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Chlorinated compounds in the muscle tissue of fish from the Croatian Adriatic: preliminary data on contamination and the associated health risks

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Levels of 17 polychlorinated biphenyl congeners (PCBs) and seven organochlorine pesticides (OCPs) were measured in the muscle tissue of 18 commercially important fish species from the eastern Adriatic Sea. PCBs [<LOD-8,866 ng g^{-1} lipid weight (lw)] accounted for over 66 % of all analysed compounds. Their pattern was dominated by PCB-138 and PCB-153. DDE (14.2-649 ng g^{-1} lw) was the prevalent DDT isomer in all samples, suggesting no recent DDT input. β-, γ- and α-HCH and HCB were found in less than 50 % of samples. The analysed organic contaminants did not seem to bioaccumulate up the food web (trophic levels 3.0 to 4.5). Our findings show no risk of chronic (non-cancerous) effects on human health.

KEY WORDS: *marine pollution; Mediterranean Sea; organochlorine pesticides; persistent organic pollutants; polychlorinated biphenyls*

Persistent organic pollutants (POPs) are chemicals of global concern, as they significantly affect the environment and human health (1-3). Even though the environmental levels of the most common POPs, such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), show a steady decline (1, 2, 4), these anthropogenic chemicals are still found in all parts of the environment at measurable levels due to their long-range transport, persistence in the environment, and ability to bioaccumulate and biomagnify in ecosystems. Ultimately, they all end in oceans and seas. These compounds can reach dangerous levels in marine organisms because of their bioaccumulation in food webs (5, 6).

The main source of human exposure to POPs is contaminated food (6). Exposure can lead to neurobehavioural impairment, reproductive disorders, increased cancer risk, changes in the immune system, endocrine disruption, genotoxicity, and birth defects (6, 7). Because of their toxic properties, POPs have been listed as the EU priority pollutants (8). Concern about the effects of these compounds on human health has led to a range of studies establishing and monitoring their levels mostly in lipid-rich but also in edible tissues of organisms worldwide. In the Adriatic, organochlorine compounds have been extensively monitored in different fish species (9-15) over the last 50 years. Most of the data refer to the western, Italian coast and northern Adriatic. Measurements from the eastern Adriatic are scarce and limited to the coastal areas before 1998 (10). Additionally, little is known about individual levels of specific PCB congeners and DDT homologues in the eastern Adriatic, as previous studies reported only total PCB levels and sums of DDT compounds (10).

To address this gap in knowledge, we investigated the distribution of the seven most common OCPs and 17 PCBs in the muscle tissue of 18 edible fish species from the eastern Adriatic Sea. The objective of this preliminary study was also to provide current information on a wide range of legacy organic pollutants in small and medium-sized fish species. As these fish species belong to different trophic levels, we also wanted to see whether the load would be carried up the food web. Finally, based on our findings, our third aim was to estimate the health risk for people consuming fish from this area using the calculations proposed by the US Environmental Protection Agency (US EPA) (16).

MATERIALS AND METHODS

Sample collection

The fish were caught with a small mid-water trawl net for sampling fish in various layers of the water column at

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17 locations along the eastern Adriatic Sea (Croatia) in September 2007 (Figure 1). Since the primary aim of this preliminary monitoring study was to identify OCPs and PCBs in 18 commonly consumed fish species of the eastern Adriatic, we decided to pool samples of fish fillets by species rather than to separately analyse whole bodies or individual specimens (Table 1). The pooled fillet samples consisted of up to 10 specimen of fish <30 cm in length or three large fish specimen (>30 cm in length) of similar size, totalling 34 pooled samples. Each fish was measured on board and dissected for analysis with high-quality stainless steel instruments on a clean glass surface following the instructions from the US EPA's fish sampling manual (18). The fillet samples were stored in PTFE containers and kept frozen at -20 °C until laboratory analysis.

Chemical analysis

Analysis of PCBs in fish samples comprised six indicator congeners (IUPAC numbers: 28, 52, 101, 138, 153, 180) and 11 toxicologically significant congeners (IUPAC numbers: 60, 74, 105, 114, 118, 123, 156, 157, 167, 170, 189). Samples were also analysed for seven OCPs: hexachlorocyclohexane isomers (α-, β-, and γ-HCH), hexachlorobenzene (HCB), 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT) and its metabolites, (1,1-dichloro-2,2-di(4-chlorophenyl)ethylene (DDE), and 1,1-dichloro-2,2-di(4-chlorophenyl)ethane (DDD). The samples were analysed using a procedure similar to Storelli et al. (14). About 1 g of lyophilisate was mixed with 2 g of sodium sulphate in a glass mortar and cold-extracted with 40 mL of *n*-hexane. The extract was passed through filter paper (Whatman No. 1) into a pre-weighted test tube and reduced under a gentle stream of nitrogen. Tissue lipid content was determined gravimetrically. The lipid extracts were dissolved in 5 mL of *n*-hexane and cleaned up with 4 mL of 96 % sulphuric acid. The clean-up was repeated two more times. The solvent was evaporated to residues under a gentle stream of nitrogen. Before gas chromatography, the residues were dissolved in 1.0 mL of *n*-hexane. For high-resolution gas chromatography we used two ATI UNICAM 610 SERIES chromatographs (Cambridge, UK) with ^{63}Ni electron capture detectors. The first chromatograph served to analyse the compounds simultaneously on two capillary columns (Supelco, Bellefonte, PA, USA): 1) 60 m x 0.25 mm, SPB-5 film thickness 0.25 µm, temperature program 100 °C, then 4 °C min^{-1} to 240 °C, 50 min isothermally; and 2) 30 m x 0.25 mm, SPB-1701 film thickness 0.25 µm, temperature program 110 °C, then 4 °C min^{-1} to 240 °C, 50 min isothermally. On the second chromatograph the compounds were separated on the 60 m x 0.25 mm capillary column (SPB-5 film thickness 0.25 µm, temperature program 100 °C, then 10 °C min^{-1} to 240 °C, 80 min isothermally). The carrier gas was nitrogen. Only compounds identified on all columns were evaluated. The mass fractions reported here are the mean values of the results obtained on all columns. Qualitative and quantitative analyses were done by comparison with external standard. Limits of detection (LOD) for the analysed compounds were 0.17 ng g^{-1} lw for PCBs, β-HCH, DDE, DDD, and DDT and 0.1 ng g^{-1} lw for HCB, α-HCH, and γ-HCH. The analytical procedure was validated through internal QA/QC and interlaboratory comparison (organised by the International Atomic Energy Agency - Marine Environment Laboratory (IAEA-MEL). Using the method blank we excluded laboratory contamination, as the level of analytes was below the detection limit.

For easier comparison with other studies, we calculated summary data for several major groups of contaminants:

Table 1 *Number of specimens (N) and pooled samples (Np); average lipid content (%); and average length (cm) per fish species*

Common name	Scientific name	N	Np	Lipid content (%)	Average length (cm)	Trophic level[a]
Bogue	*Boops boops*	10	1	0.74	17.5	3.0
Chub mackerel	*Scomber japonicus*	10	2	0.29	26	3.1
European anchovy	*Engraulis encrasicolus*	10	2	0.66	14	3.1
Sardine	*Sardina pilchardus*	10	6	10.45	14.9	3.1
Red mullet	*Mullus barbatus*	10	1	1.93	16.5	3.2
Annular seabream	*Diplodus annularis*	10	1	4.22	12	3.4
Comber	*Serranus cabrilla*	10	2	0.34	18	3.4
Common pandora	*Pagellus eryhtrinus*	10	1	27.09	11.5	3.4
Brown comber	*Serranus hepatus*	10	1	0.67	10.5	3.5
Horse mackerel	*Trachurus mediterraneus*	10	6	0.80	22	3.6
Red gurnard	*Aspitrigla cuculus*	10	1	1.06	11	3.9
Blue whiting	*Micromesistius poutassou*	10	1	0.15	12	4.0
European barracuda	*Sphyraena sphyraena*	3	1	6.34	40	4.0
Spotted flounder	*Citharus linguatula*	10	1	0.66	17	4.0
Common stingray	*Dasyatis pastinaca*	3	1	0.17	52	4.1
Picarel	*Spicara flexuosa*	10	2	9.60	14	4.2
European hake	*Merluccius merluccius*	10	3	0.31	16	4.4
John dory	*Zeus faber*	10	1	0.44	21	4.5

[a]*Trophic level was assessed electronically at www.fishbase.org (17)*

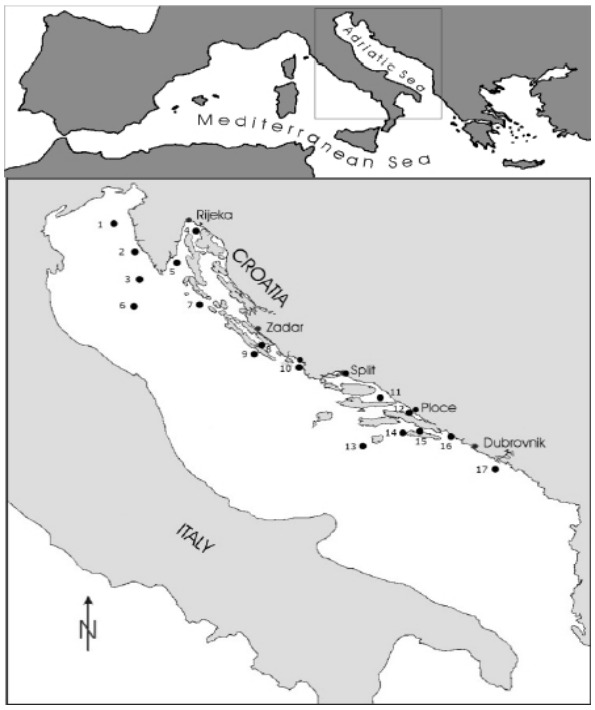

Figure 1 *Sampling sites on the Croatian Adriatic*

total HCHs (ΣHCHs) as the sum of the α-, β-, and γ-HCH; total DDTs (ΣDDTs) as the sum of *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE; total PCBs (ΣPCBs) as sum of levels of all analysed congeners; and ΣInd PCBs as the sum of six indicator PCBs (PCB-28, -52, -101, -138, -153, and -180), whose selection is based on their prevalence in technical mixtures, environment, and animal and human tissues (19). They serve to predict total PCB levels, since the sum of the six indicator PCBs accounts for about 50 % of all non-dioxin like-PCBs in food (19). We also calculated the sum of the toxicologically relevant PCBs (ΣToxRel PCBs), which are the more toxic fraction of PCBs in samples and include mono- and di-ortho substituted PCBs (PCB-60, -74, -105, -114, -118, -123, -156, -157, -167, -170, and -189).

Calculation of health risk

Human health risk was assessed by: a) comparing our findings with maximum permissible levels (MPLs) for organochlorine compounds in fish for human use (19-21) and b) calculating the risk of carcinogenic and non-carcinogenic effects from organic contaminants in fish. The methodology used for the calculation of consumption limits has been defined by the US EPA (16) and is based on the US EPA screening table (available at http://www2.epa.gov/risk/risk-based-screening-table-generic-tables), with assumptions which include a 70 kg adult, average fish meal size of 0.227 kg, and an averaged 30.44-day month.

For carcinogenic effects, daily consumption limit for a single contaminant was calculated using Eq. 1:

$$CRlim=(ARL \times BW)/CSF \times Cm$$

where CRlim is the maximum allowable fish consumption rate (kg per day); ARL the maximum acceptable individual lifetime risk level (unitless; we used the risk level of 10^{-5}); BW consumer's body weight (kg); CSF cancer slope factor (mg kg^{-1} day^{-1}); and Cm the level of chemical contaminant *m* measured in a given species of fish [mg kg^{-1} wet weight (ww)].

Since daily consumption limits may be more conveniently expressed as the allowable number of fish meals of a specified meal size over a given time (16), we converted the number of allowable kilograms per day to the allowable meals per month using Eq. 2:

$$CRmm=(CRlim \times Tap)/MS$$

where CRmm is the maximum allowable fish consumption rate (meals per month); CRlim the maximum allowable fish consumption rate (kg per day); MS meal size (0.227 kg per fish meal); and Tap is the averaged month expressed in days (365.25 days per 12 month = 30.44 days per month).

For non-carcinogenic health effects, we calculated an allowable daily consumption (CRlim) of contaminated fish using Eq. 3:

$$CRlim= (RfD \times BW)/Cm$$

where CRlim is the maximum allowable fish consumption rate (kg per day); RfD is the reference dose (mg kg^{-1} day^{-1}); BW is the consumer's body weight (70 kg); and Cm is the level of chemical contaminant *m* measured in a given species of fish (mg kg^{-1} ww).

We also converted daily consumption limits, expressed in kilograms, to meal consumption limits over one month as a function of meal size using Eq. 2.

Since individuals who eat contaminated fish are exposed to several chemicals at once, we also calculated the consumption limits for multiple chemical exposures. For the carcinogenic effects we used Eq. 4:

$$CRlim=(ARL \times BW)/\Sigma Cm \times CSF$$

where CRlim is the maximum allowable fish consumption rate (kg per day); ARL the maximum acceptable lifetime risk level (unitless; 10^{-5}); BW is consumer's body weight (kg); Cm is the level of chemical contaminant *m* in fish (mg kg^{-1}); and CSF is the cancer slope (mg kg^{-1} day^{-1}).

Daily consumption rate for non-carcinogenic chemical mixtures in a single or multiple fish species was calculated using Eq. 5., assuming that all the chemicals act additively:

$$CRlim=\Sigma(RfDm/Cm) \times BW$$

(see the above explanation of parameters).

Statistical analysis

For statistical analysis we used STATISTICA, version 12 (StatSoft, Inc., Tulsa, USA). Before statistical analysis, all biological variables and contaminant levels outside normal distribution were normalised using square root transformation on PCB-60, PCB-114, PCB-118, PCB-167, and PCB-170 data, and natural-log transformation for the remaining contaminants. Contaminant levels <LOD were replaced with half the value of the respective detection limit.

To identify differences between the trophic levels we used the Kruskall-Wallis test. For this purpose we grouped our results by trophic levels ≤3.1; 3.1-3.9; and ≥4.0, where the lower and the upper quartiles of the grouped data served as boundaries. Possible differences between species were not analysed in this study since we did not have enough composite samples per species to perform such statistical analysis.

RESULTS AND DISCUSSION

Contaminant levels

This preliminary survey provides the baseline levels of seven OCPs and 17 PCBs in the muscle tissue of 18 commonly consumed fish species from the eastern Adriatic (Table 2). All results are reported in terms of lipid weight and wet weight. Lipid-normalised data are common in

Table 2 *OCP and PCB levels in fish muscles collected at 17 locations in the eastern Adriatic*

Compound	Lipid weight basis (ng g^{-1} lw)				Wet weight basis (ng g^{-1} ww)				Positive samples (N)
	Mean	Median	Min	Max	Mean*	Median	Min	Max	
OCPs**									
HCB	0.189	<LOD	<LOD	2.79	0.021	<LOD	<LOD	0.250	4
α-HCH	0.135	<LOD	<LOD	1.87	0.017	<LOD	<LOD	0.209	4
β-HCH	97.5	<LOD	<LOD	1,823	0.277	<LOD	<LOD	1.65	15
γ-HCH	15.6	<LOD	<LOD	529	0.023	<LOD	<LOD	0.478	3
ΣHCH	113	<LOD	<LOD	2,352	0.319	<LOD	<LOD	2.12	
DDE	110	54.6	14.2	649	1.61	0.79	0.047	6.38	34
DDT	288	9.52	<LOD	6,949	0.865	0.46	<LOD	6.71	18
DDD	150	2.74	<LOD	4,592	0.368	0.14	<LOD	4.44	18
DDE/DDT	3.4	3.16	0.09	8.8	3.4	3.16	0.09	8.8	18
ΣDDTs	548	74.1	14.4	12,190	2.85	1.58	0.047	11.8	
PCBs									
Indicator PCBs (Ind PCBs)									
PCB-28	164	89.3	<LOD	965	0.863	0.76	<LOD	3.31	33
PCB-52	163	88.2	5.30	657	0.886	0.81	0.297	2.07	34
PCB-101	29.7	0.043	<LOD	306	0.399	0.01	<LOD	3.05	33
PCB-138	496	104	22.3	8,866	3.43	2.02	0.095	14.4	34
PCB-153	234	115	11.0	902	4.54	1.95	0.042	30.6	34
PCB-180	65.8	31.6	3.93	366	0.921	0.40	0.046	4.52	34
ΣInd PCBs	1,151	481	80.9	11,324	11.0	6.90	1.26	46.4	
Toxicologically relevant PCBs (ToxRel PCBs)									
PCB-74	32.3	<LOD	<LOD	873	0.276	<LOD	<LOD	3.73	15
PCB-60	16.8	<LOD	<LOD	188	0.175	<LOD	<LOD	0.691	16
PCB-105	7.26	1.62	<LOD	55.3	0.073	<LOD	<LOD	0.403	19
PCB-114	3.49	<LOD	<LOD	23.4	0.146	<LOD	<LOD	0.709	21
PCB-118	25.8	7.79	<LOD	299	0.567	0.19	<LOD	3.27	15
PCB-123	10.5	1.88	<LOD	121	0.287	0.08	<LOD	1.94	22
PCB-156	1.69	<LOD	<LOD	17.7	0.084	<LOD	<LOD	0.700	22
PCB-157	0.265	<LOD	<LOD	6.32	0.012	<LOD	<LOD	0.373	8
PCB-167	21.0	1.55	<LOD	196	0.187	0.15	<LOD	0.814	2
PCB-170	11.7	5.88	<LOD	56.6	0.165	0.09	<LOD	0.871	31
PCB-189	0.084	<LOD	<LOD	2.85	0.005	<LOD	<LOD	0.180	1
ΣToxRel PCBs	131	52.1	<LOD	1,083	1.98	1.10	<LOD	8.80	
ΣPCBs	1,283	524	106	11,326	13.0	8.98	1.33	53.0	

*LOD-limit of detection; *wet weight means were used to calculate health risk (see Table 5); **OCP findings have already been presented at the 31st International Symposium on Halogenated Persistent Organic Pollutants - POPs' Science in the Heart of Europe (22)*

literature as POPs accumulate in lipids, whose content can be affected by nutritional status, season and reproductive status, but we also wanted to assess human intake; hence the wet weight data.

We found no significant differences in POP levels between the three trophic groups ($p>0.05$; results not shown), which suggests that, in the range of trophic levels in this study (TL=3.0-4.5), the organic contaminants did not bioaccumulate up the food web. This is probably because our analysis did not include fish species at the top of the food web such as large predatory fish, which can not be caught with the small mid-water trawl we used for our study. Top marine predators with long life span, such as tuna and sword fish, can contain high organochlorine levels and pose the highest risk to humans (23, 24).

PCBs were dominant among the analysed compounds, accounting for 66 % (lw) of the total analysed POPs in the fish meat. The share of OCPs was lower, ranging from 0.01 % for HCB to 28.2 % for DDTs (lw). This order of the main groups of organic contaminants (PCBs>DDTs>HCHs>HCB) in fish from Croatian waters is in agreement with other reports for different fish species and different Mediterranean and Atlantic coastal regions (25-27).

In the group of DDT isomers, only DDE, a major metabolite of DDT, was detected in all samples, while more than 35 % of DDT and 47 % of DDD values were <LOD. DDE accounted for more than 74 % of ∑DDT levels. The DDE/DDT ratios are often used as an indicator of recent DDT input into the environment. The prevalence of *p,p'*-DDE in this study (DDE/DDT>0.6 in more than 91 % of samples) is in line with the reports on DDT metabolites in fish species from other European and Mediterranean countries (24-26, 28-31), and indicates that DDT in our study is mostly owed to historical use or remote sources and that it has not recently been used in agriculture. The obtained trend of the DDT isomers (DDE>DDT≈DDD) is consistent with the high chemical stability and long half-life of DDE in the aquatic environment in comparison to the parent DDT (25). The DDTs levels found in this study are similar to recent reports for different fish species from the Ionian Sea (29), Gulf of Naples (25), Marmara Sea (30), and Atlantic coastal regions (27) and are higher than those reported for other coastal areas of the Mediterranean (26, 31-33) (Table 3).

Although HCH-technical mixtures were banned in Croatia 43 years ago and lindane (γ-HCH) 14 years ago (37), 44 % of the analysed samples contained measurable levels of β-HCH, even though muscle tissue is not rich in lipids. This finding is consistent with the high persistence of β-HCH in the aquatic environment in comparison to other HCH isomers (38). Similar to the findings of Coelhan et al. (30) in the Marmara Sea fish species, β-HCH dominated, accounting for 86.1 % (lw) of the total analysed HCHs in fish meat. α-HCH and γ-HCH had relatively low levels with occurrence

Table 3 *Mass fractions of persistent organic pollutants [average (range); ng g^{-1} lw] in the muscle tissue of fish species from different areas of Europe and Mediterranean*

Study	Region	Species	ΣHCH	HCB	ΣDDTs	ΣPCBs
This study	Eastern Adriatic, Croatia	18 demersal and pelagic species	113 (<LOD-2,352)	0.189 (<LOD-2.79)	548 (14.4-12,190)	1283 (106-11,326)
(13)	Southern Adriatic Sea	10 demersal fish species	-	-	-	(134-1,210)
(15)	Adriatic Sea	17 benthic, demersal and pelagic species	-	-	-	(116-1,980)[a]
(25)	Gulf of Naples, Italy	6 demersal and pelagic species	-	(<LOD-93.1)	(<LOD-2,095)	(57-47,910)[b]
(26)	Tunis; Mediterranean	Common sole	15.4 (14.5-16.5)[c]	6.30 (3.4-8.5)	62.1 (55.2-74.9)	299 (257-319)
(27)	Atlantic coastal regions; rivers mouth	European hake	(1-197)	-	(1-1,219)	(296-20,185)
(29)	Ionian Sea (Mediterranean)	European conger eel	-	-	543 (271-865)	891 (518-1,724)
(30)	Marmara Sea, Turkey	12 edible species	(17.6-225)	(4.9-15.6)	(195-694)	(63.3-509)[d]
(31)	Catalan coast, NE Spain	European hake	-	(<LOD-1.0)	(2.1-16.0)	8.6-51.8[d]
(32)	Black Sea, Turkey	Bonito, Anchovy	<LOD	<LOD	(2.96-26.3)	(<LOD-17.5)[d]
(33)	Orbetello Lagoon, Italy	European conger eel	(<LOD-1,208)	(0.12-6.89)	(9.95-172)	(62.7-263)
(36)	Samsun region, Turkey	Red mullet	(54.7-85.9)	(<LOD-36.1)	(<LOD-4,188)	(1,063-3,235)e
(37)	Gironde Estuary, France	6 edible species	-	-	-	(1,530-12,449)f

LOD - limit of detection; [a] sum of 10 analysed PCBs; [b] sum of 18 analysed PCBs; [c] sum of α- and β-HCH; [d] sum of 7 ICES PCBs (PCB-25, -52, -101, -118, -138, -153, -180); [e] sum of 16 analysed PCBs; [f] sum of 21 analysed PCBs

frequencies of 9 % and 12 %, respectively. The HCH pattern (β-HCH>γ-HCH≈α-HCH) is consistent with our previous report on HCH patterns in mussels from the Croatian coast (34). Mass fractions of ΣHCHs in this study are similar to the values recorded for Orbetello Lagoon (33), the Marmara Sea (30), and Atlantic coastal regions (27) and higher than the values reported for the Tunisian coastal area (26) and the Black Sea (32) (Table 3).

Similar to α-HCH and γ-HCH, HCB mass fractions in fish from the Croatian coastal area were low, ranging from <LOD (more than 88 % of data) to 2.8 ng g^{-1} lw (11.8 % of data). Our results are in the range of the lowest values recorded in fish from the Mediterranean and European coastal area (Table 3), which suggests that the Croatian coastal region had not been exposed to high HCB emissions in the past.

Among PCB contaminant profiles ΣInd PCBs dominated, accounting for 70-99.9 % of total congener levels (Table 2). PCB-153, and PCB-180 were found in all samples, and PCB-28 in 97 % of the samples. Also, PCB-138 (38.7 %) and PCB-153 (18.2 %) were dominant congeners (Table 2). These findings are expected, since these congeners had been abundantly used in commercial PCB mixtures (Aroclor 1254 and 1260) in Europe and Croatia. As to the group of ToxRel PCBs, the most frequent congener was hepta-chlorinated PCB-170 (found in 91 % of the samples), while the highest median was that of PCB-118. The dominance of PCB-153, PCB-138, and PCB-118 is in agreement with other reports on marine organisms from the Adriatic (9, 25, 28, 29, 31, 35), reflecting their high lipophilicity, stability, and persistence, which favour accumulation in aquatic animals. The overall levels are consistent with those recently found in fish species from the Adriatic Sea (13, 15, 29) and Atlantic coastal regions (27), and are higher than the values for the Black Sea (32), Catalan coast (31), Tunis (26), and Orbetello Lagoon (33) (Table 3).

Compared to earlier measurements in edible fish parts by the Croatian Institute for Public Health (37) or Picer (10) (Table 4), our levels of chlorinated pesticides in fish from Croatia have declined over the last 30 years thanks to the worldwide ban. The decrease is slower for DDT than for other chlorinated pesticides, which is consistent with the longer half-life of DDT. Similar findings were obtained for the entire Mediterranean area (2, 4). As regards PCBs, it appears that after the decline in the 1980s, PCB levels in fish (Table 4) remained relatively constant.

Health risk assessment

Health risk from PCBs and OCPs was assessed using several limits and guidelines. We first compared our results with the EU and Croatian regulations (16-18) which define maximum permissible limits (MPLs) for dioxins and dioxin-like PCBs and six indicator PCBs in fish and mussels, while OCP limits have not yet been regulated by law. Since the sum of indicator PCBs in our study (1.3-46.4 μg kg^{-1} ww) was 1.6 to 57 times lower than the MPL for fresh meat (<75 μg kg^{-1} fresh meat), this comparison suggests that the consumption of fish species from our study is not likely to increase health risk from exposure to indicator PCBs.

Table 5 shows risk-based consumption limits for carcinogenic and non-carcinogenic health effects. Our calculations (equations 4 and 5) show no risk of cancer from chronic exposure to any of the compounds or to their chemical mixtures. However, they point to increased cancer risk from combined exposure if the consumption limit of more than 13 meals (1 meal=0.227 kg) per month is exceeded. This risk increases further if the 95th percentile levels are taken into account, and the consumption limit drops to only two meals per month (see the figures in boldface in the bottom row).

Generally, our results indicate that average consumers are unlikely to have health problems associated with fish meat consumption. Considering our findings and the related risks of consuming fish from the Croatian Adriatic, the beneficial effects of fish consumption (such as those from omega 3-polyunsaturated fatty acids) greatly outweigh the risks.

Table 4 *Mass fractions of persistent organic pollutants [average or median (range); ng g^{-1} ww] in the edible part of fish from Croatia from 1983 to 2007*

Study	Year	*N*	*HCB*	*α-HCH*	*γ-HCH*	*ΣDDTs*	*ΣPCBs*
(37)	1983	-	-	-	-	(1-12)	(48-79)
(37)	1987	-	-	-	-	(<LOD-6.2)	(16-120)
(37)	1984/1988	-	-	-	-	-	(59-287) (?-2,303)
(37)	1986/1989	153	5	2	25	127	-
(37)	1992/1996	-	<LOD (<LOD-0.3)	<LOD (<LOD-2.1)	1 (?-10.2)	1.6 (?-159)	46 (?-117)
(10)	1997	-	-	-	-	5.4 (0.6-36)	631 (36-4,004)
(37)	1999	46	0.1	0.1	0.5	4.7	-
This study	2007	34	0.021 (<LOD-0.250)	0.017 (<LOD-0.209)	0.023 (<LOD-0.48)	2.85 (0.047-11.8)	13.0 (1.33-53)

LOD - limit of detection;? – data not available

Table 5 *Health risk assessment from the consumption of fish from the eastern Adriatic based on average and high (95th percentile) levels (reported on wet weight basis), 70 kg adult, average fish meal size of 0.227 kg, and time-averaged month of 30.44 days. Chronic oral reference doses and cancer slope factors necessary for the calculation were obtained from the US EPA screening tables (http://www2.epa.gov/risk/risk-based-screening-table-generic-tables)*

Compound	Risk estimates based on average exposure					Risk estimates based on high-end exposure				
		Carcinogenic effects		Non-carcinogenic effects			Carcinogenic effects		Non-carcinogenic effects	
	Average contaminant level (mg kg^{-1} ww)	CRlim* (kg day^{-1})	AFM** (meals month^{-1})	CRlim (kg day^{-1})	AFM (meals month^{-1})	Maximum contaminant level (mg kg^{-1} ww)	CRlim (kg day^{-1})	AFM (meals month^{-1})	CRlim (kg day^{-1})	AFM (meals month^{-1})
DDT	0.00087	3.37	452	-	-	0.00671	0.434	58.3	-	-
DDE	0.00161	1.28	171	-	-	0.00638	0.323	43.2	-	-
DDD	0.00037	5.59	750	95	12,745	0.00444	0.464	62.2	7.9	1,058
HCB	0.00002	20.06	2,689	2,567	344,246	0.00025	1.742	233.6	223	29,905
λ-HCH	0.00002	6.08	815	30,637	4,108,340	0.00021	0.532	71.3	2,681	359,517
β-HCH	0.00028	1.40	188	-	-	0.00165	0.236	31.7	-	-
γ-HCH	0.00002	26.17	3,509	863	115,788	0.00048	1.333	178.7	44	5,897
PCB-105	0.00007	2.45	328	22	2,944	0.00040	0.445	59.7	3.99	535
PCB-114	0.00015	1.23	165	11	1,478	0.00071	0.253	33.9	2.27	305
PCB-118	0.00057	0.32	42	2.8	381	0.00327	0.055	7.4	0.49	66
PCB-123	0.00029	0.62	84	5.6	751	0.00194	0.092	12.4	0.83	111
PCB-156	0.00008	2.09	281	19	2,518	0.00070	0.257	34.4	2.30	309
PCB-157	0.00001	11.66	1,564	105	14,029	0.00037	0.481	64.5	4.32	579
PCB-167	0.00019	0.96	129	8.61	1,154	0.00081	0.221	29.6	1.98	265
PCB-189	0.00001	21.15	2,836	190	25,440	0.00018	0.995	133.5	8.93	1,197
ΣCRlim*		**0.101**	**13.6**	34,526	4,629,815		**0.016**	**2.17**	2,981	399,745

CRlim - daily consumption limit;AFM - allowable number of fish meals per month; ΣCRlim*** - consumption limit for exposure to multiple contaminants in multispecies diet (based on equations 4 and 5)*

CONCLUSION

This preliminary study provides the baseline information on the occurrence of OCPs and PCBs regulated by the Stockholm convention in the meat of frequently consumed fish species from the Eastern Adriatic. Organic contaminants in fish tissue decreased in the order: PCBs>DDTs>HCHs>HCB. Our results indicate that average consumers will have no health problems associated with meat consumption of fish from the Croatian Adriatic.

However, considering that OCPs and PCBs are persistent in the marine environment, their levels should be monitored all the time. As the number of pooled samples per species in our study was insufficient to make a comparison between the species, this calls for further research based on statistically justifiable sample size that could map differences and health risks by species or identify unknown pollution sources using sedentary species.

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Klorirani spojevi u mišićnom tkivu riba iz istočnog Jadranskog mora: preliminarni podaci o zagađenosti i zdravstvenim rizicima

Maseni udjeli 17 poliklorbifenila (PCB) i 7 organoklorovih pesticida (OCP) izmjereni su u mišićnom tkivu 18 komercijalno važnih ribljih vrsta iz istočnog Jadranskog mora. Maseni udjeli PCB-a (<LOD do 8.866 ng g^{-1} masti) činili su više od 66 % svih analiziranih spojeva. U njihovu profilu PCB-138 i PCB-153 dominantni su kongeneri. DDE (14,2-649 ng g^{-1} masti), glavni izomer DDT-a, jedini je detektiran u svim uzorcima. U manje od 50 % analiziranih uzoraka nađeni su β-, γ- i α-HCH te HCB. U rasponu trofičkih razina analiziranih vrsta (3,0-4,5) nije bilo bioakumulacije organskih zagađivala u hranidbenom lancu. Rezultati procjene rizika za ljudsko zdravlje pokazali su da nema rizika od kroničnih (nekancerogenih) utjecaja na ljudsko zdravlje.

KLJUČNE RIJEČI: *Mediteran; organoklorovi pesticidi; poliklorbifenili; postojana organska zagađivala*