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PBDE flame retardants and PCBs in migrating Steller sea lions (*Eumetopias jubatus*) in the Strait of Georgia, British Columbia, Canada

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) were measured in blubber biopsy samples from 22 live-captured Steller sea lions (*Eumetopias jubatus*) that had just entered the Strait of Georgia, British Columbia, Canada, for their overwintering feeding season. ∑PBDE ranged from 50 μg kg^{-1} (lipid weight) in adult females to 3780 μg kg^{-1} in subadult individuals. ∑PCBs ranged from 272 μg kg^{-1} in adult females to 14280 μg kg^{-1} in subadult individuals. While most PBDE and PCB congeners were transferred through milk to pups, PCBs with logK_{OW} > 7.0 (PCBs 206, 207, 208 and 209) appeared constrained, resulting in a lighter mixture in pups compared to adult females. The ratio of individual PCB congeners by metabolic group (Groups I, II, III, IV and V) to PCB-153 regressed against length of males suggested poor biotransformation of these compounds (slopes did not differ from zero, $p > 0.05$). PBDE congeners 49, 99, 153 and 183 appeared bioaccumulative (slopes of ratio BDE/PCB 153 versus length were higher than zero, $p < 0.05$), but the dominance of the single congener, BDE-47 (64% of total PBDEs), likely due in part to debromination pathways, reduced our ability to explore congener-specific dynamics of PBDEs in these pinnipeds. With 80% of our Steller sea lions exceeding a recent toxicity reference value for PCBs, the fasting-associated mobilization of these contaminants raises concerns about a heightened vulnerability to adverse effects during annual migrations.

1. Introduction

Persistent organic pollutants (POPs) represent a threat to marine mammals due to their recalcitrance, bioaccumulative nature and toxicity. Polychlorinated biphenyls (PCBs) are legacy industrial POPs that were banned during the late 1970s in North America and are today subject to the terms of the Stockholm Convention. More recently, polybrominated diphenyl ethers (PBDEs) have emerged as a significant concern, having been extensively used as flame retardants in foams, textiles, coatings, furniture, construction materials, electronic devices, plastics and paints since the 1970s (de Boer et al., 1998; de Wit, 2002; Alaee et al., 2003).

There are three primary commercial PBDE products, including the penta-BDE, octa-BDE and deca-BDE formulations (La Guardia et al., 2006). In Europe and North America, production of two PBDE products (penta- and octa-BDE formulations) ceased in 1998 and 2004, respectively. The third (deca) formulation was recently banned in Europe and Canada, and is subject to some state-based bans in the US and increasing voluntary restrictions (La Guardia et al., 2006; Birnbaum, 2009; de Boer, 2009; Ross et al., 2009). The tetra, penta, hexa and heptabromodiphenyl mixtures are currently classified as POPs under the terms of the Stockholm Convention, and the octa BDE formulation may be added eventually to the list of banned POPs (de Boer, 2009).

Despite having been banned, PCBs are still found at high concentrations in some marine biota of northern hemisphere (Hall and Thomas, 2007; Kelly et al., 2007). The NE Pacific Ocean is no exception, with very high PCB concentrations having been observed in killer whales, *Orcinus orca* (Ross et al., 2000; Ylitalo et al., 2001), and to a lesser extent harbor seals, *Phoca vitulina* (Ross et al., 2004). PBDEs have also been detected in marine mammals from the NE Pacific Ocean, although at lower concentrations than the PCBs (Rayne et al., 2004; Krahn et al., 2007; Ross et al., 2012).

High levels of POPs have been implicated in adverse effects on immune and endocrine systems of marine mammals, with the PCBs, in particular, being of concern (Ross et al., 1996; De Guise

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et al., 1998; Tabuchi et al., 2006; Mos et al., 2006). While many of the measured endpoints are considered sub-lethal, the fitness of individuals is also being affected. High levels PCBs have been associated with a high prevalence of neoplasms and carcinoma, causing mortality in California sea lions, *Zalophus californianus* (Ylitalo et al., 2005). PCBs have been widely implicated in reduced reproduction in pinnipeds in the North and Baltic Seas (Helle et al., 1976; Reijnders, 1986). While less is known about the toxicity of PBDEs, this flame retardant has been implicated in carcinogenicity and the disruption of steroid and thyroid hormones (Meerts et al., 2000, 2001; Hallgren and Darnerud, 2002).

The Steller sea lion (*Eumetopias jubatus*) is a piscivorous pinniped that inhabits the Pacific coastal waters of Canada, the USA and Asia. There are two populations, with the Eastern and Western stocks being genetically distinct and geographically separated at approximately 145° W longitude (Bickham et al., 1996). While the eastern stock is considered stable, the western stock has declined by 80% during the last 30 years across its entire range National Research Council (2003). In addition to the hypotheses involving nutritional stress and shifts in ocean-climate, which might explain this decline (Rosen and Trites, 2000; Trites et al., 2007), contaminants have also been suggested as a possible contributing factor (Barron et al., 2003). Low to moderate concentrations of PCBs have been observed in Steller sea lions from both the declining western stock (Varanasi et al., 1992; Lee et al., 1996; Krahn, 1997, Krahn et al., 2001) and the stable eastern stock (Krahn, 1997, Krahn et al., 2001). To date, there have been no studies on PCBs or PBDEs in Steller sea lions from British Columbia and adjacent southern coastal US states.

The total Steller sea lion population in British Columbia during the breeding season is estimated to be approximately 20 000 individuals , with an overall growth rate of 3.5% per year (Olesiuk, 2008). Of these, approximately 3000 individuals migrate into the waters off southern Vancouver Island and into the Strait of Georgia (Olesiuk, 2004; A. Trites, pers. comm.). Although the British Columbia population has been increasing, Steller sea lions are listed as "Special Concern" under the terms of the Species at Risk Act (SARA) because of human disturbance, risk of oil spills and environmental contaminants (COSEWIC, 2003; Olesiuk, 2008).

As part of a larger effort to characterize the feeding ecology of Steller sea lions frequenting the Strait of Georgia, British Columbia, 22 animals were live-captured and telemetry devices attached prior to release (Jeffries et al., 2004; North Pacific Universities Marine Mammal Research Consortium, 2006). This capture provided a valuable opportunity to measure contaminants and to characterize this potential conservation threat.

2. Materials and methods

2.1. Capture and sampling

Steller sea lions were live-captured at Norris Rocks (49°29′00″N, 124°39′00″W) in the Strait of Georgia, British Columbia, Canada, in February 2005 and January 2006, using a floating mobile trap described elsewhere (Jeffries et al., 2004). After capture, sea lions were moved into a transfer cage and weighed, and then moved into a squeeze cage, where they were physically restrained. Valium was administered (0.02 to 0.11 mg kg^{-1}, mean dosage of 0.06 mg kg^{-1}) via intramuscular injection in the shoulder area to those individuals upon which telemetry devices were being attached. Valium was given 10–20 min prior to general anesthetic using isoflorane, administered via a cone over the head. Intubation of the stomach was performed if a stomach sensor was to be inserted. Monitoring was done with a Heska G2Digital pulse-oximeter and temperature probe.

Blubber biopsy samples were collected from 22 individuals, including a freshly aborted fetus, pups (n = 3), subadults (n = 10), adult females (n = 6) and adult males (n = 2). Blubber samples were obtained with a 6 mm-biopsy punch from a cleansed (betadine and isopropyl alcohol) site 20 cm lateral to the spinal column and anterior to the pelvis as described elsewhere (Tabuchi et al., 2006; Mos et al., 2006). These samples were wrapped in hexane-rinsed aluminum foil, placed in plastic bags, and temporarily stored on wet ice in the field. After transfer to the laboratory, samples were frozen within 4 h at −80° C at the Institute of Ocean Sciences (Fisheries and Ocean Canada) until further analysis.

No teeth were extracted for age determination, such that sea lions in this study were grouped by age class for interpretation of contaminant concentrations. We defined a nursing pup as an individual with an estimated age of 0–1.5 years (one deceased pup was a known-age 1.5 year individual, WDFW0206-01, which had milk in its stomach at the time of sampling). Nursing dependency can last up to three years in Steller sea lions (Pitcher and Calkins, 1981). Sampling data, including dates, age and sex categories, morphometrics and lipid content are reported in Table 1.

2.2. Contaminant analyses

Blubber samples were analyzed by AXYS Analytical Services Ltd. (Sidney, BC, Canada), using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) as described elsewhere (Christensen et al., 2005). Briefly, blubber samples (ranging 75–440 mg wet weight) were analyzed using an Ultima HRMS equipped with a Hewlett–Packard 5890 GC and a DB-5 Durabond capillary column (60 m × 0.25 mm, 0.10 μm film). Percent of lipid in samples was determined at using the gravimetric lipid determination by weight of extract method with dichloromethane (DCM).

Briefly, samples were spiked with ^{13}C-labeled surrogate standards (n = 12 PBDEs; n = 29 PCBs) and then ground with anhydrous sodium sulfate. Samples were transferred to a Soxhlet thimble, surrogate standard was added, and samples were refluxed for 16 h with DCM. The extract was eluted through a gel permeation column with 1:1 DCM:hexane. The extract was applied to a partially deactivated Florisil column and eluted with hexane followed by 15:85 DCM:hexane. Elutes were then combined and eluted with 1:1 DCM:hexane and each fraction was concentrated. Included with each batch of samples was a procedural blank. The lab blank had concentrations above detectable levels (<25 pg g^{-1}) for 20 PBDE congeners, while for most of the PCB congeners the lab blank had concentrations above <5 pg g^{-1}.

Limits of detections (LODs) for PBDE congeners generally ranged from <10 to <60 pg g^{-1} wet weight, with exception of BDE-209 which had LODs ranging from 66.2 to 2480 pg g^{-1}. For PCBs, the LODs were in general <10 pg g^{-1}, and, in most cases, <5 pg g^{-1}. For PBDEs, a total of 34 individual PBDE congener peaks ranging from dibromodiphenyl ethers through decabromodiphenyl ether and six co-eluting bands (each composed of two congeners) were identified and quantified in the blubber samples, constituting a data set of 40 congeners overall: BDE-7, -8/11, -10, -12/13, -15, -17/25, -28/33, -30, -32, -35, -37, -47, -49, -51, -66, -71, -75, -77, -85, -99, -100, -105, -116, -119/120, -126, -128, -138/166, -140, -153, -154, -155, -181, -183, -190, -203, -206, -207, -208, -209.

2.3. Data treatment and statistical analysis

Concentrations of PBDEs and PCBs were calculated and reported as the sum of the concentrations congeners (i.e., $\sum$PBDE and $\sum$PCB) that were detectable in at least 15 out of 22 individual sea lions ($\geqslant$68% of samples). When congeners were not detected, detection limit substitutions were made using half the limit of