Levels of Tris (4-chlorophenyl) methane in seals and sediments from the Estuary and Gulf of St. Lawrence, Canada

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Introduction

Tris (4-chlorophenyl) methane (TCPMe) is among the most recently reported organochlorine contaminants in environmental samples. This compound may originate from a variety of sources including agrochemicals such as technical DDT and compounds used in the production of synthetic dyes (1). TCPMe is the presumed precursor of tris (4-chlorophenyl) methanol (TCPM), a compound that is globally distributed in the environment (2). In Canadian samples, levels of TCPM have been reported in high trophic level birds and mammals (1) but TCPMe has only been quantified in beluga blubber (3). In this paper, we report levels of TCPMe in blubber samples of four seal species and in surface sediments from the Estuary and Gulf of St. Lawrence, Canada.

Methods

Sampling. Thirty three blubber samples were obtained from adult males of four different seal species. Harbour seals (*Phoca vitulina*) (n=4) were captured in the western region of the Estuary whereas hooded seals (*Cystophora cristata*) (n=9) and harp seals (*Phoca groenlandica*) (n=11) were captured near the Magdalen Islands in the centre of the Gulf and grey seals (*Halichoerus grypus*) (n=9) were sampled from the southern part of the Gulf near Port Hood and Amet Island. Blubber samples from harbour and hooded seals were obtained as biopsies whereas harp and grey seal samples were obtained by dissection of killed animals. Blubber samples extended the entire depth of the blubber layer and excluded the skin. They were stored in solvent rinsed aluminum foil and kept on ice for up to 12 hours before being frozen at -20°C . Surface sediment samples were collected from eight stations in the Estuary, using a grab sampler from which two 3 cm thick layers of sediment were recovered. Sediment cores were also collected from each of five stations in the Gulf, using a box corer. Each core was sliced into one centimetre thick layers which were transferred into solvent cleaned glass jars and immediately frozen at - 20°C.

Analyses. The blubber samples were thawed at room temperature, chemically dried with sodium sulphate and then transferred to a glass column for extraction. A mixture of labelled surrogate compounds including D_8-4,4'-DDE were added to the column before the lipids and lipophilic

compounds were extracted from the sample with dichloromethane-hexane (50:50). About a third of the sample was used for the gravimetric determination of lipid content and lipids were removed from the rest of the extract by gel permeation chromatography (GPC). The extracts were further cleaned by passing each extract through a multi-layer column packed with acidic, neutral and basic silica. The final extract was reduced in volume and spiked with an instrument performance solution containing two $^{13}C_{12}$ PCBs. The sediment samples were thawed at room temperature, partially air-dried in an oven at 40°C and chemically dried with sodium sulphate. After addition of surrogate compounds, the samples were soxhlet extracted with toluene and treated with Cu and Hg. The remainder of the sample cleanup was the same as the procedures used for the seal blubber.

Quantification was performed using Varian's Saturn ion trap equipped with a Varian 3400CX series gas chromatograph, a Varian 1078 split/splitless programmable injector (5 µl injection volume) operated in splitless mode, and a Varian 8200CX autosampler. Chromatographic separation of the contaminants was achieved using a 30m DB-5MS column (0.25 mm ID, 0.25 µm film thickness) with helium (He) as the carrier gas. The ion source was operated in electron impact (EI) ionization mode and the ion trap in MS/MS mode to first isolate a characteristic parent ion and upon further fragmentation to monitor two daughter ions of each compound of interest. Concentrations of TCPMe were calculated on the base of RRFs determined from a four point calibration curve using D_8-4,4'-DDE as internal standard. Σ-DDT (sum of 2,4' and 4,4'-DDT, DDD and DDE) were also analysed in the samples. Precision and accuracy were confirmed with SRM1941a (marine sediment) and SRM1945 (whale blubber). TCPMe was quantified against a synthesized standard of previously confirmed purity (4). Differences in contaminant levels among seal species were assessed by analysis of variance (ANOVA) on logarithmic transformed data, followed by a Scheffé's multiple comparisons test.

Results and Discussion

Seal blubber. TCPMe concentrations in blubber samples of seals from eastern Canada range from 0.2 to 14 ng/g lipid (Figure 1). To our knowledge, the only data on TCPMe in marine mammals were reported by Rahman et al. (5) and Muir et al. (3). Rahman et al. (5) reported 0.3 ng TCPMe/g of fat in the blubber of one harbour seal collected in the Kattegat (between the North Sea and the Baltic Sea), which falls at the lower end of the range of values reported in this study. Muir et al. (3) reported much higher levels in beluga whale (*Delphinapterus leucas*) blubber from the St. Lawrence Estuary, with concentrations ranging from 172 to 873 ng/g lipid. Zook et al. (2) also found TCPMe in mature and juvenile ringed seal (*Phoca hispida*) adipose tissue from the Baltic Sea but no quantitative estimates were reported.

Levels of TCPMe in blubber samples of seals from eastern Canada vary significantly between species (Figure 1). For instance, average levels of TCPMe in harbour and hooded seals are the highest among the four species, however, they are not statistically different from each other. By comparison, levels in harp seals are 10-20 times lower than in harbour seals while grey seals show intermediate levels. Significant variation in levels of Σ-DDT were also found in blubber samples among these species (Figure 1). As with TCPMe, levels of Σ-DDT are highest in harbour and hooded seals, intermediate in grey seals and lowest in harp seals. Average levels of TCPMe are significantly different between harbour and grey seals while levels of Σ-DDT are not. Harp seals show the lowest levels of both TCPMe and Σ-DDT. They spend approximately 6 months in Estuary and Gulf and reside in the Arctic the rest of the year. Thus, these findings are in

agreement with the lower levels of most organic contaminants in northern compared to temperate regions. Harbour seals are permanent residents of the more contaminated St. Lawrence Estuary whereas grey seals reside in both the Estuary and the Gulf of St. Lawrence. As with harp seals, hooded seals also migrate from the Arctic to the Gulf, however, their levels of organic contaminants are among the highest. Possible differences in the migratory paths of these two species, with the migration of hooded seals to southern Greenland, as compared to that of harp seals to the Canadian Arctic do not appear to explain their divergent contaminant levels, since similar Σ-DDT levels were found in the blubber of ringed seals from the Canadian Arctic and Greenland (6). Harp and hooded seals were 10±3 years old animals which eliminates the possible age effect on contaminant levels. These results suggest that other considerations such as the type of prey consumed or metabolic differences have to be taken into account in order to explain the different levels of contamination found in blubber samples among seal species. For instance, harp seals tend to feed lower on the food chain than the other seals, eating more pelagic fishes while hooded seals tend to feed on large desmersal fishes.

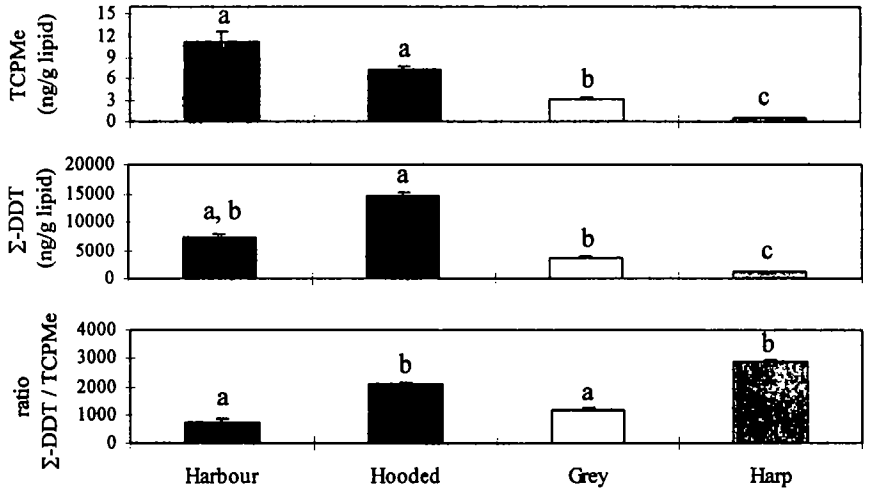

Figure 1. Concentration of TCPMe (± SE), Σ-DDT (± SE) and ratio of Σ-DDT / TCPMe in blubber samples of four seal species captured in the St. Lawrence, Canada. Species with dissimilar letters above them are significantly different ($p < 0.05$) from each other.

Recently, Buser (7) reported the first evidence of a potential link between environmental TCPMe and DDT by showing that TCPMe was formed under conditions such as those used in the synthesis of technical DDT. It was not possible, however, to establish whether technical DDT is the major source for environmental TCPMe or whether there are significant additional sources. From the levels of TCPMe and Σ-DDT in seal blubber, the average ratio (Σ-DDT / TCPMe) was calculated for each seal species (Figure 1). The results indicate that Σ-DDT / TCPMe ratios are significantly lower in harbour and grey seals than in hooded and harp seals. It is particularly interesting to see that the two seals species that are permanent residents of the St. Lawrence system and leaving closer to various sources of pollution show the lowest Σ-DDT / TCPMe

ratios. The Σ-DDT / TCPMe ratios calculated from the beluga data reported by Muir (3) are even lower. These observations suggest that DDT is likely not the only important source of TCPMe in eastern Canada, unless hooded and harp seals possess a more efficient way to eliminate TCPMe relative to DDT than do harbour and grey seals and beluga whales or alternatively, harbour and grey seals and beluga whales may be better at eliminating DDT than hooded and harp seals. The degradation or transformation of TCPMe during its transport to northern regions could also explain the different Σ-DDT / TCPMe ratios among seal species.

Sediments. Levels of TCPMe in surface sediments (0-3 cm) were below the detection limits estimated at 0.04 ± 0.01 and 0.11 ± 0.01 ng/g dry weight for samples from the Estuary and the Gulf, respectively. However, Σ-DDT levels were detectable in estuarine surface sediment samples (average of 8 stations: 2.5 ± 0.2 ng/g dry wt) as well as in surface sediments from the Gulf (average of 5 stations: 1.2 ± 0.1 ng/g dry wt). Based on the average Σ-DDT / TCPMe ratio in blubber samples (value of 1820; Figure 1) and using the average Σ-DDT levels found in surface sediments, TCPMe was estimated to 0.014 and 0.007 ng/g dry weight in surface sediments from the Estuary and the Gulf of St. Lawrence, respectively. These predicted values are 4-10 lower than the detection limits of the method used.

Conclusion

TCPMe was detected in all blubber samples of the four seal species captured in the Estuary and Gulf of St. Lawrence but was not detectable in any surface sediment samples. Levels of TCPMe in seal blubber were lower than TCPM levels reported in other marine mammals from the same area (1, 3). Lower Σ-DDT / TCPMe ratios were observed in seal species residents of the Estuary and Gulf of St. Lawrence than in species migrating to the Arctic, suggesting that technical DDT was not the only source of TCPMe or that different seals species possess different metabolic capabilities. It is also possible that TCPMe undergoes higher rates of degradation or transformation during transportation to the Arctic.

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