

Contents lists available at ScienceDirect

# Marine Pollution Bulletin



journal homepage: www.elsevier.com/locate/marpolbul

Baseline

# On mobulid rays and metals: Metal content for the first *Mobula mobular* record for the state of Rio de Janeiro, Brazil and a review on metal ecotoxicology assessments for the *Manta* and *Mobula* genera



Rachel Ann Hauser-Davis<sup>a,\*</sup>, Catarina Amorim-Lopes<sup>b,c</sup>, Nathan Lagares Franco Araujo<sup>c,d</sup>, Manasi Rebouças<sup>e</sup>, Ricardo Andrade Gomes<sup>d</sup>, Rafael Christian Chávez Rocha<sup>f</sup>, Tatiana Dillenburg Saint'Pierre<sup>f</sup>, Luciano Neves dos Santos<sup>b,c</sup>

 <sup>a</sup> Laboratório de Avaliação e Promoção da Saúde Ambiental, Instituto Oswaldo Cruz, Fiocruz, Av. Brasil, 4.365, Manguinhos, Rio de Janeiro, RJ 21040-360, Brazil
<sup>b</sup> Programa de Pós-graduação em Ecologia e Evolução, Universidade Estadual do Rio de Janeiro, Rua São Francisco Xavier, 524, Maracanã, 20550-900 Rio de Janeiro, RJ, Brazil

<sup>c</sup> Laboratório de Ictiologia Teórica e Aplicada, Instituto de Biociências, Universidade Federal do Estado do Rio de Janeiro, Avenida Pasteur, 458, Urca, 22290-255 Rio de Janeiro, RJ, Brazil

<sup>d</sup> Instituto Mar Urbano, Rua Sérgio Porto 23, Gávea, 22451-430 Rio de Janeiro, RJ, Brazil

<sup>e</sup> Colônia de Pescadores Z-13, Praça Coronel Eugênio Franco, Copacabana, 220070-020 Rio de Janeiro, RJ, Brazil

<sup>f</sup> Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Chemistry Department, Rua Marquês de São Vicente, 225, Gávea, 22451-900 Rio de Janeiro, RJ, Brazil

# ARTICLE INFO

Keywords:

Manta

Mobula

Giant Devil Ray

Southeastern Brazil

Ecotoxicology

Metals and metalloids

ABSTRACT

This study comprises the first record of a juvenile Giant Devil Ray specimen for Rio de Janeiro, Southeastern Brazil, and its metal and metalloid contents. A scientometric assessment was also performed for the *Manta* and *Mobula* genera. Only five records were found, and only As, Cd, Pb, Hg, Pt, Pd and Rh have been assessed. All studies but one concerned human consumption. A significant knowledge gap on metal and metalloid ecotoxicology for mobulid rays is noted, indicating the emergence of a new field of research that th may be applied for wildlife conservation and management in response to anthropogenic contamination. Our study is also the first to provide Al, Cr, Cu, Fe, Mn, Sr, Ti, V and Zn contents for muscle, liver, brain and kidney for a mobulid ray and one of the scarce reports concerning As, Cd, Hg and Pb in muscle, liver and kidney.

Elasmobranchs, comprising sharks and batoids (stingrays, skates, guitarfishes and sawfishes), notably suffer intense pressures such as finning practices, unsustainable fisheries, both targeted, aimed at meat consumption and the sale of elasmobranch-derived products, or captured as bycatch, climate change and chemical contamination (Navia et al., 2016; Pacoureau et al., 2021; Simpfendorfer and Dulvy, 2017). Chemical contamination, in particular, is a severe problem for many elasmobranchs, as many species are intermediate to top predators, primarily exposed to contaminants via the dietary route (Navia et al., 2016), while several batoids are highly exposed to pollutants through intimate contact with contaminated sediment due to their benthic habits (Horvat et al., 2013). Ecotoxicological assessments for this group are, however, notably lacking. This is particularly true for batoids, which remain severely understudied in this regard, especially concerning metal and metalloid evaluations (Bezerra et al., 2019).

Mobulid rays (Myliobatidae family) comprise two distinctive genera, *Manta* and *Mobula* (Eschmeyer et al., 2020). All mobulid rays are classified as either Data Deficient, Near Threatened, Vulnerable or Endangered by the International Union for Conservation of Nature (IUCN) (IUCN, 2020), indicating the need for urgent conservation actions.

One of the world's largest batoids, the Giant Devil Ray (*Mobula mobular*, previously described as *Mobula japonica*), exhibits an apparent circumglobal epipelagic distribution in warm waters found over continental shelves and near oceanic islands (Whitehead et al., 1984). It is classified as Endangered by the IUCN (Froese and Pauly, 2021). Reports for southeastern Brazil are noted for the state of São Paulo (Menezes, 2011), but no record is available for the state of Rio de Janeiro, considered a transitional region between Tropical and Subtropical zones (Santos et al., 2021). In this context, we describe herein a first record of a juvenile *M. mobular* specimen caught by artisanal fishery activities in

\* Corresponding author. *E-mail address:* rachel.hauser.davis@gmail.com (R.A. Hauser-Davis).

https://doi.org/10.1016/j.marpolbul.2021.112472

Received 22 March 2021; Received in revised form 3 May 2021; Accepted 5 May 2021 Available online 15 May 2021 0025-326X/© 2021 Elsevier Ltd. All rights reserved. Rio de Janeiro, Brazil and its toxic and essential metal and metalloid contents in kidneys, liver, brain and muscle tissue as determined by inductively coupled plasma mass spectrometry. Since metal and metalloids are among the main classes of marine fish contaminants worldwide (Zuluaga Rodríguez et al., 2015), ecotoxicological metal and metalloid assessments in the *Mobula* and *Manta* genera were also addressed and discussed, through a literature survey. Despite their susceptibility to bycatch and occasional consumption by small-scale fishery communities, the ecology and biology of mobulids remain poorly understood (Luiz et al., 2009) and this ecotoxicological field of research can be used to investigate, protect and manage wildlife conservation in response to anthropogenic contamination (Peterson et al., 2017),

The juvenile Giant Devil Ray reported in this study (n = 1) was captured on November 24th, 2020 (spring) by an artisanal gillnet fishery, the Z-13 Copacabana Colony, located in the metropolitan area of the city of Rio de Janeiro, in the state of Rio de Janeiro, southeastern Brazil ( $22^{\circ}$  59' 10" S, 43° 11' 19" W, Fig. 1). The specimen was landed displaying signs of feeding by other animals, with missing eyes. The animal was kindly donated for scientific assessments by the local fishers.

At the laboratory, the captured individual was confirmed as *M. mobular* (Gomes et al., 2019), sexed and the following measurements were taken using a metric measuring tape: right and left cephalic horn lengths (CHL), distance between cephalic horns (DCH), stinger length (SL), disk length (DL) and mouth size (MS) (Fig. 2). Unfortunately, the specimen's pectoral fins had been previously removed by the local fishers for sale, so no disk width was recorded.

Following the morphometric determinations, kidney, liver, brain and

muscle tissue were removed for metal and metalloid determinations. Approximately 100 mg of each sample were weighed in 15 mL sterile polypropylene tubes, mixed with 1 mL of bidistilled nitric acid (67% v/v, p.a. grade, Hexis, São Paulo, Brazil) and left capped overnight to react. The following day, the samples were heated on a heating block for 4 h at 100 °C in the closed polypropylene tubes, thus avoiding loss of volatile elements (USP, 2013). After cooling slowly at room-temperature, the samples were adequately made-up with ultra-pure water (resistivity > 18.0 M $\Omega$  cm), diluted and analysed employing an NexIon 300× spectrometer (PerkinElmer, USA). Multielemental external calibration was conducted through appropriate dilutions of a mixed Merck IV standard solution and <sup>103</sup>Rh was introduced online from a 20 mg L<sup>-1</sup> solution and used as the internal standard. All sample determinations were performed in triplicate. Analytical curve correlation coefficients were accepted only when above 0.995.

The limit of quantification (LOQ) for each investigated element followed the Brazilian National Institute of Metrology, Quality and Technology standards (Inmetro, 2016) as follows:  $LOQ = (10 \times SD \times df) / slope$  of the line (SD - standard deviation of the ratio of the analytical signal to the internal standard signal of 10 blanks; df - sample dilution factor).

Procedural blanks and three certified reference materials (BCR-668 – mussel tissue, DORM-2 - fish tissue and ERMBB422 - fish tissue, both from the European Commission) were analysed, in triplicate, to assure method accuracy. Table 1 displays the observed and certified values for the certified reference materials and elemental recovery percentages. All recoveries considered were adequate for this type of study, ranging from



Fig. 1. Map indicating the sampling location of the Mobula mobular individual reported herein, in the metropolitan area of the city of Rio de Janeiro, state of Rio de Janeiro, southeastern Brazil.



Fig. 2. Schematic illustration of M. mobular measurements taken using a metric measuring tape in the present study.

Table 1	
Observed and certified concentrations (mg kg <sup>-1</sup> dry weight, d.w.) for the three certified reference materials used in this study and	d their elemental recoveries (%).

Element	BCR-668			ERM-BB422			DORM-2			
	Certified value	Observed value	% recovery	Certified value	Observed value	% recovery	Certified value	Observed value	% recovery	
As	$7.1\pm0.50$	$\textbf{7.3} \pm \textbf{0.13}$	102.7	$12.7\pm0.70$	$12.7\pm0.15$	100.4	$16.4\pm1.1$	$17.1\pm2.6$	104.5	
Ca	-	-	-	342	$367.5\pm0.9$	107.5	-	-	-	
Cd	$0.28\pm0.01$	$0.23\pm0.01$	84.1	$0.0075 \pm 0.0018$	$0.005\pm0.001$	69.4	$0.04 \pm 0.01$	$0.03\pm0.01$	83.8	
Со	0.31	$0.34\pm0.01$	108.9	-	-	-	-	-	-	
Cu	-	-	-	$1.67\pm0.16$	$1.41\pm0.01$	84.6	-	-	-	
Fe	84.70-93.50	$\textbf{96.83} \pm \textbf{0.19}$	103.6-114.3	$\textbf{9.4} \pm \textbf{1.4}$	$8.6\pm0.3$	91.3	-	-	-	
Hg	-	-	-	$0.601\pm0.03$	$\textbf{0.47} \pm \textbf{0.01}$	78.1	$4.47\pm0.032$	$\textbf{3.45} \pm \textbf{0.44}$	77.2	
Mg	-	-	-	1370	$1450\pm36$	106.1	-	-	-	
Mo	$1.99 \pm 0.15$	$\textbf{2.25} \pm \textbf{0.03}$	113.2	-	-	-	-	-	-	
Mn	-	-	-	$0.37\pm0.03$	$0.30\pm0.02$	81.5	-	-	-	
Na	-	-	-	2800	$2980\pm60$	106.4	-	-	-	
Pb		-	-	-	-	-	$0.06\pm0.01$	$0.077\pm0.001$	127.9	
Zn	$\textbf{70.70} \pm \textbf{0.40}$	$51.54 \pm 0.23$	72.9	$16\pm1.1$	$11.8\pm0.1$	74.1	$\textbf{25.6} \pm \textbf{2.3}$	$16.6 \pm 2.7$	64.9	

70 to 120%, as per Eurachem standards (Eurachem, 1998; Ishak et al., 2015).

Information regarding ecotoxicological metal and metalloid assessments of mobulid rays was obtained from the scientific literature by performing a search on three scientific databases (Table 2), using the keywords Metal\* AND "mobulid", Metal\* AND "*Mobula*", and Metal\* AND "*Manta*", as well as their common names in English and Portuguese ("giant devil ray" and "raia manta", respectively). After a manual screening and the exclusion of duplicates and articles that did not report metal or metalloid data, the obtained records were selected and included in the final quantitative analyses. Citations within the reports were also investigated and added when adequate. Table 2 depicts the search strategy applied herein.

The M. mobular individual was a male, presenting small flexible

Applied search strategy concerning metal contents in mobulid rays.

Scientometric search strategy	
Subject	Metal and metalloid contents in mobulid rays
Scientific databases	Google Scholar (Google), Pubmed (NCBI), Scopus
	(Elsevier)
Descriptors and Boolean	Metal* AND mobulid; Metal* AND Mobula; Metal*
operators	AND Manta
Language	English
Document types	All types of reports
Research areas	All research areas
Timespan	All years

claspers. The obtained biometric measurements are displayed in Table 3, and images of the specimen are exhibited in Fig. 3.

The observed disk length of 55.5 cm indicates a juvenile Giant Devil Ray, as sexually mature individuals reach up to 5.2 m in length (McEachran and Séret, 1990). The mouth to disk length ratio, calculated instead of disk width (non-available), was 25.23%. No comparison to disk length is, however, reported in the literature, only to disk width, reported as 11.9% (Notabartolo Di Scaria, 1987). Ray identification and size assessments through the investigation of fin to body ratios have only been successfully applied in cases of isolated fins and shown to be a valuable tool in this regard (Almeida Marques et al., 2020; Appleyard et al., 2018). Therefore, the mouth to disk length may be an interesting complementary ratio to account for missing pectoral fins in future studies and should be further investigated and routinely reported in studies on manta rays.

Concerning elemental concentrations in the captured *M. mobular* individual, cobalt (Co), cadmium (Cd), lead (Pb), nickel (Ni), mercury (Hg), palladium (Pd), platinum (Pt), selenium (Se) and tin (Sn) concentrations were below the LOQs of 0.02, 0.05, 0.07, 0.18, 0.09, 0.01, 0.05, 1.45 and 0.06 mg kg<sup>-1</sup> wet weight (w.w.). in all evaluated *M. mobular* organs. The concentrations for the other investigated elements are displayed in Table 4, expressed as mg kg<sup>-1</sup> (w.w.).

Only one sample of each tissue was analysed, precluding statistical analyses. Some points may be noted concerning elemental concentrations. Aluminium, for example, was higher in muscle compared to liver, brain and kidney, which may indicate low clearance rates and bioaccumulation of this element. Arsenic levels were higher in liver, followed by brain, kidney and muscle, with muscle content very near the maximum permissible limit of 1.00 mg  $\mathrm{kg}^{-1}$  w.w. recommended for human consumption by Brazilian authorities (ANVISA, 2013) and the Food Standards applied in Australia and New Zealand (FSANZ, 2017), and higher than the 0.5 mg kg<sup>-1</sup> limit established by the Ministry of Health of the People's Republic of China (MHPRC, 2012). Strontium was higher in brain, followed by muscle, kidney and liver, indicating a similar behaviour to aluminium and possible bioaccumulation. Chromium in muscle was also slightly above the maximum permissible limit recommended for human consumption by Brazilian authorities, of 0.1 mg kg<sup>-1</sup> w.w. (ANVISA, 2013). Of course, these are baseline data with only one sampled individual, and further studies are required to adequately assess human consumption risks. In addition, it was a very young animal, and metal and metalloid concentrations are known to

### Table 3

Biometric measurements for the *M. mobular* specimen captured by an artisanal gillnet fishery in the metropolitan area of the city of Rio de Janeiro, state of Rio de Janeiro, southeastern Brazil.

Measurement	Size (cm)
Right cephalic horn length	15.0
Left cephalic horn length	15.0
Distance between cephalic horns	21.0
Stinger length	3.0
Disk length	55.5
Mouth size	14.0

vary with ontogenetic stage, so this must also be taken into account.

Although it is known that rays have been, in general, much less studied than sharks, and especially so concerning metal and metalloid contamination (Escobar-Sánchez et al., 2014), we were extremely surprised to find that ecotoxicological assessments of mobulid rays are virtually missing, except for five records (Table 5), wherein only As, Cd, Pb, Hg, Pt, Pd and Rh have been assessed.

The first assessment evaluated As, Cd and Hg concentrations in kidney, liver, and muscle samples from six Giant Oceanic Manta rays M. birostris individuals captured off the coast of Ghana, using the neutron activation analysis method (Essumang, 2009). This species is routinely consumed in Ghana, and the increasing number of cancer cases noted in this country motivated the authors to investigate this mobulid ray regarding toxic and carcinogenic metal and metalloid contents. In general, the authors observed metal and metalloid contents in all three analysed tissues, with higher As and Cd concentrations in liver, kidney and muscle compared to Hg in the same tissues, which were, in turn, much lower than the values detected in the present study for As, while Cd and Hg values were below our method LOQ, indicating low contamination values for the latter two elements. Calculated hazard indices for the Ghanian specimens for children were less than 1 for Cd and Hg, but higher than 1 for As, indicating a carcinogenic hazard risk for children who consume M. birostris. The authors stressed that the sample size of their study was relatively low, and that M. birostris is migratory, and, thus, the specific pollution sources to Ghana cannot be directly related to the findings, although they do indicate that illegal gold-mining activities are widespread, probably releasing Hg to the environment. In addition, they also state that the use of antifoulant paint on the hulls of seafaring vessels is prevalent, which may account for the As and Cd contents detected in the M. birostris individuals.

The same *M. birostris* specimens evaluated in the first study (n = 6) were also analysed regarding their Pt, Pd and Rh concentrations (Essumang, 2010), determined by the neutron activation method. Relatively high mean levels of all three metals were reported by the authors in kidney, liver and muscle samples, higher in fact than the limits for the human dietary intakes stipulated by international legislation, indicating potential health risks to consumers. This was not observed in the present study, as the findings for the individuals assessed herein concerning platinum and palladium levels were lower in muscle, liver, brain and kidney than our method LOQ, of 0.01 and 0.05 mg kg<sup>-1</sup> (w.w.) (rhodium was not analysed).

The third report assessed As, Cd, Pb and Hg in the highly sought-out and marketed branchial plate, used in traditional Chinese medicine against chickenpox, and in the muscle tissue of 15 Spinetail Devil ray Mobula japonica individuals and in the muscle tissue of 12 Reef Manta rays Manta alfredi individuals caught off the coast of Sri Lanka by inductively coupled plasma mass spectrometry (ICP-MS) (Ooi et al., 2015). Significant differences were observed for the elemental levels between the two species from two different locations, and mean As in M. japonica muscle tissue, mean Cd in M. japonica muscle tissue and branchial plate, and Cd and Pb in some individual M. alfredi muscle samples were above maximum permissible limits concerning food safety, while Hg concentrations in all tissues were below those limits. All metal and metalloid levels for both Spinetail Devil ray Mobula japonica and Reef Manta rays Manta alfredi muscle tissue. Arsenic (the single element among the four reported elements in our study above the method LOQ in the Rio de Janeiro individual), was much lower compared to Spinetail Devil rays Mobula japonica from Sri Lanka, but within the range reported for Sri Lankan Reef Manta rays Manta alfredi, and higher than the means for that species. The authors also indicate that, although the calculated intake of inorganic As for a vulnerable age group consuming branchial plates was below the acute duration limits, and no acute duration limit is set concerning oral exposure to Cd, Pb or Hg, further assessments concerning human health risks from the consumption of mobulid branchial plates should be carried out.

The fourth assessment evaluated the Hg contents of the muscle and



Fig. 3. *M. mobular* specimen captured by an artisanal gillnet fishery in the metropolitan area of the city of Rio de Janeiro, in the state of Rio de Janeiro, southeastern Brazil. (A) Dorsal view, (B) dorsal colouring detail, (C) eye detail, (D) rostrum detail.

Elemental concentrations in the muscle, liver, brain and kidney of an *M. mobular* specimen captured by an artisanal gillnet fishery in the metropolitan area of the city of Rio de Janeiro, state of Rio de Janeiro, southeastern Brazil. Data are expressed as mg kg<sup>-1</sup> wet weight. Sample size is of one (1) for each tissue. The Limit of Quantification (LOQ) for each element is also presented.

Organ	Al	As	Cr	Cu	Fe	Mn	Sr	Ti	V	Zn
Muscle	0.83	0.86	0.21	0.46	<loq< td=""><td><loq< td=""><td>1.21</td><td>0.59</td><td>0.03</td><td>5.46</td></loq<></td></loq<>	<loq< td=""><td>1.21</td><td>0.59</td><td>0.03</td><td>5.46</td></loq<>	1.21	0.59	0.03	5.46
Liver	<loq< td=""><td>22.38</td><td><loq< td=""><td>3.59</td><td>172.7</td><td>0.28</td><td>0.66</td><td>0.45</td><td>0.02</td><td>8.60</td></loq<></td></loq<>	22.38	<loq< td=""><td>3.59</td><td>172.7</td><td>0.28</td><td>0.66</td><td>0.45</td><td>0.02</td><td>8.60</td></loq<>	3.59	172.7	0.28	0.66	0.45	0.02	8.60
Brain	<loq< td=""><td>2.23</td><td>0.24</td><td>1.19</td><td>37.5</td><td><loq< td=""><td>1.32</td><td>1.11</td><td>0.06</td><td>9.41</td></loq<></td></loq<>	2.23	0.24	1.19	37.5	<loq< td=""><td>1.32</td><td>1.11</td><td>0.06</td><td>9.41</td></loq<>	1.32	1.11	0.06	9.41
Kidney	<loq< td=""><td>1.78</td><td>0.45</td><td>1.47</td><td>26.8</td><td><loq< td=""><td>0.92</td><td>1.16</td><td>0.08</td><td>12.03</td></loq<></td></loq<>	1.78	0.45	1.47	26.8	<loq< td=""><td>0.92</td><td>1.16</td><td>0.08</td><td>12.03</td></loq<>	0.92	1.16	0.08	12.03
LOQ	0.76	0.20	0.18	0.20	4.41	0.19	0.03	0.35	0.01	0.91

Articles reporting metal and metalloid contents in mobulid rays in the scientific literature.

Record ID	Publication year	Journal	Title	Authors
1	2009	Human and Ecological Risk Assessment: An International Journal	Analysis and human health risk assessment of arsenic, cadmium, and mercury in <i>Manta birostris</i> (manta ray) caught along the Ghanaian coastline	Essumang
2	2010	Bulletin of Environmental Contamination and Toxicology	First determination of the levels of platinum group metals in <i>Manta</i> <i>birostris</i> (manta ray) caught along the Ghanaian coastline	Essumang
3	2015	Marine Pollution Bulletin	Levels of arsenic, cadmium, lead and mercury in the branchial plate and muscle tissue of mobulid rays	Ooi et al.
4	2014	Environmental Monitoring and Assessment	Mercury levels in myliobatid stingrays (Batoidea) from the Gulf of California: Tissue distribution and health risk assessment	Escobar- Sanchez et al.
5	2019	Environmental Research	Effect of body length, trophic position and habitat use on mercury concentrations of sharks from contrasted ecosystems in the southwestern Indian Ocean	Le Bourg et al.

liver by cold vapor atomic absorption spectrophotometry using an Hg analyser in batoids frequently caught in selected areas of the Gulf of California, which includes *Mobula japonica* (n = 3), the smoothtail mobula *M. thurstoni* (n = 8) and the Munk's Devil ray *Mobula munkiana* (n = 5) (Escobar-Sánchez et al., 2014). The authors also aimed to assess human health risks for the Mexican population. All mobulid rays contained Hg concentrations below international and Mexican limits concerning fish for human consumption in muscle and liver values were mostly higher than in muscle, as expected. Both muscle and liver values reported by those authors were higher than those reported herein for the Rio de Janeiro samples, lower than the method LOQ of 0.09 mg kg<sup>-1</sup> (w. w.).

The fifth report investigated the effects of body size, trophic position, and broad habitat characteristics (coastal, open ocean and bathyal) on Hg concentrations in elasmobranchs, including *Mobula japonica*, from the southwestern Indian Ocean, by applying stable isotope analyses. The authors reported that the evaluated bathyal sharks presented high Hg concentrations almost similar to those of oceanic species, despite their lower relative trophic position, but did not report the trophic position for the *Mobula japonica* specimens, only the detected Hg concentration, of 0.14 mg kg<sup>-1</sup> d.w., higher than the values reported herein even when taking into account wet to dry unit conversion.

Comparisons between the metal and metalloid levels determined in the obtained records and the present study are displayed in Table 6.

The four first assessments focused mostly on human health risks due to mobulid ray consumption, and not on potential deleterious effects on the species themselves. The fifth assessment only reported Hg concentrations and did not discuss the data any further for mobulid rays. No reports, for example, on subcellular metal and metalloid bioavailability assessments were found, which is paramount in assessing deleterious cellular effects, as total metal and metalloid contents may not accurately represent the bioavailable fraction of these contaminants (Hauser-Davis et al., 2020a). Evaluations concerning biochemical cellular effects, such as oxidative stress enzymatic (such as glutathione system enzymes) and non-enzymatic (reduced glutathione, metallothionein) biomarkers and endpoints (i.e., lipid peroxidation, reactive oxygen species production) are also of interest to detect mobulid health effects concerning metal and metalloid contamination.

In this regard, it is important to note that mobulid rays have long life expectancies, i.e., about 30 years for M. birostris, but extremely low population growth rates. For example, *M. birostris* produces only one pup on average every 4–5 years, which has been considered one of the lowest population growth rates among elasmobranchs. Currently, this species has been experienced a population decline of 50-79% over the past three generations (87 years), with further decreases predicted over the next three generations, from 2018 to 2105 (Marshall et al., 2020). Therefore, any contamination which may lead to reproductive impairments is noteworthy and important to assess in order to undertake conservation actions, since several metals and metalloids have been reported as accumulating to high degrees in elasmobranch gonads, which can lead to negative fish reproduction effects, including low sperm motility and decreased hormone secretions (Ebrahimi and Taherianfard, 2011; Popek et al., 2006). Furthermore, most mobulid rays exhibit the aplacental viviparity reproduction mode, where embryos initially feed on yolk, followed by additional nourishment from the mother by indirect absorption of uterine fluid enriched with mucus, fat or protein through specialised structures (Dulvy and Reynolds, 1997). Therefore, maternal-embryo transfer through maternal offloading is even more likely, reported for several species of both rays and sharks (Amorim-Lopes et al., 2020; Dutton and Venuti, 2019; Hauser-Davis et al., 2020b; Lyons and Adams, 2015; Walker et al., 2014), leading to further ecotoxicological concerns regarding metal and metalloid contamination through maternal transference.

Furthermore, mobulid rays usually occur in near-shore waters, along productive coastlines displaying upwelling phenomena (Marshall, 2009), due to high prey density thresholds requirements (Armstrong et al., 2016) and the fact that these types of areas usually display high productivity (NOOA, 2020). This, in turn, leads to further vulnerability concerning chemical contamination, as the majority of human activities are concentrated in coastal regions (EEA, 2020), leading to high chemical contaminant loads in these areas. This is the case of the area where the M. mobular specimen was caught, as Guanabara Bay comprises an intensely contaminated region due the input of vast amounts of untreated sewage from domestic and industrial sources, including many industries and shipyards (Fistarol et al., 2015), with many diffuse contamination sources, such as river contamination plumes, atmospheric deposition, landfill runoff, and a chlor-alkali plant on the northwestern side of the bay (Covelli et al., 2012), to which the captured mobulid individual could have been exposed to. However, despite these conditions, Guanabara Bay still remains of the most important and productive estuaries in Brazil (da Silva et al., 2016).

Furthermore, upwelling phenomena contribute significantly to heightened metal and metalloid bioavailability, due to the transport of deep waters rich in these elements to the euphotic region (Afandi et al., 2018), comprising another important variable concerning mobulid ray metal and metalloid contamination. This is also a potential source of contamination for our mobulid individual, as an annual low-intensity upwelling event is noted at Guanabara Bay during late spring and summer, between November and March, the same period the *M. mobular* specimen was caught (da Silva et al., 2016).

Comparisons between the metal and metalloid levels determined in the obtained records and the present study for Mobula specimens worldwide. All data are expressed as mg kg $^{-1}$  wet weight. Dashes indicated non-analysed elements. LOQ – limit of quantification. LOD – limit of detection.

Data	Species	Number of	Analytical technique	Tissue	Element						
source		individuals			As	Cd	Hg	Pb	Pt	Pd	Rh
Present	Mobula	1	Inductively coupled plasma	Liver	22.38	<loq< td=""><td><loq< td=""><td><loq< td=""><td><loq< td=""><td><loq< td=""><td>-</td></loq<></td></loq<></td></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""><td><loq< td=""><td><loq< td=""><td>-</td></loq<></td></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""><td><loq< td=""><td>-</td></loq<></td></loq<></td></loq<>	<loq< td=""><td><loq< td=""><td>-</td></loq<></td></loq<>	<loq< td=""><td>-</td></loq<>	-
study	mobular		mass spectrometry	Kidney	1.78						-
				Muscle	0.86						-
Record ID	Mobula	6	Neutron activation	Liver	$1.10~\pm$	0.016 $\pm$	$0.03\pm0.002$	-	-	-	-
1	birostris				0.69	0.03					
				Kidney	0.75 $\pm$	0.010 $\pm$	$0.0010~\pm$	-	-	-	-
					0.61	0.003	0.0005				
				Muscle	0.26 $\pm$	$0.006~\pm$	$0.003~\pm$	-	-	-	-
					0.17	0.003	0.002				
Record ID	Mobula	6	Neutron activation	Liver	-	-	-	-	0.246	1.17	0.04
2	birostris			Kidney	-	-	-	-	0.912	0.70	0.07
				Muscle	-	-	-	-	2.525	1.68	0.027
Record ID	Mobula	15	Inductively coupled plasma	Muscle	7.29 $\pm$	$0.06 \pm$	$0.04\pm0.04$	$0.07~\pm$	-	-	-
3	japonica		mass spectrometry		3.74	0.04		0.04			
	Manta alfredi	12		Muscle	$0.52 \pm$	$0.03 \pm$	$0.01 \pm 0.01$	0.43 $\pm$	-	-	-
					0.57	0.03		0.25			
Record ID	Mobula	3	Cold vapor atomic absorption	Liver	-	-	0.21 - 0.22	-	-	-	-
4	japonica		spectrophotometry	Muscle	-	-	<lod< td=""><td>-</td><td>-</td><td>-</td><td>-</td></lod<>	-	-	-	-
							(0.011)				
	Mobula	5		Liver	-	-	0.08 to 0.30	-	-	-	-
	munkiana			Muscle	-	-	0.03 to 0.28	-	-	-	-
	Mobula	8		Liver	-	-	<lod td="" to<=""><td>-</td><td>-</td><td>-</td><td>-</td></lod>	-	-	-	-
	thurstoni						0.21				
				Muscle	-	-	0.03 to 0.28	-	-	-	-
Record ID 5	Mobula japonica	1	Solid sample atomic absorption spectrometer	Muscle	-	-	0.14	-	-	-	-

Concerning conservation actions for mobulid rays, specifically inplace research and monitoring, unfortunately no Action Recovery Plan and no systematic monitoring scheme are yet in place for this species (Marshall et al., 2020). In addition, regarding in-place land/water protection, no conservation site has been identified and no area-based regional management plan has been tracked, although these species occur in at least one protected area (Marshall et al., 2020). Therefore, little or no efforts to monitor or regulate mobulid fisheries are in place. Ecotoxicological assessments display the potential to aid in conservation actions by acting as predictors of detrimental environmental effects, such as reproductive success alterations and generational contaminant loads (Ankley et al., 2010; Hauser-Davis et al., 2020b), and should, therefore, be taken into consideration in these types of evaluations. In sum, the baseline metal and metalloid data reported herein may be applied to future biomonitoring efforts and conservation measures, comprising a valuable tool to further knowledge on environmental metal and metalloid contamination in endangered mobulid rays.

# CRediT authorship contribution statement

Rachel Ann Hauser-Davis: Supervision, Conceptualization, Resources, Data curation, Writing – original draft, Writing – review & editing. Catarina Amorim-Lopes: Investigation, Formal analysis. Nathan Lagares Franco Araujo: Investigation, Formal analysis. Manasi Rebouças: Resources, Investigation. Ricardo Andrade Gomes: Investigation, Formal analysis. Rafael Christian Chávez Rocha: Formal analysis, Data curation. Tatiana Dillenburg Saint'Pierre: Supervision, Resources, Data curation, Writing – original draft, Writing – review & editing. Luciano Neves dos Santos: Supervision, Conceptualization, Resources, Data curation, Writing – original draft, Writing – review & editing.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

The authors would like to thank Sérgio C. Moreira for kindly preparing the map used in this report. Special thanks are due to all fishers from the Z-13 Copacabana colony for kindly donating the *M. mobular* individual for scientific evaluations. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior -Brasil (CAPES) - Finance Code 001. CAL acknowledges CAPES for financial support in the form of a graduate scholarship. TDSP acknowledges FAPERJ and CNPq for the conceded research grants. RAHD acknowledges FAPERJ for financial support - research grant process number E-26/010/002505/2019.

# References

- Afandi, I., Talba, S., Benhra, A., Benbrahim, S., Chfiri, R., Labonne, M., Masski, H., Lae, R., Morais, L.T., Bekkali, M., Buthir, F.Z., 2018. Trace metal distribution in pelagic fish species from the north-west African coast (Morocco). Int. Aquat. Res. 10, 191–205.
- Almeida Marques, R., Guimarães Julio, T., Sole-Cava, A.M., Vianna, M., 2020. A new strategy proposal to monitor ray fins landings in south-east Brazil. Aquat. Conserv. Mar. Freshwat. Ecosyst. 1–18 https://doi.org/10.1002/aqc.3203.
- Amorim-Lopes, C., Willmer, I.Q., Araujo, N.L.F., de S. Pereira, L.H.S., Monteiro, F., Rocha, R.C.C., Saint' Pierre, T.D., dos Santos, L.N., Siciliano, S., Vianna, M., Hauser-Davis, R.A., 2020. Mercury screening in highly consumed sharpnose sharks (*Rhizoprionodon lalandii* and *R. porosus*) caught artisanally in southeastern Brazil. Elem. Sci. Anthr. 8, 022. https://doi.org/10.1525/elementa.022.
- Ankley, G.T., Bennett, R.S., Erickson, R.J., Hoff, D.J., Hornung, M.W., Johnson, R.D., Mount, D.R., Nichols, J.W., Russom, C.L., Schmieder, P.K., Serrrano, J.A., Tietge, J. E., Villeneuve, D.L., 2010. Adverse outcome pathways: a conceptual framework to support ecotoxicology research and risk assessment. Environ. Toxicol. Chem. 29, 730–741. https://doi.org/10.1002/etc.34.
- ANVISA, 2013. Resolução RDC Nº 42, de 29 de agosto de 2013. In: Diário Of. da União, pp. 33–35.
- Appleyard, S.A., White, W.T., Vieira, S., Sabub, B., 2018. Artisanal shark fishing in Milne Bay Province, Papua New Guinea: biomass estimation from genetically identified shark and ray fins. Sci. Rep. 8, 6693. https://doi.org/10.1038/s41598-018-25101-8.
- Armstrong, A.O., Armstrong, A.J., Jaine, F.R.A., Couturier, L.I.E., Fiora, K., Uribe-Palomino, J., Weeks, S.J., Townsend, K.A., Bennett, M.B., Richardson, A.J., 2016. Prey density threshold and tidal influence on reef manta ray foraging at an aggregation site on the Great Barrier Reef. PLoS One 11, e0153393. https://doi.org/ 10.1371/journal.pone.0153393.

#### R.A. Hauser-Davis et al.

Bezerra, M.F., Lacerda, L.D., Lai, C.-T., 2019. Trace metals and persistent organic pollutants contamination in batoids (Chondrichthyes: Batoidea): a systematic review. Environ. Pollut. 248, 684.

Covelli, S., Protopsalti, I., Acquavita, A., Sperle, M., Bonardi, M., Emili, A., 2012. Spatial variation, speciation and sedimentary records of mercury in the Guanabara Bay (Rio de Janeiro, Brazil). Cont. Shelf Res. 35, 29–42. https://doi.org/10.1016/j. csr.2011.12.003.

- da Silva, D.R., Paranhos, R., Vianna, M., 2016. Spatial patterns of distribution and the influence of seasonal and abiotic factors on demersal ichthyofauna in an estuarine tropical bay. J. Fish Biol. 89, 821–846. https://doi.org/10.1111/jfb.13033.
- Dulvy, N.K., Reynolds, J.D., 1997. Evolutionary transitions among egg-laying, livebearing and maternal inputs in sharks and rays. Proc. R. Soc. B Biol. Sci. 264, 1309–1315. https://doi.org/10.1098/rspb.1997.0181.

Dutton, J., Venuti, V.M., 2019. Comparison of maternal and embryonic trace element concentrations in common thresher shark (*Alopias vulpinus*) muscle tissue. Bull. Environ. Contam. Toxicol. 103 https://doi.org/10.1007/s00128-019-02667-1.

Ebrahimi, M., Taherianfard, M., 2011. The effects of heavy metals exposure on reproductive systems of cyprinid fish from Kor River. Iran. J. Fish. Sci. 10, 13–24.EEA, 2020. Coastal zone threats and management. URL. https://www.eea.europa.eu/

publications/92-826-5409-5/page035new.html (WWW Document). Eschmeyer, W.N., van der Laan, R., Fricke, R., 2020. Eschmeyer's Catalog of Fishes

Eschmeyer, W.N., van der Laan, K., Fricke, K., 2020. Eschmeyer's Catalog of Fisnes [WWW Document]. Calif. Acad, Sci.

- Escobar-Sánchez, O., Ruelas-Inzunza, J., Patrón-Gómez, J.C., Corro-Espinosa, D., 2014. Mercury levels in myliobatid stingrays (Batoidea) from the Gulf of California: tissue distribution and health risk assessment. Environ. Monit. Assess. 186, 1931–1937. https://doi.org/10.1007/s10661-013-3506-7.
- Essumang, D.K., 2009. Analysis and human health risk assessment of arsenic, cadmium, and mercury in *Manta birostris* (manta ray) caught along the Ghanaian coastline. Hum. Ecol. Risk. Assess. 15, 985–998. https://doi.org/10.1080/ 10807030903153451.

Essumang, D.K., 2010. First determination of the levels of platinum group metals in Manta birostris (Manta Ray) caught along the ghanaian coastline. Bull. Environ. Contam. Toxicol. 84, 720–725. https://doi.org/10.1007/s00128-010-0019-8.

Eurachem, 1998. The Fitness for Purpose of Analytical Methods, Eurachem Guide. ISBN: 0-94948926-12-0. https://doi.org/978-91-87461-59-0.

Fistarol, G.O., Coutinho, F.H., Moreira, A.P.B., Venas, T., Cánovas, A., de Paula, S.E.M., Coutinho, R., de Moura, R.L., Valentin, J.L., Tenenbaum, D.R., Paranhos, R., do Valle, R. de A.B., Vicente, A.C.P., Amado Filho, G.M., Pereira, R.C., Kruger, R., Rezende, C.E., Thompson, C.C., Salomon, P.S., Thompson, F.L., 2015. Environmental and sanitary conditions of Guanabara Bay, Rio de Janeiro. Front. Microbiol. https:// doi.org/10.3389/fmicb.2015.01232.

Froese, R., Pauly, D., 2021. FishBase. URL. www.fishbase.org (WWW Document).

FSANZ, 2017. Australia New Zealand Food Standards Code – schedule 19 – maximum levels of contaminants and natural toxicants. URL. https://www.legislation.gov.au/ Details/F2017C00333. (Accessed 21 February 2021).

Gomes, U.L., Santos, R.S., Gadid, B.F., Signori, C.N., Vicente, M.M., 2019. Guia para identificação dos Tubarões, Raias e Quimeras do Rio de Janeiro. Rev. Nord. Biol. 27, 268. https://doi.org/10.22478/ufpb.2236-1480.2019v27n1.47122.

Hauser-Davis, R.A., Figueiredo, L., Lemos, L., Moura, J.F., Rocha, R.C.C., Saint'Pierre, T., Z., R.L., Salvatore, S., 2020a. Subcellular cadmium, lead and mercury compartmentalization in Guiana dolphins (*Sotalia guianensis*) from southeastern Brazil, Front. Mar. Sci. 7, 584195.

- Hauser-Davis, R.A., Pereira, C.F., Pinto, F., Torres, J.P.M., Malm, O., Vianna, M., 2020b. Mercury contamination in the recently described Brazilian white-tail dogfish Squalus albicaudus (Squalidae, Chondrichthyes). Chemosphere 250, 126228. https://doi.org/ 10.1016/j.chemosphere.2020.126228.
- Horvat, M., Degenek, N., Lipej, L., Tratnik, J.S., Faganeli, J., 2013. Trophic transfer and accumulation of mercury in ray species in coastal waters affected by historic mercury mining (Gulf of Trieste, northern Adriatic Sea). Environ. Sci. Pollut. Res. 21, 4163–4176.

Inmetro, 2016. Orientação sobre validação de métodos analíticos: documento de caráter orientativo. DOQ-CGCRE-008.

Ishak, I., Rosli, F.D., Mohamed, J., Mohd Ismail, M.F., 2015. Comparison of digestion methods for the determination of trace elements and heavy metals in human hair and nails. Malays. J. Med. Sci. 22, 11–20.

IUCN, 2020. The IUCN Red List of Threatened Species. Version 2019-2.

- Luiz, O.J., Balboni, A.P., Kodja, G., Andrade, M., Marum, H., 2009. Seasonal occurrences of *Manta birostris* (Chondrichthyes: Mobulidae) in southeastern Brazil. Ichthyol. Res. 56, 96–99. https://doi.org/10.1007/s10228-008-0060-3.
- Lyons, K., Adams, D.H., 2015. Maternal offloading of organochlorine contaminants in the yolk-sac placental scalloped hammerhead shark (*Sphyrna lewini*). Ecotoxicology 24, 553–562. https://doi.org/10.1007/s10646-014-1403-7.

Marshall, A.D., 2009. Redescription of the genus Manta with resurrection of Manta alfredi. Zootaxa 2301, 1–28.

Marshall, A., Barreto, R., Carlson, J., Fernando, D., Fordham, S., Francis, M.P., Derrick, D., Herman, K., Jabado, R.W., Liu, K.M., Rigby, C.L., Romanov, E., 2020. Mobula birostris. In: The IUCN Red List of Threatened Species 2020: e. T198921A68632946. https://doi.org/10.2305/IUCN.UK.2020-3.RLTS. T198921A68632946.en (WWW Document).

McEachran, J.D., Séret, B., 1990. Mobulidae, in: Quero, J.C., Hureau, J.C., Karrer, C., Post, A., Saldanha, L. (Eds.), Check-list of the Fishes of the Eastern Tropical Atlantic. JNICT, Lisbon; SEI, Paris; and UNESCO, Paris. pp. 73–76.

Menezes, N.A., 2011. Checklist dos peixes marinhos do Estado de São Paulo. Brasil. Biota Neotrop. 11, 33–46. https://doi.org/10.1590/s1676-06032011000500003.

- MHPRC, 2012. National Food Safety Standard: Maximum Levels of Contaminants in Food. GB 2762-2012.
- Navia, A.F., Mejía-Falla, P.A., Hleap, J.S., 2016. Zoogeography of elasmobranchs in the Colombian Pacific Ocean and Caribbean Sea. Neotrop. Ichthyol. 14, e140134 https://doi.org/10.1590/1982-0224-20140134.
- NOOA, 2020. What is upwelling? URL. https://oceanservice.noaa.gov/facts/upwelling. html (WWW Document).
- Notabartolo Di Scaria, G., 1987. A revisionary study of the genus Mobula Rafinesque, 1810 (Chondrichthyes: Mobulidae) with the description of a new species. Zool. J. Linnean Soc. 91, 1–91. https://doi.org/10.1111/j.1096-3642.1987.tb01723.x.
- Ooi, M.S.M., Townsend, K.A., Bennett, M.B., Richardson, A.J., Fernando, D., Villa, C.A., Gaus, C., 2015. Levels of arsenic, cadmium, lead and mercury in the branchial plate and muscle tissue of mobulid rays. Mar. Pollut. Bull. 94, 251–259. https://doi.org/ 10.1016/j.marpolbul.2015.02.005.
- Pacoureau, N., Rigby, C.L., Kyne, P.M., Sherley, R.B., Henning, W., Carlson, J.K., Fordham, S.V., Barreto, R., Fernando, D., Francis, M.P., Jabado, R.W., Herman, K.B., Liu, K.-M., Marshall, A.D., Riley, H.K.K., Dulvy, N.K., 2021. Half a century of global decline in oceanic sharks and rays. Nature 589, 567–571.

Peterson, E.K., Buchwalter, D.B., Kerby, J.L., Lefauve, M.K., Varian-Ramos, C.W., Swaddle, J.P., 2017. Integrative behavioral ecotoxicology: bringing together fields to establish new insight to behavioral ecology, toxicology, and conservation. Curr. Zool. 63. 185–194. https://doi.org/10.1093/cz/zox010.

Popek, W., Dietrich, G., Glogowski, J., Demska-Zakeś, K., Drag-Kozak, E., Sionkowski, J., Łuszczek-Trojan, E., Epler, P., Demianowicz, W., Sarosiek, B., Kowalski, R., Jankun, M., Zakeś, Z., Król, J., Czerniak, S., Szczepkowski, M., 2006. Influence of heavy metals and 4-nonylphenol on reproductive function in fish. Reprod. Biol. 6, 175–188.

- Santos, L.N., Franco, A.C.S., de Souza, J.S., et al., 2021. Using richness of native and nonnative aquatic species along a climatic gradient to test the intermediate disturbance hypothesis. Hydrobiologia 848, 2055–2075. https://doi.org/10.1007/s10750-021-04525-w
- Simpfendorfer, C.A., Dulvy, N.K., 2017. Bright spots of sustainable shark fishing. Curr. Biol. 27, R97–R98.
- USP, 2013. <233> elemental impurities procedures, 38–NF 33 second supplement. URL. https://www.usp.org/sites/default/files/usp/document/our-work/chemicalmedicines/key-issues/c233.pdf. (Accessed 21 February 2021) (WWW Document).
- Walker, C.J., Gelsleichter, J., Adams, D.H., Manire, C.A., 2014. Evaluation of the use of metallothionein as a biomarker for detecting physiological responses to mercury exposure in the bonnethead, *Sphyrna tiburo*. Fish Physiol. Biochem. https://doi.org/ 10.1007/s10695-014-9930-y.
- Whitehead, P.J.P., Bauchot, M.-L., Hureau, J.-C., Nielsen, J., Tortonese, E., 1984. In: McEachran, J.D., Capapé, C. (Eds.), Fishes of the North-Eastern Atlantic and the Mediterranean, vol. 1. UNESCO, Paris, pp. 210–211.
- Zuluaga Rodríguez, J., Gallego Ríos, S.E., Ramírez Botero, C.M., 2015. Content of Hg, Cd, Pb and as in fish species: a review. Rev. Vitae 22, 148–159. https://doi.org/ 10.17533/udea.vitae.v22n2a09.