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Exposure of Peregrine Falcons to Halogenated Flame Retardants: A 30 Year Retrospective Biomonitoring Study across North America

Yan Wu, Kim J. Fernie, Robert J. Letcher, Kathleen E. Clark, June-Soo Park, Bryan D. Watts, Patricia M. Barber, and Da Chen*

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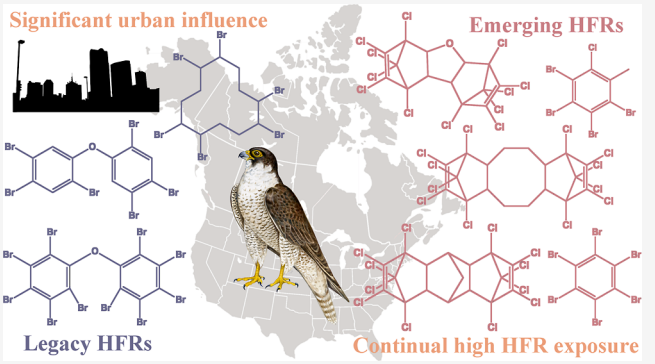
ABSTRACT: Compared to aquatic ecosystem, terrestrial systems have been subjected to fewer investigations on the exposure to halogenated flame retardants (HFRs). Our study utilized peregrine falcon eggs collected from multiple habitats across North America to retrospectively explore both spatial distribution and temporal changes in legacy (e.g., polybrominated diphenyl ethers) and alternative HFRs over a 30 year period (1984−2016). The results reveal intensive HFR exposure in terrestrial ecosystems and chemical-specific spatiotemporal distribution patterns. The correlations between egg levels of the selected HFRs and human population density clearly illustrated a significant urban influence on the exposure of this wildlife species to these HFRs and subsequent maternal transfer to their eggs. Temporal analyses suggest that, unlike aquatic systems, terrestrial ecosystems may undergo continual exposure to consistently high levels of legacy HFRs for a long period of time. Our findings collectively highlight the effectiveness of using peregrine eggs to monitor terrestrial exposure to HFRs and other bioaccumulative chemicals and the need for continuous monitoring of HFRs in terrestrial ecosystems.



KEYWORDS: *North American terrestrial ecosystem, peregrine falcon eggs, halogenated flame retardants, large-scale spatiotemporal analysis, human impacts*

INTRODUCTION

Halogenated flame retardants (HFRs) are a large suite of halogenated hydrocarbon chemicals added to commercial products to reduce flammability.[1] Their global production has increased dramatically due to the implementation of flammability standards for synthetic materials.[2] As most HFRs are not chemically blended in the polymer, they can leach out of the consumer products and partition out into the surrounding environment.[3] Several decades of high-volume manufacturing and large-scale use of HFRs have resulted in HFR-contamination of nearly all environmental compartments (e.g., air, water, soil, sediment, and biota including humans) and global ecosystems.[4]

Compared to data from aquatic systems, knowledge of the spatial and temporal distributions of HFRs has remained much more limited in terrestrial ecosystems, especially for emerging HFRs. Unlike aquatic ecosystems where fish or mammals can be employed for biomonitoring, there is difficulty in selecting efficient biomonitoring species for tracking large-scale exposure patterns of persistent organic pollutants (POPs), including HFRs, in terrestrial ecosystems over a long-term period or across large geographical ranges. This has contributed to a general lack of regional or continental programs to monitor HFRs in North American terrestrial ecosystems, subsequently leading to a paucity of relevant data that is necessary for effective risk assessments and management of chemical pollutants.

Peregrine falcons (*Falco peregrinus*) are the top predators that are globally distributed.[5] It is a cosmopolitan species, inhabiting North America, Asia, western South America, and the Western Palearctic from the tropics to the high Arctic.[6] Increasing numbers of peregrine falcons have adjusted to urban surroundings, and this adaptation appears to be an important contributor to their renewed success in coexistence with humans.[7] Although this species was removed from the U.S. list of threatened and endangered species in 1999, and was delisted in Canada in 2017, after decades of recovery efforts, high levels of pesticides [e.g., 1,1′-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene)(*p*,*p*′-DDT) and the metabolite, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p*,*p*′-DDE)], and polychlorinated biphenyls were still seen in peregrine eggs and nestlings

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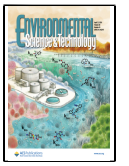

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collected in recent years.[5,8] However, urban influences on the exposure and bioaccumulation of HFRs in peregrine falcons are not well characterized, as several studies previously found comparable or even higher HFR levels in falcons nesting in suburban areas relative to those in urban environments.[5,9,10]

Peregrines generally feed on medium-sized terrestrial birds (e.g., pigeons, starlings, thrushes, owls, and birds of prey), while aquatic birds (e.g., waders, ducks, and gulls) constitute larger portions of diet for those nesting in coastal areas.[8,11,12] Their apex predator status results in greater accumulation of halogenated POPs in their tissues through food web magnification and subsequently in their eggs through maternal transfer.[13] This makes peregrines vulnerable to adverse effects produced by bioaccumulative and toxic POPs (e.g., *p,p′*-DDE leading to eggshell thinning and near extirpation of peregrines), but also makes it an ideal species for monitoring anthropogenic contamination in terrestrial ecosystems.[14] Their broad distribution in rural and urban regions is also very useful for large-scale spatial and temporal biomonitoring by using addled/unhatched eggs, and for the evaluation of anthropogenic impacts on terrestrial wildlife.[9,15,16] Some of North American peregrines inhabit the Midwest, the Northeast, the Southwest, and along the western and eastern coastlines year-round, while the others migrate from the South America to the Alaska tundra annually; the eggs are produced by adult falcons that are largely nonmigratory once they begin nesting, and thus, the eggs reflect the peregrine prey consisting of both local and migrating birds.[17,18]

The major objective of our study was to comprehensively investigate the contaminant accumulation and unprecedentedly large-scale spatiotemporal trends of an extended suite of both legacy and emerging HFRs in North American terrestrial ecosystems, using peregrine falcon eggs collected from multiple locations in the Unites States and Canada (i.e., New Jersey, California, Chesapeake Bay, and Pennsylvania in the United States, as well as Ontario, Quebec, British Columbia, and New Brunswick in Canada) between 1984 and 2016 (Figure 1). We sought to characterize the *in ovo* profiles of a broad range of HFRs in peregrine eggs and investigate spatial variations in the contamination status across eight study sites located in the U.S. and Canada. We also aimed at determining the potential temporal trends of HFRs among the study sites over the 20−30 years of this study. We hypothesized that the HFR burdens in peregrine eggs were substantial and exhibited significant spatiotemporal trends due to inter-regional variations in anthropogenic impacts and changes in regulation on their use over the investigated period.

MATERIAL AND METHODS

Sample Information. A total of 101 addled (i.e., postincubation) peregrine falcon eggs were collected from nests in New Jersey from 1990 to 2015. Additional eggs were collected from the Chesapeake Bay, northeastern U.S. (n = 15, 2010−2014), Pennsylvania (n = 39, 2010−2016), California (n = 16, 2000−2013), British Columbia (Canada, n = 4, 1986 and 2011), New Brunswick (n = 3, 1995 and 2006), Ontario (n = 56, 1995−2015), and Quebec (n = 41, 1984−2012). Tables S4 and S5 provide detailed information, namely, collection sites, sampling years, as well as lipid and water content of individual peregrine falcon egg samples. All eggs were collected by participating agencies with the required permits. Egg contents were transferred to precleaned glass jars and stored at −80 °C.

Figure 1. Map of peregrine falcon egg sampling sites across North America. The collection years at individual regions: Ontario, 1995−2015; Quebec, 1984−2012; British Columbia, 1986 and 2011; New Brunswick, 1995 and 2006; New Jersey, 1990−2015; California, 2000−2013; Chesapeake Bay 2010−2014; and Pennsylvania, 2010−2016.

Before an aliquot of the egg content was taken, the sample was thawed overnight and stirred for thorough homogenization.

Sample Preparation. All samples were analyzed with the same analytical protocol in Cooperative Wildlife Research Laboratory at Southern Illinois University Carbondale. Determination of flame retardant residues in peregrine eggs followed our previous methodology with slight modifications.[19−21] In brief, approximately 0.5−1.0 g of the wet egg sample was spiked with 50 ng each of a mixture of surrogate standards, homogenized with diatomaceous earth, and then subjected to accelerated solvent extraction (Dionex ASE 350, Sunnyvale, CA, USA), employing two 5 min static cycles with dichloromethane (DCM). After moisture removal by anhydrous sodium sulfate, one-tenth of the dehydrated extract was transferred to a preweighted aluminum foil pan for determination of lipid content. The remaining extract was further purified using a Shimadzu Prominence Semi-Prep high-performance liquid chromatograph (HPLC) (Shimadzu America Inc., Columbia, MD, USA) equipped with a phenogel gel permeation chromatography column (300 × 21.2 mm, 5 μm, 100 Å; Phenomenex, Inc., Torrance, CA, USA) coupled to a phenogel guard column (50 × 21.2 mm, 10 μm, 100 Å). The resulting fraction was then cleaned up on a 2 g isolute silica solid phase extraction cartridge (Biotage Inc., Charlotte, NC, USA). The silica gel sorbent was preconditioned with 10 mL of hexane (HEX). After the sample was loaded, the first fraction was eluted with 3 mL HEX and then discarded. The second fraction containing target analytes was eluted with 11 mL of a mixture of HEX and DCM (60:40, v/v). The latter fraction was concentrated to approximately 200 μL and transferred into a gas chromatography vial. Internal standards were added prior to instrumental analysis. For hexabromocyclododecane (HBCDD) analysis on liquid chromatography−tandem mass spectrometry, the samples were dried under nitrogen and

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reconstituted with 200 μL methanol (MeOH) and filtered through a nylon centrifugal filter (VWR, Radnor, PA, USA).

Instrumental Analysis. Table S1 lists our targeted HFRs and corresponding surrogate and internal standards. Instrumental analyses of selected HFRs except for HBCDDs were conducted on an Agilent 7890B GC (Agilent Technologies, Palo Alto, CA) interfaced with a single quadrupole mass analyzer (Agilent 5977A MS) under electron-capture negative ionization (ECNI) and selected ion monitoring (SIM) modes. The separation of FRs was achieved using a 15 m DB-5HT column (0.25 mm i.d., 0.1 μm, J&W Scientific, Agilent Tech.). The injector was operated in pulsed-splitless mode, held at 240 °C. The flow rate of carrier gas was set as 1.2 mL/min. The initial oven temperature was held at 50 °C for 3 min and then ramped to 300 °C at 8 °C/min (held for 10 min). Characteristic SIM ions of HFRs are summarized in Table S1.

The samples after solvent-exchange from HEX to MeOH were analyzed for HBCDD using an Agilent 1260 HPLC interfaced with a 3200 Q Trap triple quadrupole/linear ion trap mass spectrometer (AB Sciex; Toronto, ON, Canada). A Kinetex EVO C18 column (100 * 2.1 mm, 5 μm, 100 Å, Phenomenex, Torrance, CA, USA) coupled to a guard column was employed to separate three HBCDD isomers. The mobile phase consisted of 2 mM ammonium acetate (NH_4Ac) in optima grade water (A) and 2 mM NH_4AC in MeOH (B). The flow rate was 200 μL/min. The following gradient was employed: initially 95% A (held for 1 min), followed with a linear decrease to 0% in 17 min (held for 5 min), and then changed back to 95% A and equilibrated for 7 min.

Quality Control and Quality Assurance. Data quality was ensured through a number of QA/QC procedures previously established with minor modifications.[22] A procedural blank was processed along with every seven samples to monitor laboratory contamination. HFR residues in blanks were subtracted from those in authentic samples on a mass basis batch-by-batch. Recovery efficiency of the analytical methodology was evaluated by spiking tests where known amounts of analytes were added to homogenized chick eggs purchased from a local supermarket. None of the target analytes was detected in the egg homogenates (after blank correction). The recoveries of target analytes through the spiking tests ranged from 72 to 111% (see Table S6). In the analysis of authentic samples, the recoveries of surrogate standards F-BDE69, F-BDE160, and 4-PC-BDE208 ranged from 71.7% to 103.4%, 81.5% to 120.3%, and 62.6% to 113.5%, respectively. Concentrations of analytes with retention times earlier than that of BDE-85 were adjusted based on the recoveries of F-BDE-69. Other FRs had concentrations adjusted with the recoveries of F-BDE160, except for BDE-209 and DBDPE which were adjusted based on the recovery of 4-PC-BDE208. The instrumental detection limit (IDL) was defined as the concentration of each analyte yielding a signal-to-noise ratio (S/N) equal to three. Analytes having responses below IDLs were considered nondetectable (nd). The method limit of quantification (MLOQ) of an analyte was assessed by multiplying a Student's t-value designated for a 99% confidence level with standard deviations in replicate analyses (n = 8).[23] The MLOQ for individual FR analyte is given in Table S6.

Data Analysis. All statistical analyses were performed using OriginPro 2017 (OriginLab Corporation) or SAS 9.4 (SAS Institute). Prior to statistical tests, a value was assigned to an individual measurement below IDL using a regression plotting method,[24] whereas MLOQ/sqrt(2) was assigned if a measurement was lower than MLOQ but higher than IDL. Previous studies have confirmed that these substitutions can provide acceptable statistical outcomes.[25−27] The dependent variables were HFR concentrations, congener compositions, and concentration ratios, while the independent variables were collection regions, human population densities (HPDs), and sampling years. Assumptions for conducting parametric statistical analyses mainly include homogeneous variances and normal distribution. The (logarithmically transformed) data meeting these preconditions were interpreted using parametric methods, otherwise equivalent nonparametric methods were used instead. A significance level of α = 0.05 was applied to all analyses.

HFR concentrations and congener/analogue profiles in samples collected from different locations were statistically analyzed using principal component analysis (PCA) or analysis of variance (ANOVA) followed by Tukey's posthoc test. Regarding the data sets without normal distributions and/or containing many outliers, the randomization test for ANOVA followed by Dunn−Bonferroni posthoc test, a nonparametric alternative to conventional ANOVA, was employed to determine statistical differences among groups. The nonparametric Kendall's tau test was used to examine the correlations of FR levels/compositions with HPD data (retrieved from US Census Bureau[28] and Statistics Canada[29]); as these associations were tested for the peregrine eggs sampled during 2004−2016, the 2010 and 2011 HPD data for the United States and Canada, respectively, were utilized here. If a nest was located on a bridge, the average HPD of towns/cities at both ends of the bridge was used. To avoid pseudoreplication, a clutch mean was calculated if more than one egg was collected from a clutch in the same year, and this mean was included as a single data point for statistical analyses.

A linear regression corrected for autocorrelated errors, which can effectively eliminate erroneous statistics due to time series structures,[30] was employed to analyze temporal trends of HFR burdens in peregrine falcon eggs collected from New Jersey, Ontario, and Quebec. Prior to the linear regression, join points (i.e., breaking points) were estimated using a two-segment regression model for data sets exhibiting significant quadratic terms. Linear regressions using the autoregressive error model were used to identify separate temporal trends before and after breaking points. Additionally, we also evaluated the time effect via a three-point running mean smoother in terms of the annual medians and tested the resulting line by ANOVA for nonlinear components.[31−33]

RESULTS AND DISCUSSION

Contamination Profiles of HFRs. Polybrominated diphenyl ethers (PBDEs) were the most abundant group and with the greatest concentrations of HFRs among the analytes of interest (see Table S1 for the analyte list; Tables S2 and S3 for the summaries of *in ovo* HFR levels; and Table S4 for the detailed concentration data). The sum concentrations of PBDEs ($\sum_{20}$PBDEs) in peregrine eggs ranged from 205 to 44,220 ng/g lipid weight (lw; median: 5520 ng/g lw), at least 1 order of magnitude greater than the sums of hexabromocyclododecanes ($\sum_3$HBCDDs), alternative brominated flame retardants ($\sum_{22}$ABFRs), and Dechlorane analogues ($\sum_{17}$DECs). The major *in ovo* PBDE congeners included BDE-153, 99, 100, 154, and 183, while a few eggs collected from urban regions had substantial contributions of BDE-209 in their profile (up to 32.9%), consistent with the finding of

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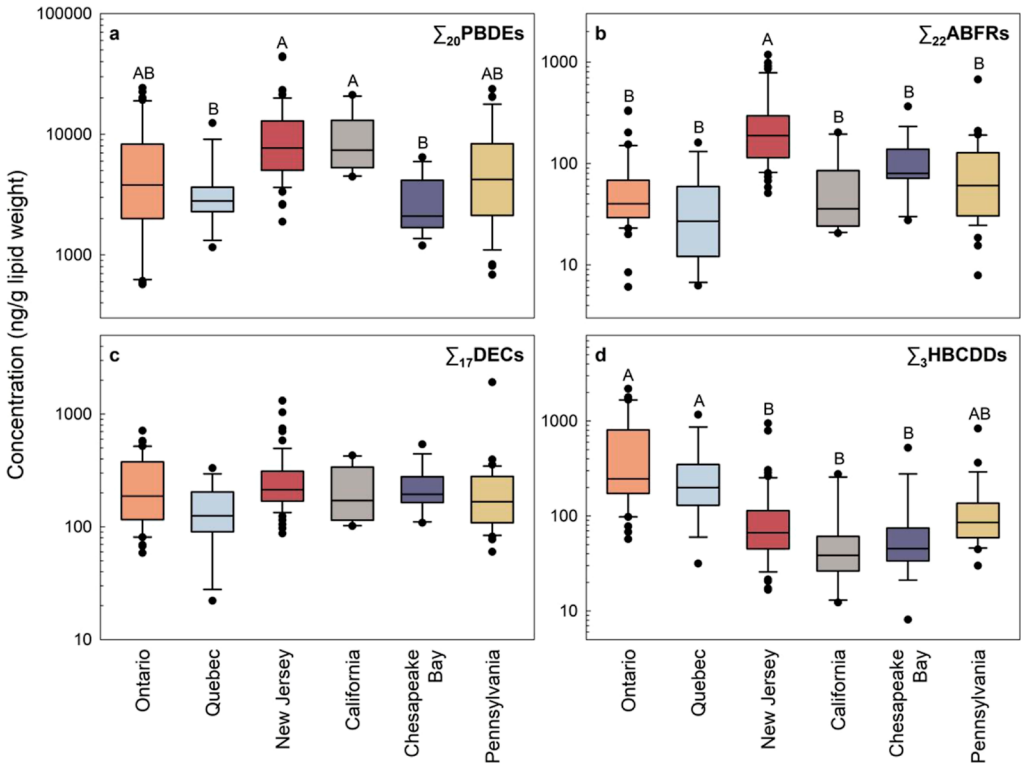

Figure 2. Burdens of HFRs in peregrine falcon eggs collected from different regions across North America during 2004−2016. (a) Sum concentrations of polybrominated diphenyl ethers ($\sum_{20}$PBDEs). (b) Sum concentrations of alternative brominated flame retardants ($\sum_{22}$ABFRs). (c) Sum concentrations of Dechlorane analogues ($\sum_{17}$DECs). (d) Sum concentrations of hexabromocyclododecanes ($\sum_{3}$HBCDDs). Boxes without a common letter suggest that their mean concentrations are significantly different ($p < 0.05$ according to the ANOVA and posthoc comparisons). Boxes represent the 25th and 75th percentiles, and the whiskers represent the 5th and 95th percentiles. The black lines represent the median. The eggs from British Columbia and New Brunswick were excluded due to their small sample size ($N = 1$ in each region).

Fernie et al. (2017)[9] demonstrating that urban peregrine chicks had higher BDE-209 levels in their blood than rural ones. By contrast, BDE-47 usually dominated PBDE profiles in aquatic species,[34−36] suggestive of dissimilar exposure scenarios between aquatic and terrestrial ecosystems.[10,37] The PBDE levels observed in our peregrine eggs were generally greater than those reported in the same species located outside of North America.[31,38,39] The regional differences that were observed in the present study were mainly due to historical usage patterns of PBDE mixtures. For the years in which data are available, the North American market has encompassed the bulk of the world's PentaBDE production (i.e., 95% in 2001 and 98% in 2003) and 44% of the world's DecaBDE production.[40] Although the production of major PentaBDE and DecaBDE mixtures ceased in North America by the end of 2004 and 2013, respectively,[21,41] continuous release of PBDEs from in-use and discarded products has consistently led to human and wildlife exposure.

Following the listing of PentaBDE and OctaBDE to the Stockholm Convention in 2004, HBCDD was also added to an amendment to Annex A (decision SC-6/13) by the Stockholm Convention listing HBCDD for production and use only in specific circumstances (enacted in November 2014).[42] In the present study, all of the peregrine eggs from the U.S and Canada contained detectable HBCDD levels, and the $\sum_{3}$HBCDDs ranged from 5.6 to 2426 ng/g lw with a median of 84.6 ng/g lw. The α-HBCDD comprised 98.2 ± 6.2% of Σ_{3}HBCDD concentrations. This diastereomer composition pattern is typically found in organisms at high trophic levels, likely due to the enhanced environmental persistence of α-HBCDD, possible biotransformation of β- and γ-HBCDD into α-HBCDD, and less efficient absorption and/or preferential metabolism of β- and γ-HBCDD relative to α-HBCDD.[38,43−45]

The combined concentrations of alternative BFRs ($\sum_{22}$ABFRs) ranged from 6.1 to 1181 ng/g lw (median: 90.1 ng/g lw) in the peregrine eggs. Among them, BTBPE, EH-TBB, HBBZ, PBEB, PBT, and TBCT were detected with a frequency of more than 80% of the peregrine eggs, with median concentrations ranging from 0.33 to 73.7 ng/g lw. Other ABFRs, such as PBBA (<MLOQ—66.5 ng/g lw), PBBZ (<MLOQ—0.74 ng/g lw), TBB (<MLOQ—20.9 ng/g lw), TBX (<MLOQ—0.64 ng/g lw), ATE (<MLOQ—25.6 ng/g lw), BEH-TEBP (<MLOQ—5.0 ng/g lw), HCCP (<MLOQ—2.62 ng/g lw), α-TBECH (<MLOQ—22.8 ng/g lw), and β-TBECH (<MLOQ—4.2 ng/g lw), were also found in the peregrine eggs with a frequency of 1.5−71%. Despite the surprisingly high overall detection rates for some of the measured ABFRs, their modest *in ovo* residues overall suggest that these ABFRs may be less bioavailable in the (terrestrial) environment than PBDEs.

As a major group of chlorinated HFRs sharing a basic bicyclo [2,2,1]-heptene structure,[46] Dechloranes exhibited a considerable degree of bioaccumulation in the peregrine eggs. The Σ_{17}DECs ranged from 22.1 to 1918 ng/g lw (median: 216 ng/g lw), even greater than Σ_{3}HBCDD concentrations in the same eggs. Among the DEC analogues, Dec-602, Dec-603, Dec-604, Dec-604CB, syn- and anti-Dechlorane Plus (DCC−CO), Cl_{11}-DCC−CO, and Cplus were detected with high frequency (all greater than 92%) in the eggs, which in total contributed to 99.4% of the $\sum_{17}$DECs. The wide detection and

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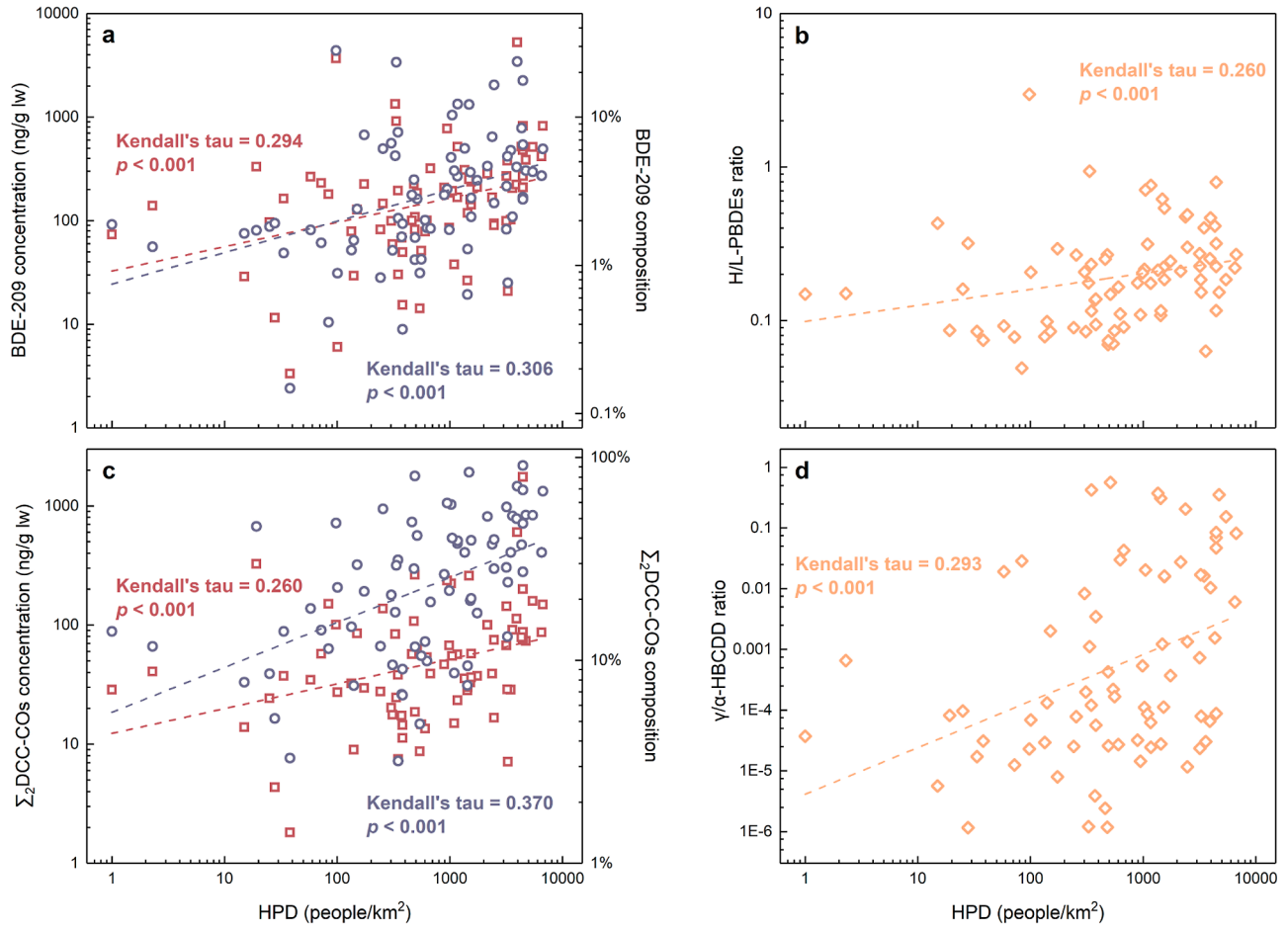

Figure 3. Human impacts on the profiles of HFRs in North American peregrine falcon eggs collected during 2004−2016. (a) Significantly positive associations of the concentrations (red squares)/compositions (blue circles) of BDE-209 with the HPD surrounding the collection sites. (b) Significantly positive correlation between the ratios of heavier PBDEs to lighter PBDEs and the HPD. (c) Significantly positive associations of the concentrations (red squares)/compositions (blue circles) of Dechlorane Plus (sums of syn-DCC−CO and anti-DCC−CO isomers, $\sum_2$DCC−COs) with the HPD. (d) Significantly positive correlation between the ratios of γ-HBCDD to α-HBCDD and the HPD. Dashed lines represent the lines of best fit.

relative abundances of DECs measured in the peregrine eggs indicate the broad exposure and substantial bioaccumulation of DECs by peregrine falcons in terrestrial ecosystems.

Similar to PBDEs, the HBCDD, ABFR, and DEC concentrations found in the peregrine eggs were greater than or comparable to those reported in peregrine falcon eggs from Southern Germany, South Greenland, Spain, the U.K., and Sweden.[31,32,38,39,44,47]

Our results clearly demonstrate widespread distributions of both legacy and alternative HFRs in North American terrestrial ecosystems. Considering the egg samples covered a time span of almost 30 years, our data indicate the long-term influence of the use of HFRs on this apex predator of the terrestrial food web.

Spatial Variations in HFRs. PBDE manufacturers in the U.S. began a voluntary phase-out of penta- and octa-BDE technical products in 2004, while the production and use of decaBDE were discontinued by 2013.[16,48] The Canadian government issued the "Polybrominated Diphenyl Ethers Regulations" to prohibit the manufacture of certain technical PBDE products in 2008 and then the "Regulations Amending the Prohibition of Certain Toxic Substances Regulations" to expand the scope of previous prohibition for PBDEs to cover all PBDE substances (including decaBDE) in 2016.[49] Therefore, only the samples collected after 2004 were used for spatial analysis to minimize the potential influences by the change of HFR manufacturing and consumption patterns over a long period in North America.

The distribution of HFR contamination in peregrine eggs exhibited chemical-dependent spatial patterns (Figure 2). Significantly greater $\sum_{20}$PBDE concentrations were observed in the eggs collected from New Jersey (median: 7674 ng/g lw) and California (7388 ng/g lw) than those from Quebec (median: 2797 ng/g lw) and Chesapeake Bay (2102 ng/g lw) (all $p < 0.05$), while $\sum_{20}$PBDEs in eggs from Ontario (median: 3793 ng/g lw) and Pennsylvania (4225 ng/g lw) were intermediate. For Σ_{22}ABFRs, the peregrine eggs from New Jersey also had significantly greater Σ_{22}ABFR burdens than the eggs from the other five regions. However, Σ_3HBCDD concentrations were significantly greater in peregrine eggs from Ontario and Quebec compared to those from California, New Jersey, or Chesapeake Bay, while no significant differences in Σ_{17}DECs were observed among the studied regions.

The exposure of peregrines to HFRs can be influenced by a number of factors, among which anthropogenic impacts are often of highest concern. Here, we employed HPDs (according to the 2010 or 2011 census data for the city/town closest to

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each nest, see Table S7) as an index of the intensity of human activities (e.g., discharge of sewage, exhaust and solid waste, energy consumption, the production, and use and disposal of consumer products)[50−52] to investigate the potential human impacts on the exposure of peregrine falcons to HFRs.[5,11,32,53]

Although Σ_{20}PBDEs by nest did not exhibit a significant relationship with the HPD, a strong correlation was observed between HPD and BDE-209 levels (Kendall's tau = 0.294, $p < 0.001$; see Figure 3a), as well as the concentrations of a few octa- and nona-BDE congeners. The proportion of BDE-209 in the *in ovo* Σ_{20}PBDEs burdens, as well as that of BDE-183, -196, -197, -203, -207, or -208, also exhibited a significant correlation with nearby HPDs (all $p < 0.01$). Similarly, the ratio of summed levels of more halogenated congeners to those of lesser brominated ones (i.e., ([octa] + [nona] + [deca])/([tetra] + [penta] + [hexa]), referred to as H/L ratio) was also significantly correlated with the HPD (Kendall's tau = 0.260, $p < 0.001$; see Figure 3b). The correlations between egg levels of selected PBDE congeners and the HPD clearly illustrate a significant urban influence on the exposure of peregrine falcons to flame retardants. Since 2004, DecaBDE had become the only commercial PBDE mixture used in North America until the end of 2013, which has been heavily used in thermoplastics and textile back-coatings.[41] Metropolitan regions with a higher HPD are thought to have more intensive use of DecaBDE-containing products, likely resulting in more substantial direct contamination of peregrines with heavier BDE congeners in urban relative to rural environments. Additionally, the more highly brominated and heavier PBDE congeners are less volatile than less brominated, lighter congeners (e.g., BDE-47, -99, and -100) and therefore less effectively disseminated from release sources. These factors subsequently resulted in elevated DecaBDE exposure for urban peregrines. The PCA analysis clearly suggests that while the urban peregrine eggs had a greater composition of heavier congeners, the rural eggs had relatively greater contributions of the less-brominated congeners (typically BDE-99, -100, and -47) (Figure 4). An urban signature may reflect that selected HFRs are prone to bioaccumulate in terrestrial ecosystems or have substantial urban release sources.

Human impacts on contamination profiles were also observed for HBCDD. While no correlation was observed between Σ_3HBCDDs and HPDs, the γ/α-HBCDD ratio did exhibit a significant relationship with the HPD (Kendall's tau = 0.293, $p < 0.001$; see Figure 3d). γ-HBCDD,the predominant diastereomer in technical HBCDD products with a composition of 75−89% by weight,[54] is subject to more degradation and/or biotransformation than α-HBCDD, leading to a general dominance of the latter diastereomer in biological tissues. However, the greater γ/α-HBCDD ratios in urban peregrine eggs may indicate their elevated exposure to HBCDD-containing products, suggesting an urban influence on the exposure and accumulation of HBCDD by the peregrines.

Although Σ_{17}DECs did not significantly differ among regions (Figure 2c), the compositions of Dechloranes exhibited large variations across regions (Figure S1). The syn- and anti-DCC−CO isomers collectively (Σ_2DCC−COs) dominated the analogue composition in peregrine eggs from California and Pennsylvania, while Dec-602 dominated the profiles in eggs from Chesapeake Bay and New Jersey. Eggs from Ontario contained similar abundances of Dec-602, Dec-603, and Σ_2DCC−COs, whereas Dec-602, Dec-604CB, and Σ_2DCC−COs had similar contributions in eggs from Quebec. Although

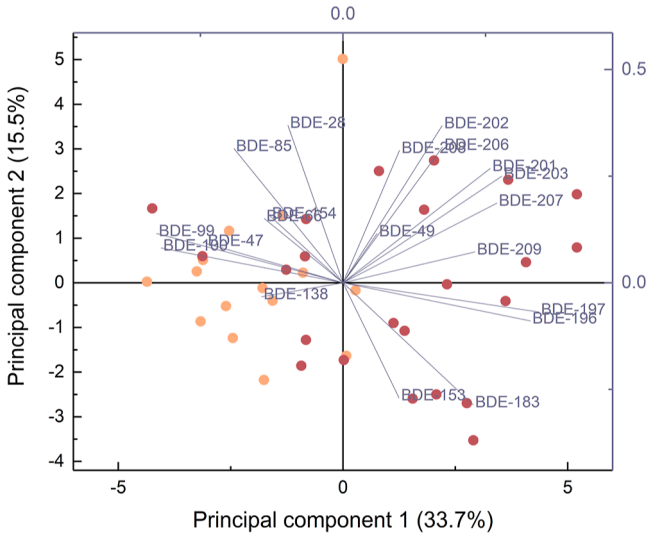

Figure 4. Biplot from the PCA of PBDE congener compositions in the peregrine falcon eggs collected during 2004−2016. Red and yellow dots represent urban and rural peregrine eggs, respectively.

there was no significant correlation between ΣDECs and the HPD in the peregrine eggs, concentrations or composition of syn-DCC−CO, anti-DCC−CO, or Cl_{11}-DCC−CO all exhibited a significant, positive correlation with HPDs (all $p < 0.05$; see Figure 3c), whereas significant, negative correlations were observed between the concentrations or compositions of Dec-601, Dec-602, Dec-603, Dec-604, Br-Dec604, and Cl_{10}-DCC−CO and HPDs (all $p < 0.05$).

It should be pointed out that other than human influence, additional factors, such as diet, migration, and proximity to contamination sources, could also exert substantial influences on the contamination profiles in the same species across different habitats.[9,48,55,56] These factors may complicate the elucidation of the exposure of peregrines to HFRs and warrant further investigation.

Temporal Trends. The peregrine eggs collected between 1984 and 2015 from New Jersey, Ontario, and Quebec were utilized to determine temporal changes in HFRs. The results revealed chemical- and region-specific temporal trends. The Σ_{20}PBDEs in peregrine eggs from Quebec showed an increasing trend from 1984 to 1999 (autoregressive error model, $t = 2.97$, $p = 0.025$), followed by a decreasing trend until 2012 ($t = -5.74$, $p < 0.001$) (Figure 5b). However, no significant trend was observed in Ontario or New Jersey (Figure 5a,c). Nonetheless, several octa-, nona-, and deca-BDEs exhibited significant increases in egg residues for all three regions (all $p < 0.05$), consistent with the regulation of the DecaBDE mixture in North America beginning in 2013, i.e., following collection of the peregrine falcon eggs in the present study. Likewise, significantly increasing nonlinear trends were also found for the heavily brominated PBDEs (all $p < 0.05$); however, $\sum_{20}$PBDEs in the Ontario eggs also exhibited a significantly nonlinear climbing trend ($F_{1,15} = 8.81$, $p = 0.010$). Following the phase-out of commercial PentaBDE mixtures (the most abundant congeners in aquatic wildlife) in the early 2000s in both North America and Europe,[48,49,57] significant declines in PBDE exposure have been demonstrated in aquatic ecosystems in these regions.[34−36,58] However, in our study, only Quebec eggs exhibited a significantly declining trend in the levels of Σ_{20}PBDEs, while no trend was observed

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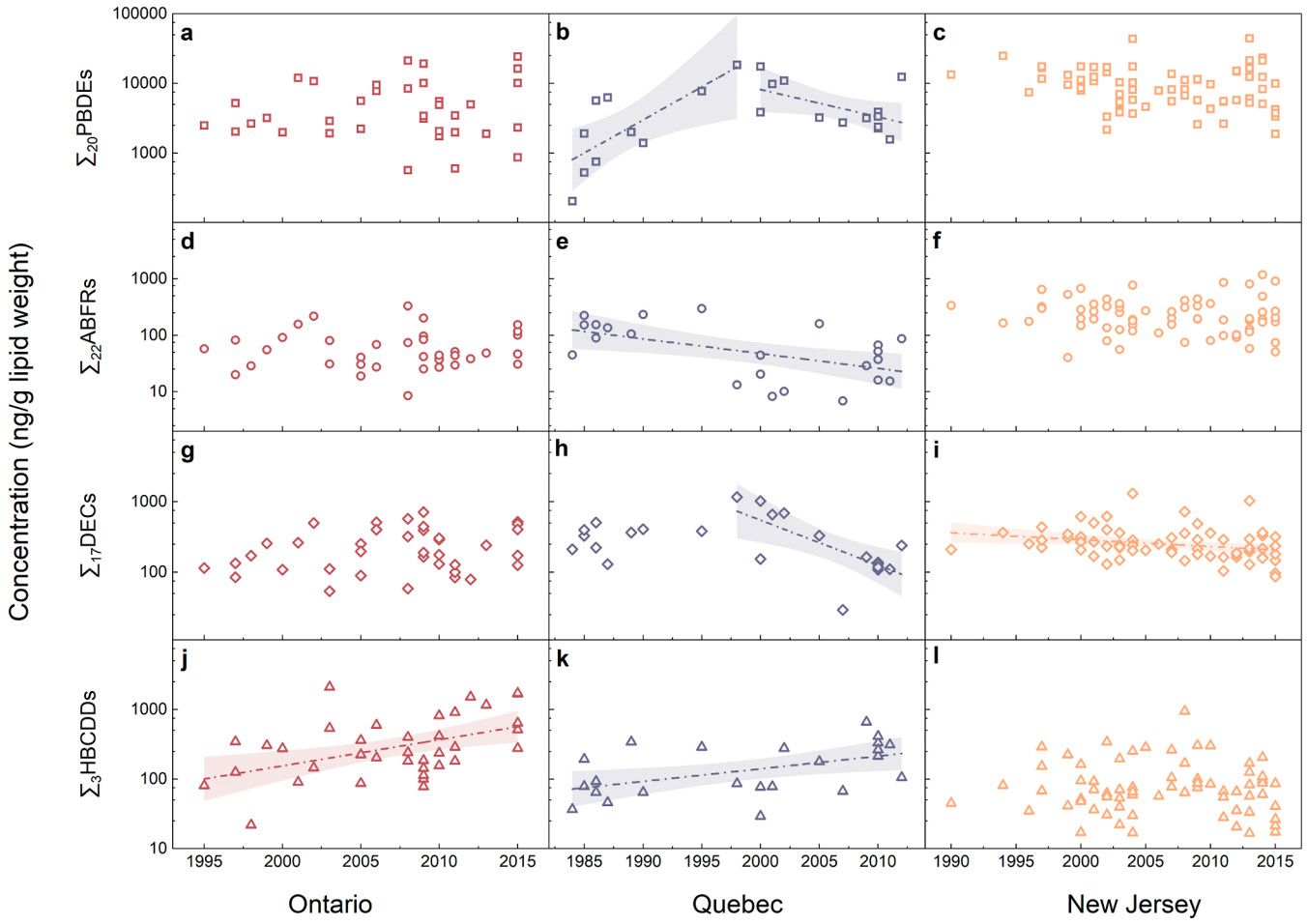

Figure 5. Temporal variations of HFRs in the peregrine falcon eggs collected from Ontario, Quebec, and New Jersey during 1984−2015. (a−c) Sum concentrations of polybrominated diphenyl ethers ($\sum_{20}$PBDEs). (d−f) Sum concentrations of alternative brominated flame retardants ($\sum_{22}$ABFRs). (g−i) Sum concentrations of Dechlorane analogues ($\sum_{17}$DECs). (j−l) Sum concentrations of hexabromocyclododecanes ($\sum_{3}$HBCDDs). The time trends were analyzed using a linear regression corrected for autocorrelated errors. Prior to the linear regression, join points (i.e., breaking points) were estimated using a two-segments regression model for data set exhibiting significant quadratic terms. Temporal trends for the data before and after a breaking point were linear-regressed separately using the autoregressive error model. Regression lines (dash-dotted) represent statistically significant alterations in the egg-associated concentrations of HFRs over time. Shaded parts represent the 95% confidence intervals.

in New Jersey and Ontario eggs during the study period. In particular, BDE-209 and several nona-BDE congeners consistently exhibited significant increases at different regions, similar to the findings in peregrine eggs from Greenland during 1986−2014.[31]

HBCDD exhibited regional temporal trends different from those of PBDEs (Figure 5j−l). Σ_3HBCDDs significantly increased in eggs from Ontario (t = 2.88, p = 0.007) and Quebec (t = 2.9, p = 0.009) during the study period, while no significant trend was observed in the eggs from New Jersey. The same temporal variations were also indicated by the nonlinear trend analyses. Although HBCDD has been phased out from the North American market since 2012, their environmental levels have shown large variations among studies and regions.[59,60] HBCDD did not decrease in any of the study regions, while aquatic studies have started to reveal significant declines in fish, birds, or mammals during the late 2000s to 2010s.[61−63]

While Dechloranes are not subject to any known regulations, their concentrations exhibited declining trends in Quebec eggs from a breaking point of 1998 (t = −4.90, p < 0.001) after an initial, marginally significant increase between 1984 and 1997 (t = 2.25, p = 0.065; see Figure 5h). Similarly, the levels of $\sum_{17}$DECs in New Jersey eggs decreased significantly during 1990−2015 (t = −2.86, p = 0.006), in line with the nonlinear trend ($F_{1,19}$ = 7.27, p = 0.014). However, no significant linear trend was observed in Ontario eggs, but a significant nonlinear increasing trend was observed ($F_{1,15}$ = 18.81, p = 0.001), which may reflect the appreciable rise in bioaccumulation of Dechloranes in Ontario terrestrial ecosystems over the study period.

While it is expected that the discontinuation of PBDEs and HBCDD would stimulate the production and use of alternative FRs, most alternative BFRs did not exhibit an increasing trend in the peregrine eggs from the three regions (Figure 5d−f). The $\sum_{22}$ABFR concentrations remained statistically unchanged in eggs from the Ontario and New Jersey (p > 0.05 in both cases). However, decreasing trends were observed for $\sum_{22}$ABFRs in the Quebec peregrine eggs (t = −3.68, p = 0.002) and several individual chemicals, including ATE, BTBPE, EH-TBB, PBEB, and PBT; concentrations of BTBPE and PBEB also declined in New Jersey peregrine

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eggs ($p < 0.05$ in all cases). The nonlinear trends for ABFRs agreed well with those from log−linear regression, except that significantly declining trends were also perceived for TBCT in the Quebec eggs ($F_{1,15} = 5.18$, $p = 0.038$).

Research Perspectives. We would like to point out some limitations of the present study which may compromise data interpretation. Since the sampling of predatory bird eggs, particularly peregrine falcons, is opportunistic in most cases,[5,9,11,13,31,32,64−66] the inclusion of different nests from various habitats and years may bring uncertainty to data analyses. Variations in diet, foraging habits, and migratory behavior among individuals or between populations from different ecosystem (i.e., urban *vs* rural *vs* coastal) could substantially influence the peregrine exposure to HFRs. Although the diet of U.S. and Canadian peregrines usually have substantial terrestrial sources, particularly for those nested in urban regions, the lack of dietary tracers (e.g., stable isotope data based on $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) prohibited an in-depth assessment of potential influences of dietary sources and trophic positions on the spatial and temporal trends of HFRs.[9,11,55,64,67] Additionally, egg-laying orders could affect the *in ovo* burdens of organic pollutants within the same nest, which has been reported in the studies of Stickel et al. (1973)[68] and Peakall and Gilman (1979).[69] Since the opportunistic sampling strategy is unable to record the laying orders of individual samples, possible egg-laying order effect may confound the interpretation of interclutch or colony variations. Moreover, better documented *in ovo* maternal transfer of HFRs, particularly the alternative substances, will further contribute to the deduction of HFR contamination sources across the sampling colonies, and of temporal alterations in North American HFR production and use over the study periods.

Despite of a number of previous studies on HFR exposure in peregrines, the present work represents one of the largest investigations in terms of the spatial (across the entire North American regions) and temporal (over 30 years) scales. It also evaluates a broad range of HFRs, allowing for the understanding of the spatiotemporal trends of both legacy and alternative HFRs in terrestrial ecosystems. In fact, knowledge on the long-term temporal changes of alternative HFRs, particularly Dechlorane analogues other than syn- and anti-DCC−CO, in terrestrial ecosystems had remained scarce. From the biomonitoring perspective, this work provides solid and large-scale data for regulatory agencies to assess historical and future contamination scenarios in North America. These aspects endow our work with sufficient novelty and significantly contribute to the understanding about HFR exposure in ecosystem. Moreover, our findings highlight the extensive HFR exposure and spatiotemporal variations in apex predators in North American terrestrial ecosystems and demonstrate the effectiveness of employing peregrine falcon eggs to monitor persistent and bioaccumulative contaminants of emerging concern (CECs) in terrestrial ecosystems.[14] As indicated by our research, peregrine falcon eggs can reveal the integrated routes of exposure to chemical pollutants on a large scale both spatially and temporally, making them an ideal species for the investigation of CEC exposure in terrestrial ecosystems, as well as for the assessment of human exposure to CECs. This, however, requires the development of a more efficient biomonitoring network with an improved sampling strategy and representative sampling sites, incorporating the efforts from government agencies, wildlife conservationists, and environmental scientists.

Temporal results suggest that HFR exposure in terrestrial ecosystems and top predators may not respond immediately to the change of HFR usage patterns. This contrasts with the trends observed in North American aquatic ecosystems where the contamination of legacy BFRs generally exhibited significant declines since early 2000s.[34−36,58] The diversity of diet across individual peregrines or different habitats and congener-specific differences in bioaccumulation and biomagnification potencies of HFRs between aquatic and terrestrial food chains may complicate the exposure scenarios and delay the response of peregrine exposure to the change of application patterns. However, our trend analysis suggests that unlike aquatic systems, terrestrial ecosystems may continue to be exposed to consistently high levels of PBDEs and HBCDD for some time. Therefore, our findings raise the need of longer-term investigation to understand the exposure trends and risks more accurately in terrestrial ecosystems. It should also be pointed out that the temporal trend analysis may be confounded by relatively moderate sample sizes and opportunistic sampling strategy. Therefore, more precise measurement of temporal trends of contamination requires continuous biomonitoring and improved sampling strategy.

The unexpected trends of ABFRs (i.e., nonchanging or declining) raise concern about other types of FRs, including nonhalogenated and polymeric FRs, which might have been increasingly applied as FRs to replace existing HFRs. Some heavily brominated substances, like tetrabromobisphenol-A-bis(dibromopropyl ether) (TBBPA-BDBPE), were suspected to be used as replacements for DecaBDE or HBCDD.[70] These chemicals usually have a high octanol−water partition coefficient (K_{OW}), less mobility, and high affinity to organic matter or lipid, while their exposure for wildlife and bioavailability has rarely been evaluated in either aquatic or terrestrial ecosystems. Their bioavailability and biomagnification potencies are predicted to be very limited since their large molecular weight/size and superhydrophobicity nature (normally with $K_{OW} > 10^8$) make these macromolecular HFRs less readily to penetrate cell membranes with very low absorption rates.[37,71−73] Nevertheless, considering the case of BDE-209, their bioaccumulation in terrestrial organisms cannot be entirely excluded as demonstrated by Gauthier et al. (2019)[70] and Eng et al. (2019).[74] Moreover, their degradation or biotransformation products could possess greater mobility and bioaccumulation potencies, which merits closer investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c10907.

> Compound-dependent parameters for HFR analyses; summary of HFR levels in the Canadian peregrine falcon eggs; summary of HFR levels in the U.S. peregrine falcon eggs; detailed HFR concentrations in individual North American peregrine falcon eggs; moisture in the peregrine falcon eggs; QA/QC results for HFRs in the peregrine falcon eggs; human population densities used to evaluate human impacts on HFR profiles in the North American peregrine falcon eggs; and compositional

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profiles of Dechlorane analogues in the peregrine falcon eggs (PDF)

AUTHOR INFORMATION

Corresponding Author

Da Chen − *School of Environment and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, Guangdong 510632, China;* orcid.org/0000-0001-5563-0091; Email: dachen@jnu.edu.cn

Authors

Yan Wu − *Key Laboratory of Geographic Information Science (Ministry of Education), School of Geographic Sciences, East China Normal University, Shanghai 200241, China;* orcid.org/0000-0001-7876-261X

Kim J. Fernie − *Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, Burlington, Ontario L7S 1A1, Canada;* orcid.org/0000-0003-3073-3208

Robert J. Letcher − *Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, National Wildlife Research Centre, Carleton University, Ottawa, Ontario K1A 0H3, Canada;* orcid.org/0000-0002-8232-8565

Kathleen E. Clark − *New Jersey Division of Fish and Wildlife, Endangered and Nongame Species Program, Woodbine, New Jersey 08270, United States*

June-Soo Park − *California Environmental Protection Agency, Department of Toxic Substances Control, Environmental Chemistry Laboratory, Berkeley, California 94710, United States; Department of Obstetrics, Gynecology and Reproductive Sciences, University of California, San Francisco, San Francisco, California 94143, United States*

Bryan D. Watts − *Center for Conservation Biology, The College of William and Mary, Williamsburg, Virginia 23185, United States;* orcid.org/0000-0001-8244-6951

Patricia M. Barber − *Pennsylvania Game Commission, Harrisburg, Pennsylvania 17110, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.3c10907

Notes

The authors declare no competing financial interest.

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