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BASELINE DATA ON RUBIDIUM (Rb) CONTAMINATION IN JUVENILE CARIBBEAN SHARPNOSE SHARK *Rhizoprionodon porosus* FROM SOUTHEASTERN BRAZIL

Dados de referência sobre contaminação por rubídio (Rb) em cações-frango *Rhizoprionodon porosus* juvenis do Sudeste brasileiro

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ABSTRACT

Although pollution has been recently identified as a priority for elasmobranch conservation, metal contamination assessments in sharks and rays are still scarce, especially in southeastern Brazil. In this regard, rubidium (Rb) is a biomagnifying non-essential element determined in only two elasmobranch assessments to date. Therefore, the aim of this study was to obtain baseline Rb data and discuss the implications of Rb concentrations in the muscle and liver of the vulnerable Caribbean Sharpnose shark *Rhizoprionodon porosus* from Southeastern Brazil. Samples from 18 juvenile specimens were analyzed by inductively coupled plasma mass spectrometry following acid decomposition. When grouping males and females, muscle concentrations (1.117 ± 0.269 mg kg^{-1} w.w.) were significantly higher than liver (0.677 ± 0.146 mg kg^{-1} w.w.), indicating probable Rb bioaccumulation. Significant differences were observed between male and female liver and muscle Rb concentrations, both higher in muscle. Females also presented significantly higher liver concentrations. A negative correlation was observed between total length and liver Rb when grouping males and females, which may indicate the contaminant dilution effect, while a positive correlation

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was noted between total length and muscle Rb for males, indicating bioaccumulation processes. Significant ecological concerns regarding Rb contamination for this group are, therefore, noted, requiring further investigations.

Keywords: Chondrichthyes, toxic elements, bioaccumulation, environmental pollution, Elasmobranchii.

RESUMO

Embora a poluição tenha sido recentemente identificada como uma prioridade para a conservação de elasmobrânquios, avaliações acerca da contaminação por metais em tubarões e raias ainda são escassas, especialmente no Sudeste do Brasil. Nesse contexto, o rubídio (Rb) é um elemento não essencial biomagnificador determinado em apenas duas avaliações em elasmobrânquios até o momento. Assim, o objetivo deste estudo foi obter dados de base de Rb e discutir as implicações das concentrações de Rb em músculo e fígados do vulnerável cação-frango, Rhizoprionodon porosus, *do Sudeste brasileiro. Amostras de 18 espécimes juvenis foram analisadas por espectrometria de massa com plasma indutivamente acoplado após decomposição ácida. Ao agrupar machos e fêmeas, as concentrações em músculo (1,117 ± 0,269 mg kg-1 w.w.) foram significativamente maiores que as em fígado (0,677 ± 0,146 mg kg-1 w.w.), indicando provável bioacumulação de Rb. Diferenças significativas foram observadas entre as concentrações de Rb no fígado e no músculo de machos e fêmeas, ambas maiores no músculo. As fêmeas também apresentaram concentrações hepáticas significativamente mais altas. Observou-se correlação negativa entre comprimento total e Rb hepático ao agrupar machos e fêmeas, o que pode indicar efeito de diluição do contaminante, enquanto uma correlação positiva foi observada entre comprimento total e Rb em músculo para machos, indicando processos de bioacumulação. Preocupações ecológicas significativas em relação à contaminação por Rb para esse grupo são, portanto, observadas, demandando maiores investigações.*

***Palavras-chave**: Chondrichthyes, elementos tóxicos, bioacumulação, poluição ambiental, Elasmobranchii.*

INTRODUCTION

Metal contamination due to anthropogenic activities has increased exponentially worldwide, especially in coastal areas, where most human activities are located (UN, 2017). These contaminants are of significant concern in aquatic ecosystems, as they exhibit high persistence in both the environment and in the biota, are able to bioaccumulate and, in some cases, biomagnify, throughout trophic webs, and, finally, may lead to several toxic effects (Singh *et al.*, 2011).

Some metals, such as lead and mercury, have been routinely assessed in marine megafauna worldwide, and their deleterious effects are well known. Others, however, are rarely determined, and little data on their mechanisms of action and concentration levels in aquatic ecosystems are available. This is the case of rubidium (Rb), who has been scarcely studied in an aquatic contamination context, especially in marine megafauna, and whose distribution and accumulation in both freshwater and marine food webs is still relatively unknown, although it has been recently reported as biomagnifying in both ecosystems (Campbell *et al.*, 2005). Because of this, its assessment has been recommended alongside other metals that consistently biomagnify in aquatic food webs in multi-element biomagnification studies (Campbell *et al.*, 2005), although this suggestion has been mostly ignored.

Rubidium (Rb) is an alkali metal whose essentiality in humans and other organisms is still disputed (Campbell *et al.*, 2005). It has, however, been reported as displaying inhibitory effects on the spermatogenesis of freshwater fish (Yamaguchi *et al.*, 2007), and, as it is a K^+ analogue, it can compete for this essential element in several enzymatic processes, in both fish and other organisms (Peters; Schultz & Newman, 1999; Tipsmark & Madsen, 2001), which may result in several deleterious biochemical processes. Studies concerning Rb in elasmobranchs, however, are almost nonexistent even though, due to some specific life history traits, such as median to high trophic positions, slow growth rates, delayed maturation and low fecundity, this group exhibits high susceptibility to metal uptake, bioaccumulation and biomagnification (Dulvy *et al.*, 2014; Gelsleichter & Walker, 2010; Navia; Mejía-Falla & Hleap, 2016; Stevens *et al.*, 2000), and many elasmobranchs exhibit coastal habits during their juvenile life stage, increasing exposure to chemical contaminants originating from these areas during this critical developmental period.

Two species of Sharpnose sharks, belonging to the *Rhizoprionodon* genus (Whitley, 1929), *Rhizoprionodon porosus* (Poey, 1861) and *Rhizoprionodon lalandii* (Muller & Henle, 1839), both categorized as vulnerable by the International Union for Conservation of Nature (Carlson *et al.*, 2021) are recorded for the Brazilian coast. In southeastern Brazil, they are the most landed species in fisheries in the Lakes Region (*Região dos Lagos*), in Rio de Janeiro (Fiperj, 2019) and widely consumed locally by human populations. Studies concerning metal contamination in these sharks are, however, severely lacking in the entire country, especially in the southeast (Rodrigues Filho *et al.*, 2020).

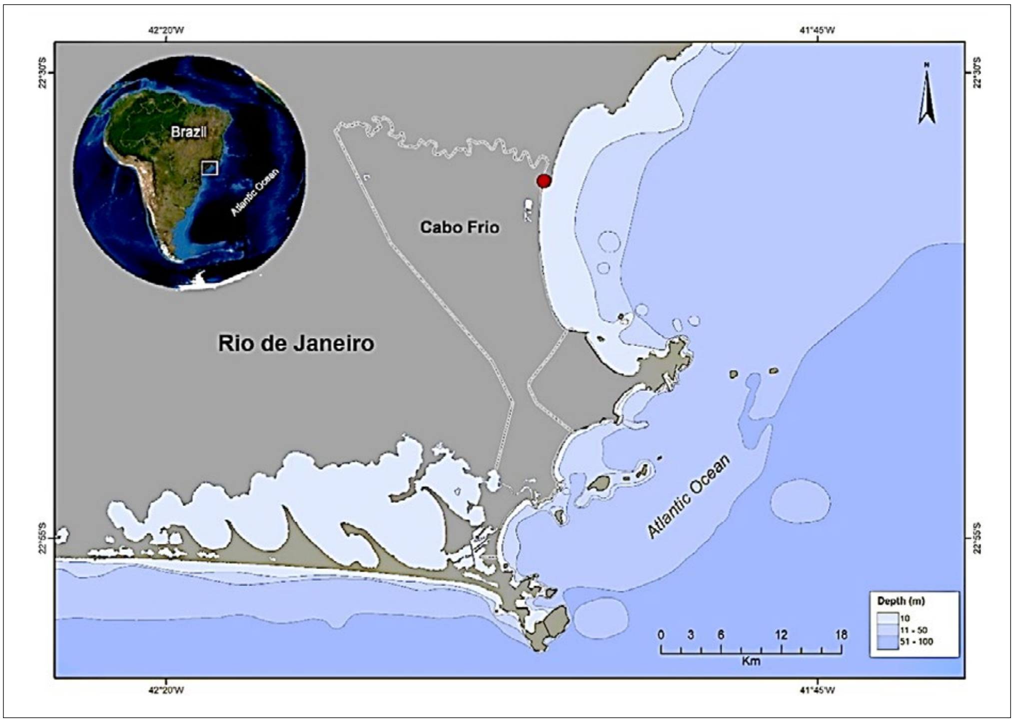
In this context, this study aims to further knowledge on Rb contamination in Caribbean sharpnose sharks *Rhizoprionodon porosus* captured by artisanal fisheries off the eastern coast of the state of Rio de Janeiro by compiling baseline data on this element and discuss the findings employing an ecotoxicological approach.

METHODOLOGY

Study area

Over 1500 registered artisanal fishers carry out artisanal fisheries activities in at least eight cities in the Região dos Lagos (*Lakes Region*) area, located in the state of Rio de Janeiro, southeastern Brazil, namely Maricá, Saquarema, Araruama, Iguaba Grande, São Pedro D'Aldeia, Cabo Frio, Armação dos Búzios and Arraial do Cabo. Concerning the municipality of Cabo Frio, (Figure 1), a year-round upwelling phenomenon is noted in area, increasing local primary production due to the resurfacing of nutrient-rich waters and making this area one of the most productive fishing areas in the state of Rio de Janeiro (Soares-Gomes *et al.*, 2016; Coelho-Souza *et al.*, 2012; Cury *et al.*, 2011; Valentin, 2001).

Figure 1 – Caribbean Sharpnose shark *Rhizoprionodon porosus* sampling site, in Cabo Frio, Rio de Janeiro, Southeastern Brazil



Source: the authors (2021).

Caribbean Sharpnose shark sampling and processing

Caribbean Sharpnose sharks were caught by artisanal fishers using bottom and surface gillnets set off the coast of Cabo Frio in the summer of 2019. Whole individuals were acquired fresh, landed at most 2 hours prior. All individuals were transported to the laboratory in Styrofoam ice boxes filled with ice, identified at the species level (Gomes *et al.*, 2020), sexed (Andrade; Silva-Junior & Vianna, 2008), and measured. Following standardized dissection procedures (EPA, 1993), muscle and liver samples were removed and stored at -20 °C in sterile polypropylene tubes until metal determinations.

Rubidium determinations

For the Rb determinations, about 100 mg of the excised liver and muscle samples were weighed using an analytical balance (0.0001 g precision) (Shimadzu, São Paulo) directly in sterile 15-mL polypropylene screw-capped tubes. Acid decomposition for each sample was performed for 12 hours, through the addition of 1.0 mL of bidistilled HNO_3 (Hexis, Rio de Janeiro, Brazil). Subsequently, the closed tubes were heated for four hours at 100 ºC on a heating block (USP, 2013), cooled and made up with Milli-Q water (resistivity > 18.0 MΩ cm) to 10 mL and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) employing a NexIon 300X mass spectrometer (PerkinElmer, Norwalk, CT, USA), following the USEPA 6020B standard method (US EPA, 2014). External multielemental calibration curves were prepared and ^{102}Rh was used as the internal standard. Analytical curve correlation coefficients were always above 0.995. Blanks and a certified reference material composed of fish muscle (ERM®-BB422, European Commission) were prepared in the same way as the samples and assessed to ensure method accuracy and precision. As no certified reference material is available for Rb, we evaluated recoveries for other elements, and all were within acceptable ranges for this type of study, from 70 to 120%, thus indicating the adequacy of our method (Cd: 72.56%, Cu: 73.54%, Fe: 84.12%, Hg: 106.54%, Zn, 76.73%, (EPA, 2000; Ishak *et al.*, 2015). All samples, blanks and certified reference materials were analyzed in triplicate. The limit of quantification (LOQ) for Rb was calculated according to the Brazilian National Institute of Metrology Standardization and Industrial Quality (Inmetro, 2016), as LOQ = (10*SD*df)/slope of the line, where SD consists of the standard deviation of the analytical signal ratio by the internal standard signal of 10 blank solutions and df comprised the sample dilution factor (Inmetro, 2016). The determined LOQ for Rb was 0.001 mg kg^{-1} wet weight (w.w.).

Statistical analyses

The GraphPad Prism v. 9 software was used for all statistical analyses. Data normality was verified by the Shapiro-Wilk test. As Rb concentrations exhibited a normal distribution, parametric tests were subsequently applied. To assess potential significant differences between element levels comparing tissues and sex, the data were analyzed by the t-test. Correlations between metal levels and total fish length and between the essential element selenium and Rb concentrations in both liver and muscle were assessed by the Pearson correlation test. The correlation strengths used were as follows: $0.00 < r < 0.19$ - very weak; $0.20 < r < 0.39$ - weak; $0.40 < r < 0.69$ - moderate; $0.70 < r < 0.89$ - strong and $0.90 < r < 1.0$ - very strong (Bryman & Cramer, 2011). A p value of < 0.05 was accepted as statistically significant for all analyses.

RESULTS AND DISCUSSION

Biometric Caribbean sharpnose shark data

Eighteen Caribbean sharpnose sharks were analyzed. Total lengths (TL) ranged from 43 to 56 cm, indicating that all specimens were juveniles (Frisk; Miller & Fogarty, 2001; Mas; Forselledo & Domingo, 2014). No significant differences ($p > 0.05$) concerning TL between males and females was observed. The biometric data for the Caribbean Sharpnose sharks sampled in the present study are presented in Table I, both grouped by sex and separately.

Table I – Total lengths and number of specimens of Caribbean Sharpnose sharks sampled at Cabo Frio, in the state of Rio de Janeiro, grouped by sex and separately

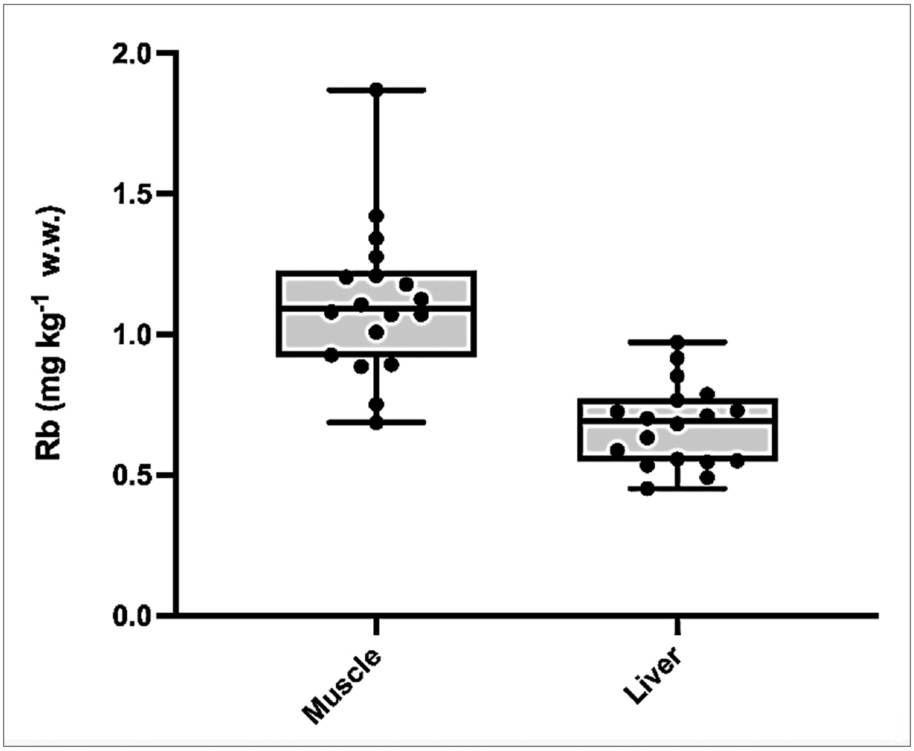
Length (cm)	Grouped	Males	Females
Minimum	43	44	43
Maximum	56	56	52
Means ± SD	49.24 ± 2.97	50.30 ± 2.71	47.71 ± 2.81
Number of specimens	18	11	7

Source: the authors (2021).

Metal contents

All samples contained Rb concentrations above the LOQ in all Caribbean Sharpnose shark muscle and liver samples. The Rb loads detected in Caribbean Sharpnose shark liver and muscle samples ranged from 0.45 to 0.97 mg kg^{-1} w.w. (0.67 ± 0.14 mg kg^{-1} w.w.) and from 0.68 to 1.87 mg kg^{-1} w.w., (1.11 ± 0.27 mg kg^{-1} w.w.), respectively.The data are displayed in Figure 2. All data are expressed as mg kg^{-1} w.w.

Figure 2 – Rb concentrations in Caribbean Sharpnose shark liver and muscle samples (as mg kg^{-1} w.w.). The box plots display the medians, and the whiskers indicate the maximum and minimum values. The filled circles represent each individual sample

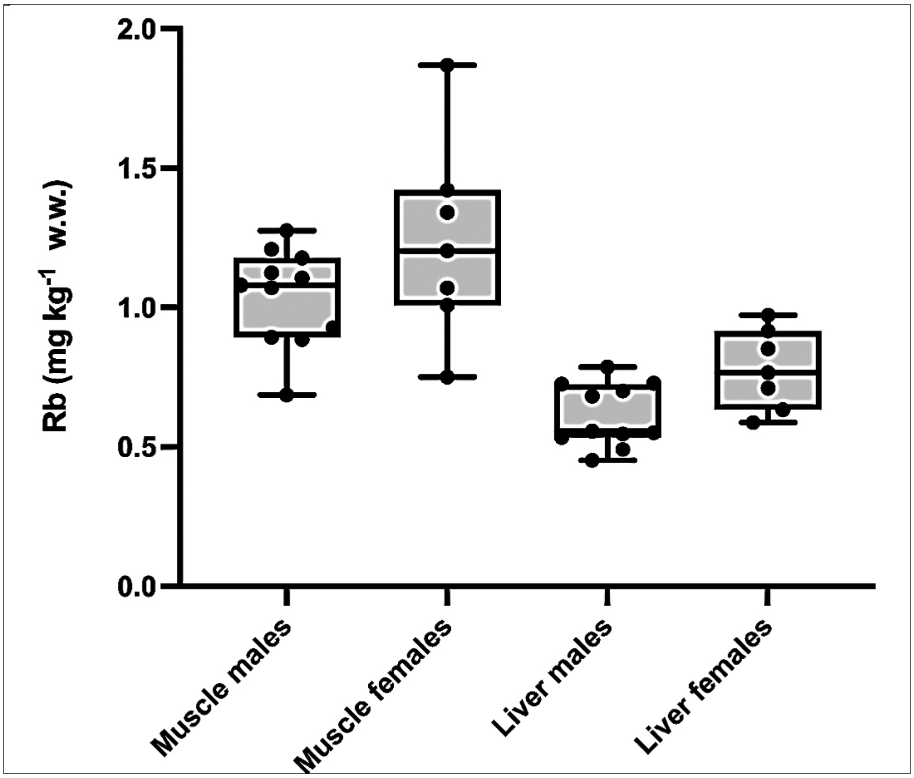


Source: the authors (2021).

When separating sexes (Figure 3), comparisons between muscle and liver Rb concentrations revealed significant differences ($p < 0.05$) for males (muscle: 1.040 ± 0.174 mg kg^{-1} w.w., range 0.686-1.276 mg kg^{-1} w.w.; liver 0.614 ± 0.113 mg kg^{-1} w.w., range 0.452-0.786 mg kg^{-1}, respectively). The same was observed for females (muscle: 1.238 ± 0.356 mg kg^{-1} w.w., range 0.751-1.869 mg kg^{-1} w.w. and liver: 0.777 ± 0.144 mg kg^{-1} w.w., range 0.587-0.972 mg kg^{-1} w.w.). Both sexes contained higher Rb concentrations in muscle. Higher muscle concentrations compared to liver may indicate Rb bioaccumulation, as this tissue displays lower contaminant accumulation rates reflecting lower metabolic activities under optimum conditions when compared to higher metabolic activity organs, such as the liver (Squadrone *et al.*, 2013; Uluturhan & Kucuksezgin, 2007). It may also, however, indicate that Rb is not significantly lipophilic, targeting organs containing less fat content compared to liver.

Regarding comparisons among the same organs between sexes, no significant difference ($p > 0.05$) was observed between female and male muscle Rb concentrations, while a significant difference ($p < 0.05$) was observed between female and male liver Rb concentrations, with female concentrations (0.777 ± 0.144 mg kg^{-1} w.w.) higher than male concentrations 0.614 ± 0.113 mg kg^{-1} w.w.). Reproductive efforts have been reported as causing differences in metal accumulation in several fish species (Marijić; Raspor & Biserka, 2014; Miramand *et al.*, 1991). However, this does not seem to be the case herein, as all specimens were juveniles, smaller than the sexual maturation lengths for the species, reported as between 76-80 cm for males and 81-85 cm for females, with the reproductive period for the species reported as from September to December (spring) in southeastern Brazil (Gadig *et al.*, 2002; Macedo; Sousa & Batista, 2012).

Figure 3 – Rb concentrations in Caribbean Sharpnose shark liver and muscle samples (as mg kg^{-1} w.w.) separated by sex. The box plots display the medians, and the whiskers indicate the maximum and minimum values. The filled circles represent each individual sample



Source: the authors (2021).

A significant moderate negative correlation was observed between total length and Rb concentrations in liver when grouping both sexes ($p = 0.003$, $r = -0.653$), and a positive strong correlation between total length and Rb concentrations in muscle for males ($p = 0.011$, $r = 0.728$). The first correlation, as it is negative, may indicate the so-called contaminant dilution effect, where contaminant loads in fish decrease with increasing fish age, as a natural detoxification mechanism (Kamunde & Wood, 2003). It is, however, important to note that this effect may not occur if chronic metal exposure is in place for the exposed organisms, or if metal concentrations in the aquatic environment are high enough that the capacity of this mechanism is inhibited (Yi & Zhang, 2012). In these cases, metal bioaccumulation may occur, and the statistical correlation between animal size and metal tissue concentrations may become altered to a positive association (Yi & Zhang, 2012). Another possibility for this association comprises ontogenetic changes in diet, reducing Rb accumulation through prey ingestion, as postulated for other metals, such as mercury (Beltran-Pedreros *et al.*, 2011). Concerning the positive male association, no robust hypothesis can be postulated, although males were slightly larger than females, and the sample size number was also slightly larger. This may indicate concerns regarding Rb contamination in this species, as this association is suggestive of increasing Rb loads with increasing age (Khansari; Ghazi-Kansari & Abdollahi, 2005). However, no significant difference concerning male and female sizes was observed. Therefore, further assessments in this regard with higher sample sizes and different life stages are paramount to understand Rb toxicokinetics in this species. For some elements, such as the essential metals copper and zinc, accumulation reaches a steady state after a certain age (Douben, 1989), indicating homeostasis regulation mechanisms. It is, however, unknown if this occurs for Rb.

Fish are exposed to metals both from the dietary route and from the surrounding water column (Lee *et al.*, 2019). Rubidium has several uses in the medical field, such as in positron emission tomographic (PET) imaging, epilepsy treatment, and the ultracentrifugal separation of nucleic acids and viruses, and is also employed in in fiber optic telecommunication systems, night-vision devices and photoelectric cells, among others (Butterman & Reese, 2003), Possible anthropogenic sources of Rb and Cs include coal-burning and space rocket fuel (Campbell *et al.*, 2005; Wosnick *et al.*, 2021), as well as electronic waste (e-waste) disposed of incorrectly and inadequately recycled and processed (Huang *et al.*, 2014), as it has been recently reported as present in high amounts in these electronic residues (Forti *et al.*, 2020). Furthermore, it may also become bioavailable in the aquatic environment due to dredging activities, that restore ancient sedimentary characteristics or expose contaminated sediments to the water column (Mill-Homens, 2013). Rb concentrations in aquatic biota, however, are still scarce. Thus, as stated by Hauser-Davis *et al.* (2021), establishing baseline elemental data is paramount in biomonitoring efforts, conservation measures and public health assessments. In this regard, concerning elasmobranchs, Rb data have only been reported for two arctic species, the Pacific sleeper shark, at 0.454 mg kg^{-1} w.w. in liver (n = 14) and the Greenland shark, at 0.38 mg kg^{-1} w.w. in liver (n = 24) (McMeans *et al*., 2007), and recently, nurse sharks (*Ginglymostoma cirratum*) from Northeastern Brazil (1.36 ± 0,64 mg kg^{-1} w.w. in muscle tissue) (Wosnick, 2021).

As the essential metalloid selenium (Se) is known to display protective effects against other metals, most notably mercury, and against oxidative stress, postulated as the main exposure effect for several metals (Betancor *et al.*, 2015), potential correlations were investigated between this element and Rb concentrations in Caribbean Sharpnose shark muscle and liver loads. No significant correlations were observed between Se and Rb for any of the analyzed tissues, both for sex and grouped. This has also been previously noted for Rb in nurse shark muscle samples (Wosnick *et al.*, 2021). Therefore, the selenium-detoxification route, either through metal complexation and/or selenoprotein action (Tapieiro; Townsend & Tew, 2003; Yoneda & Suzuki, 1997) does not seem to be significant for Rb detoxification in this species, although further assessments in this regard are, of course, required. Interesting assessments would include metallothionein and reduced glutathione evaluations, as both are known detoxification routes for other metals and have been demonstrated as efficient excretion mechanisms in other elasmobranch species (Hauser-Davis *et al.*, 2021; Walker *et al.*, 2014; Wosnick *et al.*, 2021).

It has been reported that Rb consistently biomagnifies in different food webs (Campbell *et al.*, 2005). It could, therefore, as a non-essential and biomagnifying element, provide information not only on environmental contamination, but also concerning elasmobranch diet and trophic level (McMeans *et al.*, 2007). However, metal biomagnification depends on homeostatic mechanisms and biochemical aspects that prevent trophic accumulation (Wang, 2002). Furthermore, these mechanisms may be species specific, and change with age, sex and due to ontogenetic feeding habit alterations. Adult *R. porosus* display a piscivorous habit, comprising an opportunistic predator, feeding on crustaceans and mollusks (Silva & Almeida, 2018). It is, therefore, a mesopredator, and in a vulnerable trophic position concerning Rb bioaccumulation exposure, although further studies are required to determine Rb toxicodynamics in the investigated food web at Cabo Frio.

Contamination assessments for elasmobranchs are, in general, still scarce, notably in southeastern Brazil (Rodrigues Filho *et al.*, 2020), and it is important to obtain baseline data for as many chemical contaminants as possible, as pollution has recently been identified as a priority for conservation efforts, especially for this group (Consales & Marsili, 2021; Cooke *et al.*, 2021). Furthermore, chemical contamination may directly affect cellular, systemic and physiological health, with several potential ecological endpoints, including metabolism and homeostatic balance, such as compromised osmoregulatory capacity, acid-base balance, metabolic energy and liver function (Wosnick *et al.*, 2021). For example, Rb has been reported as substituting K in processes catalyzed by Na^+/K^+–ATPase, $K^+/Na^+/2Cl^-$–transporter, and K^+–channels (Jilkina; Kuzio & Kupriyanov, 2003), which may result in severe homeostatic imbalances. It has also been noted as toxic for certain taxonomic groups, such as oysters (Salaun & Truchet, 1996). Furthermore, gonad metal accumulation can, in turn, reduce the survival of unborn individuals, due to negative embryo physiology effects, which can lead to malformations and an increase in the instantaneous natural mortality rate for the species, potentially impacting population recruitment (Hauser-Davis & Wosnick, 2021). It has been reported, for example, that low Rb concentrations (0.018 mg kg^{-1} w.w.) significantly inhibit spermatogenesis in male teleost fish testes in in vitro assessements, and significant negative correlations between this element and the Gonadossomatic Index have been observed when studying the catfish *Pangasianodon hypophthalmus* in the Mekong River delta, in Vietnam (Yamaguchi *et al.*, 2007), indicating significant ecological concerns regarding Rb contamination in fish. No further assessments, however, are noted in the literature concerning toxic effects in fish.

It is also important to draw attention to note that the current climate change scenario will both directly and indirectly affect the water environment in the near future, altering currents and the transformation and transport of pollutants and as well as their toxic effects (Bussi *et al*., 2016; Glibert *et al*., 2014; Hua *et al*., 2015; Ockenden *et al*., 2016; Yuan *et al*., 2016; Wu *et al*., 2014a, 2014b). Furthermore, global warming and extreme weather events will significantly aggravate the ecological risks of these contaminants in the aquatic environment, mainly due to increased leaching and diffuse pollution sources, as well as greater release of sediment contaminants to the water column (Wu *et al*., 2017). Thus, further investigations into the toxic effects of these contaminants become extremely necessary, especially for poorly studied groups, such as elasmobranchs. Concerning Rb, this element is rapidly depurated at higher temperatures (Campbell *et al*., 2005), and some studies have reported decreased Rb levels in bony fish tissues at higher temperatures (Barbosa *et al*., 2017; Peters; Schultz & Newman, 1999), although other assessments indicate the opposite, due to intense Na metabolism and higher Rb uptake, due to higher respiratory activity of certain fish species in warmer water (Gashkina & Moiseenko, 2020). Further assessments are, therefore, paramount to evaluate potential risks concerning Rb contamination in elasmobranchs due to altered Rb toxicodynamics caused by climate change effects.

CONCLUSION

This is only the third ecotoxicological Rb assessment carried out for elasmobranchs, indicating a severe knowledge gap in this regard. Thus, our baseline elemental data is valuable in furthering knowledge on Rb contamination in this group, applicable in biomonitoring efforts and conservation measures. In this regard, even though a negative correlation was observed between total length and liver Rb concentrations when grouping both male and female juvenile Caribbean Sharpnose sharks from Rio de Janeiro, southeastern Brazil, significantly higher muscle Rb concentrations compared to liver in both sexes and a positive correlation between total length and muscle Rb for males seemingly indicate Rb bioaccumulation processes in this vulnerable species. This leads to significant ecological concerns, as Rb accumulation is known to affect vital homeostatic processes and interfere with reproductive efforts. Therefore, further ecotoxicological Rb investigations are paramount in order to further knowledge on Rb toxicodynamics and toxicokinetics in this vulnerable taxonomic group, as pollution is now a priority for elasmobranch conservation efforts.

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