



## Tree taxa and pyrolysis temperature interact to control pyrogenic organic matter induced native soil organic carbon priming

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### ABSTRACT

Few studies have quantitatively assessed the interacting controls of taxa-specific properties and PyOM production temperature on native soil C (NSC) stabilization/de-stabilization dynamics (i.e. priming effects - PE) because of difficulty in distinctly assessing NSC reactivity apart from added PyOM-C. To quantify PyOM-induced PE, we incubated <sup>13</sup>C-enriched jack pine (JP) or red maple (RM) wood and associated <sup>13</sup>C-PyOM produced at 200 (PyOM200), 300 (PyOM300), 450 (PyOM450) and 600 (PyOM600) °C in soil from a northern temperate forest (Michigan, U.S.A.) for 10 months. We found that (1) net PE was negative with addition of both wood and PyOM from both taxa, with a 3–40% suppression in mineralization across treatments, (2) RM200, RM450, and RM600 exhibited initial positive PE in the first week of incubation, (3) PyOM300 of both taxa, the temperature associated with initial aromatization and carbohydrate conversion, induced the most negative PE and exhibited the largest increase in soil oxidative enzyme activity in JP300, (4) addition of sucrose to the incubations as labile C, offset negative PE in JP treatments but not in RM treatments and, (5) mean residence times of the fast cycling C pool of NSC were lower (1.4–1.6 d) for RM than for JP (2.9–8.3 d) additions. These results suggest that future changes in tree taxa dominance in fire prone systems could alter soil C stability through introduction of PyOM of distinct, taxa-specific, chemical properties that may be largely controlled by taxa specific temperature thresholds in thermochemical conversion of woody tissues to PyOM.

### 1. Introduction

Fire is an important controller of C and N cycling in terrestrial ecosystems (Bowman et al., 2009, 2013; Landry et al., 2015; Weise et al., 2015) and can affect global and regional C cycling via direct emissions of combustion products, e.g. gases, aerosols and pyrogenic organic matter (PyOM) (Sommers et al., 2014), and indirectly via PyOM deposition (de Groot et al., 2013a, 2013b; Santín et al., 2015) to soil resulting in changes to soil biogeochemical processes (Maestrini et al., 2014; Singh et al., 2014). Fire is also a major ecosystem disturbance and can temporarily shift a forest from being a net C sink to a large source of CO<sub>2</sub> and aerosols to the atmosphere thus impacting global greenhouse gas and radiative budgets (IPCC, 2013). As fire frequency and intensity are projected to increase with future climate change, increased PyOM

production may significantly impact forest C cycling in fire-prone boreal and temperate ecosystems (IPCC, 2013; Reich et al., 2015; Santín et al., 2015). A knowledge gap exists in how the introduction of PyOM to soil alters soil organic carbon (SOC) dynamics (Tammeorg et al., 2016). PyOM contributes on average between ~10 and 20% of SOC (Baldock and Smernik, 2002; Singh et al., 2012), and as a result, the effects of changes in PyOM production on SOC dynamics could have important implications on regional and global C cycling.

The persistence of PyOM in soil is well documented (Lehmann et al., 2015) with estimated centennial and even millennial mean residence times (MRTs) reported (Fang et al., 2014; Singh et al., 2012). The stability of PyOM in soil is in sharp contrast to nearly all chemical components of the un-altered plant parent materials (Schmidt et al., 2011) and, as such, its presence in soil is thought to be important for long-

**Abbreviations:** <sup>13</sup>C DPMAS NMR, <sup>13</sup>C Direct polarization magic angle spinning nuclear magnetic resonance spectroscopy; (DOC), Dissolved organic carbon; (JP), Jack pine; (NOA), Normalized oxidative enzyme activity; (MRT), Mean residence time; (NSC), Native soil carbon; (PE), Priming effect; (PYOM), Pyrogenic organic matter; (RM), Red maple

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term soil organic C stabilization (Bird et al., 1999; Hernandez-Soriano et al., 2015; Kerré et al., 2016). However, the impact of PyOM on soil is not merely limited to an increase in the proportion of long MRT C, as there are a myriad of PyOM-related properties and processes that may act to stabilize and destabilize SOC (Maestrini et al., 2015; Wang et al., 2015a,b; Weng et al., 2017; Wang et al., 2017).

PyOM can influence soil chemical properties such as pH and CEC (Laird et al., 2010), it can alter microbial community activity and composition (Gibson et al., 2016; Gomez et al., 2014; Santos et al., 2012), and it can influence the rate of native soil C (NSC) decomposition (Maestrini et al., 2015; Wang et al., 2015a,b). One of the primary influences of PyOM on soil C reservoirs, other than its direct addition to soil C stocks, is its potential to change the rate of microbial NSC decomposition (i.e. priming). An observed positive PE after PyOM addition to soil often occurs at the onset of an incubation experiment (< 20 days) (Maestrini et al., 2015; Wang et al., 2015a,b). Positive PEs have been attributed to the co-metabolism of NSC and labile PyOM-C fractions. Similar increases in NSC mineralization rates have been observed after the simultaneous addition of PyOM and additional labile C sources such as low molecular weight (LMW) compounds (non-lignin phenols, glucose, or sucrose), which can be released via root exudation or added to laboratory incubations (Wang et al., 2016; Zimmerman et al., 2011). Changes in substrate preferences have also been suggested as a mechanism driving positive PE (Farrell et al., 2013; Thies et al., 2015). A negative PE typically occurs after a positive priming phase; the pattern most commonly reported in long-term incubations (~ > 200 days) (Maestrini et al., 2015). Proposed mechanisms for a negative PE after PyOM addition include the leaching of compounds from PyOM that inhibit microbial activity (Smith et al., 2012; Uchimiya et al., 2015) as well as the strong surface sorption of microbial signaling compounds (Masiello et al., 2013), extracellular enzymes (Lammirato et al., 2011, 2011), or labile NSC compounds (Kasozzi et al., 2010; Keith et al., 2011). Additional negative PE could be facilitated by greater physical protection of NSC that results from increased soil aggregation after PyOM addition (Sun and Lu, 2014). While efforts have been made to elucidate the net effects of PyOM on NSC, a consensus has yet to be reached as there are multiple interacting controls including PyOM source and production temperature, soil properties, PyOM C loading rates, and incubation duration and conditions (Maestrini et al., 2015; Wang et al., 2015a,b). Furthermore, there have been even fewer efforts to observe a NSC PE in field studies due to the difficulty in measuring root production vs PyOM induced priming (Maestrini et al., 2015; Singh et al., 2014; Wang et al., 2015a,b; Wang et al., 2017; Whitman et al., 2015).

Among plant taxa in fire-prone environments the structure and chemical composition of plant tissue can vary extensively; compounds exhibiting a broad range of lability in soil (Pereira et al., 2011) including extractable sugars, lignins, non-lignin phenols, and non-polar extractives (Hatton et al., 2016; Kaal et al., 2012; Pereira et al., 2011) vary in concentration and presence in PyOM sources. The initial plant chemistry is only marginally altered at pyrolysis temperatures < 300 °C (Hatton et al., 2016) and thus PyOM produced at low temperatures may impart similar effects on the microbial communities as the original plant tissues. For example, grass-derived PyOM has been shown to be more labile than wood-derived PyOM at the same production temperature. This has been attributed to residual grass chemistry being higher in oxygenated functional groups and lower in condensed lignin and tannins than woody tissue (Ippolito et al., 2015; Pereira et al., 2011; Pignatello et al., 2015). Consequently, grass-derived PyOM more consistently promotes positive NSC priming compared with wood-derived PyOM, particularly at > 300 °C (Whitman et al., 2015; Zimmerman et al., 2011). Initial biomass physicochemistry may be especially relevant in ecosystems that are fire-prone and contain a wide variety of taxa, such as woodland-grassland boundaries (Archer et al., 2001) and where ecosystems are shifting in species composition. The high latitude forests of North America represent a particularly relevant case as red maple is gaining in dominance over pine varieties while the

system is simultaneously experiencing increased pressure from forest fires (Reich et al., 2015).

At high PyOM production temperatures, e.g., > 500 °C, many physicochemical characteristics of initial biomass that affect C cycling are diminished as pyrolysis temperatures > 400 °C cause chemistry (Kleber et al., 2015), surface area, and internal pore structure (Chia et al., 2015) of PyOM to converge (Hatton et al., 2016). The physical characteristics of high temperature PyOM (> 500 °C) promote the surface sorption of dissolved soil organics and facilitate aggregate formation, thus reducing NSC accessibility to microbes and leading to negative PE on NSC (Whitman et al., 2015). PyOM produced at low and intermediate pyrolysis temperatures (~ 100–400 °C) is expected then to retain many of the initial source biomass properties but exhibit transitional temperatures, which may differ among taxa where chemical and physical changes dramatically alter PyOM-NSC interaction (Hatton et al., 2016; Keiluweit et al., 2010). Such temperature thresholds help to explain recent studies reporting that NSC priming response among taxa does not co-vary with pyrolysis temperature (Wang et al., 2015a,b).

The purpose of this study was to investigate the potentially interactive effects of PyOM tree taxa source and pyrolysis temperature as controls on NSC PE in a fire-prone temperate forest soil from northern Michigan, USA. To quantitatively differentiate between mineralized C, measured as CO<sub>2</sub>, derived from NSC or added PyOM (as well as source wood), we produced PyOM from artificially <sup>13</sup>C-enriched red maple (RM) and jack pine (JP) wood (Hatton et al., 2016). These substrates were then added to forest soil of natural <sup>13</sup>C abundance in a 300 d laboratory incubation. The RM or JP wood as well as the PyOM, produced by pyrolyzing RM and JP wood at 200, 300, 450, or 600 °C, were previously characterized (Hatton et al., 2016) for physical (skeletal density, envelope density, porosity, surface area, and thermal stability) and chemical (elemental, isotopic, molecular and supramolecular) properties to assess how production temperature altered the properties of the PyOM for each taxa. We hypothesized that: (1) in the sandy soil investigated, the introduction of both RM and JP wood and PyOM will result in a positive NSC PE for wood and low temperature (< 300 °C) PyOM, but a neutral to negative PE for the higher temperature (> 450 °C) PyOM, (2) the difference in the magnitude of the PE between RM and JP will decrease with increasing pyrolysis temperature as the physicochemical properties of the PyOM become more similar, but temperatures reflective of significant thermally-induced physicochemical transitions will show distinct PE attributes, and (3) the presence of an additional labile C source, in the form of sucrose, will promote a comparatively greater suppression of the NSC PE for JP treatments versus RM, as JP is significantly depleted in labile sugars with respect to RM and soil microbes are expected to shift substrate metabolism to the labile sucrose.

## 2. Materials and methods

### 2.1. <sup>13</sup>C-enriched PyOM and source wood production

Understory plants are the most susceptible to PyOM formation in a wildfire and as such saplings were chosen to be representative of the woody PyOM formed (Santín et al., 2015; Hatton et al., 2016). We produced highly enriched (<sup>13</sup>C) stems from the saplings of two tree species, jack pine (*Pinus baksiana*, hereafter reported as JP) and red maple (*Acer rubrum*, hereafter reported as RM), commonly found in both northern temperate and boreal forests according to Bird and Torn (2006). Briefly, we grew 1-yr-old JP saplings (30–40 cm height; Itasca Greenhouse Inc, Cohasset, MN) and 2-yr-old RM saplings (30–60 cm height; Cold Stream Farms, Freesoil, MI) in an inorganic soil matrix consisting of washed sand and fritted clay under <sup>13</sup>CO<sub>2</sub> (25 atom% <sup>13</sup>C) (Bird and Torn, 2006). Dried stems from JP and RM saplings at 25 °C and cut into 1–2 cm pieces before being pyrolyzed (in the absence of oxygen) under a stream of N<sub>2</sub> for 5 h as described by Hammes et al. (2006) at 200, 300, 450 and 600 °C. The resulting PyOM material and

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