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Accumulation of PBDEs in an urban river otter population and an unusual finding of BDE-209

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HIGHLIGHTS

- ∑PBDE concentrations were highest in Victoria Harbour relative to the rest of the study areas.
- Consistently high levels of BDE-47 were reported across the study area.
- Higher brominated congeners were only observed in Victoria Harbour and only in river otter scat.
- Select congener patterns in scat samples were consistent with those in blood (circulation).
- There were extremely high levels of BDE-209 measured in 2 scat samples from Victoria Harbour.

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ABSTRACT

River otter scat samples ($n = 77$) and blood samples ($n = 16$) collected through non-invasive field collections and live-capture activities (November 2009 to October 2010) along the coastline of Southern Vancouver Island, near Victoria, British Columbia (BC) were analyzed for polybrominated diphenyl ethers (PBDEs). ∑PBDEs were highest in urbanized regions of Victoria Harbour for blood (1.12 μg/g lipid weight) and scat (0.35 μg/g lipid weight). A location effect between zones was confirmed statistically for blood but not for scat. Specific congeners with the highest concentrations overall were BDE-47 in blood samples (0.37 μg/g lipid weight) and BDE-206 (0.18 μg/g lipid weight) and BDE-47 (0.16 μg/g lipid weight) in scat samples. There was also an unusual finding of extremely high levels of BDE-209 in 2 scat samples (163 and 956 μg/g lipid weight). The patterns of select congeners (BDE 47, 99, 100, 153, 154) measured in blood and scat were found not to be significantly different (Chi-square Test, $X^2 = 21.08$, DF = 4, $p = 0003$). The most prominent congeners within Victoria Harbour were BDE-47 for both blood (0.82 mg/kg lipid weight) and scat (0.26 mg/kg lipid weight) followed by BDE-206 (0.18 μg/g lipid weight) and BDE-207 (0.10 μg/g lipid weight) for scat only. Comparable levels of BDE-47 were reported across the study area whereas BDE 206 and 207 were only observed in Victoria Harbour (scat). Toxicological effects of PBDEs in rivers otters from Victoria, BC are still unknown however the predominance of BDE-47 could have negative implication as an endocrine disruptor.

1. Introduction

Biodiversity hot spots such as estuaries, riverine corridors and sheltered coastlines have been preferentially selected for human settlement and have commonly grown into urban centers. In addition to habitat degradation caused by urban sprawl, cities generally have increased pollution from, for example, heavy metals, polycyclic aromatic hydrocarbons (PAHs) and rodenticides (Albert et al., 2010; Sun et al., 2010; Cizdziel et al., 2013). Of particular consequence to wildlife species are the persistent organic pollutants (POPs) which are defined by their tendency to bioaccumulate in food chains, making top predators most vulnerable (Leonards et al., 2008; Ross et al., 2008).

Certain wildlife species inhabit and even thrive in large and intensely urbanized areas where they appear to breed and survive successfully (Luniak, 2004). The highly urbanized region of Victoria Harbour, on southern Vancouver Island, British Columbia (BC), is a

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contaminated site where a variety of POPs, including polychlorinated biphenyls (PCBs), have accumulated in the marine ecosystem from past anthropogenic activities (Ikonomou et al., 2002; Elliott et al., 2008). Elliott et al. (2008) reported that river otters inhabiting Victoria Harbour were exposed to elevated levels of PCBs but potential toxicological consequences were not clear. There is some evidence that despite having been essentially banned in Canada since 1977, PCBs continue to cause detectable physiological effects in populations of top predator species, such as the harbour seal (*Phoca vitulina*) and the bald eagle (*Haliaeetus leucocephalus*) in the Salish Sea region (Tabuchi et al., 2006; Cesh et al., 2010).

Polybrominated diphenyl ethers (PBDEs) are polyhalogenated compounds that have been widely used as flame retardants. Although similar in chemical structure to PCBs, PBDEs are less stable. There are three commercial formulations of PBDEs; Penta-, Octa- and Deca-BDE. Lower brominated formulations (Penta- and Octa-BDE) which are more persistent, bioaccumulative and toxic were removed from the European and Canadian market in 1998 and 2004, respectively (Ross et al., 2009). Deca-BDE formulations continue to be used and are largely made up of the specific congener BDE-209 (Ross et al., 2009). In recent history North America was consuming approximately half (50%) of the world's production of PBDEs (Rahman et al., 2001). Studies have shown PBDE contamination to be associated with urban centers in both abiotic (Jaward et al., 2004) and biotic matrices (Park et al., 2011). Potential sources of PBDE contamination include landfill runoff and the use of sewage sludge in agricultural practices (Eens et al., 2013). BDE-209 is a significant component of total PBDEs in air, water and sediment and contributes 80% of the total PBDE in Strait of Georgia sediments (Ross et al., 2009). Highly brominated Deca-PBDE tends to be more tightly bound and are therefore less bioactive relative to Penta-PBDE congeners which tend to be more easily partitioned in aquatic systems (Muresan et al., 2010).

In the Salish Sea, a number of avian and mammalian species have been studied to monitor for impacts of environmental contamination in the marine environment. Significant levels of toxic xenobiotic chemicals have been reported in harbour seals (Ross et al., 2004), killer whales (Ross et al., 2000) and bald eagles (Elliott and Norstrom, 1998). Localized contaminant sources, in and around urban centers, are difficult to investigate using wider ranging avian and mammalian predators. The river otter is well suited for monitoring local sources of contamination as they have relatively small and seasonally constant home ranges and do not hibernate or migrate over long distances (Melquist and Dronkert, 1987). River otters inhabiting areas of high industrial and other anthropogenic activities have been reported to have contaminant levels "comparable" to coastal cetaceans (Kannan et al., 1999) which are thought to be among the most highly contaminated marine mammals in the world. River otters on Southern Vancouver Island were selected as biological monitors to investigate the finer scale dynamics of new and residual POPs in and around Victoria, BC.

River otters are exposed to contaminants primarily through their diet (Clark et al., 1981; Henny et al., 1981; Harding et al., 1999) and as a top-predator they are particularly prone to accumulation of toxicants which biomagnify with trophic level (Ruus et al., 2002). PBDEs have been reported in mustelid species, including the North American river otter, *Lutra canadensis* (Basu et al., 2007; Stansley et al., 2010; Guertin et al., 2010a) and the Eurasian River Otter, *Lutra lutra* (Walker et al., 2013).

This paper investigated the spatial patterns and congener profiles of PBDE exposure in free-ranging river otters inhabiting an urban area using non-invasive scat sampling (field collected) combined with traditional live animal sampling of blood.

2. Methods

River otters deposit feces, anal jelly and/or a mixture of both at latrine sites. Anal jellies are a mucous-like substance produced in the intestinal tract of the otter, likely to facilitate the passing of bones and shells from their prey. Elliott et al. (2008) showed that jellies contain the same concentration of contaminants relative to scat or mixed feces/jelly samples. Guertin et al. (2010a) reported a higher success rate for fecal DNA genotyping in jellies relative to scat. Based on these broader research objectives, it was determined that fresh anal jellies would be the most suitable sample type for this study. These samples will be referred to as scat here after. This sample type would not be suitable if the objective was to determine diet, as jellies contain minimal prey material.

River otter scat samples were field collected between November 2009 and October 2010 at latrine sites along the coastline (marine-terrestrial interface) of Southern Vancouver Island, near Victoria, BC. River otters use multiple latrine sites within their range and tend to show high site fidelity. The study area spans approximately 80 km of coastline and consists of 4 distinct sections along an urban-industrial gradient.

The study area was divided into 4 zones; Oak Bay (A), Victoria Harbour (B), Esquimalt Harbour (C) and Colwood-Metchosin (D). The centrally located harbours (B & C) are characterized as highly urbanized and historically industrial areas, in contrast to the relatively undisturbed areas in Colwood-Metchosin (D) and the residential yet natural settings in Oak Bay (A).

Scat samples were placed in chemically-rinsed (acetone/hexane) amber glass jars and stored at −20 °C for several months until shipment to the Great Lakes Institute for Environmental Research, Windsor, Ontario (ON), where they were stored at −40 °C until analyzed. Hormone samples were placed in plastic bags and stored at −20 °C until analyzed. Samples for genetic analysis were stored at −4 °C until analyzed.

Blood was collected from 16 river otters (5, 6, and 5 samples from zones A, B, and D respectively) during the capture of animals for the related telemetry study. Blood was centrifuged and the plasma portion was stored in chemically-rinsed amber glass vials at −20 °C until shipment to the National Wildlife Research Center, Ottawa, ON, where they were stored at −20 °C until analyzed.

Scat samples were sent for contaminant analysis to the Great Lakes Institute for Environmental Research (GLIER), University of Windsor. There, samples were prepared and analyzed for ΣPBDEs (20 congeners: 7, 15, 28, 47, 49, 85, 99, 100, 119, 126, 138, 153, 154, 183, 191, 196, 197, 206, 207, and 209). Chemical extraction and cleanup of OCs, PCBs, and PBDEs followed the procedures of (Lazar et al., 1992), and are described in further detail in (Guertin et al., 2010a) with some modifications as outlined below.

Briefly, samples (approximately 1–2 g of homogenate) were extracted by solid/liquid chromatography using dichloromethane:hexane (1:1 v/v). Prior to extraction each column was spiked with 200 ng of PCB 34 and BDE 71 used as recovery standards. After extraction and evaporation of extracts, 10% of the extracts were removed for neutral lipid determination (Drouillard et al., 2004). The remaining extracts were cleaned up by gel permeation chromatography (GPC) followed by activated Florisil chromatography as described in Lazar et al. (1992). Modifications to the procedure described above included elution of Florisil columns with 50 mL hexanes followed by another 50 mL (hexane/dichloromethane 85/15 v/v) collected as separate fractions, evaporated to 1 mL and capped in a 2 mL GC-vial. Each fraction was first analyzed for PCBs and organochlorine pesticides by gas chromatography–electron capture detection (GC–ECD) as part of a concurrent study. Following injection on the GC–ECD, the vials were recapped and injected on a high resolution mass spectrometer system