

Seasonal functioning of dissolved mercury dynamics in the Ebrié lagoon (Côte d'Ivoire)

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Abstract

Dissolved mercury (Hg) is the most mobile and reactive form of mercury in aquatic ecosystems, yet it is poorly documented in tropical lagoons. This study examines the seasonal dynamics of dissolved total Hg (THg) in the water column and sediment pore waters of the Ebrié lagoon (Côte d'Ivoire), a tropical estuarine system under intense anthropogenic pressure. Sampling occurred at eight stations during the dry (February 2017) and rainy (July 2017) seasons. Total dissolved Hg was measured using thermal decomposition atomic absorption spectrometry and analyzed in relation to physicochemical parameters, microbial activity, and Hg concentrations in Tilapia sp. Dissolved Hg in pore waters ($0.07\text{--}0.33\text{ }\mu\text{g.L}^{-1}$) was consistently higher than in the water column ($0.03\text{--}0.11\text{ }\mu\text{g.L}^{-1}$), confirming sediments as a labile Hg reservoir. Seasonal differences were limited, whereas spatial variability reflected local anthropogenic inputs and hydrodynamic conditions. Correlations showed distinct seasonal controls: during the rainy season, dissolved organic carbon and oxygen availability were closely linked to Hg solubilization in pore waters; in the dry season, microbial activity, salinity, temperature, and redox conditions more strongly influenced water-column Hg. No direct relationship existed between pore-water and water-column Hg, indicating sediment–water transfer is not systematic. Compared with other lagoonal systems, Ebrié lagoon's dissolved Hg falls within the upper global range. These results highlight dissolved Hg's critical role in Hg mobility and bioavailability and underscore the need to integrate dissolved Hg measurements into ecological and human health risk assessments in tropical coastal environments.

Keywords: Dissolved mercury; Seasonal dynamics; Coastal lagoon; Biogeochemical cycling; Ebrié lagoon

1. Introduction

Mercury (Hg) is one of the most toxic contaminants in aquatic environments due to its persistence [1, 2], its wide range of chemical forms, and its strong bioaccumulative potential. In lagoon ecosystems, the dissolved phase represents the most mobile mercury compartment, and its dynamics are strongly governed by biogeochemical conditions such as pH, redox potential, dissolved organic matter, and microbial activity [3, 4]. These factors control the transformation of inorganic Hg into methylmercury (MeHg), a highly toxic and bioavailable form that readily accumulates in aquatic food webs [5]. In a recent study conducted in the Ebrié Lagoon, we demonstrated that seasonal variability modulates

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mercury distribution in fish (Tilapia sp.) and sediments [6]. As Tilapia is a filter-feeding species [7] that primarily inhabits the water column, it is particularly exposed to dissolved Hg, suggesting that this compartment may play a key role in mercury bioavailability. Despite its importance, dissolved mercury in the water column and in sediment pore waters remains poorly documented in the Ebrié Lagoon, although it represents a critical link in trophic transfer processes. A better understanding of this compartment is essential for assessing human health risks associated with fish consumption and for improving environmental monitoring strategies in a system subjected to intense anthropogenic pressures. Accordingly, the present study builds upon previous work by focusing on the seasonal dynamics of dissolved mercury in both the water column and sediment pore waters. By explicitly addressing this overlooked compartment, this study provides key insights into mercury mobility and supports the integration of dissolved Hg into ecological and human health risk assessments.

2. Material and methods

2.1. Study area and sampling design

The Ebrié Lagoon, located along the southern coast of Côte d'Ivoire, is a tropical estuarine system characterized by pronounced seasonal hydrological variability. Sampling was conducted at eight representative stations—Cosrou, Port, Cocody, Koumassi, Biétri, Yopougon, Banco, and Marcory—selected to capture a range of anthropogenic pressures and hydrodynamic conditions within the lagoon. Field campaigns were carried out during two contrasting hydrological periods: the dry season (February 2017) and the rainy season (July 2017).

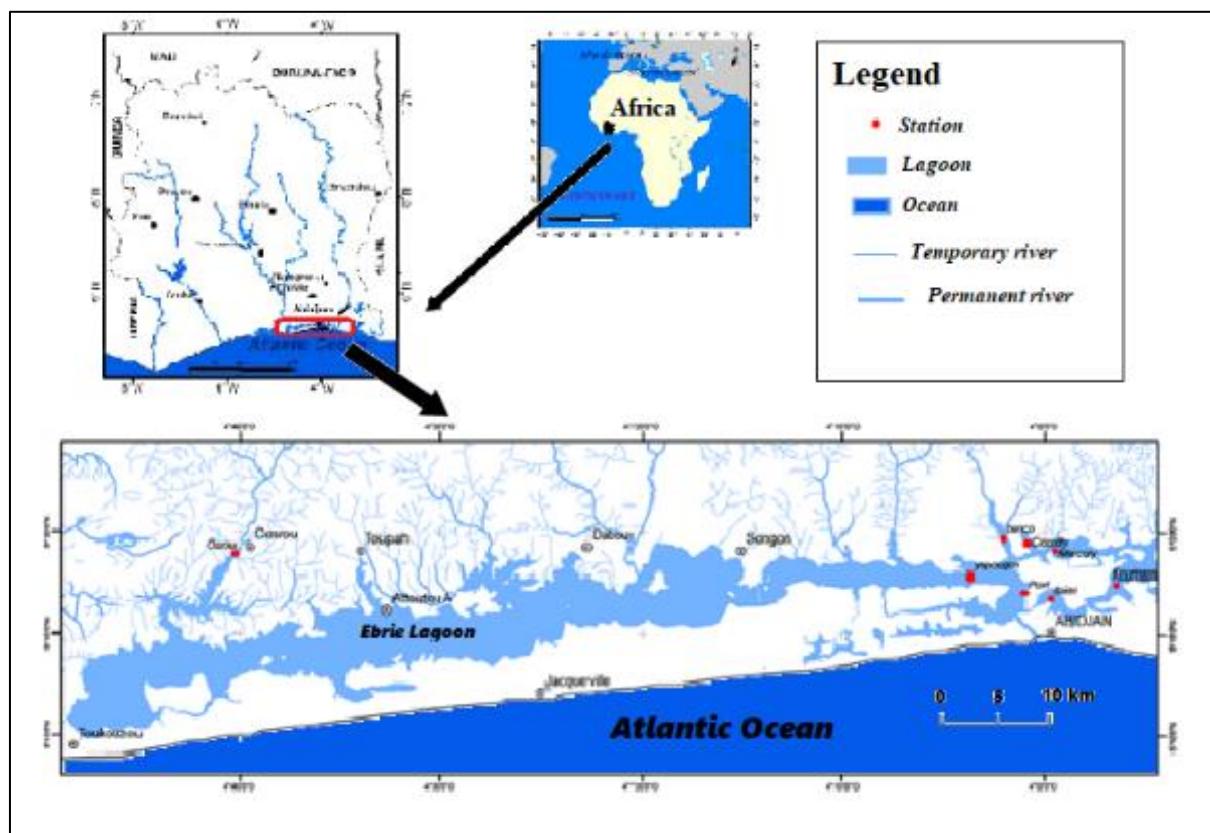


Figure 1 Localization map of the different sampling sites of the Ebrié Lagoon

2.2. Sampling and preparation of samples

Samples of sediment pore water and water were collected during two sampling campaigns in the dry season (February 2017) and then in the wet season (July 2017). The sediments were collected using a Van Veen grab sampler at the surface. Each sediment sample was split into two parts. The first portion of sediment was used for microbiological analyses and samples were collected in sterile Falcon® vials and then stored at -18°C before analysis. The second part of the sample was used for chemical analysis and was stored in freezer bags before analysis. For chemical analyses,

samples were centrifuged at 10 000 rpm for 30 min to extract the pore water. Sediment pore waters were then filtered at 0.45 μm (Teflon filter, VWR) and stored in Falcon® tubes at -18°C until analysis.

Water samples were collected at three depths (at the surface, in the middle and at 0.5 m from the bottom) from each site using a 2-L Niskin® bottle. Then, the samples were transferred to Nalgene® polyethylene bottles, which were previously rinsed with a 5% nitric acid solution, rinsed thoroughly with distilled water in the laboratory and rinsed again with an aliquot of the sample from the site before sampling. In the laboratory, the solutions were vacuum filtered using the Whatman® filtration system and a nylon filter (0.45 μm diameter). The filtered samples were stored in Falcon® tubes at -18°C until analysis.

2.3. Total mercury content in sediment pore water and water

Total mercury (Hg) in water and sediment pore water samples was measured using the AMA 254® Automatic Mercury Analyzer, based on thermal decomposition atomic absorption spectrometry (AAS) with gold amalgamation. This method allows direct quantification of Hg in liquid samples without chemical pre-treatment, offering high sensitivity regardless of the sample matrix. For each analysis, a known volume of sample was placed in the combustion boat, dried, and thermally decomposed in the catalytic tube. Mercury vapors released during decomposition were selectively trapped in a gold amalgam, while other gases were removed. This technique was used by several authors [8, 9] to quantify the total Hg in soils as well as in soil solutions.

2.4. Physicochemical and Biogeochemical Parameters

The following physicochemical and biogeochemical parameters, previously measured in the first study, were used to assess their influence on dissolved mercury in the water column and sediment pore water:

- total mercury in fish (THg_{fish}), used as a reference for bioavailability;
- DOC (Dissolved Organic Carbon, $\text{mg}\cdot\text{L}^{-1}$), influencing Hg complexation and solubility;
- DO (Dissolved Oxygen, $\text{mg}\cdot\text{L}^{-1}$), affecting redox conditions;
- Salinity (ppm) and Temperature (°C), controlling Hg mobility and water column stratification;
- pH and Eh (mV), key redox parameters affecting Hg speciation;

FDA (Fluorescein Diacetate hydrolysis), AWCD (Average Well Color Development), and cultivable cells, indicators of microbial activity controlling Hg transformation and release.

All parameters were measured in situ or in the laboratory using the same protocols as in the previous study to allow direct comparison across seasons and sites [6].

2.5. Data treatment

Data were analyzed using XLSTAT software version 2018. Each analysis was performed in triplicate. Significant differences between each sample were determined by analyzing the variance (one-factor ANOVA) and by the Tukey HSD test (significance threshold of $P<0.05$, with $n=3$). Principal component analysis (PCA) was performed on all the factors studied. Thus, the Pearson correlation coefficient was calculated between the biogeochemical characteristics of the medium and the dissolved mercury for each sampling point.

All results are expressed as mean \pm standard deviation (SD).

3. Results

3.1. Total dissolved mercury in sediment pore water and water column

The total Hg content in sediment pore water (THg_{pore}) ranged from $0.07 \pm 0.01 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ to $0.33 \pm 0.15 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, with an overall mean of $0.17 \pm 0.06 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, showing similar values in both dry and rainy seasons. Among the sampling sites, Port consistently exhibited the highest THg_{pore} , while the lowest values were observed at Cosrou during the dry season and Cocody during the rainy season. Although THg_{pore} was slightly lower during the rainy season (average difference: $-0.03 \pm 0.02 \text{ }\mu\text{g}\cdot\text{L}^{-1}$), ANOVA and Tukey's test revealed no significant differences between seasons or sites ($p = 0.05$).

Total Hg in the water column ($\text{THg}_{\text{water}}$) varied between $0.03 \pm 0.01 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ and $0.11 \pm 0.01 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, with a mean of $0.08 \pm 0.02 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ for both seasons. During the dry season, Yopougon showed the lowest $\text{THg}_{\text{water}}$, while Cosrou had the highest. In the rainy season, the lowest $\text{THg}_{\text{water}}$ was recorded at Koumassi, and the highest at Marcory. Seasonal differences were modest: $\text{THg}_{\text{water}}$ increased slightly at Biétri, Yopougon, Banco, and Marcory (average difference: 0.01 ± 0.02

$\mu\text{g}\cdot\text{L}^{-1}$) but decreased at Cosrou, Port, Cocody, and Koumassi (average difference: $-0.04 \pm 0.03 \mu\text{g}\cdot\text{L}^{-1}$). Except for Koumassi, no significant seasonal or spatial differences were observed according to ANOVA ($p = 0.05$).

Overall, THg_{pore} was consistently higher than $\text{THg}_{\text{water}}$, indicating that sediments act as a reservoir for labile Hg, while water column concentrations reflect dynamic exchanges influenced by local environmental factors.

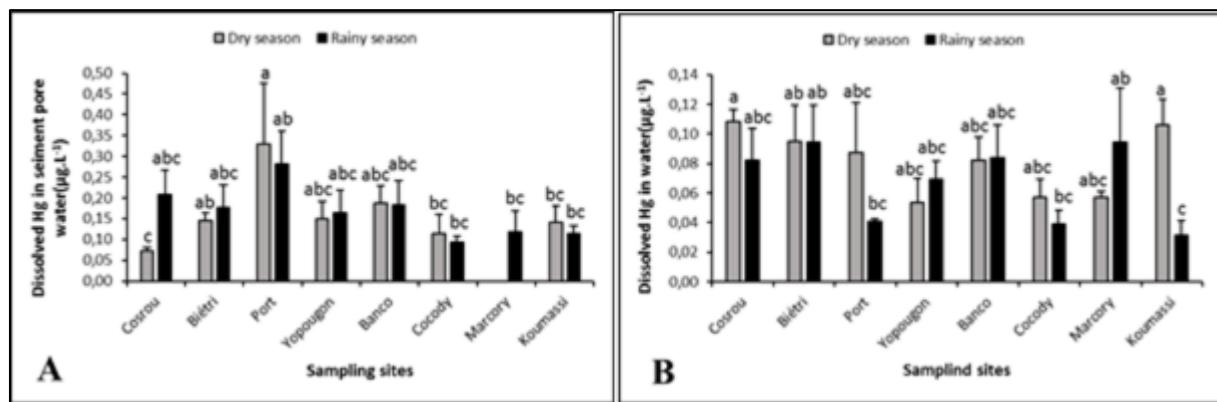


Figure 2 Seasonal variation of the dissolved Hg content ($\mu\text{g}\cdot\text{L}^{-1}$) in Ebrie lagoon (A: dissolved Hg content in sediment pore water, B: dissolved Hg content in the water column) for the different sampling sites. Each bar corresponds to the average, and the standard deviation is determined from 3 replicates. The symbols a to k correspond to the different groups of significance obtained by analysis of variance and the Tukey test ($p = 0.05$) on 3 replicates

3.2. Seasonal correlations between dissolved mercury, environmental parameters, and bioaccumulation

Correlation analyses revealed marked seasonal differences in the factors associated with dissolved Hg distribution. During the rainy season, Hg concentrations in sediment pore water (THg_{pore}) were positively correlated with dissolved organic carbon (DOC; $r = 0.48$) and dissolved oxygen (DO; $r = 0.38$), whereas dissolved Hg in the water column ($\text{THg}_{\text{water}}$) showed a negative correlation with Hg concentrations in fish (THg_{fish} ; $r = -0.43$) and only weak relationships with microbial activity indicators. In contrast, during the dry season, $\text{THg}_{\text{water}}$ was positively correlated with microbial metabolic activity, as indicated by average well color development (AWCD; $r = 0.42$), while salinity and temperature exhibited negative correlations with both $\text{THg}_{\text{water}}$ and THg_{pore} ; redox-related parameters (Eh and pH) displayed moderate correlations with dissolved Hg in sediment pore water and the water column across seasons. Overall, correlation patterns differed between seasons, with DOC and oxygen-related parameters more closely associated with dissolved Hg during the rainy season, whereas microbial activity, salinity, temperature, and redox conditions were more strongly associated with dissolved Hg during the dry season. Although THg_{pore} concentrations were consistently higher than those measured in the water column, no direct correlation was observed between THg_{pore} and $\text{THg}_{\text{water}}$ ($r = -0.003$ in the rainy season; $r = -0.22$ in the dry season), indicating that Hg transfer from sediments to the water column is not systematic. Considering the filtering feeding behavior of Tilapia, these results suggest that even moderate dissolved Hg concentrations may influence Hg bioavailability, particularly in areas and seasons characterized by elevated microbial activity and DOC levels.

Table 1 Pearson correlation coefficient ($n=1$) between total Hg contents in all compartments (sediment pore water, water column, fish), chemical parameters (pH, Eh, dissolved organic carbon and dissolved oxygen) and microbial activity (FDA total enzymatic activity, AWCD catabolic diversity, number of cultivable bacteria) based on 24 observations in the rainy season for all sampling sites. Values in bold are different from 0 to a level of significance of $\alpha = 0.05$

Variables	THg_{fish}	THg_{pore}	$\text{THg}_{\text{water}}$	DOC	DO	Salinity	pH	Eh	FDA	AWCD	cultivable cells	T°C
THg_{fish}	1											
THg_{pore}	0.110	1										
$\text{THg}_{\text{water}}$	-0.432	-0.003	1									
DOC	0.301	0.480	-0.305	1								
DO	0.085	0.383	-0.189	0.365	1							

Salinity	0.046	-0.181	-0.002	0.119	0.020	1							
pH	-0.033	-0.260	-0.086	-0.015	-0.131	0.744	1						
Eh	0.027	0.208	0.157	0.029	0.140	-0.730	-0.978	1					
FDA	0.105	0.367	-0.216	0.337	0.192	0.200	0.182	-0.185	1				
AWCD	-0.555	-0.064	-0.211	0.053	-0.067	-0.040	0.124	-0.210	0.133	1			
cultivable cells	-0.032	-0.415	-0.491	-0.062	-0.043	-0.283	0.012	-0.025	-0.212	0.532	1		
T°C	0.116	0.375	-0.077	0.004	-0.024	-0.834	-0.627	0.563	-0.020	0.085	0.141		1

Table 2 Pearson correlation coefficient (n-1) between total Hg contents in all compartments (sediment pore water, water column, fish), chemical parameters (pH, Eh, dissolved organic carbon and dissolved oxygen) and microbial activity (FDA total enzymatic activity, AWCD catabolic diversity, number of cultivable bacteria) based on 24 observations in the dry season for all sampling sites. Values in bold are different from 0 to a level of significance of alpha = 0.05

Variables	THg _{fish}	THg _{pore}	THg _{water}	DOC	DO	Salinity	pH	Eh	FDA	AWCD	cultivable cells	T°C
THg _{fish}	1											
THg _{pore}	0.021	1										
THg _{water}	-0.588	-0.221	1									
DOC	-0.013	0.074	-0.131	1								
DO	-0.162	0.169	0.248	0.095	1							
Salinity	0.359	0.479	-0.420	-0.253	-0.253	1						
pH	0.285	0.509	-0.067	-0.209	0.269	0.701	1					
Eh	-0.217	-0.381	-0.055	0.116	-0.409	-0.500	-0.868	1				
FDA	-0.205	-0.553	0.310	0.066	-0.080	-0.858	-0.711	0.663	1			
AWCD	-0.306	-0.215	0.422	-0.203	0.439	-0.580	-0.148	0.071	0.421	1		
cultivable cells	-0.266	-0.067	0.368	-0.265	0.439	-0.159	0.141	-0.120	0.036	0.777	1	
T°C	-0.396	-0.460	0.271	0.237	0.273	-0.808	-0.736	0.665	0.717	0.540	0.308	1

4. Discussion

4.1. Seasonal and Spatial Dynamics of Dissolved Mercury in a Tropical Lagoon

Dissolved mercury concentrations in the Ebrié Lagoon exhibited moderate spatial variability and limited seasonal contrasts, both in sediment pore waters and in the water column. The consistently higher Hg concentrations observed in pore waters compared to the overlying water column confirm the role of sediments as a persistent reservoir of labile mercury, while the water column reflects more transient and locally controlled conditions. The absence of statistically significant seasonal differences in THg_{pore} and THg_{water} suggests that, despite strong hydrological contrasts between dry and rainy seasons, the dissolved Hg pool remains relatively buffered at the lagoon scale. Similar patterns have been reported in other lagoonal and estuarine systems, where sedimentary Hg pools exhibit long residence times and weak short-term responses to seasonal forcing [3, 10]. However, the seasonal variations of dissolved mercury within tropical lagoon systems, according to the physicochemical factors that influence its distribution can give an insight for the potential for methylation [11]. This organic form of mercury, known as methylmercury, is a potent neurotoxin that bioaccumulates and biomagnifies up the food chain, posing severe risks to ecosystem health and human populations [12]. In these environments, seasonal fluctuations in rainfall and water disturbance can mobilize mercury from sediments, enhancing its bioavailability and trophic transfer within the food web [13]. Moreover, dry periods in mangrove wetlands have been shown to release substantial amounts of dissolved organic Hg into the water, while

particulate Hg is primarily transported to the nearshore marine environment during heavy rainfall [14]. These dynamic processes underscore the importance of continuous monitoring of mercury contamination, especially in susceptible ecosystems such as lagoons, which provide critical habitats for diverse aquatic life [13]. Consequently, the observed higher concentrations of total mercury in sediments during the dry season, compared to the rainy season, suggest a seasonal influence on its sequestration and release dynamics [13]. Similarly, eutrophication, often exacerbated by seasonal nutrient inputs, can also alter mercury cycling by promoting anoxic conditions conducive to methylation [15].

Spatially, higher dissolved Hg concentrations at sites such as Port and Marcory likely reflect localized anthropogenic pressures combined with restricted hydrodynamic renewal, whereas lower concentrations at sites such as Cosrou and Koumassi may be associated with greater dilution or weaker sediment–water exchanges. The lack of a direct correlation between THg_{pore} and $\text{THg}_{\text{water}}$ across sites and seasons further indicates that Hg transfer from sediments to the water column is not systematic, but instead modulated by local physicochemical gradients and short-term processes. This spatial decoupling highlights the importance of considering dissolved Hg as a dynamic compartment whose distribution cannot be inferred solely from sedimentary concentrations. Anthropogenic activities continually release mercury into the environment, contributing to elevated concentrations in various media, with coastal sediments acting as long-term reservoirs and potential secondary sources for methylmercury production. For instance, the Marano-Grado Lagoon, heavily contaminated by historical mercury mining operations, exemplifies how coastal sites can become long-term sources of methylmercury to broader marine systems [16].

4.2. Biogeochemical Controls on Mercury Mobility and Bioavailability

Correlation analyses revealed clear seasonal shifts in the biogeochemical processes controlling dissolved Hg mobility. During the rainy season, positive relationships between THg_{pore} , dissolved organic carbon (DOC), and dissolved oxygen indicate that organic matter complexation under predominantly oxic conditions enhances Hg solubilization in sediment pore waters. Such DOC-mediated stabilization of dissolved Hg is well documented and plays a key role in maintaining Hg in the aqueous phase while limiting its immediate transfer to higher trophic levels [17, 18]. In contrast, the negative correlation between $\text{THg}_{\text{water}}$ and Hg concentrations in fish suggests that water-column Hg during this season does not directly translate into biological accumulation, possibly due to dilution effects and rapid turnover of dissolved Hg.

During the dry season, microbial activity emerged as a dominant control on dissolved Hg in the water column, as indicated by the positive correlation between $\text{THg}_{\text{water}}$ and AWCD. Enhanced microbial metabolism, combined with higher temperatures and reduced water renewal, likely promotes Hg remobilization through redox-driven transformations and organic matter degradation [19, 20]. The observed negative correlations of dissolved Hg with salinity and temperature further suggest that evaporative concentration, stratification, and changing redox conditions influence Hg speciation and partitioning. Moderate correlations with pH and redox potential across seasons confirm that Hg mobility is strongly governed by speciation-sensitive processes, consistent with established conceptual models of mercury cycling in aquatic environments [21, 5].

From a bioavailability perspective, the lack of direct coupling between sediment pore water and water-column Hg implies that exposure pathways for filter-feeding fish such as Tilapia are controlled primarily by conditions within the water column. Even moderate dissolved Hg concentrations may therefore contribute to biological uptake when microbial activity and DOC availability favor Hg persistence in the dissolved phase.

4.3. Global Comparison and Environmental Implications

When placed in a global lagoonal context (Fig. 3), dissolved Hg concentrations measured in the Ebrié Lagoon (30–110 ng L⁻¹) fall within the upper range reported for lagoon and coastal systems worldwide. These values exceed those observed in relatively weakly impacted lagoons such as Thau (<1 ng L⁻¹; [22]) and are markedly higher than concentrations reported for several tropical lagoons, including those of Rio de Janeiro (~4–11 ng L⁻¹; [23]). Instead, they are comparable to concentrations reported for the Ria de Aveiro, a system historically affected by intense industrial mercury inputs [24, 10]. This positioning indicates that the Ebrié Lagoon functions as a moderately to strongly impacted tropical lagoon, where chronic urbanization and industrial activities contribute to sustained Hg availability in the dissolved phase.

The wide min–max range observed further emphasizes the influence of local environmental conditions on Hg dynamics, reinforcing the idea that dissolved Hg represents a critical interface between long-term sedimentary storage and short-term biological exposure. From an environmental and management perspective, these findings underscore the need to explicitly integrate dissolved mercury into monitoring and risk assessment frameworks, particularly in tropical lagoon systems subjected to intense anthropogenic pressure. Considering the central role of the dissolved compartment in

mediating Hg bioavailability, failure to account for this pool may lead to underestimation of ecological and human health risks associated with fish consumption [5, 2].

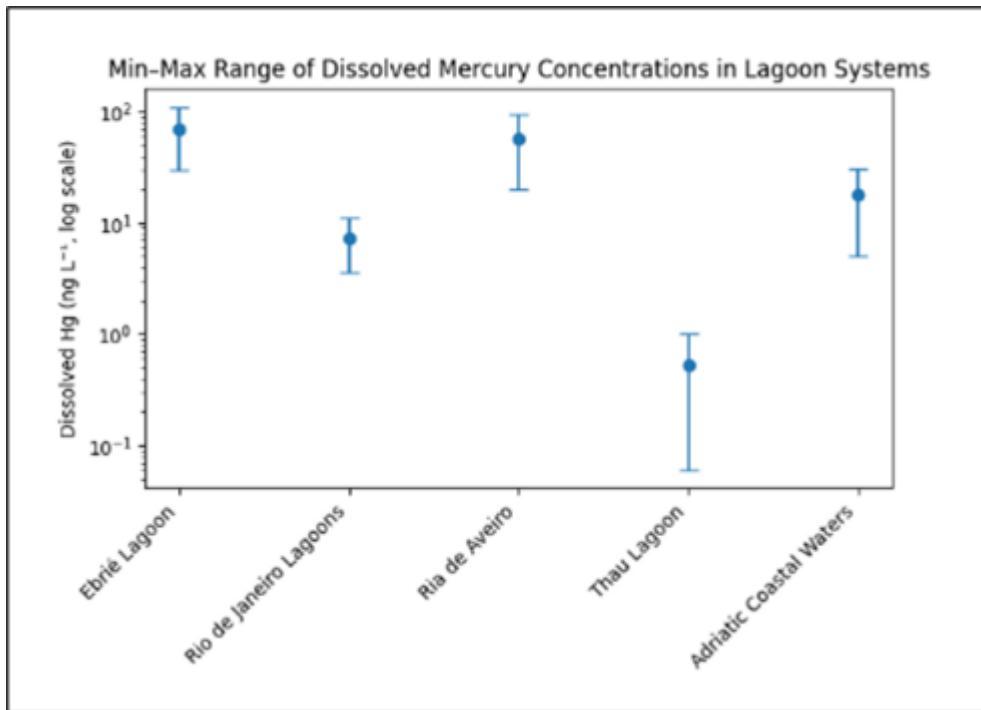


Figure 3 Min-max ranges of dissolved total mercury concentrations (ng L^{-1}) reported for the Ebrié Lagoon (this study) and for selected lagoonal and coastal systems worldwide. Symbols represent mean values, while error bars indicate minimum and maximum concentrations reported in the literature. The y-axis is displayed on a logarithmic scale. [22, 23, 24, 10]

5. Conclusion

This study provides the first comprehensive assessment of the seasonal dynamics of dissolved mercury in both sediment pore waters and the water column of the Ebrié Lagoon, thereby addressing a critical gap in the understanding of mercury cycling in tropical lagoon systems. The consistently higher dissolved Hg concentrations observed in sediment pore waters confirm the role of sediments as a long-term reservoir of labile mercury, while the water column acts as a more dynamic compartment governed by short-term physicochemical and biological processes. Despite pronounced hydrological contrasts between dry and rainy seasons, dissolved Hg concentrations exhibited limited seasonal variability, suggesting that the dissolved mercury pool is relatively buffered at the lagoon scale. In contrast, correlation analyses revealed strong seasonal shifts in the mechanisms controlling Hg mobility. During the rainy season, organic matter complexation under oxic conditions promoted Hg solubilization in pore waters, whereas during the dry season, enhanced microbial activity, redox-sensitive processes, and changes in salinity and temperature favored Hg remobilization in the water column. The absence of a direct relationship between pore-water and water-column Hg indicates that sediment-water exchanges are locally regulated and cannot be inferred solely from sedimentary Hg concentrations. From a bioavailability perspective, these findings demonstrate that even moderate levels of dissolved Hg in the water column may contribute to mercury uptake by filter-feeding fish such as Tilapia, particularly under conditions that favor microbial activity and dissolved organic matter availability. In a global context, the elevated dissolved Hg concentrations measured in the Ebrié Lagoon place this system among the more impacted lagoonal environments worldwide, reflecting sustained anthropogenic pressure. Overall, this study highlights the central role of dissolved mercury as an interface between sedimentary storage and biological exposure. Incorporating this compartment into monitoring programs and risk assessment frameworks is therefore essential to accurately evaluate ecological and human health risks associated with mercury contamination in tropical lagoon ecosystems.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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