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Key Points:
- $\Delta^{14}C_{POC}$ is well correlated with %POC consistent with a two-source mixing model
- Global flux-weighted %POC suggests a median $\Delta^{14}C_{POC}$ age of ~1800 years B.P.
- DOC is generally younger than POC and largely dominated by modern C

Supporting Information:
- Data Set S1
- Figure S1 and Tables S1 and S2

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The age of river-transported carbon: A global perspective

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Abstract The role played by river networks in regional and global carbon (C) budgets is receiving increasing attention. Despite the potential of radiocarbon measurements ($\Delta^{14}C$) to elucidate sources and cycling of different riverine C pools, there remain large regions for which no data are available and no comprehensive attempts to synthesize the available information and examine global patterns in the ^{14}C content of different riverine C pools. Here we present new ^{14}C data on particulate and dissolved organic C (POC and DOC) from six river basins in tropical and subtropical Africa and compiled >1400 literature $\Delta^{14}C$ data and ancillary parameters from rivers globally. Our analysis reveals a consistent pattern whereby POC is progressively older in systems carrying higher sediment loads, coinciding with a lower organic carbon content. At the global scale, this pattern leads to a proposed global median $\Delta^{14}C$ signature of −203‰, corresponding to an age of ~1800 years B.P. For DOC exported to the coastal zone, we predict a modern (decadal) age ($\Delta^{14}C = +22$ to +46‰), and paired data sets confirm that riverine DOC is generally more recent in origin than POC—in contrast to the situation in ocean environments. Weathering regimes complicate the interpretation of ^{14}C ages of dissolved inorganic carbon, but the available data favor the hypothesis that in most cases, more recent organic C is preferentially mineralized.

1. Introduction

While the analysis of the natural abundance of radiocarbon (^{14}C) is mainly conducted in the context of dating of archaeological remains or reconstructing paleo-environments, the use of ^{14}C for investigating contemporary aquatic C biogeochemistry date back to the midtwentieth century [e.g., *Rafter*, 1955; *Arnold and Anderson*, 1957; *Fonselius and Östlund*, 1959; *Broecker et al*., 1985], and given the increasing accessibility of accelerator mass spectrometry (AMS) facilities and the decreasing sample size requirements for accurate analysis, there has been a burgeoning database of ^{14}C measurements for different C pools in aquatic ecosystems (i.e., particulate organic carbon (POC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC)) since these early investigations. When used in combination with carbon stable isotope ratios ($\delta^{13}C$ [e.g., *Craig*, 1954]) and/or other proxies, $\Delta^{14}C$ ratios ($\Delta^{14}C_{POC}$, $\Delta^{14}C_{DOC}$, and $\Delta^{14}C_{DIC}$) offer a particularly powerful tracer of the origin of C pools and their cycling within aquatic ecosystems. Rivers are now well acknowledged in playing an important role in regional and global carbon budgets, as a significant fraction of the terrestrial subsidies they receive are processed along their transit to the coastal zone, temporarily (re-) deposited and stored in floodplains or reservoirs or degraded by microbial communities. Thus, only a small fraction of the carbon entering river networks ultimately reaches the ocean, although quantitative constraints on this fraction is still under debate [*Cole et al*., 2007; *Aufdenkampe et al*., 2011; *Raymond et al*., 2013].

The power of characterizing the ^{14}C content of aquatic C reservoirs lies in the fact that it provides additional resolution where $\delta^{13}C$ signatures of different sources may overlap (e.g., recent vegetation versus soil-derived organic matter (OM), top soils versus deeper soil layers) (Figure 1). Moreover, it has been demonstrated that the degradability of OM can be a function of its age [*Raymond and Bauer*, 2001a], whereby recent material is typically found to be more readily degradable and may provide the main substrate for overall aquatic metabolism [*Mayorga et al*., 2005; *Rosenheim et al*., 2013]. To the contrary, recent evidence from northern temperate and high-latitude regions suggest significant, and selective, degradation of very old (1000 to >21000 yr B.P.) biolabile terrestrial OC [*McCallister and del Giorgio*, 2012; *Vonk et al*., 2013], with similar observations also reported from the tropics of northern Australia [*Fellman et al*., 2014] and thus highlighting the biological link between ancient sources of C and contemporary aquatic C biogeochemistry.

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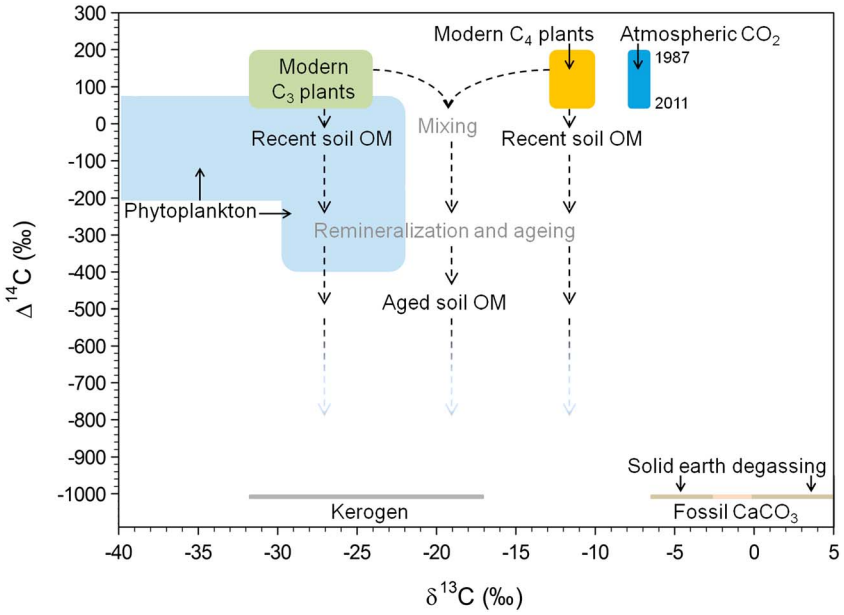

Figure 1. Major sources of carbon to global riverine C pools defined by natural abundance stable ($\delta^{13}C$) and radio C ($\Delta^{14}C$) isotopes. The $\delta^{13}C$ of plants fixing atmospheric carbon ($\delta^{13}C \sim -8$ to -6.5‰) is determined by the photosynthetic pathway followed. For example, fractionation during atmospheric C fixation by the globally dominant C_3 pathway results in biomass $\delta^{13}C$ between -32‰ and -24‰ [*Kohn*, 2010], whereas decreased fractionation through the C_4 pathway leads to biomass $\delta^{13}C$ values between -13‰ and -10‰ [*Cerling et al.*, 1997] (the CAM pathway has been excluded as it contributes insignificantly to global net primary productivity relative to the C_3 and C_4 pathways). Phytoplankton assimilate H_2CO_3 with fractionation of ~ -20‰, with biomass $\delta^{13}C$ values depending on the DIC source (range determined from global ^{14}C data set; see Figure 6). ^{14}C-dead sources include kerogen ($\delta^{13}C \sim -32$‰ to -17‰) [*Whiticar*, 1996], carbonate rocks ($\delta^{13}C \sim -2.5$‰ to 0‰) [*Whiticar*, 1996], and solid Earth degassing ($\delta^{13}C \sim -6.5$‰ to +10‰ dependent on source rock) [*Clark and Fritz*, 1997; *Wang et al.*, 1994]. The soil OC pool is highly variable and difficult to succinctly define, though will be generally reflective of the evolving history of overlying vegetation (C_3 or C_4 biomass), mixing between terrestrial OM sources, as well as remineralization and aging within the soil stock. Excluding soils disturbed by agriculture, urbanization, or other anthropogenic alterations, the age of soil OM tends to increase with depth.

Despite the growing number of ^{14}C measurements in river systems over the past few decades, there have been few attempts to synthesize the available information or to derive regional or global patterns [e.g., *Raymond and Bauer*, 2001b; *Blair and Leithold*, 2013]. On a smaller scale, however, numerous studies elucidate basin-level controls on the ^{14}C content of different riverine C pools [*Longworth et al.*, 2007; *Blair et al.*, 2010; *Bouchez et al.*, 2010; *Galy and Eglinton*, 2011; *Moore et al.*, 2013]. For instance, freshwaters draining large areas underlain by OM-rich lithology and/or containing widespread agricultural land use may contain aged POC relative to streams draining more forested, OM-poor lithology [*Longworth et al.*, 2007]. Similarly, human-driven landscape alteration is recognized as driving increased export of aged DOC from disturbed peat swamp forest compared to the predominance of recently photosynthesized OM export from the undisturbed predecessor [*Moore et al.*, 2013].

Here we present an extensive new set of ^{14}C data on different OC pools from six tropical river basins in Africa, a continent from which only a handful of ^{14}C data are currently reported [*Bouillon et al.*, 2009; *Spencer et al.*, 2012]. In addition, we conducted an extensive literature search and digitized all published ^{14}C data (>1400) on the main riverine C pools (POC, DOC, and DIC; Figure 2) in order to compile a global ^{14}C data set. These combined data sets are used to explore global patterns in the ^{14}C signatures of riverine carbon pools and to draw attention to some of the factors driving their variability. Prior to discussing the patterns in the globally compiled data set, we briefly outline the newly gathered $\Delta^{14}C$ data on riverine C pools of African river basins.

2. Materials and Methods

2.1. Literature Survey

The literature was extensively screened for data on the ^{14}C composition of POC, DOC, and DIC for lotic inland waters ranging in size from small streams [e.g., *Billett et al.*, 2007; *Moore et al.*, 2013; *Tittel et al.*, 2013] to the

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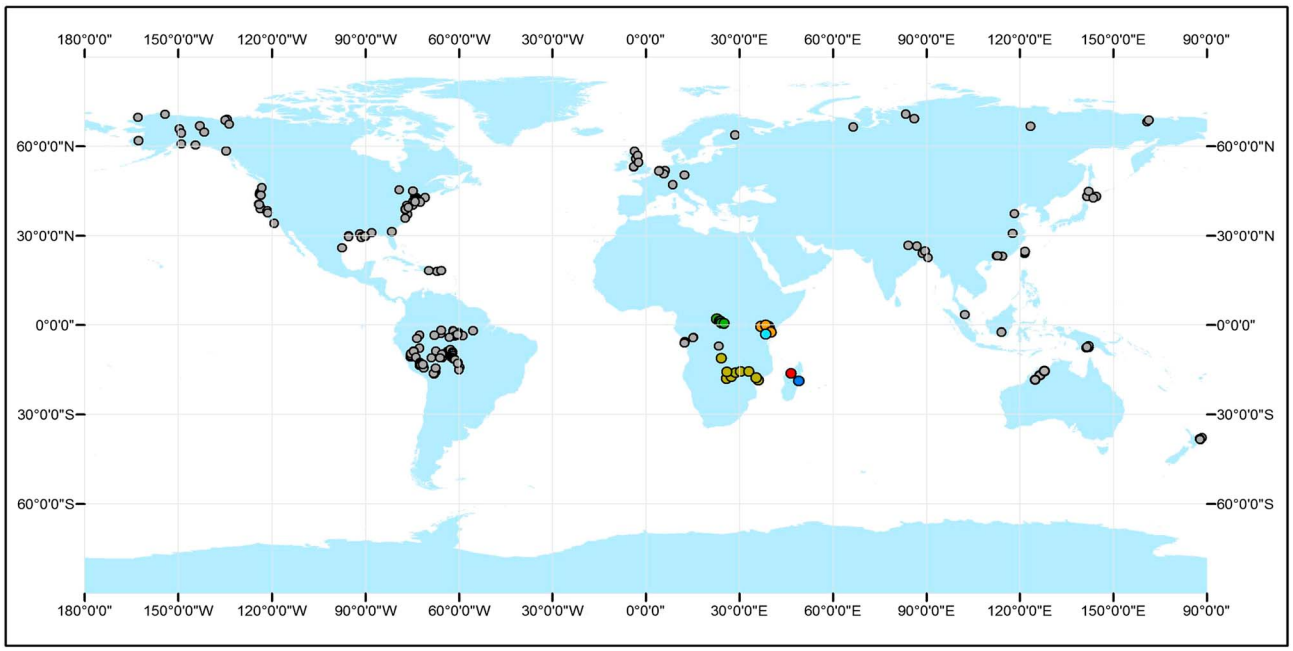

Figure 2. Site locations for the global distribution of riverine ^{14}C measurements in the POC, DOC, and DIC data sets. Literature data locations (grey circles) were either (i) reported by authors at publication or (ii) where these data were not provided, the site locality has been roughly estimated from information gleaned from the literature by the authors here. On occasion, where detailed basin-wide studies were conducted in smaller river basins and the exact geographic coordinates were not provided, only a single data point was included due to the scale of the figure. Sampling locations for the new African ^{14}C data of riverine POC and DOC presented here are as follows: Congo River basin = green circles, Zambezi River basin = yellow circles, Tana River basin = orange circles, Betsiboka River basin = red circles, Rianila River basin = dark blue circles, and A-G-S River basin = light blue circles. A full reference list for the ^{14}C literature compilation is provided in Data Set S1.

largest river globally [e.g., *Mayorga et al*., 2005; *Galy et al*., 2008; *Spencer et al*., 2012]. Overall, 60 studies were found to report ^{14}C data on riverine C pools of interest (see Data Set S1 in the supporting information for literature reference list), from which 1435 individual $\Delta^{14}C$ data points could be extracted: 466 data points on $^{14}C_{POC}$ (Figure 3a), 668 data points on $^{14}C_{DOC}$ (Figure 3b), and 209 data points on $^{14}C_{DIC}$ (Figure 3c), in addition to the new African data presented here.

Where data from estuaries were reported, only data from stations with salinities <1 have been incorporated and are considered to represent the riverine end-member. Data were taken directly from tables or requested from the authors; otherwise, data presented in figures were digitized with Plot Digitizer (v1.9). The quality of the digitization is assumed to be variable, depending on the resolution of figures and their scale, but estimated to be better than ± 5‰ for $\Delta^{14}C$ data (in addition to a similar analytical uncertainty in the original data) and better than ± 0.4‰ for $\delta^{13}C$ data, which we consider to be adequate for the purpose of this study. In cases where figures were of insufficient detail to extract some of the data unambiguously, these data were excluded. We restricted the literature data compilation to ^{14}C data of bulk OC pools, i.e., data on specific size fractions of dissolved organic matter were not considered nor were compound-specific ^{14}C data. Bulk ^{14}C data from *Rosenheim et al*. [2013], who employ the ramped pyrolysis technique, were calculated by the fractional yield (of bulk CO_2) and associated isotopic signature of CO_2 produced over each temperature interval. Some studies reported ^{14}C data on both coarse and fine POC, and in these cases the data from the fine POC fraction (i.e., $< 63\,\mu m$) have been included since this typically represents the bulk of the POC pool [*Mayorga et al*., 2005]. Where ^{14}C data from a single site were collected during different sampling events, some studies only present average values (with or without standard deviations), while others provide fully resolved data, we opted to use as much information as possible and thus did not average seasonal data in the latter case. In order to maintain compatibility of data, we excluded from our analyses the ^{14}C data reported for CO_2 evading from rivers and streams [e.g., *Billett et al*., 2007, 2012a, 2012b; *Vihermaa et al*., 2014]. Ancillary parameters, such as concentrations of total suspended matter (TSM), DOC, POC, DIC, %POC, or $\delta^{13}C$ ratios, were included when available and where they could be nonambiguously linked to the ^{14}C data. Unfortunately, while many of such data are undoubtedly collected as part of ^{14}C

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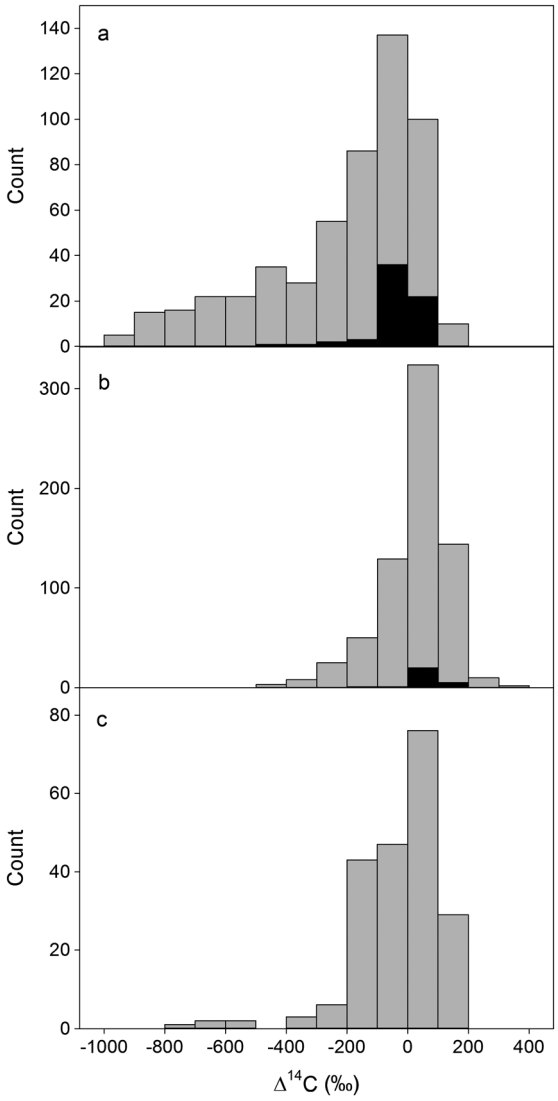

Figure 3. Stacked frequency distribution plots for global riverine $\Delta^{14}C$ of (a) POC ($n = 531$), (b) DOC ($n = 695$), and (c) DIC ($n = 209$). The new African riverine POC ($n = 65$) and DOC ($n = 27$) data are represented by the black stacks. Note the scale difference of the y axes.

studies, a substantial number of studies do not report (all) relevant data along with the ^{14}C data. Figures and statistical analyses in this synthesis paper therefore often rely on a different number of samples.

Radiocarbon data are variably reported as $\Delta^{14}C$ values, f_M values (fraction modern), and/or as radiocarbon ages. In order to achieve a consistent unit to explore all data, we opted to convert all data where applicable to obtain both $\Delta^{14}C$ values and f_M values. To convert data, we used the following formulations [see *Stuiver and Polach*, 1977; *McNichol and Aluwihare*, 2007]:

$$\Delta^{14}C = 1000 \times \left(f_M \times \exp^{-\lambda(y-1950)} - 1\right) \quad (1)$$

or, to calculate f_M when $\Delta^{14}C$ data are reported,

$$f_M = \left(\left(\Delta^{14}C/1000\right) + 1\right) \times \exp^{\lambda(y-1950)} \quad (2)$$

whereby $\lambda = 1/8267\ y^{-1}$, f_M = fraction modern, and y = the year of sample collection and measurement. Note that we assume that the year of collection and measurement are identical, such data are typically not reported, but any minor differences (<5 years) do not introduce a significant error in the context of this study. Where sampling years were not reported (only one study), 2 years prior to publication year was chosen. In some cases [e.g., *Galy et al.*, 2008; *Bouchez et al.*, 2010], data are reported as pMC, i.e., percent modern carbon, which refers to the percent of modern C expressed per unit weight of the sample (not of the total quantity of C). Here pMC values were first converted into f_M values using the provided %POC data. While the use of pMC as defined above is increasing in the literature, we prefer to avoid this notation as it can be confused with pMC as defined originally by *Stuiver and Polach* [1977] and as used in other disciplines.

2.2. Original Data

New $\Delta^{14}C$ data reported here were collected between 2009 and 2012 across a gradient of environmental and climatic settings, during field campaigns in six different African river basins (Figure S1 in the supporting information), including the Congo River basin (DR Congo), the Zambezi River basin (Zambia and Mozambique), the Tana and the Athi-Galana-Sabaki (A-G-S) River basins (Kenya), and the Betsiboka and Rianila River basins (Madagascar). All samples were collected from the upper 0.5 m of the water column. The full data set can be found in Data Set S1.

Samples for $^{14}C_{POC}$ were collected on 142 mm membrane filters (0.45 μm nominal pore size) or on precombusted GF/F filters (0.7 μm nominal pore size) and either air dried or stored in liquid nitrogen until arrival at the home laboratory, where they were stored frozen (−25°C). Samples were combusted to CO_2 in a Carlo Erba element analyzer, with blanks interspersed between each sample. The CO_2 was cryogenically trapped and immediately purified on a custom-built vacuum line. Graphitization was done with H_2 over an Fe catalyst. Targets were prepared at the Royal Institute for Cultural Heritage in Brussels, Belgium [*Van Strydonck*

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and Van der Borg, 1990–1991], and analyzed by AMS at the Leibniz Laboratory for Radiometric Dating and Isotope Research in Kiel, Germany [*Nadeau et al*., 1998].

Samples for $^{14}C_{DOC}$ were processed immediately after collection by prefiltration on precombusted GF/F filters, further filtration on 0.2 μm syringe filters (discarding the first fractions to avoid possible DOC blanks from the filter membranes), and subsequently acidified in the field with H_3PO_4 and stored cold as soon as possible. Between 250 and 1000 mL of filtered water was later rotary evaporated to a small volume (<4 mL), dried, and transferred to Ag cups. The dried material was acidified in the Ag cups and processed further as described above for $^{14}C_{POC}$ analyses. Analytical uncertainty for $\Delta^{14}C$ measurements of POC and DOC were always better than ± 7‰.

3. Results and Discussion

3.1. Sources and Age of OC in African Rivers

Basin vegetation cover has long been identified as a key driver of riverine OC pools in the tropics [*Hedges et al*., 1986; *Mariotti et al*., 1991; *Bird et al*., 1998; *Marwick et al*., 2014a]. The tropical and subtropical river basins presented here range from forested C_3-dominant basins (e.g., the Congo and the Rianila) to ones containing significant C_4-dominated grassland and savannah components (e.g., the Betsiboka and the A-G-S basins). This variability is clearly pronounced in the gradient of $\delta^{13}C$ signatures found in both DOC (−29.9 to −15.9‰) and POC (−29.6 to −17.0‰) pools of the studied basins (Table S1). Riverine OC samples containing significant quantities of C_4-derived C are not well represented within the literature ^{14}C compilation, with only four measurements of riverine $\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$ more enriched in ^{13}C than −20‰ [see *Massielo and Druffel*, 2001; *Hossler and Bauer*, 2012; *Moyer et al*., 2013]. These elevated $\delta^{13}C$ values reported here highlight the relevance of the C_4 photosynthetic pathway (which accounts for > 30% of sub-Saharan biomass cover [*Still and Powell*, 2010]) to riverine OC pools in Africa.

Given the range of environmental settings encountered across the African continent, the gradient of riverine $\Delta^{14}C_{POC}$ (−410 to +93‰, ~4200 years B.P. to modern) encompasses the spectrum from heavily aged OC (or a mixture of fossil and modern C sources) to OC recently assimilated through either terrestrial or aquatic photosynthesis, with pronounced intrabasin and interbasin variability (Table S1). The average $\Delta^{14}C_{POC}$ signature (−37 ± 89‰, ~250 years B.P., $n = 65$) is somewhat younger than previous reports from African freshwaters (Congo = −62 ± 13‰, $n = 5$ from *Spencer et al*. [2012] and Tana = −86 ± 27‰, $n = 7$ from *Bouillon et al*. [2009]), although the median $\Delta^{14}C_{POC}$ signature suggests a slightly younger age (−16‰, <100 years B.P.).

Heavily ^{14}C depleted POC was not uncommon in these African freshwaters, despite the overall prevalence of modern and partially aged POC (Figure 3a, Table S1, and Data Set S1). The Tsavo River, emanating from the northern slopes of Mount Kilimanjaro [*Oosterom*, 1988], carries POC with a $\Delta^{14}C$ composition of −177‰ (~1500 years B.P.) during the wet season. Extreme concentrations of total suspended matter (TSM; 25.1 g L^{-1}) and POC (264 mg L^{-1}) have been reported in one of the primary tributaries of the Tsavo River when under high discharge [*Marwick et al*., 2014b], evoking substantial conveyance of aged POC. Also, within the headwaters and main channel of the heavily forested Rianila basin of eastern Madagascar, $\Delta^{14}C_{POC}$ signatures indicate the presence of aged C during both the dry (−244‰; ~2200 years B.P.) and wet (−303 to −252‰; ~2800 to 2300 years B.P.) seasons, with an average $\Delta^{14}C_{POC}$ value of −143 ± 134‰ ($n = 7$). Small contributions to the riverine POC pool from ^{14}C depleted graphite, extraction of which is carried out within the headwater region of the Rianila basin [*Sodikoff*, 1996; *McConnell*, 2002], would be a probable driver of these depleted riverine $\Delta^{14}C$ values.

In contrast to the POC pool, the DOC pool was largely of modern origin ($\Delta^{14}C_{DOC}$ range = −2 to +155‰), excluding one aged sample ($\Delta^{14}C$ −126‰; ~1000 years B.P.) collected from the Athi River during baseflow. Among other factors, ^{14}C depleted riverine $\Delta^{14}C_{DOC}$ signatures have been linked with the deep erosion of old soils [*Massielo and Druffel*, 2001], disturbance of older soil profiles by agriculture and the application of (^{14}C-dead) agrochemicals to croplands [*Sickman et al*., 2010], contributions of ^{14}C-dead DOC from wastewater treatment plants [*Griffith et al*., 2009], as well as urban development [*Lu et al*., 2014]. Indeed, the headwaters of Athi River receive an influx of agricultural, industrial, and urban pollutants in the vicinity of Nairobi [*Kithiia and Ongwenyi*, 1997], while contributions of ^{14}C-depleted DOC from the upstream

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Dandora wastewater treatment plant (Nairobi River) is also likely, and even a minor contribution of fossil C can have a significant impact on an otherwise modern bulk OC pool (see discussion below). Comparatively ^{14}C-enriched DOC ($\Delta^{14}C = -2‰$) measured during the wet season suggests the flushing of a younger DOC fraction which has accumulated over the course of the dry season within the basin hinterlands. The average ($67 \pm 51‰$, $n = 27$) and median (68‰) $\Delta^{14}C$ values for these African freshwaters are comparable to that of *Spencer et al*. [2012] for the Congo basin ($73 \pm 16‰$, $n = 5$), the sole study reporting $^{14}C_{DOC}$ data for the African continent to date.

Where paired $^{14}C_{DOC}$ and $^{14}C_{POC}$ sampling was performed ($n = 19$), the dissolved fraction was in the main ($n = 17$) strongly enriched in ^{14}C compared to the particulate fraction ($\Delta^{14}C_{DOC} - \Delta^{14}C_{POC} = 104 \pm 103‰$), indicating, on average, almost a millennial-scale difference between the ^{14}C age (846 ± 841 years B.P.) of the two OC pools. Only for the Athi River sample discussed above was riverine POC significantly more enriched in ^{14}C than the DOC pool ($\Delta^{14}C_{DOC} - \Delta^{14}C_{POC} = -97‰$).

3.2. Controls on Global Riverine POC Sources and Age

The riverine POC pool constitutes an amalgam of three primary sources: (i) contemporary OM from terrestrial and/or aquatic primary producers, (ii) aged and diagenetically altered OM from deeper soil horizons, and (iii) contributions from weathered sedimentary rocks containing ^{14}C-dead OM (i.e., fossil C or kerogen) [*Blair and Aller*, 2012]. Additionally, it should be kept in mind that these C inputs may cycle through deposition-resuspension cycles (e.g., through floodplain deposition and river bank erosion) as portrayed by the "POC spiraling" concept [see *Newbold et al*., 1982], thereby enhancing remineralization and aging of OM during transit through the river basin and providing C inputs of intermediate ages. The composition of riverine POC in a given basin is largely driven by a complex interplay of lithology, tectonics, climate, hydrology, geomorphology, and ecology [*Blair and Leithold*, 2013].

The overall distribution of $\Delta^{14}C_{POC}$ data ($n = 531$; Figure 3a) shows a strongly skewed distribution yet spanning the full range between fossil and modern C, although the majority of data fall between −200 (~1700 years B.P.) and +100‰ (modern). It must be stressed here that given the relic nature of fossil C sources (where the age of kerogen, for example, is in millions of years), even a small contribution to an otherwise modern POC pool will lead to significant depletion of ^{14}C in the measured bulk $\Delta^{14}C$ ratio. This can confound the interpretation of bulk $\Delta^{14}C$ data, whereby it is impossible to discern whether a partially aged bulk POC pool is indicative aged soil OC, for example, or a combination of predominantly recently photosynthesized terrestrial C which has been marginally diluted by a minor, though ^{14}C-free, fossil C component.

The oldest riverine POC is reported from small mountainous rivers (SMR) of Taiwan (LiWu: $\Delta^{14}C_{POC} \geq -956‰$ from *Hilton et al*. [2008b] and Lanyang Hsi: $\Delta^{14}C_{POC} \geq -873‰$ from *Kao and Liu* [1996]), and New Zealand (Waiapu: $\Delta^{14}C_{POC} \geq -824‰$ from *Leithold et al*. [2006]), with a significant fossil C component common in active margin basins and SMR [*Massielo and Druffel*, 2001; *Komada et al*., 2004; *Mayorga et al*., 2005; *Hilton et al*., 2008b; *Blair et al*., 2010; *Gomez et al*., 2010; *Clark et al*., 2013; *Goñi et al*., 2013; *Smith et al*., 2013]. Despite only covering ~3% of global landmass, it is estimated that SMR contribute between 17 and 35% of the global riverine POC load [*Lyons et al*., 2002], much of which is highly aged C rapidly eroded from OM-rich (e.g., shale) bedrock and regolith. The episodically high-sediment export rates of SMR and narrow shelves typical of active margin basins [*Milliman and Syvitski*, 1992] lends these regions to being a significant source of fossil C to the marine C pool. Fossil C export is not limited to active continental margins [*Longworth et al*., 2007], with some of the world's largest rivers [*Goñi et al*., 2005; *Galy et al*., 2008; *Wang et al*., 2012], including major tributaries to the Amazon River [*Bouchez et al*., 2010], as well as numerous smaller passive margin rivers [*Megens et al*., 2001; *Raymond and Bauer*, 2001b; *Raymond et al*., 2004; *Longworth et al*., 2007] transporting significantly ^{14}C-depleted POC. Less than 20% of all riverine $\Delta^{14}C_{POC}$ measurements indicated a completely modern origin, with the most ^{14}C-enriched values reported from tributaries and the main channel of the Amazon River ($\Delta^{14}C_{POC} \leq +139‰$ from *Mayorga et al*. [2005]) and from the Hudson River basin ($\Delta^{14}C_{POC} \leq +132‰$ from *Longworth et al*. [2007]) and Cottage Hill Sike, UK ($\Delta^{14}C_{POC} \leq +107‰$ from *Billett et al*. [2012a]). ^{14}C-enriched riverine POC pools have been correlated with the absence of OM-rich sedimentary bedrock and decreased agricultural intensity in the basin, in the sense that agriculture may lead to the disturbance and subsequent export of older OC stored in deeper soil profiles [*Raymond et al*., 2004; *Longworth et al*., 2007].

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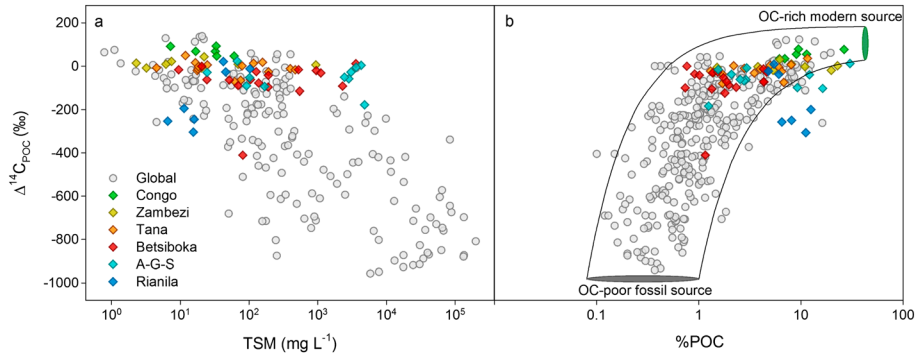

Figure 4. The relationship between $\Delta^{14}C_{POC}$ and (a) total suspended matter (TSM; $n = 250$) and (b) %POC of the TSM ($n = 376$) in the global riverine C data compilation. In Figure 4b a simple two-source mixing model constrains the majority of global $\Delta^{14}C_{POC}$ observations as a function of riverine %POC, employing (i) a modern OC-rich source (i.e,. recent terrestrial OM; %C = 42, $\Delta^{14}C = +40$ to +200‰) and (ii) a ^{14}C-dead OC-poor source (i.e., kerogen; %C = 0.08 to 1.0, $\Delta^{14}C = -1000$‰).

The global data set reveals a consistent pattern of progressively older riverine POC age with increasing suspended sediment load (Figure 4a). As the relative POC content of TSM typically decreases with higher TSM loads [*Meybeck*, 1982; *Ittekkot*, 1988; *Ludwig et al*., 1996; *Mayorga et al*., 2010], this also translates into a pattern of lower $\Delta^{14}C_{POC}$ at low %POC values (Figure 4b). Both relationships are consistent with a scenario whereby there are two main sources of TSM and associated POC to river networks: (i) an organic-rich component consisting of direct litter inputs or surface soil (humus) material, i.e., an end-member with high %POC content and a $\Delta^{14}C$ signature reflecting recently photosynthesized material which would dominate under low-relief settings with low TSM, and (ii) an end-member reflecting bedrock erosion of fossil POC dominating in highly erosive, steep gradient, SMR basins of active margin regions mentioned previously, with low %POC and devoid of ^{14}C. These two end-members are separated by the intermediary and highly variable subsurface soil-derived component, dominating in highly turbid river systems, with %POC in the range of those observed in subsurface soil layers and variable but more ^{14}C-depleted $\Delta^{14}C$ signatures. These patterns are in line with earlier observations, at smaller scales, between POC age and sediment yield [*Komada et al*., 2004; *Leithold et al*., 2006] and basin denudation rates [*Gomez et al*., 2010].

A second mechanism by which both $\Delta^{14}C_{POC}$ and %POC would simultaneously decrease is the preferential mineralization of the more recent and, assumed, more labile C reservoir during the residence time of material within the river network. Preferential mineralization of the younger C pool has been demonstrated experimentally for DOC at least [*Raymond and Bauer*, 2001c] and has also been proposed as the predominant driver of ^{14}C-enriched CO_2 outgassing in medium to large rivers of the humid tropics [*Hilton et al*., 2008a], to which a rapidly cycling, contemporary organic matter pool is considered central. Somewhat conflicting this viewpoint, however, are the recent reports of microbe-mediated contributions of highly aged, yet bioavailable, C from environments ranging from glacial to tropical conditions [see *Hood et al*., 2009; *Fellman et al*., 2014] as well as the high lability of OC released from the ancient Siberian Yedoma deposits [*Vonk et al*., 2013].

Despite the high complexity of riverine C sources and potential contributions by in-stream production at certain sites, a simple scenario with recent plant-derived POC and older, soil-derived C appears to encapsulate the majority of riverine $^{14}C_{POC}$ data (Figure 4b). Notable exceptions to this general pattern include the previously discussed Rianila streams and rivers, as well as a single sample from the mountainous headwaters of the Amazon [*Mayorga et al*., 2005], considered to be strongly influenced by solid Earth degassing (%POC = 16.2, $\Delta^{14}C_{POC} = -257$‰), all of which contain ^{14}C-depleted POC at relatively elevated %POC content. Additionally, the available ^{14}C data for bed load OC (not included here), including measurements from the Ganges-Brahmaputra basin [*Galy et al*., 2008] and major tributaries of the Amazon River [*Bouchez et al*., 2010], are typically ^{14}C-depleted and low in OC content.

Several authors have suggested that $\Delta^{14}C_{POC}$ data show strong relationships with $\delta^{13}C$ signatures [*Massielo and Druffel*, 2001; *Komada et al*., 2004; *Gomez et al*., 2010; *Clark et al*., 2013], and in certain cases $\delta^{13}C$ measurements have even been used to estimate the relative contribution of fossil and nonfossil C to riverine C loads [*Hilton et al*., 2008a; *Hilton et al*., 2010], based on the observation that the bedrock end-member often has substantially higher $\delta^{13}C$ values (and low %OC) than recent vegetation. Arguments supporting the

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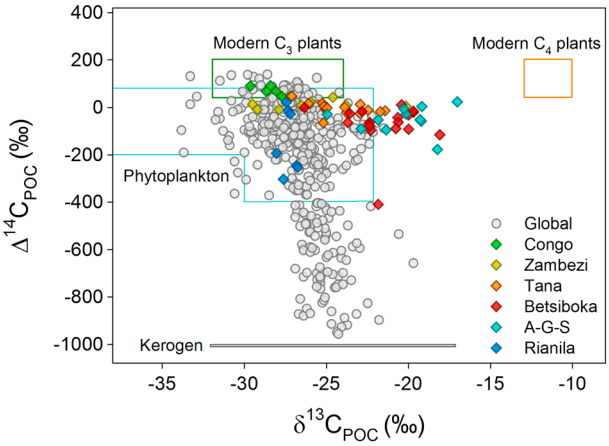

Figure 5. Delineating major sources of carbon to global riverine POC pools with the use of natural abundance stable ($\delta^{13}C$) and radio C ($\Delta^{14}C$) isotopes ($n = 483$). Although the majority of data appear constrained within the phytoplankton range, this source rarely contributes significantly to total riverine OC, and we expect that the majority of these data are, in fact, reflective of fresh and degraded terrestrial soil OM. The end-members are as defined in Figure 1.

idea that older C pools should show ^{13}C-enriched signatures include the Suess effect (i.e., the addition of ^{13}C-depleted CO_2 to the atmosphere over the past ± 150 years due to fossil fuel combustion) and the often-observed ^{13}C-enrichment during progressive degradation of OM in soil profiles—at least where C_3 vegetation is the dominant C source [e.g., *Ehleringer et al.*, 2000; *Acton et al.*, 2013]. The global data set of paired $\delta^{13}C_{POC}$-$\Delta^{14}C_{POC}$ data ($n = 483$, Figure 5), however, shows a more complex pattern and cautions against the use of $\delta^{13}C$ as a universal proxy for the age of riverine C pools. In particular, the inclusion of data from basins with mixed C_3-C_4 vegetation demonstrates the presence of a modern end-member with high $\delta^{13}C$ signatures, reflecting recent inputs derived from C_4 vegetation. While most published $\Delta^{14}C$ data sets have been gathered in C_3-dominated systems, C_4 vegetation is globally important in terms of areal cover and productivity [*Keeling et al.*, 2001; *Still et al.*, 2003; *Woodward et al.*, 2004]. Despite this, few authors report substantial contribution of C_4 OM to riverine OC pools [*Mariotti et al.*, 1991; *Bird et al.*, 1992; *Bird and Pousai*, 1997; *Wynn and Bird*, 2007; *Tamooh et al.*, 2012], even within tropical grasslands and savannah grasslands [see *Torello-Raventos et al.*, 2013] where C_4 biomass has been systematically shown to spatially dominate basin vegetation cover [*Marwick et al.*, 2014a]. This pattern is reflected in the absence of $\Delta^{14}C_{POC}$ values indicative of pure C_4 origin (as are present for the C_3 end-member) in the global data set.

Unlike the apportionment of bulk riverine POC between C_3 and C_4 end-members, which is relatively unencumbered owing to their distinct $\delta^{13}C$ signatures, isolating an autochthonous OC source at the global scale (in the absence of suitable proxies, such as POC:Chlorophyll *a* ratios) is considerably more convoluted. This is due to the large source and age variation of DIC pools utilized by emergent and submerged photoautotrophs, including ^{14}C-enriched atmospheric C, ^{14}C-depleted C associated with dissolution of carbonaceous materials, as well as variably aged soil respired CO_2 transported to freshwaters from the surrounding basin, itself dependent on the terrestrial photosynthetic pathway through which atmospheric C was originally assimilated (i.e., C_3 and C_4 pathway). Assuming the lowest $\delta^{13}C$ value representative of C_3 vegetation at the basin scale would be close to −32‰, some of the observations show that a contribution of in-stream autotrophic sources may be necessary to adequately constrain global riverine POC pools. Indeed, it has been posited that recent autochthonous production may contribute to the highly ^{13}C-depleted contemporary POC observed within the Hudson basin [*Longworth et al.*, 2007], while mixing models employing $\delta^{13}C$ and $\Delta^{14}C$ signatures have shown that the temporal variation of POC can be driven by seasonal variation of algal production in certain systems [*Hossler and Bauer*, 2012].

In summary, from the available literature data of paired $\delta^{13}C$ and $\Delta^{14}C$ signatures of POC, we conceive at least three primary OM sources are required for constraining global riverine POC origin: (i) a ^{14}C-dead end-member consistent with fossilized C_3 OM, (ii) a contemporary terrestrial C_3 end-member, and (iii) a contemporary terrestrial C_4 end-member. In-stream autotrophic production may provide a fourth end-member, though this source is at times difficult to extricate from the terrestrial C_3 end-member for reasons outlined above and, nevertheless, generally accounts for a minor component of OM exported by high-sediment yield systems [*Blair and Leithold*, 2013].

3.3. DOC Represents a Younger C Pool

We consider primary sources of DOC as for POC previously, including a recently fixed atmospheric component from the degradation of terrestrial and aquatic autotrophs, a variably aged soil component

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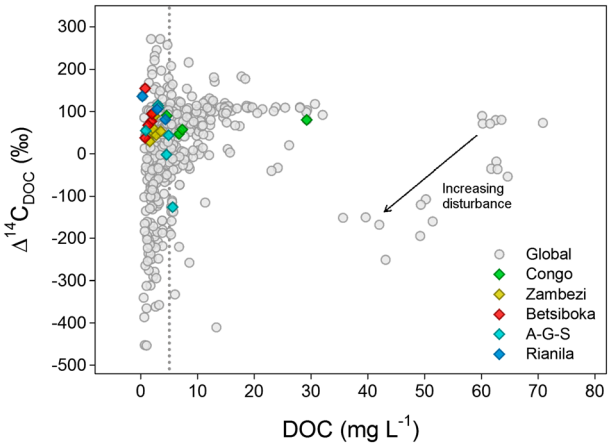

Figure 6. The relationship between riverine $\Delta^{14}C_{DOC}$ and bulk DOC concentration in the global $^{14}C_{DOC}$ compilation ($n = 443$). The circled, high DOC load, data highlight the transition of DOC source along a gradient of increasing anthropogenic disturbance in peat swamp forests of Borneo from *Moore et al.* [2013]. The dotted vertical line represents the global average riverine DOC concentration [see *Meybeck*, 1982; *Dai et al.*, 2012].

derived from OM breakdown, as well as natural and anthropogenic inputs of fossil C, with the contributing fraction of each to the bulk riverine DOC pool a function of multiple drivers, including climate, discharge, vegetation cover, soil C stocks, and the degree of anthropogenic disturbances within the contributing watershed. The $\Delta^{14}C_{DOC}$ distribution ($n = 695$; Figure 3b) is appreciably constrained toward contemporary origin (72% of the data are modern) compared to POC (22%), with the majority of $\Delta^{14}C_{DOC}$ data falling between −100 and +200‰. The most ^{14}C-depleted DOC pools have been measured within glacial meltwaters of Canada and Alaska ($\Delta^{14}C_{DOC} \geq -453$‰ in *Aiken et al.* [2014]; also, see *Hood et al.* [2009]), from a groundwater-fed stream in the ancient Kimberly region of northwest Western Australia ($\Delta^{14}C_{DOC}$ −452‰ in *Fellman et al.* [2014]), in freshwaters sourced from drained tropical peatlands of Indonesia ($\Delta^{14}C_{DOC} \geq -410$‰ in *Moore et al.*[2013]), as well as the agriculturally impacted San Joaquin River (−361‰ from *Sickman et al.* [2010]), corresponding to ^{14}C ages between 3500 and 4800 years B.P. The release of aged DOC, often linked to basins more strongly impacted by anthropogenic pressures [*Wang et al.*, 2012], has been attributed to deep erosion of old soil OM [*Massielo and Druffel*, 2001], destruction of wetlands [*Raymond et al.*, 2004], thawing permafrost soils [*Guo and Macdonald*, 2006], fossil fuel combustion [*Stubbins et al.*, 2007], municipal waste water contributions [*Griffith et al.*, 2009], and contributions from ancient, OM-rich sedimentary rocks [*Raymond et al.*, 2004]. Also, utilization of ^{14}C-depleted C within subterranean food webs and release of this old bioavailable DOC to above ground inland waters has been suggested for some oligotrophic regions [*Fellman et al.*, 2014]. The most ^{14}C-enriched riverine DOC measurements have come from throughout the Amazon basin ($\Delta^{14}C_{DOC} \leq +336$‰, modern C from *Mayorga et al.* [2005]) and rivers of the northeast U.S. ($\Delta^{14}C_{DOC} \leq +257$‰, modern C [see *Raymond and Bauer*, 2001a; *Raymond et al.*, 2004; *Longworth et al.*, 2007]), with $\Delta^{14}C_{DOC}$ values heavier than +100‰ regularly observed in waters sourced from northern latitude C-rich soils and peatlands [*Schiff et al.*, 1997; *Neff et al.*, 2006; *Billett et al.*, 2007; *Evans et al.*, 2007; *Raymond et al.*, 2007; *Billett et al.*, 2012a, 2012b].

The proportion of aged DOC typically decreases as the bulk concentration of riverine DOC increases (Figure 6). Considering a global mean riverine DOC concentration of ~5.5 mg L^{-1} [*Meybeck*, 1982; *Dai et al.*, 2012], DOC samples exceeding this generally exhibit modern $\Delta^{14}C_{DOC}$ signatures (average = +47 ± 93‰, median = +74‰, modern C; $n = 177$). The majority of these samples are from "blackwater" systems draining OC-rich soils and peats of forests and wetlands across a range of climatic settings (tropical (data presented here) [*Spencer et al.*, 2012; *Moore et al.*, 2013], temperate [*Evans et al.*, 2007; *Tittel et al.*, 2013], and boreal/arctic [*Schiff et al.*, 1997; *Raymond et al.*, 2007; *Billet et al.*, 2012b; *Aiken et al.*, 2014]). For example, *Raymond et al.* [2007] observed export of a DOC pool slightly depleted in ^{14}C during baseflow for a number of high-latitude basins feeding the Arctic Ocean, yet they also predicted as much as 90% DOC export that was fixed within the previous 20 year, with this modern C export strongly linked to the flushing of OC-rich soils during the spring-thaw period. The clear exception here are the samples of *Moore et al.* [2013] (Figure 6). Their bulk riverine DOC measurements from freshwaters of both undrained (i.e., undisturbed) and drained (i.e., disturbed) tropical peat swamp forest consistently exceeded 30 mg L^{-1}, though DOC from the latter was considerably older (^{14}C age of ~1300 to 1700 years B.P., dry and wet season averages, respectively) than the consistently modern C exported from undrained sites.

Bulk riverine DOC concentrations of ≤5.5 mg L^{-1}, on the other hand, have far more variable and aged $\Delta^{14}C$ signatures (average = −11.5 ± 134‰, median = +22‰, modern C; $n = 266$; Figure 6). Across small and

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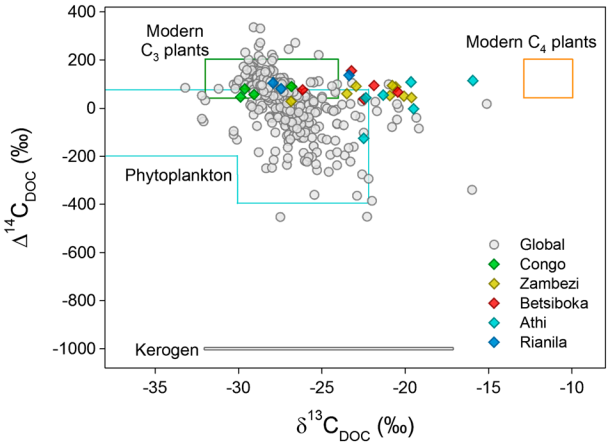

Figure 7. Delineating major sources of carbon to global riverine DOC pools with the use of natural abundance stable ($\delta^{13}C$) and radio C ($\Delta^{14}C$) isotopes ($n = 502$). Although the majority of data appear constrained within the phytoplankton range, this source rarely contributes significantly to total riverine OC, and we expect that the majority of these data are, in fact, reflective of fresh and degraded terrestrial soil OM. The end-members are as defined in Figure 1.

large drainage basins, a shift toward more depleted $\Delta^{14}C_{DOC}$ signatures during baseflow conditions has been explained by a greater proportion of riverine DOC sourced from the interaction of groundwater with deeper, older, and often more recalcitrant soil OC stock [*Schiff et al.*, 1997; *Neff et al.*, 2006; *Raymond et al.*, 2007]. As water tables rise, seepage of progressively younger DOC from shallow soil layers masks the minor ^{14}C-depleted baseflow fraction, resulting in comparatively ^{14}C-enriched riverine DOC during elevated discharge conditions [*Schiff et al.*, 1997]. Others have identified the role of land clearing and agriculture as potential drivers of ^{14}C-depleted riverine DOC [*Raymond and Bauer*, 2001c; *Sickman et al.*, 2010; *Moore et al.*, 2013], practices which may disturb and/or elevate older OC in the soil profile, and additionally, as a land use class, may contribute a disproportionate quantity of OC to riverine C loads [*Howarth et al.*, 1991]. In other cases, the preferential mineralization of a younger, and presumably more labile, DOC fraction also leads to ^{14}C-depletion of DOC pools [*Raymond and Bauer*, 2001c].

The global data set of paired $\delta^{13}C_{DOC}$-$\Delta^{14}C_{DOC}$ signatures ($n = 502$, Figure 7) shows more scatter than in the POC pool (see Figure 4), supporting the previous caution against the use of $\delta^{13}C$ as a universal proxy for the age of riverine C pools. The majority of data fall within the bounds for the three primary OC sources discussed for POC, these being modern terrestrial C_3 and C_4 vegetation as well as ^{14}C-dead fossil OC. Regions enriched in C_4 biomass [see *Still et al.*, 2003, Figure 4] are scarcely represented in the global $\Delta^{14}C$ data set, though where there is considerable C_4 influence (for example, $\delta^{13}C > -20‰$, $n = 8$) the DOC is not older than ~660 years B.P., except for an isolated measurement from glacial meltwaters in Alaska ($\delta^{13}C = -16.0‰$, ~3200 years B.P.) which may be attributed to contamination by fossil fuel burning [*Aiken et al.*, 2014]. Incubation experiments of C_3- and C_4-derived soils have shown that the OC of the latter may decompose at a rate twice that of the total soil OC pool [*Wynn and Bird*, 2007]. This would diminish the proportion of C_4-derived C available for long-term soil storage and supports the limited observations of aged C_4-derived riverine OC thus far. An increased sampling intensity in these regions may help elucidate the quantitative flux of aged C from C_4-rich basins.

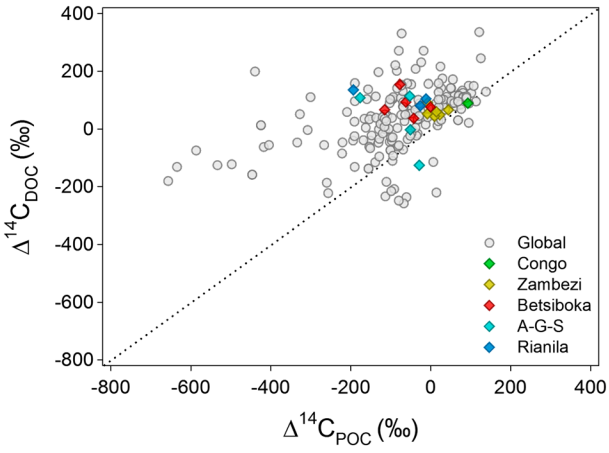

Figure 8. Comparison of paired $\Delta^{14}C_{POC}$ and $\Delta^{14}C_{DOC}$ measurements within the global riverine ^{14}C compilation ($n = 213$). The data clearly highlight the typical disconnection between riverine POC and DOC age across a variety of environmental settings. Identical age of the two pools is defined by the 1:1 dotted line.

While the global data compilation contains more $\Delta^{14}C$ data on DOC than on POC, relatively few paired sets of data are available ($n = 213$; Figure 8). A direct comparison confirms the different frequency distributions (Figures 3a and 3b): in the majority of cases (90%), DOC has a younger $\Delta^{14}C$ signature than POC, with an average relative enrichment of +139 ± 117‰ (median = +108‰; $n = 192$), whereas when POC was younger than DOC,

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the difference in $\Delta^{14}C$ was more constrained (+77 ± 72‰; median = +72‰; $n = 21$). The consistent enrichment of ^{14}C in DOC comparative to POC was previously reported in a data set comprising fewer basins [*Raymond and Bauer*, 2001b], from which it was proposed that differences in the dominant weathering and transport mechanisms drive the observed age separation between the POC and DOC pools. While mechanical weathering controls POC inputs to freshwaters, at times providing significant quantities of aged OM from deep soil erosion, DOC export from soils is controlled by the chemical weathering of recently fixed C and below ground production [*Bloom*, 1991; *Raymond and Bauer*, 2001b]. Although aged DOC export from soil pore waters may be assumed with deep soil erosion (concomitantly with aged POC export), it is reasonable to expect that the quantitative proportion of total OC mobilized to be heavily weighted toward the POC fraction under these circumstances. The characteristic transport pathways of DOC and POC upon entering a drainage system also lead to age separation between the two riverine OC pools [*Raymond and Bauer*, 2001b]. As a dissolved fraction in moving waters, DOC is conveyed rapidly to the basin outlet (if not remineralized in transit), with its residence time equal to that of the water. The transport of POC from the source to the outlet, on the other hand, is interrupted by deposition/resuspension cycles (the POC "spiraling" mentioned earlier [see *Newbold et al*., 1982]) along the drainage continuum, presenting greater opportunity for aging of this fraction within the basin relative to the more transient DOC fraction. Finally, physical protection mechanisms [*Oades*, 1988; *Torn et al*., 1997; *Six et al*., 2002] may also contribute to the generally older $\Delta^{14}C$ signatures in particle-bound C [e.g., *Goñi et al*., 2005].

3.4. Constraining the Age of Riverine C Export to the Global Oceans

The global ^{14}C compilation offers a first opportunity to quantitatively constrain the age of riverine-transported OC to the ocean. Within the open ocean, DOC has been shown to be relatively old [*Williams and Druffel*, 1987; *Bauer et al*., 1992; *Druffel et al*., 1992; *Druffel and Bauer*, 2000], leading to mean residence time estimates of ~6000 years for open ocean DOC. In contrast, oceanic POC typically has substantially more recent signatures [e.g., *Druffel et al*., 1996; *Bauer et al*., 2002; *Griffith et al*., 2012], converse to the relationship observed between $^{14}C_{DOC}$ and $^{14}C_{POC}$ in riverine settings here, although the lateral advection of resuspended sediments to the open ocean, especially from continental margin deposits, has recently been stressed [*Hwang et al*., 2010]. Additionally, estuarine zones are important physical-biogeochemical reactors acting as a nexus between inland waters and the marine system [*Bauer et al*., 2013], and modulate the quantities and quality of riverine OM reaching the open ocean [*Keil et al*., 1997] while simultaneously emitting significant quantities of CO_2 to the atmosphere [*Borges and Abril*, 2012]. Constraining the $\Delta^{14}C$ signatures of riverine OC pools is thus not only important to further our understanding of riverine C cycling but also for interpretation of estuarine and oceanic $\Delta^{14}C$ data.

3.4.1. Particulate OC

In the case of sediment-bound (particulate) OC, the distribution of $\Delta^{14}C$ is highly skewed, and average and median $\Delta^{14}C$ within the global data set differ substantially (−204 and −115‰ or ~1800 and 900 years B.P., respectively). Moreover, average suspended sediments loads in rivers vary over several orders of magnitude [*Alvarez-Cobelas et al*., 2010], and it is well established that certain regions contribute disproportionately to global sediment delivery to the oceans [*Milliman and Syvitski*, 1992], with SMR basins draining to active margins in SE Asia, typified by high suspended sediment loads and low sediment storage capacity, being major sources at the global scale [*Lyons et al*., 2002].

To provide a first-order estimate of $\Delta^{14}C_{POC}$ transported by rivers globally, we combined the patterns observed between %POC and $\Delta^{14}C_{POC}$ with a global database of riverine sediment and POC fluxes based on the Global Nutrient Export from WaterSheds 2 model [see *Mayorga et al*., 2010] from which we calculated the cumulative contribution of different river systems to global POC export. Basins were divided into five classes according to their TSM load (Table S2). Combining these with the median $\Delta^{14}C_{POC}$ values for each class, we estimate a global riverine $\Delta^{14}C_{POC}$ signature of −203‰ ($n = 251$), or corresponding to an average contribution of fossil C sources of 20% ($f_M = 0.80$ or ~1800 years B.P.). This value is substantially lower than the median ^{14}C age riverine $\Delta^{14}C_{POC}$ data compilation and stresses the important role played by highly turbid rivers in the delivery of aged C to the coastal zone, despite the generally lower %POC in such systems. Our interpretation here assumes a simple two-source mixing scenario for the sake of simplicity in reporting the median global $\Delta^{14}C_{POC}$ ratio in the form of an f_M value, yet in reality the estimated $\Delta^{14}C_{POC}$ signature of −203‰ could represent a infinite range in combinations of the relative quantities of the four

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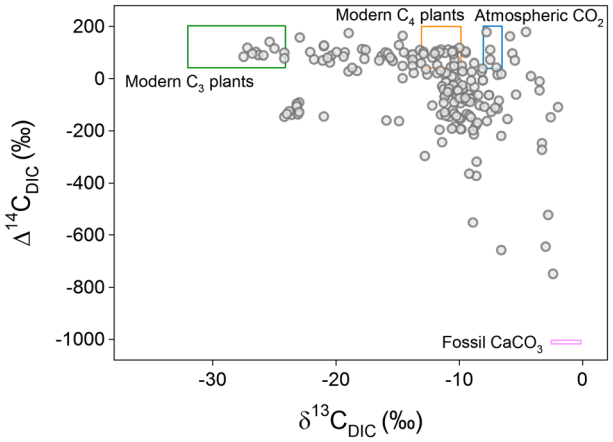

Figure 9. Delineating major sources of carbon to global riverine DIC pools with the use of natural abundance stable ($\delta^{13}C$) and radio C ($\Delta^{14}C$) isotopes ($n = 197$). The end-members are as defined in Figure 1.

primary POC sources outlined in section 3.2. These estimates will require refinement in the future, and the possible effects of within-river processing may result in an underestimate of the fossil C contribution, as discussed below for DOC.

3.4.2. Dissolved OC

For riverine DOC, the symmetric frequency distribution (Figure 3b) suggests that the average or median value in the global data compilation (+22 and +46‰, respectively; i.e., modern C) offers a reasonable approximation of the $\Delta^{14}C$ signatures of global riverine DOC export. One possible caveat in this approach is that the compilation contains data collected throughout river basins—from small headwater streams to higher-order lowland rivers. If in-river processing was to lead to consistent downstream changes in $\Delta^{14}C_{DOC}$, we may anticipate that this still overestimates the contribution of modern C, since the latter fraction would likely be preferentially mineralized [*Raymond and Bauer*, 2001c]. Few opportunities exist to assess this possibility within the global data set, particularly for large basins draining passive margins (where, relative to SMR of active margins, for example, longer residence time within larger passive margin basins will increase potential for in situ cycling of the DOC pool), as most major studies reporting riverine DOC ^{14}C data have either been conducted in small watersheds [*Schiff et al.*, 1997; *Billett et al.*, 2007; *Evans et al.*, 2007; *Billett et al.*, 2012a, 2012b; *Moore et al.*, 2013; *Moyer et al.*, 2013; *Tittel et al.*, 2013], focus on export at the basin outlet and/or conducted sampling at one or two stations per basin [*Raymond et al.*, 2007; *Hood et al.*, 2009; *Sickman et al.*, 2010; *Butman et al.*, 2012; *Hossler and Bauer*, 2012; *Wang et al.*, 2012]. The data reported here for the Zambezi River and that of *Mayorga et al.* [2005] for the Amazon basin are two large passive margin basins for which extensive longitudinal gradient is covered. Indeed, some cases in the latter (e.g., for the Madeira and Juruá Rivers) suggest a link between preferential remineralization of young OM and ^{14}C depletion in the downstream direction [*Mayorga et al.*, 2005]. Recently though, the reverse scenario has been observed in some inland waters of northwest Australia [*Fellman et al.*, 2014], albeit associated with unique subterranean conditions where microbial communities utilize old C in groundwater feeding above ground springs and where a combination of preferential remineralization of old C by in-stream microbes, lateral inputs of younger floodplain OM, and in situ autochthonous contributions lead to the downstream ^{14}C-enrichment in the riverine DOC pool [*Fellman et al.*, 2014]. As more riverine ^{14}C data comes to light in the future, revisiting this question through an integrated geographic information system-assisted approach (for example, incorporating stream ordering and/or length) could be beneficial in further illuminating the influence of in-stream processing on riverine OC age at the global scale.

3.4.3. Dissolved Inorganic Carbon

Rivers are generally heterotrophic systems and globally act as a significant source of CO_2 to the atmosphere [*Raymond et al.*, 2013]. The extent to which these CO_2 emissions are sustained by respiration in the terrestrial system or wetlands or by aquatic mineralization, however, remains largely unresolved [*Abril et al.*, 2013]. Radiocarbon measurements on the DIC pool may help to constrain the origin of C being mineralized and has been instrumental in demonstrating that most of the CO_2 emitted from the lower Amazon is of decadal age [*Mayorga et al.*, 2005]. The interpretation of $\Delta^{14}C_{DIC}$ data are, however, complicated by processes such as gas exchange with the atmosphere and by the fact that it is highly influenced by the dominant chemical weathering mechanisms (hence the underlying geology) in the basin. For example, weathering of 1 mol of fossil marine carbonates ($CaCO_3$) results in the production of 2 mol of bicarbonate (HCO_3^-), of which half originates from CO_2 while the other half is from the $CaCO_3$ itself (and hence ^{14}C-dead). Silicate weathering, in contrast, produces dissolved HCO_3^- in which the C originates entirely from the CO_2 driving its dissolution.

The overall pattern in the coupled $\delta^{13}C_{DIC}$-$\Delta^{14}C_{DIC}$ data (Figure 9) is largely consistent with a continuous spectrum between two main end-members, consisting of modern DIC with low $\delta^{13}C$ signature (representing

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silicate weathering driven by respiration of modern, C_3-derived organic matter) and an old end-member with a ^{13}C-enriched signature representing waters in which weathering of fossil carbonates dominate. Thus, considering that the median $\Delta^{14}C_{DIC}$ value is modern (+2‰, $n = 209$) and that the global dataset is partially influenced by contributions of fossil carbonate weathering, these data at least hint at the prevalence of relatively recent sources of respiratory CO_2 in most river systems. However, accurate information on the ^{14}C composition of the respiratory CO_2 can only be obtained from $\Delta^{14}C_{DIC}$ data in systems where carbonate weathering is minimal [e.g., *Mayorga et al*., 2005] or through experiments whereby only newly produced respiratory CO_2 is sampled and analyzed [*McCallister and del Giorgio*, 2012]. Such data have so far not been measured across a range of contrasting systems and thus remain an interesting pathway for future research.

4. Final Remarks

While the data compilation presented here represents the most exhaustive synthesis of riverine $\Delta^{14}C$ data to date, ancillary data (e.g., C concentrations, $\delta^{13}C$ data) are unfortunately not always reported, leading to a crucial loss of information. Future progress in our understanding of the controls on the age of riverine C pools would thus benefit from reporting such ancillary data and will also benefit from a more in-depth analysis of ^{14}C data as a function of basin characteristics. As alluded earlier, most studies have focused on the lower reaches of river systems (see Figure 2) and, specifically, quantify and characterize OC export at the basin outlet, whereas a greater basin-wide focus will undoubtedly provide further direction as to the extent of within-river processing of the aged versus modern C fractions. Finally, recent advances in both compound-specific ^{14}C measurements [*Blair et al*., 2010; *Culp*, 2013] and ramped pyrolysis ^{14}C analyses (which provide insights into continuous distribution of ^{14}C ages within a composite sample) [e.g., *Rosenheim et al*., 2013] will no doubt contribute to a more refined understanding of the transport and fate of fossil C in the aquatic environment.

Acknowledgments

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