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Wastewater dilution index partially explains observed polybrominated diphenyl ether flame retardant concentrations in osprey eggs from Columbia River Basin, 2008–2009

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Abstract Several polybrominated biphenyl ether (PBDE) congeners were found in all 175 osprey (*Pandion haliaetus*) eggs collected from the Columbia River Basin between 2002 and 2009. ΣPBDE concentrations in 2008–2009 were highest in osprey eggs from the two lowest flow rivers studied; however, each river flowed through relatively large and populous metropolitan areas (Boise, Idaho and Spokane, Washington). We used the volume of Wastewater Treatment Plant (WWTP) discharge, a known source of PBDEs, as a measure of human activity at a location, and combined with river flow (both converted to millions of gallons/day) created a novel approach (an approximate Dilution Index) to relate waterborne contaminants to levels of these contaminants that reach avian eggs. This approach provided a useful understanding of the spatial osprey egg concentration patterns observed. Individual osprey egg concentrations along the Upper Willamette River co-varied with the Dilution Index, while combined egg data (geometric means) from rivers or segments of rivers showed a strong, significant relationship to the Dilution Index with one exception, the Boise River. There, we believe osprey egg concentrations were lower than expected because Boise River ospreys foraged perhaps 50–75% of the time off the river at ponds and lakes stocked with fish that contained relatively low ΣPBDE concentrations. Our limited temporal data at specific localities (2004–2009) suggests that ΣPBDE concentrations in osprey eggs peaked between 2005 and 2007, and then decreased, perhaps in response to penta- and octa-PBDE technical mixtures no longer being used in the USA after 2004. Empirical estimates of biomagnification factors (BMFs) from fish to osprey eggs were 3.76–7.52 on a wet weight (ww) basis or 4.37–11.0 lipid weight. Our earlier osprey study suggested that ΣPBDE egg concentrations >1,000 ng/g ww may reduce osprey reproductive success. Only two of the study areas sampled in 2008–2009 contained individual eggs with ΣPBDE concentrations >1,000 ng/g, and non-significant ($P > 0.30$) negative relationships were found between ΣPBDEs and reproductive success. Additional monitoring is required to confirm not only the apparent decline in PBDE concentrations in osprey eggs that occurred during this study, but also to better understand the relationship between PBDEs in eggs and reproductive success.

Keywords Osprey · Polybrominated diphenyl ethers · Oregon · Washington · Idaho · Wastewater treatment plants · Biomagnification factors · Productivity · Dilution index

Introduction

Polybrominated diphenyl ethers (PBDEs) are compounds that have been used since the 1970s as additive flame retardants in thermoplastics, textiles, polyurethane foams and electronic circuitry. Individual PBDE congeners

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comprise commercially produced technical mixtures. As the names imply with respect to PBDE congener constitution, the three most widely used types are deca-BDE, octa-BDE and penta-BDE mixtures. PBDEs persist in the environment and bioaccumulate and biomagnify up the food web to the top predatory fish, mammal and bird species (de Wit 2002), including birds of prey as recently reviewed by Chen and Hale (2010).

ΣPBDE concentrations in mountain whitefish (*Prosopium williamsoni*) from the Columbia River increased 12-fold between 1992 and 2000, with a doubling period of 1.6 years (Rayne et al. 2003). Two osprey (*Pandion haliaetus*) eggs collected on the Columbia River near Castlegar, British Columbia in 1997 increased 15-fold over ΣPBDE concentrations reported for two collected in the area in 1991, prompting concerns over toxicological effects if residues continued to increase (Elliott et al. 2005). Analyses of fish collected in the Great Lakes between 1979 and 2005 showed that while long-term trends of ΣPBDE concentrations in each lake and fish species increased exponentially beginning in the early 1980s, a leveling-off or decrease of concentrations started in the mid-1990s, but with variability among lakes and species (Batterman et al. 2007). Herring gull (*Larus argentatus*) eggs collected from the Great Lakes between 1982 and 2006 showed a similar pattern, with no increasing trend post-2000 (Gauthier et al. 2008). Though these later studies indicate PBDEs may be leveling off or declining, Braune et al. (2007) reported PBDE concentrations in ivory gull (*Pagophila eburnea*) eggs from the Canadian arctic, steadily increased between 1976 and 2004, and the increase was primarily driven by BDE-47.

Between 2002 and 2007, all 120 osprey eggs collected from Oregon and Washington (including 82 from Columbia River Basin) contained PBDEs (Henny et al. 2009b). In contrast to DDE and other banned pesticides and polychlorinated biphenyls (PCBs), which decreased in recent years in fish-eating osprey eggs from the Columbia River Basin and elsewhere (Henny et al. 2008, 2009a, 2010), PBDEs increased in osprey eggs from Puget Sound, Washington (2003 vs. 2006/2007) and the Lower Columbia River, Oregon/Washington (2004 vs. 2007) (Henny et al. 2009b). River Mile (RM) is used in this report to define locations on rivers. RM 0 begins at the ocean or where the river joins another river. Only in 2006 and 2007 (Upper Willamette River, RM 61–157 and Lower Columbia River, RM 29–84) did PBDE concentrations in individual osprey eggs exceed 1,000 ng/g ww. In those 2 years, there was evidence that PBDE concentrations may adversely affect osprey reproductive rates. We hypothesized in our earlier paper that a small river with low flow associated with a high human population may lead to higher PBDE concentrations in osprey eggs.

Studies of biosolids from Wastewater Treatment Plants (WWTPs) (Hale et al. 2001; Anderson and MacRae 2006; Sullivan et al. 2007) reported the presence of extremely high concentrations of PBDEs. Song et al. (2006) reported that the bulk ($\sim$91%) of the average ΣPBDE concentration (ΣPBDEs; BDE 47, 99, 100, 153 and 154) leaving/entering the WWTP on the Little River and discharging into the upper Detroit River in Windsor, Ontario, Canada, ended up in the primary sludge and waste activated sludge, while the remaining $\sim$9% was discharged with the final effluent. Thus, liquid releases into rivers from WWTPs were suspected important PBDE sources.

The European Union banned the use of octa- and penta-BDEs, and the American manufacturer voluntarily stopped production in 2004 (Manugian 2004). The only PBDE mixture currently used in the US is the technical deca-BDE product. The State of Washington's PBDE Law (RCW 70.76) legislated bans on certain uses of deca-BDE (no use in mattresses after January 1, 2008, and no use in televisions, computers and upholstered furniture after January 1, 2011). Evidence indicates, including in Great Lakes herring gulls (Gauthier et al. 2008), that deca-BDE can undergo reductive debromination in the environment to congeners BDE-206, 207, 208, which can then be further debrominated (Gerecke et al. 2005; Stapleton et al. 2006; Kuo et al. 2010). With changes in PBDE use in the United States occurring post-2004, with evidence that PBDE concentrations may adversely affect osprey reproductive rates, and with published long-term studies cited above terminated in 2007 or earlier, we were especially concerned about possible recent changes (2008, 2009) in osprey egg concentrations.

This study was designed to: (1) describe regional PBDE and other brominated flame retardant concentration patterns in osprey eggs (one sample egg collected at random per nest) and congener profiles at locations within the Columbia River Basin in Oregon, Washington and Idaho in 2008 and 2009, (2) evaluate a possible relationship between observed PBDE residue concentrations in osprey eggs with river flow (cubic feet/second, converted to millions gallons/day, MGD) and wastewater discharge (MGD) from major WWTPs, i.e., a dilution effect, (3) investigate temporal trends in PBDE concentrations and congener profiles in osprey eggs collected during this study and earlier investigations at four locations (Upper Willamette River 2006 vs. 2008, and three segments of the Lower Columbia River between 2004 and 2009), (4) study PBDE residue concentrations in fish and osprey eggs from the Spokane and Boise Rivers to estimate biomagnification factors from fish to osprey eggs, and (5) investigate reproductive success (number of young produced) at each nest to determine if an association exists with PBDE concentrations in the sample egg from that nest.

Materials and methods

Four of the original study areas (Upper Willamette River and three segments of Lower Columbia River) were resampled in this study (2008–2009) to determine residue trends, and additional study areas were added. Washington Department of Ecology reported that fish from the Spokane River contained the highest PBDE concentrations in the state (Johnson et al. 2006); and Willamette River osprey eggs collected during the earlier study (the highest concentrations reported) were only obtained from the upstream portion of the river with relatively high human populations and generally lower flows. Thus, in addition to the original study areas, two smaller tributaries of the Upper Columbia River Basin (Spokane River in eastern Washington and Boise River in western Idaho) and a series of small Reference Lakes south of Spokane, as well as the Lower Willamette River (Portland Harbor and Multnomah Channel, Oregon) were added (Fig. 1). Both of the upper basin tributaries have relatively low river flows (less water dilution effect) and relatively high human populations, while the Portland Harbor and Multnomah Channel represent urban areas with large river flow near the mouth of the Willamette River.

We located occupied osprey nests by boat, car and aircraft. Nests were visited at least two to four times, but often at weekly intervals to determine nesting activity and reproductive success following definitions of Postupalsky (1977). One partially incubated egg (usually about 10 days into incubation) was randomly collected from each nest (usually 3-eggs laid per clutch) to determine exposure to contaminants. Egg contents were placed in chemically clean jars and frozen for subsequent contaminant analysis. In this study we evaluated reproductive success at individual osprey nests by comparing residue concentrations in a sample egg collected from each nest to the number of advanced-age young (40–45 days) produced from the remaining eggs in the nest, i.e., the sample egg technique (Blus 1984). A helicopter flight scheduling conflict on the Spokane River in 2009 resulted in an earlier than normal flight. This resulted in some young being smaller than usual, with the final production count perhaps biased slightly high.

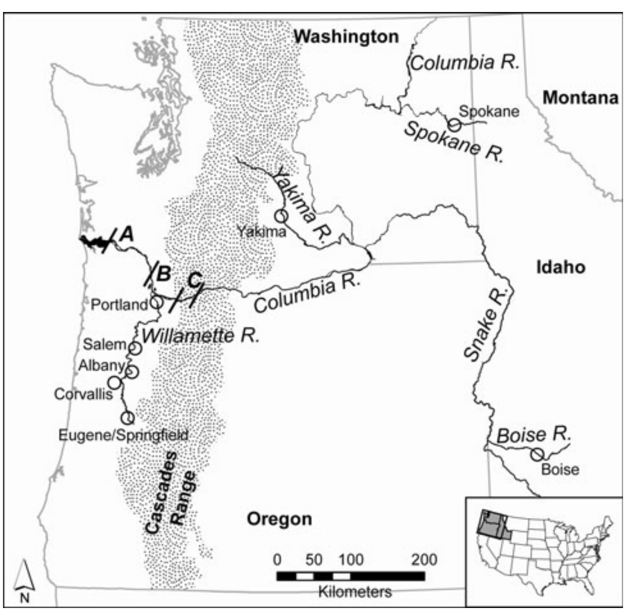

Fig. 1 Map of the Columbia Basin study area. (*A*) Lower Columbia River (RM 29–84), (*B*) Lower Columbia River (RM 85–122), (*C*) Lower Columbia River (RM 124–143). *Open circles* represent urban areas

We report on major, persistent and bioaccumulative PBDEs in 93 osprey eggs randomly collected (one per nest) during this 2008–2009 study in Oregon, Washington and Idaho, and compare them to 82 eggs previously reported from the Columbia River Basin between 2002 and 2007 (Henny et al. 2009b). Contaminants other than PBDEs can potentially influence osprey reproductive success. Osprey literature was reviewed to evaluate critical concentration levels for reproductive effects of organochlorine pesticides, polychlorinated biphenyls, dioxins, furans and mercury (see Henny et al. 2008). However, of the eggs collected earlier (2002–2007), only four contained other contaminants, in this case *p,p′*-DDE, at concentrations believed to adversely influence osprey productivity. The four eggs all came from nests along the Yakima River (an intensive agriculture area) in 2002, and were excluded from the earlier analysis (Henny et al. 2009b) and not used in this study. All eggs collected in 2008 were routinely analyzed for several legacy contaminants (organochlorine pesticides and 42 polychlorinated biphenyl congeners), but no concentrations were found at levels believed to influence osprey productivity, with concentrations continuing their pattern of decrease over time (see Henny et al. 2010). No eggs were analyzed for legacy contaminants in 2009.

As previously mentioned, liquid releases from WWTPs were suspected important PBDE sources. Furthermore, the size of human populations associated with various WWTPs in this study were highly correlated with the volume of wastewater discharge (Fig. 2). We do not believe that effluent entering the rivers from WWTPs is the only PBDE source, but the volume provides an approximate measure of human and perhaps industrial activity in a given area. PBDE concentrations in effluent could be modified by degree of wastewater treatment, but for purposes of this paper unaltered discharge values were used. Data provided 12 July 2010 by Daniel Wise, Hydrologist, U.S. Geological Survey (USGS), Portland, Oregon, listed the estimated 2002 mean discharge in

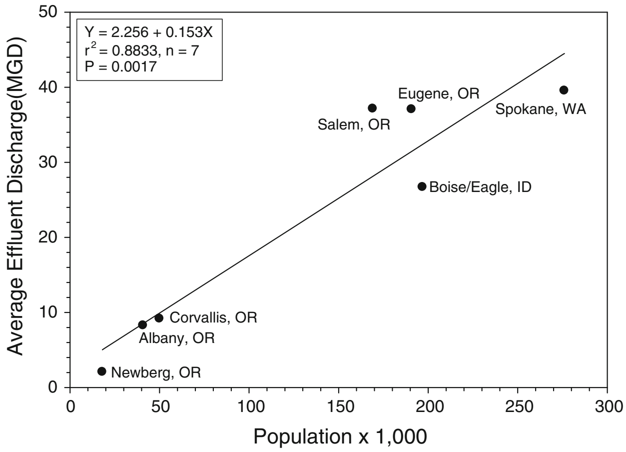

Fig. 2 Relationship between human population size and Wastewater. Treatment Plant effluent discharge at Columbia Basin osprey study areas. *MGD* million gallons per day

millions gallons/day (MGD) for 216 WWTPs in the Pacific Northwest. About one-half of the WWTPs discharge over 1.0 MGD. Although this list was incomplete, all of the major WWTPs were included and probably most of the smaller facilities. The USGS stream flow estimates (converted from cubic feet/second to MGD) for the receiving rivers at each WWTP site represent USGS modeled mean annual values for 1974–2004. Although years for the discharge data from WWTPs (2002), the average stream flow estimates (1974–2004) and osprey egg concentrations (2008–2009) were not the same, we attempt to understand general patterns in this analyses and believe our simplified approach is useful. Then, the discharge from each WWTP divided by the stream flow estimate at each site was multiplied by 1,000 to provide a Dilution Index for each WWTP to compare with observed osprey ΣPBDE egg concentrations.

$$\text{Dilution Index} = (\text{Wastewater Discharge[MGD]}/\text{River Flow[MGD]}) \times 1,000$$

This Dilution Index permits an evaluation of osprey ΣPBDE egg concentrations at various river miles along a specific river, or a general comparison of geometric mean egg concentrations among rivers. We suspected that ΣPBDE concentrations in osprey eggs may be a function of this approximate index. This initial approximation approach assumes that wastewater discharge from all WWTPs contains equal concentrations of ΣPBDEs, which may not be true. Concentrations at specific WWTPs could depend upon degree of wastewater treatment or unique PBDE use patterns; however, this simple evaluation should be instructive. Oregon Department of Environmental Quality is now in the process of evaluating PBDE concentrations in discharges at selected WWTPs in Oregon (J. Coyle, personal comm.).

Analytical chemistry

Eggs collected in 2008 and 2009 were shipped to the National Wildlife Research Centre (NWRC), Science and Technology Branch, Environment Canada, Carleton University, Ottawa, Ontario for analysis by the Letcher Organics Research Lab. As described elsewhere (Gauthier et al. 2007, 2008), sample eggs were analyzed for BDE congeners: 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190, 209 and total-α-HBCD, and polybrominated biphenyls (BB) 101 and 153 (co-eluted with BDE154). In 2009, an additional twenty BDE congeners and six non-PBDE, brominated flame retardants (BFRs) were evaluated (Table 1), but were either not detected or found at very low, parts-per-billion concentrations and, for comparative purposes, were not reported or discussed further in this paper (except see Biomagnification Factors where BDE 71 and 184 were used).

Egg analysis was comprehensively described in Gauthier et al. (2008). Briefly, homogenized osprey egg samples (about 1 g) were spiked with BDE30, BDE71, BDE156, and/or $^{13}C_{12}$-BDE-209 internal standards (200 pg/μl each and in a 100 μl spike). After clean-up and isolation of the PBDE/BFR containing fraction, the brominated compounds were determined by GC–MS (in the electron capture negative ionization (ECNI) mode). An Agilent Gas Chromatograph (GC) 6890 equipped with a 5973 quadrupole mass spectrometer (MS) detector was used. Full details are detailed in Gauthier et al. (2008), but briefly, bromine-containing compounds were identified based on their ^{79}Br and ^{81}Br anion isotopic response (overwhelmingly the major fragment ion), and on the basis of their full chromatographically resolved retention times on a DB-5HTcolumn (15 m × 0.25 mm i.d. × film thickness of 0.10 μm), and relative to that of authentic standards, i.e., total-α-HBCD, BB-101, and PBDEs (14 congeners). The α-HBCD is total-α-HBCD as β- and γ-HBCD thermally isomerize to α-HBCD at GC temperatures >160°C.

Quantification of the brominated compounds was performed using an internal standard method based on the relative ECNI response factor (RRF) of the corresponding internal standard and target compounds. The quantification analysis was based on *m/z* 79 and 81 for the bromine anion fragment, and the response of the internal standard BDE30, for the fourteen PBDE congeners, BB-101 and HBCD, which were of focus in the present study. In the case of BDE209, the *m/z* 487 and 489 isotope ions of the abundant pentabromophenoxy anion fragment were used for identification and quantification. Ion *m/z* 495 was used for the quantification (and *m/z* 497 for identity confirmation) of the internal standard of $^{13}C_{12}$-BDE-209, and used as the internal standard for BDE-209.

Table 1 The incidence, geometric mean and highest concentration (ng/g, ww) of additional PBDE congeners and other brominated flame retardants analyzed in osprey eggs from Lower Columbia River (LCR), Spokane River (SR) and Reference Lakes near Spokane, 2009

Location (N)	Incidence, geometric mean, high concentration				
	LCR RM 29-84 (10)	LCR RM 124-143 (5)	SR upper segment (8)	SR lower segment (7)	Reference lakes (8)
BDE-2	1, NC, 0.35	ND	ND	ND	ND
BDE-3	ND	ND	ND	1, NC, 1.66	ND
BDE-7	ND	ND	ND	1, NC, 2.29	1, NC, 0.44
BDE-15[a]	2, NC, 1.01	ND	1, NC, 0.40	4, 0.06, 2.29	ND
BDE-71	2, NC, 1.01	ND	ND	3, NC, 6.22	1, NC, 0.32
BDE-77[b]	ND	ND	3, NC, 0.99	4, 0.07, 1.88	ND
BDE-119	4, NC, 3.58	2, NC, 1.54	8, 1.17, 8.34	7, 2.95, 14.2	1, NC, 0.35
BDE-140	5, 0.04, 1.10	ND	6, 0.16, 2.38	6, 0.40, 7.04	1, NC, 0.35
BDE-155	10, 1.74, 5.42	5, 0.80, 1.33	7, 0.76, 4.49	7, 3.01, 9.74	1, NC, 0.79
BDE-170	1, NC, 1.01	ND	1, NC, 0.56	ND	1, NC, 0.94
BDE-179	1, NC, 0.36	ND	1, NC, 0.42	1, NC, 0.51	ND
BDE-184	ND	ND	ND	1, NC, 0.74	ND
BDE-188	2, NC, 2.34	ND	1, NC, 3.85	3, NC, 1.88	ND
BDE-194	ND	ND	ND	ND	2, NC, 3.51
BDE-195	ND	ND	1, NC, 0.32	ND	1, NC, 0.51
BDE-196	ND	ND	ND	ND	1, NC, 0.74
BDE-197	ND	ND	1, NC, 0.37	1, NC, 0.90	ND
BDE-201	ND	ND	1, NC, 0.82	2, NC, 2.05	ND
BDE-202	4, NC, 0.74	ND	1, NC, 1.56	4, 0.07, 3.19	ND
BDE-203	1, NC, 0.92	ND	ND	ND	ND
PBEB	ND	ND	ND	1, NC, 0.5	ND
PBAE	1, NC, 0.6	ND	ND	3, NC, 1.2	ND
HBB	ND	ND	ND	3, NC, 4.3	ND
BB-101	7, 0.16, 1.1	ND	1, NC, 0.7	3, NC, 3.1	1, NC, 0.5
PBBA	1, NC, 0.5	ND	ND	2, NC, 2.6	ND
HBCD	1, NC, 3.1	ND	ND	ND	ND
BTBPE	ND	ND	ND	ND	1, NC, 0.5
OBTMI	ND	ND	2, NC, 0.5	1, NC, 0.8	2, NC, 0.6

Other BDE congeners analyzed but not detected included 1, 10, 28[c], 54, 139, 171[d], 180, 181, 182, 191, 205, 206, 207, 208

[a] BDE-15 coeluted with β-TBECH

[b] BDE-77 coeluted with BB-101

[c] BDE-28 coeluted with PBT

[d] BDE-171 coeluted with BDE-190

Additional non-PBDE flame retardants analyzed and not detected included β-TBECH, PBT[d], TBPAE, α-TBECH, pTBX, TBCT, and DBDPE

ND not detected, *NC* not calculated, present in <50% of eggs, *BB-101* brominated biphenyl-101, *HBCD* hexabromocyclododecane, *TBECH* 1,2-dibomo-4-(1,2-dibromoethyl)-cyclohexane, *PBT* pentabromotoluene, *TBPAE* 2,4,6-tribromo allyl ether, *pTBX* tetrabromo-*p*-xylene, *TBCT* tetrabromochlorotoluene, *PBEB* pentabromoethylbenzene, *PBPAE* pentabromophenyl allyl ether, *HBB* hexabromobenzene, *PBBA* pentabromobenzyl acrylate, *BTBPE* 1,2-bis-(2,4,6-tribromophenoxy)ethane, *OBTMI* octabromo-1,3,3-trimethyl-1-phenyl-indane, *DBDPE* decabromodiphenyl ethane

Data analysis and quality control

In general, and as surrogates of all PBDEs and non-PBDE BFRs that were determined, the recoveries of BDE30, BDE71, BDE156 and/or $^{13}C_{12}$-BDE209 internal/recovery standards that were used were close to or greater than 75%. Concentrations were inherently recovery-corrected as an internal standard method of quantification was used to reduce heterogeneity within and between analyte classes. Method blank samples were analyzed with each batch of five samples. The method limit of quantification was generally about 0.005 ng/g wet weight (ww). To assess the precision and accuracy of the concentrations of major PBDEs under study (and by extension to other BFR), an in-house reference material (IHRM) of double-crested cormorant (*Phalacrocorax auritus*) egg pool homogenate was analyzed ($n = 5$ replicates), where one IHRM sample was analyzed per batch of osprey egg samples. Also, a standard reference material (SRM) of NIST 1947 Lake Michigan Fish Tissue homogenate was analyzed ($n = 5$ replicates), where one SRM sample was analyzed per batch of osprey egg samples. For both the IHRM and SRM used, good reproducibility of PBDEs was obtained with a % RSDs of <10%. For the NIST 1947 SRM, concentrations of applicable PBDEs were also within 10% of the actual NIST values.

PBDE residue concentrations in eggs were corrected to an approximate fresh wet weight using egg volumes determined by water displacement (Stickel et al. 1973), and reported as geometric means and log-transformed for statistical analyses. Because of unequal sample sizes, the General Linear Models Procedure (SAS Institute, Cary, NC, 2003) was used for analysis of variance. Tukey's Studentized Range Test ($\alpha = 0.05$) was used to separate means. We used the Jonckheere–Terpstra Test with a one-sided test, because a priori we wanted to test for a negative association in productivity versus ΣPBDE concentrations in the sample egg from each nest (Hollander and Wolfe 1973). Unless otherwise noted, differences were considered significant when $P \leq 0.05$.

Results and discussion

Regional pattern in osprey egg ΣPBDE concentrations, 2008–2009

Osprey eggs collected in the Pacific Northwest in 2002–2007 indicated that ΣPBDEs were lowest from the forested headwater reservoirs of the Willamette River, while those from the Upper Willamette River (RM 61–157) contained the highest concentrations (Henny et al. 2009b). Concentrations in eggs from the Columbia River progressively increased downstream from rural Umatilla, OR (RM 286) to Skamokawa, WA (RM 29) downstream of Portland, OR and Vancouver, WA metropolitan areas, which suggested additive PBDE sources along the river.

We collected osprey eggs in 2008–2009 at several of the same river reaches sampled in earlier years, but also new locations (Boise River, Spokane River, Portland Harbor and Multnomah Channel [lower Willamette River], and Reference Lakes located south of the city of Spokane in Northeastern Washington) (Fig. 1). Eggs from the two smaller rivers (Boise R. and Spokane R.) flowing through relatively large metropolitan areas contained the highest ΣPBDE concentrations (893 and 616 ng/g) in 2008 and 2009, with the Reference Lakes (61.9 ng/g) being the lowest (Table 2; Fig. 3). ΣPBDE egg concentrations at the other sites (Lower Columbia River, Portland Harbor and Multnomah Channel, and Upper Willamette River) were all within a relatively narrow range (170–427 ng/g). However, consistent with our earlier findings in 2002–2007 (Henny et al. 2009b), the lower segments of the Columbia River in both 2008—RM 29–84 (427 ng/g) versus RM 85–122 (308 ng/g), and 2009—RM 29–84 (308 ng/g) versus RM 124–143 (170 ng/g), contained higher ΣPBDE concentrations (Fig. 4). Eggs from 2008 collected at Portland Harbor (378 ng/g) and Multnomah Channel (262 ng/g) near the mouth of the Willamette River were similar to those from the adjacent Lower Columbia River (RM 85–122) (308 ng/g) and the Upper Willamette River (RM 69–181) (405 ng/g).

ΣPBDEs in osprey eggs, wastewater treatment plants and river flow

In the earlier study (Henny et al. 2009b), differences in ΣPBDE concentrations in osprey eggs along three rivers studied (Columbia, Willamette and Yakima) seemed to reflect differences in river flow (as a function of a dilution effect) and the extent of human population and industry (source inputs) along the rivers. We attempted to further understand the observed ΣPBDE concentrations in osprey eggs collected at fairly regular intervals downstream, as nest sites permitted, of several WWTPs, e.g., see Fig. 5. We evaluated the amount of wastewater discharge from each WWTP (suspected important PBDE source based upon high concentrations in WWTP biosolids and final effluent, see Song et al. 2006) and river flow data at the site of each WWTP with our Dilution Index.

Dilution based upon river flow and WWTP discharges may be less complicated to evaluate in terms of influence on osprey ΣPBDE egg concentrations at the upper portions of the three smaller rivers studied (Willamette, Boise and Spokane) in the Columbia River Basin. The main stem of the lower Columbia River may be influenced by many WWTPs. The largest series of 23 osprey eggs was collected along 112 River Miles of the Upper Willamette River in 2008 (Fig. 5). The WWTPs at both Eugene/Springfield and Salem had similar discharges (37.05 and 37.13 MGD, respectively); however, the flow of the river was considerably higher at Salem because additional tributaries flowed into the river upstream of Salem. Therefore, with the added flow, the WWTP discharge was more diluted at Salem. Both Corvallis and Albany are much smaller cities with lower WWTP discharges (9.16 and 8.26 MGD, respectively) into the river. Individual osprey egg concentrations along the Willamette River co-varied with the dilution gradient based upon major WWTP inputs (Fig. 5). Ten osprey eggs collected in the same general area in 2006

Table 2 Geometric means and ranges (in parentheses) of PBDE concentrations (ng/g, ww) in osprey eggs collected from rivers and lakes in the Columbia Basin of the Pacific Northwest, 2008–2009

Location	Year	*N*	% Lipid	PBDE congener					
				17	28	47	49	66	85
Boise R. (RM 19–45)	2008	11	3.1	3.19 A (1.35–7.05)	12.1 A (6.51–30.4)	383 A (213–807)	2.99 AB (1.55–6.00)	6.48 A (2.73–19.5)	NC [1] (ND-0.48)
Lower Columbia R. (RM 29–84)	2008	6	3.0	0.48 B (0.28–0.81)	3.65 B (2.11–7.30)	254 AB (176–411)	0.41 C (ND-1.14)	0.33 B (ND-1.14)	ND
Lower Columbia R. (RM 29–84)	2009	10	2.9	1.73 AB (0.44–4.78)	2.96 BC (1.54–7.81)	147 BC (108–292)	0.46 C (ND-1.55)	0.70 AB (ND-9.19)	NC [2] (ND-0.55)
Lower Columbia R. (RM 85–122)	2008	5	2.8	0.46 B (0.25–0.66)	3.78 B (1.72–9.66)	184 ABC (95.0–311)	0.59 BC (0.30–0.97)	0.55 B (0.35–0.79)	ND
Lower Columbia R. (RM 124–143)	2009	5	2.9	NC [2] (ND-1.24)	1.20 C (0.70–1.95)	91.6 C (70.4–145)	0.32 C (ND-0.54)	0.51 B (ND-2.05)	ND
Upper Willamette R. (RM 69–178)	2008	23	2.9	1.39 AB (0.24–7.37)	3.88 B (0.91–13.9)	250 AB (90.0–523)	0.38 C (ND-2.04)	0.33 B (ND-2.57)	ND
Multnomah Channel, OR	2008	5	2.4	1.35 AB (0.80–2.24)	4.27 AB (2.58–8.99)	163 BC (114–219)	0.78 ABC (0.45–1.89)	0.48 B (0.32–0.99)	ND
Portland Harbor, OR	2008	5	3.2	0.87 AB (0.23–2.32)	2.67 BC (0.82–3.97)	200 AB (123–314)	0.73 BC (0.33–1.03)	0.65 B (0.35–0.95)	ND
Spokane R. (RM 47–67)	2009	7	3.7	2.87 A (0.96–27.7)	4.99 AB (2.17–16.9)	295 AB (207–494)	4.46 A (1.86–10.7)	2.82 AB (ND-29.8)	ND
Spokane R. (RM 68–96)	2009	8	3.4	1.16 AB (ND-4.44)	1.83 BC (0.49–8.61)	263 AB (90.0–678)	1.83 ABC (ND-3.99)	2.82 AB (0.32–22.4)	NC [1] (ND-0.63)
Reference Lakes, Spokane, WA	2009	8	3.3	NC [1] (ND-0.32)	NC [1] (ND-0.35)	32.1D (16.1–59.4)	NC [3] (ND-2.19)	0.38 B (ND-1.23)	NC [1] (ND-0.40)

Location	PBDE congener						
	99	100	138	153	154/BB 153	183	ΣPBDEs
Boise R. (RM 19–45)	270 A (119–728)	126 A (68.4–298)	0.40 A (ND-1.23)	49.3 AB (19.7–176)	38.5 AB (16.2–102)	0.53 A (0.28–1.48)	893 A (536–2,171)
Lower Columbia R. (RM 29–84)	20.2 DE (14.2–30.8)	93.6 AB (61.9–179)	NC [1] (ND-0.27)	26.0 ABC (15.7–39.6)	26.4 BC (16.5–52.8)	NC [2] (ND-0.17)	427 ABC (330–723)
Lower Columbia R. (RM 29–84)	23.0 DE (11.2–49.0)	77.5 AB (37.7–211)	NC [2] (ND-0.63)	20.6 ABC (1.95–97.4)	24.8 BC (9.82–82.3)	ND	308 CD (172–747)
Lower Columbia R. (RM 85–122)	17.1 DE (9.45–30.8)	66.7 AB (28.8–120)	NC [1] (ND-0.18)	13.6 BCD (4.23–25.7)	18.5 BC (5.93–31.6)	0.09 B (ND-0.21)	308 CD (148–523)
Lower Columbia R. (RM 124–143)	11.5 E (2.78–31.0)	36.8 B (18.0–67.2)	NC [1] (ND-0.52)	10.7 CD (3.32–18.9)	10.9 CD (4.22–18.8)	ND	170 D (106–265)
Upper Willamette R. (RM 69–181)	31.6 CDE (5.29–201)	61.4 AB (16.4–163)	NC [3] (ND-1.30)	19.4 ABC (3.37–75.5)	23.1 BC (4.75–70.8)	NC [9] (ND-0.38)	405 ABC (125–980)
Multnomah Channel, OR	18.2 DE (8.91–25.0)	51.3 AB (33.4–71.0)	NC [1] (ND-0.33)	9.45 CD (6.95–11.7)	11.9 BCD (9.03–14.6)	ND	262 CD (186–351)
Portland Harbor, OR	44.8 BCD (14.8–78.0)	67.4 AB (21.4–120)	NC [2] (ND-1.46)	21.1 ABC (4.11–58.3)	30.2 ABC (7.41–87.4)	0.15 AB (ND-0.45)	378 BCD (172–665)
Spokane R. (RM 47–67)	131 AB (51.0–396)	131 A (72.0–294)	0.43 A (ND-1.64)	67.2 A (22.0–228)	90.4 A (34.8–251)	0.53 A (ND-3.93)	749 AB (401–1,674)
Spokane R. (RM 68–96)	88.3 ABC (17.7–210)	73.8 AB (19.3–331)	NC [1] (ND-2.26)	35.6 ABC (8.91–78.5)	36.3 ABC (8.75–68.7)	NC [3] (ND-0.82)	518 ABC (147–1,391)
Reference Lakes, Spokane, WA	9.50 E (1.14–31.0)	7.03 C (3.20–16.3)	NC [3] (ND-1.03)	3.47 D (0.68–14.5)	4.51 D (1.74–15.1)	ND	61.9 E (33.2–120)

Congeners 190 and 209 were not detected in any samples. ΣPBDE = sum of BDE congeners 17, 28, 47, 66, 85, 99, 100, 138, 153, 154/BB153, and 183. BDE 154 co-eluted with BB153. *NC* not calculated (<50% above detection limit), *ND* not detected, number of samples with detectable residues shown in []. Percent lipid presented as arithmetic mean. Columns sharing the same letter are not significantly different, Tukey's Studentized Range ($\alpha = 0.05$)

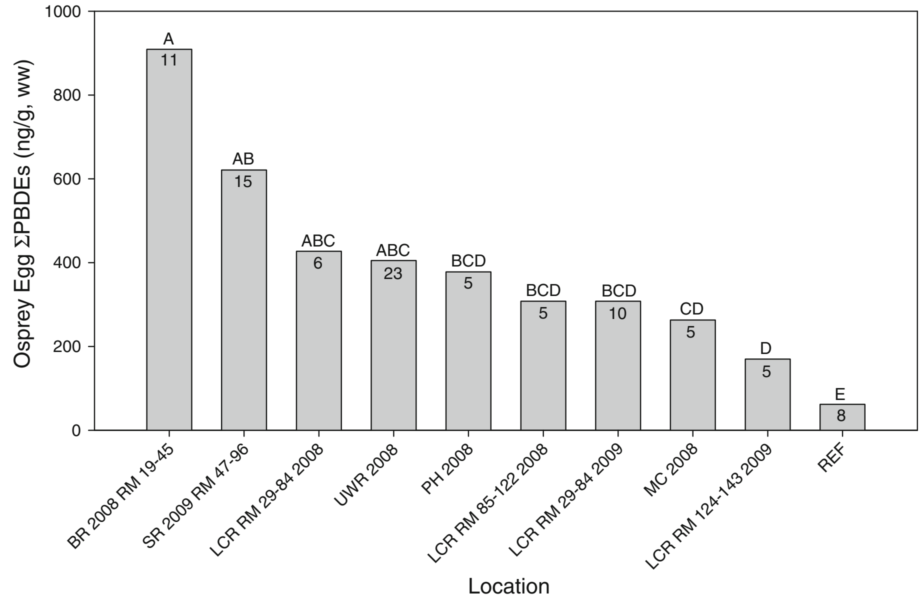

Fig. 3 ΣPBDE concentrations (geo. means) in osprey eggs collected from the Columbia River Basin, 2008–2009. *Bars* sharing the *same letters* are not significantly different from each other (alpha = 0.05). *N* values shown inside *bars*. *BR* Boise River, *SR* Spokane River, *LCR* Lower Columbia River, *MC* Multnomah Channel, *PH* Portland Harbor, *REF* Reference Lakes near Spokane, WA., *UWR* Upper Willamette River, *RM* River Mile

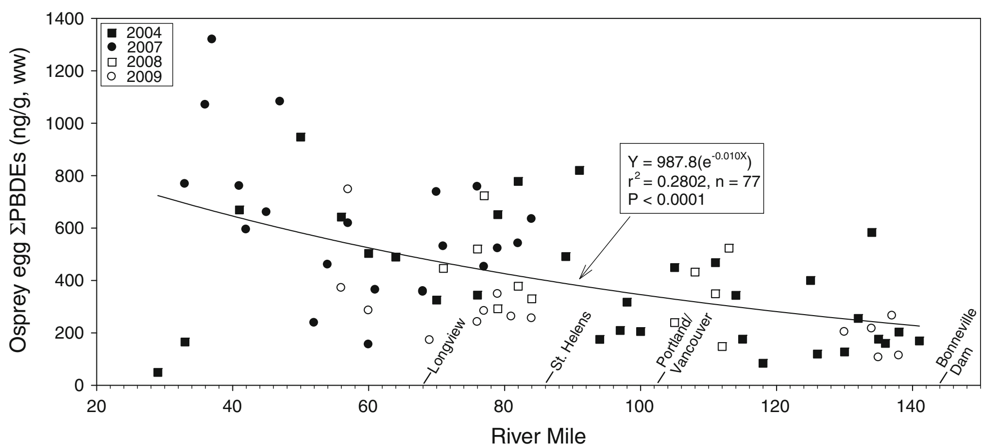

Fig. 4 Relationship between River Mile and ΣPBDE concentrations in osprey eggs along the Lower Columbia River (data from 2004, 2007, 2008, 2009)

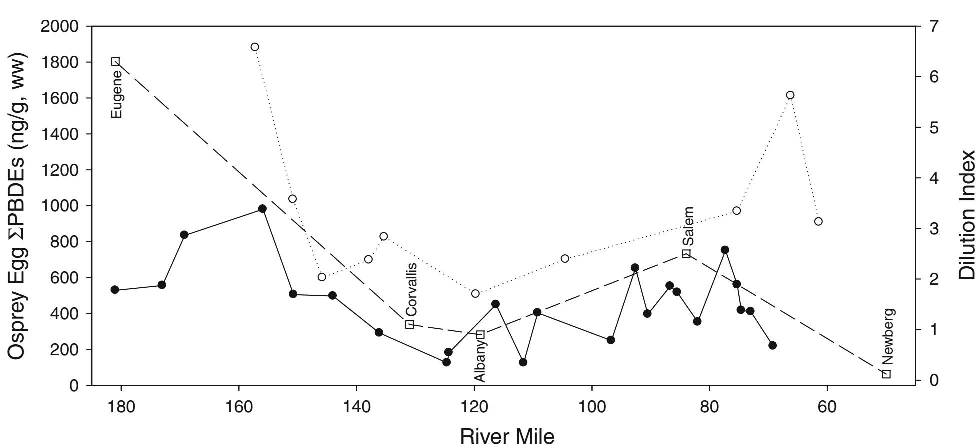

Fig. 5 Relationship between major municipal Wastewater Treatment Plant (WWTP) inputs (MGD) as a percentage of river flow (MGD) ×1,000 (Dilution Index, *open squares*, *dashed line*) and ΣPBDE concentrations in individual osprey eggs collected along the Upper Willamette River, Oregon in 2006 (*open circles*, *dotted line*) and 2008 (*closed circles*, *solid line*). *MGD* million gallons per day

contained significantly higher ΣPBDE concentrations (see later Results), but showed the same spatial pattern along the river.

Data from the Upper Willamette River, Boise River and Spokane River were then evaluated together in an attempt to better understand relationships among WWTP discharges, river flow and osprey egg concentrations (Fig. 6). To evaluate the data obtained from the three smaller rivers into one analysis, the rivers were divided into segments. The two smaller rivers studied in 2008 and 2009 had shorter study areas (Boise River with 26 RMs and Spokane River with 49 RMs) with fewer osprey eggs collected, 11 and 15, respectively. All Boise River data were combined together (no data collected above the two Boise WWTPs, while the Spokane River was subdivided into two segments (above and below the WWTP at Spokane). The Reference Lakes south of Spokane, and at least 17 miles from the Spokane River, likely represent atmospheric-sourced ΣPBDE inputs (no WWTPs nearby, and at least with legacy contaminants, concentrations in osprey eggs reflect the breeding grounds, not the wintering grounds, see Elliott et al. 2007). The study areas of the longer Willamette River (see Fig. 5) were subdivided into three segments (Eugene/Springfield, Corvallis/Albany, and Salem segments) with splits occurring near Corvallis and Salem.

Egg residue concentrations from Boise River ospreys did not follow the pattern observed at the other study areas (Fig. 6), i.e., egg concentrations were much lower

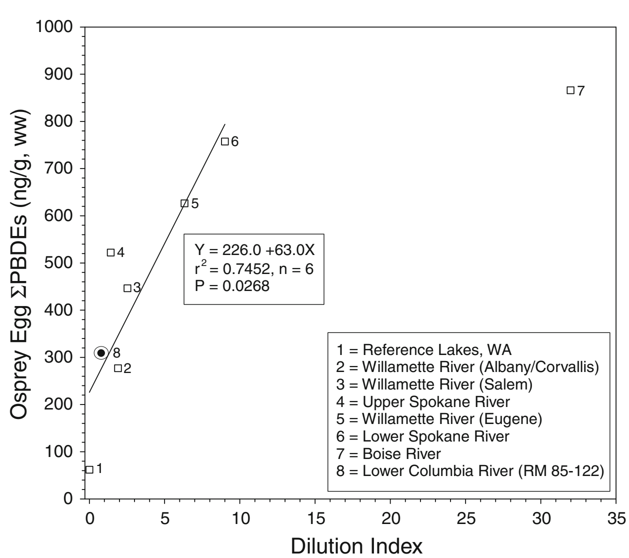

Fig. 6 Relationship at smaller rivers between major municipal Wastewater Treatment Plant (WWTP) inputs (MGD) as a percentage of river flow ×1,000 (Dilution Index) and geometric mean ΣPBDE concentrations in osprey eggs collected along the Boise, segments of the Spokane and Willamette Rivers, and a series of small reference lakes. *Points 1–6* used to determine regression line. *Point 8* added to show a high flow river site. *MGD* million gallons per day

than expected given the Dilution Index measurements based upon WWTP discharge and river flow. The relationship observed among the other study areas, excluding the Boise River, shows a strong linear relationship (Fig. 6). The Boise River, when compared to the other rivers studied, is unique because of the large number of adjacent ponds and lakes stocked with fish. We believe that perhaps 50–75% of osprey foraging in the Boise River study area occurred off river on relatively clean fish which accounts for the much lower ΣPBDE egg concentrations observed when compared to the expected relationship based upon the other two rivers. Few off-river foraging sites were available along the Spokane River and for the nesting pairs studied along the Willamette River. The maximum ΣPBDE concentration recorded in an osprey egg (2,171 ng/g) during this study was from the Boise River and approximated the Boise River mean value (2,241 ng/g) predicted by the equation in Fig. 6. The egg probably represents a pair that consistently foraged in the Boise River. Furthermore, 5 of 11 eggs from the Boise River contained ΣPBDEs >1,000 ng/g. Thus, the high ΣPBDE concentration predicted for the Boise River osprey eggs was reached with one pair, while other pairs fell short (based upon observed egg concentrations) providing evidence for varying degrees of off-river foraging.

The high flow Lower Columbia River (RM 85–122) with a river flow estimated at 120,309–141,640 MGD between Troutdale and Portland/Vancouver (especially when compared to the low flow Boise River at 835 MGD and Spokane River at 4,388 MGD) and a combined WWTP discharge in that Columbia River segment of 106.02 MGD resulted in a Dilution Index of 0.75–0.88 (mean 0.815). Osprey eggs from that segment were collected in 2008 (see Point 8 in Fig. 6, which was not used in the equation). Somewhat to our surprise, the observed geometric mean ΣPBDE egg concentration in 2008 (308 ng/g) for ospreys was a good fit with the expected findings based upon the smaller rivers (277 ng/g). Further upstream (RM 124–143), where limited WWTP discharge occurs, in 2009 egg concentrations were lower (170 ng/g), in fact, only 108 ng/g above that reported in eggs from our Reference Lakes in 2009, or only 73 ng/g above Willamette Headwater Reservoirs in 2002 (Henny et al. 2009b). Downstream from RM 85–122 at RM 29–84 in 2008 osprey egg concentrations were higher (427 ng/g), but decreased in 2009 to 308 ng/g. Additional WWTPs exist downstream of RM 85, which may account for the increase in 2008; however, it needs to be noted that this portion of the river is influenced by tide which also may be involved. The same general downstream pattern of increase in osprey eggs from the Lower Columbia River was reported in 2004 (Henny et al. 2009b).

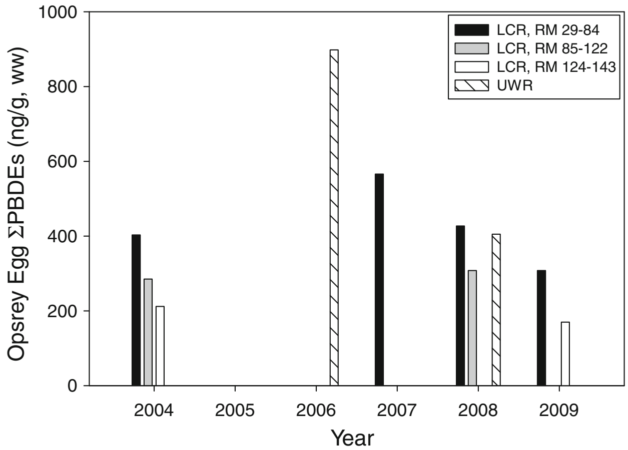

Fig. 7 Temporal pattern of ΣPBDE residues (geo. means) in osprey eggs for the Lower Columbia River (LCR) and Upper Willamette River (UWR), 2004–2009. *RM* River Mile

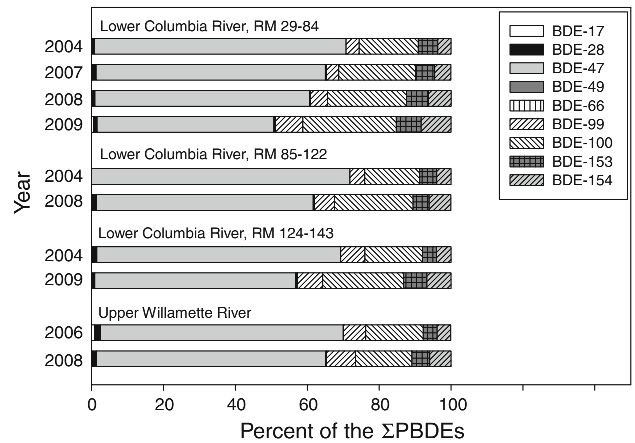

Fig. 8 Temporal patterns associated with mean percent contributions of individual PBDE congeners to the ΣPBDEs quantified in osprey eggs collected from the Lower Columbia River and Upper Willamette Rivers, 2004–2009. *RM* River Mile

Temporal changes in osprey egg ΣPBDE concentrations

With concern about possible PBDE-related reproductive effects on ospreys, but also recognizing that penta- and octa-PBDEs were no longer produced in the United States after 2004, understanding possible changes in osprey exposure over time was of paramount importance. Segments of the Lower Columbia River initially sampled in 2004 were again sampled in 2007, 2008 and 2009, together with the Upper Willamette River in 2006 and 2008 (Fig. 7).

ΣPBDE concentrations in osprey eggs decreased 55% along the Upper Willamette River (UWR) from 2006 to 2008 (897 vs. 405 ng/g) ($F = 16.86$, $P = 0.0003$). Likewise, eggs collected along the Lower Columbia River (LCR, RM 29–84) showed a general decrease in ΣPBDEs from 2007 (566 ng/g) to 2008 (427 ng/g) to 2009 (308 ng/g), with a concentration in 2004 (403 ng/g) similar to 2008 ($F = 2.68$, $P = 0.0587$). These findings imply a ΣPBDE increase from 2004 to 2007 followed by a decrease (Fig. 7). The more limited data from LCR, RM 85–122 (285 ng/g in 2004; 308 ng/g in 2008) and from LCR, RM 124–143 (212 ng/g in 2004; 170 ng/g in 2009) (two collection years) show similar concentrations in 2004 and 2008–2009, which are consistent with concentrations observed at LCR, RM 29–84 during the same time periods. Available information from this study suggests that ΣPBDE concentrations in osprey eggs peaked somewhere between 2005 and 2007, and then decreased in 2008 and 2009. ΣPBDE concentrations in largescale suckers (*Catostomus macrocheilus*) (whole body) from the Spokane River in 2009 were about 40% lower (wet weight) and about 24% lower (lipid weight) than reported in 2005 (Furl and Meredith 2010). This PBDE finding in suckers, a key osprey prey species, agrees with our recent (2008–2009) downward trend for PBDEs in osprey eggs at several other sites including the Lower Columbia River and Upper Willamette River (Fig. 7).

The congener profiles in the above time series of osprey eggs were of special interest (Fig. 8). In spite of ΣPBDE concentrations in LCR, RM 29–84 first increasing from 2004 to 2007, then decreasing in 2008 and again in 2009, the contribution of BDE 47 (as a percentage of the total) steadily decreased during the years (68.6, 62.0, 58.9, and 46.1%, respectively). Corresponding increases during the years were found in BDE 100 (16.5, 22.0, 22.5 and 26.1%), BDE 99 (3.81, 3.61, 4.64 and 7.62%), BDE 153 (5.93, 6.10, 6.09 and 8.89%) and BDE 154 (3.85, 4.71, 6.38 and 8.83%). These congener patterns were also consistent at other sites including LCR, RM 85–122 (BDE 47 in 2004, 72%; in 2008 59%), LCR, RM 124–143 (BDE 47 in 2004, 66%; in 2009 52%) and UWR (BDE 47 in 2006, 62%; in 2008 60%).

Biomagnification factors for PBDEs (fish to osprey eggs)

Three of the six largescale sucker collection sites on the Spokane River in 2009 were upstream of the Spokane WWTP to the Idaho Stateline, while three collection sites were downstream to Lower Long Lake (Fig. 9). The highest PBDE concentrations in largescale suckers were found in the lower three sub-segments downstream of the WWTP (Furl and Meredith 2010), which adds additional support to our earlier decision to separate the Spokane River into two segments (above and below the WWTP). Thus, fish residue data and the osprey egg residue data from the Spokane River were separated into two segments for calculating biomagnification factors.

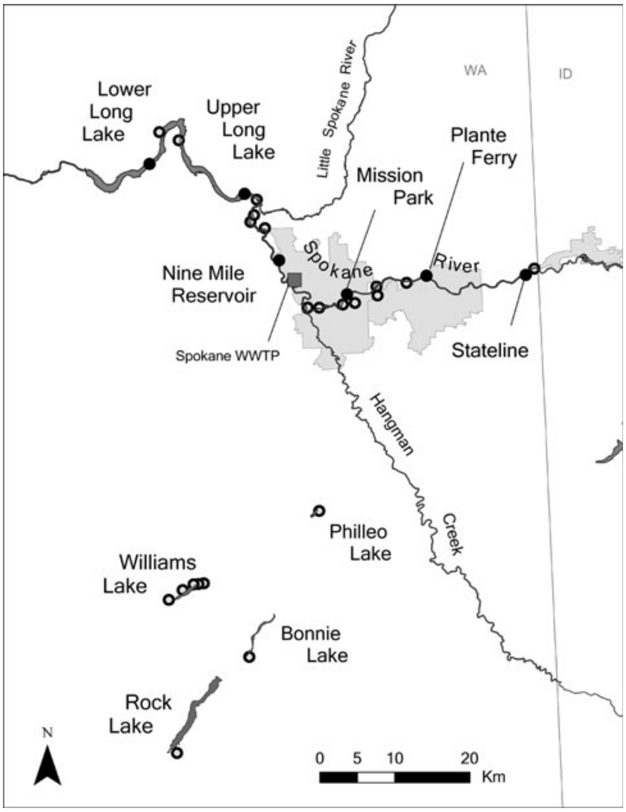

Fig. 9 Spokane River and Reference Lakes. *Closed circles* are fish collection sites and *open circles* are osprey egg collection sites

In addition to fish and osprey eggs collected along the Spokane River in 2009, a similar set of data was collected from the Boise River in 2008. Eggs from these two rivers contained the highest ΣPBDE concentrations in 2008–2009, relative to other sampling sites (Fig. 3). Prey remains were collected near osprey nest sites along the Spokane River in 2009 using standard protocol (see Johnson et al. 2008). Remains of 109 fish were collected with findings from each nest site weighted equally ($N = 7$). Suckers (primarily largescale suckers) were the dominant prey species (72.0% of the biomass), followed by bullheads/catfishes 14.1%, northern pikeminnows (*Ptychocheilus oregonensis*) (10.7%), bass (2.1%), trout (0.4%) and others (1.9%) (Table 3). Earlier studies of the osprey diet along the Lower Columbia River and Upper Willamette River also indicated that native largescale suckers were the dominant fish species preyed upon (Johnson et al. 2008). The Washington Department of Ecology emphasized the collection of largescale suckers including 18 composites (3–5 fish) at 6 sites along the Spokane River in both 2005 and 2009 (Furl and Meredith 2010). Several other fish species, including 6 composites of northern pikeminnows, 6 composites of mountain whitefish, 1 composite of smallmouth bass (*Micropterus dolomieu*) and 1 composite of rainbow trout (*Oncorhynchus mykiss*), were also collected in 2009. The mountain whitefish, a non-prey item of osprey (Table 3), had consistently higher ΣPBDE concentrations than largescale suckers, but all other fish prey species had comparable concentrations to the suckers (Furl and Meredith 2010). Therefore, to estimate fish to osprey egg biomagnification factors (BMFs), we used only the largescale sucker data. On a wet weight basis in 2009, we estimated the BMF from fish to osprey eggs for ΣPBDEs on the Spokane River at 3.76–7.52, but on a lipid basis 4.37–11.0 (Table 4). Variation in the osprey diet above and below the WWTP could account for differences observed, although sampling error was likely a factor.

Data collected along the Boise River in 2008 included 11 osprey eggs and single composites of 7 largescale suckers, 10 mountain whitefish, and 3 rainbow trout (Table 5). Although no prey data were collected at osprey nests on the Boise River in 2008, we assumed largescale suckers were again the dominant prey species and represented contaminant loading for the river. The BMF for ΣPBDEs from the Boise River was estimated at 2.62 using wet weight values and 7.88 using lipid weight. With respect to our earlier concern about the many lakes and ponds adjacent to the Boise River when evaluating ΣPBDE egg concentrations in relation to WWTPs and river flow, the same issue is of concern when calculating BMF estimates based only upon fish residues from the river. Many of these lakes were stocked with fish and provided ospreys an additional source of fish. With the adjacent lakes not directly associated with the river, we hypothesize that exposure of those fish to ΣPBDEs would be much less than from the river. Quantitative information on the percentage of fish in the osprey diet obtained from these lakes, as well as ΣPBDE concentrations in those fish, remain unknown. To provide some understanding of possible effects from foraging off-river on BMF calculations for the Boise River, we assumed that 50% of the fish were taken off-river with residue concentrations 25% of those in largescale suckers from the Boise River which yielded BMFs of 4.19 (wet weight basis) and 12.9 (lipid weight basis).

BMFs (wet weight basis) from the Spokane River (3.76–7.52) and Boise River (2.62, but likely higher, e.g., 4.19) are within a relatively narrow range and imply that ΣPBDEs do not biomagnify from fish to osprey eggs as much as *p,p*′-DDD (18-23) and *p,p*′-DDE (79–87), but appear more similar to dieldrin (3.2–6.7) and ΣPCBs (8.4–11) (Henny et al. 2009a). BMF estimates on a lipid basis from the Spokane River (4.37–11.0) and Boise River (7.88, but likely higher, e.g., 12.9) again were less than *p,p*′-DDD (25–28) and *p,p*′-DDE (103–112), and similar to dieldrin (5.0–7.9) and ΣPCBs (12–13). Chen et al. (2010) examined ΣPBDE biomagnification from fish to osprey

Table 3 Prey remains collected from osprey nests along the Spokane River, Washington, 2009

River Mile	*N*	Fish family (% Incidence)					
		Bass *Micropterus* spp.	Bullhead *Ictalurus* spp.	N. Pikeminnow *Ptychocheilus* spp.	Trout *Salmonid* spp.	Sucker *Catostomus* spp.	Other species[a]
Reference Lake[b]	12	33.3	16.7		16.7		33.3
RM 95.9	22	13.6	59.1	18.2		4.5	4.5
RM 93.2	34	17.6	61.8	8.8	5.9	2.9	2.9
RM 80	13	7.7	38.5	7.7		46.2	
RM 79.4	14		92.9			7.1	
RM 73.6	5			20.0		60.0	20.0
RM 59.6	11	9.1				90.9	
RM 56.3	10	10.0	20.0	20.0		50.0	
Mean mass (g)[c]		102	146	362	190	777	194
% Incidence[d]		8.3	38.9	10.7	0.84	37.4	3.9
% biomass		2.1	14.1	9.6	0.40	72.0	1.9

[a] Includes peamouth ($N = 2$), sandroller ($N = 1$), pumpkinseed ($N = 1$), black crappie ($N = 1$), tench ($N = 1$), and common carp ($N = 1$)

[b] Lake south of Spokane, not included in % Incidence or % biomass calculations for Spokane River

[c] Mass determined using opercula lengths (*sucker* spp., northern pikeminnow, bass), weight for 8–12 inches (203–305 mm) determined by Oregon Department of Fish and Wildlife (bullhead/catfish, salmonid, peamouth species), previously published information (Henny et al. 2004: black crappie; Johnson et al. 2008: common carp), and estimated according to Wydoski and Whitney (2003) (tench, pumpkinseed, sandroller)

[d] All nests on Spokane River weighted equally on nest by nest basis, $N = 7$

eggs from the James River, Virginia, using a similar procedure, and reported a BMF of 23.7 (lipid basis).

Osprey reproductive success and ΣPBDE concentrations

During our earlier 2002–2007 study at 120 osprey nests in Oregon and Washington, we examined the relation between concentrations of PBDEs as well as other contaminants (relative to their known toxicity) in sample eggs and reproductive success at each nest (Henny et al. 2009b). Of the other contaminants, only DDE concentrations were reported at an effect level (Yakima River in 2002) with those four eggs excluded from the analyses. The initial study provided no evidence that ΣPBDE concentrations below 1,000 ng/g adversely influenced reproductive success of ospreys; however, in 2006 (Upper Willamette River) and 2007 (Lower Columbia River) ΣPBDE concentrations were first reported to exceed 1,000 ng/g in some eggs and those nests were less successful. We analyzed those two locations separately. A negative relationship was found between young/active nest and ΣPBDEs for the 10 nests from the Upper Willamette ($P = 0.008$) and the 20 nests on the Lower Columbia ($P = 0.057$) with Henny et al. (2009b) concluding that observed PBDE concentrations “may” reduce reproductive success of ospreys.

In 2008 and 2009, a sample egg was again collected at an additional 93 nests with data summarized in a manner similar to the earlier study (Table 6). With residues of organochlorine pesticides, PCBs, dioxins and furans decreasing dramatically in the Pacific Northwest in the early 2000s, and mercury (although increasing) far below effect concentrations for osprey reproduction (Henny et al. 2008, 2009a), legacy contaminants were only evaluated in the 2008 eggs. None of the egg concentrations were reported at a reproductive effect level for ospreys (unpublished data). With ΣPBDE concentrations appearing to peak in the study areas between 2005 and 2007 (Fig. 7), only the Boise River and Spokane River populations in 2008–2009 contained some eggs with ΣPBDEs > 1,000 ng/g.

In reviewing the reproductive data in Table 6, it becomes obvious that 2008 was a “bad year” for osprey productivity at several locations studied on the west side of the Cascade Mountains including the Lower Columbia River (LCR, RM 29–84, RM 85–122; 0.20 and 0.40 young/active nest attempt, respectively), and Willamette River (UWR, RM 69–178, Portland Harbor, Multnomah Channel; 0.48, 0.80 and 1.20 young/active nest, respectively). In earlier years, when productivity was high, similar productivity rates were also reported at adjacent segments of the Lower Columbia River (Henny et al. 2008). In contrast, the Boise River study area in 2008, located on the east side of the Cascade Mountains, showed excellent productivity (1.73 young/active nest). The 2009 studies included two segments of the Lower Columbia River (RM 29–84 and RM 124–143) (1.30 and 1.60 young/active nest), the

Table 4 ΣPBDE (ng/g, ww and lw) concentrations in osprey eggs and whole body largescale suckers from two segments of the Spokane River, with calculated Biomagnification Factors (BMFs), 2009

Location	ΣPBDEs					
	Suckers		Osprey eggs		BMFs	
	ww	lw	ww	lw	ww	lw
Upper segment (RM 68–96) (Stateline, ID to Spokane wastewater treatment plant)	81.6	1,169	520	20,000		
	108	1,578	323	8,972		
	156	3,503	775	18,452		
	72.6	1,228	1,382	53,154		
	98.0	2,108	147	5,250		
	99.0	1,480	430	17,200		
	30.6	712	741	15,438		
	33.1	1,195	620	14,762		
	36.0	1,115				
Geometric mean	68.9 B	1,420 B	518 A	15,663 A	7.52	11.0
Lower segment (RM 47–67) (Spokane wastewater treatment plant to lower long lake)	130	4,305	1,637	49,606		
	145	3,198	939	19,979		
	348	19,137	826	28,483		
	143	3,482	639	14,860		
	254	5,394	849	27,387		
	314	4,421	485	13,472		
	125	2,169	397	10,730		
	163	3,840				
	320	6,806				
Geometric mean	199 A	4,753 A	749 A	20,757 A	3.76	4.37

Value for a sucker does not correspond to the adjacent osprey egg. Columns sharing the same letter are not significantly different, Tukey's Studentized Range (α = 0.05). BDE 47, 49, 66, 71, 99, 100, 138, 153, 154, 183, 184, 191 (all non-detects) and 209 (all non-detects) were analyzed in suckers (Furl and Meredith 2010); therefore, for direct comparison, the same congeners were used in osprey eggs (egg data for BDE 17, 28, 85 and 190 not used)

Table 5 ΣPBDE (ng/g, ww and lw) concentrations in osprey eggs and whole body composite fish samples from the Boise River, with calculated biomagnification factors (BMFs), 2008

River Mile (Osprey eggs)	ΣPBDEs	
	ww	lw
RM 45.5	1,187	43,945
RM 45.3	641	17,311
RM 44.9	1,057	33,032
RM 44.3	1,463	43,025
RM 43.9	711	14,515
RM 41.0	1,005	47,865
RM 34.0	604	16,337
RM 33.0	2,134	88,910
RM 28.8	707	32,143
RM 26.0	713	59,437
RM 19.5	525	12,499
Geometric mean	893	31,070
Fish (Whole body)		
Boise River (study area, RM 47.3)[a]		
Largescale sucker $N = 7$, 1,214–1,714 g	341	3,942
Mountain whitefish $N = 10$, 140–390 g	683	5,701
Rainbow trout $N = 3$, 94–159 g	65.5	4,517
Boise River (Upstream city of Boise, RM 93.3)[b]		
Largescale sucker $N = 5$, 418–995 g	0.02	0.69
Largescale sucker $N = 2$, 1,065–1,660 g	0.01	0.41
Mountain whitefish $N = 8$, 63–426 g	0.39	2.9
BMF using osprey eggs, RM 19.5–45.5	2.62	7.88

We used the same BDE congeners as in Table 4 for the Spokane River with the exception of BDE 71, 184 and 191 which were not analyzed in 2008. These congeners were of minor importance in the Spokane River and reported in low concentrations in only 3, 1 and 0 eggs, respectively

[a] Boise wastewater treatment plants located at RM 44 and 50, with fish collected at RM 47.3

[b] Location where no osprey nested

Spokane River (RM 47–96) (1.60 young/active nest) and Reference Lakes (1.50 young/active nest) all showing excellent productivity. Production rates at LCR RM 29–84 improved from 2008 to 2009 (0.20 and 1.30 young/active nest) with eggs containing low and decreasing ΣPBDE residues (427 and 308 ng/g) with none >750 ng/g. This implies that PBDEs were not related to the low productivity reported at several locations in 2008. Similarly, another segment of the Lower Columbia River (LCR RM 124–143) showed excellent productivity in 2009 (1.60 young/active nest), while an adjacent segment in 2008 (RM 85–122) had poor productivity (0.40 young/active nest) with no ΣPBDE residues in either segment or year >750 ng/g.

Following the above descriptive assessment of productivity on the west side of the Cascade Mountains, we evaluated (Jonckeere–Terpstra Test) five datasets in Table 6 with 10 or more nests studied in 2008 and 2009 to determine if any relation existed between ΣPBDEs and young/active nest. The Lower Columbia River in 2008 (RM 29–84 and RM 85–122 combined) and 2009 (RM 29–84 and RM 124–143 combined), the Upper Willamette River (RM 69–181) and Lower Willamette River (Portland Harbor and Multnomah Channel combined) in 2008 ($N = 10$, $N = 15$, $N = 23$, $N = 10$) yielded no significant relationships between ΣPBDEs and young/active nest ($Z = 0.2582$, $P = 0.40$; $Z = -1.2197$, $P = 0.11$; $Z = 0.4927$, $P = 0.31$; $Z = 0.3873$, $P = 0.35$). No eggs from these 48 nests contained ΣPBDE residues >1,000 ng/g with only two eggs >750 ng/g. Of special interest were the ospreys nesting along the Boise River in 2008 ($N = 11$) and Spokane River in 2009 ($N = 15$) where seven eggs

Table 6 Distribution of ΣPBDE concentrations (ng/g, ww) in sample eggs from 93 osprey nests and associated young/nesting attempt from remaining eggs in clutch, 2008–2009

Location[a]	Year	*N*	ΣPBDE (ng/g, ww) category					Mean
			0–250	251–500	501–750	751–1,000	>1,000	Productivity
A	2008	6		4	2			0.20[b]
A	2009	10	2	7	1			1.30
B	2008	5	2	2	1			0.40
C	2009	5	4	1				1.60
D	2008	23	5	8	8	2		0.48
E	2008	5	1	2	2			0.80
F	2008	5	1	4				1.20
G	2008	11			6		5	1.73
H	2009	15	1	4	3	5	2	1.60
I	2009	8	8					1.50

ΣPBDEs includes BDE 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 190, and 209

[a] A = Lower Columbia River (RM 29–84), OR and WA; B = Lower Columbia River (RM 85–122), OR and WA; C = Lower Columbia River (RM 124–143), OR and WA; D = Upper Willamette River (RM 69–181), OR; E = Willamette River, Portland Harbor, OR; F = Multnomah Channel, OR; G = Boise River (RM 19–45), ID; H = Spokane River (RM 47–96), WA; I = Reference Lakes, Spokane, WA

[b] Productivity based on 5 nests (1 nest not rechecked)

contained ΣPBDE residues >1,000 ng/g; however, again no significant relationship was found ($Z = -0.241$, $P = 0.42$; $Z = -0.4827$, $P = 0.31$). Both of these sites had excellent productivity (1.73 and 1.60 young/active nest), especially when considering that one egg was collected from each nest. Osprey reproductive rates for population maintenance are now estimated at between 0.8 and 1.30 young/active nest depending upon breeding age structure of the population (Poole 1989; Watts and Paxton 2007).

Conclusions

All 175 osprey eggs collected in the Columbia River Basin between 2002 and 2009 contained quantifiable PBDE concentrations. ΣPBDE concentrations in eggs during 2008–2009 were highest at the two smallest rivers (Boise and Spokane) with relatively large cities and lowest at a series of small lakes (a Reference Area) in northeastern Washington (south of Spokane). Concentrations at other locations studied were within a relatively narrow range. In an attempt to better understand ΣPBDE concentrations observed in osprey eggs from various rivers, we evaluated volume of effluent discharge from major WWTPs and river flow (a Dilution Index). Although WWTPs may not be the sole source of PBDEs, their volume of discharge provides a measure of human activity in a locality. Osprey egg concentrations along 109 miles of the Willamette River paralleled the Dilution Index (WWTP Discharge/River Flow) ×1,000 (Fig. 5). By combining information from segments of the Willamette and Spokane Rivers and the Reference Lakes, a strong relationship ($Y = 226.0 + 63.0X$, $r^2 = 0.7452$, $P = 0.0268$) was observed between osprey egg concentrations and the Dilution Index (Fig. 6). This study is novel with the information gained valuable and useful for improving our understanding of the PBDE contaminant patterns observed in osprey eggs, thereby outweighing any limitations of the fairly simple approach. Data from the Boise River could not be used in the above evaluation because ospreys there often foraged off river in adjacent lakes and ponds which resulted in lower than expected egg concentrations. Still, some of the highest PBDE concentrations occurred in Boise River eggs, apparently laid by ospreys that foraged more frequently in the river. It was fortuitous for ospreys nesting along the Boise River that adjacent ponds and lakes were available for foraging. If stocking of these lakes and ponds with fish is continued, it will likely benefit ospreys in terms of lower exposure to PBDEs.

Several study areas were sampled during more than 1 year with ΣPBDE egg concentrations decreasing 55% ($P = 0.0003$) along the Upper Willamette River from 2006 to 2008, and 46% ($P = 0.0587$) along the Lower Columbia River (RM 29–84) from 2007 to 2009. Our limited data suggests that ΣPBDE concentrations in osprey eggs probably peaked between 2005 and 2007, and then decreased (Fig. 7). In addition to concentration changes over time, congener profiles also changed with the Lower Columbia River site mentioned above showing a steady decrease in the contribution of BDE 47 (as a percentage of the total) from 2004 to 2007 to 2008 to 2009 (68.6, 62.0, 58.9 and 46.1%). The difference was made up by percentage increases in BDE 100, BDE 99, BDE 153 and BDE 154, which was also consistent at other locations. The only American manufacturer voluntarily stopped production of penta-BDE and octa-BDE in 2004. Are we observing a fairly rapid decline in osprey egg residue concentrations as a result of that production stoppage? Continued monitoring is necessary in order to confirm these trends in the Pacific Northwest.

An empirical estimate of the BMF for ΣPBDE concentrations from fish to osprey eggs was estimated at 3.76–7.52 wet weight or 4.37–11.0 lipid weight from the Spokane River study area. Boise River data were confounded by ospreys foraging off river, but a crude adjustment for off-river foraging suggested that BMFs for the Boise River were in the same general range. These BMFs are lower than reported in ospreys for p,p'-DDD and p,p'-DDE, and more similar to dieldrin and ΣPCBs.

Our earlier study in Oregon and Washington provided no evidence of reduced osprey reproductive success when ΣPBDE egg concentrations were <1,000 ng/g; however, at two locations (Upper Willamette in 2006 and Lower Columbia River in 2007) (RM 29–84) some eggs contained >1,000 ng/g with negative relationships indicated at both locations between productivity and ΣPBDE concentrations in eggs ($P = 0.008$, $P = 0.057$) (Henny et al. 2009b). Eggs exceeding 1,000 ng/g were only reported from the Boise and Spokane Rivers in 2008–2009. Osprey production rates on the Boise and Spokane Rivers were both considered excellent with no negative relationship found between productivity and ΣPBDE concentrations ($P = 0.42$, $P = 0.31$). Low production rates for ospreys nesting west of the Cascade Mountains in 2008, based on the results of this study, were not related to ΣPBDE concentrations. This lack of a relationship between PBDEs and reproductive rates is based on short-term datasets and additional monitoring is essential to confirm not only the trend of declining PBDE concentrations in these ospreys, but also the apparent lack of a relationship with reproductive success of these birds.

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