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

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

5 *¹Institut de Physique du Globe de Paris, CNRS-UMR 7154, 4, place Jussieu 75252 Paris cedex*
6 *05, France*

7 *²Université Paris Diderot, 75205 Paris cedex 13*

8 *³Laboratoire de Géologie, Ecole Normale Supérieure, CNRS-UMR 8538, 24 rue Lhomond,*
9 *75231 Paris cedex 05*

10 *⁴Woods Hole Oceanographic Institution, 360 Woods Hole Rd, Woods Hole, Massachusetts*
11 *02543, USA*

12 *⁵Centre de Recherches Péetrographiques et Géochimiques, CNRS-UPR 2300, BP 20, 54501*
13 *Vandoeuvre-lès-Nancy, France*

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

16 *⁷IRD-UR 154, 93140 Bondy, France*

17 **ABSTRACT**

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

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

30 INTRODUCTION

31 CO_2 degassed from Earth's interior is partly scavenged by chemical reactions occurring
32 during weathering of silicate rocks and subsequent carbonate precipitation in the ocean (Garrels
33 et al., 1976). It is also consumed by photosynthesis followed by burial of organic matter in
34 marine sediments (Hayes and Waldbauer, 2006). These two mechanisms have respectively built
35 up the two major carbon reservoirs of Earth's surface: limestones (50×10^6 GtC), and ^{14}C -free
36 organic matter disseminated in sedimentary rocks, or petrogenic OC (OC_{petro} , 12.5×10^6 GtC;
37 Berner, 1990). The oxidation of petrogenic OC is a source of CO_2 to the atmosphere (Berner,
38 2004). However, quantifying the modern rates of OC_{petro} oxidation remains a challenge for
39 understanding and modeling the geological carbon and oxygen cycles. Although a few studies
40 based on soil profiles have attempted to determine rates of OC_{petro} oxidation (e.g., Keller and
41 Bacon ; 1998, Petsch et al., 2000), budgets of fossil organic carbon oxidation at river catchment
42 scale have not received much attention (e.g., Galy et al., 2008b ; Hilton et al., 2008).

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

46 2004 ; Leithold et al., 2006). The oxidation of OC transported in rivers is thought to mostly
47 affect OC_{recent} and to have no effect on the geological budget of atmospheric CO₂. In their study
48 on the Amazon river, Hedges et al. (1986) showed that the organic material transported by the
49 Amazon river mostly consists in OC_{recent} derived from the highly productive lowland ecosystems.
50 During fluvial transport, the oxidation of this dissolved and particulate organic matter results in
51 the escape of ca. 500 MtC/yr to the atmosphere (Richey et al., 2002). Most of this oxidation
52 derives from OC_{recent} (Mayorga et al., 2005) and has therefore no impact on the long-term
53 regulation of atmospheric CO₂. However, a significant fraction of particulate organic matter can
54 be of petrogenic origin. Distinguishing between OC_{petro} and OC_{recent} in rivers is thus of prime
55 importance because only the oxidation of OC_{petro} represents an input of C to the active reservoirs
56 at Earth's surface.

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

65 **SETTING, SAMPLING AND ANALYTICAL METHODS**

66 The Amazon is the world largest river in terms of drainage area and water discharge to
67 the ocean (Meybeck and Ragu, 1997). Isotopic studies (Allègre et al., 1996) have clearly shown
68 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.

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

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

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

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

111 Since the Beni contributes to ca. 40% of the Madeira sedimentary budget (Guyot et al.,
112 1996), potential addition of supposedly OC_{petro} -free sedimentary material by other tributaries of
113 the Madeira River could only lead to an OC_{petro} content decrease by a factor of slightly more than

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

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

127 **ESTIMATE OF THE MAGNITUDE OF THE CO₂ SOURCE**

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

137 OC_{petro} flux of 0.02 MtC/yr that exits the plain. The difference of ca. 0.25 MtC/yr is thus the
138 oxidation flux of OC_{petro} in the Madeira floodplain. This is a first order estimate but also a lower
139 bound of the OC_{petro} oxidation flux of the Madeira basin as we assumed that no OC_{petro} is
140 delivered to the Madeira floodplain by its two other main tributaries. In addition, this estimate
141 does not take into account the oxidation of OC_{petro} upstream Rurrenabaque and in Andean soils
142 which we are not able to address here. Moreover, we assume that no oxidation affects the
143 sediments buried in the foreland basin. The flux of 0.25 MtC/y is thus a minimum bound of the
144 OC_{petro} -derived CO_2 outgassing flux. This number is in the same order of magnitude as the net
145 CO_2 sequestration flux in this basin associated to silicate weathering (0.8 MtC/yr; Gaillardet et
146 al., 1997).

147 OC_{petro} STRUCTURAL CHARACTERIZATION

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

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

163 **DISCUSSION AND CONCLUSION**

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

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

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

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

192 We speculate that, in response to an atmospheric CO_2 rise, increased global temperature
193 would probably enhance oxidation of petrogenic OC in large river floodplains and associated
194 CO_2 outgassing. This mechanism possibly constitutes a new positive feedback in the
195 long-term carbon cycle.

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

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

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

$$208 \quad \% \text{Modern C} = POC \times pMC_{\text{recent}} - \% OC_{\text{petro}} \times pMC_{\text{recent}},$$

209 where pMC_{recent} is the ^{14}C activity of OC_{recent} and $\% OC_{\text{petro}}$ is the absolute content of OC_{petro} . In a
210 $\% \text{Modern C}$ vs. POC plot, samples having the same pMC_{recent} and the same $\% OC_{\text{petro}}$ define a
211 single straight line. The pMC_{recent} is given by the slope of the line and allows the calculation of
212 the age of the recent component. Moreover, the absolute content of OC_{petro} is given by the
213 opposite of the intercept/slope ratio.

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

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

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305 **FIGURE CAPTIONS**

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

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

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

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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		Rising	Bedload	77.3	0.65			
AM-05-04		Solimões	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		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			

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