Direct measurement of riverine particulate organic carbon age structure

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[1] Carbon cycling studies focusing on transport and transformation of terrestrial carbon sources toward marine sedimentary sinks necessitate separation of particulate organic carbon (OC) derived from many different sources and integrated by river systems. Much progress has been made on isolating and characterizing young biologically-formed OC that is still chemically intact, however quantification and characterization of old, refractory rock-bound OC has remained troublesome. Quantification of both endmembers of riverine OC is important to constrain exchanges linking biologic and geologic carbon cycles and regulating atmospheric CO2 and O2. Here, we constrain petrogenic OC proportions in suspended sediment from the headwaters of the Ganges River in Nepal through direct measurement using ramped pyrolysis radiocarbon analysis. The unique results apportion the biogenic and petrogenic fractions of bulk particulate OC and characterize biogenic OC residence time. Compared to the same treatment of POC from the lower Mississippi-Atchafalaya River system, contrast in age spectra of the Ganges tributary samples illustrates the difference between small mountainous river systems and large integrative ones in terms of the global carbon cycle. Citation: Rosenheim, B. E., and V. Galy (2012), Direct measurement of riverine particulate organic carbon age structure, Geophys. Res. Lett., 39, L19703, doi:10.1029/2012GL052883.

1. Introduction

[2] River transport of particulate organic carbon (POC) links biologic and geologic carbon cycles and plays a crucial role in regulating atmospheric chemistry over geologic timescales. Rivers provide a pathway for the transfer of organic carbon (OC) from the biosphere (OCbiomass, biologic OC fixed by primary producers and moved rapidly through trophic levels until transport, storage, or metabolic release to the atmosphere) to storage in sediments and the transfer of aged, petrogenic OC (OCpetro, chemically refractive rockbound carbon derived from erosion of carbonate rocks) to marine environments. In the marine environment some fraction of OCbiomass and OCpetro can be assimilated and remineralized, and the remainder buried. The remineralization of OCbiomass represents a biologic transfer that bypasses the geologic carbon cycle; whereas the burial of OCpetro represents transfer from one geologic reservoir (continental bedrock) to another (marine sediments). Conversely, the remineralization of OCpetro [e.g., Caraco et al., 2010] and the burial of OCbiomass represent transfers between the geologic and biologic carbon cycles. Thus, the ratio of recent OCbiomass to OCpetro transported to marine ecosystems and depositional centers by rivers, as well as changes in this ratio through time, are important in determining the accumulation of dioxygen (O2) and carbon dioxide (CO2) in the atmosphere over Earth’s history [Berner, 1982].

[3] Much has been learned through characterization of the younger OCbiomass pool in recent decades, but large portions of riverine OC remain uncharacterizable. Isolation of components of OCbiomass has succeeded using compound specific and compound class methods [Eglinton et al., 1996]. An example is the isolation of lignin phenols and plant waxes that are only produced by terrestrial vascular plants; lignin extraction has yielded much information about the storage of terrestrial OC in marine sediments [Goni et al., 1997; Hedges and Parker, 1976; Hedges et al., 1997]. Extraction of alkanes and individual plant wax fatty acids has served to constrain OCbiomass [Drenzek et al., 2007] and to demonstrate that OCbiomass can have long (>1000 y) residence times in soils and sediments associated with river channels, floodplains, and deltaic deposits [Drenzek et al., 2009; Galy and Eglinton, 2011; Galy et al., 2011]. On the other hand, the compounds comprising the oldest portions of OC carried by rivers are difficult to chemically isolate and/or define. These constituents of the riverine OC were resistant to microbial degradation upon deposition and rendered chemically recalcitrant because of structural rearrangement at high temperature and pressure [Buseck and Huang, 1985; Hedges and Keil, 1995]. As a result, inference of the amount of OCpetro in lieu of extraction and measurement is necessary to constrain riverine OCpetro flux [Galy et al., 2008b; Hilton et al., 2008]. Radiocarbon dating of bulk riverine OC has been extensively used to tease apart petrogenic and biogenic contributions in absence of chemical separations [Meybeck, 1982; Blair et al., 2003; Komada et al., 2004; Leithold et al., 2006]. Recently, two approaches have been developed to infer the amount of OCpetro — characterization of bulk OC radiocarbon from sediments subsampled from the continuum created by sorting and mixing processes during fluvial transport, coupled with spectroscopic isolation of graphitic C [Galy et al., 2008b], and constraint using unique C:N values of petrogenic and biospheric carbon sources in a binary mixture [Hilton et al., 2008, 2011]. Both approaches represent significant developments in source-to-sink carbon-cycling studies. However, broad application of these solutions is difficult: the Galy et al. [2008b] approach is limited by logistical constraints of depth profile sampling,
pyrolysis analysis, decarbonated sediment was heated linearly. For ramped pyrolysis analysis of the sediment. For ramped pyrolysis analysis, we employed novel ramped-pyrolysis radiocarbon analysis [Rosenheim et al., 2008] to suspended sediment from the Narayani River – one of the largest Himalayan tributaries to the Ganges River – during monsoonal flow (Figure 1). This technique allows separation, based on thermochemical stability, of the bulk OC in a sample during linearly-ramped pyrolysis (5 K-min⁻¹ temperature ramp). The result is a spectrum of radiocarbon ages that provides a better sense of the age distribution of all OC in a sample that neither bulk nor compound specific radiocarbon measurements provide. Following a first order model of pyrolysis decomposition, this method allows determination of the proportion of OCpetro that closely matches previous inference of OCpetro. Furthermore, the method produces a clear separation of both young and old OCbiosph from OCpetro based on radiocarbon ages. The role of the Narayani River in the global carbon cycle is likely small; however it is similar to many tributaries of one of the most significant terigenous sediment sources to the world ocean – the Ganges-Brahmaputra river system.

2. Methods

[5] Samples were collected at the surface of the Narayani River near the outflow from the Himalayas [Galy et al., 2008b] during two monsoon seasons (2005 and 2007). Samples were decarbonated to isolate OC from detrital carbonates abundant in this river system [Galy et al., 2007]. Bulk results from these samples have been previously reported [Galy and Eglinton, 2011; Galy et al., 2008b]; here we focus on additional ramped pyrolysis analysis of the sediment. For ramped pyrolysis analysis, decarbonated sediment was heated linearly (ramped smoothly, not stepped) at a rate of 5 K-min⁻¹, from ambient laboratory temperature to 1000°C, and then held constant for 15 minutes. Volatile decomposition products were oxidized and carbon dioxide was integrated over 5–7 temperature intervals defined by both the sample size necessary to analyze radiocarbon content and the reaction shape recorded by a flow-through infrared CO2 analyzer (Figure 2). Samples of CO2 were then graphitized by standard procedures of the National Ocean Sciences Accelerator Mass Spectrometer (NOSAMS) facility and measured for radiocarbon content. More details of sample preparation and data treatment can be found in Rosenheim et al. [2008].

[6] For comparison, we also present a compilation of samples from the lower Mississippi-Atchafalaya river system (B. E. Rosenheim et al., The influence of river discharge on carbon transport by the Mississippi/Atchafalaya River System, submitted to Global Biogeochemical Cycles, 2012). These samples were collected from different depths, times and locations and filtered to recover particulates >0.7 μm nominal radius. The results of similar analyses are summarized below without respect to differences in depth, time, and space in order to provide a comparison to the samples analyzed from the Narayani River.

3. Results

[7] For the Narayani River samples, the 2007 sample yielded 93% of the expected CO2 (calculated from elemental analysis) while the 2005 sample yielded only 78%. Elemental analysis of 214 mg of recovered pyrolysis residue from the 2005 monsoon sample yielded only 0.64 μmol of carbon, which corresponds to 0.003% TOC and 99.997% non-carbonaceous components within the residue and does not account for the low yield. However, for both samples, the calculated bulk radiocarbon composition from ramped pyrolysis (the geometric mean of fractions modern fM = \[
\left( \frac{\Delta^1}{} \right)_{\text{modern, 2000 AD}}
\] , where the modern value is 95% of the radiocarbon content in 1950 of NBS Oxalic Acid I normalized to δ¹³C = −19‰ PDB) from each temperature interval (in a single sample) closely matched the measured bulk radiocarbon age, illustrating isotopic mass balance (Table 1). Stable carbon isotope values of OC constituents are likely fractionated during the ramped pyrolysis process, as indicated by calculated bulk δ¹³C values systematically slightly lower than measured values (Table 1). Fractionation is supported by the calculation of δ¹³C of the carbon necessary to improve the yield of the 2005 sample to 100% - this carbon would have an isotope ratio of −18.4‰, more than 5 standard deviations heavier than the other fractions measured. This would, however, not affect the radiocarbon values as the latter are corrected for isotope fractionation.

[8] Whereas calculation of bulk radiocarbon age from ramped pyrolysis is important for mass balance and comparison to conventional data in the literature, analysis of the spectrum of radiocarbon content with respect to the pyrolysis reaction temperature is the major contribution of these data. Figure 2 shows that the radiocarbon age spectra of OC from Narayani River sediment, plotted on pyrolysis temperature, are bimodal and span a large portion of the radiocarbon dynamic range. In fact, the oldest measurement is 30,100 ¹⁴C yr (Δ¹⁴C = −976.5‰), close to the limit of Δ¹⁴COCpetro = −1000‰. Such separation is remarkable from
Figure 2. Ramped pyrolysis data from two different monsoons in the Narayani River (Figure 1). (a) Ramped pyrolysis and age measurements for the 2005 monsoon and (b) the same for the 2007 monsoon. Both data sets show similarities: they are both bimodal and the different modes show both very young $^{14}$C ages and very old $^{14}$C ages. (c, d) Data from Figures 2a and 2b, respectively, decomposed into simple Gaussian models consisting of 4 major components. These components are each treated as binary mixtures of 2 of three endmembers previously isolated from Ganges River and tributary POC (modern biospheric, old biospheric, and petrogenic carbon [Galy et al., 2011]).

Table 1. Isotopic Values of Individual Splits, Bulk Samples and Compound Classes From Narayani River POC

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu$mol CO$_2$ (RP)</th>
<th>Max T (°C)</th>
<th>$f_0$ (1σ)</th>
<th>$\delta^{13}$C (PDB)</th>
<th>Age, $^{14}$C y</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005 Narayani Bulk</td>
<td>n/a (0.33% TOC)</td>
<td>n/a</td>
<td>0.39 (0.006)</td>
<td>−24.5</td>
<td>7,540</td>
</tr>
<tr>
<td>2007 Narayani Bulk</td>
<td>n/a (0.40% TOC)</td>
<td>n/a</td>
<td>0.31 (0.002)</td>
<td>−23.9</td>
<td>9,350</td>
</tr>
<tr>
<td>2005 C24+ FA Average</td>
<td>n/a</td>
<td>n/a</td>
<td>0.846 (0.019)</td>
<td>n/a</td>
<td>1,350</td>
</tr>
<tr>
<td>2007 C24+ FA – Lignin phenols Average</td>
<td>n/a</td>
<td>n/a</td>
<td>0.997 (0.022)</td>
<td>n/a</td>
<td>24</td>
</tr>
<tr>
<td>RP 1, 2005</td>
<td>12.2</td>
<td>365</td>
<td>0.9746 (0.0069)</td>
<td>−26.92</td>
<td>205</td>
</tr>
<tr>
<td>RP 2, 2005</td>
<td>12.1</td>
<td>510</td>
<td>0.6705 (0.0058)</td>
<td>−28.02</td>
<td>400</td>
</tr>
<tr>
<td>RP 3, 2005</td>
<td>12.3</td>
<td>630</td>
<td>0.0768 (0.0014)</td>
<td>−27.48</td>
<td>20,500</td>
</tr>
<tr>
<td>RP 4, 2005</td>
<td>12.2</td>
<td>703</td>
<td>0.0316 (0.0008)</td>
<td>−24.38</td>
<td>27,800</td>
</tr>
<tr>
<td>RP 5, 2005</td>
<td>5.5</td>
<td>1000</td>
<td>0.0774 (0.0032)</td>
<td>−25</td>
<td>20,600</td>
</tr>
<tr>
<td>Geometric Mean/Sum</td>
<td>54.3 (0.26% TOC)</td>
<td>n/a</td>
<td>0.3870 (0.0097)</td>
<td>−26.54</td>
<td>7,626</td>
</tr>
<tr>
<td>RP 1, 2007</td>
<td>14.8</td>
<td>355</td>
<td>0.909 (0.0021)</td>
<td>−26.58</td>
<td>765</td>
</tr>
<tr>
<td>RP 2, 2007</td>
<td>10.8</td>
<td>428</td>
<td>0.7535 (0.0023)</td>
<td>−27.12</td>
<td>2,270</td>
</tr>
<tr>
<td>RP 3, 2007</td>
<td>10.7</td>
<td>501</td>
<td>0.28 (0.0016)</td>
<td>−27.51</td>
<td>10,250</td>
</tr>
<tr>
<td>RP 4, 2007</td>
<td>12.4</td>
<td>550</td>
<td>0.0807 (0.0013)</td>
<td>−26.51</td>
<td>20,200</td>
</tr>
<tr>
<td>RP 5, 2007</td>
<td>11.6</td>
<td>600</td>
<td>0.03 (0.0012)</td>
<td>−25.76</td>
<td>28,200</td>
</tr>
<tr>
<td>RP 6, 2007</td>
<td>11.8</td>
<td>663</td>
<td>0.0237 (0.0012)</td>
<td>−24.73</td>
<td>30,100</td>
</tr>
<tr>
<td>RP 7, 2007</td>
<td>8.9</td>
<td>1000</td>
<td>0.04826 (0.0025)</td>
<td>−23.39</td>
<td>24,300</td>
</tr>
<tr>
<td>Geometric Mean/Sum</td>
<td>80.96 (0.37% TOC)</td>
<td>n/a</td>
<td>0.3289 (0.0048)</td>
<td>−26.03</td>
<td>8,934</td>
</tr>
</tbody>
</table>

$^a$RP stands for ramped pyrolysis.
a natural sample that likely undergoes some chemical mixing between different-aged constituents during pyrolysis.

4. Discussion

Recent work identifying protracted storage of OC\textsubscript{biosph} in the Ganges-Brahmaputra system [Galy and Eglinton, 2011] shows that OC\textsubscript{biosph} can be up to 17,400 14C y old (Δ14C = −885‰). This is similar to analysis of Eel River margin sediments suggesting that the contribution of pre-aged OC should be assigned to old biospheric material in addition to petrogenic material [Drenzek et al., 2009], however in a rather insignificant proportion of the bulk carbon as previously illustrated [Blair et al., 2004]. The two modes apparent in ramped pyrolysis data represent two dominant regimes of thermochemical stability over a continuum of thermal decomposition until temperatures have exceeded 900°C (Figure 2). However, relationship to chemical composition of OC benefits from comparison of ramped pyrolysis data to existing estimates of OC\textsubscript{petro} to constrain the relative contributions of OC\textsubscript{petro}, recent OC\textsubscript{biosph}, and pre-aged OC\textsubscript{biosph}.

For both samples, a first-order kinetics model of Gaussian pyrolysis activation energy distributions [Burnham and Braun, 1999; Cramer, 2004; Cramer et al., 2001] yields four components (Figures 2c and 2d). We assume that these components are comprised of young OC\textsubscript{biosph} defined by radiocarbon ages of long chain fatty acids and lignin phenols [Feng et al., 2011; Galy and Eglinton, 2011], aged OC\textsubscript{biosph} defined by Δ14C = −885‰ [Galy and Eglinton, 2011], and OC\textsubscript{petro} with Δ14C = −100‰, and that each Gaussian component can be comprised of a binary mixture of two of these known OC components. Such a calculation for each sample suggests separations of predominantly recent OC\textsubscript{biosph} (C1, 75–96% recent OC\textsubscript{biosph}), predominantly aged OC\textsubscript{biosph} (C2, 93–97% aged OC\textsubscript{biosph}), and mixtures of OC\textsubscript{petro} and aged OC\textsubscript{biosph} (C3 and C4, 21–46% OC\textsubscript{petro}). The amount of OC\textsubscript{petro} combined in C3 and C4 is 0.08% and 0.17% of the mass of suspended sediment (31% and 47% of the suspended particulate OC) for the 2005 and 2007 samples, respectively. The calculated OC\textsubscript{petro} concentration for the 2005 sample (0.08%) is essentially identical to the OC\textsubscript{petro} estimated in Galy et al. [2008b] of 0.067 ± 0.017%. For the 2007 sample, the calculated OC\textsubscript{petro} concentration (0.17%) is considerably higher than the OC\textsubscript{petro} of 0.076 ± 0.017% estimated for suspended sediments collected one week later [Galy and Eglinton, 2011]. However, the similarity in measured ages between the two samples despite the relatively larger high-temperature peak in the 2007 sample is consistent with the larger OC\textsubscript{petro} amount found in 2007. Thus, ramped pyrolysis treated with a Gaussian decomposition model, similar to other pyrolysis studies [Burnham and Braun, 1999; Cramer, 2004; Cramer et al., 2001], lends more detail to the inferred proportion of OC\textsubscript{petro} in sediment from the headwaters of the Ganges River. Specifically, our results suggest that OC\textsubscript{petro} concentrations in Narayani River sediments are more temporally variable than initially inferred by previous work [Galy et al., 2008b; Galy and Eglinton, 2011]. Moreover, the ramped pyrolysis method is based on actual analysis of CO\textsubscript{2} derived from OC\textsubscript{petro} that is otherwise difficult to chemically extract.

These data also successfully constrain the residence time of OC\textsubscript{biosph} critical for understanding the role of OC cycling over timescales such as glacial-interglacial cycles and the anthropocene. Figures 2c and 2d illustrate that the first component (mostly recent OC\textsubscript{biosph}) has −24‰ < Δ14C < −224‰. These values can be compared with 14C content of vascular plant biomarkers extracted from the same samples. Overall, C1 has Δ14C values in the same range as two classes of vascular plant biomarkers (long chain fatty acids – C24 FA’s - and lignin phenols) (Table 1). In detail, the value of the C1 component from the 2005 monsoon sample (Figure 2c) is younger than the average of long chain fatty acids (Table 1), whereas that from the 2007 monsoon is older than both long chain fatty acids and lignin phenols (Table 1) [Feng et al., 2011; Galy and Eglinton, 2011]. Ramped-pyrolysis therefore characterizes the age structure of OC\textsubscript{biosph} in a manner that is complementary with compound-specific radiocarbon dating of OC that is chemically extractable. Indeed, ramped-pyrolysis allows characterizing a wider portion of the OC\textsubscript{biosph} spectrum than compound specific measurements while the latter allows specifically targeting a fraction of OC\textsubscript{biosph} (e.g., vascular plants).

The Narayani River samples were taken from a tributary within a large river system integrating parts which can each be characterized differently in terms of riverine carbon cycling. Considered in isolation of the large river system of which it is part, the Narayani River is more like a small mountainous river (SMR) that contains carbon mainly from two unique sources displaying different radiocarbon signatures [Blair and Aller, 2012; Blair et al., 2004]. This type of system differs from large, integrating river systems such as the Ganges, Mississippi/Missouri, and Amazon, all of which contain more complex mixtures of POC. Such rivers with extensive networks of tributaries spanning various geologies not only mix different sources of POC, but they also provide enough OC residence time for different degrees of in situ reworking of OC, including OC\textsubscript{petro} [Bianchi, 2011; Bouchez et al., 2010; Caraco et al., 2010; Galy et al., 2008a, 2011; Raymond et al., 2004]. We thus compare the ramped pyrolysis data from the Narayani River POC samples to several similar analyses of Mississippi-Atchafalaya POC (Figure 3). Comparison of the age differences between youngest and oldest measured 14C ages (Figure 3) of the two systems shows that the Narayani River samples have a much wider age spectrum that relates to a much different pyrolysis profile. Furthermore, the Mississippi-Atchafalaya data (Rosenheim et al., submitted manuscript, 2012) are internally consistent compared to the Narayani River data even though they are sampled over different flow regimes and at different locations within the distributary system. The temperature of maximum CO\textsubscript{2} evolution (T\textsubscript{max}) is always lower in the Mississippi-Atchafalaya POC, despite some small but significant variability, and the ages are always less extreme at both ends of the spectrum than in the Narayani River POC. This contrast between the two types of river systems supports theories concerning river basin size, geology, and age of exported POC [Blair and Aller, 2012].

5. Conclusions

The separation of two distinct pools of riverine OC within the bulk OC is unique. Generally, it is difficult to analyze the more stable, refractory portions of bulk carbon samples because they are too chemically complex [Hedges et al., 2001; Burdige, 2007]. Information from that portion of riverine POC represents an advance with potential to
increase our understanding of river - ocean carbon cycling. Furthermore, we use a unique dataset to illustrate the difference in age spectrum between a SMR incising old, carbon-bearing bedrock and a large river system meandering through a relatively low-slope floodplain. Milliman and Syvitski [1992] showed that SMRs are important in global carbon cycling due to their collective erosive capability; here we illustrate that they are likely significantly different in terms of the age spectrum of POC transported toward the sea.

[14] In sum, these results from “SMR-like” POC, 1) apportion OC\textsubscript{petro} and OC\textsubscript{biosph} contributions to bulk POC and, 2) characterize OC\textsubscript{biosph} residence time. Application of ramped-pyrolysis radiocarbon dating to additional SMRs as well as to larger, integrative river systems will enable constraint of river processes that alter OC. Furthermore, comparison between ramped-pyrolysis data from river sediments and cored deltaic and marine deposits will enable determination of the contribution of riverine and marine processes in the transformation and burial of terrigenous OC, an important link in the global carbon cycle. It is expected that incorporation of ramped pyrolysis radiocarbon analysis into compositional riverine POC investigations will further shape emerging theories about the relationships between basin geometry, geology, and carbon cycling [Blair and Aller, 2012].

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