

Distribution and Flux of Trace Metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon and Pará River Estuary and Mixing Plume

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Abstract

The Amazon River has the largest volume on earth, making up 15–20% of the annual fluvial discharge into oceans. The neighboring Pará River mixes with the Amazon River waters in the Amazon Estuary before forming a plume that extends into the Atlantic. Despite the global importance of these rivers, dissolved trace metal fluxes from this estuary remain unknown. Here we present data for dissolved ($<0.2 \mu\text{m}$) trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon Estuary during the high discharge season (April–May 2018). We observed distinct trace metal signatures for the Amazon and Pará Rivers, reflecting different catchment areas. Concentrations of the particle-reactive elements (Mn, Fe and Pb) decreased rapidly at low-salinity ($S[?]$ 2), resulting in the highest estuarine removal (86–94% in the Amazon; 61–70% for the Para). Co, Ni and Cu removal was comparatively low in both river transects (6–39%), while Cd was the only element with a consistent net input. Chemical fluxes were estimated using (a) endmember concentrations and estuarine removal and (b) combining trace element concentrations with ^{228}Ra fluxes. Relative to global total river fluxes, the Amazon and Para Rivers combined contribute 21% of dissolved Cu and 18% of dissolved Ni during the high discharge season, but account for comparatively low fractions of Mn, Fe, Co and Zn. These data quantify, for the first time, the trace metal output from the world's largest and 5th largest river into the Atlantic Ocean, filling a critical gap in knowledge of this globally-important region.

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Title: Distribution and Flux of Trace Metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon and Pará River Estuary and Mixing Plume

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Key point

We determined, for the first time, dissolved fluxes of 10 major trace metals from the Amazon and Pará Rivers into the Atlantic Ocean.

Fluxes agreed well using methods by (a) simple endmember – removal calculations and (b) ²²⁸Ra isotopes.

The Amazon-Pará estuary contributes 18% and 21% of the global river supply of dissolved Ni and Cu to the oceans, respectively.

Abstract

The Amazon River has the largest volume on earth, making up 15–20% of the annual fluvial discharge into oceans. The neighboring Pará River mixes with the Amazon River waters in the Amazon Estuary before forming a plume that extends into the Atlantic. Despite the global importance of these rivers, dissolved trace metal fluxes from this estuary remain unknown. Here we present data for dissolved (<0.2 µm) trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon Estuary during the high discharge season (April–May 2018). We observed distinct trace metal signatures for the Amazon and Pará Rivers, reflecting different catchment areas. Concentrations of the particle-reactive elements (Mn, Fe and Pb) decreased rapidly at low-salinity (S 2), resulting in the highest estuarine removal (86–94% in the Amazon; 61–70% for the Pará). Co, Ni and Cu removal was comparatively low in both river transects (6–39%), while Cd was the only element with a consistent net input. Chemical fluxes were estimated using (a) endmember concentrations and estuarine removal and (b) combining trace element concentrations with ²²⁸Ra fluxes. Relative to global total river fluxes, the Amazon and Pará Rivers combined contribute 21% of dissolved Cu and 18% of dissolved Ni during the high discharge season, but account for comparatively low fractions of Mn, Fe, Co and Zn. These data quantify, for the first time, the trace metal output from the world's largest and

5th largest river into the Atlantic Ocean, filling a critical gap in knowledge of this globally-important region.

1. Introduction

The Amazon estuary, fed by the Amazon River as well as the Pará River to the south, is a major source of trace metals and organic matter to the Atlantic Ocean (**Fig. 1**). The Amazon River is the largest on Earth and accounts for 15–20% of riverine freshwater input (Meybeck 1982; Richey et al. 1986; Smoak et al. 2006; Espinoza-Villar et al. 2009). The catchment area extends through the Amazon Rainforest and experiences distinct wet and dry seasons (yearly flow range: 100,200–240,000 m³ s⁻¹ at station Óbidos; Richey et al. 1986; Espinoza-Villar et al. 2009). On the other hand, the Pará River (flow: 9,000–38,000 m³ s⁻¹; Prestes et al. 2020) is the earth’s 5th largest river (Prestes et al. 2020) and is fed by a combination of the Amazon River, Tocantins River and other minor tributaries. The Tocantins River (mean flow: 11,000 m³ s⁻¹; Costa et al. 2003) reflects a comparatively dryer catchment area with heavier anthropogenic influence. The Amazon estuary is further influenced by a large mangrove forest to the southeast, which provides an additional source of DOM (Dittmar and Lara 2001) and some trace metals (de Carvalho et al. 2021; Hollister et al. 2021) through groundwater exchange. The water masses from the Amazon and Pará rivers and mangrove belt mix in the estuary and form an aging river plume that travels to the northeast during the high discharge study period. Offshore, the estuary is bordered by the North Brazil Current (NBC), which we defined as the seawater endmember.

Here we present concentration distributions and fluxes for the biologically-relevant trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) as well as the conservative element U in the Amazon and Pará estuary, mangrove belt and mixing plume during the high discharge season. Trace metals act as both essential nutrients and, in high concentrations, toxins. The metals Mn, Fe, Co, Ni, Cu and Zn are utilized in a variety of enzymes (see e.g. Sunda 2012). Large regions of the open ocean (~ 40%) are growth-limited by an absence of trace metals, including Fe-limited high-nutrient-low-chlorophyll (HNLC) regions (Moore et al. 2001). Phytoplankton growth may also be limited or co-limited by insufficient Mn (Browning et al. 2021; Peers and Price 2004), Co (Saito et al. 2005; Browning et al. 2017; Browning et al. 2018) or Zn (Morel et al. 1991; Saito and Goepfert 2008). On the other hand, Pb is primarily an anthropogenic contaminant (Wu and Boyle 1997; Boyle et al. 2014). In addition, increased levels of Co, Ni, Cu, Zn and other metals can occur in rivers and estuaries as a result of anthropogenic pollution, including e.g. antifouling paints on ships, agricultural runoff, industrial waste and pharmaceutical products that accumulate in urban wastewater (McComb et al. 2014; Samanta and Dalai 2018; Pérez-Cid et al. 2021). The Amazon and Pará catchment area have been subject to increasing anthropogenic impacts (Coe et al. 2009; Davidson et al. 2012; Castello et al. 2013); however, little is known about the effect that this has on trace metals in the estuary. For example, forest fires and gold mining

in the region have been found to increase levels of Mn, Cu and Zn pollution in the atmosphere and soils (Rodrigues Filho and Maddock 1997; Yamasoe et al. 2000; Lacerda et al. 2004; Cesar et al. 2011). Therefore, it is crucial to establish trace metal levels in the Amazon and Pará estuary in order to monitor anthropogenic impacts.

Trace metal behavior in estuaries is governed by a variety of factors including physical mixing and dilution, porewater exchange, colloidal flocculation, particle adsorption/desorption, biological activity and organic matter interactions. The particle-reactive elements Fe and Pb often show high removal in estuaries, while Ni, Cu, Zn and Cd are often largely retained in the dissolved phase (e.g., Chiffoleau et al. 1994; Tang et al. 2002). Fe is heavily influenced by colloidal flocculation and subsequent removal at increasing salinity due to interaction with seawater cations (Boyle and Edmond 1977; Sholkovitz 1978; Kraepiel et al. 1997; Tang et al. 2002; Joung and Shiller 2016). Al is also particle reactive and often shows an initial sharp decrease at low salinity estuarine mixing (Zhang et al. 1999; Takayanagi and Gobeil 2000; Xu et al. 2002) sometimes followed by mobilization at higher salinity (Mackin and Aller 1986; Morris et al 1986; Upadhyay and Gupta 1995). Al is commonly incorporated into (authigenic) aluminosilicate clays, and dissolved Al in estuaries may be lost/gained from incorporation into or resuspension from sediments (Mackin and Aller 1984a,b; Mackin and Aller 1986; Xu et al. 2002; Wang et al 2015; Simonsen et al. 2019).

Mn and Fe are also heavily influenced by microbial oxidation to form ox(yhydrox)ides in estuaries (Joung and Shiller 2016; Mori et al. 2019; Pérez-Cid et al. 2021). Co (and more weakly Ni) can also be incorporated with Mn ox(yhydrox)ides and is often correlated with Mn (Zwolsman and Van Eck 1999; Takata et al. 2010; Teuchies et al. 2013; Joung and Shiller 2016). These Mn or Fe ox(yhydrox)ides can in turn enhance the removal of other particle-reactive metals such as Pb (Jiann and Wen 2009). Increased salinity may also cause particle reactivity to decrease, enhancing trace metal mobilization in some metals. For example, Cd can be mobilized from particulate matter due to reaction with Cl^- ions of seawater (Comans and van Dijk 1988). As a result, a mid-estuarine dissolved Cd maximum is commonly observed in estuaries (Elbaz-Poulichet et al. 1987; Boutier et al. 1993; Zwolsman et al. 1997; Chiffoleau et al. 1999), although this phenomenon has also been observed for Co, Ni, Cu and Zn (Zwolsman et al. 1997; Chiffoleau et al. 1999; Takata et al. 2010; Samanta and Dalai 2018). Unlike the other metals studied, U in estuaries is generally conservative and correlates positively with increasing salinity (Palmer and Edmond 1993; Windom et al. 2000; Joung and Shiller 2016), although some non-conservative removal at low salinity has also been observed in the Amazon estuary due to adsorption to Mn or Fe ox(yhydrox)ides (McKee et al. 1987; Swarzenski and McKee 1998).

Trace metal fluxes in a river cross-section (Flux_M) may be calculated by integrating trace metal concentration (M) and water velocity (V) over time (t) and depth (z), expressed as follows (Prego et al. 2010).

$$(1) \text{ Flux}_M = \int_{t,z} V_{(t,z)} M_{(t,z)} (dt)(dz)$$

In the results presented, we simplify the riverine flux calculation by ignoring the depth dimension and using the rainy season river discharge and dissolved concentrations of trace metals in the Amazon and Pará River endmembers. Estuarine removal of trace metals, e.g. by partitioning to the particulate phase and subsequent sedimentation, can be calculated by interpolating concentrations between the endmembers and then finding the deviation from the expected river-seawater mixing line (Scholkovitz 1993; Skrabal 1995; Kipp et al. 2020; Vieira et al. 2020; Zhang et al. 2020). The estuarine flux may therefore be represented as:

$$(2) \text{ Flux}_M = V * M_{\text{river}} - M_{\text{removal}}$$

where V is the river volume flux at the time of sample collection, M_{river} is the dissolved concentration in the riverine endmember and M_{removal} is the dissolved trace metal removed from the estuary.

Alternatively, Ra isotopes can be used to quantify fluxes of chemical species at the continent-ocean interface. Charette et al (2016) thus proposed a method based on the use of radium-228 (half-life of 5.75 years) as a shelf flux gauge to quantify shelf-ocean flux of chemical elements. This method has been successfully used in various places of the world to estimate shelf-ocean fluxes of dissolved trace metals. This includes the Western North Atlantic Ocean margin (Charette et al. 2016), the Congo River estuary (Vieira et al. 2020), Bering Strait (Vieira et al. 2019), the Peruvian Shelf (Sanial et al. 2018), and Argentine and Cape shelves (Hsieh et al., 2020).

Despite its global importance, trace metal data from the Amazon and Pará estuary is limited (Boyle et al. 1982; Mackin and Aller 1986; de Carvalho et al. 2021; Hollister et al. 2021), and no data exist for fluxes of dissolved transition metal in this region. Herein, we fill this gap using a dual approach to calculate dissolved trace metal fluxes using endmember concentrations and (a) removal from the conservative mixing line and (b) ^{228}Ra isotope distribution. In April-May 2018, a GEOTRACES process cruise (GAPr11) was conducted in the Amazon and Pará outflow regions, mangrove belt, mixing plume and NBC. Trace metal samples were collected in the dissolved ($<0.2 \mu\text{m}$) fraction and analyzed in home laboratories using preconcentration (seaFAST) followed by inductively coupled plasma-mass spectrometry (ICP-MS). Fluxes and estuarine removal were calculated using extrapolation based on riverine and seawater endmembers.

2. Methods

2.1 Sampling

A GEOTRACES process study (GApr11) was conducted aboard the RV Meteor in April–May 2018 (cruise M147) during a period of high river discharge. Surface samples (2–3 m depth) were collected using a towed-fish and pumped into a trace metal clean shipboard laboratory as described elsewhere (de Carvahlo et al. 2021; Hollister et al. 2021). Samples were taken from the full salinity gradient ($S = 0.3$ to 35) (**Fig. 1**), encompassing the Amazon and Pará River outflow regions (labeled the Amazon and Pará Transects), a mangrove belt to the southeast (“Mangrove Belt”), a mixing plume that aged as it flowed northward (“Plume North”) and the North Brazil Current seawater endmember (“NBC”). Briefly, samples were filtered shipboard to the dissolved fraction (<0.2 μm) using $0.8/0.2$ μm cartridge filters (AcroPak1000TM). Filtered samples were stored in acid-cleaned low-density polyethylene (LDPE) bottles and immediately acidified to pH 1.8 using ultrapure HCl (UPA, Romil). All sample handling was conducted using trace metal clean protocol (see GEOTRACES cookbook: <https://www.geotraces.org/methods-cookbook/>). For ^{228}Ra (Ra in the following) measurements, surface (~ 2 – 3 m water depth) seawater samples (16–236 L) were collected by WASP-5 underwater pumps into barrels. Seawater was first passed through a $1\mu\text{m}$ cartridge filter and then through MnO_2 coated-fibers at a flow rate $< 1\text{L min}^{-1}$ to quantitatively adsorb Ra. The Mn-fibers were then rinsed with Ra-free water.

2.2 Analytical methods

Trace metals were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) following seaFAST preconcentration as described elsewhere (Rapp et al. 2017; Hollister et al. 2021; de Carvalho et al. 2021). Briefly, the acidified samples were UV-irradiated for 4 h in order to break down organic matter that can interfere with the recovery of Co and Cu (Biller and Bruland 2012). Samples were then preconcentrated using an automated Elemental Scientific Inc. (ESI) seaFAST system (seaFAST-picoTM) as follows. Sample water was mixed with an ammonium acetate buffer (pH 8.5 ± 0.05) to reach a pH of 6.2 ± 0.05 and then loaded onto a chelating column (Wako or Nobias). The column was rinsed with ultrapure water (Milli-Q®; $18.2\text{ M}\Omega\text{ cm}$). Trace metals were eluted at a preconcentration factor of 20 in 1 mol L^{-1} nitric acid (UpA, Romil) with an In internal standard at 1 ppb. Manifold blanks were collected by drawing air instead of sample through the autosampler. A mixed metal standard addition curve was run at the start and end of seaFAST curve and between every 10 samples. Each seaFAST run was also accompanied by the certified reference materials (CRMs) CASS-6 and NASS-7 (National Research Council Canada; NRC-CNRC).

Preconcentrated samples were then analyzed on ICP-MS for counts of ^{55}Mn , ^{56}Fe , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{62}Ni , ^{63}Cu , ^{65}Cu , ^{66}Zn , ^{68}Zn , ^{110}Cd , ^{111}Cd , ^{115}In , ^{207}Pb and ^{208}Pb . Concentrations of Fe, Ni, Cu and Cd were determined using isotope spikes, while Mn, Co, Zn and Pb were determined by standard addition. In all cases, trace metal counts were normalized to ^{115}In and manifold blanks were subtracted prior to calculating concentrations. Accuracy was determined

using CASS-6 and NASS-7 CRMs, and error was determined using the Nordtest method (**Table 1**). Limit of detection (LOD) was determined to be three times the standard deviation of the manifold blank (**Table 1**). For Co, Ni and Cu, we have used previously published data from the same research cruise and study area (Hollister et al. 2021, de Carvahlo et al. 2021). Uranium was analyzed by direct measurement of diluted samples by ICP-MS (Perkin Elmer NexIONTM 350X). The ICP-MS instrument was connected to APEXQ desolvating nebulizer (Elemental Scientific Inc.) to increase the sensitivity of the measurement. Three U calibration standards (0.05, 0.50 and 1.0 $\mu\text{g L}^{-1}$) were prepared using diluted 0.60 mol L⁻¹ sodium chloride (NaCl, supra pure Merck) in 0.5 mol L⁻¹ HNO₃ (Supra pure Roth). The acid blank in salt matrix (diluted 0.60 mol L⁻¹ NaCl in 0.5 mol L⁻¹ HNO₃) and certified reference material (CRM, e.g., NASS-7 and SLEW-3 or NASS-7 and SLRS-6) were analyzed for every batch of 4 samples. Data quality was assessed by comparing the results with the calculated method limit of quantitation (MLOQ, 0.22 nmol L⁻¹) for each run and the recovery (%) of the CRMs (**Table 1**).

Aluminum was analyzed by fluorescence after derivatization with lumogallion (Hydes and Liss, 1976). Beryllium and *o*-phenanthroline were used to eliminate interferences from fluoride and Fe respectively, whilst Triton X-100 was used to enhance and stabilize the fluorescence signal (Ren et al. 2001). The fluorometer settings were adjusted to give a linear range up to 2 $\mu\text{mol L}^{-1}$ Al. We determined Al concentrations of $1.09 \pm 0.04 \mu\text{mol L}^{-1}$ (n=5) in a riverine certified reference material (SLRS-6, National Research Council, Canada; certified value = $1.25 \pm 0.08 \mu\text{mol L}^{-1}$) (**Table 1**).

For Ra analysis, the Mn-fibers were dried and placed into counting boxes (75 mm diameter and 15 mm height). The Ra analyses were performed at the LAFARA underground laboratory in the French Pyrénées, located under 85 m of rock that protect the detectors from cosmic radiations, thus providing a very low background to the facility (van Beek et al., 2013). We used a low-background, semi-planar germanium detector to quantify ²²⁸Ra activities using the 338 keV, 911 keV and 969 keV peaks of ²²⁸Ac (van Beek et al., 2010).

2.3 Determination of chemical fluxes

Method 1:

For trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U), the estuary removal fraction was calculated as:

$$(3) \text{ removal fraction} = \left(M_{\text{sample}} - S_{\text{sample}} * \frac{(M_{\text{river}} - M_{\text{sw}})}{(S_{\text{river}} - S_{\text{sw}})} + M_{\text{river}} \right) / M_{\text{sample}}$$

where M_{sample} and S_{sample} are the measured trace metal concentration and salinity in a given sample, M_{river} and S_{river} represent the trace metal concentration and salinity for the riverine endmember and M_{sw} and S_{sw} represent the trace

metal and salinity for the NBC seawater endmember. Flux was then calculated by subtracting removal from total riverine flux as:

$$(4) \text{ Flux}_M = V_{\text{river}} * (M_{\text{river}} - M_{\text{river}} * \text{removal fraction}_{\text{avg}})$$

where Flux_M is the net dissolved trace metal flux from the estuary, $\text{removal fraction}_{\text{avg}}$ is the average removal calculated from the samples in the Amazon or Pará transects using equation (3) and V_{river} is the Amazon or Pará river volume flux at high discharge.

Method 2:

Alternatively, Ra isotopes can be used to quantify fluxes of chemical species at the continent-ocean interface.

First, we calculated the flux of ^{228}Ra ($F_{228\text{Ra}}$) that was determined as follows (equation 5):

$$(5) F_{228\text{Ra}} = I_{228\text{Ra}} / \tau$$

where $I_{228\text{Ra}}$ is the ^{228}Ra inventory in the Amazon plume on the Brazilian continental shelf and τ is the residence time of the Amazon waters on the shelf.

The Ra inventory was determined by interpolating the data using QGIS software and considering a uniform ^{228}Ra distribution within the river plume thickness at each station. The plume thickness was estimated according to the vertical profiles of salinity on the shelf and ranged between 5 and 25 m. The strong density stratification over the continental shelf (Léon et al. 2022) likely limits the input of Ra from bottom sediments within the river plume. The Flux of ^{228}Ra was estimated using a residence time over the Brazilian continental shelf ranging from 12 to 21 days (Léon et al., 2022), providing upper and lower ends for the ^{228}Ra flux estimates.

To convert the ^{228}Ra flux into a trace metal flux, we then used equation (6) as follows, following Charette et al. (2016):

$$(6) \text{ Flux}_M = \text{Flux}_{228\text{Ra}} \frac{(M_{\text{shelf}} - M_{\text{ocean}})}{(^{228}\text{Ra}_{\text{shelf}} - ^{228}\text{Ra}_{\text{ocean}})}$$

where M_{shelf} and $^{228}\text{Ra}_{\text{shelf}}$ are the average concentrations of the trace metal of interest and ^{228}Ra over the shelf; M_{ocean} and $^{228}\text{Ra}_{\text{ocean}}$ are the average dissolved trace metal and ^{228}Ra concentrations in the open ocean, outside the shelf.

3. Results and Discussion

3.1 Different source signatures of the Amazon, Pará River and mangrove transects

The Pará River endmember ($S = 0.36$) was higher than the Amazon River endmember ($S = 0.31$) in dissolved Al, Ni, Co, Zn, Pb and U (**Table 2**). Al concentration was an order-of-magnitude higher in the Pará endmember compared to the Amazon endmember, likely reflecting a catchment area with higher aluminosilicate weathering. Dissolved U concentration was also roughly twice as high in concentration in the Pará in than in the Amazon, possibly reflecting the more highly contaminated catchment area of the Pará, although U concentrations both river endmembers were lower than global river averages (1.3 nmol kg^{-1} ; Palmer and Edmond 1993).

On the other hand, the Amazon River endmember was higher than the Pará River endmember for dissolved Cu, Fe and Mn. For all metals, the separate riverine signatures of the Amazon and Pará transects were not distinguishable at salinities ≥ 15 , indicating thorough estuarine mixing. The endmember differences likely reflect the different catchment areas of the Amazon and Pará River. The Pará River takes approximately 5% of the Amazon River volume by the Breves Straight, and thus contributes to 34–72% of the Pará River volume (Prestes et al. 2020). The remainder of the Pará water volume stems from the Tocantins River to the south, which reflects a drier catchment area with higher anthropogenic influence. The contribution of the more contaminated Tocantins may therefore account for the higher Pará endmember concentrations for Zn, Ni, Co and Pb which are known anthropogenic contaminants (Wu and Boyle 1997; Poulton and Raiswell 2000; Boyle et al. 2014; Samanta and Dalai 2018; Pérez-Cid et al. 2021).

Trace metal speciation during early estuarine mixing of the Amazon and Pará transects may be influenced by differences in dissolved organic matter content (through enhanced solubilization and/or colloidal flocculation) and overall particle load (through particle adsorption/desorption). In the Amazon transect, dissolved ($<0.2 \mu\text{m}$) Fe, Pb and Mn were highest in the riverine endmember and rapidly declined with increasing salinity (**Fig. 2**). This observation was in agreement with previously-reported estuarine behavior of Pb (Chiffoleau et al. 1999; Jiann and Wen 2009; Li et al. 2018; Kipp et al. 2020) and Fe (Joung and Shiller 2016; Priya and Haddout 2020; Vieira et al. 2020; Zhang et al. 2020). The decrease may be due to flocculation of riverine colloids upon mixing with seawater (Boyle and Edmond 1977; Kraepiel et al. 1997; Bergquist and Boyle 2006; Zhang et al. 2020).

In the Pará Transect on the other hand, elevated dissolved concentrations of Al, Mn, Fe, Co, Ni, Zn and Pb were observed at low to mid salinity ($S \sim 7\text{--}10$). The elevated trace metal concentrations may reflect possible mixing of benthic porewaters due to resuspension and desorption from sediments (Zwolsman and Van Eck 1999; Takata et al. 2010; Joung and Shiller 2016; Mori et al. 2019). Moreover, Mn and Fe are both redox sensitive and highly subject to ox(yhydrox)ides formation (Aucour et al. 2003; Teuchies et al. 2013; Priya and Haddout 2020; Pérez-Cid et al. 2021). The decrease in dissolved trace metals following the mid-salinity peak ($S \sim 10$) likely reflects colloidal flocculation (Sholkovitz 1978;

Tang et al. 2002) or Mn or Fe ox(yhydrox)ide formation (Teuchies et al. 2013) and subsequent scavenging of other particle-reactive metals. Co and Pb were both tightly correlated with Mn in the Pará transect ($R = 0.99$, $p < 0.0001$, **Fig. 3, Supplemental Table S1**). Co is often correlated with Mn due to incorporation into Mn ox(yhydrox)ides and mobilization from sediments (Takata et al. 2010; Joung and Shiller 2016). Mn (and Fe) ox(yhydrox)ides can also enhance Pb removal (Jiann and Wen 2009). Moreover, a major fraction of Ni in the Amazon River is incorporated into Mn-Fe ox(yhydrox)ides (Revels et al. 2021), which is reflected in the correlation of Ni and Fe with Mn in both transects (**Fig. 3, Supplemental Table S1**). On the other hand, Al did not correlate significantly with Mn in either transect ($p > 0.05$). The behavior of dissolved Al may instead be influenced by authigenic aluminosilicate formation, in addition particle adsorption and colloidal flocculation (Mackin and Aller 1984b; Takayanagi and Gobeil 2000; Simonsen et al. 2019). Although an Al-Si plot did not show significant correlation in either the Amazon or Pará Transect ($p > 0.05$; **Supplemental Fig. S1**), the overabundance of Si relative to Al may mask this effect.

Cd displayed a dissolved concentration maximum in the mid-salinity range ($S \sim 7-14$) in both transects (**Fig. 2**), a well-documented phenomenon in estuaries (Chiffoleau et al. 1999; Tang et al. 2002; Teuchies et al. 2013; Priya and Haddout 2020). As salinity increases, Cd^{2+} forms complexes with Cl^- , resulting in mobilization of Cd from particles (Comans and van Dijk 1988). Dissolved Cd had a similar mid-salinity maximum as dissolved phosphate in the same study area (Hollister et al. 2021). The Amazon and Pará River concentrations of Cd were in error of each for the endmembers and at low salinity ($S \sim 5$), but the mid-salinity Cd peak ($S = 7-14$) was much higher in the Amazon transect, indicating a higher degree of desorption from Amazon derived sediments. This could reflect a higher particle load of Cd from the Amazon, although future investigations measuring the particulate phase ($>0.2 \mu m$) are needed to verify this.

Mangroves are also a source of trace metals (Thanh-Nho et al. 2018; Mori et al. 2019; Matos et al. 2022) and DOC (Dittmar and Lara 2001; Dittmar et al. 2006), attributed to groundwater exchange and desorption from sediments. Moreover, published data from this same cruise showed an increase in DOC and Cu-associated organic matter in the Mangrove belt transect (Hollister et al. 2021). Here we observed elevated concentrations of dissolved Al, Ni, Co, Fe, Zn and Pb in the mangrove belt relative to other transects at the same salinities (**Fig. 2**). A recent study showed evidence of anthropogenic Cu and Zn in sediments of another tropical mangrove estuary in northeast Brazil (Miola et al. 2016). Although the source of these metals (natural vs. anthropogenic) cannot be discerned using our methods, future studies of sediments, as well as isotopic analysis, may elucidate this further.

3.2 Trace metal removal in the Amazon and Pará transects

Trace metals that enter the estuary from the Amazon and Pará rivers may

experience removal due to partitioning to the particulate phase (e.g. through particle adsorption, formation of ox(yhydrox)ides or colloidal flocculation). In addition, estuaries may experience additional input through particle desorption, aeolian input or fluxes from sediment porewaters. Thus, to calculate the trace metal flux from the Amazon and Pará estuary into the Atlantic Ocean, it is necessary to account for both riverine input, as well as additional sources and sinks of trace metals throughout the estuary.

Although the methods of this paper do not allow us to fully define all sources and sinks of dissolved trace metals in the study area, we can approximate the net estuarine input and removal of trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) by measuring deviation from the expected conservative mixing line. We calculated the slopes of the two-endmember mixing line (in mol L⁻¹ per unit salinity) by using the lowest salinity Amazon ($S = 0.31$) and Pará ($S = 0.36$) stations for the riverine endmember and the average concentrations of the NBC stations ($S = 35.9$) for the seawater endmember. Deviation from the expected mixing line was then calculated for each station along the Amazon and Pará transects by subtracting the measured trace metal concentration from the concentration predicted based on the conservative-mixing slope as described in equation (3) (Table 2).

The average removal percentages presented in Table 2 contain a combined loss and remobilization effect along the salinity gradient. Negative values correspond to net input (e.g., due to desorption from particles in the case of Cd). The net dissolved metal flux could then be calculated by subtracting the estuarine removal from the riverine flux (see equation 2). Error was based on the analytical error reported in Table 1.

In the Amazon transect, the greatest removal was seen for Fe (94%), Mn (92%) and Pb (86%). This is in agreement with their observed behavior in other estuaries (Boyle et al. 1977; Church et al. 1986; Figüeres et al. 1978; Jiann and Wen 2009; Zhang et al. 2020). For most metals, there was lower removal from the Pará transect than the Amazon, with only 70% removal for Fe, 61% for Mn and 69% for Pb. An exception was Al, which had 64% removal in the Pará transect but only 7% removal in the Amazon transect. The higher removal of Fe and Mn in the Amazon and Al in the Pará is likely at least partly related to the endmember concentrations, as higher endmember concentration may result in high early-estuary removal due to particle adsorption, ox(yhydrox)ide formation and/or colloidal flocculation. The lower overall Pará removal for Fe, Mn and Pb may be due to the additional input observed at mid-salinities ($S \sim 7-10$). The apparently low Al removal, especially in the Amazon transect, may have been partly due to missing the “true” endmember ($S = 0$) during sample collection. As Al is one of the hardest metals, it can be expected to experience the greatest removal low salinity (Gledhill et al. 2022), possibly resulting in some of this removal being missed in our calculations. While the imperfect endmembers may have resulted in some error in removal calculations for hard metals such as Al, Fe and Mn, it is unlikely that this had a large effect on overall flux calculations,

since both the percent removal and the endmember would be higher (equation 4).

Cd was the only element to consistently show a net input in the dissolved fraction (69% in the Amazon and 13% in Pará River). In both transects, Cd experienced net input likely due to desorption from particles upon seawater mixing. Cd removal in estuaries is rather variable (10–90%; Millward and Glegg 1997; Church et al. 1986), and negative Cd removal values have also been reported (Jiann and Wen 2009). Our findings indicate a mid-estuary desorption ($S \sim 7$ –14) from river-derived particles, which is commonly observed for Cd in estuaries (Elbaz-Poulichet et al. 1987; Chiffoleau et al. 1994; Zwolsman et al. 1997; Chiffoleau et al. 1999). The higher removal of particle-reactive elements in the Amazon transect compared to the Pará (except Al), as well as the higher input of Cd, possibly reflect a particle load from the Amazon River (Lima et al. 2005).

We also observed differences in Zn input and removal between the Amazon and Pará transects. The high removal of Zn in the Pará transect (79%) is in good agreement with some studies (82–94%; Millward and Glegg 1997; Church et al. 1986), while the net input of Zn in the Amazon is in agreement with others (Jiann and Wen 2009). An increase at $S \sim 5$ –7 (**Fig. 2**) may reflect particle desorption upon reaction with Cl (Zwolsman et al. 1997), similar to the behavior previously described for Cd.

Cu, Ni and Co all showed comparatively low loss in both transects (6–39%). Cu, which was largely conservative, had a lower removal (6% in Pará and 34% in Amazon) than that reported in other estuaries of the rivers Humber (72–88%; Millward and Glegg 1977), Delaware (84%; Church et al. 1986) or Danshuei (53–100%; Jiann and Wen 2009). On the other hand, Ni removal in estuaries is highly variable and may even be negative (net addition) in some river systems (Jiann and Wen 2009). The low overall removal of Cu may be attributed its low particle affinity, or to the excess of Cu-binding ligands which keep Cu in solution (Hollister et al. 2021). Nevertheless, some non-conservative removal was detected at low ($S \sim 6$) salinity and attributed to colloidal flocculation (Sholkovitz 1978; Zwolsman et al. 1997; Hollister et al. 2021). Metal binding with sulfide compounds may also play a role in removal of Cd and Cu (Jiann and Wen 2009), although no sulfide data are available from this cruise.

Other metals also showed some degree of remobilization at increasing salinity (**Fig. 2**). After the rapid decline in dissolved Pb at low salinity, concentrations increased in all transects from mid salinity ($S \sim 10$) to the NBC endmember. Cd also showed a secondary increase at high salinity from $S \sim 21$ –33. In addition, Al, Ni, Co, Zn, Mn, Pb were all elevated in the mangrove belt ($S \sim 28$ –35). Mangroves contribute trace metals and organic matter through porewater exchange with the surrounding estuarine water (Dittmar and Lara 2001; Dittmar et al. 2006; Thanh-Nho et al. 2018; Mori et al. 2019). The increase in this region may therefore reflect a combination trace metal contribution from mangrove derived sediments, as well as remobilization from riverine particles upon estuarine mixing (Takata et al. 2010; Samanta and Dalai 2018).

Unlike the other metals in this study, U concentrations increased with increasing salinity, reflecting its known estuarine behavior in the Amazon and elsewhere (McKee et al. 1987; Palmer and Edmond 1993; Swarzenski and McKee 1998; Windom et al. 2000; Joung and Shiller 2016). U generally displays conservative estuarine behavior, although it has been shown to experience removal at low salinity in estuaries including the Amazon due to adsorption to Fe and Mn ox(hydrox)ides (McKee et al. 1987; Swarzenski and McKee 1998). Indeed, we observed deviation below the conservative mixing line at low salinity (S 2), corresponding with the rapid decrease in Fe and Mn, and consistent with the previous Amazon studies. Overall, U had a net removal of 22% in the Pará transect but a net input in the Amazon transect. The apparent Amazon input can be partly attributed to three higher-than-expected samples at S ~4–9 however, and therefore may not reflect overall estuarine processes.

In some cases (e.g. Mn and Fe), the Amazon endmember is only represented by a single high datapoint, which heavily influences the overall removal calculation. Having a single endmember datapoint may not fully capture processes occurring at low salinity. To help address this, the Amazon endmember concentrations were compared to time series data from Station Óbidos (SO-HyBam: <http://www.ore-hybam.org>). When the time series (1994 to 2019) was averaged over the same time of year, the concentrations at Station Óbidos were higher than in our measured endmembers for all the metals reported here, although our data are still within range (**Table 2**). Our lower concentration values indicate that some removal processes occurred in the river or early estuary (S 0.3). For Al, Fe, Co and Zn, average concentrations in station Óbidos were at least an order of magnitude higher than measured in our Amazon endmember. Only Cu, a mostly conservative element was comparable in concentration between station Óbidos ($37.8 \pm 13.3 \text{ nmol L}^{-1}$) and the Amazon endmember ($35.3 \pm 4.0 \text{ nmol L}^{-1}$). Thus, the true endmember concentrations, and therefore, estuarine removal of these elements may be higher than estimated based on our lowest salinity station, particularly for Al. It should be noted however, concentrations for most elements at Station Óbidos are highly variable as a result of yearly fluctuation.

3.3 Trace metal flux estimates using two methods

Dissolved fluxes of trace metals are highly dependent on estuarine input and removal, with higher removals resulting in lower overall fluxes. To calculate the total flux, we first calculated the dissolved trace metal flux at each of the river mouths before entering the estuary using the trace metal endmember concentrations and volume from the high discharge period ($240,000 \text{ m}^3 \text{ s}^{-1}$ for the Amazon (Espinoza-Villar et al. 2009) and $38,000 \text{ m}^3 \text{ s}^{-1}$ for the Pará (Prestes et al. 2020)). We then subtracted average estuarine removal to estimate the total dissolved metal flux from the estuary into the Atlantic Ocean as described in equation (4) (**Table 2**).

As a second method of calculating fluxes, we used ^{228}Ra data. The ^{228}Ra distribution in the river plume on the Brazilian continental shelf is shown on **Fig.**

4. Close to the Amazon mouth, at salinity <1 , the ^{228}Ra activities are below $10.2 \text{ dpm.100L}^{-1}$. Activities then increase along the salinity gradient, reaching a maximum value of $80.3 \text{ dpm.100L}^{-1}$ at a salinity of 9.6. When freshwater mixes with saltwater, radium isotopes desorb because of ion exchange competition with the major cations present in seawater and are thus released into the dissolved phase (see e.g. Moore and Krest, 2004). ^{228}Ra then decreases with increasing distance from the mouth due to radioactive decay and mixing with seawater. As a comparison, the ^{228}Ra activities in the open ocean outside the shelf are $\sim 2.3 \pm 0.8 \text{ dpm.100L}^{-1}$ (**Table 3**).

We calculated a ^{228}Ra inventory for the Amazon plume on the shelf ($I_{^{228}\text{Ra}}$) of $1.82 \times 10^{14} \text{ dpm}$, or 7.9×10^{20} atoms, using equation (5) (**Table 3**). Hence, the ^{228}Ra flux estimated is $6.6 \times 10^{19} \pm 1.7 \times 10^{19} \text{ atoms d}^{-1}$ and $3.8 \times 10^{19} \pm 1.1 \times 10^{19} \text{ atoms d}^{-1}$ for 12 and 21 days residence time, respectively. The uncertainty associated with these two ^{228}Ra fluxes is ca. 25 % considering errors associated with the shelf inventory and the residence time. The range of ^{228}Ra fluxes estimated here are in good agreement with the one reported by Moore et al (1995) on the Amazon shelf during the high discharge season of the Amazon River (15×10^{14} atoms for 3 months, equivalent to $16.5 \times 10^{12} \text{ atoms d}^{-1}$). We then combined the ^{228}Ra flux with water column trace metal to ^{228}Ra ratios to quantify shelf-ocean input rates (equation 6).

The trace metal fluxes derived from Ra are comparable to the sum of Pará and Amazon fluxes derived from equation (4) (**Fig. 5**). For all metals except U, the Pará plus Amazon fluxes derived from equation (4) are within error of Ra fluxes determined using the 12 days residence time (upper end). For Ni and Cd, the sum of Pará and Amazon fluxes are slightly higher than both the 21 and 12-day residence time flux estimates derived from Ra (shelf-ocean flux), although still within error. This might reflect additional contribution from the mangrove belt, which eventually mixes with the Amazon and Pará transects (**Fig. 2**).

In general, fluxes derived from a 12-day residence time slightly overestimate, while fluxes derived from the 21-day residence time slightly underestimate relative to the equation (4) derived values, as demonstrated in **Fig. 6**. This plot shows the relationship between the chemical fluxes derived from the two different methods and highlights the good agreement between the fluxes, considering either the 12-days or the 21-days estimates (significant R; $p < 0.0001$). It is also clear from this plot that the 12-days and 21-days estimates can be considered as upper and lower estimates, since the linear regressions are just above and below the 1:1 relationship (dotted line), respectively. A 1:1 relationship would be obtained by considering a residence of ~ 16 -17 days, instead of the range that was used here in the calculations.

The trace metal fluxes calculated with equation (4) are the fluxes associated with the Amazon and Pará rivers only. On the other hand, the fluxes derived from Ra potentially include all the sources that may exist on the shelf (submarine groundwater discharge; diffusion from sediments, release from sediment resuspension). Additionally, the shelf-ocean fluxes derived from Ra may not

equal the sum of the inputs along the boundary (rivers, SGD, sediment diffusion) due to water-column shelf processes along the shelf. Biological uptake, scavenging, precipitation may remove trace elements and isotopes while resuspension, desorption, sediment diffusion may release trace elements and isotopes in the water column. Therefore, the two fluxes reported here (Ra shelf-ocean fluxes versus river fluxes) may be considered as two different approaches for TE flux estimates.

3.4 Global flux comparisons

A comparison of our calculated fluxes with fluxes from other major river estuaries is shown in **Table 4**. It should be noted that the calculated fluxes for the Amazon and Pará Rivers are based on our data from the high-discharge period, while the available global totals are reported as annual fluxes (Martin et al. 1979; Poulton and Raisewell 2000; Carey et al. 2002). This may influence the calculated contribution to global totals. Nevertheless, our data provides a useful estimate of flux and global percentages based on the high-discharge season in the Amazon estuary.

With this caveat in mind, the Amazon estuary had relatively low fluxes of the particle-reactive elements Mn, Fe, Co and Pb compared to other major rivers, given the Amazon’s enormous water volume. The Congo River is the second largest river by discharge on earth (mean: $39\,100\text{ m}^3\text{ s}^{-1}$; Gaillardet et al. 2003), following the Amazon. However, despite the much higher river volume discharge of the Amazon ($100\,200\text{--}240\,000\text{ m}^3\text{ s}^{-1}$; Espinoza-Villar et al. 2009), the Fe flux calculated in our study was within error of the annual offshore flux reported in a recent study in the Congo River plume (Vieira et al. 2020). This can be attributed to the higher endmember concentration ($7400 \pm 3100\text{ nmol L}^{-1}$ in the Congo compared to $1700 \pm 500\text{ nmol L}^{-1}$ in this study) and the unusually low estuarine removal of Fe ($\sim 50\%$) which was attributed to potential mid salinity sources of Fe, such as benthic remobilization (Vieira et al. 2020). It is also possible that the extensive peatlands in the Congo basin (Crezee et al. 2022) could supply large amounts of Fe-binding ligands (e.g., humic substances), therefore solubilizing Fe in the Congo River and estuary. Given the striking difference between the world’s two largest rivers in terms of trace metal output, further study of Fe-organic matter interaction in both estuaries is recommended.

Mn and Co fluxes were also lower in the Amazon than in the Congo, reflecting comparatively high removal of Mn and low riverine endmember concentrations of Co in the Amazon. Pb was not measured in the Congo but comprised a very small percent of global totals (0.1% ; based on Martin and Meybeck 1979). Interestingly, the flux of Pb was roughly equal in the Amazon and Pará Rivers, despite the higher Amazon volume, owing to the higher Pará endmember concentrations and lower estuarine removal. Overall, the comparatively high Pb flux in the Pará compared to the Amazon is consistent with a more heavily-contaminated catchment area (see **3.1**).

Al was not reported in the Congo, so our data were compared to other major rivers. Fluxes of Al in the Pará were similar to those than those reported in the Yangtze, a river of similar size (Ren et al. 2006). Fluxes of Al in the Amazon were roughly double that of the Yangtze, but lower-than-expected relative to river size. Considering that Al is primarily sourced by aluminosilicate weathering, this may reflect differences in geochemistry of the respective catchment areas.

The Amazon and Pará had the highest fluxes relative to global totals for Cu and Ni (**Table 4**). Cu and Ni in the Amazon surpassed major Asian rivers including the Ganga-Brahmaputra system, Yangtze, Irrawaddy, and Mekong (Samanta and Dalai 2018). In fact, Cu flux in the Amazon estuary alone surpassed the sum total of all major rivers in South Asia (Samanta and Dalai 2018). As Cu is a potential toxin for phytoplankton (Brand et al. 1986), this could have potentially biologically important implications, although Cu in the Amazon estuary never reached toxic levels due to extensive organic complexation (Hollister et al. 2021).

A comparison to annual global totals by Martin and Maybeck 1979 showed that the Amazon contributes 3% of the global dissolved riverine Cu and Fe, but <0.1 % of the global Zn and Pb. In contrast, comparison to a more recent global estimate (Poulton and Raisewell 2000; Carey et al. 2002) showed a contribution of roughly 19% for Cu and 15% for Ni, but only 4% for Co and 3% Zn and Mn by the Amazon in terms of annual global dissolved river flux. U comprised 9% of global flux (Windom et al. 2000). Using the high-discharge data, we estimate that the combined Amazon and Pará Rivers contribute up to 21% (Cu), 18% (Ni), 10% (U), 5% (Zn), 5% (Co) and 3% (Mn) to river-derived dissolved trace metals to the oceans. Based on global freshwater outputs (<https://www.bafg.de/GRDC>), the rivers listed in **Table 4** represent up 36% of global discharge. For the rivers with available Cu and Ni data, this decreases to 32%, with the combined Amazon and Pará Rivers making up 68–69% of this total. Notably, several important rivers are missing from this 32%, including the Congo, South American Rivers (Orinoco, Paraná), northern Asian Rivers (Yenesei, Lena), and North American Rivers (Mississippi, St. Lawrence). However, using this limited dataset, the Amazon-Pará estuary contributes roughly 29% of Ni and 55% of Cu. Given that the Amazon makes up 15–20% of the global river volume output, these values are in line for our global estimates for Cu, but lower-than-expected for Ni.

Conclusion

As Earth’s largest and 5th largest rivers, the Amazon and Pará represent important sources of trace metal flux to the Atlantic Ocean, following estuarine mixing. Here we show that the Pará River represents an important, and largely overlooked, source of trace metals to the Amazon estuary. Our removal and flux data are only available for the wet season (April-May 2018), which has roughly twice the river discharge for dry season in the Amazon River, so the full yearly flux cannot be calculated. Trace metals are known to experience distinct

seasonal behavior in the Amazon (Swarzenski and McKe 1998) and estuaries worldwide (Michel et al. 2000; Jiann and Wen 2009; Joung and Shiller 2016; González-Ortegón et al. 2019; Priya and Haddout 2020; Zhang et al. 2020). To fill this gap, a future GEOTRACES cruise has been approved for the dry season in the Amazon estuary. Data from this cruise will complement this paper and provide a full picture of annual (wet and dry season) fluxes.

Based on wet season data, we showed that the Amazon and Pará Rivers both contributed significant fluxes of dissolved trace metals to the Amazon estuary, reflecting the distinct catchment areas, with the Pará River showing an area of heavier anthropogenic influence. In addition to the Amazon and Pará Rivers, a large mangrove forest to the southeast contributed a minor but important source of dissolved trace metals to the estuary, e.g. through groundwater exchange. By the mid-salinity range, thorough estuarine mixing was apparent, and waters from the Amazon and Pará Rivers and mangrove belt became indistinguishable from each other before forming a mixing plume.

All metals experienced some degree of removal from the dissolved phase during estuarine mixing, occurring primarily in the low-salinity region. This removal to the particulate phase was attributed to processes such as adsorption to particles, ox(ihydrox)ide formation and/or colloidal flocculation. Consequently, estuarine removal was highest for particle-reactive elements (Al, Mn, Fe, Pb), but comparatively lower removal for Cu, Ni and Co. Even U, a mostly conservative element, displayed minor low-salinity removal. Only Cd had a net addition in both transects due to a mid-salinity increase, likely reflecting Cd^{2+} adsorption from particles upon seawater mixing.

Based on the high-discharge season data from this study, the Amazon and Pará combined represent a highly important source of dissolved Cu and Ni (up to 21% and 18% respectively, relative to global annual totals). On the other hand, Al, Mn, Fe, Co and Pb were comparatively lower, relative to other major rivers and global totals. Although this study provides only data from the wet season, it provides the first evaluation of flux for dissolved transition metal fluxes from these two globally important rivers. Given the increasing anthropogenic impact in this area and the influence of climate change, we assert that continued study is needed, including an evaluation of dry season fluxes.

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Data availability statement

Data for trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) and ^{228}Ra have been submitted to Pangea. U data are provided by Schneider et al. (in revision). Additional cruise station data are available in the M147 cruise report (https://doi.org/10.2312/cr_m147). Station Óbidos data are available through the SO-HYBAM Amazon Water Basin Resources Observation Service online (<http://www.ore-hybam.org>).

Figure captions

Figure 1. Map of sample area. (A) Surface samples collected in the Amazon and Pará River transects, mangrove belt, plume north and North Brazil Current (NBC). (B) Surface salinity (PSU scale).

Figure 2. Concentrations of dissolved ($<0.2\ \mu\text{m}$) Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U plotted against salinity. Symbols correspond to the transects as described in **Fig. 1a**. Predicted conservative mixing lines are shown for the Amazon (black) and Pará (green) River transects, using the Amazon ($S = 0.31$) and Pará ($S = 0.36$) River endmembers and the average of NBC stations as the seawater endmember ($S = 35.9$). Data for Cu is replotted from Hollister et al. 2021. Data for Co and Ni are replotted from de Carvalho et al. 2021. Data for U are replotted from Schneider et al. (in revision). Note the logarithmic scales for Mn, Fe, Co and Pb.

Figure 3. Concentrations of dissolved ($<0.2\ \mu\text{m}$) Al, Fe, Co, Ni, Cu, Zn, Cd, Pb and U plotted against Mn. Linear regression lines are shown for the Amazon (black) and Pará (green). Symbols correspond to the transects as described in **Fig. 1a**.

Figure 4. ^{228}Ra distribution (in $\text{dpm}\cdot 100\ \text{L}^{-1}$) on the Brazilian continental shelf.

Figure 5. Fluxes of dissolved ($<0.2\ \mu\text{m}$) Al, Fe, Co, Ni, Cu, Zn, Cd and Pb from the Amazon River estuary determined by ^{228}Ra -metal ratios using 12 day (blue) and 21 day (yellow stripes) residence times for ^{228}Ra , compared fluxes determined using trace metal using trace metal input/removal alone; bars for the Amazon (grey with hashed lines) and Pará (white) transects are stacked. Uranium had a negative flux when calculating using ^{228}Ra methods and is not shown. Error bars are based on the error calculated for trace metals (**Table 1**) and ^{228}Ra (**Table 3**).

Figure 6. Trace metal fluxes (kg day^{-1}) derived from Ra using 12 and 21-day

residence times plotted against fluxes derived using trace metal concentrations only (equation 4). The dashed line represents the 1:1 line.

Table captions

Table 1.

Limit of detection (LOD), error and certified reference material (CRM; CASS-6, NASS-7, SLEW-3 and/or SLEW-6) values for trace metal analysis.

Note. The LOD is considered three times the error of the manifold blank corrected for preconcentration. Data for Cu is from Hollister et al. 2021, Co and Ni are from de Carvalho et al. 2021 and U is from Schneider et al. (in revision).

Table 2.

Endmember concentrations, estuary removal and flux for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U.

Note. Trace metal concentration data for Cu is from Hollister et al. 2021, Co and Ni are from de Carvalho et al. 2021 and U is from Schneider et al. (in revision). The seawater endmember concentrations are calculated using the average of NBC stations ($S = 35.9$). The river endmember concentrations are shown for Amazon ($S = 0.31$) and Pará ($S = 0.36$) stations. For comparison, time series data at Station Óbidos are shown (average $\pm$ standard deviation of values from 1994 to 2019 from the equivalent time of year, 29 April–19 May) (<http://www.ore-hybam.org>). Estuarine removal and addition are calculated using the difference between the actual concentration and expected concentration from conservative mixing. Dissolved flux for the Amazon and Pará transects are calculated using the riverine endmember concentrations times the high-discharge volume flux (Amazon: $240\,000\text{ m}^3\text{ s}^{-1}$, Pará: $38\,000\text{ m}^3\text{ s}^{-1}$) minus net input and removal (equation 4).

Table 3.

Fluxes of dissolved ($<0.2\text{ }\mu\text{m}$) Al, Fe, Co, Ni, Cu, Zn, Cd, Pb and U from the Amazon River estuary determined by ^{228}Ra -metal ratios using 12 day and 21 day residence times for Ra.

Table 4.

Comparison of dissolved trace metal flux (kg day^{-1}) in estuaries worldwide.

Note. River discharge volumes are based on the reported values from the in the studies referenced. Total global fluxes are given as annual averages. Percentages of global fluxes are calculated based on our wet season data and therefore likely provide a high-end “upper limit” estimate of annual flux from the Amazon.

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