# Thirty years of Persistent Bioaccumulative Toxics in Puget Sound: time trends of PCBs and PBDE flame retardants in three fish species

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## Introduction and Methods

Polychlorinated biphenyls (PCBs) are a well known class of persistent bioaccumulative toxics (PBTs) that have been studied in the Puget Sound ecosystem for the past 30 years. The Puget Sound Assessment and Monitoring Program (PSAMP) has tracked PCBs in a benthic (bottom-dwelling) flatfish (English sole) from 1992 to present, and in two pelagic species (coho salmon and Pacific herring) since 1992 and 1999, respectively.

In order to better understand the fate and transport of PCBs in the Puget Sound ecosystem, and to assess the recent trends we have observed in PSAMP monitoring within a larger historical context, we combined and analyzed PSAMP monitoring data with a number of previously published studies and unpublished data dating back to 1975. This has allowed us, in a few cases, to assess trends in PCBs for a 30 year time period in Puget Sound.

In addition, we analyzed archived and recent samples of Pacific herring for flame retardant chemicals known as polybrominated diphenylethers, a more recent PBT in the Puget Sound ecosystem.

Measuring time trends of PBTs in organisms requires the application of carefully evaluated protocols, including species selection, appropriate spatial scale, consistent chemical analysis methodologies, and rigorous evaluation of the effects of biological covariates such as fish age, gender, tissue fat content, and migration patterns. Because the preponderance of available data was our own (PSAMP), and we were confident that the protocols selected for PSAMP time-tend analyses were sound, we evaluated the compatibility of other historical data with the PSAMP standard.

We evaluated PCB data from 21 studies for potential inclusion in the time-trend data set, and found impediments related to 1) significant changes in methodologies for analyzing organic compounds like PCBs over the past 30 years, 2) analysis of a variety of tissues, wherein it was sometimes unclear whether tissues taken were compatible (e.g., skin-on vs. skin-off fillets), 3) lipid analysis methodologies were often undescribed, or lipid data were not reported, 4) covariate information such as fish size (or age) were often lacking, and 5) specific sampling location information was sometimes lacking.

After careful screening of these studies to ensure compatibility, we chose to construct time trend datasets for adult English sole muscle tissue from the Duwamish River (1977

through 1997), Seattle Waterfront (1985 through 2003), and groups of non-urban sampling sites within the Central Puget Sound basin, and within the South Puget Sound basin, which we termed "CPS Reference" (1985 through 1998), and "SPS Reference" (1991 through 2003), respectively (Figure 1). The Duwamish River and Seattle Waterfront sites had been sampled prior to PSAMP, and by PSAMP, because of their high PCB-contamination, and the CPS and SPS reference sites were selected by all studies as reference sites because they were far removed from urban point sources. All data reported here prior to 1991 are from historical references, and data from 1991 onward are PSAMP data, except for several English sole samples from the Seattle waterfront taken from Ylitalo et al. (1999).

We evaluated adult coho salmon muscle tissue from Central Puget Sound stocks from 1975 through 2002, and in whole bodies of Pacific herring representing three Puget Sound stocks ranging from South Puget Sound (Squaxin stock), through Central Puget Sound (Port Orchard stock), to Northern Puget Sound (Semiahmoo stock) (Figure 1). We also measured PBDEs in archived tissue from these three herring stocks, with the oldest samples taken in 1994.

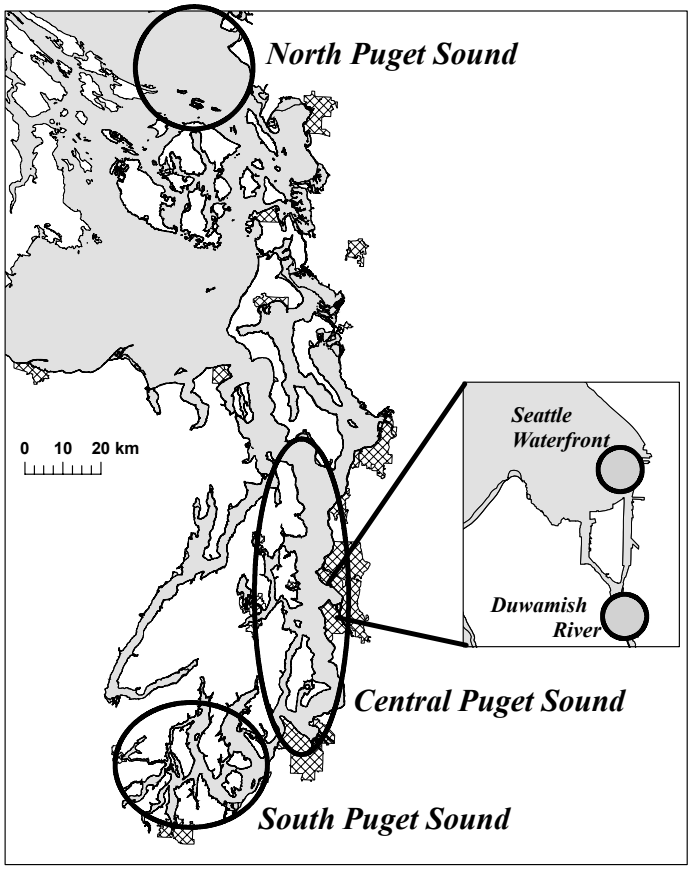


**Figure 1. Location of collection areas for English sole, coho salmon, and Pacific herring**

Where possible, we initially analyzed data using lipid-normalized PCB concentrations (i.e., concentrations expressed on a lipid basis), however, because of the ambiguity in lipid methods mentioned above, and missing lipid data, we could not confidently report those trends. When lipid data were available, the lipid-normalized trends we observed were essentially the same as the trends expressed using wet weight, so for clarity and brevity, we have expressed all results in this paper on a wet weight basis only.

Most historical PCB data were reported as sum of Aroclors, including PSAMP data from 1992 through 1997. In 1997, PSAMP monitoring adopted a High Performance Liquid Chromatography with photodiode array (HPLC/PDA) congener-based screening method for PCBs that reported 15 commonly encountered congeners, as well as an estimate of

total PCBs. We estimated the bias associated with the change in methods, by analyzing 93 samples using both the HPLC/PDA method, and our previous Aroclor analyses, which reported PCBs as the sum of Aroclors 1254 and 1260. The two methods correlated well, using the linear regression model:

$$\text{Sum2ARwet} = 4.3492 * (\text{TPCBwet}^{0.8117}),$$

where: Sum2AR = the sum of Aroclors 1254 and 1260
TPCB = the sum of PCBs by HPLC/PDA, and
$r^2 = 0.72$ and $p < 0.0001$.

We converted PSAMP data from 1998 through 2003 from HPLC/PDA to their Sum2AR equivalent, using this predictive model.

PBDE data were analyzed by gas chromatography with mass spectrometry, and total PBDEs calculated as the sum of the ten congeners, PBDEs 28, 47, 49, 66, 85, 99, 100, 153, 154, and 183.

## Results and Discussion

PCBs in English sole from the highly contaminated Duwamish River (near Kellogg Island) and Seattle Waterfront locations have dropped moderately from the 1970s and 1980s, to the 1990s and 2000 (Figures 2a and 2b). Early Duwamish River data were characterized by high variability, with median PCB concentration measured in English sole ranging from 280 ng/g (Sherwood 1981) and 420 ng/g (Puget Sound Estuary Program 1988) to 1100 ng/g, wet wt. in 1980 (Malins et al. 1982). All PSAMP samples taken from the Duwamish River site in the 1990s showed concentrations less than 250 ng/g (range of medians was 78 to 201 ng/g), or roughly one-fourth the highest median concentration prior to 1990.

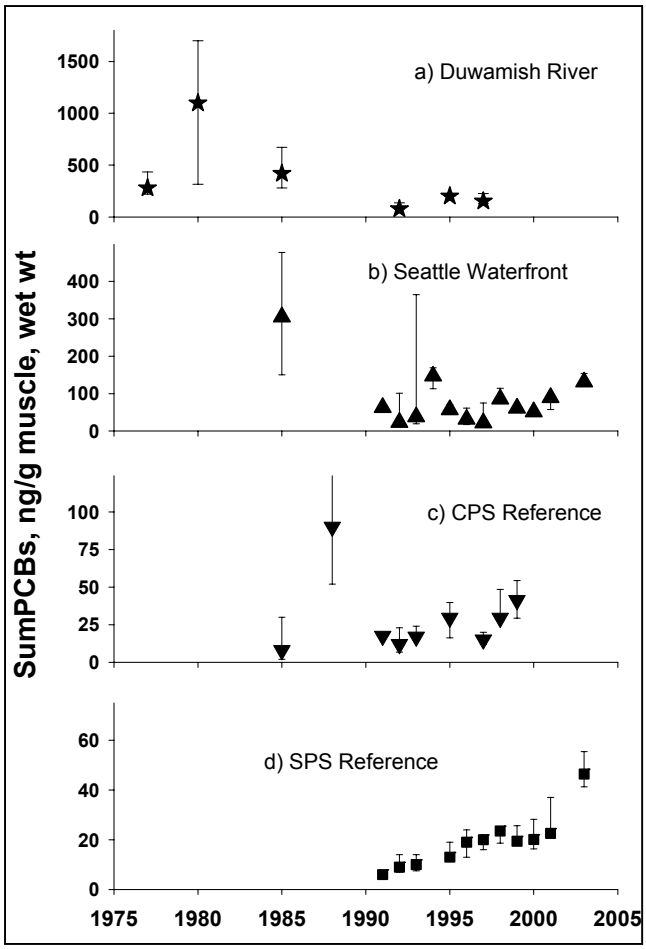


**Figure 2. PCBs in English sole from four sampling areas though time. (a) Duwamish River and (b)Seattle Waterfront in Elliott Bay, and reference sites from (c) Central Puget Sound (CPS) and (d) South Puget Sound (SPS). Medians with 25th and 75th percentiles.**

Only one historical sample prior to

PSAMP data was available for the Seattle Waterfront, which showed a drop from approximately 300 ng/g wet wt in 1985 (Puget Sound Estuary Program 1988) to less than 150 ng/g in the 1990s, through 2003 (PSAMP).

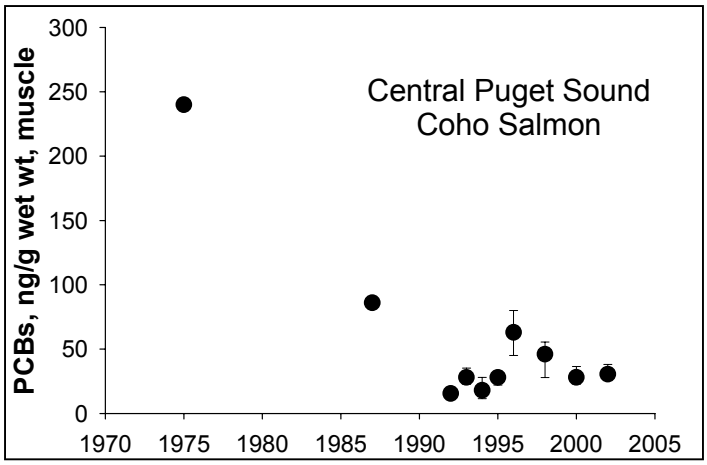


**Figure 3. PCBs in coho salmon from Central Puget Sound through time. Medians with 25th and 75th percentiles.**

Overall, PCB concentrations in CPS and SPS Reference basins were substantially lower than the Duwamish or Seattle Waterfront (Puget Sound Estuary Program 1988, Puget Sound Estuary Program 1989), with medians less than 100 ng/g (CPS) and 50 ng/g (SPS) (Figure 2c and d). However, except for one CPS sample in 1987, PCBs appeared to increase in English sole from both reference basins. PCB concentrations increased consistently from less than 10 ng/g in the early 1990s to between 20 and 40 ng/g in the early 2000s.

PCBs in muscle tissue of coho salmon, a pelagic species, dropped from over 200 ng/g wet wt in one composite sample from 1975 (Stout & Beezhold 1981) to 86 ng/g in 1987 (Tetra Tech. Inc. 1988), and mostly less than 50 ng/g in the 1990s (PSAMP -- Figure 3). Pacific herring from CPS and SPS stocks have remained relatively high, roughly three times that of coho salmon from CPS, at approximately 160 ng/g wet wt. from 1999 through 2006, while herring from the NPS stock, Semiahmoo, have remained relatively low (<40 ng/g) during this period (Figure 4).

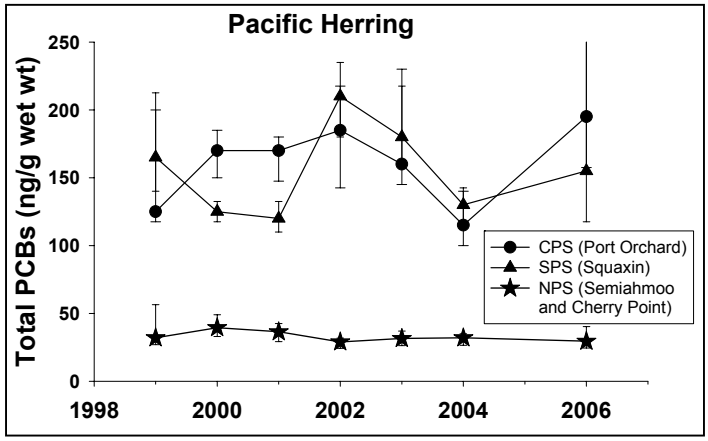


**Figure 4. PCBs in Pacific herring from three stocks through time. Median values with 25th and 75th percentiles.**

Concentrations of PBDEs in Pacific herring were roughly one-half to one-third of their PCB concentrations, with CPS herring ranging from 40 to 85 ng/g wet wt., total PBDEs (Figure 5). PBDEs in SPS herring from the year they were sampled (2006) were comparable to CPS herring from that same year. PBDEs in NPS herring were roughly one third of the CPS and SPS stocks, with all medians less than 30 ng/g. No time trend was apparent in any stock,

although these early data are very limited in temporal scope, and so were presented as bars in Figure 5.

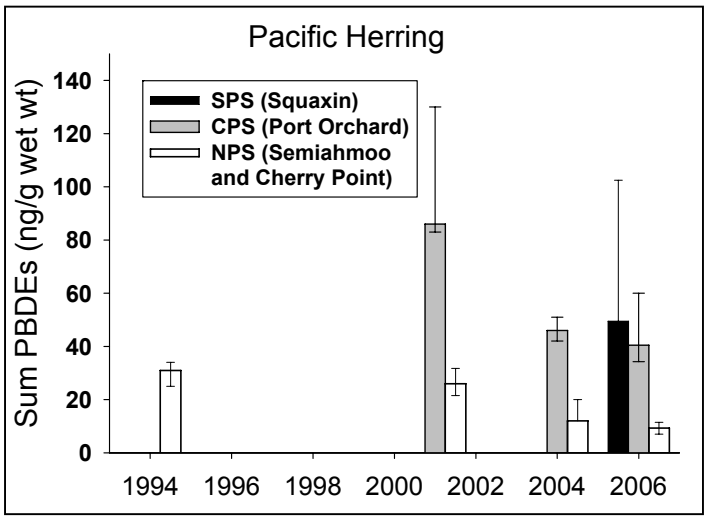


**Figure 5. Polybrominated diphenylether flame retardants in Pacific herring from three stocks in Puget Sound. Median values with 25th and 75th percentiles.**

Although high and inconsistent variability in the English sole PCB data precluded fitting typical exponential decay models, it seems clear from these historical data that PCB exposure in English sole has declined somewhat in the urban locations we analyzed over the past 30 years. This is consistent with expectations based on declines observed in other ecosystems such as the Great Lakes (Stow et al. 1994) and Baltic Sea (Bignert et al. 1998). Interestingly, we observed little or no decline in English sole from the CPS reference locations, and a significant (albeit small) increase in SPS sole. This could possibly result from (1) new sources of PCBs entering the SPS basin, or (2) long-term diffusion of existing PCBs from the highly contaminated hot spots in CPS, via biota and physical processes into previously uncontaminated SPS.

No species we analyzed exhibited a decline in PCBs in the 15 year period from 1990 through 2005. We hypothesize that the lack of a declining trend in PCBs over the past 15 years is the result of biotic recycling of PCBs through the food web, wherein once PCB molecules enter biota, they tend to stay there, rather than becoming buried in sediments or otherwise leaving the system.

We observed no obvious trend in PBDE flame retardants in herring extending from 1994 to present, in one stock. These data are very limited, and unless we identify additional archived tissue prior to the early 1990s, it may be impossible to observe the increase in this class of contaminants in Puget Sound biota. We have, however, established a baseline from 2001 onward, that we can use to compare future trends.

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