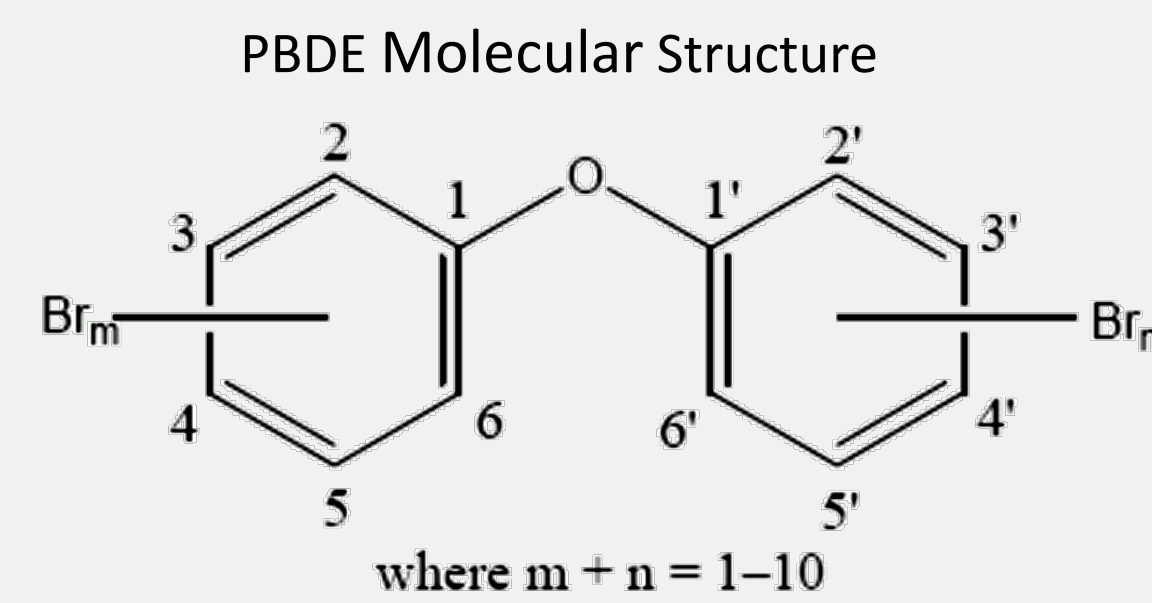


ABSTRACT

PBDEs are commercial flame retardants that were phased out over the past 10 years due to health concerns. However, they continue to persist in the environment. The Delaware River Basin Commission gathered data on PBDE levels in Channel Catfish and White Perch of the Delaware Estuary from 2004 to 2012 and in water samples from 2007. Four PBDE congeners (BDE 47, 99, 153, 209) with toxicity profiles on IRIS were the focus of this project. These data were used to draft Ambient Water Quality Criteria for the Estuary. However, some fish species have been found to metabolically debrominate certain congeners into others. Due to the effects of metabolic debromination on Bioaccumulation Factors used to determine the draft AWQC, fish tissue data were also used to draft Tissue Residue Criteria which do not require BAFs. Total Hazard Indices based on the Tissue Residue Criteria were found to decrease over the sampling years to below 1.0, and lipid normalized fish tissue concentrations were found to have significant negative associations with sampling year for all four congeners in Channel Catfish and for BDE 47,153, and 209 in White Perch.

INTRODUCTION

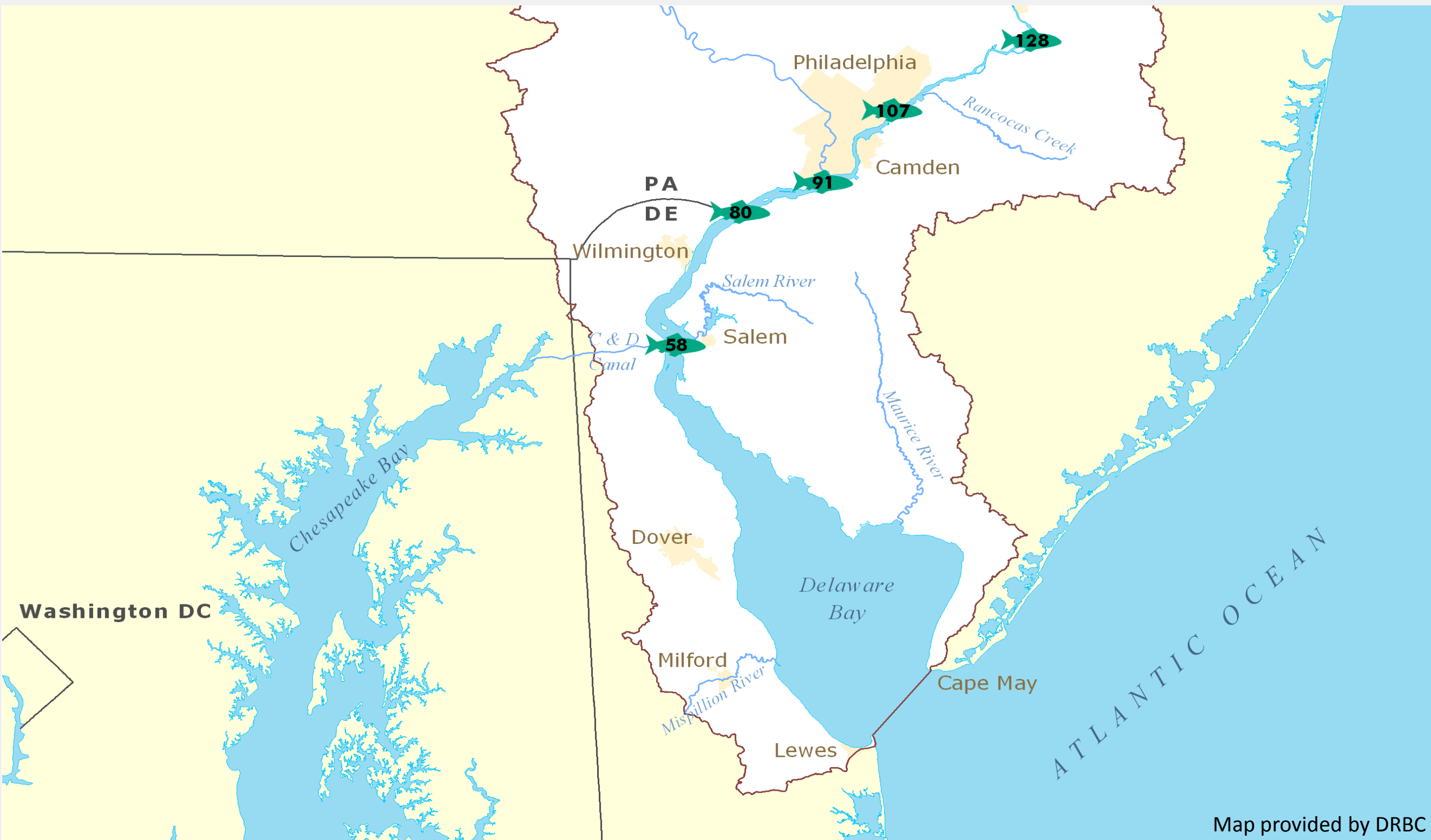
- Polybrominated diphenyl ethers (PBDEs) are flame retardants used on several consumer products such as television casings and polyurethane foam inside furniture cushions. They are not chemically bound to the products in which they are used, so they can easily shed off of them and into the environment.
- Indoor dust is believed to be the primary source of human exposure (~ 90%) but dietary exposure is also a concern (EPA, 2010a).
- PBDEs are characterized as persistent, bioaccumulative, toxic compounds.
- Human epidemiological studies have associated high PBDE levels in serum to altered steroid hormones levels and thyroid function, and to motor and cognitive deficits in children (Eskenza, 2013).
- Four PBDE congeners have toxicity profiles on EPA's Integrated Risk Information System (IRIS): BDE 47, 99, 153, and 209.
- Commercial production of PBDEs began in 1976 (EPA, 2010a). In 2004, the formulations containing BDE 47, 99, and 153 were phased out (Sutton, 2014). A phase-out of the formulation containing primarily BDE 209 was announced in 2009, with all uses due to end by 2014 (EPA, 2010a).
- The 209 possible PBDE congeners are often grouped by the number of bromine atoms they contain. There are 10 possible bromine binding sites as shown in the figure to the right (EPA, 2008a). BDE 47 contains 4, BDE 99 has 5, BDE 153 has 6, and BDE 209 has 10 bromine atoms.
- Fish have been shown to bioaccumulate PBDEs and some species biotransform certain congeners into others by debromination (Roberts, 2011). For example, BDE 153 can be debrominated to BDE 99, and BDE 99 to BDE 47.
- Debromination of certain congeners into others by some fish species affects calculations of bioaccumulation since intake of one congener can result in bioaccumulation of another. For example, in the Common Carp, no BDE 99 is stored in tissue but 10% of ingested BDE 99 is stored as BDE 47(Stapleton, 2004b).
- PBDEs have been detected in the water, sediment, and fish of the Delaware Estuary (Ashley, 2007).
- Concerns over the health effects of PBDEs require safety guidelines to be developed such as human health ambient water quality criteria (AWQC) and fish tissue residue criteria (TRC).
- BDE 47, 99, 153, and 209 all have Reference Doses (RfDs) on IRIS for neurobehavioral effects and BDE 209 also has an oral slope factor for liver cancer (EPA, 2008). Therefore, health criteria were drafted for these four congeners and hazard indices over the sampling years were determined. Due to the phase-out of PBDEs, declining levels in fish tissue over the years of data collection (2004-2012) were hypothesized.



METHODS

- Available data from the Delaware River Basin Commission consisted of fish tissue samples from five sites of the tidal Delaware River (shown on map to the right) taken in 2004-2007, 2010, and 2012 that were analyzed for PBDEs. Channel Catfish (a benthic species) and White Perch (a pelagic species) samples were available. Samples were composites of five fish, fillet portion only. 2007 whole water samples taken from nearby sites were also used to calculate the draft Ambient Water Quality Criteria.
- Bioaccumulation factors (BAFs) were calculated for each congener and fish species. These BAFs were then used with updated exposure assumptions of 80 Kg body weight and 3l/d drinking water intake. A site-specific fish consumption rate of 17.5 g/d and a relative source contribution of 20% were also used to draft Human Health Ambient Water Quality Criteria for the Delaware Estuary in accordance with 2000 EPA Methodology (EPA, 2000a) and the Draft 2014 Update.
- Tissue Residue Criteria were also determined for all four congeners using EPA methodology (EPA, 2001) and Hazard Indices for each year sampled were determined by Maximum Environmental Contamination (MEC)/Tissue Residue Criterion (TRC).
- To determine whether PBDE fish tissue concentrations have a significant negative association with sampling year, a one-tailed Spearman Correlation was performed on SPSS statistical software.
- Mean tissue concentration levels for all five sampling sites over the six sampling years are shown by line graph.

Tidal Portion of the Delaware River



Fish tissue samples taken in 2004-2007, 2010, and 2012 from the sites marked above with fish icons were used to determine bioaccumulation factors of four BDE congeners. 2007 water samples were taken from nearby sites (as listed in the table below) and also used to calculate the drafted Ambient Water Quality Criteria.

Fish Sampling Site	River Mile	Water Sampling Site	River Mile	DRBC Zone
Crosswicks Creek	128	Biles Channel	131	2
Tacony-Palmyra Bridge	107	Pennsauken	105	3
Woodbury Creek	91	Schuylkill River	90	4
Raccoon Creek	80	Marcus Hook	80	4
Salem River	58	South of DE Memorial Bridge	68	5
		Liston Point	50	5

RESULTS

Bioaccumulation Factors and draft Ambient Water Quality Criteria, Estuary-wide

BDE Congener	Catfish BAF Mean (L/KG-lipid)	Perch BAF Mean (L/KG-lipid)	Draft AWQC Geometric Mean of all sites (pg/L)	Max water conc. 2007 (pg/L)	2007 Hazard Index
BDE 47	1,496,328	1,165,193	129	216	1.70
BDE 99	769,248	11,804	394	154	0.40
BDE 153	639,728	64,783	692	18	0.026
BDE 209	573	965	34,455,494	7630	0.00022

Water data represent all six sampling sites of the Estuary for BDE 47 and BDE 99. BDE 153 represents five sites (Liston Point missing) and BDE 209 four sites (Marcus Hook and Biles Channel missing) due to field blank contamination of water samples. Fish tissue sample data were used from all sites and years sampled except no data were available for catfish from Raccoon Creek or Salem River in 2007.

Tissue Residue Criteria (TRC) and Yearly Hazard Index

BDE Congener	TRC (mg/kg)	Hazard Indices					
		2004	2005	2006	2007	2010	2012
BDE-47	0.09143	0.8266	0.7098	0.6770	0.8706	0.6562	0.5829
BDE-99	0.09143	0.4437	0.4385	0.5752	0.4003	0.3008	0.2395
BDE-153	0.18286	0.0458	0.0375	0.0411	0.0298	0.0259	0.0173
BDE-209	6.40	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001

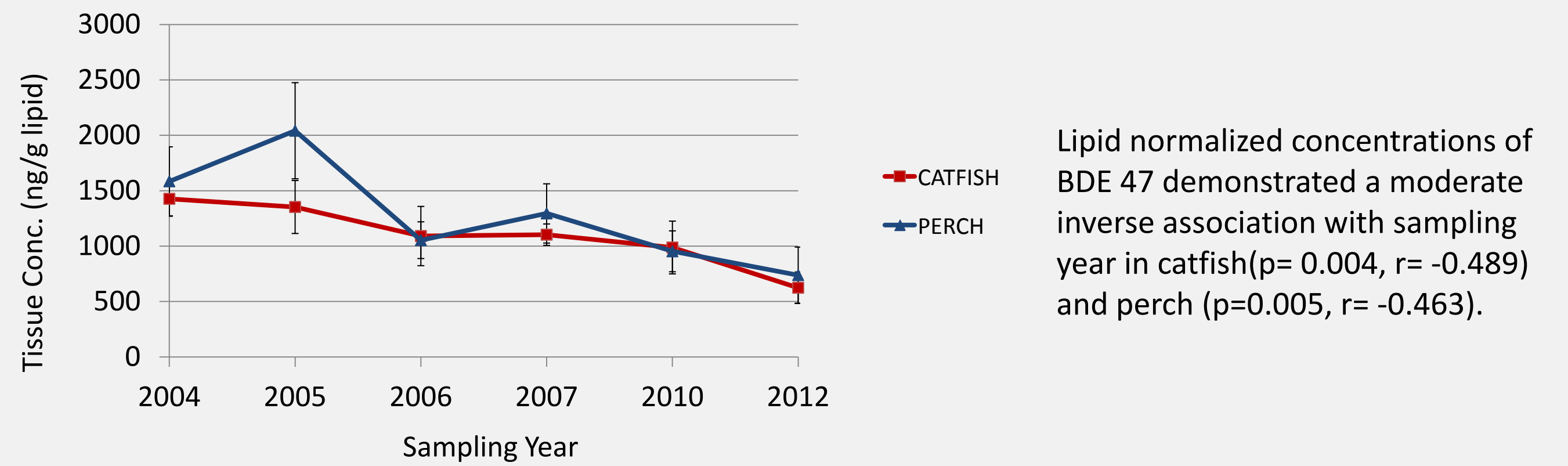
TOTAL HI 1.3163 1.1859 1.2935 1.3009 0.9829 0.8397

Hazard Index (HI) was calculated by Maximum Environmental Contamination/Tissue Residue Criterion (TRC). Total HI is the total hazard index for each year based on the 4 congeners measured.

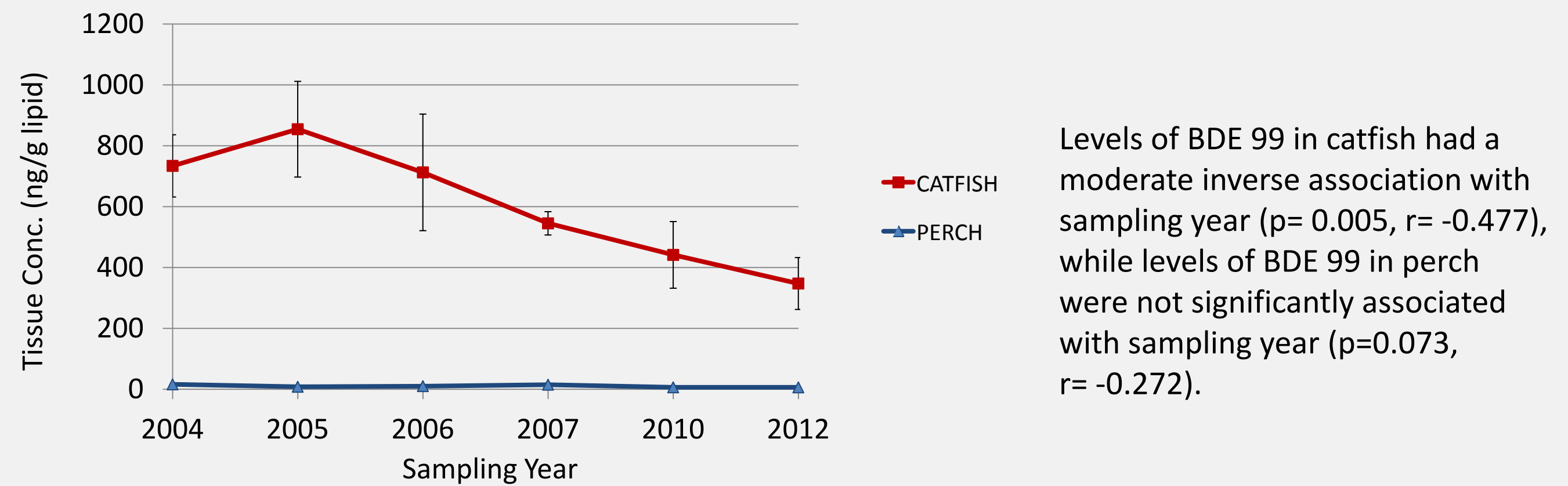
- BDE 47 was the congener that contributed most to the Hazard Index for both water (80%) and fish tissue (an average of 62% over the sampling years).
- Catfish samples from Crosswicks Creek (Zone 2) and Tacony-Palmyra Bridge (Zone 3) were the most contaminated fish sampled for all congeners in every year with only one exception.
- In contrast, 2007 water samples were most contaminated at the Schuylkill River site in Upper Zone 4.
- The Total Hazard Index from fish tissue contamination exhibits a decreasing trend from 2004 to 2012.
- 2007 whole water samples exceeded the drafted AWQC for BDE 47. However, some BDE 153 and 99 may be debrominated to BDE 47 before being stored in fish tissue. This effect appears to be more pronounced in perch, as shown by its lower BAF for BDE 99 and 153. This may result in draft AWQC that is artificially lower for BDE 47 and higher for BDE 153 and 99.

The graphs below display lipid normalized concentrations of the congeners analyzed over the sampling years in Channel Catfish and White Perch tissue. For each year, one sample (5 fish composite) was available from each sampling site in the Delaware Estuary. Mean concentrations of all 5 sites are shown with standard error bars. Data was not available for catfish in 2007 from Raccoon Creek or Salem River. Spearman Correlation results are given to the right of each graph (n=28 for catfish and n=30 for perch).

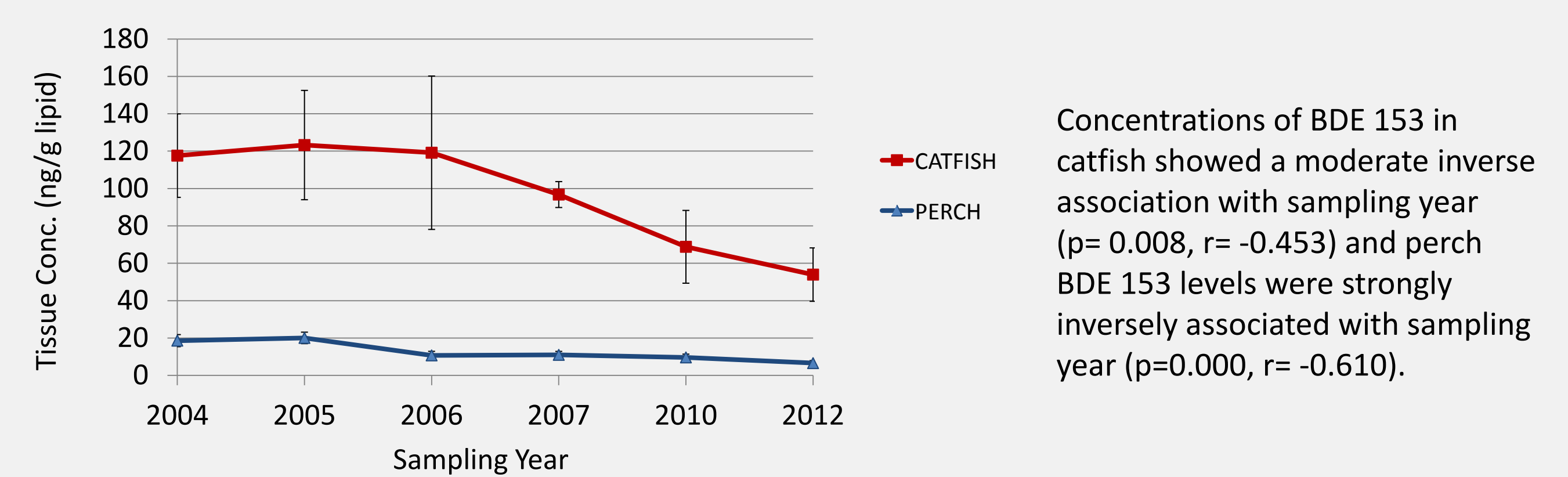
Lipid normalized tissue concentrations of BDE 47 in catfish and perch by year sampled



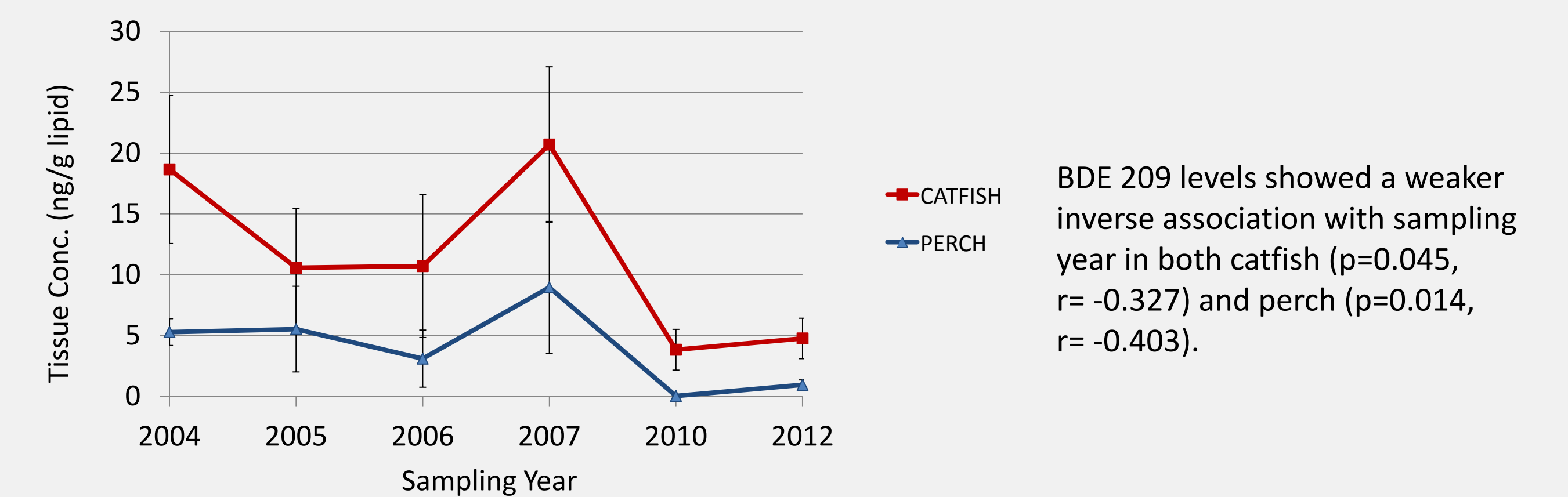
Lipid normalized tissue concentrations of BDE 99 in catfish and perch by year sampled



Lipid normalized tissue concentrations of BDE 153 in catfish and perch by year sampled



Lipid normalized tissue concentrations of BDE 209 in catfish and perch by year sampled



CONCLUSION

- Although the drafted AWQC was exceeded in 2007 water samples for BDE 47, a more recent sample may be lower as suggested by the decline in fish tissue concentrations.
- Total Hazard Indices based on the calculated TRC exceeded 1.0 from 2004-7, indicating the need for remediation, but were below this level in 2010 and 2012.
- The Hazard Indices presented here indicate the risk of the four congeners analyzed only, but there are likely other congeners that contribute significantly to risk. BDE 100 is present at high levels in both fish tissue and human serum (Stapleton, 2012). This congener may have toxic properties similar to those in this study but could not be included because it is not currently listed on IRIS. Other congeners present at lower levels are also present in fish tissue and contribute to total body burden of PBDEs (EPA, 2010a).
- Lipid normalized fish tissue concentrations of all congeners significantly declined over the sampling years in both species, with the exception of BDE 99 levels in perch which remain low likely due to debromination to BDE 47. Fish tissue will need to be analyzed for PBDEs in future years to determine whether this trend continues.
- While the decline of these congeners in fish tissue is good news and may indicate decreasing environmental contamination by PBDEs, flame retardants currently being used to replace them are not necessarily safe alternatives (Webster, 2012).

The authors would like to thank Site Supervisor Dr. Ron MacGillivray and Dr. Tom Fikslin and Greg Cavallo of the DRBC for their assistance.