Assessment of concentrations and effects of organohalogen

American environment occurred primarily over the past 30 years (Chen and Hale, 2010; de Wit, 2002; Law et al., 2003). In Canada, regulations prohibit the manufacture of all PBDEs and restrict the use of penta-BDE and octa-BDE mixtures (Canada Gazette, 2008). However, PBDEs persist in the environment and will continue to leach from existing products that are in use or have been disposed of in land lls, and deca-BDE is still in use in Canada. Legacy persistent organic pollutants that have been heavily restricted in North America since the 1970s, such as polychlorinated biphe nyl ethers (PCBs), dichlorodiphenyltrichloroethane (p,p -DDT) and its metabolite 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (p,p -DDE), and other organochlorine (OC) pesticides, are also commonly detected in the environment. The presence of PBDEs, PCBs and OCs in the environment is a concern, as they are known to cause a wide range of toxicological effects in birds (Blus, 2011; Chen and Hale, 2010; Elliott and Bishop, 2011; Harris and Elliott, 2011). Penta- and octa-BDEs, PCBs, DDT and other OCs are all further regulated internationally under the Stockholm Convention on

2.4. Plasma analysis

Total and free thyroxine (T4 and FT4) and total and free triiodothyronine (T3 and FT3) levels in plasma samples were determined using

were used for BDE-207, -208 and -209. Ions of m/z 485 and 487 were used to monitor BDE-197, -201 and -202. Ions of m/z 495 and 497 were used for the internal standard of $^{13}C_{12}$-labeled BDE-209.

OCs and PCBs in the isolated chemical fractions were analyzed using gas chromatography ..mass spectrometry working in electron ionization mode (GC/EI-MS). Analytes were separated and quanti ed on an Agilent 6890 series GC equipped with a 5973 quadrupole MS detector The analytical column was a 30 m × 0.25 mm × 0.25 m DB-5HT fused-silica column (J & W Scienti c, Brockville, ON, Canada). Helium and methane were used as the carrier and reagent gases, respectively. For OCs, a sample volume of 1 l was introduced to the injector operating in pulsed-splitless mode (injection pulse at 40.0 psi until 1 min; purge ow to split vent of 23.5 ml/min), with the injector held at 250 °C. The GC oven ramping temperature program was as follows: initial 100 °C for 3.0 min, 20 °C/min until 180 °C, and 5 °C/min until 300 °C. The GC to MS transfer line was held at 280 °C, ion source temperature was 230 °C, and the quadrupole temperature was 150 °C. For PCBs, a sample volume of 1 l was introduced to the injector operating in splitless mode (purge ow to split vent of 53.7 ml/min to 1.5 min), with the injector held at 250 °C. The GC oven ramping temperature program was as follows: initial 100 °C for 3.0 min, 20 °C/min until 180 °C, and 2.5 °C/min until 300 °C. The GC to MS transfer line was held at 280 °C, ion source temperature was 230 °C, and the quadrupole temperature was 150 °C.

The analytes were identi ed on the basis of their retention times on the DB-5HT column, and veri ed by matching retention times with those of authentic standard mixtures. Mean internal standard recoveries were 78% ± 11% for BDE-30 and -156, 54 ± 22% for BDE-209, 94% ± 11% for OCs, and 97% ± 25% for PCBs. Analytes were quanti ed using an internal standard approach, thus all reported values were inherently recovery-corrected.

The limits of detection (LODs) for PBDE, OC and PCB analysis, based on a signal-to-noise ratio of 3, were 0.2, 0.1 and 0.06 ng/g wet weight (ww), respectively, with the exception of a LOD of 0.6 ng/g ww for dieldrin. Method blanks were included for each sample batch to assess background interference and possible contamination, and a blank subtraction was done for BDE-2, 7, 10, 15, 17, 28, 47, 49, 54, 66, 71, 77, 99, 100, 153, 154, 155, 183, 195, 196, 197, 203, 206 and 209, as well as for CB-66, 99, 101/90, 118, 138, 153, 170/190, 180 and 187, and a blank subtraction was done for hexachlorobenzene and p,p -DDE. In-house standard reference material (double-crested cormorant [Phalacrocorax auritus] egg and Lake Michigan sh tissue) was also included in each

present starling study, the lack of a strong correlation between p,p -DDE and PBDEs or PCBs, and the positive correlation between PBDEs and PCBs, may also be linked to differences in the historical spatial patterns

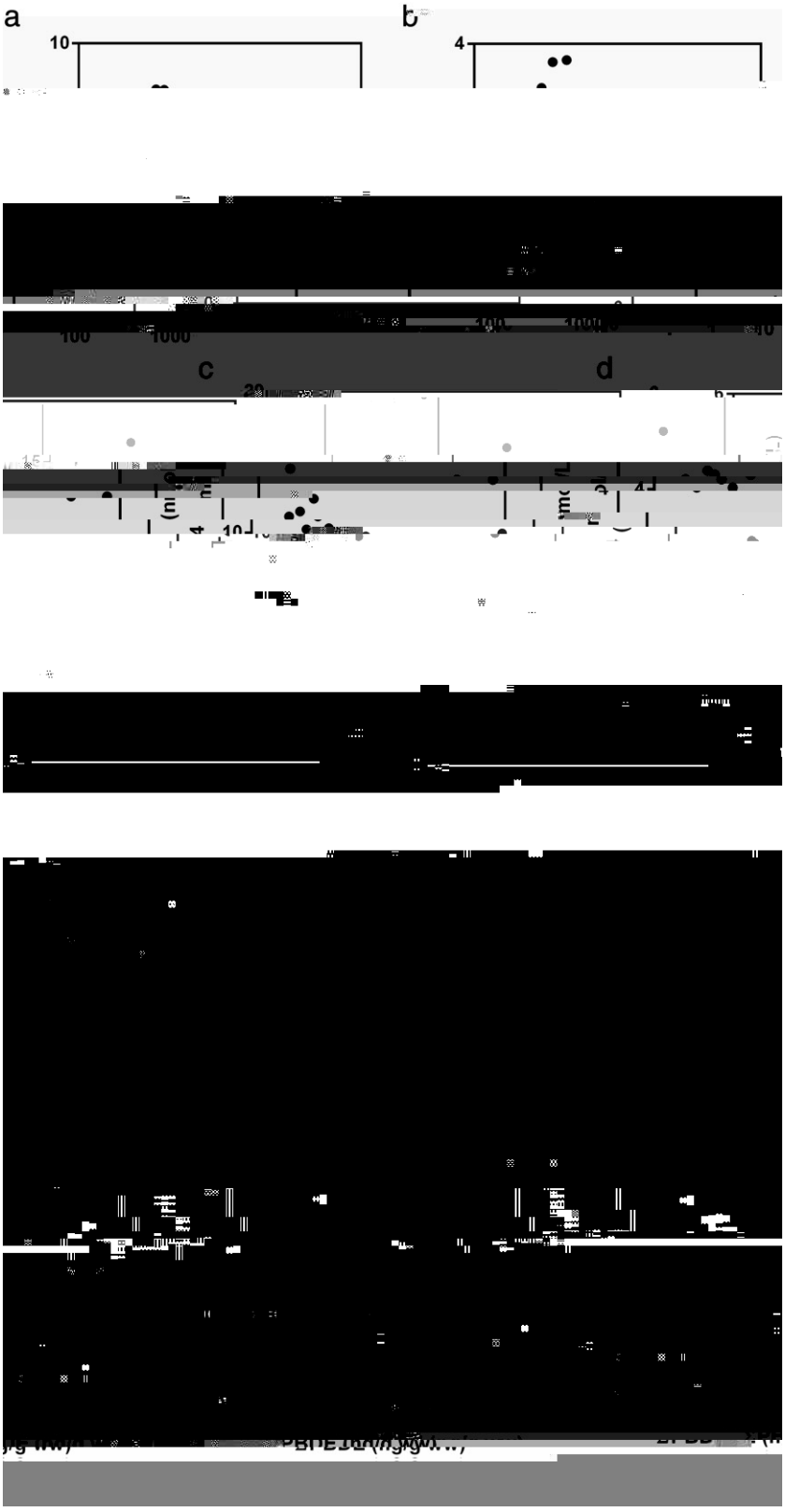

Fig. 1. Relationship between PBDEs in European starling eggs and (a) BCI of day 15 nestlings, (b) BCI of adult females, (c) plasma T4 at day 15, (d) plasma T4 of adult females, (e) OSI at day

Stable isotope studies have shown that both trophic level (Elliott et al., 2010; Sun et al., 2012) and habitat type (Elliott et al., 2009; Newsome et al., 2010) can in uence PBDE accumulation. Starlings primarily feed on soil invertebrates and are a mid-trophic level species in terrestrial food chains. Concentrations of PBDEs in our starling eggs (AM = 46.9 ng/g ww, 3.6% lipid) fell within the range of values reported for top predators in British Columbia. Arithmetic mean PBDEs were from 1.78 to 8.49 ng/g ww in bald eagle nestling (Haliaeetus leucocephalus) plasma (~1% lipid) on the west coast (McKinney et al., 2006), 47.9 ng/g ww in great blue heron (Ardea herodias) eggs (avg.

6.15% lipid) on Vancouver Island, 62.5 ng/g ww in double-crested cormorant (P. auritus) eggs (avg. 6.58% lipid) on the west coast, 185 ng/g ww in osprey (Pandion haliaetus) eggs (avg. 4.67% lipid) from southern

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