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Original Research Article

Heavy metal concentrations in two important fishes caught in artisanal fisheries of southeastern pacific waters

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Sebastian A. Lopez[1*], Nicole Abarca[1], Francisco Concha[2,3] and Roberto Meléndez[1]

[1]Centro de Investigacion Marina Quintay CIMARQ. Escuela de Ciencias del Mar, Universidad Andres Bello. Republica # 440, Santiago, Chile.
[2]Laboratorio de Biología y Conservación de Condrictios, Universidad de Valparaíso, Chile.
[3]Department of Ecology and Evolutionary Biology, University of Connecticut. # 75 North Eagleville – unit 3043, Storrs CT, U.S.A.

*Corresponding Author
E-mail: s.lopez@uandresbello.edu
Tel.: +56322362055

Muscle tissues of 102 yellownose skate (*Zearaja chilensis*) and 51 plownose chimaera (*Callorhinchus callorhynchus*) caught as bycatch in the artisanal fisheries of common hake were analyzed to determine the concentrations of mercury (Hg) and lead (Pb) measured by cold vapour and acetylene flame methods, respectively. Mercury concentration showed no differences in the studied species (p=0.1413) with 0.088 ± 0.05 μg·g^{-1} w.w. for *Z. chilensis* and 0.044 ± 0.18 μg·g^{-1} for *C. callorhynchus*. The same situation occurred in lead concentration (p=0.986) for the skate and chimaera. However, the two studied species showed higher values of Pb, with 2.48 ± 2.50 μg·g^{-1} and 2.47 ± 3.11 μg·g^{-1}. Based by WHO values, mercury concentrations reported in this study will not constitute a risk for human health, in contrast to the high contributions of lead that were found in the different tissues of the yellownose skate and the plownose chimaera, in which there will be a risk for human consumption.

Key words: Public health, fish human consumption, fisheries, elasmobranchs

INTRODUCTION

The yellownose skate *Zearaja chilensis* (Guichenot, 1848) and plownose chimaera *Callorhinchus callorynchus* (Linnaeus, 1758) are two important artisanal fishery resources (SUBPESCA, 2012) operating in the continental slope from eastern South America (central Peru) to southwest Atlantic waters (south Brazil) (DiGiacomo and Perier, 1996; Bustamante et al., 2012). In this fishing zone these target species show an annual mean landing of 3000 and 4700 tons for *Z. chilensis* and *C. callorynchus*, respectively (DiGiacomo and Perier, 1996; Aedo et al., 2009; Alarcon et al., 2011; Bustamante et al., 2012; SUBPESCA, 2012). Additionally, these fishes also are highly frequent as bycatch in the artisanal fisheries of common hake and flounder (Lamilla et al., 2011) and according to reports of (Agnew et al., 2000 and Lamilla et al., 2011) these cartilaginous fishes constitute more than 60% of the total species captured by the artisanal fisherman.

The concern based on worldwide fishing pressures on elasmobranch fishes has been widely reported (Myers et al., 2007; Baum and Worm, 2009; Tremblay-Boyer et al., 2011), mainly due to their *K*-selected life history parameters (Cortes, 1999; Navia et al., 2010) such as low fecundity and slow growth, and also due to the important role they play in the marine food webs which give structure to the ecosystem and also provide balance in the trophic cascade (Lopez et al., 2009; Lopez et al., 2010).

Despite the importance of these fishes in South American waters, few studies have been done on the exploited

Table 1. Mean values of mercury and lead concentration of different elasmobranch species around the world

Species	Mercury	Lead	Region	References
	µg·g^{-1}			
Skates				
Raja kenojei	0.17	0.072	East China Sea	Asante et al., 2008
Raja kwangtungensis	<0.05	0.085	East China Sea	Asante et al., 2008
Bathyraja spinicauda	0.03	<0.3	Barents Sea	Zauke et al., 1999
Raja radiata	0.18	<0.3	Barents Sea	Zauke et al., 1999
Raja fyllae	0.45	<0.3	Barents Sea	Zauke et al., 1999
Chimaeras				
Chimaera lignaria	0.9	-	Southeast Australian waters	Pethybridge et al., 2010
Rhinochimaera pacifica	0.5	-	Southeast Australian waters	Pethybridge et al., 2010
Other demersal sharks				
Heptranchias perlo	0.3	0.152	East China	Asante et al., 2008
Etmopterus lucifer	<0.05	0.17	East China	Asante et al. 2008

populations of *Z. chilensis* and *C. callorynchus*. For instance in the southeastern Pacific waters, (Licandeo et al., 2006; Quiroz et al., 2009; Bustamante et al., 2012 and Concha et al., 2012) studied reproductive aspects. (Bahamonde et al., 1996) conducted a preliminary stock assessment and (Quiroz et al., 2011) concluded the vulnerability of the yellownose skate to fishing effort, whereas in Atlantic waters no biological information is available. On the other hand, the biological data reported for the plownose chimaera are similar in Pacific and Atlantic waters; including feeding (DiGiacomo and Perier, 1996), morphological studies (Alarcon et al., 2011; Reiser and Ferry, 2011), geographical distribution (Lopez et al., 2000) and biogeographic studies (Luque and Iannacone, 1991; Lisney, 2010).

The elasmobranch fishes accumulate trace elements in their tissues such as mercury (Hg), arsenic (As), lead (Pb) and cadmium (Cd) (Pethybridge et al., 2010; Barrera-García et al., 2012), largely through the diet (Maz-Courrau et al., 2012). Mercury and lead are volatile and highly toxic contaminants present in marine ecosystems (Pethybridge et al., 2010). Elasmobranch fishes are more susceptible to the uptake and biomagnification of these heavy metals because they have a very efficient process to incorporate those metals and a slow mechanism for eliminating them (Wang, 2002; Wang et al., 2002; Xu and Wang, 2002; Maz-Courrau et al., 2012). Even though batoids and chimaeras are highly exploited around oceans, the knowledge about heavy metals in them is very poor and studies on trace metal concentrations in tissues of *Z. chilensis* and *C. callorynchus* have been not conducted. A few studies reported the concentration of heavy metals in different benthic sharks and skates, which are summarized in Table 1.

In the southeastern Pacific Ocean off Chile, there is no current regulation on concentrations of Hg and Pb in tissues of fishes for human consumption. The European Union (EU) and the Food and Agriculture Organization (FAO)/World Health Organization (WHO) have established limits for these heavy metals, which are 1.0 µg·g^{-1} and 0.3 µg·g^{-1} wet weight for Hg and Pb, respectively (WHO, 2003; Official European communities, 2006; Official European communities, 2008). Incidents of heavy metal exposures in human communities are well documented in Japan and Iraq, indicating severe toxic effects (Harada, 1995).

There has been widespread public concern over the bioaccumulation of heavy metals through the consumption of shark meat by humans; following this idea, the main goal of this study was to determine the mercury and lead concentration in muscular tissues of two elasmobranch species of the southeastern Pacific waters that are consumed by humans.

MATERIALS AND METHODS

Between January 2009 and February 2012 one hundred and fifty three individuals were collected as a *by*-catch in the artisanal fisheries of common hake (*Merluccius gayi*) and flounder (*Paralichthys* spp.) off Valparaíso, Chile (33°S, 75°W). Of these specimens, 102 (60 females [f] and 42 males [m]) were *Z. chilensis* and 51 (21f/30m) were *C. callorynchus*. Sexes were determined on-board; ~1.0 g of muscle from the dorsal part of the body was taken and frozen at -20 °C until processing in the laboratory.

Laboratory analysis

All laboratory material was previously decontaminated for two days with HNO_3 (20%) (Branco et al., 2007) and later washed with milli-Q water. The tissues were digested with 65% HNO_3 using a microwave system (Gutleb et al., 2002; Boscher et al., 2010) and analyzed with a Shimadzu AA-6200 atomic absorption spectrophotometer (AAS). Hg was measured by a hydride vapor system HV-1(cold vapour technique) and Pb via acetylene flame (Gutleb et al., 2002;

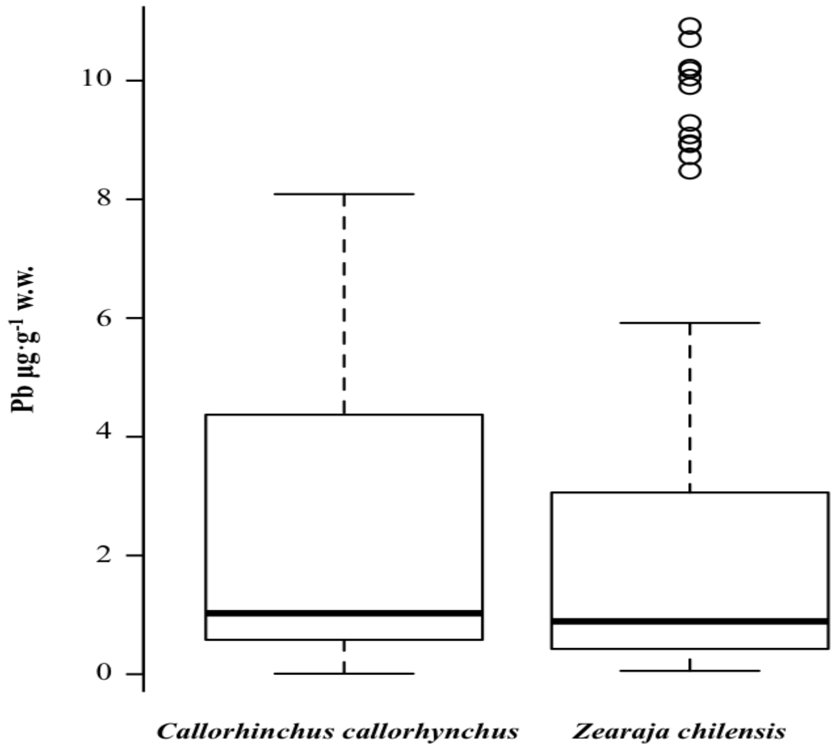

Figure 2. Lead comparison between yellownose skate (*Zearaja chilensis*) and plownose chimaera (*Callorhinchus callorhynchus*) off Valparaíso, Chile. (O = outliers).

Branco et al., 2007; Boscher et al., 2010). The AAS was calibrated using Custom Grade standards, with detection limits of 0.007 $\mu g \cdot g^{-1}$ for mercury (CertiPUR® Merck 1000 mg/L) and 0.0088 $\mu g \cdot g^{-1}$ for lead ($PbCl_2$). For quality control periodic analysis of an aliquot from a large sample of known concentration was included that represented about 15% of the total samples analysed.

Data analysis

The Shapiro-wilks test was used to verify the normality of data and a one-way ANOVA followed by a Tukey *post hoc* test (Zar, 2010) was used to compare the concentrations of heavy metals between species and sexes. The R software (R Core Team, 2013) was used to perform the statistical analyses.

RESULTS

All tissues from the analyzed specimens presented values above the limit indicated by AAS (0.007 $\mu g \cdot g^{-1}$ Hg and 0.0088 $\mu g \cdot g^{-1}$ Pb). The mean concentration of mercury in individuals of *Z. chilensis* was 0.088 ± 0.05 (± standard deviation) $\mu g \cdot g^{-1}$ while the mean concentration of lead was 2.48 ± 2.5 $\mu g \cdot g^{-1}$. The plownose chimaera showed a mercury mean concentration of 0.044 ± 0.18 $\mu g \cdot g^{-1}$ and a mean lead concentration of 2.47 ± 3.11 $\mu g \cdot g^{-1}$ in their muscle tissues. Mercury concentration was not different between *Z. chilensis* and *C. calloryncbus* (F=2.19, p=0.1413). However it should be noted that the yellownose skate presented a high concentration of Hg (Figure 1) in comparison with the chimaera. No significant value was found in the lead concentration between the two species (p=0.986) (Figure 2).

According to international agencies (EU and FAO/WHO), the mean values found of Hg in both species were below the permissible limit for human consumption (<1.0 $\mu g \cdot g^{-1}$). However, two individuals of *Z. chilensis* of the sampled population showed values above the permissible limit (Figure 3). In contrast, the lead concentrations in both species were above the limit proposed by the international agencies (<0.3 $\mu g \cdot g^{-1}$). Thus 82.4% (n=42) of the population sampled of *C. callorynchus* presented high values of lead, while the 73.5% (n=75) of *Z. chilensis* individuals showed values above the standard approved for human consumption (Figure 4).

The values of lead and mercury in the sexes of *Zearaja chilensis* and *Callorhinchus callorynchus* are summarized in Table 2, showing that females and males of *Z. chilensis* presented a mean of mercury of 0.049 ± 0.05 and 0.02 ± 0.005 $\mu g \cdot g^{-1}$ respectively. The statistical analysis showed no difference between the sexes in the studied species (p=0.1022). The mean of lead found in males of the

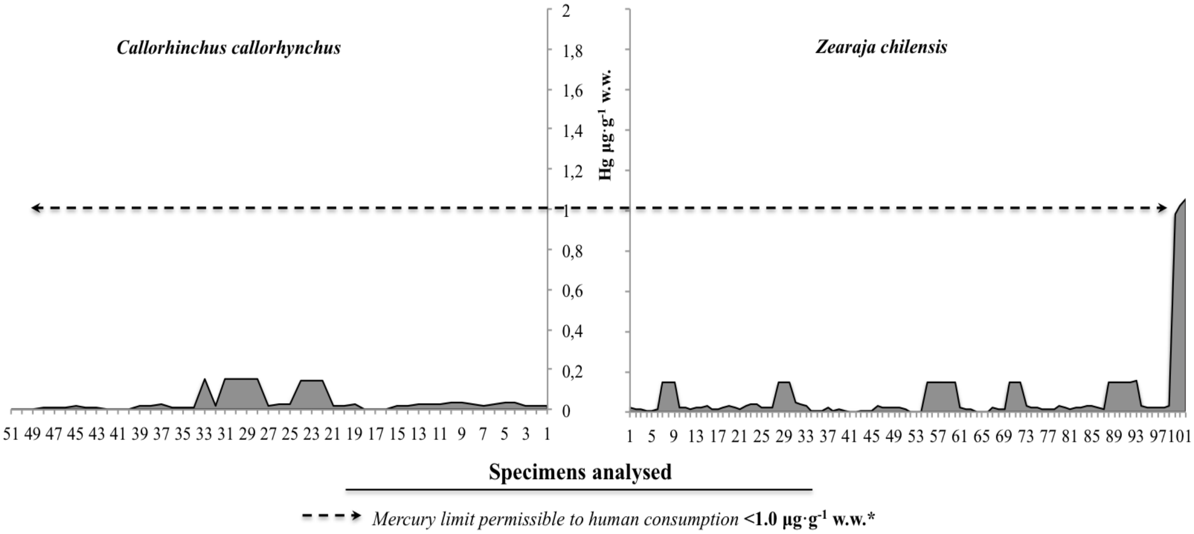

Figure 3. Individual accumulation of mercury in the tissues of yellownose skate (*Zearaja chilensis*) and plownose chimaera (*Callorhinchus callorhynchus*) off Valparaíso, Chile

Table 2. Mean values of Hg and Pb from males and females of *Zearaja chilensis* and *Callorhinchus callorhynchus* off Valparaíso, Chile. ± Standard deviation and *n,* number of individuals sampled.

	Hg	Pb	*n*
	$\mu g \cdot g^{-1}$ w.w.		
Z. chilensis female	0.049 ± 0.05	2.48 ± 3.1	60
Z. chilensis male	0.02 ± 0.005	1.35 ± 1.93	42
C. callorhynchus female	0.015 ± 0.009	1.96 ± 2.74	21
C. callorhynchus male	0.052 ± 0.06	2.43 ± 2.32	30

yellownose skate was 2.48 ± 3.01 and in females was 1.35 ± 1.93 $\mu g \cdot g^{-1}$. Likewise with values of the mercury, no statistical differences were found between the sexes (p=0.2308).

The females of the plownose chimaera showed a mercury concentration of 0.02 ± 0.009 $\mu g \cdot g^{-1}$, while males presented a concentration of 0.05 ± 0.06 $\mu g \cdot g^{-1}$, which is statistically different (F=7.86, p=0.007). The mean lead value found in females was 1.96 ± 2.74 $\mu g \cdot g^{-1}$ and in males was 2.43 ± 2.32 $\mu g \cdot g^{-1}$; the difference was not significant (p=0.4338). On the individual level, 66.7% (n=14) of the females showed high levels of lead and 93.3% (n=28) of males exhibited values above the permissible limit for human consumption.

DISCUSSION

This study is a first approach in the study of heavy metal concentrations in yellownose skate and plownose chimaera. Both species showed a lower concentration of mercury in their tissues (<1.0 $\mu g \cdot g^{-1}$) and higher levels of lead, above the limits permitted by the EU and FAO/WHO (<0.3 $\mu g \cdot g^{-1}$). Females and males of both species also showed a lower concentration of mercury and a higher concentration of lead, respectively. However, chimaera males accumulated more mercury than females. This difference may be due to the type of food consumed and their type of habitat, as suggested by Barrera-García et al. (2012), who attributed these parameters to the differences in food habits between the sexes. Therefore, we also infer that the prey of males have a greater mercury concentration compared to the prey of females. In this vein, McIntyre and Beauchamp, (2007) suggested that there are differences between the types of habitat, thus benthic individuals show high mercury concentration compared with fishes that have pelagic habits. This is consistent with Aedo et al., (2009), who reported that males of plownose chimaera spend more time in the benthic zone than females, who inhabit the water column, which is coherent with the type of food consumed by plownose chimeara individuals (Di Giacomo and Perer, 1996).

Compared to other species of skates and chimaeras (Table 1), *Z. chilensis* showed similar values of mercury but a higher concentration of lead, while *C. callorhynchus*

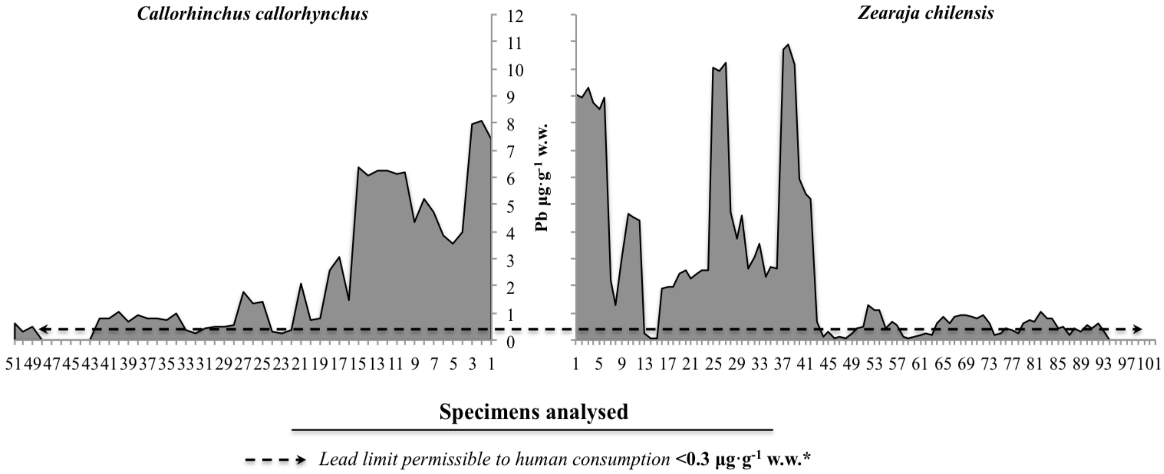

Figure 4. Individual accumulation of lead in the tissues of yellownose skate (*Zearaja chilensis*) and plownose chimaera (*Callorhinchus callorhynchus*) off Valparaíso, Chile

showed a low value of mercury compared to other chimaeras such as *Chimaera lignaria* and *Rhinochimaera pacifica*. Unfortunately no data are available to compare the values of lead. In comparison with other demersal sharks the mercury shown by the sampled individuals was similar, (Table 1). The low mercury concentration in the marine environment is an expected situation because of its high volatility (Pethybridge et al., 2010). On the other hand, recently studies (Calderon and Valdes, 2012, Muñoz , 2012, Valdes, 2012) found high levels of lead and cadmium in South Pacific waters, which is totally consistent with the high levels of lead found in this work. This is probably the best reason why mercury is low in the tissues of studied specimens. In fact, Blazka et al. (1992) found in isolated hepatocytes cells of the skate *Raja erinacea* that mercury was inhibited by cadmium and rather was increased in with presence of mercury (Blazka and Shaikh, 1992) which is coherent with the enrichment of cadmium for the Pacific waters in the last decades (Muñoz, 2012).

The concentration of lead reported in this study probably constitutes a risk for human health because the concentration exceeded the limit value proposed by international agencies (Figure 3 and 4), confirming the potential risk to human health. Lamilla et al. (2011) identified the final destination of elasmobranch landings in the artisanal fisheries as fin-sale, local consumption and fishmeal. Thus it is not safe to consume fins, meat or fishmeal from yellownose skate and chimaera. Fishmeal of these fishes is used to make pellet food given to farm fishes such as salmon, which is an important component in the human diet (Vizzini et al., 2010). The risk to humans by lead because of fish consumption is poorly known; it may involve cancer (mainly gastrointestinal), neurotoxicity, immunotoxicity, cardiotoxicity, reproductive toxicity, teratogenesis and genotoxicity (González et al., 2012).

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