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Trophic magnification of legacy persistent organic pollutants in an urban terrestrial food web

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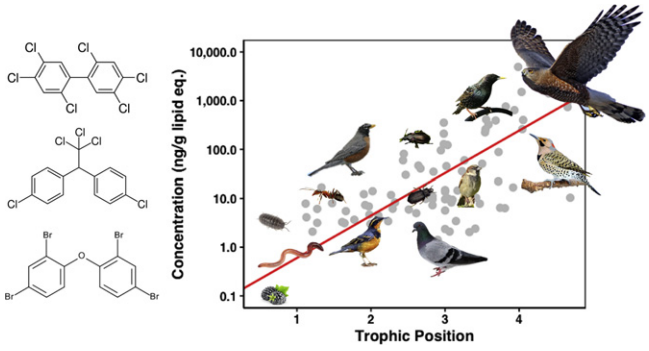
HIGHLIGHTS

- Over 100 samples of Cooper's hawks, songbirds, invertebrates, berries, and soil collected from terrestrial food-web
- Samples analysed for 38 PCB congeners, 20 OCPs, 20 PBDE congeners, and 7 BFRs
- TMFs of several legacy POPs in terrestrial food web similar or higher than those in some aquatic food chains

GRAPHICAL ABSTRACT



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ABSTRACT

Legacy persistent organic pollutants (POPs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), persist for generations in the environment and often negatively impact endocrine functions in exposed wildlife. Protocols to assess the bioaccumulation potential of these chemicals within terrestrial systems are far less developed than for aquatic systems. Consequently, regulatory agencies in Canada, the United States, and the European Union rely primarily on aquatic information for the bioaccumulation assessment of chemicals. However, studies have shown that some chemicals that are not bioaccumulative in aquatic food webs can biomagnify in terrestrial food webs. Thus, to better understand the bioaccumulative behaviour of chemicals in terrestrial systems, we examined trophic magnification of hydrophobic POPs in an urban terrestrial food web that included an avian apex predator, the Cooper's hawk (*Accipiter cooperii*). Over 100 samples were collected from various trophic levels of the food web including hawk eggs, songbirds, invertebrates, and berries and analysed for concentrations of 38 PCB congeners, 20 OCPs, 20 PBDE congeners, and 7 other brominated flame retardants listed on the Government of Canada's Chemicals Management Plan. We determined trophic magnification factors (TMFs) for contaminants that had a 50% or greater detection frequency in all biota samples and compared these terrestrial TMFs to those observed in aquatic systems. TMFs in this terrestrial food web ranged between 1.2 (0.21 SE) and 15 (4.0 SE), indicating that the majority of these POPs

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are biomagnifying. TMFs of the legacy POPs investigated in this terrestrial food web increased in a statistically significant relationship with both the logarithm of the octanol-air (log K_{OA}) and octanal-water partition (log K_{OW}) coefficients of the POPs. POPs with a log K_{OA} >6 or a log K_{OW} >5 exhibited biomagnification potential in this terrestrial food web.

1. Introduction

Protocols to assess bioaccumulation of persistent organic pollutants (POPs) are far less developed for terrestrial systems than aquatic systems (Gobas et al., 2015). At present, regulatory agencies in Canada, the USA, and the EU primarily use chemical concentration data from fish studies to assess the bioaccumulation potential of chemicals expressed as either a bioconcentration factor (BCF) or bioaccumulation factor [BAF; 1, 2, 3]. However, BCF and BAF metrics apply only to aquatic or water-respiring organisms and the BCF does not consider chemical exposure from the diet of an organism. Moreover, chemicals are known to behave differently in terrestrial ecosystems due to differing physicochemical properties, such as the octanol-water partition coefficient (K_{OW}) and the octanol-air partition coefficient (K_{OA}) (Kelly et al., 2007). For example, contaminants with a low K_{OW} (log K_{OW} ~2 to 5) and high K_{OA} (log K_{OA} ~6 to 12) can biomagnify in air-respiring organisms because of a low rate of respiratory elimination while they generally do not biomagnify in water-respiring organisms (Kelly et al., 2007). Thus, separate models and metrics for terrestrial systems need to be developed for evaluating the total bioaccumulation potential of a chemical. However, there is lack of empirical terrestrial data to develop these models.

Bioaccumulation metrics most relevant for describing bioaccumulation in terrestrial food webs include biomagnification or trophic magnification factors (BMF or TMF, respectively), as they account for dietary exposure and can be applied to both air-respiring and water-respiring organisms (Borgå et al., 2012; Conder et al., 2012). However, TMFs are often difficult to determine if the range of trophic positions of organisms in the food-chain is too small or if chemicals are not present at detectable concentrations in the environment, which is common at the lower levels of the food-chain (Conder et al., 2012). For instance, a study in China evaluated biomagnification of POPs in an urban, terrestrial food web (Yu et al., 2011), but was unable to determine TMFs because the trophic position of the main predator overlapped with its prey. Additionally, the few studies that have evaluated biomagnification of POPs in terrestrial environments have estimated TMFs using simple models (Armitage and Gobas, 2007; Kelly and Gobas, 2003) or used data collected from a limited number of trophic levels or species groups (Kelly and Gobas, 2001; Voorspoels et al., 2007; Morris et al., 2018). Consequently, many scientists (Gobas et al., 2015; van den Brink et al., 2013) have stressed that there is a critical need for more terrestrial field studies that assess biomagnification and provide essential empirical field data on ionic and ionogenic chemicals like POPs.

Legacy POPs, such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs), are hydrophobic substances banned or restricted in usage since the early 1970s but still in circulation. These were the initial POPs listed under the Stockholm Convention on POPs, a United Nations treaty signed in 2001 (www.pops.int). Emergent POPs, such as polybrominated diphenyl ethers (PBDEs), were not recognized as global contaminants until 1987 as they effectively began commercial production in 1965 and have just recently been discontinued over the last decade (Chen and Hale, 2010; Chen et al., 2012a; Vonderheide et al., 2008); thus, these emergent POPs were added later to the Stockholm Convention. However, even after decades of restrictions, legacy POPs combined with emergent POPs continue to be detected at elevated levels in apex predators posing a significant toxicological risk (Newsome et al., 2010; Park et al., 2011; Elliott et al., 2015; USEPA, 2009; Best et al., 2010; Cesh et al., 2010). Avian apex predators are particularly at risk because legacy and emergent POPs are often detected at much higher concentrations in raptors than compared to many mammalian apex predators (Yu et al., 2011; Chen and Hale, 2010; Connell, 1990; Kelly et al., 2008). For instance, a Cooper's hawk (*Accipiter cooperii*) from Metro Vancouver, British Columbia contained the highest ΣPBDE concentration recorded to date for a wild bird at 194 μg/g lipid (Elliott et al., 2015), which is also considerably higher than most ΣPBDE concentrations reported in large mammalian predators (Morris et al., 2018; Kelly et al., 2008). As terrestrial raptors like the Cooper's hawk often exhibit higher concentrations of POPs than many aquatic species (Kunisue et al., 2008; Jaspers et al., 2006), we suspect that their terrestrial food webs may also generate higher levels of biomagnification of these contaminants (Elliott et al., 2015; Yu et al., 2013; Brogan et al., 2017).

To investigate the biomagnification of legacy and some emergent POPs in a terrestrial food web, we designed a terrestrial field study that included a primary producer, detritivores, primary and secondary consumers, and an avian apex predator, the Cooper's hawk. We estimated the trophic positions of berries, invertebrates, songbirds, and Cooper's hawks using a literature-based trophic position model and stable nitrogen isotope comparisons. Over 100 biota samples were analysed for concentrations of 38 PCB congeners, 20 OCPs, 20 PBDE congeners, and 7 brominated flame retardants (BFRs) listed on the Government of Canada's current Chemicals Management Plan (CMP; Supplementary Data File – Appendix 1). We determined TMFs for legacy and emergent POPs that had a 50% or greater detection frequency in all biota samples and compared these terrestrial TMFs to those reported for aquatic systems. This study also provides a reference point for evaluating the trophic magnification of other emerging contaminants of concern, such as perfluoroalkyl substances (PFASs) and cyclic methyl siloxanes (CMSs), which will be reported in future work.

2. Methods

2.1. Study area

We assessed the trophic transfer and biomagnification of legacy POPs within a terrestrial food web in urbanized regions of Metro Vancouver, British Columbia, Canada. We chose an urban area primarily because previous studies in Metro Vancouver showed relatively high concentrations of POPs in Cooper's hawks (Elliott et al., 2015; Brogan et al., 2017) increasing the likelihood of observing detectable concentrations in the lower trophic levels of the food web. As Cooper's hawks in rural areas are known to have more diverse diets compared to urban hawks (Roth and Lima, 2003; Roth et al., 2006; Estes and Mannan, 2003), an urban food web is likely less diverse resulting in a more linear or direct transfer of contaminants up the food-chain. We focused collection efforts in urban parks and residential areas of Metro Vancouver, which is comprised of 21 municipalities. However, our food web sampling was limited to 5 municipalities with known active Cooper's hawk nests: District of North Vancouver, City of Vancouver, City of Burnaby, City of Richmond, and City of Delta (Fig. S1).

2.2. Study design & sample collection

Our primary study area included 6 sampling regions within 5 municipalities (Fig. S1). The Supplementary Information includes

comprehensive details about the study design, sample collection methods, and the number of samples obtained for each trophic level (Table S1). The designated apex predator in our terrestrial food web was the Cooper's hawk as they are tolerant to nest site disturbance and well-adapted to urban environments (Cava et al., 2012; Curtis et al., 2006a; Stout and Rosenfield, 2010; Brogan, 2014; Boal and Mannan, 1998). We obtained tissue samples of Cooper's hawk by collecting eggs from active nests ($n = 17$; Fig. S1; Table S1). Eggs were chosen to represent the apex predator trophic level because eggs represent a maternal transfer of contaminants from the female hawk to the eggs and are frequently used as a matrix for environmental contamination monitoring (Miller et al., 2014; Henny and Elliott, 2007; Elliott and Martin, 1994). Cooper's hawk egg collection was approved by the University Animal Care Committee of Simon Fraser University and authorized by the Ministry of Forests, Lands and Natural Resource Operations (Surrey, BC) under permit SU16-225842.

In southwestern BC, urban Cooper's hawk typically prey upon American Robins (*Turdus migratorius*), European Starlings (*Sturnus vulgaris*), and House Sparrows [Passer domesticus; 30]; thus, we focused collections efforts on these primary prey species (Table S1). However, we also supplemented our targeted prey species collection efforts with samples of 12 other known Cooper's hawk prey species, including Varied Thrush (*Ixoreus naevius*), Hermit Thrush (*Catharus guttatus*), Swainson's Thrush (*Catharus ustulatus*), Spotted Towhee (*Pipilo maculatus*), Song Sparrow (*Melospiza melodia*), White-crowned Sparrow (*Zonotrichia leucophrys*), Golden-crowned Sparrow (*Zonotrichia atricapilla*), Dark-eyed Junco (*Junco hyemalis*), Fox Sparrow (*Passerella iliaca*), Rock Pigeon (*Columba livia*), Eurasian-collared Dove (*Streptopelia decaocto*), and Northern Flicker (*Colaptes auratus*) that were euthanized by a wildlife rehabilitation facility, Wildlife Rescue Association (Table S1). In order to manage the cost of the analytical chemistry and to have enough biomass for each sample, we pooled bird samples into six avian groups per sampling region as follows: American Robin ($n = 9$), European Starling ($n = 5$), Sparrow spp. ($n = 6$), Thrush spp. ($n = 6$), Pigeon/Dove ($n = 6$), and Northern Flicker ($n = 6$; Table S1). Songbird egg collection and animal capturing, handling, and euthanasia were approved by the Animal Care Committee of Simon Fraser University and authorized by the Canadian Wildlife Service – Environment and Climate Change Canada under permit BC-16-0010.

As most of these songbirds predominately eat terrestrial invertebrates and seasonal wild fruit or berries, we collected several species of ground beetles (Coleoptera; $n = 12$); detritivores, including earthworms (Lumbricidae; $n = 25$) and isopods (Oniscidae; $n = 6$); and other insects ($n = 5$), such as millipedes, centipedes, spiders, and ants, by using pitfall traps or applying a chemical expellant to the soil surface (Table S1). Songbirds and ground beetles generally comprised the secondary and primary consumers in our terrestrial food web while detritivores were assumed to be the baseline consumers. The representative primary producer in our food web was Himalayan blackberry (*Rubus armeniacus*; $n = 6$), an invasive shrub that is consumed by numerous mammal and bird species, such as American Robin, European Starling, and Spotted Towhee (Tirmenstein, 1989; Gaire et al., 2015). We obtained invertebrate and berry samples from five subsampling stations within each sample region collecting samples from a total of 30 stations (Fig. S1; Table S1). Samples of ground beetles, isopods, other insects, and berries were eventually pooled into 5–6 separate pools (Table S1). All biota samples within this terrestrial food web were collected from May to September 2016 and frozen at −20 °C.

To account for the potential influence of spatial variation in contaminant concentrations, we also collected abiotic samples of soil and air within each sampling region. We obtained one soil sample from each of the 30 subsampling locations that we collected earthworms, but we analysed only 24 soil samples due to limited funding (further details in Supplementary Information). Soil samples were collected from May to September 2016 and frozen at −20 °C. Within each sampling region, one passive air monitor with a polyurethane foam (PUF) disk was deployed within 125–900 m of a Cooper's hawk nest (Fig. S2). Air samples were collected from September to December 2016 and from January to April 2018 (further details in Supplementary Information).

2.3. Sample preparation

We shipped all frozen biota and soil samples on dry ice to the National Wildlife Research Centre (NWRC) in Ottawa, ON. There, we homogenized eggs by whisking the yolk and albumen together and for the songbirds, we plucked them of feathers and clipped off large keratinized or boney tissues (e.g. beaks, wings, legs, and feet) as Cooper's hawks typically pluck their prey then eat the head, viscera, and muscle tissues in sequence (Curtis et al., 2006b). All frozen or semi-thawed biota samples were processed by cutting tissues into small pieces and homogenizing them with a ball-mill (Retsch™ MM400 Mixer Mill, Fisher Scientific). One to seven individual birds from each species group within each sampling region were pooled and homogenized for a total of 35 pools (Table S1 and Supplementary Data File – Appendix 2). Prior to and after homogenization, we stored all the samples at −40 °C.

2.4. Stable isotope analysis

Stable isotope ($\delta^{15}N$ and $\delta^{13}C$) analyses were performed at the G. G. Hatch Stable Isotope Laboratory (G. G. Hatch) at the University of Ottawa (Ottawa, ON, Canada). Briefly, homogenized subsamples of the biotic samples ($n = 98$) were freeze-dried and then approximately 1.0 mg of each subsample was weighed into tin capsules (~6 mm). Samples were combusted at 1800 °C in a Vario EL Cube elemental analyzer (Elementar, Germany) interfaced to a Delta Advantage isotope ratio mass spectrometer (IRMS; Conflo III, Thermo Scientific, Germany). The resulting gas products are carried by helium through columns of oxidizing/reducing chemicals optimized for CO_2 and N_2, then the gases are separated by a "purge and trap" absorption column and eventually sent to the IRMS. Further details about the internal standards used and the analytical precision are provided in the Supplementary Information.

2.5. Chemical analysis

The avian prey, invertebrates, berry, and soil samples were transferred to the Great Lakes Institute for Environmental Research (GLIER) in Windsor, ON for chemical analysis and the Cooper's hawk eggs were analysed for contaminants at NWRC. Air samples were shipped to the Air Quality Research Division in Toronto, ON for processing and chemical analysis.

2.5.1. National Wildlife Research Centre

Sample extraction methods used at NWRC have been described in detail in comparative studies on POPs within eggs of various species (Gauthier et al., 2008, 2007; Chen et al., 2013). Approximately 0.25–3.0 g of biota sample homogenate was ground with diatomaceous earth (J.T. Baker, NJ, U.S.A.), spiked with 25 μL of a standard solution, and then extracted with a 50:50 dichloromethane:hexane (DCM:HEX) solvent mixture using an accelerated solvent extraction system (ASE, Dionex ASE 350, CA, USA). After gravimetric determination of lipid content using 10% of the extract, the remaining extract was subjected to gel-permeation chromatography (GPC; GX-271 Liquid Handler, Gilson, Inc., WI, USA), followed by cleanup with solid phase extraction (SPE) to remove any remaining small lipids that were not removed using GPC. The cleaned-up sample was concentrated to 100 μL using nitrogen evaporation, then 400 μL of iso-octane was added to the sample prior to instrumental analysis.

PCBs/OCPs in the hawk eggs were analysed using an Agilent 7890 gas chromatograph (Agilent Technologies, CA, USA) coupled to a single quadruple mass analyzer (Agilent 7000 MS) in electron impact

ionization (MS-EI) mode. We used a 15 m DB-5MS column (0.25 mm ID, 0.25 μm film thickness; J&W, Agilent Technologies) with the injector in splitless mode and held at 280 °C. Initial oven temperature was held at 60 °C for 1 min, increased to 120 °C at 40 °C/min, and finally to 310 °C at 5 °C/min. OCP/PCB quantification was determined via selected ion monitoring (MRM). The internal standards for quantification were carbon labelled and were selected to cover the range of tri- to octa-PCBs: ^{13}C-PCB28, ^{13}C-PCB52, ^{13}C-PCB118, ^{13}C-PCB153, ^{13}C-PCB180 and ^{13}C-PCB194. Congeners that co-elute are reported as a sum and are listed in the form PCB xx/xx (e.g. PCB 28/31 is the sum of the co-eluting congeners PCB-28 and PCB-31).

PBDEs were analysed using an Agilent 7890 gas chromatography (Agilent Technologies, CA, USA) coupled to a single quadruple mass analyzer (Agilent 5977 MS) in electron capture negative chemical ionization (MS-NCI) mode [similar to methods used in 41, 42, 43, 44]. The column used was a 15 m DB-5ht fused silica column (0.25 mm ID, 0.10 μm film thickness; J&W, Agilent Technologies) with the injector in pulsed splitless mode and held at 280 °C. Initial oven temperature was held at 100 °C for 2 min, increased to 250 °C at 25 °C/min, then to 260 °C at 1.5 °C/min, and finally to 325 °C at 25 °C/min and held for 7 min. PBDE quantification was determined via selected ion monitoring (SIM) for $^{79}Br^-$ and $^{81}Br^-$, except for BDE-209 (m/z 487) and $^{13}C_{12}$-BDE-209 (m/z 495). The molecular ion (m/z 652) was used for quantifying *syn*– and *anti*-Dechlorane Plus (DP) isomers.

2.5.2. Great Lakes Institute for Environmental Research

Homogenized biota samples sent to GLIER underwent similar extraction and analysis methods with some exceptions (refer to Supplementary Information for more details). Soil samples were also sent to GLIER for chemical analysis (refer to Supplementary Information for more details).

2.5.3. Air Quality Research Division

Processing and analysis of PUF disks used for air sampling was completed in the Hazardous Air Pollutants (HAPs) Laboratory of the Air Quality Research Division (refer to Supplementary Information for more details).

2.5.4. Standards and chemicals

All PCB, OCP, and PBDE standards were purchased from Wellington Laboratories (Guelph, ON, Canada) or from the National Institute of Standards Technology (Gaithersburg, MD). All solvents used were HPLC or Optima grade and purchased from Fisher Scientific (Ottawa, ON).

2.5.5. Quality control and assurance

Refer to Supplementary Information for further details about Quality Control and Assurance.

2.6. Lipid equivalent concentrations

We measured the lipid content in all biological samples using the 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). As some organisms, such as earthworms and Isopods, 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; 4, 45].

Total organic carbon (TOC) in soil samples was measured by loss on ignition (LOI) procedures. Pre-dried sediment samples were combusted at 450 °C for 24 h and the organic carbon content was determined gravimetrically. Comparisons between TOC as derived by LOI and a Carlo-Erba Elemental Analyzer for sediment samples revealed no differences in technique as described in Drouillard et al. (2006). We expressed the dry weight concentrations as lipid-organic carbon equivalent fractions as determined by following (Kelly et al., 2007)

$$C_{lipid-OC\ eq.} = \frac{C_{dry}}{OC_{dry}(0.35)} \quad (1)$$

in which OC is the fraction of total organic carbon (g of OC/g of dry weight) determined by LOI procedures. The constant 0.35 represents the findings of Seth, Mackay (Seth et al., 1999) that organic carbon has approximately 35% the sorptive capacity of octanol.

2.7. Trophic position of organisms within the food web

We used two methods to measure the trophic position of organisms within the food web: 1) an estimate based on dietary preferences of each species obtained from the literature (Roth and Lima, 2003; Roth et al., 2006; Estes and Mannan, 2003; Cava et al., 2012; Curtis et al., 2006b; Arcese et al., 2002; Cabe, 1993; Campbell et al., 1990; Eastman, 2000; Government of Canada, 2017; Holland, 2017; Judd, 1901; Lowther and Cink, 2006; Lowther and Johnston, 2014; Reynolds, 2017; Saul, 2010; Spennemann and Watson, 2017; Vanderhoff et al., 2014a; Wiebe and Moore, 2017; Beal, 1911; Beal, 1907; Fawki et al., 2003; Moulton, 2011; Wheelwright, 1986; White and Stiles, 1990; Witmer, 1996; Baumeister, 2002; Larochelle, 1990; Vanderhoff et al., 2014b; Currier et al., 2020) and 2) an estimate inferred from stable nitrogen isotope comparisons (Mackintosh et al., 2004; Vander Zanden et al., 1997). Based on the dietary preferences, the trophic position (TP) of each species was calculated according to Eq. (2) (Vander Zanden et al., 1997)

$$TP_{predator} = \left(\sum_{i=1}^{n} TP_{prey\ i} \times p_{prey\ i}\right) + 1 \quad (2)$$

in which $p_{prey\ i}$ is the proportion of prey item i in the diet of the predator (Table S2). We assumed detritivores, i.e. earthworms and sowbugs/pillbugs, had a dietary trophic position of 2.00 and the primary producer, Himalayan blackberries, to have a dietary trophic position of 1.00.

For the stable nitrogen isotope comparison, the $\delta^{15}N$ of each consumer was compared to an average $\delta^{15}N$ of the detritivores and/or primary producer and calculated as per Eqs. (3) and (4), respectively [Table S3; Supplementary Data File – Appendix 5; 2]:

$$TP_{consumer} = \left(\frac{\delta^{15}N_{consumer} - \delta^{15}N_{detritivore}}{\Delta^{15}N}\right) + 2 \quad (3)$$

or

$$TP_{detritivore} = \left(\frac{\delta^{15}N_{detritivore} - \delta^{15}N_{berry}}{\Delta^{15}N}\right) + 1 \quad (4)$$

in which 2 or 1 are the assumed isotopic trophic positions of the detritivores or berries, respectively, and $\Delta^{15}N$ is the isotopic enrichment factor constant.

2.8. Statistical analysis

2.8.1. Stable isotopes and isotopic enrichment

To compare the average stable nitrogen and carbon isotopes between species groups and to identify differences between the species groups, we used a one-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 $\alpha = 0.05$. We also assessed the linear relationship between $\delta^{15}N$ and $\delta^{13}C$ with a simple linear model.

To determine our study-specific isotopic enrichment factor constant ($\Delta^{15}N$), we compared the average $\delta^{15}N$ of each predator to an overall

average $\delta^{15}N$ of prey with a linear mixed effects model that included sample region as a random effect (Nakagawa and Schielzeth, 2013). For example, we compared the average $\delta^{15}N$ of Cooper's hawks ($n = 2$) in Richmond to an overall average $\delta^{15}N$ of all songbird groups ($n = 6$) in Richmond (Supplementary Data Files – Appendix 4). We did not use a predator-specific proportional average of the $\delta^{15}N$ of each prey species since we had a limited representation of the prey species that each bird or insect is known to eat.

2.8.2. Contaminant concentrations with non-detect data

We calculated average concentrations of legacy POPs detected within each species, using 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 or concentration data with values below MDLs (Helsel, 2012). We calculated the mean concentration, standard deviation, and standard error of each legacy POP detected within each trophic level using a Kaplan-Meier (KM) statistical model (cenfit) in the NADA package (further details in Supplementary Information).

2.8.3. Spatial analysis of legacy POPs

Within the soil samples collected from the six sampling regions across Metro Vancouver, we determined the mean concentrations for the predominant legacy POPs found in the trophic organisms, which included PCB-153, DDE, and BDE-99 (Supplementary Data Files – Appendices 8b, 9b, and 10b). We used a one-way ANOVA with a Tukey's HSD in the R program (R Core Team, 2017) to compare the average concentrations of the legacy POPs within soil samples in each sampling region and to identify differences between sampling regions. However, if a legacy POP was not detected in all of the soil samples (i.e. had a concentration below the detection limit), we used the non-parametric Peto-Prentice score test (cendiff) in the NADA package to compare differences in legacy POP concentrations in soils between sampling regions. We performed a separate hypothesis test for each dominant legacy POP. Each null hypothesis assumed that there was no statistical difference between the mean soil concentrations in the sampling regions. 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 $\alpha = 0.05$.

2.8.4. Trophic magnification factor

We determined trophic magnification factors (TMFs) for contaminants that were detected in >50% of all samples by using a log-linear regression between the natural logarithm of a contaminant's lipid equivalent concentration and the trophic position of each sample as per equation $\ln C_{lipid\ eq.} = m\mathrm{TP} + b$, in which m is the estimated slope and b is the y-intercept (Borgå et al., 2012; Kidd et al., 2019). We only determined TMFs for POPs that had a detection frequency >50% because the error in the estimated TMF will increase as the detection frequency decreases. We used a censored regression function (cenreg) in the NADA package, which uses maximum likelihood estimation and an assumed log-normal distribution of the residuals (i.e. observed concentrations minus the predicted concentrations), to estimate the slope coefficient that had the highest likelihood of producing the observed values for the detected observations and the observed proportion of data that were below each detection limit (Helsel, 2012). The TMF is then computed based on the antilog of the slope m (i.e. $\mathrm{TMF} = e^m$). A TMF >1 indicates that the contaminant is biomagnifying in the food web; whereas, <1 indicates trophic dilution (further details in Supplementary Information). Statistical significance of *p*-values for slope estimates were assessed at $\alpha = 0.05$.

As there is considerable debate in how to appropriately handle non-detect concentrations in a data set, we evaluated three scenarios that use substitution for the non-detect (ND) concentration when determining the TMF: ND = ½ method detection limit, ND = 0, and ND = NA or ignored. We compared the TMFs determined from these scenarios with the TMF determined from the NADA package to test how non-detects may affect the TMF. Six POPs with varying total detection frequencies were used in this evaluation – DDE (95%), PCB-153 (89%), Dieldrin (90%), BDE-47 (78%), PCB-95 (40%), and Mirex (45%).

The variation in trophic magnification observed between many POPs can often be explained by differences in their chemical properties, such as K_{OW} and K_{OA}. To better understand the variation in trophic magnification observed, we examined the relationship between our estimated TMF and log K_{OA} and log K_{OW} of each legacy POP using a linear-mixed effects model with type of POP (e.g. PCB, OCP, or PBDE) as a random effect. K_{OA} and K_{OW} values of each legacy POP were compiled from various sources (Kelly et al., 2008; Mackintosh et al., 2004; Houde et al., 2008; Kelly et al., 2009; Muir et al., 2003; US EPA, 2018; Verhaert et al., 2017; Walters et al., 2011).

3. Results & discussion

3.1. Stable isotopes and isotopic enrichment

The stable nitrogen and carbon isotope analysis for a total of 98 samples from across the food web is summarized in Table S3, Fig. S3, and in Appendix 3 of the Supplementary Data File. $\delta^{15}N$ varied between the species groups ($F_{11,86} = 54.64$, $p < 0.001$; Fig. 1a; Table S2; Fig. S3) with average $\delta^{15}N$ values ranging from 0.48‰ in Himalayan blackberry to 9.23‰ in Cooper's Hawks. $\delta^{13}C$ also varied between the species groups ($F_{11,86} = 20.29$, $p < 0.001$; Fig. 1a; Table S3) yet also showed considerable overlap between the species groups (Fig. 1a; Table S3). In addition, we observed a positive relationship between the $\delta^{15}N$ and $\delta^{13}C$ values from the samples in the food web ($\delta^{15}N = 1.05(\delta^{13}C) + 32.55$; $F_{1,96} = 102.7$, $p < 0.001$, $r^2 = 0.51$; Fig. 1a). From our linear mixed effects model, we determined the isotopic enrichment factor to be 2.88 (0.35 SE) ‰ (Fig. 1b; Supplementary Data File – Appendix 4).

Very few bioaccumulation studies have estimated a study-specific isotopic enrichment factor from organisms within food webs since a factor of 3.4‰ is often used for biomagnification assessments (Borgå et al., 2012; Müller et al., 2011). We used 2.88‰ because it represented the $\delta^{15}N$ enrichment that was measured within our isotope data set and was comparable to 2.4‰ estimated for muscle tissue $\delta^{15}N$ enrichment of captive, adult common cormorants (*Phalacrocorax carbo*; Mizutani et al., 1991). In addition, pooled estimates of $\Delta^{15}N$ commonly used in bioaccumulation studies range from 2.0–3.4‰ (Jardine et al., 2006). We recommend calculating a $\Delta^{15}N$ enrichment factor specific to the organisms sampled in the food web rather than simply using the general 3.4‰ as variation in this value can greatly affect the TP calculated for each organism due to its position in the denominator of Eqs. (3) and (4). For example, when we used either 2.4‰, 2.88‰, or 3.4‰ as the $\Delta^{15}N$ enrichment factor, the average isotopic TP calculated for the Cooper's hawk varied from 4.72 (0.06 SE), 3.88 (0.04 SE), to 3.92 (0.04 SE), respectively (Supplementary Data File – Appendix 5). Although it is a costly and labour-intensive process, studies should ideally maintain each study species on a known diet then analyze and calculate $\Delta^{15}N$ directly for each species (Jardine et al., 2006). However, estimating $\Delta^{15}N$ from the average predator and prey $\delta^{15}N$ signatures within a sampled food web is a simpler and still effective way to accurately reflect $\Delta^{15}N$ across a given food web.

Our approach improves on previous bioaccumulation studies that have simply used $\delta^{15}N$ to assess biomagnification or used a general $\Delta^{15}N$ enrichment factor of 3.4‰ to calculate integer-based TPs (Borgå et al., 2012; Elliott et al., 2015; Brogan et al., 2017; Mackintosh et al., 2004) as it accounts for the baseline variation in $\delta^{15}N$ within our local food web and incorporates isotopic enrichment unique to this terrestrial system. However, there are some limitations in our method that may have underestimated or biased our derived $\Delta^{15}N$ enrichment factor. First, due to limited biomass availability we did not analyze the Insecta samples for $\delta^{15}N$ and $\delta^{13}C$ values, so those organisms were not included

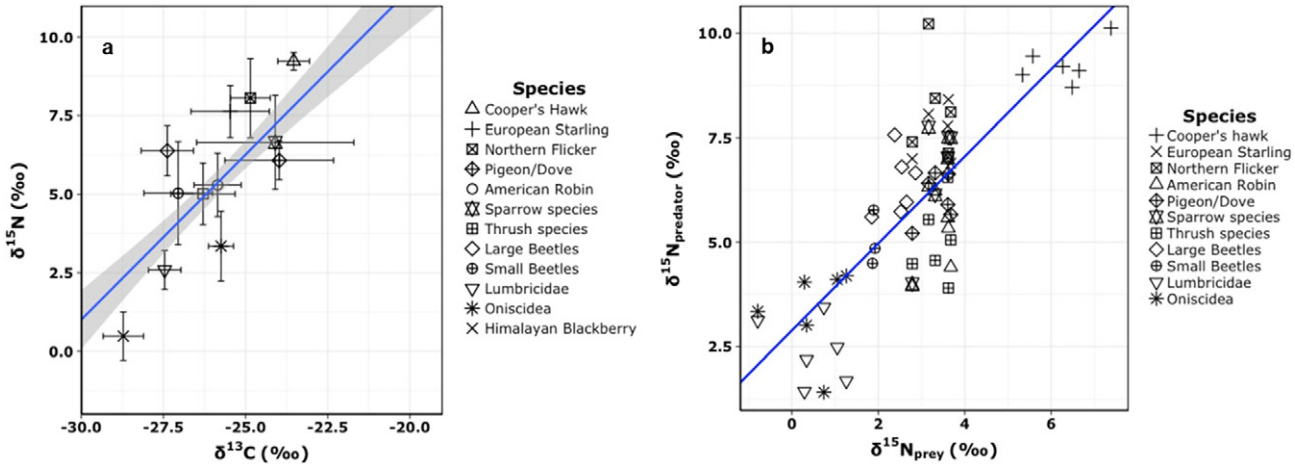


Fig. 1. a) Stable $\delta^{13}C$ and $\delta^{15}N$ isotope signatures within food web expressed with strong proportional relationship (blue line). Error bars represent 95% confidence limits. b) Isotopic enrichment factor constant represented by relationship between average $\delta^{15}N$ of each predator species and overall average $\delta^{15}N$ of prey species within six sampling regions ($\delta^{15}N$predator $= (1.04 \times \delta^{15}N$ prey$) + 2.88$; $F_{1,55} = 101.3$; $p < 0.001$).

in our isotopic enrichment assessment. Second, we used an overall average for the $\delta^{15}N$ prey signatures of each predator rather than a proportional average. However, a proportional average likely would have overestimated our $\Delta^{15}N$ enrichment factor because it required extensive modification of the proportions of each available prey item due to limited representation and sampling of the potential prey species that each bird or insect is known to eat (Supplementary Data File - Appendix 5).

3.2. Dietary versus isotopic trophic position

The estimated dietary trophic positions of the species groups ranged from 1 in the primary producer up to 4.03 in the Cooper's hawk (Tables S2; S4). Average isotopic trophic positions ranged from 1.96 (0.10 SE) in the earthworms to 4.27 (0.05 SE) in the Cooper's Hawk (Table S4, Supplementary Data File – Appendix 5). The isotopic trophic positions were generally equivalent to, or slightly higher, than the dietary trophic positions, indicating that both methods provide a reasonable estimate of trophic position in this food web (Table S4, Supplementary Data File – Appendix 5). We were unable to estimate the isotopic trophic position for Insecta species because there was insufficient biomass for stable isotope analysis, so we used the dietary trophic position of 3.00 for estimating trophic magnification.

The literature-based and average $\delta^{15}N$-determined TPs were comparable indicating that both methods are reasonable indicators of trophic position (Table S4). However, there were some notable discrepancies between the estimated TPs for some species groups, such as Sparrow spp. and Pigeons/Doves, likely due to assumptions regarding local diet and the trophic positions of various invertebrate prey items (Table S4). Therefore, we encourage using a $\delta^{15}N$-determined TP because it corrects for the baseline variation in $\delta^{15}N$ that occurs between or within systems due to natural or anthropogenic inputs of N (Borgå et al., 2012). Whereas, dietary TPs require considerable background knowledge of each species and their prey items, which is not always known or available. The $\delta^{15}N$-determined TPs also have the additional advantage of incorporating enrichment factors unique to ecosystems, species, or animal groups to improve estimates of TP and consequently TMFs (Borgå et al., 2012; Conder et al., 2012).

However, the accuracy of $\delta^{15}N$-determined TPs will depend on the choice of baseline organisms and $\Delta^{15}N$ used in Eqs. (3) and (4); an issue that continues to be debated (Jardine et al., 2006; Vander Zanden and Rasmussen, 1999). Aquatic studies have typically used bivalves although gastropods, copepods, and other invertebrates (Jardine et al., 2006; Vander Zanden and Rasmussen, 1999) have also been used. Nevertheless, Vander Zanden and Rasmussen (Vander Zanden and Rasmussen, 1999) advocate the use of a long-lived baseline consumer rather than a primary producer because their longevity results in less seasonality in $\delta^{15}N$ signatures. Thus, we used earthworms and woodlice as our baseline consumers, since the most widespread earthworm species, *Lumbricus terrestris*, has an average lifespan of 6 years in the wild (National Geographc Society, 2018) and their low $\delta^{15}N$ signatures confirm that earthworms and woodlice are near the base of the food web.

3.3. Legacy POP concentrations

We detected 83 of the 85 contaminants we selected from the Government of Canada's CMP within at least one trophic level, and 30 were detected within most (>60%) of the species groups in the food web. This high level of detection demonstrates that although they have been eliminated or restricted in use for >40 years, these contaminants are still ubiquitous within the environment. Many of these contaminants were frequently detected at high concentrations within several species groups across the food web, but particularly within our apex predator. A summary of the detection frequencies and average concentrations of contaminants detected in all the species groups is provided in the Supplementary Information and the raw data can be viewed in the Supplementary Data File (specifically Appendix 6, 7, 8a, 9a, and 10a).

3.4. Spatial analysis of legacy POPs

Mean concentrations of PCB-153 in soils from each sampling region ranged from 3.58 (0.28 SE) ng/g lipid-OC eq. in Ladner to 9.77 (2.11 SE) ng/g lipid-OC eq. in Richmond showing limited variation ($F_{5,18} = 0.95$, $p = 0.48$; Fig. 2; Table S8). Mean concentrations of DDE in soils from North Burnaby – Vancouver East and Vancouver – South were quite high compared to the other sampling regions at 549 (481 SE) ng/g lipid-OC eq. and 452 (217 SE) ng/g lipid-OC eq., respectively (Fig. 2; Table S8). However, we did not detect a difference in mean concentrations of DDE in soil samples between the sampling regions ($F_{5,18} = 1.16$, $p = 0.37$). Mean concentrations of BDE-99 in soil samples also showed limited variation between sampling regions ranging from 6.14 (4.81 SE) ng/g lipid-OC eq. in North Vancouver to 18.6 (15.9 SE) ng/g lipid-OC eq. in Vancouver – West ($\chi^2_{5,24} = 3.5$, $p = 0.3$; Fig. 2; Table S8). As there were no statistically significant differences in mean soil concentrations for the dominant legacy POPs between the sampling regions, we are confident that the spatial differences in contaminant

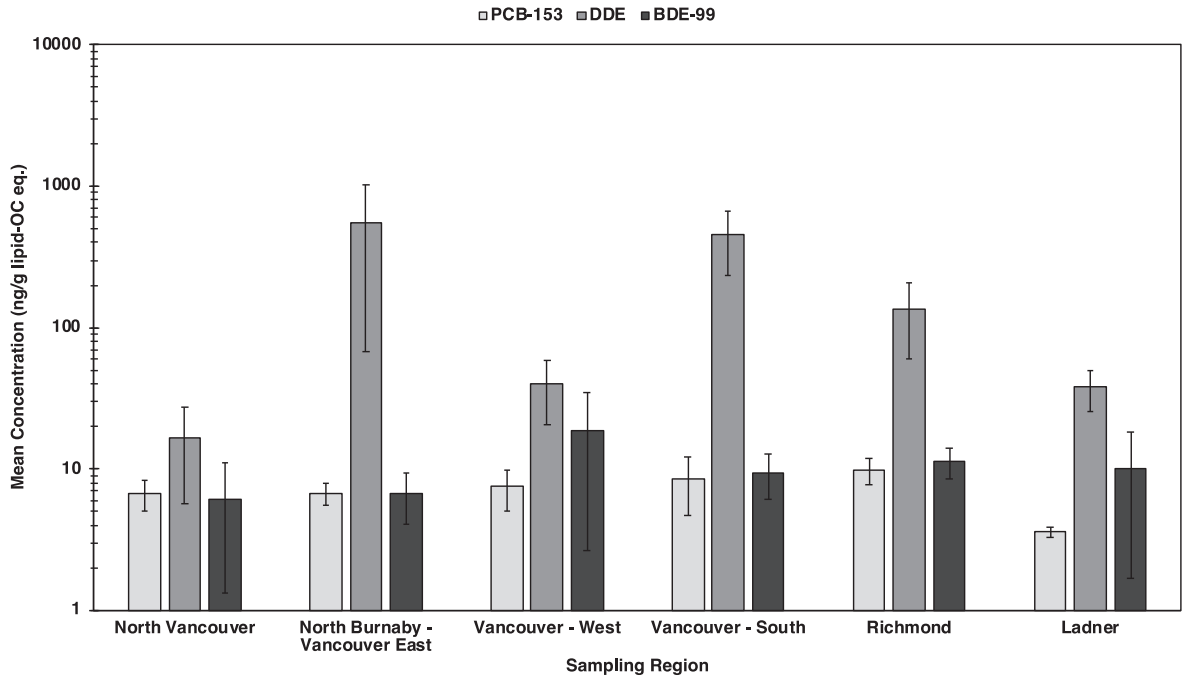


Fig. 2. Mean concentrations of the predominant legacy POPs within soil samples collected from six sampling regions across Metro Vancouver, 2016. Error bars represent standard error of the mean.

concentrations across Metro Vancouver are too small to be a confounding factor in the determination of the TMFs.

As we collected just one air sample per region, we do not have an estimate of variance for concentrations of legacy POPs in air (Fig. 3; Supplementary Data Files – Appendices 8c, 9c, and 10c). Moreover, due to a chemical analysis error, we do not have sample concentrations for PCBs in North Burnaby – Vancouver East, Vancouver – West, and Richmond. Nonetheless, concentrations of PCB-153 in air were consistently detected in the regions we did sample, and generally showed limited concentration variation ranging from 0.61 pg/m^3 in North Vancouver to 1.82 pg/m^3 in Vancouver – South (Fig. 3). Concentrations of DDE in air were also consistently detected across Metro Vancouver and ranged from 2.70 pg/m^3 in North Vancouver to 11.9 pg/m^3 in Richmond (Fig. 3). Notably, concentrations of DDE in air were highest in areas that were historically and/or currently used for agricultural purposes in Metro Vancouver. Concentrations of BDE-47 and -99 in air were also consistently detected across Metro Vancouver and ranged from 2.81–13.6 pg/m^3 and 2.95–12.9 pg/m^3, respectively, with Vancouver – West having the highest concentrations (Fig. 3). Even though we did not confirm if there were statistically significant differences in air concentrations for each legacy POP between the sampling regions, there were no overly large spatial concentration gradients that could directly interfere with the determination of the TMFs.

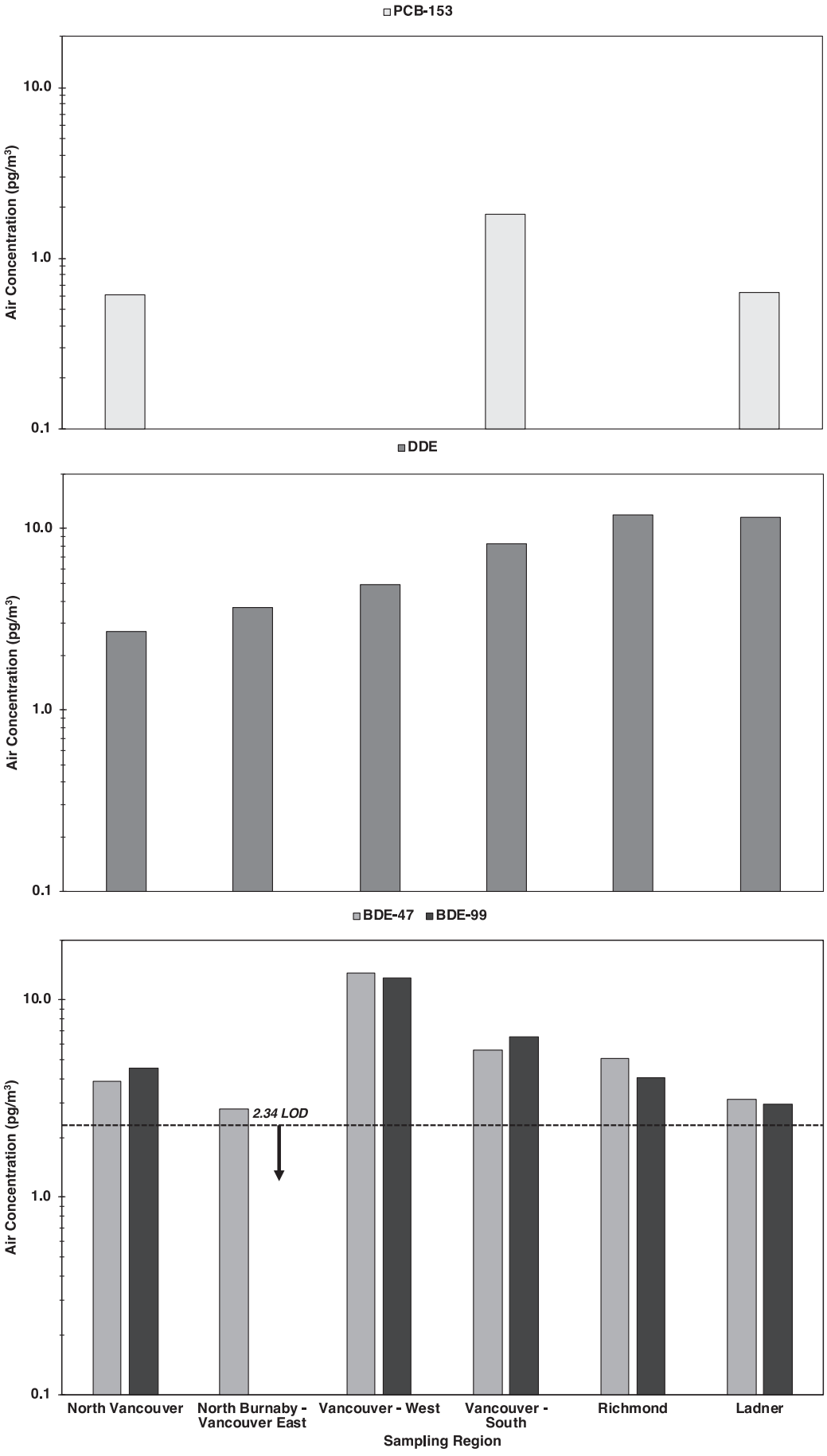
Overall, our soil and air concentration data indicated that the spatial concentration gradients for most of the legacy POPs were relatively homogenous across Metro Vancouver and thus likely did not overtly bias our estimates of trophic magnification. In addition, since our sampling effort was limited to an area of roughly 175 km^2 this also likely helped to reduce bias in our TMF estimates.

3.5. Trophic magnification of legacy POPs

Most of the PCB congeners had TMFs >1 indicating biomagnification in the food web (Tables 1; S9; Supplementary Data File – Appendix 11). However, PCB-28/31 had a TMF approximately equal to 1 ($p = 0.311$) with a 95% confidence interval that bounded 1 indicating that on average those congeners were not biomagnifying in the food web (Fig. 4). Of the three PCBs known to dominate in avian tissues, PCB-180 had the highest TMF at 16 (4.1 SE; Fig. 4). PCB-153, which had the highest average concentrations detected across the food web, had a lower TMF at 7.4 (1.2 SE; Fig. 4). All of the OCPs we evaluated had TMFs >1 indicating biomagnification in the food web (Tables 1; S9; Supplementary Data File – Appendix 11). OCPs *p,p*-DDE and *trans*-NON had high TMFs at 7.8 (1.4 SE) and 6.6 (1.7 SE) and also had some of the highest average concentrations detected across the food web (Table 1; Fig. 5; Table S9). BDE-47 and -99 both had TMFs >1 indicating biomagnification in the food web (Tables 1; S9; Supplementary Data File – Appendix 11). However, BDE-99 had a higher TMF than BDE-47 at 7.3 (1.8 SE), which was comparable to many of the high TMFs for PCBs as well as for *p,p*-DDE and *trans*-NON (Table 1; Fig. 6; Table S9). We were unable to examine trophic magnification of several legacy OCPs; such as β- and γ-HCH, *cis*-and *trans*-chlordane, or Mirex, due to low detection rates. However, some aquatic and terrestrial biomagnification studies have shown that β-HCH and Mirex can biomagnify in both aquatic and terrestrial systems (Kelly et al., 2007; Kelly and Gobas, 2001; Hoekstra et al., 2003; Elliott, 2005).

We did not detect any statistical differences between the TMFs for DDE, PCB-153, DIEL, BDE-47, and PCB-95 determined by the three substitution scenarios and the MLE method as indicated by overlapping 95% confidence intervals (Table S10; Fig. S7). However, the TMF for Mirex determined by the MLE method was considerably higher than some of the TMFs determined with substitution for Mirex (Table S10; Fig. S7). This difference was likely caused by an imbalance in the detection frequencies across the food web, for instance, Cooper's hawks and the avian prey species had extremely high detection frequencies ranging from 80 to 100% while all the invertebrate groups and the berries had zero detected concentrations (Supplementary Data File – Appendix 6). Conversely, PCB-95, which had a lower total detection frequency than Mirex, had detection frequencies ranging from 20 to 100% across the food web for each species group (Supplementary Data File – Appendix 6). Nevertheless, since we determined TMFs only for POPs that were detected in >50% of all samples, we are confident that the MLE method did not overtly bias our TMF values.

Legacy POPs that we examined typically had high log K_{OA} and log K_{OW} values (i.e. >5) indicating that they have the potential to biomagnify in both terrestrial and aquatic environments unless they


PCB-153
DDE
BDE-47
BDE-99
Air Concentration (pg/m3)
10.0
1.0
0.1
2.34 LOD
North Vancouver
North Burnaby - Vancouver East
Vancouver - West
Vancouver - South
Richmond
Ladner
Sampling Region

are biotransformed by an organism in the food web (Table 1; Kelly et al., 2007). Log K_{OA} values reported in the literature for PCBs ranged from 8.45 for PCB 28/31 up to 10.95 for PCB 187, and log K_{OW} values ranged from 5.67 for PCB 28/31 up to 7.62 for PCB 158 (Table 1). Log K_{OA} values for OCPs ranged from 7.11 for HCB up to 10.75 for DDT and log K_{OW} values ranged from 5.03 for QCB up to 6.96 for DDE (Table 1). Log K_{OA} values for BDE-47 and -99 were 9.90 and 10.70, respectively, and log K_{OW} values were 7.30 and 7.60 (Table 1). We saw a strong positive relationship between log K_{OA} and the TMF of each legacy POP ($F_{1,22.15} = 6.93$; $p = 0.0152$) indicating that the TMF increased by 1.55 (0.59 SE) units for every unit increase in log K_{OA} (Fig. 7a). There was also a strong positive relationship between log K_{OW} and TMF ($F_{1,23} = 10.40$; $p = 0.004$) indicating that the TMF increased by 2.64 (0.82 SE) units for every unit increase in log K_{OW} (Fig. 7b). PCBs generally had the highest TMFs and log K_{OA} and K_{OW} values, which both increased with chlorination (Table 1; Fig. 7a).

When we compared the correlations between log K_{OA} and log K_{OW} versus our estimated TMFs, log K_{OW} had a marginal improvement over log K_{OA} with slightly smaller AIC and BIC values (Table 2). However, both models exhibited equally strong correlations of fixed effects with TMF at −0.994 for log K_{OW} and −0.985 for log K_{OA} indicating that both variables are reasonable predictors of terrestrial trophic magnification for our contaminants of interest, which may be due to the fact that log K_{OA} and log K_{OW} values of many legacy POPs often exhibit a positive correlation with each other. Nonetheless, we recommend primarily using log K_{OA} to initially assess the bioaccumulation potential of new hydrophobic chemicals in terrestrial systems since they are comprised of air breathing organisms.

Borgå et al., (2012) and Mackintosh et al. (2004) recommend using TMF estimation of PCB-153 as a positive control to evaluate the efficiency of a study design since TMFs for PCB-153 are consistently >1 in almost all studied food webs. Therefore, if PCB-153 is present at detectable levels across the food web but does not result in a statistically significant TMF, there may be a problem with the study design or statistical method used. As most legacy POPs have high log K_{OA} and log K_{OW} values, we expect them to biomagnify in both aquatic and terrestrial systems (Gobas et al., 2015; Kelly et al., 2007; Armitage and Gobas, 2007). However, two co-eluting legacy POPs, PCB-28/31, did not biomagnify in this terrestrial food web even though they have high log K_{OA} and K_{OW} values. This was surprising since PCB-28/31 concentrations within the Cooper's hawk were relatively high at 125 (114 SE) ng/g lipid. Yet, since PCB-28/31 are lower chlorinated congeners, they were likely more readily metabolized and biotransformed by the avian prey species. In our terrestrial bioaccumulation study, we confirmed that most of the legacy POPs we examined biomagnified along the food web as we expected, including PCB-153, indicating that our study design and statistical method were effective for evaluating the biomagnification potential of other chemicals.

TMFs reported in aquatic food webs for most of the legacy POPs were generally >1 demonstrating biomagnification and were comparable to the TMFs we estimated in our terrestrial food web (Table 2). Surprisingly, even though BDE-99 has high log K_{OW} (7.6) and log K_{OA} (10.7) values, the aquatic TMF reported by (Kelly et al., 2008) was considerably lower at 0.76 (0.10 SE) in contrast to our terrestrial TMF at 7.3 (1.8 SE) demonstrating a biomagnification difference between aquatic and terrestrial environments (Table 1). This biomagnification difference between aquatic and terrestrial environments may be due to several factors. First, some air respiring organisms may exhibit higher biomagnification levels than water respiring because of their greater ability to absorb and digest their diet (Kelly et al., 2007), thus, the mixed composition of both air and water respiring organisms in the aquatic food web versus only air respiring in the terrestrial may have biased the aquatic TMF of BDE-99. Indeed, some water respiring organisms may be able to depurate BDE-99 via their gills more easily than air respiring organisms due to a log $K_{OA} > 6$ and a log $K_{OW} > 2$ (Kelly et al., 2007). Second, the aquatic food web contained mammals, which generally have increased biotransformation via debromination and/or hydroxylation of higher brominated congeners like BDE 99 resulting in elevated concentrations of lower molecular weight PBDEs like BDE-47 (Kelly et al., 2008; Weijs et al., 2015). Whereas, our terrestrial food web is dominated by bird species and some groups of birds have been shown to have higher biomagnification than mammals (Fisk et al., 2001) due to lower mono-oxygenase enzyme activity, which limits their elimination of hydrophobic contaminants (Connell, 1990). For example, TMFs reported for BDE-47 and -99 in an arctic, terrestrial food web indicated that BDE-47 diluted and BDE-99 did not biomagnify in a food web comprised of large mammals (Morris et al., 2018). Third, contaminants do not occur in isolation within organisms and likely interact either by inhibiting (Cantu, 2013) or by inducing (Elliott et al., 1996) enzymatic biotransformation of other contaminants. Consequently, contaminants in mixture may either increase or decrease their own bioaccumulative behaviour. Fourth, our terrestrial food web is within an urban environment with a large human population, and bird populations living in close proximity to urban environments typically have higher concentrations of contaminants than birds living in remote or rural places (Newsome et al., 2010; Park et al., 2011). For instance, European starling eggs collected from nest boxes adjacent to Canadian landfills had concentrations of flame retardants almost 12 times higher than eggs collected from nest boxes in rural areas (Chen et al., 2013). Also, previous research in Metro Vancouver indicated that as land use became more urbanized, ΣPCB concentrations in the blood plasma of adult Cooper's hawks also increased (Brogan et al., 2017). Lastly, the marine arctic study by (Kelly et al., 2008) had a much larger geographical range compared to our urban one, which likely increased the spatial concentration gradient of BDE-99 and thus may have systematically biased the TMF to be <1 (Borgå et al., 2012; Kim et al., 2016).

3.6. Conclusions

Despite 40 years of severe restrictions on the use of most legacy POPs, such as OCPs and PCBs, they still remain prevalent and continue to biomagnify in aquatic and terrestrial systems. In comparison, PBDEs are considered an emergent POP as they were not recognized as global contaminants until 1987 and have since become widespread causing a general repeat of the global contamination crisis created by the legacy POPs (Vonderheide et al., 2008). The biomagnification of legacy and emergent POPs we observed in our study emphasizes that these contaminants could continue to have sub-lethal effects on apex predators if exposure levels exceed toxicity thresholds. Avian species in our urban, terrestrial food web had higher biomagnification of PBDEs than mammalian species in an arctic, terrestrial environment (Morris et al., 2018) emphasizing a need for more biomagnification studies with a diversity of terrestrial species. Previous research reported that the elevated levels of legacy POPs within this urban population of Cooper's hawks appear to be affecting circulating thyroid hormone levels and individual reproduction as fledging success declined with increasing dieldrin concentrations in the blood plasma of adult Cooper's hawks (Brogan et al., 2017). However, it would appear that biomagnification and POP exposure levels in this population of Cooper's hawk is generally below threshold concentrations that would affect population stability (Table S11). Yet, as more commercial chemicals are introduced into the global market, there is an evident need to understand how they will behave in both aquatic and terrestrial environments. Moving

Fig. 3. Concentrations of the predominant legacy POPs within air samples collected from six sampling regions across Metro Vancouver, 2016 and 2017. No concentrations of PCBs in air are available for North Burnaby – Vancouver East, Vancouver – West, and Richmond. Black dashed line represents the limit of detection for BDE-99 at 2.34 pg/m^3: concentrations of BDE-99 in air in North Burnaby – Vancouver East were below LOD.

Table 1
Estimated terrestrial and aquatic TMFs and log K_{OA} and K_{OW} for each legacy POP. NA = Value was not available/provided in reference.

Analyte	Terrestrial TMF	LCL	UCL	Log K_{OA}	Log K_{OW}	Aquatic TMF	SE	LCL	UCL	Reference
PCB-28/31	1.20	0.85	1.69	8.45	5.67	2.90	NA	2.40	3.40	(Kelly et al., 2008)
PCB-99	8.30	5.35	12.90	9.71	6.39	5.94	NA	2.68	13.14	(Mackintosh et al., 2004)
PCB-101	3.88	2.80	5.39	8.60	6.40	9.80	NA	6.80	14.00	(Kelly et al., 2008)
PCB-105	4.53	3.33	6.15	10.00	6.65	4.01	NA	3.23	4.79	(Walters et al., 2011)
PCB-110	1.78	1.33	2.37	8.64	6.48	3.26	NA	2.82	3.70	(Walters et al., 2011)
PCB-118	8.63	5.64	13.20	8.50	6.74	4.10	NA	3.38	4.82	(Walters et al., 2011)
PCB-128	8.97	5.32	15.13	10.59	6.74	6.00	NA	4.23	7.77	(Walters et al., 2011)
PCB-138	6.35	4.55	8.86	9.20	6.80	10.00	NA	7.60	13.00	(Kelly et al., 2008)
PCB-149	3.43	2.41	4.89	8.53	6.67	4.18	NA	3.44	4.92	(Walters et al., 2011)
PCB-153	7.40	5.33	10.28	9.80	6.90	11.10	NA	8.60	14.00	(Kelly et al., 2008, 2009)
PCB-156	11.34	6.41	20.05	9.83	7.18	6.24	NA	4.38	8.10	(Walters et al., 2011)
PCB-158	5.08	3.58	7.22	10.17	7.62	–	–	–	–	(US EPA, 2018)
PCB-180	15.66	9.44	25.99	10.70	7.50	10.00	NA	7.20	14.00	(Kelly et al., 2008, 2009)
PCB-187	8.17	5.21	12.79	10.95	7.17	5.60	NA	4.28	6.92	(Walters et al., 2011)
QCB	2.31	1.74	3.06	8.17	5.03	–	–	–	–	(US EPA, 2018; Hoekstra et al., 2003)
HCB	2.54	2.05	3.16	7.11	5.50	2.90	1.70	NA	NA	(Houde et al., 2008)
HEP	5.37	3.62	7.95	10.53	5.40	–	–	–	–	(US EPA, 2018; Hoekstra et al., 2003)
OXY	2.95	2.20	3.97	10.53	6.02	9.63	2.76	NA	NA	(Muir et al., 2003)
trans-NON	6.55	3.93	10.91	10.00	6.35	3.60	1.50	NA	NA	(Houde et al., 2008)
DIEL	2.97	2.11	4.19	8.73	5.40	1.50	0.50	NA	NA	(Houde et al., 2008)
DDE	7.79	5.50	11.03	9.44	6.96	6.28	NA	3.07	12.80	(Kelly et al., 2009)
DDT	2.66	1.70	4.15	10.75	6.91	4.90	NA	NA	NA	(Verhaert et al., 2017)
DDD	4.41	2.66	7.32	10.34	6.50	7.10	NA	NA	NA	(Verhaert et al., 2017)
BDE-47	3.11	2.19	4.43	9.90	7.30	1.60	NA	1.20	2.00	(Kelly et al., 2008, 2009)
BDE-99	7.32	4.55	11.76	10.70	7.60	0.76	NA	0.57	1.00	(Kelly et al., 2008, 2009)

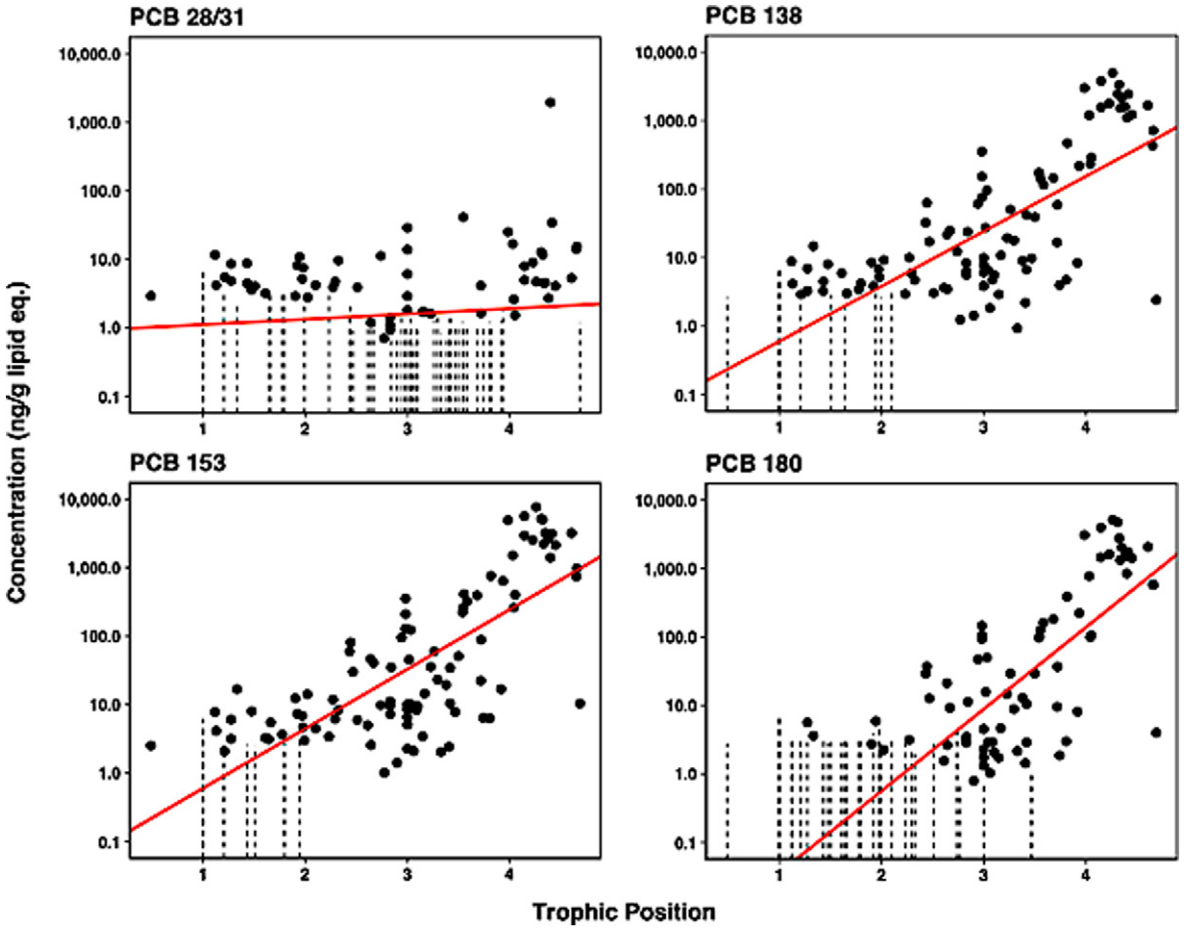


Fig. 4. PCB concentrations in organisms within an urban, terrestrial food web (ng/g lipid eq.) versus trophic position (TP) for PCB 28/31 and PCBs 138, 153, and 180, which are known to dominate in avian tissues. Black circles represent detected observations and dashed lines represent non-detected observations below a sample specific, lipid normalized MDL. Red lines represent the log-linear regression of lipid equivalent concentration to TP across the food web.

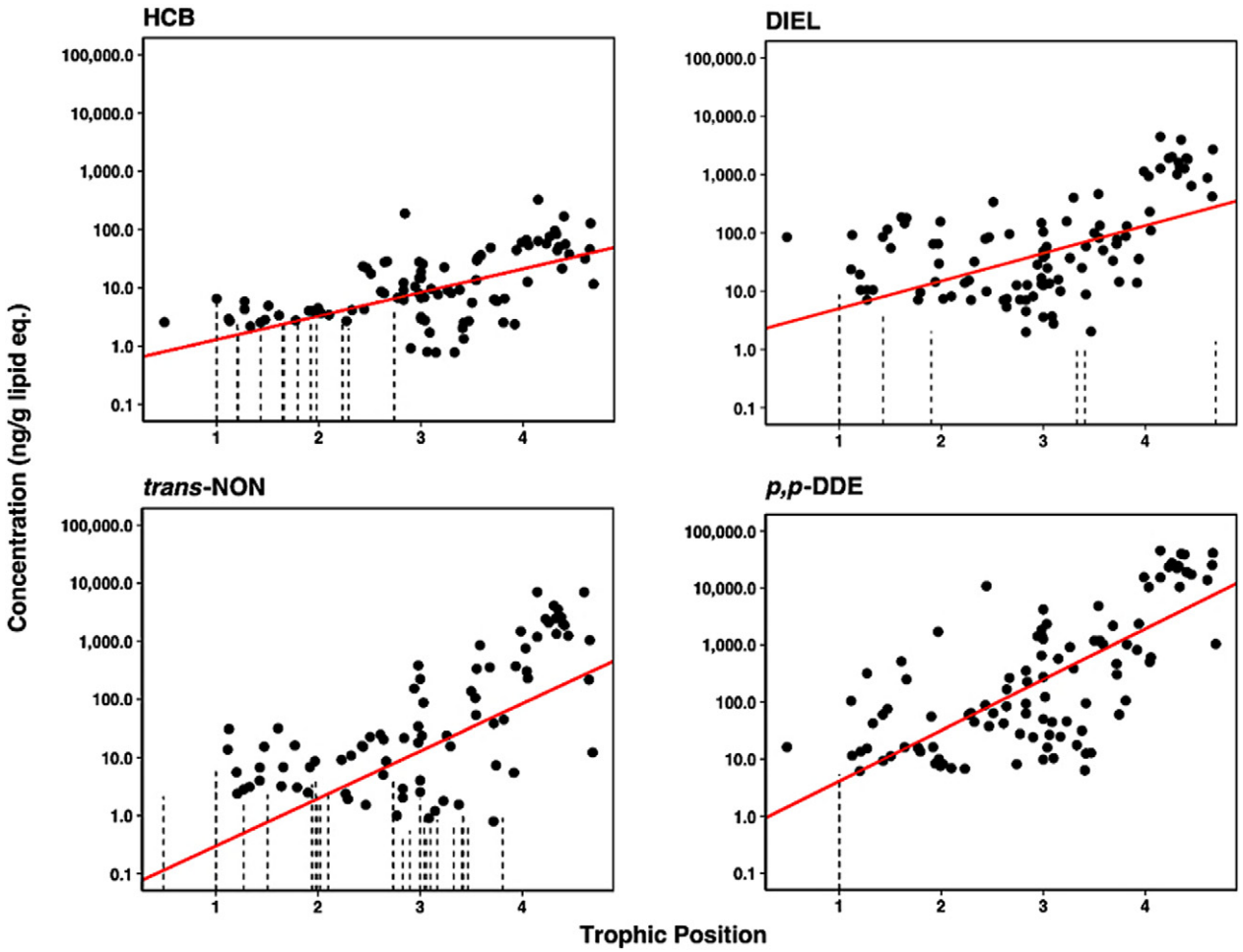


Fig. 5. OCP concentrations in organisms within an urban, terrestrial food web (ng/g lipid eq.) versus trophic position (TP) for HCB, trans-NON, DIEL and p,p-DDE, which were dominant types of OCPs in the food-web. Black circles represent detected observations and dashed lines represent non-detected observations below a sample specific, lipid normalized MDL. Red lines represent the log-linear regression of lipid equivalent concentration to TP over the entire food web.

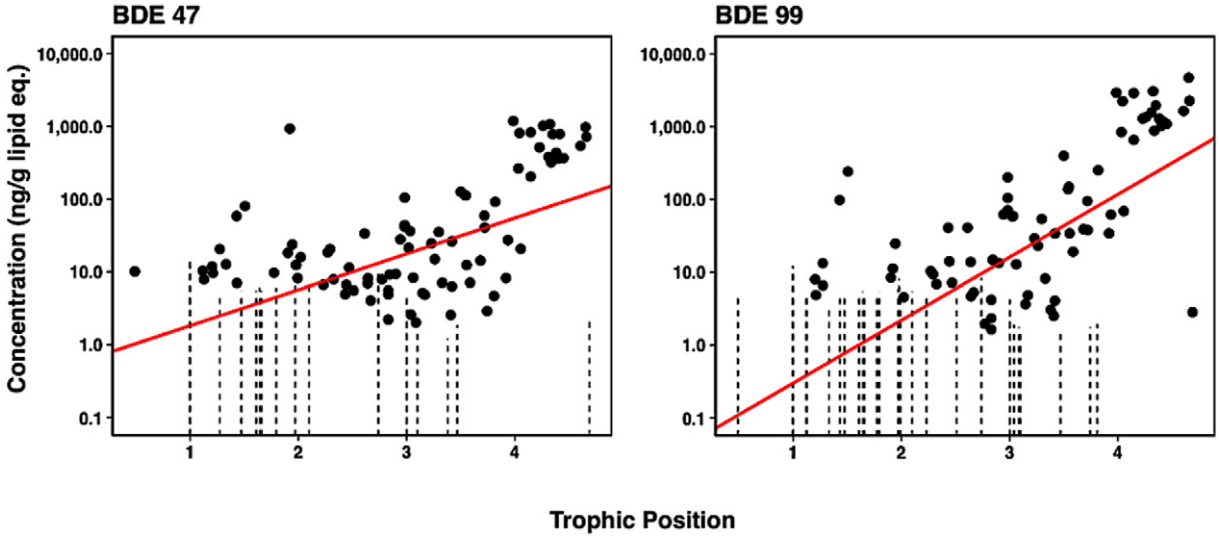


Fig. 6. PBDE concentrations in organisms within an urban, terrestrial food web (ng/g lipid eq.) versus trophic position (TP) for BDE 47 and 99, which were the dominant congeners in the food-web. Black circles represent detected observations and dashed lines represent non-detected observations below a sample specific, lipid normalized MDL. Red lines represent the log-linear regression of lipid equivalent concentration to TP over the entire food web.

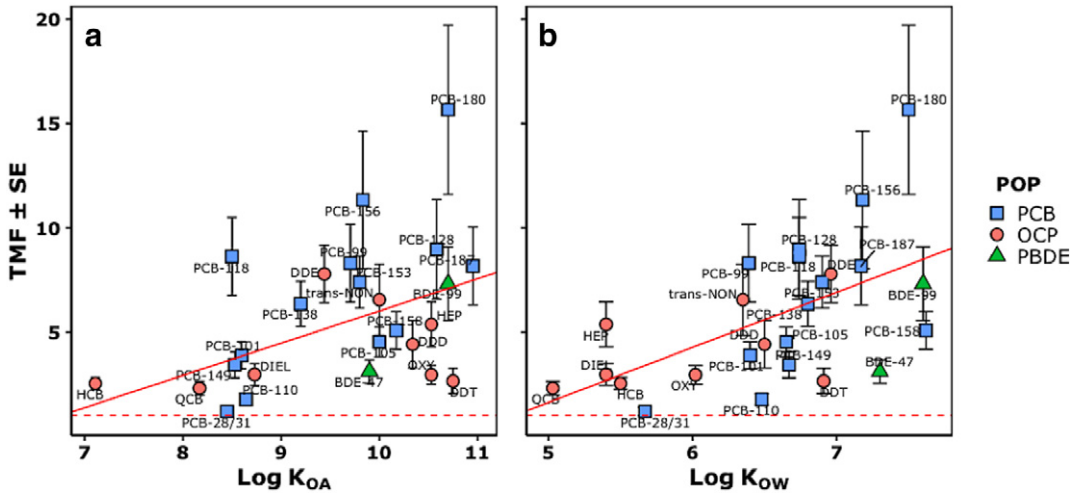


Fig. 7. a) Relationship between estimated TMF and log K_{OA} of each legacy POP (TMF = 1.55(Log K_{OA}) – 9.44; $F_{1,22.15} = 6.93$; $p = 0.0152$). b) Relationship between estimated TMF and log K_{OW} of each legacy POP (TMF = 2.64(Log K_{OW}) – 11.57; $F_{1,23} = 10.4$; $p = 0.004$). Solid red line represents the linear relationship between TMF and log K_{OA} or log K_{OW}, and the dashed red line represents a TMF of 1, indicating no biomagnification.

forward we plan to use our empirical data to develop a field-derived bioaccumulation model that would ideally be used as a regulatory tool to predict bioaccumulation potential of new chemicals in terrestrial environments.

Overall, our terrestrial study provides novel empirical data to the field of bioaccumulation. It also highlights the value of obtaining direct measures of trophic magnification of emergent POPs like PBDEs in terrestrial systems. Particularly, as PBDEs appear to have greater biomagnification in food webs with terrestrial air-breathing organisms than aquatic water- or air-breathing organisms. Our results also stress the importance of establishing separate standards and bioaccumulation criteria for terrestrial systems.

CRediT authorship contribution statement

Kate M. Fremlin: Data curation, Formal analysis, Investigation, Methodology, Project administration, Visualization, Writing - original draft, Writing - review & editing. **John E. Elliott:** Conceptualization, Project administration, Resources, Supervision, Funding acquisition, Writing - review & editing. **David J. Green:** Formal analysis, Resources, Supervision, Writing - review & editing. **Kenneth G. Drouillard:** Data curation, Investigation, Resources. **Tom Harner:** Data curation, Resources. **Anita Eng:** Data curation, Investigation. **Frank A.P.C. Gobas:** Conceptualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 2
Comparison between linear mixed effects model (LMM) for log K_{OA} and K_{OW} and terrestrial TMFs.

LMM	df	AIC	BIC	logLik	Deviance	χ^2	p-Value
Log K_{OA}	4	132.3	137.2	−62.17	124.3	2.84	<0.0001
Log K_{OW}	4	129.5	134.4	−60.75	121.5		

Appendix A. Supplementary Information

Supplementary information for this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.136746.

Supplementary Data File – Appendices 1 – 11 for this article can be found online at https://doi.org/10.25314/ffb4a6f5-fc0f-44c5-bbe0-4c7a6db66722.

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