Biological assessment and metals concentration in blue shark (*Prionace glauca*) caught in the southeast-south coast of Brazil

Gabriela Vignatti¹, Vania Elisabete Schneider^{1*}, Matheus Poletto^{1*}

Abstract

Sharks are suffering from fishing industry pressure, mostly by human consumption of meat and fins, causing a great impact on its population. These top predators can bioaccumulate metals in its tissues, which brings risks to human health and indicates aquatic pollution. The objective of this work is to determine metallic trace elements as chromium, copper, zinc and aluminium in *Prionace glauca*, while studying the biological aspects such as fork length and approximate age to indicate if there is a metal accumulation in shark tissues evaluated. Nine specimens were obtained through commercial fishing in the Southeast and South regions of Brazil, using pelagic longline fishing. On arrival at the port, specimens were weighed and sexed in its commercial weight (headed, finned and gutted). About 100 g of muscular flesh from dorsal region between the dorsal and caudal fin was removed. Metal determination in muscle tissue (wet weight basis) was performed through acid digestion (mixture of HNO₃ and H₂O₂). After the acid digestion, the metals concentration was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES). The results indicated that *Prionace glauca* capture during the winter in the Southeast-South regions of Brazil, consists mostly by small adult males. Copper, zinc and aluminium concentration was well below de maximum limits permitted by Brazilian and international agencies. Chromium average (0.14 mg/kg) was above the limits permitted by Brazilian legislation (0.10 mg/kg). A significant positive correlation was found between some metals (Al, Cr and Cu) and sharks fork length. These results corroborate the bioaccumulation of some metals in *Prionace glauca*, showing the need for more studies about metal determination in shark tissues.

Keywords Blue Shark. Metals, South Atlantic, Bioaccumulation.

I. INTRODUCTION

Metal accumulation in seafood shows great concern, mainly because it indicates the high levels of pollution in the aquatic environment [1,2] and when associated with increased worldwide production of fish in the past five decades, where fish supply as food is growing at an average annual rate of 3.2% [3] also raises concern about the human health.

Essential metals as chromium, copper, zinc and aluminum in small amounts, are needed for most, if not all organisms, but in excess may be toxic [4,5]. Metals can often cause carcinogenic and neurotoxic effects to humans, although the real physiological consequences vary from one metal to another [5]. Usually chromium, copper, zinc and aluminium are associated to metal plating processes [6], reaching the aquatic ecosystem from industrial wastewater, drainage of agricultural areas, mining activities and fossil fuels [5, 7, 8].

Although copper, zinc and aluminium are essential in small doses for humans, they are known to be very toxic, even at low concentration, for some fish and plants [6, 9]. Both marine and freshwater algae species are especially sensitive to copper, being adversely impacted at concentrations as low as 1-5 mg/L. Chromium toxicity in aquatic environment is increased with decreasing pH, alkalinity and hardness [10]. An aquatic organism may present two basic types of behavior

towards metal: it is sensitive to the toxic effect of a given metal or is not sensitive, but bioaccumulate increasing its harmful effects along the food chain [7]. Sharks are susceptible to heavy metals due to the slow elimination and large capacity to incorporate metals [11].

The wide-ranging, oceanic blue shark (*Prionace glauca*) is the main pelagic species captured by Brazilian commercial fishing and locally targeted species. The fins are exported to east Asia and the meat is consumed by Brazilians without real knowledge that is shark meat, since it is marketed as "cação" for better customer acceptance. In addition, Brazil is the largest importer of shark meat and possibly the major consumer of large pelagic shark meat in the world, using imported shark meat as children's meals at public schools financed by the government [12]. United States Environmental Protection Agency - EPA [13] advice women of childbearing age, pregnant and breastfeeding women, and young children to avoid shark meat since it has the highest mercury levels.

It is important to realize that sharks are facing intense fishing pressure, therefore its proper management and conservation are related to more biological studies associated with quantity monitoring of inorganic contaminants in shark meat, as a mean to show the risks that may come to human health by consuming it and at the same time expose marine

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¹ Universidade de Caxias do Sul – Instituto de Saneamento Ambiental (ISAM)

^{*}Email: mpolett1@ucs.br and Vania Elisabete Schneider

environment pollution. Thus, the main goal of present work is to determine metallic trace elements as chromium, copper, zinc and aluminium in *Prionace glauca* using a ICP-OES equipment, while studying the biological aspects such as fork length and approximate age to indicate if there is a metal accumulation, as well as to show the need for further studies of metal concentration in sharks, since the field is currently deficient in Brazil as other authors often evaluate only mercury levels in sharks [14, 15, 16, 17, 18].

II. MATERIAL AND METHODS

A. Sampling

In July 2016, nine blue shark samples were donated by a fishing company from the port region of Itajaí, in the state of Santa Catarina, which operates in the Territorial Sea and the Exclusive Economic Zone (EEZ) of the Southeast and South regions of Brazil, as can be seen in Figure 1, using pelagic longline fishing.

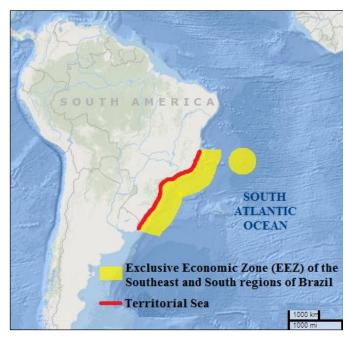


Fig. 1: Map showing the Territorial Sea and the Exclusive Economic Zone (EEZ) of the Southeast and South regions of Brazil.

On arrival at the port, specimens were weighed and sexed in its commercial weight, that is, without head, viscera and dorsal, ventral and caudal fins.

Biometric parameters such as age and fork length (FL) were obtained through equations proposed in the literature. These equations consider the weight of the carcass (commercial weight).

The age of each individual was estimated using the function proposed by von Bertalanffy:

$$Lt = L_{\infty} \left[1 - e^{-k (t-t0)} \right]$$
 (1)

Where Lt is the estimated total length; t represents age in years, the total asymptotic length, $L_{\infty} = 352.1$ cm; the growth coefficient K = 0.157 and the age where the length is theoretically equal to zero, t0 = -1.01 [19].

The fork length (FL) was obtained from the total length through the equation proposed by Hazin et al. [20]:

$$FL = 11.27 + 0.78 \, Lt \tag{2}$$

B. Metal determination

The metal concentration was determined taking about 100 g of skinless muscle from the dorsal region of each shark, between the dorsal and caudal fin, removed with the aid of a scalpel with stainless steel blade and then frozen in plastic bags and transported to the laboratory. The metal determination in the muscle tissue was performed on a wet weight basis through an acid digestion adapted from AOAC Official Method 999.10 [21] and Dias et al. [15], where a mixture of 10 mL of nitric acid (HNO₃), 0.25 mL of hydrogen peroxide (H₂O₂) and 1 g of the sample (taken with a scalpel from the central part of the muscle) kept in a bath-water at 60° C for one hour to perform acid digestion. The resulting solution was filtered and increased to 100 mL with distilled and deionized water. To avoid contamination, all glassware used was previously washed with 10% (v/v) HNO₃ solution according to the procedure recommended by AOAC Official Method 999.10 [21]. After the acid digestion, the metals concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in duplicate.

III. RESULTS

Among the biological aspects obtained from nine evaluated specimens consisted by 8 males and 1 female, ranging from 189 to 230 cm fork length (mean = 202.3 cm), as shown in Table 1, with eight individuals classified as small adults and only one individual classified as a large adult, with a fork length greater than 230 cm, based on classification proposed by Montealegre-Quijano and Vooren [22] with four categories: small young (FL \leq 129 cm); large young (FL 130 to 179 cm), small adults (FL from 180 to 219 cm) and large adults (FL \geq 220 cm). This result indicate that all fish specimens have reached adulthood and corroborate with the approximated age average found of 6.4 years, since sexual maturity of *Prionace glauca* is attained at approximately 6 years of age for males, while females occurs at age 7 [23], although four male sharks presented ages from 5.5 to 5.8 years and the estimated age of the single female evaluated was 6.6 years. This paper even with a small sample found results approximated with other authors, like Montealegre-Quijano and Vooren [22] that captured 4,511 specimens in the same region of this study, being 4,068 males and 443 females with a majority of large young sharks during the winter and Hazin et al. [24] that sampled 810 specimens in the southwestern region of the equatorial Atlantic Ocean, where 652 specimens were males and 158 females with most individuals classified as small adults during the winter.

Sex	Shark fork length (cm)	Shark total length (cm)	Approximated age (years)	
Male	189.56	226.36	5.545	
Male	191.51	228.71	5.665	
Male	191.51	228.71	5.665	
Male	193.42	231.00	5.784	
Male	200.59	239.63	6.254	
Male	203.95	243.62	6.487	
Female	205.58	245.62	6.603	
Male	214.71	256.62	7.297	
Male	230.49	275.60	8.708	

Tab. 1: Biological aspects obtained from the nine shark specimens evaluated.

The results for chromium (Cr), copper (Cu), zinc (Zn) and aluminium (Al) average concentrations measured in muscle of the blue shark for the present work and similar studies are presented in Table 2. The maximum allowable regulatory limits for metals in Brazil and by international agencies can be seen in Table 3.

Tab. 2: Metal concentrations (mg/kg) found in muscle samples from different studies with *Prionace glauca*.

Reference	n	Cr	Cu	Zn	Al	Geographic region
Present work	9	0.14	0.98	5.38	1.70	S Atlantic
Machado [25]	6	-	0.12	2.98	1.03	Unknown
Alves et al. [26]	20	2.58	1.15	24.61	23.77	N Atlantic
Olmedo et al. [27]	11	-	0.14	1.95	-	N Atlantic
Vas [28]	5	-	0.24	0	-	N Atlantic
Stevens & Brown [29]	8	-	4.40	35.00	-	N Atlantic
Barrera-García et al. [30]	44	-	1.64	6.10	-	Pacific

*n = number of sharks evaluated.

Tab. 3: Maximum			

Contaminant	Brazil (1965)	SCF (2006)	IOM (2001)	EFSA (2008)		
Chromium	0.10 mg/kg	0.25 mg/day	-	-		
Copper	30.00 mg/kg	5.00 mg/day	10.00 mg/day	-		
Zinc	50.00 mg/kg	25.00 mg/day	40.00 mg/day	-		
Aluminium	-	-	-	1.00 mg/Kg *bw/week		
Source: $\operatorname{Brazil}[21]$: SCE [22]: IOM [22] and EESA [24] *by = body weight						

Source: Brazil [31]; SCF [32]; IOM [33] and EFSA [34]. *bw = body weight.

Average total chromium content was 0.14 mg/kg (wet weight), which exceeds maximum limit legalized by Brazilian decree n. 55871 [31] of 0.10 mg/kg for any kind of food. The European Food Safety Authority – EFSA on the Scientific Committee on Food [32] regulates the maximum amount of total chromium intake at 0.25 mg/day for adults in all kind of food. The samples ranged from 0.0 to 0.44 mg/kg, with 44% of samples above the Brazilian legislation and one sample almost 5 times above permitted by law. Alves et al. [26] recently assessed 20 specimens of blue sharks from North Atlantic Ocean at the southwest coast of Portugal, finding an alarming total chromium average of 2.58 mg/kg, result that overcome seventeen times this study average concentration.

Total copper average concentration was 0.98 mg/kg (wet weight), result much lower than the Brazilian legislation limit that is 30 mg/kg for any kind of food [31] and the United States Institute of medicine recommends 10 mg/day intake, from food and supplements [33]. The present work results are similar with those found by Alves et al. [26] who determined total copper average of 1.15 mg/kg and Barrera-García et al.

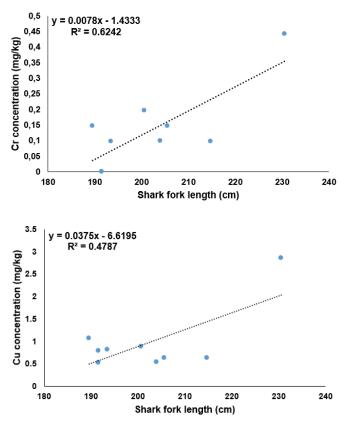
[30] who found average of 1.64 mg/kg in blue sharks fished from Pacific Ocean at Mexico west coast. Machado [25] determined lower levels of copper 0.12 mg/kg (mean) in blue sharks purchased in São Paulo state (Brazil) of the municipal market, therefore, the fishing location is very difficult to determine, since shark meat may derive from many cities, states and countries.

The average of total zinc concentration determined was 5.38 mg/kg (wet weight) within the parameters of maximum limit legalized by Brazilian decree n. 55871 [31] of 50 mg/kg, pointing out that it has not been revised since 1965. International agencies like the Institute of Medicine – IOM [33] and the European Food Safety Authority – EFSA [32] indicate the tolerable upper intake level for adults as 40.00 mg/day and 25.00 mg/day, respectively. Barrera-García et al. [30] obtained very similar results, determined a total zinc average concentration of 6.10 mg/kg. However, Alves et al. [26] and Stevens & Brown [29] who caught blue sharks from North Atlantic Ocean, had extremely high results when compared to the present study, presenting total zinc trace

elements of 24.61 mg/kg and 35.00 mg/kg, respectively. Large amounts of ingested zinc can inhibit the absorption of copper in humans, causing copper deficiency.

Total aluminium average content was 1.70 mg/kg (wet weight), ranging from 0.24 to 6.34 mg/kg. Brazilian laws do not regulate aluminium intake levels in food, although the European Food Safety Authority establish a value of 1.00 mg/kg body weight per week [34]. Recent studies as Alves et al. [26] and Machado [25] determined aluminium trace elements in blue shark's muscles, finding averages of 23.77 mg/kg and 1.03 mg/kg, respectively.

As data shown in Figure 2, a significant positive correlation was found between some metals and sharks fork length. Aluminium had the most significant positive correlation ($r^2 = 0.80$, p < 0.001), followed by chromium ($r^2 = 0.62$, p < 0.05), copper ($r^2 = 0.47$, p < 0.05) and zinc, which presented no significant correlation ($r^2 = 0.15$, p > 0.05). These results corroborate the bioaccumulation of some metals in *Prionace glauca* muscle tissue, a phenomenon where toxic substances accumulate in tissues as the specimen grows and can promote biomagnification as these substances are transferred into the food chain, changing environment and its populations, destroying communities of organisms and causing effects on the ecosystem as a whole [6].



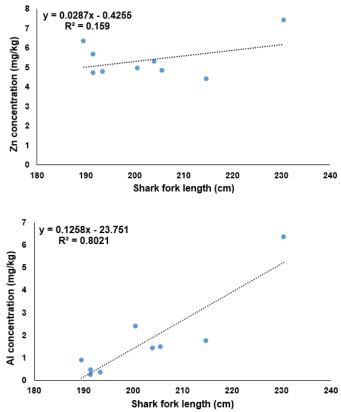


Fig. 2: Relationship between shark fork length and metal concentrations (chromium, copper, zinc and aluminium).

IV. CONCLUSIONS

The analyzed data in the present study showed that Prionace glauca capture during the winter in the Southeast-South regions of Brazil, consists mostly by small adult males (considering fork length), which can trigger an imbalance in the species population structure. The metal determination indicated that total chromium tops the maximum limit permitted by Brazilian legislation in 44% of the tested samples and that total copper, zinc and aluminium was well below the tolerable levels by Brazilian and international agencies, who have different metals intake recommendations, mainly because there is no consensus on the information obtained in several studies and sparse data on some metals (chromium e.g.) essentiality and metabolism. Positive correlation between some metals analyzed (aluminium, chromium and copper) and fork length showed that specimens evaluated can bioaccumulate metals in their muscle tissue, presenting the need for further studies in this field.

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