



1 **Potential bioavailability of pyrogenic organic matter resembles**  
2 **natural dissolved organic matter pools**

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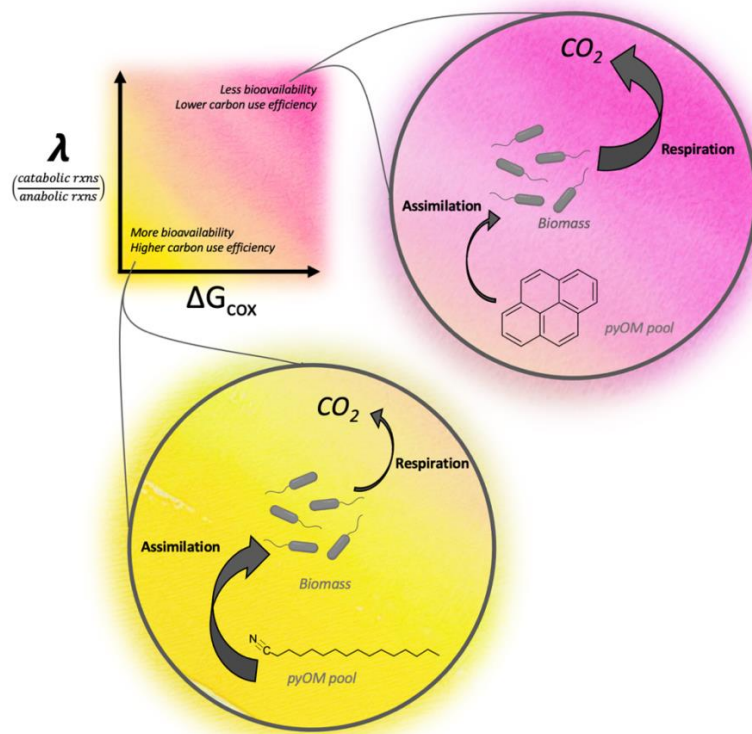
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## 20 GRAPHICAL ABSTRACT



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23 **ABSTRACT**

24 Pyrogenic materials generated by wildfires are negatively impacting many aquatic  
25 ecosystems. At least ~10% of dissolved organic matter (DOM) pools may be comprised of  
26 pyrogenic organic matter (PyOM) that is generally considered to be more refractory than DOM  
27 from other sources. However, there has been no systematic evaluation of bioavailability across a  
28 full spectrum of PyOM chemistries. We assessed the potential bioavailability of PyOM in  
29 relation to measured and globally ubiquitous DOM compounds using a substrate-explicit model  
30 to predict the energy content, metabolic efficiency, and aerobic decomposition of representative  
31 PyOM compounds. Overall, we found similar potential bioavailability between PyOM and  
32 sediment and surface water DOM. Predicted thermodynamics and carbon use efficiencies of  
33 PyOM and DOM were statistically indistinguishable. Within PyOM, phenols and black carbon  
34 (BC, defined by Wagner et al. (2017)) had lower metabolic efficiency than other PyOM and  
35 DOM compounds, and oxygen limitation had less impact on BC metabolism than on other  
36 PyOM classes. Our work supports the recent paradigm shift where PyOM bioavailability may be  
37 more comparable to natural organic matter than previously thought, highlighting its potential role  
38 in global C emissions and providing a basis for targeted laboratory investigations into the  
39 bioavailability of various PyOM chemistries.



## 40 **1 Introduction**

41 Wildfires have burned an average of 1.8-million ha year<sup>-1</sup> in the United States alone over the past  
42 80 years, dramatically impacting terrestrial and aquatic ecosystems (Bladon et al., 2014;  
43 Shakesby and Doerr, 2006; Randerson et al., 2006; Verma and Jayakumar, 2012). As wildfire  
44 activity continues to increase in response to climate change (Pierce et al., 2004; Bowman et al.,  
45 2020; Flannigan et al., 2009), its impact on river corridor biogeochemistry is receiving  
46 significant attention (Wagner et al., 2018; Abney et al., 2019).

47 Pyrogenic organic matter (PyOM) generated by wildfires, in particular, can strongly  
48 influence river corridor biogeochemistry due to the importance of organic matter as a carbon (C)  
49 and energy source in rivers. Though there is substantial uncertainty in the quantification of  
50 PyOM, estimates suggest that 116–385 Tg C is generated per year of its most common  
51 constituent—black carbon (BC: defined herein, per Wagner et al. (2017), as condensed aromatic  
52 core structures polysubstituted with O-containing functionalities). This amounts to 300 to 500  
53 giga-metric tons of C stored in sediments, soils, and waters (Jaffé et al., 2013; Dittmar et al.,  
54 2012; Hockaday et al., 2007; Santín et al., 2016) and ~10% of dissolved organic C pools in  
55 surface waters (Jaffé et al., 2013). Given that OM drives biogeochemical cycles in most aquatic  
56 ecosystems, the loading of PyOM into river corridors has the potential to produce substantial  
57 impacts on ecosystem functions and downstream drinking water treatability (Emelko et al., 2011;  
58 Hohner et al., 2017).

59 Historically, PyOM has been considered refractory, passively transported and deposited  
60 throughout landscapes. While some estimates place aquatic residence times at thousands of years  
61 (Meyer and Wells, 1997; Elliott and Parker, 2001; Bigio et al., 2010; Kuzyakov et al., 2014),  
62 recent work has shown that PyOM may be more bioavailable than previously thought (Myers-



63 Pigg et al., 2015; Norwood et al., 2013; Zimmerman and Ouyang, 2019). This inference is also  
64 supported by research on biochars, highlighting the diverse reactivities of combustion by-  
65 products (Sohi et al., 2010; Mia et al., 2017). PyOM bioavailability may, therefore, play an  
66 unrecognized role in global biogeochemical cycles and climate feedbacks. Yet, there has been no  
67 systematic evaluation of the bioavailability of different constituents within the heterogeneous  
68 compounds that comprise PyOM (Zimmerman and Mitra, 2017).

69 Due to the wide chemical continuum of PyOM (Wozniak et al., 2020; Masiello, 2004),  
70 we hypothesized that a range of known PyOM compounds (i.e., from primary literature) would  
71 show more similar potential bioavailability to a global dataset of dissolved organic matter  
72 (DOM) pool composition than expected based on historical literature. We used a new substrate-  
73 explicit model to assess the potential bioavailability of PyOM across its different chemical  
74 classes and in comparison to DOM in global surface waters and sediments. The model provides a  
75 systematic way to formulate reaction kinetics and is agnostic of many factors that have  
76 complicated a universal understanding of OM bioavailability; including molecular structure,  
77 chemical inhibition, mineral-associations and physical protection, terminal electron acceptors,  
78 microbial community composition and accessibility, and abiotic reactions (reviewed in Arndt et  
79 al. (2013)). Because it relies only on the elemental composition of individual OM molecules,  
80 substrate-explicit modelling also enabled us to compare known PyOM compounds to detailed  
81 characterizations of natural DOM pools that lack structural information (i.e., derived from  
82 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, FTICR-MS). Our work  
83 supports an emerging paradigm in wildfire science in which PyOM is relatively bioavailable and  
84 provides a baseline for targeted laboratory experiments that examine PyOM bioavailability  
85 across environmental contexts and compound chemistries.



86

## 87 **2 Results and discussion**

88 We used a substrate-explicit model to evaluate PyOM potential bioavailability and  
89 compared model outputs to global DOM pool composition (Garayburu-Caruso et al., 2020a;  
90 Song et al., 2020). In contrast to previous characterizations of PyOM bioavailability, the model-  
91 based approach enabled us to directly compare known combustion products to thousands of  
92 ubiquitous DOM compounds, which would have been unfeasible to directly assess in a  
93 laboratory setting.

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### 95 *2.1 Potential Bioavailability of Pyrogenic Organic Matter*

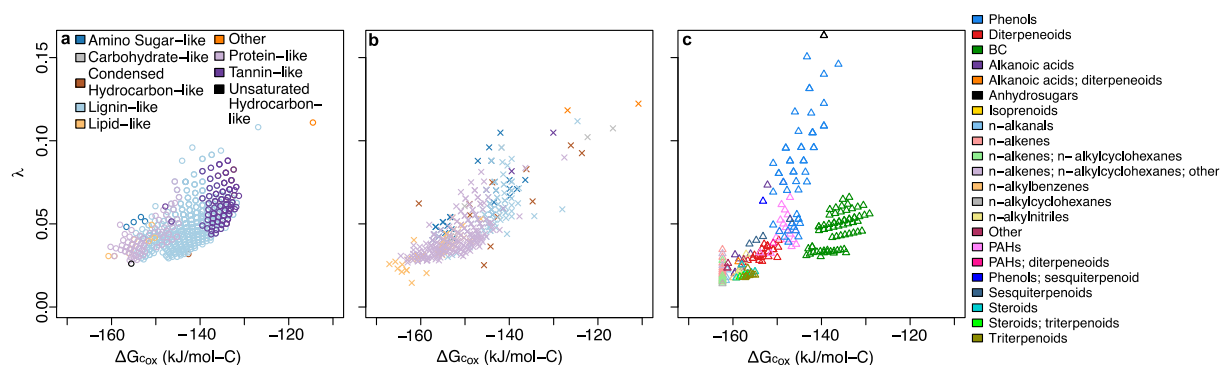
96 Though previous work has shown that sediment and surface water DOM is altered by  
97 wildfires (Cawley et al., 2018; Jaffé et al., 2013; Wagner et al., 2018), our results suggest that the  
98 chemically distinct pools of PyOM may have similar potential bioavailability to DOM. We found  
99 that the ranges of  $\Delta G_{Cox}$ ,  $\lambda$ , and CUE were similar between PyOM and DOM in sediments and  
100 surface waters (Figure 1 and 2a). Predicted CUE of PyOM classes was also comparable to  
101 literature values reported by others (Saifuddin et al., 2019; Domeignoz-Horta et al., 2020; Pold et  
102 al., 2020). Similarly,  $\lambda$  did not vary across groups of organic molecules (ANOVA  $p = 0.09$ , and  
103 Tukey HSD  $p$  (PyOM-sediment) = 0.92,  $p$  (PyOM-water) = 0.40,  $p$  (water-sediment) = 0.10).  
104 While  $\Delta G_{Cox}$  and CUE were significantly different when comparing all three groups (ANOVA,  $p$   
105  $< 0.001$ ), surface water and sediment DOM had greater dissimilarity in these parameters than any  
106 comparison involving PyOM. For example, the mean difference in  $\Delta G_{Cox}$  and CUE between  
107 surface water and sediment DOM was 7.34 kJ/mol-C and 0.058. The differences between PyOM  
108 and both surface water and sediment were less than 7.4 kJ/mol-C for  $\Delta G_{Cox}$  and 0.058 for CUE.



109 Further, there was no evidence that CUE was different between PyOM and sediment DOM  
 110 (Tukey HSD,  $p = 0.20$ ).

111 These results signal a strong overlap between the potential bioavailabilities of PyOM and  
 112 DOM pools; however, within PyOM compounds, there was variability in  $\Delta G_{Cox}$ ,  $\lambda$ , and CUE  
 113 consistent with a heterogeneous continuum of organic matter (Figure 1 and S1). This is not  
 114 surprising, given the diversity of PyOM chemistries generated by wildfires of different burn  
 115 severities and source materials (Wagner et al., 2015; Wagner et al., 2018; Neary et al., 2005),  
 116 some of which overlap with chemical classes in unaltered DOM.

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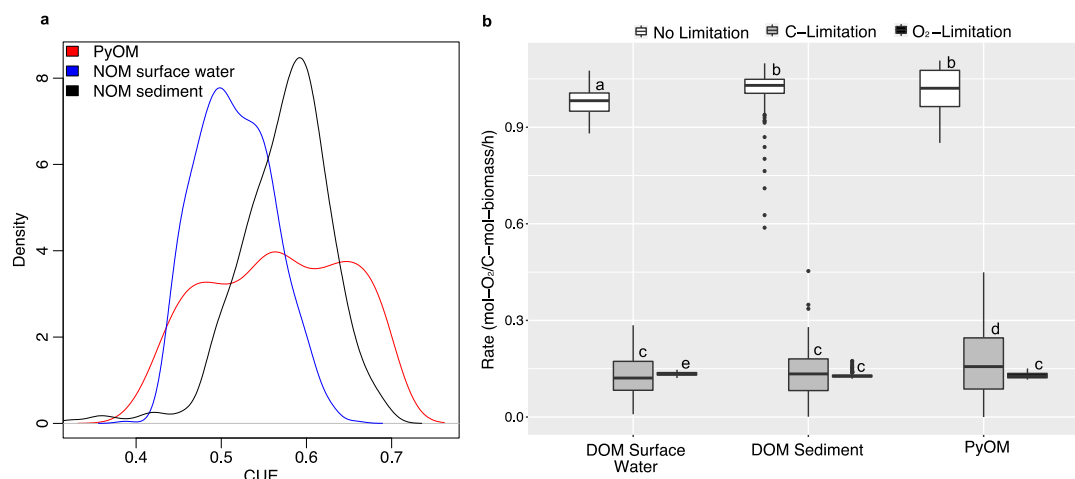


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120 **Figure 1.** Comparison of PyOM energy content ( $\Delta G_{Cox}$ ) and metabolic efficiency ( $\lambda$ ) to global  
 121 DOM. Ubiquitous DOM molecules detected via FTICR-MS in global (a) surface water and (b)  
 122 sediment are colored by inferred chemical class. (c) Representative PyOM molecules are colored  
 123 by known chemical properties. Because PyOM molecules were from primary literature, we could  
 124 assign chemical properties at higher resolution than inferred classes from measured DOM pools.  
 125 Details on inferred chemical class assignment are provided in the Supporting Information.

126 Legends are inset in (a) for (a) and (b), and to the right of (c).



127

128 **Figure 2.** Predicted CUE and metabolism of DOM and PyOM. (a) shows the probability density  
 129 function (PDF) of CUE in PyOM (red) and ubiquitous surface water (blue) and sediment (black).  
 130 The PDF reflects the relative likelihood that value of a random sample drawn from a particular  
 131 group would equal the value on the x-axis. (b) depicts the predicted metabolism of surface water  
 132 DOM, sediment DOM, and PyOM. Letters in denote statistical groups. Median values are  
 133 denoted by a bar, hinges correspond to the first and third quartiles (25th and 75th percentiles),  
 134 and whiskers extend from the hinge to the largest/smallest value no further than 1.5 \* IQR from  
 135 the hinge (where IQR is the inter-quartile range, or distance between the first and third quartiles),  
 136 and data beyond the end of the whiskers are plotted individually.

137

138

139 Interestingly, the relative equivalence of predicted CUE across PyOM and DOM pools  
 140 suggests that PyOM decomposition in rivers could emit comparable amounts of CO<sub>2</sub> per mole of  
 141 C to extant DOM pools. CUE is used in many microbially-explicit decomposition models to  
 142 constrain organic matter bioavailability (reviewed in Graham and Hofmockel, 2022). Therefore,





143 predicted CUE offers a path for assimilating PyOM in microbially-explicit models. Such an  
144 approach could be used to directly evaluate the impact of PyOM on global C cycles, and help  
145 lead to better incorporation of PyOM impacts in models (Santin et al., 2020).

146         Within PyOM, two clusters of compounds were distinctly separated from the energetic  
147 and metabolic properties of most PyOM (Figure 1c). Phenols had higher  $\lambda$  than the majority of  
148 PyOM and DOM compounds (all  $\lambda > 0.039$ , mean  $\lambda = 0.084$ ), while BC molecules were less  
149 energetically favorable than other PyOM classes (all  $\Delta G_{Cox} > -143.42$ , mean  $\Delta G_{Cox} = -136.40$ ).  
150 However, both were within the range of variability in DOM pools (Figure 1). Phenols and BC  
151 also had among the lowest CUE (means, BC = 0.47, phenols = 0.54). Phenols are traditionally  
152 associated with refractory organic matter, such as lignin and tannins, that exhibit long residence  
153 times in soils (Thevenot et al., 2010), although they have also been reported to be bioavailable in  
154 soils and waters in recent years (e.g., Thevenot et al., 2010; Ward et al., 2013). Additionally, BC  
155 in this study is defined by inferred aromaticity (i.e., the presence of condensed aromatic  
156 structures), which is also considered to have low reactivity (Kuzyakov et al., 2014; Wagner et al.,  
157 2017). Although the potential bioavailability of phenols and BC is consistent with refractory  
158 PyOM, it is within the potential bioavailability range observed in DOM, and these compounds  
159 represent only a small portion of the PyOM continuum (Wagner et al., 2018; Masiello, 2004).  
160 We note that the comparatively low predicted CUE of phenols and BC indicates that, if  
161 metabolized, their decomposition could have a greater impact on river corridor CO<sub>2</sub> emissions  
162 than other PyOM and DOM compounds. As a result, current understanding may substantially  
163 underestimate the size, reactivity, and hydrobiogeochemical role of PyOM (Wagner et al., 2018).  
164 *2.2 Inferred Metabolism of Pyrogenic Organic Matter.*



165 Predicted PyOM metabolism was also similar to DOM pools (Figure 2b), reinforcing  
166 comparable bioavailability between the two pools. Pairwise comparison of metabolic rates  
167 revealed no differences between PyOM and sediment DOM under oxygen limitation (Tukey  
168 HSD,  $p = 0.23$ ) or without C or oxygen limitations (Tukey HSD,  $p = 0.34$ ). However, the  
169 metabolic rates of both PyOM and sediment DOM were different than surface water DOM  
170 (Tukey HSD, all  $p < 0.001$ ). Aquatic sediments can reach anoxia within millimeters of the  
171 sediment-water interface such that model predictions under oxygen limitation may translate to no  
172 meaningful difference between PyOM and DOM in natural sediments. Under C-limitation,  
173 PyOM had statistically elevated metabolism relative to both surface water and sediment DOM  
174 (Tukey HSD, all  $p < 0.001$ ). However, we noted only small differences in rate values (means,  
175 surface water: 0.13, sediment: 0.13, PyOM: 0.17), with a similar range in sediment DOM  
176 (0.0008–0.45) and PyOM (4.75e-08–0.45). Statistical differences were not surprising given an  
177 extremely large sample size for DOM (sediment  $n = 398$ , surface water  $n = 811$ ), and the low  
178 effect sizes denote that overall differences in metabolism between PyOM and DOM were  
179 minimal despite statistical separation.

180 When considering the impact of elemental limitations on PyOM metabolism, rate  
181 predictions were strongly inhibited under low C and oxygen conditions. Predicted PyOM  
182 metabolism was approximately six times lower when C or oxygen was scarce. Low  
183 decomposition rates under C and oxygen limitation could be one reason for the observed  
184 persistence of PyOM in depositional features that tend to be anoxic. Still, it is worthwhile to note  
185 that metabolism of all PyOM classes under low C or oxygen was predicted to be substantially  
186 slower than without elemental limitations, indicating PyOM compounds may both actively cycle



187 in well-oxygenated surface waters with fresh C inputs and persist over long periods of time in  
188 O<sub>2</sub>-limited sediments.

189         Among PyOM chemistries, BC was less negatively impacted by oxygen limitation than  
190 any other group (Figure S2). Previous work has demonstrated that microorganisms are capable of  
191 decomposing chemically complex organic molecules, such as long-chained and/or aromatic  
192 hydrocarbons under low oxygen availability (Bushnell and Haas, 1941; Pozdnyakova, 2012;  
193 Rabus et al., 2016; Coates et al., 1997). Similar microbial metabolic pathways may also be  
194 capable of degrading BC molecules in natural settings and could be investigated with future  
195 laboratory work. Notably, our work also supports the notion that black nitrogen could be more  
196 bioavailable than BC. We posit this may be due, in part, to its chemical structure that includes  
197 pyrrole-type moieties, which are relatively biodegradable (Knicker, 2010; De La Rosa and  
198 Knicker, 2011). While we only examined one class of PyOM molecules containing nitrogen (n-  
199 alkylnitriles), it had among the highest predicted CUE and metabolic rate.

200

### 201 *2.3 Correspondence to Empirical Investigations.*

202         While the substrate-explicit modelling approach used here has been validated in natural  
203 settings and enabled comparison to environmental DOM, its underlying assumptions preclude  
204 accounting for DOM structure and size, abiotic reactions, and chemical complexation with  
205 minerals and particulates. Some aspects of model predictions are inconsistent with experimental  
206 evidence, highlighting the role of laboratory studies in evaluating PyOM bioavailability. For  
207 instance, n-alkenes and related compounds tended to have high modelled bioavailability despite  
208 being relatively stable in the environment (including useage as paleoproxies, Wiesenberg et al.,  
209 2004; Smittenberg et al., 2004). These compounds are characterized by carbon-carbon double



210 bond functional groups, which are not considered by the model and may decrease bioavailability.  
211 However, n-alkanes generated through combustion tend to have reduced chain length in  
212 comparison to their un-burned counterparts (Knicker et al., 2013), and thus may be relatively  
213 bioavailable compared to un-burned n-alkanes. Additionally, we note that previous work has  
214 shown fast degradation of combustion-derived lipids in soils (Knicker et al., 2013); as well as  
215 high n-alkene metabolism under anaerobic conditions and in natural sediments and a range in  
216 lipid reactivities at the sediment-water interface (Grossi et al., 2008; Wilkes et al., 2016;  
217 Yongdong et al., 2015; Mbadinga et al., 2011; Canuel and Martens, 1996). While work on  
218 aerobic n-alkene metabolism is limited, the comparative bioavailability of n-alkenes and known  
219 degradation pathways suggests that sediment microbiomes may metabolize them as part of  
220 natural biogeochemical cycles. Another notable discrepancy is the low potential bioavailability  
221 of anhydrosugars when compared to other PyOM compounds. Experimentally, anhydrosugars  
222 are highly bioavailable in oxic conditions, with a half-life of less than seven days (Norwood et  
223 al., 2013). The model may therefore not adequately account for some enzyme-catalyzed  
224 reactions such as levoglucosan kinase or levoglucosan dehydrogenase that may be common  
225 enzymes in aquatic microorganisms (Bacik and Jarboe, 2016; Suciu et al., 2019).

226       Because of these nuances, the analysis presented here is best used as bounding estimates  
227 for experimental validation and as a holistic comparison to DOM bioavailability. Still, the span  
228 of compounds investigated here, and their comparison to DOM pools, provides a breadth of  
229 investigation that is unfeasible without model-based approaches.

230

231 **3 Conclusions**



232 Our work supports the recent paradigm shift towards greater PyOM bioavailability than  
233 previously thought and provides a foundation for targeted experiments investigating specific  
234 components of the PyOM continuum. Globally intensifying wildfires are increasing the  
235 production of PyOM with potential implications for source water supplies, which are critical for  
236 domestic, industrial, agricultural, and ecological needs. Yet, many fundamental questions such as  
237 “how much” PyOM exists in ecosystems, “how fast” it cycles, and “how old” it is remain largely  
238 unknown (Abiven and Santin, 2019). Our work provides the first comprehensive computational  
239 assessment of the potential bioavailabilities of various PyOM chemistries in comparison to  
240 natural DOM pools. The comparable potential bioavailability to DOM revealed that PyOM may  
241 be actively transformed within the river corridor and may be an increasing source of C emissions  
242 to the atmosphere as the prevalence of wildfires increases.

243

#### 244 **Code and Data Availability**

245 Code is available at: <https://github.com/hyunseobsong/lambda>. Data describing DOM pool  
246 chemistry are published as a data package (Goldman et al., 2020) (available at:  
247 doi:10.15485/1729719) and are discussed in more detail by Garayburu-Caruso et al. (2020a).

248

#### 249 **Author Contributions**

250 EBG conceived of the manuscript and was responsible for writing the manuscript and generating  
251 all figures. HSS performed all modelling. SG determined PyOM compounds for modelling based  
252 on extensive literature review, with guidance from AMP. VGC and JCS contributed data and  
253 insight on DOM pool chemistry. All authors contributed to revisions.

254



255 **Competing Interests**

256 The authors declare that they have no conflict of interest.

257

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266 Environmental Molecular Science Laboratory User Facility.

267

268 **APPENDIX. Materials and methods**

269 An extended version of our methods is available in the Supporting Information.

270 To assess the potential bioavailability of PyOM, we searched primary literature for  
271 representative compounds of the PyOM continuum. Specifically, we targeted characteristic  
272 organic compounds from controlled burns of various fuel types representing a range of moisture,  
273 temperature, and oxygen conditions (Table S1). The chosen compounds focused on biomass  
274 burning alteration products, which are often used to characterize PyOM in the environment. This  
275 included compounds such as theoretical BC compounds, anhydrosugars, and polycyclic aromatic  
276 hydrocarbons (PAHs). The list also included compounds created and/or transformed from  
277 biomass burning, such as those derived from biopolymers like lignin (e.g., methoxyphenols),



278 waxes (e.g., n-alkenes from thermal dehydration of n-alkanols), and resins (e.g., thermally  
279 oxidized diterpenoids) (Oros and Simoneit, 2001a, b). While we recognize that recent research  
280 has applied new technologies to inferring PyOM compound presence in environmental samples  
281 (e.g., FTICR-MS), there remains high uncertainty in the confidence of formula assignment and  
282 structural information with some of these techniques. Therefore, we focused only on known,  
283 chemically identified compounds from controlled burns to represent PyOM chemistries. The  
284 selected set of compounds spans the chemical continuum of PyOM but was not intended to be  
285 exhaustive. In total, our literature search for PyOM chemistries yielded 389 compounds with 207  
286 unique chemical formulae.

287         After generating a set of representative compounds, we used a substrate-explicit  
288 modelling framework developed by Song et al. (2020) to characterize the potential  
289 bioavailability of each compound and predict its rate of decomposition. The model uses  
290 molecular formulae to predict energetic content, metabolic efficiency, and rates of aerobic  
291 metabolism, while it does not account for structural components of organic molecules (e.g.,  
292 double bonds, folding patterns, cross-linkages). This enables flexibility in application to high-  
293 throughput mass spectrometry techniques that yield chemical formulae but not structural  
294 information (e.g., FTICR-MS) for comparison to environmental DOM. Despite its limitations,  
295 the substrate-explicit model used here has proven useful in linking DOM composition to aerobic  
296 metabolism in natural environments (Song et al., 2020; Graham et al., 2017; Garayburu-Caruso  
297 et al., 2020b), and its structure is consistent with Harvey et al. (2016) who argued for the  
298 importance of thermodynamic estimates of PyOM bioavailability that underlie this model. It was  
299 chosen to allow for comparison of PyOM to the most comprehensive assessment of global  
300 aquatic DOM pools to date (Garayburu-Caruso et al., 2020a).



301 Briefly, the substrate-explicit model uses the elemental stoichiometry of organic  
302 molecules, based on molecular formulae, to predict the number of catabolic reactions that must  
303 occur to provide the energy required for the synthesis of one mole of biomass carbon. This  
304 quantity is described by the parameter lambda ( $\lambda$ ) in which lower  $\lambda$  values denote more efficient  
305 energetics of catabolism in producing biomass through anabolism. The model also predicts the  
306 Gibbs free energy of C oxidation ( $\Delta G_{Cox}$ ), under standard conditions with a modification to pH 7  
307 adjusted from LaRowe and Van Cappellen (2011) by Song et al. (2020), as well as C use  
308 efficiency (CUE) as defined by Saifuddin et al. (2019). Lower  $\Delta G_{Cox}$  denotes higher  
309 thermodynamic favorability in an electron donor half reaction associated with organic matter,  
310 and higher CUE reflects more C assimilated into biomass per unit C respired. We also predicted  
311 the rate of aerobic metabolism (as oxygen consumed per mol-C biomass produced) under three  
312 scenarios commonly observed in aquatic ecosystems: (a) C-limitation, (b) oxygen ( $O_2$ )  
313 limitation, and (c) both C and  $O_2$ -limitation. For more details of the substrate-explicit modelling  
314 approach used, please see Song et al. (2020). Each metric ( $\lambda$ ,  $\Delta G_{Cox}$ , CUE, metabolic rates)  
315 denotes a different aspect of potential bioavailability. Though the relative magnitude of the  
316 metrics in comparison to each other will vary based on the specific stoichiometry of a molecule,  
317 highly bioavailable compounds are indicated by low  $\lambda$  and  $\Delta G_{Cox}$  coinciding with high CUE and  
318 metabolic rates.

319 Three sets of organic molecules were used as model inputs: measured global dissolved  
320 (1) surface water and (2) sediment DOM pools, extracted in  $H_2O$  and analyzed by FTICR-MS as  
321 per Garayburu-Caruso et al. (2020a); and (3) literature-derived PyOM compounds as described  
322 above. Inputs to the model from the PyOM compounds were unique molecular formulae,  
323 grouped in subsequent analysis by their corresponding compound classes (Table S1). If one





324 molecular formula was represented by several PyOM compounds (e.g.,  $C_{10}H_{16}O_2$ , which  
325 corresponds to the sesquiterpenoid cis-Thujan-10-oic acid and 3-, 4- substituted methylcatechol  
326 phenols), we assigned multiple compound classes to that molecular formula. Surface water and  
327 sediment DOM pools were filtered to compounds occurring in 95% of samples to yield a dataset  
328 of globally ubiquitous DOM. Formulae assignment and inferred chemical classes via van  
329 Krevelen diagrams in DOM pools are described by Garayburu-Caruso et al. (2020a). We  
330 compared modelling outputs from representative PyOM to outputs of ubiquitous DOM pools to  
331 infer relative bioavailability using ANOVA and Tukey HSD statistical tests with R software. All  
332 model outputs are available in Tables S2–S4.

333



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