Marine Mammals as Global Pollution Indicators for Organochlorines

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1. Introduction

The global distribution of xenobiotics and the xenobiotic burden of marine mammals, due to their position at the top of the food chain and their rather long life-spans, are well established [1,2,3]. Marine mammals are thus an important tool to monitor the long-term effects concerning the pollution of the marine environment worldwide. They can also be used as global pollution indicators. Persistent pollutants, like the polychlorinated biphenyls (PCBs) and several chlorinated pesticides (e.g. HCHs and DDTs), reach the aquatic organisms mainly by way of the food chain (biomagnification). Because of their physicochemical properties (K_{OW}, lipophilicity, vapor pressure) these compounds accumulate in the fatty tissue of the body (bioaccumulation). Particularly significant is the carry-over of part of the body burden of female marine mammals to their neonatals, by prenatal transplacental transfer and/or postnatal transfer via lactation [4,5]. This additive behavior of xenobiotic concentrations for marine mammals at their earliest stages of life is very alarming, because the long-term consequences cannot be predicted. Marine mammals can be considered as model systems for low-dosis long-term effects of environmental pollutions.

We have analyzed various marine mammals differing in their geographic distribution (North Atlantic, North Pacific and Bering Sea/Arctic Ocean), age (mature, neonatal), trophic level, and feeding habits. Most of the investigations concerning marine mammals in recent years have been done with either toothed whales [6,7], like dolphins, porpoises, and white whales, or seals [8]. As far as we know no investigations concerning xenobiotic burden have been done with baleen whales. It was the aim of our analyses to show the differences and similarities in xenobiotic levels and patterns in different marine mammals, all deriving from the Northern hemisphere, and to correlate the results with the trophic levels and the geographic distribution of the mammals.

2. Experimental

2.1 Samples

Two seal species (harbor seals - *Phoca vitulina*, northern fur seals - *Callorhinus ursinus*), three toothed whale species (white whales - *Delphinapterus leucas*, one common dolphin - *Delphinus delphis*, one pilot whale - *Globicephala melaena*), and one baleen whale specie (a bowhead whale - *Balaena mysticetus*) were analyzed. The tissue analyzed was in all cases blubber.

2.2 Sample preparation and clean-up

Cold column extraction

Sample portions between 1 and 10 g (wet weight) were taken from the tissues. The sample portion was put into a mortar together with 25-50 g anhydrous sodium sulfate and 10-30 g coarse sea sand (Merck, Darmstadt, Germany; both heated at 600°C for 24 h). This mixture was homogenated carefully until a free flowing powder was obtained. This was then placed in a glass column (2.4 cm x 50 cm) and extracted for 2 hours using 110 ml/g fat content of a hexane-acetone mixture (7/4) [9]. To control the extraction step, the column was finally extracted with another 50 ml of the hexane-acetone-mixture, the eluate concentrated and injected into the GC-system. If the extraction was complete, the first 110 ml/g fat content hexane-acetone-mixture was concentrated to dryness and the residue (extractable lipids) determined gravimetrically. All solvents used were residue analysis grade (Promochem, Wesel, Germany). The sample preparation and the clean-up steps were all done under clean-bench conditions.

Clean-up

The clean-up was done using a gel-chromatography system. Bio-Beads gel S-X3 (Bio-Rad Laboratories Inc., Brussels, Belgium) was used with a cyclohexane-acetone mixture (3/1) as eluent to separate the lipids from the polychlorinated hydrocarbons [10].

Adsorption chromatography with silica gel

Liquid chromatography on a silica column (silica gel 60, particle size 63-200 µm, Merck, Darmstadt, Germany) was used to separate the organic residues into two fractions. The silica gel was heated at 350°C for 24 h, deactivated by adding 3% H_2O and left to equilibrate for a couple of days. A glass column (1.2 cm x 20 cm) was slurry-packed with 4.5 g of the deactivated silica gel in hexane. For the first fraction, 30 ml of hexane were used as mobile phase. This fraction (LC1) contained the PCB congeners and lower polarity chlorinated pesticides, as pentachlorobenzene, hexachlorobenzene, octachlorostyrene as well as 4,4'-DDE and Mirex. The second fraction (LC2) was eluted with 40 ml 25% methylene chloride in hexane. It contained the more polar pesticides as the HCHs, the remaining DDT-group, the chlordane compounds and the toxaphenes [11]. The two fractions were each concentrated to a sample volume of 200-600 µl and injected into the GC-system.

2.3 Gaschromatographic analysis

The quantitative analysis was done by high-resolution capillary gas chromatography (HRGC) with electron capture detection (ECD) using PCB 103 (LC1) and tetrachloronaphthalene (LC2) as internal standards. The analysis of the metabolic PCB pattern was done by high-resolution capillary gas chromatography (HRGC) and mass selective detection (MSD). The stationary phase used in both cases was a SPB-octyl capillary (50% methyl - 50% octylpolysiloxane, Supelco, Bad Homburg, Germany; length: 90 m, inner diameter: 0.32 mm, film thickness: 0.1 µm).

3. Results and Discussion

The xenobiotics which were quantified are the seven indicator congeners of the polychlorinated biphenyls (PCB 28, 52, 101, 118, 138, 153, and 180) [12], three isomers of the hexachlorocyclohexanes (α-, β-, and γ-HCH) as well as six components of the DDT-group (4,4'-DDT, 4,4'-DDD, 4,4'-DDE, 2,4'-DDT, 2,4'-DDD, and 2,4'-DDE). These 16 xenobiotics are summed up as the total organochlorine burden.

3.1 Comparison of the total organochlorine burden between marine mammals from the North Pacific and Bering Sea/Arctic Ocean and marine mammals from the North Atlantic

Three marine mammal species came from the North Pacific and the Bering Sea/Arctic Ocean (northern fur seal, white whale, and bowhead whale), while the other three marine mammal species originated from the North Atlantic (harbor seal, pilot whale, and common dolphin). When comparing these two groups with each other, it becomes obvious that the animals from the North Atlantic are much more contaminated with organochlorines than the animals from the North Pacific and the Bering Sea/Arctic Ocean. The total organochlorine burden of an adult northern fur seal from the North Pacific was 4730 ng/g extractable lipids in contrast to 70380 ng/g extractable lipids for an adult harbor seal from the North Atlantic. The North Pacific seal has only about 6% of the overall organochlorine burden of the North Atlantic seal from Massachusetts (see Figure 1). On the average, comparable marine mammal species are roughly fiveteen times higher polluted in the North Atlantic than they are in the western North Pacific.

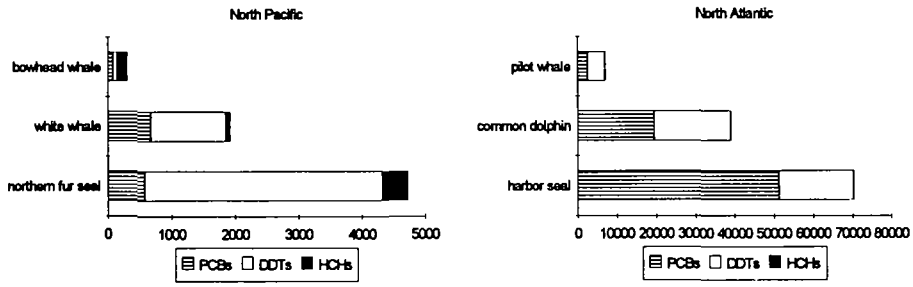

Figure 1: Correlation of total organochlorine burden in blubber (ng/g extractable lipids) with the trophic level of marine mammals from the eastern North Pacific and the western North Atlantic

3.2 Comparison of the total organochlorine burden of marine mammals and their different trophic levels

As shown in Figure 1, there is a definite correlation between the total organochlorine burden of the marine mammals analyzed and their position within the marine food chain. The two seal species both belong to the order of predatory animals. In the North Pacific as well as in the North Atlantic the two seal species have the highest organochlorine contamination

compared to the whales and therefore are on a higher trophic level. In contrast to the filter-feeding mode of life of baleen whales, seals and toothed whales are predators at the end of the marine food chain, taking a wide variety of prey, which consists mainly of herring, squid and cod [13]. The predatory seals and the toothed whales reflect a significantly higher trophic level than the bowhead whale, who stands close at the beginning of the marine food chain.

3.3 Comparison of the 4,4'-DDE-percentage (relativ to the sum of 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE) in marine mammals and their different trophic levels

The metabolite 4,4'-DDE is an indicator for biotransformation reactions within the body of marine mammals. 4,4'-DDE, the main metabolite of 4,4'-DDT, accumulates very easily in the fatty tissue of the body. Therefore it is possible to relate the concentration of 4,4'-DDE to the metabolic activity of an animal. It is known that mammals belonging to a higher trophic level metabolize to greater degree than mammals belonging to a lower trophic level. The bowhead whale, which feeds exclusively on plankton, has only a 4,4'-DDE-percentage of 56% in contrast to the two seals, which have the highest 4,4'-DDE-percentage (85 and 96%). The three toothed whales show percentages between 60 and 77% and therefore have a position between the baleen whale and the seals.

3.4 Comparison of the extent of PCB metabolism and the trophic level of marine mammals

The suggested order (baleen whales - toothed whales - seals) concerning the body burden and the different trophic levels of the marine mammals analyzed was also confirmed by GC/MS studies of the metabolic PCB patterns. The PCB patterns of the two seal species depict only the very persistent PCB congeners [14], while the pattern of the baleen whale has little difference to the technical Aroclor mixtures. These results suggest that the higher body burden of organochlorines in marine mammals leads to an elevated level of enzymatic activity of monooxygenases in PCB metabolism. Marine mammals of a higher trophic level will also feed on a premetabolized pattern of PCBs. Both factors have to be discussed when explaining the differences in the extent of PCB metabolism in mammals of different trophic levels. Surprisingly, terrestrian mammals of a low trophic level like sheeps give the same results in terms of a minimized PCB metabolism [15].

4. Conclusions

Comparing the xenobiotic levels of marine mammals from different geographical places, it showed that the animals from the western North Atlantic were significantly higher contaminated with organochlorines than the animals from the eastern North Pacific and the Bering Sea/Arctic Ocean. In addition, it was possible to correlate the total organochlorine burden, the 4,4'-DDE-percentage as well as the metabolic PCB patterns with the different trophic levels of the marine mammals analyzed.

5. References

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