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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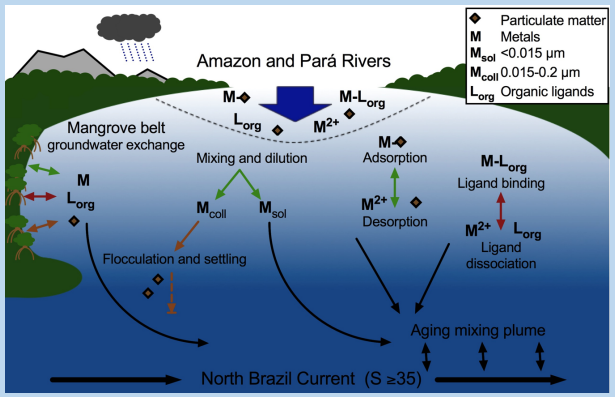
Abstract

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 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. Co, Ni and Cu removal was comparatively low in both river transects, while Cd was the only element with a consistent net input. Relative to global totals, 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.

Introduction

- Amazon has the highest river discharge (wet season ouput: 240 000 m^3 s^{-1}). The Pará to the south is Earth's 5th largest river (38 000 m^3 s^{-1})
- Trace elements enter the Atlanic Ocean after estuarine mixing and are controlled by a variety of chemical and physical factors (see figure below).
- Trace metal flux from the Amazon and Pará Rivers is currently unknown.

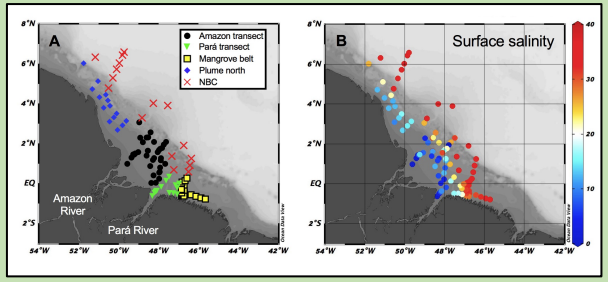
Controls on trace metal cycling in the Amazon Estuary. Metals enter the estuary from the Amzon and Pará Rivers and mangrove belt. Concentrations are influenced by mixing and dilution, colloidal flocculation and settling, particle adsorption and ligand binding.



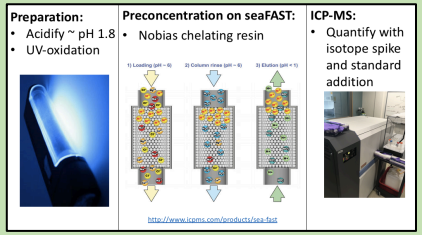
Methods

- Cruise M147 (GApr11) was conducted in April-May 2018 during the high discharge season
- Samples were collected using a trace metal clean tow-fish and filtered and acidified shipboard
- Trace metals were analyzed in the home laboratory by seaFAST-ICP-MS

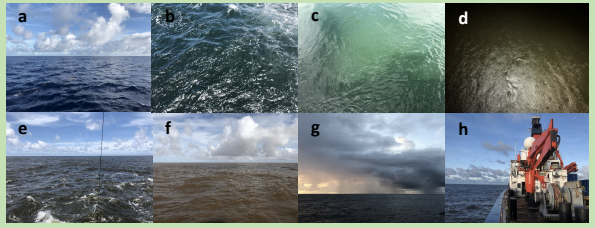
Map of sample area. (a) Surface samples collected in the Amazon and Pará River transects, mangrove belt, plume north and North Brazil Current (NBC). (B) Surface salinity (PSU scale).



Trace metal analysis. Samples were acidified shipboard, oxidized in the home laboratory and preconcentrated on seaFAST prior to analysis on the ICP-MS.

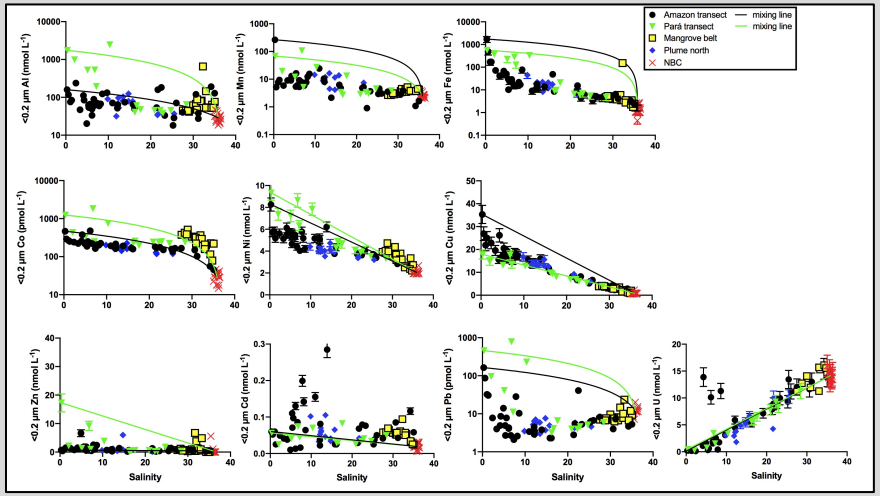


Shades of the Amazon Estuary. (a) high salinity plume waters, (b-d) green coloration at mid-salinity reflecting phytoplankton growth, (e) increased turbidity at low salinity, (f) Amazon endmember, (g) one of many rainstorms encountered in the estuary, (h) the RV Meteor (photos taken on cruise M174 in April-May 2021)



Results

Below: Concentrations of dissolved (<0.2 µm) Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U plotted against salinity. Predicted conservative mixing lines are shown for the Amazon (black) and Pará (green) River transects. Data for Cu is from Hollister et al. 2021. Data for Co and Ni are from de Carvalho et al. 2021.



Trace metal distribution:

- Fe and Pb are primarily influenced by particle scavenging.
- Al, Mn, Co and Pb have a Pará maximum at S ~ 7.
- Co and Pb correlate strongly with Mn (R = 0.87 and 0.93), especially in the Pará transect.
- Cd has a mid-salinity maximum (desorption: Cd^{2+} mixing with Cl^- in seawater).
- Cu and Ni are primarily governed by mixing.
- U is mostly conservative and correlates positively with salinity.
- Additional mangrove belt influence is observed.

Right: Estuary removal and flux for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U. Estuarine removal is calculated using the difference between the actual concentration and expected concentration from conservative mixing. Flux is calculated using the riverine endmember concentrations times the high-discharge volume flux minus net input and/or removal.

		Al, nmol L^{-1}	Mn, nmol L^{-1}	Fe, nmol L^{-1}	Co, pmol L^{-1}	Ni, nmol L^{-1}	Cu, nmol L^{-1}	Zn, nmol L^{-1}	Cd, nmol L^{-1}	Pb, pmol L^{-1}	U, nmol L^{-1}
Amazon	Average Amazon transect removal (%)	8.0	92.2	94.0	22.0	16.3	34.3	-82.7	-68.9	86.1	-71.5
Amazon	Amazon dissolved flux (kg/day)	81632 ± 2449	23634 ± 758	119161 ± 34524	443 ± 43	8413 ± 612	30584 ± 3441	1716 ± 311	236 ± 18	98 ± 13	1862 ± 23
Pará	Average Pará transect removal (%)	63.9	61.2	69.8	38.7	12.2	5.7	78.8	-13.3	68.6	22.79
Pará	Pará dissolved flux (kg/day)	55620 ± 1669	4740 ± 152	30807 ± 8926	147 ± 14	1579 ± 115	3505 ± 394	786 ± 143	24 ± 2	98 ± 13	290 ± 36

Global comparisons:

- The **Congo** is the second largest river by volume (41 200 m^3 s^{-1}), slightly larger than the Pará. Our study showed roughly equal contribution of Fe and lower Co and Pb in Amazon compared to Congo (Vieira et al, 2020).
- On a **global scale** the Amazon contributes relatively little of global river totals for dissolved Zn (3%), Mn (3%) and Co (4%) (Poulton and Raisewell, 2000)
- Cu and Ni in the Amazon make up 19% (+2% Pará) and 15% (+3% Pará) of the global riverine totals.
- Cu in the Amazon alone excedes combined output from all major Asian Rivers (Samanta and Dalai, 2018).
- A future cruise approaved for dry season will provide a more complete picture.

References: (1) de Carvalho, L.M., Hollister, A.P., Trindade, C., Gledhill, M., and Koschinsky, A. 2021. Distribution and size fractionation of nickel and cobalt species along the Amazon estuary and mixing plume. Marine Chemistry, 236: 104019. (2) Hollister, A.P., Whitby, H., Seidel, M., Lodeiro, P., Gledhill, M. and Koschinsky, A., 2021. Dissolved concentrations and organic speciation of copper in the Amazon River estuary and mixing plume. Marine Chemistry, 234: 104005. (3) Poulton, S.W. and Raiswell, R., 2000. Solid phase associations, oceanic fluxes and the anthropogenic perturbation of transition metals in world river particulates. Marine chemistry, 72(1): 17-31. (4) Samanta, S. and Dalai, T.K., 2018. Massive production of heavy metals in the Ganga (Hooghly) River estuary, India: Global importance of solute-particle interaction and enhanced metal fluxes to the oceans. Geochimica et Cosmochimica Acta, 228: 243-258. (5) Vieira, L.H., Krisch, S., Hopwood, M.J., Beck, A.J., Scholten, J., Liebetrau, V. and Achterberg, E.P., 2020. Unprecedented Fe delivery from the Congo River margin to the South Atlantic Gyre. Nature communications, 11(1): 1-8.