PBDEs and other POPs in urban birds of prey partly explained by trophic level and carbon source

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HIGHLIGHTS
• As urban areas expand, many animal species are adapting and invading urban areas.
• Urban colonists encounter many new stressors, especially chemical pollution.
• Urban birds of prey in Canada had high levels of brominated flame retardants (PBDEs).
• One individual had the highest level of PBDEs ever recorded for wildlife.
• Such high levels may have had toxicological implications.

ABSTRACT
As urban sprawl and agricultural intensification continue to invade prime wildlife habitat, some animals, even apex predators, are managing to adapt to this new environment. Chemical pollution is one of many stressors that wildlife encounter in urban environments. Predators are particularly sensitive to persistent chemical pollutants because they feed at a high trophic level where such pollution is biomagnified. To examine levels of pollution in urban birds of prey in the Lower Mainland region of British Columbia, Canada, we analyzed persistent organic contaminants in adult birds found dead of trauma injury. The hepatic geometric mean concentration of sum polybrominated diphenyl ethers (∑PBDEs) in 13 Cooper's hawks (Accipiter cooperii) from Greater Vancouver was 1873 ng/g (lipid weight) with one bird reaching 197,000 ng/g lipid weight, the highest exposure reported to date for a wild bird. Concentrations of ∑PBDEs, ∑PCBs (polychlorinated biphenyls) and, surprisingly, cyclo-diene insecticides were greatest in the urban environment while those of DDE (1,1-dichloroethylene bis[p-chlorophenyl]) were highest in a region of intensive agriculture. The level of most chlorinated and brominated contaminants increased with trophic level (δ15N). The concentrations of some contaminants, PBDEs in particular, in these birds of prey may have some toxicological consequences. Apex predators in urban environments continue to be exposed to elevated concentrations of legacy pollutants as well as more recent brominated pollutants.

1. Introduction
Human activity in the Anthropocene has been so pervasive that it has an overriding influence on global biogeochemical cycles comparable only with the greatest forces of nature (Steffen et al., 2007; Zalasiewicz et al., 2010). In particular, intensive urban and agricultural developments have caused rapid global habitat loss and degradation as such developments generally occur in biodiversity hotspots, particularly estuaries and riverine corridors (McKinney, 2002). In addition to deteriorated habitat, 21st century farming practices and urbanization can lead to indirect threats to biodiversity via chemical pollution from, for example, heavy metals, polycyclic aromatic hydrocarbons, rodenticides and persistent organic pollutants (Liu et al., 2010; Albert et al., 2010; Cizdziel et al., 2013). Those stressors are most evident when studying top predators, such as large birds of prey.

Top predators require extensive resources and usually have large home ranges, and are consequently often inherently rare (Sergio et al., 2005, 2008). Rarity coupled with large home ranges and direct competition with humans makes top predators particularly susceptible to the multiple stressors of habitat loss, over-exploitation and direct persecution (Johnson et al., 2007; Sergio et al., 2008). Furthermore, because many forms of pollution biomagnify through food webs, they occur in greatest concentrations in top predators (Cabana and Rasmussen...
1994; Henny and Elliott, 2007; Elliott and Elliott, 2013). Nonetheless, those same traits mean that the ecology of top predators can be used to track anthropogenic change; top predators integrate signals over large scales and across entire communities, and can therefore be good indicators of chemical pollution in the environment (Noble and Elliott, 1990; Peakall et al., 1990; Henny and Elliott, 2007; Grove et al., 2009; Elliott and Elliott, 2013).

Although urban and industrial-scale agricultural development has caused the extinction or global population decline of many animals, a suite of adaptable, generalist species have taken advantage of these novel habitats to become relatively abundant (Bird et al., 1996; Gompper, 2002; Bonier et al., 2007). At the apex of those food chains are predators which have successfully adapted to human-altered landscapes, often by being nearly invisible to humans (Bird et al., 1996; Gompper, 2002). For instance, the densest populations of some bird-eating birds of prey occur in urban environments, where they consume large numbers of abundant, often introduced, bird species (Bird et al., 1996; Boal and Mannan, 1998; Rutz, 2008).

As many chemical pollutants originate from point source industrial and agricultural applications, urban and near-urban top predators may be exposed to particularly high levels of pollution (Wiesmuller et al., 2002; Chen et al., 2007, 2013; Cesh et al., 2010; Yu et al., 2011). Indeed, birds of prey nesting near agricultural areas were among the species most-impacted by organochlorine pesticides in the mid 20th century, with many birds of prey showing dramatic population declines associated with high levels of DDT (dichlorodiphenyl-trichloroethane) and/or dieldrin (Grier, 1982; Spitzer et al., 1978; Peakall et al., 1990; Sibly et al., 2000; Elliott and Harris, 2002). However, chemical pollution in those environments may transfer in complex ways through anthropogenic food webs as urban human food, regardless of trophic level, is normally low in chemical pollution due to human health concerns. For instance, in urban environments, the degree of anthropogenic input (as assessed by enrichment of heavy carbon isotopes, δ13C, representative of a high-corn diet) is a better predictor of levels of brominated flame retardant levels in some raptor populations than trophic level (as assessed by enrichment of heavy nitrogen isotopes, δ15N), and individuals feeding in food webs high in anthropogenic input have higher levels of brominated flame retardants (Park et al., 2009; Elliott et al., 2009; Newsome et al., 2010).

Of particular consequence to those birds of prey are the POPs (persistent organic pollutants) that are defined by their tendency to persist and bioaccumulate (Henny and Elliott, 2007). Although the legacy persistent organic pollutants (POPs) have been virtually banned for nearly fifty years, and are slowly disappearing from the global environment (Elliott and Elliott, 2013), levels remained sufficiently high that they continued to limit the recolonization of birds of prey, such as the peregrine falcon, in some systems (Elliott et al., 2005a). Moreover, while concerns about exposure to chlorinated legacy POPs continue, there are more recent conservation issues regarding contamination by brominated flame retardants, particularly polybrominated diphenyl ethers (PBDEs), which increased exponentially in the environment over the twenty years leading up to the 2000s (e.g. Lindberg et al., 2004; Elliott et al., 2005b; Miller et al., 2014, 2015). Applied to furniture and other human environments, PBDE levels are often highest in wildlife from urban regions, especially those using landfills where PBDEs may accumulate via air particulates (Elliott et al., 2009; Newsome et al., 2010; Gentes et al., 2012; Chen et al., 2012) or into aquatic systems via sewage (Henny et al., 2009, 2011). Following restrictions on their use in the early 2000s, PBDEs peaked during the mid-2000s and have now declined in the environment (Miller et al., 2014, 2015). Some authors have questioned the degree to which PBDEs bioaccumulate and biomagnify in homeotherms (Kelly et al., 2008; Elliott et al., 2009; but see Yu et al., 2011), and there is a need to identify the source of the high levels of PBDEs and other flame retardants in urban wildlife (Gentes et al., 2012). Furthermore, effect concentrations for PBDEs are often greater than those routinely measured in the wild, and it is unclear whether wild animals were harmed during the peak era of PBDE contamination, or if release and, so, broad exposure of top predators was contained prior to harm occurring (Harris and Elliott, 2011; Henny et al., 2009, 2011).

Our objectives were to measure exposure of two bird-eating top predators, the Cooper’s hawk (Accipiter cooperii) and the peregrine falcon (Falco peregrinus), to legacy POPs and polybrominated diphenyl ethers (PBDEs) in human-altered environments in British Columbia, Canada. As the highest levels of PBDEs among British Columbia seabirds (Miller et al., 2014, 2015) and British Columbia eagles (Cesh et al., 2008; Elliott et al., 2009) occur in the urbanized south coast, we speculated that urban birds of prey sampled in south-coastal British Columbia in the 2000s also would have elevated levels of PBDEs. We used two species from phylogenetically-distant orders to examine whether similar trends appeared among distantly related species, with presumably different physiological systems for metabolizing contaminants. We used carbon and nitrogen stable isotope ratios to help understand sources of legacy POPs and PBDEs. Although such patterns have been well quantified in aquatic birds of prey, few studies have quantified POPs and PBDEs in terrestrial systems (Yu et al., 2011; Chen et al., 2007; Voorspoels et al., 2007) and less is known of trends in these systems. We predicted that (1) organochlorine pesticides would be highest in the agricultural region; (2) brominated flame retardants would be highest in the urban environments; (3) levels of both contaminants would increase with trophic level (as approximated by δ15N); and (4) levels of brominated flame retardants would increase with anthropogenic input (as approximated by δ13C).

2. Methods

2.1. Study areas

We included an ‘urban’ (Lower Mainland), ‘agricultural’ (Okanagan) and ‘mixed’ (Vancouver Island) study site (Fig. 1). The Lower Mainland region of British Columbia, Canada, includes the largest city in British Columbia (Vancouver) and is a complex landscape of urban development and intensive agricultural (Hanna, 1997). The region is also home to the largest wintering population of raptors in Canada due to the warm temperatures and highly productive Fraser River delta (Butler and Campbell, 1987). We previously documented poisoning of birds of prey from use of anticholinesterase insecticides in areas of intensive agriculture of the Lower Mainland (Elliott et al., 2008), and from lead poisoning throughout the region (Elliott et al., 1992; Wayland et al., 2003). In addition, bald eagle (Haliaeetus leucocephalus) numbers have recovered from persecution and the organochlorine era, and the densest concentration of eagles in the world now occurs in this region during late winter (Elliott et al., 2011a; Jones et al., 2013). The Okanagan is a region of intensive agriculture with some fast-growing urban development. The residual contamination of wildlife in the Okanagan from past use of DDT continues to impact some raptor populations (Elliott et al., 1994, 2005a). Southeastern Vancouver Island is a mixture of intensive agriculture and urban centers.

2.2. Sample collection

Specimens were obtained opportunistically as part of a broader monitoring program for exposure of birds of prey to various contaminants, including insecticides (Elliott et al., 2008), rodenticides (Albert et al., 2010), mercury (Wheech et al., 2003) and lead shot (Elliott et al., 1992; Wayland et al., 2003). All specimens were autopsied for cause of death. Adults in good body condition were selected for analysis to avoid the influence of age and contaminant mobilization on liver residue concentrations. Analysis of raptor liver tissue included determination of chlorobenzenes ($\sum ClBz = 1.2,4,5$-tetrachlorobenzene, 1.2,3,4-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene),
hexachlorocyclohexanes ($\sum$HCH = $\alpha$-, $\beta$-, and $\gamma$-hexachlorocyclohexane), chlordane-related compounds ($\sum$CHLOR = oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor), dichlorodiphenyltrichloroethane (DDT) and its metabolites ($\sum$DDT = $p,p^\prime$-dichlorodiphenyltrichloroethane ($p,p^\prime$-DDT), $p,p^\prime$-dichlorodiphenyldichloroethylene ($p,p^\prime$-DDE), and $p,p^\prime$-dichlorodiphenyldichloroethane ($p,p^\prime$-DDD)), mirex, PCBs ($\sum$PCBs = 39 congeners identified according to IUPAC numbers: 17/18, 28/31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105/132, 110, 118, 128, 138, 149, 153, 156/171, 158, 170, 177, 180, 183, 187, 191, 194, 195, 201, 205, 206, 208, and 209), and PBDEs ($\sum$PBDEs = 12 congeners according to IUPAC numbers: 17, 28, 49, 47, 66, 100, 99, 85, 154, 153, 138 and 183). Congeners separated by a slash chromatographically co-eluted during the separation process and are therefore reported together.

Chemical analysis was performed at the analytical laboratory of the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor, which has been accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL), and followed procedures described in Guertin et al. (2010). Briefly, 2–4 g of liver homogenate was ground and added to a glass chromatography column containing hexane/dichloromethane (50% V/V, VWR, St. Catherines, Ontario, Canada) and overlaid with anhydrous sodium sulfate (VWR). Each column was spiked with 200 ng of 1,3,5-tribromobenzene (TBB; AccuStandard, New Haven, Connecticut, USA) for use as a surrogate recovery standard. The column was eluted and further extracted with hexane/dichloromethane (50% V/V) and the eluant roto-evaporated and made up to a volume with hexane. Extracts were removed for lipid determination by gravimetric methods. Clean-up of the extracts was performed by Florisil chromatography. Fractions 1 and 2 were analyzed for OCPs and PCBs by gas chromatography–electron capture (GC–ECD). Following sample injection on GC–ECD and re-capping GC-vials, the fraction 2 extracts were analyzed for PBDEs by gas chromatography–time of flight mass spectrometry (GC–TOF). For OCPs and PCBs, a Hewlett-Packard 5890 gas chromatograph with a 63Ni-electron capture detector, 7673 autosampler and DB-5 column (60 m × 0.250 mm ×0.1 μm DB-5; Chromatographic Specialties, Brockville, Ontario, Canada) was used for analysis. For PBDEs, a Hewlett-Packard HP 6890 gas chromatograph (GC) coupled with a Waters GCT-premier Time of Flight (TOF) high resolution mass spectrometer was used. Samples were extracted and analyzed in batches of five or six. With each batch, a method blank (containing 5 g sodium sulfate) and an in-house reference sample [Detroit River carp (Cyprinus carpio) homogenate] were co-extracted and analyzed. For OCPs and PCBs, analytes were quantified using a single point external standard (Quebec Ministry of Environment PCB mixture and a custom ordered certified OCP mixture; AccuStandard; Chromatographic Specialties, Brockville, Ontario, Canada) injected at the start of each sample batch analysis. Quality assurance and control procedures were outlined in Guertin et al. (2010). The cyclodiene insecticides were also calculated as dieldrin equivalents using a toxicity reference scheme (Elliott and Bishop 2011). DieldrinEQs were calculated as: DieldrinEQ = dieldrin + (0.8 × oxychlordane) + (0.5 × heptachlor epoxide).

2.3. Statistical analysis

All statistical analyses were performed with the statistical program R 2.15.1. Samples with concentrations below the detection limit were assigned a value of 0.5 times the lowest detectable limit for that chemical (LOQ/2). Residue concentrations were log-transformed to achieve normality. One-way ANOVA was used to test differences in contaminant concentrations, $\delta^{15}$N, and $\delta^{13}$C between species: Cooper’s hawk and peregrine falcon and among regions. Multiple regressions were computed with residue concentrations as the dependent variables and $\delta^{15}$N, $\delta^{13}$C and lipid content as the independent variables. We used separate principal components analysis for PCB congeners, PBDE congeners, OC
congeners and main groups to determine associations among different log-transformed contaminants. Because there were many, intercorrelated contaminants, we used a discriminant analysis to discriminate between species and sexes (for Cooper’s hawks only; there was only a single known female falcon). The discriminant analysis attempts to determine whether there is an overall difference between the groups by maximizing the Euclidean distance between the groups within the multivariate space. We then conducted a redundancy analysis to examine how variation in contamination was determined by stable isotope values and lipids. Redundancy analyses are a multivariate analogue to regression.

3. Results

Some individual birds had very high levels of pollutants, but the highest levels were not necessarily in the same individual. For example, one adult male Cooper’s hawk collected in the Vancouver suburb of Langley had 196 μg/g (lipid weight) ∑PBDE while an adult female collected in the nearby suburb of Surrey had 104 μg/g (lipid weight). An adult female collected in Comox, on Vancouver Island, had 763 μg/g (lipid weight) DDE and 128 μg/g (lipid weight) DieldrinEQs. All three birds were collected in April–May when they should have been on their breeding territories (Cooper’s hawks are generally year-round residents although they may undergo partial migration). An adult male collected in the Vancouver suburb of Richmond had the highest level of ∑BDEs (34.1 μg/g) and also fed on a food chain most enriched in 13C (−19.7‰).

Lipid content, δ13C and DDE did not vary between species or among sites (Table 1). Peregrine falcons had a higher δ15N than Cooper’s hawks, but δ13C did not vary among sites (Table 1). ∑PBDEs, ∑PCBs, DieldrinEQs and, marginally, TBB, varied among sites but not species, with levels lower in the agricultural site than other regions. As the urban and mixed sites did not differ in any of these analyses, and due to small sample sizes at the mixed site, we pooled data from mixed and urban sites in all additional analyses. When we merged the entire dataset and employed a general linear model with δ13C, δ15N and lipids simultaneously as covariates, TBB did not co-vary with any factor (δ13C: t23 = −1.80, P = 0.09; δ15N: t23 = 1.38, P = 0.18; lipids: t23 = −0.51, P = 0.62). ∑PCB, ∑PBDE, DDE and DieldrinEQ increased with δ13C (∑PCB: t23 = 3.38, P = 0.003; DieldrinEQ: t23 = 3.94, P = 0.007; ∑PBDE: t23 = 2.67, P = 0.01; DDE: t23 = 2.08, P = 0.05; Fig. 2) but not δ15N (∑PCB: t23 = 0.22, P = 0.83; DieldrinEQ: t23 = 0.32, P = 0.75; ∑PBDE: t23 = 0.34, P = 0.74; DDE: t23 = 1.82, P = 0.08) or lipid content (∑PCB: t23 = −1.12, P = 0.28; DieldrinEQ: t23 = −0.37, P = 0.72; ∑PBDE: t23 = −0.58, P = 0.57; DDE: t23 = −1.88, P = 0.07).

The first axis of all four principal component analyses (PC congeners, PBDE congeners, organochlorines and ‘main contaminant groups’ as shown in Fig. 2) explained 68–96% of the total variance, demonstrating that contaminants were highly intercorrelated with one another. Principal component 1 (PC1) for all four groups (with the sign of each principal component flipped to provide a more intuitive parameter) increased with δ13C (PCB: t23 = 3.34, P = 0.003; OC: t23 = 3.26, P = 0.003; BDE: t23 = 2.02, P = 0.05; Main: t23 = 3.43, P = 0.002) but not δ15N (∑PCB: t23 = 0.22, P = 0.83; OC: t23 = 0.34, P = 0.73; BDE: t23 = 0.82, P = 0.42; Main t23 = 0.30, P = 0.77) or lipid content (∑PCB: t23 = −1.10, P = 0.28; OC: t23 = −1.07, P = 0.30; BDE: t23 = −0.64, P = 0.53; Main: t23 = −0.15, P = 0.30). Only the principal component analysis including main contaminants had a second axis explaining more than 10% of the total variance, and was analyzed in more detail (Fig. 3). Principal component 2 (PC2) for that group decreased with δ13C (t23 = −2.67, P = 0.01) but not δ15N (t23 = 0.25, P = 0.80) or lipid content (t23 = 0.48, P = 0.63).

Male Cooper’s hawk livers (δ13C = −22.03 ± 1.34‰) were more enriched in δ13C than female livers (δ13C = −23.68 ± 1.30‰; t16 = 2.58, two-tailed P = 0.02; excludes the Okanagan birds due potential differences in δ13C baselines). However, male livers (9.36 ± 0.90‰) were no different from female livers (8.73 ± 1.95‰) in δ15N (t16 = 0.36, P = 0.94). Males (2.98 ± 1.28%) also did not differ from females (3.68 ± 0.85%) in lipid content (t16 = 1.28, P = 0.22). Likewise, there

![Fig. 2. Principal components analysis of the main contaminant groups in Cooper’s hawk livers from urban/mixed sites (coastal British Columbia; black symbols) and agricultural sites (interior British Columbia, open symbols) and in peregrine falcon livers from urban/mixed sites (gray symbols). Each arrow represents a contaminant with the direction representing where the contaminant loads within the principal component space and the length representing the magnitude of the loading. All analyses were run on log-transformed standardized data with values below the detection limit set to half the detection limit. A representation of what the different components mean is also shown (‘High in TBB’, ‘High in contaminants’, etc.).](image-url)
was strong overlap in a redundancy analysis of male and female liver contaminant burdens, but not between falcons and hawks (Figs. 4, 5).

4. Discussion

4.1. High levels of POPs in urban birds of prey

Forty years following essential cessation of DDT and cyclodiene pesticide use in the study area, metabolite and parent compound residues still persist at relatively high concentrations in these terrestrial raptors. Furthermore, levels of $\sum \text{PBDE}$ were also among the highest reported from anywhere, and were equal to the levels of $\sum \text{PCBs}$. Indeed, $\sum \text{PBDE}$ of 196 g/l lipid weight in a Cooper’s hawk is the highest level recorded, that we are aware of, in any wildlife. Concentrations of $\sum \text{PBDE}$ were greater in the urban environment (Table 1), as had been previously found in California and elsewhere, where $\sum \text{PBDE}$ increased with population size (Newsome et al., 2010; Chen et al., 2008). A Californian city-dwelling peregrine falcon contained $\sum \text{PBDE}$ of 94.4 g/l lipid weight, previously the highest concentration recorded in the literature (Park et al., 2009).

Studies of terrestrial birds of prey from Europe, China and North America reported elevated PBDEs in those species (Jaspers et al.,...
Although many of the polybrominated biphenyls (PCBs) and organochlorine (OC) pesticides were effectively banned from any substantial usage in the 1970s, food chain contamination continued in avian top predators, sometimes with detectable effects on physiological responses and even on reproduction (Best et al., 2010; Cesh et al., 2010; Helander et al., 2002; Murvoll et al., 2006). POPs of more recent origin, such as PBDE flame retardants, increased steadily in aquatic wildlife indicator species from across North America and the Baltic Sea since the early 1980’s (Norstrom et al., 2002; Elliott et al., 2005b; Jaspers et al., 2006; Miller et al., 2014, 2015). Indications now are of declines at least in Penta-BDEs as a result of voluntary and regulatory constraints on use (Gauthier et al., 2008; Crosse et al., 2013; Miller et al., 2014, 2015).

A comparison of BDE congener profiles between the Cooper’s hawk and the peregrine falcon demonstrated differences between species (see Figs. 2, 4), with hawks slightly more positive on PC2 than falcons. Such differences likely reflected differences in aquatic input. Terrestrial sparrow hawks shared a similar BDE congener patterns as this study’s Cooper’s hawks (Voorspoels et al., 2007); in particular, identical patterns were found in Voorspoels et al. (2007) of BDE99 > BDE47 > BDE153 > BDE100 > BDE183 > BDE154. In contrast, BDE153 was the most dominating congener in peregrine falcons. Similar congener patterns in Swedish peregrines were found with BDE153 > BDE 99 > BDE100 (Lindberg et al., 2004). Higher levels of BDE-47 are found in terrestrial habitats while higher levels of BDE-153 are found in marine habitats, likely representing the relative ability of different congeners to adhere to dust and move short distances within urban terrestrial environments compared with the ability to evaporate into the atmosphere and move long distances (Yu et al., 2011). Falcons prey substantially upon aquatic birds, including ducks and shorebirds, leading to higher levels of BDE-153. The proportion of aquatic input would vary with the amount of shoreline in a particular territory leading to variable BDE congener patterns (Park et al., 2009).

The persistence of the organochlorine pesticides, both the DDT and cyclodiene compounds, in the food webs of these terrestrial birds of prey even in urbanized areas of Metro-Vancouver, almost certainly derives from usage primarily during the 1950s to 1970s and persistence in local soils. Much of the landscape of the Metro-Vancouver municipalities of Delta and Langley and to a lesser degree, Surrey, remains as agricultural land. In the past, land use even in parts of Vancouver city proper included intensive agricultural production and associated use of insecticides to control soil pests, until the 1970s mainly dieldrin and heptachlor (Elliott et al., 1996; Boyle et al., 1997; Elliott et al., 2011b; Szeto and Price, 1991; Wan et al., 1995). DDT was also used for mosquito control and applied to wetlands and even sprayed regularly in residential neighborhoods. The low pH clay soils of the Lower Fraser Valley and adjacent former flood plain are also prone to retain pesticide residues for decades (Szeto and Price, 1991; Wan et al., 1995; Wilson et al., 2002).

### 4.2. Associations with stable isotope ratios

Most of the contaminants were inter-correlated with one another, and all groups of contaminants increased with trophic level as inferred by δ15N. For most groups, about 30% of the variation in contaminant level was associated with δ15N (Fig. 3). Those persistent organic pollutants are of concern specifically because they tend to bioaccumulate in tissues, especially lipids, and are only slowly eliminated from the body, leading to biomagnification within the food web (Elliott and Shutt, 1993; Elliott and Martin, 1994; Wiesmüller et al., 2002). It is therefore not surprising that many previous studies alongside the current study have demonstrated a positive association between trophic level and contaminant levels in birds, particularly birds of prey (Elliott et al., 2009; Henny et al., 2009; Guiguero et al., 2012; Elliott et al., 2012) and even in non-aquatic food webs (Chen et al., 2007; Voorspoels et al., 2007; Yu et al., 2011). Biomagnification is generally lower for brominated than chlorinated compounds due to

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**Fig. 4.** Discriminant analysis of log-transformed contaminants in raptor livers. The ellipses represent the 95% confidence intervals. The discriminant analysis examines the overlap between the different groups within the multivariate space occupied by the different contaminants.

**Fig. 5.** Redundancy analysis of log-transformed contaminant levels (text) on environmental variables (percent lipids, δ13C, δ15N, represented by vectors) in peregrine falcon (open symbols) and female (black symbols) and male (gray symbols) Cooper’s hawk livers. The redundancy analysis is a multivariate analogue of regression and shows associations between the three environmental variables shown by vectors and the contaminants shown by the text.
biotransformation and/or because they are less lipophilic (Elliott et al., 2009; Henny et al., 2009; Yu et al., 2011), and likewise the relationships are somewhat weaker for PBDEs than organochlorines and PCBs in our dataset (Fig. 3). Furthermore, baseline δ13C may vary by at least 5‰ due to variation in anthropogenic input, which tends to be enriched in 13C, and other factors influencing baseline levels of δ13N, likely explaining some of the residual variation in the relationship.

Much of the remaining variation in contaminant patterns were likely spatial. For instance, urban birds of prey had higher levels of PBDEs, PCBs and DieldrinEQs. As the first two contaminants are primarily associated with industrial and commercial applications, this is perhaps not surprising. DDE levels did not vary significantly with location due to high trophic level falcons from the urban site having high levels of DDE; if one examines only DDE in Cooper’s hawk, levels are clearly highest in agricultural area reflecting high levels of past application. Elliott et al. (1994, 2005a) argued that levels are so high in that region that they explain why falcons currently still cannot reproduce successfully in that region. In contrast to Newsome et al. (2010), who found that high levels of the highly brominated PBDEs in peregrine falcons from California were associated with anthropogenic food sources (corn-based food webs with enriched δ13C), we found no association between δ13C and PBDEs with the exception of the one hawk with high ∑PBDEs and enriched in δ13C. Thus, although urbanization appeared to be associated with high PBDEs, δ13C did not appear to be a good indicator of urbanization. None of our birds of prey had δ13C greater than −19‰ while most urban birds of prey in California fell above that threshold; human food webs in Canada are less corn-based than in the United States, and consequently δ13C is less enriched. Thus, the smaller range of δ13C and lack of discrimination between anthropogenic and natural food webs may have confounded such relationships within our dataset, although it is also possible that most of the birds in our study were feeding largely on ‘natural’ food webs within urban green spaces and associated ‘feeder birds’. The high level of contamination implies that contaminants are dispersing from anthropogenic food webs into neighboring food webs.

4.3. Urbanization of high quality natural environments

Urbanization is a global threat to biodiversity as humans often prefer the same high quality natural environments required by wildlife. At our urban site, yellow-billed cuckoos, western screech-owls and ruffed grouse are three species that have been extirpated from the urban–suburban matrix in the past century due to multiple stressors compounded by urbanization. On the other hand, many species including apex predators are able to adapt to the new environments and colonize urban ecosystems, especially cities with extensive green spaces and corridors. For instance, populations of some species birds of prey are now densest in some cities (Bird et al., 1996; Boal and Mannan, 1998; Rutz, 2008). Peregrine falcons are particularly numerous in some cities, nesting on skyscrapers, as they were originally hacked there as part of species conservation programs. Likewise, bald eagle populations have recovered from the organochlorine era, and some of the densest populations of eagles in the world winter and breed in the Fraser Delta, where they sometimes nest in backyards and industrial complexes (e.g. Elliott et al., 2009, 2011a; Jones et al., 2013). Such colonists can be sustained in the long-term as shown by, for instance, monkeys in Indian cities.

Urban wildlife encounter multiple stressors including high levels of parasites, high mortality due to domestic animals and collisions with vehicles and windows (Bishop and Brogan, 2013; Krone et al., 2005; Mannan et al., 2008; Hager, 2009; Hindmarch et al., 2012), and, as we demonstrate, toxic contamination. As reported in other recent studies of avian terrestrial top predators, this ‘guild’ of birds is exposed to elevated ‘concentrations’ of PBDEs as well as lingering legacy POPs. To maintain healthy populations of urban wildlife with associated social benefits to humans, it will be necessary to monitor and restrict levels of chemical pollution.

4.4. Implications for ecological differences

Both the Cooper’s hawk and peregrine falcon have similar diets of small to medium terrestrial birds (Roth et al., 2005), although peregrines prey on larger birds and often on aquatic species, such as shorebirds, waterfowl and gulls (Elliott et al., 2005a). The average δ14N of the peregrine was significantly higher than that of the Cooper’s hawk, suggesting that peregrines are feeding at a higher trophic level and in more marine environments. As such, it is not surprising that the overall mix of contamination discriminates from the mix in Cooper’s hawks (Fig. 5).

Like most birds of prey, Cooper’s hawks show reversed sexual size dimorphism, with females larger than males. One explanation for this trend is that it allows for high feeding rates to offspring as the male targets smaller prey than the female. In our study, males actually fed at a slightly higher trophic level and there was no difference in the contaminant mixture between the two sexes (Fig. 5). However, male livers were more enriched in 13C than female diets, which may indicate that males are more likely to selectively target “dumpster birds”, starling flocks in agricultural fields, or other locations where birds congregate on anthropogenic food. Females, meanwhile, may be more likely to target native species in green spaces within the overall urban matrix. That observation could be expanded with additional work directly observing prey delivered at nests by each sex. In any case, our work provides some support for the hypothesis that reversed sexual size dimorphism is driven by segregation in sexual foraging niche.

4.5. Toxicological implications

It is uncertain whether the relatively high levels of ∑PBDEs present in urban birds of prey are having any reproductive or other sub-lethal effects, for example, on thyroid or other endocrine functions. A minimum avian reproductive effectiveness threshold for ∑PBDEs, in the range of 1–2 μg/g ww in eggs was suggested by Harris and Elliott (2011). In the present study, five Cooper’s hawks and two peregrine falcons had concentrations within or exceeding that threshold, assuming an egg/liver ratio of one (Braune and Norstrom, 1989). Despite some evidence of effects in laboratory studies at putative environmentally relevant exposures (Fernie et al., 2006; Harris and Elliott, 2011), indications of any effects of PBDEs on wild birds are limited (Cesh et al., 2010; Henny et al., 2009, 2011). More research would be needed on wild populations, but is now likely to be limited given the clear indications that PBDEs are generally decreasing in most foodchains (Crosse et al., 2013), including those in British Columbia (Miller et al., 2014 2015). Some recent data on captive zebra finches (Taeniopygia guttata) reported that exposure during early development had significant effects on later adult behavior and reproductive parameters such as clutch size (Eng et al., 2012; Winter et al., 2013). However, assessment of such endpoints in the field, particularly in raptors, would be logistically challenging.

Additionally, one Cooper’s hawk had levels of DDE above the level of 10 μg/g ww estimated to thin egg shells by 20% in Eurasian sparrowhawks (Accipiter nisus) (Newton et al., 1986; Elliott and Martin, 1994). More than anything, that result is another example of the extreme persistence of DDE in these terrestrial foodchains, more than 40 years since cessation of usage (Elliott et al., 1994, 2005a).

5. Conclusions

Samples of two urban raptors species taken from urban Vancouver exceeded the highest concentrations of ∑PBDEs reported in the literature for wild birds, with some individuals exceeding putative effect levels for ∑PBDEs (Harris and Elliott, 2011). Our findings indicate that Cooper’s hawk and peregrine falcons of southern British Columbia continue to be exposed to relatively elevated concentrations of legacy POPs. The more urbanized Cooper’s hawks have been exposed to greater...
concentrations of these chemicals as rural hawks. Currently, further research is underway focused on a population of Cooper’s hawks breeding in the Metro-Vancouver region, in order to investigate sources and potential effects of those chemicals.

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