

# The Pyrogenic Carbon Cycle

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## Keywords

biomass burning, black carbon, charcoal, biochar, carbon cycle, carbon isotopes

## Abstract

Pyrogenic carbon (PyC; includes soot, char, black carbon, and biochar) is produced by the incomplete combustion of organic matter accompanying biomass burning and fossil fuel consumption. PyC is pervasive in the environment, distributed throughout the atmosphere as well as soils, sediments, and water in both the marine and terrestrial environment. The physicochemical characteristics of PyC are complex and highly variable, dependent on the organic precursor and the conditions of formation. A component of PyC is highly recalcitrant and persists in the environment for millennia. However, it is now clear that a significant proportion of PyC undergoes transformation, translocation, and remineralization by a range of biotic and abiotic processes on comparatively short timescales. Here we synthesize current knowledge of the production, stocks, and fluxes of PyC as well as the physical and chemical processes through which it interacts as a dynamic component of the global carbon cycle.

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**Pyrogenic carbon**

**(PyC):** the thermochemically altered organic carbon fraction of pyrogenic carbonaceous material

**Radiocarbon ( $^{14}\text{C}$ ):**

radioactive isotope of carbon with a half-life of  $5,730 \pm 40$  yr

**Biochar:** a pyrogenic carbonaceous material that is the engineered, solid product of controlled pyrolysis, produced specifically for use as a soil amendment and carbon sequestration tool

**Teragram (Tg):** unit of mass equivalent to  $1 \times 10^{12}$  g, or 0.001 Pg

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## 1. INTRODUCTION

Pyrogenic carbon (PyC) is a general term describing thermochemically altered (pyrolyzed) carbon derived from the incomplete combustion of organic matter during biomass burning and the consumption of fossil fuels. Ranging in size from macroscopic fragments to individual pyrogenic molecules, PyC is present in atmosphere, soils, sediments, ice, terrestrial water bodies, and the ocean (Schmidt & Noack 2000). PyC has been produced, and preserved in the geologic record, since the atmosphere first contained sufficient oxygen to sustain the process of combustion 420 Myr ago (Scott & Glasspool 2006).

PyC is important as (a) a poorly understood, potentially slow-cycling component of the global carbon cycle (Schmidt & Noack 2000, Forbes et al. 2006); (b) a component of global aerosols capable of climate forcing (McConnell et al. 2007, Bond et al. 2013); (c) a source of paleoenvironmental information (Conedera et al. 2009); (d) a material commonly used for radiocarbon dating (Bird & Ascough 2012); and (e) a soil amendment (as biochar) potentially capable of providing long-term, engineered carbon sequestration (Lehmann et al. 2006). Owing to the broad significance of PyC across soil science, atmospheric science, carbon cycle science, ecology, paleoecology, geoarchaeology, and the geosciences, research on PyC has originated in different disciplines at different times and for very different reasons.

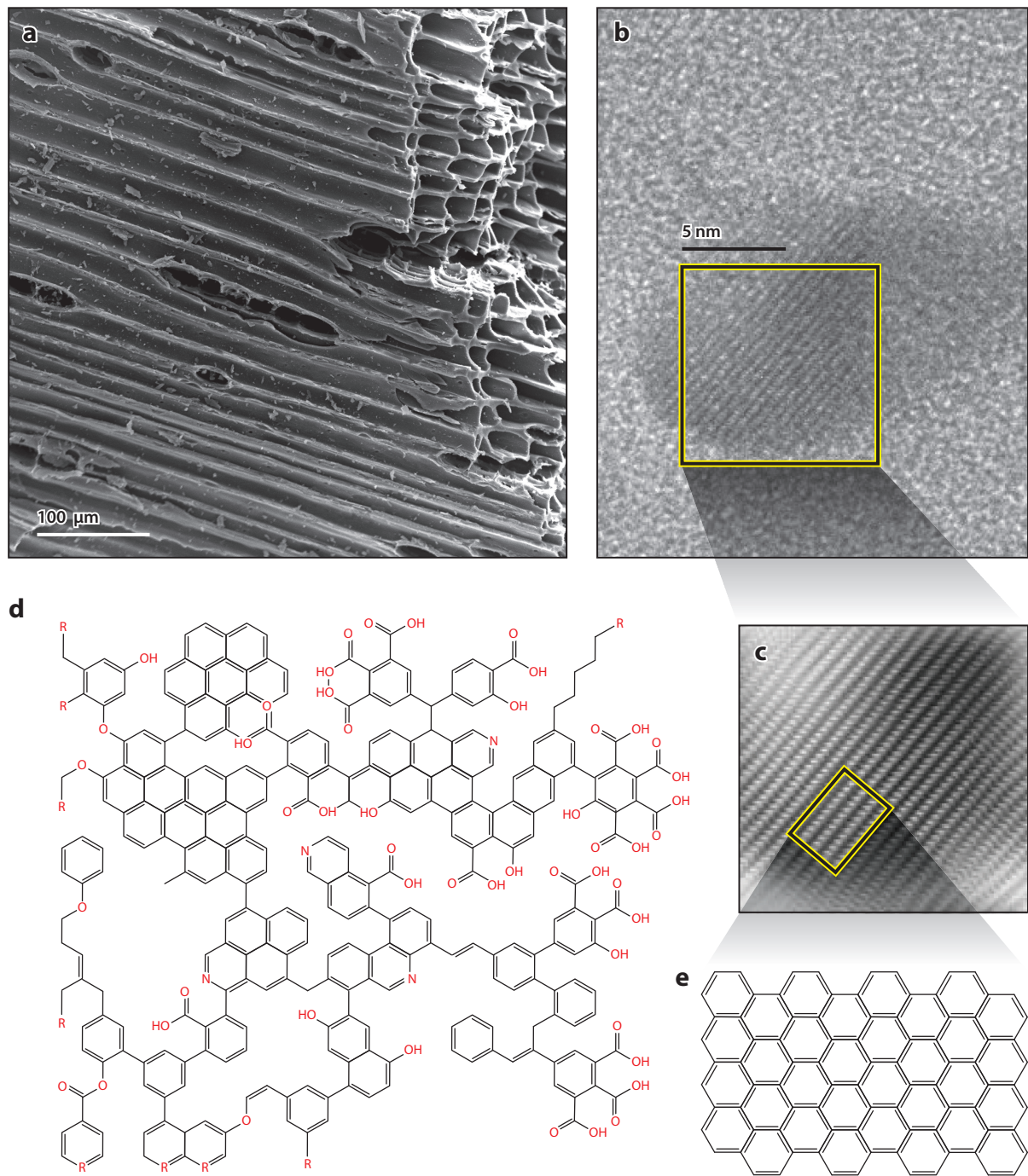
Our understanding of a PyC cycle dates back at least a century to the observation by Glinka (1914), who found that “there was almost no soil profile in which charcoal particles did not occur in the upper horizon” in parts of Asiatic Russia (p. 295). The identification by Smith et al. (1973) of elemental carbon in ancient deep-sea sediments framed the view of PyC as a recalcitrant material with an extremely long environmental lifetime. The first estimate of global PyC production from biomass burning was provided by Seiler & Crutzen (1980), who used a mass balance approach to deduce a figure of 500–1,700 Tg yr<sup>-1</sup> of elemental carbon PyC, later revised down substantially to 50–270 Tg yr<sup>-1</sup> by Kuhlbusch & Crutzen (1996).

Kuhlbusch (1998) introduced the important concepts of a life cycle and distinct reservoirs for PyC, based on the observation by Masiello & Druffel (1998) that an intermediate point of storage was required between the point of production and ultimate burial in ocean sediments in order to explain the fact that black carbon PyC in marine sediments was up to 13,900 yr older than contemporaneous sedimentary organic carbon.

Hedges et al. (2000) introduced the pivotal concept of the combustion continuum (**Figure 1**), recognizing that PyC represents a wide range of compounds of varying reactivity, from lightly charred plant material to highly condensed soot and microcrystalline graphite. This concept left open the possibility that not all PyC is highly recalcitrant and reconciled to some extent the paradox that PyC is highly resistant to degradation over thousands to millions of years (e.g., Smith et al. 1973) but also apparently susceptible to degradation over decades (e.g., Bird et al. 1999).

In the past decade it has been recognized that PyC is a significant component of anthropogenic, highly fertile, Amazonian dark earth (*terra preta*) soils (Glaser et al. 2001). This observation has stimulated interest in biochar PyC as a tool for improving soil fertility and crop yields and, as a result of its apparent environmental stability, to provide significant long-term (centennial and longer) soil sequestration (Lehmann 2007). The prospect that biochar PyC may provide long-term carbon sequestration, able to offset a significant fraction of anthropogenic emissions (Woolf et al. 2010), has provided a recent stimulus to research factors controlling PyC stability and degradation potential and interactions between PyC and the environment more generally.

This review synthesizes current knowledge regarding the sources, stocks, fluxes, stability, and interactions of PyC in the global biosphere, building on the previous seminal reviews by Schmidt & Noack (2000), Masiello (2004), Preston & Schmidt (2006), and Forbes et al. (2006).



**Figure 1**

From macroscopic to molecular: (a) scanning electron micrograph of wood pyrogenic carbon; (b) transmission electron micrograph of pine pyrogenic carbon showing disorganized and organized domains; (c) close view of an organized domain showing microcrystalline graphitic sheets; (d) hypothetical pyrogenic carbon molecular structure (redrawn with permission from Kaal 2011); and (e) molecular representation of micrographitic structure in panel c.

## 2. DEFINITION, MEASUREMENT, AND TRACERS OF PYROGENIC CARBON

### Pyrogenic carbonaceous material (PCM):

all materials produced by pyrolysis of organic matter, including the C, H, N, O, S, and mineral components

**Black carbon:** a term synonymous with PyC that is used to describe pyrogenic carbonaceous materials dispersed in the environment from biomass burning and fossil fuel combustion

**Soot:** a secondary pyrogenic carbonaceous material that derives specifically from gas phase condensation and is generally of small particle size

**Char:** the solid pyrogenic carbonaceous material remaining as a result of incomplete combustion processes such as those that occur in natural and man-made fires

**Charcoal:** pyrogenic carbonaceous material produced by the deliberate pyrolysis of biomass (mainly but not exclusively wood) for cooking and energy generation

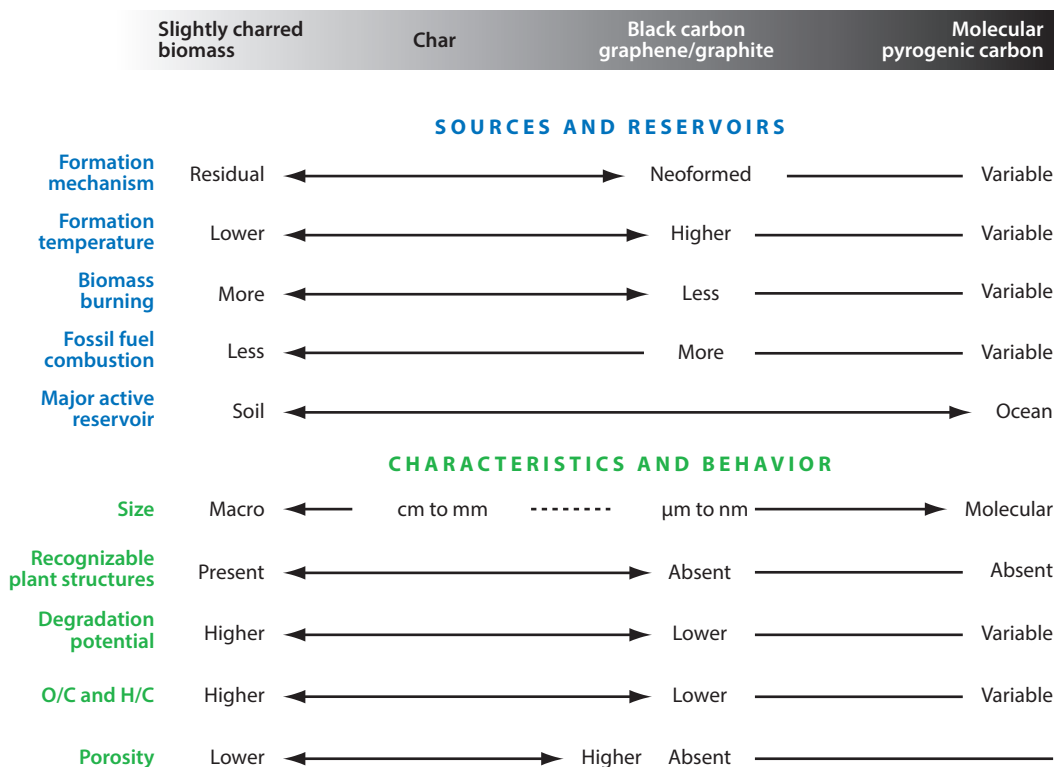
**Pyrolysis:** the irreversible thermochemical alteration and decomposition of organic matter at elevated temperatures in an atmosphere of reduced or no oxygen

PyC refers to the pyrolyzed carbon component of any pyrogenic carbonaceous material (PCM), and these two terms are here intended as inclusive of many other terms, including black carbon, micrographite, elemental carbon, soot, char, charcoal, fusain/inertinite, and a range of individual compounds of pyrogenic origin. PCM comprises a wide range of chemical compounds produced both in situ from the thermochemical rearrangement of precursor organic compounds and from gas-phase condensation of compounds volatilized during pyrolysis and/or combustion.

PyC is generally dominated by polycyclic aromatic hydrocarbons (PAHs); the size of PAH clusters increases with temperature (McBeath & Smernik 2009), leading ultimately to the formation of micrographitic sheets (Schmidt & Noack 2000). PCMs formed by biomass burning are often heterogeneous in nature, with both organized micrographitic domains and disorganized domains of variably thermochemically altered organic material (**Figure 1**) (Cohen-Ofri et al. 2006). This continuum of potential thermochemical reorganization confers a variable degree of stability to subsequent degradation. At one end of the PyC continuum, small PAHs are readily degradable by microorganisms (e.g., Kanaly & Harayama 2000), whereas at the other, microcrystalline graphite is likely to be highly resistant to degradation by any mechanism operating in the surficial environment. Thus it is appropriate to conclude that, associated with the PyC continuum, there is a PyC degradation continuum (**Figure 2**). This conclusion is of significance in understanding the operation of the global PyC cycle in terms of PyC residence times and remineralization pathways as well as the PyC alteration and transport pathways linking sites of production (sources) to intermediate and ultimate sites of storage and burial (sinks).

Along with the increasing interest in PyC, the number of techniques available to isolate, quantify, and/or characterize PyC in a range of sample matrices (e.g., soils, sediments, rocks, water, and aerosols) has grown substantially in the past decade. These techniques can be grouped into five major classes. Physical techniques are largely nondestructive and rely on a difference in density or size as the basis for separating PCM from other components for subsequent analysis. Chemical oxidation techniques are destructive and rely on the greater resistance of some components of the PyC continuum to an oxidant relative to other components of a sample. Thermal techniques are destructive and rely on the greater resistance of some components of the PCM continuum to decomposition at elevated temperature relative to other components in a sample. Spectroscopic techniques are nondestructive and rely on stimulating a sample with a magnetic field or infrared or X-ray radiation and measuring a magnetic or photon response from the sample. This can be used to infer the nature and abundance of chemical bonds in a sample, including those that are characteristic of PCM. Molecular marker techniques are destructive, decomposing a sample chemically and/or thermally to measure the abundances and types of the multiple compounds liberated in the process of decomposition. There are several reviews and intercomparisons of these techniques, which demonstrate that different techniques target different components within the PyC continuum (Hammes et al. 2007, Meredith et al. 2012). Accordingly, judgment is required in selecting a technique appropriate to an application and in comparing results derived from different techniques (Bird 2015); for example, spectroscopic techniques are likely to indicate higher PyC abundance than more aggressive thermal oxidation techniques.

Elucidation of a PyC cycle requires the ability not only to identify and quantify PyC, after degradation and remobilization from its site of production, but also to determine its source. In this regard molecular markers such as levoglucosan and benzene polycarboxylic acids have enabled the identification of PyC compounds present in complex organic mixtures in soils, sediments, aerosols, and water (Ziolkowski & Druffel 2010, Schneider et al. 2011).



**Figure 2**

The pyrogenic carbon continuum. Figure modified and updated after Hedges et al. (2000) and Masiello (2004).

Carbon isotopes represent one of the main tracers that can provide a fingerprint of the origin of PyC and indicate its longevity in the environment. The use of the stable carbon isotope composition [ $^{13}\text{C}/^{12}\text{C}$  expressed as a  $\delta^{13}\text{C}$  value relative to the international Vienna Pee Dee Belemnite (VPDB) standard] for tracing the source of PyC relies on the fact that trees use the  $\text{C}_3$  photosynthetic pathway, with  $\delta^{13}\text{C}$  values generally less than  $-24\text{‰}$ , whereas grass in tropical savanna and grasslands primarily uses the  $\text{C}_4$  photosynthetic pathway, with  $\delta^{13}\text{C}$  values generally greater than  $-15\text{‰}$  (O'Leary 1988). Randerson et al. (2005) estimated that 31% of modern global fire emissions have a  $\text{C}_4$  origin, and the  $\delta^{13}\text{C}$  value of PyC can thus provide a sensitive measure of tree versus grass sources in both modern and past environments (Bird & Cali 1998, Wurster et al. 2012). However, the discrimination of source using the stable isotope composition of carbon in PyC requires an understanding of the impact that pyrolysis may have on the  $\delta^{13}\text{C}$  value of the PyC compared with the original biomass.

Numerous studies have now suggested that the formation of PyC from  $\text{C}_3$  biomass results in comparatively small changes in the  $\delta^{13}\text{C}$  value (generally less than  $\sim 1\text{--}2\text{‰}$ ) due to preferential incorporation of biomass components, which themselves have distinct  $\delta^{13}\text{C}$  values, into the PyC, with fractionation primarily a function of temperature (e.g., Wurster et al. 2012 and references therein). In contrast, several studies have now suggested that significant decreases in  $\delta^{13}\text{C}$  values occur during the production of fine PyC (particulates  $<125\text{ }\mu\text{m}$ ) from  $\text{C}_4$  biomass (Krull et al. 2003, Das et al. 2010). Over a range of savanna environments with 30–100%  $\text{C}_4$  biomass, Saiz et al. (2014b) found that PyC was generally depleted by 2–4‰ compared with precursor biomass,

**Carbon isotope composition ( $\delta^{13}\text{C}$  value):** the ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$ , expressed as parts per thousand (per mil, ‰) deviations from a standard with a defined value of 0‰



but was depleted by up to 7‰ for fine PyC from the most C<sub>4</sub>-dominated sites. Thus, although the  $\delta^{13}\text{C}$  value can be used to infer the source of PyC, this link is not direct, and the PyC  $\delta^{13}\text{C}$  value in an environmental context will underestimate the contribution of C<sub>4</sub> biomass in most cases.

In contrast to the stable isotopes of carbon,  $^{14}\text{C}$  (radiocarbon) is an unstable isotope that decays with a half-life of 5,730 yr (Godwin 1962).  $^{14}\text{C}$  is produced in the upper atmosphere from cosmic ray spallation and is then rapidly oxidized to  $^{14}\text{CO}_2$ , distributed throughout the biosphere, and ultimately, over time, incorporated in the organic and carbonate components of soils and sediments. Natural radiocarbon can be used to date PyC from  $\sim 50,000$  yr ago to  $\sim 1960$  (e.g., Masiello & Druffel 1998, Bird 2013). Atmospheric nuclear testing in the mid-twentieth century introduced a pulse of  $^{14}\text{C}$  into the atmosphere, which is progressively also being taken up into the biosphere and provides a tracer for modern carbon in the environment. In the context of PyC, radiocarbon provides a tool that can be used from the macroscopic to the molecular level to discriminate between biosphere-derived PyC, which contains  $^{14}\text{C}$ , and fossil fuel-derived PyC and lithogenic graphite, which do not. It can also be used to estimate the residence time of PyC as it cycles through soils, sediments, aerosols, and waters (Bird & Ascough 2012, Gierga et al. 2014).

### 3. PYROGENIC CARBON IN EARTH HISTORY

As long as there has been reduced carbon at Earth's surface, sufficient atmospheric oxygen, at least periodically dry conditions, and a source of ignition, PyC has been produced in the terrestrial biosphere (Scott & Glasspool 2006, Scott et al. 2014). Evidence of the operation of a PyC cycle in the past can be found in the occurrence of PyC in the sedimentary record (Jones & Chaloner 1991). This record suggests dramatic changes in the production of PyC that can be linked to changes in the main drivers of fire activity—atmospheric oxygen, climate, vegetation, episodic catastrophic events (e.g., meteorite impacts), and, more recently, human activity.

The earliest occurrence of char in the geologic record dates from the late Silurian (420 Ma; Cressler 2001), shortly after the development of the first vascular plants and coincident with atmospheric O<sub>2</sub> content increasing beyond the minimum required to sustain combustion ( $\sim 16$ – $18.5\%$ ; Belcher et al. 2010). The production of PyC in the later Paleozoic appears to have been driven by feedbacks between increased biomass, associated with the development of extensive forests from the Late Devonian, and atmospheric O<sub>2</sub>, which peaked at levels probably  $>25\%$ , high enough to support combustion even of wet biomass. The combination of extensive peat forests, extensive burial of organic matter, and consequently high atmospheric oxygen concentrations in the Carboniferous (Berner 2006), for example, resulted in the development of major coal formations that commonly contain an average of  $\sim 18\%$  inertinite PyC derived from wildfire (Scott & Glasspool 2006).

Atmospheric oxygen probably played a significant role in controlling PyC production through the Mesozoic, with periods of potentially very low fire activity during the Early–Middle Triassic (ca. 250–240 Ma) and significantly enhanced fire activity during the Cretaceous (ca. 145–65 Ma) (Belcher et al. 2010), the latter possibly also associated with the rise of angiosperms during this period (Bond & Scott 2010, Bond & Midgley 2012). A spike in PyC abundance at the Cretaceous–Paleogene boundary (65 Ma) originally thought to have resulted from global wildfire accompanying a meteorite impact (Wolbach et al. 1988) has more recently been attributed to the combustion of hydrocarbons associated with a meteorite impact (Belcher et al. 2009), a conclusion that has itself been questioned (Premović 2012, Robertson et al. 2013).

Throughout the Cenozoic, atmospheric O<sub>2</sub> concentrations have remained near or above modern concentrations, and it is likely that the dominant control on PyC production shifted from O<sub>2</sub> to climate through control on biomass distribution and curing as well as through lightning

distribution. In comparison, the expansion of closed-canopy rainforest in the early Cenozoic may have dampened PyC production (Bond & Scott 2010). From 8 Ma, a trend toward lower atmospheric CO<sub>2</sub> followed by increasing aridity and seasonality in the later Neogene and the Quaternary promoted the expansion of pyrophilic grasslands and savannas, biomes for which fire is integral to ecosystem function and maintenance (Keeley & Rundel 2005, Edwards et al. 2010). Numerous marine and terrestrial records indicate a progressive increase in PyC abundance, and in C<sub>4</sub> grass-derived PyC, particularly since the Pliocene (e.g., Herring 1985, Jia et al. 2003, Hoetzel et al. 2013), with variations broadly associated with the glacial interglacial cycles since 2 Ma (e.g., Bird & Cali 1998, Jia et al. 2003).

The ability of humans to manipulate the PyC cycle evolved incrementally, beginning around 1 Ma with the ability to change fire frequency through the use of fire ignited by lightning (Berna et al. 2012). Before 100 ka, humans learned to make fire and thus garnered the ability to control the timing of fires. With the rise of agriculture and pastoralism in the late Pleistocene–Holocene, humans also achieved an increasing measure of control over fuel loads and connectivity (Archibald et al. 2012). Increasing human influence on the PyC cycle is evident in an increase in PyC abundance in numerous sedimentary records over the last glacial period (e.g., Kershaw 1986, Thevenon et al. 2010, Bird & Cali 1998). Since the industrial revolution, human manipulation of the PyC cycle has increased substantially through activities that either enhance (fossil fuel combustion, land clearing) or suppress (active fire management, overgrazing, landscape segmentation) PyC production (Bowman et al. 2011).

#### 4. SOURCES OF PYROGENIC CARBON IN THE MODERN ENVIRONMENT

Fires are a natural phenomenon in many ecosystems, particularly prevalent in seasonally dry savannas and grasslands, which constitute 90% and 82% of burnt area in the Northern and Southern Hemispheres, respectively (Giglio et al. 2013). Human-lit fires have also extended PyC production into areas not usually subject to burning, such as tropical rainforests and peat forests (e.g., Page et al. 2013). Giglio et al. (2013) reported an average annual burnt area of 348 Mha (1997–2011), equivalent to ~2.7% of the global land area. Millennial-scale trends in biomass burning, and hence in PyC production, suggest the complex interplay between climate and human factors. In combination, these have resulted in global biomass burning activity in the modern environment being broadly similar in magnitude to, or slightly higher than, that in preindustrial times (Marlon et al. 2008, Mooney et al. 2011), though focused in different areas and resulting from a different mix of drivers.

The PyC produced by biomass burning is partitioned into fine aerosols that disperse in the atmosphere (atmospheric PyC, or APyC) and can move far from the site of production, and coarse solid residues (residual PyC, or RPyC) that remain (initially) close to the site of production. The estimate most often quoted for global PyC production is that of Kuhlbusch & Crutzen (1996), who estimated the annual production of PyC from biomass burning at 50–270 Tg yr<sup>-1</sup>. Kuhlbusch (1998) reported 44–194 Tg yr<sup>-1</sup> as RPyC and 5–6 Tg yr<sup>-1</sup> as APyC (excluding APyC from fossil fuel combustion), whereas Forbes et al. (2006) estimated 40–241 Tg yr<sup>-1</sup> as RPyC and 6–28 Tg yr<sup>-1</sup> as APyC (including fossil fuel-derived aerosols).

Due to APyC's ability to absorb incoming solar radiation, and hence its role in modulating global climate, significant attention has been paid to determining the APyC inventory in the last decade. Bond et al. (2013) provided a summary of current source strengths for APyC. They concluded, using three inventory-modeling approaches, that average open (biomass) burning emissions total 2.8 Tg yr<sup>-1</sup>, with ~50% derived from savanna and woodland burning, ~40%

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##### Aerosol pyrogenic carbon (APyC):

thermochemically altered carbon from biomass burning or fossil fuel combustion transported through the atmosphere

##### Residual pyrogenic carbon (RPyC):

thermochemically altered carbon produced by biomass burning as particles that remain (initially) close to the site of production

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from forest and peat fires, and the remainder from agricultural waste burning. This value is significantly lower than previous estimates (e.g., Kuhlbusch 1998), but the range associated with the estimate is large (0.8–13.8 Tg yr<sup>-1</sup>). Bond et al. (2013) also reported a model-based estimate of total APyC production of 17 Tg yr<sup>-1</sup>, implying 6.2 Tg yr<sup>-1</sup> (36.6% of total emissions) of APyC from open burning. By taking the likely range of averages for biomass burning–derived APyC to be 2.8–6.2 Tg yr<sup>-1</sup> and combining that with estimates of the ratio of APyC production to RPyC production, a new estimate of global RPyC production can be developed. Combining the estimates of APyC/RPyC from Kuhlbusch et al. (1996) with more recent estimates from Saiz et al. (2014b) yields an average of 4.8% ± 3.5% (SD; *n* = 28) for the proportion of total PyC produced by biomass burning that is APyC, which in turn enables a central estimate of global RPyC production of 56–123 Tg yr<sup>-1</sup>, at the lower end of previous estimates.

In contrast to biomass burning, fossil fuel and residential fuel use produces APyC but little RPyC, and this production is dominated by environmentally recalcitrant black carbon PyC. Bond et al. (2013) estimated the total for all sources from bottom-up inventory models at 4.8 Tg yr<sup>-1</sup>, with 48% of emissions due to residential solid fuel use, 27% to diesel engines, and 14% to other sources (gasoline engines, aviation shipping, flaring, etc.). In total, these authors estimated annual APyC emissions from all sources at 6.7–8.0 Tg yr<sup>-1</sup>, but they also estimated the full range of possible emissions given all uncertainties to be 2–29 Tg yr<sup>-1</sup>. Their best inventory estimate of 7.5 Tg yr<sup>-1</sup> is lower than Jurado et al.'s (2008) 12 Tg yr<sup>-1</sup> estimate of annual PyC deposition over the oceans, which, if simply scaled to a global deposition rate by relative land-ocean area, implies a global PyC deposition rate of 17 Tg yr<sup>-1</sup>—a figure identical to Bond et al.'s (2013) modeled PyC emissions estimate.

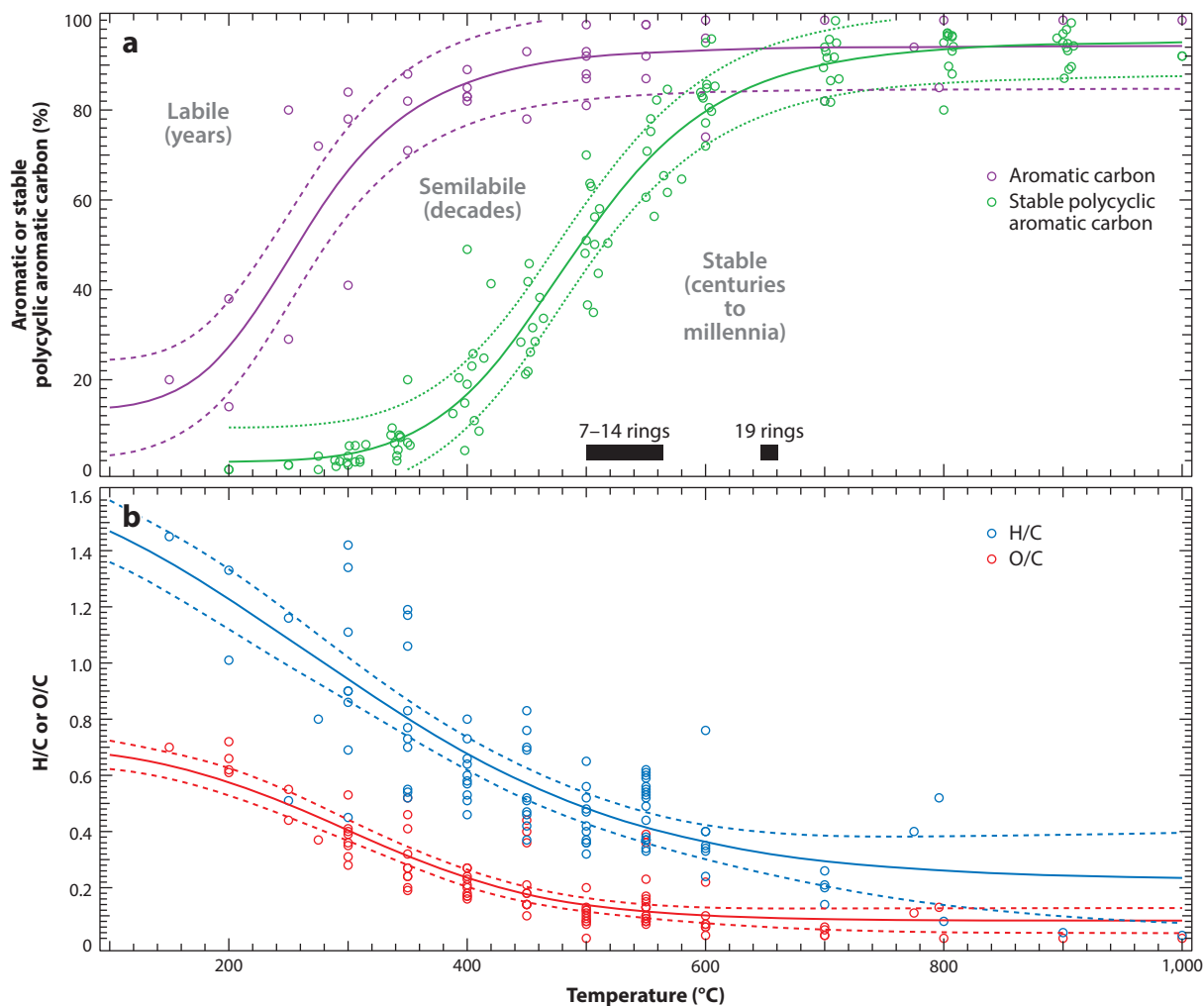
One emerging source of PyC is biochar, produced by pyrolysis of waste biomass for the purpose of carbon sequestration. Current production is negligible, but Woolf et al. (2010) estimated that if biochar production were taken up globally as a carbon sequestration tool, 110–220 Tg yr<sup>-1</sup> of PyC could be produced from waste feedstocks, a figure similar to or larger than current annual PyC production from biomass burning sources. The potential doubling of annual PyC production through biochar manufacture renders an accurate understanding of the global PyC cycle all the more urgent.

## 5. DEGRADATION AND TRANSMUTATION OF PYROGENIC CARBON IN THE MODERN ENVIRONMENT

The paradigm that PyC is an inert and environmentally recalcitrant form of carbon has been replaced over the past decade by a more nuanced understanding that PyC represents a range of materials with a range of degradation potentials by a range of mechanisms. This must be the case, as accumulation of PyC since the last glacial maximum, with no remineralization, would lead to implausible perturbations in atmospheric oxygen (Masiello & Druffel 2003).

It is therefore more appropriate to consider PyC in the context of a degradation continuum ranging from relatively degradable lightly charred materials to highly condensed aromatic materials that are indeed likely to persist in the environment for millennia (**Figure 3**). Evidence that at least a component of PyC is not inert comes from observations of loss of PyC from soils over time (Bird et al. 1999, Hammes et al. 2008), changes to the surface functionality of PyC (Cheng et al. 2006), and changes in susceptibility of environmentally exposed PyC to dissolution (Braadbaart et al. 2009, Ascough et al. 2011); from a large number of studies that have shown that PyC can support microbial respiration (e.g., Fang et al. 2014, Kuzyakov et al. 2014); from the demonstration that PyC abundance is decreased in oxic versus anoxic marine sediments (Masiello & Druffel 2003); and from the detection of molecules of original pyrogenic origin in soil humus (Haumaier





**Figure 3**

The pyrogenic carbon degradation continuum. Best-fit sigmoid regressions of the data (solid lines) and  $\pm 68\%$  confidence intervals (dashed lines) are shown. (a) Nuclear magnetic resonance (NMR) estimates of polycyclic aromatic carbon (Wang et al. 2013), hydrogen pyrolysis data from McBeath et al. (2015) and Wurster et al. (2013) defining stable polycyclic aromatic carbon, and aromatic carbon ring size estimates defined by ring current NMR (McBeath et al. 2011). The labile, semilabile, and stable zones identified on the plot are indicative only; specific sample behaviors will be biomass/feedstock and process dependent. (b) Compilation of molar H/C and O/C as a function of temperature of pyrolysis (data from Keiluweit et al. 2010, Cross & Sohi 2013, Wang et al. 2013, Whitman et al. 2013).

& Zech 1995) and a range of natural waters (Jaffé et al. 2013). The degree to which PyC is susceptible to any of these processes is dependent on the nature of the material itself (e.g., material pyrolyzed, particle size, temperature, time of pyrolysis) and local environmental conditions (e.g., soil type, land use, temperature, moisture).

Aerosol-sized soot APyC can be transported thousands of kilometers (Jurado et al. 2008), 3–50- $\mu\text{m}$  particles can be transported tens of kilometers, and 50–150- $\mu\text{m}$  particles can be transported a few kilometers (Duffin et al. 2008). Larger particles, constituting  $>91\%$  of total PyC in natural

fires (Kuhlbusch et al. 1996, Saiz et al. 2014b), remain on the ground close to the site of production. Loss of PyC can occur by several mechanisms. Chrzazvez et al. (2014) has shown that macroscopic particles fragment under compression (e.g., trampling, burial), and Braadbaart et al. (2009) have demonstrated accelerated fragmentation under alkaline conditions. This finely comminuted material is susceptible to remobilization away from the site of production by erosion or to illuviation into the soil profile (Rumpel et al. 2006, 2009; Major et al. 2010; Foereid et al. 2011); however, although such processes redistribute PyC, they do not constitute loss through remineralization.

Although recombustion of PyC by subsequent fires has been suggested as a significant remineralization process (e.g., Czimeczik et al. 2003, Kane et al. 2010), two studies have now demonstrated loss of 6.6% of prefire macroscopic charcoal for boreal forest (Santín et al. 2013) and 3.3–7.6% for tropical savanna (Saiz et al. 2014a), suggesting that recombustion does occur but is not an efficient sink for PyC. This is likely because charcoal requires sustained temperatures above 500°C in order to ignite, and these conditions are only sporadically met in many fires (Saiz et al. 2014a).

Abiotic oxidation of PyC has been reported as a result of photooxidation (Stubbins et al. 2012), oxidation by ozone (Smith & Chughtai 1997), and a range of chemical reactions to form oxidized *O*-aryl and carboxylic groups on the surface of the PyC with attendant evolution of CO<sub>2</sub> (Cheng et al. 2006, Zimmerman 2010). Microbial utilization and respiration of PyC has been directly demonstrated in numerous studies using both <sup>13</sup>C (e.g., Fang et al. 2014) and <sup>14</sup>C (e.g., Kuzyakov et al. 2014) as tracers of PyC into CO<sub>2</sub>, microbial biomass, and soil organic carbon (SOC). The available studies suggest an approximate equivalence in the significance of biotic and abiotic processes in PyC degradation, although this is likely to be highly variable and dependent, again, on PyC characteristics and environmental conditions (Cheng et al. 2006, Zimmerman 2010).

The degradation of particulate PyC (PPyC) by physical, biotic, and abiotic processes should lead to the generation of successively smaller PyC fragments and ultimately of free individual pyrogenic compounds, with all components subject to illuviation into the soil, immobilization by interactions with other soil components, and translocation by erosion or in solution (e.g., Major et al. 2010). Thus, over time, macroscopic PyC will be partly lost through remineralization and partly reduced to physical and chemical forms that are of greater environmental recalcitrance but are no longer readily identifiable as macroscopic PyC.

The rate at which PyC is remineralized to CO<sub>2</sub> by either biotic or abiotic processes, rather than transmuted into other reduced forms, is key to understanding the PyC cycle. Numerous studies have now attempted to quantify rates of mineralization of PyC from both laboratory incubations and field-based studies examining sites that have been protected from fire over known time frames (Hammes et al. 2008, Cheng & Lehmann 2009, Kuzyakov et al. 2014). Measurements of PyC abundance and age in sediments can be used to demonstrate that a proportion of PyC is not remineralized on millennial timescales (Masiello & Druffel 1998), but such measurements cannot reveal the amount of PyC remineralized prior to deposition. Field studies of PyC in soil can measure loss over time but cannot separate loss by remineralization from loss by translocation (Major et al. 2010). Laboratory studies can determine mineralization rates, but only over relatively short time frames, of years (Fang et al. 2014, Kuzyakov et al. 2014), under conditions not necessarily reflective of field conditions (Zimmerman 2010). As a result of these ambiguities, estimates of PyC remineralization rates remain poorly constrained, with mean residence times (MRTs) ranging from decades to millennia (Gurwick et al. 2013, Fang et al. 2014, Kuzyakov et al. 2014).

It is abundantly clear that the dominant control on PyC remineralization, regardless of local environmental conditions, is temperature of pyrolysis, with the stability of PyC increasing as pyrolysis temperature increases (e.g., McBeath et al. 2015). This is likely due to an increasing stable polycyclic aromatic carbon (i.e., more than seven aromatic ring clusters) component of the

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**Particulate pyrogenic carbon (PPyC):**  
thermochemically altered carbon present in the environment as a component of particulate organic carbon as particles >0.45 µm in diameter

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PyC (Wurster et al. 2013, McBeath et al. 2015). It is also likely that the time at maximum pyrolysis temperature is important up to a point, after which point no further change in PyC structure occurs. The type of material pyrolyzed may also control the stability of the PyC produced, as different organic components (e.g., lignin, cellulose, extractives) exhibit different responses to pyrolysis and potentially interact with variable ash contents in a range of ways (Nguyen & Lehmann 2009, McBeath et al. 2015).

After formation, environmental temperature (where sufficient moisture is available) is directly and positively related to CO<sub>2</sub> production from PyC (Cheng et al. 2006, Zimmermann et al. 2012). Soil conditions should also influence PyC remineralization, directly through control of moisture and oxygen availability as well as indirectly and interactively through parameters that influence the activity of microbial and fungal communities and organomineral interactions (Pietikäinen et al. 2000, Hockaday et al. 2007).

For the above reasons, identifying a simple rate constant for PyC mineralization is difficult. Nevertheless it is possible to propose a general model for PyC mineralization that reconciles the apparently contradictory observations of both PyC stability and instability in the environment. The model assumes that as well as a combustion continuum there is a PyC degradation continuum, which involves many pools, each with individual degradabilities. This complexity has previously been represented in models of soil organic matter turnover with several discrete pools (cf. Jenkinson & Rayner 1977) and for PyC can be approximated by three pools. The first pool is a small pool of labile carbon that survived pyrolysis in comparatively labile forms such as anhydrosugars and methoxylated phenols, decreasing in abundance as pyrolysis temperature increases (Kuo et al. 2011). This labile pool has been observed in incubation studies, is generally <5% of the total PyC (e.g., <1.2%; Fang et al. 2014), and has a half-life of weeks to months. The second pool is stable PyC that has been converted to polycyclic aromatic carbon with a ring size greater than seven (coronene) and can be approximated by the PyC component isolated by hydrogen pyrolysis (McBeath et al. 2015). This pool is likely highly resistant to mineralization, with a half-life measured in centuries to millennia, potentially extending to geologic timescales.

The third pool is intermediate semilabile PyC (Woolf et al. 2010, Foereid et al. 2011, Mašek et al. 2013). Here we assume this pool is approximated by the proportion of carbon that is quantifiable as polyaromatic carbon by nuclear magnetic resonance (NMR), but it is composed of small polycyclic aromatic compounds (ring size less than seven) that are degradable by microbes (Kanally & Harayama 2000). The half-life of semilabile PyC is probably in the range of years to decades. The proportion of each pool in a biochar will depend primarily on the temperature at which it formed, but also on the material that was pyrolyzed and the time over which it was pyrolyzed. The indicative size of each pool as a function of pyrolysis temperature is shown in **Figure 3**, which compiles observations of NMR aromatic carbon and hydrogen pyrolysis-determined stable polycyclic aromatic carbon as a function of temperature for a range of starting materials. The relative sizes of these pools are also reflected in the decreasing O/C and H/C ratios of the material with increasing temperature.

Most natural fires achieve temperatures of ~500°C (Wright & Bailey 1982), often for a few minutes only (Saiz et al. 2014b). **Figure 3** suggests that for this temperature PyC might be composed of around 10% labile carbon, 40% semilabile carbon, and 50% stable carbon. Below 400°C the PyC will be dominated by semilabile carbon, and above 600°C it will be dominated by stable carbon. Transmission electron microscope studies have shown that domains of semilabile, disorganized PyC are intimately associated with domains of stable, organized PyC at the sub-micrometer scale (Cohen-Ofri et al. 2006). This suggests that as labile PyC and semilabile PyC are degraded, small domains of stable PyC will be released to the environment, likely as mobile <0.45-μm particles, hence classified as dissolved PyC (DPyC).

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**Dissolved pyrogenic carbon (DPyC):** thermochemically altered carbon present in the environment as a component of dissolved organic carbon in the <0.45-μm fraction of natural waters

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Cross & Sohi (2013) and Mašek et al. (2013) employed controlled accelerated aging using a comparatively mild oxidant (0.01 M H<sub>2</sub>O<sub>2</sub>) to examine biochar stability. They found that stable carbon in biochar PyC ranged from 38% to 90% of biochar PyC made from a range of feedstocks at temperatures from 350°C to 550°C and time at maximum temperature from 20 to 80 min. Hence, labile plus semilabile PyC determined by this approach ranged from 10% to 62%, consistent with the pool sizes over the same temperature interval in **Figure 3**.

Most incubation studies have calculated PyC stability assuming a single (small) labile pool and a single (large) stable pool, but this approach may mask the significance of the intermediate semilabile pool in determining the time course of PyC remineralization. The longest-running incubation to date is the 8.5-yr incubation study by Kuzyakov et al. (2014), using PyC produced at 400°C over 13 h, which reported a single apparent half-life for stable PyC of 278 yr.

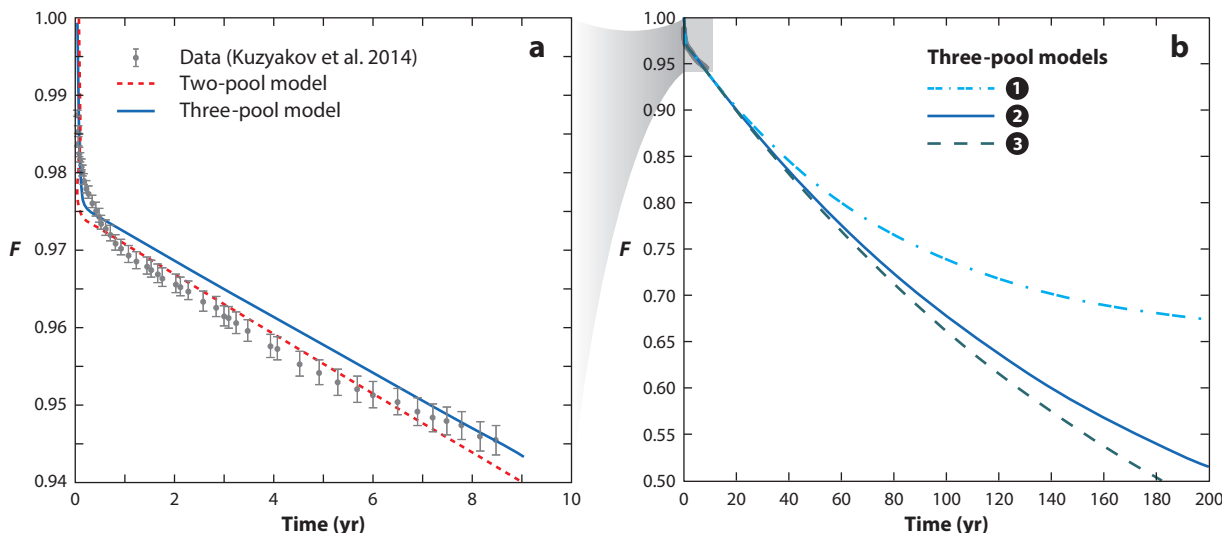
**Figure 4** compares models of multipool decomposition fit to Kuzyakov et al.'s (2014) long-term incubation data with two and three pools and illustrates that extrapolation from these long-term incubations to model predictions on millennial timescales is poorly constrained by existing data. **Figure 4a** shows that over such a short experimental time frame, the results are equally consistent with models of decomposition determined by two pools (a labile pool with  $f_l = 2.5\%$  and  $MRT_l = 13$  days, and a stable pool with  $f_s = 97.5\%$  and  $MRT_s = 248$  yr) and with any number of unconstrained three-pool models, all with similar parameters for the labile pool ( $f_l = 2.5\%$  and  $MRT_l = 13$  days). However, **Figure 4b** shows that the variation within these pools is unconstrained by the time frame of the incubation, and an equally good fit to the data may be provided by three examples of three-pool models with variable fractions of semilabile and stable pools. Clearly, the labile pool will always have a short half-life and the stable pool a very long half-life, but what determines the amount of PyC surviving to the 100-yr time frame of significance to biochar carbon sequestration is critically dependent on the proportion and half-life of the semilabile PyC pool.

The above model suggests that PyC particles will have distinct inherent degradation potentials set by the nature of the material and conditions under which the PyC is produced. The actual rate of degradation will depend on the environmental conditions where the PyC is deposited. For example, PyC produced in large quantities in tropical savannas with high year-round surface temperatures and a high fire-return interval will likely have comparatively high rates of remineralization. In contrast, PyC produced in boreal forests will likely remineralize slowly due to comparatively low average temperatures and low fire-return intervals, offset to some degree by slow mixing into the soil profile and hence longer exposure to potential recombustion (Czimczik et al. 2003). Burial in soil or sediments will likely reduce the rate of PyC mineralization.

## 6. STOCKS AND FLUXES OF PYROGENIC CARBON IN THE MODERN ENVIRONMENT

### 6.1. Pyrogenic Carbon in the Atmosphere

The total flux of APyC is 7.5–17 Tg yr<sup>-1</sup> (see above), but as the lifetime of APyC in the atmosphere is comparatively short (3.3–10.6 days; Bond et al. 2013), the stock of APyC at any one time is much smaller. Bond et al. (2013) presented a range of values for APyC column load of 0.11–0.53 mg m<sup>-2</sup>, which translates to a global average load of 0.06–0.27 Tg—equivalent to ~1–4% of the annual flux to the atmosphere. This figure is substantially lower than the 1.2-Tg atmospheric transport stock determined by Schmidt & Noack (2000).



**Figure 4**

Modeled simulations of pyrogenic carbon degradation fit to the soil data of Kuzyakov et al. (2014), assuming either two or three pools. Model curves show the fraction  $F$  remaining after time  $t$ . (a) Comparison of two- and three-pool models, both fit with least-squares regression to nonlinear exponential decay models. Each pool has a variable fraction ( $f_i$ ; total = 100%) and mean residence time (MRT). The subscripts l, s, and m denote labile, stable, and intermediate pools, respectively. Use of MRT follows that of Kuzyakov et al. (2014) and is defined for each pool as the inverse of mean decomposition rate for the pool. Best fit parameters of two-pool model are as follows:  $f_l = 2.5\%$ ,  $f_s = 97.5\%$ ,  $MRT_l = 0.035$  yr (13 days), and  $MRT_s = 248$  yr; both show an equal goodness of fit ( $R^2 = 0.94$ ). Best fit parameters of three-pooled model are underconstrained but are described in detail in panel b. (b) Comparison of three three-pool models, all fit as in panel a (the gray box shows the area depicted in panel a), with the addition of an intermediate pool. For all models,  $f_l = 2.5\%$  and  $MRT_l = 0.035$  yr, as in panel a. For model ①,  $f_s = 34\%$ ,  $MRT_s = 145$  yr,  $f_m = 63\%$ , and  $MRT_m = 100$  yr; for model ②,  $f_s = 26\%$ ,  $MRT_s = 2,069$  yr,  $f_m = 71\%$ , and  $MRT_m = 174$  yr; and for model ③,  $f_s = 87\%$ ,  $MRT_s = 172$  yr,  $f_m = 11\%$ , and  $MRT_m = 100$  yr. All three models show an equal goodness of fit ( $R^2 = 0.94$ ).

## 6.2. Pyrogenic Carbon in the Soil

The flux of PyC to the soil is dominated by RPyC from biomass burning ( $56\text{--}129 \text{ Tg yr}^{-1}$ ), with a smaller component from APyC deposited on land ( $0.6\text{--}8.4 \text{ Tg yr}^{-1}$ ), as discussed above. Soil is the major terrestrial carbon reservoir (Hiederer & Köchy 2011) and likely also represents the major terrestrial reservoir of PyC. There have been no attempts to date to estimate the amount of PyC stored in the soil, although Forbes et al. (2006) estimated that 1–35% of SOC in soil is PyC.

Preston & Schmidt (2006) reviewed estimates of PyC in soils available at that time, noting a large range of values (<1–60% of SOC) due to natural variability and to the range of techniques used in quantification, whereas Hockaday et al. (2007) concluded that PyC was generally 5–15% of SOC. Several studies have more recently widened the range of soils and biomes that have been investigated (Lehmann et al. 2008, Ohlson et al. 2009, Kane et al. 2010, Rodionov et al. 2010, Zhan et al. 2013). Some of these studies have estimated soil PyC stocks for particular regions or ecosystems. For example, Rodionov et al. (2010) estimated storage of PyC in grassland and steppe ecosystems at 4–17 Pg (top 100 cm), Ohlson et al. (2009) estimated storage in boreal forest soils at 1 Pg (macroscopic charcoal; top <20 cm), and Zhan et al. (2013) estimated storage in the soils of the loess plateau in China at 0.46 Pg (top 100 cm).

Refining an estimate for soil PyC storage is difficult, as significant uncertainty remains, primarily due to methodological differences, limited spatial coverage, and uncertainty in the variation

**Petagram (Pg):** unit of mass equivalent to  $1 \times 10^{15}$  g, or 1,000 Tg



of PyC concentration with depth in the soil. As a starting point we take the inventories of SOC aggregated according to Intergovernmental Panel on Climate Change (IPCC) climate regions by Scharlemann et al. (2014), using the Harmonized World Soil Database of SOC stocks (Hiederer & Köchy 2011) for 0–30 cm (699 Pg SOC) and 30–100 cm (497 Pg SOC). The IPCC climate regions do not map well onto biome types, but they can be related in gross terms to patterns of biomass burning (e.g., Archibald et al. 2013, Giglio et al. 2013). Based on the published estimates of the fraction of SOC that is PyC (PyC/SOC) for a range of soils and ecosystems discussed above in the assumed 0–30-cm interval,  $\text{PyC}/\text{TOC} = 0.15$  for the most flammable tropical moist and dry climate classes; 0.1 for warm/cool, temperate, moist/dry climate regions; and 0.05 for the boreal moist climate region. Although natural burning is uncommon in tropical wet/montane and boreal dry climate regions, we have assigned a nominal 0.01; these regions can burn infrequently, and they receive APyC from other regions that do burn, which accumulates in the soil over time. This yields an estimate of 54 Pg of PyC in the 0–30-cm interval.

Data for PyC abundance in the 30–100-cm depth interval are particularly sparse. PyC is clearly present in deeper soil layers (e.g., Rodionov et al. 2010, Zhan et al. 2013) and, at least in some soils, is present in proportions similar to those in the surface soil. However, in some environments, such as boreal forests, there is very little PyC in the deep soil (Czimczik et al. 2003, 2005). Here we make two endmember assumptions. First, we assume that there is no PyC in the deep soil, which is patently incorrect but allows for overestimation of the 0–30-cm inventory. Second, we assume that  $\text{PyC}/\text{SOC}$  is the same in the deep soil as in the surface soil. This is likely an overestimate, given that all PyC (unlike SOC) must enter the deep soil from the surface soil, but it allows for underestimation of the 0–30-cm inventory. On the basis of these two assumptions we calculate a total PyC inventory from 0–100 cm ranging from 54–109 Pg, or 3.8–7.7% of global SOC. Approximately 42% of this PPyC is stored in the tropical moist/dry climate zones that broadly equate to tropical woodlands, savannas, and grasslands, which cover only 25% of the land surface. A further ~42% is stored in temperate regions, covering 42% of the land surface, and ~16% is stored in the boreal zone, covering 12% of the land surface.

The loss of PPyC from the soil, as discussed in the previous sections, occurs by physical translocation (wind and water), biotic and abiotic mineralization to  $\text{CO}_2$ , or transformation into forms that can then be transported from the soil in DPyC or PPyC form. These processes likely operate at a faster rate on PPyC recently added to the soil surface, and progressively more slowly on PPyC that remains on the soil surface after the more labile components are removed and on PPyC that has been removed from the soil surface to depth.

There are no estimates of the magnitude of the remineralization flux for PyC, but it is possible to make a crude estimate. Although the MRT of PyC in hot, seasonally wet, and frequently burned areas (tropical savannas and grasslands) could be <100 yr (Bird et al. 1999, Zimmermann et al. 2012, Saiz et al. 2014a), it is unlikely that an MRT of <100 yr applies at the global scale. For PyC that has undergone significant environmental exposure and/or burial, which constitutes most of the PyC stored in soils above 1 m depth, we assume an MRT of 1,000 yr is applicable. Applying arbitrary but sensible remineralization rates of 0.01%  $\text{yr}^{-1}$  to 10% and 0.001%  $\text{yr}^{-1}$  to 90% of the terrestrial PyC stock yields a total terrestrial PyC remineralization flux of 103–207 Tg  $\text{yr}^{-1}$ , or ~0.18–0.36% of the terrestrial organic matter decomposition flux of  $\text{CO}_2$  to the atmosphere (Houghton 2007).

### 6.3. Pyrogenic Carbon in Terrestrial Sediments

Significant redistribution of soil (and therefore PPyC) occurs in the terrestrial environment as a result of natural erosion, greatly enhanced in the modern environment by human activities

associated with land clearance and agriculture (Rumpel et al. 2006, 2009). Some of this PPyC is transported to the ocean (see section 6.4), but most of it is likely buried at sites of terrestrial sediment accumulation.

Natural erosion of sediment is dominated by high fluxes from steep lands at high elevation (Wilkinson & McElroy 2007). This flux likely contains a component of lithogenic graphite (Galy et al. 2008) that most techniques will quantify as PyC but that actually contains little SOC or PPyC. Erosion related to human activities associated with land-use change (e.g., agriculture, grazing, forest clearance) amounts to  $75 \text{ Pg yr}^{-1}$  of sediment, almost entirely derived from land below 2,000 m elevation (Wilkinson & McElroy 2007). These low-altitude erosive fluxes provide the majority of remobilized SOC (Quinton et al. 2010), and therefore of PPyC as a component of SOC. Only  $\sim 20 \text{ Pg yr}^{-1}$  of the total  $96 \text{ Pg yr}^{-1}$  of eroded sediment is delivered to the ocean;  $\sim 75 \text{ Pg yr}^{-1}$  is redeposited on land, of which 80% ( $58 \text{ Pg yr}^{-1}$ ) is derived from lower elevations with soils likely to contain PPyC (Rumpel et al. 2006, 2009). Most of this erosive flux of SOC does not reach the ocean but is stored on land (Aufdenkampe et al. 2011) either locally in colluvial deposits (Hoffmann et al. 2013, Chaopricha & Marín-Spiotta 2014), in floodplain and delta sediments (e.g., Hoffmann et al. 2009), or in lakes and behind dams (Cole et al. 2007, Wilkinson & McElroy 2007). The same is probably true of PPyC.

There have been no estimates of the amount of PPyC stored in sediments on land, but using the above sediment fluxes, and assuming that the sediments contain 1% SOC of which 5–15% is PPyC, yields a crude estimate of  $29\text{--}87 \text{ Tg yr}^{-1}$  of PPyC eroded and redeposited on land. Using the farmland-only data collated by Quinton et al. (2010), who estimated the SOC flux from farmlands globally (assuming 1.4% TOC), and 5–15% PPyC yields a range of  $17.5\text{--}97.5 \text{ Tg yr}^{-1}$  for annual PPyC erosion. According to Cole et al.'s (2007) estimates of organic carbon storage in lakes and dams,  $9.5\text{--}40.5 \text{ Tg yr}^{-1}$  of eroded PPyC (around half of the total) is deposited in lakes or dams, with the rest, by difference, being deposited in colluvial or alluvial deposits.

In part, this flux represents a simple redistribution of PPyC in the terrestrial soil environment, as soil formation is ongoing on colluvial and alluvial deposits. This term is significant, however, because over time PPyC must be buried below the 100-cm soil zone, dramatically slowing its rate of degradation and/or remobilization. It is not currently possible to directly estimate the size of the terrestrial sedimentary PPyC pool, but to a first approximation it is likely to be at least equivalent to the size of the soil PPyC pool (and probably larger), given the significant quantity of sediments accumulated in internal basins, floodplains, and the landward part of deltas.

## 6.4. Fluvial Pyrogenic Carbon Transport to the Ocean

A proportion of the PPyC that is eroded from the land surface is delivered by fluvial transport to the global ocean, either directly or after a period of storage in terrestrial sediments; Druffel (2004) estimated this flux at  $20 \text{ Tg yr}^{-1}$ . Elmquist et al. (2008), using PPyC data from Arctic rivers and a compilation of other results available up to that time, suggested that PPyC represents 1.9–17% of total organic carbon (TOC) in riverine sediments and calculated an annual global flux of riverine PPyC to the oceans of  $26 \text{ Tg yr}^{-1}$ . The same authors used radiocarbon measurements to demonstrate that a significant fraction of the PPyC was derived from fossil fuel combustion or bedrock erosion or was delivered after a period of storage in soil or sediments. Only 20% of the PPyC was considered to have derived from biomass burning, but as Elmquist et al. (2008) used the aggressive CTO-375 technique (chemothermal oxidation at  $375^\circ\text{C}$ ) to quantify PPyC, this may be underestimated by up to 90% (Hammes et al. 2007). Galy et al. (2008) demonstrated that sediments derived from weathering of the Himalayas contain significant lithogenic graphite,

## PYROGENIC CARBON FROM VANISHED FORESTS

Brazil's Atlantic forests once covered over a million square kilometers, but they were cleared and burned in the nineteenth and twentieth centuries, up to about 1973, producing 200–500 Tg of pyrogenic carbon. Dittmar et al. (2012) measured dissolved pyrogenic carbon in rivers draining the former area of the Atlantic forests and found that it is still leaking from the forest soils at a rate of 0.05–0.07 Tg yr<sup>-1</sup>.

**Particulate organic carbon:** all organic carbon in a sample of soil, sediment water, or pyrogenic carbonaceous material

**Dissolved organic carbon (DOC):** all organic carbon in the <0.45- $\mu$ m fraction of natural waters

amounting to ~10% of TOC, suggesting that fossil carbon, with characteristics similar to PyC, can be present in significant quantities.

The review by Cole et al. (2007) concluded that 380–530 Tg yr<sup>-1</sup> of particulate organic carbon is delivered by rivers to the ocean. Assuming that 5–15% of this is PPyC, a flux of 19–80 Tg yr<sup>-1</sup> of PPyC is exported by rivers to the ocean. This estimate overlaps with previous estimates but extends to higher fluxes. The flux probably represents a maximum value, as a component of the PPyC delivered to the ocean is lithogenic graphite (Galy et al. 2008). However, the dominant sources of lithogenic graphite are highstanding, rapidly exhuming regions such as the Himalayas, where the apparent contribution of petrogenic graphite to TOC is high due to sparse vegetation and limited organic carbon production.

In the past decade in particular, it has been demonstrated that a component of PyC degrades to produce DPyC (Hockaday et al. 2006, Abiven et al. 2011). DPyC is a significant component of dissolved organic carbon (DOC) in many natural waters (Kim et al. 2004, Mannino & Harvey 2004), and some DPyC is comparatively labile (Norwood et al. 2013). The fact that DPyC remains a significant component of DOC even in rivers where forests were cleared and burned prior to 1973 further suggests that a component of DPyC is comparatively stable (Dittmar et al. 2012) (see sidebar, Pyrogenic Carbon from Vanished Forests). Jaffé et al. (2013) used DPyC estimates from 27 major and minor rivers to estimate the global flux of DPyC at 24.7–28.3 Tg yr<sup>-1</sup>, amounting to 10% of the global riverine DOC flux. Ziolkowski & Druffel (2010) have demonstrated using radiocarbon that DPyC from the Suwannee River is essentially modern in age (<100 yr).

### 6.5. Pyrogenic Carbon in the Global Ocean

Preceding sections have estimated the total annual amount of PyC delivered to the global ocean by direct atmospheric deposition and by fluvial transport as 50–120 Tg yr<sup>-1</sup>. The importance of different PPyC transport pathways varies between the coastal and deep ocean and with proximity to terrestrial PyC sources. Thus, rates of accession of PPyC to the ocean vary widely (Lohmann et al. 2009, Sánchez-García et al. 2013). Several studies have investigated PPyC in ocean sediments and have attempted to estimate accession of PPyC in a number of ways.

Masiello & Druffel (1998) found that PPyC was 12–31% of organic carbon at two deep ocean sites and that the PPyC component was 2,400 to 13,900 yr older than contemporaneously deposited organic carbon, indicating storage in an intermediate reservoir. Middelburg et al. (1999) reported that PPyC represented 15–30% of TOC in surface marine sediments from both the coastal and deep ocean. Both Masiello & Druffel (1998) and Middelburg et al. (1999) reported significant degradation of PyC in marine sediments under oxidizing conditions. More recently, Sánchez-García et al. (2013) reviewed several studies and found a range of mean PPyC/TOC values of 5–19%, whereas Lohmann et al. (2009) reported 3–35% for South Atlantic sediments (recognizing, again, that a range of techniques were used in these studies, introducing additional uncertainty into estimates). Dickens et al. (2004) concluded that a significant component of marine PPyC

(20–60%) may actually be lithogenic graphite derived from weathering of rocks and that the rate of burial of PyC in ocean sediments may therefore be significantly lower than implied by earlier studies.

There have been several regional estimates of PPyC sedimentation rates. For example, Sánchez-García et al. (2012) estimated that 0.97–1.3 Tg yr<sup>-1</sup> of soot PyC is deposited on the Northern European continental shelf, mostly derived from atmospheric deposition. Lohmann et al. (2009) estimated a burial flux of 0.48–0.7 Tg yr<sup>-1</sup> for the south Atlantic, with relatively more deposition close to the African and South American coastlines. Coppola et al. (2014) used benzene polycarboxylic acid analysis (which does not capture lithogenic graphite) and concluded that most PPyC is delivered to the ocean floor either in particulate form from resuspended sediments or as DPyC adsorbed onto sinking particulate organic matter.

It is likely that burial fluxes are higher in the coastal ocean than in the deep ocean, but quantification remains difficult. Coppola et al. (2014) extrapolated a PyC flux of 0.12 mg m<sup>-2</sup> day<sup>-1</sup> for one Pacific site to the global deep ocean and calculated a burial flux of 16 Tg yr<sup>-1</sup>. Lohmann et al. (2009) estimated a lower flux for the central south Atlantic, as representative of deep ocean burial, of 5 Tg yr<sup>-1</sup>. We therefore assume a range of 5–16 Tg yr<sup>-1</sup> for PPyC flux to the deep ocean. Although continental shelves make up only 7.5% of the total ocean area, fluxes to the coastal ocean are probably higher than flux to the deep ocean due to proximity to terrestrial sources. Lohmann et al. (2009) reported central African coastal fluxes of approximately twice the deep ocean flux, but still more than an order of magnitude less than fluxes determined using Northern European shelf data (Sánchez-García et al. 2012). Taking Lohmann et al.'s (2009) estimate as the likely minimum flux remote from industrial centers and Sánchez-García et al.'s (2012) estimate as the maximum flux close to industrial centers yields a range of 0.7–27.5 Tg yr<sup>-1</sup> for PyC burial on the continental shelf. Thus, the total burial flux to the ocean is estimated to be in the range of 5.7–43.5 Tg yr<sup>-1</sup>. There is a significant flux of organic carbon (dissolved and particulate) from the coastal ocean to the deep ocean, of 150–350 Tg yr<sup>-1</sup> (Bauer et al. 2013), that is likely to include PyC, but the magnitude of this flux is not known.

Kuhlbusch (1998, figure 1) estimated the stock of PPyC to be 2,000–5,000 Pg in coastal ocean sediments and 400–1,000 Pg in the deep ocean, based on the assumption that 20–50% of organic carbon in marine sediments is PPyC. Based on the more recent research presented above, PPyC/TOC in marine sediments is probably closer to 20%. If 20–60% of this lower amount actually derives from lithogenic graphite (Dickens et al. 2004), then it is more likely that PPyC stored in coastal ocean sediments amounts to 400–1,200 Pg and in deep ocean sediments amounts to 80–240 Pg. Therefore, approximately an order of magnitude more PPyC is stored in ocean sediments than is stored on land.

The global ocean contains  $662 \pm 32$  Pg C as DOC, 97% of which is considered refractory in nature, with apparent radiocarbon ages of 4,000–6,000 yr (Hansell et al. 2012). Dittmar & Koch (2006) identified a thermogenic component in marine DOC that was present as >2.4% of the total DOC pool. Dittmar & Paeng (2009) reported 2% for this component. Ziolkowski & Druffel (2010) calculated that 26–145 Pg of DOC could be DPyC, and demonstrated that this component was significantly older than bulk DOC, with apparent ages ranging from 10,400–20,100 yr.

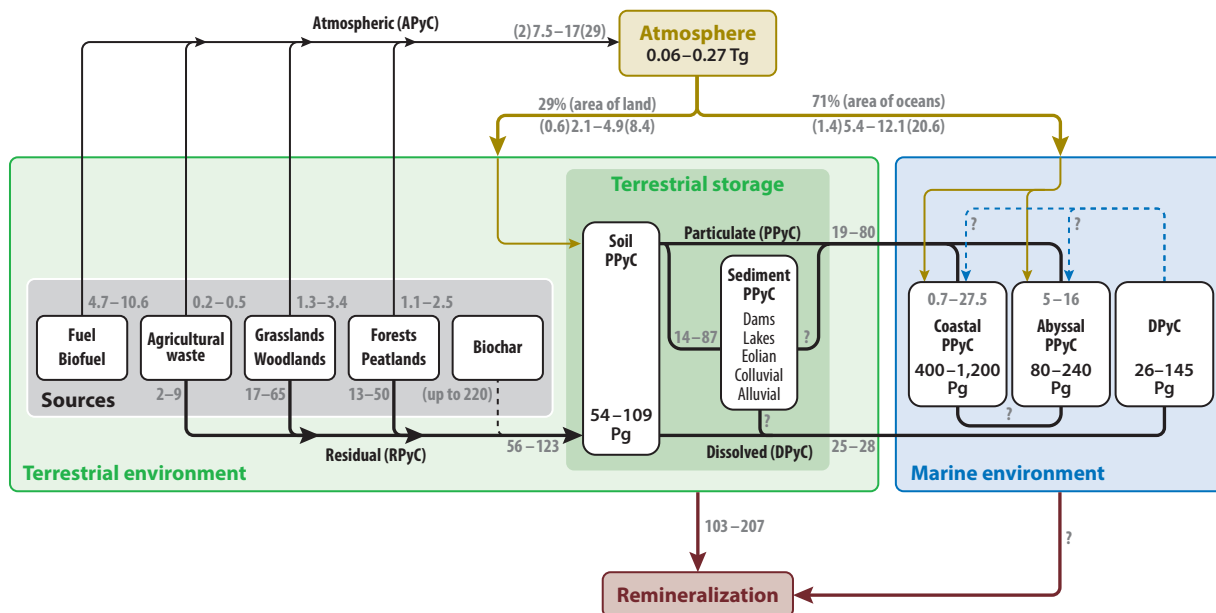
The potential origins of DPyC include the terrestrial sources discussed in preceding sections and, possibly, a component derived from thermochemical alteration of deeply buried organic carbon delivered to the deep ocean by hydrothermal vents (Dittmar & Paeng 2009). Assuming that DPyC in the ocean is derived only from riverine DPyC input suggests a residence time of 1,000–5,400 yr for DPyC in the ocean. Even with a contribution to ocean DPyC from degradation of PPyC and APyC inputs to the ocean, this is substantially younger than the apparent ages for DPyC measured by radiocarbon, suggesting a probable contribution from hydrothermal vents.

It is clear that DPyC has a very long residence time in the ocean, but that it ultimately can be removed both by adsorption to sinking particles to be buried as PPyC (Coppola et al. 2014) and by photooxidation in the surface ocean (Stubbins et al. 2012).

## 7. SUMMARY: THE MODERN PYROGENIC CARBON CYCLE

From the view that PyC is largely an inert, recalcitrant form of carbon, we have moved to a view that at least a component of PyC is dynamically involved in a range of chemical and biological processes that fundamentally alter its chemical and physical form over time and lead to its dispersal throughout the environment. This shift in thinking has been catalyzed to a large degree by interest over the past decade in the potential of PyC as a tool for long-term carbon sequestration in the soil as biochar.

The PyC produced from fossil fuel combustion may be relatively recalcitrant due to its formation at relatively high temperature. Much of the PyC in the environment is produced by natural biomass burning under a range of conditions and from a range of materials. Most PyC from biomass burning is produced at temperatures between 400°C and 600°C (Miranda et al. 1993; Saiz et al. 2014a,b). The characteristics of PyC produced over this temperature range vary dramatically, and, at the lower end of the temperature range, a significant proportion of the PyC produced is likely in the form of relatively small polycyclic aromatic compounds that are not recalcitrant. It has become clear, particularly in the past decade, that this semilabile component can be remineralized or transformed by both biotic and abiotic processes and probably has a lifetime measured in years to decades rather than centuries to millennia. All PyC is potentially subject to



**Figure 5**

The global pyrogenic carbon (PyC) cycle, showing the major sources, pathways, and reservoirs of PyC with estimates of production, storage, redistribution, and loss from the terrestrial environment, atmosphere, and oceans. Fluxes (gray text) are in Tg yr<sup>-1</sup>; stocks (black text) are in Tg or Pg, as indicated. Numbers in parentheses indicate the total range of estimates.



physical and chemical remobilization after formation, and a component becomes solubilized and is ultimately transported to comparatively long-term storage in the ocean DOC pool.

Knowledge of the size of PyC pools and fluxes of PyC between these pools remains relatively poor, due in part to the continued use of multiple methods that quantify different components of the PyC continuum as well as to the limited number of field studies. Although many estimates are little more than educated guesses based on reasonable assumptions, consideration of **Figure 5** suggests that, if these guesses are approximately correct, then the global PyC cycle is approximately in balance. Biochar production on the scale identified as possible by Woolf et al. (2010) would constitute a new and major sink of PyC.

The estimated annual inputs of APyC and RPyC to the terrestrial environment (34–128 Tg) are lower than the annual outputs of DPyC and PPyC to the ocean plus the estimated remineralization flux (147–315 Tg). It is not currently possible to isolate the cause of this mismatch. Possibly PyC production is as high as Kuhlbusch & Crutzen's (1996) estimate of 50–270 Tg yr<sup>-1</sup>, but the remineralization flux is very poorly constrained, and the PPyC flux to the ocean likely includes a component of lithogenic graphite that is currently quantified as PPyC. The estimate of PPyC and APyC delivered to the ocean (24–92 Tg) overlaps with the independent estimate of PPyC burial in the ocean (6–43 Tg), which provides a measure of confidence that these fluxes are realistic. Although this article has identified storage in terrestrial sediments as a significant long-term reservoir for PyC, it is not possible to quantify the size of this sink.

PyC is pervasively distributed throughout the atmosphere, geosphere, cryosphere (Bisiaux et al. 2012), terrestrial biosphere, and oceans in aerosols, soils, sediments, and water. As a result, it plays a significant and active role in the global carbon cycle.

## SUMMARY POINTS

1. PyC is best conceptualized as a continuum of thermochemically altered organic matter, from lightly charred to highly condensed polycyclic aromatic materials, present in the environment in forms that range from macroscopic char fragments to micrometer-sized soot particles to individual compounds of pyrogenic origin.
2. The PyC continuum is also a degradation continuum of labile, semilabile, and stable components; the proportion of each depends primarily on the temperature of formation and the nature of the precursor material, with only the stable component likely to survive environmental exposure under surficial conditions for centuries to millennia.
3. PyC can undergo a range of physical and chemical, biotic, and abiotic interactions and transformations after formation, leading to remineralization and/or to the physical disintegration and translocation of PyC in both particulate and dissolved form.
4. The major sources of PyC are biomass burning and fossil fuel combustion, which deliver 7.5–17 Tg yr<sup>-1</sup> to the atmosphere as fine aerosols and 56–123 Tg yr<sup>-1</sup> to the soil surface as char.
5. PyC is transported from the land to the ocean in particulate (19–80 Tg yr<sup>-1</sup>) and dissolved (25–28 Tg yr<sup>-1</sup>) form; the remineralization flux from PyC on land is estimated at 103–207 Tg yr<sup>-1</sup>.
6. The major pools of PyC are ocean sediments (480–1,440 Pg), marine dissolved organic carbon (26–145 Pg), and soils (54–109 Pg), plus an additional pool in terrestrial sediments for which no estimate of size is available.

## FUTURE ISSUES

1. Although considerable progress has been made in comparing and benchmarking methodologies for PyC analysis, there is an ongoing need to standardize protocols within individual methods and to more precisely identify the analytical windows of different methodologies to facilitate comparison.
2. As the sizes of many PyC pools and fluxes are constrained by comparatively few data, there is a need for further field investigations of PyC production during biomass burning as well as of the abundance of PyC in a broader range of soils, sediments, and waters.
3. There is a need to develop techniques that can separately determine the proportions and residence times of labile, semilabile, and stable components of individual samples of PyC as well as differentiate PyC from lithogenic graphite.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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First field demonstration of rapid PyC degradation in the environment.

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Comprehensive assessment of black carbon PyC in the atmosphere.

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Assessment of dissolved PyC transport to the oceans.

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First attempt to construct a global PyC budget.

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Longest-running PyC degradation study by incubation.

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Benchmark review of research on PyC to 2000.

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Comprehensive assessment of biochar PyC for carbon sequestration.

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## RELATED RESOURCES

Global fire emissions database: <http://www.globalfiredata.org>

NASA animation of global distribution of active fires by month from 2000 to 2014: [http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MOD14A1\\_M\\_FIRE](http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MOD14A1_M_FIRE)

NASA animation of aerosol optical depth, showing relationship to fire: [http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MOD14A1\\_M\\_FIRE&d2=MODAL2\\_M\\_AER\\_OD](http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MOD14A1_M_FIRE&d2=MODAL2_M_AER_OD)

NASA's 2013 Reel Science Communications program video outlining the role of biomass burning in the modern environment: [https://www.youtube.com/watch?v=\\_SujP8jInac](https://www.youtube.com/watch?v=_SujP8jInac)