Chemosphere 238 (2020) 124577

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Bioaccumulation and biomagnification of PBDEs in a terrestrial food chain at an urban landfill

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HIGHLIGHTS

- BDE concentrations were higher in starling eggs and chicks from an urban landfill than a rural farm.
- Human refuse and soil invertebrates were dominant dietary sources of BDE exposure to starlings at the landfill.
- BSAFs for BDE-47, -99, −100, and −154 were >1 indicating bioaccumulation in earthworms and refuse at the landfill.
- BMFs for BDE-47, -99, −100, −153, and −154 were >1 indicating biomagnification in starlings from their diet.

ARTICLE INFO

Article history:
Received 26 April 2019
Received in revised form
8 August 2019
Accepted 10 August 2019
Available online 16 August 2019

Handling Editor: Myrto Petreas

Keywords:
PBDEs
Terrestrial food-chain
Bioaccumulation
Biomagnification
Stable isotopes
European starling

ABSTRACT

Biota samples from the Vancouver municipal landfill located in Delta, BC, Canada, have some of the highest polybrominated diphenyl ether (PBDE) levels reported from North America. We followed a population of European starlings (*Sturnus vulgaris*) breeding in a remediated area in the landfill to identify exposure routes and bioaccumulation of PBDEs in a simple terrestrial food chain. This population was compared to a reference farm site located 40 km east in Glen Valley. We analyzed samples of European starling eggs and nestling livers as well as invertebrate prey species consumed by starlings for PBDE concentrations. We also collected soil samples from starling foraging areas. All samples from the Delta landfill had higher PBDE congener concentrations compared to the Glen Valley reference site and were dominated by BDE-99 and BDE-47. Stable nitrogen (δN^{15}) and carbon (δC^{13}) isotope analysis of starling blood samples and provisioned invertebrates revealed that stable $\delta\zeta^{3}$ signatures differed between the sites indicating that the diet of starlings in the Delta landfill included a component of human refuse. Biota-soil accumulation factors (BSAFs) > 1 demonstrated that PBDEs were bioaccumulating in soil invertebrates, particularly earthworms, which were readily accessible to foraging starlings in the landfill. Biomagnification factors (BMFs) calculated from foraged food items and starling egg and liver samples were >1, indicating that a diet of soil invertebrates and refuse contributed substantially to the PBDE exposure of local starlings.

1. Introduction

Previous studies have shown that landfills are a source of elevated polybrominated diphenyl ethers (PBDEs) to biota that frequent such sites such as European starlings (*Sturnus vulgaris*) (Chen and Hale, 2010; Chen et al., 2013; Eens et al., 2013). The potential for these compounds to bioaccumulate in biota and biomagnify in food chains is a key feature defining their behaviour in the environment and in classifying them for regulatory purposes (Weisbrod et al., 2009). However, the detailed sources and pathways of PBDE uptake and transfer to biota that use landfills, including wild birds, have not been examined. In terrestrial ecosystems, soil is frequently the primary reservoir of contaminants, which is transferred through biotic compartments (plants and

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https://doi.org/10.1016/j.chemosphere.2019.124577
0045-6535/

animals) within a given food-chain starting with the first transfer from PBDE treated products to soil, from soil to soil invertebrates and plants, and so on up the food-chain (van den Brink et al., 2013). Bioaccumulation and biomagnification potential of PBDEs can be determined by measuring PBDE levels throughout a given food-chain. In this study, we examine a relatively simple food-chain that involves the transfer of PBDEs from soil to soil invertebrates and on to European starlings. Knowledge of the contaminant levels at each of these trophic levels was established through the collection of food items brought back to starling nests, as well as with identification of favoured foraging areas used by the starlings through radio telemetry (Currier, 2014). The Vancouver municipal landfill, located in Delta, British Columbia (BC), has elevated levels of PBDEs and other persistent contaminants (Chen et al., 2013). It is known that the resident starling population at this landfill incorporates a considerable amount of refuse in their diet (Currier, 2014).

Integration of stable isotopes into bioaccumulation studies can aid in deciphering food-chain dynamics by identifying potential routes of movement of contaminants (Kelly, 2000). Nitrogen isotopes can be used to identify an animal's relative position within its food-chain, thereby herbivores generally have lower $\delta^{15}N$ values than carnivores (Kelly, 2000). Carbon isotopes indicate how a food-web is related to its primary producers and whether they utilize the C4 (higher $\delta^{13}C$ values) or C3 (lower $\delta^{13}C$ values) photosynthetic pathways (Weiser and Powell, 2011; Kelly, 2000). Stable isotope signatures have helped identify persistent contaminant pathways in terrestrial systems with urban peregrine falcons (*Falco peregrinus*) (Newsome et al., 2010; Park et al., 2011), common kestrels (*Falco tinnunculus*) (Yu et al., 2011) and Cooper's hawks (*Accipiter Cooperi*) (Elliott et al., 2015). Our reference starling population is situated in a rural environment, therefore, will likely have different stable isotope signatures compared to the landfill starlings, which have greater access to anthropogenic food sources (Currier, 2014).

In this study, we examined the foraging locations and diet of European starlings residing in a large urban landfill and compared them to a rural population. We set out primarily to examine the extent to which consumption of soil invertebrates and/or human refuse contribute to persistent contaminant exposure of PBDEs in the starling food-chain. Our objectives were to 1) measure the levels of PBDEs in the soil, starlings, and their diet to determine if PBDEs are biomagnified; and 2) identify routes of exposure. For reference, we compared European starlings in Delta to a reference population located 40 km east in the Fraser Valley in an agricultural area called Glen Valley. We measured stable isotopic signatures in blood samples from European starling adults and chicks and in foraged food items from both study sites to establish if there are differences in the diet of European starlings in landfills versus rural areas.

2. Methods

2.1. Study site and species

We carried out observations and sample collections between April and July 2012 at the Vancouver Municipal Landfill (Delta Landfill) in Delta (49° 5′ 58.1964″ N, 123° 0′ 10.5480″ W) and at the Glen Valley Farm in Fort Langley (49° 9′ 13.62224″ N, 122°28' 4.4544" W), British Columbia, Canada (see Chen et al., 2013 for site details). Handling and collections of European starlings were conducted under a Simon Fraser University Animal Care permit (829B-96) following guidelines of the Canadian Council on Animal Care. We checked starling nest boxes on a daily basis to determine clutch initiation and clutch completion dates. European starlings lay an average of six eggs per clutch within a synchronous period covering 7–8 days, incubate for 10.3 ± 0.1 days, and fledge nestlings 21 ± 0.6 days following hatch (Love et al., 2005; Cabe, 1993). We used these time periods as a guideline for monitoring the breeding progress of European starlings in Delta and Glen Valley.

On day 8 of incubation between 03:30–05:00 h, we captured 20 adult females from their respective nest boxes in the Glen Valley ($n = 10$) and Delta ($n = 10$) study sites and marked them with aluminum and colour bands for later identification. During capture, we collected blood samples for stable isotope analysis and fitted each female with radio transmitters in order to locate their preferred foraging areas. Transmitters were produced by Holohil Systems Ltd. (model PD-2, Holohil ON Canada) and weighed approximately 2.8 g (including harness), which is less than 5% of the total bird mass (average female mass [range] Delta: 87.23 g [80.78–96.08 g], Glen Valley: 84.28 g [77.36–92.40 g]). We attached transmitters onto the birds via a harness, which consisted of a length of catheter tubing fitted to the transmitter in a "Fig. 8" pattern. We observed the females daily for 30 min during the first 10 days of chick rearing to determine the location of their preferred foraging sites within both study sites. During their foraging trips from the nest boxes, we followed focal females via radio telemetry (to identify specific breeding birds) and visual observation to their preferred foraging areas. We then selected six areas with the highest number of foraging visits from each study site for soil sampling. At the Delta Landfill the six areas included: two locations adjacent to the open dumping area called the active face; the compost area where residential yard and tree trimmings were collected from Metro Vancouver; a field adjacent to the compost area; and two locations in the remediated area which had been capped with clean soil and allowed to overgrow with vegetation. The remediated area is also where nest boxes were established at the Delta landfill. At Glen Valley, the six areas selected were situated in a hobby farm and included five different livestock fields used for grazing by sheep and horses, and one construction site adjacent to the farm where recent excavation had occurred.

2.2. Soil and soil invertebrate collection

We collected a total of 12 soil samples, one from each of the preferred foraging locations in Delta ($n = 6$) and Glen Valley ($n = 6$). We used soil core samples to collect and identify soil invertebrates and to calculate biota-soil accumulation factors. We collected soil core samples as per methods described in Tinbergen (1980); each soil core was approximately 10 cm in diameter by 5 cm depth and represented the depth that starlings could actively forage.

Invertebrates were removed from soil samples and rinsed with distilled water to remove excess soil. Earthworms were cut open and rinsed with distilled water to remove soil from the gut as soil can influence the stable isotope analysis of the organic sample (Harris et al., 2000). We identified all soil invertebrates to family, placed them in glass jars, and stored at −20 °C until they could be analyzed for contaminants or dried and prepared for stable isotope analysis. Invertebrates of the same species from the same soil sample were pooled for PBDE analysis. A sub-sample of each homogenized soil core was collected (approximately 5 g) and stored at −20 °C until it could be analyzed for PBDEs.

2.3. European Starling egg, chick, and provisioned invertebrate collection

We collected one European starling egg from 8 nest boxes in Delta and 9 nest boxes in Glen Valley. Eggs were used to represent a maternal transfer of contaminants from the adult female to the eggs and are frequently used as a matrix for environmental contaminants monitoring (Miller et al., 2014; Henry and Elliott, 2007;

Elliott and Martin, 1994). In the laboratory, we separated the egg contents from the shell and stored samples in glass jars at −20 °C until they could be shipped on dry ice for chemical analysis.

When the mean age of the nestlings was 8–10 days-post-hatch, we examined the occurrence of provisioned prey items in the chicks' diet by using a collaring method at each nest box (Wright et al., 1998). After a 30 min observation period, we fitted all chicks within a subsample of nest boxes at each study site with collars made from pipe cleaners that were tight enough to prevent the chicks from ingesting any prey items brought back by the parent. We watched the nest boxes for an additional 30 min and retrieved the prey items from the nestlings after each visit from a parent. All collected invertebrate prey items were cleaned of soil debris, identified to family, and stored in glass jars. Earthworms were prepared as described in the previous section. To determine the percent composition of each invertebrate family in the diet, we compared the count data of each family to the combined total count of all invertebrates collected at each study site. We pooled invertebrates of the same family that were returned to the nest during the same provisioning trip to ensure that each sample had enough biomass for contaminant analysis. In Delta, samples retrieved from nestlings consisted of a number of anthropogenic "refuse" items which had been foraged from the landfill site. Most of these items appeared to be processed meat of beef or chicken origin. We stored all provisioned diet samples in glass jars at −20 °C until preparation for chemical analysis or stable isotope analysis.

When the nestlings reached the age of 17-days-post-hatch, we randomly selected seven chicks from different nest boxes at each study site and anaesthetized them with 15 μL of rompun:ketamine (1:1). Once the chicks were anaesthetized, we euthanized them by exsanguination via the jugular and collected the blood for stable isotope analysis. In the laboratory, we dissected the livers from the chicks, placed the liver samples in glass jars, and stored them at −20 °C until chemical analysis.

2.4. Sample preparation for stable isotopes analysis

We collected blood samples from 20 adult female European starlings and from 19 chicks when they were 17-days post-hatch to analyse for stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes. As dietary-derived $\delta^{13}C$ has a half-life of 29.8 days in red blood cells of the American crow (*Corvus brachyrhynchos*) (Hobson and Clark, 1993), we assumed a similar half-life for starlings. Consequently, the blood samples we collected should reflect the diet available during both the egg-laying and chick rearing stages. Whole blood samples were centrifuged to separate red blood cells from plasma. We also selected a subsample of invertebrates collected from the soil samples and from the nest boxes for stable isotope analysis. We dried the blood and invertebrate samples at 60 °C for 24 h, ground each sample into a fine powder with a mortar and pestle, then encapsulated approximately 1 mg of each sample into tin capsules. Samples were analyzed by the University of California Davis Stable Isotope Facility for $\delta^{13}C$ and $\delta^{15}N$ concentrations using standard methods as described by Elliott et al. (2009). Analyses were performed with a continuous flow system using a PDZ Europa ANCA-GSL elemental analyzer and a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). The final values of the samples were expressed in delta notation, parts-per-thousand (‰). Long-term facility measurement precision is 0.2‰ for $\delta^{13}C$ and 0.3‰ for $\delta^{15}N$. Commercially produced foods typically contain higher $\delta^{13}C$ values than natural ecosystems, due to the incorporation of corn or corn syrup (Suits et al., 2005, Jahren and Rebecca Kraft, 2008). It has also become a common practice to rear commercial meat (i.e. cattle, pork, and poultry) on a corn-based diet (Schmidt et al., 2005; Schwertl et al., 2005); therefore, stable isotope values for chicken and beef previously reported by Jahren and Kraft (2008) were used to represent anthropogenic food sources that could be incorporated into the starling diet through consumption of meat refuse.

2.5. Sample preparation for contaminant analysis

All soil and biological samples were analyzed for 25 PBDE congeners including BDE 3, 7, 15, 17, 28, 47, 49, 66, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, 184, 191, 196, 206, 207, and 209 at the Great Lakes Institute for Environmental Research (GLIER), Windsor, Ontario. However, European starling blood samples were not analyzed for PBDE contaminants as there was insufficient biomass left after completion of other required assays (e.g. plasma metabolites and stable isotopes).

Chemical extraction and clean-up followed the procedures of Lazar et al. (1992) for biological samples and Drouillard et al. (2006) for soil samples (further details in Supplementary Information). PBDE quantitation methods are described in further detail in Guertin et al. (2010). Approximately 2.0–5.0 g of biological homogenate was ground with anhydrous sodium sulphate (Na_2SO_4), spiked with a recovery internal standard of either 50 μL of PCB-34 or 100 μL of BDE-71, extracted with a 50% dichloromethane:hexane (DCM:HEX; 1:1 by volume) solvent mixture, rotary-evaporated (Bühi Rotavapor RE 111) to approximately 5 mL, and then mixed with 25 mL of hexane. Approximately 2 mL of this sample extract was removed for lipid content determination; the remaining 23 mL of extract was rotary-evaporated to 2 mL and subjected to GPC and/or Florisil® cleanup and separation. During Florisil® cleanup, the remaining sample extract was transferred to a glass column, plugged with glass wool, filled with hexane and 6 g of activated Florisil® absorbent (60–100 mesh), and then topped with 50 g of sodium sulphate as a moisture trap. As the sample extract passed through the column to the top, the column was rinsed with 50 mL of hexane, followed by 50 mL of 15% DCM:HEX, and eluted to a flat bottom flask. Afterwards, 150 mL of 60% DCM:HEX was added to the column and the remaining extract was eluted. Finally, approximately 5 mL of iso-octane was added to each flask and concentrated to roughly 1 mL by rotary evaporation.

Quantitation of PBDEs was performed as described in Guertin et al. (2010) using a Hewlett-Packard HP 6890 gas chromatograph (GC) coupled with a Waters GCT-premier Time of Flight (TOF) high-resolution mass spectrometer. For the TOF analysis, a 30 m Rtx-1614 fused silica column (0.25 mm ID, 0.10 μm film thickness; Restek Corporation) and 15 m Rtx-1614 (0.25 mm ID, 0.10 μm film thickness; Restek Corporation) were each injected with 1 μL of sample using splitless injection mode and held at 260 °C. In the 30 m Rtx-1614 column, initial oven temperature was held at 100 °C for 1 min, then increased to 180 °C at 20 °C/min, and finally to 325 °C at 5.0 °C/min and held for 10 min. In the 15 m Rtx-1614 column, initial oven temperature was held at 100 °C for 1 min then increased to 320 °C at 13 °C/min and held for 3 min. The shorter Rtx-1614 column is used for analyzing highly brominated PBDEs.

2.6. Quality control and assurance

Method blanks were processed to monitor interferences and contamination (further details in Supplementary Information). For biological samples, the analytical accuracy and precision were evaluated by running an aliquot of an Environment and Climate Change Canada supplied reference material (DCCO-RM, pool homogenates of Great Lakes double crested cormorant (*Phalacrocorax auratus*) eggs) and an in-house reference material (GLCARP; pool homogenates of Detroit River, Ontario, CAN common carp (*Cyprinus carpio*) muscle and liver), as well as duplicates of randomly selected

starling liver and egg samples. PBDE concentrations in the DCCO and GLCARP homogenate ranged from 0.48 to 37.9 ng/g wet weight and 0.45–31.8 ng/g wet weight, respectively. For soil, NIST SRM 1944 New York/New Jersey Waterway Sediment was utilized as a certified reference material. The mean % recoveries in analyzed NIST 1944 SRMs ranged between 69.7 and 106.3%, except for BDE 209, which had a lower recovery of 43.5% (BDE 209 was not detected in the present set of samples). Method detection limits ranged from 0.015 to 1.685 ng/g for PBDEs as generated by method validation studies (note detection limits >1 ng/g were only for highly brominated BDE's 207, 206 and 209 owing to degradation on the column during analysis). The mean ± standard deviation sample recoveries for surrogate spiking standards of PCB 34 and BDE 71 were 92.1 ± 4.3% and 91.5 ± 9.3%, respectively.

2.7. Lipid equivalent concentrations

We measured lipid content of all biological samples using a gravimetric method. Wet weight concentrations for all biological samples were lipid normalized and expressed as lipid equivalent concentrations ($C_{lipid\ eq.}$; ng/g of lipid equivalent) to remove the effect of differences in lipid contents or other sorbing matrices between organisms (further details in Supplementary Information). However, as some organisms, such as earthworms and tipulids, had very low lipid contents but high organic carbon contents, we also included non-lipid organic matter as an important matrix for chemical accumulation (further details in Supplementary Information; Mackintosh et al., 2004; Kelly et al., 2007). For the soil samples, we expressed the dry weight concentrations as lipid-organic carbon equivalent fractions ($C_{lipid\text{-}OC\ eq.}$; ng/g of lipid-OC equivalent; further details in Supplementary Information).

2.8. Statistical analysis

2.8.1. Stable isotopes

To compare the average stable nitrogen and carbon isotopes between species and to identify differences between the study sites, we used a two-way ANOVA (Type III for unbalanced data) with a Tukey's Honestly Significant Difference (HSD) test in the R program (R Core Team, 2017). Statistical significance of p-values for mean estimates were assessed at $\alpha = 0.05$.

2.8.2. Contaminant concentrations with non-detect data

For all statistical analyses involving contaminant concentrations, we used the Nondetects and Data Analysis for Environmental Data (NADA) package (Lee, 2017) in the R program (R Core Team, 2017) as recommended for left censored data (Helsel, 2012). We calculated the mean concentration, standard deviation, and standard error of each BDE congener within each species per study site using a Kaplan-Meier (KM) statistical model in the NADA package (cenfit). Since we had small sample sizes for each species per study site, we used the non-parametric Peto-Prentice score test (cendiff) to compare differences in BDE congener concentrations in soils and tissue samples between study sites. As the test statistic for the Peto-Prentice test provides a two-sided p-value, we divided the reported value in half to get a one-sided p-value. Statistical significance of p-values for concentration differences were assessed at $\alpha = 0.05$.

We calculated biota-soil accumulation factors (BSAFs) and biomagnification factors (BMFs) for BDE congeners that were detected in at least 50% of samples in a given study site. To calculate BSAFs for provisioned prey items and invertebrates, we divided the mean lipid-organic carbon equivalent concentration in the soil samples by the mean lipid-equivalent concentration in each type of prey item. To calculate BMFs for European starling eggs and chicks, we divided the lipid-equivalent concentration in the eggs or chicks by that in its diet. For the lipid-equivalent concentration in the diet, we calculated a proportional average of all prey items in the diet (Franklin, 2015) based on their respective occurrences in the collared European starling chicks. We assumed that eggs and chicks had comparable proportions and compositions of prey items in the diet as adult European starlings are known to primarily feed on invertebrate species (particularly *Tipula* spp.) rather than plant matter (e.g. fruits or berries) during the breeding season (Cabe, 1993; Fischl and Caccamise, 1987; Tinbergen, 1980; Chen et al., 2013); thus, we used the same weighted average of the diet in the BMF calculations for eggs and chicks.

3. Results

3.1. European Starling diet composition and stable isotope analysis

Chick collaring revealed quantitative and qualitative differences in preferred provisioned food items between Delta and Glen Valley European starlings. In Delta, Coleoptera made up the majority of the chick diet, followed by meat refuse (consisting of processed meat products that appeared to be composed of chicken and beef), Tipulids, Lepidoptera, Lumbricidae (earthworms), and other, which included unidentifiable pieces of invertebrates (Fig. 1). In Glen Valley, the chick diet was comprised mainly of Tipulids, followed by Lepidoptera, earthworms, Coleoptera, and other (Fig. 1). Average stable $\delta^{15}N$ and $\delta^{13}C$ signatures did not differ between study sites for most of the invertebrate species (Fig. 2; SI Table 1). At the Delta site, starling chicks had lower average $\delta^{15}N$ signatures than chicks ($t = -3.64$; $p = 0.0268$) and adult females ($t = -3.87$; $p = 0.0138$) from Glen Valley (Fig. 2; SI Table 1). Average $\delta^{13}C$ signatures of European starling chicks and adult females did not differ between study sites (Fig. 2; SI Table 1). We did not analyse stable $\delta^{15}N$ and $\delta^{13}C$ signatures in the meat refuse samples but assumed they would be comparable to $\delta^{15}N$ and $\delta^{13}C$ signatures of chicken and beef taken from Jahren and Kraft (2008). Chicken had a noticeably lower $\delta^{15}N$ signature but higher $\delta^{13}C$ signature compared to starlings from both study sites as indicated by the overlapping 95% confidence limits (Fig. 2). Beef also had a higher $\delta^{13}C$ signature compared to the starlings from both study sites, but there were no differences in $\delta^{15}N$ signatures between beef and starlings from Delta or between beef and starling chicks from Glen Valley as indicated by the overlapping 95% confidence limits (Fig. 2).

3.2. Soil and invertebrate PBDE profiles and biota-soil accumulation factors

A total of 14 BDE congeners were detected within soil samples collected from the two study sites; however, only three of those congeners (BDE-47, -99, and −100) were detected in soil samples from Glen Valley (SI Table 2). At both study sites, BDE-47 and -99 were the most frequently detected congeners and had the highest mean concentrations at 17.5 (2.94 SE) ng/g lipid-OC eq. and 23.3 (4.41 SE) ng/g lipid-OC eq., respectively at the Delta landfill and 8.76 ng/g lipid-OC eq. and 2.40 (2.33 SE) ng/g lipid-OC eq., respectively at the Glen Valley farm (SI Table 2). Mean concentrations of BDE-47 and -99 were roughly 2–12 times higher in Delta soil samples than in Glen Valley soil samples (SI Table 2). Overall, soil samples in Delta had statistically higher mean concentrations of BDE-47, -99, and −100 than soil samples in Glen Valley (SI Table 2; $p < 0.005$). Additionally, compost soil from Delta contained some of the highest concentrations of highly brominated congeners, such as BDE-207, compared to the other soil samples collected in the Delta Landfill (Fig. 3). Whereas, the remediated soil samples had fewer PBDE congeners detected in them and generally

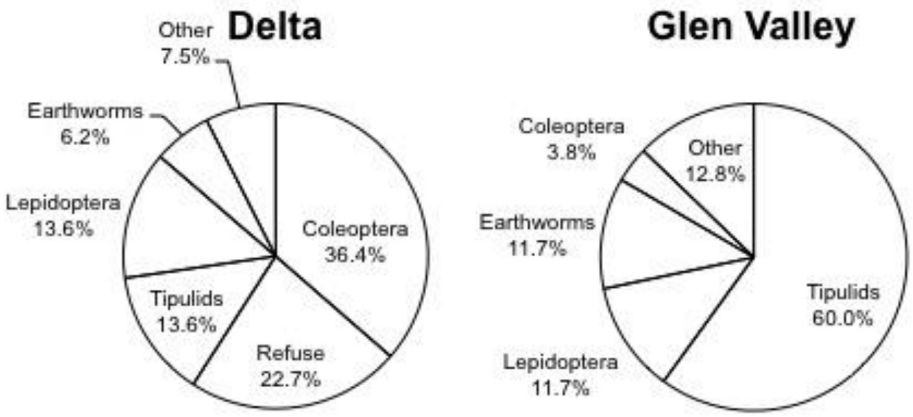

Fig. 1. Percent composition of prey items collected from European starling chicks during parental foraging visits collected from two sites in the Lower Mainland Region of British Columbia, Canada, 2012. All collection events were combined for each site to calculate the percentages of each prey category.

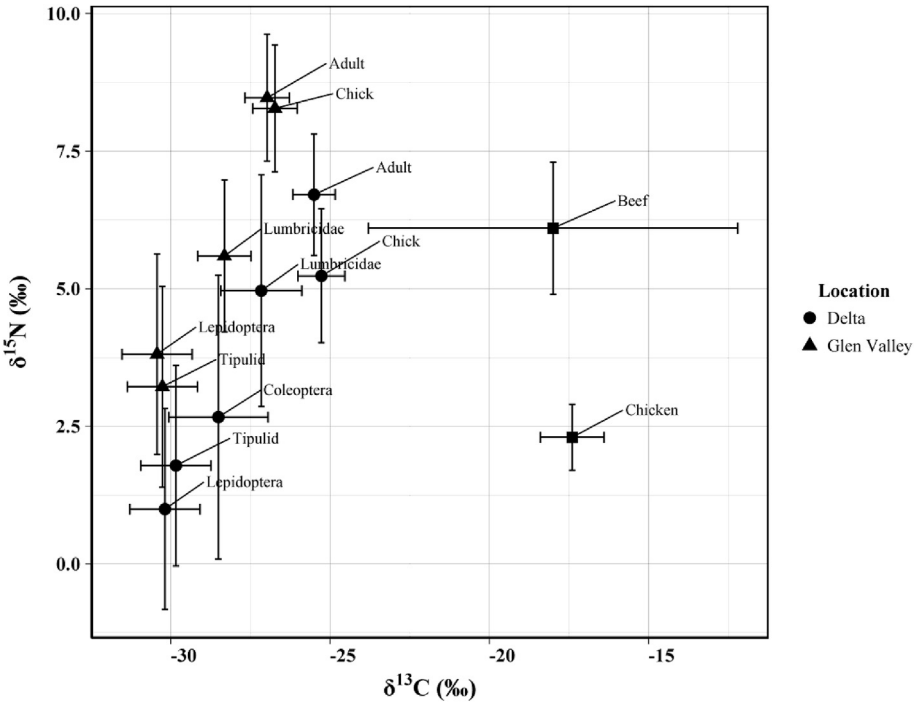

Fig. 2. Average stable $\delta^{15}N$ and $\delta^{13}C$ isotope signatures of European starling chicks, European starling adult females, and provisioned food items collected from Delta and Glen Valley study areas, 2012. Beef and chicken stable isotope values were taken from Jahren and Kraft (2008). Error bars represent ±95% confidence limits. Lumbricidae represent earthworms.

had lower congener concentrations than the active face soil samples (Fig. 3).

A total of 7 BDE congeners were detected within provisioned food items and invertebrates collected from soil samples with BDE-47, -99, and −100 as the most frequently detected congeners (SI Table 3). Meat refuse and earthworms collected from soil samples in Delta had the highest number of BDE congeners detected in them as well as the highest mean concentrations across all food items (SI Table 3). However, earthworms from soil samples in Delta had mean concentrations for BDE-47, -85, −99, and −100 roughly twofold higher at 83.1 ng/g lipid eq., 40.8 ng/g lipid eq., 59.6 ng/g lipid eq., 12.8 ng/g lipid eq., respectively, compared to meat refuse at 31.2 (14.4 SE) ng/g lipid eq., 1.28 ng/g lipid eq., 52.8 (26.4 SE) ng/g lipid eq., and 6.26 (4.91 SE) ng/g lipid eq., respectively (SI Table 3). Most food items in Glen Valley did not have any BDE congeners detected in them with the exception of one sample of Lepidoptera, which had a BDE-47 concentration of 1.04 ng/g lipid eq. (SI Table 3).

BSAFs were calculated for BDE congeners that had sufficient detection data in food items and soil samples from each study site, which included BDE-47, -85, −99, −100, −153, and −154 (Table 1). In Delta, earthworms and meat refuse had BSAFs >1 for BDE-47, -85, −99, and −100 while Coleopterans had BSAFs <1 for BDE-47 and -99 (Table 1). Earthworms from soil samples had the highest BSAFs compared to the other provisioned prey items in Delta. BSAFs for BDE-153 and -154 could only be calculated for meat refuse and were 0.293 and 1.41, respectively (Table 1). In Glen Valley, Lepidoptera had a BSAF of 0.119 for BDE-47, but BSAFs could not be calculated for the other BDE congeners as they were not detected in any Lepidoptera samples.

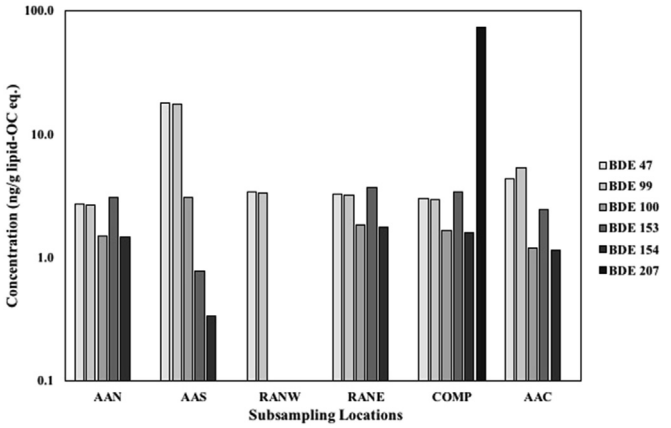

Fig. 3. Concentrations of dominant BDE congeners in soil samples collected from six subsampling locations within the Delta Landfill, British Columbia, 2012. AAN = Adjacent to Active Face North; AAS = Adjacent to Active Face South; RANW = Remediated Area Northwest; RANE = Remediated Area Northeast; COMP = Compost; AAC = Adjacent to Compost.

3.3. European Starling PBDE profiles and biomagnification factors

A total of 18 BDE congeners were detected in European starling eggs from Delta ($n = 12$) while only 5 congeners (BDE-15, -47, −99, −100, and −153) were detected in eggs from Glen Valley ($n = 13$; SI Table 4). BDE concentration profiles in the eggs were dominated by BDE-47, -99, −100, −153, and −154. However, starling eggs from Delta had average concentrations for BDE-47, -99, −100, −153, and −154 more than two orders of magnitude higher at 541.2 (111.1 SE) ng/g lipid eq., 1426.1 (282.7 SE) ng/g lipid eq., 378.6 (78.8 SE) ng/g lipid eq., 306.7 (76.7 SE) ng/g lipid eq., and 106.8 (27.7 SE) ng/g lipid eq., respectively, than in eggs from Glen Valley at 8.84 (0.78 SE) ng/g lipid eq., 14.2 (1.29 SE) ng/g lipid eq., 2.66 (0.26 SE) ng/g lipid eq., 1.20 (0.02 SE) ng/g lipid eq., and <MDL, respectively (SI Table 4). In liver samples from starling chicks, a total of 10 BDE congeners were detected across both sites with concentration profiles dominated by BDE-47, -99, and −100. Similar to the eggs, chick livers from Delta ($n = 7$) had average concentrations for BDE-47, -99, −100 one to two orders of magnitude higher at 52.0 (10.5 SE) ng/g lipid eq., 89.9 (15.5 SE) ng/g lipid eq., and 20.0 (3.41 SE) ng/g lipid eq., respectively, than in chick livers from Glen Valley ($n = 7$) at 1.91 ng/g lipid eq., 1.16 (0.24 SE) ng/g lipid eq., and <MDL, respectively (SI Table 4). Interestingly, the highest BDE concentrations in chick livers from Glen Valley were for BDE-15 and -126 at 3.62 (0.20 SE) ng/g lipid eq. and 2.53 (0.31 SE) ng/g lipid eq., respectively, whereas, chick livers from Delta had no detected concentrations of these lower brominated congeners (SI Table 4). Overall, average BDE concentrations in eggs were considerably higher than in chicks at both sites.

In Delta, European starling eggs and chicks had BMFs >1 for the most frequently detected BDE congeners, which included BDE-47, -85, −99, −100, −153, and −154 (Table 2). European starling eggs in Delta had BMFs that were almost two orders of magnitude higher than the BMFs of European starling chicks (Table 2). BDE-153, -154, and −100 had the highest BMFs in eggs at 1953.9, 579.1, and 485.9, respectively, and in chicks at 78.0, 30.3, and 25.6, respectively (Table 2). In Glen Valley, BMFs could only be determined for BDE-47 in both European starling eggs and chicks as the other predominant BDE congeners were not detected in the pooled dietary items (Table 2). European starling eggs in Glen Valley had a BMF of 72.8 for BDE-47, which was more than fourfold higher than the BMF of European Starling chicks at 15.7 (Table 2).

4. Discussion

We examined the bioaccumulative potential of PBDEs in a terrestrial food chain using European starlings as a biomonitoring tool (Chen et al., 2013; Eens et al., 2013) to better understand the pathways by which PBDEs enter the food-web at a landfill site. Overall, PBDE levels were considerably higher in soil and biological samples from the Delta Landfill than from the rural Glen Valley farm. We also found that European starling eggs and chicks from the Delta Landfill exhibited pronounced biomagnification (i.e. BMFs >1) of 6 PBDE congeners, specifically BDE-47, -85, −99, −100, −153, and −154. Whereas, European starling eggs and chicks from Glen Valley only exhibited biomagnification of BDE-47 as the other predominant BDE congeners were not detected in the diet.

4.1. Stable isotopes

European starling chicks in Delta had lower average $\delta^{15}N$ signatures than the chicks and adult females from Glen Valley; however, average $\delta^{13}C$ signatures of European starling chicks and adult females did not differ between study sites. The lower nitrogen signatures we observed in the European starlings from Delta suggests they were foraging at lower trophic levels than the European

Table 1
Biota-soil accumulation factors (BSAF) calculated for BDEs detected in soil invertebrates or provisioned food items and soil samples from Delta and Glen Valley, British Columbia, Canada, 2012. BSAF values were calculated using mean lipid-normalized concentration values in biota (ng/g lipid eq.) and organic content-normalized contaminant values in soil (g/g lipid-OC eq.). NA/– = Not available/applicable; ND = Non-detect (i.e. all sample concentrations < MDL). BSAFs >1 are in bold.

Delta	Soil		Lumbricidae - Soil			Coleoptera			Meat Refuse		
PBDE	Mean	SE	Mean	SE	BSAF	Mean	SE	BSAF	Mean	SE	BSAF
BDE 47	17.5	2.94	83.1	NA	4.74	12.5	NA	0.712	31.2	14.4	1.78
BDE 85	1.24	0.270	40.8	NA	33.0	ND	–	–	1.28	NA	1.04
BDE 99	23.3	4.41	59.6	NA	2.56	3.97	NA	0.171	52.8	26.4	2.27
BDE 100	5.18	0.701	12.8	NA	2.47	ND	–	–	6.26	4.91	1.21
BDE 153	2.95	1.29	ND	–	–	ND	–	–	0.866	0.352	0.293
BDE 154	1.32	0.475	ND	–	–	ND	–	–	1.86	1.728	1.41

Glen Valley	Soil		Lepidoptera		
PBDE	Mean	SE	Mean	SE	BSAF
BDE 47	8.76	NA	1.04	NA	0.119
BDE 85	ND	–	ND	–	–
BDE 99	2.40	2.33	ND	–	–
BDE 100	1.92	NA	ND	–	–
BDE 153	ND	–	ND	–	–
BDE 154	ND	–	ND	–	–

Table 2
Biomagnification factors calculated for European starling chicks and eggs from Delta and Glen Valley, British Columbia, Canada, 2012. Diet concentration (ng/g lipid eq.) was an average of all of the provisioned food items, weighted according to their respective contributions to the collared chicks. Eggs were assumed to have a similar diet concentration to that of chicks. ND = Non-detect (i.e. all sample concentrations < MDL).

Delta	**Diet**	**Egg**		**Chick**	
n	**10**	**8**		**7**	
PBDE	**Mean**	**Mean**	**BMF**	**Mean**	**BMF**
BDE 47	3.60	541.2	150.3	51.95	14.43
BDE 85	0.74	44.6	60.4	1.98	2.69
BDE 99	4.00	1426.1	356.2	89.86	22.5
BDE 100	0.92	378.6	411.9	19.97	21.7
BDE 153	0.20	306.7	1560.1	12.24	62.3
BDE 154	0.42	106.8	253.0	5.59	13.2
Glen Valley	**Diet**	**Egg**		**Chick**	
n	**10**	**9**		**7**	
PBDE	**Mean**	**Mean**	**BMF**	**Mean**	**BMF**
BDE 47	1.00	8.84	8.84	1.91	1.91
BDE 85	ND	ND	–	ND	–
BDE 99	ND	14.2	–	1.16	–
BDE 100	ND	2.66	–	ND	–
BDE 153	ND	1.20	–	ND	–
BDE 154	ND	ND	–	ND	–

starlings from Glen Valley, but it is more likely that the lower nitrogen signatures are influenced by the consumption of anthropogenic food sources, which are depleted in $\delta^{15}N$ (Caron-Beaudoin et al., 2013). For example, ring-billed gulls (*Larus delawarenis*) foraging primarily in anthropogenic habitats had lower $\delta^{15}N$ levels in blood cells than gulls that foraged from the St. Lawrence River (Caron-Beaudoin et al., 2013). Lower $\delta^{15}N$ signatures have also been observed in colonies of yellow-legged gulls (*Larus michahellis*) that were confirmed to be consuming meat refuse from anthropogenic sources (Ramos et al., 2009). The marginally higher $\delta^{13}C$ signature we observed in the European starlings from Delta suggests that there may be an input of carbon isotopes from a C4 pathway. The $\delta^{13}C$ signatures for beef and chicken we obtained from Jahren and Kraft (2008) indicate that incorporation of these types of meats products into the diet of European starlings may be responsible for the slightly higher $\delta^{13}C$ signature we observed in the European starlings from Delta. However, this argument assumes that the refuse items we observed in the diet of European starlings from Delta were, in fact, of chicken or beef origin. Unfortunately, we could not analyse the refuse items we collected for $\delta^{15}N$ and $\delta^{13}C$ signatures due to limited biomass. Nevertheless, Newsome et al. (2010) observed higher $\delta^{13}C$ signatures in urban Peregrine falcons (*Falco peregrinus*) compared to non-urban falcons and suggested that the urban falcons consumed prey with correspondingly higher $\delta^{13}C$ signatures. Since urban peregrine falcons' primary food items were identified as common urban bird species, such as rock pigeons (*Columba livia*) and European starlings (Newsome et al., 2010), concluded that these prey species were likely foraging on anthropogenic food sources in urban environments.

4.2. Soil, soil invertebrates, and biota-soil accumulation factors

It is estimated that 80% of consumer goods with additive PBDEs eventually end up in landfills (Alcock et al., 2003; Petreas and Oros, 2009) leading to high levels of PBDEs in local biota (Chen et al., 2013). In the Delta Landfill, BDE-47 and -99 were the dominate congeners we detected in all of the soil samples (Fig. 3), which is typical of environmental PBDE profiles documented in many other studies (de Wit, 2002; Söderström et al., 2004; Eens et al., 2013). Generally, BDE-47 is the predominant congener reported in biological samples followed by BDE-99 and -100; however, higher-brominated congeners, such as BDE-209, have become more prevalent in urban-adapted wildlife species, such as peregrine falcons (Newsome et al., 2010; Park et al., 2011) and Cooper's hawks (*Accipiter cooperii*) (Brogan et al., 2017; Elliott et al., 2015). Interestingly, we also detected high concentrations of higher-brominated congeners, such as BDE-153, -154, and −207, within the soil sample and earthworms collected from the compost area in the Delta Landfill indicating a potential source of PBDEs as well as a trophic linkage within the food-chain of European starlings.

As PBDEs are not chemically bound to consumer products, they will gradually escape from treated products over time (Gaylor et al., 2013). Plastics, one of the most common PBDE treated materials discarded into landfills, readily lose structural integrity and disintegrate into microparticles subsequently ingested by soil invertebrates (Gaylor et al., 2013). Soil invertebrates like earthworms are known to move contaminated surface soil to deeper depths, and thus, reduce the concentration of contaminates at the surface (Farenhorst et al., 2000). Thus, differences in soil invertebrate density and composition, weathering, aging, and organic carbon content (van den Brink et al., 2013) can contribute to variation in PBDE concentrations detected in soil samples.

Even though we did not observe obvious PBDE concentration differences between the surface soil samples collected from the sampling locations in the Delta Landfill, there may be PBDE concentration gradients present. For instance, the remediated soil at the landfill is much older than the soil on the active face of the landfill so has likely undergone a longer period of aging and subsequent turn over by soil invertebrate movement. Thus, we expected the remediated soil to have lower PBDE concentrations than the active landfill face soil samples. However, we only saw slightly higher concentrations of BDE-47 and -99 in the surface soil from the active landfill face compared to the remediated soil while all other PBDE congeners had similar concentrations (Fig. 3). These comparable congener concentrations at each foraging location may indicate that much of the soil at the landfill is at steady-state; however, we would need to collect replicate soil samples over a long-term period to confirm this.

Soils with high organic carbon content generally have higher sorptive properties, which greatly limits the accumulation of organic contaminants in soil organisms (van den Brink et al., 2013). Hence, low organic carbon content favours increased soil bioaccumulation. Yet, we surprisingly did not detect any PBDE congeners within invertebrates collected from the remediated or active landfill face soil samples, which contained much lower organic carbon content at 5.6% and 36.6%, respectively, compared to the compost soil (56.4%). However, we likely did not detect PBDEs in earthworms from these areas because the bioavailability of PBDEs within soil is reduced with both aging (Liang et al., 2010) and increasing organic carbon content (van den Brink et al., 2013). In addition, soil properties such as the type of organic carbon content can also greatly affect the availability of PBDEs to be absorbed by soil organisms; for instance, carbonaceous materials, such as black carbon, coal, or kerogen, are 10−100 times more absorptive than amorphous organic matter (Cornelissen et al., 2005). The compost soil and its associated invertebrates likely had higher detected concentrations of highly brominated PBDEs than the other soil types due to high amorphous organic carbon content, the presence of mixed plant matter (Mueller et al., 2006), and higher internal soil temperature (Ribes et al., 2002; Kim et al., 2013). Unfortunately, since we only collected one soil sample from each of the foraging areas at the Delta landfill, we were unable to determine BSAFs for each foraging area. Ideally, we should have collected more soil samples in each area in order to assess bioaccumulation variation across the Delta landfill. Further study should determine where

PBDE concentration gradients are present in soils at or near the Vancouver landfill. The finding that the compost soil sample contained PBDEs with some of the highest concentrations of highly brominated congeners merits further sampling at the landfill, as well as from compost soil at other municipal locations.

4.3. Provisioned food items, European Starlings, and biomagnification factors

We assumed that European starling chicks and eggs had comparable diet compositions and proportions as adult starlings mostly consume invertebrates during the breeding season (Cabe, 1993; Fischl and Caccamise, 1987; Tinbergen, 1980; Chen et al., 2013). However, it is apparent that urban starlings at the Delta landfill are highly opportunistic foragers (Park et al., 2009; Mennechez and Clergeau, 2006) that incorporated a substantial proportion of human refuse (23%) into their diet given the close proximity of the active landfill face. Much of this refuse resembled processed meat products and had some of the highest concentrations of PBDEs observed across the provisioned food items. Consequently, starling chicks and eggs at the Delta landfill also had significantly higher PBDE concentrations compared to chicks and eggs from Glen Valley.

As a high percentage of the starling diet at the Delta landfill consisted of refuse, it likely represented a dominant exposure route contributing to the elevated PBDE levels detected in the eggs and chicks. However, soil invertebrates, specifically earthworms, often contained higher PBDE levels than the refuse items so represented another major exposure route contributing to the high PBDE levels in this starling food-chain. Nonetheless, a third route of PBDE exposure that was not addressed by our sampling design, but which should be considered, is ingestion of contaminated dust through feather preening. For instance, inhalation and dermal exposure of house dust can account for 60–80% of the total PBDE intake in humans (Lorber, 2007; Wu et al., 2007; Johnson-Restrepo and Kannan, 2009). Moreover, several raptor researchers have also identified preening as a potential source of PBDE exposure in peregrine falcons living in urban habitats (Park et al. 2009, 2011; Newsome et al., 2010).

Congeners BDE-47, -99, −100, −153, and −154 in our starling eggs from the landfill had mean concentrations (541 ng/g lipid eq., 1426 ng/g lipid eq., 379 ng/g lipid eq., 307 ng/g lipid eq., and 107 ng/g lipid eq., respectively) almost threefold greater than concentrations reported in starlings collected from other urban areas across Metro Vancouver (230 ng/g lipid eq., 613 ng/g lipid eq., 114 ng/g lipid eq., 91 ng/g lipid eq., and 42 ng/g lipid eq., respectively; Fremlin et al., 2019). Starlings are income breeders (Meijer and Drent, 1999), so they rely on nutritional inputs gathered from the breeding ground to form their eggs. In glaucous gulls (*Larus hyperboreus*), which are also income breeders, PBDE contaminant levels observed in eggs were positively associated with increasing levels observed in females (Verreault et al., 2006). However, maternal transfer in gulls appeared to favour compounds with low K_{OW}, while persistent, higher-halogenated compounds transferred less readily (Verreault et al., 2006). Additionally, Eng et al. (2013) showed that more highly exposed zebra finches (*Taeniopygia guttata*) transferred proportionately less BDE-99 to their eggs suggesting that maternal transfer of BDE-99 involves a saturable transport process. Consequently, eggs from highly exposed birds may actually underestimate adult exposure. Thus, the PBDE levels observed in the Delta starling eggs could suggest that the contaminants accumulated rapidly in the females during nest building just prior to egg formation. However, we know from sampling our reference site during other studies that starlings are resident and remain in the Lower Mainland all year round (Williams et al., 2015). Therefore, it is possible for birds inhabiting the Delta landfill area to accumulate elevated amounts of PBDEs throughout the year.

BMF values in starling eggs were one to two orders of magnitudes higher than those observed in chicks. The BMFs for starling eggs were extremely high with the highest at 1560 for BDE-153 and were much higher than any other BMFs reported in the literature for other avian species or mammals (Table 3). Whereas, the BMFs for starling chicks were comparable to values reported in the literature (Table 3). The high BMFs for the starling eggs may simply be due to chicks and adult birds having a greater ability to biotransform hydrophobic contaminants than compared to eggs. Furthermore, debromination within the adult female or chicks likely enhances the depuration of higher brominated congeners but slows the depuration of lower brominated congeners resulting in inflated tissue concentrations of BDE-47 and -99 in the adult female and thus her eggs (Kelly et al., 2008). Also, starlings are homeotherms while their invertebrate prey are poikilotherms, so the starlings will generally have much higher bioaccumulation than invertebrates due to their higher energy requirements and feeding rates (Fisk et al., 2001). This biotransformation discrepancy will thus inflate the BMF values. In addition, many bird species will often exhibit higher biomagnification than mammals (Fisk et al., 2001) due to lower mono-oxygenase enzyme activity (Connell, 1990).

Nonetheless, lower PBDE concentrations in chicks could result from growth dilution, lack of time to equilibrate with diet, increase in chick body fat, and excretion via urine and feces (Drouillard et al., 2007). Also, despite BDE-47 and -99 having the highest concentrations in both eggs and chicks, they actually had some of the lowest BMFs; whereas, BDE-153 had the highest BMF in both chicks and eggs followed by BDE-154. However, our results are comparable with other food-chain studies. In an aquatic, Arctic food-chain with ringed seals (*Pusa hispida*) and polar bears (*Ursus maritimus*), BDE-47, -99, −100, and −153 all had BMFs > 1, but BDE-153 had the highest BMF at 130 (Muir et al., 2006). In a terrestrial food-chain with great tits (*Parus major*) and sparrowhawks (*Accipiter nisus*) and another with bank voles (*Clethrionomys glareolus*) and common buzzards (*Buteo buteo*), the higher brominated congeners BDE-153 and BDE-183 had higher BMFs than the lower brominated congeners despite the lower brominated congeners generally having higher concentrations in the animal tissues (Voorspoels et al., 2007). Furthermore, even though PBDE concentrations reported for aquatic bird species were dominated by BDE-47 and -99, terrestrial bird species, such as the peregrine falcon, tended to show higher concentrations of BDE-99, -100, and −153 (Drouillard et al., 2007; Law et al., 2003).

Our study had several limitations that likely impacted our BSAF and BMF calculations. First, we had small sample sizes of soil samples and dietary items. Ideally, we should have collected at least three soil samples from each foraging location in Delta and Glen Valley in order to statistically determine concentration differences between the foraging locations and soil types at the landfill. The small sample size of invertebrates in the starling diet likely contributed to the low detection frequencies we observed and thus may have biased the BSAF and BMF values. However, this was the best sampling effort that could be accomplished at the time of the field study as we were limited by time and budgetary constraints. Second, we did not analyse the dietary refuse items for stable isotopes of $\delta^{15}N$ and $\delta^{13}C$ signatures due to limited biomass so we could not confirm if those items strongly influenced $\delta^{15}N$ and $\delta^{13}C$ signatures in the starlings from the landfill. Nonetheless, we did analyse the refuse items for PBDE concentrations confirming that they were a dominant exposure route. Future studies could increase the sampling effort of invertebrates and dietary items by using pitfall traps, applying a chemical expellant such as allyl

Table 3
Biomagnification factors for starling eggs and chicks in present study compared to values reported in the literature.

BDE	EUST − EGG	EUST − CHICK	COKE −GRASS[a]	SPHA −PASS[b]	BUZZ −RODT[b]	FOX −RODT[b]	OSPR −FISH[c]	COKI−FISH[d]	EUST − DIET[e]
BDE 47	150	14	2.7	10	12	<1	29	5.7	12
BDE 85	60	2.7	NA	NA	NA	NA	NA	NA	8.3
BDE 99	356	22	7.3	20	14	<1	32	3.6	72
BDE 100	412	22	5.8	25	17	<1	19	1.5	4.6
BDE 153	1560	62	100	21	22	<1	46	6.2	8.2
BDE 154	253	13	NA	24	NA	NA	20	2.1	2.5

[a] COKE = Common Kestrel; GRASS = Grasshopper; Yu et al. (2011).
[b] SPHA = Sparrowhawk; PASS = Passerine; BUZZ = Buzzard; FOX = Red Fox; RODT = Rodent; Voorspoels et al. (2007).
[c] OSPR = Osprey; Chen et al. (2010).
[d] COKI = Common Kingfisher; Mo et al. (2012).
[e] EUST = European Starling; DIET = Terrestrial Invertebrates; Fremlin (2018).

isothiocyante (Zaborski, 2003) to the soil surface, and increasing the number of days/events of chick collaring. Third, as the starling diet composition was based on counts of prey items rather than mass, this may have partially biased the estimate of dietary exposure to PBDEs for chicks and eggs. However, we likely circumvented this limitation by lipid normalizing the PBDE concentrations in each of the prey items. Finally, our assumption that the eggs and chicks had the same proportion and composition of prey items in their respective diet may have biased the BMF values for the eggs. Generally, it is recommended to use a proportional average to represent the diet in BMF calculations (Franklin, 2015); however, since we did not definitively know the diet of the adult starling prior to egg laying, an arithmetic average may have also sufficed and would lower the estimated BMFs for the eggs. Currently we are completing a study of a comprehensive terrestrial food-chain that includes soil and air sources, invertebrates and secondary consumers like the European starling, as well as a top predator, and incorporates many of the recommendations previously mentioned (Fremlin et al., 2019).

5. Conclusions

PBDEs were found to bioaccumulate in the food web at a large urban landfill and two important dietary routes of exposure to starlings were identified. BSAF values confirmed that several PBDE congeners were accumulating in earthworms found in the landfill, which are readily available for consumption by starlings. Another major route of exposure was via consumption of anthropogenic food sources. We confirmed the incorporation of refuse in the starling diet by using both a conventional collaring method and stable isotope analysis. High concentrations of PBDE congeners in starling eggs and chicks demonstrated that the Delta landfill is a significant source of PBDEs indicating that it may be a direct source of environmental contaminants to wildlife.

CRediT authorship contribution statement

Heidi A. Currier: Investigation, Writing - original draft. **Kate M. Fremlin:** Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization. **John E. Elliott:** Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Writing - review & editing. **Ken G. Drouillard:** Resources, Investigation, Data curation. **Tony D. Williams:** Investigation, Resources, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Acknowledgements

This research was funded by Environment and Climate Change Canada through the Chemical Management Plan and by the Natural Science and Engineering Research Council of Canada. The authors would like to thank E. Chin, A. Ellison, and L. Ferguson for their help conducting observations and collecting samples in the field.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124577.

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