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A preliminary study on mercury levels in the soft tissues of the Guiana dolphin (*Sotalia guianensis*) and edible fish from southern Lake Maracaibo, Venezuela

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Abstract

Coastal ecosystems around the world are facing increasing mercury pollution from various anthropogenic activities, which are affecting many aquatic mammals such as dolphins. Lake Maracaibo receives discharges of industrial water, wastewater, pesticides and herbicides from runoff, and constant oil spills; these discharges include several contaminants. In this paper, we highlight the extent of mercury accumulation in the soft tissues of Guiana dolphins and some fish species from southern Lake Maracaibo. A total of 17 fish species were analyzed. All but one of the species had traces of mercury, but only the mercury level in *Gobioides broussonnetii* (mean ± standard deviation = 0.9209 ± 0.0134 mg kg^{-1} wet weight (ww)) exceeded the limit established as safe for human consumption. In Guiana dolphins, mercury levels in four of six individuals exceeded the maximum limit considered safe for human consumption (0.5 mg kg^{-1} ww), with the highest level of 2.9611 ± 0.1637 mg kg^{-1} ww in the liver of one individual, suggesting biomagnification through diet and possible adverse effects in this species. It is important to note that the dolphins from which samples were collected were juveniles. There is evidence of a correlation between mercury accumulation and the size and age of dolphins, emphasising the ecological risks posed by anthropogenic pollutants. The wider ecological impacts, including threats to endangered fish species and public health risks associated with mercury-contaminated marine resources are also discussed. This study emphasises the urgent need for comprehensive management strategies to reduce mercury pollution and to protect coastal ecosystems and public health.

Keywords:
bycatch, consumption, Lake Maracaibo, mercury, *Sotalia guianensis*

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Introduction

Mercury is a contaminant of great concern in the marine environment because it is easily absorbed by detritivorous organisms, accumulating in significant quantities in fish and mammals (Seixas et al., 2014; Harding et al., 2018). This, in turn, poses a threat to the people who feed on them (Porto et al., 2005; Castilhos et al., 2006).

Some metals occur naturally in the environment, but due to industrial and agricultural activities, wastewater discharges and oil spills, they have increased to levels that are harmful to biota (Walker et al., 2014). In marine mammals, high levels of Hg can suppress the immune system, cause neurotoxicity, and even reduce fitness (Tanabe, 2002; López-Berenguer et al., 2020).

Species with coastal habits and a high degree of site fidelity, such as the Guiana dolphin (*Sotalia guianensis*; Flores & Bazzalo, 2004; Azevedo et al., 2007), are particularly vulnerable to anthropogenic impacts, as coastal areas are often areas of interest for artisanal fishing, harbour construction, and human and industrial settlements. The extensive and degraded Lake Maracaibo is the main occurrence of this dolphin species in

Venezuela. The resident population has been proposed as a separate management unit, which highlights the importance of protecting this population (Caballero et al., 2007).

The southern region of Lake Maracaibo is characterised by economic activities such as blue crab (*Callinectes sapidus*) fishing and large-scale agricultural and livestock development. The latter activities are a major source of organic and inorganic waste, which in turn may contain cadmium (Cd), mercury (Hg), and lead (Pb) which, together with the constant oil spills, degraded the ecosystem (Conde & Rodríguez, 1999; Meléndez et al., 2005). Concentrations of some contaminants have been analyzed in the past on blue crabs from southern Lake Maracaibo and fish from the Catatumbo River (Hermoso & Márquez, 2005), but never been explored in Guiana dolphins. Thus, the main goal of this study was to document the presence of total Hg in soft tissue samples of six dead Guiana dolphins and in 17 fish species, some of which are prey for Guiana dolphins, and others with economic importance. Considering its position in the food chain as a top predator, the exploration and evaluation of the health status of Guiana dolphins is of great importance as it provides insight into the entire ecosystem and human health. Dolphins consume many of the same fish species caught by commercial fisheries, and consumption of Guiana dolphins has also been reported in southern Lake Maracaibo (Briceño et al., 2021).

Methods

Study area

The southern region of Lake Maracaibo in the Colón municipality covers 3,470 km^2. The area extends from 09°14′ (Boca del Escalante) to 08°31′ S (border with Táchira State) latitude and from 71°41′ (Punta Garcitas) and 72°10′ W (Caño Caimán) longitude. The water is oligohaline (0.5–5 ppm) and limnetic (< 0.5 ppm). The area is made up of a complex of swamps covered by herbaceous and arboreal vegetation, with wetlands comprising two large alluvial systems: the Santa Ana River and its tributaries to the north, and the Catatumbo River and its tributaries to the south. The Catatumbo River has the higher flow of the two rivers and provides 60% of the fresh water in Lake Maracaibo. Moreover, it is the main source of detrital sediments in the lake (Rodríguez, 2001). The depth of the southern area of Lake Maracaibo is 1–30 m. The selected study area covers 150 km^2 of the southeast region of the lake, and within those 150 km^2 there is a 70-km^2 polygon corresponding to the southern part of the Ciénagas de Juan Manuel National Park, and 35 km^2 of the Ciénagas de Juan Manuel, Aguas Blancas y Aguas Negras Wildlife Reserve. The main economic activities in the region are blue crab fishing, agriculture, and cattle ranching on the coast. In addition, there are oil platforms of the state company Petróleos de Venezuela, S.A, some of which are in disuse, near the study area.

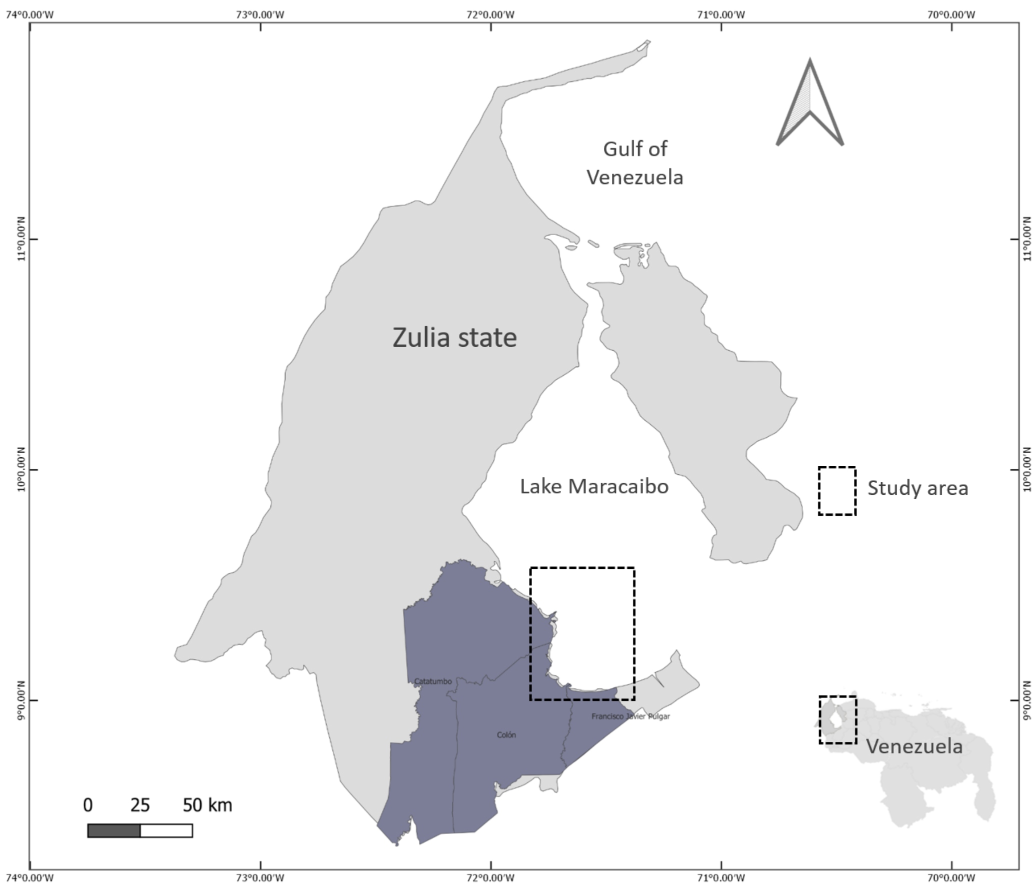

Figure 1. Map of the study area in southern Lake Maracaibo where fish and dolphin samples were collected for the Hg analysis.

Table 1. Calibration curves and correlation coefficients calculated for each detection cell of the DMA-80 (milestone) used in the determination of HgT in the samples evaluated.

Detection	Equation of the line	Coefficient of determination (r^2)
Cell 0	y = 0.1185x + 0.0269	0.9932
Cell 1	y = 0.0458x + 0.0139	0.9959
Cell 2	y = 0.0007x + 0.0266	0.9904

Table 2. Evaluation of the accuracy of the method used for the quantification of HgT using certified reference materials (SRM).

SRM	SRM 2976 Trace elements and methylmercury in mollusc tissue (μg kg^{-1} ± SD) (n = 3)	NIST 1573a Tomato leaves (μg kg^{-1} ± SD) (n = 3)
Certified value	61.0 ± 3.6	34.000 ± 4.000
Value obtained	60.6 ± 3.6	33.567 ± 1.200

NBS (National Bureau of Standards), NIST (National Institute of Standards & Technology), SD (standard deviation)

Table 3. Equations used to determine the figures of merit: limit of detection (LOD), limit of quantification (LOQ), and relative standard deviation (RSD).

Figure of merit	Equation (Eq)
LOD	$\frac{3SD_b}{m}$
LOQ	$\frac{10SD_b}{m}$
% RSD	$\frac{SD_{[Hg]}}{[Hg]} x100\%$

m: slope of the calibration curve, ([Hg]): average mercury, SD: Standard deviation, SD_b: Standard deviation of the blank (matrix without analyte)

Fieldwork

In 2018, two field trips were undertaken to search for fresh samples of fish species in southern Lake Maracaibo (Fig. 1). A preliminary meeting was held with the fishermen in the presence of the head of the fishermen's council to inform them about the study to be conducted in the area and to request their collaboration in providing fish and dolphin. On each trip, the tour started at 06:00 h to locate fishermen in the selected study area.

Each fish was measured and its weight taken using a tape measure and spring scale, respectively. A piece of muscle about 5 cm long was cut from each specimen with scalpels and wearing gloves, and then placed in a labelled plastic bag and refrigerated until further analysis. The number of specimens varied depending on the species and what the fishermen had caught in their nets.

It was necessary to select fishermen who were more trustworthy and willing to provide samples of incidentally captured dolphins, either from themselves or their colleagues. They were explained the importance of reporting the size of the individual and the place of capture. Also, they were notified that the study required a sample of approximately 5 x 5 cm of muscle and, if possible, liver samples.

Samples were obtained of six juvenile Guiana dolphins from bycatch in southern Lake Maracaibo; all of them were fresh (code 2, freshly dead) (Bermúdez, 2025). The samples received were stored in sterile plastic bags, previously labelled and then frozen at -80 °C until further processing in the laboratory.

Laboratory analysis

Analytical determination was carried out directly in a Direct Mercury Analyzer DMA-80 Tricell (Milestone Inc., Italy), using the thermal decomposition and amalgamation technique with detection by atomic absorption spectrophotometry (TDA-AAS) described in Method 7473 (U.S. Environmental Protection Agency, 2007). Approximately 100 mg of fresh muscle were weighed in a nickel bucket and placed in the DMA-80 autosampler. Then, the programmed analysis for total Hg was started at a wavelength of 253.7 nm and with a detection limit of 0.0015 ng. This procedure was performed in triplicate for each species; the results are expressed in mg kg^{-1} of wet weight. The accuracy of the analytical method was assessed with direct analysis of reference materials certified by the National Institute of Standards and Technology (NIST) for trace elements and methylmercury in mollusc tissue (SRM 2976) and by the National Bureau of Standards (NBS) for tomato leaves (SRM 1573a). The results were consistent with the certified values for each case. The precision of the method was evaluated based on the relative standard deviation (RSD) of the replicas of the certified materials (n = 3). The results confirmed the precision of the method (RSD < 5%).

A robust quality assurance and control framework was implemented of the data, focused on preventing potential errors, through appropriate planning and procedures and the testing and verification steps such as calibration curve and coefficient of determination (Table 1), accuracy evaluation using standard reference materials (SRM), and determination of limit of detection (LOD), limit of quantitation (LOQ), and RSD.

No recovery study was performed, as accuracy and precision (in terms of repeatability, %RSD) were assessed by direct analysis of certified reference materials. The results obtained are shown in Table 2.

The limit of detection (LOD) and limit of quantification (LOQ) (Table 3) were determined by calculating three and ten times the standard deviation (SD, n = 10) of the blank, respectively, considering the slope in the zero cell, which has the highest sensitivity. The blank used was deionized water obtained from

Table 4. Calibration curves and correlation coefficients calculated for each detection cell of the DMA-80 (milestone) used in the determination of HgT in the samples evaluated.

Measurements	SRM 2976 Trace elements and methylmercury in mollusc tissue (μg kg^{-1})	NIST 1573a Tomato leaves (μg kg^{-1} ± DE)
X1	63.0262	32.455
X2	58.4859	33.952
X3	62.2083	34.989
Average	61.2401	33.799
SD	2.4201	1.274
RSD (%)	3.9518	3.7693

Table 5. Values calculated for the limit of detection (LOD), limit of quantification (LOQ), and sensitivity in each detection cell of the DMA-80 (Milestone) used in the determination of HgT in the samples evaluated

LOD (ng HgT)	LOQ (ng HgT)	Detection	Sensitivity
0.0132	0.1322	Cell 0	0.1185
		Cell 1	0.0458
		Cell 2	0.0007

the Mili-Q 18 MΩ cm, Millipore (Tables 4 and 5).

The detection and quantification limits of the analytical method were calculated from the instrumental LOD and LOQ of the DMA-80 (Milestone) and the 100 µL sample volume used for the analysis. The resulting values were a detection limit (LOD) of 0.0001 mg kg^{-1} HgT and a quantification limit (LOQ) of 0.0013 mg kg^{-1} HgT.

Results

In this study, the presence of Hg was detected in all analyzed samples. We evaluated Hg levels in eight samples (six muscle and two liver) obtained from six Guiana dolphins. The individuals examined were classified as juveniles, based on our own observations and the knowledge of local fishermen.

It is important to note that in four of these samples (Table 6: a, b, c, d) Hg levels are at or exceed the 0.5 mg kg^{-1} ww limit established by the World Health Organization (WHO) as safe for human consumption. The highest value recorded was 2.9611 ± 0.1637 mg kg^{-1} ww. These findings are summarized in Table 6.

In addition, we processed samples from 17 species from 15 genera of fish (Table 7): twelve carnivorous (70.5%), three detritivorous (17.6%), one omnivorous (*Hemibrycon jabonero*), and one herbivorous (*Schizodon corti*). We found Hg in all the fish species analyzed. It ranged from 0.005 mg kg^{-1} ww (*Platysilurus malarmo*) to 0.92 mg kg^{-1} ww (*Gobioides broussonnetii*) (Table 7).

Discussion

Many coastal areas are influenced by anthropogenic activities that may increase the Hg concentrations in coastal waters and thus in the species that inhabit them (Evans & Crumley, 2005). Previous studies on sediments from Lake Maracaibo, which included many sampling stations from the north to the south, have revealed the presence of high levels of heavy metals—a result similar to what has been found in other aquatic ecosystems with great oil extraction activity, which constitutes a high ecological risk to biota (Ávila et al., 2010; Marín et al., 2022). Another study on fish tissue from the Catatumbo River revealed that most species had heavy metal levels that exceeded the limits established as safe for human consumption according to different health agencies (WHO, Food Standards Australia New Zealand, and the Agency for Toxic Substances and Disease Registry [ATSDR]; Hermoso & Márquez., 2005). In 1995, a study conducted by the Institute for the Control and Conservation of the Lake Maracaibo Basin (ICLAM, 1995) reported mercury levels of 0.03–2.01 mg kg^{-1} ww in fish from the Catatumbo River. By 2005, the levels were 0.06–2.62 mg kg^{-1} ww; although they had not changed much, the values exceeded what is considered suitable for human consumption.

It is important to note that the six dolphins from which we collected samples were juveniles (< 1.8 m). This fact could influence the amount of Hg found in their tissues. It has been shown that size and age correlate positively with the accumulation of Hg. A study analyzing mercury (Hg) contamination in 27 Guiana dolphins from Amapá state, North Brazil, found a significant positive correlation ($p < 0.05$) between mercury concentration and body length. This relationship was observed in both male ($r^2 = 0.318$) and female ($r^2 = 0.427$) dolphins, but no significant correlation was found with the sex of the dolphins (de Moura et al., 2012a). Other examples of this relation between length and Hg accumulation have been reported in Brazil (Monteiro-Neto et al., 2003; Carvalho et al., 2008), and also a positive correlation with age (Kunito et al., 2004).

Multiple studies on *Sotalia guianensis* from Brazil have reported mercury concentrations in muscle tissue ranging from 0.7 to 1.8 mg kg^{-1} ww) (Kehrig et al., 2004, 2009; Carvalho et al., 2008; Lopes et al., 2008; de Moura et al., 2012b). These values could provide a comparative baseline for assessing mercury accumulation in this species across different geographical locations considering the variables age, length and size, and those that may affect the accumulation of pollutants.

In addition, it is normal to find higher levels of Hg in liver samples because the detoxification occurs mainly in this organ, followed by the kidney, lung, and muscle (Augier et al., 1993). We could only obtain two liver samples from the dolphin carcasses. When dolphins are part of bycatch, fishermen will often extract the *longissimus* muscles and then discard the rest of the body in the water to avoid punishment from the authorities. One of the liver samples showed the highest Hg concentration of all analyzed samples: 2.9611 ± 0.1637 mg kg^{-1} ww. Another study showed a higher Hg concentration in a liver (137.15 mg kg^{-1}) in an adult male (193 cm) of Guiana dolphin from Paraná State (Brazil) and a mean in muscle (n = 30) of 0.73 mg kg^{-1} ww with a maximum value of 1.93 mg kg^{-1} ww in an adult female (Beloto, 2010).

The results of other investigations have revealed that although small cetaceans have a varied diet that may include shrimp and crabs, fish contribute more to Hg biomagnification (Seixas et al.,

Table 6. Total mercury (HgT) levels (mean ± standard deviation of three replicates) reported in tissue samples of Guiana dolphins (*Sotalia guianensis*) from southern Lake Maracaibo Lake. Samples a, b, c and d are those with the highest concentration of Hg.

Tissue sample	Code	HgT (mg kg^{-1} ww)	Age
Muscle	SG1	0.1117 ± 0.0063	Juvenile
Liver	SG1.1	0.3288 ± 0.0278	Juvenile
Muscle	SG2	0.1673 ± 0.0065	Juvenile
Muscle	SG3	0.4966 ± 0.0152	Juvenile (a)
Muscle	SG4	0.1737 ± 0.0157	Juvenile
Liver	SG4.1	2.9611 ± 0.1637	Juvenile (b)
Muscle	SG5	0.6392 ± 0.0195	Juvenile (c)
Muscle	SG6	0.5485 ± 0.0162	Juvenile (d)

Table 7. Total mercury (HgT) levels in tissue samples from fish and crabs in southern Lake Maracaibo. Species with an asterisk (*) have been identified as part of the dolphins' diet but also of interest for human consumption. The species identified with the letter e corresponds to the sample with the highest concentration of Hg.

Fish species	Length (cm)	Weight (g)	Common name (Spanish)	HgT (mg kg^{-1}) (ww)	Feeding strategy
**Eugerres plumieri*	19	120	Carpeta	0.1293 ± 0.0156	Carnivore
**Potamorhina laticeps*	19.3	130	Manamana	0.0190 ± 0.0039	Detritivore
Potamorhina laticeps	22.2	240	Manamana	0.0116 ± 0.0005	Detritivore
Potamorhina laticeps	21.3	220	Manamana	0.0136 ± 0.0021	Detritivore
Schizodon corti	30.5	400	Coti	0.0227 ± 0.0038	Hervibore
Pimelodus navarroi	21	150	Bagre	0.0489 ± 0.0007	Carnivore
Hemibrycon jabonero	27	200	Sardina, jabonero	0.0263 ± 0.0050	Omnivore
**Mylossoma acanthogaster*	31	350	Pámpano	0.1312 ± 0.0029	Carnivore
Mylossoma acanthogaster	23.2	200	Pámpano	0.0048 ± 0.0005	Carnivore
Hoplias teres	33	280	Guabina	0.0184 ± 0.0002	Carnivore
**Prochilodus reticulatus*	23.5	280	Bocachico	0.0167 ± 0.0059	Detritivore
Prochilodus reticulatus	24	320	Bocachico	0.0155 ± 0.0020	Detritivore
Sorubim cuspicaudus	43.5	700	Bagre paletón	0.1477 ± 0.0040	Carnivore
**Cynoscion acoupa*	33	340	Curvina	0.1155 ± 0.0037	Carnivore
Cynoscion acoupa	39.3	700	Curvina	0.0919 ± 0.0042	Carnivore
Cynoscion acoupa	42.8	850	Curvina	0.1023 ± 0.0050	Carnivore
**Caquetaia kraussii*	17	120	Viejita/mojarra amarilla	0.0661 ± 0.0008	Carnivore
Caquetaia kraussii	18.2	160	Viejita/mojarra amarilla	0.0506 ± 0.0033	Carnivore
**Centropomus undecimalis*	52.4	2000	Robalo	0.1486 ± 0.0025	Carnivore
Platysilurus malarmo	38.4	750	Bagre malarmo	0.0032 ± 0.0002	Carnivore
Pimelodidae	35.6	655	Bagre	0.0709 ± 0.0086	Carnivore
Hypostomus sp.	20	350	Armadillo	0.0093 ± 0.0002	Carnivore
Notarius sp.	36	700	Bagre	0.1226 ± 0.0095	Carnivore
**Gobioides broussonnetii*	12.5	95	Lamprea	0.9209 ± 0.0134	Detritivore (e)

2009). A diet study of Guiana dolphin carried out in northern Lake Maracaibo (Vílches, 2006) and other areas of its range showed that fish are its main source of food, which would explain the presence of Hg in their tissues, considering that all the fish we analyzed also had traces of Hg.

The effects of Hg on marine mammals have not yet been fully elucidated (Cardellicchio et al., 2002), but there is scientific evidence of damage to cetaceans such as immune suppression, bone injury, and damage to reproductive organs. An example of this can be seen after the Deepwater Horizon oil spill in the Gulf of Mexico. A health evaluation was carried out on the bottlenose dolphins in the Sarasota and Barataria bays. In the latter population, there were more individuals with rare diseases and damage to the respiratory system associated with exposure to toxic hydrocarbons (Schwacke et al., 2014). Therefore, the mere presence of high levels of Hg found in the tissues of juvenile Guiana dolphins from southern Lake Maracaibo suggests there may be underlying damage as a result of constant exposure to pollutants.

In 2017 a population density of 1.1 individual/km² was estimated for *Sotalia guianensis* in the southern part of the lake (Briceño et al., 2017). This data offers a reference point to analyze how various anthropogenic pressures, including pollution, may influence the population status and overall viability.

Of the 18 species analyzed, six are on the regional red list of threatened species. Specifically, the Guiana dolphin and three fish (*Potamorhina laticeps, Mylossoma acanthogaster* and *P. malarmo*) are vulnerable, and *Sorubim cuspicaudus* and *Prochilodus reticulatus* are endangered (Rodríguez et al., 2015). The latter species is endemic to Lake Maracaibo and represents its most commercially important species. The presence of Hg is another threat to these and other species. Given the current deficiency in data regarding the production volumes per fishery and fishery statistics, the future of these endangered species is uncertain.

Among the fish species analyzed, the highest mercury concentration was found in *G. broussonnetii* (0.9209 ± 0.0134 mg kg^{-1} ww). This detritivorous species feeds on organic matter, plant and animal remains from the water bottom, and can incorporate contaminants such as mercury present in sediments and food particles. The southern portion of Lake Maracaibo is characterized by a muddy, marshy bottom that can act as an important reservoir, trapping this kind of contaminants and facilitating their bioaccumulation in the ecosystem.

It is likely that the pesticides and herbicides used in crops in southern Lake Maracaibo contribute to the entry of Hg into this estuarine ecosystem which, combined with the constant oil spills for more than twenty years, are creating a negative impact. The presence of Hg and methylmercury in sediments and biota (mussels, crabs, fish, and dolphins; Hermoso & Márquez, 2005; Ávila et al., 2010; Colina et al., 2011; Lara et al., 2018; Marín et al., 2022) from Lake Maracaibo shows the level of pollution of this body of water. Moreover, the presence of Hg in the fish and Guiana dolphins we studied represents a threat to these organisms, a key focus of our investigation. While the data on mercury concentrations in fish that are also part of the human diet could serve as a valuable reference for future studies on public health, the primary scope of this study is to assess bioaccumulation in wildlife.

Conclusions

In conclusion, our analysis revealed the ubiquitous presence of Hg in the tissues of both fish and Guiana dolphins in the Lake Maracaibo ecosystem. This infiltration of toxic elements is a major concern not only for the health of dolphins and fish species, but also for human populations that rely on these species as a food source. Of particular concern is the higher concentrations of Hg we found in dolphin tissues compared with fish tissues, highlighting the capacity of bioaccumulation and biomagnification.

The co-occurrence of Hg with other anthropogenic threats exacerbates the vulnerability of species such as the Guiana dolphin, which is already listed as vulnerable in the country. Such cumulative pressures could lead to the collapse of these populations. To address this pressing issue, it is imperative to extend sampling efforts to different regions of Lake Maracaibo, covering both fish and Guiana dolphins, be able to determine the age and length of the dolphins, a parameter related to the amounts of accumulated pollutants and thus carry out a comprehensive assessment of the presence of toxic elements and organochlorines. These data are essential for formulating health advisories and issuing timely warnings regarding the consumption of certain fish species and dolphin meat. In addition, a comprehensive health assessment of the Guiana dolphin population is urgently needed to identify potential diseases and to assess their impact within the wider ecosystem.

Understanding the health of these dolphins provides a crucial window into the overall health of the ecosystem. As a top predator, their condition reflects the cumulative impacts of environmental stressors. In the face of increasing threats such as mercury contamination, concerted efforts are vital to protect both human and ecological well-being. To enhance future research and obtain more accurate data, it is imperative to have access to complete dolphin carcasses. This requires a coordinated approach: the active support of local fishing communities is essential for information dissemination and carcass recovery, while the collaboration of environmental authorities is critical to facilitate this process and ensure its success, and for developing and communicating advisories and preventive measures to ensure the safe consumption of local fish, thereby mitigating risks to public health.

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