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 bio-physicochemical 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

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☆ 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

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