

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

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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.

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2 **Global Review and Meta-analysis**

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17 **Key Points:**

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

23

24

25 Abstract

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27 longer environmental persistence than other soil organic matter components. Despite PyC's
28 persistence in soil, recent work has indicated that it is susceptible to loss processes such as
29 mineralization and leaching, with the significance and magnitude of these largely unknown at the
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31 transport in soil and freshwater. Our analysis found the primary environmental controls on
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35 reported, the slope of these correlations was pool-dependent (i.e., soil-water, precipitation, lakes,
36 streams, rivers), suggesting site-specific environmental controls. However, the lack of
37 consistency in analytical techniques and sample preparation remains a major challenge to
38 quantifying environmental controls on dPyC fluxes. We propose that future research should
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41 and aquatic systems, and (4) improved understanding of how mechanisms controlling the fate of
42 dPyC in dynamic post-fire landscapes interact. With more refined quantitative information about
43 the controls on dPyC transport at the hillslope and landscape scale, we can increase the accuracy
44 and utility of global carbon models.

45 1. Introduction

46 1.1 Significance of dissolved pyrogenic carbon in the global C cycle

47
48 Wildfire is a a major ecosystem disturbance that has been progressively getting more severe and
49 intense in many areas of the world ([Descals et al., 2022](#); [Feurdean et al., 2020](#); [Turco et al., 2018](#);
50 [Westerling et al., 2006](#)). Additionally, significant increases in the use of prescribed fire have
51 been observed across the US in the past few decades, especially in the southeast ([Kolden, 2019](#)).
52 Natural and anthropogenic fires transform carbon (C) into a range of materials across the burn
53 continuum including lightly charred material to charcoal, soot, and ash, collectively known as
54 pyrogenic carbon, or PyC ([Bird et al., 2015](#); [Masiello, 2004](#)). This PyC is initially deposited on
55 the soil surface and emitted to the atmosphere. Pyrogenic C has received considerable research
56 attention over the past decades due to its generally longer persistence times in soil relative to
57 other soil organic matter components, which has implications for C storage ([Abney and Berhe,
58 2018](#); [Bird et al., 2015](#); [Santín et al., 2016](#)).

59
60 There has been limited research synthesizing the production, pools, and fluxes of PyC across
61 large spatial scales ([Coppola et al., 2022](#); [Wagner et al., 2018](#)) to better constrain the role of PyC
62 in the global C cycle. It has been estimated that approximately 2.7% of the global land area is
63 burned annually ([Giglio et al., 2013](#)), resulting in 50-270 Tg y⁻¹ of PyC produced ([Kuhlbusch
64 and Crutzen, 1995](#)). At a global scale, PyC can account for a significant portion (~10%) of
65 dissolved organic carbon (DOC) fluxes in rivers ([Jaffé et al., 2013](#); [Wagner et al., 2018](#)). The
66 global annual transport of particulate PyC from rivers into oceans ranges from 19-80 Tg/yr
67 ([Druffel, 2004](#); [Elmquist et al., 2008](#); [Jaffé et al., 2013](#)), although this is most frequently reported
68 as 26-27 Tg/yr ([Elmquist et al., 2008](#); [Jaffé et al., 2013](#)). However, current estimates of dPyC

69 export from terrestrial to inland aquatic systems range over several orders of magnitude, from
70 ~0.4-18 Tg/yr ([Bowring et al., 2022](#); [Jones et al., 2020](#)), likely reflecting both the variability in
71 processes (e.g., decomposition, photooxidation, water availability, etc.) influencing PyC
72 dynamics at the terrestrial- aquatic interface and insufficient PyC measurements.

73
74 While parameterization of global PyC models typically includes annual production, stocks,
75 large-scale fluxes, and some smaller-scale controls (i.e., decomposition ([Bird et al., 2015](#);
76 [Reisser et al., 2016](#); [Santín et al., 2016](#)), several critical knowledge gaps remain regarding what
77 controls those fluxes, especially at smaller scales. In particular, we need a more detailed
78 understanding of how PyC is transported from source burned material into the soil system, across
79 hillslopes and watersheds, and into aquatic environments ([Myers-Pigg et al., 2015](#); [Wagner et al.,
80 2019c](#); [Wagner et al., 2015b](#)). Some recent research has demonstrated inconsistencies between
81 the sources and ages of dPyC flowing from rivers and those from PyC measured in the ocean
82 ([Wagner et al., 2019b](#)), which indicates limitations in our mechanistic understanding of (1) the
83 cycling of dPyC within terrestrial systems, (2) cycling within freshwater aquatic systems, and (3)
84 connections between terrestrial and aquatic systems. This paper addresses this limitation by
85 synthesizing our current knowledge of dPyC fluxes and the processes that control its
86 transformation within and between terrestrial and aquatic ecosystems to inform research
87 communities involved in management, modeling, and description of PyC.

88

89 **1.2 Aims**

90

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

97

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

104 **1.3 Defining dPyC**

105

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

115 of environmental research considers materials $<0.45 \mu\text{m}$ to be dissolved, these materials may in
116 fact be very small colloidal organic matter. Benzene, which makes up the backbone of many PyC
117 molecules, is only slightly soluble in water, but it is small enough that it would easily pass
118 through a $0.45 \mu\text{m}$ filter (diameter of benzene ring is 2.49 \AA or approximately $0.000249 \mu\text{m}$). Of
119 course, most PyC does not exist as single benzene rings but is comprised of large, complex
120 macromolecules with some soluble functional groups ([Bird et al., 2015](#)), and much of what is
121 often described as dPyC are chemical fragments and colloids ([Wagner et al., 2017](#)). In this work,
122 we are using “dPyC” to indicate both fully dissolved and colloidal PyC within an aqueous matrix
123 due to inconsistencies in analytical approaches used for quantifying PyC pools and fluxes.
124

125 **2. Methods**

126 **2.1 Data acquisition**

127
128 Publications were selected for the meta-analysis following a modification of the PSALSAR
129 (research protocol and reporting results) method adapted by [Mengist et al. \(2020\)](#) from the
130 SALSA (search, appraisal, synthesis, and analysis) method ([Grant and Booth, 2009](#)), which
131 outlines organized methods for systematic literature reviews. Complete search and selection
132 criteria can be found in **Table S1**. The scope of the meta-analysis was defined as original
133 research papers that either quantified dPyC or characterized its chemical composition within
134 terrestrial or freshwater systems, including in-lab simulations and extractions. The search for
135 publications was initiated on August 23, 2021, via Web of Science and returned 12,776
136 publications, which we narrowed to 175 final publications via three successive rounds of filtering
137 (**Figure S1**).

138 **2.2 Data processing and analysis**

139 **2.2.1 Extraction of dPyC values and other relevant information**

140
141
142 Data were extracted from the 175 meta-analysis publications (**Figure 1** and **Table S1**) and
143 organized in Microsoft Excel as study- and observation-level information, where the study-level
144 information was applicable to the entire publication (e.g., publication year) and observation-level
145 information was specific to individual data points (e.g., pyrolysis temperature for a single PyC
146 type). Observations were included when they were reported concentrations of dPyC or
147 concentrations of DOC when only PyC (charcoal, biochar) was extracted in the laboratory. Data
148 which were presented only in figures (e.g., a bar graph of dPyC concentration means) were
149 extracted using Web Plot Digitizer ([Rohatgi, 2022](#)).
150

151 **2.2.2 Assignment of location and climate regions to dPyC field observations**

152
153 Latitude and longitude were assigned to each field study observation using provided coordinates,
154 map figures (using Web Plot Digitizer as described earlier), or via Google Earth using
155 descriptions in the manuscript text. Climate assignments were made by entering coordinates into
156 ClimateCharts.net ([Laura Zepner, 2020](#)), a web-based application which generates climate
157 classifications based on the Geiger-Köppen system. These assignments may contain some error
158 at locations where regional or local scale climate variation exists at too fine a resolution to be

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

162
163 The map figure was generated in R version 4.2.1 using the `geom_map()` function in the `ggplot2`
164 package. To reduce noise in the map, observations were binned by river basin using ArcMap
165 from ArcGIS Desktop 10.8.1 (2020) with the World Wildlife Fund hydroSHEDS level 5 basins
166 dataset (Lehner and Grill, 2013). Detailed workflows for processing of spatial data are provided
167 in the Supplemental Materials.

168

169 **2.2.4 Statistical analyses**

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

183

184 **3. Results**

185 **3.1 Overview of dataset**

186 Here we provide an overview of the meta-analysis based on 175 studies on dPyC, which yielded
187 2084 individual observations of dPyC (**Table 1**). The majority of observations (66%) were from
188 the field setting, and they were reported across five different non-convertible units. We analyzed
189 the data in light of methodological differences (Section 3.2), field measurements (Section 3.3),
190 and laboratory-based measurements (Section 3.4) to quantify the relative magnitude of different
191 dPyC pools and fluxes across the terrestrial to aquatic interface and to identify important
192 mechanisms driving these fluxes.

193

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

200

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

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

210
 211

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

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

217

218 3.2. The influence of methodological approaches on dPyC measurements

219 3.2.1 Detection and measurement of dissolved PyC

220

221 A major obstacle to closing the gaps in the global PyC cycle is associated with the
 222 methodological difficulty in measuring PyC, because there are a broad suite of methods used to
 223 quantify PyC and dPyC, and each method only captures a small portion of the PyC continuum
 224 (Bird et al., 2015; Masiello, 2004; Wiedemeier et al., 2015). As such, a suite of analytical
 225 methods was used by the studies selected for our meta-analysis. Many studies utilized qualitative
 226 methods for identification of the chemical composition of PyC in solution, including ultrahigh
 227 resolution mass spectrometry, Nuclear Magnetic Resonance spectroscopy (NMR), X-ray
 228 photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). For additional
 229 details on how these methods can be utilized for dPyC, see (Chen et al., 2022; Hameed et al.,
 230 2023; Wagner et al., 2018). Quantitative methods provide a measurement of PyC concentration
 231 in solution, which we further investigated in our meta-analysis, and included molecular markers
 232 (Benzene Polycarboxylic Acid or BPCA, levoglucosan, and polycyclic aromatic hydrocarbons or
 233 PAHs), chemo-thermal oxidation, as well as analytical and hydrogen pyrolysis, all of which have
 234 been extensively discussed elsewhere (Ascough et al., 2009; Gustafsson et al., 2001; Hameed et
 235 al., 2023; Hammes et al., 2007; Schmidt et al., 2001; Wagner et al., 2018). In 3.2.2, we examined
 236 the most common methods applied for the chemical characterization and quantification of dPyC
 237 in field and laboratory studies.

238

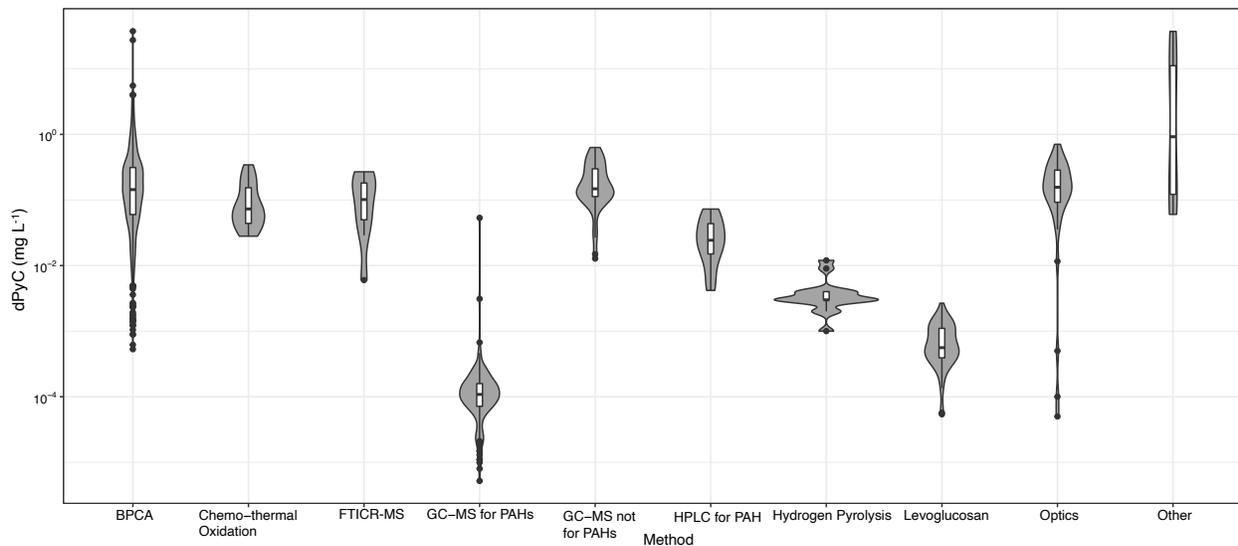
239 3.2.2 The impact of methodological approach on measured dPyC concentration

240 To assess how the use of different methodological approaches may influence dPyC values, we
 241 examined concentrations (in mg L^{-1} or mg kg^{-1}) across field- and lab-based observations (**Figure**
 242 **2**). Field measurements of dPyC ranged over six orders of magnitude, and the lowest reported
 243 concentrations were in some of the methods that describe the narrowest section of the PyC
 244 continuum, namely GC-MS for PAHs and levoglucosan. BPCA is a widely used method across
 245 many sample types and this is reflected in the concentrations reported from this method.
 246 Approximately 50% of all data points were derived from the BPCA method, the majority of
 247 which were from field-based studies. The majority of field observations were obtained from the
 248 BPCA method (71%), while the majority of laboratory observations were made by quantifying
 249 total DOC from PyC (as charcoal, biochar, etc. extractions), followed by GC-MS techniques.
 250 The GC-MS techniques were also common in field studies (16% of observations). The vast
 251 majority (>80%) of laboratory studies quantified dPyC on char extracts, and the remainder
 252 quantified dPyC on soil extracts.

253

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

258



259

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

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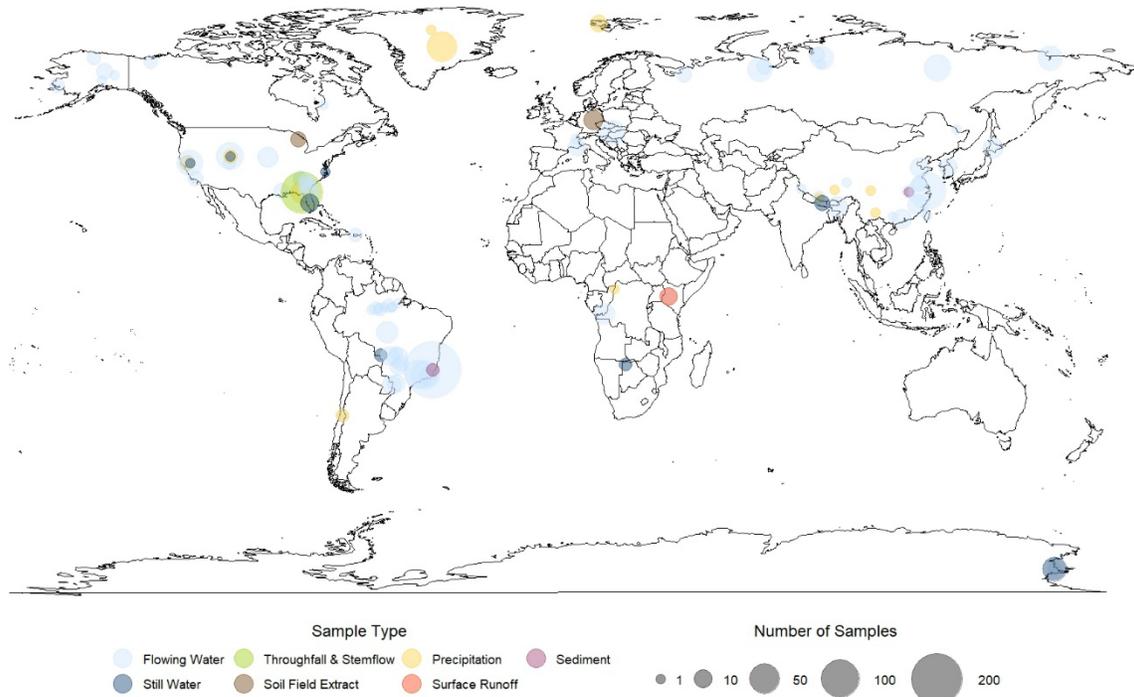
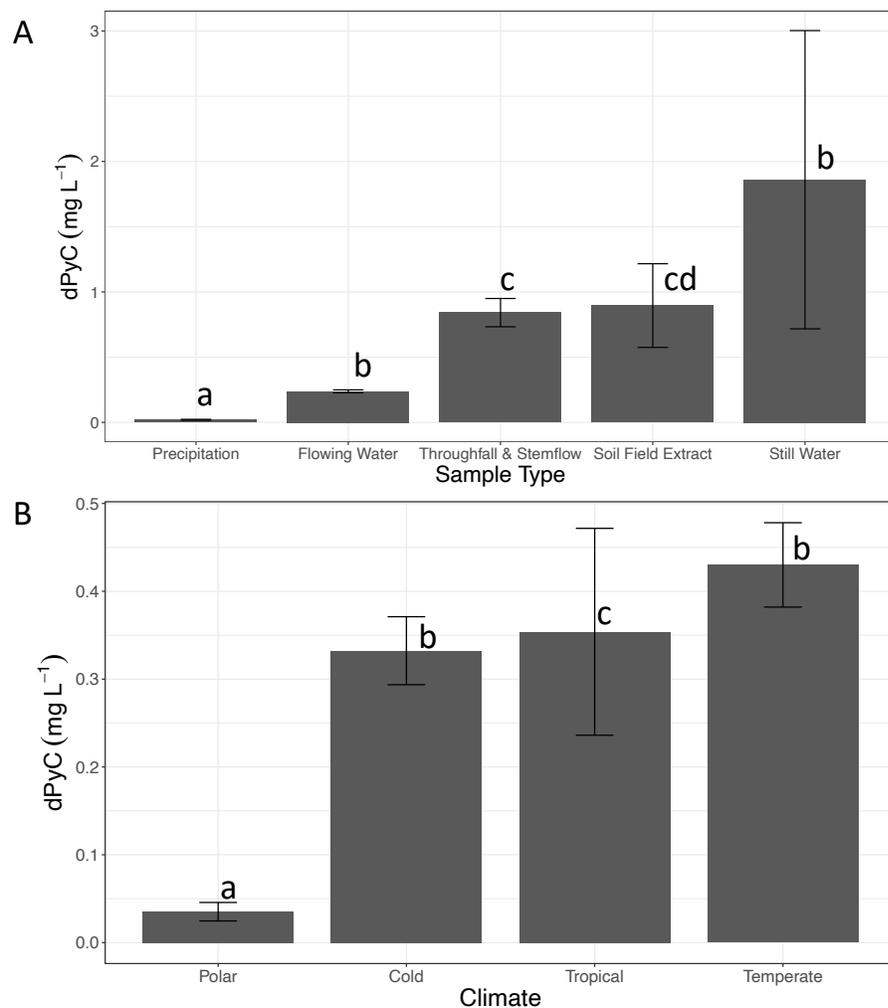


Figure 3. Field-based measurements of dPyC across all methods with color indicating sample type and size of point denoting the number of observations.

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.

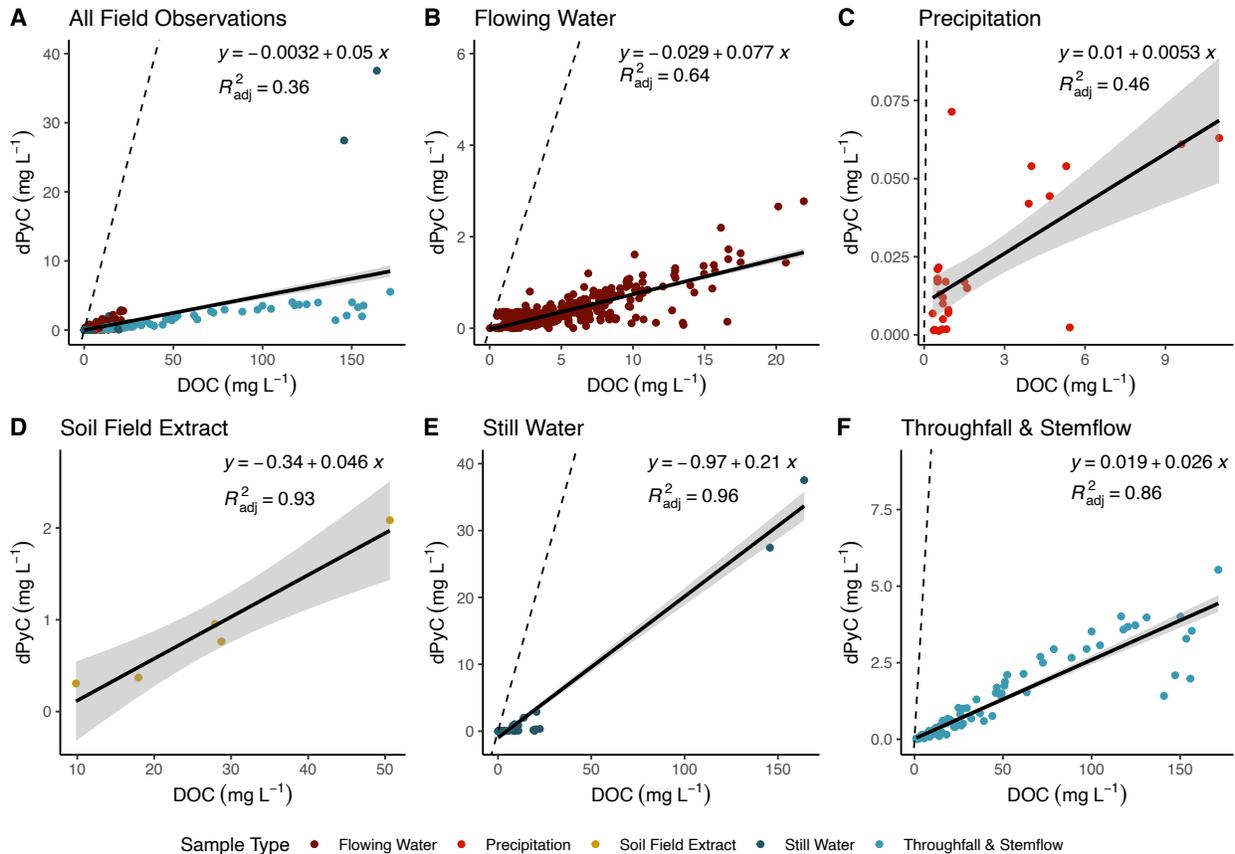


295 **Figure 4A and B.** Mean concentration with standard error of dPyC across different sample types
 296 (A) and climate zones (B) observed in the field derived from the BPCA method. Letters denote
 297 significant differences based on Wilcoxon rank sum test.
 298

299 **Correlation of dPyC with DOC**

300 In field-based studies across all sample types, dPyC comprised approximately 5% of DOC. In
 301 sample types where water has more contact time with PyC (i.e., soil water, still water, see **Figure**
 302 **4A**), dPyC makes up a greater proportion of DOC. In many of the flowing water studies the
 303 dPyC was correlated with discharge rates ([Dittmar et al., 2012](#); [Drake et al., 2020](#)), as is DOC,
 304 but some found a dilution effect of higher precipitation with lower dPyC concentrations under
 305 certain hydrologic conditions ([Bao et al., 2019](#); [Jones et al., 2019](#)). Together, this suggests that
 306 the mobility of dPyC is controlled by many of the same processes as DOC; hence the positive
 307 correlations between dPyC and DOC (**Figure 5**). However, studies that incorporate
 308 measurements of urban and anthropogenic sources of dPyC have noted a decoupling of dPyC
 309 from DOC where there are higher combustion activities ([Bi et al., 2018](#)).
 310

311



312
313 **Figure 5.** Dissolved PyC as measured by the BPCA method was correlated with DOC in field
314 data from all sample types (panel A) and separated by different sample types (panels B-F). Solid
315 black lines indicate linear fit with grey shaded area indicating 95% CI. The dashed line
316 represents a 1:1 ratio of dPyC to DOC.

317 318 3.4 Laboratory-based measurements

319
320 For laboratory studies, we considered measurements of DOC from char-extracts as a measure of
321 dPyC since the source material would be classified as PyC. This was the most frequently used
322 method in laboratory studies that measured dPyC, followed by the BPCA method. The highest
323 concentrations of dPyC measured in the lab were with the DOC method, which generated values
324 approximately 1-2 orders of magnitude higher than the next highest concentrations, which were
325 determined via the BPCA method. We found two categories of sample types in laboratory
326 studies – soil extracts and charcoal extracts ($n = 35$ and 86 , respectively). The soil extract had a
327 not significantly lower concentration of dPyC compared with charcoal extracts (in units dPyC
328 mg/kg; $p = 0.11$; $\chi^2 = 2.5347$; $df = 1$).

329
330 There were significant differences in dPyC concentrations across different filter sizes (**Figure**
331 **S2**), but these did not increase with filter pore size, therefore these differences were more likely
332 due to differing methodological approaches and/or sample characteristics. For laboratory studies,
333 the BPCA method was most frequently used ($n = 69$ observations), followed by GC-MS for
334 PAHs ($n = 46$). There were significant differences in the dPyC concentration based on the
335 analytical method used to quantify dPyC ($p < 0.05$; $\chi^2 = 40.268$; $df = 3$), with BPCA having

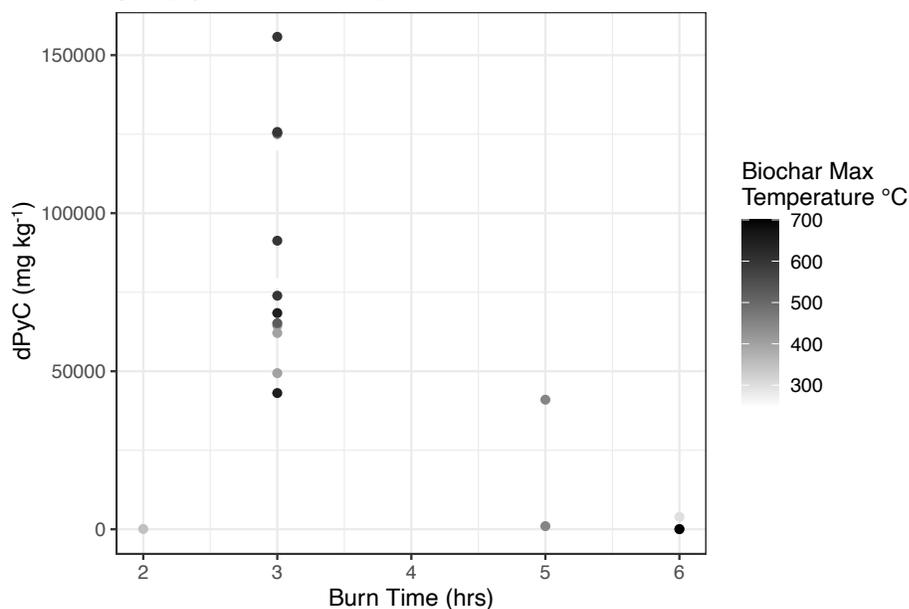
336 significantly higher concentrations than GC-MS and GC-MS specifically applied for PAHs
 337 (Figure S3).

338

339 3.4.1 Inferences from char extracts

340

341 We also examined drivers of dPyC by analyzing data from charcoal extractions, with feedstocks
 342 categorized as woody or herbaceous. There were no significant differences in dPyC
 343 concentration based upon feedstock type (woody vs herbaceous) alone ($\chi^2 = 0.011081$; $df = 1$; p
 344 > 0.05) or on extraction time ($\chi^2 = 5.1529$, $df = 5$; $p > 0.05$). Extraction by shaking released
 345 significantly more dPyC than other methods ($\chi^2 = 22.512$; $df = 1$; $p < 0.05$). There was a
 346 significant negative correlation between the solid to solution ratio ($p < 0.05$; $F = 5.648$; $df = 65$),
 347 which reflects more PyC available for dissolution, although this only explained a small portion
 348 of the variability in this data (Adjusted $R^2 = 0.068$). For extraction solvents, organic solvents
 349 resulted in significantly lower concentrations of dPyC than water or other solvents ($\chi^2 = 33.883$;
 350 $df = 2$; $p < 0.05$). We did find significant negative relationships between dPyC and burn time ($F =$
 351 10 ; $df = 18$; $p < 0.05$) and maximum charring temperature ($F = 8.57$; $df = 40$; $p < 0.05$). This is
 352 consistent with freshly produced charcoal at high charring intensities being some of the least
 353 soluble PyC (Pyle et al., 2015).



354

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

356

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

358

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

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

367

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

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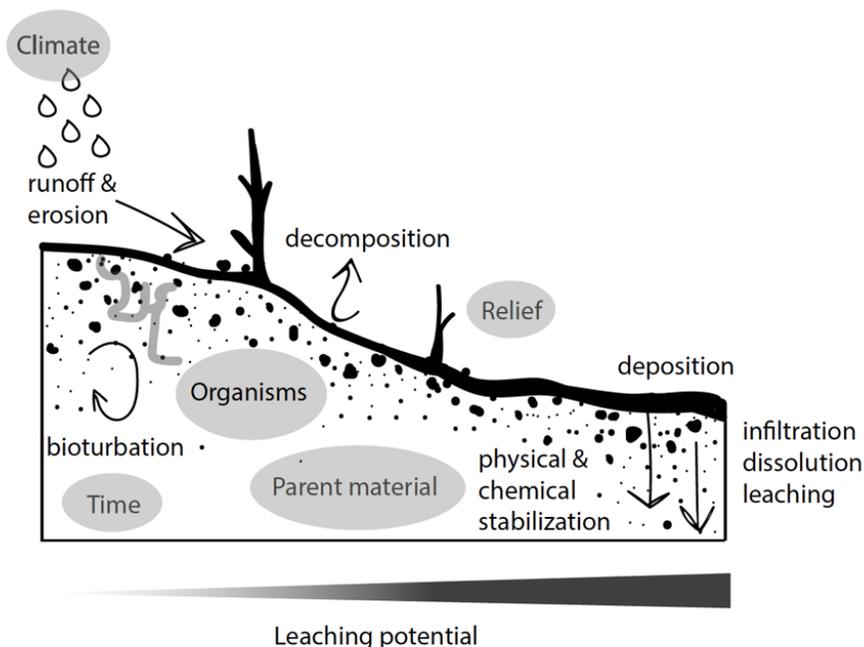
375 **4.1 Properties of PyC and dPyC that impact persistence and cycling in soil**

376

377 Once PyC is deposited on the soil surface after a fire, its physical and chemical properties dictate
378 how it may be transformed by the many processes that control its cycling and long-term fate.
379 Earlier work on PyC suggested that it persists in soil on the millennial time scale; however recent
380 work indicates that it has a centennial mean residence time in soil ([Bird et al., 2015](#); [Dittmar,
381 2015](#); [Wagner et al., 2015a](#)). The persistence of PyC in soil is typically longer when it is formed
382 at higher temperatures and/or longer burning durations, and there is evidence that when formed
383 at lower temperatures (<250 °C), it may breakdown over relatively shorter time scales (6 months;
384 [Abney et al., 2019a](#); [Whitman et al., 2015](#)). [Santos et al. \(2012\)](#) showed that this early
385 breakdown can occur even when PyC is formed in the laboratory at relatively higher controlled
386 temperatures (450 °C). This more rapid breakdown has been mainly attributed to decomposition;
387 however, some loss is likely due to leaching ([Hockaday et al., 2006](#); [Hockaday et al., 2007](#);
388 [Major et al., 2010](#)) and erosion ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Abney et al.,
389 2019b](#); [Abney et al., 2017](#)). In this section we discuss how chemical and physical properties of
390 PyC and leached dPyC impact its transport in soils. We propose the following function can be
391 used to understand the controls on the fate and properties of PyC and dPyC throughout post-fire
392 landscapes (**Figure 7**).

393

394 $f = \text{Burn conditions} + \text{Climate} + \text{Topography} + \text{Organisms} + \text{Parent material} + \text{Time} + \text{post-}$
395 $\text{fire soil properties}$



396
 397 **Figure 7.** The interaction of soil forming factors and burn conditions and severity likely dictate
 398 the fate and transport of dissolved pyrogenic carbon across dynamic landscapes. By studying
 399 post-fire landscapes through these two lenses, we can build predictive models of post-fire PyC
 400 dynamics.
 401

402 4.1.2 Chemical composition

403 The chemical composition of solid PyC before dissolution influences the quantity and quality of
 404 dPyC. At lower burn temperatures, the resulting PyC formed is high in nutrients and oxygenated
 405 functional groups, while higher burn temperatures tend to produce more condensed aromatic
 406 PyC with low H:C and O:C ratios ([Baldock and Smernik, 2002](#); [Hammes et al., 2006](#); [Schneider
 407 et al., 2010](#)). [Bostick et al. \(2018\)](#) investigated dPyC from PyC formed from oak wood and grass
 408 and reported that the leachates were mostly chemically composed of a complex mixture of C
 409 groups such as carbohydrates, aliphatics, and low molecular mass compounds, suggesting that
 410 the DOM resulting from PyC is not solely comprised of condensed aromatics. [Wozniak et al.
 411 \(2020\)](#) demonstrated the chemical heterogeneity of dPyC derived from low (250 °C) heating
 412 temperatures exhibits a wide range of O/C values and the presence of highly unsaturated
 413 aliphatics, polyphenolic formulas, and condensed aromatic C compounds, whereas compounds
 414 with low O/C ratios dominated the composition of dPyC from higher heating temperatures (400
 415 °C). Taken together, these recent findings suggest that DOM leached from solid PyC is
 416 heterogeneous and exists also along a chemical continuum ([Wagner et al., 2021](#)).

417 4.1.3 The influence of burn conditions

418
 419 The physical structure of PyC has been described by porosity, density, and particle size, each of
 420 which can impact the stability of PyC and its potential for dissolution. For many biochars,
 421 increasing charring temperature increases skeletal density and porosity, which may alter the
 422 availability of the char for microbial decomposition or leaching ([Brewer et al., 2014](#)). We found

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

437 **4.2 Environmental and soil factors controlling transport and fate of dPyC along a** 438 **terrestrial to aquatic gradient**

439
440 In addition to the properties of PyC, there are a number of environmental and soil factors that
441 play a role in the transport of dPyC across landscapes. Below we discuss the relative importance
442 of site factors, such as climate, topography, biotic factors, parent material, time, and burn
443 conditions, in dPyC formation and transport. Additionally, these factors are frequently
444 interacting across dynamics landscapes and are often difficult to disentangle in natural systems.

445 **4.2.1 Climate: precipitation and temperature**

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

458
459 From this meta-analysis, studies that measured dPyC concentrations in precipitation samples
460 found some of the lowest ratios of dPyC to DOC and the weakest correlation between DOC and
461 dPyC (**Figure 5**). The variability in dPyC in precipitation is likely due to the movement of air
462 masses containing particulate PyC (either from fire ash and soot or fossil fuel burning) and
463 variability in timing of precipitation events. The timing of the initial interaction of PyC and water
464 is critical for its fate in the post-fire landscape ([Masiello and Berhe, 2020](#)).

465
466 Environmental temperatures likely impact the potential for PyC leaching via a few key
467 mechanisms, mainly through the form of precipitation (snow vs rain fall), the speed of

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

473

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

482 **4.2.2 Topography and Erosion**

483

484 Topographic landform positions are likely significant controls on dPyC and SOM dynamics, as
485 previous research has reported an increase in SOC in depositional landform positions, which
486 receive eroded material from upslope landform positions ([Berhe et al., 2018](#); [Berhe et al., 2007](#)).
487 Additionally, the preferential erosion of PyC likely indicates that it can accumulate in these
488 depositional landform positions ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Rumpel et al.,
489 2009](#); [Rumpel et al., 2006](#)). An unanswered question, however, is whether PyC in depositional vs
490 eroding landform positions could be more susceptible to leaching when there are higher nutrient
491 concentrations and higher water content. The impacts of erosion on the long-term fate of PyC in
492 soil are complex and depend on the landscape erosion and deposition dynamics along with the
493 soil water conditions and precipitation events ([Abney and Berhe, 2018](#); [Masiello and Berhe,
494 2020](#)).

495

496 Elevated rates of post-fire erosion are widely reported across a range of different ecosystem
497 types ([Carroll et al., 2007](#); [de Dios Benavides-Solorio and MacDonald, 2005](#); [Johansen et al.,
498 2001](#); [Robichaud et al., 2007](#)). The magnitude of post-fire erosion is dependent on a number of
499 soil and precipitation factors, which also control the (1) amount of PyC available for leaching
500 and (2) the soil-water conditions to allow for leaching to occur. Furthermore, there is a direct
501 relationship between burn severity, SOM chemical composition, and erosion ([Abney and Berhe,
502 2018](#); [Abney et al., 2019b](#)), such that areas that experience higher burn severities have SOM that
503 is more aromatic and more erosion prone. This suggests that conversely, areas that experience
504 moderate- to low-severity burning may have SOM that is more prone to leaching due to both its
505 chemical composition and higher soil infiltration rates ([de Dios Benavides-Solorio and
506 MacDonald, 2005](#); [Morris and Moses, 1987](#); [Robichaud, 2000](#); [Torreano and Morris, 1998](#)).
507 Several studies have indicated that PyC is preferentially transported post-fire ([Abney et al.,
508 2019b](#); [Rumpel et al., 2009](#); [Rumpel et al., 2006](#)). However, since most SOM that is transported
509 via erosion is deposited within the same or adjacent watershed ([Stallard, 1998](#)), this transported
510 PyC may still be available for and susceptible to leaching, depending on where in the landscape
511 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

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

561

562 **4.2.5 Time**

563 Time is a critical factor in controlling the availability of PyC for forming dPyC. Some research
564 has shown that dPyC increases over time, as the processes of chemical, physical, and biological
565 breakdown of PyC progress, leading to more soluble DOC and dPyC with increasing time since
566 fire ([Bostick et al., 2021](#); [Wagner et al., 2017](#); [Wagner et al., 2018](#)). This increase in solubility is
567 due to introduction of oxygen and nitrogen containing functional groups ([Hilscher and Knicker,
568 2011](#)). There are also lags in between the formation and deposition of PyC and the transport of
569 dPyC into adjacent and further downstream aquatic systems, as evidenced by increasing ages of
570 PyC and dPyC (see **Table S2, Figure 9**) along terrestrial to aquatic gradients to the ocean
571 ([Wagner et al., 2019a](#); [Wagner et al., 2018](#)). Contrastingly, some evidence indicates that PyC is
572 more bioavailable immediately after production than previously considered, in part because PyC
573 also contains C compounds that are readily available for microorganisms and leaching ([Cheng et
574 al., 2008](#); [Schiedung et al., 2020](#)). In addition, the amount of soil PyC available for forming
575 dPyC is highest in the time immediately post fire. There are many environmental factors that
576 may control dPyC concentrations in soils and streams post-fire, such as soil PyC concentrations,
577 hydrological connectivity of a watershed, potential for decomposition of PyC, etc. At least one
578 study has found no significant relationship between time since fire or between fire return interval
579 and dPyC concentration in stream water ([Ding et al., 2013](#)), which may be reflective of these
580 complexities. [Wagner et al. \(2015a\)](#) show different timing of particulate PyC compared with
581 dPyC peak fluxes in a fire-impacted watershed in Colorado, USA. With this variability in timing
582 of export of dPyC from fire-impacted watersheds, we need more mechanistic understanding of
583 the hillslope-scale processes that are driving this export.

584 **4.3 Fire-driven changes in soil properties that impact mobilization of PyC**

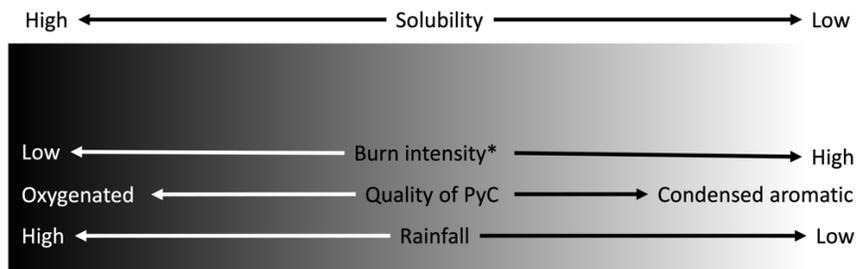
585

586 Fire has long been described as a major disturbance and driver of changes in soil properties,
587 including pH, hydrophobicity, texture, nutrient availability, organic matter, and vegetation
588 dynamics, among others ([DeBano, 1991](#); [Gonzalez-Perez et al., 2004](#); [MacDonald and Huffman,
589 2004](#); [Mataix-Solera et al., 2011](#)). Increases in pH may shift the solubility of PyC, as shown by
590 [Rebollo et al. \(2008\)](#). Increases in hydrophobicity post-fire have frequently been reported in low
591 to moderate burn severity fires ([MacDonald and Huffman, 2004](#); [Mataix-Solera and Doerr,
592 2004](#)), and increases in hydrophobicity may at least temporarily reduce the leaching of PyC into
593 the soil matrix, as there is reduced infiltration (with potential for increased runoff of dPyC).
594 Reduced infiltration and increased runoff post-fire due to loss of vegetation also can lead to
595 elevated rates of erosion, at least until vegetation cover has returned ([de Dios Benavides-Solorio
596 and MacDonald, 2005](#)). As vegetation regrows post-fire and the hydrophobic layer begins to
597 breakdown, it is not yet clear what timescales are relevant for processes of dissolution, within
598 soil redistribution, and hydrologic export of dPyC or how these processes are moderated by burn
599 severity to impact the transport of dPyC.

600

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

604 burns or more decomposed/oxidized). For example, as PyC ages, its surfaces may be broken into
 605 more digestible aliphatic functional groups, which are more soluble, but as these are consumed,
 606 this can leave behind a more aromatic PyC (Hockaday et al., 2007) that is less soluble and more
 607 persistent in soil. Rainfall can also drive fluxes of dPyC, as multiple papers monitoring dPyC in
 608 rivers noted positive correlations with higher discharge (Jaffé et al., 2013; Wagner et al., 2019c;
 609 Wagner et al., 2015a). Bao et al. (2019) argue that different pools of DOC are accessed at
 610 different flow rates through soil, so we often find higher DOC and dPyC with higher flows. The
 611 actual solubility (or potential for leaching) of PyC across landscapes is controlled by the
 612 interaction of several environmental factors, including the burn intensity, chemical and physical
 613 properties of the PyC, and amount and timing of rainfall (**Figure 8**).
 614



*Burn intensity = temperature + duration of burning

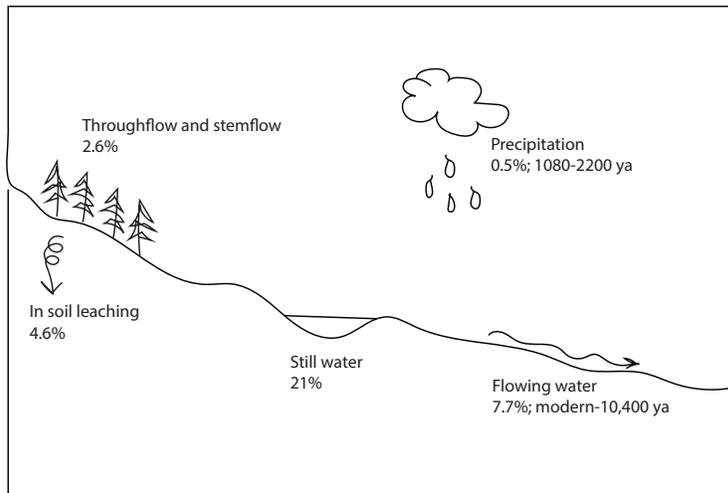
615 **Figure 8.** Controls on the solubility (leaching potential) of PyC in soil. There are other factors
 616 controlling the leaching of PyC, including decomposition, sorption, fire return intervals, aging of
 617 PyC etc. However, these are complex and likely do not follow linear relationships.
 618

619 5. Ecosystem implications

620

621 5.1 Fluxes and internal cycling of dPyC between ecosystem components

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



629 **Figure 9.** Transport of dPyC across different global pools is presented as percent of dissolved
 630 organic carbon. The range of radiocarbon ages of the dPyC in each pool is reported in years (see
 631 **Table S2** for more details).
 632

633
 634 In terrestrial waters, there is an increase in dPyC age reported with increasingly larger and more
 635 mixed pools (rivers and oceans compared with tributaries). The age of dPyC in tributaries was
 636 also highly variable, which is likely reflective of the significance of individual watershed
 637 properties on controlling DOM release and quality. The proportion of PyC that makes it from
 638 deposition on soil surface post-fire to ocean dPyC is likely infinitesimally small. [Bostick et al.](#)
 639 [\(2018\)](#) report that between 1-14% of dPyC in soil is leached to river dPyC, so the vast majority is
 640 internally recycled. However, the controls on the variability and rates of transport of soil dPyC to
 641 riverine dPyC need further investigation.

642 643 **5.2 Future research directions**

644 There are numerous needs for future research on dPyC in soil and across the terrestrial-aquatic
 645 interface. Arguably the most urgent of these is for more quantitative measurements of dPyC in
 646 soil and in fluxes between soil and aquatic systems. For example, two previous studies showed
 647 that PyC can be redistributed through leaching at rates of 1-17% of soil PyC ([Boot et al., 2015](#);
 648 [Major et al., 2010](#)), however considerable further quantification is required before we can predict
 649 dPyC leaching across different soil and precipitation regimes. There is also a need for better
 650 intercomparison between quantitative approaches, or perhaps wider adoption of a smaller
 651 number of methodologies. In field studies, the BPCA method has been widely used and has the
 652 advantage of being able to measure PyC in both solid and liquid samples, as well as provide
 653 information about the condensation of PyC. However, BPCA is time consuming, somewhat
 654 expensive, and is quantitative only for higher burn intensity dPyC. Combining BPCA with
 655 methods that are more sensitive to the lower burn intensity portion of the dPyC continuum will
 656 allow for a more complete understanding of transport of dPyC in the natural environment. BPCA
 657 can also be used to train models that enable researchers to obtain more quantitative measurements
 658 from less costly, high-throughput methods such as mid-infrared spectroscopy([Cotrufo et al.,](#)
 659 [2016](#); [Sanderman et al., 2020](#)).

660

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

674

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

687

688 **6. Conclusions**

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

698

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

707 consistent with chemical controls of dPyC solubility. We have also identified a significant need
708 for (1) more mechanistic understanding of the environmental controls of movement of dPyC
709 from soil to aquatic systems, (2) more soil-water measurements of dPyC, and (3) better
710 understanding of the temporal scales relevant to environmental fluxes of dPyC. Future research
711 on dPyC that provides quantitative measures of the fate of dPyC in soils will be useful for
712 models of soil C and can potentially provide critical information to land managers seeking to
713 increase soil C storage.
714

715

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729

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.

733

734

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

3
4
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17 **Key Points:**

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

23

24

25 Abstract

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

45 1. Introduction

46 1.1 Significance of dissolved pyrogenic carbon in the global C cycle

47
48 Wildfire is a a major ecosystem disturbance that has been progressively getting more severe and
49 intense in many areas of the world ([Descals et al., 2022](#); [Feurdean et al., 2020](#); [Turco et al., 2018](#);
50 [Westerling et al., 2006](#)). Additionally, significant increases in the use of prescribed fire have
51 been observed across the US in the past few decades, especially in the southeast ([Kolden, 2019](#)).
52 Natural and anthropogenic fires transform carbon (C) into a range of materials across the burn
53 continuum including lightly charred material to charcoal, soot, and ash, collectively known as
54 pyrogenic carbon, or PyC ([Bird et al., 2015](#); [Masiello, 2004](#)). This PyC is initially deposited on
55 the soil surface and emitted to the atmosphere. Pyrogenic C has received considerable research
56 attention over the past decades due to its generally longer persistence times in soil relative to
57 other soil organic matter components, which has implications for C storage ([Abney and Berhe,
58 2018](#); [Bird et al., 2015](#); [Santín et al., 2016](#)).

59
60 There has been limited research synthesizing the production, pools, and fluxes of PyC across
61 large spatial scales ([Coppola et al., 2022](#); [Wagner et al., 2018](#)) to better constrain the role of PyC
62 in the global C cycle. It has been estimated that approximately 2.7% of the global land area is
63 burned annually ([Giglio et al., 2013](#)), resulting in 50-270 Tg y⁻¹ of PyC produced ([Kuhlbusch
64 and Crutzen, 1995](#)). At a global scale, PyC can account for a significant portion (~10%) of
65 dissolved organic carbon (DOC) fluxes in rivers ([Jaffé et al., 2013](#); [Wagner et al., 2018](#)). The
66 global annual transport of particulate PyC from rivers into oceans ranges from 19-80 Tg/yr
67 ([Druffel, 2004](#); [Elmquist et al., 2008](#); [Jaffé et al., 2013](#)), although this is most frequently reported
68 as 26-27 Tg/yr ([Elmquist et al., 2008](#); [Jaffé et al., 2013](#)). However, current estimates of dPyC

69 export from terrestrial to inland aquatic systems range over several orders of magnitude, from
70 ~0.4-18 Tg/yr ([Bowring et al., 2022](#); [Jones et al., 2020](#)), likely reflecting both the variability in
71 processes (e.g., decomposition, photooxidation, water availability, etc.) influencing PyC
72 dynamics at the terrestrial- aquatic interface and insufficient PyC measurements.

73
74 While parameterization of global PyC models typically includes annual production, stocks,
75 large-scale fluxes, and some smaller-scale controls (i.e., decomposition ([Bird et al., 2015](#);
76 [Reisser et al., 2016](#); [Santín et al., 2016](#)), several critical knowledge gaps remain regarding what
77 controls those fluxes, especially at smaller scales. In particular, we need a more detailed
78 understanding of how PyC is transported from source burned material into the soil system, across
79 hillslopes and watersheds, and into aquatic environments ([Myers-Pigg et al., 2015](#); [Wagner et al.,
80 2019c](#); [Wagner et al., 2015b](#)). Some recent research has demonstrated inconsistencies between
81 the sources and ages of dPyC flowing from rivers and those from PyC measured in the ocean
82 ([Wagner et al., 2019b](#)), which indicates limitations in our mechanistic understanding of (1) the
83 cycling of dPyC within terrestrial systems, (2) cycling within freshwater aquatic systems, and (3)
84 connections between terrestrial and aquatic systems. This paper addresses this limitation by
85 synthesizing our current knowledge of dPyC fluxes and the processes that control its
86 transformation within and between terrestrial and aquatic ecosystems to inform research
87 communities involved in management, modeling, and description of PyC.

88

89 **1.2 Aims**

90

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

97

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

104 **1.3 Defining dPyC**

105

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

115 of environmental research considers materials $<0.45\ \mu\text{m}$ to be dissolved, these materials may in
116 fact be very small colloidal organic matter. Benzene, which makes up the backbone of many PyC
117 molecules, is only slightly soluble in water, but it is small enough that it would easily pass
118 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
119 course, most PyC does not exist as single benzene rings but is comprised of large, complex
120 macromolecules with some soluble functional groups ([Bird et al., 2015](#)), and much of what is
121 often described as dPyC are chemical fragments and colloids ([Wagner et al., 2017](#)). In this work,
122 we are using “dPyC” to indicate both fully dissolved and colloidal PyC within an aqueous matrix
123 due to inconsistencies in analytical approaches used for quantifying PyC pools and fluxes.
124

125 **2. Methods**

126 **2.1 Data acquisition**

127
128 Publications were selected for the meta-analysis following a modification of the PSALSAR
129 (research protocol and reporting results) method adapted by [Mengist et al. \(2020\)](#) from the
130 SALSA (search, appraisal, synthesis, and analysis) method ([Grant and Booth, 2009](#)), which
131 outlines organized methods for systematic literature reviews. Complete search and selection
132 criteria can be found in **Table S1**. The scope of the meta-analysis was defined as original
133 research papers that either quantified dPyC or characterized its chemical composition within
134 terrestrial or freshwater systems, including in-lab simulations and extractions. The search for
135 publications was initiated on August 23, 2021, via Web of Science and returned 12,776
136 publications, which we narrowed to 175 final publications via three successive rounds of filtering
137 (**Figure S1**).

138 **2.2 Data processing and analysis**

139 **2.2.1 Extraction of dPyC values and other relevant information**

140
141
142 Data were extracted from the 175 meta-analysis publications (**Figure 1** and **Table S1**) and
143 organized in Microsoft Excel as study- and observation-level information, where the study-level
144 information was applicable to the entire publication (e.g., publication year) and observation-level
145 information was specific to individual data points (e.g., pyrolysis temperature for a single PyC
146 type). Observations were included when they were reported concentrations of dPyC or
147 concentrations of DOC when only PyC (charcoal, biochar) was extracted in the laboratory. Data
148 which were presented only in figures (e.g., a bar graph of dPyC concentration means) were
149 extracted using Web Plot Digitizer ([Rohatgi, 2022](#)).
150

151 **2.2.2 Assignment of location and climate regions to dPyC field observations**

152
153 Latitude and longitude were assigned to each field study observation using provided coordinates,
154 map figures (using Web Plot Digitizer as described earlier), or via Google Earth using
155 descriptions in the manuscript text. Climate assignments were made by entering coordinates into
156 ClimateCharts.net ([Laura Zepner, 2020](#)), a web-based application which generates climate
157 classifications based on the Geiger-Köppen system. These assignments may contain some error
158 at locations where regional or local scale climate variation exists at too fine a resolution to be

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

162
163 The map figure was generated in R version 4.2.1 using the `geom_map()` function in the `ggplot2`
164 package. To reduce noise in the map, observations were binned by river basin using ArcMap
165 from ArcGIS Desktop 10.8.1 (2020) with the World Wildlife Fund hydroSHEDS level 5 basins
166 dataset (Lehner and Grill, 2013). Detailed workflows for processing of spatial data are provided
167 in the Supplemental Materials.

168

169 **2.2.4 Statistical analyses**

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

183

184 **3. Results**

185 **3.1 Overview of dataset**

186 Here we provide an overview of the meta-analysis based on 175 studies on dPyC, which yielded
187 2084 individual observations of dPyC (**Table 1**). The majority of observations (66%) were from
188 the field setting, and they were reported across five different non-convertible units. We analyzed
189 the data in light of methodological differences (Section 3.2), field measurements (Section 3.3),
190 and laboratory-based measurements (Section 3.4) to quantify the relative magnitude of different
191 dPyC pools and fluxes across the terrestrial to aquatic interface and to identify important
192 mechanisms driving these fluxes.

193

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

200

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

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

210
 211

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

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

217

218 **3.2. The influence of methodological approaches on dPyC measurements**

219 **3.2.1 Detection and measurement of dissolved PyC**

220

221 A major obstacle to closing the gaps in the global PyC cycle is associated with the
 222 methodological difficulty in measuring PyC, because there are a broad suite of methods used to
 223 quantify PyC and dPyC, and each method only captures a small portion of the PyC continuum
 224 ([Bird et al., 2015](#); [Masiello, 2004](#); [Wiedemeier et al., 2015](#)). As such, a suite of analytical
 225 methods was used by the studies selected for our meta-analysis. Many studies utilized qualitative
 226 methods for identification of the chemical composition of PyC in solution, including ultrahigh
 227 resolution mass spectrometry, Nuclear Magnetic Resonance spectroscopy (NMR), X-ray
 228 photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). For additional
 229 details on how these methods can be utilized for dPyC, see ([Chen et al., 2022](#); [Hameed et al.,](#)
 230 [2023](#); [Wagner et al., 2018](#)). Quantitative methods provide a measurement of PyC concentration
 231 in solution, which we further investigated in our meta-analysis, and included molecular markers
 232 (Benzene Polycarboxylic Acid or BPCA, levoglucosan, and polycyclic aromatic hydrocarbons or
 233 PAHs), chemo-thermal oxidation, as well as analytical and hydrogen pyrolysis, all of which have
 234 been extensively discussed elsewhere ([Ascough et al., 2009](#); [Gustafsson et al., 2001](#); [Hameed et](#)
 235 [al., 2023](#); [Hammes et al., 2007](#); [Schmidt et al., 2001](#); [Wagner et al., 2018](#)). In 3.2.2, we examined
 236 the most common methods applied for the chemical characterization and quantification of dPyC
 237 in field and laboratory studies.

238

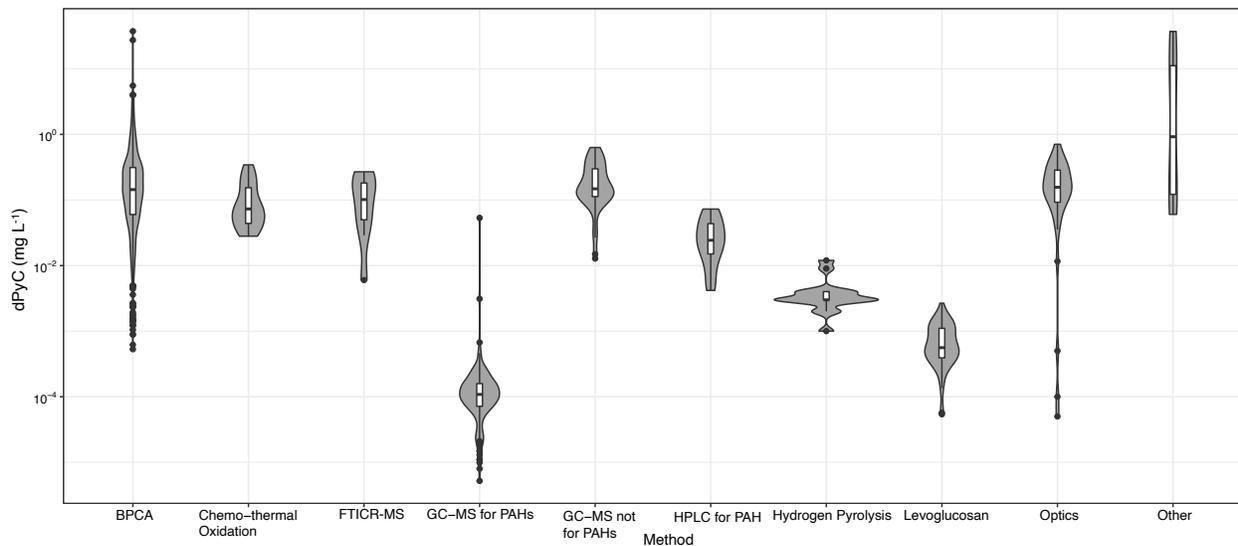
239 **3.2.2 The impact of methodological approach on measured dPyC concentration**

240 To assess how the use of different methodological approaches may influence dPyC values, we
 241 examined concentrations (in mg L^{-1} or mg kg^{-1}) across field- and lab-based observations (**Figure**
 242 **2**). Field measurements of dPyC ranged over six orders of magnitude, and the lowest reported
 243 concentrations were in some of the methods that describe the narrowest section of the PyC
 244 continuum, namely GC-MS for PAHs and levoglucosan. BPCA is a widely used method across
 245 many sample types and this is reflected in the concentrations reported from this method.
 246 Approximately 50% of all data points were derived from the BPCA method, the majority of
 247 which were from field-based studies. The majority of field observations were obtained from the
 248 BPCA method (71%), while the majority of laboratory observations were made by quantifying
 249 total DOC from PyC (as charcoal, biochar, etc. extractions), followed by GC-MS techniques.
 250 The GC-MS techniques were also common in field studies (16% of observations). The vast
 251 majority (>80%) of laboratory studies quantified dPyC on char extracts, and the remainder
 252 quantified dPyC on soil extracts.

253

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

258



259

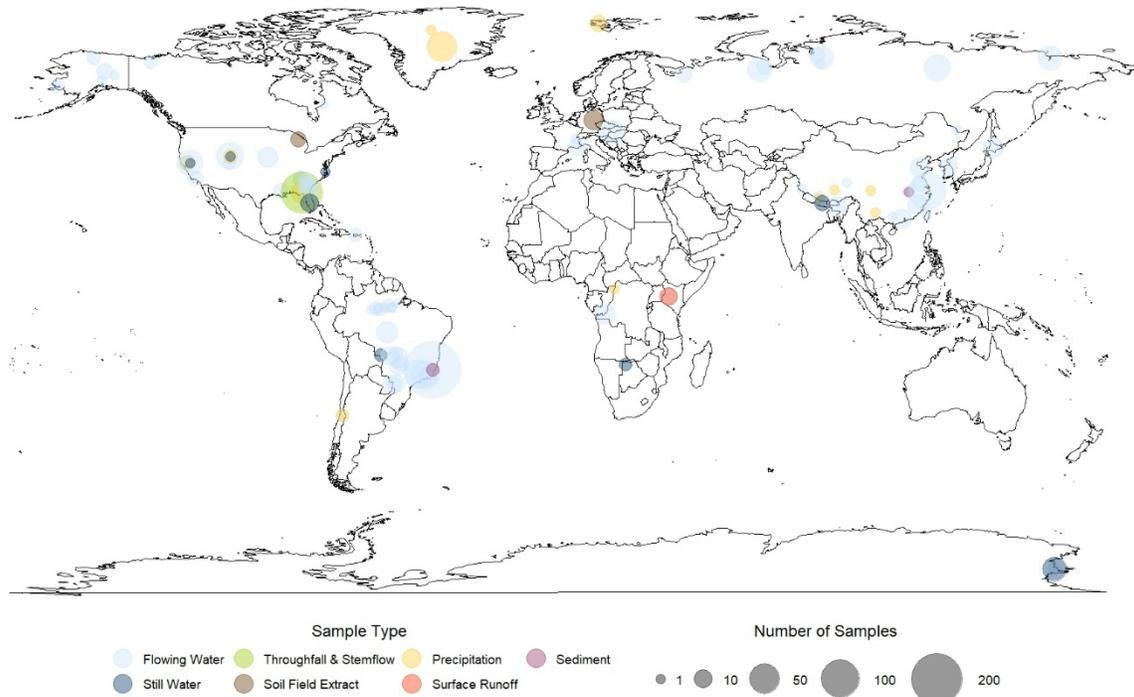
260 **Figure 2.** Field measurements of dPyC across different methodologies (n.b. Y axis is in log
 261 scale). Methods included in this figure are: BPCA (benzene polycarboxylic acid), Chemo-thermo
 262 oxidation, FTICR-MS (Fourier-transform ion cyclotron resonance mass spectrometry), GC-MS
 263 (gas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

268

269

270

271



272
 273 **Figure 3.** Field-based measurements of dPyC across all methods with color indicating sample
 274 type and size of point denoting the number of observations.
 275

276

277 3.3 Field-based measurements

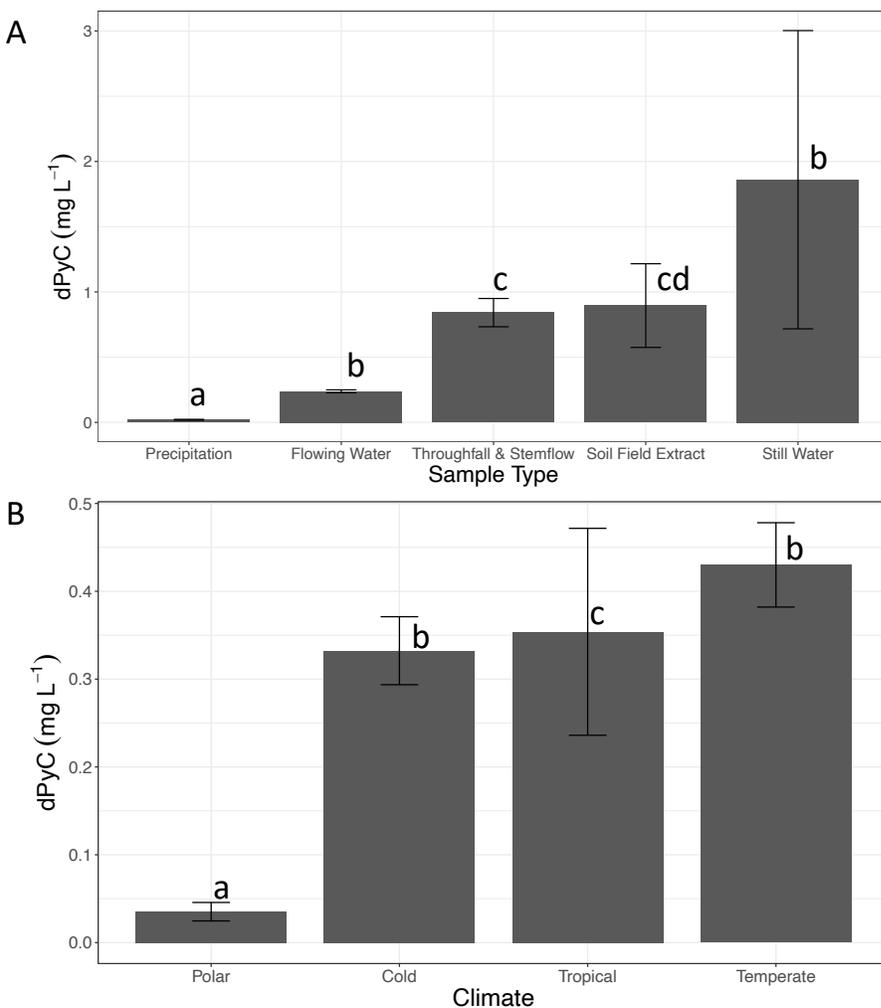
278

279 Field-based observations of dPyC were distributed globally, including six of seven continents
 280 (excluding Australia). We extracted dPyC observations from several locations, including central
 281 and western Asia, eastern Europe, central America, and northern Africa (**Figure 3**). The majority
 282 of field-based observations of dPyC using the BPCA method were made in flowing water ($n =$
 283 734; 78%), with only a few that were soil related ($n = 5$; 0.5%). There were significant
 284 differences in dPyC concentration across different sample types ($p < 0.05$; $\chi^2 = 109.42$, $df = 4$;
 285 Kruskal-Wallis, **Figure 4A**). A pairwise Wilcoxon rank sum test indicated that each sample type
 286 was significantly different from each other ($p < 0.05$), except for soil field extract and
 287 throughfall and stemflow. The highest concentrations of dPyC in the field were found in water
 288 that had more time to interact with PyC (e.g., still water, soil pore water, throughfall and
 289 stemflow vs. precipitation and flowing water (**Figure 4A**). Additionally, there were significant
 290 differences in dPyC concentration across different climate zones ($p < 0.05$; $\chi^2 = 78.434$, $df = 3$;
 291 Kruskal-Wallis; **Figure 4B**). This likely reflects differences in burn season length, vegetation
 292 available for burning, and mean air temperature and availability of water for dissolution.

293

294

295



295 **Figure 4A and B.** Mean concentration with standard error of dPyC across different sample types
 296 (A) and climate zones (B) observed in the field derived from the BPCA method. Letters denote
 297 significant differences based on Wilcoxon rank sum test.
 298

299 300 **Correlation of dPyC with DOC**

301 In field-based studies across all sample types, dPyC comprised approximately 5% of DOC. In
 302 sample types where water has more contact time with PyC (i.e., soil water, still water, see **Figure**
 303 **4A**), dPyC makes up a greater proportion of DOC. In many of the flowing water studies the
 304 dPyC was correlated with discharge rates ([Dittmar et al., 2012](#); [Drake et al., 2020](#)), as is DOC,
 305 but some found a dilution effect of higher precipitation with lower dPyC concentrations under
 306 certain hydrologic conditions ([Bao et al., 2019](#); [Jones et al., 2019](#)). Together, this suggests that
 307 the mobility of dPyC is controlled by many of the same processes as DOC; hence the positive
 308 correlations between dPyC and DOC (**Figure 5**). However, studies that incorporate
 309 measurements of urban and anthropogenic sources of dPyC have noted a decoupling of dPyC
 310 from DOC where there are higher combustion activities ([Bi et al., 2018](#)).
 311

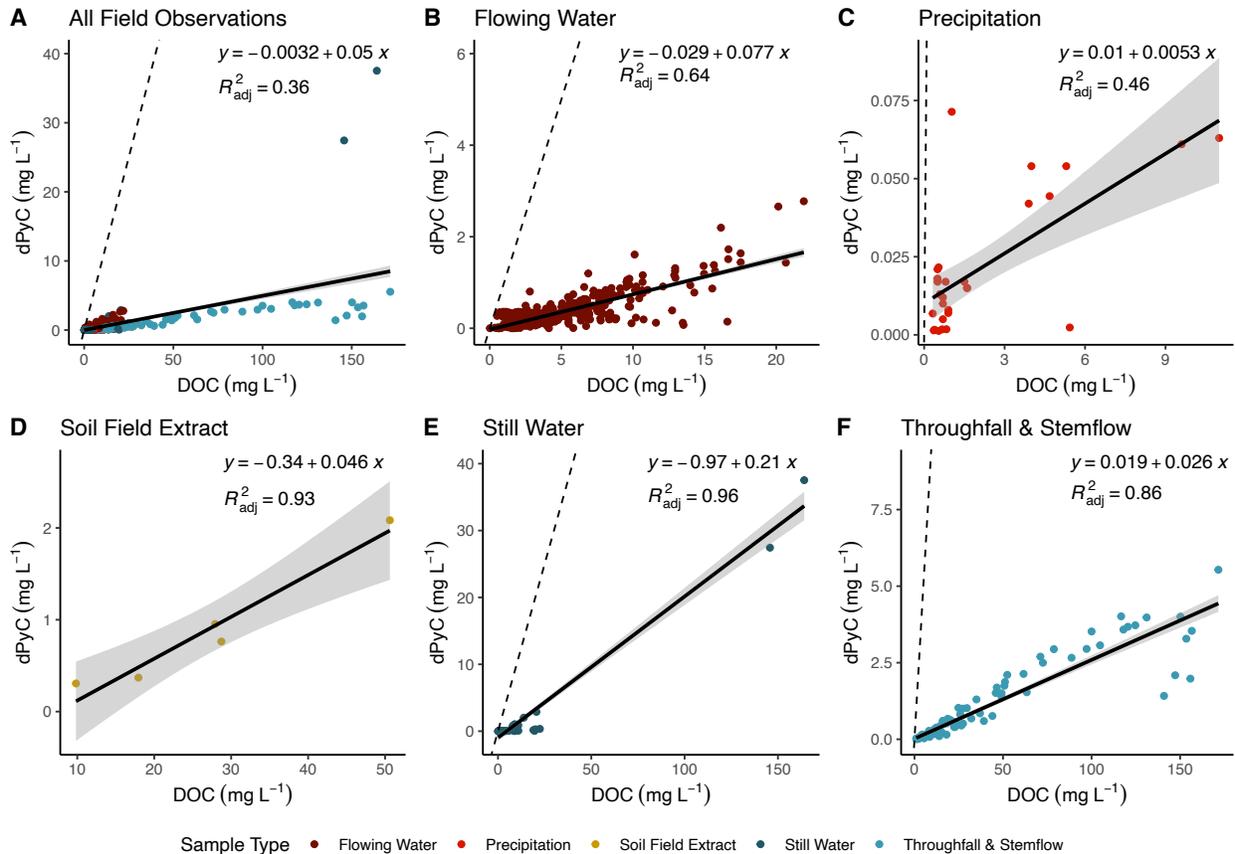


Figure 5. Dissolved PyC as measured by the BPCA method was correlated with DOC in field data from all sample types (panel A) and separated by different sample types (panels B-F). Solid black lines indicate linear fit with grey shaded area indicating 95% CI. The dashed line represents a 1:1 ratio of dPyC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

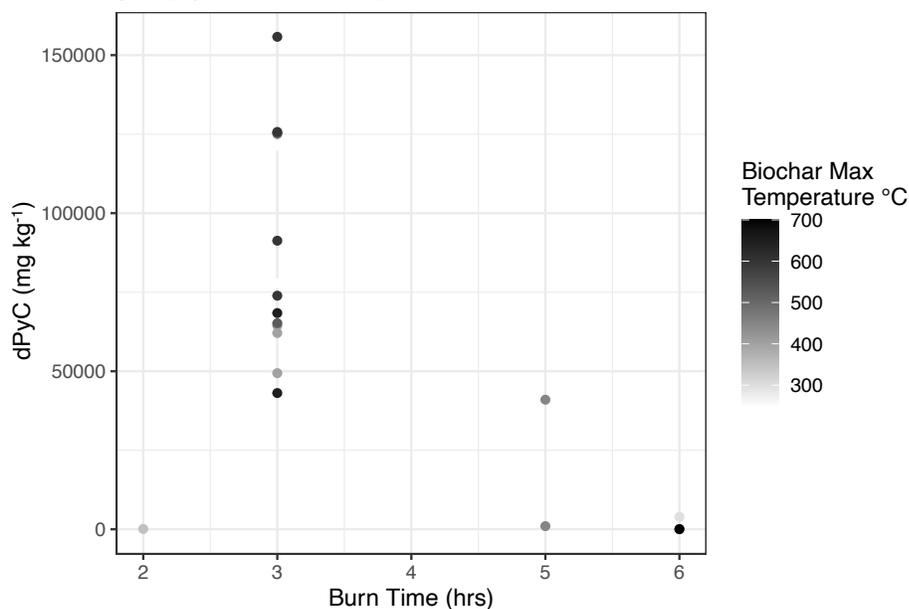
336 significantly higher concentrations than GC-MS and GC-MS specifically applied for PAHs
 337 (Figure S3).

338

339 3.4.1 Inferences from char extracts

340

341 We also examined drivers of dPyC by analyzing data from charcoal extractions, with feedstocks
 342 categorized as woody or herbaceous. There were no significant differences in dPyC
 343 concentration based upon feedstock type (woody vs herbaceous) alone ($\chi^2 = 0.011081$; $df = 1$; p
 344 > 0.05) or on extraction time ($\chi^2 = 5.1529$, $df = 5$; $p > 0.05$). Extraction by shaking released
 345 significantly more dPyC than other methods ($\chi^2 = 22.512$; $df = 1$; $p < 0.05$). There was a
 346 significant negative correlation between the solid to solution ratio ($p < 0.05$; $F = 5.648$; $df = 65$),
 347 which reflects more PyC available for dissolution, although this only explained a small portion
 348 of the variability in this data (Adjusted $R^2 = 0.068$). For extraction solvents, organic solvents
 349 resulted in significantly lower concentrations of dPyC than water or other solvents ($\chi^2 = 33.883$;
 350 $df = 2$; $p < 0.05$). We did find significant negative relationships between dPyC and burn time ($F =$
 351 10 ; $df = 18$; $p < 0.05$) and maximum charring temperature ($F = 8.57$; $df = 40$; $p < 0.05$). This is
 352 consistent with freshly produced charcoal at high charring intensities being some of the least
 353 soluble PyC (Pyle et al., 2015).



354

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

356

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

358

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

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

367

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

374

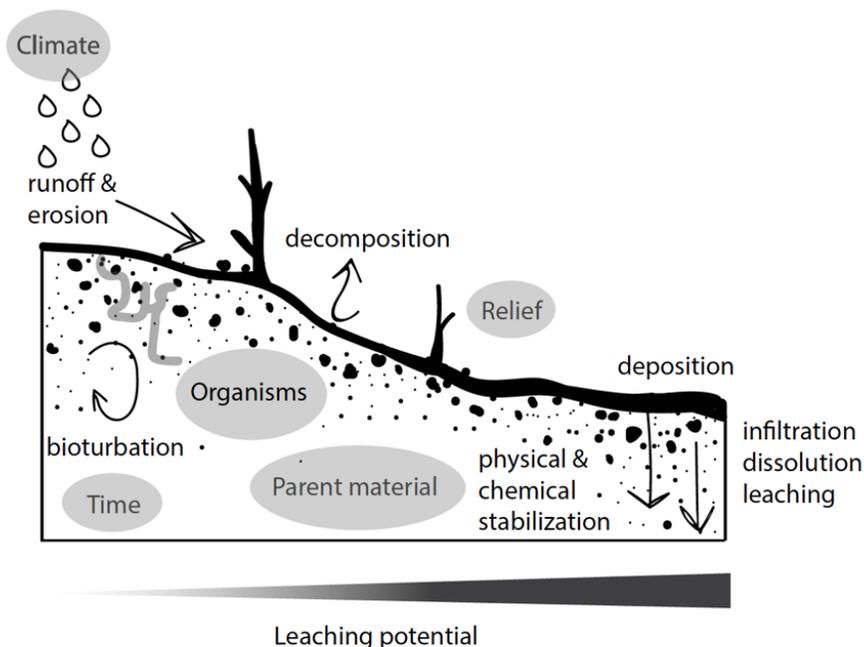
375 **4.1 Properties of PyC and dPyC that impact persistence and cycling in soil**

376

377 Once PyC is deposited on the soil surface after a fire, its physical and chemical properties dictate
378 how it may be transformed by the many processes that control its cycling and long-term fate.
379 Earlier work on PyC suggested that it persists in soil on the millennial time scale; however recent
380 work indicates that it has a centennial mean residence time in soil ([Bird et al., 2015](#); [Dittmar,
381 2015](#); [Wagner et al., 2015a](#)). The persistence of PyC in soil is typically longer when it is formed
382 at higher temperatures and/or longer burning durations, and there is evidence that when formed
383 at lower temperatures (<250 °C), it may breakdown over relatively shorter time scales (6 months;
384 [Abney et al., 2019a](#); [Whitman et al., 2015](#)). [Santos et al. \(2012\)](#) showed that this early
385 breakdown can occur even when PyC is formed in the laboratory at relatively higher controlled
386 temperatures (450 °C). This more rapid breakdown has been mainly attributed to decomposition;
387 however, some loss is likely due to leaching ([Hockaday et al., 2006](#); [Hockaday et al., 2007](#);
388 [Major et al., 2010](#)) and erosion ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Abney et al.,
389 2019b](#); [Abney et al., 2017](#)). In this section we discuss how chemical and physical properties of
390 PyC and leached dPyC impact its transport in soils. We propose the following function can be
391 used to understand the controls on the fate and properties of PyC and dPyC throughout post-fire
392 landscapes (**Figure 7**).

393

394 $f = \text{Burn conditions} + \text{Climate} + \text{Topography} + \text{Organisms} + \text{Parent material} + \text{Time} + \text{post-}$
395 $\text{fire soil properties}$



396 **Figure 7.** The interaction of soil forming factors and burn conditions and severity likely dictate
 397 the fate and transport of dissolved pyrogenic carbon across dynamic landscapes. By studying
 398 post-fire landscapes through these two lenses, we can build predictive models of post-fire PyC
 399 dynamics.
 400
 401

402 4.1.2 Chemical composition

403 The chemical composition of solid PyC before dissolution influences the quantity and quality of
 404 dPyC. At lower burn temperatures, the resulting PyC formed is high in nutrients and oxygenated
 405 functional groups, while higher burn temperatures tend to produce more condensed aromatic
 406 PyC with low H:C and O:C ratios ([Baldock and Smernik, 2002](#); [Hammes et al., 2006](#); [Schneider
 407 et al., 2010](#)). [Bostick et al. \(2018\)](#) investigated dPyC from PyC formed from oak wood and grass
 408 and reported that the leachates were mostly chemically composed of a complex mixture of C
 409 groups such as carbohydrates, aliphatics, and low molecular mass compounds, suggesting that
 410 the DOM resulting from PyC is not solely comprised of condensed aromatics. [Wozniak et al.
 411 \(2020\)](#) demonstrated the chemical heterogeneity of dPyC derived from low (250 °C) heating
 412 temperatures exhibits a wide range of O/C values and the presence of highly unsaturated
 413 aliphatics, polyphenolic formulas, and condensed aromatic C compounds, whereas compounds
 414 with low O/C ratios dominated the composition of dPyC from higher heating temperatures (400
 415 °C). Taken together, these recent findings suggest that DOM leached from solid PyC is
 416 heterogeneous and exists also along a chemical continuum ([Wagner et al., 2021](#)).

417 4.1.3 The influence of burn conditions

418
 419 The physical structure of PyC has been described by porosity, density, and particle size, each of
 420 which can impact the stability of PyC and its potential for dissolution. For many biochars,
 421 increasing charring temperature increases skeletal density and porosity, which may alter the
 422 availability of the char for microbial decomposition or leaching ([Brewer et al., 2014](#)). We found

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

437 **4.2 Environmental and soil factors controlling transport and fate of dPyC along a** 438 **terrestrial to aquatic gradient**

439

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

445 **4.2.1 Climate: precipitation and temperature**

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

458

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

465

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

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

473

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

482 **4.2.2 Topography and Erosion**

483

484 Topographic landform positions are likely significant controls on dPyC and SOM dynamics, as
485 previous research has reported an increase in SOC in depositional landform positions, which
486 receive eroded material from upslope landform positions ([Berhe et al., 2018](#); [Berhe et al., 2007](#)).
487 Additionally, the preferential erosion of PyC likely indicates that it can accumulate in these
488 depositional landform positions ([Abney et al., 2019a](#); [Abney and Berhe, 2018](#); [Rumpel et al.,
489 2009](#); [Rumpel et al., 2006](#)). An unanswered question, however, is whether PyC in depositional vs
490 eroding landform positions could be more susceptible to leaching when there are higher nutrient
491 concentrations and higher water content. The impacts of erosion on the long-term fate of PyC in
492 soil are complex and depend on the landscape erosion and deposition dynamics along with the
493 soil water conditions and precipitation events ([Abney and Berhe, 2018](#); [Masiello and Berhe,
494 2020](#)).

495

496 Elevated rates of post-fire erosion are widely reported across a range of different ecosystem
497 types ([Carroll et al., 2007](#); [de Dios Benavides-Solorio and MacDonald, 2005](#); [Johansen et al.,
498 2001](#); [Robichaud et al., 2007](#)). The magnitude of post-fire erosion is dependent on a number of
499 soil and precipitation factors, which also control the (1) amount of PyC available for leaching
500 and (2) the soil-water conditions to allow for leaching to occur. Furthermore, there is a direct
501 relationship between burn severity, SOM chemical composition, and erosion ([Abney and Berhe,
502 2018](#); [Abney et al., 2019b](#)), such that areas that experience higher burn severities have SOM that
503 is more aromatic and more erosion prone. This suggests that conversely, areas that experience
504 moderate- to low-severity burning may have SOM that is more prone to leaching due to both its
505 chemical composition and higher soil infiltration rates ([de Dios Benavides-Solorio and
506 MacDonald, 2005](#); [Morris and Moses, 1987](#); [Robichaud, 2000](#); [Torreano and Morris, 1998](#)).
507 Several studies have indicated that PyC is preferentially transported post-fire ([Abney et al.,
508 2019b](#); [Rumpel et al., 2009](#); [Rumpel et al., 2006](#)). However, since most SOM that is transported
509 via erosion is deposited within the same or adjacent watershed ([Stallard, 1998](#)), this transported
510 PyC may still be available for and susceptible to leaching, depending on where in the landscape
511 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

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

561

562 **4.2.5 Time**

563 Time is a critical factor in controlling the availability of PyC for forming dPyC. Some research
564 has shown that dPyC increases over time, as the processes of chemical, physical, and biological
565 breakdown of PyC progress, leading to more soluble DOC and dPyC with increasing time since
566 fire ([Bostick et al., 2021](#); [Wagner et al., 2017](#); [Wagner et al., 2018](#)). This increase in solubility is
567 due to introduction of oxygen and nitrogen containing functional groups ([Hilscher and Knicker,
568 2011](#)). There are also lags in between the formation and deposition of PyC and the transport of
569 dPyC into adjacent and further downstream aquatic systems, as evidenced by increasing ages of
570 PyC and dPyC (see **Table S2, Figure 9**) along terrestrial to aquatic gradients to the ocean
571 ([Wagner et al., 2019a](#); [Wagner et al., 2018](#)). Contrastingly, some evidence indicates that PyC is
572 more bioavailable immediately after production than previously considered, in part because PyC
573 also contains C compounds that are readily available for microorganisms and leaching ([Cheng et
574 al., 2008](#); [Schiedung et al., 2020](#)). In addition, the amount of soil PyC available for forming
575 dPyC is highest in the time immediately post fire. There are many environmental factors that
576 may control dPyC concentrations in soils and streams post-fire, such as soil PyC concentrations,
577 hydrological connectivity of a watershed, potential for decomposition of PyC, etc. At least one
578 study has found no significant relationship between time since fire or between fire return interval
579 and dPyC concentration in stream water ([Ding et al., 2013](#)), which may be reflective of these
580 complexities. [Wagner et al. \(2015a\)](#) show different timing of particulate PyC compared with
581 dPyC peak fluxes in a fire-impacted watershed in Colorado, USA. With this variability in timing
582 of export of dPyC from fire-impacted watersheds, we need more mechanistic understanding of
583 the hillslope-scale processes that are driving this export.

584 **4.3 Fire-driven changes in soil properties that impact mobilization of PyC**

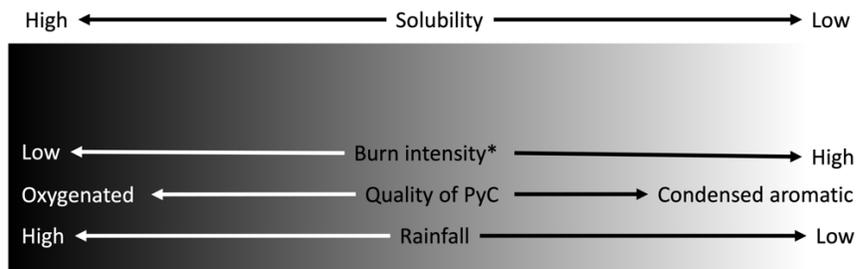
585

586 Fire has long been described as a major disturbance and driver of changes in soil properties,
587 including pH, hydrophobicity, texture, nutrient availability, organic matter, and vegetation
588 dynamics, among others ([DeBano, 1991](#); [Gonzalez-Perez et al., 2004](#); [MacDonald and Huffman,
589 2004](#); [Mataix-Solera et al., 2011](#)). Increases in pH may shift the solubility of PyC, as shown by
590 [Rebollo et al. \(2008\)](#). Increases in hydrophobicity post-fire have frequently been reported in low
591 to moderate burn severity fires ([MacDonald and Huffman, 2004](#); [Mataix-Solera and Doerr,
592 2004](#)), and increases in hydrophobicity may at least temporarily reduce the leaching of PyC into
593 the soil matrix, as there is reduced infiltration (with potential for increased runoff of dPyC).
594 Reduced infiltration and increased runoff post-fire due to loss of vegetation also can lead to
595 elevated rates of erosion, at least until vegetation cover has returned ([de Dios Benavides-Solorio
596 and MacDonald, 2005](#)). As vegetation regrows post-fire and the hydrophobic layer begins to
597 breakdown, it is not yet clear what timescales are relevant for processes of dissolution, within
598 soil redistribution, and hydrologic export of dPyC or how these processes are moderated by burn
599 severity to impact the transport of dPyC.

600

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

604 burns or more decomposed/oxidized). For example, as PyC ages, its surfaces may be broken into
 605 more digestible aliphatic functional groups, which are more soluble, but as these are consumed,
 606 this can leave behind a more aromatic PyC (Hockaday et al., 2007) that is less soluble and more
 607 persistent in soil. Rainfall can also drive fluxes of dPyC, as multiple papers monitoring dPyC in
 608 rivers noted positive correlations with higher discharge (Jaffé et al., 2013; Wagner et al., 2019c;
 609 Wagner et al., 2015a). Bao et al. (2019) argue that different pools of DOC are accessed at
 610 different flow rates through soil, so we often find higher DOC and dPyC with higher flows. The
 611 actual solubility (or potential for leaching) of PyC across landscapes is controlled by the
 612 interaction of several environmental factors, including the burn intensity, chemical and physical
 613 properties of the PyC, and amount and timing of rainfall (**Figure 8**).
 614



*Burn intensity = temperature + duration of burning

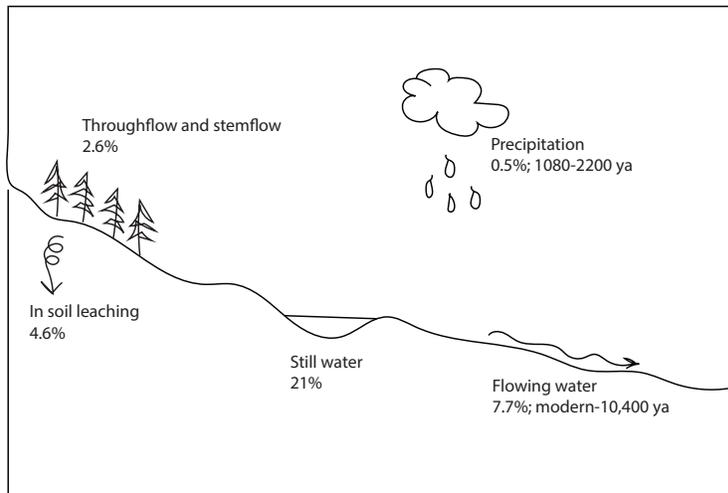
615 **Figure 8.** Controls on the solubility (leaching potential) of PyC in soil. There are other factors
 616 controlling the leaching of PyC, including decomposition, sorption, fire return intervals, aging of
 617 PyC etc. However, these are complex and likely do not follow linear relationships.
 618

619 5. Ecosystem implications

620

621 5.1 Fluxes and internal cycling of dPyC between ecosystem components

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



629
 630 **Figure 9.** Transport of dPyC across different global pools is presented as percent of dissolved
 631 organic carbon. The range of radiocarbon ages of the dPyC in each pool is reported in years (see
 632 **Table S2** for more details).

633
 634 In terrestrial waters, there is an increase in dPyC age reported with increasingly larger and more
 635 mixed pools (rivers and oceans compared with tributaries). The age of dPyC in tributaries was
 636 also highly variable, which is likely reflective of the significance of individual watershed
 637 properties on controlling DOM release and quality. The proportion of PyC that makes it from
 638 deposition on soil surface post-fire to ocean dPyC is likely infinitesimally small. [Bostick et al.](#)
 639 [\(2018\)](#) report that between 1-14% of dPyC in soil is leached to river dPyC, so the vast majority is
 640 internally recycled. However, the controls on the variability and rates of transport of soil dPyC to
 641 riverine dPyC need further investigation.

642 643 **5.2 Future research directions**

644 There are numerous needs for future research on dPyC in soil and across the terrestrial-aquatic
 645 interface. Arguably the most urgent of these is for more quantitative measurements of dPyC in
 646 soil and in fluxes between soil and aquatic systems. For example, two previous studies showed
 647 that PyC can be redistributed through leaching at rates of 1-17% of soil PyC ([Boot et al., 2015](#);
 648 [Major et al., 2010](#)), however considerable further quantification is required before we can predict
 649 dPyC leaching across different soil and precipitation regimes. There is also a need for better
 650 intercomparison between quantitative approaches, or perhaps wider adoption of a smaller
 651 number of methodologies. In field studies, the BPCA method has been widely used and has the
 652 advantage of being able to measure PyC in both solid and liquid samples, as well as provide
 653 information about the condensation of PyC. However, BPCA is time consuming, somewhat
 654 expensive, and is quantitative only for higher burn intensity dPyC. Combining BPCA with
 655 methods that are more sensitive to the lower burn intensity portion of the dPyC continuum will
 656 allow for a more complete understanding of transport of dPyC in the natural environment. BPCA
 657 can also be used to train models that enable researchers to obtain more quantitative measurements
 658 from less costly, high-throughput methods such as mid-infrared spectroscopy([Cotrufo et al.,](#)
 659 [2016](#); [Sanderman et al., 2020](#)).

660

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

674

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

687

688 **6. Conclusions**

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

698

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

707 consistent with chemical controls of dPyC solubility. We have also identified a significant need
708 for (1) more mechanistic understanding of the environmental controls of movement of dPyC
709 from soil to aquatic systems, (2) more soil-water measurements of dPyC, and (3) better
710 understanding of the temporal scales relevant to environmental fluxes of dPyC. Future research
711 on dPyC that provides quantitative measures of the fate of dPyC in soils will be useful for
712 models of soil C and can potentially provide critical information to land managers seeking to
713 increase soil C storage.
714

715

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729

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.

733

734

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Global Biogeochemical Cycles

Supporting Information for

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

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Additional Supporting Information (Files uploaded separately)

Captions for Dataset 1

Introduction

This supporting information includes some detailed methodological information, two supporting figures, two supporting tables, and metadata information for supporting dataset that is uploaded separately.

Text S1. Detailed methodology for meta-analysis

In 2021, we conducted a meta-analysis of peer-reviewed publications using Web of Science. The search terms we used were "dissolved OR particulate OR colloidal" and "PyC OR pyrogenic carbon OR black carbon OR BC OR PyOM OR pyrogenic organic matter OR charcoal OR biochar". We limited our search to papers written or translated to English and that were books, articles, and reviews. This search yielded 12,776 articles, and we removed 442 duplicates. In the following appraisal steps, we included papers that (1) concern the aqueous transport of PyC in natural systems including inland/terrestrial waters and within the soil system; (2) where aqueous transport is in the dissolved and/or particulate and/or colloidal phase; (3) concern in-lab PyC studies with dissolution, when the PyC was from plant derived material; (4) that described the chemical composition of DOM that includes a method to quantify or characterize PyC; (5) focus on biochar and they measure the dissolved concentration or quality of PyC. We excluded papers that met the following criteria: (1) dPyC was in salt marshes, ocean, atmosphere, estuaries (exclusion keywords: aerosol, PM2.5, sewer sludge); (2) dPyC was not quantified or characterized (e.g., only DOC is measured); (3) non-plant derived biochar or charcoal as a source of dPyC; (4) key terms "black carbon," "pyrogenic," "charcoal," "biochar," or "fire" are not found in the text; and (5) papers were reviews or syntheses. In the extraction step, we read the papers in detail and used the questions in Table S1 to extract data, which were inputted into excel.

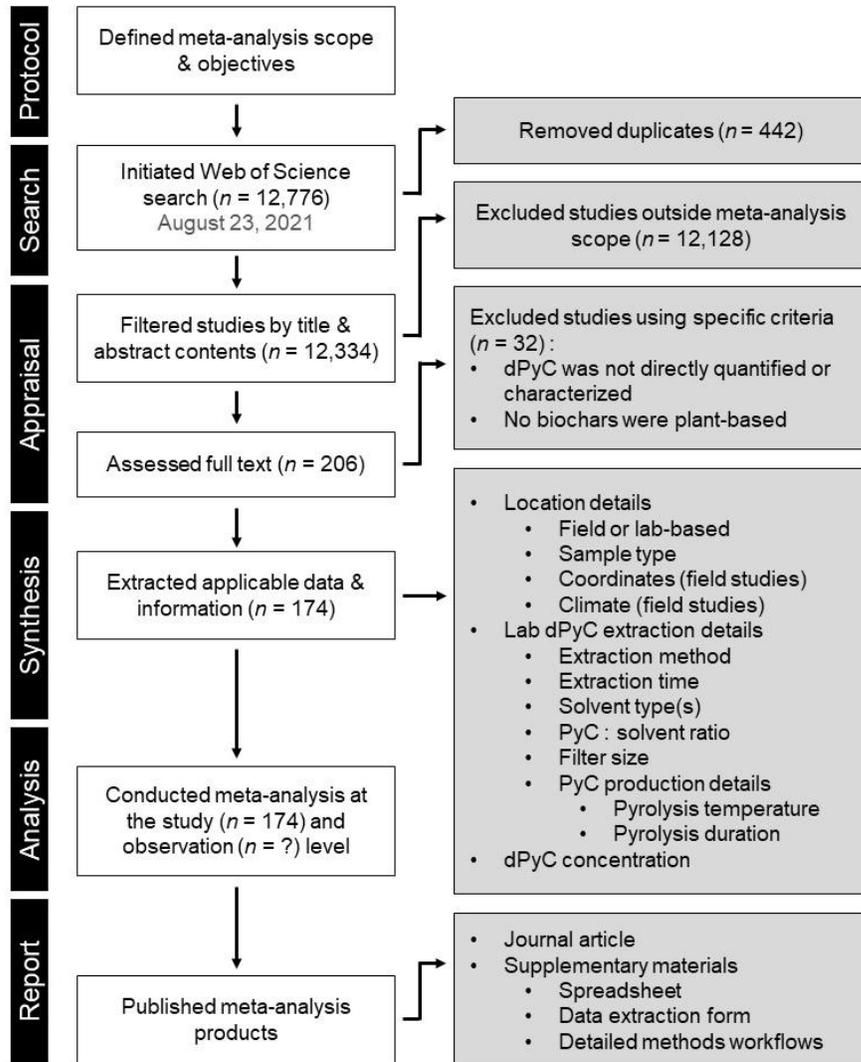


Figure S1. Flowchart depicting the steps of systematic literature review and meta-analysis based on the PSALSAR method outlined by Mengist et al. (2020).

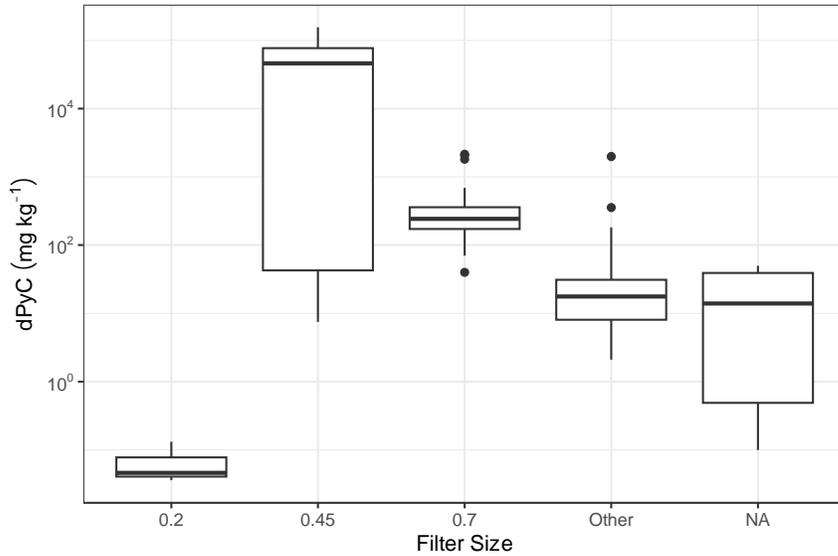


Figure S2. Relationship between reported filter size and dPyC concentration in laboratory-based studies. There are significant differences in dPyC concentration between each of the filter sizes ($\chi^2 = 40.268$; $df = 3$; $p < 0.05$).

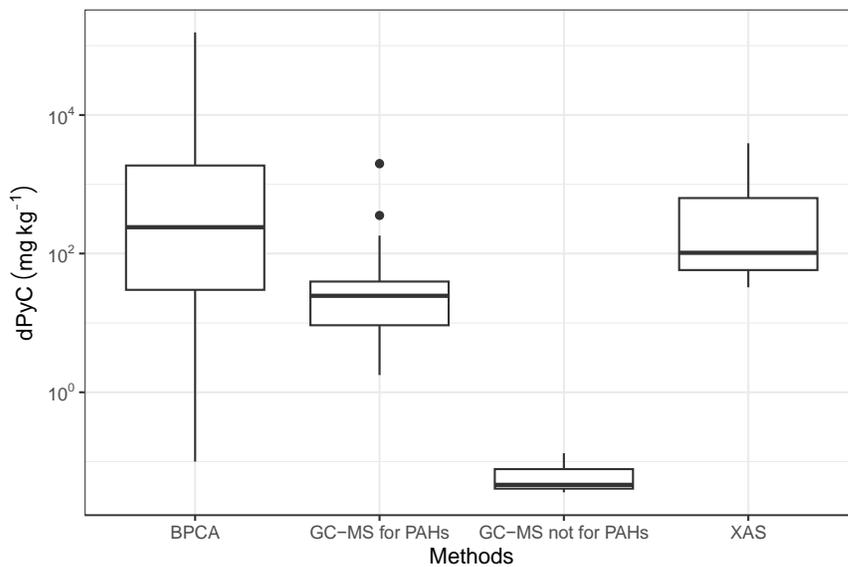


Figure S3. Relationship between method and dPyC concentration in laboratory-based studies. There are significant differences in dPyC concentration between BPCA and each of the PAH methods, but not between XAS and any of the other methods ($\chi^2 = 26.953$; $df = 3$; $p < 0.05$).

1.	Citation information
2.	Publication year
3.	What country were field observations made in?
4.	What location were field observations made in (state, province, etc.)?
5.	Latitude of individual observation
6.	Longitude of individual observation
7.	Was this observation collected in the field or lab?
8.	What koppen climate zone does this Lat/Long correspond to?
9.	What climate bin does this observation belong in (Polar, Temperate, etc.)?
10.	How did the study report the climate?
11.	Study reported MAT (C)?
12.	Study reported MAP (cm)?
13.	Vegetation type (study reported)?
14.	Soil type (study reported)?
15.	Soil depth for collected sample?
16.	Sample type of the following: Soil Lab Extract, Char Lab Extract, Precipitation, Flowing Water, Still Water, Soil Water.
17.	Biochar feedstock, of the following types: wood, herbaceous, other.
18.	Methods, of the following categories:
19.	Filter size
20.	Concentration of dPyC in mg/L
21.	Concentration of dPyC in mg/kg
22.	Concentration of dPyC in % of spectrum (1H and 13C NMR)
23.	Concentration of dPyC in DOC in mg/L
24.	Concentration of dPyC in DOC in mg/kg
25.	Was PyC measured in bulk soil? (Yes/No)
26.	Concentration of PyC in bulk soil
27.	Was carbon concentration measured in charcoal? (Yes/No)
28.	Concentration of C in charcoal?
29.	Was PyC measured in charcoal? (Yes/No)
30.	Concentration of PyC in charcoal.
31.	What method was used for solid PyC characterization (in charcoal or soil)?
32.	What was the ratio of solid to liquid for extraction of dPyC (lab studies)?
33.	What solvent type was used to extract dPyC from the following categories (lab studies):
34.	What was the maximum temperature reached for lab-made biochar (C)?
35.	How long was the biochar burned (hours)?
36.	Other notes
37.	What journal was the study published in?

Table S1. Data extraction template for dPyC meta-analysis.

Sample name	dPyC $\Delta^{14}\text{C}$	dPyC Age (years)	Reference
Precipitation			
Nam Co	-	1080	Li et al. (2018)
Lhasa	-	1750	
Chengdu	-	2300	
Kunming	-	2600	
Kathmandu	-	2200	
Tributary			
Negro	-20	-	Coppola et al. (2019)
Trombetas	14	-	
Tapajós	-771	-	
River			
Solimões	0	-	Coppola et al. (2019)
Amazon	-293 (307)	-	
Santa Clara River	-567 (184)	-	Masiello and Druffel (2001)
Changjiang (CRO3)	-64.9	475	Wang et al. (2016)
ECS-P02	-152	1230	
ECO-P04	-283	2620	
Huanghe River - January	-138 (19)	1142 (179)	
Suwannee River	-202	410	Ziolkowski and Druffel (2010)
Amazon influenced	-629	10,400	
Ocean			
Surface ocean	-450	4800 (620)	Coppola and Druffel (2016)
Deep ocean	-945	23,000 (3000)	

Table S2. Radiocarbon aging of dPyC across different sample types with standard deviation in parentheses when means are reported.

Data Set S1. Metadata for Table S3

Study or Observation: Data are organized into study level-information and individual observations (data points)

UniqueID: each line in this dataset has a unique identifier

Study Number: each study included in this dataset has a unique number identifier

Citation: Full citation information for each study

Publication year: year of publication

StudyCountry: Country where study was conducted or data were collected

Study Location: Reported location of study in manuscript

Latitude: latitude coordinate either study-reported or extracted as described in the section above

Longitude: longitude coordinate either study-reported or extracted as described in the section above

FieldorLab: data were collected in field or laboratory settings, study level may be both

Climate: Geiger-Köppen climate classification based on latitude and longitude

Climate Bin: Climate zones were binned into larger climate bins, including polar, cold, tropical, temperate, etc.

Study reported climate: Climate details reported by study

MAT: mean annual temperature, as reported by study

MAP: mean annual precipitation, as reported by study

Vegetation: any vegetation as reported by study

Soil Type: soil description information

Soil Depth: depth of sampling

Sample Type: we categorized our extracted data into the following categories of sample type: flowing water, precipitation, sediment, soil field extract, still water, surface runoff

Biochar feedstock: we characterized the biochar feedstocks into woody, herbaceous, and other. Woody plants have stem that doesn't go away, herbaceous does go away

Methods: BPCA, Chemo-thermal oxidation, FTICR-MS, GC-MS for PAHs, GC-MS not for PAHs, HPLC for PAH, hydrogen pyrolysis, levoglucosan, optics, other

Filter size: 0.2 μm , 0.45 μm , 0.7 μm , not filtered, other, N/A (filtered, but size not reported)

dPyC mg/L: reported concentration of dPyC in mg/L

dPyC mg/kg: reported concentration of dPyC in mg/kg

dPyC % ("dPyC."): reported concentration of dPyC in %

DOC mg/L: reported concentration of DOC in mg/L

DOC mg/kg: reported concentration of DOC in mg/kg

PyC in bulk soil: did the authors report the concentration of PyC in bulk soil (yes/no)

PyC in bulk soil concentration: reported concentration of PyC in bulk soil

Carbon in Charcoal: did the authors report the concentration of C in charcoal (yes/no)

Carbon in Charcoal concentration: reported the concentration of C in charcoal

PyC in Charcoal: did the authors report the concentration of PyC in charcoal (yes/no)

PyC in charcoal concentration: reported concentration of PyC in charcoal

Solid PyC method: method used to determine PyC in bulk soil or charcoal

Lab Extraction Time: extraction times were binned into the following categories (hours): 0-1.4; 1.5-4; 4.1-11.4; 11.5-24; 24.1-48; and >48

Lab Extraction Solvent: Solvents used to extraction dPyC from soils and charcoal were categorized as: acidic, basic, hot water, organic, salt, water, other, N/A

Lab Extraction Method: Mixing, settling, shaking, sonicating, stirring, other, and N/A

Lab Extract Solid to Solution ratio: ratio of solids to solution for extraction

Biochar Maximum Temperature: maximum temperature that the biochar experienced during production ($^{\circ}\text{C}$)

Biochar Burn Time (hours): duration of charring for biochar production

Extract Ratio Group: bin for ratio of solid to solution for dPyC extraction from charcoal

Temp Group: bin for temperature of PyC production for dPyC extraction from charcoal

Time Group: bin for time extracted for dPyC extraction from charcoal

Journal: Journal that published the manuscript

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