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Concentrations of chlorinated and brominated contaminants and their metabolites in serum of harbour seals and harbour porpoises

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ABSTRACT

Harbour seals (*Phoca vitulina*) and harbour porpoises (*Phocoena phocoena*) are top predators in the North Sea and consequently accumulate a variety of pollutants in their tissues. Concentrations of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and their hydroxylated metabolites (HO-PCBs and HO-PBDEs) were measured in serum of wild harbour seals ($n=47$) and captive harbour porpoises ($n=21$). Both species exhibit long life spans and do not have extreme situations, such as complete fasting during periods of lactation, in their annual cycles. For PCBs, concentrations in adult males were slightly higher than in juveniles and lowest in juvenile females. For PBDEs, juveniles have higher levels than adult males and females, probably as a consequence of lactational transfer. However, differences between these age–gender groups were not statistical significant, indicating that individual variation was limited within each species, even without knowing the feeding status of the animals. Body condition, particularly emaciation, has a major influence on the levels of chlorinated and brominated contaminants in serum. Profiles of PCBs were CB 153>CB 138>CB 187>CB 180 and CB 153>CB 138>CB 149>CB 187>CB 180 for harbour seals and porpoises respectively. For PBDEs, BDE 47 was the predominant congener followed by BDE 100 and 99 in both species. In harbour seals, concentrations of sum PCBs (median: 39,200 pg/ml) were more than 200 times higher than levels of sum PBDEs (median: 130 pg/ml) and almost 10 times higher than concentrations of sum HO-PCBs (4350 pg/ml). In harbour porpoises, concentrations of sum PCBs (median: 24,300 pg/ml) were about 20 times higher than concentrations of PBDEs (median: 1300 pg/ml). HO-PCBs were detected in only 4 harbour porpoises and this at very low concentrations. Naturally-produced MeO-PBDEs were only found in harbour porpoises at concentrations ranging from 120 to 810 pg/ml. HO-PBDEs were not found in any species. In general, harbour seals accumulate less compounds and have mostly lower concentrations than harbour porpoises possibly as a result of a better developed metabolism.

1. Introduction

The bioaccumulative potential and toxicity of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) as well as pesticides (hexachlorobenzene (HCB), dichloro-diphenyl-trichloroethane (DDT) and metabolites) in marine mammals have been the focus of numerous papers worldwide (Tanabe et al., 1994; Bruhn et al., 1995; Reijnders and Aguilar, 2002; Reijnders and Simmonds, 2003; Thron et al., 2004; Ross, 2006). These types of chlorinated and brominated contaminants have been associated with immunological, reproductive and mostly endocrine/cytotoxic (e.g. thyroid hormone action) effects in various marine mammal species and, due to their persistence in the environment, are still a threat to the health condition of aquatic organisms in general (Damstra et al., 2002; Beineke et al., 2005; Das et al., 2006; Bossart, 2007). Among these, PCBs and PBDEs are assumed to have comparable toxic action mechanisms since they have similar chemical properties (de Boer et al., 1998; Birnbaum and Staskal, 2004). Despite their ban in Europe (PCBs in 1970s, most PBDE congeners in 2004), both types of contaminants can still be found at all levels of the aquatic food chains (Ruus et al., 1999; Boon et al., 2002).

PCBs and PBDEs may undergo metabolic/enzymatic breakdown resulting in methylsulfone and hydroxylated PCB and PBDE metabolites

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(Letcher et al., 2000) or lower brominated PBDE congeners (Letcher et al., 2000; Birnbaum and Staskal, 2004). Debromination of PBDEs into lower brominated congeners has been shown to occur in a few terrestrial and aquatic organisms such as birds (Pirard and De Pauw, 2007; Van den Steen et al., 2007), rats (Huwe and Smith, 2007) and fish (Stapleton et al., 2004; Benedict et al., 2007). Although methylsulfone and hydroxylated metabolites are more polar and consequently easier to eliminate from the body than their parent compounds, considerable amounts of these metabolites are retained in the body of several species (Sandala et al., 2004; Gebbink et al., 2008; Jaspers et al., 2008). Hydroxylated metabolites can be formed by direct insertion of a HO-group or by formation of an arene oxide intermediate that rearranges to a HO-group. Both ways are possible, but the extent to which each pathway occurs is probably highly dependent of the species (Letcher et al., 2000). Effects of these metabolites are mostly related to disturbances of hormonal and endocrine systems as they can bind to and interact with several hormone receptors and transport proteins (Cheek et al., 1999; Birnbaum and Staskal, 2004; Shimokawa et al., 2006). As a result, toxic effects can have a great impact on the health condition of organisms in general. Hydroxylated metabolites are not particularly associated with lipids as can be seen for the parent compounds, but have a high affinity for plasma proteins. Therefore, they can primarily be found in blood (Gebbink et al., 2008).

Harbour seals (*Phoca vitulina*) and harbour porpoises (*Phocoena phocoena*) are common marine mammals in West-European waters (Burns, 2002; Hammond et al., 2002). They are known to accumulate high contaminant concentrations in their tissues because of their longer life spans and top-position in aquatic food chains (Shaw et al., 2005, 2007). Although seasonal changes in blubber thickness may occur, both species do not have extreme fasting periods in their annual cycles as both species continue eating during their reproductive and lactational periods (Kastelein et al., 1997; Burns, 2002; Lockyer, 2007). Weijs et al. (2009a) suggested a higher capacity in harbour seals for metabolizing PCBs and PBDEs compared to harbour porpoises. However, considering the assumed toxicity of the resulting metabolites (Meerts et al., 2000; Birnbaum and Staskal, 2004) and their presence in blood, concerns have been raised about the higher metabolic capacity of harbour seals in terms of their global health and the conservation of marine mammals on a longer term.

While extensive studies described PCBs and PBDEs in blubber and other tissues of caught or stranded marine mammals, fewer data were documented in blood of free-ranging seals and harbour porpoises (Bang et al., 2001; Sørmo et al., 2003; Sørmo, 2005). Levels of persistent organic pollutants (POPs) in blood depend not only on environmental contamination; but also numerous biotic factors are suspected to modulate concentrations: gender, diet, age, pregnancy, lactation and weaning (Debier et al., 2006). The objective of the present study was to investigate the occurrence and distribution of PCBs, PBDEs, their hydroxylated metabolites (HO-PCBs and HO-PBDEs), HCB and DDTs (*p,p′*-DDE, *p,p′*-DDT and *p,p′*-DDD) in blood of free-ranging harbour seals, harbour porpoises held in captivity and a stranded harbour porpoise in order to elucidate the metabolism of these compounds. Several factors including species, age class, gender and year of sampling were apprehended to get further understanding of PCB and PBDE kinetic in harbour seals and harbour porpoises.

2. Materials and methods

2.1. Samples, chemicals and target compounds

Serum samples of 21 harbour porpoises in captivity from 2006–2008 were provided by SOS Dolfijn, Dolfinarium Harderwijk (The Netherlands), and were taken for regular medical purposes from the tail fluke. Information about the medical situation of these animals at the time of sampling can be found in Table 1. Serum was isolated by centrifugation at 4000 rpm during 15 min (Hettich EBA-20) and kept at −20 °C until further analysis. A serum sample of an adult harbour porpoise, stranded on the North Sea coast in 2003 was also analyzed. Serum samples of free-ranging harbour seals were collected from 47 animals caught in the frame of monitoring programs for the health assessment organized on Helgoland and Lorenzenplate (North Sea, Germany) in 2006–2008 and in Rømø (Denmark) in 2008. Seals were physically restrained and blood was drawn from the extradural venous sinus into sterile evacuated blood collection tubes (serum tubes Monovette®, Germany) and kept at −20 °C. Serum was isolated by centrifugation at 1500 g during 20 min at 20 °C (Multifuge 3S-R, Kendro) (Hasselmeier et al., 2008).

In all samples, target compounds were PCBs (IUPAC-numbers: 52, 74, 95, 99, 101, 105, 110, 118, 128, 138, 149, 153, 156, 170, 180, 183, 187,

Table 1
Medical information of the harbour porpoises, held in captivity during rehabilitation, at the time of sampling.

Code	Days in rehabilitation	Gender	Estimated age at time of sampling (years)	Length (cm)	Weight (kg)	Condition at time of sampling
P1	3247	M	9	132.5	40.25	Healthy
P2	1946	M	6	120	29.55	Slightly anaemic due to blood loss associated with a urogenital lesion/ inflammation
P3	571	F	2	140	35.8	Healthy
P4	117	M	1	116.5	27.8	Healthy
P5	0	M	Adult	145	44	
P6	5	M	Adult	149	42.3	Sample on day of death, very severe inflammatory reaction probably due to pneumonia
P7	434	F	2	126	38.05	Anaemic
P8	37	F	1	113	26.46	Healthy, on antibiotics after recent stranding
P9	0	M	Adult	142	41.3	Sample shortly after stranding, inflammatory reaction in blood
P10	128	F	1	122	29.9	Healthy (animal at the end of treatment with antibiotics)
P11	42	M	1	110–114	22.85	Severe anaemia and inflammation
P12	9	F	1	118	19.6	Pneumonia, sepsis and gastric impaction, emaciation
P13	7	F	Adult	146	48.8	Anaemic and pregnant. Animal dies a month later due to acute hepatic lipidosis
P14	30	M	1	108–112.5	22.25	Severe anaemia, antiparasitic treatment
P15	174	F	2	136	34	Healthy (animal at the end of treatment)
P16	355	F	3	133–134.5	39.04	Healthy
P17	34	M	2	117–123	26.15	Laryngitis
P18	183	F	1	105	29.24	Anaemic due to lungworm infection (at time of sampling only on antibiotics after lungworm treatment)
P19	1	M	2	116	29.55	Healthy
P20	77	F	1	108.5	26.95	Chronic hepatitis of unclear significance
P21	32	F	2	116	27.2	Healthy