



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in : *Global Change Biology*

Cronfa URL for this paper: http://cronfa.swan.ac.uk/Record/cronfa25033

Paper:

Santín, C., Doerr, S., Kane, E., Masiello, C., Ohlson, M., de la Rosa, J., Preston, C. & Dittmar, T. (2016). Towards a global assessment of pyrogenic carbon from vegetation fires. *Global Change Biology*, *22*(1), 76-91.

http://dx.doi.org/10.1111/gcb.12985

This article is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Authors are personally responsible for adhering to publisher restrictions or conditions. When uploading content they are required to comply with their publisher agreement and the SHERPA RoMEO database to judge whether or not it is copyright safe to add this version of the paper to this repository. http://www.swansea.ac.uk/iss/researchsupport/cronfa-support/

Global Change Biology (2015), doi: 10.1111/gcb.12985

RESEARCH REVIEW

Towards a global assessment of pyrogenic carbon from vegetation fires

CRISTINA SANTÍN¹, STEFAN H. DOERR¹, EVAN S. KANE², CAROLINE A. MASIELLO³, MIKAEL OHLSON⁴, JOSE MARIA DE LA ROSA⁵, CAROLINE M. PRESTON⁶ and THORSTEN DITTMAR⁷

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 Ås, 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

Correspondence: Cristina Santín, tel. +44 (0)1792 295147, fax +44 (0)1792 295955, e-mail: csantinwildfire@gmail.com

sion 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

© 2015 The Authors. Global Change Biology Published by John Wiley & Sons Ltd.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Fig. 1 Carbon fluxes driven by fire over time and through a whole fire cycle (i.e. complete recovery of vegetation). Emissions to the atmosphere are represented as negative fluxes. The timescale ranges from a few years to many decades depending on the ecosystem type and the severity of the fire (modified from Conard & Solomon, 2009).

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 PvC 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 (Bodí 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 woodderived 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 woodderived 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 standreplacing 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 PvC pools deserves further attention as most PvC 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)



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).

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 \sim 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 μ m) 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 μ m) 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 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 PvC' 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 μ m 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 μ m 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 onsite 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;



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 or 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 longterm 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 PvC 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 physicochemical 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 subsoils points to soil physicochemical 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 gelifluction 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 μ m).

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 recalcitrant 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.*, 2008; Wang *et al.*, 2014a). It has been suggested that, through reactions with atmospheric oxidants, solubilization of atmospheric PyC could result in it entering the dissolved organic C pool (Masiello, 2004); however, the exact mechanisms still need to be identified.

PyC mobilization

The reservoir that a PyC particle initially enters and its further mobility are primarily determined by its size: for small PyC particles emitted during burning (atmospheric PyC, size <1–2 μ m), the initial reservoir is predominantly the atmosphere, whereas for larger PyC particles, it is the burnt area and surroundings (although some large charred particles may become airborne during fire; Tinner *et al.*, 2006; Oris *et al.*, 2014). Following this basic division by size, atmospheric transport would be the main mobilization pathway for emitted PyC particles and transport by water for on-site PyC particles (Scott, 2010). In some cases aeolian transport may also contribute to mobilization of PyC particles that have initially been deposited on-site (Pereira *et al.*, 2015).

Mobilization of atmospheric PyC. Atmospheric PyC is transported globally through atmospheric circulation, which allows its deposition in remote environments such as deep-sea sediments (Lohmann *et al.*, 2009) or on ice sheets (McConnell *et al.*, 2007). Residence times

of PyC in the atmosphere are in the order of a few days, much shorter than the long-lived greenhouse gases (Feichter & Stier, 2012). Atmospheric deposition and fluvial fluxes are the main mechanisms for delivery of atmospheric PyC to marine sediments (Suman et al., 1997), which are considered to be the final PyC sink (Masiello & Druffel, 1998). The relative importance and spatial patterns of these fluxes in the global context are still a subject of debate. Data 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 in terrestrial systems and deposition in intermediate pools also warrant further investigation (Masiello & Druffel, 1998). For example Bisiaux *et al.* (2011) examined the inputs of atmospheric PyC nanoparticles in a lake after a large wildfire and found that most of this PyC reached the lake immediately after the fire by direct atmospheric deposition, rather than by fluvial transport and subsequent deposition.

Mobilization of on-site 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 (Certini, 2005; Shakesby & Doerr, 2006). Given that PvC 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.*, 2005; Rumpel *et al.*, 2006). 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 gelifluction 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 PvC 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 lowtemperature 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 Elmquist 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 ¹⁴C-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.*, 2007).

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 $\sim 16 \text{ Tg C yr}^{-1}$ (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 necessary 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– 1.200 Pg in coastal and 80–240 Pg 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 PvC can be used to elucidate the longer-term implications of biochar as a tool for C sequestration and climate change mitigation (Woolf 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.*, 2013), 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

- Abiven S, Hengartner P, Schneider MPW, Singh N, Schmidt MWI (2011) Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal. Soil Biology & Biochemistry, 43, 1615–1617.
- Akagi SK, Yokelson RJ, Wiedinmyer C et al. (2011) Emission factors for open and domestic biomass burning for use in atmospheric models. Atmospheric Chemistry and Physics, 11, 4039–4072.
- Alexis MA, Rasse DP, Rumpel C *et al.* (2007) Fire impact on C and N losses and charcoal production in a scrub oak ecosystem. *Biogeochemistry*, **82**, 201–216.

- Ascough PL, Bird MI, Francis SM, Thornton B, Midwood AJ, Scott AC, Apperley D (2011) Variability in oxidative degradation of charcoal: influence of production conditions and environmental exposure. *Geochimica et Cosmochimica Acta*, 75, 2361– 2378.
- Baldock JA, Smernik RJ (2002) Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Organic Geochemistry, 33, 1093–1109.
- Berhe AA, Harte J, Harden JW, Torn MS (2007) The significance of erosion-induced terrestrial carbon sink. *BioScience*, 57, 337–346.
- Bird MI, Ascough PL (2012) Isotopes in pyrogenic carbon: a review. Organic Geochemistry, 42, 1529–1539.
- Bird MI, Moyo C, Veenendaal EM, Lloyd J, Frost P (1999) Stability of elemental carbon in a savanna soil. Global Biogeochemical Cycles, 13, 923–932.
- Bird MI, Wynn JG, Saiz G, Wurster CM, McBeath A (2015) The pyrogenic carbon cycle. Annual Review of Earth and Planetary Sciences, 43, 273–298.
- Bisiaux MM, Edwards R, Heyvaert AC et al. (2011) Stormwater and fire as sources of black carbon nanoparticles to Lake Tahoe. Environmental Science & Technology, 45, 2065–2071.
- Boden TA, Marland G, Andres RJ (2012) Global, Regional, and National Fossil-Fuel CO2 Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN, USA. doi 10.3334/CDIAC/ 00001_V2012
- Bodí MB, Martin DA, Balfour VN et al. (2014) Wildland fire ash: production, composition and eco-hydro-geomorphic effects. Earth-Science Reviews, 130, 103–127.
- Bond TC, Streets DG, Yarber KF, Nelson SM, Woo J-H, Klimont Z (2004) A technology-based global inventory of black and organic carbon emissions from combustion. *Journal of Geophysical Research*, 109, D14203. doi:10.1029/2003JD003697.
- Bond TC, Doherty SJ, Fahey DW et al. (2013) Bounding the role of black carbon in the climate system: a scientific assessment. Journal of Geophysical Research: Atmospheres, 118, 5380–5552. doi:10.1002/jgrd.50171.
- Boot CM, Haddix M, Paustian K, Cotrufo MF (2015) Distribution of black carbon in Ponderosa pine litter and soils following the High Park wildfire. *Biogeosciences*, 12, 1–11.
- Bowman DMJS, Balch JK, Artaxo P et al. (2009) Fire in the earth system. Science, 324, 481–484.
- Braadbaart F, Poole I, van Brussel AA (2009) Preservation potential of charcoal in alkaline environments: an experimental approach and implications for the archaeological record. *Journal of Archaeological Science*, 36, 1672–k1679.
- Brewer N, Smith AMS, Hatten JA, Higuera PE, Hudak AT, Ottmar RG, Tinkham WT (2013) Fuel moisture influences on fire-altered carbon in masticated fuels: an experimental study. *Journal of Geophysical Research: Biogeosciences*, **118**, 30–40.
- Brewer CE, Chuang VJ, Masiello CA et al. (2014) New approaches to measuring biochar density and porosity. Biomass and Bioenergy, 66, 176–185.
- Brodowski S, John B, Flessa H, Amelung W (2006) Aggregate-occluded black carbon in soil. European Journal of Soil Science, 57, 539–546.
- Brunn S, EL-Zehery T (2012) Biochar effect on the mineralization of soil organic matter. Pesquisa Agropecuária Brasileira, 47, 665–671.
- Bruun S, Jensen ES, Jensen LS (2008) Microbial mineralization and assimilation of black carbon: dependency on degree of thermal alteration. Organic Geochemistry, 39, 839–845.
- Bruun S, Clauson-Kaas S, Bobulska L, Thomsen IK (2014) Carbon dioxide emissions from biochar in soil: role of clay, microorganisms and carbonates. *European Journal* of Soil Science, 65, 52–59.
- Buseck PR, Adachi K, Gelencsér A, Tompa E, Posfai M (2012) Are black carbon and soot the same? Atmospheric Chemistry and Physics Discussions, 12, 24821–24846.
- Campbell J, Donato D, Azuma D, Law B (2007) Pyrogenic carbon emission from a large wildfire in Oregon, United States. Journal of Geophysical Research, 112, G04014.
- Carcaillet C (2001) Soil particles reworking evidences by AMS ¹⁴C dating of charcoal. *Earth and Planetary Sciences*, **332**, 21–28.
- Cerda A, Doerr SH (2008) The effect of ash and needle cover on surface runoff and erosion in the immediate post-fire period. *Catena*, 74, 256–263.
- Certini G (2005) Effects of fire on properties of forest soils: a review. *Oecologia*, **143**, 1–10.
- Chaplot V, Coadou L, Brozec E, Silvera N, Valentin C (2005) Spatial and temporal assessment of linear erosion in catchments under sloping lands of Northern Laos. *Catena*, 63, 167–184.
- Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH (2006) Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry, 37, 1477–1488.
- Ciais P, Sabine C, Bala G et al. (2013) Carbon and other biogeochemical cycles. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (eds Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V,

14 C. SANTÍN et al.

Midgley PM). Cambridge University Press, Cambridge, UK and New York, NY, USA.

- Conard SG, Solomon AM (2009) Effects of wildland fire on regional and global carbon stocks in a changing environment. In: *Developments in Environmental Science, Vol 8, Wild Land Fires and Air Pollution, Andrzej Bytnerowicz A, Arbaugh MJ, Riebau AR, Andersen C (ed Krupa SV), pp. 109–138. Elsevier, The Netherlands.*
- Coppola AI, Ziolkowski LA, Masiello CA, Druffel ERM (2014) Aged black carbon in marine sediments and sinking particles. *Geophysical Research Letters*, **41**, 2427–2433.
- Crawford AJ, Belcher CL (2014) Charcoal morphometry for paleoecological analysis: the effects of fuel type and transportation on morphological parameters. *Applications in Plant Sciences*, **2**, 1400004.
- Cross A, Sohi SP (2011) The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biology and Biochemistry*, 43, 2127–2134.
- Cusack DF, Chadwick OA, Hockaday WC, Vitousek PM (2012) Mineralogical controls on soil black carbon preservation. *Global Biogeochemical Cycles*, 26, GB2019.
- Czimczik CI, Masiello CA (2007) Controls of black carbon storage in soils. Global Biogeochemical Cycles, 21, GB3005.
- Czimczik CI, Schmidt MWI, Schulze ED (2005) Effects of increasing fire frequency on black carbon and organic matter in Podzols of Siberian Scots pine forest. *European Journal of Soil Science*, 56, 417–428.
- De la Rosa JM, Knicker H (2011) Bioavailability of N released from pyrogenic organic matter: an incubation study. Soil Biology and Biochemistry, 43, 2368–2373.
- De la Rosa JM, Martins JM, Monge Soares A, Araújo MF (2015) Assessment of distribution and sources of pyrogenic carbon in the low course of the Guadiana River (SW Iberian Peninsula). *Journal of Soils and Sediments*, **15**, 759–768.
- DeLuca TH, Aplet GH (2008) Charcoal and carbon storage in forest soils of the Rochy Mountain West. Frontiers in Ecology and the Environment, 6, 18–24.
- DeLuca TH, Boisvenue C (2012) Boreal forest soil carbon: distribution, function and modeling. *Forestry*, 85, 161–184.
- Dickens AF, Gélinas Y, Masiello CA, Wakeham S, Hedges JI (2004) Reburial of fossil organic carbon in marine sediments. *Nature*, **427**, 336–339.
- Ding Y, Yamashita Y, Dodds WK, Jaffé R (2013) Dissolved black carbon in grassland streams: is there an effect of recent fire history? *Chemosphere*, **90**, 2557–2562.
- Ding Y, Cawley Nunes, da Cunha C, Jaffé R (2014) Environmental dynamics of dissolved black carbon in wetlands. *Biogeochemistry*, 119, 259–273.
- Dittmar T, Paeng J (2009) A heat-induced molecular signature in marine dissolved organic matter. Nature Geoscience, 2, 175–179.
- Dittmar T, Rezende CE, Manecki M, Niggemann J, Ovalle ARC, Stubbins A, Bernardes MC (2012a) Continuous flux of dissolved black carbon from a vanished tropical forest biome. *Nature Geoscience*, 5, 618–622.
- Dittmar T, Paeng J, Gihring TM, Suryaputra IGNA, Huettel M (2012b) Discharge of dissolved black carbon from a fire-affected intertidal system. *Limnology and Ocean*ography, 57, 1171–1181.
- Donato DC, Campbell JL, Fontaine JB, Law BE (2009) Quantifying char in postfire woody detritus inventories. *Fire Ecology*, 5, 104–115.
- Dungait JA, Hopkins DW, Gregory AS, Whitmore AP (2012) Soil organic matter turnover is governed by accessibility not recalcitrance. *Global Change Biology*, 18, 1781– 1796.
- Elmer WH, Lattao CV, Pignatello JJ (2015) Active removal of biochar by earthworms (*Lumbricus terrestris*). *Pedobiologia Journal of Soil Ecology*, **58**, 1–6.
- Elmquist M, Semiletov I, Guo LD, Gustafsson O (2008) Pan-Arctic patterns in black carbon sources and fluvial discharges deduced from radiocarbon and PAH source apportionment markers in estuarine surface sediments. *Global Biogeochemical Cycles*, 22, GB2018.
- Feichter J, Stier P (2012) Assessment of black carbon radiative effects in climate models. WIREs Climate Change, **3**, 359–370.
- Flannigan MD, Cantin AS, de Groot WJ, Wotton M, Newbery A, Gowman LM (2013) Global wildland fire season severity in the 21st century. *Forest Ecology and Management*, **294**, 54–61.
- Foereid B, Lehmann J, Major J (2011) Modeling black carbon degradation and movement in soil. Plant and Soil, 345, 223–236.
- Forbes MS, Raison RJ, Skjemstad JO (2006) Formation, transformation, and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Science of the Total Environment*, **370**, 190–206.
- Gavin DG (2003) Forest soil disturbance intervals inferred from soil charcoal radiocarbon dates. Canadian Journal of Forest Research, 33, 2514–2518.
- Gerlach R, Fischer P, Eckmeier E, Hilgers A (2012) Buried dark soil horizons and archaeological features in the Neolithic settlement region of the Lower Rhine area,

NW Germany: formation, geochemistry and chronostratigraphy. Quaternary International, 265, 191–204.

- GFED4s (2015) Global Fire Emissions Database Version 4 with Small Fires. Available at: http://www.globalfiredata.org/ (accessed on May 2015).
- Giglio L, Randerson JT, van der Werf GR (2013) Analysis of daily, monthly, and annual burned area using the fourth-generation global fire emissions database (GFED4). Journal of Geophysical Research- Biogeosciences, 118, 317–328.
- Glaser B, Birk JJ (2012) State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (terra preta de Índio). *Geochimica* et Cosmochimica Acta, 82, 39–51.
- Goldberg ED (1985) Black Carbon in the Environment. John Wiley, New York, NY.
- Golding CJ, Smernik RJ, Birch GF (2004) Characterisation of sedimentary organic matter from three south-eastern Australian estuaries using solid-state ¹³C-NMR techniques. *Marine and Freshwater Research*, 55, 285–293.
- González-Pérez JA, González-Vila FJ, Almendros G, Knicker H (2004) The effect of fire on soil organic matter–a review. *Environment international*, **30**, 855–870.
- Graça PMLA, Fearnside PM, Cerri CC (1999) Burning of Amazonian forest in Ariquemes, Rondonia, Brazil: biomass, charcoal formation and burning efficiency. Forest Ecology and Management, 120, 179–191.
- de Groot WJ, Landry R, Kurz WA et al. (2007) Estimating direct carbon emissions from Canadian wildland fires. International Journal of Wildland Fire, 16, 593–606.
- Guggenberger G, Rodionov A, Shibistova O et al. (2008) Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in Northern Siberia. Global Change Biology, 14, 1367–1381.
- Haefele SM, Konboon Y, Wongboon W, Amarante S, Maarifat AA, Pfeiffer EM, Knoblauch C (2011) Effects and fate of biochar from rice residues in rice-based systems. *Field Crops Research*, **121**, 430–440.
- Hamer U, Marschner B, Brodowski S, Amelung W (2004) Interactive priming of black carbon and glucose mineralisation. Organic Geochemistry, 35, 823–830.
- Hammes K, Schmidt MWI, Smernik RJ et al. (2007) Comparison of quantification methods to measure fire-derived (black-elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochemical Cycles*, 21, GB3016.
- Hammes K, Torn MS, Lapenas AG, Schmidt MWI (2008) Centennial black carbon turnover observed in a Russian steppe soil. *Biogeosciences Discussions*, 5, 661–683.
- Hatten J, Warrick J, Goñi M, Wheatcroft R, Pasternack G, Gray A, Watson E (2012) The role of wildfire in the export of particulate and pyrogenic organic carbon from a small mountainous river. *Geophysical Research Abstracts*, 14, EGU2012-198.
- Hilscher A, Heister K, Siewert C, Knicker H (2009) Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil. Organic Geochemistry, 40, 332–342.
- Hockaday WC, Grannas AM, Kim S, Hatcher PG (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. *Organic Geochemistry*, 37, 501–510.
- Hockaday WC, Grannas AM, Kim S, Hatcher PG (2007) The transformation and mobility of charcoal in a fire-impacted watershed. *Geochimica et Cosmochimica Acta*, 71, 3432–3445.
- Huston MA, Wolverton S (2009) The global distribution of net primary production: resolving the paradox. *Ecological Monographs*, **79**, 343–377.
- Inoue J, Inoue Y (2009) Comparison of the reflectance of black plant fragments in melanic Andisols with those of fresh charcoal from modern fires. *Soil Science and Plant Nutrition*, 55, 358–362.
- Jaffé R, Ding Y, Niggemann J et al. (2013) Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. Science (New York, N.Y.), 340, 345– 347.
- Jeffery S, Bezemer TM, Cornelissen G *et al.* (2015) The way forward in biochar research: targeting trade-offs between the potential wins. *Global Change Biology Bioenergy*, **7**, 1–13.
- Jones DL, Murphy DV, Khalid M, Ahmad W, Edwards-Jones G, Deluca TH (2011) Short-term biochar-induced increase in soil CO2 release is both biotically and abiotically mediated. Soil Biology & Biochemistry, 43, 1723–1731.
- Kaiser JW, Heil A, Andreae MO et al. (2012) Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power. Biogeosciences, 9, 527–554.
- Kane ES, Hockaday WC, Turetsky MR, Masiello C, Valentine DW, Finney BP, Baldock JA (2010) Topographic controls on black carbon accumulation in Alaskan black spruce forest soils: implications for organic matter dynamics. *Biogeochemistry*, **100**, 39–56.
- Kasin I, Ohlson M (2013) An experimental study of charcoal degradation in a boreal forest. Soil Biology and Biochemistry, 65, 39–49.

PYROGENIC CARBON FROM VEGETATION FIRES 15

- Keane R (2012) Describing wildland surface fuel loading for fire management: a review of approaches, methods, and systems. *International Journal of Wildland Fire*, 22, 51–62.
- Kinney TJ, Masiello CA, Dugan B, Hockaday WC, Dean MR, Zygourakis K, Barnes RT (2012) Hydrologic properties of biochars produced at different temperatures. *Biomass and Bioenergy*, 41, 34–43.
- Knicker H (2010) "Black nitrogen" an important fraction in determining the recalcitrance of charcoal. Organic Geochemistry, 41, 947–950.
- Knicker H (2011) Pyrogenic organic matter in soil: its origin and occurrence, its chemistry and survival in soil environments. *Quaternary International*, 243, 251–263.
- Knicker H, González-Vila FJ, González-Vázquez R (2013) Biodegradability of organic matter in fire-affected mineral soils of Southern Spain. *Soil Biology and Biochemistry*, 56, 31–39.
- Knoblauch C, Maarifat AA, Pfeiffer EM, Haefele SM (2011) Degradability of black carbon and its impact on trace gas fluxes and carbon turnover in paddy soils. *Soil Biology and Biochemistry*, 43, 1768–1778.
- Kuhlbusch TAJ, Crutzen PJ (1995) Toward a global estimate of Black Carbon in residues of vegetation fires representing a sink of atmospheric CO₂ and a source of O₂. Global Biogeochemical Cycles, 9, 491–501.
- Kuzyakov Y, Subbotina I, Chen H, Bogomolova I, Xu X (2009) Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. Soil Biology and Biochemistry, 41, 210–219.
- Kuzyakov Y, Bogomolova I, Glaser B (2014) Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14C analysis. *Soil Biology and Biochemistry*, 70, 229–236.
- de Lafontaine G, Asselin H (2011) Soil charcoal stability over the Holocene across boreal northeastern North America. Quaternary Research, 76, 196–200.
- de Lafontaine G, Couillard P, Payette S (2011) Permineralization process promotes preservation of Holocene macrofossil charcoal in soils. *Journal of Quaternary Science*, 26, 571–575.
- Le Quere C, Raupach MR, Canadell JG *et al.* (2009) Trends in the sources and sinks of carbon dioxide. *Nature Geoscience*, **2**, 831–836.
- Lehmann J, Skjemstad J, Sohi S et al. (2008) Australian climate–carbon cycle feedback reduced by soil black carbon. Nature Geoscience, 1, 832–835.
- Lohmann R, Bollinger K, Cantwell M, Feichter J, Fischer-Bruns I, Zabel M (2009) Fluxes of soot black carbon to South Atlantic sediments. *Global Biogeochemical Cycles*, 23, 1–13.
- Lorenz K, Lal R (2014) Biochar application to soil for climate change mitigation by soil organic carbon sequestration. *Journal of Plant Nutrition and Soil Science*, 177, 651– 670.
- Maestrini B, Abiven S, Singh N, Bird J, Torn MS, Schmidt MWI (2014a) Carbon losses from pyrolysed an original wood in a forest soil under natural and increased N deposition. *Biogeosciences Discussions*, **11**, 1–31.
- Maestrini B, Nannipieri P, Abiven S (2014b) A meta-analysis on pyrogenic organic matter induced priming effect. *Global Change Biology Bioenergy*. doi: 10.1111/ gcbb.12194.
- Major J, Lehmann J, Rondon M, Goodale C (2010) Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biology*, 16, 1366–1379.
- Marin-Spiotta E, Chaopricha NT, Plante AF, Diefendorf AF, Mueller CW, Grandy AS, Mason JA (2014) Long-term stabilization of deep soil carbon by fire and burial during early Holocene climate change. *Nature Geosciences*, 7, 428–432.
- Marschner B, Brodowski S, Dreves A et al. (2008) How relevant is recalcitrance for the stabilization of organic matter in soils? *Journal of Plant Nutrition and Soil Science*, 171, 91–110.
- Masiello CA (2004) New directions in black carbon organic geochemistry. Marine Chemistry, 92, 39–64.
- Masiello CA, Druffel ERM (1998) Black carbon in deep-sea sediments. Science, 280, 1911–1913.
- Matthews JA, Seppälä M (2015) Holocene colluvial chronology in a sub-arctic esker landscape at Kuttanen, Finnish Lapland: kettleholes as geo-ecological archives of interactions amongst fire, vegetation, soil, climate and geomorphological instability. Boreas, 44, 343–367.
- McBeath AV, Wurster CM, Bird MI (2015) Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. *Biomass and Bioenergy*, 73, 155–173.
- McConnell JR, Edwards R, Kok GL et al. (2007) 20th-Century industrial black carbon emissions altered arctic climate forcing. Science, 317, 1381–1384.
- Michelotti LA, Miesel JR (2015) Source material and concentration of wildfire-produced pyrogenic carbon influence distinctively post-fire nutrient dynamics. *For*ests, 6, 1325–1342.

- Moody JA, Shakesby RA, Robichaud PR, Cannon SH, Martin DA (2013) Current research issues related to post-wildfire runoff and erosion processes. *Earth-Science Reviews*, **122**, 10–37.
- Moritz MA, Batlori E, Bradstock RA et al. (2014) Learning to coexist with wildfire. Nature, 515, 58–66.
- Moss RH, Edmonds JA, Hibbard KA et al. (2010) The next generation of scenarios for climate change research and assessment. Nature, 463, 08823.
- Mukome FND, Kilcoyne ALD, Parikh SJ (2014) Alteration of biochar carbon chemistry during soil incubations: SR-FTIR and NEXAFS investigation. Soil Science Society of America Journal, 78, 1632–1640.
- Myers-Pigg AN, Louchouarn P, Amon RMW, Prokushkin A, Pierce K, Rubtsov A (2015) Labile pyrogenic dissolved organic carbon in major Siberian Arctic rivers: implications for wildfire-stream metabolic linkages. *Geophysical Research Letters*, 42, 377–385.
- Naisse C, Girardin C, Davasse B, Chabbi A, Rumpel C (2015a) Effect of biochar addition on C mineralisation and soil organic matter priming in two subsoil horizons. *Journal of Soils and Sediments*, **15**, 825–832.
- Naisse C, Girardin C, Lefèvre R, Pozzi A, Maas R, Stark A, Rumpel C (2015b) Effect of physical weathering on the carbon sequestration potential of biochars and hydrochars in soil. *Global Change Biology Bioenergy*, 7, 488–496. doi:10.1111/gcbb.12158.
- Nguyen BT, Lehmann J (2009) Black carbon decomposition under varying water regimes. Organic Geochemistry, 40, 846–853.
- Nguyen BT, Lehmann J, Hockaday WC, Joseph S, Masiello CA (2010) Temperature sensitivity of black carbon decomposition and oxidation. *Environmental Science & Technology*, 44, 3324–3331.
- Nocentini C, Certini G, Knicker H, Francioso O, Rumpel C (2010) Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. Organic Geochemistry, 41, 682–689.
- Norwood MJ, Louchouarn P, Li-Jung K, Harvey OR (2013) Characterization and biodegradation of water-soluble biomarkers and organic carbon extracted from low temperature chars. Organic Geochemistry, 56, 111–119.
- Ohlson M, Tryterud E (2000) Interpretation of the charcoal record in forest soils: forest fires and their production and deposition of macroscopic charcoal. *The Holocene*, **10**, 519–525.
- Ohlson M, Dahlberg B, Økland T, Brown KJ, Halvorsen R (2009) The charcoal carbon pool in boreal forest soils. *Nature Geoscience*, 2, 692–695.
- Ohlson M, Brown KJ, Birks HJB et al. (2011) Invasion of Norway spruce diversifies the fire regime in boreal European forests. *Journal of Ecology*, 99, 395–403.
- Ohlson M, Kasin I, Wist AN, Bjune AE (2013) Size and spatial structure of the soil and lacustrine charcoal pool across a boreal forest watershed. *Quaternary Research*, 80, 417–424.
- Oris F, Ali AA, Asselin H, Paradis L, Bergeron Y, Finsinger W (2014) Charcoal dispersion and deposition in boreal lakes from 3 years of monitoring: differences between local and regional fires. *Geophysical Research Letters*, **41**, 6743– 6752.
- Ottmar RD (2014) Wildland fire emissions, carbon and climate: modeling fuel consumption. Forest Ecology and Management, 317, 41–50.
- Pereira P, Cerdà A, Úbeda X, Mataix-Solera J, Arcenegui V, Zavala LM (2015) Modelling the impacts of wildfire on ash thickness in a short-term period. Land Degradation and Development, 26, 180–192.
- Possell M, Jenkins M, Bell TL, Adams MA (2015) Emissions from prescribed fires in temperate forest in south-east Australia: implications for carbon accounting. *Bio*geosciences, 12, 257–268.
- Preston CM, Schmidt MW (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeo*sciences, 3, 397–420.
- Randerson JT, Chen Y, van der Werf GR, Rogers BM, Morton DC (2012) Global burned area and biomass burning emissions from small fires. *Journal of Geophysical Research*, 117, G04012.
- Regnier P, Friedlingstein P, Ciais P et al. (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean. Nature Geoscience, 6, 597–607.
- Riedel T, Zak D, Biester H, Dittmar T (2013) Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proceedings of the National Academy of Sciences of the United States of America, 110, 10101–10105.
- Righi CA, Gráça PMLA, Cerri CC, Feigl BJ, Fearnside PM (2009) Biomass burning in Brazil's Amazonian 'arc of deforestation': burning efficiency and charcoal formation in a fire after mechanized clearing at Feliz Natal, Mato Grosso. Forest Ecology and Management, 258, 2535–2546.
- Roth PJ, Lehndorff E, Brodowski S, Bornemann L, Sanchez-García L, Gustafsson O, Amelung W (2012) Differentiation of charcoal, soot and diagenetic carbon in soil: method comparison and perspectives. Organic Geochemistry, 46, 66–75.

© 2015 The Authors. Global Change Biology Published by John Wiley & Sons Ltd., doi: 10.1111/gcb.12985

16 C. SANTÍN et al.

Rumpel C, Kögel-Knabner I (2011) Deep soil organic matter-a key but poorly understood component of terrestrial C cycle. Plant and Soil, 338, 143–158.

- Rumpel C, Chaplot V, Planchon O, Bernadou J, Valentin C, Mariotti A (2006) Preferential erosion of black carbon on steep slopes with slash and burn agriculture. *Catena*, 65, 30–40.
- Rumpel C, Ba A, Darboux F, Chaplot V, Planchon O (2009) Erosion budget and process selectivity of black carbon at meter scale. *Geoderma*, 154, 131–137.
- Rumpel C, Leifeld J, Santín C, Doerr SH (2015) Movement of biochar in the environment. In: *Biochar for Environmental Management. Science, Technology and Implementation*, 2nd edn (eds Lehmann JL, Joseph S), pp. 283–299. Routledge, Tatlor & Francis, London and New York.
- Ryan SE, Dwire KA, Dixon MK (2011) Impacts of wildfire on runoff and sediment loads at Little Granite Creek, western Wyoming. *Geomorphology*, **129**, 113–130.
- Saiz G, Goodrick I, Wurster C, Zimmermann MPN, Bird MI (2014a) Charcoal recombustion efficiency in tropical savannas. *Geoderma*, 219, 40–45.
- Saiz G, Wynn JG, Wurster CM, Goodrick I, Nelson PN, Bird MI (2014b) Pyrogenic carbon from tropical savannah burning: production and stable isotope composition. *Biogeosciences Discussions*, **11**, 15149–15183.
- Sánchez-García L, Cato I, Gustafsson Ö (2012) The sequestration sink of soot black carbon in the Northern European Shelf sediments. *Global Biogeochemical Cycles*, 26, 1–12.
- Santín C, Doerr SH, Shakesby RA et al. (2012) Carbon loads, forms and sequestration potential within ash deposits produced by wildfire: new insights from the 2009 "Black Saturday" fires, Australia. European Journal of Forest Research, 131, 1245– 1253.
- Santín C, Doerr SH, Preston C, Bryant R (2013) Consumption of residual pyrogenic carbon by wildfire. *International Journal of Wildland Fire*, **22**, 1072–1077.
- Santín C, Doerr SH, Preston C, González-Rodríguez G (2015) Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. *Global Change Biology*, 21, 1621–1633.
- Santos F, Torn MS, Bird JA (2012) Biological degradation of pyrogenic organic matter in temperate forest soils. Soil Biology & Biochemistry, 51, 115–124.
- Scharlemann JPW, Tanner EVJ, Hiederer R, Kapos V (2014) Global soil carbon: understanding and managing the largest terrestrial carbon pool. *Carbon Management*, 5, 81–91.
- Schmidt WI, Noack AG (2000) Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles, 14, 777–793.
- Schmidt MWI, Skjemstad JO, Czimczik CI, Glaser B, Prentice KM, Gelinas Y, Kuhlbusch TAJ (2001) Comparative analysis of black carbon in soils. *Global Biogeochemical Cycles*, 15, 163–167.
- Schmidt MWI, Torn MS, Abiven S et al. (2011) Persistence of soil organic matter as an ecosystem property. Nature, 478, 49–56.
- Scott AC (2000) The pre-Quaternary history of fire. Palaeogeography, Palaeoclimatology, Palaeoecology, 164, 281–329.
- Scott AC (2010) Charcoal recognition, taphonomy and uses in palaeoenvironmental analysis. Palaeogeography, Palaeoclimatology, Palaeoecology, 291, 11–39.
- Shakesby RA, Doerr SH (2006) Wildfire as a hydrological and geomorphological agent. Earth-Science Reviews, 74, 269–307.
- Singh N, Abiven S, Torn MS, Schmidt MWI (2012) Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences*, 9, 2847–2857.
- Singh N, Abiven S, Maestrini B, Bird JA, Torn MS, Schmidt MWI (2014) Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment. *Global Change Biology*, 20, 1629–1642.
- Skjemstad J, Spouncer L, Cowie B, Swift R (2004) Calibration of the Rothamsted organic carbon turnover model (RothC ver 26.3), using measurable soil organic carbon pools. Australian Journal of Soil Research, 42, 79–88.
- Spokas KA, Novak JM, Masiello CA, Johnson MG, Colosky EC, Ippolito JA, Trigo C (2014) Physical disintegration of biochar: an overlooked process. *Environmental Sci*ence & Technology Letters, 1, 326–332.
- Springer GS, Nivanthi Mihindukulasooriya L, Matthew White D, Rowe HD (2012) Micro-charcoal abundances in stream sediments from buckeye Creek Cave, West Virginia, USA. Journal of Cave and Karst Studies, 74, 58–64.
- Steinbeiss S, Gleixner G, Antonietti M (2009) Effect of biochar amendment on soil carbon balance and soil microbial activity. Soil Biology and Biochemistry, 41, 1301–1310.

- Stewart CE, Zheng J, Botte J, Cotrufo MF (2013) Co-generated fast pyrolysis biochar mitigates greenhouse gas emissions and increases carbon sequestration in temperate soils. GCB Bioenergy, 5, 153–164.
- Stubbins A, Niggemann J, Dittmar T (2012) Photo-lability of deep ocean dissolved black carbon. *Biogeosciences*, 9, 1661–1670.
- Suman DO (1986) Charcoal production from agricultural burning in Central Panama and its deposition in the sediments of the Gulf of Panama. *Environmental Conservation*, **13**, 51–60.
- Suman DO, Kuhlbusch TAJ, Lim B (1997) Marine sediments: a reservoir for black carbon and their use as spatial and temporal records of combustion. Sediment Records of Biomass Burning and Global Change. NATO ASI Series, 51, 271–293.
- Thevenon F, Williamson D, Bard E, Anselmetti FS, Beaufort L, Cachier H (2010) Combining charcoal and elemental black carbon analysis in sedimentary archives: implications for past fire regimes, the pyrogenic carbon cycle, and the human–climate interactions. *Global and Planetary Change*, **72**, 381–389.
- Tinker DB, Knight DH (2000) Coarse woody debris following fire and logging in Wyoming lodgepole pine forests. *Ecosystems*, **3**, 472–483.
- Tinner W, Hofstetter S, Zeugin F, Zimmermann L, Zweifel R (2006) Long-distance transport of macroscopic charcoal by an intensive crown fire in the Swiss Alps implications for fire history reconstruction. *The Holocene*, **16**, 287–292.
- Urbanski S (2014) Wildland fire emissions, carbon, and climate: emission factors. Forest Ecology and Management, 317, 51–60.
- Van Der Werf GR, Randerson JT, Giglio L et al. (2010) Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009). Atmospheric Chemistry and Physics, 10, 11707–11735.
- Van Oost K, Quine TA, Govers G et al. (2007) The impact of agricultural soil erosion on the global carbon cycle. Science (New York, N.Y.), 318, 626–629.
- Wagner S, Cawley KM, Rosario-Ortiz FL, Jaffé R (2015) In-stream sources and links between particulate and dissolved black carbon following a wildfire. *Biogeochemistry*, **124**, 145–161.
- Wang D, Zhang W, Hao X, Zhou D (2013) Transport of biochar particles in saturated granular media: effects of pyrolysis temperature and particle size. *Environmental Science & Technology*, **47**, 821–828.
- Wang X, Heald CL, Ridley DA et al. (2014a) Exploiting simultaneous observational constraints on mass and absorption to estimate the global direct radiative forcing of black carbon and brown carbon. Atmospheric Chemistry and Physics, 14, 10989– 11010.
- Wang Q, Zhang PJ, Liu M, Deng ZW (2014b) Mineral-associated organic carbon and black carbon in restored wetlands. Soil Biology & Biochemistry, 75, 300–309.
- Wardle DA, Nilsson M-C, Zackrisson O (2008) Fire-derived charcoal causes loss of forest humus. *Science*, 320, 629.
- Whitman T, Enders A, Lehmann J (2014) Pyrogenic carbon additions to soil counteract positive priming of soil carbon mineralization by plants. Soil Biology & Biochemistry, 73, 33–41.
- Wilkinson MT, Richards PJ, Humphreys GS (2009) Breaking ground: pedological, geological, and ecological implications of soil bioturbation. *Earth-Science Reviews*, 97, 257–272.
- Woolf D, Lehmann J (2012) Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon. *Biogeochemistry*, **111**, 83– 95.
- Woolf D, Amonette JE, Street-Perrott FA, Lehmann J, Joseph S (2010) Sustainable biochar to mitigate global climate change. *Nature communications*, 1, 56.
- Zhang R, Khalizov AF, Pagels J, Zhang D, Xue H, McMurry PH (2008) Variability in morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing. Proceedings of the National Academy of Sciences of the United States of America, 105, 10291–10296.
- Zimmerman AR (2010) Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environmental Science and Technology, 44, 1295–1301.
- Zimmerman AR, Gao B, Ahn MY (2011) Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*, **43**, 1169–1179.
- Zimmerman M, Bird MI, Wurster C et al. (2012) Rapid degradation of pyrogenic carbon. Global Change Biology, 18, 3306–3316.
- Ziolkowski LA, Druffel ERM (2010) Aged black carbon identified in marine dissolved organic carbon. *Geophysical Research Letters*, 37, 4–7.