

Source and Distribution of Mercury in Sediments of the Brazilian Amazon Continental Shelf with Influence from Fluvial Discharges

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Authors' contributions

This work was carried out in collaboration between all authors. Authors GWS and FA designed the study, participated of the samples collection, wrote the protocol and performed the statistical analysis. All authors wrote and revised the draft of the manuscript, and read and approved the final manuscript.

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ABSTRACT

Place and Aims: Total concentrations of Hg and geochemical analysis of sediments from the Amazon Continental Shelf (47°52'W-4°19'N, 51°04'W-2°16'S) were determined in 25 sampling sites, during the months of lowest flow of the Amazon River. The aim of this study was to determine the influence of fluvial discharge on mercury distribution and deposition in the environment.

Duration of Study: Between 1999 and 2011.

Analyzes: The marine sediments were used to identify heavy minerals, and determine grain size, organic content (organic matter and organic carbon), SiO₂, Fe₂O₃, Al₂O₃ and MnO, and Hg levels using standard methods.

Results and Conclusion: The Hg concentrations varied from 14 to 160 ng g⁻¹. The highest Hg

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concentrations occurred in the inner shelf. Both analysis of major oxides and identification of mineral composition in the sediments confirmed the influence of river discharge on Hg deposition in the inner shelf. The geochemical results suggested that the main Hg source in the study area was from natural origins due to erosion and subsequent leaching of tropical lateritic soils, although mining in the Madeira and Tapajos river basins is also a contributing factor.

Keywords: Total mercury; mineralogy; deposition; oceanic currents; Brazilian Amazon.

1. INTRODUCTION

The Amazon River is the largest river in the world, with a flow ratio ranging between 1.2 and $2.5 \times 10^5 \text{ m}^3 \text{ s}^{-1}$ (average discharge of 1.5 to $1.7 \times 10^5 \text{ m}^3 \text{ s}^{-1}$) and a drainage area of approximately $7 \times 10^6 \text{ km}^2$ [1,2]. The total sediment load transported by the Amazon River toward the Amazon Continental Shelf (ACS) reaches 10^9 tons per year [1,3,4], with 97% of that cargo originating from drainage areas of the Andean region of Peru and Bolivia [5].

Sediments transported to the ACS from the Amazon River basin are deposited mainly in the inner shelf, due to resistance force from the ocean. In contrast, the presence of sandy material originating from marine sediments is deposited primarily on the outer shelf [6,7]. This characteristic of finer sediments accumulating on the inner part of the shelf has important consequences for the complexation of metal elements such as mercury.

In the Amazon, discussion regarding whether the main source of mercury contamination is natural or anthropogenic is both classic and longstanding, with different authors emphasizing the existence of a large Hg reservoir in the Amazon [8-14], while others argue that the main anthropogenic source is mining activity [10,12,15-22], especially in the Madeira, Tapajós and Trombetas river basins. The sum of these two sources results in an enormous amount of mercury, which is partly carried by the current associated with suspended materials, toward the mouth of the Amazon and Pará rivers.

There is already ample information regarding Hg concentrations in water and sediments of the continental Amazon; however, little is known about Hg accumulation in the region between the mouth of the Amazon and Pará rivers and the ACS. The objectives of this study were to determine the influence of fluvial discharge on Hg distribution and deposition in the ACS and nearby coastal zone and to identify the main source of total Hg in the ACS, mapping the flow

of Hg and suspended materials to the ocean shelf.

2. MATERIALS AND METHODS

2.1 Study Area

The study was conducted in the ACS and nearby coastal zone ($47^{\circ}52'W$ - $4^{\circ}19'N$ and $51^{\circ}04'W$ - $2^{\circ}16'S$) between Orange Cape and Maguari Cape (Fig. 1). It is an intensely dynamic region, conditioned by the meeting of continental water bodies of the world's largest river with the Atlantic Ocean, and influenced by the Equatorial North Current and North Brazil Current (NBC), which according to Nittrouer & DeMaster [23] results from the impingement of the South Equatorial Current on the Brazilian coast. The result of the conjunction of hydrological and atmospheric forces is an apparently unstable framework, which determines the function, structure and geomorphology of the coastal zone. The tidal system and trade winds, in conjunction with a high suspended sediment load transported and deposited along the ACS, diminishes in importance with increased distance away from the epicenter of these forces. Moving south along the coast, mangroves can be found alternating with terraces formed by peat and muddy materials from fluvial sedimentation, as well as patches of sandy banks more evident farther towards the Northeast region of Brazil. According to the Köppen-Geiger classification, the regional climate varies between "Am" hot and constantly humid (monsoon climate) and "Af" equatorial, with a mean temperature of $28^{\circ}C$ and rainfall exceeding $2000 \text{ mm year}^{-1}$ ($2600 \text{ mm year}^{-1}$ in the coastal zone), especially between December and February.

2.2 Sampling Sites

500 g of superficial sediments (0.0-0.1 m) were sampled with a "Van-Veen" collector at 25 sampling sites between 5 and 100 m isobaths during the months of lowest flow of the Amazon River (May and June) during 1999-2002, 2005-2007 and 2011, totaling 141 samples analyzed, all in triplicates.

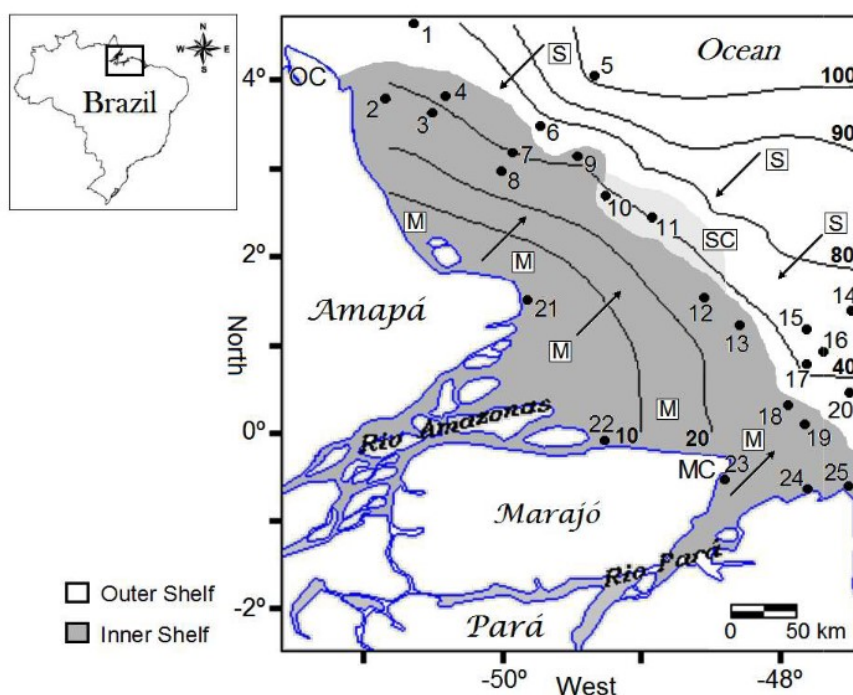


Fig. 1. Amazon continental shelf between orange cape and maguari cape, with sampling sites and their isobath locations indicated. Sedimentary loads: Continental (muddy = M) and oceanic (sand = S)

After samples were collected, the sediments were stored in plastic bags in the freezer at -20°C until time of analysis. At each sampling site, water salinity was measured with a digital salinometer to identify fluvial and marine waters. The first stage of sampling (1999-2002) was performed as part of the project titled National Assessment of the Potential Sustainable Development in the Exclusive Economic Zone (REVIZEE-SCORE/NO), and the second and third stages were performed with the logistical support of the Federal University of Pará (UFPA).

2.3 Analytical Procedures

In the chemistry lab at UFPA, the samples were dried at 45°C for a period of 48 h, homogenized, pulverized and sieved, and the very fine sand fraction ($125\text{--}63\ \mu\text{m}$) being used to identify heavy minerals and determine organic content, silicate and oxide concentrations. The same sand fraction was also used separately to analyze total Hg at Lakefield Geosol Laboratories Ltda.

Grain-size analysis was determined by the mechanical – gravimetric method using sodium

hexametaphosphate solution, and the clay fraction ($< 4\ \mu\text{m}$) was determined in a test tube via separation of suspended material [24]. The mineralogical investigation was performed using the sedimentation method, with separation of light and heavy minerals by gravity, using a tetrabromoetano solution in demineralized water [25]. After the materials had been separated and oven-dried, glass slides were assembled containing approximately 200 mineral grains per plate. Analyzes were then performed using a petrographic microscope, where grains were counted and classified in terms of estimated proportions [26].

Organic matter (OM) content was determined according to already well recognized technique of hot acidic extraction, with calculation of the weight difference before and after dry digestion. Organic carbon (OC) was determined with the use of an LECO CNS-2000 analyzer model. The analysis followed protocols for sample preparation described in the EMBRAPA Manual of Soil Analyzes [24] and the results were expressed as percentages (%). Silicates were determined by the gravimetric method (Standard Method 4500-Si C) [27]. The sample was

weighed and then volatilized as silicon tetrafluoride. The residue was weighed again and silica was determined as volatilization loss. Acid digestion followed by spectrophotometric reading was applied to estimate the following oxide concentrations: SiO₂ – by digestion with sulfuric NaOH solution and subsequent reduction of molybdate with ascorbic acid; Fe₂O₃ and Al₂O₃ – by digestion with sulfuric acid solution with sulfosalicylic acid as an indicator, titration with EDTA for iron and CDTA for aluminum; and MnO – by manganese peroxidation with potassium periodate in HNO₃ – H₂PO₄ [24,28]. The oxide values were normalized as aluminum to report variations in grain-size among the samples. Therefore, we assumed that Si/Al ratios in the sandier sediments would be high and the Si/Al ratios in the muddier sediments would be low.

To determine total concentrations of Hg, a modified cold-vapor atomic absorption method was used (Standard Method 3112 B and 3500-Hg B) [27] adding 1.0 g of dry sediment sample (< 0.063 mm), 0.1 g of V₂O₅, 10 mL of HCl:HNO₃ 3:1 and 15 mL of H₂SO₄ in a closed test tube for conservation and to promote recycling of the volatilized fumes. The material was then heated at 80°C for 60 minutes. After, the extract was quantitatively transferred to a 100 mL volumetric flask and made up to the mark using deionized water (Milli-Q). Aliquots were removed from the flasks for reading using an atomic absorption spectrometer with cold-vapor generation and a detection limit of 10 ppb. The results were certified with the international standards MAG-1 Geostandards Newsletter and NIST 1646a and were expressed in ng g⁻¹. Additionally, medium shale was used as a reference value for data interpretation [29].

2.4 Data Analysis

From the results, a Pearson correlation analysis was applied to investigate relations between total Hg and the geochemical variables. Differences in the values of each geochemical variable among the plots were tested using analysis of variance (ANOVA). To test for influence of fluvial discharge on mercury distribution and deposition, the geochemical variables were combined to form an axis using principal component analysis (PCA), and were then tested using non-parametric multivariate analysis of variance (MANOVA). A suspended material and sedimentation flux model was also developed from the results, in association with the ocean circulation model of the NBC.

3. RESULTS AND DISCUSSION

3.1 Organic Content

OM content analyzed from sediments in the study area for the entire sampling period varied between 0.3 and 4.9% (average 1.6±1.1%). The average OM content found exclusively in the inner shelf was almost 70% higher than the average content in the outer shelf (Fig. 2). The same trend was noted for OC concentrations, where levels ranged from 0.1 to 2.7% (average 0.9±0.6%), with a 1.0% average for the inner shelf and a 0.7% average for the outer shelf (Fig. 2). The high OM and OC concentrations in the inner shelf are indicative of the contribution of suspended material transported via discharge from the Amazon and Pará rivers. Recently deposited sediments normally have an OC percentage between 1–5% [30], which would mean that there are areas of recent deposition within the continental shelf with higher OC concentrations, while older deposited areas tend to have lower OC concentrations, as was observed in the N–NO axis between sampling sites 1 and 3 (near the Orange Cape) in the outer shelf (sampling site 5), and outside of the equatorial shelf between sampling sites 15–17. OC concentrations determined from sediments in the ACS (1.1±0.5%) corroborate the results obtained in literature [31,32], who reported concentrations of 1.1 and 2.0%, respectively, for the same region. Significantly positive correlations ($p < 0.050$) were found between Hg and OM concentrations (Pearson $r = 0.861$, $p = 0.001$) and between Hg and OC ($r = 0.862$, $p = 0.001$).

Organic content concentrations can be highly variable in marine sediments due to physical processes such as the degree of sediment deposition and current speed, as well as biological processes, including variations in autochthonous primary productivity. We consider that the main source of organic content found in ACS sediments is allochthonous, due to the immense load of suspended materials transported annually by the Amazon River [4,33-35], and also to a lesser extent by the Pará River. We believe that low organic content concentrations occasionally observed in coastal marine sediments in the region may be related to tide variations in discharge from the Amazon River, as well as from influence by the NBC, which occasionally causes mixing of water layers and general homogeneity of surface sediments.

3.2 Oxides

Oxide concentrations of aluminum (Al_2O_3), iron (Fe_2O_3), manganese (MnO) and silica (SiO_2) for each sampling site were first determined, then normalized based on aluminum content, before being finally presented as a ratio (Fig. 2). The $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio for the ACS was approximately 0.54, while the ratio for the inner shelf was 0.57, slightly higher than the 0.48 ratio obtained from the outer shelf. The muddy waters from the Amazon and Madeira rivers carry large amounts of suspended material with iron in abundance. An analysis of the results showed that river discharges contributed to a 41% increase in Al concentrations (mg g^{-1}) and a 60% increase in Fe concentrations (mg g^{-1}) in sediments from the inner shelf. The sampling area in the coastal zone revealed a $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio equal to 0.61, slightly higher than the ACS. Calculations for the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio did not indicate significant differences between sampling sites, maintaining a 0.01 ratio for the whole shelf and nearby coastal zone. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio obtained for the ACS was 9.96, while the inner shelf and nearby coastal zone both expressed ratios smaller than the overall average, with 6.48 and 7.20, respectively. The most notable difference came from the sampled area on the outer shelf, which calculated a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 16.41. These values confirm the results of the grain-size analysis, indicating that the high Si/Al ratio in the outer shelf is due to the presence of sediments predominantly formed by sand fractions, mainly quartz, resulting from the breakdown or decomposition of rocks with silica. Similarly, the

low Si/Al ratio found in the inner shelf is explained by the predominance of muddy sediments (clay) with high organic content. Studies developed in the Amazon Fan [36], the third largest modern 'mud-rich' submarine fan system in the world, located on the equatorial Atlantic margin and abyssal plain, revealed $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratios between 0.40 and 0.90 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 5 and 13, where the highest silicon oxide ratios were observed with some degree of sedimentation in the outer shelf.

3.3 Hg Levels

Total concentrations of Hg of sediment ranged from 14 to 160 ng g^{-1} (mean $84 \pm 30 \text{ ng g}^{-1}$). ACS sediments of both estuarine and coastal influence did not show large variations in Hg concentrations compared with the general mean, and always presented low standard deviations. The highest mercury concentrations were observed inside the ACS, particularly at sampling sites 3, 9, 13 and 18 (Fig. 3), which showed concentrations greater than 100 ng g^{-1} . Overall, the results also presented variation (maximum-minimum), with a standard deviation of approximately 16 ng g^{-1} , confirming the trend of a standard mercury concentration along the continental shelf, which could indicate an absence of heavy metal pollution in the region. Total concentrations of Hg determined for the coastal region remained near $77 \pm 6 \text{ ng g}^{-1}$, a high value considering that the deposition rates are much lower, due to remobilization from the strong tidal currents and waves. Mercury, like most of the metallic elements, has a

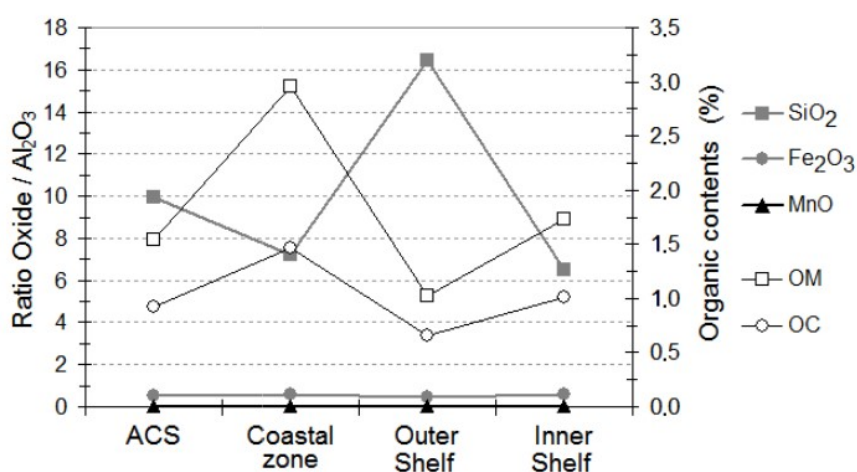


Fig. 2. Average oxide ratios/ Al_2O_3 for SiO_2 , Fe_2O_3 and MnO , and average organic content (%) for the ACS and adjacent coastal zone ($n = 141$)

high capacity to accumulate in biological tissues, and the sediments of the coastal zone are the main source of Hg to fish, crabs, shrimps, lobsters and other seafood for local populations in Pará State, including the region of Marajó Island. Besides, mangrove sites located to the south may be serving as an accumulator compartment of mercury, due to the high sedimentation ratio that occurs in this region. Significantly negative correlations were observed between Hg concentrations and sand content (Pearson $r = -0.688$, $p = 0.005$) in ACS sediments (Table 1). Results confirm that the metal elements have a high affinity for organic compounds and little or no affinity for silicates and quartzites, as the Si correlations were not significant ($p > 0.050$). Due to variations in total concentrations of Hg in relation to water depth, Pearson's correlation analysis showed no significant relationship among the variables ($r = 0.115$, $p = 0.614$), although higher Hg concentrations were observed in shallower water. Vergotti et al. [21] demonstrated a negative correlation between soil organic matter and silicate, which is similar to the negative

correlation encountered here between silicate concentrations and specific sediment surfaces. These results corroborate the trend distribution of sediments in the ACS, as the highest OM levels were concentrated in the muddy sediments of the inner shelf, compared with sandy silicate sediments found in the outer shelf.

Several studies have reported that the global Hg average ('Clarke' geochemist) and the average Hg concentrations in shale are higher than one would expect to represent "background" values in different sedimentary basins [37]. In fact, the concentration of 180 ng g^{-1} reported for shale by Bowen [29] is higher than the highest concentration found in the ACS during the study period, which was 160 ng g^{-1} (at site 9). Mason [38] reported that the average mercury concentration found in crustal rocks was 80 ng g^{-1} . Given this variation, we decided to set the reference value based on the average Hg concentration found in sediment samples from Amazonian areas free from anthropogenic metal contamination (*regional background*).

Table 1. Pearson's correlations for Hg and the geochemical variables. Marked correlations are significant at $p < 0.050$ and $n = 141$ (casewise deletion of missing data)

	OM	OC	Si/Al	SiO ₂	Fe ₂ O ₃	Sand	Silt	Clay	Depth
Hg	0.861	0.862	-0.034	0.027	0.192	-0.688	0.675	0.684	0.115
	$p=0.001$	$p=0.001$	$p=0.870$	$p=0.899$	$p=0.411$	$p=0.005$	$p=0.011$	$p=0.008$	$p=0.614$

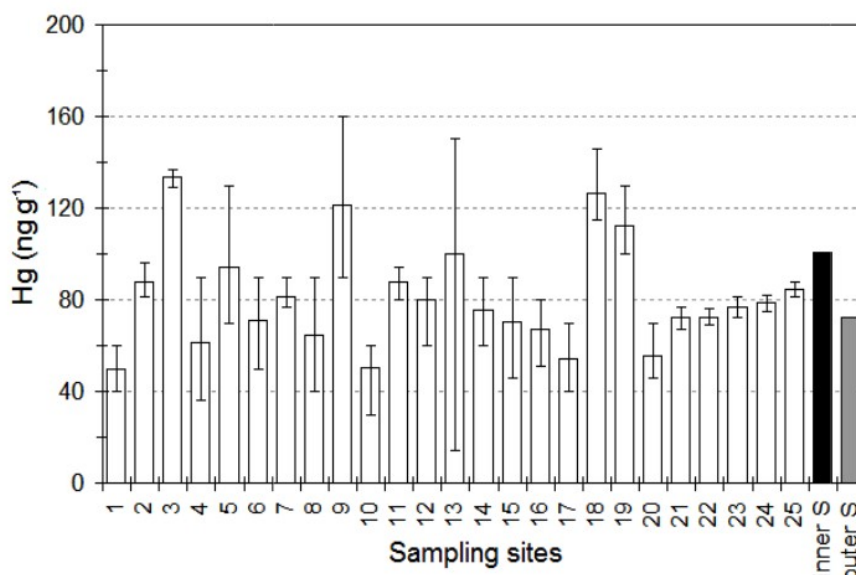


Fig. 3. Average concentrations (ng g^{-1}) with maximum-minimum bars for total Hg in the ACS sampling sites ($n = 141$). Black bar = inner shelf; gray bar = outer shelf

In order to determine whether a regional background value of an element is reliable, it is necessary to cross-check with all other reported values in the given region [39], detailing all natural and anthropogenic variations encountered. However, the idea of a global geochemical background value for any given element is illusory, given the large variations in geochemical composition and sources of human-made contamination from region to region. For a regional background value of mercury concentration in the Eastern Amazon, several works have been consulted [15,16], which analyzed total Hg levels in sediments of the Madeira River basin. They estimated Hg concentrations between 50 and 2620 ng g⁻¹ for the main river channel and between 200 and 19,830 ng g⁻¹ for forest-rivers. According to the authors, the high Hg concentrations in forest-rivers were associated with relative flow/load of suspended material, sediment pH and acidic waters. Lacerda et al. [40] established a correlation between Hg concentrations and organic matter content in the fine sediment fraction (< 63 µm), which was 330 ng g⁻¹ Hg to 3.9% OM in muddy water rivers, 130 ng g⁻¹ Hg to 5.2% OM in clear water rivers, and 490 ng g⁻¹ Hg to 9.0% OM in black water rivers of Western Amazonia. Bonotto & Silveira [41] measured Hg values in sediments of the Madeira River basin between 30 and 160 ng g⁻¹, while Vergotti *et al.* [21] determined mean mercury content in lake sediments of the same basin at 50 ng g⁻¹ and 128 ng g⁻¹ for fluvial sediments.

Comparatively, it is clear that the average total concentration of Hg determined in the ACS between 1999 and 2011 was far below the range proposed for Amazonian rivers [15,16,40], being closer to the reference value proposed by Mason [38] for the crust. Also, considering that total concentrations of Hg determined in this study resemble those obtained by other authors for the Madeira River [41], where intense mining activity occurs, regional background value of 4.5 ng g⁻¹ proposed by these authors was chosen, appearing to be an acceptable reference value for environmental conditions in the ACS. Marins et al. [39], who studied the role of total mercury as an indicator of urban and industrial pollution in the eastern and southern parts of the Brazilian coast, reported Hg values between 1 and 15 ng g⁻¹ for the eastern part and between 20 and 35 ng g⁻¹ for the southern part, both in fine sediments (< 63 µm) and at depths characteristic of pre-industrial deposition. From their results,

the authors established a regional background mercury value of 15 ng g⁻¹ for the East Coast and 35 ng g⁻¹ for the South Coast of Brazil.

3.4 Grain-size and Mineralogical Composition

Regarding the type of sediment found in the ACS, the grain-size analysis revealed the presence of three groups: sandy sediments (2000vcs – 250 ms µm) found in the outer shelf; sandy-clayey and clay-sanded sediments in transition area between the outer and inner shelf; and muddy sediments formed by thin particles, being a mixture of clay, silt and small fractions of organic matter in the inner shelf and in the nearby coastal zone (Fig. 1). Overall, the results showed a trend of higher Hg concentrations in muddy sediments, which are probably due to Hg affinity to anionic clay minerals and organic matter, thereby forming an aggregate component. Both clay and OM display an intrinsic characteristic of attracting positively charged elements.

The mineralogical composition analysis revealed slightly different patterns between the area influenced directly by river discharge on the inner shelf and the area influenced by the ocean in the outer shelf. In the inner shelf and coastal zone the following minerals predominated: very stable heavy minerals such as tourmaline (borosilicate with complex structure) and zircon [ZrSiO₄]; less stable heavy minerals including amphibole [hornblende Ca-Mg-Fe-Al-silicate], epidote [pistacite Ca-Fe-Al-(SiO₄ and Si₂O₇)] and pyroxene [augite Ca-Mg-Fe aluminum silicate]; and also significant concentrations of kaolinite [Al₂Si₂O₅(OH)₄], montmorillonite (clay mineral) and quartz [SiO₂]. In the outer side of the ACS, very abundant, stable heavy minerals such as zircon and garnet [Ca-Mg-Fe-Mn aluminum silicate] were found, as well as less stable heavy minerals including epidote, pyroxene and amphibole, and high levels of quartz. The results of this analysis are directly related to variations in sediment particle size (Fig. 4 and Table 2). The results also corroborate findings by Rimington et al. [36] in the Amazon Shelf and Fan, which determined that the most abundant, less stable minerals in the shelf within Amapá State were pyroxene, amphibole and epidote.

Although mineralogical composition analysis can be hampered by the impacts of leaching and sediment redistribution, in this study it was

possible to infer some assumptions about sediment origins and erosion processes. Translucent detrital species of heavy minerals are very common, making them ideal candidates as source indicators [25]. An interpretation of the results obtained by other authors [8,42,43] for sediments of various rivers in the Amazon basin, allowed us to establish a connection between different minerals and their specific geological areas and depositional histories, proposing possible origins for mineral elements within a given watershed. The results showed that amphibole and epidote, both heavy minerals found in the ACS, originated from the Guianan Shield (Precambrian), with likely significant contributions from the Negro and Trombetas rivers. Additionally, there is also with a possible contribution from the Brazilian Shield (Precambrian) by way of the Xingu and Tapajós river discharges. Furthermore, it is important to note that montmorillonite and zircon are abundant in muddy water rivers of Andean sediment origins. However, other abundant elements such as kaolinite and pyroxene in the ACS did not show conclusive results regarding their geological origins.

The last two major droughts in the Amazon River basin (2005 and 2010) acted as a strong disturbance on the hydrological cycle, affecting the volume of sediment discharged to the ACS. These disturbances apparently impacted the concentrations of some geochemical variables within the study period. Therefore, an ANOVA was used to investigate variations in the values of each geochemical variable, to see whether differences could be found related to environmental heterogeneity. Overall, the analysis revealed that discrepancies (errors) were distributed randomly and independently. Additionally, with the exception of OC and zircon concentrations, all other variables did not show high variability among the sampling periods (Table 3), ensuring data reliability.

The trend of mineralogical composition was confirmed by Principal Component Analysis, with component axis 1 explaining 62.6% and axis 2 12% of the behavior (Table 4). Component 1 was responsible for the separation between the fluvial and marine discharges, while component 2 presented the sampling sites based on distance away from the Amazon River mouth.

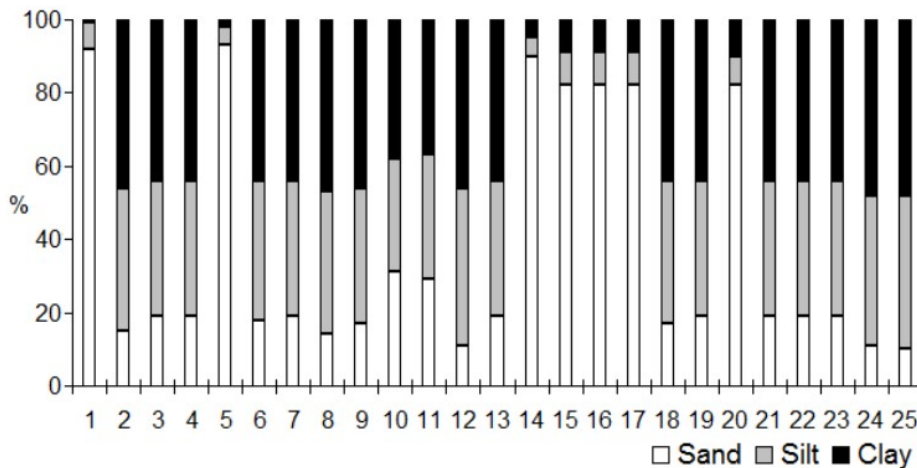


Fig. 4. Proportions of sand, silt and clay in the ACS sediments and adjacent coastal zone (n = 141)

Table 2. Results of the mineralogical investigation in the sediment fraction of very fine sand (VFS 125 – 63 µm) for ACS

Inner shelf	Outer shelf	Abundance
Kaolinite, montmorillonite	Quartz	Elevated
Epidote, amphibole, pyroxene	Epidote, amphibole, pyroxene	High
Quartz	Zircon	Abundant
Zircon, tourmaline	Garnet, kaolinite	Medium
Garnet, feldspars, Illite	Feldspars, Illite, mica, goethite	Little
Mica	Hematite	Very little

Table 3. Variance analysis (ANOVA) and non-parametric analysis of variance (Kruskal-Wallis) tests comparing the means of the samples for geochemical variables ($p= 0.05$)

Variable	n	SS _{tot}	df	MS _{tre}	F	p
Hg	141	37235.6	140	1.7	0.002	0.963
OM	141	36.7	140	2.0	2.762	0.103
OC	141	19.3	140	1.9	5.345	0.025
Si	141	1262.9	140	0.2	0.008	0.930
SiO ₂	141	120793.4	140	22.6	0.009	0.925
Fe ₂ O ₃	139	115.9	138	0.048	0.020	0.888
Al ₂ O ₃	141	144.8	140	1.3	0.435	0.513
MnO	141	0.038	140	0.0	0.021	0.887
Kaolinite	24	69.7	23	1.3	0.893	0.349
Montmorillonite	25	237.2	24	1.6	0.328	0.570
Epidote	25	42.1	24	1.1	1.290	0.262
Amphibole	25	34.4	24	0.050	0.070	0.793
Pyroxene	25	50.6	24	3.3	3.354	0.073
Quartz	25	68.7	24	1.0	0.710	0.404
Zircon	25	19.0	24	8.4	37.797	1.49E-07
Sand	141	6.0	140	0.0	0.002	0.965
Silt	141	1.2	140	0.003	0.123	0.727
Clay	141	2.0	140	0.002	0.040	0.842

* SS_{tot} = Total sum of squares; MS_{tre} = Treatment mean square. Bold = There is no difference between the periodic means

Table 4. Principal component analysis (PCA) of the geochemical variables*

Axis	Eigenvalue	Total variance (%)	Cumulative eigenvalue	Cumulative (%)	Meaning
1	16.9	62.6	16.9	62.6	Discharge influence
2	3.2	12.0	20.1	74.6	Discharge distance
3	2.9	10.8	23.0	85.3	
4	1.4	5.1	24.4	90.4	

*27 active variables to 25 sampling sites and 141 active cases

The MANOVA tested the PCA results based on all environmental variables, relating them to seasonal variations (hydrological cycle), flood pulse, sediment discharge volume and location of sampling sites. The results showed a significant difference ($p < 0.0001$) between the inner and outer shelves, confirming clear distinctions between river and marine sediment load. The projection of environmental variables observed from the PCA results showed that quartz and silicon oxide levels were predominant during isolation of the oceanic shelf sampling sites (Fig. 5).

3.5 Sediment Dynamics

In order to understand the sediment dynamics inside the ACS, it is necessary to examine the mineralogical composition of all sediments in the Amazon River basin. In the Upper Amazon, an area located more than 3000 km upstream from the river's mouth, where the Napo, Yucatali,

Javari, Jutai and Iça rivers can be found, the predominant composition of both sediments and suspended material includes: ultra-stable to stable minerals, such as tourmaline, zircon, magnetite and ilmenite [FeTiO₃]; less stable heavy minerals such as amphibole and pyroxene; and light minerals such as kaolinite, illite and montmorillonite [8,42,43]. From the Upper Amazon to the Lower Amazon, the amount of suspended material changes in relation to contributions from black water and clear water river discharges.

According to personal observations and some author [8,42,43], in the Lower Amazon, an area influenced by both the muddy waters of the Amazon and Madeira rivers and also the clear water rivers of the Trombetas, Tapajós, Xingu and Tocantins, there is a higher frequency of heavy minerals such as epidote and staurolite, light minerals such as montmorillonite and kaolinite, including punctual fractions of goethite,

illite and feldspars, and a large percentage of quartz. This change in mineralogical composition is accompanied by variations in texture and grain size. From the Lower Amazon towards the mouth of the Amazon and Pará rivers, which passes through the coastal zone to reach the inner part of the ACS, the sediment load is enhanced by reduced current speed in the lower part of the slope, and also by pressure imposed by oceanic water masses.

In the region situated between the mouths of the Amazonas and Pará rivers and the open ocean, the tidal zone acts like a strong physical barrier to river flow. In such conditions, drastic changes in pH and salinity accelerate the process of sediment deposition, forming an immense string of muddy sediments rich in clay minerals, associated with metallic elements, along the Atlantic coast (Fig. 1). Accumulated organic matter inside the shelf also exerts an important influence on the complexation of metal elements. Organic matter reduces sediment density, while increasing its porosity and specific surface. As a result of increased specific surface area, sediments rich in organic matter are able to adsorb more cations. In other words, an increase

in cation exchange capacity occurs with increasing OM content [44].

Research conducted in the ACS between North Cape and Cassiporé Cape in Amapá State confirm the presence of extensive ranges of sand and mud sedimentation alternated with erosion processes due to wind action, which is dominated by the easterly trades, and also wave action, associated with the North Brazilian Current [23]. These sedimentary deposits are concentrated in the inner part of the shelf reflecting sedimentary dynamics resulting from discharge of the Amazonas and Pará rivers in the region [45,46].

Although the Amazon River basin transports the world's highest volume of suspended material, most of that material remains in the basin itself, due to an average river gradient of only 2 cm per km [43], which results in low current speed, allowing the formation of a large floodplain. The geomorphological characteristic of winding river channels in the Amazon basin also contributes to reduced current velocity, which would explain why mercury levels found in sediments of the Madeira River, for example, are higher than concentrations found in the continental shelf.

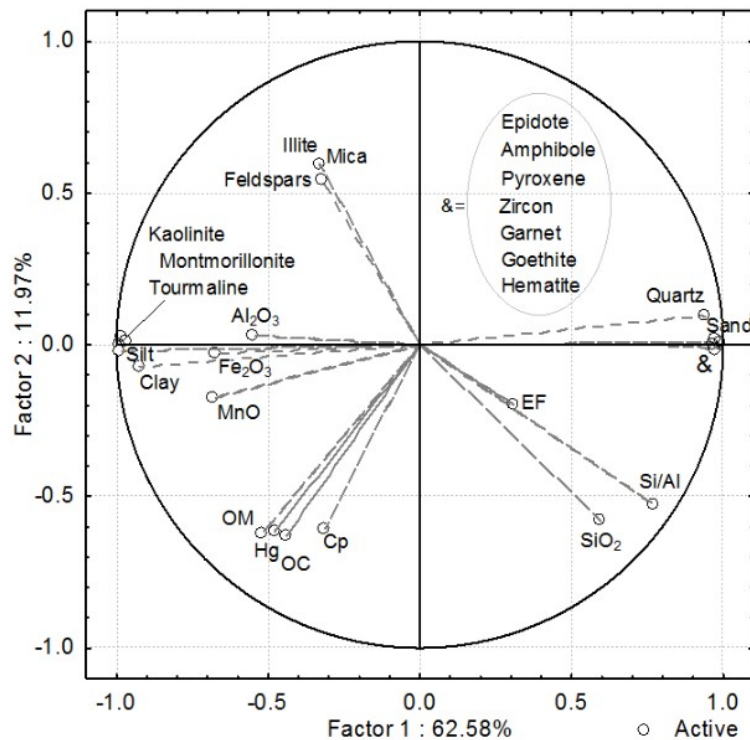


Fig. 5. PCA analysis with the variables projected on a factor-plane 1 x 2

3.6 Mercury Origin and Deposition

Mercury deposition in bottom sediments of aquatic ecosystems can become more bioavailable in the marine environment. Mercury, like most metallic elements, has low solubility with regards to certain physicochemical properties, including pH, salinity, potential redox, anionic concentration, type and character of ionic salts present in the water column, especially chloride and sulfide concentrations, and the presence of sulfur-reducing bacteria [47-49]. Moreover, aspects related to sediment type, size and texture, current speed and organic content concentration also influence metal solubility and complexation. Greater residence time and low transport speed enables deposition of suspended particulate material in sediments, where metal bioavailability becomes controlled by physicochemical factors.

Identification of sediment type at the mouth of the Amazon River, and in the continental shelf confirmed the assumption that metallic elements have a special association with clay, and that this association is enhanced in the presence of organic matter. Similarly, high Hg concentrations occurring naturally in soils of the Negro and Tapajós river basins and their release by way of

podzolization [10,50], allow spontaneous bioavailability of metals to aquatic ecosystems. Therefore, this explains why high mercury concentrations can be found in areas far removed from point sources of contamination, mainly mining. Likewise, the same arguments justify the particularly high mercury levels encountered in the inner shelf, an area which extends from Orange Cape to Maguari Cape and receives enormous quantities of fluvial sedimentation from the Amazonas and Pará rivers (Fig. 1).

The podzolization process is responsible both for movement dynamics and variations in metal concentrations, such as mercury, in horizontal and vertical soil profiles. The high total mercury concentrations found in Amazonian soils and sediments suggests that Hg origins and mobility are both directly related to erosion, transport and depositional processes. The Hg mass balance proposed (Fig. 6), which compares the results obtained in this study with a literature review, indicates the occurrence of naturally-produced mercury concentrations caused by destruction of the lateritic soil cover. In other words, the presence of Oxisols – Latosols in the Amazon basin may be the main Hg source for spodic horizons in podzols.

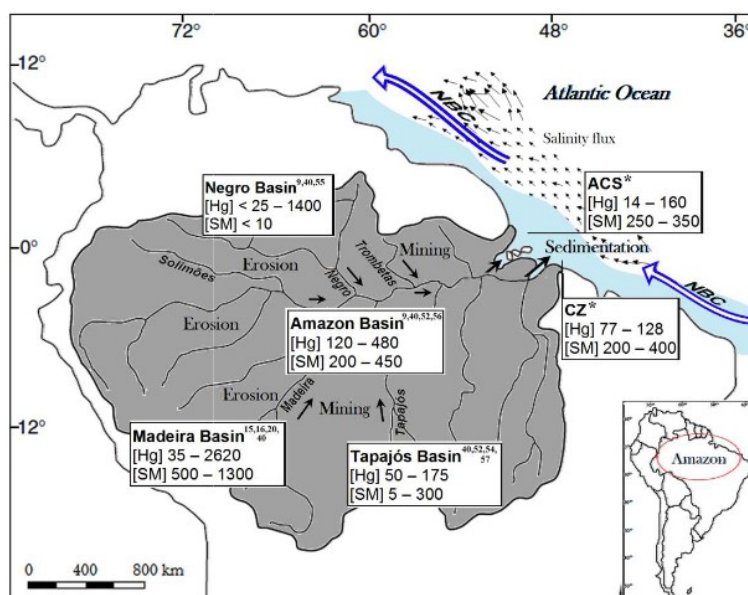


Fig. 6. Estimation of mass to total Hg (ng g⁻¹) in sediments and total suspended material (SM mg L⁻¹) of the Amazon River basin and ACS

Legend: gray color – Drainage basin = $7 \times 10^6 \text{ km}^2$ (Tardy et al. [1]). Data references: Roulet et al. [9,52]; Pfeiffer et al. [15,16]; Bastos et al. [20]; Lacerda et al. [40]; Cordeiro et al. [54]; Diniz [55]; Do Valle et al. [56] (in diverse soil fractions); Farella et al. [57]; this paper*

There is evidence that the main source of total mercury in the Eastern Amazon, including the Amazonas and Pará river estuaries, is of geochemical origins due to soil erosion in muddy river basins, with significant contributions from the Negro and Tapajós rivers as well. Additionally, current mining activities in the Madeira River basin in the Western Amazon cannot be overlooked, as they represent an important component of Hg accumulation in river sediments.

In the Tapajós River basin, Roulet et al. [51] determined that Hg concentrations from mining activity were insufficient to explain the high mercury levels found in soils. Furthermore, they determined that mining only contributed approximately 3% of total Hg found in the surface horizons of local soils. Since then, studies have further confirmed the existence of a large reservoir of natural Hg in the Amazon, and particularly in the Negro and Tapajós river basins [8,10]. However, anthropogenic activities associated with deforestation and human settlement are disrupting the natural mercury cycle, increasing surface erosion and Hg transport associated with fine soil particles to aquatic ecosystems, especially during the rainy season [52]. According to Molisani et al. [53], which investigated Hg concentrations in Sepetiba Bay and at the Paraíba do Sul river mouth, the main sources of total Hg in these ecosystems are the erosion processes associated to anthropogenic activities. There are many points of views on the main source of total Hg in the Amazonian, and more studies must be developed to understand the influence of fluvial discharge on Hg distribution and deposition in the coastal zone and ocean.

4. CONCLUSION

The results indicated high Hg concentrations in the Amazon Inner Continental Shelf, stretching from Orange Cape situated to the north of the Amazonas and Pará river mouths to Maguari Cape in the south. The increase of Hg in ocean sediments can be directly associated with discharge of muddy sediments from the Amazon River. Correlation analyses revealed a direct relation between mercury, organic matter and organic carbon concentrations, and with grain-size, indicating strong geological influence. Due to continued intense mining activity in some Amazonian rivers, it is necessary to implement further studies investigating mercury accumulation and deposition in the region.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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