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Metal(loid) contamination in tiger sharks (*Galeocerdo cuvier*) from a remote oceanic island in the Equatorial Atlantic Ocean and potential impacts on physiological parameters

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HIGHLIGHTS

- Metal(oid)s were detected in the blood of tiger sharks from Fernando de Noronha.
- Blood concentrations of Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn were positively correlated with each other.
- Blood As concentration was positively correlated with plasma triglyceride levels.
- Increasing anthropogenic activity may be affecting shark health condition.

GRAPHICAL ABSTRACT

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ABSTRACT

We investigated the relationship between blood metal(loid) concentrations and plasma levels of glucose, proteins, triglycerides, cholesterol, lactate, urea, and polyunsaturated fatty acids in tiger sharks (*Galeocerdo cuvier*) sampled off the Fernando de Noronha Archipelago, a remote oceanic marine protected area in the Equatorial Atlantic Ocean. Results revealed that Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn were detected in the whole blood of tiger sharks and no sexual differences in blood metal(loid) concentrations were observed. Females had higher concentrations of plasma proteins and docosahexaenoic acid. In females, all analyzed elements were

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positively correlated with each other, except As. Only As was positively correlated with triglycerides, suggesting a potential impact of As exposure on the nutritional condition of this species. The results presented herein reinforce that sharks, even from remote sites, are exposed to metal(loid)s and that such exposure might elicit physiological responses.

1. Introduction

In virtually all marine environments, the increasing concentrations of metals and metalloids, hereafter metal(loid)s, have become a major concern due to their potential biological effects (Islam and Tanaka, 2004; Martinez et al., 2022). Although some of these elements are considered essential to aquatic organisms, others can be toxic, even at low concentrations (Wood et al., 2011). Essential metals such as Cr, Cu, Fe, Mn, and Zn are involved in physiological functions, including metabolism, cellular processes in the central nervous system, and enzymatic activity (Jomova et al., 2022). In contrast, toxic, and potentially toxic, elements such as Al, As, Cd, Pb, Hg, and Ni have been associated with several disturbances in marine animals, such as reproductive (Crump and Trudeau, 2009; Kar et al., 2021) and behavioral (Henry and Atchinson, 2020) impairments, as well as reactive oxygen species generation (Valko et al., 2005; Sevcikova et al., 2011; Lushchak, 2016).

The Fernando de Noronha Archipelago is an isolated group of volcanic islands located 345 km off north-eastern Brazil (03°51′S, 32°25′W). This region is under the influence of the South Equatorial Current and experiences a warm tropical oceanic climate, with marked rainy (March–July) and dry (August–February) seasons (Barcellos et al., 2011). The seawater temperature is relatively steady year-round, averaging 26 °C. Part of the archipelago consists of a sustainable use area, known as the "Fernando de Noronha - Rocas - São Pedro and São Paulo Environmental Protected Area", where fishing is partially allowed. Other areas constitute a no-take marine protected area, which preserves nearshore ecosystems up to the 50 m isobath. Recent studies suggest the occurrence of anthropogenic impacts in the archipelago, such as the discharge of solid wastes and untreated sewage, associated with growing urbanization and tourism activity (Araújo et al., 2017; Braga et al., 2018; Grillo and Mello, 2021). These impacts were particularly observed in marine fauna (Prazeres et al., 2012; Prioste et al., 2015), including sharks (Araújo et al., 2023, 2024).

Sharks often accumulate substantial concentrations of metal(loid)s in their tissues due to their long lifespan and high position in the food web (Gelsleichter and Walker, 2010). This seems to be particularly true for epipelagic, oceanic species, in which Hg concentration can be 2- to 3-fold higher than those observed in coastal sharks of similar trophic positions (Le Bourg et al., 2019; Gelsleichter et al., 2020). Due to their susceptibility to accumulate metal(loid)s, these organisms have been considered reliable bioindicators of marine pollution (Alves et al., 2022).

Despite the increasing interest and, consequently, publications on metal(loid) concentrations in sharks in the last decades, changes in body and/or health conditions associated with exposure to these contaminants have been less frequently investigated (Tiktak et al., 2020; Wosnick et al., 2021). Several parameters have been proposed for assessing elasmobranch health as a consequence of environmental contamination. However, those are mostly analyzed in liver and muscle samples (Alves et al., 2022), which usually require lethal sampling. Measurements of these metal(loid)s in blood and its subcomponents (*i.e.*, red blood cells and blood plasma) represent a valuable nonlethal biological matrix (Hammerschlag and Sulikowski, 2011) for assessing short-term exposure to metal(oid)s (Merly et al., 2019; Gelsleichter et al., 2020). Although the concentrations of these elements in the blood are low, they have been reported to be positively correlated with levels in other tissues, such as liver and muscle (van Hees and Ebert, 2017; Gelsleichter et al., 2020). Additionally, plasma samples can also provide insightful information on reproductive physiology (Awruch et al., 2008), energetic status (Moorhead et al., 2020), nutritional quality (Rangel et al., 2021), stress status (Marshall et al., 2012), and other biological aspects, which can be related to contaminant exposure.

In the context described above, the present study aimed to quantify whole blood concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn and investigate the potential impact of these elements on plasma health parameters in tiger sharks (*Galeocerdo cuvier*) sampled from the Fernando de Noronha Archipelago. As these parameters might be influenced by metal(loid) concentrations, we hypothesize that the elements analyzed herein would elicit physiological responses in tiger sharks, translated to low energy state and nutritional quality, and alterations in lactate and urea levels. Specifically, the objectives of this study were: (1) to quantify metal(loids) in the whole blood of tiger sharks; (2) to explore the relationships between metal(loid)s aiming to detect any potential exposure patterns; and (3) to evaluate the potential relationships between energy state and nutritional quality (glucose, proteins, triglycerides, cholesterol, polyunsaturated fatty acids), metabolism (lactate), and osmoregulation (urea) plasmatic parameters in tiger sharks.

2. Materials and methods

2.1. Shark sampling

In January 2022, ten tiger sharks (seven females and three males) were actively captured off the Fernando de Noronha Archipelago. Shark capture was performed using drumlines ranging from 40 to 60 m deep and consisted of a mooring with two attachment points, as described by Rangel et al. (2023). All sharks were sexed and measured for total length (TL). Blood was collected via caudal vein puncturing using a 10-mL heparinized syringe with an 18-gauge needle. Blood samples were immediately stored on ice on the boat and blood plasma aliquots were obtained through centrifugation at 3000 rpm for 15 min. Whole blood and blood plasma samples were kept at −20 °C until analysis.

After blood sampling, sharks were opportunistically tagged with conventional tags (Hallprint, www.hallprint.com) for individual identification in case of recapture and then released. Two female tiger sharks (shark #497: TL = 210 cm; shark #519: TL = 260 cm) were tagged on January 18, 2022 with Smart Position and Temperature Transmitting tags (SPOT, Wildlife Computers) to monitor their spatial movement patterns. Prior to deployment, SPOT tags were tested and confirmed for location accuracy at land-based facilities. These tags were coated with antifouling materials (IPM-AST4 from Interphase Materials) to minimize biofouling (Hammerschlag et al., 2022) and fixed to the shark's first dorsal fin.

All procedures were previously approved by the Brazilian Ministry of Environment (ICMBio #80761) and the Committee on Ethics for the Use of Animals of the Instituto de Biociências of the Universidade de São Paulo (CEUA #362/2020).

2.2. Metal(loid) concentrations determination

A suite of 11 metal(loid)s (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) were measured in whole blood samples of female and male tiger sharks. The essential metals Cr, Cu, Fe, Mn and Zn were selected based on their key roles in fish physiology, but also due to their potential toxicity at high concentrations (Wood et al., 2011). Toxic (As, Cd, Hg, and Pb) and potentially toxic (Al and Ni) elements were analyzed due to their potential toxicity to marine fish. In this context, we aimed to screen potential elements inducing physiological alterations and report a set of essential elements as a baseline for further studies.

Subsamples of 0.5–1.5 mL were lyophilized and then completely digested with 500 μL of 65% ultrapure (SupraPur®) nitric acid (HNO_3) (Merck, Darmstadt, Germany) for 24 h at 60 °C. The final volume of each digested sample was adjusted to 1 mL by adding high ultrapure (resistivity of 18.2 MΩ cm) water (MasterSystem MS-2000, Gehaka, São Paulo, SP, Brazil). Samples were then appropriately diluted (10 times for Hg and 5 times for the other elements) prior to analysis. Determination of metal(loid)s was performed using inductive coupled plasma mass spectrometry (ICP-MS, PlasmaQuant MS Q, Analytik Jena, Jena, Germany). ICP-MS parameters were adjusted as follows: radio frequency (RF) power: 1300 W; plasma (argon) flow: 15 L min^{-1}; auxiliary flow: 1.2 L min^{-1}; argon flow in the nebulizer: 0.42 L min^{-1}; replicate readings: 5; dwell time: 50 ms; and detector operation mode: dual mode. Yttrium-*89* ($^{89}Y^+$) was used as an internal standard. The following isotopes and respective gases were employed for metal(loid) quantification: ^{27}Al[He], ^{75}As[H_2], ^{114}Cd [H_2], ^{52}Cr[He], ^{65}Cu[He], ^{57}Fe[He], ^{202}Hg[H_2], ^{55}Mn[He], ^{60}Ni [He], ^{206,207,208}Pb[He], and ^{66}Zn [He]. Concentrations were determined based on calibration curves built for each element analyzed, using a serial dilution of a multielement standard (1000 mg L^{-1}) solution (Merck, Darmstadt, Germany). Coefficients of determination (R^2) of the calibration curves were 0.999556 (Al), 0.999989 (As), 0.999605 (Cd), 0.999940 (Cr), 0.999971 (Cu), 0.999870 (Fe), 0.999996 (Hg), 0.999964 (Mn), 0.999986 (Ni), 0.999984 (Pb) and 0.999967 (Zn).

Quality assurance and control comprised the regular analysis of blanks and spiked matrices, as well as of a certified reference material (CRM) for fish protein (DORM-5) from the National Research Council Canada (Ottawa, Canada). Mean recovery rates for metal(loid)s analyzed in the CRM corresponded to 92% (Al), 81% (As), 84% (Cd), 89% (Cr), 87% (Cu), 88% (Fe), 82% (Hg), 84% (Mn), 90% (Ni), 83% (Pb), and 90% (Zn). It is worth mentioning that, for most residue analytical method guidelines, an acceptable recovery range is 70%–120% (1–3) with means from 70% to 120% or 70%–110%, depending on the regulatory guideline (Schoenau, 2019). The limit of detection (LOD) was calculated as three times the standard deviation (SD) value of the blank signals (3 × SD; n = 10). The LOD corresponded to 0.26, 0.035, 0.0014, 0.033, 0.057, 0.76, 0.0017, 0.12, 0.018, 0.19 and 0.21 μg L^{-1} for Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn, respectively. The limit of quantification (LOQ) was ten times the SD value of the blank signals (10 × SD; n = 10). The LOQ was 0.85, 0.12, 0.0047, 0.11, 0.19, 2.5, 0.0057, 0.40, 0.060, 0.64 and 0.71 μg L^{-1} for Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn, respectively. Results are expressed as μg L^{-1}.

2.3. Biochemical parameters analyses

Metabolic parameters of the energetic state in tiger sharks were assessed through the quantification of concentrations of glucose, total proteins, total triglycerides, and total cholesterol (Ballantyne, 1997; Gallagher et al., 2014a, 2014b, 2017). Other parameters, such as lactate and urea, were also analyzed in plasma samples as metabolites of acid–base balance and osmoregulation (Hammerschlag, 2006; Skomal and Bernal, 2010). The above-mentioned blood plasma biochemical parameters were measured using commercial reagent kits based on colorimetric methods and following the manufacturer's instructions (Labtest®, Lagoa Santa, MG, Brazil). Readings were performed using an ELISA spectrophotometer (Spectra Max 250, Molecular Devices, San Jose, CA, USA). Results were expressed as mg dL^{-1} (glucose, triglycerides, cholesterol, lactate), g dL^{-1} (total proteins), or mM (urea). The ratio between triglycerides and cholesterol (triglycerides/cholesterol) was also considered because it has been described as an indicator of body condition in sharks (Gallagher et al., 2014a, 2017; Rangel et al., 2021).

The blood plasma profile of essential polyunsaturated fatty acids (PUFAs) was measured to assess the nutritional status of *G. cuvier*. PUFAs were analyzed using direct transmethylation, as described by Parrish et al. (2015). Briefly, blood plasma samples were homogenized and directly transmethylated in 3 mL of a methanol: dichloromethane: concentrated hydrochloric acid (10:1:1 v/v) solution for 2 h at 80–85 °C. After cooling, 1.5 mL of Milli-Q® water and 1.8 mL of a hexane: dichloromethane (4:1 v:v) solution was added to the test tubes, which were then vortexed and centrifuged at 2000 rpm for 5 min. The supernatant was then collected and transferred to a 2 mL injection vial, and the volume was reduced under a nitrogen stream. Fatty acid analysis was carried out in a Varian gas chromatograph (GC, Model 3900, Palo Alto, CA, USA) coupled with a flame ionization detector and a CP-8410 autosampler, as described by Rangel (2018). Essential PUFAs [AA (C20:4n6), EPA (C20:5n3), and DHA (C22:6n3)] were used as markers of nutritional quality due to their physiological importance (Tocher, 2010). Results are expressed as % of total fatty acid methyl-esters based on peak area analysis.

2.4. Shark tracking

Regarding tracking of female shark displacement, the raw tag locations were first filtered using a correlated random walk model applying 3 m s^{-1} speed filters with the "*aniMotum*" R package (Jonsen et al., 2023) to obtain the most likely daily locations for each shark tracked (i.e., filtered tracks). Kernel utilization distribution (KUD) heatmaps were then calculated for each shark using the filtered tracks. Calculation was performed using the "*adehabitatHR*" R package (Calenge, 2006). Distances traveled by each shark were calculated using the geosphere R package (Hijmans, 2022).

2.5. Statistical analyses

Normality and homoscedasticity assumptions were tested, and data were log-transformed when necessary. A significance level of 0.05 was adopted for all statistical analyses. The correlation between individual body size (TL) and metal(loid) concentrations, as well as plasma health parameters, were investigated using Spearman's correlation test (Zar, 2010). A principal component analysis (PCA) was applied to characterize the metal(loid) concentrations and plasma health parameters of females and males and, especially, to search for patterns regarding any of these parameters. For that, data were standardized and the PCA plots represented the covariance matrix, where distances between objects reflect Euclidian distances. Sexual differences regarding whole blood metal(loid) levels and plasmatic biochemical measures were also tested. These analyses were made using the Student's *t*-test or the non-parametric Mann–Whitney's Test, according to the data normality and homoscedasticity. As sex might be a confounding factor influencing the accumulation and potential impacts of contaminants, only females were selected for further analysis.

Spearman's correlation test was applied to assess the correlations between metal(loid) concentration in whole blood samples of females only (Zar, 2010). The goal of this analysis was to investigate the sources and patterns of exposure. Relationships among female whole blood concentrations—as independent variables—and plasma health parameters—as dependent variables—were fitted using generalized linear models (GLMs) considering a gamma distribution to assess the potential influence metal(loids) on organisms' health (Zuur et al., 2009).

To test the hypothesis that essential [(arachidonic acid (AA), eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA)] PUFA profiles would be influenced by metal(loid) exposure, a permutation multivariate analysis of variance (PERMANOVA) was applied. Therefore, 119 permutations were carried out on a Bray–Curtis dissimilarity matrix, considering the matrix of blood plasma PUFA concentrations as the dependent variable and the metal(loid) concentration as the exploratory variables (Legendre and Legendre, 1998). All analyses were performed using R Studio (Posit, PBC), employing the package "*lmer*" for the GLM fitting and the packages "*vegan*" and "*ggvegan*" for the multivariate approaches.

3. Results

Shark TL ranged from 140 to 260 cm in females and 220–273 cm in males. This metric was not correlated to any analyzed parameter. Therefore, this variable was not further included in the fitted models described in the present study.

The characterization of female and male sharks according to blood metal(loid) levels and plasma biochemical parameters was explored using a PCA (Fig. 1). The two principal components explained 66% of the data variability in PC 1 (51%) and PC 2 (16%). Most metal(loid)s were associated with the first axis (PC 1), whereas biochemical parameters were mostly associated with the second axis (PC 2). Despite the low sample size and consequent variability, a few patterns could be explored in this analysis. Female and male sharks did not cluster as a function of sex. For example, the male shark #521 was characterized by high concentrations of several metal(loid)s, while the other male sharks (#476 and #484) showed lower concentrations of these elements. Regarding female sharks, a potential cluster, represented by sub-adults (TL = 140–210 cm) was identified, in which the largest specimen (#519) was characterized by whole blood concentrations of metal(loid)s, remarkably Cu and Zn.

Descriptive statistics of metal(loid) concentrations measured in the whole blood of female and male individuals sampled around the Fernando de Noronha Archipelago are presented in Table 1. All metal(loid)s analyzed in the present study (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) were detected in all whole blood samples of female and male tiger sharks (Table 1). As, followed by Al, presented the highest concentrations among non-essential elements. Mean concentrations of As corresponded to 37 and 81 μg L^{-1} in females and males, respectively. Regarding Al, they were 51 and 70 μg L^{-1}, respectively. Among essential metals, the highest levels were observed for Fe (651–1040 μg L^{-1} for females and males, respectively), followed by Zn (100–1400 μg L^{-1} for females and males, respectively). Despite the apparent higher concentrations in males, significant sexual differences were not observed for any element analyzed. In turn, blood plasma concentrations of total proteins and docosahexaenoic acid (DHA) were significantly higher in females than in male tiger sharks (Table 2).

Results from Spearman's rank correlation analysis performed for female tiger sharks indicated that all metal(loid)s evaluated, except As, strongly and positively correlated to each other (Fig. 2). GLMs fitted to assess the effect of metal(loids) on plasmatic parameters in female sharks only indicated a significant and positive relationship between As and triglycerides ($p = 0.019$; Table S1). Contrarily, the PERMANOVA

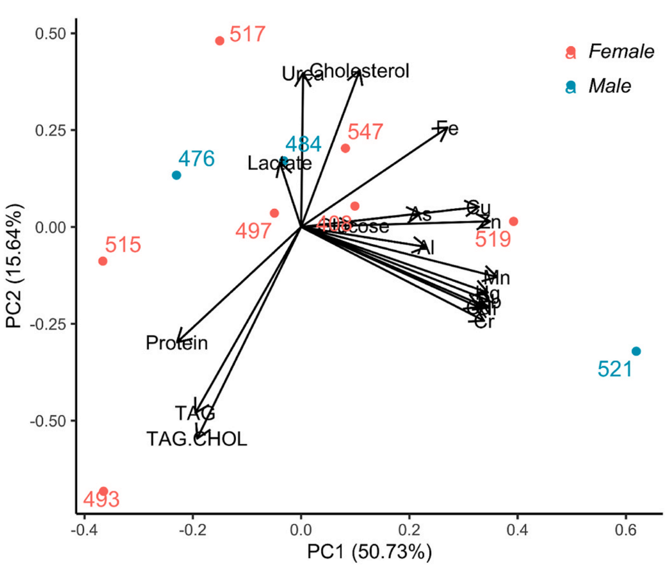

Fig. 1. Principal Component Analysis (PCA) carried out for whole blood concentrations of metal(loid)s and blood plasma concentrations of biochemical parameters in male (blue circles) and female (coral circles) tiger sharks (*Galeocerdo cuvier*) sampled around the Fernando de Noronha Archipelago (Northeastern Brazil). TAG: total triglycerides; CHOL: total cholesterol; TAG.CHOL: TAG/CHOL ratio.

Table 1
Descriptive statistics of whole blood concentrations (μg L^{-1}) of metal(loid)s in female (n = 10) and male (n = 3) tiger sharks (*Galeocerdo cuvier*) sampled around the Fernando de Noronha Archipelago (Northeastern Brazil). Minimum (Min), maximum (Max), mean, standard deviation (SD) and median values are shown. Mean values were not significantly different between female and male sharks for all elements analyzed (Student's t-test; $p > 0.05$).

Element	Sex	Min	Max	Mean	SD	Median
Al	*Female*	3.9	165	51	66	19
	Male	16	155	70	75	16
As	*Female*	9.1	85	37	25	35
	Male	32	115	81	43	95
Cd	*Female*	0.031	0.072	0.049	0.015	0.042
	Male	0.031	0.12	0.063	0.053	0.041
Cr	*Female*	0.23	0.61	0.39	0.13	0.40
	Male	0.15	0.82	0.44	0.34	0.37
Cu	*Female*	15	125	52	37	42
	Male	38	93	65	27	65
Fe	*Female*	43	1531	651	523	567
	Male	926	1200	1040	143	993
Hg	*Female*	0.40	1.7	0.95	0.41	0.91
	Male	0.63	1.8	1.1	0.62	0.85
Mn	*Female*	2.5	8.1	4.8	1.9	4.5
	Male	2.6	10	5.6	4.1	3.9
Ni	*Female*	12	29	19	6.1	17
	Male	11	46	24	19	16
Pb	*Female*	0.22	0.75	0.38	0.18	0.32
	Male	0.23	0.90	0.46	0.38	0.30
Zn	*Female*	11	288	100	92	83
	Male	37	248	140	106	137

Table 2
Descriptive statistics of blood plasma concentrations of biochemical parameters in female (n = 10) and male (n = 3) tiger sharks (*Galeocerdo cuvier*) sampled around the Fernando de Noronha Archipelago (Northeastern Brazil). Results are expressed as mg dL^{-1} [glucose, triglycerides, cholesterol and lactate], g dL^{-1} (total proteins) or mM (urea). The triglycerides/cholesterol ratio and PUFAs profile are expressed in %. Minimum (Min), maximum (Max), mean, standard deviation (SD) and median values are shown. Significant different mean values for female and male sharks are indicated with an asterisk (Student's t-test or Mann Whitney test; $p < 0.05$).

Blood plasma parameter	Sex	Min	Max	Mean	SD	Median
Glucose	*Female*	83	129	101	17	96
	Male	71	105	93	19	104
Protein	*Female*	1.3	2.0	1.6*	0.22	1.5
	Male	1.2	1.4	1.3	0.12	1.2
Triglycerides	*Female*	8.6	41	21	13	17
	Male	14	23	17	4.8	15
Cholesterol	*Female*	30	93	63	21	70
	Male	47	53	50	32	51
Triglycerides/ Cholesterol ratio	*Female*	0.12	1.3	0.42	0.43	0.24
	Male	0.28	0.45	0.35	0.09	0.31
Arachidonic acid	*Female*	0.60	1.7	0.95	0.46	0.88
	Male	1.3	2.1	1.6	0.42	1.4
Eicosapentaenoic acid	*Female*	2.6	5.0	3.4	1.0	3.1
	Male	3.5	6.9	4.7	1.9	3.6
Docosahexaenoic acid	*Female*	12	21	16*	3.0	15
	Male	8.9	12	9.8	1.5	9.0
Lactate	*Female*	30	161	74	46	72
	Male	44	92	71	25	77
Urea	*Female*	292	493	339	71	319
	Male	296	318	309	12	313

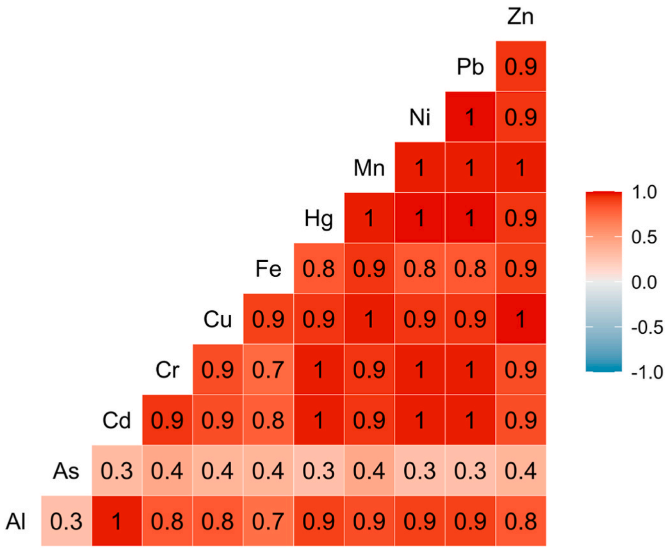

Fig. 2. Spearman's Rank Correlation Coefficient values of metal(loid)s concentrations in whole blood of female tiger sharks (*Galeocerdo cuvier*) sampled around the Fernando de Noronha Archipelago (Northeastern Brazil).

performed to assess the effect of the concentrations of metal(loid)s on essential PUFA profiles in plasma showed a lack of significant effect for all elements analyzed (Table S2).

Regarding the satellite tracking, results showed that the female tiger shark #497 was tracked for 84 days, whereas the female tiger shark #519 was monitored for 116 days. During these periods, they traveled total distances of 8201 km (97 km/day) and 7995 km (69 km/day), respectively. Despite moving considerably long daily distances, these two organisms remained mostly within the vicinity of the Fernando de Noronha Archipelago and showed high spatial range. However, there is a noticeable difference in the area explored by the two specimens. The female tiger shark #497 explored all the area around the archipelago, including both the northern and southern sides of the archipelago. The female tiger shark #519 explored only the area associated with the northern side of the archipelago, which faces the North Atlantic Ocean (Fig. 3).

4. Discussion

This study provides insights into the exposure and potential consequences of metal(loid) intake in tiger sharks off the Fernando de Noronha Archipelago in Brazil. The high concentrations of metal(loid)s in this species, compared to other sharks in the same region, were previously documented by Araújo et al. (2024). However, the levels found herein are considerably lower. For instance, the mean concentration of

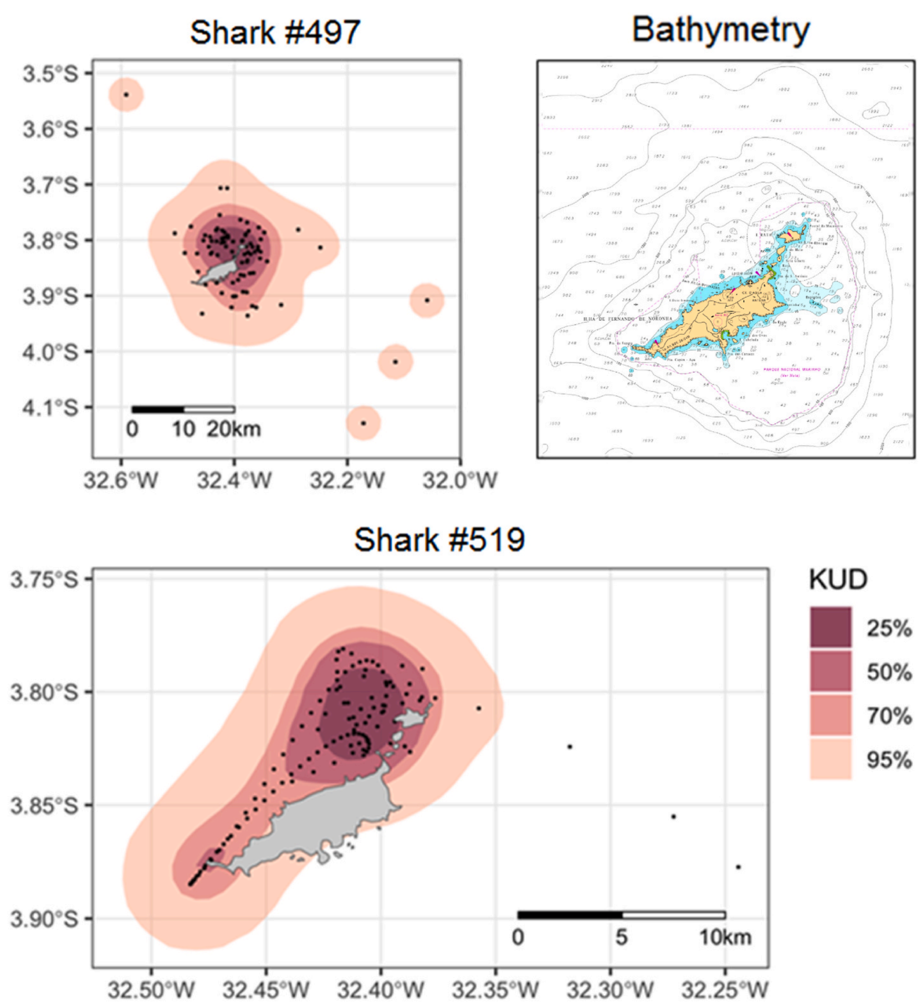

Fig. 3. Kernel Utilization Distribution (KUD) for two (Shark #497 and Shark #519) female tiger sharks (*Galeocerdo cuvier*) tracked in the Fernando de Noronha Archipelago (Northeastern Brazil) and the bathymetric chart of the study area. Available at: https://www.marinha.mil.br/chm/sites/www.marinha.mil.br.chm/files/geotiff/52geotiff.zip.

As in tiger sharks reported by Araújo et al. (2024) was 171 μg L^{-1}, whereas in this study, it was 50 μg L^{-1}. In addition, the mean concentrations of Fe (4436 μg L^{-1}) and Zn (198 μg L^{-1}) reported by Araújo et al. (2024) were 4- and >2-times higher than those found in the present study. Such differences might reflect divergences in the sex and life stage of the organisms sampled in these two studies, as these features influence metal exposure and accumulation (Merly et al., 2019; Crawford et al., 2023).

Other than tiger sharks, other organisms such as turtles and foraminifers have been studied regarding metal(loid) exposure in the Fernando de Noronha Archipelago. High median concentrations of As (205 μg L^{-1}) were found in the blood serum of green turtles (*Chelonia mydas*) (Prioste et al., 2015). Important impacts on the health and ecological parameters of marine invertebrates from the Fernando de Noronha Archipelago associated with elevated concentrations of Cu and Zn in seawater were also reported (Prazeres et al., 2012).

To the best of our knowledge, the only study reporting metal(loid) concentrations in the whole blood of sharks analyzed scalloped hammerhead sharks (*Sphyrna lewini*) off La Paz Bay, Mexico (Whitehead et al., 2024). The mean concentrations of metal(loid)s observed in the whole blood of tiger sharks sampled in Fernando de Noronha were much higher than those found in *S. lewini* sampled in Mexico. For instance, concentrations of As, Cr, Fe, and Ni were 2- to 4-fold higher in tiger sharks than in scalloped hammerhead sharks. Furthermore, the Hg concentration was 6-fold higher in the specimens analyzed herein. The Cu and Zn concentrations were 75- and 24-fold higher, respectively, in tiger sharks than in *S. lewini*. Cd (0.21 μg L^{-1}) and Pb (1.8 μg L^{-1}) were the only elements found in higher concentrations in the scalloped hammerhead sharks from Mexico. These differences are likely not only explained by different levels of contamination in the study sites but also by biological factors, such as feeding habits and trophic position (McKinney et al., 2016; Boldrocchi et al., 2021).

Several ecotoxicological studies have reported the influence of biometric parameters, body condition, and sex on concentrations of tissue contaminants in fish (Arantes et al., 2016; Varol et al., 2022), including sharks (Crawford et al., 2023). For instance, blood plasma concentration of total Hg measured in Northwest Atlantic white sharks (*Carcharodon carcharias*) was previously found to be significantly correlated with their precaudal length (Crawford et al., 2023). Conversely, blood plasma concentrations of 14 metal(loid)s (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, and Zn) were not correlated with shark body size, body condition, and sex in white sharks sampled in South Africa (Merly et al., 2019). Furthermore, no significant relationship was observed between blood cell Hg concentration and body size in blacktip sharks (*Carcharhinus limbatus*) (Reistad et al., 2021), suggesting that the influence of biological features on metal(loid) concentration is highly variable among sharks and/or locations. Similarly, in the present study, no significant relationship was observed between the whole blood concentrations of any of the 11 metal(loid)s analyzed with total body length, body condition (using the ratio triglycerides/cholesterol as a proxy; Gallagher et al., 2017) and sex of tiger sharks evaluated. In this case, it is worth noting that the sample size and range of body lengths evaluated were relatively limited (females: 140–260 cm; males: 220–273 cm). Based on established size-at-maturity estimates (Ebert et al., 2021), tiger sharks sampled and analyzed in the present study were either sub-adults or adults. Therefore, significant changes in blood concentrations of metal(loid)s as a function of age, sex, or biometry were not expected.

Urea and lactate are indicators of acute stress, with urea also serving as an important osmolyte in sharks. Lactate mean concentrations reported for female (74 ± 46 mg dL^{-1}) and male (71 ± 25 mg dL^{-1}) tiger sharks were lower than those reported previously for this species in Fernando de Noronha (126 ± 15; Wosnick et al., 2017). Concerning variations induced by metal(loid) exposure, lactate did not change significantly in the spiny dogfish (*Squalus acanthias*) experimentally exposed to Pb (Eyckmans et al., 2013) but varied transiently in individuals exposed to high concentrations of Cu (De Boeck et al., 2007). Again, blood plasma urea concentrations were also lower than those reported previously in tiger sharks from Fernando de Noronha (464 ± 11; Wosnick et al., 2017). In this study, urea concentrations were not related to any element analyzed. The same was observed in *S. acanthias* experimentally exposed to Ag (De Boeck et al., 2007). Specimens exposed to above environmental concentrations of Cu, however, experienced decreased urea concentrations (De Boeck et al., 2001). Wosnick et al. (2021) observed a positive correlation between Fe and urea, and Hg and lactate in sharks' gills. In this study, however, these parameters were not affected by metal(loid) concentrations, possibly due to their direct association with capture stress, which can vary significantly between individuals (Gallagher et al., 2014b; Wosnick et al., 2017).

Total protein concentration was not influenced by any element analyzed, as has been found in white sharks from South Africa (Merly et al., 2019). The mean concentrations of total protein in female (1.6 ± 0.23 g dL^{-1}) and male tiger sharks (1.3 ± 0.12 g dL^{-1}) reported in this study were also lower than those reported by Wosnick et al. (2017). Plasma glucose was similarly not affected by metal(loid)s in tiger sharks from Fernando de Noronha. The mean concentrations (±SD) of blood plasma glucose observed in female (101 ± 17 mg dL^{-1}) and male (93 ± 19 mg dL^{-1}) tiger sharks from Fernando de Noronha were below the values reported by Wosnick et al. (2017) for this species in the same study area (129 ± 19 mg dL^{-1}). As sharks rely mostly on the oxidation of ketonic bodies as energy fuel (Ballantyne, 1997), these short-term dietary indicators might be less responsive to pollution.

Triglycerides, on the other hand, were positively influenced by As concentrations. Triglycerides concentrations in blood plasma likely reflect lipid reserves stored in the shark's liver (Gallagher et al., 2017; Shipley et al., 2021). Triglyceride levels are positively related to body condition in tiger sharks (Gallagher et al., 2014a) and health, therefore the positive effect of As on plasma triglycerides was unexpected. Interestingly, a positive correlation between hepatic Fe and triglycerides was also reported for sharks from the Brazilian Amazon coast (Wosnick et al., 2021). The triglyceride concentrations in this study were lower than those found in the blood serum (108 ± 5.6 mg dL^{-1}) of tiger sharks previously sampled in Fernando de Noronha (Wosnick et al., 2020). The same was observed for cholesterol, which is also a marker of nutritional health in sharks (Gallagher et al., 2017; Wosnick et al., 2023). The observed relationship between As blood levels and plasma triglycerides concentration in tiger sharks could be a direct result of dietary exposure to As. At this point, it is important to note that metal(loid) concentrations in circulating blood are likely more transient as compared to other tissues, such as muscle and liver (Burger et al., 2007; Merly et al., 2019). Therefore, the elevated concentration of blood As in tiger sharks can be a result of acute dietary exposure to As. Still, the lack of information on other organs' metal(loid) concentration is a limitation in this study. As triggered genomic damage in sharks from the same study site (Araújo et al., 2024), reinforcing that shark exposure to this metalloid must be monitored.

The PUFAs profile was not related to any element analyzed here, as shown by the PERMANOVA outputs, possibly because the association between metal(loid) levels and the fatty acid profile is only evident when analyzing tissues, as the plasma profile is more closely linked to recent dietary intake (e.g., McMeans et al., 2012). Additionally, metabolic and nutritional parameters are species-specific and might vary as a function of ontogeny, season, and reproduction (Gallagher et al., 2017). For instance, triglycerides and fatty acids are mobilized during exercise (Ballantyne, 2015), being potentially influenced by sampling procedures. Cholesterol, on the other hand, is also involved in other physiological processes, such as reproduction (Ballantyne, 1997; Moorhead et al., 2020). In this context, the parameters assessed in this study are not specific to metal(loid) exposure and, therefore, are subject to other stressors.

Blood plasma/serum concentrations of biochemical parameters employed as indicators of health, nutritional, and/or body condition in sharks are quite variable. Variations observed in glucose, lactate, total proteins, and urea concentrations in the blood plasma of tiger sharks in the present study may be due to a stress response associated with capture and handling stress (Skomal, 2007; Skomal and Bernal, 2010). In turn, changes observed in lipids (triglycerides, total cholesterol, and fatty acids) may be associated with body conditions, as previously shown in tiger sharks (Gallagher et al., 2014a). These patterns are reinforced by the fact that no significant relationship was observed between the blood plasma concentrations of biochemical parameters analyzed and the whole blood concentrations of metal(loid)s investigated, except for triglycerides and As. Also, stronger correlations might be found in other tissues, such as the liver and gills, which are more prone to bioaccumulation (Gelsleichter and Walker, 2010). For instance, positive associations between metals and plasmatic physiological markers were observed in the internal organs of tiger sharks (Wosnick et al., 2021). Therefore, the use of blood plasma and whole blood as matrixes for ecotoxicological assessments, although important from a conservation perspective, has its limitations.

It is important to note that the plasma health biomarkers implied in this study are responsive to several stressors despite contaminant exposure. These markers might be influenced by the stress of exhaustive exercise during capture and handling procedures (Skomal and Mandelman, 2012; Borucinska and Skomal, 2022). For instance, glucose was proven to be a very variable parameter and should, therefore, be used with caution (Wosnick et al., 2017). On the other hand, lactate is closely associated with capture-induced stress responses as a metabolite of anaerobic metabolism (Skomal and Bernal, 2010). In this context, plasma marker responses to environmental contamination must be carefully discussed. Studies linking plasmatic stress responses to contaminants are scarce (Alves et al., 2022); therefore, establishing such relationships is challenging. Still, these approaches are crucial for understanding the outcomes of metal exposure in elasmobranchs, either as direct effects, especially because pollution might attenuate such responses (Lyons and Wynne-Edwards, 2019).Significant positive correlations were observed between all metal(loid)s analyzed in the whole blood of tiger sharks from Fernando de Noronha, except for As (Fig. 3), indicating that As uptake might not be related to the other elements analyzed. The satellite tracking data obtained from the two opportunistically tagged females aided in understanding how these animals used the area for over 100 days and the potential linkages between space use and metal(loid) exposure. Our data showed that the two female tiger sharks monitored (shark #497 and shark #519) remained most of the time in the vicinity of the Fernando de Noronha Archipelago, presenting a large spatial range of movement. However, there was a noticeable difference in the area explored by the two specimens. The female tiger shark #497 explored all the area around the archipelago. In turn, the female tiger shark #519 explored only the area associated with the northern side of the archipelago, which faces the North Atlantic Ocean (Fig. 3). Remarkably, they had different whole blood concentrations of As, with the shark #519 showing a much higher blood As contamination than the shark #497. This differential response could be explained, at least in part, by the bathymetry of the Fernando de Noronha Archipelago. The southern side of this archipelago is characterized by shallower waters than its northern side. Furthermore, the southern side of the archipelago is a protected marine area and, thus, supposedly less contaminated than the northern portion (Fig. 3). A recent review of the As occurrence and cycling in the marine environment reported that, normally, the concentration of this metalloid is lower in the upper water layer than in the deep-water layer (Wang et al., 2023), potentially explaining the higher concentrations in shark #519. In addition, it has been demonstrated that unpolluted nearshore marine sediments have much lower concentrations of As than deep-sea sediments (Masuda et al., 2019). These conditions would imply higher levels of As bioaccumulation in biota living in deep waters than in shallower ones. Taken together, it is possible that the higher As values seen in shark #519, which used areas of deeper water than shark #497, could result from acute dietary exposure at depth. However, this hypothesis assumes that shark movements during the tracking period were indicative of their movements prior to sampling (i.e., the period of exposure). Either way, this hypothesis needs to be tested with larger dataset.

In summary, the results from the present study show that tiger sharks from the Fernando de Noronha Archipelago are being exposed to metal (loid)s. The positive correlation observed between blood As concentration and plasma triglyceride levels in female tiger sharks sampled in this area also suggests that exposure to this specific metalloid might elicit physiological changes. Therefore, the potential impact of environmental exposure to As on the health condition of organisms occurring in the Fernando de Noronha Archipelago certainly deserves special attention in future studies. Due to the scarcity of studies related to plasma health parameters, remarkably, PUFAs, responses to contaminant exposure, this study aids in understanding this topic not only in tiger sharks but potentially also in other sharks.

The metal(loid) concentrations reported herein highlight the need for a monitoring of the sources and concentrations of metal(loid) contamination, especially Al, As, Cu, Fe, and Zn, around the archipelago. A limitation of this study is the fact that metal(loid)s were measured from whole blood, which is a transient tissue. Accordingly, investigations that evaluate metal(loid) concentrations in internal organs, such as the liver and gills might provide better for relating to physiological endpoints in these organisms. Finally, the results reported herein also indicate that oceanic islands, such as the Fernando de Noronha Archipelago, might not be pristine environments, void of environmental contaminants, due to the constant and increasing anthropogenic activities taking place both inland and offshore.

CRediT authorship contribution statement

Bianca de Sousa Rangel: Writing – review & editing, Writing – original draft, Resources, Methodology, Investigation, Data curation, Conceptualization. **Mariana da Fontoura Martins:** Writing – review & editing, Writing – original draft, Validation, Formal analysis, Data curation. **Neil Hammerschlag:** Writing – review & editing, Validation, Conceptualization. **Yuri Vieira Niella:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Patrícia Gomes Costa:** Writing – review & editing, Methodology, Investigation, Data curation. **Renata Guimarães Moreira:** Writing – review & editing, Validation, Resources, Conceptualization. **Adalto Bianchini:** Writing – review & editing, Writing – original draft, Validation, Resources, Formal analysis, Data curation.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2025.144250.

Data availability

Data will be made available on request.

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