Potential bioavailability of pyrogenic organic matter resembles natural dissolved organic matter pools

Emily B. Graham+* [1,2], Hyun-Seob Song+ [3], Samantha Grieger[1,4], Vanessa A. Garayburu-Caruso[1,5], James C. Stegen[1], Kevin D. Bladon[6], and Allison Myers-Pigg [1,4]

+equal contributors

*Correspondence: Emily B. Graham (emily.graham@pnnl.gov)

[1] Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA, USA

[2] School of Biological Sciences, Washington State University, Richland, WA USA

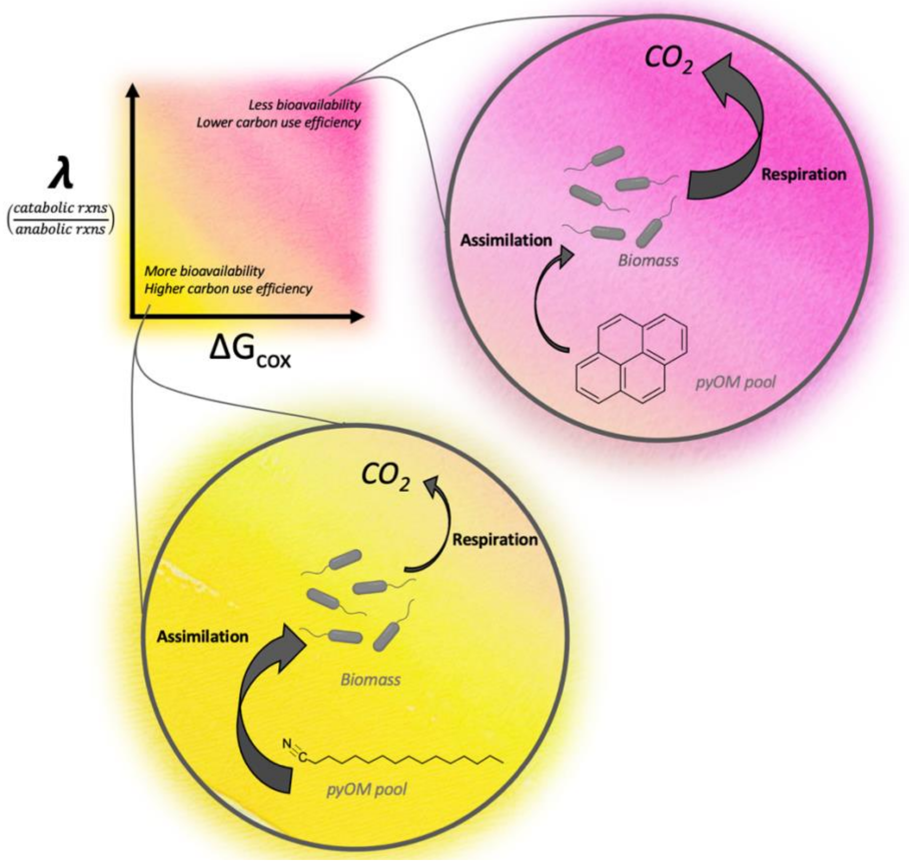
[3] Department of Biological Systems Engineering, Department of Food Science and Technology, Nebraska Food for Health Center, University of Nebraska, Lincoln, NE, USA

[4] Marine and Coastal Research Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA

[5] School of the Environment, Washington State University, Richland, WA USA

[6] Department of Forest Engineering, Resources, and Management, Oregon State University, Corvallis, OR, USA

GRAPHICAL ABSTRACT



ABSTRACT

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

1 Introduction

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

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

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

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

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

2 Results and discussion

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

2.1 Potential Bioavailability of Pyrogenic Organic Matter

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

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

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

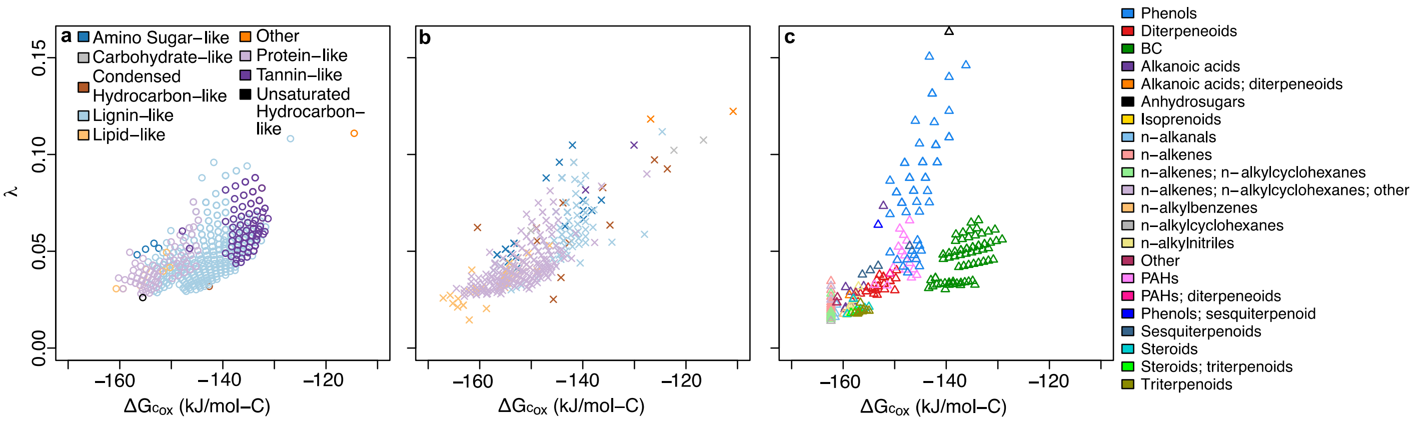


Figure 1. Comparison of PyOM energy content (ΔG_{Cox}) and metabolic efficiency (λ) to global DOM. Ubiquitous DOM molecules detected via FTICR-MS in global (**a**) surface water and (**b**) sediment are colored by inferred chemical class. (**c**) Representative PyOM molecules are colored by known chemical properties. Because PyOM molecules were from primary literature, we could assign chemical properties at higher resolution than inferred classes from measured DOM pools. Details on inferred chemical class assignment are provided in the Supporting Information. Legends are inset in (**a**) for (**a**) and (**b**), and to the right of (**c**).

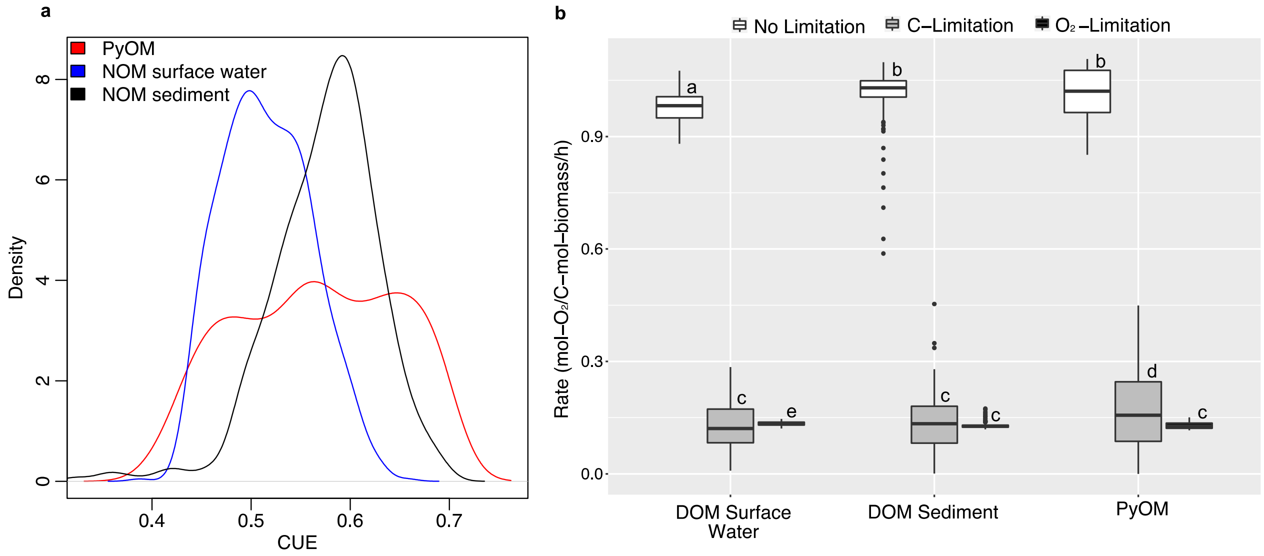


Figure 2. Predicted CUE and metabolism of DOM and PyOM. (**a**) shows the probability density function (PDF) of CUE in PyOM (red) and ubiquitous surface water (blue) and sediment (black). The PDF reflects the relative likelihood that value of a random sample drawn from a particular group would equal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

Interestingly, the relative equivalence of predicted CUE across PyOM and DOM pools suggests that PyOM decomposition in rivers could emit comparable amounts of CO_2 per mole of C to extant DOM pools. CUE is used in many microbially-explicit decomposition models to constrain organic matter bioavailability (reviewed in Graham and Hofmockel, 2022). Therefore, predicted CUE offers a path for assimilating PyOM in microbially-explicit models. Such an approach could be used to directly evaluate the impact of PyOM on global C cycles, and help lead to better incorporation of PyOM impacts in models (Santin et al., 2020).

Within PyOM, two clusters of compounds were distinctly separated from the energetic and metabolic properties of most PyOM (Figure 1c). Phenols had higher λ than the majority of PyOM and DOM compounds (all $\lambda > 0.039$, mean $\lambda = 0.084$), while BC molecules were less energetically favorable than other PyOM classes (all $\Delta G_{Cox} > -143.42$, mean $\Delta G_{Cox} = -136.40$). However, both were within the range of variability in DOM pools (Figure 1). Phenols and BC also had among the lowest CUE (means, BC = 0.47, phenols = 0.54). Phenols are traditionally associated with refractory organic matter, such as lignin and tannins, that exhibit long residence times in soils (Thevenot et al., 2010), although they have also been reported to be bioavailable in soils and waters in recent years (e.g., Thevenot et al., 2010; Ward et al., 2013). Additionally, BC in this study is defined by inferred aromaticity (i.e., the presence of condensed aromatic structures), which is also considered to have low reactivity (Kuzyakov et al., 2014; Wagner et al., 2017). Although the potential bioavailability of phenols and BC is consistent with refractory PyOM, it is within the potential bioavailability range observed in DOM, and these compounds represent only a small portion of the PyOM continuum (Wagner et al., 2018; Masiello, 2004). We note that the comparatively low predicted CUE of phenols and BC indicates that, if metabolized, their decomposition could have a greater impact on river corridor CO_2 emissions than other PyOM and DOM compounds. As a result, current understanding may substantially underestimate the size, reactivity, and hydrobiogeochemical role of PyOM (Wagner et al., 2018).

2.2 Inferred Metabolism of Pyrogenic Organic Matter.

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

When considering the impact of elemental limitations on PyOM metabolism, rate predictions were strongly inhibited under low C and oxygen conditions. Predicted PyOM metabolism was approximately six times lower when C or oxygen was scarce. Low decomposition rates under C and oxygen limitation could be one reason for the observed persistence of PyOM in depositional features that tend to be anoxic. Still, it is worthwhile to note that metabolism of all PyOM classes under low C or oxygen was predicted to be substantially slower than without elemental limitations, indicating PyOM compounds may both actively cycle in well-oxygenated surface waters with fresh C inputs and persist over long periods of time in O_2-limited sediments.

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

2.3 Correspondence to Empirical Investigations.

While the substrate-explicit modelling approach used here has been validated in natural settings and enabled comparison to environmental DOM, its underlying assumptions preclude accounting for DOM structure and size, abiotic reactions, and chemical complexation with minerals and particulates. Some aspects of model predictions are inconsistent with experimental evidence, highlighting the role of laboratory studies in evaluating PyOM bioavailability. For instance, n–alkenes and related compounds tended to have high modelled bioavailability despite being relatively stable in the environment (including useage as paleoproxies, Wiesenberg et al., 2004; Smittenberg et al., 2004). These compounds are characterized by carbon-carbon double bond functional groups, which are not considered by the model and may decrease bioavailability. However, n-alkanes generated through combustion tend to have reduced chain length in comparison to their un-burned counterparts (Knicker et al., 2013), and thus may be relatively bioavailable compared to un-burned n-alkanes. Additionally, we note that previous work has shown fast degradation of combustion-derived lipids in soils (Knicker et al., 2013); as well as high n-alkene metabolism under anaerobic conditions and in natural sediments and a range in lipid reactivities at the sediment-water interface (Grossi et al., 2008; Wilkes et al., 2016; Yongdong et al., 2015; Mbadinga et al., 2011; Canuel and Martens, 1996). While work on aerobic n-alkene metabolism is limited, the comparative bioavailability of n-alkenes and known degradation pathways suggests that sediment microbiomes may metabolize them as part of natural biogeochemical cycles. Another notable discrepancy is the low potential bioavailability of anhydrosugars when compared to other PyOM compounds. Experimentally, anhydrosugars are highly bioavailable in oxic conditions, with a half-life of less than seven days (Norwood et al., 2013). The model may therefore not adequately account for some enzyme-catalyzed reactions such as levoglucosan kinase or levoglucosan dehydrogenase that may be common enzymes in aquatic microorganisms (Bacik and Jarboe, 2016; Suciu et al., 2019).

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

3 Conclusions

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

Code and Data Availability

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

Author Contributions

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

Competing Interests

The authors declare that they have no conflict of interest.

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APPENDIX. Materials and methods

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

To assess the potential bioavailability of PyOM, we searched primary literature for representative compounds of the PyOM continuum. Specifically, we targeted characteristic organic compounds from controlled burns of various fuel types representing a range of moisture, temperature, and oxygen conditions (Table S1). The chosen compounds focused on biomass burning alteration products, which are often used to characterize PyOM in the environment. This included compounds such as theoretical BC compounds, anhydrosugars, and polycyclic aromatic hydrocarbons (PAHs). The list also included compounds created and/or transformed from biomass burning, such as those derived from biopolymers like lignin (e.g., methoxyphenols), waxes (e.g., n-alkenes from thermal dehydration of n-alkanols), and resins (e.g., thermally oxidized diterpenoids) (Oros and Simoneit, 2001a, b). While we recognize that recent research has applied new technologies to inferring PyOM compound presence in environmental samples (e.g., FTICR-MS), there remains high uncertainty in the confidence of formula assignment and structural information with some of these techniques. Therefore, we focused only on known, chemically identified compounds from controlled burns to represent PyOM chemistries. The selected set of compounds spans the chemical continuum of PyOM but was not intended to be exhaustive. In total, our literature search for PyOM chemistries yielded 389 compounds with 207 unique chemical formulae.

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

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

Three sets of organic molecules were used as model inputs: measured global dissolved (1) surface water and (2) sediment DOM pools, extracted in H_2O and analyzed by FTICR-MS as per Garayburu-Caruso et al. (2020a); and (3) literature-derived PyOM compounds as described above. Inputs to the model from the PyOM compounds were unique molecular formulae, grouped in subsequent analysis by their corresponding compound classes (Table S1). If one molecular formula was represented by several PyOM compounds (e.g., $C_{10}H_{16}O_2$, which corresponds to the sesquiterpenoid cis-Thujan-10-oic acid and 3-, 4- substituted methylcatechol phenols), we assigned multiple compound classes to that molecular formula. Surface water and sediment DOM pools were filtered to compounds occurring in 95% of samples to yield a dataset of globally ubiquitous DOM. Formulae assignment and inferred chemical classes via van Krevelen diagrams in DOM pools are described by Garayburu-Caruso et al. (2020a). We compared modelling outputs from representative PyOM to outputs of ubiquitous DOM pools to infer relative bioavailability using ANOVA and Tukey HSD statistical tests with R software. All model outputs are available in Tables S2–S4.

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