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Persistent organic pollutants (POPs) in edible fish species from different fishing zones of Croatian Adriatic

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ABSTRACT

High-risk contaminants, OCPs and PCBs, were investigated in marine fish from the Adriatic Sea, from which retail fish in Croatia is commonly sourced. The pollutant levels in sardine, horse and chub mackerel, anchovy and round sardinella were analysed based on a two-year sampling and the joint use of generally accepted statistics and advanced clustering methods − self-organizing maps (SOM) and decision tree analysis (DT). Both the SOM and DT suggested fish mass and length rather than fat along with α-HCH, *p,p′*-DDT, PCB-74 and PCB-189 to cause variable pollutant uptake among species. Main distinctions of sardines occur in coastal and off coast regions rather than in a particular fishing zone and they are associated with both fish characteristics, levels of γ-HCH and PCBs: −60, −105, −150, −170, and −189. The results, mutually compatible or in agreement, could be useful for the design and implementation of the abatement strategies of fish pollution.

1. Introduction

Persistent organic pollutants (POPs) are compounds highly persistent in the environment, prone to transport through air, soil, water, and sediments. They accumulate in fatty tissue and consequently have adverse impacts on wildlife and human health. That is why the use of POPs was banned in many countries in the 1970s. Polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP) are the POPs of main concern and they are still present in the all parts of environment.

In the aquatic environment, owing to their lipophilic properties, POPs tend to sorb on suspended matter and sediments, and because of slow degradation processes persist for a long time. As a result, sediments act as secondary sources of pollution; thus, PCBs and OCPs can enter the aquatic organisms and consequently bio-accumulate through the marine food chain. Until now, in the Adriatic, POP levels in pelagic (Bayarri et al., 2001; Perugini et al., 2004), deep-sea (Storelli et al., 2009) fish and marine predators (Corsolini et al., 1995) have been well investigated and reported (Picer, 2000).

Fish consumption could be one of the important sources of POPs in humans (Pan et al., 2016). The sardine (*Sardina pilchardus*, Walbaum 1792) is a pelagic fish, rich in omega-3 and omega-6 unsaturated acids and is therefore very healthy for consumption. As an important seafood for humans, it occupies about 60% of the total catch of fish in the Adriatic. Together with the sardine, the European anchovy (*Engraulis encrasicholus*, Linnaeus, 1758) constitutes up to one half of the total landings in the Mediterranean sea, and both these small pelagic foraging species as well as round sardinella *Sardinella aurita* (Valenciennes, 1847), chub mackerel (*Scomber japonicas*, Houttuyn, 1782) and horse mackerel (*Trachurus trachurus*, Linnaeus, 1758) are of high ecological relevance because they transfer energy from the lower to the upper levels of the trophic chain (Sinovčić et al., 2009; Fernandes et al., 2018; Tugores et al., 2016). In our previous study, occurrences of OCPs and PCBs in different edible fish species were preliminarily investigated (Kljaković-Gašpić et al., 2015). The results demonstrated a need for investigations involving larger sample sizes.

In this paper, the objective was to study the distribution of PCBs and OCPs in fish species sampled by a fishing fleet along the Croatian Adriatic in 2014 and 2016. The study combines widely accepted and traditionally used statistical tests along with advanced classification methods to enable a more detailed interpretation of the results and

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strives to achieve a better description of the spatio-temporal distribution of POPs in marine fish species. Furthermore, this paper elaborates on the possibility of implementing onward algorithms such as the Kohonen self-organizing maps (SOM) and Decision Tree Learning (DT) for an improved approach to the pollutant apportionment primarily in *S. pilchardus*, which further enhance the overall conclusions presented herein. We note that both methods were verified in the available literature as a reliable means for the evaluation and exploration of contaminants such as POPs in air, water, soil, plant and lake fish species (Herceg Romanić et al., 2018a; Herceg Romanić et al., 2018b; Mari et al., 2010; Olkowska et al., 2014), but also as the tools that exhibited advantages over commonly applied clustering techniques (e.g., Budayan et al., 2009).

2. Materials and method

2.1. Sampling

A total of 45 fish samples were collected in the period 2014 to 2016. A random sample of *ca* 50 specimens was taken by purse seine catches (mesh size: 8 mm/bar length) in the eastern Adriatic Sea. Each fish sample was pooled from a fillet of specimen, totalling 45 pooled samples (Table 1). The fish was caught in various fisheries zone (coastal: A, E, and F, and off coast: B and C) of the Adriatic Sea (Fig.1).

2.2. Chemical analysis

Two aliquots were analysed from each pool and about 5 g were ground with 2 g of sodium sulphate in a glass mortar, dissolved in 40 mL of n-hexane. The details were described in a paper by Kljaković-Gašpić et al. (2015).

Analysed compounds: OCPs: (HCB (hexachlorobenzene), α-HCH, β-HCH, γ-HCH (α-, β-, γ-hexachlorocyclohexanes), *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT). PCB is a group of 209 congeners and methods of analysis usually include six indicator PCBs, whose selection is based on their dominant presence in technical mixtures, the environment, and animal and human tissues. The selection of toxicologically relevant congeners that mostly include some mono- and di-ortho substituted PCBs represents the more toxic fraction of PCBs in the sample. Six indicator PCBs: PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180; toxicologically relevant PCB congeners: PCB-60, PCB-74, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-170, and PCB-189.

High-resolution gas chromatography with electron capture detector

Table 1
Biometry and fisheries zone of sardine samples collected in 2016 (1 – 22), and pelagic fish samples in 2014 (A – anchovy, L – chub mackerel, M – horse mackerel, OS - round sardinella, and S – sardine).

S	Sampling date	Fisheries zone	Total length range (cm)	Average total length (cm) and standard deviation	Average body mass (g) and standard deviation
1S	28.7.2016.	B2	13–16	14.28–0.61	21.58–3.11
2S	06.05.2016.	B3	13.5–15.5	14.45–0.58	21.67–3.25
3S	13.06.2016.	B2	12.5–16	13.83–0.82	30.31–3.97
4S	13.06.2016.	F1	11.5–15	13.09–0.62	16.85–2.46
5S	30.06.2016.	B2	12.5–15	13.71–0.77	18.96–3.59
6S	30.04.2016.	B2	12–16	13.81–0.85	20.11–2.89
7S	13.04.2016	F1	12–15.5	13.47–0.76	18.45–2.88
8S	06.05.2016	B3	14–17.5	15.23–0.74	27.85–4.07
9S	31.05.2016.	B2	13–16	14.75–0.73	26.19–3.96
10S	04.07.2016.	B2	13.5–17	14.81–0.73	24.50–4.11
11S	30.08.2016.	B2	11.5–15	13.30–0.70	17.89–2.69
12S	30.08.2016.	F1	12.5–16.5	14.42–0.54	23.64–4.35
13S	09.08.2016.	B3	14–16.5	14.94–0.58	25.37–2.99
14S	17.03.2016.	F2	11–16	13.94–0.89	18.73–3.86
15S	15.03.2016.	F1	11.5–16	13.73–0.86	17.58–3.02
16S	04.07.2016.	B3	13–16.5	14.71–0.72	24.45–3.69
17S	08.03.2016.	B3	12.5–15	13.66–0.68	18.76–2.69
18S	30.06.2016.	B2	12.5–17	14.34–0.81	21.58–4.37
19S	05.08.2016.	A1	12–15	12.80–0.45	15.68–1.71
20S	28.07.2016.	B3	13.5–17	14.80–0.81	23.72–3.82
21S	29.4.2016.	B3	12.5–17	14.43–1.10	21.62–7.28
22S	20.11.2015	E7	12–16	14.5–0.97	22.56–4.87
23A	2.6.2014.	B3	13–16.6	14.55–0.66	19.93–3.08
24S	3.7.2014.	B3	13.5–15.5	14.72–0.57	25.46–3.05
25A	3.7.2014.	B3	12.5–15	13.59–0.52	16.37–1.82
26M	3.7.2014.	B3	11–14	14.06–0.75	21.81–3.61
27L	3.7.2014.	B3	26.5–28.5	27.5–1.41	183.66–26.67
28S	25.8.2014.	E5	13–14.5	13.64–0.44	19.0–2.09
29A	25.8.2014.	E5	12–15	13.16–0.44	13.78–1.32
30OS	25.8.2014.	E5	21–26	23.42–1.14	96.75–12.51
32M	25.8.2014.	E5	13.5–16	14.55–0.77	23.60–4.43
33A	29.9.2014.	B2	10–15	13.24–0.75	13.93–2.23
34L	29.9.2014.	B2	11–25	16.45–3.79	41.76–36.66
35S	29.9.2014.	B2	13–17	14.59–0.76	23.51–3.85
36S	28.10.2014.	B3	15–17	15.91–0.67	31.71–3.72
37OS	28.10.2014.	B3	22–25	23.86–0.84	109.41–15.39
38M	28.10.2014.	B3	16–21.5	18.7–2.36	56.85–19.94
39S	29.10.2014	E2	13.5–15.5	14.72–0.56	26.19–3.05
40M	29.10.2014	E2	16–19	17.2–1.25	25.83–48.71
41L	29.10.2014	E2	19.5	19.5	62.41
42A	25.11.2014.	F2	12–15	13.71–0.59	14.41–2.04
43S	25.11.2014.	F2	13–16.5	14.09–0.66	20.74–3.71
44L	25.11.2014.	F2	16–32.5	25.92–5.42	140.32–108.28
45S	19.12. 2014.	C1	12.5–15	13.69–0.62	19.27–3.09
46A	19.12. 2014	C1	13–14.5	13.75–0.44	18.61–2.63