Significance of perylene for source allocation of terrigenous organic matter in aquatic sediments

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ABSTRACT

Perylene is a frequently abundant, and sometimes the only polycyclic aromatic hydrocarbon (PAH) in aquatic sediments, but its origin has been subject of a longstanding debate in geochemical research and pollutant forensics because its historical record differs markedly from typical anthropogenic PAHs. Here we investigate whether perylene serves as a source-specific molecular marker of fungal activity in forest soils. We use a well-characterized sedimentary

record (1735 to 1999) from the anoxic-bottom waters of the Pettaquamscutt River basin, RI, USA to examine mass accumulation rates and isotope records of perylene, and compare them with total organic carbon and the anthropogenic PAH fluoranthene. We support our arguments with radiocarbon (^{14}C) data of higher plant leaf-wax *n*-alkanoic acids. Isotope-mass balance-calculations of perylene and *n*-alkanoic acids indicate that ~40 % of sedimentary organic matter is of terrestrial origin. Further, both terrestrial markers are pre-aged on millennial time-scales prior to burial in sediments and insensitive to elevated ^{14}C concentrations following nuclear weapons testing in the mid-20th Century. Instead, changes coincide with enhanced erosional flux during urban sprawl. These findings suggest that perylene is definitely a product of soil-derived fungi, and a powerful chemical tracer to study spatial and temporal connectivity between terrestrial and aquatic environments.

INTRODUCTION

Perylene is found in marine [1–5] and lacustrine sediments [6–8], in soils [9,10], and also in petroleum [11,12] and fuel emissions [13,14] often associated with other distinctive anthropogenic combustion-derived polycyclic aromatic hydrocarbons (PAHs). However, most studies report that sediment records of perylene differ greatly from those of anthropogenic PAHs [15–19]. The latter are typically most abundant in sediments post-dating the Industrial Revolution, particularly those deposited during the latter half of the 20th Century, whereas perylene abundances are lowest near the sediment-water interface and tend to increase with depth, particularly in anoxic sedimentary settings [18,20]. This depth-related increase in concentration implies abiotic or biologically mediated *in situ* production from precursor natural product(s) [2,21] by either a first- or second-order reaction under anaerobic conditions [20].

The origin of perylene has remained unclear for decades, during which has previously been argued for terrestrial [1,2,22,23] and diagenetic [6,16,24], as well as petrogenic [12,25] and pyrogenic [13,14] sources. It was only recently that Itoh and collaborators [23] determined that the fungal species *Cenococcum geophillum* produces 4,9-dihydroxyperylene-3,10-quinone, confirming a longstanding hypothesis [1,22] that there is a naturally produced precursor. This ectomycorrhizal fungus appears almost ubiquitous in boreal, temperate and subtropical regions, and present in the rhizosphere of woody-plant roots and more generally in forest soils [26]. A fungal origin can explain the widespread abundance of perylene in the environment even over geological time-scales [27], since mycorrhizal associations with vascular plants evolved about 400 million years ago [28].

Besides *C. geophyllum*, other mycorrhiza also produce similar perylene precursor compounds [29,30] as toxins involved in pathogenesis of their host plant [31]. Prior stable carbon isotopic ($\delta^{13}C$) measurements of perylene found values similar to those terrestrial sources (C_3-vegetation: $\delta^{13}C \approx -27$ ‰), supporting a wood-degrading origin from the rhizosphere [32]. This is further supported by dual-isotope analyses of perylene ($\delta^{13}C$ and δD) in sediments showing similar δD values as methoxy groups in lignin while $\delta^{13}C$ values are consistent with the expected fractionation range in saprophytic fungi[22]. In addition, natural abundance radiocarbon (^{14}C) analyses allows a comparison of the ^{14}C age of perylene with that of other organic matter constituents [25], including total organic carbon (TOC) and specific markers of terrigenous organic matter co-deposited in aquatic sediments. Such analyses shed light on the origin and provide further evidence on the origin of perylene and its use in environmental forensics.

Our motivation is to reconcile existing hypotheses on the source of perylene and assess the potential of this marker compound as a biogeochemical tracer to follow the trajectories of terrigenous organic matter mobilization and transport within watersheds. Specifically, we investigate whether it serves as a molecular marker for rhizosphere carbon from catchment soils and thus facilitates source approximation of terrigenous organic matter in sediments. Moreover, while researchers currently tend to exclude perylene from forensic investigations involving the apportionment of PAHs due to its incongruent behaviour, perylene may have mutagenic effects on organisms [33,34]. Thus, an improved understanding of the provenance and dynamics of perylene may be pertinent to mapping inventories of natural and anthropogenic pollutants, delineating transport pathways, and reconstructing historical land-use.

In this study, we construct historical records of perylene and TOC abundances and isotope compositions from the anoxic sediments of the suburban Pettaquamscutt River basin, RI, USA. We chose these sediments because they provide an exceptionally detailed chronological record and a wealth of background information on the catchment area, including human influence on local to regional scales [15,35–38]. In addition, this sedimentary record extends over 260 years, from the pre-industrial (~1735) until 1999, including an interval characterized by frequent above-ground nuclear-bomb testing (resulting in elevated atmospheric ^{14}C concentrations peaking in 1963 when the testing ceased), thus offering the opportunity to study the rate at which specific organic carbon species incorporate atmospheric CO_2 and are sequestered in aquatic sediments. These characteristics of the study site, when coupled with down-core $\delta^{13}C$ and ^{14}C records, provide a novel perspective on perylene biogeochemistry, yielding constraints on its source and on the burial efficiency of terrigenous organic matter in aquatic sediments. We compare mass accumulation rates (MAR) of perylene and TOC to the combustion-derived

PAH marker fluoranthene. While several non-alkylated PAHs could be used to trace past-combustion practices, we choose fluoranthene because its quantitative down-core profile resembles the temporal evolution of the sum of 15 parent PAHs in this watershed[15]. We further support our interpretation with down-core data of particle size and leaf wax (C_{30-32}; *n*-alkanoic acids) ^{14}C variations. We then carefully assess whether the rhizosphere of wooded land serves as the direct source for perylene in the environment and discuss the process of pre-ageing of terrestrial organic matter prior to delivery into the aquatic environment in the context of parallel sedimentary records.

EXPERIMENTAL SECTION

A series of seven freeze cores were collected in the depocenter of the lower basin of the Pettaquamscutt River basin, RI, USA (41.503100; -71.450500) in 1999. The catchment area covers 35 km^2 of forest, wetlands and open water of which today about 30 % is residential land [37]. Ocean water flooded the basin about 1700 ± 300 years ago leading to a stratified water column and sustained anoxic conditions in bottom waters and underlying sediments [36]. A detailed description on the sediment chronology and sample processing is presented elsewhere [15,39]. Sediment chronology was obtained from varve counting of x-ray radiographs as well as from ^{137}Cs and ^{210}Pb profiles using the model of constant rate of supply that yielded a sequence of about 260 years (1735-1999 AD) and an average sedimentation rate of 0.44 ± 0.10 cm yr^{-1} [39].

Sections from the cores were combined after aligning x-radiograph images including hurricane layers in 1938 and 1954 to a reference chronology of varve counting, ^{210}Pb, and ^{137}Cs. This was necessary to obtain enough sediment for trace molecular isotopic-analyses [35]. Hence, we pooled

126 the samples in eight horizons for all isotopic analyses: H1 (1999−1982), H2 (1981−1962), H3
127 (1960− 1931), H4 (1929−1898), and H5 (1896−1873), H6 (1871−1842), H7 (1840−1768), and
128 H8 (1764−1735) respectively, except *n*-alkanoic acids that were analyzed in four individual
129 samples: 1885±5, 1947±33, 1972±2, and 1991±1. Quantitative measurements for the
130 calculation of the mass accumulation rates as well as grain size analyses were performed on
131 individual samples as well.
132
133 **Grain size analyses**
134 One freeze-core slab was sub-sectioned using a scalpel blade, transferred into 50-mL round
135 bottom flasks and treated with a 30% hydrogen peroxide solution at a ratio of 40 ml per 1 g
136 sediment, and heated in a water bath to 70 °C as a means to support mineralization of the
137 organic matter. Subsequently, samples were freeze dried, and a subsample of about 11 mg was
138 suspended in water and measured on a Beckmann Coulter LS13 320 Laser Diffraction Particle
139 Analyser (Indianapolis, USA) in triplicate.
140
141 **Total Organic Carbon and Nitrogen**
142 A Fisons 1108 elemental analyzer was used to measure the TOC content of the samples. To
143 remove the inorganic carbon fraction, about 2 mg of dry sample was weighed into a silver
144 capsule and acidified with 20 µL of 2N HCl. TOC content was calculated in relation to the
145 whole sediment dry weight while organic carbon/organic nitrogen TOC/TN ratios were
146 calculated on an atomic basis. Samples were run in triplicate and all reported weight
147 percentages represent the mean ± one standard deviation with an instrumental blank of 0.004
148 mg for C and smaller than 0.005 mg for N.
149

Isotope ratio monitoring mass spectrometry

The stable carbon isotopic composition of bulk sample TOC was determined in triplicate by automated on-line solid combustion interfaced to a Finnigan Delta Plus isotope ratio mass spectrometer. Isotope ratios were calculated relative to CO_2 reference gas pulses, with standard deviations for replicate measurements were always better than 0.6 ‰ and usually within 0.3 ‰.

Extraction, purification and isotope analyses of perylene, fluoranthene and *n*-alkanoic acids

Dry sediment samples (0.5-1.5 g) were extracted by pressurized fluid extraction (Dionex ASE 200) using a mixture of acetone and *n*-hexane (1:1) at 1000 psi at 100 ºC. Molecular identification and quantification was achieved using an Agilent 6890 Plus GC System interfaced to a mass selective detector operating at 70 eV in SIM mode using a DB-XLB capillary column (60 m × 0.25 mm × 0.25 μm) [15].

Compound-specific radiocarbon analyses (CSRA) of perylene and fluoranthene were performed on eight pooled horizons by first using high-pressure liquid-chromatography (HPLC) to separate pure perylene (98% purity or greater) from the sample extracts. The HPLC procedure isolated PAHs into 2-ring and the combined 3+4-ring and 5+6-ring PAHs. The resulting 16 HPLC fractions (8 horizons x 2 ring classes) were subjected to two-dimensional preparative capillary gas chromatography for isolation and purification of individual PAHs via HP 7683 auto-injector and a multi-column switching system (Gerstel MCS 2) connected to a HP 6890 series gas chromatograph, and Gerstel preparative fraction collector (PFC; further details in SI). Purified samples were transferred to pre-combusted quartz tubes (7 mm I.D. x 20 cm), dried under nitrogen before adding copper oxide (50 mg). Each tube was then evacuated on a vacuum

line while samples were kept at -90ºC to prevent sublimation, sealed, and combusted at 850ºC for five hours. About 95% of the purified carbon dioxide was reduced to graphite, pressed and analyzed for ^{14}C at NOSAMS, Woods Hole, U.S. and the remaining 5% was used for $\delta^{13}C$ measurements.

The $\delta^{13}C$ values of perylene were determined in triplicate on a Finnigan Delta Plus isotope ratio mass spectrometer with attached Finnigan GC combustion III interface and Hewlett-Packard 6890 GC (irm-GC/MS). Compounds were separated on a CP-Sil 5CB capillary column (50 m × 0.25 mm × 0.25 µm) and isotope ratios for PAH peaks were calculated relative to CO_2 reference gas pulses. The standard deviation for replicate measurements of perylene was better than 0.6 ‰ and mostly around 0.2 ‰.

The isotopic composition of leaf wax *n*-alkanoic acids ($C_{30\text{-}32}$) were determined for four individual sediment samples deposited in 1885±5, 1947±33, 1972±2, and 1991±1 following the analytical procedure described elsewhere [40]. In brief, *n*-alkanoic acids were extracted, isolated, and purified using a preparative Hewlett Packard 5890 series II capillary gas chromatograph [41]. Following the chromatographic purification of individual compounds, samples were graphitized and measured at NOSAMS, Woods Hole, U.S.

Evaluation of isotope data

Isotope mass-balance calculations provide quantitative estimates for source apportionment of organic matter. To constrain the sources of TOC and perylene in Pettaquamscutt River sediments, we calculated the relative contribution of possible organic carbon sources in the sediments using the measured ^{14}C and $\delta^{13}C$ values for TOC (Figure 2). We report the ^{14}C data

as $F^{14}C$ which is the fraction modern independent from the year of measurement [42]. We assumed a simple mixing model to retrieve an average value for the lag-time of perylene and leaf wax *n*-alkanoic acids; the details of which are published elsewhere [35]. In brief, these source-specific molecular markers facilitate approximations of the contributions of terrigenous organic matter in aquatic sediments (further details on the concept are included in SI).

To account for the potential variability under increasing human pressure on the coastal environment, we determined average values of our terrestrial end-members for two time periods: the pre-industrial (1735 to 1840) and the post-'bomb' (1960 to 1999) period (see SI for more detail). Regarding ^{14}C data evaluation, the post-1960s period also is a benchmark to test for the resilience and short-term dynamics of catchment processes. In contrast, the aquatic end-member is only affected by the marine reservoir effect, which is about 400 ± 40 ^{14}C years lower than the atmospheric ^{14}C concentration at the time of burial [43]. Furthermore, we neglect a potential impact of petrogenic carbon [44] in the Pettaquamscutt River because of the absence of post-glacial erosion and due to the absence of carbonaceous metasedimentary rocks in the basin [45]. We constrain our model by $\delta^{13}C$ = -21.0 ‰ for aquatic production [46] and use local records of perylene, pyrogenic carbon [35] and *n*-alkanoic acids ($C_{30\text{-}32}$) to define terrestrial end-members. We further obtained the contemporary atmospheric ^{14}C concentrations from the extended Intcal13 reference chronology [43,47].

RESULTS AND DISCUSSION

The exceptionally well-constrained chronology of the Pettaquamscutt River sediments along with detailed reconstructions of the provenance of combustion-derived PAHs [15,35] and Hg [38] provide key constraints that allow us to determine whether perylene signatures are consistent with its production in the rhizosphere of catchment soils [23,26]. To characterize the export of

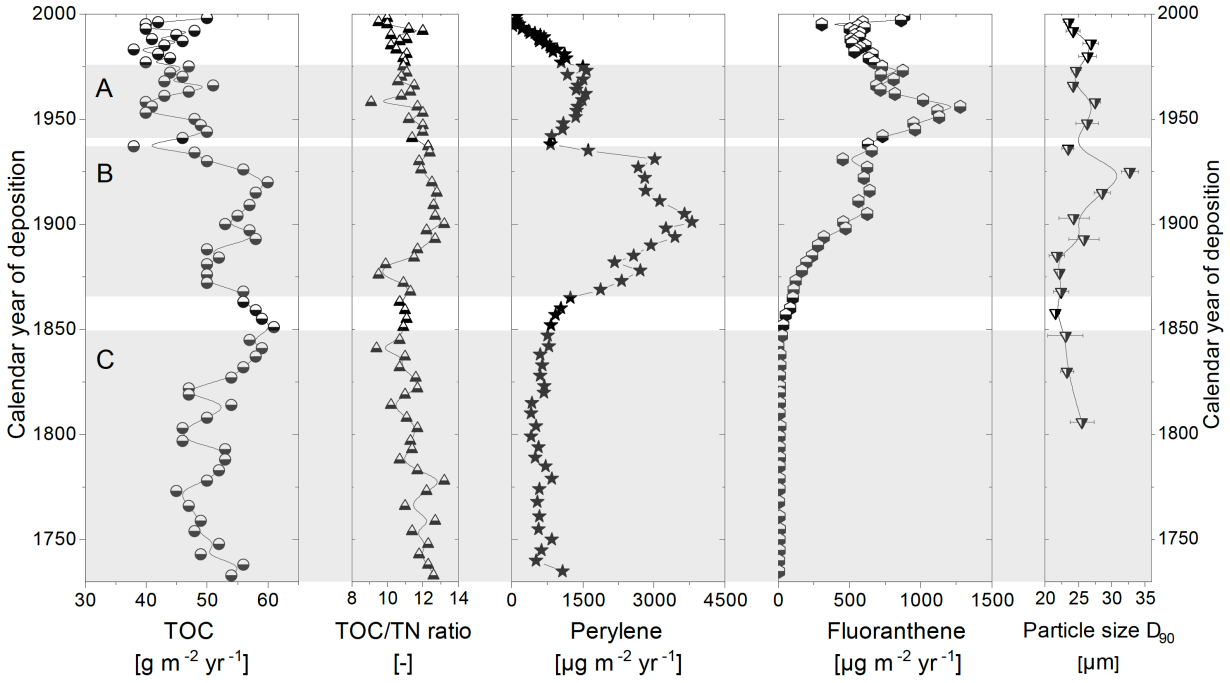
terrigenous organic matter, including the putative precursors of perylene, and its subsequent burial in aquatic sediments, we report MAR for TOC, perylene, and fluoranthene. Isotopic mass balance calculations for $\delta^{13}C$ and ^{14}C records are employed to further constrain the main source of perylene precursors. With reference to recent research and our results, we then provide a synthesis aiming to merge the existing concepts, reconciling the origin of perylene (i.e., terrestrial, diagenetic or petro-/pyrogenic).

Down-core mass accumulation rates of TOC and perylene

The burial rate of TOC in the sediments of the Pettaquamscutt River ranges from 38 to 61 g m^{-2} yr^{-1} (average = 49 ± 6 g m^{-2} yr^{-1}, *n* = 71). The lowest TOC burial flux is observed in ca. 1938 (Figure 1) and is related to a 16.7 % shift in burial flux from 53.0 ± 43 g m^{-2} yr^{-1} prior to ca. 1927 to 44.0 ± 3.7 g m^{-2} yr^{-1} for sediments deposited thereafter. The timing of this change coincides with the construction of the Lacey Bridge on the ocean side of the lower basin in 1934 [45] (Figure 1B) that likely caused a restriction in seawater intrusion, affecting the influx of both marine as well as the terrestrial matter. We argue that this exemplifies the accelerated development of the catchment area beginning early in the last century and the related infrastructure projects that changed the natural flow paths of materials within the watershed.

The N_{org} down-core record reveals only small variations, here illustrated as C_{org}/N_{org} profiles (n = 71; Figure 1) where three trends are delineated: decreasing C/N from 1730s (12.6) to 1840s (9.4), a ~50-year reversal towards higher C/N ratios (13.2 in 1900), and a century-long C/N secular decrease in the upper core (10.0 in 1999). This rather narrow range in C/N ratios suggests that organic matter is predominantly yet not exclusively composed of labile material with C/N values similar to aquatic organic matter (C/N = 4 to 10) [48]. However, we refrain from

246 further speculations on this bulk-level information due to the absence of a robust reference for
247 C/N values of terrigenous organic matter from this area.
248



249
250 Figure 1: Mass accumulation rates for total organic carbon (TOC), perylene, and fluoranthene as well as carbon to nitrogen
251 (TOC/TN) ratios and down-core shifts in coarse particle abundance (D_{90}) with shaded area **A** representing the maximum PAH
252 flux in this area, **B** the period of amplified erosion due to infrastructure development, and **C** the pre-industrial era prior to
253 1840s.
254
255 MARs for perylene/proto-perylene, which corresponds to the reduced perylene quinone, vary
256 from 29 to 3800 µg m^{-2} yr^{-1}, while its down-core profile differs markedly from the combustion-
257 marker fluoranthene (Figure 1). The values were low before 1938, reached a maximum between
258 ca. 1938 and 1973 (1580 µg m^{-2} yr^{-1}), before diminishing again in most recent decades (~ 100
259 µg m^{-2} yr^{-1}) (Figure 1). This contrasting accumulation behaviour implies a different origin for
260 perylene relative to combustion-derived PAHs, here illustrated by fluoranthene (Figure 1). This
261 non-alkylated PAH appears lower in abundance varying from 1 to 1280 µg m^{-2} yr^{-1} and also

exhibits significant variability [35], however the temporal evolution of MARs of this pyrogenic PAH differs sharply with that of perylene. Specifically, fluoranthene's MAR was low until the mid-19th century (Figure 1C), increased steadily to a maximum in the late-1950s, then declined in the post-1970s due to cleaner burning fuels and as consequence of environmental regulations [15,37]. Such down-core profiles of combustion-derived PAHs are also observed in other sedimentary records, including the upper basin of the Pettaquamscutt River [16,19,49].

The observed decline in perylene/proto-perylene MAR between 1927-1938 coincides with the abrupt decrease in TOC accumulation rate (Figure 1B). We attribute the latter to a dilution in organic carbon content resulting from a higher proportion of clastic material due to erosion of soil mineral horizons (Figure 1). Perylene is a trace constituent of TOC, never accounting for more than 0.1 % of TOC, and consequently perylene/TOC ratios shift by 500 % relative to before or after this time interval. These observations thus support the link between a decrease in perylene's MAR resulting from an increase in erosional flux (Figure 1B).

A striking feature of the perylene profile is that fluxes remain nearly constant (665 ± 180 μg m^{-2} yr^{-1}; n = 26) prior to 1865, indicating either steady-state erosional conditions or quantitative conversion of precursor material (Figure 1) [23]. Due to the large variations in perylene burial rates in our sedimentary record we refrain from attempting to derive kinetic parameters for conversion of perylenequinone (proto-perylene) precursor to perylene. However, Slater and collaborators [50] compared two perylene profiles from Lake Siskiwit collected in 1983 and 2005. They found a reaction rate constant (0.048 yr^{-1}), ca. 75 % higher than previously reported [20] while another study reported much lower rates [18]. All of the above studies suggest that the conversion of perylenequinone to perylene follows first-order kinetics. Nevertheless, the strong

(~ 97%) decrease in perylene abundance in Pettaquamscutt River sediments from 1973 to 1999 likely reflects incomplete conversion of precursor compounds (Figure 1).

Isotope mass balance calculations

The $\delta^{13}C$ TOC profile (Figure 2) appears relatively invariant throughout the core (-25.4 to –23.0 ‰, average -24.1 ± 0.5 ‰, n = 36), indicating the absence of large variations in organic matter composition. Although the TOC MAR decreased in the 1930s, $\delta^{13}C$ values do not suggest this was accompanied by a shift in the nature of organic matter supplied to Pettaquamscutt River basin. Instead, the observed changes in burial flux in this catchment are attributed to a shift in land use stemming from an increase in the local human population and the accompanied development of infrastructure. The $\delta^{13}C$ values of perylene (-28.9 to -28.3 ‰; average -28.6 ± 0.6 ‰; Figure 2) were similarly invariant, while significantly lower than TOC and similar to that reported for terrestrial C_3 plants (-29 to -25, average -28 ‰) [51].

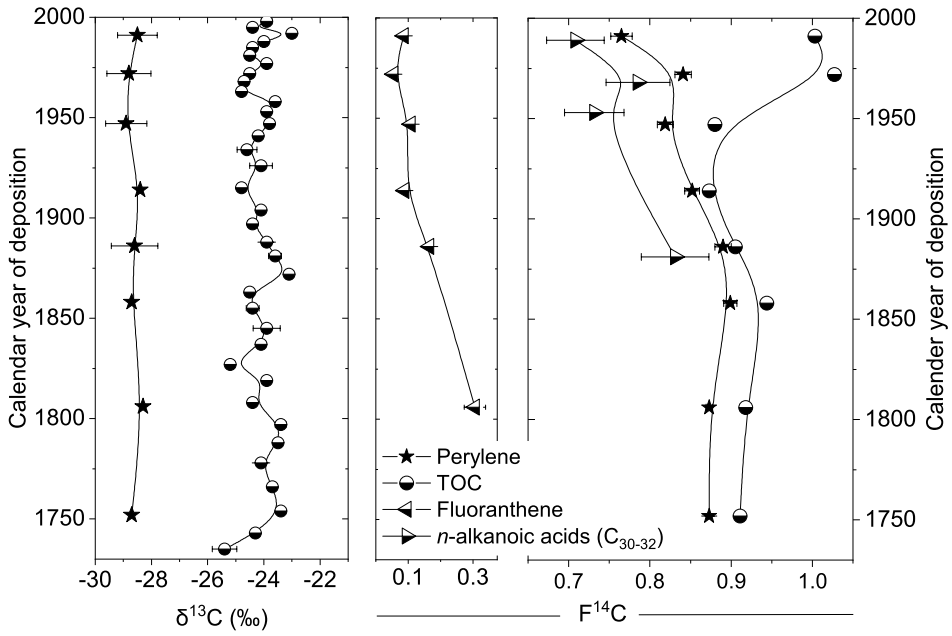


Figure 2: High-resolution $\delta^{13}C$ record for TOC and pooled sample results for perylene (left); molecular ^{14}C data for the combustion-derived fluoranthene (middle) and results on perylene, leaf wax n-alkanoic acids as well as TOC (right).

In contrast, the ^{14}C record of TOC for pooled samples (n = 8; Figure 2) reveals only small variations in pre-industrial time (1735 to 1840) but then tends to shift towards more ^{14}C depleted values between 1839 and 1958. This change is thought to integrate the increasing use of fossil fuels slightly diluting the natural atmospheric ^{14}C concentration (the so-called 'Suess effect') as well as on-going infrastructural development and constructions within the catchment resulting in the mobilization of deeper mineral soils. Thereafter, we observed a drastic (~15 %) increase in $F^{14}C$ TOC values reflecting the shift in atmospheric ^{14}C derived from thermonuclear weapons testing in the post-1960s. The uppermost sediment layer signals declining ^{14}C concentrations similar to the atmosphere [47].

Compound-specific radiocarbon analysis reveals that the ^{14}C profile of perylene follows that of TOC from the pre-industrial period until ~1950. Thereafter, ^{14}C of TOC increases due to the incorporation of atmospheric bomb ^{14}C, while perylene trends to more ^{14}C-depleted values. This could reflect a pyrogenic (fossil fuel) contribution to perylene, mitigating the impact of 'bomb' carbon in the Pettaquamscutt River sediments. However, CSRA of leaf wax *n*-alkanoic acids ($C_{30\text{-}32}$) from the same sediments reveals a concomitant ^{14}C trend with perylene (Figure 2). We infer, therefore, that leaf waxes and perylene share a common source and mode of export, implying that local erosional fluxes and mobilization of soil organic matter are responsible for the decoupled TOC and perylene post-1950s signals rather than global-scale perturbations such as 'Suess effect' or above-ground nuclear weapons testing.

In the mainly wooded catchment area of Pettaquamscutt River, organic molecules are produced during photosynthetic activity, translocated and metabolized in plants, as well as released into the rhizosphere. In the soil, plant and animal residues can be assimilated, stabilized and

metabolized until they eventually become respired to carbon dioxide [52], or they can be eroded and redistributed within the watershed [53]. Source-specific molecular markers allow delineation of specific processes associated with organic matter cycling, while molecular ^{14}C data provide additional information on the timescales of organic matter storage and transport from its source to the 'ultimate' site of burial. This "residence time" has been determined for several markers of terrestrial primary productivity [54–56], as well as charred plant biomass [35,57], and range from centuries to several millennia. The underlying processes resulting in organic matter 'pre-aging' prior to burial in aquatic depocenters can complicate source apportionment because the ^{14}C concentration of various organic matter components differs from that of the corresponding atmospheric ^{14}C reference value.

We determined an average ^{14}C residence time for perylene of 1300 ± 300 ^{14}C years for samples pre-dating the industrialization (1735-1840, n = 3) and 2000 ± 500 ^{14}C years for the post-'bomb' era (1960-1999; n = 3). These values agree well with leaf wax *n*-alkanoic acids (C_{30-32}) that showed a 2700 ± 700 ^{14}C year residence time for the post-'bomb' era (Figure 2), and a record of biomass-derived pyrogenic carbon from the same core revealed an average age of 1460 ± 490 ^{14}C years for the pre-industrial era [35]. The apparent average age or residence time over the pre-industrial and the post-'bomb' era for perylene and higher plant *n*-alkanoic acids of ca. 2000 ^{14}C years is slightly higher than has been reported for (micro) charcoal in the same catchment [35] as well as for leaf wax *n*-alkanoic acids in the Bengal fan [55] yet similar to that of Cariaco basin [56]. However in the post-'bomb' era we observed a decoupling of ^{14}C concentrations among molecular markers and TOC. Specifically, the increase in atmospheric ^{14}C concentrations post-1960s is not apparent in perylene or *n*-alkanoic acids, suggesting that soil carbon storage on millennial timescales may conceal or delay the legacy.

Isotope mass balance calculations based on TOC ^{13}C and ^{14}C data yield similar values for the proportion of organic matter of terrestrial origin ($\delta^{13}C$: -43 ± 10 % and ^{14}C: -37 ± 10 %), with the remaining carbon derived from aquatic productivity. These results for the Pettaquamscutt River basin are slightly higher than an estimated global average of one-third of sedimentary organic of terrestrial origin [58]. The similar estimates obtained from dual-carbon isotope evaluations based on perylene reinforce its value in constraining the terrestrial end-member in source apportionment.

New constraints on the source of perylene

The origin and widespread distribution of perylene in the environment has been a subject of scientific debate for decades, although its conversion from the precursor molecule, 4,9-dihydroxyperylene-3,10-quinone, has long been suspected [1,2,23,29]. In particular, it has remained unclear whether perylene is formed during *in-situ* diagenesis [6,16] or is of petro-/pyrogenic origin [11,14,25,59]. The former hypothesis was stimulated by the presence of perylene in Antarctic marine sediments [60] and by large similarities between perylene and total organic matter down-core profiles, fueling the notion of *in-situ* synthesis from TOC [16]. Along these lines, Gschwend and collaborators [20] calculated kinetic parameters necessary to yield perylene from biogenic precursor concentrations that are consistent with results from a recent study comparing down-core profiles 20 years apart in Lake Siskiwit [50], and both are in line with the observed reduction of perylenequinones [23]. The second alternative hypothesis is based on the abundance of perylene in ancient sediments [22,61], fossil fuels [11,12] or combustion emissions [13,14,59]. Regarding the latter sources, perylene concentrations remain below 1.4% of the total PAH and thus are negligible for the overall budget. Its presence in these matrices, however, raises the question of

373 whether perylene is exclusively of fungal origin. A possible explanation for the occurrence of
374 perylene in fossil fuels lies in the evolutionary development of fungi. The symbiotic interaction
375 between fungi and vascular plants evolved about 400 Ma ago, and ectomycorrhiza have existed
376 for at least 56 Ma [62], while the divergence and evolution of the mycorrhiza gene pool remains
377 largely unexplored [28]. However, Blumer proposed the conversion of pigments to hydrocarbons
378 through a geochemically irreversible deoxygenation of functional groups and hydrogenation
379 under sustained reducing conditions [63]. Even though this was exemplified for fossil crinoids in a
380 pigment-rich Triassic oil shale, these reactions likely also apply to the precursors of biogenic
381 PAH. We deduce, therefore, that fungal-derived perylenequinone is deoxygenated during
382 sediment diagenesis and, at least partly, survives coalification. This could explain the
383 occurrence of perylene in fossil deposits [32] and could explain its abundance in combustion
384 residues. One evolutionary rationale for the occurrence of perylene in scletoria, the resting
385 structures of *C. geophyllum* [64], is the extreme mutagenic activity of the unsaturated nucleus of
386 perylenequinones on gram-negative bacteria [33] , protecting the reproductive function of fungal
387 spores. Overall, the preponderance of evidence [17,22,32], reinforced by our new data, indicates that
388 perylene is a remnant of wood degradation or fungal activity in the rhizosphere – a hotspot of
389 biological activity on land, and source of organic matter to aquatic systems.
390
391 **Parallels between perylene and TOC**
392 Sedimentary organic matter is a highly complex mixture composed of aquatic and terrigenous
393 organic carbon, and this complexity complicates source apportionment calculations, as well as
394 determination of carbon fluxes and thus the carbon burial efficiencies [65,66]. Measurement of the
395 abundance and isotopic composition of source-specific molecular markers can provide
396 constraints on terrigenous organic matter in sediments [65]. In addition to source constraints from

397 $\delta^{13}C$ and ^{14}C signatures, the latter also yields information on whether organic matter is of
398 modern or fossil origin[44], as well as on timescales of terrigenous organic matter between
399 formation on land and burial in aquatic depocenters (i.e., "average residence times") [35]. The
400 process of 'pre-aging' implies a lag between biosynthesis and export of organic matter from
401 land to depocenter, with natural as well as anthropogenic molecules being retained in catchment
402 soils from annual to millennial time-scales [35,55,56]. Here, we find that this pre-aging process
403 occurs on similar time-scales for leaf wax fatty acids (*n*-alkanoic acids), biomass-derived
404 pyrogenic carbon and the rhizosphere tracer perylene – all together terrestrial markers with
405 different modes of formation, chemical structures and functionalities. This agreement between
406 these different source-specific markers suggests that retention within soils regulates the export
407 of most terrigenous organic matter and associated carbon-based pollutants that enter the soil
408 column.
409
410 TOC and perylene MARs co-vary in the pre-industrial era until about 1850 despite some
411 variability in the TOC flux (Figure 1). We attribute the latter to the increasing pressure by
412 extensive farming, as well as potential changes in aquatic productivity. The dual carbon isotope
413 records for TOC and perylene (Figure 2) support the absence of drastic compositional shifts
414 throughout the record, despite the influence of the 'Suess effect' and nuclear weapons testing
415 on the latter part of the TOC ^{14}C record. Notably, perylene shows large variation in MAR after
416 1850, which we suspect is due to the conversion of the catchment from a rural into a sub-urban
417 landscape that was accompanied by an enhanced erosional flux of carbon from bare soils.
418
419 Similarities between TOC and perylene records have been observed previously [6,16,22,61], yet in
420 these cases it was suspected to reflect direct *in-situ* microbial production of perylene [16] rather

than the reduction and conversion of a precursor into perylene. This depletion of the precursor pool may continue over geological time scales [63], thus limiting comprehensive quantitative assessment of perylene in recent sediments [50]. In contrast, the isotopic composition of perylene is expected to be insensitive to conversion efficiency, and thus can serve as a robust tracer of soil-derived terrestrial organic matter.

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Supporting Information. Provides details on the preparative chromatographic isolation of PAHs for compound-specific isotope analysis, the concept of two modes of terrigenous organic matter export from land to oceans, the impact of the nuclear weapon testing on the atmospheric and marine ^{14}C partitioning over time and results for grain size analyses, respectively.

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