



Trial by Fire: On the Terminology and Methods Used in Pyrogenic Organic Carbon Research

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Our understanding of the cycling of fire-derived, i.e., pyrogenic organic matter (pyOM), as well as the goals of the community of researchers who study it, may be inhibited by the many terms and methods currently used in its quantification and characterization. Terms currently used for pyOM have evolved by convention, but are often poorly defined. Further, each of the different methods now used to quantify solid and dissolved pyrogenic carbon (pyC) comes with its own biases and artifacts. That is, each detects only a fraction of the total pyrogenic products produced by fire, while, at the same time, include some fraction of non-pyrolytic OM. This may be evident in the commonly observed correlations between pyC and total organic C reported for both soils and dissolved OM in many different systems. We suggest that our research area can be placed on a stronger footing by: (1) agreement upon a common set of terms tied to the method used for detection (e.g., of the form pyC_{method}), (2) implementation of another “ring trial” study with a wider set of natural soil and water samples that cross-compare more recently developed methods, and (3) further investigation of the processes which preserve/degrade/transport pyOM in the environment.

Keywords: pyrogenic carbon, black carbon, quantification, artifacts, biochar, ring trial

INTRODUCTION

The understanding that fire and pyrogenic organic matter (pyOM) have contributed to shaping Earth's biosphere is one that has evolved within a number of disparate fields including geology, ecology, atmosphere science, agriculture/soil science, and anthropology. In each field, this realization, along with associated terminology and methodology, has tended to evolve separately, with limited cross-disciplinary communication. Humans have been using pyOM in industry (charcoal used in the smelting of copper as early as 5,000 BCE) and medicine for thousands of years (Scott and Damblon, 2010). However, formal research into charcoal's properties began as early as the beginning of the twentieth century (e.g., Hedin, 1907; Sweetser, 1908; Homfray, 1910). Charcoal was noted in soils even earlier (e.g., Heer, 1866; Fliche, 1907; Godwin and Tansley, 1941), but was not treated quantitatively and used as an indicator of past vegetation and human settlement by paleoecologists and archeologists, respectively, until much later (Western, 1963; Camps, 1971). Detection and quantification of charcoal in marine and lake sediments led to the first use of pyOM as a proxy for past fire-frequency and climate in the 1970's (Smith et al., 1973; Herring, 1976; Swain, 1978), though there was some debate at this time as to its pyrogenic origin (Schopf, 1975).

Consideration of the pyrogenic component of aerosols and the development of the first instrument to measure aerosol soot concentrations (Thomas, 1952) was sparked by the “London fog” of December 1952 which killed at least 4,000 (Wilkins, 1954). The dark color of the filters used to collect the “soot” derived from coal-burning led to use of the term “black carbon” (BC) within the field of atmospheric chemistry (e.g., Novakov, 1981, 1984; Gundel et al., 1984). Novakov (1981, 1984) defined BC as “combustion-produced black particulate carbon having a graphitic microstructure” and soon, the term “BC” was applied more broadly to pyOM in both its atmospheric and geological forms (Goldberg, 1985). However, the term “elemental carbon,” reflecting its C-rich character, was and is still also widely used by the atmospheric community, which has largely been concerned with its light absorption and associated direct radiative forcing of Earth’s climate (Bond et al., 2004). Although there have been quite a few inter-laboratory comparisons of methods used to quantify aerosol BC (e.g., Countess, 1990; Birch, 1998; Hitzenberger et al., 1999, 2006; Schmid et al., 2001; ten Brink et al., 2004), there is still no universally accepted method for isolating aerosol pyOM (discussed further in next section).

Awareness of elevated atmosphere CO₂ and other atmosphere greenhouse gas concentrations in the 1970’s led to consideration of the role of fire in the global C cycle. The first estimate of global biomass burning and charcoal production, 500–700 Tg yr⁻¹ (Seiler and Crutzen, 1980) was an attempt to balance the poor match between C inputs to the atmosphere with known removal mechanisms. This estimate was since revised downward and is now generally agreed to be in the range of 50–300 Tg yr⁻¹ (Kuhlbusch and Crutzen, 1996; Forbes et al., 2006; Bird et al., 2015; Santin et al., 2016). Another turning point in geochemists’ understanding of pyOM was the “BC combustion continuum” first proposed by Hedges et al. (2000) and Schmidt and Noack (2000) and later elaborated upon by others (Masiello, 2004; Elmquist et al., 2006; Preston and Schmidt, 2006). It maintained that pyOM is composed of a wide range of materials from slightly charred biomass to highly condensed graphite and soot. With this “continuum perspective” came the wider recognition that pyOM cannot be wholly refractory, but is degraded to different extents through a variety of abiotic and microbially-enhanced processes.

A call to compare methods used to quantify pyrogenic carbon (pyC) in soils and sediments, which requires the use of techniques different from those used in atmospheric sciences due to the presence of interfering matrices, came at much the same time. The first method comparison efforts examined a limited range of sample types (Currie et al., 2002) or resulted in widely ranging values for individual samples (Schmidt et al., 2001). Thus, a “Steering Committee for Black Carbon Reference Materials” was established and recommended a larger set of pyrogenic and non-pyrogenic test materials (Schmidt et al., 2003). The resulting comprehensive evaluation of pyC quantification methods (Hammes et al., 2007), the so called “BC ring trial,” made it clear that each analytical method is selective for a different part of the pyOM continuum.

At the same time that soil scientists and agronomists were realizing the potential of soil amendments of pyC to enhance soil fertility and mitigate climate change through C sequestration

(Lehmann et al., 2002; Lehmann, 2007a,b), environmental scientists identified substantial amounts of pyC in an ever-widening range of settings including river water (Ding et al., 2013; Jaffe et al., 2013), marshes (Dittmar et al., 2012b) and the ocean (Dittmar, 2008; Stubbins et al., 2010; Ziolkowski and Druffel, 2010). However, all of these pursuits require the ability to accurately quantify pyC and to track the chemical evolution and transport of pyOM in the environment.

PYROGENIC SUBSTANCES QUANTIFICATION METHODS

The methods used to quantify pyC vary widely in their cost, ease of application, and unfortunately, in the pyOM fraction that they target. These methods can be categorized as those that rely on pyOM detection of: (1) morphology, (2) light absorption, (3) thermal or chemical stability, and (4) chemical composition. Archeologists and some geoscientists commonly use light microscopy and particle morphology to count the number and size of charcoal particles (e.g., Smith et al., 1975; Figueiral and Mosbrugger, 2000; Scott and Damblon, 2010). However, these methods cannot quantify pyC and are biased toward detection of particles of larger sizes (Masiello, 2004; Crawford and Belcher, 2016). Atmospheric scientists quantify pyC using optical techniques (Rosen and Novakov, 1977), thermal heating combined with optical methods, or laser-induced incandescence (Watson et al., 2005; for a historical perspective, see Novakov and Rosen, 2013). While many of these methods are subject to interferences introduced during mixing of combustion-derived aerosols with non-pyrogenic OM (Bond et al., 2013), quantification of pyC in soil or sedimentary matrices is even more difficult due to the even greater presence of minerals and complex non-pyrogenic geopolymers. To cope with this, many approaches assume pyOM to be the most refractory OM fraction. Thus, different thermal and/or chemical oxidation techniques (e.g., CTO-375, dichromate oxidation, UV oxidation, catalytic hydrogen pyrolysis (hy-py) have been used to remove more labile OM and assume the residual to be pyOM (e.g., Lim and Cachier, 1996; Gustafsson et al., 1997, 2001; Thevenon et al., 2010).

A final group of methods identify pyOM using some aspect of its chemical structure. The abundance of both levoglucosan, an anhydrous sugar formed during cellulose combustion (Elias et al., 2001; Kuo et al., 2008), and benzenepolycarboxylic acids (BPCAs) which are formed via nitric acid oxidation (Glaser et al., 1998; Brodowski et al., 2005; Dittmar, 2008) have been used as chemical markers for lower temperature charred OM and condensed aromatic C, respectively. Another technique infers the pyC content of a sample using the sorptive characteristics of pyrene onto the sample (Flores-Cervantes et al., 2009a,b). Spectroscopic tools such as ¹³C-nuclear magnetic resonance (NMR) and mid-infrared (MIR) spectroscopy provide information on the structure and chemical bonds of OM present in a material. In the case of NMR, it is generally aromatic C that is quantified and associated with pyC (Simpson and Hatcher, 2004; Nelson and Baldock, 2005), though specialized techniques have been

developed to estimate the condensed aromatic fraction (Knicker et al., 2005; McBeath et al., 2011). Though MIR also examines a sample's spectral characteristics, it requires calibration using one of the other pyC methods in order to be quantitative (Janik et al., 2007; Bornemann et al., 2008; Cotrufo et al., 2016). More detailed reviews of methods used to quantify pyC can be found elsewhere (Meredith et al., 2012; Bird et al., 2015).

PROBLEMS AND PERPLEXITIES

While the methods used to study pyOM production and cycling have advanced greatly in the last decade, we believe that there are still terminology, methodology/conceptual impediments to further progress that urgently need to be addressed. This inhibits both research funding opportunities and implementation of the fire-science community findings and recommendations, be they in settings of agriculture, policy, or climate/geochemical model incorporation.

Terminology Issues

From the discussion above, it should be clear that different fire research sub-communities have adopted various terms for pyOM or pyOM fractions, often for historical reasons only. Confusion arises because these terms are often not associated with specific definitions, or because terms have been adopted across research community boundaries without regard for their original narrow definitions. For example, the atmospheric community refers to BC as combustion-generated aerosols that absorb visible light, are insoluble in water, and exist as aggregates of carbon spherules (Novakov, 1984; Bond et al., 2013). On the other hand, BC has come to be used by many as shorthand for pyrogenic C of all forms. The term "dissolved black carbon" conflicts with the atmospheric community's definition that BC should not be soluble in water. Organic compounds detected in the aqueous fraction of combustion-derived aerosols are typically referred to by the atmospheric community as water soluble organic carbon (Decesari et al., 2000; Mayol-Bracero et al., 2002). In the past, soot was defined as the total carbonaceous material produced by combustion (Novakov, 1984). However, for others, soot is the condensate of combustion gases and has graphitic structure (Hammes et al., 2007). The materials referred to as charcoal, biochar, and agrichar may all be the same, or somewhat different (Lehmann and Joseph, 2015). While it is understood that different analytical methods target different pyC fractions, there is as yet no consistent method or property-based terminology applied across different research communities. This lack of consistency may inhibit cross-disciplinary communication and fertilization of new concepts.

Methodology/Conceptual Issues

Several methodological issues and recent observations should cause us to question our ability to quantify the amount of pyOM (or pyC) in natural samples. The first issue is that many of these methods require a "*conversion factor*" of some type to transform measured parameters such as a post-treatment residue weight or compound abundance to an amount of pyOM or pyC present in a sample. For example, a conversion factor has been calculated based on theoretical BPCA yields of organic

structures of marine DOM observed via ultrahigh-resolution mass spectrometry (about 3, Dittmar, 2008; Stubbins et al., 2012) or from the BPCA yields of various aromatic substances including activated C (2.27, Glaser et al., 1998) PAHs, soot and C nanotubes (about 4, Ziolkowski et al., 2011). However, application of any single BPCA conversion factor to a variety of pyOM types has been called into question (Brodowski et al., 2005). For the dichromate oxidation procedure, a correction factor derived from the residual yield of plant char oxidation was used to account for pyC losses during the chemical treatment (Knicker et al., 2008). A degree of uncertainty has been generated in the fire science community because of the variety and range of conversion and correction factors used, even within specific analytical methods.

The second issue is that pyC can be falsely identified as non-pyC and vice versa. Underestimates in pyC quantification certainly occur because not all pyC is recalcitrant or purely condensed aromatic, as assumed by most analytical methods (e.g., Bostick et al., this issue, Nguyen and Lehmann, 2009; Zimmerman, 2010; Singh et al., 2012). Some portion of pyC is likely destroyed in the harsh thermal and chemical oxidation steps used. Overestimates can occur in a number of ways. Not all non-pyC is removed by thermal/chemical oxidation steps (e.g., Knicker et al., 2007). Oxidative treatments can even generate apparently "pyrogenic" OM (e.g., Derenne and Largeau, 2001; Hammes et al., 2007; Novakov and Rosen, 2013). This has been shown to occur, for example, during the oxidation required to form BPCA compounds (Brodowski et al., 2005; Kappenberg et al., 2016) as well as in steps used to remove non-pyrolytic aromatic C prior to NMR analysis (Simpson and Hatcher, 2004). Other NMR quantification approaches use spectral editing or molecular mixing models to separate condensed aromatic from non-condensed aromatic biomolecules, both of which require assumptions or corrections that have not been fully validated (Cusack et al., 2012; Paetsch et al., 2017). Light absorption-based methods used mainly by atmosphere chemists suffer from uncertainties related to non-linearities in the light attenuation coefficient which vary with filter loading and particle type, as well as to interferences from non-pyrolytic OM (reviewed in Kirchstetter and Novakov, 2007).

Light absorption, BPCA and some NMR quantification techniques use the assumption that only pyOM, takes the form of condensed aromatics structures. But increasingly, this has been shown not to be the case. For instance, melanoidins, several plants, fungi and pigments yielded quantities of BPCAs (even highly-carboxylated BPCAs which are indicative of very condensed aromatic OM) like that of charred plant material (Brodowski et al., 2005; Glaser and Knorr, 2008). These may be derived from lignin or tannin, which include a wide variety of polycondensed aromatics (Hernes and Hedges, 2000; Waggoner et al., 2015). Other non-pyrolytic OM sources of condensed aromatic OM are abundant in the geosphere, including woody peat, coal, kerogen, and oil (Yoshioka and Ishiwatari, 2005; Hammes et al., 2007; Wang et al., 2012; Hartman et al., 2015; Li et al., 2017). Still other studies have found that non-pyrolytic OM can be readily transformed to condensed aromatic OM, which would appear to be pyrolytic, through photolytic,

microbial, or chemical degradative processes (Glaser and Knorr, 2008; Chen et al., 2014; Waggoner et al., 2015; DiDonato et al., 2016).

Given that we are finding ever more ways in which pyOM can cross the analytical window into non-pyOM and vice versa, it is perhaps not surprising that many have observed correlations between pyC and total C concentrations in soils regionally (Glaser and Amelung, 2003; Jauss et al., 2015; Ahmed et al., 2017; Qi et al., 2017) and globally (Reisser et al., 2016), and dissolved in natural waters regionally (Dittmar et al., 2012a; Ding et al., 2013, 2014, 2015; Guerena et al., 2015) and globally (Jaffe et al., 2013; Wagner et al., 2015) and even in aqueous leachates of marine aerosols (Bao et al., 2017). These correlations indicate, as do other more detailed statistical examinations (in the same studies), a lack of dependence of pyC concentrations on fire history or climate. A plot of data compiled by a recent literature review (Reisser et al., 2016) shows a significant relationship between pyC and total C in global soils across all quantification methods and within each method (except CTO-375, **Figure 1**). The strongest correlations are found for data derived from BPCA and NMR, suggesting that these methods may have the greatest likelihood for artifacts that misidentify pyC. Alternatively, the finding of correlation between pyC and total C regardless of the analytical method used, might suggest the relationship is present in nature. That is, production, degradation/preservation or mobilization processes may act on pyC and non-pyC in ways that cause them to co-vary. For example, regions of higher productivity, thus higher soil C, also have more biomass to burn and are therefore likely to have greater pyC in soils and drainage waters (Alexis et al., 2007; van Leeuwen et al., 2014). Soils with greater amounts of clay or metal oxide mineral or even charcoals, are likely to sorb and therefore protect both pyOM and non-pyOM from microbial mineralization through sorptive protection (Kasozi et al., 2010; Zimmerman et al., 2011) or aggregate stabilization (Wang et al., 2017). And soil translocation, erosion, leaching, and other hydrologic/climatic-related processes of a region are likely to act to mobilize both pyOM and non-pyOM in similar ways (Hilscher and Knicker, 2011; Jien and Wang, 2013), though not necessarily to equal extents (Rumpel et al., 2009). Finally, it has been suggested that pyC mobilization may occur via association with other OM in dissolved (Jaffe et al., 2013) or perhaps colloidal (Zand and Grathwohl, 2016; Kumari et al., 2017) form, but the controlling mechanisms are still unknown (Wagner et al., 2017).

RECOMMENDATIONS

Despite, or possibly even because of the many issues facing the pyC cycling research community, we may be on the brink of making great advances in this field, but only if these issues are acknowledged and dealt with. First, we suggest more stringent use of terminology. The terms “pyOM” or “pyC” should be used when referring to the totality of fire-derived carbonaceous substances. These terms represent the broadest short forms for the total substance of pyrogenic origin and the carbon in these substances, respectively. When reporting analytical results, we suggest that terms tied to the method or properties used

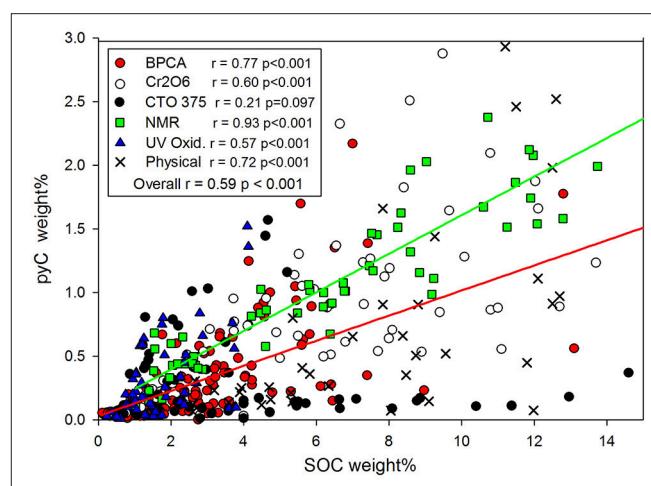


FIGURE 1 | Relationships between total soil organic carbon (SOC) and pyrogenic carbon (pyC) as determined by different methods. Pearson linear correlation coefficients (r) and levels of significance (p) are given in the legend. Data are taken from Reisser et al. (2016), a compilation of results of global soil data from 55 studies.

for detection should be used. For greatest clarity, we these terms could take the form “ $\text{pyC}_{\text{method}}$ ” (**Figure 2**). For example, substances quantified via light microscopy might be referred to as pyC_{mic} . Substances isolated based on their chemical or thermal resistance could be designated pyC_{CTR} . The term “ pyC_{LE} ” should be used for substances detected based upon their near complete light extinction properties, but failing to convince the mainly atmospheric community of this, we suggest that terrestrial and aquatic scientists leave the term “black carbon” to them. Use of these terms will serve as continuous reminder that a quantity of C refers only to a portion of the substances produced by fires and may even contain a non-pyrogenic portion.

Regarding the potential for analytical artifacts that plague pyC cycling research, we recommend, first, that another “ring trial” study be conducted so that techniques that have been developed since the last ring trial (such as MIR spectroscopy and catalytic hydrogen pyrolysis and improvements in NMR and BPCA analytical methods) can be compared and their relative strengths and weaknesses re-evaluated. This ring study should include not just geochemists, but also those that study pyOM from the anthropology, atmosphere and agriculture communities. Moreover, the new ring trial should also make use of modern analytical techniques that can deconvolve composition of pyOM at unprecedented levels (e.g., aerosol mass spectrometer, Fourier transform ion cyclotron resonance mass spectrometer). In addition to the set of pyrogenic and “potentially interfering” materials included in the first ring trial (Hammes et al., 2007), this new ring trial should include a biochar thermal series, which would be expected to have a regularly increasing degree of aromatic condensation (Cao et al., 2012). Furthermore, we recommend a broader set of atmosphere-derived samples such as the diesel soot standard (NIST

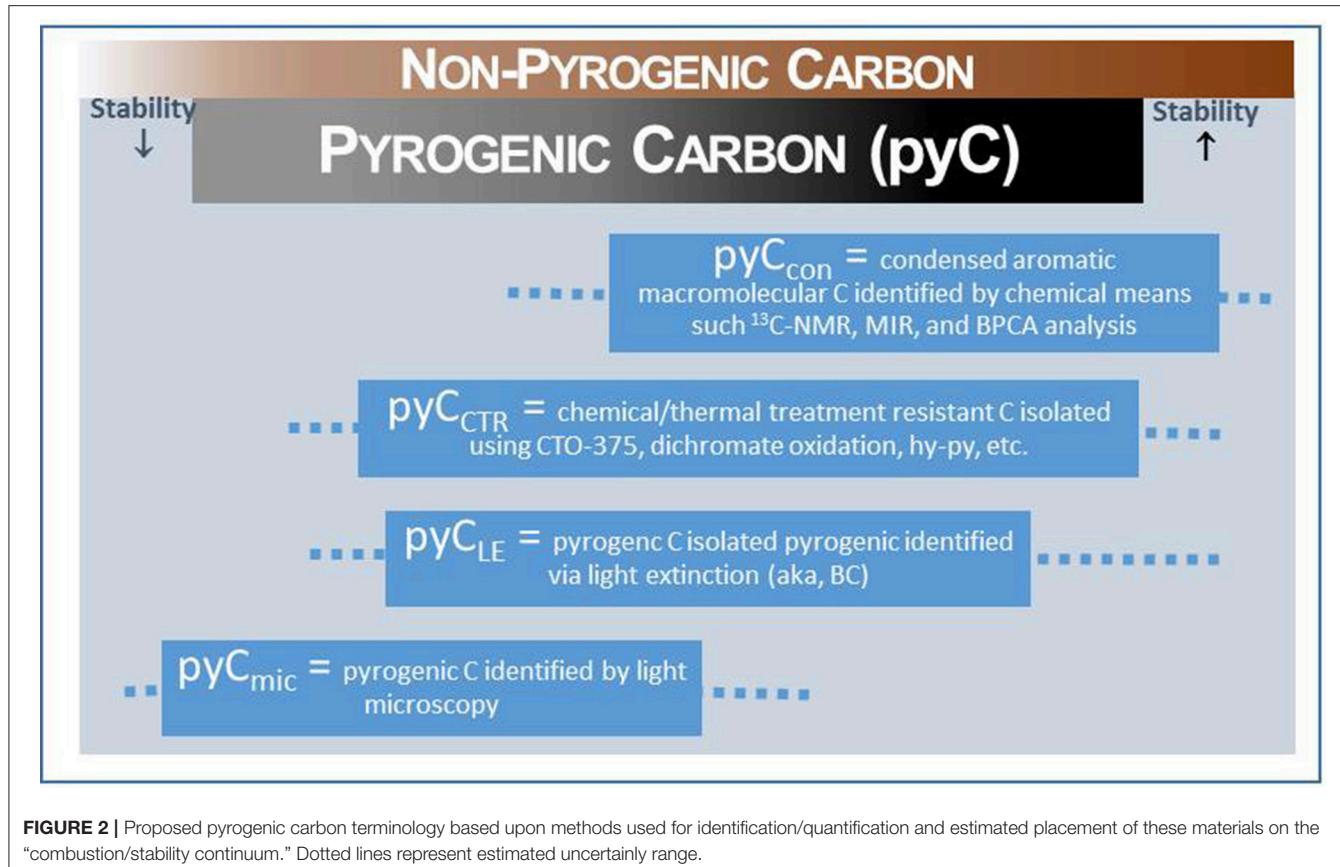


FIGURE 2 | Proposed pyrogenic carbon terminology based upon methods used for identification/quantification and estimated placement of these materials on the “combustion/stability continuum.” Dotted lines represent estimated uncertainly range.

SRM 2975) and aqueous samples (preferably not freeze-dried) isolated from river and ocean water. Additional non-pyrogenic materials such as wood biomass, leachate from this biomass, and photodegraded biomass leachate should also be considered for analyses. To evaluate matrix effects associated with each method, a standard addition experiment should be added to the method intercomparison, whereby different amounts of a pyOM, such as wood char, are added to a soil-like mixture containing no pyOM. This ring trial should be followed up not only with a report of results, but with a best-practices paper that includes consensus recommendations for use of terminology.

Until now, the focus of many fire science studies has been to establish properties of pyrogenic substances and their inventories in different systems. Given the major question of the cause of the often-observed pyC/TOC correlation, a greater focus should be placed on studies that compare transformation and movement of pyrogenic relative to different types of non-pyrogenic substances. Mechanistic pyOM investigations are needed to understand both preservation processes such as adsorption, metal-complexation and aggregate formation, and transformation processes such as solubilization, volatilization, and microbial, chemical and photo-degradation. In addition, pyC mobilization studies should focus not just on particle movement in soil via translocation and erosion, but transport in aerosol, colloid, and dissolved forms

via atmosphere and aqueous processes. We hope this comment stimulates greater dialog between research communities that study various aspects of pyrogenic substances. The desired result would be not only a more complete understanding of the production and cycling of pyC, but also a greater application of these insights in such areas as agriculture and climate modeling.

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

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