Brominated flame retardant trends in aquatic birds from the Salish Sea region of the west coast of North America, including a mini-review of recent trends in marine and estuarine birds

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HIGHLIGHTS

- Seabird eggs have been used to monitor POPs on the west coast of Canada since 1979.
- Samples of these eggs were analysed retrospectively for PBDEs and HBCDD.
- Regulations exist in North America to control PBDEs, but not HBCDD.
- PBDEs decreased significantly since regulations were applied.
- HBCDD was not detected pre-2003, but is now found in low concentrations.

ARTICLE INFO

ABSTRACT

Polybrominated diphenyl ethers (PBDEs) increased in many matrices during the 1990s and early 2000s. Since voluntary restrictions and regulations on PBDEs were implemented in North America circa early 2000s, decreases in PBDEs have occurred in many of these same matrices. To examine temporal trends in the North Pacific, we retrospectively analysed PBDEs and eight non-PBDE flame retardants (FR) in eggs of two aquatic bird species, great blue herons, *Ardea herodias*, and double-crested cormorants, *Phalacrocorax auritus*, collected along the British Columbia coast, Canada from 1979 to 2012. Increasing PBDE concentrations were observed in both species followed by significant decreases post-2000 for all dominant congeners and ΣPBDE. Non-PBDE FRs were generally undetected in cormorant eggs, or detected at very low levels in heron eggs, except for hexabromocyclododecane (HBCDD). HBCDD, currently unregulated in North America, was not detected in early sampling years; however low concentrations were observed in both species in recent sampling years (2003–2012). Dietary tracers (δ^{13}C and δ^{15}N) did not change significantly over time, indicating that temporal changes in PBDEs are likely caused by implemented regulations. A comparison with recently published temporal trends of ΣPBDE in marine birds from North America and Europe is given.

1. Introduction

Coastal marine environments are the interface between terrestrial and oceanic ecosystems. They are vulnerable to environmental contaminants originating from land-based anthropogenic activities (e.g., manufacturing or specific industrial activities), as well as from marine transport accidents or ocean dumping. Compared to remote sites, biota and other matrices such as air, rain and particulates from more populated coastal environments often have higher contaminant concentrations (Elliott et al., 2005; Gauthier et al., 2007, 2008; Noël et al., 2009). Monitoring of nearshore environments is important because emerging contaminants and any changes due to regulations are normally first detected closer to urban and industrial sources. Seabird species utilise a wide range of environments, from coastal urban habitats to uninhabited offshore islands, making them ideal indicator species for such work, including determination of spatial and temporal trends and patterns (Elliott and Elliott, 2013).

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Long-term monitoring of seabird eggs allows for temporal trends in contaminants to be investigated (Bignert et al., 1995; Elliott et al., 2005; Burgess et al., 2013) and allows for examination of the efficiency and efficacy of implemented policy and regulations.

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) represent two classes of brominated flame retardants (BFR). PBDEs were produced to purportedly decrease the flammability of various materials (e.g., plastics, rubbers, building materials and other textiles) (Alaee et al., 2003; Sjödin et al., 2003). They were manufactured commercially at three different degrees of bromination — penta-, octa- and deca-BDEs (de Wit, 2002; Alaee et al., 2003). Produced as a mixture of three stereoisomers – α, β and γ (Alaee et al., 2003; Covaci et al., 2006) – HBCDDs are largely used in building materials as foams and expanded polystyrene (de Wit, 2002). Both PBDEs and HBCDDs are persistent and bioaccumulative (de Wit, 2002), making higher trophic level biota particularly susceptible to biomagnification (Braune et al., 2007). PBDEs are now virtually ubiquitous throughout environmental media, including humans, terrestrial, aquatic and marine biota, sewage sludge and air (de Wit, 2002; Darnerud, 2003; Sellström et al., 2003; Chen and Hale, 2010; Daso et al., 2010; de Wit et al., 2010; Kefeni et al., 2011). In 1999, PBDEs were declared toxic under the Canadian Environmental Protection Act (Environment Canada, 2004). The penta- and octa-BDE commercial mixtures were voluntarily phased out in Canada in the early 2000s, quickly followed by regulatory restrictions in both Canada and the USA (Canadian Gazette, 2006; Environment Canada, 2008). Since 2009, penta- and octa-BDEs have been included as "new" persistent organic pollutants (POPs) under the Stockholm Convention. Currently, the manufacture of tetra- to deca-BDEs and the use, sale and import of tetra-, penta- and hexa-BDE congeners in Canada are prohibited (Environment Canada, 2008). In contrast, HBCDD is not regulated in North America, although it has been slated for inclusion under the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention on Persistent Organic Pollutants, 2008), and the Long Range Transboundary Air Pollution Protocol on POPs (Arnot et al., 2009).

Around the time of the voluntary PBDE phase outs in North America, two offshore seabird species found in British Columbia (BC), rhinoceros auklets (*Cerorhinca monocerata*) and Leach's storm-petrels (*Oceanodroma leucorhoa*), showed decreasing PBDE concentrations at the majority of examined sites, which were likely the result of decreases associated with these regulations rather than, for example, dietary changes (Miller et al., 2014). In contrast, dietary changes often factor into changes in contaminant concentrations in other species (Jarman et al., 1997; Hebert et al., 2000; Burgess et al., 2013). Isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) are commonly used to examine the role of carbon source and determine trophic position (TP) respectively in uptake of contaminants by biota (e.g., Burgess et al., 2013; Christensen et al., 2005; Elliott et al., 2009; Fisk et al., 2001; Hebert and Weseloh, 2006; Ikemoto et al., 2008; Riget et al., 2007; Weseloh et al., 2011), and are a valuable tool for the analysis of food web structure in evaluating biomagnification potential of environmental contaminants (Jarman et al., 1997; Hop et al., 2002; Ruus et al., 2006; Braune, 2007; Bodin et al., 2008; Morrissey et al., 2010).

Up until 2002, PBDE concentrations in coastal BC populations of double-crested cormorants (*Phalacrocorax auritus*, hereafter cormorants) and great blue herons (*Ardea herodias*, hereafter herons) were increasing exponentially (Elliott et al., 2005). Given that voluntary phase outs of PBDEs in North America were introduced in the early 2000s, the situation in coastal-urban dwelling cormorants and herons requires reappraisal, especially in light of results seen in offshore BC seabirds (Miller et al., 2014). Here we examine temporal trends of PBDE concentrations in cormorant and heron eggs. We compare the concentration of dominant congeners in the most recently sampled year to three offshore seabird species collected on remote BC islands (Miller et al., 2014), to examine spatial differences in ΣPBDE and HBCDD between coastal and offshore seabirds, and provide a mini-review of recently published temporal trends of PBDEs in marine birds from North America and Europe.

2. Materials and methods

2.1. Study species

Double crested cormorants are widely distributed across North America (Mercer et al., 2013). They are habitat generalists, being found from coastal near-shore to inland aquatic environments (Mercer et al., 2013). In BC, they are a coastal-breeding aquatic bird that feeds on a variety of benthic and mid-water schooling fish. Unlike most of North America, cormorants may be experiencing declines in the breeding population in BC (Chatwin et al., 2002; Mercer et al., 2013) and are a protected species under the BC Wildlife Act (1996) (Courtot et al., 2012).

Great blue herons are also widely distributed across North America. They are found in freshwater and marine habitats, and are widely used as an indicator species (Custer et al., 1997; Elliott et al., 2001; Champoux et al., 2006). Herons are opportunistic, primarily piscivorous feeders (Harris et al., 2003b) preying mostly on fish, e.g., sea perch (*Helicolenus percoides*), but also on amphibians, invertebrates and small mammals. Although migratory, herons remain in the BC coastal area year-round (Butler et al., 1995). The BC heron population is blue listed, meaning it is vulnerable and at risk of local decline (Harris et al., 2003b).

2.2. Sites, sampling matrix and design

Since 1979, cormorant eggs have been collected at Mandarte Island, an uninhabited island of approximately 6 ha, located approximately 6 km off the east coast of Vancouver Island, and 60 km south-west of Vancouver, BC (Fig. 1, Table 1). Those cormorants forage in the South Salish sea in the vicinity of the colony (Harris et al., 2003a). Heron eggs were collected from a colony formerly on the grounds of the University of British Columbia, later Pacific Spirit Park, from 1987 to 2004, a 763 ha urban park near the metropolitan centre of Vancouver. This colony re-located to Stanley Park in downtown Vancouver, approximately 6–8 km north-east from the original colony site and has subsequently been sampled from here since 2008. Stanley Park is approximately 400 ha, located in downtown Vancouver, a city with a greater metropolitan population comprising >2 million people. Herons breeding at both sites forage along the foreshore of the Fraser River estuary and Burrard inlet, site of the port of Vancouver (Elliott et al., 2001), and are thus referred to as the Fraser River colony throughout. The total number of eggs collected each year has varied (see Table 2).

2.3. Chemical analysis and quality assurance

Egg homogenates were analysed at the National Wildlife Research Centre as per methods described previously (Chen et al., 2013; Miller et al., 2014). A total of 33 PBDE congeners were analysed for BDE 7, 8, 10, 15, 17, 25, 28, 35, 37, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 140, 153, 154, 155, 181, 183, 190, 206, 207, 208, and 209. Analyte standards were purchased from Wellington Laboratories (Guelph, ON, Canada) and Cambridge Isotope Laboratory (Cambridge, MA, USA). Briefly, approximately 1.5 g wet weight (ww) of aliquots were homogenized with anhydrous sodium sulphate (Na_2SO_4) followed by neutral extraction with DCM:hexane (1:1). The homogenate was spiked with labelled internal standards (BDE-30, BDE-71, BDE-156 and/or ^{13}C-BDE-209) and a portion of the resulting extract was removed for lipid determination. Further cleanup was performed on a Florisil column containing 8 g of deactivated Florisil in a Borosilicate glass column (1 cm ID × 24 cm length). Purified sample extracts were analysed for BFRs using a capillary gas chromatograph (Agilent 6890 N), coupled with a mass selective detector (Agilent 5973N) operated in selected ion monitoring mode. The determination of α-HBCDD by GC–MS is
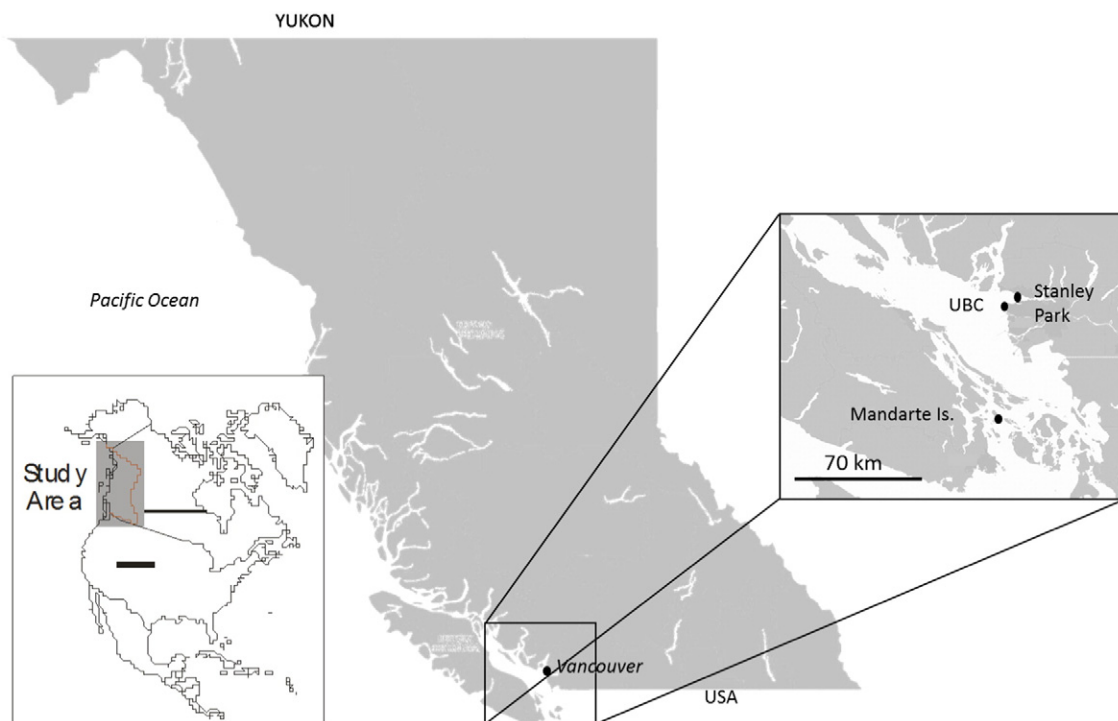
Fig. 1. Map of North America showing British Columbia, Canada (inset, bottom left, grey shading), indicating the approximate location of the studied colonies (black dots, inset, right). Double crested cormorant eggs were collected from Mandarte Island, and great blue heron eggs were collected from a colony at the University of British Columbia (UBC) until 2004, and since 2008 from Stanley Park (collectively referred to as the Fraser River colony).

representative of total-HBCDD as any β- and γ-HBCDD residues are thermally isomerized to α-HBCDD at temperatures exceeding 160 °C in the injection port. Contaminant recovery values for BDE-30 were 43–69%; for BDE-156, 41–75%; and for ^{13}C-BDE-209, 13–41%.

For quality assurance, a standard reference material (Lake Michigan fish tissue homogenate from the National Institute of Standards and Technology) was analysed with each batch of samples. All reported PBDE congeners were within ±20% of the certified values, except for co-eluted BDE 154/BB (brominated biphenyl) 153. Duplicate extractions, cleanups and injections were performed. In most years the method limit of detection (LOD) was <0.10 ng/g for all congeners, except for hexabromocyclododecane (HBCDD) (1.0 ng/g) and BDE 209 (from 1.0 to < 5.0 ng/g). BDE-15 and β-TBECH, and BDE-154 and BB-153 coeluted. Non-PBDE FRs analysed for were alpha and beta tetrabromoethylcyclohexane (α-TECH, b-TECH/BDE 15), hexabromobenzene (HBB), HBCDD, BB 101, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and stereoisomers of dechlorane plus (*syn*-DP, *anti*-DP).

2.4. Stable isotope analysis

Stable isotope analysis for ^{13}C/^{12}C and ^{15}N/^{14}N isotopes was carried out using the same egg homogenate as used for chemical analyses and described elsewhere (Elliott et al., 2014; Miller et al., 2014). Sub-samples of 1 mg were freeze-dried, loaded into tin cups and

analysed using a PDZ Europa ANCA-GSL elemental analyser interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (IRMS; Sercon Ltd., Cheshire, UK) at the Stable Isotope Facility at the University of California, Davis (http://stableisotopefacility.ucdavis.edu). Samples were interspersed with replicates of at least two different laboratory standards during analysis. Final delta values were presented in parts per thousand (‰) relative to international standards Vienna PeeDee Belemnite and Vienna Cañon Diablo Troilite (δ^{13}C) and air (δ^{15}N). The δ^{13}C values were lipid normalised (Elliott et al., 2014) as variation in lipid content can obscure variation in δ^{13}C (Elliott et al., 2014).

2.5. Statistics

Concentrations are presented on a wet weight (ww) basis with standard error of the mean (SEM) where appropriate. Values below limit of quantification (LOQ) were replaced with half the limit of detection (LOD) to give a conservative estimate of the concentration. Where >50% of reported values were below the LOQ, or were non-detects, the congener was removed from analyses. This situation occurred only for trace congeners, or non-PBDE FRs. Arithmetic means were calculated for each year where multiple pooled samples were available. BDE 154 was replaced by co-eluted BDE 154/BB 153 in 2003 in heron eggs and in 2006 for cormorant eggs, and is thus treated as a single continuous congener.

A principal component analysis (PCA) was used to examine the pattern of distribution of log transformed dominant PBDE congeners and HBCDD between cormorant and heron eggs for the most recent year of sampling, using each pooled sample for the final year (n = 5 for both species). HBCDD was included as it was the only trace congener above the LOQ for all samples for both species in the final year. The proportion contribution of each dominant congener to ΣPBDE was calculated. A general linear model (GLM) was used to examine the relationship between log-transformed ΣPBDE and species (cormorant and heron), lipid percentage, year and year^2. Year^2 was included as a possible effect because of the potential for nonlinear change in contaminant values.

Table 1
Species and years sampled at each site. All sampling occurred between April and July.

Species	Site, coordinates	Years sampled
Double crested cormorant	Mandarte Island 43° 38′N; 123° 17′W	1979, 1985, 1990, 1994, 1995, 1998, 2002, 2006, 2011
Great blue heron	Fraser River 49° 30′N; 123° 14′W/49° 26′N, 123° 25′W	1987, 1988, 1991, 1992, 1993, 1994, 1996, 1998, 2000, 2002, 2003, 2004, 2008, 2012

Table 2

Arithmetic mean lipid and moisture percentages, dominant congener concentrations, and sum of PBDEs (ΣPBDE) (ng/g ww) for both species in each monitored year. Proportion (%) contribution of each dominant congener to ΣPBDE is shown in parenthesis. All values are presented to 1 decimal place. BDE 154/BB 153 replaced BDE 154 for double crested cormorants since 2006, and since 2003 for great blue herons.

Species	Double crested cormorant																			
Site	Mandarte Island																			
Year	1979	1985	1987	1988	1990	1991	1992	1993	1994	1995	1996	1998	2000	2002	2003	2004	2006	2008	2011	2012
N	1	5			11				3	10		6		3			15		15	
Moisture %	83.8								83.7			84.1					83.5		84.2	
Lipid %	4.9	5.6			5.4				5.5	6.1		6.1		6.6			4.3		3.2	
BDE 47	0.1 (45.1)	1.9 (25.4)			6.9 (26.3)				172.2 (44.7)	81.5 (38.7)		53.7 (27.6)		16.3 (25.8)			9.2 (26.4)		8.4 (25.3)	
BDE 99	0.1 (25.1)	2.6 (35.5)			7.5 (28.4)				57.3 (14.9)	41.1 (19.5)		44.0 (22.6)		9.2 (14.5)			4.4 (12.5)		2.4 (7.1)	
BDE 100	<0.1 (13.0)	1.3 (17.4)			7.0 (26.6)				88.3 (22.9)	57.8 (27.4)		55.1 (28.3)		22.3 (35.3)			13.7 (39.0)		14.2 (42.8)	
BDE153	<0.1 (11.3)	0.6 (7.7)			2.1 (8.2)				39.2 (10.2)	16.2 (7.7)		25.8 (13.2)		9.7 (15.3)			3.6 (10.2)		2.9 (8.7)	
BDE 154, BDE154/BB153	<0.1 (4.2)	0.5 (6.5)			2.1 (7.8)				25.6 (6.7)	11.8 (5.6)		15.0 (7.7)		4.2 (6.6)			2.8[a] (8.1)		2.6[a] (7.9)	
ΣPBDE	0.2	7.3			26.3				384.9	210.7		194.6		63.4			35.7		31.3	

Species	Great blue heron																			
Site	Fraser River estuary																			
Year	1979	1985	1987	1988	1990	1991	1992	1993	1994	1995	1996	1998	2000	2002	2003	2004	2006	2008	2011	2012
N			27	16	5	10	6	5			5	5	10	5	5	5	5	5		5
Moisture %			81.5	81.9	81.3	81.9	82.9	82.1			82.4	80.9	81.7		82.3	81.5		79.9		81.4
Lipid %			6.0	6.8	6.7	6.4	5.8	6.1			6.0	7.0	5.7	5.9	6.1	5.5		6.2		6.3
BDE 47			4.4 (35.0)	4.7 (32.9)	20.0 (37.2)	28.3 (28.4)	42.9 (39.5)	53.8 (43.5)			120.0 (41.8)	64.8 (32.1)	53.9 (27.8)	82.8 (18.2)	97.1 (41.6)	37.3 (34.0)		38.8 (41.1)		26.9 (37.5)
BDE 99			2.2 (17.3)	2.0 (14.2)	12.3 (22.9)	11.7 (11.8)	21.4 (19.7)	17.4 (14.1)			54.4 (18.9)	34.8 (17.2)	28.9 (14.9)	174.0 (38.3)	35.0 (15.0)	22.1 (20.2)		16.1 (17.1)		11.8 (16.5)
BDE 100			1.4 (11.3)	1.5 (10.9)	9.0 (16.7)	10.3 (10.4)	21.8 (20.1)	25.9 (20.9)			56.1 (19.5)	51.2 (25.4)	56.1 (29.0)	88.6 (19.5)	58.4 (25.1)	25.7 (23.4)		23.9 (25.4)		16.3 (22.7)
BDE153			2.6 (21.1)	3.5 (24.8)	7.0 (13.0)	6.4 (6.4)	11.8 (10.9)	15.1 (12.2)			34.2 (11.9)	30.9 (15.3)	32.9 (17.0)	67.7 (14.9)	18.6 (8.0)	12.0 (10.9)		7.1 (7.6)		8.9 (12.4)
BDE 154, BDE154/BB153			1.6 (12.7)	1.8 (12.5)	4.6 (8.6)	40.7 (40.8)	8.2 (7.6)	8.9 (7.2)			18.8 (6.5)	18.5 (9.2)	19.0 (9.8)	35 (7.7)	19.5[a] (8.4)	10.5[a] (9.5)		6.7[a] (7.1)		5.4[a] (7.5)
ΣPBDE			12.5	14.3	53.6	99.6	108.5	123.6			287.5	201.9	193.7	457.0	248.9	114.9		94.3		71.7

[a] Indicates where BDE 154 was replaced by coeluted BDE154/BB 153.

Only log (ΣPBDE) is presented for the entire time series. Temporal trends in natural log transformed dominant congeners and log (ΣPBDE) concentrations were examined using quadratic regression, and the untransformed data were plotted using two-year running smoothers. Initial voluntary restrictions on production and use of penta-BDEs occurred in the early 2000s, and were soon followed by regulatory restrictions in Canada and the USA (Environment Canada, 2008). Thus, doubling times pre- and post-2000 were calculated from the slope of a simple regression line and assume first-order (exponential) increases. Temporal trends of stable isotopes of δ^{13}C and δ^{15}N from cormorant eggs were examined using simple linear regression. Natural log transformed dominant congeners and ΣPBDE were examined for any relationship with δ^{13}C, δ^{15}N and lipid percentage over time using multiple linear regression. Statistical analyses were conducted in Excel 2010 and R version 3.0.3.

2.6. Comparison of recent published ΣPBDE trends

A mini-review of recent temporal trends of ΣPBDE in marine birds was conducted by searching the Web of Science database using the key words "marine birds", "seabirds", "PBDE", "polybrominated diphenyl ethers", "BFR", "brominated flame retardants", "temporal trends" and any combination of these. No specific start year was applied for the temporal trends. Trends could be based on as few as two years (She et al., 2008; Herzke et al., 2009) to annual collections for more than 30 years (Sellström et al., 2003). Published articles describing temporal trends of ΣPBDE in marine or estuarine birds at quantifiable levels were included. Most of the articles included used eggs as the matrix, although two articles used liver (Law et al., 2002; Braune and Simon, 2004), and one article reported both egg and liver concentrations (Herzke et al., 2009), resulting in 14 published articles and one article in press (Miller et al., 2014) being included alongside data presented here. Data from this mini-review are presented on a lipid weight basis given the differences in lipid percentage in eggs between species.

3. Results and discussion

Concentrations of PBDEs in eggs of double crested cormorants from the Salish Sea near Victoria and great blue herons from the Fraser River estuary near Vancouver increased in the early years of monitoring (Elliott et al., 2005, and here) and subsequently decreased since the late 1990s (cormorant eggs) or early 2000s (heron eggs). The timing of those decreases coincides with voluntary phase-outs of penta- and octa-BDE mixtures in Canada, which later became regulation and was extended to include tetra- and hexa-BDE congeners (Canadian Gazette, 2006). There was no significant change over time in either δ^{15}N or δ^{13}C from cormorant eggs, or any significant relationship with ΣPBDEs or the majority of dominant congeners, indicating that the observed decreasing trends in PBDEs in this species were not driven by diet, but were probably due to the restrictions introduced in North

America. Those findings are in line with temporal trends recently reported in two offshore seabird species, rhinoceros auklets and Leach's storm-petrels from the Pacific coast of Canada, where increases followed by decreasing concentrations corresponding to regulations were observed (Miller et al., 2014).

3.1. Dominant congeners

Penta-BDEs, found in technical PBDE products, were dominant in both species here, with BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154 (later replaced by co-eluted BDE154/BB153) the most dominant congeners. In heron eggs, BDE 47 was dominant in most years, with exceptions seen in 1992 (surpassed by BDE 154/BB 153), 2000 (surpassed by BDE 100) and 2002 (surpassed by both BDE 99 and BDE 100) (Table 2). In the late 1980s, BDE 153 was the second most dominant congener. However, concentrations of BDE 99 and BDE 100 gradually surpassed BDE 153. In cormorant eggs, the dominant congener was more variable — BDE 99 was dominant in 1985 and 1990, BDE 47 was dominant in 1994 and 1995, and BDE 100 became dominant for the remaining four sampling years (Table 2). Lower brominated BDEs, such as BDE 47, tend to be volatile and thus more likely to disperse in the environment (Hale et al., 2006).

Penta-BDE congeners are dominant in many biota, including fish (e.g., Christensen et al., 2002; Ma et al., 2013; Rice et al., 2002; Ross et al., 2009) and piscivorous birds (e.g., Braune et al., 2002, 2007; Chen et al., 2012; Elliott et al., 2005; Helgason et al., 2009; Karlsson et al., 2006; Lavoie et al., 2010; Sellström et al., 2003). BDE 47 and BDE 99 were the two most dominant congeners reported from herring gull (*Larus argentatus*) eggs in the North and Baltic Sea (Fliedner et al., 2012), whereas BDE 47 alone was dominant in ivory gull (*Pagophila eburnea*) eggs from the Canadian Arctic (Braune et al., 2007). In captive and wild peregrine falcon populations from Sweden, BDE 153 was the dominant penta-congener, with a suggestion that the half-life of BDE 153 is very long (Lindberg et al., 2004). De-bromination of higher-brominated congeners, e.g., BDE 209, could also be contributing to the dominance of penta-BDE congeners (Gauthier et al., 2007, 2008; Gauthier et al., 2009).

A PCA showed some variation in congeners in the most recent year of sampling between the two species, with ~95% of the variance explained by the first two axes. HBCDD, BDE 47 and BDE 99 formed a group, while BDE 100, BDE 153 and BDE 154/BB 153 formed a group. Cormorants and herons did not overlap within those congener groups. Herons tended to have higher levels of all brominated flame retardants than cormorants (heavier loading on axis 1) and a higher ratio of the more brominated compounds (BDE 100, BDE 153, BDE 154/BB 153) to the less brominated compounds (BDE 99, HBCDD; heavier loading on axis 2) compared with cormorants (Fig. 2). In particular, cormorants do not seem to be especially influenced by any one congener or group of congeners (Fig. 2). Reasons for these differences are not clear and may be due to diet or variations in sources.

3.2. Non-polybrominated diphenyl ether flame retardants

Non-PBDE FRs in cormorant eggs were generally not detected, except for HBCDD. However, HBB was quantified in one of four pooled samples in 2011 (0.11 ng/g ww). HBB was historically used in Japan as an additive to paper, plastic and electronic goods (Verreault et al., 2007). In herons, all non-PBDE FRs analysed were detected, but at low levels, since 2003 when they were first analysed. Gauthier et al. (2009) reported that non-PBDE FRs have accumulated in herring gull eggs over the last 25 years. Comparably, Chen et al. (2012) found that HBCDD was common, while DP *syn-* and *anti*-isomers were detected at <1.0 ng/g ww in marine samples of glaucous gull (*Larus glaucescens*) and herring gull eggs from Pacific and Atlantic Canada colonies. BB101 was quantifiable in 40% of the colonies examined, however, the other non-PBDE FRs were generally below the LOD or LOQ (Chen et al., 2012).
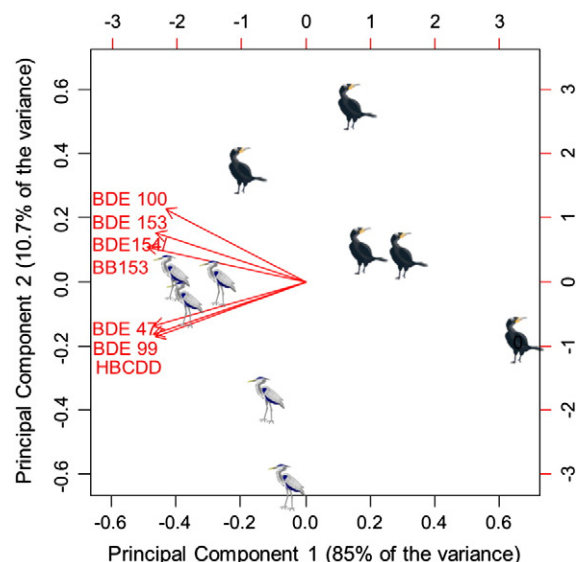

Fig. 2. Principal component analysis on log transformed dominant congeners (BDE 47, 99, 100, 153, BDE154/BB153) and HBCDD in the most recent year of sampling for double crested cormorant (black birds, n = 5) and great blue heron eggs (pale birds, n = 5).

In early years of sampling, HBCDD was either not analysed for or was below the LOQ once analysis began (2006 for cormorants and 2003 for herons). Of concern however, HBCDD was quantified in most pooled samples since 2006 in cormorants (2006: 0.77 ng/g ww ± 0.1 SEM; 2011: 0.57 ng/g ww ± 0.2 SEM) and since 2003 in herons (2003: 15.5 ng/g ww ± 9.9 SEM; 2004: 5.2 ng/g ww ± 1.2 SEM; 2008: 12.2 ng/g ww ± 7.3 SEM: 2012: 1.7 ng/g ww ± 0.2 SEM). By contrast, HBCDD was a dominant congener in rhinoceros auklet, ancient murrelet and Leach's storm-petrel eggs off the coast of BC from 1990 to 2011 (Miller et al., 2014). That indicates different sources of some BFRs for offshore and coastal seabirds along the Pacific coast of BC, which may be due to their different life histories. The offshore birds are believed to feed off the coast of Asia before returning to breeding colonies in BC; whereas the colonies of coastal BC birds examined here remain in coastal BC areas year round. Since the withdrawal of some PBDE-containing products in Japan, concentrations of HBCDD have begun to exceed PBDE concentrations (Tanabe et al., 2008), which may explain the high HBCDD concentrations observed over time by Miller et al. (2014) in the offshore birds, and the recent increases in HBCDD concentration observed here. In agreement with results here, temporal trends observed by Chen et al. (2011) in fish collected within the US mid-Atlantic region suggest that HBCDD use has risen in North America as penta-BDE use declined following regulations to halt US manufacture.

3.3. Temporal trends

Prior to the voluntary phase outs in Canada in the early 2000s, concentrations of all dominant congeners and ΣPBDE were increasing in both cormorant and heron eggs. In 1979 when cormorant egg monitoring began, all BDE congener concentrations were extremely low (≤0.1 ng/g ww). However, by the mid-1990s concentrations had increased, with ΣPBDE peaking in 1994 at 384.9 ng/g ww (Table 2). In heron eggs, concentrations remained comparatively low in the late 1980s before ΣPBDE peaked in 2002 at 457 ng/g ww (Table 2). The dominance of the lower-brominated congeners during this period is likely explained by the high demand for penta-BDE in North America during the examined period (Hale et al., 2003), i.e., the North American market comprised 98% of the world's penta-BDE production in 2003 (Chen and Hale, 2010).

In cormorant eggs, BDE 47 has consistently contributed >25% and up to ~45% to ΣPBDE, while the contribution of BDE 100 to ΣPBDE has

shown a steady increase since 1994 (Table 2). In heron eggs, contribution of BDE 47 to ΣPBDE was >25% and up to ~43%, with the exception of 2002, where proportion contribution was lower (18.2%). In 1992, BDE 154 contributed >40% to ΣPBDE, subsequently contributing <10% each year (Table 2). Log (ΣPBDE) varied with year (GLM, $t_{18} = 7.98$, $p < 0.001$) and $year^2$ ($t_{18} = -7.96$, $p < 0.001$) but not species ($t_{18} = 0.77$, $p = 0.45$) or lipid content ($t_{18} = 0.29$, $p = 0.77$). Pre-2000, ΣPBDE doubling times were 4.2 years (cormorants) and 5.4 years (herons). In agreement with the increasing concentrations seen pre-2000 here, PBDEs in ringed seal (*Phoca hispida*) blubber from the Canadian Arctic showed exponential increases in concentration up to 2000 (Ikonomou et al., 2002), as did PBDE concentrations in beluga whale (*Delphinapterus leucas*) blubber collected from the St Lawrence Estuary, Canada between 1988 and 1999 (Lebeuf et al., 2004). Similarly, increasing concentrations of PBDEs, primarily driven by BDE 47, were observed in ivory gull eggs from the Canadian Arctic collected between 1976 and 2004 (Braune et al., 2007)

Post-2000, significant decreases in all dominant congeners and log (ΣPBDE) were observed in cormorant and heron eggs (Fig. 3, Table 3). ΣPBDE halving times were 23.1 years (cormorants) and 13.2 years (herons) (Table 3). BDE 47 contributed less to ΣPBDE post-2000, while contributions of BDE 100 generally increased for both species, although overall concentrations were decreasing. A significant increasing trend was seen for BDE 100 in heron eggs ($p = 0.02$) prior to the observed significant decrease (Table 3). Decreases observed here are consistent with findings from offshore BC bird eggs (Miller et al., 2014). Other aquatic bird species have also shown temporal declines of PBDEs, e.g., murre (*Uria aalge*) eggs from the Baltic Sea (Sellström et al., 2003) and herring gull eggs collected from German coastal regions (Fliedner et al., 2012), where observed decreases were attributed to reduction in use prior to the implementation of regulations in the EU (Fliedner et al., 2012; Sellström et al., 2003). Gauthier et al. (2008) noted increases in penta-BDEs prior to 2000 in herring gull eggs from the Laurentian Great Lakes, and a subsequent lack of increasing concentrations, also attributed to regulations. In harbour seal (*Phoca vitulina*) blubber samples collected from the Salish Sea in north-western North America, PBDE concentrations have been declining since 2003, again credited to regulations (Ross et al., 2013).

3.4. Stable isotope analysis

Stable isotope values from cormorant eggs sampled at Mandarte Island indicate that birds from this colony are piscivorous coastal feeders, with relatively stable yearly average $\delta^{15}N$ values (15.1 ± 0.4‰ SEM; range 13.6 to 17.3) and more variable yearly average $\delta^{13}C$
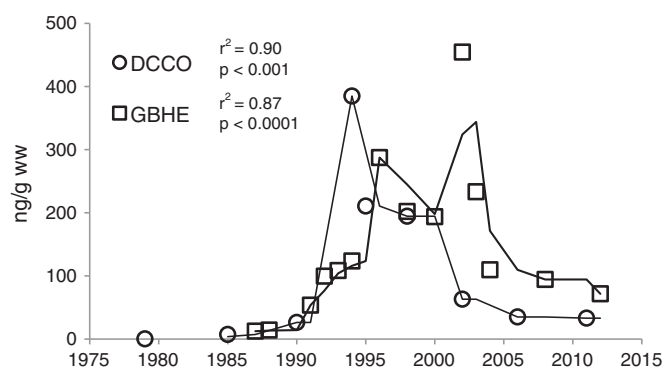

Fig. 3. ΣPBDE (ng/g ww) showing 2 year moving smoothers for double crested cormorant eggs (DCCO, circles) from Mandarte Island and great blue heron eggs (GBHE, squares) from the Fraser River estuary.

Table 3
Quadratic regression and r^2 value for the whole time series, and doubling times or half-life (in years) pre- and post-2000 (from simple linear regression) for log (dominant congeners) and log (ΣPBDE) for double crested cormorants and great blue herons. Values in parenthesis indicate halving times.

Double crested cormorant, Mandarte Island, df = 6		Doubling time/half-life (years)	
Congener	r^2	Pre-2000, n = 6	Post-2000, n = 3
BDE 47	0.85[*]	4.3	(22.2)
BDE 99	0.92[*]	4.5	(10.7)
BDE 100	0.93[*]	3.8	(33.2)
BDE 154/BB153–BDE 154	0.92[*]	4.0	(31.8)
BDE 153	0.91[*]	4.2	(12.2)
ΣPBDE	0.90[*]	4.2	(23.1)
Great blue herons, Fraser River estuary, df = 11		Doubling time/half-life	
Congener	r^2	Pre-2000, n = 8	Post-2000, n = 6
BDE 47	0.85[**]	5.3	(19.2)
BDE 99	0.80[**]	5.3	(11.5)
BDE 100[a]	0.93[**]	4.3	(12.6)
BDE 154/BB153–BDE 154	0.69[*]	6.7	(11.3)
BDE 153	0.75[**]	6.5	(10.7)
ΣPBDE	0.87[**]	5.4	(13.2)

[*] $p < 0.001$.
[**] $p < 0.0001$.
[a] Showed a significant linear increase prior to decrease.

values (-14.9 ± 0.5‰ SEM; range -13.9 to -17.6) observed over the sampled time period. This is consistent with the known feeding ecology of this species, preying mostly on sub-surface schooling fish (Ainley et al., 1981; Dunn, 1975; Robertson, 1974). No relationship was observed between $\delta^{13}C$ and $\delta^{15}N$ ($r^2 = 0.001$, $p = 0.9$).

In 1994, both $\delta^{15}N$ and $\delta^{13}C$ decreased to their lowest values observed. $\delta^{13}C$ decreased to -17.6‰, -2.7‰ lower than the overall average value, and $\delta^{15}N$ decreased to 13.6‰, 1.5‰ lower than the overall average value and also the lowest yearly average value observed for both variables. The cause of these decreases is unclear. However, one possibility could be weather patterns and fluctuations. In 1994, a weak El Niño-Southern Oscillation (ENSO) event occurred in the waters off British Columbia (Gaston and Smith, 2001). ENSO events bring warmer waters and milder weather to the Pacific coast of British Columbia, which may reduce zooplankton stocks, eventually affecting higher trophic level feeders (Bertram et al., 2000; Goldblatt et al., 1999; Hipfner, 2008; Mackas and Tsuda, 1999). However in other years when ENSO events occurred e.g., 1982–1983, 1997–1998 (see Gaston and Smith, 2001) data for these two seabird species was either not available or available for 1998 only, making it difficult to say if weather patterns were the cause.

Nonetheless, the highest concentrations of dominant PBDE congeners and ΣPBDE in cormorant eggs were observed in 1994 (Table 2), coinciding with these lower stable isotope values. However, multiple linear regression analyses showed non-significant relationships between log (ΣPBDE) and $\delta^{13}C$, $\delta^{15}C$ and lipid content ($p = 0.08$, $p = 0.07$, $p = 0.5$ respectively, df = 8). No significant relationships were observed between log transformed dominant congeners and any of these three variables, with the exception of log (BDE 99), where a significant relationship with $\delta^{15}N$ was seen ($p < 0.03$). Cormorant diet was therefore not the primary driver of temporal changes in PBDE concentrations, despite the apparent relationship observed in this single year. This finding is consistent with results seen from rhinoceros auklet and Leach's storm-petrel eggs from the Pacific coast of BC, whereby temporal trends in PBDE concentrations were unlikely to have been caused by dietary changes (Miller et al., 2014). Further support comes from Chen et al. (2011), wherein freshwater fish species sampled from the Atlantic coast of the USA showed a temporal increase in HBCDD and a simultaneous decrease in PBDE concentrations.

3.5. Comparison of recent published ΣPBDE trends

Temporal trends from North America all show initial increases, with ten trends (from British Columbia, Canada and the San Francisco Bay, USA) showing subsequent decreases occurring from the mid to late-1990s to the early 2000s (Table 4), in line with regulations introduced in North America in the early 2000s (Canadian Gazette, 2006). This trend was reported by Elliott et al. (2005), Miller et al. (2014) and in data presented here, where seabirds were sampled from British Columbia, and in She et al. (2008), where sampling occurred in San

Francisco Bay, USA, despite this being a short time series (four years). Maximum ΣPBDE concentration from the North American region was observed in Forster's tern, *Sterna fosteri*, sampled in the San Francisco Bay (63,000 ng/g lw) (She et al., 2008). By contrast, steady increases in ΣPBDE were seen in ivory gull (*P. eburnea*) eggs sampled from the Canadian Arctic (Braune et al., 2007) and in Leach's storm-petrel eggs sampled at Hippa Island, a remote British Columbian island. Due to their distance from industrial or urban influence, it is possible that a lag period in observing decreasing concentrations may occur in remote locations.

Table 4
ΣPBDE concentrations and temporal trends in other published seabird species studies.

Country	Site (year)	Species	ΣPBDE range ng/g lw	Temporal trend	Reference
North America					
Canada	Seymour Island (Arctic) (1976–2004)	Ivory gull, *Pagophila eburnea*	18.3–44.5	+	Braune et al. (2007)
	Fraser River Estuary (1987–2002)	Great blue heron, *Ardea herodias*	206.9–7685.8	+	Elliott et al. (2005)
	Mandarte Island, British Columbia (1979–2002)	Double-crested cormorant, *Phalacrocorax auritus*	4.9–7064.2	+, − post-1995	
	Pitt River, British Columbia (1991–2000)	Osprey, *Pandion haliaetus*	187.1–4545.5	+, − post-2000	
	Cleland Island, British Columbia (1990–2010)	Rhinoceros auklet, *Cerorhinca monocerata*	51–491.8	+, − post-2000	Miller et al. (2014)
	Lucy Island, British Columbia (1990–2010)	Rhinoceros auklet, *Cerorhinca monocerata*	39.6–251.7	+, − post-2000	
	Cleland Island, British Columbia (1990–2011)	Leach's storm-petrel, *Oceanodroma leucorhoa*	28.1–266.1	+, − post-2000	
	Hippa Island, British Columbia (1991–2011)	Leach's storm-petrel, *Oceanodroma leucorhoa*	20.3–52	+, − post-2000 +	
	Fraser River estuary, British Columbia (1987–2012)	Great blue heron, *Ardea herodias*	206.8–7719.6	+, − post-2002	This study
	Mandarte Island, British Columbia (1979–2011)	Double-crested cormorant, *Phalacrocorax auritus*	4.9–7062.6	+, − post mid-1990s	
USA	San Francisco Bay (2000–2003)	Caspian tern, *Sterna caspia*	1200–36,100	+, −	She et al., (2008)
	(2000–2002)	Forster's tern, *Sterna fosteri* California least tern, *Sterna antillarum brownii*	666–63,300 5420–5870	+, − +	
Europe					
Germany	North Sea, Trischen Island (1988–2008)	Herring gull, *Larus argentatus*	116–1722 232–2021	−	Fliedner et al. (2012)
	North Sea, Mellum Island (1988–2008)	Herring gull, *Larus argentatus*		−	Fliedner et al. (2012)
	Baltic Sea, Heuwiese Island (1991–2008)	Great skua, *Stercorarius skua*	282–2059	−	Leat et al. (2011)
UK	Shetland Islands (1980, 2008)	Great skua, *Stercorarius skua*		No change	Leat et al. (2011)
	England and Wales, multiple sites (1996–2000)[a]	Cormorants, *Phalacrocorax carbo*	85.7–4375 µg/kg lw	No change +	Law et al. (2002)
	Ailsa Craig, western Atlantic (1977–2007)	Gannet, *Morus bassanus*	139.7–1755.6	+, − post-1994 +, − post-1994	Crosse et al. (2012)
	Bass Rock, North Sea (1977–2007)		118.4–1661	+, − post-1994	
Sweden	Stora Karlsö, Baltic Sea (1970–1989)	Murre (guillemot), *Uria aalge*	158.2–1909	+	Sellström et al. (1993)
	(1969–2001)		48–1348	+ 1970s–1980s, −	Sellström et al. (2003)
	(2000–2002)		70.6–83.3	No change	Lundstedt-Enkel et al. (2006)
	Baltic Proper, Baltic Sea (1994–2001)	White-tailed sea eagle, *Haliaeetus albicilla*	4300 (mean)–13,600 (maximum)	−, + −, +	Nordlöf et al. (2010)
Norway	Munkholmen (2003–2004)	Common eider duck, *Somateria mollissima*	27.4–48.2	+	Herzke et al. (2009)
	Ekne (2003–2004)		13.6–23.2	+	
	Sklinna (2003–2004)		7.2–5.5	−	
	Sklinna (2003–2004)	European shag, *Phalacrocorax aristotelis*	90.1–97.3	−	
	Sklinna (2003–2004)[a]		2–4.6	−	
	Røst and Hornøya (1983–2003)	Herring gulls, *Larus argentatus*	457–759	+, −	Helgason et al. (2009)
	(1983–2003)			+, −	
	(1983–2003)			+, −	
	Røst and Hornøya (1983–2003)	Atlantic puffins, *Fratercula arctica*	144–308	+, −	
	(1983–2003)	Black-legged kittiwakes, *Rissa tridactyla*	90–217	+, −	
	(1983–2003)			+, −	

[a] Liver samples.

In Europe in the early 1990s, several countries considered phasing out or restricting PBDE use due to concerns about these chemicals (Sellström et al., 2003). By the mid-1990s, this issue had passed to the level of the European Union, and in 2003 a European-wide directive had been passed restricting the marketing and use of penta- and octa-BDEs (European Parliament L 42/45, 2003). By July 2008, deca-BDEs were also banned in Europe (European Parliament C 116/2, 2008), and in 2009 tetra- and penta-BDEs were added to the Stockholm Convention on Persistent Organic Pollutants. Despite this, temporal trends from European countries have not been especially consistent, showing a mixture of stable, increasing and even decreasing trends, with five trends showing subsequent decreases since the late-1980s (Sweden), mid-1990s (UK) and late 1990s/early-2000s (Norway). Two trends for white tailed sea eagles from the Baltic Sea, Sweden, show increases in ΣPBDE since the late-1990s (Table 4). These inconsistencies could be due to e.g., species differences in life history, diet, and local marine food chains. One anomaly appears to be great skua from the Shetland Islands, UK (Leat et al., 2011). Here, no temporal trend was observed; however, eggs of this species were sampled in only two years – 1980 and 2008 – thus trends in the intervening three decades have been missed. The maximum ΣPBDE concentration seen from the European region was in great skuas, *Stercorarius skua*, sampled from the Shetland Islands (22,128.6 ng/g lw) (Leat et al., 2011). Nonetheless, the overall picture from Europe and North America generally show decreasing trends when time series for ΣPBDE have been evaluated post-2000.

When comparing the most recent year of sampling in BC seabirds only (2010–2012), ΣPBDE concentrations were considerably higher in double-crested cormorants and great blue heron eggs, both of which are coastal species, compared to rhinoceros auklets and Leach's storm-petrel eggs, which are offshore species (Miller et al., 2014). Mean ΣPBDE in heron eggs (71.6 ng/g ww) was more than ten times higher than the lowest mean ΣPBDE (5.9 ng/g ww) seen from Leach's storm-petrel eggs at Hippa Island (Fig. 4). By contrast, HBCDD concentrations were highest in the offshore bird eggs compared to the coastal species (Fig. 4). HBCDD was highest in Leach's storm-petrel eggs (9.5 ng/g ww), where ΣPBDE was lowest. HBCDD concentrations in the coastal seabird eggs were only at trace concentrations (0.5 ng/g ww in cormorant eggs, 1.7 ng/g ww in heron eggs).

PBDE contamination is typically higher in urbanised areas (Yogui and Sericano, 2009), i.e., in coastal-based biota (Gauthier et al., 2007, 2008), due to their proximity to sources, e.g., production factories or municipal waste sites. Sources of PBDEs in North America have predominantly been from flame-retardant polyurethane foam, electronics, automobile padding (Hale et al., 2003), furniture and textiles (Yogui and Sericano, 2009), most of which are commonly found in homes and workplaces (Chen and Hale, 2010). Release of PBDEs into the environment can occur at any point during the life cycle of these products, from synthesis to disposal/recycling (Hale et al., 2003). Historically, the US has led world-wide production of these chemicals (Yogui and Sericano, 2009). Given the North American population size, consumer-driven demand for products containing flame-retardants has been high and the dense collection of PBDE-containing products in highly populated areas would result in a greater release of these chemicals to the surrounding environment (Chen and Hale, 2010), thus driving up concentrations of these chemicals in urban-dwelling species. This idea is further supported by the maximum ΣPBDE concentration observed from a North American seabird, coming from San Francisco Bay (Forster's tern, 63 000 ng/g lw), another densely populated urban area. Differences in concentrations between the BC coastal and offshore birds are most likely due to exposure patterns and sources, largely attributable to location. Thus, local i.e., North American sources rather than long-range transport of PBDEs are likely to have driven penta-BDE concentration in the two coastal species.
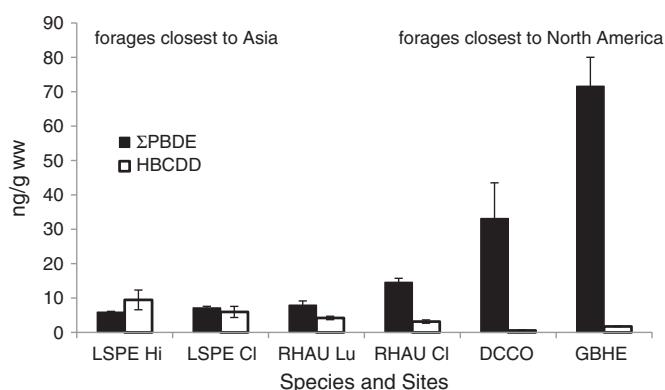
3.6. Conclusion

Here we report temporal increases in PBDEs followed by decreases, in line with the introduction of voluntary and regulatory restrictions on use, sale and import of the tetra-, penta- and hexa-BDE congeners in Canada. Trends here are comparable to those seen elsewhere in North America. Temporal trends in European seabirds generally also exhibit decreases after regulations were introduced there. Dietary change has played little role in observed temporal brominated flame retardant trends in BC cormorants, and points to voluntary and regulatory restrictions as the driver of the decreasing PBDE concentrations observed. A point of concern is that HBCDD concentrations are now being found at low concentrations in both cormorant and heron eggs. This may be an early indicator of an increasing trend in this flame retardant, which is currently unregulated in North America but slated for inclusion under the Stockholm Convention on POPs (2008) under Annex A for elimination, and the Long Range Transboundary Air Pollution Protocol on POPs (Arnot et al., 2009). These results are in line with increasing HBCDD trends seen in offshore BC birds (Miller et al., 2014), and warrants continued monitoring and action to assess risk from HBCDD in the same manner as has been done for PBDEs.

Acknowledgements

Fig. 4. ΣPBDE and HBCDD (ng/g ww) in coastal and offshore seabird species from British Columbia for the most recent years. Species/site are positioned in the order of most remote (LSPE Hi) to most urban breeding colony sampled (GBHE). LSPE Hi — Leach's storm-petrel, Hippa Island, n = 5 pools of 3 eggs; LSPE Cl — Leach's storm-petrel, Cleland Island, n = 6 pools of 3 eggs; RHAU Lu — rhinoceros auklet, Lucy Island, n = 5, 4 pools of 3 eggs, 1 pool of 2 eggs; RHAU Cl — rhinoceros auklet, Cleland Island, n = 5 pools of 3 eggs; DCCO — double crested cormorant, n = 5 pools of 3 eggs; GHBE — great blue heron, n = 5 individual eggs.

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