

**Constraints and Drivers of Dissolved Fluxes of Pyrogenic Carbon in Soil and Freshwater Systems: a
Global Review and Meta-analysis**

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Key Points:

- Burn intensity of pyrogenic carbon (PyC) controls its dissolution and aqueous transport.
- From headwater streams to oceans, dissolved PyC increases in radiocarbon age, implying environmental persistence.
- Environmental controls, including climate, topography, biota, parent material, and time impact the pool size and flux of dissolved PyC.

Abstract

Pyrogenic carbon (PyC) is a significant component of the global soil carbon pool due to its longer environmental persistence than other soil organic matter components. Despite PyC's persistence in soil, recent work has indicated that it is susceptible to loss processes such as mineralization and leaching, with the significance and magnitude of these largely unknown at the hillslope and watershed scale. We present a review of the work concerning dissolved PyC transport in soil and freshwater. Our analysis found the primary environmental controls on dissolved PyC (dPyC) transport are the formation conditions and quality of the PyC itself, with longer and higher temperature charring conditions leading to less transport of dPyC. While correlations between dPyC and dissolved organic carbon in rivers and other pools are frequently reported, the slope of these correlations was pool-dependent (i.e., soil-water, precipitation, lakes, streams, rivers), suggesting site-specific environmental controls. However, the lack of consistency in analytical techniques and sample preparation remains a major challenge to quantifying environmental controls on dPyC fluxes. We propose that future research should focus on the following: (1) consistency in methodological approaches, (2) more quantitative measures of dPyC in pools and fluxes from soils to streams, (3) turnover times of dPyC in soils and aquatic systems, and (4) improved understanding of how mechanisms controlling the fate of dPyC in dynamic post-fire landscapes interact. With more refined quantitative information about the controls on dPyC transport at the hillslope and landscape scale, we can increase the accuracy and utility of global carbon models.

1. Introduction

1.1 Significance of dissolved pyrogenic carbon in the global C cycle

Wildfire is a major ecosystem disturbance that has been progressively getting more severe and intense in many areas of the world ([Descals et al., 2022](#); [Feurdean et al., 2020](#); [Turco et al., 2018](#); [Westerling et al., 2006](#)). Additionally, significant increases in the use of prescribed fire have been observed across the US in the past few decades, especially in the southeast ([Kolden, 2019](#)). Natural and anthropogenic fires transform carbon (C) into a range of materials across the burn continuum including lightly charred material to charcoal, soot, and ash, collectively known as pyrogenic carbon, or PyC ([Bird et al., 2015](#); [Masiello, 2004](#)). This PyC is initially deposited on the soil surface and emitted to the atmosphere. Pyrogenic C has received considerable research attention over the past decades due to its generally longer persistence times in soil relative to other soil organic matter components, which has implications for C storage ([Abney and Berhe, 2018](#); [Bird et al., 2015](#); [Santín et al., 2016](#)).

There has been limited research synthesizing the production, pools, and fluxes of PyC across large spatial scales ([Coppola et al., 2022](#); [Wagner et al., 2018](#)) to better constrain the role of PyC in the global C cycle. It has been estimated that approximately 2.7% of the global land area is burned annually ([Giglio et al., 2013](#)), resulting in 50-270 Tg y⁻¹ of PyC produced ([Kuhlbusch and Crutzen, 1995](#)). At a global scale, PyC can account for a significant portion (~10%) of dissolved organic carbon (DOC) fluxes in rivers ([Jaffé et al., 2013](#); [Wagner et al., 2018](#)). The global annual transport of particulate PyC from rivers into oceans ranges from 19-80 Tg/yr ([Druffel, 2004](#); [Elmquist et al., 2008](#); [Jaffé et al., 2013](#)), although this is most frequently reported as 26-27 Tg/yr ([Elmquist et al., 2008](#); [Jaffé et al., 2013](#)). However, current estimates of dPyC

export from terrestrial to inland aquatic systems range over several orders of magnitude, from ~0.4-18 Tg/yr ([Bowring et al., 2022](#); [Jones et al., 2020](#)), likely reflecting both the variability in processes (e.g., decomposition, photooxidation, water availability, etc.) influencing PyC dynamics at the terrestrial-aquatic interface and insufficient PyC measurements.

While parameterization of global PyC models typically includes annual production, stocks, large-scale fluxes, and some smaller-scale controls (i.e., decomposition ([Bird et al., 2015](#); [Reisser et al., 2016](#); [Santín et al., 2016](#)), several critical knowledge gaps remain regarding what controls those fluxes, especially at smaller scales. In particular, we need a more detailed understanding of how PyC is transported from source burned material into the soil system, across hillslopes and watersheds, and into aquatic environments ([Myers-Pigg et al., 2015](#); [Wagner et al., 2019c](#); [Wagner et al., 2015b](#)). Some recent research has demonstrated inconsistencies between the sources and ages of dPyC flowing from rivers and those from PyC measured in the ocean ([Wagner et al., 2019b](#)), which indicates limitations in our mechanistic understanding of (1) the cycling of dPyC within terrestrial systems, (2) cycling within freshwater aquatic systems, and (3) connections between terrestrial and aquatic systems. This paper addresses this limitation by synthesizing our current knowledge of dPyC fluxes and the processes that control its transformation within and between terrestrial and aquatic ecosystems to inform research communities involved in management, modeling, and description of PyC.

1.2 Aims

The aim of this paper is two-fold. The first aim is to conduct a meta-analysis of available primary literature on dPyC to synthesize the state of knowledge of pools and fluxes in soils and freshwater systems. We use the meta-analysis to quantify methodological differences in measurements of dPyC and examine whether they confound our understanding of reported dPyC fluxes. We also assess the interactive effects of precursor material, burn conditions, and environmental factors on the magnitude and quality of reported dPyC fluxes.

The second aim is to synthesize known and unknown processes that affect the aqueous transport and composition of dPyC across the terrestrial to aquatic interface. We conclude this paper by identifying gaps in our understanding of processes that drive dPyC retention and mobility in soils and freshwater. By providing a more quantitative understanding of dPyC in soil and freshwater carbon cycles, this work should provide useful information for researchers, land managers, and for land models that handle fire disturbances used to predict future climates.

1.3 Defining dPyC

Pyrogenic C is a continuum of materials that range from lightly charred organic matter to highly charred and condensed organic matter ([Bird et al., 2015](#); [Masiello, 2004](#); [Santín et al., 2016](#)). Therefore, dPyC also exists on such a continuum ([Wagner et al., 2017](#)). In a review paper on the PyC cycle, [Bird et al. \(2015\)](#) define dPyC as the “thermochemically altered carbon present in the environment as a component of dissolved organic carbon in the <0.45 μm fraction of natural waters.” However, current methodological approaches restrict measurement of PyC or dPyC to only subsections of the continuum ([Wiedemeier et al., 2015](#)). Thus, by selecting a single method, most studies are operationally defining PyC or dPyC. Previous studies have measured dPyC using filter sizes ranging from 0.1 μm to 0.7 μm (see section 3.2.2, **Figure S2**), and while much

of environmental research considers materials $<0.45\ \mu\text{m}$ to be dissolved, these materials may in fact be very small colloidal organic matter. Benzene, which makes up the backbone of many PyC molecules, is only slightly soluble in water, but it is small enough that it would easily pass through a $0.45\ \mu\text{m}$ filter (diameter of benzene ring is $2.49\ \text{\AA}$ or approximately $0.000249\ \mu\text{m}$). Of course, most PyC does not exist as single benzene rings but is comprised of large, complex macromolecules with some soluble functional groups ([Bird et al., 2015](#)), and much of what is often described as dPyC are chemical fragments and colloids ([Wagner et al., 2017](#)). In this work, we are using “dPyC” to indicate both fully dissolved and colloidal PyC within an aqueous matrix due to inconsistencies in analytical approaches used for quantifying PyC pools and fluxes.

2. Methods

2.1 Data acquisition

Publications were selected for the meta-analysis following a modification of the PSALSAR (research protocol and reporting results) method adapted by [Mengist et al. \(2020\)](#) from the SALSA (search, appraisal, synthesis, and analysis) method ([Grant and Booth, 2009](#)), which outlines organized methods for systematic literature reviews. Complete search and selection criteria can be found in **Table S1**. The scope of the meta-analysis was defined as original research papers that either quantified dPyC or characterized its chemical composition within terrestrial or freshwater systems, including in-lab simulations and extractions. The search for publications was initiated on August 23, 2021, via Web of Science and returned 12,776 publications, which we narrowed to 175 final publications via three successive rounds of filtering (**Figure S1**).

2.2 Data processing and analysis

2.2.1 Extraction of dPyC values and other relevant information

Data were extracted from the 175 meta-analysis publications (**Figure 1** and **Table S1**) and organized in Microsoft Excel as study- and observation-level information, where the study-level information was applicable to the entire publication (e.g., publication year) and observation-level information was specific to individual data points (e.g., pyrolysis temperature for a single PyC type). Observations were included when they were reported concentrations of dPyC or concentrations of DOC when only PyC (charcoal, biochar) was extracted in the laboratory. Data which were presented only in figures (e.g., a bar graph of dPyC concentration means) were extracted using Web Plot Digitizer ([Rohatgi, 2022](#)).

2.2.2 Assignment of location and climate regions to dPyC field observations

Latitude and longitude were assigned to each field study observation using provided coordinates, map figures (using Web Plot Digitizer as described earlier), or via Google Earth using descriptions in the manuscript text. Climate assignments were made by entering coordinates into ClimateCharts.net ([Laura Zepner, 2020](#)), a web-based application which generates climate classifications based on the Geiger-Köppen system. These assignments may contain some error at locations where regional or local scale climate variation exists at too fine a resolution to be

captured by the raster cell size from ClimateCharts.net or within the Geiger-Köppen classification system itself. We further binned the climate assignments into broader classes, such as temperate, tropical, polar, etc.

The map figure was generated in R version 4.2.1 using the `geom_map()` function in the `ggplot2` package. To reduce noise in the map, observations were binned by river basin using ArcMap from ArcGIS Desktop 10.8.1 (2020) with the World Wildlife Fund hydroSHEDS level 5 basins dataset (Lehner and Grill, 2013). Detailed workflows for processing of spatial data are provided in the Supplemental Materials.

2.2.4 Statistical analyses

We subset the data to analyze field and laboratory studies separately, and for field studies we only used dPyC observations measured by the benzene polycarboxylic acid (BPCA) method to maintain comparability across studies, and because this method comprised ~71% of the field observations. Data were found not normal using the Shapiro-Wilk test and were analyzed using non-parametric tests: the Kruskal-Wallis rank sum test and pairwise comparisons using the Wilcoxon rank sum test. For field studies dissolved pyrogenic carbon was the dependent variable and sample type (Flowing Water, Still Water, Precipitation, Soil Field Extract, and Throughflow and Stemflow), methodology, filter size, and climate bin (Cold, Polar, Temperate, and Tropical) were independent variables. For laboratory studies, we used observations across all methodologies to increase our sample size and because no method was employed to produce a majority of the observations. For some continuous variables in the laboratory observations (charring temperature, time, extraction ratios), we used linear regression to describe their relationship with dPyC. Significance was determined at the $p < 0.05$ level.

3. Results

3.1 Overview of dataset

Here we provide an overview of the meta-analysis based on 175 studies on dPyC, which yielded 2084 individual observations of dPyC (Table 1). The majority of observations (66%) were from the field setting, and they were reported across five different non-convertible units. We analyzed the data in light of methodological differences (Section 3.2), field measurements (Section 3.3), and laboratory-based measurements (Section 3.4) to quantify the relative magnitude of different dPyC pools and fluxes across the terrestrial to aquatic interface and to identify important mechanisms driving these fluxes.

The most frequently published journals were *Science of the Total Environment* ($n = 20$); *Environmental Science and Technology* ($n = 17$); *Chemosphere* ($n = 13$); *Journal of Hazardous Materials* ($n = 9$); *Organic Geochemistry* ($n = 8$); *Global Biogeochemical Cycles* ($n = 6$); *Biogeochemistry* ($n = 5$); *Frontiers in Earth Science* ($n = 5$); and *Water Research* ($n = 5$); The remainder had fewer than five studies included in this meta-analysis. This wide range in scope of journal topics reflects our broad search aims to connect terrestrial and aquatic research on dPyC.

Of the studies selected for this meta-analysis, only 12 measured soil, sediment, or other PyC source concentration in combination with dPyC. Many of these reported positive correlations

between dPyC with DOC and source PyC concentration (Bi et al., 2018; Güereña et al., 2015; Jones et al., 2019). Contrastingly, several studies reported a reduction in DOC export after biochar or charcoal amendment (e.g. (Abdelrahman et al., 2018; Braun et al., 2020; Zand and Grathwohl, 2016), suggesting initial sorption of OM to the added PyC surface. Furthermore, many of these papers noted or measured variability in time post-fire or post-addition of charcoal as factors in leaching of PyC (e.g. (Bi et al., 2018; Jones et al., 2019; Santos et al., 2017), highlighting the need for investigation on the controls on the timing of post-fire dPyC fluxes.

Table 1. Number of dPyC measurements (n) across all methods that were extracted in this meta-analysis. A measurement of dPyC was considered whenever the observation was associated with a quantitative measurement of dPyC concentration. Dissolved organic C was considered a measurement of dPyC when charcoal only was extracted in the laboratory setting. Proportion of dPyC in DOC is denoted as %.

Sample Type	Individual Observations (n)	dPyC	dPyC	DOC	DOC	dPyC
		mg L ⁻¹ (n)	mg kg ⁻¹ (n)	mg L ⁻¹ (n)	mg kg ⁻¹ (n)	% (n)
Field	1389	1300	64	NA	NA	25
Lab	695	67	121	302	159	46
Total	2084	1367	185	302	159	71

3.2. The influence of methodological approaches on dPyC measurements

3.2.1 Detection and measurement of dissolved PyC

A major obstacle to closing the gaps in the global PyC cycle is associated with the methodological difficulty in measuring PyC, because there are a broad suite of methods used to quantify PyC and dPyC, and each method only captures a small portion of the PyC continuum (Bird et al., 2015; Masiello, 2004; Wiedemeier et al., 2015). As such, a suite of analytical methods was used by the studies selected for our meta-analysis. Many studies utilized qualitative methods for identification of the chemical composition of PyC in solution, including ultrahigh resolution mass spectrometry, Nuclear Magnetic Resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). For additional details on how these methods can be utilized for dPyC, see (Chen et al., 2022; Hameed et al., 2023; Wagner et al., 2018). Quantitative methods provide a measurement of PyC concentration in solution, which we further investigated in our meta-analysis, and included molecular markers (Benzene Polycarboxylic Acid or BPCA, levoglucosan, and polycyclic aromatic hydrocarbons or PAHs), chemo-thermal oxidation, as well as analytical and hydrogen pyrolysis, all of which have been extensively discussed elsewhere (Ascough et al., 2009; Gustafsson et al., 2001; Hameed et al., 2023; Hammes et al., 2007; Schmidt et al., 2001; Wagner et al., 2018). In 3.2.2, we examined the most common methods applied for the chemical characterization and quantification of dPyC in field and laboratory studies.

3.2.2 The impact of methodological approach on measured dPyC concentration

To assess how the use of different methodological approaches may influence dPyC values, we examined concentrations (in mg L^{-1} or mg kg^{-1}) across field- and lab-based observations (**Figure 2**). Field measurements of dPyC ranged over six orders of magnitude, and the lowest reported concentrations were in some of the methods that describe the narrowest section of the PyC continuum, namely GC-MS for PAHs and levoglucosan. BPCA is a widely used method across many sample types and this is reflected in the concentrations reported from this method. Approximately 50% of all data points were derived from the BPCA method, the majority of which were from field-based studies. The majority of field observations were obtained from the BPCA method (71%), while the majority of laboratory observations were made by quantifying total DOC from PyC (as charcoal, biochar, etc. extractions), followed by GC-MS techniques. The GC-MS techniques were also common in field studies (16% of observations). The vast majority (>80%) of laboratory studies quantified dPyC on char extracts, and the remainder quantified dPyC on soil extracts.

Most of the samples were filtered prior to analysis, with approximately a third of samples ($n = 742$) filtered using a $0.7 \mu\text{m}$ filter size, followed by 664 samples filtered with a $0.45 \mu\text{m}$ filter. Laboratory studies most frequently used the $0.45 \mu\text{m}$ filter ($n = 412$), whereas field-based studies most frequently used the $0.7 \mu\text{m}$ filter size ($n = 670$).

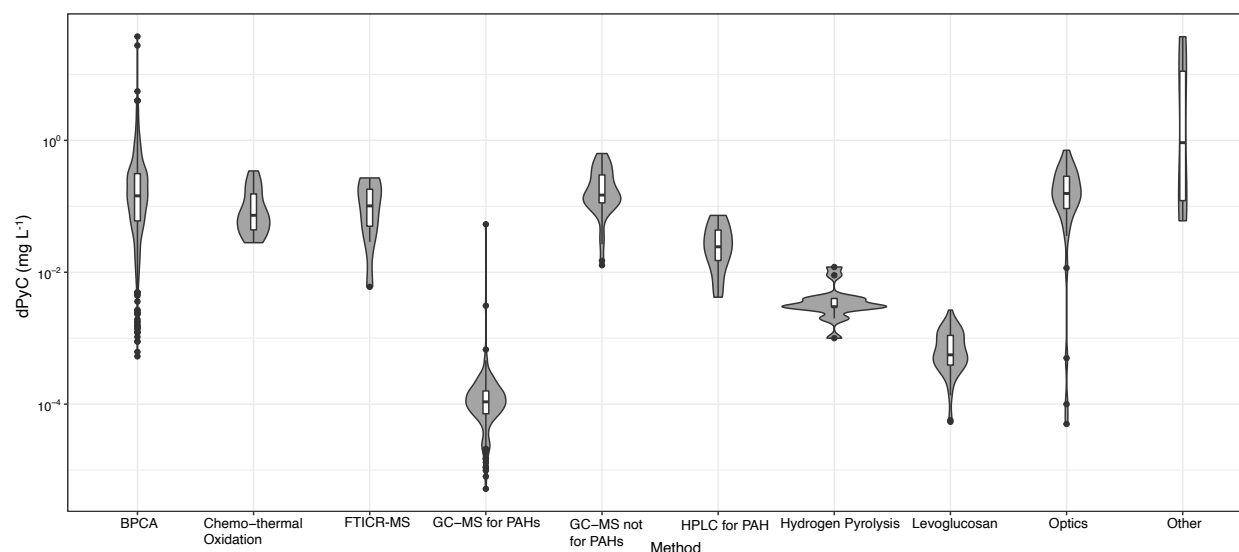


Figure 2. Field measurements of dPyC across different methodologies (n.b. Y axis is in log scale). Methods included in this figure are: BPCA (benzene polycarboxylic acid), Chemo-thermo oxidation, FTICR-MS (Fourier-transform ion cyclotron resonance mass spectrometry), GC-MS (gas chromatography mass spectrometry) for PAHs (polycyclic aromatic hydrocarbons), HPLC (High-performance liquid chromatography) for PAHs, hydrogen pyrolysis, levoglucosan, optics (includes fluorescence excitation-emission matrix-parallel factor analysis and other optical techniques), and other (includes liquid-chromatography for organic carbon detection and dichromate sulfuric acid oxidation).

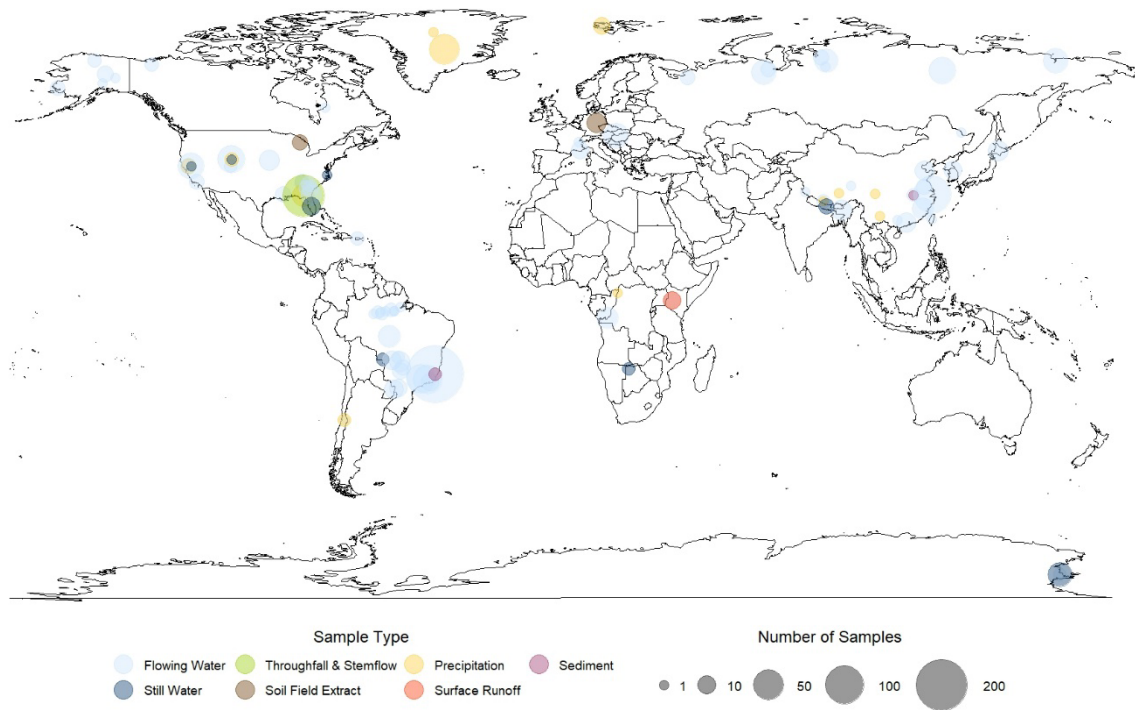


Figure 3. Field-based measurements of dPyC across all methods with color indicating sample type and size of point denoting the number of observations.

3.3 Field-based measurements

Field-based observations of dPyC were distributed globally, including six of seven continents (excluding Australia). We extracted dPyC observations from several locations, including central and western Asia, eastern Europe, central America, and northern Africa (**Figure 3**). The majority of field-based observations of dPyC using the BPCA method were made in flowing water ($n = 734$; 78%), with only a few that were soil related ($n = 5$; 0.5%). There were significant differences in dPyC concentration across different sample types ($p < 0.05$; $\chi^2 = 109.42$, $df = 4$; Kruskal-Wallis, **Figure 4A**). A pairwise Wilcoxon rank sum test indicated that each sample type was significantly different from each other ($p < 0.05$), except for soil field extract and throughfall and stemflow. The highest concentrations of dPyC in the field were found in water that had more time to interact with PyC (e.g., still water, soil pore water, throughfall and stemflow vs. precipitation and flowing water (**Figure 4A**). Additionally, there were significant differences in dPyC concentration across different climate zones ($p < 0.05$; $\chi^2 = 78.434$, $df = 3$; Kruskal-Wallis; **Figure 4B**). This likely reflects differences in burn season length, vegetation available for burning, and mean air temperature and availability of water for dissolution.

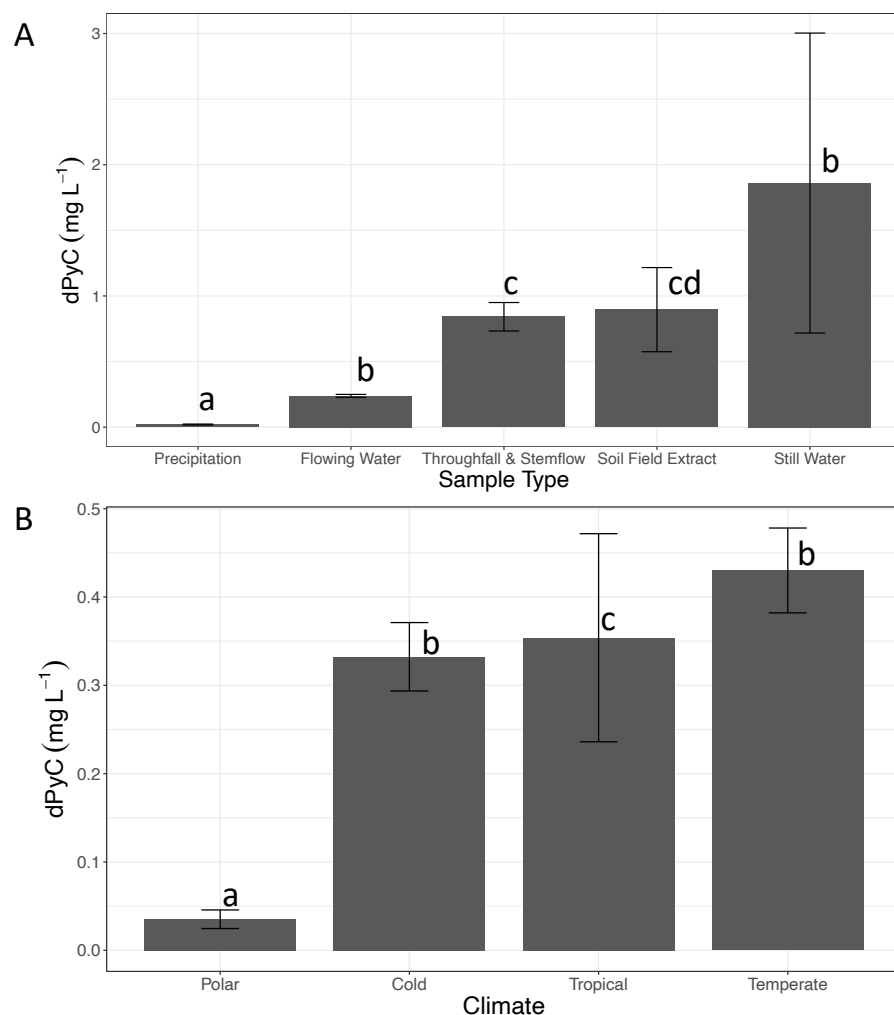


Figure 4A and B. Mean concentration with standard error of dPyC across different sample types (A) and climate zones (B) observed in the field derived from the BPCA method. Letters denote significant differences based on Wilcoxon rank sum test.

Correlation of dPyC with DOC

In field-based studies across all sample types, dPyC comprised approximately 5% of DOC. In sample types where water has more contact time with PyC (i.e., soil water, still water, see **Figure 4A**), dPyC makes up a greater proportion of DOC. In many of the flowing water studies the dPyC was correlated with discharge rates ([Dittmar et al., 2012](#); [Drake et al., 2020](#)), as is DOC, but some found a dilution effect of higher precipitation with lower dPyC concentrations under certain hydrologic conditions ([Bao et al., 2019](#); [Jones et al., 2019](#)). Together, this suggests that the mobility of dPyC is controlled by many of the same processes as DOC; hence the positive correlations between dPyC and DOC (**Figure 5**). However, studies that incorporate measurements of urban and anthropogenic sources of dPyC have noted a decoupling of dPyC from DOC where there are higher combustion activities ([Bi et al., 2018](#)).

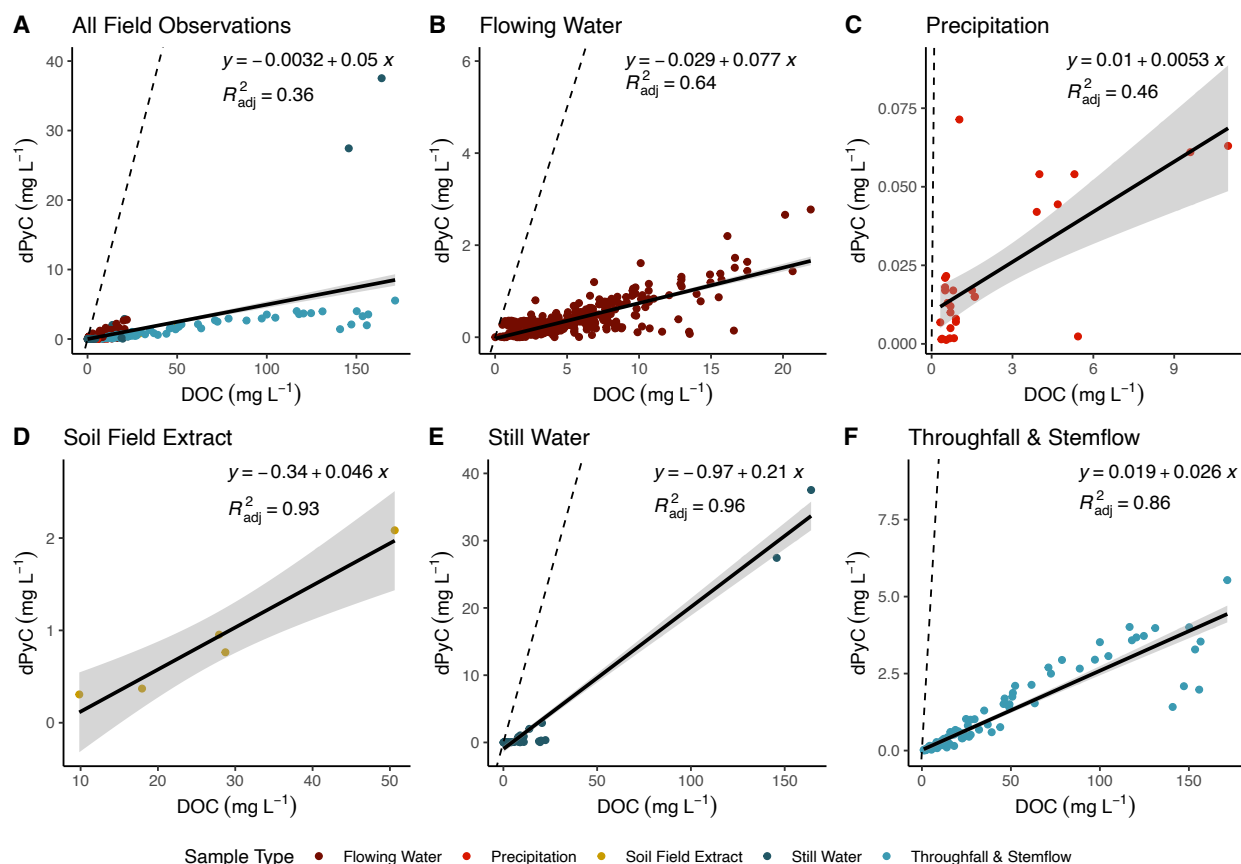


Figure 5. Dissolved PyC as measured by the BPCA method was correlated with DOC in field data from all sample types (panel A) and separated by different sample types (panels B-F). Solid black lines indicate linear fit with grey shaded area indicating 95% CI. The dashed line represents a 1:1 ratio of dPyC to DOC.

3.4 Laboratory-based measurements

For laboratory studies, we considered measurements of DOC from char-extracts as a measure of dPyC since the source material would be classified as PyC. This was the most frequently used method in laboratory studies that measured dPyC, followed by the BPCA method. The highest concentrations of dPyC measured in the lab were with the DOC method, which generated values approximately 1-2 orders of magnitude higher than the next highest concentrations, which were determined via the BPCA method. We found two categories of sample types in laboratory studies – soil extracts and charcoal extracts ($n = 35$ and 86 , respectively). The soil extract had a not significantly lower concentration of dPyC compared with charcoal extracts (in units dPyC mg/kg; $p = 0.11$; $\chi^2 = 2.5347$; $df = 1$).

There were significant differences in dPyC concentrations across different filter sizes (**Figure S2**), but these did not increase with filter pore size, therefore these differences were more likely due to differing methodological approaches and/or sample characteristics. For laboratory studies, the BPCA method was most frequently used ($n = 69$ observations), followed by GC-MS for PAHs ($n = 46$). There were significant differences in the dPyC concentration based on the analytical method used to quantify dPyC ($p < 0.05$; $\chi^2 = 40.268$; $df = 3$), with BPCA having

significantly higher concentrations than GC-MS and GC-MS specifically applied for PAHs (Figure S3).

3.4.1 Inferences from char extracts

We also examined drivers of dPyC by analyzing data from charcoal extractions, with feedstocks categorized as woody or herbaceous. There were no significant differences in dPyC concentration based upon feedstock type (woody vs herbaceous) alone ($\chi^2 = 0.011081$; $df = 1$; $p > 0.05$) or on extraction time ($\chi^2 = 5.1529$, $df = 5$; $p > 0.05$). Extraction by shaking released significantly more dPyC than other methods ($\chi^2 = 22.512$; $df = 1$; $p < 0.05$). There was a significant negative correlation between the solid to solution ratio ($p < 0.05$; $F = 5.648$; $df = 65$), which reflects more PyC available for dissolution, although this only explained a small portion of the variability in this data (Adjusted $R^2 = 0.068$). For extraction solvents, organic solvents resulted in significantly lower concentrations of dPyC than water or other solvents ($\chi^2 = 33.883$; $df = 2$; $p < 0.05$). We did find significant negative relationships between dPyC and burn time ($F = 10$; $df = 18$; $p < 0.05$) and maximum charring temperature ($F = 8.57$; $df = 40$; $p < 0.05$). This is consistent with freshly produced charcoal at high charring intensities being some of the least soluble PyC (Pyle et al., 2015).

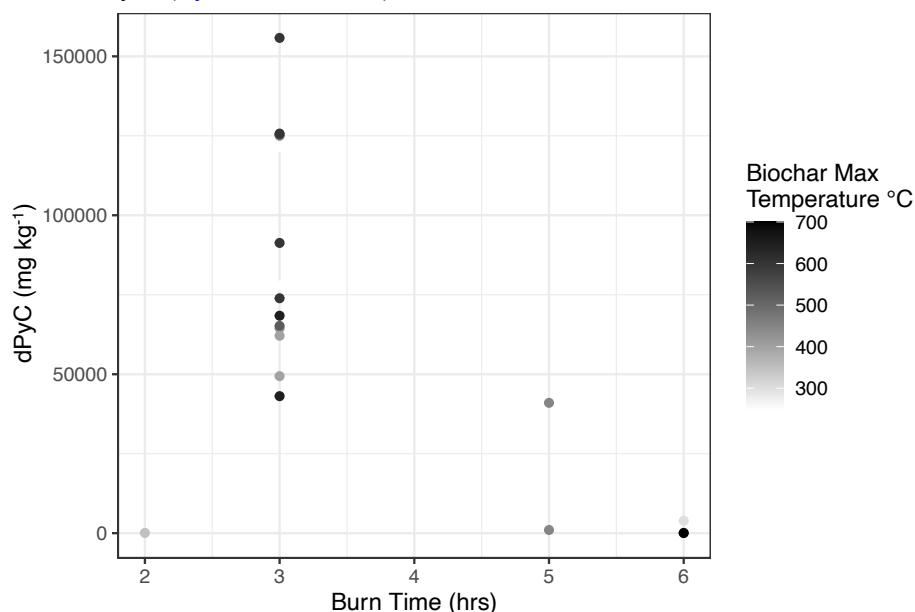


Figure 6. Concentration of dPyC across a range of burn time (hours) from charcoal extractions.

4. Synthesis: factors affecting the fate of dPyC in terrestrial ecosystems

Through this meta-analysis we have identified some key factors controlling the observed magnitudes of dPyC fluxes reported by previous studies, including formation properties of PyC and the method used to quantify dPyC. We found that methods that quantify a smaller component of the dPyC continuum report lower concentrations of dPyC, and we found that higher solid to solution ratios resulted in higher dPyC concentrations. We found that higher charring time and temperature produced PyC that yielded lower amounts of dPyC (Figure 6).

These results make intuitive sense in terms of mechanistic controls on decomposition and already described properties of the solubility of PyC.

In the following sections we synthesize the controls on pools and fluxes of dPyC along the terrestrial to aquatic continuum. We will explore the main chemical and physical properties of dPyC that impact its transport, discuss the role of fire in changing soil and landscape properties that guide dPyC movement through terrestrial to aquatic systems, and finally describe how the soil forming factors can be applied as a model for understanding the relevant environmental controls on dPyC formation, transformation, and loss in watersheds.

4.1 Properties of PyC and dPyC that impact persistence and cycling in soil

Once PyC is deposited on the soil surface after a fire, its physical and chemical properties dictate how it may be transformed by the many processes that control its cycling and long-term fate. Earlier work on PyC suggested that it persists in soil on the millennial time scale; however recent work indicates that it has a centennial mean residence time in soil ([Bird et al., 2015](#); [Dittmar, 2015](#); [Wagner et al., 2015a](#)). The persistence of PyC in soil is typically longer when it is formed at higher temperatures and/or longer burning durations, and there is evidence that when formed at lower temperatures (<250 °C), it may breakdown over relatively shorter time scales (6 months; [Abney et al., 2019a](#); [Whitman et al., 2015](#)). [Santos et al. \(2012\)](#) showed that this early breakdown can occur even when PyC is formed in the laboratory at relatively higher controlled temperatures (450 °C). This more rapid breakdown has been mainly attributed to decomposition; however, some loss is likely due to leaching ([Hockaday et al., 2006](#); [Hockaday et al., 2007](#); [Major et al., 2010](#)) and erosion ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Abney et al., 2019b](#); [Abney et al., 2017](#)). In this section we discuss how chemical and physical properties of PyC and leached dPyC impact its transport in soils. We propose the following function can be used to understand the controls on the fate and properties of PyC and dPyC throughout post-fire landscapes (**Figure 7**).

$$f = \text{Burn conditions} + \text{Climate} + \text{Topography} + \text{Organisms} + \text{Parent material} + \text{Time} + \text{post-fire soil properties}$$

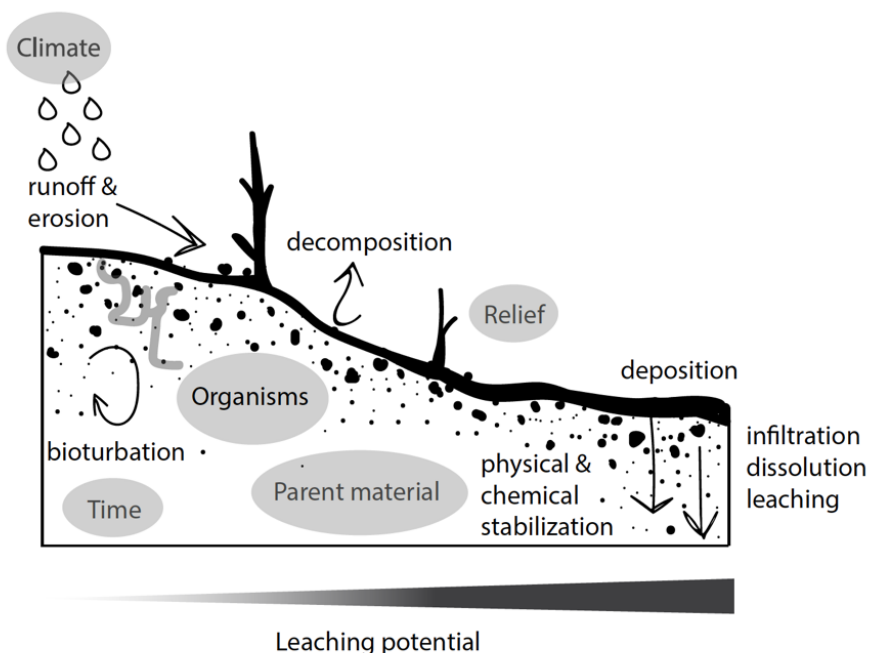


Figure 7. The interaction of soil forming factors and burn conditions and severity likely dictate the fate and transport of dissolved pyrogenic carbon across dynamic landscapes. By studying post-fire landscapes through these two lenses, we can build predictive models of post-fire PyC dynamics.

4.1.2 Chemical composition

The chemical composition of solid PyC before dissolution influences the quantity and quality of dPyC. At lower burn temperatures, the resulting PyC formed is high in nutrients and oxygenated functional groups, while higher burn temperatures tend to produce more condensed aromatic PyC with low H:C and O:C ratios (Baldock and Smernik, 2002; Hammes et al., 2006; Schneider et al., 2010). Bostick et al. (2018) investigated dPyC from PyC formed from oak wood and grass and reported that the leachates were mostly chemically composed of a complex mixture of C groups such as carbohydrates, aliphatics, and low molecular mass compounds, suggesting that the DOM resulting from PyC is not solely comprised of condensed aromatics. Wozniak et al. (2020) demonstrated the chemical heterogeneity of dPyC derived from low (250 °C) heating temperatures exhibits a wide range of O/C values and the presence of highly unsaturated aliphatics, polyphenolic formulas, and condensed aromatic C compounds, whereas compounds with low O/C ratios dominated the composition of dPyC from higher heating temperatures (400 °C). Taken together, these recent findings suggest that DOM leached from solid PyC is heterogeneous and exists also along a chemical continuum (Wagner et al., 2021).

4.1.3 The influence of burn conditions

The physical structure of PyC has been described by porosity, density, and particle size, each of which can impact the stability of PyC and its potential for dissolution. For many biochars, increasing charring temperature increases skeletal density and porosity, which may alter the availability of the char for microbial decomposition or leaching (Brewer et al., 2014). We found

that the formation conditions (burn time and temperature) of dPyC were most critical for predicting the concentration of dPyC (**Figure 6**). Together, burn temperature and duration represent burn intensity, which controls solid PyC properties, such that increasing burn temperature and duration generate PyC that is increasingly aromatic and condensed, contributing to lower solubility. Solid PyC can physically break down via comminution that leads to its dissolved transport, and there is evidence that weaker portions of the solid PyC structure are responsible for the production of dPyC ([Spokas et al., 2014](#)). Some of the variability in strength in char structure reflects the precursor plant material structure, which is often retained in PyC ([Brewer et al., 2014](#); [Hockaday et al., 2007](#)), although we found no effect of precursor material on resulting dPyC concentration. Additionally, size of the solid PyC controls the distance it can be transported via erosion ([Bellè et al., 2021](#)), which may result in the PyC being eroded into a landform position with more favorable leaching conditions. The physical properties of charcoal have been linked to its persistence in soil, however more research is needed on how and if these properties dictate quantity and quality of leached dPyC.

4.2 Environmental and soil factors controlling transport and fate of dPyC along a terrestrial to aquatic gradient

In addition to the properties of PyC, there are a number of environmental and soil factors that play a role in the transport of dPyC across landscapes. Below we discuss the relative importance of site factors, such as climate, topography, biotic factors, parent material, time, and burn conditions, in dPyC formation and transport. Additionally, these factors are frequently interacting across dynamics landscapes and are often difficult to disentangle in natural systems.

4.2.1 Climate: precipitation and temperature

The climate of an area regulates vegetation type, biomass (see **section 4.2.3**) and the availability and quantity of water required for leaching, erosion, and microbial functioning. We found dPyC concentration varied with climate (**Figure 4B**). Precipitation can affect erosion of PyC and transport of dPyC. However, we found no significant relationship between MAP and field-reported concentration of dPyC ($p > 0.05$). This is likely because climate describes average expected weather for an area, whereas leaching is largely driven by individual precipitation events. Climate does dictate the amount of time throughout the year that precipitation-driven erosion events can occur (i.e., rainfall vs snowfall), which can drive overall sediment transport ([Nearing et al., 2004](#)). Importantly, extreme precipitation events can be major drivers of erosion in post-fire landscapes, and previous research has described how rain-on-snow events, can lead significant erosional losses of PyC ([Abney et al., 2019b](#); [Carroll et al., 2007](#)), and increase runoff (see **Section 4.2.2**).

From this meta-analysis, studies that measured dPyC concentrations in precipitation samples found some of the lowest ratios of dPyC to DOC and the weakest correlation between DOC and dPyC (**Figure 5**). The variability in dPyC in precipitation is likely due to the movement of air masses containing particulate PyC (either from fire ash and soot or fossil fuel burning) and variability in timing of precipitation events. The timing of the initial interaction of PyC and water is critical for its fate in the post-fire landscape ([Masiello and Berhe, 2020](#)).

Environmental temperatures likely impact the potential for PyC leaching via a few key mechanisms, mainly through the form of precipitation (snow vs rain fall), the speed of

decomposition, and interactively through controlling the vegetation available to serve as fuel for a fire (formation quantity and quality of PyC). Slow rates of snow melting or rainfall could possibly drive more downwards migration of PyC through leaching than the rapid runoff of an intense rainfall event. The role of precipitation intensity as a driver of leaching is also moderated by soil type ([Bellè et al., 2021](#)).

Temperature is a significant driver of the rate of decomposition. Due to the higher temperature sensitivity of PyC and other more persistent SOM components to rising temperatures ([Conant et al., 2011](#); [Davidson and Janssens, 2006](#); [von Lützow and Kögel-Knabner, 2009](#)), these materials may have increased decomposition that leads to greater dissolution of PyC ([Abiven et al., 2011](#); [Hockaday et al., 2006](#)). Temperature also impacts the solubility of DOM, where considerably higher temperatures may lead to greater solubility of PyC. We did not find a significant relationship between mean annual temperature and field dPyC concentrations ($p > 0.05$), but we expect that this is due to confounding site-specific environmental and methodological factors.

4.2.2 Topography and Erosion

Topographic landform positions are likely significant controls on dPyC and SOM dynamics, as previous research has reported an increase in SOC in depositional landform positions, which receive eroded material from upslope landform positions ([Berhe et al., 2018](#); [Berhe et al., 2007](#)). Additionally, the preferential erosion of PyC likely indicates that it can accumulate in these depositional landform positions ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Rumpel et al., 2009](#); [Rumpel et al., 2006](#)). An unanswered question, however, is whether PyC in depositional vs eroding landform positions could be more susceptible to leaching when there are higher nutrient concentrations and higher water content. The impacts of erosion on the long-term fate of PyC in soil are complex and depend on the landscape erosion and deposition dynamics along with the soil water conditions and precipitation events ([Abney and Berhe, 2018](#); [Masiello and Berhe, 2020](#)).

Elevated rates of post-fire erosion are widely reported across a range of different ecosystem types ([Carroll et al., 2007](#); [de Dios Benavides-Solorio and MacDonald, 2005](#); [Johansen et al., 2001](#); [Robichaud et al., 2007](#)). The magnitude of post-fire erosion is dependent on a number of soil and precipitation factors, which also control the (1) amount of PyC available for leaching and (2) the soil-water conditions to allow for leaching to occur. Furthermore, there is a direct relationship between burn severity, SOM chemical composition, and erosion ([Abney and Berhe, 2018](#); [Abney et al., 2019b](#)), such that areas that experience higher burn severities have SOM that is more aromatic and more erosion prone. This suggests that conversely, areas that experience moderate- to low-severity burning may have SOM that is more prone to leaching due to both its chemical composition and higher soil infiltration rates ([de Dios Benavides-Solorio and MacDonald, 2005](#); [Morris and Moses, 1987](#); [Robichaud, 2000](#); [Torreano and Morris, 1998](#)). Several studies have indicated that PyC is preferentially transported post-fire ([Abney et al., 2019b](#); [Rumpel et al., 2009](#); [Rumpel et al., 2006](#)). However, since most SOM that is transported via erosion is deposited within the same or adjacent watershed ([Stallard, 1998](#)), this transported PyC may still be available for and susceptible to leaching, depending on where in the landscape it is deposited and if it is buried after erosion.

4.2.3 Organisms

Vegetation can play a role in controlling the fate of dPyC through several pathways including acting as fuel for PyC formation and regulating burn severity, moderating microbial decomposition/cycling of PyC, and dictating post-fire erosion via soil stabilization and ground cover ([Cerdà and Doerr, 2005](#); [Kim et al., 2021](#)). These factors will vary with functional type, diversity, and structure of vegetation, along with pre- and post-fire growth, and likely will drive shifts in SOM composition and stability ([Hart et al., 2005](#); [Viedma et al., 2020](#)).

In addition to vegetation growing in soil, soil fauna can impact the fate of PyC and dPyC. Soil macro- and meso-fauna can fragment PyC into smaller particle sizes and remobilize it ([Domene, 2016](#); [Domene et al., 2015](#); [Elmer et al., 2015](#)), likely increasing the availability of PyC to be microbially degraded and/or to enter the dissolved phase. However, the specific role of bioturbation in controlling dPyC production has, to the authors' knowledge, not yet been demonstrated. The addition of PyC to soil also has been demonstrated to increase microbial biomass and cause shifts in microbial community composition ([Dove et al., 2021](#); [Lehmann et al., 2011](#)). While in some cases bacteria can be more sensitive to fire relative to fungi ([Brown et al., 2019](#)), emerging general trends suggest that fungi are more sensitive to fire than bacteria ([Beals et al., 2022](#); [Pressler et al., 2019](#); [Qin and Liu, 2021](#)), and may ([Dove and Hart, 2017](#)) or may not ([Miyamoto et al., 2021](#)) recover to pre-fire levels over a decade post burn. These microbial and other organismal community changes can alter soil functioning, possibly leading to shifts in dPyC formation and leaching.

4.2.4 Parent material and mineralogy

A soil's parent material will influence the soil texture, structure, and reactivity, among other soil characteristics. Coarse, sandy soils formed under granodiorite parent material may have a low cation exchange capacity (CEC) and little aggregation. These soils can have high infiltration and hydraulic conductivity, with potential for rapid leaching of PyC; however, clay-rich soils may have lower hydraulic conductivity, with lower potential for leaching ([Barnes et al., 2014](#)). The parent material also influences the hydrologic properties of a soil, including depth to ground water, hydrologic flow paths, and connectivity to nearby aquatic systems. In soils where surface water is connected to groundwater, post-fire leaching can transport dPyC to groundwater, with some concerns regarding contamination (i.e., with PAHs) of aquifers ([Mansilha et al., 2014](#)).

Mineral-PyC associations have been demonstrated by several studies ([Brodowski et al., 2005](#); [Glaser et al., 2000](#); [Hockaday et al., 2007](#)), but it is not yet known if these form from the interaction of dPyC or solid PyC with soil minerals. [Cusack et al. \(2012\)](#) found positive correlations between PyC, SOC, and short range order minerals. They did not find selective preservation of PyC over non-pyrogenic SOC, but they indicate that physical protection is likely an important stabilization mechanism for PyC. A study by [Brodowski et al. \(2006\)](#) found that PyC was preferentially stored in the occluded particulate matter fraction. Some labeling studies have also found PyC associated with heavy fractions or aggregate-protected fractions in less than a year post-application ([Singh et al., 2014](#); [Soong and Cotrufo, 2015](#)). In subsurface soils, increasing mineral surface area and soil aggregates ([Lehmann and Kleber, 2015](#)) may control dPyC mobility or stabilization via sorption. Mineral stabilization of PyC needs more

investigation to fully understand how mineral-PyC associations are similar to other mineral-OM interactions, how important the quality and quantity of dPyC is for the formation of these associations, and how these interactions impact the long-term fate of PyC in soil.

4.2.5 Time

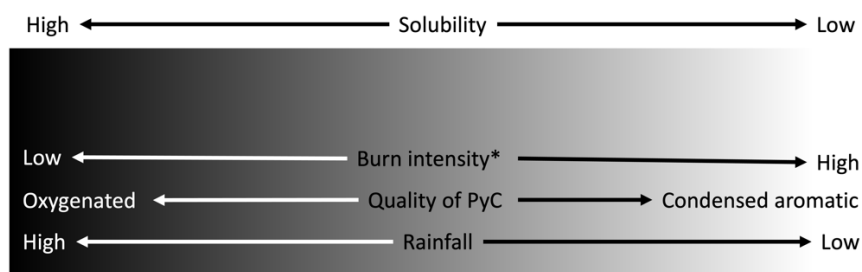
Time is a critical factor in controlling the availability of PyC for forming dPyC. Some research has shown that dPyC increases over time, as the processes of chemical, physical, and biological breakdown of PyC progress, leading to more soluble DOC and dPyC with increasing time since fire ([Bostick et al., 2021](#); [Wagner et al., 2017](#); [Wagner et al., 2018](#)). This increase in solubility is due to introduction of oxygen and nitrogen containing functional groups ([Hilscher and Knicker, 2011](#)). There are also lags in between the formation and deposition of PyC and the transport of dPyC into adjacent and further downstream aquatic systems, as evidenced by increasing ages of PyC and dPyC (see **Table S2, Figure 9**) along terrestrial to aquatic gradients to the ocean ([Wagner et al., 2019a](#); [Wagner et al., 2018](#)). Contrastingly, some evidence indicates that PyC is more bioavailable immediately after production than previously considered, in part because PyC also contains C compounds that are readily available for microorganisms and leaching ([Cheng et al., 2008](#); [Schiedung et al., 2020](#)). In addition, the amount of soil PyC available for forming dPyC is highest in the time immediately post fire. There are many environmental factors that may control dPyC concentrations in soils and streams post-fire, such as soil PyC concentrations, hydrological connectivity of a watershed, potential for decomposition of PyC, etc. At least one study has found no significant relationship between time since fire or between fire return interval and dPyC concentration in stream water ([Ding et al., 2013](#)), which may be reflective of these complexities. [Wagner et al. \(2015a\)](#) show different timing of particulate PyC compared with dPyC peak fluxes in a fire-impacted watershed in Colorado, USA. With this variability in timing of export of dPyC from fire-impacted watersheds, we need more mechanistic understanding of the hillslope-scale processes that are driving this export.

4.3 Fire-driven changes in soil properties that impact mobilization of PyC

Fire has long been described as a major disturbance and driver of changes in soil properties, including pH, hydrophobicity, texture, nutrient availability, organic matter, and vegetation dynamics, among others ([DeBano, 1991](#); [Gonzalez-Perez et al., 2004](#); [MacDonald and Huffman, 2004](#); [Mataix-Solera et al., 2011](#)). Increases in pH may shift the solubility of PyC, as shown by [Rebollo et al. \(2008\)](#). Increases in hydrophobicity post-fire have frequently been reported in low to moderate burn severity fires ([MacDonald and Huffman, 2004](#); [Mataix-Solera and Doerr, 2004](#)), and increases in hydrophobicity may at least temporarily reduce the leaching of PyC into the soil matrix, as there is reduced infiltration (with potential for increased runoff of dPyC). Reduced infiltration and increased runoff post-fire due to loss of vegetation also can lead to elevated rates of erosion, at least until vegetation cover has returned ([de Dios Benavides-Solorio and MacDonald, 2005](#)). As vegetation regrows post-fire and the hydrophobic layer begins to breakdown, it is not yet clear what timescales are relevant for processes of dissolution, within soil redistribution, and hydrologic export of dPyC or how these processes are moderated by burn severity to impact the transport of dPyC.

Results from this meta-analysis indicate that burn intensity (energy x duration, **Figure 6**) is a significant driver of formation and quality of dPyC in soils. Other works have suggested that quality of PyC is important for formation of dPyC (more aliphatic, from either lower temperature

burns or more decomposed/oxidized). For example, as PyC ages, its surfaces may be broken into more digestible aliphatic functional groups, which are more soluble, but as these are consumed, this can leave behind a more aromatic PyC (Hockaday et al., 2007) that is less soluble and more persistent in soil. Rainfall can also drive fluxes of dPyC, as multiple papers monitoring dPyC in rivers noted positive correlations with higher discharge (Jaffé et al., 2013; Wagner et al., 2019c; Wagner et al., 2015a). Bao et al. (2019) argue that different pools of DOC are accessed at different flow rates through soil, so we often find higher DOC and dPyC with higher flows. The actual solubility (or potential for leaching) of PyC across landscapes is controlled by the interaction of several environmental factors, including the burn intensity, chemical and physical properties of the PyC, and amount and timing of rainfall (Figure 8).



*Burn intensity = temperature + duration of burning

Figure 8. Controls on the solubility (leaching potential) of PyC in soil. There are other factors controlling the leaching of PyC, including decomposition, sorption, fire return intervals, aging of PyC etc. However, these are complex and likely do not follow linear relationships.

5. Ecosystem implications

5.1 Fluxes and internal cycling of dPyC between ecosystem components

If we assume that the main sources of dPyC for soil water include precipitation and dissolution of *in situ* charcoal or PyC, then our data currently suggest that *in situ* dissolution is much more important than precipitation, which has a dPyC concentration three orders of magnitude lower than reported soil extract dPyC concentrations (Figure 6). The radiocarbon age of dPyC in precipitation was, however, older than reported in some tributaries and rivers (Figure 9, Table S2), which likely suggests that there is some contribution of very old pyrogenic material (i.e., fossil fuel combustion) with more modern fuel burning to this dPyC pool.

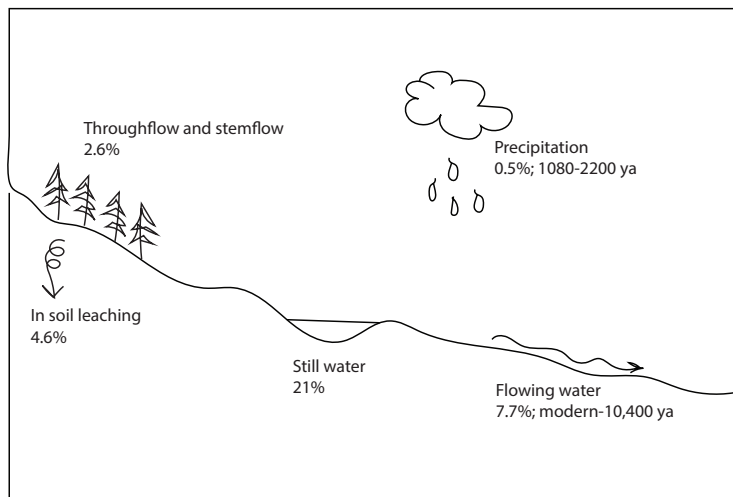


Figure 9. Transport of dPyC across different global pools is presented as percent of dissolved organic carbon. The range of radiocarbon ages of the dPyC in each pool is reported in years (see **Table S2** for more details).

In terrestrial waters, there is an increase in dPyC age reported with increasingly larger and more mixed pools (rivers and oceans compared with tributaries). The age of dPyC in tributaries was also highly variable, which is likely reflective of the significance of individual watershed properties on controlling DOM release and quality. The proportion of PyC that makes it from deposition on soil surface post-fire to ocean dPyC is likely infinitesimally small. [Bostick et al. \(2018\)](#) report that between 1-14% of dPyC in soil is leached to river dPyC, so the vast majority is internally recycled. However, the controls on the variability and rates of transport of soil dPyC to riverine dPyC need further investigation.

5.2 Future research directions

There are numerous needs for future research on dPyC in soil and across the terrestrial-aquatic interface. Arguably the most urgent of these is for more quantitative measurements of dPyC in soil and in fluxes between soil and aquatic systems. For example, two previous studies showed that PyC can be redistributed through leaching at rates of 1-17% of soil PyC ([Boot et al., 2015](#); [Major et al., 2010](#)), however considerable further quantification is required before we can predict dPyC leaching across different soil and precipitation regimes. There is also a need for better intercomparison between quantitative approaches, or perhaps wider adoption of a smaller number of methodologies. In field studies, the BPCA method has been widely used and has the advantage of being able to measure PyC in both solid and liquid samples, as well as provide information about the condensation of PyC. However, BPCA is time consuming, somewhat expensive, and is quantitative only for higher burn intensity dPyC. Combining BPCA with methods that are more sensitive to the lower burn intensity portion of the dPyC continuum will allow for a more complete understanding of transport of dPyC in the natural environment. BPCA can also be used to train models that enable researchers to obtain more quantitative measurements from less costly, high-throughput methods such as mid-infrared spectroscopy ([Cotrufo et al., 2016](#); [Sanderman et al., 2020](#)).

A second methodological need is for studies designed to provide information within relevant timescales for dPyC pools and fluxes post fire. Many studies have reported some “aging” required for PyC to become dissolved ([Abiven et al., 2011](#); [Hockaday et al., 2007](#)), but these do not frequently have more than two or three timepoints for comparing dissolution. Additionally, we know that some of this aging is related to photooxidation, microbial processing, and physical comminution ([Abney et al., 2019a](#); [Spokas et al., 2014](#); [Ward et al., 2014](#)), but these processes likely operate on different timescales and interact with one another to dynamically impact the fate of PyC in soil. Some post-fire soil changes have been well-described, such as increases in pH, weakening of soil aggregation, and decreases in infiltration due to increases in hydrophobicity, and these post-fire changes can be short (<1 year) or medium term (>10 years), depending on burn severity and post-fire vegetation recovery ([Abney et al., 2017](#); [Gonzalez-Perez et al., 2004](#); [Mataix-Solera and Doerr, 2004](#)). Longer-term experiments and field studies which encompass repeated burn events are needed to capture the time component of dPyC transformation.

There is also a need for a better understanding of dPyC cycling within soils and watersheds – in particular, the fate of PyC once it becomes dissolved in soil water. We hypothesize that PyC can also form mineral-organic interactions and become stabilized, but there is only limited evidence for this process ([Brodowski et al., 2006](#)). We also hypothesize that dPyC is more susceptible to decomposition than solid PyC, but this needs further evidence. We also need a better understanding of the transport and connectivity of DOC and dPyC between different aquatic reservoirs (i.e., soil water to stream to lake, etc.). There is considerable research attention on DOC at the terrestrial-aquatic interface ([Rasilo et al., 2015](#); [Tank et al., 2018](#)), but this has yet to focus on the transport of dPyC, which may be a significant persistent source of OC in this pool. Future research should also focus on the interaction between disturbances and loss processes impacting PyC and dPyC, such as erosion, leaching, decomposition, land management activities, and climate change.

6. Conclusions

The concentration and flux of dPyC from soils represents a critical soil C loss mechanism that has received a limited amount of research attention. In rivers and the ocean, dPyC has been well characterized, but more investigation is needed to understand the connections between terrestrial and aquatic dPyC. One major challenge to integrating current research on dPyC is the range of different methodological approaches used to quantitatively and qualitatively describe dPyC. In this meta-analysis we found over ten different methodologies used to quantify dPyC, but in field studies BPCA was the most frequently used method. We found that methods that quantify a smaller component of the dPyC continuum reported smaller concentrations of dPyC, which indicates that these may be underestimating dPyC more than other methods.

Due to the variability in the data in this meta-analysis, we found only a few significant trends in controlling factors for dPyC. In field studies, sample types where PyC was in contact with water for longer periods had higher concentrations of dPyC (i.e., still water vs flowing water), and samples from areas with more fire-prone climates had higher dPyC concentrations (i.e., temperate vs polar). Across sample types we also found high correlations between DOC and dPyC, which suggests that these are controlled by many of the same environmental processes, although these processes need further elucidation. From laboratory studies, we found that burn temperature and burn time were negatively correlated with freshly extracted dPyC, which is

consistent with chemical controls of dPyC solubility. We have also identified a significant need for (1) more mechanistic understanding of the environmental controls of movement of dPyC from soil to aquatic systems, (2) more soil-water measurements of dPyC, and (3) better understanding of the temporal scales relevant to environmental fluxes of dPyC. Future research on dPyC that provides quantitative measures of the fate of dPyC in soils will be useful for models of soil C and can potentially provide critical information to land managers seeking to increase soil C storage.

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730 **Open Research**

731 The data extracted from the meta-analysis are available in a table uploaded in the supplemental
732 information of this manuscript as a .xlsx file.

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