Prescribed fire effects on soil chemical properties in wind-damaged coastal forests

by

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Abstract

Coastal forests in the southeastern United States are vital carbon sinks that provide essential ecosystem services. However, decades of fire suppression and increasing hurricane activity have led to altered vegetation structures, increased fuel loads, and overall ecosystem degradation. Prescribed fires have been reintroduced as a management strategy to restore these ecosystems, but frequent hurricane-induced wind damage complicates fuel distribution and fire application, impacting carbon cycling and soil chemical properties in ways that remain unclear.

This study provides a comprehensive analysis of the changes in soil chemical properties and carbon dynamics following prescribed fires in hurricane-impacted coastal forests. We conducted quantitative and qualitative assessments of dissolved organic matter (DOM) and soil organic matter (SOM) before, immediately after, and up to one year post-fire at two sites along the Gulf of Mexico: Perdido River Preserve in Florida and Weeks Bay National Estuarine Research Reserve in Alabama.

At Perdido, a positive correlation was observed between fire severity and immediate increases in dissolved organic carbon (DOC), dissolved nitrogen (DN), and the carbon-to-nitrogen (C : N) ratio. DOC levels returned to pre-fire conditions within a year, while DN remained elevated. Elevated nitrate and reduced phosphate levels were also noted one year post-fire at both locations. These findings highlight the impact of prescribed fires on DOM and SOM dynamics and nutrient cycling in hurricane-affected coastal forests. By discerning the relationships between fire severity, organic matter transformations, and soil chemical properties, this study contributes insights into the unique relationships between the various variables of these critical ecosystems.

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List of Abbreviations

DOM	Dissolved Organic Matter
SOM	Soil Organic Matter
EEM	Excitation Emission Matri
FTIR	Fourier Transform Infrared Spectroscopy
PARAFAC	Parallel Factor Analysis
UV-Vis	Ultraviolet-Visible Spectroscopy

Chapter 1 : Introduction

Coastal forest ecosystems are vital components of global biodiversity and play a crucial role in regulating climate and nutrient cycles. They act as crucial carbon sinks, provide habitat for a diverse range of species, and protect against coastal erosion and storm surge (Barbier et al., 2011). The health of coastal forests has significant implications for the overall health of our planet and for our efforts to combat climate change. Coastal forests of the southeastern United States have long been subject to the destructive impacts of hurricanes. These extreme weather events are a key driver of forest dynamics in the region. Hurricanes can create significant disturbances in forest ecosystems, causing widespread defoliation, snapping or uprooting of trees, and changes in forest structure and composition (Turner et al., 1998). Additionally, the increased frequency and intensity of hurricanes in recent decades, driven by climate change, are leading to more severe impacts on coastal forest ecosystems (Kossin, 2020). Hurricanes not only affect the above-ground vegetation but also significantly alter the below-ground environment, affecting the hydrology, soil properties, and nutrient cycling, which, in turn, have cascading impacts on forest recovery and succession (Camargo, 2013).

Natural and anthropogenic fire has been an integral part of the coastal forest ecosystems in the southeastern U.S. Historically, the region's coastal areas experienced regular fires due to lightning ignitions associated with a high frequency of thunderstorms, a pronounced dry season, and extensive intentional burning by Native Americans (Fowler and Konopik, 2007). However, decades of changes in land use practices and fire suppression have led to pronounced changes in the composition and structure of these systems, associated with the deterioration of ecosystem function and services, including biodiversity loss, increased fuel loads, and altered hydrology (Mitchell et al., 2006; Guyette et al., 2002). In response to these alterations, prescribed burning has emerged as a prevalent management to restore and sustain the vitality and functionality of these coastal forests (Brockway et al., 2005). Prescribed fires can also effectively reduce extreme fire occurrences by preventing high fuel load accumulation, leading to highly intense disastrous fires. Wildfires that occur naturally in extremes can contribute to twice the loss in Nitrogen and Carbon compared to prescribed fire (Homann et. al., 2011).

Fire acts as a rapid mineralizing agent (St. John and Rundel, 1976) that releases nutrients instantaneously in contrast to natural decomposition processes, which may require years or, in some cases, decades. Frequent intense fires can also combust the aboveground mass and leaf litter leading to the lower input of organic matter into the soil and to an overall decline in soil organic matter (SOM) concentrations. (Knicker, 2007). Despite the potential of prescribed fire as a management tool, understanding its intricate interactions with other coastal disturbances, particularly hurricanes, and its overall impact on coastal ecosystem processes, especially carbon cycling, presents a complex challenge. An increased understanding of the mechanisms underlying the interactions between common forest disturbances, such as wind damage and fire, can considerably enhance our predictive models of ecosystem change and inform forest management practices following natural disturbances (Cannon et al., 2017). Wind damage and wildfire, which affect over two million ha of forest annually in the U.S., each has profound ecological impacts, and their interactions can significantly alter the behavior and effects of disturbances like prescribed fires. For instance, severe wind damage can lead to increased fuel for intense wildfires, while also potentially altering the behavior and impacts of prescribed fires with consequential effects on forest management (Cannon et al., 2017). The mechanisms through which these disturbances interact form a crucial part of our understanding of how ecological changes occur following disturbances.

Soil acts as a sink for atmospheric carbon dioxide through a process known as carbon sequestration. Carbon sequestration in soils involves the uptake and long-term storage of atmospheric CO_2. Plants absorb CO_2 during photosynthesis and convert it into organic compounds. Some of this carbon is transferred to the soil as plant residues and root exudates, where it can be stabilized and stored for years to centuries (Post and Kwon, 2000; Minasny et al., 2017). Fire frequency may shift ecosystem carbon storage by changing soil carbon pools and nitrogen limitations on plant growth, altering the carbon sink capacity (Pellegrini, et. al., 2018). For example, frequent fires can lead to a net loss of soil carbon as the combustion of organic matter results in the immediate release of stored carbon into the atmosphere. Moreover, by causing a substantial loss of soil nitrogen, a key nutrient for plant growth, frequent fires can further limit the ecosystem's ability to sequester carbon due to diminished plant productivity and reduced litter inputs to the soil. Fire can also help in stabilizing carbon within the soil. It creates charcoal, which is very resistant to decomposition. Fire can also increase the amount of carbon bound tightly to minerals in the soil. (Abney and Berhe, 2018) If the right balance of prescribed fire is achieved, it can lock in or increase carbon which can tip the carbon balance towards carbon sequestration in the long term. (Association of Fire, 2013). Thus, soil carbon sequestration can mitigate greenhouse gas emissions and help combat climate change (Paustian et al., 2016). Moreover, prescribed fires can alter the levels and availability of essential soil nutrients, particularly cations like calcium, potassium, and magnesium (Certini, 2005). The intense heat generated by the fire can cause the release of these nutrients from organic matter and increase their availability in the short-term post-fire environment. However, such effects are often temporary as the leaching caused by rainfall or the uptake by vegetation can reduce these levels over time (Covington and Sackett, 1992).

As a restorative and management tool, the prescribed fire profoundly influences soil properties, with particular relevance to carbon, organic matter, and nutrient cycling. In the terrestrial ecosystem, soil organic matter is a significant reservoir of stored carbon (Davidson and Janssens, 2006). Soil comprises the largest carbon pool on the earth’s surface. (Gonza´lez-Pe´rez et. al, 2004). SOM is a complex heterogenous substances derived from decomposed plants, animals, and microbial materials. It is essential to soil health because it affects several soil properties, including nutrient availability, water retention, and overall fertility. It enhances soil structure by encouraging the aggregation of soil particles, which increases the soil's ability to retain water and nutrients (Lehmann and Kleber, 2015). Furthermore, as a major reservoir for carbon, it plays a key role in the global carbon cycle by sequestering atmospheric CO_2, thus helping mitigate climate change. (Lal, 2016; Smith, 2016)

Dissolved organic matter (DOM), a component of SOM, is the fraction of organic matter that is water-soluble. This includes a complex mixture of compounds derived from plant and microbial materials, such as sugars, amino acids, and aromatic compounds (Kalbitz et al., 2000). DOM plays a significant role in soil biogeochemical processes by influencing nutrient availability, metal mobility, and microbial activity (Jones and Willett, 2006). Furthermore, the molecular composition of DOM can influence the mobility and bioavailability of pollutants in the soil (Jones and Willett, 2006). The dynamic nature of SOM and DOM, especially under disturbances like fire, plays a crucial role in shaping soil properties and functions, making the understanding of their behavior vital for effective ecosystem management. Humus, often considered the end product of organic matter decomposition, is characterized by its resistance to further decomposition, providing long-term storage of carbon in the soil (Batjes, 1996). SOM and humus are particularly noteworthy, as they serve as cation exchange sites.

Prescribed fire in longleaf pine (Pinus palustris Mill.) plantation elevated soil pH and instigated a flux of carbon (C), nitrogen (N), and other elemental nutrients in the upper strata of the soil (0-5 cm). (Butnor et al. 2020). This nutrient surge, intriguingly, peaks approximately 1 to 3 months post-fire. However, a decline was observed 12 months post-fire, with levels of C and N falling beneath pre-fire levels at soil depths between 5 and 10 cm. Furthermore, fire events cause the formation of novel, particulate C entities, notable for their resistance to oxidation and biological degradation (Gonza´lez-Pe´rez et al., 2004). These are pyrogenic carbon, often referred to as biochar, which is a form of carbon produced through the thermal decomposition of organic matter in an oxygen-limited environment, such as during a fire event.

Pyrogenic carbon (PyC) is a form of carbon produced by the incomplete combustion of organic matter, such as biomass and fossil fuels. It is a significant component of soil organic carbon (SOC) and plays a crucial role in soil biogeochemical processes, carbon sequestration, and contaminant immobilization. Chemically, it is composed of a poly-condensed aromatic structure that is much more resistant to degradation compared to other organic matter, which is why it can persist in the environment for hundreds to thousands of years (Lehmann et al., 2011). This chemically robust structure is a result of the charring process, where organic material is exposed to high temperatures in the absence of oxygen, leading to the transformation of its molecular composition. Physically, pyrogenic carbon has a porous structure, which increases its surface area, enhancing its ability to adsorb and hold nutrients, water, and pollutants. Therefore, improving soil fertility and quality (Lehmann et al., 2011). In addition to its longevity, pyrogenic carbon can also significantly influence soil chemical properties, enhancing nutrient retention and availability (Liang et al., 2010). Moreover, previous studies have shown that pyrogenic carbon can interact with other soil organic matter, potentially leading to a protective effect and further enhancing soil carbon sequestration (Wang et al., 2016). However, its precise impact on soil organic matter dynamics, particularly in the context of post-fire scenarios in wind damaged forests, remains under-explored.

Given the intricate dynamics of hurricanes, prescribed fires, and their combined influence on soil properties – especially in terms of carbon cycling – there remains a pressing need to unpack these interactions. This research aims to delve deeper into understanding how these disturbances shape soil organic matter, particularly the behavior of DOM and pyrogenic carbon, and consequently influence the potential of these ecosystems for carbon sequestration.

Goals:

The primary goal of this study is to explain the intricate effects of prescribed fire on soil chemical properties within coastal forests impacted by recent hurricane disturbance. The ultimate purpose is to broaden our understanding of soil chemical responses to prescribed fires applied to wind damage coastal forests. This will not only enhance our knowledge of carbon cycling dynamics under such disturbances but also provide critical insights for improving restoration efforts and maximizing ecosystem services delivered by these coastal habitats.

Research Questions and Hypothesis:

1) How do hurricane disturbances and fire intensity interactively influence the SOM and DOM content and molecular characteristics in coastal forest ecosystems?

H - Hurricane disturbances are hypothesized to influence the distribution and availability of fuels in coastal forest ecosystems. This altered fuel distribution, in turn, is anticipated to modulate fire behavior, determining its severity, and spread. Specifically, areas with higher fuel accumulation due to hurricanes might witness more intense fires, leading to pronounced changes in the soil's chemical composition. Upon this fire disturbance, an initial surge in soil organic carbon concentration is expected, resulting from the deposition of partially combusted biomass (Neary and DeBano, 1999). As the ecosystem undergoes natural recovery and potentially faces further hurricane disturbances, this elevated carbon concentration may stabilize or even decrease. The interplay between hurricanes and fires can also lead to the formation of more resistant forms of organic matter, such as black carbon, thus enhancing carbon sequestration (Schmidt and Noack, 2000). Moreover, fires might transform complex organic molecules into smaller, more soluble compounds, elevating the DOM content. This transformation can give rise to new fluorescent substances like polycyclic aromatic hydrocarbons (PAHs) and alter the dynamics of protein-like substances due to combustion and subsequent microbial and plant recovery processes.

2) How do hurricane disturbances and fire events influence soil chemistry?

H - Prescribed fires in hurricane-disturbed areas can temporarily alter soil chemistry, notably by decreasing pH due to the release of acid-forming gases like CO_2 and SO_2 during combustion (DeBano, Neary, & Ffolliott, 1998). Ash deposition following fires may introduce sulfur and nitrogen compounds, which, through reactions with water, can form sulfuric and nitric acids, further lowering soil pH. We hypothesize that fire will increase the availability of soil cations and anions through the combustion of organic materials, although nutrient leaching could reduce these effects in the high-drainage, high-precipitation environments typical of coastal ecosystems (Certini, 2005).

3) What role does prescribed fire play in the formation of pyrogenic carbon within the top layer of the soil profile, and what implications does this have for carbon sequestration?

H - Wind disturbances, such as hurricanes, alter fuel distribution and density, potentially increasing fuel concentrations in localized areas. We hypothesize that prescribed fires following these disturbances will result in intensified burning in areas with greater fuel loads, promoting pyrogenic carbon formation, especially in anoxic conditions. This PyC, being more resistant to decomposition, is expected to increase the soil's long-term carbon storage capacity, thus enhancing carbon sequestration potential within these coastal forest ecosystems.

4) What are the molecular-level transformations in soil organic matter, as observed through FTIR and BPCA markers, resulting from the combined effects of hurricanes and fire?
H - Fire-induced transformations are hypothesized to yield distinct FTIR spectral signatures and BPCA profiles in SOM, reflecting changes in functional groups and molecular structure. We expect that higher fire severities, associated with hurricane-modified fuel loads, will increase the abundance of aromatic carbon compounds (such as B5CA and B6CA), indicating more condensed, stable forms of PyC. Additionally, FTIR spectra should reveal shifts toward functional groups linked to recalcitrant carbon, capturing the chemical changes that enhance SOM stability and support long-term carbon storage within these coastal soils.

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Chapter 2: Prescribed Fires Effects on Dissolvable Organic Matter in Wind-Damaged Coastal Forest Ecosystems of the Southeastern United States

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Highlights

- Prescribed fires modify soil DOM in coastal forests.
- Fire severity directly influences DOC and DN levels post-fire.
- UV-Vis and fluorescence spectroscopy track changes in DOM post-fire.
- Comparative analysis of two sites shows distinct soil responses.

Abstract

Prescribed fire is a common management practice for restoring and preserving coastal forest ecosystems in the southeastern U.S., which face complications due increasing impact of wind damage on fuel distribution. In this study, we quantified variations in dissolvable organic matter (DOM) to identify changes in carbon and nutrient cycling before, immediately after and up to a year after prescribed. Two coastal forests impacted by hurricanes were selected along the Gulf of Mexico, USA, Perdido River Preserve (FL), and Weeks Bay National Estuarine Research Reserve (AL). At Perdido, a positive correlation was observed between fire severity and immediate increased dissolvable organic carbon (DOC), nitrogen (DN), and carbon-to-nitrogen ratio (C:N). DOC returned to pre-fire levels within a year, while DN levels remained elevated, resulting in a decrease in C:N. The molecular size of DOM reflected by the ratio between absorbance at wavelength 465 to 665 nm increased by 34% at Perdido. At Weeks Bay, the specific absorbance at 254 of DOM decreased by 88% during the first-month post-fire, suggesting a relative decrease in aromatic moieties. Increase in humic-like and decrease in small aromatic DOM at Weeks Bay, a year after fire was measured by fluorescence spectroscopy. Increases in potassium and sodium were observed at both sites after the fire. Constant declines in magnesium, silicon, and aluminum at Weeks Bay were seen up to one-year post-fire. Both sites experienced elevated nitrate and reduced phosphate levels one-year post-fire. These findings highlight the critical role of prescribed fire in influencing DOM and nutrient dynamics.

Keywords: EEMs, Carbon cycling, PARAFAC.

Introduction

Preservation and restoration of coastal forest ecosystems across the southeastern U.S. depend on frequent, low-intensity prescribed fires. Maintaining their composition and structure provides vital ecosystem services, including carbon sequestration, and improves water quality (Song et al., 2013). However, the increasing frequency of hurricane disturbances modifies fuel loads by increasing leaf and woody debris (Suzuki et al., 2019) and enhancing live understory vegetation

(Angulo-Sandoval et al., 2004). These variations in fuel loads distribution can lead to differences in fire behavior (Berlin et al.,1980), directly affecting standing carbon stocks by removing wood, vegetation, and surface organic soils. Variations in fire severity can be reflected in alterations in the concentration and composition of dissolvable organic matter (DOM) and nutrients. Understanding these changes provides insight into the impact of prescribed fire on carbon and nutrient cycling in wind-damaged forests.

Within the coastal forests of the southeastern U.S., the Longleaf pine (*Pinus palustris*) savannas and slash pine (*Pinus elliottii*) ecosystems are particularly noteworthy for their carbon sequestration capabilities (Bracho et. al., 2012; Samuelson et. al., 2014). Historically, natural, lightning-ignited fires and indigenous practices have played a crucial role in shaping the successional trajectories, forest composition, and structure of these ecosystems. Longleaf and slash pine flatwoods, characterized by a sparse canopy and a rich understory of grasses and forbs, depend on frequent, low-intensity surface fires to maintain an open structure and prevent woody encroachment from fire-sensitive, shade-tolerant species (Fowler and Konopik, 2007). Fire also significantly influences the germination and growth of pyrophytic plant species, such as those found in longleaf and slash pine ecosystems. These species thrive in the presence of fire, which enhances their dominance and contributes to the unique biodiversity of these ecosystems (Hiers et. al., 2014). Moreover, acting as an ecological process, fire is essential for clearing decaying plant matter and enhancing the growth of native species found within fire-prone habitats (USGS National Wetlands Research Center, 2000).

Fire suppression started with modern human settlements and intensified by agriculture and urban development in the past century, resulting in the transitioning of open savanna-woodlands into closed-canopy forests with dense midstory dominated by opportunistic species (Varner et al., 2005). These forest structural changes compromise essential ecosystem services, such as carbon sequestration, soil fertility, water regulation, and biodiversity. To restore and maintain forest ecosystem services, the use of prescribe fire dramatically increased in the past few decades across various fire-dependent in the southeastern U.S. (Brockway et. al., 2005, Hahn et. al., 2019). These routinely implemented frequent, low-intensity surface fires are integral to maintaining ecosystem health and vitality, not only to mimic natural fire regimes but also to mitigate the risk of uncontrolled large-scale wildfires (Ryan et. al., 2013). Contrary to intuition, prescribed fire can increase carbon stocks by reducing the likelihood of future high-intensity wildfires, which are far more destructive and carbon-releasing (Hurteau and North, 2010). Prescribed fire can also promote the formation of more stable forms of soil organic carbon, such as char and black carbon, which are more resistant to decomposition and can remain in the soil for extended periods (Certini, 2005; Paustian et al., 2016). Moreover, by maintaining a healthy forest structure and promoting regrowth, prescribed fires can enhance forests' long-term carbon sequestration potential (Hurteau et al., 2010; Ryan et al., 2013).

The application of prescribed fire in the southeastern U.S. is complicated by another form of disturbance, wind damage. Hurricanes have historically made landfall predominantly in southern coastal states — accounting for approximately 94% of U.S. hurricane impacts over the past century (National Oceanic and Atmospheric Administration, 2021) — wreak havoc on these landscapes, causing extensive defoliation and uprooting of trees. Climate change exacerbates this threat, as evidenced by the unprecedented twelve tropical cyclone landfalls in 2020, a record number for over 170 years (National Oceanic and Atmospheric Administration (NOAA, 2021); Benedetto and Trepanier, 2020). These events, coupled with the possibility of increased tornado activity, place southeastern U.S. forests at a heightened risk of transitioning from carbon sinks to carbon sources (Coulston et. al., 2015). The destructive power of hurricanes (and tornados) alters the fuel landscape by increasing the amount of dead and downed woody material. Fuel accumulation, depending on the type, location, and age of the fuel, can lead to hotter and more intense prescribed fires due to increased fuel availability (Cannon et. al., 2017). On the other hand, wind also has buffering effects, such as disrupting the continuity of fuel, which can reduce the intensity of subsequent fires (Cannon et. al., 2017). The interplay between these intensified prescribed burns and wind damages poses unique challenges and uncertainties for forest management, especially in the context of soil organic matter and the carbon storage potential of soil.

Fire acts as a rapid mineralizing agent (St. John and Rundel, 1976) that releases nutrients instantaneously, offering a sharp contrast to the gradual nutrient release from natural decomposition processes, which may span years (Prescott et. al., 2005). High-intensity fire can consume a larger portion of the soil organic matter (SOM) concentrations (Knicker, 2007). Fire can also alter the stability of SOM by affecting both its physicochemical properties and the environmental drivers of decomposition. For example, it can increase the abundance of more recalcitrant forms of carbon, such as pyrogenic carbon, lignin, and polyphenols (Keiluweit et. al., 2010, Pellegrini et. al., 2022, Certini, 2005). The frequency of fire events modifies the dynamics of ecosystem carbon storage by influencing soil carbon reservoirs and the nitrogen availability that underpins plant growth, thereby affecting the capacity of these soils to act as carbon sinks (Pellegrini et. al., 2018). Properly managed prescribed fires can prevent the net decline in soil carbon levels caused by uncontrolled, high-intensity fires, which rapidly release carbon stored in the soil back into the atmosphere (Pellegrini et. al., 2017).

DOM is the most reactive fraction of SOM and is highly sensitive to ecological disturbances including fire (Kalbitz et. al., 2000, Jaffé et. al., 2008). DOM is heterogeneous and has varying molecular weights, functional groups, aromaticity, and hydrophilicity (Nebbioso and Piccolo, 2013). Lado et al. (2023) observed that laboratory-based soil heating at 300°C increased DOM aromaticity; while heating at 600°C reduced the water-soluble aromatic fraction due to oxidation and condensation reactions, demonstrating non-linear changes with temperature**.** Knicker et al. (2006) found that moderate fires reduced aliphatic carbon and increased aromatic carbon due to partial charring. As fire intensity increased, there was a further rise in aromatic carbon and a continued decline in aliphatic carbon, showing that these changes vary with fire severity. DOM is highly mobile and can leach into deeper soil horizons or be removed from the soil system through surface or groundwater flow (Shen et. al., 2014). Fire-driven changes in DOM, such as increased aromaticity and altered molecular weight, influence SOM stability and nutrient cycling. Post-fire pulses of DOM and nutrients have been suggested to trigger eutrophication in connected water bodies (Waters et. al., 2023).

The relationships between fire severity resulting from heterogeneous fuel load, and the quantity and properties of DOM are under-investigated. Particularly in forest systems that are subjected to frequent wind disturbances. In this work, we investigated the changes in concentration and molecular composition of DOM to provide insight into carbon and nutrient cycling in Southeastern US coastal forest ecosystems, which are subjected to hurricane damage and managed by prescribed fires. We selected sites with a wide fuel load gradient created by hurricane damage. We hypothesized that increased fire severity due to higher fuel load would increase the concentration of DOM, particularly low molecular weight aromatic compounds released from incomplete combustion of fuels. We anticipated a pulsed release of non-volatile elements such as P, K, Si, and Al.

Materials and Methods

2.1 Site Descriptions

The study was conducted at two distinct sites with recent (< two years) exposure to hurricane damage and a history of fire management: Weeks Bay National Estuarine Research Reserve (Weeks Bay) (30° 25' 9.3504" N, 87° 49' 49.944" W) in Alabama, and Perdido River Preserve (Perdido) (30° 27' 56" N, 87° 24' 34" W) in Florida, USA (Figure 1). Both sites are located in a humid subtropical climate region with warm summers exhibiting an average high of 33ºC and mild winters (average 16ºC), with occasional cold waves. precipitation from a combination of winter storms, thunderstorms, and tropical systems with an average annual accumulation of 170 cm (NOAA, 2024).

Weeks Bay is a mature (60–80-year-old) stand (13.4 ha) of coastal slash pine (*Pinus elliottii*). Soils are predominantly of the Okenee and Hyde series (fine-silty, mixed, active, thermic Typic Umbraquults; Web Soil Survey, USDA). This site experienced Category 2 Hurricane Sally on September 15, 2020, and Category 3 Hurricane Zeta on October 23, 2020, and underwent prescribed burns in July 2016, June 2020, and April 2022. At Perdido, we sampled a young (~20-year-old) longleaf pine (*Pinus palustris*) stand (12.3 ha) Soils are primarily of the Hurricane (sandy, siliceous, thermic Oxyaquic Alorthods) and Albany (siliceous, subactive, thermic Aquic Arenic Paleudults), respectively (Web Soil Survey, USDA). Prior to sampling, this site faced Category 3 Hurricane Zeta on October 23, 2020, and underwent prescribed burns in March 2019 and March 2022.

We selected study plots within each site to represent a gradient of wind damage. At Weeks Bay, we used stratified random sampling to ensure plots were distributed from the bay to further inland. First, we used satellite imagery from Google Earth to subdivide the stand into six 70-m x 280-m sections running parallel to the bay. We then subdivided each of the six sections into 16 grid cells (35-m x 35-m) and randomly selected five cells for plot locations (n = 30 plots centered on the grid cell). Based on visual detection of downed trees, this approach represented an array of wind damage. At Perdido, we used satellite imagery to select eight plots within the central part of the burn unit dominated by longleaf pine (0.062 km^2) that represented a gradient of hurricane impact based on the prevalence of downed trees, ranging from no obvious wind damage to high damage. For both sites, we ensured that downed trees were produced by the hurricanes by comparing imagery before and after the wind events.

Although both study sites have a history of prescribed fire as noted above, the burns evaluated here were the first to be conducted after the 2020 hurricanes. At Weeks Bay, the prescribed fire occurred on April 27, 2022. The fire was ignited by drip torch by hand or ATV at 13:30 on the southeastern edge of the unit and was mostly out, except for smoldering dead wood, by 17:00. During the burn, winds were out of the NNW at 5-8 km/s. Relative humidity was 25-55%, and air temperature was 25-27 °C. Flame length ranged from 0.4 to 1.6 m. At Perdido, the burn occurred on March 21, 2022 and was ignited on the west/northwest side of the unit starting at 10:40 by hand using drip torches. Winds were out of the ESE at 5-8 km/s with gusts to 11 km/s. Relative humidity was 29-51%, and air temperature was 22-28 °C.

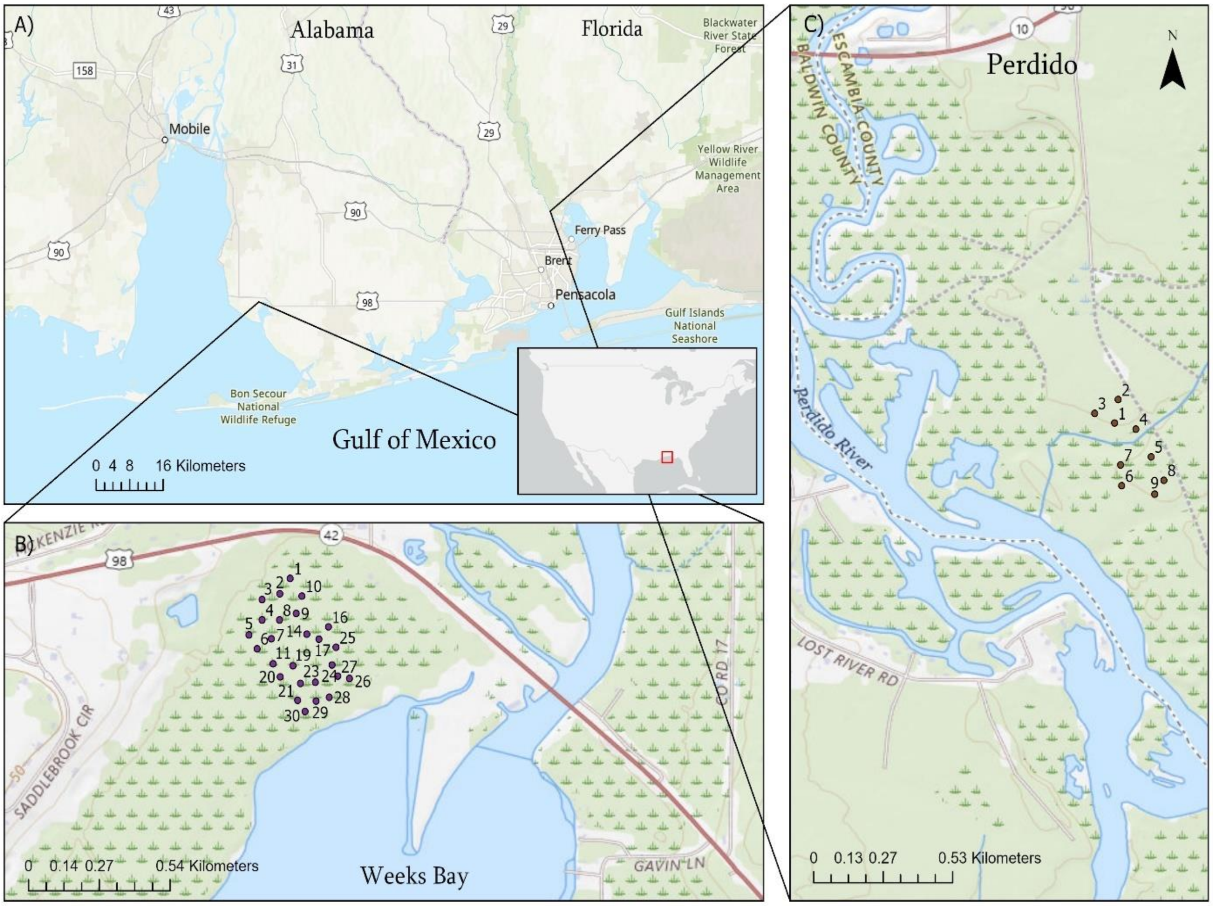

Figure 1Geographic depiction of the Weeks Bay (B) and Perdido (C) sampling sites situated in Southern Alabama and the Florida Panhandle, respectively, including the specific locations of sampling plots.

2.2 Sampling Methods

Soil sample collection was strategically scheduled to ascertain the chronological impact of post-wind event fire on soil conditions. At Perdido, samples were gathered before the prescribed fire on March 8, 2022. Post-fire sampling first occurred on March 22, 2022, to document changes immediately after the fire. A follow-up collection occurred on March 7, 2023, to observe soil characteristics one year post-fire. At Weeks Bay, we sampled pre-fire conditions from March 5 to 7, 2022 immediately after the fire on April 26, 2022, one month after the fire on May 31, 2022, and one year after the fire on March 10, 2023.

Soil samples (0-5 cm depth) were excavated using a soil auger at the 9-m mark along each of three 15-m long transects radiating from the plot center at 0°, 135°, and 225° and placed in labeled Ziploc bags. All samples were stored in a cooler before processing in the lab within 48 hours. In the lab, the soil was air-dried, sieved (< 2 mm), and stored in the dark before subsequent analyses.

2.3 DOM Extraction

Dissolved organic matter (DOM) was extracted by agitating 10 g of air-dried soil with 60 mL of ultrapure water (18.2 MΩ) in a 250 mL polypropylene bottle. The suspension was agitated using a Labline 3527 Orbital Incubator Shaker (Lab-Line Instruments Inc, Thermo Scientific, Iowa, USA) at 90 RPM. The suspensions were then decanted into 50 mL centrifuge tubes and centrifuged at 4000 rpm for 10 minutes at 25°C. The supernatant was filtered through 0.45µm Supor® polyether sulfone membranes. The filtered DOM solutions were stored in pre-combusted amber glass bottles at 4 °C and analyzed within 24 hours.

2.4 DOM Quantification and Characterization

Electrical conductivity (EC) and pH were measured using an Accument Basic AB30 Conductivity Meter (Fisher Scientific, Waltham, MA) and a SevenCompact S220-Basic pH/Ion benchtop meter (Mettler Toledo, Columbus, OH), respectively. The quantification of Dissolved Organic Carbon (DOC) and Dissolved Nitrogen (DN) was conducted using a multi-C/N 3100 analyzer (Analytik Jena, Jena, Germany). Ultraviolet-visible (UV-vis) absorbance was recorded over a wavelength range of 250 to 700 nm at 0.5 nm intervals on a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) using a 1.0 cm quartz cuvette. The absorbance ratios E2:E3 (250 nm:365 nm) and E4:E6 (465 nm:665 nm) were measured. The E2:E3 ratio is an indicator of the molecular weight of DOM (Wang et. al., 2015), where a low ratio suggests higher molecular size (Hautala et. al., 2000). The E4:E6 identifies the degree of aromatic ring condensation in humic acids, with higher values suggesting greater aromaticity and higher degrees of condensation. (Saab et. al., 2007). Specific UV-absorbance at 254 nm ($SUVA_{254}$ L mol^{-1} cm^{-1}) was calculated by normalizing the absorbance at 254 nm to the DOC concentration, indicating DOM aromaticity. (Minor et. al., 2014; Weishaar et. al., 2003). Fluorescence excitation-emission matrices (EEMs) were collected with an FP-8500 spectrofluorometer (JASCO, Easton, MD). To minimize inner filter effects, samples were diluted with ultrapure water, ensuring the UV-absorbance at 254 nm remained below 0.10 (Gilchrist and Reynolds, 2014; Lakowicz, 2006). EEMs were acquired by exciting samples from 250 to 585 nm at 5 nm intervals and recording emissions from 260 to 600 nm at 2 nm intervals. Ultrapure water blanks were measured daily before beginning the experiments for background subtraction and Raman normalization, along with correction for Rayleigh scattering. (Murphy et. al., 2014)

Major cations and metals (Na, Mg, Al, Si, K, and Ca) were measured with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Spectro Ciros, Spectro Analytical Instruments Inc. Mahwah, NH). Anions (NO_3^-, Cl^-, and PO_4^{3-}) were analyzed using the Dionex Ion Chromatography (IC) system (Dionex ICS 3000, Thermo Fisher Scientific, Waltham, MA). Ammonium (NH_4^+) concentration was measured using a colorimetric method (Mulvaney, 1996), using MQX200 Microplate Spectrophotometer (Bio-Tek Instruments, Winooski, VT).

2.5 Data Analysis

Fuel load change, calculated by subtracting post-fire fine fuel biomass from initial fine fuel biomass, and initial fuel biomass data; calculated by adding understory, fine woody debris, and litter biomass (Supplemental Method S1), were interpolated using Empirical Bayesian Kriging (EBK) for Perdido and Inverse Distance Weighting (IDW) for Weeks Bay in ArcGIS software (2023, Esri, Redlands, CA). The interpolation method was selected based on the Exploratory Interpolation Tool in ArcGIS Pro, which ranks methods based on Root Mean Square Error (RMSE).

Statistical analyses were performed using R (R Core Team, 2024) in RStudio (Posit Team, 2024). Pearson's correlation coefficients (r), coefficient of determination (r^2), and p-values were used to assess the significance and explanatory power of the correlations between fire severity and the immediate change in concentrations of DOC, DN and C:N. The change in the studied variables over time, we used a one-way repeated measures ANOVA. Given the larger spatial heterogeneity in fuel load change at Weeks Bay, we binned the plots into three categories of fuel load change, defined as low (0 to 14.79 tons/ha), medium (14.80 to 31.26 tons/ha), and high (31.27 to 49.88 tons/ha), based on an equal division of the range from the lowest to the highest fuel load change. Here, we utilized a mixed-design repeated ANOVA, considering both within-subjects factors (timeframe) and between-subjects factors (fuel load change category). Tukey's HSD post hoc test was applied to determine significant differences between each pair of samples.

We used Parallel Factor Analysis (PARAFAC) to decompose EEMs into individual fluorophores that could explain the variability of EEMs across the whole dataset of soil extracts (Murphy et. al., 2014). PARAFAC analysis was executed utilizing the R package staRdom (Pucher, 2023).

Results

3.1 Fuel distribution and load change.

Fuel load change was used to assess the fire severity across hurricane-affected coastal forests. (Supplemental Method S1, Figure 2) While the fine fuel fractions (fine woody debris, understory vegetation, and leaf litter), were largely consumed by the prescribed fire, the biomass of coarse woody debris remained unchanged or increased post-fire, likely due to inputs of fallen branches, twigs, and trunks from dead trees (Supplemental Table S2).

3.2 Spatial and Temporal Dynamics of DOM

At Perdido, fire severity correlated with elevated concentrations of DOC, DN, and C:N immediately after fire. Specifically, the relationship between fuel load change and DOC change (Δ DOC) before and after fire was the strongest ($r^2 = 0.85$, $p < 0.01$; Figure 3A), followed by Δ DN ($r^2 = 0.68$, $p < 0.01$; Figure 3A) and ΔC:N ($r^2 = 0.51$, $p < 0.05$; Figure 3C). A weaker negative correlation was seen between fuel load change and DOC change at Weeks Bay ($r^2 = 0.2$, $p < 0.05$; Figure 3A). No significant correlation was observed between fuel load change and change in DN, and C:N at Weeks Bay.

A positive correlation was observed between pre-fire fine fuel load and fuel change at both sites (Supplemental Figure S3, with Perdido exhibiting a stronger correlation ($r^2 = 0.81$, $p < 0.001$) than Weeks Bay ($r^2 = 0.73$, $p < 0.001$).

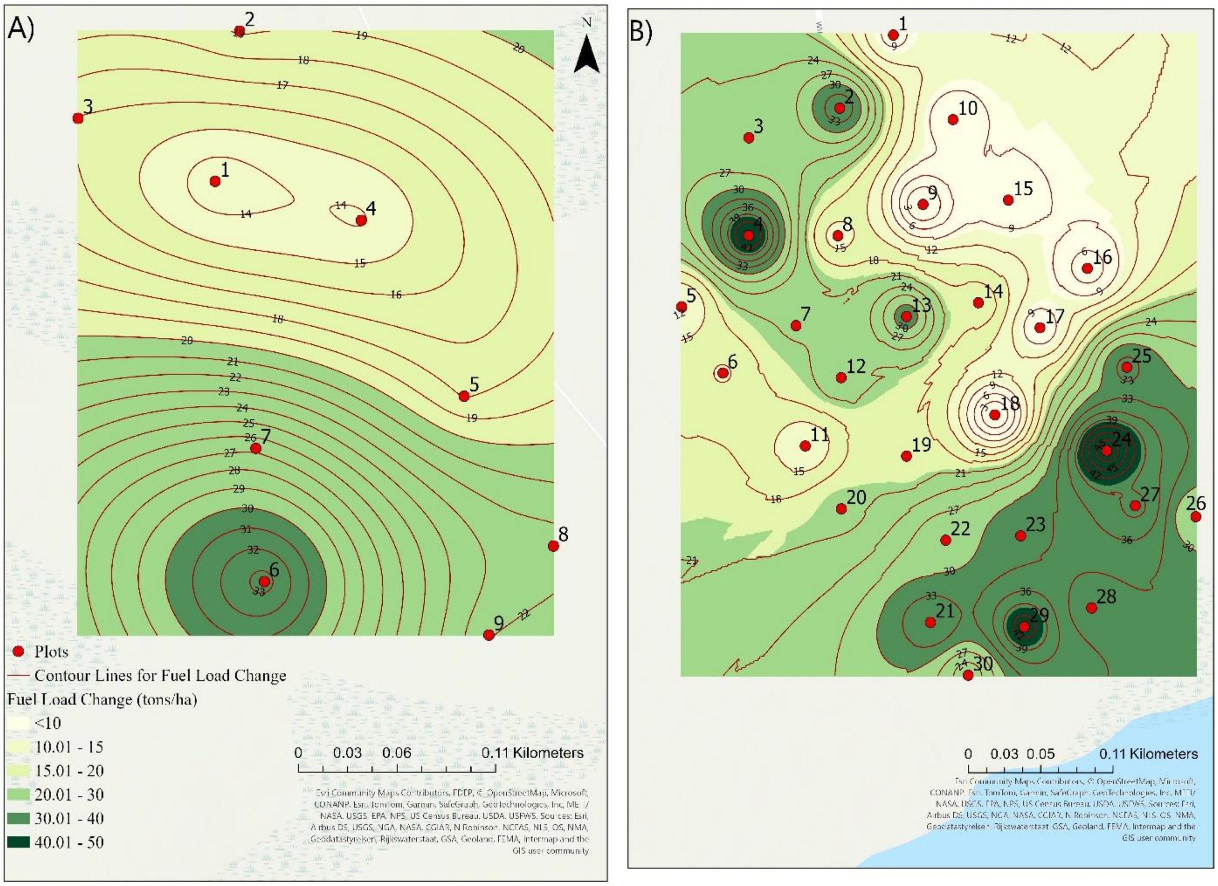

Figure 2Spatial interpolation maps displaying fuel load change (tons/ha) for Perdido (A) and Weeks Bay (B). Fuel load change, indicative of fire severity, was calculated as the reduction in fine fuel biomass—comprising understory vegetation, fine woody debris, and leaf litter—post-prescribed fire compared to pre-fire conditions.

At Perdido, DOC levels initially increased but reverted to pre-fire conditions within one year ($p < 0.05$, repeated measures ANOVA) (***Error! Reference source not found.***). DN levels, however, increased from 4.1 mg/L pre-fire to 10.3 mg/L one year after the fire ($p < 0.01$). This resulted in a two-fold decrease in the C:N from 15.3 to 7.8. ($p < 0.001$).

For Weeks Bay, significant changes were observed in DOC concentrations for the high fuel load change category ($p < 0.05$, repeated measures ANOVA) (Figure 4), though no specific time point comparisons showed statistically significant differences (Tukey's post hoc test, S4). Plots with medium fuel load change exhibited a significant change in DN post-fire ($p < 0.05$, repeated measures ANOVA), with the increase from post-fire to one-month post-fire being a significant difference (Tukey's post hoc test, S4). The C:N ratio across all fuel load categories decreased one year post-fire ($p < 0.05$, repeated measures ANOVA, S5). All plots, regardless of fuel load change category, converged to similar C:N ratios by the end of the first year post-fire.

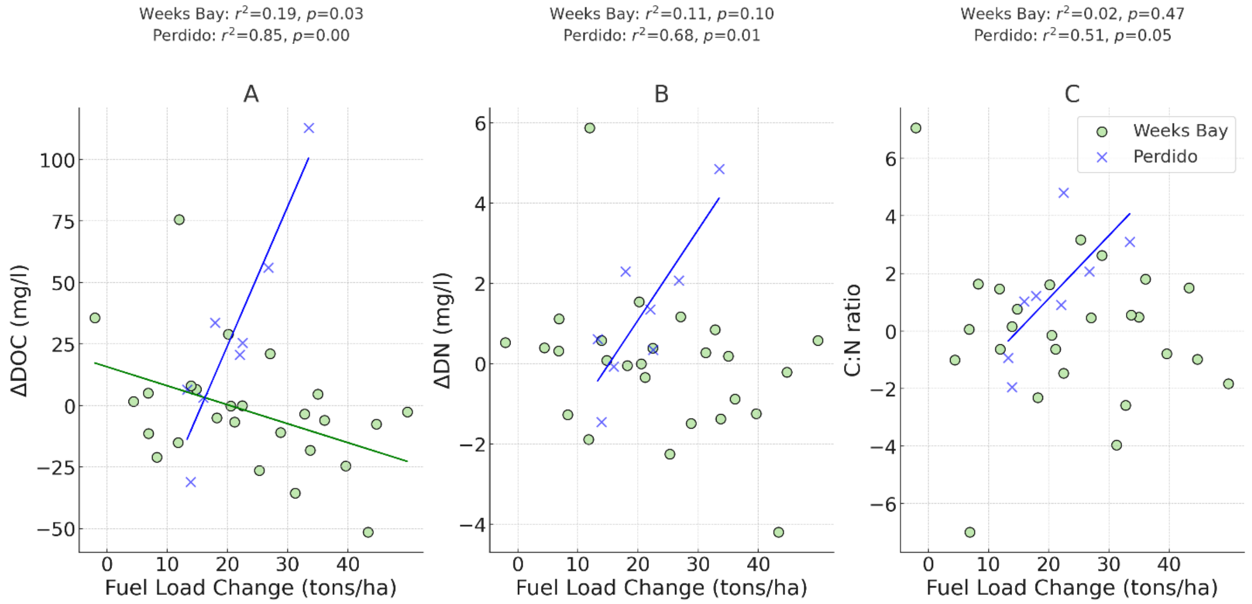

Figure 3Relation between fire severity (estimated as the change in fuel load) and the difference in DOC, DN, and C: N ratio, pre- and immediately post-fire values. Solid lines represent the linear regression, and the r² and p-values are reported for each line.

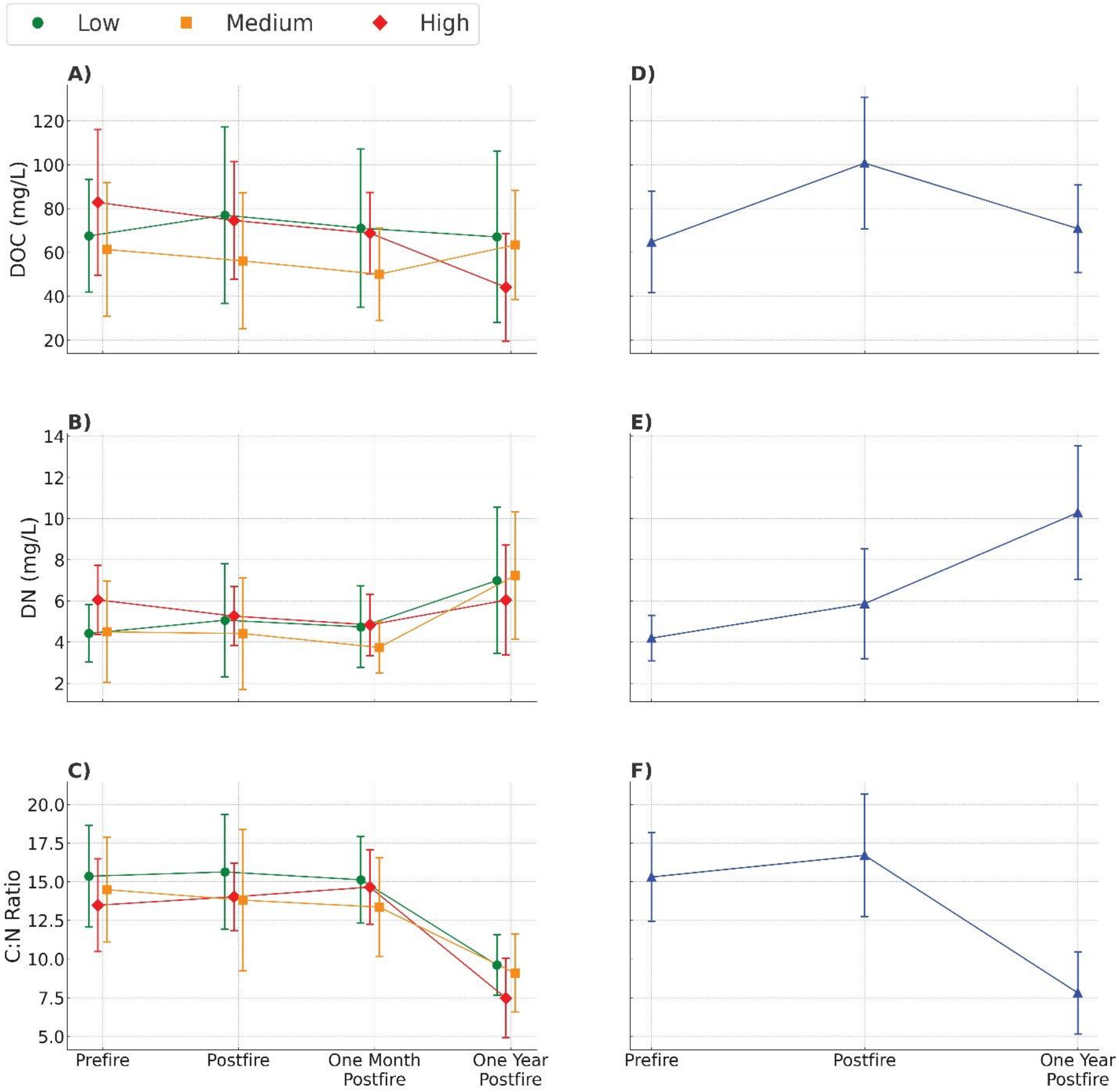

Figure 4Temporal changes in DOC (mg/L), DN (mg/L), and C:N in plots with low (green circles), medium (yellow squares), and high (red diamonds) fuel load change at the Weeks Bay site (A, B, C) and Perdido (D, E, F). Points represent mean values for each timeframe post-fire, with error bars depicting standard error.

3.3 Changes in the molecular composition of DOM

In addition to bulk concentration changes, fire affected the molecular composition of DOM. At Perdido, the E4:E6 ratio increased by 34% one year post-fire (Table 1, $p < 0.001$, repeated measures ANOVA), suggesting a decrease in the average molecular size of DOM (Thomsen et. al., 2002, Chen et. al., 1977). At Weeks Bay, $SUVA_{254}$, an indicator of DOM aromaticity (Wang et. al., 2015), experienced a significant decrease by 88% between immediate post-fire (480 L mol C^{-1} cm^{-1}) and one-month post-fire (36 L mol C^{-1} cm^{-1}, $p < 0.001$, repeated measures ANOVA), indicating either a substantial loss of aromatic compounds initially or a relative increase in non-aromatic compounds. Furthermore, at Weeks Bay, the E2:E3 ratio increased by 65% one year post-fire ($p < 0.001$, repeated measures ANOVA), suggesting alterations in the molecular character of DOM over time.

Table 1Temporal Changes in UV-Vis Spectroscopic Indicators of DOM. Mean values are presented, and standard deviations are shown in parentheses.

	Perdido			Weeks Bay			
	Pre fire	Postfire	One Year Postfire	Pre fire	Postfire	One Month Postfire	One Year Postfire
E2:E3	4.41 (0.45)	4.46 (0.58)	3.88 (1.37)	3.29 (0.99)	2.87 (1.06)	3.88 (1.52)	5.44 (1.38)
E4:E6	22.11 (3.95)	23.71 (5.11)	29.69 (3.82)	15.53 (1.75)	15.97 (3.19)	13.02 (4.81)	19.54 (10.86)
$SUVA_{254}$ (L mol-C^{-1} cm^{-1})	240.2 (72.06)	240.2 (48.04)	360.3 (228.19)	460.5 (125.4)	480.4 (120.1)	36.03 (48.04)	240.2 (120.1)

The PARAFAC model decomposed the EEMs into five fluorophore components (Figure 5 and Supplemental Figure S6). The first component (C1) is associated with humic-like substances known for their significant molecular weight, ranging up to a few thousand Daltons (Jamieson et. al., 2014; Zhang et. al., 2022). It has been previously described as a microbial-derived humic-like substance composed of relatively aliphatic compounds with low molecular weight (Lado et al., 2023, Lambert et al., 2016; Podgorski et al., 2018). The second fluorophore component (C2) is reflective of humic acids characterized by a molecular weight exceeding 1000 Dalton (Huang et. al, 2019, Ishii and Boyer 2012, He et. al. 2016). C2, exhibiting longer Ex and Em wavelengths, likely encompasses complex structures with conjugated aromatic groups (Huang et. al., 2018; Zhang et. al., 2022). Its elongated emission wavelengths suggest a molecular structure potentially enriched with phenolic molecules of low molecular weight and highly unsaturated aliphatic compounds (Uchimiya et. al., 2013; Kellerman et. al., 2015; Huang et. al., 2019). The third fluorophore component (C3) is indicative of a humic-like substance (Lin et. al., 2020; Zhang et. al., 2022), similar to those previously identified as humic-like components found in various environments, including soils, and streams (Lado et al., 2023; Baghoth et al., 2011; Sharma et al., 2017a). This component has also been characterized as having a large molecular size (Ishii and Boyer, 2012) and described as organic matter derived from plants by microbial transformations (Hunt and Ohno, 2007; Sharma et al., 2017a). The fourth fluorophore component (C4) aligns with tyrosine-like fluorescence (Marhuenda-Egea et. al., 2007; Dubnick et. al., 2010). The fifth fluorophore component (C5) displays shorter Ex peak than those typically associated with tyrosine and tryptophan fluorescence identified by some researchers (Coble, 1996; Yamashita et. al., 2008) yet extends beyond the wavelength range noted by others (Marhaba et. al., 2000), as discussed by Dubnick et. al., (2010). It has been previously described as a small-sized, low-biodegradability component with limited adsorption to soils and sediments (Lado et al., 2023; Ishii and Boyer, 2012; Sharma et al., 2017a). Given the association of lower emission wavelengths with substances of lower molecular weight (Uchimiya et. al., 2013; Kellerman et. al., 2015), C4 and C5 may denote the presence of smaller aromatic DOM components.

Table 2Excitation (Ex) and Emission (Em) range and maxima of the five components identify by PARAFAC analysis.

Component (C)	Ex. Range nm	Em. Range nm	Ex. maxima nm	Em. maxima nm
1	225-275	300-380	260/310	422
2	225-275	380-480	270	490
3	250-300	420-520	360/265	438
4	225-300	300-380	285	304
5	250-300	420-520	250	290

At Weeks Bay, significant changes in the fluorescence components were not observed immediately or one month post-fire; however, notable changes became apparent after one year. Specifically, C1, C2, and C3 increased by 97%, 92%, and 104%, respectively one year after the fire ($p < 0.001$), while C4 decreased by 47% ($p < 0.05$) (At Perdido, an immediate but non-significant increase was observed in the C4 and C5 components post-fire, with C4 increasing by 49% and C5 by 50% ($p = 0.11$ for both) (*Table* 3). No significant *changes* were seen for C1, C2, and C3. While these changes were not statistically significant, they may reflect a rapid release of materials due to the fire. However, these levels returned to pre-fire states within a year.

). When discerning the impacts of fire load change on DOM molecular characteristics, the magnitude of change varied among fuel categories (Supplemental Table S7). In the high fuel category, substantial transformations were observed one year post-fire, with increases of 146%, 111%, and 156% in C1, C2, and C3, respectively. However, decreases were noted in C4 and C5 (60% and 50%, respectively). The increases in the medium fuel category were more modest, with C1 rising by 62%, C2 by 54%, and C3 by 64%, while C4 and C5 showed a smaller change with a 14% decrease and a 20% increase, respectively. Similarly, in the low fuel category, C1 increased by 107%, C2 by 120%, and C3 by 100%, whereas C4 and C5 decreased by 63% and 33%, respectively. These changes across all categories and components were statistically significant ($p < 0.05$, repeated measures ANOVA).

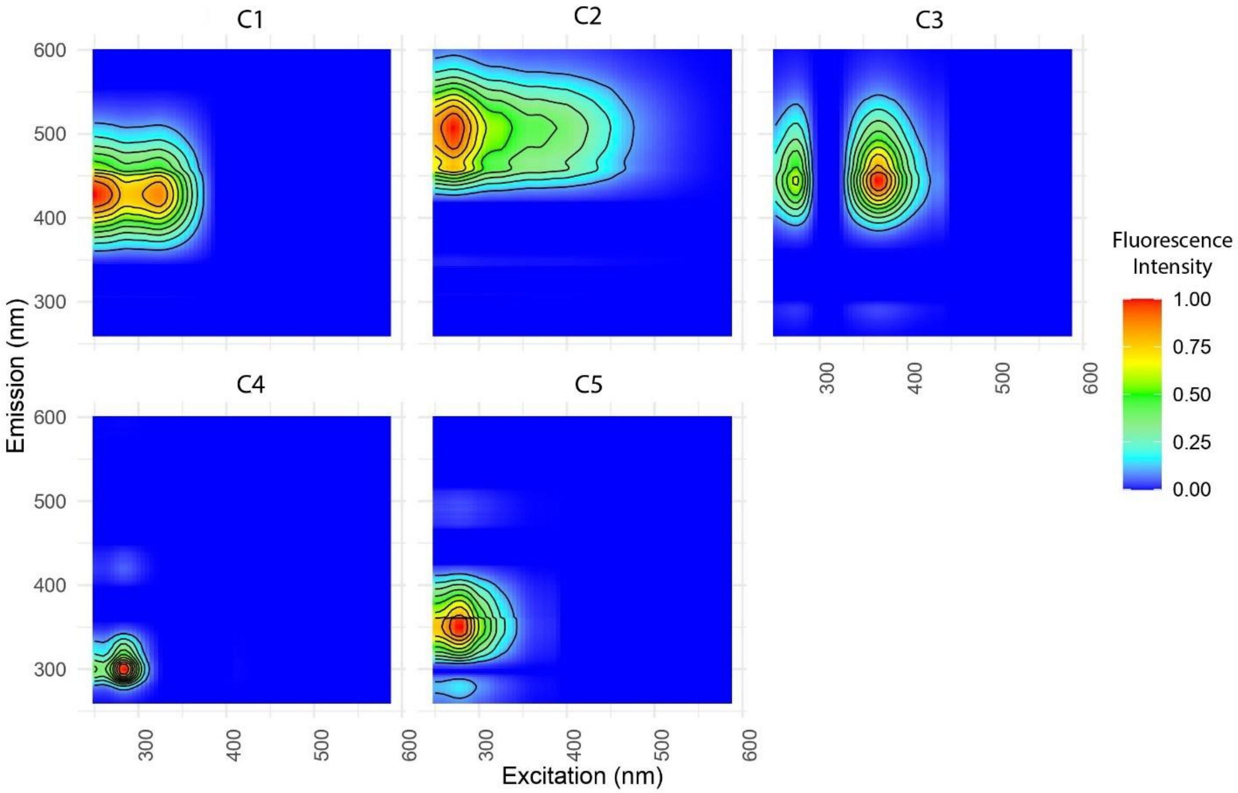

Figure 5 The five fluorophore components of DOM identified using PARAFAC analysis.

At Perdido, an immediate but non-significant increase was observed in the C4 and C5 components post-fire, with C4 increasing by 49% and C5 by 50% ($p = 0.11$ for both) (Table 3). No significant changes were seen for C1, C2, and C3. While these changes were not statistically significant, they may reflect a rapid release of materials due to the fire. However, these levels returned to pre-fire states within a year.

Table 3 Temporal changes in fluorophore intensities at Perdido and Weeks Bay. Values are means of the Ramman intensity normalized to DOC concentration. Standard deviations are shown in parentheses.

	Perdido			Weeks Bay			
	Pre fire	Postfire	One Year Postfire	Pre fire	Postfire	One Month Postfire	One Year Postfire
C1	0.324	0.309	0.295	0.166	0.179	0.185	0.326
	(0.09)	(0.06)	(0.08)	(0.10)	(0.12)	(0.11)	(0.11)
C2	0.226	0.215	0.241	0.106	0.116	0.127	0.204
	(0.06)	(0.04)	(0.07)	(0.06)	(0.06)	(0.07)	(0.05)
C3	0.175	0.166	0.152	0.108	0.116	0.120	0.222
	(0.05)	(0.03)	(0.05)	(0.07)	(0.08)	(0.08)	(0.08)
C4	0.032	0.048	0.023	0.084	0.081	0.068	0.045
	(0.01)	(0.02)	(0.01)	(0.03)	(0.03)	(0.03)	(0.03)
C5	0.030	0.044	0.033	0.058	0.054	0.046	0.046
	(0.01)	(0.02)	(0.01)	(0.02)	(0.02)	(0.01)	(0.03)
Total Fluorescence	0.787	0.782	0.744	0.522	0.546	0.546	0.843

3.4 Temporal Variations in Soil Dissolved Inorganic Ions

We observed significant changes in cation concentrations at both Perdido and Weeks Bay. The data captured immediate and long-term effects, offering insights into the soil's response to fire. (At Perdido, the immediate post-fire K+ increased by 124% ($p < 0.01$) and Mg2+ by 91.6% ($p < 0.05$). One year post-fire, Na+ increased by 400% ($p < 0.01$) and NH4+ by 88% ($p < 0.01$) compared to pre-fire levels, while Mg2+ decreased by 20.4% ($p < 0.05$). At Weeks Bay, immediate post-fire changes were less pronounced, but one-year post-fire, Mg2+ decreased by 47.26% ($p < 0.05$), Si by 67.15% ($p < 0.01$), Al by 91.64% ($p < 0.01$), and NH4+ by 39% ($p < 0.01$). Na+, K+, and Ca2+ did not change significantly. Differences between sites included significant increases in Na+ and K+ at Perdido, with relatively stable levels at Weeks Bay. Conversely, Al and Si levels remained stable at Perdido but decreased significantly at Weeks Bay one year post-fire.

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At Perdido, the immediate post-fire K^+ increased by 124% ($p < 0.01$) and Mg^{2+} by 91.6% ($p < 0.05$). One year post-fire, Na^+ increased by 400% ($p < 0.01$) and NH_4^+ by 88% ($p < 0.01$) compared to pre-fire levels, while Mg^{2+} decreased by 20.4% ($p < 0.05$). At Weeks Bay, immediate post-fire changes were less pronounced, but one-year post-fire, Mg^{2+} decreased by 47.26% ($p < 0.05$), Si by 67.15% ($p < 0.01$), Al by 91.64% ($p < 0.01$), and NH_4^+ by 39% ($p < 0.01$). Na^+, K^+, and Ca^{2+} did not change significantly. Differences between sites included significant increases in Na^+ and K^+ at Perdido, with relatively stable levels at Weeks Bay. Conversely, Al and Si levels remained stable at Perdido but decreased significantly at Weeks Bay one year post-fire.

Table 4 Summary of pH, electrical conductivity (EC: $\mu S\ cm^{-1}$), and ion concentrations ($mg\ L^{-1}$) at Perdido and Weeks Bay Pre- and Post-Fire. Mean values are presented, and standard deviations are shown in parentheses.

Perdido				Weeks Bay			
	Pre fire	Postfire	One Year Postfire	Pre fire	Postfire	One Month Postfire	One Year Postfire
pH	4.18 (0.34)	4.12 (0.26)	4.22 (0.05)	4.43 (0.66)	4.36 (0.58)	4.45 (0.52)	4.17 (0.01)
EC	61.29 (27.74)	72.62 (28.62)	46.18 (19.52)	54.93 (23.97)	67.89 (39.38)	53.79 (37.14)	94.73 (70.10)
Na^+	0.64 (0.26)	0.98 (0.52)	3.21 (1.55)	4.08 (2.19)	4.22 (1.48)	3.65 (1.51)	5.83 (2.43)
K^+	1.57 (0.73)	3.53 (2.23)	5.49 (7.20)	2.93 (2.11)	3.17 (2.14)	2.79 (1.60)	2.81 (1.63)
Ca^{2+}	0.89 (0.73)	1.90 (1.54)	0.98 (0.71)	1.39 (0.97)	1.82 (2.48)	1.56 (2.44)	1.56 (2.44)
Mg^{2+}	0.45 (0.19)	0.86 (0.55)	0.35 (0.34)	2.24 (1.01)	2.18 (1.14)	1.96 (0.97)	1.18 (0.88)
Al	2.03 (1.54)	2.04 (1.28)	1.93 (0.66)	29.16 (19.01)	25.4 (13.2)	27.22 (18.70)	2.42 (0.96)
Si	4.45 (3.27)	4.31 (2.83)	6.36 (1.26)	40.54 (22.39)	36.14 (15.00)	38.11 (13.31)	13.31 (13.10)
NH_4^+	0.82 (0.44)	1.13 (0.72)	1.55 (0.63)	1.89 (0.48)	1.85 (0.57)	1.87 (0.31)	1.15 (0.70)

Cl^-	1.80 (0.63)	2.78 (1.92)	0.61 (0.55)	2.00 (1.61)	2.61 (1.97)	2.09 (1.64)	3.42 (2.99)
NO_3^-	0.19 (0.04)	0.21 (0.10)	0.52 (0.21)	0.18 (0.04)	0.18 (0.06)	0.18 (0.06)	0.41 (0.31)
PO_4^{3-}	4.23 (3.29)	9.13 (8.49)	0.94 (0.84)	0.81 (0.08)	0.85 (0.16)	0.83 (0.14)	0.71 (0.44)

Cl^- levels remained unchanged at Perdido, but NO_3^- levels increased by 168% ($p < 0.01$) and PO_4^{3-} decreased by 77% ($p < 0.05$) one-year post-fire compared to pre-fire levels. At Weeks Bay, NO_3^- levels increased by 128% ($p < 0.05$) one year post-fire.

Discussions

4.1 Impact of Fire Severity on Soil Organic Matter Dynamics

A key finding from our study is the correlation between fire severity and DOC levels. At Perdido, increased fuel load change was associated with elevated DOC concentration immediately after the fire, but a decrease in DOC one year post-fire. This trend indicates the potential transport of DOM to the bay through surface runoff or shallow groundwater. Alternatively, DOM could be utilized by the soil's heterotrophs (Vries et al., 2016). The DOM response to fuel load change categories at Weeks Bay is particularly noteworthy. Immediately following low and medium fuel load changes, post-fire DOC and DN levels remained constant or increased slightly. Still, both decreased in high fuel load change, indicating that higher fire severities increased the mineralization and volatilization of organic matter (Knicker et al., 2006). This finding suggests that targeted fire severity in prescribed burns could be strategized to avoid fire behaviors that cause substantial organic matter loss (Chen et. al., 2022, Pellegrini et. al., 2022). Despite the varied trajectories initially observed across different fuel load change categories, DN and DOC levels converged to similar values across the load change categories one year post-fire, indicating the ecosystem's capacity to recover and stabilize after the disturbance. This resilience suggests that with careful prescriptions, fire can be used to maintain and enhance the carbon storage potential of these forests (Johnstone et. al., 2010). However, compared to pre-fire levels, DN increased significantly one year post-fire on both sites, potentially due to reduced uptake by vegetation after the fire, resulting in higher DN levels in the soil, as was also seen in a study by Koyama et. al. (2010). Additionally, changes in the activity of nitrogen-fixing bacteria due to alterations in vegetation and rhizosphere interactions post-fire may have contributed to the increased DN levels (Vitousek & Hobbie, 2000). Another study by Wan et. al., (2001) showed elevated NO_3^- levels a year after fire. Increased concentrations of DN in these nitrogen-depleted ecosystems may positively impact the accrual of soil organic carbon (De Vries et al 2006). However, soluble nitrogen may be transported to the connected waters and bay, promoting eutrophication (Jani & Toor, 2018).

4.2 Interpreting Changes in DOM Composition Post-Fire

The increase in the E4:E6 ratio at Perdido one year post-fire suggests a reduction in the average molecular weight and particle size of DOM (Weishaar et. al., 2003). The reduction in aromaticity at Weeks Bay, identified by a reduction in $SUVA_{254}$ in the first-month post-fire, may indicate the leaching of small aromatic DOM or the gradual release of less aromatic DOM from biomass. Lado et. al. (2023) found that heating soil at 300 °C led to an increase in $SUVA_{254}$, indicating higher aromaticity in some soils, while higher temperatures reduced the proportion of aromatic compounds due to more intense oxidation and polymerization processes. However, it was also mentioned that the trend seen between fire intensity and $SUVA_{254}$ is soil-specific. The subsequent recovery to pre-fire levels of $SUVA_{254}$ a year after fire indicates a possible replenishment or reconstitution of aromatic compounds within the soil DOM, possibly from new aromatic material from plant and biomass regrowth, highlighting the dynamic nature of organic matter transformation in response to fire. The rise in the E2:E3 ratio at Weeks Bay a year after the fire suggests an increase in smaller, less aromatic, and more aliphatic molecules in the DOM pool, which may result from the selective decomposition of larger, more complex aromatic molecules. Larger aromatic molecules are more complex and recalcitrant (Kleber 2010). Organic compounds, including aliphatic compounds, contribute essential nutrients during decomposition, influencing nutrient availability for plants and microbes (Berg and McClaugherty, 2014). While various organic molecules play a role in carbon storage, Lorenz et al. (2007) suggested that an increase in the proportion of certain biomolecules, such as aliphatic compounds, may enhance soil carbon's stability and long-term storage.

The molecular fluorescence data further illuminates the changes in DOM. Components C1, C2, and C3, which are representative of humic-like substances, showed a general increase in intensity post-fire, especially at Weeks Bay. This rise in humic-like substances suggests that fire induces transformations in soil organic matter, contributing to the accumulation of more resistant organic compounds within the dissolved fraction. The observed decrease in fluorescence intensity of components C4 and C5 at Weeks Bay one year after the fire may be due to enhanced microbial load change (Berg and McClaugherty, 2014) or leaching of these smaller aromatic compounds. (Shen et al., 2014). Changes in vegetation composition affect the types of organic matter entering the soil (Knicker, 2007). We observed an increase in C5 immediately post-fire but only at Perdido, suggesting site-specific differences in the post-fire response of smaller aromatic DOMs. The increase in C5 at Perdido could imply that the fire-induced changes at this site favored the accumulation or formation of these smaller, more labile DOM components. The decrease of C5 fluorescence intensity at both Perdido and Weeks Bay aligns with findings by Lado et al. (2023) and Hunt and Ohno (2007), who observed that components similar to C5 typically decrease in fluorescence intensity during the decomposition of biomass.

4.3 Understanding the Temporal Variations in Dissolved Ions

Soil cation concentrations post-fire at Perdido and Weeks Bay offer valuable insights into the temporal variations in soil chemistry following prescribed burns. At Perdido, we observed a significant increase in base cations like Na^+ and K^+ over time. An immediate increase in K^+ levels was noted, potentially tied to ash deposition and the release of cations from burnt organic matter, with K^+ levels increasing shortly after the fire (Certini, 2005). Weeks Bay exhibited a notable decrease in Mg^{2+} a year after the fire. This decrease might be related to leaching or altered cation exchange capacity in the fire-influenced soil (Ulery et al., 2017). Weeks Bay showed a drastic decrease in Al and Si concentrations one year post-fire, possibly due to leaching or precipitation of secondary phases as previously described in coastal ecosystems (Angel et al., 2016). Vegetation recovery and subsequent uptake by regenerating plants might have also contributed to the reduction in Si. Nitrate increased in both sites one year post-fire. This increase aligns with the measured increase in DN. However, the majority of the DN was dissolved organic nitrogen (DON), with nitrate contributing only about 5% of the DN at Perdido and Weeks Bay one year post fire. Ammonium contributed around 15% at Perdido and 13% at Weeks Bay out of total DN. Increased nitrogen mineralization after the fire might have also increased nitrate content over time (Matson et. al. 1987).

Perdido exhibited a significant decrease one year post-fire in phosphorous content. This observation is important in terms of water quality; changes in P to N ratio have been suggested as a driver of eutrophication (Correll, 1998; Waters et al., 2023). Eutrophication results in harmful algal blooms, reduced water quality, loss of habitat and natural resources, and increased hypoxia severity in estuaries and coastal waters (Rabalais et al., 2009).

Conclusions

This study provides insights into the impact of prescribed fire on soil organic matter and nutrient dynamics in wind-damaged coastal forest ecosystems. At Perdido, where fire severity was comparatively more evenly distributed, we observed a transient increase in DOM immediately post-fire. However, this was not mirrored at Weeks Bay, where higher fire severity was linked to a decrease in DOM concentrations, possibly due to the volatilization or mineralization of organic matter. The molecular composition of DOM also exhibited notable changes. In Weeks Bay, we observed an increase in humic-like substances one year post-fire, while smaller, protein-like aromatic DOM components decreased, likely due to leaching. At Perdido, there was an immediate post-fire increase in these protein-like aromatic DOM components, indicating that the fire-induced changes at this site may have promoted the formation of smaller, more labile organic molecules. The increase in nitrate levels one year post-fire could be attributed to nitrogen mineralization, while the overall increase in DN could be due to reduced vegetation uptake and possible changes in nitrogen-fixing bacteria due to shifts in vegetation. The decrease in phosphorus one year post-fire at the more phosphorus-rich Perdido site emphasizes the risk of nutrient imbalances that could affect connected water bodies. This reduction, alongside the overall increase in nitrogen species, presents the potential for fire-derived leaching of DOM, nitrogen, and phosphorus into nutrient-sensitive waters, raising concerns about the ecological impacts on these connected aquatic systems. These findings highlight the complex interplay between fire severity, soil chemistry, and ecosystem recovery. The distinct responses observed at each site showcase the importance of considering local environmental factors, such as soil type and fire severity, when managing prescribed burns.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplemental Information

Supplemental Method S1

Fuel Biomass Collection and Estimation

Understory vegetation biomass was quantified using a destructive harvesting approach. In each of the three transects (N, SE, SW) of a circular plot, all understory vegetation biomass (less than 2 m in height and stems without a diameter at breast height) within a 0.5-m x 0.5-m quadrat was harvested at either the 9-m or 4-m location. Immediate post-fire harvesting was done avoiding pre-fire harvested area to ensure accuracy in estimation. Clippers were used to clip and collect the understory biomass, which was then stored in labeled paper bags. In the laboratory, samples were dried at 60 °C for ~ 48 hours to attain a constant weight. Oven-dried biomass was then used to calculate understory vegetation biomass per hectare. The plot-level understory vegetation biomass was obtained by averaging the biomass values from three transects within each plot.

Dead fine woody debris (FWD) biomass was estimated using Brown's planar intercept method along each transect line (Brown et al., 1974). Wood pieces of different sizes and time lags (1-hour, 10-hour, and 100-hour) were tallied along the transects between 2-m and 7-m. Woody debris biomass (tons/ha) was calculated using standard formulas (Brown, 1974) and specific gravity values (Anderson, 1978). Plot-level FWD biomass was determined by first summing the biomass across all size classes within each transect, then averaging these sums across the three transects per plot.

To quantify leaf litter biomass, leaf litter depth measurements were taken at the 4-m and 9-m marks along each transect. Leaf litter depth was then multiplied by site-specific leaf litter bulk densities obtained from leaf litter samples collected from 20 plots at Weeks Bay and 14 plots at Perdido using a 25-cm x 25-cm quadrat near plot center. Collected samples were placed in labeled paper bags. In the lab, twigs (> 6 mm in diameter) were removed, and litter samples were oven dried at 60 °C for ~ 48 hours to attain a constant weight for bulk density estimation, which was determined as the mean g dry weight of leaf litter per unit volume sampled. Bulk density values used were 28 kg/m^3 for Weeks Bay and 24 kg/m^3 for Perdido. Plot-level leaf litter biomass was determined by averaging the calculated biomass values from multiple sampling points within each plot.

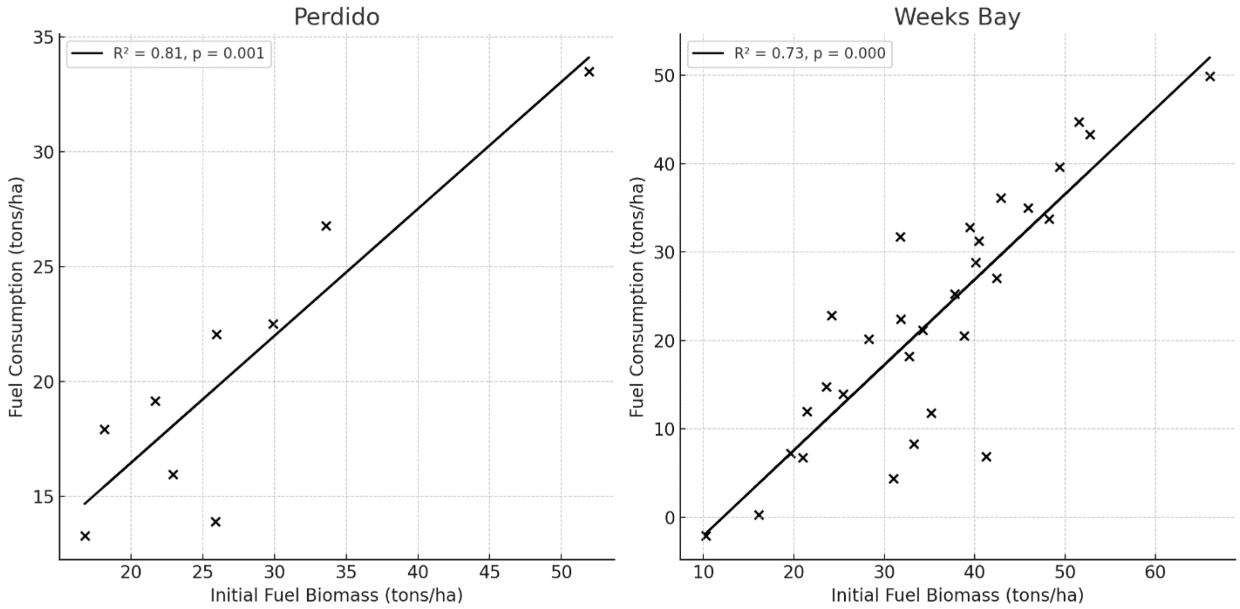
Fuel Biomass and Change in Fuel Load Calculation

Total fuel biomass was calculated by summing the initial biomass of fine woody debris, leaf litter, and understory vegetation. After the prescribed fire, change in fuel load was determined by subtracting the post-fire biomass of these components from their pre-fire biomass. This calculation provided the magnitude of change in amount of biomass during fire, which was used as an indicator of fire severity across different plots. Coarse woody debris (CWD) and soil organic layer (SOL) were not considered as part of fuel load changes. Post-fire CWD biomass was higher than pre-fire CWD biomass in most of the plots due to input from dead-standing trees during the prescribed fire. This made it difficult to estimate how much CWD was consumed and also suggested that CWD might not have been consumed during the fire as anticipated. Similarly, pre-fire SOL biomass was also similar to post-fire biomass in most plots.

Supplemental Table 1 Mean Fuel Load Distribution Across Plots Before and After Prescribed Fire at Perdido and Weeks Bay.

	Perdido		**Weeks Bay**	
	Pre fire (tons/ha)	Post-fire (tons/ha)	Pre fire (tons/ha)	Post-fire (tons/ha)
Fine Woody Debris	10.37	4.12	16.08	10.52
Understory	6.66	1.94	6.57	1.42

Litter	10.39	0.80	12.59	1.0



Supplemental Figure 1 Linear Regression Analysis of Fuel Consumption as a Function of Initial Fuel Biomass. Solid lines represent the linear regression, and the r^2 and p-values are reported for each line.

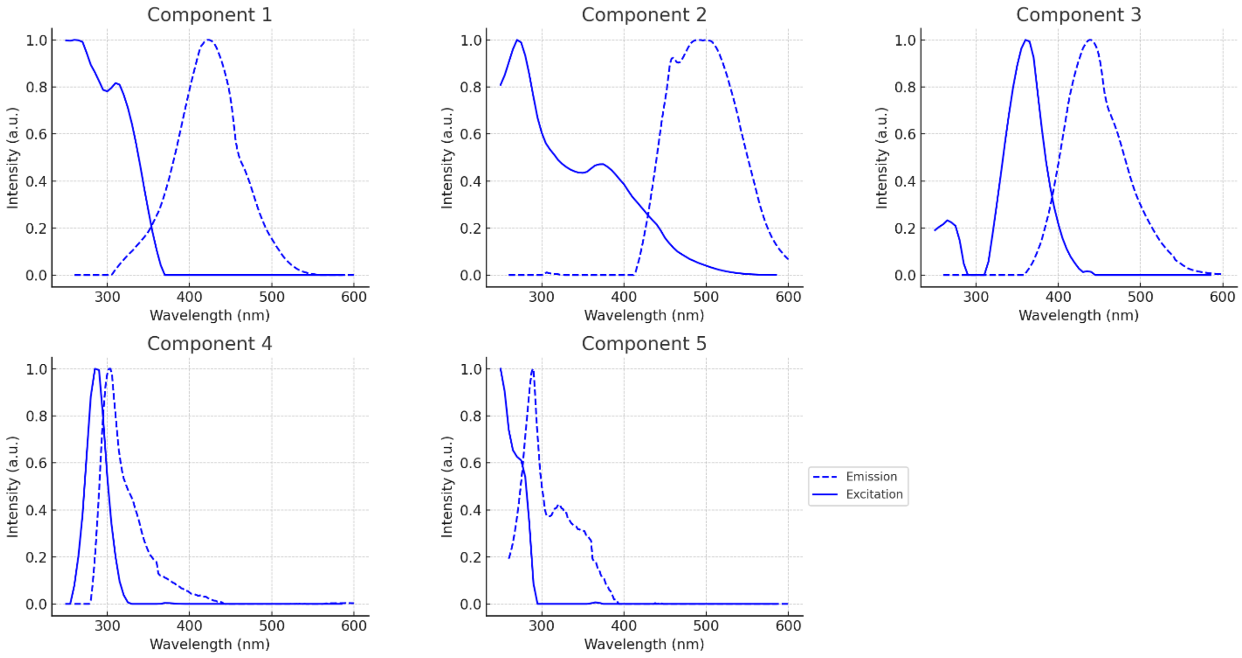
Supplemental Table 2: Tukey's Post Hoc Analysis of Dissolved Organic Carbon (DOC) and Dissolved Nitrogen (DN) Concentrations Across Time Points for Different Fuel Consumption Categories

Time Comparison	DOC High	DN Medium
Pre fire vs. Postfire	not significant	not significant
Pre fire vs. 1 Month Postfire	not significant	not significant
Pre fire vs. 1 Year Postfire	not significant	not significant
Postfire vs. 1 Month Postfire	not significant	$p < 0.05$
Postfire vs. 1 Year Postfire	not significant	not significant

1 Month Postfire vs. 1 Year Postfire	not significant	not significant

Supplemental Table 3 Tukey's Post Hoc Analysis of Carbon: Nitrogen (C:N) Ratio Across Time Points for Different Fuel Consumption Categories

Time Comparison	**Low**	**Medium**	**High**
Pre fire vs. Postfire	not significant	not significant	not significant
Pre fire vs. 1 Month Postfire	$p < 0.05$	$p < 0.05$	$p < 0.05$
Pre fire vs. 1 Year Postfire	not significant	not significant	not significant
Postfire vs. 1 Month Postfire	$p < 0.05$	not significant	$p < 0.0001$
Postfire vs. 1 Year Postfire	not significant	not significant	not significant
1 Month Postfire vs. 1 Year Postfire	$p < 0.05$	$p < 0.05$	$p < 0.05$



Supplemental Figure 2 Excitation and Emission Spectra of PARAFAC-Derived Components

Supplemental Table 4 Mean and Standard Deviation of Soil Components Fluorescence Across Fuel Categories and Time Post-Fire in Weeks Bay

	Component	Prefire Mean	Prefire SD	Postfire Mean	Postfire SD	One Month Postfire Mean	One Month Postfire SD	One Year Postfire Mean	One Year Postfire SD
Low	1	0.15	0.12	0.2	0.16	0.17	0.14	0.31	0.1
	2	0.1	0.06	0.13	0.08	0.12	0.09	0.22	0.06
	3	0.1	0.09	0.13	0.12	0.11	0.1	0.2	0.07
	4	0.08	0.04	0.08	0.03	0.07	0.03	0.03	0.03
	5	0.06	0.02	0.05	0.01	0.05	0.01	0.04	0.02
High	1	0.13	0.04	0.12	0.04	0.17	0.09	0.32	0.12
	2	0.09	0.03	0.08	0.02	0.12	0.06	0.19	0.06
	3	0.09	0.03	0.08	0.02	0.12	0.07	0.23	0.09
	4	0.1	0.03	0.08	0.02	0.07	0.03	0.04	0.01
	5	0.06	0.02	0.05	0.01	0.05	0.01	0.03	0.01

Medium	1	0.21	0.12	0.2	0.12	0.21	0.13	0.34	0.12
	2	0.13	0.07	0.13	0.07	0.14	0.07	0.2	0.05
	3	0.14	0.09	0.13	0.08	0.12	0.08	0.23	0.1
	4	0.07	0.04	0.09	0.04	0.06	0.03	0.06	0.03
	5	0.05	0.02	0.06	0.02	0.04	0.02	0.06	0.03

Chapter 3: Characterization and Quantification of Organic Matter and Pyrogenic Carbon in Coastal Forest Soils

Abstract

Prescribed fires play a pivotal role in shaping soil organic matter (SOM) dynamics and carbon cycling and stabilization processes in coastal forest ecosystems. This study investigates the effects of prescribed burns on the molecular composition of solid-phase SOM in wind-damaged southeastern U.S. coastal forest soils, focusing on total carbon (TC), total nitrogen (TN), and pyrogenic carbon (PyC) markers. At Weeks Bay, significant post-fire increases in TC and TN were observed one year after the fire, likely driven by vegetation regrowth and microbial activity. Conversely, no significant changes were detected at Perdido, highlighting site-specific responses influenced by variations in soil properties and fire severity. BPCA analysis revealed a dominance of less-condensed PyC immediately post-fire, suggesting the formation of more labile PyC fractions that were subsequently lost through leaching or microbial degradation. The decrease in the B5CA to B6CA ratio one year post-fire indicated a transition toward a more stable, highly condensed PyC pool. These findings highlight the transient nature of less-condensed PyC, the resilience of highly condensed PyC, and the site-specific impacts of prescribed fires on soil carbon stability and nutrient cycling.

1. Introduction

In the southeastern United States, coastal forests have historically relied on frequent, low-intensity prescribed burns to maintain their open structure, enhance biodiversity, and prevent the dangerous accumulation of fuels (Brockway et al., 2005; Fowler and Konopik, 2007). Over time, shifts in land use and fire suppression altered these fire regimes, compromising its carbon sink capacity and other key ecosystem services. Hurricanes and other wind-related disturbances add complexity, as the influx of woody debris and changes in understory vegetation after storm events reshape fuel distributions and potentially intensify subsequent fires (Cannon et al., 2017; Suzuki et al., 2019). Strategically implementing prescribed fires in wind-damaged coastal forests can mitigate the risk of severe, uncontrolled wildfires, foster the production of stable pyrogenic carbon, and maintain or even enhance the soil's long-term carbon storage capacity (Hurteau and North, 2010; Ryan et al., 2013).

Coastal forests play a vital role in carbon sequestration, acting as significant carbon sinks that help balance atmospheric CO_2 levels (Barbier et al., 2011). The soil organic matter (SOM) within these ecosystems serves as a critical carbon reservoir, with its stability greatly influenced by fire dynamics (Certini, 2005). When effectively managed, prescribed fires can transform SOM into more recalcitrant forms, such as pyrogenic carbon, which is highly resistant to decomposition and can contribute to long-term carbon storage (Certini, 2005; Lehmann et al., 2011). SOM serves as a critical carbon reservoir, underpinning the carbon cycling processes within ecosystems, with fire altering its stability and molecular structure to produce pyrogenic carbon (PyC), a highly recalcitrant form that can resist decomposition for centuries (Abney and Berhe, 2018).

Pyrogenic carbon (PyC) is a form of carbon produced by the incomplete combustion of organic matter, such as biomass and fossil fuels. It is a significant component of soil organic carbon (SOC) and plays a crucial role in soil biogeochemical processes, carbon sequestration, and contaminant immobilization. The stability of PyC is attributed to its condensed polyaromatic structure, which makes it significantly more resistant to microbial and chemical degradation than other forms of soil organic carbon (Schmidt et al., 2001; Brodowski et al., 2005; Lehmann et al., 2011). Hence, PyC offers the potential to bind carbon within the global carbon cycle over the long term, thereby reducing greenhouse gas concentrations in the atmosphere (Glaser et al., 1998; Brodowski et al., 2005).

This chemically robust structure is a result of the charring process, where organic material is exposed to high temperatures in the absence of oxygen, leading to the transformation of its molecular composition. Fuel type, combustion temperature, and the availability of oxygen during charring can profoundly influence the resultant chemical and physical properties of PyC. For instance, woody biomass often produces more condensed, aromatic PyC, while herbaceous fuels may yield forms with higher surface functionality and reactivity (Masiello, 2004; Preston and Schmidt, 2006). Elevated combustion temperatures tend to increase aromatic condensation and reduce volatile components, thereby enhancing the chemical stability of PyC (Enders et al., 2012; Kuhlbusch and Crutzen, 1995). Moreover, limited oxygen conditions promote the formation of highly polyaromatic and porous PyC structures with increased resistance to degradation (Keiluweit et al., 2010; Preston and Schmidt, 2006). Physically, pyrogenic carbon has a porous structure, which increases its surface area, enhancing its ability to adsorb and hold nutrients, water, and pollutants. Therefore, improving soil fertility and quality (Lehmann et al., 2011). In addition to its longevity, pyrogenic carbon can also significantly influence soil chemical properties, enhancing nutrient retention and availability (Liang et al., 2010). Moreover, previous studies have shown that pyrogenic carbon can interact with other soil organic matter, potentially leading to a protective effect and further enhancing soil carbon sequestration (Wang et al., 2016). However, its precise impact on soil organic matter dynamics, particularly in the context of post-fire scenarios in wind damaged forests, remains under-explored.

The production of PyC from the incomplete combustion of vegetation biomass not only contributes to PyC formation but also helps mitigate carbon (C) and nitrogen (N) losses from volatilization by creating a stable form of these elements that can resist gaseous losses during and after fires when incorporated into the soil (Bird et al., 2012; Torres-Rojas et al., 2020; Santín et al., 2015). In this way, the presence of PyC in soils can improve the long-term carbon sink potential by reducing the rapid release of CO2 during fires and enhancing soil nutrient retention (Santín et al., 2015; Jones et al., 2019).

This study aims to explore the impact of prescribed fires on the molecular composition of soil organic matter in wind-damaged southeastern U.S. coastal forest soils. Specifically, we examine whether prescribed burns contribute significant amounts of PyC to the soil, how PyC formation correlates with fire severity, and whether the PyC added to the soil remains stable or is lost over time through leaching or transport. In addition, we investigate whether FTIR (Fourier Transform Infrared) spectroscopy can effectively measure fire-induced changes in soil, including shifts in PyC markers and broader molecular transformations in soil organic matter. Furthermore, we assess whether BPCA formation leads to shifts in FTIR spectra, how fire severity influences FTIR patterns, and the potential connections between BPCA markers and FTIR spectral characteristics. By addressing these questions, this study seeks to explain the mechanisms underlying post-fire carbon dynamics in fire-managed ecosystems.

2. Method

2.1 Site Description and Sampling Method

The research was conducted at two coastal forests, both recently affected by hurricanes and managed using prescribed fire. These sites include the Weeks Bay National Estuarine Research Reserve (Weeks Bay) in Alabama (30° 25' 9.3504" N, 87° 49' 49.944" W) and the Perdido River Preserve (Perdido) in Florida (30° 27' 56" N, 87° 24' 34" W). Situated within a humid subtropical zone, the region experiences hot summers with peak temperatures averaging 33°C and mild winters averaging 16°C, though brief cold spells may occur. The area receives approximately 170 cm of rainfall annually, influenced by seasonal storms, summer thunderstorms, and tropical weather patterns (NOAA, 2024).

Weeks Bay features a mature coastal slash pine (Pinus elliottii) forest, 60–80 years old, encompassing an area of 13.4 ha. The soils in this area are primarily classified as Okenee and Hyde series (fine-silty, mixed, active, thermic Typic Umbraquults; Web Soil Survey, USDA). The site was impacted by two hurricanes: Category 2 Hurricane Sally on September 15, 2020, and Category 3 Hurricane Zeta on October 23, 2020. Prescribed burns were conducted in July 2016, June 2020, and April 2022. In comparison, Perdido contains a younger longleaf pine (Pinus palustris) stand, approximately 20 years old, covering 12.3 ha. Its soils are predominantly of the Hurricane series (sandy, siliceous, thermic Oxyaquic Alorthods) and Albany series (siliceous, subactive, thermic Aquic Arenic Paleudults; Web Soil Survey, USDA). This site also faced Hurricane Zeta in 2020, with prescribed burns carried out in March 2019 and March 2022.

Study plots were established at both sites to capture a range of wind damage caused by hurricanes. At Weeks Bay, stratified random sampling was employed, dividing the forest into six sections (70 m × 280 m) aligned parallel to the bay using satellite imagery from Google Earth. Each section was further divided into 16 grid cells (35 m × 35 m), from which five cells were randomly selected, resulting in a total of 30 plots. This approach ensured representation across varying levels of wind damage, which was visually confirmed by identifying downed trees. In contrast, Perdido plots were selected from a central 0.062 km² area dominated by longleaf pine, with eight plots chosen to encompass a gradient of hurricane damage ranging from minimal to severe, based on pre- and post-hurricane imagery analysis.

Both locations had a history of prescribed fire management, but the burns evaluated in this study were the first conducted after the hurricanes in 2020. At Weeks Bay, the prescribed burn took place on April 27, 2022, beginning at 13:30 and concluding by 17:00, aside from smoldering. Fire ignition was performed using drip torches, both by hand and via ATV, starting from the southeastern edge of the unit. Weather conditions during the burn included NNW winds at 5–8 km/s, relative humidity ranging from 25% to 55%, and air temperatures between 25°C and 27°C, with flame lengths varying from 0.4 to 1.6 m. The Perdido burn occurred earlier, on March 21, 2022, with ignition starting at 10:40 on the west/northwest side of the unit using drip torches. Conditions included ESE winds at 5–8 km/s, gusting up to 11 km/s, relative humidity of 29% to 51%, and temperatures ranging from 22°C to 28°C.

Soil sampling schedules were carefully designed to evaluate the effects of prescribed fires on soil properties over time. At Perdido, pre-fire soil samples were collected on March 8, 2022, followed by immediate post-fire sampling on March 22, 2022, and a final collection on March 7, 2023, one year after the burn. At Weeks Bay, pre-fire samples were obtained from March 5 to 7, 2022, with additional collections immediately after the burn on April 26, 2022, one month later on May 31, 2022, and one-year post-fire on March 10, 2023.

Soil samples (0–5 cm depth) were extracted using a soil auger at the 9-m mark along three 15-m transects radiating from the plot center at angles of 0°, 135°, and 225°. Samples were stored in labeled Ziploc bags, kept in coolers during transport, and processed within 48 hours in the lab. There, they were air-dried, sieved to <2 mm, and stored in the dark for subsequent analysis.

2.2 Total Carbon and Nitrogen Measurement

Samples were freeze-dried and finely ground using a mortar and pestle to ensure homogeneity. Approximately 10–20 mg of each ground sample was weighed using a VWR microbalance (Model VWR2U, VWR International, Radnor, PA, USA) with a precision of ± 0.001 mg. The samples were then placed into tin capsules. The encapsulated samples were then loaded into the autosampler of Costech Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, CA, USA). This analyzer operates based on the principle of dynamic flash combustion, where the samples are burned in the presence of excess oxygen at high temperatures (1000 °C), converting the organic and inorganic carbon and nitrogen into carbon dioxide (CO_2) and nitrogen gases (N_2), respectively. The results from the elemental analyzer were calibrated using acetanilide standards at five distinct weights: 0.5 mg, 1 mg, 2 mg, 3 mg, and 4 mg. The instrument had a detection limit of 0.02%, and the precision of the measurements is reported to be ±0.1% relative standard deviation (RSD) for repeated analyses of standards, and the accuracy is within ±0.2% of certified values for reference materials. The total weight of carbon and nitrogen in milligrams per gram of soil was calculated by multiplying the percentage of each element (%C and %N) by the weight of the soil sample analyzed, then converting the result to its equivalent per gram of soil.

2.3 FTIR Measurement

Fourier-transform infrared (FTIR) spectroscopy offers a valuable method for identifying fire-induced changes in SOM by detecting specific functional groups such as carbonyl, hydroxyl, and aromatic groups. These functional groups provide insight into the chemical transformations occurring within SOM post-fire (Nguyen et al., 2008). By measuring the absorbance of infrared light across a range of wavelengths, FTIR reveals shifts in the presence and intensity of various organic compounds, indicating changes in carbon stability and composition (Artz et al., 2006). For instance, increased absorbance in the aromatic region suggests higher PyC formation, while reductions in aliphatic content may signal combustion-related changes (Keiluweit et al., 2010; Certini, 2005). This capability makes FTIR particularly useful for distinguishing labile from recalcitrant carbon forms, enhancing our understanding of fire's impact on SOC dynamics (Artz et al., 2006). The soil samples were prepared by finely grinding them to achieve a uniform particle size suitable for infrared analysis. Each ground sample was thoroughly mixed with potassium bromide (KBr) powder, which is a diluent due to its broad infrared transmission range and low mid-infrared absorption (Coates, 2000). A mixture ratio of 10% (w/w) soil sample to 90% KBr was used to ensure adequate dilution and prevent oversaturation of absorbance bands.

The FTIR spectra were collected with a JASCO FT/IR-6800 Fourier Transform Infrared Spectrometer (JASCO Corporation, Easton, MD) equipped with a diffuse reflectance accessory (DiffusIR™, PIKE Technologies, Madison, WI). Before analyzing the samples, a background spectrum was collected using pure KBr. The background was subtracted from each spectrum to account for atmospheric contributions (Griffiths and de Haseth, 2007).

The soil-KBr mixture was carefully placed into the diffuse reflectance accessory sample cup. Excess material was gently leveled off with a flat-edged blade to create a smooth, even surface, which is critical for optimal diffuse reflectance measurements. During data acquisition, the sample chamber was continuously purged with high-purity nitrogen gas (N_2) to minimize carbon dioxide (CO_2) and water vapor interferences, as these gases have absorbance bands that can overlap with those of the samples (Stuart, 2004).

Spectral data were collected over the mid-infrared range of 4,000–600 cm^{-1} with a resolution of 4 cm^{-1}. Post-acquisition processing, including baseline correction and spectral smoothing, was performed using Spectra Manager™ Suite Version 2 software (JASCO Corporation).

2.4 Benzene polycarboxylic acids (BPCA) Analysis

Benzene polycarboxylic acids (BPCAs) are widely used as molecular markers for the analysis of pyrogenic carbon (PyC) (Glaser et al., 1998). BPCA analysis was used to quantify PyC in the soil samples. The principle of this method is the oxidation of polyaromatic structure with concentrated nitric acid solution (65% w/w) under high pressure and temperature. The oxidation products are BPCAs (Hammes et al., 2007). The number and position of carboxylic acids in the BPCA products depend on the condensed polyaromatic structure. Benzene hexacarboxylic acid (mellitic acid, B6CA) forms from the complete oxidation of an interior benzene ring that is completely surrounded by other benzene rings, indicating the highest level of aromatic condensation. benzene pentacarboxylic acid (B5CA), is the product of the oxidation of a benzene ring that is surrounded by adjacent aromatic rings, leaving one position unoccupied. This structure reflects a slightly lower level of condensation compared to B6CA but still indicates significant aromaticity and stability. B4CAs, such as pyromellitic, mellophanic, and prehnitic acids, result from benzene rings with four carboxylic acid groups. These compounds indicate intermediate condensation levels, where the aromatic ring is less surrounded than in B5CA and B6CA but still suggest partial aromatic linkage within the polyaromatic matrix. B3CAs, including hemimellitic, trimellitic, and trimesic acids, contain three carboxylic acid groups attached to a single benzene ring, representing lower degrees of aromaticity and structural integration within the PyC framework. This classification—from B3CAs to B6CA—illustrates the increasing degree of aromatic condensation and stability in PyC structures, with B6CA being the most stable and condensed form (Glaser et al., 2021). The differentiation of BPCA structures also provides information about pyrolysis temperatures, which further influence PyC's stability and carbon sequestration potential (Brodowski et al., 2005).

Soil samples from Section 2.2 were used for the oxidative digestion process. Due to time constraints, only soil samples from Plot 6 at Perdido were used for BPCA analysis. This plot was specifically chosen based on its highest fire severity, as indicated by the greatest change in fuel load. Each air-dried and sieved soil sample (≤2 mm) was ground to a fine powder using a mortar and pestle or ball mill. Approximately 2.5 g of the powdered soil was weighed and placed into Teflon reaction vessels compatible with the CEM MARS Xpress microwave digestion system (CEM Corporation, Matthews, NC). Five milliliters of concentrated nitric acid (65% HNO_3) was added to each sample to ensure complete sample wetting. The vessels were sealed and subjected to microwave-assisted digestion at 190°C for 60 minutes to ensure the complete breakdown of organic material. After digestion, the sample was filtered through glass fiber filters (VWR, Radnor, PA).

Following filtration, samples were subjected to cation exchange chromatography to remove multivalent cations. Glass columns (400 mm height, 15 mm diameter) were packed with 11 g of Dowex cation exchange resin. The resin was conditioned with two column volumes of water, followed by one column volume of 2 M NaOH, and then rinsed with 2 column volumes of water, followed by one column volume of 2 M HCL and further 2 column volumes of water. The digested sample solutions were then passed through the conditioned columns by gravity, and rinsed five times with 10 ml water, and the eluents were collected in glass bottles. The samples were then freeze-dried for 48 hours.

To remove apolar compounds, solid phase extraction (SPE) was performed using C18 SPE cartridges. The cartridges were conditioned with methanol and equilibrated with a methanol/water (1:1, v/v) solution. The digested and cleaned samples were redissolved in 3 mL of methanol/water (1:1, v/v) and passed through the SPE cartridges. The eluents were collected, and the cartridges were further rinsed with ultrapure water to ensure complete recovery of the analytes. The combined eluents were dried using a nitrogen gas blow-down system at 60°C until only dry residues remained.

The final residues were redissolved in 1 mL of ultrapure water and transferred to autosampler vials for ultra-performance liquid chromatography (UPLC) analysis. The Waters Acquity UPLC system (Waters Corporation, Milford, MA), equipped with a C18 reversed-phase column, was used to separate and quantify benzene polycarboxylic acids (BPCAs). The mobile phase consisted of 85% orthophosphoric acid (solvent A) and HPLC-grade acetonitrile (solvent B). UV absorbance was monitored at 216 nm, and calibration curves were constructed using standard solutions of BPCA compounds: benzene-1,2,3-tricarboxylic acid (trimellitic acid), benzene-1,2,4-tricarboxylic acid, benzene-1,3,5-tricarboxylic acid (hemimellitic acid), benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid), benzene-1,2,3,4,5-pentacarboxylic acid, and benzene-1,2,3,4,5,6-hexacarboxylic acid (mellitic acid).

Results were expressed as BPCA-C per unit dry weight of the sample and as a percentage of total organic carbon (TOC). The concentrations of BPCAs in mg/g were converted to their corresponding carbon concentrations (mg/g) by accounting for the total number of carbon atoms in each BPCA molecule. This included the six carbons in the aromatic ring and additional carbons from the attached carboxylic acid (-COOH) groups. The carbon contribution of each BPCA was calculated as the product of its concentration (mg/g) and the fraction of its molecular weight attributable to carbon, determined by dividing the total carbon weight by the molecular weight of the BPCA. The ratio of benzenepentacarboxylic acid (B5CA) to benzenehexacarboxylic acid (B6CA) was also calculated, which is used to assess the degree of aromatic condensation, representing the formation of stable, resistant carbon structures crucial for long-term carbon sequestration as B5CA and B6CA represent the most thermally mature fractions of PyC, formed under higher combustion temperatures compared to other BPCAs (Glaser et al., 1998).

2.5 Data Analysis

Fuel load change was used to assess the fire severity across hurricane-affected coastal forests. Fuel load change was calculated by subtracting post-fire fine fuel biomass from initial fine fuel biomass. Initial fuel biomass data was calculated by adding understory, fine woody debris, and litter biomass. (Supplemental Method S1)

To better quantify fire-induced changes in SOM, we correlated FTIR spectra with BPCA analysis. While FTIR identifies broader compositional changes, BPCA analysis provides molecular-level specificity related to PyC formation (Glaser et al., 1998). By integrating these methods, we aim to assess carbon stability and transformations under varying fire intensities.

Statistical analyses were performed using R (R Core Team, 2024) in RStudio (Posit Team, 2024). Pearson's correlation coefficients (r), coefficient of determination (r^2), and p-values were used to assess the significance and explanatory power of the correlations between fuel load change and the immediate change in concentrations of TC, TN, and C:N. For the change in the studied variables over time, we used a one-way repeated measures ANOVA for each site individually. Tukey's HSD post hoc test was applied to determine significant differences between each pair of samples.

Partial Least Squares Regression (PLSR) was employed to model the relationship between the FTIR spectra and the measured fuel load change, which served as an indicator of fire severity. PLSR is a multivariate statistical method that projects both the predictor variables (spectral data) and the response variable (fuel change) into a new latent space, maximizing the covariance between them (Wold et al., 2001). This method is particularly suitable for handling datasets with a large number of collinear predictors relative to the number of observations, as is common with spectral data. In this study, the FTIR absorbance values at different wavenumbers served as predictor variables, while the Total C and N concentration, and fuel change measurements were the response variables. The spectral data were preprocessed by mean-centering and scaling to unit variance to ensure that all variables contributed equally to the model. Cross-validation was performed using a 10-fold approach to prevent overfitting and to assess the model's predictive performance. The optimal number of latent variables was determined based on the minimum Root Mean Squared Error (RMSE) obtained during cross-validation.

Partial Least Squares Discriminant Analysis (PLS-DA) was applied to classify samples into three time points: before fire, immediately after fire, and one month after the fire. To improve the modeling power and enhance the ability to detect patterns and trends, FTIR spectra from both Weeks Bay and Perdido sites were combined for analysis. PLS-DA is an extension of PLSR tailored for classification tasks, where the response variable is categorical (Barker & Rayens, 2003). It works by finding a linear regression model that maximizes the separation between predefined classes while accounting for the covariance structure of the predictors.

The same preprocessed FTIR spectral data were used as predictors in the PLS-DA model. The categorical time point labels served as the response variable. The model's performance was evaluated using overall accuracy, Cohen's kappa statistic, and class-specific metrics such as sensitivity and specificity. Cross-validation with 10 folds was again utilized to ensure the robustness of the classification results.

Principal Component Analysis (PCA) was conducted on the FTIR spectral data to explore patterns and identify potential clustering among samples based on their spectral characteristics. PCA is an unsupervised multivariate statistical technique that reduces the dimensionality of the data by transforming the original correlated variables into a new set of uncorrelated variables called principal components (Jolliffe & Cadima, 2016). This method is particularly useful for high-dimensional datasets like spectral data, where it helps to reveal underlying structures and visualize variance in the data.

In this study, PCA was performed on the preprocessed and scaled FTIR spectra to assess whether samples from different time points exhibited distinct clustering patterns in the principal component space, which could indicate changes in chemical composition due to the fire event. The PCA was performed using data from both Weeks Bay and Perdido sites combined to improve modeling power and capture broader trends in soil organic matter composition. The analysis focused on the first few principal components that captured the most variance in the data. Score plots were generated to visualize the distribution of samples and to examine any potential groupings or trends.

3. Results

3.1 Spatial and Temporal Dynamics of Total Carbon and Nitrogen

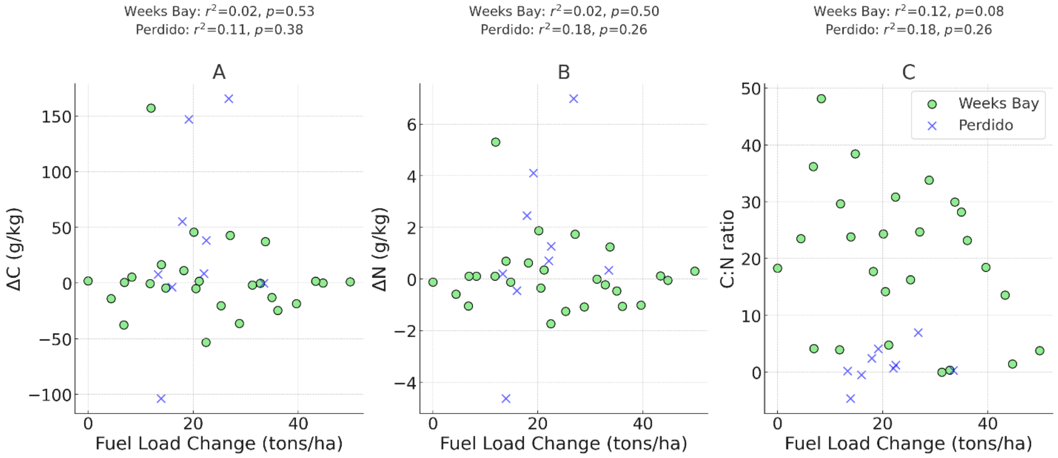


Figure 1. Relation between fire severity (estimated as the change in fuel load) and the difference in C, N, and C: N ratio, pre- and immediately post-fire values.

No significant correlation was observed between fuel load change and change in C, N, and C: N at both Weeks Bay and Perdido sites.

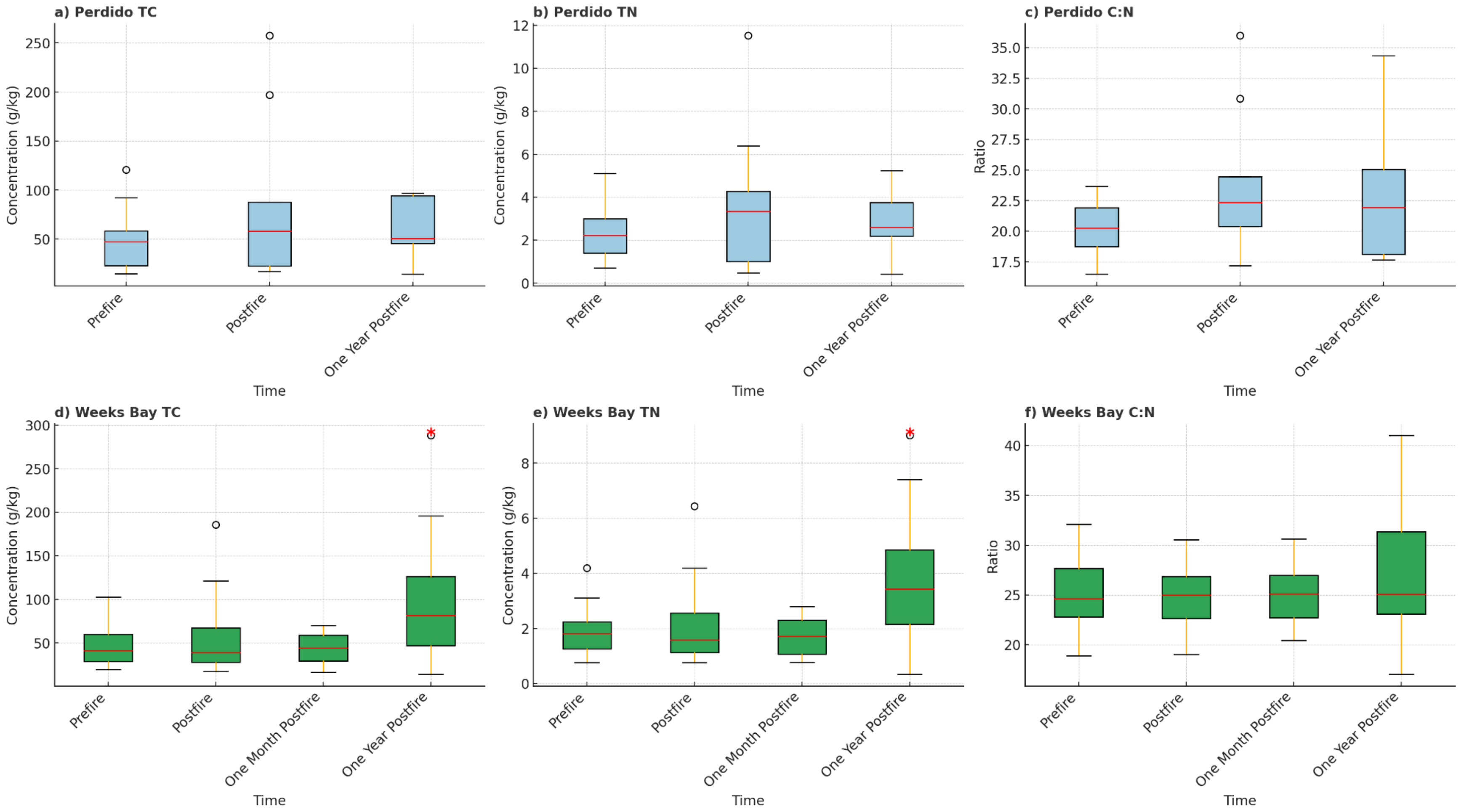


Figure 2. Box and whisker plots showing concentrations of Total carbon (TC), Total nitrogen (TN), and carbon-to-nitrogen (C: N) ratios at different time points for Perdido (a–c) and Weeks Bay (d–f) study sites. Significant differences between time periods, as determined by Tukey's HSD post hoc test, are denoted by red asterisks in each panel.

At Perdido, no significant changes were observed for TC, TN, or C: N ratio across the time frames (Figure 2 A, B, C).

In Weeks Bay, for TC, concentrations increased from 67.5 g/kg pre-fire to 71.1 g/kg immediately post-fire and rose substantially to 118.8 g/kg one year post-fire, reflectin a significant overall trend. ($p < 0.001$, repeated measures ANOVA, Figure 2D). One year post-fire TC levels were significantly higher than pre-fire ($p < 0.001$), immediately post-fire ($p < 0.001$), and one month post-fire ($p < 0.001$), while no significant differences were observed among the other time points. TN concentrations increased from 3.2 g/kg pre-fire to 3.4 g/kg immediately post-fire and further to 5.1 g/kg one year post-fire ($p < 0.001$, Figure 2E). Significant increases in TN concentrations was measured between one year post-fire compared to pre-fire ($p < 0.001$), immediately post-fire ($p < 0.001$), and one month post-fire ($p < 0.001$). In contrast, the C: N ratio showed no significant changes over the observed periods (Figure 2F).

3.2 PLSR and PLS-DA Analyses on FTIR Data

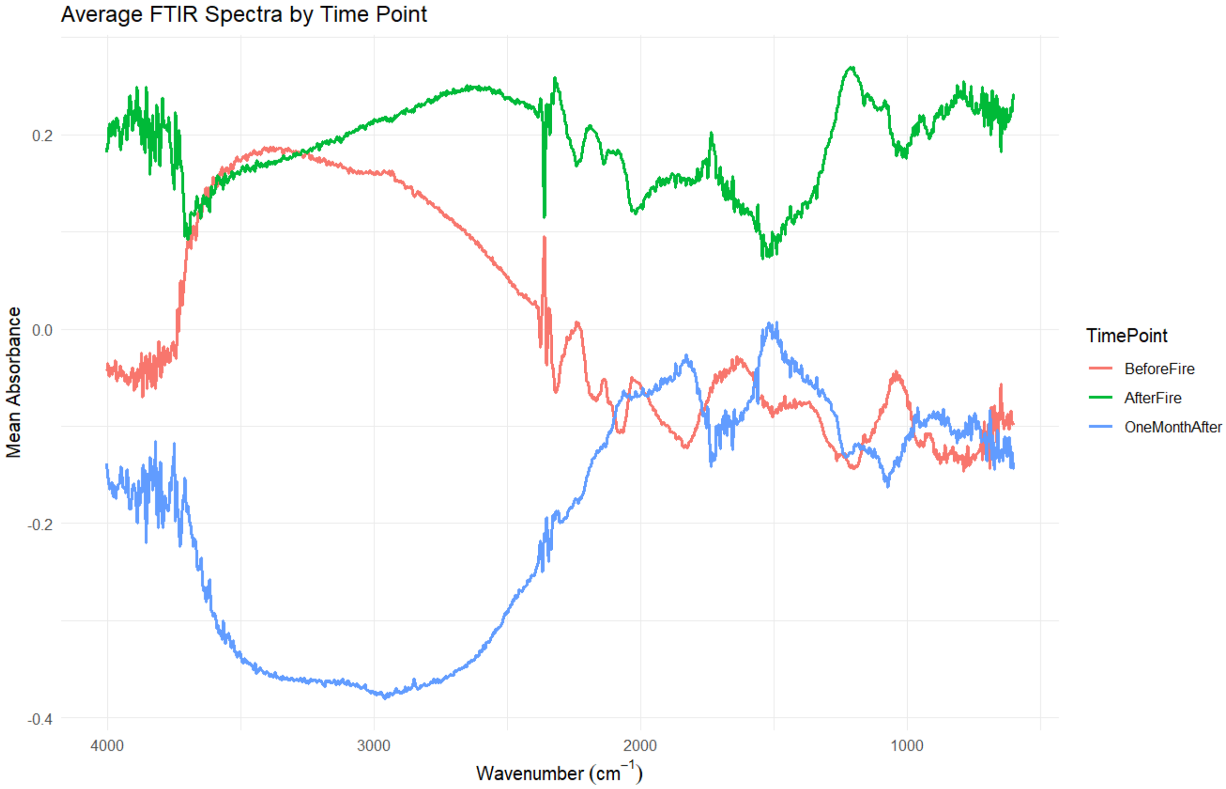


Figure 3. PLS-DA loading plots derived from FTIR spectral data of soil samples at different time points, combining data from both Weeks Bay and Perdido sites. Red represents soil samples collected before the fire, green represents immediately after the fire, and blue represents one month after the fire. The x-axis represents wavenumbers (cm^{-1}), which correspond to molecular vibrational frequencies, while the y-axis represents mean absorbance, indicating the relative abundance of functional groups.

Partial Least Squares Regression (PLSR):

We employed PLSR to model and find the relationship between fuel change and FTIR spectra comprising 3,528 wavenumbers for all the samples. The optimal model selected had 3 components, resulting in a cross-validated RMSE of 6.3. However, the model's performance on the test set was suboptimal, with an RMSE of 5.6171, and an R-squared value of 0.0042. This indicates that the model explained less than 1% of the variance in Fuel Change.

PLS-DA was utilized to classify samples into before-fire, after-fire, and one-year after-fire categories based on their FTIR spectra. The model achieved an overall accuracy of 28.57%, lower than the no-information rate of 33.33%. The Kappa statistic was -0.0714, suggesting no agreement beyond chance. Sensitivity for the classes ranged from 14.29% to 42.86%, indicating poor predictive capability.

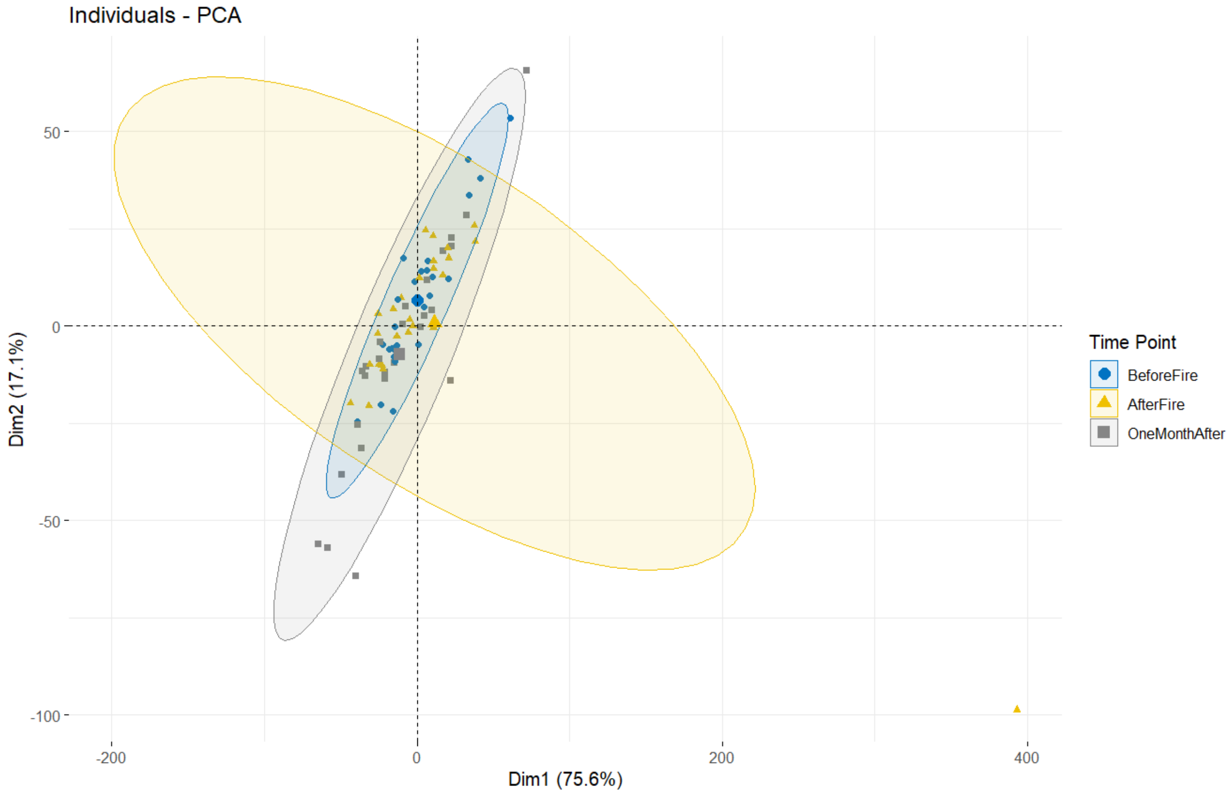


Figure 4 Principal Component Analysis (PCA) score plot showing PC1 (x-axis) versus PC2 (y-axis), with samples colored by time point: blue (before fire), yellow (immediately after fire), and gray (one month after fire). The axes, labeled as Dim1 and Dim2 in the plot, represent the first two principal components (PC1 and PC2), which explain 75.6% and 17.1% of the variance in the dataset, respectively. Ellipses represent 95% confidence intervals for each time point, highlighting group separations based on time since the prescribed fire.

The PCA of the FTIR spectral data did not reveal distinct patterns or clustering based on time since fire events. The lack of significant separation indicates that the FTIR spectra did not capture substantial changes in soil chemistry attributable to the fire or the short-term ecological processes following it. Therefore, the PCA results align with the findings from the PLSR and PLS-DA analyses, further indicating that FTIR spectroscopy, under the conditions and timeframes studied, may have limited sensitivity in detecting the immediate or short-term impacts of fire on soil chemical properties.

3.3 Quantitative and Qualitative changes in pyrogenic carbon through BPCA markers

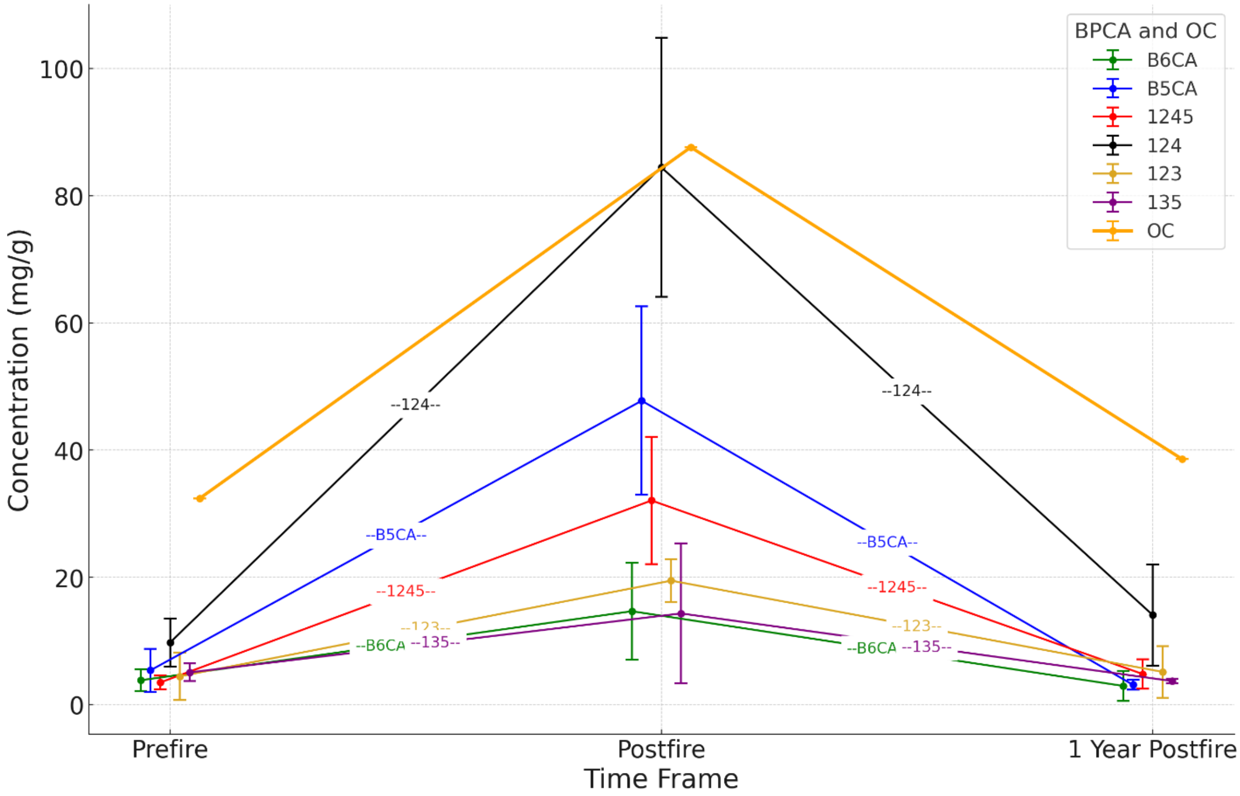


Figure 5 Concentration changes of benzene polycarboxylic acids (BPCAs) over time in Plot 6 at the Perdido site (4 replicates).

All BPCA compounds showed a general trend of significant increases immediately post-fire, followed by declines to near or below pre-fire levels one year post-fire. The total BPCA contribution to organic carbon (OC) increased from 35.6% pre-fire to 82.3% post-fire, then declined to 29.7% one year post-fire. Among the BPCAs, 1,2,4-BPCA and B5CA were the most dominant, collectively contributing over 70% of the total BPCA content.

For B6CA, concentrations increased nearly 4-fold from 3.82 mg/g prefire to 14.68 mg/g immediately postfire, before dropping to 2.93 mg/g one-year postfire ($p < 0.01$), falling below prefire levels. Similarly, B5CA showed a dramatic rise, increasing nearly 9-fold from 5.38 mg/g prefire to 47.76 mg/g postfire, but declined sharply to 3.10 mg/g one year postfire ($p < 0.001$). Concentrations of 1,2,4,5-BPCA rose from 3.48 mg/g prefire to 32.08 mg/g immediately after the fire—a nearly 10-fold increase—before decreasing to 4.80 mg/g one year postfire ($p < 0.001$). In contrast, 1,2,4-BPCA exhibited the highest postfire levels, surging from 9.75 mg/g prefire to 84.46 mg/g postfire, then declining to 14.09 mg/g by one year postfire ($p < 0.001$). For 1,2,3-BPCA, concentrations increased more moderately, rising from 4.45 mg/g prefire to 19.48 mg/g postfire before declining to 5.15 mg/g after one year ($p < 0.001$). Lastly, 1,3,5-BPCA showed a smaller increase, rising from 4.81 mg/g prefire to 14.09 mg/g postfire, with a subsequent decrease to 2.93 mg/g one year postfire ($p = 0.08$).

The ratio of B5CA to B6CA, which indicates the relative dominance of less condensed to highly condensed aromatic carbon structures, increased from 1.41 prefire to 3.25 immediately postfire, follow by a decreased to 1.06 one year postfire.

4. Discussion

4.1 Post-Fire Dynamics of Total Carbon and Nitrogen

The lack of a significant relationship between fire severity (as measured by changes in fuel load) and shifts in total carbon (TC), total nitrogen (TN), and the carbon-to-nitrogen (C:N) ratio suggests that for bulk organic matter in the soil, factors beyond fire severity might have influenced these changes and that high variability within the samples was seen in the results. Unlike dissolved organic matter (DOM), where a significant correlation with fuel load change was observed at the Perdido site, TC and TN did not exhibit such patterns at either study location. This discrepancy may stem from the differences in mobility and reactivity between bulk soil organic matter and dissolved organic matter fractions (Don and Schulze, 2008; Certini, 2005).

At Weeks Bay, the observed increases in TC and TN over time could reflect ensuing post-fire processes. Altered understory vegetation could have disrupted nitrogen uptake by plants and facilitated nutrient redistribution, particularly through enhanced liable organic matter deposition and microbial nitrogen fixation (Neary et al., 1999). The substantial rise in TC levels suggests contributions from vegetation regrowth, litter deposition, and microbial processing of organic matter. These processes align with the observed increase in humic-like fluorophores (components C1, C2, and C3) one year post-fire seen in Chapter 2, which indicates the accumulation of more resistant organic compounds in the dissolved organic matter (DOM) pool. The increase in humic-like substances likely reflects enhanced microbial activity and the transformation of plant-derived organic inputs into more stable forms. (Lehmann and Kleber, 2015) Additionally, increased soil aggregation may have stabilized carbon within organo-mineral complexes (Six et al., 2002).

In contrast, Perdido showed no significant temporal changes in TC, TN, or the C:N ratio, possibly due to site-specific differences. Variations in soil properties, vegetation types, or fire severity between the two sites may account for this divergence.

4.2 Post-Fire Dynamics of Pyrogenic Carbon: Formation, Transformation, and Stabilization in Soil

The observed dominance of B5CA and 1,2,4,5-BPCA in the BPCA analysis immediately post-fire highlights changes in the quantity and molecular structure of PyC. These BPCAs reflect intermediate levels of aromatic condensation within the PyC pool (Nguyen et al., 2008; Brodowski et al., 2005) and may represent transient forms of PyC that contribute to short-term nutrient cycling before being further oxidized, leached, or stabilized within the soil matrix (Brodowski et al., 2005). The post-fire increase observed across all BPCA compounds, including B6CA, reflects the production of PyC during combustion. Interestingly, 1,2,4-BPCA contributed the largest proportion of the carbon pool immediately after the fire, highlighting its role as a key fire-generated thermal product. The relatively high levels of B3CA and 1,2,4-BPCA reflect the production of PyC with a mix of structural complexities, where less-condensed PyC dominates due to the incomplete combustion of organic matter during the fire. These compounds, while aromatic, represent labile forms of PyC that are more susceptible to degradation and transport. All BPCA compounds showed a general trend of significant increases immediately post-fire, followed by declines to near or below pre-fire levels one-year post-fire.

The gradual decrease in the B5CA to B6CA ratio from post-fire to one year post-fire reflects changes in the composition and stability of the PyC pool. The immediate post-fire PyC pool was dominated by less-condensed, labile aromatic structures, as indicated by the relatively high levels of B5CA and 1,2,4,5-BPCA. Over time, the reduction in the B5CA to B6CA ratio suggests a transition toward a PyC pool enriched in more highly condensed aromatic structures, despite the overall decline in PyC concentrations. This trend implies the selective loss of less-condensed, labile PyC fractions through microbial degradation or transport, while more condensed and stable PyC structures persisted.

These observations emphasize the dynamic nature of the PyC pool, with initial formation favoring labile fractions that are gradually depleted, leaving behind more stable aromatic compounds. These trends highlight the dual processes of PyC formation and selective loss, which shape the long-term stability of soil organic carbon in fire-affected ecosystems. This interpretation is consistent with the gradual reduction in fluorescence intensity of smaller, aromatic DOM components (e.g., C5) observed in Perdido and Weeks Bay in Chapter 2, which may indicate similar mechanisms of transport or degradation of labile PyC.

4.4 Limitations of the Study

Due to time constraints, this study faced certain limitations, particularly in the scope of BPCA characterization. Analysis was conducted on a single plot, and for this chapter, we chose a plot from Perdido with the highest fuel load change to assess the impact on pyrogenic carbon changes over time. FTIR analysis in this study was restricted to samples collected within one-month post-fire, limiting the temporal resolution of spectral changes over time. While multivariate analyses such as PCA, PLSR, and PLS-DA were applied, the current performance of these models could be improved by refining the analysis of existing FTIR spectra. Enhanced preprocessing and advanced chemometric approaches may yield more robust insights.

This study aimed to establish a correlation between FTIR and BPCA data, to use FTIR—a rapid and cost-effective method—to predict pyrogenic carbon characterization. While this correlation could not be fully achieved due to limited BPCA data, it represents a promising direction for future work. Expanding this analysis with additional data could strengthen the correlation and further validate the approach. While the findings presented here are preliminary, I plan to continue this research beyond my master's degree, incorporating additional data to address these gaps and ultimately publish the outcomes in a comprehensive paper.

A more extensive temporal and depth-wise analysis would enable a deeper understanding of long-term pyrogenic carbon dynamics, nutrient cycling, and leaching potential. Additionally, environmental factors such as microbial activity, moisture levels, and other abiotic processes were not directly monitored but are likely to have influenced the observed changes in soil organic matter and pyrogenic carbon. Including these variables in future studies would provide more mechanistic insights into the transformations occurring within the soil system. These limitations, while inherent to the scope and timeframe of this research, highlight opportunities for further exploration and refinement of the methodologies to enhance the understanding of soil organic matter dynamics postfire.

5. Conclusion

The study revealed significant post-fire dynamics in carbon and nitrogen concentrations and pyrogenic carbon (PyC) markers, highlighting the complexity of soil chemical transformations following fire events. At Weeks Bay, significant increases in total carbon (TC) and total nitrogen (TN) one year post-fire suggest nutrient input and organic matter accumulation, potentially driven by vegetation regrowth and microbial activity. These findings indicate that fire may stimulate processes that enhance soil organic matter stabilization and contribute to ecosystem recovery. In contrast, at Perdido, no significant changes were observed in TC or TN, reflecting site-specific differences in ecosystem responses, possibly due to variations in soil properties, vegetation, or fire intensity.

Significant shifts in BPCA markers provide insights into the post-fire transformation and stability of PyC. The dominance of less-condensed BPCAs such as 1,2,4-BPCA and B5CA immediately post-fire highlights the formation of potentially more labile PyC fractions, likely due to incomplete combustion processes. However, the subsequent decrease in these markers one year post-fire suggests the selective loss of less-condensed PyC through leaching or microbial degradation. The decrease in the B5CA to B6CA ratio over this period indicates a transition toward a PyC pool enriched in highly condensed, stable aromatic structures.

These findings emphasize the transient nature of less-condensed PyC and the resilience of highly condensed PyC under environmental conditions. By distinguishing between site-specific responses and broader post-fire dynamics, this study contributes to understanding how fire impacts soil carbon stability and nutrient cycling, with implications for managing fire-affected ecosystems and enhancing soil carbon storage.

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Appendix

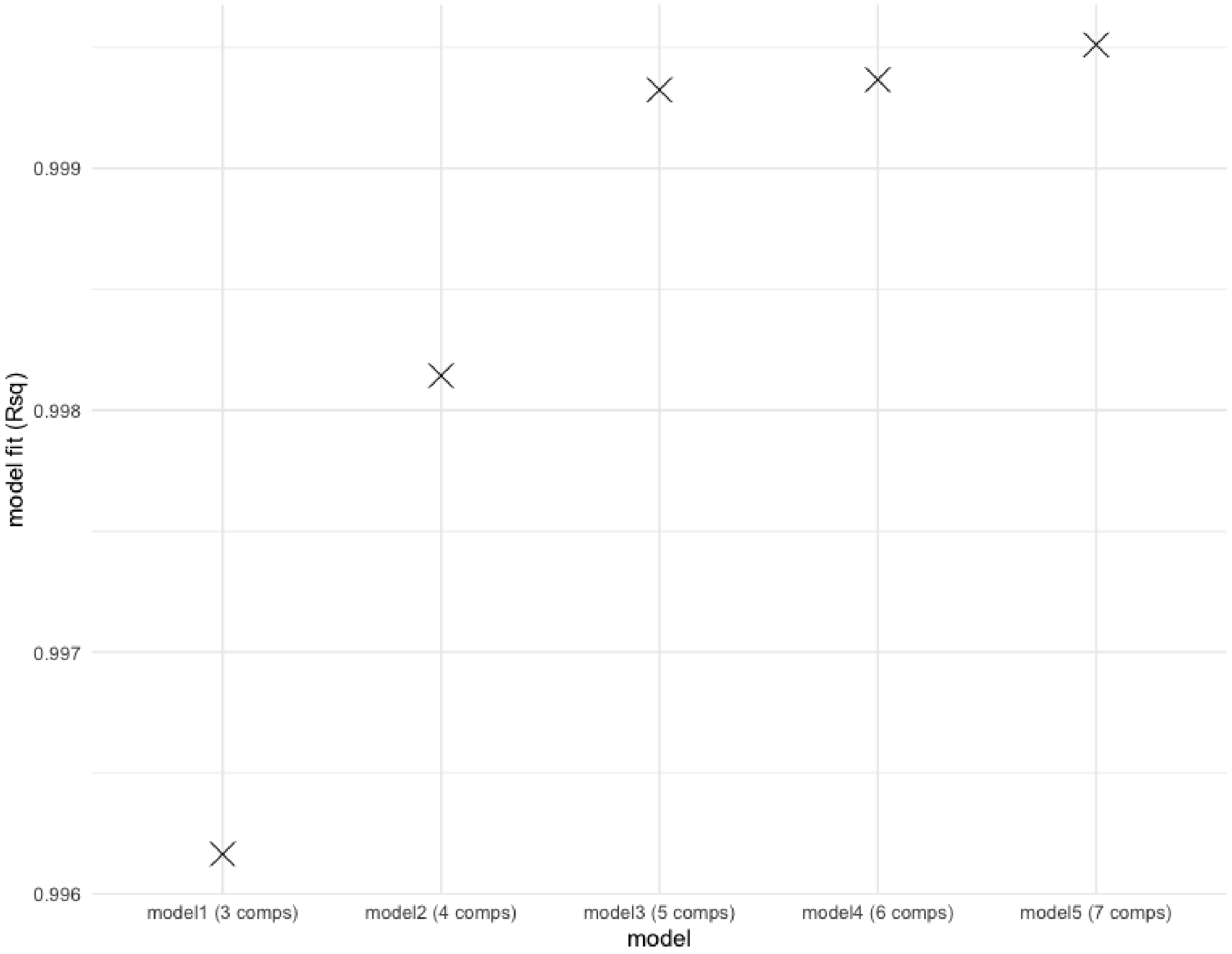


Figure 6 R-square of all 5 different PARAFAC models.

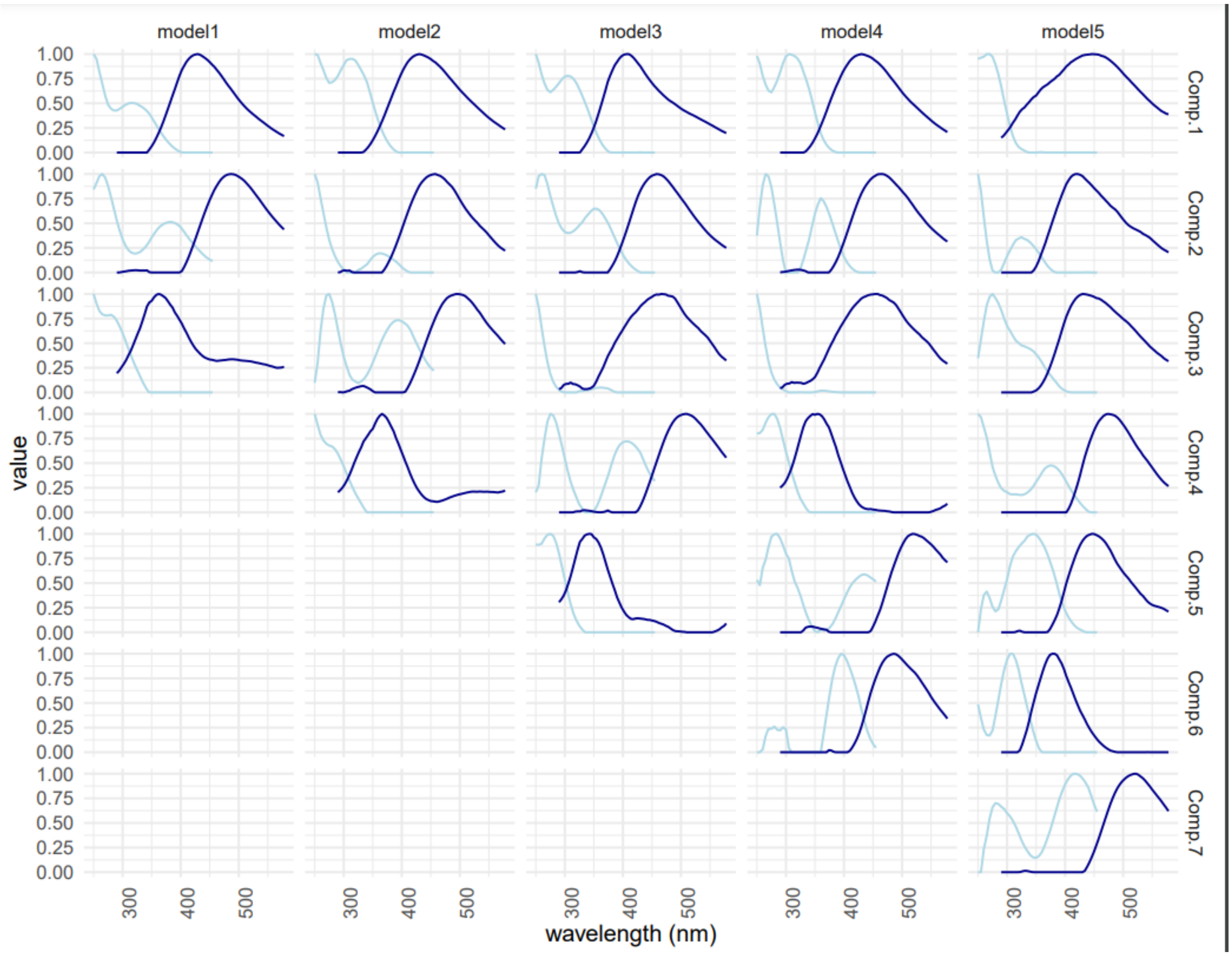


Figure 7 Signature of all 5 different PARAFAC models.

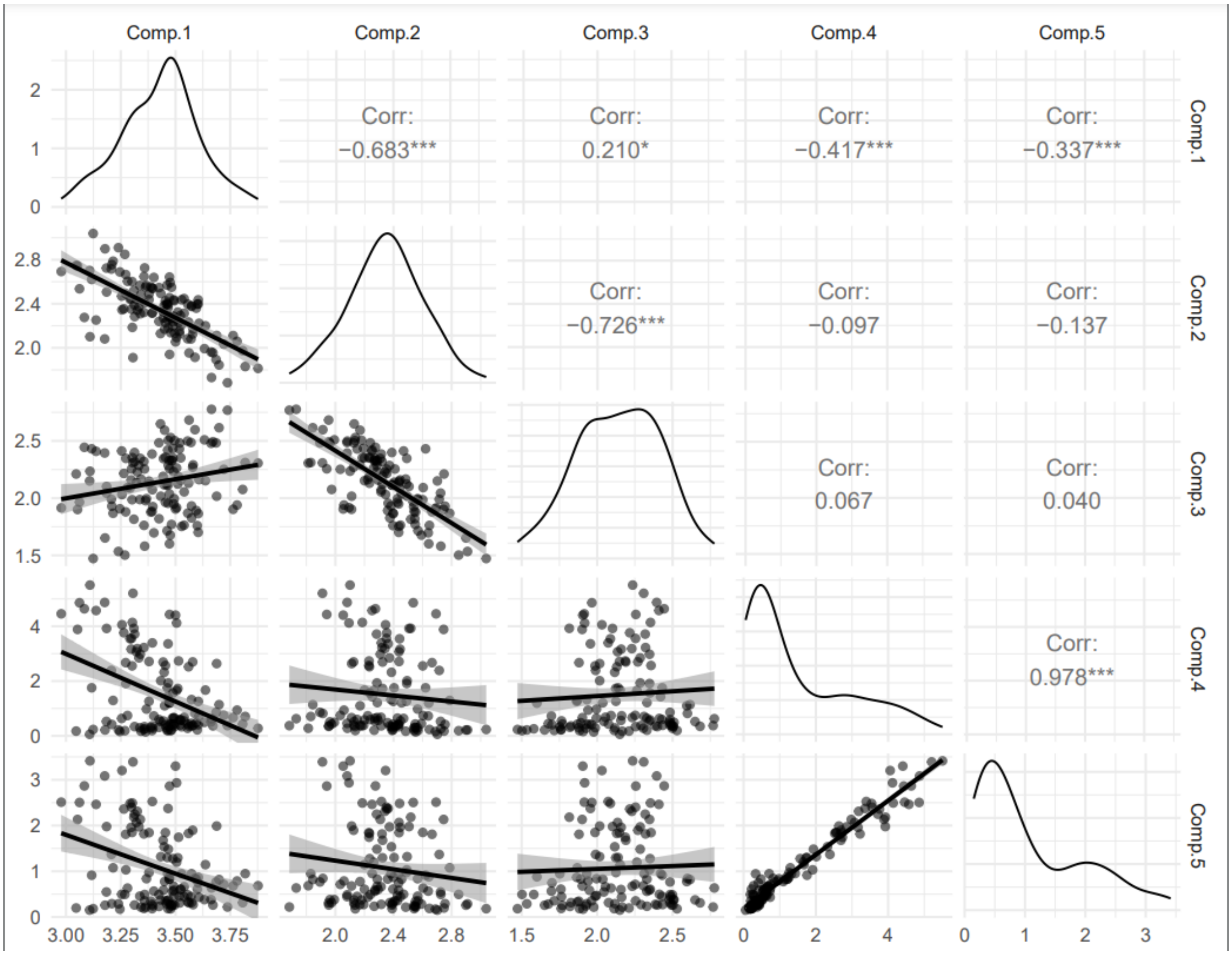


Figure 8 Correlation plot of the 5-component PARAFAC model.

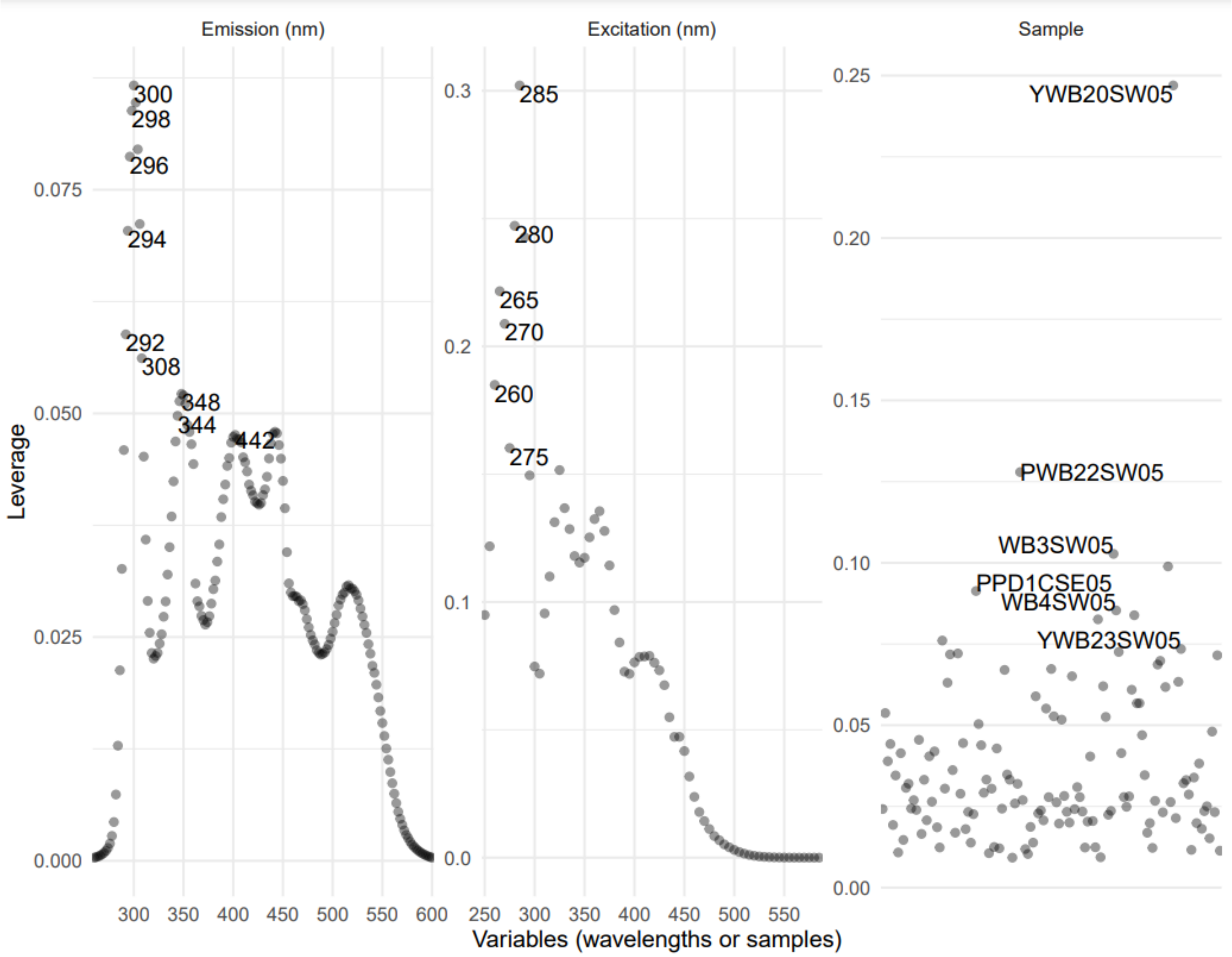


Figure 9 Leverage of the 5-component model before removing outlier

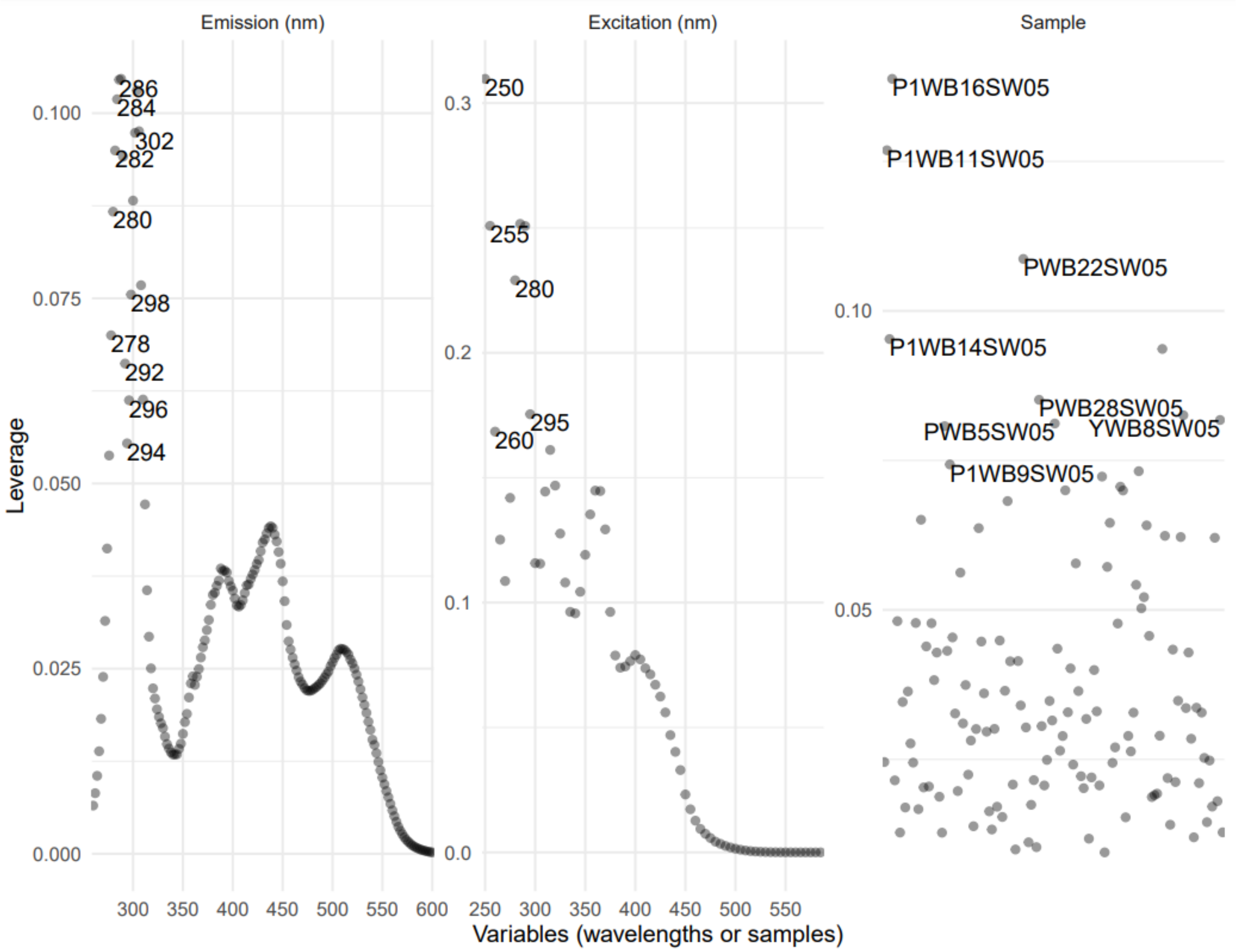


Figure 10 Leverage of the 5-component model after removing outlier

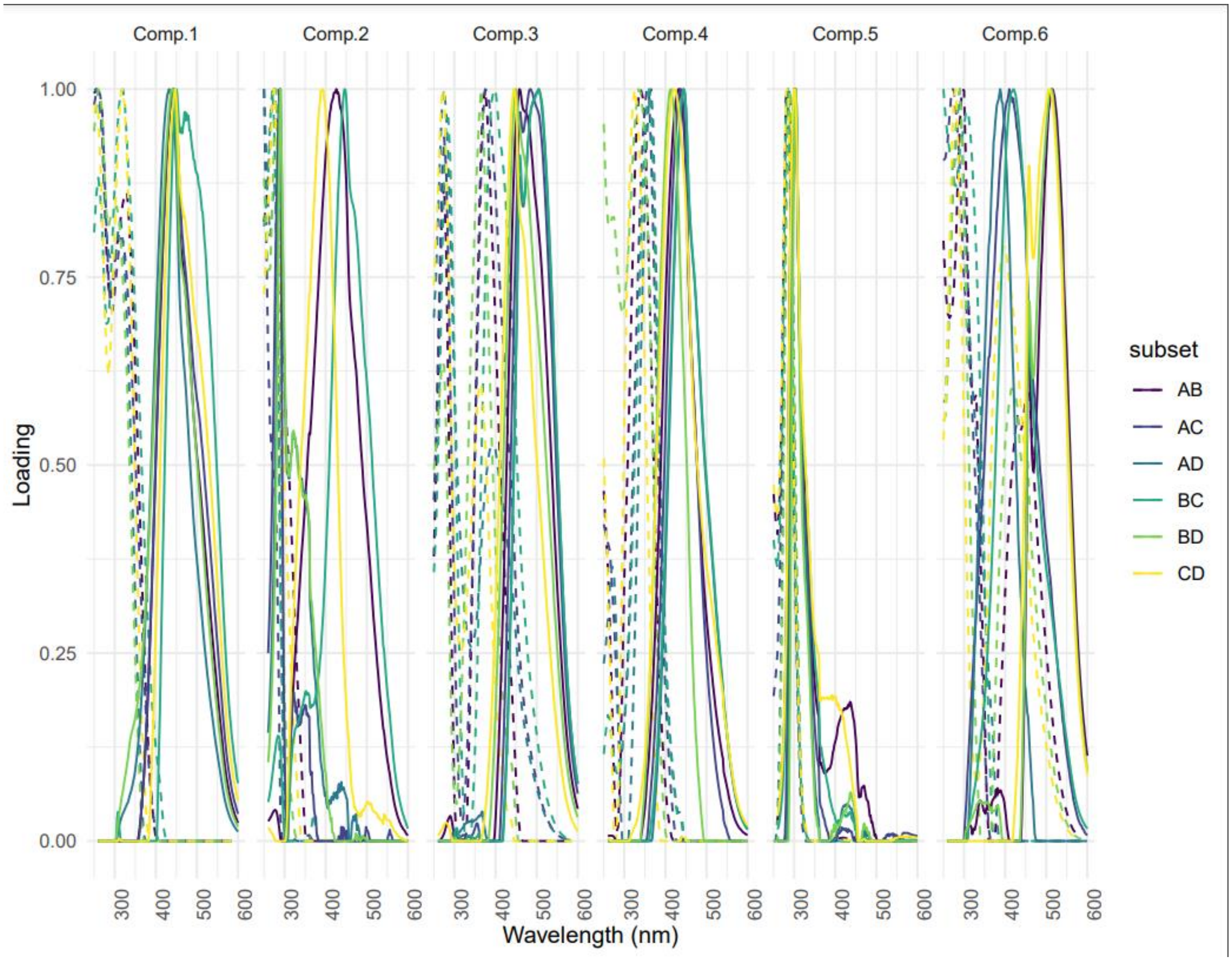


Figure 11 Split-half analysis from validation of 5-component PARAFAC model. Emission is represented by dashed lines while excitation is represented by solid.

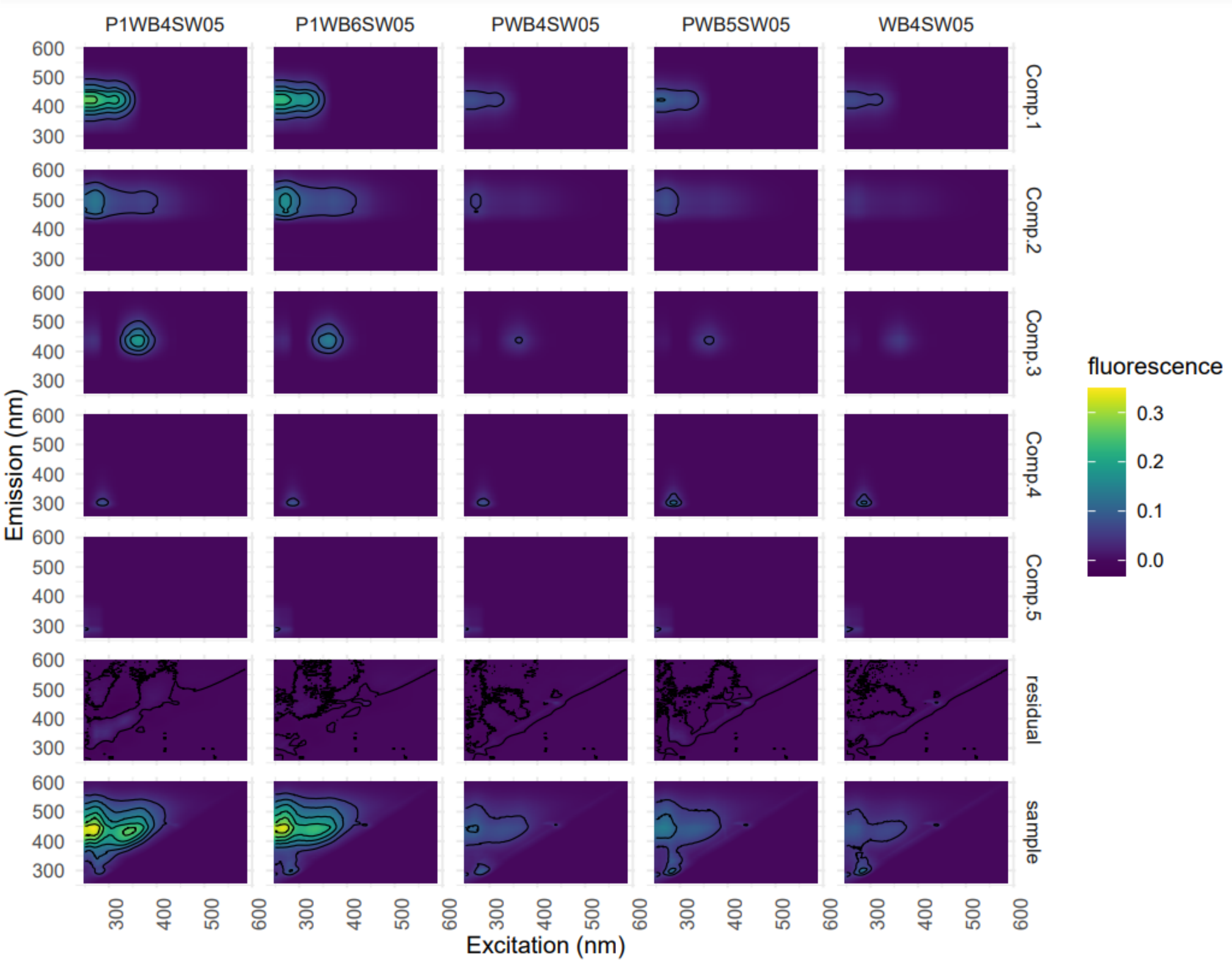


Figure 12 Plot of five DOM samples residuals from derived 5 component PARAFAC model

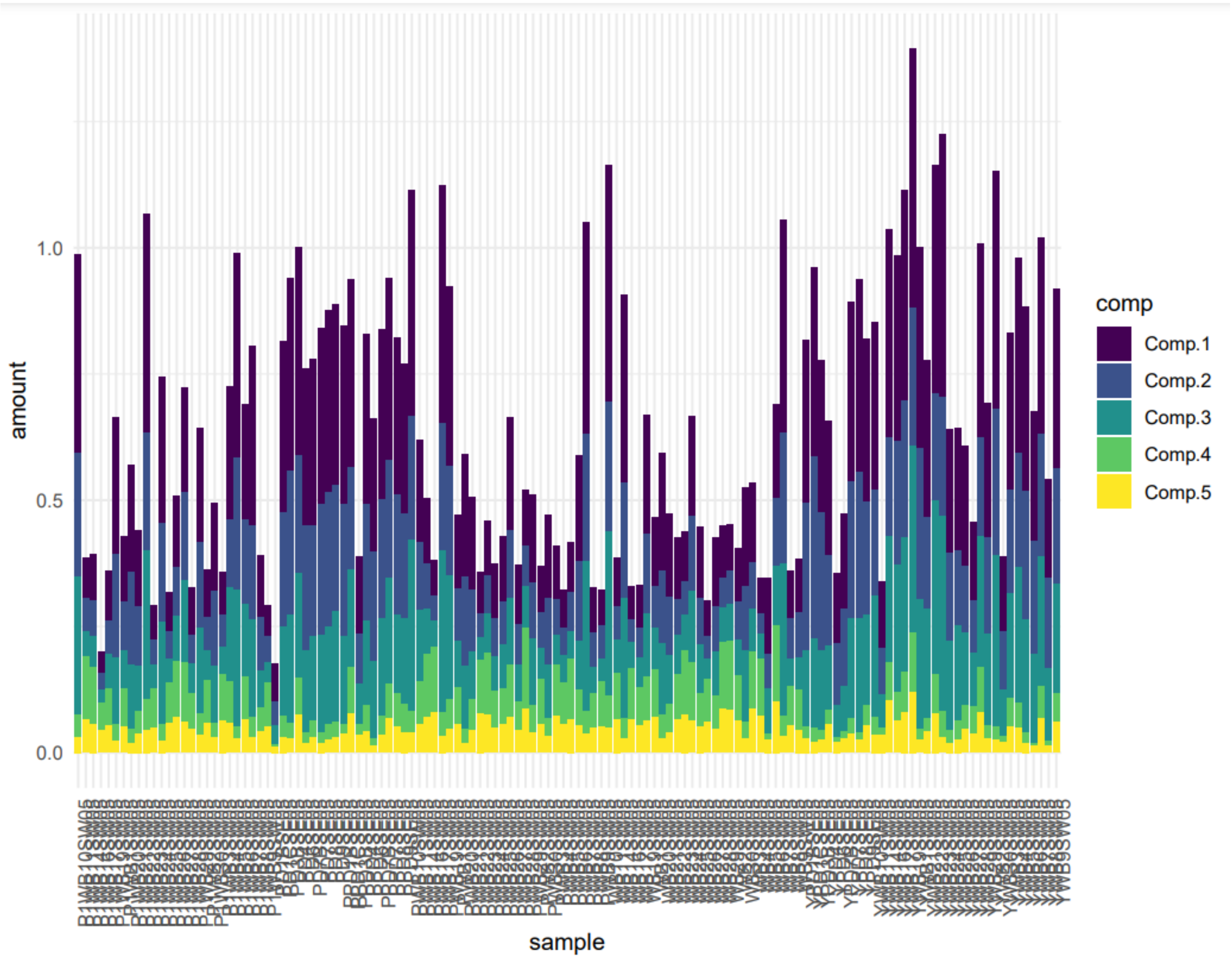


Figure 13 Loading of all components in PARAFAC analysis

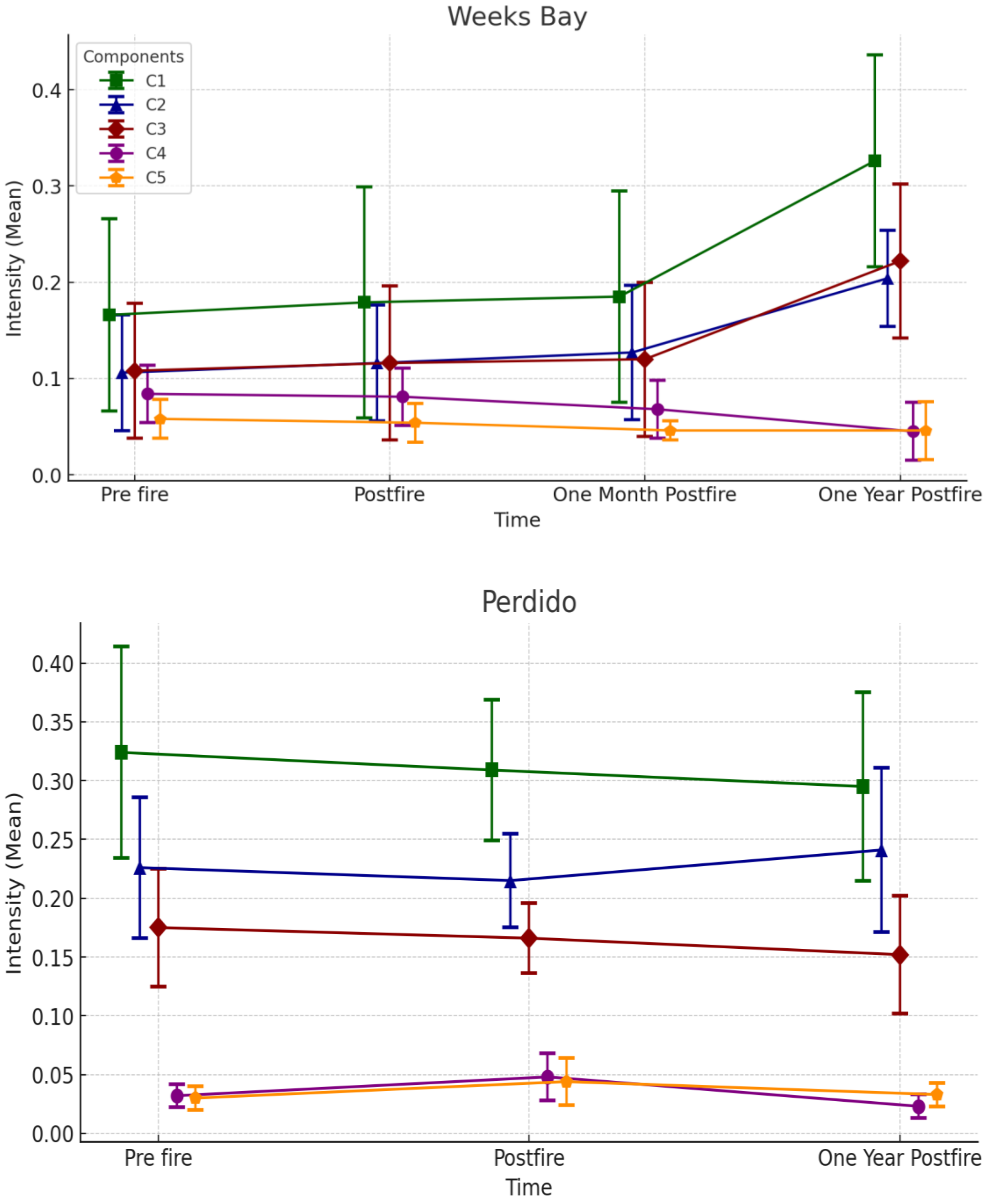
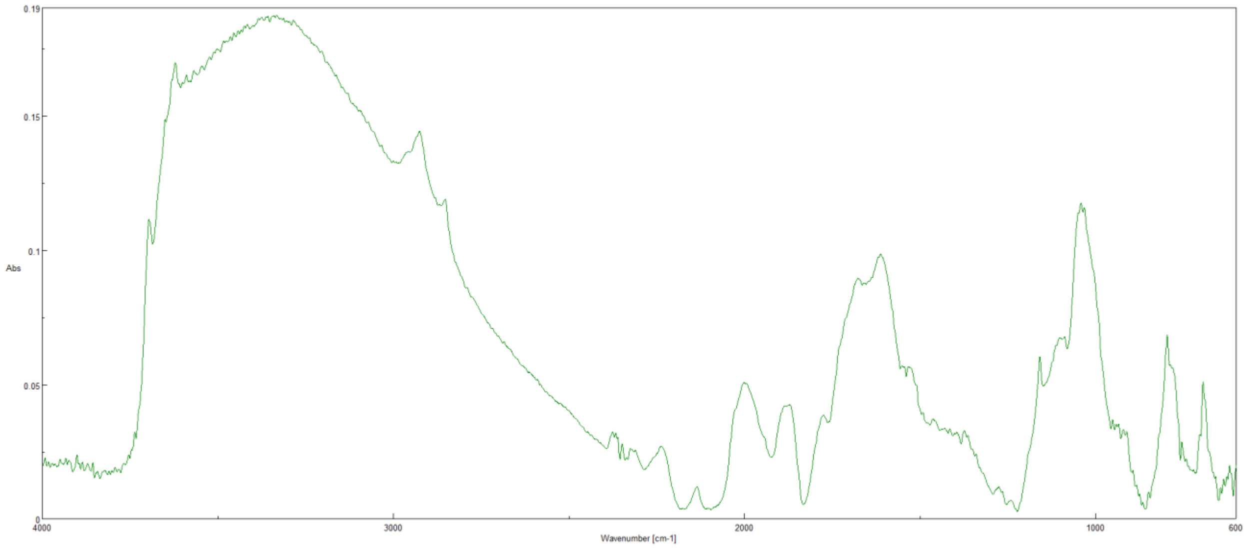
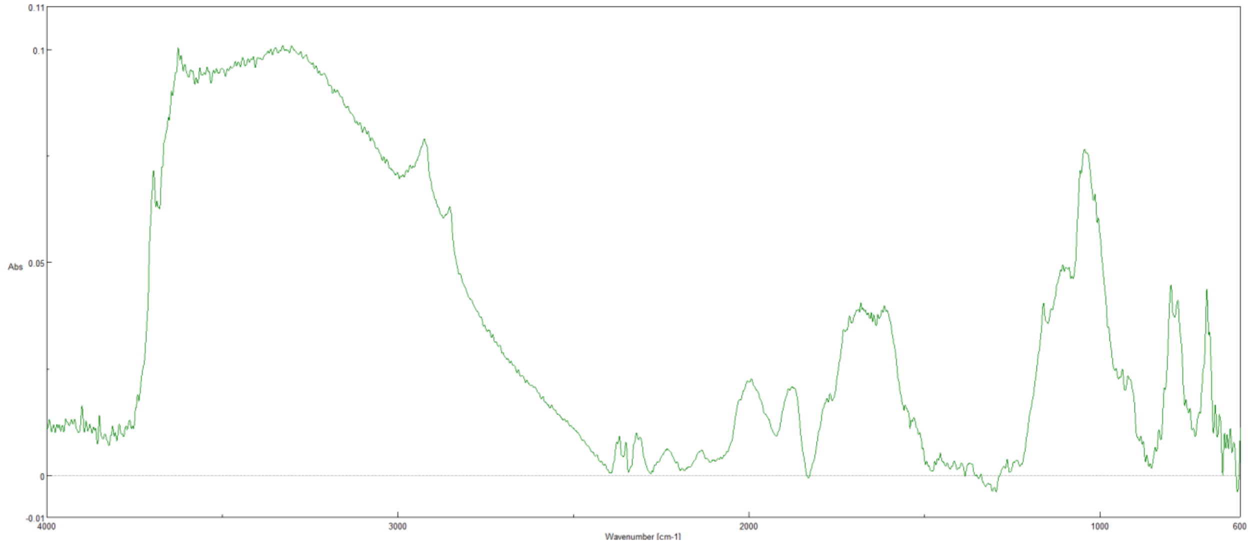


Figure 14 Temporal change in components intensity over time for Weeksbay (top) and Perdido (bottom)


0.19
0.15
0.1
0.05
0
Abs
4000
3000
2000
1000
600
Wavenumber [cm-1]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0.1
0.05
0
-0.01
Abs
4000
3000
2000
1000
600
Wavenumber [cm-1]

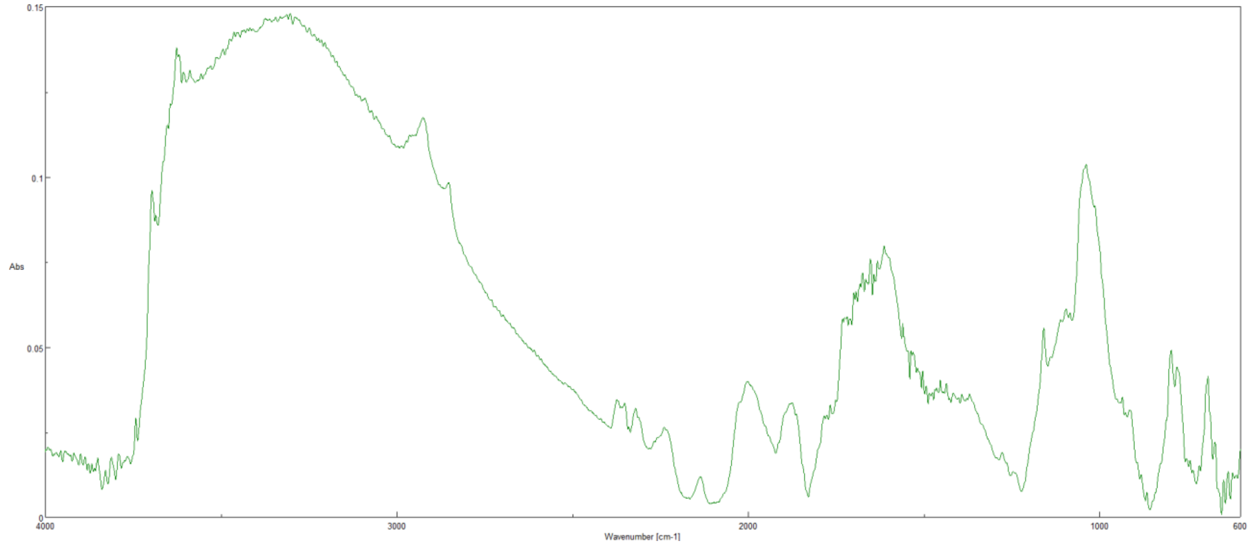
0.15
0.1
0.05
0
Abs
4000
3000
2000
1000
600
Wavenumber [cm-1]

Figure 15 Pre fire (Top), Post fire (Middle) and 1 Month Post fire (Bottom) FTIR Spectra in a Weeksbay sample.