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Intra and interannual variability in the Madeira River water chemistry and sediment load

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Abstract Concentrations of cations (Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+), anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) and suspended sediments in the Madeira River water were determined near the city of Porto Velho (RO), in order to assess variation in water chemistry from 2004 to 2007. Calcium and bicarbonate were the dominant cation and anion, respectively. Significant seasonal differences were found, with highest concentrations occurring during the dry season, as expected from the drainage of Andean carbonate-rich substratum. Interannual variations were also observed, but became significant only when annual average discharge was 25% less than normal. Under this atypical discharge condition, bicarbonate was replaced by sulfate, and higher suspended sediment concentrations and loads were also observed. Compared to previously published studies, it appears that no significant changes in water chemistry have occurred during the last 20–30 years, although differences in approaches and sampling designs among this and previous studies may not allow detection of modest changes. The calculated suspended sediment load reported here is close to the values presented elsewhere, reinforcing the relative importance of this river as a sediment supplier for the Amazon Basin. Seasonality has a significant control on the chemistry of Madeira River waters, and severe decrease in discharge due to anthropogenic changes, such as construction of reservoirs or the occurrence of drier years—a plausible consequence of global climate change—may lead to modification in the chemical composition as well in the sediment deliver to the Amazon River.

Keywords Amazonia · Madeira River · Rondonia · River water chemistry · Suspended sediment

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Introduction

The Madeira River is the largest tributary of the Amazon River, contributing about 16% of the Amazon discharge at Óbidos (Mortatti and Probst 2003). It is formed by the confluence of the rivers Beni (Bolivia) and Mamore (Bolivian-Brazilian border) at Villa Bella, Bolivia. In Brazil, it runs along the northwest of Rondonia state and enters the state of Amazonas, where it joins with the Amazon River, downstream of the city of Manaus. Porto Velho is the largest city along the Madeira's course, with a population of approximately 426,000 inhabitants (IBGE 2010).

Since the 1960s researcher have reported a large number of studies about Amazonian rivers, starting with assessments of discharge at the mainstem of the Amazon River (Oltman 1968; Sternberg 1975), followed by water classification schemes designed according to common physical and chemical features (Sioli 1968; Gibbs 1970; Stallard and Edmond 1983) and more detailed studies on several aspects of the structure and functioning of these systems (summarized by Sioli 1984 and McClain et al. 2001).

Interest in the chemistry of the Madeira River increased in the 1980s due to intensive gold mining and concerns about potential mercury contamination (Malm et al. 1990; Pfeiffer et al. 1991; Bastos et al. 2006), although its high sediment load and transport has also drawn attention (Gaillardet et al. 1997; Guyot et al. 2007). Fewer studies have focused on the chemical composition (Pessenda et al. 1986; Ferreira et al. 1988; Martinelli et al. 1988), and they were usually based on short sampling periods (1 or 2 years).

In the near future the Madeira water chemistry and sediment load might present yet unknown changes due to the construction of the Madeira Hydroelectric Complex, composed of four hydroelectric power plants, two of them in the Brazilian state of Rondonia—Santo Antonio and Jirau, nearby Porto Velho (Porto et al. 2005). Together these two power plants are designed to generate 6,450 megawatts (MW) of electricity, becoming the third largest hydroelectric complex in Brazil. Damming of rivers can have severe effects on the functioning of these systems (Tundisi 2005; Tundisi and Straškraba 1999).

Madeira headwaters are located in Andean region geology which is covered with sedimentary and metamorphic rocks (Stallard and Edmond 1983; Lyons and Bird 1995), carrying relatively high ionic concentrations and about 40×10^6 ton $year^{-1}$ of suspended sediment itself (Guyot et al. 1999), which corresponds to nearly half of the total suspended load transported by the Amazon River into the Atlantic Ocean (Latrubesse et al. 2005).

Hence, the main purpose of this study was to characterize major ion chemistry and sediment load in the Madeira River on a seasonal basis, in order to compare with previous studies. To achieve that goal, we measured the concentration of major cations (Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+) and anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}) and suspended sediment in the city of Porto Velho during the period between 2004 and 2007.

Study area and methods

Study area

The Madeira River is the largest tributary of the Amazon River, about 1,450 km in length (Bastos et al. 2006) if its tributary Beni is considered or 3,350 km if the headwaters of Mamoré River are included (Lyons and Bird 1995). According to the Brazilian National Water Agency (ANA), Madeira River basin area is about 1.4×10^6 km^2 whereas the drainage area until Porto Velho station is around 954×10^3 km^2, which corresponds to approximately 69% of the basin (http://snirh.ana.gov.br/snirh.asp). Other basin estimates, although similar, are reported by different authors elsewhere (Bastos et al. 2006, 2007; Dorea and Barbosa 2007; Latrubesse et al. 2005; Moreira-Turcq et al. 2003; Ferreira et al. 1988), with values spanning from 1.30 to 1.42×10^6 km^2.

The study was carried out in one transect between the two banks of the Madeira River (8°44′54″ S and 63°55′01″ W), about 2 km upstream of the city of Porto Velho, with one sampling at the middle of the river channel and another two equidistant from the margins (Fig. 1). Samples were taken biweekly between September 2004 and June 2005 and monthly from November 2005 to December 2007 with a total of 49 sampling dates. Similar multi-year uninterrupted time series are not common for the Amazon region, where usually most studies are based on short (Bonotto and da Silveira 2003; Biggs et al. 2004) or widely spaced (Richey et al. 1986; Martinelli et al. 1988; Roulet et al. 2001; Moreira-Turcq et al. 2003) sampling periods.

The Madeira basin has a humid tropical climate (Aw type, according to Köppen's classification), exhibiting a mean annual precipitation of 1,900–2,200 mm (Bastos et al. 2007; Moreira-Turcq et al. 2003). The wet season occurs between October and April, whereas the dry season goes from May to September (Rondônia 2010; Bastos et al. 2007; Liebmann and Marengo 2001).

Geological information regarding Madeira River basin is scarce, and most of studies use the

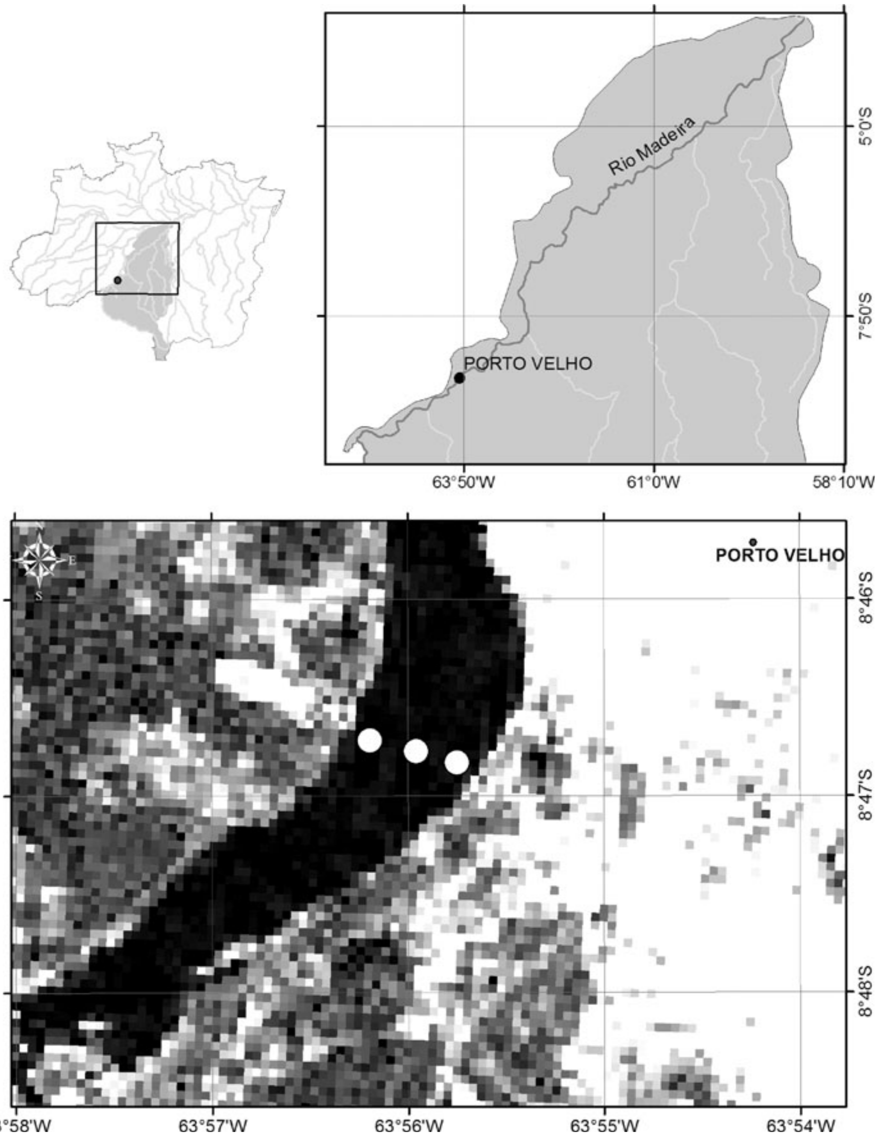


Fig. 1 Location of the studied site in Rondonia with three sampling locations within the Madeira River. Image obtained by Landsat-5 TM, band 5

classification described by Stallard and Edmond (1983), as Mortatti and Probst (2003), Elbaz-Poulichet et al. (1999), and Lyons and Bird (1995).

Briefly, both the important tributaries Mamoré and Beni start in Bolivia, draining approximately 75% Ordovician dark shales and sandstones with some carbonates (Lyons and Bird 1995). The Madeira also drains fluvio-lacustrine sediments and red beds that can contain dispersed evaporites. The southeastern portion of the drainage contains Precambrian metamorphic rocks (Stallard and Edmond 1983). In the other main tributary, Madre de Dios, there is also a predominance of carbonates and some evaporites (Barthem et al. 2003).

Bastos et al. (2007) divided the Madeira River basin into two different sections: (1) Upper Madeira River (between the confluence of the Mamoré and Beni rivers and Porto Velho city) running through pre-Cambrian and Cenozoic sediments, with rocky outbursts in its bed responsible for various waterfalls and rapids (Silveira et al. 2000); (2) Lower Madeira River (between the cities of Porto Velho and Itacoatiara), draining the Brazilian shield and the central plains (Moreira-Turcq et al. 2003).

The annual-averaged discharge (19×10^3 m^3 s^{-1}) was calculated based on a data series spanning from 1970 to 2007 and measured twice a day by CPRM—Brazilian Geological Service (available online at ANA website—http://hidroweb.ana.gov.br/), on a fluvial station 5 km from the sampling sites (named Porto Velho gauging station). In addition to daily measurements of river water stage, CPRM also performed periodical measurements of discharge using conventional current meter methods (area × velocity), in order to calibrate the station rating curve.

Field sampling and laboratory analysis

Fieldwork was performed with a small motorized boat, crossing the river (average width = 1,100 m) and stopping at each sampling site, at which a submersible pump was used to obtain samples from a standard depth (60% of total depth obtained at the staff gage and measured from the surface), as suggested by Hauer and Lamberti (2007).

Electrical conductivity, pH, and water temperature were measured using an Amber Science 2052 conductivity meter and an Orion 250A pH meter, respectively. In order to avoid gas exchange, the end of the tube from the pump was inserted at the bottom of a graduated flask on the boat and continuously flushed while probes were placed inside the same flask.

Using a 60 ml syringe aliquots were then taken and filtered in the field through PALL Supor-450 membrane filters (0.45 μm pore size), stored in HDPE flasks, preserved with thymol and kept cool prior to transport for analysis. Concentrations of major ions (Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}) and nutrients (NO_3^-, NH_4^+ and PO_4^{3-}) were determined with by ion chromatography (Dionex DX-500).

To check the accuracy of our analysis, every time a sample was run we also analyzed a certified water sample (Pérade-70, National Water Research Institute, Canada). The difference between total cations and anions given by the formula, $TZ^+ - TZ^-\ \% = 200(TZ^+ - TZ^-)/(TZ^+ + TZ^-)$ slightly exceeds 10%, indicating the presence of organic anions, which were not accounted for in this study.

Samples for dissolved organic and inorganic carbon (DOC and DIC) were collected concurrently with major ions. Triplicate DOC samples were collected by filtering water samples through ashed glass-fiber filters (Whatman GF/F, 0.7 μm nominal pore size), stored into 20 ml glass vials, and preserved in the field with mercury chloride ($HgCl_2$). DIC was analyzed using the same aliquot collected for major ions (preserved with thymol). DOC and DIC were determined in a Shimadzu total carbon analyzer (Model TOC-VCPH). DOC was measured on preserved samples after the extraction of DIC by acidification and sparging. DIC fractions (HCO_3^-, CO_3^-, and free CO_2) were calculated based on DIC concentrations, pH and temperature, using thermodynamic equilibrium equations (Stumm and Morgan 1996; Skirrow 1975).

Suspended sediment concentrations (SSC) were determined gravimetrically from another aliquot of water sample collected from the same pump. Using a churn splitter to homogenize the samples, 10 l of water were first passed trough a sieve to obtain the coarse fraction (>0.63 μm) and then filtered through membrane filters to obtain the fine fraction (<0.63 and >0.45 μm). Previously dried (to constant weight) and weighted cellulose acetate membrane filters (0.45 μm pore size) were used in triplicates for the fine fraction and in a single replicate for the coarse fraction.

Statistical analysis

A summary of data was performed by using descriptive statistics. Normal distribution was evaluated by Shapiro–Wilk's test (significance set to $p < 0.05$) using Univariate procedure of SAS (O'Rourke et al. 2005). Since data exhibited non-normal distribution and heteroscedasticity, Box-Cox transformation was used to achieve both homoscedasticity and normality, in order to proceed with parametric tests. Seasonality effects on solute and sediment concentrations was evaluated by two-way ANOVA ($p < 0.001$) which also allowed us to examine its interaction with the years. Pearson correlation was used to generate the matrix of correlations between variables. Statistical analyses were carried out using the software SAS® 9.2.

Results

Hydrological settings

Average discharge time series for years 2004–2007 at the CPRM station in the city of Porto Velho is illustrated in Fig. 2 (ANA 2009). In general, average discharge was remarkably lower in the first 2 years, with a deficit of 16% (2004) and 25% (2005) in relation to both the long-term series (1969–2007) and also for the two last years of this study (2006–2007), showing a mean discharge of 19 × 10^3 m^3 s^{-1}. Such differences can be attributed to the 2005 drought observed in the Amazon region (Marengo et al. 2008; Zeng et al. 2008).

The low-water phase typically occurred between August and October for all years (2004–2007), with a minimum discharge of 2.45 × 10^3 m^3 s^{-1} in September 2005. Rising water was observed from November to January, when river level increased continuously, particularly for the period 2006–2007. The high-water period (inundation) encompasses February to April reaching a maximum discharge of 42.6 × 10^3 m^3 s^{-1} in April 2007. The receding water takes place from May to July.

The monitored discharge of the Madeira River, based on daily measurements acquired from CPRM station, showed similar annual mean values (19 × 10^3 m^3 s^{-1} in Porto Velho) when compared with other previous studies such as Bastos et al. (2006) (23 × 10^3 m^3 s^{-1}), Guyot et al. (1999) (18 × 10^3 m^3 s^{-1} at the Brazilian/Bolivian frontier), Dorea and Barbosa (2007) (32 × 10^3 m^3 s^{-1} at the Madeira's mouth), Moreira-Turcq et al. (2003) (31.2 × 10^3 m^3 s^{-1} at the Madeira's mouth), and Richey et al. (1986) (25.4 × 10^3 m^3 s^{-1} at the Madeira's mouth) but different than the value reported by Martinelli et al. (1989) (31.3 × 10^3 m^3 s^{-1} in Porto Velho). This discrepancy could result from the fact that Martinelli et al. (1989) made only six measurements of discharge in their study.

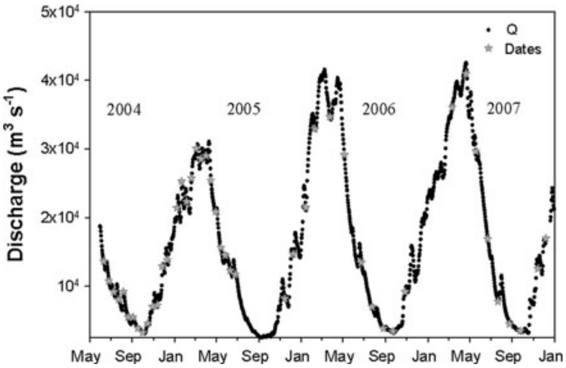


Fig. 2 Daily discharge (Q) and precipitation (P) at the CPRM station in Porto Velho city between May 2004 and December 2007. *Stars* correspond to the sampling dates

Overall water chemistry

A total of 142 water samples were collected in the period 2004–2007 in the Madeira River at Porto Velho city. Of these, 35 samples were obtained during base flow condition, 31 during rising water, 36 at the peak discharge, and 40 during the recession limb.

Transverse measurements made along the Madeira River ($n = 3$) revealed a good homogeneity of the water masses in regard with the different parameters (both physical and chemical), indicating that the mixing of the river water at this sector is fairly complete. Results were analyzed using one-way ANOVA, between subjects design. This analysis revealed no significant effect of site location (along the transect) for all solutes and both coarse and fine suspended sediments (Table 1).

Since river sections (center and left/right margins) did not show significant differences for all measured variables, daily mean values were calculated for each sampling day, assuming the three available results (sampling sites) as replicates.

Table 1 Obtained statistic (F) and probability (p) value for one-way ANOVA (between subjects design) used to determine whether there was a difference among three sampling sites in relation to several water samples variables

Variable	F value	Pr > F
HCO_3^-	$F(2,126) = 0.04$	0.96
Cl^-	$F(2,126) = 0.16$	0.85
SO_4^{2-}	$F(2,126) = 0.53$	0.59
NO_3^-	$F(2,126) = 1.29$	0.28
Na^+	$F(2,126) = 0.56$	0.57
K^+	$F(2,126) = 0.52$	0.59
Ca^{2+}	$F(2,126) = 0.10$	0.90
Mg^{2+}	$F(2,126) = 0.78$	0.46
DIC	$F(2,126) = 0.09$	0.91
DOC	$F(2,126) = 0.45$	0.64
FSS	$F(2,132) = 2.42$	0.51
CSS	$F(2,119) = 1.02$	0.36
TSS	$F(2,126) = 2.38$	0.10

$p < 0.05$ indicates significant differences from at least one river sector in relation to the others

Table 2 Physical–chemical variables and dissolved and suspended load of Madeira River waters near Porto Velho city, from 2004 to 2007

	2004			2005			2006			2007		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
EC	68.3	136.5	94.8	39.8	79.4	70.7	32.9	140.9	79.1	65.4	142.5	77.1
Temperature	25.8	30.3	28.6	25.9	28.7	27.3	27.4	31.7	28.5	26.7	29.7	28.0
pH	6.2	7.6	6.8	4.8	7.2	6.9	6.4	7.5	6.9	6.2	7.6	6.5
DOC	128.3	733.7	210.5	170.1	1024.2	436.7	135.7	534.7	370.9	190.6	547.0	351.1
DIC	78.9	624.8	211.3	247.5	505.7	381.1	376.6	862.0	500.9	400.7	1060.0	756.3
HCO_3^-	43.3	576.3	142.3	14.2	357.5	297.5	210.0	810.9	396.1	173.8	1002.2	518.9
Cl^-	4.5	54.3	11.9	11.7	21.3	14.7	8.6	47.3	15.1	4.9	74.9	29.7
NO_2^-	4.3	21.6	6.3	8.6	14.5	11.1	10.2	21.8	13.7	0.4	12.4	1.0
SO_4^{2-}	7.5	189.0	43.3	74.2	124.9	88.7	25.4	133.4	70.8	26.1	143.0	76.8
NO_3^-	0.6	16.6	4.2	6.9	14.9	9.4	1.9	14.5	6.6	3.1	18.2	9.2
PO_4^{3-}	na	na	na	na	na	na	1.0	2.4	1.7	0.9	1.2	1.1
Na^+	8.7	189.2	45.4	48.0	111.3	90.9	12.6	215.4	160.0	90.5	258.5	126.3
NH_4^+	0.1	4.8	0.3	0.9	7.5	3.9	na	na	na	2.2	2.2	2.2
K^+	2.0	30.9	9.3	25.9	40.0	31.1	6.3	58.8	34.8	30.1	51.4	39.0
Mg^{2+}	11.2	161.0	42.4	27.5	100.7	79.7	7.4	158.1	96.6	71.0	174.7	94.0
Ca^{2+}	55.4	270.9	100.2	39.5	188.7	122.6	13.4	236.3	135.0	108.1	293.9	132.4
FSS	36.9	578.4	208.6	174.7	1201.8	654.3	22.3	945.6	329.3	22.8	919.7	370.7
CSS	1.3	309.4	52.0	12.2	123.8	68.0	0.6	114.2	38.3	1.3	224.9	42.3
TSS	42.5	855.9	260.5	196.6	1299.0	717.8	23.0	1059.8	367.6	24.2	975.2	413.0

Solute data expressed in μM, suspended sediments in mg l^{-1}, electrical conductivity in μS cm^{-1}, and temperature in °C

Variations and averages in the chemical composition and suspended load of the Madeira River for the years 2004–2007 are shown in Table 2.

Electrical conductivity, or conductance, is the ability of a substance to conduct an electrical current, and several authors use this variable as an indicator of the total content of ions (and of dissolved inorganic components) on a given solution (Negrel and Lachassagne 2000; Meybeck 1986; Hem 1970). The Madeira River showed a mean annual value of 83.8 ± 23.6 μS cm^{-1}, and a large variation, ranging from 32.9 to 146.1 μS cm^{-1} for the entire period ($n = 146$), with the largest variation in 2006 (32.9–140.9) and the lowest in 2005 (39.8–79.4).

Stream water temperature showed a mean annual value of 28.0 ± 1.2°C ($n = 146$) ranging from 25.4°C to 31.9°C, with no significant differences among the years.

The dissolved organic carbon concentration exhibited a wide range from 128.3 to 1,024.2 μM and a mean annual value of 359.3 μM. The lowest variation was observed for both 2006 and 2007 and the largest in 2005.

These values are in agreement with the world average of 441.7 μM estimated by Meybeck (Berner and Berner 1996), evidencing a substantial organic content.

On a charge equivalence, HCO_3^- accounts for 54% of the total anions, its concentrations varying between 14.2 and 1,002.2 μM. HCO_3^- is followed by SO_4^{2-}, which accounts for 39% of the total anions, its concentrations varying between 7.5 and 189.0 μM.

Ca^{2+} and Mg^{2+} are the dominant cations accounting for 48 and 28% of the total cations. Ca^{2+} concentration ranges from 13.4 to 293.8 μM, while Mg^{2+} ranges between 7.4 and 174.7 μM.

Mean suspended sediment concentration during the study period was 402 mg l^{-1} at a mean discharge (Q_{mean}) of 19 × 10^3 m^3 s^{-1}. Maximum concentrations reached 1,645 mg l^{-1} under 30 × 10^3 m^3 s^{-1} during the March 2005 flood. The highest fraction of the suspended sediment was always the fine (<0.63

and >0.45 μm), comprising about 90% of the total suspended sediment for all studied years (Table 2), except for 2004, when only the 6 last months of data is available.

The remaining 10% corresponds to the coarse suspended sediment, and Guyot et al. (1999) attributed these low concentrations at this sector of the river to accumulation of suspended material delivered by the Andes at the transitional region at the Andean piedmont, which discharges only the fine particles toward the Amazon.

Discussion

General geochemical characteristics

The Madeira River may be chemically classified according to different schemes: (1) as white-water type, rich in suspended matter (>200 mg l^{-1}) with neutral pH values and moderate electrical conductivity (>40 μS cm^{-1}), accordingly to Sioli's classification (1950); (2) as a rock-dominated river type, as stated by Gibbs (1970); or (3) as an Andean-supplied river, draining metamorphosed dark shales, carbonates, red beds, andesitic volcanics, fluvio-lacustrine sediments, and some evaporites with $7{,}000 > TZ^{+} > 400\ \mu eq\ l^{-1}$, as suggested by Stallard and Edmond (1983).

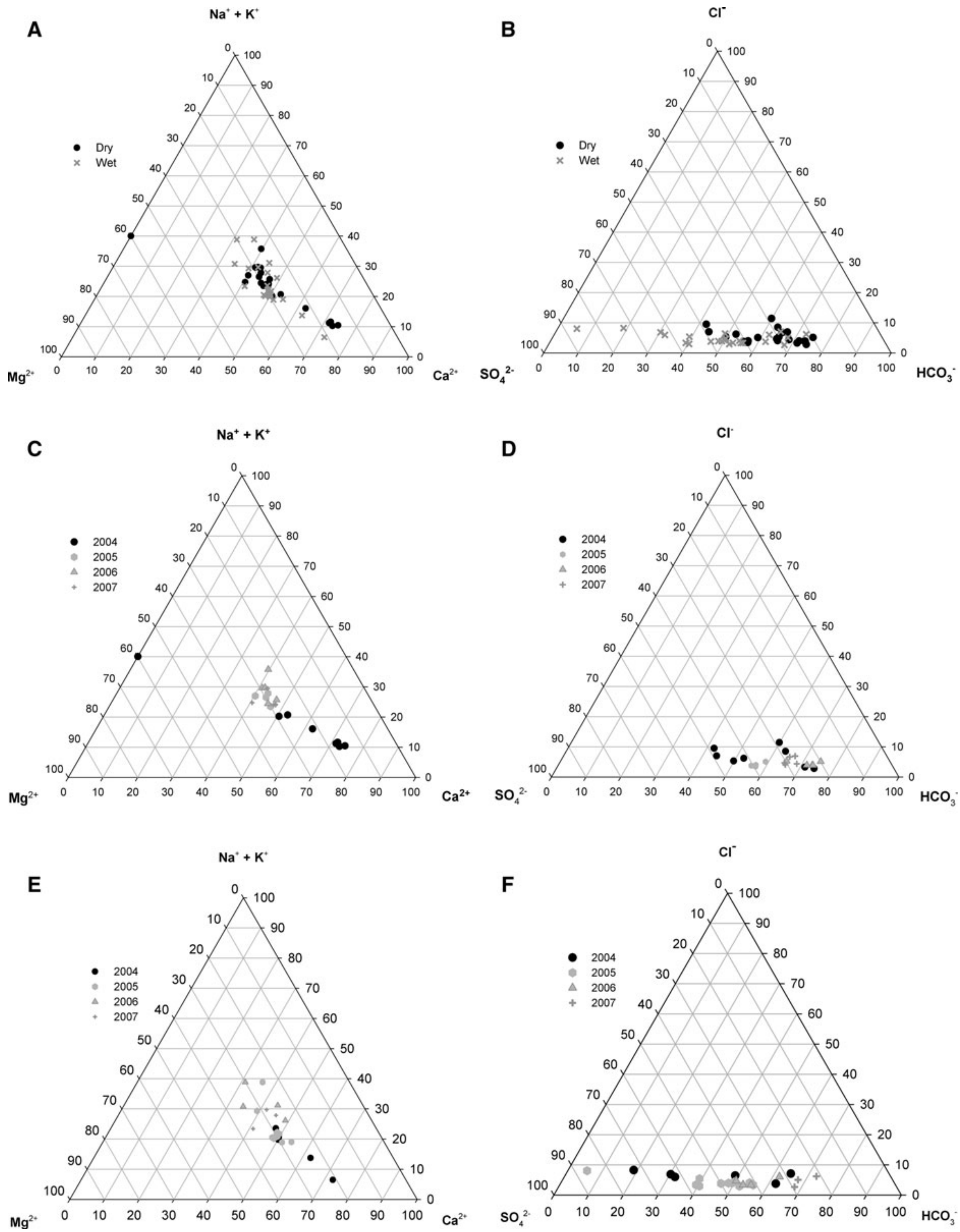
In general, most of the Madeira waters plot in the calcium bicarbonate field (Fig. 3), which represents 48% (Ca^{2+}) and 54% (HCO_3^{-}) of the sum of cations (TZ^{+}) and anions (TZ^{-}), respectively. However, the dissolved solid concentrations and the type of waters do not remain constant throughout the year, with highly variable and sometimes substantial contribution from SO_4^{2-} (Fig. 3). The fact that Na^{+} appears in higher concentrations than Mg^{2+} indicate that not only carbonates but also silicates are important sources of solutes in this basin (Stallard and Edmond 1983, 1987).

The concentrations of bicarbonate in the Madeira River showed strong association to calcium (Spearman rank correlation, $r_s = 0.63$) reflecting carbonate weathering in the upstream portion of the watershed. Mortatti and Probst (2003) and Ferreira et al. (1988) have found the same pattern for Madeira River waters at a station closer to its mouth (Urucurituba, Amazonas State), suggesting that this river still preserves the same chemical composition found at the headwaters as well as those observed here on a middle reach of its course (Porto Velho).

The importance of carbonate weathering in the Andes is also shown by a comparison between dissolved load of Madeira at Porto Velho with that of Beni River at Rurrenabaque (data available online at the Hybam Project website: http://www.ore-hybam.org/index.php/eng/). Beni River at this sector corresponds to only 7% of the basin, but contributes respectively with 35 and 26% of the dissolved load of SO_4^{2-} and Ca^{2+} measured at Porto Velho.

The constituent end-members for the ternary plots are chosen to reflect different processes within the watershed which have the potential to control the chemical composition of the Madeira River. For example, in the triangular diagrams for the major anions (Fig. 3), a straight line between the sulfate and bicarbonate apex indicates a mixture of two very distinct weathering sources such as carbonaceous rocks (bicarbonate) and evaporite sediments (sulfate). Chloride does not show significant contribution to total anions. For cations, dispersion is observed, but there are some trends in direction to calcium apex. This pattern indicates water with chemical composition resulting from a combination of different sources and origins (Drever 1997), as it should be expected in this reach of the river, which receives contributions from three major tributaries with Andean drainage and an unknown amount of less cation-rich waters from the lowlands.

Using these diagrams it appears that anion dominance is related to the season, with the drier period exhibiting a higher proportion of bicarbonate in relation to the wet season, which actually has a higher proportion of sulfate (Fig. 3b). This pattern of high bicarbonate in the dry season but a higher proportional contribution from sulfate in the wet season is much more evident when comparing years individually. For example 2006 and 2007, which exhibited discharges close to the long term average, showed a clear trend in the direction of the bicarbonate apex, for both dry and wet season, whereas 2005, which presented the highest discharge deficit (−25%) among the studied years, plotted closer to the bicarbonate apex at the dry season (Fig. 3d) but closer to sulfate apex during the wet season (Fig. 3f). This could result from changes in the relative importance of the dissolved load from each of the main tributaries and lowland drainage along the year,


A
Na+ + K+
Dry
Wet
Mg2+
Ca2+
B
Cl-
Dry
Wet
SO42-
HCO3-
C
Na+ + K+
2004
2005
2006
2007
Mg2+
Ca2+
D
Cl-
2004
2005
2006
2007
SO42-
HCO3-
E
Na+ + K+
2004
2005
2006
2007
Mg2+
Ca2+
F
Cl-
2004
2005
2006
2007
SO42-
HCO3-

◀ **Fig. 3** Ternary plots representing the relative abundance of cations and anions in the Madeira River. (**a** and **b**) corresponds to the entire 2004–2007 dataset presented by season; (**c** and **d**) and (**e** and **f**) represents dry and wet season data, respectively, presented by year. All units are in meq l^{-1}

as well as changes in the balance between atmospheric and weathering inputs.

Therefore, an interannual variability must be considered in addition to the seasonal variability, and atypical events, such as strong and prolonged dry periods (as observed throughout 2005), may lead to different chemical composition in this river.

From a comparison of the mean composition of the Madeira River as observed in this study (2004–2007) with the mean composition of several other studies (Mortatti and Probst 2003; Bonotto and da Silveira 2003; Mortatti et al. 1989; Ferreira et al. 1988; Stallard 1980), it appears that no apparent change in the bulk water chemistry has occurred, but it must be taken into account that available data result from studies with different approaches and levels of detail (Table 3). The results of Bonotto and da Silveira (2003) registered much higher values for all solutes than all other studies, but these results were based on only one sampling in August 1996, which comprises the drier period in Madeira's region where the highest solute concentrations are usually registered.

Overall, HCO_3^- is the dominant anion whereas Ca^{2+} is the dominant cation for all selected studies.

Seasonal trends in chemical composition and suspended load

Ion and sediment concentrations were related with discharge to calculate predictive regression equations (Table 4). The results indicate that all solutes and suspended sediment may be predicted by discharge, except nitrate.

There was a significant correlation between temperature and discharge (Spearman rank correlation, $r_s = 0.70$), with higher temperatures occurring in the drier months (September–November).

The Madeira waters were characteristically more basic during low water periods, with higher pH values (ranging from 6.3 to 7.6) than in high waters (4.8–7.4)

Table 4 Linear regression relationships between water chemistry variables and discharge at the Madeira River (Porto Velho, Rondônia)

Regression equation	R	R^2	p Value
EC = 323.968 − (58.637 log(Q))	0.76	0.58	<0.001
pH = 9.492 − (0.653 log(Q))	0.49	0.24	<0.001
HCO_3^- = 1602.548 − (311.875 log(Q))	0.47	0.22	<0.001
Cl^- = 115.767 − (23.102 log(Q))	0.53	0.28	<0.001
SO_4^{2-} = 214.010 − (32.312 log(Q))	0.25	0.06	0.003
NO_3^- = −1.791 + (2.558 log(Q))	0.15	0.02	0.078
Na^+ = 340.513 − (57.611 log(Q))	0.32	0.10	<0.001
K^+ = −26.038 + (13.512 log(Q))	0.29	0.09	<0.001
Mg^{2+} = 220.574 − (34.301 log(Q))	0.27	0.07	0.001
Ca^{2+} = 420.600 − (71.655 log(Q))	0.35	0.13	<0.001
DOC = −1103.803 + (373.246 log(Q))	0.17	0.03	0.044
DIC = 1372.343 − (228.470 log(Q))	0.32	0.10	<0.001
FSS = −2327.242 + (652.798 log(Q))	0.65	0.42	<0.001
CSS = −212.170 + (60.125 log(Q))	0.38	0.15	<0.001
TSS = −2534.774 + (711.492 log(Q))	0.66	0.44	<0.001

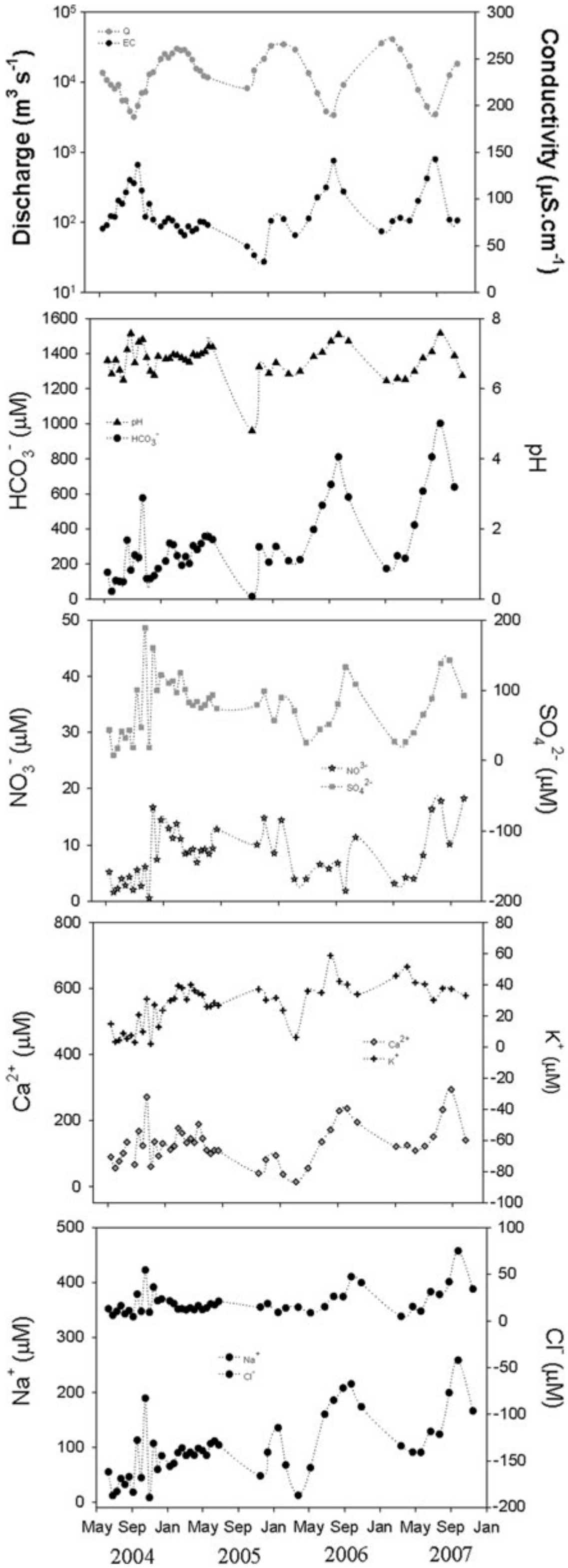
Q discharge, *EC* electrical conductivity, *DOC* dissolved organic carbon, *DIC* dissolved inorganic carbon, *FSS* fine suspended sediment, *CSS* coarse suspended sediment, *TSS* FSS + CSS

$p < 0.05$ indicates that the independent variable (Q) can be used to predict the dependent variable

Table 3 Comparison of major ion chemical composition in the Madeira River based on different studies

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-
This study	123.2	79.8	90.9	30.6	249.0	15.1	79.8	8.3
Mortatti and Probst (2003)	133.0	79.0	95.0	38.0	378.0	27.0	56.0	–
Bonotto and da Silveira (2003)	250.5	158.0	123.5	41.4	545.5	309.9	113.5	5.0
Mortatti et al. (1989)	173.9	99.6	109.6	38.3	–	–	–	–
Ferreira et al. (1988)	141.0	75.0	138.0	39.0	395.0	47.0	73.0	12.0
Stallard (1980)	139.7	8.2	113.1	40.9	636.4	22.5	58.3	–

All values in μM



◀ **Fig. 4** Variations in ion concentrations (*right y* axis) at the Madeira River between June 2004 and December 2007. All values are given in µM. The *upper line* indicates river discharge ($m^3\ s^{-1}$) at Porto Velho, expressed in logarithmic scale

(Fig. 4). The linear regression between discharge and pH confirm an inverse relationship between these variables (Table 4). However, when individual years are considered, this pattern is clearer in years when discharge was normal, exhibiting a higher correlation (Spearman rank correlation, $r_s = -0.92$ and -0.93, for 2006 and 2007, respectively).

Leite (2004) observed the same pattern of decreasing pH with increasing discharge in the Ji-Paraná River, the largest tributary of the Madeira in the state of Rondonia and which drains cation-rich soils on its central reaches (Ballester et al. 2003; Krusche et al. 2005).

This inverse relation was also observed for electrical conductivity, which had higher values during drier months, but no significant correlation with discharge in the atypical 2005 (Table 4). Higher pH and electrical conductivity during the low water period indicate a predominance of carbonate weathering in the Andean headwaters region of the watershed, which results in a relative increase in dissolved carbonates. During the rainy season, relatively more ion depleted and acidic precipitation and lowland drainage increase, changing water chemistry. This type of seasonal variations in water chemistry is common to many rivers in the world (Gibbs 1970; Hem 1970; Carbonnel and Meybeck 1975; Berner and Berner 1996).

Except for K^+, the relationships of discharge with ion concentrations were negative. Dissolved organic carbon, and suspended sediment exhibited an inverse trend, with concentrations increasing with discharge (Fig. 4).

Limiting nutrients, such as K^+ and dissolved inorganic N (NH_4^+) have an opposite pattern, with highest concentrations during the wet season, which indicates that precipitation and/or lateral exchanges with floodplains and terrestrial compartments are a significant component of the overall annual cycle of these elements in the Madeira River.

The processes controlling fluvial water chemistry are in agreement with those suggested by several

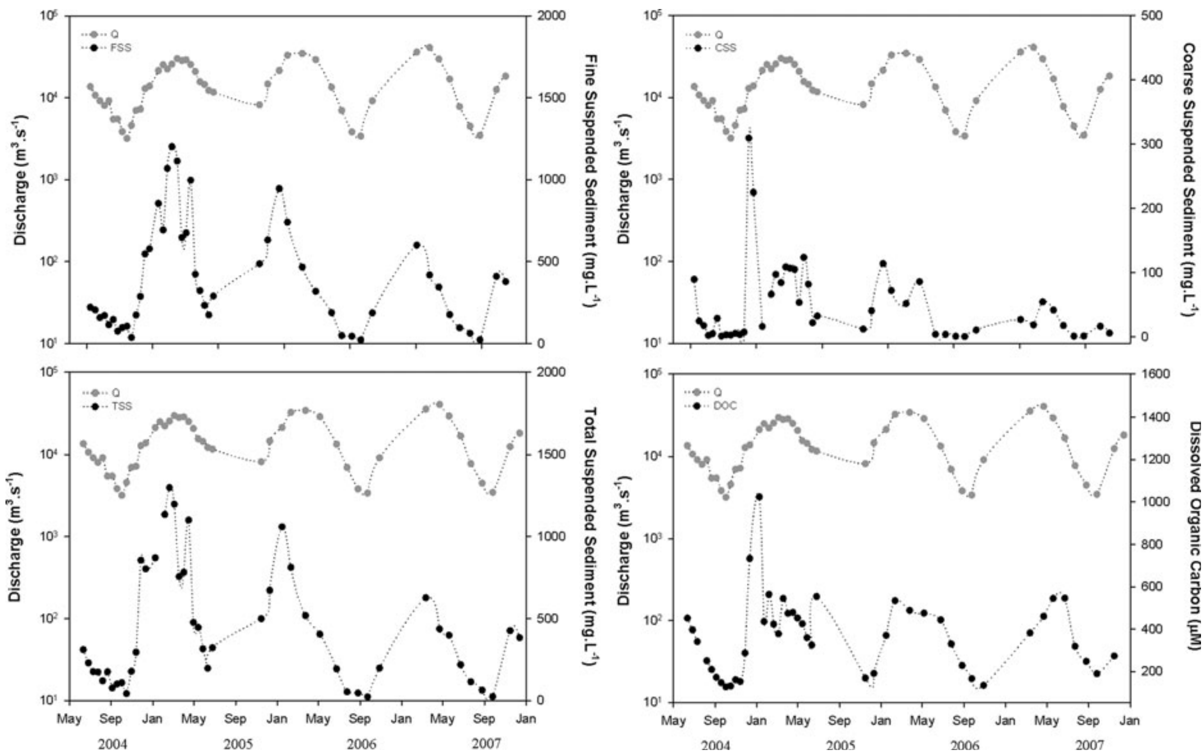


Fig. 5 Time of sampling versus suspended sediment and dissolved organic carbon concentration (*right y* axis) in Madeira water samples collected at Porto Velho city between June 2004 and December 2007. All concentrations are given in mg l^{-1}, except DOC in µM. The *upper line* indicates river discharge (m^3 s^{-1}) in Porto Velho (*left y* axis, note the logarithmic scale)

authors (Stallard and Edmond 1983; Markewitz et al. 2001; Williams et al. 2001), where the chemical composition is primarily controlled by the source of the input of major ions no matter whether they result from atmospheric precipitation, groundwaters or if they are supplied by the chemical weathering of underlying rocks and erosion processes.

Suspended load and transport rates in the Madeira River as compared to world rates

The pattern of increased suspended sediment concentrations during high water stage (Fig. 5) results from increased erosion upstream. Minimum concentrations were below 30 mg l^{-1} and were typically observed during baseflow (usually in the beginning of October).

Sediment load estimates for the Madeira River were based on the measured sediment concentrations, cross-multiplied with water discharge, for the period 2004–2007.

Regression of sediment load on water discharge for the 47 sampling dates (Fig. 6a) provided a rating curve (Power Regression, $r^2 = 0.89$; $s_\alpha^2 = 130 \times 10^3$, $s_\beta^2 = 6.9$) which was used to estimate daily sediment load. This is the most commonly used procedure for estimating suspended sediment concentration from discharge in the absence of actual SSC data (Horowitz 2003) and was extremely useful to fill missing dates, especially for some months in 2005 (July–October) and transitional 2006–2007 (Nov/2006–Feb/2007). The daily water discharge, obtained from CPRM station, was then used in conjunction with the rating curve to calculate the annual sediment load.

In the mainstem of Madeira River the calculated suspended sediment load (Q_{ss}) for the period 2004–2007 was 319 × 10^6 ton $year^{-1}$ (standard error = 482 × 10^3), with a mean discharge of 19 × 10^3 m^3 s^{-1} and a mean suspended sediment concentration of 446 mg l^{-1}.

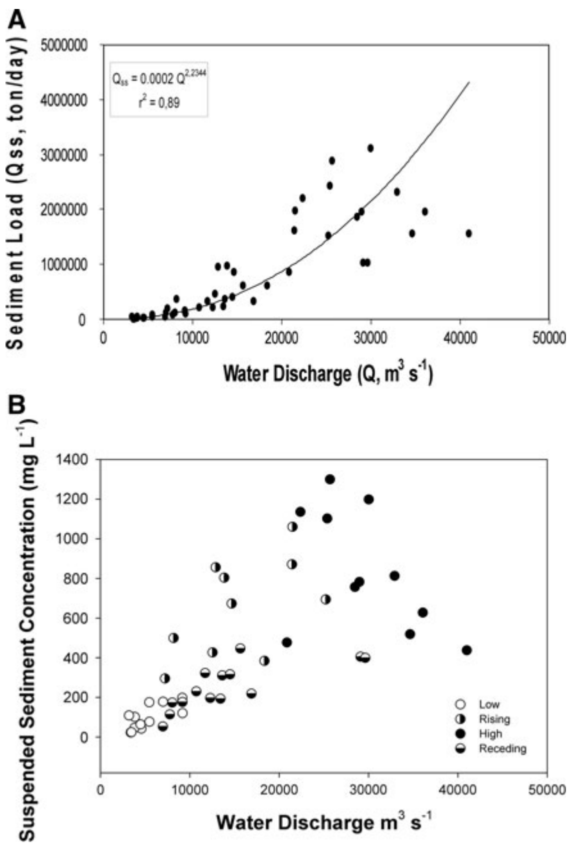


Fig. 6 Based on dataset sampled in Madeira River at Porto Velho during 2004–2007 period ($n = 47$), we chart: **a** Measured sediment load (Q_{ss}, ton day^{-1}) versus measured discharge (Q, m^3 s^{-1}); **b** measured sediment concentration (mg l^{-1}) versus measured discharge (Q, m^3 s^{-1}) showing distinct periods of the annual hydrograph

Table 5 presents a comparison of suspended sediment concentration and load for several studies in the Madeira River. The mean suspended sediment concentration is close to the value presented by Guyot et al. (1996), slightly higher than Filizola and Guyot (2009) but much lower than observed by Martinelli et al. (1993), although the value presented by the latter author is based on only two sampling dates.

The distinct stages of hydrograph indicate that seasonality between suspended sediment concentration and river water discharge in the Madeira River forms a clockwise loop or hysteresis (Fig. 6b). According to Meade (1994), this pattern is very well defined being characteristic of the hydrological regime of the largest Amazonian rivers. It could also in part explain differences in sediment load estimates for this river, since the sediment concentration is very variable for similar discharges at similar stages. For example, at rising stage (range between 10×10^3 and 15×10^3 m^3 s^{-1}, the concentration can oscillate between ~350 and 900 mg l^{-1} (Fig. 6). During high stage in the range between ~28×10^3 and ~32×10^3 m^3 s^{-1} the concentration can range between 1,300 and 500 mg l^{-1} (Fig. 6). The concentration values are in the order of more than 100% variability for the same range of discharges. That can partially explain the high variability in the results provided for different authors when calculating the total sediment transport applying a correlation curve (discharge-transport).

Conclusions

An updated database shows that over the last three decades no change in the chemical composition was detected for Madeira River in comparison with previous works, given the various in sampling regime across studies.

Table 5 Comparison of suspended sediment loads in the Madeira River based on different studies

Location	Period	Q ($\times 10^3$ m^3 s^{-1})	TSS (mg l^{-1})	Q_{ss} ($\times 10^6$ ton year^{-1})	Reference
PVH	2004–2007	19.0	450	319	This study
PVH	Feb/1978–Aug/2000	19.4	165	277	Filizola and Guyot (2009)
PVH	1978–1993	20.1	483	306	Guyot et al. (1996)
PVH	Apr/1984	41.7	791	1022	Martinelli et al. (1993)
PVH	Jan/1986	20.9	1700	1105	Martinelli et al. (1993)
Mouth	Average (1982–1985)	29.2	627	488	Martinelli et al. (1989)
Mouth	1977	40.0	330	396	Meade et al. (1979)
Mouth	na	31.4	na	157	Gibbs (1967)

A relatively large number of measurements in the current study also reinforce the earlier assessment of a strong seasonal pattern in suspended sediment load.

Seasonality further appears to have a significant control on the chemistry of the Madeira River. The current study is unique, however, in showing the role of discharge to be critical not only seasonally but interannually with the drier-than-normal year of 2005 presenting different anion distribution relative to 2006 and 2007, which had discharges closer to long-term averages. Severe decreases in discharge, natural or anthropogenic based, may lead to modification in the chemical composition as well as in deliver of sediment toward Amazon River, with yet unknown consequences in river functions.

This study presents important information having the potential to serve as background in future works evaluating the impacts of the installation of hydro-electric power plant complex in the Madeira River. For example, fine suspended sediments carry adsorbed carbon and nutrients such as amino-acids that can be important for food webs downstream, decreases in suspended sediments concentrations can favor light penetration in water, enabling enhanced phytoplankton growth, changes in chemistry might change microbial loops, all affecting fisheries on which Indian and riverine populations depend.

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