Effects of illegal gold mining on Hg concentrations in water, *Pistia stratiotes*, suspended particulate matter, and bottom sediments of two impacted rivers (Paraíba do Sul River and Muriaé River), Southeastern, Brazil

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Received: 4 May 2022 / Accepted: 10 September 2022 / Published online: 17 September 2022
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Abstract Recent reports of illegal small-scale alluvial gold mining activities (locally called *garimpo*) by miners working on rafts in the Paraíba do Sul River (PSR) and in one of its tributaries (Muriaé River (MR)) have raised concerns about Hg contamination. This study aimed to evaluate the impact of *garimpo* activities on Hg contamination in three environmental compartments. Water, sediment, and aquatic macrophytes (*Pistia stratiotes*) were sampled during the rainy season in PSR, forming a 106-km transect from the point where *garimpo* rafts were seen and/or seized by the Federal Police. They were also sampled in the MR. Total and dissolved mercury (Hg) concentrations in water and total Hg in the suspended particulate matter (SPM) sampled in the PSR increased by 1.7, 1.5, and 2.1 times at the points where the rafts were seen compared to the point immediately upstream. In the MR, Hg concentrations were higher than those in the PSR, but most values in the environmental compartments were below the safe limits (174–486 ng·g⁻¹, threshold and probable effect level, respectively), with the exception of Hg in the SPM of one of the MR sampling points (256 ng·g⁻¹) and the mining tailings (197 ng·g⁻¹). Sediment granulometry was exponentially associated with Hg concentrations in the sediment (\(R^2=0.75, p<0.0001\)) and is also essential to understand the physical impacts of *garimpo* on PSR. Future studies should focus on assessing the seasonal variability of Hg concentrations in the studied compartments, especially if *garimpo* is identified during the dry season.

Keywords Gold mining · Mercury · Sediment · Paraíba do Sul River · Muriaé River

Introduction

Environmental contamination by metals poses a serious threat to the environment and to food security due to the accelerated development of agriculture and industry, as well as the disturbance of natural ecosystems due to the high increases in the worldwide population (Sarwar et al., 2017). High concentrations of metals in soils, sediments, and water resulting from anthropogenic activities can lead to harmful biota and human health effects (Franz et al., 2013; Gamvroula et al., 2013; Alexakis, 2020; Dall’Agnol et al., 2022). Indeed, arsenic, lead, mercury, and cadmium are...
ranked among the top ten pollutants in the priority list ranking of the American Agency for the Toxic Substances and Diseases Registry (ATSDR, 2019), a list that employs compound toxicity and human exposures as criteria for ranking the frequency in which toxic substances are found in facilities containing hazardous waste. Among these elements, mercury (Hg) has been classified for 30 years as the third leading pollutant in this ranking.

Environmental contamination by Hg is associated with several anthropogenic activities, such as fossil fuel burning, industrial activities, solid waste disposal, and forest clearing (Selin, 2009; Dall’Agnol et al., 2022). Among these activities, small-scale alluvial gold mining (locally called garimpo) is noteworthy, known as the most significant Hg pollution source worldwide (Esdaile & Chalker, 2018). Because of this, the reform of this activity is considered a priority in the Minamata Convention on Hg that aims to reduce and eliminate Hg use and the production of Hg-containing products (UNEP, 2013). Brazil acceded to the treaty in 2018 (Brasil, 2018). The main actions taken by the countries participating in this treaty include banning the opening of new mines for Hg extraction, regulating the use of Hg in garimpo activities and in the production of everyday items, such as fluorescent lamps and batteries (UNEP, 2017).

Garimpo activities carried out by rafts dredge the bottom sediments from rivers and employ metallic Hg (Hg0) to form a gold-Hg amalgam that is later burned using a gas torch in the open to volatilize the Hg and recover the gold (Guimaraes, 2020; Pestana et al., 2022). Estimates indicate that for each 1 kg of gold produced through garimpo activities, 1.3 to 1.7 kg of Hg are released into the environment (Hacon et al., 1990; Pestana et al., 2022; Pfeiffer & Lacerda, 1988), with emissions from this activity higher in South America compared to all other regions of the globe (UNEP, 2019). It is estimated that all of the Hg employed in this activity, 54% are released into the atmosphere in the form of vapor and 46% are released into rivers as Hg0 (Hacon et al., 1990; Pfeiffer & Lacerda, 1988), which can become methylated and bioaccumulate in exposed biota (Lacerda & Malm, 2008). Epidemiological studies indicate that the Amazon region is one of the most Hg-exposed areas worldwide (Passos & Mergler, 2008), and studies in southeastern Brazil have already reported contamination of sugarcane workers exposed to organomercurial pesticides in the past (Câmara, 1986, 1990, 2017). In addition to environmental Hg contamination, gold miner exposure to Hg vapors during gold-Hg amalgam burning causes severe damage to the central nervous system, as these vapors accumulate in the brain (Lauthartte et al., 2018; Li et al., 2015).

In the scientific literature, gold mining in the Paráiba do Sul River (PSR), located in southeastern Brazil, and consequent Hg contamination of surrounding aquatic ecosystems have been reported as a past event until now. Indeed, the PSR has a history of Hg contamination due to two anthropogenic activities that took place in the 1970s and 80s: i.e., widespread garimpo activities and the use of organomercurial fungicides in sugarcane plantations, as stated previously (Almeida & Souza, 2008; Lacerda et al., 1993). Chronologically, this garimpo activity began in the Muriaé River (MR), a tributary of the PSR, and later extended to the Itabapoana River (Lima, 1990). In 1980, the use of Hg agrochemicals was banned due to the intoxication of sugarcane workers by Hg (Brasil, 1980; Câmara, 1986, 1990). Seven years later, garimpo activities were prohibited in the PSR and its tributaries, in view of the risk of Hg contamination (Almeida & Souza, 2008). Indeed, Hg atmospheric deposition has decreased from the late 1970s to the present (15–30 µg·m−2·year−1) as a result of emission control measures implemented at that time (Lacerda & Ribeiro, 2004).

The events listed above and the prohibitions that resulted from them limited the activities of the gold miners in the PSR in the ensuing years. However, the context of the COVID-19 pandemic, associated with economic and political factors, motivated a new wave of garimpo in the PSR and MR at the end of 2021 (Folha): (a) the price of gold increased by 90% compared to pre-pandemic values, reaching R$ 320 per gram (Pontes, 2021), making the activity even more attractive; (b) the reduction in the number of people for environmental control in Brazil, favoring the advancement of illegal garimpo activities throughout the country, such as the recent invasion of the Madeira River (Amazonas) by hundreds of rafts and dredges (Pestana et al., 2022; Prazeres, 2021; Thomas, 2021); and (c) the federal government’s pro-garimpo agenda, especially in the Amazon region, which has implicitly encouraged miners across the country to return to the
activity (Guimaraes, 2020; Pestana et al., 2022). For example, the government issued two decrees (Brasil, 2022a; Brasil, 2022b) that encourage garimpo in the Amazon and proposed the development of the state through this activity. This is in the opposite direction of preservation, not only in the Amazon, but elsewhere in the country, since garimpo is unsustainable by definition (Guimaraes, 2020).

In October 2021, the Environmental and Military Police identified an illegal mining raft located in the PSR near the city of Itaocara, in the state of Rio de Janeiro (Trindade, 2021). One month later, the Federal Police launched “Operação Paraíba Dourado” (which means “Golden Paraíba,” in a literal translation) and four rafts were seized between the city of Cambuci and Pureza, a district of the city of São Fidélis (Folha de Itaíva, 2021a; Trindade, 2021). In the MR, there were also reports of an increase in garimpo activities since July 2021 (Folha de Itaíva, 2021b; Jornal Terceira Via, 2021). Previous studies conducted in this drainage basin indicated high Hg concentrations in several fish species, especially demersal ones (up to 0.3 µg·g⁻¹), indicating the significant role of garimpo activities concerning Hg biota exposure (Azevedo et al., 2017, 2018; Rocha et al., 2015).

In this context, this study aimed to evaluate the impact of garimpo activities on Hg contamination in three environmental compartments (sediment, water, and aquatic macrophytes) along a 106-km transect, starting from the point where the mining rafts were seized. Monitoring the impact of small-scale alluvial mining gold mining on Hg contamination is paramount, as garimpo remains the main source of Hg contamination for aquatic ecosystems in Latin America (Meneses et al., 2022). Higher Hg concentrations near the points where garimpo rafts were seized and/or seen are expected, as (I) the Hg⁰ used in the amalgamation of gold is insoluble in water, and (II) the effects of garimpo are spatially limited (Lechler et al., 2000; Guimaraes, 2020).

Material and methods

The PSR is formed by the union of the Paraibuna and Paraitinga rivers, whose sources are located in the state of São Paulo. It travels a distance of approximately 1100 km to its mouth, located at Atafona Beach (municipality of São João da Barra), where it flows into the Atlantic Ocean (Fig. 1). Its watershed is located in the most populous and industrialized area of the country (Southeast Brazil), with a total drainage area of 61,307 km², divided among the states of Rio de Janeiro (26,674 km²), São Paulo (13,934 km²), and Minas Gerais (20,699 km²). In addition, its upper and middle watersheds are constituted by rocks formed during the Precambrian period, predominantly migmatites, biotite, biotite-gneiss schists, granitoid gneisses, and quartztite invasions. The lower coastal plain basin is formed by tertiary and quaternary lands (DNPM, 1983). It is a river under federal control and its main tributaries are the rivers Pomba, Muriaé, and Paraibuna Mineiro (on the left bank), and Piabanha, Piraí, and Dois Rios (on the right bank) (AGEVAP, 2018). The highest flows are observed in the rainy season (December to February), with an average of 4624 m³·s⁻¹, and the lowest in the dry season (June to August), with an average of 115 m³·s⁻¹ (Almeida & Souza, 2008).

Campos dos Goytacazes is the largest city in the state of Rio de Janeiro and the penultimate city that the PSR passes through before flowing into the ocean. Its estimated population is of over 500,000 people (IBGE, 2021). Solid waste produced by the population of Campos dos Goytacazes and five other neighboring cities is collected and taken to a sanitary landfill in the district of Conselheiro Josino, which receives approximately 450 tons·day⁻¹ (Almeida et al., 2019). Although solid waste is a potential source of Hg contamination, mainly due to the disposal of fluorescent lamps and batteries (Cheng & Hu, 2012), this contribution is not relevant to the study areas, as the landfill is located more than 35 km away from the PSR.

Watershed Hg sources may include the runoff of legacy Hg in soils from past activities, including the use of organomercurials in sugarcane plantations and garimpo activities (Câmara, 1986; Lacerda et al., 1993), in addition to industrial discharges in the upper part of the river, in the city of Rio de Janeiro (Veeck et al., 2007). Although two small hydroelectric plants are located at the lower part of the PSR (namely Santa Cecilia and Ilha dos Pombos), which could limit Hg suspended particulate matter (SPM) transport downstream, they are located at 184 and 357 km from the study area and, therefore, their impacts on Hg dynamics should not be locally significant (AGEVAP,
Furthermore, as Hg$^0$ is insoluble, a significant influence from sources distant from the study area on the data interpretation is not expected.

The MR is one of PSR tributaries and is located in the lower portion of the basin (Fig. 1). It has a length of 300 km and a total drainage area of 8162 km$^2$. It is formed by the union of the Bom Sucesso and Samambaia rivers. It flows in a flat region, forming a floodplain in periods of large floods from the municipality of Italva to its mouth. It covers 26 municipalities, the most representative in terms of population being Muriaé, Itaperuna, and Carangola (ANA, 2022). Approximate channel width and depth for the PSR and MR are 494 and 96 m, and 7 and 2 m, respectively.

In the PSR, six sampling points were defined, forming a transect of 106 km between them. The sampling was carried out in December 2021 and P2 and P4 are the sampling points where illegal mining rafts were seized and/or seen, in the districts of Batatal and Pureza, respectively (Folha de Italva, 2021a; Trindade, 2021). At the MR, three points were sampled in January 2022, when illegal mining rafts were sighted (Fig. 2a, b). Points P8 and P7 are located upstream and downstream of the garimpo area, respectively. Local MR residents denounced the presence of illegal mining rafts that had been operating in the region since June 2021 (Folha de Italva, 2021b; Jornal Terceira Via, 2021). At the sampling points, the engine of one of the rafts’ dredges was observed in active operation (Fig. 2b). In addition, garimpo tailings were observed on the banks of the river (Site P9; photo image in Fig. 2c), which were also sampled concerning Hg concentrations. As stated previously, the samplings were carried out in view of denunciations and reported raft sightings. In this sense, seasonality, river discharges, and land use effects on Hg dynamics could not be included in the sample design.

Water and surface sediment samples were collected at all sampling points (P1 to P8) during the morning (09 AM–12 PM). Surface water (±10 cm) and surface sediment were sampled in the main channel of each river ($n=5$ independent samples for both matrices at each sampling point). Water samples were stored in pre-rinsed bottles with water from the same sampled point and sediment samples were stored in plastic bags. Aquatic macrophytes were only present at P1 and P2, where *Pistia stratiotes* specimens were sampled. The macrophytes were separated into roots.
and shoots and stored in plastic bags. At P9, only tailings from *garimpo* activities located on the banks (less than 1 m away from the river) of the MR were sampled. All samples were packed in thermal boxes and transported to the laboratory for processing.

The physicochemical parameters of the water column, such as pH, temperature (DM-2P, Digimed, Brazil), electrical conductivity (DM-3P, Digimed, Brazil), and dissolved oxygen (Model 55-12FT, YSI, USA) were measured in situ at all sampling points, with the exception of P9 (S1). The electrodes were periodically calibrated with buffer solutions to avoid measurement errors and the precision was of ±0.01 for all physicochemical parameters.

At the laboratory, the water samples were filtered using GF/F Whatman® filters (0.7-µm porosity) (Pestana et al., 2019). During the entire procedure, gloves were used to avoid Hg contamination. Likewise, all glassware was previously washed with nitric acid (HNO₃) and hydrochloric acid (HCl, 24-h baths for each acid) and subsequently rinsed with ultrapure water three times. Hg determinations were performed on the same day of sample filtering, in order to prevent Hg losses (Kasper et al., 2015). The filters were dried and weighed beforehand on an analytical balance (Model ME-5, Sartorius, Germany), and after filtration they were once again dried in an oven (<40 °C) and then weighed to obtain the mass of SPM.
Total Hg concentrations were determined in both unfiltered (total Hg in water) and filtered water samples (dissolved Hg in water <0.7 µm). The Hg concentrations in the SPM were obtained by subtracting the dissolved Hg concentrations from the total Hg concentrations, and the result was divided by the SPM concentrations.

For the analysis of total and dissolved Hg, 300 µL and 150 µL of 0.2 N bromine chloride (BrCl) were added in 30-mL aliquots of the unfiltered and filtered water samples, respectively. Prior to the determination, 150 µL of BrCl, 60 µL of hydroxylamine hydrochloride (NH₂OH•HCl), and 150 µL of stannous chloride (SnCl₂) were added to the samples. Analytical blanks were included (n = 3) in all analyses. The determination of total and dissolved Hg was performed by atomic fluorescence spectrophotometry using the cold vapor generation technique (CV-AFS Mercury Analysis System, Model 2600, Tekran Instruments Corporation, Toronto, Canada) calibrated with a 7-point curve (0.33, 0.83, 1.66, 3.33, 8.32, 16.35, and 33.33 ng·L⁻¹). The method detection and quantification limits were 0.06 and 0.2 ng·L⁻¹, respectively. A certified estuarine sediment sample (NIST 1646A) was used to evaluate the accuracy of the method and the obtained Hg recovery was 96.22±0.02% (n = 5). Reproducibility was assessed using analytical triplicates every 20 samples (coefficient of variation <15%).

The surface sediments were lyophilized (Freeze-Dry System, Labconco, Model 7,522,900, Kansas City, USA) and then separated into the fraction of interest (sieve <2 mm) for Hg determination and for granulometric analysis. For Hg determination, the samples were macerated with the aid of a mortar and pestle and then packed in polyethylene bags and stored until analysis.

The aquatic macrophyte (Pistia stratiotes) samples were lyophilized, separated into roots and leaves, and ground in a knife mill (Model MA048, Moinho Marconi, SP, Brazil) for homogenization. The samples were packed in polyethylene bags and stored until analysis.

Dry aliquots of 0.3 g of sediment were solubilized in 8 mL of aqua regia (3 HCl: 1 HNO₃), and 0.3 g aliquots of macrophyte tissues (leaf and root) were solubilized with 4 mL of ultrapure water + 2 mL of hydrogen peroxide (H₂O₂)+6 mL of H₂SO₄:HNO₃ (1:1) (according to the protocol described by Silva-Filho et al. (2006)). The extracts were solubilized in a microwave oven (Mars Xpress, CEM, Model 907,501, USA). The total digestion time for the sediment and macrophyte tissues was 35 min (10 min, until reaching 95 °C; and 25 min with constant temperature of 95 °C) with power of 1600 W (adapted from Bastos et al., 1998).

After cooling for 30 min, the extracts (sediment and macrophyte tissues) were filtered through Whatman® 40 paper and placed in tubes, which were filled to 25 mL with ultrapure water (Milipore Milli-Q, Integral model A10, Molsheim, France). After that, 1 mL of each final extract was added to 29 mL of ultrapure water and then 150 µL of BrCl, 60 µL of NH₂OH•HCl, and 150 µL of SnCl₂ were added. In all analyses, analytical blanks were included (n = 3). The Hg determination in the sediment and tissues of the macrophytes was also performed by atomic fluorescence spectrophotometry using the cold vapor generation technique.

The granulometric analysis of the sediment samples was performed using a laser diffraction particle analyzer (Model SALD-3101, Shimadzu, Japan). Each sample was subjected to ultrasonic agitation for 10 min to disaggregate the particles before determining the particle size distribution (Blott et al., 2004; McCave et al., 1986). Fractions were classified according to Krumbtein and Aberdeen (1937).

To evaluate Hg dynamics in the water column, a geochemical partition coefficient (Kd–Hg) between the particulate and dissolved fraction was determined by the following formula:

\[
\text{Kd – Hg (L g}^{-1}) = \log (\text{Hg in SPM (ng g}^{-1})/\text{dissolved Hg (ng L}^{-1})) \quad (1)
\]

Statistical analyses were performed using the R statistical program (R Core Team, 2021). Empirical combinatorial analyses (Monte Carlo Method; Khitalishvili, 2016) were used to calculate the ratios of Hg concentrations between the sampled environmental compartments, including the Kd–Hg, in order to incorporate the variability of Hg concentration in each compartment in the final result.

An analysis of variance (ANOVA) was used to evaluate the effect of the distance from the PSR mouth on total, dissolved, particulate, and sediment Hg concentrations. When an effect was detected,
multiple comparisons among the sampling points were performed using the Tukey test and significant differences were reported using the compact letter display (Mendiburu, 2021).

Regressions between total Hg concentrations and the silt-clay content of the sediments were used to assess the association between these two variables. The model equation, determination coefficient ($R^2$), and $p$-values were computed. A maximum likelihood function (Venables & Ripley, 2002) was used to perform transformations of the data, when necessary, in order to meet the premises of ANOVA and regressions (normality, linearity, homoscedasticity of residuals). ANOVA and regression results were validated using diagnostic plots (Altman & Krzywinski, 2016). In all cases, an a priori type I error of 5% ($\alpha = 0.05$) was assumed.

Results and discussion

The behavior of Hg concentrations along the transect of the PSR indicated the limited effect of garimpo activities on Hg dynamics in aquatic ecosystems, with the detected patterns independent of water column physicochemical parameters (pH, electrical conductivity, dissolved oxygen and temperature; S2) and SPM loads (S3). The total, dissolved, and particulate Hg concentrations (Fig. 3) were higher at the points where the rafts were seen and/or seized compared to the immediately previous (upstream) point of the transect by factors of $1.7 \pm 0.7$, $1.5 \pm 0.2$, and $2.1 \pm 0.8$ times, respectively (Fig. 3). At these same points, where the rafts were located, the highest Hg concentrations were observed for each of these environmental compartments. The behavior of dissolved Hg concentrations along the transect is even more noteworthy: there was a continuous increase in Hg concentrations from the point where the first raft was observed to the point where the second raft was observed, followed by a sharp decrease after the latter.

The pattern of a local increase in Hg concentrations in the water column at the site of garimpo activity followed by a rapid decrease has previously been observed by other authors (Diringer et al., 2015; Limbong et al., 2003). This spatial limitation of garimpo effects was discussed by Lechler et al. (2000), who analyzed Hg in the

Fig. 3 Total, particulate, and dissolved Hg concentrations in the Paraíba do Sul River water column, SPM, and bottom sediments. a Total and dissolved Hg ($<0.7 \mu m$) in water; b total Hg in SPM and bottom sediments. Lowercase letter denotes significantly different mean Hg concentration among the sampling points. The numbers are the mean $\pm$ SD of the ratio between total and dissolved Hg in water and between total Hg in SPM and bottom sediments for each of the sampling points. The points where the rafts were seen and/or seized are highlighted in gray. Each point represents 5 independent samples ($n = 5$)
water column in a 900-km transect of the Madeira River (corresponding to 62.07% of its length), where garimpo activities were and still are intense (Pestana et al., 2022). Comparatively, this study evaluated a transect of only 106 km (corresponding to only 9.38% of the PSR extension). The findings indicate spatial variations in Hg concentrations (coefficients of variation of 74% and 84% for total and dissolved Hg, respectively), but lower when compared to those of Lechler et al. (2000) (coefficients of variation of 85% and 108% for total and dissolved Hg, respectively), suggesting that garimpo effects on the PSR are less pronounced than on the Madeira River. This is in line with Guimaraes (2020), who considered that the “limited spatial effects of garimpo” apply to specific geographic and social contexts. For example, Lechler et al. (2000) carried out sampling in the Amazon Basin, where Hg concentrations are among the highest in the world, and remarked that the region’s soils play a major role in the Hg cycle, acting as the largest natural reservoir. For southeastern Brazil, on the other hand, the main sources of Hg are from garimpo and the use of Hg agrochemicals (Almeida & Souza, 2008; Câmara, 1986, 1990; Lacerda et al., 1993), so this should be taken into account in this type of comparison. In addition, on the Madeira River, hundreds of rafts have been reported (350 rafts; Branches, 2021) when there is garimpo activity, while in the PSR the number of rafts was much smaller (four rafts; Folha de Itália, 2021a; Trindade, 2021).

Total Hg concentrations in the PSR’s sediments exhibit different behaviors from those observed for the mentioned environmental compartments. In this compartment, concentrations were lower at the points where the rafts were seen (Fig. 3b). This result was opposite to what was expected, as gold miners use Hg to amalgamate gold, which has low solubility and accumulates in sediments (Lacerda & Malm, 2008). In this case, the granulometric analysis of the sediment helps to understand this result.

The granulometry data showed that in most sampling points, there was a large percentage of silt + clay content (Fig. 4c), with the exception of precisely the point where one of the rafts was observed (P4, Fig. 4c). The relationship between the silt + clay content and Hg concentrations in the PSR sediment was direct and exponential (Fig. 4b), showing a clear effect of granulometry on Hg concentrations. Normalizing the Hg concentrations in the sediments by the silt + clay content (Fig. 5a), the results indicate that, proportionally to the amount of silt + clay, P4 presented the highest Hg concentrations in the sediment.

This demonstrates a garimpo effect also on Hg concentrations in sediments. The modification of sediment granulometry in garimpo areas has been described by other authors (Guimaraes, 2020; Serapião & Ladeira, 2022). According to Guimaraes (2020), garimpo areas have a major impact in the silting of rivers, which not only increases the sand content in the sediment but also impacts the diversity and abundance of fish on a spatial scale wider than that described for the impacts of Hg contamination (Mol & Ouboter, 2004).

All Kd–Hg values were greater than 1 (Fig. 5b), demonstrating the high Hg affinity with SPM, which is in line with expectations for the region (Almeida & Souza, 2008). It is also possible to infer that Hg transport occurred preferentially associated with SPM. The Kd–Hg values were within the range (3.1 to 5.9) described by Picado and Bengtsson (2012), who evaluated the Artiguas River (Nicaragua), where garimpo activities also occur.

In general, total (2 to 3 ng·L⁻¹) and dissolved Hg (0.2 to 0.9 ng·L⁻¹) concentrations in water were lower than the limits described by Brazilian regulations (2000 ng·L⁻¹–class III freshwater) (CONAMA, 2005). Furthermore, Hg concentrations in the SPM (38 to 95 ng·g⁻¹) and sediments (5 to 86 ng·g⁻¹) were below the levels at which a small probability of adverse effects on the biota is expected (threshold effect level (TEL) 174 ng·g⁻¹ and probable effect level (PEL) 486 ng·g⁻¹), and lower than the TEL (CCME, 2002), demonstrating little or no risk to the biota. On the other hand, the high values found in sediments (86 ng·g⁻¹) were over twofold Hg background levels in PSR basin sediments (40 ng·g⁻¹; Souza, 1994).

Hg concentrations were higher in the roots compared to the leaves of the sampled aquatic macrophytes (Table 1). The calculated translocation factors (leaf to root ratio) were less than 1, demonstrating low translocation of Hg to the aerial parts. This was expected, since the roots of these macrophytes are in direct contact with the water column and have a high surface area to adsorb Hg-rich particles (Molisani et al., 2006). The higher Hg accumulation in the roots of macrophytes is a protective strategy, since the restriction of Hg transport to the aerial parts prevents possible damage to the photosynthetic apparatus (Lominchar et al., 2019). This not only indicates that
Hg is mostly accumulated in the roots, but also that it can enter the food chain through ingestion, especially by herbivorous fish (Suárez et al., 2001). It is important to highlight that the macrophytes sampled at the point where the raft was seen (P2) showed higher Hg concentration in all tissues in comparison with those at P1, which further indicates that the *garimpo* activity also affects the aquatic plant biota.

**Fig. 4** a Association of Hg concentrations with silt + clay content of Garimpo tailings (P9) and sediments from the Muriaé River (P7 to P9). The dashed and solid lines represent the regression models associated with the tailings and sediments samples respectively. b Association of Hg concentrations with the silt + clay content of sediments from the Paraíba do Sul River (P1 to P6). The blue shading indicates the 95% regression model confidence interval and the regression statistics. c Granulometry of sediment samples for each sampling point from Paraíba do Sul River (rafts were seen/seized at P2 and P4) and the Muriaé River (rafts seen at P9)
In the MR, the mean (± SD) total Hg concentrations in water (10 ± 0.4 ng L⁻¹), SPM (256 ± 11 ng g⁻¹), and bottom sediments (131 ± 11 ng g⁻¹) were higher at the sampling point upstream of the garimpo area (p = 0.002, 0.003, 0.004, respectively), while the inverse pattern was observed for dissolved Hg (5 ± 1 ng L⁻¹; p = 0.052) (Fig. 6). In the sediments of these points (P7 and P8), there was predominance of silt + clay content (Fig. 4c), which has a direct and exponential relationship with Hg concentrations (R² = 0.67, p < 0.0001; Fig. 4a). This may explain the higher Hg concentrations upstream from the garimpo area, since at that point the silt + clay content corresponded to ≈100%, while at the point downstream from the garimpo area, this value was slightly lower (Fig. 4a). Higher silt + clay contents were expected to be associated with higher Hg⁰ accumulations, since this granulometric fraction is an important support for Hg adsorption and immobilization (Moreno-Brush et al., 2020). Besides the granulometry effect, another factor must be considered to explain the higher Hg concentration detected upstream the garimpo area: the rafts do not stand still. Instead, they travel along the river channel. It is possible that the higher Hg concentrations observed upstream from the garimpo area is due to remnants of previous activities further upstream, where the flow may have resuspended contaminated sediments that then transported the Hg downstream.

Comparatively, Hg concentrations in the SPM were higher than those in the sediments at both MR sampling points (Fig. 6). This can be explained by the Kd–Hg values upstream (3.95 ± 0.20 L g⁻¹) and downstream (2.90 ± 0.37 L g⁻¹) the garimpo area, demonstrating higher Hg affinity with SPM.

In both graphs, the lowercase letters indicate significantly different mean Hg concentrations of each environmental compartment among the sampling points. The sampling points where the rafts were seen and/or seized are highlighted in gray. Each point represents 5 independent samples (n = 5).

**Table 1** Total Hg concentration in the tissues of the aquatic macrophyte *Pistia stratiotes* sampled in the Paraíba do Sul River at the points where it was present. Values are mean ± SD. Sample size is in parenthesis.

| Variable                        | P1       | P2       |
|---------------------------------|----------|----------|
| Hg concentration in leaves (ng g⁻¹) | 5 ± 2 (5) | 23 ± 8 (5) |
| Hg concentration in the roots (ng g⁻¹) | 28 ± 19 (5) | 55 ± 23 (5) |
| Translocation factor (root/leaf) | 0.2      | 0.4      |
| Distance of the sampling point from PSR mouth (km) | 145      | 138      |
compared to the dissolved fraction of the water column, as observed in the PSR data (Fig. 5b). In fact, the Kd–Hg values calculated for the RM were in the same range (2.9 to 3.8) and order of magnitude as the PSR values. Since both rivers present forests adjacent to their banks, organic matter most likely plays an important role increasing Hg affinity to the SPM (Figueiredo et al., 2011). Furthermore, reports of high Hg concentrations in the gills of detritivorous fish species in the RPS basin were attributed to the direct contact of these species with the sediment, indicating the significant role of this compartment in Hg biota exposure (Azevedo et al., 2017), especially during the dry season (Azevedo et al., 2018). Based on the maximum Hg concentrations detected among species with different feeding habits in the region (0.3 µg·g⁻¹ wet weight; Azevedo et al., 2017) for which the safe ingestion limit established by the WHO should be exceeded (4 µg·kg⁻¹ per week per body weight; WHO, 2008), an average person (70 kg body weight) would need to eat between 1.0 and 1.5 kg of fish per week. Fish consumption in Southeastern Brazil does

Fig. 6 Total Hg in sediments, SPM and dissolved concentrations from the Muriaé River, upstream (P8) and downstream (P7) of the Garimpo areas where the rafts were seen. The $p$ value indicates the statistical level of significance.
not exceed 43 g per week (IBGE, 2010), so no major Hg-related health problems are expected for the population around the study areas.

Garimpo tailings contained higher sand contents (P9, Fig. 4c) compared to the samples from the other points, and a non-significant association between Hg concentrations and silt–clay content was observed (R² = 0.11, p = 0.58; Fig. 4a), demonstrating a different behavior from that observed in the PSR (Fig. 4b) and at the other points of the RM (Fig. 4a). Furthermore, the tailings exhibited the highest mean Hg concentration among all environmental compartments evaluated in this study (197 ± 4 ng g⁻¹), higher than the MR sediment samples (131 ± 11 and 96 ± 5 ng g⁻¹), in agreement with expectations. This was also observed by Odumo et al. (2014), but the Hg concentrations determined in the tailings by those authors were about 46-fold higher compared to this study. Those authors studied an area that constitutes a mining complex with a long history of this activity. Comparatively, only four rafts were identified in the sampling areas of this study, which partially explains the differences in Hg values between this study and those reported by Odumo et al. (2014).

Van Straaten (2000) reported that 20 to 30% of Hg is lost to tailings during the amalgamation process, which may explain the higher Hg concentrations observed herein. The Hg-enriched tailings on the banks of the MR can act as point sources of contamination for the ecosystem through soil leaching processes and flooding during rainy periods.

As in the PSR, the total (8 and 10 ng L⁻¹) and dissolved Hg concentrations (4 and 5 ng L⁻¹) in water of the MR were lower than the limits set by Brazilian regulations (2000 ng L⁻¹–class III freshwater) (CONAMA, 2005). The Hg concentrations in the sediments (96 and 131 ng g⁻¹) and in the SPM downstream the garimpo area (101 ng g⁻¹, Fig. 6) were lower than those in the TEL (174 ng g⁻¹, CCME, 2002), indicating little or no risk to the biota. However, the values observed in the SPM upstream the garimpo area (256 ng g⁻¹, Fig. 6) and in the tailings (197 ng g⁻¹) were in the range between TEL and PEL (486 ng g⁻¹, CCME, 2002), suggesting possible risks to the biota.

Overall, the PSR and MR had different Hg dispersion patterns. According to Moreno-Brush et al. (2020), variations in Hg concentrations in tropical river systems affected by garimpo activity are rarely systematic, since there is a complex network of factors (e.g., watershed characteristics, hydrology, and specific biogeochemistry of each water body) that control the dispersion in the ecosystem. This is in line with which was observed herein. Conversely, in both rivers, Hg dynamics in the water column were mainly related to raft location, which was also reported by other studies in rivers affected by garimpo activity (Diringer et al., 2015; Moreno-Brush et al., 2016; Picado & Bengtsson, 2012).

Conclusion

Illegal small-scale alluvial gold mining activities in the PSR locally impacted Hg concentrations in both fractions of the water column, sediment, and macrophytes, with limited spatial impacts. The SPM was the environmental compartment that presented the highest Hg concentration (95 ng g⁻¹). Sediment granulometry was essential to understand the physical impacts of garimpo activities on PSR silting and helped to understand the Hg dynamics in this environmental compartment, due to a high affinity to Hg. Despite the effects of garimpo being clear in the data, Hg concentrations in water and sediment did not exceed the limits of Brazilian and international regulations. However, it is important to emphasize that the number of mining rafts in these locations was small, so the increase in this activity can increase the environmental and health risks of the regional population. Furthermore, as only 9.38% of the entire length of the PSR was sampled, our findings are limited concerning the impacts of garimpo activities throughout the entire drainage basin.

Mercury concentrations in the environmental compartments of the MR were higher than those in the PSR, which may be associated with the longer time of garimpo activity in this river. Garimpo tailings contained the highest Hg concentrations in this study and they could act as a point source of Hg contamination for the water body. Mercury concentrations in SPM and tailings from the MR have the potential to pose risks to biota. Despite a different Hg dispersion pattern in the two rivers, the SPM stands out as the main fraction of the water column in both rivers regarded Hg dynamics.

Our data demonstrate the clear effect of illegal garimpo activities on Hg concentrations in the environmental compartments of both rivers. It is important
to note the need for increased personnel for environmental control and monitoring and more stringent public policies aimed at the conservation of these ecosystems, since the presence of Hg poses a potential environmental risk to biota and human health. In addition, new samples should be obtained during the dry season, as the lower water column levels are expected to favor Hg remobilization. Furthermore, other Hg species should also be assessed, especially methylmercury, due to its higher bioaccumulation potential and toxicity to both wildlife and humans.

Acknowledgements The authors thank the Programa de Pós-Graduação em Ecologia e Recursos Naturais e Laboratório de Ciências Ambientais (LCA) of the Universidade Estadual Norte Fluminense Darcy Ribeiro (UENF) for the assistance, and the field and laboratory logistics. This work was supported by Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ; grant numbers: E-26/111.790/2013; E-26/010.001272/2016; E-26/200.586/2022; and E-26/210.350/2022), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES; grant number: 001), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq; grant number: 305.217/2017-8). UENF also supports the maintenance contract for the employed equipment. The authors also thank the anonymous reviewers for their valuable suggestions.

Funding Philine R. Gomes and Inácio A. Pestana received financial support from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES; financing code 001). Inácio A. Pestana and Carlos Eduardo de Rezende received financial support from the Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ; grant codes E-26/200.586/2022 and E-26/010.001272/2016, respectively). Carlos Eduardo de Rezende received financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq; grant code 305.217/2017-8).

Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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