Sources and effects of persistent organic pollutants and brominated flame retardants in Cooper’s hawks (*Accipiter cooperii*) of Vancouver, British Columbia

by

Jason M. Brogan

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Name: **Jason M. Brogan**

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Title: ***Sources and effects of persistent organic pollutants and brominated flame retardants on Cooper's hawks (Accipiter cooperii) of Vancouver, British Columbia***

Examining Committee: **Chair: Dr. Leah Bendell**
Professor

Dr. Ron Ydenberg
Senior Supervisor
Professor

Dr. John Elliott
Supervisor
Adjunct Professor

Dr. David Green
Supervisor
Professor

Dr. Tony Williams
Internal Examiner
Professor

Date Defended/Approved: October 14, 2014

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Abstract

Birds of prey are excellent indicators of environmental health. Since they are top predators, they accumulate a high concentration of persistent organic pollutants (POPs). Cooper's hawks (*Accipiter cooperii*) are abundant in urban areas but these environments have been associated with POPs known to cause adverse physiological effects. To investigate the exposure and effects of POPs and flame retardants in Vancouver, British Columbia, we assess the influence of diet, and landscape variables, such as land use and population density on plasma concentrations of pollutants in adult and nestling Cooper's hawks. We then examined how these pollutant influence thyroid hormones and the fledge success. Our results suggest that: 1) concentrations of DDE are relatively high, 2) urbanized areas were most associated with industrial chemicals; ΣPCB and ΣPBDE, which were also negatively influencing thyroid hormone concentrations, and 3) diet most influenced dieldrin concentrations, which were associated with fledge success.

Keywords: persistent organic pollutants; PBDEs; thyroid hormones; Cooper's hawk; urbanization; fledge success

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Chapter 1. General Introduction

1.1. Urbanization

Human population growth puts increased stress on natural areas. One major human activity which threatens wildlife and their habitats is urbanization, leading to loss of biodiversity and species extinction (McKinney, 2002; Pimm & Raven, 2000). Currently, in 2013, the world population is approximately 7.2 billion and it is projected to grow to 9.6 by 2050 (United Nations, 2013). There is a growing trend for the world's population to concentrate increasingly in larger and larger cities. World-wide, 50% of people now live in urban areas, and in North America, 80% inhabit cities and their satellite communities (World Bank, 2013).

Urban areas contain many hazards to wildlife, allowing some species to adapt better to the anthropogenic environment than others. Urbanization has led to a loss of biodiversity in highly urbanized areas with an abundance of non-native species in those environments, such as European starlings (*Sturnus vulgaris*) and house sparrows (*Passer domesticus*; Blair, 1999, 2007; McKinney, 2002). Urban environments are associated with increased threats to health and survival of wildlife caused by window strikes and vehicular collisions, (Bishop & Brogan, 2013; Hager, 2009; Hindmarch et al., 2012), disease (Mannan et al., 2008), and exposure persistent organic pollutants (POPs; Morrissey et al., 2013, 2014). Some raptor species have adapted to urban areas, taking advantage of abundant prey, protection from their predators, and availability of man-made structures for nests and perches (Bird, Varland, & Negro, 1996). Some species of raptors have been found in higher densities and are more successful in urban areas versus the natural habitats (Boal & Mannan, 1998). These top predators are ideal monitors of environmental pollution.

1.2. Background of persistent organic pollutants

The Stockholm Convention describe a persistent organic pollutant as a group of chemicals that are persistent in the environment, bioaccumulate in biota, can be toxic, and easily transported over long distances (UNEP, 2001). POPs can be grouped as pesticides, industrial chemicals and by-products of chemicals. Pesticides include many organochlorine compounds such as dichloro-diphenyl-trichloroethane (DDT), chlordane, and dieldrin. Industrial chemicals include polychlorinated biphenyls (PCBs). A class of POPs of recent concern is brominated flame retardants particularly formulations of polybrominated diphenyl ethers (PBDEs).

Legacy POPs, such as DDT and dieldrin, have been banned since the 1970 and 1980s respectively, but they are still being detected at potentially harmful level in eggs and blood of birds of prey. Clark et al. (2009) recently reported a maximum concentration of DDE, the metabolite of DDT, in a peregrine falcon (*Falco peregrines*) egg exceeding the critical level known to cause eggshell thinning and embryotoxicity (Peakall et al. 1990). Cesh et al. (2008) observed three bald eagles (*Haliaeetus leucocephalus*) containing levels of DDE which surpassed a critical limit where productivity falls below a minimal sustainable rate (Elliott & Harris, 2002). After DDT was banned and concentrations of DDT and DDE were declining, there was delay in the recovery of some birds of prey. Research in the United Kingdom and North America suggest that dieldrin, a pollutant known to cause negative affects to the central nervous system, was the cause of the repressed population growth of Accipiters, after the banning of DDT (Elliott & Martin, 1994; Newton & Wyllie, 1992).

The Great Lakes, known for areas of heavy PCB pollution, has been used to investigate the effects of PCB on wildlife. A long term monitoring program of Great Lakes waterbirds has reported adverse behavioural and physiological effects related to increased concentrations PCBs (Fox et al., 1998; Gilbertson et al., 1991; Grasman et al., 1998). Those effects were not limited to only waterbirds, as there is evidence that PCBs reduced the reproduction of bald eagles along the Great Lakes (Best et al., 2010).

The more recent industrial chemical compounds, PBDEs, share similar structure and effects as PCBs, but may have different accumulation dynamics. PDBEs are similar in that they are lipophilic, bioaccumulate (Vonderheide, Mueller, Meija, & Welsh, 2008) and they act as endocrine disrupters causing growth alterations (Chevrier et al. 2010; McKernan et al., 2009; Van den Steen et al., 2010). ΣPBDEs, however were found to not be linked with trophic level ($\delta^{15}N$) unlike ΣPCBs (Elliott et al., 2009). Over a period of 20 years concentrations of ΣPBDE have increased in California peregrine falcon eggs while ΣPCB concentrations, although found in greater concentrations, did not change significantly (Park et al. 2009). This is indicative of a different mode of accumulation.

1.2.1. Factors determining toxicity

If duration and quantity of exposure are equal, toxicity can vary within and between species based on life history traits, and genetic variation in the sensitivity of individuals and species. The age, sex, and body condition can be general predictors of the relative concentration of a pollutant (Elliott & Shutt, 1993; Newton et al., 1981). Older males tend to have the greatest concentration of pollutants in their tissues while the female offloads her pollutant body burden into her eggs thus lowering her residue concentrations (Van den Steen et al., 2009; Verreault et al., 2006). Between species, habitat and prey preference play a role in exposure (Klaassen, 2008; Walker, 1983). Species specific metabolism of pollutants also influences the body burden (Letcher et al., 1998, Hoekstra et al., 2003). There is variation in the sensitivity to dioxin-like compounds, such as PCBs, due to genetic differences in protein receptor composition (Head et al., 2008).

The environmental fate and movement of a pollutant is influenced by its' chemical properties. One of the most important factors is the chemical's polarity, which leads to another important factor used to determine environmental fate - the octanol-water coefficient ($K_{OW;}$ Walker, 2012). When a pollutant is less polar the more lipid soluble it is and the higher it's $K_{OW.}$ The K_{OW} is used to determine the persistence of a pollutant in soil, sediment and wildlife (Walker, 2012). Other important factors include the chemical's other medium partition coefficients (e.g. octanol-air), vapour pressure, Henry's Law coefficient, and chemical stability (Klaassen, 2008; Walker, 2012). These variables with the inclusion of the chemical's fugacity, or tendency to move from one environmental medium to another, have been used in predictive models of a pollutants environmental fate (Gobas, 1993; Walker, 1987). Armitage et al., (2007) designed a model estimating the biomagnification potential of POPs in a terrestrial food chain using and testing a predictive model based on K_{OW} and K_{OA}.

1.3. Thyroid hormones

Many pollutants have been found to cause endocrine disruption, some of them are known to affect thyroid function (McNabb & Fox, 2003). The chemical structures of endocrine disrupting chemicals are similar to the body's natural hormones. In the case of the thyroid hormones, they mimic thyroxine (T4). The resulting effect of endocrine disrupting chemicals interactions can lead to less circulating T4 through interaction with thyroid hormone metabolism and transport and altered thyroid gland function (Brouwer et al., 1998; McNabb & Fox, 2003). In juvenile birds, thyroid function is necessary for proper growth and development. In adult birds, thyroid function is necessary for reproduction, behaviour, and metabolism function (McNabb, 2007).

1.4. The Cooper's hawk

The Cooper's hawk (*Accipiter cooperii*) has many characteristics that make it an ideal candidate for monitoring POP exposure in urban wildlife. First, they are resilient to human intrusions and rarely abandon their nests if disturbed, even early in the nesting cycle (A. Stewart pers. comm.). Between 1980 to 1993, over 3500 nest were visited and only 4 of the 350 nests failed due to research related disturbance (Curtis et al., 2006). Second, they exhibit high nest fidelity (Rosenfield et al., 1995; Mannan et al., 2000) which allows for multiple observations over time. Third, they are year round residents to the Vancouver area (Campbell et al., 1990) and thus exposure to pollutants is local. Fourth, Cooper's hawks are high on the terrestrial food chain, which puts them at greater risk to of accumulating persistent bioaccumulative contaminants (Jaspers et al., 2006).

Accipiters are known to be vulnerable to POP poisoning due to their life history characteristics (Elliott and Martin, 1994; Newton and Wyllie, 1992; Noble and Elliott, 1990; Sibly et al., 2000; Snyder et al., 1973). For example, mortalities observed in

Cooper's hawks of New Jersey coincided with passerine poisonings due to chlordane, leading researchers to believe that the Cooper's hawks were also negatively affected by the pesticide (Stansley and Roscoe, 1999). Recently, data has been obtained from Cooper's hawk and peregrine falcon liver tissues from the Lower Mainland, Vancouver Island, and the Okanagan Valley. Elliott et al. (2010) reported that ΣPBDE concentrations in five of 21 Cooper's hawks sampled from the Lower Mainland averaged greater than an effects level of 1.8ug/g ΣPBDE ww (Harris & Elliott, 2001). The study also reported the highest concentration in wildlife of ΣPBDEs in literature: 197 µg/g lipid weight, compared to 94 µg/g lipid weight in peregrine falcons (Park et al., 2009).

1.5. Thesis structure

The now widespread presence of POPs and PBDEs in the environment and their bioaccumulation in wildlife top predators warrants further assessment of threats, whether there is need for stricter management of PBDE containing materials in waste streams and municipal landfills, and if continued remediation of legacy pollutants is necessary. This thesis aims to identify potential routes of exposure and possible effects of POPs and ΣPBDEs on Cooper's hawks across the Metro Vancouver area.

We investigate the sources of pollutants in the plasma of Cooper's hawks of Metro Vancouver in chapter 2. There have been reports of increased concentrations of both ΣPCBs and ΣPBDEs associated with the level of urbanization and population density (Morrissey et al, 2013; Newsome et al., 2010). Our objective is to determine which class of variables, urbanization or diet, best explains the variability of the OC pollutants; dieldrin, trans-nonachlor, and DDE, ΣPCBs, and ΣPBDEs found in plasma of Cooper's hawks. Urbanization is defined by population density, or land use (agriculture, recreation, lakes and water, institutional, undeveloped, industrial, and residential/commercial) found within the average home range of each Cooper's hawk. Diet is defined as the carbon and nitrogen isotope signatures of each bird measured.

In chapter 3 we investigate effects of pollutants on thyroid hormones and reproductive success of Cooper's hawk. There is evidence that certain pollutants affect the proper thyroid function. All pollutants under investigation have been associated, either directly or indirectly, with reduced reproductive success in birds of prey (Brouwer et al., 2008; McNabb & Fox, 2003). Our objective is to determine which pollutant; DDE, ΣPCBs, ΣPBDEs or total contaminant load was most associated with concentrations of thyroid hormones total thyroxine (TT4) and total triiodothyronine (TT3). We further examined which variable; dieldrin, trans-nonachlor, DDE, ΣPCBs, ΣPBDEs, total contaminant load, TT4, TT3 was most associated with the fledge success of the Cooper's hawk.

The 4th and final chapter is a summary of the previous chapters and discusses directions for future research in this field.

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Chapter 2. Sources of persistent organic pollutant and flame retardant exposure in Cooper's hawks (*Accipiter cooperii*) of Metro Vancouver, British Columbia.

2.1. Abstract

Increases of a centralized human population leads to increased concentrations of some persistent organic pollutants (POPs; Morrissey et al., 2013; Newsome et al., 2010). POPs have been reported to cause adverse physiological effects and lowered reproductive success in birds from many field and laboratory studies. We investigated the potential sources of legacy POPs and more recently used contaminants in Cooper's hawks (*Accipiter cooperii*) in the mainly urbanized Vancouver, British Columbia area. Over a two year period, 2012-2013, we collected blood samples from 21 adult and 15 nestlings Cooper's hawks associated with 22 nest sites. Nine adults were radio tracked to determine the average home range. We examined how spatial variables, such as land use and population density within the home range, and diet ($\delta^{13}C$ and $\delta^{15}N$) was associated with concentrations of dieldrin, trans-nonachlor, dichlorodiphenyldichloroethylene (DDE), total polychlorinated biphenyls (ΣPCBs), and total polybrominated diphenyl ethers (ΣPBDEs) in plasma of adult and nestling Cooper's hawks. We found the average home range of Vancouver's Cooper's hawks to be 4.71 ± 1.40 km^2. Plasma dieldrin concentrations were positively associated with $\delta^{15}N$, and ΣPCBs and ΣPBDEs were positively associated with increased urbanization. Our results suggest that legacy pollutants are still apparent in the food chain and the environment, with industrial chemicals most associated with urban areas.

2.2. Introduction

As the global human population increases to over nine billion by 2050 (United Nations, 2013; World Bank, 2011) urbanization of land is expected to similarly increase leading to degradation and loss of natural habitats and biodiversity (Blair, 1999; McKinney, 2002). Some wildlife species, however, have been adapting and thriving in large urban centers. These urban exploiters are usually dependant on human food subsidies, are non-native, and do not need the vegetation that urban-avoiding species depend on (Blair, 1999). For example, the Norway rat (*Rattus norvegicus*) and European starling (*Sturnus vulgaris*) can be found in urban areas across Europe and North America (McKinney, 2002).

Urban dwelling avian species can face increased threats from disease (Boal & Mannan, 1999), trauma from striking buildings and vehicles (Bishop & Brogan, 2013; Boal & Mannan, 1999; Roth et al., 2005), along with increased exposure to pollutants (Morrissey et al., 2013; Newsome et al., 2010; Wiesmüller et al., 2002; Yu et al., 2011). There is nonetheless a less diverse but abundant community of urban adapted species which can be useful as monitors of environmental pollution.

Urban pollutants of concern include persistent organic pollutants (POPs) such as the polychlorinated biphenyls (PCBs) used for decades in many industrial processes. Urban environments can also be residually contaminated by organochlorine (OC) pesticides as intensively used agricultural land is turned into urban development (Harris et al., 2000). Countries in North America and Europe imposed heavy restrictions on these legacy POPs in the 1970s to early 1980's, while the Stockholm Convention imposed global restrictions or bans on production and use since 2004 (Hagen & Walls, 2005). Nevertheless, these chemicals continue to be reported in wildlife, particularly top predators, and are often correlated with health effects (Bustnes et al., 2002; Cesh et al., 2008; Henny et al., 2009; Morrissey et al., 2014).

In recent decades the polybrominated diphenyl ethers (PBDEs) have emerged as important contaminants of both urban and remote environments (Chen & Hale, 2010). PBDEs are widely used as additive flame retardants on household and office furnishings and equipment. Commercial production began in the 1970's, by 1989 approximately

100,000 tonnes were produced and 10 years later production of PBDE's had doubled (Alaee, 2003). Since 2008, under the *Canadian Environmental Protection Act, 1999* Canada has banned all PBDE congener manufacturing but the importation of the *deca-BDE* is still is allowed in Canada. In 2010, however, a voluntary commitment among the largest deca-BDE producers to phase out exportation to Canada began (Environment Canada, 2013). Currently tetra-BDE, penta-BDE, hexa-BDE and hepta-BDE are listed in Annex A of the Stockholm Convention; where governments signed in agreement with the Convention agreed to eliminate the production and use of these pollutants (UNEP, 2001).

Pollutants in urban environments need to be monitored due to the increasing human population growth and input of man-made pollutants. Due to the bioaccumulative properties of POPs, monitoring would best be conducted in top predators, such as birds of prey; representing the maximum concentration in that food-chain. While most ecotoxicology studies on raptors have focused on non-urban, piscivorous species; urban adapted birds of prey are advantageously easily assessable for research (Bird et al. 1996).

The Cooper's hawk (*Accipiter cooperii*) is an abundant bird of prey which has moved into more urbanized areas in the past few decades, preying mainly on terrestrial birds Cooper's hawks are a useful model to examine urban environmental pollutants; 1) they have successfully adapted to urban areas over the past few decades and can routinely be found in greater densities than in adjacent rural or forested areas (Boal & Mannan, 1998; Rosenfield et al., 1995; Stewart, 1996), 2) they are resilient to human intrusions; rarely abandon their nests if disturbed, 3) they exhibit high nest fidelity allowing for multiple observations over time (Rosenfield et al., 1995; Mannan et al., 2000), 4) they prey almost exclusively on medium sized terrestrial birds (Boal & Mannan, 1998; Cava et al., 2012; Stout et al., 2007; Stout & Rosenfield, 2010).

In this study, we assess exposure of Cooper's hawks to legacy pollutants and brominated flame retardants in the area of Vancouver, British Columbia, Canada. Specifically, we quantified land-use variables and average population density found within the home range of sampled nests, and diet variables; $\delta^{12}C$ and $\delta^{15}N$ of individual sampled hawks, to find the most important variable influencing the concentrations of organochlorine pesticides; dieldrin, trans-noncahlor, and DDE, ΣPCBs, and ΣPBDEs.

2.3. Methods

2.3.1. Nest searching

Potential nest site were located throughout the western Metro Vancouver region through the use of citizen science and call-playback. We compiled at dataset of potential nesting sites for Cooper's hawks throughout Metro Vancouver area using information from eBird.com, BC Breeding Bird Atlas, from local naturalists. We visited each site and used call-playbacks to determine if Cooper's hawks were present (Rosenfield et al., 1985). Playbacks were conducted 15 minutes before sunrise until one hour after sunrise. If a hawk responded to playback the hawk was observed until a nest was located.

2.3.2. Capturing and blood sampling of adults and chicks

We captured adult Cooper's hawks between June 19th and July 17th in 2012 (when chicks were approximately 10-15 days old), between April 17th to the April 26th 2013 (during pre-incubation), and again from July 3rd to July 6th 2013 (when chicks were approximately 10-15 days old). Adults were captured using a doh gazza method (Bloom et al., 2007). A 100mm nylon mesh mist net (2.6 m x 6 m; avinet.com), occasionally two in a V – shape formation, was lightly attached to poles with clothes-pins and placed in the territory of the Cooper's hawk, within 10 m of the nest tree. The lure - a great-horned owl (*Bubo virginianus*) tethered to a perch, was place between the nest tree and the mist-net(s). Cooper's hawk call-playback was used to get the attention of the to-be-captured Cooper's hawk. We captured nestlings by having a professional tree climber access the nest when nestlings were approximately 10 to 21 days of age. Nests were accessed from June 14th to 28th 2012 and 2013.

We banded and measured adults and nestlings captured. We attached a USFS band to the left tarsus. We weighed each individual with a Newton scale (± 1 gram), measured the halux (± 0.1mm), tarsus length (± 0.1 mm), bill length (± 0.1 mm), and bill depth (± 0.1 mm) with analog calipers, and measured the wing chord (± 1 mm), and tail length (± 1 mm) with a wing rule. We collected a maximum of 3ml, and never more than 1% of the individual's body weight, using a 3ml syringe and a 26 gauge needle. We transferred the blood to a 4ml heparin coated Vacutainer tube which was kept on ice until centrifuged within 6 hours of collection. We transferred the plasma of the centrifuged samples to acetone/hexane rinsed glass vials for contaminant analysis, microcentrifuge tubes for stable isotope analysis, and nalgene cryovial tubes for thyroid hormone analysis. We stored the glass vials and microcentrifuge tubes in -20^{o}C freezer and the cryovials in -80^{o}C freezer until they were to be analyzed. All data was collected according to the following permits: BC Ministry of Environment permit SU12-7796, sub banding permit 10761A, and Animal Care permit 1026B-11.

2.3.3. Stable isotope (δ13C and δ15N) processing

We dried approximately 100µL of plasma in an oven at 60^{o}C for two days. We crushed the dried plasma to a powder using a sterilized mortar and pestle and enclosed between 0.8–1.2 mg of ground, dried plasma in a tin capsule that was shipped to University of California-Davis Stable Isotope Facility for analysis. Using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK), the samples are reacted with chromium oxide and silvered copper oxide at 1000^{o}C. The oxides were removed, and N_2 and CO_2 are trapped and separated on a Carosieve GC column before the IRMS.

2.3.4. Contaminant Analysis

We obtained data on the concentrations of pollutants in plasma from the laboratory services at the National Wildlife Research Center (NWRC) in Ottawa, Ontario according to standard protocol (Environment Canada, 2007). Samples were prepared for extraction by denaturing the plasma with formic acid (1:1) then extracted for OCs/PCBs/BDEs/BFRs with an activated C18 Cartridges and elution with DCM/Hexane (1:1). Those extracts were cleaned by Florisil column chromatography. Using the capillary gas chromatograph (Agilent 6890N) and a mass selective detector (Agilent

5973N) operated in selected ion monitoring mode, the purified samples were analyzed. Background contamination was corrected for by subtracting the method blank concentration values. The chemicals analyzed were organochlorine (OC) pesticides: 1,2,4,5-Tetrachlorobenzene, 1,2,3,4-Tetrachlorobenzene, Pentachlorobenzene, α-Hexachlorocyclohexane, Hexachlorobenzene, β-Hexachlorocyclohexane, γ-Hexachlorocyclohexane, Octachlorostyrene, Heptachlor epoxide, Oxychlordane, trans-Chlordane, cis-Chlordane, trans-Nonachlor, p,p'-DDE, Dieldrin, p,p'-DDD, cis-Nonachlor, p,p'-DDT. Heptachlor epoxide and oxychlordane were successfully quantified for the 2013 plasma samples, but interference during analysis occurred for the 2012 samples. They are both metabolites of primary constituents of the insecticide, chlordane. Polychlorinated biphenyls (PCBs) included: PCB-16/32, PCB-18/17, PCB-22, PCB-31/28, PCB-33/20, PCB-42, PCB-44, PCB-47/48, PCB-49, PCB-52, PCB-56/60, PCB-64/41, PCB-66, PCB-70/76, PCB-74, PCB-85, PCB-87, PCB-92, PCB-95, PCB-97, PCB-99, PCB-101/90, PCB-105, PCB-110, PCB-114, PCB-118, PCB-128/167, PCB-130, PCB-137, PCB-138, PCB-141, PCB-146, PCB-149, PCB-151, PCB-153, PCB-156, PCB-157, PCB-158, PCB-170/190, PCB-171, PCB-172, PCB-174, PCB-176, PCB-177, PCB-187, PCB-178, PCB-179, PCB-180, PCB-183, PCB-189, PCB-194, PCB-195, PCB-196/203, PCB-199, PCB-200, PCB-201, PCB-202, PCB-205, PCB-206, PCB-207, PCB-208, PCB-209, ΣPCB was calculated from the summation of the above PCB congeners, and total PCBs as Aroclor as 1:1 Aroclor 1254:1260 and Aroclor 1260 were also determined. Polybrominated diphenyl ethers (PBDEs) and other brominated flame retardants included: BDE-15/ 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (β-TBECH), BDE-17, BDE-28, BDE-47, BDE-49, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154/2,2',4,4,5,5'-hexabromobiphenyl (BB-153), BDE-183, BDE-190, BDE-209, 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (α-TBECH), hexabromobenzene (HBB), 2,2',4,5,5'-pentabromobiphenyl (BB-101), Hexabromocyclododecane (HBCDD), 1,2,-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), syn-Dechlorane Plus (syn-DP), anti-Dechlorane Plus (anti-DP), ΣPBDE was calculated from the summation of BDE congeners, and ΣBDE/BFR was calculated from the summation of BDE congeners and other brominated flame retardants.

2.3.5. Radio Telemetry and Home Range Analysis

We determined the home range of urban adult Cooper's hawks using radio telemetry. We fitted 6 g radio transmitters (Holohil, Ontario, Canada. Model RI-2C) to adults using a pelvic harness in 2012. We tracked from August 2012 to March 2013, twice a week, by car using a whip antenna, and then on foot to triangulate the location using a yagi antenna and receiver (Advanced Telemetry Systems Scientific Receiver, Isanti, MN). We determined the kernel density estimate using Geospatial Modelling Environment (GME, version 0.7.2.1, Spatial Ecology LLC) extension for ArcGIS. We used the kernel density estimation function with a least-squared cross validation bandwidth, to calculate the 95% contour level, or home range.

2.3.6. Land-use and Population Density Calculations

We quantified land use and average population density within a 1.23 km radius of each contaminant sampled nest using Geographic Information Systems software (ArcGIS 10.1). We used a 1.23 km radius because that was found in this study it to be the average home range of Cooper's hawks. We obtained a 2006 land use data layer of the Vancouver Regional District (Metro Vancouver, 2012). We amalgamated 11 land use categories into the following seven groupings: rural/agriculture, recreation, lakes and water, industrial, institutional/utility, undeveloped/open, and residential/commercial. We further obtained a 2006 population density data layer of the Vancouver Regional District (Metro Vancouver, 2012). We determined the area of each land use category and average population density with average home range. Average population density was calculated by multiplying the percent of area covered within the home range by the associated population density, than summing all the multiples together.

2.3.7. Statistical Analysis

We transformed our data to comply with the assumptions of normality and reduce correlated variables. All contaminants below the level of detection (LOD) were given a value of half the LOD (Detection limit for all contaminants = 0.1 ng/g except BDE.209 = 1.0 ng/g). There was no difference in results when zero was used instead of half the LOD. Concentrations were $\log_{10}$ transformed to approximate normal distribution, prior to analysis. The spatial variables; area of land use categories and average population density, were combined using a principal component analysis into PC1 and PC2.

We used Akaike Information Criterion (AIC) to examine how the concentrations of dieldrin, trans-nonachlor, DDE, ΣPCBs, and ΣPBDEs in plasma of adult and nestling Cooper's hawks varied with spatial variables: PC1, and PC2, diet: $\delta^{15}N$, and $\delta^{13}C$, and gender. Due to the small sample size we used a corrected AIC (AICc; Burnham and Anderson, 2002). The AICc method selects the best model based on the overall support of that model among other, competing models. The model with the lowest AIC is considered the most influential and the AIC weight (AICwt) indicates the level of support for that model. We ran a mix effect model on nestling samples, due to sampling of two chicks at four nests - a potential nest effect; however, only the intercept was different when comparing with fixed effects models. For each dependant variable (dieldrin, trans-nonachlor, DDE, ΣPCBs, and ΣPBDEs) we created a candidate set of 10 mixed models for adults that included spatial variables PC1, and PC2; $\delta^{15}N$, $\delta^{13}C$, and null, which was repeated with the addition of the fixed effect gender. We only used five univariate models, however, for examining contaminant concentrations nestlings (spatial variables PC1, and PC2; $\delta^{15}N$, $\delta^{13}C$, and null). We assumed all models greater than two ΔAICc have support in influencing the dependant variable.

A value for $\delta^{15}N$ was beyond Cook's distance and, therefore, it had a large effect on the data for adult Cooper's hawks. Two separate AICc analyses were done to explain the effects of the high $\delta^{15}N$ value (data not shown). Since there was no major differences in results, the larger dataset was used in this study.

2.4. Results

We located 40 Cooper's hawk territories and nest sites throughout the greater Vancouver area. In 2012 we found 27 nest sites and three territories, and in 2013 we found nine new sites and one new territory. These territories and nest sites included 16 in Vancouver, nine in Burnaby, seven in Richmond, five in Surrey, two in Delta, and one in Port Moody. The majority of sites were found in parks (70%), along heavily treed residential boulevards (23%) and next to golf courses (8%). Nests were built mainly in a variety of deciduous trees (72%, n=40) including London plane trees (*Platanus orientalis x Platanus occidentalis*), sweet gum (*Liquidambar styraciflua 'Worplesdon'*) and black cottonwood (*Populus trichocarpa*). Nest height averaged 16.7 ± 5.86 m in trees which averaged 20.6 ± 6.01 m in height with an average diameter at breast height (dbh) of 53.3 ± 19.6 cm.

2.4.1. Territories and Land Use

Cooper's hawks in the greater Vancouver area remain year-round in the vicinity of their nesting territories. Eight of the nine hawks released with radio tags were successfully followed through the non-breeding season. One of the eight individuals occupied a second location 6 km away from its nest site for one month, and then returned to its original nest site during the breeding season. This bird was excluded when calculating average home range size. We estimated the mean home range (95% KDE) of seven individuals to be 4.71 ± 1.4 km^2 (see Fig. 2-1).

The land use and population density was calculated for a subset of Cooper's hawk nests (n = 22; Fig. 2-1). The land use which covered the most area within their home range was residential/commercial land-use categories (mean = 2.63km^2), followed by recreational land-use (mean = 0.75 km^2; see Table 2-1). The average population density was in the home range of Cooper's hawks was 2970 people/km^2 with a range of 17.8 - 6750 people/ km^2 (see Table 1). Principle Component one of the spatial elements explained 43% of the variation and represented a gradient from more urban (i.e. high population density) to less urban (i.e. agriculture and recreational land-use) and Principal Component two explained 17.5% of the variation (Fig. 2-2).

2.4.2. Contaminants

We obtained blood samples from 21 adults and 15 nestlings associated with 22 nests in 2012 and 2013 (Fig. 2-1.) and measured contaminant concentrations, focusing on dieldrin, trans-nonachlor, DDE, ΣPCBs and ΣPBDE (Table 2-2). All contaminants are highly correlated to each other (Table 2-3); however, we focused on major POPs in this study to isolate ones with the most influence. DDE was high, while the other contaminants were similar in plasma concentrations relative to other studies.

A total of 15 OC pesticides were detected in plasma samples: 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, heptachlor epoxide, oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, dieldrin, p,p'-DDT, p,p'-DDE, p,p'-DDD, mirex (see Table A-1 for details). Heptachlor epoxide and oxychlordane were successfully quantified for the 2013 plasma samples, but were recorded to have interference for the 2012 samples. They are both metabolites of primary constituents of chlordane. Both are usually included in quantifying chlordane exposure, so we used trans-nonachlor, a major constituent, to reflect the concentration of chlordane in plasma. Further, we focused on select major OC pesticides: dieldrin, trans-nonachlor and DDE. Concentrations of dieldrin were significantly greater in adults (M = 62.6 ng/g, SD = 77.27) than nestlings (M = 9.21 ng/g, SD = 8.39; $t(20.32) = 3.3$. $p = 0.004$). There was no significant difference in concentrations of dieldrin between male (M = 82.8 ng/g, SD = 90.3) and female (M = 35.5 ng/g, SD = 47.9) adult Cooper's hawks; $t(17.56) = 1.59$, $p = 0.13$. Also, concentrations of trans-nonachlor were significantly greater in adults (M = 82.1 ng/g, SD = 78.61) than nestlings (M = 10.3 ng/g, SD = 10.05; $t(33.24) = 5.96$. $p < 0.001$). There was no significant difference in concentrations of trans nonachlor between male (M = 96.0 ng/g, SD = 92.5) and female (M = 63.4 ng/g, SD = 54.8) adult Cooper's hawks; $t(12.92) = 1.17$, $p = 0.26$. Lastly, concentrations of DDE were significantly greater in adults (M = 1225 ng/g, SD = 1103) than nestlings (M = 68.8 ng/g, SD = 54.62; $t(33.02) = 9.27$. $p < 0.001$). There was no significant difference in concentrations of trans nonachlor between male (M = 1671 ng/g, SD = 1261) and female (M= 630 ng/g, SD = 397.15) adult Cooper's hawks; $t(2.37) = 17.89$, $p = 0.03$.

A total of 60 PCB congeners were measured and summed to the ΣPCB (The 54 congeners which were detected in the majority of samples are presented in Table A-2). Concentrations of ΣPCB were significantly greater in adults (M = 509 ng/g, SD = 357) than nestlings (M = 54.9 ng/g, SD = 44.84; $t(29.31) = 8.05$. $p <0.001$). There was no significant difference in concentrations of ΣPCB between male (M = 570 ng/g, SD = 376) and female (M = 427 ng/g, SD = 333) adult Cooper's hawks; $t(13.84) = 1.15$, $p = 0.27$.

The most abundant six PCB congeners in adult Cooper's hawks were CB-153 > 138 > 180 > 183 > 170/190 > 187 and in nestlings were CB-153 > 138 > 183 > 170/190 > 179 > 180.

A total of 14 PBDE congeners were summed as ΣPBDE (Table A-3). Concentrations of ΣPBDE were significantly greater in adults (M = 118 ng/g, SD = 83.9) than nestlings (M = 18.8 ng/g, SD = 15.93; $t(26.52) = 7.87$. $p < 0.001$). There was no significant difference in concentrations of ΣPBDE between male (M = 121 ng/g, SD = 88.9) and female (M = 114 ng/g, SD = 81.8) adult Cooper's hawks; $t(17.47) = 0.85$, $p = 0.85$. The most abundant PBDE congeners in 2012 nestling hawks were BDE-99 > 47 > 100 > 153 > 154. The PBDE congener profile for adult hawks was BDE-99 > 153 > 47 > 100 > 154. The appropriate congener proportions could only be calculated for 2012 as lab results were inconclusive for BDE 153 in 2013, a prominent congener.

2.4.3. Factors Influencing Contaminant Concentrations in Adult Hawks

Four of 10 models examining the influence of spatial variables, diet, and gender on concentrations of dieldrin received strong support (ΔAIC_C <2; Fig. 2-3; Table 2-4, 2-6). The top ranked model, the diet variable $\delta^{15}N$ + gender, received 4.6 times the support of the null model. The second ranked model $\delta^{13}C$ + gender, and the third ranked model, gender, received 4.2 time the support of the null, and 0.91 time the support of the top model. The fourth ranked model, $\delta^{15}N$, received 3.2 times the support of the null, and 0.7 times the support of the top model. The data suggests that as $\delta^{15}N$, and indicator of trophic level, and $\delta^{13}C$ increases as dieldrin concentrations increase. Gender is also influencing the concentrations of dieldrin where males have a greater concentration overall.

Three of the ten models examining the influence of spatial variables, diet, and gender on concentrations of trans-nonachlor received strong support (ΔAIC_C <2; Table 2-4, 2-6). The top was the null model and received 1.8 times the support of the second and third ranked models; gender and spatial PC1, respectively.

One of ten models examining the influence of spatial variables, diet, and gender on concentrations of DDE received strong support (ΔAIC_C <2; Table 2-4). The top model was gender and received 5.4 times the support of the null model. Gender alone explained the variation in DDE concentrations, with males having a significantly ($p < 0.05$) greater concentrations than females.

Two of the 10 models examining the influence of spatial variables, diet, and gender on concentrations of ΣPCBs received strong support (ΔAIC_C <2; Fig. 2-4; Table 2-4, 2-6). The top model was spatial PC1, which received 17 times the support of the null. The second ranked model, spatial PC1 + gender received 13 times the support of the null and 77 time the support of the null. The data suggest that as the concentrations of ΣPCBs increase, the coefficient for spatial PC1 decreases, or the landscape becomes more urban. Gender also influences the concentrations of ΣPCBs uptake, where males have a greater concentration than females.

Four of the 10 models examining the influence of spatial variables, diet, and or gender on concentrations of ΣPBDEs received strong support (ΔAIC_C <2; Fig. 2-4; Table 2-4, 2-6). The top model, spatial PC1, received 1.1 times the support of the null, which was the second ranked model. The third ranked model, gender, received 0.45 times the support of the null and 0.42 times the support of the top model. The fourth ranked model, spatial PC1 + gender received 0.45 times the support of the null and 0.42 times the support of the top model. The data suggest that concentrations of ΣPBDEs increase, the coefficient for spatial PC1 decreases, or the landscape becomes more urban.

2.4.4. Factors Influencing Contaminant Concentrations in Nestling Hawks

Three of five models examining the influence of diet and spatial variables on concentrations of dieldrin received strong support (ΔAIC_C <2; Table 2-5, 2-7). The top ranked model was the null, which received 1.7 times the support of the second ranked model. The second ranked model, $\delta^{15}N$, received 0.61 times the support of the top model, the null. The third ranked model, $\delta^{13}C$, received 0.47 times the support of the top model, the null.

Two of five models examining the influence of diet and spatial variables on concentrations of trans-nonachlor received strong support (ΔAIC_C <2; Table 2-5, 2-7). The top ranked model was the null which received 1.3 times the support of the second ranked model, spatial PC1.

One of five models examining the influence of diet and spatial variables on concentrations of DDE received strong support (ΔAIC_C <2; Table 2-5, 2-7). The top ranked model was the null which received 3.2 times the support of the second ranked model, spatial PC1.

One of five models examining the influence of diet and spatial variables on concentrations of ΣPCBs received strong support (ΔAIC_C <2; Table 2-5, 2-7). The top ranked model was the null which received 2.9 times the support of the second ranked model, spatial PC1.

One of five models examining the influence of diet and spatial variables on concentrations of ΣPBDEs received strong support (ΔAIC_C <2; Table 2-5, 2-7). The top ranked model was the null which received 2.9 times the support of the second ranked model, $\delta^{13}C$.

2.4.5. Relationship between Adult and Nestlings

There was no evidence of a nest site effect since a contaminant concentrations in nestling and adult Cooper's hawks were not significantly correlated (p-value = 0.06). Concentrations of contaminants in plasma were significantly greater in adults than in nestlings (Welch's t-test, maximum p-value $\leq$ 0.004). There was no significant difference mean $\delta^{13}C$ in plasma between adults (M = -24.4‰, SD = 0.69) and nestlings (M = -24.6‰, SD = 0.83) t = 0.63, df = 27.4, p-value = 0.54. There was a small but significant difference for $\delta^{15}N$ between adult and nestlings (M = 9.17‰, SD = 0.73; M = 8.44‰, SD = 0.52, respectively), t = 3.22, df = 27.1, p-value = 0.003.

2.5. Discussion

Cooper's hawks were found nesting throughout the Metro Vancouver region in parks, along boulevards and around golf courses. That is similar to reports from other North American and European cities of Accipiters increasingly occupying and appearing to thrive in urbanized environments (Endo et al., 1991; Newton et al., 1986; Rosenfield et al., 1995; Rutz, 2008). Based on the small home range and over winter residency of these Cooper's hawks, we can infer that contaminant exposure is localized. The Cooper's hawks contained a variety of legacy contaminants, particularly the OC pesticides such as dieldrin, trans-nonachlor and DDE, industrial chemicals, specifically PCBs, as well as the flame retardant PBDEs of more recent origin. Concentrations of ΣPCBs and ΣPBDEs in plasma increased with the level of development. Whereas the pesticide dieldrin increased in males and with trophic level, as $\delta^{15}N$ and DDE concentrations were most influenced by gender alone. Overall, there was little variation in trophic level, as $\delta^{15}N$, or carbon source, as $\delta^{13}C$, indicating that there is likely little dietary variation, probably as most hawks are feeding on common city birds (Cava et al., 2012) within this regional population.

2.5.1. Organochlorine Insecticides

In the present study we measured continuing elevated concentrations of a range of organochlorine insecticides in a Cooper's hawk population nesting in an urbanized environment. We have documented that these hawks are year round residents in their home ranges. The bulk of their prey species includes house sparrows (*Passer domesticus*), European starlings (*Sternus vulgaris*), and other common year round song birds (Cava et al., 2012; Brogan personal observations). We argue, therefore, that these pesticides are derived from agricultural usage primarily from the 1950s to 1970s even though the land has now been developed In the past, land use was dominated by intensive agricultural production and associated intensive use of insecticides to control soil pests, until the 1970s mainly dieldrin and heptachlor (Elliott et al., 1996; Elliott et al., 2012; Szeto & Price, 1991; Wan, Kuo, & Pasternak, 1995). In the recent past, areas of Vancouver and Burnaby also had large tracts of intensive agricultural land, particularly along the Fraser River (Boyle et al., 1997). DDT in particular was widely used for public health and applied to wetlands and even sprayed regularly in residential neighborhoods. All of that usage leaves a legacy of residual soil contamination. 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 & Price, 1991; Wan et al., 1995; Wilson & Tisdell, 2001).

There are a limited number of studies quantifying plasma concentrations of cyclodiene pesticides (dieldrin and trans-nonaclor) as most studies use other tissues, such as egg or liver. Migrating adult sharp-shinned hawks (*Accipiter striatus*) reported arithmetic mean plasma dieldrin concentrations of (20ng/g dieldrin (8 – 69); Elliott & Shutt, 1993) compared to the present study (62.6 ng/g dieldrin (4.8 – 271 ng/g)). Although there is little variation of $\delta^{15}N$, dieldrin was the one compound which was influenced by trophic level. Also, Elliott and Shut (1993) reported an arithmetic mean of 8 ng/g trans-nonachlor (2 – 16 ng/g) in plasma of sharp-shinned hawks. This study found a relatively greater arithmetic mean concentration of trans-nonachlor (82.1 ng/g trans-nonachlor (4.3 – 271 ng/g)). The large range of these chemicals is likely resulting from patchiness in residual soil contamination and local uptake in resident Cooper's hawk food chains. The sharp-shinned hawks, sampled over 25 years ago, are migratory and picked up pesticides from areas in Latin America with supposed ongoing OC usage (Elliott and Shutt, 1993). Thus the persistence of these cyclodiene insecticides in the Metro Vancouver food chain after such a long hiatus in local usage is a testimony to the extreme environmental persistence of these chemicals.

This study also detected concentrations of cyclodiene pesticides in nestling Cooper's hawks at greater concentrations found in bald eagles of British Columbia. We found dieldrin in Cooper's hawk nestling plasma at a geometric mean of 2.47 ng/g dieldrin (below detection limit – 24.2 ng/g) and trans-nonachlor (7.06 ng/g trans-nonachlor (1.8 – 37.9 ng/g). Bald eagle nestlings of the Fraser Valley and those sampled from British Columbian freshwater sites both quantified trans-nonachlor, which had concentrations of trans-nonachlor no greater than 8.4 ng/g. Further, at B.C. freshwater sites, nestlings accumulated a maximum concentration of 1.5 ng/g dieldrin (Elliott et al., 2009). This further supports that cyclodienes are found in higher concentrations in terrestrial feeding birds of prey (*Accipiters*) rather than aquatic feeding species (Elliott & Martin, 1994). This is speculated to be due to soil applications of these compounds and the subsequently relatively high exposure of birds feeding at high trophic levels in terrestrial food chains (Elliott & Martin, 1994). The extreme recalcitrance of the cyclodiene insecticides is further demonstrated by evidence that up to four decades after use they continue to affect birds. In New Jersey parks, chlordane residues from past use for soil pests have accumulated through the food chain to poison raptors, including Cooper's hawks, and other birds (Stansley & Roscoe, 1999). At the Rocky Mountain Arsenal a former cyclodiene manufacturing facility, residues of dieldrin in particular continue to poison birds, despite billions spent in remediation (Edson et al., 2011).

The variation in concentrations of DDE was best explained by the gender. There was a significant difference in DDE concentrations, whereby the males had significantly greater concentrations than females. That is likely due to maternal offloading of the contaminants into the eggs, a process by which lipophilic compounds are transferred from the female into her eggs (Van den Steen, 2009). For example, blood concentrations of DDT related compounds in gravid female American kestrels dropped after she laid her eggs (Henny and Meeker, 1981). That mechanism obviously is not available to males and they retain, therefore, a higher overall body burden.

The geometric mean concentrations of DDE in nestling Cooper's hawks was 51.5 ng/g DDE (12.8 – 204 ng/g), higher then concentrations found in the plasma of nestling bald eagles (19.9 ng/g DDE (2.85 – 62.6 ng/g; Venier et al., 2010) and in peregrine falcons (2.7 ng/g DDE (0.08 – 15.4 ng/g); Fernie & Letcher, 2010) of the Great Lakes area. As well, the Vancouver area Cooper's hawk nestlings had higher concentrations then nestling bald eagles from the Fraser Valley and western British Columbia, which had a geometric mean not exceeding 33 ng/g (Elliott et al., 2009; Gill & Elliott, 2003). However, nestling bald eagles found at BC freshwater sites, ones more likely to be subject to agricultural influences, had a maximum concentration of 479 ng/g DDE, exceeding the maximum found in nestling Cooper's hawks. Adult Cooper's hawks did, however, have higher average concentrations (824 ng/g DDE (88.9 – 3800 ng/g)) than sharp-shinned hawks trapped while migrating through the Great Lakes and after wintering in areas of putative ongoing DDT usage in Latin America (280 ng/g DDE; Elliott

& Shutt, 1993), peregrine falcons of southern Greenland (140 ng/g DDE; Jarman et al., 1994), as well as bald eagles of coastal BC (251.5 ng/g DDE (48.6 – 1532 ng/g; Elliott et al., 2009). However, the maximum DDE concentration in coastal BC bald eagles exceeded the concentration in Cooper's hawks. While terrestrial feeding Accipiters generally have a higher concentration of OC pesticides (Jaspers et al., 2006) the maximum value of these compounds found in bald eagles is possibly due to individual body fat percentage and lipid mobilization, and species metabolism (Bogan & Newton, 1977; Bustnes et al., 2010; Henriksen et al., 1998). That may also potentially be due to sampling immediately following a feeding event and elevated plasma lipids (Elliott & Norstrom, 1998).

2.5.2. Polychlorinated Biphenyls

Concentrations of PCBs found in the plasma of Cooper's hawks are similar to that found in other species across Canada. The geometric mean concentration of 40.5 ng/g ΣPCBs (6.4 -179 ng/g) in nestling Cooper's hawks was similar to those reported in nestling birds of prey from the Great Lakes area: peregrine falcons (35.16 ng/g ΣPCBs (3.52 – 368 ng/g); Fernie & Letcher, 2010) and bald eagles (73.8 ng/g ΣPCBs, (5.4 - 254 ng/g); Vernier et al, 2010). While bald eagle nestlings from the Delta/Richmond area had lower, but not statistically different concentrations of 10.3 ng/g ΣPCBs, (3 – 18.6 ng/g; McKinney et al., 2006). It has been suggested that PCBs have been essentially in environmental equilibrium for some time (Elliott et al., 1996; Park et al., 2009), which may explain the similar concentrations found in similar birds of prey across the country, with the exception of samples from PCB contaminated sites, for example, around Victoria Harbour, British Columbia (Harris et al., 2003). The congener profile is similar to that of other terrestrial feeding birds, such that CB-153 is in the greatest proportion (Jaspers et al., 2006). However, the variability within the adult Cooper's hawks was best explained by the level of development. The association with urbanization and increased concentrations of PCBs has also been found in birds from other studies (Morrissey et al., 2013; Potteret al., 2009). This link is likely due to past usage of PCBs in urban areas, including electrical transformers and a great variety of other uses including PCB laden paints and light ballasts. Fernie and Letcher (2010) reported lower PCB concentrations in nestling peregrine falcons from urban areas and speculated that it was due to feeding on urban pigeons, which are at lower trophic levels (e.g. Newsome et al., 2010) than shore and water birds - prey of non-urban peregrines. They go on further to hypothesize that the non-urban prey is thought to be migrating from areas of historically high PCB concentrations leading to elevated PCB levels in peregrines (Fernie & Letcher, 2010). This study is of a relatively small scale; dealing with primarily urban and suburban hawks that mainly feed on resident song birds, which may explain the low variation in PCB concentrations among individuals.

2.5.3. Polybrominated Diphenyl Ethers

Our finding of a mean concentration of 14.1 ng/g ΣPBDEs, (3.6 – 60.1 ng/g) in nestling hawks is similar to that reported in plasma of nestling peregrine falcons at sites around the Great Lakes (15.4 ng/g ΣPBDEs, (0.87 – 195 ng/g); Fernie & Letcher, 2010). In comparison to bald eagles, however, of both the Great Lakes (5.7 ng/g ΣPBDEs, (0.35 – 29.3 ng/g); Venier et al., 2010) and in Delta/Richmond B.C. (3.76 ng/g ΣPBDEs, (1.23 – 7.08); McKinney et al 2010), the Cooper's hawk had greater PBDE plasma concentrations. The differences are likely explained by diet and less so to metabolic differences (Newton et al., 1993; Walker, 1983). The congener profile in adults was similar to other studies on terrestrial feeding birds of prey, with high proportions of BDE-153 and BDE-99 (Jaspers et al., 2006; Law et al., 2006). Researchers speculated that PBDEs would be attached to dust, falling on to, and ingested by urban birds during feather preening, and thus contributing to the concentrations found in urban peregrines (Newsome et al., 2010; Park et al., 2009, 2011). The diet of the Californian urban peregrines consisted of rock dove, European starlings and mourning doves (Newsome et al., 2010), which is comparable to that of west coast urban Cooper's hawks (Cava et al., 2012; Brogan personal observation). This pathway seems to be the most parsimonious exploitation for accumulation of PBDEs in our Cooper's hawks, further supported by our finding that variation in concentration of PBDEs was best explained by the degree of urban development.

2.6. Conclusion

Cooper's hawks nesting in the large urban area of Metro-Vancouver were contaminated with a wide variety of POPs of both legacy and recent origins. Ongoing exposure to relatively elevated levels of organochlorine insecticides, both DDT-related compounds and cyclodienes, can likely be explained by a legacy of residual soil contamination from past agricultural land use. Variation in dieldrin exposure was partially explained by $\delta^{15}N$ and thus some variation in trophic level of prey. Industrial contaminants both the legacy PCBs and the more recently used PBDEs were explained by the degree of development, consistent with sources of those chemicals from industrial and urban activities.

Cooper's hawks are a useful monitor of urban pollutants due to their high trophic position, large North American distribution, bird specific diet, and their high urban nesting density. Raptors have been successfully used as a long term monitor of pollutants in the UK, especially in the Eurasian sparrowhawk (*Accipiter nisus*), a conspecific of the Copper's hawk (Crosse et al., 2012; Newton et al., 1993). Continued monitoring of Cooper's hawks should be considered in Vancouver and in other urban areas, not only to see the changes in this environment, but to potentially compare to conspecific species on other continents.

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2.8. Figures

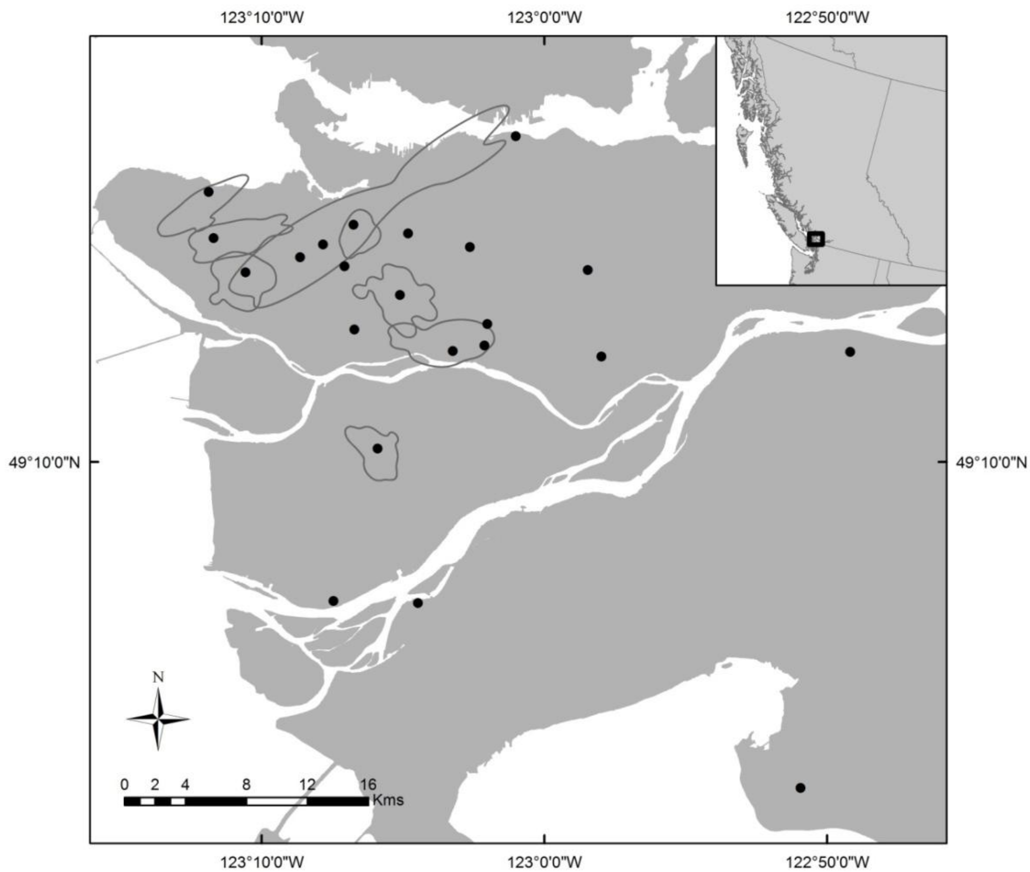

Figure 2-1. Sampled nest location and home range (95% Kernal Density Estimate) of 8 individually tracked adult Cooper's hawks in the Metro Vancouver area, British Columbia, 2012-2013. Points represent nests. Some nests were not associated with radio tracked individuals.

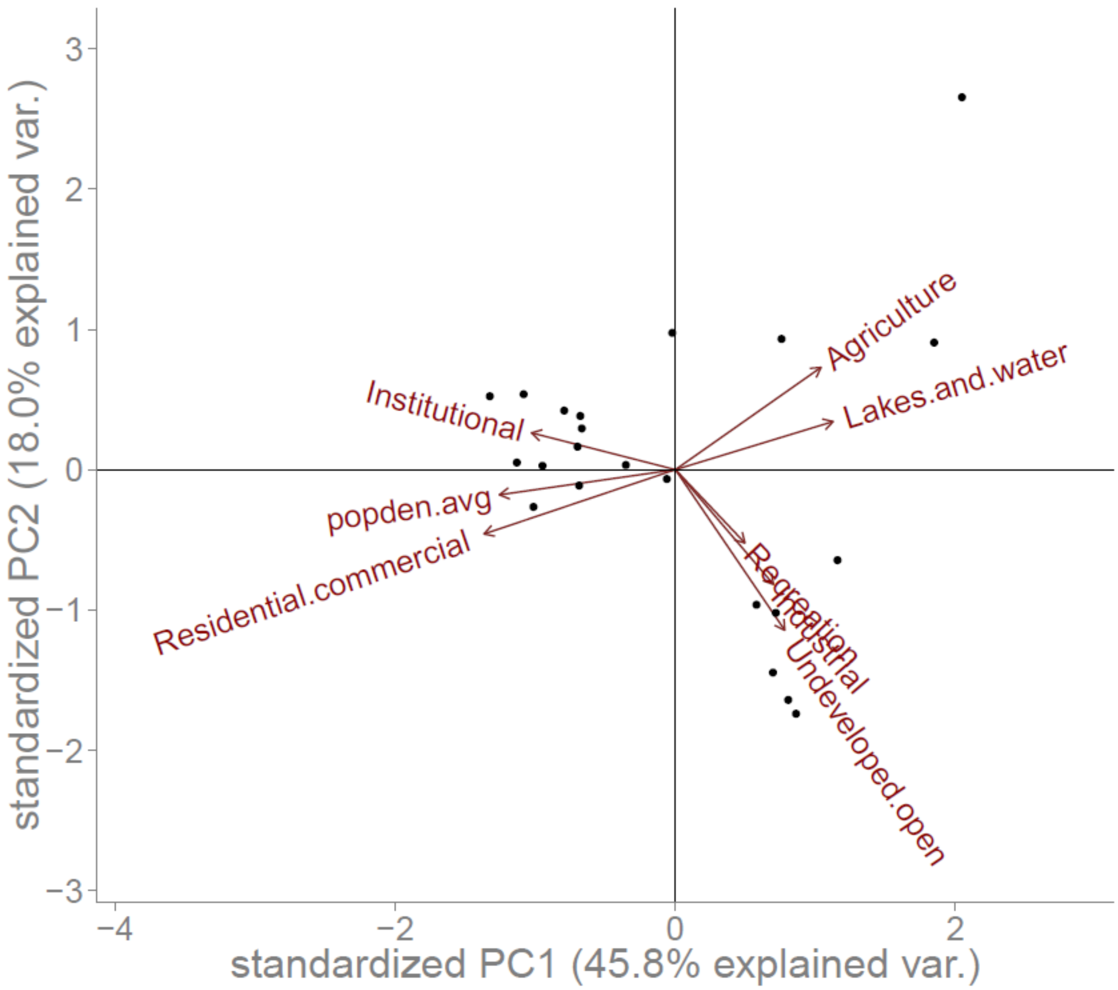

Figure 2-2. **Principal Component Analysis of spatial elements (land-use and population density) within the average home range of sampled Cooper's hawks nests of the Metro Vancouver area, British Columbia (see Table 3).**

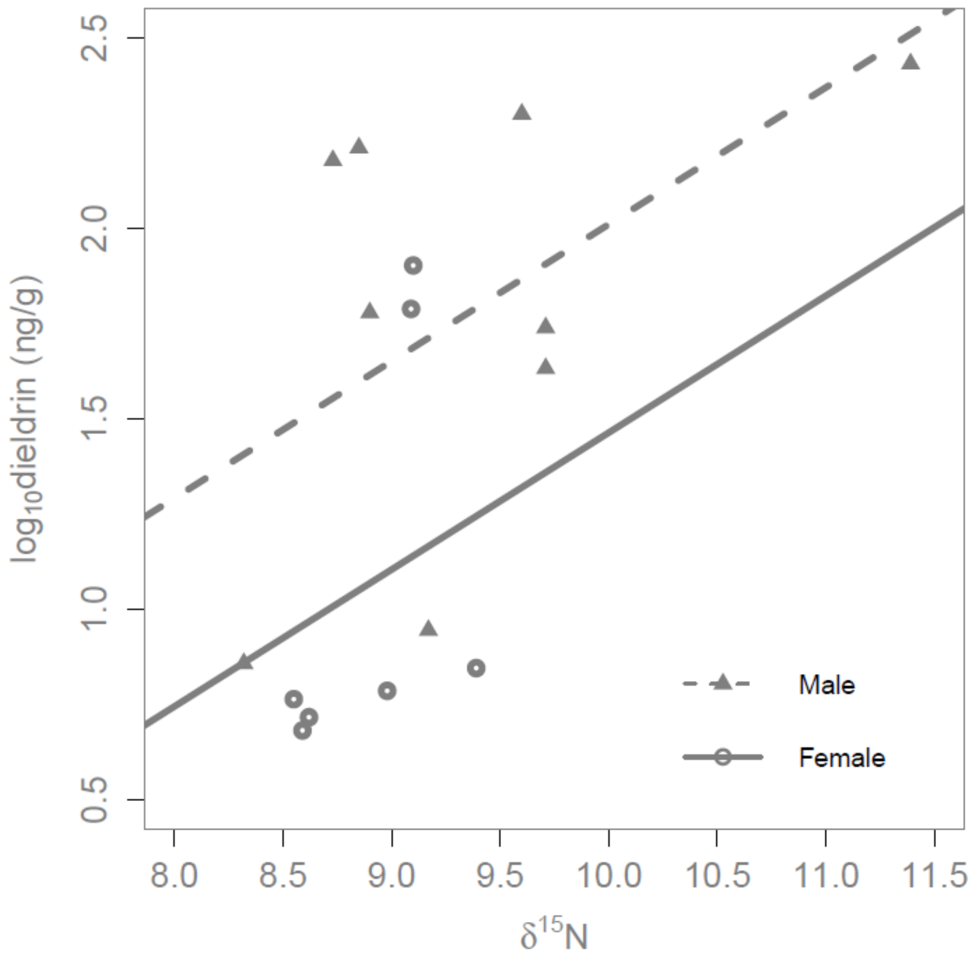

Figure 2-3. Linear regression of top ranked model, $\delta^{15}N$ + gender, influence on plasma concentration of dieldrin in adult Cooper's hawks of Metro Vancouver, British Columbia (n = 16).

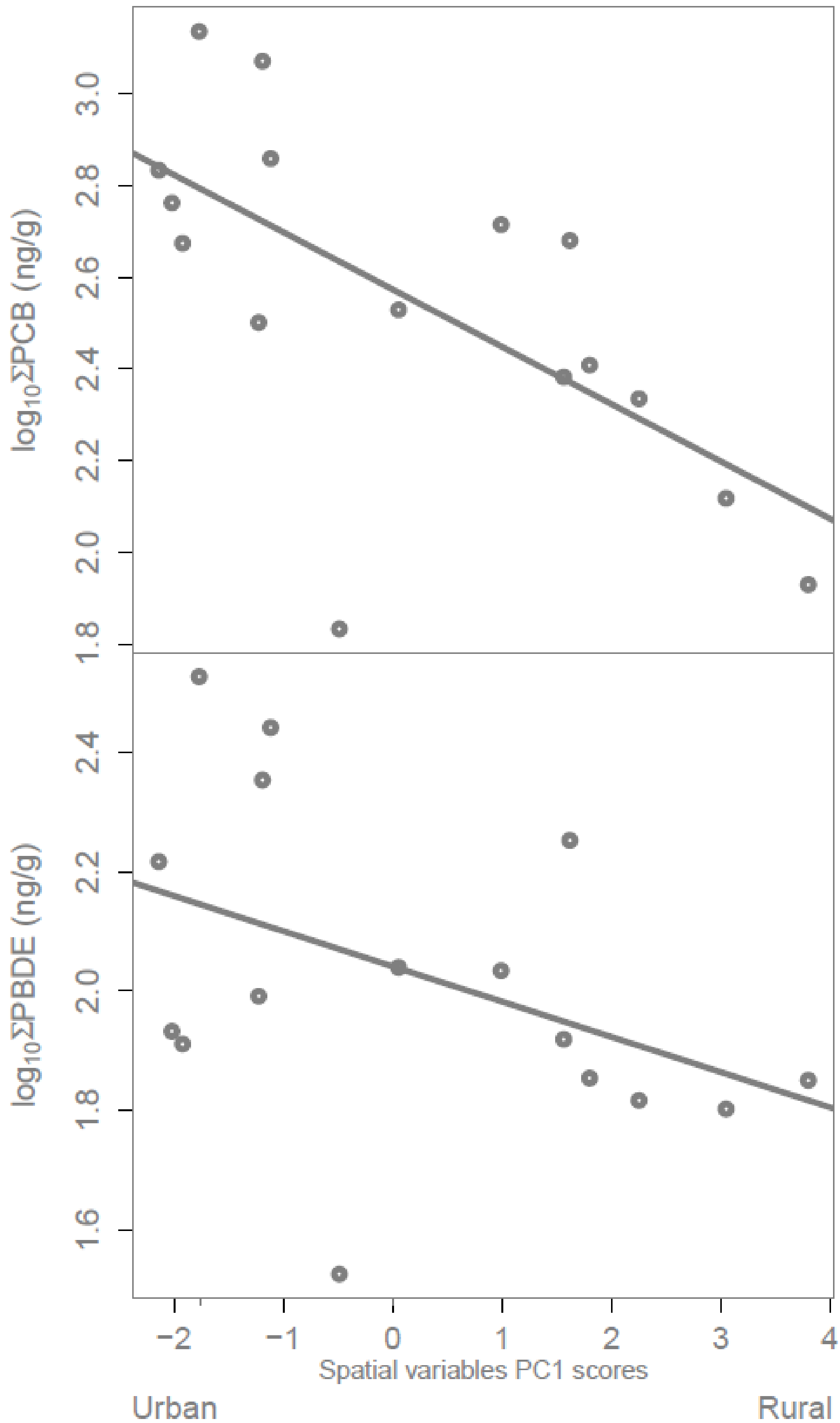

Figure 2-4. **Linear regression of top ranked variable, PC1 of spatial elements influence on plasma concentration of a) ΣPCB and b) ΣPBDE in adult Cooper's hawks of Metro Vancouver, British Columbia (n = 16).**

2.9. Tables

Table 2-1. The mean, median and range of human population density (people/km^2) and area (km^2) of seven land use types in the home ranges of Cooper's hawks, measured in Metro Vancouver, British Columbia, 2012 to 2013 (n=22).

	Median	Mean	Range
Population density	2693	2967	(17.8 - 6750)
Agriculture	0	0.301	(0 - 2.75)
Recreation	0.784	0.781	(0.161 - 2.02)
Lakes and water	0.002	0.374	(0 - 2.04)
Institutional	0.3	0.295	(0 - 0.627)
Undeveloped	0.03	0.09	(0 - 0.417)
Industrial	0.101	0.301	(0 - 1.14)
Residential/commercial	2.87	2.59	(0 - 4.29)

Table 2-2. Contaminant concentrations found in the plasma of adult and nestling Cooper's hawks from the Metro Vancouver area, British Columbia, 2012 to 2013. (geometric mean (range)).

	Adult (n=21)		**Nestling (n = 15)**	
dieldrin	26.5	(4.8 - 271)	2.47	(DL - 24.2)
trans-nonachlor	51.5	(4.3 - 271)	7.06	(1.8 - 37.9)
DDE	824	(88.9- 3800)	51.5	(12.8 - 203)
ΣPCB	390	(66 - 1370)	40.5	(6.4 - 179)
ΣPBDE	96.6	(33.6 - 336)	14.1	(3.6 - 60.1)

Table 2-3. Pearson's Correlation Coefficients (r-value) and associated p-values of contaminants found in plasma of adult and nestling Cooper's hawks from the Metro Vancouver area, British Columbia (df = 35).

	dieldrin	**trans-nonachlor**	**DDE**	**ΣPCB**	**ΣPBDE**
dieldrin		0.485	0.716	0.385	0.502
trans-nonachlor	**$p < 0.01$**		0.595	0.774	0.580
DDE	**$p < 0.01$**	**$p < 0.01$**		0.551	0.495
ΣPCB	*$p < 0.05$*	**$p < 0.01$**	**$p < 0.01$**		0.811
ΣPBDE	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	

Table 2-4. Summary of AICc models examining the relationship between plasma concentrations of pollutants (dieldrin, trans-nonachlor, DDE, ΣPCB, and ΣPBDE) and PC1 and PC2 of spatial variables, diet ($\delta^{15}N$ and $\delta^{13}C$), and gender based on adult Cooper's hawks from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwt$_{top\ model}$, r^2: coefficient of determination (n = 16).

	Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
dieldrin	deltaN+gender	4	32.35	0	0.23	1.00	0.38
trans-nonachlor	null	2	26.4	0	0.28	1	0
	gender	3	27.61	1.21	0.15	0.54	
	spatial PC1	3	27.62	1.22	0.15	0.54	0.05
DDE	gender	3	18.73	0	0.43	1.00	
ΣPCB	spatial PC1	3	12.1	0	0.52	1.00	0.38
	spatial PC1+gender	4	12.62	0.52	0.4	0.77	0.45
ΣPBDE	spatial PC1	3	6.68	0	0.26	1.00	0.12
	null	2	6.82	0.14	0.24	0.92	
	gender	3	8.38	1.71	0.11	0.42	
	spatial PC1+gender	4	8.4	1.72	0.11	0.42	0.16

Table 2-5. Summary of AICc models examining the relationship between plasma concentrations of pollutants (dieldrin, trans-nonachlor, DDE, ΣPCB, and ΣPBDE) and PC1 and PC2 of spatial variables, and diet ($\delta^{15}N$ and $\delta^{13}C$) based on nestling Cooper's hawks from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: $AICwt/AICwt_{top\ model}$, r^2: coefficient of determination (n = 15).

	model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
dieldrin	null	2	49.14	0	0.38	1.00	0.00
	$\delta^{15}N$	3	50.16	1.02	0.23	0.61	0.13
	$\delta^{13}C$	3	50.63	1.49	0.18	0.47	0.11
trans-nonachlor	null	2	18.35	0	0.39	1.00	0.00
	spatial PC1	3	18.89	0.54	0.30	0.77	0.16
DDE	null	2	15.43	0	0.51	1.00	0.00
ΣPCB	null	2	16.65	0	0.50	1.00	0.00
ΣPBDE	null	2	13.91	0	0.49	1.00	0.00

2.10. Akaike information criterion (AIC) tables in full

Table 2-6. Summary of AICc models examining the relationship between contaminants and PCA of spatial elements (land use and populations density), diet ($\delta^{15}N$ and $\delta^{13}C$) and gender, followed by each variables coefficient (Coeff), standard error (SE), and lower and upper confidence intervals (L CI and U CI respectively) based on adult Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: $AICwt/AICwt_{top\ model}$, r^2: coefficient of determination (n = 16).

dieldrin

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
deltaN+gender	4	32.35	0	0.23	1.00	0.38
deltaC+gender	4	32.46	0.11	0.21	0.91	0.37
gender	3	32.49	0.14	0.21	0.91	-
deltaN	3	33	0.64	0.16	0.70	0.25
open+gender	4	35.13	2.78	0.06	0.26	0.26
null	2	35.56	3.2	0.05	0.22	0.00
spatial PC1+gender	4	36	3.65	0.04	0.17	0.22
deltaC	3	37.05	4.7	0.02	0.09	0.03
open	3	37.98	5.63	0.01	0.04	-0.03
spatial PC1	3	38.56	6.21	0.01	0.04	-0.07

Variable	Coeff	SE	L CI	U CI
intercept	1.699	5.318	-8.725	12.123
open	0.103	0.117	-0.127	0.332
spatial PC1	-0.024	0.077	-0.175	0.128
δ15N	0.414	0.207	0.009	0.819
δ13C	0.346	0.198	-0.042	0.735
gender - male	0.682	0.288	0.116	1.247

trans-nonachlor

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	26.4	0	0.28	1.00	0.00
gender	3	27.61	1.21	0.15	0.54	-
spatial PC1	3	27.62	1.22	0.15	0.54	0.05
deltaN	3	28.69	2.28	0.09	0.32	-0.02
deltaC	3	28.72	2.32	0.09	0.32	-0.02
spatial PC1+gender	4	29.11	2.7	0.07	0.25	0.10
open	3	29.44	3.04	0.06	0.21	-0.07
deltaC+gender	4	30.04	3.63	0.05	0.18	0.05
deltaN+gender	4	31.01	4.6	0.03	0.11	-0.01
open+gender	4	31.2	4.8	0.03	0.11	-0.02

Variable	Coeff	SE	L CI	U CI
intercept	1.999	2.255	-2.421	6.418
open	0.019	0.101	-0.180	0.218
spatial PC1	-0.082	0.061	-0.202	0.039
δ15N	0.133	0.180	-0.221	0.486
δ13C	0.162	0.183	-0.196	0.520
gender - male	0.318	0.243	-0.157	0.793

DDE

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
gender	3	18.73	0	0.43	1.00	-
deltaN+gender	4	21.1	2.37	0.13	0.30	0.29
spatial PC1+gender	4	22.03	3.3	0.08	0.19	0.25
null	2	22.15	3.42	0.08	0.19	0.00
open+gender	4	22.25	3.53	0.07	0.16	0.24
deltaC+gender	4	22.31	3.58	0.07	0.16	0.23
deltaN	3	22.36	3.63	0.07	0.16	0.10
spatial PC1	3	24.99	6.26	0.02	0.05	-0.06
deltaC	3	25.02	6.29	0.02	0.05	-0.06
open	3	25.16	6.43	0.02	0.05	-0.07

Variable	Coeff	SE	L CI	U CI
intercept	2.331	1.380	-0.373	5.035
open	0.023	0.078	-0.131	0.176
spatial PC1	0.025	0.050	-0.073	0.123
δ15N	0.175	0.147	-0.112	0.462
δ13C	-0.038	0.146	-0.324	0.249
gender - male	0.471	0.188	0.104	0.839

ΣPCB

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
spatial PC1	3	12.1	0	0.52	1.00	0.38
spatial PC1+gender	4	12.62	0.52	0.4	0.77	0.45
null	2	17.71	5.61	0.03	0.06	0.00
gender	3	19.11	7.01	0.02	0.04	-
deltaC	3	19.57	7.48	0.01	0.02	0.01
deltaN	3	20.39	8.29	0.01	0.02	-0.05
open	3	20.52	8.42	0.01	0.02	-0.05
deltaC+gender	4	20.97	8.88	0.01	0.02	0.07
deltaN+gender	4	21.33	9.24	0.01	0.02	0.05
open+gender	4	22.47	10.37	0	0.00	-0.02

Variable	Coeff	SE	L CI	U CI
intercept	2.586	0.704	1.207	3.965
open	-0.037	0.077	-0.188	0.114
spatial PC1	-0.121	0.037	-0.194	-0.048
δ15N	-0.107	0.140	-0.382	0.169
δ13C	0.152	0.137	-0.117	0.421
gender - male	0.234	0.144	-0.047	0.515

ΣPBDE

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
spatial PC1	3	6.68	0	0.26	1.00	0.12
null	2	6.82	0.14	0.24	0.92	0.00
gender	3	8.38	1.71	0.11	0.42	-
spatial PC1+gender	4	8.4	1.72	0.11	0.42	0.16
deltaC	3	8.85	2.17	0.09	0.35	0.00
open	3	9.83	3.15	0.05	0.19	-0.07
deltaN	3	9.88	3.2	0.05	0.19	-0.07
deltaC+gender	4	10.5	3.82	0.04	0.15	0.05
deltaN+gender	4	11.68	5	0.02	0.08	-0.03
open+gender	4	11.94	5.26	0.02	0.08	-0.04

Variable	Coeff	SE	L CI	U CI
intercept	2.332	1.206	-0.032	4.696
open	0.014	0.055	-0.094	0.122
spatial PC1	-0.057	0.032	-0.120	0.006
δ15N	-0.023	0.101	-0.221	0.174
δ13C	0.101	0.099	-0.093	0.294
gender - male	0.160	0.130	-0.094	0.415

Table 2-7. Summary of AICc models examining the relationship between contaminants and PCA of spatial elements (land use and populations density) and diet ($\delta^{15}N$ and $\delta^{13}C$) and each variables coefficient (Coeff), standard error (SE), and lower and upper confidence intervals (L CI and U CI respectively) based on nestling Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwt$_{top\ model}$, r^2: coefficient of determination (n = 15).

dieldrin

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	49.14	0	0.38	1.00	0.00
$\delta^{15}N$	3	50.16	1.02	0.23	0.61	0.13
$\delta^{13}C$	3	50.63	1.49	0.18	0.47	0.11
spatial PC1	3	51.14	2	0.14	0.37	0.08
spatial PC2	3	52.32	3.17	0.08	0.21	0.00

Variable	Coeff	SE	L CI	U CI
spatial PC2	0.022	0.285	-0.537	0.581
spatial PC1	-0.224	0.217	-0.650	0.201
$\delta^{15}N$	0.772	0.544	-0.294	1.838
$\delta^{13}C$	0.432	0.347	-0.248	1.111

trans-nonachlor

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	18.35	0	0.39	1.00	0.00
spatial PC1	3	18.89	0.54	0.3	0.77	0.16
$\delta^{15}N$	3	20.59	2.24	0.13	0.33	0.06
$\delta^{13}C$	3	20.93	2.58	0.11	0.28	0.04
spatial PC2	3	21.47	3.12	0.08	0.21	0.00

Variable	Coeff	SE	L CI	U CI
spatial PC2	0.024	0.102	-0.176	0.224
spatial PC1	-0.117	0.074	-0.262	0.028
$\delta^{15}N$	0.186	0.203	-0.212	0.584
$\delta^{13}C$	0.094	0.129	-0.159	0.346

DDE

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	15.43	0	0.51	1.00	0.00
spatial PC1	3	17.71	2.28	0.16	0.31	0.06
$\delta^{13}C$	3	18.46	3.03	0.11	0.22	0.02
spatial PC2	3	18.51	3.09	0.11	0.22	0.01
$\delta^{15}N$	3	18.58	3.15	0.11	0.22	0.00

Variable	Coeff	SE	L CI	U CI
spatial PC2	-0.081	0.090	-0.257	0.096
spatial PC1	0.021	0.073	-0.123	0.164
$\delta^{15}N$	0.031	0.190	-0.341	0.403
$\delta^{13}C$	-0.043	0.119	-0.275	0.190

ΣPCB

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	16.65	0	0.5	1.00	0.00
spatial PC1	3	18.84	2.18	0.17	0.34	0.06
spatial PC2	3	19.56	2.91	0.12	0.24	0.02
$\delta^{15}N$	3	19.79	3.14	0.11	0.22	0.00
$\delta^{13}C$	3	19.83	3.18	0.1	0.20	0.00

Variable	Coeff	SE	L CI	U CI
spatial PC2	0.047	0.096	-0.141	0.235
spatial PC1	-0.070	0.074	-0.215	0.075
$\delta^{15}N$	0.038	0.198	-0.349	0.426
$\delta^{13}C$	-0.006	0.124	-0.249	0.237

ΣPBDE

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	13.91	0	0.49	1.00	0.00
$\delta^{13}C$	3	15.97	2.06	0.17	0.35	0.07
$\delta^{15}N$	3	16.4	2.48	0.14	0.29	0.05
spatial PC2	3	17.09	3.17	0.1	0.20	0.00
spatial PC1	3	17.09	3.18	0.1	0.20	0.00

Variable	Coeff	SE	L CI	U CI
spatial PC2	0.008	0.088	-0.165	0.180
spatial PC1	0.003	0.070	-0.134	0.139
$\delta^{15}N$	0.139	0.177	-0.207	0.485
$\delta^{13}C$	0.110	0.109	-0.104	0.324

Chapter 3. Potential effects of persistent organic pollutants on Cooper's hawks (*Accipiter cooperii*) of Metro Vancouver, British Columbia.

3.1. Abstract

Persistent organic pollutants (POPs) have been reported to have a negative impact in wildlife in particular to top predators. Many of these contaminants affect a species central nervous system and the endocrine system. We investigated how legacy POPs and more recently used contaminants influence the level of thyroid hormones and the fledge success of Cooper's hawks (*Accipiter cooperii*) in Vancouver, British Columbia. Over a two year period, 2012-2013, we collected blood samples from 21 adult and 15 nestlings associated with 22 nest sites. We examined how dichlorodiphenyldichloroethylene (DDE), total polychlorinated biphenyls (ΣPCBs), and total polybrominated diphenyl ethers (ΣPBDEs) influences concentrations of total thyroxine (TT4) and total triiodothyronine (TT3) and how dieldrin, trans-nonachlor, DDE, ΣPCBs, ΣPBDEs, TT4, and TT3 influenced nest success. Cooper's hawks were present in most of the available ideal habitat, with the closest nest to nest distance of approximately one kilometer. Average nest success; in 2012, 71% of active nests fledged an average of 1.95 fledglings/ active nest, and in 2013, 82% of active nests fledged an average of 1.64 fledglings/ active nest. We found evidence that increases in ΣPCB and ΣPBDEs was negatively associated with TT4. All contaminants tested had a negative influence on concentrations of TT3. Dieldrin, was most associated negatively with fledge success, rather than thyroid hormone levels or other contaminants Our results suggest some impacts of legacy POPs, such as ΣPCBs, ΣPBDEs and dieldrin; influencing thyroid concentrations and reproductive success of, urban Cooper's hawkss.

3.2. Introduction

The 20th century witnessed a huge rise in the development and use of synthetic pesticides and industrial chemicals, many of which persist for years and even decades in environmental compartments. In the 1960's scientists and the public became concerned with the ubiquitous use of polychlorinated biphenyls (PCBs), pesticides, such as dichlorodiphenyl-trichloroethane (DDT), and cyclodiene compounds, such as dieldrin and chlordane, and the negative consequences to wildlife and the environment (Carson, 1963; Rattner, 2009). A more recent group of chemicals of concern are brominated flame retardants, particularly polybrominated diphenyl ethers (PBDEs), which have been in major use only since the 1990s. Evidence of widespread contamination of both legacy and new contaminants has led to them being banned and/or restricted. However, these chemicals continue to be detected in air and soil samples of western North America (Bidleman et al., 2006; Harris et al., 2000) and have been transported to wildlife of the high arctic (Letcher et al., 2010; Rigét et al., 2010). Although concentrations of these contaminants have experienced a decreasing trend following their ban and restriction (Law, 2014) there are instances of continuing elevated exposure of top predators (Elliott, Wilson, & Drouillard, 2010; Elliott et al., 2009; Park et al., 2009).

Terrestrial top predators are more exposed to some classes of chemical due to their bioaccumulative properties, such as PBDEs (Chen & Hale, 2010; Chen et al., 2007). Captive American kestrels (*Falco sparverius*) have been used to study effects of some chemicals under controlled conditions (Bardo & Bird, 2009). In some early work, Porter & Wiemeyer (1969; 1972) further investigated the negative relationship of organochlorine pesticides, such as DDT and its metabolite dichlorodiphenyldichloroethylene (DDE), and eggshell thickness, reproduction, and survival.. Later studies showed some evidence of PCBs altering behaviour, such as increases in male courtship displays and flights, while decreasing male parental care, or a "lazy male" effect occurs (Fisher et al., 2001; 2006). Concentrations of PBDEs considered to be environmentally relevant at the time (the average concentration found in Great Lake herring gull (*Larus smithsonianus*) eggs were administered to captive kestrels which resulted in impacts to the kestrel's immune response (Fernie et al., 2005; 2006).

Legacy pollutants, such as DDT, DDE, and ΣPCBs and more recent contaminants such as ΣPBDEs, can affect thyroid hormones concentrations due to their structure as hormone mimics (Blus, 2011; Harris & Elliott, 2001). Due to their structural similarity to thyroxin (T4) these chemicals can impact the thyroid hormone system. These pollutants have been found to affect the thyroid glands function and regulation, thyroid hormone metabolism, and binding with blood transport proteins with the last two mechanisms decreasing T4 concentrations (Boas et al., 2006; Brouwer et al., 1998; McNabb & Fox, 2003). Alterations to the proper functioning of the thyroid can affect juvenile growth, tissue development, and thermoregulation, among other endpoints (McNabb, 2007).

Given the concentrated human activities urban environments can be sources of elevated exposure to many contaminants. A positive relationship has been demonstrated between population density and PCBs in Eurasian dipper (*Cinclus cinclus*) eggs and with PBDEs and peregrine falcons (*Falco peregrines*) eggs (Morrissey et al., 2013; Park et al., 2009). Recently, high concentrations of PBDEs and other POPs have been reported in tissues of Cooper's hawks found dead of southwestern British Columbia (Elliott et al., 2010). This study investigates if the concentrations of select organochlorines; dieldrin, trans-nonachlor and DDE, ΣPCBs, and ΣPBDEs in the plasma of adult and nestling Cooper's hawks are having an influence on fledging success and on circulating concentrations of thyroid hormones; TT4 and total triiodothyronine (TT3)

3.3. Methods

3.3.1. Nest Searching

We compiled at dataset of potential nesting sites for Cooper's hawks throughout Metro Vancouver area using information from eBird.com, BC Breeding Bird Atlas, and discussions with local naturalists. We visited each site and used call-playbacks to determine if Cooper's hawks were present (Rosenfield et al., 1985). Playbacks were conducted 15 minutes before sunrise until one hour after sunrise. If a hawk responded to playback the hawk was observed until a nest was located.

3.3.2. Capturing and Blood Sampling of Adults and Nestlings

We captured adult Cooper's hawks between June 19th and July 17th in 2012 (when chicks were approximately 10-15 days old), and between 17th April to the 26th April (during pre-incubation), and again from 3rd July to 6th July (when chicks were approximately 10-15 days old) in 2013. Adults were captured using a doh gazza method (Bloom et al., 1992). A 100mm nylon mesh mist net (2.6 m x 6 m; avinet.com), occasionally two, to from a V - shape, was lightly attached to poles with clothes-pins, and placed in the territory of the Cooper's hawk, within 10 m of the nest tree. The lure - a great-horned owl (*Bubo virginianus*) tethered to a perch, was place between the nest tree and the mist-net(s). Cooper's hawk call-playback were used to initiate a response by the Cooper's hawk. We captured nestlings by having a professional tree climber access the nest when nestlings were approximately 10 to 21 days of age. Nests were accessed from June 14th to 28th 2012 and 2013.

We weighed, measured and banded adults and nestlings. We weighed each individual (± 1gram) with a Newton scale , measured the halux (± 0.1mm), tarsus length (± 0.1 mm), bill length (± 0.1 mm), and bill depth (± 0.1 mm) with analog calipers, and measured the wing chord (± 1 mm), and tail length (± 1 mm) with a wing rule. We attached a USFS band to the left tarsus. We collected up to 3ml of blood from each individual using a 3ml syringe and a 26 gauge needle, ensuring that our sample did not exceed 1% of the individual's body weight. We transferred the blood to a 4ml heparin coated vacutainer tube which was kept on ice until centrifuged within 6 hours of collection. We transferred the plasma of the centrifuged samples to acetone/hexane rinsed glass vials for contaminant analysis, microcentrifuge tubes for stable isotope analysis, and nalgene cryovial tubes for thyroid hormone analysis. We stored the glass vials and microcentrifuge tubes in -20^{o}C freezer and the cryovials in -80^{o}C freezer until they were to be analyzed. All data was collected according to the following permits: BC Ministry of Environment permit SU12-7796, sub banding permit 10761A, Animal Care permit 1026B-11.

We recorded the number of young that fledge for all nests with a female incubating or a delivery of prey to the nest was observed. To be consistent with other studies on Cooper's hawks (Rosenfield et al. 2007, Steenhof et al. 2010), we determined fledge success as the number of young present when nestlings were 21-24 days old based on their plumage, based on drawings by Meng (1951).

3.3.3. Contaminant Analysis

Plasma contaminants were analyzed for adults (n = 21) and nestlings (n = 15) as described in chapter 2. Contaminants under examination varied across adults: dieldrin 4.8 – 271 ng/g ww, trans-nonachlor 4.3 – 271 ng/g ww, DDE 88.9 – 1370 ng/g ww, ΣPCBs 66 – 1370 ng/g ww, and ΣPBDEs 33.6 – 336 ng/g ww; and nestlings: dieldrin detection limit – 24.2 ng/g ww, trans-nonachlor 1.8 – 37.9 ng/g ww, DDE 12.8 – 203 ng/g ww, ΣPCBs 6.4 - 179 ng/g ww, and ΣPBDEs 3.6 – 60.1 ng/g ww.

3.3.4. Thyroid Hormone Analysis

Concentrations of total thyroid hormones thyroxine (TT4) and triiodothyronine (TT3) in plasma were analyzed by laboratory services at the National Wildlife Research Center (NWRC) in Ottawa, Ontario. The frozen plasma aliquots was gradually brought to room temperature and analyzed on two consecutive days to minimize degradation. TT3 and TT4 was analyzed by radioimmunoassay (RIA) using Coat-a-count TT3 and Coat-a-count canine TT4 (Seimens kits, InterMedico). The radioactivity, determined with a Canberra-Packard gamma counter E-5002, was counted during 1 minute with results calculated using linear regression log-logit representation of the calibration curves of T3 and T4. When the percent coefficient of variation (%CV) between replicates was over 5% for the counts (CMP = counts per min) and/or higher than 20% for the calculated results (log-logit extrapolation), the assay was repeated when there was enough sample volume. Analysis was completed in duplicate.

3.3.5. Statistical Analysis

We transformed our data to comply with the assumptions of normality. All contaminants below the level of detection were given a value of half the detection limit, after which they were $\log_{10}$ transformed to approximate normal distribution prior to analysis. Preliminary analysis of contaminant effects on thyroid hormones (TT3 and

TT4) and fledge success used mixed effects models with nest identity specified as a random term. We found little evidence that the random term was influencing results since the slopes did not differ from the models without the random term, so we used fixed effects models to assess the effects of contaminants on thyroid hormones and fledge success.

We first asked how contaminants influenced TT4, TT3 and the TT4:TT3 ratio in adult and nestling plasma samples. Candidate model sets for these analyses all 7 univariate models which included trans-nonachlor, dieldrin, DDE, ΣPCB, ΣPBDE, total contaminant load, and the null as explanatory variables. We did not evaluate multivariate models because our sample sizes were limited.

We next evaluated the relative importance of thyroid hormones (TT4, TT3, TT4:TT3), contaminants (trans-nonachlor, dieldrin, DDE, ΣPCB, ΣPBDE, and total contaminant load), and the null in explaining variation in fledging success by developing a candate model set with 10 univariate models.

We used an information theoretic approach to rank and identify the best-supported models within each model set (Burnham & Anderson, 2002). We calculated Akaike's Information Criterion adjusted for small sample sizes (AICc) and AICc weights (AICwt) for each model. Models with AICc scores within 2 of the best model and with high AICwt were considered to have strong support (Burnham & Anderson, 2002). We calculated the parameter estimate, the standard error and the 95% confidence interval.

3.4. Results

3.4.1. Cooper's hawk reproductive success

During 2012 and 2013 we found a total of 40 territorial and/or breeding Cooper's hawks around the Vancouver BC area (Table 3-1.). In 2012, a total of 24 nests were monitored of 27. Of the monitored nests, 88% were active, and 71% of the active nests produced young. Nest success was 1.95 fledglings/ active nest. In 2013, a total of 23 of

25 nests were monitored. Of the monitored nests, 96% were active, and 81% produced young. The nest success was 1.64 fledglings/ active nest.

3.4.2. Thyroid Hormone Concentrations in Plasma

We found that there was no significant difference in concentrations of TT4 between adult (M = 4.8 ng/mL, SD = 2.48) and nestling Cooper's hawks (M 4.8 ng/mL, SD = 2.59; t(17.75) = -0.05, p = 0.96). However, TT3 was significantly lower in adult (M = 1.1 ng/mL, SD = 0.33) than nestling Cooper's hawks (M = 2.2 ng/mL, SD = 0.69; t(12.58) = -4.64, p = 0.0005).

Adults

Three of the five models examining influence contaminants have on concentrations of TT4 in adult Cooper's hawks received strong support (ΔAIC_C <2; Table 3-2, 3-5). The highest ranked model, ΣPCBs, had two times the support of the null model. The data suggests that TT4 was negatively associated with concentrations of ΣPCBs (Fig. 3-3). The second ranked model, the null model, received 0.51 the support of the top model. The third model, ΣPBDEs, received 0.39 time the support of the top model and 0.76 times the support of the null model.

All five models examining the influence of contaminant concentrations on levels of TT3 received strong support (ΔAIC_C <2; Table 3-2, 3-5). The top ranked models, total contaminant load and ΣPBDEs, were equally weighted and received 2.2 times the support of the null model. The third model, DDE, received 0.9 times the support then the top models and 1.9 times the support of the null model. The forth model, ΣPCBs received 0.5 times the support of the top models and 1.1 times the support of the null model. The data suggest that TT3 decreases as total contaminant load, ΣPBDEs, DDE, and ΣPCBs increases (Fig. 3-2).

One model of the five candidate models examining the influence of contaminant concentrations on the TT4:TT3 ratio received strong support. The top ranked model was the null model (Table 3-2, 3-5).

Nestlings

Four of the five models examining the influence of contaminant concentrations on levels of TT4 received strong support (ΔAIC_C <2; Table 3-3, 3-6). The top ranked model, ΣPBDEs received 1.1 times the support of the null model. The top model suggests ΣPBDE concentrations have a negative influence on level of TT4 (Fig. 3-4). The second ranked model, the null model, received 0.91 times the support of the top model. The third ranked model, ΣPCBs, received 0.53 times the support of the top model and 0.58 times the support of the null model. The fourth ranked model, total contaminant load, received 0.44 times the support of the top model and 0.48 times the support of the null model.

Two of the five models examining the influence of contaminant concentrations on levels of TT3 received strong support (ΔAIC_C <2; Table 3-3, 3-6). The top model, the null model, received 1.5 times the support of the second ranked model. The second ranked model, DDE received 0.67 times the support of the top model.

One of the five models examining the influence of contaminant concentrations on the ratio of TT4:TT3 received strong support (ΔAIC_C <2; Table 3-3, 3-6). The top model, the null model, received 3.5 times the support of the second ranked model.

3.4.3. Contaminants and Fledging Success

Based on the adult samples (n = 17), three of the 10 models examining the influence of contaminants and thyroid hormones on the fledge success of Cooper's hawks received strong support (ΔAIC_C <2; Table 3-4). The top model, dieldrin received the same support of the null model, which was the second ranked model (AICwt = 0.24; Fig.3-5). The data suggests that the fledge success is negatively influenced by increasing concentrations of dieldrin. The third ranked model, ΣPBDE, received 0.5 times the support of the top model and the null model.

3.5. Discussion

Cooper's hawks from primarily urbanized areas of Vancouver nested in relatively high density, had average nest and fledge success, and were contaminated with a variety of POPs, principally DDE, cyclodiene insecticides, PCBs and PBDEs. Nest success measured as the number of chicks fledged per active nest, was variable and appears to be affected by contaminant exposure, Models indicate that fledge success was best explained by variation in the legacy compound dieldrin. TT4 concentrations in adults were negatively associated with concentrations of ΣPCBs in adults, while in nestlings; TT4 was most associated with ΣPBDEs.

In the Vancouver area, the distance between the closest Cooper's hawk nests was within the variable range reported in literature. The actual nest density of Vancouver's' Cooper's hawks could not be determined due to the likelihood we did not identify all nesting sites, however, the closest nest-to-nest distance observed was approximately 1km. This is within the bounds of other sites around North America (Wisconsin: 0.5 – 2.4 km, Rosenfield et al., 1995; New York: closest distance = 2.4 km, Meng, 1951).

The nest success and fledge success of the Cooper's hawks of Vancouver, BC, fall within the range of results previously reported in their breeding range. We found a nest success of 71% with 1.95 fledging per active nest in 2012, and 82% produced young with 1.64 fledglings per active nest. In Arizona, a high nest success of 85% was reported; with a corresponding high fledge success of 2.6 fledglings per active nest (Milisap, 1981). In contrast, a nest success rate of 53% and a fledge success of 1.6 fledglings per active nest was recorded in Utah (Hennessey, 1978). There are multiple routes that may affect fledge success, some which has been investigated in this study. Newton (1979) suggests that once in the nesting stage a raptors success can be affected by: 1) the age of parents, where older, more experienced adults produce more offspring, 2) weather, were wetter breeding seasons will reduce the number of chicks fledged, 3) food quality and availability, 4) parasites and disease, 5) human disturbance, 6) predation, and 7) contaminants. There is an abundance of prey in urban area for Cooper's hawks (Cava et al., 2012; Stout & Rosenfield, 2010), however, these prey include the abundant Columbidea (pigeons and doves) which can be infected with an upper digestive tract disease trichomoniasis. Urban Cooper' hawks in Arizona experienced low success rates due to this parasitic protozoan, *Trichomonas gallinae*, killing almost half of offspring leading researchers to suspect an ecological trap (Boal & Mannan, 1999). In spite of this outbreak, more recent studies demonstrated that there was in fact no ecological trap and that there is low presence and no mortality due to trichomoniasis across North America, including British Columbia (Mannan et al., 2008; Rosenfield et al., 2002). It has been observed that the Cooper's hawks of Metro Vancouver have been victim to predation at one nest and potentially human disturbance, causing a reduction in fledge success.

3.5.1. Effects of Contaminants on Reproductive Success

Concentrations in wildlife of legacy cyclodienes, such as dieldrin, have caused negative effects in the past and have declined since being banned; however, this study has found that dieldrin is continuing to have an influence on the success of Cooper's hawks. There is little published evidence of dieldrin affecting reproduction directly; however, a number of authors have hypothesized, and there is evidence to support, an indirect impact of dieldrin and other cyclodienes on reproduction of wild birds by poisoning of adults, particularly males, during the energetic stress of chick provisioning, particularly as dieldrin appears to be an anorexic agent (see review in Elliott & Bishop, 2011). Walker and Newton (1998) also speculated that, as a neuro-toxin, dieldrin could impact motor skills and coordination thus impacting hunting ability and increased risk of impacts with trees, vehicles, and power lines (Bishop & Brogan, 2013; I Newton & Wyllie, 1992; Walker & Newton, 1998). An Accipiter relies on its quick reaction and mobility to acquire prey, which if impaired can lead to less nest returns, and overall less parental care. Based on an examination of the available literature, Elliott and Bishop (2011) suggested a critical threshold of 1000 ng/g dieldrin in adult plasma associated with anorexic effects which could lead to reduced provisioning or even survival. In the present study, adult plasma dieldrin concentrations were elevated but did not exceed 271 ng/g dieldrin. Such thresholds provide guidance to interpret contaminants exposure data, but need to be weighed against statistical analysis of empirical data, such as from the present study where information theoretic decision making suggests that dieldrin exposure may have some lingering effects on reproductive success in Cooper's hawks. Such determinations also have to be considered in context of the overall nesting success and apparent saturation of the Metro Vancouver environment by these hawks. If there are minor impacts of legacy and newer POPs on nesting success of the more highly exposed individual hawks, the impact does not extend to the population level.

While there is strong evidence that North American populations of Cooper's hawks were impacted by organochlorine pesticides during the 1950s to 1980s, the species received much less attention than the European sparrowhawk (see, however, Elliott & Bishop, 2011; Elliott & Martin, 1994; Elliott & Shutt, 1993; Newton & Wyllie, 1992; Noble & Elliott, 1990; Sibly, Newton, & Walker, 2000; Snyder, et al., 1973; Stansley & Roscoe, 1999). Among the issues surrounding the role of contaminants in the documented declines of Cooper's hawks and other raptors during the OC era is the relative importance of DDT (specifically the metabolite, DDE) on reproduction, due to the its negative impact on eggshell thickness, reducing it to the point of being crushed under the weight of the incubating parent (Lincer, 1975; Peakall & Kiff, 1979; Ratcliffe, 1967, 1970), versus the impact of cyclodienes, such as dieldrin, chlordane on adult survival.

The European conspecific and ecological equivalent, the sparrowhawk (*Accipiter nisus*), has been extensively studied as a model species in population ecology and an indicator of the impact of chronic organochlorine contamination on wildlife (I Newton et al., 1986, 1993). Based on long term studies of a marked population, Newton et al. (1986) attributed population decline of sparrow hawks throughout many areas of Britain to adult mortality, primarily from soil and seed treatment use of dieldrin. Elliott and Martin (1994) made a case for a similar scenario in North America based in part on the stronger coincidence in timing of Cooper's hawk (and sharp-shinned hawk, *Accipiter striatus*) population trends with North American sales, and therefore usage, of dieldrin compared to DDT. They supported their argument with evidence of the relatively higher contamination of Accipiters with the cyclodienes, likely related to their soil use and therefore preferential bioaccumulation in terrestrial food chains. That is in contrast to the aerial application and likely fate of DDT compounds in aquatic systems, where they impacted species such as peregrine falcons (*Falco peregrines*), bald eagles (*Haliaeetus* *leucocephalus*) and osprey (*Pandion haliaetus*; Elliott et al., 2001; Elliott & Norstrom, 1998; Henny et al., 2010; Peakall & Kiff, 1979).

To consider how other contaminants in Cooper's hawk plasma compared to threshold values, we had to turn mainly to available criteria for eggs. Plasma to egg conversions have been determined for DDE and PCBs in nestling bald eagles and great horned owls (Strause et al., 2007) and for DDE only in adult Accipiters and kestrels (Henny & Meeker, 1981). Those authors analyzed concentrations of DDE eggs and nestlings or adults, and used linear regression to formulate the relationship. Newton et al. (1986) found that a DDE concentration in sparrowhawk eggs of 10 ug/g ww lead to a 20% reduction in eggshell thickness, as well, reproductive failure occurred in merlin (*Falco columbarius*) eggs at similar concentrations. When applying the egg to nestling plasma formula (Strause et al., 2007) the critical DDE plasma concentration is 215 ng/g. Applying the formula found by Henny and Meeker (1981) to convert egg to adult plasma concentrations, we get a critical threshold concentration of 1599 ng/g DDE in adults. Nestling Cooper's hawk geometric mean DDE concentration of 51.5 ng/g DDE (12.8 – 203 ng/g), which is below the critical threshold. Adult Cooper's hawk's concentrations were 824 ng/g DDE (88 – 3800 ng/g), with 3 individuals over the critical threshold of 1599 ng/g DDE. While this concentration is concerning, there is little evidence that that DDE is causing an effect, as this study found a no association with DDE and fledge success, or thyroid hormones. Furthermore, lab based dietary studies reported a critical threshold concentration of 34000 ng/g ΣPCB in the egg can cause lowered hatch success in American kestrels (Fernie et al., 2001). That converts to a plasma concentration in hatchlings of 1024 ng/g ΣPCB (Strause et al., 2007). Nestling ΣPCB concentrations did not exceed 179 ng/g ΣPCB, well below the critical threshold. Further, kestrels were again used to determine a threshold concentration of lowered parental care of 4000 ng/g ΣPCB in adult male plasma (Fisher et al., 2001, 2006; Harris & Elliott, 2011). This study found a maximum concentration of 1370 ng/g ΣPCB in adult plasma, again below the threshold concentration.

3.5.2. POPs and Thyroid Hormone Concentrations

There are multiple mechanisms by which pollutants, such as DDE, PCBs, and PBDEs, can alter circulating levels of thyroid hormone. Those contaminants can interfere with thyroid metabolizing enzymes in the liver, such as induction of uridine diphosphate glucuronosyltransferase (UDP-GT), leading to the formation of T4-glucuronide which is excreted in bile (McNabb and Fox, 2003). As well, the pollutants can alter plasma transport by competitive binding with T4 to the transport protein transthyretin, leading to an increase in free T4 which is excreted in urine or bile (Boas et al., 2006; Brouwer et al., 1998; McNabb & Fox, 2003; Ucán-Marin et al., 2010). It would be predicted that there would be a negative relationship between these thyroid disrupting compounds and thyroid hormones.

The relationship between known thyroid disrupting pollutants and thyroid hormone concentrations has been reported previously in birds, however, with varying results. We found that there was a negative relationship between ΣPCBs and TT4 in adults and between ΣPBDE and TT4 in nestlings, as well as a negative relationship between all contaminants and TT3 in nestlings. Similarly, adult glaucous gulls (*Larus hyperboreus*) and adult herring gulls (*Larus argentatus*) were reported to have a negative relationship with T4 and ΣPCBs (Fox et al., 2007; Verreault et al., 2007). The only recent study to find a negative relationship between PBDEs and T4 was an egg based lab study (Fernie et al., 2005). Concentrations of T3 in nestlings have also been found to be negatively influenced by contaminants. PCBs have been found to influence T3 in great blue heron (*Ardea herodias*) in the wild and American kestrels in the lab (Champoux et al., 2006; Fernie et al., 2005). T3 was also negatively associated with DDE and OH-PCBs in Bald eagles (Cesh et al., 2010). In a mini-review of correlations of pollutants and thyroid hormones, Cesh et al. (2010) found that nine of 14 studies in which T4 was negatively correlated to ΣPCBs, and only one lab based study out of three field and one lab studies found a negative relationship between T4 and ΣPBDE. They also found that six of 26 studies found a negative relationship between contaminants (PCB, DDE, PBDEs, OH-BDEs and OH-PCBs) and one study found a positive relationship. Although the majority of studies do find a negative relationship with PCBs and T4, the varying results may be due to the lower binding affinity of T4 to transthyretin in birds, rather than in mammals where the relationship is consistent (Cesh et al., 2010; Dawson, 2000). The negative association between all contaminants in this study and TT3 and no effect on TT4 in nestling signals that individuals may be experiencing inhibition of deiodinase with increasing concentrations of contaminants (Boas et al., 2006; Brouwer et al., 1998). The mechanism affecting TT4 in adults, however, could not be determined given the limited biomarkers quantified in this study. Given that there is little evidence of an effect occurring to the success of the Cooper's hawks, we believe that the concentrations of thyroid hormones, although influenced by pollutants, are within a healthy range.

3.6. Conclusion

Legacy pollutants, particularly cyclodiene insecticides such as dieldrin appear to be having a lingering effect on nesting success of Cooper's hawks in the Vancouver area. There is also some evidence of minor perturbation of circulating thyroid hormone concentrations by PCBs and possibly PBDEs. There were also three individual adult Cooper's hawks with concentrations of DDE surpassing a critical threshold known to cause eggshell thinning. Although the population seem to be healthy; taking up residency in most available habitat in the Vancouver area, contaminants, particularly in concert with other urban stress factors such as car strikes and increased parasite load (Boal & Mannan, 1999) may have an impact on the health of individual birds. The collection of eggs and blood are good mediums to measure residue levels, contaminant trends, per se, could also be done without further disturbing nesting birds by monitoring residue levels in the liver of birds found dead (e.g. the Predatory Bird Monitoring Scheme of the United Kingdom). It is recommended that one of these methods be employed to further monitor POPs in Cooper's hawks and other terrestrial birds of prey to further understand if there are long term negative impacts to top predators.

3.7. References

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3.8. Figures

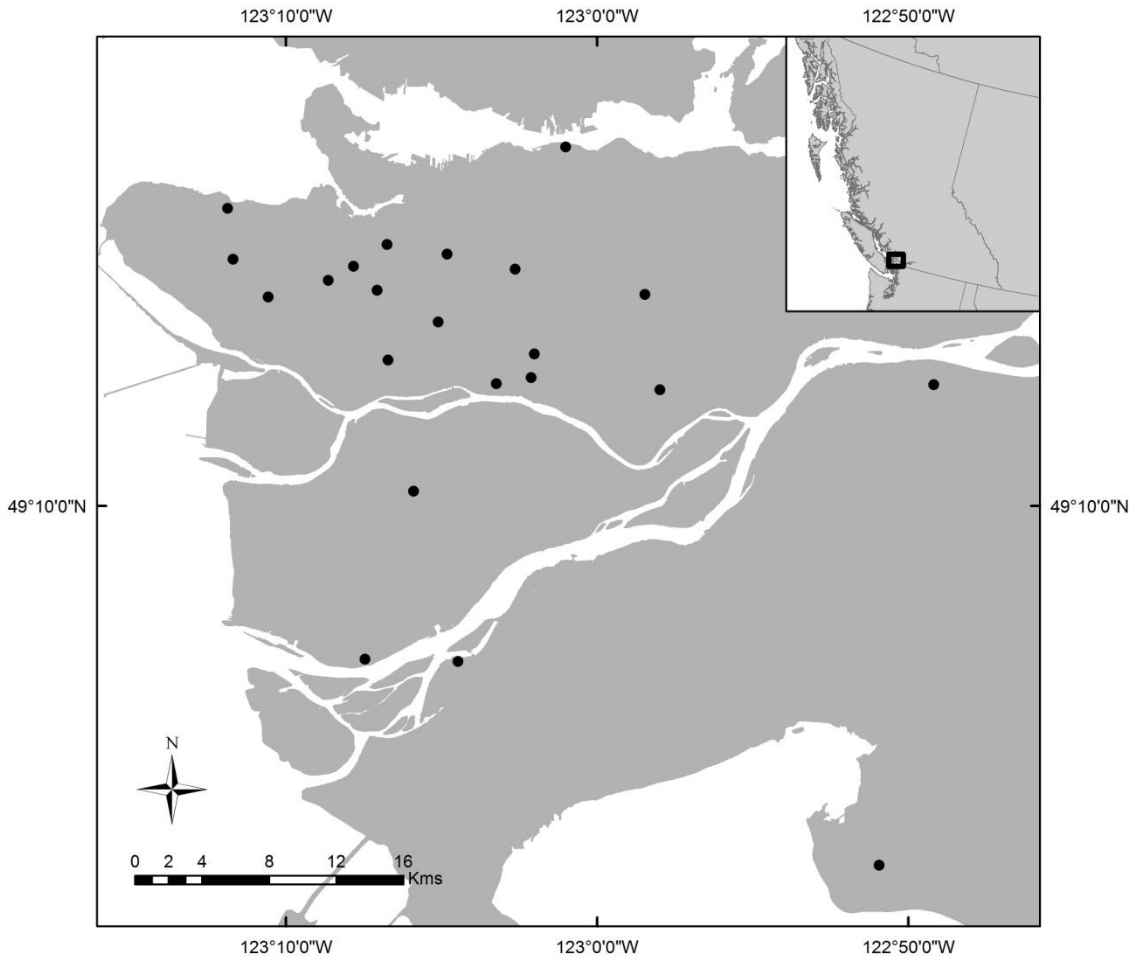

Figure 3-1. Sampled nest locations (points) of Cooper's hawks in the Metro Vancouver area, British Columbia, 2012- 2013.

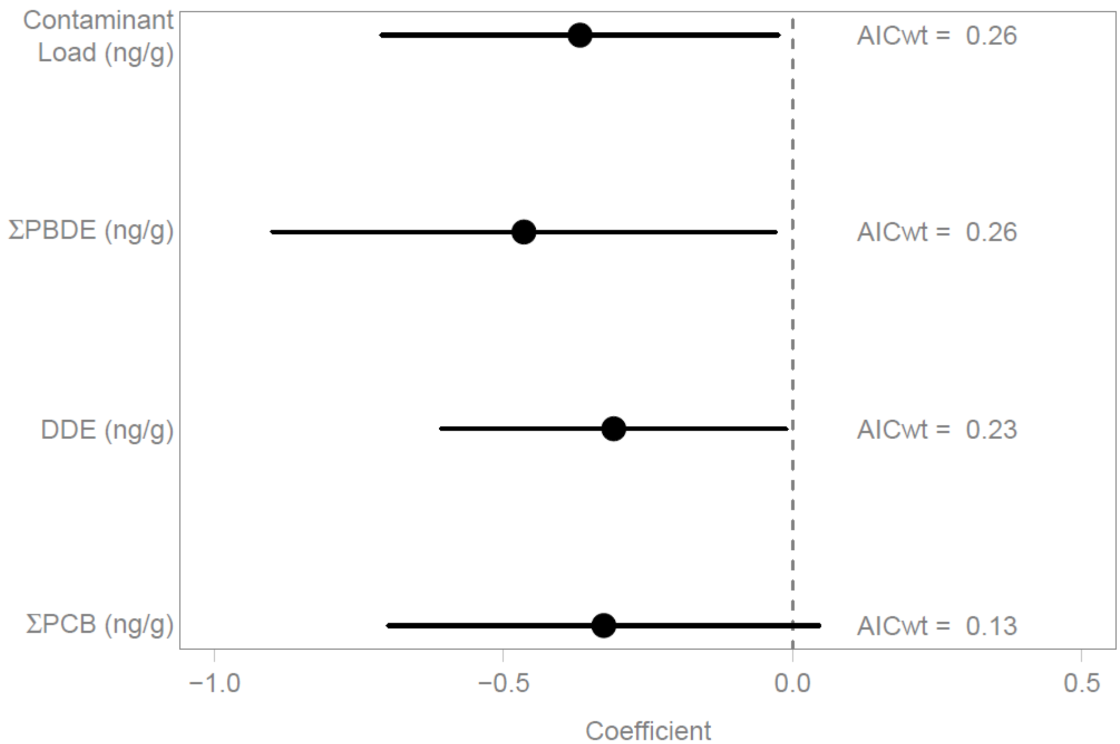

Figure 3-2. Coefficients (±95CI) and AICwt of $\log_{10}$ transformed contaminants influence (ΔAICc < 2) on TT3 in adult Cooper's hawks of Metro Vancouver, British Columbia (n = 19).

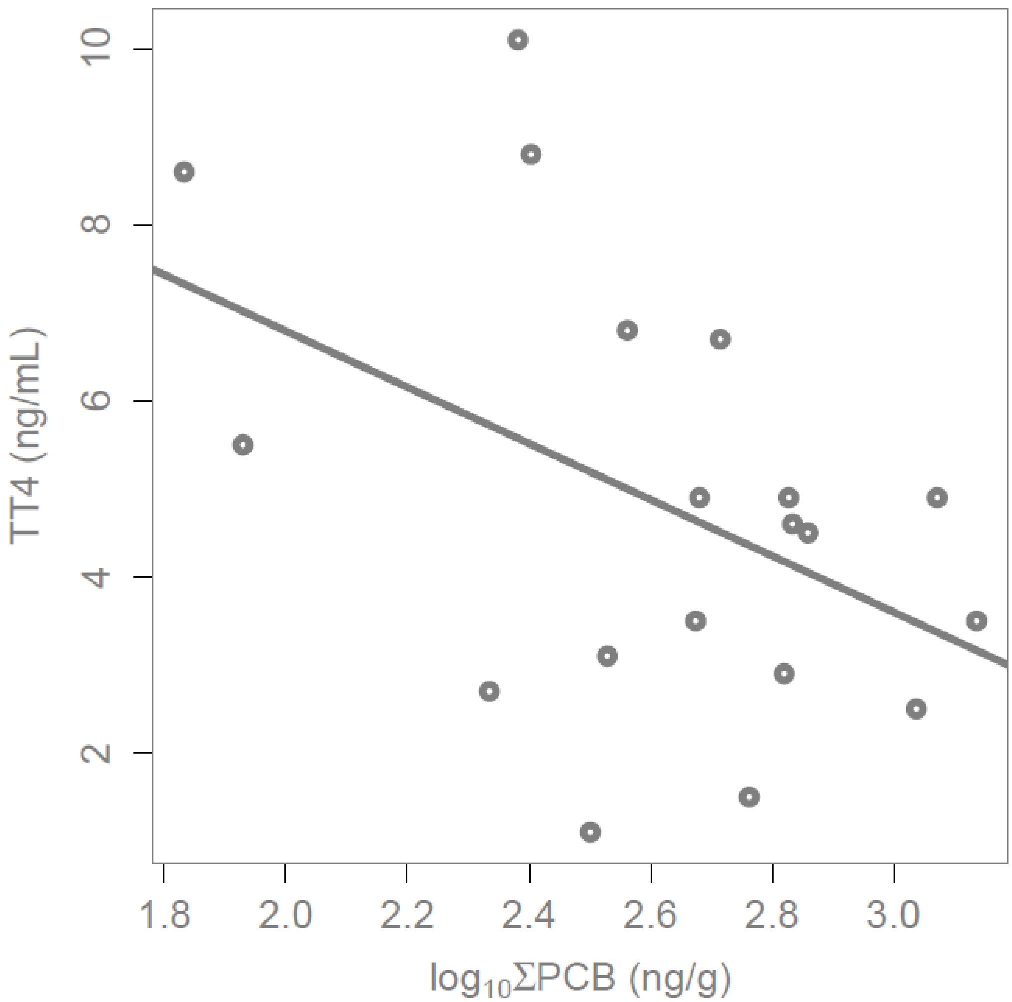

Figure 3-3. Linear regression of the top ranked variable, ΣPCB, influencing concentrations of TT4 based on plasma contaminant concentrations in adult Cooper's hawks of Metro Vancouver, British Columbia (n = 19).

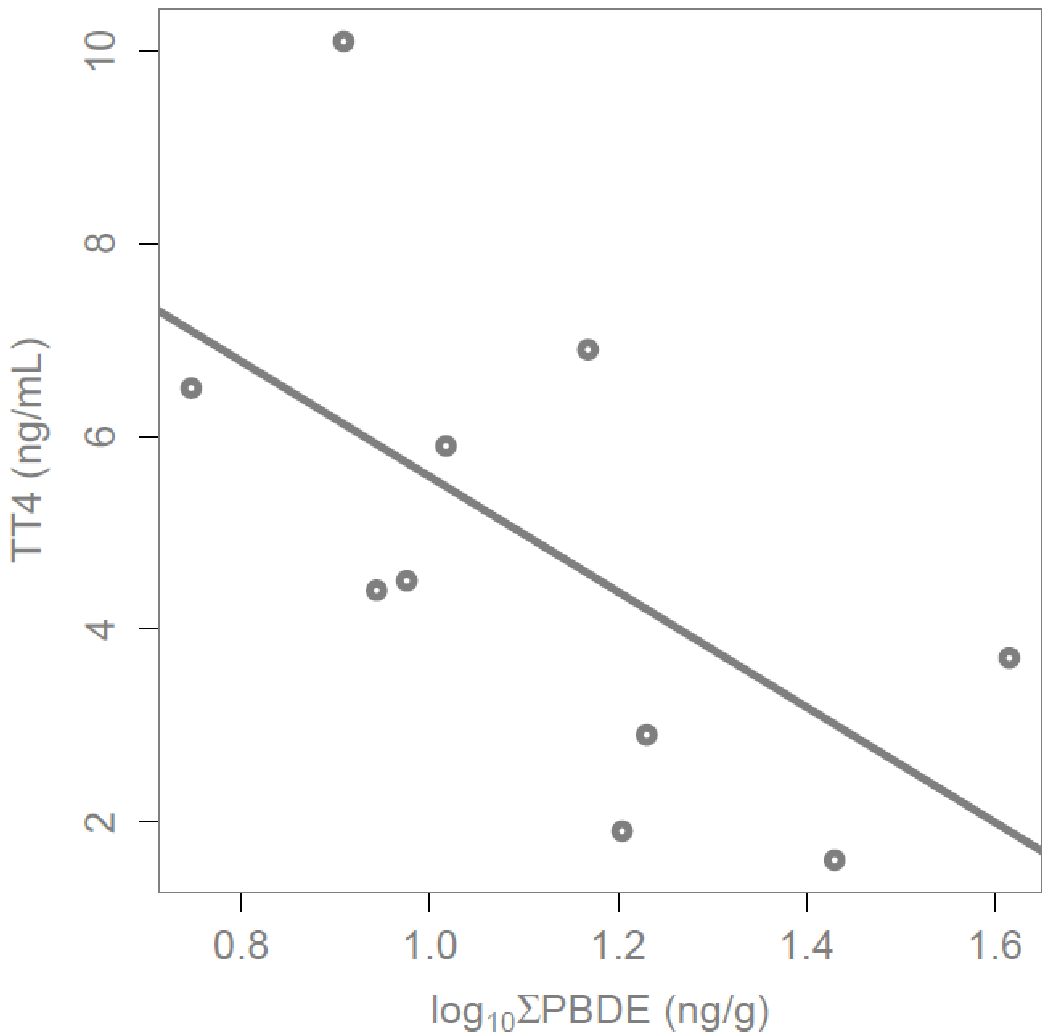

Figure 3-4. **Linear regression of the top ranked variable, ΣPBDE, influencing concentrations of TT4 based on plasma contaminant concentrations in nestling Cooper's hawks of Metro Vancouver, British Columbia (n = 10).**

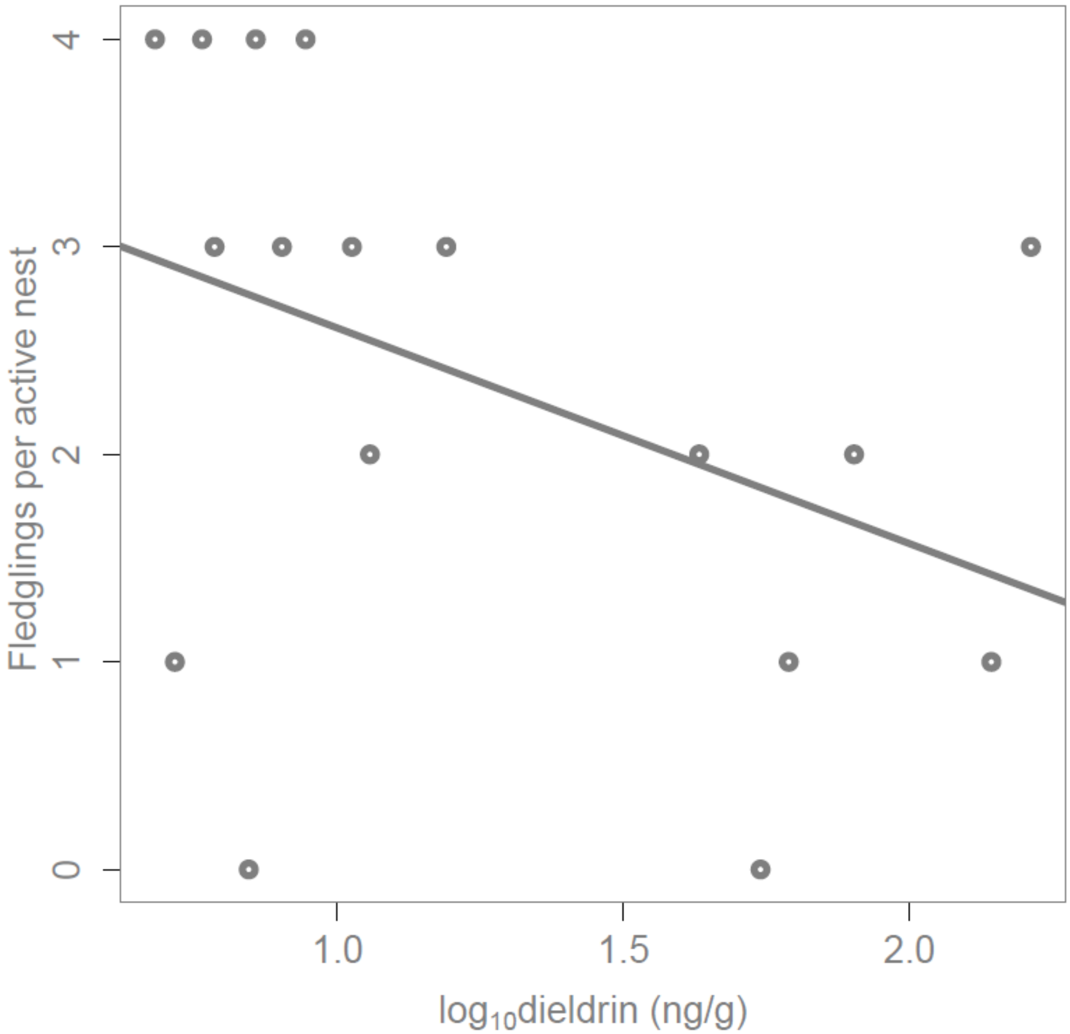

Figure 3-5. **Linear regression of the top ranked variable, dieldrin, influencing fledge success based on plasma contaminant concentrations in adult Cooper's hawks of Metro Vancouver, British Columbia (n = 17).**

3.9. Tables

Table 3-1. Nest activity and fledge success of Cooper's hawks of the Metro Vancouver area, British Columbia, 2012 and 2013.

	2012	2013
Total nests found	27	25
Territorial non-breeders	3	1
Confidently assessed active nests*	21	22
Proportion produced fledged young	0.71	0.82
Fledge success (fledged birds/active nest)	1.95	1.64

Table 3-2. Summary of most influential models, < 2 ΔAICc, examining the relationship between thyroid hormones; TT4, TT3 and the ratio of TT4:TT3 and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) based on adult Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: $AICwt/AICwt_{top\ model}$, r^2: coefficient of determination (n = 19).

	Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
TT4	ΣPCB	3	90.82	0	0.41	1.00	0.20
	null	2	92.2	1.38	0.21	0.51	0.00
	ΣPBDE	3	92.68	1.86	0.16	0.39	0.12
TT3	toxload	3	9.75	0	0.26	1.00	0.21
	ΣPBDE	3	9.78	0.02	0.26	1.00	0.21
	DDE	3	9.99	0.24	0.23	0.88	0.20
	ΣPCB	3	11.1	1.35	0.13	0.50	0.15
	null	2	11.29	1.54	0.12	0.46	0.00
TT4:TT3	null	2	89.62	0	0.49	1.00	0.00

Table 3-3. Summary of most influential models, < 2 ΔAICc, examining the relationship between thyroid hormones; TT4, TT3 and the ratio of TT4:TT3 and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) based on nestling Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwt$_{top\ model}$, r^2: coefficient of determination (n = 10).

	Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
TT4	ΣPBDE	3	51.86	0	0.32	1.00	0.36
	null	2	52.06	0.2	0.29	0.91	0.00
	ΣPCB	3	53.14	1.28	0.17	0.53	0.27
	toxload	3	53.47	1.61	0.14	0.44	0.25
TT3	null	2	26.47	0	0.42	1.00	0.00
	DDE	3	27.25	0.78	0.28	0.67	0.30
TT4:TT3	null	2	32.74	0	0.6	1.00	0.00

Table 3-4. Summary of AICc models examining the relationship between fledge success and thyroid hormones (TT4, TT3, and the ratio of TT4:TT3), and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) based on adult Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwt$_{top\ model}$, r^2: coefficient of determination (n = 17).

	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
dieldrin	3	62.66	0	0.24	1.00	0.16
null	2	62.69	0.03	0.24	1.00	0.00
ΣPBDE	3	64.14	1.48	0.12	0.50	0.09
TT4	3	65.08	2.42	0.07	0.29	0.03
TT3:TT4	3	65.37	2.71	0.06	0.25	0.02
TT3	3	65.56	2.9	0.06	0.25	0.01
ΣPCB	3	65.63	2.98	0.05	0.21	0.00
toxload	3	65.63	2.98	0.05	0.21	0.00
trans-nonachlor	3	65.68	3.02	0.05	0.21	0.00
DDE	3	65.68	3.02	0.05	0.21	0.00

3.10. Akaike information criterion (AIC) tables in full

Table 3-5. Summary of AICc models examining the relationship between thyroid hormones; TT4, TT3 and the ratio of TT4:TT3 and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) and each variables coefficient (Coeff), standard error (SE), and lower and upper confidence intervals (L CI and U CI respectively) based on adult Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwttop model, r2: coefficient of determination (n = 19).

TT4

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
ΣPCB	3	90.82	0	0.41	1.00	0.20
null	2	92.2	1.38	0.21	0.51	0.00
ΣPBDE	3	92.68	1.86	0.16	0.39	0.12
toxload	3	93.16	2.35	0.13	0.32	0.09
DDE	3	93.89	3.07	0.09	0.22	0.06

Variable	Coeff	SE	L CI	U CI
toxload	-2.094	1.572	-5.175	0.987
DDE	-1.429	1.383	-4.140	1.281
ΣPCB	-3.191	1.550	-6.229	-0.154
ΣPBDE	-2.954	1.966	-6.807	0.899

TT3

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
toxload	3	9.75	0	0.26	1.00	0.21
ΣPBDE	3	9.78	0.02	0.26	1.00	0.21
DDE	3	9.99	0.24	0.23	0.88	0.20
ΣPCB	3	11.1	1.35	0.13	0.50	0.15
null	2	11.29	1.54	0.12	0.46	0.00

Variable	Coeff	SE	L CI	U CI
toxload	-0.368	0.175	-0.711	-0.025
DDE	-0.310	0.152	-0.608	-0.012
ΣPCB	-0.327	0.190	-0.700	0.046
ΣPBDE	-0.465	0.222	-0.900	-0.030

TT4:TT3

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	89.62	0	0.49	1.00	0.00
ΣPCB	3	91.93	2.3	0.15	0.31	0.00
ΣPBDE	3	92.41	2.79	0.12	0.24	0.03
DDE	3	92.43	2.81	0.12	0.24	0.00
toxload	3	92.47	2.85	0.12	0.24	0.00

Variable	Coeff	SE	L CI	U CI
toxload	-0.044	1.544	-3.070	2.982
DDE	0.251	1.331	-2.357	2.860
ΣPCB	-1.125	1.596	-4.253	2.002
ΣPBDE	-0.462	1.952	-4.289	3.364

Table 3-6. Summary of AICc models examining the relationship between thyroid hormones; TT4, TT3 and the ratio of TT4:TT3 and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) and each variables coefficient (Coeff), standard error (SE), and lower and upper confidence intervals (L CI and U CI respectively) based on nestling Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwttop model, r2: coefficient of determination (n = 10).

TT4

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
ΣPBDE	3	51.86	0	0.32	1.00	0.36
null	2	52.06	0.2	0.29	0.91	0.00
ΣPCB	3	53.14	1.28	0.17	0.53	0.27
toxload	3	53.47	1.61	0.14	0.44	0.25
DDE	3	54.48	2.62	0.09	0.28	0.17

Variable	Coeff	SE	L CI	U CI
toxload	-4.160	2.547	-9.152	0.832
DDE	-3.247	2.535	-8.214	1.721
ΣPCB	-3.341	1.922	-7.108	0.425
ΣPBDE	-5.982	2.810	-11.490	-0.474

TT3

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	26.47	0	0.42	1.00	0.00
DDE	3	27.25	0.78	0.28	0.67	0.30
toxload	3	28.64	2.18	0.14	0.33	0.19
ΣPCB	3	29.36	2.9	0.1	0.24	0.13
ΣPBDE	3	30.27	3.8	0.06	0.14	0.05

Variable	Coeff	SE	L CI	U CI
toxload	-1.009	0.736	-2.452	0.433
DDE	-1.190	0.650	-2.463	0.083
ΣPCB	-0.639	0.585	-1.786	0.509
ΣPBDE	-0.602	0.955	-2.473	1.269

TT4:TT3

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
null	2	32.74	0	0.6	1.00	0.00
ΣPBDE	3	35.27	2.52	0.17	0.28	0.16
ΣPCB	3	36.78	4.04	0.08	0.13	0.02
DDE	3	36.97	4.22	0.07	0.12	0.01
toxload	3	36.98	4.23	0.07	0.12	0.01

Variable	Coeff	SE	L CI	U CI
toxload	-0.226	1.117	-2.414	1.963
DDE	0.237	1.056	-1.832	2.307
ΣPCB	-0.379	0.848	-2.041	1.284
ΣPBDE	-1.523	1.226	-3.926	0.879

Table 3-7. Summary of AICc models examining the relationship between fledge success and thyroid hormones (TT4, TT3, and the ratio of TT4:TT3), and contaminants (total contaminant load, DDE, ΣPCB, and ΣPBDE) and each variables coefficient (Coeff), standard error (SE), and lower and upper confidence intervals (L CI and U CI respectively) based on adult Cooper's hawk's plasma samples from Metro Vancouver, British Columbia, 2012 - 2013. K: number of parameters estimated, ΔAICc : the difference between the AICc of each model and the top model, AICwt: AIC weight for that model, Evidence Ratio: AICwt/AICwttop model, r2: coefficient of determination (n = 17).

Model	k	AICc	ΔAICc	AICwt	Evidence Ratio	r^2
dieldrin	3	62.66	0	0.24	1.00	0.16
null	2	62.69	0.03	0.24	1.00	0.00
ΣPBDE	3	64.14	1.48	0.12	0.50	0.09
TT4	3	65.08	2.42	0.07	0.29	0.03
TT3:TT4	3	65.37	2.71	0.06	0.25	0.02
TT3	3	65.56	2.9	0.06	0.25	0.01
ΣPCB	3	65.63	2.98	0.05	0.21	0.00
toxload	3	65.63	2.98	0.05	0.21	0.00
trans-nonachlor	3	65.68	3.02	0.05	0.21	0.00
DDE	3	65.68	3.02	0.05	0.21	0.00

Variable	Coeff	SE	L CI	U CI
dieldrin	-1.039	0.608	-2.231	0.153
t - nonachlor	-0.010	0.719	-1.420	1.400
DDE	0.010	0.860	-1.676	1.695
toxload	-0.204	1.007	-2.177	1.770
TT4	0.099	0.135	-0.165	0.363
TT3	0.366	1.127	-1.843	2.575
TT4:TT3	0.042	0.080	-0.115	0.200
ΣPCB	-0.209	1.024	-2.216	1.798
ΣPBDE	-1.474	1.234	-3.892	0.945

Chapter 4. Conclusion

4.1. Thesis Summary

There is evidence of lingering effects of chemicals that have been banned for decades. During the 1950s to 1980s, raptor populations in many parts of the world were impacted by contamination, mainly from organochlorine insecticides and other persistent organic pollutants (POPs; Newton, 1979). Because of the extreme persistence of many of these compounds exposure is determined by past usage. Although the concentrations of many pollutants have decreased in wildlife or have equilibrated with the surrounding environment (Crosse et al., 2012; Harris et al., 2003; Newton et al., 1986; Park et al., 2009) our findings provide evidence that some of these chemicals still affect health of bird populations (Cesh et al., 2010; Henny et al., 2009; Morrissey et al., 2014).

In this study the Cooper's hawk (*Accipiter cooperii*) was used to investigate the sources and effects of pollutants in the metro Vancouver area. A recent study reported that Cooper's hawks of south western British Columbia were exposed to high concentrations of PBDE and other pollutants (Elliott et al., 2010). Based on those findings a more thorough investigation was necessary. We first investigated sources of POP and PBDE exposure based on land-use, population density and diet (Chapter 2). We then investigated potential effects of exposure based on concentrations of thyroid hormone biomarkers and fledge success (Chapter 3).

Chapter one focused on the sources of POP and PBDE exposure. Using radio telemetry, Cooper's hawks were followed throughout the non-breeding season, allowing us to discover their home range, and that they are year round residents to the area, thus, exposure is local. We found that concentrations of both ΣPCBS and ΣPBDE were most associated with increasing level of development. This association has also been reported in other birds around the world where the source of pollution is more urbanized (Morrissey et al., 2013; Newsome et al.,2010). As well, concentrations of DDE were best explained by gender of Cooper's hawk and dieldrin was most associated with the nitrogen isotope signature $\delta^{15}N$ which is associated with trophic level and, therefore, bioaccumulation from the diet.

In chapter two, we focused on the potential effects that the pollutants may be causing. Firstly, we found that concentrations of DDE were relatively high, with three individuals surpassing a critical threshold associated with reduced eggshell thickness. We found that the thyroid hormone total thyroxine (TT4) was most associated with PCBs and PBDEs, and that total triiodothyronine (TT3) received support from all tested contaminants negatively. The negative relationship between TT4 and ΣPCBs and ΣPBDEs are predicted given the proposed mechanism of hormone mimicry, particularly by the structural similarities. Results in birds, however, have varying interactions which are likely due to the binding affinity of T4 to transthyretin, a transport protein (Dawson, 2000). Interestingly, the relationship between TT3 and all the pollutants was negative and ranked above the null model. This may be due to an altered deiodonase enzyme, not allowing T4 to be metabolized to T3, with the limited biomarkers investigated, we only speculate. We also measured nest success of Cooper's hawks throughout our study area. In general, the hawks in this study had a low to average fledge success which was most influence by concentrations of dieldrin. Dieldrin has been attributed to causing reduced fledge success in Accipiters in the UK and eastern North America and still may be having an impact (Elliott & Martin, 1994; Newton & Wyllie, 1992).

Research should expand the temporal and spatial aspects of this project to obtain a broader scope of the exposure and health of the Cooper's hawk population throughout southwestern B.C. Given that this was a two year study, a few hawks may not have been found, which blood samples could taken from to create a larger picture of the status of POPs and PBDEs. As well, sampling another population away from a large metropolis would allow for a comparative study and help better understand the dynamics of the residue concentrations.

Pollutants which are banned will only be replaced with other chemicals with unknown consequences and it is therefore necessary to have in place an effective method to monitor these chemicals distribution and effects. A species or population of organisms that are used to detect environmental health is termed a biomonitor, of which birds have been successfully utilized. Recently the European starling (*Sturnus vulgaris*) has begun to be used to monitor flame retardants and other POPs in a terrestrial system (Chen et al., 2012; Eens et al., 2013; Eng et al., 2014). The starling, however, does not represents the exposure of a top predator, like a bird of prey does. The United Kingdom has implemented a success long term raptor monitoring program which has been able to identify the temporal and spatial qualities of many POPs and emerging pollutants (Crosse et al., 2012; Wienburg & Shore, 2004). North America could benefit from a similar program, using a top predator to monitor exposure to environmental contaminants.

4.2. References

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Appendix.

Plasma contaminant concentrations

Organochlorines

Table A-1. Concentrations of organochlorine pesticides (ng/g) in adult and nestling Cooper's hawks from the Metro Vancouver area, British Columbia, Canada, 2012 to 2013 (geometric mean (range))

	Adult (n = 21)		Nestling (n = 15)	
Pentachlorobenzene	0.1	(DL - 1.3)	0.05	(DL - 0.1)
t.Chlordane	0.12	(DL - 1.2)	0.06	(DL - 0.6)
c.Chlordane	0.50	(DL - 4.7)	0.09	(DL - 0.7)
y.Tetrachlorobenzene	0.28	(DL - 2.2)	0.11	(DL - 3.2)
x.Tetrachlorobenzene	0.25	(DL - 2.9)	0.12	(DL - 3.5)
Mirex	17.5	(1.9- 327)	0.19	(DL - 2.3)
*Heptachlor epoxide	40.7	(15.3- 313)	0.19	(DL - 9.4)
Hexachlorobenzene	2.1	(0.5- 19.8)	0.20	(DL - 1)
c.Nonachlor	6.77	(0.5- 31)	0.89	(0.3- 4.5)
p.p.DDD	6.47	(1.1- 48.2)	1.14	(0.2- 2.6)
*Oxychlordane	49.1	(13.8- 164)	2.20	(DL - 10.3)
Dieldrin	26.5	(4.8- 271)	2.47	(DL - 24.2)
t.Nonachlor	51.5	(4.3- 271)	7.06	(1.8- 37.9)
sumChlro	70.6	(4.4- 560)	9.61	(2- 38.5)
p.p.DDE	824	(88.9- 3800)	51.5	(12.8- 203)
p.p.DDT	0.33	(DL - 11.3)	<DL	

* concentrations for 2013 only

Detection Limit (DL) = 0.1 ng/g

Polychlorinated biphenyls (PCBs)

Table A-2. Concentrations of polychlorinated biphenyl congeners (ng/g) in adult and nestling Cooper's hawks from the Metro Vancouver area, British Columbia, Canada, 2012 to 2013 (geometric mean (range)).

	Adult (n = 21)		Nestling (n = 15)	
PCB.16.32	<DL		0.06	(DL - 0.1)
PCB.18.17	0.06	(DL - 4.3)	<DL	
PCB.22	0.05	(DL - 0.3)	0.05	(DL - 0.1)
PCB.31.28	0.17	(DL - 1.1)	0.1	(DL - 0.9)
PCB.33.20	<DL		0.07	(DL - 0.3)
PCB.44	0.06	(DL - 0.3)	0.05	(DL - 0.1)
PCB.47.48	0.37	(DL - 1.7)	0.06	(DL - 0.4)
PCB.49	0.12	(DL - 0.6)	0.06	(DL - 0.3)
PCB.52	0.52	(DL - 1.6)	0.18	(DL - 0.9)
PCB.56.60	0.07	(DL - 0.5)	0.07	(DL - 1.8)
PCB.64.41	0.06	(DL - 0.8)	<DL	
PCB.66	0.62	(0.2- 1.7)	0.14	(DL - 1.8)
PCB.70.76	0.1	(DL - 1.)	0.08	(DL - 1.9)
PCB.74	0.99	(DL - 3.8)	0.44	(DL - 1.7)
PCB.85	1.24	(0.4- 6.5)	0.1	(DL - 0.8)
PCB.87	0.22	(DL - 2.1)	0.05	(DL - 0.1)
PCB.92	0.59	(DL - 2.)	0.11	(DL - 0.6)
PCB.95	0.29	(0.1- 1.4)	0.08	(DL - 0.4)
PCB.97	0.09	(DL - 0.5)	0.09	(DL - 0.4)
PCB.99	7.39	(1.9- 27.2)	0.8	(0.2- 3)
PCB.101.90	3.8	(1.2- 13.1)	1.06	(0.3- 2.7)
PCB.105	1.27	(DL - 5.2)	0.08	(DL - 1.5)
PCB.110	0.61	(DL - 2.5)	0.09	(DL - 0.8)
PCB.114	0.18	(DL - 0.9)	0.05	(DL - 0.1)
PCB.118	8.81	(2.5- 29.9)	1.34	(0.2- 4.5)
PCB.128.167	6.88	(1.6- 22.7)	0.68	(DL - 3.6)
PCB.130	1.51	(0.2- 6.7)	0.12	(DL - 1)
PCB.137	2.21	(0.7- 5.9)	0.11	(DL - 1.2)
PCB.138	42.9	(8.79- 183)	4.46	(0.6- 19.2)
PCB.141	1.46	(0.3- 5.3)	0.18	(DL - 1.2)
PCB.146	10.6	(1.6- 41.1)	1.25	(DL - 4.5)
PCB.149	3.95	(0.1- 18)	0.6	(DL - 2.9)

PCB.151	0.69	(0.2- 4.5)	0.13	(DL - 1.2)
PCB.153	70.3	(10.7- 272)	7.42	(1.3- 31)
PCB.156	3.87	(0.8- 14.1)	0.22	(DL - 1.7)
PCB.157	0.18	(DL - 1.3)	0.06	(DL - 0.3)
PCB.158	2.76	(0.7- 12.4)	0.35	(DL - 1.1)
PCB.170.190	19.2	(3- 66.4)	1.75	(0.3- 10.3)
PCB.171	3.42	(0.7- 11.4)	0.25	(DL - 1.7)
PCB.172	5.13	(0.7- 15.6)	0.36	(DL - 2.8)
PCB.174	1.9	(0.3- 7)	0.24	(DL - 2.1)
PCB.176	0.07	(DL - 0.4)	<DL	
PCB.177	6.21	(0.8- 24)	0.61	(DL - 3.9)
PCB.187	14.8	(1.3- 114)	1.04	(0.3- 19.4)
PCB.178	0.59	(DL - 9.5)	0.09	(DL - 2.9)
PCB.179	1.59	(DL - 206)	1.46	(DL - 13.1)
PCB.180	25.6	(2.8- 105)	1.37	(0.3- 26)
PCB.183	23.2	(1.8- 167)	3.36	(0.2- 11.5)
PCB.189	1.2	(0.2- 4.6)	0.06	(DL - 0.5)
PCB.194	12.3	(1.5- 44)	0.67	(DL - 4.9)
PCB.195	2.78	(0.4- 10.4)	0.11	(DL - 1.4)
PCB.196.203	10.5	(1.5- 39.2)	0.98	(0.2- 4.6)
PCB.199	14.2	(1.8- 50.2)	0.89	(DL - 6.4)
PCB.200	0.16	(DL - 1.1)	0.06	(DL - 0.3)
PCB.201	0.18	(DL - 2)	<DL	
PCB.202	1.46	(0.3 5.1)	0.14	(DL - 1)
PCB.205	0.18	(DL - 1.6)	0.08	(DL - 8.8)
PCB.206	3.42	(0.6 - 11.9)	0.22	(DL - 1.5)
PCB.207	0.11	(DL - 0.8)	0.05	(DL - 0.1)
PCB.208	0.39	(DL - 2.7)	0.06	(DL - 0.4)
PCB.209	0.98	(0.2- 5)	0.21	(DL - 0.7)
ΣPCB	390	(66 - 1370)	40.5	(6.4- 179)

Detection Limit (DL) = 0.1 ng/g

Polybrominated diphenyl ethers (PBDEs)

Table A-3. Concentrations of polybrominated diphenyl ether congeners (ng/g) in adult and nestling Cooper's hawks from the Metro Vancouver area, British Columbia, Canada, 2012 to 2013 (geometric mean (range))

	Adult (n = 21)		Nestling (n = 15)	
BDE.28	0.12	(DL - 1)	0.05	(DL - 0.2)
BDE.47	14.9	(6.7- 61.5)	1.97	(DL - 13.9)
BDE.49	0.09	(DL - 3.4)	0.07	(DL - 0.8)
BDE.66	0.2	(DL - 6.5)	0.08	(DL - 1.7)
BDE.85	0.43	(DL - 2.7)	0.09	(DL - 0.5)
BDE.99	46.4	(13.4- 208)	5.54	(0.5- 31.8)
BDE.100	12.3	(2.5- 50.3)	1.17	(DL - 5.3)
BDE.138	0.16	(DL - 1.4)	0.05	(DL - 0.2)
*BDE.153	10.7	(4.5- 32.6)	0.85	(0.3- 2.3)
BDE.154.BB.153	7.17	(1.2- 25.6)	0.44	(DL - 3.1)
BDE.17	0.11	(DL - 0.6)	0.05	(DL - 0.1)
BDE.183	0.84	(DL - 5.7)	0.07	(DL - 0.7)
BDE.190	0.08	(DL - 0.5)	<DL	
BDE.209	<DL		<DL	
ΣPBDE	96.6	(33.6- 336)	14.1	(3.6- 60.1)

* concentrations for 2012 only

Detection Limit (DL) = 0.1 ng/g, except BDE.209 DL = 5 ng/g