventory
Canada DSL	: On the inventory, or in compliance with the inventory
Australia AICS	: On the inventory, or in compliance with the inventory
New Zealand NZIoC	: On the inventory, or in compliance with the inventory
Japan ENCS	: On the inventory, or in compliance with the inventory
Korea KECI	: On the inventory, or in compliance with the inventory
Philippines PICCS	: On the inventory, or in compliance with the inventory
China IECSC	: On the inventory, or in compliance with the inventory

SECTION 16: Other information

NFPA Classification : Health Hazard: 1
Fire Hazard: 2
Reactivity Hazard: 0

Further information

Legacy MSDS Number : 663320

Significant changes since the last version are highlighted in the margin. This version replaces all previous versions.

The information in this MSDS pertains only to the product as shipped.

The information provided in this Material Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed

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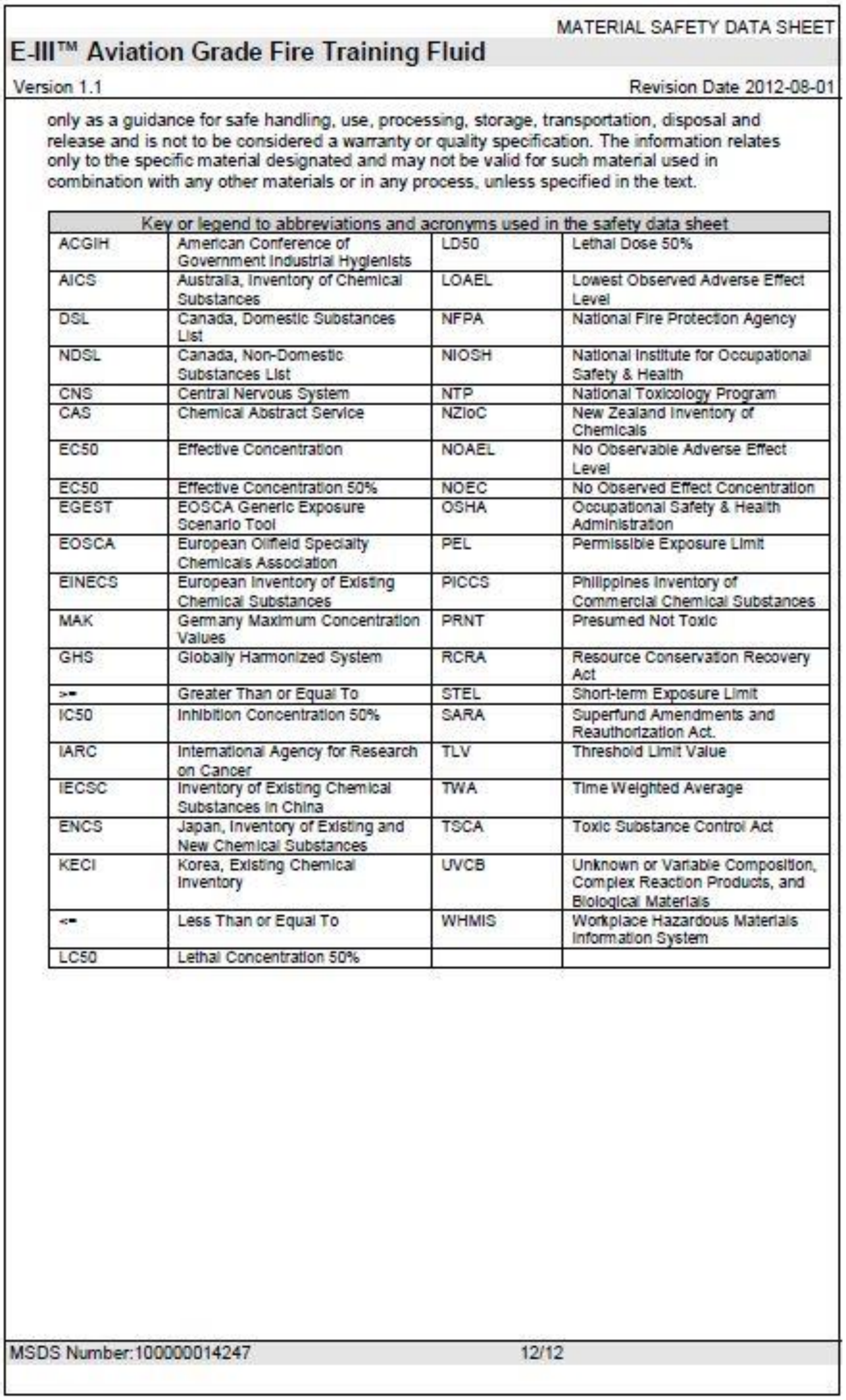

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only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Key or legend to abbreviations and acronyms used in the safety data sheet			
ACGIH	American Conference of Government Industrial Hygienists	LD50	Lethal Dose 50%
AICS	Australia, Inventory of Chemical Substances	LOAEL	Lowest Observed Adverse Effect Level
DSL	Canada, Domestic Substances List	NFPA	National Fire Protection Agency
NDSL	Canada, Non-Domestic Substances List	NIOSH	National Institute for Occupational Safety & Health
CNS	Central Nervous System	NTP	National Toxicology Program
CAS	Chemical Abstract Service	NZIoC	New Zealand Inventory of Chemicals
EC50	Effective Concentration	NOAEL	No Observable Adverse Effect Level
EC50	Effective Concentration 50%	NOEC	No Observed Effect Concentration
EGEST	EOSCA Generic Exposure Scenario Tool	OSHA	Occupational Safety & Health Administration
EOSCA	European Oilfield Specialty Chemicals Association	PEL	Permissible Exposure Limit
EINECS	European Inventory of Existing Chemical Substances	PICCS	Philippines Inventory of Commercial Chemical Substances
MAK	Germany Maximum Concentration Values	PRNT	Presumed Not Toxic
GHS	Globally Harmonized System	RCRA	Resource Conservation Recovery Act
>=	Greater Than or Equal To	STEL	Short-term Exposure Limit
IC50	Inhibition Concentration 50%	SARA	Superfund Amendments and Reauthorization Act.
IARC	International Agency for Research on Cancer	TLV	Threshold Limit Value
IECSC	Inventory of Existing Chemical Substances in China	TWA	Time Weighted Average
ENCS	Japan, Inventory of Existing and New Chemical Substances	TSCA	Toxic Substance Control Act
KECI	Korea, Existing Chemical Inventory	UVCB	Unknown or Variable Composition, Complex Reaction Products, and Biological Materials
<=	Less Than or Equal To	WHMIS	Workplace Hazardous Materials Information System
LC50	Lethal Concentration 50%		

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APPENDIX B: Data from Lab-Scale Bio-separator Tests

Table A.1: Data for small crushed limestone replicate A test. Test run on 8/30/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	N/A
	Length	N/A in
	Type	N/A
	Moisture Content	N/A $g{\cdot}g^{-1}$
	Pack Density	N/A $kg{\cdot}m^{-3}$
	Dry Bulk Density	N/A
Aggre-gate	Material	Crushed Limestone
	Length	12 in
	Pack Density	1143 $kg{\cdot}m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	453.87 g
	Influent Fuel Concentration:	868 $mg{\cdot}L^{-1}$
	Flowrate:	3.87 $L{\cdot}min^{-1}$
	Fuel Mass Flowrate:	3362 $mg{\cdot}min^{-1}$
	Breakthrough Time:	104 min
	Total Samples Collected:	10
	Max. Fuel Effluent Concentration:	ND $mg{\cdot}L^{-1}$
	Concentration Reduction:	ND
	Removal Efficiency:	ND %

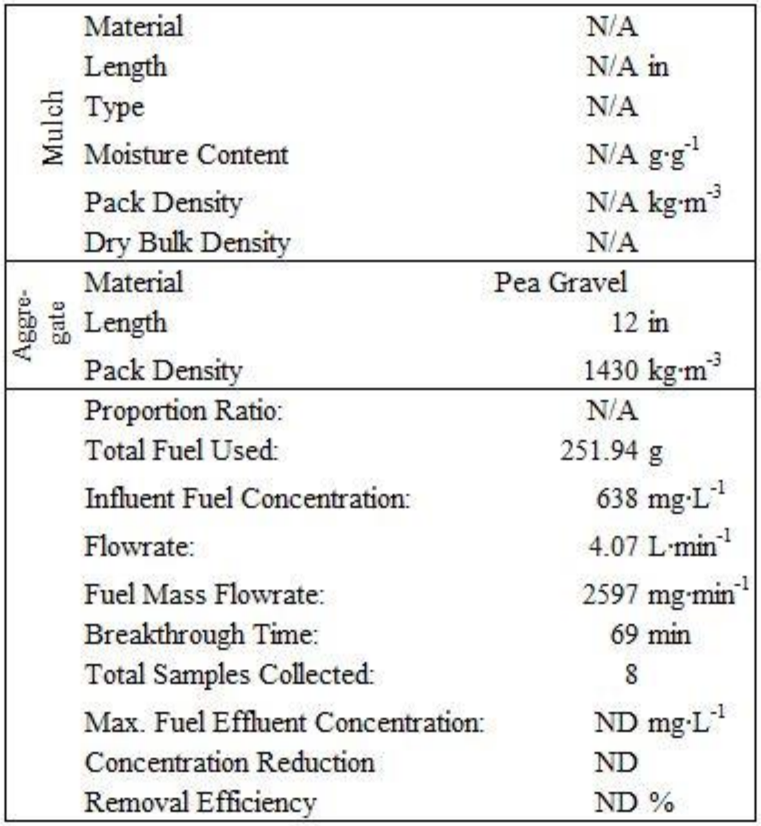
Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg{\cdot}L^{-1}$
0	0	BD	ND	BD
1	15	error	ND	error
2	30	error	ND	error
3	45	error	ND	error
4	60	error	ND	error
5	75	error	ND	error
6	90	error	ND	error
7	105	error	ND	error
8	120	error	ND	error
9	135	error	ND	error

Table A.2: Data for small crushed limestone replicate B test. Test run on 1/4/2016. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

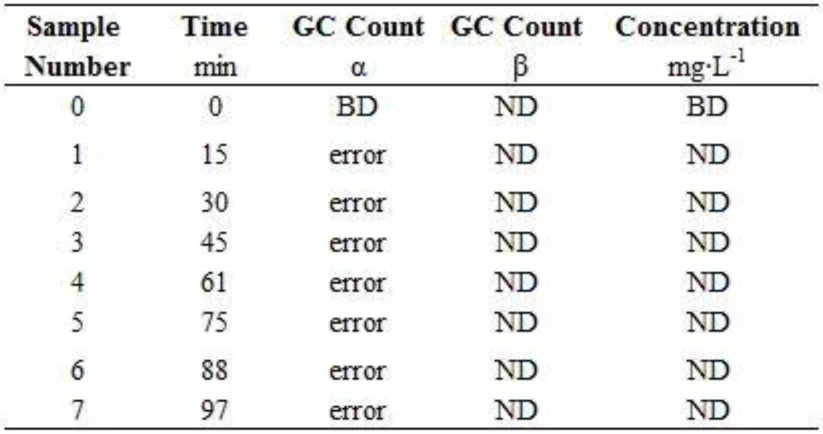
Mulch	Material	N/A
	Length	N/A in
	Type	N/A
	Moisture Content	N/A $g \cdot g^{-1}$
	Pack Density	N/A $kg \cdot m^{-3}$
	Dry Bulk Density	N/A
Aggre-gate	Material	Crushed Limestone
	Length	12 in
	Pack Density	1287 $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	172.41 g
	Influent Fuel Concentration:	862 $mg \cdot L^{-1}$
	Flowrate:	4.00 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	3448 $mg \cdot min^{-1}$
	Breakthrough Time:	42 min
	Total Samples Collected:	5
	Max. Fuel Effluent Concentration:	16.1 $mg \cdot L^{-1}$
	Concentration Reduction	1.73
	Removal Efficiency	98.1 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	190000	ND	11.3
2	30	270000	ND	16.1
3	45	204000	ND	12.1
4	50	204000	320000	12.1

Table A.3: Data for pea gravel replicate A test. Test run on 9/14/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.



Mulch	Material	N/A
	Length	N/A in
	Type	N/A
	Moisture Content	N/A g·g^{-1}
	Pack Density	N/A kg·m^{-3}
	Dry Bulk Density	N/A
Aggregate	Material	Pea Gravel
	Length	12 in
	Pack Density	1430 kg·m^{-3}
	Proportion Ratio:	N/A
	Total Fuel Used:	251.94 g
	Influent Fuel Concentration:	638 mg·L^{-1}
	Flowrate:	4.07 L·min^{-1}
	Fuel Mass Flowrate:	2597 mg·min^{-1}
	Breakthrough Time:	69 min
	Total Samples Collected:	8
	Max. Fuel Effluent Concentration:	ND mg·L^{-1}
	Concentration Reduction	ND
	Removal Efficiency	ND %



Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	BD	ND	BD
1	15	error	ND	ND
2	30	error	ND	ND
3	45	error	ND	ND
4	61	error	ND	ND
5	75	error	ND	ND
6	88	error	ND	ND
7	97	error	ND	ND

Table A.4: Data for concrete sand replicate A test. Test run on 9/7/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	N/A
	Length	N/A in
	Type	N/A
	Moisture Content	N/A $g \cdot g^{-1}$
	Pack Density	N/A $kg \cdot m^{-3}$
	Dry Bulk Density	N/A
Aggregate	Material	Concrete sand
	Length	12 in
	Pack Density	1605 $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	297.21 g
	Influent Fuel Concentration:	4751 $mg \cdot L^{-1}$
	Flowrate:	0.41 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	1970 $mg \cdot min^{-1}$
	Breakthrough Time:	N/A min
	Total Samples Collected:	8
	Max. Fuel Effluent Concentration:	0.0 $mg \cdot L^{-1}$
	Concentration Reduction	> 3.98
	Removal Efficiency	> 99.99 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	16	BD	ND	BD
2	30	BD	ND	BD
3	45	BD	ND	BD
4	60	BD	ND	BD
5	90	BD	ND	BD
6	120	BD	ND	BD
7	150	BD	ND	BD

Table A.5: Data for large crushed limestone replicate A test. Test run on 8/31/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	N/A
	Length	N/A in
	Type	N/A
	Moisture Content	N/A $g{\cdot}g^{-1}$
	Pack Density	N/A $kg{\cdot}m^{-3}$
	Dry Bulk Density	N/A
Aggre-gate	Material	Crushed Limestone #4
	Length	12 in
	Pack Density	1335 $kg{\cdot}m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	123.9 g
	Influent Fuel Concentration:	688 $mg{\cdot}L^{-1}$
	Flowrate:	4.00 $L{\cdot}min^{-1}$
	Fuel Mass Flowrate:	2753 $mg{\cdot}min^{-1}$
	Breakthrough Time:	44 min
	Total Samples Collected:	3
	Max. Fuel Effluent Concentration:	ND $mg{\cdot}L^{-1}$
	Concentration Reduction	ND
	Removal Efficiency	ND %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg{\cdot}L^{-1}$
0	0	BD	ND	BD
1	15	error	ND	-
2	30	error	ND	-

Table A.6: Data for medium degraded chipped mulch replicate A test. Test run on 9/5/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.35 $g \cdot g^{-1}$
	Pack Density	254 $kg \cdot m^{-3}$
	Dry Bulk Density	166
Aggregate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	279 g
	Influent Fuel Concentration:	821 $mg \cdot L^{-1}$
	Flowrate:	3.82 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	3135 $mg \cdot min^{-1}$
	Breakthrough Time:	63 min
	Total Samples Collected:	7
	Max. Fuel Effluent Concentration:	BD $mg \cdot L^{-1}$
	Concentration Reduction	> 3.22
	Removal Efficiency	> 99.94 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	12200	ND	BD
2	30	9330	ND	BD
3	45	11100	ND	BD
4	60	17900	ND	BD
5	75	13300	ND	BD
6	89	18010	ND	BD

Table A.7: Data for medium degraded chipped mulch replicate B test. Test run on 9/23/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.35 $g \cdot g^{-1}$
	Pack Density	254 $kg \cdot m^{-3}$
	Dry Bulk Density	166
Aggregate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	612.08 g
	Influent Fuel Concentration:	373 $mg \cdot L^{-1}$
	Flowrate:	4.04 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	1507 $mg \cdot min^{-1}$
	Breakthrough Time:	363 min
	Total Samples Collected:	19
	Max. Fuel Effluent Concentration:	8.8 $mg \cdot L^{-1}$
	Concentration Reduction	1.63
	Removal Efficiency	97.7 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	BD	ND	BD
2	30	35620	ND	BD
3	45	40980	ND	BD
4	60	error	45110	BD
5	75	81440	ND	BD
6	90	139030	ND	BD
7	105	error	94810	BD
8	121	187300	ND	BD
9	150	126530	ND	BD
10	180	219050	ND	BD
11	200	142170	ND	BD
12	210	110180	ND	BD
13	240	109040	ND	BD
14	270	123600	ND	BD
15	300	125190	ND	BD
16	330	error	113340	BD
17	375	390711	ND	8.8
18	390	-	ND	BD

Table A.8: Data for medium degraded chipped mulch replicate C test. Test run on 1/5/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.27 $g{\cdot}g^{-1}$
	Pack Density	159 $kg{\cdot}m^{-3}$
	Dry Bulk Density	117
Aggre-gate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg{\cdot}m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	251.94 g
	Influent Fuel Concentration:	255 $mg{\cdot}L^{-1}$
	Flowrate:	3.82 $L{\cdot}min^{-1}$
	Fuel Mass Flowrate:	973 $mg{\cdot}min^{-1}$
	Breakthrough Time:	210 min
	Total Samples Collected:	17
	Max. Fuel Effluent Concentration:	8.9 $mg{\cdot}L^{-1}$
	Concentration Reduction	1.45
	Removal Efficiency	96.5 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg{\cdot}L^{-1}$
0	0	BD	BD	BD
1	15	9300	ND	BD
2	30	92000	ND	5.5
3	45	84000	ND	5.0
4	60	95000	ND	5.7
5	75	90000	ND	5.4
6	90	110000	ND	6.5
7	105	90000	ND	5.4
8	120	150000	ND	8.9
9	135	90000	ND	5.4
10	150	BD	100000	6.0
11	165	110000	ND	6.5
12	180	150000	ND	8.9
13	195	120000	ND	7.1
14	210	120000	ND	7.1
15	250	120000	ND	7.1
16	260	120000	ND	7.1

Table A.9: Data for high degraded chipped mulch replicate A test. Test run on 1/27/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	High Degradation
	Moisture Content	0.44 g·g^{-1}
	Pack Density	302 kg·m^{-3}
	Dry Bulk Density	169
Aggre-gate	Material	N/A
	Length	N/A in
	Pack Density	N/A kg·m^{-3}
	Proportion Ratio:	N/A
	Total Fuel Used:	296.63 g
	Influent Fuel Concentration:	641 mg·L^{-1}
	Flowrate:	3.85 L·min^{-1}
	Fuel Mass Flowrate:	2472 mg·min^{-1}
	Breakthrough Time:	120 min
	Total Samples Collected:	7
	Max. Fuel Effluent Concentration:	36.3 mg·L^{-1}
	Concentration Reduction	1.25
	Removal Efficiency	94.3 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	BD	ND	BD
1	15	405000	ND	24.1
2	30	300000	ND	17.9
3	42	490000	ND	29.2
4	60	450000	ND	26.8
5	90	420000	ND	25.0
6	120	610000	ND	36.3

Table A.10: Data for low degraded chipped mulch replicate A test. Test run on 2/3/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	High Degradation
	Moisture Content	0.51 $g \cdot g^{-1}$
	Pack Density	286 $kg \cdot m^{-3}$
	Dry Bulk Density	142
Aggre-gate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	139.73 g
	Influent Fuel Concentration:	593 $mg \cdot L^{-1}$
	Flowrate:	3.68 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	2183 $mg \cdot min^{-1}$
	Breakthrough Time:	51 min
	Total Samples Collected:	5
	Max. Fuel Effluent Concentration:	83.4 $mg \cdot L^{-1}$
	Concentration Reduction	0.85
	Removal Efficiency	85.9 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	570000	ND	33.9
2	45	1100000	ND	65.5
3	52	1200000	ND	71.4
4	60	1400000	ND	83.4

Table A.11: Data for medium degraded shredded mulch replicate A test. Test run on 7/14/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Shredded Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.18 $g \cdot g^{-1}$
	Pack Density	270 $kg \cdot m^{-3}$
	Dry Bulk Density	222
Aggre-gate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	309.81 g
	Influent Fuel Concentration:	977 $mg \cdot L^{-1}$
	Flowrate:	4.10 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	4004 $mg \cdot min^{-1}$
	Breakthrough Time:	38 min
	Total Samples Collected:	7
	Max. Fuel Effluent Concentration:	5.8 $mg \cdot L^{-1}$
	Concentration Reduction	< 1.24
	Removal Efficiency	99.4 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	16	13248	ND	BD
2	30	57772	ND	BD
3	45	24000	ND	BD
4	60	349240	error	5.8
5	75	108231	ND	BD

Table A.12: Data for medium degraded shredded mulch replicate B test. Test run on 9/21/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Shredded Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.18 $g \cdot g^{-1}$
	Pack Density	318 $kg \cdot m^{-3}$
	Dry Bulk Density	261
Aggre-gate	Material	N/A
	Length	N/A in
	Pack Density	N/A $kg \cdot m^{-3}$
	Proportion Ratio:	N/A
	Total Fuel Used:	252.46 g
	Influent Fuel Concentration:	643 $mg \cdot L^{-1}$
	Flowrate:	4.18 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	2686 $mg \cdot min^{-1}$
	Breakthrough Time:	71 min
	Total Samples Collected:	7
	Max. Fuel Effluent Concentration:	6.0 $mg \cdot L^{-1}$
	Concentration Reduction	2.03
	Removal Efficiency	99.1 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	16	198290	ND	BD
2	30	167160	ND	BD
3	45	47380	ND	BD
4	60	252850	ND	BD
5	75	339208	ND	5.1
6	90	351220	ND	6.0

Table A.13: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:3 replicate A test. Test run on 2/15/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	7.2 in
	Type	Medium Degradation
	Moisture Content	0.40 $g{\cdot}g^{-1}$
	Pack Density	265 $kg{\cdot}m^{-3}$
	Dry Bulk Density	160
Aggre-gate	Material	Crushed Limestone
	Length	10.8 in
	Pack Density	1360 $kg{\cdot}m^{-3}$
	Proportion Ratio:	2:3
	Total Fuel Used:	595.21 g
	Influent Fuel Concentration:	1271 $mg{\cdot}L^{-1}$
	Flowrate:	3.53 $L{\cdot}min^{-1}$
	Fuel Mass Flowrate:	4487 $mg{\cdot}min^{-1}$
	Breakthrough Time:	94 min
	Total Samples Collected:	8
	Max. Fuel Effluent Concentration:	50.6 $mg{\cdot}L^{-1}$
	Concentration Reduction	1.40
	Removal Efficiency	96.0 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg{\cdot}L^{-1}$
0	0	BD	ND	BD
1	15	410000	360000	24.4
2	30	93000	400000	5.5
3	60	error	ND	BD
4	90	450000	570000	26.8
5	105	700000	ND	41.7
6	120	850000	ND	50.6
7	130	760000	ND	45.2

Table A.14: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:3 replicate B test. Test run on 2/16/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	7.2 in
	Type	Medium Degradation
	Moisture Content	0.38 g·g^{-1}
	Pack Density	238 kg·m^{-3}
	Dry Bulk Density	148
Aggre-gate	Material	Crushed Limestone
	Length	10.8 in
	Pack Density	1395 kg·m^{-3}
	Proportion Ratio:	2:3
	Total Fuel Used:	367.5 g
	Influent Fuel Concentration:	1239 mg·L^{-1}
	Flowrate:	3.62 L·min^{-1}
	Fuel Mass Flowrate:	4482 mg·min^{-1}
	Breakthrough Time:	62 min
	Total Samples Collected:	6
	Max. Fuel Effluent Concentration:	13.1 mg·L^{-1}
	Concentration Reduction	1.98
	Removal Efficiency	98.9 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	BD	ND	BD
1	15	88000	ND	5.2
2	30	170000	ND	10.1
3	60	220000	ND	13.1
4	73	190000	ND	11.3
5	80	210000	ND	12.5

Table A.15: Data for medium degraded chipped mulch and small crushed limestone length proportion 5:4 replicate A test. Test run on 1/7/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	10 in
	Type	Medium Degradation
	Moisture Content	0.25 $g \cdot g^{-1}$
	Pack Density	191 $kg \cdot m^{-3}$
	Dry Bulk Density	143
Aggregate	Material	Crushed Limestone
	Length	8 in
	Pack Density	1335 $kg \cdot m^{-3}$
	Proportion Ratio:	5:4
	Total Fuel Used:	737.09 g
	Influent Fuel Concentration:	695 $mg \cdot L^{-1}$
	Flowrate:	4.00 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	2781 $mg \cdot min^{-1}$
	Breakthrough Time:	248 min
	Total Samples Collected:	11
	Max. Fuel Effluent Concentration:	10.7 $mg \cdot L^{-1}$
	Concentration Reduction	1.81
	Removal Efficiency	98.5 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	30	140000	ND	8.3
2	60	140000	ND	8.3
3	90	110000	ND	6.5
4	120	150000	ND	8.9
5	150	150000	ND	8.9
6	180	180000	ND	10.7
7	210	140000	ND	8.3
8	240	160000	ND	9.5
9	248	170000	ND	10.1
10	251	170000	ND	10.1

Table A.16: Data for medium degraded chipped mulch and small crushed limestone length proportion 5:4 replicate B test. Test run on 2/24/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	10 in
	Type	Medium Degradation
	Moisture Content	0.26 g·g^{-1}
	Pack Density	229 kg·m^{-3}
	Dry Bulk Density	170
Aggre-gate	Material	Crushed Limestone
	Length	8 in
	Pack Density	1287 kg·m^{-3}
	Proportion Ratio:	5:4
	Total Fuel Used:	380.15 g
	Influent Fuel Concentration:	445 mg·L^{-1}
	Flowrate:	3.62 L·min^{-1}
	Fuel Mass Flowrate:	1611 mg·min^{-1}
	Breakthrough Time:	227 min
	Total Samples Collected:	10
	Max. Fuel Effluent Concentration:	10.1 mg·L^{-1}
	Concentration Reduction	1.64
	Removal Efficiency	97.7 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	BD	ND	BD
1	15	170000	ND	10.1
2	30	83000	ND	4.9
3	60	130000	ND	7.7
4	90	84000	ND	5.0
5	120	97000	ND	5.8
6	150	105000	ND	6.3
7	180	95000	ND	5.7
8	224	130000	ND	7.7
9	234	170000	ND	10.1

Table A.17: Data for medium degraded chipped mulch and small crushed limestone length proportion 5:4 replicate C test. Test run on 2/25/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	10 in
	Type	Medium Degradation
	Moisture Content	0.40 $g \cdot g^{-1}$
	Pack Density	286 $kg \cdot m^{-3}$
	Dry Bulk Density	171
Aggre-gate	Material	Crushed Limestone
	Length	8 in
	Pack Density	1406 $kg \cdot m^{-3}$
	Proportion Ratio:	5:4
	Total Fuel Used:	477.15 g
	Influent Fuel Concentration:	429 $mg \cdot L^{-1}$
	Flowrate:	3.64 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	1559 $mg \cdot min^{-1}$
	Breakthrough Time:	303 min
	Total Samples Collected:	11
	Max. Fuel Effluent Concentration:	11.6 $mg \cdot L^{-1}$
	Concentration Reduction	1.57
	Removal Efficiency	97.3 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	BD	ND	BD
2	30	BD	ND	BD
3	60	90000	ND	5.4
4	90	90000	ND	5.4
5	120	90000	ND	5.4
6	150	96000	ND	5.7
7	180	100000	ND	6.0
8	210	94000	ND	5.6
9	270	120000	ND	7.1
10	303	195000	ND	11.6

Table A.18: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:1 replicate A test. Test run on 1/18/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.35 g·g^{-1}
	Pack Density	191 kg·m^{-3}
	Dry Bulk Density	124
Aggre-gate	Material	Crushed Limestone
	Length	6 in
	Pack Density	1271 kg·m^{-3}
	Proportion Ratio:	2:1
	Total Fuel Used:	1056.34 g
	Influent Fuel Concentration:	600 mg·L^{-1}
	Flowrate:	3.87 L·min^{-1}
	Fuel Mass Flowrate:	2322 mg·min^{-1}
	Breakthrough Time:	433 min
	Total Samples Collected:	15
	Max. Fuel Effluent Concentration:	27.4 mg·L^{-1}
	Concentration Reduction	1.34
	Removal Efficiency	95.4 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	BD	ND	BD
1	30	130000	ND	7.7
2	60	150000	ND	8.9
3	90	150000	ND	8.9
4	120	170000	ND	10.1
5	150	220000	ND	13.1
6	180	200000	ND	11.9
7	210	310000	ND	18.5
8	240	250000	ND	14.9
9	270	430000	ND	25.6
10	300	320000	ND	19.1
11	360	260000	ND	15.5
12	420	370000	ND	22.0
13	433	180000	260000	15.5
14	455	460000	ND	27.4

Table A.19: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:1 replicate B test. Test run on 2/11/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.47 $g \cdot g^{-1}$
	Pack Density	286 $kg \cdot m^{-3}$
	Dry Bulk Density	152
Aggre-gate	Material	Crushed Limestone
	Length	6 in
	Pack Density	1303 $kg \cdot m^{-3}$
	Proportion Ratio:	2:1
	Total Fuel Used:	397.36 g
	Influent Fuel Concentration:	509 $mg \cdot L^{-1}$
	Flowrate:	3.70 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	1883 $mg \cdot min^{-1}$
	Breakthrough Time:	158 min
	Total Samples Collected:	9
	Max. Fuel Effluent Concentration:	10.7 $mg \cdot L^{-1}$
	Concentration Reduction	1.68
	Removal Efficiency	97.9 %

Sample	**Time**	**GC Count**	**GC Count**	**Concentration**
Number	min	α	β	$mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	BD	ND	BD
2	30	90000	ND	5.4
3	60	120000	ND	7.1
4	90	120000	ND	7.1
5	120	130000	ND	7.7
6	150	180000	ND	10.7
7	180	180000	ND	10.7
8	210	150000	ND	8.9

Table A.20: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:1 replicate C test. Test run on 3/14/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.30 g·g^{-1}
	Pack Density	222 kg·m^{-3}
	Dry Bulk Density	155
Aggre-gate	Material	Crushed Limestone
	Length	6 in
	Pack Density	1367 kg·m^{-3}
	Proportion Ratio:	2:1
	Total Fuel Used:	822.35 g
	Influent Fuel Concentration:	281 mg·L^{-1}
	Flowrate:	1.96 L·min^{-1}
	Fuel Mass Flowrate:	553 mg·min^{-1}
	Breakthrough Time:	1458 min
	Total Samples Collected:	18
	Max. Fuel Effluent Concentration:	6.6 mg·L^{-1}
	Concentration Reduction:	1.63
	Removal Efficiency:	97.7 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	0	-	14000	BD
1	30	-	12000	BD
2	60	-	BD	BD
3	120	21000	ND	1.3
4	180	20000	ND	1.2
5	240	37000	ND	2.2
6	300	29000	ND	1.7
7	360	55000	ND	3.3
8	420	54000	ND	3.2
9	480	62000	ND	3.7
10	540	59000	ND	3.5
11	600	83000	ND	4.9
12	720	41000	ND	2.4
13	840	82000	ND	4.9
14	1080	96000	ND	5.7
15	1320	51000	ND	3.0
16	1463	107000	92000	5.5
17	1485	error	111000	6.6

Table A.21: Data for medium degraded chipped mulch and small crushed limestone length proportion 3:1 replicate A test. Test run on 1/22/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	13.5 in
	Type	Medium Degradation
	Moisture Content	0.43 $g \cdot g^{-1}$
	Pack Density	- $kg \cdot m^{-3}$
	Dry Bulk Density	-
Aggregate	Material	Crushed Limestone
	Length	4.5 in
	Pack Density	1229 $kg \cdot m^{-3}$
	Proportion Ratio:	3:1
	Total Fuel Used:	1011.53 g
	Influent Fuel Concentration:	538 $mg \cdot L^{-1}$
	Flowrate:	4.00 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	2152 $mg \cdot min^{-1}$
	Breakthrough Time:	450 min
	Total Samples Collected:	13
	Max. Fuel Effluent Concentration:	17.3 $mg \cdot L^{-1}$
	Concentration Reduction:	1.49
	Removal Efficiency:	96.8 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	150000	ND	8.9
2	45	-	110000	6.5
3	60	120000	ND	7.1
4	90	150000	ND	8.9
5	120	180000	ND	10.7
6	180	190000	ND	11.3
7	240	250000	ND	14.9
8	300	290000	ND	17.3
9	360	170000	ND	10.1
10	420	210000	ND	12.5
11	452	180000	ND	10.7
12	470	190000	ND	11.3

Table A.22: Data for medium degraded chipped mulch and small crushed limestone length proportion 3:1 replicate B test. Test run on 3/27/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	13.5 in
	Type	Medium Degradation
	Moisture Content	0.25 $g \cdot g^{-1}$
	Pack Density	268 $kg \cdot m^{-3}$
	Dry Bulk Density	202
Aggregate	Material	Crushed Limestone
	Length	4.5 in
	Pack Density	1271 $kg \cdot m^{-3}$
	Proportion Ratio:	3:1
	Total Fuel Used:	765.35 g
	Influent Fuel Concentration:	120 $mg \cdot L^{-1}$
	Flowrate:	3.88 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	468 $mg \cdot min^{-1}$
	Breakthrough Time:	1632 min
	Total Samples Collected:	14
	Max. Fuel Effluent Concentration:	9.5 $mg \cdot L^{-1}$
	Concentration Reduction:	1.10
	Removal Efficiency:	92.1 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	BD	48000	2.9
2	30	28000	ND	1.7
3	60	42000	ND	2.5
4	120	52000	ND	3.1
5	180	51000	ND	3.0
6	240	50000	ND	3.0
7	360	69000	ND	4.1
8	480	62000	ND	3.7
9	720	160000	ND	9.5
10	960	72000	ND	4.3
11	1200	99000	ND	5.9
12	1440	86000	ND	5.1
13	1632	140000	ND	8.3

Table A.23: Data for medium degraded chipped mulch and small crushed limestone length proportion 3:1 replicate C test. Test run on 3/29/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	13.5 in
	Type	Medium Degradation
	Moisture Content	0.43 $g \cdot g^{-1}$
	Pack Density	283 $kg \cdot m^{-3}$
	Dry Bulk Density	161
Aggre-gate	Material	Crushed Limestone
	Length	4.5 in
	Pack Density	1271 $kg \cdot m^{-3}$
	Proportion Ratio:	3:1
	Total Fuel Used:	437.25 g
	Influent Fuel Concentration:	937 $mg \cdot L^{-1}$
	Flowrate:	3.79 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	3555 $mg \cdot min^{-1}$
	Breakthrough Time:	120 min
	Total Samples Collected:	6
	Max. Fuel Effluent Concentration:	6.0 $mg \cdot L^{-1}$
	Concentration Reduction:	2.20
	Removal Efficiency:	99.4 %

Sample **Number**	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	15	43000	ND	3
2	30	19000	ND	1
3	60	18000	ND	1
4	90	16000	ND	-
5	120	100000	ND	6

Table A.24: Data for medium degraded chipped mulch and small crushed limestone length proportion 3:1 replicate D test. Test run on 3/30/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	13.5 in
	Type	Medium Degradation
	Moisture Content	0.45 $g \cdot g^{-1}$
	Pack Density	311 $kg \cdot m^{-3}$
	Dry Bulk Density	170
Aggregate	Material	Crushed Limestone
	Length	4.5 in
	Pack Density	1271 $kg \cdot m^{-3}$
	Proportion Ratio:	3:1
	Total Fuel Used:	465.8 g
	Influent Fuel Concentration:	1653 $mg \cdot L^{-1}$
	Flowrate:	1.75 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	2893 $mg \cdot min^{-1}$
	Breakthrough Time:	85 min
	Total Samples Collected:	7
	Max. Fuel Effluent Concentration:	7.1 $mg \cdot L^{-1}$
	Concentration Reduction:	2.36
	Removal Efficiency:	99.6 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	0	BD	ND	BD
1	30	ND	ND	ND
2	60	74000	120000	4.4
3	70	96000	ND	5.7
4	85	120000	ND	7.1
5	120	110000	ND	6.5
6	160	120000	ND	7.1

Table A.25: Data for medium degraded chipped mulch and small crushed limestone length proportion 2:1 flow-event 2. Test run on 3/18/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	12 in
	Type	Medium Degradation
	Moisture Content	0.30 $g \cdot g^{-1}$
	Pack Density	222 $kg \cdot m^{-3}$
	Dry Bulk Density	155
Aggregate	Material	Crushed Limestone
	Length	6 in
	Pack Density	1367 $kg \cdot m^{-3}$
	Proportion Ratio:	2:1
	Total Fuel Used:	136.25 g
	Influent Fuel Concentration:	284 $mg \cdot L^{-1}$
	Flowrate:	3.94 $L \cdot min^{-1}$
	Fuel Mass Flowrate:	1117 $mg \cdot min^{-1}$
	Breakthrough Time:	N/A min
	Total Samples Collected:	9
	Max. Fuel Effluent Concentration:	7.1 $mg \cdot L^{-1}$
	Concentration Reduction:	1.60
	Removal Efficiency:	97.5 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** $mg \cdot L^{-1}$
0	1	37000	ND	2.2
1	5	120000	ND	7.1
2	10	90000	ND	5.4
3	20	93000	ND	5.5
4	30	110000	ND	6.5
5	45	95000	ND	5.7
6	60	99000	ND	5.9
7	90	105000	ND	6.3
8	120	104000	ND	6.2

Table A.26: Data for medium degraded chipped mulch and small crushed limestone length proportion 3:1 flow-event 2. Test run on 4/3/2015. Test information on the left and water sample results on the right. N/A = Not applicable, ND = No data, and error = Gas Chromatograph error.

Mulch	Material	Chipped Mulch
	Length	13.5 in
	Type	Medium Degradation
	Moisture Content	0.45 g·g^{-1}
	Pack Density	311 kg·m^{-3}
	Dry Bulk Density	170
Aggregate	Material	Crushed Limestone
	Length	4.5 in
	Pack Density	1271 kg·m^{-3}
	Proportion Ratio:	3:1
	Total Fuel Used:	334.25 g
	Influent Fuel Concentration:	1591 mg·L^{-1}
	Flowrate:	1.74 L·min^{-1}
	Fuel Mass Flowrate:	2762 mg·min^{-1}
	Breakthrough Time:	N/A min
	Total Samples Collected:	9
	Max. Fuel Effluent Concentration:	6.0 mg·L^{-1}
	Concentration Reduction:	2.43
	Removal Efficiency:	99.6 %

Sample Number	**Time** min	**GC Count** α	**GC Count** β	**Concentration** mg·L^{-1}
0	1	21000	ND	1.3
1	5	84000	ND	5.0
2	10	63000	ND	3.8
3	20	31000	65000	3.9
4	30	35000	ND	2.1
5	45	39000	ND	2.3
6	60	23000	35000	2.1
7	90	61000	ND	3.6
8	120	100000	ND	6.0

VITA

Michelle Ann Melone

Candidate for the Degree of

Master of Science

Thesis: BIOSEPARATOR DESIGN IMPROVEMENTS FOR REMOVAL OF PETROLEUM HYDROCARBONS FROM RUNOFF

Major Field: Biosystems and Agricultural Engineering

Biographical:

Education:

Completed the requirements for the Master of Science in Biosystems and Agricultural Engineering at Oklahoma State University, Stillwater, Oklahoma in July, 2016.

Completed the requirements for the Bachelor of Science in Biosystems and Agricultural Engineering at Oklahoma State University, Stillwater, Oklahoma in May, 2014.

Experience:

Graduate Research Assistant, City of Tulsa Stormwater Manual
Graduate Research Assistant, EPA 319(h) Nonpoint Source Grant #: 00F56701
Graduate Teaching Assistant, ENSC 3233: Fluid Mechanics for Engineers
Undergraduate Research Assistant, Department of Plant and Soil Sciences

Professional Memberships:

American Society of Agricultural and Biological Engineers
Theta Tau, Professional Engineering Fraternity
Alpha Epsilon, Biosystems and Agricultural Engineering Honor Society