Biogeochemical characterization of carbon sources in the Strickland and Fly rivers, Papua New Guinea

Simone R. Alin,[1] Rolf Aalto,[2] Miguel A. Goni,[3] Jeffrey E. Richey,[1] and William E. Dietrich[4]

[1] The highstanding islands of Oceania are recognized as a source of significant particulate organic carbon delivered to nearshore marine environments. The existing data on carbon export in Oceania are largely derived from small mountainous watersheds (<10,000 km^2) with little or no sediment storage capacity and located in subtropical to temperate regions. The Fly-Strickland fluvial dispersal system is the largest in tropical Oceania and has high sediment yields, aged organic matter in its suspended-sediment load, and lowland sediment storage capacity. The Fly River system also has very high soil organic carbon content and conditions favorable to perennially high production, oxidation, and discharge within the watershed. We used stable and radiogenic isotopes (δ^{13}C, Δ^{14}C, and δ^{15}N), lignin phenols, and X-ray photoelectron spectroscopy to examine the organic and inorganic composition of particulate and dissolved carbon at several lowland sites in the Fly and Strickland rivers and on the Strickland River floodplain. Isotopic, elemental, and biomarker results suggest that organic carbon in the Strickland River was more degraded than in the Fly River, with a greater input of ancient organics from upland sources, and that aquatic production constituted a larger source in the Fly River. Radiocarbon results indicate that all carbon fractions were older in the Strickland than in the Fly and that Strickland floodplain sediments were also depleted in radiocarbon. Collectively, these results suggest that rivers of New Guinea export a comparable amount of particulate organic carbon to the Amazon, with a significant contribution from radiocarbon-depleted sources.

1. Introduction

[2] The wet, mountainous watersheds of Oceania are estimated to discharge perhaps as much as half of the global sediment flux from rivers to the marine environment as well as 17–35% of the global riverine POC flux to the ocean [*Milliman and Syvitski*, 1992; *Lyons et al.*, 2002]. The Fly-Strickland fluvial dispersal system is the largest river basin in tropical Oceania, ranking among the top 25 rivers in the world for water and sediment discharge at 189×10^9 m^3 a^{-1} and 85 Mt a^{-1}, respectively [*Harris et al.*, 1993; *Wolanski et al.*, 1997]. In addition, the Fly River basin has the highest soil organic carbon content in a database of 60 major world river basins (34.9 kg C m^{-3}) [*Ludwig et al.*, 1996]. On the basis of these data, the delivery of particulate organic carbon from this system to the ocean should be substantial.

[3] The bulk of the riverine flux of sediment and carbon to marine environments in Oceania is carried by small mountainous rivers (SMR), defined as having a basin area <10,000 km^2 and source elevations of 1000–3000 m. SMR typically discharge particulate organic carbon (POC) with depleted radiocarbon contents that are consistent with elevated contributions from aged or ancient sources and have minimal lowland sediment storage capacity in their watersheds [e.g., *Blair et al.*, 2003; *Leithold et al.*, 2006]. Sediment yield appears to be a critical predictor in determining the radiocarbon content of POC exported by small mountainous rivers [*Komada et al.*, 2004], although it has been argued that the use of sediment yield as a proxy for sediment transport processes breaks down at larger basin sizes because of the contribution of increasing lowland area to sediment storage [*Aalto et al.*, 2006]. In a study of eight subtropical to temperate SMR, sediment yields ranging from 125 to 20,520 t km^{-2} a^{-1} generated riverine POC loads with Δ^{14}C values decreasing from +70 to −870‰ (average ± SD = −383 ± 308‰, with the range equivalent to values of 1.05 to 0.1 fraction modern ^{14}C) [*Leithold et al.*, 2006]. The interpretation of this relationship has been

[1]School of Oceanography, University of Washington, Seattle, Washington, USA.
[2]Department of Geography, University of Exeter, Exeter, UK.
[3]College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.
[4]Department of Earth and Planetary Science, University of California, Berkeley, California, USA.

that the large loads of sediment and ancient organic matter mobilized from the uplands of these small, steep watersheds are transported to marine environments on timescales too short for significant alteration or storage to occur en route.

[4] In river systems with more modest relief, the magnitude of sediment delivery per unit watershed area and the contribution of aged/ancient POC to the sediment load exported to the ocean may decrease as sediment storage and chemical weathering rates increase [*Stallard*, 1995; *Dunne et al.*, 1998; *Smith and Alsdorf*, 1998; *Petsch et al.*, 2000; *Aalto*, 2002; *Aalto et al.*, 2006]. Radiocarbon analyses of particulates from more lowland influenced or dominated rivers, including the Amazon, Hudson, Delaware, York, Parker, Susquehanna, Mississippi/Atchafalaya, and Mackenzie rivers, show that these rivers also export POC with variable and fairly depleted $\Delta^{14}C$ compositions, consistent with contributions from modern, aged, and ancient sources (+47 to −714‰, average ± SD = −207 ± 210‰) [*Raymond and Bauer*, 2001; *Gordon and Goni*, 2004; *Raymond et al.*, 2004; *Goni et al.*, 2005; *Mayorga et al.*, 2005]. Among this group of rivers, the radiocarbon content of exported POC does not appear to be related to either sediment yield or watershed size. Land use and the prevalence of ancient sedimentary matter in each watershed account for some of the variation, particularly among the smaller rivers [e.g., *Raymond and Bauer*, 2001; *Raymond et al.*, 2004]. The three largest rivers in this group (Amazon, Mississippi, and Mackenzie) have watershed areas greater than a million km^2 and integrate across regions with more diverse geology and land cover/land use than the smaller rivers. Across these largest rivers, the radiocarbon content of exported POC appears to become increasingly depleted as latitude increases. Differences in carbon cycle processes affected by temperature between low- and high-latitude river systems, such as rates of OC accumulation and degradation in floodplain soils, may account for this trend and play a role in controlling the quantity and radiocarbon content of POC exported from larger and/or lowland-dominated watersheds [cf. *Eglinton et al.*, 2006].

[5] The Fly-Strickland river system of Papua New Guinea (PNG) provides an interesting comparison to previously studied sediment delivery systems. As a relatively large tropical river, its basin area is substantially larger than SMR (75,000 km^2), yet only about a tenth as large as the Amazon basin. The Fly River basin has a sediment yield comparable to SMR, corresponding to the largest values for a basin of its size globally (1500 t km^{-2} a^{-1}) [*Milliman and Syvitski*, 1992], and radiocarbon values from the Fly River Delta clearly suggest that the system exports POC that is substantially depleted in ^{14}C [*Goni et al.*, 2006, 2008].

[6] The lowland reaches of the Fly-Strickland river system are occupied by a narrow but well-developed floodplain, representing the opportunity for significant sediment storage between sediment mobilization and delivery to the marine environment, as well as the potential for altering upland ancient organic matter composition by the addition of contemporary lowland sources [*Dietrich et al.*, 1999; *Aalto et al.*, 2008; *Swanson et al.*, 2008]. The Fly-Strickland river system represents another important datum in the study of the interacting factors of latitude and basin geomorphology on the ultimate age of exported POC. Within the Fly-Strickland system, the Strickland floodplain has

sediment accumulation and lateral migration rates roughly an order of magnitude higher than does the Fly, although a smaller percentage of the Strickland's total sediment load is deposited in its floodplain annually [*Dietrich et al.*, 1999; *Aalto et al.*, 2008; *Swanson et al.*, 2008]. The large difference in the rates of dynamic exchange of sediment between the Fly and Strickland rivers and their floodplains also presents an interesting opportunity to contrast carbon cycle processes between these two main tributaries within the Fly-Strickland system [e.g., *Dietrich et al.*, 1999; *Aalto et al.*, 2008; *Day et al.*, 2008].

[7] Furthermore, debate over whether carbon diagenesis and remineralization in the Fly River delta operate at rates and with efficiency tantamount to those observed in the Amazon River delta [e.g., *Aller et al.*, 1996; *Keil et al.*, 1997; *Aller and Blair*, 2004] cannot be fully resolved without better characterization of the organic load being delivered to the nearshore marine environment. Recent results suggest that the carbon burial in the Fly River delta may operate more similarly to the Eel River delta, where a significant portion of the terrestrial organic carbon delivered to the delta, mostly during large floods, is buried without substantial diagenetic alteration or losses [*Leithold and Blair*, 2001; *Goni et al.*, 2006, 2008]. Previous studies comparing the composition of organic matter in the Fly River delta with samples from the river itself have been hindered by the scarcity of river samples and by the lack of samples from upriver of the mouth [e.g., *Bird et al.*, 1995; *Keil et al.*, 1997; *Aller and Blair*, 2004; *Goni et al.*, 2006, 2008].

[8] Here we present an analysis of the carbon biogeochemistry of the lowland portion of the Fly River and its major tributary, the Strickland River (Figure 1). The samples were collected in June 2003 during a falling stage of the hydrograph at a time of year that typically has intermediate discharge [cf. *Ogston et al.*, 2008]. Earlier in the year, the river system experienced both low flows associated with the El Niño/Southern Oscillation (ENSO) (January 2003 [*Goni et al.*, 2006]) and periods of widespread overbank flood flooding (late March to early April and May 2003) (Figure 2). This study focuses in particular on characterizing the particulate organic matter transported by the Fly and Strickland rivers, in order to facilitate comparisons between organic material reaching the delta and its watershed sources.

2. Study Area

[9] The Fly-Strickland river system drains a 75,000 km^2 basin on the southern margin of the island of New Guinea. From the New Guinea highlands (maximum elevation ~4000 m), these rivers flow >1000 km across lowland tropical floodplains to the Gulf of Papua, with an average annual depth of runoff more than an order of magnitude higher than that of the Amazon (1300 versus 100 mm a^{-1}) [*Milliman and Syvitski*, 1992]. Rainfall ranges from 10 m a^{-1} in the mountainous headwaters to 2 m a^{-1} at the coast and is not strongly seasonal [*Harris et al.*, 1993]. As a result, average freshwater discharge into the delta is high with relatively low variability (6000 ± 1500 m^3 s^{-1}), with the exception of El Niño years, when strong drought
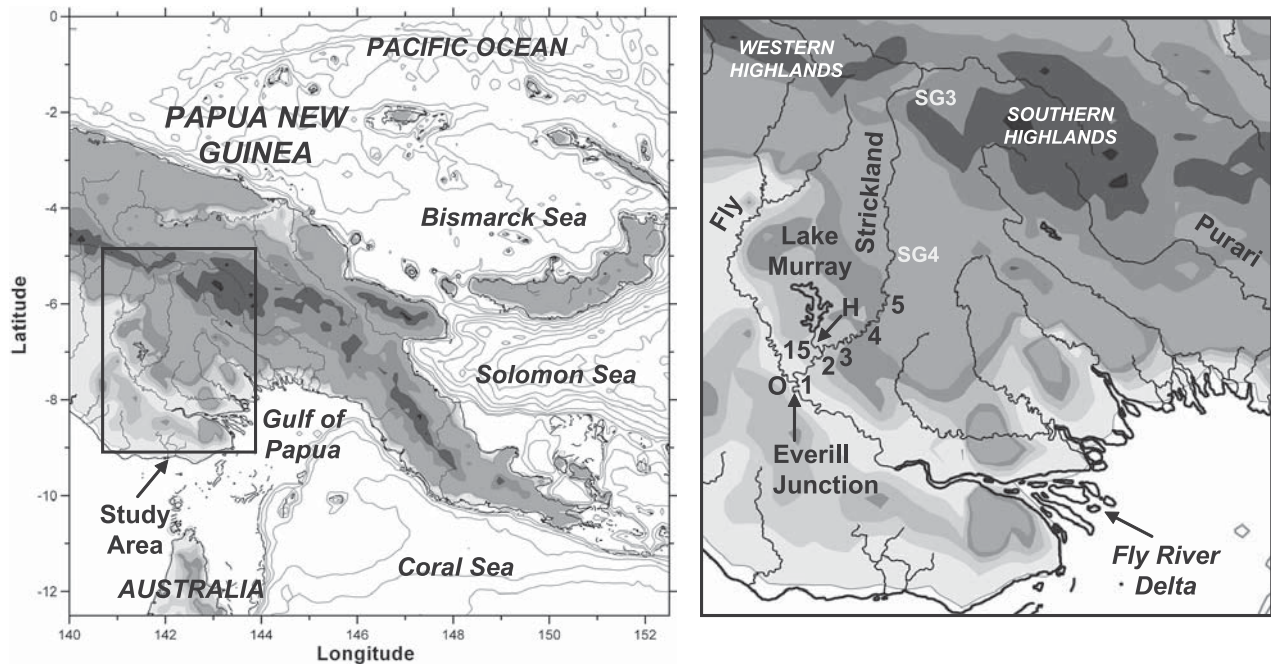
Figure 1. (left) Location of the study area within Papua New Guinea. (right) All Fly River sampling occurred near the village of Obo (O). Locations of Strickland River sites STR1–5 and coring transect 15 are shown by numerals 1–5 and 15, and the Herbert River sampling location is indicated by H. Gauging stations SG3 and SG4 upstream of sampling sites on the Strickland are also shown. Shaded elevation contours occur at 500-m intervals.
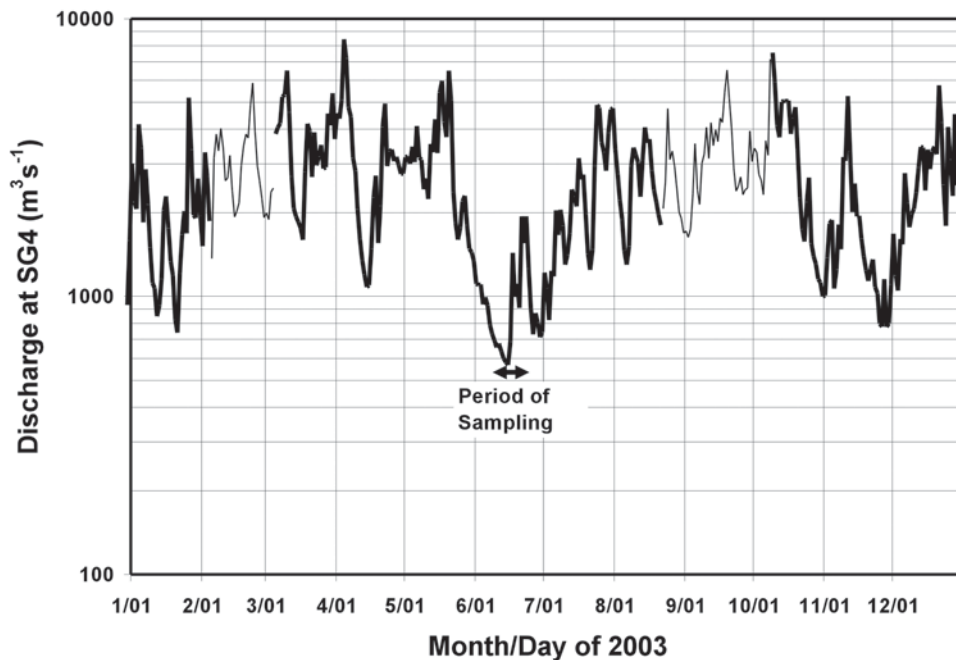

Figure 2. Daily discharge recorded at gauging station SG4 during 2003, located 100–400 km upstream of the study sites along the lower Strickland River. Thick line represents discharge derived from stage measured at SG4, and thin line represents discharge from a correlation to discharge measured upstream at SG3. The flood in early April (8400 m^3 s^{-1}) is one of the four largest on record (see *Aalto et al.* [2008] for further discussion). Period of sampling (denoted) coincides with the lowest recorded discharge in 2003, and immediately follows an extraordinary fall in discharge from 6450 m^3 s^{-1} in the weeks preceding the sampling to 550 m^3 s^{-1} in mid-June. Data provided by Porgera Joint Venture.

Table 1. Location of Sampling Sites

Location	River	Date	Latitude, °S	Longitude, °E
Water and Suspended-Sediment Sampling				
STR1	Strickland	17 June 2003	7.500	141.384
STR2	Strickland	9 June 2003	7.371	142.082
STR3	Strickland	15 June 2003	7.255	141.693
STR4	Strickland	14 June 2003	7.134	141.929
STR5	Strickland	20 June 2003	6.901	142.045
FLY1	Fly	8 June 2003	7.586	141.318
FLY2	Fly	17 June 2003	7.588	141.324
FLY3	Fly	17 June 2003	7.582	141.314
HERB1	Herbert	23 June 2003	7.277	141.506
Floodplain Coring Transects[a]				
15	Strickland		7.388	141.486

[a]Coring transect locations are given as the river location from which transects began; that is, coring transects 1, 3, 4, and 5 were at sites STR1, STR3, STR4, and STR5.

conditions reduce discharge substantially [*Wolanski et al.*, 1997; *Dietrich et al.*, 1999].

[10] Sediment supply stems from very high rates of erosion in the mountainous headwater regions of the Fly and Strickland. Denudation rates of $3-4$ mm a^{-1} have been calculated for some upland areas [*Pickup*, 1984]. Source rocks in the Southern Fold Mountains include limestones, sandstones, and shales of marine origin, and both mass wasting and runoff deliver large quantities of weathered material of all size classes to upland tributaries [*Pickup*, 1984]. Suspended-sediment concentration in rivers correlates well with discharge in upland areas, where the influence of localized rainfall events is discernible, but less well in lower stretches of the rivers, where the integration of inputs from discrete localized events upstream is reflected [*Pickup*, 1984; *Swanson et al.*, 2008].

[11] Water chemistry samples were collected from five sites (STR1–5; Table 1 and Figure 2) along a 250-km reach of the Strickland River upstream from its confluence with the Fly River at Everill Junction. The STR sites are regular sampling locations for the Porgera gold mine, which is located in the headwater region of the Strickland River and maintains a water quality monitoring program. Floodplain sediments were collected at the five STR sites in 1997 and 2003 by coring along transects extending away from the river [*Aalto et al.*, 2008; *Swanson et al.*, 2008]. In addition, three sites on the Fly River just upstream from its confluence with the Strickland were sampled near the village of Obo (FLY1–3). FLY1 and FLY3 were upstream of the village a short distance, whereas FLY2 samples were taken at the village. A large mine also exists on a tributary to the upper Fly, the Ok Tedi Mining Company on the Ok Tedi River, which has increased sediment flux through the Fly River by three- to five-fold since it opened in 1985 [*Dietrich et al.*, 1999].

[12] Within the system, the Strickland carries seven times the sediment load across a slope that is about ten times steeper than the Fly, providing an opportunity to investigate biogeochemical differences associated with particulate flux. Site STR5, the furthest upstream, lies at the end of the gravel bedded section of the Strickland River channel and thus represents a zone of transition from higher to lower gradient. In addition to water chemistry samples from the

Strickland sites, we also present data on organic carbon concentration and composition in the Strickland River floodplain between sites 1 and 5. Finally, a single sampling was done on the sediment-impoverished tributary connecting Lake Murray to the Strickland, the Herbert River. This river experiences bidirectional flow, with most of the sediment in the Herbert River system derived from the Strickland. At the time of sampling, the Herbert was draining from Lake Murray into the Strickland.

3. Methods

[13] During the floodplain coring campaign in June 2003 [see *Aalto et al.*, 2008], water and suspended-sediment samples were opportunistically collected from the three sampling stations on the Fly River and five stations on the Strickland River in Papua New Guinea (Table 1) to characterize the organic and inorganic chemistry of various carbon fractions. At the time of sampling, water level in the Strickland River was approximately one meter below bankfull conditions, receding after widespread overbank flooding between March and May. In the weeks leading up to the period of sampling there was a dramatic decrease in discharge as recorded at gauging station SG4 (Figure 2). While such a tenfold decrease in discharge was not observed in the lower Strickland, probably owing to the buffering effects of floodplain storage, river water level did fall meters to decimeters during the field campaign at upstream and downstream locations, respectively. Field surveys of fresh sediment deposits and sharp silt lines on trees across the floodplain indicated a recent inundation of many floodplain locations to depths of $\sim$1 m, indicating in turn a recent drop in stage of $4-6$ m (upstream sections) to $2-4$ m (downstream sections), as discussed by *Aalto et al.* [2008]. Floodplain lakes on the lower middle Fly River were draining into the Fly River at the time of sampling, representing an important possible carbon source there.

3.1. Field Work

[14] At each site in Papua New Guinea, water chemistry parameters were assessed as follows. Dissolved oxygen concentrations and water temperature were measured directly at the river surface with a portable Thermo Orion DO meter (model 810Aplus) calibrated with water-saturated air. In-stream pH was measured using a portable Thermo Orion meter (model 290Aplus) calibrated with pH 7.00 and pH 10.00 buffers.

[15] Water and suspended-sediment samples were collected from intermediate depths in the rivers using a battery-powered pump attached to Teflon-lined tubing to fill 4-L polyethylene sample bottles through a 63-μm sieve. Water samples were generally filtered within 12 hours of collection and were kept refrigerated between the times of collection and filtration if a longer interval was necessary. At the time of filtration, a churn splitter was used to generate homogenous subsamples from the 4-L sample bottles. Known volumes of water were filtered through preweighed 0.45-μm cellulose membrane filters (in triplicate) to determine fine suspended-sediment (FSS) concentrations. Filtrate from membrane filters was retained for measurement of alkalinity and nutrient concentrations. Known volumes of churn-homogenized water were also

filtered through precombusted 0.7-μm glass fiber filters for analyses of the organic composition (%C, %N, δ^{13}C, δ^{15}N) of the fine particulates (0.7–63 μm). Filtrate from the glass fiber filters was retained and preserved with mercuric chloride for analysis of dissolved organic carbon (DOC) concentrations. Coarse suspended-sediment samples for elemental and isotopic analysis were collected at the river surface by deploying a 63-μm plankton net for several minutes. Unfiltered water samples were collected in 125-mL polycarbonate bottles for analysis of dissolved inorganic carbon (DIC) and preserved with 100 μL saturated mercuric chloride solution.

[16] Floodplain sediments were collected manually in 1-inch diameter core liners and were stored refrigerated, except during shipping, between the time of collection and analysis. Details of core sampling are given by *Aalto et al.* [2008]. Floodplain core chronologies were established by ^{210}Pb geochronology following R. Aalto and C. A. Nittrouer (Application of fallout ^{210}Pb geochronology to river-floodplain systems, manuscript in preparation, 2007) and *Aalto et al.* [2008]. The cores were subsampled within 2-cm intervals displaying relatively constant ^{210}Pb-unsupported activity levels, reflecting rapid deposition events associated with major floods occurring during the last century. An independent set of cores were collected and analyzed for particulate Pb and Ag derived from upstream mine tailings release; these cores indicate average deposition rates of approximately 1.7 cm a^{-1} in the Strickland River floodplain out to 1 km from the bank [*Swanson et al.*, 2008].

3.2. Sample Analysis: Inorganic Chemistry

[17] Alkalinity was measured by micro-Gran titration on 1-mL aliquots from filtered samples [*Edmond*, 1970]. Carbon dioxide concentrations are expressed as pCO$_2$ in units of μatm and were calculated from all possible combinations of pH, alkalinity, and DIC data using freshwater dissociation constants in the program CO2SYS [*Lewis and Wallace*, 1998].

[18] Preserved DIC samples were stored refrigerated for 3 annums before analysis, at which time 100-mL aliquots were acidified and bubbled with helium to strip inorganic carbon from the solution. Concentrations were measured manometrically in the Oceanography Stable Isotope Laboratory at University of Washington. Carbon stable isotope ratios (δ^{13}C) of DIC were measured on a Finnigan MAT 251 mass spectrometer and are reported relative to the VPDB standard (reproducibility: $\pm$0.025‰) [*Quay and Stutsman*, 2003]. CO$_2$ remaining in ampoules from DIC analyses was graphitized by the iron/zinc reduction method and analyzed for radiocarbon content at the NSF Arizona Accelerator Mass Spectrometry Laboratory. All radiocarbon results are reported here as Δ^{14}C in per mil units (‰), where Δ^{14}C = δ^{14}C$-2(\delta^{13}$C + 25)(1 + δ^{14}C/1000), δ^{14}C = (F$_{mod}$ − 1) × 1000, and F$_{mod}$ = fraction modern [*Stuiver and Polach*, 1977]. Results reported as Δ^{14}C have been normalized to account for fractionation in the sample based on δ^{13}C values (precision $\approx$ 0.5%). The δ^{13}C of CO$_2$ was calculated on the basis of δ^{13}C$_{DIC}$, the calculated distribution of DIC among species [*Zeebe and Wolf-Gladrow*, 2001], and fractionation factors from *Zhang et al.* [1995].

[19] Plastic bottles are generally thought to be unsuitable for DIC storage on the basis that they are known to leak dissolved gases. We compared the performance of the standard 250-mL glass bottles with ground glass stoppers to the same type of Nalgene polycarbonate bottles used to store our samples over an incubation period of 2 months. The bottles were filled with seawater from Puget Sound filtered through sand and a fine filter and treated with UV (obtained from Seattle Aquarium). The seawater was siphoned into the bottles from a drum and subsequently poisoned with 100 μL saturated mercuric chloride. At the end of the 2-month period, the concentrations of DIC were 1964.6 ± 3.7 μmol/kg seawater (n = 3) in the glass bottles and 1966.6 ± 0.2 μmol/kg seawater (n = 3) in the polycarbonate bottles. Carbon stable isotope values were −0.03 ± 0.02‰ and −0.01 ± 0.01‰ in the glass and polycarbonate bottles, respectively. If we extrapolate the magnitude of these changes in concentration and isotopic composition over the 3-annum storage period that our samples experienced, we might expect to see changes of ∼36 μmol/kg seawater (<2%) and +0.3‰ in δ^{13}C. While these results would clearly be unacceptable for ocean carbonate chemistry work, where great precision and accuracy are required to detect the small changes in DIC typical of marine environments, we argue that errors of <5% in concentration and <1‰ in δ^{13}C are acceptable (albeit clearly not desirable) in the present work, as the observed differences are much larger, both between the Fly and Strickland Rivers and among sampling stations along the Strickland (Table 2).

[20] Nutrient samples were analyzed spectrophotometrically for phosphate, silicate, nitrate, nitrite, and ammonium (PO$_4$, Si(OH)$_4$, NO$_3$, NO$_2$, and NH$_4$, respectively) according to the Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements [*UNESCO*, 1994].

3.3. Sample Analysis: Organic Composition

[21] Membrane and glass fiber filters were dried at 60°C. All membrane filters were weighed to ±0.00001 g to determine the concentration of fine suspended sediments.

[22] All fine and coarse particulate samples as well as the floodplain core samples were analyzed for organic elemental and stable isotopic composition (% organic carbon [OC], % total nitrogen [TN], δ^{13}C, δ^{15}N) at the UW Stable Isotope Laboratory (fine particulates) or the University of Arizona Environmental Isotope Laboratory (coarse particulates and floodplain samples). Precision of stable isotope analyses are 0.1‰ and 0.25‰ for carbon and nitrogen, respectively. Filters with fine particulates were acidified with 1 N hydrochloric acid to remove inorganic carbon and allowed to air dry prior to packaging in sample tins. Coarse particulates from the rivers and floodplain core samples were soaked overnight in 1 N hydrochloric acid to remove carbonates. After acid treatment, sediments were centrifuged, the supernatant decanted, and the sediments rinsed, mixed by vortexing, and centrifuged twice more. Sediments were then dried at 60°C and pulverized prior to elemental and isotopic analysis. Large root fragments (>2 mm) were removed from floodplain samples prior to homogenizing.

[23] Lignin and nonlignin reaction products in coarse particulate and floodplain samples were quantified using alkaline CuO oxidation following the method of *Goni and Montgomery* [2000] (for details, see also *Goni et al.*

Table 2. Water Chemistry Data for River Sampling Stations in Papua New Guinea

Sampling Location	Water Temperature, °C	pH	Dissolved O_2, mg L^{-1}	O_2 Saturation (× Atmospheric)	pCO_2 (Calculated), [a] μatm	CO_2 Saturation (× Atmospheric)	Alkalinity, μeq L^{-1}	DIC, μmol kg^{-1}	$\delta^{13}C_{DIC}$, ‰	$\delta^{13}C_{CO2}$, ‰	$[PO_4]$, μM	$[Si(OH)_4]$, μM	$[NO_3]$, μM	$[NO_2]$, μM	$[NH_4]$, μM
STR1	27.5	7.48	3.14	0.39	2220–2500	5.9–6.7	1095	1040.8	−9.84	−16.82	0.01	140.07	2.74	0.12	0.24
STR2	27.7	7.48	2.54	0.32	2010–2810	5.4–7.5	893	1335.2	−8.63	−15.61	0.00	131.15	2.65	0.12	0.84
STR3	26.9	7.85	3.70	0.46	1790–1860	4.8–5.0	1888	2013.6	−10.34	−17.72	0.22	215.73	4.19	0.11	0.97
STR4	18.2	7.03	3.97	0.42	10480	27.9	1842	n.a.	n.a.	n.a.	0.05	221.34	3.91	0.11	0.44
STR5	25.1	7.69	5.48	0.66	1910–2030	5.1–5.4	1493	1461.1	−8.82	−16.26	0.18	174.51	3.32	0.08	0.00
Average	*25.1*	*7.50*	*3.77*	*0.45*	*3070*	*8.2*	*1442*	*1462.7*	*−9.41*	*−16.60*	*0.09*	*176.56*	*3.36*	*0.11*	*0.50*
SE	*1.8*	*0.14*	*0.49*	*0.06*	*930*	*2.5*	*198*	*203.7*	*0.41*	*0.45*	*0.05*	*18.62*	*0.31*	*0.01*	*0.18*
FLY1	29.0	7.24	1.10	0.14	3250–4770	8.7–12.7	1180	901.8	−10.81	−17.27	0.01	116.04	1.11	0.08	0.98
FLY2	28.5	6.95	1.64	0.21	6620–7370	17.7–19.7	949	1057.5	−10.53	−16.32	0.01	106.87	1.04	0.11	0.10
FLY3	28.1	6.92	1.54	0.19	7270–8760	19.4–23.4	1044	1094.3	−10.60	−16.30	0.02	108.85	1.11	0.10	1.26
Average	*28.5*	*7.04*	*1.43*	*0.18*	*6340*	*16.9*	*1058*	*1017.8*	*−10.65*	*−16.63*	*0.01*	*110.59*	*1.09*	*0.10*	*0.78*
SE	*0.3*	*0.10*	*0.17*	*0.02*	*810*	*2.2*	*67*	*59.0*	*0.08*	*0.32*	*0.00*	*2.79*	*0.02*	*0.01*	*0.35*
p values[b]	0.20	0.06	0.01	0.01	0.16	0.16	0.20	0.13	0.05	0.97	0.24	0.04	0.001	0.37	0.45
HERB1	28.1	7.06	n.a.	n.a.	1110–1410	3.0–3.8	234	219.7	−8.36	−14.49	0.00	94.73	1.17	0.06	1.20

[a]The pCO_2 values were calculated twice, once using pH and alkalinity as known carbonate system variables and again using pH and DIC as knowns to generate the range shown here.
[b]The p values are for t-tests comparing STR and FLY samples.

[2008]). Because of the interference of the glass-fiber filter material with the alkaline oxidation, the fine particulate river samples, which were collected on glass-fiber filters, were not analyzed by the CuO procedure. After CuO oxidation and derivatization of the reaction products with bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 1% trimethylchlorosilane (TMCS), we quantified the yields of individual lignin and nonlignin oxidation products using GC-MS selective ion monitoring. Of the resulting lignin-derived CuO oxidation products (COP), we quantified the yields of vanillyl (V_{COP}; vanillin, acetovanillone, vanillic acid), syringyl (S_{COP}; syringealdehyde, acetosyringone, syringic acid), and cinnamyl (C_{COP}; p-coumaric acid, ferulic acid) products. The yields of several nonlignin COP were also quantified, including p-hydroxybenzenes (P_{COP}; p-hydroxybenzaldehyde, p-hydroxyacetopheone, p-hydroxybenzoic acid) and other benzoic acids (B_{COP}; benzoic acid, m-hydroxybenzoic acid, 3,5-dihydroxybenzoic acids).

[24] Lignin is a phenolic molecule synthesized by vascular plants such as trees and grasses and that can be used to quantitatively trace terrestrial inputs of organic matter to aquatic environments [e.g., *Hedges et al.*, 1986; *Goni and Thomas*, 2000; *Benner and Opsahl*, 2001; *Gordon and Goni*, 2004]. The nonlignin oxidation products we quantified derive from various biochemical precursors, including aromatic amino acids and phenolic polymers such as tannins. Several types of organisms, representing potential sources of organic matter in the samples analyzed, can biosynthesize these nonlignin compounds, including algae, vascular plants, fungi, and bacteria [e.g., *Goni and Hedges*, 1995; *Goni and Thomas*, 2000].

[25] Fine suspended sediments on membrane filters were analyzed by X-ray photoelectron spectroscopy (XPS) in standard as well as high-resolution carbon (C1s) modes to characterize the surface elemental composition and carbon oxidation state in the fine particulates. XPS spectra allow estimation of the compositional abundance for all elements present in >0.1 atomic percent abundance in the outer 10 nm of sediment particles (precision <10%), as well as giving information about the bonding environment of carbon atoms in the surface organic material associated with mineral sediments [*Ratner and Castner*, 1997]. Two, millimeter-scale spots were measured on one filter per site, with typical reproducibility of ±10%. Unfortunately, prior handling of coarse particulate and floodplain samples (i.e., homogenization) made it impossible to perform XPS analyses on these samples.

[26] High-resolution C1s XPS spectra indicate what percentage of carbon atoms in the surface layers of the organic matter is engaged in different functional groups (Figure 3). Spectra are standardized such that peak 1, the lowest binding energy (BE, in units of electron volts (eV)) peak, falls at 285.0 eV. This peak represents carbon atoms in hydrocarbon bonds (C-H, C-C) [*Ratner and Castner*, 1997]. Aromatic carbon bonds fall in approximately the same location as aliphatic bonds, so are indistinguishable from each other for our purposes. Peak 2 (centered at BE 286.6 eV in this analysis) represents alcohol and ether type carbon bonds (C-O-H, C-O-C); peak 3 (BE 288.3 eV) includes carbonyl and amide bonds (C = O, N-C = O); and peak 4 (BE 289.4 eV) comprises carbon atoms in acid or ester bonds (O-C = O) [*Ratner and Castner*, 1997].
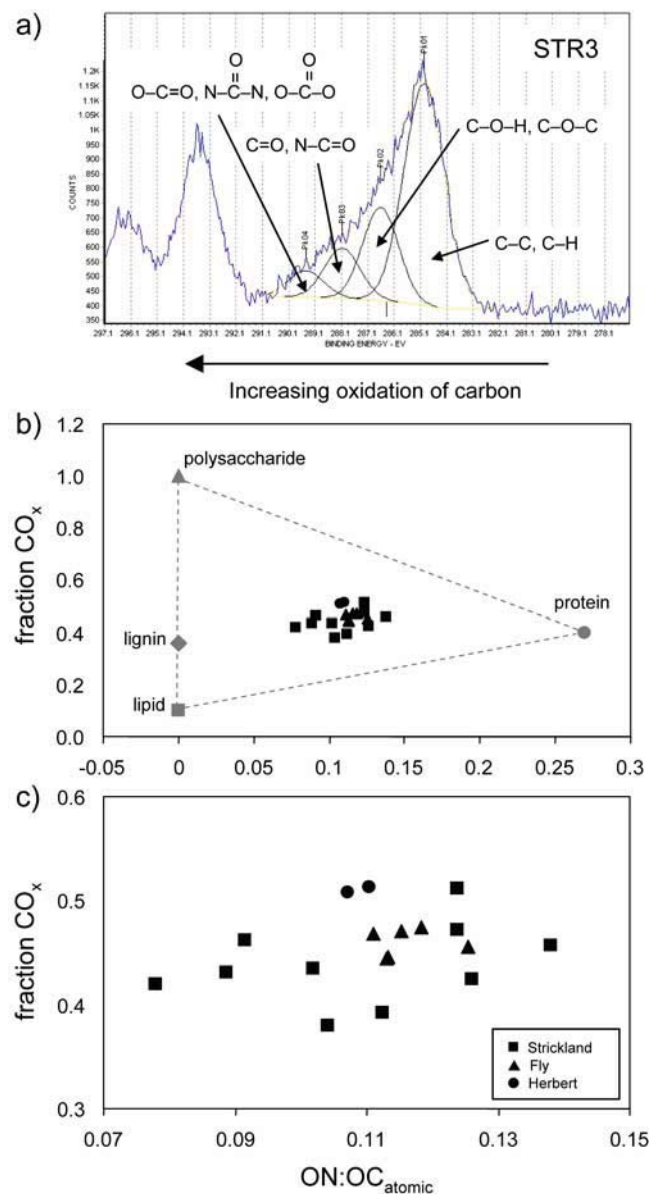
existed between the Fly and Strickland river samples and included the resulting p values in each table. The Herbert River was not included in statistical tests, as there was only one sample from this location. In addition, we compared proximal and distal floodplain samples for compositional differences using t-tests. All data were checked for normality and were log-transformed prior to analysis if they were not normally distributed. In the few cases where the data were not normal after log transformation, the data were not compared statistically (indicated by "NC" in Table 5). Finally, many results were not statistically significant even when an apparent difference existed as a result of the low statistical power associated with the small number of samples.

4. Results

4.1. Inorganic Chemistry

[29] Measured pH for all sites in the Fly, Strickland, and Herbert Rivers was neutral to slightly alkaline, with values between 6.9 and 7.9 (Table 2). On average, pH was 0.5 units lower in the Fly than in the Strickland, reflecting the influence of drainage of the extensive blackwater lake system on its floodplain upstream of the sampling site and/or high levels of mine waste on the Fly River (mine waste is ~5 times background on the Fly). Generally, pH in the Strickland fell between 7.4 and 7.9, although it was roughly 7.0 at site STR4 when it was sampled. Gran-titration alkalinity values fell in the range of $893-1888$ μeq L^{-1} for all Fly and Strickland sites. The Strickland had higher alkalinity and dissolved inorganic carbon concentrations than the Fly on average. The Herbert River had neutral pH and the lowest alkalinity and DIC values sampled (Table 2).

Figure 3. (a) Representative high-resolution carbon spectrum (C1s) for fine particulate sediment fraction in the Strickland River. The unlabeled peaks to the left of the C1s peaks correspond to the potassium content of the surface sediment. (b) Van Krevelen-style plot of ON:OC versus fraction CO_x (fCO_x) from X-ray photoelectron spectroscopy analysis of fine particulate suspended sediments relative to biochemical end-members (polysaccharides, proteins, and lipids) [following *Arnarson and Keil*, 2001] as well as lignins and (c) a magnified view of the data.

[27] Dissolved organic carbon concentrations were measured by high-temperature combustion (750°C) on an MQ Scientific TOC analyzer (MQ-1001) [*Peterson et al.*, 2003]. Reproducibility of measurements with this method is <5%.

3.4. Statistical Analyses

[28] All statistical analyses were done using SYSTAT. For all basic data presented here (i.e., Tables 2–6), we used t-tests to determine whether significant differences

Table 3. Radiocarbon Results for Select Dissolved and Particulate Carbon Fractions

Sample Location or ID	Sample Type	Arizona AMS Number	$\Delta^{14}C$, ‰	$^{14}C_{CO2}$ Age, ^{14}C a B.P.	Fraction Modern ^{14}C
Water Column					
STR1	DIC	70240	−194.3	1490	0.83
STR2	DIC	70237	−372.5	3515	0.65
STR3	DIC	70238	−183.4	1390	0.84
STR5	DIC	70241	−214.3	1670	0.81
Average			*−241.1*	*2016*	*0.78*
SE			*44.3*	*503*	*0.05*
FLY1	DIC	70235	−146.8	1040	0.88
FLY2	DIC	70239	−119.9	790	0.91
FLY3	DIC	70234	−128.5	870	0.90
Average			*−131.8*	*900*	*0.89*
SE			*7.9*	*74*	*0.01*
p values[a]			0.04	0.04	0.09
HERB1	DIC	70236	−102.4	600	0.93
STR1	FPOM	70892	−371.1	3780	0.62
FLY3	FPOM	70893	−275.1	2500	0.73
STR1	CPOM	70435	−184.5	1690	0.81
FLY1	CPOM	70436	−96.8	850	0.90
Floodplain (Distal)					
5 LFB 150 34−36	floodplain	70437	−235.5	2230	0.76
1C LFS 200A 28−30	floodplain	70438	−261.6	2420	0.74
		Average	*−248.6*	*2325*	*0.75*

[a]The p values are for t-tests comparing STR and FLY DIC samples.

Table 4. Organic Carbon Composition of River Water Samples

Sampling Location	DOC, mg L^{-1}	FSS, mg L^{-1}	FPOC, mg L^{-1}	Bulk FPOM OC, %	Bulk FPOM ON, %	Bulk FPOM OC:ON	Bulk FPOM δ^{13}C, ‰	Bulk FPOM δ^{15}N, ‰	Surface C, %	Surface N, %	Surface C:N	C$_{surface}$:OC$_{bulk}$	N$_{surface}$:ON$_{bulk}$	Bulk CPOM OC, %	Bulk CPOM ON, %	Bulk CPOM OC:ON	Bulk CPOM δ^{13}C, ‰	Bulk CPOM δ^{15}N, ‰
STR1	2.95	49.4	1.52	3.08	0.25	14.4	−28.5	n.a.	19.4	2.4	8.1	6.3	9.6	1.60	0.14	11.5	−28.2	1.0
STR2	2.80	231.1	5.01	2.17	0.18	14.1	−28.4	1.9	14.3	1.5	9.5	6.6	8.4	1.41	0.11	12.6	−28.1	0.6
STR3	1.88	95.6	0.95	0.99	0.12	9.6	−28.6	0.6	9.2	1.5	6.1	9.3	12.5	0.71	0.06	11.1	−26.5	0.6
STR4	2.50	91.6	0.96	1.05	0.13	9.5	−29.5	0.9	9.8	1.6	6.1	9.3	12.4	n.a.	n.a.	n.a.	n.a.	n.a.
STR5	7.30	160.4	2.70	1.68	0.17	11.9	−28.6	−0.7	12.7	1.4	9.1	7.5	8.5	2.21	0.14	16.3	−28.9	−0.4
Average	*3.49*	*125.6*	*2.23*	*1.80*	*0.17*	*11.9*	*−28.7*	*0.7*	*13.1*	*1.7*	*7.8*	*7.8*	*10.3*	*1.48*	*0.11*	*12.9*	*−27.9*	*0.5*
SE	*0.97*	*31.8*	*0.76*	*0.39*	*0.02*	*1.1*	*0.2*	*0.5*	*1.8*	*0.2*	*0.7*	*0.6*	*0.9*	*0.28*	*0.02*	*1.06*	*0.5*	*0.3*
FLY1	3.35	19.5	0.99	5.06	0.46	13.0	−30.3	0.8	24.3	3.3	7.4	4.8	7.2	0.78	0.06	12.4	−29.7	2.2
FLY2	4.10	23.9	2.16	9.03	0.44	24.1	−31.1	0.2	29.7	3.9	7.6	3.3	8.9	0.75	0.05	14.7	−29.0	0.1
FLY3	4.10	59.6	1.38	2.32	0.19	14.2	−30.4	0.8	28.9	3.6	8.0	12.5	18.9	1.02	0.09	11.6	−30.9	2.2
Average	*3.85*	*34.3*	*1.51*	*5.47*	*0.36*	*17.1*	*−30.6*	*0.6*	*27.6*	*3.6*	*7.7*	*6.9*	*11.7*	*0.85*	*0.07*	*12.9*	*−29.9*	*1.5*
SE	*0.25*	*12.7*	*0.34*	*1.95*	*0.09*	*3.5*	*0.3*	*0.2*	*1.7*	*0.2*	*0.2*	*2.8*	*3.6*	*0.08*	*0.01*	*0.95*	*0.6*	*0.7*
p values[a]	0.51	0.08	0.64	0.04	0.04	0.12	0.001	0.91	0.002	0.000	0.91	0.69	0.84	0.15	0.12	0.99	0.05	0.19
HERB1	n.a.	21.9	1.84	8.39	0.78	12.6	−30.4	1.5	33.6	3.4	9.9	4.0	4.4	11.57	1.86	6.2	−30.3	4.6

[a]The *p* values are for *t*-tests comparing STR and FLY samples.

[30] Isotope values for DIC also differed among rivers (Table 2). Fly River samples had the most depleted and consistent δ^{13}C values for DIC. Strickland DIC samples were slightly more enriched, and the Herbert River sample was the most enriched. Calculated δ^{13}C values of CO_2 were very similar in the Fly and Strickland Rivers, both of which had more depleted values than the Herbert (Table 2).

[31] Radiocarbon analysis of DIC yielded generally old ages for CO_2 in the water column, as well as interesting differences among the rivers sampled (Table 3). Measured Δ^{14}C values were most depleted (oldest) in the Strickland and most enriched (youngest) in the Herbert River, corresponding to average radiocarbon ages ranging from 2100 to 600 a B.P. (^{14}C annums before present, where "present" by convention is 1950 AD). The first samples collected in both the Strickland and Fly rivers (STR2 and FLY1) had significantly older ages than those collected a week or more later, possibly reflecting a changing source of water during this falling stage of the hydrograph.

[32] In terms of dissolved gases, both the Fly and Strickland Rivers were highly supersaturated with carbon dioxide (ranging from ~5 to 28 times atmospheric equilibrium concentrations) and undersaturated with oxygen (~15–70% of equilibrium values) (Table 2 and Figure 4). The Fly had higher CO_2 and lower O_2 concentrations than the Strickland River. These pCO_2 and O_2 concentrations are comparable to and on the low end of the range, respectively, of typical values in the main stem of the Amazon River and its largest tributaries, where observed values of pCO_2 are typically 1500–13,000 μatm and O_2 concentrations in the range of 2.6–7.0 mg L^{-1} [*Devol et al.*, 1995; *Richey et al.*, 2002]. The pCO_2 values calculated using pH and either alkalinity or DIC as known variables were fairly consistent with each other, whereas those calculated using total alkalinity (TA) and DIC were erratic and ranged from 9 to 14,000 μatm (Figure 4a). Using pH and either TA or DIC to calculate the other (TA or DIC), we found that the results were relatively consistent internally, whereas using TA and DIC to calculate pH gave wildly variable results that were inconsistent with observations (Figures 4b and 4c). We have observed similar inconsistencies in other tropical river systems, suggesting that the use of TA and DIC to calculate the other carbonate system variables is unreliable (S. R. Alin et al., unpublished data, 2007).

[33] Nutrient concentrations from the Strickland and Fly River sites are presented in Table 2. PO_4 concentrations ranged from 0.00 to 0.22 μM, NO_3 concentrations from 1.04 to 4.19 μM, NO_2 from 0.08 to 0.12 μM, NH_4 from 0.00 to 1.26 μM, and $Si(OH)_4$ from 107 to 221 μM. Nutrient concentrations were higher in individual measurements and on average in the Strickland than in the Fly River, with the exception of NH_4 and $Si(OH)_4$, for which values were comparable between rivers. For comparison, the concentrations of PO_4 and NO_3 over a 10-annum time series in the Amazon main stem were substantially higher at 0.5–1.2 μM and 4–20 μM, respectively, while silica concentrations had comparable values of 130–180 μM [*Devol et al.*, 1995].

4.2. Organic Chemistry: River

[34] Fine suspended-sediment (FSS) concentrations ranged from 20 to 231 mg L^{-1} and were higher in the Strickland than in the Fly, with the Herbert River having a

Table 5. CuO Oxidation Parameters[a]

Sample ID	Yields, mg/100 mg OC						Compositional Ratios, mg/mg						
	V_{COP}	S_{COP}	C_{COP}	B_{COP}	P_{COP}	Λ_{COP}	P/V	B/V	S/V	C/V	Vd/Vl	Sd/Sl	3,5Bd/V
					River Coarse Particulates								
STR1	2.54	1.73	0.21	0.26	0.58	4.48	0.23	0.10	0.68	0.08	0.17	0.22	0.05
STR2	2.41	1.67	0.21	0.22	0.51	4.29	0.21	0.09	0.69	0.09	0.18	0.20	0.04
STR3	2.28	1.77	0.20	0.33	0.58	4.26	0.25	0.14	0.78	0.09	0.24	0.28	0.07
STR5	3.54	2.40	0.21	0.21	0.57	6.15	0.16	0.06	0.68	0.06	0.17	0.22	0.03
Average	*2.69*	*1.89*	*0.21*	*0.26*	*0.56*	*4.80*	*0.21*	*0.10*	*0.71*	*0.08*	*0.19*	*0.23*	*0.05*
SE	*0.29*	*0.17*	*0.00*	*0.03*	*0.02*	*0.46*	*0.02*	*0.02*	*0.02*	*0.01*	*0.02*	*0.02*	*0.01*
FLY1	3.39	2.27	0.31	0.39	0.96	5.98	0.28	0.11	0.67	0.09	0.21	0.27	0.05
FLY3	2.88	1.95	0.25	0.33	0.89	5.07	0.31	0.11	0.68	0.09	0.23	0.22	0.05
FLY2	2.66	1.77	0.24	0.34	0.78	4.66	0.29	0.13	0.67	0.09	0.22	0.21	0.07
Average	*2.98*	*1.99*	*0.27*	*0.35*	*0.87*	*5.24*	*0.29*	*0.12*	*0.67*	*0.09*	*0.22*	*0.23*	*0.06*
SE	*0.22*	*0.15*	*0.02*	*0.02*	*0.05*	*0.39*	*0.01*	*0.01*	*0.00*	*0.00*	*0.00*	*0.02*	*0.01*
p values[b]	0.49	0.68	0.11	0.04	0.001	0.51	0.02	0.39	NC[c]	NC	0.20	0.90	0.46
					Proximal Floodplain Samples[d]								
15 RFC 5 34−36	2.53	1.47	0.18	0.28	1.00	4.18	0.40	0.11	0.58	0.07	0.33	0.42	0.05
3 LFS 5A 16−18	0.75	0.60	0.11	0.21	0.20	1.46	0.27	0.27	0.79	0.15	0.46	0.32	0.08
3 LFS 5A 34−36	1.16	0.92	0.11	0.26	0.31	2.19	0.27	0.23	0.79	0.09	0.52	0.29	0.10
3 LFS 5A 64−66	1.11	0.87	0.12	0.26	0.31	2.10	0.28	0.23	0.79	0.11	0.50	0.26	0.10
4 RFS 5A 70−72	0.44	0.51	0.12	0.43	0.20	1.08	0.45	0.96	1.16	0.27	0.80	0.26	0.18
5 LFB 5A 34−36	2.15	2.11	0.24	0.33	0.37	4.50	0.17	0.15	0.98	0.11	0.85	0.56	0.08
5 LFB 5A 64−66	1.68	1.27	0.16	0.16	0.40	3.11	0.24	0.10	0.76	0.10	0.33	0.29	0.07
Proximal average	*1.40*	*1.11*	*0.15*	*0.27*	*0.40*	*2.66*	*0.30*	*0.29*	*0.84*	*0.13*	*0.54*	*0.34*	*0.09*
Proximal SE	*0.28*	*0.21*	*0.02*	*0.03*	*0.10*	*0.50*	*0.04*	*0.11*	*0.07*	*0.02*	*0.08*	*0.04*	*0.02*
					Distal Floodplain Samples								
15 RFC 100 34−36	0.36	0.43	0.17	0.21	0.21	0.96	0.59	0.58	1.20	0.48	0.60	0.30	0.12
5 LFB 150 34−36	0.86	0.72	0.10	0.25	0.23	1.68	0.27	0.29	0.84	0.11	0.50	0.32	0.11
1C LFS 200A 28−30	0.34	0.25	0.07	0.25	0.24	0.66	0.70	0.74	0.72	0.21	0.52	0.37	0.20
1C LFS 200A 44−46	0.19	0.43	0.20	0.18	0.24	0.82	1.26	0.94	2.24	1.05	1.28	0.40	0.28
5 LFB 250A 14−16	1.30	1.48	0.24	0.33	0.22	3.01	0.17	0.26	1.14	0.18	0.85	0.40	0.18
5 LFB 250A 34−36	0.52	0.46	0.13	0.15	0.21	1.11	0.41	0.29	0.88	0.25	0.66	0.36	0.14
5 LFB 250A 64−66	0.61	0.57	0.16	0.34	0.28	1.34	0.45	0.56	0.93	0.27	0.88	0.42	0.16
3 LFS 350A 28−30	0.20	0.22	0.10	0.17	0.10	0.52	0.51	0.85	1.10	0.50	1.00	0.44	0.23
Distal average	*0.55*	*0.57*	*0.15*	*0.24*	*0.22*	*1.26*	*0.55*	*0.56*	*1.13*	*0.38*	*0.79*	*0.38*	*0.18*
Distal SE	*0.13*	*0.14*	*0.02*	*0.03*	*0.02*	*0.28*	*0.12*	*0.09*	*0.17*	*0.11*	*0.10*	*0.02*	*0.02*
p values[e]	0.01	0.03	0.93	0.34	NC	0.02	0.08	0.03	0.11	0.01	0.07	0.48	0.01

[a]Abbreviations are as follows: V_{COP}, sum of CuO oxidation products (vanillin + acetovanillone + vanillic acid); S_{COP}, syringyl COP (syringealdehyde + acetosyringone + syringic acid); C_{COP}, cinnamyl COP (*p*-coumaric acid + ferulic acid); B_{COP}, benzoic acid COP (benzoic acid + *m*-hydroxybenzoic acid + 3, 5-dihydroxybenzoic acid); P_{COP}, *p*-hydroxybenzene COP (*p*-hydroxybenzaldehyde + *p*-hydroxyacetophenone + *p*-hydroxybenzoic acid); Λ_{COP}, sum of all lignin COP (V_{COP} + S_{COP} + C_{COP}).
[b]The *p* values are for *t*-tests comparing STR and FLY samples.
[c]NC denotes that the data were not compared statistically.
[d]See Table 7 for more detailed information about floodplain sample locations.
[e]The *p* values are for *t*-tests comparing proximal and distal samples.

low concentration as expected (Table 4). Bulk OC content of fine particulates, which varied from 0.99 to 9.03%, was lowest in the Strickland and highest in the Herbert and at site FLY2. Combining FSS concentrations and bulk OC content yielded fine particulate organic carbon (FPOC) concentrations ranging from 0.95 to 5.01 mg L^{-1}, with the highest and most variable values measured in the Strickland and somewhat lower values in the Fly and Herbert. Bulk nitrogen contents ranged from 0.12 to 0.46% and, similar to the bulk OC content, had the lowest values in the Strickland, intermediate values in the Fly, and the highest value in the Herbert. A plot of %TN versus %OC for all fine particulate samples had a negative %TN intercept at zero %OC (not shown), indicating a lack of inorganic nitrogen [cf. *Goni et al.*, 1998]. Hence %TN is considered to represent %ON for fine particulate samples. Atomic C:N ratios for bulk analyses fell in the range of 9.5 to 24.1 (Table 4). The

higher value for Fly River samples is due to the outlying value of 24.1, which may reflect enhanced organic inputs from a large blackwater lake actively draining into the Fly along the right bank during the time of sampling, within 1 km upstream of the sampling site FLY2.

[35] Stable isotope analysis of fine particulates revealed consistently depleted δ^{13}C values, ranging from −31.1 to −28.4‰ (Table 4). The Fly and Herbert rivers had the most negative δ^{13}C values. The δ^{13}C signatures from Strickland FPOM were slightly enriched relative to the other rivers. Nitrogen isotope values varied from −0.7 to +1.9‰ and were fairly similar between the Fly and Strickland. The Herbert sample was slightly enriched relative to the Fly and Strickland averages, but was within the range of variability of Strickland River samples.

[36] In general, the coarse particulates were lower in organic content than the fine particulates, suggesting a

Table 6. High-Resolution C1s Spectra Results for Carbon Bond Types Present in Surface Organic Matter

Sampling Location	Hydrocarbons (285.0 eV)	One O, N Bond (286.6 eV)	Two O, N Bonds (288.3 eV)	Three O, N Bonds (289.4 eV)	fCO_x
STR1	48.4	32.4	13.6	5.6	0.49
STR2	56.4	26.3	12.1	5.3	0.42
STR3	60.4	21.7	11.7	6.2	0.39
STR4	54.3	27.2	13.6	5.1	0.45
STR5	54.2	25.2	13.7	7.0	0.45
Average	*54.7*	*26.5*	*12.9*	*5.8*	*0.44*
SE	*1.9*	*1.7*	*0.4*	*0.4*	*0.02*
FLY1	49.9	30.9	15.8	3.4	0.47
FLY2	51.0	31.0	14.2	3.9	0.46
FLY3	51.5	30.3	13.5	4.8	0.45
Average	*50.8*	*30.7*	*14.5*	*4.0*	*0.46*
SE	*0.5*	*0.2*	*0.7*	*0.4*	*0.01*
p values[a]	0.11	0.07	0.09	0.02	0.41
HERB1	45.3	35.3	15.9	3.6	0.51

[a]The *p* values are for *t*-tests comparing STR and FLY samples.

contribution of sand to the coarse suspended fraction. The OC content of coarse particulates ranged from 0.71 to 11.57%, with the most organic-poor found in the Fly River and the most organic-rich sample from the Herbert (Table 4). Visually, the Herbert sample appeared to be comprised almost completely of low-density algal remains. Concentration of coarse suspended sediments (CSS) was not measured, though the contribution of CSS to fluvial particulate OM is typically <10% in other large tropical rivers [*Keil et al.*, 1997]. Thus it is not possible to compute a coarse particulate organic carbon concentration. Nitrogen in CSS samples also had a negative TN intercept at 0% OC, so all nitrogen was deemed to be of organic origin in CSS samples. Atomic C:N ratios for coarse particulate organic matter (CPOM) varied from 6.2 to 16.3 and were lowest in the Herbert and equal in the Fly and Strickland. The $\delta^{13}C$ signatures of CPOM ranged from -30.9 to $-26.5‰$ and were most enriched in the Strickland and most depleted in the Fly and Herbert rivers. The opposite was true for $\delta^{15}N$ values, which ranged from -0.4 to $+4.6‰$, with more depleted values in the Strickland than elsewhere.

[37] Radiocarbon analysis of select FPOM samples from both the Fly and Strickland rivers revealed $\Delta^{14}C$ values of $-275‰$ and $-371‰$, corresponding to calendar ages of 2500 and 3800 a B.P., respectively (Table 3). CPOM samples exhibited enriched $\Delta^{14}C$ values relative to their FPOM counterparts, yielding ages from 850 to 1690 a B.P. (Table 3). As was the case for DIC radiocarbon composition, both FPOM and CPOM samples from the Fly River had younger ^{14}C ages than their respective Strickland samples.

[38] Yields of lignin (V_{COP}, S_{COP}, C_{COP}) and nonlignin (P_{COP}, B_{COP}) CuO oxidation products from CPOM samples ranged from 0.20 to 3.54 mg/100 mg OC (Table 5). The highest yields were consistently those of V_{COP}, followed by S_{COP} and P_{COP}. The total yields of lignin-derived products (Λ_{COP}) ranged from 4.26 to 6.15 mg/100 mg OC. Overall, the CPOM samples from both the Fly and Strickland rivers had comparable yields of the different CuO oxidation products. Compositionally, all of the CPOM samples were characterized by moderate C_{COP}/V_{COP} ratios of less than

0.1 mg/mg and elevated S_{COP}/V_{COP} ratios greater than 0.6 mg/mg (Table 5). Additionally, all CPOM samples exhibited low vanillyl and syringyl acid:aldehyde ratios that were consistently less than 0.3 mg/mg, suggesting the presence of relatively intact lignin. Notably, other parameters indicative of the diagenetic state of the lignin, such as B/V and 3,5Bd/V, also display low values of less than 0.2 mg/mg and 0.08 mg/mg, respectively.

[39] XPS analysis revealed carbon and nitrogen concentrations on the surface of fine particulates that ranged from 9.2 to 33.6% and 1.4 to 3.9%, respectively (Table 4). These C and N contents are higher than those in the bulk samples, yielding surface enrichment factors ($C_{surface}:OC_{bulk}$,
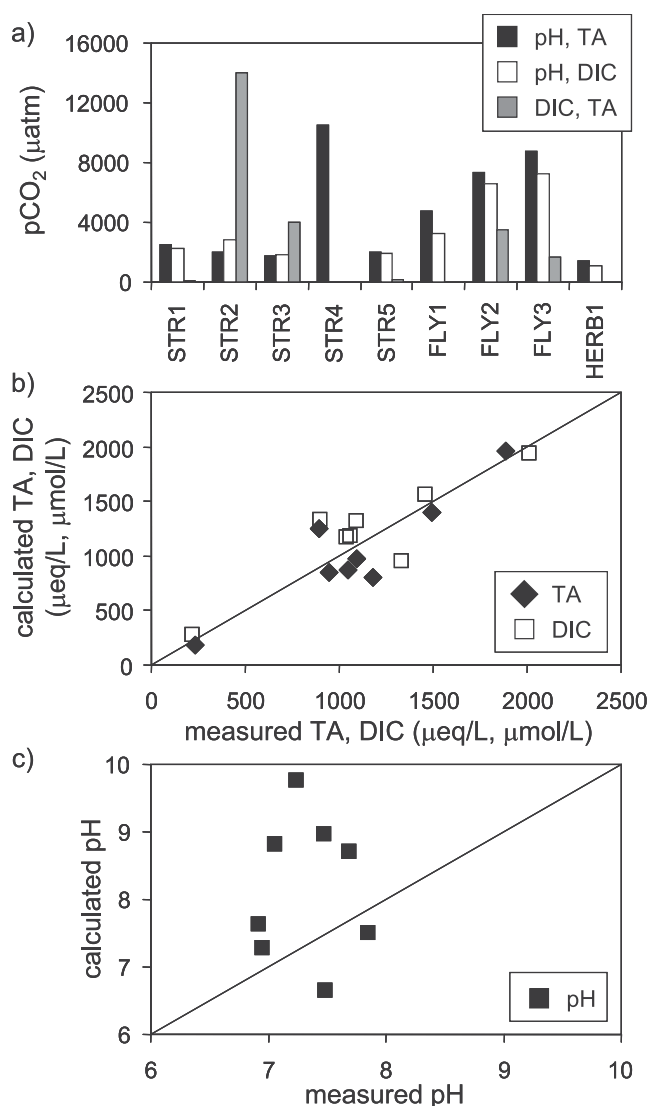

Figure 4. Carbonate system calculations using measured variables pH, alkalinity (TA), and dissolved inorganic carbon (DIC). (a) The pCO_2 values calculated with each of the three possible combinations of two known variables: pH, TA; pH, DIC; and DIC, TA. (b) Comparison of measured and calculated values of TA, using pH and DIC and DIC using pH and TA as givens. (c) Comparison of measured and calculated values of pH, using TA and DIC as known values.

Table 7. Organic Composition of Floodplain Core Samples

Sample ID	Transect Location	Bank	Distance From Channel, m	Depth in Core, cm	Deposition Year	Error, annums	Bulk OC, %	Bulk ON, %	Bulk OC:ON	Bulk δ^{13}C, ‰	Bulk δ^{15}N, ‰
					Proximal Samples						
3 LFS 5A 16−18	3	L	5	16−18	1998	4	1.67	0.131	12.8	−26.01	0.82
3 LFS 5A 34−36	3	L	5	34−36	1995	5	1.01	0.090	11.2	−26.77	1.43
3 LFS 5A 64−66	3	L	5	64−66	1970	5	0.97	0.088	11.0	−25.90	1.55
4 RFS 5A 70−72	4	R	5	70−72	1968	7	0.49	0.056	8.8	−26.19	1.05
5 LFB 5A 34−36	5	L	5	34−36	2003	4	0.72	0.056	12.9	−26.88	0.78
5 LFB 5A 64−66	5	L	5	64−66	1998	5	1.33	0.097	13.7	−27.89	0.65
15 RFC 5 34−36	15	R	5	34−36	2003	4	1.21	0.081	15.0	−28.11	1.22
Proximal average							1.06	0.085	12.2	−26.82	1.07
Proximal SE							0.15	0.010	0.8	0.33	0.13
					Distal Samples						
15 RFC 100 34−36	15	R	100	34−36	1995	6	0.41	0.037	10.9	−25.45	1.13
5 LFB 150 34−36	5	L	150	34−36	1990	4	1.01	0.096	10.5	−28.69	1.18
1C LFS 200A 28−30	1	L	200	28−30	1971	7	0.79	0.109	7.2	−26.94	2.95
1C LFS 200A 44−46	1	L	200	44−46	<1940		0.56	0.089	6.2	−25.47	2.26
5 LFB 250A 14−16	5	L	250	14−16	1991	4	1.48	0.139	10.6	−27.13	1.32
5 LFB 250A 34−36	5	L	250	34−36	1991	4	1.12	0.121	9.2	−25.88	2.29
5 LFB 250A 64−66	5	L	250	64−66	1950	8	0.77	0.095	8.1	−23.77	1.52
3 LFS 350A 28−30	3	L	350	28−30	<1940		0.64	0.076	8.4	−26.30	1.50
Distal average							0.85	0.095	8.9	−26.20	1.77
Distal SE							0.12	0.011	0.6	0.51	0.23
p values[a]							0.30	0.52	0.005	0.35	0.02

[a]The *p* values are for *t*-tests comparing proximal and distal samples.

$N_{surface}$:ON_{bulk}) of 3−13 in carbon and 4−19 in nitrogen in the Fly-Strickland system. As with the bulk measurements, %C was significantly higher in Fly River samples than in the Strickland and was highest in the Herbert sample. Percent N content in the outer 10 nm of fine particulates was highest in the Fly. The corresponding atomic C:N ratios of surface organics are somewhat lower than the bulk values.

[40] High-resolution C1s spectra revealed the following patterns. Hydrocarbon bonds comprised 45−60% of the organic matter in each surface sample, with the Herbert having the lowest values, the Strickland the highest, and the Fly River falling in between (Table 6). Carbons involved in a single oxygen bond, alcohols and ethers, comprised the next most abundant group, with the opposite trend among rivers. Carbon atoms with double bonds to oxygen atoms, carbonyls and amides, had similar relative abundance patterns to alcohols and ethers. Carbons with three bonds to oxygen, acids and esters, comprised the smallest category for all samples, always falling below 10% abundance.

[41] Dissolved organic carbon (DOC) concentrations in the Fly and Strickland Rivers ranged from 1.9 to 7.3 mg L^{-1} (Table 4). The averages were similar between the two rivers, but variability was higher in the Strickland.

4.3. Organic Chemistry: Floodplain

[42] The organic composition of floodplain core samples is described in Table 7. Average percentages of organic carbon in the floodplain samples fell in the range of 0.41 to 1.67% and were generally lower than in river particulates. The regression of %OC against TN had a positive intercept of 0.174 at a zero %OC value. This value is presumed to represent inorganic nitrogen in the floodplain sediment, and was subtracted from TN values to give %ON [*Goni et al.*, 1998]. Percent organic nitrogen values were relatively high considering the low OC content, ranging from 0.037 to

0.139%. The resulting OC:ON ratios for floodplain soils varied from 6.2 to 15.0 and were slightly lower than in bulk river-borne fine and coarse particulates. The OC:ON ratios of floodplain soils proximal to the river channel (5 m from the channel) were significantly higher than those from more distal sites (100−350 m from the channel). Finally, stable isotope measurements showed that the δ^{13}C signatures of organic matter in floodplain sediments ranged from −28.7 to −23.8‰, and δ^{15}N values of floodplain organics from +0.65 to +2.95‰. Proximal floodplain samples displayed slightly enriched δ^{13}C signatures and significantly depleted δ^{15}N signatures relative to their distal counterparts. Overall, the organic matter in floodplain sediments displayed substantially enriched δ^{13}C and δ^{15}N values relative to FPOM and CPOM samples, a trend that may reflect contrasts in the source and diagenetic history of the organic materials present in each fraction.

[43] Radiocarbon analyses on select Strickland floodplain organic samples yielded Δ^{14}C values of −236‰ and −262‰. These values translate into calendar ages of 2200−2400 a B.P., making them younger than FPOM ages and older than CPOM and DIC sample ages (Table 3). The particular floodplain deposits dated were collected on topographically lower portions of the point bar side of the channel, which experiences more regular inundation, and thus may not reflect the character of the organic matter deposited during the largest flood events [cf. *Aalto et al.*, 2003].

[44] The yields of total lignin-derived CuO oxidation products (Λ_{COP}) from floodplain sediment samples ranged from 0.52 to 4.50 mg/100 mg OC, with significantly lower yields in distal sites relative to proximal ones (Table 5). Furthermore, the Λ_{COP} yields of floodplain samples were significantly lower than those of the CPOM samples ($p <$ 0.0001). The exception was several proximal floodplain
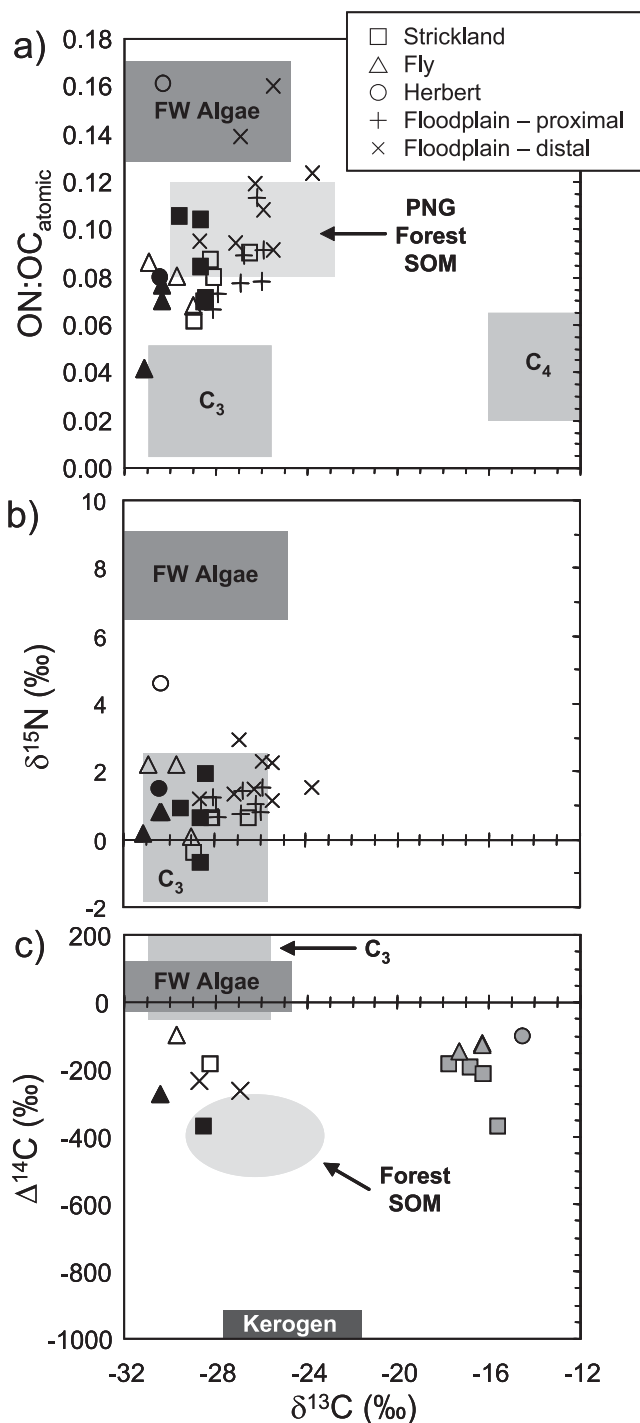
Figure 5. Organic composition of river suspended sediment and floodplain core samples, as well as isotope composition of dissolved inorganic carbon (DIC). All samples are plotted relative to end-members used by *Goni et al.* [2006, 2008] and from *Forsberg et al.* [1993] and *McCallister et al.* [2004]. Solid symbols represent river FPOM samples, and open symbols denote CPOM samples, and gray solids in panel c represent DIC samples. Carbon stable isotope values ($\delta^{13}C$) plotted against (a) the atomic ratio of organic nitrogen to organic carbon, which is displayed as ON:OC to allow comparison to *Goni et al.* [2006, 2008], (b) the nitrogen stable isotopic signature ($\delta^{15}N$), and (c) the radiocarbon content ($\Delta^{14}C$).

samples exhibiting Λ_{COP} values greater than 4 mg/100 mg OC, comparable to those obtained from CPOM samples. The yields of nonlignin oxidation products from floodplain samples were significantly lower than those for CPOM in the case of P_{COP} ($p < 0.0001$) but not for B_{COP} ($p = 0.23$). Compositionally, the S/V, C/V, and vanillyl acid:aldehyde ratios of floodplain sediments exceeded those from CPOM and increased with distance from the river. Other diagenetic lignin indicators, such as B/V and 3,5Bd/V, also showed this trend of elevated values in floodplain sediments relative to CPOM and were significantly elevated at distal sites compared to proximal ones.

[45] Contrasts in lignin and nonlignin COP compositions between the coarse particulate load in the river and the floodplain sediments suggests that different sources contribute to both pools and/or that postdepositional degradation in the floodplain may alter the composition of organic matter relative to the suspended load in the river. Since we were only able to characterize the coarse particulate fraction, it is impossible to say whether the fine particulate fraction, which makes up the majority of the suspended load in most rivers, is more compositionally similar to the floodplain sediments with respect to CuO oxidation products.

5. Discussion and Implications

5.1. Provenance of Organic Matter in the Fly-Strickland River System

[46] The elemental, isotopic and biomarker compositions obtained as part of the previously described analyses can be used to evaluate the provenance of OM pools in the Fly-Strickland river/floodplain system. For example, the $\delta^{13}C$ compositions of the OM can be combined with the ON:OC ratios to graphically discriminate among different types of OM, i.e., end-members (Figure 5a). Because diagenesis can alter both signatures, and there may be end-members that are not considered, this type of assessment is semiquantitative. Nevertheless, these types of plots can provide valuable insight into the nature and provenance of OM in geochemical samples [e.g., *Goni et al.*, 2006; *Hedges et al.*, 1986]. For example, most of the FPOM and CPOM samples from the Fly and Strickland rivers and the proximal floodplain samples plot in a region between the C_3 vascular plant and freshwater algal end-members, which also overlaps the compositional range of PNG soils. In contrast several of the distal floodplain samples and the Herbert CPOM sample display higher ON:OC ratios, which may be indicative of higher contributions from freshwater algae or other N-rich sources of organic matter such as microorganisms (e.g., bacteria, fungi). On the basis of the observed composition of samples, we can conclude that C_4 plants, including natural grasses as well as cultivars such as sugar cane, contribute little to the OM of floodplain and suspended-sediment samples.

[47] Carbon stable isotopes of FPOM are consistent with a strong contribution of algal production in both the Herbert and Fly rivers (-31 to $-30‰$), whereas the somewhat more enriched $\delta^{13}C$ in Strickland River FPOM may reflect a greater importance of soil organic matter (SOM) and/or C_3 plant material in the suspended load of the more sediment-rich Strickland. Nitrogen isotope values of FPOM in all three rivers would also be consistent with terrestrial C_3

inputs or nitrogen fixation. C:N ratios (shown as ON:OC in Figure 5) suggest that FPOM in all river samples represents a mix between freshwater algae and C_3 vascular plant remains, such that even algae-rich samples incorporate other sources of OM.

[48] The $\delta^{13}C$ signatures of CPOM were most enriched in the Strickland River, consistent with a dominant SOM source, and more depleted in the Fly and Herbert rivers, suggesting a greater role for freshwater production. Indeed, the coarse particulate sample from the Herbert River, which was observed to contain a large fraction of algal material, plots well within the end-member space for freshwater algae. The more enriched ^{15}N values in the Fly and particularly the Herbert are again suggestive of an algal source (Figure 5b). Finally, C:N atomic ratios for CPOM were lowest in the Herbert, consistent with an algal source, and somewhat higher and similar in the Fly and Strickland rivers, suggesting a mix of terrestrial and aquatic or microbial sources (Figure 5a).

[49] Floodplain soils/sediments are formed through the interacting processes of riverine sediment deposition on the floodplain, terrestrial processes associated with soil development, and aquatic ecosystem processes that occur during periods of inundation. Strickland River floodplain samples contained roughly half the organic content of suspended sediments in the river contained (river $\approx 1.8\%$ OC, floodplain $\approx 0.9\%$ OC). This difference may be the result of efficient remineralization of OC with the repeated wet-dry alternation experienced in the floodplain environment. However, data from loss-on-ignition (LOI) on an independent series of cores collected at the same Strickland transect sites indicate a wide range of %OC values in floodplain sediments, from 0.2 to 45.2% [*Watson*, 2006]. Although LOI can overestimate organic content in clay-rich sediments like those on the Strickland floodplain [e.g., *Barillé-Boyer et al.*, 2003], these results suggest that our sampling may have missed the more OC-rich lenses of sediment and buried organic materials preserved within the depositional lenses that construct the floodplain.

[50] Strickland floodplain sediments were enriched in $\delta^{13}C$ relative to fine suspended sediments in the river, with a tendency toward greater enrichment further from the river channel. The enrichment in $\delta^{13}C$ seen in Strickland floodplain sediments with respect to suspended sediments is comparable to that seen between suspended sediments and surface sediments in the Fly River delta, and may be related to diagenetic changes [*Goni et al.*, 2006]. Enriched $\delta^{13}C$ values in floodplain samples would also be consistent with a soil OM source. Intermediate values of $\delta^{15}N$ are difficult to interpret, as depleted values may derive from either C_3 vegetation or nitrogen fixation (terrestrial or aquatic). More enriched sources include soil organic matter and freshwater phytoplankton other than nitrogen fixers [*McCallister et al.*, 2004, and references therein]. Finally, ON:OC ratios of floodplain soils proximal to the river channel are consistent with a mix of C_3 and SOM sources, whereas more distal floodplain sites have values consistent with SOM and soil microbes or freshwater algae as organic matter sources. Overall, Figure 5 indicates that the isotopic signatures and elemental ratios of floodplain sediment samples are consistent with a mixed source of C_3 plants, freshwater algae or soil microbes, and soil organic matter.

[51] Lignin CuO oxidation products are exclusively derived from vascular plants, predominantly of terrestrial origin. In combination with $\delta^{13}C$ compositions, the yields of these biomarkers can provide a semiquantitative estimate of organic matter contributions from different terrestrial and aquatic sources. Figure 6 shows the carbon-normalized yields of lignin CuO oxidation products (Λ_{COP}) typical of end-members present in the Fly-Strickland river system relative to their carbon stable isotopic signatures. In this type of graph, C_3 vegetation is characterized by relatively depleted $\delta^{13}C$ values and elevated Λ_{COP} values, which can range from 5 to over 20 mg/100 mg OC depending on the type of tissue (woods are generally richer in lignin than nonwoody tissues such as leaves). Degradation and alteration of lignin in soils and the addition of microbial and fungal biomass result in lower Λ_{COP} for soil OM relative to the overlying vegetation [e.g., *Kogel-Knabner et al.*, 1991]. In contrast, neither algae, which do not synthesize lignin, nor kerogen, which loses most recognizable biochemical structures during the thermal maturation process, yield lignin oxidation products. Among the Fly/Strickland samples, the high Λ_{COP} yields and relatively depleted $\delta^{13}C$ compositions of CPOM are consistent with a mixture of C_3 and algal sources. In contrast, the lower Λ_{COP} yields and more enriched $\delta^{13}C$ values of floodplain soil/sediment signatures are more typical of soil OM.

[52] The ratios of syringyl and cinnamyl COP to vanillyl COP (i.e., S_{COP}/V_{COP} and C_{COP}/V_{COP}) generate insight into the type of vascular plant source contributing lignins to our sediment samples and can differentiate among angiosperm, gymnosperm, woody, and nonwoody sources [e.g., *Hedges et al.*, 1986]. The relative abundances of acid and aldehyde syringyl and vanillyl compounds also yield information about the degradation state of a lignin sample, with higher acid:aldehyde ratios reflecting more degraded samples and vice versa. In addition, increasing ratios of benzoic acid or *p*-hydroxybenzene nonlignin COP to vanillyl COP (i.e., B_{COP}/V_{COP} and P_{COP}/V_{COP}) can indicate the importance of nonvascular plant OM sources, such as algae, fungi, or bacteria to organic matter in sediment samples. Coarse particulates in both the Fly and Strickland rivers appear to be derived from relatively undegraded woody-nonwoody angiosperm sources, whereas floodplain signatures ranged from woody-nonwoody angiosperm mixes to more nonwoody dominance at sites distal from the channel. Also, a tendency toward more degraded lignin and elevated nonlignin COP yields was noted with increasing distance from the river channel, which may be attributable to the lower sediment accumulation rates, more active soil microbial and fungal communities, and longer oxygen exposure times at more distal floodplain locations [cf. *Aalto et al.*, 2008]. While there was some variation in topography away from the channel, in general the distal coring sites were lower in elevation and thus subjected to frequent flooding and long periods of standing water that presumably fostered some algal production.

[53] The new methodology of using X-ray photoelectron spectroscopy to study organic matter composition in sediments has the capacity to reveal the composition of surface compounds in particulate organic matter and thereby yield information about the relationship between organic matter and minerals in sediment samples as well as the degradation
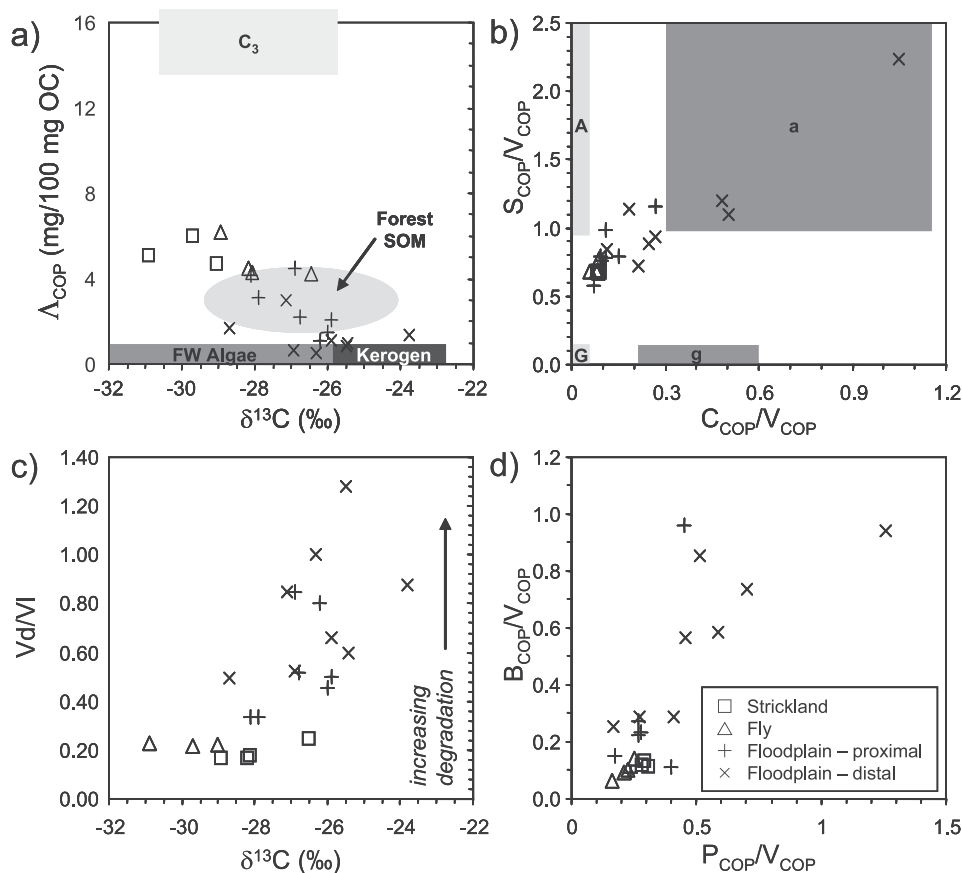
Figure 6. Lignin composition of coarse suspended particulates from the Fly, Strickland, and Herbert rivers and the Strickland River floodplain. Carbon stable isotope values ($\delta^{13}C$) plotted against (a) total yield of vanillyl, syringyl, and cinnamyl lignin CuO oxidation products (Λ_{COP}) and (b) the acid:aldehyde ratio of vanillyl COP ([Ad/Al]$_V$). The ratios of various classes of lignin COP relative to vanillyl COP: (c) syringyl and cinnamyl plotted relative to lignin end-members: A, angiosperm wood; G, gymnosperm wood, a, angiosperm leaves and grasses, and g, gymnosperm needles [from *Goni et al.*, 1998] and (d) *p*-hydroxybenzene and other benzoic acid products.

history of particles [*Arnarson and Keil*, 2001, 2007; *Yuan et al.*, 1998]. XPS yields clear and quantifiable differences among FPOM samples from the Fly, Strickland, and Herbert rivers (Tables 4 and 6), with significantly higher surface concentrations of carbon and nitrogen in samples from the Fly and Herbert than in the Strickland. The surface to bulk carbon ratio calculated with XPS data (C$_{surface}$:OC$_{bulk}$) can also yield insight into whether organic matter in the fine particulate fraction dominantly occurs in the form of discrete organics or as organic matter associated with mineral particles, either through aggregation or sorption. A careful study of organic matter from marine environments revealed that C$_{surface}$:OC$_{bulk}$ increased as organic carbon to surface area ratio (OC:SA) decreased with increasing sediment density interval and degradation state [*Arnarson and Keil*, 2007]. Although we were not able to perform density fractionation or OC:SA analyses, we can compare our results to the *Arnarson and Keil* [2007] study to assess the average/bulk character of organic matter in our samples relative to the density intervals they examined. FPOM from the Strickland River samples generally had higher surface to bulk carbon ratios than the Fly and Herbert rivers, with the exception of the FLY3 outlier (Table 4). Values of C$_{surface}$:OC$_{bulk}$ between

6 and 10, such as those observed at STR sites were typical of intermediate- to high-density sediment fractions (1.9–2.2 and 2.2–2.5 g cm^{-3}) [*Arnarson and Keil*, 2007]. Lower values, in the range of 2 to 5 as observed in the Fly and Herbert rivers, were more typical of their intermediate density fraction (1.9–2.2 g cm^{-3}). Along the full gradient from low-density to high-density sediment fractions (from < 1.6 to >2.5 g cm^{-3}), the physical form of organic matter shifts from discrete OM to organic-mineral aggregates to sorbed material, and its presumed preservation mechanism shifts along the same gradient from recalcitrance or encapsulation to material that is protected within a matrix (e.g., diatoms) or by sorption [*Arnarson and Keil*, 2007]. The intermediate C$_{surface}$:OC$_{bulk}$ values of our samples suggest that they were composed of either a mix of fresh, discrete, low-density OM and degraded, aggregated or sorbed, high-density OM or a more homogenous sample of intermediate density and degradation state. Without measuring OC:SA on density-fractionated sediments, it is not possible to definitively differentiate between these alternatives. However, observations of ancient carbon sources in the uplands and of aged, degraded OM in the subaqueous delta environment downstream

suggest that our samples contain a mixture of fresh and aged OM [cf. *Goni et al.*, 2006, 2008]. The somewhat higher surface enrichment of C in the Strickland may reflect a greater role for inputs of ancient or degraded OM than in the Fly.

[54] High-resolution carbon data from XPS also suggest variation in OM degradation state among rivers. For instance, carboxylic acid groups may bond more strongly than other functional groups with positively charged clay minerals in suspension and thus become more enriched in more degraded samples as other functional groups are consumed [cf. *Arnarson and Keil*, 2000; T. Arnarson, personal communication, 2006]. Although there is no consensus on whether lipid or protein molecules are more resistant to microbial degradation [cf. *Aufdenkampe et al.*, 2001, 2006; *Macko et al.*, 1993], polysaccharides are agreed to be the most prone to degradation by microbial processes in the water column.

[55] A van Krevelen-style plot of the fraction of carbon bonded to oxygen (fCO_x) and the atomic ON to OC ratio can be used to evaluate the relative contributions of proteins, lipids, and polysaccharides to the organic matter on the surface of fine sediments, as well as other biochemical compounds such as lignins (Figures 3b and 3c) [cf. *Arnarson and Keil*, 2001]. To calculate the fraction of carbon bonded to oxygen (fCO_x), we followed *Arnarson and Keil* [2001] in assuming the nitrogen to be dominantly amide and subtracting the total percent nitrogen contribution from the composition spectra from the high-resolution C1s peak 3 totals. None of the samples had significant inorganic nitrogen present; nitrate appears at BE = 408 eV in the composition spectrum, and only one filter had even trace amounts of inorganic nitrogen present (0.2%). Samples for all three rivers had fCO_x values of $0.380-0.511$ and ON:OC ratios of $0.023-0.126$. Solving a mixing model for fCO_x and ON:OC based on the three biochemical end-members yields the percent protein in each sample. According to this calculation, the protein content for fine particulates from the Strickland River falls in the range of $28-50\%$ of the surface carbon, while surface protein content in Fly and Herbert fine particulates span smaller ranges of $40-46\%$ and $39-40\%$, respectively. Because lignins have intermediate fCO_x and the same ON:OC values as lipids and polysaccharides, we cannot calculate percentages of the other constituents in these samples. Thus the remaining $50-72\%$ of the surface carbon in all river-borne fine particulates is composed of some mixture of carbohydrates, lignins, and lipids.

[56] Samples from all sites plot closer to the lipid-protein axis than to the polysaccharide pole of the van Krevelen plot, suggesting some history of exposure to degradation in the fine particulate samples. Among sites, those from the Strickland River are closest to the lipid-protein axis, while those from Fly and Herbert rivers appear somewhat closer to the polysaccharide pole. These results would suggest a trend of increasing degradation in the particulates from the Herbert to the Fly and Strickland rivers. For comparison, samples collected from the Mekong and Chao Phraya rivers of Southeast Asia at various elevations and throughout the annual hydrological cycle showed much greater variation in fCO_x and ON:OC values, ranging from 0.386 to 0.698 and 0.035 to 0.181, respectively (S. R. Alin et al., manuscript in preparation, 2007). These compositions translate to surface

protein contents of $13-66\%$ and combined lignin, lipid, and carbohydrate contents of $34-87\%$. The data from the Fly-Strickland river system plot closer to the protein-lipid axis than many samples from SE Asia and have thus been interpreted to reflect relatively degraded particulate organic sources.

[57] In summary, elemental, isotopic, and biomarker analyses all suggest that particulate organic matter transported by the Fly, Strickland, and Herbert rivers is composed predominantly of a mixture of terrestrial C_3, algal, and soil organic matter. Carbon stable isotopes and XPS data suggest that organic matter transported in the Strickland River may be more degraded than that in the Fly and Herbert rivers. Lignin COP and $\delta^{13}C$ values reveal greater degradation among floodplain samples than suspended sediments, particularly at sites more distal to the river channel.

5.2. Radiocarbon Constraints on Carbon Cycling in the Fly-Strickland System

[58] Radiocarbon analyses can provide additional constraints on the provenance of carbon fractions in river systems by revealing the average age of carbon in various pools. The results presented here demonstrate the presence of organic and inorganic carbon in the particulate and dissolved carbon loads of the Fly-Strickland system with bulk ages on the order of hundreds to thousands of years. The presence of relatively aged organic carbon in riverine particulates suggests a combination of (1) fresh terrestrial and/or aquatic sources of organic matter, (2) contributions of ancient carbon from weathering of sedimentary rocks in the upper elevations of the watershed, and (3) contributions of carbon altered during storage through long residence times in floodplains. Similarly, aged inorganic carbon in the Fly-Strickland system indicates that sources significantly older than modern atmospheric CO_2, such as carbonate weathering, groundwater inputs from floodplain or upland soils, or respiration of aged organics, contribute a fraction of the DIC to this system.

[59] All carbon fractions measured in the river (DIC, FPOM, CPOM) were older in the Strickland than in the Fly, reflecting differences in sediment and carbon provenance, transport processes, and floodplain dynamics between the two subbasins. Consistent with elemental, stable isotopic, and XPS evidence presented above, radiocarbon results indicate that suspended particulates transported by the Strickland River are older and probably more degraded than those in the Fly. All indicators suggest that the youngest, freshest OC was found in the Herbert River. In each river, CPOM ages were the youngest, average DIC ages intermediate, and FPOM ages the oldest. The two radiocarbon dates from Strickland floodplain sediments, one from the most upstream floodplain site (STR5) and the other from the furthest downstream site (STR1), were close to the estimated turnover time for floodplain sediments of approximately 2 ka [*Aalto et al.*, 2008].

[60] Differences in the nature and magnitude of river-floodplain interactions between the Fly and Strickland rivers may explain the age differences observed in all carbon fractions between rivers. The channel of the Strickland River migrates laterally at a rate of 5 m a^{-1}, generating a vigorous sediment exchange flux of $30-50$ Mt a^{-1} between

cut-bank erosion and point-bar deposition, thereby recycling approximately half its sediment load on an annual basis [*Aalto et al.*, 2008]. In contrast, recent lateral migration rates on the Middle Fly range from $1-2$ m a^{-1} in the upper reaches to undetectable rates in the lower reaches where our sampling occurred [*Dietrich et al.*, 1999; *Day et al.*, 2008]. As a result of the low migration rates in the middle Fly River, the 40% of its net annual sediment load that is deposited on its floodplain constitutes a net loss and is not compensated by cut-bank erosional inputs to the river as occurs in the Strickland [*Day et al.*, 2008]. Thus, while the Strickland floodplain may represent an important source of stored organic carbon to its lowland river reaches, the strength of this source in the Fly River should be much smaller.

[61] Sampling on the Strickland River occurred during a receding limb of the hydrograph when river sediment concentrations were not at their peak and saturated flood-plain banks were collapsing into the channel. Thus it is possible that a substantial portion of the suspended sediments in the river at the time of sampling were entrained from the floodplain. The organic signatures of the river FSS suggest that they were composed of a mix of floodplain bank sediment, freshwater algae either from floodplain lakes or the river, and an upland OM contribution. However, because the Strickland is generally quite sediment-rich, the river itself may not have high rates of primary production owing to insufficient light penetration [cf. *Wissmar et al.*, 1981].

[62] Another potentially important difference between the two rivers is that extensive floodplain lakes are more prevalent on the floodplain of the middle Fly River than on the Strickland floodplain, as a result of the lower elevational gradient of the Fly River. These blackwater lakes may represent a significant source of organic carbon to the Fly River when the floodplains are draining into the river, as they were during our sampling. In addition, the lower sediment load typical of the Fly River may favor primary production within the river channel. Whether production occurs in the floodplain lakes or within the river itself, all evidence suggests that the aquatic primary production source is larger in the Fly than the Strickland, which may partially explain the younger ages found for all carbon pools there.

[63] The isotopic values of DIC and CO_2 may also give some insight into the age and source of organic material respired within the rivers. Dissolved carbon dioxide concentrations were higher than atmospheric equilibrium concentrations at all sampling sites, suggesting that outgassing from river channels in the lowland Fly-Strickland system may be another significant carbon flux in this river system and other rivers of New Guinea [cf. *Richey et al.*, 2002]. This supersaturation occurs despite any contribution of ancient inorganic carbon from the weathering of sedimentary rocks in the watersheds, because weathering alone cannot create supersaturated conditions. The average bulk ages of dissolved CO_2 across rivers ranges from $\sim$600 a B.P. (-102‰) in the Herbert, to the Fly at $\sim$900 a B.P. (-132 ± 14‰), and finally the Strickland at >2100 a B.P. (-250 ± 106‰). These radiocarbon results are more similar to $\Delta^{14}C$ values of DIC (-240 ± 233‰) measured at mountain sites in the Amazon basin, defined as sites where the percentage of drainage area higher than 1000 m in

elevation exceeds 50%, than those measured at mixed or lowland sites, having $10-50$% and <10% of drainage area >1000 m in elevation, respectively (mixed: -14 ± 99‰, lowland: 89 ± 44‰) (data from *Mayorga et al.* [2005]). Data from the Mekong and Chao Phraya rivers in Southeast Asia also show older ages in DIC samples from higher elevation sites than lower elevation sites (-57 ± 36‰ versus 21 ± 33‰, respectively) (S. R. Alin et al., unpublished data, 2007). Upland sources of carbon from marine sedimentary rocks may contribute either ancient inorganic (carbonates) or organic (shales) carbon to the Fly and Strickland Rivers, lending an old radiocarbon signal to the DIC. The older age of the dissolved inorganic carbon in the Strickland, along with the higher alkalinity and pH values there, suggest that carbonate weathering or respiration of ancient organic matter from the headwater regions contributes more to the inorganic carbon load of the Strickland than of the Fly. The 600 a B.P. age of Herbert River DIC seems at odds with the observed high contribution of algal production to POM there. However, sediment in the Herbert River system largely stems from the Strickland River at flood stage, including along a recent "breakout" that connects the upper Strickland to Lake Murray, and thus is ultimately derived from upland sedimentary sources as well. Erosion related to overgrazing, population pressure, and lack of forest cover may contribute to inputs of older material of sufficient quantity to yield an older DIC age than would be expected on the basis of algal abundance in the water sample. The depleted radiocarbon content characteristic of lowland DIC in the Strickland River suggests that either aged organic matter is actively being respired in the river as it passes through the floodplain, adding aged/dead DIC to the water column, or that turnover of the riverine DIC pool is not sufficient to replace the highland weathering signature by the respiration of young organic matter in lowland environments [cf. *Mayorga et al.*, 2005].

[64] Falling discharge during the period of sampling may explain why the oldest DIC ages were recorded during the first days of sampling along both systems (Tables 1 and 3). During the first days of sampling in early June (STR2 and FLY1), discharge would have been primarily derived from a decrease in the upstream in-channel storage, water that had been supplied directly from upland sources with a greater fraction of old carbon. Furthermore, the rapidly falling river water level in the upper portions of the study area would have led to both the physical collapse of and robust groundwater return from the saturated river banks (field evidence for this mechanism was prevalent at sites STR3–5). The accelerated return of this particulate material of older ^{14}C age (Table 3) and associated groundwater to the channel could also help maintain older ^{14}C ages for material conveyed farther downstream and sampled in early June. As stage continued to fall throughout the sampling campaign and heavy rains began, the effects of floodplain drainage increased in significance (we saw many small floodplain channels discharging water into the Strickland). As the largest example of this process, toward the end of the campaign we estimated the discharge of the Herbert River into the lower Strickland to be on the order of 800 m^3 s^{-1}. If the young ^{14}C age of the Herbert (Table 3) is representative of the water draining into the Strickland and Fly rivers from other floodplain lakes, it seems plausible that the decrease in

ages observed for the later samples could be due to a switch in the primary source of water and sediment supplied to the Strickland and Fly rivers.

[65] In order to explain the relatively high OC-loadings observed in sediments from the Fly Delta, *Goni et al.* [2006] suggested that the Fly-Strickland river system may be a more direct conduit for the delivery of sediment from highlands to the marine environment than other large rivers such as the Amazon and the Mississippi. Small mountainous river systems such as the Eel (USA), Santa Clara (USA), and Lanyang Shi (Taiwan) typically do not have floodplains of sufficient size to accommodate the high yields of sediment mobilized from their watersheds [e.g., *Blair et al.*, 2003; *Kao and Liu*, 1996; *Komada et al.*, 2004]. In contrast, in the Amazon Basin, a large proportion of sediment weathered out of Andean headwater regions, especially during high rainfall ENSO events, is retained in long-term storage in foreland basin floodplains [*Aalto*, 2002; *Aalto et al.*, 2003]. Sediment accumulation in Amazonian lowlands comprises a net flux about 15% of the annual input to that section of the river, integrating the dynamic interplay between bank erosion and overbank deposition [*Dunne et al.*, 1998]. A chief difference in lowland floodplain storage between the Amazon and the Strickland is that the width of floodplains available for sediment accumulation is much narrower in the Strickland and active tectonic deformation is not creating new accommodation space, as in the case of a foreland basin.

[66] In the coupled watershed-continental margin model of *Blair et al.* [2004], SMR systems like the Eel River represent the reservoir bypass end of the continuum, with low residence times of mobilized sediment within the watershed, and the Amazon represents the other end of this continuum with extensive storage in bioactive reservoirs. It is also critical to consider differences in the rates of organic matter cycling between tropical and higher-latitude environments as a result of temperature differences [cf. *Eglinton et al.*, 2006]. For instance, in the tropics, fluxes of carbon into and out of soils are higher than at higher latitudes, and organic carbon stocks are generally much younger, with typical residence times of less than a decade in the tropics compared to soil profiles with organic constituents of decades to millennia in age at higher latitudes [*Trumbore*, 1993; *Smittenberg et al.*, 2006]. Although the turnover time estimated for sediment across the entire width of the Strickland floodplain is estimated to be circa 2 ka, it is reasonable to assume that a substantial portion of the material returned to the channel may comprise more recently deposited, and thus less altered floodplain deposits. This recently deposited material may be some mix of ancient organic matter or SOM mobilized from upland sources and freshly produced organic matter. Overall, it is unclear whether storage in floodplain sediments can be expected to increase or decrease the radiocarbon age of organic matter in the Fly-Strickland system. OM deposited during large flood events may effectively bury associated and underlying organic matter to a sufficient depth that it escapes the rapid turnover typical of surface layers of tropical soils. In contrast, organic matter deposited during background sedimentation conditions may be rapidly oxidized in the bioactive soil environment and replaced by contemporary OM, tending to decrease the age of the SOM overall. Therefore, although

the exchanges of sediment and carbon between the Strickland River and its floodplain are large, and residence time in the floodplains does appear to alter the stable isotopic and biochemical composition of organic matter, it is not clear that this process results in consistent increases or decreases in the age the transported POC as in other large river systems. Further research is needed to resolve where the Fly-Strickland river system falls on the continuum between reservoir bypass and extensive storage and reworking in reservoirs, keeping in mind the critical implications of climate conditions for rates of organic matter cycling.

5.3. Quantitative Assessment of Particulate OC Sources

[67] By applying a mass balance approach, we can make a preliminary estimate of the relative contributions from various end-member sources to the organic carbon in the Fly-Strickland river system. The dominant organic carbon end-members in the system include: (1) upland sources of ancient organic matter (i.e., kerogen) from upland sedimentary rocks, (2) aged carbon from upland and floodplain soils, and modern production from both (3) terrestrial and (4) aquatic sources. We used two different three-source mixing models with the variables $\Delta^{14}C$ and $\delta^{13}C$ to constrain the range of reasonable values for the contribution of each source to the six samples for which we had both stable and radiocarbon data. Model 1 included modern C_3 vascular plants (VP), C_3 freshwater algae (FA), and soil organic matter (SOM) as organic sources. Model 2 also included VP and FA, but substituted kerogen (KER) for SOM as the third source. The three mixing model equations were as follows:

$$\delta^{13}C_{sample} = f_{VP} \times \delta^{13}C_{VP} + f_{FA} \times \delta^{13}C_{FA} + f_x \times \delta^{13}C_x, \quad (1)$$

$$\Delta^{14}C_{sample} = f_{VP} \times \Delta^{14}C_{VP} + f_{FA} \times \Delta^{14}C_{FA} + f_x \times \Delta^{14}C_x, \quad (2)$$

$$1 = f_{VP} + f_{FA} + f_x, \quad (3)$$

where f values represent the fractional contribution of each end-member and x represents SOM in model 1 and KER in model 2. Mixing model results that returned negative f values were eliminated from consideration, as they represent the inability of the model to generate the observed sample composition with the end-members used.

[68] End-member composition for the mixing models was estimated on the basis of published values. For each end-member, default $\delta^{13}C$ and $\Delta^{14}C$ values were chosen, along with a likely range of variation. We first ran both mixing models with all default values, and subsequently varied each parameter individually using the selected end values for each range. Soil $\delta^{13}C$ values for forest sites vary with elevation and range from −30.8 to −23.5‰ in Papua New Guinea [*Bird et al.*, 1994]. The default SOM $\delta^{13}C$ value was chosen to be the average across elevations in the watershed, −27.2‰, with a 2σ range of −29.9 to −24.5‰. Freshwater algae in the Amazon have $\delta^{13}C$ values ranging from −40 to −26‰, with an average of −33.3‰ [*Forsberg et al.*, 1993]. Initial trials with the mixing model suggested that the

Table 8. Fractional Contributions of Organic End-Members Based on $\Delta^{14}C$ and $\delta^{13}C$ Mixing Models[a]

Sample Location or Identification	Sample Type	Model 1 (VP, FA, SOM)			Model 2 (VP, FA, KER)		
		f_{VP}	f_{FA}	f_{SOM}	f_{VP}	f_{FA}	f_{KER}
FLY1	CPOM	0.43	0.25	0.32	0.57	0.30	0.14
		(0.29−0.60)	(0.05−0.41)	(0.20−0.40)	(0.40−0.82)	(0.03−0.48)	(0.08−0.18)
STR1	CPOM	0.38	0.09	0.53	0.61	0.16	0.23
		(0.23−0.49)	(0.07−0.24)	(0.42−0.67)	(0.47−0.70)	(0.06−0.32)	(0.16−0.28)
FLY3	FPOM	n.s.[b]	n.s.	n.s.	0.27	0.43	0.29
		(0.05−0.16)	(0.13−0.34)	(0.56−0.72)	(0.03−0.40)	(0.31−0.70)	(0.26−0.32)
STR1	FPOM	n.s.	n.s.	n.s.	0.34	0.26	0.39
		(0.00−0.11)	(0.14)	(0.76−0.86)	(0.18−0.51)	(0.09−0.43)	(0.35−0.42)
1C LFS 200A 28−30	floodplain	n.s.	n.s.	n.s.	0.64	0.06	0.31
		(0.15−0.26)	(0.05−0.16)	(0.68−0.70)	(0.49−0.73)	(0.03−0.22)	(0.24−0.36)
5 LFB 150 34−36	floodplain	0.22	0.15	0.63	0.49	0.24	0.27
		(0.00−0.31)	(0.05−0.25)	(0.52−0.80)	(0.38−0.71)	(0.01−0.38)	(0.22−0.31)

[a]Results in the upper row for each sample were obtained using default values for all parameters. The values in parentheses represent the full range of values observed during permutation tests that returned valid results.

[b]Here n.s. means no solution.

average value was too enriched for the PNG sites, so we used −36.5‰ as the default, with a range of −40 to −33‰. Observed $\delta^{13}C$ signatures in C_3 vegetation also vary with elevation and latitude, with values ranging from approximately −30.5to −24.5‰ at elevations and latitudes similar to those in the Fly River basin [*Körner et al.*, 1991]. We used the midpoint of this range, −27.5‰, as our default value and also tested both ends of this range. A wide range of published $\delta^{13}C$ values exist for kerogen (−35 to −20‰) [*Lewan*, 1986]. Without data directly from kerogen deposits in PNG highlands, we chose to use the average value observed in the Eel River watershed, approximately −24‰ [*Blair et al.*, 2003]. We also tested values ranging from −28 to −20‰.

[69] Default values and ranges for the radiocarbon ($\Delta^{14}C$) content of end-members were estimated on the basis of *Goni et al.* [2003, 2005, 2006, and references therein]. For SOM, the default was chosen to be −400‰ and the range −500 to −300‰. Vascular plant matter was assumed to have been produced in the year of sampling, bearing a signature of +70‰ for 2003 [*Levin and Kromer*, 2004], with a range of +170 to −30‰. Freshwater algae was also assumed to have grown in the year produced, but a lower default value (0‰) was chosen to reflect the likely uptake of some portion of the aged DIC present in the rivers. Alternate values of +70, −100, and −200‰ were used to represent CO_2 source contributions from the atmosphere, DIC in the Fly River, and DIC in the Strickland River. The age of kerogen in sedimentary rocks is typically on the order of hundreds of thousands of years or more, so it contains no radiocarbon and has a $\Delta^{14}C$ of −1000‰.

[70] Because of the uncertainty in end-member composition, the mixing models generally yielded wide ranges for possible source contributions (Table 8). However, some general patterns emerged. Model 1 default values failed to generate valid fractional contribution values for FPOM samples and the downstream floodplain sample, suggesting that the organic sources for these samples cannot be parsed without accounting for the input of kerogen. For the CPOM samples, model 1 suggests that roughly equal contributions of SOM and vascular plant matter dominated organic sources at both the Fly and Strickland sites, with a smaller contribution of freshwater algae. Between the two sites, the combined contribution of VP and FA was higher in the Fly

CPOM sample. Although the default values performed poorly for FPOM and floodplain samples, the alternate values tested suggest that SOM inputs in these samples may be significant (>50%).

[71] In contrast, model 2 yielded viable results for all samples using default values (Table 8). Model 2 suggests that coarse particulate organics at both sites were dominated by VP inputs (∼60%), with the remainder divided between algal and kerogen sources. As expected, kerogen inputs appear to be somewhat more important in the Strickland sample, as were algal inputs in the Fly sample. Fine particulate organic sources appear to be split roughly equally among the three sources, with algae comprising the dominant FPOM source in the Fly sample and kerogen in the Strickland sample. Finally, model 2 results suggest that floodplain organic matter represents contributions of approximately 50−60% vascular plant remains, 25−35% kerogen, and 5−25% algal inputs.

[72] The differences between models 1 and 2 in the estimated contributions of OC sources highlight the need to improve characterization of watershed end-member composition in the Fly-Strickland river system in order to resolve the sources of organic matter to suspended sediments, floodplain soils, and ultimately to delta sediments. We attempted a four-source mixing model, incorporating all four end-members and using ON:OC as the third variable. Default ON:OC values used were 0.10 for both kerogen and SOM, 0.03 for vascular plants, and 0.14 for algae. Four of the six results were invalid, pointing to poor end-member constraints for ON:OC.

[73] Taken en masse, these results suggest that organic matter in the Fly-Strickland river-floodplain system represents a mixture of fresh OM inputs from C_3 vegetation and algal production as well as aged and/or ancient organic matter from soils and upland kerogen deposits. The mixing models suggest that it is not possible to account for the composition of all suspended sediment and floodplain samples without including a kerogen source. The model without the SOM term did adequately explain the observed sample compositions, which suggests that SOM composition may itself represent a combination of the other end-members.

[74] The results presented here may not be typical of the transported sediment load in the Fly-Strickland river system

on an annual basis, as the samples were collected at the end of a falling stage in the hydrograph and not during the period of peak runoff in the uplands when the majority of sediment transport occurs. This may explain the greater relative influence of C_3 vegetation and freshwater algae on the composition of suspended sediments than that of kerogen. Overall, it appears that the sediment-rich Strickland, which has the highest sediment yield, higher inputs of sediment from channel migration, and lowest average OC content, also has a higher contribution of ancient organic matter from upland sources. At their confluence, the Strickland drains twice the watershed area of the Fly River (36,740 versus 18,400 km^2 [*Dietrich et al.*, 1999]). Within the Fly-Strickland river system, both major tributaries have significant lowland floodplains, but modification of organic matter through river-floodplain interactions appears to play a more important role in organic matter cycling the Strickland than in the Fly and is a significant factor in the organic matter cycling in the system as a whole.

5.4. Estimated Flux of Particulate Carbon to the Ocean

[75] The sampling for this study was conducted during moderate discharge conditions, when suspended-sediment concentrations and organic composition would not necessarily represent those associated with peak delivery of sediment to the delta environment. Nonetheless, because the sediment efflux in this region of the world is globally significant, we will tentatively extrapolate the results of the present work to generate a preliminary estimate of the organic carbon delivery to the ocean from the Fly-Strickland river system and, by analogy, rivers throughout New Guinea.

[76] If we accept the estimate of mean discharge on the Strickland to be 3110 m^3 s^{-1} and the average sediment yield to be 70 Mt a^{-1}, the average sediment concentration in the river would be 714 mg L^{-1} [*Dietrich et al.*, 1999]. Similarly, for average discharge and sediment yield estimates of 2244 m^3 s^{-1} and 30 Mt a^{-1}, respectively, on the Fly River, the average sediment concentration would be 424 mg L^{-1}.

[77] Overall, the rivers studied here were characterized by high organic content: 3.8% OC by mass on average, which is 2–3 times higher than the average organic carbon content of suspended sediments in the Amazon River system [*Devol and Hedges*, 2001]. In the Amazon main stem, the fine and coarse sediment loads and their weight percent OC contents vary in a complex manner that is roughly inverse to discharge [*Devol et al.*, 1995]. Thus the high weight percentages observed in this study may simply reflect the less-than-peak discharge and suspended-sediment concentrations at the time of sampling. For the Fly-Strickland suspended-sediment data presented here, a power function describes the relationship between FSS concentration and weight %OC (wt %OC = $32.31 \times$ FSS$^{-0.5897}$, $r^2 = 0.7156$). This equation agrees quite well with relationships constructed for TSS versus weight %OC documented in the Amazon main stem [*Devol and Hedges*, 2001] and a global compilation of river data [*Meybeck*, 1982], although our relationship uses FSS in place of TSS because we lack CSS concentration data. If we assume that CSS accounts for 10% of TSS concentration and augment our totals accordingly, a new relationship between TSS and weight %OC can be defined for the Fly-Strickland system (wt %OC = $45.82 \times$ TSS$^{-0.6559}$, $r^2 = 0.6361$). This relationship is unconstrained

by data at higher sediment concentrations, so this equation is not suitable for use at the average TSS concentrations calculated above on the basis of mean discharge and sediment yield. However, at the lower end of TSS concentration, Fly-Strickland data appear to be intermediate to those of *Devol and Hedges* [2001] and *Meybeck* [1982], so we use values intermediate to those extrapolated by their curves to TSS concentrations of $\sim$425 mg L^{-1} and $\sim$715 mg L^{-1} ($\sim$1.5 and 1.0 wt %OC for the Fly and Strickland, respectively). Combining the above estimates yields an estimated delivery of 0.7 Mt a^{-1} of organic carbon from the Strickland and 0.45 Mt a^{-1} from the Fly River, for a total of $\sim$1.2 Mt a^{-1}, to the Fly River delta. This represents a realistic, but perhaps conservative, estimate.

[78] If, on the other hand, it turns out that the measured %OC values at the time of sampling are typical of these rivers during higher flow and sediment transport conditions than those based on an extrapolation of the global river data compilation, the organic carbon delivery to the delta may be much higher. This may be reasonable, as discharge and rainfall do not vary as significantly on a seasonal basis in the Fly River drainage basin as they do in other river basins, and the soil organic carbon content appears to be substantially higher in the Fly River basin than in other major world rivers [*Ludwig et al.*, 1996]. Also, if our samples do represent a bias toward sediment mobilized from banks and bars during the falling limb of a flood, as appeared to be occurring in the field, they might also represent the OC characteristics of this material in transport and exchange during the highest stages of the flood. Using our averages of 1.8% OC for the Strickland and 3.7% OC for the Fly (excluding the outlier associated with floodplain drainage), we would get annual fluxes of $\sim$1.3 Mt OC a^{-1} from the Strickland and 1.1 Mt OC a^{-1} from the Fly River, for a total of $\sim$2.4 Mt OC a^{-1} from the entire system.

[79] The island of New Guinea, at 800,000 km^2 in area, represents just over one tenth of the land area included in the Amazon Basin ($\sim$7 million km^2). Being in a collisional tectonic environment, topography on the island is generally quite high, and rates of uplift and denudation are also high [*Pickup*, 1984; *Milliman*, 1995]. Estimates of sediment discharge to the ocean from New Guinea rivers alone, including large rivers such as the Fly and the Purari, as well as the many small rivers draining the steep northern margin of the island, suggest that the island is a source of 1700 Mt of sediment to the marine environment annually. These estimates are essentially equivalent to the combined loads of all rivers draining North America and greater than the estimated the 1200 Mt a^{-1} of sediment delivered by the Amazon River to its delta [*Milliman*, 1995]. Furthermore, on the basis of the measured %OC contents of suspended particulates measured in this study and those from sediment exiting the non−tidally influenced Amazon at Obidos ($\sim$1.0% OC [*Keil et al.*, 1997]), it appears that rivers draining New Guinea alone may lead to the delivery of a comparable or greater amount of OC to the ocean than the Amazon River.

[80] The most detailed work to date on mountainous rivers in Oceania has been done on subtropical and temperate ecosystems (i.e., Taiwan and New Zealand) [e.g., *Kao and Liu*, 1996; *Leithold et al.*, 2006]. Climatic conditions in the small tropical river basins in Oceania favor perennially high

terrestrial primary production and oxidation rates as well as discharge conditions. In addition, the organic carbon content of soils in the Fly and Purari Rivers in Papua New Guinea represent two of the three highest values in a database of major world rivers [*Ludwig et al.*, 1996], reflecting large reservoirs of soil carbon within these watersheds available for export to marine environments. This real potential for enormous sediment effluxes and large organic carbon stocks in the watersheds of tropical Oceania underscores the need for further research into carbon cycling in rivers of this tectonically active region and their role in the global carbon budget.

References

Aalto, R. (2002), Geomorphic form and process of mass flux within an active orogen: Denudation of the Bolivian Andes and sediment transport and deposition within the channel-floodplain systems of the Amazonian foreland, Ph.D. thesis, 365 pp., Univ. of Wash., Seattle.

Aalto, R., L. Maurice-Bourgoin, T. Dunne, D. R. Montgomery, C. A. Nittrouer, and J.-L. Guyot (2003), Episodic sediment accumulation on Amazonian flood plains influenced by El Niño/Southern Oscillation, *Nature*, *425*, 493–497.

Aalto, R., T. Dunne, and J.-L. Guyot (2006), Geomorphic controls on Andean denudation rates, *J. Geol.*, *114*, 85–99.

Aalto, R., J. W. Lauer, and W. E. Dietrich (2008), Spatial and temporal dynamics of sediment accumulation and exchange along Strickland River floodplains (PNG), over decadal-to-centennial timescales, *J. Geophys. Res.*, doi:10.1029/2006JF000627, in press.

Aller, R. C., and N. E. Blair (2004), Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes, *Geochim. Cosmochim. Acta*, *68*, 1815–1825.

Aller, R. C., N. E. Blair, Q. Xia, and P. D. Rude (1996), Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments, *Cont. Shelf Res.*, *16*, 753–786.

Arnason, T. S., and R. G. Keil (2000), Mechanisms of pore water organic matter adsorption to montmorillonite, *Mar. Chem.*, *71*, 309–320.

Arnason, T. S., and R. G. Keil (2001), Organic-mineral interactions in marine sediments studied using density fractionation and X-ray photoelectron spectroscopy, *Org. Geochem.*, *32*, 1401–1415.

Arnason, T. S., and R. G. Keil (2007), Changes in organic matter—Mineral interactions for marine sediments with varying oxygen exposure times, *Geochim. Cosmochim. Acta*, *71*, 3545–3556.

Aufdenkampe, A. K., J. I. Hedges, J. E. Richey, A. V. Krusche, and C. A. Llerena (2001), Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin, *Limnol. Oceanogr.*, *46*, 1921–1935.

Aufdenkampe, A. K., E. Mayorga, J. I. Hedges, C. Llerena, P. D. Quay, J. Gudeman, A. V. Krusche, and J. E. Richey (2006), Organic matter in the Peruvian headwaters of the Amazon: Compositional evolution from the Andes to the lowland Amazon mainstem, *Org. Geochem.*, *38*, 337–364, doi:10.1016/j.orggeochem.2006.06.003.

Barillé-Boyer, A.-L., L. Barillé, H. Massé, D. Razet, and M. Héral (2003), Correction for particulate organic matter as estimated by loss on ignition in estuarine ecosystems, *Estuarine Coastal Shelf Sci.*, *58*, 147–153.

Benner, R., and S. Opsahl (2001), Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume, *Org. Geochem.*, *32*, 597–611.

Bird, M. I., S. G. Haberle, and A. R. Chivas (1994), Effect of altitude on the carbon-isotope composition of forest and grassland soils of Papua New Guinea, *Global Biogeochem. Cycles*, *8*, 13–22.

Bird, M. I., G. J. Brunskill, and A. R. Chivas (1995), Carbon-isotope composition of sediments from the Gulf of Papua, *Geo Mar. Lett.*, *15*, 153–159.

Blair, N. E., E. L. Leithold, S. T. Ford, K. A. Peeler, J. C. Holmes, and D. W. Perkey (2003), The persistence of memory: The fate of ancient sedimentary organic carbon in a modern sedimentary system, *Geochim. Cosmochim. Acta*, *67*, 63–73.

Blair, N. E., E. L. Leithold, and R. C. Aller (2004), From bedrock to burial: The evolution of particulate organic carbon across coupled watershed-continental margin systems, *Mar. Chem.*, *92*, 141–156.

Day, G., W. E. Dietrich, J. C. Rowland, and A. Marshall (2008), The depositional web on the floodplain of the Fly River, Papua New Guinea, *J. Geophys. Res.*, doi:10.1029/2006JF000622, in press.

Devol, A. H., and J. I. Hedges (2001), Organic matter and nutrients in the mainstem Amazon River, in *The Biogeochemistry of the Amazon Basin*, edited by M. E. McClain, R. L. Victoria, and J. E. Richey, pp. 275–306, Oxford Univ. Press, New York.

Devol, A. H., B. R. Forsberg, J. E. Richey, and T. P. Pimentel (1995), Seasonal variation in chemical distributions in the Amazon (Solimões) River: A multiyear time series, *Global Biogeochem. Cycles*, *9*, 307–328.

Dietrich, W. E., G. Day, and G. Parker (1999), The Fly River, Papua New Guinea: Inferences about river dynamics, floodplain sedimentation and fate of sediment, in *Varieties of Fluvial Form*, edited by A. J. Miller and A. Gupta, pp. 345–376, John Wiley, Chichester, U. K.

Dunne, T., L. A. K. Mertes, R. H. Meade, J. E. Richey, and B. R. Forsberg (1998), Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil, *GSA Bull.*, *110*, 450–460.

Edmond, J. M. (1970), High precision determination of titration alkalinity and total carbon dioxide of sea water by potentiometric titration, *Deep Sea Res.*, *17*, 737–750.

Eglinton, T. I., N. J. Drenzek, A. F. Dickens, P. Poussart, E. Schefuss, D. Montlucon, E. R. Druffel, J. Southon, G. dos Santos, and K. Hughen (2006), Temporal constraints on the transfer of particulate organic carbon from the continents to the oceans, *Eos Trans. AGU*, *87*(52), Fall Meet. Suppl., Abstract OS14A-01.

Forsberg, B. R., C. A. R. M. Araujo-Lima, L. A. Martinelli, R. L. Victoria, and J. A. Bonassi (1993), Autotrophic carbon sources for fish of the central Amazon, *Ecology*, *74*, 643–652.

Goni, M. A., and J. I. Hedges (1995), Sources and reactivities of marine-derived organic matter in coastal sediments as determined by alkaline CuO oxidation, *Geochim. Cosmochim. Acta*, *59*, 2965–2981.

Goni, M. A., and S. Montgomery (2000), Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples, *Anal. Chem.*, *72*, 3116–3121.

Goni, M. A., and K. A. Thomas (2000), Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (north inlet, South Carolina, USA), *Estuaries*, *23*, 548–564.

Goni, M. A., K. C. Ruttenberg, and T. I. Eglinton (1998), A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico, *Geochim. Cosmochim. Acta*, *62*, 3055–3075.

Goni, M. A., M. J. Teixeira, and D. W. Perkey (2003), Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA), *Estuarine Coastal Shelf Sci.*, *57*, 1023–1048.

Goni, M. A., M. B. Yunker, R. W. Macdonald, and T. I. Eglinton (2005), The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean, *Mar. Chem.*, *93*, 53–73.

Goni, M. A., N. Monacci, R. Gisewhite, A. Ogston, J. Crockett, and C. Nittrouer (2006), Distribution and sources of particulate organic matter in the water column and sediments of the Fly River delta, Gulf of Papua (Papua New Guinea), *Estuarine Coastal Shelf Sci.*, *69*, 225–245.

Goni, M. A., N. Monacci, R. Gisewhite, J. Crockett, C. Nittrouer, A. Ogston, S. R. Alin, and R. Aalto (2008), Terrigenous organic matter in sediments from the Fly River delta–clinoform system (Papua New Guinea), *J. Geophys. Res.*, doi:10.1029/2006JF000653, in press.

Gordon, E. S., and M. A. Goni (2004), Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin, *Mar. Chem.*, *92*, 331–352.

Harris, P. T., E. K. Baker, A. R. Cole, and S. A. Short (1993), A preliminary study of sedimentation in the tidally dominated Fly River Delta, Gulf of Papua, *Cont. Shelf Res.*, *13*, 441–472.

Hedges, J. I., W. A. Clark, P. D. Quay, J. E. Richey, A. H. Devol, and U. M. Santos (1986), Compositions and fluxes of particulate organic material in the Amazon River, *Limnol. Oceanogr.*, *31*, 717–738.

Kao, S.-J., and K.-K. Liu (1996), Particulate organic carbon export from a subtropical mountainous river (Lanyang Shi) in Taiwan, *Limnol. Oceanogr.*, *41*, 1749–1757.

Keil, R. G., L. M. Mayer, P. D. Quay, J. E. Richey, and J. I. Hedges (1997), Loss of organic matter from riverine particles in deltas, *Geochim. Cosmochim. Acta*, *61*, 1507–1511.

Kogel-Knabner, I., W. Zech, P. G. Hatcher, and J. W. de Leeuw (1991), Fate of plant components during biodegradation and humification in forest soils: Evidence from structural characterization of individual biomacromolecules, in *Advances in Soil Organic Matter Research: The Impact on Agriculture and the Environment*, edited by W. S. Wilson and T. R. G. Gray, pp. 61–70, R. Soc. of Chem., Cambridge, U. K.

Komada, T., E. R. M. Druffel, and S. E. Trumbore (2004), Oceanic export of relict carbon by small mountainous rivers, *Geophys. Res. Lett.*, *31*, L07504, doi:10.1029/2004GL019512.

Körner, C., G. D. Farquar, and S. C. Wong (1991), Carbon isotope discrimination follows latitudinal and altitudinal trends, *Oecologia*, *88*, 30–40.

Leithold, E. L., N. E. Blair, and D. W. Perkey (2006), Geomorphologic controls on the age of particulate organic carbon from small mountainous and upland rivers, *Global Biogeochem. Cycles*, *20*, GB3022, doi:10.1029/2005GB002677.

Levin, I., and B. Kromer (2004), The tropospheric $^{14}CO_2$ level in mid-latitudes of the Northern Hemisphere (1959–2003), *Radiocarbon*, *46*, 1261–1272.

Lewan, M. D. (1986), Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks, *Geochim. Cosmochim. Acta*, *50*, 1583–1591.

Lewis, E., and D. Wallace (1998), *Program Developed for CO_2 System Calculations*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn.

Ludwig, W., J.-L. Probst, and S. Kempe (1996), Predicting the oceanic input of organic carbon by continental erosion, *Global Biogeochem. Cycles*, *10*, 23–41.

Lyons, W. B., C. A. Nezat, A. E. Carey, and D. M. Hicks (2002), Organic carbon fluxes to the ocean from high-standing islands, *Geology*, *30*, 443–446.

Macko, S. A., M. H. Engel, and P. L. Parker (1993), Early diagenesis of organic matter in sediments: assessment of mechanisms and preservation by the use of isotopic molecular approaches, in *Organic Geochemistry: Principles and Applications*, edited by M. H. Engel and S. A. Macko, pp. 185–210, Plenum, New York.

Mayorga, E., A. K. Aufdenkampe, C. A. Masiello, A. V. Krusche, J. I. Hedges, P. D. Quay, J. E. Richey, and T. A. Brown (2005), Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers, *Nature*, *436*, 538–541.

McCallister, S. L., J. E. Bauer, J. E. Cherrier, and H. W. Ducklow (2004), Assessing sources and ages of organic matter supporting river and estuarine bacterial production: A multiple-isotope ($\Delta^{14}C$, $\delta^{13}C$, and $\delta^{15}N$) approach, *Limnol. Oceanogr.*, *49*, 1687–1702.

Meybeck, M. (1982), Carbon, nitrogen, and phosphorus transport by world rivers, *Am. J. Sci.*, *282*, 401–450.

Milliman, J. D. (1995), Sediment discharge to the ocean from small mountainous rivers: The New Guinea example, *Geo Mar. Lett.*, *15*, 127–133.

Milliman, J. D., and J. P. M. Syvitski (1992), Geomorphic/tectonic control of sediment discharge to the ocean: The importance of small mountainous rivers, *J. Geol.*, *100*, 525–544.

Ogston, A. S., R. W. Sternberg, C. A. Nittrouer, D. P. Martin, M. A. Goñi, and J. S. Crockett (2008), Sediment delivery from the Fly River tidally dominated delta to the nearshore marine environment and the impact of El Niño, *J. Geophys. Res.*, doi:10.1029/2006JF000669, in press.

Peterson, M. L., S. Q. Lang, A. K. Aufdenkampe, and J. I. Hedges (2003), Dissolved organic carbon measurement using a modified high-temperature combustion analyzer, *Mar. Chem.*, *81*, 89–104.

Petsch, S. T., R. A. Berner, and T. I. Eglinton (2000), A field study of the chemical weathering of ancient sedimentary organic matter, *Org. Geochem.*, *31*, 475–487.

Pickup, G. (1984), Geomorphology of tropical rivers: I.Landforms, hydrology and sedimentation in the Fly and lower Purari, Papua New Guinea, in *Channel Processes: Water, Sediment, Catchment Controls*, edited by A. P. Schick, *Catena Suppl.*, *5*, 1–17.

Quay, P. D., and J. Stutsman (2003), Surface layer carbon budget for the subtropical N. Pacific: $\delta^{13}C$ constraints at station ALOHA, *Deep Sea Res., Part I*, *50*, 1045–1061.

Ratner, B. D., and D. G. Castner (1997), Electron spectroscopy for chemical analysis, in *Surface Analysis—The Principal Techniques*, edited by J. C. Vickerman, pp. 43–98, John Wiley, Chicester, U. K.

Raymond, P. A., and J. E. Bauer (2001), Riverine export of aged terrestrial organic matter to the North Atlantic Ocean, *Nature*, *409*, 497–500.

Raymond, P. A., J. E. Bauer, N. F. Caraco, J. J. Cole, B. Longworth, and S. T. Petsch (2004), Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers, *Mar. Chem.*, *92*, 353–366.

Richey, J. E., J. M. Melack, A. K. Aufdenkampe, V. M. Ballester, and L. L. Hess (2002), Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, *Nature*, *416*, 617–620.

Smith, L. C., and D. E. Alsdorf (1998), Control on sediment and organic carbon delivery to the Arctic Ocean revealed with spaceborne synthetic aperture radar: Ob' River, Siberia, *Geology*, *26*, 395–398.

Smittenberg, R. H., T. I. Eglinton, S. Schouten, and J. S. Sinninghe Damsté (2006), Ongoing buildup of refractory organic carbon in boreal soils during the Holocene, *Science*, *314*, 1283–1286.

Stallard, R. F. (1995), Relating chemical and physical erosion, *Rev. Mineral.*, *31*, 543–564.

Stuiver, M., and H. A. Polach (1977), Discussion: Reporting of ^{14}C Data, *Radiocarbon*, *19*, 355–363.

Swanson, K. M., E. Watson, R. Aalto, J. W. Lauer, M. T. Bera, A. Marshall, M. P. Taylor, S. C. Apte, and W. E. Dietrich (2008), Sediment load and floodplain deposition rates: Comparison of the Fly and Strickland Rivers, Papua New Guinea, *J. Geophys. Res.*, doi:10.1029/2006JF000623, in press.

Trumbore, S. E. (1993), Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements, *Global Biogeochem. Cycles*, *7*, 275–290.

UNESCO (1994), *Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements*, *IOC Manual Guides*, vol. 29, Paris.

Watson, E. W. (2006), The use of mine-derived trace element signatures to study recent sedimentation on a tropical floodplain, Honors thesis, 106 pp., Dep. of Phys. Geogr., Macquarie Univ., Sydney, Australia.

Wissmar, R. C., J. E. Richey, R. F. Stallard, and J. M. Edmond (1981), Plankton metabolism and carbon processes in the Amazon River, its tributaries, and floodplain waters, Peru-Brazil, May-June 1977, *Ecology*, *62*, 1622–1633.

Wolanski, E., B. King, and D. Galloway (1997), Salinity intrusion in the Fly River estuary, Papua New Guinea, *J. Coastal Res.*, *13*, 983–994.

Yuan, G., M. Soma, H. Seyama, B. K. G. Theng, L. M. Lavkulich, and T. Takamatsu (1998), Assessing the surface composition of soil particles from some Podzolic soils by X-ray photoelectron spectroscopy, *Geoderma*, *86*, 169–181.

Zeebe, R. E., and D. Wolf-Gladrow (2001), *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*, 346 pp., Elsevier, New York.

Zhang, J., P. D. Quay, and D. O. Wilbur (1995), Carbon isotope fractionation during gas-water exchange and dissolution of CO_2, *Geochim. Cosmochim. Acta*, *59*, 107–114.

————————————

R. Aalto, Department of Geography, University of Exeter, Exeter EX4 4RJ, U.K.

S. R. Alin and J. E. Richey, School of Oceanography, University of Washington, Seattle, WA 98195, USA. (salin@u.washington.edu)

W. E. Dietrich, Department of Earth and Planetary Science, University of California, Berkeley, Berkeley, CA 94720, USA.

M. A. Goni, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA.