Environmental Pollution 235 (2018) 771–779

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Distribution and availability of mercury and methylmercury in different waters from the Rio Madeira Basin, Amazon☆

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ARTICLE INFO

Article history:
Received 22 May 2017
Received in revised form
17 November 2017
Accepted 8 January 2018

Keywords:
Mercury
Methylmercury
Amazon
Sediments
Water color
pH
Plankton

ABSTRACT

Waters from the Amazon Basin have distinct physicochemical characteristics that can be optically classified as "black", "clear" and "white". We studied the distribution of total-Hg (THg) and methyl-Hg (MeHg) in these waters and respective suspended solids, sediment, phytoplankton, zooplankton, and benthic macroinvertebrates (BM) in the Madeira River Basin. Compared with the other types of water, the more acidic "black" kind had the highest THg and MeHg concentrations. The trend (black > clear > white) occurred for the concentrations of THg and MeHg in sediments and in the biotic compartment (plankton, macroinvertebrates). Organic Hg accounted for a small percentage (0.6–0.4%) of the THg in sediments but was highest in water (17–15%). For plankton and BM, the biota sediment accumulation factor (BSAFs) of MeHg (53–125) were greater than those of THg (4.5–15); however, the BSAF trend according to water type (black > clear > white) was only significant for MeHg. Sediment THg is correlated with all forms of Hg in biotic and abiotic matrices. The results indicate that water acidity in the Amazon is an important chemical characteristic in assessing Hg contamination of sediments and bioaccumulation in the aquatic food web. The differences in the BSAFs between THg and MeHg support the use of this factor for evaluating the bioaccumulation potential of sediment-bound Hg. The results add information critical to assessing environmental and health risks related to Hg methylation and potential fish-MeHg contamination, especially in tropical aquatic environments.

1. Introduction

The Amazon rain forest has an exceptionally complex aquatic environment, which is readily recognized by the optical classification of its water bodies as "black", "white", and "clear" (Sioli, 1950; Gragson, 1992). These optical characteristics impart certain biophysicochemical properties (Furch et al., 1982) that are linked to the bio-geo-chemical origin (Gibbs, 1967) and to the drainage of the river basins (Lechler et al., 2000). These types of water have different chemical (pH, Eh) conditions, content of organic matter, and suspended solids (Fadini and Jardim, 2001; López-Siangas et al., 2012).

"Black" waters have pH below 4.0, very low suspended solids, and low dissolved element concentration (Junk and Furch, 1980, 1985). The reason for the dark coloration of the water is the presence of soluble organic matter (Sioli, 1965). Vegetation influences the chemical composition of this water type (Sioli, 1968). "Clear" waters are found where relief is more regular, thus possessing low erosion and low transport of clay sediments (Santos and Ribeiro, 1988). They can have a visibility of more than 4 m (transparency) and pH between 4.0 and 7.0 (Irion, 1984). In the "white" water there are abundant suspended solids, and pH close to neutral. The white waters of Western Amazon have suspended sediment concentration and dissolved Andean salts and sediments eroded by the river channel (Sioli, 1968). Chemical conditions in acidified lakes seem to favor Hg methylation, allowing Hg to be bio-accumulated as methyl-Hg (MeHg) (Watras et al., 1995). Therefore, physical and chemical compositions of these waters modulate their optical

☆ This paper has been recommended for acceptance by Dr. Harmon Sarah Michele.

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https://doi.org/10.1016/j.envpol.2018.01.020
0269-7491/

difference. These types of water are important factors in the availability and mobilization of metals and Hg (Furch, 1984), including Amazonian rivers (Maurice-Bourgoin et al., 2003).

Environmental Hg in the Amazon rain forest is mainly from natural sources (Fadini and Jardim, 2001) such as geochemical characteristics of soils, biological decay, and to a lesser extent anthropogenic inputs from artisanal gold mining in some rivers. The sources of Hg in the Western Amazon are mainly from the atmosphere (Lacerda and Pfeiffer, 1992; Hacon et al., 1995), transported by suspended solids in the waters from the Andes (Meade, 1994; Maurice-Bourgoin et al., 2000, 2003; Galvão et al., 2009), and the stock of the naturally enriched soils (Roulet et al., 1998). In addition, there are anthropic sources such as gold-mining operations, deforestation and forest fires (Martinelli et al., 1988; Lacerda and Salomons, 1998; Malm, 1998). In the aquatic environment, Hg is readily bound by particulate matter and deposited into bottom sediments. This compartment serves as a natural sink where most of the methylation occurs, thus regulating the amount of MeHg that goes into the aquatic food web.

In the sediments of water-bodies (streams, rivers, and lakes), Hg is methylated mainly by bacteria, thus becoming bioavailable to be accumulated and magnified by species throughout the structure of the aquatic food webs (Compeau and Bartha, 1985; Rudd, 1995; Baeyens et al., 2003; Siqueira and Aprile, 2012). Sediments provide the ideal ecological habitat for a number of organisms, including benthic macroinvertebrates (BMs) (Pisanello et al., 2016). Sediments are the main reservoir of Hg in freshwater systems, providing stability to Hg dynamics (Ullrich et al., 2001). In the Amazon waters they represent the main environmental compartment for the production and bioaccumulation of MeHg (Brito et al., 2017). However, the concentrations of total-Hg (THg) in waters may not represent the immediate risk of contamination which is specific to its bio-accumulative and toxic chemical form – MeHg (Chapman et al., 2013). Methylation of Hg and MeHg bioavailability factors depend on local environmental conditions (Ehlers and Loibner, 2006; Xu et al., 2007).

Plankton (phyto- and zooplankton) plays an important role as primary consumer and is responsible for the transfer of Hg (as MeHg) to the higher levels of the trophic web during the biomagnification process (Back et al., 1995). The BMs can be considered as the link between the intermediate trophic levels and the top of the food chain (Browder et al., 1994) and can serve as food for fish and birds (Ponyi, 1994; Paterson et al., 2006; Edmonds et al., 2012). The BMs are part of several food chains leading to several trophic levels, thus becoming an important biomarker of pollutant contamination (Buckland-Niks et al., 2014). Bioaccumulation of Hg results from its trophic transfer through the aquatic food web; therefore, predictive factors become central in Hg contamination and risk assessment. In the Amazonian ecosystem, interactions of Hg between water and sediments are complex, and little is known regarding the different types of waters. Therefore, biota-sediment accumulation factors (BSAF), as proposed by Ankley et al. (1992), were used in this study.

BSAF is defined as the ratio of the concentration of Hg in an organism to that in the sediment of the studied waters. This is a good algorithm, useful for interpreting the Hg and MeHg accumulation patterns in these complex aquatic environments. Burkhard (2003) tested the BSAF performance in several simulations to evaluate the underlying factors, such as number of samples, temporal variation, spatial variation, metabolism of organisms, and the structure of the trophic web.

The Rio Madeira is formed in Peru and Bolivia and runs through the Brazilian Amazon. Its main tributaries are: Madre de Dios (Peru), Mamoré and Beni (Bolivia) and Guaporé (Brazil) (Fig. 1). In addition to their large dimensions, their headwaters are located in the Andes, where we find sedimentary and metamorphic rocks, and later cross ancient areas of the Amazon Craton with granite rocks and enter the Amazon Basin (Bonotto and Vergotti, 2015). The predominant soils in the study area are the *Argissolo* (Ultisols), *Latossolo* (Oxisols) and *Plintossolos* (Plinthic Oxisols), all of which are dystrophic haplotypes (IBGE, 1977). The cover vegetation of the Madeira River basin corresponds to open and dense lowland rainforest and the "*cerrado*" (savanna vegetation) covering most of the basin.

Furthermore, the Rio Madeira Basin presents distinctive physicochemical characteristics and has a recent history of gold-mining activities and hydroelectric dams along its tributaries (Fig. 1). Its main course is mostly "white" water from the Andean piedmont, running through sedimentary and metamorphic rocks (Gomes et al., 2006; Queiroz et al., 2011). Clear waters are found in ancient formations such as areas of the Shields (Irion, 1984). Previous studies have shown calcium-bicarbonate, bicarbonate, sodium-potassium-bicarbonate and sodium-potassium-sulfate compositions, resulting in low acidity (Queiroz et al., 2011).

Therefore, we took advantage of finding the three types of optically identifiable waters ("black", "white", and "clear") in the same river basin to measure entry of Hg (THg and MeHg) into the food chain interface (water, SS, and sediments) and in the food web basic-trophic-levels (plankton and BM).

2. Materials and methods

2.1. Study area

The study area is located in the Madeira River, which has a geologically and geographically complex basin. The map in Fig. 1 illustrates the 20 sites representing the three types of water. The data collection was carried out on 18 occasions over four consecutive years (2009–2012). We sampled four times during the hydrological seasons of drought, flood, full and ebb. Sampling of water, suspended sediments (SS), bottom sediment (BS), planktons (phyto- and zoo-), and BMs occurred 360 times representing black water (54 samples) in the rivers Castanho (P9), Mutum Paraná (P10), and Foz do Mutum Paraná (P20). There were 144 samples for clear water in the rivers Mamoré (P1), Araras (P3), Abunã (P4), Simãozinho (P6), São Simão (P7), Cotia (P11), São Lourenço (P13), and Caiçara (P14). For white water there were 162 samples distributed in the Madeira (P2, P5, P8, P12, P15, P16, P19, P20) and Jirau (P17) Rivers.

2.2. Sample collection

2.2.1. Water

At the time of water sampling, the pH monitoring was done with in Horiba multi-parameter probe (Kyoto, Japan). Precautions were taken in order to avoid contamination during sampling; bottles of polyethylene terephthalate (PET) commercialized for mineral water were used following the recommended procedure of Fadini and Jardim (2001). The bottles were washed several times at the sampling site and filled up to 10 cm below the surface. The water samples were collected, properly identified, and conditioned with nitric acid solution (65% ultra-pure HNO3, Merck), maintaining the pH of the sample lower than 2.0 until the time of analysis according to the Environmental Protection Agency recommendations (EPA, 2002). The samples intended for MeHg determination were extracted according to laboratory protocol (Bisinoti et al., 2007).

2.2.2. Suspended sediment (SS)

Samples of SS were obtained from sub-surface water (about 20 cm depth) collected in 5-L polyethylene bottles and kept under

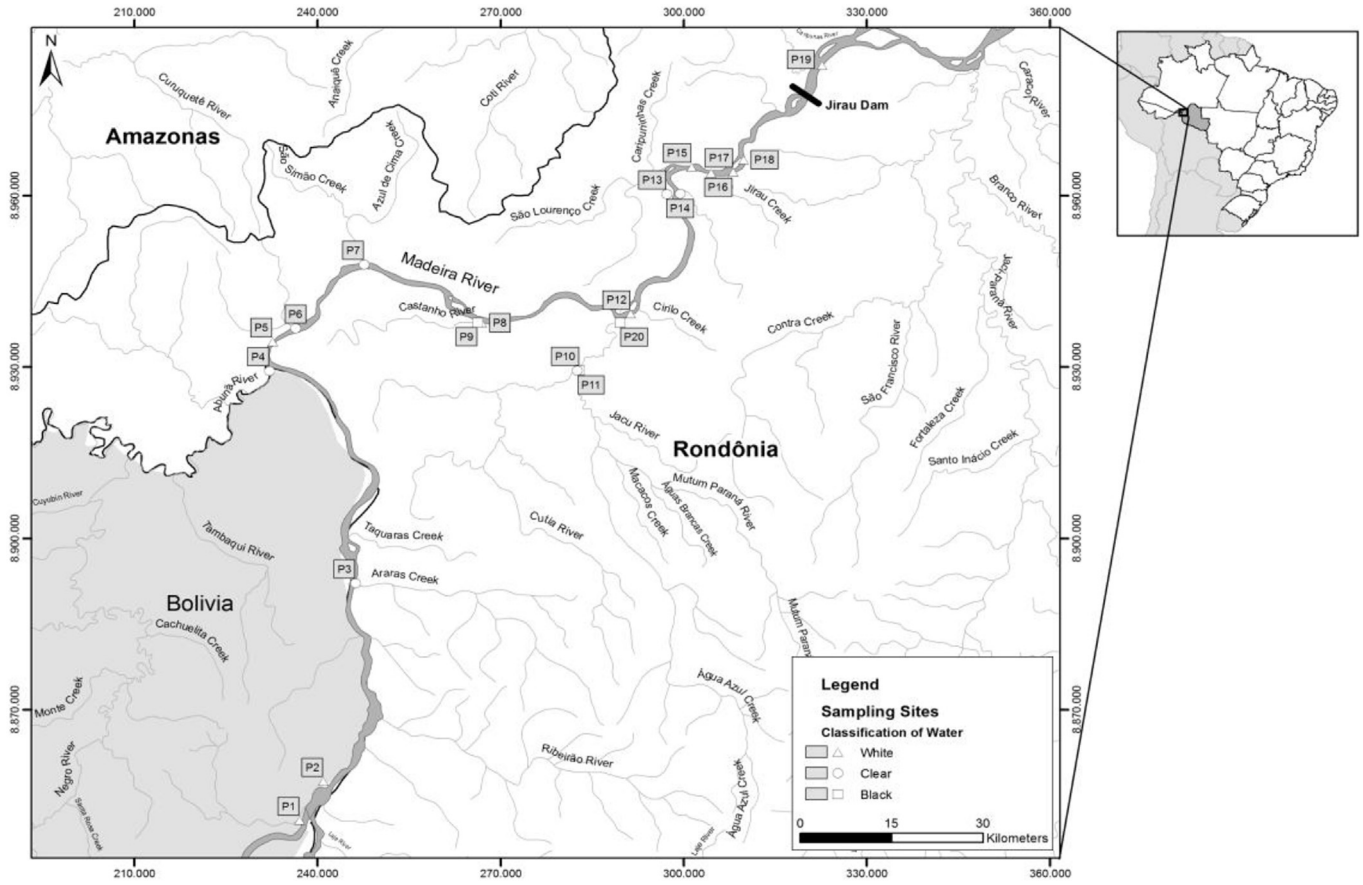

Fig. 1. Map showing projected coordinates of the sampling locations.

refrigeration. In the laboratory, the SS was filtrated through glass fibers of 0.45 μm (GF/C), and weighed to determine the mass of particulate material retained in the filters; the filters were subjected to chemical extraction for MeHg determination.

2.2.3. Bottom sediment (BS)

The bottom sediment samples were collected using the Eckman dredge which allows harvesting the most reactive sediment layer. After collection, the samples were conditioned in polyethylene bags and sent to the laboratory and kept cool (4 °C) until sample preparation and chemical analysis.

2.2.4. Phytoplankton and zooplankton

Two plankton nets (1 m × 30 cm) were equipped in a boat to haul (3 km/h) horizontally the water surface for about 5 min. The plankton samples collected with a 20 μm mesh net for phytoplankton and a 70 μm mesh net for zooplankton. The planktons (5 L) from both nets were packed in polyethylene bottles. Samples were identified in the field, taken to the laboratory and stored at 4 °C until time of preparation and chemical analysis.

2.2.5. Benthic Macroinvertebrates (BMs)

The BMs were collected from the water column and from the surface of the bottom sediment. In a depth of approximately 1 m, a 250 μm mesh net was used in order to capture the surface of water column and the surface of the bottom sediment. The surfaces of the bottom sediment in deep waters were sampled with a Eckman dredge. When appropriate the samples were sieved to separate the BMs from the macrophites, leaves, and litter. Samples were identified in the field, taken to the laboratory and stored at 4 °C until the time of analysis.

2.3. Sample treatment and mercury determination

All glassware used for both sample storage and analyses was submitted to rigorous cleaning procedures that included acid washings and milli-Q (Millipore) water rinsing. Before analysis all samples were chemically extracted for organic Hg determination. The procedure for organic Hg extraction is based on acidification with 10% (m/v) HCl followed by step wise CH_2Cl_2 extraction and back-extraction into water. Total mercury (THg) represents the sum of all mercury species present in the analyzed samples.

Determination of mercury (inorganic and MeHg) in all matrices (SS, BS and water samples) was done according to the routine laboratory protocol in the Department of Chemistry (Laboratory of Environmental Chemistry in Araraquara, at UNESP, São Paulo, Brazil). Analytical results were run in duplicate, and blanks were prepared as appropriate to check any contamination. The coefficient of variation between replicates was 5 to 10%, and the accuracy was determined through validated standards (NIST 1646a). The detection limits for THg and MeHg were 0.1 and 0.002 $ng.L^{-1}$ for water, and 0.2 and 0.0002 $ng\,kg^{-1}$ in sediments respectively.

2.3.1. Abiotic samples

The THg concentrations followed the procedure described by Bisinoti et al. (2007); it starts with the determination of reactive Hg (all Hg species) which can be reduced by $SnCl_2$. 100 mL of water samples were placed in a bottle and added with 2 mL of 10% (m/v)

$SnCl_2$ solution. Briefly, THg was determined according to the adapted EPA method 1631 (EPA, 2002). The formed Hg is stripped out with argon and trapped. The quantification was done using fluorescence spectrophotometry coupled to the system of cold vapor generation and gold pre-concentration (CVFAS). Total mercury (THg) represents the sum of all mercury species.

The extraction and quantification of organic Hg from water samples is done with 10% (m/v) HCl followed by CH_2Cl_2 extraction and back-extraction (Bisinoti et al., 2007). The MeHg quantification was done by gas chromatography in a Shimadzu model GC-14 B equipped with an electron-capture detector (ECD) (Shimadzu Corporation, Japan).

Hg determination in both sediments (SS and BS) was preceded by the extraction of organic Hg. The procedure for THg described in Bisinoti et al. (2007) is carried out in a 1–2 g of sediment sample mixed in a 10 mL of MilliQ water, and then added with 5 mL of concentrated H_2SO_4, 2.5 mL of concentrated HNO_3 and 15 mL of 7% (m/v) $KMnO_4$ solution. The mixture is put to rest for 15 min and added with 10 mL of 8% (m/v) potassium persulfate solution, and heated for 2 h at 80 °C and left to cool to room temperature. The excess of permanganate was eliminated with 6 mL of 15% (m/v) $HONH_2 \cdot HCl$ solution. Then the final volume was adjusted to 50 mL with ultrapure water. Sediment samples were analyzed on a wet basis to avoid losses associated with drying. THg was quantified by the fluorescence spectrophotometry coupled to the EVA 1631 (adapted) gold column (CVAFS) cold vapor pre-concentration system (EPA, 2002).

The determination of MeHg was described by Bisinoti et al. (2007) and involves digestion with KOH 25% (m/v) solution in alcoholic medium, extraction with dithizone-toluene and quantification by gas chromatography in a Shimadzu model GC-14 B equipped with an electron-capture detector (ECD) (Shimadzu Corporation, Japan). THg was calculated as the sum of concentrations of inorganic and MeHg.

2.3.2. Biotic samples: planktons and BMs

The samples were digested following Bastos et al. (1998) and the determination of mercury (THg and MeHg) according to an analytical method developed and validated for biotissue. Aliquots of the biotic sample (planktons or BMs) were extracted and processed for MeHg and for THg determination respectively. BMs were digested following the methodology described by Malm et al. (1989) and THg quantified by the fluorescence spectrophotometry coupled to the EPA 1631 (adapted) gold-vapor pre-concentration (CVAFS) system. The determination of MeHg was done according to the methodology described by Bisinoti et al. (2007), involving digestion, dithizone-toluene extraction and quantification by gas chromatography (Shimadzu Corporation, Japan) as described for the abitotic samples.

2.4. Biota sediment accumulation factors (BSAFs)

The magnitude of bio-accumulation of each Hg form of was evaluated through the BSAFs calculated as follows: BSAF = [Hg] in organism/[Hg] in each type of aquatic environment after Ankley et al. (1992). Hg concentrations refer to THg and MeHg in organisms (phytoplankton and zooplankton and BMs).

2.5. Statistical analysis

The Kolgomorov-Smirnov test was used to check the normality of the variables in order to define the hypothesis test to be used in the groups; the data were not normally distributed. The Kruskal-Wallis ANOVA by Ranks test was chosen to compare the concentrations of Hg, MeHg and BSAF of the taxa in different types of water. The *post-hoc* Bonferroni was run to identify which of the groups (water) differed among themselves for the measured variables (Statistica Version 10). To infer the interactions of variables (species) of Hg the Spearman correlation was used for each group of waters. Statistically significant differences were accepted at $p \leq .05$.

3. Results

Results of Hg chemical species (THg and MeHg) are shown in Table 1 for all types of water. Black water showed more acidity than the other types. Although THg and MeHg concentrations showed variation, there was a noticeable pattern in relation to the water classification (black > clear > white). Overall, the highest concentrations for all variables were found in black water, except for the SS-THg and sediment-THg, which had the highest THg concentrations in white water and clear water, respectively. The statistical significance was found for SS-THg, sediment-THg and sediment-MeHg, phytoplankton-THg, and phytoplankton-MeHg, zooto-plankton-THg, and zooplankton-MeHg, and BM-MeHg (Table 1). However, no significant difference was found for BM-THg among the water types. In all compartments the Hg was mainly in the inorganic form; the greatest proportion of MeHg was found in water (mean percent ranged from 17 to 15%), whereas in sediments the mean MeHg proportion of THg (range, 0.6 to 0.4%) was the lowest (Fig. 2). According to the type of water environment, the mean MeHg percentages of the THg were comparable in plankton (range of 6.3 to 4.4%), but were higher in the water column (range of 9.4 to 5.6%). In all cases the black water environment showed higher percentage values.

The BSAF results for THg in plankton (phyto- and zooplankton) showed no statistically significant difference between different types of waters; however, the trend for BSAF-MeHg (black > clear > white) in both types of plankton was statistically significant (Table 1). For macroinvertebrates, the results were the opposite; there was a significant difference (black > clear > white) for BSAF-THg but not for BSAF-MeHg (Table 1). The highest BSAF, as expected, were seen for MeHg (BM > zooplankton > phyto-plankton) with mean ranges of 181.9–255.6 (BM), 68.5 to 125.6 (zooplankton) and 53.0 to 107 (zooplankton). The BSAFs for THg were 1–2 orders of magnitude less than MeHg (Fig. 3). However, significant differences between water types were seen only for plankton BSAF-MeHg. The opposite trend was observed for BM-BSAF, and only THg was significantly different (Table 1). Actually, all the tested organisms were seen to bio-accumulate MeHg better than THg (Fig. 3). This also explains the variation in the increase in concentration through the trophic web. The BSAF results (Fig. 3) suggest a more complex process of bioaccumulation in BM in the clear waters, as no relationship was observed in patterns seen for planktons. Despite differences in MeHg:THg ratios in the tested organisms, the contrast between black and white waters remained across the tested waters (Fig. 2).

Summaries of the correlations between variables for each type of water are shown in Tables 2–4. In all types of water there was a significant correlation between S-THg and other measured Hg variables. Among the three types of water, “white” showed the largest number of statistically significant correlated variables. In both water and sediments the correlations between THg and MeHg were high and statistically significant compared to other variables. The correlations between the variables in black water and clear water showed that the relationships between geological and biological variables were not significant (Tables 2 and 3). Biological variables (phytoplankton-THg, phytoplankton-MeHg, zooplankton-THg, zooplankton-MeHg, BM-THg, BM-MeHg) had the highest number of significant correlations with each other (Tables 2 and 3). Except for water THg, the water-MeHg component had no

Table 1
Summary of pH and Hg chemical forms measured in biotic and abiotic compartments as a function of optically classified water environments.

Variable	Black	Clear	White	p
	mean ± sd	mean ± sd	mean ± sd	
N	54	144	162	
pH	3.60 ± 0.31^{a}	5.10 ± 0.22^{b}	6.70 ± 0.5^{c}	.00001
Water THg, $ng.l^{-1}$	2.41 ± 0.014^{a}	2.02 ± 0.015^{b}	2.23 ± 0.013^{b}	.004
Water MMHg, $ng.l^{-1}$	0.43 ± 0.0005^{a}	0.31 ± 0.0002^{b}	0.33 ± 0.0001^{b}	.051
SS THg, $\mu g.Kg^{-1}$	107.16 ± 78.1^{a}	122.39 ± 131.9^{a}	159.27 ± 88.1^{b}	.00001
Sediment THg, $\mu g.Kg^{-1}$	77.52 ± 43.6^{a}	76.41 ± 52.1^{a}	55.33 ± 30.4^{b}	.0005
Sediment MMHg, $\mu g.Kg^{-1}$	0.44 ± 0.47^{a}	0.33 ± 0.4^{b}	0.24 ± 0.3^{c}	.007
Ppk-THg, $\mu g.Kg^{-1}$	322.35 ± 276.4^{a}	274.60 ± 199.5^{a}	211.60 ± 147.4^{b}	.001
Ppk-MMHg, $\mu g.Kg^{-1}$	19.20 ± 16.8^{a}	12.90 ± 9.9^{b}	9.40 ± 8.8^{c}	.00001
Zpk THg, $\mu g.Kg^{-1}$	388.15 ± 280.1^{a}	333.87 ± 235.1^{a}	246.34 ± 167.0^{b}	.00001
Zpk-MMHg, $\mu g.Kg^{-1}$	24.60 ± 18.3^{a}	15.94 ± 12.7^{b}	11.43 ± 9.9^{c}	.00001
BM-THg, $\mu g.Kg^{-1}$	701.39 ± 489.8	636.91 ± 418.6	645.73 ± 372.6	.7232
BM-MMHg, $\mu g.Kg^{-1}$	65.80 ± 82.5^{a}	44.38 ± 60.3^{b}	36.74 ± 72.1^{b}	.00001
Ppk-BSAF, THg	6.55 ± 11.2	5.49 ± 6.2	4.54 ± 3.8	.899
Zpk-BSAF, THg	6.17 ± 6.2	6.43 ± 6.2	5.37 ± 4.4	.624
BM-BSAF, THg	10.79 ± 10.7^{a}	12.94 ± 13.6^{a}	14.96 ± 13.7^{b}	.005
Ppk-BSAF, MeHg	107.92 ± 148.4^{a}	82.99 ± 85.9^{ab}	53.00 ± 51.4^{b}	.024
Zpk-BSAF, MeHg	125.68 ± 165.9^{a}	105.86 ± 126.9^{ab}	68.51 ± 89.8^{b}	.050
BM-BSAF, MeHg	255.61 ± 345.8	305.48 ± 705.6	181.95 ± 263.7	.0917

Biota sediment accumulation factor: BSAF; THg: total Hg; MeHg: methylmercury; S: sediment; SS: suspended solids; Ppk: Phytoplankton; Zpk: Zooplankton; BM: benthic macroinvertebrates; a,b,c: different letter superscripts denote statistically significant differences by Bonferroni correction test; we accepted $p < .05$ as statistically significant.

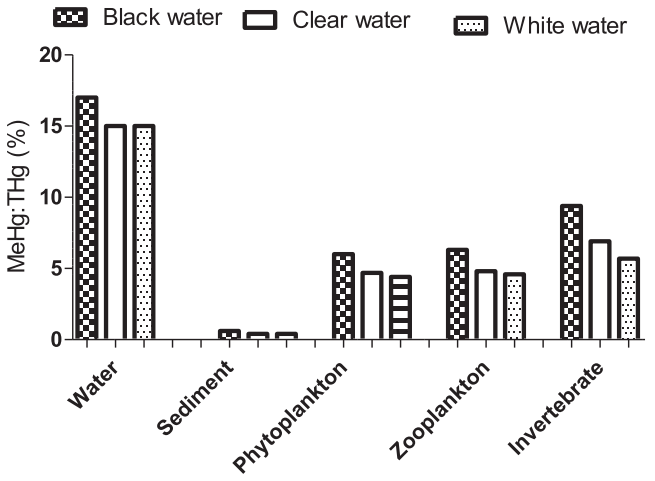

Fig. 2. Percentage of methylmercury (MeHg) from total-Hg (THg) and types of water.

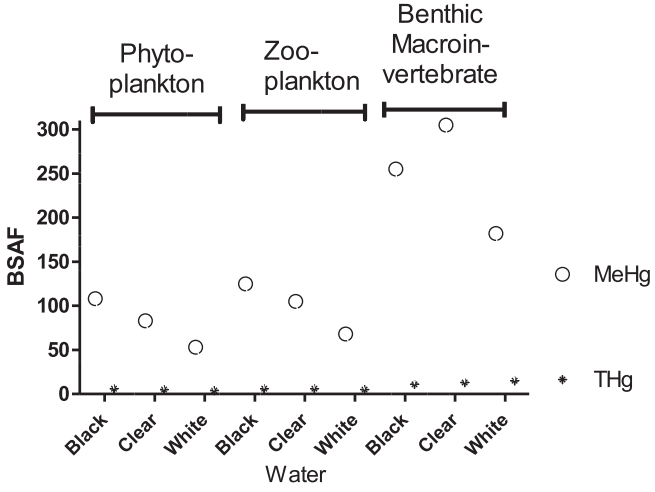

Fig. 3. Biota sediment accumulation factor (BSAF) for total-Hg (THg) and methyl-Hg (MeHg) in Phytoplankton, Zooplankton, and Benthic Macroinvertebrates (BM).

significant correlation with any variable in any type of water.

4. Discussion

We compared three types of water and estimated the availability and distribution of Hg (THg and MeHg) in biotic and abiotic samples from the Madeira River Basin. Optically classified waters, respective sediments and biota showed significant differences in Hg (THg and MeHg) concentrations. A contrast between "black" and "white" water was seen in all measured parameters. Hg availability and methylation was higher in "black" water environments with the lowest pH. The significant differences in the concentrations of THg and MeHg found between the water types (Table 1) were probably due to other physical-chemical characteristics, beside pH. In relation to pH gradient observed in the three types of water, our results are in full agreement with those observed in the Amazonian Rivers (Jepsen and Winemiller, 2007; Cooke et al., 2012). Jepsen and Winemiller (2007) reported that poverty in nutrients drives longer trophic webs in "black" water rivers which contrast with more productive "white" water rivers. Therefore, the trophic status of the body of water seems to be another influencing factor for Hg biomagnification in aquatic Amazonian ecosystems.

The extreme pH between the "black" and "white" waters formed a predominant pattern in Hg-associated variables. Mercury concentrations in different types of water have been studied in the different rivers of the Amazon rain forest; most of these studies have been done in only one type of aquatic environment ("black"/"clear"/"white"). The more acidic conditions of the "black" waters seem to favor Hg mobilization and methylation (Maurice-Bourgoin et al., 2003). Nevertheless it is important to mention that these aquatic (optically classified) environments are also characterized by the differences in richness of nutrients which also affect bioaccumulation of Hg in the food web (Azevedo Silva et al., 2016). Furthermore, Jardim et al. (2010) studied the unique environment of "black waters" (in the Negro River) identifying a dynamic redox chemistry affecting the mobility of mercury due to the formation of the dissolved elemental species (Hg^{0}).

In the waters of the Madeira River, the concentrations found of both Hg and MeHg are within the range reported in the Amazon region by several authors (Pfeiffer et al., 1991; Aula et al., 1995;

Table 2
Summary of Spearman correlations among measured variables in "black" waters.

	W-HgT	S THg	SS THg	Ppk- THg	Zpk- THg	BM THg	W MeHg	S MeHg	Ppk- MeHg	Zpk- MeHg	BM-MeHg
W-THg	–	0.330*	0.476**	−0.128	0.230	0.441**	−0.152	0.362**	0.104	0.290*	0.230
S-THg	0.330*	–	0.393**	0.301*	0.522**	0.462**	0.289*	0.298	0.345**	0.531*	0.450*
SS-THg	0.476**	0.393**	–	0.004	0.042	0.408**	−0.144	0.260	0.390**	0.377**	0.410*
Ppk-THg	−0.128	0.301*	0.004	–	0.643**	0.298*	0.142	−0.071	0.734**	0.459**	0.230
Zpk- THg	0.230	0.522**	0.042	0.643**	–	0.689**	0.071	0.194	0.573**	0.796**	0.490*
BM -THg	0.441**	0.462**	0.408**	0.298*	0.689**	–	−0.083	0.429**	0.507**	0.677**	0.810*
W-MeHg	−0.152	0.289*	−0.144	0.142	0.071	−0.083	–	0.141	0.070	0.027	−0.100
S-MeHg	0.362**	0.298*	0.260	−0.071	0.194	0.429**	0.141	–	0.110	0.200	0.550*
Ppk-MeHg	0.104	0.345**	0.390**	0.734**	0.573**	0.507**	0.070	0.110	–	0.713**	0.430*
Zpk-MeHg	0.290*	0.531**	0.377**	0.459**	0.796**	0.677**	0.027	0.200	0.713**	–	0.510*
BM-MeHg	0.230	0.450*	0.410*	0.230	0.490*	0.810*	−0.100	0.550*	0.430*	0.510*	–

*Statistically significant at the <0.05 level (2-tailed); ** statistically significant at the <0.01 level (2-tailed); W: water; S: sediment; SS: suspended solids; Ppk: phytoplankton; Zpk: zooplankton; BM: benthic macroinvertebrates.

Table 3
Summary of Spearman correlation among measured variables in "clear" waters.

	W-HgT	S THg	SS THg	Ppk- THg	Zpk- THg	BM THg	W MeHg	S MeHg	Ppk- MeHg	Zpk- MeHg	BM-MeHg
W-THg	–	0.321**	0.140	0.095	0.098	0.084	−0.057	0.193*	0.306**	0.170*	0.220*
S-THg	0.321**	–	0.689**	0.393**	0.276**	0.555**	0.358**	0.265**	0.240**	0.271**	0.330*
SS-THg	0.140	0.689**	–	0.077	0.201*	0.145	−0.143	−0.036	0.236**	0.236**	−0.030
Ppk-THg	0.095	0.393**	0.077	–	0.635**	0.258**	−0.046	−0.181*	0.713**	0.488**	0.130
Zpk- THg	0.098	0.276**	0.201*	0.635**	–	0.563**	0.089	−0.182*	0.491**	0.753**	0.400*
BM -THg	0.084	0.555**	0.145	0.258**	0.563**	–	0.088	−0.103	0.247**	0.469**	0.700*
W-MeHg	−0.057	0.358**	−0.143	−0.046	0.089	0.088	–	0.055	−0.085	0.074	0.160
S-MeHg	0.193*	0.265**	−0.036	−0.181*	−0.182*	−0.103	0.055	–	−0.040	−0.065	0.010
Ppk-MeHg	0.306**	0.240**	0.236**	0.713**	0.491**	0.247**	−0.085	−0.040	–	0.720**	0.440*
Zpk-MeHg	0.170*	0.271**	0.236**	0.488**	0.753**	0.469**	0.074	−0.065	0.720**	–	0.590*
BM-MeHg	0.220*	0.330*	−0.030	0.130	0.400*	0.700*	0.160	0.010	0.440*	0.590*	–

Statistically significant at the <0.05 level (2-tailed); ** statistically significant at the <0.01 level (2-tailed); W: water; S: sediment; SS: suspended solids; Ppk: phytoplankton; Zpk: zooplankton; BM: benthic macroinvertebrates.

Table 4
Summary of Spearman correlation among measured variables in "white" waters.

	W-HgT	S THg	SS THg	Ppk- THg	Zpk- THg	BM THg	W MeHg	S MeHg	Ppk- MeHg	Zpk- MeHg	BM-MeHg
W-THg	–	0.658**	0.361**	0.423**	0.363**	0.507**	−0.075	0.680**	0.605**	0.600**	0.642**
S-THg	0.658**	–	0.379**	0.415**	0.418**	0.518**	0.311**	0.767**	0.561**	0.562**	0.551**
SS-THg	0.361**	0.379**	–	0.312**	0.234**	0.287**	−0.146	0.333**	0.291**	0.284**	0.597**
Ppk-THg	0.423**	0.415**	0.312**	–	0.748**	0.549**	−0.070	0.407**	0.852**	0.687**	0.480**
Zpk- THg	0.363**	0.418**	0.234**	0.748**	–	0.568**	−0.058	0.374**	0.720**	0.802**	0.474**
BM -THg	0.507**	0.518**	0.287**	0.549**	0.568**	–	−0.010	0.442**	0.581**	0.591**	0.821**
W-MeHg	−0.075	0.311**	−0.146	−0.070	−0.058	−0.010	–	−0.029	−0.063	−0.058	0.070
S-MeHg	0.680**	0.767**	0.333**	0.407**	0.374**	0.442**	−0.029	–	0.551**	0.527**	0.553**
Ppk-MeHg	0.605**	0.561**	0.291**	0.852**	0.720**	0.581**	−0.063	0.551**	–	0.870**	0.706**
Zpk-MeHg	0.600**	0.562**	0.284**	0.687**	0.802**	0.591**	−0.058	0.527**	0.870**	–	0.718**
BM-MeHg	0.642**	0.551**	0.597**	0.480**	0.474**	0.821**	0.070	0.553**	0.706**	0.718**	–

*Statistically significant at the <0.05 level (2-tailed); ** statistically significant at the <0.01 level (2-tailed); W: water; S: sediment; SS: suspended solids; Ppk: phytoplankton; Zpk: zooplankton; BM: benthic macroinvertebrates.

Malm et al., 1989; Kannan et al., 1998; Bastos et al., 2006). It seems that past anthropogenic sources of Hg associated with gold extraction and hydroelectric reservoirs (in the Madeira River) had less impact on the measured Hg variables than the natural environmental conditions associated with water pH (Table 1).

Only a few studies have compared "black" and "white" water environments for Hg concentrations (Guimarães et al., 1995; Lechler et al., 2000; Fadini and Jardim, 2001; Bisinoti et al., 2007; Lindell et al., 2010). Guimarães et al. (1995) reported differences in Hg methylation rates between "black" and "white" waters in the Madeira River Basin; they showed a depressed Hg methylation rate in the sediment of black waters. In the Negro River Basin, studies have found that "black" water had higher concentrations of THg than "white" water (Fadini and Jardim, 2001; Bisinoti et al., 2007). Others comparing "black" and "white" waters also found higher concentrations of Hg in the former type in the Negro River (Maurice-Bourgoin et al., 2003). In regard to Hg in water, Maia et al. (2009) reported the opposite; "white" waters showed higher THg concentrations than "black" waters. Pouilly et al. (2012) compared "white" and "clear" waters (in the Itenez and Blanco Rivers-Madeira River Basin), reporting neither pH nor THg concentration differences.

Sediment is the ideal ecological habitat for BMs and studies have shown that Hg-contaminated sediments can affect benthic organisms (Chapman et al., 2013). However, in estuarine studies, Hg bioaccumulation and drivers of MeHg production can vary within a region (Buckman et al., 2017). In our study, sediments collected from the more acidic waters had higher contents of both forms of

Hg than those from the less acidic ones (Table 1). Sediment Hg (THg and MeHg) concentrations from the "white" waters were significantly less than in "black" waters. However, suspended solids showed an opposite trend. It is worth noting that the ratios of MeHg:THg in water were higher than those of sediments (Fig. 2). The proportion of MeHg to THg is within the expected range observed by others (Ullrich et al., 2001). Sediments represent the major environmental compartment for methylation of inorganic Hg. Furthermore, sediment THg was the only variable that was significantly correlated with all the other Hg variables (Tables 2–4), thus indicating that sediment is central in Hg availability, regardless of the type of water. Therefore, direct analysis of Hg in sediments seems a more reliable indicator of its distribution and bioavailability.

Phytoplankton is a primary producer, thus affecting the upper levels of the trophic web (Mason et al., 1996; Lacerda and Malm, 2008); as such, it is an indicator of the chemical characteristics and/or changes occurring in aquatic environmental Hg (Uherkovich, 1984). In our study, the concentrations of Hg in phytoplankton, zooplankton and BM (Table 1) showed different bioavailability. Regarding Hg compounds, MeHg is expected to bioaccumulate more than THg.

Regarding Hg bioaccumulation comparing different types of 'water' in the Amazon, only work done on fish can be found in a variety of species; the results in fish are not consistent. Azevedo-Silva et al. (2016) compared "black" and "white" waters, Pouilly et al. (2012) compared "clear" and "white" waters; and Jepsen and Winemiller (2007) compared the three types of water. Barbosa et al. (2003) did not find differences in fish Hg concentrations related to pH. Despite that, BSAFs are useful estimators of the bioaccumulation potential of pollutants and suitable indicators of sediment-Hg availability in Amazonian water systems. In this study, the calculated mean of BSAFs for the Hg compounds (THg and MeHg) was different for the measured organisms and type of water (Fig. 3). BSAFs revealed values higher for the organic Hg form as well as the contrast between "black" and "white" waters (Fig. 3).

The mobilization of the sediment-bound Hg depends on environmental conditions related to pH and bacterial activity, among others (Jardim et al., 2010; Brito et al., 2017). Methylation activity in our study was favored by acidic conditions, which explained the significant differences in BSAF-MeHg for plankton not seen for THg (Table 1). In our study, availability of Hg and MeHg for benthic organisms, however, showed different profiles related to types of water. It seems that the THg concentration "*per se*" in any water-type sediment is not a good general predictor of Hg fate or bioaccumulation. Uptake of Hg expressed as BSAF showed that in BM organisms there is variability indicative of other mediating factors in the mobility and/or chemical forms of Hg in sediments. This is in line with recent findings by Buckman et al. (2017) on the ecological complexities of MeHg production and fate. In our study, acidity was a strong environmental determinant driving Hg bioavailability in optically classified waters.

The Madeira River Basin has been impacted by anthropic activities due to intense gold-mining activities, agricultural projects (forest fire) and man-made reservoirs for hydroelectric plants. Nevertheless, as inferred from the present results, pH was a key factor in the mobility of Hg from sediment to organisms in Amazon waters. Although the THg concentration in sediments is correlated to other Hg-related variables, its bioavailability (accumulation factor for aquatic biota), *i. e*, its uptake by plankton and BMs, is greatly influenced by water acidity. This is in agreement with the general role of sediments in Hg availability (Chakraborty et al., 2014).

These are useful results that compare the three types of optically classified waters in the Amazon. And, when considering the Hg concentrations and bioavailability in primary interfaces (water, suspended sediment, and sediment) and primary consumers, these results are unique in the Amazon rain forest. Our results suggest that water-THg concentration *per se* is not sufficient to predict Hg bioavailability, bioaccumulation and/or environmental toxicity; attention should be paid to influential factors in the methylating potential of inorganic Hg in sediments, especially water acidity.

This study has notable strengths that include direct comparison of specific physical and chemical characteristics of water (optical classification) driving Hg methylation potential and/or biomagnification. Another strength is the measurement of the entry of Hg (THg and MeHg) into the food chain interface (water, SS, and sediments) and in the food web basic-trophic-levels (plankton and BM). Given the role of particle size and organic matter in controlling the geochemical behavior of Hg and its methylation potential, not having this complementary data is a limitation of this study. Another limitation is not having species identification and quantification of BMs; it is only possible to affirm that they were mostly composed of aquatic insects (coleoptera, odonata), crustaceans (shrimp group) and shellfish (prawns group).

5. Concluding remarks

- This study asserted that bio-physical-chemical components determining optical characteristics of water had a detectable influence on the distribution and availability of Hg species. Thus, it makes the optical characterization of Amazon waters an easy way to assess Hg contamination of primary feeders (plankton) and BMs.
- Water pH and respective sediments were determinants of Hg methylating activity which modulated the BSAFs of MeHg in the tested biota.
- The results are of interest in evaluating Hg contamination in the Amazon Basin adding information critical to assessing environmental and health risks associated with potential fish Hg contamination.
- Considering the legacy of small scale gold mining activity in the Madeira River (predominantly 'white' waters) these are useful findings.

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