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Spatiotemporal patterns and relationships among the diet, biochemistry, and exposure to flame retardants in an apex avian predator, the peregrine falcon[☆]

Kim J. Fernie[a,*], Dominique Chabot[b], Louise Champoux[c], Samantha Brimble[a,d], Mehran Alaee[d], Sarah Marteinson[a], Da Chen[e], Vince Palace[f], David M. Bird[b], Robert J. Letcher[g]

[a] Ecotoxicology & Wildlife Health Division, Science & Technology Branch, Environment and Climate Change Canada, Burlington, Ontario, Canada
[b] Avian Science and Conservation Centre, Department of Natural Resource Sciences, McGill University, Ste-Anne-de-Bellevue, Quebec, Canada
[c] Ecotoxicology & Wildlife Health Division, Science & Technology Branch, Environment and Climate Change Canada, Quebec City, Quebec, Canada
[d] Aquatic Contaminants Research Division, Science & Technology Branch, Environment and Climate Change Canada, Burlington, Ontario, Canada
[e] Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University, Carbondale, IL, USA
[f] International Institute for Sustainable Development – Experimental Lakes Area (IISD-ELA), Winnipeg, Manitoba, Canada
[g] Ecotoxicology & Wildlife Health Division, Science & Technology Branch, Environment and Climate Change Canada, National Wildlife Research Centre, Ottawa, Ontario, Canada

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ABSTRACT

Flame retardants (FR) are industrial chemicals and some are proven environmental contaminants that accumulate in predatory birds. Few studies have examined the influence of diet on FR profiles in nestling raptors and the possible physiological implications of such FR exposure. The objectives of this research were (1) to determine spatial patterns of ≤ 48 polybrominated diphenyl ether (PBDE) congeners and ≤ 26 non-PBDE FRs, including organophosphate esters (OPEs), in nestling peregrine falcons (*Falco peregrinus*) across the Canadian Great Lakes-St. Lawrence River Basin (GL-SLR; 2010) and in the eastern Canadian Arctic (2007); (2) to identify temporal changes in FR concentrations from the mid-2000s to 2010 in GL-SLR peregrine nestlings; (3) to investigate the role of diet using stable isotopes on exposure patterns of quantifiable FRs; and (4) to assess possible associations between circulating FRs and total (T) thyroxine (TT_4) and triiodothyronine (TT_3), tocopherol, retinol and oxidative status (isoprostanes). The summed concentrations of the top 5 PBDEs (Σ_5) (BDE-47, -99, -100, -154, -153) were significantly higher in rural nestlings than urban nestlings in the GL-SLR, followed by the eastern Arctic nestlings. The PBDE congener profile of rural nestlings was dominated by BDE-99 (34‰), whereas BDE-209 (31‰) became dominant in the 2010 urban PBDE profile marking a shift since the mid-2000s. Low (ppb) concentrations of 25 novel non-PBDE FRs (e.g., 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE)) were measured in the nestlings in at least one region, with the first report in peregrines of 15 novel non-PBDE FRs (e.g., 2-ethyl-1-hyxyl 2,3,4,5-tetrabromobenzoate (EHTBB), pentabromo allyl ether (PBPAE), tetrabromoethylcyclohexane (α-, β-DBE-DBCH)) as well as of tris (2-butoxyethyl) phosphate (TBOEP) (0–7.5 ng/g ww) > tris(2-chloroisopropyl) phosphate (TCIPP) (0.1–5.5 ng/g ww) > tris(2-chloroethyl) phosphate (TCEP) (0.02–2.0 ng/g ww) > tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) (0–1.0 ng/g ww). Within the GL-SLR, the urban nestlings' diet had significantly more terrestrial sources (greater $\delta^{13}C$ values) than the broader, more aquatic-based diet of rural peregrines. Dietary source ($\delta^{13}C$) was significantly associated with concentrations of Σ_5PBDE, BDE-209, EHTBB, and 2,2–4,4′,5,5′-hexabromobiphenyl (BB-153), with trophic level ($\delta^{15}N$) also positively associated with BDE-209 levels. Compared to urban nestlings, the rural nestlings had significantly lower circulating concentrations of thyroxine (TT_4), triiodothyronine (TT_3), a greater proportion of TT_3 relative to TT_4 (TT_3:TT_4), tocopherol and oxidative status (isoprostanes), but higher retinol levels; the most recalcitrant PBDE congener, BDE-153, in combination with low concentrations of some novel FRs, particularly

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* Corresponding author.

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octabromotrimethylphenyllindane (OBIND), may influence circulating thyroid hormones, especially TT_4, and retinol levels of peregrine falcon nestlings. These associations of FR-endocrine-biochemical measures suggest possible exposure-related changes in these birds and further study is warranted.

1. Introduction

Industrial chemicals used as flame retardants (FRs) are incorporated into a wide variety of commercial products, and many are persistent environmental contaminants. Historically, the most prevalently used FRs were brominated compounds, particularly polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), and tetrabromobisphenol A (TBBPA) (Covaci et al., 2011). PBDEs were additive FRs having the highest production volume and prolonged usage through the 1970s, until the voluntary withdrawal of the technical mixture in 2004; the production of BDE-209 continued until it was phased out in 2013. PBDEs are bioaccumulative and continue to be found at the greatest concentrations relative to all other FRs. The three major commercial PBDE technical mixtures, penta-BDE, octa-BDE and deca-BDE, are now listed under the Stockholm Convention, with the acceptance of deca-BDE for risk management in June 2016 (http://chm.pops.int/). Since being listed under the Stockholm Convention, decreasing levels of PBDE congeners have been reported in birds (e.g., Law et al., 2014), although congeners associated with the deca-BDE mixture, mainly BDE-209, generally continue to be reported as increasing (e.g., Letcher et al., 2014). The various regulatory measures of these prominent BFRs have resulted in the development and use of novel FRs as alternative replacements: many are reported as emerging environmental contaminants capable of long-range transport and deposition (Covaci et al., 2011; Bergman et al., 2012), including 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE) and bis(2-ethyl-1-hexyl-tetrabromophthalate (BEHTBP).

Organophosphate esters (OPEs) are a large group of chemicals that are also used as FRs and plasticizers (van der Veen and de Boer, 2012), and are replacement FRs for PBDEs. As a result, their production and use has increased considerably, as for example in North America where the annual production of the OPEs, tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and tris(2-chloroethyl) phosphate (TCEP), increased from less than 14,000 t per year in 1986, to 38,000 t per year in 2012 (Schreder et al., 2016). Several OPEs have varied in the eggs, plasma, and other tissues of herring gulls (*Larus argentatus*) across the Great Lakes (Greaves and Letcher, 2014) over the past two decades (Greaves et al., 2016a, 2016b). Very recently, Greaves and Letcher (2017) reviewed the occurrence and levels of OPEs in the environment with a focus on avian wildlife. Overall, reports on the bioaccumulation and toxicity to wildlife, including birds, of novel FRs have been increasing in recent years but remain limited.

Birds at elevated trophic levels are useful sentinel species of FR accumulation (e.g., Guerra et al., 2011, 2012; Gentes et al., 2012; Su et al., 2015, 2017; Greaves et al., 2016a, 2016b; Champoux et al., 2017) some of which have shown biochemical changes and toxicological effects (e.g., Smits and Fernie, 2013). Peregrine falcons (*Falco peregrinus*) and Cooper's hawks (*Accipiter cooperi*) are obligate apex avian predators having an exclusively avian diet and occupying the highest trophic level. They have also accumulated the highest recorded concentrations of HBCDD (Guerra et al., 2011, 2012) and PBDEs (Elliott et al., 2015) of any biota. Peregrines are known to accumulate historical FRs (e.g., Lindberg et al., 2004; Chen et al., 2008; Park et al., 2009; Potter et al., 2009; Fernie and Letcher, 2010). Yet, there is limited knowledge concerning their exposure to novel FRs (Guerra et al., 2011, 2012; Johansson et al., 2009; Newsome et al., 2010; Park et al., 2011), and that of other raptors (e.g., Chen et al., 2012a, Eulaers et al., 2014), and there have been no studies examining the linkages among FR profiles, diet, and potential biochemical changes in apex predatory birds. In the mid-2000s, spatial differences were evident across the Canadian Great Lakes Basin in the exposure of nestling peregrines to PBDEs, hydroxylated (OH)-PBDE metabolites, and other non-FRs (Fernie and Letcher, 2010), some which were correlated with the nestlings' circulating triiodothyronine (T_3), retinol, and biochemical measures relating to hepatic function, bone dynamics and growth (Smits and Fernie, 2013). In other studies with wild predatory birds, concentrations of OH-PBDE metabolites were similarly associated with T_3 and retinol concentrations in nestling bald eagles (*Haliaeetus leucocephalus*) (Cesh et al., 2010), and testosterone was associated with PBDE and methoxylated (MeO)-PBDE concentrations in the eggs of glaucous gulls (*L. hyperboreus*) (Verboven et al., 2008).

Given the environmental persistence of certain PBDEs, and the increasing use of novel FRs despite limited knowledge of their toxicity, further research is warranted to characterize the exposure of apex predatory birds to these FRs and the subsequent potential physiological effects to these species. Using the peregrine falcon as a model for apex avian predators, the objectives of the current study were: (1) to determine spatial patterns of historical and novel FR exposure, including OPEs, in the plasma of nestling peregrine falcons from urban and rural sites across the Canadian Great Lakes-St. Lawrence River Basin (GL-SLR; sampled in 2010) and remote sites in the eastern Canadian Arctic (2007); (2) to compare temporal changes in FR concentrations in GL-SLR peregrine nestlings in 2010 to those in the mid-2000s (Fernie and Letcher, 2010); (3) to investigate the role of diet (using stable carbon and nitrogen isotope ratios) on the 2010 exposure patterns of quantifiable FRs; and (4) to assess possible associations between concentrations of circulating FRs and total (T) thyroxine (TT_4), TT_3, tocopherol, retinol and oxidative status (isoprostanes) in the GL-SLR nestlings.

2. Materials and methods

2.1. Field data collection

This research was conducted with appropriate permits and in compliance with the guidelines of the Canadian Council of Animal Care. Peregrines nest repeatedly at the same location (Murphy, 1990) and most of the current 30 nest sites (2010) were monitored previously in the mid-2000s (Fernie and Letcher, 2010) across the GL-SLR. In addition, nestlings from 9 nests were sampled in the eastern Canadian Arctic (Ungava Bay, Quebec; 2007) (Fig. 1). In the GL-SLR, 14 nests were located within large urban centers ("urban"), specifically in the Greater Toronto-Hamilton Metropolitan Area (GTHA) (N = 7 nests), the Montreal Metropolitan Area (N = 4), and the Montreal peri-urban area (N = 3). The 15 remaining nests in the Canadian GL-SLR were located in "rural" areas (N = 13 nests, Lake Superior; N = 2 nests, eastern Quebec). Blood samples were collected for laboratory analyses (GL-SLR: FR concentrations, stable isotopes and biomarkers; Ungava Bay: FR concentrations only) from up to 2 randomly selected nestlings, preferably one male and one female, from each brood of up to 5 possible nestlings (18–30 days old). Blood samples were taken from the brachial vein using a heparinized 27-gauge ½" needle and 3 cc syringe. The blood was immediately stored on ice until centrifuged, with subsequent plasma aliquoted, frozen in a dry shipper and then at −80 °C, until the

E-mail address: kim.fernie@canada.ca (K.J. Fernie).