

Article

Source Material and Concentration of Wildfire-Produced Pyrogenic Carbon Influence Post-Fire Soil Nutrient Dynamics

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Abstract: Pyrogenic carbon (PyC) is produced by the thermal decomposition of organic matter in the absence of oxygen (O). PyC affects nutrient availability, may enhance post-fire nitrogen (N) mineralization rates, and can be a significant carbon (C) pool in fire-prone ecosystems. Our objectives were to characterize PyC produced by wildfires and examine the influence that contrasting types of PyC have on C and N mineralization rates. We determined C, N, O, and hydrogen (H) concentrations and atomic ratios of charred bark (BK), charred pine cones (PC), and charred woody debris (WD) using elemental analysis. We also incubated soil amended with BK, PC, and WD at two concentrations for 60 days to measure C and N mineralization rates. PC had greater H/C and O/C ratios than BK and WD, suggesting that PC may have a lesser aromatic component than BK and WD. C and N mineralization rates decreased with increasing PyC concentrations, and control samples produced more CO₂ than soils amended with PyC. Soils with PC produced greater CO₂ and had lower N mineralization rates than soils with BK or WD. These results demonstrate that PyC type and concentration have potential to impact nutrient dynamics and C flux to the atmosphere in post-fire forest soils.

Keywords: pyrogenic carbon; black carbon; nitrogen; soil respiration; N mineralization; wildfire; *Pinus banksiana*

1. Introduction

Wildfire frequency, severity, and fuel availability are predicted to increase in many areas of the world as a result of global climate change [1,2]. Wildfires may exacerbate climate change by releasing carbon dioxide (CO₂) via the combustion of organic matter during fires and via post-fire microbial decomposition of plants killed by fire. However, pyrogenic carbon (PyC, also known as black carbon) is produced during the thermal decomposition of organic matter in the absence of oxygen (O) (*i.e.*, pyrolysis) and may represent an important carbon (C) pool in fire-affected forests [3–5]. PyC is composed of a labile and soluble component, and an aromatic component [6]. Thus, PyC inputs to soils from forest fires have the potential to influence overall soil respiration rates. PyC has been shown to have a positive priming effect on soil respiration in the short-term, as the labile component is utilized, but PyC may also have a long-term negative priming effect due to the aromatic component [7]. By decreasing soil respiration rates, PyC addition may promote C sequestration in forest soil [3,8]. PyC can also affect N dynamics in forests. For example, wildfires produce ammonium during the burning of biomass, and increase nitrification because they remove vegetation that compete with nitrifying bacteria [9]. However, PyC can increase nitrogen (N) mineralization rates [10] and interact physically with organic compounds that may affect N cycling [11]. PyC is produced from various source materials and at differing temperatures within individual wildfires [12,13], yet the current scientific understanding of how variation in PyC influences post-fire C and N ecosystem dynamics is limited.

Variation in PyC characteristics is influenced by both charring conditions and source material [3,4,14–16]. The structure of PyC is a function of its charring conditions, in which an increase in temperature results in greater overall aromaticity [4,15,16]. The number of O- and H- containing functional groups that are important for biological degradability decreases continuously as the source material becomes more charred [14]. Furthermore, the interaction of charring temperature and source material influences the ultimate characteristics of the PyC [3,15]. Current knowledge of the chemical and physical characteristics of PyC produced by wildfire (hereafter, wildfire PyC) is primarily from studies investigating the properties of PyC produced experimentally (hereafter, experimental PyC) [3,17]. Therefore, there is limited understanding of how charring conditions during wildfires influence PyC characteristics produced from various source materials, or how variations in PyC characteristics affect post-fire nutrient dynamics.

Experimental PyC (including biochar) is produced by pyrolysis similar to wildfire PyC, however, charring conditions and source material are held constant during the formation of experimental PyC. In contrast, wildfire PyC is produced under fluctuating conditions of temperature, heating duration, and oxygen availability during wildfires and originates from mixed sources of organic matter, including standing live or dead trees (with bark, woody tissue, foliage, and seed-bearing structures such as cones), shrubs, herbaceous vegetation, forest litter (dead foliage, bark, and other plant components) and dead woody debris on the forest floor (hereafter, woody debris). These source materials experience different fire environments depending on their physical location within a forest, such as being located at the base of standing trees or in the forest canopy. Thus, experimental PyC may not be representative of the range of wildfire PyC that occurs in natural fire-prone forest ecosystems [18] because of the differences in charring conditions and source materials that exist between experimental PyC and wildfire PyC. The few studies that have investigated variability in wildfire PyC have found large variability in the degree

of aromatic condensation, likely due to variation in source material and temperature [13,18]. These potential differences in PyC characteristics may influence the extent to which PyC addition to soil alters soil respiration rates and stimulates gross N mineralization rates (*i.e.*, indices of microbial activity) [3,4,7], with important implications for post-fire nutrient dynamics in soils and ultimately C sequestration rates by the recovering forest. Here we present data on a suite of major types of wildfire PyC produced in a high-severity, stand-replacing wildfire in jack pine (*Pinus banksiana* Lamb.) forest in the northern lower peninsula of Michigan, USA. Our overarching objective was to characterize the PyC produced from major contrasting types of aboveground source material (bark, pine cones, and woody debris) during wildfire in a fire-dependent forest type, and to identify effects on microbially-mediated post-fire nitrogen C and N cycling after fire. Our specific objectives were to (1) characterize PyC produced by wildfires and (2) examine the influence that contrasting types and concentrations of PyC have on soil C and N mineralization rates. We hypothesized that the addition of PyC to soils would decrease soil respiration and increase N mineralization, and that the extent to which this occurs would depend on the type and concentration of wildfire PyC.

2. Experimental Section

2.1. Study Site and Sample Collection

Our study was focused in jack pine forests in Michigan. These forests are primarily monocultures of even-aged jack pine trees. Jack pine is an ecologically similar species to the widespread lodgepole pine (*P. contorta* Douglas ex Loudon) in the western US. These two closely related species are also major components of boreal forest ecosystems. The fire regime for jack pine forests in our study region is high-severity (*i.e.*, stand-replacing) fires (Figure S1) with a fire return interval of approximately 31 years [19]. Fires may become increasingly severe in many forest types as the climate continues to warm [20,21]. Thus, we used a stand-replacing fire in jack pine forest to represent PyC produced in high-severity fire and its effect on forest ecosystem function.

We collected our samples in autumn 2013 from the stand-replacing Howes Lake wildfire. The Howes Lake wildfire was ignited by lightning and lasted from 7 June to 8 June 2011. The fire burned a total of 352 ha in even-aged jack pine forest in Crawford County, Michigan (44°42'39.6" N, 84°48'54" W). The total amount of precipitation between the wildfire and the time of sample collection was 226 cm [22]. This forest is dominated by jack pine with a minor component of *Quercus alba* L., *Q. velutina* Lam., and *Q. ellipsoidalis* E.J. Hill intermixed. The understory consists of *Arctostaphylos uva-ursi* (L.) Spreng., *Vaccinium angustifolium* Aiton, *Carex pensylvanica* Lam., *Schizachyrium scoparium* (Michx.) Nash, and *Andropogon gerardii* Vitman. Soils are classified as sandy Entisols following the USDA soil classification system, which is related to the World Reference Base Arenosol. Specifically, the soil in our study area predominantly represents the Grayling series (Typic Udipsamments), which is characterized by excessively drained, acid, relatively undeveloped medium to medium-fine sand [23]. The Graycalm series (Lamellic Udipsamments) occurs intermixed with the Grayling series and is characterized by the presence of thin, fine-textured bands of loamy sand to sandy clay loam in the lower horizons. The mean annual temperature is 6.7 °C and the average temperature during the growing season (May through September) is 16.9 °C [22].

We collected three types of wildfire PyC (Figure 1): charred bark (BK), charred pine cones (PC), and charred woody debris (WD). The charred bark was collected from the stem of standing dead jack pine trees, from ground level to 1.37 m. We collected WD from ground level that was between 1.3 and 10.8 cm in diameter. We collected only WD pieces without bark and with evidence of charred stemwood, which together indicate that the woody debris was dead and on the ground surface before and during the fire. We collected the PC from tree limbs on the soil surface that retained charred bark.

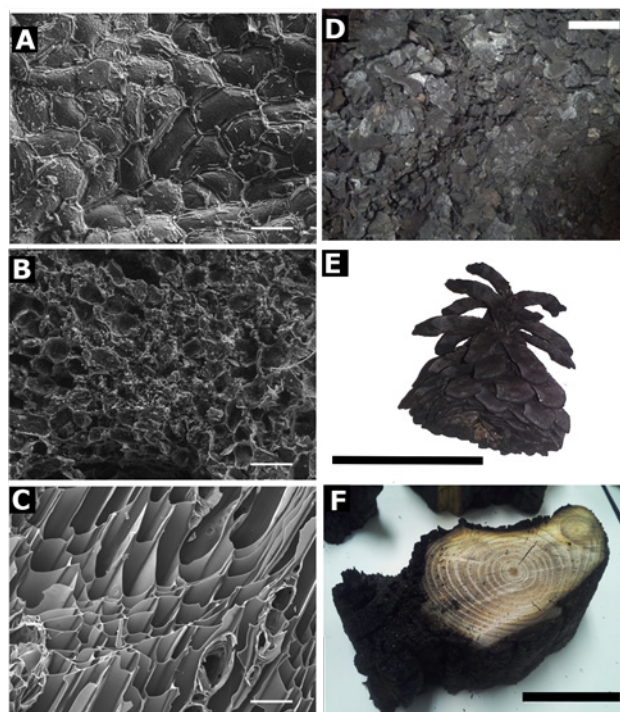


Figure 1. Scanning electron microscopy (SEM) images of charred bark (A), charred pine cones (B), and charred woody debris (C). Scale bars for the SEM images = 50 µm. Photos to the right of the SEM images (D–F) are images of the corresponding charred material. Scale bar for images shown in panels D, E and F = 4 cm.

The presence of charred bark on the limbs indicates that the pine cones were charred in the forest canopy on trees that were alive at the time of the fire and that fell after the fire. BK and PC were each composited in the field, whereas WD was returned to the lab as individual pieces, from which all blackened material was removed manually from each piece using a small steel plane (Microplane, Grace Manufacturing, Inc., Russellville, AR, USA). From the unburned jack pine forest of the same age outside the Howes Lake fire perimeter, we collected uncharred bark from standing dead trees, and uncharred woody debris and pine cones from the ground surface. The uncharred material was collected to test that differences in chemical composition between the charred materials was due to charring and not simply due to the difference chemical composition of the source material. Because the properties of freshly-produced char can differ from aged char [24,25], we focused on naturally aged PyC collected two years after fire. This approach provides information that is most relevant to understanding relatively persistent effects of wildfire PyC on soil processes in a recovering forest, rather than very short-term impacts that may result from transient chemical characteristics of fresh PyC.

2.2. Laboratory Analysis

We oven-dried all materials at 60 °C until constant mass. We composited the BK material by mixing all of the BK that was collected from various trees and we composited the PC material by mixing all of the pine cones that were collected. The WD was processed and retained as individual samples. For charred and uncharred bark, pine cones, and woody debris, we pulverized a subsample to fine powder and determined the weight percent C, N, hydrogen (H), and oxygen (O) with an elemental analyzer at Atlantic Microlabs (Norcross, GA). We determined percent ash following ASTM E1755-01 [26] and calculated element ratios following established methods [27,28]. We measured pH with a 1:2 w/v ratio of PyC:water [29] using pulverized PyC material.

2.3. Laboratory Incubations

We established a 60-day laboratory incubation using a full factorial design of the three types of wildfire PyC and two concentrations of wildfire PyC (1% and 0.1% of soil mass, hereafter high and low concentrations, respectively). We followed Deluca, *et al.* [10] to identify our lowest PyC concentration. Although Deluca, *et al.* [10] investigated soils from ponderosa pine (*Pinus ponderosa* Lawson and C. Lawson), there have been no estimates of PyC concentrations in jack pine forest mineral soils to date. We implemented our high concentration as 10× base PyC concentration to evaluate potential impacts of greater amounts of PyC addition to soil, which may occur in forests that experience an increase in fire frequency or severity. We used three replicates per treatment per time point (Table S1). Each type of wildfire PyC was ground and passed through a 1.0 mm sieve in order to homogenize the particle size. We incorporated each type and level of wildfire PyC into field moist mineral soil collected from an unburned area within the same soil classification adjacent to the perimeter of the Howes Lake fire to create a homogenized 300 g stock media of soil and wildfire PyC for each treatment. The field-moist soil was collected from 0–15 cm depth and had a pH of 4.7 ± 0.0 and C and N concentrations of $1.13\% \pm 0.04\%$ and $0.05\% \pm 0.00\%$, respectively ($N = 2$ replicates of composited soil). For each treatment we used 20.0 g (± 0.1 g) of stock soil for each sample. The soils were incubated in the dark at constant ambient temperature (25 °C).

We measured CO₂ concentrations using a LiCOR LI-820 (Lincoln, NE, USA) on days 10, 20, 40, and 60 (T₁₀, T₂₀, T₄₀, and T₆₀, respectively) of the incubation [29]. The samples were sealed for 10 days for T₁₀ and T₂₀, and for 20 days for T₄₀ and T₆₀. The headspace of each sample was flushed with ambient air after each CO₂ measurement. On days 0, 20, 40, and 60, three replicates of each treatment combination (10.0 ± 0.01 g each) were extracted with 50 ml 2M potassium chloride (KCl), to determine changes in ammonium (NH₄⁺), nitrate (NO₃[−]), and total inorganic N concentrations over time, and N mineralization rates over the 60-day period [29]. NH₄⁺ concentrations were measured in accordance to Sinsabaugh, *et al.* [30], such that the KCl extracts, ammonia cyanurate, and ammonia salicylate were mixed in microplate wells and incubated at room temperature for 20 minutes. NO₃[−] concentrations were measured in accordance to Doane and Horwath [31], such that the KCl extracts and a saturated vanadium solution were mixed in microplate wells and incubated in the dark at room temperature for 5 hours. After incubation, the microplates were read on a BioTek ELX808 (Winooski, VT, USA) reader at 595 nm.

2.4. Statistical Analysis

We used a Pearson's Correlation test to determine if the elemental composition of the uncharred material was a significant covariate for the charred material. We used an ANOVA (C, percent ash, O/C, and H/C), and an ANCOVA with uncharred material as a covariate (N, H, and O) to identify statistically significant differences among the wildfire PyC type using R 3.0.2. We analyzed C and N mineralization rates from the incubations using repeated measures ANOVA in SAS 9.3 (SAS Institute, Cary, NC, USA) with PROC MIXED. We used Tukey's adjustment for multiple comparisons to identify statistically significant differences among treatment means and time points. We considered differences to be statistically significant at $p < 0.05$.

3. Results

3.1. Chemical Composition

Using the Pearson's Correlation test, we determined that the elemental composition of the uncharred material was a significant covariate for H, N, and O. H/C and O/C ratios can be used to indirectly measure the aromaticity of a substance [32] and a van Krevelen plot (Figure 2) is a convenient way to visualize the difference in these two ratios between the samples. PC was less aromatic than BK and WD, as indicated by the ratios of C, H, and O (Figure 1 and Table 1). The O/C ratio and H/C ratio for PC were 24% and 25% greater than WD, respectively, and 12% and 39% greater than BK (Table 1). The H concentrations and mineral component (% ash) were 12% and 83% greater in PC than WD, respectively. In addition, PC had 79% more ash than BK. However, PC had 18% and 14% less C than WD and BK, respectively. Lastly, the C/N ratio in PC was 60% lower than in WD. The C/N ratio of BK was 27% greater than WD.

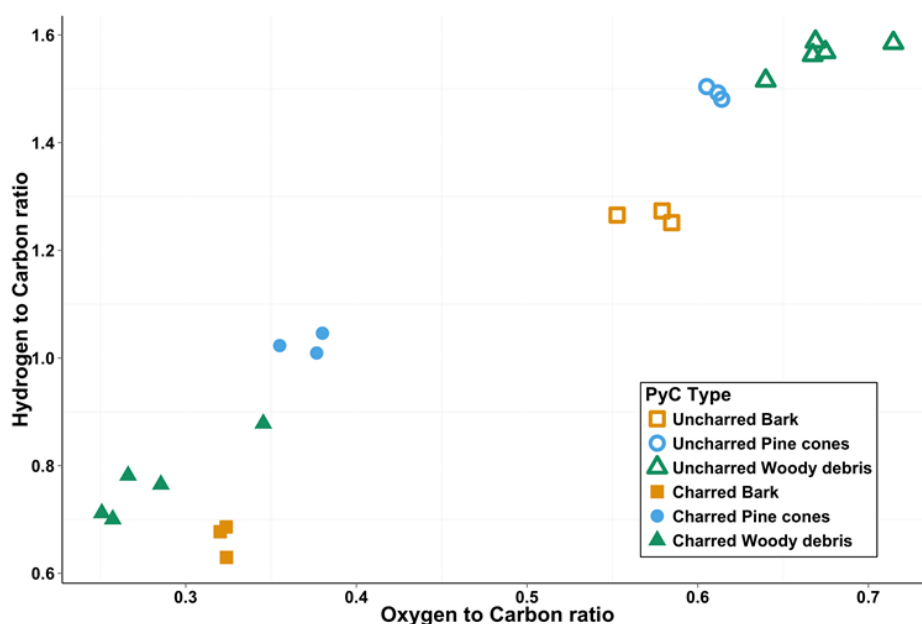


Figure 2. Van Krevelen diagram of uncharred and charred (open and filled symbols, respectfully) bark (yellow), charred pine cones (blue), and charred woody debris (green). The ratios on the axes are expressed as atomic percent of the elements.

Table 1. Summary table of the mean and standard error (one standard error) of the chemical composition and atomic ratios of charred bark (BK), charred pine cones (PC), charred woody debris (WD), uncharred bark, uncharred pine cones, and uncharred woody debris.

Material	<i>n</i>	%C	%H *	%N *	%O	%Ash	O/C	H/C	C/N *	pH
<i>Charred</i>										
BK	3	50.22 ± 0.43 a	33.34 ± 0.60 ab	0.23 ± 0.01 a	16.20 ± 0.17 a	1.40 ± 0.19 ab	0.32 ± 0.00 ab	0.66 ± 0.018 b	214.97 ± 8.68 ab	4.4 ± 0.0
PC	3	41.62 ± 0.25 b	42.70 ± 0.26 a	0.25 ± 0.01 ab	15.43 ± 0.27 ab	8.54 ± 0.6 a	0.37 ± 0.01 a	1.03 ± 0.011 a	169.83 ± 5.39 a	3.8 ± 0.0
WD	5	48.83 ± 1.10 a	37.34 ± 0.67 b	0.18 ± 0.01 b	13.65 ± 0.50 b	1.77 ± 0.41 b	0.28 ± 0.01 b	0.77 ± 0.032 b	272.27 ± 17.06 b	4.3 ± 0.0
<i>Uncharred</i>										
Bark	3	35.20 ± 0.12 a	44.46 ± 0.22 a	0.20 ± 0.01 a	20.14 ± 0.30 ab	1.39 ± 0.12 a	0.57 ± 0.01 a	1.26 ± 0.01 a	175.87 ± 7.17 ab	3.7 ± 0.0
Pine cones	3	32.14 ± 0.05 b	47.97 ± 0.15 b	0.27 ± 0.00 b	19.62 ± 0.11 a	1.02 ± 0.18 a	0.61 ± 0.00 a	1.49 ± 0.01 b	118.53 ± 1.42 b	3.5 ± 0.0
Woody debris	5	30.85 ± 0.22 c	48.24 ± 0.14 b	0.15 ± 0.01 c	20.76 ± 0.23 b	1.00 ± 0.13 a	0.67 ± 0.01 b	1.56 ± 0.01 c	219.67 ± 20.89 a	3.7 ± 0.0

Lower case letters indicate significant differences within column by category (charred, uncharred) ($p < 0.05$, ANOVA, after Tukey-Kramer correction). An * indicates that the uncharred material was used as a covariate when analyzing the charred material.

3.2. Incubations

3.2.1. CO₂ Flux (in Terms of Soil-C)

To compare differences in soil respiration rates between treatments we investigated the amount of CO₂ produced per g of soil-C per day ($\mu\text{g CO}_2 \text{ soil-C}^{-1} \text{ day}^{-1}$, Figure 3A) in order to account for the different amount of C added to each treatment. Throughout the 60 days of the incubation, the control samples produced more CO₂ than each of the wildfire PyC treatments at all time points (Figure 3A, Table 2, and Table S1). Specifically, the control samples produced 11%–54% more CO₂ than the soils amended with wildfire PyC at a given time point. Overall soils amended with low wildfire PyC concentrations produced more CO₂ than soils amended with high wildfire PyC concentrations. Also, at all time points except T₁₀, soils amended with PC produced more CO₂ than soils with BK or WD, irrespective of concentration. Specifically, soils with low concentrations of PC produced 7%–19% and 11%–18% more CO₂ than soils with BK or WD, respectively. Soils with low concentrations of BK or WD produced similar amounts of CO₂. However, at high wildfire PyC concentrations, soils with WD produced 20%–48% more CO₂ than soils with BK. Soils amended with high concentrations of BK produced 36%–62% less CO₂ than soils amended with low concentrations of BK.

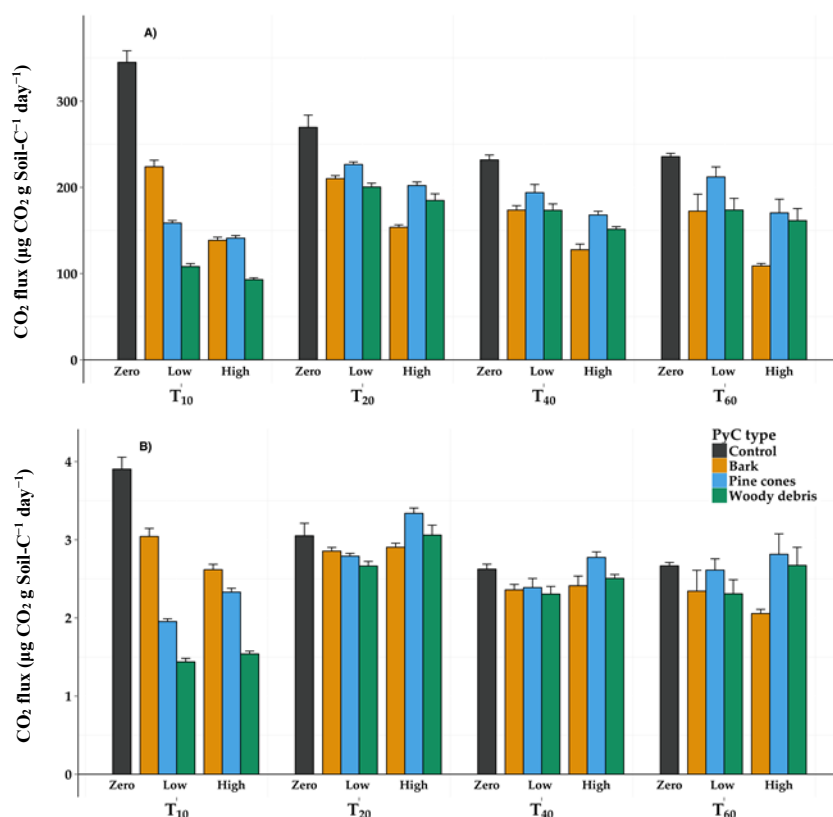


Figure 3. CO₂ flux, in terms of (A) g soil C per day and (B) g soil per day, of soils incubated with charred bark (yellow), charred pine cones (blue), or charred woody debris (green) at either zero (black, control), low (0.1%), or high (1.0%) PyC concentrations. The CO₂ concentrations were measured on days 10, 20, 40, and 60 (T₁₀, T₂₀, T₄₀, T₆₀, respectively). The error bars represent one standard error. Results from means separation tests are reported in Table S1.

Table 2. Table of F-statistics and *p*-values for ANOVAs of soil respiration for treatment, time, and treatment $\times$ time. All PyC types and concentrations fall under treatment.

	Main Effect	F Value	<i>p</i> Value
$\mu\text{g CO}_2 \text{ g soil-C}^{-1} \text{ day}^{-1}$	Treatment	87.81	<0.0001
	Time	55.08	<0.0001
	Treatment $\times$ Time	30.65	<0.0001
$\mu\text{g CO}_2 \text{ g soil}^{-1} \text{ day}^{-1}$	Treatment	18.58	<0.0001
	Time	79.38	<0.0001
	Treatment $\times$ Time	32.58	<0.0001

3.2.2. CO₂ Flux (in Terms of g Soil)

At the beginning (T₁₀) of the incubation the control soils produced 22%–50% more CO₂ than any of the soils amended with wildfire PyC. For all time points (T₂₀–T₆₀) soils amended with high concentrations of PC and WD produced 7%–16% and 6%–14% (respectfully) more CO₂ than soils with low concentrations of PC and WD (Figure 3B and Table S2). Furthermore, the control soils produced more CO₂ than soils amended with low concentrations of wildfire PyC. Specifically, the control samples produced 6%–22%, 2%–50%, and 12%–63% more CO₂ than soil amended with low concentrations of BK, PC, and WD, respectfully.

3.2.3. Nitrogen Flux

At the beginning of the incubation, soils with low concentrations of wildfire PyC had greater N mineralization rates than soils with high concentrations of wildfire PyC (Figure 4, Table 2). Specifically, soils with low concentrations of BK, PC, and WD had 23%, 50%, and 37% higher N mineralization rates, respectively, than soils with high concentrations (Figure 4, Tables 3 and 4). Of the soils with high concentrations of wildfire PyC, soils with BK had the greatest N mineralization rates at all time points (26%, 15%, 20% at T₂₀, T₄₀, T₆₀, respectively). At T₂₀ and T₄₀ the soils with low concentrations of wildfire PyC had 17% and 60% higher N mineralization rates than the control soils. However, at T₆₀ the N mineralization rates of the control soils were 8%–60% greater than all wildfire PyC treatments (Figure 4, Table 2).

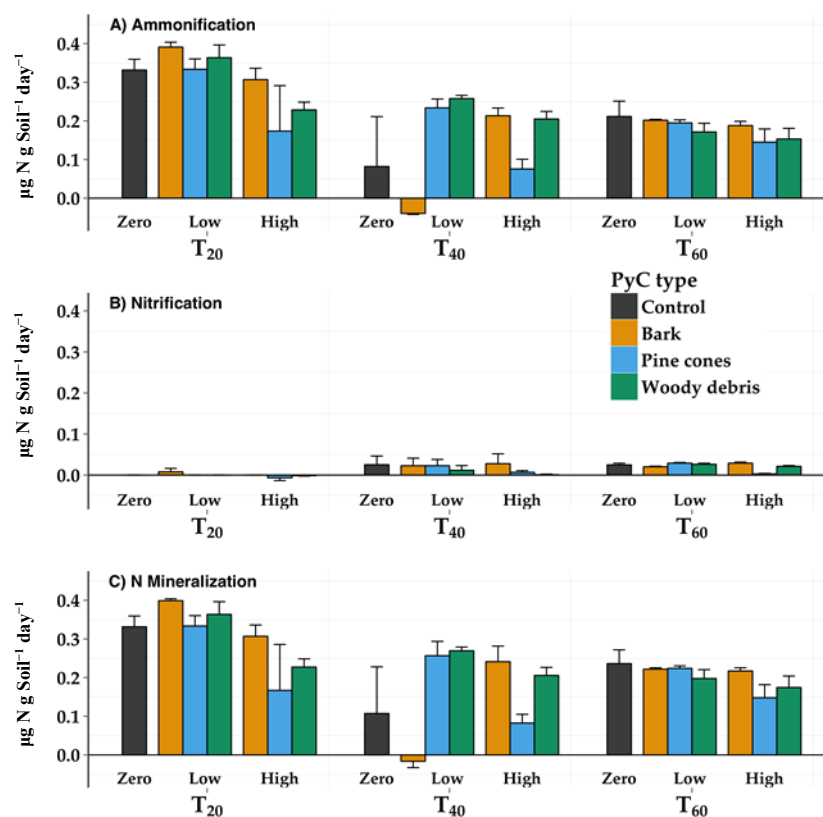


Figure 4. (A) Ammonification rate, (B) nitrification rate, and (C) total N mineralization rate of soils incubated with charred bark (yellow), charred pine cones (blue), or charred woody debris (green) at either zero (black, control), low (0.1%), or high (1.0%) PyC concentrations. The soils were incubated for 20, 40, 60 days (T₂₀, T₄₀, T₆₀, respectively). The error bars represent one standard error.

Table 3. Summary table of means $\pm$ standard errors (one standard error) for N mineralization rates ($\mu\text{g N g Soil}^{-1} \text{ day}^{-1}$) of soils incubated for 20, 40, and 60 days with charred bark (BK), charred pine cones (PC), or charred woody debris (WD) at zero (control), low (0.1%), or high (1.0%) PyC concentrations.

		PyC Type			
Time	Concentration	Control	BK	PC	WD
20	Zero	0.33 $\pm$ 0.03 c	—	—	—
	Low	—	0.40 $\pm$ 0.01 d	0.33 $\pm$ 0.03 c	0.36 $\pm$ 0.03 cd
	High	—	0.31 $\pm$ 0.03 bc	0.17 $\pm$ 0.12 abc	0.23 $\pm$ 0.02 bc
40	Zero	0.11 $\pm$ 0.12 abc	—	—	—
	Low	—	-0.17 $\pm$ 0.16 a	0.26 $\pm$ 0.04 bc	0.27 $\pm$ 0.01 bc
	High	—	0.24 $\pm$ 0.04 bc	0.08 $\pm$ 0.02 ab	0.21 $\pm$ 0.02 abc
60	Zero	0.24 $\pm$ 0.04 bc	—	—	—
	Low	—	0.22 $\pm$ 0.00 bc	0.22 $\pm$ 0.01 bc	0.20 $\pm$ 0.02 abc
	High	—	0.22 $\pm$ 0.01 abc	0.15 $\pm$ 0.03 abc	0.18 $\pm$ 0.03 abc

Significant differences among all time, concentration and PyC type comparisons are indicated by letters next to each mean ($p < 0.05$, ANOVA). Treatment combinations that did not exist (i.e. soils with zero concentration of BK, which were functionally equivalent to the Control) are indicated by —.

Table 4. Table of F-statistics and *p*-values for ANOVAs of ammonification, nitrification, and N mineralization for treatment, time, and treatment $\times$ time. All PyC type and concentrations fall under treatment.

	Main Effect	F Value	<i>p</i> Value
Ammonification	Treatment	3.26	0.0101
	Time	24.77	<0.0001
	Treatment $\times$ Time	3.15	0.0029
Nitrification	Treatment	1.47	0.2108
	Time	10.22	0.0002
	Treatment $\times$ Time	0.43	0.9437
N mineralization	Treatment	3.96	0.0032
	Time	18.94	<0.0001
	Treatment $\times$ Time	2.95	0.0047

All PyC type and concentrations fall under treatment.

4. Discussion

Our research provides an assessment of variability in naturally produced PyC collected from a high-severity wildfire in jack pine forest in Michigan. Our use of naturally aged PyC (2 years post-fire) provides information on intermediate-term PyC effects on soil processes rather than short-term effects that result from transient chemical properties [24,33], or long-term effects of PyC >100 years old, which over time becomes heavily occluded by senescent fungal hyphae and humic debris [11]. The addition of all types and concentrations of wildfire PyC to soil increased N mineralization rates when compared to the control samples. This finding is consistent with Deluca, *et al.* [10], who found that charred wood PyC increased nitrification in ponderosa pine forest soils. This increase in N mineralization rates indicates an increase in microbial activity. Microbial abundance has been found to increase with the addition of experimental PyC from wood [3,4]. Increases in microbial abundance may be due to the physical and chemical characteristics of PyC. For example, PyC may increase soil moisture, provide microhabitats for some microbial communities, and increase the pH of soil [4]. Although we did not measure microbial communities, we found that all types of PyC we used had a lower pH than the un-amended soil. Thus, two year old PyC in our jack pine forests may decrease pH in sandy soils. In contrast, other studies have shown that PyC may have a liming potential and may buffer acidic soils, thereby increasing pH and facilitating an increase in microbial abundance [4]. These contrasting results further suggest that the type of PyC incorporated into soil has an important effect on soil processes. It is possible that the increase in N mineralization we observed may have been influenced by changes in microbial abundance, which may increase due to release of nutrients from experimental PyC [3].

We observed a decrease in soil respiration, compared to the control soils, when low concentrations of all PyC types were added to soils (Figure 3B). However, soils with high concentrations of PyC produced more CO₂ than the control soils. T₁₀ does not fit the same trend as the other time points because it is most likely capturing the initial disturbance of establishing the incubation. In order to accurately represent the fact that there were different amounts of C in the soils due to the addition of PyC, we also evaluated soil respiration in terms of $\mu\text{g CO}_2 \text{ g soil-C}^{-1} \text{ day}^{-1}$ (Figure 3A). We observed a decrease in soil respiration in soils amended with wildfire PyC, which indicates a decrease in microbial activity.

This decrease in soil respiration may be due to the fact that all wildfire PyC types collected for this study were collected from a site that experienced a high severity crown fire. Zimmerman, *et al.* [34] found that experimental PyC produced at low temperatures (250–400 °C) increased soil respiration, whereas experimental PyC produced at high temperatures (525–650 °C) caused decreased soil respiration. Wildfires can have a greater range in temperature than prescribed fires. For example, Hartford and Frandsen [35] found that the litter surface, duff, and soil surface reached 300, 515, and 400 °C, respectively, in a prescribed ground fire in mixed-conifer forests (*Larix occidentalis* and *P. contorta*) in western Montana, whereas Santín, *et al.* [12] found that the mean temperature during an experimental stand-replacing crown fire in a jack pine forest in Canada was <70 °C at the mineral soil surface and 750 °C at the surface of the forest floor. Furthermore, Schneider, *et al.* [36] in a study of experimental fire in pitch pine (*P. rigida* Mill) forest in New Jersey, found that temperatures in the canopy can reach 510–650 °C during a crown fire whereas temperatures in the canopy during surface fire range between 0 and 260 °C. Together, the temperature ranges reported from these experimental fires suggest that the mean temperature at the floor forest during fire in conifer forests may range between 300 and 750 °C and that the temperature in the canopy may reach 650 °C. Although the study conducted by Santín, *et al.* [12] also focused on jack pine forest, their study was conducted in the boreal region and their study site supported a deep moss layer and saturated mineral soil. Jack pine forests in our study site are more ecologically similar to the pitch pine forests in the New Jersey, USA pine barrens because both forest types have thin forest floors and are found on dry sandy soils [37]. Therefore, the forest in our study site probably experienced fire temperatures more similar to those reported from crown fire in pitch pine forest in New Jersey.

If wildfire PyC increases microbial activity we would expect to see increases in N mineralization and soil respiration rates (indices for microbial activity) with the addition of PyC to soils. When comparing N mineralization rates (Figure 4C) and soil respiration rates (in terms of g soil, Figure 3B) there was an increase in N mineralization but a decrease in soil respiration for soils amended with low concentrations of PyC. However, soils amended with high concentrations of PyC had lower N mineralization rates than the controls but greater soil respiration rates. This opposite response between the two microbial activity indices we used presents a paradox [3]. In some cases, decreases in soil respiration rates may be caused by CO₂ precipitating onto high-pH surfaces of PyC [3,7]. However, because our PyC was acidic it is unlikely that this chemical reaction is occurring in our study. Another possible explanation is that the PyC may be sorbing the CO₂ due to its porous structure [7]. This may be occurring in our samples even though our PyC was collected two years post-fire because we ground the PyC, thereby opening new pore spaces and/or surfaces that were previously protected from the atmosphere or interaction with the soil matrix. However, the differences in soil respiration rates among PyC types followed the differences in pH of the PyC types. PC was the most acidic type of PyC and soils amended with PC had the highest soil respiration rates, whereas BK was the most basic and soils amended with BK had the lowest soil respiration rates (Figure 3). The lower pH in soils amended with PC may have increased fungal growth and therefore increased soil respiration. This paradox may also result from PyC increasing microbial C utilization and thus decreasing the need for enzyme production, as Bailey, *et al.* [38] observed decreased microbial enzyme activity after the addition of experimental PyC. Although we did not investigate microbial biomass and/or phospholipid fatty acid analysis, this type of information would provide valuable insight on additional indices of microbial community composition and activity in future studies.

Linking additional information on PyC characteristics (e.g., relative contributions of benzene polycarboxylic acid molecular markers [36]) with its effects on ecosystem processes represents a major knowledge gap. This information would help refine current understanding of fire effects on soil function, and would be relevant for understanding interactions among climate, fire and forest C dynamics.

Our results show that the magnitude of the effect of wildfire PyC on soil C and N mineralization rates differs among type and concentration of wildfire PyC added to the soil. Of all three types of wildfire PyC, different concentrations of BK had the largest effects on nutrient dynamics in soils. High concentrations of BK added to soils caused a significant decrease in soil respiration. In a study of PyC production in a stand-replacing fire boreal jack pine forest in Canada, Santín, *et al.* [12] found that one third (1.4 t ha^{-1}) of PyC produced is in the form of BK. Santín, *et al.* [12] reported similar % C for charred bark (62.9%) and similar percent increase in C due to charring (15.6%) compared to the 15.0% change we observed. BK represents a large pool of PyC in jack pine forests, and may be added to soils at high concentration after a fire. However, charred bark can also stay attached to the tree for a few years after a fire (*L. Michelotti, personal observation*). Thus, there is a need to identify the rate of PyC input to the soil ecosystem over time after a fire as well as how differences among forest types influence the rates of PyC input to soil.

Other researchers have shown that PyC aromaticity increases with charring temperature [4,5,15,16,36] and have suggested that it may be possible to approximate the relative maximum temperatures experienced by specific source materials during charring [13,14,36]. To date, controlled investigation of relationships between combustion conditions and PyC characteristics have involved prescribed fires or laboratory heating experiments. Interpreting the characteristics of wildfire PyC, or inferring its formation conditions, may be more challenging because combustion conditions in unplanned wildfires remain poorly understood. A laboratory heating experiment using red pine (*Pinus resinosa*) wood indicated that C and N concentrations increased with heating temperature from 70 °C to 350 °C, whereas H and O concentrations decreased [28]. The C concentration in our WD PyC was similar to the experimental red pine wood PyC produced at the lowest temperatures, whereas our H concentrations were greater than the lowest-temperature experimental PyC and our O concentrations were much lower than those reported for the highest-temperature experimental PyC [28]. The differences in the elemental concentrations of our wildfire-produced PyC relative to those reported for experimentally charred red pine wood highlights the potential danger of inferring wildfire-produced PyC characteristics from experimental studies, and also highlights a major need for information to characterize variability in wildfire-produced PyC. Although BK and WD in our study exhibited different chemical characteristics than PC, we are unable to confidently assume that these characteristics resulted from more similar charring temperatures to each other than to PC (Table 1). However, our PyC types fall under different portions of the PyC continuum [39]. Specifically, BK and WD have an H/C (0.66 and 0.77, respectively) similar to black carbon whereas PC has H/C that is similar to partly charred biomass [40]. However, the soils we amended with PC had greater soil respiration rates than soils amended with the other wildfire PyC types, and soil respiration has been found to decrease as charring temperature of experimental PyC increases [8]. Together, our results suggest that differences in source material influence wildfire PyC physical and chemical characteristics and the resulting effects on nutrient dynamics. We emphasize that additional research is needed to differentiate between the effects of temperature and source material in wildfire PyC.

Changes in fire frequency, severity or seasonality have occurred or are anticipated to occur as a result of climate change in many parts of the world. For example, increased occurrence of drought and increased fire season length can both contribute to increased fire frequency [1,2]. Increased wildfire activity will result in more CO₂ released to the atmosphere by fires and an increase in the overall strength of fires as a net C source [41]. Santín, *et al.* [12] reported that 4.8 t ha⁻¹ PyC were produced in a stand-replacing fire in boreal jack pine forest, whereas DeLuca and Aplet [42] estimated that 0.18–1.84 t ha⁻¹ and 0.34–3.36 t ha⁻¹ were produced in wildfires in ponderosa pine and lodgepole pine forests, respectively, in the western U.S. Together, these studies show that the total mass of PyC differs among forest type—which encompasses differences in fire regime, elevation and/or climate, and aboveground biomass—and that the ecologically similar jack pine and lodgepole pine forests reflect both high-severity fire and the upper end of aboveground PyC mass estimates that are available to date. We focused on wildfire in jack pine forest as an example study system for investigating how the production of PyC in high severity fires may affect post-fire nutrient dynamics.

It is reasonable to expect that changes in fire frequency, season, size and severity that result from changes in regional to global climate would also lead to changes in combustion conditions relative to historic fire conditions that would in turn influence PyC formation rates and characteristics. In our study area, high-severity fire in jack pine forest results in bark that is charred from the base to top of standing trees [43]. If forests that historically experienced lower-severity fires (e.g., surface fires) undergo shifts in disturbance regimes to include high-severity fire (e.g., canopy fire) as is already the case in many forests of the western U.S. [20,21,44,45], we suggest that a greater proportion of the aboveground forest may be converted to PyC. Although it has been suggested the PyC produced during a fire may be consumed in subsequent fires [46], recent studies have found limited PyC consumption in subsequent fires [47,48]. Thus, the effects of climate change on fire regimes may lead to increased PyC stocks produced in each forest fire. However, decreases or no change in fire severity in response to climate change may also occur, depending on forest biome [49]. Our results suggest that PyC may decrease C flux from soils, and that this effect is influenced by the concentration of PyC in soil. High concentrations of wildfire PyC that become incorporated into the mineral soil over the longer term after fire may actually decrease C flux from the soil to the atmosphere. We note that vegetation recovery also has an important influence on post-fire C dynamics [50,51], and is not addressed by our study.

5. Conclusions

Our data showed that differences in wildfire PyC source material and concentration in soil influence post-fire nutrient dynamics. The availability of wildfire fuels across broad geographical regions is predicted to increase due to greater frequency of droughts [2]. Wider ranges in types of wildfire fuels may lead to greater variation in PyC characteristics produced during wildfire, as more types of forest fuels will be available for combustion and pyrolysis. Our study indicates that wildfire PyC produced from different tissues of a single tree species causes significant variation in nutrient dynamics in soil. It is likely that there is even greater variation in PyC produced from different tree and understory species in mixed-species or multi-age forests. Therefore, an understanding of how PyC differs by species and source material type is necessary to elucidate how variability in wildfire PyC affects post-fire nutrient dynamics. Our study provides support for addressing the contributions of particular types and

concentrations of PyC added to soils from wildfires in order to accurately understand the impact of wildfire on post-fire forest C budgets.

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Author Contributions

Lucas A. Michelotti developed the research design, collected the data, and led the interpretation of the results, figure generation, and manuscript writing. Jessica R. Miesel provided assistance with the research design, data collection and interpretation, and writing.

Conflicts of Interest

The authors declare no conflict of interest.

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