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# Seasonal dissolved rare earth element dynamics of the Amazon River main stem, its tributaries, and the Curuaí floodplain

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[1] We present a comprehensive dissolved rare earth element (REE) data set for the Amazon River and its main tributaries, Rio Negro, Solimões, and Madeira, as well as the Curuaí floodplain. The two-year time series show that REE vary seasonally with discharge in each of the tributaries, and indicate a hydrologically dominated control. Upper crust normalized REE patterns are relatively constant throughout the year, with Ce/Ce\* anomalies being positively related to discharge. We propose revised annual dissolved REE fluxes to the surface Atlantic Ocean based on an integration of the seasonal data. For Nd (<0.22  $\mu\text{m}$ ) this results in an average flux of  $607 \pm 43$  T/yr, which is at least 1.6 times larger than the previous estimate of 374 T/yr (<0.45  $\mu\text{m}$ ) based on low water stage data. Moreover, during the high water season the maximum Nd flux measures  $1277 \text{ t.yr}^{-1}$ , constituting 30% of the required flux to the Atlantic Ocean (Tachikawa et al., 2003). Consequently, a smaller contribution of Nd from atmospheric and river particle desorption is required than was previously suggested. A mass balance of Amazon tributaries and observed fluxes at Óbidos indicates that dissolved LREE behave quasi-conservatively. Conversely, the HREE mass balance presents a deficit during the high water stages, which could be related to the passage of water through the floodplain system accompanied by solid/dissolved phase transfer.

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## 1. Introduction

[2] The rare earth elements (REE) form a coherent group of trace elements whose chemical properties gradually change with their decreasing ionic radii across the series, from lanthanum (La) to lutetium (Lu). As a result, REE concentration patterns may change during solid-solution phase transitions at the Earth's surface, as has been observed for mineral weathering in soils [Nesbitt, 1979; Duddy, 1980; Braun *et al.*, 1998; Aubert *et al.*, 2001] and REE transport in natural waters [Elderfield *et al.*, 1990; Sholkovitz, 1995; Johannesson *et al.*, 2004]. These changes in REE patterns, i.e., fractionation of the REE relative to some reservoir, such as the upper crust (UC), are commonly used for deciphering REE sources [Hannigan and Sholkovitz, 2001], and weathering and transport mechanisms [Braun *et al.*, 1998; Viers and Wasserburg, 2004], or to evaluate mixing process between water masses in oceanic or continental environments [Stordal and Wasserburg, 1986; Johannesson *et al.*, 1999].

[3] Many studies carried out on the Amazon River illustrate the complex functioning of this river in terms of geochemistry [Stallard and Edmond, 1983; Devol *et al.*, 1995; Gaillardet *et al.*, 1997; Aucour *et al.*, 2003]. Concerning the REE, Sholkovitz and Szymczak [2000] and Hannigan and Sholkovitz [2001] summarized the actual knowledge we have on the Amazon River with the following main features: the dissolved REE fractionation pattern of the Amazon River has a distinct middle REE enrichment that is likely related to the weathering of phosphate minerals (i.e., apatite/rhabdophane) [Hannigan and Sholkovitz, 2001]. Studies available in the literature are based on single sampling, which does not allow relating REE behavior to important control parameters, such as temperature, discharge, pH, suspended sediments (SS). Establishing such relationships requires seasonal data, which for the REE has been illustrated in detail for the Kalix and Mississippi Rivers [Ingri *et al.*, 2000; Shiller, 2002]. For the Amazon River at Óbidos, a recent study by Seyler and Boaventura [2003] showed three types of seasonal concentration trends for dissolved trace elements: correlated (Co, Cd, Mn), anti-correlated (Sr, Ba, Mo, Sb, V, Cu) and invariant (U, Rb, Ni, Cr) with water discharge. These authors proposed that Mn, an element that is enriched in the dominant (80% of Amazon basin) lateritic soils, is mobilized by flood flows during the high water season. They also argued that Co and Cd concentrations at Óbidos cannot be explained by

simple tributary mixing, and that internal sources possibly involving the “várzea” floodplains are necessary.

[4] In this study we present a 2-year time series on dissolved REE geochemistry in the Amazon River at Óbidos, its three major tributaries: the Rio Negro, Rio Solimões, and Rio Madeira, and the Curuaí floodplain, one of the largest várzea located in between Manaus and Óbidos. The seasonal REE fluxes to the Atlantic Ocean will be discussed in the context of tributary contributions, internal processes, and floodplain functioning. This study is a part of a larger project (HyBAm) on the hydrology and geochemistry of the Amazon basin [Gerard *et al.*, 2003; Moreira-Turcq *et al.*, 2003; Seyler and Boaventura, 2003; Dosseto *et al.*, 2006; Martinez and Le Toan, 2006].

## 2. General Features

[5] The Amazon ranks first among the world's rivers in terms of drainage area ( $6 \cdot 10^6 \text{ km}^2$ ) and annual discharge ( $5.5 \cdot 10^9 \text{ m}^3 \cdot \text{yr}^{-1}$ ), the latter representing about 20% of the global fresh water flux from land to ocean [Baumgartner and Reichel, 1975; Shiklomanov and Sokolov, 1983; Callède *et al.*, 2004]. Dissolved and particulate fluxes carried by the Amazon River are therefore of prime importance in biogeochemical cycling between land and ocean. Within the Amazon River basin, tributaries exhibit contrasted chemical characteristics. They have long been classified into three types on the basis of their appearance as “whitewaters”, “clearwaters” and “blackwaters” [Sioli, 1967]. Two major tributaries are the Rio Solimões and Rio Negro, which combine at Manaus to form the Amazon River. The “blackwaters” from the Rio Negro are relatively acidic (pH 4 to 5), poor in total major cations, rich in dissolved organic carbon (from 7 to  $10 \text{ mg} \cdot \text{L}^{-1}$ ) and poor in suspended sediment ( $<10 \text{ mg} \cdot \text{L}^{-1}$ ). The “whitewaters” from Rio Solimões show a near neutral pH and are relatively rich in total cations and in suspended sediments (from 60 to  $200 \text{ mg} \cdot \text{L}^{-1}$ ). Two hundred kilometers downstream of the Solimões-Negro confluence, the Amazon River receives water from the Madeira River, which drains the Bolivian Andes and passes through the central Amazon plain. The main tributaries of the lower course, the Trombetas, Tapajós and Xingú Rivers drain the Brazilian shield.

[6] Annual mean precipitation in the Amazon basin is  $\sim 2000 \text{ mm} \cdot \text{yr}^{-1}$  and the water regime of



**Figure 1.** Location of the sampling point in the Amazon Basin. Focus on the Óbidos area and on the floodplain of Curuaí with special attention to Sale Lake.

the main channel is characterized by one high water stage (between April and September) and one low water stage (between October and March). During the period 1965–1990, the mean discharge at Óbidos was estimated at  $209\,000\text{ m}^3\text{ s}^{-1}$  (standard deviation [SD] is 30%) (DNAEE 1994) with  $103\,000\text{ m}^3\text{ s}^{-1}$  (SD = 30%) from the Solimões River, at Manacapuru,  $28\,000\text{ m}^3\text{ s}^{-1}$  (SD = 40%) from the Negro River at Manaus and  $31\,200\text{ m}^3\text{ s}^{-1}$  (SD = 60%) from the Madeira River at the confluence with the Amazon River. Relative seasonal tributary contributions change, however, as the Madeira maximum discharge precedes those of the Solimões and Negro Rivers by two months [Callède *et al.*, 2004]. During the rising water stage (February–April) the river overflows and fills the surrounding floodplains, thereby creating a seasonal ecosystem of flooded forests and connected lakes during the high water stage. The floodplains (so-called várzeas) of the Amazon River and its tributaries are one of the largest riverine wetlands in the world [Junk, 1997]. Surface area estimates vary between 100000 [Junk, 1985] to 300000  $\text{km}^2$  [Junk, 1997] and between 20 and 30% of the annual Amazon discharge passes through the floodplains [Richey *et al.*, 1989; Bonnet *et al.*, 2004].

[7] Concerning sediment transport, recent results obtained by Filizola and Guyot [2004] give a mean annual suspended sediments (SS) flux close to  $600\,10^6\text{ t}\cdot\text{yr}^{-1}$  at Óbidos. Ninety-seven percent of this amount is contributed by Andean tributaries (62% from the Solimões and 35% from the Madeira). The contributions of the Negro, Trombetas, Tapajos and Xingú account for less than 3%. During the hydrological period, SS concen-

trations show high frequency variations (10 days) and the sediment peak discharge precedes by three months the maximum water discharge [Seyler and Boaventura, 2003].

### 3. Sampling and Analytical Methods

[8] Within the ORE (Environmental Research Observatory) HyBam (Hydrology of the Amazon Basin) Program (<http://www.ore-hybam.org>) monthly samples are collected from the Amazon River at Óbidos station ( $S01^{\circ}56'50''$ ,  $W55^{\circ}30'40''$ ; Para State, Brazil), which is the chief gauging station on the Amazon River upstream from the marine influence (Figure 1). Monthly samples are also collected on the three main Amazon River tributaries, The Negro River at Serrinha station ( $S00^{\circ}28'55''$ ,  $W064^{\circ}49'48''$ ) and at Caracaraí ( $N01^{\circ}49'17''$ ,  $W061^{\circ}07'25''$ ) for the Branco River, the Solimões River at Manacapuru station ( $S03^{\circ}20'43''$ ,  $W60^{\circ}33'12''$ ) and the Madeira River at Fz. Vista Alegre ( $08^{\circ}44'12''$ ,  $W63^{\circ}55'13''$ ). In this study we will consider data from March 2003 to May 2005. Some samples have been collected during additional sampling campaigns, in March 2003 and June 2003. From March 2003 to August 2003 the Rio Negro was sampled 50 km upstream from Manaus and therefore covers the entire Negro Basin. Contrarily, Rio Negro samples from September 2003 and onward were collected at Serrinha (Negro) and Caracaraí (Branco) which is  $\sim 600$  km upstream from Manaus, and results in 90% coverage of the drainage area. The várzea “Lago Grande do Curuaí” has been selected as a pilot site to study the relation between the floodplains and the

**Table 1.** Results of ICP-MS Analysis of International Geostandard SLRS-4<sup>a</sup>

Element	Recommended Value (1)		Measured Average Value		
	Concentration, ppb	SD, %	Concentration, ppb	SD, %	Internal Error, %
La	0.2870	3	0.2903	2	3
Ce	0.3600	3	0.3672	2	3
Pr	0.0693	3	0.0704	3	5
Nd	0.2690	5	0.2694	3	7
Sm	0.0574	5	0.0573	3	8
Eu	0.0080	8	0.0072	34	19
Gd	0.0342	6	0.0286	2	12
Tb	0.0043	9	0.0037	14	13
Dy	0.0242	7	0.0227	5	13
Ho	0.0047	6	0.0046	9	18
Er	0.0134	4	0.0128	5	17
Tm	0.0017	12	0.0018	20	31
Yb	0.0120	3	0.0114	6	12
Lu	0.0019	5	0.0016	20	27

<sup>a</sup>River water; National Research Council of Canada. One sigma standard deviations are given, based on 5 replicate analysis over a 2-year time period. Our measurements are in good agreement with the values proposed by *Yeghicheyan et al.* [2001] (1).

Amazon River mainstream (Figure 1). This floodplain, with more than 2500 km<sup>2</sup> of wetlands, is representative of the floodplains between Manaus and Óbidos. Samples have been collected monthly in the Sale Lake of this várzea from July 2002 to December 2003.

[9] In order to avoid contamination, water samples were taken upstream from a small boat, at ~0.5 m depth in the middle of river sections. Samples were collected in acid-cleaned high density polyethylene (HDPE) containers and filtered immediately through 0.22 μm Millipore<sup>®</sup> membranes. We did not encounter clogging filtration problems. Filtered solutions for trace element analyses were acidified to pH 2 with double-distilled 10 N HNO<sub>3</sub> and stored in HDPE bottles, previously washed with 1 N double-distilled HCl and rinsed with MilliQ deionized water.

[10] REE concentrations were measured by ICP-MS (Perkin Elmer, Elan 6000) using a single point calibration against a synthetic solution of known REE concentrations. Indium and rhenium were used as internal standards in order to correct for instrumental drift and potential matrix effects. Appropriate corrections for oxide and hydroxide isobaric interferences were made for the REE [*Aries et al.*, 2000]. The international geostandard SLRS-4 (Riverine water reference material for trace metals, certified by the National Research Council of Canada) was used to check the validity and reproducibility of the ICP-MS analyses. Although, the concentrations of REE are not certified or recommended in the SLRS-4 standard, our measurements are in

good agreement (LREE better than 5%, HREE better than 12%) with the values proposed by [*Yeghicheyan et al.*, 2001] (Table 1). These authors have compiled and evaluated data from several laboratories. Eu, Tb, Ho, Tm and Lu concentrations in a number of samples were close to the ICP-MS detection limits and had problematic interference corrections. These data are therefore omitted from the data set. Potential suspended sediment contamination was evaluated from Ti and Zr concentrations, and suspect samples omitted as well.

## 4. Results

### 4.1. Amazon River at Óbidos Station, Para State, Brazil

[11] Dissolved REE (i.e., <0.22 μm) concentrations at Óbidos Station from March 2003 to May 2005 are reported in Table 2. The seasonal variation of water discharge (water discharge data from ORE and “Agencia Nacional de Agua “(ANA) Brazil), and concentrations of lanthanum, neodymium and ytterbium from March 2003 to May 2005 are shown in Figure 2e. Overall, the concentrations correlate with river discharge at Obdios Station. During the falling water stages of both 2003 and 2004 (August and October respectively) this relationship is interrupted with a brief rise in REE concentrations. A comparison of our upper crust (UC) [*Taylor and McLennan*, 1985] normalized REE concentrations to published REE trends for the Amazon River (Figure 2a) shows that our



**Table 2.** Rare Earth Element Concentrations and Discharge of the Amazon River Water<sup>a</sup>

Amazon River Obidos Station	La, $\mu\text{g/L}$	Ce, $\mu\text{g/L}$	Pr, $\mu\text{g/L}$	Nd, $\mu\text{g/L}$	Sm, $\mu\text{g/L}$	Gd, $\mu\text{g/L}$	Dy, $\mu\text{g/L}$	Er, $\mu\text{g/L}$	Yb, $\mu\text{g/L}$	Discharge, $\text{m}^3/\text{s}$
29/03/2003	0.065	0.175	0.022	0.103	-	0.024	0.023	0.014	0.012	178,700
01/06/2003	0.109	0.276	0.035	0.157	-	0.039	0.036	0.021	0.018	228,600
10/07/2003	0.053	0.145	0.018	0.088	0.026	0.026	0.022	0.013	0.012	224,400
10/09/2003	0.064	0.154	0.021	0.092	0.026	0.026	0.023	0.012	0.012	170,900
10/12/2003	0.042	0.088	0.013	0.060	0.018	0.018	0.015	0.009	0.008	109,300
10/01/2004	0.035	0.081	0.012	0.058	0.015	0.017	0.015	0.008	0.007	113,500
10/04/2004	0.087	0.206	0.029	0.133	0.035	0.035	0.030	0.015	0.012	201,800
10/05/2004	0.130	0.325	0.041	0.178	0.049	0.046	0.037	0.022	0.018	224,000
10/06/2004	0.122	0.299	0.037	0.174	0.045	0.045	0.039	0.022	0.019	233,073
10/07/2004	0.108	0.300	0.036	0.163	0.040	0.042	0.035	0.020	0.016	221,396
10/08/2004	0.063	0.158	0.021	0.098	0.023	0.030	0.024	0.013	0.011	184,835
10/09/2004	0.077	0.178	0.024	0.114	0.029	0.028	0.026	0.016	0.013	156,331
10/10/2004	0.078	0.166	0.022	0.102	0.026	0.027	0.025	0.014	0.014	115,335
10/11/2004	0.060	0.113	0.017	0.070	0.022	0.029	0.020	0.012	0.009	101,634
10/12/2004	0.037	0.069	0.010	0.047	0.014	0.013	0.011	0.007	0.004	112,269
10/01/2005	0.041	0.090	0.013	0.065	0.021	0.017	0.015	0.009	0.008	135,696
10/02/2005	0.062	0.115	0.017	0.085	0.027	0.027	0.021	0.012	0.010	158,744
10/03/2005	0.081	0.190	0.027	0.122	0.038	0.035	0.032	0.016	0.013	180,293
10/04/2005	0.091	0.165	0.022	0.105	0.028	0.031	0.024	0.016	0.013	207,885
10/05/2005	0.069	0.191	0.024	0.112	0.027	0.031	0.027	0.016	0.014	229,004
Flux to the ocean, T/yr	396.6	956.7	126.4	580.8	165.9	158	136.2	76.9	65.8	

<sup>a</sup> Concentrations are for  $<0.22 \mu\text{m}$ . From Óbidos station, Brazil. The sampling was done from March 2003 to May 2005.

observations nearly span the range of REE concentrations in the Amazon River reported in the literature [Goldstein and Jacobsen, 1988b; Elderfield et al., 1990; Sholkovitz, 1993, 1995; Gaillardet et al., 1997; Deberdt et al., 2002; Gerard et al., 2003]. Literature data for which sampling dates were reported have REE concentrations that correspond remarkably well to our seasonal observations (Figure 2e; original month retained, yet superimposed on the year 2003) [Goldstein and Jacobsen, 1988b; Elderfield et al., 1990; Sholkovitz, 1993; Gaillardet et al., 1997; Deberdt et al., 2002; Gerard et al., 2003]. UC normalized REE fractionation trends (Figure 2a) also closely resemble published work and illustrate the typical MREE enriched dissolved REE phase. Figure 3a shows the seasonal variation of the UC normalized  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ratio, which is a measure of HREE/LREE fractionation. An increase in  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  from  $\sim 1.0$  at the start of the rising water stage (January–April) to 1.5 during the low water stage (November–

January) can be observed for the year 2004, and partially for the years 2003 and 2005.  $\text{Gd}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ratios (not shown), which are a measure of MREE/LREE fractionation, do not show any seasonal trends. We also show in Figure 3a the cerium anomaly ( $\text{Ce}/\text{Ce}^*$ ), calculated from La and Nd concentrations ( $\text{Ce}/\text{Ce}^* = 3\text{Ce}/(\text{La} + 2\text{Nd})$ ) [Shiller, 2002].  $\text{Ce}/\text{Ce}^*$  appears to be weakly correlated with discharge (Figure 3a) and Ce concentrations (Table 2;  $r^2 = 0.54$ ). The high water stage has  $\text{Ce}/\text{Ce}^*$  around 1.0 and the low water stage has  $\text{Ce}/\text{Ce}^*$  of 0.75.

#### 4.2. Amazon Tributaries (Rio Negro, Rio Solimões, and Rio Madeira) $< 0.22 \mu\text{m}$

[12] Except for the samples March 2003 and June 2003 which were collected during field campaigns, all the other samples are from the ORE sampling network. REE data are summarized in Table 3 for the Negro River, in Table 4 for the Solimões River and in Table 5 for the Madeira River.

**Figure 2.** Dissolved ( $<0.22 \mu\text{m}$ ) REE patterns of (a) the Amazon River, (b) the Rio Negro and Rio Branco, (c) the Rio Solimões, and (d) the Rio Madeira. REE concentrations have been normalized to the Upper Crust [Taylor and McLennan, 1985]. (e–h) Seasonal variations of dissolved REE concentrations ( $\mu\text{g}\cdot\text{L}^{-1}$ ), illustrated for La, Nd, and Yb. Discharge data ( $\text{m}^3\cdot\text{s}^{-1}$ ) are included in Figures 2e–2h (gray areas) for each river. Literature data for REE trends (Figures 2a–2d) and seasonal Nd concentrations (Figures 2e–2h) are shown in color in Figures 2a–2h. Nd concentration literature data (Figures 2e–2h) are all plotted in the year 2003, but in the month they were originally collected.

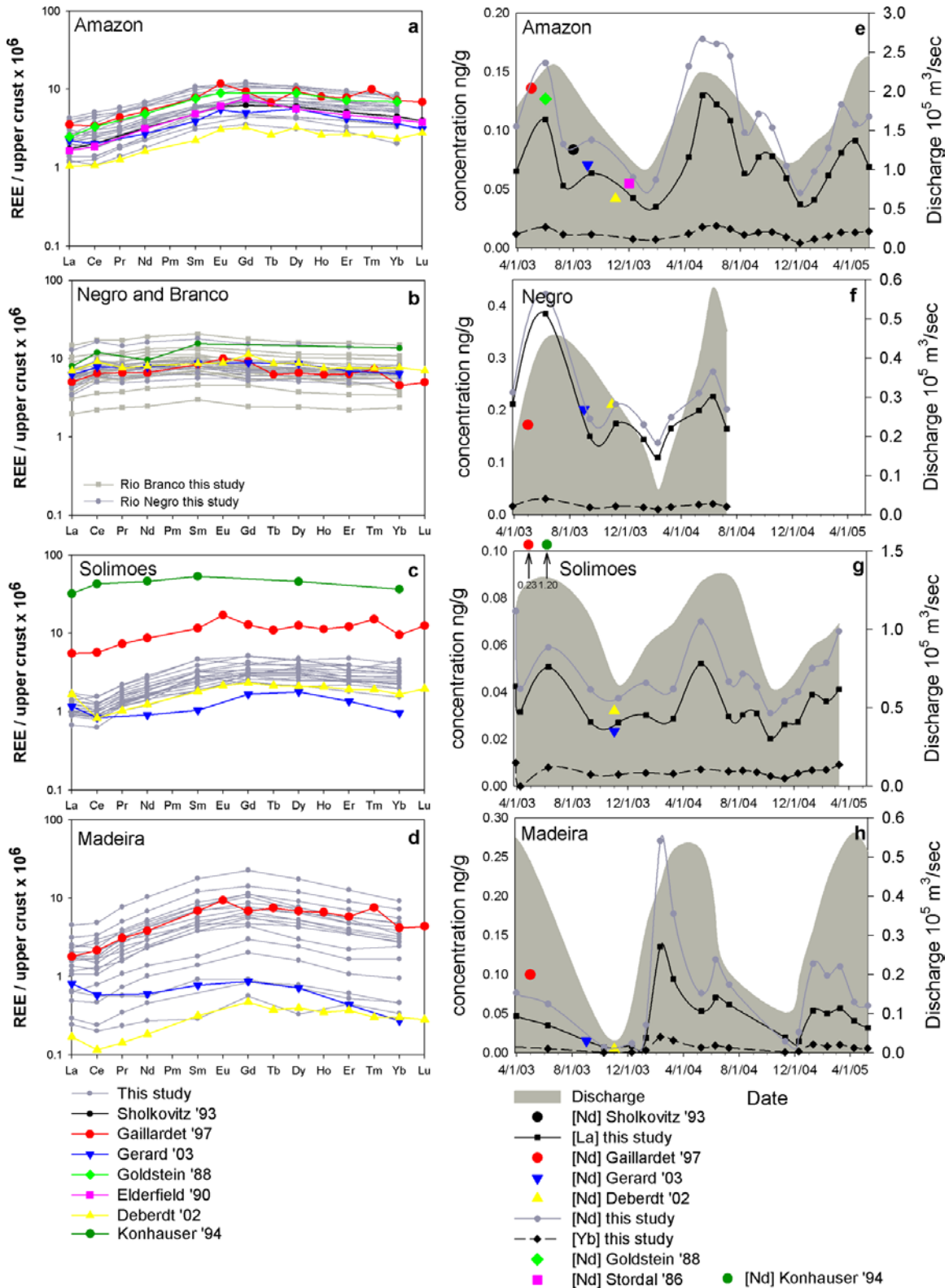
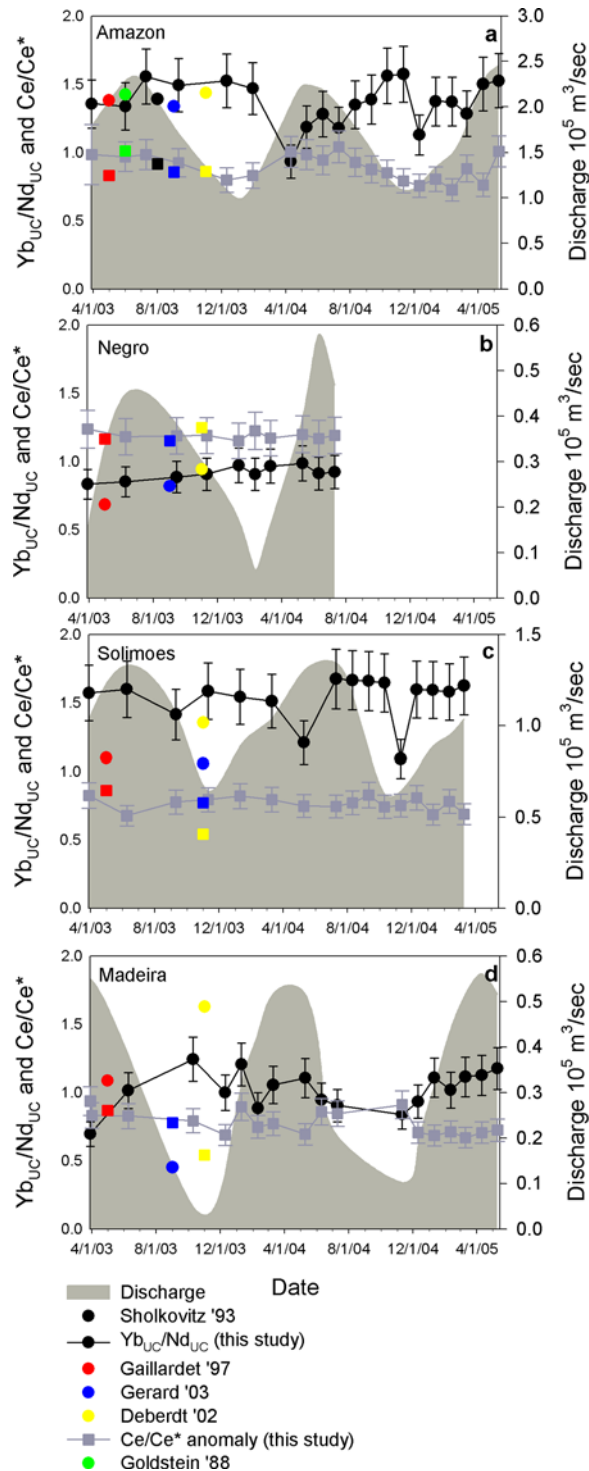


Figure 2



**Figure 3.** Yb/Nd ratio and Ce/Ce\* (both on left axis) seasonal variation for the Amazon River at (a) Obdios, (b) the Negro River, (c) the Solimões River, and (d) the Madeira River. Discharge ( $10^5 \text{ m}^3 \cdot \text{sec}^{-1}$ ) is indicated as gray surface area for each river. Error bars indicate 2 sigma standard deviations.

[13] The Negro River (from March 2003 to July 2004) exhibits higher REE concentration than any of the other tributaries (Figure 2f:  $1 \mu\text{g} \cdot \text{L}^{-1}$  for Ce and lowest is  $0.01 \mu\text{g} \cdot \text{L}^{-1}$  for Yb). This is a typical feature of organic-rich river waters in tropical environments [Viers *et al.*, 1997]. Negro River concentrations vary with discharge (Figure 2f) and the UC normalized REE patterns (Figure 2b) are flat with no significant variation in  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  and a positive Ce/Ce\* anomaly of 1.2–1.3 (Figure 3b). This is in good agreement with Gaillardet *et al.* [1997], Deberdt *et al.* [2002] and Gerard *et al.* [2003]. Superimposing published REE trends (Figure 2b, colors) and monthly sorted published Nd concentrations (Figure 2f, colors, May, September, November) onto our seasonal REE trends and Nd evolution shows a good agreement. [Goldstein and Jacobsen, 1988b; Sholkovitz, 1993; Gaillardet *et al.*, 1997; Deberdt *et al.*, 2002; Gerard *et al.*, 2003].

[14] The Solimões River (from March 2003 to March 2005) has relatively low REE concentrations and relatively modest concentration variations (within a factor 2) compared to the other rivers (Figure 2c). The UC normalized REE patterns for the Andean Solimões show an enrichment in MREE and HREE (Figure 2c). Fractionation between LREE and HREE is reflected by the relatively high  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  values of 1.5 (Figure 3c), yet no temporal variations are observed for either  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  or Ce/Ce\*. Two anomalously low  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ratios of 1.1 and 1.2 occurred during May (high water) and November (low water) 2004. REE trend and Nd concentration results (Figures 2c and 2g) during the low water stage are similar to observations by Deberdt *et al.* [2002] and Gerard *et al.* [2003]. The high water stage Solimões REE concentrations from Gaillardet *et al.* [1997] (May 1989) and Konhauser *et al.* [1994] (May/June 1991) are respectively  $\sim 3$  and  $\sim 16$  times more concentrated than our maximum (high water stage) Solimões REE concentrations. The Konhauser *et al.* [1994] data have a suspiciously low  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ratio of 0.79 (Figure 3c), which is similar to the average Amazonian Rivers suspended matter  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  of 0.77 [Gaillardet *et al.*, 1997]. This suggests that suspended sediment contamination may be responsible for the high dissolved Solimões REE concentrations of Konhauser *et al.* [1994]. However, this argument does not apply to the three-fold higher REE concentration of Gaillardet *et al.* [1997] with a  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ratio of 1.10 that is within the range of our  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  (1.09–1.67). Given that the 2003 and 2004 high water stage





**Table 3.** REE Concentrations Measured in the Dissolved Phase and Discharge of the Rio Negro From March 2003 to July 2004<sup>a</sup>

Negro River Serrinha Station	La, $\mu\text{g/L}$	Ce, $\mu\text{g/L}$	Pr, $\mu\text{g/L}$	Nd, $\mu\text{g/L}$	Sm, $\mu\text{g/L}$	Gd, $\mu\text{g/L}$	Dy, $\mu\text{g/L}$	Er, $\mu\text{g/L}$	Yb, $\mu\text{g/L}$	Discharge, $\text{m}^3/\text{s}$
29/03/2003	0.212	0.612	0.060	0.234	0.043	0.034	0.029	0.017	0.017	17956
09/06/2003	0.385	1.058	0.103	0.422	0.081	0.058	0.053	0.032	0.031	46274
14/09/2003	0.124	0.384	0.039	0.156	0.029	0.020	0.019	0.013	0.012	32756
10/11/2003	0.172	0.520	0.053	0.211	0.042	0.028	0.027	0.016	0.017	24719
10/01/2004	0.151	0.424	0.046	0.182	0.034	0.025	0.023	0.014	0.015	15105
10/02/2004	0.103	0.323	0.035	0.134	0.025	0.021	0.018	0.011	0.011	5506
10/03/2004	0.168	0.467	0.050	0.188	0.037	0.026	0.024	0.015	0.016	14212
10/05/2004	0.168	0.522	0.054	0.201	0.040	0.032	0.026	0.017	0.018	34063
10/06/2004	0.152	0.479	0.050	0.198	0.036	0.027	0.025	0.016	0.017	49610
10/07/2004	0.132	0.404	0.042	0.165	0.036	0.023	0.021	0.014	0.014	40305

<sup>a</sup> Concentrations are for  $<0.22 \mu\text{m}$ .

REE concentration maximums in the Negro (Figure 2f) and Madeira (Figure 2h; see below) tributaries vary by a factor 2, it is plausible that the threefold difference also reflects a natural variation in REE concentrations either on a year-to-year or on a shorter frequency, i.e., weekly, basis.

[15] The Madeira River (from March 2003 to June 2005) shows large seasonal concentration variations (from 0.01 to 0.1  $\mu\text{g.L}^{-1}$  for La) with a strong increase at the beginning of the rising water stage, followed by a decrease toward the low water stage (Figure 2h). The UC normalized REE patterns for the Andean Madeira River show

the most pronounced MREE enrichment of all rivers (Figure 2d). Despite an overall variation in  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  (0.7–1.2) and  $\text{Ce}/\text{Ce}^*$  (0.7–0.9), no seasonal trends are observed (Figure 3d).

#### 4.3. “Sale” Lake from the “Lago Grande de Curuai” Floodplain (Para State, Brazil)

[16] Samples from the “Sale” Lake of the várzea do Curuai are reported in the Table 6. Again concentrations vary strongly as a function of time (Figure 4b); La concentrations are close to 0.03  $\mu\text{g.L}^{-1}$  in March 2003 and up to 0.25  $\mu\text{g.L}^{-1}$  in August and September 2002 and September 2003. During the latter period, the floodplain is

**Table 4.** REE Concentrations Measured in the Dissolved Phase and River Discharge of the Solimões River From March 2003 to March 2005<sup>a</sup>

Solimões River Manacapuru Station	La, $\mu\text{g/L}$	Ce, $\mu\text{g/L}$	Pr, $\mu\text{g/L}$	Nd, $\mu\text{g/L}$	Sm, $\mu\text{g/L}$	Gd, $\mu\text{g/L}$	Dy, $\mu\text{g/L}$	Er, $\mu\text{g/L}$	Yb, $\mu\text{g/L}$	Discharge, $\text{m}^3/\text{s}$
27/03/2003	0.042	0.100	0.016	0.074	0.021	0.015	0.017	0.008	0.010	103211
08/04/2003	0.032	0.066	0.009	0.041	-	0.009	0.011	-	-	123200
09/06/2003	0.051	0.082	0.013	0.059	0.015	0.016	0.013	0.009	0.008	132949
10/08/2003	0.033	0.068	0.011	0.050	0.012	0.012	0.011	0.007	0.006	138900
10/09/2003	0.027	0.056	0.009	0.041	0.013	0.010	0.009	0.006	0.005	106800
10/11/2003	0.027	0.055	0.008	0.037	0.009	0.010	0.009	0.006	0.005	64168
10/12/2003	0.028	0.052	0.009	0.043	0.009	0.011	0.009	0.006	0.004	75119
10/01/2004	0.030	0.065	0.010	0.044	0.010	0.012	0.011	0.006	0.006	88610
10/03/2004	0.029	0.060	0.009	0.041	0.008	0.011	0.011	0.006	0.005	103565
10/04/2004	0.041	0.081	0.012	0.054	0.014	0.015	0.014	0.009	0.007	118990
10/05/2004	0.052	0.098	0.015	0.070	0.021	0.019	0.016	0.009	0.007	129942
10/07/2004	0.030	0.059	0.009	0.044	0.011	0.012	0.012	0.006	0.006	134458
10/08/2004	0.030	0.063	0.010	0.048	0.015	0.013	0.012	0.007	0.007	116984
10/09/2004	0.031	0.065	0.010	0.042	0.011	0.011	0.010	0.007	0.006	86276
10/10/2004	0.020	0.040	0.007	0.031	0.009	0.009	0.007	0.005	0.004	62793
10/11/2004	0.026	0.050	0.008	0.036	0.012	0.009	0.008	0.004	0.003	64168
10/12/2004	0.027	0.058	0.009	0.040	0.013	0.011	0.010	0.005	0.005	75119
10/01/2005	0.039	0.066	0.012	0.050	0.012	0.013	0.012	0.008	0.007	88610
10/02/2005	0.036	0.074	0.012	0.053	0.015	0.011	0.013	0.008	0.007	94528
10/03/2005	0.041	0.078	0.014	0.066	0.017	0.020	0.016	0.011	0.009	103565

<sup>a</sup> Concentrations are for  $<0.22 \mu\text{m}$ .

**Table 5.** REE Concentrations Measured in the Dissolved Phase and River Discharge of the Madeira River From March 2003 to June 2005<sup>a</sup>

Madeira River Porto Velho Station	La, $\mu\text{g/L}$	Ce, $\mu\text{g/L}$	Pr, $\mu\text{g/L}$	Nd, $\mu\text{g/L}$	Sm, $\mu\text{g/L}$	Gd, $\mu\text{g/L}$	Dy, $\mu\text{g/L}$	Er, $\mu\text{g/L}$	Yb, $\mu\text{g/L}$	Discharge, $\text{m}^3/\text{s}$
27/03/2003	0.070	0.192	0.027	0.129	0.035	0.044	0.027	0.012	0.008	51186
01/04/2003	0.047	0.108	0.015	0.077	0.021	0.018	0.015	-	-	54650
09/06/2003	0.035	0.084	0.011	0.062	0.017	0.017	0.010	0.005	0.005	38178
10/10/2003	0.007	0.013	0.002	0.007	0.001	0.002	0.001	0.001	0.001	4877
10/12/2003	0.009	0.015	0.002	0.012	-	0.003	0.003	0.001	0.001	12170
10/01/2004	0.019	0.051	0.008	0.036	0.008	0.011	0.008	0.004	0.004	31590
10/02/2004	0.136	0.311	0.055	0.271	0.080	0.086	0.061	0.029	0.020	42700
10/03/2004	0.094	0.216	0.036	0.178	0.055	0.054	0.042	0.021	0.016	51720
10/04/2004	0.076	0.148	0.028	0.136	0.040	0.042	0.032	0.016	0.012	56094
10/05/2004	0.053	0.096	0.017	0.076	0.023	0.023	0.018	0.009	0.007	51607
10/06/2004	0.071	0.170	0.025	0.119	0.036	0.040	0.025	0.011	0.010	34110
10/07/2004	0.061	0.134	0.021	0.087	0.021	0.026	0.018	0.009	0.007	20398
10/11/2004	0.020	0.036	0.004	0.014	0.004	0.003	0.003	0.001	0.001	10191
10/12/2004	0.015	0.030	0.005	0.026	0.006	0.008	0.006	0.002	0.002	17983
10/01/2005	0.054	0.116	0.022	0.114	0.032	0.030	0.023	0.013	0.011	31159
10/02/2005	0.050	0.109	0.019	0.099	0.026	0.028	0.022	0.011	0.008	43809
10/03/2005	0.057	0.114	0.023	0.110	0.031	0.033	0.026	0.013	0.010	51524
10/04/2005	0.041	0.078	0.014	0.065	0.020	0.022	0.015	0.008	0.006	56094
10/05/2005	0.032	0.069	0.012	0.060	0.017	0.021	0.017	0.008	0.006	51607
10/06/2005	0.085	0.186	0.027	0.121	0.037	0.036	0.025	0.011	0.006	34110

<sup>a</sup>Concentrations are for  $<0.22 \mu\text{m}$ .

discharging into the Amazon main stem and individual dissolved REE concentrations in floodplain water exceed those of the Amazon main stem. By contrast, the lowest values are encountered during the low water stage at the onset of inundation (January to March 2003). The UC normalized REE patterns are shown in Figure 4a and display variations in  $\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  from 0.71–1.44 and in  $\text{Ce}/\text{Ce}^*$  from 0.55–0.92. Moderate correlations between individual REE concentrations and

$\text{Yb}_{\text{UC}}/\text{Nd}_{\text{UC}}$  ( $r^2 = 0.55$ ) and  $\text{Ce}/\text{Ce}^*$  ( $r^2 = 0.50$ ) can be observed.

## 5. Discussion

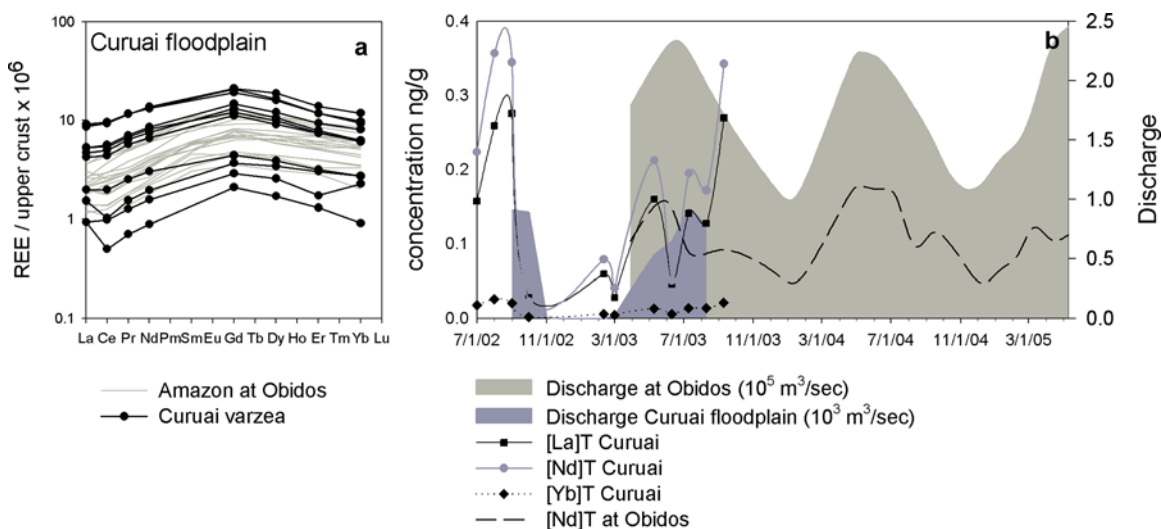
### 5.1. REE Concentration–Discharge Relationships

[17] One of the most prominent features of the seasonal REE concentration variations is that, to

**Table 6.** REE Concentration in the Sale Lake Dissolved Phase From July 2002 to September 2003<sup>a</sup>

Curuai's Floodplain Sale Lake	La, $\mu\text{g/L}$	Ce, $\mu\text{g/L}$	Pr, $\mu\text{g/L}$	Nd, $\mu\text{g/L}$	Sm, $\mu\text{g/L}$	Gd, $\mu\text{g/L}$	Dy, $\mu\text{g/L}$	Er, $\mu\text{g/L}$	Yb, $\mu\text{g/L}$
01/07/2002	0.157	0.363	0.050	0.223	-	0.056	0.042	0.022	0.018
01/08/2002	0.259	0.598	0.082	0.357	-	0.080	0.066	0.032	0.026
01/09/2002	0.276	0.616	0.082	0.345	-	0.079	0.058	0.027	0.021
10/10/2002	0.028	0.032	0.005	0.023	-	0.008	0.006	0.003	0.002
10/02/2003	0.059	0.127	0.018	0.079	-	0.017	0.014	0.007	0.006
01/03/2003	0.028	0.063	0.009	0.041	-	0.011	0.009	0.004	0.005
10/05/2003	0.160	0.345	0.048	0.212	-	0.046	0.035	0.017	0.013
10/06/2003	0.046	0.066	0.011	0.051	-	0.014	0.012	0.007	0.006
10/07/2003	0.141	0.319	0.045	0.195	-	0.050	0.037	0.018	0.014
10/08/2003	0.127	0.281	0.041	0.172	-	0.043	0.032	0.017	0.014
10/09/2003	0.270	0.614	0.083	0.343	-	0.073	0.056	0.027	0.021
Flux to the Amazon River, T/yr	1.6	3.3	0.5	2.0	-	0.5	0.4	0.2	0.1

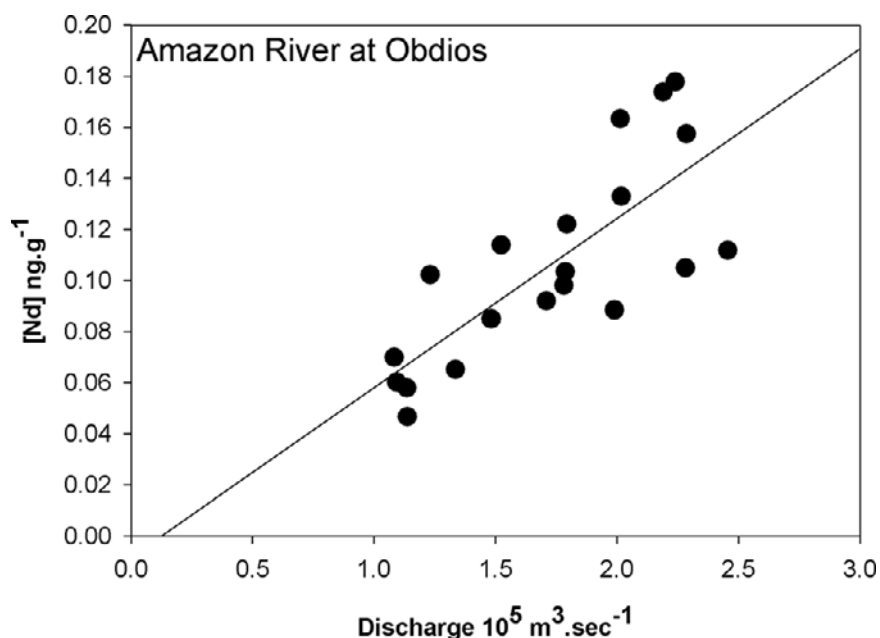
<sup>a</sup>Concentrations are for  $<0.22 \mu\text{m}$ . Average REE fluxes are also reported in  $\text{t}\cdot\text{yr}^{-1}$ .



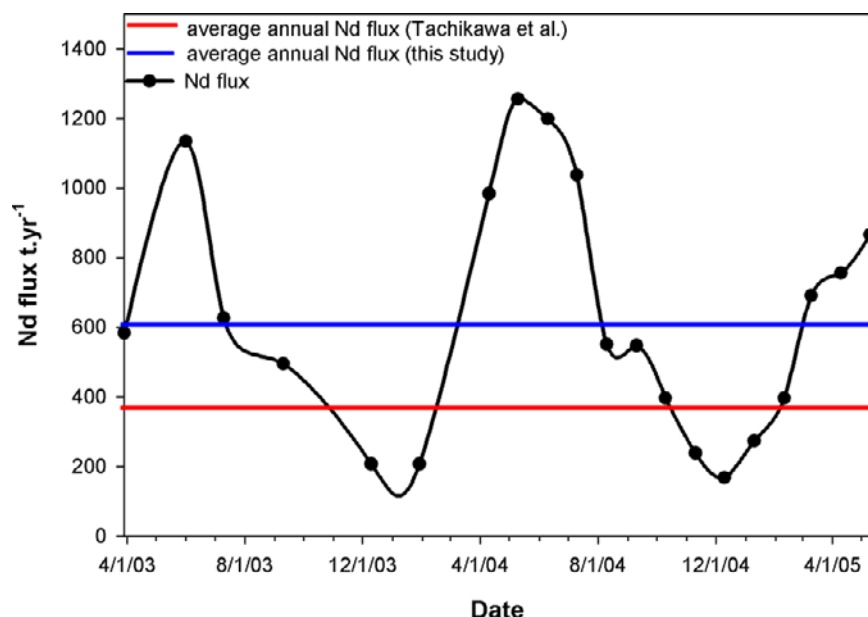
**Figure 4.** (a) Upper crust normalized REE patterns for the Curuai várzea and (b) seasonal concentration trends for the period July 2002 to September 2003. Included for reference are the observed REE patterns at Obidos (Figure 4a, gray) and the seasonal Nd concentrations at Obidos (Figure 4b, dashed black line) as well as the discharge at Obidos (Figure 4b, gray area). Note difference in discharge units between Obidos and Curuai in the legend.

first order, they follow the River discharge trends (Figure 2). For all tributaries, the REE concentrations display their highest levels during the high water season and vice versa. Within the high and lower water seasons the relationship is more complex. This is reflected in the overall correlation coefficients of discharge versus Nd concentrations (for example), which yield values of 0.64, 0.29, 0.35 and 0.41 for the Amazon, Negro, Solimões, and Madeira River respectively. Figure 5 illustrates

the linear discharge versus Nd flux relationship for Obidos station ( $r^2 = 0.79$ ). Linear relationships between chemical fluxes and annual run-off are typically observed on the watershed scale [White and Blum, 1994] and reflect transport limited chemical weathering conditions. Transport limitation, where the maximum weathering rate exceeds the ability of transport processes to remove material, has been suggested to take place in the plains of the Amazon Basin, and lead to development of



**Figure 5.** Linear correlation between monthly discharge ( $10^5 \text{ m}^3 \cdot \text{sec}^{-1}$ ) and Nd Flux ( $\text{T} \cdot \text{yr}^{-1}$ ) of the Amazon River at Obidos station.



**Figure 6.** Monthly interpolated dissolved Nd flux ( $\text{T.yr}^{-1}$ ) at Óbidos (black line) and annual average of  $607 \text{ T.yr}^{-1}$  (blue line). The previous estimate used in global Nd ocean box models [Tachikawa *et al.*, 2003] is based on data from Stordal and Wasserburg [1986] and is shown in red.

thick soils [Stallard and Edmond, 1983, 1987]. Under the transport limited scenario intense high water season rainfall and flooding mobilize particles, including colloids from topsoils and intermediate soil layers. To extend transport limited weathering to the REE, a key factor is the REE speciation in soil solutions and river water. Recent progress in ultra-filtration, experimental and speciation modeling studies of REE-colloid interactions suggest that REE speciation in natural waters is dominated by colloids [Viers *et al.*, 1997; Ingri *et al.*, 2000; Tang and Johannesson, 2003; Pokrovsky *et al.*, 2005; Sonke and Salters, 2006]. Particle and colloid mobilization during rainfall events is therefore a plausible explanation for the observed discharge–REE concentration relationships in the Amazon River and its tributaries. An 18-month time series of the boreal Kalix River (Sweden) REE fluxes has been presented by Ingri *et al.* [2000]. They found, similar to our observations that dissolved REE concentrations were highly correlated with discharge.

[18] Shiller [1997, 2002] has shown that Mississippi dissolved REE and Mn concentrations oscillate on a seasonal basis governed by water temperature. His study shows that for the Mississippi River, REE and Mn fluxes are highest during November–April when water temperature is at its lowest ( $5^{\circ}\text{C}$ ), and REE are lowest during May–October coinciding with high water temperature

( $25^{\circ}\text{C}$ ). Shiller suggested that the Mississippi’s seasonal dissolved Mn and REE oscillations are linked to intensified microbial Mn oxidation during summer and subsequent high trace metal scavenging by  $\text{MnO}_2$  particles. Mississippi Ce/Ce\* anomalies correlate with Ce concentrations and are lowest (0.3) during the summer temperature maximum. This supported the geomicrobiological interpretation that inorganic Ce(III) oxidation by  $\text{MnO}_2$  and/or microbial Ce(III) oxidation are involved. Compared to the Mississippi, the Amazon River at Óbidos integrates multiple, but predominantly (sub-) tropical climate zones that are characterized by minor seasonal temperature fluctuations (e.g., 3–4 degrees C at Óbidos). Nevertheless, dissolved Mn [Seyler and Boaventura, 2003] and REE concentrations, and Ce/Ce\* anomalies at Óbidos correlate similarly as in the Mississippi River. The temperature-independent linear correlation between particle reactive trace metals (Mn, Co, Cd and REE), Ce/Ce\*, and discharge suggests that hydrological, rather than microbial control factors, dominate their dissolved river concentrations in the Amazon Basin.

## 5.2. Dissolved REE Fluxes to the Ocean

[19] The two-year time series of dissolved REE and Amazon discharges at Óbidos allows us to calculate monthly fluxes to the Atlantic, as well as



**Table 7.** Summary of Published Nd Inputs to the Surface Atlantic and Global Oceans<sup>a</sup>

Source	Surface Atlantic		Global Oceans		Reference
	T/yr	%	T/yr	%	
Total	4300	100	8600	100	<i>Tachikawa et al.</i> [2003]
2% dust leaching	133	3	400	5	<i>Tachikawa et al.</i> [2003]
Rivers	600	14	1719	20	<i>Tachikawa et al.</i> [2003]
Missing	3567	83	6482	75	<i>Tachikawa et al.</i> [2003]
Amazon literature	374	9	374	4	<i>Stordal and Wasserburg</i> [1986]
Amazon annual	607	14	607	7	this study
Amazon min	165	4	165	2	this study
Amazon max	1277	30	1277	15	this study

<sup>a</sup>Our annual, minimum, and maximum fluxes of dissolved Nd to the surface Atlantic (this study) are compared to the current Amazon input [*Stordal and Wasserburg*, 1986] (used by *Goldstein and Jacobson* [1988a, 1988b] and *Tachikawa et al.* [2003]). Dissolved river Nd inputs are assumed to desorb 100% from coagulated colloids in estuaries [*Tachikawa et al.*, 2003].

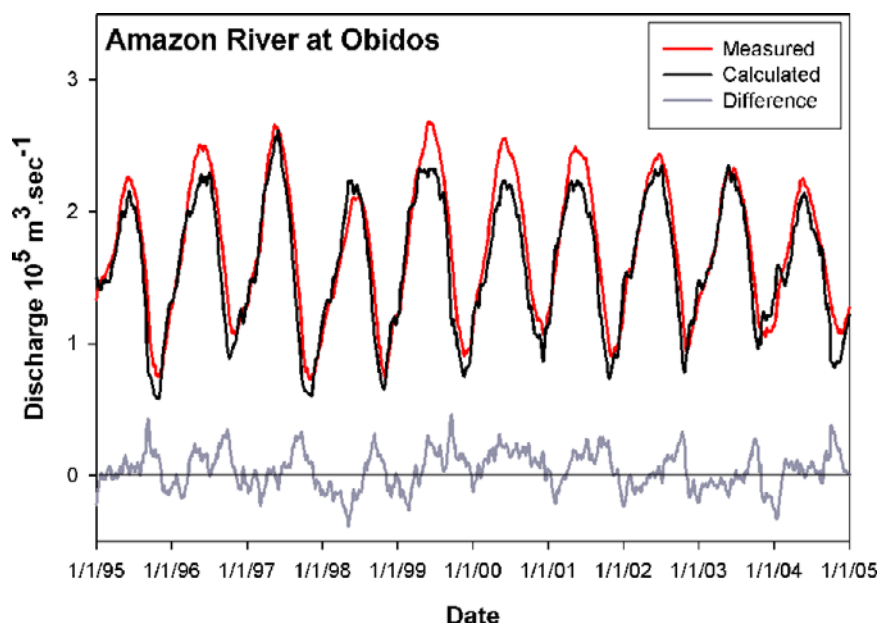
a revised annual flux that integrates the seasonal fluctuations (Table 2). This is of particular interest for Nd, whose isotopic composition is used as a tracer of global ocean circulation and continent-ocean interaction [*Piegras and Wasserburg*, 1982; *Jeandel*, 1993; *Sholkovitz et al.*, 1994]. The annual dissolved REE fluxes (Table 2) have been obtained by the integration of interpolated concentrations on a bi-weekly river discharge scale, during the 2 years of study. These fluxes vary from 996 t.yr<sup>-1</sup> to 68 t.yr<sup>-1</sup> for Cerium and Ytterbium respectively. Figure 6 illustrates the results for the seasonal dissolved Nd flux, which averages 607 ± 43 t.yr<sup>-1</sup> over the period June 2003–May 2005. This flux is 1.6 times larger than the typically used estimate of 375 t.yr<sup>-1</sup> [*Goldstein and Jacobson*, 1988a] which is based on the <0.45 μm dissolved Nd concentration of 54 ng.L<sup>-1</sup> obtained during the low water stage of 1982 (TTO-TAS cruise, leg 1, 30 December 1982 [*Stordal and Wasserburg*, 1986]). In addition to the temporal difference between the *Stordal and Wasserburg* TTO-TAS data and our study, two operational differences remain: (1) The TTO-TAS sample was obtained near the mouth of the Amazon River and therefore includes minor REE flux additions from the Tapajos and Xingú Rivers. (2) Our study uses 0.22 μm filters, whereas the TTO-TAS study used 0.45 μm filters. Had we used larger pore size 0.45 μm filters, then an average annual Nd flux in excess of 607 t.yr<sup>-1</sup> could be expected. Oceanic Nd budget evaluations typically use 0.45 μm pore size data sets, suggesting that our revised annual dissolved Nd flux to the Atlantic Ocean constitutes a minimum estimate.

[20] Using its current estimate of 375 t.yr<sup>-1</sup>, the Amazon River contributes 4% of the global dissolved Nd flux and 9% of the surface Atlantic flux

(assuming 100% re-dissolution of coagulated REE bearing colloids in estuaries [*Tachikawa et al.*, 2003]). Balancing the dissolved Nd budget of the oceans therefore requires REE desorption from shelf sediments and atmospheric dust inputs, both of which are ill-known [*Tachikawa et al.*, 2003]. On the basis of our monthly weighted average dissolved Nd flux of 607 t.yr<sup>-1</sup>, Amazon River contribution to global ocean increases to 7% of dissolved Nd, and 14% of dissolved Nd to the Atlantic Ocean, on an annual basis, and could be respectively as high as 15% and 30% during peak discharge on a month basis (Table 7). It is of interest here to note that for the surface Atlantic Ocean, the missing Nd fluxes in *Tachikawa's* budget require ε<sub>Nd</sub> signatures that correspond to the dissolved and particulate ε<sub>Nd</sub> values of the dominant Amazon River input [*Tachikawa et al.*, 2003]. For the surface Atlantic Ocean, a higher average dissolved Nd flux from the Amazon can therefore be straightforwardly assimilated into Oceanic Nd budget models without violating Nd isotopic constraints. Clearly more seasonal data for the world's major rivers are required to re-evaluate the dissolved Nd flux and its impact on global ocean circulation model calibration. Our new data suggest that at least for the surface Atlantic Ocean, a smaller Nd input from shelf sediments and atmospheric dust desorption is required than was previously thought.

### 5.3. Tributary Mixing and Related Processes

[21] In terms of water budget, the Amazon River can be considered as the result of the mixing of its three main tributaries, the Rio Negro, The Rio Solimões and the Rio Madeira. Together they represent 89% (low water stage) – 100% (high



**Figure 7.** Hydrograph of the Amazon River at Óbidos station. A comparison is made between measured (blue) and calculated (red) discharge, with the latter based on summing the Negro, Solimoes, and Madeira tributaries. The difference (black) between measured and calculated discharge reflects the floodplain filling and discharging dynamics after a 4% correction for missing tributaries.

water stage) of the discharge of the Amazon River at Óbidos (water discharge data from ORE and “Agencia Nacional de Agua” (ANA) Brazil). Figure 7 shows the water discharge of the Amazon River at Óbidos Station (blue line) over the past 10 years. Tributary mass balance calculations are limited by the Negro River data set for which only eight samples during an 18 month period were available. As the transfer time of water between Manaus and Óbidos is around one week, we consider that mixing is instantaneous. The (1 sigma) uncertainty calculated for discharges are 5%, and vary for REE fluxes from 15% to 22% based on the uncertainties of 5 and 12% for the LREE concentration and HREE concentration. The observed discharge at Óbidos at time “t,”  $Q_{ob}(t)$ , can be compared to the sum of tributary discharge  $Q_{sum}(t)$ :

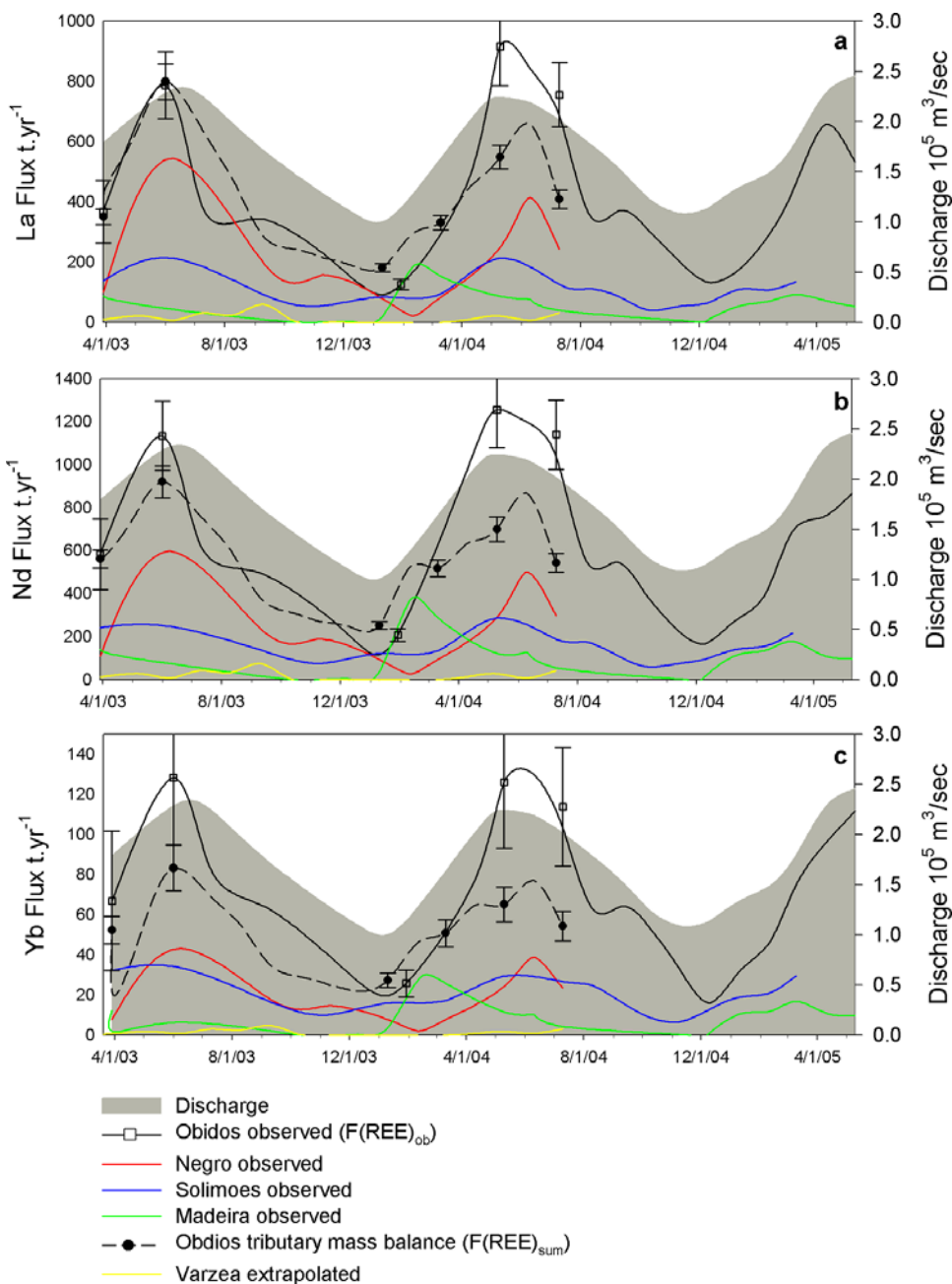
$$Q_{sum}(t) = Q_{sol}(t) + Q_{neg}(t) + Q_{mad}(t)$$

Figure 7 shows that generally during the rising water stages, the measured discharge (blue) is lower than the calculated discharge (red) at Óbidos station, and vice versa during the falling water stages. The difference between the two (corrected for 4% missing tributaries) reflects the floodplain filling and emptying dynamics [Bonnet *et al.*, 2006; Tardy *et al.*, 2005]. Similarly, we can formulate flux equations for the REE based on the observed flux at Óbidos,  $F(REE)_{ob}$  and the

sum of tributary fluxes,  $F(REE)_{sum}$ , here written for La:

$$F(La)_{sum} = Q_{sol}(t)[La]_{sol} + Q_{neg}[La]_{neg} + Q_{mad}(t)[La]_{mad}$$

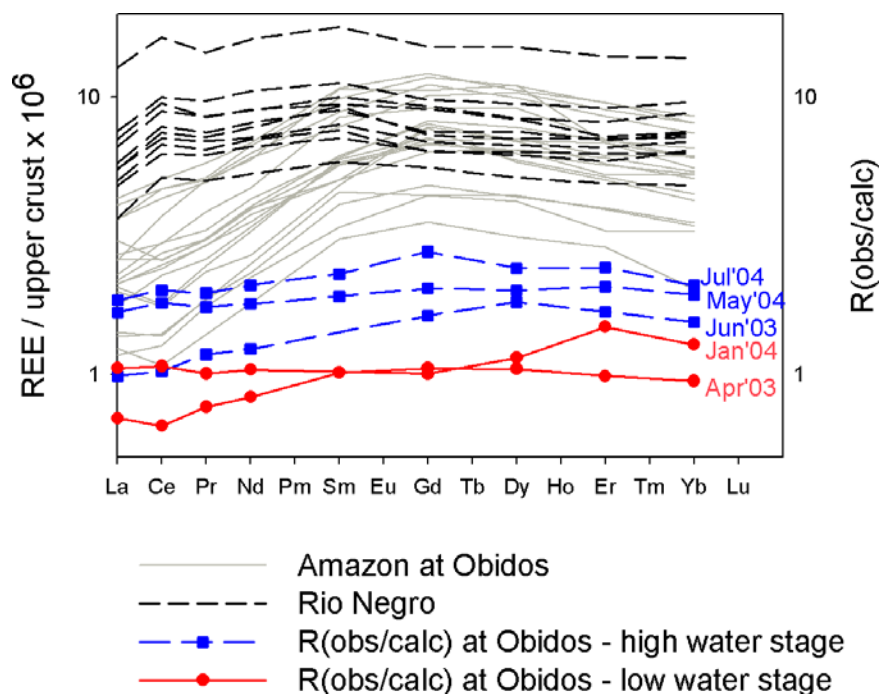
Figures 8a–8c show that for La, Nd and Yb the  $F(REE)_{sum}$  curve reproduces the seasonal features of  $F(REE)_{ob}$ . Only for five individual months do we have data from all stations; these are shown by symbols in Figure 8 and will be discussed hereafter. Overall, the LREE, represented by La (Figure 7a) display a better agreement between the  $F(REE)_{ob}$  and  $F(REE)_{sum}$  than the HREE, represented by Yb (Figure 7c), which are deficient in  $F(HREE)_{sum}$ . All dissolved REE behave conservatively over the period March 2003 to March 2004. However, during the high water stage of 2004 (May–July) the observed  $F(REE)_{ob}$  significantly exceeds the calculated  $F(REE)_{sum}$ . We can define a mismatch factor between observed and calculated fluxes:  $R(obs/calc) = F(REE)_{ob}/F(REE)_{sum}$ . Examining in more detail this mismatch factor, shows similar results for all REE (Figure 9). The REE patterns of  $R(obs/calc)$  during the 2004 high water stage (May 2004 and July 2004) approximate a value of 2 in Figure 9. The  $R(obs/calc)$  pattern directly reflect the patterns of the missing REE source during the high water stage of 2004. Figure 9 includes the UC normalized patterns for the Amazon and Negro Rivers and indicates that the “missing”



**Figure 8.** Mass balance results for (a) La, (b) Nd, and (c) Yb fluxes ( $T.yr^{-1}$ ). Solid curves represent the observed fluxes for the Amazon at Óbidos (black), the Negro (red), the Solimões (blue), and the Madeira (green). The calculated flux at Óbidos is given by the dashed black line. The five months for which all tributaries as well as the Amazon at Óbidos were sampled are indicated by square (observed) and round (calculated) symbols, including their 1 sigma standard deviations. Extrapolated várzea floodplain fluxes between Manaus and Óbidos are shown in yellow.

REE source for the 2004 high water stage is more similar to the Negro (and Branco) shield Rivers than to the Andean MREE enriched patterns. From September 2003 onward, the Negro discharge contribution to the Amazon at Manaus involves a correction for the missing drainage area between

Serinnha and Manaus. However, the REE contribution (i.e., REE concentrations in the missing discharge) remains unaccounted for. The mass balance mismatch for 2004 therefore may be partly related to an ill-constrained Negro (Manaus) time series for 2004. If we assume that the 2004 Negro



**Figure 9.** Mismatch factors,  $R(\text{obs}/\text{calc})$ , between the observed and the calculated dissolved REE fluxes of the Amazon River at Óbidos during the high water (blue lines, square symbols) and low water (red lines, round symbols) stages. The UC normalized Amazon (gray solid lines) and Negro patterns (black dashed lines) are included for reference.

fluxes are similar to those for 2003 for all REE, and then the LREE deficit for 2004 disappears, however the HREE deficit remains. Thus, regardless of an ill-constrained 2004 Negro budget, there appears to be another source of REE, and HREE in particular, which we missed so far in our mass balance.

[22] The detailed study into the Amazon River chemistry by Gaillardet *et al.* [1997] includes REE data obtained during May 1989 for all relevant tributaries. We can therefore apply the same mass balance to their data set. This results in a balanced HREE budget for May 1989 and a slight (25%) excess of  $F(\text{LREE})_{\text{calc}}$ . In summary then, REE budgets are balanced within 30% (significant at 2 sigma level) during the 2004 low water stage, the 1989 and 2003 high water stages, but not during the 2004 high water stage. Several explanations can be considered: (1) our assumption that sampling date mismatch and water transit time can be neglected is flawed, (2) trace metal transport in the Amazon River system is simply not uniform from one year to the next due to differential expression of several REE sinks and sources, (3) samples that are collected and analyzed by different people over long periods of time introduce internal inconsistencies in the data set. Whereas 1 and 3 are

difficult to evaluate, we will discuss several potential REE sources for the missing dissolved REE at Óbidos during the high water stage of 2004. The MREE and HREE enriched nature of the missing source (Figure 9) is similar to suspended sediment REE patterns and to leached REE from SS ‘fractions [Sholkovitz, 1995; Hannigan and Sholkovitz, 2001]. A REE transfer from SS to the dissolved phase could take place at two particular locations: (1) sites of tributary mixing and (2) floodplains.

[23] Between the two main mixing zones, Negro – Solimões and Madeira – Solimões, the first is of most interest as it involves the mixing of low pH (4–5), low SS ( $<10 \text{ mg.L}^{-1}$ ), high DOC ( $7\text{--}10 \text{ mg.L}^{-1}$ ) Negro waters mix with the neutral pH ( $\sim 7$ ), high SS ( $60\text{--}200 \text{ mg.L}^{-1}$ ), low DOC ( $3\text{--}5 \text{ mg.L}^{-1}$ ) Solimões waters. Recent work on the confluence between Negro and Solimões has shown a redistribution of trace metals from the particulate to the dissolved phase [Benedetti *et al.*, 2002; Aucour *et al.*, 2003]. This transfer reflects a re-equilibration among surface complexed and dissolved (including colloidal) trace metals upon mixing. Recent filtration and modeling studies on REE complexation by humic substances show that HREE bind relatively stronger to DOC compo-



nents (e.g., humic substances) than LREE and that average river water REE speciation is dominated by organic complexes [Ingri *et al.*, 2000; Tang and Johannesson, 2003; Johannesson *et al.*, 2004; Sonke and Salters, 2006]. Therefore a potential particulate → DOC transfer of REE at the Negro-Solimões confluence might be more pronounced for HREE than LREE. A similar transfer scenario can be hypothesized to explain the elevated REE concentrations of the Curuaí floodplain lake relative to the Amazon main stem at the end of the high water stage (Figure 4b). Primary productivity related DOC production within floodplain lakes provide the conditions for a particulate → DOC bound REE transfer, with the várzea floodplains acting as a chemical reactor.

[24] Floodplains discharge dynamics have so far been neglected in our calculations. Previous studies [Richey *et al.*, 1989; Dunne *et al.*, 1998] reported that one third of the Amazon River water passes annually through these floodplains and [Bonnet *et al.*, 2004] recently estimate this flooding to 20%. Figures 8a–8c include the estimated La, Nd and Yb fluxes (yellow curves) from the floodplains between Manaus and Óbidos, based on an extrapolation of the Curuaí floodplain observations (Figure 4b) for the period of September 2002 to September 2003. These calculations were made by interpolation of the Sale lake Nd concentrations and the output water discharge calculated by Bonnet *et al.* [2006] from the hydrological model of the floodplain of Curuaí. While imports are negligible, the Curuaí floodplain exports 2 t.yr<sup>-1</sup> Nd between July and October 2002, which is 0.4% of the total Amazon River Nd flux. The Curuaí floodplain flooded area represents at least 13% of the total flooded area (19500 km<sup>2</sup>) between Manaus and Óbidos [Martinez and Le Toan, 2006]. If we extrapolate the Nd flux we calculated for Curuaí to all floodplains situated between Manaus and Óbidos, then a flux of 15,5 t.yr<sup>-1</sup>, representing 3% of the Amazon River flux, is obtained and shown in yellow in Figure 8. Although significant, the monthly floodplain contribution does not close the REE deficit for 2004. It is of interest to note that further extrapolation to the entire Amazon Basin, where floodplains represent 300000 km<sup>2</sup> [Junk, 1982; Sippel *et al.*, 1992; Shimabukuro *et al.*, 2002], generates a total Nd flux of 200 t.yr<sup>-1</sup>, representing 35% of the exported Nd to the ocean, that passes through or originates in the floodplains. Given the sparse floodplain data, as well as the simplifications and extrapolations, more work is needed to evaluate the

REE mass balance status of the Amazon and the role of the floodplains.

## 6. Summary and Conclusions

[25] A two-year times series (March 2003 – March 2005) of dissolved REE in the Amazon basin shows the following main features:

[26] 1. A substantial seasonal variation in dissolved REE concentrations that is correlated with discharge for the Amazon main stem, and its Negro, Solimões, and Madeira River tributaries. This variation repeats itself from 2003 to 2004, and is also reflected in a compilation of literature data that reflects different years and dates of sampling. We suggest therefore that our observations reflect the long-term seasonal variation, and that they relate to transport limited weathering conditions.

[27] 2. A monthly weighted annual Nd flux to the surface Atlantic Ocean of  $607 \pm 43$  T.yr<sup>-1</sup>, which is at least 1.6 times larger than the currently used estimate based on one single measurement during the low water stage. The observation on temperate (Mississippi [Shiller, 2002]), boreal [Ingri *et al.* 2000] and tropical rivers (this study) that REE fluxes display large seasonal variations necessitates similar studies on other dominant REE riverine sources, in order to properly evaluate the dissolved Nd input to the Oceans.

[28] 3. A mass balance of the major tributaries shows quasi-conservative behavior of the LREE and an excess of observed HREE during the 2004 high water stage. Additional observations are necessary to see if this feature is recurrent. Persistence of such a HREE excess would require a source such as suspended matter sorbed REE that transfer to the dissolved phase at tributary confluences or during passage through the Amazon River floodplain lakes. This hypothesis is qualitatively supported by the observation that during the high water and falling water stage the floodplain exit waters display higher REE concentrations than Amazon mainstream.

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