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Iron isotope composition of the bulk waters and sediments from the Amazon River Basin



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ABSTRACT

The present study provides iron concentrations and isotopic compositions determined by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), along with key chemical, mineralogical and physical properties of 35 representative bulk (unfiltered) waters and bulk sediments from the Amazon River Basin. These samples from the Amazon River, five of its main tributaries (the Solimões, Negro, Madeira, Tapajós and Trombetas rivers) and four sub-tributaries (the Purus, Jaú, Ucayali and Napo rivers) were essentially collected during seven field missions conducted for over two years. These encompassed the centennial flood of May 2009 and the exceptional low water stage of September-October 2010, thereby providing the most extreme hydrological situations that have been recorded over the last hundred years. While the data confirmed massive losses of iron (up to ~19000 tons/day, ca. 50% of the Amazon River bulk water budget) in the Solimões and Negro rivers mixing zone, the Fe isotope signatures of these bulk waters behaved conservatively. This property allows the use of bulk water Fe isotope signature to track iron sources and explain such isotopic signature in terms of simple mixing. Unfiltered samples from the organic-rich black water rivers present light δ^{57} Fe relative to the average continental crust composition. This contrasts with the composition of the bulk white waters carrying a high mineral suspended load that have δ^{57} Fe values undistinguishable from the crustal isotopic signature (~0.1‰ relative to IRMM-14). This observation indicates that the Fe isotopic composition represents a reliable direct tracer of the iron speciation and, therefore, of the host phases of iron in its sources. Specifically, the white water δ^{57} Fe most likely trace the signatures of igneous and sedimentary sources, as well as of their lateritic soil minerals, while the bulk black water δ^{57} Fe track a preferential release of Fe that has gone through a reduction step in the organic-rich horizons of tropical podzols as a result of the biological activity. This study shows that the total iron transferred by the Amazon River represents between 5 and 30% of the world's ocean Fe input by rivers, and this Amazon bulk water iron displays an isotopic composition indistinguishable from that of the average continental crust.

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1. Introduction

Iron is the fourth most abundant element in the Earth's crust and as such, it plays a key role in many biogeochemical processes at the Earth's surface, notably through its changes in redox states. Iron oxyhydroxide particles are an important carrier for other metals in aquatic systems, and Fe is key for plant and animal metabolism (Langmuir, 1996;

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Crichton, 2001). Its oxyhydroxide minerals also constitute hill-forming lateritic ferruginous crusts that affect continental water flows in inter-tropical zones.

Despite extensive studies for over half a century, some important questions pertaining to the iron cycling on continental surfaces remain unanswered. For instance, the role of the vegetation in iron transfer from soils to rivers is still poorly quantified (Pokrovsky et al., 2006). The Amazon River Basin, which is the largest watershed in the world, delivers ~17% of riverine freshwater to the oceans (Callède et al., 2010) and therefore a large fraction of the metals coming from rivers. Despite the significance of the Amazon River Basin, the iron cycling remains little known in this watershed. This is partly because the sources

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and fluxes of this element still have to be properly determined and quantified (see e.g., Benedetti et al., 2003). Furthermore, an improved knowledge of the amount of iron transferred by rivers to the oceans is essential to understand continental erosional/weathering mechanisms given its redox chemistry combined with the abundance of this element in rocks, soils and in the river loads. Such an improved understanding applied to the sedimentary record may in turn provide keys in the characterization of ancient climates. Similarly, this element is an essential, yet sometimes limiting nutrient for the oceanic phytoplankton that plays a key role in the atmospheric carbon pump (Martin, 1990). The forms and fluxes of the Fe delivered to the ocean by major tropical rivers such as the Amazon are among the clues for a better understanding of this biogeochemical process.

For such source and mass balance questions, the isotopic approach brings a new dimension relative to the study of iron concentrations only. Furthermore, stable isotopes may also provide information on the nature of the chemical reactions involved in the cycling of this element (e.g., Hoefs, 2004). Hence, the last decade has seen a growing number of studies aiming at the understanding of the mechanisms that fractionate iron isotopes on the Earth's surface. Such studies were made possible by analytical developments using plasma source mass spectrometry (Belshaw et al., 2000). They have shown the importance of redox reactions on the Fe isotope fractionation (e.g., Johnson et al., 2002; Wiederhold et al., 2006), making this isotopic approach well suited to study processes like reductive iron dissolution or the interaction with ligands from the organic matter in soils (e.g., Brantley et al., 2001; Fantle and DePaolo, 2004; Emmanuel et al., 2005; Wiederhold et al., 2007). Additionally, these soil processes may, in turn, be traced using the Fe isotope composition of the suspended and dissolved loads of rivers (Ingri et al., 2006; Ilina et al., 2013). Promising first results also suggest that the role of plants in the iron transfer from soil to surface water is likely to leave an imprint on the isotope composition of river-born Fe, since different types of iron metabolism in plants result in contrasting iron isotope signatures (Guelke and von Blanckenburg, 2007; Kiczka et al., 2010).

Besides its global importance, the Amazon River Basin is an interesting target to study the iron cycling because a pioneering study on the suspended and dissolved load of the Amazon River and its two major tributaries (the Solimões and the Negro rivers) has uncovered a large Fe isotope fractionation (~1.8% in δ^{57} Fe; Bergquist and Boyle, 2006). However, this study was based on only three sampling stations, making it difficult to have a comprehensive overview on the possible range of Fe isotope signatures and on their likely causes. Bergquist and Boyle (2006) concluded that the iron isotope signature delivered by the Amazon to the Atlantic Ocean was lighter than that of the average continental crust, which seems to be in contradiction with previous work on other rivers rich in clastic sediments (Beard et al., 2003) or inferences based on lateritic soils (Poitrasson et al., 2008) that dominate tropical regions. From these two latter studies, it can be argued that a river such as the Amazon, with a high mineral suspended load, and that drains ferralitic soils, should rather deliver to the Atlantic Ocean an iron with δ^{57} Fe values close to that of the continental crust overall (~0.1‰ relative to IRMM-14; Poitrasson, 2006).

Given the importance of this question towards a better definition of the isotopic composition of Fe sources feeding the oceans (Lacan et al., 2008; John and Adkins, 2010) as well as the remaining unknowns on the Fe cycling in a major intertropical watershed, we have conducted an iron isotopic study of bulk waters and sediment samples taken in various representative locations of the Amazon River Basin in order to provide a comprehensive picture of this continental-scale watershed. To avoid potential biases on the Fe stable isotope composition induced by water filtrations, we worked with bulk samples instead of filtered waters, although our recently published study on this topic suggests that filtration processes do not appear to produce a significant isotopic shift (Ilina et al., 2013). This work is part of an integrated research program that also focuses on the spatial and temporal variation of the suspended matter (dos Santos Pinheiro et al., 2013), the importance of speciation of Fe in waters (Mulholland et al., 2014) and the role of the vegetation and soil transformation on the iron cycling in the Amazon Basin using the isotopic approach.

2. Study site and samples

The Amazon River Basin is a continental scale watershed (Fig. 1) that covers more than 6×10^6 km² (Molinier et al., 1996), i.e., comprising approximately one third of South America. The intertropical Amazon River is the largest in the world in terms of drained surface area and mean annual water discharge $(206000 \pm 6\% \text{ m}^3/\text{s})$ to the ocean (Callède et al., 2010). The water discharge varies by at least a factor of two as a function of the hydrological cycle (Martinez et al., 2009) with the low water level period in October-November and the high water level in May-June. The Peruvian Amazon River is renamed Solimões River at the border between Peru and Brazil, where its water discharge already equates that of the second largest river in the world, the Congo (Molinier et al., 1996), even though it is still ca. 3000 km upstream the Atlantic Ocean. The river is named Amazon in Brazil only from the confluence between the Negro River and the Solimões River (Fig. 1). The latter represents already up to half of the total discharge of the Amazon River at its mouth during the flood season. Besides the Negro River, which represents up to one third of the Amazon water discharge at low waters, other important tributaries include the Madeira, Tapajós, Xingu and Trombetas rivers (Fig. 1).

In order to obtain a complete picture of the rivers variability in terms of chemistry and sources, we investigated bulk water samples from the Amazon River and some of its main tributaries, including the Solimões, Negro, Madeira, Trombetas and Tapajós (Fig. 1). The Solimões and Madeira are classified as white water rivers because of their abundant sedimentary suspended load that results from high erosional rates in the Andes (e.g., Stallard and Edmond, 1983; Seyler and Boaventura, 2003). The Napo and Ucayali rivers, which are tributaries of the Solimões River, drain the Ecuadorian and Peruvian part of the Andes, while the Madeira River drains the Bolivian Andes (e.g., Molinier et al., 1996). These two latter rivers carry 93% of the suspended load found in the Amazon mainstream (Filizola and Guyot, 2009). The Negro is a black water river, rich in both dissolved and suspended organic matter. Although it notably drains giant tropical podzols (Fritsch et al., 2009), its mineralogical and chemical sources are varied (Molinier et al., 1996) since, for example, some of its tributaries come from the Guyana Shield (e.g., the Branco River). More representative rivers that flow over the rainforest soils are the Jaú River (Allard et al., 2011), a tributary of the Negro River, and the Purus River, a tributary of the Solimões River, which has a "blackish" water (Bouchez et al., 2010) with small amounts of suspended matter and low organic content. Lastly, we sampled the Tapajós and the Trombetas rivers that are both clear waters, with low amounts of suspended matter and low organic content, representative of the highly weathered Brazilian and Guyana shields, respectively (e.g., Stallard and Edmond, 1983; Gaillardet et al., 1997).

In order to characterize the rivers suspended load that is lost during its transport to the ocean, we also took sediment samples along the banks of the Solimões, Negro, Madeira and Amazon rivers.

3. Methods

Unfiltered, bulk water and bulk sediment samples were collected during seven multidisciplinary cruises along the Amazon River and its tributaries, from May 2009 to September 2010. Additional sediment samples were collected during previous field missions (Guyot et al., 2007). The types of measurements and sampling varied according to the main objective of the cruises, but they typically involved water discharge rates, measured by Acoustic Doppler Current Profiler (ADCP) with a 2SD uncertainty better than 4%, following the methods reported by Filizola and Guyot (2004). Water temperature, conductivity and



Fig. 1. Map of the Amazon River Basin. The red dots correspond to the water sample locations (coordinates are reported in Table 1). The three cities along the Amazon River referred to in the text are also shown (black squares). From www.ore-hybam.org.

pH were also measured immediately after sampling using a WTW pH/conductimeter 340i and/or multi-parameter sensors (YSI 6820 V2 or Hydrolab DS5X). Repeated measurements in the field using the same equipment or comparing the values from different devices suggest that conductivity was measured with an uncertainty of $\pm 1 \mu$ S/cm and pH < ± 0.2 units.

When they were not measured directly with ADCP at the time of sampling, or to make accurate mass balance calculation of the water input from different tributaries at the same date, discharges at the gauging stations were assessed from the HYBAM (hydrology of the Amazon basin program) database. They were computed using:

 $Q = A \cdot V$

in which V can be obtained through the Manning-Strickler equation:

 $V = 1/n \cdot R^{2/3} \cdot S^{1/2}$

where:

Q	is the	water	discharge	(m³/	/s)
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- A is the cross-section area (m^2)
- *V* is the cross-section average velocity (m/s)
- *n* is the Manning coefficient
- *R* is the hydraulic radius (m)
- *S* is the slope of the water surface

The Manning coefficient n is calibrated for each gauging station as a function of the water stage, using the available ADCP discharge measurements (at least 30 per station). The geometric parameters R and A are deduced from the cross-sections obtained during discharge measurements. Finally, the water slope is computed for a given day using a downstream gauging station at reasonable distance (no more than

300 km), whose depth gauge altitude has been obtained through Differential Global Positioning System (DGPS) monitoring.

For the present study, typically one liter of river water was taken using Nalgene high-density polyethylene (HDPE) bottles, pre-cleaned in the clean lab with pro analysis HCl and milli-Q water. Water was sampled ~50 cm below the river surface (unless indicated otherwise in Table 1), after three bottle rinses, with a 300 μ m net covering the mouth of the bottle to avoid large particles. Sampling was carried out from the bow of a small boat located upstream the main boat, to ensure that engine pollution did not occur with the river current. Other water samplings were also performed for immediate onboard filtration using 0.45 μ m pore size filters to conduct particulate matter or dissolved ion studies that are beyond the scope of the present paper, but described elsewhere (dos Santos Pinheiro et al., 2013; Mulholland et al., 2014). Water samples were frozen onboard at -18 °C to minimize water chemistry transformations under the Amazonian tropical climate.

The samples were thawed in the laboratory immediately before further chemical processing. The freezing step proved to coagulate some of the organic matter in samples where it was abundant. For this reason, all bulk water samples rich in organic or mineral suspended matter were vigorously shaken after thawing to ensure that all particulate matter was re-suspended in the bottle, just before taking the water aliquots for the analyses. This way, the aliquots taken were representative of the dissolved and particulate content of these unfiltered natural water samples. Water freezing was preferred over acidification as it affects less metal speciation upon sample storage. Typically, 10 to 100 ml of water were evaporated on hotplates in a class 10000 clean laboratory at the University of Brasília, Geosciences Institute (IG-UnB) and at the laboratory Géosciences Environnement Toulouse (GET). The decomposition of waters and their particulate content initially involved Merck Suprapur H₂O₂ at room temperature in open Savillex vials. The next day, bidistilled HNO₃ was added, the vials were closed and put on a hotplate at 100 °C. After evaporation, bidistilled HF and HNO₃ were added and like for the remaining steps, put for 24 h on a hotplate in

Table 1

Physical, chemical and Fe isotope data of unfiltered water samples from the Amazon River and its tributaries.

River name	Site/sample	Latitude ^a	Longitude ^a	Sampling date	Sampling time	River diso (m ³ /s)	charge rate	T° (C)	Conductivity (µS/cm)	рН	Fe (ppm)	δ ⁵⁷ Fe (‰)	Uncertainty (2SE) ^b	δ ⁵⁶ Fe (‰)	Uncertainty (2SE) ^b	Number of analyses
						ADCP ^c	Calculated									
Solimoes River an	d tributaries:															
Napo	Canada	S3.99644	W73.1695	11/6/2010	11h30	7140		26.5	41	7.1	7.76	0.016	0.107	0.011	0.072	3
Ucayali	Requena	S4.49185	W73.4243	10/6/2010	09h00	9360		27.2	238	7.5	6.92	0.090	0.051	0.066	0.046	3
Solimoes	Tabatinga			23/10/2009	11h00			~~~			3.31	0.076	0.045	0.044	0.029	6
Purus	Foz do Purus	S3.90446	W61.39317	24/6/2010	10h00	16100	150000	28.5	24	6.1	1.37	-0.200	0.094	-0.140	0.070	6
Solimoes	Manacapuru	\$3,32333	W60.55495	26/5/2009	16h30	138500	156000	28.5	/5	8.6	2.92	0.076	0.067	0.044	0.048	9
Negro River and t	ributary:															
Jau	JAU1001	S1.86841	W61.54251	27/9/2010	07h30	_		33.1	31	6.1	1.12	-0.179	0.014	-0.119	0.009	3
Negro	Paricatuba			26/5/2009	07h30	30700	26400	25.0	11	5.3	0.169	-0.056	0.074	-0.044	0.048	9
Negrod	Paricatuba	S3.07203	W60.26109	3/10/2009	21h15	29500	8810 ^e	32.3	8	4.7	0.420	-0.022	0.071	-0.016	0.040	3
Negro ^a	Paricatuba 30 m deep ^r	S3.07203	W60.26109	3/10/2009	22h00	29500		31.2	8	-	0.540	0.043	0.051	0.029	0.029	6
Madeira River:																
Madeira	Porto Velho	S8.78043	W63.91982	20/11/2009		12100		28.8	72	7.2	14.3	0.131	0.110	0.075	0.054	3
Madeira	Humaïta	S7.52632	W63.00586	22/11/2009		14300		29.5	74	7.1	10.4	0.076	0.108	0.048	0.072	9
Madeira ^d	Manicoré	S5.80992	W61.36462	25/11/2009	09h40	14500		30.1	66	7.0	12.5	0.166	0.046	0.108	0.020	6
Madeira	Borba	S4.36681	W59.65014	28/11/2009	13h30	13200	16300	30.9	71	7.1	10.1	0.093	0.115	0.065	0.049	3
Madeira	Foz do Madeira			30/5/2009	09h00	39700	46200	27.9	43	6.3	4.00	0.139	0.095	0.117	0.054	9
Tromhetas River:																
Trombetas	CBH530	\$1 75363	W55 87955	2/7/2009	16b00	_		28.4	14	53	0.512	0.097	0 108	0.057	0.086	3
Trombetab	ebribbo	511105005	1100107000	2,7,2000	101100			2011	••	0.5	01012	0.007	01100	01007	0.000	5
Tapajos River:																_
Tapajos	CBM541	S2.47455	W55.01570	7/7/2009	16h30	14900		29.9	18	6.4	0.307	0.118	0.057	0.061	0.058	6
Amazon River:																
Amazon ^g	ENC1001	S3.12804	W59.89713	29/9/2010	08h20	64900		31.4	69	7.0	0.880	0.084	0.043	0.056	0.029	3
Amazon	ENC1010	S3.22831	W59.21124	30/9/2010	11h40	-		33.0	49	6.9	0.992	0.060	0.086	0.052	0.044	6
Amazon	ENC1012	S3.33183	W58.79639	30/9/2010	17h00	70200		31.7	56	7.1	0.912	0.077	0.068	0.052	0.045	6
Amazon	Itacoatiara	S3.17356	W58.40438	30/5/2009	16h15	197900	236000	27.9	54	6.3	2.07	0.036	0.035	0.013	0.023	9
Amazon	Parintins	S2.59310	W56.66275	4/12/2009	18h00	72700	76900	31.1	73	7.3	2.78	0.143	0.060	0.094	0.031	3
Amazon	Obidos CBM531	S1.97130	W55.47040	3/7/2009	11h30	-	250300	28.8	47	6.3	2.12	-0.031	0.105	-0.013	0.060	3
Amazon ^d	Obidos	S1.91985	W55.5146	6/12/2009	08h10	69200	76900	30.4	85	7.2	2.00	0.082	0.040	0.067	0.019	6
Amazon	Santarem	S2.44377	W54.5598	7/12/2009	16h15	-		30.6	42	7.4	3.41	0.170	0.057	0.112	0.034	6
Average Amazon												0.078	0.052	0.057	0.039	8

n/a: not applicable; -: no datum. ^a Decimal degrees, WGS84.

^b The iron isotope composition and two standard error uncertainties quoted are calculated from the number of analyses indicated and using the Student's *t*-correcting factors (Platzner, 1997).

^c Measured by ADCP. See text for details.

^d Temperature, conductivity and pH from dos Santos Pinheiro et al. (2013). ^e 1/12/2009.

^f Depth beneath the river surface where the sample was taken.
^g 50 liter sample taken at the limit between white and black water mixing zone.

closed Savillex vials. After evaporation, an additional dissolution step with aqua regia was carried out, followed by a final step with 6 M HCl. After the last evaporation, the samples were taken in 0.5 ml of 6 M HCl for anion exchange chromatography in HCl medium, following the procedure described in Poitrasson et al. (2004). Sediments were decomposed and Fe was purified following methods designed for samples rich in organic matter, like carbonaceous chondrites (Poitrasson et al., 2005). It notably involved H_2O_2 during sample dissolution and centrifugation before column loading to avoid graphitized organic matter. Overall, procedural blanks for waters and sediments ranged from 8 to 60 ng for Fe, which is less than 1% of the processed sample iron, even in the most Fe-poor bulk waters.

Isotopic compositions were determined using Thermo-Electron Neptune, high mass resolution, multi-collector inductively coupled plasma mass spectrometers at IG-UnB, Brasília and Observatoire Midi-Pyrénées, CNRS-IRD Toulouse, following the procedure detailed in Poitrasson and Freydier (2005). It involved a mass bias correction using a combination of sample-standard bracketing and Ni-doping of the purified Fe samples. This approach was found to accurately correct for mass bias deviations due to residual matrix effects. Iron concentrations were determined with an uncertainty usually better than 5% using the same instrument. For instance, three MC-ICP-MS determinations of a 100 ml aliquot of the SLRS-4 certified river water for trace metals from the National Research Council of Canada after sample evaporation, decomposition and iron purification yielded 98.3 \pm 1.5 ppb (2SD), in good agreement with the 103 \pm 5 ppb certified iron concentration. The Fe isotope compositions are reported in Tables 1 and 2, following the standard delta notation, and given in ‰ relative to the European isotopic standard IRMM-14. Analytical reproducibility was estimated on the basis of 103 individual analyses of our hematite standard from Milhas, Pyrénées (sometimes referred in the literature as "ETH hematite standard") conducted for over three years in the same analytical sequences as the samples reported in Tables 1 and 2. Given that most samples are typically analyzed six times on average (see "Number of analyses" columns in Tables 1 and 2), the long term reproducibility of such pooled measurements can be estimated on the basis of the hematite analyses pooled by groups of six individual measurements (see details in Poitrasson and Freydier, 2005). In Brasília, 50 pooled analyses gave δ^{57} Fe = 0.753 \pm 0.079‰ and δ^{56} Fe = 0.508 \pm 0.056‰, whereas in Toulouse, 53 pooled analyses yielded δ^{57} Fe = 0.766 \pm 0.072‰ and δ^{56} Fe = 0.509 \pm 0.053‰, with uncertainties reported as 2 standard

Table 2

Sediment samples from the Amazon River Basin.

deviation (2SD). These values are undistinguishable from previous measurements performed in various laboratories (see Poitrasson et al., 2013, for a recent update). Three individual MC-ICP-MS analyses of the SLRS-4 riverine water reference material (0.2 µm filtered Ottawa River, Canada, taken 100 km upstream the city of Ottawa) discussed above to evaluate Fe concentration determination accuracy yielded δ^{57} Fe = 0.564 \pm 0.108‰ and δ^{56} Fe = 0.380 \pm 0.081‰, with uncertainties reported as two standard error (2SE) using the *t*-correcting factor given the small number of measurements.

4. Results

4.1. Waters

4.1.1. Physical and chemical properties

The water discharge rates measured by ADCP in the same locations where the samples were taken (Table 1) range from 7140 m^3/s in June 2010 in the Napo River, a tributary of the Solimões River from Equator and Peru, to 197900 m³/s in May 2009 in the Amazon River at Itacoatiara, 40 km downstream the Madeira confluence. The latter value is at the high end of what is normally found there, since this period corresponded to a centennial flooding. Besides the Solimões River, other main Amazon tributaries like the Negro River or the Madeira River can show up to a measured threefold decrease between May and November 2009 (Table 1). In fact, data computed from the HYBAM program (www.ore-hybam.org) reveal that the seasonal water discharge variations for the Negro River is within a factor of 4 and ranges from three times for the Solimões River up to 20 times for the Madeira River flowing from the Andes. It should also be noted that the water discharge in the lower Negro River at Paricatuba may be affected by a backwater effect from the Solimões and Amazon rivers (Meade et al., 1991; Filizola and Guyot, 2009).

The measured river surface temperatures show a range of 8 °C, with a mean value of ~29 °C, varying depending on the time of the day and season. At a given period of the year, the Madeira and Solimões rivers and tributaries point to a tendency towards cooler temperatures upstream (Table 1).

Conductivity values show large variations among the river samples studied, ranging from 8 to 238 μ S/cm. The highest numbers are found in the white waters with elevated suspended and dissolved salts, such as the Solimões and its Andean tributaries, the Madeira River and the

Site	Sample	Latitude ^a	Longitude ^a	Lithology	Fe (wt%)	δ ⁵⁷ Fe (‰)	Uncertainty (2SE) ^b	δ ⁵⁶ Fe (‰)	Uncertainty (2SE) ^b	Number of analyses
Solimoes River: Manacapuru	MAN1001	S3.34329	W60.53948	Fine clayey sand	1.56	0.141	0.062	0.084	0.051	6
<i>Negro River:</i> Paricatuba	PA1001	S3.07974	W60.23812	Organic matter-rich fine sand	0.608	-0.229	0.091	-0.153	0.061	3
<i>Madeira River:</i> Rio Coroico, teoponte Alto Beni, Sapecho Rio Marmore, Guayaramerin Grande, Puerto Pailas Vista Alegre	76 ^c 86 ^c 118 ^c 110 ^c 132 ^{c,d}	S15.5015 S15.5612 S10.8078 S17.6546 S4.8917	W67.8470 W67.3713 W65.3458 W62.7773 W60.0283	Coarse gray sand Fine sand Soil Fine clayey sand Coarse sand	2.39 1.28 2.21 1.34 0.891	0.049 0.085 0.074 0.069 0.227	0.108 0.043 0.063 0.076 0.033	0.036 0.053 0.058 0.049 0.112	0.077 0.011 0.046 0.056 0.050	6 3 6 3 9
Amazon River: Encontro das aguas Encontro das aguas Parintins Obidos	AM1001 AM1002 PARI ^d 135 ^c	S3.24644 S3.31705 S1.9120	W59.22730 W58.79350 W55.5433	Fine clayey sand Fine clayey sand Coarse sand Coarse sand	1.46 1.51 2.47 0.286	-0.014 0.163 0.274 0.135	0.047 0.072 0.056 0.073	-0.010 0.103 0.181 0.108	0.031 0.043 0.037 0.056	3 6 8 3

n/a: not applicable; -: no datum. ^a Decimal degrees, WGS84.

^b The iron isotope composition and two standard error uncertainties quoted are calculated from the number of analyses indicated and using the Student's *t*-correcting factors (Platzner, 1997).

^c Samples equivalent to those of Guyot et al. (2007).

^d Includes two sample decomposition and Fe purification, the second set starting from a more finely ground powder.

Amazon River itself, which show conductivity values always above 40 μ S/cm (Table 1). The highest value is found in the Ucayali River, which is known to drain some evaporitic geological formations (Stallard and Edmond, 1983). In contrast, black and clear waters from the Purus, Jaú, Trombetas and Tapajós rivers have lower conductivities, with the lowest values in the Negro River (Table 1). These black and clear water river samples are acid and have a pH that ranges from 4.7 to 6.1, while white waters have near neutral pH at 7 \pm 1 (Table 1), in agreement with previous studies (e.g., Gaillardet et al., 1997; Seyler and Boaventura, 2003).

4.1.2. Iron concentrations and isotopic compositions

In the bulk water samples, iron concentrations range from 0.169 to 14.3 ppm, the highest values being found in white water rivers such as the Madeira and the Solimões (from 2.92 to 14.3 ppm; Table 1). In these waters, ~95% of the iron is in the particulate form (Benedetti et al., 2003; Bergquist and Boyle, 2006; Mulholland et al., 2014). On the other hand, clear and black water rivers like the Trombetas, Tapajós, Purus, Jaú and Negro have lower Fe concentrations (0.169 to 1.37 ppm; Table 1). In the Negro black waters, the latest studies have shown that 40 to 50% of the iron is found in the dissolved form (i.e., <0.45 µm filtrate; Bergquist and Boyle, 2006; Mulholland et al., 2014) and this presumably applies to other black water rivers. Bulk water iron concentrations in the Amazon River are essentially lower than those of other white water rivers, like the Solimões and the Madeira Rivers, but higher than the clear and black water rivers, like the Negro, Purus, Trombetas or Tapajós (Table 1). Only three samples taken from the Solimões and Negro Rivers mixing zone show bulk water Fe concentrations below 1 ppm (samples ENC1001, ENC1010 and ENC1012, Table 1) due to the influence of the Negro River waters. Another noteworthy feature is the lower Fe concentration observed in the unfiltered waters of the Negro and Madeira rivers at the high water season (samples taken in May) relative to the low water season (November and December, Table 1). Seasonal variations in Fe concentrations were also found in the suspended particulate matter (dos Santos Pinheiro et al., 2013), as well as in the amount of particulate matter (e.g., Guyot et al., 2005). This effect is particularly obvious on time series of more than one year from the Negro and Amazon Rivers, although a temporal shift of 1–2 months was observed between the amount of suspended particulate matter and water discharge rates (Guyot et al., 2005).

Overall, the bulk water samples from the Amazon River and its tributaries display a δ^{57} Fe range within $\pm 0.2\%$ (Table 1; Fig. 2). All the white waters and the clear waters studied show iron isotope compositions undistinguishable from that of the continental crust (δ^{57} Fe = $0.10 \pm 0.03\%$; Poitrasson, 2006). Exceptions to this are some black waters such as those of the Jaú and the Purus rivers (Table 1 and Fig. 2). The Negro River samples, which are of the same water type, also tend to be lighter than the continental crust composition (Fig. 2). The Amazon River water samples seem to show some scatter relative to other white water rivers, but this remains within uncertainty.

4.2. Sediments

The iron concentration of the sediments analyzed range from 0.3 to 2.5 wt.% (Table 2), with no specific relationship with location or lithology. Out of the eleven samples analyzed for their Fe isotope composition (Table 2), seven yielded δ^{57} Fe values undistinguishable from that of the continental crust (Fig. 3). Two sediment samples taken from the banks of the Madeira and Amazon rivers (samples 132 and PARI, respectively) have their iron isotope composition significantly heavier than the continental crust (Fig. 3). To check whether this was a sampling issue with the ~8 to 16 mg aliquots taken for the Fe isotope analysis because of the coarse nature of these two samples, they were more finely ground and new sample aliquots were subjected to independent acid decomposition, Fe purification and mass spectrometry. The Fe isotope results so obtained were undistinguishable from previous determinations, however, and the numbers of individual MC-ICP-MS analyses reported in Table 2 include the fully duplicated determinations for these two samples. Further mineralogical investigations by X-ray diffraction suggest that at least for the PARI sample, this could be due to a concentration of ilmenite during sedimentation. Although initially debated (Poitrasson, 2007) on the basis of the first theoretical predictions (Polyakov and Mineev, 2000), recent work has shown that this iron oxide tends to show a heavy Fe isotope composition relative to coexisting mineral phases in rocks like iron-bearing silicates (Craddock et al., 2010). Two other sediment samples taken from the banks of the Amazon and Negro rivers (samples AM1001 and PA1001,



Fig. 2. Bulk water iron isotope composition of the Amazon River and its main tributaries arranged from the Western Andean springs to the river mouth, in the Atlantic Ocean to the East. The continental crust baseline (black line; δ^{57} Fe_{IRMM-14} = 0.10 ± 0.03%; Poitrasson, 2006) is shown for reference. It is undistinguishable from the mean value of the bulk Amazon River waters (red line and its 2SE envelope: 0.078 ± 0.052‰). Three bulk black water samples are significantly lighter than the Amazon mean value, from W to E: the Purus, a tributary of the Solimões River, the Jaú, a tributary of the Negro River and one sample from the Negro itself. They are labeled directly on the figure. Data are from Table 1.



Fig. 3. Bulk sediment iron isotope composition taken from the Amazon River banks and from its main tributaries arranged from West to East. The continental crust baseline (black line and its 2SE envelope; δ^{57} Fe_{IRMM-14} = 0.10 ± 0.03‰; Poitrasson, 2006) is shown for reference. Note that most sediment samples have an iron isotope composition undistinguishable from the continental crust baseline. Exceptions are sediments that may show isotopically heavy mineral concentrations (samples 132 and PARI) or that incorporated isotopically light suspended matter from the organic rich waters in the Negro River or at its confluence with the Solimões River, at the start of the Amazon River (samples PA1001 and AM1001). Data are from Table 2.

respectively) yielded δ^{57} Fe values significantly lighter than the continental crust value (Table 2). This is especially obvious for the Negro River sediment sample PA1001 (Fig. 3). Sample AM1001 was taken in the mixing zone between the Negro and Solimões rivers, at the beginning of the Amazon River, downstream the junction. It is therefore possible that its light Fe isotope composition also results from the influence of the Negro River waters, though to a lesser extent than for sample PA1001, as is discussed in more detail below.

5. Discussion

5.1. Elemental iron transfer in bulk waters

The data obtained allow to estimate the mass transfer to the Amazon River from its tributaries. The sum of the water discharge rates of the Solimões, Negro and Madeira rivers measured in May 2009 (Table 1) is only 5% above the discharge rate measured in the same month on the Amazon River at Itacoatiara, which is 40 km downstream the confluence between the Madeira and the Amazon rivers (Fig. 1). There is thus a good consistency between the various discharge rates, as this small difference can be due to the uncertainties related to the ADCP measurements over a four-day period (Table 1). The mismatch is greater when a similar comparison is made using ADCP data of the low water level season of 2009. The sum of the discharge rates of the Solimões (46 200 m³/s on the 30th November 2009; Martinez, 2009), Negro and Madeira (Table 1) exceeds the discharge rate measured on the Amazon at Parintins and Obidos in early December 2009 (Table 1) by 22% and 28%, respectively. The spread in time for the measurements (up to two months) is likely the reason for the lesser agreement compared to the end of May 2009 measurements. When calculated discharge rates are used instead (see Table 1, and adding a recalculated value of 51070 m³/s on the 30th November 2009 for the Solimões River at Manacapuru), the mass balance calculations can be made on a narrower period. As a result, the discrepancy between the sum of the discharge rates of the tributaries and that of the Amazon does not exceed 5%, for both high and low water seasons, which is within water discharge calculation uncertainties.

The combination of these computed water discharge and of our data for bulk water iron concentrations (Table 1) allows us to give a first estimate of the daily iron fluxes (Table 3) for both the high and low water seasons. In May 2009, which corresponds to the high water season, these were around 39400, 400 and 16000 tons of Fe per day for the Solimões, Negro and Madeira rivers, respectively. The sum of these iron flux of 55700 tons/day from these Amazon tributaries comes down to 41600 tons of Fe per day measured at the same time on the Amazon River at Itacoatiara (Table 3). Clearly, a quarter of the iron brought by these three main Amazon River tributaries is lost at their confluence and cannot be recovered from bulk water analyses downstream, at Itacoatiara. This non-conservative behavior of insoluble metals like iron during the mixing of natural waters of contrasted properties has been previously reported in the Amazon River Basin (Aucour et al., 2003; Benedetti et al., 2003). Similar computations conducted during the low water season (November-December 2009) indicated a total of 39000 tons of iron per day brought by the Negro, Solimões and Madeira rivers together, but only 19600 tons/day are found in the Amazon River at Itacoatiara (Table 3). In this case, it means that half of the iron brought by the main tributaries has been lost in the mixing zone. These calculations carried out further downstream the Amazon River, near Parintins and Óbidos show some further deviation (Table 3). However, they are not vastly different (i.e., $\leq 16\%$) from the losses computed at Itacoatiara. They may therefore not be significant given the uncertainties attached to these Fe transfer estimates, as

Table	3
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Iron fluxes of the main rivers from the Amazon River Basin

River	Iron flux (tons/day)						
	High waters (May 2009)	Low waters (Nov-Dec 2009)					
Solimoes	39400	24400 ^a					
Negro	385	320					
Madeira	16000	14300					
Amazon at Itacoatiara	41600	19600					
Amazon at Parintins	_	18500					
Amazon at Obidos	45100 ^b	19600					
Amazon iron deficits at:							
Itacoatiara	25%	50%					
Parintins	_	53%					
Obidos	19%	66%					

Computed with data from Table 1 using calculated water discharge rates, except for ^aCalculated from Fe concentrations from dos Santos Pinheiro et al. (2014) and ^bCalculated from Fe concentrations from dos Santos Pinheiro et al. (2013). -: no data.

discussed in more detail below. This means that although water and suspended matter do flow through lateral floodplain lakes (e.g., Mangiarotti et al., 2013), the impact of these "varzeas" on the iron transfer in the Amazon main channel remain small. These calculations nevertheless confirm the seasonal pattern of Fe loss, which is twice more important in low waters relative to the flooding season (Table 3).

Such iron losses (from ~14000 tons/day in the 2009 high water season up to ~19000 tons/day in the 2010 low water season) are massive, yet they represent little in terms of deposited sediment thickness at the scale of the Solimões and Negro rivers mixing zone, that is often more than 2 km wide and extends until Itacoatiara, 160 km downstream the start of the confluence. Considering an average suspended matter Fe concentration of 4 wt.% (dos Santos Pinheiro et al., 2013) and a sediment density of 2.5, this translates into a yearly deposition of up to ~20 cm of sediment, which is less than 0.5% of the Amazon water column depth in this area. This value is close to previous sedimentation rate estimates (~16 cm/year) for this reach of the Amazon River channel (Dunne et al., 1998), although it was attributed to the Madeira River sediment input. Albeit possibly at the high end because this sediment deposition estimate corresponds to very low water levels associated with the extreme 2010 drought, ~20 cm of annual sediment deposition rate in the Amazon channel would mean that such a process may affect the Amazon River flow and channel location only after several centuries if we assume a steady state.

The water discharge rate estimates will not affect much the uncertainty of these iron transfer computations because of the good balance of the water mass transfer achieved when water discharges computed at the same time for all Amazon River tributaries are used, as described above. On the other hand, the variations in iron concentration through lateral and depth river cross-sections will have a stronger influence on these iron flux estimates. For instance, dos Santos Pinheiro et al. (2013) found that the suspended matter content and its Fe concentration may vary by up to a factor of two along depth and lateral profiles of the Amazon, Solimões and Madeira River cross-sections. Given that ~95% of the iron is carried by the suspended matter in the white waters like the Amazon River and its main tributaries (i.e., the Solimões and Madeira rivers, since the Fe from the black water Negro River represents less than 1% of the Amazon Fe budget; Table 3), this heterogeneity has to be considered in our estimates. Accordingly, another study by Bouchez et al. (2011) concluded that depth-integrated Fe flux is more than twice as high as the one estimated from a surface sample only. Furthermore, dos Santos Pinheiro et al. (2013) also showed notable iron concentration variations along river cross-sections, perpendicular to the water flow. Hence, all water samples taken for this study are subsurface samples taken near the center of river cross-sections to minimize this lateral heterogeneity effect. Therefore, the relative difference of the Fe flux figures (percentage data presented in Table 3) is probably more accurate than the above mentioned factor of two, but only river cross-section sampling using lateral and depth profiling can minimize this uncertainty for absolute metal flux estimates (expressed in tons/ day). The good uncertainty of our estimates in relative terms is illustrated by a comparison with previous literature results: the iron loss in the Amazon River mixing zone, after the Solimões and Negro rivers confluence was noted by several previous studies (e.g., Aucour et al., 2003; Benedetti et al., 2003), and their estimate of Fe loss (between 30 and 40%) is very similar to ours at Itacoatiara, the closest station we have after this confluence (from ~25 to 50%, depending on the season; Table 3).

Although Óbidos is 800 km away from the Amazon estuary in the Atlantic Ocean, this station has frequently been used to estimate the dissolved and suspended material transfer from the Amazon River to the ocean. Part of the reason lies with the difficulty to estimate water discharge rates downstream Óbidos due to the influence of the tides. If we take our estimates of the daily iron flux at Óbidos (Table 3) in high (May 2009) and low (Nov–Dec 2009) water seasons (Table 3) to compute the annual iron output assuming that each value will be

representative for half of the year, this would amount to ~11.8 \times 10⁶ tons of Fe that are sent by the Amazon to the ocean every year, with ~95% of this being in the particulate form. Given that Fe represents 4 wt.% of the suspended matter at Óbidos on average along the year (dos Santos Pinheiro et al., 2014), this would translate into over 280 \times 10⁶ tons of suspended material that is sent to the Atlantic Ocean every year. Our value is lower than previous estimates ranging from ~500 to 1200×10^6 tons/year, depending on the authors (see review in Filizola and Guyot, 2009), because we based our calculations on surface samples in which the suspended matter has lower Fe concentrations compared to deeper samples in the Amazon at Óbidos (Bouchez et al., 2011; dos Santos Pinheiro et al., 2013). Hence, our underestimated amount of Fe sent to the Atlantic Ocean by the Amazon every year should be reevaluated to take these limitations into account. A more accurate value should lie $\sim 34 \times 10^6$ tons of Fe per year if the estimate of the suspended matter annual discharge of ~800 \times 10^{6} tons/year from Martinez et al. (2009), based on several years, different methodologies and close to the most recent estimates of sediment discharge in the Amazon estuary (see review in Filizola et al., 2011) is taken as a reference in our calculation. Interestingly, this correcting factor of ~2.9 relative to our initial value is close to that found by Bouchez et al. (2011) required to make a correct estimate of the Amazon Fe flux from surface sampling only. This therefore shows the good consistency of our study with those of Martinez et al. (2009) and Bouchez et al. (2011).

Such quantities of iron will not travel over long distances across the seas since experiments and field observation reveal that from 70 to 90% of the riverine dissolved and particulate Fe will preferentially flocculate with organic matter upon mixing between freshwater and marine water (Sholkovitz et al., 1978; Bergquist and Boyle, 2006; Escoube et al., 2009). Regardless, our estimation of the annual Amazon Fe output (that consists in ~95% of suspended matter) is between 5 and 30% of the Fe delivered by the world rivers, if the global estimates (that also include riverine Fe occurring in the dissolved and particulate form) of Fantle and DePaolo (2004) and Beard et al. (2003) are used, respectively.

It is noteworthy that the Fe concentration measured in the exposed sediments along the Amazon River banks (Table 2) are less than half the value measured in the suspended matter (dos Santos Pinheiro et al., 2013), suggesting that these sediments do not represent the simple, direct sedimentation of this suspended matter. Riverbed sand mineral assemblage may vary if there is a preferential sedimentation of denser, Fe-rich minerals or if, to the opposite, currents lead to the preferential deposition of Fe-free quartz and feldspars (e.g., Franzinelli and Potter, 1983). This mineral sorting, together with the non-conservative behavior of iron in the Amazon River waters shows that the isotopic approach will be useful to go further into our understanding of the Fe cycling in the Amazon River Basin.

5.2. Conservative Fe isotope signatures in bulk waters

The nearly constant iron isotope compositions measured in bulk water samples of the Amazon River and five of its main tributaries (Table 1 & Fig. 2) are in sharp contrast with the large variations found in iron concentrations and fluxes (Tables 1 and 3). For instance, the Negro and Solimões rivers mixing zone, at the start of the Amazon River, which is characterized by a loss of 25 to 50% of the bulk waters Fe depending on the season (see above and Table 3), has no effect on the bulk water Fe isotope signatures of the Amazon (Fig. 2). This is consistent with the findings made in estuaries where, despite important Fe loss due to particle flocculation upon freshwater and seawater mixing, this process has only a minor effect on δ^{57} Fe values for both the dissolved (Bergquist and Boyle, 2006) and the particulate fractions (Escoube et al., 2009), and therefore, on bulk water Fe. In fact, the Amazon bulk iron isotope composition is essentially that of its two tributaries overwhelming the Fe budget of the river: the Solimões and the Madeira Rivers (Table 3). This value is close to that of the continental crust (δ^{57} Fe = 0.1 \pm 0.03‰; Poitrasson, 2006), and the Amazon River mean δ^{57} Fe is undistinguishable from this reference value (Fig. 2). This certainly reflects the nature of the main Fe carriers in these white waters: as previously stated, ~95% of this element is locked within particles (e.g., Benedetti et al., 2003; Bergquist and Boyle, 2006; Mulholland et al., 2014) that are made of over 80% of material eroded from the Andes (Gibbs, 1967) or even up to 93% if their foreland sedimentary basins are taken into account (Filizola and Guyot, 2009).

Even though they account for up to 35% of the water discharge of the whole Amazon Basin, the black waters of the Negro River do not represent much in the Amazon River total Fe budget (<1%; Table 3). Yet these rivers, and especially the Jaú and the Purus, have bulk water Fe isotope compositions that are lighter than the continental crust reference value (Fig. 2). This likely stems from the particulate suspended matter of these black waters which represents ca. 50% of the bulk water iron budget and that is characterized by light Fe isotope signatures (Bergquist and Boyle, 2006; dos Santos Pinheiro et al., 2013). This possibly reflects the occurrence of podzolic soils in the source region of the black waters that contain Fe²⁺ in their organic-rich horizons (e.g., Allard et al., 2011), which is typically isotopically light in soils (Fantle and DePaolo, 2004; Wiederhold et al., 2007). This light Fe extracted from soils that arises from the headwaters can therefore be traced in the bulk Fe isotope signatures of black waters (Fig. 2).

Hence, while the bulk water δ^{57} Fe is a conservative tracer during water mixing and Fe loss at the Negro-Solimões confluence, it appears to faithfully trace the nature of the iron sources. If continental crust-like isotopic signature in white waters shows the little processed nature of a suspended matter mostly derived from the erosion of igneous and sedimentary rocks in the Andes, the light δ^{57} Fe found in black waters reflect its source as the reduced, ferrous form in organic-rich horizons of podzols.

Bulk water samples δ^{57} Fe do not seem to vary according to the hydrological cycle along the year either (Table 1). Thence, isotopic seasonal effects observed in the particulate matter of organic-rich rivers (Ingriet al., 2006; dos Santos Pinheiro et al., 2013, 2014) appear to be canceled by opposite isotopic variations in the dissolved Fe fraction. Further work on the Fe isotope composition of the dissolved fraction of Amazonian black waters is required to study this effect in more detail.

5.3. Origin of sediment Fe isotope compositions

Like the bulk waters, most of the Amazon River Basin sediments are characterized by a homogeneous Fe isotope composition, undistinguishable from the continental crust δ^{57} Fe value, whatever their location and nature (Table 2 and Fig. 3). There are, however, some exceptions yielding δ^{57} Fe significantly lighter than the continental crust (Fig. 3). These correspond to sediments taken in the Negro River, and in the Amazon River, in the mixing zone after the Negro and the Solimões rivers confluence. These results are consistent with sediment deriving from suspended matter of black waters, like the Negro River, which have light δ^{57} Fe values (Bergquist and Boyle, 2006; dos Santos Pinheiro et al., 2013). From the Negro River to 120 km downstream in the Amazon River, just before the confluence with the Madeira River, it seems that the sediments are progressively less light isotopically, which is consistent with the incorporation of increasingly heavier suspended particles as the mixing process occurs (Mulholland et al., 2014). On the other hand, two other sediment samples from the Madeira and the Amazon rivers near Parintins display a heavy δ^{57} Fe relative to the continental crust (Table 2 and Fig. 3). We interpret this feature as resulting from the sedimentary concentration of minerals having a heavy iron isotope composition. As discussed above, at least one of these two samples contains ilmenite that is potentially isotopically heavy.

Hence, and in contrast to the iron concentration recorded in the sediments that are systematically lower by at least a factor of two compared to that of the riverine suspended matter (compare data in Table 3 with those of dos Santos Pinheiro et al., 2013), their δ^{57} Fe appear to record more faithfully the iron isotope composition of the river suspended matter, unless isotopically heavy minerals are concentrated during sedimentation.

5.4. Implications

Our data thus suggest that while the iron isotope composition of unfiltered river water behaves conservatively during water mixing and suspended matter sedimentation processes, it records the isotopic signature of the iron sources in igneous rocks, sediments and/or soils. These results on the Amazon River support previous conclusions that bulk waters from rivers rich in clastic, suspended detrital material, like the Amazonian white waters, will have a composition close to that of the continental crust (Beard et al., 2003; Fantle and DePaolo, 2004). This conclusion also agrees with inferences derived from lateritic soil studies. Given that lateritic soils cover one third of the continents (Tardy, 1997) and that these soils from tropical and equatorial areas show very little Fe isotope variations (Poitrasson et al., 2008), it was inferred that intertropical rivers such as the Amazon, which constitutes a basin that drains up to 80% of lateritic soils (Bernoux et al., 2001) should deliver to the ocean an iron that has a composition close to that of the continental crust (Poitrasson et al., 2008). Given the lack of notable Fe isotopic fractionation in the dissolved and particulate loads of estuarine areas (Bergquist and Boyle, 2006; Escoube et al., 2009), it can be confirmed from the present study that the continental crust-like δ^{57} Fe values measured in bulk waters of the Amazon River (Fig. 2) will be that of the Fe delivered to the Atlantic Ocean. Admittedly, black water rivers that are organic-rich and contain half of their Fe in the dissolved form may have a lighter bulk Fe isotope signature (Fig. 2). However, their contribution to the Fe budget is small at the Amazon Basin scale (see e.g., Gaillardet et al., 1997; and Table 3) and therefore, their isotopic influence is negligible. Such a study should be conducted on other major world rivers since the isotopic composition of the various Fe sources to the ocean is required to improve our understanding of the oceanic Fe cycle with its isotopes (Lacan et al., 2008; John and Adkins, 2010).

Our conclusion, based on a large bulk water dataset, is at variance with those of Bergquist and Boyle (2006). These authors inferred on the basis of the iron isotope determination of the suspended and dissolved fraction of water samples taken in only three different locations, that the Amazon River carries a negative δ^{57} Fe overall. Our mean bulk water values for the Negro, Solimões and Amazon Rivers are compared in Fig. 4 to the corresponding dissolved and particulate fraction of the three samples studied by Bergquist and Boyle (2006). These new bulk water data, along with those of the Madeira River, unambiguously point to a continental crust-like isotope composition. We also recalculated bulk water Fe isotope compositions from the determinations of Bergquist and Boyle (2006), and complemented, when those data were missing, with the elemental dissolved and particulate results of Gaillardet et al. (1997). While the Amazon River data of Bergquist and Boyle (2006) cannot be distinguished from the continental crust δ^{57} Fe considering the uncertainties, their Solimões River data are clearly lighter than the continental crust (Fig. 4). The reason for this discrepancy is difficult to account for, since our data are based on bulk samples of this river taken from near the headwaters in the Andes to its mouth, right after Manacapuru (Fig. 1 and Table 1), and δ^{57} Fe values remain constant (Table 1). Depth profiles, lateral profiles and temporal series of the suspended matter from the Solimões River and other Amazonian white waters, for which over 95% of the iron is in the suspended matter, point to δ^{57} Fe ~ 0.1‰ (dos Santos Pinheiro et al., 2013), which is similar to the continental crust value (δ^{57} Fe = 0.1 \pm 0.03‰; Poitrasson, 2006). Hence, the light values of Bergquist and Boyle (2006) cannot be linked to an isotopic heterogeneity in space or time in the white waters and the discrepancy might therefore be of analytical nature. It is possible the MC-ICP-MS instrument and methodology employed by these authors, involving simple sample-standard bracketing without Ni-



Fig. 4. Mean bulk water Fe isotope composition of the Negro River (excluding the Jaú), the Solimões River (excluding the Purus), the Madeira and the Amazon rivers obtained in this study. They are all undistinguishable from the continental crust baseline (black line and its 2SE envelope; $\delta^{57}Fe_{IRMM-14} = 0.10 \pm 0.03\%$; Poitrasson, 2006) shown for reference. These values are compared to previously published data on the suspended and particulate fractions of these rivers (from B&B, 2006; Bergquist and Boyle, 2006) and the recalculated bulk water $\delta^{57}Fe_{IRMM-14}$ values using the results from these authors and other Fe concentration of dissolved and suspended matter data from the literature (G, 19997; Gaillardet et al., 1997). Note that while the new measured bulk water iron isotope composition data for the Amazon agrees within uncertainties with the recalculated values from the literature, this is not the case for Solimões and the Negro rivers: computed bulk water iron isotope compositions from the previous literature are significantly lighter than the continental crust baseline for the Negro and the Solimões rivers. See text for discussion.

doping for mass bias correction might lead to shifted isotope compositions due to a residual matrix effect. Similarly, our mean of bulk water data from the Negro is in between the dissolved and particulate data of Bergquist and Boyle (2006), but significantly heavier than the bulk value computed from these authors' data (Fig. 4). On the other hand, our bulk mean is in excellent agreement from computed bulk water data based on ultrafiltration experiments of a sample taken in October 2010 (Mulholland et al., 2014). For these black waters however, dos Santos Pinheiro et al. (2013, 2014) found a significant seasonal variation on the suspended matter δ^{57} Fe that might explain the difference between our mean Negro River data and the results of Bergquist and Boyle (2006).

6. Conclusions

This comprehensive survey on the bulk water and sediments of the Amazon River, five of its main tributaries and four sub-tributaries, reveals that while iron concentrations show massive losses (of at least ~25%) when contrasting water masses mix, the iron isotopic signatures of unfiltered waters remain unaffected. Similarly, whereas the sediment Fe concentrations are systematically lower by at least a factor of two relative to that measured in the rivers suspended load, probably due to particle sorting reasons, the δ^{57} Fe values of bulk sediments sampled on the river banks faithfully record the suspended matter isotopic signatures in most cases. Hence, unfiltered river Fe isotope compositions do not seem to register iron biogeochemical cycling in the water. Rather, they appear to trace the δ^{57} Fe values from the river headwater terranes, which can either be detrital rock fragments from the Andes, recording the crustal isotopic composition, or the light iron extracted from the podzols in the case of rivers (Jaú and Purus) draining rainforest soils. However, the white water Fe budget overwhelms that carried by the black waters at the Amazon Basin scale. Thus, the \sim 34 \times 10⁶ tons of Fe delivered to the Atlantic Ocean by the Amazon River every year has an iron isotope composition close to the continental crust value (~0.1‰ in δ^{57} Fe), in agreement with previous inferences based on tropical lateritic soil studies.

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