The Pennsylvania State University

The Graduate School

ANTHRACITE AS A FILTER MEDIA TO REMOVE PETROGENIC HYDROCARBONS FROM STORMWATER

A Thesis in

Agricultural and Biological Engineering and International Agriculture and Development

by

Carlos Rolando Fernandez Pulido

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

May 2020

The thesis of Carlos Rolando Fernandez Pulido was reviewed and approved* by the following:

Rachel A. Brennan
Associate Professor of Civil and Environmental Engineering/Agricultural and Biological Engineering
Thesis Advisor

Margaret Hoffman
Assistant Professor of Plant Science

Lauren McPhillips
Assistant Professor of Civil and Environmental Engineering/Agricultural and Biological Engineering

Paul Heinemann
Professor of Agricultural and Biological Engineering
Head of the Department of Agricultural and Biological Engineering

ABSTRACT

Environmental water pollution is a global threat, and the major contributors are the agricultural, domestic and industry sectors. Stormwater pollution, a dominant form of water pollution in urban and semi-urban areas, is surface water generated by heavy rain or melted snow, that is collected and/or diverted into natural water bodies or infiltrated into aquifers carrying pollutants of concern. Nitrogen, and phosphorus, the main pollutants driving eutrophication around the globe, along with hydrocarbons and heavy metals, acute toxic and carcinogenic compounds that represent a threat to humans and wildlife, are major stormwater contaminants. Classic stormwater management, along with green infrastructure, relies on a set of technologies and solutions to address this issue. Techniques like biological degradation, utilized in wet ponds and constructed wetlands, aim for the removal of nutrient-based pollutants such as nitrogen and phosphorus. Filtration, another treatment option utilized in stormwater management, sometimes enhanced by biological activity carried out within the filtration media, is utilized for the removal of sediments, less degradable compounds, as well as nutrients. Some of these techniques remove petrogenic hydrocarbons attached to sediments, but they are not designed for removing soluble petrogenic hydrocarbons. Anthracite, a type of coal, has been investigated in the removal of petrogenic hydrocarbons, and as a component of multi-stage filters, but more research must be done in order to parameterize anthracite as a filter media for removing petrogenic hydrocarbons from stormwater. The purpose of this study was to evaluate anthracite as a filter media option for removing used motor oil from artificial stormwater. Material characterization, a batch experiment, and a filtration experiment were utilized. Anthracite utilized in this study exhibited a Brunauer-Emmett-Teller (BET) surface area of 0.628 m^2/g for particles with a diameter of 1.18 mm < d_1 < 2.36 mm, and 0.335 m^2/g for particles with a diameter of 2.36 mm < d_2 < 4.75 mm. The Fourier-transform infrared spectroscopy (FTIR) spectrum showed no functional groups that could favor any type of chemical

sorption, but two sharp peaks in the infrared spectrum of the anthracite sample that treated used motor oil (UMO) water accommodated fraction (WAF) appear at 2856 and 2924. These peaks are consistent with CH stretches of hydrocarbons, meaning that there is evidence of physical sorption of hydrocarbons. WAF of UMO contained approximately 18 % of the original motor oil that was utilized to make it, which is consistent with the literature on crude oil, where WAF utilization is the norm. Batch experiments performed with 1 gram and 5 grams of anthracite, and shaking times of 2, 6, 12, 24 and 48 hours, showed UMO removal above 99 %. Similar results were found for three preliminary filtration column experiments, the percentages of removal were: above 99 % for the fast flow column, the 5-minute intermittent saturated column and the 15-minute intermittent saturated column.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to use I would like to use this section to truly thank Dr. Margaret Hoffman and Dr. Robert Berghage for giving me this new opportunity at Penn State that allowed me to provide for my family. Dr. Lauren McPhillips accepted to serve as a committee member and provided meaningful feedback for this work, thanks to her too. I would also like to thank Dr. Rachel Brennan for accepting me in her group again (second Master of Science and sixth year working together), for the advice, for the kindness and for giving me freedom. Rachel is an exceptional person and a better boss, you changed my life and I will be grateful to you forever. Special thanks to Dr. Sara Lincoln, she saved this experiment, she taught me so much, and she knows that I was lost without her, and thanks for all of the great moments in the lab. TJ, thanks for our friendship and for all of the help with the FTIR, I still owe you that favor. Judy Heltman, Devon Johnson and Amy Case, thanks again for all of these years in which I had the privilege to work close to you. I also want to thank Alejandro Lococo "La Bestia del Hardcore" and some other MC's for all of their music and rap battles in the FMS Argentina, all of my nights in the laboratory where better because of the rap and hip-hop that they do so well. Torey, great friend, thanks for talking to me about State College. Thanks to my State College family: Sandra, Clarisa, Miguel Schievenin, Ilse, Antonella, Michele and Harrison. I do not want to forget Lucilla and Sandee, thanks for everything, bo I am so happy that we are still friends and we will continue to do so. Zeque, thank you for being there for me when I was alone. Thanks to Uruguay, Argentina (especially Mar del Plata) and United States, Ezequiel Maschwitz, I almost forgot you. Castel, thanks for being my friend for such a long time, you are part of this. I also want to thank all the anime and cartoons that I watched (I still do), my desire to become a better person was shaped by several characters that I really admire, Goku, Klilin, Maestro Roshi, L, Vegeta, Gon, Hanamichi, Batman, Spider Man, Kenshin, Tony Stark, and many more, thank you all. I am grateful to all the problems and difficult situations that I had to face in my life.

Thanks God, for being there for me always. To my parents, thank you for teaching me how not to give up and for giving me everything that you had. Thanks to State College and its people, a beautiful and magical town. Thanks to Mount Nittany Hospital for bringing my son to this world. Thanks to all of the parks in which we had amazing moments with my family. Thanks to the Schlow Library for being the perfect place for my family and especially for my son. Thanks to Cozy Thai and Galanga for their amazing gluten free food. Thanks to Sowers Harvest for their kindness and excellent food, and thanks to Jan for her friendship and for making our weekend breakfast perfect. Thanks to Nuria for being a good friend, and for always being there for us. Big thanks to Sims, Juanjuli, Kira, Loki and Kichi (Kitzzy) for being there for us along the years, for visiting us in every important moment of our life, for celebrating perfect Christmas with us, and for opening the doors of your house to help us when we needed that the most, you are a big part of this. Finally, thanks to my beautiful wife Clara and my beloved son Icaro, they make my life amazing and everything that I do, I do for you. You make me a better person every day, thanks for all the help that you gave me during this process and for believing in me, I could not have done this without you.

Chapter 1

Introduction

Environmental pollution in streams, rivers, lakes, and oceans is often generated by the agricultural, industrial, and domestic sectors (WWAP, 2014). Depending on the area in which industries and residential neighborhoods/cities are located, the amount of pollution discharged into bodies of water may vary. Where infrastructure is in place, stormwater (surface water generated by heavy rain or melted snow) is collected and/or diverted into natural water bodies or infiltrated into aquifers. As mentioned by Brabec (Brabec et al., 2002), Stankowski (Stankowski 1972) stated that, as urban development increases, the impervious surface area, that is, structures covered by almost non-porous materials, also increases. Thus, stormwater pollution from domestic gardens, automobiles, parking lots, service stations, roads, and other types of point and non-point source generators is concentrated (Brabec et al., 2002). Green infrastructure, man-made solutions such as, bio-swales, constructed wetlands and detention ponds, enhances the treatment of stormwater pollution reducing the flow velocity and controlling the volume, while filtering some of the pollutants present in stormwater before it reaches the environment. The utilization of suitable filter media can also help to remove specific pollutants while reducing the peak flow and the velocity of stormwater (Clark & Pitt, 2012; Kramer, 2014).

The source of the stormwater will dictate the combination of different pollutants present in it (WWAP, 2014). Contaminants of importance, based on their impact on the environment, include:

- Nutrients: mostly nitrogen (N) and phosphorus (P), causing eutrophication (excessive amount of nutrients in a water body generates a proliferation of photosynthetic organisms that deplete oxygen when decaying) (Paerl et al., 2014);
- Heavy metals: which in high levels can be toxic for plants and fish (Karlsson et al., 2010); sediments, which if accumulated in rivers can disrupt the food chain;

- Hydrocarbons: which can be lethal to aquatic life even at low concentrations (Kennedy, Allen, and Wilson, 2016) and also be toxic for humans (IARC, 1988), with used motor oil the most abundant, toxic, and non-regulated one.

There is no "one-size-fits-all" solution to address stormwater pollution, for this reason, new treatments based on the different mix of pollutants present in the water must be explored. The selection of appropriate media is key for the effective management of stormwater. For example, a constructed wetland for treating stormwater runoff from a service station (containing heavy metals and hydrocarbons) may require different filter media than one designed to filter pollutants from a small community garden in the city (containing pesticides, as well as inorganic and organic fertilizers).

Because green infrastructure is widely applied in current and new stormwater management systems (WWAP, 2014), filter materials utilized in this endeavor should be versatile enough to treat different types of pollutants, while simultaneously supporting the growth of plants which can provide additional environmental functions (e.g. in the case of wetlands and bioswales). Commonly used filter materials include activated carbon (AC), organoclays (containing anthracite), sand, and charcoal, among others (Al-Anbari et al., 2008; Alther, 2008; Wendling et al., 2013), all of them exhibiting different characteristics and effectiveness to remove stormwater pollution. In addition, a few investigations have utilized anthracite as a fill material. Anthracite, the purest form of coal, is commercialized in the United States for water, wastewater, and stormwater treatment. It has been investigated as a possible component of multi-stage filters for treating stormwater and wastewater (Mueller et al., 2003; Ncube et al., 2018), as a main component for removing hydrocarbons from stormwater (Okiel et al., 2011), and combined with other types of media to remove a variety of contaminants from real stormwater (Al-Anbari et al., 2008). Due to the relatively large size of hydrocarbon molecules, the efficacy of materials like activated carbon (one of the most versatile materials for water and wastewater treatment) to filter water containing this type of pollutant could

be compromised. Because of the difference in size between hydrocarbon molecules and the porous channels of activated carbon (hydrocarbon molecules are bigger than the internal pores of AC), the interior pores become ineffective and only the exterior surface area is available for adsorption (Clark & Pitt, 2012). Utilizing anthracite as a filter media in multi-stage filters or bioswales could represent a viable option for removing petrogenic hydrocarbons from stormwater. After its filtering capabilities were exceeded, the anthracite could be burned "cleanly", due to its high percentage of carbon and low percentage of impurities (besides the ones removed from stormwater).

Results using anthracite as a filter media are promising; however, further efforts are needed to study and characterize the effectiveness of anthracite as a filtration material to remove petrogenic hydrocarbons from stormwater.

The purpose of this study was to evaluate the ability of anthracite to remove petrogenic hydrocarbon pollution from stormwater. Anthracite material characterization (particle size distribution, surface area, FTIR, physical and chemical parameters) along with a batch (isotherm) and column experiments were utilized to assess the ability of anthracite to remove used motor oil from artificial stormwater.

Chapter 2

Literature Review

Introduction to stormwater pollution

Individual households, industries or farms can generate stormwater. It usually originates in urban and semi-urban environments, when rainwater or melted snow flows in large quantities transporting pollutants discharged by point or non-point generation sources. As a response to this phenomenon, several techniques have been explored as treatment options to reduce stormwater volume, velocity, and pollutant concentrations before reaching natural water bodies. Depending on the objective, volume control or pollution abatement, different techniques can be utilized, such as reservoirs, bioswales, filters, or constructed wetlands. Another factor, commonly considered to define the type of stormwater treatment, is proximity of the collection or discharge point to the targeted water body. The closer the system is to an aquatic environment; the more complex and expensive the infrastructure should be in order to prevent pollution from entering the environment (in an ideal case scenario when stormwater is treated). Pollutants of concern for research and government legislation are inorganic fertilizers, which are heavily utilized by intensive agriculture and landscaping, and heavy metals that migrate from roads and some industries that do not meet regulation standards. The former compounds are of importance because of their environmental negative impact, contributing to eutrophication, and the latter due to their acute toxicity for wildlife and humans. Research has been carried out focusing mostly in these two categories due to the complexity of treatment options needed to remove the combination of contaminants in stormwater, and the wide extent of land generating such pollutants (Clark & Pitt, 2012).

Constructed wetlands, retention basins, bio and physical filtration are some of the systems utilized to treat stormwater, which exhibit different degrees of effectiveness depending on the type

of pollutants and the filter/support media utilized (Butler & Davies, 2004; Kramer, 2014). Stormwater management is far from being perfected for removing every pollutant present in the water; for this reason, more research is needed, especially for the removal of petrogenic hydrocarbons. This type of contaminant poses a technical challenge for treatment, due to the size of the molecules, presence of several heavy metals, point and non-point generation nature (erosion from road, car leaks, service stations leaks and tire wear), and acute toxicity potential.

Government regulations for reducing stormwater pollution

The 1948, the Federal Water Pollution Control Act was the first law to address water pollution in the United States. It was amended in 1972, since then it is known as the Clean Water Act (CWA), and the Environmental Protection Agency (EPA) was appointed as the institution in charge of enforcing the laws and regulations defined in it. From 1972 until 1987, the CWA was designed to address water pollution generated by point sources, but after an amendment in 1987, the CWA also started to consider water pollution generated from non-point sources. Thus, agricultural runoff, construction sites, urban areas, and even forest where included in the scope of the CWA. This federal law is a complete and comprehensive law designed to address water pollution since the start of an activity or the modification of an ongoing one. It provides guidelines and requirements for the control of pollution sources and the design and maintenance of infrastructure destined to treat polluted water before it is discharged into the environment. Some of the components of the CWA are:

- The National Pollutant Discharge Elimination System (NPDES): a system to regulate pollution generated at point sources; that includes programs such as Municipal Separate Storm Sewer Program (MS4) and Combined Sewer Overflow (CSO), oriented to generate green infrastructure to increase stormwater management while improving water quality;

- Technology based standards: establishing a discharge limit per activity based on the best available technology, thus creating national standards that have nothing to do with the current state of the water body in which polluted water is discharged;
- Water quality standards: a tool to limit even more the level of pollution discharged to a water body in case those technology-based standards are not sufficient to ensure non-degradation of the environment.

Currently, the EPA, implementing the CWA and the NPDES, regulates the pollution discharges of construction and industrial activities, municipal and transportation sources, oil and gas stormwater activity. In 2017, the first draft for long-term stormwater planning was released by the EPA, providing a tool-kit to assist communities in the design of their stormwater infrastructure. Despite being an excellent tool for regulation and control of water pollution, the CWA is not oriented to work towards prevention, which generates a disconnection between state-of-the-art research, monitoring and enforcement, and policymaking. Another aspect that was not considered by the CWA, since its creation, was the interaction between different pollutants, the majority of the water quality standards are design based on the effect of a particular compound, not considering the multiplier effect that two or more of these pollutants could have over the environment.

The Clean Water Act is one of the most complete water environmental laws in the world that has prevented further damage to the environment since it was created, but a new approach considering prevention and the interaction of multiple compound must be taken, considering all of the research data gathered since it was last amended in 1987.

The following sections aim to describe the current state of knowledge related to stormwater pollution, treatment options, and opportunities to explore new techniques for reducing environmental petrogenic hydrocarbon pollution from stormwater.

Sources of stormwater pollution: agricultural, industrial, and residential

Stormwater pollution is generated by a variety of sources within urban and semi-urban environments, with agriculture, residential areas, and industry (including commercial activities such as downtown areas) being the main contributors. The distinctive characteristic of landscapes in which stormwater is generated is the area covered by impervious surfaces: the higher the percentage of land covered, the higher the risk for water quality to be negatively impacted. There is not an exact method to quantify at which percentage of area covered the environment starts to be degraded, but the concept of threshold limit is utilized to determine approximately when water environments are being degraded (Brabec et al., 2002).

Urban and semi-urban environments are special areas because stormwater pollution can originate in farms that are close to roads, or in residential landscaping and urban gardens (Ellis et al., 2014), discharging different concentrations of pollutants but with similar composition. This is an advantage since the same treatment option can be utilized at different scales, thus the management complexity can be reduced.

Among the three biggest contributors to stormwater pollution, industry is expected to be the smallest, due to regulations imposed to their activities (West et al., 2015). However, depending on the size of the industry, the capabilities of the government agencies to enforce environmental laws, as well as the type of industry, the environmental damage that this sector can generate could be substantial.

Technical and political processes, such as urban planning, exist that aim that human settlements are designed in harmony with the environment, conserving the balance between human activity and the natural surroundings. Nevertheless, urban planning generally does not consider the health of the water bodies surrounding land developments as a priority. On the contrary, stormwater is quickly diverted into the natural water bodies to avoid floods and infrastructure damage in roads,

towns or cities (Brabec et al., 2002), which is considered an old-fashioned approach in stormwater management practices.

The limitations of the current tools for assessing water quality impact in places with high impervious surface coverage along with the "old fashioned" approach utilized by governments to regulate land development by the private sector, creates a scenario in which new media filter alternatives must be explored to be utilized in stormwater management. Different cities in the United States, such as, Baltimore, Phoenix and Portland, have been working towards the implementation of new, diverse, and more efficient technologies for stormwater management paying attention to enhanced filter media options (McPhillips & Matsler, 2018). However, due to the absence of a national plan for implementing mandatory green stormwater infrastructure (GSI), and the lack of documentation of the ecosystem services that these systems provide, a gap on the research exists that must be closed. Thus, enhancing the capabilities of current treatment technologies for treating stormwater pollution, while new and revolutionary treatment options and regulations become available for reducing and eliminating stormwater pollution should be a priority for scientists.

Point and non-point sources of pollution

Stormwater pollution is generated by either a "point source" or a "non-point source". As its name indicates, a point source of pollution is an identifiable source of contamination from where pollutants are discharged into the environment, for example, wastewater treatment plant effluents, factory discharges, and service station spills. On the contrary, a non-point source of pollution is spread over a large area in which superficial runoff carries pollutants as it moves towards natural or artificial water bodies (Ellis et al., 2014). Roads, highways, bridges, and agricultural land are

examples of non-point sources of pollution, where applying treatment technologies is challenging due to the extension of land that they represent (Hilpert & Breysse, 2014).

Due to existent infrastructure, urban environments are equipped to capture most of the stormwater generated within the city's boundaries, point or non-point source generated, but this water is not always properly treated, and it is usually discharged untreated into water bodies. On the contrary, more rural environments lack in infrastructure and application of treatment technologies due to the high cost associated with those practices, and as a result, water quality degradation is more likely to take place in those areas. For agricultural areas, best management practices (BMPs) are the best tool for control and mitigation of stormwater pollution. Due to the rapid degradation of bodies of water in the last two decades, for example, the Chesapeake Bay, green infrastructure applied to stormwater management and agriculture BMP's have become powerful tools utilized by the government and private companies for pollution control.

Most common stormwater pollutants

Numerous compounds can create negative impacts in the environment, but not all of them are released in quantities that can create short- or medium-term effects capable of generating irreparable damage. Thus, some substances are of more importance for enforcement agencies like EPA due to their rapid impact on the environment (such as N and P), acute toxicity (such as hydrocarbons and heavy metals), and other types of substances that are resistant to environmental degradation (such as persistent organic pollutants).

Stormwater pollutants that promote biological activity and eutrophication: nitrogen and phosphorus

Inorganic fertilizers, animal manure, and excessive organic matter from dead vegetation and food processing activities releases amounts of N and P that could produce irreparable damage to the environment (Yang & Lusk, 2018). After the agricultural application of nitrogenous inorganic fertilizers, 50 % of the nitrogen (N) applied ends up as water pollution or as atmospheric nitrogen (N_2) or nitrous oxide (N_2O) (Smil, 1999), while crops take up the rest. This type of water pollution contributes to the creation of eutrophicated water bodies, commonly called “dead zones”. Eutrophication is caused by high concentrations of limiting nutrients for aquatic life, mostly N and P (Paerl et al., 2014). Algae utilize these nutrients to proliferate rapidly, and after they die and settle in the benthic zone, heterotrophic organisms use them along with dissolved oxygen (DO) to grow. If the DO is depleted, the survival of organisms that need certain levels of oxygen (O_2) to survive like crustaceans or fish is threatened. This represents irreparable damage to a water body and could have negative consequences on human and aquatic life.

Stormwater pollutants with high toxicity and possible carcinogenicity: hydrocarbons

Hydrocarbons are compounds that can be produced in nature, either biologically (phytogenic) when plants or animals decompose, or geologically (petrogenic) when petroleum is formed. They can also be produced by anthropogenic activities, when petrogenic hydrocarbons are refined or transformed into products such as oil or gas. Another category is pyrogenic hydrocarbons, which result from the intentional or unintentional combustion of different types of fuel or materials. Some examples of each category are mentioned below (Kennedy, Allen, and Wilson, 2016):

- Phytogenic hydrocarbons: chemical compounds originating from the decomposition of animals, bacteria, plants and fungi.
- Petrogenic hydrocarbons: monocyclic and polycyclic aromatic hydrocarbons, alkanes, and naphtenes. These compounds can be found in coal, gas, and oil. They usually reach stormwater when spills occur.
- Pyrogenic hydrocarbons: heavier and more complex than petrogenic hydrocarbons. Their molecular size and structure make them less degradable in the environment, and therefore they tend to fix into sediments and have less mobility. They are typically persistent organic pollutants.

The hydrocarbons present in stormwater pollution will depend on site characteristics and the type of hydrocarbons dominating that site. Thus, runoff generated in a forest area will contain more phytogenic hydrocarbons than in an urban area, in which the predominant form of hydrocarbon will be petrogenic (Kennedy, Allen, and Wilson, 2016).

The chemical composition of petrogenic and pyrogenic hydrocarbons present in stormwater, in addition to the presence of heavy metals in such contaminated waters make them extremely toxic for humans and the environment. They are associated with increased cancer rates according to one study carried out by the International Agency for Research on Cancer (IARC) part of the World Health Organization (WHO). Data collected from mice studies and limited human data were analyzed to evaluate the carcinogenicity of hydrocarbons in different areas of its production and utilization, from refining to automobile use. Gasoline was cataloged as carcinogenic for humans and experimental animals. Other types of fuel, such as jet fuel or diesel could not be proven to cause cancer in humans (IARC, 1988). However, the exposure data was limited, and due to the similarities with oil, these types of fuels could generate similar negative effects on living creatures.

The IARC monograph (IARC, 1988) provides evidence of the different ways in which humans and the environment can be exposed to petrogenic hydrocarbons. Based on this study, it can be concluded that stormwater must be treated to remove petrogenic hydrocarbons and reduce the exposure of humans and wildlife to these contaminants of concern.

Motor oil and total petroleum hydrocarbons

United States consumes around 20 % of the total petroleum extracted and refined in the world (US, Energy and Information Administration, 2019) As shown in Table 2-1 (adapted from: Petroleum and Other Liquids, Product Supplied U.S. Energy Information Administration, 2019) 20.5 million barrels day^{-1} of petroleum products were consumed in the United States in 2018. Petrogenic hydrocarbons (mostly gasoline and oil) are mainly released into the environment through vehicle leaks, followed by tire and asphalt erosion, and engine emissions among others. Pollutants released into stormwater contain heavy metals and polycyclic aromatic hydrocarbons (PAH's), constituting the worst and most difficult to compounds to degrade (Göbel et al., 2007). Industrial leaks are considered another potential contributor, but due to regulations and controls, this type of pollution can be mitigated more easily.

Table 2-1. Petroleum products consumed in The United States in 2018

Product	Annual consumption (million barrels/day)
Finished motor gasoline[1]	9.329
Distillate fuel oil (diesel fuel and heating oil)[1]	4.146
Hydrocarbon gas liquids (HGL)	3.007
Kerosene-type jet fuel	1.707
Still gas	0.703
Petrochemical feedstocks	0.346
Petroleum coke	0.327
Asphalt and road oil	0.327
Residual fuel oil	0.318
Lubricants	0.117
Miscellaneous products and other liquids[2]	0.094
Special napthas	0.048
Aviation gasoline	0.012
Waxes	0.006
Kerosene	0.005
Total petroleum products	20.504

[1] Includes fuel ethanol in gasoline and biodiesel in distillate fuels
[2] Others includes other liquids not included in the table
Note: Sum of individual products may not equal total because of independent rounding

Literature about oil water pollution in the United States is scarce and California is one of the states that started measuring it and pushing for more and better regulation for such contaminants. Approximately 150 million gallons of lubricating oil, along with and 145 million gallons of industrial oil were commercialized in California in 2004 (California Integrated Waste Management Board (CIWMB)), where 58 % and 23 % of these oils were recycled. Up to 40 % of the lubricating oil utilized in California is leaked or expelled as combustion products by cars (Denton et al., 2006). The oil that is not properly disposed of or recycled, plus the oil that is leaked and released in emissions, may constitute stormwater pollution. The quantities of oil that are being released into the environment are unknown and difficult to estimate due to the large areas in which they are being released, the complexity of the mixtures, and the transport and degradation processes that take place in the environment (Denton et al., 2006).

Petrogenic hydrocarbons (also called petroleum hydrocarbons) are derived from crude oil. They constitute a group of compounds that can have different chemical structures that affect their transport properties, toxicity, and biodegradability. Higher molecular weight compounds in this category tend to bind with soil particles and be less degradable, while lower molecular weight petrogenic hydrocarbons tend to be more mobile, soluble in water, and highly toxic. This group of compounds are classified as total petroleum hydrocarbons (TPH), and usually include PAH's. Unlike some PAH's, TPH does not have any aquatic or human health standard associated with it, thus, its monitoring and mitigation is not regulated within a solid legislative framework in the United States. Some states or municipalities have narrative standards for TPH, for example: "no visible sheen" being arbitrary and difficult to measure (Schueler & Youngk, 2015). Table 2-2 (adapted from Aerial Observations of Oil At Sea, Branch, Response, Division, & Oceanic, 1996) shows the general glossary of terms developed by The National Oceanic Atmospheric Administration (NOAA); it summarizes the terminology utilized to identify the appearance of oil in water (Branch et al., 1996). The EPA in section 304 (a) of the CWA, states that oil and grease should not be present in stormwater in a quantity that produces a visible oily sheen (Weiner, 2000). A concentration of oil and grease smaller than 1 mg/l could produce a visible sheen (Denton et al., 2006).

Table 2-2. Oil spill observation glossary.

Description of sheen	Approx. thickness of layer	Approx. volume of oil per area
Barely visible	0.00004	50
Silver sheen	0.00007	100
First color trace	0.0001	200
Iridescent rainbow	0.0003	400
Dull colors	0.001	1,200
Dark colors	0.003	3,600
Brown oil	0.1 – 1.0	- - -

Table 2-3 (adapted from Schueler & Youngk, 2015) presents a summary of TPH concentrations observed in different sampling locations. Depending on the generation source and sampling place, TPH concentration can vary considerably. A detention pond for runoff can exhibit TPH ranges of 0.1 to 0.3 mg/l, while runoff from an impervious surface can carry stormwater with a TPH concentration as high as 22 mg/l.

Table 2-3. Total petroleum hydrocarbon concentration in stormwater

Sample location	TPH concentration (mg/l)	Country	Year	Author
Trafficked area	0.51 – 6.5	Germany	2007	Gobel
Highway runoff	1.4	United States (CA)	2007	Kayhanian
Pervious runoff	5	Unite States (TN)	2010	James
Impervious runoff	22			James
Detention pond runoff	0.1 – 0.3	England	2014	Ronias

Comparing the impact of petrogenic hydrocarbon stormwater pollution is not a straightforward task, due to the lack of standardized methods for producing artificial stormwater in the laboratory to run experiments simulating this type of pollution. On the other hand, such standards exist for seawater pollution from crude oil. After the “Deepwater Horizon” oil spill, scientists started to work towards defining a technique to prepare artificial polluted water with crude oil. The concept surrounding this technique is called the water-accommodated fraction (WAF).

Water accommodated fraction (WAF)

After reaching the environment, petrogenic hydrocarbons in stormwater partition into soil particles, water, and air. Unlike what is popularly believed, some proportions of these compounds are soluble in water, exhibiting low molecular weight and high toxicity. When petrogenic hydrocarbons are released into nature, they experience a weathering process that will control partitioning, possible chemical changes, photo-oxidation, biodegradation, and sometimes the formation of emulsions (when released in turbulent waters) (Atlas & Hazen, 2011; Brakstad et al., 2014; Faksness et al., 2015). The water accommodated fraction (WAF) is the solution that contains the soluble hydrocarbons present in the original sample, after a mixing process that ensures reaching equilibrium while avoiding creating an emulsion. Once the soluble hydrocarbons (alkanes and aromatic compounds) have partitioned into the water, they become available for natural degradation processes, exhibiting high bioavailability and representing a threat for aquatic life (Pollino & Holdway, 2002; Rosenkrantz et al., 2008; Rowland et al., 2005). The utilization of WAF as a method for achieving stable hydrocarbon solutions represents an opportunity for establishing valid comparisons between results generated with different filter media or set-ups for removing hydrocarbons from stormwater.

Treatment technologies for addressing petrogenic hydrocarbon stormwater pollution

Different techniques exist to treat stormwater pollution, with biological degradation, settling/sedimentation, and filtration being the most utilized (Clark & Pitt, 2012). The objective of these alternatives is to use facilities such as retention ponds, constructed wetlands, or single/multimedia filters to achieve stormwater pollution removal. Biological degradation offers better performance for the removal of nutrient-based pollutants such as N, P, and organic carbon

that can serve as nutrients for plants and photosynthetic organisms. Depending on the foundation of the retention ponds or constructed wetlands, some non-nutrient pollutants like heavy metals and low soluble hydrocarbons can be trapped in the sediments as well. The second technique, filtration, offers the possibility to primarily trap, either by absorption or adsorption, different contaminants that are not biologically degradable such as sediments, synthetic organics, hydrocarbons, heavy metals (Clark & Pitt, 2012), and persistent organic contaminants such as endocrine disruptors and disinfection byproducts.

Biological degradation in wet/dry retention ponds and constructed wetlands

Artificial ponds are excavated structures that can be lined to prevent infiltration of polluted water into the soil. There are three types of ponds destined to control and filter stormwater: wet and dry ponds, and a combination of the two. The operation principle is to control the excess of superficial runoff created for storms or snow melted events, not focusing in water quality. Wet ponds have an inlet and outlet that are aligned, and they usually have a fixed volume of water in them. In contrast, dry ponds do not necessarily have an outlet point, and they do not have water stored in them in between storm events. Wet ponds, due to their stored water and bottom slope (for accumulation of sludge), are more effective for pollution removal. Since some pollutants tend to bind with suspended solids, becoming part of the sediments, outlet water tends to be less polluted after it is decanted. If biodegradable, those pollutants on the bottom undergo microbial degradation. Conversely, dry ponds have a reduced ability to degrade pollutants due to the lack of water stored in them, their bottom is usually porous, and they are not connected to the stormwater grid. Their main function is to control the stormwater volume during huge rain events (Butler & Davies, 2004; Yang & Lusk, 2018).

Constructed wetlands are shallow excavated structures, where a variety of media can be utilized in the bottom, such as sand, rock, soil, or combinations of them in different layers. This media is saturated with water or sometimes covered by shallow water flowing during runoff events. Plants are established to add a biological unit of treatment/filtration. Well-designed constructed wetlands have good oxygen diffusion provided by plant roots to enhance microbial growth, thus enhancing degradation and pollutant removal. Despite simple design and construction, artificial wetlands must be monitored and maintained in order to perform properly (Butler & Davies, 2004; Yang & Lusk, 2018). Hydrocarbons can undergo aerobic microbial degradation (anoxic conditions in detention ponds represent an obstacle for tackling hydrocarbon pollution), being this an option when designing stormwater infrastructure. However, these systems are not designed considering hydrocarbons as pollutants of concern and for that reason more research need to be done for justifying including hydrocarbons in the matrix of decision when defining GSI technologies.

Chemically active filtration: anthracite, peat, compost, soil, and activated carbon

Stormwater filtration systems consist of regular infrastructure to collect water plus a filtration media unit to trap pollutants. These types of systems also have a chamber to handle large volumes of water during major rain events. The most common media utilized is sand, due to its availability and ability to retain suspended solids (Ellis et al., 2014). However, media such as peat, compost, activated carbon, or anthracite can replace or supplement this option in order to target specific contaminants to ensure water quality before discharging into natural water bodies.

Al-Anbari (Al-Anbari et al., 2008) studied the effectiveness of different filter media for removing pollutants from real stormwater, filtered and non-filtered, with high and low concentration of contaminants. Targeted contaminants measured were N and P along with heavy metals. Media tested was anthracite (A), clean river sand, garden compost, granular activated

carbon (GAC), lignite, perlite, vermiculite (V), and zeolite (Z). Anthracite and GAC exhibited higher adsorptive capacities when tested alone. The second part of the experiment included eleven different combinations of A, GAC, V, and Z. The best performance in overall removal was observed in double GA and double Z (GA_2Z_2), GA and double V (GAV_2) and GA and double Z (GAZ_2). Despite the laboratory nature of the experiment, it was demonstrated that the different filter media tested were capable of effectively removing stormwater pollutants and justifies full-scale application to test the utilized media.

According to Clark & Pitt (2012), the treatment proposed for the reduction or elimination of polyaromatic hydrocarbons, oil and grease was chemically active filtration, where removal can be enhanced by microbial activity in the porous space of the filtration media. Peat, compost, and soil, along with granular activated carbon, were listed as filter media to be utilized in this type of treatment. This comprehensive review stated clearly the huge potential that non-sand filter media could have in the removal of pollutants from stormwater.

Filter adsorption: anthracite, activated carbon, and organoclays

Okiel (Okiel et al., 2011) evaluated the effectiveness of powdered activated carbon, bentonite and deposited carbon effectiveness in removing oil from water emulsions. Adsorption was proposed as the removal mechanism. Activated carbon was able to perform better than bentonite and deposited carbon. Due to the high surface area of activated carbon, this type of filter media can be utilized to remove small molecular weight pollutants. Alther (Alther, 2008) utilized organoclays as a treatment alternative to remove oil from water, stating that, besides mechanical filtration, organoclays offer ion exchange capabilities as well as hydrophilic and lipophilic capabilities. Anthracite was utilized for preventing early blockage of the filter media and for adding heat capacity to organoclays, increasing the value of the exhausted material after filtration.

Anthracite coal

One of the most distinctive coal classifications is the one based on carbon content, where coal is grouped in two categories:

- *Brown coals*: lignite and sub-bituminous coal, carbon content 25 - 45 %
- *Hard coals*: bituminous and anthracite coal, carbon content 45 - 98 %.

Brown coals are usually lower in carbon content, and higher in impurities (such as sulfur), while hard coals have the opposite properties. Anthracite is the purest form of coal, with a carbon content of up to 98 %, one of the lowest sulfur contents, 0.6 - 0.8 %, and one of the highest heat of combustion values, up to 15,000 BTU/lb (Oakey, J. (Ed.). (2015). These characteristics make anthracite the best and most expensive type of coal (see Table 2-4 (adapted from: Coal explained, coal prices and outlook, 2018. United States Energy Information Organization, and Coal characteristics, Indiana Center for Coal Technology Research)) in the market, being primarily utilized as industrial (coke products) and residential material for electricity generation and heating.

Table 2-4. Characteristics of four main categories of coal

Type of coal	Carbon content (% w/w)	Sulfur (% w/w)	Heat capacity (BTU/lb)	Price United States, 2018 (US$/short ton)
Lignite	25-35	0.4-1.0	4,000-8,300	20.21
Sub-bituminous	35-45	< 2 %	8,500-13,000	13.64
Bituminous	45-85	0.7-4.0	11,000-15,000	59.43
Anthracite	85-98	0.6-0.8	13,000-15,000	99.97

As can be seen in Table 2-5 (adapted from: BP Statistical Review of World Energy, 67th edition), the biggest reservoirs of anthracite are in United States (7.2 %), China (4.52 %), India (3.2 %), Russian Federation (2.4 %) and Australia (2.36 %), representing approximately 20 % of the total reservoirs worldwide (BP statistical review of world energy. London, 2018). Pennsylvania is the biggest anthracite producer in the United States, where most of the mines are located in Luzerne,

Northumberland, and Schuylkill counties, as can be seen in Figure 2-1 (source: Department of Environmental Protection. Coal Mining in Pennsylvania). This anthracite region produced 4.6 million tons of coal from surface coalmines in 2015.

Table 2-5. Total proved coal reserves at the end of 2017

Country	Anthracite and bituminous (million tonnes)	Sub-bituminous and lignite (million tonnes)	Total	Share of total
United States	220800	30116	250916	24.2
Canada	4346	2236	6582	0.6
Mexico	1160	51	1211	0.1
Total North America	226306	32403	258709	25
Brazil	1547	5049	6596	0.6
Colombia	4881	–	4881	0.5
Venezuela	731	–	731	0.1
Other S. and Central America	1784	24	1808	0.2
Total Other S. and Central America	8943	5073	14016	1.4
Bulgaria	192	2174	2366	0.2
Czech Republic	1099	2541	3640	0.4
Germany	8	36100	36108	3.5
Greece	–	2876	2876	0.3
Hungary	276	2633	2909	0.3
Poland	19808	6003	25811	2.5
Romania	11	280	291	< 0.05 %
Serbia	402	7112	7514	0.7
Spain	868	319	1187	0.1
Turkey	378	10975	11353	1.1
United Kingdom	70	–	70	< 0.05 %
Other Europe	1108	5172	6280	0.6
Total Europe	**24220**	**76185**	**100405**	**9.7**
Kazakhstan	25605	–	25605	2.5
Russian Federation	69634	90730	160364	15.5
Ukraine	32039	2336	34375	3.3
Uzbekistan	1375	–	1375	0.1
Other CIS	1509	–	1509	0.1
Total CIS	**130162**	**93066**	**223228**	**21.6**
South Africa	9893	–	9893	1
Zimbabwe	502	–	502	< 0.05 %

Country	Anthracite and bituminous (million tonnes)	Sub-bituminous and lignite (million tonnes)	Total	Share of total
Other Africa	2756	66	2822	0.3
Middle East	1203	–	1203	0.1
Total Middle East and Africa	**14354**	**66**	**14420**	**1.4**
Australia	68310	76508	144818	14
China	130851	7968	138819	13.4
India	92786	4942	97728	9.4
Indonesia	15068	7530	22598	2.2
Japan	340	10	350	< 0.05 %
Mongolia	1170	1350	2520	0.2
New Zealand	825	6750	7575	0.7
Pakistan	207	2857	3064	0.3
South Korea	326	–	326	< 0.05 %
Thailand	–	1063	1063	0.1
Vietnam	3116	244	3360	0.3
Other Asia Pacific	1326	687	2013	0.2
Total Asia Pacific	**314325**	**109909**	**424234**	**41**
Total World of which	**718310**	**316702**	**1035012**	**100**
OECD	320377	177608	497985	48.1
Non-OECD	397933	139094	537027	51.9
European Union	22913	53416	76329	7.4

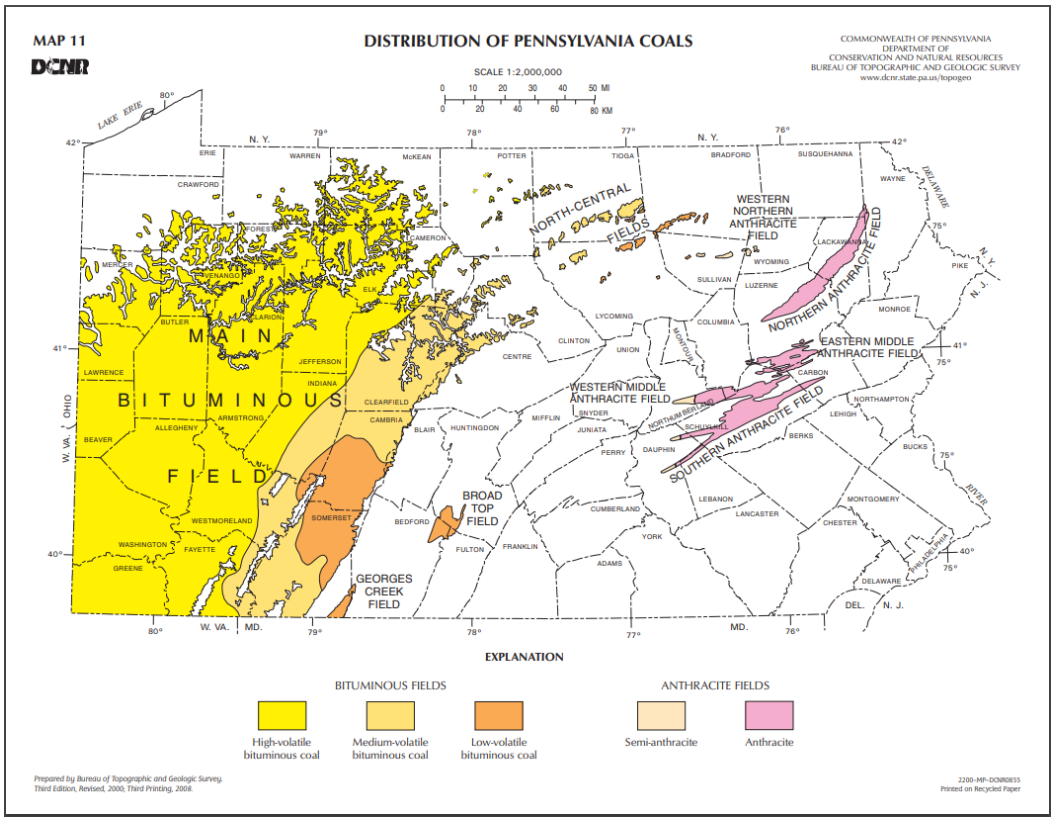

Figure 2-1. Distribution of Pennsylvania coals

Even though anthracite is well established as a product that it is utilized to generate energy, coal companies such as Blaschak Coal Corporation in Pennsylvania are exploring its utilization in water treatment and water filtration. This is based on the low impurity content and the possibility of generating energy after the material is saturated with pollutants present in the water after filtration. Few studies have explored anthracite in depth as a filter media option for removing hydrocarbons from stormwater, and this represents an opportunity for this industry to incorporate a “greener” use of its product.

Anthracite as a filter media

Goals

Based on the scientific data present in current literature, there is an opportunity to investigate anthracite as a potential filter media option for addressing petrogenic hydrocarbon stormwater pollution. Thus, the following goal is key for starting to build the framework for anthracite to be considered as a technically and economically attractive filter media option:

- Investigate the use of anthracite as a material to adsorb petrogenic hydrocarbons from stormwater;

Objectives

In order to achieve the stated goals, the performance of anthracite as filter media for stormwater management must be evaluated based on anthracite particle size, treatment time during batch experiment, and stormwater retention time during filtration. The following objectives were defined to accomplish this task:

- Quantify material properties of anthracite to understand sorption mechanisms;
- Quantify the performance of anthracite in removing petrogenic hydrocarbons from simulated stormwater in batch sorption systems;
- Evaluate the performance of anthracite in removing petrogenic hydrocarbons in a filtration experiment under different flooding times.

Chapter 3

Anthracite material characterization

General description

Anthracite, mined/extracted from Blaschak Coal Corporation mines in northeastern Pennsylvania, was utilized in this experiment. Bags of 18 kg of commercial anthracite were used. In order to understand its chemical characteristics and physical properties, a sieve analysis, a FT-IR analysis, a Zeta potential analysis, along with the interpretation of a compost analysis (performed by Dr. Duiker, Professor of Soil Management and Applied Soil Physics at Penn State) were carried out.

Materials and methods

Anthracite sieve analysis

A sieve analysis method was utilized to quantify the distribution of particles of anthracite (Braja Das, 1992). An air-dried composite sample of 500 grams of Blaschak anthracite, from three different bags, was utilized. Eight stainless steel/brass sieves, 3/8-inch, N° 4, 8, 10, 16, 20, 30 and 50 (ordered from bigger to smaller openings), plus a bottom pan for collecting fines (Figure 3-1) were stacked together and place on a motorized Humboldt sieve shaker (1/4 HP motor, 115V, 60Hz). The composite sample was slowly added into the 3/8-inch sieve and capped, and the shaker operated for 30 minutes to ensure complete separation of particle sizes. After separation was complete, the weight of the anthracite particles present in each sieve was recorded and the percentage of every category calculated.

Figure 3-1. A stack of sieves with a cover on top and a pan for fines at the bottom

Anthracite composition analysis (compost analysis)

A composite sample of Blaschak anthracite was sent for a compost analysis (Penn State Agricultural Analytical Laboratory). The following parameters were measured: pH, soluble salts, organic matter, total nitrogen, organic nitrogen, ammonium nitrogen, carbon, C:N ratio, phosphorus (P_2O_5), potassium (K_2O), calcium (Ca), magnesium (Mg), sodium (Na), aluminum (Al), iron (Fe), manganese (Mn), arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn). A summary of the analytical methods can be found in the Penn State Agricultural Analytical Services Laboratory webpage.

Surface area and pore volume

Surface area, pore volume, and pore size were measured for three different composite samples: 1.18 mm, 2.36 mm, and a sample containing all the diameters present in the original anthracite bag (Materials Characterization Laboratory, Penn State University). The instrument utilized for performing the measurements was the ASAP 2020 Plus Accelerated Surface Area and Porosimetry System, and the gas used was N_2. The parameters measured were:

Surface area: BET surface area (m^2/g), t-plot micropore area (m^2/g), t-plot external surface area (m^2/g), BJH Adsorption cumulative surface area (pores between 17.000 Å and 3,000.000 Å width) (m^2/g);

Pore volume: single point adsorption total pore volume (pores less than 9.506 Å width at p/p° = 0.010856992) (cm^3/g), BJH Adsorption cumulative volume (pores between 17.000 Å and 3,000.000 Å width) (cm^3/g);

Pore size: adsorption average pore diameter (4V/A by BET) (Å), BJH Adsorption average pore width (4V/A) (Å).

Zeta potential of one composite sample ground at a diameter lower than 100 microns was measured (Materials Characterization Laboratory, Penn State University). Electrophoretic Light Scattering (ELS) was performed utilizing the Malvern Zetasizer ZS following a modified procedure utilized by Johnson (Johnson et al., 1996).

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were collected utilizing a vertex 70 infrared spectrometer (Bruker Optics, Billerica, MA) equipped with a praying mantis diffuse reflectance accessory using a liquid nitrogen

cooled mercury cadmium telluride (MCT) detector. 500 scans at 6 cm^{-1} resolution were averaged per spectrum and absorbance calculated by referencing to clean KBr. The sample was diluted using clean KBr to prevent total beam attenuation. A fragment of anthracite was pulverized and mixed with potassium bromide (KBr) to produce a diluted sample (~1%). Black samples pose a challenge to infrared spectroscopy as IR is absorbed at all IR frequencies without necessarily being related to a specific functional group. Dilution of the sample allowed for signal from the sample to be detected over background absorbance. An additional sample that was exposed to WAF containing 20 µl of used motor oil (UMO) was analyzed in order to compare the spectra of anthracite with and without adsorbed UMO.

Results

Anthracite sieve analysis

Table 3-1 shows the results of anthracite sieve analysis. It can be observed that almost 98 % of the particles have a diameter between 1.18 mm and 2.36 mm. The percentage of fines present in the samples, particles with a diameter smaller than 0.3 mm, is less than 0.6 %. This constitutes an advantage when utilizing this material for filtration applications, eliminating the risk of clogging within the filter. On the contrary, the high percentage of particles in the 1.18 mm to 2.36 mm range, pose a challenge when trying to utilize this commercial anthracite as a media in stormwater filters, where 0.5 mm to 1 mm sand is typically used (Massachusetts Department of Environmental Protection, 2008). This particular particle size distribution of anthracite does not provide the retention time that is usually desired in stormwater filters. More configuration could be proposed where a pre-filter could be utilized before the anthracite, adding retention time and particle catchment abilities, thus complementing this anthracite particle size. In addition, different particle

sizes of anthracite could be utilized. Commercial anthracite provided by Blaschak Coal Corporation was utilized.

Table 3-1. Anthracite sieve analysis

Sieve Number	Sieve opening (mm)	Weight retained on each sieve (g)	% weight retention on sieve	Cumulative percentage retained	Percent finer
3/8 inch	9.5	0	0	0	100
# 4	4.75	2	0.4	0.4	99.6
# 8	2.36	327.2	65.44	65.84	34.16
# 10	2	84.7	16.94	82.78	17.22
# 16	1.18	74.1	14.82	97.6	2.4
# 20	0.85	6.4	1.28	98.88	1.12
# 30	0.6	1.6	0.32	99.2	0.8
# 50	0.3	0.7	0.14	99.34	0.66
pan		2.2	0.44	99.78	0.22

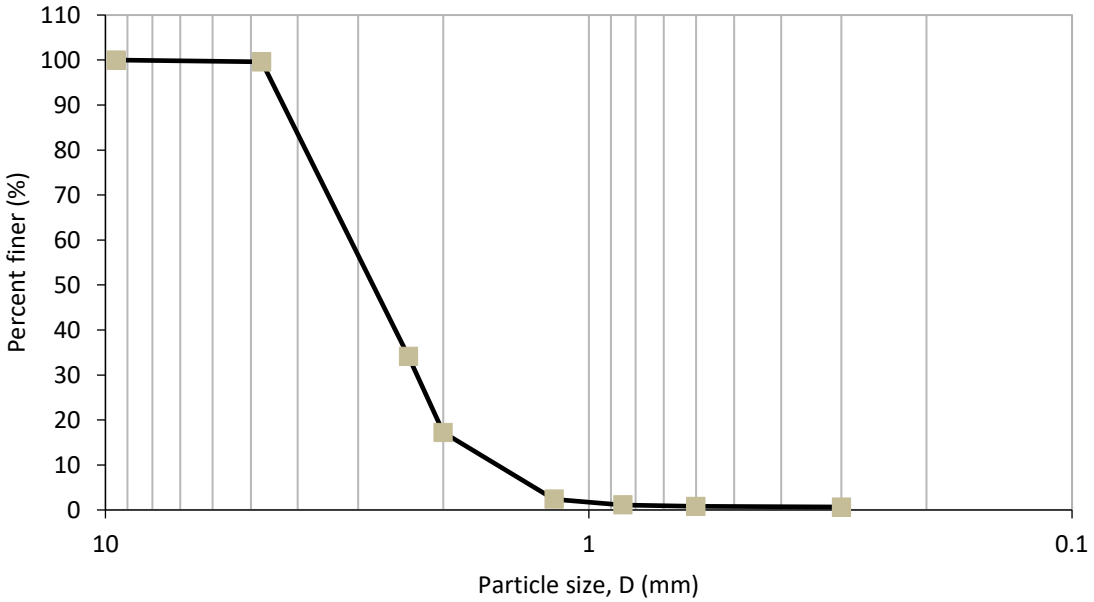

Figure 3-2. Anthracite particle size distribution curve

Based on anthracite particle size distribution curve (Figure 3-2), and with the objective of calculating the uniformity coefficient (C_u) and the coefficient of gradation (C_c), see equation 2 and

3, the diameters corresponding to percentages finer than 10 %, 30 % and 60 % were calculated (D_{10}, D_{30} and D_{60}) see equation 3.

$$\%\ Finer = 100 - \ Cumulative\ \%\ retained \quad (1)$$

$$C_u = \frac{D_{60}}{D_{10}} \quad (2)$$

$$C_c = \frac{{D_{30}}^2}{D_{60} \times D_{10}} \quad (3)$$

These characteristics are key for filter media to exhibit a particle distribution with a wide range of particles sizes, allowing the media to be utilize in a versatile way, detaining sediments, allowing longer residence times, and preventing clogging. The parameters C_u (2.06) < 4, and C_c (0.97) < 1 (see Table 3-2), calculated for anthracite show that this type of coal, as it is sold in the market, is a poorly graded filter media, and does not represent a good option to replace sand in bioswales, for example.

Table 3-2. Uniformity coefficient and coefficient of gradation

Parameter	**Value**
D_{10}	1.6
D_{30}	2.27
D_{60}	3.30
C_u	2.06
C_c	0.97

Coal composition analysis (compost analysis)

Anthracite utilized for this experiment was also utilized in an agricultural application performed by Dr. Sjoerd Duiker, Professor of Soil Management and Applied Soil Physics at Penn State. He provided the data that is presented in Table 3-3. As expected, the carbon content is high at 87.3 %, and impurities such as cadmium (Cd), copper (Cu), lead (Pb), and mercury (Hg), are present and could pose a threat to wildlife and human health if they migrate to the ground water or

the ground when used as a potential filter. This needs further investigation. In addition, the presence of nutrients such as N, P, K, and salts, are not considerable, and do not pose an environmental risk. Thus, anthracite could be considered as a potential filter media option to treat stormwater after more experiments are performed to understand the potential fate of compounds such as Cd, Cu, Hg and Hg.

Table 3-3. Anthracite composition analysis

Parameter	**Value**
pH	2.9
Soluble salts	0.78 mmhos/cm
Organic matter	873 g/kg
Total nitrogen	8 g/kg
Organic nitrogen	8 g/kg
Ammonium nitrogen	<0.005 g/kg
Carbon	774 g/kg
C:N ratio	97
Phosphorus (P_2O_5)	0.2 g/kg
Potassium (K_2O)	0.9 g/kg
Calcium (Ca)	0.3 g/kg
Magnesium (Mg)	0.1 g/kg
Sodium (Na)	26 mg/kg
Aluminum (Al)	2183 mg/kg
Iron (Fe)	2407 mg/kg
Manganese (Mn)	12 mg/kg
Arsenic (As)	2.1 mg/kg
Cadmium (Cd)	<0.5 mg/kg
Copper (Cu)	18.8 mg/kg
Lead (Pb)	12.9 mg/kg
Mercury (Hg)	0.18 mg/kg
Molybdenum (Mo)	<1.5 mg/kg
Nickel (Ni)	7.0 mg/kg
Selenium (Se)	2.5 mg/kg
Zinc (Zn)	8.0 mg/kg

Anthracite surface area

Anthracite sample called d_1 (1.18 mm < d < 2.36 mm), d_2 (2.36 mm < d < 4.75 mm), and a non-sieved sample were analyzed to quantify surface area (Table 3-4), pore volume (Table 3-5) and pore size (Table 3-6), in order to understand the available area for physical sorption of petrogenic hydrocarbons. The BET surface area of the d_1 sample was 87 % higher than the d_2 sample. Similar results of d_1 vs. d_2 were observed for t-plot external surface area (79.5 % increase) and BJH adsorption cumulative surface area (82 % increase). A similar trend was observed for pore volume, where single point adsorption total pore volume, and BJH adsorption cumulative volume for the d_1 sample were 88 %, and 96 % higher than for d_2. However, this was not observed for pore size, where adsorption average pore diameter and BJH adsorption average pore width for sample d_1 registered only a 0.9 % and a 7.6 % increase when compared with the d_2 sample. These results are expected due to the homogeneity of the anthracite, where the dominant difference in composition would be in particle size but not in internal composition and pore size distribution. Thus, surface adsorption could be controlled by arranging the particle size distribution for a potential filter application, but the sizes of the particles that could be adsorbed internally by particles of anthracite would be controlled by the same type of pore distribution.

Table 3-4. Anthracite surface area.

	Anthracite particle size		
Parameter	**d_1**	**d_2**	**Heterogeneous original sample**
BET surface area (m^2/g)	0.628	0.335	0.315
t-plot micropore area (m^2/g)	0.017	*	0.063
t-plot external surface area (m^2/g)	0.655	0.365	0.252
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3,000.000 Å width (m^2/g)	0.431	0.236	0.176

Table 3-5. Anthracite pore volume.

	Anthracite particle size		
Parameter	**d_1**	**d_2**	**Heterogeneous original sample**
Single point adsorption total pore volume of pores less than 9.506 Å (cm^3/g)	0.000143	0.000076	0.000071
BJH Adsorption cumulative volume of pores between 17.000 Å and 3,000.000 Å width (cm^3/g)	0.001482	0.000756	0.001053

Table 3-6. Anthracite pore size diameter and width.

	Anthracite particle size		
Parameter	**d_1**	**d_2**	**Heterogeneous original sample**
Adsorption average pore diameter (4V/ Å by BET) (Å)	8.5	8.4	9.0
BJH Adsorption average pore width (4V/ Å) (Å)	137.6	127.9	239.8

Fourier Transform Infrared Spectroscopy (FTIR)

Results for this section were provided by Dr. Zimudzi, Tawanda from the Research Characterization Laboratory, from the Millennium Science Complex at Penn State. The anthracite flake that was not in contact with UMO WAF did not exhibit many spectra features due to the strong background absorbance of carbon. As a result, the flake was crushed to increase the surface area for analysis, and hence the sensitivity of the IR measurement. Upon crushing, combination of peaks from the surface of the flake and the bulk of the flake were observed. The crushed flake was mixed with KBr to dilute the sample and further increase sensitivity (Figure 3-3).

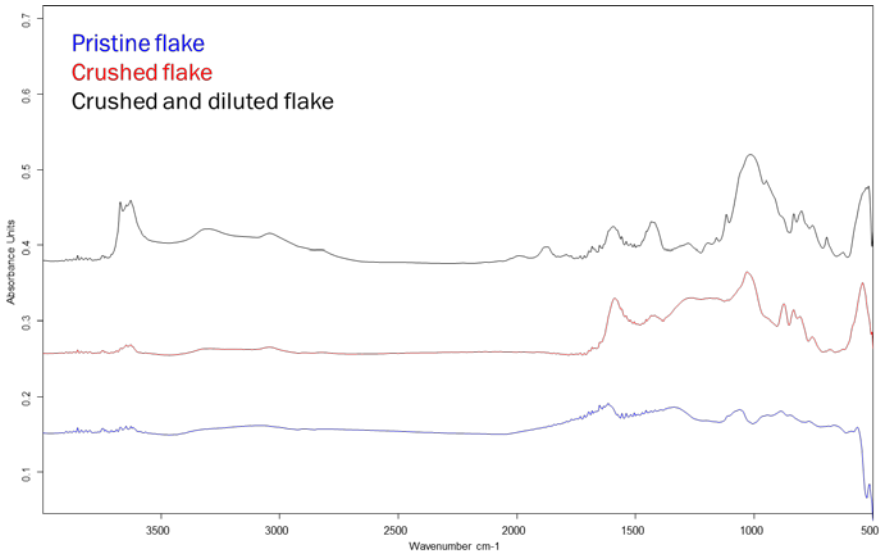

Figure 3-3. Diffuse reflectance infrared spectra of an anthracite flake before and after crushing and mixing with KBr.

The infrared spectrum of a new flake (different than the one showed in Figure 3-3), after crushing and diluting with KBr, is shown in Figure 3-4. Peaks in the range of 3700-3500 are indicative of structural OH, which is typical of free OH groups where hydrogen bonding is not possible, and OH groups associated with metal oxides and hydroxides. The peak at 3307 falls in the range where hydrogen bonded OH is typically observed (3200-3500).

While the peak at 2829 falls in the range for C-H groups for organics (located between 2750-2900), organic C-H peaks often appear as a sharp doublet unlike the broad peak observed for the anthracite sample.

The peak at 1870 can be attributed to C=O, and its high frequency is an indication of a carbonyl group in close proximity (1 or two bonds away) from nitrogen or an electron withdrawing group.

The strong band at 1017 is characteristic of an inorganic oxide such as silicon oxide or iron oxide. The precise origin of the rest of the peaks observed in Figure 3-4 would require further

investigation in order to determine their origin. However, the majority of the peaks identified are consistent with inorganic species and carbon oxygen functional groups, which would impart hydrophilicity to the anthracite sample. It is important to note that the peak intensities corresponding to different functional groups do not necessarily correspond to the relative concentration of the functional group, as different functional groups have different molar extinction coefficients. For example, the C=O bond has a higher extinction coefficient than the N-H bond, and as a result, if C=O and N-H are present in equal amounts, the C=O peak on the IR spectrum would appear much more intense than that of N-H. Consequently, results from Figure 3-4 cannot be used to interpret the relative amounts of the functional groups in the anthracite sample.

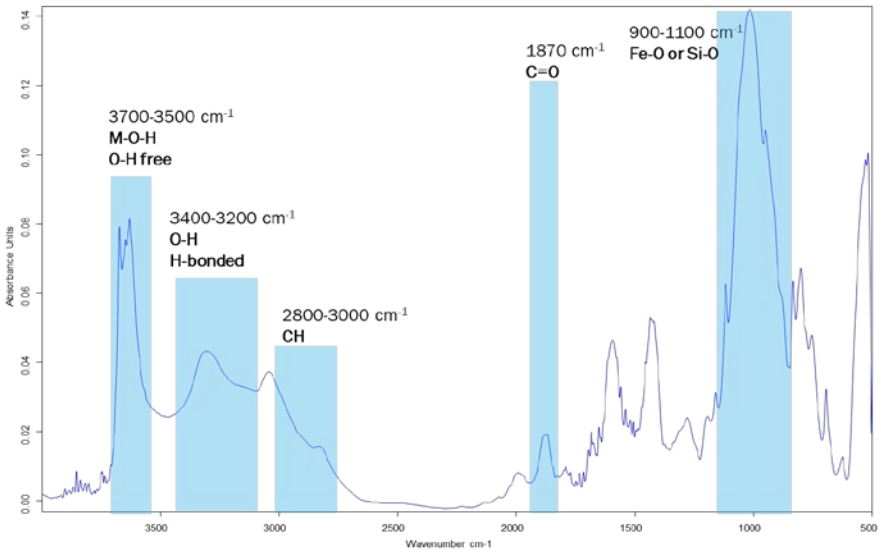

Figure 3-4. Diffuse reflectance infrared spectrum of KBr diluted anthracite sample.

After exposure of 5 grams of 1.18 mm to 2.36 mm anthracite to 20 µl UMO WAF, an anthracite flake was dried using dry N_2. The sample infrared spectrum of this post treatment sample was compared to that of pristine anthracite (Figure 3-5). The most evident difference is that most of the inorganic peaks observed in the pristine sample disappeared. Interestingly, a peak at 3435

was observed indicative of stretching mode of OH from water (vOH). The presence of water is confirmed by the presence of a peak at 1630. In addition to water, two sharp peaks appear at 2856 and 2924, which are consistent with CH stretches of hydrocarbons. These hydrocarbon and water peaks are likely from adsorbed WAF. The IR spectra presented do not show any evidence of chemical interaction between the anthracite and oil as no peak shifts were observed in the post treatment sample. Although several peaks disappeared, this can be attributed to physical washing of the anthracite sample.

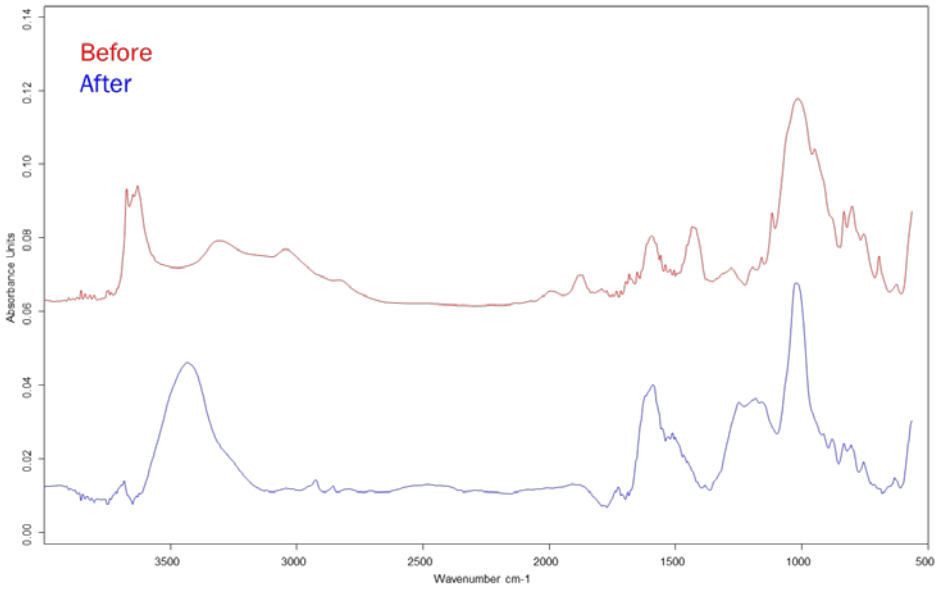

Figure 3-5. Diffuse reflectance infrared spectrum of anthracite sample before and after treating WAF.

Conclusions

Anthracite is a material with a high percentage of carbon in its composition, with a low surface area compared to other adsorbents such as activated carbon, a dominant pore size that appears to be independent from the particle size, and is defined as a poorly graded material based

on the sieve analysis performed on a commercial sample. However, isotherm adsorption experiments testing different loads of anthracite with different UMO concentrations must be run in order to build a comprehensive kinetic study and scientifically assess the ability of anthracite to adsorb these types of pollutants. FTIR data do not show evidence of chemical sorption, but there is evidence of WAF on the surface of the samples that were in contact with WAF, suggesting that physical sorption could be a sorption mechanism. Additional FTIR measurements of pristine samples and samples exposed to WAF must be performed in triplicate to get statistical data to support the findings. This is particularly important since the anthracite appears not to be completely homogeneous. In addition, a combination of FTIR and x-ray photoelectric spectroscopy (XPS) is recommended to confirm the precise surface molecular composition. Elemental analysis could also be utilized to simplify the interpretation of FTIR measurements.

Chapter 4

Batch experiment: used motor oil adsorption into anthracite

General description

In order to quantify the ability of anthracite to adsorb petrogenic hydrocarbons present in stormwater (used motor oil), two batch adsorption experiments were performed utilizing a variable mass for the adsorbent (anthracite) and maintaining the concentration of the pollutant (used motor oil) constant. WAF was prepared immediately before every sample run, in order to avoid chemical degradation of the oil or microbial activity that could change the final concentration after treatment. Filtration of samples was performed prior to liquid-to-liquid extraction with dichloromethane (DCM) which took place before samples were analyzed with GC-MS to quantify the relationship between the concentration at equilibrium and the mass adsorbed by anthracite. Freundlich isotherms were used to illustrate the adsorption mechanisms between anthracite and used motor oil over time. The anthracite used for the batch experiments was from the same bag utilized for material characterization.

Materials and methods

WAF preparation

Literature lacks on methods for producing WAF utilizing used automobile motor oil, thus, a method described by Singer (Singer et al., 2000) for crude oil was modified in order to produce the artificial stormwater for this experiment. An amount of 20 µl of Motul USA® 6100 Save-Lite™ SAE 5W-20 Synthetic Blend Motor Oil (changed after 3,000 miles of use in a Dodge Avenger,

2011) was transferred in a 100-µl glass syringe into a liter of deionized water (DW) in an amber wide mouth jar with PTFE lined cap. The contents of the jars were mixed for 24 hours on a shaking table at 175 rpm, preventing the formation of emulsions, and then were set to rest for 24 hours allowing equilibration and separation of the non-soluble components of oil. Based on crude oil literature, it is expected that approximately 10 % to 30 % of the initial used motor oil would be soluble in water (Singer et al., 2000). Considering motor oil density of 0.88 ± 0.01 g/ml (calculated for this experiment and consistent with literature), a 2 mg/l to 6 mg/l final WAF concentration was expected (aligned with the expected range for urban TPH stormwater pollution for trafficked area, see Table 2-3 (Schueler & Youngk, 2015)). After the equilibration time was reached, caps were removed allowing the volatile compounds trapped in the headspace to be released into a hood. A custom-made u-shape glass siphon (Figure 4-1), was utilized to transfer the WAF to clean jars. For every extraction, the first 80 ml were discarded, and approximately 200 ml were not extracted to avoid suctioning the supernatant. The final volume of WAF was projected to be between 650 ml and 700 ml.

In order to remove traces of organic materials that could interfere with the measurements, the glassware was rinsed with DCM between samples. After rinsing with DCM, the glassware was put in the oven at 550 °C for up to 8 hours to remove all traces of organic compounds.

Figure 4-1. U-shape glass siphon utilized for removing the WAF from amber mixing jars.

Anthracite mixing and filtration

Two isotherm treatments were utilized: 1 g and 5 g of anthracite were placed in 1-liter amber jars with PTFE caps, and were placed on a mechanical shaker at 250 RPM for 2, 6, 12, 24, and 48 hours in order to understand the sorption kinetics of UMO into anthracite (see Table 4-1). Samples were run in triplicates, a blank sample (DW + anthracite) and three WAF samples (no treatment) were run to perform comparison and a baseline to quantify UMO adsorption. The selection of these two treatments was made based on the small surface area that anthracite possess in comparison with other adsorbents commonly used, such as biochar or activated carbon. In order to quantify how much UMO would migrate into the WAF, 10, 20, 50, and 100 µl of UMO per liter of DW were prepared.

Table 4-1. Batch experiment samples

	Time					
Samples	**0 hrs.**	**3 hrs.**	**6 hrs.**	**12 hrs.**	**24 hrs.**	**48 hrs.**
WAF 10 µl UMO/l	1	-	-	-	-	1
WAF 20 µl UMO/l	1	-	-	-	-	1
WAF 50 µl UMO/l	1	-	-	-	-	-
WAF 100 µl UMO/l	1					
WAF 20 µl/l + 1-gram anthracite	1	-	-	-	-	-
WAF 20 µl/l + 5-gram anthracite	1	-	-	-	-	-
WAF 20 µl/l + 20-gram anthracite	1	-	-	-	-	-
DI water + 5 grams anthracite	1	-	1	-	1	-
WAF (20 µl /l) + 1-gram anthracite	-	3	3	3	3	3
WAF (20 µl /l) + 5-gram anthracite	-	3	3	3	3	3

After the shaking period, samples were filtered utilizing two 5.5 cm diameter binderless glass filter papers: Whatman® glass microfiber filter, Grade GF/D, 2.7 µm, and Starlitech ® glass microfiber filter Grade F, 0.7 µm. The addition of the filter with smallest pore size was considered after the first batch of trial samples was contaminated, presumably with anthracite fines. Filtered WAF was directed to clean and fired at 550 °C amber jar with PTFE lined cap. The filtration apparatus utilized is presented in Figure 4-2. A new clean and fired at 550 °C side arm flask was utilized for every different sample, and the same was done for the filtering cup and head when possible (smaller number of available items). In order to remove traces of organic materials that could interfere with the measurements, DCM was utilized to rinse the glassware that had to be utilized for multiple samples and was not fired at 550 °C.

Figure 4-2. Borosilicate glass filtration apparatus

Gas chromatography–mass spectrometry

Samples were analyzed on a Trace 1310 GC coupled to an ISQ LT single quad mass spectrometer (Thermo Scientific). The PTV inlet was operated in CT splitless mode and held at 320°C. Separation was achieved on a fused silica column (TG-1 MS, Thermo, USA; 30 m, 0.25 mm ID, 0.25µm film) with a constant He carrier flow rate of 1.5 ml/min using the following temperature program: 2 min hold at 60°C; 15°C/min to 330°C; 14 min hold at 320°C. The ISQ LT was operated in electron ionization mode with the source held at 230°C, scanning a mass range of 43-800 Da with a 0.2 s dwell time.

Used motor oil adsorption and percentage of removal

Since this project represents a preliminary experiment and was run on a tight budget, it aimed to collect data that will serve for designing a more comprehensive study, more replication

and further characterization of WAF will be needed for future experiments (see Chapter 6) . For this reason, the mass of used motor oil (UMO) removed by anthracite was quantified as follows:

$$Mass\ UMO_{Removed\ by\ anthracite} = Mass\ UMO_{WAF} - Mass\ UMO_{WAF\ after\ treatment} \quad (4)$$

$$\%\ UMO_{Removed} = \frac{(Mass\ UMO_{Removed\ by\ anthracite})}{Mass\ UMO_{WAF}} \times 100 \quad (5)$$

$Mass\ UMO_{WAF}$ refers to mass of UMO measured in WAF samples that where not treated with anthracite, and $Mass\ UMO_{WAF\ after\ treatment}$is the mass of UMO present in the samples after anthracite treatment. $\%\ UMO_{Removed\ by\ anthracite}$ is the percentage of UMO removed in reference to UMO present in WAF. Isotherms and kinetic studies were not run for this experiment due to financial reasons, and future studies modeling adsorption with the mentioned techniques will be based on the data collected during this experiment.

Liquid to liquid extraction of used motor oil

A separation funnel liquid-to-liquid extraction was used to extract the mass of UMO remaining in the solution of the filtered WAF. Due to economic limitations, different sizes of separation funnels were utilized, which defined the volume of sample to be extracted, approximately 250 ml, or 40 % of the original sample. Samples were shaken for up to two minutes prior to extractions to ensure homogeneity, poured into the glass funnels, and 25 ml of DCM were added. Three extractions were performed to increase the effectivity of the process and help recover all of the UMO present in the samples. DCM was later evaporated in a heated evaporator at 45 °C under a continuous flow of nitrogen gas (N_2). After completing the evaporation, the vials were

rinsed with up to 1.5 ml of DCM and transferred to 1.5 ml GC-MS vials to perform a second evaporation. Samples were stored at -20 °C until the moment of analysis.

Results

Used motor oil adsorption and percentage of removal

The first step for evaluating the variability of the process of making WAF was to quantify the mass of used motor oil present after performing the extraction. To achieve this goal, WAF with initial loadings of 10, 20, 50, and 100 µl of UMO per liter of DW were prepared.

Table 4-2. Mass of UMO migrating to WAF and percentage of original UMO migrated to WAF. Errors represent one standard deviation.

WAF (µl UMO/l)	**Mass UMO_{WAF} (mg)**	**% Error**	**% $UMO_{from\ initial\ to\ WAF}$**
10	6.41 ± 1.92	29.9	72.87
20	3.11 ± 0.77	24.7	17.66

As seen in Table 4-2 the mass of UMO present in the WAF for the 20 µl UMO/l (17.6 mg/l) sample is 17.66 % of the original oil dispensed into the DW, this number is between the expected values based on the literature. On the other hand, for the 10 µl UMO/l, the mass of UMO migrated to the WAF represents approximately 73 %, this number seems unrealistic, and maybe it is the result of contamination from the non-soluble layer of oil in the jar when of the WAF siphoning. It can also be observed that the percentage of error is higher for the 10 µl UMO/l sample. This along with the lack of accuracy obtained when loading 10 µl of oil with a 100 µl syringe, were the basis of deciding to use 20 µl of used motor oil per liter of DW as initial loading for the following experiments. Samples with initial oil load of 50 µl and 100 µl presented thick uneven layers of non-soluble oil on the surface after the 24-hour resting period, this could be due to a

possible saturation of the water or the formation of emulsions. For this reason, they were not extracted. More experiments will need to be performed to define the cause of this problem.

A control sample, "DW + anthracite" was run to quantify possible hydrocarbon compounds leached from the anthracite, but no hydrocarbon signature was identified in the GC-MS chromatogram.

The following step was to test three different masses of anthracite to evaluate their ability to remove UMO from the artificial stormwater. Three 1-liter samples containing 1, 5, and 20 grams of anthracite, loaded with 20 µl of UMO were prepared, extracted and analyzed. Figure 4-3 shows the effect of anthracite mass over relative abundance of UMO. Due to economic constraints, the internal standard (dodecane) was not utilized, and singlets were run. Nonetheless, the evidence suggests that there were not significant differences on UMO removal between 5 grams and 20 grams of anthracite. The results also indicate that 1 gram was less effective than 5 grams when removing UMO. Thus, treatments utilizing 1 gram and 5 grams of anthracite were chosen going forward.

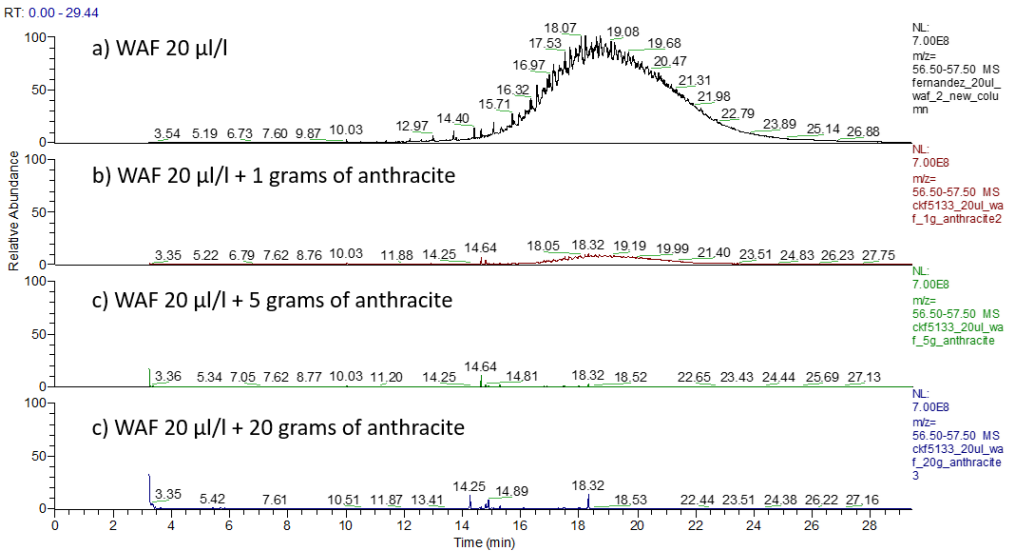

Figure 4-3. Effect of different masses of anthracite on the removal of UMO from WAF.

Following the procedures described in the materials and methods section of this chapter, triplicates of each sample were prepared, extracted and analyzed (see Table 4-1). The results are presented in Table 4-3 and Table 4-4. Unexpectedly, both treatments were equally effective, performing above 99 % UMO removal even at the lowest shaking time, 2 hours. This was not expected due to the characteristics of the material, lower surface area, a dominating pore size, and unclear indications (based on FTIR information) that anthracite could be as effective on removing petrogenic hydrocarbons from artificial stormwater.

Table 4-3. Mass and percentage of UMO removed by 1 gram of anthracite in batch experiment. Errors represent one standard deviation.

Time (hours)	$\boldsymbol{Mass\ UMO_{WAF\ after\ treatment}}$ **(mg)**	% $\boldsymbol{UMO_{Removed}}$
2	0.00095 ± 0.00017	99.97 ± 24.69
6	0.00800 ± 0.00209	99.74 ± 24.69
12	0.02506 ± 0.02084	99.19 ± 24.70
24	0.00637 ± 0.00444	99.79 ± 24.69
48	0.01355 ± 0.01217	99.56 ± 24.70

Table 4-4. Mass and percentage of UMO removed by 5 grams of anthracite in batch experiment. Errors represent one standard deviation.

Time (hours)	$\boldsymbol{Mass\ UMO_{WAF\ after\ treatment}}$ **(mg)**	% $\boldsymbol{UMO_{Removed}}$
2	0.01558 ± 0.00155	99.50 ± 24.70
6	0.00194 ± 0.00014	99.94± 24.69
12	0.00687 ± 0.00766	99.78± 24.69
24	0.00082 ± 0.00062	99.97± 24.69

Conclusions

The mass adsorption and percent removal of UMO by anthracite results were promising. It was observed that 99% UMO removal was achieved by 1 gram of anthracite in just 2 hours, providing evidence that anthracite is an excellent adsorbent for petrogenic hydrocarbons. Since no literature about anthracite as a filter media for petrogenic hydrocarbons was found to decide on the

shaking time, a conservative approach was utilized, and 2 hours was selected as the minimum shaking time. These results showed evidence that adsorption kinetics for this type of experiment are fast when using anthracite. This is solid evidence the shorter shaking times should be utilized for future experiments. However, the level of error for percent removal is around 25 %, suggesting that something is systematically incorrect in one or several steps of the procedure from making the WAF until analyzing it with GC-MS, and it needs to be investigated further to properly quantify the ability of anthracite to adsorb petrogenic hydrocarbons from stormwater.

Chapter 5

Filtration experiment

General description

This experiment was designed for testing anthracite in a filtration set-up with the objective of getting useful information for building a breakthrough curve for anthracite and UMO. After the results from the batch experiment were evaluated, it was decided to test anthracite in a non-favorable situation, where contact time was significantly smaller than in the previous experiment. Three different treatment configurations were utilized: a fast flow column; intermittent saturation for 5 minutes; and intermittent saturation for 15 minutes. The same concentration of UMO in the WAF, 20 ul/l, and the same mass of anthracite, 50 grams, were utilized for the three column tests. The anthracite and UMO utilized were the same as used in the batch experiment.

Materials and methods

WAF preparation, filtration, liquid-to-liquid extraction and GC-MS analysis

The same methods and materials utilized in Chapter 4 for WAF preparation, filtration, liquid-to-liquid extraction, and GC-MS analysis were utilized for this section. Samples were not run in triplicate due to economic reasons.

Colum set-up

Borosilicate glass columns (40 cm in length, 3 cm of internal diameter), equipped with PTFE O-rings and stainless steel outlet valve were utilized (see Figure 5-1). With the intention of distributing the flow evenly, and avoiding short-circuiting of the stormwater, 40 grams of glass beads were placed before the outlet and on top of the anthracite column. Anthracite (50 grams of d_2 diameter, see Chapter 2) utilized as filter media. The packed anthracite column, with a void volume of 35 ml, was washed utilizing 100 void volumes of water, aiming for elimination of fine particles. The ratio of column diameter to mean sediment grain diameter was 12. Columns were operated in a down flow direction.

Fast flow column: anthracite was saturated with DW, then WAF was added at the same rate that the outflow (138 ml/min) and collected under the column in a clean amber jar (the initial volume of DW was discarded). This was repeated for the six WAF samples. Due to economic reasons, only sample 1, 4, and 6 were analyzed.

Intermittent saturation columns: anthracite was saturated with WAF at 45 degrees by pouring the WAF against the column wall, thus, generating an artificial flooding from bottom to top displacing air trapped in the filter media. This was done for three consecutive WAF samples of 300 ml each.

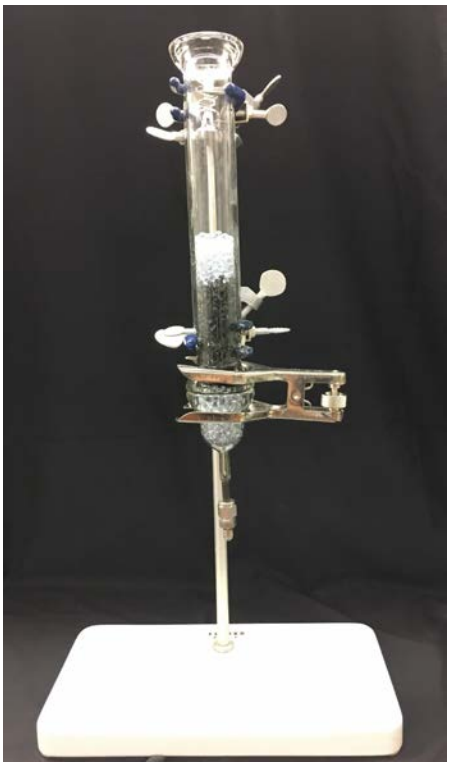

Figure 5-1. Columns utilized for filtration experiment

Results

The filtration experiment showed comparable results to those of the batch experiment: percentages of UMO removal were above 99 % for all of the cases, making it impossible to identify any trend that may explain removal mechanisms. The fast column treatment (Table 5-1) was expected to exhibit the lowest performance (there was not enough contact time for anthracite to act), followed by the 5 minute intermittent saturated column (Table 5-2). The 15-minute intermittent saturated column (Table 5-3) was expected to be the better at removing UMO from WAF. This was not observed and there was no significant difference between treatments. Triplicates were not run so statistical data was not utilized to explain discrepancies but based on

the standard deviation of the WAF triplicates, the differences observed in the decimal places for percent removal should not be consider as significant.

Table 5-1. Mass and percentage of UMO removed by fast column filled with anthracite.

Sample	$\boldsymbol{Mass\ UMO_{WAF\ after\ treatment}}$ **(mg)**	$\boldsymbol{UMO_{Loaded}}$ **(mg)**	% $\boldsymbol{UMO_{Removed}}$
1	0.0154	3.11	99.50
4	0.0133	12.43	99.89
6	0.0096	18.64	99.95

Table 5-2. Mass and percentage of UMO removed by 5-minute intermittent saturated column filled with anthracite.

Sample	$\boldsymbol{Mass\ UMO_{WAF\ after\ treatment}}$ **(mg)**	$\boldsymbol{UMO_{Loaded}}$ **(mg)**	% $\boldsymbol{UMO_{Removed}}$
1	0.0066	1.332	99.50
2	0.0057	5.327	99.89
3	0.0041	7.991	99.95

Table 5-3. Mass and percentage of UMO removed by 15-minute intermittent saturated column filled with anthracite.

Sample	$\boldsymbol{Mass\ UMO_{WAF\ after\ treatment}}$ **(mg)**	$\boldsymbol{UMO_{Loaded}}$ **(mg)**	% $\boldsymbol{UMO_{Removed}}$
1	0.001	1.332	99.93
2	0.008	2.664	99.71
3	0.002	3.995	99.94

Conclusions

Results for the column test suggest that anthracite is an excellent filter media for removing UMO from artificial stormwater, even with a short contact time like the one in the fast column treatment. For this reason, no differences could be found in the percentage of UMO removal for any of the treatments run in this chapter. In these experiments, 50 grams of anthracite where utilized for relatively small loads of UMO (when comparing the mass of anthracite to concentration ratio between this experiment and the batch experiment), and this could generate the false impression

that anthracite is performing extremely well. In addition, the short contact time proposed for the first treatment was thought as a way to compensate for this imbalance in the relationship between the mass of anthracite and mass of UMO. It is evident that more experiments need to be performed before considering anthracite as an excellent filter media option for removing petrogenic hydrocarbons from stormwater.

Chapter 6

International and Agricultural Development (INTAD)

Sharp population growth is a problem that every country and city is experiencing worldwide, and world population is expected to be 8.5 billion by 2030 (UN, 2019). Developed countries are creating plans for expanding and improving their infrastructure in order to ensure that their population will not be negatively impacted by food shortages, lack of affordable housing, and access to basic services such as sanitation and water access (Gogate & Rawal, 2012; UN, 2015). Stormwater management is a key service to take into consideration when planning the expansion of a city or town, and for reducing the impact of heavy rains that create floods. Developed countries are implementing green infrastructure for reducing the ratio between impervious to permeable surfaces to increase water percolation, thus reducing the impacts that heavy rains or melted snow can have in the daily dynamics of their populations. However, developing countries are not planning or engineering their growth, they are (in the best-case scenarios) building infrastructure to accommodate people and to provide basic services, sometimes forgetting about ecosystem services, not considering contingency plans for natural disasters or simply not providing services like sewer or stormwater piping (Goldenfum et al., 2007). This lack of planning have negative ramifications that affect all of the systems in a city or town negatively affecting quality of life and the environment. Population density is increasing dramatically in developed cities, where people from the farms arrive in order to get better access to the labor market. Thus, systems such as sewer, water and stormwater infrastructure are pushed to their limits or sometimes non-existing. Stormwater, if not handle properly, can accumulate in urban and semi-urban environment in the form of floods becoming a risk for human and fauna health (Goldenfum et al., 2007) being the perfect environment for disease vectors to spawn.

Developing cities, due to financial constraints, are more oriented to set up goals to control flow and quantity of stormwater, over quality, and for this reason, their drinking water supply is sometimes polluted when heavy storms carry contaminants from the surface into the water sources. Moreover, sewer waste is usually mixed with regular stormwater and this brings more complexity to the problem of maintaining stormwater infrastructure. Along with lack of planning, low budget and population increase, another common problem is the implementation of solutions that require high maintenance, such as detention basins, where sediments accumulate reducing the performance over time, leading to the complete failure of the system. In combination with the issues mentioned previously, political tensions due to conflict of interests for urban planning, along with difficulties to pass new legislation to manage stormwater, wastewater and allocate water rights contribute to generate a scenario in which solution are not being implemented (Goldenfum et al., 2007).

Small improvements in infrastructure for sewage and stormwater treatment can lead to significant increments in quality of life, for example a significant reduction in diarrheal cases in children (Moraes et al., 2004). In the same way, prevalence of mosquitos, vectors that transmit diseases such as dengue fever, zica, malaria and chikungunya, can be eradicated if accumulated waters are drained utilizing properly design infrastructure, thus reducing water bodies in which mosquitos can lay their eggs (Lines, 2002). Along with these two problems, management of solid and hazardous waste in developing communities contributes to make the problematic more complex, being of extreme importance to include this factor in designing solutions to manage stormwater and reduce the pollution that eventually reaches sources of drinking water (Armitage & Rooseboom, 2000). The combination of the factors mentioned above show how challenging could be to implement differentiated filter media to treat stormwater in developing countries, where the basic stormwater management infrastructure is not yet implemented.

Treatment alternatives such as sand filtration, multi-media filtration, constructed wetland and the utilization of specialty filter media to target specific contaminants is a luxury for countries

in which wastewater is not yet separated from stormwater (Gogate & Rawal, 2012; Moraes et al., 2004; Parkinson, 2003). Thus, findings of this work are not applicable to the currents efforts that are being implemented in developing countries; however, these findings have potential to be implemented in places where medium to high investment in wastewater management infrastructure is put in place.

Chapter 7

General conclusions and future work

Anthracite, when used in batch and column experiments, achieved percentages of UMO removal close to 99.9 %, this demonstrates the potential of this material for being used as a filter media for removing petrogenic hydrocarbons, despite the high particle size that was utilized for the experiments. In addition, no strong evidence of chemisorption was found, unveiling that the physisorption was the mechanism for removing the UMO. This suggests that smaller particle sizes could perform similarly or better considering that surface area was responsible for the adsorption of UMO into anthracite.

It is important to mention as a first comment, that the experiments presented in this document were run under severe economic constraints, not allowing the run of multiple trials in order to define the boundaries and capabilities of anthracite for removing UMO from stormwater. It was not possible to achieve replication of the samples to show statistical comparisons in all of the cases, making it difficult to identify trends or methodological error during sampling. It was not possible to acquire the custom made glassware necessary to prepare WAF in a precise and timely manner, and for this reason glassware had to be washed and fired in between sampling points, generating the perfect scenario for contamination of the glassware that could have affected the results, even under different treatments. Not enough separation funnels of 1 liter were available, and for this reason a fraction of the original WAF had to be extracted, something that is advised against by the literature. Quality control measures and strict protocols were applied in order to avoid the mentioned problems, but the possibility of losing some of the UMO on the walls of the jars, or maybe, not achieving full mix when shaking before using 33% of the sample for liquid-to-liquid extraction are high. This could explain the extremely high percentages of removal observed in all of the cases.

For all of the reasons mentioned above, it would be vital to run future experiments under the following recommendations:

- Utilize custom-made 1.25-liter borosilicate glass jars with a Teflon valve in the bottom to make WAF and extract without disturbing the upper non-soluble layer of oil. This will allow equal volumes of WAF and visual inspection of the supernatant (in order to avoid it), thus reducing the sampling error.
- WAF for UMO should be studied in more detail before utilizing one particular concentration for the experiments. In addition, the effect of shaking power (RMP), headspace volume in the jars, and temperature must be evaluated. It could be possible that the protocols utilized for crude oil are not necessarily accurate for UMO. In addition, the UMO/water saturation concentration must be known in order to avoid being close to that range when sampling.
- Several samples with different ratios of mass of anthracite to UMO concentration in WAF must be run prior to the principal experiment in order to define the boundaries of the experiment. This is key for understanding the point of saturation of the anthracite when performing UMO adsorption. Masses of anthracite from 0.05 grams to 5 grams are recommended in combination with concentrations of UMO in water from 10 µl/l to saturation concentration must be evaluated before the principal experiment.
- Columns utilized for filtration/column experiments must have the proper diameter to accommodate the particle size utilized. In addition, since more anthracite is utilized in this type of set-up, a way to make large volumes of WAF must be devised in order to achieve several bed volumes without introducing discrepancies of different batches of WAF.

- Column experiments must be performed controlling the volume of water with peristaltic pumps, and in order to do so, special tubing that is non-reactive and specially designed to not interact with hydrocarbons must be used. Such tubing is expensive, but this type of experiment cannot be performed with regular tubing.
- A more complex method for measuring mass of UMO after liquid-to-liquid extraction must be utilized, and more internal standards must be utilized in order to track the possible loss of mass in between steps. This was not done due to economic constraints.
- Along with the quantification of UMO, heavy metal analysis for samples involving UMO is necessary. Also identification of specific compounds such as some relevant PAH's must be performed in order to provide a comprehensive conclusion about anthracite as a filter media. Petrogenic hydrocarbon pollution in stormwater is more complex than just total mass of hydrocarbons present in the water.
- The effect of anthracite particle size must be evaluated when building the isotherms and the kinetic curves fitted to different models present in the literature.

Bibliography

Al-Anbari, R. H., Wootton, K. P., Durmanic, S., Deletic, A., & Fletcher, T. D. (2008). Evaluation of media for the adsorption of stormwater pollutants. *11th International Conference on Urban Drainage*, 1–9.

Alther, G. (2008). Cleaning wastewater: Removing oil from water with organoclays. *Filtration and Separation*, *45*(3), 22–24. https://doi.org/10.1016/S0015-1882(08)70057-0

Armitage, N., & Rooseboom, A. (2000). The removal of urban litter from stormwater conduits and streams: Paper 1 - The quantities involved and catchment litter management options. *Water SA*, *26*(2), 181–187.

Atlas, R. M., & Hazen, T. C. (2011). Oil biodegradation and bioremediation: A tale of the two worst spills in U.S. history. *Environmental Science and Technology*, *45*(16), 6709–6715. https://doi.org/10.1021/es2013227

BP statistical review of world energy. London, B. P. C. (2018). 67 th edition Contents is one of the most widely respected. *Statistical Review of World Energy*, 40.

Brabec, E., Schulte, S., & Richards, P. L. (2002). Impervious surfaces and water quality : A review of current literature and its implications for watershed planning impervious surfaces and water quality : A review of current literature and its implications. *Journal of Planning Literature*, *16*(MAY 2002), 499–514.

Brakstad, O. G., Daling, P. S., Faksness, L. G., Almås, I. K., Vang, S. H., Syslak, L., & Leirvik, F. (2014). Depletion and biodegradation of hydrocarbons in dispersions and emulsions of the Macondo 252 oil generated in an oil-on-seawater mesocosm flume basin. *Marine Pollution Bulletin*, *84*(1–2), 125–134. https://doi.org/10.1016/j.marpolbul.2014.05.027

Branch, S. S., Response, H. M., Division, A., & Oceanic, N. (1996). *Aerial Observations of Oil At Sea*. *April*.

Butler, D., & Davies, J. w. (2004). *Urban Drainage 2nd Edition*.

Clark, S. E., & Pitt, R. (2012). Targeting treatment technologies to address specific stormwater pollutants and numeric discharge limits. *Water Research*, *46*(20), 6715–6730. https://doi.org/10.1016/j.watres.2012.07.009

Denton, J. E., Ph, D., Mazur, L., & Salocks, C. (2006). Characterization of used oil in stormwater runoff in California. In *California Environmental Protection Agency Office of Environmental Health Hazard Assessment (OEHHA) Integrated Risk Assessment Branch (IRAB)* (Issue September).

Ellis, K., Berg, C., Caraco, D., Dresher, S., Hoffman, G., Keppler, B., LaRocco, M., & Turner, A. (2014). *Low Impact Development in Coastal South Carolina: A Planning and Design Guide*. 462. http://www.northinlet.sc.edu/LID/

Faksness, L., Altin, D., Nordtug, T., Daling, P. S., & Henrik, B. (2015). Chemical comparison and acute toxicity of water accommodated fraction (WAF) of source and field collected Macondo oils from the Deepwater Horizon spill. *Marine Pollution Bulletin*, *91*(1), 222–229. https://doi.org/10.1016/j.marpolbul.2014.12.002

Göbel, P., Dierkes, C., & Coldewey, W. G. (2007). *Storm water runoff concentration matrix for urban areas*. *91*, 26–42.

Gogate, N. G., & Rawal, P. M. (2012). Sustainable Stormwater Management in Developing and Developed Countries: A Review. *Proceedings of the International Conference on Advances in Design and Construction of Structures 2012*, 1–6. https://doi.org/02.ADCS.2012.1.515

Goldenfum, J. A., Tassi, R., Meller, A., Daniel, G., & Silveira, A. L. (2007). Challenges for the sustainable urban stormwater management in developing countries : from basic education to technical and institutional issues Défis pour la gestion durable des eaux pluviales urbaines dans les. *Novatech 2007*, 357–364.

Hilpert, M., & Breysse, P. N. (2014). In filtration and evaporation of small hydrocarbon spills at gas stations. *Journal of Contaminant Hydrology*, *170*, 39–52.

https://doi.org/10.1016/j.jconhyd.2014.08.004

IARC. (1988). Evaluation of carcinogenic risk to humans. Occupational exposures in petroleum refining; crude oil and major petroleum fuels. In *International Agency for Research on Cancer* (Vol. 45).

Johnson, P. R., Sun, N., & Elimelech, M. (1996). Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environmental Science and Technology*, *30*(11), 3284–3293.

Karlsson, K., Viklander, M., Scholes, L., & Revitt, M. (2010). Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks. *Journal of Hazardous Materials*, *178*(1–3), 612–618.

Kennedy, Allen, and Wilson, N. (2016). *The management of hydrocarbons in stormwater runoff: A literature review* (Issue October).

Kramer, G. (2014). Enhancing sustainable communities with green infrastructure a guide to help communities better manage stormwater while achieving other environmental , public health , social, and economic benefits. *Office of Sustainable Communities, US Environmental Protection Agency*, *October*, 2–4.

Lines, J. (2002). How not to grow mosquitoes in African towns. *Waterlines*, *20*(4), 16–18.

Massachusetts Department of Environmental Protection. (2008). Structural BMP Specifications for the Massachusetts Stormwater Handbook. *Stormwater Handbook Volume 2*, *2*.

McPhillips, L. E., & Matsler, A. M. (2018). Temporal evolution of green stormwater infrastructure strategies in three us cities. *Frontiers in Built Environment*, *4*(May), 1–14.

Moraes, L. R. S., Cancio, J. A., & Cairncross, S. (2004). Impact of drainage and sewerage on intestinal nematode infections in poor urban areas in Salvador, Brazil. *Transactions of the Royal Society of Tropical Medicine and Hygiene*, *98*(4), 197–204.

Mueller, S. A., R.Kim, B., E. Anderson, J., Gaslightwala, A., Szafranski, M. J., & A.Gaines, W.

(2003). Removal of oil and grease and chemical oxygen demand from oily automotive wastewater by adsorption after chemical de-emulsification. *American Society of Civil Engineers*, *7*(3), 156–162.

Ncube, P., Pidou, M., & Jarvis, P. (2018). The impact of filter bed depth and solids loading using a multimedia filter. *Separation Science and Technology (Philadelphia)*, *53*(14), 2249–2258.

Okiel, K., El-Sayed, M., & El-Kady, M. Y. (2011). Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. *Egyptian Journal of Petroleum*, *20*(2), 9–15.

Paerl, H. W., Gardner, W. S., Mccarthy, M. J., Peierls, B. L., & Wilhelm, S. W. (2014). *Algal blooms : Noteworthy nitrogen algal blooms : Proactive strategy ocean acidification foils chemical signals*. *346*(6206).

Parkinson, J. (2003). Drainage and stormwater management strategies for low-income urban communities. *Environment and Urbanization*, *15*(2), 115–126.

Pollino, C. A., & Holdway, D. A. (2002). Toxicity testing of crude oil and related compounds using early life stages of the crimson-spotted rainbowfish (Melanotaenia fluviatilis). *Ecotoxicology and Environmental Safety*, *52*(3), 180–189.

Rosenkrantz, R. T., Pollino, C. A., Nugegoda, D., & Baun, A. (2008). Toxicity of water and sediment from stormwater retarding basins to Hydra hexactinella. *Environmental Pollution*, *156*(3), 922–927.

Rowland, S. J., Scarlett, A., & Canty, M. N. (2005). Potential ecological effects of chemically dispersed and biodegraded oils. *Report RP*, *August 2015*.

Schueler, T., & Youngk, A. (2015). *Part 1 : Removal of Urban Toxic Contaminants in Stormwater BMPs*. 1–88.

Singer, M. M., Aurand, D., Bragin, G. E., Clark, J. R., Coelho, G. M., & Sowby, M. L. (2000). *Standardization of the Preparation and Quantitation of Water-accommodated Fractions of*

Petroleum for Toxicity Testing. *40*(11), 1007–1016.

Smil, V. (1999). Nitrogen in crop production: An account of global flows. *Global Biogeochemical Cycles*, *13*(2), 647–662.

UN. (2015). UN adopts new Global Goals, charting sustainable development for people and planet by 2030. *United Nations Department of Economic and Social Affairs*.

UN. (2019). World Population Prospects 2019. In *Department of Economic and Social Affairs. World Population Prospects 2019.* (Issue 141).

Weiner, E. (2000). National Recommended Water Quality Criteria. *Applications of Environmental Chemistry*.

Wendling, L. A., Douglas, G. B., Coleman, S., & Yuan, Z. (2013). Nutrient and dissolved organic carbon removal from natural waters using industrial by-products. *Science of the Total Environment*, *442*, 63–72.

West, M., Wenzel, M., Mpca, B. S., Flynn, L., Smith, T., Wenzel, M., Moore, A., & Gaffey, T. (2015). *Industrial Stormwater*. *April*.

WWAP. (2014). *The United Nations world water development report 2014: water and energy* (Vol. 1).

Yang, Y., & Lusk, M. G. (2018). Nutrients in urban stormwater runoff : Current state of the science and potential mitigation options. *Current Pollution Reports*, *April*, 112–127.