# Direct measurement of riverine particulate organic carbon age structure

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[1]  Carbon cycling studies focusing on transport and transformation of terrigenous 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 $CO_2$ and $O_2$. 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 biospheric and petrogenic fractions of bulk particulate OC and characterize biospheric 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 ($OC_{biosph}$, 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 ($OC_{petro}$, chemically refractive rock-bound carbon derived from erosion of carbonaceous rocks) to marine environments. In the marine environment some fraction of $OC_{biosph}$ and $OC_{petro}$ can be assimilated and remineralized, and the remainder buried. The remineralization of $OC_{biosph}$ represents a biologic transfer that bypasses the geologic carbon cycle; whereas the burial of $OC_{petro}$ represents transfer from one geologic reservoir (continental bedrock) to another (marine sediments). Conversely, the remineralization of $OC_{petro}$ [e.g., *Caraco et al.*, 2010] and the burial of $OC_{biosph}$ represent transfers between the geologic and biologic carbon cycles. Thus, the ratio of recent $OC_{biosph}$ to $OC_{petro}$ 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 ($O_2$) and carbon dioxide ($CO_2$) in the atmosphere over Earth's history [*Berner*, 1982].

[3]  Much has been learned through characterization of the younger $OC_{biosph}$ pool in recent decades, but large portions of riverine OC remain uncharacterizable. Isolation of components of $OC_{biosph}$ 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 [*Goñi et al.*, 1997; *Hedges and Parker*, 1976; *Hedges et al.*, 1997]. Extraction of alkanes and individual plant wax fatty acids has served to constrain $OC_{biosph}$ [*Drenzek et al.*, 2007] and to demonstrate that $OC_{biosph}$ 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 $OC_{petro}$ in lieu of extraction and measurement is necessary to constrain riverine $OC_{petro}$ flux [*Galy et al.*, 2008b; *Hilton et al.*, 2008]. Radiocarbon dating of bulk riverine OC has been extensively used to tease apart petrogenic and biospheric 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 $OC_{petro}$ – 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,

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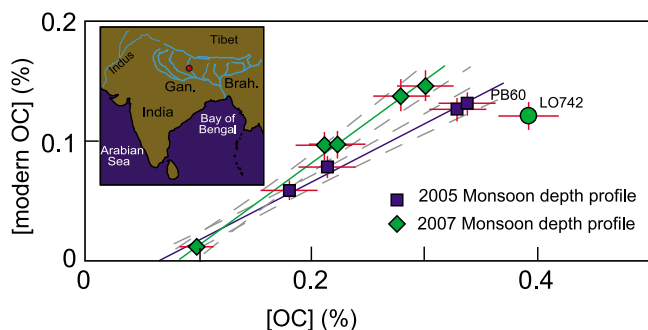
**Figure 1.** Modern carbon content (%$C_{org}$ × Fm) as a function of the total OC content for depth profiles of Narayani River sediments (see inset). In this diagram, sediments with similar $OC_{petro}$ concentration and age of $OC_{biosph}$ plot on linear mixing lines, with the $OC_{petro}$ concentration given by the intercept of the mixing lines [from *Galy et al.*, 2008a, 2008b; *Galy and Eglinton*, 2011]. Statistical analysis demonstrates this is the case for the two series of samples considered (2005 and 2007 monsoon). This approach estimates $OC_{petro}$ concentration of 0.067 ± 0.017% for the 2005 monsoon sampling, and 0.076 ± 0.017% for the 2007 monsoon sampling. LO742 (green circle) - the sample analyzed in Figures 2b and 2d – was collected one week before the depth profile sampling of the 2007 monsoon.

and the *Hilton et al.* [2008] approach applied to larger systems than those studied in Taiwan and New Zealand relies on the assumption that such systems would only mix two sources of POC.

[4] Here, we employ 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 $OC_{petro}$ that closely matches previous inference of $OC_{petro}$. Furthermore, the method produces a clear separation of both young and old $OC_{biosph}$ from $OC_{petro}$ 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 terrigenous 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 $CO_2$ analyzer (Figure 2). Samples of $CO_2$ 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 $\mu$m 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 $CO_2$ (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 $\mu$mol 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 $f_M$ = $\left[ \dfrac{\left(\frac{^{14}C}{^{12}C}\right)_{sample}}{\left(\frac{^{14}C}{^{12}C}\right)_{modern,1950}} \right]$, [where the modern value is 95% of the radiocarbon content in 1950 of NBS Oxalic Acid I normalized to $\delta^{13}C = -19$‰ 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 $\delta^{13}C$ values systematically slightly lower than measured values (Table 1). Fractionation is supported by the calculation of $\delta^{13}C$ 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 chronometer's dynamic range. In fact, the oldest measurement is 30,100 $^{14}C$ y ($\Delta^{14}C = -976.5$‰), close to the limit of $\Delta^{14}C_{OCpetro} = -1000$‰. Such separation is remarkable from
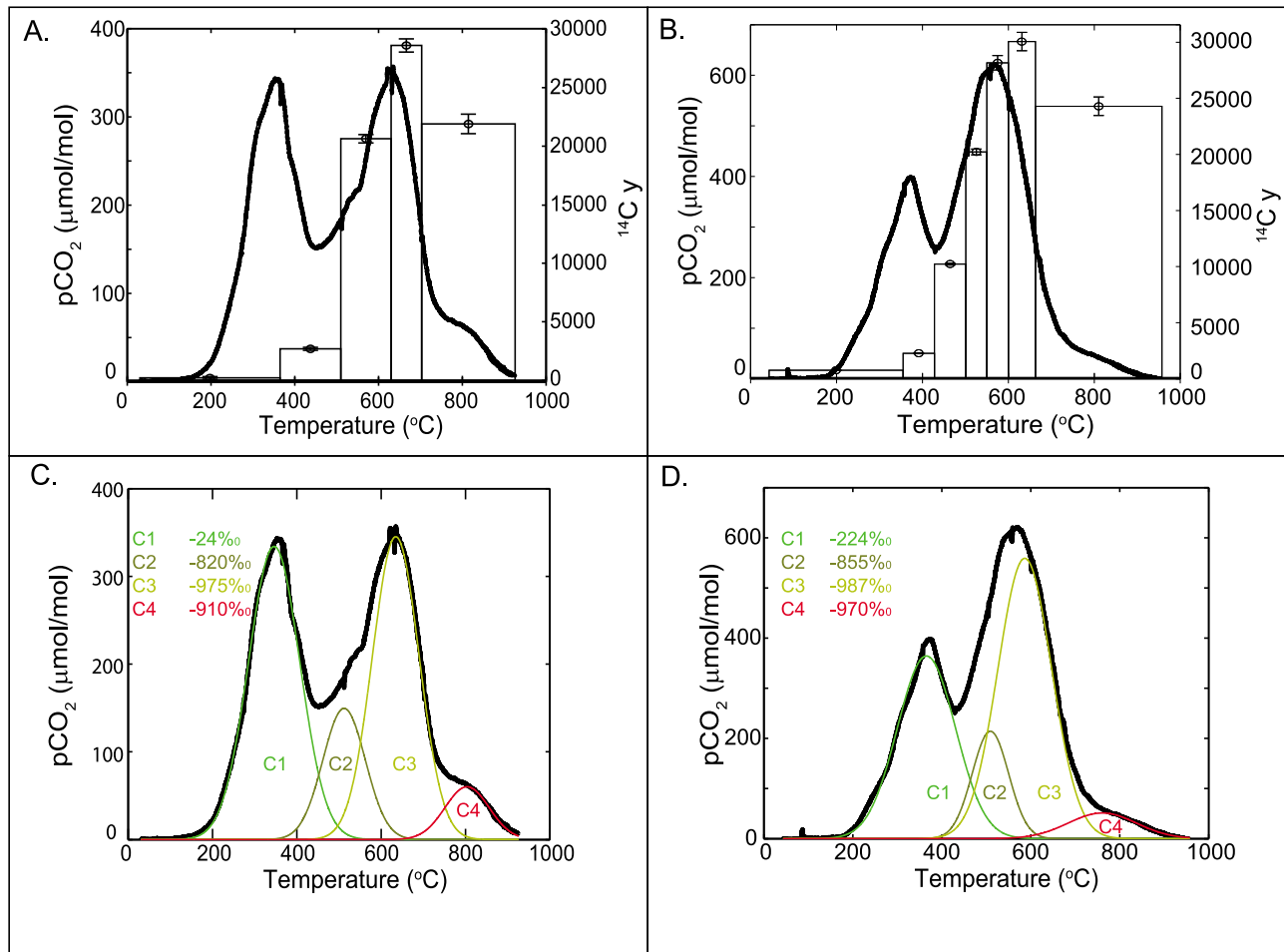
**Figure 2.** Ramped pyrolysis data from two different monsoons in the Narayani River (Figure 1). (a) Ramped pyrolysis and age measurements for the 2005 monsoon and (b) the same for the 2007 monsoon. Both data sets show similarities: they are both bimodal and the different modes show both very young $^{14}C$ 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[a]

| Sample | $\mu$mol $CO_2$ (RP) | Max T (°C) | $f_M$ (1$\sigma$) | $\delta^{13}C$ (PDB) | Age, $^{14}C$ y |
|---|---|---|---|---|---|
| 2005 Narayani Bulk | n/a (0.33% TOC) | n/a | 0.39 (0.006) | −24.5 | 7,540 |
| 2007 Narayani Bulk | n/a (0.40%TOC) | n/a | 0.31 (0.002) | −23.9 | 9,350 |
| 2005 C24+ FA Average | n/a | n/a | 0.846 (0.019) | n/a | 1,350 |
| 2007 C24+ FA – Lignin phenols Average | n/a | n/a | 0.997 (0.022) | n/a | 24 |
| RP 1, 2005 | 12.2 | 365 | 0.9746 (0.0069) | −26.92 | 205 |
| RP 2, 2005 | 12.1 | 510 | 0.6075 (0.0058) | −28.02 | 4000 |
| RP 3, 2005 | 12.3 | 630 | 0.0784 (0.0014) | −27.48 | 20,500 |
| RP 4, 2005 | 12.2 | 703 | 0.0316 (0.0008) | −24.38 | 27,800 |
| RP 5, 2005 | 5.5 | 1000 | 0.0774 (0.0032) | −25 | 20,600 |
| Geometric Mean/Sum | 54.3 (0.26% TOC) | n/a | 0.3870 (0.0097) | −26.54 | 7,626 |
| RP 1, 2007 | 14.8 | 355 | 0.909 (0.0021) | −26.58 | 765 |
| RP 2, 2007 | 10.8 | 428 | 0.7535 (0.0023) | −27.12 | 2,270 |
| RP 3, 2007 | 10.7 | 501 | 0.28 (0.0016) | −27.51 | 10,250 |
| RP 4, 2007 | 12.4 | 550 | 0.0807 (0.0013) | −26.51 | 20,200 |
| RP 5, 2007 | 11.6 | 600 | 0.03 (0.0012) | −25.76 | 28,200 |
| RP 6, 2007 | 11.8 | 663 | 0.0237 (0.0012) | −24.73 | 30,100 |
| RP 7, 2007 | 8.9 | 1000 | 0.04826 (0.0025) | −23.39 | 24,300 |
| Geometric Mean/Sum | 80.96 (0.37% TOC) | n/a | 0.3289 (0.0048) | −26.03 | 8,934 |

[a]"RP" stands for ramped pyrolysis.

a natural sample that likely undergoes some chemical mixing between different-aged constituents during pyrolysis.

## 4. Discussion

[9] Recent work identifying protracted storage of $OC_{biosph}$ in the Ganges-Brahmaputra system [*Galy and Eglinton*, 2011] shows that $OC_{biosph}$ can be up to 17,400 [14]C y old ($\Delta^{14}C = -885‰$). 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 $OC_{petro}$ to constrain the relative contributions of $OC_{petro}$, recent $OC_{biosph}$, and pre-aged $OC_{biosph}$.

[10] 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 $OC_{biosph}$ defined by radiocarbon ages of long chain fatty acids and lignin phenols [*Feng et al.*, 2011; *Galy and Eglinton*, 2011], aged $OC_{biosph}$ defined by $\Delta^{14}C = -885‰$ [*Galy and Eglinton*, 2011], and $OC_{petro}$ with $\Delta^{14}C = -1000‰$, 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 $OC_{biosph}$ (C1, 75–96% recent $OC_{biosph}$), predominantly aged $OC_{biosph}$ (C2, 93–97% aged $OC_{biosph}$), and mixtures of $OC_{petro}$ and aged $OC_{biosph}$ (C3 and C4, 21–46% $OC_{petro}$). The amount of $OC_{petro}$ 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 $OC_{petro}$ concentration for the 2005 sample (0.08%) is essentially identical to the $OC_{petro}$ estimated in *Galy et al.* [2008b] of 0.067 ± 0.017%. For the 2007 sample, the calculated $OC_{petro}$ concentration (0.17%) is considerably higher than the $OC_{petro}$ 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 $OC_{petro}$ 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 $OC_{petro}$ in sediment from the headwaters of the Ganges River. Specifically, our results suggest that $OC_{petro}$ 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 $CO_2$ derived from $OC_{petro}$ that is otherwise difficult to chemically extract.

[11] These data also successfully constrain the residence time of $OC_{biosph}$, 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 $OC_{biosph}$) has $-24‰ < \Delta^{14}C < -224‰$. These values can be compared with ^{14}C content of vascular plant biomarkers extracted from the same samples. Overall, C1 has $\Delta^{14}C$ 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 $OC_{biosph}$ 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 $OC_{biosph}$ spectrum than compound specific measurements while the latter allows specifically targeting a fraction of $OC_{biosph}$ (e.g., vascular plants).

[12] 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 $OC_{petro}$ [*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 ^{14}C 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 $CO_2$ evolution ($T_{max}$) 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

[13] 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
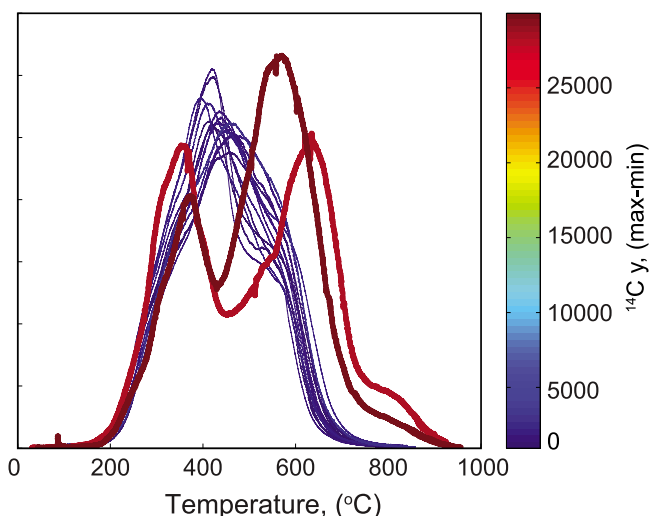
**Figure 3.** Normalized thermographs from the Narayani River (thick lines, same data as Figure 2) compared to analysis of several samples from the lower Mississippi and Atchafalaya Rivers. Here, the y-axis values are normalized so that the area under each curve is equal; therefore it is a unitless estimation of decomposition rate during pyrolysis measured as the ultimate product ($CO_2$). Colors represent the age difference ($^{14}C$ y) between the oldest measured sample and the youngest measured sample. Differences between the Mississippi-Atchafalaya samples are evident, however they are internally consistent compared to the Narayani River data. Differences in shape and temperature of maximum $CO_2$ evolution ($T_{max}$) relate strongly to differences in the age spectrum between the youngest and oldest measurements. Comparison of these two river systems yields no age differences in the middle of the spectrum.

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 SRMs 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 $OC_{petro}$ and $OC_{biosph}$ contributions to bulk POC and, 2) characterize $OC_{biosph}$ 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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