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1 **What on Earth have we been burning? Deciphering sedimentary records**  
2 **of pyrogenic carbon**

3

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22 molecular markers, BPCAs, PAHs

23

24 **Abstract**

25 Humans have interacted with fire for thousands of years, yet the utilization of  
26 fossil fuels marked the beginning of a new era. Ubiquitous in the environment,  
27 pyrogenic carbon (PyC) arises from incomplete combustion of biomass and  
28 fossil fuels, forming a continuum of condensed aromatic structures. Here we  
29 develop and evaluate <sup>14</sup>C records for two complementary PyC molecular  
30 markers, benzene-polycarboxylic-acids (BPCAs) and polycyclic-aromatic-

31 hydrocarbons (PAHs) preserved in aquatic sediments from a sub-urban and a  
32 remote catchment in the United States (U.S.) from mid-1700s to 1998. Results  
33 show that the majority of PyC stems from local sources and is transferred to  
34 aquatic sedimentary archives on sub-decadal to millennial time scales.  
35 Whereas a small portion stems from near-contemporaneous production and  
36 sedimentation, the majority of PyC (<90%) experiences delayed transmission  
37 due to 'pre-aging' on millennial timescales in catchment soils prior to its ultimate  
38 deposition. BPCAs (soot) and PAHs (precursors of soot) trace fossil fuel-  
39 derived PyC. Both markers parallel historical records of the consumption of  
40 fossil fuels in U.S., yet never account for more than 19% total PyC. This study  
41 demonstrates that isotopic characterization of multiple tracers is necessary to  
42 constrain histories and inventories of PyC, and that sequestration of PyC can  
43 markedly lag its production.

44

## 45 1. **Introduction**

46 Combustion processes have played a major role in the biogeochemical cycling  
47 of carbon (C) for more than four hundred million years <sup>1</sup>. Yet the utilization of  
48 fossil fuels marked the beginning of a new era (post-1840s) when humans  
49 dramatically accelerated the cycling of fossil C. Today, carbon dioxide  
50 emissions from fossil fuel burning are more than twice that from biomass  
51 burning <sup>2</sup>. However, 'the Anthropocene epoch' <sup>3</sup> has also ushered in enhanced  
52 combustion efficiencies and emission controls, as well as the use of cleaner  
53 burning fuels (petroleum and natural gas), attenuating or changing  
54 environmental impacts.

55

56 Incomplete combustion processes cause the formation of solid residues,  
57 frequently termed “black carbon” or “pyrogenic carbon” (PyC) <sup>4-5</sup>. PyC  
58 corresponds to a continuum of condensed aromatic structures with different  
59 chemical and physical properties <sup>6-8</sup>. In addition to macromolecular or ‘bulk’  
60 forms of PyC, which typically describes the solid residues of combustion  
61 including charcoal and soot, the lower-molecular-weight precursors of  
62 combustion condensates, such as polycyclic aromatic hydrocarbons (PAHs),  
63 are a class of widespread environmental contaminants, some of which are  
64 notorious for their carcinogenic and mutagenic properties <sup>9-10</sup>. Moreover, while  
65 PAHs are directly identifiable in chromatographic analyses, ‘bulk’ PyC can only  
66 be assessed via operationally-defined measurements.

67

68 PyC is ubiquitous in the environment <sup>11-12</sup> due to its transport and widespread  
69 dispersal by wind and water <sup>5</sup>. Subsequent to its production and redistribution,  
70 PyC may engage in a cascade of processes the culmination of which is either  
71 degradation <sup>13</sup> or (ultimate) burial in sediments <sup>14-16</sup>. Estimates of the global PyC  
72 stocks and fluxes carry large uncertainties stemming from diverse methods of  
73 detection and quantification. Some methods are prone to analytical artefacts  
74 and thus hinder precise quantitative assessment of environmental PyC <sup>17-19</sup>,  
75 while others, such as the precursors of combustion condensates, e.g., PAHs,  
76 only trace a restricted portion of the combustion continuum.

77

78 The depositional fluxes of combustion-derived (pyrogenic) PAHs parallel  
79 industrialization on a regional scale <sup>20</sup>. PAHs are however trace level PyC  
80 products, with concentrations typically two or more orders of magnitude lower

81 than 'bulk' PyC<sup>21</sup>. In contrast, benzene polycarboxylic acids (BPCAs) are more  
82 quantitative tracers of 'bulk' PyC which are liberated by laboratory-based  
83 chemical oxidation of combustion residues<sup>19, 22</sup>. Specifically, in contrast to  
84 PAHs that reflect vapour-phase combustion processes, BPCAs appear to track  
85 macromolecular PyC residues, such as charcoal and soot, that comprise a  
86 greater fraction of the PyC burden delivered to and sequestered in the  
87 environment<sup>21</sup>.

88

89 The combined application of both PAHs and BPCAs as molecular markers of  
90 combustion can facilitate development of more comprehensive records of  
91 combustion from sedimentary archives. When coupled with molecular-level  
92 natural abundance radiocarbon (<sup>14</sup>C) measurements, they can provide  
93 quantitative constraints in sources of PyC derived from either biomass burning  
94 or fossil fuel combustion. The success of this approach, however, requires high-  
95 fidelity sedimentary archives with well-defined catchments. In a prior  
96 investigation of an exceptionally well-dated sedimentary sequence from the  
97 northeastern USA (Pettaquamscutt River estuary, Rhode Island), we observed  
98 incongruent PAH and BPCA flux variations<sup>21</sup>, suggesting that these two well-  
99 established groups of PyC markers differ markedly in provenance and mode of  
100 transport and deposition. Specifically, we found that records of combustion are  
101 clearly decoupled in the (pre-)industrial era and chronicle local and regional  
102 combustion practices<sup>21</sup>.

103

104 Here, our objectives were to (1) use <sup>14</sup>C characteristics to reconcile previously  
105 observed decoupled records for these two suites of complementary molecular

106 markers of combustion; (2) constrain the provenance and transport pathways of  
107 pyrogenic carbon in sediment deposited since the pre-industrial era; (3)  
108 compare results from a urbanized catchment with that from a remote location in  
109 the context of local and regional land-use and fuel consumption history.

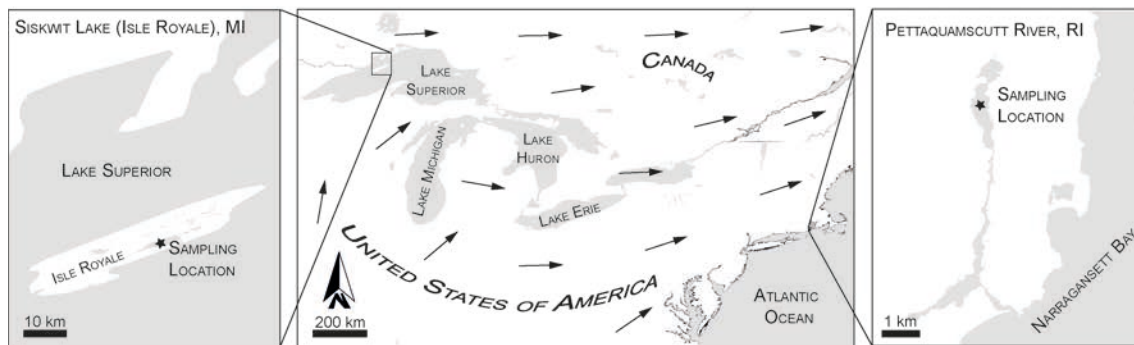
110

## 111 **2. Experimental Section**

### 112 **Study Area**

113 *Pettaquamscutt River basin* is a suburban setting located in South  
114 Kingston, southern Rhode Island, USA (Figure 1). This 9.7 km long estuary  
115 ranges in width from 100 to 700 m, and has a small watershed (~35 km<sup>2</sup>)  
116 dominated by oak woodland, wetlands and open waters<sup>23-24</sup>. This system can  
117 be geographically divided into two remnant kettle lakes (upper and lower basin)  
118 and a 6.4-km long channel that connects it to the main source of salt water to  
119 this estuary, Narragansett Bay in Rhode Island Sound<sup>25</sup>. Samples were  
120 collected in the deepest point (20 m) of the lower basin of the River<sup>20</sup>.

121 *Siskiwit Lake* is a remote site located on Isle Royale in the northwestern  
122 portion of Lake Superior, close to the USA-Canada border (Figure 1). Isle  
123 Royale is distal from major urban and industrialized centers, the nearest being  
124 55 km away, and over 98% of its land is designated wilderness<sup>26</sup>. More than 50  
125 lakes are located on the Isle, of which Siskiwit Lake is the largest with an  
126 approximate area of 16.8 km<sup>2</sup> and a maximum depth of 46 m. This lake is  
127 situated 17 m higher than, and 600 m inland from Lake Superior, preventing  
128 exchange between these two water bodies. Atmospheric deposition is  
129 considered the only source of contamination to Siskiwit Lake<sup>26</sup>.



130

131 Figure 1: Overview on study sites (made with Natural Earth) with *left* Siskiwit Lake, *centre* northeastern  
 132 North America with prevailing vector mean wind composites from 1871-1998 (NOAA/ESRL) and *right*  
 133 Pettaquamscutt River.

134 **Sampling and Sediment Dating.** In Pettaquamscutt River basin, four

135 rectangular aluminum freeze corers (90x30x10 cm) were collected, immediately

136 packed with dry ice, x-rayed for age chronology and kept frozen until at the

137 laboratory <sup>27</sup>. While maintained frozen by applications of liquid nitrogen, the

138 cores were sectioned at 0.5-cm intervals using a tile saw equipped with a

139 diamond wafering blade (0.63-mm thickness). After subsequent freeze-drying,

140 homogenized sediment samples of equivalent depth (correlated based on varve

141 patterns reveals in X-ray and visual images) were combined. Sedimentation

142 rates were calculated using the constant rate of supply (CRS) <sup>28</sup> model, and the

143 results were then compared to a remarkably detailed high-resolution varve

144 chronology by Lima, et al. <sup>27</sup>. Eight depth-age intervals were defined for the

145 Pettaquamscutt River basin sediments as follows: in the industrialized era, P1

146 (1999-1982), P2 (1981-1962), P3 (1960-1931), P4 (1929-1898) and P5 (1896-

147 1873), and prior to significant industrial activities, P6 (1871-1842), P7 (1840-

148 1768) and P8 (1764-1735).

149

150 In Siskiwit Lake, seven gravity cores (ca. 20-30 cm length and a diameter of 10

151 cm) were collected, sliced at 2-cm intervals, placed into plastic freezer bags,

152 sealed and stored in ice for transport. Sediment samples were later transferred

153 to combusted glass jars and freeze-dried prior to analysis. Unfortunately, the  
154 upper 8 cm of the record (i.e., post-1954) was lost during coring due to the  
155 aggressive nature of gravity coring. Sediment chronology was then established  
156 with the constant initial concentration (CIC) model to estimate the missing top  
157 sediments deposited over 43 years.<sup>29</sup> The calculated sedimentation rate (0.18  
158 cm yr<sup>-1</sup>) was in close agreement with a previous study<sup>26</sup>. The Siskiwit Lake  
159 sediments were combined at a coarser resolution. Four horizons were defined  
160 for BPCAs: S1 (1954-1926), S2 (1915-1882), S3 (1871-1837) and S4 (1826-  
161 1793); and three for PAHs: S1x (1954-1932), S2x (1921-1887), and S3x (1832-  
162 1798). The latter chronology was extended by a <sup>14</sup>C PAH record of the same  
163 location published by Slater, et al.<sup>30</sup>.

164

165 **Total Organic Carbon (TOC).** A Fisons 1108 elemental analyzer was used to  
166 measure the total organic carbon (TOC) content of the sediments after removal  
167 of carbonates<sup>27</sup>. Samples were run in triplicate and all reported weight  
168 percentages represent the mean  $\pm$  one standard deviation. Carbon  
169 concentration were determined through a 5-point calibration curve (0.1 to 1 mg)  
170 of a sulfanilamide standard. Instrumental blanks were run after sets of 12  
171 analyses, yielding blanks better than 0.004 mg C.

172

173 **Extraction and purification of benzene polycarboxylic acids (BPCAs).**  
174 BPCAs are specific measures of combustion residuals, liberated by chemical  
175 oxidation of residues such as char and soot<sup>21,31</sup>. Briefly, oxidative degradation  
176 (170°C, 8 h) of PyC was achieved via nitric acid treatment of air dried  
177 sediments<sup>32</sup>. BPCAs were purified from the products by removal of polyvalent



178 ions and non-polar organic compounds using cation exchange (Dowex®  
179 50WX8) and solid phase extraction (Discovery® DSC-18, 500 mg) columns and  
180 then separated by preparative liquid chromatography using an Agilent 1290  
181 infinity HPLC system equipped with a 2.7µm Agilent Poroshell 120 C-18  
182 column. Quantification of BPCAs was achieved from seven-point calibration  
183 curves (2 to 200ng µl<sup>-1</sup>) using commercially available BPCA standards including  
184 pentacarboxylic acid (Aldrich S437107) and hexacarboxylic acid (Aldrich  
185 M2705). All measurements were carried out in duplicate. To demonstrate that  
186 the BPCA methodology is insensitive to the presence of petrogenic (rock-  
187 derived) graphitic C, a limitation of other PyC methods <sup>33</sup>, we processed and  
188 sought to quantify BPCAs liberated from natural graphite, type: Sri Lankan,  
189 99.7% C (Asbury Carbons). The lack of detectable BPCAs implies that we can  
190 exclude possible interferences from lithogenic material in <sup>14</sup>C-based source  
191 apportionment using BPCAs.

192 **Isolation of BPCAs for <sup>14</sup>C analysis.** Briefly, according to Hanke, et al. <sup>32</sup>,  
193 target analytes were collected in repetitive runs yielding amounts of about 30 µg  
194 C while injection volumes were adjusted per sample (1 to 20 µl per inj.<sup>-1</sup>) <sup>32</sup>. The  
195 purified fractions were dried (3 hours) on a hot plate (~70°C) using ultrapure  
196 nitrogen stream and stored at 6 °C. Samples were then oxidized to CO<sub>2</sub> with  
197 sodium persulfate in 12 ml Exetainer vials and measured on a gas ion source <sup>34</sup>  
198 equipped MICADAS AMS at ETH Zürich <sup>35</sup>. All measured samples were  
199 conveyed with process standards (<sup>14</sup>C modern and depleted charcoals in  
200 various concentrations) that span over the entire analytical procedure facilitating  
201 the correction of measured data for constant contamination <sup>32</sup>. Reported results  
202 on BPCAs are mean values with the standard deviation of duplicates.

203

204 **Extraction, Purification and Combination of pyrogenic PAHs.** Non-alkylated  
205 (pyrogenic) PAHs are formed as precursors of condensates during combustion  
206 processes and represent intermediates in soot formation <sup>12</sup>. Each 0.5-cm  
207 sediment interval total lipid extract was separated on a column packed with 100-  
208 200 mesh fully-activated silica gel where PAHs were eluted with a mixture of  
209 toluene and hexane (1:1). After extraction and purification, the PAH fractions  
210 were concentrated and further combined yielding fractions corresponding to  
211 coarser depth intervals in order to obtain sufficient amounts of individual PAHs  
212 for <sup>14</sup>C analysis. The resulting fractions were subjected to preparative capillary  
213 gas chromatography (PCGC) for isolation of individual PAHs. The measurement  
214 precision was better than 5%.

215

216 **Preparative Capillary Gas Chromatography (PCGC).** Automated preparative  
217 capillary gas chromatography (PCGC; Eglinton, et al. <sup>36</sup>) was used to isolate  
218 non-alkylated PAHs through repetitive injections (~100) from sedimentary  
219 extracts. PAHs in Siskiwit Lake extracts were isolated using the one-  
220 dimensional PCGC system <sup>37</sup>. For the Pettaquamscutt River extracts it was  
221 necessary to use a two-dimensional system PCGC because the samples  
222 contained interfering biogenic organic compounds <sup>38</sup>. For Pettaquamscutt River  
223 basin, we report phenanthrene, fluoranthene, pyrene, benz[a]anthracene,  
224 chrysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, and  
225 benzo[g,h,i]perylene as an integrated pyrogenic PAH signal, and for Siskiwit  
226 Lake the sum of phenanthrene, anthracene, fluoranthene, pyrene,  
227 benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene,

228 benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[123-*cd*]pyrene  
229 and benzo[*ghi*]perylene. Here, reported values are the sum of measured PAHs  
230 and standard deviation.

231

232 **Radiocarbon Measurements.** Compound-specific radiocarbon analyses and  
233 initial processing of data of BPCAs were performed at the laboratory of Ion  
234 Beam Physics, ETH Zürich, Switzerland, while PAHs were measured at the  
235 National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility,  
236 Woods Hole Oceanographic Institution, Woods Hole, USA. All samples were  
237 corrected for extraneous carbon<sup>32,37</sup> and reported as  $F^{14}C$ <sup>39</sup>, which is percent  
238 modern carbon but independent from the year of measurement<sup>39</sup>. Calculations  
239 of mean residence time and  $^{14}C$  ages were retrieved from the atmospheric  $^{14}C$   
240 calibration curve (Intcal13)<sup>40-41</sup>.

### 241 **3. Results and Discussion**

242 **Pettaquamscutt River basin.** The sedimentary record spans the time interval  
243 from 1738 to 1998 AD (Table 1)<sup>27</sup>, capturing what moments in “human history”.  
244 Combustion history in this sedimentary archive was reconstructed in eight  
245 depth-intervals tracing periods influenced by both local (e.g., land-use) and  
246 more widespread (regional industrialization) phases of change. We find BPCA  
247 concentrations vary by over a factor of two, from 0.347 to 0.826 g kg<sup>-1</sup>  
248 throughout the record with a general decrease in concentrations towards the  
249 latter half of the 20<sup>th</sup> Century (Table 1). In contrast, prior to the industrial era  
250 (before 1840s) PAH concentrations were very low (about 0.0001 g kg<sup>-1</sup>), and  
251 varied between with 0.006 g kg<sup>-1</sup> (1983 – 1998 AD) and 0.062 g kg<sup>-1</sup> (1932-  
252 1961 AD) during the industrial era. Thus, these quantities reproduce the time

253 trends observed by individual measurements in high-temporal resolution from  
254 the same sediments <sup>21</sup>. Summarizing, pyrogenic PAHs are two orders of  
255 magnitude lower in abundance than BPCAs, with the sharply contrasting  
256 temporal evolution patterns of these two PyC tracers indicating they are  
257 decoupled <sup>21</sup> similar to previous research using operationally-defined PyC  
258 methods <sup>42-44</sup>.

259

260 The uppermost TOC <sup>14</sup>C samples show the highest <sup>14</sup>C concentrations  
261 corresponding to the 'bomb peak', where <sup>14</sup>C was added to the atmosphere  
262 through thermo-nuclear 'bomb' testing in the late 1950s and early 1960s (Table  
263 1). The atmospheric inventory of <sup>14</sup>C doubled during this period and manifests  
264 itself, albeit in a muted fashion, in the TOC <sup>14</sup>C record. While this bomb <sup>14</sup>C  
265 signal would have been transferred to vegetation via photosynthetic C fixation,  
266 and subsequently to products of biomass burning, it is, if at all, only very weakly  
267 pronounced in the PyC records (Table 1). However, this increase is strongly  
268 muted relative to concomitant atmospheric <sup>14</sup>C variations <sup>40</sup>, with values that are  
269 consistently lower than its corresponding atmospheric signature at the time of  
270 deposition. The low-amplitude 'bomb spike' and depressed <sup>14</sup>C values may  
271 reflect reservoir (incl. hard water) effects and or supply of pre-aged organic  
272 matter to the sediments. The term 'pre-aged' describes the time lag between  
273 production and the subsequent transport trajectory until deposition in  
274 sedimentary archives. PyC is an excellent tracer of pre-aged organic matter  
275 because it is uniquely terrestrial in origin, and corresponding <sup>14</sup>C records allow  
276 for more facile attribution of inputs. In contrast, TOC reflects a myriad of organic  
277 matter sources and processes associated with its transformation and

278 decomposition in the water column and sediments <sup>45</sup>. For BPCAs (tracers of  
 279 'bulk' PyC) we attribute a fraction of 'pre-aged' PyC in deciphering origins of  
 280 sedimentary PyC.

281

282 The BPCA records in Pettaquamscutt River sediments coincide with our  
 283 historical knowledge on the catchment. Europeans colonized the catchment  
 284 throughout the 17<sup>th</sup> Century first building ships and then started to establish  
 285 farmland with both these activities promoting deforestation and land clearance  
 286 that peaked in the mid-1700s <sup>46</sup>. The sediments deposited between 1738 and  
 287 1766 reflect this biomass-derived PyC inputs with relatively modern BPCA <sup>14</sup>C  
 288 values ( $F^{14}C = 0.836 \pm 0.035$ ). In the late 1700s, agricultural land use started to  
 289 develop to residential land <sup>46</sup>, and no obvious manifestation of this change  
 290 occurs in the sedimentary BPCA record (1770-1841). Abandonment of local  
 291 farmland continued throughout the 19<sup>th</sup> century, while on a regional scale,  
 292 consumption of fossil fuels in U.S. started and already accounted for 9.3% of  
 293 energy consumption in U.S. by 1850 AD <sup>47</sup>. BPCA concentrations increase  
 294 between the periods 1770-1841 and 1843-1872 AD yet there is no substantial  
 295 accompanying change in the BPCA <sup>14</sup>C record due to the increasing use of  
 296 fossil fuels implying that this increase is due to enhanced local re-mobilization  
 297 processes.

298 Table 1 Results on quantities and <sup>14</sup>C concentrations for TOC, BPCAs and PAHs in Pettaquamscutt River  
 299 basin sediments over eight periods of time ( $F^{14}C$  reads as percent modern C)

Time range	Depth interval	Total organic carbon		Benzene-[penta+hexa]-carboxylic acids		Polycyclic aromatic hydrocarbons	
		[%]	$F^{14}C$	[g kg <sup>-1</sup> ]	$F^{14}C$	[g kg <sup>-1</sup> ]	$F^{14}C$
1983-1998	0 - 9.5	7.3±0.2	1.003±0.004	0.347±0.006	0.713±0.019	0.006	0.198±0.010
1962-1981	10 - 19	7.7±0.4	1.027±0.004	0.457±0.011	0.686±0.014	0.047	0.071±0.004
1932-1961	19.5 - 29	7.9±0.2	0.880±0.003	0.633±0.017	0.633±0.013	0.062	0.066±0.003

1898-1930	29.5 - 36	9.8±0.5	0.873±0.004	0.841±0.007	0.610±0.015	0.039	0.131±0.007
1874-1897	36.5 - 42	9.2±0.1	0.905±0.003	0.763±0.031	0.673±0.014	0.007	0.183±0.009
1843-1872	42.5 - 49	9.9±0.3	0.944±0.005	0.826±0.077	0.819±0.014	n/a	n/a
1770-1841	49.5 - 64	8.9±0.1	0.918±0.003	0.680±0.011	0.822±0.020	n/a	n/a
1738-1766	64.5 - 70	8.9±0.1	0.911±0.004	0.694±0.072	0.826±0.035	n/a	n/a

300

301 As fossil fuel consumption increased from 1874 to 1897, and coal superseded  
302 wood as the primary fuel source by 1885 AD <sup>47</sup>, the sediments reveal marked  
303 increases in PAH concentrations ( $\sim 0.007 \text{ g kg}^{-1}$ ). This allowed for enough  
304 material for  $^{14}\text{C}$  analysis ( $0.183 \pm 0.002 \text{ F}^{14}\text{C}$ ). This interval corresponds to a  
305 notable decline in BPCA  $^{14}\text{C}$  compared to the previous years, and together with  
306 the PAH data this change is consistent with increased accumulation of soot and  
307 associated condensation residues of fossil fuel burning in the Pettaquamscutt  
308 River basin sediments. During the interval between 1898 and 1930, the  
309 sedimentary deposits recorded an increased concentration and further  
310 decreases in  $\text{F}^{14}\text{C}$  values of both PAHs and BPCAs, the latter reaching its  
311 minimum value over the entire record. These changes are consistent with  
312 increased dependence on fossil fuels at both local and regional scales. By this  
313 time, the proportion of fuel use from biomass burning was already less than  
314 10% on a regional scale, and petroleum was increasingly used, ultimately  
315 exceeding coal consumption by 1950 AD <sup>47</sup>. Locally, the residential land  
316 increased by at least 4.7% from 1930s to 1950s <sup>46</sup>. During this phase 1932-  
317 1961, the BPCA  $^{14}\text{C}$  increased slightly, while that of the PAHs decreased  
318 further.

319

320 The subsequent period from 1962 to 1981 also corresponds to increasing  
321 consumption of petroleum and natural gas and subordinate use of coal ( $\sim 20\%$ )

322 in terms of overall fuel consumption<sup>47</sup>. Additionally, implementation of stricter  
323 emission controls and catalytic converters during this period led to reduced  
324 particulate emissions, coinciding with decreasing BPCA and PAH abundances,  
325 molecular markers with lower quantities and slightly increasing <sup>14</sup>C signatures  
326 indicating either less  $\text{PyC}_{\text{fossil fuel}}$  or supply of very small portion of bomb <sup>14</sup>C-  
327 affected  $\text{PyC}_{\text{contemporary}}$ . This trend of decreasing PyC concentrations and  
328 increasing  $F^{14}\text{C}$  values continues in the sediments for the period 1983 to 1998,  
329 consistent with changing combustion practices on a regional scale that resulted  
330 in increasing combustion efficiency and tighter environmental regulations.  
331 However, different modes of combustion (gas phase vs. pyrolysis) cause the  
332 formation of different PyC qualities, which again greatly depend on fuel type,  
333 reaction times and the combustion efficiency<sup>48-49</sup>. On local scale, land-use  
334 change may only have a minor influence on the sedimentary PyC deposits  
335 during the era of industrialization, although the catchment has undergone  
336 reforestation and residential land now accounts for about 30% of the catchment  
337 <sup>50</sup>.

338

339 **Pre-aging of PyC prior to burial.** The sedimentary legacy of combustion, as  
340 manifested in the concentrations and <sup>14</sup>C values of PAHs and BPCAs, reveals  
341 clear changes in quantity and sources of PyC over time. PAHs signals appear  
342 to closely follow regional-scale patterns in fossil fuel consumption, whereas  
343 BPCAs appear to track more local biomass combustion practices and runoff  
344 from the catchment<sup>21</sup>. However, the BPCA <sup>14</sup>C values ( $<0.826 \pm 0.035 F^{14}\text{C}$ ) are  
345 systematically lower, i.e. ~16% in the preindustrial era, than the corresponding  
346 atmospheric <sup>14</sup>C values ( $>0.982 \pm 0.008 F^{14}\text{C}$ ), implying that they could not have

347 been produced from burning of contemporaneously synthesized biomass. The  
348  $^{14}\text{C}$  offset is apparent even prior to the industrial era and associated utilization  
349 of fossil fuels. Thus BPCAs must trace at least a portion of biomass-derived  
350 PyC that is pre-aged and supplied to 'ultimate' site of burial with a certain lag  
351 time. During the three time intervals recording the pre-industrial era (1738-1766,  
352 1770-1841, 1843-1872), we observed BPCA  $F^{14}\text{C}$  values of  $0.826 \pm 0.009$ , which  
353 corresponds to  $1290 \pm 160$   $^{14}\text{C}$  years. Given that at least some fraction of the  
354 BPCA signature reflects near instantaneous (i.e., on seasonal to decadal  
355 timeframe) burning and translocation from biomass source to sedimentary sink,  
356 the observed  $^{14}\text{C}$  age likely represents mixed aged PyC components, with some  
357 exhibiting ages greater than  $\sim 1300$   $^{14}\text{C}$  years. Sedimentary signatures of  
358 combustion thus reflect inputs not only from different sources in the catchment,  
359 but also similar sources but differing pre-depositional histories. Here we  
360 observe this pre-aging for BPCAs and our findings ought to be supported by  
361 studies employing other 'bulk' PyC approaches. However, the phenomenon of  
362 pre-aging has also been seen in other molecular-level studies tracing the  
363 carbon cycle and its trajectory in the environment <sup>51-52</sup>.

364

365 We define three PyC inventories yet two of which supply biomass-derived PyC  
366 (Table 2): the immediate post-fire input ( $\text{PyC}_{\text{contemporary}}$ ) and an integrated  
367 signature reflecting the mean residence time (MRT) of a certain catchment  
368 ( $\text{PyC}_{\text{pre-aged}}$ ). Additionally, the usage of fossil fuels with the onset of  
369 industrialization has left its signature on the environment <sup>15, 53-54</sup>, introducing an  
370 additional source of PyC since the mid-1800s.

371 Table 2: Conceptual framework of inventories that supply PyC to sediments from local and regional  
372 sources of combustion.  $\text{PyC}_{\text{contemporary}} + \text{PyC}_{\text{pre-aged}}$  equals PyC from biomass burning and PyC derived  
373 from fossil fuel combustion becomes only active with the onset of industrialization.



Characteristics	PyC <sub>contemporary</sub>	PyC <sub>pre-aged</sub>	Fossil fuel combustion
Time [years]	0 to 60	60 to 10,000	> 60,000
Origin	Local sources	Catchment soils	Domestic and industrial combustion and transport
F(t)	Direct	e <sup>-kt</sup>	Direct
Transport pathways	Atmospheric deposition, surface runoff	Erosional (sub-) surface processes	Primarily atmospheric deposition

374

375 Three pools must therefore be taken into consideration in order estimate and  
376 allocate the sources of PyC supplied to sediments in the Pettaquamscutt River  
377 and Siskiwit Lake catchment (Table 2; Equations 1 & 2).

378

379 Equation (1) 
$$F^{14}C_{\text{measured}} = F^{14}C_{\text{contemporary}} * f_1 + F^{14}C_{\text{pre-aged}} * f_2 + F^{14}C_{\text{fossil fuel}} * f_3$$

380 Equation (2) 
$$F^{14}C_{\text{biomass}} = F^{14}C_{\text{contemporary}} * f_1 + F^{14}C_{\text{pre-aged}} * f_2$$

381

382 The following boundary conditions were chosen to determine the contribution of  
383 pre-aged PyC to the total pool of PyC from biomass burning: (1) the maximum  
384 period of time since deposition assuming that vegetation growth and soil build-  
385 up did not commence following glacial retreat earlier than 10,000 years before  
386 present in both catchments; (2) an absence of ancient (fossil) PyC due to a lack  
387 of post-glacial erosion processes in Pettaquamscutt River basin <sup>25</sup> and the  
388 Great Lakes region; and (3) the PyC<sub>contemporary</sub> <sup>55</sup> is assumed to be small  
389 accounting for only about 10% of the total PyC produced during a fire event  
390 because, the greater part of PyC will remain in immediate proximity of a fire and  
391 deplete in stocks only over the long term <sup>56-57</sup>. Given that the mean fire return  
392 interval is, in average, about 300 years for Pettaquamscutt River catchment and  
393 about 150 years for Siskiwit Lake catchment <sup>58</sup>, this may coincide with the

394 average  $^{14}\text{C}$  ages for the respective pre-aged PyC. To account for disparities in  
395 the catchment location and variable factors that influence rate and extent of  
396  $\text{PyC}_{\text{contemporary}}$  mobilization (e.g., precipitation, relief), we consider a variation of  
397 10% for the two pools:  $f_{\text{contemporary}} = 10\pm 10\%$  and  $f_{\text{pre-aged}} = 90\pm 10\%$ . These  
398 conditions facilitated to explain more than 98% of biomass-derived PyC  
399 (supporting information).

400

401 We used the advanced source apportionment model based on three scenarios  
402 (Table 3) to estimate the pre-aged PyC pool. The time lag between production  
403 and burial is given by retention within intermediate reservoirs (e.g., soils, rivers)  
404 and decelerated transport of PyC in the catchment. These processes may  
405 explain the lag time (pre-aging) of PyC between production and deposition. We  
406 argue that contemporary inputs account for only a minor fraction yet is variable,  
407 and thus we report  $\text{PyC}_{\text{pre-aged}}$  within the range  $90\pm 10\%$  resulting in the mean  
408 value and standard deviation for pre-aged PyC of the three possible scenarios.  
409 We further expect the average pre-industrial age of PyC of  $\sim 1300$   $^{14}\text{C}$  years to  
410 remain steady throughout the industrialized era because of (1) the low age  
411 variability ( $\pm 160$   $^{14}\text{C}$  years) in the three reference intervals (*1738-1766*, *1770-*  
412 *1841*, *1843-1872 AD*) and (2) the variable pool size of  $\text{PyC}_{\text{pre-aged}}$  resulting in a  
413 total uncertainty that is three times larger than the initial value (Table 3). The  
414 model thus is robust against possible variation in the present-day mean  
415 residence time (MRT) as modest changes would be undetectable.  
416 Subsequently, we retrieve an average MRT of  $1,500\pm 210$  years for PyC within  
417 the Pettaquamscutt River basin catchment, which agrees well with the limited  
418 data available in literature ( $<1500$  years)<sup>59-60</sup>. In this study we can exclude

419 sources of 'pre-aged' dissolved PyC circulating in the marine environment, but  
 420 this could substantially influence the results in other environmental settings.

421

422 Table 3: Scenarios of varied composition for pool  $\text{PyC}_{\text{biomass}}$  in Pettaquamscutt River basin sediments  
 423 resulting in different PyC catchment mean residence times (MRT) depending on active entry of  
 424  $\text{PyC}_{\text{contemporary}}$  (0-30 years before deposition)  
 425

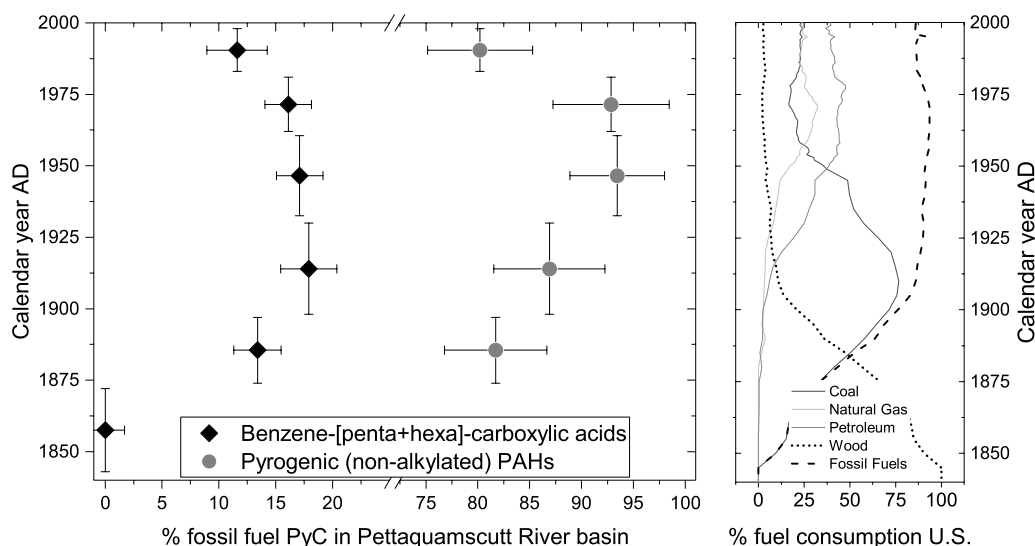
#	$F^{14}\text{C}_{\text{measured}}^{\text{a)}$	$f_{\text{contemporary}}$	$F^{14}\text{C}_{\text{contemporary}}^{\text{b)}$	$f_{\text{pre-aged}}$	$F^{14}\text{C}_{\text{pre-aged}}$	Catchment MRT <sup>c)</sup> [years]
1	0.826±0.043	0.00	0.982±0.008	1.00	0.826±0.05	1290±480
2	0.826±0.043	0.10	0.982±0.008	0.90	0.808±0.05	1460±490
3	0.826±0.043	0.20	0.982±0.008	0.80	0.787±0.05	1710±510

<sup>a)</sup> Average  $F^{14}\text{C}$  of BPCAs (1738-1872); <sup>b)</sup> Average atmospheric  $F^{14}\text{C}$  in 1790±50 AD derived from Intcal13<sup>40-41</sup> <sup>c)</sup> Uncertainties derived from atmospheric  $^{14}\text{C}$  concentrations and of BPCA  $^{14}\text{C}$  data

426

427 **Legacy of fossil fuel combustion in sedimentary deposits.** Fuel  
 428 consumption in U.S. started to change with the onset of industrialization, and  
 429 this change is clearly reflected by the marked increase in PAH fluxes from the  
 430 late 1800s onwards recorded in a high-resolution record from Pettaquamscutt  
 431 River basin sediments <sup>20</sup> as well as in our  $^{14}\text{C}$  BPCA and PAH data (Figure 2).  
 432 Assuming a constant age of biomass-derived PyC obtained from samples pre-  
 433 dating the industrialization it is possible to apply isotope mass balance  
 434 calculations to retrieve the contribution from fossil fuels (Equations 1 & 2). We  
 435 found concentrations of fossil fuel-derived PyC vary between 12 and 18% for  
 436 BPCAs and between 80 and 93% for PAHs over this time interval. The latter of  
 437 which is similar to recent findings by Jautzy, et al. <sup>49</sup>.

438



439 Figure 2: Pettaquamscutt River basin. (left) PyC from combustion of fossil fuels increases in late 1800s in  
 440 BPCAs and PAHs (vertical error bars indicate depth interval; horizontal error bar the analytical error) and  
 441 corresponds to the (right) consumption of fossil fuels in U.S. (dashed line) and biofuel wood (dotted line).  
 442 The declining contribution in both PyC markers from 1970s reflects the increasing usage of cleaner  
 443 burning fuels as well as emission control.  
 444

445

446 With respect to char and soot measured by BPCAs, the above estimates are  
 447 similar to dissolved PyC in a Chinese river (15-23%  $\text{PyC}_{\text{fossil fuel}}$ ) but much lower  
 448 than its particulate counterpart ( $\sim 50\% \text{PyC}_{\text{fossil fuel}}$ )<sup>61</sup>. The portion of fossil PyC  
 449 in arctic surface sediments accounted for 80%<sup>62</sup>, yet this study used a different  
 450 method that is susceptible to measure lithogenic graphite as PyC<sup>63</sup>.  
 451 Surprisingly, the absolute quantities of BPCAs and PAHs differ by several  
 452 orders of magnitude, yet both estimates of  $\text{PyC}_{\text{fossil fuel}}$  follow a similar trend and  
 453 parallel the proportional consumption of fossil fuels (coal, petroleum and natural  
 454 gas) during the industrial era (Figure 2). We find divergence between the  
 455 percent amounts of  $\text{PyC}_{\text{fossil fuel}}$  and fuel consumption post-1970s due to  
 456 increased combustion efficiency and stricter emission controls resulting in  
 457 reduced production of soot particles<sup>64</sup>.

458

459 Thus, isotope mass balance-derived proportions of  $\text{PyC}_{\text{fossil fuel}}$  based on both  
 460 PAHs (binary mixture) and BPCAs (ternary mixture) trace the consumption of

461 fossil fuels throughout the industrial era. However, the proportion of fossil PyC  
462 in PAHs always is much larger than in BPCAs. Using BPCAs <sup>14</sup>C records of  
463 'bulk' PyC reveals relatively uniform inputs and a time lag ('pre-aging') from the  
464 source of local biomass-derived PyC to the sink, whereas the amounts of fossil  
465 fuel-derived PyC change with time. There are two implications for this finding.  
466 First, fossil fuel consumption represents only a minor fraction (<20%) of the  
467 overall PyC burden in Pettaquamscutt River basin sediments as represented by  
468 BPCAs <sup>19, 65</sup>. In contrast, pyrogenic PAHs show markedly different temporal  
469 behaviour and predominantly trace fossil fuel combustion processes. Second,  
470 fossil fuel-derived PyC record is defined by regional-scale processes, which  
471 implies this signal is carried by atmospheric transport. Previous studies have  
472 found that PAHs adsorb onto soot and exhibit atmospheric transport times of  
473 about 10 days <sup>66-67</sup>. The Pettaquamscutt River catchment is located downwind  
474 of industrial centres <sup>21, 68</sup>, and thus records the regional combustion activity  
475 through transport and deposition of atmospheric particulates.

476

477 **Siskiwit Lake.** The sedimentary profile of BPCAs and PAHs <sup>14</sup>C spans over the  
478 time interval from 1793 to 1954 AD, and is augmented by additional PAH data  
479 for four time points (1950-2000 AD) reported by Slater, et al. <sup>30</sup> (Figure 3).  
480 Concentrations of 'bulk' PyC (given by BPCAs) range from 0.85 to 0.93 g kg<sup>-1</sup>  
481 for BPCAs thus are similar to those for the Pettaquamscutt River basin. In  
482 contrast, maximum PAH concentrations (0.0013 g kg<sup>-1</sup>) between 1793 and 2000  
483 <sup>30</sup> are considerably lower than those of the Pettaquamscutt basin (0.062 g kg<sup>-1</sup>).  
484 Thus, the PAH inventory in Siskiwit Lake correspond to ~ 21% of the suburban  
485 catchment, highlighting the pristine location out of reach to centres of industrial

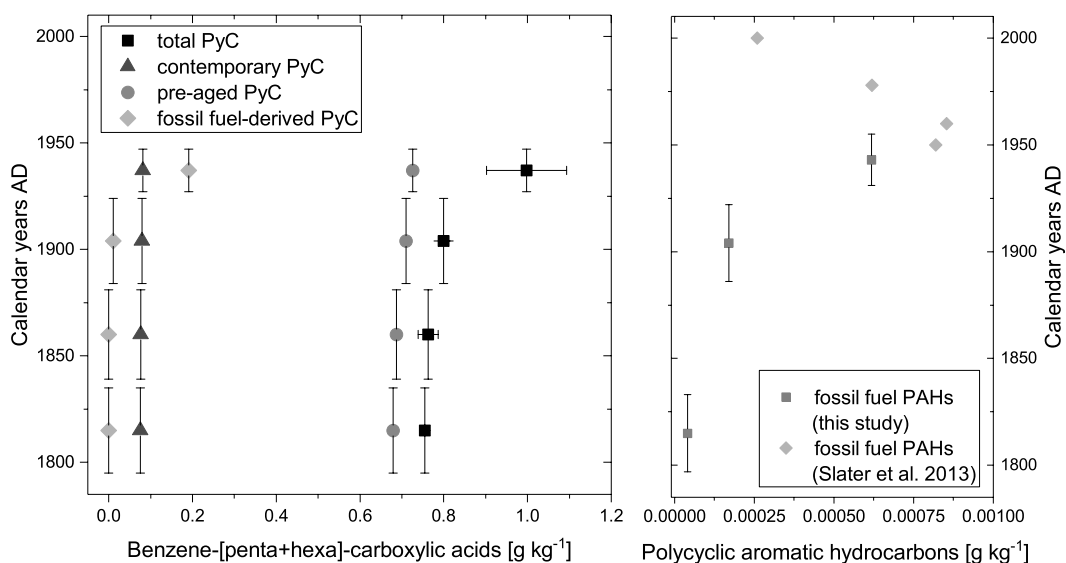
486 activity. BPCA  $^{14}\text{C}$  values are near constant between 1793 and 1871 ( $F^{14}\text{C}$  of  
487  $0.905\pm 0.019$ ) and decrease thereafter to  $F^{14}\text{C}$  of  $0.658\pm 0.022$  between 1926  
488 and 1954 (Table S2). The PAH  $^{14}\text{C}$  record shows a similar profile, with  $F^{14}\text{C}$  of  
489  $0.895\pm 0.014$  between 1798 and 1832, decreasing to  $0.528\pm 0.005$  between  
490 1926 and 1954 (Figure 3, Table S3).

491

492 The sampling location on Isle Royale within the Lake Superior, U.S. is ca. 55  
493 km from the nearest populated area <sup>26</sup>. Locally, the catchment was extensively  
494 deforested by fishermen and mineworkers in the 19<sup>th</sup> century, the record of  
495 which is preserved in two sediment samples from 1793-1826 and 1837-1871  
496 AD. Large-scale forest fires cleared more than 50% of the forest area in 1847  
497 and roughly 80% in 1936 AD <sup>69</sup>. Since 1940, Isle Royale has been a designated  
498 wilderness area, with near total restrictions on use of combustion engines.

499

500 Adopting the same approach and assumptions used for the Pettaquamscutt  
501 River basin, we report a catchment MRT of  $860\pm 110$  years for  $\text{PyC}_{\text{pre-aged}}$  pool.  
502 Thus the lag time in Siskiwit Lake catchment is 630 years shorter than in  
503 Pettaquamscutt River basin. This implies more rapid transfers of  $\text{PyC}$  to its  
504 burial site. This difference may reflect contrasting residence times in soils  
505 and/or transport pathways but can also be linked to the shorter fire return  
506 interval, which here is only 50% of that in the Pettaquamscutt catchment.



507

508 Figure 3: PyC from biomass burning remains uniform in Siskiwit Lake sediments yet PyC from fossil fuel  
 509 combustion adds additional carbon in mid-1900s, which reflects similar in BPCAs (*left*) and PAHs (*right*).  
 510 Additional PAH data in blue and magenta were taken from Slater, et al. <sup>30</sup>.

511

512 In contrast to the suburban catchment, the Siskiwit Lake BPCA-based record of  
 513  $\text{PyC}_{\text{fossil fuel}}$  begins later with a more abrupt change from  $0.022 \text{ g kg}^{-1}$  (1.1% of  
 514 total PyC) in 1882 - 1915 AD to  $0.198 \text{ g kg}^{-1}$  (19.1%) for the interval 1926 - 1954  
 515 AD, which is similar to that observed for Pettaquamscutt River basin for  
 516 approximately the same period of time. Given the remote setting of Siskiwit  
 517 Lake we infer that the fossil fuel-derived quantities of PyC predominantly  
 518 derives from long-range atmospheric transport <sup>67</sup>.

519

520 In summary, the <sup>14</sup>C records constructed in this study for two complementary  
 521 groups of molecular markers of combustion (PAHs and BPCAs) provide novel  
 522 constraints on the sources and transport pathways of PyC during the pre-  
 523 industrial and industrial era. Contrasts between urbanized (Pettaquamscutt  
 524 River basin) and a remote, relatively pristine location (Siskiwit Lake) enable  
 525 further insights to be gained on PyC sources and cycling. Surprisingly, these

526 different catchments receive similar quantities and sources of “bulk” PyC  
527 (reflected by BPCAs), with “pre-aged”  $\text{PyC}_{\text{biomass}}$  representing the dominant  
528 input to the sediments. The similar proportions of  $\text{PyC}_{\text{fossil fuel}}$  estimated for both  
529 PAHs and BPCAs from isotopic mass balance suggests that (a) they are  
530 transported together (e.g., PAHs sorbed onto soot particles) via atmospheric  
531 processes<sup>70</sup>, (b) that  $\text{PyC}_{\text{fossil fuel}}$  comprises a minor component of “bulk PyC” in  
532 these sedimentary records, and (c) that the PAH component is predominantly  
533 derived from fossil fuels, confirming the decoupling between the precursors of  
534 combustion condensates and bulk PyC. These findings have implications for  
535 local vs. regional-scale assessments of combustion practices and their impact  
536 on biogeochemical cycles, as well as with respect to the sources and fate of  
537 persistent organic pollutants, and their relevance to environmental quality in  
538 watersheds. Furthermore, the erosional transport of PyC following a local fire  
539 event may be a prolonged temporal process lasting at least for decades and  
540 thus smoothing out pronounced signals in deposits at the ‘ultimate’ sites burial.  
541 This predominance of pre-aged PyC in aquatic sediments bears strongly on our  
542 understanding of the biogeochemical cycling of PyC on local to global scales.

543

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552 **Supporting information**

553 Further details on sediment dating procedures, the determination of the pre-  
554 aged pyrogenic carbon fraction and numerical values are provided in the SI.

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556

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766 Supporting information

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768 **What on Earth have we been burning? Deciphering sedimentary records**  
769 **of pyrogenic carbon**

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774 Ulrich M. Hanke<sup>1\*</sup>, Christopher M. Reddy<sup>2</sup>, Ana L.L. Braun<sup>2, †</sup>, Alysha I. Coppola<sup>1</sup>, Negar

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795 The supporting information includes the data shown in plots in the manuscript and details on the

796 calculation of the pre-aged pyrogenic carbon (PyC) fraction.

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799 Pages: 7

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## 806 **Detailed Sampling and Sediment Dating Procedures.**

807 Four out of seven freeze-cores were selected for the compound-specific radiocarbon study

808 based on their integrity and number of identifiable features on the X-radiographs. Each 0.5-cm

809 sample ( $n = 554$ ) was placed in a combusted glass-jar, freeze-dried and homogenized with a

810 mortar and pestle. Because the cores were aligned before sectioning, dried samples of

811 equivalent depth could be combined and stored for the compound-specific  $^{14}\text{C}$  analyses.

812 Sediment chronology calculations for the Pettaquamscutt River have been detailed elsewhere <sup>1-</sup>

813 <sup>2</sup>. Briefly,  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$  and  $^{137}\text{Cs}$  were measured in dry samples by direct  $\gamma$ -counting using a high

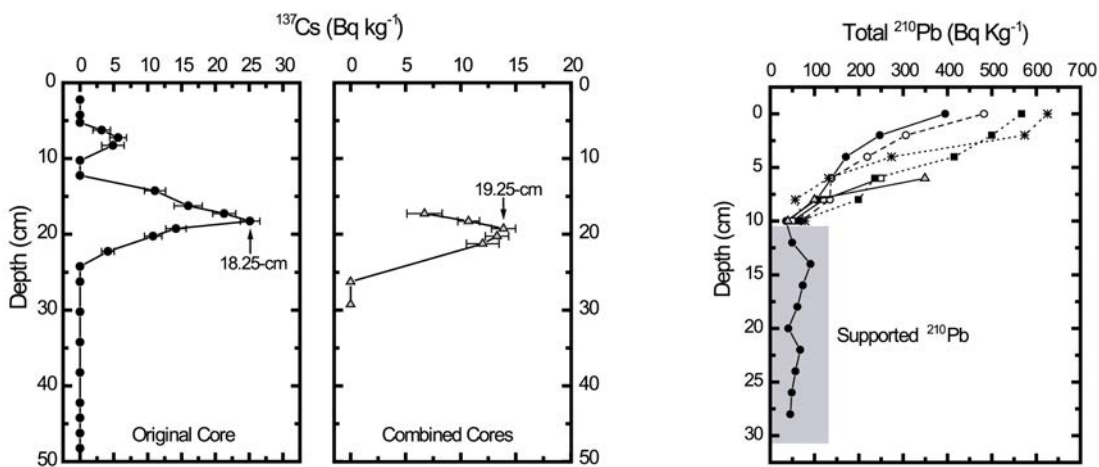
814 purity germanium detector. The constant rate of supply (CRS) <sup>3</sup> model was applied to the

815 calculated excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{Excess}} = ^{210}\text{Pb}_{\text{Total}} - ^{214}\text{Pb}$ ) and the results obtained were compared

816 to an independent varve chronology. The good age agreement between the CRS model and the  
 817 varve counts allowed the extension of the sediment chronology beyond the limit of the  $^{210}\text{Pb}$   
 818 method (100-150 years). Because the depth-age evaluation was performed for a single core,  
 819  $^{137}\text{Cs}$  measurements were conducted on samples from the composite horizons to verify if the  
 820 stratigraphic resolution had been preserved. The results obtained show a 1-cm shift in the  
 821 depth of maximum fallout of  $^{137}\text{Cs}$ , from 18.25 cm to 19.25 cm (Figure 1a), corresponding to a  
 822 2-year difference in chronology between the combined cores and the original high-resolution  
 823 record of PAHs <sup>4</sup>. This difference is within the range of resolution of  $^{210}\text{Pb}$ -ages, hence no  
 824 correction was applied to account for this small shift.

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826 Sediments collected in Siskiwit Lake were also dated by  $^{210}\text{Pb}$ . Excess  $^{210}\text{Pb}$  was measured at  
 827 2-cm intervals and showed that  $^{210}\text{Pb}$  supported levels were reached at approximately 10 cm for  
 828 all seven cores (Figure 1b). Even though an apparently intact sediment-water interface was  
 829 observed at the time of collection,  $^{210}\text{Pb}$  measurements revealed that the upper portion of the  
 830 sediment cores had been lost during sampling. A plot of the natural logarithm of the excess  
 831  $^{210}\text{Pb}$  against depth (cm) for one of the cores showed no obvious slope inflections characteristic  
 832 of a change in sedimentation rate or the surficial mixing previously reported by <sup>5</sup>. Therefore, we  
 833 used the constant initial concentration (CIC) model <sup>6</sup> to estimate that the top 8-cm of sediment  
 834 of that core had been deposited over 43 years. Neither compaction nor sediment focusing were  
 835 taken into account during these calculations. However, the calculated sedimentation rate (0.18  
 836  $\text{cm yr}^{-1}$ ) was in close agreement with values reported by McVeety <sup>5, 7</sup> (0.19  $\text{cm yr}^{-1}$ ) for that  
 837 location. We then assumed that  $^{210}\text{Pb}$  achieved supported levels within 100 years of deposition  
 838 and reasoned that because these levels were observed 10 cm from the top, the surficial layer of  
 839 the sediment column was dated at 1954. As a result, we estimated that approximately 44 years  
 840 (8-cm) of the sediment record were not retrieved by the gravity coring procedure. Because  $^{210}\text{Pb}$   
 841 supported levels were reached at approximately 10 cm for all seven cores, we presumed that a  
 842 comparable amount of sediment was lost from the upper most portion of all seven cores.



a. Pettaquamscutt River

b. Siskiwit Lake

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845 **Figure S1:** (a)  $^{137}\text{Cs}$  activity in the combined horizons differs from that of the original core by  
846 only 1-cm, or approximately 2 years; (b) Total  $^{210}\text{Pb}$  activity in seven cores collected in Siskiwit  
847 Lake. Supported levels were achieved at 10-cm for all cores.

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### 851 **Determining the pre-aged pyrogenic carbon fraction**

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853 The conventional binary source apportionment approach using radiocarbon ( $^{14}\text{C}$ )<sup>8</sup> differentiates  
854 between biomass burning and fossil fuel combustion in environmental samples. However,  
855 similar to Douglas, et al.<sup>9</sup>, we found  $^{14}\text{C}$  values of benzene polycarboxylic acids (BPCAs)  
856 derived from pyrogenic carbon (PyC) were at least about 15 % lower than the corresponding  
857 atmospheric  $^{14}\text{C}$  concentrations in the pre-industrial age. This finding cannot be explained with  
858 the combustion of fossil fuels. A detailed record on the consumption of fossil fuels in the United  
859 States (late 1600s to 2000) reveals that biomass was used for combustion<sup>10</sup> before the 1840s.  
860 Thus, the offset between the BPCA  $^{14}\text{C}$  data and the corresponding atmospheric  $^{14}\text{C}$  data<sup>11-12</sup>  
861 suggests the two pool assumption is not valid, and requires a different interpretation. Here we  
862 suggest that biomass-derived PyC is aging by temporary storage in catchment soils en-route to  
863 deposition in sediments. To account for this lag time, we used the pre-industrial samples of our  
864 archives from prior to the late 1800s.

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866 For Pettaquamscutt River sediments, the average  $F^{14}\text{C}$  value was  $0.826\pm 0.043$  in the pre-  
867 industrial era. If 100 % of biomass-derived PyC would be pre-aged before being deposited in  
868 sediments, then this pool would have a mean residence time in the catchment of 1200  $^{14}\text{C}$   
869 years. There is certain chance that a portion of PyC produced during a fire is quickly transported  
870 to its burial site in aquatic sediments. This fraction carries the average  $^{14}\text{C}$  signatures of modern  
871 biomass at the time of deposition (> 30 years)<sup>13</sup>. Here we argue that the majority of PyC is  
872 older and is supplied on centennial scale to millennial time scales (see Figure S1). However, the  
873 contribution of PyC from contemporary sources might vary over time. We introduce an  
874 uncertainty of  $\pm 10\%$  for natural variability, such as, flood events, which enhance soil erosion.  
875 We found that the scenarios 100, 90, 80 % pool size explained 98 % and more of the total  
876 biomass-derived PyC (Figure S1). Thus we rather report a conservative age of the 'pre-aged'  
877 PyC fraction ( $90\pm 10\%$ ) with  $1423\pm 231$  years for the Pettaquamscutt River catchment.

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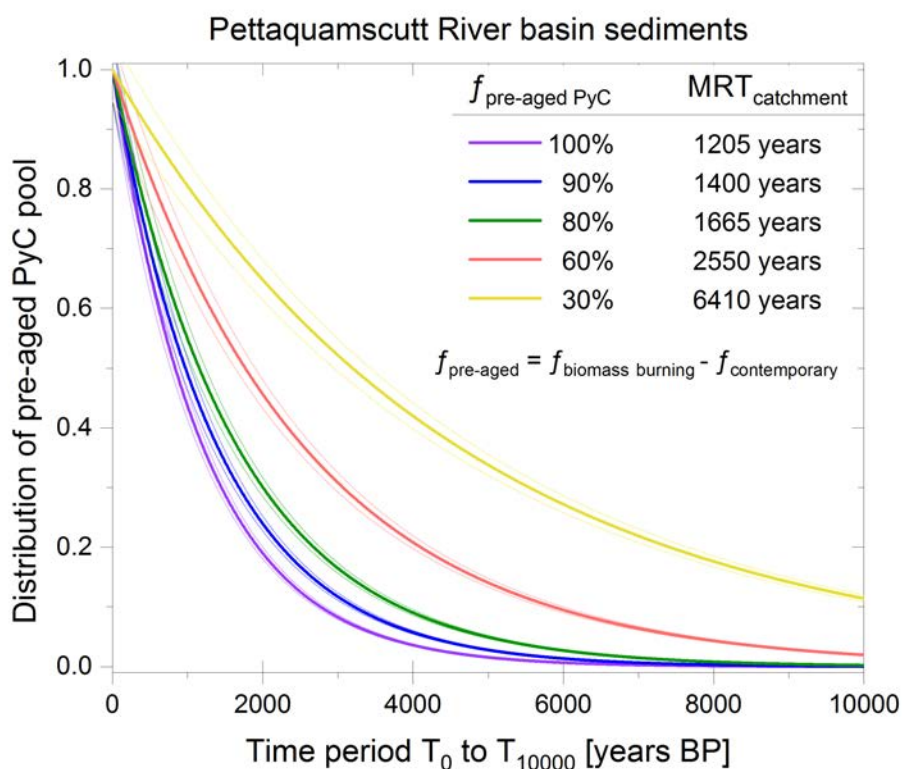
879 Surprisingly, the 'pre-aged' PyC  $^{14}\text{C}$  signature remained constant in deposits from the pre-  
880 industrial era in the Pettaquamscutt River basin and Siskiwit Lake, U.S. However, the two  
881 catchments have different ages. Thus we concluded that the 'pre-aged' fraction of PyC provides  
882 information about certain catchment characteristics that might be similar to reservoir age offsets  
883 and allow here to retrieve the fossil fuel derived- PyC fraction during the industrialization. This  
884 implies that local land-use changes may not be instantly recorded in high-temporal sedimentary  
885 sequences. The reconstruction of combustion history during industrialization using the refined

886 source apportionment concept requires a pre-industrial reference sample from the same  
 887 catchment.

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892 **Figure S2:** Visualization of the different pool sizes of 'pre-aged' PyC in the Pettaquamscutt River  
 893 sediments from the pre-industrial age. The illustrated uncertainties are empirical errors

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899 **Table S1:** Individual data from Pettaquamscutt River sediments for pre-aged, contemporary and  
 900 fossil fuel-derived PyC

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Age range	Depth interval	Benzene-[hexa+penta]-carboxylic acids derived from PyC			
		[g kg <sup>-1</sup> ]	% contemporary	% pre-aged	% fossil fuel
[years AD]	[cm]				
1983-1998	0 - 9.5	0.347	8.8	79.6	11.6
1962-1981	10 - 19	0.457	8.4	75.5	16.1
1932-1961	19.5 - 29	0.633	8.3	74.6	17.1
1898-1930	29.5 - 36	0.841	8.2	73.9	17.9

1874-1897	36.5 - 42	0.763	8.7	77.9	13.4
1843-1872	42.5 - 49	0.826	10.0	90.0	0.0
1770-1841	49.5 - 64	0.680	10.0	90.0	0.0
1738-1766	64.5 - 70	0.694	10.0	90.0	0.0

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**Table S2:** Results of BPCAs derived from PyC in Siskiwit Lake sediments and the relative contribution of contemporary, pre-aged and fossil fuel derived PyC

Age range [years AD]	Depth interval [cm]	TOC [%]	Benzene-[penta+hexa]-carboxylic acids derived from PyC				
			[g kg <sup>-1</sup> ]	F <sup>14</sup> C	% contemporary	% pre-aged	% fossil fuels
1926-1954	2-4	8.8±0.01	0.998±0.096	0.658±0.022	8.0	73.0	19.0
1882-1915	8-10	8.3±0.02	0.800±0.013	0.881±0.033	10.0	88.8	1.3
1837-1871	16-18	7.5±0.03	0.763±0.024	0.918±0.034	10.4	89.6	0.0
1793-1826	24-26	7.9±0.09	0.755±0.002	0.892±0.037	10.5	89.5	0.0

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**Table S3:** TOC and PAHs data for Siskiwit Lake sediments in three depth intervals

Age range [years AD]	Depth interval [cm]	TOC			PAHs *	
		[%]	C/N ratio	δ <sup>13</sup> C	[g kg <sup>-1</sup> ]	F <sup>14</sup> C
1932-1954	0-4	8.8±0.1	18.6	-25.4	0.0004	0.528±0.005
1887-1921	6-12	8.3±0.2	17.6	-23.7	0.0002	0.733±0.008
1798-1832	22-28	8.2±0.3	17.2	-22.4	0.0001	0.895±0.139

\* PAHs = sum of 13: Phen, Anth, Fla, Py, BaA, Chry, BbF, BbF, BbF, BaP, BeP, IP and BghiP

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