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Time-Trends and Congener Profiles of PBDEs and PCBs in California Peregrine Falcons (*Falco peregrinus*)

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Abstract

High levels (μg/g lw) of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) were measured in peregrine falcon eggs from California (n = 90 eggs from 52 birds, 38 nest sites, collected 1986–2007, ΣPBDEs median = 4.53, range = 0.08–53.1). Over the past 22 years, PBDE levels more than tripled each decade in the eggs, whereas PCB levels had no significant changes. PBDE levels were highest in eggs from major California cities ("Big Cities"), whereas PCBs showed no difference across the regions. For PBDEs, Big City eggs had markedly different patterns from Coastal eggs:BDE-209 and the higher brominated PBDEs (hexa–nona) were dominant congeners in Big City eggs, while BDE-47 and -99 were dominant in Coastal eggs. In many of the birds that gave multiple eggs over time ("time series"), PBDE patterns changed over time: the high proportions of BDE-209 and higher brominated PBDEs (short half-lives) in young birds contrasted with increasingly higher proportions of BDE-153 (long half-life) and other lower brominated PBDEs as the birds aged. These data are consistent with metabolic debromination of BDE-209 ($t_{1/2}$ = 1–2 weeks) to the lower brominated PBDEs, with accumulation over time of BDE-153 ($t_{1/2}$ = 3–4 years). In contrast, PCB patterns showed no differences by locations, and did not change over time. Diet (prey birds) may explain the urban PBDE pattern, as the patterns in urban pigeons and peregrines were similar, with high proportions of BDE-209 and the higher-brominated PBDEs. Also, our prey data (feathers from peregrine nests) showed urban peregrines having a higher proportion (>2 fold) of granivorous/opportunistic birds (e.g., "introduced feral" pigeons, mourning doves, starlings) in their diet than coastal peregrines. In summary, these data indicate that BDE-209 exits consumer products as an environmental contaminant to be taken up by wildlife (particularly in urban locations), and undergoes metabolic debromination to the banned lower-brominated PBDEs. High levels of the higher-brominated PBDE congeners, especially in urban locations, permitted accurate measures of relative proportions of homologues in each of the hexa–nona congener classes. Using the major hexa–nona homologues in each of these classes, we propose a pathway for the stepwise, metabolic debromination of BDE-209.

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Supporting Information Available

S1 describes the experimental section in detail; Tables S1A, S1B, S2A, and S2B list the concentrations of PBDEs and PCBs (ng/g lipid wt) measured from all California peregrine falcon eggs (n = 90) and chicks (n = 7); Figure S1 illustrates the postulated debromination pathways. This information is available free of charge via the Internet at http://pubs.acs.org.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardant additives in synthetic textiles in rugs, draperies, and upholstery, and in polyurethane foam and thermoplastics found in a variety of consumer products and electronics. Presently, PBDEs are widely dispersed in the abiotic and biotic environments (1). Three technical PBDE formulations (penta, octa, and deca) were produced in large volumes in the United States (7.1, 1.5, and 30 million tons/yr, respectively, in 2001), representing about half of the world's PBDE production since the 1970s (2). Penta- and octa-BDE mixtures are now banned in the European Union (EU) and California. However, production and use of the deca-BDE mixture (the major commercial PBDE formulation comprising 65–70% of total production) continues in North America and most of the U.S. This may pose a threat to wildlife and public health because BDE-209, the major component (>97%) of deca-BDE (3), bioaccumulates in wildlife, especially in the terrestrial food web (4–10), and breaks down either via photolysis (11,12) or enzymatic transformation (13–15) to lower brominated PBDEs. These PBDEs are known to be more bioavailable, persistent, and toxicologically active than the parent compound.

PBDEs are structurally similar to polychlorinated biphenyls (PCBs), and share many physicochemical properties (e.g., lipophilicity and persistence), although they are somewhat less stable. As with PCBs, elevated levels and distributions of PBDEs would be expected to continue for decades after any reduction in use or production. PBDE levels in wildlife and humans have been increasing over the past several decades (16–19), and these increases may continue as PBDEs exit from flame-retarded consumer products that are in use, or have been disposed of and/or recycled. PBDEs exert toxicological effects in humans and wildlife similar to those of the PCBs, including perturbed thyroid homeostasis; neurodevelopmental deficits; irreversible motor and behavior effects that worsen with age; altered reproductive function; immunotoxicity; deformed thyroid, liver, and kidney; and fetal toxicity/teratogenicity (1,20).

Our Wildlife Early Warning System (WEWS) has a long history (approximately 20 years) of measuring levels of industrial chemicals in California wildlife. We have measured levels of PBDEs in wildlife from the San Francisco Bay region, e.g., harbor seals (18), fish (21,22), and terns (23), as well as in adipose (18), serum (24,25) and breast milk samples from Californians (26,27). PBDE levels in California residents and aquatic wildlife were found to be among the highest in the world, with tetra-, penta-, and hexa-BDEs (BDE-47, -99, -100, -153, and -154) as the major congeners. In these samples (aquatic biota and humans), the more highly brominated hepta–deca congeners (e.g., BDE-183) were only minor components, with nondetect or trace levels of BDE-209. As a part of the WEWS program, PBDE and PCB levels were measured in peregrine falcon (*Falco peregrinus*) eggs and chicks. Peregrine falcons are a useful sentinel species for monitoring environmental organic contaminants because, as bird-eating raptors, they sit high on the aquatic/marine and terrestrial food chains, consuming prey from the aquatic (waders and ducks) and terrestrial (pigeons, starlings, and thrushes) environments, as well as migratory birds (28). Peregrines can serve as indicators of regional differences in chemical pollution because they have strong pair-bonds with a single mate; long life spans of 12–15 years; stable nest locations with long-term residency (7–9 years); and yearly clutches of 3–5 eggs. In the 1960s, peregrines suffered almost complete reproductive failure (California's peregrine population at one point was reduced to a few breeding pairs) because of high DDT levels and consequent egg shell thinning (28), and were placed on the endangered species list (29).

In this study, we measured levels of PCBs and PBDEs in peregrine falcon eggs and chicks that were collected and archived in California during 1986–2007. We compared levels and patterns of congeners in peregrine eggs collected in different California ecological regions (Big City, Rural, and Coastal). We also examined changes in levels and patterns over time, both in the

population and in individual raptors. Based on the prevalence of BDE-209 and higher brominated congeners, we postulate a metabolic pathway for the transformation of BDE-209 to the lower brominated PBDEs.

Materials and Methods

Sample Collection

Peregrine falcon eggs and chicks were collected and archived in California over a 22-year period (1986–2007) as part of the Peregrine Recovery Program in response to DDT-induced egg-shell thinning and population collapse in the 1960s (29). Some samples were collected as addled eggs in nests when nestlings were banded. Other eggs were brought in for captive incubation after two weeks of nest incubation, and eggs that did not hatch were frozen and archived. Ninety eggs and 7 chicks collected from 56 peregrine falcons at 41 nest locations were used for analysis. Chick and egg data were assessed separately. Some birds ($n = 33$) were represented by a single egg, while others ($n = 19$) were represented by multiple eggs ("time-series" eggs, $n = 57$), with each egg collected during a different year. Eggs were received frozen and were stored at −20 °C until analysis.

Materials

The following internal standards were purchased from Wellington Laboratory (TerraChem Inc., USA): surrogate standards ($^{13}C_{12}$ BDE-28, -47, -100, -99, -153, -183, -197, -209, and $^{13}C_{12}$ PCB-28, -52, -101, -105, -114, -118, -138, -153, -156, -157, -167, -180, -194, and -209) and recovery standards ($^{13}C_{12}$ BDE-77, -154, -207, and $^{13}C_{12}$ PCB-47, -178). Other chemicals and solvents used for the analysis include hexane, methylene chloride (Ultra-Resi Analyzed, Mallinckrodt-Baker Chemicals, Philipsburg, NJ), tetradecane (Sigma-Aldrich Inc., St. Louis, MO), sodium sulfate (anhydrous, granular, reagent grade, Spectrum Chemical Mfg. Co., Gardena, CA), silica gel (60–100 mesh Mallinckrodt-Baker Chemicals), sulfuric acid (E M Science, Princeton, Canada), potassium hydroxide, (Fisher Sci., USA), and silica (200–400 mesh) (Sigma-Aldrich Inc.). A matrix-free standard (Predominant Congener Mix, Cambridge Isotope Laboratories, Andover, MA) was used to assess accuracy for PBDE analysis.

Sample Analysis and Quality Assurance

Detailed information about sample analysis and quality assurance is provided in Supporting Information (S1). In summary, samples were lyophilized and extracted in an accelerated solvent extraction system (ASE200, Dionex, Sunnyvale, CA). A portion (3%) of extract was used for gravimetric fat determination. The remaining extract was cleaned up using a glass column and fractionated on a gel permeation column. PCBs and PBDEs were measured by isotope dilution/HRGC-HRMS using an Agilent 6890 GC (Agilent Technology Palo Alto, CA) coupled to a ThermoFinngan MAT95 (Bremen, Germany). Recoveries of PCB and PBDE internal standards (spiked after lyophilization) ranged from 42.9 ± 1.4% for $^{13}C_{12}$ PCB-28 to 82.8 ± 1.5% for $^{13}C_{12}$ PCB-105, and from 59.6 ± 4.3% for $^{13}C_{12}$ BDE-209 to 90.7 ± 3.4% for $^{13}C_{12}$ BDE-153.

Statistical Analysis

The concentrations of PCBs and PBDEs were expressed on a lipid weight basis (lw) and log-transformed to make the data distributions more symmetrical. For ease of interpretation and comparison with other literature, thesummarystatistics presented throughout this text, and in Table 1, are based on the untransformed values. These summaries are based on 52 eggs; in cases where there are multiple eggs from one bird, the geometric mean is used to present a single value. Parametric and nonparametric tests for the logged-PCB and PBDE data were conducted to determine differences between the ecological groups. *t* tests, Wilcoxon rank sum

tests, and Generalized Estimating Equations (GEEs) (30) were used to test the difference in measures of location between the various groups. The *p*-values presented hereafter will refer to the *p*-value from the *t* tests. Unless stated otherwise, it may be assumed that similar *p*-values were also obtained from the other tests. GEEs were also used to explore temporal trends in PBDE and PCB levels, which were based on all 90 eggs. GEEs use a generalized linear model to estimate regression parameters and are relevant for longitudinal studies as they account for within-subject correlation. The R package, a language and environment for statistical computing, was used for all statistical analyses. Individual egg and chick data are provided in the Supporting Information (Tables S1 and S2).

Results and Discussion

Concentrations and Temporal Trends

ΣPBDE levels in peregrine falcon eggs and chicks are reported for the first time in California, and are among the highest ever found in biota, with levels in chicks significantly higher than those in eggs (*p*-value = 0.0018) (Table 1). The maximum Σ_{15}PBDE value of 94.4 μg/g lw measured in a California peregrine chick is the highest PBDE level ever reported for wildlife. TheΣPBDE levels (μg/g lw) of California peregrine eggs (median 4.53, this study) and northeast U.S. peregrine eggs (median 7.66) (31) exceed those reported for eggs from European and Arctic peregrines (medians 1.90–3.10) (4,32–34), reflecting the greater usage of PBDEs in the U.S (2). Eggs were assigned to four ecological classifications based upon nest location: Big City, Coastal, Rural, and Other. For example, “Big City” refers to nest sites on high-rise office buildings in downtown areas of California’s major cities (e.g., San Francisco, Los Angeles, San Diego, San Jose); “Coastal” refers to nest sites on California’s coastal cliffs that are not near major cities (e.g., nests on Big Sur coastal cliffs); “Rural” refers to nest sites in remote rural areas, far from major population centers. The measure of the location of the ΣPBDE levels (μg/g lw) were significantly higher in Big City eggs (10.1) than in Coastal (2.38) or Rural samples (1.61), as were BDE-209 levels, where *p*-value < 0.001 for all four comparisons. BDE-209 was detected in all of our California samples, and exceeded 1.0 μg/g lw in 14 eggs and 2 chicks. A median BDE-209 level (1.00 μg/g lw) in Big City eggs is the highest median ever reported for eggs from peregrines or other species. Whereas most Big City eggs were collected during 1987–1999, five of the 31 Big City eggs were collected during 2000–2007. However, the difference in the median BDE-209 levels of Big City eggs from the early versus later collection periods is not statistically significant (at a 1% level of significance). Thus, the high median BDE-209 level seen in Big City eggs is not the consequence of a later collection dates. More likely, it represents high urban exposures to BDE-209.

The upper plot of Figure 1 shows the linear relationship between the sample collection year and the logged-PBDE data for both ΣPBDEs and BDE-153. Similarly, the lower plot of Figure 1 shows the relationship between the sample collection year and the logged-PCB data. GEE analysis (which allows for within-bird correlations) confirms the findings of these graphical representations. Over the 22-year period during which the egg samples were collected, ΣPBDE levels in the California peregrine population more than tripled each decade. The GEE analysis showed a significant (*p*-value < 0.001) increase of 0.13 units of log(PBDE) per year; this corresponds to an increase of 3.67 per unit PBDE over 10 years $(\exp(0.13)^{10} = 3.67)$. BDE-153 was a major driving congener for this trend, as it has a long half-life (years) (35) and the time trend may reflect increasing BDE-153 bioaccumulation. Temporal increase of BDE-209 was not as significant (*p*-value = 0.1) as that reported for peregrine eggs from the northeastern U.S. (31). BDE-209 has a short half-life (weeks) in humans and starlings (35,36) and, consequently, the BDE-209 time trends may reflect increasing BDE-209 exposures. Other studies show ΣPBDE levels increasing over several decades: San Francisco harbor seals (1989–1999) (18); Greenland peregrine eggs (1986–2003) (34); Canadian Arctic ringed seals (1981–2000) (37);

and Great Lakes herring gull eggs (1982–2006) (38). In contrast, levels of ΣPBDEs in European biota seem to be leveling off (39), likely due to banned production and use of the PBDE mixture formulations.

In contrast, the GEE analysis indicates that PCB levels do not significantly change over the collection period (Figure 1, bottom). Nevertheless, median PCB levels in peregrine eggs and chicks are much higher than median PBDE concentrations (12- and 7-fold, respectively), even 30 years after the PCB ban (Table 1). This differential will narrow over the next decades if the PCBs and PBDEs continue their respective time-trends. Similar temporal changes in PBDE and PCB levels were also seen in several individual "time-series" birds. PBDE levels were higher in Big City peregrines than in Coastal and Rural peregrines, while PCB levels were not significantly different across the groups, indicating different sources and pathways of exposure for these two families of contaminants.

Congener Patterns

PBDE congener patterns varied according to nest location, with Big City and Coastal eggs presenting striking contrasts: BDE-209 and the higher brominated PBDEs (hexa-nona) are dominant congeners in Big City eggs, while BDE-47 and -99 are dominant in Coastal eggs. Figure 2 shows congener patterns for the 90 California eggs, with eggs arranged in increasing order of percent fraction of BDE-47 + -99. Most Big City eggs are found on the left, where percent fraction of BDE-47 + -99 is low and higher-brominated congeners predominate. In contrast, most Coastal eggs are on the right, where lower-brominated congeners predominate. These data support findings from other studies, which indicated that terrestrial species experience greater exposure to the heavier PBDE congeners than do aquatic biota (6,7,10, 40). PBDE patterns of the Coastal peregrine eggs mimic patterns found in our earlier studies of California's aquatic biota (fish, harbor seals, terns from San Francisco Bay), where lower brominated PBDEs (BDE-47, -99, and -100) predominated and BDE-209 was at nondetect or trace levels. The BDE-209 and other higher brominated PBDEs found in terrestrial species and Big City peregrine eggs must arise from consumption of either deca-or octa-BDE commercial mixtures, likely via preening and/or prey diet. The deca-mixture is the more likely source, as it has comprised 65–70% of total PBDE production over the past two decades. Additional support for the deca mixture comes from our prey data. We classified feathers of prey at 38 peregrine nest sites for different years, creating 181 nest-years of prey data (unpublished). We grouped the 185 prey species into 15 prey categories based upon diet. Our prey data indicate that the diet of Big City peregrines differs from that of Coastal or Rural peregrines, with more than two times higher percentage of granivorous/opportunistic birds (e.g., "introduced feral" pigeons, mourning doves, starlings).

Why the striking difference in PBDE patterns in Big City versus Coastal peregrines? The major PBDE "starting materials" in both the terrestrial and marine food webs are the same, with BDE-209 the dominant PBDE congener in both marine sediments and urban dusts. Why then are there such divergent PBDE patterns in the Big City versus Coastal peregrines, each at the top of their respective food web? We believe bioconcentration factors and stabilities of the higher versus lower PBDE congeners contribute, along with characteristics of the two food webs. In biota BDE-209 and the hepta–nona BDEs have lower rates of uptake and shorter half-lives (higher rates of debromination) than do the lower brominated PBDEs (33). Thus, biota are enriched with lower-brominated PBDEs relative to higher-brominated congeners with each biological transfer, as well as over the passage of time. Fewer biological transfersmeanless preferential uptake of lower-brominated PBDEs against BDE-209; and shorter residence times mean less breakdown of BDE-209. Thus, the Big City food web, with fewer biological transfers, fewer (~2) trophic levels, and shorter residence times than the marine food web, would favor the passage of BDE-209 from urban dust to urban peregrines. For example, since

the urban pigeon's daily diet is food debris coated with BDE-209-containing urban dust, the Big City peregrine will eat an urban pigeon that consumed BDE-209 earlier in the day. The short residence time of the urban BDE-209 in the pigeon minimizes its metabolism to lower-brominated PBDEs. The single trophic level, and the two biological transfers, offer minimal barriers to uptake, and minimize the preferential uptake of lower-brominated PBDEs. The result is a relatively BDE-209 enriched Big City peregrine.

In contrast, the greater number of biological transfers and trophic levels in the marine food web favors preferential uptake of the lower-brominated PBDEs during passage up the food chain. Because of the many biological transfers, it takes much longer for the starting material of BDE-209 in marine sediment to reach the coastal peregrine, providing a greater opportunity for metabolism of the BDE-209 starting material to lower-brominated PBDEs. The result is a Coastal peregrine enriched with the lower-brominated PBDEs.

Possible Evidence of Debromination?

PCB and PBDE congener patterns in eggs from a single California peregrine falcon, a "Big City" time-series bird nesting on Union Bank in downtown Los Angeles during 1987–1994, are shown in Figure 3. As the bird aged, proportions of heavier-brominated PBDEs (BDE-209, -207) decreased and proportions of lesser-brominated congeners (BDE-153 and -183) increased (Figure 3, top). Similar changes with age in PBDE patterns were seen in several other time-series peregrines, with proportions of BDE-153 increasing as the birds got older. BDE-153 has a longer half-life than the other PBDEs (35), and the increase seen with age could come from either uptake of the penta-BDE commercial mixture or from debromination of the higher-brominated PBDEs. The fact that the proportions of higher-brominated PBDEs decrease as the proportion of BDE-153 increases suggests that debromination is an important source. This change in PBDE congener patterns seen in Big City peregrines could have come from a change in prey (e.g., from urban to aquatic prey) as the birds aged, but this is not supported by our prey data (unpublished). We found a similar change in PBDE patterns (from higher- to lower-brominated PBDEs) in our study of serum PBDEs from fledgling versus adult urban kestrels: in younger vs older birds BDE-209 proportions decreased and proportions of higher-brominated PBDEs increased (10). These data sets from peregrines and kestrels are consistent with metabolic debromination of BDE-209, and are supported by other studies (4,35,41,42). In contrast, PCBs behaved quite differently from PBDEs. PCB congener patterns were not nearly so varied as PBDEs at urban versus coastal nest locations (not shown), and PCB patterns showed no changes in the "time-series" peregrines as the birds aged (Figure 3, bottom). These results suggest PCBs are in environmental equilibrium.

High levels of the higher-brominated PBDE congeners, especially in urban locations, permitted accurate measures of relative proportions of homologues in each of the hexa–nona congener classes. Based on the relative abundance of homologues in each of the hexa–nona congener classes (n = 90 eggs), we postulated a pathway for the stepwise metabolic debromination of BDE-209 to BDE-153. This pathway involves sequential debromination at the meta-, meta-, ortho-, and ortho-positions (dark arrow), with intermediates of BDE-207, BDE-197, and BDE-183 (Figure S1). In support of this, ratios of BDE-183, -197, and -207 in their homologue groups were higher than ratios found in commercial PBDE mixtures (3). In addition, new congeners (hepta-unknown and BDE-202), which are not seen in technical commercial mixtures (3), were found in California peregrine falcons. BDE-202 was also found in other U.S. peregrine studies (7, 42).

In summary, we found California peregrine falcon eggs/chicks contaminated with high levels of PBDEs, when compared to other wildlife. In other studies of wild birds, PBDE levels such as these were associated with a variety of significant toxicological effects (e.g., impaired growth, reduced brood size, long-term reproductive effects, and neurodevelopmental deficits)

(33,35,43,44). Further, our data support the ideas that (1) BDE-209 exits consumer products to become an environmental contaminant; (2) BDE-209 bioaccumulates in wildlife (particularly in urban locations); and (3) BDE-209 undergoes metabolic debromination to the lower banned brominated PBDEs (e.g., BDE-153, -183).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank the many ornithologists and bird enthusiasts who have enabled the U.S. peregrine populations to survive DDT-induced egg-shell thinning and reproductive failure in the mid-1950s-60s, and to restore the California breeding pair population from a low of 2 known to >200 over the past thirty years. The views expressed herein are those of the authors and do not necessarily reflect those of the Department of Toxic Substances Control, California Environmental Protection Agency.

Literature Cited

1. Vonderheide AP, Mueller KE, Meija J, Welsh GL. Polybrominated diphenyl ethers: Causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. Sci. Total Environ 2008;400:425–436. [PubMed: 18571221]
2. Birnbaum LS, Staskal DF. Brominated flame retardants: cause for concern. Environ. Health Perspect 2004;112:9–17. [PubMed: 14698924]
3. La Guardia MJ, Hale RC, Harvey E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol 2006;40:6247–6254. [PubMed: 17120549]
4. Lindberg P, Sellstrom U, Haggberg L, de Wit CA. Higher brominated diphenyl ethers and hexabromocyclododecane found in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden. Environ. Sci. Technol 2004;38:93–96. [PubMed: 14740722]
5. Jaspers V, Covaci A, Maervoet J, Dauwe T, Voorspoels S, Schepens P, Eens M. Brominated flame retardants and organochlorine pollutants in eggs of little owls (*Athene noctua*) from Belgium. Environ. Pollut 2005;136:81–88. [PubMed: 15809110]
6. Voorspoels S, Covaci A, Lepom P, Escutenaire S, Schepens P. Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (*Vulpes vulpes*). Environ. Sci. Technol 2006;40:2937–2943. [PubMed: 16719094]
7. Chen D, Mai B, Song J, Sun Q, Luo Y, Luo X, Zeng EY, Hale RC. Polybrominated diphenyl ethers in birds of prey from Northern China. Environ. Sci. Technol 2007;41:1828–1833. [PubMed: 17410771]
8. Kunisue T, Takayanagi N, Isobe T, Takahashi S, Nakatsu S, Tsubota T, Okumoto K, Bushisue S, Shindo K, Tanabe S. Regional trend and tissue distribution of brominated flame retardants and persistent organochlorines in raccoon dogs (*Nyctereutes procyonoides*) from Japan. Environ. Sci. Technol 2008;42:685–691. [PubMed: 18323088]
9. Hu GC, Luo XJ, Dai JY, Zhang XL, Wu H, Zhang CL, Guo W, Xu MQ, Mai BX, Weit FW. Brominated flame retardants, polychlorinated biphenyls, and organochlorine pesticides in captive giant panda (*Ailuropoda melanoleuca*) and red panda (*Ailurus fulgens*) from China. Environ. Sci. Technol 2008;42:4704–4709. [PubMed: 18677994]
10. Park JS, Holden A, Wang Y, Chang J, Heckly S, McKeown K, Jewell N, Hooper K. Metabolic fate of polybrominated diphenyl ethers (PBDEs) in California kestrel blood. Organohalogen Compd 2008;70:1566–1569.
11. Stapleton HM, Dodder NG. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. Environ. Toxicol. Chem 2008;27:306–312. [PubMed: 18348638]
12. Soderstrom G, Sellstrom U, de Wit CA, Tysklind M. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ. Sci. Technol 2004;38:127–132. [PubMed: 14740727]

13. Kierkegaard A, Asplund L, de Wit CA, McLachlan MS, Thomas GO, Sweetman AJ, Jones KC. Fate of higher brominated PBDEs in lactating cows. Environ. Sci. Technol 2007;41:417–423. [PubMed: 17310701]
14. Stapleton HM, Alaee M, Letcher RJ, Baker JE. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. Environ. Sci. Technol 2004;38:112–119. [PubMed: 14740725]
15. Holden A, Park J-S, Chu V, Kim M, Choi G, Shi Y, Chin T, Chun C, Linthicum JW, Walton BJ, Hooper K. Unusual hepta- and octa-brominated diphenyl ethers and nona-brominated diphenyl ether profile in California, USA, peregrine falcons (*Falco peregrinus*): More evidence for brominated dipheny ether-209 debromination. Environ. Toxicol. Chem 2009;28:1906–1911. [PubMed: 19374475]
16. Norstrom RJ, Simon M, Moisey J, Wakeford B, Weseloh DV. Geographical distribution (2000) and temporal trends (1981–2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. Environ. Sci. Technol 2002;36:4783–4789. [PubMed: 12487300]
17. Hale RC, Alaee M, Manchester-Neesvig JB, Stapleton HM, Ikonomou MG. Polybrominated diphenyl ether flame retardants in the North American environment. Environ. Int 2003;29:771–779. [PubMed: 12850095]
18. She J, Petreas M, Winkler J, Visita P, McKinney M, Kopec D. PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. Chemosphere 2002;46:697–707. [PubMed: 11999793]
19. Hites RA. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ. Sci. Technol 2004;38:945–956. [PubMed: 14998004]
20. Darnerud PO. Toxic effects of brominated flame retardants in man and in wildlife. Environ. Int 2003;29:841–853. [PubMed: 12850100]
21. Brown FR, Winkler J, Visita P, Dhaliwal J, Petreas M. Levels of PBDEs, PCDDs, PCDFs, and coplanar PCBs in edible fish from California coastal waters. Chemosphere 2006;64:276–286. [PubMed: 16455130]
22. Holden A, She J, Tanner M, Lunder S, Hooper K. PBDEs in the San Francisco Bay Area: measurements in fish. Organohalogen Compd 2003;61:255–258.
23. She J, Holden A, Adelsbach TL, Tanner M, Schwarzbach SE, Yee JL, Hooper K. Concentrations and time trends of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in aquatic bird eggs from San Francisco Bay, CA 2000–2003. Chemosphere 2008;73(1 Suppl):S201–S209. [PubMed: 18466953]
24. Petreas M, She J, Brown FR, Winkler J, Windham G, Rogers E, Zhao G, Bhatia R, Charles MJ. High body burdens of 2,2′, 4,4′-tetrabromodiphenyl ether (BDE-47) in California women. Environ. Health Perspect 2003;111:1175–1179. [PubMed: 12842770]
25. Fischer D, Hooper K, Athanasiadou M, Athanassiadis I, Bergman A. Children show highest levels of polybrominated diphenyl ethers in a California family of four: a case study. Environ. Health Perspect 2006;114:1581–1584. [PubMed: 17035146]
26. She J, Holden A, Sharp M, Tanner M, Williams-Derry C, Hooper K. Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in breast milk from the Pacific Northwest. Chemosphere 2007;67:S307–S317. [PubMed: 17280703]
27. Hooper K, She J, Sharp M, Chow J, Jewell N, Gephart R, Holden A. Depuration of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in breast milk from California first-time mothers (primiparae). Environ. Health Perspect 2007;115:1271–1275. [PubMed: 17805415]
28. Ratcliffe DA. Decrease in eggshell weight in certain birds of prey. Nature 1967;215:208–210. [PubMed: 6049131]
29. The Santa Cruz Predatory Bird Research Group. Santa Cruz: University of California; http://www2.ucsc.edu/scpbrg/pefacensus.htm
30. James, WH.; Joseph, MH. Generalized Estimating Equations. New York: Chapman & Hall/CRC; 2003.
31. Chen D, La Guardia MJ, Harvey E, Amaral M, Wohlfort K, Hale RC. Polybrominated diphenyl ethers in peregrine falcon (*Falco peregrinus*) eggs from the northeastern U.S. Environ. Sci. Technol 2008;42:7594–7600. [PubMed: 18983080]

32. Herzke D, Berger U, Kallenborn R, Nygard T, Vetter W. Brominated flame retardants and other organobromines in Norwegian predatory bird eggs. Chemosphere 2005;61:441–449. [PubMed: 16182862]
33. Johansson AK, Sellstrom U, Lindberg P, Bignert A, de Wit CA. Polybrominated diphenyl ether congener patterns, hexabromocyclododecane and brominated biphenyl 153 in eggs of peregrine falcon (*Falco peregrinus*) breeding in Sweden. Environ. Toxicol. Chem 2009;28:9–17. [PubMed: 18717624]
34. Vorkamp K, Thomsen M, Falk K, Leslie H, Moller S, Sorensen PB. Temporal development of brominated flame retardants in peregrine Falcon (*Falco peregrinus*) eggs from South Greenland (1986–2003). Environ. Sci. Technol 2005;39:8199–8206. [PubMed: 16294855]
35. Van den Steen E, Covaci A, Jaspers VL, Dauwe T, Voorspoels S, Eens M, Pinxten R. Accumulation, tissue-specific distribution and debromination of decabromodiphenyl ether (BDE 209) in European starlings (*Sturnus vulgaris*). Environ. Pollut 2007;148:648–653. [PubMed: 17239511]
36. Thuresson K, Bergman K, Rothenbacher K, Herrmann T, Sjolin S, Hagmar L, Papke O, Jakobsson K. Polybrominated diphenyl ether exposure to electronics recycling workers-a follow up study. Chemosphere 2006;64:1855–1861. [PubMed: 16524616]
37. Ikonomou MG, Rayne S, Addison RF. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. Environ. Sci. Technol 2002;36:1886–1892. [PubMed: 12026966]
38. Gauthier LT, Hebert CE, Weseloh DV, Letcher RJ. Dramatic changes in the temporal trends of polybrominated diphenyl ethers (PBDEs) in herring gull eggs from the Laurentian Great Lakes: 1982–2006. Environ. Sci. Technol 2008;42:1524–1530. [PubMed: 18441798]
39. Law RJ, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit CA. Levels and trends of brominated flame retardants in the European environment. Chemosphere 2006;64:187–208. [PubMed: 16434081]
40. Christensen JR, MacDuffee M, Macdonald RW, Whiticar M, Ross PS. Persistent organic pollutants in British Columbia grizzly bears: consequence of divergent diets. Environ. Sci. Technol 2005;39:6952–6960. [PubMed: 16201616]
41. Drouillard KG, Fernie KJ, Letcher RJ, Shutt LJ, Whitehead M, Gebink W, Bird DM. Bioaccumulation and biotransformation of 61 polychlorinated biphenyl and four polybrominated diphenyl ether congeners in juvenile American kestrels (*Falco sparverius*). Environ. Toxicol. Chem 2007;26:313–324. [PubMed: 17713220]
42. Potter KE, Watts BD, La Guardia MJ, Harvey EP, Hale RC. Polybrominated diphenyl ether flame retardants in Chesapeake Bay region, USA, peregrine falcon (*Falco peregrinus*) eggs. Environ. Toxicol. Chem 2009;28:973–981. [PubMed: 19102579]
43. Fernie KJ, Laird Shutt J, Ritchie IJ, Letcher RJ, Drouillard K, Bird DM. Changes in the growth, but not the survival, of American kestrels (*Falco sparverius*) exposed to environmentally relevant polybrominated diphenyl ethers. J. Toxicol. Environ. Health, A 2006;69:1541–1554. [PubMed: 16854784]
44. Fernie KJ, Shutt JL, Mayne G, Hoffman D, Letcher RJ, Drouillard KG, Ritchie IJ. Exposure to polybrominated diphenyl ethers (PBDEs): changes in thyroid, vitamin A, glutathione homeostasis, and oxidative stress in American kestrels (*Falco sparverius*). Toxicol. Sci 2005;88:375–383. [PubMed: 16120752]

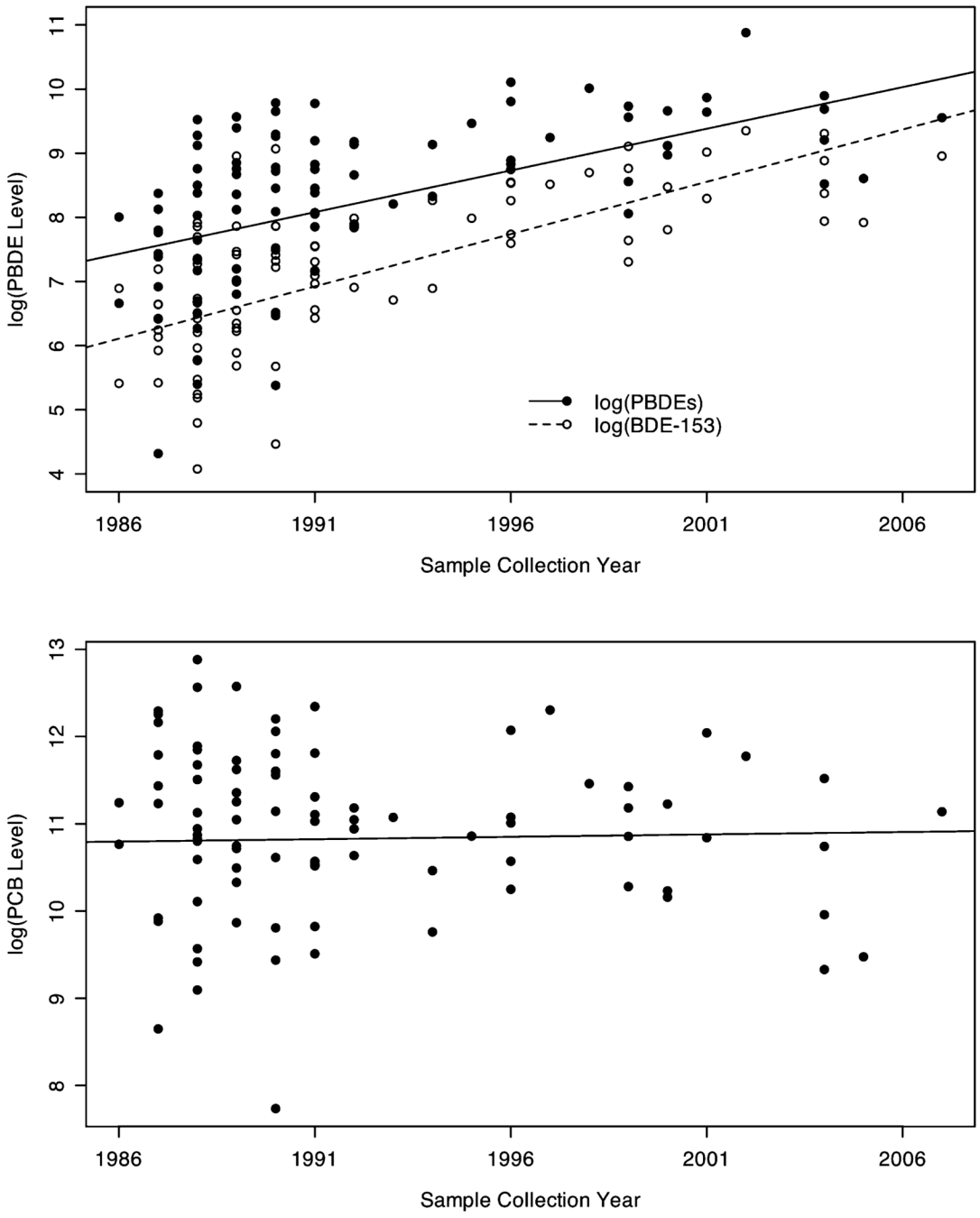

FIGURE 1.

Temporal changes in the log (natural logarithm) of levels (ng/g lipid wt) of ΣPBDEs and BDE-153 (top), and ΣPCBs (bottom) in peregrine falcon eggs from California (*n* = 90).

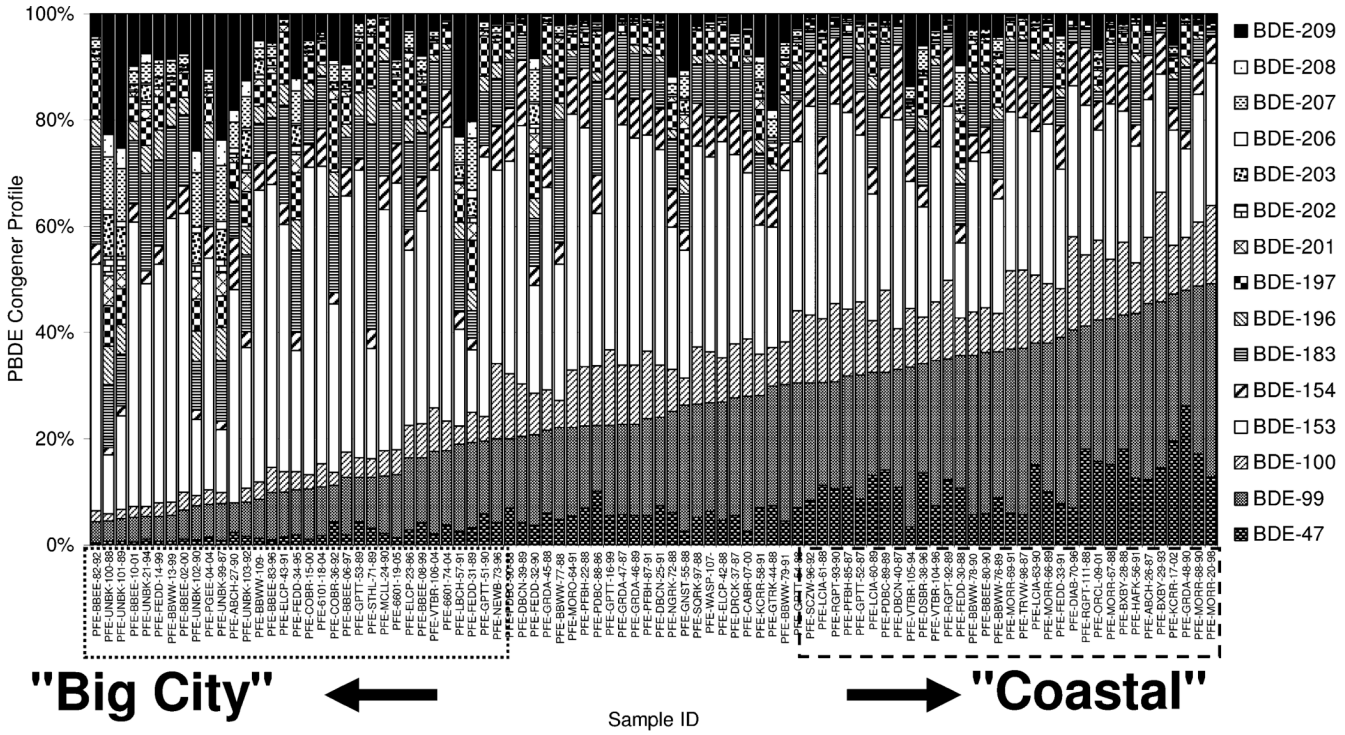

FIGURE 2.

PBDE patterns in peregrine falcon eggs from California (1986–2007; *n* = 90): eggs arranged in increasing order of Σ(% BDE-47 + % BDE-99).

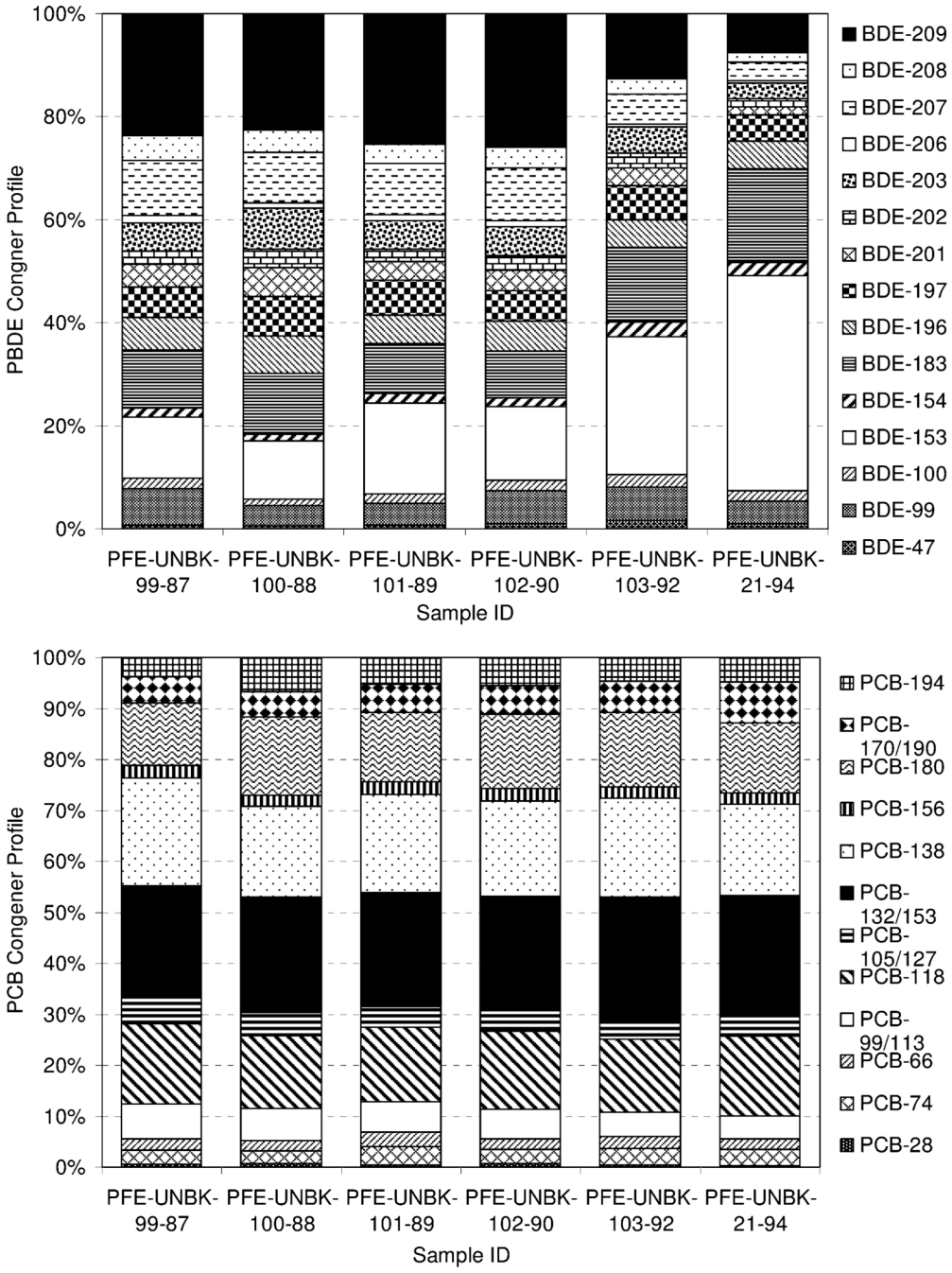

FIGURE 3.

Temporal changes in PBDE and PCB patterns in eggs collected during the period 1987–1994 from one California peregrine falcon nest (Union Bank building, Los Angeles, CA).

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TABLE 1

Levels (μg/g lipid) of PCBs and PBDEs Measured from California Peregrine Falcon Eggs (PFEs) and Chicks[a]

	"Big City" PFEs (*N* = 10)				"Coastal" PFEs (*N* = 18)				"Rural" PFEs (*N* = 13)				"Other" PFEs (*N* = 11)				total CA PFEs (*N* = 52) Big City + Coastal + Rural + Other						peregrine falcon chicks (*N* = 7)			
	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	mean	sd	min	med	max	geo mean
PBDEs																										
PBDE-47	0.08	0.18	3.33	0.24	0.00	0.19	4.07	0.18	0.00	0.07	0.85	0.06	0.08	0.74	10.4	0.71	0.00	0.21	10.4	0.19	0.68	1.63	0.10	0.74	10.9	0.86
PBDE-99	0.44	0.83	5.05	1.18	0.01	0.53	3.38	0.40	0.02	0.22	2.18	0.24	0.55	2.00	14.7	2.45	0.01	0.71	14.7	0.63	1.54	2.49	0.76	3.51	23.6	3.24
PBDE-100	0.16	0.38	2.15	0.45	0.00	0.30	1.55	0.00	0.01	0.12	0.66	0.10	0.23	0.89	4.88	1.09	0.00	0.32	4.88	0.00	0.65	0.96	0.30	1.52	11.4	1.44
PBDE-153	0.62	3.21	7.08	2.94	0.09	0.66	8.19	0.75	0.03	0.62	2.58	0.44	1.06	4.00	11.5	3.82	0.03	1.41	11.5	1.20	2.37	2.65	1.51	7.19	29.2	7.49
PBDE-154	0.14	0.49	0.97	0.43	0.02	0.19	0.54	0.17	0.01	0.10	0.35	0.07	0.25	0.63	2.14	0.72	0.01	0.28	2.14	0.23	0.39	0.42	0.31	0.92	4.48	1.13
PBDE-183	0.25	1.17	2.50	1.05	0.00	0.10	1.85	0.10	0.01	0.14	1.30	0.15	0.31	0.52	2.95	0.66	0.00	0.35	2.95	0.26	0.64	0.74	0.44	3.08	8.05	2.22
PBDE-196	0.09	0.42	0.77	0.31	0.00	0.01	0.57	0.02	0.00	0.02	0.27	0.00	0.06	0.11	0.60	0.15	0.00	0.09	0.77	0.00	0.16	0.20	0.06	0.81	1.41	0.48
PBDE-197	0.15	0.54	1.75	0.55	0.00	0.03	1.36	0.05	0.00	0.04	0.86	0.07	0.15	0.25	1.47	0.34	0.00	0.21	1.75	0.13	0.34	0.41	0.21	1.77	4.16	1.18
PBDE-201	0.03	0.11	0.36	0.12	0.00	0.01	0.13	0.01	0.00	0.01	0.24	0.00	0.02	0.05	0.24	0.06	0.00	0.03	0.36	0.00	0.06	0.09	0.02	0.17	0.50	0.14
PBDE-202	0.02	0.03	0.22	0.05	0.00	0.00	0.03	0.01	0.00	0.00	0.06	0.00	0.01	0.03	0.15	0.03	0.00	0.01	0.22	0.00	0.03	0.05	0.00	0.03	0.26	0.00
PBDE-203	0.04	0.12	0.44	0.13	0.00	0.00	0.10	0.00	0.00	0.00	0.19	0.00	0.02	0.04	0.26	0.05	0.00	0.02	0.44	0.00	0.06	0.10	0.02	0.10	0.96	0.10
PBDE-206	0.01	0.02	0.09	0.03	0.00	0.00	0.01	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.06	0.01	0.00	0.00	0.09	0.00	0.01	0.02	0.00	0.01	0.23	0.01
PBDE-207	0.08	0.25	0.96	0.28	0.00	0.01	0.21	0.01	0.00	0.01	0.38	0.01	0.02	0.07	0.65	0.09	0.00	0.03	0.96	0.03	0.12	0.21	0.02	0.26	1.48	0.20
PBDE-208	0.03	0.10	0.29	0.10	0.00	0.00	0.04	0.00	0.00	0.00	0.10	0.00	0.01	0.02	0.18	0.03	0.00	0.01	0.29	0.00	0.04	0.07	0.00	0.04	0.48	0.04
PBDE-209	0.26	1.00	4.06	0.85	0.00	0.03	0.22	0.02	0.00	0.02	0.97	0.02	0.04	0.22	3.13	0.28	0.00	0.07	4.06	0.08	0.40	0.78	0.04	0.25	3.51	0.28
Σ15PBDEs	3.71	10.1	24.5	10.2	0.22	2.38	15.9	2.17	0.08	1.61	9.14	1.34	4.37	12.1	53.1	12.0	0.08	4.53	53.1	3.72	7.57	9.12	4.08	20.6	94.4	21.6
PCBs																										
PCB-28	0.08	0.20	0.64	0.21	0.02	0.16	1.57	0.15	0.03	0.13	0.76	0.11	0.03	0.16	0.44	0.15	0.02	0.16	1.57	0.15	0.21	0.24	0.16	0.32	1.18	0.33
PCB-74	0.44	1.05	2.90	1.24	0.04	0.99	3.05	0.85	0.12	0.38	3.20	0.47	0.23	0.96	2.34	0.87	0.04	0.95	3.20	0.79	1.08	0.80	0.88	1.76	4.83	1.76
PCB-66	0.40	1.02	2.93	0.99	0.03	0.84	3.57	0.71	0.08	0.38	1.73	0.36	0.13	1.02	1.78	0.65	0.03	0.80	3.57	0.63	0.93	0.77	0.57	1.01	4.44	1.32
PCB-99/113	1.07	2.11	8.38	2.39	0.06	2.49	6.82	2.18	0.25	0.78	8.87	1.10	0.42	1.91	10.1	2.18	0.06	2.11	10.1	1.87	2.71	2.23	2.28	5.59	20.8	5.28
PCB-118	2.40	4.88	15.8	5.18	0.14	6.19	19.9	5.37	0.50	1.73	14.9	2.31	1.04	4.68	14.2	4.69	0.14	4.88	19.9	4.20	6.10	4.72	3.21	12.7	35.7	10.6
PCB-105/127	0.72	1.34	3.81	1.36	0.02	1.22	3.78	1.05	0.10	0.36	2.75	0.47	0.26	1.23	2.96	1.09	0.02	1.11	3.81	0.91	1.31	0.94	0.70	2.58	8.36	2.31
PCB-132/153	4.81	11.8	76.0	14.7	0.69	29.2	67.1	22.1	1.64	9.29	92.3	10.1	3.84	15.0	44.5	17.1	0.69	18.0	92.3	15.9	24.3	21.1	23.9	39.9	91.3	44.4
PCB-138	3.25	6.89	44.8	9.24	0.24	11.7	30.4	9.14	1.08	5.66	47.6	5.00	1.50	6.95	32.8	8.43	0.24	7.70	47.6	7.74	11.8	10.7	11.4	20.5	109	25.6

	"Big City" PFEs (*N* = 10)				"Coastal" PFEs (*N* = 18)				"Rural" PFEs (*N* = 13)				"Other" PFEs (*N* = 11)				total CA PFEs (*N* = 52) Big City + Coastal + Rural + Other						peregrine falcon chicks (*N* = 7)			
	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	min	med	max	geo mean	mean	sd	min	med	max	geo mean
PCB-156	0.45	0.93	4.48	1.16	0.07	1.28	2.83	1.02	0.13	0.59	5.17	0.56	0.26	1.01	2.72	1.02	0.07	0.94	5.17	0.90	1.27	1.06	1.05	2.12	8.11	2.57
PCB-180	2.50	6.75	42.0	8.50	0.52	14.5	41.3	11.5	0.84	7.29	63.6	6.77	2.44	9.46	40.3	9.54	0.52	9.62	63.6	9.13	14.0	13.3	11.5	34.8	109	30.0
PCB-170/190	1.50	3.01	17.2	3.80	0.26	5.81	16.2	4.63	0.37	2.94	24.5	2.66	1.07	3.33	9.49	3.95	0.26	3.73	24.5	3.75	5.59	5.18	4.42	13.7	65.0	12.9
PCB-194	0.83	2.15	9.97	2.57	0.20	3.62	10.7	2.74	0.20	1.52	20.8	1.90	0.17	2.16	10.0	2.12	0.17	2.21	20.8	2.34	3.70	3.77	3.11	7.69	27.9	8.37
Σ15PCB	19.9	39.9	227	53.4	2.29	77.8	199	62.2	5.71	36.1	286	32.4	12.1	46.2	170	52.9	2.29	52.3	286	49.6	73.1	62.6	71.1	146	453	152

[a]The eggs from multiple prey habitats were classified as "Other". *N* = number of eggs, with eggs in a time-series represented by a single geometric mean value. Data for individual peregrine falcon eggs and chicks are provided in Tables S1A, S1B, S2A, and S2B.