CHARACTERIZATION OF THE IMPACT OF FIRE ON TERRESTRIAL ORGANIC CARBON AND ITS FATE IN THE ENVIRONMENT

A Dissertation

by

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ABSTRACT

Pyrogenic carbon (PyC) is a heterogeneous continuum of compounds resulting from incomplete combustion of organic matter. The understanding of PyC in the environment has mainly focused on high-temperature combustion by-products. However, the portion of this continuum produced at low temperatures, mainly during wildfire and prescribed burning events, is particularly labile and water-soluble. Therefore, low-temperature PyC is imperative to study during dynamic transport across environmental interfaces. This dissertation presents new characterization of low-temperature PyC at the interfaces of terrestrial, aquatic and atmospheric environments. I use biomarkers of biomass combustion, plant materials, and inorganic tracers to elucidate sources, composition, and degradation of PyC during transport within and between environmental reservoirs.

In large Arctic rivers, low-temperature PyC biomarkers are present in detectable concentrations during all flow regimes. PyC export occurs predominately in the dissolved phase and is an intrinsic component of the DOC pool mobilized by hydrologic events. Around half of the low-temperature PyC exported may be remineralized during transit time from fire source to river mouth, implying a labile source of PyC to these watersheds. Phase partitioning of low-temperature PyC suggests that it sorbs to particles at levels orders of magnitude higher than what equilibrium theory would predict. The higher than expected association of these soluble components with particles may help explain the recorded presence of these biomarkers in sedimentary deposits, which have helped track historical wildfire signatures in watersheds. However, as partitioning coefficients of low-temperature PyC biomarkers are lower than those reported for high-temperature PyC biomarkers, there is a higher potential for exchange with the aqueous phase and thus accessibility to microbial degradation during transport to the coastal ocean, especially during the spring freshet.

In the atmosphere, low-temperature PyC biomarkers may be more labile than previously considered, with potential abiotic degradation (such as hydroxyl radical reactions) occurring on time scales relevant to atmospheric transport (days). As this could affect the composition of PyC biomarkers at depositional sites, the assumption that they are conservative in the atmosphere must be questioned.

This dissertation quantifies PyC dynamics to help solidify flux and pool estimates and missing parameters in model assessments of carbon cycling.

DEDICATION

For all of my role models from pre-school to doctorate-

My accomplishments are yours.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Vegetation fires affect carbon cycling in the atmosphere, as well as within soils and riverine environments. These fires release 1.6-2.8 petagrams of carbon (Pg C) to the atmosphere worldwide (Santín et al. 2016), mostly as gaseous CO_2. However, environmental combustion conditions also result in a proportion of fire-affected carbon to be incompletely combusted, generating a range of carbonaceous residues, called pyrogenic carbon (PyC), which varies in molecular structure and environmental functionality. Through these incomplete combustion conditions, fires create a spectrum of chemically unique carbon species with different physicochemical characteristics than the parent material, leading to distinct degradation potential in earth systems through biotic or abiotic processes (such as photodegradation). As wildfires are increasing in all major earth systems and are projected to increase in the future (Bowman et al. 2009, Krawchuk et al. 2009), it is particularly important to quantify the pools of organic carbon altered by fires in the environment. Additionally, a holistic approach to understanding PyC dynamics will help constrain flux and pool estimates that could directly apply to missing parameters in model assessments of carbon cycling.

Understanding the entire PyC continuum has been a main challenge in PyC research, due to many differences in PyC detection methods, terminology, and little crossover between different disciplines (Masiello 2004, Santín et al. 2016, Conedera et al. 2009). Since the first PyC continuum model proposed almost 20 years ago (Hedges et al. 2000), research has focused on understanding PyC as a chemically heterogeneous pool.

Limitations and strengths for different methodology to determine PyC structure and content have been studied in reference materials (e.g. Hammes et al. (2007), Louchouarn et al. (2009)) and laboratory charcoals (e.g. Wiedemeier et al. (2015), Kuo et al. (2008a)) for all portions of the PyC continuum. However, only a handful of research has been dedicated to understanding the entire PyC continuum in environmental settings. This is primarily done by simultaneously measuring markers for different portions of the continuum in depositional records (e.g. Hanke et al. (2016), Hunsinger et al. (2008), Kuo et al. (2011b), Louchouarn et al. (2007)). Understanding the entire PyC continuum in environmental settings is a key process that needs to be addressed if we are to understand how PyC affects global carbon cycling (Santín et al. 2016).

The field of organic geochemistry often uses source selective molecules, i.e. biomarkers, to understand the presence and impact of these different sources of carbon in global carbon pools, fluxes, and cycling (Hedges and Prahl 1993). Biomarkers of PyC are as heterogeneous as the bulk materials created during combustion events, and their mean residence times in the environment vary depending on their structure and chemical functionality. These biomarkers can be used to study the importance of PyC on different reactivity time scales, and can help elucidate the role that the heterogeneous pool of PyC plays in the carbon cycle.

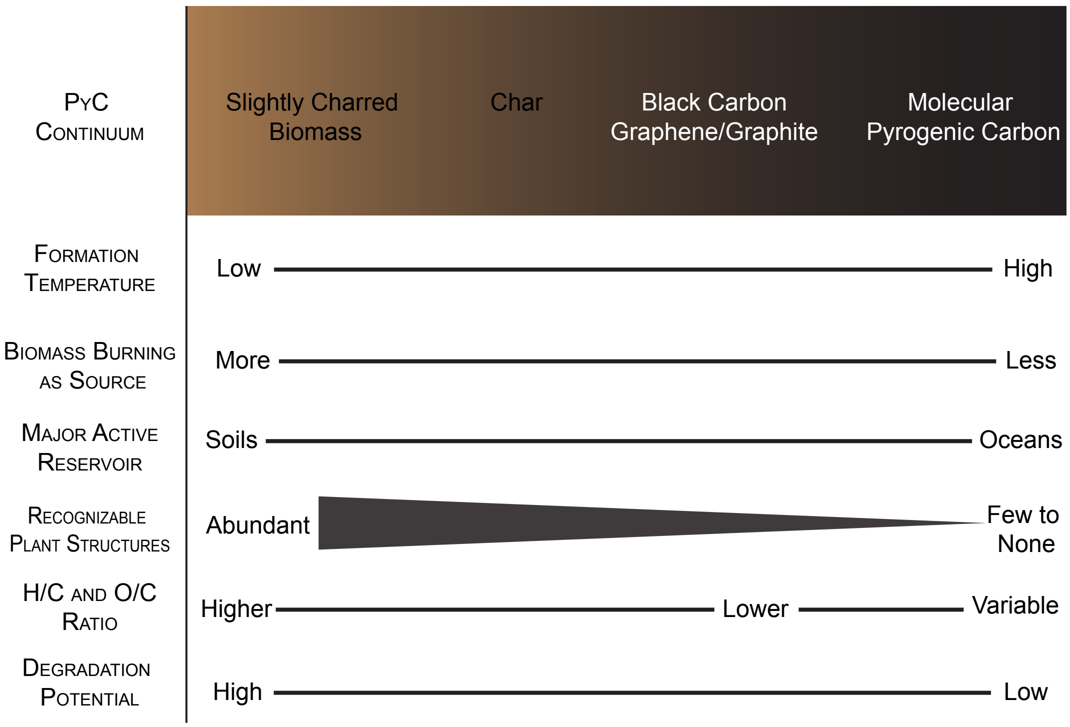

Figure 1.1: The Pyrogenic Carbon (PyC) continuum first proposed by Hedges et al. (2000). This figure is modified to include updates by Masiello (2004) and Bird et al. (2015).

1.2 Background on PyC Biomarkers

Fire events create modified pools of carbon, with structural characteristics dependent on temperature of combustion and burning efficiencies (Figure 1.1) (Masiello 2004, Harvey et al. 2012a). While black carbon aerosol emissions are an important contributor to reducing surface albedo and other positive climate forcings (Simoneit 2002), they have been recently suggested to comprise a smaller fraction of the carbon produced from biomass burning events than other combustion by-products (such as charcoals or other forms of pyrogenic carbon) (Santín et al. 2016). Therefore, these other forms of PyC, as well as transport of these constituents, must be constrained in order to develop a holistic understanding of how fires affect climatic changes.

The majority of forest fire temperatures fall within 200-600˚C (Cheng and Lehmann 2009). Crown fires, which dominate severe fire seasons in forests (Conard and Ivanova 1997), burn at such high temperatures (≥ 500˚C) that they predominantly produce the more condensed portions of PyC. These in turn have been the focus of nearly all previous quantifications in many terrestrial and aquatic systems (Preston and Schmidt 2006, Bird et al. 2015). However, many forest fires in heavily fire-affected regions burn less intensely; for example, around 80% of the area burnt in boreal forests is due to surface fires (Conard and Ivanova 1997), which burn much longer and at lower temperatures (100-400 ˚C) than necessary to create the highly condensed portions of the PyC continuum (Alexis et al. 2006, Czimczik and Masiello 2007, Masiello 2004). Additionally ground fires, such as peat fires, smolder at temperatures less than 300˚C (Usup et al. 2004).

Biomarkers of this low-temperature combustion, such as levoglucosan, have been observed in all reservoirs of all major systems, including soil organic matter (SOM) in sub-boreal forests, e.g. Otto et al. (2006), ice cores, e.g. Kawamura et al. (2012), and lake sedimentary organic matter, e.g. Kirchgeorg et al. (2014). These low-temperature PyC biomarkers are unique to source materials, and can give information about the type of material that was burnt. Levoglucosan, mannosan, and galactosan are monosaccharide combustion by-products of cellulose and hemicelluloses, and are unambiguous tracers of biomass combustion (Simoneit 2002, Kuo et al. 2008a). They are produced exclusively over a low temperature range (150-400 ˚C) (Kuo et al. 2008a), such as that experienced during surface wildfires (Figure 1.1). Free lignin methoxyphenols, which can be released by thermal degradation of the lignin macromolecule, can also be used to study terrestrial input of fires (Simoneit 2002). Diterpenoids, conifer-derived biomarkers, are derived from resin acids and can be used as a tracer specifically for coniferous combustion (Simoneit 2002). These low-temperature PyC biomarkers can be used to study the impact of PyC produced from lower temperature wildfires in a variety of ecosystems.

At intermediate temperatures (350-500ºC), these low-temperature PyC indicators, easily recognizable from parent plant macromolecules, sharply decline due to increasing proportions of aromatic structure condensation (Kuo et al. 2008a, Kuo et al. 2008b, Harvey et al. 2012b, Schneider et al. 2011, Keiluweit et al. 2010) (Figure 1.1). This can be seen with the decrease in H/C ratios and the rise in benzene polycarboxylic acids (BPCA), biomarkers of larger aromatic clusters (Schneider et al. 2011, Ziolkowski and Druffel 2010) (Figure 1.1). These intermediate temperatures are still within the range of temperatures produced during forest fires, especially crown fires (which can reach temperatures ≥ 500˚C), and therefore can also be used to study the impact of PyC on ecosystems worldwide. However, as larger condensed aromatics can also be formed through photochemical processing in environmental settings (e.g. Chen et al. (2014)), low temperature PyC markers may be the best biomarkers to unambiguously ascertain the influence of fires on carbon cycling. However, as these molecules contain higher functionality and lability than their condensed-aromatic counterparts, we must first understand their environmental reactivity and cycling on environmental timescales to assess their relative usefulness as environmental tracers of PyC.

1.3 PyC in the Environment

PyC is produced in natural environments from wildfires. Current estimates suggest a global production of 0.1-0.4 Pg C yr^{-1} of PyC, equal to 0.2-0.6% of annual terrestrial net primary production (Santín et al. 2016). Most research and attention of PyC has focused on source or sink measurements, i.e. PyC interactions in soils and PyC burial in marine sediments (Santín et al. 2016). As fires alter carbon reservoirs in terrestrial ecosystems, accelerate transfers across all reservoirs, and modify carbon residence times within them (Conard and Ivanova 1997), it is important to consider and understand PyC dynamics in intermediate reservoirs (Santín et al. 2016, Masiello and Druffel 1998, Masiello and Louchouarn 2013), such as the atmosphere and rivers. However, through estimates of PyC stocks and fluxes in and through all environments, especially intermediate reservoirs, are still scarce. These estimates will help to put PyC cycling in context for overall global carbon cycling.

1.3.1 Aerosols

Studies of PyC in the atmosphere are traditionally focused on the emissions of highly condensed, small particulates, known as soot carbon, black carbon, or elemental carbon (Bird et al. 2015), as this portion of PyC affects the radiative balance of Earth, and is especially detrimental to health and safety. Estimates of this type of aerosol carbon released worldwide are between 2-3 Tg C yr^{-1} (Table 1.1 and references therein). However, emissions of a variety of PyC components are released during fire events

(Santín et al. 2016). For example, low-temperature emissions of PyC in the form of levoglucosan is estimated to be between 1-2 Tg C yr^{-1} based on emission factors and biomass affected by fire from Andreae and Merlet (2001) and Crutzen and Andreae (1990) (Table 1.1). How other components released from biomass burning events (included in the definition of primary organic aerosols, POA), such as levoglucosan and other aerosol emissions, react in the atmosphere is important to consider in order to understand secondary organic aerosol (SOA) formation, and the effects of these emissions on air quality and their importance in global climate models (Jimenez et al. 2009). Emissions from wildfire events can affect air quality in downwind systems. For example, biomass burning from the Russian boreal forest affect air quality in the entire Arctic, contributing to the springtime aerosol concentrations double that of the "Arctic Haze", a well known wintertime build-up of organic aerosols, in the region (Warneke et al. 2010). In fact, the flux of organic carbon to the Arctic from aerosols is around 1.7 Tg yr^{-1}, which suggests that the Aeolian input of particulate organic and black carbon may be an important source of particulate carbon to the Arctic (Shevchenko and Lisitzin 2004). Atmospheric deposition is considered to be a main mechanism for PyC into its final sink, marine sedimentary deposits (Masiello and Druffel 1998, Santín et al. 2016).

1.3.2 Soils

Soils are thought to be the largest terrestrial reservoir of PyC (Bird et al. 2015), with estimates of 54- 212 Pg C as a part of the soil organic carbon (SOC) pool (Bird et al. 2015, Santín et al. 2016). The evolving idea, that PyC is not merely a recalcitrant pool of carbon created during burning conditions and buried *in-situ*, has partially come to light due to observed losses of PyC from soils over time (Bird et al. 2015). These losses can be due to remineralization within the soils, or translocation from soils. Understanding the amount of PyC that is transported from soils is understudied, and export mechanisms are thought to comprise an important flux of carbon on a global scale (Hockaday et al. 2007).

1.3.3 Rivers

Rivers export ~0.2-0.4 Pg C yr^{-1} to marine environments (Raymond and Spencer 2015). While terrestrial organic matter is the main source of carbon to rivers, this carbon pool becomes highly altered by the time it reaches the marine environment, due to both land-based and *in-situ* processing. One large source of chemically altered terrestrial carbon to enter aquatic systems is PyC. Transport through river systems is a main process thought to control PyC fluxes to marine sediments (Santín et al. 2016). Riverine PyC has been recently identified as a major component of dissolved organic carbon (DOC) in rivers worldwide (Jaffé et al. 2013). The flux of Py-DOC from rivers to the oceans has been estimated to be 25-28 Tg C yr^{-1} (Jaffé et al. 2013) (Table 1.1). The cycling of riverine pyrogenic DOC (Py-DOC) has implications for overall riverine DOC fluxes, as many of the more chemically labile components, or photo-oxidized aromatics from the PyC continuum may aid in accelerating riverine metabolisms (i.e. priming) (Masiello and Louchouarn 2013, Wagner and Jaffé 2015).

It should be noted that in some studies, fires have been suggested to decrease total amount of DOC export from fire-affected streams and rivers, particularly in Arctic environments (Kicklighter et al. 2013, Prokushkin et al. 2009). However, in Alaskan

Arctic streams, regional differences in watershed characteristics has a larger effect on DOC concentrations and bioavailability than fire (Larouche et al. 2015). In grassland streams, there are no strong correlations between DOC concentrations, Py-DOC fluxes, and fire frequency (Ding et al. 2013). Therefore, the relationship between total DOC export, Py-DOC export, and fire events need to be further examined before final conclusions on the effects of fire frequency on DOC and Py-DOC concentrations and export can be drawn.

Additionally, there is a dearth of information on the export of pyrogenic particulate organic carbon (Py-POC) from river systems (Wagner et al. 2015). As Py-POC is a precursor for PyC buried in sedimentary records, it is important to understand Py-POC fluxes from river systems. A recent estimate for Py-POC export from rivers is ~5 Tg C yr^{-1} (Santín et al. 2016) (Table 1.1), although this number is based on estimates from sedimentary PyC in river margins (Elmquist et al. 2008).

1.3.4 Oceans

Ocean sediments are considered to be the final sink for PyC (Masiello and Druffel 1998, Masiello 2004), with estimates of 480-1440 Pg PyC in marine sediments (Santín et al. 2016), while oceanic Py-DOC is a major intermediate reservoir for PyC (Ziolkowski and Druffel 2010, Coppola and Druffel 2016). Loss processes from oceanic Py-DOC may include sorption onto particulates and subsequent “rain-out” and burial into marine sediments (Coppola et al. 2014), and may account for a flux of 16 Tg C yr^{-1} (Table 1.1) (Coppola et al. 2014). It is currently unknown if low-temperature PyC components survive transit and burial in marine sediments, as current literature focuses on characterization of the more chemically recalcitrant portion of PyC in the oceans (Figure 1.1). However, as low-temperature PyC biomarkers (such as levoglucosan) have been observed in estuarine (Kuo et al. 2011b) and coastal margin (Hunsinger et al. 2008) sediments, this is certainly a portion of the PyC continuum that should be further explored in oceanic settings.

It has recently been suggested that there are two distinct pools of recalcitrant Py-DOC in the world's oceans, cycling on centennial and millennial timescales, respectively (Coppola and Druffel 2016). These pools may be sourced from different depositional regimes, such as atmospheric and riverine PyC entering the ocean, which each have unique physical properties and aromatic structures (Coppola and Druffel 2016, Ding et al. 2014b).

1.4 Importance of Low-Temperature PyC

It should be clear from the above discussion that PyC is a dynamic pool of carbon, and that our knowledge of its transportation and transformation during transport is still in its infancy. This pool of carbon is large, and is getting larger with a changing climate. Low-temperature PyC is especially important to study as it has the chemical functionality to be reactive in the environment (Masiello and Louchouarn 2013), and this reactivity may be of importance on transport timescales (Norwood et al. 2013).

To begin to understand the importance of low-temperature PyC on global-scale carbon cycling, we must first elucidate if and how this material is being transported, if the degradation of this material is relevant on transport timescales, as well as possible transport mechanisms. The objectives of this dissertation to address the issues raised above are as follows: 1) to explore the lability and contribution of low-temperature Py-DOC in rivers, 2) to investigate the relative abundances of low-temperature pyrogenic biomarkers in the dissolved and particulate phases in rivers to elucidate how this PyC is exported, 3) to understand the potential sources and fate of low-temperature PyC biomarkers in intermediate reservoirs (both riverine and atmospheric) 4) to assign revised flux estimates of PyC cycling in the environment to aid in assessing importance of PyC on global carbon cycling.

Table 1.1 Current estimates of PyC fluxes worldwide.

	Flux TgC yr^{-1}	Fluxes Derived From
Biomass as Fire Fuel	2000-5000	Crutzen and Andreae (1990)
CO_2, from fire	1812	van der Werf et al. (2010), Crutzen and Andreae (1990)
$PyC_{aerosol,BC}$ Emissions	2-3	Santín et al. (2016), Andreae and Merlet (2001)
Levoglucosan Emissions	1-2	Crutzen and Andreae (1990),Santín et al. (2016), Andreae and Merlet (2001)
Atmospheric Deposition of $PyC_{aerosol,BC}$ &	2	Jurado et al. (2008)
On-site $PyC_{charcoal}$ production	114-383	Santín et al. (2016)
Theoretical Solubilization of $PyC_{charcoal}$	3.6-17.2	Santín et al. (2016), Norwood et al. (2013), Hilscher and Knicker (2011)
Respiration of Py-DOC during riverine transport	??	??
$Py\text{-}DOC_{DBC}$ exported to Ocean	25-28	Jaffé et al. (2013)
$Py\text{-}POC_{PBC}$ exported to Ocean	5	Santín et al. (2016)
$Py\text{-}DOC_{DBC}$ in Ocean to Sediments	16	Coppola et al. (2014)

& dry deposition to oceans only

CHAPTER II

LABILE PYROGENIC DISSOLVED ORGANIC CARBON IN MAJOR SIBERIAN ARCTIC RIVERS: IMPLICATIONS FOR WILDFIRE-STREAM METABOLIC LINKAGES *

2.1 Introduction

Siberian Arctic rivers (Lena, Ob, Yenisey, and Kolyma) are estimated to contribute almost half (14.2 ± 1.1 Tg C yr^{-1}) of the 30.5 ± 5.5 Tg of carbon delivered annually to the Arctic Ocean in the form of dissolved organic carbon (DOC), and their vast watersheds are currently a net sink of CO_2 (Holmes et al. 2012, Amon et al. 2012, Raymond et al. 2007, McGuire et al. 2009). Yet, the seasonal nature of DOC fluxes, and inter-annual variability of large-scale carbon emissions from wildfires (50-230 TgC yr^{-1}) (Shvidenko et al. 2011), suggest that climatic change and environmental disturbances could alter the lateral transport of DOC to these Arctic rivers. Since changes in carbon sources and sinks affect climate forcing (Randerson et al. 2006, Soja et al. 2007), understanding the fluxes and composition of DOC in Arctic rivers is important for comprehending carbon cycling in this dynamic region. Although wildfires initially affect carbon stocks in terrestrial ecosystems, they also accelerate transfers across all reservoirs and modify carbon residence times within them (Conard and Ivanova 1997). Given that Arctic watersheds contain large carbon stocks in both permafrost regions (~350 PgC) (Tarnocai et al. 2009) and boreal forests (60-70 PgC) (McGuire et al. 2009), understanding the impact of fires on the biogeochemical cycling of carbon at the

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ecosystem level is paramount to unraveling the role of such environmental perturbations on terrestrial and aquatic ecosystem functioning. As wildfires are recognized as the most significant cause of forest loss in boreal forests (Hansen et al. 2013) and lead to significant disturbances to this region's carbon cycle (Preston and Schmidt 2006, Shvidenko et al. 2011), quantifying the input of pyrogenic DOC (Py-DOC) to Arctic rivers is necessary to better understand their impacts on climate change in high latitude ecosystems (Preston and Schmidt 2006).

Although there are now a few examples demonstrating significant fluxes of refractory Py-DOC components to streams and the coastal ocean (Dittmar et al. 2012b, Ding et al. 2014b, Ding et al. 2013, Jaffé et al. 2013, Dittmar et al. 2012a), little is known about the potential role that wildfires play in the transfer of labile, combustion-derived Py-DOC to these systems. Current estimates of total pyrogenic carbon (PyC) production in boreal forests are poor, but it has been estimated that fires devour up to one-third of net primary production in boreal forests (Preston and Schmidt 2006, Bond and Keeley 2005). With projected increased frequency and intensity of wildfires expected in boreal forests (Kasischke 1995, Running 2006, Soja et al. 2007), it becomes vital to better constrain the amount of labile and refractory carbon released to the aquatic environment. Highly condensed Py-DOC components, which are mostly biologically refractory in the environment (Masiello 2004, Dittmar et al. 2012a), have been recently shown to contribute ~10% of DOC fluxes to the world's ocean (dissolved black carbon, DBC) (Jaffé et al. 2013). However, it is unknown if inputs of the more labile portion of Py-DOC, produced at lower temperatures, contribute substantially to the total DOC pool in aquatic systems (Masiello and Louchouarn 2013). Crown fires, which dominate severe fire seasons in boreal forests (Conard and Ivanova 1997), burn at such high-temperatures (≥ 500˚C) that they predominantly produce the more condensed portions of Py-DOC previously quantified in arctic forests (Preston and Schmidt 2006). However, about 80% of the area burnt in boreal forest fires is due to surface fires (Conard and Ivanova 1997), which burn much longer and at lower temperatures (100-400 ˚C) than necessary to create the highly condensed portions of the PyC continuum (Alexis et al. 2006, Czimczik and Masiello 2007, Masiello 2004). In fact, Alexis et al. (Alexis et al. 2006, Alexis et al. 2010) suggest that the majority of combustion by-products produced from forest fires (75% of the total PyC flux to soils) have structural characteristics that are closer to slightly thermally altered organic matter ("brown carbon"), than condensed structures characteristic of high-temperature PyC. In addition, much of this PyC seems to be mobilized from the soils with very little physical mixing or storage through hydrological cycling (Czimczik and Masiello 2007). Because 2.5-15% of the charcoals produced at low to intermediate temperatures have been found to be water soluble (Norwood et al. 2011), and low-temperature PyC components decompose on timescales of days to weeks (Norwood et al. 2013), wildfires may contribute to increased carbon cycling in fire-affected ecosystems as well as increased watershed respiration rates (Masiello and Louchouarn 2013). Monitoring the sources and fate of the labile fraction of Py-DOC is therefore critical in rivers worldwide in order to understand changing watershed dynamics, under evolving fire regime conditions.

Biomarkers of low-temperature combustion have been observed in many portions of the boreal ecosystem, including soil organic matter (SOM) in sub-boreal forests (Otto et al. 2006), ice cores (Kawamura et al. 2012, Zennaro et al. 2014), and boreal aerosols (Saarnio 2010). Levoglucosan, mannosan, and galactosan are combustion by-products of cellulose and hemicelluloses, and are unambiguous tracers of biomass combustion (Simoneit 2002). They are produced exclusively over a low-temperature range (150-400 ˚C) (Kuo et al. 2008a), such as that experienced during surface wildfires. Another fire-derived biomarker, dehydroxyabietic acid, can be used as a specific tracer of coniferous combustion, as it is a by-product of thermally-altered conifer resin (Simoneit 2002). The presence of anhydrosugars and other fire-derived biomarkers in natural waters provides evidence for inputs of soluble low-temperature PyC to the aquatic environment. Here, we measure low-temperature PyC biomarkers in river water from four Arctic rivers from 2004-2006 to constrain distribution of low-temperature Py-DOC. We also measure low-temperature biomarkers in aerosols from heavily burned forests in 2012 to constrain the biomass source signatures present in river samples. Using a first-order degradation model, we then estimate the potential loss of Py-DOC from source to mouth, which correspond to the first projection of losses of low-temperature PyC within transit time along major Arctic rivers.

2.2 Materials and Methods

Arctic river samples were collected as a part of the PARTNERS Project during various flow regimes in 2004-2006 (Amon et al. 2012). The samples analyzed for this study were sub-aliquots of river water samples used by Amon et al. (2012) from high and low flow periods between 2004-2006. Briefly, samples were collected near gauging stations in each river basin. The sampling/gauging stations are as follows: Salekhard in the Ob watershed (about 1000 km upstream from Arctic Ocean), Dudinka in the Yenisey, (600 km upstream from Arctic Ocean), Zhigansk in the Lena (850 km upstream from Arctic Ocean), and Cherskiy in the Kolyma (100 km upstream from Arctic Ocean). Free lignin phenols and anhydrosugars were sequentially extracted from acidified (pH < 2.0) waters, pre-spiked with *d7*-trans-cinnamic and *d7*-levoglucosan as surrogate standards, respectively, according to Norwood et al. (2013). Briefly, free phenols were first extracted by liquid: liquid extraction into ethyl acetate. The extracted water was then saved and freeze-dried for anhydrosugar analysis. Ethyl acetate extracts were chemically dried with sodium sulfate, then dried in a LabConco solvent concentrator and re-suspended in pyridine. Previously extracted, freeze-dried waters were re-suspended in pyridine. Both free phenol and anhydrosugar extracts were then derivatized for 15 minutes using O-bis (trimethylsilyl) trifluoroacetamide containing 1% trimethylchlorosilane (9:1 BSTFA: TMCS) at 75˚C and immediately analyzed on a Varian triple quadrupole 480-300 GC-MS system using a fused silica column (J&W DB-5MS, 30m x 0.25mm i.d., 0.25µm film thickness; Agilent Technologies, Santa Clara, CA, USA). Each sample was injected splitless using helium as a carrier gas. Free phenol and levoglucosan analyses were performed independently under single ion monitoring (SIM) mode, and using specific ions for compound determination. The MS was operated in electron ionization (EI) mode with the detector held at 1200 V or varied in Extended Dynamic Range (EDR). Dehydroxyabietic acid concentrations were determined by relative ratios to internal standards in full scanning mode.

Atmospheric samples were collected on filters as a part of the ZOTTO Project in the Western Siberian Lowlands, on a tower located at 60˚47’55” N, 89˚21’12” E, about 20 km west of the Yenisey river, during a large wildfire event in the summer of 2012. GFF filters, with a nominal pore size of 0.45 μm, were placed on the 300 m tall long-term tower. Filters were removed as they became saturated, with a sampling flow rate of ~ 40 L min^{-1} (Heintzenberg et al. 2008). Combustion biomarkers were extracted from the GFF filters according to Shakya et al. (2011) and Louchouarn et al. (2009) with slight modification. Briefly, aerosol samples were extracted via solvent extraction using 9:1 dichloromethane: methanol using an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA, USA) at 1500 PSI and 100˚C. Samples were then concentrated in a RapidVap at 50˚C, then dried completely in a LabConco solvent concentrator (LabConco, Kansas City, MO, USA) and re-suspended in pyridine. The same internal standards and GC-MS methods were used to determine free-phenols and anhydrosugars in these samples as in the river samples.

Low-temperature pyrogenic DOC (Py-DOC) concentrations were determined using experimental degradation rates derived from incubation of water soluble organic matter produced from laboratory charcoals (Norwood et al. 2013). In river waters, levoglucosan degrades at a rate of 0.09-0.15 day^{-1} and low-temperature Py-DOC degrades at a rate of 0.2 day^{-1} (Norwood et al. 2013). Measured levoglucosan concentrations, and the ratio of levoglucosan to Py-DOC in combustion end-members (the ratio at 250˚C represents the maximum ratio between 150-350˚C for most plant types, following a normal distribution) (Kuo et al. 2008a, Norwood et al. 2013) can be applied as a simple model to estimate the upper range of low-temperature Py-DOC potentially present in Arctic rivers at our sampling sites, Py-DOC$_t$ (Table 2.2). Sample locations and total river lengths were derived from Amon et al. (2012). The ranges of fire locations in each watershed were estimated by MODIS/Terra (Giglio et al. 2006) and AVHRR/NOAA (Sukhinin et al. 2004) satellite imagery (Figure 2.1b, Table 2.1). These locations were determined from the highest frequency of fires from the years 2003-2006, using the heaviest fire years (2003 and 2006) to determine extent of the range of concentrated fire location. The length the river traveled between these fire locations was determined via fire map location overlay onto Google Earth imaging. Based upon these projections, the amount of low-temperature Py-DOC$_t$ was determined, taking in account potential degradation between fire sources and sampling site assuming fresh input at fire sources. This degradation factor was calculated using the transit time derived from high riverine velocity of 1.5 m s^{-1} (Holmes et al. 2012) and the calculated ratio of levoglucosan to Py-DOC at this transit time based on degradation in a 250˚C charcoal (Norwood et al. 2013). To estimate the original input of Py-DOC from the southern fire regions, Py-DOC$_o$, the calculated concentrations of Py-DOC at the source of the fires for each river accounting for potential degradation, the following first-order kinetic degradation model was used to solve for Py-DOC_o:

$$\mathbf{Py\text{-}DOC_t = Py\text{-}DOC_o e^{-kt}} \qquad \mathbf{(2.1)}$$

where Py-DOC_t is the median Py-DOC_t calculated from above range at the sampling site, Py-DOC_o is the initial concentration, k is the degradation constant from Norwood et al. (2013) and t is the average transit time from fire sources to sampling site (Holmes et al. 2012) (Table 2.2). Py-DOC_m, the calculated Py-DOC concentrations at the mouth of the river, is calculated using the same first-order model, substituting Py-DOC_m for $\text{Py-DOC}_{t,}$ Py-DOC_t for $\text{Py-DOC}_{o,}$ and transit times from sample sites to the river mouths based upon river velocities from Holmes et al. (2012) and sample locations from Amon et al. (2012) (Table 2.2). Percentage lost was calculated from the estimated material left at the different stages (sample location, river mouth) subtracted from estimated Py-DOC_o (100%).

2.3 Results and Discussion

2.3.1 Fire Activity

Within our study area, geographic reconstructions using satellite imagery of forest fires from 2003-2006 shows that the majority of forest fires occurred in the central and southern reaches of the watersheds, between the 50° and 55° N parallels, in predominately forested regions, regardless of the overall yearly burn areas (Figure 2.1b, Table 2.1). Of this burnt region, about half of fire fuel is spatially characterized as deciduous needle-leaf forests (Figure 2.1, Table 2.1). Deciduous needle-leaf forests, which are comprised predominantly of deciduous gymnosperms, the larch species (*Larix* *spp.*), are most abundant in the central and southern reaches of all arctic watersheds, with their distribution and abundance increasing across the watersheds in the eastward direction (Figure 2.1a). The majority of deciduous needle-leaf forests burn as surface fires, and they burn more frequently in the central and southern portions of these watersheds (Kharuk et al. 2011, Kharuk et al. 2013, Soja et al. 2006, Czimczik et al. 2003). Angiosperm dwarf shrub and carbohydrate-rich mosses tend to prevail in tundra and northern taiga ecosystems, while evergreen and conifer forests are more abundant in the most southern portions of the basins (Figure 2.1a). Therefore, the majority of forest fire fuel for these watersheds appears, based on satellite data, to be southern gymnosperm forests.

Although high-temperature Py-DOC components have not been well correlated to fire history (Ding et al. 2013), little is known about the immediate effects of fires and fire frequency on the export of PyC to aquatic systems. In boreal regions, there are two main seasonal occurrences of fires, late summer fires and spring fires (Shvidenko et al. 2011). Given these differences in fire regimes, one might expect a dynamic flux of surface PyC to aquatic systems dependent on fire severity during the spring and late summer fires, timed with the yearly spring freshet high flow period. In fact, increases in export of high-temperature Py-DOC components have been linked to peak flow in large tropical river systems (Dittmar et al. 2012a), suggesting that this dynamic release of Py-DOC does occur for a portion of the spectrum on long time scales. Due to scarcity of high-resolution time series data in Siberian watersheds, this rapid cycling and intra-annual variability needs to be further investigated in Arctic environments and for low-temperature Py-DOC.

2.3.2 Fire Biomarkers and Sources

Isomer ratio signatures of anhydrosugars (e.g. levoglucosan to mannosan: L/M) combined with those from free lignin methoxyphenol monomers (e.g. syringyl to vanillyl: S/V) distinguish source materials at the clade level of combustion materials (Kuo et al. 2011a, Louchouarn et al. 2009), and therefore can help to identify fire fuel sources within each watershed (Figure 2.2). To better constrain source endmember signatures, recent atmospheric samples were collected from smoke plumes, originating from crown fires within conifer forests and surface fires in conifer and mixed forests, during major fire events in 2012 in the south-central portion of the Yenisey watershed (60˚47’55” N, 89˚21’12”E). Levoglucosan emissions from crown fires (1.97 ± 1.13 µg m^{-3}) were in the same range as those reported for a Montana gymnosperm wildfire in 2003 (Ward et al. 2006). The presence of levoglucosan in the crown fires first confirms that these fires produce fractions from the entire PyC continuum, including low-temperature components, and therefore, validates using low-temperature PyC biomarkers as tracers of biomass combustion from all types of wildfires. Emissions from surface fires, which may contain volatilized burnt soil organic matter (OM), show levoglucosan concentrations (14.40 ± 9.75 µg m^{-3}) that are among the highest ever reported for forest wildfires (Lee et al. 2008, Pio et al. 2008, Saarnio 2010, Ward et al. 2006). This may be related to the lower temperature of combustion in surface fires and/or the fuel type in soil OM layers which is proportionally richer in cellulose/hemicellulose (mosses and litter) than the woody biomass that burns during crown fires. In addition, the ratios of free lignin monomers and anhydrosugars in all of these aerosols point to a pure softwood end-member (S/V of 0.34 ± 0.09 and L/M of 4.04 ± 0.42; Figure 2.2), consistent with gymnosperm source signatures reported in charcoal end members (Kuo et al. 2011a) and atmospheric aerosols from the referenced Montana gymnosperm wildfire in 2003 (S/V of 0.19 ± 0.08 and L/M of 5.08 ± 0.28) (Ward et al. 2006).

The source signature ratios of riverine samples indicate that, in spite of representing only a fraction of the watersheds, boreal forest fires occurring in the southern reaches of these arctic watersheds are the predominant source of PyC to these major Arctic rivers (Figure 2.2). Source signatures show a strong gymnosperm input at our sampling sites, which are located 2000-4000 kilometers downstream of the main gymnosperm forests affected by wildfires (Figure 2.1). The polymeric lignin phenols in the same samples, previously analyzed and reported by Amon et al. (2012), also point to gymnosperm vegetation as the predominant input of total DOC to the Arctic rivers. In addition to these biomarkers, our river samples contain detectable quantities of dehydroxyabietic acid, produced exclusively from the thermal alteration of gymnosperm resin (Simoneit 2002).

Table 2.1: Annual fire area by year (in 10^3 km) from 2003-2006, ordered by watershed size. The largest total proportion of each watershed burnt in 2003. Burnt vegetation area by watershed is classified by land-cover classes using GLC2000 (Bartalev et al. 2003). The largest area burnt of the forest biome is deciduous needleleaf forest, which is the largest area burnt proportionally of any biome. Although grass and cropland account for a much larger area burnt overall, the majority of area is due to the Ob's urbanization, which contains a much higher proportion of cropland than any of the other watersheds.

		Annual fire area, 10^3 km^2					Burnt vegetation (2003-2006), 10^3 km^2						
							Forests						
River name	Watershed area, 10^3 km^2	2003	2004	2005	2006	Total (2003-2006)	Evergreen needleleaf	Deciduous broadleaf	Deciduous needleleaf	Mixed	Tundra	Grass-/croplands and steppe	Shrubs
Ob	2914	19.2	45.4	40.9	69.2	174.7	10.4	21.9	0.7	5.5	0.3	118.9	0.3
Yenisey	2763	53.5	8.9	20.3	37.4	120.1	22.3	9.3	36.5	15.2	0.9	23.5	1.0
Lena	2623	50.7	2.9	17.5	27.3	98.3	11.7	0.7	59.9	4.6	1.9	10.3	1.9
Kolyma	653	7.2	0.0	0.1	0.1	7.4	0.0	0.0	4.9	0.0	0.8	0.0	0.7
Total	8954	130.6	57.2	78.8	134	400.5	44.4	31.9	102	25.3	3.9	152.7	3.9

Table 2.2: Py-DOC loss estimates during riverine transport. Pyrogenic DOC (Py-DOC) input and loss estimates for each river for the sampling years 2004-2006. Py-DOCt (mg L^{-1}) represents the Py-DOC concentration at our sampling sites determined by the ratios of levoglucosan to Py-DOC concentrations in solutions during degradation experiments (Norwood et al. 2013). The transit time from fire location to sampling site was used to select the appropriate levoglucosan/Py-DOC ratio (see Methods section for further information). Py-DOC_o (mg L^{-1}) represents the concentration at the fire source determined by back-calculations and using first-order degradation rates of measured levoglucosan and estimated Py-DOC concentrations at the sampling site (degradation rates determined by Norwood et al. (2013) and further explained in the Methods section). Py-DOCm (mg L^{-1}) are estimates of Py-DOC concentrations at each river mouth based upon first order degradation of Py-DOC and transit time from sampling sites to river mouths (Norwood et al. 2013) and Py-DOC_t estimates. Rivers are ordered by their length in kilometers (Amon et al. 2012).

River	River Length (km)	Measured Levoglucosan Average 2004-2006 (µg L^{-1})	Py-DOC_o (mg L^{-1})	Py-DOC_t (mg L^{-1})	Percent Loss from Fire Source to Sample Site (%)	Py-DOC_m (mg L^{-1})	Percent Loss from Fire Source to River Mouth (%)
Yenisey	4803	0.8 ± 0.5	0.5 ± 0.3	0.3 ± 0.2	40	0.3 ± 0.2	49
Lena	4387	0.7 ± 0.4	0.4 ± 0.3	0.3 ± 0.2	39	0.2 ± 0.1	51
Ob	3977	0.8 ± 0.4	0.4 ± 0.2	0.2 ± 0.1	48	0.2 ± 0.1	62
Kolyma	2091	0.6 ± 0.4	0.1 ± 0.1	0.1 ± 0.1	19	0.1 ± 0.1	21
Average	3814.5	0.7 ± 0.4	0.4 ± 0.3	0.2 ± 0.2	37 ± 10	0.2 ± 0.1	47 ± 15

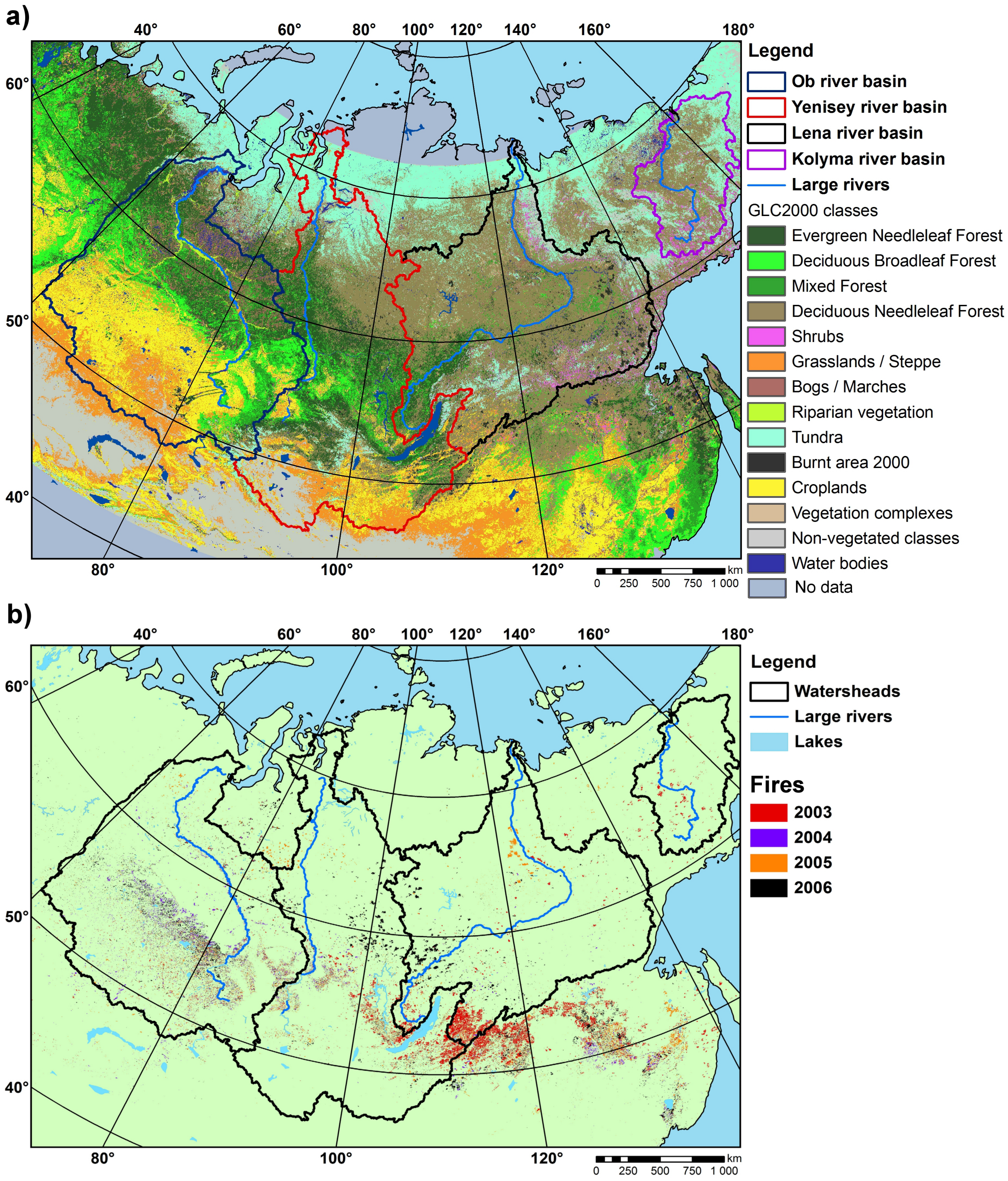


Figure 2.1: Spatial distribution of a) vegetation types using GLC2000 (Bartalev et al. 2003) and b) fire locations by year using AVHRR and MODIS (Sukhinin et al. 2004, Giglio et al. 2006) occurring in the major Siberian watersheds for the years 2003-2006.

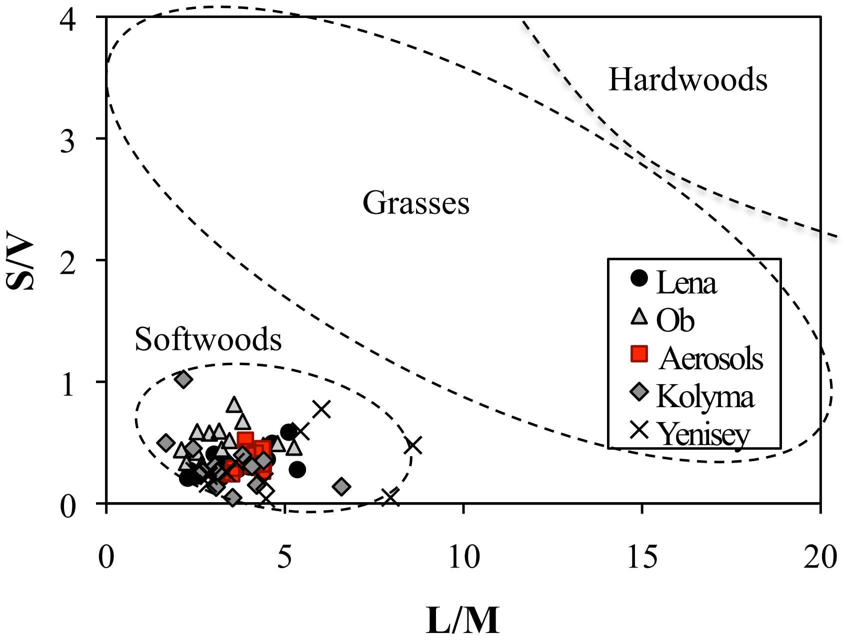


Figure 2.2: Ratios of syringyl to vanillyl (S/V) and levoglucosan to mannosan (L/M) for river samples and aerosols (in red). All river and aerosols samples show characteristic softwood signatures.

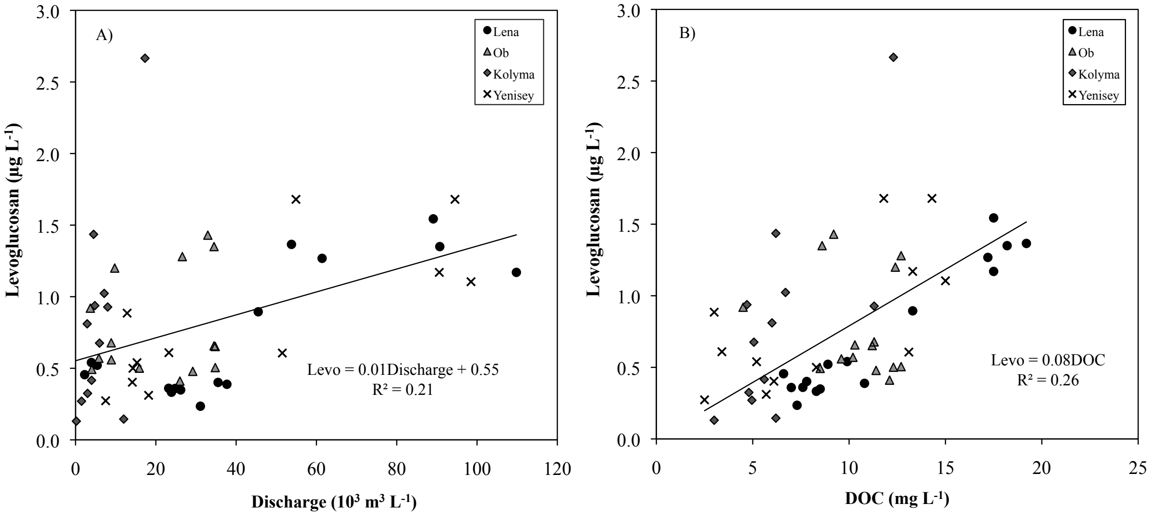


Figure 2.3: a) Relationship between levoglucosan and DOC concentrations and b) between levoglucosan and discharge. Watershed variability can be attributed to differences in export due to different hydrodynamics.

The presence of multiple independent biomarkers of gymnosperm combustion confirms that these forest ecosystems are the main source of low-temperature Py-DOC to these Arctic rivers. However, the majority of burnt material in the Ob watershed is characterized spatially as grassland and croplands (Table 2.1), but does not contain a significantly different biomarker signal of transported Py-DOC than the other watersheds. Therefore, an alternative explanation for the uniform signature observed across watersheds may include the selective preservation of gymnosperm material in the Py-DOC pool (i.e. (Smith et al. 2013)). The role of source vs. selective degradation on Py-DOC signature thus needs to be further constrained before a final conclusion on source inputs can be drawn.

2.3.3 Potential Loss of Py-DOC During Riverine Transit

The rivers in this study confirm a connection between watershed dynamics and PyC transport throughout riverine systems (Czimczik and Masiello 2007, Jaffé et al. 2013, Ding et al. 2013). Levoglucosan concentrations peak during maximum river discharge events demonstrating that peak export of Py-DOC is related to peak stream flow, similarly to peak DOC export (Amon et al. 2012). The concentration of levoglucosan in these rivers varies according to streamflow and watershed type, consistent with variations in polymeric lignin phenol concentrations (Amon et al. 2012). Levoglucosan concentrations averaged 0.73 ± 0.42 $\mu g\ L^{-1}$ for all rivers throughout the study, and are significantly correlated to DOC with watershed level differences, most likely due to differences in basin hydrology and sampling year (Figure 2.3).

Py-DOC is strongly correlated to discharge in all watersheds (combined $r^2= 0.62$), suggesting that fire-altered carbon is an intrinsic component of the DOC pool mobilized by hydrologic events (Figure 2.4). This is consistent with recent studies (Ding et al. 2013, Ding et al. 2014a) reporting that in fire impacted watersheds recent fire history was found to be less important in controlling the black carbon and black nitrogen dynamics than the environmental drivers that control DOC dynamics, suggesting coupled soil-to-water translocation mechanisms and/or a physicochemical association between DOC and Py-DOM.

2.3.4 Watershed Dynamics of Py-DOC

Given that the half-life of low-temperature Py-DOC in river water ranges from 30-40 days (Norwood et al. 2013), which is the mean transit time of the Arctic rivers, we can anticipate that a significant portion of Py-DOC must be lost during transport to the Arctic Ocean. Based upon our calculations, the median of our low-temperature Py-DOC estimates was 2.5% of the DOC pool (± 0.4 % on a 95% confidence interval, n=55, $p < 0.05$) for all rivers studied at our sampling sites. Assuming that ~10% of the total DOC is recalcitrant DBC (Jaffé et al. 2013, Ding et al. 2014b), then up to ~13% of the total DOC entering Arctic rivers may be of pyrogenic origin.

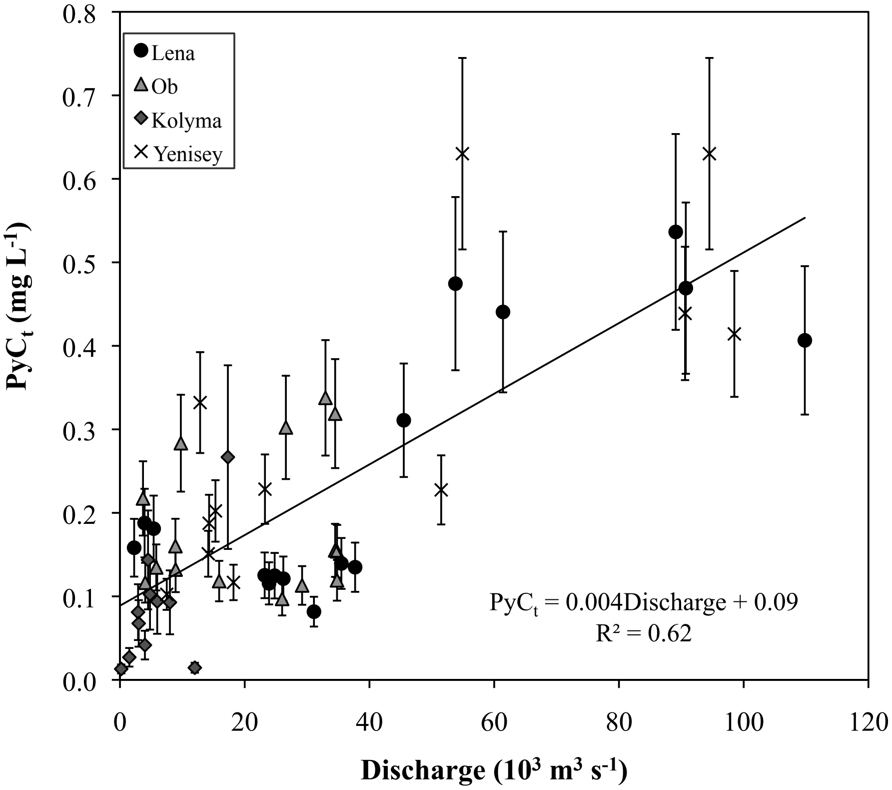


Figure 2.4: Relationship between Py-DOC and river discharge at our sampling sites. Errors determined based on maximum and minimum transit time from fire region in each watershed (see discussion in text for explanation). Py-DOC is well correlated to discharge for all rivers.

The quality and concentration of Py-DOC supplied to the Arctic Ocean from each river feasibly depends on the overall hydrodynamics of each system, similarly to bulk DOC (Amon et al. 2012). River-scale differences are more pronounced in the measured levoglucosan concentrations (Figure 2.3a and b), whereas PyC$_t$ calculations “normalize” watershed processes through the integration of transit time degradation within each river (Norwood et al. 2013) (Figure 2.5, Table 2.2). The estimated loss of 47.1 ± 14.9 % of the Py-DOC during transit time from fire source to river mouth in these watersheds (Table

2.2), suggests that PyC is a more dynamic and reactive pool of carbon added to aquatic systems than originally thought.

Of the low-temperature Py-DOC inputs at upstream fire sites, only 53 ± 15% actually enters the Arctic Ocean, corresponding to 0.35 ± 0.02 Tg Py-DOC yr^{-1}. Although this flux represents only 4.5-6% of the total annual estimated production of PyC from Siberian boreal forests (5.1-7.1 Tg PyC yr^{-1}, using the same methodology as Preston and Schmidt (2006) based on PyC/CO_2 ratios of 5-7%, and using CO_2 emissions and annual areal extent of fires in the region from Shvidenko et al. (2011)), it may nevertheless have a significant influence on DOC cycling in these rivers. For example, if the presence of Py-DOC accelerates the re-mineralization of bulk DOC through a process of 'priming' (accelerated loss of bulk DOC due to increased metabolism stimulated by labile Py-DOC) during riverine transport, then it is important to better constrain its fluxes if we are to understand the influence of wildfires on additional CO_2 releases from aquatic systems. If the Py-DOC degraded during riverine transit is respired into CO_2, the additional flux of CO_2 from the Eurasian basin could be 0.2 ± 0.01 Tg C yr^{-1}, which represents 3-4 % of estimated PyC production in this region (Preston and Schmidt 2006, Shvidenko et al. 2011). The total labile Py-DOC pool, 0.56 ± 0.02 Tg C yr^{-1}, corresponds to roughly 0.5% of the total combustion by-products (gaseous and particulate) estimated from forest fire production in the area (121 Tg C yr^{-1} over the period 1998-2010) (Shvidenko et al. 2011). This is consistent with the component of fire emissions from such regional fires, classified as organic carbon and elemental carbon (1.3% combined) (Shvidenko et al. 2011).

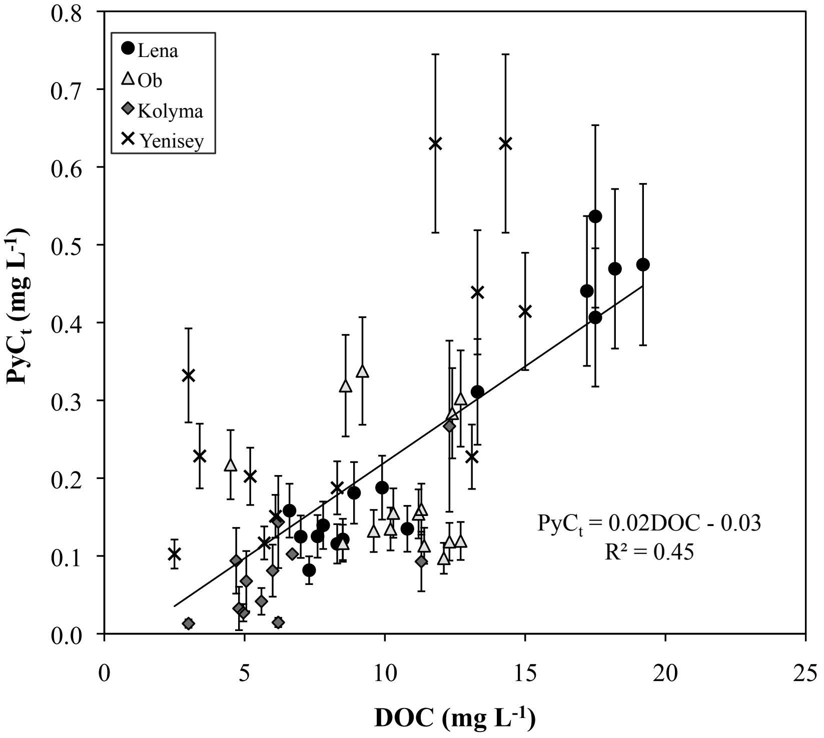


Figure 2.5: Relationship between estimated Py-DOC and DOC at the sampling sites. Errors determined based on maximum and minimum transit time from fire region in each watershed (see discussion for explanation). Most likely, river scale differences in inputs of PyC and DOC affect the relationships of PyC$_t$ and DOC between rivers.

Our data confirm the ubiquitous nature of dissolved PyC on seasonal and geographical scales in global rivers (Jaffé et al. 2013), and also establish that fire-derived material contains multiple carbon pools of various reactivities, as proposed by Masiello and Louchouarn (2013). The dynamics of total DOC within Arctic rivers are complex, with labile components degradable on timescales of riverine transport (Amon et al. 2012). The presence of dissolved PyC may add to this complexity, with its transformations during transit time from fire source to river mouth potentially priming (accelerating bulk organic carbon degradation) more refractory DOC constituents (Masiello and Louchouarn 2013), increasing overall riverine respiration rates. To understand the fate of PyC, we need to better characterize its heterogeneous nature and what types of residues/constituents cycle through different environmental reservoirs (soils, ground and surface waters, atmosphere). With recent advancements to quantify Py-DOC, the gap in our knowledge of the flux of PyC from soils into the DOC pool has begun to be addressed worldwide. However, with increased frequency and intensity of forest fires expected in future years, research to quantify the fate of combustion-derived organic matter on geographical and temporal scales is necessary in order to better understand carbon cycling in fire-impacted watersheds.

CHAPTER III

ENVIRONMENTAL PARTITIONING OF LEVOGLUCOSAN IN TWO HIGH-LATITUDE RIVERS ACROSS THE SPRING FRESHET HYDROGRAPH

3.1 Introduction

Wildfires are an important source of pyrogenic carbon (PyC) to Arctic environments (Hansen et al. 2013, Preston and Schmidt 2006, Santín et al. 2015). PyC formation and resulting chemical structures are temperature dependent, resulting in a continuum of materials produced during wildfire events (Masiello 2004). The continuum of PyC is marked by the sequential changes in the proportion of chemical markers of combustion by-products, and increased aromatic condensation level (decreasing the ratio of Hydrogen to Carbon; H/C ratios) in PyC along temperature gradients (0-1000˚C) (Kuo et al. 2008a, Kuo et al. 2008b, 2011a, Keiluweit et al. 2010) (Figure 3.1). At low-temperatures (150-300˚C), macropolymer dehydration and fragmentation leads to the release of free monomers and oligomers rich in –OH and –COOH functionalities (Kuo et al. 2008a, Kuo et al. 2008b, 2011a, Keiluweit et al. 2010, Harvey et al. 2012b, Norwood et al. 2013). At these temperatures, the formation of anhydrosugars (levoglucosan and isomers) is prevalent (Kuo et al. 2008a) (Figure 3.1). At intermediate temperatures (350-500˚C), the rapid disappearance of recognizable plant lignocellulosic macromolecules, and the decrease of levoglucosan yields before 400˚C (Kuo et al. 2008a, Kuo et al. 2011a), occurs synchronously with a steep increase in the proportion of amorphous aromatic structures (Keiluweit et al. 2010, Schneider et al. 2011, Harvey et al. 2012b) as noted by the rapid decrease in H/C ratios and the rise in benzene polycarboxylic acids

(BPCA), selective molecular markers of aromatic clusters (Schneider et al. 2011, Ziolkowski and Druffel 2010) (Figure 3.1). The highest temperature portion of the PyC continuum is characterized by increasing graphene-like structures in highly condensed turbostratic aromatics, marked by the increase in condensation levels of molecular markers such as BPCAs (Schneider et al. 2010, Keiluweit et al. 2010). This PyC-derived turbostratic carbon is relatively unordered (Nguyen et al. 2010) and is therefore structurally different than graphite found in natural environments of high temperature and pressure (such as within metamorphic rock), which is likely more ordered and highly crystalline in nature (Brandes et al. 2008). High-temperature PyC can also be formed from the condensation of gas-phase intermediates (i.e. soot carbon) (Hammes et al. 2007, Schmidt and Noack 2000). As the lability of organic matter is decreased along the PyC continuum (Ascough et al. 2011), the potential for reactivity in the environment is decreased with higher combustion temperatures (Masiello 2004).

Given the high potential for biological degradation of levoglucosan and other low-temperature PyC on environmentally relevant time scales (Norwood et al. 2013), one might expect that low-temperature PyC produced in the environment is quickly degraded *in-situ*. The fact that levoglucosan is observed in depositional environments 100's-1000's of years old could be attributed to mineral associations (Kuo et al. 2008a), or association of low-temperature PyC with higher temperature, more recalcitrant components, as a wide range of combustion conditions are present in environmental settings, resulting in heterogeneous PyC byproducts (Knicker 2007, McBeath et al. 2013). Observations of levoglucosan in the sedimentary record raises it as a potential candidate for a proxy of PyC in the environment (Elias et al. 2001, Conedera et al. 2009, Kuo et al. 2011b), as it is an unambiguous biomarker of cellulose burning (Simoneit 2002, Kuo et al. 2008a), and is relatively easy to measure in the laboratory (e.g. Louchouarn et al. (2009), Hopmans et al. (2013)). However, before assessing it as a proxy for PyC storage in the long-term carbon pool, we must first understand the transportation, transformation and export characteristics of levoglucosan and how it relates to the entire PyC continuum. Here, using levoglucosan as a proxy for low-temperature PyC, we assess the relative importance of dissolved versus particulate PyC export from high-latitude river systems.

Recent studies have documented the transfer of PyC to river systems in the dissolved and particulate phases, originating from all portions of the PyC continuum, from highly resistant PyC to more soluble, labile components (Jaffé et al. 2013, Myers-Pigg et al. 2015, Dittmar et al. 2012a, Wagner et al. 2015). Understanding the transfer of PyC to aquatic systems is especially pertinent for Arctic regions, given the projected increase in frequency and intensity of boreal forest fires (Kasischke 1995, Running 2006, Soja et al. 2007) and a larger proportion of PyC created in these environments (Santín et al. 2015). The phase in which these materials are mobilized throughout the environment has implications on its availability for *in-situ* degradation/transformation, and ability for PyC to be stored in the long-term carbon pool (Czimczik and Masiello 2007, Santín et al. 2016). For example, PyC in dissolved phase can be quickly remineralized (Myers-Pigg et al. 2015, Ward et al. 2014, Stubbins et al. 2012), while PyC in the particulate phase may be buried in intermediate carbon pools along transport (such as river sediments) or on continental margins (Hunsinger et al. 2008, Cotrufo et al. 2016b). A few studies have shown that biomarkers of low-temperature biomass combustion by-products (levoglucosan and isomers) can be found in sedimentary and soil records 100's-1000's of years old and help trace fire events induced by climate cyclicity and/or anthropogenic activities (Elias et al. 2001, Kirchgeorg et al. 2014, Hunsinger et al. 2008, Kuo et al. 2011b, Gao et al. 2016). However, chemical functionality of low-temperature PyC should favor mobilization and transport in the aqueous phase and therefore, preservation of low-temperature PyC and deposition into sedimentary records may be a function of sorption disequilibrium within the environment.

Two-phase partitioning models are often used environmental organic chemistry to understand the distribution of organic molecules in the environment, usually in the context of environmental contaminant fate. The distribution coefficient, or partition coefficient (K_d), is a parameter of phase distribution/partitioning of a constituent throughout environmental transport between two phases. This phase distribution is particularly important to understand in aquatic systems, as the carrier phase of the constituent has implications for *in-situ* degradation and deposition. Here, we determine particulate-dissolved phase distribution of molecular markers of PyC within river waters by calculating distribution coefficients observed in the environment. Distribution coefficients are often used in laboratory or environmental settings to understand the sorption of organic pollutants to particulate matter (e.g. planar hydrophobic contaminants such as polychlorinated biphenyls- PBCs- e.g. Lohmann et al. (2005), Cornelissen et al. (2008)) and their subsequent fate in environmental settings (especially with relation to understanding remediation practices- e.g. Burgess et al. (2013), Oen et al. (2012)). Here, we present the first study to our knowledge that analyzes the distribution of low-temperature PyC, using levoglucosan as a biomarker proxy, in two high-latitude systems: a small sub-Arctic Canadian River, the Great Whale River, in northern Québec, and the largest Arctic River, the Yenisei River, in north-central Siberia. We consider the environmental partitioning of levoglucosan throughout various flow regimes, to discover the evolution and relative importance of low temperature PyC in these high-latitude systems.

3.2 Materials and Methods

For each river, we collected particulate and dissolved organic matter across the spring freshet period. Approximately 100L of river water, was pre-filtered for gross particulates (64µm) in the field and transported to a field laboratory station in either in the village of Whapmagoostui-Kuujjuarapik for the Great Whale River (2012), or Igarka for the Yenisei River (2014), and immediately filtered using tangential flow filtration (TFF, 0.45µm filter size) to separate the particulate and dissolved/colloidal phases. The particulate portion, ≥ 0.45µm, was concentrated and frozen, then transported to the EcoLab laboratory in Toulouse, France, for further analysis. The dissolved portion, < 0.45µm, was isolated using a portable reverse osmosis system (Serkiz and Perdue 1990), and the concentrate was also frozen and transported to the EcoLab laboratory in Toulouse, France, for further analysis. The samples were all freeze-dried in Toulouse, France, and analyzed for carbon stable isotopes ($\delta^{13}C$) on an IR-MS before sub-samples were transported to Texas A&M University Galveston Campus for further analysis.

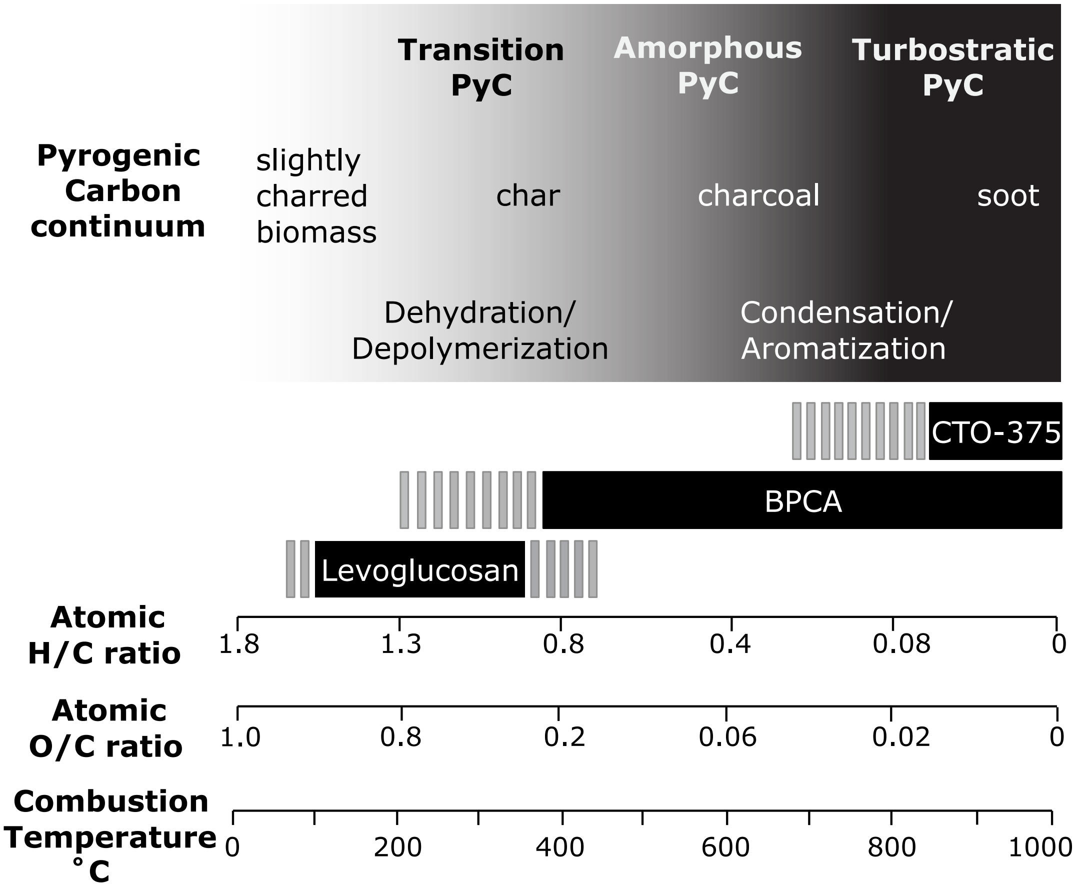


Figure 3.1: Updated pyrogenic carbon continuum inspired by Masiello (2004), including modifications inspired by Kuo et al. (2008a) and Hammes et al. (2007). This figure includes changes in the proportion of chemical markers of combustion by-products and the increased aromatic condensation level observed in biomass chars along a heat treatment temperature (HTT) gradient (0-1000˚C) (Keiluweit et al. 2010, Harvey et al. 2012b). Decreasing H/C ratios and O/C ratios along the HTT are synthesized from Kuo et al. (2008a), Schneider et al. (2011), Keiluweit et al. (2010). Note that these vary dependent on feedstock and the scales on this figure are non-linear. Biomarker ranges derived from a variety of sources: benzene polycarboxylic acids (BPCA) from Schneider et al. (2011), Schneider et al. (2010), levoglucosan range from Kuo et al. (2008a) and upper limit uncertainty from Lakshmanan et al. (1970), Chemo-thermal oxidation (CTO-375) range from Kuo et al. (2008a).

Percent OC (% OC) was determined on vapor-phase acidified freeze-dried sub-samples (to remove carbonates) on a Costech Elemental Analyzer. Freeze-dried samples were then analyzed for fire-derived biomarkers, monomeric lignin phenols and anhydrosugars, following methods outlined in Louchouarn et al. (2009), (Shakya et al. 2011), and Myers-Pigg et al. (2015). Briefly, biomarkers were extracted from freeze-dried materials pre-spiked with *d*-7 levoglucosan (NIST SRM 2267) using 9:1 dichloromethane:methanol on an accelerated solvent extractor (ASE 200; Dionex) at 1500 PSI and 100˚C. Sample were then concentrated in a RapidVap (LabConco) under Argon gas at 50˚C, dried to completion in a CentriVap centrifugal concentrator (LabConco) at 50˚C, and re-suspended in pyridine. Extracts were then derivativized for 15 minutes using O-bis (trimethylsilyl) trifluoroacetamide containing 1% trimethylchlorosilane (9:1 BSTFA:TMCS) at 75˚C, and analyzed on a Varian triple quadrupole 480-300 GC-MS system using a fused silica column (J&W DB-5MS, 30m x 0.25mm i.d., 0.25µm film thickness; Agilent Technologies). Each sample was injected splitless using helium as a carrier gas. Monomeric lignin phenol and anhydrosugar analyses were performed independently under single ion monitoring (SIM) mode, and using specific ions for compound determination. Sample detection limits, recoveries, and precision are within the ranges presented in Louchouarn et al. (2009).

Mass-weighted distribution coefficients (K_ds) and organic carbon-weighted distribution coefficients (K_{OC}s) in L kg^{-1} are determined by the following equations:

$$\mathbf{K_d = [\mathit{l}\ in\ POM\ mg\ kg^{-1}]/[\mathit{l}\ in\ DOM\ mg\ L^{-1}]} \qquad (3.1)$$

where the concentrations of levoglucosan (*l*) is measured in the isolated particulate and dissolved matter from each river, and

$$\mathbf{K_{oc} = K_d/\mathit{f}_{oc}} \qquad (3.2)$$

where K_d is determined in equation 3.1 and f_{OC} is the particulate organic carbon concentration in kg OC kg $^{-1}$, determined by elemental analysis. The equations 3.1 and 3.2, above, were also used to calculate distribution coefficients for high-temperature PyC from literature values of high-temperature PyC biomarkers (BPCA and PAHs) from dissolved and particulate concentrations in various environments. Values included in Table 3.1 are calculated from reported concentrations of biomarkers presented in the literature. For the PAHs presented, these values are derived from the sum of PAHs measured in DOM and POM, respectively (see Yunker et al. (2002), Yunker et al. (1994) for details). Distribution coefficients in Table 3.1 are presented as the natural log of K_d values ($\log K_d$), which is a common way to represent distribution coefficients in the literature, and allows for quick orders of magnitude comparisons between sampling periods, sites, and biomarkers used. Theoretical equilibrium K_{OC} values were determined for levoglucosan using the molecular connectivity index from the US Environmental Protection Agency (EPA) model KOCWIN (EPA 2012). Theoretical K_d values presented in Table 3.2 are calculated using equation 3.2, the K_{oc} value from the EPA model (EPA 2012), and the concentrations of POC in each river sample.

New flux estimates of Py-POC from the pan-Arctic were derived from K_d values calculated here (Table 3.1), assuming that bulk PyC is distributed in the environment similarly to the respective biomarkers- this assumption is based on apparent correlation of biomarker to bulk functionality of PyC from both low and high temperatures (Norwood et al. 2013, Wiedemeier et al. 2015). Equation 3.1 was used to calculate the concentration of Py-POC using K_d values from Table 3.1 and average literature concentrations of Py-DOC for low- and high-temperature PyC (Myers-Pigg et al. 2015, Stubbins et al. 2015), then scaled to a pan-Arctic flux by multiplying calculated Py-POC concentrations by annual pan-Arctic POC fluxes from McClelland et al. (2016). These new flux estimates are compared to Py-POC fluxes calculated from methodology outlined in Elmquist et al. (2008), updated with new pan-Arctic POC fluxes from McClelland et al. (2016). Briefly, Elmquist et al. (2008) use the ratio of PyC to sedimentary organic carbon and literature POC flux estimates to calculate Py-POC fluxes from major Arctic Rivers (see discussion in Elmquist et al. (2008) for further details). Pan-Arctic Py-DOC fluxes from low-temperature PyC was calculated using low-temperature Py-DOC fluxes from Myers-Pigg et al. (2015) and scaling to the pan-Arctic by assuming yields of low-temperature Py-DOC are the same from the gauged Siberian Arctic Rivers studied in Myers-Pigg et al. (2015) (40.6% of pan-Arctic watershed) as the rest of the pan-Arctic watershed (Stubbins et al. 2015).

3.3 Results

Concentrations of levoglucosan increased with increasing discharge in both rivers (Figure 3.2). Environmental K_d values of levoglucosan varied throughout the freshet period, but differently dependent on the river (Figure 3.2). Theoretical K_d values were determined from equation 3.2, using the concentration of POC in each sample, and the theoretical K_{OC} value from the EPA model, 10 L kg^{-1} (EPA 2012). Theoretical LogK_d values are 1.1 ± 0.7 L kg^{-1} for both rivers (Table 3.2).

3.3.1 Arctic River

LogK_d values were nearly one order of magnitude lower during peak flow in the Yenisei River (Figure 3.2c) than during base flow. LogK_d values of levoglucosan are within the same range as estimated logK_d values for higher temperature PyC markers (BPCA) in rivers (Table 3.1 and references therein). Particulate organic carbon (POC) in the Yenisei River was 0.08 ± 0.02 kg OC kg^{-1} throughout the sampling period. Environmental logK_{oc} values were an order of magnitude higher than logK_d values, and varied throughout the freshet periods in a similar fashion as logK_d values (Figure 3.2c). The average $\delta^{13}C$ of POM in the Yenisei River during this study is -28.9 ± 1.2 ‰ (Figure 3.3a). Monomeric lignin phenol ratios (syringyl/vanillyl: S/V) are 0.44 ± 0.21 in the Yenisei River (Table 3.2), and the ratios of levoglucosan to its isomer mannosan (L/M) are 4.2 ± 1.2 (Table 3.2).

3.3.2 Sub-Arctic River

In the Great Whale River, logK_d values decreased with increasing discharge (Figure 3.2d). POC in the Great Whale River was 0.17 ± 0.08 kg OC kg^{-1} throughout the sampling period. LogK_{oc} values were an order of magnitude higher than logK_d values, but followed the same trends as logK_d values (Figure 3.2d).

The average $\delta^{13}C$ of POM in the Great Whale River is -26.8 ± 0.6 ‰ (Figure 3.3b). Monomeric lignin phenol ratios S/V are 0.29 ± 0.19 in the Great Whale River (Table 3.2), and L/M ratios are 3.2 ± 3.7 (Table 3.2).

Table 3.1: LogK_d and LogK_{oc} values for various PyC biomarkers in different systems. Systems are ordered by watershed/basin size. Note the similarities of LogK_d values of high and low-T PyC biomarkers in rivers, suggesting the export of the entire PyC continuum is linked. Data for partition coefficients is from Coppola et al. (2014), Wagner et al. (2015), Yunker et al. (2002), Yunker et al. (1994), Ziolkowski and Druffel (2010) and this study (Table 3.2), and calculated using equations 3.1 and 3.2.

	Watershed Size 10^6 km^2	Biomarker Used	Average LogK_d	Average LogK_{OC}
Poudre River (Wagner et al., 2015)	0.005	BPCA	3.99 ± 0.62	N/A
Great Whale River (This study)	0.043	Levoglucosan	4.38 ± 0.24	5.20 ± 0.28
Small Rivers in Northwest Territories and Nunavut (Yunker et al., 2002)	0.083 ± 0.045	PAHs	4.49 ± 0.16	5.09 ± 0.16
Mackenzie River/Delta (Yunker et al., 1994, 2002)	1.78	PAHs	4.79 ± 0.76	6.63 ± 0.27
Yenisei River (This study)	2.54	Levoglucosan	3.67 ± 0.30	4.79 ± 0.28
	Ocean Size 10^6 km^2			
Beaufort Sea (Yunker et al., 1994, 2002)	0.18	PAHs	6.26 ± 0.38	7.71
Pacific Ocean (Coppola et al., 2014; Ziolkowski and Druffel, 2010)	165.2	BPCA	5.78	7.00 ± 0.05

Table 3.2: Average levoglucosan concentrations, suspended particulate matter (SPM), source signature ratios from free phenols and anhydrosugars (syringyl/vanillyl: S/V and levoglucosan/mannosan: L/M) and theoretical K_d values for the Yenisei River and Great Whale River.

	Yenisei River	Great Whale River	Total Average For This Study
Dissolved Levoglucosan μg L^{-1}	0.057 ± 0.032	0.054 ± 0.053	0.054 ± 0.044
Particulate Levoglucosan μg $gPOM^{-1}$	0.27 ± 0.14	0.94 ± 0.34	0.73 ± 1.1
Particulate Levoglucosan μg L^{-1}	0.002 ± 0.002	0.008 ± 0.011	0.005 ± 0.009
SPM mg L^{-1}	11 ± 6.4	19 ± 32	15 ± 24
Theoretical Partitioning, K_d	0.78 ± 0.20	1.7 ± 0.75	1.1 ± 0.69
S/V	0.42 ± 0.18	0.29 ± 0.23	0.36 ± 0.21
L/M	4.5 ± 1.5	5.8 ± 4.7	5.1 ± 3.3

3.4 Discussion

3.4.1 Characterization of Organic Matter and PyC

In general, the export of organic matter (OM) from Arctic river systems occurs predominantly in the dissolve phase (DOM). The $\delta^{13}C$ of POM in the Yenisei River is indicative of increasing terrestrial input throughout the freshet period (Figure 3.3a), and is within the range previously reported for the Yenisei River (McClelland et al. 2016). The lower $\delta^{13}C$ values in the Yenisei during the summer months observed by McClelland et al. (2016) from 2003-2012 (-31.7 ± 0.4 ‰) are also observed here in 2014 (Figure 3; July-October: -30.7 ± 1.1 ‰).

Younger $\Delta^{14}C$ ages observed in the Yenisei River POM compared to other Arctic Rivers is attributed to organic matter contributions from surface soil layers (McClelland et al. 2016). The $\delta^{13}C$ of POM in the Great Whale River, in contrast, does not correlate well with discharge (Figure 3.3b). However, it remains within the range previously reported for POM in North American Arctic Rivers (-26.8 ± 0.6 ‰ for the Great Whale River, this study; -26.2 ± 0.7 ‰ for the Yukon River (Guo and Macdonald 2006) and -26.5 ± 0.5 ‰ for the Mackenzie River (Goñi et al. 2005)). River-bank erosion is particularly strong during the ice flow period of spring freshet discharge, and may be a substantial source of terrestrial POM in the Great Whale River (Hudon et al. 1996).

Free monomeric lignin phenol ratios (syringyl/vanillyl: S/V), coupled with levoglucosan and its isomer, mannosan (L/M), are within the range of gymnosperm source reconstruction in aerosols, soils, and charcoals, suggesting that low-temperature PyC in the Yenisei River and the Great Whale River in both phases are influenced predominately by gymnosperm fire fuels (Table 3.2, source ratios from (Kuo et al. 2011a)). These ratios are consistent with previously reported source reconstruction for Py-DOC in Arctic Rivers (Myers-Pigg et al. 2015).

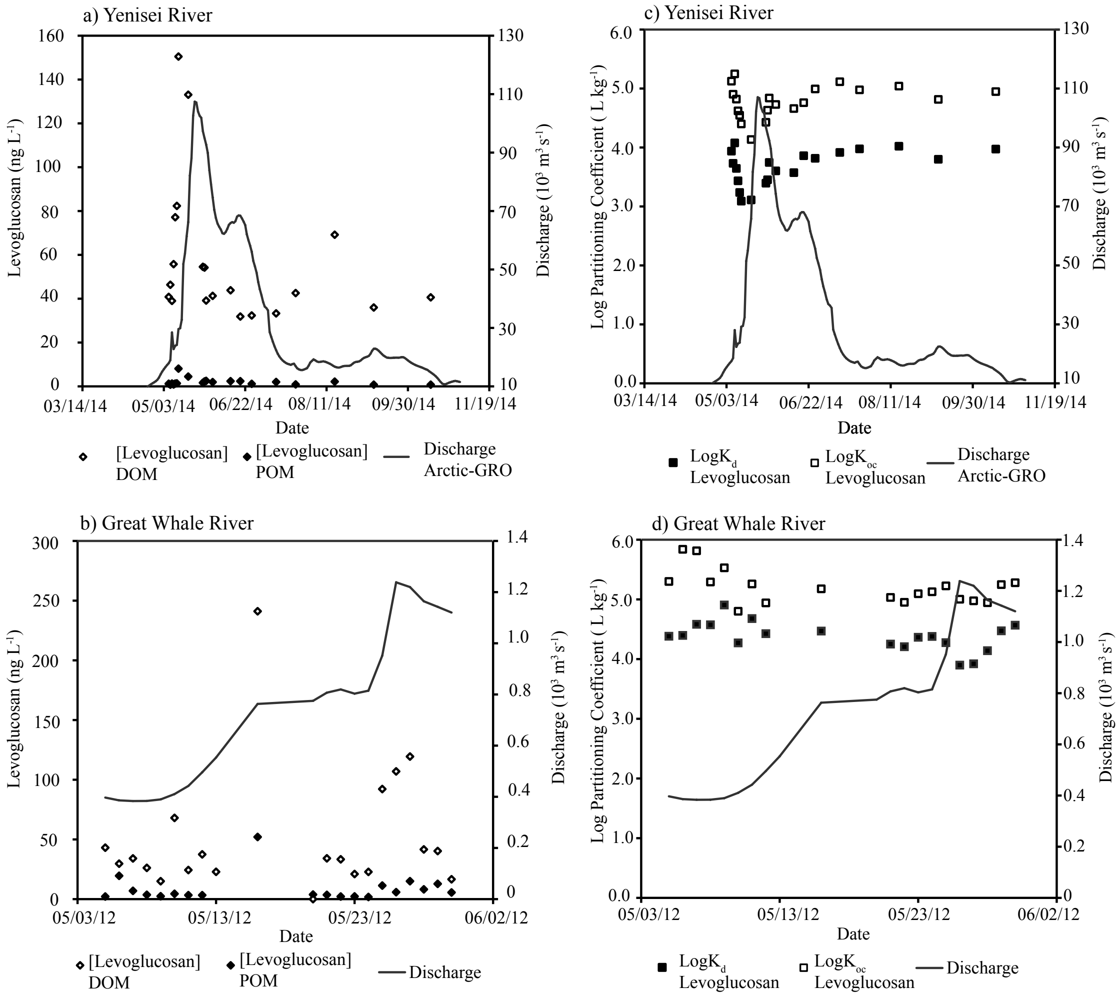


Figure 3.2: a) Levoglucosan concentrations throughout the freshet hydrograph in the Yenisei River 2014, b) the Great Whale River in 2012. c) Environmental partitioning coefficients (K_d and K_{oc}) throughout the hydrograph for the Yenisei River in 2014 and d) the Great Whale River in 2012.

Absolute concentrations of levoglucosan are on the lower end of the range previously reported in river DOM (0.06 ± 0.04 μg L^{-1} in this study versus 0.7 ± 0.4 μg L^{-1} from 2004-2006 in Siberian Arctic Rivers (Myers-Pigg et al. 2015)) and may reflect inter-annual variability, dependent on hydrographic regimes and/or extent and severity of prior fire events. Concentrations of levoglucosan in the particulate phase of the studied rivers are low (Figure 3.2; Table 3.2, 0.73 ± 1.1 μg $gPOM^{-1}$) compared to concentrations of levoglucosan in surface sediments from a river plume (1.3 – 6.9 μg gdw^{-1}) of a small, mountainous stream (Hunsinger et al. 2008). Environmental $logK_d$ values are 4.4 ± 0.24 L kg^{-1} for the Great Whale River and 3.7 ± 0.30 L kg^{-1} for the Yenisei River during this study (Table 3.1; Figure 3.2). These values are within a similar range of calculated $LogK_d$s determined by PAH concentrations from a variety of other Canadian sub-Arctic and Arctic Rivers (Yunker et al. 1994, Yunker et al. 2002) (Table 3.1), but are two order of magnitude lower than calculated $LogK_d$ values for PAHs in the Beaufort Sea (Yunker et al. 1994, Yunker et al. 2002) (Table 3.1).

Theoretical $logK_d$ values for levoglucosan are 1.1 ± 0.7 L kg^{-1}, using the EPA contaminant model KOCWIN (EPA 2012) K_{oc} value, and fraction of organic carbon in river POM (Table 3.2). The KOCWIN modeled partitioning can be treated as a theoretical partitioning of a constituent, because it does not consider factors that affect environmental partitioning such as association with minerals or physical properties of particles present such as surface area, porosity, number of reactive sites, etc. The fact that we observe 3-4 orders of magnitude higher $logK_d$ values than predicted in both rivers, 4.0 ± 0.5 L kg^{-1} (total average for this study), indicates orders of magnitude higher association of levoglucosan with particulate matter in these systems than anticipated based on chemical functionality alone. Similarly, environmental partitioning of PAHs are 2-3 orders of magnitude higher than predicted at the sediment-pore water interface in estuaries and lakes (Gustafsson et al. (1997)and references therein). This has been attributed to PAH-soot particle association in natural sediments (Gustafsson et al. 1997). Therefore, the association of levoglucosan with particulate matter suggested by environmental partitioning coefficients may be indicative of a connection of combustion biomarkers with particulate organic matter upon export, either within charcoal particles or sorbed to exported bulk soil organic matter (SOM).

3.4.2 PyC Release Mechanisms to Aquatic Systems

Although very little research has been done on the transport of particulate PyC from river systems, it has been suggested that transport in this phase may be of importance in recently fire-affected ecosystems (Wagner et al. 2015), where increased surface run off (Moody et al. 2013), soil erosion (Shakesby and Doerr 2006), and total suspended solids (TSS) (Ryan et al. 2011) have been observed. In our study regions, particulate carbon export is often a small proportion of the total carbon export; POC export accounts for ~15% of the total OC flux from the pan-Arctic per year (Holmes et al. 2012, McClelland et al. 2016). Around 23% of the total POC export occurs during the spring freshet period in both the Yenisei River and Great Whale River (McClelland et al. 2016, Hudon et al. 1996). As previous work estimates that Py-POC export in Arctic Rivers is between 3-9% of total POC fluxes (Elmquist et al. 2008), transport of Py-POC may be an important portion of the total POC flux in Arctic Rivers.

The sources of bulk POC in Arctic Rivers include soil organic matter and erosion (Guo et al. 2007). Around 16% of global soil area is within the northern circumpolar permafrost region (Tarnocai et al. 2009). In watersheds that contain permafrost coverage (such as the watersheds in this study), the permafrost can act as a boundary layer, causing rapid translocation of water to river systems during spring thaw events, which influences soil organic matter transport to rivers (Prokushkin et al. 2009). Although the soil active layer, in which organic matter has the ability to exchange with the surface terrestrial ecosystem when thawed, is generally quite shallow in these regions, depth of the active layer varies dependent on location within a basin (Osawa et al. 2010). PyC content has been found in a sub-watershed of the Yenisei River to be the highest in soils in areas with shallow active layer depths, compared to those with thick active layers and no permafrost (Guggenberger et al. 2008). Therefore, there should be a strong relationship between PyC concentrations and hydrological regime. This may help to explain the observed lack of relationship between fire frequency and riverine export of dissolved black carbon (DBC as determined by BPCAs) (Ding et al. 2014a, Ding et al. 2013), and the strong reported relationships between DBC and hydrological cycling (Jaffé et al. 2013), particularly in Arctic systems (Stubbins et al. 2015).

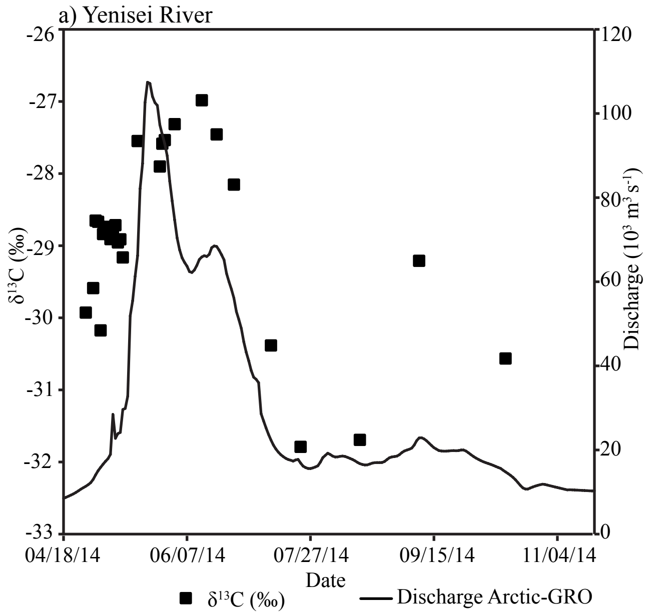
In boreal ecosystems, the turn-over time of soil PyC is <100 yrs (Hammes et al. 2008). This turnover time accounts for all loss processes (decomposition, leaching, erosion). This is much less than the millennial time-scales traditionally thought for PyC turnover in soils, and may also reflect the translocation of PyC from soils into riverine systems. Export of DBC does not appear to be controlled by fire history (Wagner et al.

2015, Ding et al. 2013), implying that high-temperature PyC needs to be functionalized before export, i.e. the solubility of high-temperature PyC is likely a function of charcoal age and exposure (Abiven et al. 2011). This idea is supported by the continual mobilization and export of DBC in deforested ecosystems long after slash-and-burn agriculture has stopped (Dittmar et al. 2012a). However, as low-temperature Py-DOC is also non-correlated to fire history (Myers-Pigg et al. 2015), the processes controlling the export of low- and high-temperature Py-DOC may be coupled. The relationship between Py-DOC and bulk DOC in these rivers (Stubbins et al. 2015, Myers-Pigg et al. 2015, Jaffé et al. 2013) indicate that the mechanisms governing their export are similar. It has been suggested that subsoil export is a primary mechanism for PyC export from terrestrial to aquatic systems (Güereña et al. 2015), which may be regulated by soil-PyC associations. Czimczik and Masiello (2007) suggest that the ability of soil minerals to sorb PyC may be a main controller of PyC storage within soils, similar to bulk soil organic matter (SOM). When PyC is incorporated into soils, it may be associated with minerals in soils (Hockaday et al. 2007, Knicker 2011). PyC-mineral interactions observed on the surface of charcoals may also influence associations of PyC with minerals in the dissolved phase within soils (Hockaday et al. 2007), as soil mineral-DOM interactions affect the quantity of DOM exported from soil layers (Kaiser and Guggenberger 2000, Kawahigashi et al. 2006). The distribution of PyC in Arctic soil profiles indicates vertical movement of PyC between soil layers (Guggenberger et al. 2008), and may be due to transport of Py-DOC within soil profiles. In many high-latitude systems, the highest PyC content within soils is associated with soil mineral layers (Rodionov et al. 2006, Guggenberger et al. 2008). In permafrost regions, DOM export is controlled by active layer thickness and extent of seasonally thawed mineral layers above permafrost regimes (Kawahigashi et al. 2004). These relationships within soils may affect both the phase and timing of PyC export to aquatic systems.

3.4.3 Differences in Partitioning Throughout the Hydrograph

The composition and bioavailability of OM exported from soils in high-latitude systems is a function of active layer depth and mineral soil association (Kawahigashi et al. 2006). A large portion of labile materials, if associated with a mineral layer, may avoid remineralization during transport (Kaiser and Guggenberger 2000, Hedges et al. 1997, Vonk et al. 2010). Terrestrial organic carbon (as determined by n-alkanoic acids) in the particulate phase has been found to associate with two distinct pools of soil carbon released during the spring freshet period; a young pool dominated by humics and an old pool with a mineral soil component (Vonk et al. 2010). This observed difference in mobilization of terrestrial OC may also influence the mobilization of PyC in high-latitude systems, which in turn, affects availability for transformations during transport. For example, K_ds of low-temperature PyC biomarkers infer different association to POM throughout the freshet period in the Yenisei River (Figure 3.2c), which indicates that the material exported throughout the freshet may have different sorptive capacity and/or equilibrium state than material exported during base-flow periods. K_{oc} values in the Yenisei River show similar trends to K_d values (Figures 3.2c), further indicating that the type of organic matter in the particulate phase, or the association of PyC to the particulate matter, shifts during the freshet period, and not just the amount of organic matter present in the system (which would alter K_d values but keep K_{oc} values constant). During the freshet period, levoglucosan is proportionally exported more in the dissolved phase than during low-flow. This may be due to hydrophilic DOM, such as levoglucosan (and presumably all low-temperature PyC; Figure 3.1), bypassing association with soils within the active layer, and directly entering the aquatic system (Kawahigashi et al. 2006) during high-flow regimes. As high-flow regimes release the largest proportion of yearly DOM and POM during a relatively short time period (Holmes et al. 2012, McClelland et al. 2016, Amon et al. 2012), the proportional release of PyC from high-latitude rivers during the spring freshet period may be of importance for the overall flux of PyC from high-latitude river systems. Additionally, as PyC is largely released in the dissolved phase, this may allow highly functionalized and hydrophilic portions of PyC to be more accessible to *in-situ* microbial degradation and lead to increased riverine respiration rates during this period (Masiello and Louchouarn 2013).

In the Great Whale River, the export phase of PyC may be intrinsically linked to soil mineral interactions and a deeper active layer associated with discontinuous permafrost that underlay most of the watershed (Kawahigashi et al. 2006, Bhiry et al. 2011), as Log K_d and K_{oc} values are higher than in the Yenisei River, and decrease nearly linearly with increasing discharge ($R^2 = 0.4$ and 0.2, respectively, $p < 0.05$, data not shown) (Figure 3.2d). This apparent association of exported PyC with soils is also congruent with high fire return intervals in the Great Whale River (Bhiry et al. 2011), as it would allow for PyC to vertically "equilibrate" within soil active layers, influencing the proportion of PyC may be exported during varying flow regimes.



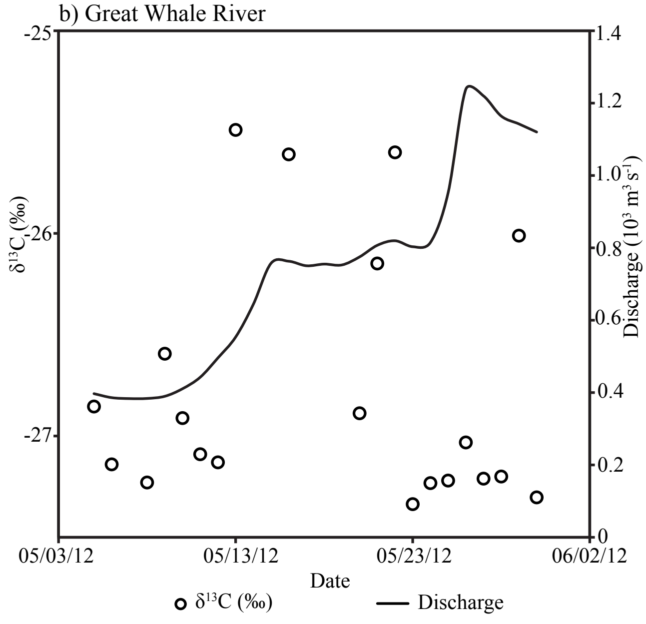


Figure 3.3: δ^{13}C values (‰) for particulate matter throughout the freshet a) in the Yenisei and b) in the Great Whale River.

3.4.4 Implications for Phase-Association of the Entire PyC Continuum

Regardless of the type of PyC biomarker used, it appears that each proxy for PyC is similarly associated to particulate matter (as determined by K_d values) throughout a system, and that changes in this association are seasonal and may reflect types of material exported or environmental conditions present. Log K_d values for low- and high-temperature PyC biomarkers in river systems are within the same range (Table 3.1), while LogK_{oc} of high-temperature PyC biomarkers show higher values than those of levoglucosan. The somewhat higher K_{oc} values for high-temperature PyC biomarkers is consistent with their higher propensity to sorb to organic matter present in a system (e.g. Lohmann et al. (2005)). The variations in LogK_ds between systems may be due to quality and source of bulk organic matter and active layer depth unique to and within each system. This suggests that POM interactions in each watershed may ultimately govern the export of PyC more than the nature of the PyC itself (as high-temperature PyC is more hydrophobic while low-temperature PyC is hydrophilic, yet their K_ds are within the same range; Figure 3.1, Table 3.1). This argument is strengthened by the fact that the phase distribution of hydrophobic PAHs varies between studied river and time of year. For example, during the freshet of the Mackenzie River, PAHs are predominately exported in the particulate phase, while during base-flow both the Rhône River and the Mackenzie River, dissolved PAHs comprise the bulk of the PAH export (Yunker et al. 1994). However, PAH composition in the Mackenzie River is distinct in the dissolved and particulate phases (Yunker et al. 1994), indicating that the chemical structure of the sorbate still plays a role on its phase association.

The similarity between Log K_d values calculated for high-temperature PyC components (BPCA and PAHs) and low-temperature PyC (levoglucosan) support the concept that low- and high-temperature PyC may be exported similarly from river systems. However, as physical weathering has been shown to be an important loss process for both high- and low-temperature charcoals, although on very different time scales (Naisse et al. 2015), understanding the ages of these exported carbon pools is necessary before final conclusions on their similarities can be determined. Additionally, as the export of dissolved and particulate black carbon (DBC and PBC, respectively) is decoupled from a fire-impacted watershed (Wagner et al. 2015), and given the fact that bulk DOC and POC in Arctic River systems have vastly different ages (e.g. Amon et al. (2012), (Goñi et al. 2005)), we must understand the sources and ages of dissolved and particulate PyC in order to fully understand how export of Py-DOC and Py-POC might be linked.

The apparent order of magnitude increase in sorption coefficients for high-temperature PyC from rivers to oceans (Table 3.1; calculated from Wagner et al. (2015), (Coppola et al. 2014), Ziolkowski and Druffel (2010)) suggests that sorption plays an increasingly important role on PyC throughout its transport, and may eventually help to determine the fate of PyC in ocean systems. This however, does not take into account the potential degradation of dissolved PyC during transit (Stubbins et al. 2012, Myers-Pigg et al. 2015, Ward et al. 2014) and therefore, may skew the importance of sorption versus loss in the dissolved phase throughout this transport. To understand loss terms and PyC cycling, the relative proportion of all component of the PyC continuum in the dissolved and particulate phases during transfer to and within ocean systems must be further explored.

3.4.5 Flux Estimates from Rivers for Arctic PyC using Partitioning Coefficients

Based on Log K_d values presented here, only 1.3 ± 6.2 % of the total flux of PyC is in the particulate phase from the pan-Arctic watershed (Figure 3.4). This is much less than a calculated distribution of Py-POC in worldwide flux estimates (~16 % of total PyC flux from rivers (Santín et al. 2016)). This is also lower than pervious estimates of Py-POC fluxes from the pan-Arctic (~8% of total PyC flux) using pan-Arctic Py-POC flux estimates (calculated using BC/POC ratios from Elmquist et al. (2008) and pan-Arctic POC fluxes from McClelland et al. (2016)) and pan-Arctic Py-DOC fluxes from Stubbins et al. (2015) (Figure 3.4). However, as our estimates measure *in-situ* phase distribution based on biomarker composition within rivers, they can represent a conservative estimate of the amount of Py-POC exported from Arctic rivers. Additionally, previous Py-POC flux estimates from Arctic Rivers rely on measurements of the most refractory PyC (using the CTO-375 method; see Figure 3.1 for range of detection within the PyC continuum) in estuarine sediments to estimate *in-situ* Py-POC fluxes (see Elmquist et al. (2008) for further explanation of previous Py-POC flux calculations). As refractory PyC analytical methods (such as CTO-375 method) may over estimate PyC contribution in environmental samples (Hammes et al. 2007), and the most refractory portion of the PyC continuum measured by these techniques may be more particle associated than other forms of PyC (due to their hydrophobic nature), the previously reported flux estimates may over estimate the actual distribution of PyC transported from Arctic Rivers. In environments where POC export is a proportionally important part of the TOC flux, the relative influence of Py-POC on the total export of PyC from the region may be of higher significance. Phase partitioning of PyC components vary with the hydrograph (Figure 3.2), implying that the export of PyC in the particulate phase varies throughout the year. This is important to consider when looking at PyC in deposited sedimentary records and estimating the impact of fire on past climate, as the records of these signatures may vary with hydrographic regimes and particulate matter loadings.

Sorption processes and transfer to sediments are attributed as one of the major loss processes for Py-DOC in the world's ocean(Coppola et al. 2014). Although our estimates of Py-POC export based on distribution coefficients from pan-Arctic rivers is much lower than previously estimated, Py-DOC could sorb to sinking particulates once within the Arctic Ocean. This has implications on how much Py-DOC may survive transport and ends up in regions of North Atlantic Deep Water formation (Stubbins et al. 2015), versus what is sorbed to sinking particles and buried on the vast Arctic continental shelves, as measures of Py-POC in Arctic Ocean sediments and sinking particles (using CTO-375 method) suggest that Py-POC quickly sinks and is stored within coastal margins (Fang et al. 2016).

Considering the changing fire regimes in the Arctic (Kelly et al. 2015), the intrinsic tie of PyC with discharge in the region (Stubbins et al. 2015, Myers-Pigg et al. 2015), and changing hydrological regimes (Wrona et al. 2016), the transport of PyC from Arctic terrestrial to aquatic systems is likely to increase. As the Arctic Ocean continental margins have recently been suggested as an efficient location for PyC burial (Fang et al. 2016), understanding the phase distribution of PyC during transport through rivers and estuaries is relevant for understanding overall PyC fluxes, the potential degradation of PyC during transit, and losses of PyC from the active carbon cycle through burial into sediments.

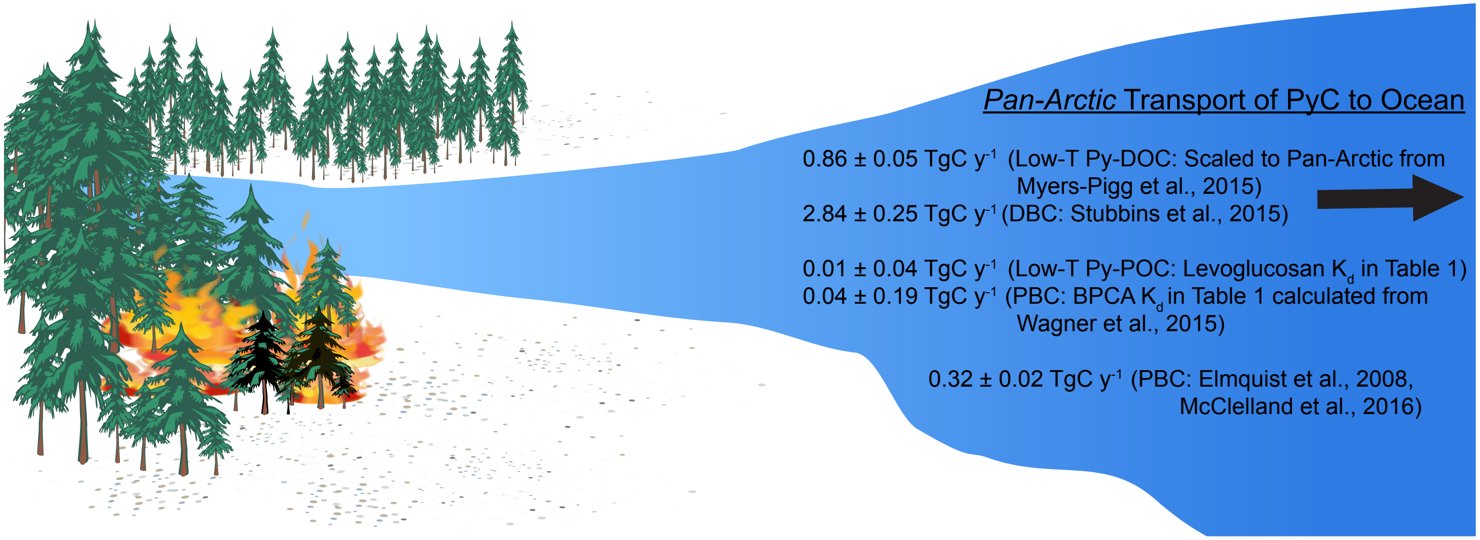


Figure 3.4: Flux estimates from the Pan-Arctic watershed to the Arctic Ocean of Py-DOC and Py-POC. See methods for flux calculation explanations.

CHAPTER IV

SIGNATURES OF BIOMASS BURNING AEROSOLS IN THE PLUME OF A SALTMARSH WILDFIRE IN SOUTH TEXAS *

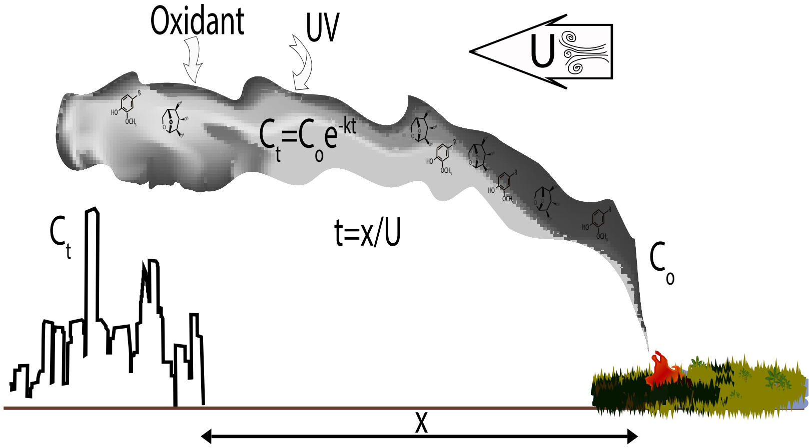


Figure 4.1: Conceptual diagram of the current study.

4.1 Introduction

Understanding the dynamics of atmospheric aerosols is of critical importance due to the impacts of particulate matter (PM) on the health of exposed populations, radiative forcing, and visibility (Griffin 2013). In most locations sampled, organic material is the PM constituent that contributes the largest fraction of observed mass concentrations (Jimenez et al. 2009, Zhang et al. 2007). Therefore, elucidating the sources, sinks, and chemistry of organic PM also is critical. On a global scale, in addition to secondary

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organic aerosol formation and direct emission from natural and industrial/anthropogenic sources, biomass burning (BB) is a large source of organic PM to the atmosphere (Andreae and Merlet 2001). Analyses show a strong relationship between fire incidence and natural inter-annual- and decadal-scale climate oscillations (Bowman et al. 2009, Kuo et al. 2011b). However, climate change and fire management practices have promoted conditions that favor the transition to larger wildfire events (Bowman et al. 2009, Westerling et al. 2006). When considering future controls on industrial/anthropogenic emissions, it is hypothesized that the relative importance of BB PM will increase.

Biomass burning has been linked to increased emissions of multiple particulate species, including potassium, elemental carbon (defined based on thermal properties as opposed to black carbon, which is defined based on optical properties), and primary organic aerosol (POA, again defined based on thermal properties) (Simoneit et al. 1999, Holzinger et al. 1999). To understand the impact of BB emissions on air quality and climate, the relative contribution of various emitted species from this source must be quantified. Unfortunately, many of the emitted species also are emitted from other anthropogenic and natural sources and do not provide a marker that is unique to BB. Specific tracers of BB events include compounds such as the anhydrosugar levoglucosan and its isomers mannosan and galactosan, among others found in BB POA. These compounds are direct and exclusive byproducts of thermal degradation of cellulosic and hemicellulosic plant polymers (Kuo et al. 2008a, Simoneit et al. 1999).

The use of these biomarkers as quantitative tracers in source apportionment models is limited by the assumption that they are conservative. Such conservative behavior seems unlikely given the rapid measured changes in the physical and chemical nature of BB aerosols during downwind plume advection (Vakkari et al. 2014). More specifically, there is debate about the actual lifetime of levoglucosan in the atmosphere, with estimates ranging from significantly less than a day to approximately one month depending on the loss processes considered (Fraser and Lakshmanan 2000, Hennigan et al. 2010, Knopf et al. 2011, Bai et al. 2013, Slade and Knopf 2014, Lai et al. 2014, Zhao et al. 2014). This uncertainty covers much of the time range of atmospheric processes, creating serious interpretation challenges. Therefore, effective application of these biomarkers to atmospheric transport and apportionment studies requires a better understanding of their chemical lifetimes and degradation products in the atmosphere, at least relative to other species.

Detailed characterization of the proportional yield of biomarkers relative to each other or to total organic matter is a common approach in organic geochemistry to identify the source and fate of organic matter input to environmental reservoirs (Hedges and Mann 1979). For example, the ratio of levoglucosan to its isomers (particularly mannosan) within POA emissions permits discrimination of fuel types (Caseiro et al. 2009, Engling et al. 2009, Fabbri et al. 2009, Kuo et al. 2011a, Schmidl et al. 2008, Ward et al. 2006, Louchouarn et al. 2009). Similarly, lignin-derived methoxyphenol ratios identify specific compositional signatures of vascular plant tissues and their degradation pathways (Louchouarn et al. 2010, Hedges et al. 2000, Hedges and Mann

1979). Such relative ratios are thus extremely useful in degradation and transport studies for characterizing the fate of biomass-derived polymers under a number of environmental conditions (Norwood et al. 2013, Hernes and Benner 2003, Amon et al. 2012).

While the relative ratios of biomarkers have seen extended use in hydrologic, soil, and marine settings, they have yet to be applied extensively to atmospheric scenarios. Jimenez et al. (2007) proposed using the ratio of anhydrosugars to methoxyphenols to differentiate smoke emissions from different types of biomass fuels. In addition, Sullivan et al. (2014) recently investigated the quantification and use of various marker ratios to elucidate plume chemistry a short distance downwind of a fire. Observed temporal variations in these ratios between day and night conditions (Hoffer et al. 2006) also point to a higher sensitivity of methoxyphenols than anhydrosugars to photochemically driven oxidation in the atmosphere.

Using a sampling opportunity during a saltmarsh wildfire event that occurred upwind of Houston, TX, during October 2013, this study seeks to address the current lack of clarity on relative marker lifetimes and the dearth of information regarding relative ratios of BB markers in plumes downwind of fires. Relative and absolute PM marker concentrations are considered, as are their isotopic signatures, to elucidate relevant processing occurring within the plume.

4.2 Materials and Methods

4.2.1 Sampling

Aerosol samples were collected on 47-mm pre-treated quartz filters. Fine aerosols ($PM_{2.5}$, aerosol diameter $\leq 2.5\mu m$) were collected every ~24hr, using a Versatile Air Pollutant Sampler (VAPS, URG, NC) located atop a two-story building on the Rice University campus. Samples were collected daily from October 23-29, 2013, as part of a month-long sampling project, during which a wildfire burned on October 25-26, 2013. This fire burned ~5,000 acres of a *Spartina alterniflora*-dominated saltmarsh ecosystem in the McFaddin National Wildlife Refuge, 125 km southeast of Houston (Figure 4.2). *Spartina alterniflora* (cordgrass) fixes carbon using a C_4 pathway (referring to the number of carbon atoms in the first molecule produced in carbon fixation), while other species present in the saltmarsh, such as *Batis maritima* (succulent shrub) and *Iva frutescens* (high-tide bush), fix carbon using the C_3 pathway. Based on Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT (Draxler and Hess 1997)) backward trajectory modeling (Figure 4.3), Houston was directly downwind of this wildfire during the peak of the burn, with an approximate travel time from source to aerosol sampling site of 12-16 hrs. Burnt and unburnt plant materials from representative populations of grasses and shrubs present at the fire site were collected approximately 1 week after the fire occurred. Burnt and unburnt areas of the marsh were divided by an access road. Charcoal material was collected from burnt plant material onsite using gloves. Unburnt plant material was collected from unburnt portions of the saltmarsh using gloves. Plant materials and charcoals were frozen upon arrival at the Texas A&M

University Galveston campus. Samples were freeze-dried and homogenized for further analysis.

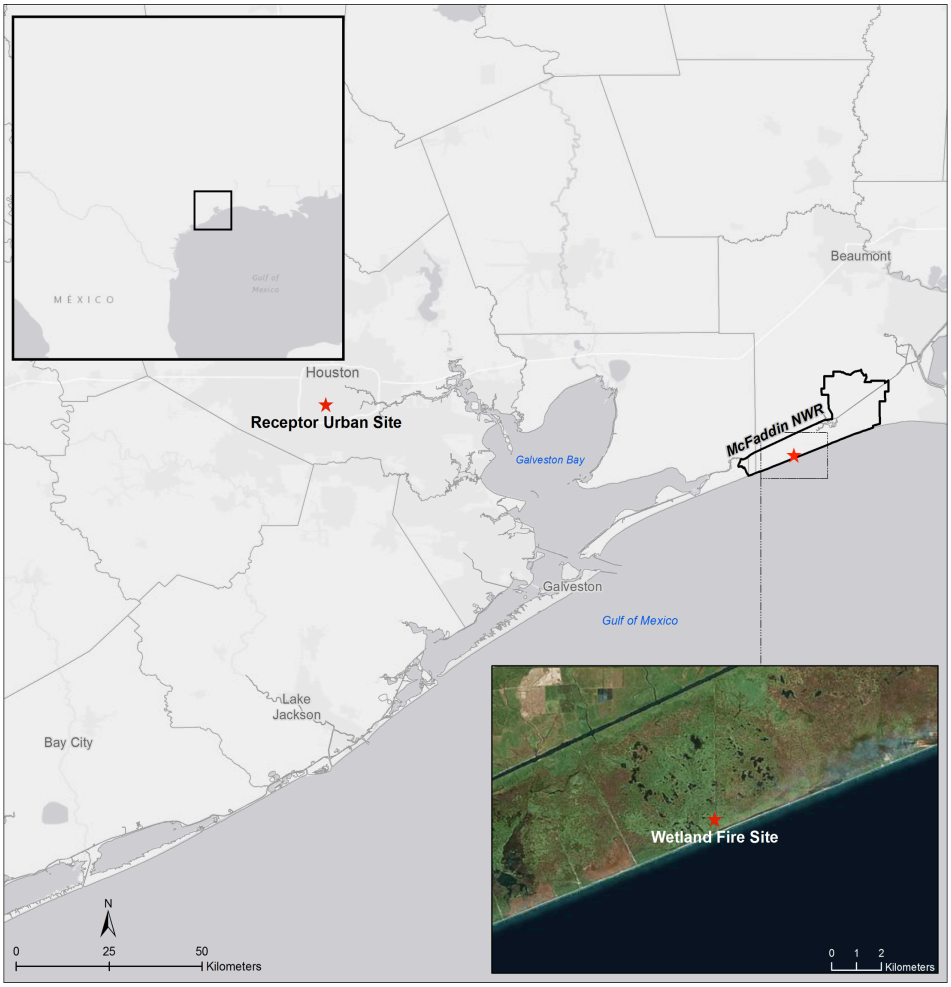

Figure 4.2: Map indicating location of fire site in McFaddin National Wildlife Refuge and receptor site in Houston. This map was created using ArcGIS with georeferenced locations of the fire and receptor sites indicated by red stars. The basemap is 2014 National Aerial Imagery Program from ESRI Map Services.

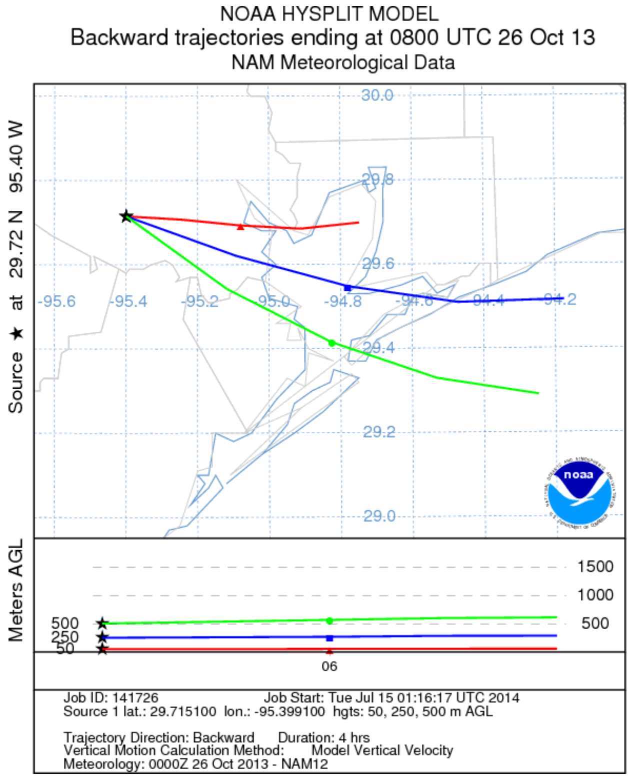

Figure 4.3: Example HYSPLIT backward trajectory indicating transport from the fire site to the receptor site. HYSPLIT model was created using ARCHIVE data.

4.2.2 Bulk Chemical Analysis

Carbon and nitrogen elemental and stable isotopic composition (%C, %N, $\delta^{13}C$ and $\delta^{15}N$) were determined from a subsample of each filter, charcoals, and plant materials using a Thermo-Electron Dual-Inlet Gas-Source Stable Isotope Mass Spectrometer at Baylor University (Waco, TX). These subsamples were pre-treated for removal of carbonates by vapor-phase acidification.

Inorganic ions were extracted from a subsample of each filter with 10 mL of deionized water using one hour of automatic shaking followed by one hour of sonication. The extracted solution was analyzed with ion chromatographs (Dionex ICS

1600) equipped with CS12 (cation) and AS12A (anion) analytical columns. Ion concentrations were determined from a calibration curve of six different standard solutions. One field blank filter treated with identical procedures was used for blank correction.

4.2.3 Plant and Fire Biomarker Analysis

Terrestrial and fire-derived biomarkers (polymeric lignin phenols, lignin methoxyphenols, and anhydrosugars) were analyzed using filter, charcoal, and plant material subsamples following the methods outlined in Louchouarn et al. (2010), Louchouarn et al. (2009) and Shakya et al. (2011). Polymeric lignin phenols and cutin acids were obtained using alkaline cupric oxide oxidation (Goñi and Hedges 1990, Hedges and Ertel 1982, Shakya et al. 2011, Louchouarn et al. 2009).

The identification and quantification of polymeric lignin phenols were performed using capillary gas chromatography-mass spectrometry (Varian triple-quadrupole GC-MS) using methodology modified from Louchouarn et al. (2010). Briefly, aliquots of extracts were derivatized for 15 minutes using O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) (9:1 BSTFA:TMCS) at 75˚C. Samples were injected splitless on a Varian triple quadrupole 480-300 GC-MS system fitted with a fused silica column (J&W DB-5MS, 30m x 0.25mm i.d., 0.25µm film thickness; Agilent Technologies), using helium as the carrier gas. The MS was operated in extended dynamic range (EDR) under selective ion mode (SIM).

The identification of cutin-derived acids was performed by re-injecting the cupric oxide aliquots in full scanning mode as detailed in Opsahl and Benner (1995). Briefly, the GC oven temperature began at 100˚C with a one-minute hold, increased at 4˚C/min to 270˚C, and held again for 16 minutes. Cutin-derived acid identification was determined from relative retention times of trimethylsilyl derivatives of saturated fatty acid standards (Goñi and Hedges 1990, Opsahl and Benner 1995) and relative response factor to the internal standard, *d*7-cinnamic acid.

"Free" lignin methoxyphenols and fire-derived anhydrosugars were solvent-extracted (Shakya et al. 2011, Louchouarn et al. 2009) from subsampled filters or charcoals with 9:1 dichloromethane: methanol using an accelerated solvent extractor (ASE 200; Dionex) at 1500 psi and 100˚C. Samples were concentrated in a rapidvap at 50˚C and dried to completion in a LabConco solvent concentrator, then re-suspended in pyridine. Samples were analyzed using capillary GC-MS (Varian triple-quadrupole GC-MS) according to methods described elsewhere (Shakya et al. 2011, Louchouarn et al. 2009). The GC-MS analyses of lignin methoxyphenols and levoglucosan were performed independently, using specific ions for compound determination.

4.2.4 Mixing and Degradation Models

To understand the contribution of burnt material to aerosols, a linear regression was performed between estimated total (non-carbonate) carbon (TC_{total}) and levoglucosan (r^2=0.63, not shown). A positive TC_{total} value at the intercept of this regression (levoglucosan concentration of 0) provides an estimate for the background TC value in the aerosols (unburnt level of TC, $TC_{background}$). For each sample, the amount of $TC_{background}$ was subtracted from the TC measured (TC_{total}) to determine the input of TC from burnt sources, TC_{burnt}. This rough approximation of TC_{burnt} does not account for any potential isotopic fractionation during the burning or the types of plant materials contributing to the TC_{burnt}. Therefore, the amount of TC_{burnt} that can be attributed to burned C_4 plants can be found from (Das et al. 2010, Boutton et al. 1999):

$$\%C_{4,burnt} = (\delta^{13}C_{BB}-\delta^{13}C_{3,burnt})/(\delta^{13}C_{4,burnt}-\delta^{13}C_{3,burnt}) \times 100\% \qquad (4.1)$$

where $\delta^{13}C_{3,burnt}$ is the end member isotopic signature present in burnt C_3 charcoals collected at the wildfire site, and $\delta^{13}C_{4,burnt}$ is the end member isotopic signature in burnt C_4 grasses collected at the wildfire site. The range in this relationship can be further constrained by considering the potential for isotope fractionation of burnt biomass as it becomes an aerosol, which only occurs in C_4 plants and usually varies from -1 to -7 ‰ (Das et al. 2010). This isotopic fractionation can be accounted for in Equation (4.1) by substituting ($\delta^{13}C_{4,burnt}$) with ($\delta^{13}C_{4,unburnt}$ + smoke fractionation). The isotopic signature of the burnt material present in the aerosols, $\delta^{13}C_{BB}$, can be determined based on a simple isotopic mixing model:

$$\delta^{13}C_{sample} = \delta^{13}C_{BB}f_{BB} + \delta^{13}C_{OA,bkg}(1-f_{BB}) \qquad (4.2)$$

where $\delta^{13}C_{sample}$ is the measured isotopic signature of the sample in ‰, $\delta^{13}C_{BB}$ is the isotopic signature of the material burnt in the sample, f_{BB} is the fraction of the sample from biomass burning, and $\delta^{13}C_{OA,bkg}$ is the isotopic signature of the organic aerosol sample before the fire, assumed to be the "background" concentration in this environment.

A pseudo first-order degradation equation:

$$(C_t/C_o) = e^{-kt} \qquad (4.3)$$

was used to explore the relative rate of degradation of a biomarker (through k, the pseudo first-order reaction rate constant) and estimates of at-source concentration, C_o. Here, C_t is the concentration of a biomarker measured at the receptor site (Houston) and t is the transit time from the fire site to the receptor site.

4.3 Results and Discussion

4.3.1 Chemical Characterization of $PM_{2.5}$

Concentrations of BB biomarkers (both anhydrosugars and monomeric lignin methoxyphenols) peak during the period of maximum burning conditions (Oct 25-26), when wind backward trajectories also coincided with the direction of the receptor site (Figure 4.3). Methoxyphenol concentrations during the plume are an order of magnitude higher than background concentrations in Houston during summer (Shakya et al. 2011), confirming that they were released during this biomass burning event in the fine aerosol fraction (Simoneit et al. 1993) (Figure 4.4a). Background concentrations of levoglucosan (determined as levoglucosan concentrations pre- and post- fire plume), 11 – 32 ng m^{-3}, are within the range of concentrations reported previously in Houston (5.03 – 141.75 ng m^{-3}) (Fraser et al. 2002). During the peak of the fire event, levoglucosan concentrations reached 400 ng m^{-3}, similar to those reported in PM_{10} in Houston aerosols from large fire events in Mexico and Central America (Fraser and Lakshmanan 2000). Source signature ratios of levoglucosan to mannosan (L/M; Figure 4.4b) in these aerosols correspond to those of grass charcoals collected at the burn site, whereas syringyl (syringic acid, Sd) to vanillyl (vanillic acid, Vd) ratios of the “free” methoxyphenols (Sd/Vd; Figure 4.3b; Table 4.1) suggest that softwood (gymnosperms) are a main contributor to the BB-derived aerosols. Gymnosperms do not contain syringyl units, while grasses and angiosperms contain larger amounts of syringyl units (S/V values > 1.0; Table 4.1) (Hedges and Mann 1979). However, it should be noted that thermal alteration may substantially lower the syringyl to vanillyl ratios from all angiosperm plant tissues and that these lower ratios have been shown to fall within the range observed in the aerosols of this study (0.35-0.45) (Kuo et al. 2008b). Hence, both biomarker ratios of solvent-extractable anhydrosugars and methoxyphenols point to the dominant vegetation (grasses and angiosperm shrubs) burned in the wetland wildfire.

In addition to levoglucosan, concentrations of other organic markers, potassium and calcium increased by factors of 2-13 within 1-2 days of the start of the fire and dropped to pre-fire levels 3 days after the peak event. Strong relationships (r^2 = 0.63-0.88, not shown) were observed between levoglucosan and potassium, "free" methoxyphenols, and TC during the entire sampling event, confirming a shift in composition of the fine aerosol fraction during the peak of the fire. The presence of cutin acids (the long-chain fatty acids that comprise the cuticle of plant materials (Goñi and Hedges 1990)) in pre-fire aerosols and their absence during the peak of the event further support a change in the composition of POA during the fire event. This suggests that cutin acids are an appropriate tracer of non-combustion plant-derived POA (e.g., plant fragments). However, further research must be done to further examine this relationship.

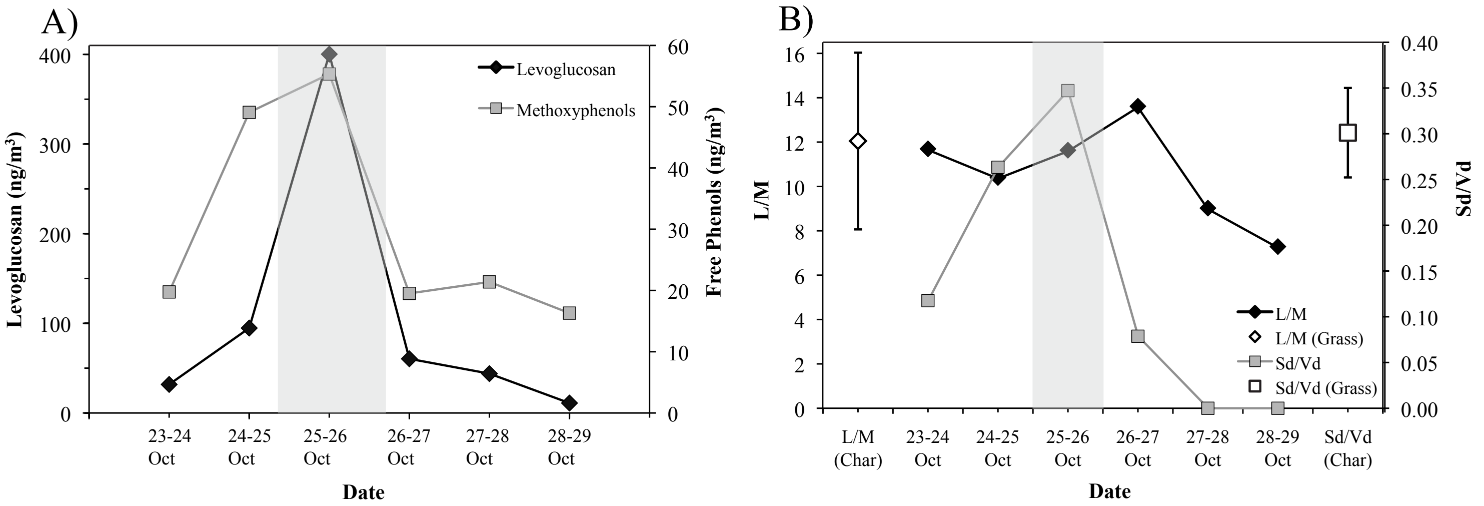

Figure 4.4: Evolution of BB biomarkers across the sampling period. Area marked in grey is the peak during the period of maximum burning conditions (Oct 25-26), when wind backward-trajectories also coincided with the direction of the receptor site. A) Levoglucosan and free methoxyphenol concentrations peak during the period of maximum burning conditions. B) Source signature ratios of levoglucosan to mannosan (L/M) correspond to those of grass charcoals collected at the burn site, whereas syringic acid to vanillic acid ratios (Sd/Vd) suggest that softwood are the main contributor to the BB-derived aerosols.

Table 4.1: Range of parameters of lignin phenols and anhydrosugars for different source materials modified from Shakya et al. (2011).

Parameter	**Gymnosperm Wood**	**Nonwoody Gymnosperm Tissue**	**Angiosperm Wood**	**Nonwoody Angiosperm Tissue**	**References**
S/V	0.01	0.03-0.24	1.90-2.44	0.10-2.00	(Alberts et al. 1991, Goñi and Hedges 1992)
C/V	0.01-0.04	0.08-0.11	0.01-0.08	0.07-1.73	(Alberts et al. 1991, Goñi and Hedges 1992)
(Ad/Al)v, (Ad/Al)s		**Fresh Plant Material**	**Altered Plant Material**		(Louchouarn et al. 1999, Hedges et al. 1988, Goñi and Hedges 1992)
		0.1-0.2	> 0.5		
L/M	**Brown Coal**	**Combustion of Angiosperm Wood**	**Combustion of Gynmosperm Wood**		(Kuo et al. 2011a, Fine et al. 2001, Louchouarn et al. 2009)
	> 50	11-83	3-6		

Despite the fact that measurements of “free” methoxyphenols is now common in atmospheric literature (e.g. (Ward et al. 2006)), to our knowledge, the measure of polymeric lignin has been performed only once in aerosols, under background summer conditions (Shakya et al. 2011). Although never quantified, it is expected that macropolymers, such as polymeric lignin, contribute a significant fraction of the PM emitted from burning (Simoneit et al. 1993). Because of the possibility of oxidation reactions (as with the individual biomarkers), the chemical functionality of model macropolymers are likely to be altered, leading to an overall shift in functionality without a significant change in total organic mass (Jimenez et al. 2009, Kroll et al. 2011). The ratios of polymeric lignin phenols (S/V, C/V) in these aerosols suggest that the main source of polymeric lignin is angiosperm material, which agrees with previously reported ratios in ambient Houston aerosols (Shakya et al. 2011) and with published ratios of source materials for angiosperms (Table 4.1) (Hedges and Mann 1979). Although source signature ratios agree with published background ratios, concentrations throughout the plume event are two orders of magnitude larger (149 ± 40 ng m^{-3}) than previously reported in fine aerosols in Houston (<1 ng m^{-3}) (Shakya et al. 2011), suggesting that polymeric lignin is released during biomass burning events. Polymeric lignin comprises 73-91% of total lignin present in aerosols over the fire event. The proportion of “free” monomeric lignin methoxyphenols to polymeric lignin is significantly higher during the period of the fire, comprising up to 30% of total lignin phenols during the peak of the event (Figure 4.5). This higher percentage of free methoxyphenols within the plume is not surprising, as polymeric lignin can be degraded into smaller components by burning conditions (Simoneit et al. 1993).

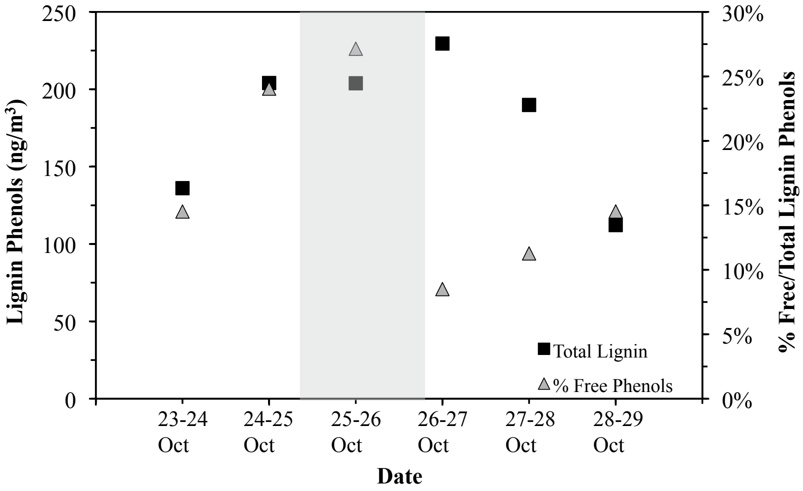

Figure 4.5: Total lignin phenol concentrations increase during the period of maximum burning, while the percent of free to total lignin phenols increase during this period as well.

Stable isotopic signatures of organic carbon in the aerosol samples varied throughout the sampling period, becoming slightly enriched during the peak fire event. The signatures measured in the aerosol samples, between -26.9 and -25.9‰, suggest a mixed source of marsh plant material contributing to the ^{13}C signature of these aerosols. The dominant salt marsh plant found within regularly flooded low marshes along the Gulf of Mexico is the C_4 plant *Spartina alterniflora* ($\delta C^{13} \approx -12.8‰$) (Benner et al. 1987, Tiner 1999). Although regularly flooded low salt marshes along the Texas Gulf Coast are dominated by monocultures of *Spartina alterniflora*, irregularly flooded high marshes are made up of multiple plant assemblages including C_3 plants *Batis maritima* ($\delta C^{13} \approx$ -26.7‰) and *Iva frutescens* ($\delta C^{13} \approx$ -25.4‰) (Winemiller et al. 2007, Ember et al. 1987). Because the ecological structure of marshes in the region includes a mixture of C_3 and C_4 plants, mixed contribution of C_3 and C_4 plant organic matter in fire aerosols can be expected. Using Equation 2, the calculated stable carbon isotopic signatures of BB aerosols range from -26.21 to -24.95‰ (Table 4.2). To further elucidate the contribution of BB on aerosol samples in the downwind plume, mixing models can be applied.

4.3.2 Mixing Models of Biomass Burning Sources

To estimate the respective inputs of each plant source to the plume aerosols, an isotope mixing model from Equation 4.1 was applied to better understand the potential input of materials burned, including potential fractionation. The data (Table 4.2) suggest that during the maximum of the plume over Houston (considering fractionation), the amount of BB aerosols attributed to C4 plants is 48.7 ± 16.4%.

Taking into account isotopic fractionation of BB aerosols (Das et al. 2010) slightly increases the appropriation to C_4 plants (Table 4.2), but it does not account for the vast majority of C_4 plants (*Spartina alterniflora*) present within the community structure of low-tide marshes expected to contribute to BB in this scenario. This apparent lack of C_4 plant contribution to BB may not reflect influences of external mixing or the community structure of the wetland but rather the differences in burning efficiency of the plant types within the wetland. For example, C_4 plants are mostly grasses, which can burn more completely than the woody plant materials of C_3 plants. If, because of different burning efficiency, one plant source contributes selectively and predominantly to POA, then that plant source will be over represented in receptor model reconstruction. Another potential cause for this discrepancy is that parent charcoals are not completely accurate end members for aerosol samples; they may in fact be a proxy end-member that is more heterogeneous than the resulting aerosols. For example, if the charcoal is depleted of much of its low-temperature BB biomarkers due to their high-water solubility and/or degradability (these components degrade on weekly time-scales in incubation studies (Norwood et al. 2013)), it may become an unsuitable end member for the BB aerosols.

One way we can explore the idea of the parent charcoals as accurate end members for aerosol samples is to examine the differences and similarities in the ratios of BB and plant-based biomarkers between the charcoals and the aerosols. Relative biomarker ratios may evolve rapidly over a span of only a few hours within a smoke plume, thus affecting the capacity of each individual biomarker, when used in isolation, to trace accurately biomass-derived POA in the atmosphere. This idea can be further explored by assessing the reactivity of BB biomarkers in the atmosphere.

Table 4.2: Proportion of aerosols attributed to BB and their sources based off isotopic mixing models.

Date (2013)	**% BB (TOC_{total}-TOC_{bkg})**	**$\delta^{13}C_{burnt}$ (Eqn 2)**	**%C_4 without fractionation (Eqn 1)**	**Average %C_4 in BBA (including fractionation range, Eqn 1)**	**Standard Deviation %C4 in BBA (from fractionation)**
10/23-10/24	0.0%	-26.86	N/A	N/A	N/A
10/24-10/25	37.1%	-26.37	16.5%	30.8%	10.4%
10/25-10/26	49.4%	-24.95	26.1%	48.7%	16.4%
10/26-10/27	0.0%	-26.53	N/A	N/A	N/A
10/27-10/28	33.7%	-25.80	20.4%	38.0%	12.8%
10/28-10/29	0.0%	-26.21	N/A	N/A	N/A

4.3.3 Reactivity of Biomass Burning Components

The ratio of anhydrosugars to free methoxyphenols can be indicative of the selective degradation and differences in sources of these components. Because it is anticipated that anhydrosugars (levoglucosan and its isomers) are less reactive than the lignin-derived methoxyphenols (Hennigan et al. 2010, Hoffer et al. 2006, Lauraguais et al. 2012), the ratio of total anhydrosugars to total methoxyphenols may offer a plume-aging tracer. Additionally, anhydrosugar isomers (particularly levoglucosan and mannosan) may show different stability to oxidative conditions (Kuo et al. 2011a), leading to altered combustion source signatures (sugar isomer ratios) during plume aging. A substantial increase was observed in the ratio of levogulocsan to free methoxyphenols (enrichment factor of ~20) between parent charcoals and POA at the receptor site, which may serve as an indication that the two biomarker groups are characterized by different degradation rates (Hennigan et al. 2010, Zhao et al. 2014). Therefore, the reactivity of both levoglucosan and the methoxyphenols must be taken into account.

Previous work showed that levoglucosan can be degraded by hydroxy radicals (OH) in the atmosphere on hourly to daily scales (Hennigan et al. 2010). If it is assumed that the reaction rate constant between levoglucosan and OH is 1.1×10^{-11} cm^3 molec^{-1} sec^{-1} (Knopf et al. 2011), that the ratio of levoglucosan to methoxyphenols in charcoal is representative of the same ratio in the emitted PM, and that the average atmospheric OH concentration is 1×10^6 molecules cm^{-3}, then the average reaction rate constant for the OH-methoxyphenol reaction is 6.1×10^{-11} cm^3 molec^{-1} sec^{-1} for a transport time of 16 hrs (based on Equation (4.3)). Methoxyphenol degradation occurs rapidly (Yang et al. 2016, Lauraguais et al. 2012), with an observed rate constant for syringol (9.7×10^{-11} cm^3 molec^{-1} sec^{-1}) being of the same order of magnitude but larger than the value presented here. This work represents one of the first efforts to track methoxyphenol degradation after a high input event. Conversely, if levoglucosan were a truly conservative tracer, as is assumed in some source apportionment models, the required reaction rate constant for methoxyphenols would decrease slightly to 5×10^{-11} (cm^3 molec^{-1} sec^{-1}). It should be stressed that it is possible that the application of the biomarker ratios in charcoal to the emitted aerosols is inappropriate as other atmospheric loss processes also may contribute to the change in the levoglucosan to methoxyphenol ratio.

Lignin monomer ratios can be used as a biomass burning plume-aging metric, similar to other airmass "ages" used in the atmospheric chemistry community (such as the ratio of nitrogen oxides to total reactive nitrogen (Kleinman et al. 2007)). For example, it is expected that the acid (Ad) to aldehyde (Al) ratios from vanillyl (V) and syringyl (S) methoxyphenol "families" ($[Ad:Al]_v$ and $[Ad:Al]_s$, respectively) increase with plume processing, whereas the total syringyl (Sd + Sl) to vanillyl (Vd + Vl) ratio (S/V) decreases. [Ad:Al] values of fresh lignin usually fall within a range of 0.1-0.2, whereas S/V values for angiosperms range between 0.1-2.44 (see Table 4.1). Shifts in these ratios in atmospheric settings are analogous to the well documented increase in [Ad:Al] and decrease in S/V during oxidative lignin degradation in soils and in aquatic systems (Hernes and Benner 2003, Houel et al. 2006, Hedges et al. 1988, Opsahl and Benner 1998). Although white rot fungi have been shown to increase the yield of acidic byproducts through side-chain oxidation (using lignin peroxidase (Hedges et al. 1988)), abiotic degradation processes (such as photooxidation, OH oxidation, or thermal degradation) also lead to side chain oxidation (Lanzalunga and Bietti 2000) . These degradation processes increase [Ad:Al] ratios and decrease S/V ratios in dissolved and particulate vascular plant matter (Hernes and Benner 2003, Kuo et al. 2008a, Opsahl and Benner 1998). Particularly, $[Ad:Al]_s$ is sensitive to thermal alteration, while unaffected by biodegradation (Kuo et al. 2008b, Opsahl and Benner 1998).

Here, we see shifts in $[Ad:Al]_s$ and [S/V] during the peak of the fire plume, which confirm that inputs of thermally-altered polymeric plant components are pronounced during the height of the event (Figure 4.6). The $[Ad:Al]_s$ increases by an order of magnitude during the peak of the plume emissions (~0.3 to ~2.7; Figure 4.6), and the relative increase is much larger than observed changes in fire soils pre- and post-burn (Kuo et al. 2008b). The value at the peak of the plume (~2.7) is similar to maximum $[Ad:Al]_s$ measured in cordgrass charcoals at 300˚C (2.4) (Kuo et al. 2008b). S/V ratios, which decrease throughout the plume and increase again afterwards, fall within the reported ranges of degraded angiosperm sources (Figure 4.6) (Kuo et al. 2008b, Opsahl and Benner 1995, 1998).

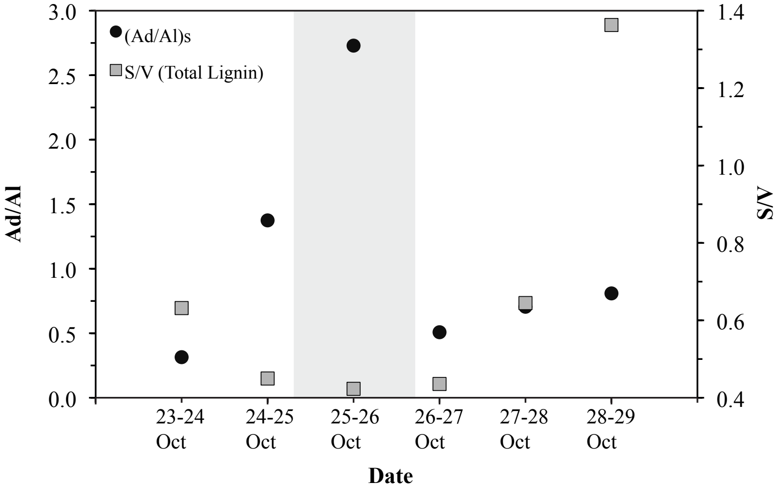

Figure 4.6: Acid (Ad) to aldehyde (Al) ratios from syringyl (S) methoxyphenols, (Ad:Al)s, increase during the period of maximum burning conditions, whereas the total syringyl (Sd + Sl) to vanillyl (Vd + Vl) ratio (S/V) decreases.

Based on peak concentrations during the sampling event and the larger reaction rate constants from the preceding analysis, the initial concentrations in the plume directly after emissions can be estimated using Equation (4.3). These values are 750 ng m^{-3} and 1.9 µg m^{-3} for levoglucosan and methoxyphenols, respectively. If a typical emission ratio of levoglucosan to organic carbon (OC) in BB emissions from softwoods of 3.45 ± 0.15% is considered (Hays et al. 2002, Engling et al. 2006), this value of 750 ng m^{-3} would indicate an approximate OC concentration at the site of the fire of 22.1 ± 13.0 µg m^{-3}, which is equal to the release of ~0.5 tons of aerosol OC (assuming plume height of 1km (Liu et al. 2013)) from the 5,000-acre burn.

The analyses presented here suggest that isotopic mixing models and degradation equations can be used to help elucidate the sources and transformation of BB aerosols in the atmosphere. Consideration of the reactivity of methoxyphenols and other tracers is critical to understand how such tracers impact secondary chemistry as BB plumes are advected downwind and are diluted. The analyses and findings shown here could be strengthened by investigating *in-situ* emissions ratios of different ratios and comparing them to the ratios observed in solid charcoal remains. For example, measures of fire source emissions and downwind plume emissions for the same fire could help to further constrain the *in-situ* degradation model of levoglucosan and methoxyphenols. Higher temporal resolution sampling for a longer duration (in this case, for example, on an hourly or sub-hourly basis over the course of a day or two) would potentially provide insights into changes in loss mechanisms for the BB tracers (e.g., OH versus nitrate radical oxidation). Based on this work, we believe that levoglucosan oxidation must be considered in source apportionment models. For example, these findings could be applied to understanding emissions from wildfires in carbon models and help to constrain mean residence times of levoglucosan and other BB by-products in the atmosphere.

CHAPTER V

NEW INSIGHTS ON THE CHARACTERIZATION AND FATE OF PYROGENIC CARBON DURING TRANSPORT IN AQUATIC AND ATMOSPHERIC ENVIRONMENTS

5.1 Introduction

Inefficient, or incomplete combustion of fire fuels yield pyrogenic carbon (PyC), a heterogeneous continuum of organic materials resulting from the alteration of organic matter due to combustion (Figures 1.1, 3.1; see Chapters 1 and 3). PyC is seldom incorporated in global models, and is left out of traditional views of fires as "net zero carbon emissions events" (i.e. that the CO_2 released from fire events will be sequestered by new generation forest growth) (Santín et al. 2016). Until recently, studies that examine the fate of PyC in the environment have mainly focused on the highly recalcitrant portion of the continuum produced during high-temperature combustion processes (e.g. soot carbon). This carbon comprises a smaller portion of the PyC continuum than historically estimated (Santín et al. 2016, Santín et al. 2015). The lower temperature portion of this continuum (e.g. combustion temperatures < 450˚C) produced mainly during wildfire and prescribed burning events may be the predominant fraction produced during such fires (Alexis et al. 2010), and has been found to be particularly labile and water-soluble (Norwood et al. 2013, Myers-Pigg et al. 2015). This makes low-temperature PyC especially relevant and important to study at environmental interfaces, such as rivers.

Boreal ecosystems hold about one third of global terrestrial carbon (McGuire et al. 2009), and have been suggested as a main region of uptake for rising atmospheric CO_2 (Qian et al. 2010). These systems are especially vulnerable to climatic shifts, and it is projected that fires are increasing in frequency and intensity in these regions (Kasischke 1995, Running 2006, Soja et al. 2007, Kelly et al. 2015). It is important to quantify the effects of disturbances such as fires on carbon cycling, as these disturbances may alter the carbon sequestration potential in boreal ecosystems (Kelly et al. 2015, Hayes et al. 2011).

In boreal forests, around 80% of the area burnt is due to surface fires (Conard and Ivanova 1997), which burn much longer and at lower temperatures (100-400 ˚C) than necessary to create the highly condensed portions of the PyC continuum (Alexis et al. 2006, Czimczik and Masiello 2007, Masiello 2004). Additionally, as forest fires are expected to increase in all major earth systems, especially boreal forests, PyC is extremely important to study in order to understand carbon cycling on a global scale (Santín et al. 2015).

Atmospheric deposition and riverine transport are considered to be the primary transport mechanisms for PyC to oceanic pools, where it is effectively sequestered in the deep ocean dissolved organic carbon pool and/or marine sediments (Santín et al. 2016, Masiello and Druffel 1998, Dittmar and Paeng 2009). During this transport, PyC can be degraded via biotic (e.g. microbial breakdown in rivers) or abiotic (e.g. photodegradation in rivers and atmosphere, hydroxyl radical reactions in atmosphere) processes (Norwood et al. 2013, Wagner and Jaffé 2015, Myers-Pigg et al. 2016, Myers-Pigg et al. 2015, Stubbins et al. 2012, Hennigan et al. 2011).

Quantitative estimates of this degradation are still a work in progress (Masiello and Louchouarn 2013). Here, I present new flux estimates of PyC in interfaces of terrestrial, aquatic and atmospheric environments, with special consideration to degradation of PyC throughout transport. I focus on the Arctic ecosystem, as new estimates of PyC production account for up to ~30% of the total fire-affected carbon in boreal forests (Santín et al. 2015).

5.2 Methods

Data used for this chapter were derived from a combination of new data, and the synthesis of literature values of PyC. For low-temperature PyC, this was determined by biomarker analysis of levoglucosan, an exclusive by-product of biomass combustion, using methods and samples from the previous chapters of this dissertation. In addition levoglucosan analysis was preformed on the same samples analyzed for BPCA in Stubbins et al. (2015). Briefly, levoglucosan was isolated from water samples by liquid-liquid extraction techniques (Norwood et al. 2013, Myers-Pigg et al. 2015), and from aerosol samples by accelerated solvent extraction (ASE) (Shakya et al. 2011, Louchouarn et al. 2009, Myers-Pigg et al. 2016). Levoglucosan concentrations in water samples were scaled to low-temperature Py-DOC estimates using ratios of levoglucosan production to Py-DOC production in experimental charcoals from 250˚C (Norwood et al. 2013, Myers-Pigg et al. 2015). Environmental partitioning coefficients (K_ds) for levoglucosan (Chapter 3; Table 3.1) were used in conjunction to dissolved PyC estimates to calculate low-T Py-POC concentrations and fluxes.

High- and low-temperature PyC biomarkers (BPCAs and levoglucosan, respectively) were also measured across a sample set from the Arctic-GRO archive from 2009. The extraction of these biomarkers followed methods outlined above for levoglucosan, and using BPCA analyses from Stubbins et al. (2015).

Degradation of low-temperature PyC was taken into account in river and aerosol samples by applying a first order degradation equation using experimental degradation rate constants from the literature (Methodology outlined in Chapter 2; Myers-Pigg et al. (2015) for rivers, and for aerosols, Chapter 4; Myers-Pigg et al. (2016)). To find the time in which potential degradation of aerosol PyC occurs in the Arctic, the degradation rate of levoglucosan by hydroxyl radicals, as determined by Knopf et al. (2011), was applied in a first order degradation equation from Myers-Pigg et al. (2016) with original concentrations of forest fire levoglucosan emissions from Myers-Pigg et al. (2015) and average summer levoglucosan concentrations in the middle of the Arctic Ocean from Yttri et al. (2014) and Fu et al. (2013), and solved for transit time.

Flux estimates in Table 5.1 were determined from literature sources (Preston and Schmidt 2006, Shvidenko et al. 2011, Samsonov et al. 2005, Conard et al. 2002, Stubbins et al. 2015, Elmquist et al. 2008, Hilscher and Knicker 2011, Myers-Pigg et al. 2015, Jurado et al. 2008, McClelland et al. 2016, Santín et al. 2015) and estimates of degradation during transport were calculated when possible. Fuel-affected by fires (CA) was determined per hectare from Santín et al. (2015) and Samsonov et al. (2005)

(average 1.9 x 10^{-3} ± 1.8 x 10^{-4} Tg C km^{-2}) and average annual areas burnt from Shvidenko et al. (2011) (Eurasian forests), Conard et al. (2002) (North American forests) and Abbott et al. (2016) (all boreal forests). PyC production from fire-affected fuels was calculated using the PyC/CO_2 range of 5-7% (Preston and Schmidt 2006), and PyC/CA ratios of 5-15% (Santín et al. 2016). CO_2 release was estimated from C-CO_2 emissions (84.6% of total carbon (C) emissions as CO_2) from Shvidenko et al. (2011) using C emissions presented in Shvidenko et al. (2011) (Eurasian forests) and Conard et al. (2002) (North American forests). Carbonaceous aerosols (50-70% of total aerosols) and EC aerosols (7-15% of total aerosols) were determined from emission ratios using total aerosol emissions per unit area (4 ± 3 x 10^{-5} Tg C km^{-2}) in Samsonov et al. (2005). Deposition of aerosol PyC for latitudes 60˚- 90˚ N were determined from Jurado et al. (2008). Theoretical PyC solubilization was calculated from water-soluble organic matter (Py-WSOM) produced from charcoals and leachates (~3-4% of PyC produced for 250-350˚C) (Norwood et al. 2013, Hilscher and Knicker 2011). Pan-Arctic estimates of exported PyC from rivers was determined by scaling literature values of low (Myers-Pigg et al. 2015) and high (Stubbins et al. 2015) temperature Py-DOC from monitored watersheds to the entire Pan-Arctic region. Estimates of Py-POC were determined from average K_d values calculated for low-temperature Py-POC biomarkers (Myers-Pigg et al. 2016- In Review) (Table 3.1), and for high-temperature Py-POC using an average of previous methods outlined in Chapter 3. Briefly, two methods were used: 1) sediment BC:SOC ratios (Elmquist et al. 2008) and recent POC flux estimates (McClelland et al. 2016) were used to calculate Py-POC fluxes, and 2) partition coefficients of PyC determined by BPCAs and levoglucosan from Chapter 3 (Table 3.1). DBC concentrations (Stubbins et al. 2015), low-temperature Py-DOC concentrations (Myers-Pigg et al. 2015), and recent POC flux estimates (McClelland et al. 2016) were used to calculate Py-POC fluxes. Numbers in Table 5.1 are presented to two signifigant digits, as signifigance levels varied throughout different studies and methods used, and the confidence in our error estimates were only availabile to this digit. Error estimates were propagated from standard deviations in concentration measurements to fluxes presented in this chapter. Additionally error in percentages used were also propagated to formulate flux measurements. For example, the calculation for theoretical solubilization of $PyC_{charcoal}$ was determined by solving for the low and high ends of possible solubilization based on $PyC_{charcoal}$ fluxes (17 ± 7.1 TgC yr^{-1}), and literature solubilization percentages- 3-4% (Norwood et al. 2013, Hilscher and Knicker 2011), then determining and average and difference (error) based on these parameters. These estimates are merely a first approximation of fluxes from the boreal system, and must be considered with caution. However, the estimates presented in Table 5.1 match fairly well with previous literature values (such as those presented in Preston and Schmidt (2006), etc).

5.3 Results and Conclusions

5.3.1 Coupling of Py-DOC in Arctic Rivers

In Arctic river systems, Py-DOC from the entire PyC continuum (based on levoglucosan and BPCA biomarkers as proxies for low- and high-temperature Py-DOC, respectively) is correlated throughout various flow regimes in 2009 (Figure 5.1, $n = 21$, $R^2 = 0.53$, $p < 0.05$). River scale differences in this relationship may be attributed to differences in contribution of DBC from fires versus anthropogenic sources (Ding et al. 2014b) in each watershed. The variation between rivers may also reflect decoupling of export characteristics between the two portions of Py-DOC at various times of the year and between different river systems.

The fact that there is a relationship between low-temperature Py-DOC and DBC in river systems is first a confirmation of the link between the export of DOC and all portions of Py-DOC (Jaffé et al. 2013, Myers-Pigg et al. 2015), and secondly, supports the suggestion that the export of these components are somehow linked (as suggested in Chapters 2, 3).

The link between PyC markers of different temperatures along the continuum has not been shown in depositional environments; for example, deposited levoglucosan and PAHs are decoupled in estuarine sediments (Kuo et al. 2011b), BPCAs and PAHs are decoupled in marine sediments (Hanke et al. 2016), and GBC and PAHs are decoupled in lake sediments (Louchouarn et al. 2007). However, the preliminary relationship in rivers between DBC and low-temperature Py-DOC (Figure 5.1) points to an apparent correlation in the export mechanisms of low-temperature Py-DOC and high temperature Py-DOC (DBC) and, therefore, confirms that independent biomarkers of low and high temperature Py-DOC are correlated (and are both correlated to DOC), and suggests that PyC is entrained as a mixture of materials with different theoretical behaviors (such as dissolution, sorption, and reactivity).

Table 5.1 PyC fluxes in the Arctic.

	Flux TgC yr^{-1}	Fluxes Derived From
Biomass as Fire Fuel in Arctic Forests	180 ± 18	Santín et al. (2015), Samsonov et al. (2005), Shvidenko et al. (2011), Conard et al. (2002), and Abbott et al. (2016)
CO_2, from fire	140 ± 13	Shvidenko et al. (2011), Conard et al. (2002)
Carbonaceous $PyC_{aerosol}$ Emissions	2.6 ± 3.1	Samsonov et al. (2005)
Atmospheric Deposition of $PyC_{aerosol}$ to Ocean (60˚-90˚N)	0.05 ± 0.02	Jurado et al. (2008)
Elemental Carbon (EC) $PyC_{aerosol}$ Emissions	0.54 ± 0.47	Samsonov et al. (2005)
On-site $PyC_{charcoal}$ production	17 ± 7.1	Preston and Schmidt (2006), Santín et al. (2016)
Theoretical Solubilization of $PyC_{charcoal}$	0.71 ± 0.38	Norwood et al. (2013), Hilscher and Knicker (2011)
Respiration of low-temperature Py-DOC during riverine transport	0.49 ± 0.025	Myers-Pigg et al. (2015)
Low-Temperature Py-DOC exported to Arctic Ocean	0.86 ± 0.049	Myers-Pigg et al. (2015)
Low-Temperature Py-POC exported to Arctic Ocean	0.013 ± 0.041	Myers-Pigg et al. (2015), Myers-Pigg et al. (2016- In Review)
High-Temperature Py-DOC exported to Arctic Ocean	2.8 ± 0.25	Stubbins et al. (2015), Myers-Pigg et al. (2016- In Review)
High-Temperature Py-POC exported to Arctic Ocean	0.18 ± 0.12	Elmquist et al. (2008), Stubbins et al. (2015), McClelland et al. (2016), Myers-Pigg et al. (2016- In Review)

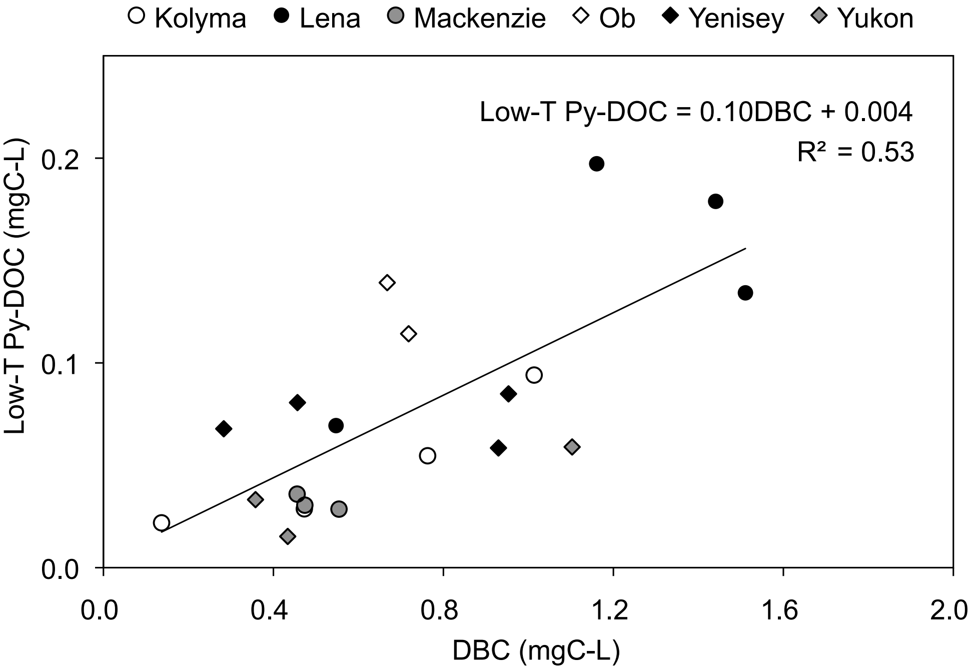

Figure 5.1: Arctic River Py-DOC as determined by low and high-temperature components is correlated in the dissolved phase for the six major Arctic Rivers. DBC concentration are from Stubbins et al. (2015).

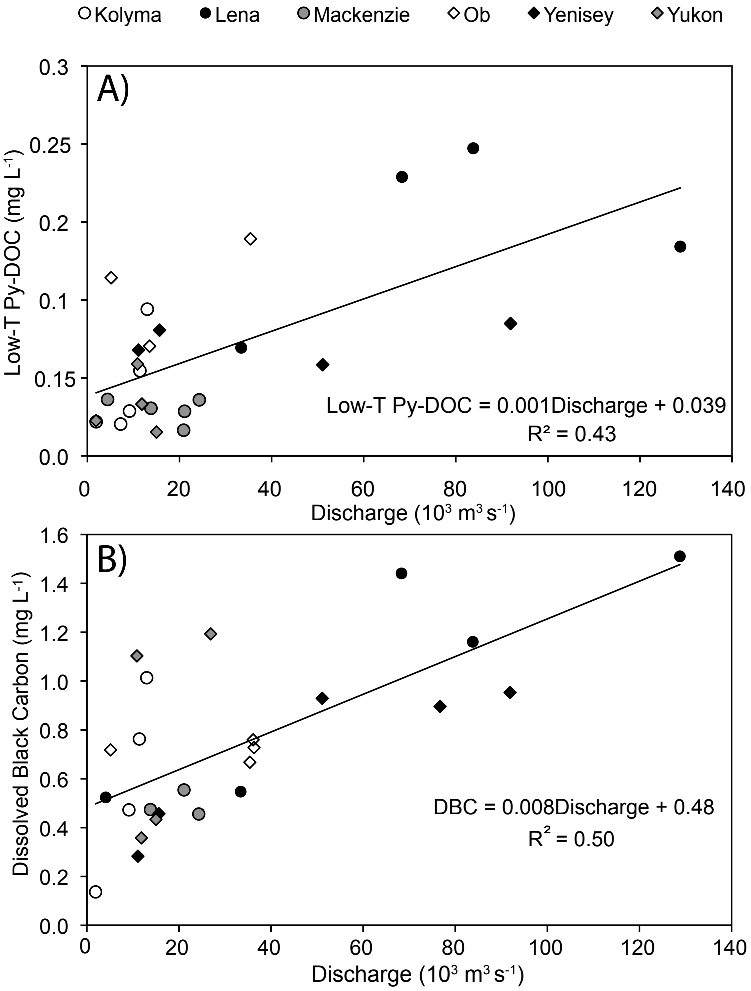

Figure 5.2 Py-DOC versus discharge in Arctic Rivers in 2009. A) Low-temperature Py-DOC versus discharge. The relationship between low-T Py-DOC and discharge follows a similar trend as the 2004-2006 samples, but with lower low-T Py-DOC concentrations. B) High-temperature (Dissolved Black Carbon, DBC) Py-DOC versus discharge in 2009. DBC concentrations increase with increasing discharge (Stubbins et al. 2015).

The relationship of low-temperature Py-DOC and discharge is similar to that reported by Myers-Pigg et al. (2015) (Figure 5.2). Differences in this relationship presented in 2009 versus the previous relationship from 2004-2006 can be attributed to changing inter-annual variability in hydrodynamics within the systems (Wrona et al. 2016). In rivers where the relationship of low-temperature Py-DOC and DBC are especially weak, i.e. the Yenisei River, the ratio of the most condensed portion of BPCAs (Benzenehexacarboxylic acid; B6) (Schneider et al. 2010) to levoglucosan increases with increasing discharge (data not shown), suggesting that as discharge increases, the quality of PyC is becoming more refractory. This may be due to different sources or mobilization of the components of PyC in this system, such as increasing contribution of PyC from deeper soil layers with increasing discharge. Additionally, the size fraction of Py-DOC may play a role in the relationship between low- and high-temperature Py-DOC, as more condensed DBC is associated more with high-molecular weight DOM (Wagner and Jaffé 2015). The composition and sources of DOM varies in the different size fractions in Arctic Ocean estuaries (high-molecular weight is more planktonic derived, while low molecular weight is terrestrial in origin) (Amon and Meon 2004), suggesting that the high-temperature Py-DOC may be preferentially degraded during transport from high to low molecular weight size fractions (Wagner and Jaffé 2015), skewing the relationship between high- and low-temperature Py-DOC in rivers. However, further research may help elucidate these varying mechanisms.

In addition, including compound specific isotopic work to determine sources and ages of the different portions of Py-DOC within the rivers may help determine if the apparent correlation of Py-DOC in rivers is an artifact of its relationship with discharge mobilizing different pools of OM from within a watershed. For example, if high-temperature PyC is more entrained in SOM, while low-temperature PyC remains on surface layers, increased discharge would still increase the export of both components, but presumably the high temperature Py-DOC would be older due to it's longer potential residence time in the environment. However, if their isotopic signatures show similar ages and/or sources, then one could conclude that they are incorporated in similar pools and exported as a whole (as suggested by Chapter 3).

5.3.2 Further Understanding for Riverine Fluxes from the Arctic

Estimates of PyC created in the boreal region in Figure 5.3 are on the higher end of the range previously estimated (7-17 Tg yr^{-1}) (Preston and Schmidt 2006). This may be a function of both including a higher range of conversion rate of CA to PyC (5-15% PyC/CA) (Santín et al. 2016) and larger areas burnt within the affected regions compared to previous decades (Shvidenko et al. 2011). However, despite this, the maximum theoretical yearly solubilization of PyC to Py-DOC much less than the yearly observed Py-DOC flux, suggesting there must be additional inputs of Py-DOC to rivers than pure solubilization of fresh charcoals. This may be due additional solubilization of older PyC from the ecosystem or from within soils (Hockaday et al. 2006, Abiven et al. 2011) during spring thaw. For example, a 100-yr old char produces 0.2% of DOM when incorporated in soils within 2 days (Hockaday et al. 2007), suggesting that older chars could add an additional 3% of Py-DOM to the system during the average length of the freshet period. This solubilization mechanism may help to explain the lack of observable chars in boreal soils (Czimczik et al. 2003), as bulk charcoal PyC is broken down into smaller, more soluble components.

Yearly Py-DOC export estimated from the entire continuum is nearly a quarter of the yearly PyC production in the Arctic (Figure 5.3- 3.7 TgC yr^{-1}, the sum of Low-T Py-DOC and DBC). Py-DOC export from the Arctic, therefore, comprises a large proportion of worldwide estimates of riverine Py-DOC fluxes (~13 % total annual worldwide Py-DOC fluxes, Santín et al. (2016)), congruent with the importance of total DOC export and discharge from the Pan-Arctic on a global stage (11% of total DOC fluxes are from the Pan-Arctic (Holmes et al. 2012, Raymond and Spencer 2015), 10% of total river discharge is from Arctic rivers (Holmes et al. 2012)).

The actual translocation of PyC from terrestrial to aquatic systems may actually be a larger proportion of the PyC produced once degradation is considered. Here, we assume that the loss of low-temperature Py-DOC estimated from Siberian Rivers (Myers-Pigg et al. 2015) is scalable to the Pan-Arctic watershed, and that this loss is due to respiration. This thought exercise represents an upper estimate of the total low-temperature Py-DOC that might be respired during transport to the Arctic Ocean (Figure 5.3). It is known that DBC is photo-degradable on time-scales of riverine transport (Stubbins et al. 2012). Ward et al. (2014) estimate that 10.5 ± 2.5 % of DBC is degraded to CO_2. If we assume that the amount of DBC degraded to CO_2 happens on riverine transport timescales, then the amount of DBC remineralized to CO_2 nearly doubles the estimated respiration of Py-DOC during riverine transport in Figure 5.3 (0.3 ± 0.07 TgC yr^{-1}).

The majority of DBC may be transformed by photodegradation into partially oxidized components (Ward et al. 2014, Stubbins et al. 2012), potentially explaining the accumulation of smaller condensed aromatics in oceans (Masiello and Louchouarn 2013, Ziolkowski and Druffel 2010). These components may also increase riverine respiration rates through priming (Wagner and Jaffé 2015). The release of partially oxidized DBC from soils may also be of critical importance for the overall flux of Py-DOC from terrestrial to aquatic systems (Hockaday et al. 2006, Abiven et al. 2011). This release of Py-DOC from soils may help explain the discrepancy of the theoretical solubilization of PyC and the measured export of Py-DOC from river systems (Figure 5.3).

High- and low-temperature PyC biomarkers are similarly associated to the particulate or dissolved phase, as determined by partition coefficients (Table 3.1), again suggesting that on basin-level scale that the export of Py-DOC and Py-POC may be coupled (Chapter 3). While PyC is primarily exported in the dissolved phase for high- and low-temperature components of the PyC continuum, Py-POC exported from Arctic systems should not be ignored and could account for ~10% of the PyC exported from Arctic watersheds (determined from averaging the results of Py-POC flux estimates from Myers-Pigg et al. (2016- In Review) and Elmquist et al. (2008); see Figure 5.3). The export of Py-POC from the Pan-Arctic may be related to erosion, which may be increasing in Arctic systems with a changing climate (Guo et al. 2007). The apparent increase in association of PyC with the particulate phase and POC content with transport from rivers to oceans (as suggested in Chapter 3) supports the theory that sorption of Py-DOC to the particulate phase may be an important loss process of Py-DOC in oceans (Coppola et al. 2014).

5.3.3 Further Understanding for Atmospheric Fluxes from the Arctic

The calculated CO_2 emissions from fires presented here (Figure 5.3) are in the same range, though slightly lower than recent flux estimates from various emission models (250 Tg yr^{-1}, error not reported) (Abbott et al. 2016), validating the methods used to calculate CO_2 emissions from the region. PyC aerosol emission flux estimates are within the range previously reported (2-2.5 Tg yr^{-1}) for the boreal region (Preston and Schmidt 2006). Deposition of aerosol PyC for latitudes 60˚- 90˚ N determined from Jurado et al. (2008) account for only ~2% of estimates of PyC aerosol emissions (Figure 5.3). Therefore, deposition of PyC from atmospheric sources needs to be further researched, with this potential for degradation relevant on transport timescales in mind. It has been estimated that around half of oceanic deposition of atmospheric PyC occurs over continental margins, but there is no clear estimate of land-based versus oceanic deposition of BB aerosols at this time (Santín et al. 2016). The apparent discrepancy between deposition and emissions based off the flux estimates here points to degradation as a main loss process of aerosol PyC during atmospheric transport.

The degradation of levoglucosan from biomass burning aerosol emissions may be of key importance when using levoglucosan as a biomarker to understand effects of fires on atmospheric aerosol concentrations (Myers-Pigg et al. 2016). For example, atmospheric concentrations of levoglucosan over the Arctic Ocean (~0.14 ng/ m^3 average from Yttri et al. (2014) and Fu et al. (2013)) can be compared to near-source concentrations from a fire plume near the ZOTTO tower in Central Siberia (average 1.97 $\mu g/m^3$ from Myers-Pigg et al. (2015)) to explore potential degradation of aerosol low-T PyC within a fire plume. If we assume that concentrations of levoglucosan is fairly consistent over the Arctic Ocean, and that air-mass trajectories from boreal forest fires reach the Arctic Ocean (e.g. Zangrando et al. (2013), Stohl et al. (2007), Hu et al. (2013), and Evangeliou et al. (2016)), then we can roughly approximate how important degradation is on estimating the contribution of biomass burning on primary organic aerosol (BB POA) concentrations. Using the first order degradation equation from Myers-Pigg et al. (2016), we estimated the transport time (t) needed to account for the 99% loss of levoglucosan observed from fire source to Arctic Ocean, which is 10 days. This is consistent with transport time for air masses from boreal zone fires to the Arctic (e.g. Warneke et al. (2010)). This confirms prior reports that levoglucosan losses are rapid and substantial during atmospheric transport (e.g. Hennigan et al. (2010), Myers-Pigg et al. (2016)). As estimates of BB POAs is primarily conducted using tracers such as levoglucosan, coupled with the current assumption that levoglucosan is a conservative tracer, it is important to understand the degradation of levoglucosan relative to bulk BB POAs. For example, if BB POA does not degrade at the same rate as levoglucosan, then its importance may be underestimated in the atmosphere. Alternatively, if bulk BB POA is degraded in a similar fashion to levoglucosan, then the degradation of BB POA during transport may be an important loss term to consider.

5.3.4 Synthesis of PyC Fluxes from the Arctic

It is especially important to understand the impacts of fire on boreal carbon cycling, as even a small change in carbon emissions from the region could turn it from a net sink into a net source of carbon to the atmosphere (Kelly et al. 2015). If we are to fully understand the impact fires have on carbon cycling, we must take into account the role of PyC in carbon budgets. To do this, we must understand fluxes and pools of the entire PyC continuum (Santín et al. 2016).

In-situ degradation of low-T PyC may be of importance when considering atmospheric and riverine PyC fluxes (Figure 5.3). This work synthesizes the current state of understanding PyC dynamics with special consideration to carbon cycling in the Arctic. It also highlights the potential importance of the degradation of PyC produced during wildfire conditions. Lower temperature components of PyC may be more susceptible to degradation and their degradation may be of importance when budgeting the impact of PyC on carbon cycling.

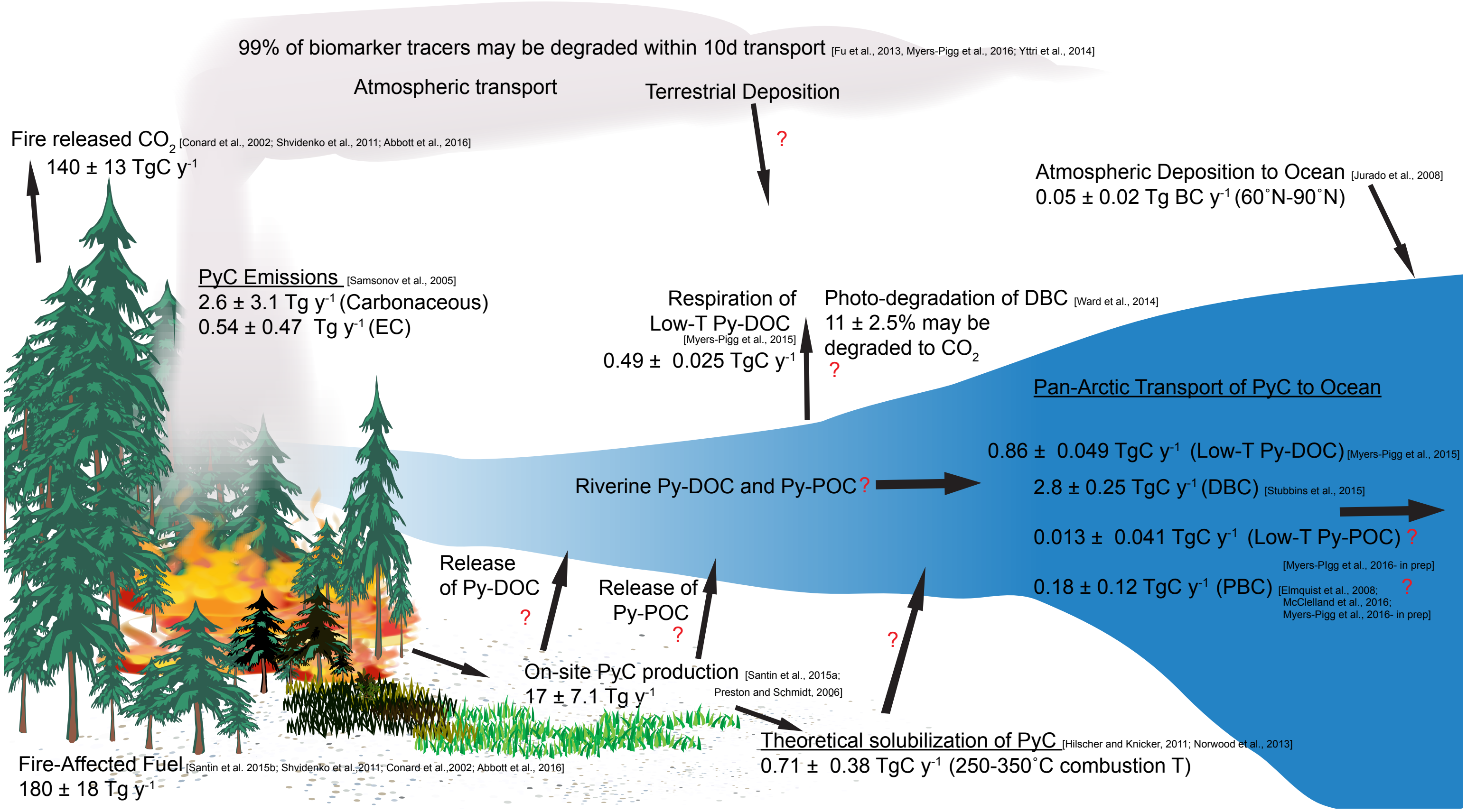

Figure 5.3: PyC fluxes with special consideration for boreal regions. See text for discussion on how numbers are derived.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

6.1 Synthesis with Special Consideration to Low-Temperature PyC

Fires create a spectrum of chemically unique carbon species with different physicochemical characteristics than the parent material through incomplete combustion conditions. This thermally altered organic carbon varies in molecular structure and environmental functionality, creating distinct analytical challenges for measuring PyC in the environment. It is now documented that there is both biodegradation and photodegradation can affect PyC pools during transfer from terrestrial to aquatic systems (Ward et al. 2014, Myers-Pigg et al. 2015), and new insights on PyC biomarkers degradation in the atmosphere suggest that degradation of PyC during atmospheric transport is of importance (Myers-Pigg et al. 2016).

Low-temperature PyC is currently understudied in the literature. The importance of the release of organic carbon from low-temperature combustion conditions, such as those experienced during natural fire events needs to be further addressed. The flux estimates presented in this dissertation represents a first attempt at understanding PyC cycling with consideration of low-temperature PyC. However, worldwide estimates need to be determined, as the importance of low-temperature PyC on the dynamics of PyC cycling may vary with environment.

The translocation of PyC from terrestrial to aquatic systems may be a key process in understanding PyC cycling and dynamics in the environment. For example, PyC in frequently burned systems comprise only ~2-5% of the SOM pool (Czimczik and

Masiello 2007), while production of PyC can reach up to ~28% of fire-affected fuels during burning events (Santín et al. 2015). Although there are a variety of Py-DOC studies in rivers (e.g. Jaffé et al. (2013), Dittmar et al. (2012a), Stubbins et al. (2015)), and now at least two studies in existence that measure suspended Py-POC in river systems (Wagner et al. 2015, Myers-Pigg et al. 2016- In Review), there is still a dearth of information on the translocation and mechanisms of transport of PyC from terrestrial to aquatic environments. However, these translocation mechanisms from terrestrial to aquatic systems may be of importance, as PyC has been observed in higher concentrations in lake sediments than surrounding soils (Ohlson et al. 2013), pointing to preferential erosion of PyC (Rumpel et al. 2006), and sediment focusing that may lead to PyC enrichment in some sedimentary environment (Cotrufo et al. 2016b).

6.2 Recommendations for Future Work

In a recent review of the state of PyC research, Santín et al. (2016) pointed towards four main directions of future research needed for the field, including an integrated view of the entire PyC continuum in the environment and how this relates to carbon cycling. These calls for future research are slowly being addressed. This dissertation contributes to a fuller understanding of PyC intermediate pools and fluxes (Chapters 2, 3, 4, 5), a preliminary understanding of how and in what phase PyC is transported in river systems through simultaneous measures of low-temperature PyC in different phases (Chapter 3), and how PyC from low- and high- temperatures are linked in river DOC (Chapters 3, 5). However, if we are to fully understand how PyC cycles in the environment on a global scale, and how this affects overall carbon cycling, we must understand how PyC cycles on different timescales, locations, and using different biomarkers.

6.2.1 Further Understanding Sources of PyC in the Environment

While work to understand the sources of PyC to the environment has significantly increased in recent years, there is still a need to further characterize PyC products and their mean residence times in the environment (Santín et al. 2016). This is especially important to discern for source appropriation, and to fully understanding the effects of PyC on carbon cycling. For example, recent work (including what is presented in this dissertation) has shown that levoglucosan degrades on environmentally relevant timescales. This degradation of levoglucosan and other PyC markers in the environment may skew source appropriation of environmental PyC. For example, selective preservation of gymnosperm-like components in Py-DOC (Smith et al. 2013), and fractionation of PyC during burning events ((Myers-Pigg et al. 2016) and references therein), may skew source appropriation, such as that presented in this dissertation. This is not unlike the potential for fractionation skewing lignin degradation signatures in environmental settings (Hernes et al. 2007). Therefore, further work to understand these potential mechanisms in the environment must be studied.

6.2.2 Further Determination of Coupling of PyC Continuum

There is a need to understand PyC dynamics from the entire PyC continuum in environmental settings (Hammes et al. 2007). There are only a few studies that look at the relationship of PyC biomarkers over the continuum in environmental settings, e.g. Hanke et al. (2016), Hunsinger et al. (2008), Kuo et al. (2011b), Louchouarn et al.

(2007). These studies suggest that different markers of PyC track different forms of combustion and differences in transportation and deposition. Therefore, we must understand and characterize the entire range of PyC continuum in order to determine environmental residence times, the role of PyC in carbon cycling, and potential for transport dynamic coupling (Santín et al. 2016). Additionally, we must characterize and compare different methodological proxies in environmental settings to more widely apply our understanding of PyC in the environment (Cotrufo et al. 2016a).

These parameters are also important to quantify if we are to reconstruct past fire regimes. However, to fully elucidate past fire regimes, understanding the stability of these biomarkers within sediments, including during different depositional and diagenetic settings, is also necessary (Conedera et al. 2009).

6.2.3 Quantitative Estimates of Carbon Cycling from Fire-Impacted Regions

While quantitative estimates of carbon fluxes from fires are present in the literature, these are often based on scarce data, making understanding fire's impact on carbon cycling as a whole is not well accounted for. Fires are especially difficult to study in terms of overall carbon cycling, as the fire event affects carbon cycling on a variety of timescales. Fire events are well documented spatially (fires are estimated to affect 3-4.6 million km^2 annually (Santín et al. 2016)), but tracking the flux of carbon from pre-fire vegetation to fire emissions and pyrogenic carbon is widely scattered within the literature, and large uncertainties in values presented exist (e.g. Table 1.1). Carbon emissions from fires are often reported as C_{total} emitted from the fire, combining emissions from major components such as CO_2 with smaller emission components, such as CH_4, CO and organic carbon (e.g van der Werf et al. (2010)). Emission factors (g constituent/kg dry weight) are present for a variety of constituents released during fire events (e.g Andreae and Merlet (2001)), but estimates of total biomass affected by fire remains sparse, making scaling these values difficult. Many studies that holistically examine the conversion of biomass during fire events are conducted with prescribed burn studies (e.g. Santín et al. (2015), Samsonov et al. (2005)), or studies of PyC in the environment after a natural burn event (e.g. Czimczik et al. (2003)), and therefore, cannot capture temporal differences. Therefore, understanding emissions throughout time (including understanding degradation of PyC) is important if we are to fully capture the effects of fires on carbon cycling.

6.3 Final Conclusions

It should be clear from the above work that a multi-proxy approach must be used in all environmental settings to help further elucidate the input, fate, and impact of PyC on the environment. Future work should also focus on a variety of environments with extreme fire events, such as those caused by anthropogenic alterations (slash-and-burn agriculture). Dissemination and collaboration of PyC research between communities, especially within modeling, must happen before PyC can be input into global carbon cycle models, such as those used for policy management purposes.

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