LEVELS AND TRENDS OF POLYBROMINATED DIPHENYL ETHERS IN PACIFIC SALMON

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Abstract
Elevated levels of certain persistent organic compounds in the environment, especially those still in production, has caused increasing concern and the need for studies to determine the source and levels as well as the potential for exposure to humans and wildlife. One such class of compounds is the Polybrominated Diphenyl Ethers (PBDEs), which are used as flame retardant compound in a wide variety of consumer products and materials. The large-scale use of these compounds has lead their accumulation in the environment and detectable levels in many marine and terrestrial organisms, including many fish species. One such group of fish is the Pacific salmon family, which is comprised of five species; Chinook (King), Chum, Coho (Silver), Pink (Humpback), and the Sockeye (Red) (8). These salmon species play an important role as both a sport and commercial food resource as the worldwide demand and consumption of fish increases. (1)

Introduction
Polybrominated Diphenyl Ethers have been used extensively as flame retardants in a wide variety of commercial and household products and applications. Due to this wide-scale use they are now considered a ubiquitous environmental contaminant. Interest and concern about these products has increased over the last several years due to the elevated levels detected in the environment and the food supplies or potential food sources of many countries worldwide. The consumption of Salmon, both wild and farmed, is an important food source for many countries throughout the world, and the rate of consumption has continued to increase worldwide over the past 15-20 years (1). Salmon fisheries, wild and hatchery raised, are also an important resource for sport and recreational activity throughout the Pacific coastal areas of the United States and Canada.

Materials and Methods
The initial phase of this study included nineteen salmon samples which were collected from along the Pacific coastal areas of California, Washington, and Alaska during the time period of 2005 -2007. Three samples were collected from California, four samples from Washington, and twelve samples from Alaska. The samples collected in California and Washington were caught by private sport fishermen and the samples from Alaska were provided by the Alaska Department of Environmental Conservation. There were three species of salmon collected in the study; Chinook, Coho, and Chum, to reflect the variety of species available from the collection locations. The samples from California were all Chinook (King) salmon, the samples from Washington were comprised of Chinook (King) and Coho (Silver) salmon, and the samples collected from Alaska included Chinook, Coho, and Chum species. The samples from California and Alaska were collected in the ocean prior to their migration to fresh water and the samples from Washington were collected from freshwater river locations after the fish had started their return to the spawning grounds.

The samples were processed as the edible portions only, but were prepared in several different ways. The samples from California and Alaska were all prepared as fillet samples that were either homogenized and frozen, or frozen as fillets and homogenized prior to analysis. Three of the four samples from Washington were prepared as fillets, cut into cubes, and canned in a light salt brine solution. The fourth sample from Washington was immediately filleted and frozen after collection.

The salmon tissue samples were analyzed by Severn Trent Laboratory in Sacramento, California for eleven predominant PBDE congeners (BDE-28, 47, 66, 85, 99, 100, 153, 154, 183, 209) using high resolution gas chromatography-mass spectrometry in accordance with EPA Method 1614. The samples were homogenized and mixed prior to removal of a nominal 20gram wet weight sample size for extraction. A mixture of eight 13C-labeled PBDE congeners was added to each sample prior to extraction by Soxhlet/Dean-Stark apparatus using toluene. The extracts were split after concentration and a 10gram aliquot was removed for PBDE determination and processed through acid/base back-wash, silica gel, and alumina column cleanup procedures.

The samples were analyzed by HRMS with an Agilent 6890N GC and an Ultima Autospec Model-M mass spectrometer. The analysis was performed using a 30m DB-5HT column with quantitation using the isotope dilution technique. The data was processed using routine laboratory reporting limits and data quality objectives. The samples were all analyzed for percent lipid content and the sample results are reported in units of concentration for both ng/g wet weight and ng/g lipid.

Results and Discussion

The total PBDE concentrations were calculated by summing the concentrations of 11 predominant congeners. Sample results were evaluated to one-half of the reporting limit, and assigned a value of zero for the purpose of the calculation of "total PBDE concentration" if not present at or above that level. Several congeners (BDE-47, 99, 100 & 209) have elevated reporting limits based on the historical background levels of these congeners present in the laboratory reagents and processes. The total concentrations using this format were found to be low (< 1ng/g wet wt.) for all three species collected from Alaska versus the level found in the samples from California and Washington. One King salmon sample from Alaska had a total concentration of approximately 0.8ng/g when using this convention, but all other Alaskan samples were less than 0.1ng/g wet wt. The samples collected from California and Washington showed higher total PBDE concentrations, ranging from a low of 1.1ng/g to a high of 8.4ng/g on a wet wt basis.

The congener patterns for the samples from California and Washington were dominated by the BDE-47, 99, and 100 congeners. The sum of the three congeners contributed to over 80% of the total PBDE concentration in the samples, with BDE-47 accounting for over 50% of the total PBDE concentration. Many of the study samples had a mixture of congeners present, but there was only one sample with BDE-183 detected above one-half of the reporting limit and no BDE-138 detected in any of the samples at a concentration greater than one-half of the reporting limit. There were many samples with concentrations detected for BDE-47, 99, and 209 but they were significantly below the reporting limit (less than one-half the reporting limit) and were not significantly different from the levels historically detected in the laboratory blanks. Further evaluation of the laboratory background levels will be performed to determine if the levels detected in the samples are significant versus recent historical background levels.

The difference in concentrations between the samples collected from the California and Washington locations versus the Alaska locations indicate that there are differences in the levels of contamination present in the environment and food sources between these areas. The congener patterns within the various species from Alaska is difficult to determine due to the overall lower concentrations present, and the potential for congeners to be present but below the reporting limit. The data does however appear to show differences across the species. The pattern in the Alaskan Chinook (King) was BDE-47>99>100>153 where as the BDE-100>154/153>85 for the Alaskan Chum and the BDE-154>153>28>85>66 for the Alaskan Coho (Silver). The difference in congener patterns may be due to diet or life cycle, or lower concentration of certain congeners that fall below the established reporting threshold. The pattern detected in the California and Washington King samples were BDE-47>>100>99. There were further differences observed between the Alaskan Coho and the Washington Coho samples. The pattern in the Washington Coho was BDE 47>>99>100. These differences may be due to their environment or food source, as cwell as their lower levels relative to the reporting thresholds used. Further evaluation of the available data or additional analyses using larger sample sizes or reduced final volumes may provide additional information. The presence of PBDE-47 being the predominant congener in many of the samples is similar to patterns observed in other recent studies. (1, 2, 3, 4, 5, 6, 7)

The results of the %-Lipid determination indicated that the Chinook (King) salmon samples had a higher lipid content than the Coho or Chum species. The average lipid content for all the Chinook samples was 9.5%, the Coho was 4.3%, and the Chum was 2.5%. One sample each of the Chinook and Coho samples had a calculated lipid content that was much higher than the others in the study. Upon further investigation it was determined that the Chinook sample from California had a larger part of the homogenized sample taken from the collar area behind the gills, but no explanation was determined for the higher lipid content of the one Coho sample. Removal of these apparent outliers from the calculation reduced the average lipid content of the Chinook samples to 8.3% and the Coho to 3.8%

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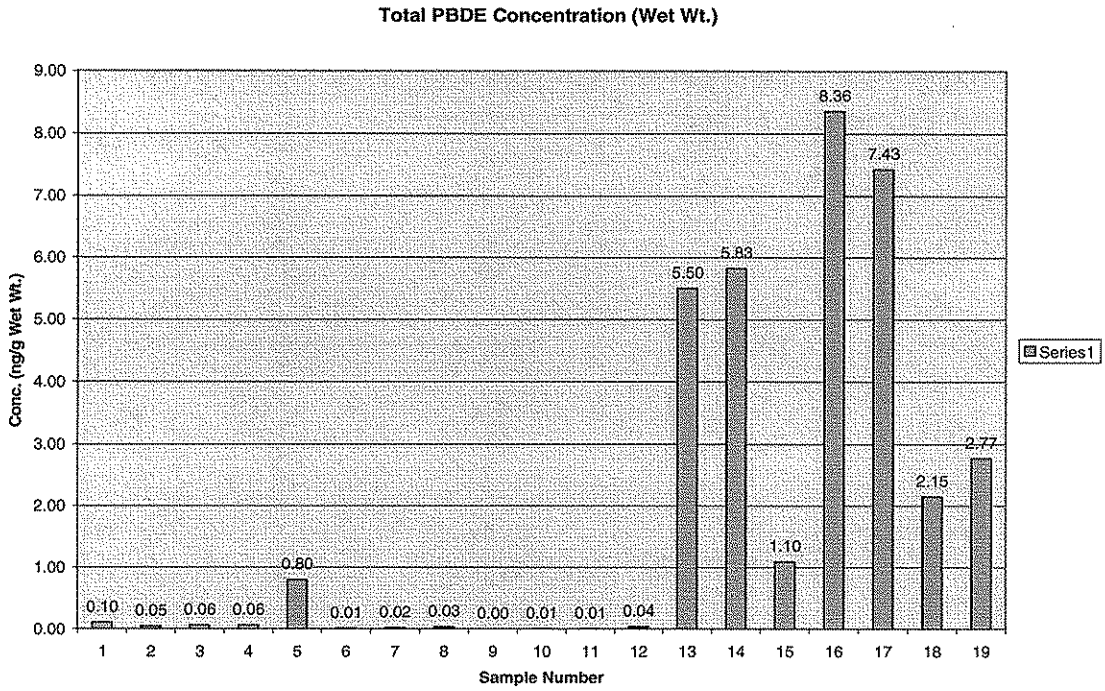

Figure 1- Total PBDE Concentration (sum of 11 congeners) ng/g wet weight. (routine reporting thresholds)
Sample 1, 2, 11- Alaskan Chum Samples 3, 4, 5- Alaskan King Samples 6, 7, 8, 9, 10, 12-Alaskan Coho
Samples 13, 14, 15-California King Sample 16, 17, 18- Washington King Sample 19- Washington Coho

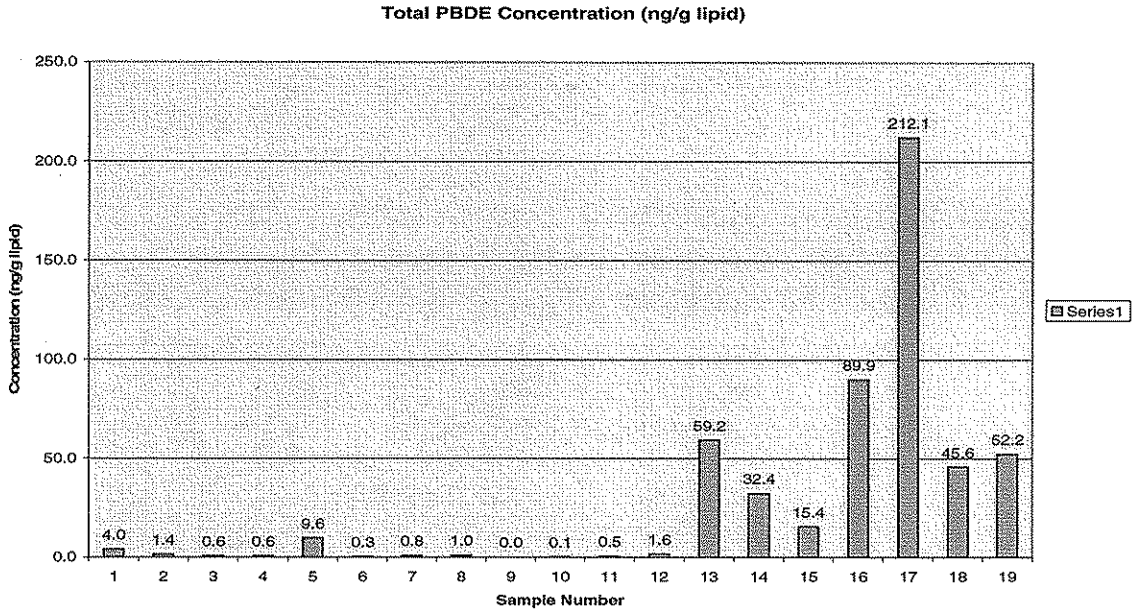

Figure 2- Total PBDE Concentration (sum of 11 congeners) ng/g lipid. (All samples)
Sample 1, 2, 11- Alaskan Chum Samples 3, 4, 5- Alaskan King Samples 6, 7, 8, 9, 10, 12-Alaskan Coho
Samples 13, 14, 15-California King Sample 16, 17, 18- Washington King Sample 19- Washington Coho

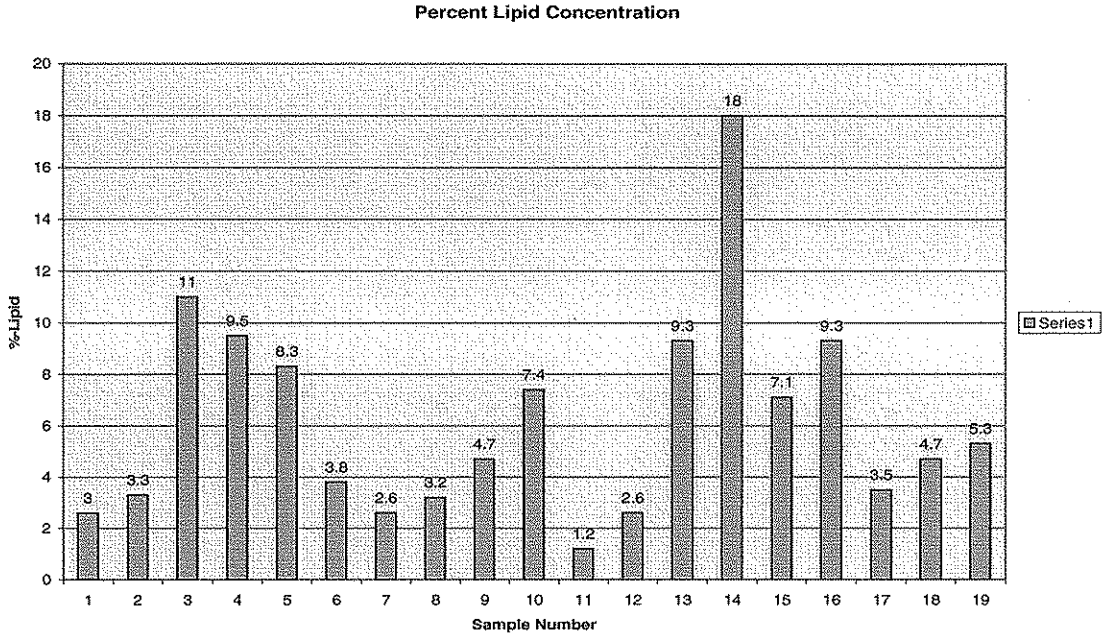

Figure 3- %-Lipid Content
Sample 1, 2, 11- Alaskan Chum Samples 3, 4, 5- Alaskan King Samples 6, 7, 8, 9, 10, 12-Alaskan Coho
Samples 13, 14, 15-California King Sample 16, 17, 18- Washington King Sample 19- Washington Coho