Wildfire impacts to soil in Alberta's southern Rocky Mountains: pyrogenic carbon abundance and character on a post-wildfire landscape

by

Nathan Storey

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Soil Science

Department of Renewable Resources

University of Alberta

© Nathan Storey, 2023

Abstract

Pyrogenic carbon (PyC) is a ubiquitous soil constituent produced as a result of wildland and anthropogenic fire. The dynamic nature of wildfire produces heterogenous chemical by-products in a broad range of sizes and chemical makeup, from lighter soots to heavier charcoals. A large component of the global soil organic carbon pool, PyC is an important component of healthy soils, particularly in fire-adapted ecosystems where flora and soil fauna make use of its many positive impacts. The stock, character, and transport of PyC is poorly understood at landscape and local scales, particularly in mountainous regions and sub-alpine ecosystems.

This study assessed watersheds of Waterton Lakes National Park affected by the Kenow Wildfire in 2017 and unburned reference watersheds in the adjacent Castle Provincial Park. Soil was sampled at two time periods, 2018 from 0-5 cm and 2021, from 0-5 and 5-15 cm in depth and analyzed for total carbon, total nitrogen, particle size distribution, and PyC quantity via chemical oxidation and chemical composition via pyrolysis-GCMS. Sites paired to sample locations chosen by Parks Canada in 2018 were assessed for slope and aspect characteristics. Relationships between time, depth, burn status, soil texture class, and total carbon were evaluated using two-sample t-tests, ANOVA, regression analysis, non-metric multidimensional scaling, and permutational analysis of variance. Analytical methods were contrasted to determine the most appropriate pyrolysis-GCMS pretreatment methodology for the determination of PyC chemical constituency by comparing results in a distance matrix.

Soils collected from burned watersheds showed enrichment of pyrolysates directly following wildfire and four years afterwards, where PyC made up a larger portion of soil TC. Levels of benzene/aromatics and PAHs were observed to decrease on short timescales in soils from 0-5cm, leading to substantial increases in these compound families in soil from 5-15 cm compared to reference soils consistent with known vertical redistribution mechanisms common

to more condensed PyC species. The PyC content of soil total carbon decreased across a gradient of time since fire, translocated and transformed via abiotic and biotic processes, and potentially diluted by OM deposition. No site characteristic was found to be a significant driver of PyC production movement or storage, however increasing percent PyC was loosely correlated with increasing soil coarseness. This study provides a first look at PyC content and character in this region of the Southern Rocky Mountains and valuable insight into the dynamics regarding movement and storage of this essential soil component.

Acknowledgements

I would like to thank my two supervisors, Dr Sylvie Quideau and Dr. Miles Dyck, for their expertise and the care they showed me throughout the project. You took it in turns to light a fire under my butt and treat the burns. Special thanks go to Dr. Uldis Silins for taking me on as a part of the Southern Rockies Watershed Project (SRWP) and never being afraid to tell it like it is, your game fajitas were delicious.

Thank you to the forWater network and the SRWP for funding this research. The experiences I had during the source-to-tap training were invaluable for me as a scientist and professional.

Thank you to my fellow graduate students, Kiah Leicht, Beckett Stark, Brittany Hynes, Jamin Achtymichuk, Qingge Zhao, and Michelle Moawad, who weathered my barrage of opinions and questions. Two colleagues in particular were invaluable to myself and my research, so thank you Emmily MacDonald for taking time away from your project to hike the mountains with me collecting my samples, your MSc is "just a little farther". Finally, thank you Laura Bony for your insight and assistance at all levels of my project, it was incredibly rewarding to work as your lab mate and fellow event coordinator.

Thank you as well to the SRWP crew, Erin Cherlet and Eamon Tuner, for your assistance throughout this project. I appreciate all your help in the short time we spent together.

This research would not have gotten off the ground without the assistance of the staff at the UofA. Thank you, Allan Harms and Claudio La Roca, for your assistance with my analyses. Special thanks to Jela Burkus, for your insight, expertise, and most of all patience, your care and concern for me always made the lab feel like home. Thank you, Christie Nohos, I would never have entered a single room in GSB without your assistance, hopefully I paid enough in coffees!

Thank you to the Land Reclamation International Graduate School (LRIGS) and Valerie Miller for their support and teaching around science communication as well as Stephanie Reddecliff of Paragon Soil and Environmental Consulting for her mentorship and advice.

To my family, Cathie Storey, Jean Storey, and Kevin Storey, thank you for always supporting and having confidence in me. Thank you to my in-laws for providing me with a huge Albertan family and listening to me talk about "my thesis" for many years. Finally, infinite thanks to my patient and loving wife, Ariana Storey, by my side during the thick and thin of this

project, always willing (despite her boredom) to listen and give me feedback. Without you and our little boy, I don't think this would have been possible.

TABLE OF CONTENTS

List of Tables

List of Figures

List of Abbreviations

C	Carbon
CL	Clay Loam
DOC	Dissolved Organic Carbon
GCMS	Gas Chromatrography Mass Spectrometry
KW	Kenow Wildfire
L	Loam
LS	Loamy Sand
N	Nitrogen
NMDS	Non-metric Multidimensional Scaling
OC	Oxidized Carbon
OM	Organic Matter
PAH	Poly-aromatic Hydrocarbons
perMANOVA	Permutational Analysis of Variance
PyC	Pyrogenic Carbon
PyGCMS	Pyrolysis Gas Chromatography Mass Spectrometry
SiCl	Silty Clay Loam
SL	Sandy Loam
SOC	Soil Organic Carbon
SRWP	Southern Rockies Watershed Project
TC	Total Carbon
TMAH	Tetramethylammonium Hydroxide
TN	Total Nitrogen
UP	Ultra Pure
WB	Walkley-Black
WBC	Walkley-Black Carbon

Chapter 1: Background and research objectives

1.0 INTRODUCTION

Pyrogenic carbon (PyC), also known as black carbon or charcoal, is a broad continuum of well over 200 thermochemically altered compounds produced during incomplete combustion of organic matter, typically plants (Bird et al., 2015). This class of fire by-products range in size from macroscopic, charcoal and biochar, to polyaromatic hydrocarbons, and graphitic carbon. These compounds occur naturally and exist in all three phases throughout the atmosphere, sediments, ice, terrestrial water bodies, the ocean, and are present in the soil as particulate or dissolved species (Schmidt & Noack, 2000). An important component of the global carbon cycle, PyC makes up approximately 13.7% of the soil organic carbon pool, though estimates vary depending on the model and can be as high as 60% (Reisser et al., 2016). The ubiquity of PyC in the carbon cycle and its recalcitrance relative to other soil organic matter underline its importance as a carbon sink globally.

Pyrogenic carbon examined in this study was produced during wildland fire, specifically the Kenow Wildfire (KW) occurring from August 30th to October 3rd, 2017, in Waterton Lakes National Park. During the third driest summer on record (Parks Canada Agency, 2023), the fire burned approximately 35,000 ha, 38% of the park area (Parks Canada Agency, 2023). Classified as a very high severity fire for the majority of its range, temperatures ranged from 450 to 650^{o}C, driven in part by the dramatically increased fuel load typical of Canadian forests after 100 years of landscape-wide fire suppression.

Fire is essential to almost all of Alberta's ecosystems, from grasslands and the boreal forest all the way to the alpine forests of the Rocky Mountains. While fire return intervals have not been extended past their natural variation, the homogeneity of mature forest at late seral stages throughout the province and the buildup of forest floor biomass will increase the size and severity of wildfire compared to natural regimes (Rogeau et al., 2016). These factors combined with increasing global temperatures, more pronounced in colder northern regions, will alter PyC production dynamics across the province. A clearer understanding of how pyrogenic carbon is produced, transported, and stored in montane environments will serve to guide research and

policy around wildfire, land reclamation, and carbon dynamics in an ecosystem that makes up a significant portion of Alberta's land area.

The effects of montane fire dynamics on soil are important to understand due to the popularity of the Rocky Mountains as tourist attractions. The overall health and beauty of this area is important both economically and culturally to Albertans, thus important factors affecting the recovery of these ecosystems need to be better understood, particularly in areas deprived of the regular PyC inputs that would have occurred without fire suppression. Additionally, humans are the main driver of wildland fire in many regions of the world (Hanes et al., 2019).

1.1 Literature Review

1.1.1 Pyrogenic Carbon

Pyrogenic carbon has been present in the geologic record since the atmosphere contained enough oxygen to support combustion processes roughly 380 Myr ago (Scott & Glasspool, 2006). These compounds represent a large and important component of the global carbon cycle (Bird et al., 2015), and make up 14% of total soil organic carbon (SOC) on average but have been observed as high as 60%, one of the largest groups of compounds present in soils (Reisser et al., 2016). Prior to the discovery of fire by humans, the sole producer of PyC was wildfire caused by lightning strikes. With the advent of fossil fuel burning humans now produce more aerosolized PyC (atmospheric or APyC) than natural fires (Kuhlbusch, 1998). Vegetation fire produces the majority of particulate PyC (residual or RPyC) deposited to soils and sediments (30-115 Tg), although in recent years the burning of agricultural waste and production of biochar have begun to contribute a larger percentage of these inputs concentrated in anthropogenically disturbed, cultivated, and reclaimed ecosystems (Bird et al., 2015). More mobile as a part of the dissolved organic carbon (DOC) pool, an estimated 0.44 Tg of dissolved PyC (DPyC) was lost from land to the aquatic environment each year from 1910-2010 (Bowring et al., 2022). Total global soil PyC stock estimates vary wildly between publications, 54-109 Pg to 71-212 Pg (Bird et al., 2015; Santín et al., 2016) within the first 1-2 m of soil, and are often calculated using global SOC stocks multiplied by a representative percentage of PyC to SOC (5-15% in these cases) depending on the ecosystem. Approximately half of all soils contain PyC and it is generated at an estimated 40-260 Gt per year (DeLuca & Aplet, 2008). Due to the recalcitrance,

and therefore long residence times of PyC, these species are potentially the longest-lived terrestrial components of global carbon sequestration that are not subject to freezing or anaerobic conditions.

Global carbon modeling has become increasingly more sophisticated with the addition and increasing knowledge of PyC and other poorly understood constituents. However, significant knowledge gaps exist in the areas of PyC production (DeLuca et al., 2020), degradation (Bowring et al., 2022), particulate PyC mobility and storage (Masiello & Berhe, 2020), and the effects of a century of fire suppression (Matosziuk et al., 2020).

1.1.2 Wildfire and PyC Production

The boreal, grassland, and montane environments of western Canada have been fire-adapted ecosystems since fire became the predominant agent of disturbance approximately 6,000 years ago (Gale & Thomas, 2021). Fire-adapted ecosystems can be found across the globe, from savannah and prairie grasslands, to boreal, temperate, subtropical and tropical forests. Contemporary fires are typically large-scale, stand-replacing events that determine various characteristics such as community composition and fuel structure (Hatten et al., 2005), as well as shape forest function and dynamics (Kelly et al., 2013), especially important factors in temperate montane forests. Most fires impact vegetation, accumulated forest floor materials, and the first few centimeters of soil as they predominantly occur at soil surface (González-Pérez et al., 2004). Areas experiencing high severity fire were found to have 82% less forest floor mass and 71% lower total carbon in a Sierra Nevada mixed-conifer forest (Adkins et al., 2019). The broad effects of wildfire include increases to soil bulk density, pH, and total phosphorus, and decreases to carbon and nitrogen content and water holding capacity through depletion of OM and enrichment of PyC primarily (Jílková et al., 2023).

Human intervention in the natural fire cycle, both fire suppression and accidental or malicious arson, has altered wildfire regimes and PyC production dynamics (Matosziuk et al., 2019). Increased fuel loads, downed trees and thicker vegetative litter layers in North America as a result of nearly a century of broad scale fire suppression have led to wildfires with greatly altered characteristics (Hatten et al., 2005; Rogeau et al., 2016). In Canada, large fires of anthropogenic origin account for approximately 50% of all wildfires and 10% of total burned area but have been on the decline since 1980 (Hanes et al., 2019). Fire suppression efforts after

1940 have disrupted the natural 60-70 yr fire return cycle on the east side of the Canadian Rocky Mountains, dramatically decreasing the burning rate and containing burns to less than 1% of government park areas (Van Wagner et al., 2006). Human impacts have possibly led to the lengthening of the fire season in Canada, due to their predominance at either end of the natural cycle where fuels are particularly susceptible to ignition (Hanes et al., 2019).

Differences in fire severity, a function of wildfire characteristics including temperature, duration, fuel type (feedstock) and quantity, and burn pattern, have been investigated as the largest driver of PyC production, though results conflict. Miesel et al., 2018 found no difference in PyC production on a fire severity gradient in California mixed-conifer forests, Huang et al., 2018 found that moderate severity fires produced the most PyC, and Matosziuk et al., 2020 found statistically larger PyC production and deposition from high severity fires. These differences could be partially attributed to the consumption of legacy PyC by subsequent fires, reducing the total PyC stored at soil surface (Doerr et al., 2018), and the slow release of charred materials from dead burnt timber. Notably, higher severity fires and smaller feedstocks (graminoids, herbaceous plants, forest floor materials) increase the amount of local biomass converted to airborne PyC, which can then accumulate elsewhere (Bird et al., 2015). Globally averaged soil PyC is enriched by 40.6% and the ratio of PyC/TC by 30.3% following wild and prescribed fires, predominantly in mixed-wood and coniferous forests of temperate and boreal climate zones (Li et al., 2021).

1.1.3 Physical and Chemical Properties

Pyrogenic carbon encompasses a broad range of compounds which vary greatly in size and chemical character even within individual pieces of charred material (Bird et al., 2015). Described as a continuum, these compounds are dominated by aromatic structures but are chemically heterogeneous, ranging from highly condensed refractory soot to larger charcoals and slightly thermochemically altered or charred plant materials that remain highly biodegradable (Masiello, 2004). Soot and charcoal are primarily differentiated by their size and the distinguishability of their biomass source. While the precise mechanism of formation has not been elucidated, soot is understood to form from condensed carbon ions and radicals that combine into polycyclic aromatic hydrocarbons (PAHs) and finally into complex ring structures (Masiello, 2004). Soot can range in molecular structure from two dimensional layers of graphene

containing very little oxygen and hydrogen (4-11%) to polymers of complex organic compounds in three dimensions containing PAHs, humified substances, and aliphatic compounds (Andreae & Gelencsér, 2006). Charcoal and charred materials retain much of their pre-burn organic structure where remaining lignin and cellulose are negatively correlated to increasing temperature and burn time, and subsequently their degradation potential and chemical recalcitrance (Belcher et al., 2018). They are unique in that they contain organized, homogeneous micrographitic structure, and disorganized, heterogeneously thermochemically altered organics, in distinct regions within individual particles (Bird et al., 2015).

Particle size ranges from single molecules and micrometer thick graphene sheets in soots to several centimeter long charcoal pieces. Deposited PyC after prescribed fire was found to consist primarily of < 2mm diameter (54.6%) and > 9mm (20.8%) by weight (Jenkins et al., 2014). Size fractionation effects constituent chemistry, with larger materials (> 9mm) containing the largest total C percentage, higher quantity of C, and associated C:N ratio. The fraction smaller than 1 mm positively prime organic matter decomposition in soils, increasing mineralization of nutrients, and contribute to a significant increase in pH. In contrast, PyC larger than 1 mm are more resistant to microbial degradation and chemical decomposition, in keeping with their general recalcitrance (Jenkins et al., 2014). Particle size also determines erosive transport distances, where millimeter scale particles will settle out of air and water sooner than micrometer sized soots which can be suspended on month-long timescales (Clark and Patterson, 1997; Ogren and Charlson, 1983 from Masiello, 2004). From fires observed in Panama, PyC larger than ~2 micron was found to make up greater than 90% of PyC deposited to soils from the atmosphere (Suman 1983, 86, 88 from Masiello, 2004).

All chemical and physical aspects of these compounds are a function of feedstock and burning temperature, where smaller and more herbaceous plants and lighter forest floor materials produce corresponding smaller and lighter PyC than larger charcoals derived from woody species (Bostick et al., 2018; Masiello, 2004). In a series of laboratory generated biochars, pyrolyzed materials were depleted in O, H and N when compared to their feedstocks. Analysis of oak- and grass-generated chars produced at the same temperature showed the latter had greater O-containing functional groups and a lower amount of aromatic C (Bostick et al., 2018). Feedstock pore structure determines the small-scale porosity of biochars pyrolyzed at temperatures below 500 ºC (Hyväluoma et al., 2018). Overall, PyC produced at higher

temperatures features increased pH, C content, porosity, degree of condensation (C/O and C/H ratios), specific surface area, and pollutant sorption capacity, alongside decreased reactivity, lability, and degradability (Bird et al., 2015; Chen et al., 2020; Masiello, 2004). Quantity of functional groups, containing mainly hydrogen or oxygen, decreases with degree of thermal alteration (Preston & Schmidt, 2006). With this increasing condensation, PyC becomes less bioavailable and more chemically resistant, and therefore more recalcitrant.

1.1.4 Effects on Soils

Pyrogenic carbon can make up approximately 28% of total carbon left on the forest floor after wildfire (Santín et al., 2015). Heterogeneous distribution on the surface and throughout the soil profile drives both community wide and local effects on many soil properties (Gale & Thomas, 2021; Hobley, 2019; Jílková et al., 2023). Impacts are predominantly regulated by PyC feedstock, pyrolysis temperature and soil texture, driven by the broad range of physicochemical properties (Edeh et al., 2020; Jílková et al., 2023; Wang et al., 2014; Wu et al., 2022). In addition, larger PyC resides preferentially in the pedosphere while smaller species are present primarily in the atmosphere and hydrosphere. This results in the effects associated with the larger fraction becoming concentrated in the primary reservoir, soils, and the smaller fraction, in air and water (Masiello et al., 2004; Bird et al., 2015; Reisser et al., 2016).

Biochar, and by extension PyC, improves several key soil hydrological properties that benefit plant growth and ecosystem recovery following fire events. On average available water content (AWC), the portion of soil water available for plant uptake, and crop water use efficiency, the biomass produced by a plant for a given amount of water, were increased by 26.8% and 4.7% with an application rate of 10 t/ha based on a meta-analysis by Wu et al., 2022, which also saw an increase in soil moisture content by 10.8%. A corresponding decrease in these hydrological variables was observed in cases where biochar amendment exceeded a threshold value, dependent on soil particle size. Soil texture is the most significant variable modifying the effect of biochar amendment, increasing the positive change to AWC and field capacity (FC) in coarse textured compared to fine-textured soils (Edeh et al., 2020), primarily driven by a bulk density decrease and increase respectively. Saturated hydraulic conductivity was found to increase by ~40% in fine-textured soils (<20% sand) and decrease by ~62% in coarse textured soils (>50% sand), where woody feedstock accounted for the majority of change, and crop

residue biochar had no effect (Edeh et al., 2020). Biochar of fine particle size fills the pores of sandy soils, increasing AWC at lower amendment rates, whereas clayey soils benefit from the increase of mesopore structure at higher biochar application rates (Wang et al., 2014; Edeh et al., 2020). Naturally produced PyC mirrors the effects on bulk density found in biochar application, significantly increasing in 2-year, post-fire stands compared to those harvested for timber (Shrestha & Chen, 2010), potentially negatively affecting soil hydraulic properties.

Soil chemistry is dramatically altered by wildfire and pyrogenic carbon addition, most notably pH, total nitrogen, and total phosphorus. Increased pH has been observed in soils (Certini, 2005) and forest floor (Jilkova et al., 2023; Shrestha and Chen, 2010) after wildfire, prescribed fire (Matosziuk et al., 2019), with biochar addition (Luo et al., 2011), and in leachates from dissolved pyrogenic organic matter (Schiedung et al., 2020), attributed to carbonates present in light PyC fractions. The largest increases occur at high fire temperatures (Certini, 2005; Matosziuk et al., 2019). Importantly these increases occur in the 6-6.4 pH range, improving availability of plant essential soil properties like base saturation and phosphorus, possibly aiding growth and re-establishment post-fire (Matosziuk et al., 2019). Total and dissolved phosphorus, and its lability in soil are higher following wild and prescribed fire (Butler et al., 2018; Fonseca et al., 2017). Dissolved phosphorus was found to be six times higher one year after wildfire but returned to levels found in unburned forest floor within 100 years (Jilkova et al., 2023) and extractable phosphorus increased after prescribed burns, staying higher than pre-fire reference up to three years after the burn (Fonseca et al., 2017). Conversely nitrogen is lost from all forms of fire, though the effect is less pronounced in low intensity fires, ranging from 2-6%, and more severe in forests of tropical and temperate regions, ranging from 14-50% (Li et al., 2021; Jilkova et al., 2023) but recovering to control levels within 10 years (Li et al., 2021). Total inorganic nitrogen and NH_4 in particular rises 6-fold following high severity wildfire relative to unburned soils, though this dramatic increase could be due to a shift to an N-fixing plant community, plant mortality, or changes in microbial nutrient consumption (Adkins et al., 2019).

Additional significant chemical change attributed to PyC includes soil organic matter (SOM) priming as a result of wildfire and biochar application. On short time scales (200 days) and most intensely ~20 days after addition, positive priming, increasing mineralization of SOM, has been observed in multiple studies of wildfire and biochar additions to soil (Gibson et al., 2018; Ling et al., 2021; Luo et al., 2017; Maestrini et al., 2014; Zimmerman et al., 2011).

Though the exact mechanisms have yet to be elucidated, this effect is commonly attributed to change in composition and increase in biomass of microbial communities (Ling et al., 2021; Maestrini et al., 2015; Zimmerman et al., 2011) driven by changes to the form and availability of N and P, increase in pH, enrichment in lighter fractions of PyC more easily decomposed by microbes, and increase in the carbon use efficiency from constituent microbes (Jiang et al., 2016). Conversely, a negative priming effect, potentially exceeding or equaling C losses from initial positive priming (Zimmerman et al., 2011; Maestrini et al., 2015), is exerted on SOM on longer timescales, inhibiting soil C mineralization. Organic matter sorption to surface and within pores may protect it from microbial activity, and this combined with other inhibitive effects on later stage microbial communities, such as physical changes to PyC surfaces and their chemistry and soil fauna diversification with further OM inputs, leads to carbon sequestration with time over and above the quantities of PyC added (Jiang et al., 2016; Maestrini et al., 2014; Zimmerman et al., 2011; Zimmerman & Ouyang, 2019).

Directly following wildfire, microbial activity is reduced as a result of mass die-off of above and below ground forest biomass and limited soil nutrient resources for reestablishment (Ling et al., 2021; Certini et al., 2005). Early colonizing species of microbes drive the pattern of priming described previously, and biochar amended soils have increased microbial biomass compared to unamended soils (Jiang et al., 2016). Early microbial composition is driven by recalcitrant components of SOM, where oligotrophic bacteria such as Actinobacteria were more abundant with higher concentration of phenolic-C compounds (Luo et al., 2017), and potentially affected by the relative toxicity of these same compounds, which produce stress responses in some early colonizers (Ling et al., 2021). In a long-term incubation it was observed that the prevalence of actinomycetes and gram-negative bacteria in soils amended with biochar increased (Ling et al., 2017). These effects also follow a fire severity gradient as the desiccating effects of high severity fire on soils may result in more intense but truncated explosions of microbial activity following precipitation events than in undisturbed soils (Adkins et al., 2019). Protective effects on microbes have also been hypothesized, with the micropores of PyC acting as refugia from microfauna, however Pingree et al., 2022, found no evidence of this mechanism using conifer derived biochar in boreal forests.

Generally, plant biomass increases with the addition of biochar in both field and lab trials with effects leveling off over time, suggesting the largest effects of PyC occur early after

deposition (Thomas & Gale, 2015). Growth responses are stronger in boreal and tropical as compared to temperate species in addition to increased response among deciduous versus coniferous trees (Thomas & Gale, 2015). Sapling diameter and height of *Pinus banksiana* was stimulated dramatically up to 45 t/ha of biochar addition, where increases stop accelerating (Gale & Thomas, 2021). Similarly, temperate tree species exhibit increased radicle extension and germination with biochar amendment (Thomas, 2021). In contrast, post-fire succession to pre-disturbance state is driven by accumulating OM rather than PyC in central European temperate forests, mediated by composition of vegetation recovery (Jilkova et al., 2023).

1.1.5 Transport and Fate

Erosion accounts for a loss of 3-5 Mt of pyrogenic carbon annually (Abney et al., 2017) and transport is dominated by precipitation occurring less than one year post-fire (Masiello & Berhe, 2020). Much of the PyC produced on the hillslope ultimately ends up stored in lake sediments, however Ohlson et al., 2013, found that atmospheric deposition to lakes was the primary mechanism, not downslope washing. Stabilization mechanisms happen on a timescale that is far too slow to prevent washout by the first post-fire rainfall (Masiello & Berhe, 2020). Several recent studies have reported significant erosion of PyC post-fire in montane environments (Abney et al., 2017, 2019; Boot et al., 2015; Cotrufo et al., 2016) with 90% of eroded topsoil transported locally within the same catchment (Berhe et al., 2018). Post-fire soil hydrophobicity can increase dramatically, contributing to soil erosion, as a result of higher quantities of alkyl C and other hydrophobic species in upper mineral and surface soil (DeBano, 2000; Neary et al., 1999). Additionally, fire affected landscapes are scoured of litter and surface vegetation, contributing to increased runoff speed and intensity (Abney et al., 2019) and a net loss of PyC from hillslopes and other eroding landforms (Abney & Berhe, 2018).

Pyrogenic carbon has a stronger affinity to sorb to mineral particles than other forms of organic matter, increasing its residence time in soil (Bellè et al., 2021). Mechanisms affecting physical pyrogenic carbon redistribution can be broadly categorized into pedoturbation, soil surface alteration, and percolation (Hobley, 2019). Within natural systems flora and soil fauna drive soil mixing, primarily in the top 30 cm (Hobley et al., 2019). Cryoturbation or the mixing caused by frost heave during the freeze thaw cycle can also occur in higher latitude regions. Cracks formed during high temperature fires can allow subsequent precipitation events to wash

PyC into deeper soil regions (Hobley, 2019). The relative position of deposited PyC can change with the reformation of litter and humus layers during post-fire recovery (Preston et al., 2017). Additionally, relative depth can be altered in mountainous regions, where landslides are common, with PyC buried under soil and rock particles or carried to streams and rivers (Claessens et al., 2006), and floodplains, where soils are layered overtop by sediments during flood events (Denis et al., 2021). Pyrogenic carbon can be washed downward through the soil profile via eluviation of particulate particles or leached via dissolution in soil solution into deeper regions and ultimately groundwater (Hobley, 2019; Liu et al., 2016). In a column experiment, 3.8 - 10.8% of PyC added to soil moved vertically up to 7 cm below the application layer, concentrated in the area from 0 - 2.3 cm (Schiedung et al., 2020), and in the field, 2 - 6% of dissolved organic carbon lost from upper horizons during a snowmelt event was mature PyC (Santos et al., 2017).

The majority of hillslope PyC ends up in depositional landforms where conditions for microbial decomposition are more favorable (Abney et al., 2017). While PyC was originally thought to be extremely resistant to all forms of physicochemical alteration, oxidation via biotic and abiotic processes can act to alter structural and chemical properties of PyC, particularly less condensed species (Velasco-Molina et al., 2016), where they become more polar and are easily dissolved into soil water (Bostick et al., 2018). Grass derived biochar was found to leach larger quantities of PyC-derived DOC than oak feedstock (4x) due to its increased degradability, with total levels decreasing with increasing formation temperature. Despite this large difference, leachate levels decreased over time, equaling the more consistent C loss of woody sources (Bostick et al., 2018). Additionally, PyC has been shown to decompose faster in poorly drained nutrient rich depositional landforms like those of river valleys than in erosional landforms such as surrounding hillslopes (Abney et al., 2019). The reactivity of BC also varies along the combustion continuum. Charcoal decomposes much more rapidly than soot when exposed to chemical oxidants in the laboratory (Masiello et al., 2002). Evidence from field experiments suggests that the environmental lability of charcoal also varies dramatically, due to a combination of microbial decay and photo-oxidation (Bird et al., 1999). Laboratory experiments using one plant type (*Pinus resinosa*, red pine) suggest that extent of charring also influences lability (Baldock & Smernik, 2002).

In the long term, PyC is stabilized by the effects of adsorption, chemical alteration, and water absorption in concert, and stored in deeper soils with a protective litter layer (Jilkova et al., 2023), depositional landforms, or the sediments of rivers, lakes, and oceans (Bird et al., 2015). The fate of pyrogenic carbon is to be transported to the oceans by ground and surface water. Storage is partitioned between terrestrial and marine reservoirs, with roughly 10 times more residing in ocean sediments than on land (Bird et al., 2015). Mean residence time, or the average age of PyC, begins at approximately 1,000 years in soils increasing to 10,400 - 20,100 years dissolved in marine waters, and possibly longer in deep ocean sediments (Bird et al., 2015). Increasingly, terrestrial stocks are dominated by anthropogenic sources, so it may be that where humans choose to deposit PyC will shape its future distribution on land.

1.1.6 Quantification and Characterization

Reliable quantification of PyC mineralization and erosion remains a missing link in the C balance of post-fire landscapes (Bowring, 2022). Most reviews and meta-analyses on the subject of PyC outline the need for accurate and comparable evaluation techniques with more consistent use of terminology and language (Bird et al., 2015; Hammes et al., 2007; Reisser et al., 2016; Zimmerman & Mitra, 2017). The number of conversion and correction factors employed is as large as the number of preparation and measurement methods, adding additional uncertainty when comparing study results even when employing the same method types (Zimmerman & Mitra, 2017). Further to this problem, each method is selective to specific parts of the PyC compound continuum, misidentifying more condensed aromatics or not capturing lighter soots, etc. (Hammes et al., 2007; Zimmerman & Mitra, 2017). Current quantification and characterization methods in soils belong to five classifications captured within two types. Destructive techniques, which alter or destroy samples, include chemical oxidation, thermal decomposition, and molecular marker evaluation. Alternatively, non-destructive techniques include physical separation and non-pyrolysis spectroscopy (Bird et al., 2015).

Chemical oxidation, like the majority of methods, is a pseudo-qualitative technique but is primarily employed for quantification. Lighter and less condensed classes of SOM and PyC are not as resistant to oxidation, and depending on the type and strength of oxidizing agent will be preferentially removed from samples, leaving behind the larger and more resistant species resulting in quantification of only those compounds remaining, acting as a heavy-handed

classification mechanism to partition lighter and heavier PyC (Bird et al., 2015). The PyC (and SOM) remaining following oxidation is then quantified via titration, elemental analyser or spectroscopy (Hammes et al., 2007). The most common methods involve pretreatment using HCl, H_2O_2, H_2SO_4, and/or HF, and oxidation by dichromate ($K_2CR_2O_7$), sodium hypochlorite (NaClO) or temperatures of 375 ^oC (Hammes et al., 2007), the last combining oxidation and thermal decomposition. Due to the nature of the method PyC is commonly misidentified (resulting in overestimation) or underestimated in many cases (Murano et al., 2021). As the field has evolved methods have been evaluated and improved, particularly in regard to the dichromate method, which Murano et al., 2021 altered to more effectively suppress PyC overestimation via humified substances.

Pyrolysis GCMS combines thermal decomposition in the form of flash heating at 500-800 ^oC, and chemical characterization via gas chromatography mass spectroscopy (Kaal & Rumpel, 2009). Drawbacks include its semi-quantitative nature where like many techniques it only provides estimates of PyC concentration (Kaal et al., 2008), and stable portions of the PyC continuum, which can be substantial, are unaffected by pyrolysis and remain undetected within runs (Kaal and Rumpel, 2009). Recently a ratio of aromatic hydrocarbons and nitrogenous compounds divided by phenolic carbon and lignin carbon has been proposed as an indicator of the level of PyC present in soils with legacy fire effects (Chen et al., 2020). When employed at high enough temperatures, the method is capable of similar separation and quantification of PyC as nuclear magnetic resonance spectroscopy combined with a molecular mixing model (Kaal and Rumpel 2009).

Unfortunately, both minor and substantive advances in established methodology serve to further weaken comparison between past and present studies and the accuracy of quantification in natural systems, where analysis is subject to multiple confounding variables. Stocks quantified in different ecosystems and at different times may not be appropriately combined to give us concrete values to enter into climate, carbon cycle, and sequestration models for predictive purposes.

1.2 Research Objectives

The goal of this research is to address the identified knowledge gaps on PyC stocks and investigate changes following wildfire. The research will evaluate the effects of fire on soil PyC,

differences over time since fire, and changes between depth classes (0-5 and 5-15 cm) using both quantitative and qualitative determination.

Specific research objectives are as follows:

- To determine the quantity and distribution of PyC within soil profiles directly following wildfire.
- To assess soil particle size, carbon and nitrogen content, and slope position and determine each component's relationship to pyrogenic carbon.
- To explore pyrogenic carbon movement and redistribution within the top 0-15 cm of soil profiles at 1-year, 4-years, and 100-years following fire.

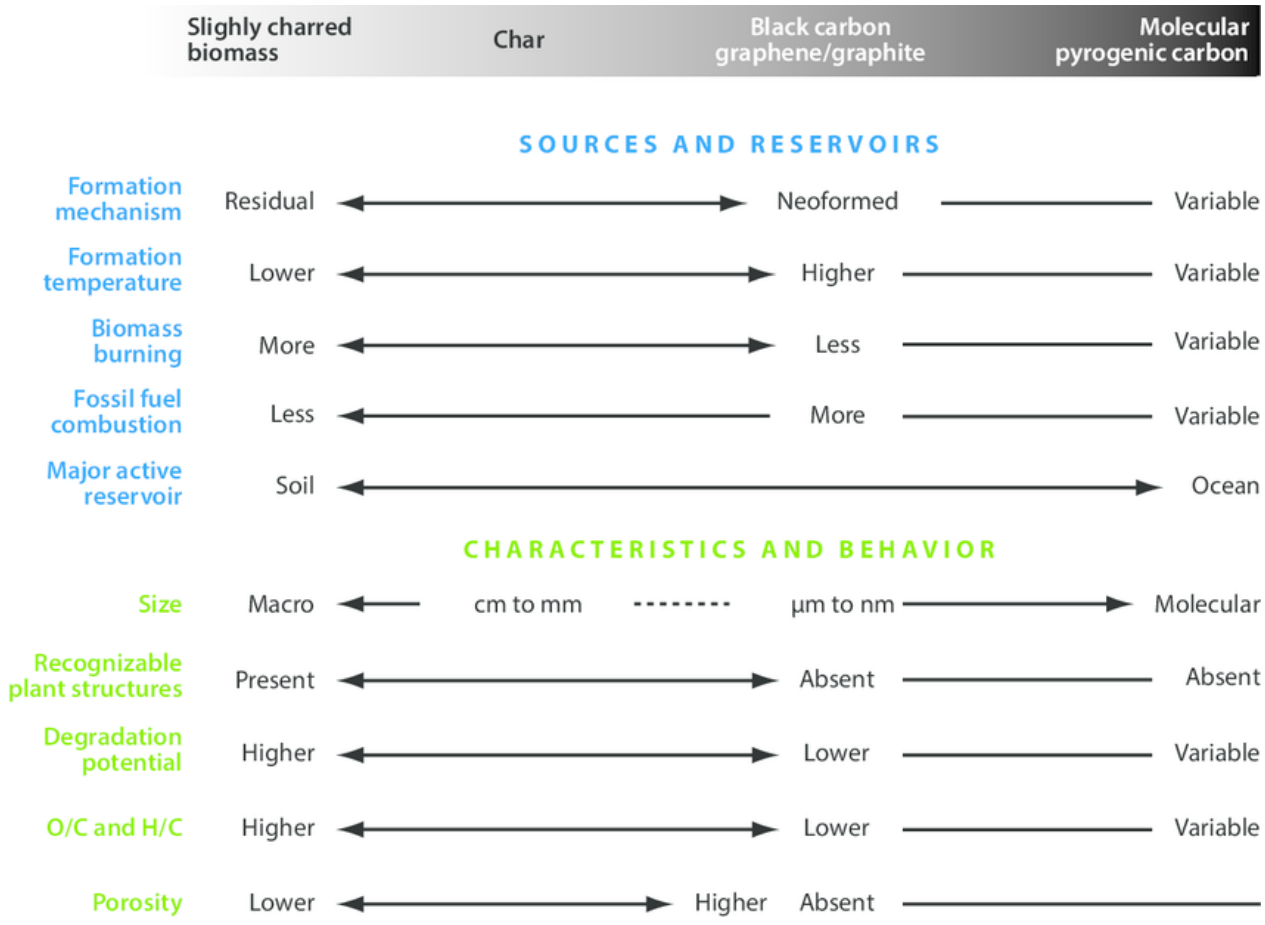

Figure 1.1 Pyrogenic carbon continuum (Bird et al.,2015)

Chapter 2: Pyrogenic carbon in the soils of burned and unburned watersheds

2.1. INTRODUCTION

Pyrogenic carbon (PyC) is a broad chemical classification term to define over 200 thermochemically altered compounds produced during incomplete combustion of organic matter, typically plants, as well as many pyrolysates of anthropogenic origin (Bird et al., 2015; Santín et al., 2015). Pyrogenic materials range in size from macroscopic charcoal to sheets of graphitic carbon a single atom thick (Jenkins et al., 2014). Produced naturally and through the burning of fossil fuels and agricultural waste, PyC can be found almost anywhere, suspended in the atmosphere or as particulate and/or dissolved species in soils, sediments, and waterbodies (Schmidt & Noack, 2000). Models have estimated PyC at 14-60% of global soil organic carbon stocks (Reisser et al., 2016). Combined with the increased recalcitrance of PyC in comparison to other SOC, it is critical that we better understand PyC production and storage as an important mechanism of carbon sequestration and climate change contravention.

The soils of temperate regions contain approximately 1% of global PyC stocks (Bird et al, 2015). Despite this relatively small amount, PyC is ubiquitous in fire-adapted ecosystems of which Alberta has a significant number, including boreal forest, prairie grassland, and the patchwork of forest, hillslope, and grassland that constitute subalpine ecosystems. One such area is Waterton Lakes National Park, where the Kenow Wildfire (KW) burned 38% of the park area (35,000 ha) from August to October of 2017 (Parks Canada Agency, 2023). The increased fuel load resulting from decades of fire suppression combined with the driest summer on record produced a very high severity fire that rapidly swept through the park, burning at temperatures of 450 to 650 ^{o}C (Parks Canada Agency, 2023).

Many studies have explored PyC in montane ecosystems, and those performed in North America have mostly focused on coniferous forests (Boot et al., 2015; Cotrufo et al., 2016; DeLuca & Aplet, 2008; Jílková et al., 2023; Matosziuk et al., 2019, 2020). To our knowledge no study of subalpine fire has investigated PyC production within multiple watersheds or employed both a chemical oxidation method and pyrolysis-GCMS to compare and contrast quantitative and qualitative properties of PyC between freshly burned soils and those belonging to unburned reference sites.

The pyrolysate production mechanisms that operate during wildfire are well established, however accurate stocks, rates of change, predictive factors, and storage mechanisms remain relatively understudied, especially in montane ecosystems (Reisser et al., 2016). Conflicting reports are widespread within the literature regarding the role of fire severity in the production of PyC and the relationship of PyC to soil depth, soil texture, and slope percentage. While PyC stocks and character have been studied extensively (Matosziuk et al., 2019; Soucémarianadin et al., 2019), comparisons between burned and adjacent unburned watersheds are less common.

Horizontal and vertical redistribution mechanisms remove significant quantities of PyC from affected surface soils post-wildfire (Abney et al., 2017; Hobley, 2019). A number of studies have established that hydrologic contact with PyC, particularly the first rainfall following high severity fire, preferentially erodes pyrolysate materials, greatly affecting the final location that PyC settles (Abney et al., 2019; Bellè et al., 2021; Masiello & Berhe, 2020). Additionally leaching, illuviation, and pedoturbation have been identified as significant drivers in soils close to surface but have been little studied in the field (Hobley, 2019; Santos et al., 2022). Currently, PyC depletion and storage patterns with depth have not been quantified in the Southern Rocky Mountains. Determining the speed at which wildfire effects are translocated down the soil profile will have important implications for soil health following the reestablishment of natural fire regimes and the degree to which wildfire might affect resources important to human health. Field studies investigating changes in PyC with depth and time are few, and no published studies have been conducted using adjacent unburned areas as a proxy for long term changes in combination with depth distribution.

The overall objective of this research project was to quantify the stock and character of PyC at 1-year, 4-years, and 100-years post wildfire, in 0-5 and 5-15 cm depth classes, and what site and soil factors correlate most strongly with PyC abundance and character. Specific research objectives were to estimate PyC concentration on a percent w/w of soil basis, the PyC content as a percentage of soil TC, and the chemical composition of PyC across five burned watersheds and 3 unburned watersheds with varying site and soil character. An additional objective was to evaluate PyGCMS pretreatment methods for suitability in PyC investigation.

2.2. MATERIALS & METHODS

2.2.1. Study area and study watersheds

The project was conducted in five watersheds affected by the 2017 Kenow Wildfire, including: the Upper and Lower Cameron, Upper and Lower Blakiston, and Bauerman watersheds located within the boundary of Waterton National Park near Waterton, Alberta (Figure 2.1). West of the town of Waterton, the Bauerman and Upper Blakiston flow into the Lower Blakiston, adjacent to the Upper Cameron which flows into the Lower Cameron, and all drain into the Lower Waterton River watershed and Waterton Lake (Figure 2.1). The mean elevation of these watersheds ranges from 1856m for the Lower Blakiston to 2025m for the Upper Blakiston covering a total area of 21,376 ha. The Upper and Lower Cameron watersheds are fed by Cameron Lake at the border of Alberta and Montana, the Lineham Lakes and creek, Carthew and Alderson Lakes, and by snowmelt, groundwater contributions, and precipitation. Additionally, Bauerman is fed in part by Twin Lakes, and the Blakiston watersheds by Lone Lake. Unburned watersheds used as a representation of long term fire recovery included the Upper and Lower Yarrow and Spionkop watersheds located within the boundary of Castle Provincial Park north of Waterton, Alberta, which last saw fire in 1934 and 1936 (Alberta Government, 2015). Captured within the Alberta Vegetation Inventory, the last stand initiating disturbance occurred in 1936 and 1920 in Spionkop and Yarrow watersheds respectively. Flows from the unburned watersheds meet with drainage from Lake Waterton in the Waterton Reservoir to the north and east, adjacent to Hill Springs, Alberta. All eight watersheds fall within the larger, long-term hydro-climatic monitoring network of the Southern Rockies Watershed Project (SRWP) (University of Alberta, 2023).

Watershed ecotypes consist of a mosaic of coniferous dominated, deciduous dominated, and mixedwood forest, grassland, and hillslope vegetation characteristic of the subalpine region. Dominant vegetation includes Lodgepole pine (*Pinus contorta*), trembling aspen (*Populus tremuloides*), and white spruce (*Picea glauca*) in the forested sampling sites and succulent and grass species in the depositional sites (personal observation).

The various landforms within the park consist of moraines, alluvial fans and terraces, and lower valleys bordered by steep mountainside slopes (Coen & Holland, 1976). Surficial geology is a complex mosaic of coarse textured colluvium, alluvium, and glacial till with plenty of coarse

fragments ranging from 5 to 95%, leading to soil textures from loamy sands (LS) to clay loams (CL), with loams (L) and sandy loams (SL) found to be the most abundant. Classified soils of the area are primarily of the Regosolic and Brunisolic orders, secondarily of Podzolic order, with small pockets of soil in the Luvisolic order in areas on the valley floor and in floodplains, in addition to Gleysolic and Organic soils which were not sampled (Coen & Holland, 1976).

2.2.2. Field sampling design

This study uses an exploratory design with a historical (2018) and contemporary (2021) field sampling campaign taken from a total of twenty-five sites in the five fire-affected watersheds and three reference watersheds to examine change in soil pyrogenic carbon content over a four-year period. Several assumptions of this design include that historical and contemporary sampling sites are comparable despite spatial differences of a maximum of 10 metres, and that degradation and erosion dynamics are similar between burned and reference watersheds. Initial plot selection was conducted with ArcGIS using map data provided by Parks Canada. These data included a stream network, vegetation map, digital elevation model, soil survey, and plotting map from their 2018 program containing 115 sites. Sampling plot choice was constrained by the location of historical samples collected by Parks Canada to allow for temporal comparison. Three sites were chosen for each of the five burned watersheds, and five within the two reference watersheds for a total of twenty-five samples. Sample sites meeting these criteria were narrowed down by stream proximity, slope position, and to create the most varied mosaic of soil great groups possible. Reference sites were clustered more closely together due to access limitations. These sites were chosen in the field based on their hillslope position and dominant vegetation type to best represent the range of sites sampled within the burned area. Two mid-high slope sites with forest and grassland vegetation, two depositional sites with forest and grassland vegetation, and a sloped site with regosolic properties, visible coarse fragments at the soil surface and moss/lichen vegetation were sampled from each watershed.

2.2.3. Sampling

Contemporary samples were collected within 10 m of historical locations using georeferenced pdf maps, with the exception of “Blakiston 5”, where the historical sample location was ~50 m south-southeast in the centre of the Blakiston river. In several cases, survey

markers (rebar with an orange plastic cap), which represented Park Canada's sample locations, were visible within a few metres and care was taken not to disturb these markers. A surface sample (0-5cm) was collected along with a deeper upper solum mineral sample (5-15cm) to match the protocol employed by Parks Canada.

Soil sampling was performed over three days during the late summer in August 2021. The local weather conditions were warm, sunny, and dry. Soil conditions were moderate to dry. Upon arriving at the sampling sites living vegetation was cleared away from the soil surface. As the litter layer, which included mosses and lichens at soil surface, often had a layer of dark charcoal material attached to the underside, these materials were collected along with 1-3 kg of surface (0-5 cm) soil in a large ziploc bag using a shovel. Mineral soil from 5-15 cm was collected in the same manner from the same small pit. Photos were taken of representative vegetation, the four cardinal directions away from the pit and the soil surface before and after sampling, Sample bags were transferred to a cooler for transport to the laboratory.

2.2.4. Laboratory Analyses

Samples were weighed in the laboratory after sieving with a 2 mm mesh to remove large woody debris and coarse fragments, which were discarded. Samples were transferred to large tin weigh boats, weighed, and set in a drying oven at 60 ºC for 48 hours. Dried samples were stored in ziploc bags at 4ºC.

Soil parameters including particle size and total carbon/nitrogen were evaluated by the Natural Resources Analytical Laboratory (NRAL) at the University of Alberta. Particle size analysis (PSA) was performed via laser diffraction using a LS 13320 Laser Particle Size Analyzer (Beckman Coulter, Brea, California, USA) based on ISO methodology (ISO 13320:2009, International Standards Organization). Soil texture class was assigned based on the soil texture triangle (The Canadian System of Soil Classification, 1998). Total carbon/nitrogen (TC/TN) was determined via combustion elemental analysis by Thermo FLASH 2000 Organic Elemental Analyzer (Thermo Scientific Inc. Bremen, Germany).

Soil organic matter chemical composition was determined through two methods, including Py-GCMS analysis using the methods described in Chen et al. (2020) with modifications as described below. All samples were run in duplicate with and without

tetramethylammonium hydroxide (TMAH). The second method utilized a modified Walkley black digestion and titration to determine the amount of non-oxidisable carbon in each sample.

Samples were ground to 5 μm using a Mixer Mill Model MM 400 ball grinder (Glenmills, Clifton, New Jersey, USA) with DI water and ethanol washes, and acid-washed sand scouring between samples. Ground samples were freeze dried and submitted for PyGCMS analysis with a portion retained for Walkley-Black oxidation. About 10 mg of ground soil was measured into an 80 μL pyrolysis cup, together with 3 μL of C17:0 internal standard (methyl heptadecanoate) and 10 μL of 25% TMAH in methanol solution (omitted for runs submitted without TMAH) and placed into an AS-1020E auto-shot sampler (Frontier Laboratories, Koriyama, Japan).

Each sample was injected in a split ratio of 25:1 in single shot mode on an EGA/Py-3030D pyrolyzer (Frontier Laboratories, Koriyama, Japan). Compounds were separated via a gas chromatograph (GC)-7890B (Agilent Technologies Inc., Santa Clara, California, USA) running an HP-5MS UI column (Agilent Technologies Inc., Santa Clara, California, USA) with an internal diameter of 60 m x 0.25 mm and a film thickness of 0.25 μm combined with a 5977A mass spectrometer (Agilent Technologies, Santa Clara, California, USA). Samples were injected to the pyrolyzer at 650 ºC for 0.20 min, with the Py/GC interface and GC injector set to 300 ºC. The GC program initial temperature was 50 ºC for 10 min, then increased 3 ºC/min to 320 ºC and held for 10 min. The mass spectrometer was run in EI mode at 70 eV ionization energy, with TIC scan of mass range 45 to 650, and He as carrier gas. Data were processed using the Agilent Mass Hunter Qualitative Analysis B.07.00 software, filtering peaks with relative area $\geq$ 2% of the largest peak. A reference list of pyrogenic and other organic compounds that may be identified in sampled soils was organized based on broad compound classes including PyC markers and compared to accounts by various publications including Chen et al. (2020).

Specific pyrolysates were assigned to families of known organic compounds, including carbohydrates, lignins, phenolics, benzene and other aromatics, aliphatics, and nitrogen containing compounds. Runs with TMAH derivatize carboxyl and hydroxyl groups to their methyl esters and ether groups. In effect, methylation with TMAH decreases the polarity of pyrolysates and improves peak resolution. As a result, TMAH has been successfully used to characterize cutin and suberin biomarkers, as well as lignin monomers. On the other hand,

TMAH cannot distinguish between free hydroxyl groups and preexisting methoxy groups and can falsely identify tannin as lignin moieties.

The second analysis utilized a Walkley-Black (WB) method similar to that employed by multiple studies to estimate PyC (Hardy & Dufey, 2017; Kurth et al., 2006). To control the variability of the method, each sample was run in duplicate with results evaluated using the coefficient of variance between runs. In brief, 0.1 - 0.5 g of air-dry soil was weighed out, 10 ml of 1N dichromate solution was added and the flask was swirled to disperse the soil. The flask was transferred to a fume hood and 20 ml sulfuric acid (98%) was added, triggering an exothermic reaction, swirled for 1 minute and then placed on a ring to limit surface contact and maintain solution temperature for 30 minutes. After 30 minutes 200 ml of Ultrapure (UP) water was added to the flask, and the solution was removed from the fume hood for titration. Titration was performed by adding three drops of "Ferroin", a redox indicator ([Fe(1,10-phenanthroline)$_3$]SO_4) and titrating with 0.5N iron (II) sulphate until the solution was reduced. The solution begins as an orange colour, potentially dark green when the solution has a higher carbon content (~ >5%) and progresses to a clearer green cast then light blue followed by a sharp change to rusty brown. Iron (II) sulphate oxidizes over time in the presence of air, reducing its concentration, and requires daily calibration. Calibration runs were completed each day by titrating 10 ml of dichromate, 20 ml of sulphuric acid, and 200 ml of UP water without soil.

Organic carbon oxidized by the method was calculated using the following formula:

$$OC\ [\%]\ = \frac{(vol_b Fe_2SO_4\ -\ vol_t Fe_2SO_4)\ *\ d\ *\ e\ *\ 100}{W_{OD}}$$

Where:

- W_{OD} = Weight of oven-dried soil (g)
- vol_b = Volume of Fe_2SO_4 used to titrate blank sample
- vol_t = Volume of Fe_2SO_4 used to titrate sample
- d = Normality of Fe_2SO_4 solution
- e = 0.003: The milliequivalent atomic weight of C is 0.003 g C/ mmolc [1 mole of C = 12 g
  and each mole of C gets oxidized from 0 to +IV oxidation state, so that 1 mole = 4 $mole_c$]

Pyrogenic carbon (PyC) within each sample was assumed to be equal to the portion of total carbon that was not oxidized by the WB method. This was calculated with the following formula:

$$WBC\ [\%] = TC\ [\%w/w] - OC\ [\%]$$

Where:

- TC = Total carbon
- OC = Oxidized organic carbon

To account for the uncertainties in the definition of PyC discussed in Chapter 1, PyC determined through chemical oxidation will be referred to as Walkley-Black Carbon (WBC), its percentage (%WBC), and the proportion of soil TC that is WBC (WBC/TC).

2.2.5 Method calibration

Biochar from a residual wood waste feedstock was used to develop a calibration curve for the WB method. The biochar was ground then weighed directly into flasks in combination with acid washed sand in weight ratios to achieve the following percentages: 0%, 1%, 5%, 10%, 20%, and 30% biochar to acid washed sand. Two replicates of each calibration mixture were run to accommodate variability. Approximately 5% of biochar was oxidized through this method.

2.2.6 Data analysis

The following statistical analyses were conducted in Excel version 2303. Both differences in WBC and differences in concentration of compound families between sample types were evaluated using paired two sample t-tests for comparisons with the same number of samples including 0-5 and 5-15 cm samples collected from 2021 burned sites (15), and surface samples collected in 2018 (15). Two sample t-tests assuming unequal variances were used to compare 0-5 and 5-15 cm soils collected from 2021 reference sites (6 and 10 respectively). Single factor ANOVA was used to evaluate the differences between soil texture class. Significant differences were reported relative to $\alpha = 0.05$.

Correlations and relationships were evaluated graphically, between % TC and % WBC etc., with the independent variable on the x-axis. Strong correlation, or accuracy of the equation of the line of best fit, was defined as an R^2-value of 0.7 or greater.

Further analyses were conducted in R version 4.4.2 (RStudio 2022). PyGCMS data were standardized using a Hellinger transformation to account for null values and extreme differences present for many of the 200+ compounds evaluated within samples. Distance matrices were created for both datasets using the Bray-Curtis method as it utilizes similarities instead of distance (Legendre & Gallagher, 2001) more appropriate for environmental data that are nonlinear and contain zeros or null values. Permutational analysis of variance (perMANOVA) was performed utilizing adonis2 in the ecodist package (Goslee & Urban, 2007) to assess significant differences between site locations, time since fire, and soil texture.

Non-metric multidimensional scaling (NMDS) was used to determine similarities and dissimilarities between sample classes and evaluate the magnitude of distance between samples for method development. NMDS makes no assumptions of normality, dimensionality, and linearity (Kruskal, 1964), and assigns ranks for dissimilarity between parameters (Legendre & Gallagher, 2001), therefore it is especially effective for species data such as those obtained via PyGCMS. NMDS goodness of fit is assessed through a stress parameter, where values < 0.05 indicate low dimensionality or a strong representation of the similarities between classes, < 0.1 fair, < 0.2 good, and < 0.3 or greater indicating weak representation (Clarke, 1993). To ensure accuracy metaMDS from the Vegan package was used, which selects the most stable result from several random starts and standardizes scaling (Oksanen et al., 2022).

2.3 RESULTS

2.3.1 Site and Soil Characteristics

Slope, aspect, landform, and broad type of vegetation is outlined in Table A.1**Error! Reference source not found.**. Slopes varied significantly between different sites between 0 and 39 degrees, with a mean of 17. Aspect for sites within both burned and reference watersheds ranged from 8 (north facing) to 310 (west facing) degrees and were primarily south facing, with a larger number of flat sites located within the two reference watersheds. Landform throughout the study area was a mosaic of hillslopes, valleys, and floodplains, and sampling sites were outlined based on their slope position, where areas defined as “depositional” were flat at the bottom of slopes. Hillslope vegetation was defined as moderate to steep slopes (10-40 degrees) dominated by grasses, forbs, and lichens with no or solitary trees. Grasslands were defined with

similar species distribution, dominated by grasses and little to no slope (0-10 degrees). Forest type was defined as coniferous (< 30% deciduous species), mixedwood (30 - 70% deciduous), and deciduous (> 70% deciduous).

Coarse- and medium-textured soils dominated within studied watersheds, consistent with soils in mountainous subregions (Table A.2). Sandy loams were the most common, followed by loams, loamy sands, clay loams and silty clay loams (25, 20, 11, 4 and 1 sites respectively) distributed between 0-5 and 5-15 cm depths and burned and reference sites with no overall pattern. Soil particle size distribution was dominated by the sand sized fraction (>2 mm), where 38 of the 61 samples exhibiting greater than 50% sand with no samples containing less than 19% sand. Soils sampled from the 5-15 cm fraction from 4-year sites were of a finer texture (mean = 48) than the 0-5 cm fraction (mean = 61%) with 100-year soils containing more sand and of coarser texture (mean = 63%, 72%) than 1-year or 4-year soils. 1-year samples collected in 2018 had the finest mean texture (mean = 43%).

Total carbon and total nitrogen ranged substantially between individual sites, with mean total carbon percentages similar between 1-year post fire and 4-year post fire soils from 0-5 cm (9.21 and 9.95%) and 4-year post fire and 100-year post fire soils from 5-15 cm (4.62 and 5.68%) with significant differences between these two groups ($p = 0.014$). Despite having only six observations, mean total carbon of 100-year soils from 0-5 cm was significantly higher than from the 5-15 cm depth (21.32%) but not the other categories of 0-5 cm soils. The TC/TN ratios followed a different trend with sample means broadly similar for 4-year and 1-year post fire sites and 5-15 cm soils with the only significantly different mean in 0-5 cm soils from 100-year post fire watersheds (23.81), likely owing to the accumulation of vegetative litter the other samples do not have (Table 2.1).

2.3.2 Analytical Method Development

The greatest uncertainties in the PyC method stem from a lack of reliable and relatable analytical methods that don't require extremely large correction factors (Zimmerman & Mitra, 2017). Chemical oxidation techniques such as the one employed in this study may misidentify humified substances as PyC and completely remove lighter less recalcitrant PyC species more common in organic rich (forest floor) soil layers (Hardy & Dufey, 2017). The WB method was calibrated using wood waste biochar in acid washed sand. An average of 95.4% of added biochar

remained following the WB oxidation regardless of PyC concentration, but generally it decreased with the increasing ratio of biochar to sand (Table 2.2).

To evaluate the most effective pyrolysis-GCMS sample preparation methodology for the determination of pyrogenic carbon quantity and constituents, all 13 samples analyzed were run with and without TMAH to determine which showed better separation between target compounds. Runs with TMAH of all samples yielded 238 unique compounds, and runs without TMAH yielded 341 unique compounds, each classified into one or more of 30 large families.

Comparing the two methods, mean values of each compound of interest as a percent of all detected compounds were roughly similar with the exception of nitrogenous compounds and carbohydrates, which were significantly higher in the TMAH and no TMAH runs respectively (Table 2.3, Figure 2.2). An NMDS performed including all numeric values showed a higher degree of separation between the five classification groups in an ordination and the resulting perMANOVA had a lower, but insignificant, p-value for runs without TMAH (Figure 2.3). In addition, significant differences in a comparison of 1-year and 4-year burned samples and all 100-year samples were only found for runs without TMAH (Table 2.3).

2.3.3 Pyrogenic Carbon Production

2.3.3.1 Walkley Black Oxidation

Enrichment of WBC by wildfire was obvious in soils from 0-5 cm but could not be evaluated in mineral soils from 5-15 cm with our dataset over the 1-year to 4-years post fire timescale. Four of ten 100-year sites evaluated had analyses performed on soils from 5-15 cm but not 0-5 cm samples. Variability of WBC content was high for all sampled watersheds, with 0-5 cm 1-year post fire samples featuring the broadest range of values compared to samples collected 4-years post fire. Mean WBC in 0-5 cm soils was 3.4% w/w of soil and ranged from 0.4 to 8.8% over 15 observations (Table 2.4) within the five watersheds representing 1-year after fire. Sample means were highest in the Bauerman watershed and lowest in the Lower Cameron (4.2, 1.7%). The WBC/TC followed a similar trend, however it painted a clearer picture of the fire effects on WBC quantity. Mean WBC was 35.1% of TC, ranging from 17.2 to 54.2%, weakly correlated with increasing WBC percentage ($R^2 = 0.229$, Figure 2.4). 100-year sites in the Yarrow and Spionkop watersheds were found to have a higher mean percent WBC (4.18%) ranging from 2.1 to 8.5% over 6 observations (Table 2.4). Despite these unusually high values

the percent pyrogenic portion of total carbon ranged from 11.9 to 37.6 with a mean of 22.7%, significantly lower than 1-year post fire ($p = 0.019$). Featuring a similarly weak correlation, 100-years post fire sites exhibited a decreasing WBC/TC with increasing WBC ($R^2 = 0.137$, Figure 2.4), an opposite relationship to that of 1 and 4 year post fire sites. Differences in mean percent WBC between the 0-5 cm soils of 1-year and 100-year sites were large in the context that they exceeded the minimum % WBC value from 1-year post fire samples but were not significant ($p = 0.49$; Table A.2). When a perMANOVA including all variables (sand, silt, and clay percentage, slope percentage, % WBC and WBC/TC) was performed, significant differences were found between sites representing 1-year and 100-years post fire ($p = 0.0075$).

WBC was highly variable for all five burned watersheds 4-years post fire, with soil from 0-5 cm ranging from 0.6 to 7.3 % WBC, with a substantially higher variance compared to soils from 5-15 cm (4.0 vs 1.6, Table A.3). The opposite trend was observed for the percent WBC/TC where soils from 5-15 cm ranged from 8.1 to 69.3 % with a much larger variance (229 vs 82, Table A.3) compared to soils from 0-5 cm. Mean %WBC in 0-5 cm soils was 2.7% over 15 observations, highest in the Bauerman (4.2 %) and lowest in the Lower Cameron (1.7 %) watersheds. Following a similar trend, the mean WBC/TC was 26.9%, highest in Bauerman (30.7 %) and lowest in Lower Cameron (23.1 %) (Table A.3). The pattern was the same for both measures in mineral soils from 5-15 cm where mean WBC was 1.2 % (Figure 2.5), with Upper Cameron at the top end (2.4 %) and Bauerman (0.4 %) at the low end, and a mean of 23.3 % WBC of TC, with the highest value falling within the Upper Cameron (34.1 %) and lowest value within the Bauerman watersheds (13.1 %). Burned soils collected 4-years following fire featured significantly higher means of WBC in 0-5 cm soils compared to those from 5-15 cm at the same sites ($p = 0.018$). Despite nearly identical minimum values but extremely different maximums, the difference in mean percent of WBC of TC however was not significant between the two depths ($p = 0.43$). 100-year soils were much the same with a significant difference between mean percentage WBC and no significant difference for means of WBC/TC ($p = 0.041$ and 0.16) despite differences being much larger than either 1-year or 4-year soils (Table A.1).

Means varied to a greater magnitude in 100-year watersheds sampled in 2021, where soil from 0-5 cm ranged from 2.0 to 8.50 % WBC, a much higher variance compared to soils from 5-15 cm (0.87 vs 2.76, Table A.3). Soils from 5-15 cm were more dissimilar, where percent WBC/TC ranged from 19.6 to 73.59 % with 3.5 times the variance (275 vs 77, Table A.3)

compared to soils from 0-5 cm and 1-year and 4-year soils, possibly owing to the smaller sample size. Mean WBC in 0-5 cm soils was 4.19% over 6 observations, highest in the Spionkop (5.35 %) and lowest in the Yarrow (3.02 %) watersheds. Observing an opposite trend, the mean WBC/TC was 22.70%, highest in Yarrow (28.70 %) and lowest in Spionkop (16.69 %) (Table A.3). In mineral soils from 5-15 cm mean WBC was 1.68 % (Figure 2.5) over 10 observations, with Yarrow at 1.71 % and Spionkop at 1.65 %, and a mean of 32.24 % WBC of TC, with Yarrow similarly higher (39.45 %) and Spionkop lower (25.03).

A regression of percent WBC of TC vs percent WBC revealed an increasing relationship but no correlation for soils from 0-5 cm ($R^2 = 0.23$) and a comparatively much stronger relationship with a 1% increase in WBC increasing its portion of TC by approximately 10%, explaining 73% of the variation in values ($R^2 = 0.73$). A positive relationship was also found for soils from 5-15cm 100-years after fire, with each 1% of percent WBC increasing its portion of WBC by approximately 12% with only 29% of variation explained by WBC ($R^2 = 0.29$), contrasting the negative relationship for 0-5 cm soils with no correlation ($R^2 = 0.14$). Even considering the lack of correlation in the case of 100-year sites, soils from 5-15 cm had very similar relationships between percent WBC and its portion of TC for 4-year sites and 100-year sites including identical intercepts (Figure 2.4).

2.3.3.2 Pyrolysis GC-MS

Soils from 0-5 cm evaluated by PyGCMS consisted of three 1-year and two 100-year samples (Table A.4). Variability among samples was substantially higher than what the Walkley-Black analyses yielded owing to the increased complexity of the 300+ constituent compounds making up organic matter found in these soils. Compounds of interest for the evaluation of pyrogenic carbon include benzene/aromatic hydrocarbons (BAh), phenolics (Ph), polyaromatic hydrocarbons (PAH) and pyrogenic C. Differences between the 1-year 0-5 cm samples and samples from the 100-year sites were not significant for any of the individual compound families despite the substantial differences between sites within the five categories, possibly due to the low sample size. When evaluated together, mean values for all compound families were significantly different between the two sample types ($p = 0.04$), however means for aromatic species were not ($p = 0.5$). Benzene and PAHs in particular showed the largest differences between the two sample groups, but differences were still not significant. Notably, sites with comparatively low and identical concentrations of PAHs, Spionkop 4 and Cameron 1 (2.07 mg/g

of carbon) share no common soil or ecosystem characteristics. Compound families were analyzed further in an NMDS, however due to the low number of samples for 100-year sites (2), distance within any given confidence interval is indeterminable. Two perMANOVAs including all compounds, and all aromatics were performed, finding no significant differences between the 1-year and 100-year sites in either case ($p = 0.4, 0.1$).

When all samples were evaluated together means for all four relevant compound groups were highest in burned soils from 5-15 cm 4-years after wildfire, and lowest for burned soils from 0-5 cm 4-years after fire (Table A.4; Table A.5), whereas means from both 0-5 and 5-15 cm depths collected from 100-year sites were very similar, with phenolics at 22.35 and 20.45 mg per g of carbon and PyC at 114 and 128 mg per g of carbon respectively (Table A.4; Table A.5). Aromatics as a whole were comparable among samples, however the lowest means of Benzene and Alkylbenzene were found in 100-year soils from 0-5 cm (1.53 and 10.58 mg/gC), and PAHs in 100-year soils from 5-15 cm (3.86 mg/gC). Further, Alkylbenzene was the most abundant aromatic compound on all sites within all classes.

Changes with depth were not significant when all 4-year samples were analyzed together in PyGCMS for both the holistic chemical composition and aromatics specifically within an NMDS. When examined independently, compound families within 4-year soils were significantly different between 0-5 cm and 5-15 cm depth classes ($p = 0.004$), and 100-year soils were also significantly higher ($p = 0.06$) (Table 2.3). In-depth analysis of the aromatic family revealed that benzene, PAHs, and alkylbenzenes were approximately three to five times higher for the 5-15 cm fraction 4-years after wildfire than 0-5 cm and 100-year 5-15 cm soils (Figure 2.6).

2.3.4 Pyrogenic Carbon Longevity

The date of most recent burn within the reference watersheds is unknown. The last recorded fire in the greater Castle area happened in 1936, however given the extent of vegetation, lack of evidence of recent surface fire, and differences in soil and WBC parameters it will be assumed that significant time, approximately 100-years, has passed since the sites last experienced wildfire for the purposes of comparison.

Total carbon, total nitrogen and total carbon to total nitrogen ratio (TC:TN) were highly variable between the 1-year and 4-year samples from 0-5 cm. Notably there were no significant

differences between 1-year and 4-year mean TC (9.21 and 9.95%) and TC (0.61 and 0.57%), and TC:TN (14.9, 17.3), however the p-value for TC/TN is on the threshold of significance ($p = 0.051$). Despite mean %WBC from 0-5 cm being higher directly after the wildfire (3.38 and 2.73%), differences were not significant from 1-year to 4-years, with the maximum and minimum differences occurring in the Upper Cameron and Lower Blakiston watersheds respectively (2.03 and 0.33%). Possibly a better measure of environmental difference, significant differences were found for the means of percent WBC/TC from 1-year to 4-years (35.1 and 26.9%, $p = 0.026$), with the maximum and minimum differences occurring in the Upper and Lower Blakiston watersheds respectively (16.91 and 0.98%). There were no significant differences between either percent WBC or its portion of TC for any single watershed. Regression lines modeled on the relationship of percent WBC/TC as a function of percent WBC featured nearly identical slopes between 1-year and 4-year soils where each 1% increase in WBC drove an increase of 2.13 and 2.20% ($R^2 = 0.229, 0.232$) in its portion of TC respectively, differing only in their y-intercepts, or baseline WBC of TC, of 27.9 and 20.9% respectively (Figure 2.4).

Reference watersheds were analyzed as a proxy for change in fire effects over long periods (100-years). While means were higher in all cases, 100-year site's TC, and TN were not significantly different in soils 0-5 cm deep from either 1-year or 4-year burn sites, whereas TC:TN ratio was higher in 4-year samples ($p = 0.046$) (Table A.1). Critically, despite a depletion in percent WBC from 1-year to 4-year, means were highest in 100-year soils but were not statistically significant ($p = 0.21$). The WBC/TC was also not statistically significant ($p = 0.33$) but decreased from 1-year to 4-year to 100-year samples. Notably the relationship of percent WBC/TC as a function of percent WBC was negative on 100-year sites, with a slope of -1.42, however the relationship was very weak, possibly owing to the small number of samples ($R^2 = 0.137$).

Means for samples collected in 2018 analyzed with PyGCMS were higher for all compound families compared to 2021 burned sites, however there were no significant differences between overall chemical composition or aromatics specifically over time in soils from 0-5 cm. Despite higher means for 100-year soils than 4-year but not 1-year for many compound families including benzene/aromatics and aliphatics and higher means of phenolics and nitrogenous compounds than 1-year soils, no differences were significant. Generally,

concentrations of benzene, PAHs, and alkylbenzene decreased along the time gradient from 1-year to 100-year soils.

2.3.5 Pyrogenic Carbon Relationship to Site and Soil Characteristics

Soil texture, in particular moderate to high clay content, has been hypothesized to store more PyC than coarser texture soils, however there were no significant differences between means of % WBC and its portion of TC for any of the five soil textures that made up 4-year sites, or the three that made up 100-year sites. Excluding SiCl as the sample size of one makes differences incalculable, means increased with increasing soil coarseness in all cases, with sandy loams the only outlier for means of WBC/TC in 4-year sites (Figure 2.7). Means of % WBC and WBC/TC were broadly similar for all soil textures found in both 4-year and 100-year sites where loams had the largest percentage differences in both cases while remaining insignificant. Pyrogenic portion of TC was strongly positively correlated with % WBC for clay loams (R^2 = 0.97, 4 observations) and weakly for loams (R^2 = 0.44, 20 observations) across all sample types. The relationship increased in strength for loams in 4-year soils from 5-15 cm (R^2 = 0.73, 6 observations) and sandy loams in 4-year and 100-year soils from 5-15 cm (R^2 = 0.66, 0.51, and 5, 3 observations). Ordinating all samples revealed an association between silt and clay and 1-year and 4 -year sites, with no clear texture relationship for 100-year sites. When a perMANOVA including all variables was performed, significant differences were found between texture classes for all comparisons within all sites from 0-5 cm (p = <0.0001) and 5-15 cm (<0.0001).

Contrary to expectation, increasing % WBC and the WBC/TC were not correlated with either increasing or decreasing slope. For all datasets maximum WBC values were observed on slopes greater than eight percent and as high as 26 and 28% for 100-year and 4-year soils respectively. An NMDS performed including all numeric values revealed a correlation between slope and % WBC for 100-year soils from 0-5 cm, slope and WBC/TC for 1-year soil from 0-5 cm, and slope and both % WBC and WBC/TC for all soils from 5-15 cm. A perMANOVA including all variables showed significant differences between samples of different slope (p = <0.0001) and the four slope positions defined as landform for soil from 0-5 cm (p = <0.0001) and 5-15 cm (p = 0.001).

2.4 DISCUSSION

2.4.1 Site Character

Differences observed between burned soils less than one year post wildfire and 100 years post wildfire both met and defied expectations. The present study found mean total carbon at 0-5 cm depth was much higher for the 100-year post-fire soils with no significant difference, owing to the accumulation of litter, decomposition products, and a broader mosaic of soil organic matter than a recently burned soil. While not directly comparable due to inconsistent geographic location, soil, and vegetation, the 11% difference in soil TC from 0-5 cm between 1-year and 100-year post-fire sites (9.21%, 21.26%) is much larger than the difference in TC among soils from the 5-15 cm depth interval (4.62, 5.68%). These results are in agreement with similar studies on Mediterranean pine forest, and ponderosa pine forest in Colorado (Boot et al., 2015; Certini et al., 2011) and are the best measurement of the consumptive effects of wildfire.

2.4.2 Contrasts in PyGCMS Pretreatment Methodology

To better elucidate the effects of PyGCMS on PyC and non-PyC chemical constituents of our soil samples, pretreatment methodologies were evaluated to determine the technique with the greatest detection and separation of pyrolysate compounds associated with PyC. Tetramethylammonium hydroxide is a chemolytic agent that acts to alter constituent compounds through hydrolysis and methylation of esters and ether linkages, allowing analysis of polar compounds in GCMS (Chefetz et al., 2000). Runs with TMAH returned nearly one third fewer compounds (238 vs 341), likely contributing to the lower stress values (0.036 vs 0.068) when evaluated in an NMDS. The overall concentration of compounds classified under the nitrogenous category were increased and carbohydrates were decreased compared to runs without TMAH, typical for this type of SOM analysis (Chefetz et al., 2000). Runs without TMAH had visibly higher separation in ordination and greater statistical separation with a lower p-value than those with TMAH ($p = 0.1813$ vs 0.2128). 100-year post-fire sites of both depth classes had two samples each, rendering distances between those and burned sites potentially uninterpretable. This is important as unburned sites more closely resemble soils analyzed with TMAH.

Greater separation, the lack of literature with TMAH utilization in the pretreatment of burned or biochar amended samples (Kaal & Rumpel, 2009), and the comparability of our results

to ratios of four compound families established in Chen et al., 2020, guided the decision to solely interpret the data obtained from runs without TMAH for the purposes of this study.

2.4.3 Wildfire Effects on Pyrogenic Carbon

Quantification of PyC suffers greatly from inconsistent terminology and technique across the literature (Bowring, 2022) making comparisons challenging. Up until very recently pyrogenic carbon stock and character in sub-alpine and other mountain ecosystems was unknown or poorly understood (Bird et al., 2015; Reisser et al, 2016). As a baseline both 1-year and 100-year post-fire soils feature a similarly strong relationship between TC and WBC (0.89 and 0.85 respectively) that agrees with a study in the southern Appalachian Mountains (Matosziuk et al., 2020), increasing our confidence in the conclusions reached through the present study in comparison with contemporary literature.

Contrary to expectations, 0-5 cm samples at the 100-year post-fire sites contained higher mean WBC by weight of soil compared to 1-year post-fire samples, although no significant difference was present. The opposite was true for WBC/TC with significantly higher means as a result of the burn (35.1, 22.7%, $p = 0.019$). The latter measure is a better indicator of pyrogenic carbon enrichment post-fire, and accounts for both the increase of PyC and reduction of other SOM. Higher variability of WBC was observed for burn sites, due likely in part to the larger sample size and greater heterogeneity in site and soil characteristics. Results are in line with studies performed on prescribed burns, where surficial soil (LFH in the Canadian System of Soil Classification) defined as O-horizon had higher BPCA, a PyC indicator similar to WBC examined in our study, per kg C but lower PyC indicator per g of soil, and differ from others on wildfire, where 100-year soils from 0-5 cm had higher values for amount of BPCA and proportion of all carbon for moderate and high severity fires, similar to the fire severity of the KW in the present study (Matosziuk et al., 2019; Boot et al., 2015). In step with the above studies, certain site parameters such as location of slopes, heterogeneity of soil textures, and fire patchiness, likely driven in this study by inconsistent vegetation coverage across sites, may have led to the wide range of values observed within 1-year post-fire sites for both WBC content and WBC/TC. Areas of greater fire intensity, more common in fall fires (Matosziuk et al., 2019), experience more complete combustion of materials, generation of lighter PyC more prone to wind erosion, and consumption of existing PyC (Bird et al., 2015). The hot weather, high winds,

increased fuel load, and early fall timeline of the KW likely contributed to heterogeneity of fire effects between sites.

Overall, enrichment of WBC was observed on 1-year compared to 100-year post-fire sites, but not to the magnitude expected or observed in similar subalpine ecosystems (Boot et al., 2015; Matosziuk et al., 2020). The present study did not evaluate localized burn severity for each sample site, which when combined with time since fire was observed to be a significant factor for the production of PyC, increasing levels 10 times in some cases (Matosziuk et al., 2020). In addition, these two studies were localized within a smaller area of relative landscape and ecosystem homogeneity, and in the case of Matosiuk et al, compared pre- and post-burn. The discontinuous nature of our study sites contributed to the higher variance observed within those sites affected by the fire and between burned and unburned watersheds. This combined with the lack of deeper soil samples available directly following the wildfire limits the conclusions we can reach about immediate soil effects as a result of the KW.

Expected chemical changes were observed in burned areas. Samples were evaluated ungrouped as individual compound signals, in broader families (carbohydrates, aliphatics etc.), and subclasses within the benzene/aromatic family. Classes of interest included fire indicators, such as benzene, other aromatics and nitrogenous compounds, and non-fire indicators such as carbohydrates, phenolics, and aliphatics. Due to the limited sample size of two for the 100-year post-fire sites, distances cannot be examined for significance. Differences in mean values of compounds sorted into families of interest were not significant, possibly due to inadequate method sensitivity, inappropriate compound classification, or simply too few samples. This result could also imply that the short time between the fire and collection of samples was sufficient for the majority of pyrolysates to erode, percolate or otherwise be transported away from soils 0-5 cm in depth. A one-year time period has been shown to eliminate significant differences in PyC content for O-horizon soils and those from 0-10cm (Matosziuk et al, 2020). Additionally, fire intensity increases the aromatic condensation of PyC, therefore increasing the proportion of benzene and similar compounds due to higher severity wildfire (Matosziuk et al., 2020), which are reflected in the slightly increased levels of benzene, alkylbenzene and PAHs found in our 1-year post-fire samples. Phenolics, typically associated with mature organic matter common in forest litters (Chen et al., 2020) were lower however, further indicating an effect by the burn that was not associated with changes in total carbon.

2.4.4 Site and Soil Characteristics as Drivers

Pyrogenic carbon stocks have been observed to be larger in fine textured soils, specifically clays, globally, possibly due to higher SOC levels associated with clay dominated soils (Czimczik & Masiello, 2007; Reisser et al., 2016). The present study observed the opposite trend with respect to means, where %WBC increased on a gradient of soil texture class from clay loam to loamy sand, but not with increasing percent sand, whereas median values decreased from loamy sand to loam soils. When considered together these indicate that the driver could be something other than particle size distribution that itself is affected by soil texture, though no patterns emerge within the number of samples examined by this study. Data resolution was low for clay loams due to their relative scarcity in the study area (n = 4), however they featured the strongest relationship of WBC/TC by %WBC and the largest slope, with each 1% of WBC corresponding to 16% WBC/TC. The magnitude of TC made up by such a small percentage of WBC could be driven by the formation of organo-mineral complexes combined with significantly lower pore space leading to preferential storage of PyC over other SOC that is subsequently shielded from degradation (Czimczik & Masiello, 2007; de Oliveira et al., 2022).

Slope percentage appeared to have no effect on WBC generation, with the highest concentrations occurring on slopes greater than 8%, up to 28%. Examined qualitatively, areas of steep slope featured no vegetative commonalities and inconsistent slope position, occurring on both backslopes and toeslopes. Both pyrogenic feedstock and hillslope location likely drive WBC production more than slope percentage (Boot et al., 2015), supported by the present study. The first significant precipitation event is the most important factor determining the ultimate location of PyC materials (Masiello & Berhe, 2020), distributing them away from eroding landform positions to downhill areas such as floodplains (Abney et al., 2017). Despite a limited effect of slope on PyC movement noted in major studies (Boot et al., 2015; Cotrufo et al., 2016), given the lag between burn and sample collection, including snowmelt and runoff in the spring season, there should be an obvious increase in PyC in toeslope and depositional hill positions. Curiously this was not observed in the present study, possibly due to the increased surface roughness characteristic of mountain hillslopes with a high percentage of coarse fragments (Belle et al., 2021), a feature on our sites with steeper slopes.

2.4.5 Aromatic Enrichment as a Legacy Fire Effect

When analyzed together, the dramatically higher means of specific families of compounds such as benzene, PAHs, and nitrogenous compounds found in 4-year soils of the 5-15 cm fraction indicate an enrichment of three to five times the background level as a short-term result of fire. Soils from 5-15 cm on 100-year sites showed a similar enrichment effect in the same families when compared to 0-5 cm soils but at much lower levels and with no significance. This effect is even more noticeable in contrast to the relative similarity of 4-year and 100-year soils from 0-5 cm collected in 2021, with the 100-year sites featuring higher means in all cases. The differences between 1-year samples and 4-year or 100-year samples are too small to account for the level of enrichment observed from 5-15 cm in the 4 years since the wildfire. This increase may have been observed directly post wildfire, likely to a lesser extent, had 5-15 cm soils from 1-year been evaluated. Possible implications include the rapid vertical translocation of these species down through the profile in the short term following wildfire (< 4 years) that has been noted in multiple studies (Chen et al., 2020; Kim et al., 2011), or that the watershed's status as a heavily trafficked national park has led to a more aggressive fire suppression regime than the 100-year sites, reducing PyC content in soils from 0-5cm below natural levels, however it is hard to tell without establishing the source of these compounds and the most accurate fire record places the last large scale fire on the 100-year sites in 1936. Despite this uncertainty our findings are within expectations and mirror the results of two other studies focused on PyGCMS (Chen et al., 2020; Kim et al., 2011).

Further to the short-term enrichment, means observed within 100-year 5-15 cm soils insignificantly higher than 0-5 cm soils from both 4-year sample types imply that sometime between four years post wildfire elevated levels of these pyrolysate compounds are consumed by soil biota, transformed to less recalcitrant species, or further translocated deeper into the soil profile, while still maintaining a higher concentration than soils from 0-5 cm due to protective mechanisms discussed earlier. Phenolics, as observed by Kim et al., 2011, are the only family that remains higher in 100-year 0-5 cm soils, likely due to their source which is commonly attributed to mature organic matter.

2.4.6 Depth Distribution of Pyrogenic Carbon

Soils collected in 2021 included both surface samples from 0-5 cm, and deeper samples from 5-15 cm allowing for comparisons with depth. Pyrogenic carbon begins to move from 0-5 cm soil layers deeper into the profile within 30 minutes of intense rainfall and has significant mobility overall within the first year post wildfire (Belle et al., 2021; Matosziuk et al., 2020). That TC explains > 80% of the variation in %WBC for 0-5 cm samples from both 4-year and 100-year sites indicates WBC storage is closely tied to initial production of PyC, which itself is a function of TC, or the interference from other OM that is not oxidizable by our method is significant. This relationship weakens with depth, explaining only 49 and 28% of variation in 5-15 cm soils respectively, illustrating a shift in the type of organic matter or size fraction of PyC that makes up WBC from 5-15 cm.

Means of %WBC for soils from 5-15 cm were significantly lower as expected (1.2 vs 2.7%, $p = 0.018$) compared to 0-5 cm on 4-year sites. A greater difference with a similar level of significance (1.7 vs 4.2%, $p = 0.02$) was observed on 100-year sites between 0-5 and 5-15 cm soils, implying a comparable relationship with depth. These results are supported by well established mechanisms of surface erosion, where first interactions with precipitation and runoff most significantly determine the ultimate location of PyC, vertical distribution via pedoturbation, burying events such as rock and mudslides, and percolation with precipitation, as well as biotic transformation resulting in loss from surface layers, potentially to deeper soils or the atmosphere (Masiello & Berhe, 2020; Belle et al., 2021; Santos et al., 2022; Hobley, 2019). Additionally, as the majority of PyC produced by fire has been observed to be < 2 mm in diameter (Jenkins et al., 2014), mountainous areas like our study which are typically dominated by coarser soils could support increased vertical redistribution of particulate PyC due to greater pore sizes (Hobley, 2019).

In regards to WBC/TC, a lack of significantly different means between depths for either 4-year or 100-year sites agrees with findings from other mountain fires (Matosziuk et al., 2020, 2019; Boot et al., 2015). This further reinforces the changing relationship between PyC and TC with depth, as important non-pyrogenic sources of TC are increasingly reduced as the soil deepens. A significantly smaller percentage of %WBC contributes to roughly the same WBC/TC ratio, as it may be subject to protective mechanisms not afforded to other SOC types or PyC present in the 0-5 cm samples (Matosziuk et al., 2020). In addition, %WBC explains 73% of the

variation in WBC/TC, indicating that increasing volumes of PyC displace and replace other SOC in deeper soils, consistent with a greater sorption affinity (Schiedung et al., 2020).

Regression lines of %WBC versus WBC/TC show very different trends between 0-5 and 5-15 cm soils for both 1-year and 100-year samples. Increasing %WBC greatly increased WBC/TC in the 5-15 cm soil fraction with a stronger relationship on 4-year sites ($R^2 = 0.73$), contrasting the 1/5th but still positive relationship weakly correlated in 4-year 0-5 cm soils, and the weak negative relationship evident in 100-year 0-5 cm soils. These results further reinforce the magnitude of protective effects available to PyC the deeper they translocate through the soil profile.

Unfortunately, these results may be subject to confounding factors, particularly those from 100-year sites, due to the accumulation of non-pyrolysed vegetative matter. Recalcitrant OM species with similar resistance to the Walkley Black Oxidation method could be masquerading as PyC within our detection range, the amount of which is incalculable in the present study.

2.4.7 Short Term Changes in Pyrogenic Carbon

Differences between 1-year and 4-year soils were compared as a measure of short-term change and to determine the longevity of fire effects. The heterogeneity of soil is high, even for samples collected a few centimeters from each other, especially in mountain soils where coarse fragments are large and numerous. These factors related to vegetative recovery and deposition of organic matter over the three year gap in sampling explain the differences in texture and elemental composition of soils paired by collection site observed in the present study.

Over the three year span the mean %WBC in soils from 0-5 cm decreased from 3.38% to 2.73% with only three of fifteen sites increasing during this period. Differences are likely due to erosive mechanics described above that move PyC deeper into the soil profile as well as lateral erosion dynamics unique to post-fire conditions (Abney et al., 2017). Recent literature is demonstrating that PyC is more highly susceptible to erosive forces than non-PyC (Abney et al., 2017; Rumpel et al., 2006; Yao et al., 2014). Field studies on erosion dynamics particular to PyC have shown that 7 to 53% of biochar applied to surface soils is lost to runoff and erosion (Kaal & Rumpel, 2009; Major et al., 2010) and an average of 11% of fire produced PyC can also be relocated (Cotrufo et al., 2016). Post-fire erosion conditions, exacerbated by vegetation removal

which increases overland flow of surface runoff, in concert with the increased hydrophobicity of PyC relative to other SOC, have reduced the stock of WBC in the time since the KW (Belle et al., 2021; Certini et al., 2005). While aeolian transport of lighter PyC (ashes, soots) was also a factor, erosion of this type likely took place immediately following the fire and the missing materials were not captured in samples 1-year afterwards (Abney & Berhe, 2018). Further to this, no significant differences were detected for depositional landforms like the Blakiston floodplain (Blakiston 1, Bauerman 1) and samples collected next to watercourses (Blakiston 3, Blakiston 5), over erosive landforms surrounding them (Cameron 4, Lineham 1), indicating that PyC relocated in this manner was minimal or simply indetectable by our methods.

The ratio of WBC/TC in soils from 0-5 cm is an entirely different story, decreasing significantly from 35.1 to 26.9% over the three year period, increasing on three sites similarly to %WBC. Normalized to each sample's TC, this is a much better indicator of the relative abundance of PyC. As mean %WBC is not significantly lower in 4-year post-fire soils vegetative recovery of these ecosystems and subsequent deposition of non-PyC OM could have led to a dilution of PyC present in the upper layer (Matosziuk et al., 2020) in addition to loss and translocation of WBC away from 0-5 cm soils.

The chronosequence is most succinctly described via the regression of WBC/TC as a function of %WBC, where the relationship is practically identical for both 1-year and 4-year burned soils, the major difference being a larger base value of WBC/TC for each 1 %WBC. This elegantly demonstrates the static nature of the relationship between overall PyC content and how much PyC contributes to SOC, despite the reduction in PyC concentration over this short time period, however the correlation is weak for both relationships (R^2 = 0.229 and 0.232) and cannot be considered representative.

2.4.8 Long Term Changes in Pyrogenic Carbon

With the last known burn taking place roughly 86 years ago in the Spionkop and Yarrow, soils collected in these watersheds were evaluated as a proxy for longer term trends in PyC. Despite the greater than 4 years, and likely close to 100-years since fire, 0-5 cm 100-year samples had the highest %WBC but were not significantly different from 1-year or 4-year post-fire samples. The high values of %WBC are likely a result of the limitations of our method, mischaracterization of other recalcitrant SOC as PyC combined with the comparatively

enormous TC but could be legacy PyC captured and protected in soils from previous fires (Walker et al., 2019). Mirroring and exceeding the magnitude of PyC dilution by OM input observed in 4-year soils WBC/TC was lowest for the same 100-year 0-5 cm samples. The magnitude of difference (- 4.2%) is roughly half that of the short term (- 8.2%), suggesting that the majority of loss and dilution takes place shortly after fire, decreasing exponentially over time to a stable point sometime between 4 and 86 years.

The 100-year post-fire deeper soil layers (5-15 cm) had higher means of both metrics as well, though insignificant, and examined solely would imply that there was little to no change in the long term at depths greater than 5 cm. The dramatically elevated concentrations of aromatics in 4-year post-fire 5-15 cm soil layers imply that not only is the WBC of an entirely different character despite being relatively less abundant but that this fire effect disappears over time in this specific soil layer, consistent with increasing PyC condensation with depth (Boot et al., 2015; Matosziuk et al., 2020).

The 100-year post-fire shallower soil layers (0-5 cm) featured the only negative relationship between %WBC versus WBC/TC, suggesting that sometime after 4 years the proportion of TC that is PyC becomes independent of any concentration of PyC present in the soil, whereas soil layers from 5-15cm do not, exhibiting a roughly similar relationship over time albeit with a much higher variance in WBC/TC as a function of %WBC.

2.5 Conclusion

Shallow soil layers (0-5 cm) burned by the Kenow Wildfire exhibited a clear and distinct enrichment in WBC that was not reflected in an increase in WBC abundance when compared to the 100-year post-fire soils. Given that severe wildfire has been observed to add significant quantities of PyC to affected soils across the literature we can be certain that despite the lower mean WBC obtained for 1-year post-fire soils the significantly increased ratio of WBC/TC does indeed reflect a considerable addition of pyrolysates to the SOM of soils from 0-5 cm immediately following wildfire. While not significant, pyrolysate indicators such as benzene and PAHs were elevated on 1-year post-fire sites while indicators of humified material such as phenolics and nitrogenous compounds remained higher in 100-year post-fire soils, further reinforcing this conclusion. Soil texture was the only factor examined that appeared to have any consistent effect on the quantity of WBC though results conflict. Increasing coarseness in soil

texture (CL to LS), but not specifically percent sand, was loosely correlated with increasing %WBC, however clay loams featured a comparable ratio of WBC/TC to other soil textures despite a lower %WBC.

Pyrogenic carbon is translocated vertically down the soil profile and away from topsoils on very short timescales. Levels of pyrolysate enrichment observed in soils from 5-15 cm over three years are inexplicable given the comparatively minor decrease between soils collected immediately post-fire and those from 4-years afterward from 0-5 cm. Similar increases in aromatic compounds were not observed in these 0-5 cm soils, implying that they were removed in the short time between fire and sampling in 2018, despite the lack of prefire reference soils or those from the 5-15 cm fraction for the same sites. Over the long term, greater than 4 years, this enrichment gradually lessens as non-pyrolysate humified substances dilute the PyC pool and condensed aromatic compounds are consumed or transformed, however significant quantities of PyC remain in the soil from 0-15 cm.

The relationship between %WBC and its portion of TC was strong for the 5-15 cm soil samples collected at the 4-year post-fire sites, with the correlation weakening dramatically in the 100-year post-fire soils at the same depth. These results agree with contemporary literature, soil horizons from 0-5 cm and those from 5-15 cm have very different roles; surficial horizons are the first point of contact for PyC materials and act as a long-term source, whereas deeper soil horizons act as a sink.

Table 2.1 Mean and standard error of carbon, nitrogen, and Walkley-Black carbon parameters

Depth (cm)	Type	Total Carbon (%)	Total Nitrogen (%)	TC/TN Ratio	Walkley-Black Carbon (%)	Walkley-Black Proportion of Total Carbon (%)
0-5	1-year	9.21 ± 1.59	0.62 ± 0.09	14.89 ± 1.10	3.38 ± 0.64	35.13 ± 2.85
	4-year	9.95 ± 1.82	0.57 ± 0.09	17.29 ± 0.89	2.73 ± 0.51	26.91 ± 2.35
	100-year	21.32 ± 5.52	0.87 ± 0.19	23.81 ± 2.43	4.18 ± 0.94	22.70 ± 3.59
5-15	4-year	4.62 ± 0.73	0.31 ± 0.06	15.62 ± 0.95	1.19 ± 0.33	23.28 ± 3.91
	100-year	5.68 ± 0.79	0.33 ± 0.05	17.45 ± 1.27	1.68 ± 0.23	32.24 ± 5.25

Table 2.2. Walkley-Black oxidation calibration values

Calibration ID	Biochar/acid washed sand (%)	Total carbon removed (g)	Total carbon remaining (g)	Resistant carbon (%)
C1	1	0.03	0.97	97
C5	5	0.27	4.73	94.6
C10	10	0.38	9.62	96.2
C20	20	1.06	18.94	94.7
C30	30	1.64	28.36	94.5

Table 2.3. Significance values for compound families of interest analyzed in PyGCMS without TMAH

	Carbohydrate	Phenolic	Benzene/A	Aliphatic	Nitrogen compounds	Pyrogenic C (pyrolysis)	PyC marker
P-value	<0.000	0.273	0.095	0.886	<0.000	0.517	0.111

Table 2.4. Total carbon, nitrogen, and Walkley-Black carbon percentages of all soils collected 1-year post fire

Type	Location	Total Carbon (%)	Total Nitrogen (%)	TC/TN Ratio	Walkley-Black Carbon (%)	Walkley-Black Proportion of Total Carbon (%)
Burned	Bauerman 1	3.74	0.28	13.37	0.89	23.79
	Bauerman 2	9.96	0.74	13.46	4.43	44.44
	Bauerman 3	3.7	0.39	9.49	1.28	34.66
	Blakiston 1	6.37	0.56	11.38	1.18	18.51
	Blakiston 2	5.26	0.41	12.84	1.17	22.25
	Blakiston 3	17.79	0.7	25.41	5.54	31.13
	Blakiston 4	4.28	0.36	11.89	1.89	44.07
	Blakiston 5	5.29	0.25	21.18	2.87	54.18
	Blakiston 6	20.33	1.15	17.62	8.78	43.21
	Cameron 1	8.16	0.49	16.66	2.93	35.94
	Cameron 2	4.72	0.42	11.24	1.98	42.01
	Cameron 3	19.41	1.23	15.78	5.96	30.72
	Cameron 4	12.85	1.18	10.89	5.91	45.98
	Carthew 1	13.92	0.94	14.81	5.43	39
	Lineham 1	2.42	0.14	17.29	0.42	17.15

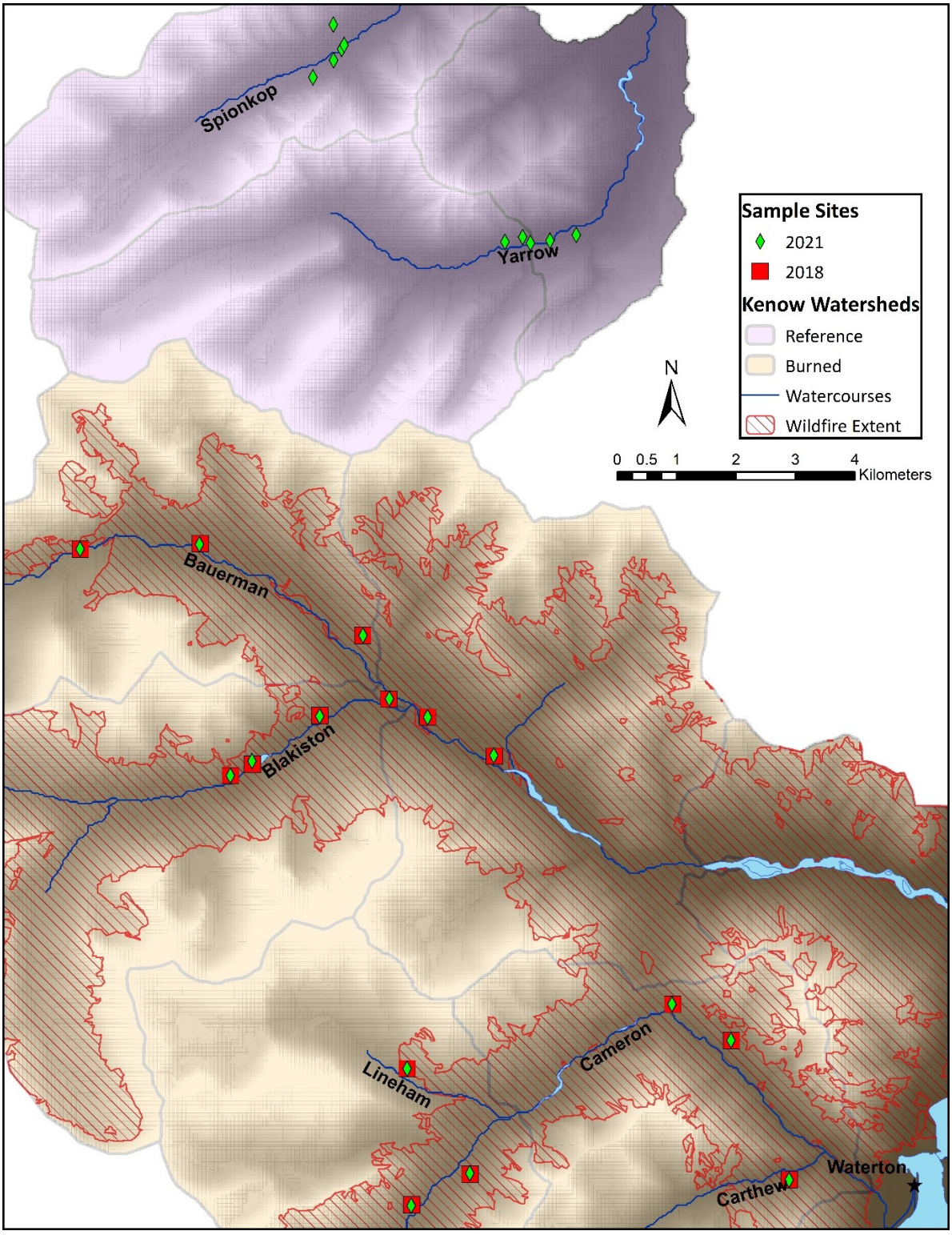

Figure 2.1. Kenow Wildfire sampling map in Waterton and Castle Provincial Parks, showing burned and unburned reference areas and extent of burn. Historical Parks Canada sampling locations (2018) shown in red, contemporary sampling locations (2021) shown in green

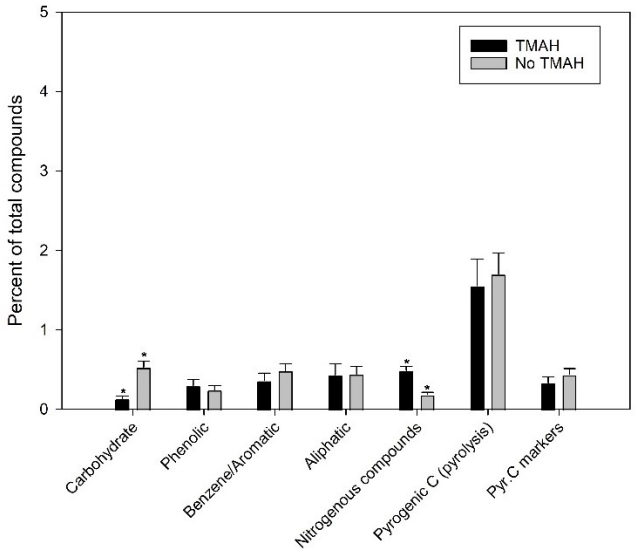

Figure 2.2. Method comparison of PyGCMS runs with and without TMAH including seven compound families of interest. Asterisks denote compound families with significant differences between run types

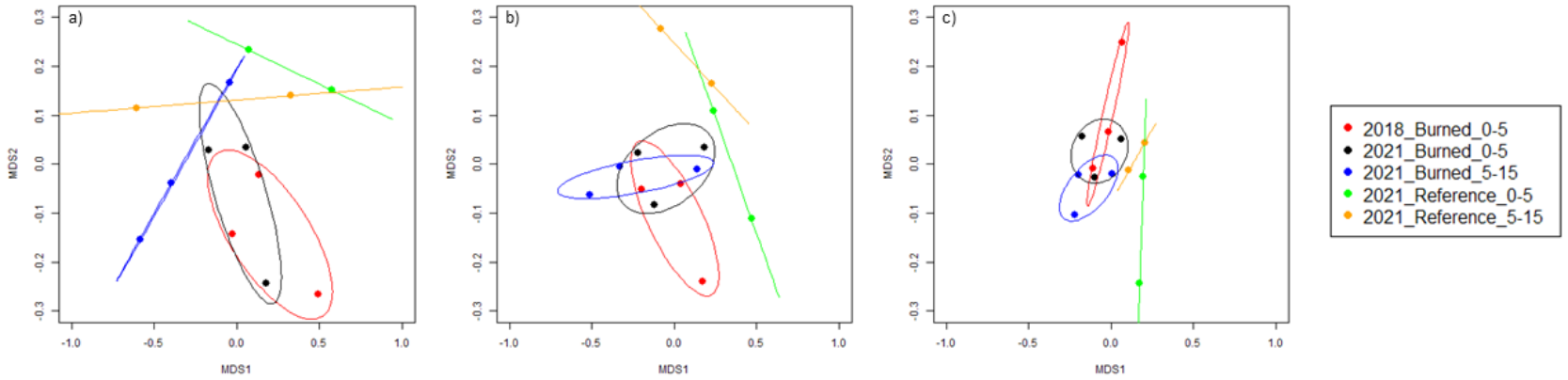

Figure 2.3. NMDS of PyGCMS runs of: all compounds run with TMAH (a), all compounds run without TMAH (b), and aromatic hydrocarbons run without TMAH (c) of 13 samples belonging to 5 groups with ellipses of 95% confidence intervals. Stress values are 0.036 (a), 0.068 (b), and 0.101 (c).

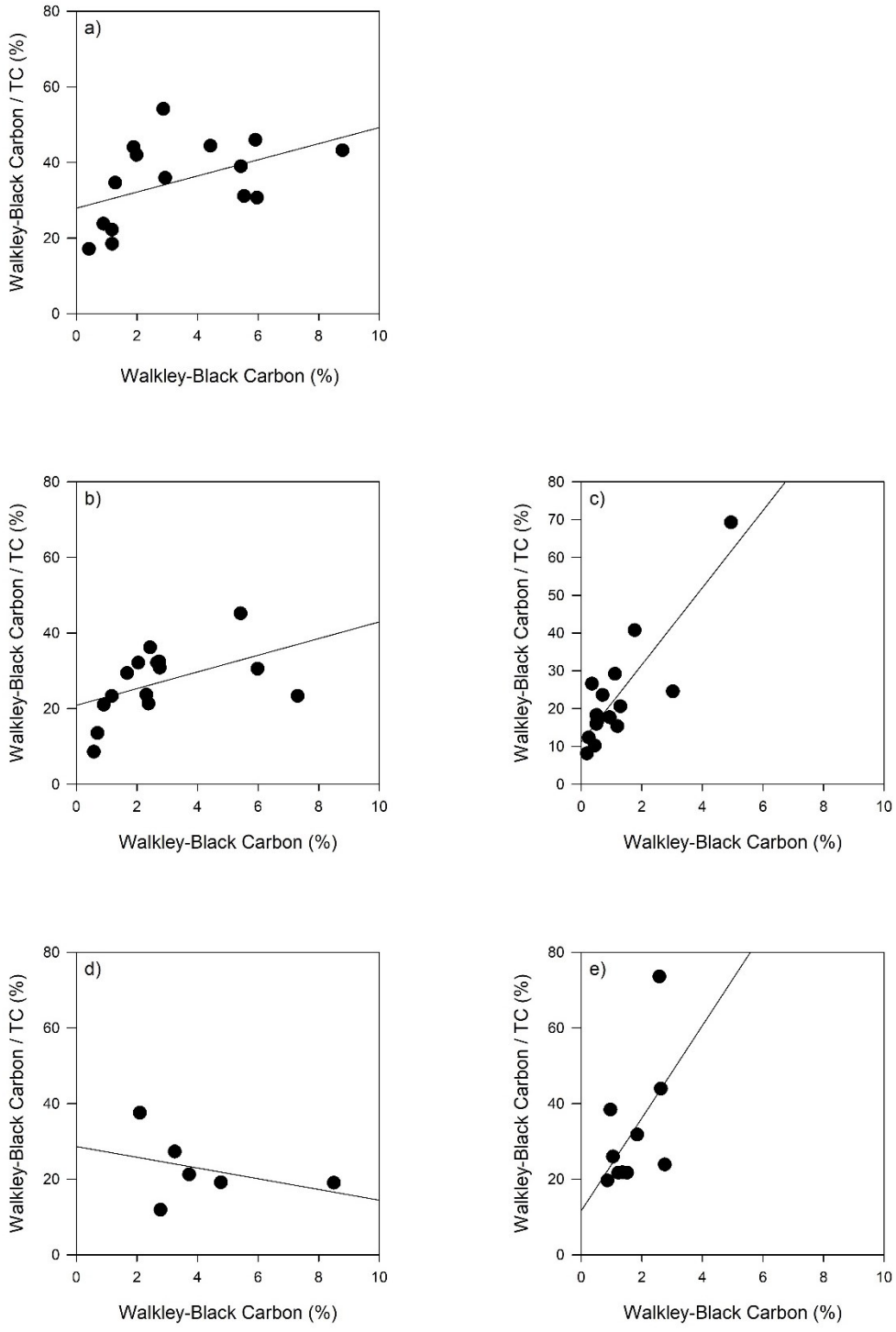

Figure 2.4. Regression plots of: 1-year post fire (a) 4-years post fire 0-5 cm (b), 4-years post fire 5-15 cm (c), 100-years post fire 0-5 cm (d), and 100-years post fire 5-15 cm (e) samples. Lines indicate best fit relationship of percentage Walkley-Black carbon proportion of total carbon as a function of percentage Walkley-Black carbon. R^2 values are 0.23 (a), 0.23 (b), 0.73 (c), 0.14 (d), 0.29 (e).

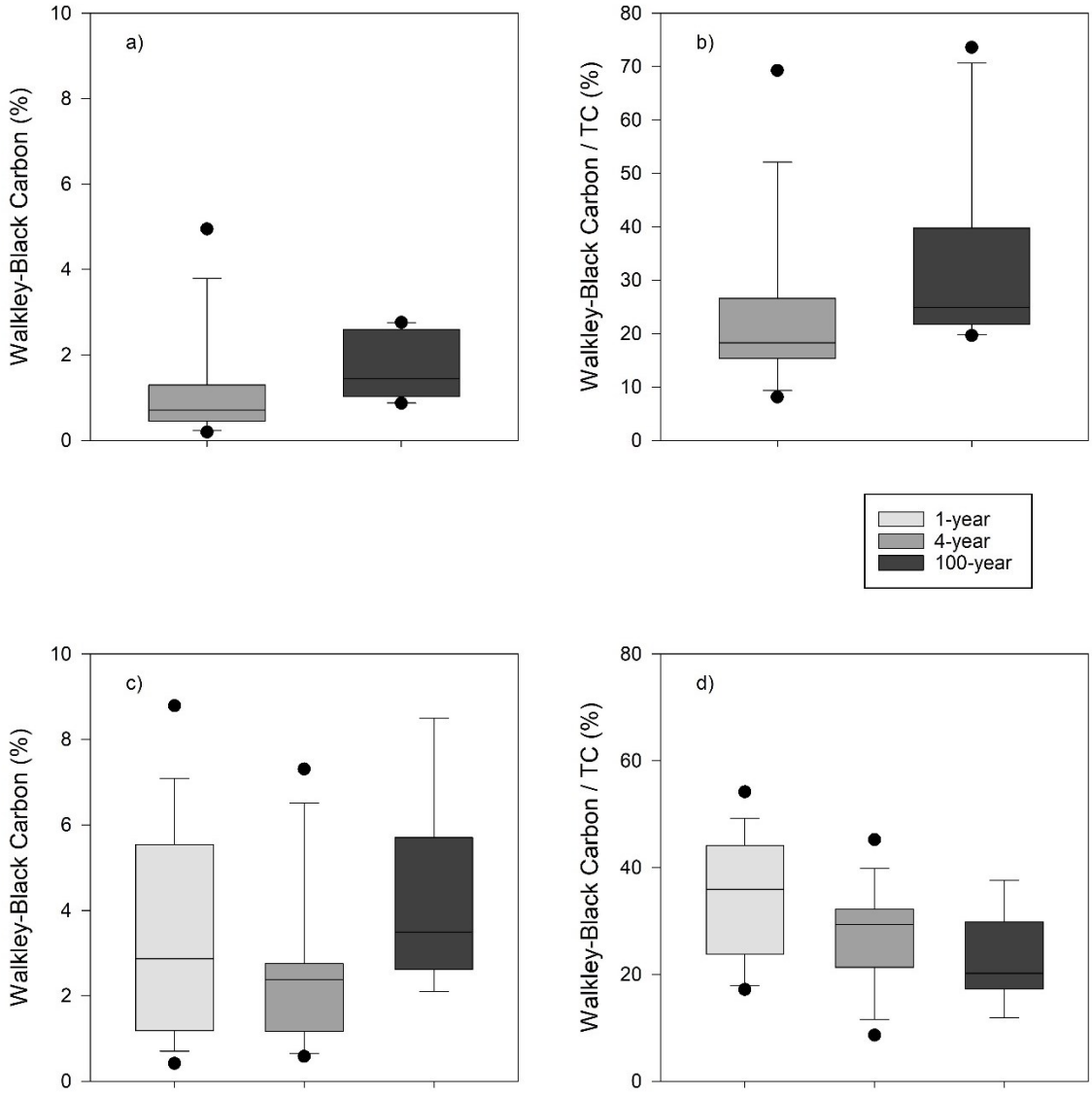

Figure 2.5. Box whisker plots of percentage Walkley-Black carbon and percentage Walkley-Black carbon of total carbon. Samples from 5-15 cm are compared between 4-years post fire and 100-years post fire samples (a, b) and samples from 0-5 cm are compared between 1-year post fire, 4-years post fire and 100-years post fire (c, d). Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and "whiskers" denote 5th and 95th percentiles.

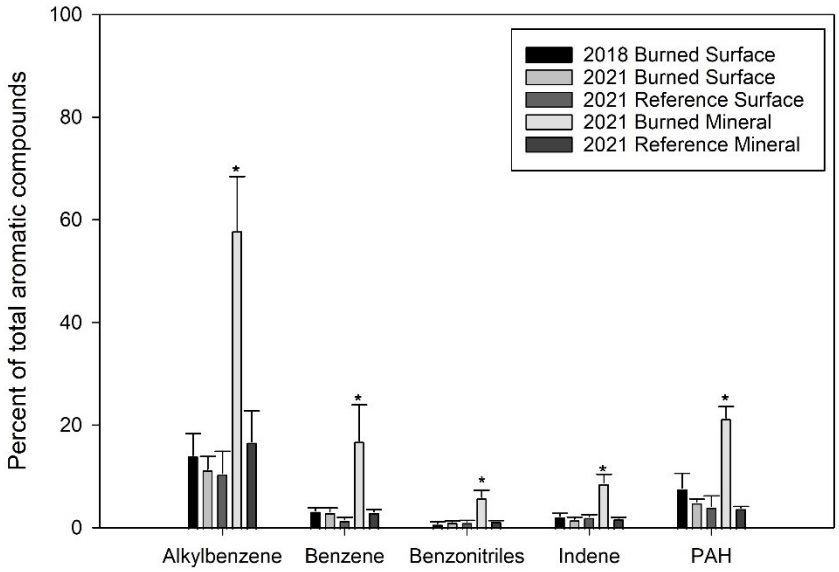

Figure 2.6. Comparison of five compounds of interest within the benzene/aromatic family in mg/g of carbon evaluated via PyGCMS run without TMAH. Asterisks denote compounds with significantly different levels.

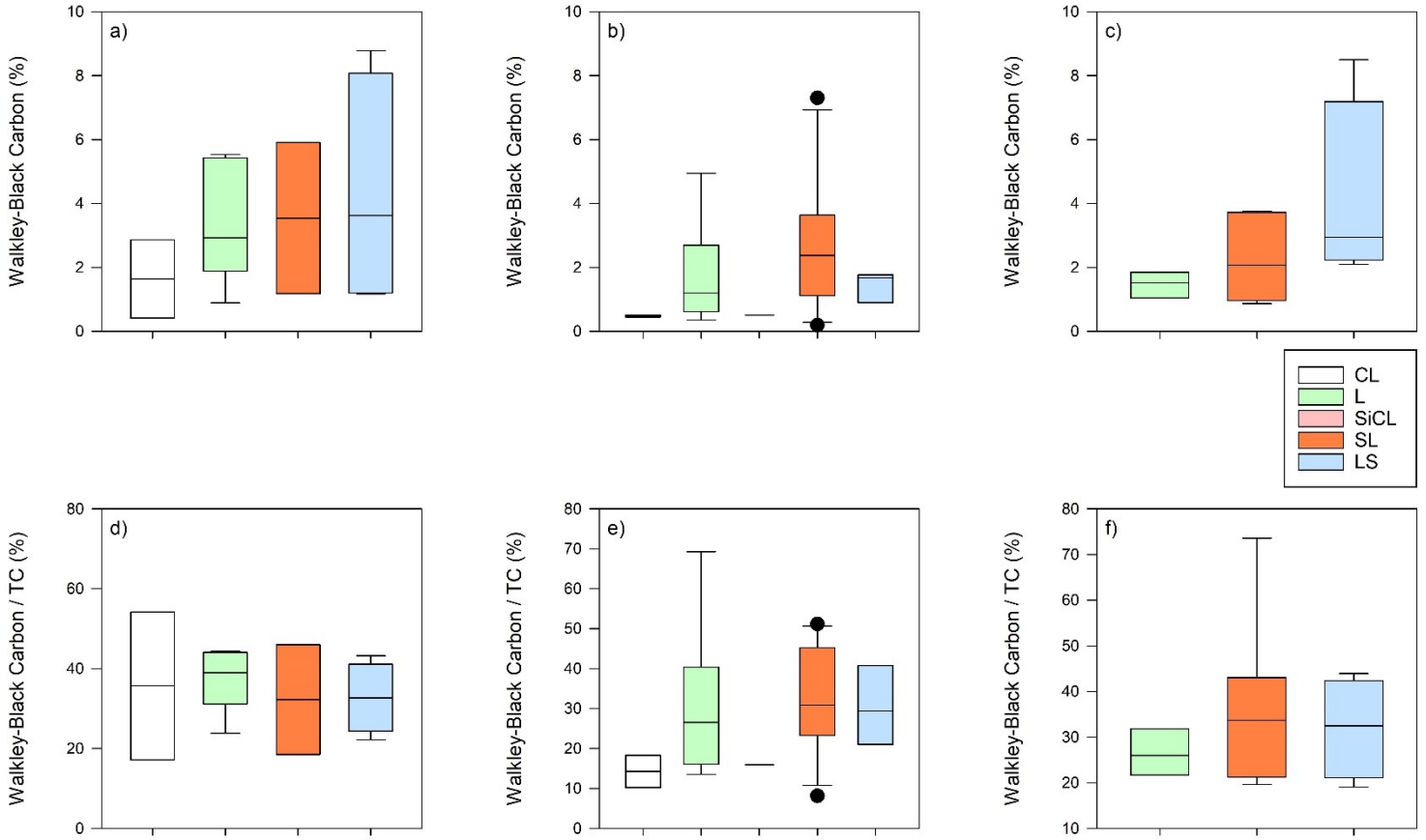

Figure 2.7. Box whisker plots of percentage Walkley-Black carbon and percentage Walkley-Black carbon / total carbon by soil texture grouped by: 1-year post fire (a, d), 4-years post fire (b, e), and 100-years post fire (c, f) samples. Abbreviations are CL = clay loam, L = loam, LS = loamy sand, SiCL = silty clay loam, SL = sandy loam. Silty clay loams were limited to a single sample. Upper and lower rectangle bounds denote 25th and 75th percentiles, the horizontal line indicates the median and "whiskers" denote 5th and 95th percentiles. Boxes without whiskers consisted of fewer than 4 samples.

Chapter 3: Summary

3.1 Research Summary

The sub-alpine watersheds of the Southern Rocky Mountains are one of many fire-adapted ecosystems within the province of Alberta. In terms of pyrogenic carbon stock, character, and production, mountainous regions represent one of the least studied areas globally, and especially within Canada. While not surprising given their relative unimportance, with lower biomass and limited agricultural potential compared to parkland, boreal forest, or prairie, they represent a large portion of the North American landmass and potentially sequester a significant amount of carbon of both pyrogenic and biomass origin. This research was conducted following the Kenow Wildfire of 2017 to better understand soil pyrogenic carbon and the dynamics surrounding it.

The overarching objectives of this research were to 1) determine the quantity and distribution of PyC within the soil profile directly following wildfire; 2) assess soil particle size distribution, carbon and nitrogen content, slope position, and broad vegetation type, and determine each component's relationship to PyC; 3) explore PyC movement and storage from 0-15 cm in the soil profile; and 4) elucidate the relationship between PyC percentage weight by weight of soil and PyC as a percentage of total carbon for watersheds representing 1-year, 4-years, and 100-years since wildfire.

These questions were addressed through the use of two analytical techniques. A quantitative chemical oxidation method adapted from the Walkley Black oxidation procedure was used that has semi-quantitative properties in that the materials it quantifies do not represent the entire spectrum of PyC and are thus referred to as WBC. Pyrolysis-GCMS was employed as a qualitative method to better understand the chemical constituents of the PyC itself. As an aside, two pretreatment methodologies, with TMAH and without, were contrasted to determine which provided the best separation and identification of pyrolysates within our samples.

3.1.1 Immediate Effects of Wildfire on Pyrogenic Carbon

This study explored PyC in soils from 0-5 cm collected from fifteen sites in 2018 following the burn and from ten sites in an adjacent unburned reference area in 2021 to establish the immediate effect of fire on mountain soils. The materials identified by the oxidation method

employed to quantify pyrogenic materials do not cover the entire spectrum of PyC and were thus referred to as WBC. 1-year and 4 -year soils contained less percent WBC than 100-year sites, likely due to legacy PyC present in the surface layers of the unburned sites, or confounding effects introduced by the modified Walkley Black oxidation method (Murano et al., 2021; Walker et al., 2019). The WBC/TC, however, was significantly increased as a result of fire, with the lower ratio observed on 100-year sites likely a result of dilution via the accumulation of humified substances, a function of their vastly increased TC over burned sites which had their vegetative litter consumed.

Soil texture was the only non-PyC characteristic that demonstrated a clear relationship with WBC shortly after wildfire. Contrary to the findings within the broader literature increasing %WBC was correlated with increasing textural coarseness (clay loam to loamy sand). Consistent with the literature however, clay loams featured the lowest average %WBC with a comparable WBC/TC to sites with other soil textures, indicating these finer textured soils may indeed store more PyC on average. Overall, no single soil or site characteristic was able to account for differences in PyC for any site.

3.1.2 Chronosequence and Depth Distribution of Pyrogenic Carbon

To determine the longevity of fire effects and the ultimate fate of PyC in the soil system PyC was examined in the same manner with the addition of burned soils collected from the same fifteen 2018 sites in 2021 as well as soils from 5-15 cm from 2021 burned and reference (100-year) areas. Mean %WBC decreased over the period from 1-year to 4-years with a significant decrease in WBC/TC, confirming erosive mechanisms and dilution by humified substances make substantial alterations to immediate post-fire conditions in topsoils (Matosziuk et al., 2020, Abney et al., 2017). Curiously, 100-year sites had the highest mean %WBC but exhibited similar WBC/TC to 4-year soils, and while a similar trend has occurred elsewhere (Matoszuik et al., 2020), arriving at conclusions about long term PyC dynamics is difficult given a lack of pre-burn data.

Soil from 5-15 cm contained significantly lower levels of WBC on both 4-year and 100-year sites, implying this relationship has stabilized to long term levels within 4 years of the KW, reinforced by the lack of difference in WBC/TC ratio between the two. The %WBC of 100-year sites, however, explained substantially less of the variation in the WBC/TC ratio, consistent with

long term enrichment of humified substances in the 5-15 cm layer that might have only just restarted 4 years after fire. Chemical character was very different, with enrichment of 3-5 times key pyrolysate compound families compared to 100-year sites, indicating a vastly different SOC composition following wildfire. The largely unchanged relationship of %WBC to WBC/TC between 1-year and 4-years, combined with this massive enrichment of aromatic species demonstrates that wildfire has profound effects at shallow and deep soil depths for at least 4 years.

3.2 Research Limitations

The research was limited most notably due to the imprecise quantification of PyC via the quantification methodology employed. Chemical oxidation techniques commonly assume PyC to be the most refractory OM contained within a given sample. This is simply not true and both underestimation due to the potential oxidation of lighter and/or less recalcitrant compounds that belong to the PyC continuum, and overestimation due to the potential survival and misidentification of more condensed or recalcitrant humified compounds, can occur (Zimmerman & Mitra, 2017). The difference could have been exacerbated by underestimation of lighter PyC, more common on sites of recent burn, potentially lowering the mean WBC from 1-year samples. Overestimation is far more likely on the 100-year sites as they feature extensive and mature litter layers that have been contributing complex humified compounds to the soil and may account for the relatively large concentration of WBC in 100-year samples. The limited application of PyGCMS was also a factor as only thirteen samples were analysed to complement existing data with qualitative determinations.

Pairing investigated sites to existing Parks Canada samples for the purposes of comparison was also a significant limitation. No single watershed contained a sufficient number of sampling sites with enough heterogeneity to focus on each individually, mostly as a result of Parks Canada collecting samples less than 20 m from existing access in almost all instances. Combined with the logistical difficulties associated with accessing sites only reachable by walking trail on foot, sites closer to major roadways had to take priority. Sample size further limited data exploration opportunities, particularly for 100-year sites and PyGCMS analysis. Evaluating site and soil characteristics was nearly impossible when certain categories of interest, such as clay loams, or hillslope vegetation, were confined to two or less samples in some of the

five categories combining time of collection, burn status, and depth. Further to this, the broad scope of variables included in the study likely introduced confounding factors not considered during lab or data analyses, including interaction effects and correlations between independent variables that could not be seen with the smaller number of samples available.

Additional sampling considerations limiting this study were the lack of preburn samples in the same or similar sites to allow for direct comparison of TC and PyC measurements, and likely most interestingly, chemical composition. Accounting for the differences between these samples and the unburned reference soil used as substitute is not currently possible within the context of this study. The same problem hampered the investigation of short-term changes in mineral soils, as the 5-15 cm samples collected by Parks Canada were not available for analysis.

3.3 Research Applications

This research has shown that major mechanisms within the broader pyrogenic carbon literature hold true for the region and ecosystems studied. Initial steps have been taken to inventory and describe the PyC residing in mountain soils of this region and the broader range as a whole. Substantial erosion, consisting of both surficial and vertical translocation were shown to take place on short and long timescales, most notably in the earliest stages following wildfire and greater than four years afterward. While no one driver or combination of drivers were uncovered for the production and/or storage of pyrogenic materials in soils, the field has been narrowed somewhat to factors that most strongly affected these parameters, or factors not investigated within this study. The relationship discovered between soil texture of increasing coarseness challenges general theories about the preferential storage of PyC with increasing clay content.

This research adds to the number of studies employing PyGCMS to assess PyC and compares pretreatment methodologies, finding that chemical composition was best elucidated by untreated (no TMAH) samples. The substantial enrichment of the chemical classes described in 5-15 cm soils of 4-year sites within the context of PyC was not found within the literature, appearing to be a novel contribution. To our knowledge, this is the first study of its kind to compare soils with such a broad range of site and soil characteristics together, particularly as most studies make comparisons within areas of homogenous vegetation.

In the context of water quality and riverine export of sediment and carbon following wildfire studied within the SRWP, this research demonstrates that the ultimate destination of a

significant quantity of PyC are not only soils but potentially watercourses and groundwater within watersheds vital to the health of Waterton Lake and the community of the Town of Waterton.

3.4 Future Research

There is much still to be studied in this region in regard to pyrogenic carbon. Research evaluating pre-burn versus post-burn conditions would more clearly elucidate the changes that these subalpine ecosystems go through as a result of wildfire. To further investigate the aromatic enrichment of soils from 5-15 cm, research should be conducted on soils to a greater depth with narrower classifications to evaluate what could potentially be a normal distribution of compound concentration with depth. Additionally, research should be conducted at regular intervals, every two to three years, to discover where and when fire-affected soils reach their equilibrium PyC level to better map the longevity of fire effects and what soils would look like without human intervention in fire dynamics. This research would have broad implications for the importance of wildfire's return as it affects carbon sequestration in the topsoils of Alberta, a temperate climatic region almost exclusively composed of fire-adapted ecosystems.

Finally, research conducted in the future should benefit from and make use of the inevitable refinement of techniques and definitions as the field of pyrogenic carbon research narrows towards a consistent description of what PyC actually is as it pertains to the health and function of fire-adapted ecosystems and the most accurate quantification and qualification methods that allow for comparison and compilation within the literature.

References

Abney, R. B., & Berhe, A. A. (2018). Pyrogenic Carbon Erosion: Implications for Stock and Persistence of Pyrogenic Carbon in Soil. *Frontiers in Earth Science*, *6*, 26. https://doi.org/10.3389/feart.2018.00026

Abney, R. B., Jin, L., & Berhe, A. A. (2019). Soil properties and combustion temperature: Controls on the decomposition rate of pyrogenic organic matter. *CATENA*, *182*, 104127. https://doi.org/10.1016/j.catena.2019.104127

Abney, R. B., Sanderman, J., Johnson, D., Fogel, M. L., & Berhe, A. A. (2017). Post-wildfire Erosion in Mountainous Terrain Leads to Rapid and Major Redistribution of Soil Organic Carbon. *Frontiers in Earth Science*, *5*, 99. https://doi.org/10.3389/feart.2017.00099

Adkins, J., Sanderman, J., & Miesel, J. (2019). Soil carbon pools and fluxes vary across a burn severity gradient three years after wildfire in Sierra Nevada mixed-conifer forest. *Geoderma*, *333*, 10–22. https://doi.org/10.1016/j.geoderma.2018.07.009

Andreae, M. O., & Gelencsér, A. (2006). Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmospheric Chemistry and Physics*, *6*(10), 3131–3148. https://doi.org/10.5194/acp-6-3131-2006

Baldock, J. A., & Smernik, R. J. (2002). Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. *Organic Geochemistry*, *33*(9), 1093–1109. https://doi.org/10.1016/S0146-6380(02)00062-1

Belcher, C. M., New, S. L., Santín, C., Doerr, S. H., Dewhirst, R. A., Grosvenor, M. J., & Hudspith, V. A. (2018). What Can Charcoal Reflectance Tell Us About Energy Release in Wildfires and the Properties of Pyrogenic Carbon? *Frontiers in Earth Science*, *6*. https://doi.org/10.3389/feart.2018.00169

Bellè, S.-L., Berhe, A. A., Hagedorn, F., Santin, C., Schiedung, M., van Meerveld, I., & Abiven, S. (2021). Key drivers of pyrogenic carbon redistribution during a simulated rainfall event. *Biogeosciences*, *18*(3), 1105–1126. https://doi.org/10.5194/bg-18-1105-2021

Berhe, A. A., Barnes, R. T., Six, J., & Marín-Spiotta, E. (2018). Role of Soil Erosion in Biogeochemical Cycling of Essential Elements: Carbon, Nitrogen, and Phosphorus. *Annual Review of Earth and Planetary Sciences*, *46*(1), 521–548. https://doi.org/10.1146/annurev-earth-082517-010018

Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J., & Frost, P. (1999). Stability of elemental carbon in a savanna soil. *Global Biogeochemical Cycles*, *13*(4), 923–932. https://doi.org/10.1029/1999GB900067

Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M., & McBeath, A. (2015). The Pyrogenic Carbon Cycle. *Annual Review of Earth and Planetary Sciences*, *43*(1), 273–298. https://doi.org/10.1146/annurev-earth-060614-105038

Boot, C. M., Haddix, M., Paustian, K., & Cotrufo, M. F. (2015). Distribution of black carbon in ponderosa pine forest floor and soils following the High Park wildfire. *Biogeosciences*, *12*(10), 3029–3039. https://doi.org/10.5194/bg-12-3029-2015

Bostick, K. W., Zimmerman, A. R., Wozniak, Andrew. S., Mitra, S., & Hatcher, P. G. (2018). Production and Composition of Pyrogenic Dissolved Organic Matter From a Logical Series of Laboratory-Generated Chars. *Frontiers in Earth Science*, *6*, 43. https://doi.org/10.3389/feart.2018.00043

Certini, G. (2005). Effects of fire on properties of forest soils: A review. *Oecologia*, *143*(1), 1–10. https://doi.org/10.1007/s00442-004-1788-8

Certini, G., Nocentini, C., Knicker, H., Arfaioli, P., & Rumpel, C. (2011). Wildfire effects on soil organic matter quantity and quality in two fire-prone Mediterranean pine forests. *Geoderma*, *167–168*, 148–155. https://doi.org/10.1016/j.geoderma.2011.09.005

Chefetz, B., Chen, Y., Clapp, C. E., & Hatcher, P. G. (2000). Characterization of Organic Matter in Soils by Thermochemolysis Using Tetramethylammonium Hydroxide (TMAH). *Soil Science Society of America Journal*, *64*(2), 583–589. https://doi.org/10.2136/sssaj2000.642583x

Chen, H., Rhoades, C. C., & Chow, A. T. (2020). Characteristics of soil organic matter 14 years after a wildfire: A pyrolysis-gas-chromatography mass spectrometry (Py-GC-MS) study. *Journal of Analytical and Applied Pyrolysis*, *152*, 104922. https://doi.org/10.1016/j.jaap.2020.104922

Claessens, L., Lowe, D. J., Hayward, B. W., Schaap, B. F., Schoorl, J. M., & Veldkamp, A. (2006). Reconstructing high-magnitude/low-frequency landslide events based on soil redistribution modelling and a Late-Holocene sediment record from New Zealand. *Geomorphology*, *74*(1), 29–49. https://doi.org/10.1016/j.geomorph.2005.07.008

Clarke, K. R. (1993). Non-parametric multivariate analyses of changes in community structure. *Australian Journal of Ecology*, *18*(1), 117–143. https://doi.org/10.1111/j.1442-9993.1993.tb00438.x

Coen, G. M., & Holland, W. D. (1976). *Soils of Waterton Lakes National Park, Alberta*. Minister of Supply and Services Canada.

Cotrufo, M. F., Boot, C., Abiven, S., Foster, E. J., Haddix, M., Reisser, M., Wurster, C. M., Bird, M. I., & Schmidt, M. W. I. (2016). Quantification of pyrogenic carbon in the environment: An integration of analytical approaches. *Organic Geochemistry*, *100*, 42–50. https://doi.org/10.1016/j.orggeochem.2016.07.007

Czimczik, C. I., & Masiello, C. A. (2007). Controls on black carbon storage in soils: BLACK CARBON IN SOILS. *Global Biogeochemical Cycles*, *21*(3), n/a-n/a. https://doi.org/10.1029/2006GB002798

de Oliveira, E. A., Feldpausch, T. R., Marimon, B. S., Morandi, P. S., Phillips, O. L., Bird, M., Murakami, A. A., Arroyo, L., Quesada, C. A., & Marimon-Junior, B. H. (2022). Soil pyrogenic carbon in southern Amazonia: Interaction between soil, climate, and above-ground biomass. *Frontiers in Forests and Global Change*, *5*. https://www.frontiersin.org/articles/10.3389/ffgc.2022.880963

DeBano, L. F. (2000). The role of fire and soil heating on water repellency in wildland environments: A review. *Journal of Hydrology*, *231–232*, 195–206. https://doi.org/10.1016/S0022-1694(00)00194-3

DeLuca, T. H., & Aplet, G. H. (2008). Charcoal and carbon storage in forest soils of the Rocky Mountain West. *Frontiers in Ecology and the Environment*, *6*(1), 18–24. https://doi.org/10.1890/070070

DeLuca, T. H., Gundale, M. J., Brimmer, R. J., & Gao, S. (2020). Pyrogenic Carbon Generation From Fire and Forest Restoration Treatments. *Frontiers in Forests and Global Change*, *3*, 24. https://doi.org/10.3389/ffgc.2020.00024

Denis, E. H., Maibauer, B. J., Bowen, G. J., Jardine, P. E., Harrington, G. J., Baczynski, A. A., McInerney, F. A., Collinson, M. E., Belcher, C. M., Wing, S. L., & Freeman, K. H. (2021). Decreased soil carbon in a warming world: Degraded pyrogenic carbon during the Paleocene-Eocene Thermal Maximum, Bighorn Basin, Wyoming. *Earth and Planetary Science Letters*, *566*, 116970. https://doi.org/10.1016/j.epsl.2021.116970

Doerr, S. H., Santín, C., Merino, A., Belcher, C. M., & Baxter, G. (2018). Fire as a Removal Mechanism of Pyrogenic Carbon From the Environment: Effects of Fire and Pyrogenic Carbon Characteristics. *Frontiers in Earth Science*, *6*, 127. https://doi.org/10.3389/feart.2018.00127

Edeh, I. G., Mašek, O., & Buss, W. (2020). A meta-analysis on biochar's effects on soil water properties – New insights and future research challenges. *Science of The Total Environment*, *714*, 136857. https://doi.org/10.1016/j.scitotenv.2020.136857

Environment, P.-G. of A. (n.d.). *History and Description of the Castle River Range Reference Area*.

Gale, N. V., & Thomas, S. C. (2021). Spatial heterogeneity in soil pyrogenic carbon mediates tree growth and physiology following wildfire. *Journal of Ecology*, *109*(3), 1479–1490. https://doi.org/10.1111/1365-2745.13571

Gibson, C., Hatton, P.-J., Bird, J. A., Nadelhoffer, K., Le Moine, J., & Filley, T. (2018). Tree taxa and pyrolysis temperature interact to control pyrogenic organic matter induced native soil organic carbon priming. *Soil Biology and Biochemistry*, *119*, 174–183. https://doi.org/10.1016/j.soilbio.2018.01.022

González-Pérez, J. A., González-Vila, F. J., Almendros, G., & Knicker, H. (2004). The effect of fire on soil organic matter—A review. *Environment International*, *30*(6), 855–870. https://doi.org/10.1016/j.envint.2004.02.003

Goslee, S. C., & Urban, D. L. (2007). The ecodist Package for Dissimilarity-based Analysis of Ecological Data. *Journal of Statistical Software*, *22*, 1–19. https://doi.org/10.18637/jss.v022.i07

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O., Masiello, C. A., Song, J., Peng, P., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C., … Ding, L. (2007). Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochemical Cycles*, *21*(3). https://doi.org/10.1029/2006GB002914

Hanes, C. C., Wang, X., Jain, P., Parisien, M.-A., Little, J. M., & Flannigan, M. D. (2019). Fire-regime changes in Canada over the last half century. *Canadian Journal of Forest Research*, *49*(3), 256–269. https://doi.org/10.1139/cjfr-2018-0293

Hardy, B., & Dufey, J. E. (2017). The resistance of centennial soil charcoal to the "Walkley-Black" oxidation. *Geoderma*, *303*, 37–43. https://doi.org/10.1016/j.geoderma.2017.05.001

Hatten, J., Zabowski, D., Scherer, G., & Dolan, E. (2005). A comparison of soil properties after contemporary wildfire and fire suppression. *Forest Ecology and Management*, *220*(1–3), 227–241. https://doi.org/10.1016/j.foreco.2005.08.014

Hobley, E. (2019). Vertical Distribution of Soil Pyrogenic Matter: A Review. *Pedosphere*, *29*(2), 137–149. https://doi.org/10.1016/S1002-0160(19)60795-2

Home. (n.d.). Southern Rockies Watershed Project. Retrieved June 12, 2023, from https://srwp.ualberta.ca/

Huang, W., Hu, Y., Chang, Y., Liu, M., Li, Y., Ren, B., & Shi, S. (2018). Effects of Fire Severity and Topography on Soil Black Carbon Accumulation in Boreal Forest of Northeast China. *Forests*, *9*(7), 408. https://doi.org/10.3390/f9070408

Hyväluoma, J., Hannula, M., Arstila, K., Wang, H., Kulju, S., & Rasa, K. (2018). Effects of pyrolysis temperature on the hydrologically relevant porosity of willow biochar. *Journal of Analytical and Applied Pyrolysis*, *134*, 446–453. https://doi.org/10.1016/j.jaap.2018.07.011

Jenkins, M. E., Bell, T. L., Norris, J., Adams, M. A., Jenkins, M. E., Bell, T. L., Norris, J., & Adams, M. A. (2014). Pyrogenic carbon: The influence of particle size and chemical composition on soil carbon release. *International Journal of Wildland Fire*, *23*(7), 1027–1033. https://doi.org/10.1071/WF13189

Jiang, X., Denef, K., Stewart, C. E., & Cotrufo, M. F. (2016). Controls and dynamics of biochar decomposition and soil microbial abundance, composition, and carbon use efficiency during long-term biochar-amended soil incubations. *Biology and Fertility of Soils*, *52*(1), 1–14. https://doi.org/10.1007/s00374-015-1047-7

Jílková, V., Adámek, M., Angst, G., Tůmová, M., & Devetter, M. (2023). Post-fire forest floor succession in a Central European temperate forest depends on organic matter input from

recovering vegetation rather than on pyrogenic carbon input from fire. *Science of The Total Environment*, *861*, 160659. https://doi.org/10.1016/j.scitotenv.2022.160659

K, B. S. P., Link to external site, this link will open in a new window, Jones, M. W., Philippe, C., Link to external site, this link will open in a new window, Bertrand, G., & Samuel, A. (2022). Pyrogenic carbon decomposition critical to resolving fire's role in the Earth system. *Nature Geoscience*, *15*(2), 135–142. https://doi.org/10.1038/s41561-021-00892-0

Kaal, J., Brodowski, S., Baldock, J. A., Nierop, K. G. J., & Cortizas, A. M. (2008). Characterisation of aged black carbon using pyrolysis-GC/MS, thermally assisted hydrolysis and methylation (THM), direct and cross-polarisation 13C nuclear magnetic resonance (DP/CP NMR) and the benzenepolycarboxylic acid (BPCA) method. *Organic Geochemistry*, *39*(10), 1415–1426. https://doi.org/10.1016/j.orggeochem.2008.06.011

Kaal, J., & Rumpel, C. (2009). Can pyrolysis-GC/MS be used to estimate the degree of thermal alteration of black carbon? *Organic Geochemistry*, *40*(12), 1179–1187. https://doi.org/10.1016/j.orggeochem.2009.09.002

Kelly, R., Chipman, M. L., Higuera, P. E., Stefanova, I., Brubaker, L. B., & Hu, F. S. (2013). Recent burning of boreal forests exceeds fire regime limits of the past 10,000 years. *Proceedings of the National Academy of Sciences of the United States of America*, *110*(32), 13055–13060. https://doi.org/10.1073/pnas.1305069110

Kim, E. j. (1), Choi, S.-D. (2), & Chang, Y.-S. (3). (2011). Levels and patterns of polycyclic aromatic hydrocarbons (PAHs) in soils after forest fires in South Korea. *Environmental Science and Pollution Research*, *18*(9), 1508–1517. https://doi.org/10.1007/s11356-011-0515-3

Kruskal, J. B. (1964). Nonmetric multidimensional scaling: A numerical method. *Psychometrika*, *29*(2), 115–129. https://doi.org/10.1007/BF02289694

Kuhlbusch, T. A. J. (1998). Black Carbon and the Carbon Cycle. *Science*, *280*(5371), 1903–1904. https://doi.org/10.1126/science.280.5371.1903

Kurth, V. J., MacKenzie, M. D., & DeLuca, T. H. (2006). Estimating charcoal content in forest mineral soils. *Geoderma*, *137*(1), 135–139. https://doi.org/10.1016/j.geoderma.2006.08.003

Legendre, P., & Gallagher, E. D. (2001). Ecologically meaningful transformations for ordination of species data. *Oecologia*, *129*(2), 271–280. https://doi.org/10.1007/s004420100716

Li, J., Pei, J., Liu, J., Wu, J., Li, B., Fang, C., & Nie, M. (2021). Spatiotemporal variability of fire effects on soil carbon and nitrogen: A global meta-analysis. *Global Change Biology*, *27*(17), 4196–4206. https://doi.org/10.1111/gcb.15742

Ling, L., Fu, Y., Jeewani, P. H., Tang, C., Pan, S., Reid, B. J., Gunina, A., Li, Y., Li, Y., Cai, Y., Kuzyakov, Y., Li, Y., Su, W., Singh, B. P., Luo, Y., & Xu, J. (2021). Organic matter chemistry and bacterial community structure regulate decomposition processes in post-fire forest soils. *Soil Biology and Biochemistry*, *160*, 108311. https://doi.org/10.1016/j.soilbio.2021.108311

Liu, Z., Dugan, B., Masiello, C. A., Barnes, R. T., Gallagher, M. E., & Gonnermann, H. (2016). Impacts of biochar concentration and particle size on hydraulic conductivity and DOC leaching of biochar–sand mixtures. *Journal of Hydrology*, *533*, 461–472. https://doi.org/10.1016/j.jhydrol.2015.12.007

Luo, Y., Durenkamp, M., De Nobili, M., Lin, Q., & Brookes, P. C. (2011). Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. *Soil Biology and Biochemistry*, *43*(11), 2304–2314. https://doi.org/10.1016/j.soilbio.2011.07.020

Luo, Y., Lin, Q., Durenkamp, M., Dungait, A. J., & Brookes, P. C. (2017). Soil priming effects following substrates addition to biochar-treated soils after 431 days of pre-incubation. *Biology and Fertility of Soils*, *53*(3), 315–326. https://doi.org/10.1007/s00374-017-1180-6

Maestrini, B., Herrmann, A. M., Nannipieri, P., Schmidt, M. W. I., & Abiven, S. (2014). Ryegrass-derived pyrogenic organic matter changes organic carbon and nitrogen mineralization in a temperate forest soil. *Soil Biology and Biochemistry*, *69*, 291–301. https://doi.org/10.1016/j.soilbio.2013.11.013

Maestrini, B., Nannipieri, P., & Abiven, S. (2015). A meta-analysis on pyrogenic organic matter induced priming effect. *Global Change Biology. Bioenergy*, *7*(4), 577–590. https://doi.org/10.1111/gcbb.12194

Major, J., Lehmann, J., Rondon, M., & Goodale, C. (2010). Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. *Global Change Biology*, *16*(4), 1366–1379. https://doi.org/10.1111/j.1365-2486.2009.02044.x

Masiello, C. A. (2004). New directions in black carbon organic geochemistry. *Marine Chemistry*, *92*(1), 201–213. https://doi.org/10.1016/j.marchem.2004.06.043

Masiello, C. A., & Berhe, A. A. (2020). First interactions with the hydrologic cycle determine pyrogenic carbon's fate in the Earth system. *Earth Surface Processes and Landforms*, *45*(10), 2394–2398. https://doi.org/10.1002/esp.4925

Masiello, C. A., Druffel, E. R. M., & Currie, L. A. (2002). Radiocarbon measurements of black carbon in aerosols and ocean sediments. *Geochimica et Cosmochimica Acta*, *66*(6), 1025–1036. https://doi.org/10.1016/S0016-7037(01)00831-6

Matosziuk, L. M., Alleau, Y., Kerns, B. K., Bailey, J., Johnson, M. G., & Hatten, J. A. (2019). Effects of season and interval of prescribed burns on pyrogenic carbon in ponderosa pine stands in the southern Blue Mountains, Oregon, USA. *Geoderma*, *348*, 1–11. https://doi.org/10.1016/j.geoderma.2019.04.009

Matosziuk, L. M., Gallo, A., Hatten, J., Bladon, K. D., Ruud, D., Bowman, M., Egan, J., Heckman, K., SanClements, M., Strahm, B., & Weiglein, T. (2020). Short-Term Effects of Recent Fire on the Production and Translocation of Pyrogenic Carbon in Great Smoky Mountains National Park. *Frontiers in Forests and Global Change*, *3*, 6. https://doi.org/10.3389/ffgc.2020.00006

Miesel, J., Reiner, A., Ewell, C., Maestrini, B., & Dickinson, M. (2018). Quantifying Changes in Total and Pyrogenic Carbon Stocks Across Fire Severity Gradients Using Active Wildfire Incidents. *Frontiers in Earth Science*, *6*. https://doi.org/10.3389/feart.2018.00041

Murano, H., Liu, G., Wang, Z., Tanihira, Y., Asahi, T., & Isoi, T. (2021). Quantification methods of pyrogenic carbon in soil with soil as a complex matrix: Comparing the CTO-375 and Cr2O7 methods. *Soil Science and Plant Nutrition*, *67*(4), 380–388. https://doi.org/10.1080/00380768.2021.1925960

Neary, D. G., Klopatek, C. C., DeBano, L. F., & Ffolliott, P. F. (1999). Fire effects on belowground sustainability: A review and synthesis. *Forest Ecology and Management*, *122*(1), 51–71. https://doi.org/10.1016/S0378-1127(99)00032-8

Ohlson, M., Kasin, I., Wist, A. N., & Bjune, A. E. (2013). Size and spatial structure of the soil and lacustrine charcoal pool across a boreal forest watershed. *Quaternary Research*, *80*(3), 417–424. https://doi.org/10.1016/j.yqres.2013.08.009

Oksanen, J., Simpson, G. L., Blanchet, F. G., Kindt, R., Legendre, P., Minchin, P. R., O'Hara, R. B., Solymos, P., Stevens, M. H. H., Szoecs, E., Wagner, H., Barbour, M., Bedward, M., Bolker, B., Borcard, D., Carvalho, G., Chirico, M., Caceres, M. D., Durand, S., … Weedon, J. (2022). *vegan: Community Ecology Package* (2.6-4). https://cran.r-project.org/web/packages/vegan/index.html

Parks Canada Agency, G. of C. (2023, March 15). *Kenow wildfire—Waterton Lakes National Park—Kenow Wildfire*. https://parks.canada.ca/pn-np/ab/waterton/nature/environment/feu-fire/feu-fire-kenow

Preston, C. M., & Schmidt, M. W. I. (2006). Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences*, *3*(4), 397–420. https://doi.org/10.5194/bg-3-397-2006

Preston, C. M., Simard, M., Bergeron, Y., Bernard, G. M., & Wasylishen, R. E. (2017). Charcoal in Organic Horizon and Surface Mineral Soil in a Boreal Forest Fire Chronosequence of Western Quebec: Stocks, Depth Distribution, Chemical Properties and a Synthesis of Related Studies. *Frontiers in Earth Science*, *5*. https://doi.org/10.3389/feart.2017.00098

Reisser, M., Purves, R. S., Schmidt, M. W. I., & Abiven, S. (2016). Pyrogenic Carbon in Soils: A Literature-Based Inventory and a Global Estimation of Its Content in Soil Organic Carbon and Stocks. *Frontiers in Earth Science*, *4*. https://doi.org/10.3389/feart.2016.00080

Rogeau, M.-P., Flannigan, M. D., Hawkes, B. C., Parisien, M.-A., Arthur, R., Rogeau, M.-P., Flannigan, M. D., Hawkes, B. C., Parisien, M.-A., & Arthur, R. (2016). Spatial and temporal variations of fire regimes in the Canadian Rocky Mountains and Foothills of southern Alberta. *International Journal of Wildland Fire*, *25*(11), 1117–1130. https://doi.org/10.1071/WF15120

Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C., & Mariotti, A. (2006). Preferential erosion of black carbon on steep slopes with slash and burn agriculture. *CATENA*, *65*(1), 30–40. https://doi.org/10.1016/j.catena.2005.09.005

Santín, C., Doerr, S. H., Kane, E. S., Masiello, C. A., Ohlson, M., de la Rosa, J. M., Preston, C. M., & Dittmar, T. (2016). Towards a global assessment of pyrogenic carbon from vegetation fires. *Global Change Biology*, *22*(1), 76–91. https://doi.org/10.1111/gcb.12985

Santín, C., Doerr, S. H., Preston, C. M., & González-Rodríguez, G. (2015). Pyrogenic organic matter production from wildfires: A missing sink in the global carbon cycle. *Global Change Biology*, *21*(4), 1621–1633. https://doi.org/10.1111/gcb.12800

Santos, F., Bird, J. A., & Asefaw Berhe, A. (2022). Dissolved pyrogenic carbon leaching in soil: Effects of soil depth and pyrolysis temperature. *Geoderma*, *424*, 116011. https://doi.org/10.1016/j.geoderma.2022.116011

Santos, F., Wagner, S., Rothstein, D., Jaffe, R., & Miesel, J. R. (2017). Impact of a Historical Fire Event on Pyrogenic Carbon Stocks and Dissolved Pyrogenic Carbon in Spodosols in Northern Michigan. *Frontiers in Earth Science*, *5*. https://doi.org/10.3389/feart.2017.00080

Schiedung, M., Bellè, S.-L., Sigmund, G., Kalbitz, K., & Abiven, S. (2020). Vertical mobility of pyrogenic organic matter in soils: A column experiment. *Biogeosciences*, *17*(24), 6457–6474. https://doi.org/10.5194/bg-17-6457-2020

Schmidt, M. W. I., & Noack, A. G. (2000). Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochemical Cycles*, *14*(3), 777–793. https://doi.org/10.1029/1999GB001208

Scott, A. C., & Glasspool, I. J. (2006). The Diversification of Paleozoic Fire Systems and Fluctuations in Atmospheric Oxygen Concentration. *Proceedings of the National Academy of Sciences of the United States of America*, *103*(29), 10861–10865.

Shrestha, B. M., & Chen, H. Y. H. (2010). Effects of stand age, wildfire and clearcut harvesting on forest floor in boreal mixedwood forests. *Plant and Soil*, *336*(1), 267–277. https://doi.org/10.1007/s11104-010-0475-2

Soucémarianadin, L., Reisser, M., Cécillon, L., Barré, P., Nicolas, M., & Abiven, S. (2019). Pyrogenic carbon content and dynamics in top and subsoil of French forests. *Soil Biology and Biochemistry*, *133*, 12–15. https://doi.org/10.1016/j.soilbio.2019.02.013

Thomas, S. C. (2021). Biochar effects on germination and radicle extension in temperate tree seedlings under field conditions. *Canadian Journal of Forest Research*, *51*(1), 10–17. https://doi.org/10.1139/cjfr-2019-0386

Thomas, S. C., & Gale, N. (2015). Biochar and forest restoration: A review and meta-analysis of tree growth responses. *New Forests*, *46*(5), 931–946. https://doi.org/10.1007/s11056-015-9491-7

Van Wagner, C. E., Finney, M. A., & Heathcott, M. (2006). Historical Fire Cycles in the Canadian Rocky Mountain Parks. *Forest Science*, *52*(6), 704–717.

Velasco-Molina, M., Berns, A. E., Macías, F., & Knicker, H. (2016). Biochemically altered charcoal residues as an important source of soil organic matter in subsoils of fire-affected subtropical regions. *Geoderma*, *262*, 62–70. https://doi.org/10.1016/j.geoderma.2015.08.016

Walker, X. J., Baltzer, J. L., Cumming, S. G., Day, N. J., Ebert, C., Goetz, S., Johnstone, J. F., Potter, S., Rogers, B. M., Schuur, E. A. G., Turetsky, M. R., & Mack, M. C. (2019). Increasing wildfires threaten historic carbon sink of boreal forest soils. *Nature*, *572*(7770), 520-523,523A-523H. http://dx.doi.org.login.ezproxy.library.ualberta.ca/10.1038/s41586-019-1474-y

Wang, Z., Liu, Z., Xu, K., Mayer, L. M., Zhang, Z., Kolker, A. S., & Wu, W. (2014). Concentrations and sources of polycyclic aromatic hydrocarbons in surface coastal sediments of the northern Gulf of Mexico. *Geochemical Transactions*, *15*(1), Article 1. https://doi.org/10.1186/1467-4866-15-2

Wu, W., Han, J., Gu, Y., Li, T., Xu, X., Jiang, Y., Li, Y., Sun, J., Pan, G., & Cheng, K. (2022). Impact of biochar amendment on soil hydrological properties and crop water use efficiency: A global meta-analysis and structural equation model. *GCB Bioenergy*, *14*(6), 657–668. https://doi.org/10.1111/gcbb.12933

Yao, J., Hockaday, W. C., Murray, D. B., & White, J. D. (2014). Changes in fire-derived soil black carbon storage in a subhumid woodland. *Journal of Geophysical Research: Biogeosciences*, *119*(9), 1807–1819. https://doi.org/10.1002/2014JG002619

Zimmerman, A. R., Gao, B., & Ahn, M.-Y. (2011). Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*, *43*(6), 1169–1179. https://doi.org/10.1016/j.soilbio.2011.02.005

Zimmerman, A. R., & Mitra, S. (2017). Trial by Fire: On the Terminology and Methods Used in Pyrogenic Organic Carbon Research. *Frontiers in Earth Science*, *5*, 95. https://doi.org/10.3389/feart.2017.00095

Zimmerman, A. R., & Ouyang, L. (2019). Priming of pyrogenic C (biochar) mineralization by dissolved organic matter and vice versa. *Soil Biology and Biochemistry*, *130*, 105–112. https://doi.org/10.1016/j.soilbio.2018.12.011

Appendix

Table A.1. Landscape characteristics of all sites in burned and reference watersheds

Type	Site	Slope (º)	Aspect (º)	Landform	Ecotype
Burned	Bauerman 1	30	184	Backslope	Hillslope Vegetation
	Bauerman 2	0	NA	Depositional	Grassland
	Bauerman 3	10	112	Toeslope	Coniferous Forest
	Blakiston 1	0	NA	Depositional	Grassland
	Blakiston 2	0	NA	Depositional	Grassland
	Blakiston 3	9	62	Depositional	Coniferous Forest
	Blakiston 4	25	133	Backslope	Forest/Grass Transition
	Blakiston 5	21	160	Footslope	Mixedwood Forest
	Blakiston 6	15	138	Backslope	Hillslope Vegetation
	Cameron 1	13	290	Footslope	Coniferous Forest
	Cameron 2	32	295	Backslope	Coniferous Forest
	Cameron 3	18	310	Footslope	Mixedwood Forest
	Cameron 4	21	114	Footslope	Deciduous Forest
	Carthew 1	39	8	Backslope	Coniferous Forest
	Lineham 1	25	173	Footslope	Coniferous Forest
Reference	Spionkop 1	27	15	Footslope	Coniferous Forest
	Spionkop 2	3	NA	Toeslope	Mixedwood Forest
	Spionkop 3	2	NA	Depositional	Grassland
	Spionkop 4	3	NA	Depositional	Grassland
	Spionkop 5	18	130	Footslope	Hillslope Vegetation
	Yarrow 1	14	160	Backslope	Hillslope Vegetation
	Yarrow 2	20	133	Footslope	Hillslope Vegetation
	Yarrow 3	4	NA	Depositional	Mixedwood Forest
	Yarrow 4	4	NA	Depositional	Mixedwood Forest
	Yarrow 5	13	11	Toeslope	Coniferous Forest

Table A.2. Particle size distribution and associated textural class for all sites

Location	Type	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Textural class*
Carthew 1	1-year	0-5	44.64	33.66	21.71	L
Lineham 1	1-year	0-5	29.7	42.13	28.17	CL
Blakiston 4	1-year	0-5	40.19	42.38	17.43	L
Blakiston 6	1-year	0-5	79.38	14.4	6.21	LS
Blakiston 5	1-year	0-5	22.59	46.23	31.18	CL
Cameron 1	1-year	0-5	31.91	47.49	20.61	L
Cameron 4	1-year	0-5	60.5	28.55	10.95	SL
Blakiston 3	1-year	0-5	27.69	44.95	27.36	L
Cameron 2	1-year	0-5	33.84	46.3	19.87	L
Bauerman 1	1-year	0-5	36.74	42.6	20.66	L
Blakiston 2	1-year	0-5	83.7	13.15	3.15	LS
Blakiston 1	1-year	0-5	68.7	24.18	7.12	SL
Cameron 3	1-year	0-5	83.52	13.01	3.47	LS
Bauerman 3	1-year	0-5	82.93	10.84	6.23	LS
Bauerman 2	1-year	0-5	41.54	40.11	18.36	L
Bauerman 1	4-years	5-15	77.15	12.78	10.07	SL
Bauerman 2	4-years	5-15	22.78	49.83	27.39	CL
Bauerman 3	4-years	5-15	51.77	31.09	17.13	L
Bauerman 1	4-years	0-5	78.62	13.8	7.59	SL
Bauerman 2	4-years	0-5	46.02	40.19	13.8	L
Bauerman 3	4-years	0-5	65.07	25.54	9.39	SL
Blakiston 1	4-years	5-15	57.18	30.16	12.66	SL
Blakiston 2	4-years	5-15	74.71	17.19	8.1	SL
Blakiston 3	4-years	5-15	48.3	31.83	19.87	L
Blakiston 4	4-years	5-15	71.49	16.73	11.78	SL
Blakiston 5	4-years	5-15	83.56	9.77	6.67	LS
Blakiston 6	4-years	5-15	59.85	26.03	14.12	SL
Blakiston 1	4-years	0-5	61.02	27.86	11.12	SL
Blakiston 2	4-years	0-5	78.72	14.02	7.26	LS
Blakiston 3	4-years	0-5	58.64	31.01	10.35	SL
Blakiston 4	4-years	0-5	82.25	11.66	6.1	LS
Blakiston 5	4-years	0-5	74.21	18.74	7.05	SL
Blakiston 6	4-years	0-5	72.27	20.24	7.49	SL
Cameron 1	4-years	5-15	31.22	39.12	29.66	CL
Cameron 3	4-years	5-15	38.01	41.66	20.33	L
Cameron 4	4-years	5-15	43.34	37.24	19.42	L
Cameron 1	4-years	0-5	44.34	34.69	20.96	L
Cameron 2	4-years	5-15	19.49	48.27	32.24	SiCL
Cameron 2	4-years	0-5	39.78	40.69	19.52	L
Cameron 3	4-years	0-5	56.88	30.79	12.33	SL
Cameron 4	4-years	0-5	60.49	28.81	10.7	SL

Table A-2. Continued

Location	Type	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Textural class*
Carthew 1	4-years	5-15	30.63	46.56	22.82	L
Carthew 1	4-years	0-5	51.49	34.57	13.94	L
Lineham 1	4-years	5-15	38.05	36.78	25.17	L
Lineham 1	4-years	0-5	54.62	31.71	13.67	SL
Spionkop 1	100-years	5-15	50.44	32.38	17.17	L
Spionkop 2	100-years	5-15	48.56	33.61	17.83	L
Spionkop 3	100-years	5-15	64.32	25.76	9.93	SL
Spionkop 4	100-years	5-15	65.06	26.07	8.87	SL
Spionkop 5	100-years	5-15	57.06	30.15	12.79	SL
Spionkop 1	100-years	0-5	81.71	12.72	5.58	LS
Spionkop 4	100-years	0-5	58.76	30.56	10.68	SL
Spionkop 5	100-years	0-5	60.63	26.47	12.9	SL
Yarrow 1	100-years	5-15	67.42	18.38	14.2	SL
Yarrow 2	100-years	5-15	72.06	18.5	9.43	SL
Yarrow 3	100-years	5-15	81.89	12.61	5.5	LS
Yarrow 4	100-years	5-15	49.51	35.9	14.59	L
Yarrow 5	100-years	5-15	60.88	27.94	11.18	SL
Yarrow 1	100-years	0-5	78.94	15.26	5.8	LS
Yarrow 3	100-years	0-5	66.16	24.77	9.07	SL
Yarrow 5	100-years	0-5	78.3	15.82	5.88	LS

* Texture class abbr: L = loam, SL = sandy loam, LS = loamy sand, CL = clay loam, SiCL = silty clay loam

Table A.3. Total carbon, nitrogen and Walkley-Black carbon percentage of soils collected in 2021

Depth (cm)	Type	Location	Total Carbon (%)	Total Nitrogen (%)	TC/TN Ratio	Walkley-Black Carbon (%)	Walkley-Black Proportion of Total Carbon (%)
0-5	Burned	Bauerman 1	6.72	0.49	13.70	2.43	36.18
		Bauerman 2	8.42	0.52	16.20	2.73	32.46
		Bauerman 3	31.31	1.69	18.50	7.31	23.33
		Blakiston 1	6.72	0.55	12.20	0.58	8.60
		Blakiston 2	4.27	0.30	14.20	0.90	21.02
		Blakiston 3	11.98	0.53	22.60	5.42	45.22
		Blakiston 4	5.69	0.41	13.90	1.67	29.38
		Blakiston 5	8.92	0.59	15.10	2.75	30.81
		Blakiston 6	19.58	0.95	20.60	5.98	30.54
		Cameron 1	5.14	0.23	22.30	0.50	15.94
		Cameron 2	6.36	0.32	19.90	2.04	32.14
		Cameron 3	11.16	0.82	13.60	2.38	21.32
		Cameron 4	5.00	0.28	17.90	1.16	23.29
		Carthew 1	9.76	0.46	21.20	2.31	23.67
		Lineham 1	8.28	0.48	17.30	2.66	32.16
	Reference	Spionkop 1	44.66	1.68	26.60	8.50	19.03
		Spionkop 2	-	-	-	-	-
		Spionkop 3	-	-	-	-	-
		Spionkop 4	24.94	1.06	23.50	4.77	19.13
		Spionkop 5	23.32	0.68	34.30	2.78	11.91
		Yarrow 1	5.58	0.31	18.00	2.10	37.57
		Yarrow 2	-	-	-	-	-
		Yarrow 3	17.52	0.88	19.90	3.72	21.25
		Yarrow 4	-	-	-	-	-
		Yarrow 5	11.90	0.58	20.50	3.25	27.30
5-15	Burned	Bauerman 1	2.02	0.18	11.20	0.25	12.36
		Bauerman 2	4.41	0.32	13.80	0.45	10.24
		Bauerman 3	3.19	0.25	12.80	0.53	16.75
		Blakiston 1	3.00	0.28	10.70	0.71	23.60
		Blakiston 2	2.39	0.19	12.60	0.19	8.13
		Blakiston 3	1.35	0.07	19.30	0.36	26.57
		Blakiston 4	3.83	0.28	13.70	1.12	29.19
		Blakiston 5	4.33	0.20	21.70	1.76	40.71
		Blakiston 6	6.28	0.36	17.40	1.30	20.62
		Cameron 1	2.78	0.14	19.80	0.51	18.30
		Cameron 2	5.32	0.37	14.40	0.94	17.68
		Cameron 3	7.79	0.55	14.20	1.20	15.36
		Cameron 4	3.16	0.15	21.10	0.69	13.51
		Carthew 1	12.34	0.95	13.00	3.03	24.55
		Lineham 1	7.14	0.38	18.80	4.95	69.27

Table A.3 Continued

Reference	Spionkop 1	5.82	0.25	23.30	1.85	31.78
	Spionkop 2	4.05	0.28	14.50	1.05	25.99
	Spionkop 3	5.67	0.35	16.20	1.23	21.72
	Spionkop 4	11.56	0.74	15.60	2.76	23.89
	Spionkop 5	6.29	0.26	24.20	1.37	21.78
	Yarrow 1	3.51	0.17	20.70	2.58	73.59
	Yarrow 2	2.51	0.21	12.00	0.96	38.37
	Yarrow 3	5.99	0.34	17.60	2.63	43.94

Table A.4. Carbon compound family values in mg/grams of carbon of soils from 0-5cm

Type	Location	Carbohydrate	Phenolic	Benzene/ Aromatics	Aliphatic	Nitrogenous compounds	Other	Abietanes, Terpenoids, Sterols	Pyrogenic C (pyrolysis)	PyC - Marker	Lignin	Lignin marker	Black C (Pyrogenic C)	Black C marker
1-year	Bauerman 1	66	29.5	51.4	53.2	22.5	0	0	200.6	53.7	52.8	0.4	148.2	5.2
	Blakiston 3	35.5	19.8	45.2	47.7	8.2	2.6	3.8	138.3	41.4	35.9	0.9	107.4	1.5
	Cameron 1	16.2	7.3	15.5	10.1	6.1	0	0.2	49.7	14.5	14.7	0.3	35.1	0
4-years	Bauerman 1	34.5	12.9	32.1	39.3	15	2	2.5	125.1	32.5	27.4	0.5	95.5	2.0
	Blakiston 3	14.2	6.1	19.2	14.9	4.5	0	0.3	53.1	17.4	13.3	0.1	38.8	0
	Cameron 1	45	16.3	32.6	26.2	15	0	0.5	123.9	30.6	31.8	0.4	83.9	0
100-years	Yarrow 1	46	28.1	44.1	40.1	20.2	2.7	3	159.2	39.7	43.4	2.7	120.9	2.9
	Spionkop 4	19.9	16.6	20.1	15.7	7.3	2.5	2.5	69.6	14.1	23.1	0	52.2	0.6

Table A.5. Carbon compound family values in mg/grams of carbon of soils from 5-15cm

Type	Location	Carbohydrate	Phenolic	Benzene/ Aromatics	Aliphatic	Nitrogenous compounds	Other	Abietanes, Terpenoids, Sterols	Pyrogenic C (pyrolysis)	PyC - Marker	Lignin	Lignin marker	Black C (Pyrogenic C)	Black C marker
4-years	Bauerman 1	133.1	34.9	97.1	138.8	47.6	2.6	3.3	420.6	93.5	77	0.8	303.8	4.7
	Blakiston 3	284.7	57.4	166	101.6	42.7	0	0	598.7	149.5	138.3	0	332.6	0
	Cameron 1	181	46.5	129.1	75.8	57.8	20.3	20.3	461.7	116.4	108	0	296.5	0
100-years	Yarrow 1	35.6	23.6	44.6	26.3	17	1	1	131.9	43.2	44.5	0.6	100.4	1.8
	Spionkop 4	37.6	17.3	30.5	34.9	21.5	2.2	2.7	124.4	27.1	28.8	0.7	94.3	0.3