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Forest Management in Coastal Pine Forests: An Investigation of Prescribed Fire Behavior, Detrital Chemical Composition, and Potential Water Quality Impacts

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FOREST MANAGEMENT IN COASTAL PINE FORESTS: AN INVESTIGATION OF PRESCRIBED FIRE BEHAVIOR, DETRITAL CHEMICAL COMPOSITION, AND POTENTIAL WATER QUALITY IMPACTS

A Dissertation
Presented to
the Graduate School of
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Forest Resources

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by
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Accepted by:
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ABSTRACT

Prescribed fire, thinning, and mastication are common forest management practices implemented in southern pine forests. These practices affect ecosystem properties differently depending upon the intensity at which they are implemented. One ecosystem property of interest is the chemical composition of forest detritus, commonly referred to as the litter and duff. This material is largely responsible for the replenishment of organic resources into soils. It may also be a primary contributor to surface water quality. In this study we were given an opportunity to evaluate two long-term forest management strategies at two sites along the South Carolina coastal plain to determine their effects on forest detrital chemical composition and potential water quality: 1) frequent prescribed fire (annual and biennial) and 2) a combination of periodic prescribed fire (every 3-4 years) and singular implementations of tree thinning and understory mastication. Based upon our analyses, we confirmed that the prescribed fires implemented on these sites display the characteristics of low intensity, low severity surface fires. As such, fuel quantities decreased as a result of forest management at both sites. At one of our sites, the Tom Yawkey Wildlife Center in Georgetown, South Carolina, the chemical functional groups of forest detritus were not greatly altered by fire. Specific compounds within these groups may have been affected by fire, but returned to or fell below long-term unburned levels within one-year post-fire. On our other site, the Santee Experimental Forest, it appears that long-term forest management has altered overstory species composition and subsequently detrital chemical composition. At both sites, potential organic pollutants were reduced by the forest management practices. This reduction may be beneficial in terms of water treatment and human health. These results add to the long list of benefits noted in the literature for active forest management, particularly the benefits of prescribed fire.

ACKNOWLEDGMENTS

First, I would like to thank those that funded this project and supported our work through the use of their equipment. This research was made possible through funding provided by the United States Joint Fire Science Program. The USDA Forest Service Southern Research Station Research Work Unit 4156 provided the thermocouples and dataloggers used to assess fire behavior during the prescribed burns in both 2015 and 2016. Without these contributions of money and equipment, this research would not have been possible.

Next, I would like to thank those that served on my doctoral committee: Drs. Alex Chow, Don Hagan, Geoff Wang, and Billy Bridges. Without their input, collaboration, and encouragement, none of this work would have been possible. I am extremely grateful to Dr. Don Hagan for the many hours he spent reviewing this document. His advice and encouragement to “stay the course” through the writing and editing process was extremely valuable. I also want to note that working alongside Dr. Alex Chow has truly been a rewarding experience. Throughout the course of this project, he has afforded me opportunities to excel in the areas in which I have already shown proficiency. He has also challenged me to learn new skills and techniques and has invested many hours of his own time teaching me those things. His intellect, experience, inquisitiveness, and calm demeanor are truly gifts to the scientific community, Clemson University, and the Baruch Institute of Coastal Ecology and Forest Science. I am very humbled by his friendship and I am equally honored to have him as a mentor.

I would also like to acknowledge Dr. Tom Waldrop. In 2001, I first heard Tom talk about prescribed fire in Table Mountain Pine communities during Clemson's Forestry Summer Camp. His passion for and knowledge of fire ecology literally "ignited" something in me that I have not been able to suppress. I was very fortunate to have Tom serve on my graduate committee as a master's student and I am grateful for all that he taught me on an academic and scientific level. Further upon life's journey now, I believe I am most grateful for the steadfast friendship he has provided. I would not have returned to academia without his encouragement and support. Much of what is represented in this work is a product of his investment in me for over 15 years, so for that I am truly humbled and grateful.

Mr. Jamie Dozier and all of the South Carolina Department of Natural Resources staff at the Tom Yawkey Wildlife Center in Georgetown, South Carolina deserve an immense amount of credit for allowing us to be on their property and conduct our prescribed burns. Jamie is truly one of the nicest and most knowledgeable professionals I've worked with and I am indebted to him for his continual support of this project. Several people spent a great deal of time with me at Yawkey collecting pre- and post-fire samples and I would like to thank them for their hard work, friendship, and good conversation: Mary-Frances Rogers, David Miller, Brian Williams, and Jennie Untener. Rob O'Neal and Ryan Marsh offered a great amount of support for the work completed on the Santee Experimental Forest and I am thankful for their efforts, as well. I would also like to thank Ms. Deanna Ruth and the Forest Protection students at Horry-

Georgetown Technical College for their assistance in the field and for allowing me to teach them about fire ecology during their laboratory sessions at Yawkey.

When asked how one completes a Ph.D. project, a good dose of Bruce Springsteen should be mentioned at the top of the list of essentials. Bruce Springsteen and the E Street Band's live performance in Chicago from January 19, 2016 sustained countless hours of analyses, writing, and editing. Thanks, Boss, for your passion, energy, drive, and contagious lyrics.

I am indebted to my family for innumerable reasons, but as I think back intentionally about this work over the last 2+ years, I am particularly grateful for a few, specific things. First, I would like to thank my mother- and father-in-law, Ken and Cheryl Berry, for allowing us to live with them during our transition from the mountains to the coast in the fall of 2014. They sacrificially allowed 5 individuals to overtake their home for 3 months and they still, amazingly, maintain steadfast love for us today. I must say that is quite a feat and is truly appreciated more than words can describe. I would also like to thank my parents, Keith and Karen Coates, for their regular visits to see us at the beach, for their assistance helping us move multiple times, and for their encouragement to pursue my dreams regardless of the circumstances. I would also like to thank my little gems, Sam, Kate, and Natalie, for being the best children a dad could ever dream to father. I am in awe of your spirit, love, generosity, and resilience. You fill my heart in ways that are unexplainable and I will forever be inspired to be and do my best because I want to make you proud. I hope this work, along with my parental guidance, inspire each of you to go, be, and do all that your heart desires.

Last, but not least, I would like to thank my wife, Erica Berry Coates, for being the best person I know and for joining me on this adventure we have called life now for 13 years as husband and wife. This accomplishment is made possible through your partnership, support, and encouragement. Thank you for loving me and for joining me on this adventure as we, in the words of Teddy Roosevelt, have “dared greatly.” I dedicate this work to you, my dear, and I love you enough that I will not require you to read the entire document.

> “It is not the critic who counts, not the man who points out how the strong man stumbled, or where the doer of deeds could have done them better. The credit belongs to the man who is actually in the arena; whose face is marred by dust and sweat and blood; who strives valiantly, who errs and comes up short again and again; who knows the great enthusiasms, the great devotions, and spends himself in a worthy cause; who, at best, knows in the end the triumph of high achievement; and who, at the worst, if he fails, at least fails while daring greatly, so that his place shall never be with those cold and timid souls who know neither victory nor defeat.” – Teddy Roosevelt

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CHAPTER ONE

INTRODUCTION

Forest harvesting and fuel reduction techniques, such as prescribed fire and mastication, are common forest management practices (Waldrop & Goodrick, 2012). These practices are continually evaluated for their impacts on the environment, influence on sustainability, and potential harm to humans. Coastal pine forests of the southern United States are no exception to this evaluation. Although much is known about the effects of these practices in these ecosystems, much is still left to be learned (Callaham et al., 2010).

One potential impact of prescribed fire is the production of black carbon (DeLuca & Aplet, 2008). Black carbon is classified as a continuum of products resulting from the incomplete or partial combustion of woody material and fossil fuels (Goldberg, 1985). It's presence in the environment ranges from soot found in the atmosphere, which can be subsequently deposited through precipitation events to Earth's surface, to charcoal found at or below Earth's surface (Masiello, 2004). The particulates in the atmosphere are monitored and measured as aromatic and polycyclic aromatic hydrocarbons (PAHs) by the Environmental Protection Agency (EPA) and many other entities around the world as a result of fossil fuel and biomass burning (Sommers et al., 2014).

Most of what is known relative to black carbon and PAH production is related to that portion of black carbon released into the atmosphere (Sommers et al., 2014). Studies suggest that black carbon in this form may alter air quality and adversely affect human health (Tobias et al., 2014). It is also understood that chemicals such as PAHs contaminate source waters that are treated and used for human consumption (Forbes et al., 2006; Abdel-Shafy & Mansour, 2016). Soot black carbon is a key contributor to global climate change due to its properties to absorb both light and heat (Goldberg, 1985). Alternatively, black carbon may be advantageous in soils as a source for long-term carbon sequestration (DeLuca & Aplet, 2008) and some researchers suggest black carbon may enhance soil cation exchange capacity (Liang et al., 2006).

Less is known about black carbon's characteristics as one observes it in its larger forms, such as those that remain on the ground following both naturally-occurring and anthropogenic wildland fires (Callaham et al., 2010). Land managers, foresters, and landowners utilize prescribed fire and other forest management practices for a host of reasons in longleaf and loblolly pine forests, including wildlife habitat management, timber production, and aesthetics (Waldrop & Goodrick, 2012).

It is well documented that prescribed fire behavior (i.e. peak burning temperature and duration of heating) is highly variable, not just in the context of pine systems (Bova & Dickinson, 2008). Fire behavior fluctuates because of differences in factors such as:

- Fire weather (wind speed and direction; ambient temperature; relative humidity)
- Firing technique (head fire, backing fire, spot fire, etc.)
- Fuels (fuel type, amount, structure, moisture content)
- Topography (Waldrop & Goodrick, 2012)

Fire weather variables differ, not only within a given day, but also day-to-day, week-to-week, season-to-season, etc. (Keeley, 2009). This creates difficulty when one seeks to define how fire might affect an ecosystem property, such as black carbon production and the chemical composition of the forest soil O Horizon, here referred to as forest detritus.

Given these factors, a large grant was obtained to investigate the implications of prescribed fire and other forest management practices on black carbon production, forest detrital chemical composition, and water quality in coastal forests of South Carolina. Chapter 2 discusses our attempt to determine the best methods for obtaining fire behavior estimates. This assessment was conducted to better understand how thermocouple-derived metrics might be affected by alterations in burning frequency and season. Chapter 3 discusses alterations in forest fuel mass and detrital chemistry as a result of burning in a frequently burned, longleaf pine forest at the Tom Yawkey Wildlife Center in Georgetown, South Carolina. Chapter 4 discusses alterations in detrital chemical composition and potential changes in water quality resulting from prescribed fire, mastication of understory vegetation, and thinning in a coastal, forested watershed on the Santee Experimental Forest of the Francis Marion National Forest in Cordesville, South Carolina. In Chapter 5 we compile the results of these studies for an integrated view of how forest management practices at these two sites has affected fuel quantity, detrital chemical composition, and potential water quality. Preliminary results to address additional questions are also presented and discussed in Chapter 5.

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CHAPTER TWO

THERMOCOUPLE ORIENTATION AFFECTS PRESCRIBED FIRE BEHAVIOR ESTIMATION

Abstract

Understanding the relationship between fire intensity and fuel mass is essential information for scientists and forest managers seeking to manage forests using prescribed fires. Peak burning temperature, duration of heating, and area under the temperature profile are fire behavior metrics obtained from thermocouple-datalogger assemblies used to characterize prescribed burns. Despite their recurrent usage in prescribed burn studies, there is no standard protocol established to guide the orientation of thermocouple installation. Our results from dormant and growing season burns in coastal longleaf pine forests in South Carolina suggest that thermocouples located horizontally at the litter-soil interface record significantly higher estimates of peak burning temperature, duration of heating, and area under the temperature profile than thermocouples extending 28 cm vertically above the litter-soil interface ($p<0.01$). Surprisingly, vertical and horizontal estimates of these measures did not show strong correlation with one another ($r^2 \leq 0.14$). Distinction of differences for these fire behavior metrics varied as a result of burning season based upon thermocouple orientation ($p<0.01$–0.97), as well. Pre-fire fuel mass, pre-fire fuel depth, and post-fire residual detrital (litter and duff) mass were not significant predictors of any fire behavior metrics, regardless of thermocouple orientation ($r^2 \leq 0.29$). Based upon these findings, we encourage scientists, researchers, and managers to carefully consider the orientation of thermocouples when investigating prescribed fire

behavior metrics as orientation may affect values and any distinction of fire treatment effects.

Introduction

Peak burning temperature (PBT) is a common measure used to describe prescribed fires (Keeley, 2009; Wotton et al., 2012). Many methods and techniques have been developed and tested to measure PBT, including pyrometers and calorimeters (Iverson et al., 2004; Kennard et al., 2005; Wally et al., 2006). Another common method involves the use of thermocouple probes attached to datalogger units. These dataloggers can be programmed to record temperature throughout the duration of a burn. Because they log temperature over an interval of time, some researchers suggest that the total duration of heating (DOH), or the amount of time the datalogger records temperatures above ambient temperature, can be just as useful, if not more useful, as a descriptor of fire behavior (Keeley, 2009; Dayamba et al., 2010). Area under the temperature profile (AUTP) can be calculated with these units as well by multiplying the change in temperature as a result of heating by the DOH (Kennard et al., 2005; Wenk et al., 2011).

Some scientists question the usefulness of the data thermocouples record (Bova & Dickinson, 2008). Peak burning temperature, for example, is questioned because it is largely dependent upon the metal used in creating the thermocouple (Kennard et al., 2005). The diameter, length, and orientation of the thermocouple are all important items to consider that may influence thermocouple readings (Dayamba et al., 2010). Thermocouple values have been shown to vary widely from flame-to-flame as a result of their metallurgical properties (Bailey & Anderson, 1980; Bova & Dickinson, 2008). It is also suggested that PBT is only a loose surrogate to describe fire intensity (Kennard et al., 2005) and thermocouple DOH values may be greatly affected by thermocouple diameter (Bova & Dickinson, 2008). Technological advancements greatly favor hyperspectral methods and other strategies to better estimate heat release, fire intensity, and other estimates of fire behavior that may be related to fire's effects on ecosystems and fire danger ratings (Roberts et al., 2003). Despite these criticisms, the inexpensive cost of thermocouples along with their ability to determine DOH make them a tool of choice for fire-related research, particularly in situations where fuel types are similar (Bova & Dickinson, 2008).

Few studies utilizing thermocouples to estimate these fire behavior metrics have investigated how differences in thermocouple orientation (vertically above the litter-soil interface or horizontally at the litter-soil interface) might affect value estimation. Dayamba et al. (2010) found that differences in orientation existed when burning was conducted at different times during the fire season in a Sudanese savanna-woodland. In early fires (December), PBT and DOH were highest and longest 20 cm above the soil surface, but that result was opposite in mid-season (mid-January) and late-season (end of March) fires as PBT and DOH were highest and longest at the ground surface. In contrast, Franklin et al. (1997) found that PBT was highest at the litter-soil interface as opposed to some distance aboveground in upland *Quercus* communities.

Thermocouple orientation became an important item of consideration as we sought to investigate potential differences in fire behavior resulting from alterations in fire frequency and season in coastal longleaf pine forests. We had difficulty determining which orientation might provide the most reliable and useful estimates of PBT, DOH, and AUTP. We decided to install thermocouples in both directions: vertically (extending 28 cm above the litter-soil interface) and horizontally (at the litter-soil interface) to see if thermocouple orientation affects fire behavior estimation and which orientation is most related to pre- and post-fire measures of fuel loading.

Our hypotheses were: 1) The parameters obtained from horizontal thermocouples are different than their vertical counterparts but there should be correlation among the parameters; 2) Pre-fire fuel loading and depth and post-fire detrital mass (litter + duff) will be significantly related to the fire behavior metrics with both orientations ($r^2>0.50$).

Materials and Methods

Study design

This study was conducted at the Tom Yawkey Wildlife Center in Georgetown, South Carolina (33.23°N, -79.22°W). The forest in the preserve has been managed with prescribed fire since 1978 and the predominant tree species present on these sites were longleaf pine (*Pinus palustris* Miller), loblolly pine (*Pinus taeda* L.), turkey oak (*Quercus laevis* Walter), and sweetgum (*Liquidambar styraciflua* L.). Six units, 1-2 ha in size were selected for burning in 2015: three to be burned during the dormant season and three to be burned during the growing season. Each of these areas was previously burned in 2014, 2013, and an additional five to eight times since 2004.

In each burn unit, a 300 m transect was established. Every 25 m, thermocouples were installed (see next section). Every 50 m, down and dead woody debris mass was determined using Brown's Planar Intercept Method (Brown, 1974) as modified by

Stottlemyer (2004). Down and dead woody debris greater than 7.62 cm (3 in) in diameter was not altered due to burning at these sites. The mass of this material is not included in our results or discussion.

Litter mass was determined at each plot within our burn units using one 0.30 x 0.30 m (1 ft x 1 ft) destructive sample obtained 1 m opposite of the middle transect azimuth. The sum of woody fuel mass (1-hr, 10-hr, and 100-hr fuels) and litter mass was tallied as one combined measure for total fuel load (Table 2.1). Heights of down and dead woody material and litter depth were visually measured using a 0.30 m (1 ft) ruler at 3.66 m (12 ft), 7.62 m (25 ft), and 12.19 m (40 ft) along each transect (Stottlemyer, 2004). Height of elevated down and dead woody debris was measured from the bottom of the litter layer to the highest intersecting woody fuel particle occurring within 0.30 m segments of the sampling plane for each transect. Litter depth was measured from the mineral soil surface to the top of the litter layer. Because of the frequent burning present on these sites, duff was rarely present but when it was present, it was included in the tally of litter. Post-burn detrital mass was determined similarly to pre-burn litter mass at each plot using one 0.30 x 0.30 m destructive sample obtained 2 m opposite of the middle transect azimuth used to establish Brown’s Transects. Post-burn detrital samples were collected within 48 hours after prescribed fires were implemented.

Thermocouple installation

Two Type K Thermocouples (4.8 mm diameter, 30 cm length) were connected to HOBO dataloggers (Onset Computer Corporation, Bourne, MA, USA) and were installed at 12 locations approximately 25 m apart yielding 24 thermocouples per burning

Table 2.1. Fuel loads (Mg ha^{-1}), soil moisture contents, fuel moisture contents, and fire weather data associated with annual dormant and annual growing season burns in 2015 at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA. * = Fuel Load calculated as the sum of litter mass, 1-hr fuel mass, 10-hr fuel mass, and 100-hr fuel mass

Season	**Fire Date**	**Fuel Load* (Mg ha^{-1})**	**Soil Moisture % (0-10 cm)**	**Fuel Moisture %**			**Fire Weather**		
				Litter	**Down & Dead Woody**	**Live Fuels**	**Ambient (^{o}C)**	**RH (%)**	**Wind Speed (km/h)**
Annual Dormant	**March 9**	11.1±2.0	24.6	45.8	38.4	181.4	18	74	6.9
	March 10	19.1±1.8	43.5	11.4	18.3	94.3	27	60	4.8
	March 11	20.6±2.2	8.9	35.9	36.5	148.4	26	70	8.2
Annual Growing	**May 5**	8.6±0.4	9.7	2.6	17.7	72.1	24	55	3.2
	May 5	10.0±0.4	17.6	2.6	3.8	40.3	30	48	5.4
	May 6	19.0±1.4	11.1	4.2	10.1	92.7	28	52	5.3

replication. At each location, a hole was dug and the dataloggers were individually placed in bags and buried, leaving the thermocouple probes outside the hole. The HOBO dataloggers were programmed to detect temperature on a 5 s interval prior to and throughout the duration of burning using HOBO BoxCar Pro 4.3 (Onset Computer Corporation, Bourne, MA, USA) as the programming software. Once the fires were extinguished, thermocouples and dataloggers were collected and removed from the field. PBT was noted and recorded for each unit. DOH was calculated for each individual dataset by determining the ambient temperature prior to burning and subsequent escalation above and return to that ambient temperature. AUTP was then calculated as the difference in heating temperature and ambient temperature multiplied by the number of seconds from DOH.

Fire implementation

Burning took place in the dormant season blocks on March 9-11, 2015 and in the growing season blocks on May 5-6, 2015. Prior to the day of the burns, down and dead woody debris, soils (0-10 cm), and live understory vegetation were sampled in three locations in each of the burn units to determine the pre-fire moisture content of each parameter. Wet mass (g) was obtained in the field using a portable, battery-operated scale. The woody fuels, soils, and live vegetation were then taken back to the lab and were oven-dried at 70°C for not less than 48 hrs. Moisture content of fuel was equal to [((wet mass – dry mass)/dry mass) x 100%]. Relative humidity and wind speed were measured before and during the burns using a Kestrel 3000 Pocket Wind Meter

(KestrelMeter, Birmingham, MI) (Table 2.1). These burns were headfires and flame lengths in all fires averaged 0.3 – 1 m (personal observation).

Statistical analyses

Matched pair t-tests were used to determine differences in mean PBT, DOH, and AUTP based upon thermocouple orientation. Simple linear regression analysis was used to determine relationships among the thermocouple orientations. Differences in mean PBT, DOH, and AUTP as a result of burning season were additionally determined using t-tests. Results shown in the following text are based on original scale variables, t-tests, and simple linear regression (as no complex regression models improved our correlations). All statistical calculations were conducted using JMP® (Version 12, SAS Institute Inc., Cary, NC, USA).

Results

Thermocouple orientation

A typical time-temperature heating curve generated from the thermocouple-datalogger assemblies at each of the burning locations is shown in Figure 2.1. Visually it appears that the horizontal thermocouples heated to a higher temperature quicker and remained above ambient temperature for a longer period of time. Statistically this was confirmed using data obtained from all of the thermocouple-datalogger assemblies as shown in Figure 2.2. Values for PBT, DOH, and AUTP were all significantly greater using the horizontal thermocouples ($p<0.01$).

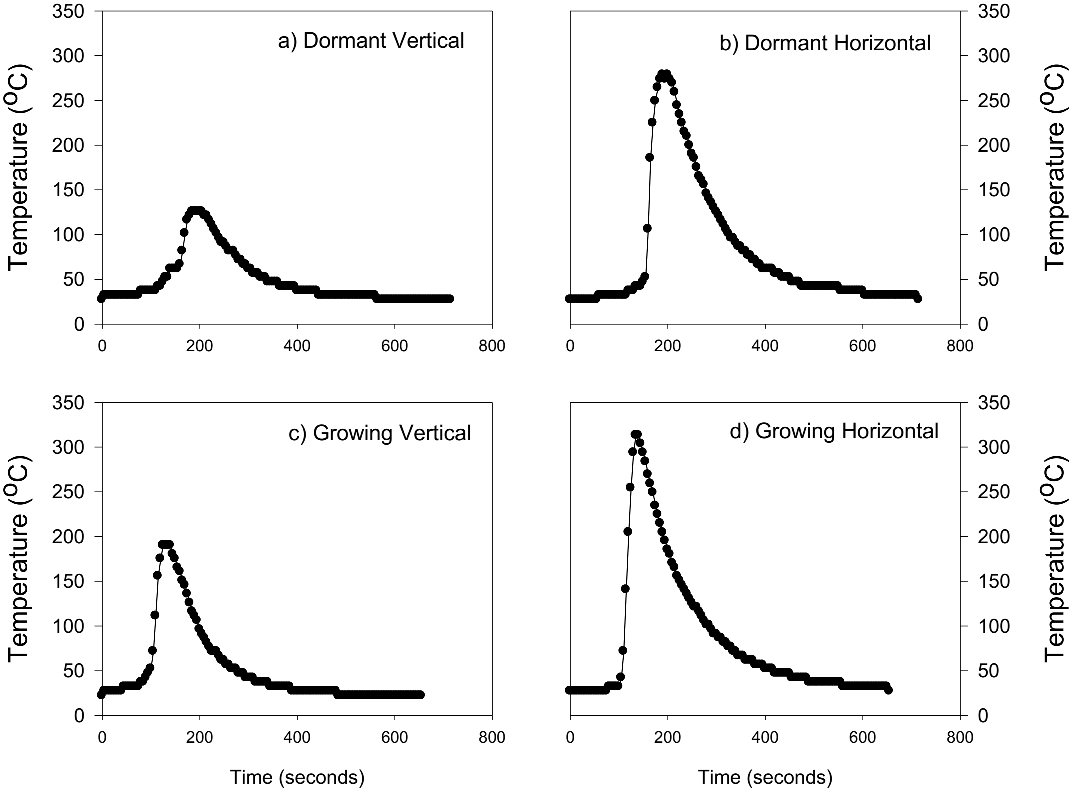

Figure 2.1 Examples of temperature data recorded every 5 seconds during prescribed burns in the dormant (a and b) and growing (c and d) seasons using vertical (a and c) and horizontal (b and d) thermocouples at the Tom Yawkey Wildlife Center in Georgetown, South Carolina, USA.

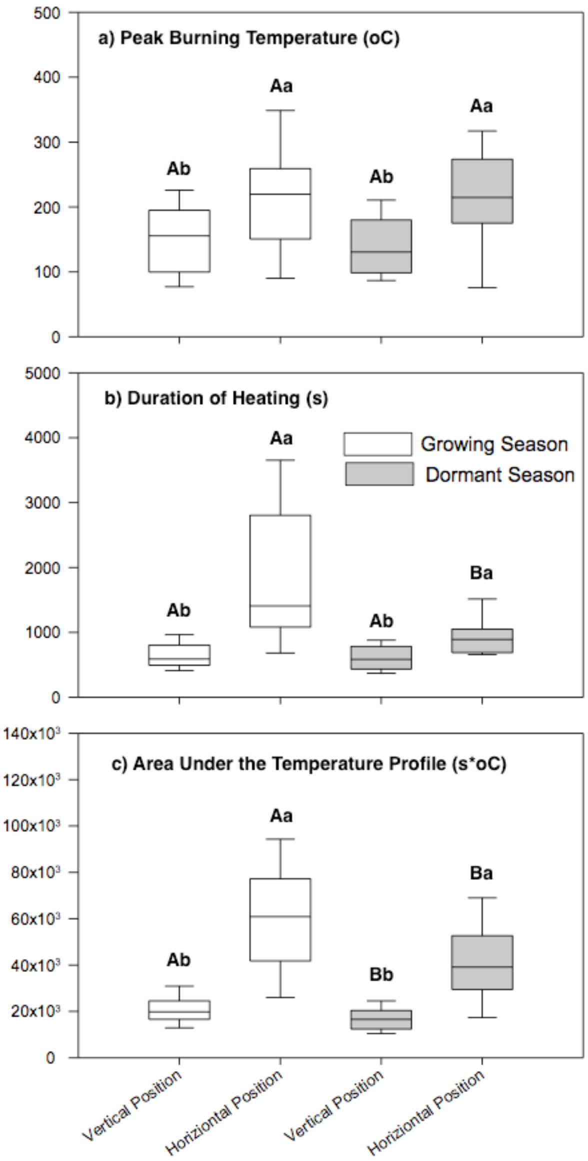

Figure 2.2. Ranges and means for peak burning temperature (a), duration of heating (b), and area under the temperature profile (c). Large letters indicate differences based upon burning season; small letters indicate differences based upon thermocouple orientation.

Using simple linear regression analysis, we also observed that vertical values of PBT, DOH, and AUTP were not significant predictors of their horizontal counterparts (PBT $r^2 \leq 0.13$; DOH $r^2=0.03$; AUTP $r^2 \leq 0.14$).

Burning season

Figure 2.2 additionally displays the ranges and means of PBT, DOH, and AUTP as a result of burning season. PBT did not differ significantly as a result of burning season with either the horizontal or vertical thermocouples ($p=0.97$ horizontal, $p=0.32$ vertical). Horizontal DOH was estimated to be significantly greater in the growing season burns than in the dormant season burns ($p<0.01$), but vertical DOH did not differ between the growing and dormant season burns ($p=0.52$). AUTP was significantly greater in the growing season both vertically and horizontally ($p \leq 0.03$ for all values).

Relationship to other field measurements

Figure 2.3 shows PBT, DOH, AUTP, pre-fire fuel (1-10-100 hr. fuels + litter) mass (Mg ha^{-1}), pre-fire fuel depth (cm), and post-fire detrital mass (Mg ha^{-1}) from one of our burn areas along the 300 m transect. It did not appear that the fire behavior metrics showed any relationship with pre-fire fuel mass, pre-fire fuel depth, or post-fire detrital mass. This was confirmed statistically as no relationships could be established with an r^2 above 0.29 (Table 2.2).

Discussion

Thermocouple orientation affects value estimates of fire behavior metrics

We found that horizontal estimates of our fire behavior metrics were significantly greater than their vertical counterparts. Few studies have investigated these metrics as

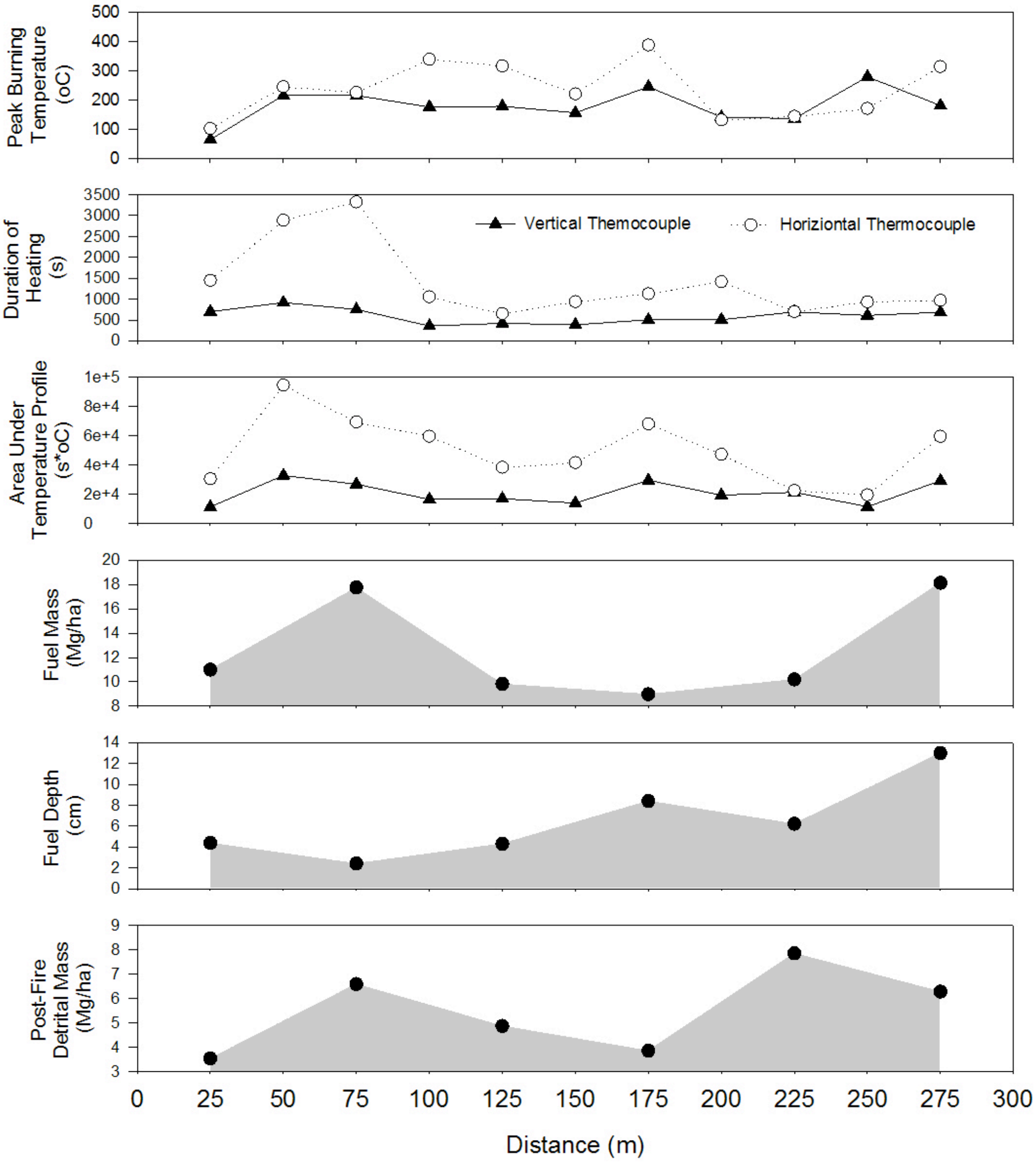

Figure 2.3. Depiction of peak burning temperature, duration of heating, and area under the temperature profile as related to pre-fire fuel mass (Mg ha^{-1}), pre-fire fuel depth (cm), and post-fire detrital mass (Mg ha^{-1}) along the 300 m sampling transect at one of the dormant season burning sites at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

Table 2.2. Correlation coefficients (r^2) of linear regressions where pre-fire fuel mass, pre-fire fuel depth, and post-fire detrital mass were used as predictors of vertical and horizontal peak burning temperature (PBT), duration of heating (DOH), and area under the temperature profile (AUTP).

Fire Behavior Variables	**Pre-fire Fuel Mass ($Mg\ ha^{-1}$)**	**Pre-fire Fuel Depth (cm)**	**Post-fire Ash Mass ($Mg\ ha^{-1}$)**
Vertical PBT (^oC)	0.07 n=31	-0.00 n=30	0.08 n=34
Horizontal PBT (^oC)	0.16 n=26	0.00 n=25	0.01 n=29
Vertical DOH (s)	0.10 n=28	0.00 n=27	0.01 n=31
Horizontal DOH (s)	0.01 n=26	0.22 n=25	0.23 n=29
Vertical AUTP (s* ^oC)	0.02 n=32	0.00 n=29	0.22 n=33
Horizontal AUTP (s* ^oC)	0.02 n=27	0.29 n=26	0.27 n=29

they fluctuate with height above the litter-soil interface within the same burn. The results from these studies are not uniform and seem to vary with both fuel type and structure. Using pyrometers, Gibson et al. (1990) found that PBT in areas burned every 5 years yielded higher temperatures at the ground surface than some degree above the ground surface in the Florida sandhills, but differences in PBT as a result of measurement location were not present in annually burned forests and forests that were burned every 3 years. In contrast, Kennard et al. (2005) found that PBT was less at the litter-soil interface than at 30 cm above the litter-soil interface in a longleaf pine ecosystem containing a significant shrub and grass understory. Bailey and Anderson (1980) found in a study of grassland fires in Canada that PBT was highest some distance aboveground as opposed to ground level.

Our differences are particularly noteworthy given the frequency of fire used at our study site. The blocks included in this portion of our study were previously burned in 2014, 2013, and at least 5 additional times since 2004 and did not contain large amounts of fuel prior to burning in 2015 (8.6–20.6 Mg ha^{-1}). Given the low fuel masses and fuel depths, these fires were considered low intensity, low severity surface fires. We hypothesize that the tips of the thermocouples installed horizontally were more uniformly exposed to flames than were the tips of the vertical thermocouples. Based upon our findings and those mentioned above, it appears horizontally oriented thermocouples provide unique insight when fuel beds are largely dominated by litter and surface fuels, as opposed to grasses and vertically oriented fuels.

Vertical and horizontal thermocouple estimates are independent

Results from our regression analyses suggest that the horizontal and vertical estimates show no strong correlation with one another. The vertical and horizontal thermocouples were located in the same location and buried in the same hole and yet their values did not seem to be related. Based upon the matched pair and regression results, one can conclude that PBT, DOH, and AUTP at the litter-soil interface are different measures than PBT, DOH, and AUTP 28 cm above the litter-soil interface.

Seasonal burning effects may not be reflected by peak burning temperature alone

Of the fire behavior metrics we investigated, PBT is the metric most utilized in studies of prescribed fire (Franklin et al., 1997). When all other variables affecting fire behavior are held constant, it is assumed that higher ambient temperatures in the growing season contribute to higher PBT in growing season fires (Whelan, 1997). Our results did not reflect this notion as PBT did not differ between the growing and dormant season burns. Our burns were conducted eight weeks apart in the late-dormant and early-growing seasons. Ambient temperature was not drastically different on the dates of our burns, which suggests that there was no difference in the amount of heat needed to reach ignition between the dormant and growing season burns. Both soil moisture and relative humidity were lower during the growing season burns, however, which might have suggested higher PBT in those burns. Nonetheless, this was not actualized in our findings.

Even though PBT did not differ as a result of burning season, we did note significantly higher values for AUTP and horizontal DOH in the growing season. With this in mind, it appears that PBT may not fully encapsulate fire dynamics within a given fire, thus making it difficult to establish differences in fire behavior metrics between fire events. Other researchers have noted the potential shortcomings of PBT for these purposes as well (Byram, 1958; Bova & Dickinson, 2008; Keeley, 2009).

Prediction of fire behavior metrics using pre-fire fuel characteristics (and post-fire detrital mass) may be difficult using thermocouples alone

Based upon the variables we assessed pre- and post-fire, we could not establish any significant predictive relationships for PBT, DOH, and AUTP. Kennard et al. (2005) found this to be true with their results as well. This is not surprising given the heterogeneity of fire events, both vertically and laterally.

When using thermocouples, consider how they are oriented

The use of thermocouples has been questioned in previous studies, particularly when PBT is the only metric considered (Bova & Dickinson, 2008). Thermocouples do not measure actual flame temperatures (Kennard et al. 2005), but instead give an estimate of the ability of a given fire in a given area to transfer heat (Bova & Dickinson, 2008). This is dependent upon the diameter and composition of the thermocouple itself (Kennard et al., 2005) and any contact made between the fuelbed and thermocouple tips. Nonetheless, when fuel type is consistent, choosing one thermocouple type to assess these metrics may be beneficial (Bova & Dickinson, 2008).

One unique advantage of using thermocouples as opposed to other methods of obtaining PBT, such as calorimeters and pyrometers (Iverson et al., 2004; Kennard et al., 2005), is that thermocouple-datalogger assemblies can be programmed to record temperature throughout the duration of a given fire event. In light of the differences we noted in burning season with DOH and AUTP, we strongly recommend the use of thermocouple-datalogger assemblies because they afford the opportunity to obtain these metrics. This benefit must be noted with the caution that metallurgical properties and thermocouple diameter do influence the rate at which thermocouples heat and cool. This may greatly influence values for DOH and AUTP (Kennard et al., 2005).

In their work, Bova and Dickinson (2008) determined that thermocouple-generated data might be more useful when raw data is calibrated with additional data, such as flame height and mean rate of spread. Fireline intensity and fuel consumption can be generated from these calibrations. We did not attempt to utilize these calibrations and instead compared the raw data generated by the thermocouples. We chose this method because our fires were conducted in the same fuel type and because we were interested in the utility of the uncalibrated values in longleaf pine-dominated systems. As stated by Bova and Dickinson (2008), uncalibrated values obtained from thermocouples vary greatly spatially along the landscape, but may serve as point estimates of fire and fuelbed characteristics in a given location. As such, the orientation comparison we conducted may provide needed insight for the deployment of thermocouples in prescribed fires occurring in longleaf pine-dominated forests and between differing fire treatments (i.e. dormant versus growing season fires) within the longleaf pine fuel type.

From our findings, it appears that thermocouple orientation may influence our determination of differences in PBT, DOH, and AUTP as a result of burning season.

These results also suggest that fire behavior metrics generated at the litter-soil interface are different metrics than those obtained some distance vertically above the litter-soil interface. Many managers and foresters are interested in quantifying the metrics that thermocouples provide. In light of this study, we highly encourage scientists and managers to carefully consider thermocouple orientation when designing studies evaluating fire behavior metrics. Thermocouple orientation may affect the values generated and the ability to determine differences in burning regimes.

Conclusions

In this study we investigated the orientation of thermocouples in six prescribed fires in southeastern coastal forests. We found that thermocouples located horizontally at the litter-soil interface obtained greater values of peak burning temperature, duration of heating, and area under the temperature profile than did thermocouples extending 28 cm vertically above the litter-soil interface. Estimates of these metrics from vertical thermocouples did not serve as significant predictors of horizontal metrics at any resolution. This suggests that thermocouples oriented horizontally and vertically may capture inherently different estimates of these fire behavior metrics. The utility of both orientations to distinguish differences between dormant and growing season burns was consistent for peak burning temperature and the area under the temperature profile. Duration of heating was only significantly greater in the growing season burns when measured with the horizontal thermocouples. Regardless of orientation, we found that none of the fire behavior metrics were significantly related to pre-fire fuel mass, pre-fire fuel depth, and post-fire detrital mass. Based upon these findings and those from other studies, we recommend careful consideration of the implications posed by the placement of thermocouple-datalogger assemblies across the landscape when evaluating prescribed burns as these details may affect the evaluation of treatment effects.

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CHAPTER THREE

FREQUENT PRESCRIBED BURNING AS A LONG-TERM PRACTICE IN LONGLEAF PINE FORESTS DOES NOT AFFECT DETRITAL CHEMICAL COMPOSITION

Abstract

The O Horizon, or detrital layer, of forest soils is directly linked to long-term forest productivity and health. Fuel reduction techniques, such as prescribed fire, can alter the thickness and composition of this important compartment of a forest ecosystem. Developing an understanding of the changes in the chemical composition of forest detritus due to prescribed fire is essential for forest managers and stakeholders seeking sustainable, resilient, and productive ecosystems. In this study we evaluated fuel quantity, fuel structure, and detrital chemical composition in longleaf pine forests that have been frequently burned for the last 40 years at the Tom Yawkey Wildlife Center in Georgetown, South Carolina. Our results suggest that frequent prescribed fire reduces forest fuel quantity ($p<0.01$) and vertical structure ($p=0.01$). Using pyrolysis-GC/MS as a molecular technique to analyze detrital chemical composition, including aromatic compounds and polycyclic aromatic hydrocarbons (PAHs), we found that the chemical composition of forest detritus was nearly uniform for both unburned and burned detritus. Our burning activities varied in the short-term, consisting of annual dormant, annual growing, and biennial dormant season burns. Seasonal distinctions were present for fuel quantity and vertical structure, but these differences were not noted for the benzene/phenol ratio. These results are significant as more managers consider burning existing longleaf stands while determining effective management practices for longleaf

stands yet to be established. Managers of such stands can be confident that frequent, low intensity, low severity prescribed burns in longleaf pine stands do little to affect the long-term chemical composition of forest detritus.

Introduction

One of the many reasons forest soils are unique is due to the presence of the O Horizon. Comprised of the Oi, Oe, and Oa subhorizons, this material is frequently referred to as litter and duff and has great value as a long-term source of organic matter (Melillo et al., 1982). Its presence helps insure site productivity and forest health (Binkley & Fisher, 2015). Countless numbers of microorganisms call it home and assist in the process of decomposition, which allows this material to be utilized by plants (Pritchett, 1979).

Wildland fire has the potential to greatly alter the O Horizon, both in quantity and quality (Agee, 1996; Neary et al., 1999). Whether the fires are ignited by nature or by humans, as fire intensity and severity increase, fire can greatly alter or consume all of the litter and duff (DeBano & Neary, 2005). Most fires do not enact the same changes across the landscape in a given fire (Bova & Dickinson, 2008). As a result of this heterogeneity, much of the material left on the forest floor is a mixture of unburned, lightly burned, and completely charred material (Bodi et al., 2014). To simplify terminology, the constituents of the O Horizon will be referred to as forest detritus for the remainder of this publication.

Any material that is at least partially charred by fire falls within the spectrum of compounds referred to as black carbon. Black carbon is known to increase in the atmosphere as a result of biomass and fossil fuel burning (Goldberg, 1985; Hedges et al., 2000). One of the key groups of compounds found in black carbon materials are polycyclic aromatic hydrocarbons (PAHs) (Kennedy, 1997; Dachs et al., 2000; Oen et al., 2006; Vila-Escale et al., 2007). The Environmental Protection Agency (EPA) and other entities around the globe monitor many of these compounds as particulate matter that may lead to respiratory and other health-related issues (Ramanathan & Carmichael, 2008; Sasser et al., 2012). The EPA also monitors PAHs and other organic substances exiting forests through forested waters as potential pollutants, some of which have been shown to be carcinogenic (Kafilzadeh et al., 2011). On the other hand, black carbon is believed to comprise a major source of long-term carbon storage and sequestration in soils (DeLuca & Aplet, 2008; Shrestha et al., 2010; Zimmerman et al., 2012) and may actually enhance cation exchange capacity in mineral soils (Liang et al., 2006).

Few studies have investigated PAH production as a result of wildland fire and the studies that were conducted have mostly been focused on wildfire effects on PAHs in mineral soil (Bodi et al., 2014). Additional studies have been conducted to relate PAH detection to differing levels of flash heating in laboratory settings (Yang et al., 2016). In general, the quantity and characteristics of burned detritus produced as a result of wildland fire depend mainly on the total burned fuel, fuel type, and combustion completeness (Bodi et al., 2014). It is believed that higher fire intensities produce the energy needed to create more recalcitrant bonds in PAH constituents (Masiello, 2004; Preston & Schmidt, 2006). It is assumed that wildfires produce the intensity needed to create these compounds, but little has been done to confirm this assertion. Furthermore, none of this research has been related to forests that are impacted by frequent prescribed burning.

Reasons to burn forest ecosystems include the reduction of hazardous fuels, improvement of conditions for specific vegetative species, wildlife habitat improvement, and aesthetics (Waldrop & Goodrick, 2012). One such ecosystem burned extensively in the southern United States is the longleaf pine ecosystem. As has been documented extensively, this ecosystem once occupied 1.2 million hectares of habitat (Outcalt & Sheffield, 1996; Van Lear et al., 2005) and represents one of the most diverse ecosystems on earth (Peet & Allard, 1993; Walker 1993). Dormant-season prescribed fire has been the prescription most utilized in longleaf pine forests throughout the southern United States to control the accumulation of highly flammable understory fuels and to prevent fine root expansion into the duff (Pyne et al., 1996; Brose &Wade, 2002) because understory fuels generally accumulate to pre-burn, hazardous levels within 5 years post-fire (Davis & Cooper, 1963). Most scientists agree that frequent wildland fires in this ecosystem contributed to its dominance across the landscape (Noss, 1989; Landers et al., 1995) and widespread fire exclusion, along with unsustainable logging practices, led to its subsequent decline (Van Lear et al., 2005).

An improved understanding of the effects of prescribed fire on fuel loading and detrital chemistry in longleaf pine stands will enable scientists and managers to implement prescribed burns to reduce wildfire hazard with an understanding of how long-term forest carbon cycling might be affected. Toward these ends we conducted a study to assess the impact of long-term, frequent, prescribed fire on forest fuel loading, structure, and detrital chemistry in coastal South Carolina. By comparing longleaf pine stands that have been burned at differing frequencies over the last 40 years, we were granted an opportunity to determine how frequent prescribed fire might affect long-term forest detrital quantity and chemistry.

Our hypotheses were: 1) Both fuel loading and fuel structure pre-fire are greatest in a long-term unburned stand than in frequently burned longleaf stands and 2) Prescribed fire alters detrital chemical composition, most notably by increasing PAH content.

Materials and Methods

Study Site

This study was conducted at the Tom Yawkey Wildlife Center in Georgetown, South Carolina (33.23°N, -79.22°W) (Figure 3.1). Nine units, approximately 1-2 ha in size, were selected for burning in 2015 and 2016. Within each unit, six 0.02 ha sampling plots were established. The dominant overstory tree species present were longleaf pine (*Pinus palustris* Miller), loblolly pine (*Pinus taeda* L.), turkey oak (*Quercus laevis* Walter), and sweetgum (*Liquidambar styraciflua* L.). Soils present on these sites consisted of both *Entisols* and *Spodosols*. The treatments were allocated as such:

1. Three units burned during the dormant seasons of 2015 and 2016 (Annual dormant)
2. Three units burned during the growing season of 2015 only (Annual growing)
3. Three units burned during the dormant season of 2016 only (Biennial dormant)

Each of these areas was previously burned in 2014, 2013, and 16-20 additional

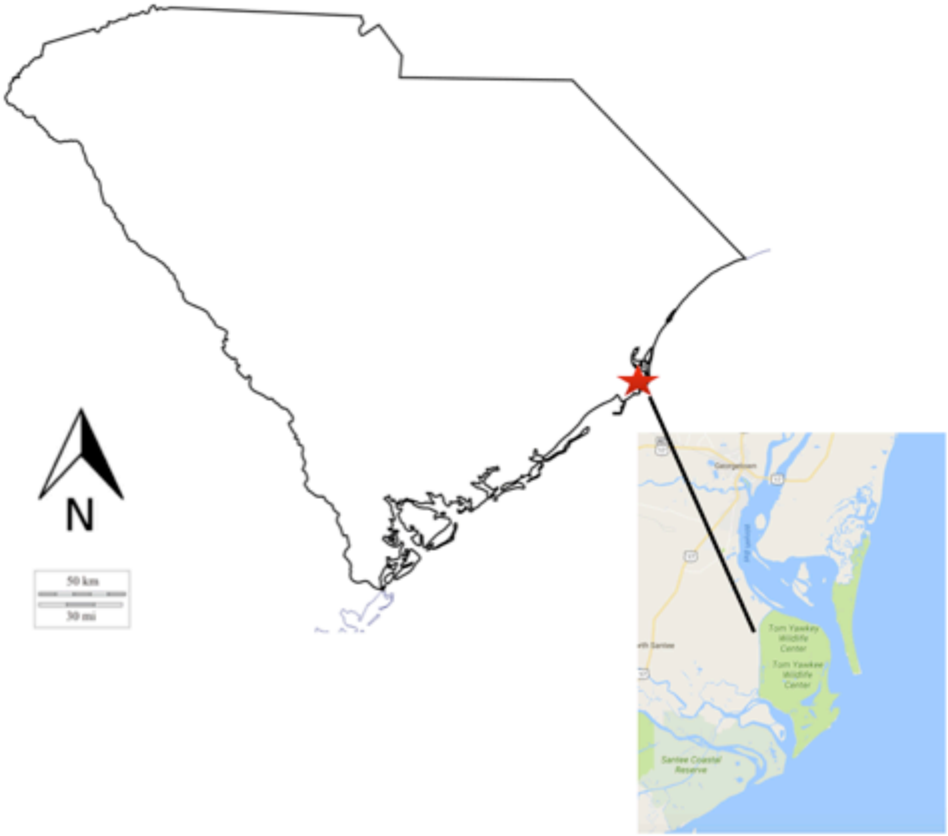

Figure 3.1. Location of the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA (33.23°N, -79.22°W).

times since 1978 (Jamie Dozier, unpublished records). One unit approximately 6-7 ha in size was used as a long-term, unburned control. This control unit has not been burned or harvested since 1978. This was the only unit within the Yawkey Wildlife Center with a documented, extended history that did not include burning. Average basal area in this long-term unburned stand was 45.6 m^2 ha^{-1} and the average basal area in the frequently burned stands was 20.86 m^2 ha^{-1}. Images of these stands prior to fire are shown in Figure 3.2.

Field Sampling

Live Fuels

Prior to burning, one 1m x 1m destructive sample of live vegetation was obtained at each of six sampling plots within each treatment unit (Figure 3.3). We measured the height of this vegetation prior to collection with a 1 m ruler. Common understory species included common bracken fern (*Pteridium aquilinum*), sweetgum (*Liquidambary styraciflua*), gallberry (*Ilex glabra*), switch cane (*Arundinaria gigantea*), highbush blueberry (*Vaccinium corymbosum*), and a variety of grasses. None of these was wiregrass (*Aristida stricta*), however, which is commonly associated with longleaf pine forests. This island property lies within the wiregrass gap (Shibu et al., 2006).

Down and Dead Woody Debris

Brown's Planar Intercept Method (Brown, 1974) was used to tally down and dead woody debris in all of our stands prior to and after burning. We specifically followed the specifications of this technique using the methods of Stottlemyer (2004). Brown's Planar Intercept Method produces estimates of 1-, 10-, 100-, and 1000-hr fuel loads; we obtained

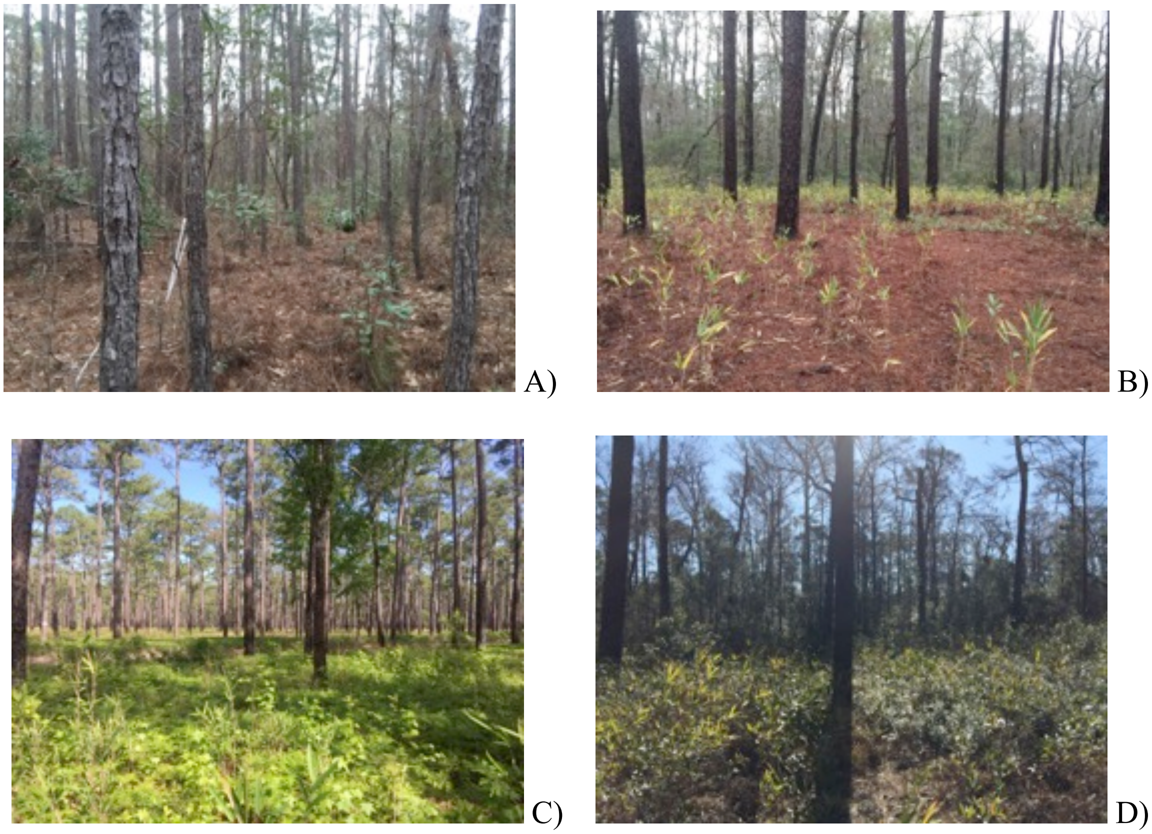

Figure 3.2. Representative pre-burn images for the A) long-term unburned stand, B) annual dormant stands, C) annual growing stands, and D) biennial dormant stands.

Figure 3.3. An example of vegetation sampling prior to burning using a 1m x 1m sampling frame at the Tom Yawkey Wildlife Center, Georgetown, South Carolina.

these estimates in both the long-term unburned and frequently burned stands. 1000-hr fuels have been excluded from our results and discussion because they were not consumed as a result of these low intensity, low severity burns. Estimates of down and dead woody debris height, litter (Oi) depth, and duff (Oe+Oa) depth (when present) were obtained in nine locations per plot prior to fire along the transects. In our post-fire samples, charred depth, litter depth, and duff depth were distinguished (when applicable); not all of the litter and duff were consumed as a result of fires in some of our sampling locations.

Detrital Samples

One m x 1 m destructive samples of both litter and duff were obtained from our stands every 50 m prior to and after burning to determine detrital mass before and after fire. Regardless of charring impact, all material remaining after burning was collected in these samples.

Fire implementation

Burning took place in the annual dormant season blocks March 9-11, 2015 and in the annual growing season blocks May 5-6, 2015. The biennial dormant season units were burned on March 9 and 16, 2016. Additionally, on these dates, two of the three annual dormant units were burned a second time. Before and after images at some of the locations are shown in Figure 3.4. Down and dead woody fuel moisture content, soil moisture content (0-10 cm), and understory vegetation moisture content were measured prior to burning. Relative humidity and wind speed were measured before and during the burns (Table 3.1). All burns were headfires. Mean flame lengths in each of the annual

Figure 3.4. Before and after images from the fire treatments: A & B) Annual dormant pre-and post-fire, C & D) Annual growing pre-and post-fire, and E& F) Biennial dormant pre- and post-fire.

Table 3.1. Soil moisture contents, fuel moisture contents, and fire weather data associated with annual dormant, annual growing, and biennial dormant season burns at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

Fire Date	**Treatment**	**Soil Moisture % (0-10 cm)**	**Fuel Moisture %**			**Fire Weather**		
			Litter	**Down Dead Fuels**	**Live Fuels**	**Ambient Temp. (^{o}C)**	**RH (%)**	**Wind Speed (km/h)**
2015/03/09	Annual Dormant	24.6	45.8	38.4	181.4	18	74	6.9
2015/03/10	Annual Dormant	43.5	11.4	18.3	94.3	27	60	4.8
2015/03/11	Annual Dormant	8.9	35.9	36.5	148.4	26	70	8.2
2015/05/05	Annual Growing	9.7	2.6	17.7	72.1	24	55	3.2
2015/05/05	Annual Growing	17.6	2.6	3.8	40.3	30	48	5.4
2015/05/06	Annual Growing	11.1	4.2	10.1	92.7	28	52	5.3
2016/03/09	Annual Dormant & Biennial Dormant	47.9	13.4	27.4	76.5	27	45	4.8
2016/03/16	Annual Dormant & Biennial Dormant	55.0	30.6	46.2	93.8	27	45	5.3

burns were estimated as 0.3-1 m. Flame lengths observed in the biennial dormant burns averaged 0.3-1 m, although some spots experienced flame lengths greater than 2 m where live fuels were greater than 30 cm in height.

Laboratory assessments of detrital chemical composition

Both pre- and post-fire detrital samples were brought back to the lab, oven-dried at 70°C for not less than 48 hrs, and ground using a Wiley mill (2 mm sieve). To determine the chemical composition of the detritus, 1-2 mg of well-mixed, oven-dried, ground material was subjected to analytical pyrolysis/gas chromatography – mass spectrometry (GC-MS). Over one hundred fifty peaks (Table 3.2) were evaluated and derived from 47 samples (3 detrital samples from the long-term unburned stand; 20 unburned, pre-fire detrital samples from our frequently burned stands; 10 detrital samples from annual dormant burns; 10 detrital samples from annual growing burns; and 4 detrital samples from biennial dormant burns). The 20 unburned detrital samples from the frequently burned stands were matched to their burned counterparts, either as annual dormant burns or annual growing burns. These pyrolyzed compounds were then placed within one of the following functional groups to better characterize detrital chemistry pre- and post-fire: 1) Aliphatic compounds (lipid-like), 2) Aromatic compounds with only one-ring structures (i.e. benzene and its derivatives excluding the hydroxyl group), 3) Polycyclic Aromatic Hydrocarbons (compounds with two or more aromatic rings), 4) Nitrogen-containing compounds (protein-like), 5) Oxygen-containing compounds excluding phenolic compounds (carbohydrate-like), and 6) Phenolic compounds (lignin-like) (i.e. benzene with at least one or more hydroxyl group). Percentages of these

Table 3.2. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
2.338	1-Hexanol	55, **56**, 69	Oxygen
2.44	3-Cyclopentene-1,2-diol	53, 81, **82**	Oxygen
2.583	Methenamine, N-hydroxy-N-methyl-	61	Nitrogen
2.837	1,3-Cyclohexadiene	77, **79**	Oxygen
3.128	Benzene	50, 77, **78**	Aromatic (one-ring)
3.272	1,4-Cyclohexadiene	77, **79**	Aliphatic
3.66	Cyclopropane, butyl	**55**, 56, 69, 70	Aliphatic
3.823	Cyclohexanol, methyl	**57**, 71, 81, 96	Oxygen
3.964	Furan, 2,5-dimethyl	53, 81, 95, **96**	Oxygen
4.853	1H-Pyrrole, methyl	53, 80, **81**	Nitrogen
5.061	Pyridine	52, **79**	Nitrogen
5.352	Pyrrole	67	Nitrogen
5.835	Toluene	**91**, 92	Aromatic (one-ring)
6.858	Cyclopentane, 1-ethyl-2-methyl	**55**, 56, 69, 70, 83, 84	Aliphatic
7.226	Cyclohexanol, dimethyl	57, 71, 84, **95**, 110	Oxygen
7.228	2-Pyrrolidinecarboxamide, 5-oxo	**84**, 85	Nitrogen
7.968	Pyridine, methyl	66, 92, **93**	Nitrogen
8.666	Furan, 2,5-dimethyl	**96**	Oxygen
8.704	2-Cyclopenten-1-one	53, 54, 82	Oxygen
9.061	1H-Pyrrole, 2-methyl	53, 80, 81	Nitrogen
9.442	1H-Pyrrole, 3-methyl	**81**	Nitrogen
10.064	Ethylbenzene	**91**, 106	Aromatic (one-ring)
10.232	Pyridine, 3-methyl	66, 92, **93**	Nitrogen
10.537	o-xylene	**91**, 106	Aromatic (one-ring)

Table 3.2. continued. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
11.665	Styrene	78, 103, **104**	Aromatic (one-ring)
11.669	p-xylene	**91**, 106	Aromatic (one-ring)
11.822	1-Nonene	**55**, 56, 69, 70, 83	Aliphatic
12.263	Decane, 2,5,6-trimethyl	56, **57**, 85	Aliphatic
12.425	2-Cyclopenten-1-one, 2-methyl	53, **67**, 96	Oxygen
13.494	1H-Pyrrole, 2,5-dimethyl	**94**, 95	Nitrogen
13.648	1H-Pyrrole, ethyl	53, 80, 95	Nitrogen
13.825	Pyridine 2,4-dimethyl-	79, 106, **107**	Nitrogen
14.189	1H-Pyrrole, 2,3-dimethyl-	**94**, 95	Nitrogen
15.008	Benzene, propyl	**91**, 120	Aromatic (one-ring)
15.439	Benzene, 1-ethyl-2-methyl	**105**, 120	Aromatic (one-ring)
15.611	2-Cyclopenten-1-one, 3-methyl	53, 67, 81, 95, **96**	Oxygen
15.893	Benzene 1,2,3-trimethyl	**105**, 120	Aromatic (one-ring)
16.299	Benzene, 1-ethyl-3-methyl	**105**, 120	Aromatic (one-ring)
16.3	Aniline	65, 66, 93	Nitrogen
16.689	Phenol	66, **94**	Phenolic
16.787	Benzonitrile	76, **103**	Nitrogen
16.848	Pyrrole-2-carboxamide	93, 94, **110**	Nitrogen
17.227	Benzene, trimethyl	**105**, 120	Aromatic (one-ring)
17.273	Benzofuran	90, **118**	Oxygen
17.281	Benzene 1-propenyl	**117**, 118, 91	Aromatic (one-ring)
17.517	Benzene 1-ethenyl-2-methyl	**117**, 115, 91	Aromatic (one-ring)
18.619	Benzene 1,2,3-trimethyl	**105**, 120	Aromatic (one-ring)
18.959	Benzene, 2-propenyl-	**117**, 118	Aromatic (one-ring)
19.281	Indane	**117**, 188	Aromatic (PAH)
19.468	2-Cyclopenten-1-one, 2,3-dimethyl	**67**, 110	Oxygen

Table 3.2 continued. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
19.792	Benzene, 1-propynyl	**115**, 116	Aromatic (one-ring)
20.606	Phenol, 3-methyl (Phenol, 2-methyl)	79, **107**, **108**	Phenolic
21.101	Ethanone, 2-hydroxy-1-phenyl-	51, 77, **105**	Phenolic
21.117	Benzoylformic acid	51, 77, 105	Oxygen
21.807	Phenol, 4-methyl	77, 79, **107**, 108	Phenolic
22.126	Phenol, 2-methoxy	53, 81, 109, **124**	Phenolic
22.353	Benzene, 1-methyl-4-(1-methylethenyl)-	91, 117, **132**	Aromatic (one-ring)
22.391	Benzonitrile, 2-methyl	**131**, 132	Nitrogen
22.568	3-Dodecene	**55**, 69, 83, 97,	Aliphatic
23.214	Benzofuran, 2- methyl	**131**, 132	Oxygen
24.838	Phenol, 2-ethyl	**107**, 122	Phenolic
24.9	Benzyl nitrile	90, **117**	Nitrogen
24.921	Phenol, 3-ethyl	**107**, 122	Phenolic
25.459	Phenol, 2,4-dimethyl	77, **107**, 121, 122	Phenolic
25.485	Phenol, 3,5-dimethyl-	51, 77, **107**, 121	Phenolic
25.594	Naphthalene, 1,2-dihydro	115, 128, 129, **130**	Aromatic (PAH)
26.33	Phenol, 3-ethyl	**107**, 122	Phenolic
26.849	Phenol, 2,3-dimethyl	77, **107**, 121, 122	Phenolic
26.974	Naphthalene	**128**	Aromatic (PAH)
27.357	Phenol, 2-methoxy-4-methyl	95, **123**, 138	Phenolic
27.893	Nonadecane	57, 71, 85	Aliphatic
28.023	1,2-Benzenediol	63, **110**	Phenolic
28.5	Ethanone, 1-(4-methylphenyl)	134	Phenolic
28.921	Benzofuran, 2,3-dihydro-	91, 119, 120	Oxygen
28.959	Naphthalenediol, 1,2,3,4-tetrahydro-, cis-	91, 120	Aromatic (PAH)

Table 3.2 continued. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
29.552	Quinoline	102, 129	Nitrogen
29.739	Phenol, 4-ethyl-3-methyl-	121, 136	Phenolic
29.741	Benzene 1-methoxy-2(methoxymethyl)	**91**, 121, 152	Aromatic (one-ring)
29.772	Benzenepropanenitrile	91,131	Nitrogen
30.849	1,2-Benzenediol, 3-methyl	124	Phenolic
31.332	1,3-Benzenedicarbonitrile	**128**	Nitrogen
31.369	Phenol, 2-ethyl-2-methoxy-	**137**, 152	Phenolic
31.421	Phenol, 4-ethyl-2-methoxy-	137, 152	Phenolic
31.533	1H-Inden-1-one, 2,3-dihydro	**104**, 132, 78, 77	Aromatic (PAH)
32.205	Naphthalene, 2-methyl	115+**141**	Aromatic (PAH)
32.22	Indole	89, 90, **117**	Nitrogen
32.347	1,2-Benzenediol, 3-methyl	124	Phenolic
32.352	3-Propenenitrile, 3-phenyl-(E), isoquinoline	102, 129	Nitrogen
32.878	Naphthalene, 1-methyl	115, **141**	Aromatic (PAH)
33.055	Phenol, 2-methoxy-4-vinyl	77, 107, **135**, **150**	Phenolic
33.681	3-Methoxy-5-methylphenol	109, **138**	Phenolic
34.787	2-Methyl-5-hydroxybenzofuran	91, 147, **148**	Oxygen
34.794	Phenol, 3,4-dimethoxy-	111, 154	Phenolic
34.843	Eugenol	164	Phenolic
35.368	Phenol, 2-methoxy-4-propyl	**137**, 166	Phenolic
36.018	Biphenyl	152, 153, **154**	Aromatic (PAH)
36.404	1,3-Benzenediol, 4-ethyl	123, 138	Phenolic
36.566	Naphthalene, 1,4-dimethyl-	**141**, 156	Aromatic (PAH)
36.956	Benzaldehyde, 3-hydroxy-4-methoxy	151, 152	Phenolic
37.117	Cn(ANE)	**57, 71, 85**	Aliphatic

Table 3.2 continued. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
37.159	Phenol, 2-methoxy-6-(1-propenyl)-	149, 164	Phenolic
37.674	Naphthalene, 1,5-dimethyl-	141, **156**	Aromatic (PAH)
38.753	1,2,4-trimethxoybenzene	**153**, 168, 125	Aromatic (one-ring)
38.982	Phenol, 2-methyoxyl-4-(1-propenyl)	91, 103, 149, **164**	Phenolic
39.091	Naphthalene, 1-ethyl	115, **141**, 156	Aromatic (PAH)
39.276	Pyridine, 2-phenyl	154, **155**	Nitrogen
40.341	1,1'-Biphenyl, 4-methyl-	167, **168**	Aromatic (PAH)
40.44	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	123, **151**, 166	Phenolic
40.712	2-naphthalenecarbonitrile	126, **153**	Nitrogen
40.807	1,1'-Biphenyl, 3-methyl-	167, **168**	Aromatic (PAH)
40.945	Hexadecanol	**55**, 69, 83, 91, 111	Oxygen
41.32	Cn(ane)	**57**, 71, 85	Aliphatic
41.637	Dibenzofuran	139, **168**	Oxygen
41.769	1-naphthalenol	115, 116, **144**	Aromatic (PAH)
43.319	Naphthalene, 1,4,6-trimethyl-	155, **170**	Aromatic (PAH)
44.253	Fluorene	**165**, 166	Aromatic (PAH)
44.356	Naphthalene, 2,3,6-trimethyl	155**, 170**	Aromatic (PAH)
44.913	1-Hexadecanol	**55**, 69, 83, 97, 111	Oxygen
45.22	Nonadecane	**57**, 71, 85	Aliphatic
48.959	Nonadecane	**57**, 71, 85	Aliphatic
49.741	1,4,5,8-tetramethylnaphthalene	169, **184**	Aromatic (PAH)
49.903	2-methyl-E-7-hexadecene	**55**, 69, 83, 97	Aliphatic
50.002	9H-Fluoren-9-one	152, **180**	Aromatic (PAH)
51.466	Phenanthrene	**178**	Aromatic (PAH)
51.89	Anthracene	**178**	Aromatic (PAH)

Table 3.2 continued. Py/GC-MS peaks evaluated for pre- and post-fire detrital samples.

Time	**Compound**	**Molecular Weights**	**Functional Group**
51.941	3-Phenanthrol	165, **194**	Aromatic (PAH)
52.247	Cn(ANE)	**55**, 69, 83, 97, 111	Aliphatic
52.504	1-Hexadecane	**57**, 71, 85	Aliphatic
53.613	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	**95**, 123	Oxygen
55.053	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	**95**, 123	Oxygen
55.664	1- Heptacosene	**55**, 69, 83, 97, 111	Aliphatic
55.77	Hexadecanenitrile	57, 97	Nitrogen
55.835	Cn(anol)	57,71,85	Aliphatic
55.863	Cn(ane)	**57**, 71, 85	Aliphatic
58.935	1-Hexacosene	**55**, 69, 83, 97, 111	Aliphatic
59.038	2-Hexadecanol	57, 71, 85	Aliphatic
59.116	Octadecane	**57**, 71, 85	Aliphatic
60.042	Phenanthrene, 1,7-dimethyl-	**206**	Aromatic (PAH)
62.019	1-Hexacosene	**55**, 69, 83, 97, 111	Aliphatic
62.029	Heptadecane, 9=hexyl-	**57**, 71, 85	Aliphatic
62.21	Octadecane 3-ethyl-5-(2-ethylbutyl)-	**57**, 71, 85	Aliphatic
63.222	Phenanthrene, 2,3,5-trimethyl-	205, **220**	Aromatic (PAH)
64.99	Cn(ANE)	**55**, 69, 83, 97, 111	Aliphatic
65.048	2-Isopropyl-10-methylphenanthrene	**219**, 220, 234	Aromatic (PAH)
65.067	1-Hexacosene	**55**, 69, 83, 97, 111	Aliphatic
65.191	Tetracontane	**57**, 71, 85	Aliphatic
67.095	1,4-Dimethyl-6-phenyl-naphthalene	217, **232**	Aromatic (PAH)
67.85	Cn(ANE)	**55**, 69, 83, 97, 111	Aliphatic
68.006	Trietracontane	**57**, 71, 85	Aliphatic
70.615	1-Hexacosene	**55**, 69, 83, 97, 111	Aliphatic

functional groups based upon peak areas within each sample were calculated. Additionally, the ratios of 1) benzene/toluene and 2) benzene/phenol were evaluated to understand the cross-link structures (Kaal & Rumpel, 2009).

Our Py/GC-MS procedures followed the methodology specified by Song & Peng (2010). Pyrolysis products were identified according to: (1) their GC retention times; (2) their mass spectra with reference to the Wiley/NIST library supplied with the instrument software; and (3) published mass spectra of pyrolysis products listed in Song & Peng (2010).

Statistical analyses

Analysis of variance (ANOVA) was used to determine differences between the treatment units for the following variables: 1) pre- and post-fire fuel loading and 2) pre- and post-fire fuel structure. A linear contrast was constructed to determine differences in all of the fire treatments as compared to the long-term unburned treatment. Due to the semi-quantitative nature of analytical pyrolysis-GC/MS (Derenne & Quenea, 2015) and the abundance of compounds, ANOVA was not conducted for the chemical functional groups. Benzene, toluene, and phenol are readily identified in the literature, having reliable time signatures. For this reason, ANOVA was utilized for these substances and their ratios. All statistics were conducted with JMP.

Results

Fuel loading and structure

The primary contributor to pre-fire fuel loading in all treatments was forest detritus (Figure 3.5a). Total fuel loading was highest in the long-term unburned control

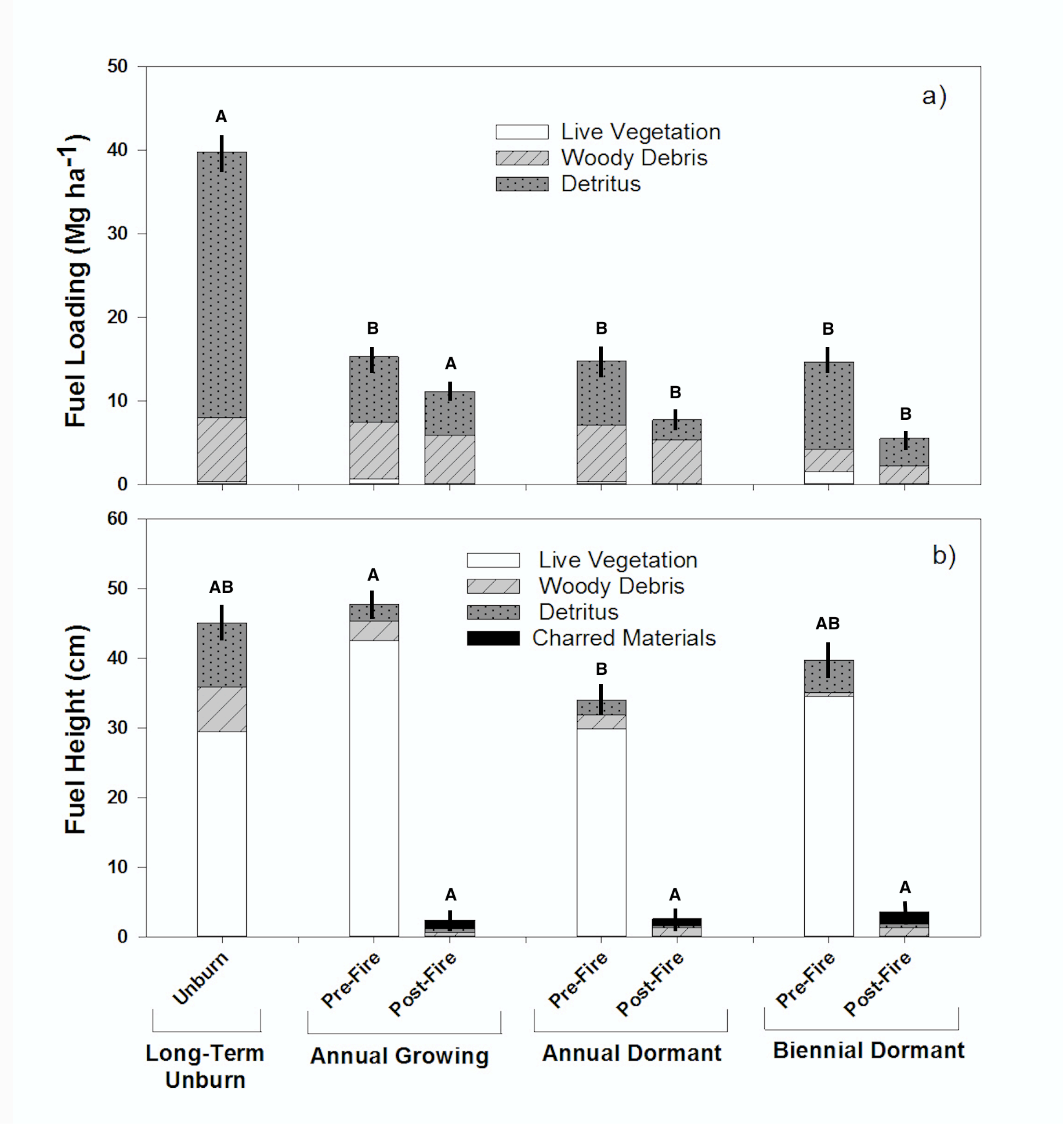

Figure 3.5. Fuel loading a) and fuel structure b) pre- and post-fire at treatment units on the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

(p<0.01). Post-fire fuel loading in our burned stands was composed of both woody debris and burned detritus (Figure 3.5a). Live fuels were essentially consumed by the fires. Detrital mass post-fire was significantly greater in the annual growing treatment units (p<0.01), but did not differ between the annual and biennial dormant units (Figure 3.5a).

Results for pre-burn fuel structure did not mirror the results for pre-burn fuel loading; total pre-burn fuel height was greatest in the annual growing burns (p=0.04), due in large part to much higher totals for live fuel height (Figure 3.5b). Down and dead woody debris height was significantly more in the long-term unburned stand than in the burned units (ANOVA p=0.01; linear contrast p-value=0.04). Detrital depth was highest in the long-term unburned stand as well (ANOVA p<0.01; linear contrast p<0.01).

Total post-burn fuel height did not differ among the burn treatments (p=0.07) (Figure 3.5b), despite differences in post-burn down and dead woody debris height (p=0.04) and charred depth (p<0.01). Charred depth was significantly greater in the biennial dormant burns (p<0.01).

Detrital characterization

Pyrograms of detrital materials produced from each treatment are displayed in Figure 3.6. The mean phenolic group percentage was 61.8-82.2% and in all samples represented the main functional group (Figure 3.7). The mean percentage of one-ring aromatic compounds was 6.6-11.9% and mean PAH percentage varied from 2.0–3.0%.

Benzene/toluene was greatest in the annual growing burns (p<0.01) (Table 3.3). Differences did not exist among the treatment units for the benzene/phenol ratio as those values equaled 0.14-0.17 in all treatments (p=0.73) (Table 3.3).

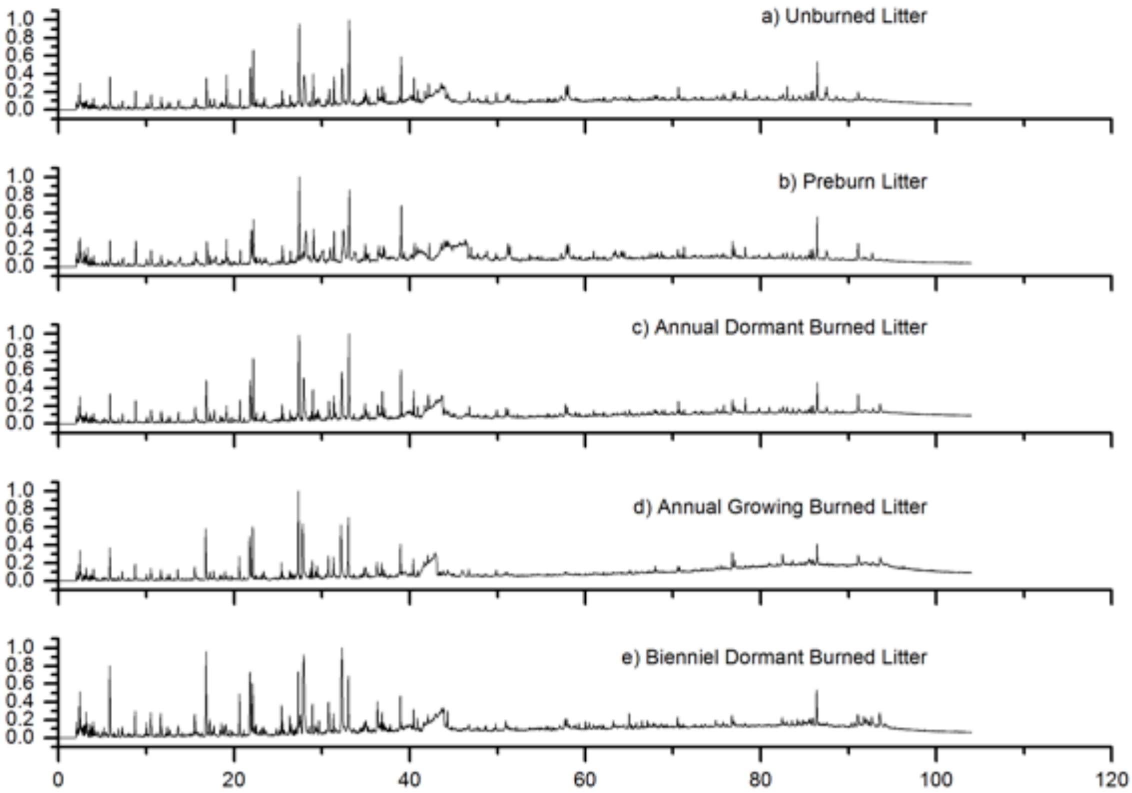

Figure 3.6. Pyrograms for detrital samples representative of each fire treatment at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

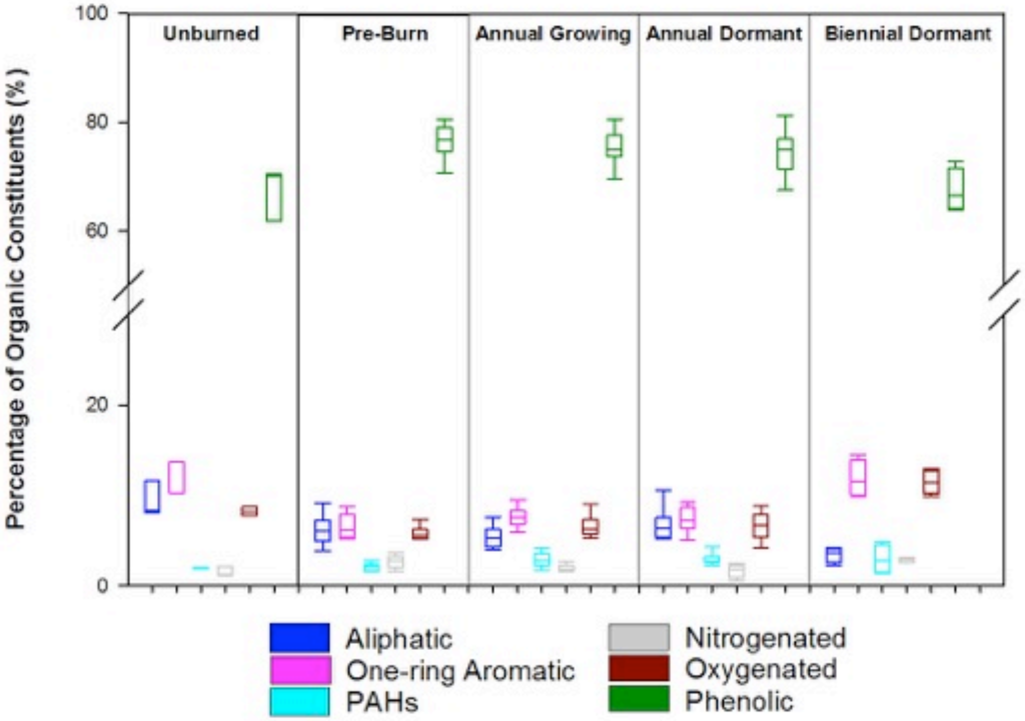

Figure 3.7. Range in percentages for organic functional groups identified in detrital samples obtained from the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

Table 3.3. Selected ratios related to detrital chemical composition before and after burning on the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

Treatment	Benzene/ Toluene	Benzene/ Phenol
Long-term unburned (n=3)	0.46±0.29 C	0.16±0.02 A
Pre-burn (n=20)	0.59±0.02 C	0.14±0.01 A
Annual dormant burn (n=10)	0.71±0.03 B	0.15±0.01 A
Annual growing burn (n=10)	0.85±0.03 A	0.17±0.01 A
Biennial dormant burn (n=4)	0.22±0.05 D	0.16±0.02 A
ANOVA p-value	**<0.01**	0.73
Linear contrast p-value (LTU vs. all fires)	0.14	0.87

Discussion

Frequent prescribed burning reduces fuel quantity

Not surprisingly, total fuel loading was significantly greater in the long-term unburned stand than in the frequently burned stands. Detrital mass was the primary contributor to this result; it was approximately 3-3.5 times greater in the long-term unburned stand. Much of this detrital material consisted of duff. In many cases duff was scarcely present in our frequently burned stands. Varner et al. (2016) suggest that frequent prescribed burning assists longleaf pine in establishing fine roots in mineral soil whereas the absence of fire affords longleaf pine the opportunity to establish more fine roots in the duff. When fire is introduced in long-term fire excluded stands, tree mortality can be expected as these roots are damaged or destroyed. In this sense, frequent prescribed fire contributes to long-term longleaf pine health if and when a wildfire is considered by accelerating decomposition and reducing duff thickness.

Frequent prescribed fire alters fuel structure

Fuel structure, defined as the vertical height of each fuel variable (i.e. live vegetation, woody debris, detritus) was an important variable we considered in these stands based upon evidence suggesting burning temperature and duration of heating may be most related to fuel structure in longleaf pine stands (Andreu et al., 2012; Cronan et al., 2015). Live fuel height differed between our treatment units and was highest in the annual growing season burns. This differed from our results for live fuel mass which was highest in the biennial dormant burns. We relate this finding to the abundance of more green, actively growing plants in the growing season than in the dormant season.

Down and dead woody debris height was greatest in the long-term unburned stand prior to fire, even though this result was not reflected in the mass of this material between the treatment units. Following the results for detrital mass, detrital depth was greatest in the long-term unburned stand. The values in the long-term unburned stand were approximately 2-4 times greater than the frequently burned stands. The differences in total fuel height were not as clearly defined, however, and differed by only 14 cm from the annual dormant (lowest) to the annual growing stands (highest). It is noted that the canopy in the long-term unburned stand is essentially closed, which is one factor limiting the presence and height of understory vegetation in this stand. Additionally, there were not significant differences in total fuel height between the annual and biennial dormant stands. This result was surprising given the additional time understory vegetation in the biennial dormant stands was given to grow. Using the results generated by the linear contrasts prior to burning, it appears that frequent prescribed fire in these stands did not affect live fuel height or total fuel structure, but both down and dead woody debris height and detrital depth were greater in the long-term unburned stand as compared to all of the frequently burned stands.

Detrital chemical composition is not affected by frequent prescribed fire

Our results suggest that frequent prescribed burning does not significantly alter detrital chemical composition in longleaf pine forests, despite altering detrital mass and vertical structure. We observed minimal differences in functional group percentages in our samples, regardless of treatment. In a general sense, proteins (nitrogen compounds), carbohydrates (oxygen compounds), and lipids (aliphatic compounds) were all minimally affected as a result of long-term, frequent prescribed fire. The phenolic compounds, or lignin-based, woody material, accounted for approximately 60-80% of all samples, regardless of treatment. This range aligned well with Song and Peng's (2010) estimate of 65.9% phenolic compounds in wood charcoal. Ecologically, the phenolic group is slow to breakdown and decompose, but does serve as a food source for microbes and will provide a source of decomposable, long-term carbon and other nutrients.

The aromatic compounds were of particular interest in this study because they are generally linked to poor air quality when emitted into the atmosphere, may have impacts as a major contributor to global climate change, and may serve as a long-term carbon sink in soils (Bird et al., 2015). Although aromatics are regularly found in naturally decomposing litter, they generally increase as a consequence of burning, particularly PAHs (Schmidt & Noack, 2000; Masiello, 2004; Santin et al., 2016). The rate at which PAHs and other black carbon constituents are degraded and decomposed is directly related to charring intensity and fuel source (Baldock & Smernik, 2002; Masiello et al., 2002; Czimczik et al., 2003; Czimczik & Masiello, 2007). In a study of burned soils in Korea, Kim et al. (2003) found that PAHs were only elevated in burned soils immediately after burning, not five months after burning. After five months, the PAH levels returned to pre-burn and control levels. This contrasts Vergnoux et al. (2010) who found that naphthalene, a PAH, was 20 times higher in burned surface soils (0-5 cm) immediately after burning. These levels remained elevated years after burning, as well. Additional studies have shown that black carbon can remain in residence in soils beyond 1000 years (Forbes et al., 2006; Schmidt & Noack, 2000).

We found PAHs in all of our samples but the overall contributions to the total biomass were relatively low (2.0-3.0%), regardless of treatment. Similar values for the PAH group were observed in the long-term unburned unit and the frequently burned units. This may be related to natural decomposition as PAHs are present in naturally, untreated, degrading litter (Placha et al., 2009). Another explanation for this may be the proximity of these units spatially at the Tom Yawkey Wildlife Center. Atmospheric deposition of PAHs over time may have led to an accumulation of these compounds within each of the treatment units, regardless of whether or not a particular unit was burned.

Another plausible explanation for this lack of differences may be related to the depth of charred and uncharred material remaining after burning. In these low intensity, low severity surface fires, incomplete combustion is common. Significant amounts of unburned or partially burned detrital materials remain post-fire as a result of non-uniform fire behavior. Not all of the pre-burn detritus was ignited in our treatment units as a result of these prescribed fires. The depth of unburned material varied across the landscape and was approximately 0.5 cm in the biennial dormant stands. Consequently, the samples we prepared and ran using analytical pyrolysis/GC-MS were not simply "ash," but were instead a mixture of both burned and unburned material. This heterogeneity has been noted in other studies of burned detritus (Jenkins et al., 2016).

While broad functional groups showed very little alteration in response to prescribed fire, we did note that individual compounds within those groups may not be identical between treatments. One example of this was noted with the one-ring aromatics (non-PAHs). Percentages for this group were highest in the long-term unburned stand (11.4%) and the biennial dormant burned stands (11.9%). This was in contrast to 6.6-7.6% for the annually burned stands. This is most likely the product of elevated values for toluene in both the long-term unburned stand and the biennial dormant burned stands, as can be seen in the lower benzene/toluene ratios for these stands. Toluene is a less condensed aromatic compound and is more difficult to breakdown over time than benzene. Kaal & Rumpel (2009) indicate that the benzene/toluene ratio falls between 0.3-0.6 with laboratory burning temperatures of 400^{o}C. This value increases with increasing heat beyond 800^{o}C. Although functionally toluene and benzene are quite similar and are both aromatics, they exemplify one of the differences we noted in compounds that function similarly but are still structurally unique compounds.

The lack of differences determined when evaluating the benzene/phenol ratio between these treatments is a strong indicator of the conservation of detrital chemistry as a result of frequent burning at the Tom Yawkey Wildlife Center. The mean benzene/phenol ratio ranged from 0.14-0.17 between the treatments, which is indicative of burning temperatures less than 800^{o}C (Kaal & Rumpel, 2009).

It has been suggested that organic matter may be volatilized at temperatures between 200^{o}C and 315^{o}C (Lide, 2004). We did place thermocouple–datalogger units in these stands to monitor burning temperature (Figure 3.8). Although our thermocouples

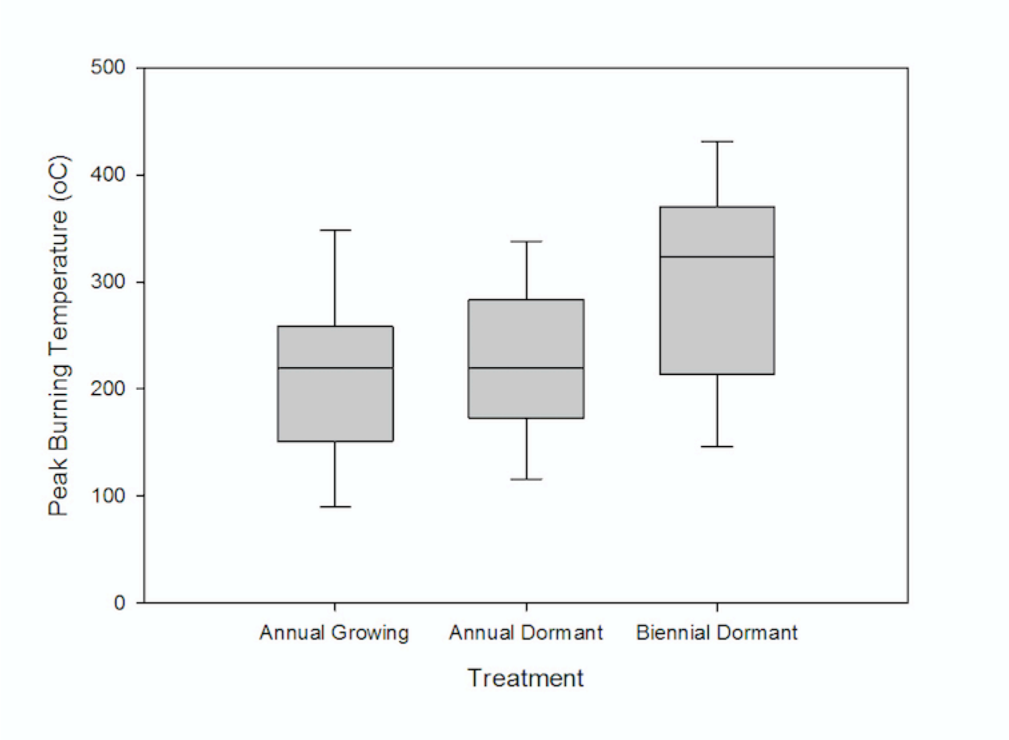

Figure 3.8. Peak burning temperature recorded using thermocouple–datalogger assemblies during prescribed fires conducted at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA. Annual growing: n=47; Annual dormant: n=49; Biennial dormant: n=26

suggest that we reached temperatures of 200-315^{o}C in most of our burn units, these values were by no means uniform.

Essentially pyrolysis of burned detritus generates a wide array of products that can be related to their origin and the structure of the organic molecules present in that substance (Leinweber & Schulten, 1995; Gonzalez-Vila et al., 2001; De la Rosa, 2012). Knicker et al. (2005) note that fire may generate new forms of carbon and nitrogen compounds while also modifying some carbon compounds. Based upon the similarities in the functional group percentages and the selected ratios we investigated between our treatment units and the lack of differences in those percentages and ratios before and after fire in the burned treatments, we are able to conclude that prescribed fire altered detrital quantity, but did not significantly alter detrital chemical composition.

This research serves to suggest that frequent prescribed fire in longleaf pine forests may alter the concentration of some individual chemicals, but does little to affect the overall chemical integrity of forest detritus. This is done while reducing wildfire hazard, adding to the extensive benefits that may be promoted by prescribed fire in these systems. Managers and landowners should feel confident that frequent prescribed fire in longleaf pine forests does little to alter the chemical character of forest detritus.

Conclusions

Despite changes in fuel loading and fuel structure as a result of short-term alterations in fire frequency and fire season in longleaf pine stands, long-term, frequent prescribed fire does not appear to significantly alter forest detrital chemical composition. Phenolic compounds, serving as a lignin surrogate, represented the dominant fraction in samples from all of our treatments. We believe this is largely the result of incomplete combustion of the detrital material, which is the product of both low fire intensity and low fire severity. These types of fires characterize the frequent low intensity, low severity fires conducted in longleaf pine forests throughout the southern United States. Fuel loading and fuel structure may be altered by prescribed fire when stands have faced fire exclusion for a long period of time. Tree mortality may result from fine root degradation as a result of duff consumption if fine roots have penetrated the duff. In this sense, frequent prescribed fire presents major benefits to maintain detrital quality while minimizing the risk of tree mortality if a wildfire were to occur in a long-term, unburned stand. These results highlight one benefit of prescribed fire in these forests and other properties and processes should be considered when discussing the benefits and impacts of frequent prescribed fire in longleaf pine forests.

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CHAPTER FOUR

FOREST MANAGEMENT ALTERS DETRITAL CHEMICAL COMPOSITION IN COASTAL WATERSHEDS AND MAY BENEFIT WATER QUALITY

Abstract

Many people around the globe depend on drinking water sources originating from forested watersheds. Forest management practices, such as prescribed fire and forest harvesting, may impact the litter and duff of forest soils. Any alterations to the litter and duff, here defined as forest detritus, may consequently affect the organic constituents and treatment regimens of source waters. We conducted a preliminary study at a pair of first-order watersheds in coastal South Carolina to better understand the impacts of long-term forest management on forest detrital chemical composition and potential water quality. By comparing the chemical composition of forest detritus originating from a managed watershed and an unmanaged watershed, we observed differences in the chemical composition of forest detritus. Aliphatic, or lipid-like, chemicals were prevalent in primary compounds identified in the detritus from the unmanaged watershed, but were not found in the primary compounds of the detritus from the managed watershed. Phenolic, or lignin-like, compounds were the predominant functional group found in the principle compounds of the managed watershed. Detritus from the unmanaged watershed contained higher percentages of a few organic pollutants (aromatic and polycyclic aromatic hydrocarbons). Fuel reduction techniques, such as prescribed fire and mastication, and harvesting have been utilized in the managed watershed since 1963. It appears that these practices might be of interest to not only reduce hazardous fuel loads

but to also reduce some of the organic pollutants that may affect forested water quality and, subsequently, human health.

Introduction

Forests cover approximately 31% (4 billion hectares) of the world's total land mass (Bladon et al., 2014). One of the ecosystem services provided by forests is the filtration of water (Brooks et al., 2013), the cost-savings of which is estimated at 4.1 trillion dollars per year globally (Bladon et al., 2014). Almost two-thirds of the municipalities in the United States and about one-third of the world's largest cities receive most of their drinking water from forested areas (Bladon et al., 2014). As such, practices that alter forests must be considered for their potential impact on water quality (Brooks et al., 2013).

Two of the practices most utilized in the management of forested watersheds are prescribed fire and harvesting (Waldrop & Goodrick, 2012). To understand the impacts of these practices on water quality, one must understand how they impact forest soils. The O Horizon of forest soils, comprised of the litter and duff, serves as a critical source of organic materials (Pritchett, 1979; Binkley & Fisher, 2015). This litter and duff, referred to in this publication as forest detritus, contributes to dissolved organic matter in forested watersheds and subsequently impacts water quality (Bladon et al., 2014).

Under the appropriate conditions, prescribed fires reduce excessive fuel loads and maintain a more open forest cover (Van Lear et al., 2005). In general, prescribed fires minimally impact forest soils and forested water quality because fire intensity and fire severity remain low (Waldrop & Goodrick, 2012). When fire intensity and fire severity are high, as is the case in wildfires, the duff layer is generally altered, reduced, or completely consumed (DeBano et al., 2005). When this occurs, surface runoff and erosion increase. Sediments, heavy metals, and pollutants may be added to forested waters in this scenario (Pereira et al., 2012; Brooks et al., 2013), leading to a host of well-documented, detrimental effects (Fulton & West, 2002).

The effects of forest harvesting on water quality are similar to the effects of prescribed fire. As the intensity of harvesting disturbance increases, more detrimental effects are actualized to forest soils and forested waters (Brooks et al., 2013). These effects may include increased water temperatures, increased sediment and heavy metal loads, and alterations in aquatic habitat (Emelko et al., 2011). The choice of equipment, timing of harvest, road construction techniques, and choices related to the management of woody debris post-harvest are critical items of consideration when determining the impacts of forest harvesting on forest water quality (Holopainen & Huttunen, 1998). Impacts are generally stated in terms of their longevity as most harvesting impacts are short-lived and localized (Fulton & West, 2002). Standard thinning operations are generally less intense and impact forest soils less (Fulton & West, 2002). It is a concern for water resources that influences the voluntary or mandatory implementation of best management practices (BMPs) in forestry operations throughout the United States (Brooks et al., 2013).

Specific compounds in water exiting forests are addressed at water treatment facilities to insure the availability of healthy drinking water (Emelko et al., 2011). This includes many nutrient concentrations and potential pollutants. Scientists have investigated both aromatic and polycyclic aromatic hydrocarbons (PAHs) for many years as potential components of long-term carbon sequestration in forest soils (DeLuca & Aplet, 2008) and as contributors to global climate change when emitted into the atmosphere (Abdel-Shafy & Mansour, 2016). These compounds are also monitored as pollutants in drinking water due to their mutagenic and potentially carcinogenic properties when ingested by humans (Olivella et al., 2006). Burning of biomass is one of the primary sources of aromatic compounds and PAHs in natural systems as these tend to increase in burned materials (Goldberg, 1985). Little is known about potential long-term alterations in the chemical composition of forest detritus and water quality resulting from forest management practices such as prescribed burning and harvesting.

To investigate this issue, we conducted a preliminary analysis of detrital chemical composition at a pair of first-order watersheds along the South Carolina coast. By identifying and comparing the chemical functional groups of detrital samples obtained from a long-term, unmanaged watershed to a long-term, managed watershed, our goal was to determine differences in detrital chemical composition that might significantly impact water quality. Our hypothesis was that the forest management practices of prescribed fire and thinning have altered detrital chemical composition in the managed watershed, mainly through an increase in aromatic and polycyclic aromatic compounds, and this may impact forested water quality.

Materials and Methods

Study site

Two experimental, coastal, first-order watersheds within the Santee Experimental Forest of the Francis Marion National Forest in Cordesville, South Carolina were utilized for this study (Figure 4.1). Lands comprising this forest have been used for agricultural and forestry purposes since the early 1700s (Dai et al., 2013). The unmanaged watershed, Watershed 80, is a 160 ha watershed that has not been subjected to active forest management practices since 1968 and serves as a control site for the USDA Forest Service Southern Research Station Center for Forested Wetlands Research (Amatya & Trettin, 2007). The managed watershed, Watershed 77, is a 160 ha watershed that has been actively managed by a host of silvicultural practices since 1963, including prescribed fire, thinning, and mastication (Amatya et al., 2006) (Table 4.1).
One large natural disturbance of note affecting both watersheds in 1989 was Hurricane Hugo; approximately 80 percent of the dominant trees in the area were broken or uprooted (Hook et al., 1991). No post-hurricane debris was removed from the unmanaged watershed and no silvicultural practices were utilized for stand recovery. The managed watershed was salvage-harvested in 1990 (Amatya et al., 2006). Since 2003, this watershed has been burned every 2-4 years (Table 4.1). These differences in management strategy have resulted in greater total fuel loading, forest floor depth, and fuelbed depth in the unmanaged watershed (Figure 4.2).

The dominant trees on both watersheds are loblolly pine (*Pinus taeda*), sweetgum (*Liquidambar syraciflua*), and many oaks (*Quercus* spp.). Basal area is currently greater in the unmanaged watershed (46.35 m^2 ha^{-1}) than in the managed watershed (33.72 m^2 ha^{-1}). Pines account for eighty-one percent of the basal area in the managed watershed and

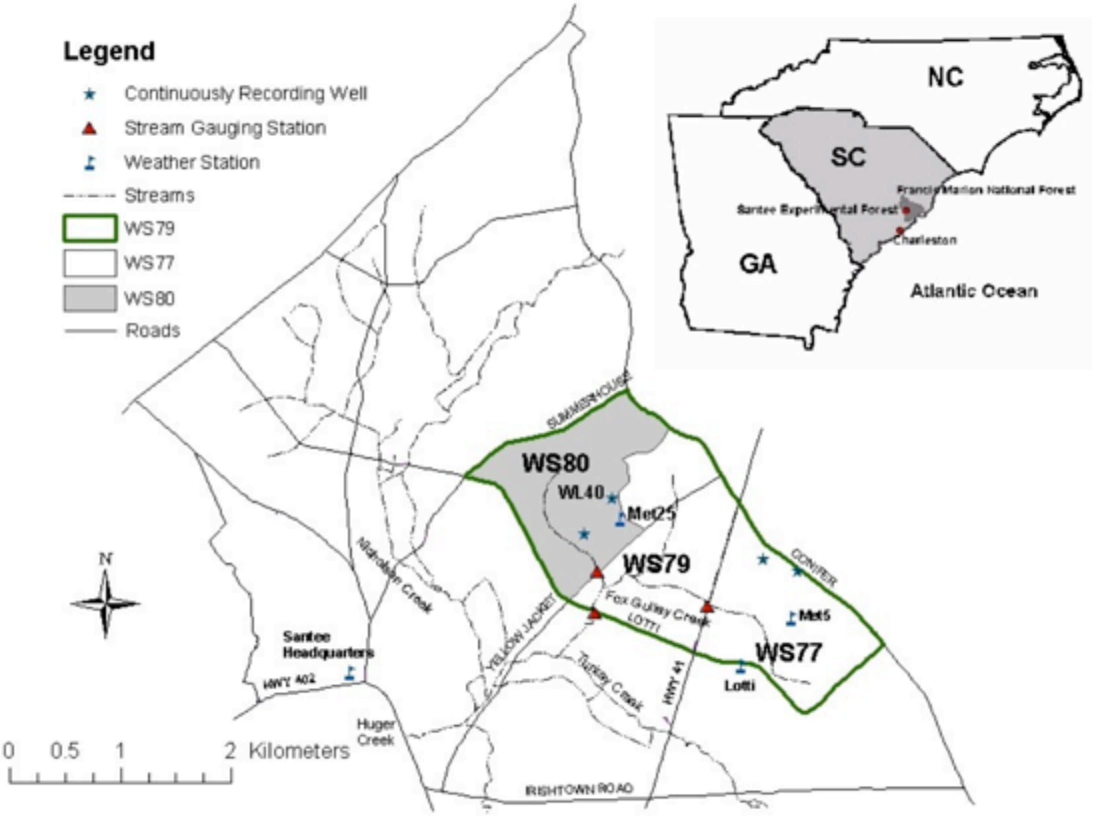

Figure 4.1. Location of the experimental watersheds (Watersheds 77 and 80) utilized for this study on the USDA Forest Service Southern Research Station's Santee Experimental Forest, Cordesville, South Carolina (Harder et al., 2006).

Table 4.1. Chronology of forest management practices and natural disturbances on both the managed (Watershed 77) and unmanaged watersheds (Watershed 80) of the Santee Experimental Forest, Cordesville, South Carolina (dates added to Table 4.1, Amatya et al., 2006).

Year (s)	**Description of treatments/disturbances**
1963	Watershed 77 established as a managed, treatment watershed
1968	Watershed 80 established as a control/unmanaged watershed
1977-1981	100% of Watershed 77 is prescribed burned at various times over 5 year period
1989	Hurricane Hugo damages 80% of forest (Sept.)
1990	Watershed 77 is salvage-harvested (entire vegetation harvested and removed) Watershed 80 is left untouched
2001	Mastication of understory vegetation occurred on Watershed 77 (Feb.-Nov.)
2003	Watershed 77 prescribed burned on May 10
2006	Watershed 77 whole-tree thinning of understory in early July
2007	Watershed 77 prescribed burned on June 7
2009	Watershed 77 prescribed burned on April 21
2013	Watershed 77 prescribed burned on March 5

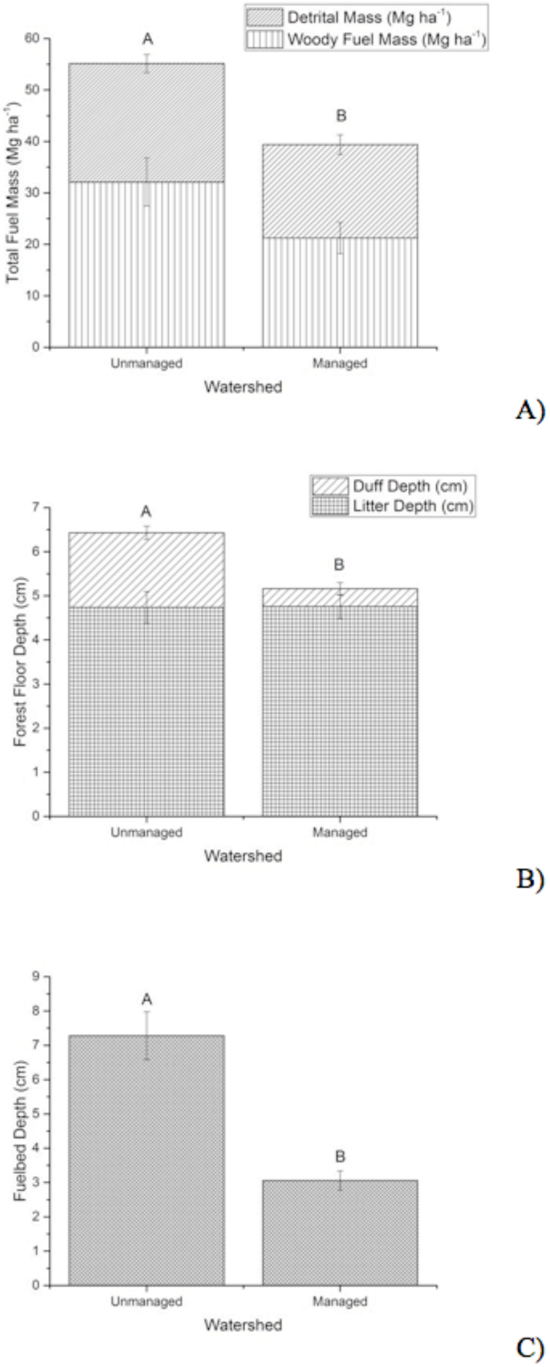

Figure 4.2. A) Total fuel mass, B) forest floor depth, and C) fuelbed depth for the Santee Experimental Forest watersheds.

forty-one percent of the basal area in the unmanaged watershed. These dynamics are depicted in the photos featured in Figure 4.3. The soils have developed in marine sediments and have drainage varying from very poorly drained in the riparian zones to moderately well drained in the uplands. They are defined as aquic *Alfisols* or *Ultisols*, containing argillic horizons (Jayakarin et al., 2014).

Detrital sampling

A randomized sampling grid was established for each watershed. Twenty locations were established approximately 300 m apart in each watershed. During January–February 2015, three 0.30 x 0.30 m (1 ft x 1 ft) destructive samples of forest detritus were taken approximately 1 m apart at each location. Each of these samples was brought back to the lab and oven-dried at 70°C for not less than 48 hrs. These samples were then ground using a Wiley mill (2 mm sieve).

Detrital chemistry

To determine the chemical composition of the detritus (litter and duff combined), 1-2 mg of well-mixed, oven-dried, and ground material was subjected to analytical pyrolysis/gas chromatography – mass spectrometry (GC-MS) for a total of four samples (two from the unmanaged watershed and two from the managed watershed).

Our Py/GC-MS procedures followed the methodology specified by Song & Peng (2010). Pyrolysis products were identified according to: (1) their GC retention times; (2) their mass spectra with reference to the Wiley/NIST library supplied with the instrument software; and (3) published mass spectra of pyrolysis products listed in Song & Peng (2010).

Figure 4.3. Images from sites at the A) unmanaged and B) managed watersheds, Santee Experimental Forest, Cordesville, South Carolina.

Using the results generated from each sample, the total identified area of each sample was calculated using the NIST software. Default parameters for calculating this area were followed, with the exception of slope. This value was adjusted to 5. Using this area calculation, the most readily identified compound by highest total area was determined. The area for this compound was then used as the denominator to calculate the total quantified peak area (TQPA) percentage for each additional compound (Kaal & Rumpel, 2009). Representative pyrograms for the managed and unmanaged watersheds depicting this notation are shown in Figure 4.4.

To better understand the chemical composition of each sample, the ten compounds with the highest TQPA in each sample were noted by name and by functional group. The potential functional groups were as follows: 1) Aliphatic compounds (lipid-like), 2) Aromatic compounds with only one-ring structures (i.e. benzene and its derivatives excluding the hydroxyl group), 3) Polycyclic Aromatic Hydrocarbons (compounds with two or more aromatic rings), 4) Nitrogen-containing compounds (protein-like), 5) Oxygen-containing compounds excluding phenolic compounds (carbohydrate-like), and 6) Phenolic compounds (lignin-like) (i.e. benzene with at least one or more hydroxyl group) (Song & Peng, 2010).

Additionally, six of the compounds most distinguished in the pyrolysis literature were identified within each of the four samples. The percentage that each compound constituted of the entire, tested sample was calculated using the integrated area. These compounds were: 1) 4-vinylsyringol (phenolic), 2) Naphthalene (PAH), 3) Phenol (phenolic), 4) Ethylbenzene (aromatic), 5) Toluene (aromatic), 6) Benzene (aromatic).

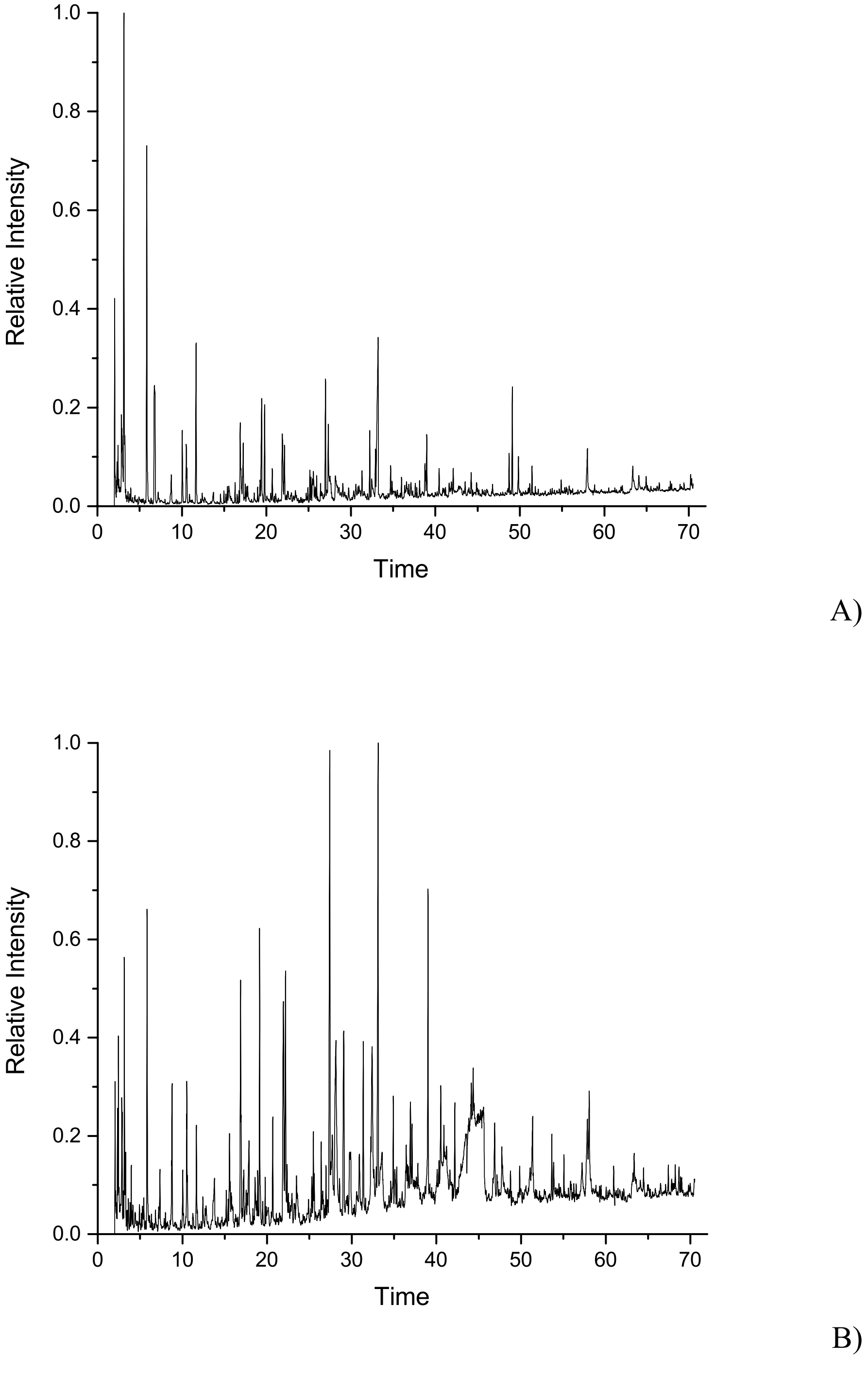

Figure 4.4. Representative pyrograms for detrital samples originating from the A) unmanaged and B) managed watersheds of the Santee Experimental Forest.

These compounds differ in aromaticity and functional grouping. Ratios of 1) benzene/toluene and 2) benzene/phenol were additionally evaluated to understand the cross-link structures (Kaal & Rumpel, 2009).

Statistical analyses

Due to the semi-quantitative nature of Py-GC/MS results and small sampling numbers, no strict statistical procedures were used to distinguish differences in detrital chemistry between the two watersheds.

Results

Detritus chemistry

None of the top ten compounds found in either of the samples from the managed watershed were noted as aliphatic compounds (lipid, fat-like) (Table 4.2), but both samples from the unmanaged watershed contained aliphatic compounds in their top ten (Table 4.3). Phenolic compounds (lignin-like) and aromatic compounds were found within the top ten in each of the four samples, but phenolic compounds were the predominant functional group found in the managed watershed's detrital samples.

Values for the TQPA of 4-vinylsyringol (phenolic), naphthalene (PAH), phenol (phenolic), ethylbenzene (aromatic), toluene (aromatic), and benzene (aromatic) in each watershed are depicted in Figure 4.5. Values for benzene, toluene, ethylbenzene, and naphthalene were higher in the unmanaged watershed than in the managed watershed. Values for phenol and 4-vinylsyringol were higher in the managed watershed. The ratios of both benzene/toluene and benzene/phenol are shown in Figure 4.6. Both ratios were higher in the unmanaged watershed.

Table 4.2. Top ten compounds distinguished by total quantified peak area (TQPA) in detrital samples from the managed watershed.

Watershed / Sample	Time	Compound	Functional Group
Managed / #1	22.179	Phenol 2-methoxy-	Phenolic
	19.116	Cyclohexanol	Oxygen
	39.023	Phenol, 2-methoxy-4-(1-propenyl)-	Phenolic
	5.827	Toluene	Aromatic
	29.045	Benzofuran, 2,3-dihydro-	Phenolic
	32.404	1,2-Benzenediol, 3-methyl-	Phenolic
	21.927	Phenol 4-methyl-	Phenolic
	28.123	1,2-Benzenediol	Phenolic
	33.115	2-Methoxy-4-vinylphenol	Phenolic
	27.405	Phenol, 2-methoxy-4-methyl-	Phenolic
Managed / #2	32.33	1,2-Benzenediol, 3-methyl-	Phenolic
	11.65	Styrene	Aromatic
	33.037	2-Methoxy-4-vinylphenol	Phenolic
	27.957	1,2-Benzenediol	Phenolic
	28.986	Benzofuran, 2,3-dihydro-	Oxygen
	16.823	Phenol	Phenolic
	27.336	Phenol, 2-methoxy-4-methyl-	Phenolic
	21.824	Phenol 4-methyl-	Phenolic
	5.828	Toluene	Aromatic
	3.138	Benzene	Aromatic

Table 4.3. Top ten compounds distinguished by total quantified peak area in detrital samples from the unmanaged watershed.

Watershed / Sample	Time	Compound	Functional Group
Unmanaged / #1	21.888	Phenol 4-methyl-	Phenolic
	2.04	Cyclopropane	Aliphatic
	19.438	Dodecane, 1-fluoro-	Aliphatic
	27.002	Naphthalene	Aromatic
	6.723	Cyclopentane	Aliphatic
	6.771	Cyclopentane	Aliphatic
	11.672	Styrene	Aromatic
	5.842	Toluene	Aromatic
	33.232	2-Methoxy-4-vinylphenol	Phenolic
	3.141	Benzene	Aromatic
Unmanaged / #2	2.827	1,3-Cyclohexadiene	Aliphatic
	49.835	1-Dodecanol, 3,7,11-trimethyl-	Oxygen
	11.641	Styrene	Aromatic
	2.032	Cyclopropane	Aliphatic
	16.815	Phenol	Phenolic
	28.121	1,2-Benzenediol	Phenolic
	29.004	Benzofuran, 2,3-dihydro-	Oxygen
	3.125	Benzene	Aromatic
	21.841	Phenol 4-methyl-	Phenolic
	5.818	Toluene	Aromatic

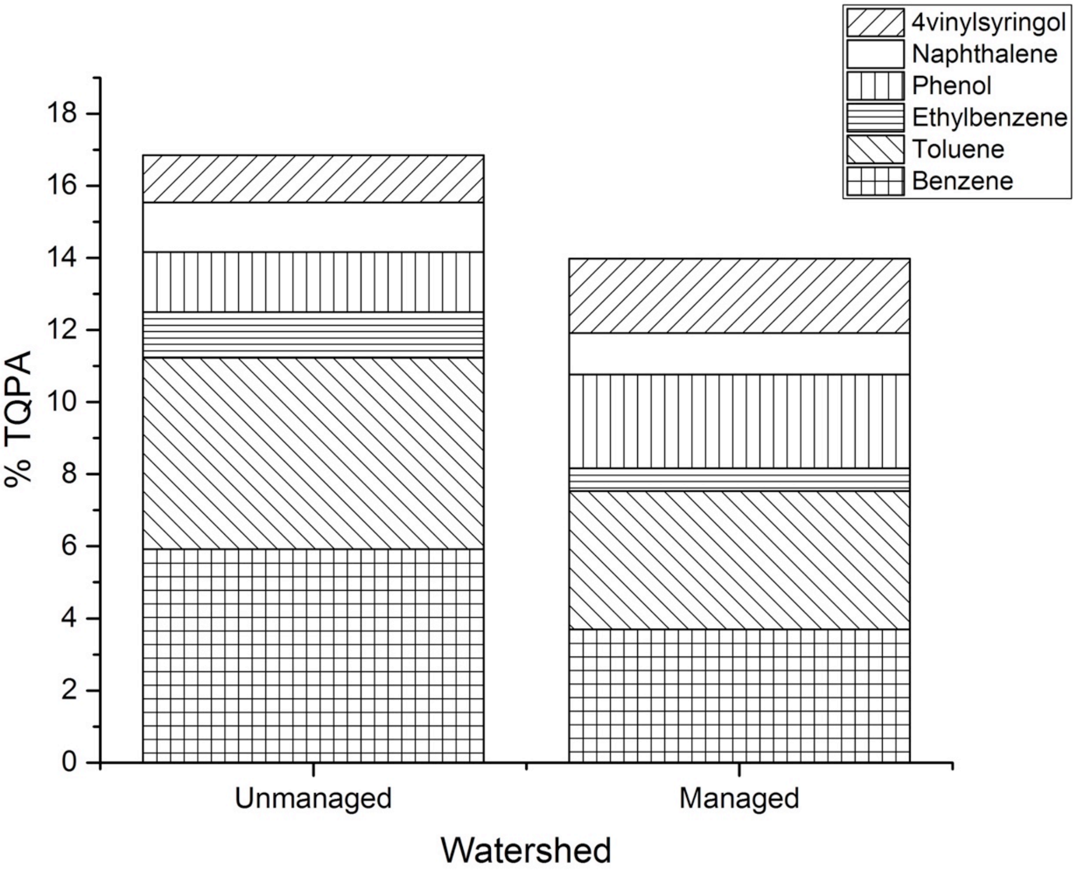

Figure 4.5. Percentage of the total quantified peak area (TQPA) for selected compounds found in detrital samples obtained from unmanaged and managed watersheds of the Santee Experimental Forest.

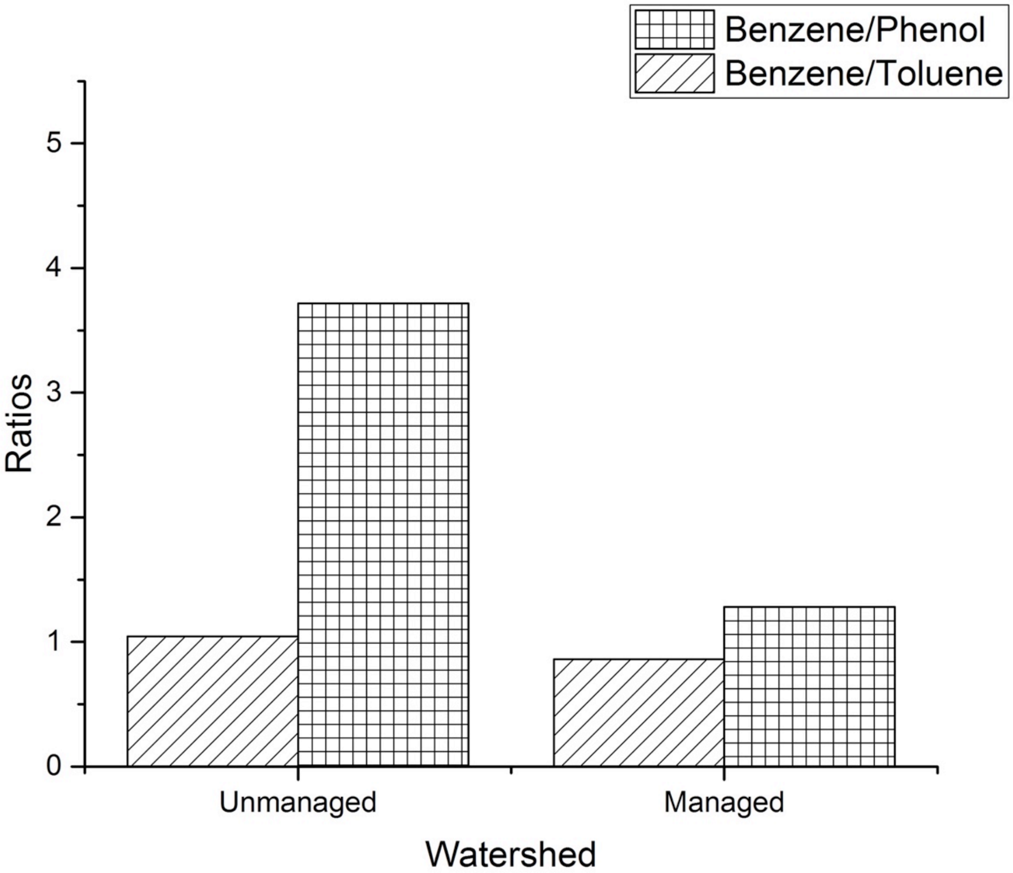

Figure 4.6. The benzene/toluene and benzene/phenol ratios for detrital samples obtained from the unmanaged and managed watersheds of the Santee Experimental Forest.

Discussion

Predominant influence of fire

A multitude of information has been generated to document the effects of harvesting on short-term nutrient loading and sedimentation in forested waters (Fulton & West, 2002), but no comparable studies of detrital chemistry related to forest harvesting could be found in the literature. Additionally, ten years have passed since non-fire related management practices have been implemented on the managed watershed (Table 4.1). Most post-harvest effects on forest soils and water quality are localized and temporary in thinning or partial harvest scenarios (Wang et al., 2006), as was practiced on the managed watershed in 2006. Our results appear to be influenced by the extended prevalence of prescribed fire across the managed watershed. It cannot be neglected, however, that the stand conditions currently experienced on the managed watershed (decreased basal area, decreased hardwoods, decreased total fuel loading, decreased forest floor depth, and decreased fuelbed depth) are the result of the combination of prescribed fire, thinning, and mastication. As a result of this distinction in the management practices, most of the subsequent discussion will highlight the effects that appear to be directly related to the inclusion or exclusion of prescribed fire on these watersheds.

Detrital chemistry differs between the watersheds

The aliphatic, or fat-like, compounds were not present in the top ten compounds identified in either of the samples from the managed watershed, but were present in both samples from the unmanaged watershed. Gonzalez-Perez et al. (2004) suggest in their review of soil organic matter that aliphatic (lipid-like) structures appear to decrease in areas that have been burned. In the absence of fire, these substances persist in the environment (Alexis et al., 2007). In some cases, aliphatic hydrocarbons are present in burned material, particularly compounds that are heated to 280^{o}C or less (Nassar et al., 1984). Beyond that threshold, aromatic compounds tend to dominate post-fire chemistry (de la Rosa, 2007). This would suggest that burning temperatures at the managed watershed have consistently exceeded 280^{o}C, leading to the volatilization of aliphatic structures; the predominant influence of aliphatic structures in the unmanaged watershed may be related to the lack of burning.

Aromatic and phenolic compounds dominated the top ten compounds derived from the managed watershed samples. These results are similar to samples obtained from pine-dominated stands that have been burned frequently at the Tom Yawkey Wildlife Center in Georgetown, South Carolina (Chapter 2). At Yawkey, aliphatic compounds were generally reduced in stands that were frequently burned as opposed to stands that were not burned. Aromatic compounds are generally present in abundance in burned detritus (Masiello, 2004). The phenolic compounds, or lignin-like structures, may be the result of the partial degradation of material that has occurred because of burning. These compounds typically persist in abundance at fire temperatures of 400^{o}C or less (Kaal et al., 2012). Not all material in these low intensity prescribed burns is completely consumed or reduced to "ash" (Goldberg, 1985). Much of the material is simply heated or partially charred and may remain in residence on the forest floor for some degree of time (Krishnaraj et al., 2016).

The abundance of the aromatics (benzene, toluene, ethylbenzene) and naphthalene (PAH) in the unmanaged watershed samples was not anticipated. This may be the result of natural humification in the unmanaged watershed with the absence of any fire-related volatilization losses. There are few sufficient methods to estimate or quantify potential losses of chemical constituents in wildland fire smoke. Most research related to this topic has been focused on quantifying emissions of CO_2, CH_4, and other potential greenhouse gases (Simpson et al., 1999). Reinhardt & Ottmar (2000) did conduct work related to wildfire emissions and the impact on wildland firefighters' health. They found that exposure to benzene could be predicted from exposure to CO, but did not focus on quantifying specific amounts of benzene in wildfire smoke. It is plausible that benzene and toluene, two aromatic compounds and monitored organic pollutants, have been emitted from the managed watershed during the prescribed fires. In the unmanaged watershed, these compounds have remained in residence because of uninterrupted humification and have not exited the site.

If a wildfire were to occur, the increased fuel loads in the unmanaged watershed are a cause for concern. This increase in fuel can also be related to an increase in these volatile compounds entering the atmosphere, which is a concern for many stands where fire has been excluded for an extended time (Varner et al., 2005). Our results do suggest that the presence of these compounds can be expected, both with and without a high degree of manipulation and management. This concurs with the findings of Placha et al. (2009) who found naphthalene in abundance in both unmanaged, forest soils and highly-managed, agricultural soils.

When interpreting these results, it must also be noted that forest composition differs at these watersheds. Hardwoods dominate the composition of the unmanaged watershed while pines dominate the composition of the managed watershed. We can only theorize potential differences in chemical functional groups based upon species composition. We have only conducted our tests on detrital chemistry with litter composed of mixed species, not pure species. However, evidence in the literature suggests that species composition is important when evaluating pyrolytic products (Ralph & Hatfield, 1991; Weise & Wright, 2014). Although their study was focused on biochars and bio-oils, evidence from Jarvis et al. (2014) suggests that different tree species contain different chemical constituents and these constituents respond differently to pyrolysis. Even further, different portions of a tree seem (i.e. bark, leaves, stem) present differing chemical signatures when heated (Das et al., 2010). It is plausible that the increase in hardwood species and detritus in the unmanaged watershed may be a factor affecting the detrital chemistry results.

The presence of more hardwoods in the unmanaged watershed is the result of the lack of active forest management since 1968. These watersheds were originally paired due in part to similar forest composition. Thin-barked species that are generally confined to bottomlands may increase in abundance across the landscape in the absence of fire and other disturbances (Waldrop & Goodrick, 2012). Fire and thinning have maintained lower stand density in the managed watershed and have most likely affected the reduction of hardwood species.

Potential Water Quality Effects

Based upon this preliminary analysis, it appears that water exiting these stands might necessitate different treatment regimens at a water treatment facility. The chemical composition of these detrital materials differs. The results of Py/GC-MS are not intended to estimate quantities of these materials but are instead used to characterize a given sample (Kaal & Rumpel, 2009). This limits our study to the characterization of detrital chemistry without practical means to estimate quantities.

Nevertheless, it appears the prevalence of potential pollutants, found in the aromatic and PAH functional groups, and the greater abundance of decomposing detritus in the unmanaged watershed might pose more hazard in waters exiting that watershed as opposed to the managed watershed. Benzene, toluene, and ethylbenzene are noted as regulated organic chemicals in drinking water by the Environmental Protection Agency (EPA) (Macler, 2007). The maximum contaminant level (MCL) for benzene, a known carcinogen (Dozier & Lesikar, 2009), in tap water is 5 ppb. Ethylbenzene carries an MCL value of 0.7 ppm and toluene’s MCL value is 1 ppm. Both compounds are currently being investigated as potential carcinogens in humans (Macler, 2007), but long-term exposure to either has been associated with spasms, tremors, liver damage, and kidney damage (EPA, 2009). Naphthalene is not a regulated organic contaminant and carries no MCL value (Macler, 2007) but is currently deemed a potential carcinogen, as well (Delaware Health and Social Services, 2013). These four chemicals were more abundant in the samples from the unmanaged watershed and are a cause of concern for both water quality and human health.

Phenol and its derivatives, such as 4-vinylsyringol, were more abundant in the detritus from the managed watershed. Phenol is not a regulated organic chemical in drinking water, but in 1974 a large incidence of human illness was reported resulting from the chemical contamination of wells in southern Wisconsin (Baker et al., 1978). Although not life threatening, these individuals experienced a host of symptoms, such as diarrhea, mouth sores, dark urine, and burning of the mouth. The estimated intake of phenol was 10-240 mg/person/day. No long-term threats to exposed individuals were noted six months after this level of exposure. Phenolic compounds accounted for more of the top ten compounds in the managed watershed and the abundance of these compounds was greater in this watershed, as well. This could lead to concerns regarding short-term illness, but does not confer potential carcinogenic effects, as do some of the compounds that may be exiting the unmanaged watershed in greater abundance.

There are many more compounds found within these functional groups (Table 3.2) that were not part of our inquiry here and many more functional groups that are considered for overall water quality (Macler, 2007; Karyab et al., 2013). Specific compounds not investigated for this study may be found in greater abundance in one watershed as opposed to another.

The results presented here are based upon an initial evaluation of a small number of samples obtained from these watersheds using one specific method: Py/GC-MS. Further evaluation of these types of sites with similar stand histories and fire regimes would be helpful to determine the long-term consequences of forest management practices as related to long-term detrital chemistry and potential water quality. Other ecosystem properties and processes should be evaluated in cohort with information regarding detrital chemistry to fully understand the implications of long-term forest management.

From this study it does appear that active forest management practices, such as prescribed fire, thinning, and mastication, may alter long-term detrital chemistry in favor of improved water quality. This adds to the list of benefits that active forest management might provide, such as fuel reduction, wildfire hazard reduction, wildlife habitat improvement, and invasive species control (Waldrop & Goodrick, 2012). In many forested watersheds, the implementation of these practices may be deemed necessary for improved forest health, as well as improved human health.

Conclusions

Based upon our evaluation, it appears that the implementation of forest management practices in a coastal forested watershed in South Carolina has altered detrital chemical composition. Aliphatic compounds represented the primary products of forest detritus from an unmanaged watershed, while aromatic and phenolic compounds constituted the primary products of forest detritus from a managed watershed. The individual aromatic compounds and potential pollutants benzene, toluene, ethylbenzene, and naphthalene were found in greater abundance than expected in the unmanaged watershed, most likely the result of unmanipulated decomposition and humification in the absence of prescribed fire. Phenolic compounds represented a greater portion of the identified components in detritus from the managed watershed which potentially agrees with the partial charring and acceleration of decomposition that occurs with prescribed burning. Water exiting these watersheds may differ in quality as a result of the long-term inclusion or exclusion of fire. This may have implications for drinking water treatment and subsequent human health as a few organic pollutants characterized more of the detrital materials from the unmanaged watershed.

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CHAPTER FIVE

CONCLUSIONS

Polycyclic Aromatic Hydrocarbons and Peak Burning Temperature

One of the initial goals of this project was to test the hypothesis that black carbon production, measured by PAH concentration, increases as peak burning temperature increases. We were not able to fully address this hypothesis because the range of temperatures obtained using our thermocouple-datalogger assemblies was narrow (Figure 3.8). All temperatures were less than 500^{o}C. This may be the result of the frequency of burning present for our treatment units at the Tom Yawkey Wildlife Center. This forest has been burned nearly every other year since 1978. Fuel accumulations are not substantial given this frequency of burning, which leads most fires to burn as low intensity, low severity surface fires.

Our range of temperature values was also affected by the thermocouples themselves. As stated by Bova & Dickinson (2008), thermocouple probes do not measure actual flame temperature. It is suggested that true flame temperatures, regardless of fuel type, fuel amount, or ignition source, approximate 1100-1300^{o}C (Martin et al., 1969; Kennard et al., 2005). Instead of measuring true flame temperature, thermocouples provide an estimate of the degree to which the thermocouples themselves are heated in a fire event (Kennard et al., 2005). These values can then be used as a surrogate for fire intensity, particularly in scenarios where thermocouples are deployed at various points within the same burn unit or when comparing multiple burns in the same fuel type (Bova & Dickinson, 2008). This was the case in our study. Our peak values were much less than those noted for actual flame temperatures and were also less than many studies citing thermocouple values resulting from prescribed fires (i.e. Wenk et al., 2011).

In this study, fire behavior metrics at Yawkey (March 2015, May 2015, March 2016) and the managed watershed (April 2016) were obtained. At all fires, little difference was noted in thermocouple values despite differences in burn frequency, burn season, fuel loads, and methods of ignition. For example, mean peak burning temperature at the managed watershed using vertical thermocouples was 170.2^{o}C (n=12). This watershed had not been burned in 4 years, was ignited aerially, and had higher fuel loads than our stands at Yawkey. Despite this, mean peak burning temperature values at Yawkey were quite similar (vertical thermocouple mean=148.2^{o}C; horizontal thermocouple mean=214.3^{o}C) (Table 5.1). We did note that values from our horizontal metrics at Yawkey were nearly identical from one year to the next when the same stands were burned in 2015 and 2016 (Table 5.1). Vertical values were significantly different in 2015 and 2016. Fire weather may have had more influence on the vertical values; in 2016, wind gusts were more prevalent during our burns.

As stated in Chapter 2, our thermocouple values were not correlated with any pre- or post-fire metrics of fuel loading, fuel depth, detrital mass, or detrital functional group percentages. In this way these values were not useful as predictors or predicted values. Bova & Dickinson (2008) recommend calibrating thermocouple values with additional data to approximate other estimates of fire behavior, such as fireline intensity. This calibration may enhance potential correlations for some of our paramaters at a later date.

Table 5.1. The means and mean differences (and associated p-values) in the fire behavior variables from both vertical and horizontal thermocouples obtained by burning the same sites in both 2015 and 2016 at the Tom Yawkey Wildlife Center.

Fire Behavior Variables	**Orientation**	**Means and Mean Differences**
PBT (^oC)	**Vertical Mean 2015**	122.7
	Vertical Mean 2016	165.7
	Vertical Mean Difference	**43.0 (p<0.01) n=21**
	Horizontal Mean 2015	229.0
	Horizontal Mean 2016	232.3
	Horizontal Mean Difference	3.3 (p=0.91) n=16
DOH (s)	**Vertical Mean 2015**	555.5
	Vertical Mean 2016	419.3
	Vertical Mean Difference	**136.19 (p<0.01) n=21**
	Horizontal Mean 2015	893.9
	Horizontal Mean 2016	938.6
	Horizontal Mean Difference	44.6 (p=0.78) n=14
AUTP ($s \cdot {}^oC$)	**Vertical Mean 2015**	15073
	Vertical Mean 2016	20015
	Vertical Mean Difference	4942 (p=0.12) n=21
	Horizontal Mean 2015	38607
	Horizontal Mean 2016	40798
	Horizontal Mean Difference	2191 (p=0.59) n=14

Management Effects on Detrital Chemistry and Potential Water Quality

Based upon our data, observations, and the assertions of many studies conducted over the years around the globe (Waldrop & Goodrick, 2012), we affirm that prescribed fire does reduce total fuel loading. The reduction of a particular class of woody fuels may not be uniform, however, depending upon the site and other disturbances affecting that site. For example, 1-, 10-, and 100-hr fuels were not always uniformly consumed by fire in our burns. This may be the reality for a given fire at a given site, but it may also be related to our measurement technique (Brown's Planar Intercept Method) (Brown, 1974). Brown's method would ideally be conducted before and after fire in exactly the same location. We had some difficultly doing that at Yawkey, even when we installed metal pins at each pre-fire sampling location. Fire made it difficult to insure we were re-sampling in the same exact location at the same exact transect angle.

These fires, both at Yawkey and the managed watershed, affected detrital mass most. Despite this reduction in detrital quantity at Yawkey, the chemical composition of this material, as noted by the functional group percentages, did not seem drastically altered. One may expect this material to degrade and enter the soil in a similar fashion, replenishing soil resources similarly long-term, regardless of fire treatment. More study is needed to confirm this, however. Some preliminary results are shown related to soils later in this chapter.

We did note that the abundance of a given compound within a given chemical functional group may differ even when percentages for the groups did not differ. This was the case with benzene and toluene, two aromatic compounds, at both sites. These compounds do differ structurally even though their function is similar. At Yawkey, with the exception of the elevated value in the biennial dormant burns, toluene appeared to increase with increasing time since fire. This was also the case at the watersheds. We relate the abundance in the biennial dormant burns potentially to the amount of material that remained unburned post-fire.

The additional individual compounds that were evaluated for the watershed samples in Chapter 4 are listed in Table 5.2 for our treatment units at Yawkey. With all of the compounds evaluated, regardless of the values found in post-fire samples, pre-fire percentages were less than or equal to the long-term unburned percentages. The post-fire samples were obtained on the day of the fires shortly after the fires cooled. This suggests that, despite short-term pulses that may increase post-fire, prescribed fire appears to reduce the accumulation of these compounds long-term. This agrees with the findings at the watersheds for naphthalene, ethylbenzene, benzene, and toluene which were all elevated on the unmanaged watershed.

To our knowledge, no significant research related to the effects of harvesting and mastication on detrital chemical composition has been published. This limits our knowledge of any potential direct harvesting effects on detrital chemical composition. Most studies suggest direct harvesting impacts to water quality, such as increased sedimentation and metal loads, are limited and short-lived when best management practices have been implemented, however (Wang et al., 2006). Given that these practices were implemented 10-15 years ago, the direct impacts of these practices have

Table 5.2. Percentage of the total quantified peak area (TQPA) for selected compounds found in detrital samples obtained from the Santee Experimental Forest and the Tom Yawkey Wildlife Center.

Treatment	**Benzene**	**Toluene**	**Ethylbenzene**	**Phenol**	**4-vinylsyringol**	**Naphthalene**	**Benzene / Phenol**	**Benzene / Toluene**
Santee Experimental Forest Watersheds								
Unmanaged (n=2)	5.91±2.90	5.31±1.19	1.27±0.16	1.66±0.13	1.31±0.12	1.37±0.88	3.72±2.04	1.04±0.31
Managed (n=2)	3.69±2.30	3.84±1.50	0.64±0.12	2.61±0.63	2.07±0.27	1.14±0.81	1.28±0.58	0.86±0.27
Tom Yawkey Wildlife Center								
Long-term unburned (n=3)	0.82±0.26 AB	3.11±1.03 A	0.61±0.07 A	5.01±0.27 B	3.64±0.22 A	0.12±0.02 B	0.16±0.02 A	0.46±0.29 A
Pre-fire (n=20)	0.60±0.03 B	1.01±0.04 B	0.13±0.01 C	4.32±0.17 B	3.52±0.28 A	0.09±0.00 B	0.14±0.01 A	0.59±0.02 A
All post-fire (n=24)	1.07±0.07 A	1.98±0.32 A	0.25±0.04 B	6.76±0.20 A	2.14±0.12 B	0.19±0.01 A	0.16±0.01 A	0.68±0.05 A
Burned Units								
Annual dormant (n=10)	0.93±0.09 A	1.30±0.08 B	0.16±0.01 B	6.23±0.19 B	2.04±0.19 A	0.17±0.02 A	0.15±0.01 A	0.71±0.04 C
Annual growing (n=10)	1.15±0.10 A	1.34±0.07 B	0.16±0.01 B	6.97±0.34 AB	2.37±0.19 A	0.21±0.02 A	0.17±0.01 A	0.85±0.04 B
Biennial dormant (n=4)	1.19±0.15 A	5.28±0.40 A	0.70±0.07 A	7.58±0.32 A	1.83±0.25 A	0.23±0.04 A	0.16±0.02 A	0.22±0.01 A

most likely been exhausted. It cannot be dismissed, however, that thinning and mastication did contribute to basal area reduction and the maintenance of trees species in the managed watershed.

It must be noted that we have not determined any approximations of smoke emissions or the constituents of the smoke exiting our study locations as a result of these fires. Smoke management is a major determinant of prescribed fire implementation for the professionals managing both the Tom Yawkey Wildlife Center and the Santee Experimental Forest. Prescribed fires are generally conducted at these locations when fire weather minimizes smoke. Nonetheless, the loss of some compounds from our burn treatments in post-fire sampling may be related to smoke losses. Additionally, when stating the effects of these treatments as they relate to human health, one must consider the impact of smoke emissions as they may be related to respiratory problems in humans (Goldberg, 1985) and contribute to climate change (Ramanathan & Carmichael, 2008; Sasser et al., 2012).

Brief Synopsis

When evaluating both sites, it appears that low intensity, low severity prescribed fires in coastal pine systems do not detrimentally alter the chemical composition of detrital materials. Using the thermocouple-datalogger assemblies, we observed fire behavior metrics characteristic of low intensity, low severity surface fires. Although specific compounds within the chemical functional groups may have been elevated immediately post-fire, those effects appeared to be short-lived, dissipating within one year post-fire at the Tom Yawkey Wildlife Center. In the long-term, it appears frequent (annual and biennial) and periodic (every 4 years) prescribed fires may reduce percentages of the potential organic pollutants (naphthalene, ethylbenzene, toluene, benzene) we evaluated. In forests that actively drain to source waters, like the watersheds of the Santee Experimental Forest, this may have implications on the cost, timing, and effectiveness of water treatability. These concerns may have direct implications on human health, not to mention the health of aquatic life. This furthers a vast body of work suggesting the benefits of prescribed fire for wildlife habitat improvement, forest health, wildfire hazard reduction, and the management of specific vegetative species.

Continued Questions

Pyrolysis GC-MS settings

The method utilized to determine detrital chemistry involved the use of analytical pyrolysis/GC-MS. This method is labor intensive in terms of the amount of time needed to collect fresh samples from the field, dry and grind those samples, prepare the quartz tubes, load the quartz tubes, run the samples through the machine, and determine the total quantified peak area. Over four months was spent defining the list of one hundred fifty compounds needed to properly evaluate the chemical functional groups present in our pre- and post-fire samples at Yawkey (Table 3.2). This list was by no means exhaustive as thousands of compounds were not included in the list because they are not well-defined in the literature. Additional weeks were spent evaluating each sample using that list. This technique was needed to generate the total quantified peak area (TQPA) based upon a thorough evaluation of all of the potential polycyclic aromatic hydrocarbons (PAHs) of interest. Within this labor, it was also determined that multiple options could be utilized to determine TQPA based upon: 1) the settings of the machine, 2) the manual integration of areas, or 3) a computer-generated integration of area.

The full, functional group classifications we obtained in Chapter 3 were very beneficial and useful. It is noted, however, that an investigation of specific compounds, as was utilized in Chapters 4 and 5, may provide the most efficient use of time and resources. For the samples described in Chapter 4, six compounds explained 45-65% of the TQPA present in those samples. Additionally, many of the compounds identified in Chapter 3 are less understood and are not noted thoroughly in the literature. This creates issues in terms of utilizing the information that was generated. When it takes a long time to generate information that may not be useful for interpretation, it may be best to shorten the list or only stick with compounds that are frequently described in the literature. We did this in Chapter 4 and at the beginning of this chapter (Table 5.2).

We would also like to note that the settings of the machine remained constant for flash pyrolysis at 700^{o}C alone for the samples used in the preceding chapters. Flash temperatures have been known to affect the detection and intensity of many compounds (Wurster et al., 2013). To investigate the effects of flash heating at different temperatures, additional samples have been evaluated using a thermosequence of temperatures on the same samples. A preliminary evaluation of those samples is shown in Tables 5.3-5.7. Based upon this initial assessment, it appears the temperature of flash pyrolysis may have an effect on the constituents observed in a given sample. More work can be done to better understand these dynamics with samples of other vegetative types and compositions.

Table 5.3. Detrital functional group designations and compositional percentages for samples obtained at the Tom Yawkey Wildlife Center. Samples were heated using flash pyrolysis; sequence distinction refers to samples heated in a 300-500-700-900°C sequence.

Functional Group	**Long-term unburned litter sequence**	**Long-term unburned litter 700°C only**	**Long-term Unburned duff sequence**	**Long-term Unburned Duff 700°C only**	**Pre-burn litter sequence**	**Pre-burn litter 700°C only**	**Post-burn litter sequence**	**Post-burn litter 700°C only**
Aliphatic compounds	2.4	7.9	5.0	8.3	2.2	4.4	3.1	6.0
Aromatic (one-ring)	27.0	11.0	31.0	9.3	25.1	6.2	33.6	9.6
Aromatic (PAH)	4.6	2.6	4.7	1.5	4.7	2.4	5.8	4.3
Nitrogen compounds	0.9	0.9	1.0	2.0	0.7	1.6	0.7	1.6
Oxygen compounds	8.5	8.9	8.0	6.1	8.8	5.2	6.7	9.2
Phenolic compounds	56.6	68.8	50.4	72.9	58.5	80.2	50.1	69.3

Table 5.4. Detrital functional group designations and compositional percentages for a long-term unburned litter sample obtained at the Tom Yawkey Wildlife Center, Georgetown, South Carolina that was heated using flash pyrolysis in a thermosequence (300-500-700-900°C). Values for a sample run at 700°C only are shown in the final column as a comparison.

Functional Group	**300°C**	**500°C**	**700°C**	**900°C**	**SUM**	**700°C only**
Aliphatic compounds	0.1	0.7	1.6	0.0	2.4	7.89
Aromatic (one-ring)	0.0	4.4	19.6	3.0	27.0	11.00
Aromatic (PAH)	0.1	1.2	3.0	0.2	4.6	2.55
Nitrogen compounds	0.5	0.2	0.2	0.0	0.9	0.91
Oxygen compounds	2.4	2.5	3.6	0.0	8.5	8.87
Phenolic compounds	15.5	20.8	20.3	0.0	56.6	68.77
SUM	18.7	29.8	48.2	3.2	100.00	100.00

Table 5.5. Detrital functional group designations and compositional percentages for a long-term unburned duff sample obtained at the Tom Yawkey Wildlife Center, Georgetown, South Carolina that was heated using flash pyrolysis in a thermosequence (300-500-700-900^{o}C). Values for a sample run at 700^{o}C only are shown in the final column as a comparison.

Functional Group	**300^{o}C**	**500^{o}C**	**700^{o}C**	**900^{o}C**	**SUM**	**700^{o}C only**
Aliphatic compounds	0.1	1.1	3.9	0.0	5.0	8.3
Aromatic (one-ring)	0.0	4.4	23.8	2.7	31.0	9.3
Aromatic (PAH)	0.1	1.0	3.4	0.2	4.7	1.5
Nitrogen compounds	0.4	0.3	0.3	0.0	1.0	2.0
Oxygen compounds	1.6	1.8	4.6	0.0	8.0	6.1
Phenolic compounds	9.2	15.6	25.5	0.0	50.4	72.9
SUM	11.4	24.2	61.5	2.9	100.0	100.0

Table 5.6. Detrital functional group designations and compositional percentages for a pre-burn litter sample obtained at the Tom Yawkey Wildlife Center, Georgetown, South Carolina that was heated using flash pyrolysis in a thermosequence (300-500-700-900°C). Values for a sample run at 700°C only are shown in the final column as a comparison.

Functional Group	**300°C**	**500°C**	**700°C**	**900°C**	**SUM**	**700°C only**
Aliphatic compounds	0.0	0.4	1.6	0.2	2.2	4.39
Aromatic (one-ring)	0.2	2.0	15.5	7.4	25.1	6.21
Aromatic (PAH)	0.3	0.8	2.5	1.1	4.7	2.38
Nitrogen compounds	0.7	0.0	0.0	0.0	0.7	1.63
Oxygen compounds	5.6	1.2	1.7	0.3	8.8	5.19
Phenolic compounds	29.2	12.0	16.6	0.7	58.5	80.21
SUM	35.9	16.5	37.9	9.7	100.0	100.00

Table 5.7. Detrital functional group designations and compositional percentages for a post-burn detrital sample obtained at the Tom Yawkey Wildlife Center, Georgetown, South Carolina that was heated using flash pyrolysis in a thermosequence (300-500-700-900°C). Values for a sample run at 700°C only are shown in the final column as a comparison.

Functional Group	**300°C**	**500°C**	**700°C**	**900°C**	**SUM**	**700°C only**
Aliphatic compounds	0.0	0.5	2.6	0.0	3.1	6.0
Aromatic (one-ring)	0.0	2.2	22.7	8.7	33.6	9.6
Aromatic (PAH)	0.2	0.7	4.2	0.6	5.8	4.3
Nitrogen compounds	0.5	0.0	0.1	0.0	0.7	1.6
Oxygen compounds	1.4	1.0	4.2	0.1	6.7	9.2
Phenolic compounds	10.7	9.8	29.7	0.0	50.1	69.3
SUM	12.9	14.2	63.5	9.4	100.0	100.0

Mineral soil chemistry

It was our intention at the onset of the study to determine potential alterations in soil organic matter chemistry as a result of prescribed fire. At Yawkey and the watersheds, pre-fire soil samples were collected in triplicate at each of the detrital sampling locations for two soil depths: 0-10 cm and 10-20 cm. Samples were taken again immediately post-fire at Yawkey and at a few locations, additional samples were collected both four months and one year post-fire. These samples were collected to determine if PAH concentrations increased as a result of fire and if they did increase, the length of time that increase was actualized and to what soil depth.

A test run of unaltered soil samples was conducted using Py/GC-MS, but the signal–to-noise ratio was not sufficient for analysis. Essentially very little organic material was present in the sandy soils at Yawkey. An extraction procedure was developed to examine the humic and fulvic acids of the soil organic matter. This procedure was quite labor intensive, but we generated data from one set of samples, which is shown in Table 5.8. Due to time constraints and our desire to continue adjusting the extraction procedure, we have not completed that analysis for all of our samples and sites. It is our goal to gain a better understanding of how fire might affect both the quality and quantity of compounds contributing to soil organic matter. This would be particularly important for PAHs and other black carbon constituents as some studies suggest they are linked to increased cation exchange capacity (Liang et al., 2006) and account for a large quantity of sequestered carbon (DeLuca & Aplet, 2008).

Table 5.8. Chemical functional group percentages for soil humic acid extractions obtained from soils influenced by prescribed fire at the Tom Yawkey Wildlife Center, Georgetown, South Carolina, USA.

Soil Depth	**0-10 cm**			**10-20 cm**		
Functional Group	**Pre-fire**	**Immediate post-fire**	**Four month post-fire**	**Pre-fire**	**Immediate post-fire**	**Four month post-fire**
Aliphatic compounds	0.5	0.5	0.5	1.2	1.8	2.1
Aromatic (one-ring)	50.5	47.7	49.7	64.3	62.1	57.5
Aromatic (PAH)	4.8	4.6	4.5	5.2	5.1	4.9
Nitrogen compounds	6.1	11.6	12.9	3.6	2.8	2.7
Oxygen compounds	7.1	6.0	5.5	7.8	7.4	7.0
Phenolic compounds	31.0	29.6	26.9	17.9	20.8	25.8

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