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Baseline

Bioaccumulation of organochlorine compounds in large, threatened elasmobranchs off northern New South Wales, Australia

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ABSTRACT

Persistent organic pollutants (POPs) include polychlorinated biphenyls (PCBs) dichlorodiphenyltrichloroethane (DDT) and hexachlorobenzene (HCB), which are resistant to biodegradation and therefore accumulate in the marine environment. In Australia, POPs occur in high concentrations primarily in costal water near farming regions and urban centres. From contaminated sediments and biota, POPs are transferred and biomagnified in larger marine organisms. We quantified POPs concentrations in 57 individuals from ten species of sharks and rays caught in bather-protection gillnets deployed off northern New South Wales, Australia. Polychlorinated biphenyls, DDTs and HCB were detected in all species. For some individuals, concentrations were at levels known to have deleterious sub-lethal effects. Overall, the POP concentrations analysed in this study were comparable to those in similar species from more polluted regions, and may have negative impacts on longer-term health. Future research is warranted to investigate spatio-temporal patterns of species-specific contaminant loads and their implications.

Polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT, and its metabolites), and hexachlorobenzene (HCB) are persistent organics pollutants (POPs) of major concern in the marine environment because of their toxicity to both humans and wildlife (El-Shahawi et al., 2010; Niimi, 1996). Persistent organic pollutants tend to occur in high concentrations throughout those marine environments close to urban centres and industrial sites, and especially in developing countries where they are legally and illegally used as pesticides (Fu et al., 2003). From these contaminated environments, POPs are transported and released into the sediments of more remote regions (e.g. *Antarctica*; Kallenborn et al. (2015)) through two main pathways termed: 'long range atmospheric transport'; or 'biological transport' (Blais et al., 2007). Once in the marine environment, POPs can be absorbed and bio-accumulated into the tissues of living organisms because of their lipophilic and persistent nature. High tissue concentrations of POPs can have deleterious sublethal effects on aquatic organisms, such as impaired reproduction and growth (Hose et al., 1989; Johnson et al., 2013) and immune suppression (Gelsleichter et al., 2006; Marsili et al., 2012).

In Australia, the use of DDT, PCBs, and HCB has been banned since the late 1970s (Bu et al., 2015). Dichlorodiphenyltrichloroethane remains a common contaminant in the environment, but its concentration in Australia waters has temporally declined (Connell et al., 2002; Stemmler and Lammel, 2009). Conversely, there has been no clear decline among PCBs, probably because they continue to be produced as combustion by-products and are released during the recycling of materials and building demolitions (Department of Environment and Energy, 2018a). In Australia, of the three contaminants, HCB is the least abundant in marine environments due to its limited use, low water solubility and rapid, almost complete degradation to pentachlorophenol and related compounds (Department of Environment and Energy, 2018b).

The monitoring of POPs in Australian marine organisms has mostly focused on economically important species inhabiting the Great Barrier Reef (Haynes and Johnson, 2000; Lewis et al., 2009) and near urbanised centres (Matthews et al., 2008; Roach and Runcie, 1998). These studies imply considerable spatio-temporal variation among POP levels. Specifically, several marine organisms sampled from the Great Barrier Reef Marine Park have shown a general enrichment of various contaminants including POPs (Jones et al., 2005; Mortimer, 2000; Van Oosterom et al., 2010), but the greatest levels were recorded from Moreton Bay, near Brisbane (Matthews et al., 2008). Similarly,

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throughout Australia's largest urban port—Sydney Harbour (New South Wales; NSW)—PCBs in several small- and medium-sized commercially and recreationally important species were above levels considered safe for human consumption (Manning et al., 2017; Roach and Runcie, 1998). By comparison, at another industrial port in Port Phillip Bay, Victoria, Australia, POPs were below detection levels in sand flathead (*Platycephalus bassensis*) (Gagnon et al., 2016).

Notwithstanding the above work, there remains a paucity of data describing baseline contaminant loads in larger marine species, including elasmobranchs in Australian waters (Niimi, 1996). In one of the few published studies, Gilbert et al. (2015) suggested that off Australia, apex predators like sharks have the potential to accumulate high PCBs levels. With global populations of most elasmobranchs in decline, understanding both the extent of contaminant exposure and potential physiological effects is critical to management and conservation.

In this study, we examined the concentration of 30 PCB congeners, op′ and pp′ forms of DDT, DDE and DDD and HCB in the muscle samples of six and four species of sharks and rays, respectively from northern NSW, Australia. The sampled species and their ICUN (2018) red list classifications included: great hammerhead (*Sphyrna mokarran*; $n = 24$; Endangered), common blacktip shark (*Carcharhinus limbatus*; $n = 9$; Near Threatened), dusky shark (*Carcharhinus obscurus*; $n = 1$; Vulnerable), white shark (*Carcharodon carcharias*; n = 2; Vulnerable), bull shark (*Carcharhinus leucas*; n = 2 plus six embryos from one gravid female; Near Threatened), greynurse shark (*Carcharias taurus*; n = 1; Critically Endangered), pygmy devilray (*Mobula kuhlii* cf. *eregoodootenkee*; $n = 8$; Near Threatened), Australian cownose ray (*Rhinoptera neglecta*; n = 1; Data Deficient), whitespotted eagle ray (*Aetobatus ocellatus*; n = 2; Vulnerable) and whitespotted guitarfish (*Rhynchobatus australiae*; n = 1; Vulnerable).

All but one sample were opportunistically collected from specimens caught (and deceased) in bather-protection gillnets (150 m long by 4 or 6 m deep) deployed off northern NSW (28.77° S, 153.60° E to 29.10° S, 153.44° E) during two fishing blocks (8 December 2016 to 30 May 2017 and 23 November 2017 to 2 May 2018). The gillnets were anchored ~500–600 m off shore in 5–13 m water depths and parallel to five beaches: Lennox Head, Sharpes, Shelly and Lighthouse beaches, Ballina; and Main Beach, Evans Head (Fig. 1). The only animal not gillnetted was the dusky shark which was reported stranded at Lighthouse Beach (Fig. 1). The use of gillnets was approved under government legislation, and all samples were collected under permit of the NSW Department of Primary Industries.

After being removed from the gillnets (or collected), all specimens were measured for total length (TL) and immediately frozen (−20 °C) in an industrial freezer. During subsequent necropsies, tissue (muscle) samples were collected from the posterior base of the dorsal fin of all sharks using a solvent-washed and distilled-water-rinsed biopsy cutter attached to a power drill. For the rays, tissue samples were collected from the pectoral fins using a sterilised knife. All samples were then stored at Southern Cross University in a −20 °C freezer.

Determination of HCB, DDTs and PCBs was performed at the Environmental Sciences Department, University of Siena, according to the U.S. Environmental Protection Agency (EPA) 8081/8082 Method modified (Marsili et al., 2016). Specifically, samples (50–300 mg) were lyophilised in an Edwards freeze drier for 2 days and extracted with n-hexane (gas chromatography grade, Merck) in a Soxhlet apparatus. Whatman cellulose thimbles (i.d. 25 mm, e.d. 27 mm, length 100 mm) used for extraction of the samples were preheated for about 30 min to 110 °C and pre-extracted for 9 h in a Soxhlet apparatus with n-hexane, in order to remove any organochlorine contamination. Each sample was spiked prior to extraction with 2,4,6-trichlorobiphenyl (International Union of Pure and Applied Chemistry; IUPAC) number 30 Ballschmiter and Zell (1980) as a surrogate compound. The concentration of PCB30 was quantified and its recovery calculated for each sample. After a 9-h extraction with n-hexane, the samples were purified with sulphuric acid to first obtain lipid sedimentation.

The extract then underwent liquid chromatography on a column containing florisil that had been dried for 1 h in an oven at 110 °C. This further purified the apolar phase of lipids that could not be saponified, such as steroids like cholesterol. Decachlorobiphenyl (DCBP - IUPAC number 209) was used as an internal standard, where it was added to each sample prior to the extraction and included in the calibration standard (a mixture of Aroclor 1260, HCB and pp′- and op′-DDT, DDD and DDE). High resolution capillary gas chromatography was performed with an Agilent 6890 N and a 63Ni ECD and an SBP-5 bonded phase capillary column (30 m long, 0.2 mm i.d.). The carrier gas was nitrogen with a head pressure of 15.5 psi (splitting ratio 50/1). The scavenger gas was argon/methane (95/5) at 40 ml/min. Oven temperature was 100 °C for the first 10 min, after which it was increased to 280 °C at 5 °C/min. The injector and detector temperatures were 200 and 280 °C respectively. The extracted organic material (EOM%; lipid content) from freeze-dried samples was calculated in all samples.

Capillary gas-chromatography revealed 30 PCB congeners (IUPAC no. 95, 101, 99,151, 144, 135, 149, 118, 146, 153, 141, 138, 178, 187, 183, 128, 174, 177, 156, 171, 202, 172, 180, 199, 170, 196, 201, 195, 194 and 206). Total PCBs (ΣPCBs) were quantified as the sum of all congeners. These congeners constituted 80% of the total peak area of PCBs in the sample. Total DDTs (ΣDDTs) were calculated as the sum of the isomers op′DDT, pp′DDT, op′DDD, pp′DDD, op′DDE and pp′DDE. The proportion of endocrine disrupting chemicals (EDCs) was calculated as the sum of the isomers: op′DDT, pp′DDT, op′DDD, pp′DDD, op′DDE, pp′DDE and PCBs IUPAC no. 95, 99, 101, 118, 153 (Fossi and Marsili, 2003; Fossi et al., 2003). The results were expressed in ng/g lipid weight (l.w.) unless differently specified. The limit of detection (LOD) for all compounds analysed was 0.1 ng/kg (ppt). For analyses purposes, censored data were replaced with LOD/2 (0.05 ng/kg) (Zeghnoun et al., 2007). Where relevant, PCB and DDT profiles in sample tissues were compared with known concentrations in the original source pollutants (e.g. Arochlor 1260 and commercial pesticides containing all DDT isomers).

Statistical analyses were performed with IBM SPSS Statistics v 22.0 (IBM Corporation, US). Owing to the small sample sizes and skewed distributions, nonparametric statistical tests were applied. Differences in ΣPCBs, ΣDDTs and HCB concentrations and EOM% (lipid content of tissues) were tested using Kruskal-Wallis for more than two group comparisons and Mann–Whitney *U* test (MWU) for pairwise comparisons. Correlations between ΣPCBs, ΣDDTs or HCB and TL were assessed using the Pearson's correlation coefficient. Significance was tested at $p < 0.05$.

With a total of 24 samples (six females and 18 males), the great hammerhead was the most represented species. Total lengths varied from 234 to 383 cm, with all individuals determined during necropsy to be mature. The EOM% ranged from 2.68 to 30.32% with no significant difference between sexes ($p > 0.05$; Table 1). Polychlorinated biphenyls and DDTs were detected in all samples, whereas HCB was below detectable concentrations in seven samples (Table 1). There was a trend of greater median concentrations of ΣPCBs, ΣDDTs and HCB in males than females, but these differences were not statically significant ($p > 0.05$; Table 1). No significant correlations were detected between TL and contaminant concentrations (PCBs: $r = -0.10$, $p = 0.63$; DDTs: $r = 0.08$, $p = 0.71$; HCB: $r = 0.07$, $p = 0.73$). The concentrations of ΣPCBs in the sampled great hammerheads were similar to those previously recorded in liver samples of the smooth hammerhead, *Sphyrna zygaena* from the Mediterranean Sea (Seventeen PCB isomers: average = 4260 ng/g l.w.) (Storelli et al., 2003).

The common blacktip shark was the second most represented shark species with nine samples (six females and three males). All individuals were mature (Table 2). The lipid percentages ranged from 9.57 to 40.30% with no significant difference between sexes (MWU = 7, $p = 0.71$). Polychlorinated biphenyls and DDTs were detected in all samples, while HCB were below detectable concentrations in two samples (Table 2). The median values of ΣPCBs, ΣDDTs and HCB were

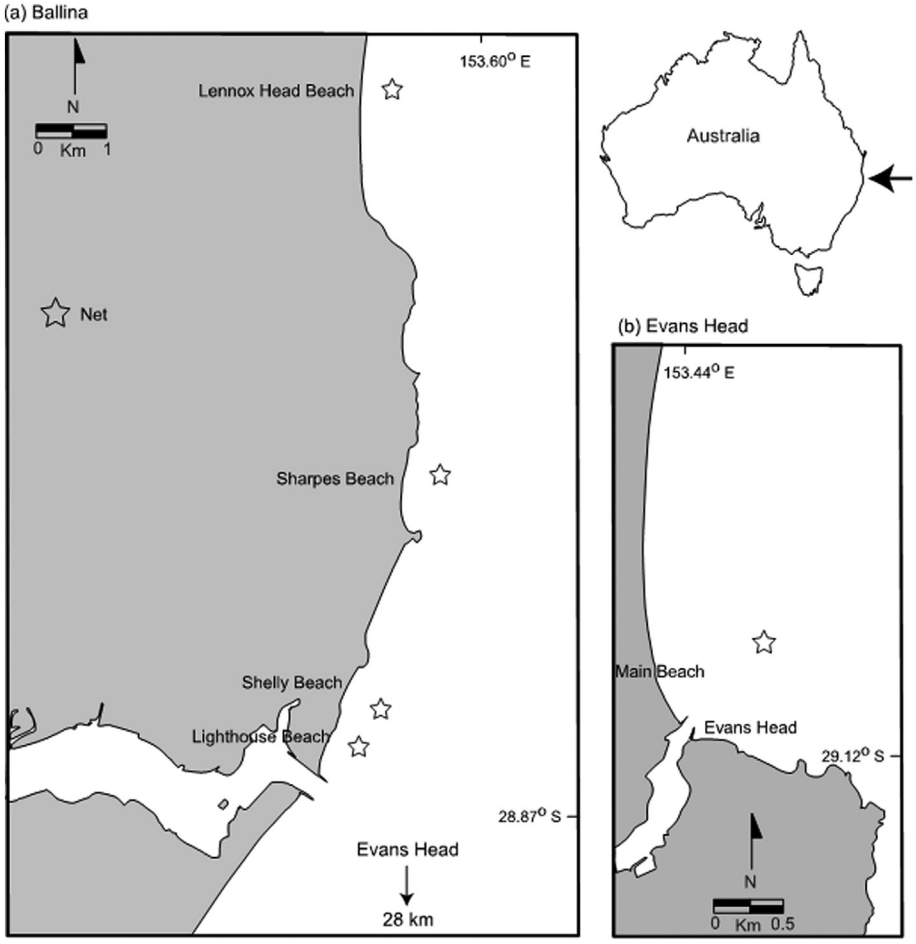

Fig. 1. Map of the fished area and location of the nets used to catch specimens examined in this study.

Table 1
Median levels and ranges of % extracted organic material (EOM), ΣPCBs[a], ΣDDTs (sum of the op′ and pp′, forms of DDT, DDD and DDE) and HCB in the muscle samples of 24 adult great hammerheads (*Sphyrna mokarran*) sampled off northern New South Wales, Australia. Values are expressed in ng/g l.w. M = male, F = female, LOD = limit of detection (0.01 ng/g l.w.), MWU = Mann–Whitney *U* test.

	Sex	Median	Range	MWU	p
EOM%	F	16.02	11.63–20.83	45	0.54
	M	15.39	2.68–30.32		
ΣPCBs	F	3559.5	129.77–12,942.05	40	0.35
	M	6883.35	488.60–22,224.26		
ΣDDTs	F	128.70	10.24–463.66	30	0.11
	M	261.70	31.65–10,780.77		
HCB	F	6.48	2.47–10.48	11	0.63
	M	10.16	< LOD–1482.65		

[a] ΣPCBs = IUPAC no. 95, 101, 99, 151, 144, 135, 149, 118, 146, 153, 141, 138, 178, 187, 183, 128, 174, 177, 156, 171, 202, 172, 180, 199, 170, 196, 201, 195, 194, 206.

greater in females (ΣPCBs: median = 7257.62 ng/g l.w.; ΣDDTs: median = 400.66.13 ng/g l.w.; HCB = 9.36 ng/g l.w.) than males (ΣPCBs: median = 6357.81 ng/g l.w.; ΣDDTs: median = 193.36 ng/g l.w.; HCB = 5.22 ng/g l.w.) but these differences were not statistically significant (ΣPCBs: MWU = 7, $p = 0.71$; ΣDDTs: MWU = 7, $p = 0.60$; HCB: MWT = 7, $p = 0.69$) (Table 2). Overall there were no significant correlations between TL and contaminant concentrations (PCBs: $r = -0.51$, $p = 0.15$; DDTs: $r = -0.41$, $p = 0.27$; HCB: $r = -0.41$, $p = 0.26$).

Table 2
The total lengths (TL in cm), sex and median levels of % extracted organic material (EOM), ΣPCBs[a], ΣDDTs (sum of the op′ and pp″, forms of DDT, DDD and DDE) and HCB in muscle samples of nine mature common blacktip sharks (*Carcharhinus limbatus*) sampled off northern New South Wales, Australia. Values are expressed in ng/g l.w. M = male, F = female, LOD = limit of detection (0.01 ng/g l.w.).

TL (cm)	Sex	EOM%	ΣPCBs	ΣDDTs	HCB
207	M	13.04	6357.81	193.36	5.22
186	F	9.57	29,635.86	2184.35	14.34
182	M	12.33	987.40	114.53	< LOD
146	F	14.29	20,291.04	1016.98	21.82
192	M	20.73	7921.34	326.51	16.18
195	F	40.30	1728.47	60.43	< LOD
223	F	18.29	11,104.55	645.29	5.10
233	F	18.16	382.44	156.03	12.51
231	F	18.14	3410.69	124.10	6.21

[a] ΣPCBs = IUPAC no. 95, 101, 99, 151, 144, 135, 149, 118, 146, 153, 141, 138, 178, 187, 183, 128, 174, 177, 156, 171, 202, 172, 180, 199, 170, 196, 201, 195, 194, 206.

The lipid percentages of the two white (both immature females), two bull (both mature females), one dusky (immature female) and one greynurse shark (mature female) ranged from 10.84 to 18.89% (Table 3). Polychlorinated biphenyls and DDTs were detected in all samples, while HCB was below detectable concentrations in one of the white sharks. Owing to the small sample size, differences among genders and species were not tested. The observed ΣPCBs, ΣDDTs and HCB in these four species were within the ranges of concentrations recorded here for the great hammerheads and common blacktip sharks.

Table 3
The total lengths (TL), sex and median levels of % extracted organic material (EOM), ΣPCBs[a], ΣDDTs (sum of the op′ and pp′, forms of DDT, DDD and DDE) and HCB in muscle samples from a dusky shark (*Carcharhinus obscurus*), two white sharks, (*Carcharodon carcharias*), two bull sharks (*Carcharhinus leucas*) including six embryos and one greynurse shark (*Carcharias taurus*) sampled off northern New South Wales, Australia. Values are expressed in ng/g l.w. MM = mature male, MF = mature female, IM = immature male, and IF = immature female, LOD = limit of detection (0.01 ng/g l.w.).

Species (common name)	TL (cm)	Sex	EOM%	ΣPCBs	ΣDDTs	HCB
White shark	290	IF	10.84	4723.05	557.28	< LOD
	345	IF	10.98	23,436.70	1295.08	155.39
Dusky shark	220	IF	18.22	2447.42	737.32	6.06
Greynurse shark	299	MF	18.02	647.85	174.91	7.37
Bull shark	244	MF	18.89	2486.99	523.42	11.94
	278 (gravid)	MF	12.55	560.60	444.44	4.94
Embryos in the gravid bull shark	78	IM	17.93	658.41	538.59	3.95
	73	IM	15.11	485.72	418.89	7.85
	78	IF	16.40	378.31	329.01	10.52
	77	IM	15.03	394.04	422.00	6.55
	80	IF	16.46	283.68	220.14	9.01
	72	IM	16.00	960.23	534.19	27.19

[a] ΣPCBs = IUPAC no. 95, 101, 99, 151, 144, 135, 149, 118, 146, 153, 141, 138, 178, 187, 183, 128, 174, 177, 156, 171, 202, 172, 180, 199, 170, 196, 201, 195, 194, 206.

Gilbert et al. (2015) analysed liver samples of white and dusky sharks collected from northern NSW for a total of seven PCBs congeners. Five of those PCBs congeners were also analysed in this study ($PCBs_5$ = 101 + 118 + 138 + 153 + 180). The concentration of $PCBs_5$ in the smaller white shark from this study (1267.38 ng/g l.w.) was below the concentrations reported by Gilbert et al. (2015) (2872.5–4972.1 ng/g l.w.), whereas the concentration of $PCBs_5$ in the larger white shark (6393.80 ng/g l.w.) was substantially greater. The dusky shark sample analysed in this study had $PCBs_5$ (1498.36 ng/g l.w.) within the lower range of those reported by Gilbert et al. (2015) (41.3–9146.4 ng/g l.w.). Of note, POP concentrations in liver samples are generally higher than in muscle samples (Storelli and Marcotrigiano, 2001).

In terms of broader spatial comparisons, Marsili et al. (2016) analysed the muscle samples of four female white sharks off South Africa and following the same protocol applied here. The concentrations of ΣPCBs reported for white sharks in Australia were within the range, and also above those values from South Africa (ΣPCBs: range = 4219.58–18,4126.99 ng/g l.w.), whereas ΣDDTs and HCB were in the lower range of concentrations reported from South African conspecifics (range ΣDDT = 963.65–31,330.43 ng/g l.w.; HCB: range = 65.05–1923.07 ng/g l.w.) (Table 3). No spatial comparisons of PCBs, DDTs and HCB are available for the greynurse shark, great hammerhead or common blacktip shark and so, to the best of our knowledge, these are the first baseline data describing the accumulation of PCBs, DDTs and HCB in these species.

Similarly, bull sharks have not been previously assessed for POPs in Australia. Of note here was that one of the two bull sharks was gravid with six embryos (two males and four females) in the left (n = 2) and right (n = 4) uteri (Table 3). The concentrations and profiles of ΣPCBs, HCB and ΣDDTs in the mother were similar to those in her embryos, and lower than the values recorded in the non-gravid conspecific (Fig. 2; Table 3). These results are more likely attributable to maternal offloading during gestation (Olin et al., 2014; Weijs et al., 2015b). Both adult female bull sharks had ΣPCB and ΣDDT concentrations within the lower range of those found in the muscle and liver samples of conspecifics from the southeastern USA (PCBs = 1780–32,000 ng/g l.w.; DDTs = 416–4320 ng/g l.w.) (Olin et al., 2014; Weijs et al., 2015a).

A total of 12 samples of four ray species were analysed, and all contained detectable PCBs, DDT and HCB (Table 4). Owing to the small sample sizes for Australian cownose rays, whitespotted eagle rays and whitespotted guitarfish, interspecific differences were not tested. However, ΣPCBs, ΣDDTs and HCB for these three species were very similar, and within the range of concentrations recorded for the pygmy devilray (Table 4). Other studies reported similar PCB concentrations in muscle samples (PCBs = 68–3160 ng/g l.w.) of Atlantic stingrays (*Dasyatis sabina*) (Weijs et al., 2015a) and in the livers of *Torpedinid* spp. from the Mediterranean Sea (PCBs = 434–1040 ng/g l.w.), whereas the mean DDT level in the *Torpedinid* spp. (mean = 234 ng/g l.w.) was lower than recorded here. Of note, in five of the twelve samples analysed here, ΣPCBs and ΣDDTs were above the concentrations (PCBs = 605 ng/g l.w.; DDTs = 80 ng/g l.w.) at which an immunosuppression effect was detected in Atlantic stingrays (Gelsleichter et al., 2006).

When compared between groups, ΣPCBs and ΣDDTs were significantly greater in sharks than rays (ΣPCBs: MWU = 76, p = 0.00; ΣDDTs: MWU = 185, p = 0.03) whereas HCB (MWU = 153, p = 0.46) was found at similar, low concentrations. The PCBs congener compositions also varied substantially among sharks (Fig. 3). In great hammerheads, white sharks, and common blacktip sharks hexa-CBs (35-23-27%) and nona-CBs (28-37-33%) were the dominant congeners followed by hepta-CBs (20-22-22%), octa-CBs (11–14-12%) and penta-CBs (3-4-4%). In the dusky and greynurse sharks, hexa-CBs accounted for at

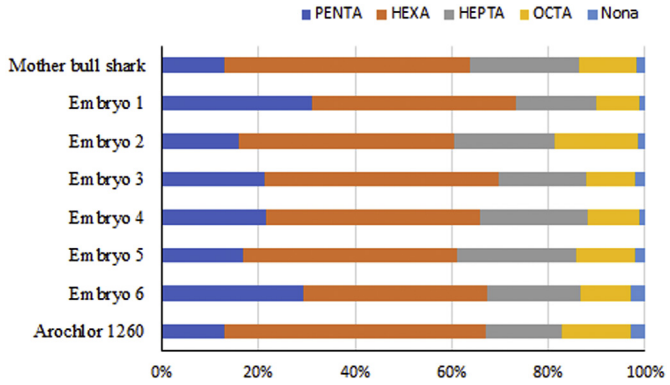

Fig. 2. Percentage composition of PCBs divided by chlorine content (penta-CBs, hexa-CBs, hepta-CBs, octa-CBs, nona-CBs) on ΣPCBs, analysed in six embryos found in a gravid bull shark (mother).

Table 4
The disc width (DW), sex (and maturation), and median levels of % extracted organic material (EOM), ΣPCBs[a], ΣDDTs (sum of the op′ and pp′, forms of DDT, DDD and DDE) and HCB in the muscle samples of mature pygmy devilray (*Mobula kuhlii* cf. *eregoodootenkee*), Australian cownose ray (*Rhinoptera neglecta*), whitespotted eagle ray (*Aetobatus ocellatus*) and whitespotted guitarfish (*Rhynchobatus australiae*) sampled off northern New South Wales, Australia. Values are expressed in ng/g l.w. MM = mature male; MF = mature female; M = male (unknown maturity), F = female (unknown maturity).

Species (common name)	DW (cm)	Sex	EOM%	ΣPCBs	ΣDDTs	HCB
Pygmy devilray	111	MF	9.65	736.54	807.26	6.17
	111	MM	13.94	579.08	323.63	8.97
	116	MF	20.73	358.57	166.16	4.07
	111	MF	12.96	470.46	235.99	7.89
	111.5	MF	15.77	354.12	264.93	4.45
	117.5	MF	15.61	2733.48	440.81	8.17
	93	MF	15.09	1038.79	771.47	21.00
	103.2	MM	18.55	670.97	609.77	10.55
Australian cownose ray	76	M	16.53	445.88	262.43	8.92
Whitespotted eagle ray	NA	F	14.85	615.06	710.72	13.32
	NA	F	15.57	359.46	314.16	8.25
Whitespotted guitarfish	243	M	16.76	372.77	351.43	7.08

[a] ΣPCBs = IUPAC no. 95, 101, 99, 151, 144, 135, 149, 118, 146, 153, 141, 138, 178, 187, 183, 128, 174, 177, 156, 171, 202, 172, 180, 199, 170, 196, 201, 195, 194, 206.

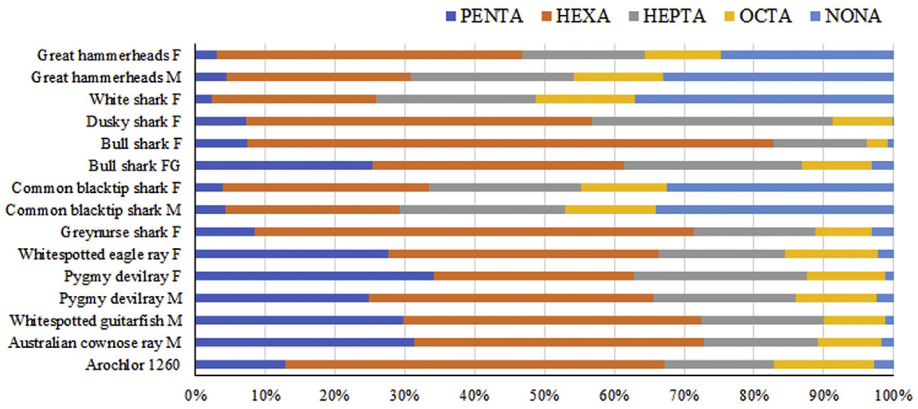

Fig. 3. Percentage composition of polychlorinated biphenyls (PCBs) divided by chlorine content (penta-CBs, hexa-CBs, hepta-CBs, octa-CBs, nona-CBs) on ΣPCBs, analysed in the muscle samples of sharks and rays divided by genders (M = males; F = females; G = gravid) and for Arochlor 1260.

least half of the total congeners (62–50%), followed by hepta-CBs (17–34%), while penta- octa- and nona-CBs accounted for < 1% of the profile. In the two bull sharks (non-gravid and gravid), hexa-CBs (36–75%) were largely the dominant congeners followed by hepta- (13–25%), penta-CBs (7–25%), octa-(2–10%) and nona-CBs (1–3%).

The PCB profiles for rays had greater inter-specific consistency and were similar to those reported for the commercial PCB congener mixture found in Arochlor 1260 (Fig. 3). Hexa-CBs (~38%) and penta-CBs (~29%) were the most abundant congeners, followed by hepta-CBs (~19%), octa-CBs (~10%) and nona-CBs (~1%). The bioconcentration potential (K_{ow} = octanol/water partition coefficient or lipophilicity) of hexa (log K_{ow}: range = 6.64–7.24) and penta-CBs (log K_{ow}: range = 6.13–6.39) congeners is lower than etpa-CBs (log K_{ow}: range = 7.08–7.36) opta-CBs (log K_{ow}: range = 7.27–7.8) and nona-CBs (log K_{ow} = 8.09) which indicates lower capacity of bioaccumulation in marine organisms. Therefore, the overall dominance of hexa-CBs and hepta-CBs in both sharks and rays seems to reflect observations made for environments proximate to Australian urban areas (Yeo et al., 2015).

The percentage of DDT and its metabolites evaluated in the muscle samples of sharks and rays are shown in Fig. 4 together with the commercial product formulation. Once in the environment, DDT undergoes slow degradation to DDE and DDD isomers; mostly, pp.'DDE is more stable and persistent than its parent compound. In our samples, pp.'DDE, was the most abundant isomer (28 and 39% in sharks and rays), and was substantially greater than the concentration in the original product formulation (4%). On contrary, pp′DDT, which was originally the major active component in the contaminants (77.1%), accounted for only 10% of the DDTs in rays and 16% in sharks. Of interest is the high proportion of op′ isomers (sharks = 50%, rays = 43%) compared to the original commercial pesticide mixture (15%) which suggests technical (non-insecticidal) sources of DDT (Nowell et al., 1999), such as manufacturing or storage facilities (Schmitt et al., 1990).

The pp′DDE/pp′DDT ratio typically is used as an indicator of degradation of pp′DDT in the environment (Qiu et al., 2004). In the commercial pesticide mixture, this ratio is 0.05, and so very high ratios are indicative of an almost complete degradation of the original compound suggesting an historical input of the pesticide (Aguilar, 1984). The pp′DDE/DDTs ratio is also an indicator of recent DDT input into the environment or metabolic 'weathering' of DDT. Values > 0.6 imply there have been no new inputs to the environment (Tsydenova et al., 2004).

In both sharks and rays, the pp′DDE/ pp′DDT ratios were quite low (sharks: range = 0.11–10.81; rays: range = 0.37–8.68) and the pp′DDE/DDTs ratios (sharks: range = 0.02–0.065; rays: range = 0.06–0.70) were, with two exceptions, lower than the critical value of 0.6; which implies recent sources of DDTs for most of the analysed specimens. Ongoing input of DDTs into the environment could be explained by emissions to the air and surface waters from manufacturing the technical mixtures, or even the deposition of long-range

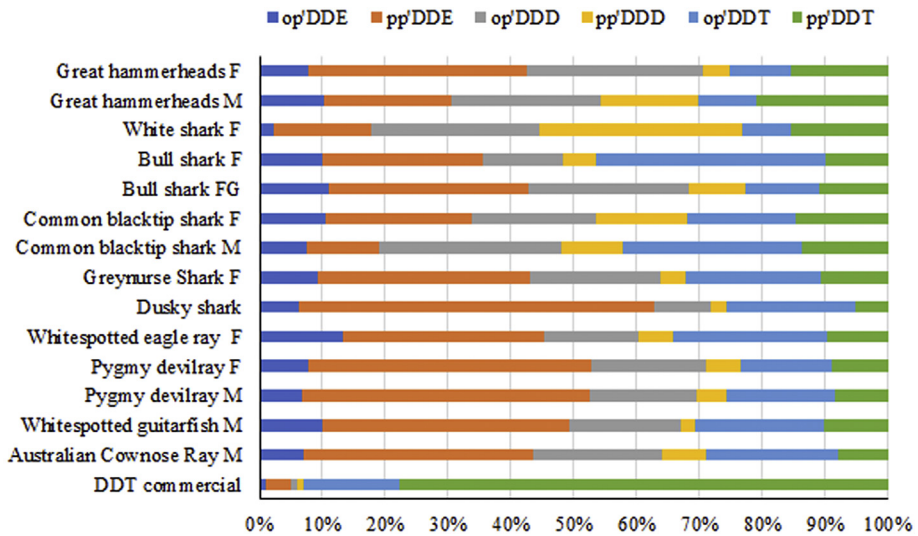

Fig. 4. Percentage composition of the op′ and pp′ forms of DDT, DDE and DDD on ΣDDTs in muscle samples of sharks and rays divided by sex (M = males; F = females; G = gravid) and for the commercial DDT mixture.

transported DDT from regions where this pesticide is still used. Until 2004 in China, technical DDT was still the predominant source of DDT in the air (Qiu and Zhu, 2010). Moreover, technical DDT was used to produce dicofol which was exported to Africa and Southeast Asia and used for malaria prevention and control (Qiu and Zhu, 2010). Internal sources of DDT cannot be excluded. It is well established that DDT remains one of the most common contaminants detected in irrigation channels and can reach marine environments during flood events (Müller et al., 2000). Unlike DDT, the low level of HCB found in the assessed specimens implies limited concentrations in the marine environment, and probably as a consequence of low solubility and degradation.

A key concern is the large proportion of EDCs which constitute about 65% of all POPs in rays (females = 64%; males = 68%) and 33% in sharks (females = 32%; males = 34%). In male rays and sharks, respectively 79% and 67% of the EDCs are composed of compounds with known estrogenic and anti-androgenic capacities (pp′DDT, op′DDT, pp′DDE and op′DDE and PCB congeners, 95, 99, 101 and 153), which can affect male reproductive processes in some species (Gray et al., 2001; Mills and Chichester, 2005). In female rays and sharks, 20 and 29% of the EDCs (pp′DDE and op′DDT and PCB congener 118), respectively have androgenic and anti-estrogenic properties and may be implicated in adverse reproductive outcomes (Gray et al., 2001; Marsili et al., 2016; Mills and Chichester, 2005).

Elasmobranchs are an evolutionarily conservative group with diverse life histories, complex reproductive strategies and divergent trophic levels (Weijs et al., 2015a, 2015b). A high degree of variability in contaminant concentrations was found among the samples here, although extremely high concentrations were only found in sharks. Sharks are apex predators with long lifespans, slow growth rates and especially large sizes which renders them more susceptible than rays to accumulating high levels of organochlorine compounds.

Migrations are also likely to expose some sharks to more POPs. For example, white sharks, great hammerheads and dusky sharks are fairly nomadic species that primarily occur along the northern NSW coast in winter and migrate to cooler waters in the summer months, often covering substantial distances (Hammerschlag et al., 2011; Rogers et al., 2013; Stevens and Lyle, 1989). In particular, white sharks are known to complete rapid transoceanic return migrations (e.g. from South Africa to Australia; Bonfil et al., 2005), and may accumulate contaminants off various countries. By comparison, common blacktip, bull, and especially greynurse sharks might exhibit greater philopatry, with movements primarily restricted to shallow nearshore areas (Hueter et al., 2005; Otway et al., 2004; Smoothey et al., 2016). Species-specific contaminant fingerprints might therefore be more indicative of the regionally sampled marine environment.

Despite being smaller in size and at lower trophic levels, rays clearly are also susceptible to accumulating contaminants at potentially dangerous levels. The species of analysed rays included primarily filter feeders (pygmy devilray) and also secondary consumers (all species). These species might accumulate contaminants directly through water filtration (including microplastics), and ingesting contaminated zooplankton and other prey including benthic species and detritivores (Stewart et al., 2018). While the pygmy devilrays predominantly reside off the bottom, the other rays species are known to primarily consume benthic species, which might make them more susceptible to the bioaccumulation of high levels of any POPs stored in the sediments.

In addition to quantifying POPs among elasmobranchs, this study also provides further support for the maternal transfer of PCBs body burdens, with a relatively high concentration of contaminants observed in the bull shark embryos (Weijs et al., 2015b). Coupled with ontogenetic changes in diet, such transfer ultimately will increase the risk of reaching high concentrations of contaminants in adults (Lyons et al., 2013).

In conclusion, the presented data provide a snapshot of the potential risks to which elasmobranch species may be exposed. Experimental and field studies have shown how exposure to POPs can have negative population effects, including birth defects, high infertility, endocrine disruption, immune system dysfunction, and other reproductive anomalies (Corsolini and Sara, 2017; Gelsleichter et al., 2006; Storelli et al., 2005). Sex-ratio imbalances in teleosts and molluscs have been associated with total concentrations of organochlorines contaminants with known endocrine disruptors (in this study: DDTs and PCBs IUPAC no. 95, 99, 101, 118, 153) (Harris et al., 2010; Jobling et al., 2002; Jobling et al., 2005; Tyler and Jobling, 2008). Unfortunately, the potential health effects of these compounds among elasmobranchs remain unknown. Such implications are of concern considering that all species analysed in this study have a high conservation protection status and generally the numbers of elasmobranchs around the world are declining (Sims, 2015; Spaet et al., 2016). We contend that while it remains unclear if the observed contaminant loads cause deleterious physiological impacts that result in lower survival or future reproductive impairment (all of which may impact population maintenance), the potential effects cannot be underestimated and deserve more attention and dedicated studies.

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