Function of Wildfire-Deposited Pyrogenic Carbon in Terrestrial Ecosystems

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Fire is an important driver of change in most forest, savannah, and prairie ecosystems and fire-altered organic matter, or pyrogenic carbon (PyC), conveys numerous functions in soils of fire-maintained terrestrial ecosystems. Although an exceptional number of recent review articles and books have addressed agricultural soil application of charcoal or biochar, few reviews have addressed the functional role of naturally formed PyC in fire-maintained ecosystems. Recent advances in molecular spectroscopic techniques have helped strengthen our understanding of PyC as a ubiquitous, complex material that is capable of altering soil chemical, physical, and biological properties and processes. The uniquely recalcitrant nature of PyC in soils is partly a result of its stable $C = C$ double-bonded, graphene-like structure and C-rich, N-poor composition. This attribute allows it to persist in soils for hundreds to thousands of years and represent net ecosystem C sequestration in fire-maintained ecosystems. The rapid formation of PyC during wildfire or anthropogenic fire events short-circuits the normally tortuous pathway of recalcitrant soil C formation. Existing literature also suggests that PyC provides an essential role in the cycling of certain nutrients, greatly extending the timeframe by which fires influence soil processes and facilitating recovery in ecosystems where organic matter inputs are low and post-fire surface soil bacterial and fungal activity is reduced. The high surface area of PyC allows for the adsorption a broad spectrum of organic compounds that directly or indirectly influence microbial processes after fire events. Adsorption capacity and microsite conditions created by PyC yields a "charosphere" effect in soil with heightened microbial activity in the vicinity of PyC. In this mini-review, we explore the function of PyC in natural and semi-natural settings, provide a mechanistic approach to understanding these functions, and examine examples of such mechanisms in published literature.

Keywords: black carbon, charcoal, carbon sequestration, surface adsorption, sorption, nutrient cycling, soil organic matter, bioactive zones

INTRODUCTION

In recent years, naturally occurring and anthropogenic pyrogenic carbon (PyC) in the environment have become a prominent area of research across scientific disciplines (Zhu et al., 2005; Hammes et al., 2007; Ding et al., 2014; Lehmann and Joseph, 2015; Alam et al., 2016), and yet, to date, there has been little effort to provide a broad ranging synthesis of this unique material that transcends individual disciplines and ecosystems (Sohi et al., 2010; Hart and Luckai, 2013). An increased

emphasis on the importance of PyC in the global carbon (C) cycle and as an amendment for agricultural soils has resulted in a rapid increase in the number of studies across managed, semi-natural, and natural environmental conditions affording a multi-disciplinary framework for improving our mechanistic understanding of PyC (Barrow, 2012; Santín et al., 2015; Dietrich et al., 2017). Applications of molecular spectroscopic analyses to PyC studies in natural environments complement the absolute quantification of PyC and any known information on molecular changes associated with wood pyrolysis (Nishimiya et al., 1998), transport and oxidation of PyC particles (Hockaday et al., 2006; Cheng et al., 2008; Inoue et al., 2017), change in soil organic matter quality due to wildfires (Miesel et al., 2015), and interactions of PyC surfaces with the surrounding soil environment (Archanjo et al., 2017). In this review, we describe these potential functions and explore the mechanisms underlying PyC functionality in natural and semi-natural environments for the advancement of multi-disciplinary research endeavors (see **Figure 1**).

BELOWGROUND SEQUESTRATION OF RECALCITRANT CARBON

Pyrogenic C is a high-C and low-nitrogen (N) byproduct of organic matter pyrolysis or incomplete combustion. The residual material consists of aromatic C rings, aliphatic C chains, and a variety of surface pores and cracks (Preston and Schmidt, 2006). Generally, the PyC material found in nature is less graphitic and more amorphous constituent of the black C continuum model (Hedges et al., 2000) which lends physical and chemical properties that convey unique functions in the soil environment.

The production of PyC by wildfires and anthropogenic fires directly adds highly recalcitrant C into soils, sediments, and aquatic systems in contrast to the tortuous pathway for formation of soil humic materials (**Figure 1**). Estimates of PyC persistence in soils and sediments range from hundreds to thousands of years (Meyer et al., 1995; Gavin et al., 2003; Laird et al., 2008; Liang et al., 2008), which provides evidence of wildfires in fossilized PyC from pre-Quaternary periods in the Earth's history (Scott, 2000). Accounting for PyC after fire events is an important aspect of quantifying the impact of fire on the global C cycle in contrasting C storage as PyC versus C loss as CO_2, CO, and CH_4 during combustion events (Ciais et al., 2013). Empirical measurements of PyC in the surface and sub-surface soils reported in over 500 studies suggest that PyC ranges from 0 to 60% of soil organic matter across forests, agriculture soils, grasslands, peat, and urban soils (Reisser et al., 2016) and yet no standard method exists to quantify PyC in soils. There are numerous PyC quantification methods commonly utilized in soils and sediments that rely on physical separation, chemical and
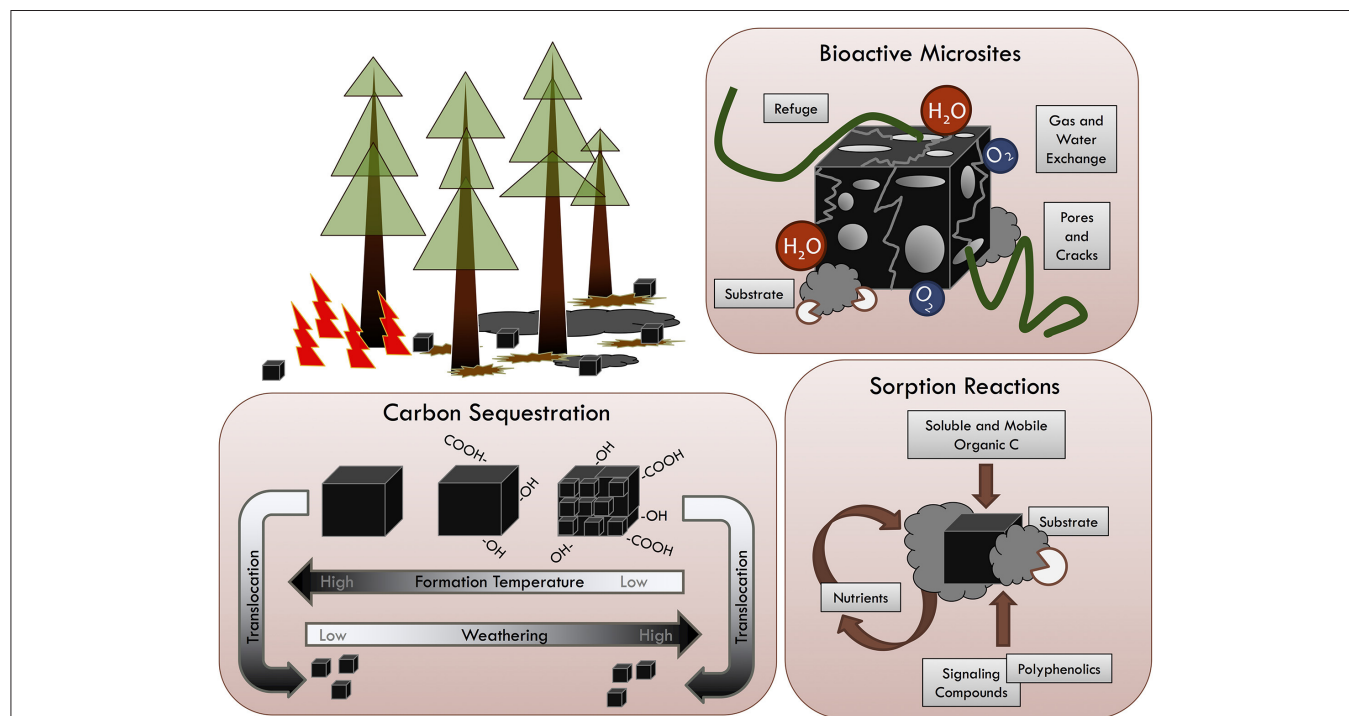
FIGURE 1 | Pyrogenic carbon (PyC) provides three primary mechanistic functions in forest soils after organic carbon (C) from aboveground vegetation is redistributed as highly recalcitrant, belowground Pyrogenic C via fire-driven pyrolysis and combustion. The sequestration of C, in the form of PyC is largely driven by formation temperature and subsequent weathering (mean annual temperature and precipitation) as PyC particles oxidize, increase in oxygen and hydrogen functional groups, and are physically disintegrated and translocated over time. As a component of mineral soils, PyC can act as a sorbent of soluble and mobile organic C, nutrients, polyphenolics, plant signaling compounds, and provide substrate for microorganisms. Lastly, PyC in soils may provide bioactive zones with various pores, cracks, and physical refuge for organisms, as well as facilitate gas, water, and nutrient exchange with surrounding mineral soil.

thermal oxidation, spectroscopy, and molecular identification (Mikutta et al., 2005; Rovira and Ramón Vallejo, 2007; Koide et al., 2011; Bird, 2015). While some methods use molecular identification of the unique PyC structure to separate PyC from humic compounds, others rely on comparisons between burned and unburned soils and are limited to a broader definition of PyC (Hedges et al., 2000).

Studies using the weak nitric acid-peroxide digestion method (Kurth et al., 2006), which quantifies chemically recalcitrant C in mineral soils, have reported PyC accounting for 3–25% (with an average of 13%) of soil C (Kurth et al., 2006; Bélanger and Pinno, 2008; MacKenzie et al., 2008; Licata and Sanford, 2012; Pingree et al., 2012; Buma et al., 2014; Soucémarianadin et al., 2014). Where unburned or pre-wildfire sites were measured in concurrence with wildfire-burned sites, PyC fractions accounted for 8% of total ecosystem C in a low fire frequency, high fire intensity subalpine forest (Buma et al., 2014), and 25% of total ecosystem C in a moderate fire frequency, moderate fire intensity temperate forest (Pingree et al., 2012). The PyC on standing boles represents an additional long-term input of PyC into soil as charred bark sloughs onto the forest floor and standing snags fall to the ground (Makoto et al., 2012; Buma et al., 2014). Wildfire-burned standing snags in the Alaskan boreal, USA, accounted for 65–248 kg charcoal ha^{-1} (if charcoal C is assumed 50% C, 33–124 kg C ha^{-1}) in a beetle-killed *Picea glauca* forest (Makoto et al., 2012). Most wildfire events are likely to increase PyC storage and PyC as a component of total ecosystem C; however, wildfires may consume PyC remaining on the forest floor from prior wildfire events (Zackrisson et al., 1996; Tinkham et al., 2016).

The resistance of PyC to chemical and biological oxidation can largely be attributed to its stacked aromatic C structure (Pierson, 1993; Cohen-Ofri et al., 2006; Ascough et al., 2011). Short and strong sigma (σ) bonds create one plane of hexagonal C while the fourth valence electron (orthogonal to the σ bonds) forms longer and weaker van der Waals bonds (π) with other hybridized electrons above and below the hexagonal plane (Pierson, 1993; Kleber et al., 2015). The result is a layered, alternating hexagonal structure unique to C.

Oxidation of PyC has been attributed to both the intrinsic structure of PyC material and environmental gradients. Temperature-dependent recalcitrance has been indirectly suggested by several laboratory incubation studies that showed reduced C mineralization in the presence of PyC produced at high temperatures (Baldock and Smernik, 2002; Bruun et al., 2008; Zimmerman, 2010; Hanan et al., 2016). These studies were unable to distinguish the effects of inherent recalcitrance from adsorption to PyC surfaces, which may concurrently reduce available C by adsorption (see next section). Long-term storage of PyC in soils and PyC elemental composition was shown to be influenced by climate variables (precipitation and temperature), which had a greater influence compared to soil characteristics (soil texture, cation exchange capacity, pH), with mean annual temperature being the best predictor of PyC oxidation (Glaser and Amelung, 2003; Cheng et al., 2008). Aged PyC particles showed slightly lower aromaticity and released larger and more aromatic clusters into solution or as colloids,

which suggests oxidation over a 10-year study period (Schneider et al., 2010). Similarly, many studies showed aged PyC particles decrease in C concentration and an increase in functional groups relative to fresh PyC (Hockaday et al., 2007; Cheng et al., 2008; Nguyen et al., 2008; Ascough et al., 2011; Singh et al., 2012), which possibly resulted from environmental weathering, microbial decomposition (Hockaday et al., 2006, 2007), or faunal bioturbation (Domene, 2016). PyC particles have been shown to decrease in specific surface area over time (Hockaday et al., 2007), although the physical fragmentation of larger particles may ultimately increase total surface areas in soil. Preferential mobilization of PyC particles has received little attention, but a recent study suggests that more highly condensed PyC may be more readily physically degraded in soils due to its physically less stable structure, leaving behind a more biologically available PyC (Inoue et al., 2017).

SORPTION INTERACTIONS

The ability for PyC particles to adsorb non-polar organic compounds lends to its function as a surface adsorption foci in soils, sediments, and solutions (**Figure 1**). This mechanism has wide ranging implications for how PyC influences myriad soil processes (Cornelissen and Gustafsson, 2004; Keech et al., 2005; Bornemann et al., 2007; Pingree et al., 2016). First, and perhaps the most obvious, is that most all soluble and mobile organic compounds in soil represent an energy source for microbes. Surface adsorption to PyC particles would concentrate organic compounds around PyC particles, thereby creating a microsite for enhanced microbial activity (Lehmann et al., 2011). Increased decomposition of C adsorbed to PyC may partially account for observations including priming effects (Hamer et al., 2004; Jones et al., 2011), an increase in the nutrient release from mineral precipitates and cation exchange sites, or increased immobilization of inorganic nutrients near PyC particles. Contrasting findings of N mineralization and N immobilization rates (see DeLuca et al., 2015) are likely related to the capacity of PyC to adsorb nutrients and organic compounds. Finally, adsorption of polyphenolic signaling compounds within the rhizosphere could influence plant pathogenic or symbiotic interactions, but to date there has been limited effort to evaluate this in natural ecosystems (Hassan and Mathesius, 2012; Hall et al., 2014; Kolton et al., 2017).

Adsorption capacity is predominantly driven by the specific surface area and pore-size distribution of PyC particles, which are determined by pyrolysis temperature and the innate chemical nature of the feedstock. As formation temperature increases and pyrolysis or combustion takes place, adsorption capacity typically increases exponentially (Zhu et al., 2005; Brimmer, 2006; Bornemann et al., 2007; Pingree et al., 2016), while pore sizes become dominated by micropores (<2 nm) (Braida et al., 2003; Bornemann et al., 2007). Wood-based PyC contains extensive porosity partly due to the partial pyrolysis of tracheid cells associated with xylem, which contributes further to the natural porosity of PyC made from wood (Keech et al., 2005). Sorption behavior as a function of formation temperature is well-documented in the laboratory (Bornemann et al., 2007),

but is likely altered by exposure to environmental influences. Direct measurements of adsorption capacity in soils show a more complicated and less predictable relationship between PyC as an adsorbent and naturally-occurring adsorbate compounds (Cornelissen and Gustafsson, 2004; Pingree et al., 2016). Terrestrial and aquatic ecosystems provide complex matrices for sorption interactions that merit a better understanding of sorption interactions in relation to surface properties of PyC.

The adsorption capacity of PyC as charcoal particles may have a significant effect on N cycling in post-fire forest soils. Previous studies of temperate and boreal forest soils have shown an increase net mineralization of N and in net nitrification with the addition of charcoal through the production of nitrate (NO_3^--N), which otherwise show minimal net nitrification (DeLuca et al., 2002, 2006; MacKenzie and DeLuca, 2006; Ball et al., 2010; Kurth et al., 2014; Michelotti and Miesel, 2015). There are multiple mechanisms that may be responsible for this observed increase in NO_3^--N after the addition of charcoal to soil. The presence of PyC may release nitrifier activity by adsorption of allelopathic C compounds which results in a total reduction of nitrification potential (Paavolainen et al., 1998; MacKenzie and DeLuca, 2006; Uusitalo et al., 2008). The presence of heterocyclic C compounds may provide a source of organic C that results in net immobilization of NH_4^+ (Bremner and McCarty, 1988). In addition, the presence of charcoal may reduce the complexation of high molecular weight compounds and indirectly alter the N and C cycles of soils via complexation of NH_4^+ and amines by polyphenolics that may eliminate NH_4^+ availability for nitrification (Hättenschwiler and Vitousek, 2000). In wildfire-burned chaparral forest soils, the addition of PyC had no significant effect on N dynamics after an incubation study, but instead may have promoted N immobilization by enhancing microbial biomass (Hanan et al., 2016). Alternatively, the surface adsorption of NH_4^+ by PyC could also reduce availability for autotrophic oxidation by nitrifying bacteria—a mechanism yet to be evaluated in PyC and soil N dynamics.

The release and reception of molecular signaling compounds is known to directly influence both symbiotic and pathogenic relationships in soils. Both mycorrhizal infection of host plants and nodule establishment in legumes is thought to be dependent upon the release and reception of signaling compounds, which are generally flavonoids or related polyphenolic compounds (Hassan and Mathesius, 2012). It is well-understood that PyC has the capacity to adsorb such compounds (Zackrisson et al., 1996; DeLuca et al., 2002; Keech et al., 2005), but the direct connection between PyC and signaling effectiveness has, to date, been largely ignored. Biochar-induced ethylene production, a plant hormone and soil microbial inhibitor, has been found in some PyC materials although most notably from non-woody sources (Spokas et al., 2010). Legume nodulation has been observed to both increase and decrease in the presence of biochar applications to surface soils, but more often wood charcoal has increased nodulation or N_2 fixation in legumes (see DeLuca et al., 2015). Further, numerous studies have demonstrated an increase in mycorrhizal infection rates in the presence of wood char (Thies et al., 2015). However, there has been no strenuous effort to date to evaluate the influence of PyC on signaling-mediated processes in natural forest or prairie ecosystems.

MICROSITE EFFECTS

The presence of PyC in soils may also serve an important function by creating bioactive zones through the addition of a heterogeneous environment facilitated by the particulate and porous nature of PyC particles, which provides nutrients, organic matter, water availability, and refuge for some organisms (**Figure 1**). Pyrogenic C particles have been cited as creating a novel substrate for microbial growth and as physical habitat for microbes (Pietikäinen et al., 2000; Quilliam et al., 2013; Thies et al., 2015), which may aid in the recovery of surface soils exposed to wildfires or intense prescribed fires. PyC microsites are likely to elicit diverse interactions with surrounding biotic and abiotic constituents in soils as they are most likely to affect plant-microbe-soil interactions in the "charosphere," the soil immediately surrounding a PyC particle (Quilliam et al., 2013).

Surface heterogeneity in naturally-produced PyC particles can further increase soil microorganism activity and abundance via adsorption of compounds utilized as substrate and physical microsites for the exchange of water and gas that may influence redox conditions. While these mechanisms have been evaluated in biochar studies wherein strict pyrolysis conditions and a narrow selection of feedstock were applied to agriculture soils, they have rarely been investigated in natural soils (Briones, 2012; Joseph et al., 2013). Evidence of microbial substrate utilization of adsorbed compounds on PyC surfaces is limited outside of biochar applications, but suggests that surface sorption may play an important role in providing microorganisms with nutrients and C compounds for metabolic oxidation as well as altering the microbial community (Zackrisson et al., 1996; Singh et al., 2014; Kolton et al., 2017). Negative C mineralization priming in high-temperature-produced biochar treatments may be related to the adsorption of C substrate (Zimmerman et al., 2011). Additionally, the similarity of dissolved organic matter released by aged PyC particles to products of polycyclic aromatic hydrocarbon biological decomposition suggests microbial oxidation of PyC (Hockaday et al., 2006, 2007). Enzymatic oxidation of aromatic C structures in lignin, humic acids, and coal are documented and utilized in the bioenergy industry (see review by Fakoussa and Hofrichter, 1999), but have yet to be explored in microbial decomposition of naturally-produced PyC in soils where regular fire events are likely to sustain the activity of microbial populations responsible for such processes. Studies of ^{14}C labeled biochar mineralization clearly show that PyC is not resistant to microbial decomposition, however, the interactions between adsorbed substrate utilization and enzymatic oxidation of PyC remain poorly understood (Hamer et al., 2004; Bruun et al., 2008; Kuzyakov et al., 2009; Jones et al., 2011; Quilliam et al., 2013; Maestrini et al., 2014).

There are numerous examples of microbial hyphae habitation of internal and external PyC surfaces via pore infiltration. Wildfire-produced PyC exposed to weathering in forest soils over many decades is often physically inhabited by fine roots, filamentous microorganisms, and coated by minerals compared to recently formed PyC (Zackrisson et al., 1996; Hockaday et al., 2007). Internal and external pores on PyC particles

have often been cited as providing the potential for microbial habitation as refuge from predators, increasing water holding capacity, providing gas exchange, and increasing redox potential (Lehmann et al., 2011; Thies et al., 2015). However, no quantitative efforts have been undertaken to directly connect microbial abundance, activity, or composition with pore size and distribution of wildfire-deposited PyC particles. Further, PyC and its pore distribution is not a static entity, but an attribute that changes with the numerous physical disturbances presented in terrestrial environment. Subsequent wildfires may further pyrolyze PyC and physical processes of freezing and thawing, wetting and drying, wind abrasion, or bioturbation all may lead to partial disintegration of PyC thereby exposing internal surfaces or degrading small pores (Gao et al., 2017). Additionally, the incorporation of PyC bark from tree boles can provide a delayed input of PyC onto soil surfaces that may exhibit larger pore sizes after prolonged physical weathering (Makoto et al., 2012; Gao et al., 2017).

FUTURE RESEARCH DIRECTIONS

The historical occurrence of wildfires and anthropogenic fires has yielded a rich *ex post facto* experimental design of varied length that allows us to evaluate both the recalcitrance of PyC as well as the functional properties of PyC in terrestrial ecosystems. Knowledge gained from these studies can be used to help elucidate the long-term fate and function of biochar in agricultural soils, which is otherwise limited to "long-term" studies of 10 years or less. Interest in PyC for its role in C storage has also created a foundation for C accounting in isolated studies; however, studies lack the use of systematic, consistent approaches to PyC quantification in post-fire surveys that could provide vital information in a thorough understanding the global C cycle (Parson et al., 2010; Santín et al., 2015). Combining fire ecology, fire science, and PyC research has the potential to directly link wildfire and prescribed fire conditions (such as temperature, duration, fuel load, etc.) to PyC production and characteristics to achieve a better understanding of how fires alter C dynamics and plant-soil-microbe relationships through the deposition of PyC. Studies of PyC occupy a unique place in science as a focal point in paleobotany, paleoecology, archeology, agriculture, and ecological research for decades, which collectively lend to a multi-disciplinary research potential that may lead to a broadened understanding of fire ecology and the role of PyC in ecosystem diversity and function.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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