Mercury in multimedia system of Itacaiúnas Basin, Brazilian Amazon: An integrated approach to understand its distribution, origin, and ecological risk

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Abstract

This study presents the first integrated study on Hg level in surface soil (SS), bottom soil (BS), stream sediments (SD), lake sediments (LS), stream water (SW), and lake water (LW)) of Itacaiúnas River Watershed (IRW), Brazil to investigate the source and distribution of Hg in different environmental media considering contrasts of geological domains and sub-basins, and its potential ecological and human risk. Hg content in most of the soils and sediments were above the upper crustal average values (0.056 mg/kg), however, when compared to the CONAMA limit (Nº420/2009), only 1 soil sample from Parauapabas sub-basin and 4 sediment samples from Violão Lake exceeded the limit. All SW and LW samples (0.2 µg/L) are not markedly contaminated by Hg. The SS and BS show similar contents and spatial distribution of Hg with higher contents being registered mostly in the Itacaiúnas and Parauapebas sub-basins, which closely correlated with SD. This suggests that Hg levels are largely geogenic origin in the IRW and its anthropogenic source is highly limited. Principal Component Analysis (PCA) results show that Hg is strongly associated with TOC, LOI, and SO_3, indicating organic matter as the main factor controlling the distribution of Hg and this is the major cause of accentuated Hg enrichment in lake sediments. In addition, lake morphometry and catchment lithology also play a role to this. The ecological risk index (ER) and contamination factor (CF) revelaed a low pollution risk for most of the solid samples, except 11% LS and <1.5% SS and SD samples, which registered moderate risk. The results of health risk assessment indicated the absence of any adverse non-carcinogenic health effect for adult and children in terms of Hg contamination. This information will be useful for Hg risk assessment in the Carajás region and future environmental research in this direction in the Amazonia.

1. Introduction

After Minamata disease was discovered in Japan, in the year 1956, mercury (Hg) poisoning has been given a serious attention worldwide. Mercury is also listed as a priority pollutant of major public health concern among all toxic elements by many organizations (WHO 2007, 2010; AMAP/UNEP, 2013). This is due to its unique toxicological and eco-geochemical properties determined by the diversity of its forms, persistence, non-biodegradability, and active transformation in the environment, which can cause a wide spectrum of serious health effects on humans (Zheng et al., 2015; Castilhos et al., 2006; Clarkson et al., 2003; WHO, 2017; Spela et al., 2018; Ullrich et al., 2001; Obrist et al., 2018). The most powerful toxic form of Hg is methyl-mercury (MeHg; organic Hg). It has high tendency of bioaccumulation and biomagnification in the topic level due to its lipophilic character, easy penetration through biological membrane, and high affinity towards proteins; thus, MeHg can be easily enriched in aquatic organisms such as benthos and fish (Castilhos et al., 2006; Clarkson and Magos, 2006; Windisch et al., 2022). Currently, consumption of Hg contaminated fish has become the main route of Hg exposure to humans in many regions (Jirsa et al., 2014; Nyholt et al., 2022; Evans et al., 2005; Hylander et al., 2006; Mergler et al., 2007). High exposure of Hg can cause adverse neurological effects and affect immune, genetic and enzyme systems, and leads to the development of sequelae in humans and wild animals (Akagi et al., 1995; Matsuyama et al., 2018).

Mercury (Hg) relased into the biosphere by varied natural or anthropogenic sources (Chen et al., 2018; Nyholt et al., 2022). The latter is contributed from industrial and traffic emmision, industrial wastewater discharges, coal burning, mining and smelting of metals, artisanal gold mining, cement production, etc. (Zhang et al., 2016; UN Environment, 2019; Wip et al., 2013; Chen et al., 2018; Sahakyan et al., 2021; Obrist et al., 2018). As such, significant contents of Hg can be transported to long distances in the atmosphere and enter into soil, sediments, and aquatic bodies through wet and dry depositions (Lyman et al., 2020). In soil, Hg tends to accumulate in surface horizon and is mainly retained by sorption onto organic matter, although several other

soil properties such as pH, redox potential, temperature, Fe-oxyhydroxide content, etc. and composition of the parent materials and soil types also control Hg concentrations (Zhang et al. 2014; Rahman and Singh 2019; Raj and Maiti 2019). After accumulation in soil, Hg can be absorbed by plants and can contaminate the aquatic and terrestrial food chain (Riaz et al. 2018; Zhong et al. 2018). Similarly, in aquatic system, sediment is considered as the best sink for Hg as it can accumulate high amounts of it, either from catchment rocks/soils and/or from atmospheric deposition (He et al., 2008; Haris et al., 2017). However, depending upon environmental conditions, sediments can further act as a source of Hg contamination in water through the re-emission of Hg from sediment via biogeochemical processes (Gambrel et al., 2001; Yang et al., 2020), which is also responsible for the conversion of Hg to methylmercury (Jensen and Jerbelov, 1969). Therefore, it is crucial to understand the fate of Hg in the soil-sediment-water system for accurate assessment of risk deriving from Hg, and to assure the protection of the ecosystem. Although, the environmental risk is commonly assessed by comparison with national/international standard or guideline values, it can be better evaluated using local geochemical values as reference and various pollution indices such as geo-accumulation index (Igeo), pollution index (Pi), enrichment factor (EF), and contamination factor (CF), and potential ecological risk (Ei), etc., which have proven to be helpful in effective pollution evaluation (Weissmannová and Pavlovský, 2017; Sahakyan et al., 2021).

Mercury contamination in several freshwater ecosystems has attracted considerable attention as a major environmental concern worldwide. This is true for the Brazilian Amazonia owing to the critical situation of Hg contamination and its consequence of human health risks. High levels of Hg have been detected in fishs of the Juruá river, a large tributary of the Amazon river, and associated lakes, in a region without significant anthropic impact (Nyholt et al., 2022). There is also increasing evidence that fish Hg contamination is the main route of contamination for Amazonian riverside populations (Berzas Nevado et al., 2010; Rodriguez Martin-Doimeadios et al., 2014; Crespo-Lopez et al., 2021). Other studies also reported or suspected serious Hg impacts to biota and human health in the region (WWF, 2018; Santos-Sacramento et al., 2021; Crespo-Lopez et al., 2021; Pestana et al., 2022). Considering this serious issue, research has been conducted to find out the source and geochemical behavior of Hg in surficial systems in the Brazilian Amazon and it was proposed that Hg enrichment in the region can result from diversified processes and sources including natural as well as

anthropogenic factors. In natural process, it can be possible to find enrichment of Hg during formation of soils from weathering of volcanic rocks (Horbe et al., 2019). Moreover, the surficial geological formations and soils of Amazon are naturally enriched in Hg (Lechler et al., 2000; Fadini and Jardim, 2001; Mascarenhas et al., 2004; Siqueira et al, 2018, Horbe et al., 2019) and their erosion and the intense run off, particularly during the raining season, favor transport of Hg to circulating waters. Some studies have also reported soils naturally enriched in Hg or high baseline concentrations of Hg in the Amazon basin could be contributing to higher Hg level in fish (Roulet et al., 1995; Akagi et al., 2000; Hacon et al., 2008). In addition, meteorological processes and atmospheric transport also exert influence in the dispersion and distribution of Hg to different biotic and abiotic compartments in the Amazon Forest (Artaxo et al., 2000; Bastos et al., 2006; Lacerda et al., 2004; Fostier et al., 2015), which ends up acting as a large reservoir of Hg and its compounds. Since some plants are a significant sink for atmospheric Hg (Zhou et al., 2021), it is also possible that Hg accumulation in forest litter occurs over time, which could be a significant source of Hg to soils and sediments in the Amazon. Anthropic actions tend to intensify the effects of soil erosion (Bonotto et al., 2018) and are also certainly responsible for Hg pollution, mostly in areas of gold mining, where Hg is commonly used for gold concentration (Lacerda et al., 1994; Akagi et al., 1995; Artaxo et al., 2000; Harada et al., 2001; Lacerda et al., 2004: Telmer et al., 2006; Faial et al., 2015; Teixeira et al., 2021). Moreover, deforestation activities related to agriculture and cattle farming expansion (Artaxo et al., 2000; Lacerda et al., 2004; Hacon et al., 2008), biomass burning and hydroelectric dams can also contribute to Hg contamination (Leino and Lodenius, 1995; Porvari, 1995; Crespo-Lopez et al., 2021; Hacon et al., 2008). Some authors emphasize that the influence of gold exploitation affect more restrict areas of the Amazon region (Lechler et al., 2000; Horbe et al., 2019), but its impact in large areas, like Tapajós basin, is well documented (Harada et al., 2001; Telmer et al., 2006: Pinheiro et al., 2007; Faial et al., 2015; Meneses et al., 2022). Hence, all these potential factors of risk must be evaluated to reduce the health hazard related to Hg contamination. Moreover, independent of its natural or anthropic origin, Hg has tendency to disperse along large areas and to accumulate locally in the environment. These aspects and the possibility of Hg bioaccumulation in the biological cycle indicate that it has potential to negatively affect humans and animals leaving in the Amazonia and must be monitored.

There are still large areas of the Amazon, which are poorly known towards Hg contamination. This is true for the Itacaiúnas River Watershed (IRW), located in the eastern portion of the Brazilian Amazon, which stands out for sheltering the Carajás National Forest (FLONA) and several other protected areas that make up the Carajás mosaic and by large mineral deposits and active mines of Fe, Cu, Mn, and Ni (Docegeo, 1988; Vasquez et al., 2008; Xavier et al., 2012), in addition to areas of extensive cattle raising and local urban occupation (Souza-Filho et al., 2016). On the decades from the 80s and 90s there was intense exploration of gold in areas of the Itacaiúnas watershed (Verde et al., 2014). Some studies discussed Hg pollution on fishes of the IRW in pristine areas or in areas under influence of mining (Lacerda et al., 1994; Borges et al., 2018; Montes et al., 2020). Lacerda et al. (1994) concluded that despite small Hg inputs and high dilution in Amazon rivers, mercury can attain high concentrations in local fishes. Borges et al. (2018) stated that geological and hydrological factor favored the entry of Hg in aquatic systems, which was increased by intense run off and erosion. However, THg contents in stream sediments and studied fishes are low and the bioavailabily of Hg is also low, because it is mainly bounded in suspended particulate matter. Notwithstanding the mentioned studies, currently there has been very little research emphasizing Hg pollution characteristics and its potential sources, either by natural process or by anthropogenic action, in the IRW and no study has carried out on the Hg in multimedia of soil-sediment-water system in the entire basin and, therefore, many questions need to be clarified. This information is not only important for better understanding the ecological risks and the preservation of natural resources, but it is also of global importance to facilitate progress towards achieving the 2030 SDG goals, expecially SDG 3.9, aiming substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination (UNEP, 2018).

In this context, the present study was carried out in the multimedia system of Itacaiúnas river basin (IRW) in which Hg along with other elements data in soil, stream and lake sediments, and stream and lake water were compiled with the objective to (1) understand the current pollution status and spatial variability of Hg in the different environmental matrices in the basin, (2) to elucidate the possible geogenic and anthropogenic contributions of Hg and occurrence of Hg in the soil-sediments-water system linked with environmental factors, and (3) to evaluate the environmental and health risks associated with it. The results now being obtained are fundamental for the

establishment of indicators of environmental sustainability and to support decision-making aimed at public health and Hg pollution control in the Itacaiúnas river basin.

2. Materials and Methods

2.1. Study area and climate

The Itacaiúnas River Basin (IRW; Fig. 1) makes part of the Tocantins River Basin and is the main drainage network in the Carajás region. The region stands out for housing the Carajás National Forest (FLONA) and several other protected areas (Fig. 1a). The IRW hosts the more prominent mineral province of Brazil, the Carajás Mining Province, located in the Amazon craton, with active mines (Fig. 1a) and vast reserves of Fe, Cu, Mn, and Ni (Figueiredo *et al.* 2011). These mines are named as S11D, N4, N5, and Serra Leste (Fe), Onça Puma (Ni), Salobo and Sossego (Cu), and Azul and Buritirama (Mn). The IRW has its headwaters in Serra da Seringa, in the municipality of Água Azul do Norte, state of Pará, and flows into the Tocantins River, near the city of Marabá (Possas et al., 2016). Its drainage area covers approximately 41,500 km². The IRW is sub-divided into 9 sub-basins (Fig. 1b): Parauapebas, Vermelho and Sororó in the eastern side; Itacaiunas in the center; and Cateté, Aquiri, Cinzento, Tapirapé, and Preto in the western site. The active upland lakes such as Violão (VL), Amendoim (AM), and Três Irmãs (TI1, TI2 and TI3) are located in the southern plateaus of the Serra dos Carajás (Fig. 1e). These lakes are hydrologically restricted and were formed over iron and iron-aluminous lateritic crusts as a result of successive weathering (chemical, physical and biological) and erosion cycles under strong tropical climate conditions (Vasconcelos et al., 1994; Costa et al., 2005; Maurity and Kotschoubey, 1995).

The regional climate of this area is tropical monsoon, hot and humid with an average annual temperature of 27.2°C and relative humidity of 80% (Alvares et al., 2013). Based on the monthly rainfall, the drier season extended from June to September with a total mean of 128 mm, while the rainy season (October to May) presented a total average of 1595 mm. The total annual precipitation was around 1723 mm (Alvares et al. 2014).

2.2. Regional geological setting and land use/land cover of the basin

Geologically, the IRW presents a very complex picture because it is located on the boundary between different tectonic blocks. The simplified stratigraphy of the four major geological domains of the basin is presented in Sahoo et al. (2020) and Salomão et al. (2020, 2021). These domains in the IRW are named as Rio Maria, Sapucaia, and Canaã

dos Carajás (RMC) domains and Carajás Basin (CB) from south to north; the Bacajá Domain (BD), in the extreme northern portion of the basin; and the Araguaia Belt (AB) that occupies the eastern portion of the basin. The CB is dominated by mafic to intermediate metavolcanic sequences and banded-iron formations (Martins et al., 2017), while BD is consist of high-grade charnockite rocks with subordinate mafic orthogranulite and metasedimentary granulites (Vasquez et al., 2008). The RMC domains are mainly formed by granitoid rocks associated with orthogranulitic units, and metamafic sequences (Vasquez et al., 2008; Dall'Agnol et al., 2017). In AB, low-grade metamorphic rocks are dominant, besides occurrence of mafic-ultramafic complexes with associated deep-sea sediments (Vasquez et al., 2008). The plateaus lakes in the Serra dos Carajás are supported by lateritic crusts derived of Neoarchean volcanic rocks, mainly basalts and basaltic andesites, interspersed with banded iron formations, constituting a volcanic-sedimentary sequence deposited on Mesoarchean granite-gnessic rocks of the crystalline basement (Teixeira et al., 2018). In the past, tropical rainforest with subordinate montane savana was entirely dominating in this region. However, over the last 45 years the accelerate increase of economic activity and human occupation significantly changed the land use pattern with a large part of the forested area being converted into pasturelands with minor urban and mining area (Fig. 1a; Souza Filho et al., 2016). At present, the basin exhibits two entirely distinct main types of land use (Fig. 1a,b), a mosaic of forest remnants composed of environmental protection areas consisting of indigenous lands and conservation units (UCs), which occupy a quarter of the area of the basin (Souza-filho et al., 2016), and a larger area that was intensely deforested and is explored mostly for livingstock breeding.

2.3. Data collection and analysis

The database of Hg and other elements in topsoil (SS), bottom soil (BS), stream sediments (SD), stream water (SW) of the IRW was taken from published literatures (Sahoo et al., 2019, 2020, Salomão et al., 2020, 2021), which are the product of the Itacaiúnas Geochemical Mapping and Background project (ItacGMB), while the database of lake lake sediments (LS) and lake water (LW) were taken from Sahoo et al. (2017, 2019), which linked with Paleoclima project. Both these projects have been developed by the Instituto Tecnológico Vale (ITV), Belém, Brazil. The sampling used in ItacGMB covers a total number of around 5284 samples, which was comprised of: SS (0-20cm; 1479 samples, plus 74 duplicates); BS (30-50cm; 1479 samples, plus 74 duplicates) (Fig.

1c); SD (761 samples, plus 27 duplicates) (Fig. 1d); SW (720 samples plus 30 duplicates in the rainy season and 638 samples plus 29 duplicates in the dry season). These samples were collected between the years 2017 and 2018 considering the division of the basin into six main sub-basins – Itacaiúnas rivers (main drainage), Sororó, Vermelho, Parauapebas, Cateté, and Tapirapé (Fig. 1b). A detailed sampling description can be found in Sahoo et al. (2019, 2020), and Salomão et al. (2020, 2021). The lake database included 143 surface sediments and 170 water samples from 5 upland lakes (Violão -VL, Amendoim -AM, and Três Irmãs -TI1, TI2 and TI3), which were sampled between the years 2013 and 2015. Based on the lithotype around the lake basins, distinct lateritic crusts viz., ferruginous lateritic crusts (Fe-LC) and aluminium-enriched ferruginous laterite crusts (Al-LC), and soils viz., ferruginous soils (Fe-Soil) and Al-enriched ferruginous soils (Al-Soil) were also collected at the surface. The detailed description of these sample types can be found in Sahoo et al. (2019). The quantification of Hg in soil and sediments was performed by ALS LTDA, and in surface water samples by Bioagri LTDA, both are certified laboratories in Brazil. In both laboratories, Hg in all samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique. Quality control was monitored for duplicates and replicated analysis of reference materials. The detailed methods for analysis can be found in the respective references. For data comparison and assessment of the Hg contamination status in different enrvironmental media, regional IRW background values for soils and sediments (Sahoo et al., 2020; Salomão et al., 2020, 2021) along with national reference values such as the Brazilian soil Prevention and Investigation levels (agriculture systems), fresh water (class II), Resolução 357/2005, groundwater limit (Resolução 396/2008), sediment L1 and L2, defined by the Brazilian Council for the Environment (CONAMA, 2009; CONAMA, 2012), and global reference values such as Upper Continental Crust (UCC; Wedepohl, 1995) and World background soils (Kabata-Pendias, 2011) were used.

2.4. Ecological risk assessment of Hg

The estimation of environmental pollution level was carried out using some quantitative indices such as contamination factor (CF) and potential ecological risk index (ER). All these indices were calculated for different sampling media using their respective regional geochemical background values (based on mMAD: soil (0.32 mg/kg), stream sediments (0.14 mg/kg), and lake sediments (0.34 mg/kg).

The contamination factor (CF) aims to determine the pollution potential of Hg in soils and sediments with respect to background/reference value. This is calculated using the following equation (Eq. 1) (Hakanson, 1980).

$$CF = C_{metal}/C_{background} \qquad (1)$$

where C_{metal} is concentration of metals in studied samples and $C_{background}$ is the GB value of the respective sampling media in the IRW. The level of contamination is classified into four categories: CF <1 indicates low contamination, 1<CF<3 is moderate, 3<CF<6 is considerable and CF> 6 is very high contamination.

The degree of potential ecological risk (ER) of Hg in soils/sediments is calculated using the contamination factor (CF) and toxic response values (Eq. 2), as suggested by Hakanson (1980).

$$ER = T_f \times CF \qquad (2)$$

where, ER is the single index of potential ecological risk, T_f is the toxic response for Hg, i.e., 40 according to Hakanson (1980); CF is contamination factor, which is calculated based on Eq. 1. The ecological risk follows the classification as: ER < 40, low ecological risk; 40 < ER < 80, moderate risk; 80 < ER < 160, high risk; ER > 160, higher risk.

The potential environmental risks of waters were determined by applying the quantitative screening of the environmental Hazard Quotient (HQ) approach (Eq. 3).

$$HQ = \frac{EEC}{Screening\ Benchmark} \qquad (3)$$

Where EEC = Estimated Hg concentration in the water sample; Screening Benchmark = generally a no-adverse effects level concentration (NOAEL); for this purpose, we have used WHO drinking water limit (1 µg/L). If the HQ <1, the contaminant is not likely to cause any adverse effect, while if the HQ value is > 1 then there is a high risk from Hg (Environmental Canada, 1995; USEPA, 1997).

2.5. Health risk assessment

Considering that local population having fishing and recreation activities along the Itacaiúnas river basin for living, human health risk of Hg on both adult and children was measured through the exposure risk assessment, i.e., average daily intake (ADI, mg/kg-day) and non-carcinogenic risk, i.e., hazard quotient (HQ) using the model developed by USEPA (USEPA, 1989, 2001). Since carcinogenic slope factors (SF) is not available for Hg, only non-carcinogenic risk was estimated. These values were calculated for surface

soil taking into account three active exposure pathways such as oral ingestion, inhalation, and dermal exposure using the equations Eqs. 4–6 (USEPA, 2002; Zeng et al., 2010). The different parameters used to calculate the health risk assessment are presented in supplementary Table S1.

$$ADI_{ing} = \frac{Csoil*IngR*EF*ED}{BW*AT*10^6} \qquad (4)$$

$$ADI_{inh} = \frac{Csoil*InhR*EF*ED}{BW*AT*PEF} \qquad (5)$$

$$ADI_{dermal} = \frac{Csoil*SA*FE*ABS*EF*ED}{BW*AT*10^6} \qquad (6)$$

where ADI_{ing}, ADI_{inh} and ADI_{dermal} are the average daily intake doses (in mg/kg/day) through soil ingestion, inhalation, and dermal exposure, respectively. C_{soil} is the Hg concentration in soils (mg/kg). IngR (mg/day) is the intake rate and InhR (m^3/day) is the inhalation rate, EF (days/year) is the exposure frequency, ED (years) is the exposure duration, BW (kg) is the body weight of the exposed individual, AT (days) is the time period over which the dose is averaged, PEF (m^3/kg) is the particulate emission factor. SA (cm^2) is the exposed skin area, FE is the fraction of the ratio to soil, ABS is the fraction of the applied dose absorbed across the skin and 10^6 is the conversion factor in kg/mg.

The non-carcinogenic hazard quotients (HQ) were calculated using the Eq. 7-9, as below:

$$HQ_{ing} = \frac{ADIing}{RfD} \qquad (7)$$

$$HQ_{inh} = \frac{ADIinh}{RfD} \qquad (8)$$

$$HQ_{dermal} = \frac{ADdermal}{RfD} \qquad (9)$$

RfD is the reference dose of Hg that was taken from the Risk Assessment Information System (Rais, 2018). The hazard index (HI) is the sum of the all target hazard quotient (HQ) that expresses a non-cancer risk for Hg (USEPA 2001; 2000; 1997; 1989). If HI is <1, there is no risk of non-carcinogenic effects, while if HI is > 1, there is a probability of a harmful health effect (RAIS, 2018).

2.6. Statistical and data analysis

The Hg data were subjected to basic and multivariate analyses following the standard methods (Filzmoser et al., 2009; Sahoo et al., 2020; Salomão et al., 2021). The basic statistical analyses include descriptive statistics (average, median, minimum, maximum, and standard deviation). Boxplot was used to analyze the data distribution and variations between the sample groups. The normality of the dataset was checked using Shapiro-Wilk's (S‑W). Depending on the normality test results, multivariate analyses such as Spearman correlation and principal component analysis (PCA) using centred log-ratio (clr) transformation were carried out to understand the relationship between Hg and other elements. Clr-transformation was used to reduce the closure effect (Filzmoser et al., 2009). All statistical data analysis was carried out using SPSS software (version 18.0) and the free statistical software R version 3.1.2. For spatial mapping, the results were georeferenced using ArcGIS 10.5 software, according to the datum World Geodetic System 1984 (WGS84) and the Inverse Distance Weighting (IDW) interpolation method was adopted to generate distribution maps.

3. Results and Discussion

3.1. Occurrence and distribution of Hg in surface and bottom soils of IRW

The descriptive statistics of T-Hg concentrations in both SS and BS in the six sub-basins are summarized in Table 1. In both soil types, there is a very small percentage of samples with concentration below LD (0.54% in SS and 0.61% in BS). There is little variability in terms of T-Hg content between the two soil types ranging from <LD to a maximum value of 540 µg/kg and 600 µg/kg in SS and BS, respectively (Table 1, Fig. 2). Most of the soil samples, except 1 from SS and 1 from BS (i.e, 0.27%), do not exceed 500 µg/kg, the reference value referring to prevention value (PV) of Hg in soil, which is considered the concentration in the soil above which soil quality may be seriously altered (CONAMA, 2009). However, when compared to the USEPA residential soil screening level (SSL) (USEPA, 1996), most of the soil samples in the study area were above and up to 100 times greater than the guidance value of 0.0023 mg/kg. Similarly, the mean values for both sample types were also above 0.056 mg/kg and 0.040 mg/kg, which are the average composition of Hg in upper continental crust according to Wedepohl (1995) and Taylor and McLennan (1985), respectively. When compared with the regional soil GB of IRW (mMAD, 0.32 mg/kg), the number of samples exceeding the threshold limit of Hg were maximum from Itacaiunas sub-basin (5), followed by Paraupebas (4) and Tapirapé (1), while no sample from Cateté, Vermelho, and Sororó sub-basin exceeded

that value. This is well corroborated with the sub-surface soil samples (Table 1). There are also records of Hg concentration in soils from different locations in the Brazilian Amazon, which indicate concentrations similar or higher to the context of IRW. Horbe et al. (2019) reported maximum levels of 420 µg/kg of Hg in the soils of the Solimões and Madeira river basins. Similar maximum concentrations of Hg in soils (406 µg/kg) of the Madeira River were also reported by Lechler et al. (2000). In the gold mining areas of Tapajós river basin, there are records of maximum values in the soil reaching 360 µg/kg of Hg (Telmer et al., 2006). However, there are also studies showed Hg concentrations lower than those found in IRW, for example, in the soils of the Rio Negro basin (232 µg/kg of Hg; Fadini, 2001) and in the forest soil in Alta Floresta, Mato Grosso state of Brazil, Southern Amazon (248 µg/kg of Hg; Lacerda et al., 2004). Moreover, the average value of Hg in the study area was relatively higher in comparison with the values reported in soils from other countries such as ASGM sites in Korea (0.204 mg/kg; Han et al., 2012), Gilgit-Baltistan in Pakistan (0.27 mg/kg; Arjumand, et al., 2018) and in Venezuela (0.049 mg/ kg; Garcıa-Sanchez et al., (2006).

The spatial distribution maps show that Hg concentrations in superficial and subsuperficial soil (Fig. 2) are highly correlated, but this is varied between sub-basins. The Paired-T test also revealed that Hg concentrations were significantly different between the sub-basins ($p < 0.05$), as well as the geological domains ($p < 0.05$). It can be also seen that the sampling points with the highest levels of Hg are located predominantly in the northern portion, in the Bacajá Domain, and in the central portion, in the Carajás Basin, of the IRW, where mafic and intermediate metavolcanic and plutonic rocks are abundant. These points are mostly concentrated in the Itacaiúnas and Parauapebas sub-basins. According to Sahoo et al. (2020), in an investigation carried out in the Parauapebas River sub-basin and IRW, the strong geochemical similarity existing between surface and sub-surface soils indicates that different chemical elements, including potentially toxic elements, are dominantly of geogenic (or natural) origin and apparently the influence of anthropogenic activities has less relevance. Carvalho et al. (2018) and Soares et al. (2015b) have obtained high concentration of Hg in basalt-derived soil. These results are in agreement with natural concentrations of Hg registered in 14 soil classes from southeast Brazil (Soares et al., 2015b), which indicated that samples with higher concentrations of Hg (150 and 200 µg/kg) are originated from basalts. Horbe et al. (2019) also determined the variability of mercury and its historical values in the western portion of the Brazilian

Amazon and showed the strong influence exerted by the tropical climate on the formation of soils and lateritic crusts, as well as the contribution of the erosion of volcanic rocks from the Andes in the accumulation of Hg. They suggested that these geological processes caused Hg to accumulate efficiently, which would explain the extensive distribution of Hg found in the Amazon. Simialrly, Lechler et al. (2000) also reported high mercury levels in Madeira River basin, Brazilian Amazon, are due largely to natural origin They also emphasized that, on a local scale, additional Hg enrichment can be related to artisanal gold mining effects. Furthermore, they argue that, in the main rivers, the dilution caused by the large volume of water and the high content of transported particles can contribute to the dispersion of Hg. The transport of Hg from soil to water and stream sediments is a prolonged process, but it can be intensified by the action of intense rainfall, which is typical of the region (tropical zone). Hence, soils can be potential sources of contamination for water and stream sediments.

3.2. Occurrence and distribution of Hg in stream sediments of IRW

The Hg concentrations in the basin ranged from 0.001-0.27 mg/kg in active stream sediments (Table 1). About 4.6% of the samples have values < LD and there is no record of any sample with values above the Brazilian reference limit (486 µg/kg; CONAMA, 2012) and, following this, present low probability risks to biota because Hg values below 170 ug/kg present a low probability of adverse effects on biota and only Hg concentrations above 486 ug/kg would cause harmful effects on organisms. When compared to the regional stream sediment GB of Hg estimated by the method mMAD for IRW (140 µg/kg; Salomão et al., 2020), only 17 samples (corresponding to 2.24% of the total samples) exceeded the threshold limit. Also, most of the sediment samples have lower level than the US-EPA value of 0.2 ppm. Similar, low level of Hg was obtained in sediments of the continental shelf of the Amazon River (14 – 160 µg/kg; Siqueira et al, 2018), as well as in the Itacaiúnas River (Borges et al., 2018) and Madeira River basin (Bonotto et al., 2018). Mercury concentrations in sediments were also compared to the Australia and New Zealand default sediment guideline value (DGV; 150 µg/kg), which is commonly used for guidance on the remediation of contaminated sediment or aims to provide a guideline for restoration of polluted sites (Water Quality Australia, 2018). Only 1.18% of total samples, concentrated in the Itacaiúnas river sub-basin, exceeded the DGV limit. Numerical sediment quality guidelines, such as threshold effect levels and probable

effect levels (PEL) have been used to screen Hg contamination of sediment (MacDonald et al., 2000).

The concentration of Hg in sediments vary significantly among different domains and sub-basins (p<0.05). The spatial distribution of Hg (Fig. 2) indicates that the highest concentrations of Hg are located, in general, in the Tapirapé and down parts of Itacaúnas and Parauapebas sub-basins, in the Bacajá Domain (north portion of IRW) and in the Carajás Basin (central portion of IRW), similarly to what happens with the spatial distribution of both soils (Fig. 2). This can also be seen in boxplots (Fig. 3) that allow the comparison between the Hg concentrations of both top and bottom soils in relation to stream sediments. It is noted that the average concentrations found in the stream sediment samples are generaly less than half of the concentrations measured in soils, and the same occurs with the maximum limits. In both cases, there is strong evidence of natural enrichment in Hg in the geological Bacajá Domain and Carajás Basin. This indicates that the soils are potential sources of Hg for stream sediments. Moreover, it should be considered that independent of Hg concentration in sediments, Hg accumulation rate and its concentrations can increase in fish due to bioaccumulation. Hunter et al. (1987) reported that Hg level in fish exceeded the WHO permissible limit (0.5 ppm) in Onondaga Lake wherein 90% of the surface sediments contained Hg concentrations > 0.1 mg/kg. However, this trend was not observed by Oppong et al. (2010) despite having high content of Hg in sediments. Similar poor correlation was observed by Rose et al. (1990). Therefore, the relationship between Hg concentrations in fish and sediments is not direct, rather Hg accumulation in fish is depending upon several other factors that affect sediment mythylation rates, Hg bioavailability in sediment/water column and trophic interaction, etc. (Oppong et al., 2010; Jackson 1990).

3.3. Occurrence and distribution of Hg in stream water of the IRW
3.3.1.   General stream water characteristics of the IRW

The basic water characteristics of the IRW did not show any significant variation between the rainy (RS) and dry (DS) seasons, except turbidity, Fe, Mn, and Al (Sahoo et al, 2019). Thus, the basic water characteristics were presented combining both seasons. As shown in Table 2, the average pH in the six sub-basins ranged from 6.93 to 7.23, indicating that the waters were mostly neutral to slightly alkaline. However, a few pH values were outside the limit established by Brazilian regulations (CONAMA Resolution No. 357/2005), and indicate the local occurrence of a moderately acidic environment

(minimum values varying between 4.32 and 6.11; Table 2), which may be related to natural processes such as erosion, surface runoff and/or changes in land use. The average temperature in the sub-basins ranged from 24.97 °C to 25.87 °C (Table 2). Similarly, the average dissolved oxygen (DO) varies from 4.89 to 6.07 mg/l, except for the Sororó sub-basin where it is of 4.89 mg/l (Table 3). The DO values are mostly compatible with the normal values of the Brazilian legislation, however, the minimum values observed in the six sub-basins were well below the minimum value required. Based on this information, along with Eh values (ranging from -229 mV to 397 mV), it can be expected the occurrence of anoxic conditions in some sampling points. The maximum electrical conductivity (EC) was registered in the Parauapebas sub-basin (1260 µS/cm), followed by Itacaiúnas River (752 µS/cm) and others. The average turbidity varies widely ranging from 14.78 NTU in Cateté to 49.74 NTU in Sororó sub-basin (Table 2). According to Sahoo et al. (2019), turbidity also showed strong seasonal variation with higher values in the rainy period (average 34.25 NUT) than in the dry period (average 23.26 NTU); similar behavior is shown for Fe (rainy period: average 3.29 mg/l; dry period: average 2.14 mg/l) and Al (rainy period: average 0.33 mg/l; dry period: average 0.24 mg/l), while Mn was higher in the dry period (average 0.42 mg/l), than in the rainy period (0.29 mg/l). Fe, Al, and Mn values in surface waters of the IRW were significantly higer than the CONAMA 357/05 limit (Sahoo et al., 2019). Higher Mn occurrence in the dry period results from redox cycling of Fe and Mn via biogeochemical processes, while higher Fe and Al in the rainy period can be explained by influence of surficial erosion of the exposed aluminous-iron crusts and soils in deforested areas with intense leaching and run-off during the rainy season, that caused concomitant increased turbidity (Sahoo et al., 2019).

3.3.2. *Distribution and concentrations of Hg in stream water*

The descriptive statistics of Hg concentrations in the six sub-basins during the rainy and dry period is summarized in Table 1 and their distribution pattern was shown in Fig. 2. It can be see that Hg concentrations in the stream water ranged from <LD (<0.1 µm/l) to 0.13 ug/l in the rainy period and is always below DL in the dry period, without significant variations between the two climatic periods. For this reason, means values of Hg do not exceed 0.05 µg/L and no significant distinct Hg distribution patterns were also observed between the different sub-basins and geological domains. In the rainy season, 5 samples which had detectable levels (0.10 - 0.13 µg/ L) – this is equivalent to 0.7% of the

analyzed data (Fig. 2). These detectable values of Hg were obtained in the Vermelho River sub-basin (two micro-basins presented values of 0.101 and 0.115 μg/L of Hg); in the Parauapebas (one sample showed a concentration of 0.11 μg/L of Hg); and in the Itacaiúnas (two microbasins showed levels of 0.108 and 0.134 μg/L of Hg). In the sub-basins of Sororó, Cateté and Tapirapé rivers, all samples exhibited Hg levels below the LD. The higher concentration in the 5 points in the rainy season possibly have resulted from run-offs from the watershed during rainfall event. Overall, the maximum Hg concentrations found in all sub-basins were below the Hg threshold value (0.2 μg/L) for freshwater of classes I and II established in CONAMA Resolution No. 357/2005 (Table 1). For drinking water, the Ministry of Health of Brazil, in its Ordinance No. 2,914 adopted the limit of 1 μg/L of Hg, the same value assumed by the WHO (2017) and by the CWQG of Canada. The U.S. EPA, on the other hand, adopts a value of 2 μg/L of Hg and Japan from 0.1 to 0.3 μg/L. Based on these legislations, the results obtained indicate that the risks of Hg poisoning related to both the ingestion of surface water from the IRW and its absorption through the skin are extremely limited or even non-existent. Many authors have also reported that drinking water with such low levels of Hg cannot be seen as significant sources of exposure to the general public (Amos et al., 2014; Jaffe et al., 2014; Quétel et al., 2014; Abass et al., 2014). Fadini and Jardim (2001) detected in 17 tributaries of the Rio Negro (Brazilian Amazon), for example, an average concentration of 0.00045 μg/L Hg. These examples confirm the idea that, in Amazon rivers, under natural conditions, Hg is present in water at very low levels (Pereira et al., 2019). Nevertheless, there is significant evidence of contents of Hg in fishes that are probably related to biomagnification processes and need precaution (Lacerda et al., 1994; Borges et al., 2018; Nyhlot et al., 2022).

3.4. Relationship between Hg and physico-chemical variables in stream water in the IRW

Although the majority of Hg concentrations in stream waters were below the DL, the few detected concentrations were correlated with water quality (Fig. 4). It can be seen that Hg showed moderate negative relation with some physico-chemical parameters such as temperature, DO, Eh, turbidity. It is generally reported that turbidity, temperature, DO, organic matter, pH, and Eh are the key variables influencing Hg in freshwater bodies (Kabata-Pendias and Mukherjee, 2007; Emmerton et al., 2018, Pestana et al., 2019). Turbidity, which is caused by suspended particles in the water column, results in the decrease of Hg in the water (Emmerton et al., 2018). High dissolved oxygen favors the

formation of Fe/Mn/Al-oxides that tend to absorb Hg, resulting lower Hg levels in waters with higher DO (Fig. 4). Hence, it was observed a negative relation of Hg with Fe, Al, and Mn (Culvin-Aralar, 1990). This indicates that Fe/Mn/Al oxyhydroxides colloids scavenge Hg and other metals and sink to the bottom sediments, resulting in lower Hg levels in conditions of high oxic conditions (Cuvin-Aralar, 1990). Although the results in this study showed that Hg in the stream sediment has no direct relation with Hg levels in the corresponding water (Fig. 2), the biochemical cycling of Hg at the sediment-water interphase can occur depending on the environmental conditions (Hamilton et al., 1984). It should be considered that the DO can suffer a drastic reduction when there is a considerable increase in the concentration of suspended material in water (Tundisi, 2008) or consumption and decomposition of organic matter (oxidation) caused by the respiration of aquatic organisms and by the oxidation of metal ions such as iron and manganese, which lead to an anoxic condition (Esteves, 2011). In the IRW, sampling points under anoxic conditions were registered (Sahoo et al., 2019) and thus it is suggested that the levels of organic matter should be checked at these points, given the fact that in these anoxic conditions, microorganisms can convert Hg^{2+} to CH_3Hg (Watras et al., 1995). The temperature follows the characteristics of tropical regions, presenting high averages in both seasons. These conditions can interfere with the concentrations of Hg vapor in surface water, as it can be more easily remobilized to the atmosphere.

3.5. Distribution of Hg in surface sediments of plateau lakes

The Hg contents in sediments of plateau lakes ranged from 80 to 590 µg/kg, with average varying from 180 to 350 µg/kg (Table 1), and are comparatively higher than those registered in soils and stream sediments of IRW. There is also a significant differentiation ($p< 0.05$) in Hg concentrations between lakes (Table 1, Fig. 5,6). Highest concentration was found in VL (130-590 ug/kg, average 350 ug/kg), followed by TI2 (150-350 ug/kg, average 240 ug/kg), AM (average 220 ug/kg), TI3 (average 200 ug/kg) and TI1 (average 180 ug/kg). The average concentrations found in the sediments of these lakes are approximately double of the concentrations measured in the catchment soils and stream sediments (Sahoo et al., 2019). This indicates that lake sediments are the best sink of Hg in the IRW. About 5% of samples have values <LD and about 2.7% values above the reference limits (486 µg/kg; CONAMA, 2012), this is mainly from VL (4 samples). When compared with the estimated geochemical background value of lake sediments (340 µg/kg of Hg, based on mMAD), around 11% of the total lake sediment samples

exceeded the limit. However, this is significantly varied lake-wise. The maximum number of samples (12) that exceeded the GB of Hg were from VL, followed by 3 from AM and 1 from TI2, while no sample from TI1 and TI3 exceeded it. Most of the lake sediments samples in the study area show Hg concentration significantly higher than the estimated average of Hg in UCC (Wedepohl, 1995; Taylor and Mclemann, 1985). When compared with the Australia and New Zealand ecotoxicological data (Water Quality Australia, 2018; cf. Table 1), the mean Hg levels of all lake sediments were higher than the default guideline value (DGV; 150 µg/kg), but they were much lower than the upper guiding value (GV-high; 1000 µg/kg) of Hg, indicating a low probability of toxic effect to benthic organism (Water Quality Australia, 2018). Moreover, THg content of several sediment samples were above Threshold Effect Level (TEL) of 0.13 µgg−1, however, all the THg concentrations of the sediments were lower than the Probable Effect Level (PEL) of 0.70 µgg−1 for Hg in sediments postulated by Smith et al. (1996) and MacDonald (1994). According to the Sediment Quality Criteria for Protection of Aquatic Life (Environment Canada, 1992, cited in Haines et al., 1994), all the sediments in this study had mean THg below the toxic threshold of 1.0 µgg−1 and minimal effects threshold of 0.20 µgg−1; thus there is a low risk from Hg.

3.6. Occurrence and distribution of Hg in lake water

In all five lake waters, Hg concentrations in both dry and rainy periods in all samples exhibited levels below the LD (< 0.1 ug/l) (Table 1), nearly similar with stream water in the IRW. These concentrations were also very low when compared to the the maximum permitted level (0.2 µg/L) for fresh water (class II; CONAMA 2005) and WHO drinking water limit (1 ug/l). In general, uncontaminated freshwaters generally contain < 0.005 ug/l total Hg, althoug 0.01 to 0.02 ug/l can be found in humic lakes (Meili et al.,). The Canadian water quality guideline (CWQG) for protection of aquatic life (0.026 ug/l; Environment Canada, 2003) was used as the basis of evaluation for Hg levels in the studied lakes. In Carajas uptake lakes, all samples were below the aquatic life protection limit and thus are considered as safe for drinking and bathing. Similar concentrations were also observed in Lake Victoria (Campbell et al., 2003). Moreover, despite having high concentration of Hg in lake sediments, the lake water quality is preserved. This indicates the existence of factors that control water-sediment interaction and prevent Hg release from sediments.

3.7. Hg in lake water and its relationship with physico-chemical characteristics

This study demonstrates that despite having Hg enrichment in lake sediments and some catchment materials, Hg level in water of all five lakes was below the DL in both dry and wet periods. This indicates that Hg in sediments did not exert significant influence on the composition of the waters. The interaction between sediments and waters could be influenced by several factors including their physico-chemical characteristics (Table 3). One controlling factor could be related to the oxic conditions of the lakes that show DO concentrations ranging from 6.1 to 13.3 mg/L in the rainy period and from 5.2 to 10.5 mg/L in the dry period (Table 3). Temperature is also a major factor controlling mercury concentration in aquatic system. The average water temperature shows little variation between the dry (25.73–30.1 °C) and rainy season (26.5–29.75 °C). Same is also observed between the surface and bottom water as the maximum temperature difference was < 2 °C, indicating that these lakes were weakly stratified in both seasons, and, in somecases, they are relatively homogenous, which favored mixing processes by wind action. All these factors may have favored low Hg concentrations in lake waters. Also, increasing concentrations of organic carbon (under suboxic overlying water) and strong positive correlation between Hg and TOC in lake Carajás sediments (Sahoo et al., 15, 2017) could indicate processes such as the well-known Hg binding capacity of humic materials in sediments removing mercury from the lake water column (Gambrell et al., 2001). Although, high concentrations of Fe in lake waters and sediments can decrease the mobility of Hg and cause low Hg in lake waters by scavening, the poor relation between Hg and Fe in lake sediments indicates that Fe-oxyhydroxides has a minor role to this (Sahoo et al., 2017). Moreover, morphological features such as shallow depth are responsible for turbid water by basin flushing and frequent re-suspension of organic matter particles from the sediment, which can influence the scavenging of Hg.

Conversely, pH and redox potential can have negative correlation with Hg concentrations in aquatic ecosystems. Lake water acidification can increase mercury concentration in water by decreasing sedimentation rates, by mobilizing mercury from sediments, or by affecting sediment-water interactions (Verta et al., 1990). However, since the studied lake water bodies are found to be acidic, it could occur an increase of bacterial decomposition of organic carbon contained in the sediments with release of Hg, stimulating methylmercury production at the sediment-water interface. This will be facilitated in anoxic conditions, which can favor methylation in sediments and could

result in a net increase of solibility, mobiluity of MeHg and its bioaccumulation in food chain (Gambrel et al., 2001; Morel et al., 1998). It has been also suggested that Hg bound to Fe-oxyhydroxides particles may be released upon reduction in the hypoxic zone in deeper lake waters (Campbell, 2001). Moreover, although, the results in this study showed that mercury content in the sediment has no direct influence on mercury levels in the water, depending on water conditions, a biochemical cycling of Hg at the sediment-water interphase could still occur, promoting release of Hg to water (Culvin-Aralar, 1990). Therefore, frequent monitoring of water and fish samples are required to assess the Hg risk in lake ecosystem.

3.8. Multivariate statistics to understand the major factors controlling Hg in soils and sediments

To understand the possible sources and factors controling Hg in the stream and lake sediments and surface soils, PCA was performed separately on each dataset including Hg and other elements (Fig. 7). Based on eigenvalues (eigenvalue > 1.0), two principal components (PCs) cumulatively explained 55.99% of the total variance in the samples in the present study. Based on this, three major groups of elemental associations were identified with one group clearly identified common Hg association in all soils, stream sediment and lake sediments. In the SS, PC 1 contributed 32.5% of the total variance and Hg was grouped with TOC, LOI, SO_3, Se, Al_2O_3. This is highly similar with bottom soils and lake and stream sediments. In general, elements of anthropogenic origin are associated with unstable fractions, thus they cannot maintain similar geochemical association. Therefore, the strong similarity between soils and sediments supports a dominant geogenic origin for their geochemical signature. Futhermore, the factor score of SS and BS demonstrates strong similar spatial variability between surface and bottom soils, which further supports geogenic control of Hg distribution. The association of Hg with Al in both top and bottom soils reinforces the hypothesis that Hg originated from geogenic sources and lake sediments indicate that organic matter exerts significant control on the Hg enrichment. A heat map of the Spearman correlations (Fig. 8) was obtained via correlation analysis as a further supplement to PCA. Significant positive relationships among Hg, TOC, and SO_3 were observed (Fig. 8) implying that Hg has high affinity for organic matter, forming complexes with both inorganic and organic forms of mercury (Driscoll et al. 1995; El Bilali et al. 2002; Arias et al. 2004; Liu et al. 2012).

Morever, the strong positive Hg-TOC relationship further suggests that sediments with high organic content may effectively scavenge of Hg. This is due to humic materials in sediments are highly effective in binding Hg, and, also organic enriched sediments are responsible for mercury methylation by proving more energy source for anaerobic microbes (Gambrell et al., 2001; Zhu et al., 2018). Therefore, organic matter plays a major role in controlling Hg in soils and sediments, which agrees well with several previous studies reported elsewhere (Bengtsson and Picado, 2008; Chakraborty et al., 2015; Sahoo et al., 2015; Chen et al., 2009). Particulate and dissolved organic matter are major transport vectors of Hg from forests to lakes owing to the enrichment of Hg present in the organic soil horizons (Klaminder et al. 2008; Biester et al. 2012; Jiang et al. 2018). Moreover, in lakes sediment organic matter, including algal-derived, dissolved, and particulate fractions, adsorbs mercury and can influence the rate of mercury delivery to lake-bottoms. This finding indicated that the increase of organic matter can be considered as an indicator of Hg enrichment, as demonstrated in the case of lake sediments (Gambrell et al., 2001). This can be further seen in different media of the IRW in binary plots of Hg vs LOI and Hg vs TOC (Fig. 9). However, it can be noticed that for sediment samples of TL2, despite having high enrichment of TOC, they do not show parallel increase of Hg. This could be due to the excessive accumulation of organic matter from autochthonous sources and additional contribution from macrophytes. The excess in TOC accumulation could be diluting the signal of Hg. Therefore, the organic fractions of soils and sediment significantly affect mobility and availability of mercury in them. Clay particles have also high capacity to adsorb mercury and this can put limits in mercury bioavailability (Desauziers et al. 1997; Ullrich et al. 2001; Arias et al. 2004; Zhu & Zhong 2015). The influence of clay minerals in Hg distribution is indicated by the positive association between Hg and Al, but this association doesn't occur in the lakes (Fig. 8). A possible explanation is that aluminous clay minerals are not abundant in lake sediments and the opposite should occur on soils and stream sediments.

Besides, the accumulation of Hg in lake sediments can be related to various allochthonous and autochthonous factors, including the catchment lithological characteristics and vegetation pattern, lake basin morphology, soil erosion, and internal lake processes, such as lake productivity and trophic state (Schutze et al., 2020). The catchment weathering can be one of the major sources of Hg by which naturally occurring Hg can be delivered to lake sediments, and this is strongly dependent on the type of bedrock geology of a lake catchment (Sahoo et al., 2019). To decipher these effects in the

lakes of the Carajás plateau, a comparison with their catchment materials such as ferruginous lateritic crust/soil and Al-enriched ferruginous lateritic crust/soils was made (Fig. 5). Mercury concentrations in the five studied lakes are higher than those found in the catchment materials. The highest Hg content was observed in the Al-enriched soils, which are a product of Al-enriched ferruginous lateritic crusts commonly orginated from meta-volcanic basaltic rocks. Carvalho et al. (2019) mentioned the occurrence of higher Hg in metabasalt-derived soils, which can result of Hg being related with volcanic activities that are a natural source of mercury (Gustin et al., 2000; Lintern et al., 2020). However, when compared between the Hg distribution in lake sediments, highest concentration was found in VL and lowest in TL1 and TL3, but the catchment of latter two lakes is dominated by meta-volvanic rocks, while the former is influenced by metamafic sills and dikes that are also mafic hypabyssal rocks but not related to the metavolcanics of Carajás. This indicates that the role catchment lithology is not predominant, rather the Hg concentrations in lake sediments are more influenced by high contents of organic matter and additional factors like internal lake productivity, phytoplankton biomass, and lake depth, which are responsible for higher sedimentary organic input. Higher level of total Hg in the shallowest lake TI2 and shallower portion of VL compared to other lakes indicates that Hg is inversely related to water depth (Fig. 6). The shallow depth favors a higher contribution of organic matter from autochthonous sources, such as siliceous sponge spicules, algae and aquatic vegetation due to the greater availability of light (Tolu et al., 2017) and leads to more decomposition of organic matters, corroborating the finding that Hg contamination is elevated in relatively shallow lake areas. Also, lake trophic state and chlorophyll-a concentrations can play a role in Hg enrichment in lake sediment, as supported by the highest chlorophyll-a average content in VL lake (Table 3). Hg concentrations in northern Lake Victoria are also correlated with chlorophyll-a concentrations, suggesting that the phytoplankton of Lake Victoria played an important role in THg cycling in sediments (Campbell, 2001). Thus, productive lakes and the relevance of organic matter sedimentation are primarily responsible for the more accentuated Hg content in the lake sediments. Since organic matter is the energy source of anaeroric bacteria, lake with high organic matter in sediments may lead to MeHg production and favor its accumulation in fish and other aquatic organism (Gambrell et al., 2001). However, there is no direct association between total Hg and MeHg dynamics in sediments, rather this is a complex process that is influenced by multiple biogeochemical and environmental factors that control the transport, bioavailability, methylation and

trophic transfer of Hg to fish ((Chen et al., 2009; Nyholt et al., 2022). For example, Hg re-emission from sediment-organic complexes can occur in area prone to hypoxia, in which Hg methylation rates increase because of the accelerated activity of anaerobic bacteria and formation of methyl-Hg that can be transferred to the aquatic food chain (Yang et al., 2020; Driscoll et al. 1995; Ullrich et al. 2001; Chen et al., 2009). Therefore, frequent monitoring of Hg in lake waters and sediments along with environmental conditions, Hg species, and their accumulation in fishes are required to managing safe ecological life in this ecosystem.

3.9. Environmental risk assessment for Hg in IRW

Although national/international reference values have been used widely in the assessment of heavy metal contamination in soils and sediments, these guidelines do not consider the GB registered in different media of distinct regions. Soil and sediment quality management frameworks in many parts of the world, including Australia, also state that pollution reduction and the contamination assessment should be based on the regional background conditions of the specific aquatic system (Canadian Council of Ministers of the Environment, 2003). Moreover, it is necessary to consider the regional GB in the respective media to more accurately evaluate Hg contamination in any environmental samples. In this study, contamination indices such as CF and ER in soils and stream sediments and lake sediments have been evaluated using the respective regional GB values of IRW (soil, 320 µg/kg; stream sediments, 140 µg/kg; and lake sediments, 340 µg/kg). The results (Table 4) showed that the CF values in SS and BS obtained in all sub-basins are predominantly <1, indicating minimum contamination, as described below: Sororó, Tapirapé and Cateté (100%), Vermelho (99.25-99.62%); Parauapebas (99.45-98.9%); Itacaiúnas (97.38-98.92). The number of samples that showed moderate contamination values (CF = 1-3) in the soils of sub-basins are highest in Itacaiúnas (11 samples in BS and 5 samples in SS), followed by Parauapebas (4 samples in SS and 2 samples in BS), and Vermelho (2 samples in SS and 1 sample in BS). Samples presenting high and very high contamination (CF = 3-6 and > 6) are completely absent in IRW. Similar contamination level was registered in stream sediments, with dominating of low contamination in most of the sub-basins with 100% samples having CF < 1, except 11 samples (4.2%) of Itacaiúnas and 1 sample (1.75%) of Tapirapé sub-basin, which registered moderate contamination (CF = 1-3). This is further evaluated using potential ecological risk index (ER) (Table 4). The 'ER values show low risk (ER≤

40) in 100% SS and BS samples for the Sororó, Tapirapé, and Cateté. In Vermelho only 2 SS and 1 BS samples (< 1% samples) exhibit a moderate risk level (ER = 40-80), while the remaining samples classify as low risk category. In contrary, a larger number of samples from Itacaiúnas (11 samples in BS and 5 samples in SS) and Parauapebas sub-basin (4 samples from SS and 2 samples from BS) are classified as moderately contaminated (ER = 40-80) and no samples considered into considerable (ER = 80-160) and very high (ER = > 160) category. Overall, the strong correlation of CF and ER values between surface and bottom soils as well as with stream sediments and their spatial correlation with respect to geological domains reflect natural Hg enrichment and support the assertion that geological characteristics are crucial to understanding the Hg concentrations present in the IRW.

Compared with the SQGs, among the 767 sediment samples in six sub-basins, Hg contents are always below the TEL and PEL values and none of the samples exceeded the CONAMA limit. These results suggest that sediments do not exhibit potential ecological risks. Similarly, all CF and ER values of all sediments were within the low risk category. However, this is different from lake sediment. This can be seen that maximum percentage of samples (54%, 14 samples) were clasisified into moderate contamination (CF= 1-3) from VL, while only 7.6 % (3 samples) and 3% (1 sample) were from AM and TI2, respectively, and no single sample has been classified into this category from TI1 and TI3, which were fully grouped into minimal contamination category. This is very similarly with ER values as the moderate ecological risk (Ei= 40-80) was mainly registered in VL (46%), while this is reduced to only 3% and 1% in AM and TI2, respectively, and no sample in this category from TI1 and TI3. Also, not a single sample from any lake is classified into considerable/high ecological risk category.

Moreover, the potential Hg risks in surface water bodies was calculated by using hazard quotient (HQ), both for river and lakes. For water bodies, the Screening Benchmark base on the WHO Standard setting establishes that the Hg contamination in drinking water should not exceed 1.00 μg/l and it was adopted. Results show that in all lake and river water samples, HQ was less than 1, indicating Hg risks in water bodies of contaminated sites were lower. However, the potential risks might be posed due to the possibility of continual bioaccumulation and long term exposure.

3.10. Hg risk to human health of adults and children living in the Carajás region

The non-carcinogenic Hazard Quotient (HQ) calculated on the basis of soil exposure pathway (e.g. inhalation, ingestion, dermal) and the sum of HQ values (HI: hazard index) are shown in Table 5. For the ingestion exposure way, HQ values in the soil vary from 1.84E-05 to 0.001985 with the mean of 0.000341 in adult and from 0.000154 to 0.016636 with the mean of 0.002861 in children. For inhalation, this varied from 1,13E-07 to 1.22E-05 and 0.005645 and 0.609664 for adult and children, respectively. While the dermal exposure ranged from 8.48E-06 to 0.000916 in adult and 0.000954 and 0.103017 for adult and children, respectively. This indicates higher exposure of children and the overall pathway decreased in the following order: ADDingestion < ADDdermal < ADDinhalation. So, the dominant exposure way could be the ingestion and this finding is consistent with other studies, which have shown that the main pathway of Hg exposure from soil was the ingestion (Huang et al. 2014; Sahakyan et al. 2018). The HQ calculated on each exposure way of soil ingestion, inhalation and dermal absorption values are far less than 1, which is the USEPA threshold limit for non-carcinogenic risk, indicating that the Hg health risk through soil ingestion and inhalation pathway are insignificant in IRW. The HI represents the following results: HI values vary from 2.7E-05 to 0.002913 with the mean of 0.000501 for adult and from 0.006753 to 0.729317 with the mean of 0.125443 for children. Based on the health risk index (HI), also no significant risk of non-carcinogenic effects is indicated for both children and adults in the study area as the values were much lower than the assumed safe level of 1 and therefore showed that Hg does not constitutes a serious non-carcinogenic risk for both adults and children exposed to the soil in the study area.

4. Conclusions

The study of multimedia (soil, stream sediments, and lake sediments and waters) Hg distribution in the IRW showed that Hg is generally present at very low levels in all the studied environmental compartments, but provided strong indications that its distribution in the IRW is essentially explained by its derivation from natural sources by geogenic processes. Multivariate analysis also confirms that Hg originated from natural sources that majorly influenced the Hg level in different media. The highest enrichment in lake sediments is due to the high organic matter contents observed in the lakes with subordinate influence of catchment Al-laterititic rocks and soils. The ecological risk index indicates low risk for soils, stream sediments, and lake sediments, except for 11% of lake sediment samples, which registered moderate risk from Hg. In case of non-carcinogenic

risk for human health, the overall hazard index estimated is much below the USEPA threshold limit. Thus, the concentrations of Hg found in soils and sediments in the IRW indicated a low probability of adverse effects on biota. Moreover, the results of this research indicate that IRW soils can be considered potential sources of Hg for water and current active sediments, and Hg release can be intensified by the frequent action of rain, a typical characteristic of the tropical zone, and by other natural phenomena. In the aquatic environment, Hg is not directly available in surface water, it is probably adsorbed to particulate matter, which justifies its very low levels of Hg. However high Hg enrichment in lake sediments indicates that the biogeochemical conditions in anaerobic lake sediments may be more favorable for MeHg production and subsequent accumulation by fish. Thus, it is considered important to deepen the future studies on the the monitoring of different forms of inporganic Hg as well as methylmercury in environmental media and their bioaccumulation in Amazon fishes to avoid misdiagnosis and to reduce the environmental risks of future intoxication of humans by Hg.

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