Drivers of the accumulation of mercury and organochlorine pollutants in Mediterranean lean fish and dietary significance

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HIGHLIGHTS

- 40% of Mediterranean lean fish had Hg concentrations above EU recommended values.
- The levels of organochlorine compounds in all specimens were below the EU threshold.
- Hg levels were correlated with specimen weight but the trend was species dependent.
- The organochlorine compound concentrations were not correlated with specimen weight.
- Mediterranean populations feeding on fish have higher EWI for Hg than the EFSA PTWIs.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 10 January 2018

Received in revised form 9 March 2018

Accepted 27 March 2018

Available online 5 April 2018

Editor: D. Barcelo

Keywords:

Mediterranean lean fish

Mercury

Organochlorine pollutants

Provisional tolerable weekly intakes

Trophic level and pollutant accumulation

Balearic Islands

ABSTRACT

An integrated assessment of lean fish of commercial value as Hg and organochlorine compound source into the population of the Balearic Islands were reported. Dependences between pollutant concentrations, trophic level, fish species, specimen weight and physical-chemical properties were evaluated.

Hg and total DDTs showed highest variability between fish species whereas PCBs and HCB displayed more constant median values. The organochlorine compounds found in highest concentrations were those with highest hydrophobicity, consistently with their higher bioaccumulation potential. These pollutant concentrations were higher in Mediterranean than Atlantic fish. Higher median total DDT and PCBs concentrations were also observed in the third than the second trophic level species. The observed concentrations were below the threshold recommended by the EU for human consumption (75 ng/g wet weight).

The Hg concentrations were higher in Mediterranean than Atlantic fish, with average values of 1.5 µg/g ww and 0.43 µg/g ww, respectively. Forty-one percent of the specimens from the Mediterranean and 25% of dusky grouper specimens from the Atlantic Ocean showed Hg concentrations above the EU recommended limits for human consumption, either 0.5 µg/g ww or 1 µg/g ww.

In the third trophic level, a significant dependence between median Hg concentrations and weight of each studied species was observed, which remained significant in specimen weight correlations. Independent species correlations of Hg concentrations vs individual weight generally showed higher concentrations at higher weight. Weight/size of the individuals was therefore an important factor for Hg accumulation but the trend was modulated by a species effect.

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Extrapolation of the observed Hg concentrations in Mediterranean fish to Provisional Tolerable Weekly Intakes (PTWIs) showed higher intakes than the thresholds recommended by EFSA for adults and children, 110% and 140%, respectively. The estimated PTWIs for MeHg corresponded to 310% and 400% of the recommended threshold values. The PTWI values for organochlorine compounds were lower than those recommended.

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1. Introduction

Fish consumption has been associated to human accumulation of mercury (Hg) and organochlorine pesticides (Llop et al., 2010; Gascon et al., 2012, 2013; Garí et al., 2013; Vizcaino et al., 2014; Costa et al., 2016; Bravo et al., 2017). Despite their different origin and structure, OCs and Hg share common properties such as (I) strong chemical stability and environmental persistence, (II) bioconcentration in living organisms and biomagnification through the food chain due to their hydrophobic character and (III) toxicity for humans and wild animals. Methylmercury is a more toxic form than the original metal whose human intake is also attributed to fish and seafood (Calatayud et al., 2012; Garí et al., 2013; Perello et al., 2014; Cano-Sancho et al., 2015; Obeid et al., 2017).

Human exposure to environmental concentrations of organochlorine compounds with high number of chlorine substituents has been associated to diverse deleterious effects, e.g. hexachlorobenzene (HCB) to attention deficit hyperactivity syndrome (Ribas-Fitó et al., 2007), alteration of thyroid hormones (Álvarez-Pedrerol et al., 2008; Sala et al., 2001), overweight (Smink et al., 2008) and thyroid cancer (Grimalt et al., 1994), DDE to increases of asthma (Ribas-Fito et al., 2006; Sunyer et al., 2006), alteration of thyroid hormones (Álvarez-Pedrerol et al., 2008) and urinary coproporphyrins (Sunyer et al., 2008), DDT to decreases of cognitive skills (Ribas-Fito et al., 2006; Morales et al., 2008), oncogene mutation (Porta et al., 1999), and polychlorobiphenyls (PCBs) to overweight (Valvi et al., 2012), oncogene mutation (Porta et al., 1999; Howsam et al., 2004), impaired liver metabolism (Sala et al., 2001) and neuropsychological development (Forns et al., 2012; Gascon et al., 2013) among others.

On the other hand, methylmercury (MeHg) targets the nervous system, especially during the children developmental stage (Grandjean et al., 1997; World Health Organization - International Programme on Chemical Safety (WHO-IPCS), 1990). Contamination episodes in Japan showed irreversible neurological damage upon exposure to this compound (Harada, 1995) and neurotoxicity and neurodevelopmental risk among children exposed to low or moderate Hg levels have been investigated (Karagas et al., 2012).

Accordingly, the production and use of OCs and Hg has been restricted and/or banned in many countries. However, these contaminants are still found in the environmental compartments (Arellano et al., 2011; Lamborg et al., 2014), foodstuff (Martí-Cid et al., 2010; Olmedo et al., 2013) and human tissues (Vizcaino et al., 2014; Garí et al., 2013).

Even though there are many sources of human exposure to these pollutants, it is well-known that ingestion is the main route (representing >90% of the total exposure) and, especially, through consumption of fatty food such as fish (Xu et al., 2017 and Vázquez et al., 2015). Until very recently, fish consumption recommendations for vulnerable population groups, such as infants and pregnant women, have focussed on certain big, migratory and oily fish species (EFSA, 2012, 2015; AESA, 2006). However, since Hg is primarily associated with muscle tissue rather than fat, predatory but non-migratory fish species, e.g. lean fish, may also accumulate this compound. This is particularly relevant for carnivorous species feeding at the top of the food chain which increase the concentrations of these pollutants by bioaccumulation. To date, few studies have assessed the potential role of predatory but non-migratory fish species regularly consumed by general and infant populations as sources of organochlorine compounds and Hg.

This concern is high in island populations for being typically high fish consumers, particularly from local markets. These populations are prone to accumulate high levels of these pollutants (Grandjean et al., 1997; Myers et al., 2000; Murata et al., 2002). Previous studies on newborns and preschool children from Mediterranean populations have shown high Hg concentrations in blood and hair (Freire et al., 2010; Garí et al., 2013; Llop et al., 2014). They evidence the need for assessment of the role of different fish species in human exposure to these pollutants.

In this sense, we performed two preliminary studies on the intake of these compounds, one on Hg in Mediterranean lean fish and seafood (Llull et al., 2017) and another on a diet evaluation of the population from Menorca (Junqué et al., 2017). Now, an integrated assessment of lean fish species of commercial value as sources of both Hg and organochlorine compounds in islander populations is reported. The Balearic Islands are adequate reference sites for their location in the western Mediterranean. Thus, most of the fish specimens were obtained from fishermen of these islands. The study has been extended to fish specimens from Tunisia and Egypt. Samples from the Atlantic Ocean, in front of Senegal and Mauritania, two big fishery areas due to upwelling, have also been collected and examined for comparison.

To acquire further data on the possible human health risks of fish consumption, this study examined the weekly intakes of both children and adults and comparison with the Provisional Tolerable Weekly Intakes (PTWIs) established by the European Food and Safety Authority (EFSA, 2012). The study is also aimed to ascertain whether the concentrations of Total Hg are compliant with the maximum values in fishery products established by the European Legislation. Taking into account the role of biotic and abiotic factors in the accumulation of these pollutants in fish (Verhaert et al., 2017 and Storelli et al., 2002), the dependences between pollutant concentrations, fish species and specimen weight have been also evaluated.

The results of the present study need to be considered to design guidelines for decreasing human incorporation of these compounds through diet which is consistent with the EFSA (2015) recommendations.

2. Materials and methods

2.1. Sampling

Between March 2016 and August 2017, 104 commercial fish samples from the Western Mediterranean Sea were collected (Fig. 1). Most of them ($n = 102$) in waters nearby the Balearic Islands (Majorca, $n = 66$; Menorca, $n = 17$; Ibiza, $n = 18$) and the rest of the samples were from Tunisia ($n = 2$) and Egypt ($n = 1$). Additional fish samples ($n = 14$) from the Atlantic Ocean, in front of the Senegal ($n = 4$) and Mauritania ($n = 10$) coasts, were also collected.

Twenty-one lean fish species from the Balearic Islands were selected considering those most consumed by the population (Table 1; SMAP, 2015). They encompassed angler (*Lophius piscatorius*), European hake (*Merluccius merluccius*), common dentex (*Dentex dentex*), common pandora (*Pagellus erythrinus*), dusky grouper (*Epinephelus marginatus*), Mediterranean moray (*Muraena helena*), red scorpionfish (*Scorpaena scrofa*), small-spotted catshark (*Scyliorhinus canicula*), conger (*Conger conger*), Mediterranean rainbow grasse (*Coris julis*), four-spot megrim (*Lepidorhombus boschii*), annular seabream (*Diplodus annularis*), common two-banded seabream (*Diplodus vulgaris*), John dory (*Zeus faber*),

Fig. 1. Map of the areas in which fish were collected.

common dolphinfish (*Coryphaena hippurus*), pearly razorfish (*Xyrichtys novacula*), white seabream (*Diplodus sargus*), comber (*Serranus cabrilla*), greater amberjack (*Seriola dumerili*), Atlantic horse mackerel (*Trachurus trachurus*) and painted comber (*Serranus scriba*). These species were obtained by both commercial and recreational fishing. Samples were collected in auction halls and local fish markets. Those from

Tunisia, Egypt and the Atlantic Ocean (belonging only to the dusky grouper species), were obtained from importer facilities in the Balearic Islands. Information on length, weight, date of sampling and catch location was obtained.

The studied fish species were grouped into two trophic levels: (i) those feeding on small fish and crustaceans (trophic level 2, encompassing 31 specimens from eleven species); and (ii) piscivorous species that feed on fish and cephalopods (trophic level 3, encompassing 87 specimens from ten species) (Riera et al., 1995).

Table 1
Lean fish analysed in this study.

Common name	Scientific name	Habitat
Second trophic level		
Mediterranean rainbow wrasse	<i>Coris julis</i>	Benthic
Four-spot megrim	<i>Lepidorhombus boscii</i>	Benthic
Annular seabream	<i>Diplodus annularis</i>	Benthic
Common two-banded seabream	<i>Diplodus vulgaris</i>	Benthic
Small-spotted catshark	<i>Scyliorhinus canicula</i>	Benthic
Common pandora	<i>Pagellus erythrinus</i>	Benthic
Pearly razorfish	<i>Xyrichtys novacula</i>	Benthic
White seabream	<i>Diplodus sargus</i>	Benthic
Comber	<i>Serranus cabrilla</i>	Benthic
Atlantic horse mackerel	<i>Trachurus trachurus</i>	Pelagic
Painted comber	<i>Serranus scriba</i>	Benthic
Third trophic level		
Angler	<i>Lophius piscatorius</i>	Benthic
Dusky grouper	<i>Epinephelus marginatus</i>	Benthic
Conger	<i>Conger conger</i>	Benthic
Common dentex	<i>Dentex dentex</i>	Benthopelagic
Mediterranean moray	<i>Muraena helena</i>	Benthic
European hake	<i>Merluccius merluccius</i>	Benthic
Red scorpionfish	<i>Scorpaena scrofa</i>	Benthic
John Dory	<i>Zeus faber</i>	Benthic
Common dolphinfish	<i>Coryphaena hippurus</i>	Pelagic
Greater amberjack	<i>Seriola dumerili</i>	Pelagic

2.2. Chemicals and analytes of interest

The following pollutants were considered for analysis: pentachlorobenzene (PeCB), hexachlorobenzene (HCB), 4 isomers of hexachlorocyclohexanes (α -, β -, γ - and δ -HCH), 2,4'-DDT, 4,4'-DDT and three metabolites (2,4'-DDE, 4,4'-DDE and 4,4'-DDD), 6 PCB congeners (28, 52, 118, 138, 153 and 180) and total Hg.

Solvents for residue analysis, *n*-hexane, dichloromethane, isooctane, acetone, concentrated 95–97% sulfuric acid, sodium sulfate and silica gel were from Merck (Darmstadt, Germany). Sulfate and silica were activated overnight by heating at 400 °C and 120 °C, respectively. The cellulose extraction cartridges (22 mm $\times$ 80 mm) were from Whatman International Ltd. (UK). The standards of PeCB, HCB, HCHs, DDTs and PCB congeners were from Dr. Ehrenstorfer (Wesel, Germany). 1,2,4,5-Tetrabromobenzene (TBB) was from (Aldrich Steinheim, Germany). The standard mixtures of organochlorine compounds, surrogate solution composed of TBB and PCB 209, and internal standard of PCB 142, were prepared in isooctane. Fish muscle certified reference material, ERM-BB422, was obtained from the Institute for Reference Materials and Measurements (Geel, Belgium).

2.3. Determination of organochlorine compounds

The extraction and clean-up of organochlorine compounds in fish samples was based on previous analytical procedures (Berdie and Grimalt, 1998; Vives and Grimalt, 2002).

Briefly, each muscle sample (3–4 g) was homogenized with activated sodium sulfate until a fine powder was obtained and then the mixtures were introduced into previously cleaned cellulose cartridges (6 h in Soxhlet). These mixtures were Soxhlet-extracted with 100 mL of *n*-hexane-dichloromethane (4:1 v/v) for 6 h. At this step, TBB and PCB 209 were added as recovery standards (50 ng/mL). The extract was concentrated with a rotary evaporator to 2 mL and then 3 mL of sulfuric acid were added. After vigorous stirring in a Vortex-mixer (2 min) the mixture was centrifuged (4000 rpm, 5 min) to remove any foam in the interface and the sulfuric acid layer was discarded. This clean-up step was repeated until a colorless transparent acid layer was obtained (3–5 times). The solvent layer was introduced into a chromatographic column packed with 1 g of sodium sulfate and silica gel column (1:1 by weight). The extract was then evaporated to dryness under a gentle stream of nitrogen (10–20 °C) and transferred to vials using 200 µL of isooctane. Before instrumental analysis, the sample was evaporated to nearly dryness under a gentle nitrogen flow and a solution of PCB 142 was added as internal standard (10 ng/mL).

OCs were quantified using a gas chromatograph with electron capture detection (GC-ECD, Agilent Technologies 7890A, Palo Alto, California, USA) equipped with a HP-5MS capillary column of 60 m length, 0.25 mm internal diameter and 0.25 µm film thickness (J&W Scientific, Folsom, CA, USA), protected with a retention gap. The oven temperature was programmed from 90 °C (holding time 2 min) to 130 °C at 15 °C/min and finally to 290 °C at 4 °C/min, keeping the final temperature for 15 min. Injector and detector temperatures were 250 °C and 320 °C, respectively. Injection (2 µL) was performed in splitless mode, keeping the split valve closed for 30 s. Helium was the carrier gas (1.5 mL/min) and nitrogen was used as the make-up gas for the detector (60 mL/min).

Structural confirmations were performed by gas chromatography (GC, Agilent Technologies 7890A, Agilent Palo Alto, USA) coupled to a mass spectrometer (MS, Agilent Technologies 5975C, Agilent Palo Alto, USA) operating in negative chemical ionization mode (GC-NICI-MS). The system was equipped with a HP-5MS capillary column of 60 m length, 0.25 mm internal diameter and 0.25 µm film thickness (J&W Scientific, Folsom, CA, USA), protected with a retention gap. Helium was used as carrier gas (1.2 mL/min). Ammonia was the reagent gas (2.5 mL/min). The oven temperature program started at 90 °C which was held for 2 min, followed by a first increase to 130 °C at 15 °C/min and a final ramp to 310 °C at 4 °C/min with a hold time of 10 min. Injector, transfer line and ion source temperatures were 280 °C, 280 °C and 176 °C, respectively. The dwell time was 50 ms/channel.

One procedural blank was included in each batch of samples. Mean recoveries of spiked standards in the samples were 56% and 77% for TBB and PCB 209, respectively. Detection and quantification limits were determined as the average signal obtained from the blanks plus three and five times the standard deviation, respectively. Detection limits ranged between 0.0050 and 0.095 ng/g wet weight (ww) and quantification limits, between 0.038 and 0.14 ng/g ww.

2.4. Determination of mercury

Total Hg was performed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies 7900, Agilent Palo Alto, USA) operating under standard conditions and using iridium as internal standard. Helium was used as a carrier gas (5 mL/min). One procedural blank was included in each sample batch. The limits of quantification (LQs) were 0.1 mg/kg ww. These analyses were performed at the Public Health Laboratory of Palma (Mallorca; ENAC accreditation 603/LE1307).

2.5. Estimated dietary intakes and threshold values

All fish species considered in the study are usually consumed by the Spanish population (BOE, 2015). In addition, 5 of the species analysed (*Conger conger*, *Lepidorhombus boschii*, *Lophius piscatorius*, *Merluccius merluccius* and *Trachurus trachurus*) are in the 30 main fishing species of commercial interest according to the Spanish Ministry of Agriculture and Fisheries (Government of Spain, 2012).

A first estimation of the dietary weekly total Hg intakes (mg Hg) through fish consumption was calculated by multiplying the median fish concentrations of all analysed samples (mg/kg ww) by the weekly average fish consumptions of the Spanish population (AES, 2006). Following the recommendations of EFSA 50th and 95th percentiles of consumption have been used to assess the middle bound (MB) and upper bound (UB) for both children (7–12 years old; MB = 46.4 g/day and UB = 383 g/day) and adults (older than 17 years: MB = 71.1 g/day and UB = 597 g/day), respectively (EFSA, 2015). Comparison of these results with those reported by EFSA for Spain gave similar figures, e.g. 36.3 g/day and 63.6 g/day for children and adults, respectively (EFSA, 2015). Estimated Weekly Intakes (EWIs; µg/kg bw) of total Hg were obtained from the dietary weekly intakes after normalization to the mean body weights of each population group, e.g. 34.48 kg for children and 68.48 kg for adults.

The EWIs were compared to the PTWIs of both THg and MeHg, 4 µg/kg bw and 1.3 µg/kg bw, respectively (EFSA, 2012). The PTWI percentages (%PTWI) were calculated as 100 · EWI/PTWI.

2.6. Statistical analysis

The statistical analyses were performed using R (R Core Team, 2015) software and Microsoft Excel (2010). The concentrations of OCs and Hg were expressed in ng/g ww and mg/kg ww, respectively. When OCs and Hg concentrations were under the limit of detection or quantification, the values were assumed to be one-half of the detection or quantification limits, respectively (ND = ½ LOD; ½ LOQ, respectively). For THg, concentrations below LQs were assumed to be ½ of the LQs, 0.05 mg/kg ww. Similar figures were obtained from the calculation of these values with a reverse Kaplan-Meier estimator (Gillespie et al., 2010). Either ww or dry weight (dw) were used for comparison with other studies.

Total HCHs were defined as the sum of α -, β -, δ - and γ -HCHs. Total DDT concentrations were the sum of 4,4'-DDT, 2,4'-DDT, 4,4'-DDE, 2,4'-DDE and 4,4'-DDD. Total PCB concentrations were the sum of 28, 52, 118, 138, 153 and 180. HCB and Hg were reported as individual compounds. Concentration means and ranges were used for data reporting. The concentrations were not normally distributed and graphics were displayed in a logarithmic scale (Figs. 2 and 4–6). Non-parametric Kruskal-Wallis test was used for assessing the differences on pollutant concentrations by location and trophic level. Pearson correlation test of log-transformed values and Spearman correlation test of non-transformed values, as well as simple linear regression models were applied for evaluation of the relationships between pollutant concentration and fish weights.

3. Results and discussion

The present study reports the concentrations of organochlorine pollutants and Hg in 118 fish specimens from 21 species (Table 1) collected at several locations of the Western Mediterranean Sea and the Atlantic coast (Fig. 1). Dusky grouper, Mediterranean moray and common dentex were the most studied species, with a total of 15 to 28 specimens for each species examined.

The distributions of the concentrations of HCB, total DDTs, PCBs and Hg of the studied species displayed in Table 1 are shown in Fig. 2. Hg and total DDTs show highest variability between species whereas PCBs and HCB display more constant median values between species (Fig. 2).

Fig. 2. Boxplots showing the hexachlorobenzene, DDTs, polychlorobiphenyls and mercury concentrations (ng/g ww and $\mu\text{g/g ww}$ for OCs and Hg, respectively) in the studied fish species. The EU mercury threshold levels of 0.5 and 1 $\mu\text{g/g ww}$ for human consumption (EC, 2006) are indicated.

Angler is the species showing the highest median concentration of Hg (1.9 $\mu\text{g/g}$) and DDTs (3.4 ng/g).

3.1. Occurrence of organochlorine compounds

The concentrations of organochlorine compounds in the fish specimens range between not detected and 32 ng/g ww (Table 2, Fig. 2). Those concentrations are lower than the European Union threshold recommended for human consumption, 75 ng/g ww (DOUE, 2011). The PCB congeners found in highest concentrations in all samples were those with highest molecular weights, PCB118, PCB138, PCB153 and PCB180, which involves those with highest hydrophobic properties (octanol-water coefficients, $\log K_{ow} > 6.9$). The predominance of these compounds is consistent with their high hydrophobicity and bioaccumulation potential. Concerning DDTs, the species average $100 \times 4,4'$ -DDT/(4,4'-DDT + 4,4'-DDE) ratios are between 3.5 and 33%, indicating that the observed DDT concentrations correspond to old spills in the Mediterranean waters.

The mean concentration of HCB in the Atlantic fish, 0.04 ng/g ww was slightly higher than in the Mediterranean fish, 0.03 ng/g ww, but the differences were not significant (Table 2, Fig. 3). For the rest of organochlorine compounds, the concentrations were higher in fish from the Mediterranean Sea than in those from the Atlantic Ocean, especially for DDTs and PCBs (Table 2). The differences were not significant for total HCHs but for total DDTs and PCBs these differences were significant ($p < 0.01$, data not shown).

In any case, the observed concentrations in the specimens captured nearby the Balearic Islands were lower than in the fish specimens consumed in Sweden, Catalonia, Austria and Russia (Table 2). The

differences were particularly significant for the DDT and the PCB groups since the average concentrations found in the fish from the Balearic Islands were about 6–7 times lower than the average concentrations reported in Catalonia (Martí-Cid et al., 2010; Llobet et al., 2003) or Russia (Polder et al., 2010) (Table 2). The concentrations of total HCHs, DDTs and PCBs were also lower than those described in Croatia (Kljakovic-Gaspic et al., 2015). With the exception of HCB the concentrations of the organochlorine compounds from fish captured near the Canary Islands were lower than those in the Balearic Islands analysed in the present study (Table 2). The average concentrations of HCB, total HCHs and total DDTs in fish captured nearby the Balearic Islands are quite similar than those observed in fish captured near Menorca (Junqué et al., 2017). However, the PCB concentrations are higher in the present case, 2.4 ng/g ww vs. 1.7 ng/g ww (Table 2). In general, decreasing concentrations in OCs have been observed (Krauthacker et al., 2009; Aguilar and Borrell, 2005), probably as the result from the application of the Stockholm Convention.

3.2. Mercury

The concentration of total Hg in the studied fish specimens ranges between not detected and 3 $\mu\text{g/g ww}$. For certain species (e.g. common dentex, John dory), the median concentrations were well above the EU threshold of 0.5 $\mu\text{g/g ww}$ (EC, 2006). This previous range does not include angler, whose specimens have values of 0.65–3.1 $\mu\text{g/g ww}$ which also have an upper limit that is above the EU threshold for this species, 1 $\mu\text{g/g ww}$. Thirty-nine percent of the specimens from the Mediterranean, excluding angler, have Hg concentrations above the EU threshold of 0.5 $\mu\text{g/g ww}$ whereas 25% of the Dusky grouper species

Table 2
Arithmetic mean concentrations of OCs in food items of Menorca and in other European sites (ng/g ww).

	Fish	Location	Reference
HCB			Present study
Mediterranean	0.03		
Atlantic	0.04		
	0.33	Canary Islands	Rodríguez-Hernández et al., 2016
	0.021	Croatia	Kljakovic-Gaspic et al., 2015
	0.45	Sweden	A. Törnkvist et al., 2011
	0.22	Catalonia	Martí-Cid et al., 2010
	0.28	Catalonia	Falcó et al., 2004
	0.053	Menorca	Junqué et al., 2017
	0.56	Russia	Polder et al., 2010
∑HCHs			Present study
Mediterranean	0.05		
Atlantic	0.039		
	0.13	Canary Islands	Rodríguez-Hernández et al., 2016
	0.32	Croatia	Kljakovic-Gaspic et al., 2015
	0.23	Sweden	Törnkvist et al., 2011
	0.20	Catalonia	Martí-Cid et al., 2010
	0.038	Menorca	Junqué et al., 2017
	0.28	Russia	Polder et al., 2010
	0.12	Xiamen (China)	Qian et al., 2017
∑DDTs			Present study
Mediterranean	1.1		
Atlantic	0.17		
	0.77	Canary Islands	Rodríguez-Hernández et al., 2016
	2.8	Croatia	Kljakovic-Gaspic et al., 2015
	3.3	Sweden	Törnkvist et al., 2011
	7.5	Catalonia	Martí-Cid et al., 2010
	1.1	Menorca	Junqué et al., 2017
	6.4	Russia	Polder et al., 2010
	6.1	Xiamen (China)	Qian et al., 2017
∑PCBs			Present study
Mediterranean	2.4		
Atlantic	0.67		
	1.3	Canary Islands	Rodríguez-Hernández et al., 2016
	4.3	Austria	Mihats et al., 2015
	11	Croatia	Kljakovic-Gaspic et al., 2015
	5.1	Sweden	Törnkvist et al., 2011
	11	Catalonia	Martí-Cid et al., 2010
	12	Catalonia	Llobet et al., 2003
	1.7	Menorca	Junqué et al., 2017
	7.4	Russia	Polder et al., 2010
	4.1	Xiamen (China)	Qian et al., 2017

from the Atlantic Ocean analysed in the present study show values above this limit.

The Hg concentrations observed in the present study were consistent with previous results reported in the same organisms from the Adriatic Sea (Storelli and Barone, 2013; Storelli et al., 2007), Farwa Island (Lybian coast; Banana et al., 2016), the Gulf of Lion (Torres et al., 2015; Cresson et al., 2014), the Aegean Sea (Yabanli and Alparslan, 2015), Menorca (Junqué et al., 2017) and deep-sea sites from the Mediterranean basin (Koenig et al., 2013; Naccari et al., 2015).

The mean THg concentrations of the angler specimens analysed in the present study (1.9 µg/g ww) were much higher than those from the Italian coast (mean of 0.13 µg/g ww; Brambilla et al., 2013) and even previous studies near the Balearic Islands (0.74 µg/g ww; Llull et al., 2017).

The concentrations of mercury in dusky groupers from the Balearic Islands, 1.5 µg/g ww ($n = 8$), are similar to those found in a previous study of the same area, 1.6 µg/g ww, and higher than those observed in Tunisia, 0.86 mg/kg ww, and Egypt, 0.92 µg/g ww, or in the Atlantic Ocean (mean 0.34 µg/g ww; $n = 14$). In the present study, fish from the Atlantic Ocean had Hg levels of 0.43 µg/g ww ($n = 14$).

Common dentex were found to have mean Total Hg concentrations of 0.78 µg/g ww which was lower than in a previous study in the western Mediterranean, 0.99 µg/g ww, and in the Egyptian coast, 1.1 µg/g ww (Llull et al., 2017).

3.3. Pollution differences between Mediterranean and Atlantic concentrations

Comparison of the differences in pollutant concentrations in dusky groupers between the specimens analysed in the Mediterranean Sea ($n = 14$) and the Atlantic Ocean ($n = 14$) shows important contrasts (Fig. 3). The mean differences of THg, total DDTs and PCBs between dusky grouper specimens from Mediterranean Sea and Atlantic Ocean are statistically significant (1.5 vs. 0.43 µg/g ww, 1.3 vs. 0.16 ng/g ww and 3.2 vs. 0.57 ng/g ww, respectively, with Kruskal-Wallis test's, p -values <0.001; Fig. 3). In contrast, no significant differences are found for HCB (0.03 vs. 0.05 ng/g ww, p -value 0.084). This contrast reflects the higher pollution inputs in the Mediterranean. However, the difference is more defined for the organic compounds with higher capacity of fish bioaccumulation, such as those with logKow >6.9, compounds with lower bioaccumulation capacity are not retained in the food web

Fig. 3. Boxplots showing the hexachlorobenzene, DDTs, polychlorobiphenyls and mercury concentrations (ng/g ww and µg/g ww for OCs and Hg, respectively) in the studied fish species in the Mediterranean Sea and the Atlantic Ocean.

and therefore no difference in accumulation of these compounds between Mediterranean and Atlantic fish specimens is observed.

3.4. Trophic level

The concentration differences between the second and third trophic levels are summarized in Fig. 4. No median difference in the concentration of HCB is observed between the two levels. For Hg, total DDTs and PCBs, higher median concentrations in the third level are found. The differences are only significant for total DDTs and PCBs (data not shown). Again, considering the physical-chemical properties of the organochlorine compounds the contrast between these two pollutant groups and HCB is related to the capacity for bioaccumulation of the former and therefore higher pollution inputs are retained in the species from higher trophic level which retain the pollutants ingested from lower food web species.

MeHg has been reported to generally increase at higher size and age which recommends to consider specimen length, weight and age for concentration data interpretation (Wiener et al., 2007). Representation of the median Hg concentrations of each Table 1 third trophic level species by median weight shows an increasing trend and the correlation is significant $r = 0.81$ ($p < 0.001$; Fig. 5). The species having larger-size individuals, higher weight, are those accumulating Hg at higher extent. Representation of the Hg concentrations vs. weight of each specimen shows again a significant correlation with nearly the same correlation coefficient and degree of significance, $r = 0.78$ ($p < 0.01$; Fig. 5). It is therefore difficult to discriminate between species or individual weight/size in the accumulation of Hg. Plotting the Hg concentrations vs individual weight for each species shows higher concentrations at higher weight in each species except in Mediterranean moray (Fig. 6).

Accordingly, the weight/size effect of the individuals is an important factor determining Hg accumulation. Nevertheless, important differences between concentration increases vs weight are observed depending on each species (Fig. 6), evidencing that there is also a species effect in the accumulation of this metal. No significant dependences between longitude of the individuals and concentrations of the organochlorine compounds are observed.

3.5. Dietary exposure assessment

According to the results of the present study, the average THg intake due to fish consumption of all collected species in the present study, $0.61 \mu\text{g/g ww}$, involves Hg EWIs of $5.7 \mu\text{g/kg bw}$ for children aged 7–12 years and $4.4 \mu\text{g/kg bw}$ for adults when referred to the infant and general Spanish population (AESA, 2006). These values are higher than the PTWI for total Hg intake recommended by FAO/WHO, $4 \mu\text{g/kg bw}$ (EFSA, 2012), 140% and 110%, respectively. In the worst case scenario (UB approach), the children and adults would be exposed to $47.25 \mu\text{g/kg bw}$ and $37.08 \mu\text{g/kg bw}$, which exceed largely the established upper limit, 1181% and 927%, respectively. For MeHg, assuming that 90% of total Hg is in this form, the EWIs are $5.2 \mu\text{g/kg bw}$ and $4.0 \mu\text{g/kg bw}$ for MB and $42.5 \mu\text{g/kg bw}$ and $33.4 \mu\text{g/kg bw}$ for UB in children and adults, respectively. The PTWI for MeHg are set to $1.3 \mu\text{g/kg bw}$ (EFSA, 2012) which is lower than the EWIs for children and adults. According to these PTWIs, the observed EWIs for children and adults are 400% and 310% of the PTWIs for MB and 3269% and 2596% for UB respectively.

These values represent the worst case scenarios in which only local fish is consumed. Fish from other Mediterranean areas and the Atlantic

Fig. 4. Boxplots showing the hexachlorobenzene, DDTs, polychlorobiphenyls and mercury concentrations (ng/g ww and $\mu\text{g/g ww}$ for OCs and Hg, respectively) in the studied fish species belonging to the second trophic level (feeding on small fish and crustaceans) or to the third trophic level (feeding on fish and cephalopods).

Fig. 5. Representation of the mercury concentrations vs. weight of the fish specimens (top) or median mercury concentrations vs median fish weight (bottom) in the species belonging to the third trophic level (see Fig. 4). The coloured area around the curve fitted line correspond to the 95% confidence interval.

Ocean is also commercialized in the Balearic Islands. Consumption from local sites is less than half of the total.

This evaluation of mercury ingestion by fish consumption may be compared with those of other Mediterranean populations. Two studies performed in Italy on target fish species found higher EWIs than in the present study (Storelli and Barone, 2013; Bonsignore et al., 2013). Studies in Valencia showed that total fish consumption contributed to 43% of PTWI (Yusa et al., 2008) whereas these contributions in Catalonia were 49.3% for adults and 38.5% for children (Llobet et al., 2003; Falcó et al., 2006).

In the case of HCB, total HCHs, DDTs and PCBs, the average concentrations, 0.027 ng/g ww, 0.047 ng/g ww, 0.93 ng/g ww and 1.7 ng/g ww, respectively, correspond to 0.03 ng/kg bw d, 0.05 ng/kg bw d, 0.96 ng/kg bw d and 1.8 ng/kg bw d, respectively, for adults and 0.03 ng/kg bw d, 0.06 ng/kg bw d, 1.1 ng/kg bw d and 2.1 ng/kg bw d, respectively, for children in the MB approach. The same estimations for HCB, total HCHs, DDTs and PCBs in high consumers, correspond to and 0.3, 0.52, 10.3, 19, 27 for children and 0.24, 0.41, 8.08 and 15.12 ng/kg bw d for adults.

The EWI in MB and UB in children and adults are much lower than the PTWIs recommended by the Joint FAO/WHO Meeting on Pesticide

Residues, 160, 5000, 10,000 and 10 ng/kg bw d, respectively (JMPR, 2000).

4. Conclusions

Hg and total DDTs showed highest variability between species whereas PCBs and HCB displayed more constant median values between species. The PCB congeners found in highest concentrations in all lean fish samples were those with highest molecular weight, PCB118, PCB138, PCB153 and PCB180, e.g. those with highest hydrophobicity ($\log K_{ow} > 6.9$). The predominance of these compounds was consistent with the high bioaccumulation potential. The DDT distributions were predominated by 4,4'-DDE which corresponded to old spills of these compounds.

The concentrations of organochlorine compounds were higher in fish from the Mediterranean Sea than from the Atlantic Ocean but the average differences were only significant for the compounds with high bioaccumulation potential, e.g. total DDTs and PCBs. Fish from the third trophic level showed higher median concentrations of DDTs and PCBs than those from the second trophic level, with statistically significant results. Again the differences were only significant for the

Fig. 6. Representation of the mercury concentrations vs. weight of the fish specimens in each species belonging to the third trophic level (see Fig. 4).

compounds with high bioaccumulation potential. In any case, the observed concentrations of organochlorine compounds were below the threshold recommended by the EU for human consumption.

The Hg concentrations were significantly higher in the dusky grouper specimens from the Mediterranean Sea than from the Atlantic Ocean. Forty-one percent of the specimens from the Mediterranean and 25% of the species from the Atlantic Ocean analysed in the present study showed Hg concentrations above the EU recommended limit for human consumption.

In the third trophic level, a significant dependence between median Hg concentrations and weight of each studied species was observed. This dependence also remained significant when representing the Hg concentrations vs. weight of each specimen. Plotting the Hg concentrations vs individual weight for each species again showed higher concentrations at higher weight in each species except for Mediterranean moray. Accordingly, the weight/size effect of the individuals was an important factor determining Hg accumulation in lean fish but the trend was modulated by a species effect.

The PTWIs of total Hg were higher than the thresholds recommended by EFSA for adults and children, 110% and 140%, respectively, and the estimated PTWIs for MeHg corresponded to 310% and 400% of the recommended threshold values. In contrast, the PTWI values for organochlorine compounds were much lower than those recommended.

Acknowledgements

We thank Francesc Riera and Antoni Maria Grau for their assistance in the species selection and sampling. Financial support has been received from the EU projects HEALS (FP7-ENV-2013- 603946), NEUROSOME (H2020-MSCA-ITN-2017 SEP-210411486) and IDEM (11.0661/2017/750680/SUB/ENV.C2). Financial support from the Spanish Ministry of Economy and Competitiveness through the Projects

Cuantox (CTM2015-71832-P) and Consolider-Redes (CTM2014-59111-REDC) is also acknowledged.

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