
RESEARCH REVIEW

Towards a global assessment of pyrogenic carbon from vegetation fires

CRISTINA SANTÍN, STEFAN H. DOERR, EVAN S. KANE, CAROLINE A. MASIELLO, MIKAEL OHLSON, JOSE MARIA DE LA ROSA, CAROLINE M. PRESTON and THORSTEN DITTMAR

1Department of Geography, College of Science, Swansea University, Singleton Park, Swansea SA2 8PP, UK, 2School of Forest Resources and Environmental Science, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA, 3Departments of Earth Science, BioSciences, and Chemistry, MS 126, Rice University, 6100 Main St, Houghton, TX 77005, USA, 4Departments of Ecology and Natural Resource Management, Norwegian University of Life Sciences, PO Box 5003, NO-1432 As, Norway, 5Institute of Natural Resources and Agrobiology of Seville (IRNAS), CSIC, Reina Mercedes Av. 10, 41012 Seville, Spain, 6Pacific Forestry Centre of Natural Resources Canada, 506 W. Burnside Rd., Victoria BC V8Z 1M5, Canada, 7Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Carl-von-Ossietzky-Str. 9–11, 26129 Oldenburg, Germany

Abstract

The production of pyrogenic carbon (PyC; a continuum of organic carbon (C) ranging from partially charred biomass and charcoal to soot) is a widely acknowledged C sink, with the latest estimates indicating that ~50% of the PyC produced by vegetation fires potentially sequesters C over centuries. Nevertheless, the quantitative importance of PyC in the global C balance remains contentious, and therefore, PyC is rarely considered in global C cycle and climate studies. Here we examine the robustness of existing evidence and identify the main research gaps in the production, fluxes and fate of PyC from vegetation fires. Much of the previous work on PyC production has focused on selected components of total PyC generated in vegetation fires, likely leading to underestimates. We suggest that global PyC production could be in the range of 116–385 Tg C yr⁻¹, that is ~0.2–0.6% of the annual terrestrial net primary production. According to our estimations, atmospheric emissions of soot/black C might be a smaller fraction of total PyC (<2%) than previously reported. Research on the fate of PyC in the environment has mainly focused on its degradation pathways, and its accumulation and resilience either in situ (surface soils) or in ultimate sinks (marine sediments). Off-site transport, transformation and PyC storage in intermediate pools are often overlooked, which could explain the fate of a substantial fraction of the PyC mobilized annually. We propose new research directions addressing gaps in the global PyC cycle to fully understand the importance of the products of burning in global C cycle dynamics.

Keywords: biochar, black carbon, carbon accounting, carbon emissions, carbon sequestration, charcoal, dissolved organic carbon, erosion, pyrogenic organic matter, wildfire

Received 23 February 2015; revised version received 14 May 2015 and accepted 18 May 2015

Introduction

Vegetation fires affect 300–460 Mha globally per year (Randerson et al., 2012; Giglio et al., 2013), emitting 1.6–2.8 Gt carbon (C) to the atmosphere, the equivalent of 25–30% of the current annual C emissions from fossil fuel consumption (Van Der Werf et al., 2010; Boden et al., 2012). Over the longer term (i.e. decades), however, vegetation fires are widely considered as ‘net zero C emission events’ because C emissions from fires are balanced by C uptake by regenerating vegetation (excluding deforestation and peatland fires) (Bowman et al., 2009; Van Der Werf et al., 2010). This zero C emission scenario is potentially flawed, however, as it does not consider the role of pyrogenic C (PyC; Fig. 1).

Incomplete combustion during fires transforms part of the fuel C into PyC. The high diversity of fuel materials as well as the wide range of combustion conditions, especially in vegetation fires, do not allow PyC to be defined as a distinct chemical component, but instead as the organic C fraction of the whole range of pyrogenic organic materials from partially charred vegetal biomass and charcoal to soot (Goldberg, 1985; Schmidt & Noack, 2000). PyC is therefore not a homogenous organic C pool, but includes a broad continuum ranging from biolabile depolymerization products to highly resistant condensation products. Charring mainly induces condensation reactions, with the resulting
polycyclic aromatic structures providing increased resistance against degradation. However, under low charring temperatures (~< 250 °C), depolymerization and dehydration of part of the biomass also occurs, which makes some of the PyC highly water soluble and biodegradable (Norwood et al., 2013; Myers-Pigg et al., 2015).

Overall, the pyrogenic process mostly confers the charred materials a longer mean residence time in the environment compared to their unburnt precursors (Schmidt et al., 2011; DeLuca & Boisvenue, 2012; Singh et al., 2014; Naisse et al., 2015a). Therefore, a large fraction of the PyC continuum can be considered a C sink on a decadal/centennial timescale (Fig. 1) (Bird et al., 2015). The enhanced resistance of PyC to degradation, for example, underpins the production of biochar (PyC intentionally produced for soil amendment) and its addition to soils as one of the most viable global approaches in offsetting C emissions to the atmosphere (Woolf et al., 2010; Jeffery et al., 2015). However, PyC produced naturally in vegetation fires is usually not considered in C budget and global warming investigations (Lehmann et al., 2008; Le Quere et al., 2009), and the net role of PyC in the global C cycle is thus not well elucidated. The main reason for this is the lack of robust knowledge on PyC production and degradation, fluxes and residence time in the environment (Masiello, 2004; DeLuca & Aplet, 2008; Schmidt et al., 2011). As small changes in C cycle dynamics can have large effects in global climate change scenarios, there is an urgent need for improvement of the representation of the terrestrial C cycle in climate and integrated assessment models (Moss et al., 2010).

In this research review we discuss the identification and quantification of PyC from vegetation fires and review current knowledge and uncertainties on its production, degradation, mobilization and long-term fate in the environment. We provide updated estimates of the current global PyC production, fluxes and pools and highlight the main research gaps in the PyC cycle. This review concludes with suggestions of new research directions aimed at achieving a more complete and integrated understanding of the role of PyC from vegetation fires in the global C cycle.

**PyC identification and quantification**

Identification and quantification of PyC in the different environmental matrixes (soils, sediments, air and waters) are essential for addressing the role of PyC in C budgets. However, these are difficult tasks as PyC is not a distinct chemical component but a continuum of C-rich solid organic materials. This represents a key challenge when studying PyC because the methodology used determines the overall amount and characteristics of the PyC quantified, and yields can also change depending on the environmental matrix the PyC is being isolated from (Schmidt et al., 2001; Hammes et al., 2007; Roth et al., 2012).

A clear definition of the specific window of the PyC continuum that each study addresses is essential to avoid uncertainty when comparing, extrapolating or
scaling up data from individual studies. Some components of the PyC continuum are measured through mutually exclusive techniques. For example, low-temperature pyrolysis can transform cellulose into anhydrosugars (e.g. levoglucosan) which have no aromatic rings, are detected by gas chromatography and can have a very short mean residence time (MRT) (Norwood et al., 2013). Conversely, fire can also produce soot, which is characterized by a stable, condensed and aromatic chemical structure and is typically measured either by nuclear magnetic resonance or by thermal analyses (Hammes et al., 2007). While these two forms of C (anhydrosugars and soot) are produced exclusively by pyrolysis, they have very different environmental pathways and MRTs. Neither can be treated as behaving in a way representative of the entire PyC pool. Currently, no technique representatively captures the entire PyC pool. Therefore, not only methodologies capturing a wide range of the PyC continuum are fundamental (e.g. visual identification, Santín et al., 2015), but also those characterizing specific parts of the PyC continuum are necessary to understand how much of the total PyC is significant as a C sink in the long term (e.g. stable polycyclic aromatic C – SPAC, McBeath et al., 2015).

**PyC production from vegetation fires**

To elucidate the PyC cycle, we need first to know how much is formed during fire. To allow inclusion of PyC production into C emission and budget models, a complete prefire fuel quantification is needed so that PyC production can be reported as a proportion of the fuel affected by fire (Fig. 2). However, comprehensive fuel data are rarely available, particularly for wildfires (Keane, 2012), and assessments often exclude relevant fuel components such as the canopy or woody debris (de Groot et al., 2007; Possell et al., 2015).

A detailed prefire fuel quantification is normally only available for small-scale experimental or prescribed fires (e.g. Alexis et al., 2007), which are usually not representative of wildfire conditions. In the low-intensity burning conditions typical of prescribed fires (Certini, 2005), burning efficiency is generally low, only a small part of the fuel is exposed to thermal degradation, and overall little PyC is produced (Graça et al., 1999; Schmidt & Noack, 2000). In contrast, high-intensity fires have a higher burning efficiency (Campbell et al., 2007) and affect a greater proportion of the fuel available. The degree to which fire intensity translates into complete fuel combustion vs. PyC generation is governed by complex factors related to intrinsic fuel properties (e.g. density and composition), extrinsic fuel properties (e.g. arrangement, moisture and loads) and burning conditions (e.g. fire weather, oxygen availability and burning duration) (Brewer et al., 2013). As a result, PyC produced in low-intensity experimental or prescribed fires may not be representative of PyC produced during the often more intense wildfires.

---

**Fig. 2** Quantification of pyrogenic C produced in a fire with respect to C affected by fire requires: (i) pre- and postfire unburnt fuel estimations and (ii) determination of pyrogenic C emitted to the atmosphere and the remaining in all fuel components (for this example of a forest fire: overstory, understory, down wood, forest floor (or litter) and mineral soil).
In addition to a complete prefire fuel assessment, the whole range of PyC materials generated needs to be considered and quantified (Fig. 2). However, PyC investigations are primarily divided into (i) on-site PyC (i.e. generated and remaining on-site immediately after the fire) and (ii) PyC emitted to the atmosphere within the smoke. To the best of our knowledge, no investigation has fully quantified simultaneously the production of on-site and emitted PyC during fire.

On-site PyC

Much of the PyC generated during a vegetation fire initially remains on-site mainly as PyC within (i) soil; (ii) the ash layer on the ground; and (iii) charred plant tissue (charcoal) on standing vegetation and downed wood (Scott, 2000) (Fig. 2).

(i) PyC in soil: When examining fire effects on soil PyC stocks, it is important to consider that most vegetation fires do not result in temperatures exceeding the minimum temperature required to initiate the charring process a few millimetres below the mineral soil surface (~200 °C; González-Pérez et al., 2004). Therefore, much of the PyC found in fire-affected soils does not originate from in situ pyrolysed soil organic matter, but from PyC produced from the burning of the litter and aboveground vegetation (Bodi et al., 2014; Boot et al., 2015). This PyC can subsequently be incorporated into the soil profile through processes such as bioturbation and freeze-thaw or into newly forming horizons in areas where eroded sediments accumulate (Gavin, 2003; Wilkinson et al., 2009). Notable exceptions are burning of tree roots, organic soils and peats, where smouldering combustion produces PyC in situ at depth (Kane et al., 2010).

Studies investigating soil PyC often address exclusively either visually detectable charcoal or one of the chemically defined PyC components (i.e. quantified through thermal, chemical or spectroscopic techniques), reflecting a research focus, respectively, on either fire history (e.g. Ohlson et al., 2011) or on mineral soil/biogeochemical issues (e.g. Czimczik et al., 2005). Either approach misses part of the soil PyC spectrum. Studies focused on visual identification of charcoal pieces miss the PyC in the finest fraction of the soil, which can contain the largest PyC soil stock (Brodowski et al., 2006). Those quantifying chemically defined PyC in soils usually examine the soil fraction <2 mm and therefore exclude macroscopic charcoal >2 mm, which can account for up to 60–90% of the visually detected charcoal (Ohlson & Tryterud, 2000; Nocentini et al., 2010). This mutual neglect tends not only to underestimate the total amount of PyC, but also to overrepresent specific fractions and their characteristics. For instance, the biggest pieces of PyC are dominated by wood-derived charcoal, while the smaller fractions typically originate from needles, leaves, herbs and organic topsoil material. These fractions differ in their physical and chemical nature. Wood-derived PyC is generally more recalcitrant than the chemically more reactive nonwoody PyC fractions (Hilscher et al., 2009; Nocentini et al., 2010; De la Rosa & Knicker, 2011). They also differ in their mobility and MRTs, with large wood-derived charcoal particles prone to being incorporated into the soil and to persist there for millennia (Gavin, 2003; Ohlson et al., 2009; de Lafontaine & Asselin, 2011; de Lafontaine et al., 2011).

(ii) PyC in the ash layer is rarely considered in PyC inventories (Fig. 3a). A major reason for the neglect of ash is its often rapid redistribution within, and removal from, burnt sites by wind and water erosion, which often occurs before the commencement of postfire field investigations (Cerda & Doerr, 2008; Bodí et al., 2014). Depending on formation conditions, ash can contain substantial amounts of PyC and should be included in PyC inventories (Forbes et al., 2006; Bodí et al., 2014). For example, Santín et al. (2012) estimated that 6–8 t PyC ha\(^{-1}\) was transferred from burnt fuels to the ash layer during the catastrophic 2009 ‘Black Saturday’ wildfires in Australia.

(iii) PyC on standing vegetation and downed wood is another important, although frequently neglected, pool of PyC (Figs 2 and 3b). Tinker & Knight (2000) estimated 6.4 t ha\(^{-1}\) of charcoal produced from coarse woody debris (>7.5 cm diameter) during a crown fire in a conifer forest in western USA. Donato et al. (2009) reported 0.3–0.6 t ha\(^{-1}\) PyC generated from downed wood in a stand-replacing conifer forest fire in north-western USA. Santín et al. (2015) quantified a PyC production of 1.9 ± 0.2 t ha\(^{-1}\) in down wood and 2.5 ± 1.3 t ha\(^{-1}\) in bark of standing trees during a conifer forest fire in the boreal Canada. The importance of these aboveground PyC pools deserves further attention as most PyC compounds originating from woody materials are expected to have long MRTs (Ohlson et al., 2009). Also large woody charcoal pieces may act as slow-release sources of PyC. The location of this woody PyC (e.g. standing timber vs. down wood) also needs consideration as it affects its persistence and mobilization.

In conclusion, for a comprehensive quantification of PyC produced, all the components discussed above need to be accounted for (Fig. 2). Santín et al. (2015) summarized the approaches used in 31 previous studies quantifying on-site PyC production and concluded that most inventories are incomplete and tend to underestimate total PyC production. Santín et al. (2015)
quantified the complete range of PyC components found on-site immediately after a boreal forest fire and estimated that over a quarter of the C affected by fire was converted to PyC. This is well above the ~1–5% commonly considered (Preston & Schmidt, 2006) and highlights the importance of including the complete range of PyC in quantitative studies.

PyC emitted to the atmosphere

Part of the PyC produced during fire is emitted to the atmosphere within smoke. This ‘atmospheric PyC’ is situated at the smallest size end of the PyC spectrum (<1–2 μm) and is chemically the most recalcitrant (Bird & Ascough, 2012). Within the atmospheric sciences, it is usually referred to as black C (BC), elemental C or soot (for a detailed discussion of these terms see Buseck et al., 2012). It is important to recognize that during fire, some macroscopic PyC (particles >120–150 μm) can also become airborne, but these are commonly not considered in PyC emissions as its mobilization is generally limited to the vicinity of the fire (Oris et al., 2014).

At regional and global scales, estimations of emitted PyC based on bottom-up inventories are much lower than concentrations estimated from atmospheric observations (Kaiser et al., 2012). Given that open biomass burning is not only one of the largest contributors to global PyC emissions, but also the one presenting the highest uncertainties (Bond et al., 2004), a better understanding of the PyC emissions to the atmosphere during vegetation fires is essential. Bond et al. (2013) point to emissions factors (i.e. C emitted with respect to fuel combusted) representing the dominant uncertainty of the role of PyC aerosols in the global climate.

There is a major gap between ‘atmospheric’ and ‘terrestrial’ PyC research. On the one hand, research on fire emissions quantifies PyC emitted to the atmosphere, but overlooks the PyC remaining on-site (Ottmar, 2014); investigations on fire emissions generally assume that all burnt C is either volatilized as gases or contained in the emitted aerosols (Akagi et al., 2011). On the other hand, research focusing on ‘terrestrial’ PyC (i.e. remaining on-site) often assumes that >80% of PyC produced remains on-site and <20% is emitted to the

Fig. 3 Examples of pyrogenic C (PyC) in the environment: (a) PyC derived mainly from burnt forest floor and down wood (boreal forest, NW Canada). Note the PyC-rich ash layer below the white ash; (b) bark-derived PyC on standing tree (dry eucalypt forest, SE Australia); (c) water erosion and redeposition of PyC-enriched sediments after a severe wildfire (wet eucalypt forest, SE Australia); (d) PyC-rich layers in reservoir sediments (excavated at low water level, pit depth 2 m, SE Australia).
atmosphere as aerosol PyC. These numerical estimates have been used extensively (e.g. Forbes et al., 2006; Alexis et al., 2007; Zimmerman et al., 2012), although their general applicability is questioned here. The ratio of 80/20% was obtained by Kuhlbusch & Crutzen (1995) by simple comparison of production rates of PyC that remained on-site following the laboratory and prescribed fires with emission factors for emitted ‘aerosol PyC’ obtained from other studies. For this calculation, emitted vs. remaining PyC was not determined for any specific fire nor was its variability with vegetation or fire characteristics examined. This ratio is likely to vary substantially with environment, fuel type and fire behaviour, and we suggest that site-specific validation studies are a critical need for future research. For example, Saiz et al. (2014a) quantified PyC produced during 16 small-scale experimental burns in tropical savannah, distinguishing between PyC remaining on the ground and ‘distal’ PyC (airbone 125–10 μm particles and some soot material). They found that the distal component was always <3% of the total amount PyC produced. Unfortunately, not all atmospheric PyC was accounted for, as particles <10 μm were not quantified.

**Global estimations of PyC production**

Updated estimates of the global PyC production from vegetation fires are presented in Fig. 4, divided into on-site PyC (charcoal) and atmospheric PyC (i.e. BC emissions). Global BC emissions from vegetation fires have recently been estimated as 1.85 Tg BC yr⁻¹ (average for the period 1997–2014 from the Global Fire Emissions Database GFED4s, 2015). These BC emissions include both BC and elemental C emissions (see Akagi et al., 2011), so for simplicity, we assume a C concentration of 100% (i.e. 2 Tg BC yr⁻¹ = 2 Tg C yr⁻¹ in Fig. 4).

Regarding our on-site PyC (charcoal) production estimations, the proportion of fuel C affected by fire (CA) that is transformed to PyC (PyC/CA) has been previously assumed to be 1–5% (e.g. Forbes et al., 2006; Alexis et al., 2007; Zimmerman et al., 2012) by simple comparison of production rates of PyC that remained on-site following the laboratory and prescribed fires with emission factors for emitted ‘aerosol PyC’ obtained from other studies. For this calculation, emitted vs. remaining PyC was not determined for any specific fire nor was its variability with vegetation or fire characteristics examined. This ratio is likely to vary substantially with environment, fuel type and fire behaviour, and we suggest that site-specific validation studies are a critical need for future research. For example, Saiz et al. (2014a) quantified PyC produced during 16 small-scale experimental burns in tropical savannah, distinguishing between PyC remaining on the ground and ‘distal’ PyC (airbone 125–10 μm particles and some soot material). They found that the distal component was always <3% of the total amount PyC produced. Unfortunately, not all atmospheric PyC was accounted for, as particles <10 μm were not quantified.

**Global estimations of PyC production**

Updated estimates of the global PyC production from vegetation fires are presented in Fig. 4, divided into on-site PyC (charcoal) and atmospheric PyC (i.e. BC emissions). Global BC emissions from vegetation fires have recently been estimated as 1.85 Tg BC yr⁻¹ (average for the period 1997–2014 from the Global Fire Emissions Database GFED4s, 2015). These BC emissions include both BC and elemental C emissions (see Akagi et al., 2011), so for simplicity, we assume a C concentration of 100% (i.e. 2 Tg BC yr⁻¹ = 2 Tg C yr⁻¹ in Fig. 4).

Fig. 4 Global cycle of pyrogenic C (PyC) from vegetation fires. PyC production (in Tg C yr⁻¹) is divided in on-site (charcoal) and atmospheric (soot/BC) PyC. Fluxes between atmosphere, terrestrial and marine environments are given in Tg C yr⁻¹. Main PyC pools are given in Pg C. Main uncertainties and unknowns are represented by red question marks. Data derived from Schmidt & Noack, 2000; Hockaday et al., 2007; Elmquist et al., 2008; Dittmar & Paeng, 2009; Jaffé et al., 2013; Coppola et al., 2014; Scharlemann et al., 2014; Bird et al., 2015 and the GFED4 database. These estimates are based on data produced using different approaches which do not account for regional variability and may not distinguish between PyC from different sources. For more details see main text.
Preston & Schmidt, 2006). However, the most recent and comprehensive studies addressing different ecosystems reported substantially higher conversion rates: 16% PyC/CA for savannah fires (Saiz et al., 2014a), 27% in a boreal forest fire (Santín et al., 2015) and 16% in tropical slash and burn fires (Righi et al., 2009). Therefore, it seems justified to apply an increased estimate here of ~5–15% of the total C affected by fire converted to PyC. Using this PyC/CA conversion rate, the annual amount of PyC can be derived from the amount of total C emitted globally (2.17 Pg C yr−1; average for the period 1997–2014 from GFED4s, 2015), according to the equation CA = ‘C emitted’ + PyC (Santín et al., 2015). This translates into an annual global PyC production of 114–383 Tg C yr−1 (Fig. 4).

The sum of on-site and atmospheric PyC production is 116–385 Tg C yr−1. This represents ~0.2–0.6% of the terrestrial annual net primary production (Huston & Wolverton, 2009), further stressing the global significance of PyC in the C cycle. Our estimations of PyC production exceed the high end of the previously reported ranges (50–270 Tg C yr−1, Kuhlbusch & Crutzen, 1995; 49–200 Tg C yr−1, Schmidt & Noack, 2000; 63–140 Tg C yr−1, Bird et al., 2015). In the present calculations, atmospheric PyC accounts only for 0.5–1.6% of the total production, a lower proportion than what has been previously estimated (e.g. 3–12% Schmidt & Noack, 2000; 5 ± 3% Bird et al., 2015).

It is essential to remember that not all produced PyC has the same MRT. Some PyC will be mineralized on the timescale of weeks (e.g. anhydrosugars, Norwood et al., 2013), while other forms may persist for millennia (e.g. woody-charcoal, Ohlson et al., 2009). Thus, as will be further discussed, an accurate incorporation of PyC into the C cycle would require consideration of this variability in MRTs.

**Degradation vs. mobilization of PyC**

Based on a simple calculation, Goldberg (1985) estimated that if all PyC produced during vegetation fires remained, all the C on the Earth’s surface would be transformed to PyC in ~100 000 years. Obviously, not all PyC remains in the environment in the medium or long term and the question arises, where does it all go? To address this fundamental issue, two main mechanisms for PyC removal need to be considered together: degradation and mobilization.

**PyC degradation**

The assumption of PyC being inert has long been demonstrated to be wrong (Goldberg, 1985). What remains clear is that many pyrogenic transformations enhance the chemical recalcitrance of the organic materials, which prolongs their MRTs in the environment (Schmidt et al., 2011; DeLuca & Boisvenue, 2012; Knicker et al., 2013). Estimated MRTs of pyrogenic materials (including biochar) are very variable, ranging from decades to centuries (e.g. Bird et al., 1999; Hammes et al., 2008; Steinbeiss et al., 2009) to millennia (e.g. Thevenon et al., 2010; de Lafontaine et al., 2011). Critically, however, the MRTs of PyC products are generally one or two orders of magnitude longer than those of their unburnt precursors (Baldock & Smernik, 2002; Knoblauch et al., 2011; Brunn & EL-Zehery, 2012; Santos et al., 2012; Maestrini et al., 2014a; Naisse et al., 2015a). Furthermore, PyC, together with fossil C, is the only form of non-mineral-associated organic matter that shows long-term persistence in mineral soils (Marschner et al., 2008). Thus, PyC is likely to be a potent C sink over the medium and long term (decades to millennia). An exception to this general statement is the water-soluble PyC fraction of low-temperature chars, with turnover rates in the order of weeks to months (Norwood et al., 2013).

Experimental results for PyC mineralization in soils have been contradictory, with reported decomposition rates ranging from rapid (e.g. 0.07% day−1, Hilscher et al., 2009) to slow (e.g. 0.0007% day−1, Kuzyakov et al., 2014). However, short-term incubation experiments can lead to unrealistically low MRTs (Woolf & Lehmann, 2012; Kuzyakov et al., 2014). In early stages, degradation of the labile and readily available compounds in PyC occurs, which is reflected in relatively fast degradation rates (Zimmerman, 2010). Mukome et al. (2014) illustrated this by showing that the labile aliphatic PyC fraction is degraded first, whereas the oxidation of the aromatic PyC portion occurs more slowly. Fast degradation of labile components also explains why PyC produced at low temperatures degrades faster than PyC from high temperatures as the labile fraction is relatively large in low-temperature PyC (Inoue & Inoue, 2009; Ascough et al., 2011). The loss of labile PyC components with ageing leads to a decrease of PyC degradation rates over time (e.g. Hamer et al., 2004; Bruun et al., 2008; Kuzyakov et al., 2009; Knoblauch et al., 2011). Therefore, realistic long-term turnover dynamics of the different PyC forms have to be considered when estimating MRTs of PyC in the environment (Foereid et al., 2011; Kasin & Ohlson, 2013). PyC degradation should not be estimated using a single-pool, single residence time model.

Recent studies investigating MRT of PyC in soils have used multipool models representing different biomolecular classes in soils (e.g. Singh et al., 2012; Woolf & Lehmann, 2012; Knicker et al., 2013; Bird et al., 2015). The most recent model for PyC mineralization
proposed by Bird et al. (2015) differentiates three PyC pools: a labile (anhydrosugars and methoxylated phenols; half-life of weeks to months), an intermediate semilabile (polycyclic aromatic compounds <7 rings; half-life of years to centuries) and a stable pool or SPAC (polycyclic aromatic compounds >7 rings; half-life of centuries to millennia). The contribution of these pools varies with the formation conditions and original material. For PyC formed in natural fires, Bird et al. (2015) speculated that contributions for labile, semilabile and stable pools maybe are around 10%, 40% and 50%, respectively, which suggests that most of PyC formed is in relatively stable forms.

A major limitation of previous work on PyC decomposition rates is that much of it has focused on processes occurring in surface soils. However, surface soil horizons are only one type of environment where PyC accumulation has been identified (e.g. Terra Preta soils; Glaser & Birk, 2012). Most ancient charcoal deposits are found in environments with low decomposition rates such as peats, lake sediments, alluvial fans, flood plain deposits or deep marine sediments (Scott, 2000). Hence, knowledge on PyC degradation in environments where PyC accumulates such as deep soil horizons or depositional sites is required (Dungait et al., 2012; Marin-Spiotta et al., 2014). As a proxy, some studies examined PyC decomposition under differing environmental conditions such as oxygen availability (Nguyen & Lehmann, 2009; Knoblauch et al., 2011), temperatures (Cheng et al., 2006; Nguyen et al., 2010) or alkalinity (Braadbaart et al., 2009). In addition, more information is needed about interaction with the matrix in which PyC is held, given that physiochemical stabilization/protection (e.g. occlusion within aggregates, adsorption onto minerals, per-mineralization) is increasingly seen as a key factor in PyC preservation (de Lafontaine et al., 2011; Cusack et al., 2012; Bruun et al., 2014). The only study to date examining the decomposition of PyC in subsoil points to soil physiochemical parameters being more critical for stabilization than microbial community characteristics (Naisse et al., 2015a).

When examining the relationship between PyC accumulation in soils and C losses to the atmosphere, the effect of PyC on soil organic matter degradation must also be considered. This is especially relevant when PyC is added to the soil for C sequestration and soil amelioration purposes (i.e. biochar application). Studies testing the hypothesis that PyC can prime the decomposition of soil organic matter have had mixed results, with effects being negative (e.g. Cross & Sohi, 2011; Jones et al., 2011; Zimmerman et al., 2011; Whitman et al., 2014; Naisse et al., 2015a), positive (Wardle et al., 2008; Zimmerman et al., 2011; Singh et al., 2014; Naisse et al., 2015a) or absent (Hilscher et al., 2009; Kuzyakov et al., 2009; Cross & Sohi, 2011; Brunn & EL-Zehery, 2012; Santos et al., 2012). The direction of the priming effects depends on several factors such as soil type, original soil organic matter quantity and quality, climate/incubation conditions, and PyC amount and characteristics (Stewart et al., 2013; Michelotti & Miesel, 2015). In a meta-analysis of 18 studies on PyC-induced priming, Maestrini et al. (2014b) suggested that overall the presence of a labile fraction in PyC may induce a positive priming effect in the short term, whereas in the long term, PyC may induce a negative priming by promoting physical protection mechanisms. The only available modelling estimates on long-term potential priming of PyC (biochar) additions on soil organic C concluded that, even for the worst-case scenario examined, the potential negative priming effect exceeds by far the potential positive priming effect (Woolf & Lehmann, 2012).

Biotic degradation is currently the better-understood pathway for PyC decomposition (Kuzyakov et al., 2009; Santos et al., 2012), although abiotic degradation is also important (Cheng et al., 2006; Spokas et al., 2014). Abiotic factors such particle disintegration during water erosion, cryoturbation or gelification are notable drivers of PyC degradation (Preston & Schmidt, 2006; : Spokas et al., 2014). For example, Naisse et al. (2015b) exposed PyC (biochar) to wetting/drying and freezing/thawing cycles and noted substantial losses (10–40% C) by leaching of dissolved and small particulate PyC (<20 μm).

Consumption of existing PyC by subsequent fires has also been highlighted as a possible major abiotic loss mechanism of PyC in soils (Ohlson & Tryterud, 2000; Czimczik et al., 2005; Preston & Schmidt, 2006; Czimczik & Masiello, 2007; Kane et al., 2010). However, none of these studies have produced direct evidence to support this suggestion. More recently, two studies measured PyC consumption by fire in contrasting environments: an experimental boreal forest fire (Santín et al., 2013) and a prescribed fire in open savannah woodland (Saiz et al., 2014b). Both found only minor losses of existing PyC (median mass losses <15% in Santín et al., 2013; average mass losses <8% in Saiz et al., 2014b), suggesting that subsequent fire is not a major cause of PyC loss.

It is essential to recognize that although PyC can be altered and degraded, only its transformation to CO₂ (and other gases) constitutes a net loss to the atmosphere. Through the alteration/degradation process, PyC can evolve into other PyC forms, which may still act as C sinks and need to be accounted for. For example, during degradation, some PyC can enter the dissolved organic matter pool (Hockaday et al., 2006; Guggenberger et al., 2008; Major et al., 2010). It is not
clear how much of the PyC becomes soluble during ageing, but some exploratory results suggested that this soluble fraction tends to increase with ageing (Abiven et al., 2011). This is consistent with the observation by Dittmar et al. (2012a) of a continuous flux of dissolved PyC from a burnt catchment decades after the fire. Ding et al. (2013) also suggested the continuous export of dissolved PyC over long timescales as a plausible explanation for the lack of correlation between dissolved PyC concentration and recent fire history (<20 years) in grassland streams. Some of this dissolved PyC is likely to become part of the relict calcitric pool of dissolved organic C in the deep ocean or sequestered in abyssal sediments where its MRT is in the order of thousands of years (Ziolkowski & Druffel, 2010; Coppola et al., 2014). From a global C accounting perspective, it is important to note that this C, effectively sequestered from the atmosphere, is largely not accounted for.

In the case of atmospheric PyC, this is subjected to a range of alteration processes during ageing, including coating by coagulation and condensation with other aerosols, oxidation and incorporation into liquid water. All these processes have profound implications not only for PyC dynamics, but also for climate forcing and human health (Zhang et al., 2014). Residence times of years (Ziolkowski & Druffel, 2010; Coppola et al., 2014) are consistent with the observation by Elmquist et al. (2008) from the Arctic Ocean point to a predominance of inputs from terrestrial systems by rivers over direct atmospheric deposition, whereas Sánchez-García et al. (2012) accounted atmospheric deposition to be much larger than fluxes from rivers for the northern European shelf. Lohmann et al. (2009) estimated both fluxes being of similar quantitative importance for the South Atlantic Ocean.

Mobilization of atmospheric PyC. Soil erosion by water is usually enhanced after fire by loss of the vegetation cover and, in some cases, increase of soil water repellence and/or the destabilization of soil structure (Certiini, 2005; Shakesby & Doerr, 2006). Given that PyC particles typically have a lower density than soil, and are located on or within the soil surface, a significant part of the PyC may thus become mobilized by postfire water erosion (Fig. 3c; Rumpel et al., 2015; Wagner et al., 2015). Rumpel et al. (2009) found that, even on a slope of only 1%, 7–55% of PyC produced in an experimental savannah fire was subject to erosion under simulated rainfall. Boot et al. (2015) did not detect substantial incorporation of PyC into the mineral soil four months after a conifer forest fire and concluded that most PyC generated aboveground was likely transported off-site through erosion events. In a study characterizing PyC pools across a boreal forest watershed, Ohlson et al. (2013) showed that the lake sediment contained more PyC per unit area than the forest soil surrounding the lake, which also supports the importance of lateral PyC mobilization.

It has also been demonstrated that ‘fresh’ PyC is preferentially transported ex situ by water erosion with respect to bulk soil organic matter, probably due to its low-density particulate nature and lack of immediate interaction with the mineral soil phase (Chaplot et al., 2015).
However, even if lateral erosion is becoming widely recognized as one of the main mechanisms for PyC removal from surface soils (Major et al., 2010; Foereid et al., 2011), PyC flux by erosion has been scarcely quantified and relationships between soil erosion and PyC movement remain poorly understood (Rumpel et al., 2015). The effects of PyC intrinsic characteristics (e.g. particle size, density, porosity, hydrophobicity; Kinney et al., 2012; Brewer et al., 2014) and environmental factors (e.g. topography, rainfall regime, soil type; Boot et al., 2015; Rumpel et al., 2015) in the transport of PyC are yet to be elucidated.

In addition to lateral movement of PyC by erosion and its potential off-site transport by wind and water, vertical transport through the soil profile can also occur (Rumpel et al., 2015). This movement can be driven by water flow and is governed by intrinsic PyC properties and soil characteristics. For example, Wang et al. (2013) observed a greater vertical mobility for PyC particles with smaller sizes and lower surface charges. Haefele et al. (2011) found that 50% of the biochar moved below 0.30 m in the soil profile within 4 years after its application to a sandy soil, whereas vertical movement was inappreciable in another soil with poor percolation rates.

Vertical movement can also occur by bioturbation or physical processes such as gelification and cryoturbation (Schmidt & Noack, 2000; Preston & Schmidt, 2006; Elmer et al., 2015). Although the main direction is downward, upward vertical movement of PyC can occur by, for example, bioturbation or uprooting of trees (Carcaillet, 2001). The oxidation of PyC with ageing may enhance vertical transport of PyC by increasing its polarity, which may promote its movement through the profile with water (Knicker, 2011). Notwithstanding this, PyC oxidation may also enhance its interaction with the soil mineral phase, which in turn could increase its stabilization within the soil (Brodowski et al., 2006). Singh et al. (2014) found that these PyC–mineral interactions were formed in <1 year in a temperate forest Cambisol.

Vertical movement and subsequent accumulation of PyC in deeper soil horizons can contribute to its preservation (Dungait et al., 2012; Lorenz & Lal, 2014), but also, in the case of very small particles or dissolved PyC, could facilitate further transportation by groundwater (Hockaday et al., 2007; Dittmar et al., 2012b). In addition to this, PyC incorporated into the soil matrix disintegrates and oxidizes into water-soluble low-molecular mass compounds (Abiven et al., 2011; Spokas et al., 2014). Water fluxes carry these dissolved PyC compounds horizontally across landscapes into rivers. This is a slow but continuous process that affects land–ocean fluxes globally (Dittmar et al., 2012a; Jaffé et al., 2013). Wagner et al. (2015) reported simultaneous measurements of dissolved and particulate PyC fluvial export one year after a wildfire. They found that their dynamics were decoupled: dissolved PyC fluxes were not significantly affected by recent fire activity, whereas particulate PyC export was substantially larger in recent fire-affected areas when surface run-off occurred. This highlights the need to understand the specific mobilization mechanisms for the different forms of PyC.

It is worth noting that transformation of PyC may take place during transport. For example, PyC particles subjected to water mobilization may suffer abrasion and fragmentation (Scott, 2010; Crawford & Belcher, 2014). Moreover, as is the case for other forms of C within soil organo-mineral complexes, PyC can become exposed during soil erosion and transport through the breaking of soil aggregates and could therefore be more susceptible to degradation (Berhe et al., 2007). Finally, the degradation of dissolved PyC can also be quantitatively and qualitatively important during its transport in surface waters. Stubbins et al. (2012) pointed to photo-degradation as being responsible for the shift from highly condensed aromatics in terrestrial waters to less condensed PyC structures in the open ocean. Myers-Pigg et al. (2015) estimated that half of the low-temperature dissolved PyC is lost in Arctic rivers during the transport from fire source to the ocean.

Global estimations of PyC fluxes

A representation of the main PyC fluxes is shown in Tg C yr$^{-1}$ in Fig. 4. For this annual timescale, atmospheric deposition is equal to atmospheric emissions, given that the residence time of PyC in the atmosphere is in the range of days (Feichter & Stier, 2012). It has been estimated that around half of the atmospheric deposition in the oceans takes place over the continental margins and the other half in the open ocean (Suman et al., 1997); however, to the authors’ knowledge, no robust data are available distinguishing between deposition on land vs. ocean. Therefore, the deposition of atmospheric PyC in Fig. 4 is given as a single value. Regarding transport from land to ocean, we focus on riverine fluxes although some minor remobilization and short-distance deposition by wind may also take place (Suman, 1986). Together, riverine fluxes of particulate and dissolved PyC to oceans may account for about 8–27% of the total annual production of PyC (Fig. 4). Riverine particulate PyC inputs to marine sediments were first estimated as 12.2 Tg PyC yr$^{-1}$ by Suman et al. (1997), with most of the PyC (94–96%) being deposited on the continental shelf. Here, we use the revised values presented by Elmqquist et al. (2008),
which increase global riverine PyC flux to 26 Tg C yr\(^{-1}\), but with only 20% derived from vegetation burning (i.e. 5.2 Tg C yr\(^{-1}\); Fig. 4), and the rest derived from \(^{14}\)C-extinct sources. This is probably a low estimate of riverine particulate PyC inputs because the method used by Elmquist et al. (2008) does not detect the less recalcitrant component of particulate PyC (Hammes et al., 2017).

For dissolved PyC, Jaffé et al. (2013) identified a global flux of 26.5 Tg C yr\(^{-1}\), corresponding to ~10% of the global riverine flux of dissolved organic C. Importantly, Jaffé et al. (2013) quantified only the most recalcitrant forms of PyC, and therefore, values would be higher if labile dissolved PyC forms were also considered (Myers-Pigg et al., 2015). Regarding mechanisms for transfer of PyC from waters into sediments, Coppola et al. (2014) suggested that sorption of dissolved PyC to sinking particulate organic C and deposition into abyssal sediments could account for ~16 Tg C yr\(^{-1}\) (Fig. 4). Other transfer mechanisms need yet to be quantified. Fluxes from terrestrial ground waters to oceans also remain unquantified (Fig. 4), representing another gap in our understanding of the global PyC cycle.

**Long-term fate of PyC**

Burial in marine sediments is usually considered the ultimate fate of PyC (Masiello, 2004). Storage conditions in this anoxic environment are ideal for PyC preservation, with estimated MRTs of several thousands of years (Masiello & Druffel, 1998). However, at the global scale, PyC concentrations measured in marine sediments do not account for all the PyC generated, even considering partial degradation of PyC in the depositional marine environments (Masiello, 2004). This points to the potential importance of ‘intermediate’ PyC reservoirs, which are poorly understood. Regnier et al. (2013) estimated the current lateral anthropogenic-induced fluxes of C from land to ocean and reported that, globally, only <20% of this C is exported to the open ocean and ~30% is emitted, whereas another ~50% is instead accumulated in ‘intermediate reservoirs’ along the continuum of freshwater, estuaries and coastal environments.

Deep soil is one of the intermediate reservoirs gaining attention in the C sequestration context (Lorenz & Lal, 2014). However, it is still not clear how quantitatively relevant the ‘deep’ PyC in soils is, as it remains unaccounted for in studies that do not consider the whole soil profile (Rumpel & Kögel-Knabner, 2011). Other poorly understood intermediate PyC reservoirs are depositional sites within terrestrial environments such as colluvial and alluvial deposits, lake and reservoir sediments, peats and other types of wetlands, and river bank and floodplain deposits (Gerlach et al., 2012; Springer et al., 2012; Wang et al., 2014b; Matthews & Seppälä, 2015).

In terrestrial depositional environments, MRTs of PyC are expected to be relatively long as environmental conditions promote low decomposition rates through, for example, oxygen deficiency, physical protection and/or substrate-driven biological rate limitation (Fig. 3d; Knicker, 2011; Dungait et al., 2012). However, these terrestrial depositional environments are not as stable as marine depositional environments. They are subjected to disturbances over a range of temporal and spatial scales, which can lead to the remobilization of PyC. For example, Ryan et al. (2011) reported PyC enriched fluvial discharges several years after a wildfire, caused by soil remobilization after intense rainfall. Hatten et al. (2012) found that flood events can lead to input of particulate PyC to rivers by mobilization of PyC stored in near-stream deposits. However, even if remobilization from intermediate terrestrial environments takes place, it is necessary to bear in mind that this is a recurring and natural geomorphological process acting at the landscape scale, with most of the material being redeposited within the landscape (Chaplot et al., 2005; Shakesby & Doerr, 2006; Rumpel et al., 2009). Therefore, fluxes between sites do not necessarily imply a net loss or export of PyC from terrestrial systems.

In addition to these terrestrial PyC reservoirs, transitional environments at ocean margins such as estuaries and other coastal wetlands may also hold substantial PyC pools, considering that most of the PyC deposition from rivers to marine sediment occurs near shore (Golding et al., 2004; Ding et al., 2014; De la Rosa et al., 2015). In these transitional environments, particulate PyC can shift from being partially saturated (and thus capable of floating and long-distance transport) to fully saturated and deposited. Also, fluctuations in water table position frequently cause changes in redox conditions in wetlands and coastal zones, which can promote coprecipitation of dissolved PyC with iron hydroxides and other minerals (Riedel et al., 2013). Once enclosed in a mineral matrix and buried in sediments, PyC may be stabilized over long periods of time (Riedel et al., 2013).

**Global estimations of PyC pools**

Robust quantifications of the global PyC pools are currently unavailable, although some estimates can be provided (Fig. 4). Hockaday et al. (2007) estimated that if the PyC contents of soil, freshwater and coastal waters and sediments are assumed to be in the order of 5–15%
of the total organic C, it would imply a global PyC reservoir of 300–500 Pg C. If the same approach is taken for soils with updated figures (global soil organic C pool 1416 Pg; Scharlemann et al., 2014), it translates into a global PyC pool in soils (0–100 cm depth) of 71–212 Pg C (Fig. 4). Past estimates of PyC stored in marine sediments were 2400–6000 Pg (Schmidt & Noack, 2000). However, those numbers did also include PyC derived from lithogenic graphite (Dickens et al., 2004), and updated estimates are now in the range of 400–1200 Pg in coastal and 80–240Pg in open ocean sediments (Bird et al., 2015) (Fig. 4). Future studies examining mechanisms of PyC stabilization in marine sediments are necessary to obtain estimates for the size of this pool.

Recent estimates for dissolved PyC in the ocean are 12 Pg C (Dittmar & Paeng, 2009) and 26–145 Pg C (Ziolkowski & Druffel, 2010). In Fig. 4, we use the more conservative estimate by Dittmar & Paeng (2009) because their study included hundreds of samples of major oceanic water masses. We stress again that estimates are still lacking for key PyC pools such as terrestrial sediments (e.g. lakes, reservoirs, floodplains), freshwaters and particulate PyC in ocean waters (Fig. 4); quantification and characterization of PyC in these pools is an important area for future research.

Conclusions

New directions and challenges: an integrated view of PyC in the environment

Fire is a globally important perturbation in the Earth system, and the extent and intensity of vegetation fires are expected to increase in some regions under predicted future climatic scenarios (Flannigan et al., 2013; Moritz et al., 2014). Thus, irrespective of current efforts for decreasing global anthropogenic PyC emissions, natural PyC production from vegetation fires will remain a major and potentially increasingly important player in the global C cycle. To quantitatively assess the role of PyC in the global C budget and climate prediction models, an integrated view including multiple pools and fluxes of PyC is required. In addition, a full understanding of PyC generation from vegetation fires can provide us with new opportunities for mitigating climate change through, for example, optimizing management of burns for maximum PyC production (Ottmar, 2014). Furthermore, the lessons learned from natural PyC can be used to elucidate the longer-term implications of biochar as a tool for C sequestration and climate change mitigation (Woollf et al., 2010; Lorenz & Lal, 2014). We conclude here by proposing further directions in PyC investigations that may help to achieve these ambitious objectives:

Complete PyC production inventories and conversion factors. Simultaneously acquired quantitative data are needed for the whole spectrum of PyC produced, both PyC remaining on-site and emitted to the atmosphere. These data are required with respect to fuel consumed for a range of fuel types and fire behaviours. When emission factors regarding gases and aerosols are estimated for different fuel types and burning conditions (e.g. Akagi et al., 2011; Urbanski, 2014), conversion factors for PyC production could be determined simultaneously. This would allow direct incorporation of PyC production into C emissions models.

Characterization of the whole range of PyC products and their MRTs. The assessment of the types and relative proportions of all PyC generated would allow not only robust estimation of total PyC produced, but also determination of their characteristics and MRTs. MRT of PyC is not only determined by chemical recalcitrance (e.g. SPAC) but also by physical properties and environmental factors; all of these parameters need to be considered for realistic estimations of MRTs for different PyC types and for accurate appraisals of their roles as C sinks. In addition to this, the importance of pyrogenic organic matter in the cycles of other elements such as nitrogen, phosphorous or sulphur deserves further attention (Knicker, 2010).

Full understanding of PyC intermediate pools and fluxes. The relative importance of the whole range of intermediate PyC pools (and their fluxes) still need to be quantified to understand how much PyC is actually lost (i.e. mineralized) and how much is just moving between reservoirs. A key step forward in this regard has been the recognition of riverine fluxes of dissolved PyC to oceans as one of the major mechanisms for mobilization of PyC from soils (Jaffé et al., 2013). Global-scale quantification of other major PyC fluxes should follow this example. In this context, simultaneous determinations of different PyC types would help elucidating whether their dynamics are coupled (e.g. Wagner et al., 2015).

Terrestrial PyC erosion–deposition as a C sink. Within terrestrial environments, the potential for soil C erosion and subsequent deposition as a C sink is widely recognized (Berhe et al., 2007; Van Oost et al., 2007). Considering the characteristics of PyC (i.e. the recalcitrant nature of some fractions combined with its high susceptibility to water erosion), PyC erosion–deposition could be one of the key mechanisms of PyC preservation. An understanding of not only how PyC is transported.
away from production sites, but also where it is deposited, is essential to quantify PyC fluxes and its ultimate role as long-term C sink. Substantial efforts have been made to measure and model postfire soil erosion and redistribution by the soil and geomorphology communities (Moody et al., 2015), but PyC has to date not been examined as a component within these fluxes. Adding PyC to monitoring studies, or applying established methods in new investigations focusing on PyC, would deliver a fundamental understanding of pathways and quantities involved.

Integration of PyC in models through interdisciplinary collaboration. The PyC production estimates presented in this review suggest that the inclusion of PyC in the global C budget estimations could identify up to 25% of the current missing or residual terrestrial C sink (~1.5 Pg C yr\(^{-1}\), Ciais et al., 2013), with the majority of this expected to survive over decades or centuries (Bird et al., 2015). However, few attempts have been made to incorporate PyC into C budgets and models. To date, this work has mainly focused on soil C models for savannah and agricultural soils (Skjemstad et al., 2004; Lehmann et al., 2008). In addition to soil C models, a wide range of advanced erosion-, fire-related emissions and sediment transport models exist that provide suitable platforms for including PyC (e.g. CASA-GFED, FO-FEM, CONSUME, CanFIRE, ERMIT, LISEM). A closer collaboration between the often distinct research communities specializing in fire behaviour and combustion, fire emissions, fire history, biogeochemical cycling, soil erosion and sediment fluxes could provide the knowledge and data required for incorporating PyC in such models. This integration would bring us closer to a robust global assessment of PyC from vegetation fires.

Acknowledgments

C.S. is grateful to the Spanish Government (EX2010–0498) and to The Leverhulme Trust (Grant RPG-2014–095), J.M.R. to the European Commission’s Marie-Curie Career Integration Grant (FP7-People-2012-CIG-333784) and C.A.M. acknowledges funding from the US National Science Foundation Grant number EAR 0911685. The authors thank two anonymous reviewers, the subject editor and R. Jaffé for helpful comments and suggestions.

References


