GLOBAL DISTRIBUTION OF *TRIS* (4-CHLOROPHENYL) METHANOL AND *TRIS* (4-CHLOROPHENYL) METHANE IN FLATFISH – IS TECHNICAL DDT THE MOST LIKELY SOURCE?

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Introduction

Tris (4-chlorophenyl) methanol (TCPM(OH)) and *tris* (4-chlorophenyl) methane (TCPMe) are among the most recently studied persistent organic pollutants (POPs) in environmental samples. TCPM(OH) was first found in marine mammal tissues in the late 1980s[1]. In the early 1990s data were reported for TCPM(OH) in both marine mammals and birds[2,3], and the qualitative presence of its presumed precursor, TCPMe, confirmed in the same samples. These two compounds were then quantified in a variety of environmental samples[4-15]. TCPM(OH) and TCPMe are now known to be globally distributed in the environment. A recent study also reported that concentrations of TCPM(OH) were about 10 times higher in blubber samples of marine mammals from Europe than in those from Asia, Russia or North America[13].

The principal source of TCPM(OH) and TCPMe in the environment is, as yet, unknown. These compounds may originate from a variety of sources including the manufacture of agrochemicals such as Dicofol and technical DDT formulations, both of which contain structurally related compounds[3,16]. In their study, Buser[17] showed that under conditions similar to those used for the synthesis of technical DDT, TCPMe isomers were formed in small amounts. Although a significant correlation has been reported between TCPMs (TCPM(OH) and TCPMe) and DDTs in animals feeding at high trophic levels[13], including humans[14], technical DDT has not been confirmed as the source of TCPMs. It is also possible that the association between the concentrations of TCPMs and DDTs in environmental samples reflects the similar properties and bioaccumulation behavior of these groups of compounds in aquatic food chains, since significant relationships have also been observed between TCPMs and PCBs[13].

The main objective of this study is to investigate the global distribution of TCPMs in flatfish species from different areas of North America and Europe. In addition, the relationship between TCPMs and DDTs is assessed in flatfish species, which generally occupy a lower trophic level than either marine mammals or humans, in order to test the hypothesis that technical DDT represents the main source of TCPMs in the marine environment.

Methods

Sampling

Samples of a number of flatfish species were obtained from different locations in North America and Europe (Table 1). The most westerly sampling site (in Canada) is located about 10 000 km from the

most easterly site (in Germany), allowing a global view of the distribution of these compounds in flatfish. All samples were collected between 1995 and 2000.

Analyses

Liver samples from flatfish were analysed, either individually or as pooled samples, for TCPM(OH), TCPMe, 4,4'-DDT, 4,4'-DDD and 4,4'-DDE. Results are reported as the sum of TCPM(OH) and TCPMe (TPCMs) and as the sum of 4,4'-DDT, 4,4'-DDD and 4,4'-DDE (DDTs). Four different laboratories undertook the analysis of these compounds (Table 1). In most cases, for a given sample, the analysis was performed in a single laboratory. The exception was for samples from the United Kingdom, where the extraction was performed at CEFAS and the remainder of the analysis at IML. Most laboratories applied very similar methods of extraction, cleanup and fractionation; however, different quantification methods were used. Although all laboratories used capillary columns (HRGC) to isolate the compounds of interest, for detection and quantification IML used EI-LRMS in MS/MS mode, RIVO used ECNI-LRMS, and IFÖ used dual column ECD. In 2000-01, the three laboratories that performed the quantification participated in an ICES-MCWG interlaboratory study on the analysis of TCPM(OH) and TCPMe in two flatfish samples (muscle) and one solution with TCPM(OH) and TCPMe in undisclosed concentrations. Results indicated that these laboratories could report TCPMs in solution to within 17% CV. Due to low levels of TCPMs in the flatfish samples, comparisons for these samples were more difficult, but when levels were detected by at least two laboratories, concentrations were within 20% CV[18].

Table 1. Sampling location, species of flatfish and characteristic of liver sample analyzed

Continent Country	Sampling location	Common name Species	Samples n	 Type	Laboratory[a]
North America					
Canada (West coast)	Iona, BC	English sole			
		Parophrys vetulus	2	pool (4; 6)[b]	IML
	ZeroRock , BC	Pacific sanddab			
		Citharichthys sordidus	4	pool (2; 3; 3; 3)[b]	IML
Canada (East coast)	St.Lawrence	Greenland halibut			
	Estuary, Qc	*Reinhardtius hippoglossoides*	5	individual	IML
	St.Lawrence	American plaice			
	Estuary, Qc	*Hippoglossoides platessoides*	4	individual	IML
	St.Lawrence	Smooth flounder			
	Estuary, Qc	*Pleuronectes putnami*	3	individual	IML
Europe					
United Kingdom	Morecambe Bay	Dab			
		Limanda limanda	3	pool (5;5;5)[b]	CEFAS/IML
	Tyne,Tees,	Flounder			
	Thames	*Platichthys flesus*	2	pool (5;5)[b]	CEFAS/IML
The Netherlands	North Sea,	Plaice			
	Dutch coast	*P. platessa*	3	individual	RIVO
	North Sea,	Sole			
	Dutch coast	*Solea solea*	1	individual	RIVO
Germany	North Sea,	Plaice			
	German Bight	*P. platessa*	48	individual	IFÖ

[a] see authors' affiliations

[b] number of individual liver tissues per pool sample

Results and Discussion

TCPM(OH) was detected in all liver samples whereas TCPMe was detected, at lower concentrations, in about half of them. Average concentrations of TCPMs in liver of flatfish species obtained from different locations are reported in Figure 1A. The highest concentrations of TCPMs were found in plaice from the North Sea (German Bight). Mean concentration of TCPMs (range) in samples from North America (mean of the 5 flatfish species/locations) was 175 (50 - 465) pg/g ww. This value is about 20 times lower than the average TCPMs concentration of 3400 (1070 - 8560) pg/g ww in samples from Europe (mean of the 5 flatfish species/locations).

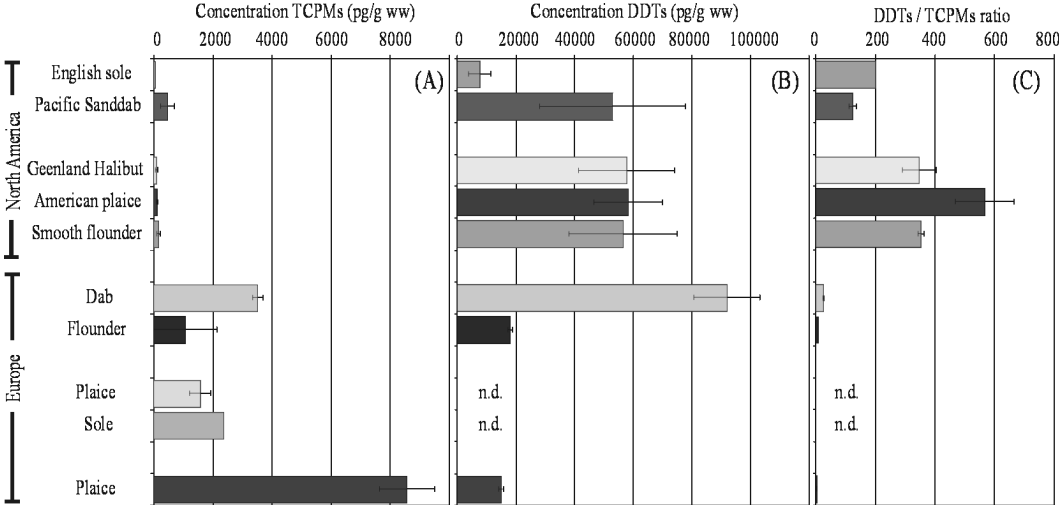

Figure 1. Average concentrations (± standard error) of TCPMs (A), DDTs (B) and average ratios ((± standard error) of DDTs / TCPMs (C) in flatfish species from North America and Europe. n.d. = not determined. (see Table 1 for sampling locations).

DDTs were also measured in the same samples (Figure 1B) allowing us to assess whether the observed differences in concentrations of TCPMs could be explained by differences in the general level of contamination of the fish between species and/or locations. In contrast to TCPMs, the average DDT concentrations in samples from North America (mean of the 5 flatfish species/locations), 46 700 (range 7 700 - 58 300) pg/g ww, was similar to the average concentration found in samples from Europe (mean of the 3 flatfish species/locations), 41 700 (range 15 000 - 92 000) pg/g ww.

The ratios of DDTs to TCPMs were also calculated for each of the flatfish samples (Figure 1C). Similar DDTs/ TCPMs ratios in all flatfish samples would strongly suggest that globally both TCPMs and DDTs originate from the same source. However, the average DDTs/TCPMs ratio (range) in flatfish species from North America, 317 (123 -566), is more than 25 times higher than that found in samples from Europe, 12 (2.6 - 26), suggesting that the production of technical DDT is probably not the main source of TCPMs in these samples.

The results of this study provide further evidence that TCPMs are globally distributed. Higher concentrations of TCPMs were found in flatfish species from Europe than in those from North America. This suggests that the European environment is more heavily contaminated by TCPMs than the North American environment, which is in agreement with previous work on marine mammals (13).

LEVELS IN BIOTIC COMPARTMENTS

Although a significant correlation is generally observed between TCPMs and DDTs in animals from high trophic levels, such a relationship was not observed in flatfish species that feed at lower trophic levels in the food chain. Study of the ratios between concentrations of these two groups of compounds suggests that technical DDT does not represent the main source of TCPMs in the marine environment. Further investigation of the origin of TCPMs in the environment is needed.

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