

## Water Contamination from Fire Events

A Major Qualifying Project Report submitted to the faculty of WORCESTER POLYTECHNIC INSTITUTE in partial fulfillment of the requirements for the Degree of Bachelor of Science

in

Civil Engineering, Environmental Engineering, and Mechanical Engineering Submitted by Luke Marcoux, Emily Mullin, and Dayna Tang

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## Abstract

As a product of climate change, fire events are becoming increasingly more common, causing concern for elevated levels of contaminants entering water distribution systems and threatening water sources used by the public. It is important to understand these types of contaminants and how they will affect populations in the future. This project aimed to improve upon a burn methodology, develop a chemical analysis procedure, and collect data on chemical contaminants released into water following fires. Spheres composed of sawdust and paraffin wax in combination with either high-density polyethylene, chemical resistant polyvinyl chloride, or neoprene rubber were burned and then suppressed in a water reservoir. Using Gas Chromatography-Mass Spectrometry, concentrations of benzene, naphthalene, ethylbenzene, anthracene, and pyrene were identified in several water samples. Benzene concentrations exceeding Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) for drinking water were detected in water samples, indicating a need for monitoring and possible treatment of water discharged after fires. Benzene concentrations were also compared to allowable daily discharges for oil companies in Massachusetts and were found to be above levels set in 2021. Concentrations of naphthalene, anthracene, pyrene, and ethylbenzene detected did not exceed EPA MCLs but are still concerning as they are known carcinogens.

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## **Capstone Design Statement**

When obtaining a degree from an accredited engineering program, a capstone design experience must be completed as mandated by the Accreditation Board for Engineering and Technology (ABET). ABET define engineering design as the process of creating systems, components, or processes that help meet a specific need and set of parameters. At Worcester Polytechnic Institute, this capstone design experience is part of the Major Qualifying Project (MQP), typically completed by students in their senior year of the program.

This MQP demonstrates the use of design processes for the development of spheres containing a mixture of sawdust, paraffin wax, and a chosen building material. When designing the burn medium, the design parameters were selected to facilitate rapid burns based on extensive research. Spheres were selected for the shape based on existing literature on the effects physical properties of a sphere burns including mass loss rates and the relationship between surface area and gas production. Sheets of neoprene rubber and high-density polyethylene (HDPE) alongside polyvinyl chloride (PVC) pipe were purchased and then powdered or diced using a coffee grinder and hand saw. This was to create similar particle sizes for each material before their addition to the spheres and resulting powders consisted of particulates from 0.5 to 1 mm. Each sphere was formed in a mold with a 2.5 in diameter. Varying masses of sawdust and building material were combined before heated paraffin wax was poured into the mold to bind the material together. Paraffin wax was selected as a binding agent due to its low melting point and high boiling point. It is also insoluble, making it easier to separate the wax from the water sample after each burn trial ended. Other adhesives were considered but many produced excess contaminants (those that were not of typical concern for water contamination) during chemical reactions that would be difficult to differentiate from the contaminants produced by the samples.

A burn system with an associated suppression method that includes mechanical components was designed. The burn system was created by suspending each sphere from a ring stand over a 500 mL water reservoir. The 500 mL water reservoir was placed on a scale to monitor mass loss as a function of time as the burn proceeded. A water reservoir was created to avoid the challenges with water application that came with designing a sprinkler system. Several suspension methods were designed and tested to determine feasibility and effectiveness. One design that was considered was using a wire to suspend the sphere from two points above the reservoir. However, a metal skewer was chosen as it was easier to insert the skewer into each sphere and let the sphere harden in the molds. In trial burns, the sphere was suspended vertically with the metal skewer, but this position allowed the paraffin wax to melt quickly, breaking apart the sphere and causing the sphere to fall and submerge itself before steady state burn conditions were achieved. Eventually, the team decided to suspend the sphere horizontally as this slowed the burning rate down and gave adequate time for steady state conditions.

Trial burns were conducted to determine ignition intervals and steady state burning durations for each sphere. A propane torch was used to ignite each sphere for a total of ten seconds, focusing the flame on the underside of the sphere. Ignition times had to be long enough to adequately ignite the entire sphere and allow the sphere to sustain the flame alone.

After collection and refrigeration of the water samples from each burn, solid contaminants were filtered using a 90 cm diameter glass fiber filter membrane with a 1.5-micro pore size in combination with a

vacuum pump. Filtration was necessary to avoid damaging the Gas Chromatograph-Mass Spectrometer machine during chemical analysis.

Finally, hypothetical parameters to design a granulated activated carbon (GAC) treatment method were established based on experimental Freundlich isotherm adsorption values. These parameters include the mass of carbon needed per liter of water treated, the bed volume of carbon needed, as well as other physical properties of a GAC column design. These parameters were established from a combination of extensive research and an established hypothetical empty bed contact time and assumed flow rates based on typical treatment plants and water temperatures.

## **Professional Licensure Statement**

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Several requirements must be met before an individual is able to acquire a PE. First, an individual must have four years of engineering experience satisfactory to the Board of Engineering or graduate from a four-year ABET-accredited engineering program. This provides the background to complete the next step of the process, taking and passing the Fundamentals of Engineering (FE) exam. After passing this exam, an individual becomes an Engineer in Training (EIT). EIT's must work under the direct supervision of a professional engineer for a minimum of four years to gain experience and exposure to engineering practices and skills. During this time, EITs will develop a comprehensive work portfolio to later submit to the PE board for approval for taking the PE exam. Each state has a licensure board and exams and required qualifications may differ between states. Once the licensure has been obtained, qualified PEs can sign, seal, and approve engineering plans. In Massachusetts, license renewal is required Biennially but the requirements for maintaining a PE license varies by state.

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## **Executive Summary**

### Introduction

In recent years, the United States has observed an increase in the number of wildfires and consequential property damage annually. The effects of this increase on public health and safety as well as the effects of water contamination from fire suppression is a relatively new field of study. This research is a continuation of previous work done by Worcester Polytechnic students in their 2021-2022 report *Contaminant Formation and Mobilization in Water Due to Fire Events*. The goal of this project was to expand on that research and complete the following objectives: Analyze and adapt the previous project's burn method to increase repeatability, quantity of data collected, and standardization of a procedure, develop a chemical analytical procedure for production and collection of samples for chemical analysis using gas chromatography and mass spectrometry, and collect data on aqueous chemical contaminations released following a fire.

#### Literature Review

The World Health Organization has indicated that fire events are increasing in frequency as climate change creates hotter and drier conditions around the world. As more fire events occur contamination in water sources has a more immediate, concerning impact on public health and safety. Most commonly, volatile organic compounds (VOCs) and polyaromatic hydrocarbons (PAHs) are found in water distribution systems, threatening water sources used by the public. Exposure to VOCs and PAHs, in both polluted air and water sources, can cause headaches, respiratory illness, fatigue, and even nerve damage. As more VOCs and PAHs are detected, communities will need to prepare for the treatment of these toxic contaminants.

These VOCs and PAHs come from materials commonly used in infrastructure and residential homes. This includes wood, cement, plastics such as polyvinyl chloride (PVC) and high-density polyethylene (HDPE), and elastomers. Each material poses different threats to water sources from the contaminations produced during the combustion process. More studies are being conducted to determine the short and long-term effects of the burning of these materials on water sources.

#### Methodology

Spheres with a 2.5" diameter were created using a mixture of sawdust, paraffin wax, and select building materials to simulate infrastructure burns. These select materials included HDPE, chemical resistant PVC, and neoprene rubber. A skewer was inserted into each sphere before being suspended with a ring stand over a 500 mL water reservoir. The reservoir was positioned on a mass balance load cell to continuously measure the mass lost by the sphere as the burn proceeded. Each sphere was burned individually before being extinguished in the reservoir once the burn had reached steady state.

The last batch created was altered to observe how the number of spheres influenced contaminant concentrations. A batch of spheres was made using a higher mass of neoprene rubber and a lower mass of sawdust and paraffin wax. Two spheres of this batch were then burned and extinguished in the same 500 mL reservoir. The samples from the burn of this batch were referred to as concentrated neoprene rubber

samples. Non-concentrated neoprene rubber samples were any samples produced from the original burn methodology.

All water samples were then collected and stored at 4°C for 72 to 120 hours. The samples were then filtered using vacuum filtration before being processed through solid phase extraction (SPE). The contaminants in the SPE cartridges were eluted using methylene chloride to produce the samples, which were then processed using GC-MS to quantify and identify contaminants. Benzene, *o*-xylene, pyrene, naphthalene, anthracene, and ethylbenzene were selected as indicator contaminants based on research surrounding contaminants of most concern found in water sources after wildfires and other fire events. Standard curves of peak area versus concentration were developed based on EPA 625 Semivolatile Calibration Mix and Supelco EPA 502/524 Volatiles Organic Calibration Mix standards. These standard curves were then used to estimate the concentrations of indicator contaminants in each water sample.

The same procedure was used to test both samples and standards in the GC-MS. The GC oven temperature was set to 40°C for four minutes, then increased to 290°C at a rate of 9°C/min and held at 290°C for six minutes. Each sample was sequenced for approximately 37 minutes. The GC-MS post-run was then set at 290°C for six minutes to allow a large window for any elution of compounds still present in the sample.

#### **Experimentation Results and Discussion**

Due to the molds used for sphere production, spheres were uniform in shape, meaning their surface areas were almost uniform. This allowed for constant mass loss as a function of time for spheres. Change in mass loss approached zero as the burn approached steady state, signaling when the sphere was submerged.

Thirteen samples of contaminated water were produced from multiple burns for chemical analysis. Naphthalene, anthracene, and pyrene were detected in all 13 samples. Benzene was detected in every sample except samples from the HDPE burns. Ethylbenzene was unique to the samples from the PVC burns. Pictured below in Figure 1 are the average concentrations of each detected indicator contaminant for the three material types.



Figure 1. Average concentrations of detected indicator contaminants by material type.

Benzene concentrations in the concentrated neoprene rubber samples exceeded the 0.5 ppb maximum contaminant level (MCL) set by the Environmental Protection Agency (EPA) for drinking water. The average anthracene and pyrene concentrations fell below the EPA's MCL of 100 ppb for PAHs in all samples but are concerning as they are considered carcinogens. Although the naphthalene concentrations in the concentrated neoprene rubber water did not violate MCLs, the increase in concentration in conjunction with the increased rubber mass is still cause for concern. Levels were also compared to NPDES permit discharge maximums allowed by the state for sample industries. Benzene concentrations in the samples from the concentrated neoprene rubber samples also exceeded these levels.

Outside of the indicator contaminants, several compounds were identified based on their probability (as assigned by the GC-MS) and feasibility of production in combustion reactions. One notable identified compound was 2-Nitrodiphenyamine, which was detected in samples from burns of neoprene rubber spheres. It is a common stabilizer for synthetic rubbers and may cause respiratory tract, skin, and eye irritation. The toxicity of this compound alongside several other compounds that have been identified by the mass spectrum library are of additional concern and should be monitored and examined in future work.

A hypothetical granulated activated carbon was designed using the Freundlich isotherm to model adsorption and experimental Freundlich coefficients from a study by Rineksa et al. in 2022. From these values, a cylindrical contactor with a height of 5.62 ft and diameter of 4.68 ft was designed to flow rate of 0.124 MGD, an empty bed contact time of 7.5 minutes, and a surface loading rate of 6 gpm/ft<sup>2</sup>. The contactor was designed to hypothetically require 0.637 mg of activated carbon (with the associated properties to the 2022 study) for every liter of water treated.

#### **Conclusions and Recommendations**

The adapted burn methodology and chemical analysis procedure helped increase repeatability of the experiment as well as amount of data points. The burning of sawdust and chosen building materials led to the increase of certain toxic and hazardous contaminants, including benzene and naphthalene, in produced water samples. When increasing the concentration of building materials in the burn sample, and consequently total mass of sawdust and building material burned, benzene concentration in samples exceeded the EPA's MCL. Anthracene and pyrene concentrations were not significantly affected by increases in mass of sawdust and neoprene rubber, indicating their presence may have been from another source.

It is recommended that further testing be done to determine how increasing mass of materials and time between sample collection and filtration influences concentration of contaminants. Future work should focus on testing other materials of concern in house fires, such as carpet and upholstery. Research should also be done into the feasibility of a burn chamber to decrease outside influences and help trap gaseous phase compounds during the burn experiment. Finally, it is recommended that further research be conducted on treatment and removal techniques through bench scale tests, such as activated carbon columns.

## **1.0 Introduction**

The United States has observed an average of 61,298 wildfires annually over the past ten years, leading to an impacted 7.4 million acres each year (United States Congress, 2022). These statistics, representing the United States alone, are staggering, and research by the World Health Organization (WHO) in 2022 has indicated that fire events are increasing in frequency as climate change creates hotter and drier conditions around the world. While the immediate consequences of wildfires, including civilian harm and property damage, are concerning, long-term effects can sometimes be a larger problem but may be neglected. These long-term effects include increased air pollution in surrounding areas, eye and respiratory tract irritation leading to more serious disorders, increase in stormwater runoff, among other consequences (Mendenhall, 2022).

Pollution in particular poses a threat to both the natural environment as well as human and animal health. Due to the scale of wildfires, large amounts of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and particulate matter are released into the atmosphere during and after fire events (World Health Organization, 2022). Studying the effects on drinking water has become increasingly more common due to serious contamination concerns.

From 2015-2019, US fire departments reported an estimated average of 346,800 home structure fires, 2,620 civilian deaths, 11,070 civilian injuries, and \$7.3 billion in property damage each year. These fires are commonly started due to "cooking, heating, electrical distribution and lighting equipment, intentional fire setting, and smoking materials" (Ahrens et al., 2021). Examining residential fires produces a unique perspective on fire contamination as the materials that burn, the duration of the fire, and the methods of sequestration differ greatly from wildfires. Subsequently, these variables can be used to study the contamination that occurs in water runoff and how this affects water distribution systems.

This project was a continuation upon the work done by the 2021-2022 Worcester Polytechnic Institute (WPI) Major Qualifying Project (MQP) team, whose work is detailed in the report *Contaminant Formation and Mobilization in Water Due to Fire Events*. The use of fire events in this project refers to both wildfires as well as industrial and residential fires. The goal of this project was to expand upon the research and experimentation done by the previous team and to further the data collected on the "contribution of thermal degradation of plastics and household materials to environmental and water contamination, as a means to promote community and environmental resilience" (Cristiano et al., 2022). To reach this goal, the following three objectives were identified:

- 1. Analyze and adapt the previous project's burn method to increase repeatability, quantity of data collected, and standardization of a procedure,
- 2. Develop a chemical analytical procedure for production and collection of samples for chemical analysis using gas chromatography mass spectrometry,
- 3. Collect data on aqueous chemical contaminants released following a fire.

To achieve these objectives procedures were developed involving the creation and burn of spheres containing a mixture of sawdust, paraffin wax, and select materials likely to be burned in a structural fire. Subsequent chemical analysis of contaminants resulting from these fire events enabled the determination of potential aqueous contamination.

## 2.0 Literature Review

To examine the long-term effects fires have on the environment as well as public health and safety, it is important to first contextualize the increasing number of fire events and the concerns surrounding them. This involves developing an understanding of water contamination from fire events and the long-term effects they may present. Although wildfires are not the focus of this project, it is still important to understand their effects on infrastructure, specifically water lines, to comprehend the danger associated with fire event runoff entering distribution systems and natural water sources. Research conducted was centered around the United States and trends seen within the country's infrastructure and regulations.

## 2.1 Increasing Trends in Fire Events

The western United States has witnessed an increase in wildfires during the last two decades, which researchers partly contribute to the severe consequences of climate change. Researchers predict that frequency, extent, and severity of wildfires will all increase alongside these conditions as well as decreased water availability during the peak summer months, which can be credited to snow melting earlier in the year. Wildfire spread depends on several factors, such as temperature and soil moisture. The extent of area burned during wildfires has also increased since the 1980s, coinciding with the highest average temperatures on record throughout the US (Environmental Protection Agency [EPA], 2022). As temperatures rise globally, there will be more extensive droughts and low moisture atmospheric conditions, creating perfect dry conditions for a wildfire to ignite and spread to devastating extents (EPA, 2022).

#### 2.2 Environmental Impact

Fire events can contaminate the environment in a variety of ways, including fire plume, water runoff containing toxic chemicals and products, and the discharge of burned material. The effects from wildfires and structural fires overlap in several ways when examining their impact on infrastructure as well as the different ways they contaminate drinking water sources.

#### 2.2.1 Environmental Impact from Wildfires

In 2022, there were a documented 68,988 wildfires that burned 7,577,183 acres (National Interagency Fire Center [NIFC], 2022). A modern-day concern over the environmental impact can be seen in the aftermaths of the Paradise, California wildfire in 2018. After the wildfire, volatile organic compounds (VOCs) were found in the town's water supplies at concentrations above the Environmental Protection Agency's (EPA) allowable limits (Meadows, 2022). This included benzene, naphthalene, toluene, alongside styrene and xylenes. VOCs were found in the service lines but not in the water at the treatment plant or in the main lines (Meadows, 2022). The majority of the town's service lines, and water meters are made of polyvinyl chloride (PVC) and high-density polyethylene (HDPE). Service lines and water meters are typically located near or above the ground, making them more vulnerable to heat degradation than deeper main lines (Meadows, 2022). This contamination was investigated further, and several explanations were developed, such as burning plastic pipes releasing VOCs into water or smoke and soot products entering the distribution system after fires (American Chemical Society [ACS], 2022).

### 2.2.2 Environmental Impact from Structural Fires

A report released by the National Fire Protection Association (NFPA) in 2021 described statistics for structural fires that occurred from 2015 to 2019 in the United States. It was found that 26% of fires during this period occurred in homes, causing 75% of civilian fire deaths and 72% of all reported injuries caused by home fires (National Fire Protection Association [NFPA], 2021). An estimated average of 346,800 home structure fires occurred during this five-year period with an annual average of 2,620 civil deaths and 11,070 civilian fire injuries (NFPA, 2021). This means an estimated \$7.3 billion in direct property damage was caused by home fires (NFPA, 2021).

The 2021 statistics were released by the NFPA that detail the amount of damage, measured in different ways, caused by structural fires. 2021 saw an estimated 1.35 million fires in the United States that required a local fire department response, with 36% of those fires occurring in or on structures (NFPA, 2021). These fires include residential fires, vehicle fires, and wildland fires (NFPA, 2021).

## 2.3 Community Health and Environment Risk

The lasting effects of wildfires and residential fires on the environment can be seen across the country. Fire events can cause threats to water supplies specifically, as ash and other contaminants settle on bodies of water such as streams, lakes, and reservoirs. Wildfires also can decrease air quality in an area, especially during the time immediately following the event. Within communities, contamination from fire events has a more immediate impact upon public health and safety.

VOCs present several dangers for community health. When present in polluted air, they may cause headaches, respiratory illness, fatigue, and even nerve damage (de Mello et al., 2022). There are increased concerns that long-term exposure to these contaminants may increase the risk of cancer. One extremely toxic VOC is benzene ( $C_6H_6$ ). Benzene is extremely volatile and soluble and can easily be introduced into water bodies. It commonly comes directly from the petrochemical industry but can also leach into groundwater from underground oil storage tank leaks and spills from oil wells (de Mello et al., 2022). Benzene is only one contaminant of many that are of concern in water discharged following fire-fighting activities.

## 2.3.1 Common Building Materials and Contaminant Risks

Aside from the materials used in piping infrastructure, there are a variety of materials in households that are commonplace across the United States that pose a serious concern in the event of a burn. Some of the most common materials used in construction in the United States include wood, cement, aggregates, metals, bricks, concrete, and clay. Wood tends to be beneficial due to its flexibility under loads and stress as well as its ability to maintain strength during bending (The Constructor, 2021).

Plastics include both synthetic or semi-synthetic organic condensation or polymerization products and depending on their structures, they can vary in heat tolerance, hardness, resiliency. The United States construction industry utilizes more than 10 billion pounds of plastics each year (Allen & Iano, 2008). Elastomers (synthetic rubber compounds) are a type of polymer with elastic properties that are typically made from organic molecules found in oil, natural gas, and cold. Modifiers are often added to different plastics to change their properties and reduce costs. Examples include plasticizers, which can influence flexibility and softness, fillers, helping decrease expenses and increase toughness and resistance to high

temperatures, and stabilizers. They are also used to help materials resist deterioration to light, heat, and oxygen. Flame retarders, which become important in the scope of this project, are often applied to materials that are intended for interior use (Allen & Iano, 2008).

PVC, which was introduced earlier, can come in its plastic form, as flexible rubberlike sheets, or a rigid, solid form. It is often used for coatings, sealants, insulating foams, and adhesives. Neoprene rubber is typically used for gaskets and waterproofing. Polyethylene is tough, flexible, and impermeable. It's utilized in vapor retarders, moisture barriers, piping, and tarps. The presence of these plastics alongside their many additives and various uses in residential construction during the last 50 years has become cause for concern as more is learned about their effects on human health through different contaminant pathways.

#### 2.3.2 Piping Infrastructure

Sink, toilet, and shower drain lines in the United States are commonly made of polyvinyl chloride (PVC) due to the material's ability to protect water from rust and corrosion. Due to its durability, it can also be used for a house's main water supply line. However, there are growing concerns about PVC's toxicity and the possible threat it presents to drinking water by releasing polyvinyl chloride chemicals, leading to respiratory and reproductive issues if consumed over longer periods (New England Institute of Technology [NEIT], 2021). PEX, sometimes referred to as cross-linked polyethylene, is an affordable alternative to PVC and has many of the same characteristics. PEX is also flexible yet strong enough to withstand average water pressures. Another common material seen in the United States is acrylonitrile butadiene styrene (ABS). ABS is useful in vent and drain lines because it is resilient to cold temperatures. However, it warps when exposed to sunlight and tends to be noisy when water runs through it (NEIT, 2021). Copper pipes tend to be a more attractive alternative as they can last over 50 years and are corrosion resistant. Copper can handle high water pressures and a range of temperatures. Copper pipes also tend to be the most expensive type, causing contractors to consider other options. Cast iron and galvanized steel pipes are seen throughout the United States but more commonly in homes built during the early 20th century. They are known for their durability, heat resistance, and ability to reduce the sound of moving water, which is why they are typically used in sewer pipes and drainage systems. However, cast iron and galvanized steel pipes are commonly replaced by copper or PEX pipes as they are prone to rust and corrosion (NEIT, 2021).

High density polyethylene (HDPE) is often used to transport hazardous wastes, slurry, and stormwater. HDPE is used in water mains, high-pressure pipelines, gas mains, sewer mains, fire system supply lines, among other pipe systems (PSC Construction, 2022). HDPE is advantageous as it is both flexible and lightweight, and it is resistant to acidic chemicals at lower temperatures. Unfortunately, HDPE is flammable, vulnerable to stress cracking, and has high thermal expansion, making it unfavorable in certain conditions (PSC Construction, 2022). PVC and PEX are typically favored when building underground water lines as they can withstand higher pressures and can be buried below the surface of the Earth. This is especially important to note when considering the types of materials that are subject to thermal degradation during fire events and how these materials contribute to contaminants found in distribution systems.

#### 2.4 Physical and Chemical Properties During Fire Events

The physical and chemical processes affecting the materials as they burn must be better understood to anticipate the outcome of each burn. This includes factors such as the mass transfer between contaminants and materials during the burn and the physics of the distribution of a burning sphere.

#### 2.4.1 Mass Transfer and Mobilization

The materials subjected to fire events produce chemical contaminants due to the reaction between the burn and the material, thus creating hazardous compounds. To analyze contaminants produced from burns it is important to understand the flashpoint, or the lowest possible temperature at which vapors above a volatile combustible substance ignite when exposed to fire. The flashpoints can be seen in Table 1 below for the materials selected by the team for analysis.

Material	Flashpoint (°C)
Neoprene Rubber	200
PVC Pipe	390
HDPE	343

Table 1: Flashpoint of materials tested.

Mass-transfer phenomena refers to the net movement of mass from one location–usually meaning stream, phase, fraction, or component–to another. A multitude of materials are capable of igniting and can burn or fuel flames, and the chemical release, due to various mass-transfer phenomena, may be mobilized. Complete combustion, however, does not always occur in these burns, meaning that the reaction does not combust into mainly H<sub>2</sub>O and CO<sub>2</sub> (Ghasemzadeh et al., 2018). During complete combustion, other byproducts may be produced depending on the composition of materials burned. During incomplete combustion, hazardous organic and inorganic compounds may be produced, leading to contamination of water sources. These include heavy metals, particulates, and polycyclic aromatic hydrocarbons (PAHs) (Ghasemzadeh et al., 2018).

#### 2.4.2 Mass Loss Rate

Mass loss rate, or the burning rate (BR), is defined in Equation 1 where m is the instantaneous value of the mass of the fuel and t represents time.

$$BR = \left|\frac{dm}{dt}\right| \tag{Equation 1}$$

To use this equation, the mass of the fuel is monitored throughout the combustion process. However, the combustion process is not typically constant throughout time *t*. In some combustion reactions, there may be a state of constant mass loss rate for a period, which would appear linear in a graph of dm (m/m<sub>0</sub>) versus time (between t<sub>1</sub> and t<sub>2</sub> in Figure 2). The slope of this line would be equivalent to the mass loss rate during that time.



Figure 2. A mass loss curve with a period of constant mass loss rate (Viegas et al., 2018).

However, Figure 3 below shows a situation where there is not a constant mass loss rate. At  $t_3$ , the second derivative of Equation 1 is equal to 0, indicating a maximum mass loss ratio. The maximum mass loss ratio can be used to represent the *BR* of the combustion process (Viegas et al., 2018). Sometimes, a global or overall *BR* can be estimated using the difference between the final and initial values of mass ( $m_f$  and  $m_0$ ) and time of the combustion process ( $t_f$ ). The global or overall *BR* is used for processes where the change in mass cannot be monitored or determined for the duration of the combustion reaction.



*Figure 3.* A mass loss curve with an inflection point corresponding to the maximum mass loss rate value (Viegas et al., 2018)

A 2020 study by Isaacson et al. examined drinking water contamination that occurred due to thermal degradation of plastics, specifically plastics that are typically seen in pipes used for drainage pipes and water distribution systems and the implications for wildfire and structure fire responses. The study looked at how plastics such as PEX, HDPE, PP, PVC contributed to VOCs found in water distribution systems. The experiment exposed plastic drinking water pipes to a range of temperatures (200°C to 400°C) in a muffle furnace and subsequently submerged the plastics in water or an organic solvent. The experiment determined mass loss rate through recording the mass of the crucible and the plastic pipe both before degradation and after the pipe had cooled, then utilized the difference per time (Isaacson et al., 2020). GC-MS was then used for chemical analysis. The study found that benzene and toluene had leached into

water at higher concentrations than ethylbenzene and xylene. These leaching rates were affected by compound production, water solubility, air volatilization, among other variables.

Isaacson et al.'s study used only one of several ways to determine the mass loss rate. Another way to determine mass loss rate is to monitor the mass of an object throughout the entire duration of the combustion process. Within the limitations of this laboratory, this could be done by using an analytical balance connected to software that graphs the mass of the burning object versus time. A constant mass loss rate (or a characteristic mass loss rate) is important to establish that the combustion process has reached a steady state burning phase, which occurs when there is no change in mass loss rate for a period. The steady-state burning phase is also referred to as the free-burning phase and is characterized by when there is sufficient oxygen and fuel for the fire to grow and spread (Fire Department City of New York [FDNY], 2017).

## 2.4.3 Spherical Burns

The procedure followed for the burn portion of this research involved the burning of a sphere. As such, it is crucial to understand the physical properties of the sphere throughout the burn. Before the burn, the geometrical properties of the sphere enable the determination of the ratio of the surface area to the volume of the sphere to be the quotient of three and the radius, a very low ratio (Tamassy, 1969). Thus, the expected rate of mass transfer for the burn of the sphere is lower than that of other configurations. Therefore, the team chose to utilize a sphere design in place of the crib construction used in the previous project.

There is existing literature on the properties of a sphere during combustion. As combustion first occurs, assuming the mixture of the sphere is uniform, the surface area changes very slightly as the gasses released by the wood during combustion are either released or are trapped inside without affecting the sphere's physical structure (FDNY, 2017). Due to this, measuring mass, not surface area, as a function of time theoretically would produce the most accurate results (FDNY, 2017).

#### 2.5 National and State Regulations

First created in 1972 under the Clean Water Act, the National Pollutant Discharge Elimination System (NPDES) exists to regulate and address water pollution in the United States. Non-Stormwater Discharge is categorized as any material discharged to water systems that is not solely from stormwater.

Fire water runoff (referred to as "Discharges from fire-fighting activities") falls under the allowable nonstormwater discharges outlined in the "NPDES General Permit for Stormwater Discharges From Construction Activities". The Municipal Separate Storm Sewer System (MS4) General Permit allows cities and counties to discharge the stormwater collected to be discharged to water bodies located in the United States (National Association of Clean Water Agencies [NACWA], 2018).

Allowable discharges can vary between circumstances and certain activities do require monitoring and clean-up of water contamination from fire suppression. The NFPA has a published list of codes and standards to help decrease the effects fire as well as other risks. One specific code, the NFPA 15: Standard for Water Spray Fixed Systems for Fire Protection, contains several standards for water discharge from water spray systems (NFPA, 2022). This includes controlling or containing water

discharge when flammable or combustible liquids are present as well as treating water to standards set by local regulations after it has been used to prevent the spread of fire in applicable situations. However, water spray systems are not required to be controlled or contained when damage to nearby water sources is expected to be minimal (NFPA, 2022). Therefore, the responsibility for treatment of contaminated water from fire runoff is often the responsibility of fire professionals.

While the existing regulations contribute to the lessening of the effects of water contamination from fire events, there are still several areas in which they are lacking. One of these areas is the regulation of building materials for future site developments based on the contaminants produced from burning. In relation to this, there is lacking regulation for site development materials based on the predisposition to fire events in the area.

#### 2.5.1 Suggested Preventative Measures and Possible Solutions

Most home fires and fire casualties result from five causes: cooking, heating, electrical distribution and lighting equipment, intentional fire setting, and smoking materials (NFPA, 2021). Existing studies and research conducted on the effects of fire contamination are invaluable to this topic. In context of the shortcomings in national and state regulations, these research studies can be used and analyzed to suggest measures to be taken to minimize the effect of fire pollution in water systems.

In a study conducted in 2021, VOCs in water were identified and compared to VOCs emitted from burned pipes and burned building materials (Solomon et al., 2021). The results of this analysis showed that the water was contaminated by plastic pipes and smoke (Solomon et al., 2021). This study suggested possible remedies to prevent pollution. The first is burying service lines deeper to insulate them from heat, thus inhibiting the chance of a fire (Solomon et al., 2021). Also, researchers recommended developing a network of isolation valves to help prevent contaminants from spreading throughout a system in case of fire (Solomon et al., 2021). One suggested innovation was creating sensors that detect when pipes reach threshold temperatures for releasing VOCs (Solomon et al., 2021).

As more communities detect VOCs in their water post-fire events, the need for emerging methods to remove these contaminants in water treatment plants becomes more apparent. Adsorption technologies have proven particularly effective in removing benzene and similar VOCs. An activated carbon filter cartridge is usually favored by water treatment facilities because as the carbon-based VOCs in the contaminated water passes through, they will adsorb to the filter. Adsorption is when a gas or liquid amasses on the surface of a liquid or solid substrate (Water Technology, 2016). Activated carbon is an attractive option for an adsorbent due to its high porosity, low cost, and accessibility. Contaminants can stick to the surface of the carbon atoms due to the Van der Waal forces and induced dipole interactions, causing the molecules to be attracted to each other. Once the molecules stick together, they can precipitate out of solution through the adsorption spaces in the carbon (Water Technology, 2016).

In a 2022 study performed by de Mello et al., removal of benzene from diluted water was tested using a combination of adsorption, desorption with methanol, and electrochemical treatment. These methods are favorable due to their simplicity, relatively low cost, and energy efficiency. The study found that methanol is a very good solvent for desorption of benzene. Granulated activated carbon (GAC) can be received and reused after the contaminant is desorbed by heating. After desorption with methanol, a solution with a high concentration of the pollutant is obtained (de Mello et al., 2022).

#### 2.6 Selection of Contaminants

Compounds were selected as indicator contaminants utilizing standards from the EPA's National Primary Drinking Water Regulations, the legally enforceable primary standards and treatment techniques that apply to public water systems and select contaminants (EPA, 2023).

This list of contaminants was then compared to contaminants commonly found after wildfires. A study by the United States Geological Survey (USGS) found that downstream water sources were found to produce higher nitrate, organic carbon, and sediment levels following wildfires (Water Resources Mission Area, 2019). Based on this information, the compounds selected to be indicators were benzene, ethylbenzene, *o*-xylene, which are polyaromatic hydrocarbons (PAHs), and pyrene, naphthalene, and anthracene, which are aromatic hydrocarbons.

The first indicator contaminant, benzene ( $C_6H_6$ ), is the simplest organic, aromatic hydrocarbon and parent compound of numerous important aromatic compounds (Carey, 2023). Therefore, the presence of benzene can indicate the presence of other aromatic compounds. Sources of benzene can be natural, such as volcanoes and forest fires, as well as caused by human production including crude oil, gasoline, and cigarette smoke (Center of Disease Control [CDC], 2018). Some industries also use benzene to make other chemicals which are then used to produce synthetic materials including plastics and resins.

Ethylbenzene ( $C_6H_5C_2H_5$ ) is another aromatic hydrocarbon composed of a benzene ring linked to an ethyl group (National Center for Biotechnology Information [NCBI], 2023). This compound is often found in products including coal tar and petroleum, as well as being used in manufactured products such as paints (Agency for Toxic Substances and Disease Registry [ATSDR], 2021). It is used primarily to make another chemical, styrene (NCBI, 2023). Thus, the presence of ethylbenzene can be indicative of the presence of styrene.

The compound *o*-xylene ( $C_6H_4(CH_3)_2$ ) is another aromatic hydrocarbon based on benzene with two methyl substituents and is a xylene substituted by methyl groups (NCBI, 2023). It is often affiliated with xylene, phthalic anhydride, and p-xylene, as such can be indicative of their presence (NCBI, 2023). Xylene is used mainly as a solvent and in the printing, rubber, and leather industries (NCBI, 2023).

The first polyaromatic hydrocarbon, anthracene ( $(C_6H_4CH)_2$ ), is also referred to as paranaphthalene or green oil. It is a solid PAH consisting of three benzene rings derived from coal-tar (NCBI, 2023). Anthracene is identified in surface and drinking water, ambient air, exhaust emissions, smoke of cigarettes and cigars, and in smoked foods and edible aquatic organisms (NCBI, 2023). It is used in wood preservatives, research, and smoke screens, but most people are exposed when they breathe in contaminated air (Minnesota Department of Health, 2019).

Pyrene ( $C_{16}H_{10}$ ) is a parent class of polycyclic aromatic hydrocarbons containing four fused rings (NCBI, 2023). It forms during incomplete combustion of organic compounds, and is used to make dyes, plastics, and pesticides (NCBI, 2023). One of the most common ways pyrene can enter the body is through breathing contaminated air. It can also get into the lungs when working in an environment with pyrene and other PAHs.

Naphthalene  $(C_{10}H_8)$  is a white, volatile, solid polycyclic hydrocarbon. It is obtained from the production of coal tar and petroleum and is primarily used to manufacture phthalic anhydride (NCBI, 2023). It is also

used in moth repellents. When a person is exposed to naphthalene, they may experience hemolytic anemia, liver and neurological damage, cataracts, and retinal hemorrhage (NCBI, 2023).

### 2.7 Worcester Polytechnic Institute Master Qualifying Project Research

This project is a continuation of the research conducted by a team of WPI students in 2021-2022 in their report titled *Contaminant Formation and Mobilization in Water Due to Fire Event*. In their project, analysis was performed on the mobilization of contaminants as a result of structure fire events. The team identified common materials in fire events, then developed a burn method for the identified materials. The procedure involved constructing cribs made of different combinations of white pine wood, high-density polyethylene, chemical resistant polyvinyl chloride, and neoprene rubber, which were burned and then suppressed with water.

The team then developed a chemical analysis method to identify contaminants and their concentrations within collected water samples from the burns using GC-MS. Benzene, pyrene, and naphthalene were detected in all their samples while *o*-xylene was only present in samples from the burn of a neoprene rubber crib. Utilizing combined influence from the previous project as well as research from existing experimental papers, a burn methodology was produced that emphasized repeatability and simplicity.

## 3.0 Methodology

Alterations were made to the previous methodology to adapt the burn method and develop a more consistent suppression application. After careful review of the previous project's crib construction and sprinkler system design, a new burn procedure was developed. Spheres containing a mixture of sawdust, paraffin wax, and selected contaminant materials were created, then burned before being extinguished by a water reservoir. The chemical analysis method was maintained due to the ability of gas chromatography and mass spectrometry to resolve complex samples containing hundreds of compounds as well as its application to volatile contaminants.

## 3.1 Procedural Setup

Before conducting the burn procedure, the spheres were produced in batches for each material. Once each material was selected, the material was procured and then refined to better fit the needs for test sphere production.

## 3.1.1 Selection of Materials

The previous MQP tested HDPE, chemical resistant PVC, and neoprene rubber. By keeping the materials consistent, the results may still be compared even with the change in burn methodology. These materials were selected due to their present abundance in residential construction projects and the limited research conducted involving their potential pollution post pyre phenomenon (Valavandis, 2007).

Paraffin wax was chosen as an adhesive agent to bind the test materials together due to its petroleum base, low melting point of 37°C and high boiling point of 370°C (Chemical Book, 2017). Alternate adhesives pose the concern of being either non-flammable or producing unnecessary toxic chemical byproducts which would otherwise not be present in the samples. The wax's insolubility separates the material from the collected water sample, simplifying the chemical analysis by reducing the number of chemical agents present. In the context of this project, paraffin wax's properties meet all requirements without posing any unnecessary risks to the samples.

For this procedure, a large volume of sawdust was required for the creation of all the spheres. The white pine wood planks used for the previous iteration of this research was substituted with already ground sawdust from the facilities of a local packaging group. This sawdust was selected due its low cost and ability to be collected and transported to the lab quickly, eliminating the time constraint of re-ordering and delivering saw dust.

## 3.1.2 Processing Materials

The first step in the creation of test spheres was the refinement of materials from their as-received form. Thin sheets of polyvinyl chloride and high-density polyethylene were obtained. Materials purchased from a hardware store or online supplier were appropriately trimmed using cutting tools before grounding the materials in the appropriate machine.

The procedure for the refinement of each material differed depending on the physical properties. These methods can be seen in Table 2 below.

Material	Procedure
Sawdust (Test Procedure)	Powdered
Neoprene Rubber	Cut
Neoprene Rubber #2	Shredded
HDPE	Powdered
Chemical Resistant PVC	Powdered

Table 2: Refinement procedure according to each material.

Applicable materials were powdered using a coffee grinder to refine them into a coarse powder. This apparatus varied depending on the physical composition of the material. PVC pipe required the use of a specific rolling grinder as well as simple hand tools for the initial cuttings.

The physical properties of neoprene rubber prevented the material from being powdered. The team avoided using chemical solvents to dissolve or powder the rubber to prevent additional contamination. To refine the material, the neoprene rubber was shredded using a grater to obtain the finest particulate size.

These powdered materials were sifted through a 10 mm sieve to remove large particulates. Then, the sifted material was put through a 1 mm sieve to remove particles larger than 1 mm. The resulting material was then put through a 0.5 mm sieve to remove any particle smaller than 0.5 mm and retain material that did not pass through. Thus, the resultant powder consisted of particulates within a range of 0.5 of 1 mm. Once each of the required materials had been successfully powdered to an appropriate particle size, they were fit for use in the creation of test spheres.

## 3.1.3 Sphere Production

The materials used to create a sphere were paraffin wax, powdered pine sawdust, and a selected contaminant. The spheres were formed using a spherical mold of 2.5" in diameter as seen in Figure 4 below.



Figure 4. The silicon mold used for creation of spheres (HONYAO, 2022).

A beaker of paraffin wax was placed above a beaker of boiling water to avoid boiling the wax during the melting process. This process can be seen below in Figure 5. Once the wax had reached a liquid state, the sawdust and selected contaminants were then added. The slurry of melted wax and solids was then poured into the mold and allowed to harden for one hour, or until cooled. Whilst cooling, a skewer was inserted into the tops of the spheres to allow for suspension while burning.



Figure 5. The initial neoprene rubber sphere production set-up.

Figure 6 below showcases the appearance of the first batch of sawdust spheres, made from sawdust and paraffin wax. Spheres that were the most spherical in shape were chosen for burning to maintain the characteristics of sphere burns described in Section 2.4.3.



Figure 6. The first batch of sawdust control spheres.

#### 3.2 Burn Procedure

After the spheres were created, they were subjected to the adapted burn methodology. This part of the procedure was defined to consist of the burn apparatus and the combustion of the sphere.

#### 3.2.1 Fire Apparatus

Each sphere was suspended using a metal skewer attached to a ring stand. The suspension apparatus was positioned on a mass balance load cell to continuously measure the mass. The sphere was suspended over a 2000 mL beaker containing 500 mL of water. A drawing of the experimental setup can be seen below in Figure 7.



Figure 7. Experimental setup designed for the sphere burn.

#### 3.2.2 Burn Procedure and Sample Collection

First, a set of preliminary control burns was performed. These burns were used to develop a standard burn time that the rest of the experiments followed. This involved igniting a sphere consisting of sawdust and paraffin wax, lacking any test contaminants. Using a propane torch, the spheres were held alight for 10 seconds with the flame focused on the underside of the suspended sphere. Following this, the sawdust spheres took an average of 30 seconds to reach a steady state burn. They were then burned for an average of three minutes. Burns under three minutes were not able to burn long enough, resulting in under approximately 5% mass loss. Burns over three minutes compromised the structure of the sphere resulting in total disintegration at anywhere from four to seven minutes. This was not suitable for the methodology due to the necessity of uniformity between experiments.

Additionally, alternate suspension orientations were designed and tested before eventually deciding to suspend the spheres horizontally with the water. This was to assist in preventing catastrophic failure because of the paraffin wax melting too quickly, causing the sphere to prematurely submerge itself.

Subsequent batches followed the same procedure. The sphere was ignited with a propane torch from underneath, followed by a 30 second ignition time to reach a steady state burn and then three minutes of steady state burning, in which the surface area of the sphere was entirely encased in visible flame. The previous MQP determined a steady state burn for each material was necessary to encourage contaminant mobilization during suppression (Cristiano et al., 2022). Figure 8 depicts an example burn for each material.



Figure 8. Sawdust, neoprene rubber, and HDPE spheres burning in the described apparatus.

Suppression occurred once the three minute and 30 second time was reached for each of the burns. This involved the removal of the suspending rod from the stand and immediately submerging the burning sphere in 500 mL of water. The spheres with a high sawdust ratio broke apart upon submersion, creating a charred sawdust slurry solution. Figure 9 below showcases a test sphere after being burnt and subsequently quenched in the water reservoir.



Figure 9. Test sphere after burning and subsequent suppression.

Later batches utilized less sawdust in the spheres to increase the concentration of testing building material. This reduction in sawdust caused the spheres to no longer break apart as they did in previous iterations. Figure 10 below illustrates the appearance of a sawdust sphere with less sawdust after burning and subsequent suppression.



Figure 10. A modified sphere with less paraffin wax after burning and subsequent suppression.

The largest difference between this project's burn procedure and its predecessor is simplicity. The adapted procedure can be performed by a single trained individual due to its reduced size and potential danger while previous projects require a team of supervision. This project also involved a less complex extinguishing procedure, which accounts for mobile contaminants only at the time of instant submersion, instead of requiring consideration of rapidly changing gas phases over a period for a sprinkler suppression method. This version of the experiment was designed with repeatability and cost in mind.

However, due to the reduced scale, burn length, and simplified suppression method, the results were found under optimal conditions, and it should be noted that real world and even large-scale applications may produce varying magnitudes of concentrations.

## **3.3 Sample Preparation**

After the burn procedure was completed, the water samples needed to be properly processed and stored. This sample preparation involved collecting the water and normalizing the samples. Samples were collected in the WPI Salisbury Combustion Lab and prepared for transport to the WPI Kaven Environmental Laboratory.

## 3.3.1 Sample Collection and Storage

Once the burn was completed, the 500 mL of contaminated water was transferred to a 1000 mL storage container. A collection bottle example is shown below in Figure 11, containing water from a neoprene rubber sphere burn. Each storage bottle held up to 1000 mL from two burns. Each batch was given its own container and burns from different batches were never combined. Reagent grade water from the WPI Kaven Laboratory was used to rinse the beaker in which the contaminated water was collected in. This reagent grade water was filtered using a Barnstead D375 Hollow Fibre Filter with a pore size rating of 0.2 µm. These flasks were sealed to prevent evaporation during the time necessary for transportation to the laboratory for chemical analysis.



Figure 11. An example collection bottle for neoprene rubber sphere burn.

## 3.3.2 Normalization of Samples

After collection, and before filtration, water samples were sealed and stored in refrigerated conditions at 4°C. Before filtration, the samples were stored in these refrigerated conditions between 72 and 120 hours to ensure saturation as well as stirred to evenly redistribute the debris that had settled at the bottom and top of the storage bottles.

## 3.3.3 Initial Filtration

The solid phase extraction (SPE) cartridges are prone to clogging if samples contain insoluble debris (Hawach Scientific, 2020). To prevent this, and to prevent damage to the Gas Chromatography-Mass Spectrometry (GC-MS) during sample testing, water samples were initially filtered using Whatman<sup>TM</sup> 150 mm diameter filter papers to remove any large particulate matter that might have been present. These samples were then processed through vacuum filtration fitted with a 90 cm diameter glass fiber filter membrane with a 1.5-micron pore size Hach Glass-microfibre disc. The filtered samples were stored in 100 mL glass vials and sealed with minimal headspace to prevent evaporation.

#### 3.3.4 Solid Phase Extraction

By using SPE, the analytes present in the collected water samples were isolated by interacting with a solid stationary phase. The methodology used was developed from the Cristiano et al. process (2022). Three mL Supelclean<sup>TM</sup> ENVI<sup>TM</sup>-18 SPE tubes were used, each with a bed weight of 500 mg. Each SPE cartridge was conditioned with 2 mL of methanol and then 2 mL of reagent grade water to activate packing before extraction. The pressure of the vacuum was maintained at approximately 10 inches Hg for the procedure. The samples were then pumped at a flow rate of 1 mL per minute. Finally, 6 mL of reagent grade methylene were drawn through each cartridge to elute the analytes. Methylene chloride samples were transferred in screw top volatile organic compound vials to prevent evaporation. These samples

were then returned to the refrigerated conditions and stored at 4°C until they were analyzed using GC-MS.

#### 3.4 Chemical Analysis

The first objective of the chemical analysis procedure was to determine which indicator contaminants would be identified. Following this, standards were prepared and processed to develop standard curves to interpret the GC-MS results.

### 3.4.1 Selection of Contaminants

Contaminants were selected for GC-MS based on severity in water resource contaminants and frequency of occurrence in the materials tested, or materials commonly found in residential structures and settings (Cristiano et al., 2022). Appendix A lists these contaminants based on research from the previous team. From this list, six indicator contaminants were chosen due to the large range of expected contaminants in the water samples: benzene, ethylbenzene, *o*-xylene, pyrene, naphthalene, and anthracene. Justification for the selection of these contaminants is described in Section 2.7 of the literature review. It was also important that the compounds could be analyzed utilizing GC-MS, which is why three VOCs were chosen and three polyaromatic hydrocarbons (PAHs). The same contaminants were tested for as the previous year's team as the materials were consistent due to ease of access and lower cost.

### 3.4.2 Standard Preparation

Following the methodology from the previous project's chemical analysis, the same two sets of standards that were utilized for the standard curve were used. These standards were purchased by Fisher Scientific covering all major contaminants considered. The first of the two standards—Supelco EPA 625 Semivolatile Calibration Mix— contained contaminant concentrations of 1000  $\mu$ g/mL each. Each component was in a methylene chloride-benzene mixture with a ratio of 3:1. For the second standard, Supelco EPA 502/524 Volatiles Organic Calibration Mix (without gasses), contaminants were in concentrations of 2000  $\mu$ g/mL each, with each component in methanol. The full list of components of each standard is listed in Appendix B. A 4-step serial dilution with reagent grade methylene chloride (UN1593 dichloromethane) was performed to create several samples of each standard at known concentrations ranging from 0.1 ppb to 100 ppb (Table 3).

	EPA 625	EPA 502/524
Initial Concentration	1000 ppb	2000 ppb
Step 1	100 ppb	100 ppb
Step 2	10 ppb	10 ppb
Step 3	1 ppb	1 ppb
Step 4	0.1 ppb	0.1 ppb

## Table 3: Serial dilution concentrations for Standards EPA 625 and EPA 502/524.

For all serial dilutions of the EPA 625 and the last three dilutions of the EPA 502/524, the dilutions were prepared in a 10 mL volumetric flask with methylene chloride and 1 mL of sample. For the first step of EPA 502/524, 0.5 mL of the standard was used. Vials and pipettes were cleaned according to the
procedures in section 3.5. The diluted standards at concentrations of 0.1, 1, 10, and 100 ppb were then refrigerated until analysis in the GC-MS.

#### 3.4.3 Gas Chromatography-Mass Spectrometry Analysis

Gas Chromatography-Mass Spectrometry (GC-MS) combines separation and detection techniques to identify unknown compounds within a sample and determine the concentrations of these contaminants. The tested sample is first vaporized into the gas phase and then separated into its components. This occurs when the sample is run through a capillary column that is coated with a stationary phase. Each component is separated from the mixture at different times, depending on their boiling points and polarity (Thermofisher, 2023). This elution time is called the compound's retention time and is plotted on the x-axis of a chromatogram. The mass spectrometer then utilizes electron or chemical ionization sources to ionize and fragment the components that leave the GC column. The instrument then analyzes these fragments, typically using a quadrupole or ion trap to separate the ions based on their mass-to-charge (m/z) ratios (Thermofisher, 2023). These values are graphed on the x-axis of the mass spectrum. These fragmented ions are graphed as functions of their m/z ratios. Peak areas produced in the gas chromatogram are proportional to the amount of compound and a corresponding mass spectrum is produced for each peak. These mass spectrums can then be compared to mass spectra libraries to identify and quantify unknown compounds (Thermofisher, 2023).

The GC-MS procedure used to identify organic contaminants in each water sample was adapted from the previous team's method. The procedure utilized an Agilent Technologies 7890B system with a 5977B MSD with an HP-5ms ultra inert 30m x 250  $\mu$ m x 0.25  $\mu$ m equipped column. A 1.5 mL GC vial filled with methylene chloride was run both before and after the samples as a blank. Each sample was transferred to a 1.5 mL GC vial using a sterile 3 mL BD PrecisionGlide<sup>TM</sup> Needle.

The GC oven temperature was initially set to 40°C for four minutes, then increased to 290°C at a rate of 9°C/min, and then held at 290°C for six minutes (Table 4). The sequencing time was approximately 37 minutes for each vial and 2.0  $\mu$ L samples were injected in splitless injector mode.

Ramp Rate (°C/min)	Temperature (°C)	Hold Time (min)
	40	4
9	290	6

Table 4: Oven program set for GC-MS analysis of each sample and standard.

The post-run of the GC-MS was set at a temperature of 290°C for six minutes. A run rate graph can be seen below in Figure 12, produced by the GC-MS based on these specifications. The thermal aux transfer line to MS was set to 200°C. Helium gas was used as a carrier gas. The split-splitless inlet had a front inlet temperature of 250°C, a pressure of 7.8 psi, and a flow rate of 1.1 mL/min. These conditions were selected based on the previous year's project (Cristiano et al., 2022), with slight alterations made to increase inlet temperature and allow optimal time for a post-run.



Figure 12. Run Time vs. Temperature ( $\mathcal{C}$ ) graph for selected gas chromatography-mass spectrometry process.

The standards produced following Section 3.4.2 were then run through the GC-MS using the same procedure as the water samples. Figure 13 below showcases how GC-MS vials were configured in the machine for analysis of samples from a neoprene rubber burn. Data collected from these chromatograms were used to produce six standard curves with four points each. These graphs were approximated using linear regression and  $R^2$  values were used to measure the appropriateness of the fit when applicable.



Figure 13. Neoprene rubber samples in gas chromatography-mass spectrometry machine before analysis.

The standard curves were created by graphing the concentration of each dilution versus the area of the peak identified by the GC-MS for each indicator contaminant. This is because the peak area is proportional to the amount of each component. The peak areas obtained from the chromatograms for each sample could then be used to estimate the concentration of each indicator chemical present in the sample.

#### 3.4.4 Chromatogram Modeler

The Restek Pro *EZGC* Chromatogram Modeler simulates retention time (minutes), resolution, peak width (minutes), and temperature (°C). The modeler allows the user to input specific conditions, including carrier gas, column dimensions, and column flow, detailed in Table 5 below. When using the modeler, the oven program was designed to reflect the conditions selected earlier.

	Table 5: Restek Pro	EZGC Chromatogram	Modeler Input	Conditions.
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Column Flow	Average Velocity	Holdup Time	Inlet Pressure	Outlet Pressure (abs)
1.00 mL/min	36.12 cm/sec	1.38 min	7.38 psi	0.00 psi

Expected outputs and retention times for each analyte were predicted by the Restek Pro *EZGC* Chromatogram Modeler and tabulated in Appendix C for both selected standards. This was done to reduce the need for repetitive recalibration and increase efficiency (Cristiano et al., 2022).

#### **3.5 Cleaning Procedure**

For proper cleaning of the glassware, to reduce cross contamination and to ensure a sterile work environment, the procedure developed by Michigan State University (2018) was followed.

Some contaminants cannot be cleaned through standard washing procedures. The contaminants would be insoluble inorganic residues and poorly extracted organic contaminants. To identify if these contaminants were present, a visual analysis of the container was performed for unusual beading that indicates their presence (MSU, 2018). If identified, containers would be rinsed with a very small amount of methylene chloride which was then drained from the container and disposed of properly (MSU, 2018). If the unusual beading is not present, the standard cleaning procedure could proceed. First, the interior and exterior of the glassware was scrubbed using a lab grade detergent (MSU, 2018). The container would then be rinsed six times using warm tap water or until detergent was no longer visible. The container would then be rinsed six more times using purified water before being allowed to dry (MSU, 2018).

The next part of the cleaning procedure was performed under a chemical fume hood for safety. To remove chemical compounds, the containers were rinsed three times with reagent grade methylene chloride (MSU, 2018). Each rinse involved filling a tenth of the container volume and swirling the methylene chloride. For the second and third rinse of each container, a fresh sample of methylene chloride was used (MSU, 2018). However, methylene chloride used once for a piece of glassware could be reused for the first rinse of another piece of glassware (MSU, 2018).

## 4.0 Burn Results and Analysis

The following sections present and discuss the findings that correspond to the burn portion of this project. Review of the preparation and composition of each sphere was documented to identify any differences between batches before considering the mass loss and mass transfer interactions in each burn.

#### 4.1 Prepared Spheres

The first point of data collection for this experiment was during the creation of the spheres for burn analysis. The physical properties of each sphere were recorded and visual analysis of the burn of each sphere was performed. The collected mass of the skewers was deducted from the measured mass of each sphere due to lack of interaction.

The spheres were produced in batches and the properties of the spheres in the batches can be found in Appendix D. Sphere composition was uniform with respect to their batch.

#### 4.2 Burn Data

#### 4.2.1 Mass Loss

Due to the nature of the experiment, a given amount of material would be lost from the combustion reaction. Mass loss as a function of time was virtually identical for all samples due to the nature of their near identical surface area. It was estimated that change in mass loss begins to approach zero as the burn approaches a steady state. It is upon reaching this steady state that the sphere is then extinguished and submerged to allow for contaminants to be collected.

#### 4.2.2 Mass Transfer

Once the test sphere was submerged into the liquid, only a portion of the total sphere would transfer contaminants or other particles to the collected water. This rate of transfer is given in Equation 2 below. The mass transfer rate is directly dependent on the radius of the sphere. As the radius of the sphere decreases, the rate of mass transfer also decreases.

$$W_a = 4\pi D_{AB} \times a c x_a \qquad (Equation 2)$$

In Equation 2,  $W_a$  is defined as the molar rate of mass transfer,  $D_{AB}$  is the diffusion coefficient as defined by Fick's law of diffusion, a is the radius of the sphere, and  $cx_a$  is the molar concentration of the fluid (Subramanian, n.d.). Under the assumption of a steady state condition at the time of submersion, it can be approximated that the size and shape of the sphere did not change after it was introduced to the water. As all the sphere's possessed identical molds with uniform diameters and were ignited for the same length of time, it can be estimated that each of the spheres underwent near identical rates of mass transfer with the collection reservoir. However, this assumes an ideal scenario where all spheres were created equally and were burned into identical forms which perfectly maintained their original shape while also undergoing identical dimensional rates of change.

Due to the complexity and variability of the composition of the spheres, the coefficient of mass transfer cannot be accurately found without extensive simulation of the internal structure of the spheres. The mechanical motion of submersion also aids the rate of mass transfer, as the fluid passing the sphere's

surface is absorbed at an accelerated rate. The influence that this effect aids or alters the rate of mass transfer was assumed insignificant and not considered for the following results. It is recommended that future teams find the rate of mass transfer for each of the tested materials independent of the compound spheres. This will allow for accurate modeling and theoretical calculations of the expected rate of mass transfer.

As the spheres combusted, their surface became a mixture of solid, liquid, and gas phases. Some of these phases existed for only mere moments as the flame rapidly heated and expanded the material. While in their non-solid phases, materials were considered mobile. In this mobile state, contaminants are typically captured by the atmosphere, other nearby mobile phases, or the environment. However, upon being submerged, the liquid and gas phases of the combusted spheres were dissolved into the water, capturing the mobile contaminants, and preventing their evaporation. Once dissolved, the solid surface of the sphere then began the absorption of the surrounding mixture of mobile particulates and water reservoir. Upon reaching full absorption, the solid phase surface of the sphere began to dissolve and desorb the mixture. This process can be seen in Figure 14 below. Once fully desorbed, the mobile contaminants are captured within the water reservoir, and will then be filtered of any remaining non-soluble solid particulates.



*Figure 14.* Illustration of the liquid & gas phases dissipation in the water reservoir, followed by the adsorption and desorption of the surrounding mixture, releasing contaminants into the water reservoir.

#### 4.2.3 Visual Analysis

Each of the burns were performed following near identical procedures, creating small variance in the appearance of the flames. The type of material being tested also appeared to have negligible impact on the shape, color, or intensity of the burn. Spheres with higher concentrations of sawdust demonstrated little to no difference time required to reach steady state, nor any change in flame intensity. Spheres created with excess testing material, i.e., concentrated neoprene rubber spheres, did not appear to have any change in flame characteristic.

Although some of the materials were treated with flame-retardant coatings, this did not appear to have any effect on any visual characteristics. This is likely because the materials were originally shipped as sheets or pipes, and any flame-proofing did not account for when the materials had been powdered or shredded, as is the case in these experiments. Overall, the appearance of the flame did not have any significant variance in color, shape, smoke production, or intensity as it relates to changes in the material being tested.

#### 4.2.4 Error in Burn Procedure

The results from initial chemical analysis showed very low concentrations of contaminants, making it difficult to detect and identify them. As a result, the burn procedure was altered to increase concentrations. The first was increasing the saturation time and decreasing the volume of water. The development of the spheres was also altered to involve manipulating material so that the sawdust, paraffin wax, and chosen material were more evenly distributed across the surface of the sphere. Lastly, for the initial procedure, each sphere was designated its own water suppression beaker. Therefore, for the final burn multiple spheres were extinguished in the same water sample to increase the concentration. The inconsistency with the burn procedure can cause variation in chemical analysis results, therefore being a source of error.

#### 4.3 Burn Procedure Recommendations and Discussion

After repeated trials, the team was able to gradually reduce the amount of paraffin wax and sawdust in each of the spheres, thus increasing the amount of testing material. This allowed for higher concentrations of contaminants to both be created and measured. It is recommended that should this experiment be repeated that sawdust and paraffin wax be kept to an absolute minimum to maintain steady state combustion, while also maximizing the potential contaminants being created.

By suspending the spheres via a horizontal skewer with proper fume hood ventilation, each of the burns performed had very small amounts of smoke produced, allowing for efficient combustion and constant, uninterrupted flame. The suppression system used was also extremely simple which maximized potential contaminant output over an instantaneous length of time. While unrealistic, as most large-scale fires are unable to be extinguished instantaneously, these results provide a baseline for small scale fires which may be repeated at larger scales over greater lengths of time for more applicable real-world results.

Additionally, more research can be devoted to improving the mass transfer rates post submersion. Due to the hydrophobic nature of paraffin wax, alternative adhesives may pose advantageous in mobile contaminant capture.

# 5.0 Chemical Analysis and Discussion

The following sections present and discuss the findings that correspond to the chemical analysis portion of this project. A review of the GC-MS results for each of the materials burned analyzed was conducted as well as the standard curves developed. The implications of these results and other contaminants of concern are also discussed.

#### 5.1 GC-MS Results

After solid phase extraction (SPE) was completed, the water samples were run through the GC-MS and organized by burn date and material type. Using the data generated by the Restek Pro *EZGC* Chromatogram Modeler (linked in Appendix C), retention times for each indicator contaminant were chosen. Since the times were solely an estimate, the team focused on order the analytes were expected to elute in and took note of peaks within a five-minute retention time window. The expected retention time used for each indicator contaminant can be seen below in Table 6. Using this information, 13 samples of contaminated water from multiple burns were collected and analyzed. Two samples of contaminated water from sawdust burns were used as control samples.

Table 6: E	Expected reter	ntion times (m	inutes) for	r the elution	ofea	ch indicator	<sup>•</sup> contaminant	estimated	using
the Restek	Pro EZGC C	Chromatogran	1 Modeler						
				1					
~			~ .		-		Absolut	e RT win	dow

Compound Name	Signal	Exp. RT (min)	Absolute RT window (min)
Benzene	MS1Front TIC SCAN EI	2.55	5.00
<i>O</i> -Xylene	MS1Front TIC SCAN EI	5.27	5.00
Ethylbenzene	MS1Front TIC SCAN EI	6.62	5.00
Naphthalene	MS1Front TIC SCAN EI	13.62	5.00
Anthracene	MS1Front TIC SCAN EI	22.47	5.00
Pyrene	MS1Front TIC SCAN EI	26.23	5.00

#### 5.1.1 Standard Curves

The standards prepared in Section 3.4.2 were used to develop standard curves to determine the concentration of contaminants in water samples for the GC-MS method. The area of each peak that corresponded with an indicator contaminant was obtained from the GC-MS software and then substituted in for the x-value in each linear regression equation, outputting concentration (ppb) as the y-value. Sample calculations for concentrations can be found in Appendix E. The adapted methodology for creating the standards added a fourth dilution, 100 ppb. This was done to help create more ideal standard curves. The chromatograms used to produce the standard curves are included in Appendix F. The standard curve for benzene can be seen in Figure 15 below. The standard curves for the other five indicator contaminants are included in Appendix G.



Figure 15. Standard curve (Concentration (ppb) vs. Peak Area) for benzene.

Benzene was the only indicator contaminant detected at each concentration (0.1 ppb, 1 ppb, 10 ppb, and 100 ppb). Ethylbenzene, *o*-xylene, naphthalene, anthracene, and pyrene were all detected at concentrations of 10 ppb and 100 ppb in their respective standards but were at too low of concentrations to be detected in the 0.1 and 1 ppb samples. For indicator contaminants that were not detected at every dilution, standard curves were less ideal and contaminant concentrations concluded are only estimated based on these results, rather than measured values. A linear trendline, equation, and R<sup>2</sup> value were developed for each graph.

#### 5.1.2 Sawdust Control Sphere GC-MS Results

To try and distinguish between the contaminants that are produced during the combustion reaction of wood and the contaminants produced by burning the selected building materials, a sawdust control sphere (SD-001) burn was conducted. Two samples from this burn were tested in the GC-MS. Indicator chemicals were determined to be detected or not detected based on the presence of peaks at expected retention times. However, the modeler was only an estimate of these retention times, therefore each chromatogram was inspected to determine if the analyte eluted earlier or later with respect to the expected time and compared to the mass spectrum library database.

Seen below in Figure 16 is the chromatogram for the first SD-001 sample. Peaks are indicated by an arrow with their retention times displayed above them. For the chromatograms included in Appendix H through Appendix K, the six indicator contaminants can be seen labeled at and around their expected retention times.



Figure 16. Chromatogram for SD-001.

Benzene, ethylbenzene, and *o*-xylene were not detected in either control sawdust sample. Included in Table 7 below are the concentrations of naphthalene, anthracene, and pyrene found in both control sphere burns. In the sample name "SD-001 #1", SD-001 refers to the batch name (Appendix D) and #1 refers to the first water sample taken from the burn of that batch. If no number follows the batch name in the sample name, then only one sample was taken from the burn of that batch. This naming convention is consistent for all samples.

Sample Name	Indicator Contaminant Found in Sample	Concentration (ppb)	Retention Time of Peak (min)
	Naphthalene	0.426	13.657
SD-001 #1	Anthracene	0.255	22.036
	Pyrene	0.509	26.147
	Naphthalene	0.403	13.657
SD-001 #2	Anthracene	0.251	22.036
	Pyrene	0.067	26.147

**Table** 7. Concentrations and retention times of indicator contaminants based on GC-MS results for the samples from the control sawdust sphere burns.

It is important to note that the blank methylene chloride run before and after these control samples identified a peak in the pyrene range. If this peak is pyrene, it would have an estimated concentration of 0.102 ppb. This may indicate that the pyrene found in the sample is present in the solvent rather than produced by the burn reaction. However, there was an increase in pyrene concentration in the first control sawdust spheres from what was identified in the blank. Methylene chloride blanks were run before and after every set of samples and pyrene was not identified in all of them. Therefore, more testing would be required to know the source of these peaks present in the pyrene range in the sawdust burn. The two chromatograms for the sawdust control spheres are included in Appendix H.

#### 5.1.3 Neoprene Rubber Samples GC-MS Results

Neoprene rubber samples NR-001, NR-002, NR-003, and NR-004 were the first four samples analyzed using GC-MS. Table 8 outlines which indicator contaminants were detected in these neoprene rubber water samples, the concentrations of each indicator contaminant, and the retention time that the peak was eluted. These neoprene rubber water samples were collected using the methodology described in Section 3.2.2 and will be referred to as the non-concentrated neoprene rubber water samples.

Benzene was found in one of the four tested GC-MS samples below. Its estimated concentration in the sample was approximately 0.453 ppb. Naphthalene was found in every sample from non-concentrated neoprene rubber burns and had an estimated concentration range of 0.297 to 1.957 ppb. Anthracene was found in all these samples, at concentrations ranging from 0.106 to 1.101 ppb as well as pyrene at concentrations between 0.024 and 1.513 ppb. Of all the detected indicator contaminants, pyrene was consistently present at the lowest concentrations. Neither ethylbenzene nor *o*-xylene were detected in any of the samples from non-concentrated neoprene rubber burns.

Sample Name	Indicator Contaminant Found in Sample	Concentration (ppb)	Retention Time of Peak (min)
	Naphthalene	0.822	13.642
NR-001	Anthracene	0.671	22.032
	Pyrene	0.059	27.108
	Benzene	0.453	2.619
NID 002	Naphthalene	0.297	13.644
NK-002	Anthracene	0.106	22.384
	Pyrene	1.513	26.131
	Naphthalene	0.913	13.643
NR-003	Anthracene	1.101	22.031
	Pyrene	0.024	26.303
	Naphthalene	1.957	13.642
NR-004	Anthracene	0.157	22.294
	Pyrene	0.057	26.303

**Table 8**: Concentrations and retention times of indicator contaminants based on GC-MS results for the samples from non-concentrated neoprene rubber burns.

Included in Table 9 are the results from the three neoprene rubber water samples from batch number NR-005. These samples differed from the first four samples from neoprene rubber burns due to how they were collected and created. To try and increase contaminant concentration, two neoprene rubber spheres were burned and quenched in the same 500 mL water reservoir. The mass of neoprene rubber in these two spheres was also increased from 10% of the total mass to 25% of the total mass. Three samples from this burn were then tested in the GC-MS and will be referred to as the samples from the concentrated neoprene rubber sphere burns. Benzene and naphthalene concentrated neoprene rubber sphere burns. Benzene and naphthalene concentrated neoprene rubber sphere burns. Benzene had an average concentration of 28.429 ppb, a large increase from the 0.453 ppb in the NR-002 sample. Naphthalene had an average concentration of 10.102 ppb between these samples from the concentrated neoprene rubber burn, an increase from the average 0.997 ppb estimated in the samples from the non-concentrated neoprene rubber burns.

On the other hand, the average anthracene concentration for these samples was 0.835 ppb whereas the samples from the non-concentrated neoprene rubber burn had an average anthracene concentration of 0.678 ppb. Although the average anthracene concentration did increase, it was not a large enough increase to theorize that it was due to the change in methodology. Pyrene saw a decrease in average concentration, with an average of 0.413 ppb between the original four samples and an average of 0.077 ppb in the NR-

005 samples. The chromatograms for the samples from the non-concentrated and concentrated neoprene rubber burns are included in Appendix I.

Sample Name	Indicator Contaminant Found in Sample	Concentration (ppb)	Retention Time of Peak (min)
	Benzene	25.616	2.561
	Naphthalene	11.247	13.652
NR-005 #1	Anthracene	0.889	22.395
	Pyrene	0.085	26.306
	Benzene	52.142	2.528
	Naphthalene	10.394	13.653
NR-005 #2	Anthracene	0.986	22.395
	Pyrene	0.087	26.307
	Benzene	7.529	2.532
	Naphthalene	8.665	13.652
NR-005 #3	Anthracene	0.630	22.390
	Pyrene	0.058	26.306

*Table 9*: Concentrations and retention times of indicator contaminants based on GC-MS results for the samples from the concentrated neoprene rubber burns.

#### 5.1.4 Chemical Resistant PVC Samples GC-MS Results

Table 10 below details the concentration of each indicator contaminant that was detected in the burns of the two PVC batches, PVC-001 and PVC-002. Two samples from the burn of each PVC batch were tested. The concentrations of the indicator contaminants as well as the retention times they were eluted are also included in Table 10.

Naphthalene (0.233 to 1.922 ppb), anthracene (0.045 to 0.220 ppb), and pyrene (0.023 to 0.176 ppb) were detected in every sample from the PVC burns. Benzene was only detected in the PVC-001 #2 sample, with an estimated concentration of 1.056 ppb. Ethylbenzene was detected in the PVC-002 #1 sample at a concentration of 1.755 ppb. This was the only sample between all three materials where ethylbenzene was detected. The chromatograms for the four samples from the PVC burns are included in Appendix J.

*Table 10*: Concentrations and retention times of indicator contaminants based on GC-MS results for the samples from the chemical resistant PVC burns.

GC-MS Label	Indicator Contaminant Found in Sample	Concentration (ppb)	Retention Time of Peak (min)
	Naphthalene	0.660	13.657
PVC-001 #1	Anthracene	0.045	22.037
	Pyrene	0.023	26.136
	Benzene	1.056	2.577
DVC 001 #2	Naphthalene	0.233	13.657
PVC-001 #2	Anthracene	0.167	22.037
	Pyrene	0.137	26.136
	Ethylbenzene	1.755	6.359
	Naphthalene	1.922	13.645
PVC-002 #1	Anthracene	0.220	22.428
	Pyrene	0.176	26.304
	Naphthalene	0.949	13.654
PVC-002 #2	Anthracene	0.133	22.383
	Pyrene	0.075	25.676

#### 5.1.5 HDPE Samples GC-MS Results

Table 11 displays the concentrations of each indicator contaminant found in the samples from the burns of the HDPE-001 batch and their respective concentrations. Naphthalene, anthracene, and pyrene were found in each sample with naphthalene having the highest concentration in both samples. The amount of pyrene in each sample was approximately an order of magnitude smaller than the other contaminants found. The chromatograms for the two HDPE tests are included in Appendix K.

*Table 11*: Concentrations and retention times of indicator contaminants based on GC-MS results for the HDPE spheres.

Sample Name	Indicator Contaminant Found in Sample	Concentration (ppb)	Retention Time of Peak (min)
	Naphthalene	1.280	13.643
HDPE-001 #1	Anthracene	0.688	22.032
	Pyrene	0.079	26.303
	Naphthalene	0.612	13.643
HDPE-001 #2	Anthracene	0.510	22.030
	Pyrene	0.057	26.303

#### 5.2 Implications and Other Contaminants

According to Equation 2 from Section 4.2.2, under the assumption that the sphere had reached steady state at the time of submersion, each sphere had identical rates of mass transfer between the sphere materials and the water. This indicates that the team would also expect identical concentrations of each contaminant between burn trials since each material would transfer between the solid and liquid phase at identical rates. However, from Tables 7 through 11, concentrations for each indicator contaminant were not identical between samples from different burns. This is most likely to do with errors with the team's assumptions, including physical variety between each sphere and batch from the nature of the molds.

#### 5.2.1 Indicator Contaminant Concentration Analysis

Higher concentrations of benzene, naphthalene, and anthracene were found in the water samples from the neoprene rubber, PVC, and HDPE burns than the samples from the control sawdust burns consistently. This indicates that some portions of contaminants were being formed due to the combustion reactions of the chosen building materials rather than only forming from the combustion of wood. When adapting the methodology to try and increase contaminant concentration, benzene and naphthalene concentrations experienced large increases, indicating that the production of these contaminants may increase with larger building structures fires containing the chosen materials. This phenomenon should be researched further by varying the masses of building materials.

Anthracene and pyrene were only found in small concentrations in both the samples from the nonconcentrated neoprene rubber burns and the samples from the concentrated neoprene rubber burns. They did not significantly change when increasing the mass of burned sawdust, paraffin wax, and neoprene rubber in the water reservoir.

The possible presence of benzene, pyrene, and naphthalene was expected as they are commonly found in plastics and rubbers and may be produced by incomplete combustion reactions (Cristiano et al., 2022). The detection of ethylbenzene in the water sample from the PVC burn was also expected, as ethylbenzene is often used to manufacture styrene, a component in plastics (International Agency for Research on

Cancer (IARC), 2000). Acute exposure to ethylbenzene can cause throat and eye irritation as well as dizziness (EPA, 2000).

The US EPA sets maximum contaminant levels (MCLs) for drinking water to minimize risks on public health by certain toxic contaminants. Although fire event runoff does not always end up directly in drinking water distribution systems, large scale fire events may affect distribution systems, eventually leading to drinking water contamination. Table 12 below details the MCLs set by the US EPA for the detected indicator contaminants.

*Table 12*: Detected indicator contaminants and their maximum contaminant level as set forth by the Environmental Protection Agency (EPA, 2018).

Contaminant	Maximum Contaminant Level
Benzene	0.005 mg/L (5 ppb)
Ethylbenzene	0.7 mg/L (700 ppb)
Naphthalene	20 µg/L (20 ppb)
Anthracene	100 μg/L (100 ppb)*
Pyrene	100 μg/L (100 ppb)*

\*Total Discharge limit for Group II Polycyclic Aromatic Hydrocarbons

The MCL set by the EPA for benzene allowed in drinking water is 0.005 mg/L or 5 ppb. The samples from the burn of the NR-005 batch had concentrations of 25.616 ppb, 52.142 ppb, and 7.529 ppb, all of which exceed this limit. No other indicator contaminant was measured above the EPA's MCLs for drinking water, but levels of ethylbenzene, naphthalene, anthracene, and pyrene are still concerning as they are considered carcinogens.

Spheres that produced benzene concentrations above the MCL were part of the NR-005 batch, which had an increased overall mass of neoprene rubber in the spheres to try and increase contaminant concentrations. One important thing to note is that paraffin wax is soluble in benzene but not water (Chemical Book, 2017). This is important for samples with higher benzene concentrations, as paraffin wax may have contributed to the contaminants of that sample. To try and counteract this, paraffin wax was removed from the water samples as it hardened on the surface of the water and was not included in large quantities within the storage bottles. However, this should still be considered when applying conclusions to real environments. Naphthalene was the second closest contaminant to violating the MCL, with an average concentration of 10.102 ppb in the samples from the burn of the NR-005 batch. The methodology used to create the higher concentration neoprene rubber spheres should be explored more in future work and repeated for PVC and HDPE.

Fire runoff often also has a chance of ending up in water sources that will not be treated directly for drinking water purposes. Therefore, a more appropriate metric for comparing the concerning levels of contaminant may be by comparing these concentrations to industrial removal goals and surface and groundwater requirements. However, there is no standardized list of these levels, making comparison difficult. For example, benzene is often found in groundwater sources following gasoline spills and leaks

from storage containers. These sources must be treated quickly as the ability of benzene to migrate through soil and water sources makes it an immediate concern and removal goals must be met.

Companies in Massachusetts must file NPDES permits under the Federal Clean Water Act and Massachusetts Clean Waters Act to discharge certain levels of contaminant. Although these limits set by the permit have changed in the past 10 years, they can be used to examine the range of levels allowed by the state for industrial discharges. One example of this is Irving Oil Terminals Inc, who filed a permit in 2014 to discharge their industrial effluent into the Chelsea River Mystic River Watershed (Massachusetts Department of Environmental Protection [DEP], 2014). The permit allowed them to discharge a maximum effluent limit of 51  $\mu$ g/L (51 ppb) per month. This limit is based off monthly testing done by the permittee. The permit also sets a maximum effluent limit of 100  $\mu$ g/L for naphthalene per month. This permit expired in 2019 and Irving Oil Terminals has since filed a new one. In this permit, the maximum effluent limit is 5  $\mu$ g/L (5 ppb) of benzene per day. For naphthalene, the new maximum daily effluent limit is 20  $\mu$ g/L (20 ppb) per day (EPA, 2022). Other companies such as the Gulf Oil Terminal have filed for NPDES permits to discharge into the Chelsea River. Their permit allows the same discharge levels as Irving Oil Terminals (EPA, 2021).

Based on these allowable discharge concentrations and the concentrations of benzene detected in the samples, concentrations detected in water following larger fire events may violate these maximum daily effluent levels. This is important to note as water sources that are contaminated after fires may be similar in size and location to those that receive effluent from industrial sources.

Since fire water runoff falls under allowable non-stormwater discharges, there is cause for concern in discharging large amounts of water used for fire suppression. Based on the concentrations detected in the samples compared to the allowable daily effluents from several NPDES permits in Massachusetts, water departments should perform water sampling at different points in the distribution system following fire events to determine if concerning concentrations are present. VOC sampling methods may be recommended based on the performed experiments in this project, such as the US EPA Method 524.2 (Munch, 1995). Since VOCs were identified in multiple samples, it may be important for more water treatment plants to prepare for treatment of compounds such as benzene and naphthalene. For future work, it may be beneficial for experimental values to be compared to actual values of contaminants measured by local departments or agencies, such as the Massachusetts Department of Environmental Protection.

#### 5.2.2 Other Contaminants

Appendix L includes the names, probability, and retention times of each compound identified using the Mass Spectrum Library Search generated by the Agilent Technologies 7890B system, separated by sample. Due to the extent of possible compounds detected by the GC-MS, listed compounds had a probability of 55 or more. The compounds identified were only included if their formation was reasonable based on research into their sources, uses, and possible hazards.

One notable compound identified was 2-Nitrodiphenylamine, detected in the samples from the burn of the NR-004 batch. It was eluted at 21.51 minutes with a probability of 85.57. It is a common stabilizer for synthetic rubbers and may cause skin and eye irritation, as well as respiratory irritation (Parchem, 2017).

This compound, among others identified by the GC-MS, are cause for concern in water distribution systems.

There were several differences between the possible contaminants identified in last year's work from this year's. Previous data identified contaminants such as n-Hexane, cyclohexane, cyclopentanone and other organic compounds. All materials remained the same between project interactions excluding white pine wood, which was replaced with sawdust in this project. The sawdust used was from a laboratory meaning it was made from several different materials mixed versus the pinewood sticks chosen for last year's crib construction. Therefore, it is important to note that the chosen wood material may have significantly altered the types of contaminants produced by the combustion reaction.

Due to the large amount of sawdust used in each sphere, several compounds were identified that are commonly found in plant and wood species. However, these compounds did not typically have hazards and were common between most samples. Examples of these compounds include guaiacol methyl ether (11.823 minutes) and herbacetin (25.129 minutes). Several compounds were also identified that are often found in pesticides and insecticides, including cyphenothrin (22.133 minutes) and acrinathrin (25.265 minutes). Although these contaminants appear as concerning as others that were identified, their presence does indicate that the use of composites in structures may cause a large range of contaminants to show up in water following fire events and the toxicity of them should be explored further.

One common disadvantage of GC-MS is the process's difficulty with detecting and correctly identifying non-volatile compounds. Only a small range of volatile, thermally stable compounds are fit for analysis (Amirav et al., 2020), which is why six researched indicator contaminants were selected. However, this may not apply to the other contaminants identified in each sample, influencing the validity of the mass spectrum library search, even with higher probability compounds. Due to this, many compounds had a large probability of matching to the MS spectrum but would not be formed by burning the sphere materials. Another disadvantage is that there is often absence or weakness of molecular ions in the samples (Amirav et al., 2020), leading to a smaller confidence level in the sample identification based on the mass spectrum library.

#### 5.2.3 Comparison to Previous Work

To understand the effects of changing the burn procedure from last year's project, the concentrations and mass spectrum identifications can be examined and compared. It was initially hypothesized that lower concentrations would be seen compared to the previous group's project because the sphere design required less material to be used overall than the wooden cribs produced last year. This meant that since less material would burn, the contaminants produced from the combustion reaction and the contaminants present in the materials would appear at lower concentrations. This was generally not true, as concentrations for the spheres created using the original methodology described in Section 3.1.3 were similar values as seen in the previous data. This may have to do with the differences in suppression methods, as quenching the spheres in a water reservoir allowed for longer contact time and consistent water application between the sphere mass and the water versus previous work that used a sprinkler-like suppression system and then collected the water only after it had passed over the cribs.

Unlike the previous group's samples, *o*-xylene was not detected in any burn water sample. This was unexpected due to the use of xylenes in rubbers and the presence of *o*-xylene in one of the previous

project's neoprene rubber burns. Several experiments by Valavnidis et al. (2008) and Chong et al. (2019) found *o*-xylene in water after the burning of PVC through different burning methodologies. Although levels were not necessarily over EPA MCLs, *o*-xylene and other VOCs were still detected using GC-MS. Therefore, further research should be conducted to determine if *o*-xylene was not present due to the change in materials or variation in burning and sampling.

Another notable difference between this year's project is that the team took steps to ensure that samples, at all parts of the procedure, were properly sealed, refrigerated, and stored with minimal headspace to avoid issues of evaporation. As a result, the samples did not require reconstitution, which may contribute to differences in results between the previous project and this work.

The previous investigative team was able to produce eight burns fit for data collection. This team decided to scale down the magnitude of the burns for ease of repeatability and creation of samples. As a result, the team was able to complete a total of nine burns and a larger volume of water was used for the adapted burns, allowing for a larger sample pool for analysis. By increasing the repeatability and the amount of data, it was easier to notice trends between burns and strengthen confidence in the conclusions.

# 6.0 Theoretical Study on Contaminant Removal from Water

Due to the nature of the water contaminants found in this report, traditional treatment methods may not be sufficient. Therefore, it is important to conduct more research into ways of effectively removing them from drinking water. The team investigated removal techniques of VOCs and PAHs to establish parameters of treatment systems future work should investigate, both through theoretical research as well as testing through experiments. As the frequency of fire events increases with climate change over the next several decades, water treatment plants may need to consider ways of filtering out these contaminants on larger scales.

#### 6.1 Activated Carbon Packing Column

Since concerning levels of benzene and naphthalene were found within the samples described in Section 5.0, treatment of this water would be required before distribution. The project team decided to look at one treatment method, a granulated activated carbon (GAC) system, and frame it within the scope of the project. This system was chosen due to its ability to treat water containing VOCs.

In a typical treatment system, metals and particulate removal will occur by several processes: coagulation, flocculation, sedimentation, and filtration. When looking at this year's data, this is important to consider due to the contribution larger masses of sawdust, wax, and building material had for contaminant concentrations. It was hypothesized that removing ash and other solid contaminants as quickly as possible may help keep contaminant concentrations lower, and further testing should be done in the future to quantify this by varying the amount of time between sample collection and filtration (Section 3.3.3).

After removing these contaminants, organic removal may occur using chemical oxidation and activated carbon adsorption. Adsorption is when material accumulates at the interface between two phases and is often used to remove contaminants from fluids and transfer them to the solid phase. In this case, the contaminants would adsorb to the GAC within a vessel. GAC is used due to its high surface area, which gives contaminants more space to accumulate. Adsorption is typically modeled by three isotherms: Freundlich isotherm, Linear isotherm, and Langmuir isotherm. These adsorption isotherms illustrate the relationship between adsorbate in the surrounding phase and adsorbate on the surface of the absorbent, in this case the GAC, at equilibrium (Saleh, 2022). These isotherms only apply at constant temperature and are important in the calculation of the mass of activated carbon needed for every liter of water treated, along with other variables.

Grieco (2021) detailed requirements for GAC systems that are not always widely publicized and may be important for water treatment systems to consider as more treatment plants find need for GAC for VOC and PFAS treatment. For water treatment, GAC system requirements include soaking requirements, backwash requirements, pH adjustment period, arsenic content, and disinfection. Soaking is required to fill the internal pore spaces with water, displacing the entrained air. Higher temperatures will help quicken this process due to the hydrophobic GAC surfaces. At ambient temperatures of around 10-15.6°C (50-60°F), soaking will take approximately 48 to 72 hours (Grieco, 2021). In places where ambient temperature may be lower, the soaking process will take longer. Failure to wet the GAC may lead to poor or very little adsorption so it is important that this step is taken properly.

Backwashing GAC is necessary to remove carbon fines and stratify the bed, allowing large carbon particles to settle and create a desired vertical particle size distribution (Grieco, 2021). For a given system, a backwash flow rate must be established based on temperature of the water and the properties of the GAC installed. Backwash requirements also depend on pH, buffering capacity of the inlet water, and target pH values. General guidelines for backwashing can be found in literature sources and altered to fit the specific requirements and goals of a system. The author Grieco also recommends consideration of a pH adjustment period and possible arsenic content. GAC systems may have effluent exceeding allowable pH levels, most likely due to surface functional groups from the GAC activation process (Grieco, 2021). Forward-flushing with influent water is recommended to help obtain a neutral pH. Arsenic content must also be considered due to the presence of pyrite and arsenic in the coal used to make bituminous and subbituminous GAC products. Grieco recommends utilizing the same flushing process as with pH adjustment requirements to decrease the arsenic concentration when needed. Chlorination is required to disinfect empty adsorption vessels, piping, and other equipment (Grieco, 2021) as GAC may become contaminated during transport.

To create a hypothetical design of an activated carbon column, several parameters must be established. Firstly, an influent benzene concentration of 1 mg/L was used to solve for hypothetical column properties. The concentrations found experimentally in Section 5.0 most likely do not represent actual magnitudes of contaminant concentrations that would be entering a distribution system due to the differences in scale (of both fires and water volumes). From the EPA maximum contaminant levels and NPDES permit allowable discharges, a treatment objective of 0.005 mg/L benzene (5 ppb) was selected.

Using experimental data, an isotherm is chosen based on the graph that has the strongest linear correlation between the q<sub>e</sub> and C<sub>e</sub> variables. Due to the lack of experimental data in a hypothetical design, the Freundlich isotherm was selected based on its ability to be used for gasses that are absorbed onto solids at low pressures. The Freundlich isotherm is also more commonly applied to multilayer adsorption on heterogenous sites (Kalam et al., 2021). The Freundlich isotherm requires an assumption for use: cations and anions are absorbed onto the same surface simultaneously, resulting in the formation of attractive forces between adsorbed cations and anions on the surface (Nakahara, 1994). The Freundlich isotherm equation is shown below in Equation 3 (Droste & Gehr, 2019).

$$q_e = K \times C_e^{1/n} \qquad (Equation 3)$$

This equation can be linearized to Equation 4 below and is used for graphing the relationship between  $log(q_e)$  and  $log(C_e)$  to determine if the Freundlich isotherm fits the associated data. This requires recorded values of  $q_e$  and  $C_e$ , where  $q_e$  is the mass of carbon adsorbed per mass solid phase (g/g) and  $C_e$  is the equilibrium concentration of the adsorbate. These equations can be applied under the assumption that equilibrium is achieved.

$$\log(q_e) = \log(K_f) + (1/n \times \log(C_e))$$
 (Equation 4)

Using an established experimental value for the removal of benzene using activated carbon from a 2022 study, a Freundlich adsorption coefficient (K) of 17.87 and a Freundlich intensity of adsorption (1/n) of 0.46 were chosen (Rineksa et al., 2022). In this study, solutions of varying concentrations of benzene and toluene were created. Then, 0.25 grams of GAC were added to each concentration and placed into an auto-shaker for two days at a speed of 27 revolutions per minute (rpm). The absorbance of each

concentration was found and plotted as  $log(C_e)$  on the x-axis and  $log(C_e)$  on the y-axis. From this, linear regression was performed to find K and 1/n.

This experiment was performed using granulated activated carbon with the following properties: a surface area of  $1062 \text{ m}^2/\text{g}$ , pore volumes ranging from 0.314 to 0.488 mL/g, a wet carbon density in bed of 1.20 g/cm<sup>3</sup> and pore diameters between 1.5 x  $10^{-9}$  and 2.3 x  $10^{-9}$  meters. The bed had a void fraction of 0.48.

Substituting these values in the Freundlich isotherm equation yields Equation 5 below.

$$q_e = 17.87 \times C_e^{0.46} \qquad (Equation 5)$$

Using Equation 5, a mass balance can be performed to determine the required dose of activated carbon for a hypothetical GAC column designed to reduce the concentration of benzene from 1 mg/L to 0.005 mg/L. The mass balance is included in Appendix M. Typically, activated carbon is packed in a column and water runs through it for treatment. From this equation, it was found that 0.637 mg of activated carbon (with the associated properties) is required for every liter of water treated.

Several assumptions were made to find these parameters, including a steady state system and average water temperatures around 20 °F. An empty bed contact time (EBCT) of 7.5 minutes was estimated by the EPA's work breakdown structure (WBS) model for granulated activated carbon treatment of benzene removal (linked in Appendix M) based on an influent flow rate of approximately 0.124 MGD. This EBCT falls in ranges recommended by the EPA (5-25 minutes) (EPA, 2020). A surface loading rate (SLR) of 6 gpm/ft<sup>2</sup> was assumed. SLR values typically range from 2 to 10 gpm/ft<sup>2</sup> (Water Filter Advisor, 2023). From these assumed values, a contactor height of 5.62 ft and contactor diameter of 4.68 ft can be estimated. Appendix M details these calculations.

It is important to note that these values are based off of assumptions and would need to be examined using a pilot-scale test design approach to determine feasibility. These contactor dimensions also depend heavily on the type of GAC selected and the specific values from this hypothetical design approach can only be applied to the GAC used in the Rineksa et al. 2022 study.

A required bed volume of 96.8 ft<sup>3</sup> was estimated from these assumptions (Appendix M). The bed density should be approximately 90% of the apparent dry density, which typically ranges from 220 to 650 kg/m<sup>3</sup> (Droste & Gehr, 2019). One important disadvantage of GAC is its limited lifetime. GAC requires regeneration as its removal efficiency decreases overtime. Regeneration is typically performed by heating carbon to high temperatures and volatizing compounds that have adsorbed onto the media (Newcombe, 2007).

These experimental adsorption coefficient and intensity of adsorption values were concluded from the results of only one study. These values vary depending on the mass of the adsorbent (and therefore the type of granulated activated carbon used), the mass adsorbed ( $C_e$ ), and the properties of the activated carbon. For the sake of these calculations, mass transfer effects were ignored in mass balance equations. Therefore, future work should aim to collect data and produce experimental values of these constants. Other parameters that experimental design could find include the run time and particle and water velocity. Parameters such as carbon bulk density can be found from the manufacturer with typical bulk densities between 400 and 500 kg/m<sup>3</sup> (Droste & Gehr, 2019).

The team also recommends that more research be done on removal methods of contaminants from fire events. Data and concentrations from both this project and the previous work can be considered. The established parameters above (soaking requirements, backwashing requirements, pH adjustment period, arsenic content, and disinfection) should be selected for the specific requirements of the system that is designed. Using experimental methods, the system could be designed, and bench scale tests could be conducted to determine the necessary variables and observe contaminant removal abilities.

# 7.0 Conclusions and Recommendations

The goals of this project were achieved through chemical analysis techniques and the engineered burn procedure. The design of the burn procedure and suppression method were determined based on increasing repeatability of the procedure to achieve multiple data points. The materials, concentration distributions, and masses of each sphere were recorded. By establishing a different burn procedure, the team was able to produce a larger volume of contaminated water and thus have a larger testing pool. This led to more data to compare and make conclusions from. The data obtained from the GC-MS identified and quantified the concentrations of contaminants in each sample. In the spheres made using the original methodology, contaminant levels were similar to those found in the previous project. However, the chemical analysis of the samples showed no *o*-xylene amongst the contaminants in this year's work. It also showed smaller amounts of anthracene and pyrene compared to benzene and naphthalene. Thus, after a fire event these contaminants may be less of a concern for the chosen building materials and water treatment facilities should focus on testing water for increased levels of naphthalene and benzene following fire events.

If this procedure is to be repeated, it is recommended to use reagent grade water for suppression of the sphere. This may be beneficial to ensure that any present contaminants in tap water do not create artificial results or show contaminants that are not actually present from the burn. Since altering the number of spheres quenched in a single 500 mL water reservoir increased concentrations, further testing with different materials using this adapted methodology should be performed. Higher concentrations of contaminants will also aid the GC-MS with detection capabilities. It is recommended that methods be explored to improve material uniformity on the surface area of the spheres, helping the burn more closely resemble literature surrounding spherical burns. To expand upon this procedure, it is recommended that future research is invested into creating a special burn and suppression chamber for the spheres. This is recommended to trap any gaseous phase compounds that might be produced and to ensure there are minimal outside influences to ensure less contaminated results.

Lastly, as future research is done into the contaminants resulting from fire events, part of the future research should be invested into the ways of removing these contaminants in a laboratory setting. Research done by this year's team concerning the requirements of a granulated activated carbon column should be considered and expanded on by finding Freundlich isotherm coefficients using bench scale tests.

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# Appendices

# Appendix A - Abbreviated List of Expected Contaminants in Water from Literature Review (Adapted from Cristiano et al., 2022)

Polyaromatic hydrocarbons

Acenaphthene	Benzo[g,h,i]perylene	Indeno[1,2,3-cd]pyrene
Anthracene	Benzo[k]fluoranthene	Irganox 1010 Constituent
Benzo[a]anthracene	Chrysene	Naphthalene
Benzo[a]pyrene	Dibenzo[a,h]anthracene	Phenanthrene
Benzo[b]fluoranthene	Fluorene	Pyrene

### Volatile Organic Compounds

Benzene	Ethyl Benzene	Methylpentane isomer
1-butene	2-ethyl-1-hexanol	OCtadecane
1,3-butadiene	Formaldehyde	N-pentane
2-butoxyethanol	N-hexane	Trimethylamine
Dimethylbutane Isomer	Hexadecane	Tetradecane
Dimethyloctane Isomer	Methylbutadiene isomer	Toluene
Docosane	Methylbutane isomer	Xylenes

## Appendix B - Analytes in Selected Standards

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Analytes in Supelco EPA 625 Semivolatile Calibration Mix 1000 μg/mL each component in a 3:1 ratio of methylene chloride to benzene (From: https://www.sigmaaldrich.com/US/en/product/supelco/506559)					
Acenaphthene Acenaphthylene Anthracene Azobenzene Benz[a]anthracene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[ghi]perylene Benzo[a]pyrene Benzyl butyl phthalate Bis(2-chloroethoxy)methane Bis(2-chloroethoxy)methane Bis(2-chloroethyl) ether Bis(2-ethylhexyl) phthalate 4-Bromodiphenyl ether Carbazole 4-Chlorodiphenyl ether Bis-(2-chloroisopropyl) ether 4-Chloro-3-methylphenol 2-Chloronaphthalene	2-Chlorophenol Chrysene Dibenz[a,h]anthracene Dibutyl phthalate 1,2-Dichlorobenzene 1,3-Dichlorobenzene 2,4-Dichlorophenol Diethyl phthalate 2,4-Dimethylphenol 2,4-Dinitrophenol 2,4-Dinitrotoluene 2,6-Dinitrotoluene Di-n-octyl phthalate Fluoranthene Fluorene Hexachlorobenzene Hexachloro-1,3-butadiene	Hexachlorocyclopentadiene Hexachlorocyclopentadiene Indeno[1,23-cd]pyrene Isophorone 2-Methyl-4,6-dinitrophenol Naphthalene Nitrobenzene 2-Nitrophenol 4-Nitrophenol N-Nitrosodimethylamine N-Nitrosodi-n-propylamine Pentachlorophenol Phenol Pyrene 1,2,4-Trichlorobenzene 2,4,6-Trichlorophenol			

Analytes in Supelco EPA 502/504 Volatiles Organic Calibration Mix (without gasses) 2000 μg/mL each component in methanol (From: https://www.sigmaaldrich.com/US/en/product/supelco/502111)					
Benzene	1,3-Dichlorobenzene	Naphthalene			
Bromobenzene	1,4-Dichlorobenzene	Propylbenzene			
Bromochloromethane	1,1-Dichloroethane	Styrene			
Bromodichloromethane	1,2-Dichloroethane	1,1,1,2-Tetrachloroethane			
Bromoform	1,1-Dichloroethylene	1,1,2,2-Tetrachloroethane			
Butylbenzene	cis-1,2-Dichloroethylene Tetrachloroethylene				
sec-Butylbenzene	trans-1,2-Dichloroethylene Toluene				
tert-Butylbenzene	Dichloromethane	1,2,3-Trichlorobenzene			
Carbon tetrachloride	1,2-Dichloropropane	1,2,4-Trichlorobenzene			
Chlorobenzene	1,3-Dichloropropane	1,1,1-Trichloroethane			
Chloroform	2,2-Dichloropropane	1,1,2-Trichloroethane			
2-Chlorotoluene	1,1-Dichloro-1-propene	Trichloroethylene			
4-Chlorotoluene	cis-1,3-Dichloropropene	1,2,3-Trichloropropane			
Dibromochloromethane	trans-1,3-Dichloropropene	1,2,4-Trimethylbenzene			
1,2-Dibromo-3-chloropropane	Ethylbenzene	Mesitylene			
1,2-Dibromoethane	Hexachlor-1,3-butadiene	m-Xylene			
Dibromomethane	Cumene	o-Xylene			
1,2-Dichlorobenzene	p-Cymene	p-Xylene			

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#### Appendix C - Expected outputs from Pro EZCG Chromatogram Modeler

Outputs were generated by inputting the following parameters into the Pro *EZGC* Chromatogram Modeler (https://www.restek.com/en/technical-literature-library/brands/EZGC-online-tools/). Selected indicator contaminants are highlighted.

EPA 625					
Peaks	Retention Time (min)	Resolution	Peak Width (min)	Temperature (°C)	
N-Nitrosodimethylamine	3.87	136	0.043	40	
Phenol	9.76	4.2	0.039	91.8	
Bis(2-chloroethyl) ether	9.93	1.2	0.04	93.3	
2-Chlorophenol	9.97	1.2	0.041	93.8	
1,3-Dichlorobenzene	10.35	4.5	0.042	97.2	
1,4-Dichlorobenzene	10.54	4.5	0.042	98.9	
1,2-Dichlorobenzene	10.92	8.9	0.042	102.3	
Bis-(2-chloroisopropyl) ether	11.31	7.7	0.04	105.8	
N-Nitrosodi-n-propylamine	11.62	3.6	0.04	108.6	
Hexachloroethane	11.77	3.6	0.042	109.9	
Nitrobenzene	11.96	4.5	0.041	111.6	
Isophorone	12.61	4.4	0.041	117.5	
2-Nitrophenol	12.79	4.4	0.042	119.2	
2,4-Dimethylphenol	13.04	5.8	0.039	121.3	
Bis(2-chloroethoxy)methane	13.27	4.1	0.04	123.4	
2,4-Dichlorophenol	13.44	4.1	0.041	124.9	
1,2,4-Trichlorobenzene	13.64	3.9	0.041	126.8	
Naphthalene	13.80	3.9	0.042	128.2	
Hexachloro-1,3-butadiene	14.23	10.3	0.042	132.1	
4-Chloro-3-methylphenol	15.39	18.3	0.04	142.5	
Hexachlorocyclopentadiene	16.12	7.6	0.042	149.1	
2,4,6-Trichlorophenol	16.44	7.6	0.042	152	
2-Chloronaphthalene	16.91	11	0.043	156.2	
2,6-Dinitrotoluene	17.92	1.4	0.044	165.3	
Acenaphthylene	17.98	1.4	0.044	165.8	

Acenaphthene	18.46	3.2	0.044	170.1
2,4-Dinitrophenol	18.60	3.2	0.042	171.4
4-Nitrophenol	18.89	1.8	0.041	174
2,4-Dinitrotoluene	18.97	8.7	0.042	174.7
Diethyl phthalate	19.73	2.1	0.041	181.6
Fluorene	19.83	2	0.044	182.4
4-Chlorodiphenyl ether	19.91	2	0.043	183.2
2-Methyl-4,6-dinitrophenol	20.03	2.8	0.043	184.3
Azobenzene	20.32	6.7	0.043	186.9
4-Bromodiphenyl ether	21.19	2.3	0.043	194.7
Hexachlorobenzene	21.29	2.3	0.045	195.6
Pentachlorophenol	21.84	12.2	0.045	200.5
Anthracene	22.47	10.6	0.046	206.2
Carbazole	22.95	10.6	0.045	210.6
Dibutyl phthalate	24.11	25.9	0.043	221
Fluoranthene	25.47	12.2	0.047	233.3
Pyrene	26.05	12.2	0.048	238.4
Benzyl butyl phthalate	28.04	26.7	0.045	256.4
Benz[a]anthracene	29.24	1.8	0.049	267.2
Chrysene	29.33	1.8	0.049	268
Bis(2-ethylhexyl) phthalate	29.68	7.2	0.043	271.1
Di-n-octyl phthalate	31.30	13.4	0.044	285.7
Benzo[b]fluoranthene	31.89	1.3	0.051	290
Benzo[k]fluoranthene	31.96	1.3	0.051	290
Benzo[a]pyrene	32.68	14	0.058	290
Indeno[1,23-cd]pyrene	36.19	1.6	0.096	290
Dibenz[a,h]anthracene	36.35	1.6	0.096	290
Benzo[ghi]perylene	37.20	8.8	0.107	290

EPA 502/524				
Peaks	Retention Time (min)	Resolution	Peak Width (min)	Temperature (°C)

1,1-Dichloroethylene	1.67	7.4	0.018	40
Dichloromethane	1.81	1.9	0.02	40
trans-1,2-Dichloroethylene	1.84	1.9	0.02	40
1,1-Dichloroethane	2.02	8.1	0.022	40
cis-1,2-Dichloroethylene	2.2	1.6	0.024	40
2,2-Dichloropropane	2.24	1.3	0.024	40
Bromochloromethane	2.27	1.3	0.025	40
Chloroform	2.31	1.5	0.025	40
Carbon tetrachloride	2.35	1.2	0.026	40
1,1,1-Trichloroethane	2.38	1.2	0.026	40
1,1-Dichloro-1-propene	2.44	2	0.027	40
Benzene	2.56	3.9	0.028	40
1,2-Dichloroethane	2.67	3.9	0.029	40
Trichloroethylene	2.91	8	0.032	40
Dibromomethane	3.2	2.3	0.035	40
1,2-Dichloropropane	3.28	2.3	0.036	40
Bromodichloromethane	3.38	2.6	0.038	40
cis-1,3-Dichloropropene	4.04	5.9	0.045	40.3
Toluene	4.31	5.9	0.046	42.8
Tetrachloroethylene	4.76	3.4	0.046	46.9
trans-1,3-Dichloropropene	4.92	3.4	0.045	48.3
1,1,2-Trichloroethane	5.11	3.1	0.046	50
Dibromochloromethane	5.3	3	0.046	51.7
1,3-Dichloropropane	5.44	1.5	0.046	53
1,2-Dibromoethane	5.51	1.5	0.046	53.6
Chlorobenzene	6.36	3.5	0.045	61.2
1,1,1,2-Tetrachloroethane	6.52	0.1	0.045	62.7
Ethylbenzene	6.53	0.1	0.045	62.8
1,1,2,2-Tetrachloroethane	8.8	1.2	0.042	83.2
p-Xylene	6.79	0.1	0.044	65.1
m-Xylene	6.78	0.1	0.044	65
Bromoform	7.4		0.045	70.6
o-Xylene	7.4		0.045	70.6

Styrene	7.5	2.1	0.044	71.5
Cumene	7.96	8.5	0.044	75.6
Bromobenzene	8.33	6.4	0.044	79
Propylbenzene	8.62	2	0.043	81.5
2-Chlorotoluene	8.71	2	0.044	82.4
1,2,3-Trichloropropane	8.86	1.2	0.043	83.7
Mesitylene	9.01	0.5	0.042	85.1
4-Chlorotoluene	8.99	0.5	0.043	84.9
tert-Butylbenzene	9.45	3	0.043	89
1,2,4-Trimethylbenzene	9.58	3	0.042	90.2
sec-Butylbenzene	9.74	3.2	0.042	91.7
1,3-Dichlorobenzene	9.88	3.2	0.043	92.9
p-Cymene	10.05		0.042	94.4
1,4-Dichlorobenzene	10.05		0.043	94.4
Butylbenzene	10.71	1.1	42	100.4
1,2-Dichlorobenzene	10.66	1.1	43	100
1,2-Dibromo-3-chloropropane	11.98	25.9	0.043	111.8
1,2,4-Trichlorobenzene	13.08	2.6	0.043	121.7
Hexachloro-1,3-butadiene	13.19	2.6	0.042	122.7
Naphthalene	13.56	6.7	0.043	126.1
1,2,3-Trichlorobenzene	13.85	6.7	0.043	128.7

#### Appendix D - Tabulated values and Characteristics of Sphere Batches

Batch	Total Mass	Neoprene Rubber Mass %	Sawdust Mass %	Paraffin Mass %
NR-001	216.1 g	10%	15%	75%
Appearance	1.0 cm <sup>2</sup> neoprene particulates, smooth, waxy surface			
Burn Date	01/19/2023			
Filter Date	01/24/2023			

Table D1: Neoprene rubber spheres properties for batch NR-001

Table D2: Neoprene rubber spheres properties for batch NR-002

Batch	Total Mass	Neoprene Rubber Mass %	Sawdust Mass %	Paraffin Mass %
NR-002	212.04 g	10%	30%	60%
Appearance	1.0 cm <sup>2</sup> neoprene particulates, rough, pocketed surface			
Burn Date	01/27/2023			
Filter Date	01/31/2023			

 Table D3: Neoprene rubber spheres properties for batch NR-003

Batch	Total Mass	Neoprene Rubber Mass %	Sawdust Mass %	Paraffin Mass %
NR-003	256.78 g	10%	20%	70%
Appearance	1.0 cm <sup>2</sup> neoprene particulates, smooth, waxy surface			
Burn Date	02/03/2023			
Filter Date	02/07/2023			
Batch	Total Mass	Neoprene Rubber Mass %	Sawdust Mass %	Paraffin Mass %
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NR-004	256.78 g	10%	20%	70%
Appearance	$0.5 \text{ cm}^2$ neoprene particulates, smooth, waxy surface			
Burn Date	02/03/2023			
Filter Date	02/07/2023			

Table D4: Neoprene rubber spheres properties for batch NR-004

Table D5: Neoprene rubber spheres properties for batch NR-005

Batch	Total Mass	Neoprene Rubber Mass %	Sawdust Mass %	Paraffin Mass %
NR-005	224.22 g	25%	15%	60%
Appearance	$0.1 \text{ cm}^2$ neoprene particulates, smooth, waxy surface			
Burn Date	02/28/2023			
Filter Date	03/15/2023			

Table D6: PVC spheres properties for batch PVC-001

Batch	Total Mass	PVC Mass %	Sawdust Mass %	Paraffin Mass %
PVC-001	204.33 g	5%	15%	80%
Appearance	0.1 cm <sup>2</sup> PVC particulates, smooth, waxy surface			
Burn Date	02/10/2023			
Filter Date	02/12/2023			

Table D7:	PVC spheres	properties fo	or batch	PVC-002
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Batch	Total	PVC	Sawdust	Paraffin
	Mass	Mass %	Mass %	Mass %
PVC-002	197.62 g	10%	13%	77%

Appearance	0.1 cm <sup>2</sup> PVC particulates, smooth, waxy surface		
Burn Date	02/14/2023		
Filter Date	02/17/2023		

 Table D8: HDPE spheres properties for batch HDPE-001

Batch	Total Mass	HDPE Mass %	Sawdust Mass %	Paraffin Mass %
HDPE-001	260.80 g	10%	20%	70%
Appearance	1.0 cm <sup>2</sup> HDPE chunks, smooth, waxy surface			
Burn Date	02/17/2023			
Filter Date	02/20/2023			

Table D9: Control sphere properties for batch SD-001

Batch	Total Mass	Sawdust Mass %	Paraffin Mass %
SD-001	131.56 g	20%	80%
Appearance	Smooth, waxy surface		
Burn Date	03/29/2023		
Filter Date	03/31/2023		

#### Appendix E - Sample Calculations for Concentrations of Indicator Contaminants in Water Samples

Benzene Concentration Calculation Example

Line of best fit from standard curve: y = 0.000009x

Rubber  $01/27/2023 \rightarrow$  Peak area for benzene was 50271.3803.

Concentration (y) =  $0.000009 \times 50271.3803 = 0.453$  ppb

Ethylbenzene Concentration Calculation Example

Line of best fit from standard curve: y = 0.00001x

PVC  $02/19/2023 \#1 \rightarrow$  Peak area for ethylbenzene was 175462.4327.

Concentration (y) =  $0.00001 \times 175462.4327 = 1.755$  ppb

Naphthalene Concentration Calculation Example

Line of best fit from standard curve: y = 0.000006x

Rubber 03/15/2023 Sample #1  $\rightarrow$  Peak area for naphthalene was 1874571.2756.

Concentration (y) =  $0.000006 \times 1874571.2756 = 11.247$  ppb

Anthracene Concentration Calculation Example

Line of best fit from standard curve: y = 0.000005x

HDPE 02/17/2023 Sample  $\#1 \rightarrow$  Peak area for anthracene was 137598.4609.

Concentration (y) =  $0.000005 \times 137598.4609 = 0.688$  ppb

Pyrene Concentration Calculation Example

Line of best fit from standard curve: y = 0.000004x

PVC 02/10/2023 Sample #1  $\rightarrow$  Peak area for pyrene was 57145.2422.

Concentration (y) =  $0.000004 \times 57145.2422 = 0.229$  ppb

## Appendix F - GC-MS Chromatograms for Standards Supelco EPA 625 Semivolatile Calibration Mix and Supelco EPA 502/524 Volatiles Organic Calibration Mix

EPA 502/524 Standards 0.1 ppb, 1 ppb, 10 ppb, and 100 ppb:





EPA 625 Standards 0.1 ppb, 1 ppb, 10 ppb, and 100 ppb:







Appendix G – Standard Curves for Six Indicator Contaminants











## Appendix H - GC-MS Chromatograms for Sawdust Control Samples

## Sample Control #1:



## Sample Control #2:



## Appendix I - GC-MS Chromatograms for Neoprene Rubber Samples

#### Sample NR-001:



#### Sample NR-002:



### Sample NR-003:



#### Sample NR-004:



Sample NR-005 #1:



## Sample NR-005 #2:



Sample NR-005 #3:



## Appendix J - GC-MS Chromatograms for Chemical Resistant Polyvinyl Chloride (PVC) Samples

## Sample PVC-001 #1:



### Sample PVC-001 #2:



## Sample PVC-002 #1:



### Sample PVC-002 #2:



## Appendix K - GC-MS Chromatograms for High Density Polyethylene (HDPE) Samples

## Sample HDPE-001 #1:



## Sample HDPE-001 #2:



# Appendix L - Contaminants Identified by the GC-MS MS Spectrum Library Database in Each Material Type

SD-001				
Compound	Probability	Retention Time		
Thioguanine	80.80	11.639		
rac-2-Des Piperidyl-2-amino repaglinide	86.92	15.629		
2-Decanol	72.85	16.833		
L-Glutamine	92.06	16.923		
Homovanillic acid sulfate	64.82	17.778		
Capsazepine	76.20	18.779		
N-Acetyl-p-fluoro-DL-phenylalanine	60.77	19.363		
N-alpha-(tert-Butoxycarbonyl)-L-proline	94.94	20.289		
Capsazepine	96.99	20.578		
Diosmetinidine cation	73.87	27.444		
Zotepine	58.08	27.773		
Bithionol	58.39	28.113		
Zotepine	57.95	29.594		
Glafenine	78.93	30.211		

NR-001, NR-002, NR-003, NR-004				
Compound	Probability	Retention Time		
Guaiacol methyl ether	71.96	11.823		
D(+)-glucuronic acid gamma-lactone	59.13	12.037		
Fluquinconazole	82.37	14.226		
rac-2-des piperidyl-2-amino repaglinide	67.25	15.612		
2,4-Dimethoxyaniline	95.92	16.16		
2-Decanol	61.09	16.832		
Azinphos-ethyl	82.16	18.949		
N-alpha-(tert-Butoxycarbonyl)-L-proline	92.05	20.266		
3alpha-Galactobiose-CH3	64.37	20.471		
4H-[1,2,4]Triazolo[4,3-a][1,4]benzodiazepine-4- acetamide, 6	77.78	27.406		
Skyrin	95.43	28.435		

Beclomethasone	98.73	30.5
Nalbuphine	88.16	34.743

NR-005				
Compound	Probability	<b>Retention Time</b>		
Fluquinconazole	80.55	14.228		
2-Bromo-4,5-methylenedioxymethamphetamine	64.01	17.188		
Chlorpromazine	89.82	18.454		
Probucol	60.14	18.516		
3,4-Dihyroxymethamphetamine	88.79	18.58		
Chlorpromazine	84.90	19.132		
2-Oxo-3-hydroxy lysergic acid diethylamide	61.51	19.694		
7,8-Dihydroxy-4-methylcoumarin-3-acetic acid	76.98	19.762		
N-alpha-(tert-Butoxycarbonyl)-L-proline	91.35	20.288		
1-Piperazineethanol, 4- dibenzo[b,f][1,4]thiazepin-11-yl	81.60	20.689		
Bromoenol lactone	69.77	20.81		
7-Methoxyisoflavone	67.89	21.798		
Benzenesulfonamine, 2-chloro-N-[3-(5-chloro- 3-methylbenzo[b	98.17	21.898		
Cyphenothrin	67.86	22.133		
Silodosin	94.12	22.395		
1,8-Diethyl-1,3,4,9-tetrahydro-4-oxo- pyrano[3,4-b]indole-1-	90.28	23.18		
Phenothiazine	81.24	23.983		
Acrinathrin	90.74	25.274		
Methanone, [1-(2-fluorohexyl)-1H-indol-3-yl]- 1-naphthalenyl	72.58	26.654		
4H-[1,2,4]Triazolo[4,3-a][1,4]benzodiazepine- 4-acetamide, 6	76.12	27.43		
Methanone, [1-(4-hydroxypentyl)-1H-indol-3- yl](4-methoxy-1-	73.25	28.723		
1H-indole-1-acetic acid, 5-fluoro-2-methyl-3- (2-quinolinylmethyl)	86.64	29.533		
1H-indole-1-acetic acid, 5-fluoro-2-methyl-3- (2-quinolinyl)	80.41	29.594		

Glafenine	93.61	29.74
Glafenine	76.75	29.94
6-Methoxy Luteolin	87.87	30.206
Beclomethasone	76.22	30.522
Beta-Alanine, N-[2-(2-pyridinyl)-6-(1,2,4,5- tetrahydro-3H-3-be	82.27	31.711
Diosmetin	73.34	31.795
Beta-Alanine, N-[2-(2-pyridinyl)-6-(1,2,4,5- tetrahydro-3H-3-be	79.14	34.014
Nalbuphine	86.83	34.776
Lappaconitine	96.46	35.801
Lappaconitine	81.36	37.516

PVC-001, PVC-002				
Compound	Probability	Retention Time		
5-iodo-2-aminoindane	75.98	10.969		
Thioguanine	67.06	11.824		
N-Acetyl-D-glucosamine	64.42	12.265		
3,4-Dimethoxy-alpha-pyrrolidinopentiophenone	55.29	14.18		
rac-2-Despiperidyl-2aminorepaglinide	87.46	15.614		
2-Decanol	69.34	16.832		
DL-Laudanosine	76.20	18.447		
Phenyltrimethylammonium cation	98.28	19.122		
N-alpha-(tert-Butoxycarbonyl)-L-proline	91.91	20.266		
Capsazepine	95.17	20.549		
Etodolac	93.85	20.678		
Diosmetinidine cation	76.46	20.984		
Daidzein	77.09	21.241		
Fenbufen	82.04	22.671		
Phytol	73.40	24.197		
Glafenine	91.21	25.687		
Damnacanthal	91.72	25.934		
4H-[1,2,4]Triazolo[4,3-a][1,4]benzodiazepine- 4-acetamide-6	86.31	27.411		
Bithionol	91.63	28.095		

Coptisine cation	97.00	29.137
4-Hydroxy-2',3,4',6'-trimethoxy chalcone	81.29	29.925

HDPE-001				
Compound	Probability	Retention Time		
(+)-Blebbistatin	70.66	9.254		
Thioguanine	68.4	11.83		
D-Glucuronic acid	67.15	15.383		
rac-2-des piperidyl-2-amino repaglinide	89.46	15.614		
2-Decanol	57.43	16.832		
L-Glutamine	94.04	16.899		
Ethanone, 1-[4-[[4'-[2,2,2-trifluoro-1-hydroxy- 1-(trifluoro	58.73	17.69		
Homovanillic acid sulfate	68.47	17.759		
Zectran	75.49	18.148		
Chlorpromazine	96.60	18.446		
Capsazepine	74.29	18.758		
n-Octadecylamine	56.38	19.069		
N-alpha-(tert-Butoxycarbonyl)-L-proline	91.87	20.266		
Capsazepine	83.81	20.533		
2,2-Bis(4-chlorophenyl)ethanol	92.96	21.353		
Hydroxyde Hydro Nifedipine Carboxylic acid	80.00	24.563		
4H-[1,2,4]Triazolo[4,3-a][1,4]benzodiazepine- 4-acetamide, 6	73.97	27.408		
Bithionol	71.24	29.923		

#### Appendix M - Calculations for the Sorption of Benzene onto Activated Carbon

WBS Model for Granulated Activated Carbon (used to estimate EBCT): https://www.epa.gov/sites/default/files/2016-03/wbs-gac.xlsm

Estimated carbon usage rate:

Mass balance

 $V(C_{initial} - C_e) = -M_{carbon}[q_{initial} - q_e]$ 

 $V(C_{initial} - C_e) = -M_{carbon} \left[q_{initial} - 17.87 \times C_e^{0.46}\right]$ 

 $(M_{carbon})/(V) = -\frac{Cinitial - Ce}{qinitial - 17.87Ce^{0.46}} = -\frac{1\frac{mg}{L} - 0.005\frac{mg}{L}}{0 - (17.87 x \ 0.005^{0.46} \frac{mg}{L})} = 0.637 \text{ mg} \text{ of activated carbon per L of water treated}$ 

Bed volume:

Bed Volume = Contact Time × Flow Rate (Droste & Gehr, 2019)

Bed Volume =  $(7.5 \text{ minutes}) \times (103.4 \text{ gallons per minute}) / 7.48 \text{ gal/ft}^3$ 

Bed Volume =  $96.8 \text{ ft}^3$ 

Dimensions of the contactor:

Typical surface loading rates for GAC filters: 2 to 10 gpm/ft<sup>2</sup>

Using a SLR of 6 gpm/ft<sup>2</sup>

SLR = Flow Rate / Area

Area = Flow Rate / SLR

Area =  $103.4 \text{ gpm} / 6 \text{ gpm/ft}^2$ 

Area =  $17.23 \text{ ft}^2$ 

For a cylinder:

Bed Volume = Area  $\times$  Height

96.8  $ft^3 = 17.23 ft^2 x$  Height

Height = 5.62 ft

Diameter of column:

Volume =  $\pi \times \text{Radius}^2 \times \text{Height}$ 

96.8 ft<sup>3</sup> =  $\pi \times \text{Radius}^2 \times 4.68$  ft

Radius = 2.3 ft

Diameter = **4.68 ft**