

Article

Particulate Mercury and Particulate Organic Matter in the Itenez Basin (Bolivia)

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Abstract: In rivers and other freshwater bodies, the presence of mercury can be due to direct contamination by anthropic activities such as gold mining. However, it can also be attributed to atmospheric deposition and erosion, runoff, or lixiviation from surrounding soils. In the case of the Amazon rainforest, high mercury contents have been reported for litter and topsoil, which could affect the mercury concentrations in water bodies. Samples of suspended particulate matter were obtained from a transect of the Itenez River, associated lakes, and some of its tributaries. The aim was to obtain information on particulate mercury's origin in the study area and determine the relationship between particulate mercury and particulate organic carbon. The concentration of mercury, organic matter, and the C:N ratio of the suspended matter was determined. The concentration of particulate mercury by water volume depended on changes in suspended matter loads, which in turn were mostly affected by the nature of the watershed or sediment resuspension. The observed values for the percentage of organic matter and the C:N ratio suggest that most of the mercury content in rivers and lakes originated from soils. A positive correlation was found between mercury concentration by weight of particulate matter and organic carbon content in particles. This correlation might be due to the direct binding of mercury to organic matter through functional groups like thiols or to an indirect effect of oxyhydroxides that can adsorb mercury and are associated with organic matter.

Keywords: particulate mercury; suspended particulate matter; particulate organic carbon; Amazon rainforest

1. Introduction

Mercury (Hg) is a significant environmental and health issue in the Amazon basin. Mercury's toxicity is particularly elevated due to the property of its organic form, methylmercury, to penetrate biological organisms and to generate accumulation during the individual's life and magnification along the trophic chain. In tropical forests, typical vegetation with broad leaves facilitates the capture of mercury from atmospheric deposition. Consequently, high contents of this metal have been reported for forest litter and topsoil [1]. In water bodies, mercury content can be related to atmospheric deposition, but most originates from the runoff or lixiviation of superficial and subterranean water from mercury-laden soils [2].

The influx of mercury to water bodies from runoff can be exacerbated by natural erosion and anthropic activities such as deforestation, agriculture, mining, or urbanization. In rivers that drain deforested watersheds, an increase in total mercury in the water column and surface sediments has been observed and attributed to the erosion of fine particles from soils [3,4]. Additionally, forest fire for

land conversion can give rise to an increase in Hg mobility [5]. However, the impact of deforestation on mercury concentrations in rivers and lakes varies in different watersheds [6].

Gold mining activities are also responsible for the discharge of mercury to the environment [6]. Exogenous (industrial) mercury used for gold mining can be emitted to the atmosphere or released into water bodies in the form of droplets and mercury-coated sediments [7]. Pollution may be worst when cyanide is used as part of the process because cyanomeric complexes are more easily transported [7]. Schudel et al. [8], using stable isotopes of mercury, showed that mercury from mines where cyanide was used could be traced 120 km downstream. Although gold mining causes deforestation in smaller areas than cattle rising or agriculture, it is one of the leading causes of deforestation in South America [9]. Moreover, informal gold mining can cause more substantial soil perturbation than other activities due to the removal of the organic layer under the trees, which increases the loads of sediments containing high mercury concentrations [10].

Pouilly and coworkers [11] reported data on mercury concentrations in fish populations from different trophic levels in the Itenez basin (Bolivia). They also reported average values for particulate mercury in Blanco, San Martín, and Itenez rivers and their associated floodplain lakes. The authors highlighted that no clear relationship between particulate mercury concentrations in water and mercury concentrations in fish muscle was observed, indicating that bioavailability must be taken into account for interpreting the results. A second study by Pouilly et al. [12] suggested that periphyton's contribution to the food web could explain higher mercury bioavailability since it is a site of mercury methylation [13]. We report additional data to those that were presented by Pouilly et al. [11] about suspended particulate matter, total particulate mercury, particulate organic carbon, and the C/N ratio. We took into account some additional sampling points directly influenced by deforestation and mining and performed a seasonal analysis (early and late dry season). These additional data were analyzed to obtain information on the origin of particulate mercury in the study area and determine the relationship between particulate mercury and particulate organic carbon.

The data that we report and analyze correspond to samples that were taken from the Itenez basin in June and September 2007. No previous or more recent data on particulate mercury in the Itenez basin has been reported to our knowledge, although this river is one of the main tributaries of the upper Madeira River and its basin covers 303,300 km² shared between Brazilian and Bolivian territories [11]. The punctual values on particulate mercury that we report are not expected to reflect the current situation. However, the information on its relationship with anthropic activities and with organic matter contributes to the characterization of mercury pollution in that particular region. Moreover, this characterization is valuable for newer studies on mercury pollution in the region, particularly given recent deforestation, which has been aggravated by the 2019 and 2020 forest burnings.

2. Materials and Methods

Water samples were taken in June (early dry season) and September (late dry season) 2007 from a longitudinal transect in the Itenez River, which is located at the frontier between Bolivia and Brasil and from the tributaries Blanco and San Martín. The sampled transect in Itenez river is 660 km long, starting at the "Piso Firme" locality (S 13°31'36.9" W 61°49'40.7") and finishing 100 km upstream of the confluence with Mamoré River (S 12°11'43.0" W 64°40'00.5"). Floodplain lakes related to the Itenez, San Martín, and Blanco Rivers were also sampled. Additional samples were obtained from three streams that cross Bolivian territory influenced by the "San Simon" goldmine and from three tributaries of Itenez that cross highly deforested Brazilian territory. The location of the sampling points can be observed in Figure 1. A more detailed description of the study area can be found in [11].

Five-liter plastic containers were used for sampling. These were conditioned by following a slight modification of the protocol proposed by Montgomery et al. [14]. The containers were first washed with tap water and metal-free detergent and rinsed with MilliQ water. After this, they soaked overnight with a 7% NaOH solution. They were then rinsed with MilliQ water and soaked with 10% HCl for an additional 12 h. Finally, they were rinsed three times with MilliQ water. Once clean, the containers

were kept in hermetic plastic bags until their use. For the sampling of SPM, GF/F (0.7 μm) filters were used. Before sampling, the filters were placed in packages wrapped with aluminum foil and heated up to 500 °C for 8 h. Upon cooling, the filters were weighted and individually placed in Petri dishes.

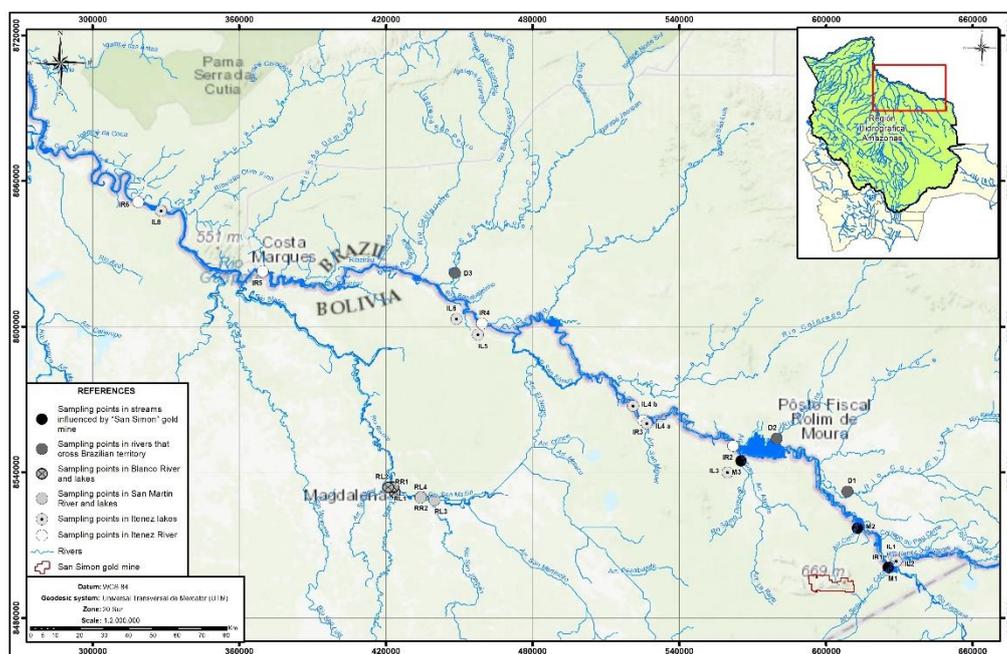


Figure 1. Location of sampling points.

Water was collected from the mainstream of rivers and the center of lakes by submerging the containers around 1 m deep. Following [13], the person in charge of sampling wore clean gloves throughout the procedure. The containers were rinsed three times with the river or lake water before being filled. Additionally, in each sampling point, temperature (°C), electric conductivity, and pH were measured with CONSORT C353 multimeter (Belgium). The depth of water was also registered.

SPM was obtained in the field by vacuum filtration of the water sample. The volume of water that caused saturation of the filter was annotated. Each filter was then placed in a Petri dish and stored at $-17\text{ }^{\circ}\text{C}$ until analysis.

Mercury content of SPM was determined at the Laboratorio de Calidad Ambiental of the University of San Andrés (La Paz, Bolivia). The filters that contained SPM were oven-dried at 40 °C for 24 h and weighted. Each filter was then introduced in a thermoresistant screw-capped 50 mL glass tube. 1 mL of nitric acid and 100 μL of hydrochloride acid were added to the tubes, and these were sealed with Teflon and capped. All tubes were heated at 100 °C for two hours. After cooling, 200 μL of hydrogen peroxide was added, and the tubes were again heated at 100 °C for two hours. 5 mL of ultrapure water was finally added.

Mercury of the digested samples was quantified with Cold Vapor Atomic Fluorescence Spectrometer (CVAFS, Brooks Rand Model III, Seattle, WA, USA) using the EPA 1631 Revision E: (EPA 2002) protocol. Reference samples were obtained from the National Research Council of Canadá: TORT-2 lobster hepatopancreas and MESS-3 Marine Sediment Reference Materials for Trace Metals (NRC-CNRC 2016). Total mercury concentration in SPM was expressed by water volume ($[\text{Hg}]_v$) and SPM weight ($[\text{Hg}]_w$). SPM from filters was additionally analyzed for particulate organic carbon (POC) and nitrogen in the Laboratorio de Medios Analíticos Cayenne- IRD in French Guyana with the CHNS THERMOQUEST AS2100 analyzer.

Wilcoxon test was applied to compare data obtained among sites (rivers and lakes) and seasons (early and late dry season). Spearman correlation coefficients between variables were calculated. All analyzes were carried out with R statistical computing freeware program (<http://www.r-project.org>).

3. Results and Discussion

A significant decrease in water depth was observed in September (late dry season, Tables S1 and S2) for most sampling points, except IR 1 and D3 (Tables S1 and S2). Most physicochemical characteristics did not vary among sites or seasons (Tables S1 and S2). The Blanco River showed a higher conductivity than the other water bodies ($50 \mu\text{S cm}^{-1}$ as compared to a mean of $27 \pm 4 \mu\text{S cm}^{-1}$ for the Itenez River and $20 \mu\text{S cm}^{-1}$ for San Martín), and this value increased during the late dry season ($80 \mu\text{S cm}^{-1}$).

Quantities of SPM showed a mean value of $5.6 \pm 1.1 \text{ mg/L}$ with minor variations along the Itenez river in June (Table S1). In September, the quantities of SPM along the Itenez River were significantly higher ($p = 0.005$) than in June (Figure 2A). For point IR6 (Vuelta Grande), the value obtained in September more than doubled the value measured in June (12.4 mg/L in September compared to 5.7 mg/L in June, Table S1). Such an increase can be related to the resuspension of sediments by physical factors or bioturbation since the water column at this point became very shallow (0.9 m) [15].

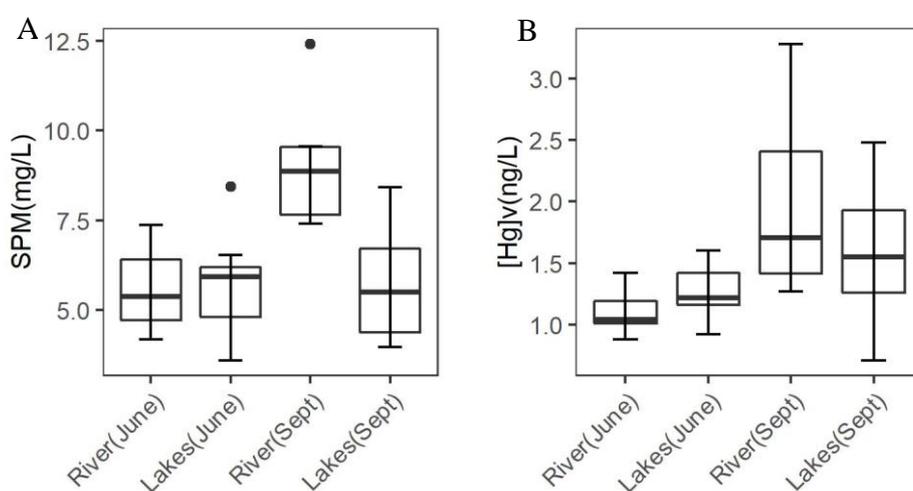


Figure 2. Comparison of suspended particulate matter (A) and particulate mercury concentration by volume (B) for the Itenez River and associated lakes in the two seasons.

In June, SPM values for the Itenez lakes were similar to those obtained for the river (Figure 2A); this is in agreement with the fact that, during the high water level season, rivers and lakes are connected. No significant difference for SPM in the Itenez lakes was observed between September and June, except for lake IL9, which showed a strong increase of suspended matter (from 4.8 mg/L in June to 100.2 mg/L in September, Table S1). In September, the connections between the river and the lakes were interrupted, and most floodplain lakes of Itenez showed slightly lower concentrations of SPM than the river, probably because of a sedimentation process and the fact that they did not receive new particulate material. Lake IL9 became very shallow in September (1.70 m), and resuspension phenomena can explain the very high value of SPM (Table S1).

Two of the sampled tributaries of Itenez, a river from Brazilian territory that crosses highly deforested areas and the Colorado stream, which is influenced by gold mining showed in June the highest values for SPM (20.7 mg/L and 15.2 mg/L , respectively) (Table S2). However, the other tributaries directly influenced by anthropic activities showed values similar to those of the Itenez river. In September, the Asunta Stream showed a very high value (36.7 mg/L) for SPM, but the other two streams influenced by the “San Simon” goldmine had low values (6.4 and 9.7 mg/L). On the other hand, in June, Blanco river, which drains white waters, contained higher amounts of particulate matter than Itenez river (27.7 mg/L), while San Martín, a clear water river, and its lakes, showed the lowest values (2.9 mg/L , Table S2). Both rivers cross territory with little anthropic influence [11]. In September, however, concentrations of SPM in San Martín increased strongly (up to 19.9 mg/L), probably due to

the resuspension of sediments [15], while this was not the case for Blanco. Although deforestation and mining give rise to disturbance of the upper horizons of soil and cause an increase in the loads of solid particles that reach water bodies [9,10], factors not related to anthropic intervention must also be taken into account in order to determine the causes of high SPM.

The concentration of particulate mercury by water volume ($[Hg]_v$) followed the same pattern as particulate suspended matter, showing little variations along the Itenez river (mean value 1.10 ± 0.19 ng/L) and its associated lakes in June (mean value 1.26 ± 0.23 ng/L, see Table S1). In September, the Itenez river had significantly higher $[Hg]_v$ than in June ($p = 0.0129$) (Figure 2B), as was observed for SPM.

Although high values for $[Hg]_v$ were measured in June for one of the rivers coming from deforested Brazilian territory and for the Colorado stream (3.83 ng/mL and 2.45 ng/L), the other tributaries influenced by anthropic activities showed concentrations of particulate mercury similar to those of Itenez river (Table S2). The lowest values for $[Hg]_v$ were observed in June for the San Martín River and its floodplain lakes (around 0.70 ng/L), while the highest value of all samples was obtained in the Blanco River (3.96 ng/L, Table S2). In September, the Asunta stream showed a substantial increase in $[Hg]_v$ (7.00 ng/L), but this was not observed for the other tributaries influenced by anthropic activities (Table S2).

The samples were taken from a very large area with different degrees of anthropic intervention, which goes from no intervention to gold-mining and deforestation. This area includes rivers and floodplain lakes, most of which contain clear water while some contain white water. No data are available for comparisons in this region, and there are few data on particulate mercury under similar conditions in the Amazonian basin. One exception is data from Roulet et al. [16] for suspended particulate matter and particulate mercury in the Tapajos river. The Tapajos river and the Itenez river are considered clear water rivers [16]. The values reported by Roulet et al. [17] for fine particulate matter and particulate mercury in the early dry season are similar to our data for the Itenez river and its lakes. The increase of SPM that we observed in the dry season (September) was also observed at Tapajos and was attributed to the decrease of water volumes. However, in our work, mercury associated with the coarse and fine particulate matter has been pooled, while Roulet et al. [17] did not report mercury concentration associated with coarse particulate matter. Comparisons must, therefore, be interpreted carefully.

More than the punctual values on particulate mercury by water volume, we were interested in the relationships between mercury and the degree and type of anthropic interventions. The relative contribution of mining activities and deforestation to mercury pollution in water bodies is still controversial and might depend on regional characteristics. Obritz et al. [18] indicate that the accumulation of mercury in soils depends on soil properties. Moreover, the accumulation in upper organic layers is different from the accumulation in mineral horizons. This implies that the contribution of soil mercury to water bodies can vary between regions. They also point out that runoff from contaminated sites such as gold mines can dominate Hg loads in water bodies. Horbe et al. [19] indicate that there are large variations in geochemical values of mercury in western Amazonia, and, by then, the contribution of different soils to Hg loads in rivers and lakes is variable. In our case, no systematic increase in $[Hg]_v$ was observed in sample points of Itenez river nearest to the mining sites or in streams affected by the "San Simon" mine. Furthermore, the obtained values for Hg loads in rivers that crossed highly deforested Brazilian territory and for rivers that crossed territories with little anthropic intervention showed no clear relationship between anthropic activities and particulate mercury loads. Phenomena such as resuspension, soil properties, and the water properties that the river drains (clear/white) must be taken into account when interpreting Hg loads.

When the concentration of total particulate mercury was evaluated by weight of SPM ($[Hg]_w$), the values obtained in June for the complete set of samples fluctuated between 133 and 327 ng g⁻¹ (Figure 3A, Tables S3 and S4). No significant variation between June and September was observed for the Itenez river or its lakes. In samples from tributaries affected by mining activities and rivers that

cross highly deforested Brazilian territory, the values for $[Hg]_w$ were similar to those of Itenez river. Such was also the case for samples from Blanco and San Martin rivers.

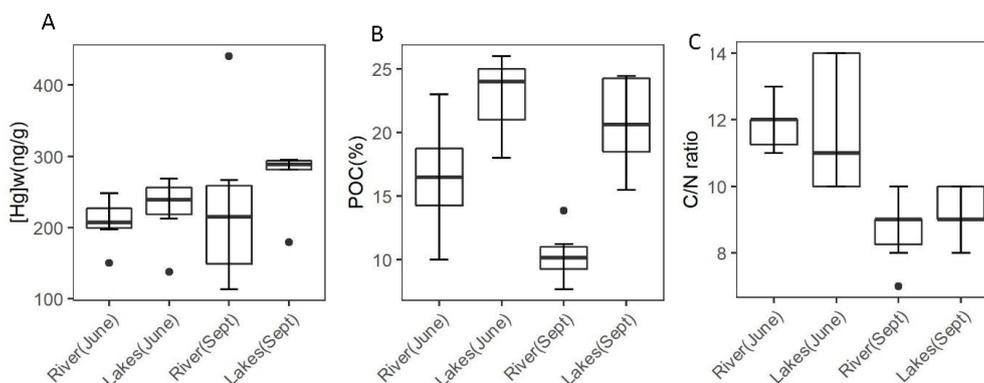


Figure 3. Characteristics of suspended particulate matter including the concentration of mercury by weight ($[Hg]_w$) (A), organic carbon (B), and C/N ratio (C) for the Itenez River and associated lakes in June (early dry season) and September (late dry season).

The percentage of particulate organic carbon (POC) in SPM in all samples from the Itenez basin varied from 6 to 26% in June (Tables S3 and S4). Samples from Itenez lakes tended to contain higher POC percentages than those from the Itenez river. POC decreased significantly ($p = 0.02$) in September in Itenez River, but no significant variation was observed for its lakes. Lower percentages of organic carbon associated with suspended matter can be due to lower organic matter inputs to water bodies in dry months and carbon turnover. Although particulate organic carbon is less bioavailable than dissolved carbon, some carbon turnover takes place [20].

In June, the C:N ratio for particulate matter from the Itenez river, lakes, and tributaries showed values between 9.9 and 14.9. In September, the C:N ratio values were lower, fluctuating between 7.4 and 11.2 for all samples (Tables S3 and S4). This decrease was significant for both the Itenez river ($p = 0.004$) and its lakes ($p = 0.009$), Figure 3C, and it can be related to preferential sorption of nitrogen compounds, as observed by Aufdenkampe et al. [21]. For both June and September, and for both habitats (lakes and rivers), the obtained C:N values are characteristic of suspended matter originated from soil [17,22]. This finding implies that the particulate organic carbon and the particulate mercury are mostly terrigenous in our study area. Terrigenous POC has a lower tendency to drive mercury methylation than autochthonous material [23], suggesting relatively low bioavailability of mercury.

A significant negative correlation was observed between SPM and POC for June ($\rho = -0.739$, $p < 0.001$) and September ($\rho = -0.739$, $p < 0.001$). Likewise, SPM and $[Hg]_w$ were negatively correlated in June ($\rho = -0.640$, $p < 0.001$) and September ($\rho = -0.709$, $p < 0.001$, see also Figure 4A,B). Maurice-Bourgoin et al. [24] have also observed a negative correlation between SPM and $[Hg]_w$ for samples from the Negro, Solimoes, Amazon, and Madeira rivers. This “dilution effect” can be due to several processes. Higher loads of SPM generally imply that water also contains higher concentrations of colloids, which are not retained by filters but could absorb part of the available mercury [25]. Hsu-Kim et al. [6] indicate that there can be a “growth dilution” of particulate mercury caused by an increase in biomass attached to particles. On the other hand, for sampling points where strong resuspension of sediments was observed, POC’s values and $[Hg]_w$ were much lower than in the other points. Sediments generally contain less organic carbon and mercury than suspended matter in the water column [3,23]. This difference can be related to high heterotrophic activity in sediments at the benthic and hyporheic zone [26]. High heterotrophic activity causes carbon turnover and can also cause mercury transformations, which leads to its separation from particles. A combination of the “dilution effect” and sediment resuspension could explain the behavior observed in Figure 4A,B.

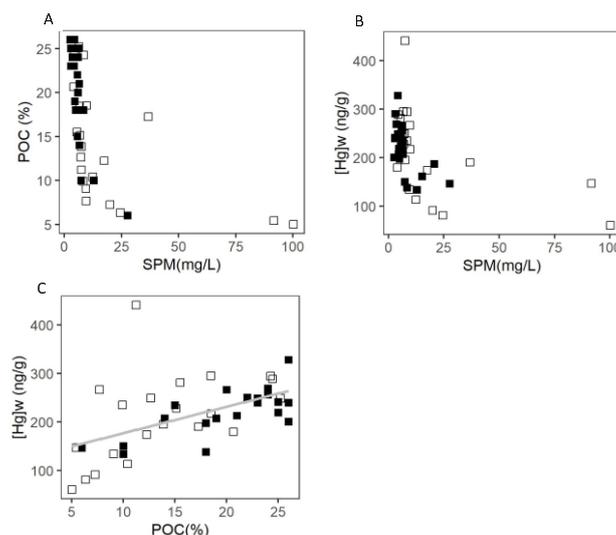


Figure 4. Relationships between particulate organic carbon (POC) and suspended particulate matter (SPM) (A), [Hg]_w and SPM (B) and [Hg]_w and POC (C) for samples taken in June (closed squares) and September (open squares).

Particulate organic carbon was positively correlated with particulate mercury (see Figure 4C) both in June ($\rho = 0.595$, $p = 0.004$) and September ($\rho = 0.595$, $p = 0.004$). Such a positive relationship was also reported by other authors [23,24], although in some other cases, no significant correlation was found [15,17]. The nature of the samples of the particulate matter probably influences this correlation. Roulet et al. [17] found no correlation between [Hg]_w and the POC percentage in fine particulate matter. The difference between this result and ours might be due to the fact that, in our case, we included coarse material in the analysis; this coarse material could contain higher percentages of organic matter. The characteristics of the water that is drained by the river could also play a role in the relationship between [Hg]_w and POC. Maia et al. [15] found no significant correlation between [Hg]_w and POC for floodplain lakes of the Amazonian river. However, these lakes contained water classified as white or black water, while the Itenez river is considered a clear water river. The fact that not all authors find a positive correlation between particulate mercury and particulate organic matter can also be due to regional differences and types of soil. Therefore, our data can contribute to a wider analysis of which conditions give rise to such a positive relationship.

Samples were taken in two seasons of the same year, at the beginning of the low water season and by the end of the low water season. The relationships between suspended particulate matter, particulate organic matter, and particulate mercury by weight [Hg]_w did not show seasonal variations. The possible terrigenous nature of particles could explain the seasonal invariance of these relationships.

The nature of the bonds between mercury and particulate suspended matter could affect mercury's fate and the possibilities of its methylation. Our results suggest that particulate mercury binds to organic carbon. However, mercury adsorption has also been related to aluminum and iron oxyhydroxides [3,27], which, in turn, are closely associated with organic matter [17]. Therefore, further studies are necessary to establish if the correlation of particulate mercury with POC is due to direct binding of mercury with organic matter or binding with the oxyhydroxides associated with this organic matter. Moreover, several studies have shown that mercury binding to organic matter is mostly through thiols, sulfides, and disulfides [25,28]. Consequently, the nature of the particulate organic matter might influence the amount of captured mercury. A study on sediment cores taken from the Titicaca lake has shown that capturing mercury on solids depends more on quality than quantity of organic matter. There is a positive correlation between bound mercury and reduced sulfur content [29]. Quantification of reduced sulfur in SPM could help establish the nature of the bonds between mercury and organic matter.

4. Conclusions

The concentration of particulate mercury by water volume $[Hg]_v$ in the studied water bodies depended on phenomena that caused changes in suspended matter loads. The effect of anthropic activities on these loads could not be established since the nature of the watershed or resuspension had a more direct effect on concentrations of SPM.

The POC values and the C:N ratio observed in suspended particulate matter suggest that most of this material in Itenez, Blanco, and San Martín rivers and lakes is terrigenous for the two sampling dates considered (early and late dry seasons), which implies that particulate mercury in these water bodies mostly comes from soils. At the same time, particulate organic matter (SPM) and $[Hg]_w$ were negatively correlated with the quantity of suspended matter, which may suggest a dilution effect.

A positive correlation was found between $[Hg]_w$ and POC. Although this suggests that mercury is bound to organic matter, further studies are needed to clarify this since organic matter could be associated with oxyhydroxides, and these minerals contain binding sites for mercury.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/10/23/8407/s1>, Table S1. Characteristics of samples from Itenez river and its floodplain lakes, Table S2. Characteristics of samples from Blanco, San Martín, and tributaries of Itenez, Table S3. Contents of mercury ($[Hg]_w$), organic matter (POC), and C/N ratio in suspended particulate matter of Itenez river and floodplain lakes, Table S4. Contents of mercury ($[Hg]_w$), organic matter (POC) and C/N ratio in suspended particulate matter of Blanco, San Martín, and other tributaries of Itenez.

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