Understanding the role of ecological factors affecting mercury concentrations in the blue shark (Prionace glauca)

Lola Riesgo a, b, Carola Sanpera b, Salvador García-Barcelona c, Moisès Sánchez-Fortún b, Marta Coll a, Joan Navarro a, *

a Institut de Ciències Del Mar (ICM), CSIC, Barcelona, Spain
b Departament de Biologia Evolutiva, Ecologia i Ciències Ambientals, Universitat de Barcelona, Barcelona, Spain
c Instituto Español de Oceanografía (IEO), CSIC, Delegación de Málaga, Fuengirola, Spain

HIGHLIGHTS

- Marine predators are good sentinels for monitoring pollutants.
- Geographic area and body size determine blue shark Hg concentrations.
- Mediterranean blue sharks showed higher Hg values than Atlantic ones.
- Most blue sharks showed Hg values exceeding the human consumption limits.

ABSTRACT

Human activities have increased environmental concentrations of pollutants in marine ecosystems, which can cause harmful effects on marine organisms. Top predators are particularly susceptible to bioaccumulation and biomagnification of pollutants through the food webs and are described as good sentinels for monitoring metal accumulation such mercury (Hg) in marine ecosystems. However, to be used as sentinels, it is important to understand the main ecological factors affecting the concentrations of pollutants in these organisms. In the present study, our main objective was to investigate the effect of body size, sex, trophic niche and geographic area on Hg concentrations in a top marine top predator, the blue shark (Prionace glauca). We analysed Hg in muscle samples from male and female blue sharks of different body sizes collected from the waters surrounding the Canary Islands and the South of Portugal, in the Atlantic Ocean, to waters of the north-western Mediterranean Sea. The results revealed that the sampling area was an important factor explaining Hg concentrations, showing higher values in the Mediterranean blue sharks. We also found a positive relationship between Hg concentrations and body size of blue sharks, indicating a bioaccumulation process of this pollutant in relation with body size. Moreover, we observed a relationship between Hg concentrations and δ13C values, a proxy of the use of inshore-offshore marine habitats. Individuals with depleted δ13C values that potentially foraged in offshore waters showed higher Hg values. Importantly, most of the analysed blue sharks presented Hg concentrations that exceeded the limits established by the European Union for human consumption.

* Corresponding author.
E-mail address: joan@icm.csic.es (J. Navarro).

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1. Introduction

The diversity and number of pollutants dispersed into the environment by anthropogenic activities has become problematic at a worldwide scale (Aktar et al., 2009; Halpern et al., 2008). Marine environments receive inputs of chemicals from irrigation waters from agriculture or industry, among others (Boehm et al., 2017; Ramirez-Llodra et al., 2011). Given their high toxicity and persistence, these pollutants cause harmful and negative effects in marine fauna, which in turn could affect human health (e.g. Alves et al., 2016; Storelli et al., 2020). Among them, mercury (Hg) is of particular concern due to its affectation on the immunological, reproductive, hormonal, and nervous systems, and, which could damage both in individuals and in whole populations (Furness, 2018).

Hg inputs from natural sources include volcanic activity and forest fires, nevertheless, the major part of the Hg present in the aquatic habitats and atmosphere has a human origin (Boening, 2000). Hg is present in different chemical compounds and forms compounds, and exhibits a particular dynamic in comparison with other pollutants as it biomagnifies along the food webs and is able to bioaccumulate in organisms (Hilgendag et al., 2022; Lavoie et al., 2013). In aquatic ecosystems, Hg can be methylated thereby transformed into methylmercury (MeHg), the most toxic form of Hg for biota. In addition to the effect of abiotic and biotic processes in mercury methylation, microbial methylation is considered the main pathway in this compound to the environment, being the sulphate-reducing bacteria the most important methylating agents. Such process occurs in sub-thermocline low-oxygen oceanic waters, and in the sediment where organic matter is highly remineralized (Bloom, 1992; Fitzgerald et al., 2007). Inorganic Hg passes through biological membranes, being available for microbial methylation in cellular cytoplasm, it gets transformed into MeHg and thereafter, it is assimilated through diet by higher trophic level organisms causing biomagnification through the food webs (Hoffman et al., 2002).

Biomagnification has been widely studied in aquatic ecosystems, being comparable among diverse ecosystems, source and concentrations of Hg (Hilgendag et al., 2022; Lavoie et al., 2013; Watras et al., 1998). In animals, dietary uptake is the main pathway for Hg assimilation (Hall et al., 1997). After passing through the intestine, given the high affinity of Hg to sulfhydryl protein groups (-SH), Hg is sequestered in muscle hindering its excretion and elimination from muscle tissues (Maulvault et al., 2016; Wang and Wong, 2003). Thus, Hg concentrations tend to bioaccumulate with size and age, which outcomes from the slow degree of removal relative to its fast degree of uptake.

Sharks play a unique and pivotal ecological role in marine ecosystems as top predators (Heithaus et al., 2008). Due to its long-lived strategies, sharks are particularly susceptible to accumulate high levels of pollutants, including Hg (Alves et al., 2016, 2022; Branco et al., 2007). However, despite the fact that information on these pollutants in top predators is paramount for improving knowledge about their biotransference, published information on metal content for shark species at global scale is scarce (McKinney et al., 2016; Pethybridge et al., 2010). Also, since the fishing captures of some shark species for human consumption have increased in recent years (Dulvy et al., 2008), it is...
through diet, the incorporation of Hg is transferred to higher trophic levels throughout ocean basins. Since Hg is transferred to higher trophic levels, it is necessary a more accurate pollutant monitoring in these species (Storelli et al., 2020).

The blue shark (Prionace glauca) is a highly mobile pelagic shark inhabiting temperate and tropical waters of all oceans frequently captured by drifting longlines or as bycatch in pelagic fisheries worldwide (Druon et al., 2022), being considered the most frequent elasmobranch in the international trade of shark fins (Clarke et al., 2006).

From a conservation point of view, steepest population declines have been documented, and therefore, differences in Hg bioaccumulation and biomagnification among different ecosystems are not yet well understood (Lavoie et al., 2013).

In this study, the main aim was to examine the Hg concentration in the muscle of blue sharks sampled in western Mediterranean Sea, South of Portugal, and the Canary Islands to determine the influence of size, sex, trophic ecology tracers (stable isotopes), and spatial distribution on Hg levels in individuals. Furthermore, based on our results, we aimed to evaluate the risk of its consumption to human health and discuss its possible use in biomonitoring programmes.

2. Material and methods

2.1. Sampling procedures

During the years 2017 and 2018, a total of 141 blue sharks were opportunistically collected as bycatch by Spanish commercial longline vessels targeted swordfish (Xiphias gladius) along a wider geographic area, between the south of the Canary Islands and the Atlantic Ocean, and the north-west of the Mediterranean Sea (Fig. 1). As the major part of the individuals were released alive after the capture, for each individual, we only measured the fork length with a ruler (±0.1 cm) and sex (visually), and collected a small portion (1 cm) of white muscle from above the dorsal fin with sterilized scalpels. Muscle samples were stored on-board at −20 °C until Hg and stable isotopic determination.

2.2. Mercury determination

Total mercury concentrations (THg) (ng/g dry weight) were determined by combustion in 20–30 mg of lyophilized dry muscle samples using a Direct Mercury Analyzer (Milestone® DMA-80). Accuracy and precision were assured by analysing dogfish liver (DOLT-3; reference from the NRCC) every 10 samples. The obtained THg recoveries for the DOLT-3 analyses ranged from 80 to 90% of the certified values, thus, we did not apply any corrections to the THg values. THg concentration levels of samples were initially expressed as THg dry weight concentration in muscle (ng/g dry weight). In addition, to allow comparisons with other studies, those values were converted into wet weight concentrations, considering a factor 1:5 dw/vw (Cresson et al., 2014).

2.3. Stable isotope analysis

After removing the urea content from the muscle samples (following the procedures of Kim and Koch, 2012), isotopic determination was conducted at LIE-EBD (Stable Isotopes Lab, Estación Biológica de Doñana, Spain) by using an isotope-ratio mass spectrometry system by means of a Flash HT Plus analyser coupled to a Delta-V Advantage isotope ratio mass spectrometer via a CONFLO IV interface (Thermo Fisher Scientific). The isotopic composition was reported in the conventional delta (δ) per mil notation (%), relative to atmospheric N2 (δ15N) and VPDB (δ13C). The analytical errors were of ±0.1% and ±0.2% for δ13C and δ15N, respectively. No lipid correction of the δ13C values was applied because the C:N ratio of the isotopic values was lower than 3.5 (Logan et al., 2008).

2.4. Statistical analyses

To examine the potential differences in total mercury concentration, body size (FL), δ15N (as a proxy of trophic position) and δ13C (as a proxy of habitat source) values between sexes and geographical sampling locations, two-way ANOVA tests were used. Post-hoc tests (Tukey tests) were applied when significant differences based on the ANOVA tests were observed. Before the ANOVA tests, all variables were checked for normality and homoscedasticity considering each sampling area.
separately by using Kolmogorov-Smirnov tests and residual plots. Based
on the normality tests, for $\delta^{13}$C values, we compared between sexes and
sampling locations by using Kruskal-Wallis and U-Mann-Whitney tests.

To investigate the effect of FL, $\delta^{15}$N values, $\delta^{13}$C values and sampling
location on the variability of Hg concentrations, Generalized Linear
Models (GLMs) were applied. FL (when considering size-related trends)
and isotopic values (when considering isotopic-related trends) were the
continuous explanatory variables in the models, while area (a categori-
cal variable) was included as an interaction factor. As it is common in
contaminants variables, GLMs were fitted to raw Hg values with log-link
function and Gamma distributions (Chouvelon et al., 2018). Differences
in Hg values between males and females were tested firstly, but since
there was no effect, the sex was removed from the final GLMs.

The models performed were based on the algorithm:
$\log \{THg\} \sim FL + Zone$ and $\log \{THg\} \sim Zone + \delta^{15}$N + Zone $\times$
$\delta^{13}$C

For each model, we retained the variables based on the Akaike In-
formation Criterion (AIC). We checked the homogeneity and normality
in model residuals, as well as the independence (Zuur et al., 2010). For
all cases, we considered a $p < 0.05$ as the level of statistical signifi-
cance. Statistical analyses were performed using R v.4.0.3 (R Development
Core Team, 2020).

3. Results

3.1. Differences between sexes and sampling areas in the stable isotopes,
body size and mercury concentrations

Total Hg concentrations (THg) in muscle of blue sharks differed
among sampling areas, showing the highest values in the western
Mediterranean, followed by Canary Islands and South of Portugal (Ta-
bles 1 and 2, Figs. 1 and 2, and Table S1 in Supplementary Information).
Regarding the fork length, we found that males presented higher values
of THg than females (Tables 1 and 2; Fig. 2), and the individuals sampled
in the western Mediterranean showed lower fork length than the in-
dividuals sampled in Atlantic waters (Tables 1 and 2, Fig. 2). Analo-
gously, we found significant differences in $\delta^{15}$N values between the
Mediterranean Sea and both Atlantic areas (Tables 1 and 2, Fig. 2). In
contrast, no differences were found in $\delta^{13}$C values among sampling areas
and only between sexes for the individuals sampled in Canary Islands
(Tables 1 and 2, Fig. 2).

3.2. GLM results

In the GLM models, the total deviance explained for the variability of
THg was high, ranging between 61.48% for size-related and 60.46% for isotopic-related trends (Table 3), showing similar effects. In the case of the size-related trends (based on the fork length), for the three sampling areas, THg concentrations increased significantly with fork length (Table 3, Fig. 3), being the intercept significantly higher for blue sharks sampled in the western Mediterranean than for Atlantic ones. The relationship between δ15N and THg did not show significant differences among areas (Table 3, Fig. 3). In the case of δ13C values, we found different relationships between THg concentrations and δ13C among areas (Fig. 3).

### 3.3. Comparison of Hg concentrations with legislation limits

The European Commission set maximum level for Hg in shark, tuna or some demersal fish for human consumption up to 1 mg kg⁻¹ ww for seafood (Commission Regulation (EC) No 1881/2006). In the present study, 71.42% of the samples from the Mediterranean Sea exceed the legal limit, 31.42% in the South of Portugal and 68.29% in the Canary Islands (Fig. 2).

### 4. Discussion

In the present study, we examined the proximate factors influencing the Hg values in blue sharks in a wide geographic area from the western Mediterranean and the Canary Islands, in the Atlantic Ocean. Specifically, we investigated the effect of biological parameters such as sex and body size, and ecological parameters related to trophic ecology and spatial distribution (Atlantic Ocean vs. Mediterranean Sea) on Hg concentrations in muscle samples of the species. Also, we discuss whether blue shark consumption could be a human health issue and the suitability of this species as a bioindicator in marine biomonitoring programmes.

Hg values for the blue sharks sampled in Canary Islands and South of Portugal were similar to those reported for pelagic sharks from Atlantic waters (Alves et al., 2022; see Table 4), as well as other Atlantic top predators such as the black scabbard fish (Aphanopus carbo) (Afonso et al., 2007), or swordfish (Xiphias gladius) (Biton-Porsmoguer et al., 2022). In contrast to the Atlantic sampling areas, the individuals analysed from the western Mediterranean Sea showed higher Hg values, as has been previously reported for other marine species (Andre et al., 1991; Chouvelon et al., 2018; Cinnirella et al., 2019; Damiano et al., 2011). Those differences may be partially explained by the “Mediterranean Hg anomaly”, that indicates that Mediterranean organisms have a high Hg bioaccumulation (Cinnirella et al., 2019; Cossa et al., 2022). It has been proposed that the differences between the Hg concentration in the Mediterranean biota compared to other oceanic regions could be explained by the presence of higher Hg methylation associated to the higher sea temperatures of this semi-enclosed sea (Bacci, 1989; Cinnirella et al., 2019; Cossa et al., 2022). The potential impact of sea-surface temperature differences could also explain the elevate Hg bioaccumulation showed in the Mediterranean blue sharks. Warmer Mediterranean waters may increase mercury bioaccumulation in biota’s tissues and, on the other hand, it could affect their ability to eliminate contaminants (Maulvault et al., 2016). Moreover, the high Hg values observed in the blue sharks sampled along the western Mediterranean Sea could be also explained by the high level of anthropogenic impact associated to the numerous mining and chemical industries placed in this region (Morillo et al., 2004; Palanques and Díaz, 1994).

### Table 3

Results of the final GLM models explaining THg concentrations variability in the muscle of blue shark. Akaike Information Criterion (AIC) values, the total deviance explained (DE) are added. Estimates and significance (p-values) for each term included are also given.

<table>
<thead>
<tr>
<th>Variables (equation terms)</th>
<th>Estimates p-value</th>
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<td>Log(</td>
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**Fig. 3.** Relationships between individual log-transformed THg concentrations and (A) fork length values, (B) δ15N, and (C) δ13C values of blue shark sampled in the Mediterranean Sea, South of Portugal, and Canary Islands.
In consumers, Hg values are related to their trophic position and also to particular biological factors such as growth, feeding rates, longevity and detoxication capability (Li et al., 2020; Senn et al., 2010). In our case, the best-fitted model included the fork length as a key variable explaining mercury variations among sampling zones. Specifically, we found that larger individuals showed higher Hg concentrations, indicating that Hg has been bioaccumulated in relation to the body size (Branco et al., 2007; de Carvalho et al., 2014; Storelli et al., 2020, 2003). The increase of Hg concentrations with length is due to the high uptake efficiency for Hg and its slow excretion rates (Dang and Wang, 2012; Trudel and Rasmussen, 1997). Interestingly, in the Mediterranean Sea, sampled blue sharks showed smaller body sizes, Hg concentrations tended to be higher than similar sized specimens from the Atlantic Ocean. This can be related to differences in growth rates between Mediterranean and Atlantic populations (Megalofonou et al., 2009). As Hg accumulation is age and size dependent, slower growth rates exhibited by the Mediterranean population may be enhancing metal bioaccumulation, since they reduce the dilution effect of the somatic build up (Cossa et al., 2012). In addition, as Hg concentrations are correlated with age (Wang and Wong, 2003), it is possible that equivalent size blue sharks in the Mediterranean could show higher mercury concentrations because they are older than Atlantic ones. However, these interpretations need to be taken carefully since other potentially factors such as different ingestion rates may occur among the different populations. Similar, although male and female elasmobranchs have been documented to differ in their Hg values (de Pinho et al., 2002), we did not find sexual differences in this pollutant for any of the sampled areas. This similitude in the Hg values between sexes could be explained by the similar trophic (isotopic) niche occupied by male and female blue sharks (Torres et al., 2014; Vidal et al., 2022).

Considering diet as the main pathway of mercury intake in predators such as elasmobranchs, tunas or cetaceans (Boening, 2000), the use of δ13C values as a proxy of trophic position (Navarro et al., 2011) allowed us the exploration of the biomagnification process of Hg along the entire food web. Here, the association between δ13C and Hg values in blue sharks was not significant, probably indicating the consistent dietary during the range of body sizes included in our study. Nevertheless, this was also observed in blue sharks from the north Atlantic waters (e.g. Biton-Pornsmoguer et al., 2018; Escobar-Sánchez et al., 2011; Torres et al., 2017). If the Hg biomagnification between trophic levels is constant upwards a food web, then the basal Hg values at the bottom of the food web will regulate Hg concentrations in apical predators. Therefore, results from the stable isotopic trend found in the Mediterranean Sea could be reflecting the presence of higher Hg values from the lowest trophic positions in this basin compared to the Atlantic Ocean. Similar findings have been published in other ecosystem-compared studies (Chouvelon et al., 2018; Cossa et al., 2012), reinforcing the hypothesis of the higher basal Hg levels in the Mediterranean than in the Atlantic ecosystems (Cossa et al., 2022). Moreover, the relationships found between the Hg and δ13C values can be indicating the habitat where blue sharks were feeding. In marine environments, δ13C values present natural spatial gradients related to the distance from the coast: depleted and enriched δ13C values reflect the use of inshore or offshore waters, respectively; Cherel and Hobson (2007). Based on these trends, the blue sharks with more depleted δ13C values and, thus, they were feeding in more offshore waters, showed higher Hg values. One potential explanation of this result could be the fact that the winds and atmospheric currents can transport and deposit Hg to offshore waters (Outridge et al., 2018).

European Union plays an important role in the international trade of shark products, exporting 30% of worldwide shark meat exports, being Spain, Portugal, France, and Germany are considered the largest shark meat traders in Europe (Niedermüller et al., 2021). Thus, to protect human health and according to national and international agreements about marine pollution (i.e. European Marine Strategy Framework and Minamata Convention of Mercury), it is important to evaluate food safety for consumers. Since significant percentages of our samples were above the safety level for Hg in seafood for human consumption (Commission Regulation (EC) No 1881/2006), the consumption of blue shark may be detrimental for human health. Moreover, as sampled blue sharks in this study were juveniles and medium sized adults, and knowing that Hg has a robust relationship with body size, this may raise a serious concerns since half of the wild shark population could exhibit higher concentrations than those found in the present study.

5. Conclusions

In marine ecosystems, life-trait of elasmobranchs make them ideal for long-term biomonitoring. The blue shark has demonstrated great potential to be used as pollution bioindicator as it merges key features. Their cosmopolitan distribution together with their high trophic position, long growth rate and longevity allows the extrapolation of relevant information on ecosystems and human health. The main constrains to use them in biomonitoring are their accessibility, as well as their high mobility. The latter characteristic makes it difficult to associate certain metal levels with a specific limited region, therefore, it would be better to use this species for large scale studies. The combination of tracking studies together with stable isotopes could improve the knowledge gap. In fact, during the last decade has been an increment of electronic tracking studies with this species, specifically in Atlantic waters (Druon et al., 2023), to better understand their movement patterns and enhance its accessibility. Nonetheless, the Mediterranean Sea seems to be a comparatively understudied area for sharks in general, including the research conducted with the blue shark. The present findings indicate a strong influence of size, system structure and habitat preference on Hg bioaccumulation in the blue shark, reinforcing the necessity for global pollutant assessments.

Credit author statement

L. Riesgo: Methodology; Formal analysis; Writing, C Sanpera:
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.

Data availability

Data will be made available on request.

Acknowledgments

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Appenix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.137642.

References


