Oxidation of petrogenic organic carbon in the Amazon floodplain as a source of atmospheric CO₂

Julien Bouchez, Olivier Beyssac, Valier Galy, Jérôme Gaillardet, Christian France-Lanord, Laurence Maurice, Patricia Moreira-Turcq

► To cite this version:

Julien Bouchez, Olivier Beyssac, Valier Galy, Jérôme Gaillardet, Christian France-Lanord, et al..
Oxidation of petrogenic organic carbon in the Amazon floodplain as a source of atmospheric CO₂.
Geology, 2010, 38 (3), pp.255-258. 10.1130/G30608 . ird-00588739

HAL Id: ird-00588739

<https://hal.ird.fr/ird-00588739>

Submitted on 26 Apr 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Oxidation of petrogenic organic carbon in the Amazon floodplain as a source of atmospheric CO₂

**Julien Bouchez^{1,2}, Olivier Beyssac³, Valier Galy⁴, Jérôme Gaillardet^{1,2}, Christian France-
Lanord⁵, Laurence Maurice⁶, and Patricia Moreira-Turcq⁷**

¹*Institut de Physique du Globe de Paris, CNRS-UMR 7154, 4, place Jussieu 75252 Paris cedex
05, France*

²*Université Paris Diderot, 75205 Paris cedex 13*

³*Laboratoire de Géologie, Ecole Normale Supérieure, CNRS-UMR 8538, 24 rue Lhomond,
75231 Paris cedex 05*

⁴*Woods Hole Oceanographic Institution, 360 Woods Hole Rd, Woods Hole, Massachusetts
02543, USA*

⁵*Centre de Recherches Pétrographiques et Géochimiques, CNRS-UPR 2300, BP 20, 54501
Vandœuvre-lès-Nancy, France*

⁶*Laboratoire des Mécanismes de Transfert en Géologie, IRD, 14 avenue Edouard Belin, 31400
Toulouse, France*

⁷*IRD-UR 154, 93140 Bondy, France*

ABSTRACT

The two long-term sources of atmospheric carbon are CO₂ degassing from metamorphic and volcanic activity, and oxidation of organic carbon (OC) contained in sedimentary rocks, or petrogenic organic carbon (OC_{petro}). The latter flux is still poorly constrained. In this study, we report Particulate Organic Carbon (POC) content and ¹⁴C-activity measurements in Amazon River sediments, which allow for estimates of the OC_{petro} content of these sediments. A large

decrease of OC_{petro} content in riverine sediments is observed from the outlet of the Andes to the mouth of the large tributaries. This loss reveals oxidation of OC_{petro} during transfer of sediments in the floodplain, and results in an escape of ca. 0.25 MtC/yr to the atmosphere, which is on the same order of magnitude as the CO_2 consumption by silicate weathering in the same area. Raman microspectroscopy investigations show that graphite is the most stable phase with respect to this oxidation process. These results emphasize the significance of OC_{petro} oxidation in large river floodplains in the global C cycle.

INTRODUCTION

CO_2 degassed from Earth's interior is partly scavenged by chemical reactions occurring during weathering of silicate rocks and subsequent carbonate precipitation in the ocean (Garrels et al., 1976). It is also consumed by photosynthesis followed by burial of organic matter in marine sediments (Hayes and Waldbauer, 2006). These two mechanisms have respectively built up the two major carbon reservoirs of Earth's surface: limestones (50×10^6 GtC), and ^{14}C -free organic matter disseminated in sedimentary rocks, or petrogenic OC (OC_{petro} , 12.5×10^6 GtC; Berner, 1990). The oxidation of petrogenic OC is a source of CO_2 to the atmosphere (Berner, 2004). However, quantifying the modern rates of OC_{petro} oxidation remains a challenge for understanding and modeling the geological carbon and oxygen cycles. Although a few studies based on soil profiles have attempted to determine rates of OC_{petro} oxidation (e.g., Keller and Bacon ; 1998, Petsch et al., 2000), budgets of fossil organic carbon oxidation at river catchment scale have not received much attention (e.g., Galy et al., 2008b ; Hilton et al., 2008).

The dissolved and particulate load transported by rivers derive from chemical weathering of rocks and physical erosion of soils and rocks. This includes organic material, which consists in a mixture of recent biospheric carbon (OC_{recent}), and OC_{petro} (Blair et al., 2004 ; Komada et al.,

2004 ; Leithold et al., 2006). The oxidation of OC transported in rivers is thought to mostly affect OC_{recent} and to have no effect on the geological budget of atmospheric CO₂. In their study on the Amazon river, Hedges et al. (1986) showed that the organic material transported by the Amazon river mostly consists in OC_{recent} derived from the highly productive lowland ecosystems. During fluvial transport, the oxidation of this dissolved and particulate organic matter results in the escape of ca. 500 MtC/yr to the atmosphere (Richey et al., 2002). Most of this oxidation derives from OC_{recent} (Mayorga et al., 2005) and has therefore no impact on the long-term regulation of atmospheric CO₂. However, a significant fraction of particulate organic matter can be of petrogenic origin. Distinguishing between OC_{petro} and OC_{recent} in rivers is thus of prime importance because only the oxidation of OC_{petro} represents an input of C to the active reservoirs at Earth's surface.

In this study, we report POC (Particulate Organic Carbon) and ¹⁴C activity measurements in river sediments collected throughout the Amazon River system. Sediments were collected along river depth-profiles in order to capture the whole range of granulometric spectrum of erosion products. Concentrations of OC_{petro} were measured in these sediments, and coupled with structural characterization of OC_{petro} by Raman microspectroscopy. This allows us to estimate the first order of carbon input to the atmosphere by OC_{petro} oxidation during transfer of sediments in the floodplains of the Amazon Basin, and gives a lower bound on the estimate of CO₂ release to the atmosphere by the oxidation of OC_{petro} in the Amazon Basin.

SETTING, SAMPLING AND ANALYTICAL METHODS

The Amazon is the world largest river in terms of drainage area and water discharge to the ocean (Meybeck and Ragu, 1997). Isotopic studies (Allègre et al., 1996) have clearly shown that most of the Amazon River sediments are derived from the Andes. There, Amazon tributaries

69 drain extensive outcrops of easily erodible sedimentary and meta-sedimentary rocks, such as
70 black shales in the Bolivian Andes.

71 We sampled the two main tributaries of the Amazon, the Solimões and the Madeira
72 rivers, at their mouth, as well as the Amazon mainstream at Obidos, in June 2005 and March
73 2006 (Fig. 1). The Beni River, which supplies most of the sediments to the Madeira River, has
74 been sampled at the outlet of the Andes, near Rurrenabaque, where it enters the Madeira
75 floodplain, in February 2001. At each location, river water was sampled at various river depths
76 along vertical profiles, from channel surface to bottom, and filtered at 0.22 μm porosity; bed
77 sediments were also dredged. Within the channel of large rivers, granulometric sorting induces
78 important variations of chemical composition of river sediments from the surface to the bottom
79 (Galy et al., 2008a). The sampling technique used here allows us to characterize the whole range
80 of erosion products in terms of grain size distribution and mineralogy.

81 POC content was determined using a modified Eurovector EuroEA3028-HT elemental
82 analyzer coupled to a GV Instruments IsoPrime continuous-flow isotope mass spectrometer at
83 the CRPG, Vandoeuvre-lès-Nancy, France (Galy et al., 2007). ^{14}C activity was determined by
84 Accelerator Mass Spectrometry at LMC14 National Facility, Saclay, France, after off-line
85 organic matter combustion and CO_2 cryogenic purification. Samples were decarbonated before
86 combustion (Galy et al., 2007). ^{14}C values are given after correction for ^{13}C fractionation
87 (normalization to a $\delta^{13}\text{C}$ of -25‰), and expressed as pMC (percentage of Modern Carbon)
88 comparatively to 95% of the ^{14}C activity of the oxalic acid standard OXI. Petrogenic carbon was
89 characterized by Raman microspectroscopy using a Renishaw InVia Raman micro-spectrometer
90 at the Laboratoire de Géologie, Ecole Normale Supérieure, Paris, France (Bernard et al., 2008).
91 Raman spectra were obtained directly on raw sediments, and on thin sections for bedrocks.

RESULTS: ^{14}C AGE OF $\text{OC}_{\text{recent}}$ AND OC_{petro} CONTENT

In depth-profile sediments, ^{14}C content shows a wide range of variation, between 37.5 and 86.2% pMC (Tab. 1). A first-order positive relation between pMC and POC is observed, the coarser bed sediments being the most depleted in both OC and ^{14}C .

In river sediments, OC can be interpreted as a binary mixture of OC_{petro} and $\text{OC}_{\text{recent}}$ with distinct ^{14}C content (e.g., Blair et al., 2004). Following the approach of Galy et al. (2008b) we plot our results in a diagram of POC * pMC (or Modern C) as a function of POC (Fig. 2). Depth-profiles from different sampling locations define linear trends, at 95% confidence level, regardless the sampling period. These correlation indicate that samples from a given depth-profile have rather constant absolute OC_{petro} concentration and ^{14}C activity of the $\text{OC}_{\text{recent}}$ component (see appendix for details). The values of OC_{petro} content in the samples and ^{14}C -age of the $\text{OC}_{\text{recent}}$ pool can be both determined from the slope and intercept of each line (Tab. 1). Similar observations were made on the Ganga-Brahmaputra system (Galy et al., 2008b).

The highest OC_{petro} content, 0.26% ($\pm 0.11\%$, 2 sigma uncertainty), is obtained for the Beni at Rurrenabaque. There, OC_{petro} makes up to 50% of the POC, and likely originates from the large outcrops of black shales drained by this river. Lowland sampling locations (Solimões, Madeira and Amazon) all display lower OC_{petro} content, between 0.02% and 0.06%, (or even lower, regarding the uncertainties reported in Tab. 1). Thus, there is a large apparent decrease in OC_{petro} concentration between the entry and the outlet of the Madeira floodplain.

Since the Beni contributes to ca. 40% of the Madeira sedimentary budget (Guyot et al., 1996), potential addition of supposedly OC_{petro} -free sedimentary material by other tributaries of the Madeira River could only lead to an OC_{petro} content decrease by a factor of slightly more than

two. Hence, the apparent 10-fold decrease in OC_{petro} content could mainly be due either to a preferential burial of OC_{petro} -rich material in the floodplain, or to a loss by oxidation.

Burial of sedimentary material occurs in the Amazon basin between the Andean source of sediments and the Amazon mouth, in particular between Rurrenabaque and the mouth of the Madeira (Guyot et al., 1996). If sediment storage is the cause of the observed decrease of OC_{petro} concentration reported here, it would imply the preferential sedimentation of an OC_{petro} enriched component. As stated above, sampling along depth-profiles allows to take into account the whole range of riverine particulate matter in size distribution and mineralogy. Our results (Fig. 2) show that absolute OC_{petro} content is the same along all depth-profiles, despite expected variations in particle size distribution with depth (Curtis et al., 1979). Selective burial of a given size fraction should therefore not affect OC_{petro} concentration of suspended sediments. This observation strongly suggests that the decrease of OC_{petro} concentration along the course of the Madeira is due to OC_{petro} oxidation.

ESTIMATE OF THE MAGNITUDE OF THE CO_2 SOURCE

Given the important amount of sediments transported in the Madeira floodplain (Guyot et al., 1996), the oxidation flux resulting from the large decrease in OC_{petro} content during the transfer of sediments in the floodplain should be significant. A first-order oxidation flux of OC_{petro} can be estimated using previous works on sedimentary budgets in the Madeira River Basin. Among the 212 Mt/yr of sediments delivered by the Beni River to the plain, ca. one half is buried in the foreland basin (Guyot et al., 1996). The amount of Beni sediments actually transiting through the plain is thus on the order of 100 Mt/yr. Hence, given the OC_{petro} concentration reported in this study, 100 Mt/yr of sediments represent a OC_{petro} flux of 0.26 MtC/yr supplied to the plain and not buried. At the outlet, 100 Mt/yr of sediments represent a

OC_{petro} flux of 0.02 MtC/yr that exits the plain. The difference of ca. 0.25 MtC/yr is thus the oxidation flux of OC_{petro} in the Madeira floodplain. This is a first order estimate but also a lower bound of the OC_{petro} oxidation flux of the Madeira basin as we assumed that no OC_{petro} is delivered to the Madeira floodplain by its two other main tributaries. In addition, this estimate does not take into account the oxidation of OC_{petro} upstream Rurrenabaque and in Andean soils which we are not able to address here. Moreover, we assume that no oxidation affects the sediments buried in the foreland basin. The flux of 0.25 MtC/y is thus a minimum bound of the OC_{petro}-derived CO₂ outgassing flux. This number is in the same order of magnitude as the net CO₂ sequestration flux in this basin associated to silicate weathering (0.8 MtC/yr; Gaillardet et al., 1997).

OC_{petro} STRUCTURAL CHARACTERIZATION

OC_{petro} is derived from organic carbon initially trapped in sediments and has been structurally and chemically transformed during diagenesis and metamorphism. Structural characterization of OC_{petro} by Raman microspectroscopy has been performed both in riverine sediments and bedrock samples. Because volcanic rocks of the high cordillera may not contain any significant amount of solid OC, the main sources of OC_{petro} are most likely the sediments, mainly black shales, drained by the Rio Beni. Three samples representative of the main bedrock lithologies from the Tipuani, Mapiri and Coroico basin have been investigated (Fig. 1). They contain two main OC_{petro} fractions (Fig. 3): one is rather disordered, exhibiting Raman spectra typical of greenschist facies (Beyssac et al., 2002), in agreement with the thermal history of these rocks. The second is highly graphitic and supposedly represents a detrital pool. Both fractions are found in all riverine sediments either as isolated particles or as inclusions or aggregates within minerals (mostly quartz, phyllosilicates or plagioclases, Fig. 3). As shown in Fig. 3, the graphitic

phases become dominant in samples of downstream sediment (Rio Beni and then Rio Madeira), while the disordered fraction progressively disappears. Graphite thus appears to be the most stable phase with respect to the oxidation process.

DISCUSSION AND CONCLUSION

This study thus shows that the oxidation of OC_{petro} during fluvial transport is a significant flux for the long-term atmospheric CO_2 budget. Fluvial oxidation of OC_{petro} may counteract the consumption flux of CO_2 by silicate weathering, which is conventionally thought to be the only significant process, with organic carbon sequestration, to control atmospheric CO_2 at geological timescales (Berner, 2004; Wallmann, 2001). The degradation of physically mobilized ancient organic matter in large fluvial systems is most probably dependent on a number of factors such as residence time of particles in floodplains (Blair et al., 2003), or on climatic conditions. This important oxidation flux found here is probably favored by the warm and oxidative conditions that prevail in the soils of Amazonian floodplains. Whether this oxidation of OC_{petro} occurs via biotic (Petsch et al., 2001) or abiotic (Chang and Berner, 1999) pathways, is beyond the scope of the paper but would need further investigations.

Galy et al. (2008b) showed that 30%–50% of the OC_{petro} present in the Himalayan source rocks were preserved and are still present in the marine sediments of the Bengal Fan. Our estimate of the OC_{petro} preservation in the Madeira floodplain, 15%, is an upper bound of the extent of OC_{petro} preservation in the Madeira basin, as it does not take into account the oxidation taking place in Andean soils, downstream the sampling locations, or even in the ocean, before or after deposition. The Amazon basin is hence a better incinerator of OC_{petro} than the Himalayan system. This is likely due to differences in the sources of OC_{petro} . Low-grade metamorphic rocks with disordered OC are common in the Andes, while high-grade metamorphic rocks generating

highly graphitic OC are widespread in the Himalaya (Beyssac et al., 2004). Disordered OC is more prone to oxidation than graphite because of its chemistry (aromatic skeleton with radicalization) and structure, as micro- and nano-porosity enhance oxidation rates.

Over geological timescale, geodynamic (metamorphic grade, erosion intensity...) settings probably control the extent of preservation of OC_{petro} during the erosion-transport-sedimentation cycle. Over shorter timescale (tens to hundreds kyrs), and for a given geodynamic context, climate is likely to control the oxidation or preservation of OC_{petro}, through erosion, temperature, and probably the nature of microbial communities (and their metabolic activity) present in the floodplain.

We speculate that, in response to an atmospheric CO₂ rise, increased global temperature would probably enhance oxidation of petrogenic OC in large river floodplains and associated CO₂ outgassing. This mechanism possibly constitutes a new positive feedback in the long-term carbon cycle.

ACKNOWLEDGMENTS

This study was funded by CNRS-INSU program Reliefs de la Terre, and realized in the frame of the HyBAm project (cooperation agreement with CNPq n° 492685/2004-5). We sincerely acknowledge the following Brazilian Institutions and Universities: ANA, UnB, UFF, CPRM. We thank C. Guilmette for technical assistance in the stable isotopes laboratory and R. Hilton for improving the quality of the text. This is IGP contribution N°2564.

APPENDIX: OC_{petro} AND ¹⁴C AGE OF OC_{recent} CALCULATION

We use a method described in Galy et al., 2008b. Briefly, we describe the OC pool as a binary mixture of OC_{petro}, derived from the rocks, and OC_{recent} derived from the biosphere (vegetation, soils and autotrophic production in the river). These two component have distinct ¹⁴C activity,

OC_{petro} being ¹⁴C-free (pMC_{petro} = 0). For each sample, the absolute content of Modern C (POC x pMC – “Modern” referring here to a present ¹⁴C standard) can thus be written as:

$$\% \text{Modern C} = \text{POC} \times \text{pMC}_{\text{recent}} - \% \text{OC}_{\text{petro}} \times \text{pMC}_{\text{recent}},$$

where pMC_{recent} is the ¹⁴C activity of OC_{recent} and %OC_{petro} is the absolute content of OC_{petro}. In a %Modern C vs. POC plot, samples having the same pMC_{recent} and the same %OC_{petro} define a single straight line. The pMC_{recent} is given by the slope of the line and allows the calculation of the age of the recent component. Moreover, the absolute content of OC_{petro} is given by the opposite of the intercept/slope ratio.

Despite the auto-correlated nature of the two plotted variables, and as shown in Tab. 1, the relationships we obtain are more significantly correlated than in the case of randomly distributed POC and pMC (either assuming an uniform or normal distribution, within boundaries defined by the ranges covered by the values measured in our samples).

Uncertainties on the determined slope and intercept (and thus on %OC_{petro} and pMC_{recent}) are yielded by a full inversion method (Tarantola and Valette, 1982). Relatively low uncertainties on pMC_{recent} (i.e. on the slope) stem from the good alignment of data points.

REFERENCES CITED

- Allègre, C.J., Dupré, B., Négrel, P., and Gaillardet, J., 1996, Sr-Nd-Pb isotope systematics in Amazon and Congo River systems: constraints about erosion processes: *Chemical Geology*, v. 131, p. 93–112, doi: 10.1016/0009-2541(96)00028-9.
- Bernard, S., Beyssac, O., and Benzerara, K., 2008, Raman mapping using advanced line-scanning systems: geological applications: *Applied Spectroscopy*, v. 62, p. 1180–1188.
- Berner, R.A., 2004, *The Phanerozoic carbon cycle*, Oxford University Press, 150 pp.

- 228 Berner, R.A., 1990, Atmospheric carbon dioxide levels over Phanerozoic time: *Science*, v. 249,
229 p. 1382–1386, doi: 10.1126/science.249.4975.1382.
- 230 Beyssac, O., Goffé, B., Chopin, C., and Rouzaud, J.-N., 2002, Raman spectra of carbonaceous
231 material in metasediments: a new geothermometer: *Journal of Metamorphic Geology*, v. 20,
232 no. 9, p. 859–871, doi: 10.1046/j.1525-1314.2002.00408.x.
- 233 Beyssac, O., Bollinger, L., Avouac, J.-P., and Goff, È., B., 2004, Thermal metamorphism in the
234 Lesser Himalaya of Nepal determined from Raman spectroscopy of carbonaceous material:
235 *Earth and Planetary Science Letters*, v. 225, p. 233–241.
- 236 Blair, N.E., Leithold, E.L., Ford, S.T., Peeler, K.A., Holmes, J.C., and Perkey, D.W., 2003, The
237 persistence of memory: the fate of ancient sedimentary organic carbon in a modern
238 sedimentary system: *Geochimica et Cosmochimica Acta*, v. 67, no. 1, p. 63–73, doi:
239 10.1016/S0016-7037(02)01043-8.
- 240 Blair, N.E., Leithold, E.L., and Aller, R.C., 2004, From bedrock to burial: the evolution of
241 particulate organic carbon across coupled watershed-continental margin systems: *Marine*
242 *Chemistry*, v. 92, p. 141–156, doi: 10.1016/j.marchem.2004.06.023.
- 243 Chang, S., and Berner, R.A., 1999, Coal weathering and the geochemical carbon cycle:
244 *Geochimica et Cosmochimica Acta*, v. 63, no. 19/20, p. 3301–3310, doi: 10.1016/S0016-
245 7037(99)00252-5.
- 246 Curtis, W.F., Meade, R.H., Nordin, C.F., Price, N.B., and Sholkovitz, E.R., 1979, Non-uniform
247 vertical distribution of fine sediment in the Amazon River: *Nature*, v. 280, p. 381–383, doi:
248 10.1038/280381a0.

- 249 Gaillardet, J., Dupré, B., Allègre, C.J., and Négrel, P., 1997, Chemical and physical denudation
250 in the Amazon River Basin: *Chemical Geology*, v. 142, p. 141–173, doi: 10.1016/S0009-
251 2541(97)00074-0.
- 252 Galy, V., Bouchez, J., and France-Lanord, C., 2007, Determination of Total Organic Carbon
253 content and ^{13}C in carbonate-rich detrital sediments: *Geostandards and Geoanalytical*
254 *Research*, v. 31, no. 3, p. 199–207, doi: 10.1111/j.1751-908X.2007.00864.x.
- 255 Galy, V., France-Lanord, C., and Lartiges, B., 2008a, Loading and fate of particulate organic
256 carbon from the Himalaya to the Ganga-Brahmaputra delta: *Geochimica et Cosmochimica*
257 *Acta*, v. 72, no. 7, p. 1767–1787, doi: 10.1016/j.gca.2008.01.027.
- 258 Galy, V., Beyssac, O., France-Lanord, C., and Eglinton, T.I., 2008b, Recycling of graphite
259 during Himalayan erosion: a geological stabilization of carbon in the crust: *Science*, v. 322,
260 no. 5903, p. 943–945, doi: 10.1126/science.1161408.
- 261 Garrels, R.M., Lerman, A., and Mackenzie, F.T., 1976, Controls of atmospheric O_2 and CO_2 –
262 past, present and future: *American Scientist*, v. 63, p. 306–315.
- 263 Guyot, J.-L., Filizola, N., Quintanilla, J., and Cortez, J., 1996, Dissolved solids and suspended
264 sediment yields in the Rio Madeira basin, from the Bolivian Andes to the Amazon: *IAHS*
265 *Publication*, v. 236, p. 55–63.
- 266 Hayes, J.M., and Waldbauer, J.R., 2006, The carbon cycle and associated redox processes
267 through time: *Philosophical Transactions of the Royal Society*, v. 361, no. 1470, p. 931–950,
268 doi: 10.1098/rstb.2006.1840.
- 269 Hedges, J.I., Quay, P.D., Groottes, P.M., Richey, J.E., Devol, A.H., Farwell, G.W., Schmidt,
270 F.W., and Salati, E., 1986, Carbon-14 in the Amazon River System: *Science*, v. 231,
271 p. 1129–1131, doi: 10.1126/science.231.4742.1129.

- 272 Hilton, R.H., Galy, A., Hovius, N., Chen, M.-C., Horng, M.-J., and Chen, H., 2008, Tropical-
273 cyclone-driven erosion of the terrestrial biosphere from mountains: *Nature Geosciences*,
274 v. 1, p. 759–762, doi: 10.1038/ngeo333.
- 275 Keller, C.K., and Bacon, D.H., 1998, Soil respiration and georespiration distinguished by
276 transport analyses of vadose CO₂, ¹³CO₂ and ¹⁴CO₂: *Global Biogeochemical Cycles*, v. 12,
277 no. 2, p. 361–372, doi: 10.1029/98GB00742.
- 278 Komada, T., Druffel, E.R.M., and Trumbore, S.E., 2004, Oceanic export of relict carbon by
279 small mountainous rivers: *Geophysical Research Letters*, v. 31, p. L07504, doi:
280 10.1029/2004GL019512.
- 281 Leithold, E.L., Bair, N.E., and Perkey, D.W., 2006, Geomorphic controls on the age of
282 particulate organic carbon from small mountainous and upland rivers: *Global*
283 *Biogeochemical Cycles*, v. 20, p. GB3022, doi: 10.1029/2005GB002677.
- 284 Mayorga, E., Aufdenkampe, A.K., Masiello, C.A., Krusche, A.V., Hedges, J.I., Quay, P.D.,
285 Richey, J.E., and Brown, T.A., 2005, Young organic matter as a source of carbon dioxide
286 outgassing from Amazonian rivers: *Nature*, v. 436, no. 28, p. 538–541, doi:
287 10.1038/nature03880.
- 288 Meybeck, M., and Ragu, A., 1997, River discharges to the oceans: an assessment of suspended
289 solids, major ions and nutrients, UNEP, WHO.
- 290 Petsch, S.T., Berner, R.A., and Eglinton, T.I., 2000, A field study of chemical weathering of
291 ancient sedimentary organic matter: *Organic Geochemistry*, v. 31, p. 475–487, doi:
292 10.1016/S0146-6380(00)00014-0.

- Petsch, S.T., Eglinton, T.I., and Edwards, K.J., 2001, ^{14}C -dead living biomass: evidence for microbial assimilation of ancient organic carbon during shale weathering: *Science*, v. 292, p. 1127–1131, doi: 10.1126/science.1058332.
- Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., and Hess, L.L., 2002, Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2 : *Nature*, v. 416, p. 617–620, doi: 10.1038/416617a.
- Tarantola, A., and Valette, B., 1982, Generalized nonlinear inverse problems solved using the least squares criterion: *Reviews of Geophysics and Space Physics*, v. 20, no. 2, p. 219–232, doi: 10.1029/RG020i002p00219.
- Wallmann, K., 2001, Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO_2 and climate: *Geochimica et Cosmochimica Acta*, v. 65, p. 3005–3025, doi: 10.1016/S0016-7037(01)00638-X.

FIGURE CAPTIONS

Figure 1. Map of the Amazon basin and sampling sites.

Figure 2. Modern C content ($\text{POC} \times \text{pMC}$, expressed in weight % of the whole sample) vs. POC for sediments collected along a depth profile in different rivers of the Amazon basin. The linear regression solution for each sampling location is also shown. Open symbols stand for bedload sediments, closed symbols for suspended load sediments. Samples are plotted regardless of their position in the hydrological cycle.

Figure 3. Representative Raman spectra of riverine and bedrock material, with the location of the main graphite G band, and the D1, D2 and D3 defect bands. Minerals associated with C are also indicated. Fossil organic matter was found as free particles, inclusions in minerals such as quartz or rutiles, or aggregates with phyllosilicates. Free particles were as large as 20 μm in diameter.

316

TABLE 1. SAMPLE LIST AND RESULTS:
ANALYTICAL ABSOLUTE UNCERTAINTIES (2σ) ARE 0.5 M
FOR SAMPLING DEPTH, 0.3% FOR PMC AND 0.02% FOR POC

Sample	River	Water stage	Depth (m)	pMC (%)	POC (%)	pMC _{recent} (%)	OC _{petro} (%)
AM-05-35	Amazon	Falling	58	78.6	0.65	84	0.06
AM-05-37		Falling	30	78.4	0.92	± 0.04	± 0.05
AM-05-39		Falling	2	81.4	1.22	$(r^2=0.995)$	
AM-06-64		Rising	20	76.9	0.93		
AM-06-66	Solimões	Rising	Bedload	77.3	0.65		
AM-05-04		High	28	86.2	0.79	87	0.03
AM-05-08		High	2	83.3	1.13	± 0.03	± 0.02
AM-05-10		High	Bedload	37.5	0.06	$(r^2=0.998)$	
AM-06-10	Madeira	Rising	22	82.7	0.95		
AM-06-36		High	15	70.6	0.62	71	0.02
AM-06-38		High	0	68.3	0.65	± 0.04	± 0.03
AM-06-44		High	Bedload	45.5	0.05	$(r^2=0.999)$	
AM-01-14-a	Beni	High	1	44.1	0.51	96	0.26
AM-01-14-b		High	3	55.1	0.61	± 0.13	± 0.11
AM-01-14-c		High	5	42.0	0.45	$(r^2=0.986)$	
AM-01-14-d		High	7	41.0	0.47		

317