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Oxidative Potential and Composition of Fine Particulate Matter at Two Locations in Mississippi

by

Victoria Claire Stevens

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford

May 2021

Approved by

Advisor: Dr. Courtney Roper

Reader: Dr. Walter Cleland

Reader: Dr. Marc Slattery

DEDICATION

To my parents and siblings, Vicki, Michael, Emily Elise, and Heath,
I could not have done any of this without your constant love and support.
You are the most important to me.

Also, in memory of Robert Stevens

ACKNOWLEDGEMENTS

I would like to thank Roper Lab for giving me the opportunity and support to research this topic. I would especially like to thank Maggie Craze for always making time to help me and for going above and beyond to make my research experience positive and fun. And to Cole Smith, thank you for always being such a great friend.

Above all else, I would like to thank Dr. Courtney Roper who has been my advisor and mentor throughout my project. Dr. Roper has been one of my strongest supporters over the two years I have known her, both in research and in my personal goals. She has given up her time to invest in me and my project, and she does so with constant kindness and patience. Thank you so much for everything you have done for me, Dr. Roper.

ABSTRACT

Air pollution exposure has negative health effects on individuals across the globe. Negative impacts on human health have been documented in studies following both short-term and long-term exposure to air pollution, and these adverse effects have been seen even at the lowest levels of exposure. Fine particulate matter ($PM_{2.5}$) has specifically been linked to these negative health effects. These effects come from many sources, but one large contribution to the negative health effects comes from oxidative stress. In this study, samples were collected from Hernando, MS and Gulfport, MS in September 2013 and November 2013. Black carbon (BC) analysis was performed on these samples to determine black carbon concentrations. $PM_{2.5}$ was extracted from filters in methanol by sonication. The samples were then divided into their methanol soluble and hexanes soluble fractions. The oxidative potential was measured for both fractions using a diothiothreitol (DTT) assay. Statistical analysis was done to measure statistical significance of data collected. There were significant differences observed between sampling dates and soluble fractions for oxidative potential. There were trends observed for $PM_{2.5}$ concentrations, black carbon concentrations, and oxidative potentials. The results of this study show that sampling date and location should be considered when studying $PM_{2.5}$.

TABLE OF CONTENTS

LIST OF TABLES & FIGURES

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BC	Black carbon
DMSO	Dimethyl sulfoxide
DTNB	5,5’-Dithiobis (2’-nitrobenzoic acid)
DTT	DL, 1,4-Dithiothreitol
EPA	Environmental Protection Agency
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
MDEQ	Mississippi Department of Environmental Quality
NAAQS	National Ambient Air Quality Standards
N-EVAP	Nitrogen-Evaporation
PB	Potassium phosphate, monobasic (KH2PO4)
$PM_{2.5}$	Particulate Matter smaller than 2.5 microns
WHO	World Health Organization

INTRODUCTION

Air pollution exposure has negative health effects on individuals across the globe. Importantly, there has been an increase in pollutants in the atmosphere that can be attributed to the increased combustion of fossil fuels throughout the last century (Kampa & Castanas, 2008). Negative impacts on human health have been documented in studies following both short-term and long-term exposure to air pollution, and these adverse effects have been seen even at the lowest levels of exposure (Brunekreef & Holgate, 2002). There is consistent evidence of an association between air pollution exposures and deaths related to cardiovascular and respiratory diseases of the elderly as well as an increase in cases of respiratory diseases (Seaton et al., 1995).

There are several types of air pollution. The Environmental Protection Agency (EPA) is required by the Clean Air Act to set National Ambient Air Quality Standards (NAAQS) for six categories of air pollutants, called criteria air pollutants in the United States. These categories include ground-level ozone, carbon monoxide, lead, sulfur dioxide, nitrogen dioxide, and particulate matter (US EPA, 2014). While researching and regulating all six groups of pollutants is important, this project focuses on particulate matter.

There are an estimated 7 million deaths per year as a result of exposure to fine particles in polluted air (WHO, 2018). Particulate matter is one component of air pollution that has well-documented adverse human health effects. Fine particulate matter

($PM_{2.5}$) is a portion of air pollution that is comprised of particulate matter that is 2.5 microns or smaller in aerodynamic diameter which are emitted either directly or indirectly. These particles are emitted directly from sources like fires, smokestacks, or construction sites, but they are more commonly formed as a result of chemical reactions from products of power plants and automobile emissions (US EPA, 2016). Due to the small size of $PM_{2.5}$, it can penetrate deep into the lungs and potentially exit the lungs and enter the bloodstream (US EPA, 2016). The health effects of $PM_{2.5}$ include chronic heart disease, lung cancer, acute respiratory infections in children, asthmatic attacks, aggravation of pre-existing heart and lung disease, chronic heart disease, chronic respiratory disease, minor upper respiratory irritation, and chronic bronchitis in adults (Kampa & Castanas, 2008).

The composition of $PM_{2.5}$ can show great variation across locations, pollutant sources, and seasonal changes. Elements, organic compounds, and metals can sorb to $PM_{2.5}$ during the formation of the particulates. What sorbs to the particulates depends on the composition of the environment at the time of formation (Bell et al., 2010). For example, in one study performed in Laiwu, China in 2016, components of $PM_{2.5}$ from different sources were identified. Components of $PM_{2.5}$ in urban dust and soil dust were Si, Fe, and Ca. SO_4^{2-} and NH_4^+ were the primary components in power plant dust. The characteristic components were distinctly different between different sources, which is important information to establish, as different compositions of $PM_{2.5}$ have varied effects on health (Zhang et al.,2020).

Different compositions of $PM_{2.5}$ can lead to different health effects. These particulates are able to travel deep into the lungs due to the size of the $PM_{2.5}$, bringing their sorbed components with them (US EPA, 2016). For example, high exposures to $PM_{2.5}$ containing large concentrations of nickel, silicon, aluminum, vanadium, and elemental carbon during the third trimester of pregnancy have been found to be associated with lower birth weights in children resulting from those pregnancies (Bell et al., 2010). In addition, communities with higher concentrations of $PM_{2.5}$ containing nickel, vanadium, and elemental carbon have been found to have higher risks of hospitalizations associated with short-term exposure to $PM_{2.5}$ (Cao Junji et al., 2012). Polycyclic aromatic hydrocarbons (PAHs) are a health-relevant component of $PM_{2.5}$ with a structure made of various configurations of two or more benzene rings (Kim et al., 2013). These particulates are formed from incomplete combustion of fossil fuels or other organic compounds (Mumtaz et al., 1996). PAHs also have detrimental human health effects due to their varying carcinogenic and mutagenic properties. These health effects include birth defects; DNA mutations; and lung, bladder, bone, brain, and scrotal cancers (Edokpayi et al., 2016). Significant amounts of PAHs have been found in both umbilical cord blood of newborn babies and the placental tissue of their mothers. These PAH residues have been found to cause damaged DNA in umbilical cord blood (Ravindra et al., 2001). PAHs and other organic molecules (hydrocarbons, thiols, mercaptans, ketones, and aldehydes) make up approximately 10 – 40 % of the $PM_{2.5}$ and PM_{10} mass of pollution in urban areas (Ravindra et al., 2001). Black carbon is another component of

$PM_{2.5}$. It is a solid form of mostly pure carbon that absorbs solar radiation at almost all wavelengths, and it is the most strongly light-absorbing component of particulate matter. Exposure to black carbon can cause harmful effects on the cardiovascular system, respiratory diseases, or premature death. (US EPA, 2016).

While the human health effects from exposure to $PM_{2.5}$ and its constituents are known, the mechanisms for how these effects occur is not fully understood. Oxidative stress is one hypothesized mechanism. Oxidative stress is an imbalance in the production of antioxidant defenses and the production of reactive oxygen species (free radicals) (Betteridge, 2000). Oxidative stress can lead to cell and tissue damage in the body like harmful effects on proteins, lipids, and nucleic acids. Oxidative stress can be responsible for the onset or progression of diseases like diabetes, metabolic disorders, atherosclerosis, cancer, or cardiovascular disease (Pizzino et al., 2017). The oxidative potential of a particle is the capability of that particle to create reactive oxygen species. The higher the oxidative potential of a particle, the more likely it will create the radicals that would create oxidative stress (Yadav & Phuleria, 2020).

In order to attribute health effects to specific sources of $PM_{2.5}$, it is important to know the composition of $PM_{2.5}$ (Dutton et al., 2009). ICP-MS (inductively coupled plasma - mass spectrometry) is one of the most effective methods for ascertaining the elemental composition of $PM_{2.5}$ (Manousakas et al., 2014). GC-MS (gas chromatography-mass spectrometry) is one of the most popular methods for determining the composition of organic molecules in $PM_{2.5}$ (Dutton et al., 2009). PAHs are a diverse class of organic molecules that can be quantified through GC-MS. PAH derivatives, which are formed in the same ways as PAHs, contain different functional groups, including hydroxy-PAHs, oxy-PAHs, and nitro-PAHs (Trine et al., 2019). PAHs that are found to have a molecular weight higher than 278 g/mol are called high molecular weight PAHs (HMW-PAHs) (Trine et al., 2019). The high molecular weight causes the compounds to shift from hydrophilic to lipophilic properties, leading to the absorption of HMW-PAHs in the gastrointestinal tract of humans and animals (Abdel-Shafy & Mansour, 2016). Black carbon concentrations can also be quantified using a non-destructive instrument called a SootScan. The analysis uses two wavelengths: 880 nm which is indicative of black carbon and 370 nm which is indicative of brown carbon. Enhanced optical absorption can indicate the presence of black or brown carbon. When these optical attenuation values are compared to a blank filter, the quantity of black carbon can be determined ("SOOTSCAN^{TM} MODEL OT21 OPTICAL TRANSMISSOMETER," n.d.). Because of the potential negative health effects on living things, it is important to develop methods to identify and quantify the different components found in $PM_{2.5}$.

In this study we analyzed the composition and oxidative potential of $PM_{2.5}$, specifically looking at $PM_{2.5}$ collected on 12 days from two areas in Mississippi, Gulfport and Hernando. The sampling days included September and November at each location. For oxidative potential both the methanol soluble and hexanes soluble (methanol insoluble) fractions were measured for oxidative potential. I hypothesized that higher black carbon concentrations will be observed at the Gulfport site in September compared to the other location, Hernando and the other sample month, November, and that higher oxidative potential will be observed in the methanol soluble fractions than in the hexane soluble fractions. Identifying how characteristics of $PM_{2.5}$ vary between days and locations will help establish methods for better understanding the associated health effects from these exposures.

Materials and Methods

1. *Obtaining Filters*

All control and $PM_{2.5}$ filters were donated from the Mississippi Department of Environmental Quality (MDEQ) from locations around the state (Table 1). The sample collection followed the Federal Reference Monitor program that is overseen by the United States EPA and all sample and control filters were 47 mm PTFE-coated filters (US EPA, 2016). At locations in both Hernando and Gulfport, Mississippi, 12 sample filters were collected on the same dates throughout the months of September and November of 2013. Date matched travel, field, and laboratory blank filters were included in this research, all blank filters did not have active collection of $PM_{2.5}$ onto them. The MDEQ provided detailed information for each sample and control including: sampler runtimes, flowrates, meteorological measurements (temperature, humidity), and notes regarding the sample collection.

Table 1: $PM_{2.5}$ Filter Collection Dates, Masses, and Concentrations from MDEQ Samples.

Filter ID	Date	Location	$PM_{2.5}$ mass (mg)	$PM_{2.5}$ conc. (µg/m^3)
T3651402	9/7/2013	Gulfport	0.507	21
T3651443	9/10/2013	Gulfport	0.355	14.7
T3651430	9/13/2013	Gulfport	0.324	13.5
T3651492	9/16/2013	Gulfport	0.291	12.4
T3651427	9/22/2013	Gulfport	0.186	7.7

T3651490	9/25/2013	Gulfport	0.232	9.6
T3651731	11/3/2013	Gulfport	0.213	8.8
T3651741	11/6/2013	Gulfport	0.197	8.2
T3651742	11/9/2013	Gulfport	0.259	10.7
T3651743	11/12/2013	Gulfport	0.306	14.6
T3651792	11/21/2013	Gulfport	0.376	15.6
T3651846	11/24/2013	Gulfport	0.172	7.1
T3651379	9/7/2013	Hernando	0.324	13.7
T3651444	9/10/2013	Hernando	0.443	18.4
T3651451	9/13/2013	Hernando	0.216	9
T3651459	9/16/2013	Hernando	0.202	10.9
T3651509	9/22/2013	Hernando	0.183	7.6
T3651518	9/25/2013	Hernando	0.187	7.7
T3651702	11/3/2013	Hernando	0.217	9
T3651697	11/6/2013	Hernando	0.181	7.5
T3651748	11/9/2013	Hernando	0.217	9
T3651756	11/12/2013	Hernando	0.127	5.2
T3651801	11/21/2013	Hernando	0.314	13
T3651802	11/24/2013	Hernando	0.176	7.3
T3651513	9/24/2013	Trip Blank (Hernando)	--	n/a
T3651508	9/20/2013	Field Blank (Gulfport)	--	n/a

1. *Black Carbon Analysis*

A Magee OT21 SootScan instrument, an optical transmissometer that analyzes two discrete wavelengths: 800nm (IR) and 370nm (UV), was used to measure the amount of

Black Carbon or “soot” collected on each filter. It also collected qualitative information about aromatic compounds. This information can be used to aid in finding potential fuel sources that contributed to the black carbon. A blank filter’s absorption was compared to each sample filter’s absorption. The difference between the two absorptions is known as “attenuation.” The standard operating procedures for the SootScan were detailed in and followed from the “Protocols for Magee OT21 SootScan.” The SootScan was first powered on. The static of each filter was removed by using an anti-static “gun” with the lid of the filter container removed. A blank filter was placed into the black slot of the filter tray, known as “position 1.” The blank was then analyzed. A sample filter was then placed into the front slot, “position 2.” The filter was then analyzed. This process was repeated in triplicate for all sample filters. Concentrations of black carbon were then determined by using precise sampler runtimes and flow rates with corrections based on the blank filter measurements.

2. *Filter Extraction*

Each filter was placed into a labeled 15 mL conical tube, and 8 mL of methanol was added. Each tube was sonicated for one hour in a water-bath sonicator (60 Hz). The filter was rinsed with 200 uL of methanol as it was removed from the tube to collect any residuals particles remaining on the filter. The resulting solution was then stored in -20°C until further use. Identical methods were used for all sample and control filters.

3. *Methanol Soluble and Hexane Soluble fractions*

The schematic for creating the methanol and hexane soluble fractions of $PM_{2.5}$ is detailed in Figure 1. A 0.5 mL aliquot of the $PM_{2.5}$ methanol solution was removed from the 15 mL tube and added to a 1.5 mL centrifuge tube. This tube was centrifuged at 13g for 5 minutes. The supernatant was removed and placed into another 1.5 mL tube labeled as methanol soluble fraction. This tube was then put into -20 degrees Celsius storage. The remaining pellet, that contained the particles and insoluble components of the sample were re-suspended in 0.5 mL of hexane to create the “hexane soluble fraction” (methanol insoluble fraction). This fraction was sonicated for 5 minutes and then the tube was centrifuged at 13g for 5 minutes. The supernatant was removed and placed in a new 1.5 mL centrifuge tube. This centrifuge tube was then placed in -20 degrees Celsius for storage. This process was repeated for all samples and controls and resulted in a methanol soluble and insoluble fraction for each filter that did not contain particles.

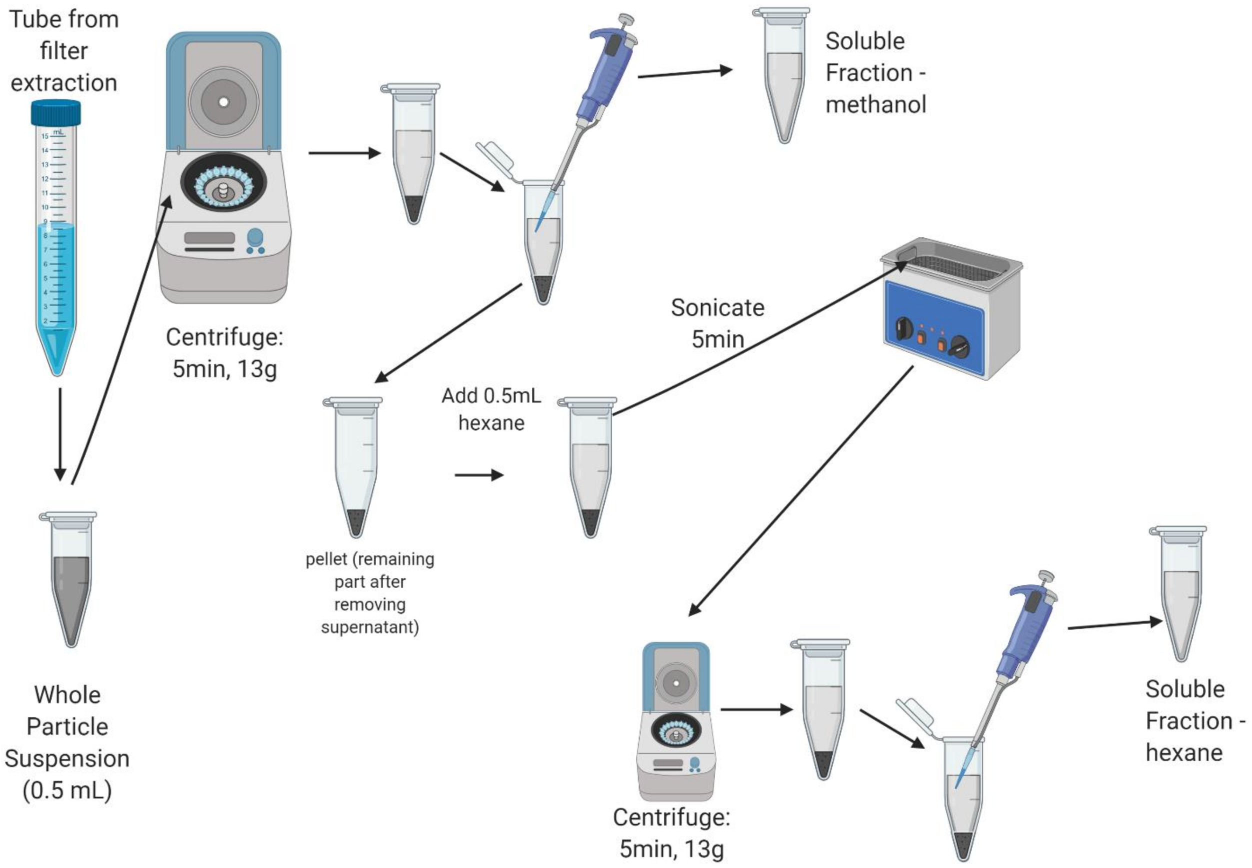


Figure 1: Generation of Methanol Soluble and Insoluble Fractions of $PM_{2.5}$. This schematic was created BioRender to demonstrate how the methanol soluble and insoluble fractions of $PM_{2.5}$ were collected for each sample and blank filters.

5. Oxidative Potential

Reagents were dissolved in specified solvents to produce the following stock concentrations.

i. DL, 1,4-Dithiothreitol (DTT) in Potassium Buffer (PB) at 5mM

ii. 5,5’-Dithiobis (2’-nitrobenzoic acid) (DTNB) in methanol at 10 mM

iii. Potassium Buffer (PB) in milli-q water at 0.05 M

DTT calibration curve: DTT dilutions in PB were created in 0.2 mL thin wall micro tubes in concentrations of 0, 0.2, 0.4, 0.6, 0.8, and 1 mM for the generation of a calibration curve. A DTT dilution for samples was also created in a 1.5 mL centrifuge tube at 0.5 mM. In a 96-well plate, 100 µL of 0.05 M PB was added into control, DTT curve, and sample wells. For the DTT curve, 5 µL of each DTT dilution was added in triplicate along with 5 µL of methanol to maintain equal volumes between all calibration curve and sample wells.

Controls: Three controls were used: PB run in triplicate (only PB), 0 mM DTT run in the curve (100 µL PB, 5 µL methanol or hexanes, 5 µL 0 mM DTT, and 10 µL DTNB) and a positive control (1µM 1,4-Napthoquinone).

Samples: Aliquots of the soluble methanol fractions for all filters were placed into wells at 5 µL, in triplicate. Following the addition of the sample, 5 µL of 0.5 mM DTT was added into each sample well. In total, each sample had 100 µL PB, 5 µL sample, and 5 µL 0.5 mM DTT. Additionally, blank filters (field, travel, lab) were placed into triplicate wells with the exact same procedures as the filter samples.

Plate Analysis: Once the calibration curve, controls, and samples were prepared a lid was placed on each 96-well plate and wrapped in foil. The plate was shaken on a vortexer for 2-3 seconds and then incubated at 37 °C for 20 minutes. After the incubation, 10 µL of 1mM DTNB was added to all wells, except the PB control wells. This quenches the reaction. The plate was shaken for 1 minute and then the consumption of DTT was read at 412 nm on a spectrophotometer. The calibration curve and absorbance values for the samples were used to calculate the DTT consumption for each sample run in triplicate. The DTT consumption was recorded as nm of DTT consumed/ reaction time in minutes/ m^3 of air, where the reaction time was 20 minutes and m^3 of air was 24 m^3 for the samples.

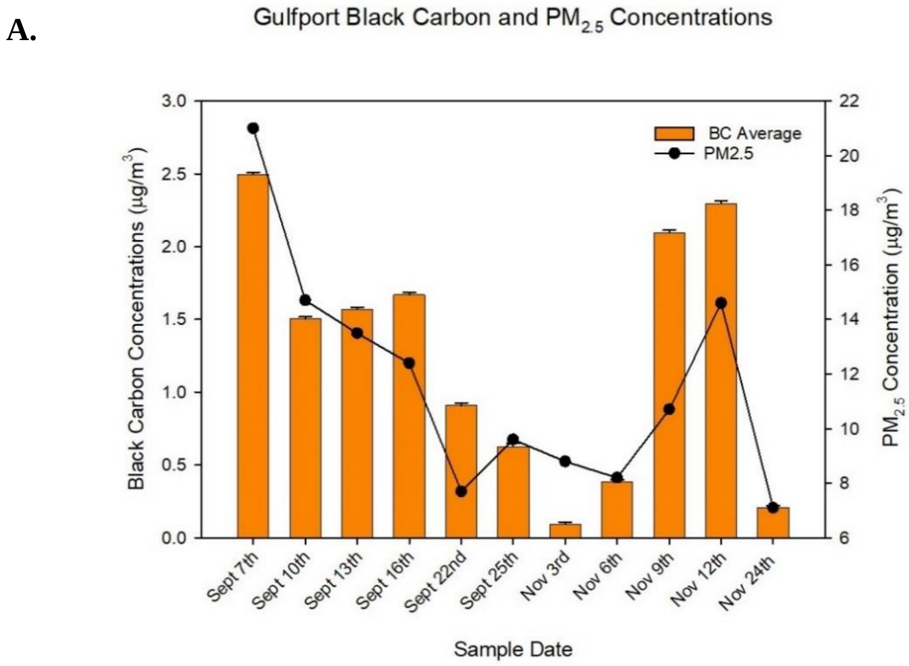
4. ***Statistical Analysis***:

All data analysis and figure generation were conducted in Excel and Sigmaplot (Version 14). All analyses were conducted in triplicate with blank filter corrections. One-way analysis of variance (ANOVA) tests was used with significance set at $p \leq 0.05$ for black carbon and the oxidative potential data. A two-way ANOVA test was used to compare between the month a sample was taken from and if it was whole particle solution or soluble fraction. Significance was also set at $p < 0.05$ for the two-way ANOVA test. Methods schematics were created using BioRender.

Results

1. Black Carbon

Black carbon concentrations were determined for each sample and compared between sample dates and $PM_{2.5}$ concentration (Figure 1). For the Gulfport location (Figure 1A), black carbon concentrations ranged from 0.0935 to 2.497 μg/m^3 over the 11 sample dates throughout September and November. Also at the Gulfport location (Figure 1A), the $PM_{2.5}$ concentrations ranged from 7.1 to 21 μg/m^3). For the Hernando location (Figure 1B), black carbon concentrations ranged from 1.459 to 3.119 μg/m^3 over the 11 sample dates throughout September and November. Also, at the Hernando location (Figure 1B), the $PM_{2.5}$ concentrations ranged from 5.2 to 18.4 μg/m^3.



B.

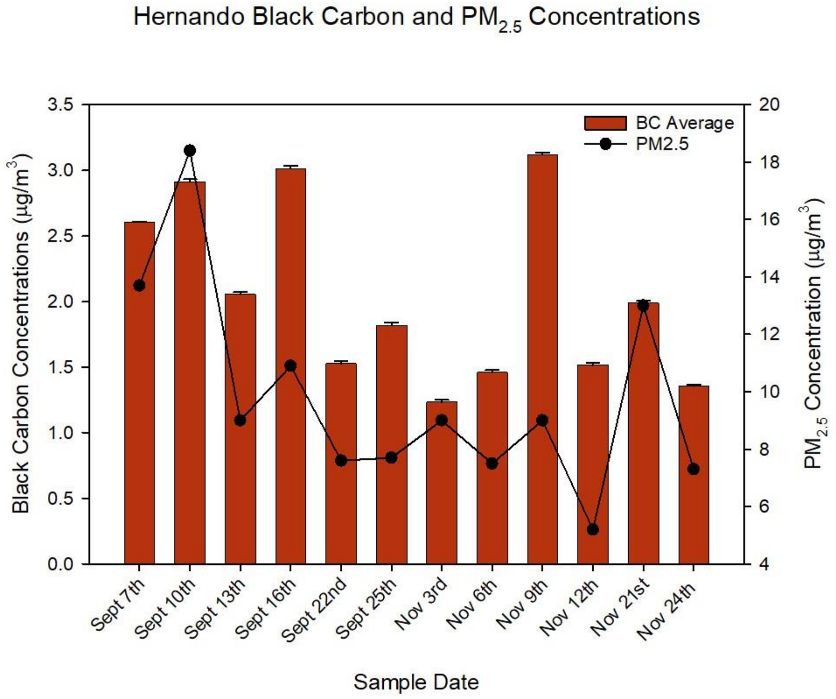


Figure 2. Black Carbon Concentrations for each sample compared between days in each month, and $PM_{2.5}$ Concentrations for each sample compared between days in each month. Black Carbon concentrations are reported ± standard deviations (sd) for A) Gulfport Black Carbon and $PM_{2.5}$ Concentrations and B) Hernando Black Carbon and $PM_{2.5}$ Concentrations.

Using the black carbon concentrations for each sample, the average concentrations for each month and location were determined (Figure 3). The black carbon concentrations were considerably larger in Hernando over both months. Also, black carbon concentrations were higher at both Gulfport and Hernando in September when compared to concentrations at the same location in November. However, even though the average black carbon concentration for Hernando was lower in November than in September, the November average was higher than the black carbon concentration of samples collected in Gulfport over both September and November.

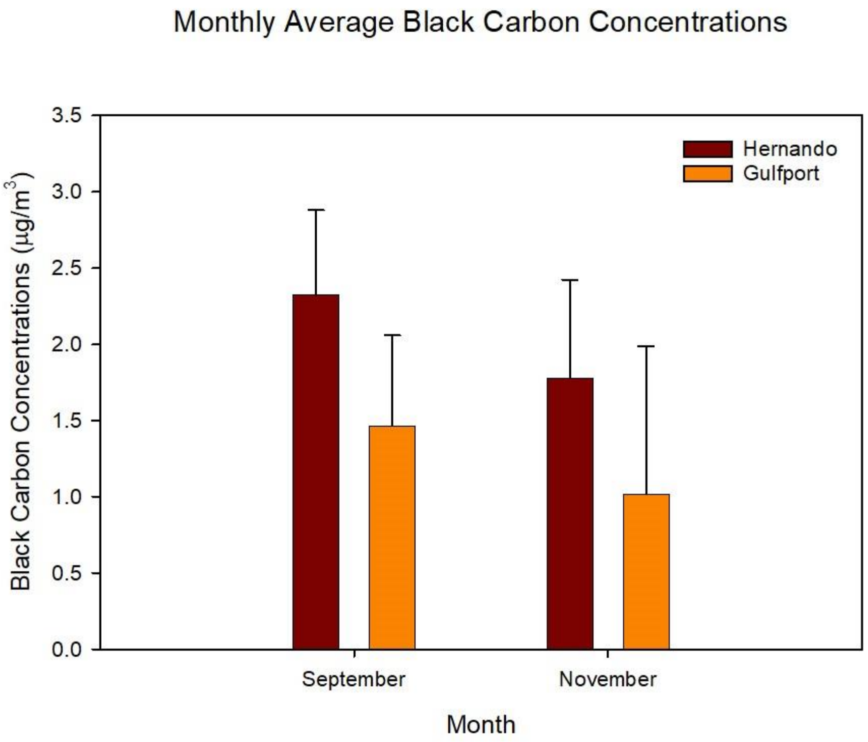
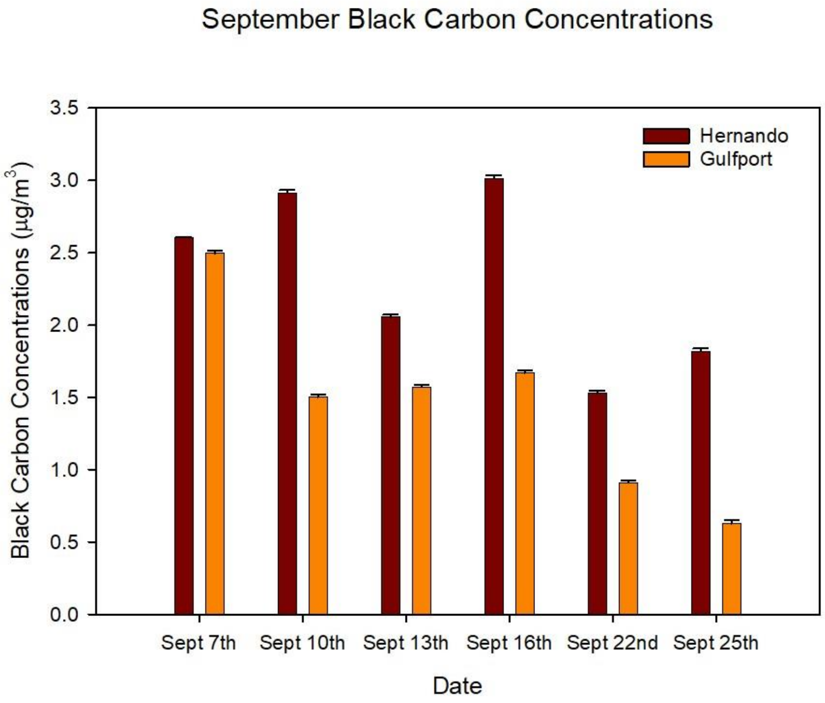


Figure 3. Average black carbon concentrations for the entire month compared between each month and sampling location. Averages are reported ± standard deviations (sd) for monthly black carbon concentrations with the number of sampling days for each month and location, September in Hernando (n=6), September in Gulfport (n=6), November in Hernando (n=6), and November in Gulfport (n=6).

Black carbon concentrations were determined for each sample and compared between the two locations, Hernando and Gulfport (Figure 4). For September, samples collected at Hernando had higher black carbon concentrations for every date in September. This trend continued during the month of November with the exception of November 12th, where the sample collected on this date in Gulfport had a higher black carbon concentration than the sample collected on the same date in Hernando.

A.


September Black Carbon Concentrations
Hernando
Gulfport
Black Carbon Concentrations (μg/m^3)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Sept 7th
Sept 10th
Sept 13th
Sept 16th
Sept 22nd
Sept 25th
Date

B.

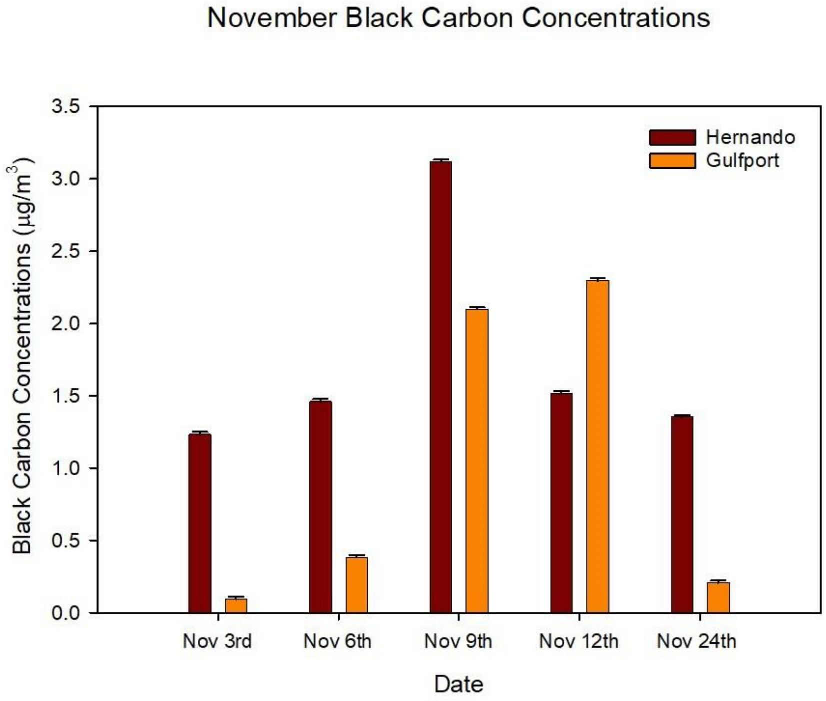
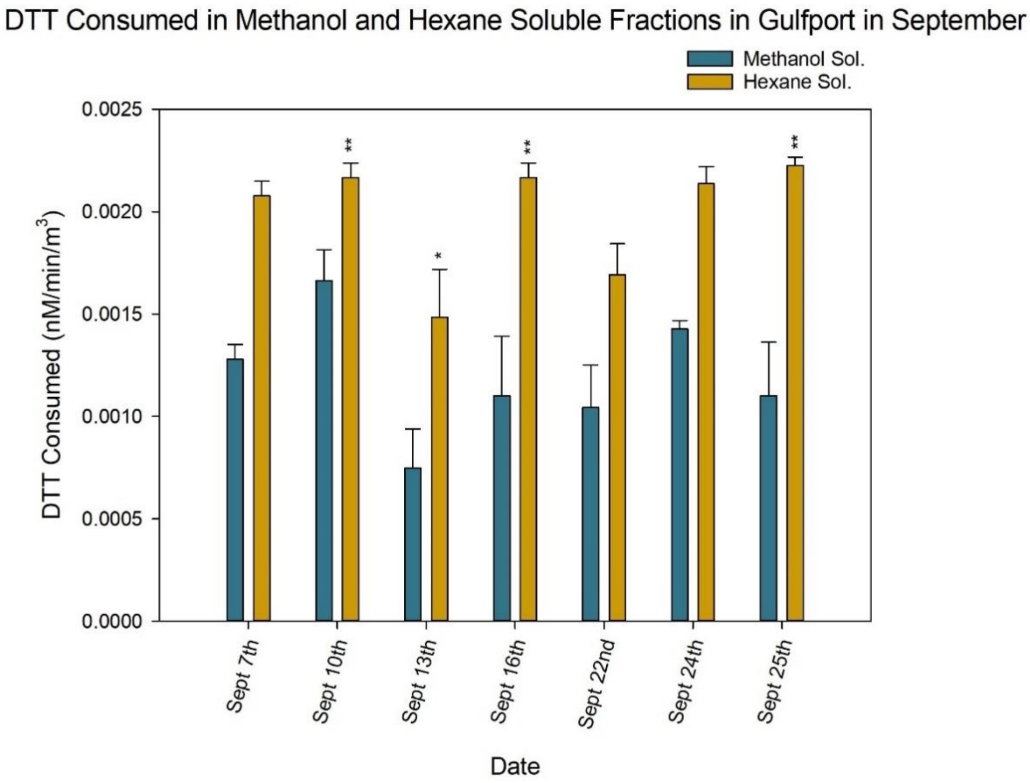

November Black Carbon Concentrations
Hernando
Gulfport
Black Carbon Concentrations (μg/m^3)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Nov 3rd
Nov 6th
Nov 9th
Nov 12th
Nov 24th
Date

Figure 4. Black Carbon concentrations for each sample date in November compared between the two separate locations. Black Carbon concentrations are reported ± standard deviations (std) for each sample date.

2. *Oxidative Potential*

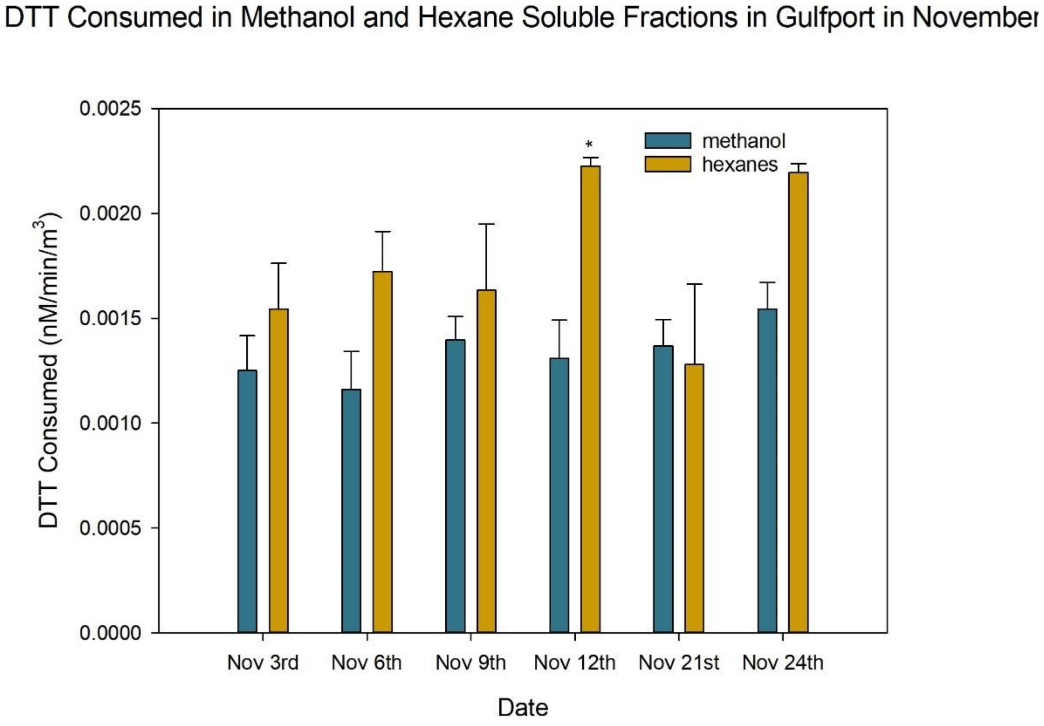
Oxidative potential was determined by calculating the DTT consumption (nm/min/m^3). A higher DTT consumption indicated a higher oxidative potential. The average amount of DTT consumed was determined for both the methanol and hexanes soluble fractions and compared across sample dates in September and November in Gulfport (Figure 5). For September (Figure 5A), there were significant differences between the methanol and hexanes soluble fractions on the following days: September 10th, September 13th, September 16th, and September 25th. The average amount of DTT consumed for Gulfport in September in methanol ranged from 0.000748 to 0.00166 nM/min/m^3 and from 0.001486 to 0.002225 nM/min/m^3 in hexanes. For November (Figure 5B), there was a significant difference between the methanol and hexanes soluble fractions on November 12th. The average amount of DTT consumed for Gulfport in November ranged from 0.00116 to 0.00155 nM/min/m^3 in methanol and from 0.00128 to 0.002225 nM/min/m^3 in hexanes.

A.



DTT Consumed in Methanol and Hexane Soluble Fractions in Gulfport in September

B.

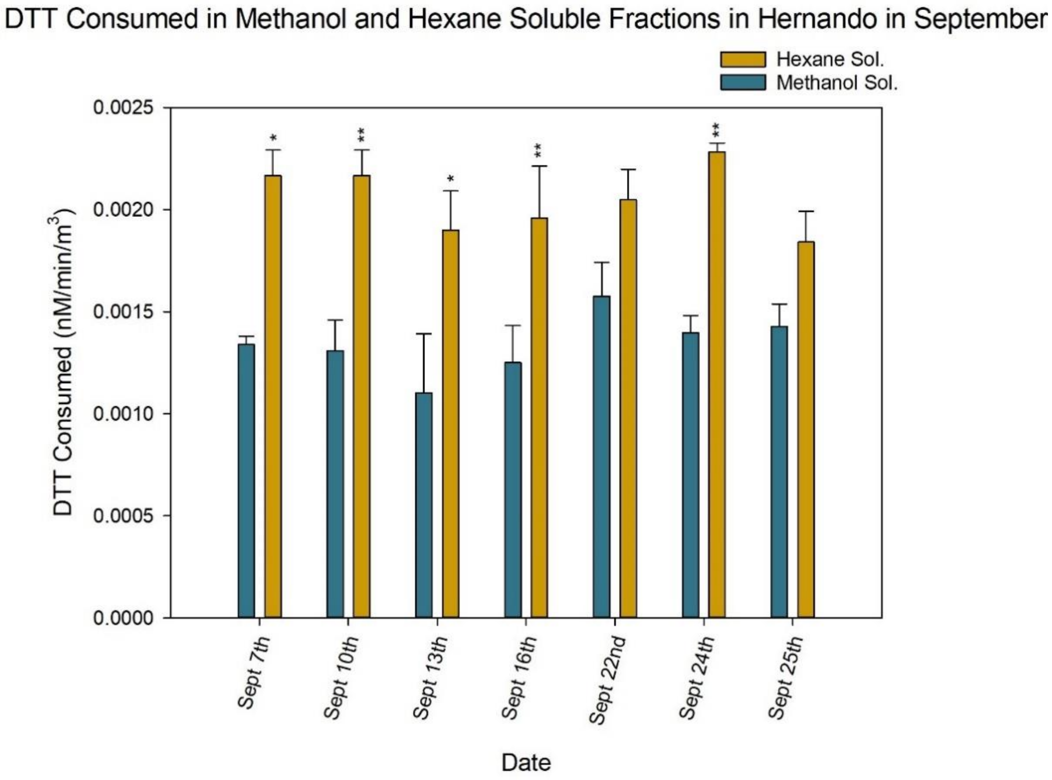


DTT Consumed in Methanol and Hexane Soluble Fractions in Gulfport in November

Figure 5. Average DTT consumed for each sample date compared between methanol soluble fractions and hexanes soluble fractions for Gulfport. Averages ± standard deviations (sd) for DTT consumed per reaction time and volume of air are reported for the methanol soluble and hexanes soluble fractions in A) September and B) November. Data for A-B were analyzed using a two-way ANOVA. Differences with a p value ≤ 0.05 were considered significant. Differences with a p value ≤ 0.05 were indicated with a single asterisk (*), and differences with a p value ≤ 0.01 were indicated with a double asterisk (**).

Oxidative potential was determined by calculating the DTT consumption (nm/min/m^3). A higher DTT consumption indicated a higher oxidative potential. The average amount of DTT consumed was determined for both the methanol and hexanes soluble fractions and compared across sample dates in September and November in Hernando (Figure 6). For September (Figure 6A), there were significant differences between the methanol and hexanes soluble fractions on the following days: September 7th, September 10th, September 13th, September 16th, and September 24th. The average amount of DTT consumed for Hernando in September in methanol ranged from 0.001102 to 0.001575 nM/min/m^3 and from 0.0019 to 0.002284 nM/min/m^3 in hexanes. For November (Figure 6B), there were no days with a significant difference between the methanol soluble fraction and hexanes soluble fraction. The average amount of DTT consumed for Hernando in November ranged from 0.001398 to 0.002107 nM/min/m^3 in methanol and from 0.001516 to 0.002137 nM/min/m^3 in hexanes.

A.


DTT Consumed in Methanol and Hexane Soluble Fractions in Hernando in September
Hexane Sol.
Methanol Sol.
DTT Consumed (nM/min/m^3)
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
*
**
*
**
**
Sept 7th
Sept 10th
Sept 13th
Sept 16th
Sept 22nd
Sept 24th
Sept 25th
Date

B.

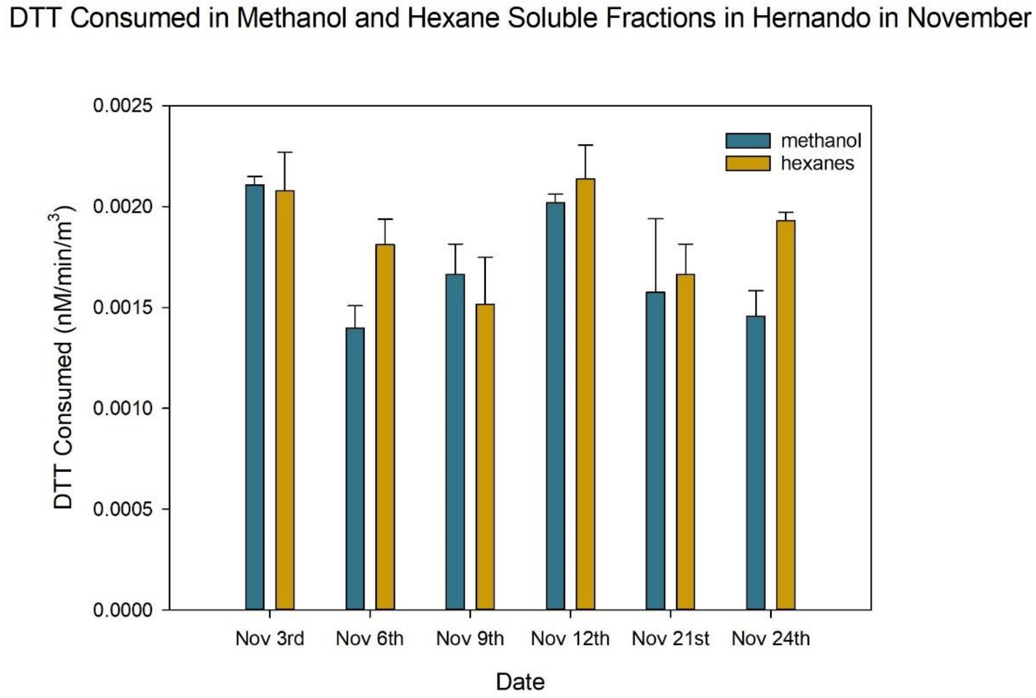
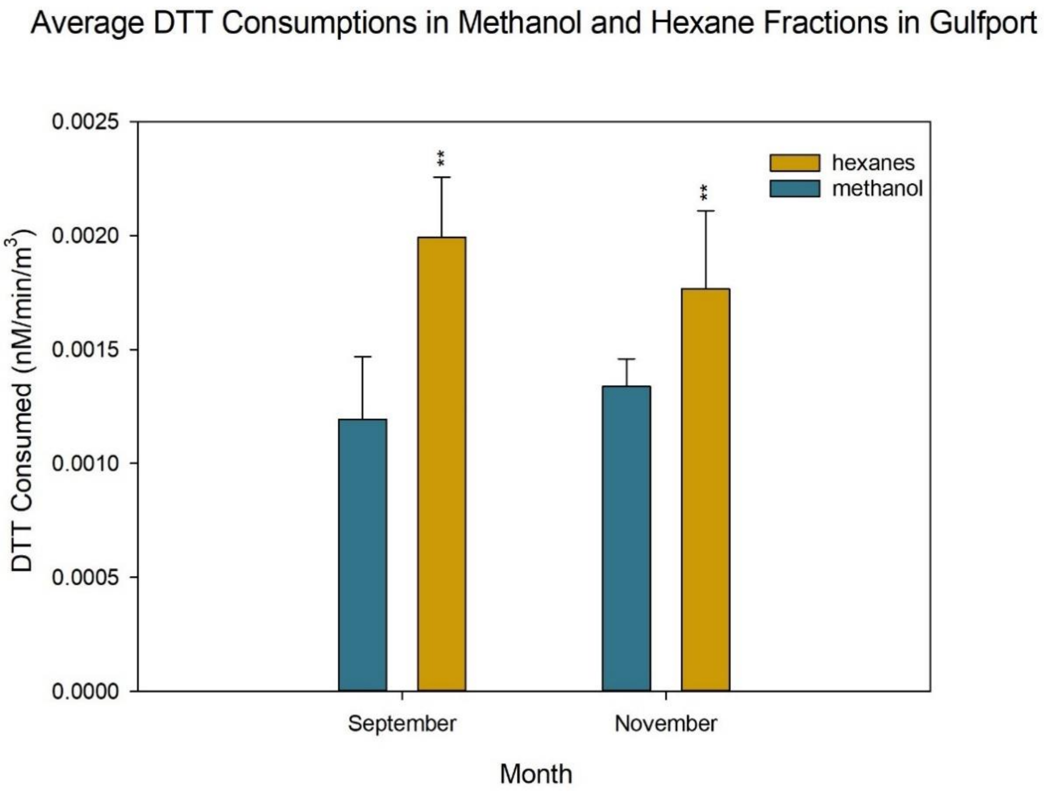


Figure 6. Average DTT consumed for each sample date compared between methanol soluble fractions and hexanes soluble fractions for Hernando. Averages ± standard deviations (sd) for DTT consumed per reaction time and volume of air are reported for the methanol soluble and hexanes soluble fractions in A) September and B) November. Data for A-B were analyzed using a two-way ANOVA. Differences with a p value ≤ 0.05 were considered significant. Differences with a p value ≤ 0.05 were indicated with a single asterisk (*), and differences with a p value ≤ 0.01 were indicated with a double asterisk (**).

The amount of DTT consumed was averaged for both months at both locations. These monthly averages were used to compare differences between methanol soluble and hexanes soluble fractions (Figure 7). In Gulfport, there is a significant difference between the DTT consumption averages for methanol soluble and hexane soluble fractions in both

September and November (Figure 7A). For Gulfport, the average DTT consumption for the methanol soluble fraction was higher in November than in September, while the average DTT consumption for the hexanes soluble fraction was higher in September than November. In Hernando, there is a significant difference between the DTT consumption averages for methanol soluble and hexane soluble fractions in both September and November. For Hernando, the average DTT consumption for the methanol soluble fraction was higher in November than in September, while the average DTT consumption for the hexanes soluble fraction was higher in September than November. This trend was consistent across both sampling locations.

A


Average DTT Consumptions in Methanol and Hexane Fractions in Gulfport
DTT Consumed (nM/min/m^3)
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
hexanes
methanol
**
**
September
November
Month

B.

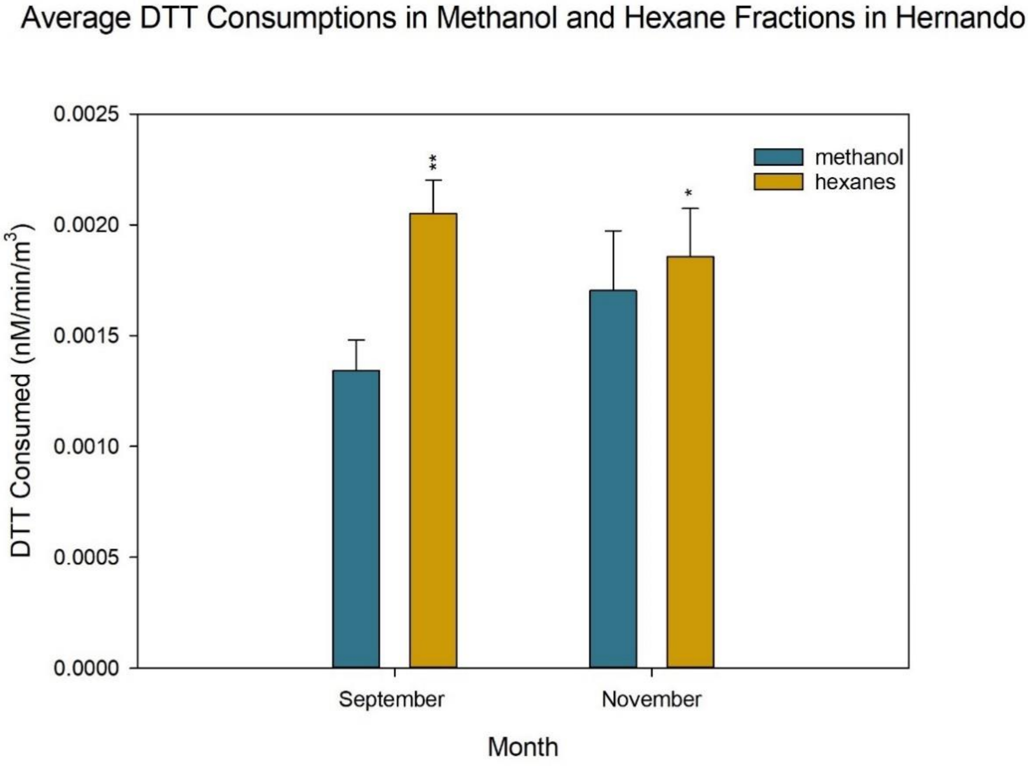


Figure 7. Average DTT consumed for each sample month compared between methanol soluble fractions and hexanes soluble fractions. Averages ± standard deviations (sd) for DTT consumed per reaction time and volume of air are reported for the methanol soluble and hexanes soluble fractions in A) Gulfport and B) Hernando. Data for A-B were analyzed using a two-way ANOVA. Differences with a p value ≤ 0.05 were considered significant. Differences with a p value ≤ 0.05 were indicated with a single asterisk (*), and differences with a p value ≤ 0.01 were indicated with a double asterisk (**).

Discussion

1.Black Carbon

Black carbon (BC) concentrations showed variation throughout dates in both September and November across both sampling locations, Hernando and Gulfport. At both locations, September samples had a higher black carbon average concentration, showing a decrease in black carbon concentration as the year progressed. Across both September and November, average black carbon concentrations were higher for the Hernando site than the Gulfport site. Black carbon concentrations were higher in Hernando for every sample date in September and November except for November 12th. November 12, 2013 fell the day after Veterans Day. The increase in black carbon concentrations may have been impacted by increased traffic and travel due to the holiday weekend. However, nothing definitive can be said. These results did not completely support my hypothesis that black carbon concentrations would be higher in Gulfport in September than other sample locations and months. The average black carbon concentration was higher in September than November for Gulfport, but the average black carbon concentrations were higher in Hernando than in Gulfport. A study done in Chungcheong Province, Korea for 8 months in 2015 to 2016 showed different results in relation to sampling months. This study found higher black carbon concentrations in November than September, which is the opposite of what was found in this study (Yu et al., 2019). The authors of the Chungcheong Province, Korea study documented a difference in wind patterns that aligned with the differences in black carbon concentrations. In September, there were as many south-easterly winds as westerly winds, but in November, there were more westerly winds. Westerly winds tended to transport Asian Dust, which likely contributed to the increase in the black carbon concentrations.

$PM_{2.5}$ concentrations showed similar trends compared to black carbon concentrations in Gulfport. For example, the date with the highest black carbon concentration, September 7th, also had the highest $PM_{2.5}$ concentrations. In Hernando, the $PM_{2.5}$ concentrations seemed to remain more constant and did not vary as much even when black carbon concentrations did. The same study in Chungcheong Province, Korea also tracked the relationship between black carbon concentrations and $PM_{2.5}$ concentrations. In this study, they found that the relationship between $PM_{2.5}$ concentrations and black carbon concentrations can vary based on the composition of $PM_{2.5}$ depending on the sources (Cha et al., 2019). This may explain why several dates in my project had variation between $PM_{2.5}$ concentrations and black carbon concentrations.

2.Oxidative Potential

Oxidative potential was analyzed for both methanol and hexanes soluble fractions for each sample date, and comparisons were made between sample dates, monthly averages, and locations. When analyzing oxidative potential for methanol soluble and hexanes soluble fractions, there were many dates in September where there was a significant difference in the DTT consumption for the two different fractions, four dates in Gulfport and five dates in Hernando. However, this number was greatly decreased in the month of November. There was only one sample from November across both locations to show a significant difference between the DTT consumption of the methanol and hexanes soluble fractions. This was November 12th in Gulfport. There were no significant differences in November in Hernando. In methanol, polar molecules dissolve, but nonpolar molecules would not. These nonpolar molecules that were not methanol soluble were dissolved in hexanes after the methanol soluble fraction was removed. In a study done in 2019 in China, they found that water-soluble potassium and water-soluble organic matter had negligible effects on oxidative potential. These two compound groups would be soluble in methanol. The study found that when compounds that would be soluble in hexanes were present, the oxidative potential values were higher (Brehmer et al., 2019). This aligns with the results in this study because the averages for oxidative potential were higher in the hexanes soluble fraction.

There were significant differences in the DTT consumption between sample months at both locations. In Gulfport, there was a significant difference between DTT consumption of the methanol soluble and hexanes soluble fractions in both September and November. This was also true of Hernando, where there was a significant difference between DTT consumption of the methanol soluble and hexanes soluble fractions in both September and November. In general, DTT consumption was higher in the hexane soluble fractions. This does not align with my hypothesis which was that oxidative potential (DTT consumption) would be higher in the methanol soluble fractions. In one study in 2018 in China, $PM_{2.5}$ composition and oxidative potentials were measured. In this study, they found that the composition of $PM_{2.5}$ varied based on the time of year which led to seasonal changes in oxidative potential (Yu et al., 2019). This is similar to the study because the oxidative potential varied between months with respect to each fraction. If the composition of $PM_{2.5}$ varies with the time of year, then the oxidative potential of each fraction would change as the composition of the fractions changed.

Future Directions

In future studies, it would be beneficial to include more sampling dates and locations to see if the trends observed in this study changed with location and date, or if they remained the same. To improve upon this study, elemental analysis should be performed on the samples to determine the elemental composition of the particulate matter, such as the composition and contribution of PAHs. PAHs and other organic molecules make up between 10 and 40% of $PM_{2.5}$ and are known to have mutagenic and carcinogenic properties. Because of their potential abundance and potential effects, this is a particularly important component of $PM_{2.5}$ to study. This analysis would be performed on both the hexane soluble and methanol soluble fractions to determine what causes the difference in oxidative potential between the two fractions.

Conclusions

In conclusion, this study found that black carbon concentration averages were higher in Hernando than in Gulfport. Also, the black carbon concentration averages were higher in September than in October. The hexane soluble fractions were found to have higher oxidative potentials than the methanol soluble fractions, and this was consistent over both locations. Overall, the results regarding $PM_{2.5}$ concentrations and black carbon concentrations did not fully support my hypothesis, but were generally supported by the results of other studies. My results regarding oxidative potential did not support my hypothesis. In order to definitively know what these trends should be and how $PM_{2.5}$ composition and concentrations affects the health of individuals; more research needs to be completed. However, regulations and monitoring for particulate matter should be prioritized. In conclusion, my project shows that the location and sampling date should be taken into consideration when studying $PM_{2.5}$ composition or concentration.

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