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Agency

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EPA

Proceedings of the 2007 National Forum on Contaminants in Fish

All sections of the 2007 Proceedings are available from our web site at:
http://www.epa.gov/waterscience/fish/forum/2007/

Section II-B
Sampling and Analysis Issues

Moderators:

Robert Brodberg, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency

Robert Gerlach, Alaska Department of Environmental Conservation

Mercury Measurements Using Direct-Analyzer Methodology

Thomas A. Hinners, Office of Research and Development, National Exposure Research Laboratory, U.S. EPA

A Biopsy Procedure for Determining Mercury in Fish Tissue with Results from a Western USA Survey

Robert Hughes, Department of Fisheries and Wildlife, Oregon State University

Mercury in Fish in the Gulf of Mexico

Tony Lowery, National Marine Fisheries Service

Report on EPA's National Lake Fish Tissue Survey

Leanne Stahl, Office of Science and Technology, Office of Water, U.S. EPA

EPA Pilot Study on Pharmaceuticals and Personal Care Products (PPCPs) in Fish Tissue:

PPCPs as Emerging Contaminants

John Wathen, Office of Science and Technology, Office of Water, U.S. EPA

EPA PPCP Fish Pilot Study

Leanne Stahl

Polybrominated Diphenyl Ethers (PBDEs) in Fish from the Delaware River Drainage Basin

Richard Greene, Delaware Department of Natural Resources and Environmental Control

Distribution of PBDE Flame Retardants in Fish and Water from Washington Rivers and Lakes

Dale Norton, Washington State Department of Ecology

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Mercury Measurements Using Direct-Analyzer Methodology

Thomas A. Hinners, Office of Research and Development,
National Exposure Research Laboratory, U.S. EPA

Biosketch

During more than 37 years as a Research Chemist with EPA's Office of Research and Development, while stationed in Research Triangle Park, NC, and, for the last 28 years in Las Vegas, NV (at what is now the Environmental Sciences Division of the National Exposure Research Laboratory), Mr. Thomas Hinners has been involved in developing, evaluating, and applying methods for measuring trace elements, including writing the original inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Inductively coupled plasma mass spectrometry (ICP-MS) methods for EPA's Office of Solid Waste. Since 1998, he has used two versions of direct analyzers to determine both total mercury and methylmercury in biological matrices. He conducted his undergraduate and graduate studies at George Washington University.

Abstract

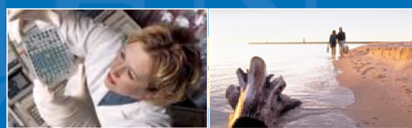
Under the Environmental Protection Agency's (EPA's) Water Quality Research Program, exposure studies are needed to determine how well control strategies and guidance are working. Consequently, reliable and convenient techniques that minimize waste production are of special interest. While traditional methods for determining mercury (Hg) in solid samples involve using aggressive chemicals to dissolve the matrix and using other chemicals to properly reduce the Hg to the volatile elemental form, pyrolysis-based analyzers can be used by directly weighing the solid in a sampling boat and initiating the instrumental analysis for total Hg. Although not well suited for trace-level analyses of liquids because of the limited capacity of the sampling boat, such pyrolysis-based Hg analyzers (EPA Method 7473) have the following advantages:

- *Throughput*: A measurement every 10–15 minutes, including the weighing and logging time
- *Learning curve*: Operation must be simple enough for those with no prior analytical skills
- *Low cost*: Capital cost about $37,000
- *Green*: Generation of waste virtually eliminated
- *Sample-size limits*: 0.5 mL for liquids and 500 mg for solids
- *Detection limit*: near 0.01 nanogram Hg (or 0.1 ppb for 100-mg sample)
- *Applications*:
  - Non-lethal monitoring of fish (by tissue biopsy)
  - Longitudinal analysis of hair (to locate peak-exposure periods)
  - Exposure assessments for other tissues (e.g., feathers, fur, toenails, botanicals)
  - Near real-time monitoring of contaminated soil and sediment during remediations
  - Assess coal-fired power plant emissions (by Hg difference in the coal and in solid waste)
  - Speciation for Hg in tissues (via suitable extracts of the methylmercury).

* NOTE: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

Mercury Measurements using Direct-analyzer Methodology

Thomas A. Hinners, Research Chemist



23 July 2007 presentation for the National Forum on Contaminants in Fish
Portland, Maine

Office of Research and Development
National Exposure Research Laboratory, Environmental Sciences Division, Environmental Chemistry Branch, Las Vegas, NV

NOTICE:

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use, including the abbreviation shown on the next slide.

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Introduction

- Because exposure studies are needed as part of EPA's Water Quality Research to determine how well control strategies and guidance are working, use of convenient methods that minimize waste production are desired.
- Traditional methods for determining mercury in samples involve the use of aggressive chemicals to dissolve the matrix and the use of other chemicals to properly reduce the mercury to the volatile elemental form.
- In contrast, ***pyrolysis-based analyzers*** can be used by pipetting solutions, or weighing solids, in a sampling boat, and initiating the instrumental analysis for total mercury.
- Although not well suited for trace-level analyses of liquids because of the limited capacity of the sampling boat (0.5 mL), such pyrolysis-based mercury analyzers have several advantages & applications, which are listed in the Abstract for this talk, and won't be itemized here to save time.

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Analyzer basics

- Sampling boat (ca 0.25 x 0.25 x 1.5 inch)
- Pyrolysis at $\geq$750 °C in air or oxygen flow
- Catalytic trap (inorganic salts to promote oxidation & trap halides & oxides)
- Amalgamator (one or more)
- Delay before amalgamator(s) heat purged
- Atomic-absorption detection at 254 nm
  (energy to move an electron to a higher orbital, & light from a Hg lamp by reverse process)
- EPA Method 7473 & instrument providers (see links on last slides)

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Results for Certified Materials

- For reference materials with Hg between 0.0058 and 32.6 µg/g, several investigators have found agreement using pyrolysis analyzers for matrices including rice powder, apple leaves, pine-needle powder, milk powder, oyster tissue, tuna & shark fillet, shark liver, mussel tissue, hair, coal fly ash, numerous sediments, and contaminated soils.

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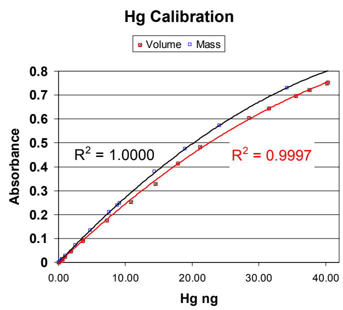
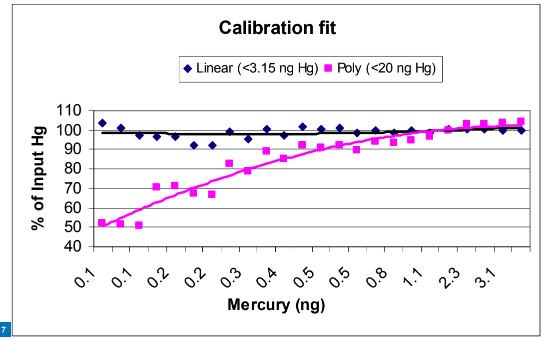
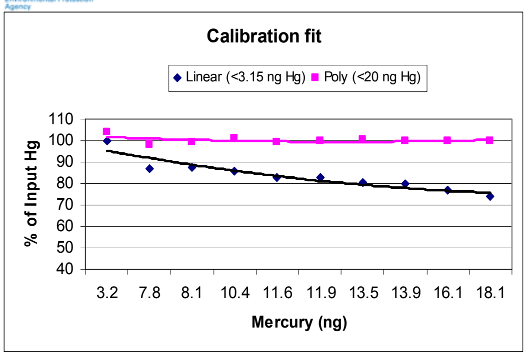


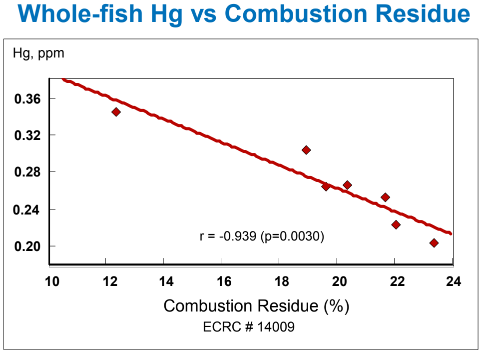




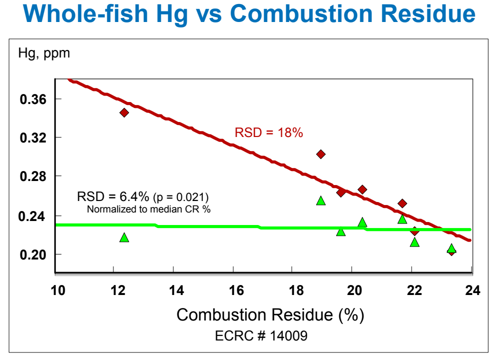
Fish investigations

- Using freeze-dried whole-fish homogenates provided by William Brumbaugh at the USGS in Missouri, statistically equivalent results were obtained in our lab by blind analyses for ten specimens containing Hg between 0.10 and 2.26 ppm Hg.
  - Contrary to some verbal reports for other such comparisons, the fact that statistically higher results were **not** obtained with the direct analyzer could reflect that these were dry specimens where moisture content was not a variable.

Whole-fish Hg vs Combustion Residue



Whole-fish Hg vs Combustion Residue



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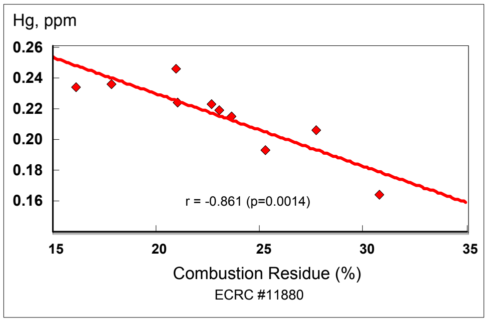
Whole-fish Hg vs Combustion Residue



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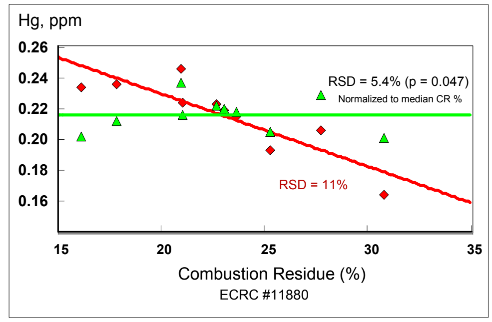
Whole-fish Hg vs Combustion Residue



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Fish investigations

- For fish from the National Park Service, fillet biopsy-plug Hg proved valid to compute whole-fish Hg (r^2 = 0.976 for 20 species across 10 parks), which could (with U.S. Senate approval) eliminate collecting & homogenizing of whole fish (when Hg is the only concern).
- EMAP whole-fish homogenates were analyzed in collaboration with EPA-Cincinnati where repeated alternating analyses (n = 5) for two samples labeled as "duplicates" clarified that the samples were statistically different in Hg, i.e. the Hg difference was not ascribable to measurement error.

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Fish investigations (citations available upon request)

- Lake Mead fish reports
  - Assess methodology
    Water, Air, and Soil Pollut. 135:355-370, **2002**
  - Hg in 339 fish
    Arch. Environ. Contam. Toxicol. 43:309-317, **2002**
  - Relationships between fish tissues
    J. Environ. Monitor 5:802-807, **2003**
  - **Fillet Hg Higher in Skinnier Fish**
    poster at the 2004 National Forum on Contaminants in Fish
    - Canadians have proposed including fish-growth rates in walleye advisories (*Environ. Res. 98*:73-82, **2005**)

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Fish investigations

- Non-lethal fillet biopsy sampling of fish has been successfully utilized for selenium (by neutron activation analysis) in an endangered species (Waddell & May, *Arch. Environ. Contam. Tox. 28*:321-326, **1995**), and is feasible for Hg using a pyrolysis analyzer
- To remove an uncertainty in fish-Hg data, the wet-tissue basis (cited in EPA and FDA guidance) could be defined as a specified moisture percentage (such as 78.5% in The National Survey of Mercury Concentrations in Fish, Summary 1990 -1995, EPA-823-R-99-014)

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Hair Investigations

- Human-research approval required for federally funded studies and states may also have requirements (See www.hhs.gov/ohrp/irb-guidebook.htm)
- Accuracy for hair-Hg verified by participation in Health Canada Mercury-in-Hair Interlaboratory Program
- Collaboration with State of Washington to assess exposure of ethnic groups (Dr. Marien)
- Longitudinal analysis can locate peak-exposure periods (and recommended by the NRC in Toxicological Effects of Methylmercury, 2000)
- Single–fiber analysis can serve to identify high samples (as shown on the next slide), but short segments of a single fiber require expressing data per unit length because of the weighing limitation.

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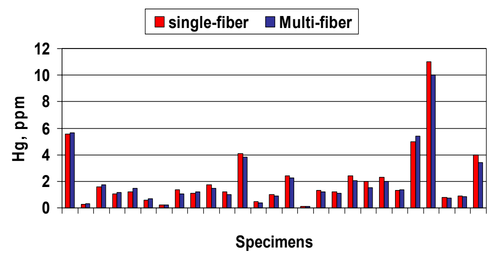
Hair-Hg analyses



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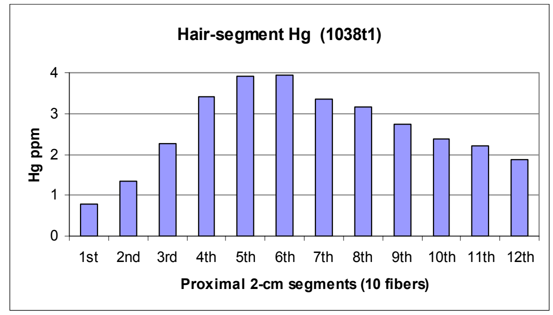

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Mercury Speciation

- Methyl mercury results for KOH digests of fish tissues followed by partitioning into toluene agreed ($r^2 = 0.998$) with results from gas chromatography (in collaboration with Steve Pyle in our branch using AOAC Method 983.20)
- Inorganic mercury values in Health Canada Mercury-in-Hair samples (via the difference between total Hg and the acid-extracted methyl mercury) have been within the acceptance ranges.

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For More Information (available by email)

- EPA Hg Method 7473 http://www.epa.gov/sw-846/pdfs/7473.pdf
- Providers of Pyrolytic (or Thermal-Decomposition) Hg analyzers (in alphabetic order):
- www.agssci.com for AGS Scientific
- www.brandtinst.com for Brandt Instruments
- www.leco.com for LECO Corporation
- www.milestonesci.com for Milestone, Inc.
- EPA guidance on fish: http://www.epa.govhttp://epa.gov/waterscience/fish/
- NRC report on methyl mercury http://books.nap.edu/catalog/9899.html
- Health Canada Mercury-in-Hair Interlaboratory Comparison Program: mhicp@hc-sc.gc.ca
- hinners.tom@epa.gov (except brown.ann@epa.gov for news media)
- c:\Tom Hinners\Fish Forum 2007 – Version #6.ppt

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A Biopsy Procedure for Determining Hg in Fish Tissue with Results from a Western USA Survey

Robert Hughes, Department of Fisheries and Wildlife, Oregon State University

Biosketch

Dr. Robert Hughes is a Senior Research Professor in the Department of Fisheries and Wildlife at Oregon State University. Dr. Hughes received an A.B. degree in Biology and Psychology and an M.Sc. degree in Resource Planning and Conservation from the University of Michigan followed by a Ph.D. in Fisheries from Oregon State University. He was employed by Western Michigan University (3 years), the University of Illinois and EPA (1 year each), and as an on-site EPA contractor (22 years). He has been an Oregon State University employee for the past 3 years. His research interests are in bioassessment and biomonitoring of aquatic ecosystems, focusing on regional scale surveys, large rivers, and fish assemblages.

Abstract

We compared biopsy and fillet mercury (Hg) concentrations from 210 fish of 13 species, including both piscivores and non-piscivores, and found that we could model fillet concentrations from biopsy samples with an r2 of 0.96. We also collected and analyzed 2,707 large fish from 626 stream/river sites in 12 western USA states using a probability design to assess the regional distribution of whole fish Hg concentrations. Large (>120 mm total length) fish Hg levels were strongly related to both fish length and trophic guild. All large fish that we sampled exceeded the wet weight detection limit of 0.0024 $\mu g \cdot g^{-1}$, and the mean Hg concentration in piscivores (0.260 $\mu g \cdot g^{-1}$) was nearly three times that of non-piscivores (0.090 $\mu g \cdot g^{-1}$). Fish tissue Hg levels were not related to local site disturbance class. After partialing out the effects of fish length, correlations between Hg and environmental variables were low ($r<0.3$) for the most common genera (trout and suckers). Stronger partial correlations with Hg ($r>0.5$) were observed in other genera for pH, stream size, and human population density, but patterns were not consistent across genera. Salmonids, the most common family, were observed in an estimated 125,000 km of stream length, exceeded 0.1 μg $Hg \cdot g^{-1}$ (deemed protective for fish-eating mammals) in 11% of the assessed stream length and exceeded the fillet equivalent of 0.3 μg $Hg \cdot g^{-1}$ (U.S. Environmental Protection Agency human consumption advisory level) in 2.3% of that length. Piscivores were less widespread (31,400 km), but they exceeded the 0.1 and 0.3 μg $Hg \cdot g^{-1}$ criteria in 93% and 57% of their assessed stream length, respectively. Our findings suggest that atmospheric transport is a key factor relative to Hg in fish across the western USA.

A Biopsy Procedure for Determining Hg in Fish Tissue with Results from a Western USA Survey

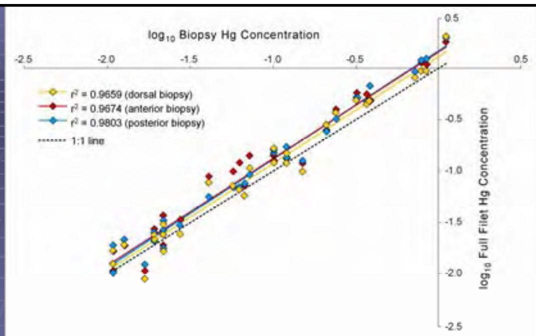
Robert M. Hughes & Alan T. Herlihy, Department of Fisheries & Wildlife, Oregon State University, Corvallis, OR

Spencer A. Peterson, John Van Sickle, & David V. Peck, U.S. Environmental Protection Agency, Corvallis, OR

EMAP

Background

- Hg in fish tissue is 95%-99% methylmercury, total Hg is a good estimate of Hg in fish tissue
- Whole fish and fish filet Hg analysis requires killing fish
- Fish tissue biopsy = small non-lethal estimate of Hg in filet
- The CAAS Hg analysis method uses only 0.25 g biopsy sample and is equivalent to CVAAS method (Cizdziel et. al., 2002)



Biopsy Hg does not differ significantly from one location to another in the filet and this does not differ significantly from the filet Hg itself.

Objectives

- Develop a model to predict whole fish Hg concentration from biopsy Hg concentration
- Assess fish tissue Hg in rivers of the conterminous western USA states

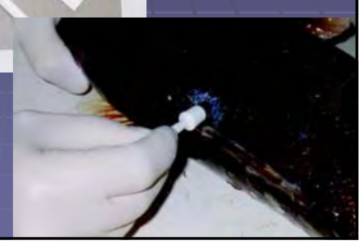
APPROACH

Collect large fish (>200mm length) of multiple sizes and species using a probability sampling design

Locations of 65 sampling sites.

Numbers are sample sizes per river site

Biopsy punch and plug expeller



Biopsy sampling immediately below and in front of dorsal fin

Photos from Pearson, 2000

- Analyze total Hg in biopsy and whole fish subsamples from the same frozen fish using CAAS
- Determine effects of freezing on biopsies over 100 days
- Develop relationship of biopsy data versus whole fish data

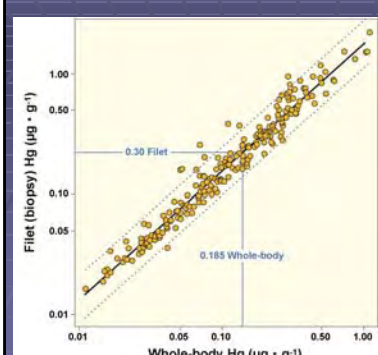
Results

- We collected and analyzed 210 piscivorous and non-piscivorous fish from 13 species of various sizes at 65 sites across 12 western USA states
- Frozen biopsy samples analyzed periodically over 100 days showed no significant difference in Hg concentration

Mean, minimum – maximum fish lengths, and biopsy Hg conc. (Peterson et.al., 2005)

Species (Common Name)	Number Fish (Total)	Length (mm) (Mean, Minimum–Maximum)	Hg Concentration (μg/g) (Mean, Minimum–Maximum)
Brook Trout	13	235, 203–290	0.051, 0.019–0.206
Brown Trout	36	270, 200–412	0.123, 0.023–0.652
Channel Catfish	1	505	0.200
Cutthroat Trout	7	242, 208–265	0.055, 0.036–0.082
Largemouth Bass	10	335, 210–415	0.642, 0.086–1.034
Northern Pike	16	405, 212–510	0.300, 0.164–0.432
Northern Pikeminnow	27	328, 208–470	0.675, 0.011–2.212
Rainbow Trout	29	292, 208–453	0.099, 0.016–0.360
Sauger	1	253	0.739
Smallmouth Bass	31	285, 201–405	0.248, 0.064–0.753
Walleye	21	334, 223–425	0.451, 0.137–0.948
White Sucker	17	293, 203–430	0.217, 0.053–0.516
Yellow Perch	1	200	0.171

Relationship Between Fish Whole Body and Filet Hg Conc.



$n = 210$,

$r^2 = 0.96$

Whole fish Hg conc.≥0.185 μg Hg/g exceeds the USEPA tissue based water quality criterion of 0.3 μg Hg/g in filets

Summary

- Biopsies are non-lethal to fish
- Biopsies are less cumbersome, less expensive, and less detrimental to fish populations than conventional techniques
- CAAS Hg analysis is a precise and accurate means to estimate filet Hg concentration and predict whole fish Hg concentration

Mercury in Fish Tissue Across the Western United States

Questions

- What is the extent of Hg contamination in fish tissue across all Western USA streams and rivers?
- What are the factors related to mercury levels in fish?

EMAP-West Survey

- Sample sites were selected using the systematic, randomized EMAP sampling design from all perennial western U.S. streams/rivers
- Additional hand-picked sites selected to characterize best sites
- Site selections from the digitized version of the 1:100,000 scale USGS maps
- Inferences to the entire stream network can be made from probability survey data using site inclusion probabilities

Field Methods

- Fish sampled by electrofishing
- Streams: backpack electrofisher on 40 channel width long sample reaches
- Rivers: raft electrofisher on 100 channel width reaches

- Associated measurements of water chemistry, physical habitat, and watershed characteristics

Tissue Samples

- Collect large and small fish sample at each site if sufficient numbers of fish were available
- Large fish: adults ≥ 120 mm total length
- Small fish: adults < 120 mm
- Samples kept on ice, shipped overnight to laboratory and then frozen until analysis.

Most Common Species Analyzed

- Large Fish (2,707 fish, 626 sites)
- Non-Piscivores (85%)
  - Rainbow, Brown, Brook, Cutthroat Trout
  - White, Largescale Sucker
  - Mountain Whitefish, Common Carp
- Piscivores (15%)
  - Smallmouth Bass
  - Northern Pikeminnow
  - Walleye, Northern Pike
- Small Fish (386 samples)
  - Mottled Sculpin
  - Common Shiner
  - Redside Shiner
  - Fathead Minnow
  - Creek Chub
  - Speckled Dace
  - Longnose Dace

Hg Laboratory Analysis

- Whole body analysis (µg Hg/g wet weight)
  - Fish ground up in blender (homogenized)
  - Sub-sampled and frozen until analysis
  - Thawed, re-homogenized and analyzed without further sample preparation

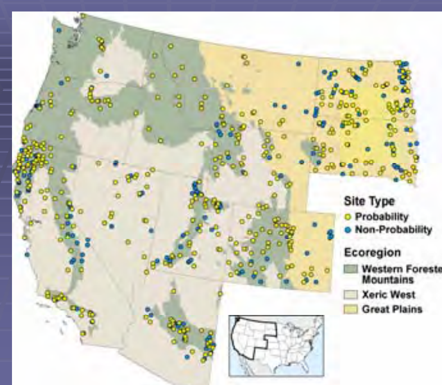
Analyzed by Combustion Atomic Absorption Spectrometry (CAAS)

QA and Detection Limits

- Samples run in duplicate and repeated if more than 10% variation between duplicates
- Method Detection Limit (MDL):
  = 0.002 µg Hg/g wet wt.

EMAP West Fish Tissue Sample Sites

n=625



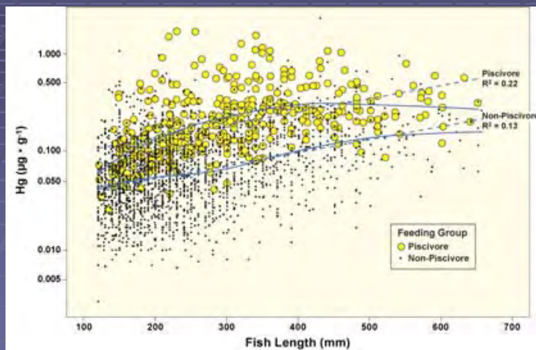
Factors Considered

- Fish Size (Total length)
- Fish Classification
  - **Species (genus)**
  - **Family**
  - **Trophic Class (piscivore, non-piscivore)**
- Site Disturbance Class (Low, Moderate, High)
  Based on:
  Physical Habitat
  Water Quality
  Air Photo Analysis

Analysis Types

- Linear and local regression (LOESS)
- ANCOVA - site condition effects tested w/fish length as covariate
- Partial correlation analysis to assess environmental variable influences
- Population estimates (stream length)

Mercury – Fish Length Relationship for Individual Large Fish



ANCOVA RESULTS

Fish Group	Length Effect (Partial F)[a]	(df)	Site Effect (Partial F)[b]	(df)
Cut./Rain. Trout	135	1, 275	0.34	2 ,206
Brown Trout	73.8	1, 157	0.22	2, 102
Mt. Whitefish	117	1, 83	0.56	2, 36
Suckers	137	1, 259	0.29	2, 179
Bullheads	19.2	1, 67	0.41	2, 49
Bass	170	1, 70	0.74	2, 36

Correlation between Hg and environmental variables after partialing out fish length

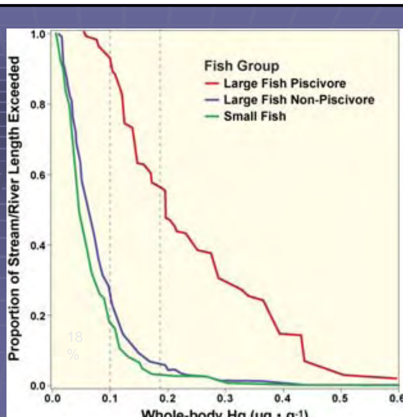
Fish Group	r_{length}	No. Fish	Top Environmental Correlates
Bass	0.72	110	Ann. Runoff (0.37), WS slope (0.37), Longitude (0.35)
Pikeminnow	0.52	100	pH (-0.60), WS area (-0.37), ANC (-0.56)
Suckers	0.48	442	None > 0.3
Br. Trout	0.33	120	None > 0.3
Cut./Rain. Trout	0.20	485	None > 0.3
Brook Trout	0.17	159	DOC (0.47), WS slope (-0.36)

Various Fish Tissue Mercury Criteria Values

- Human Health
  - 0.35 µg/g (Oregon Health Div., 1997)
  - 0.30 µg/g filet, 0.185 whole body (USEPA, 2001)
  - 0.10 µg/g (Faroe Island Study, 1998)
- Wildlife protection values - Lazorchak et al. 2003
  - 0.10 µg/g whole body (Otter)
  - 0.07 µg/g (Mink)
  - 0.03 µg/g (Kingfisher)

Cumulative Distribution Frequency (CDF) for Site Mean Mercury in Fish Tissue

(from Peterson et al. 2007)



Summary (1/4)

- Fish tissue mercury concentrations were most strongly related to trophic group and fish length
- Site disturbance effect was non-existent
- Other environmental factors influence Hg in fish to different degrees and with no consistent pattern
- % stream length exceeding criteria:
- Piscivores
  - 57% > 0.185 µg Hg/g
  - 93% > 0.1 µg Hg/g
- Non-piscivores
  - 6% > 0.185 µg Hg/g
  - 26% > 0.1 µg Hg/g

Summary (2/4)

- Fish tissue mercury concentrations in Western U.S. streams and rivers were found in a fairly narrow range (90% = 0.02 to 0.2 µg/g) and all fish were above the detection limit (0.002 µg Hg/g)
- High concentration "hot spots" (Hg > 0.5 µg/g) were rare (< 2% of stream resource)
- The above (plus Jaffy et al., 1999; Hope, 2006) strongly suggests a broad diffuse source of mercury from atmospheric deposition.

Summary (3/4)

Consumption of large game fish from extensive lengths of western streams/rivers presents a potential risk to sensitive consumers relative to the current fish tissue criterion

- Both wildlife and humans (particularly children & females of child bearing age).

Summary (4/4)

Probability survey results are:

- Inferable to an entire population of water bodies
- Capable of providing regional contamination estimates with known confidence

Questions and Answers

Q. *Did you assess mercury levels in whole fish and biopsy plugs and then infer the relationship between filets and whole fish? (Brodberg)*

A. No, we took three samples (filet, whole fish, and biopsy) and assessed the relationship of all three.

Q. *Were there no major mercury issues found in the mining areas of California? (Brodberg)*

A. It was a probability-based survey, which might not have assessed the mercury levels in fish in mining areas.

Q. *The survey must have taken some time to complete. Is it likely the differences in sample dates/time have impacted the mercury levels?*

A. Some repeat sampling was performed at later dates, but the sample size was too small to confirm a difference or lack of difference across the multiple dates. It did not appear to be an issue, however.

Q. *Did any of the sampling, specifically in Utah, suggest any sources or source types?*

A. The study was probabilistic relative to the entire Western United States, not to any one state. We did not specifically sample near mines or possible sources.

Synoptic Survey of Mercury in Recreational Fish of the Gulf of Mexico

Tony Lowery, National Marine Fisheries Service

Biosketch

Dr. Tony Lowery (Ph.D.) is the Program Coordinator for NOAA Fisheries' National Seafood Inspection Laboratory (NSIL). Dr. Lowery earned his B.S. degree in Biology and M.S. degree in Marine Biology from the University of Southern Alabama. He earned his Ph.D. in Marine Estuarine Environmental Sciences from the University of Maryland. He previously worked for NOAA's National Ocean Services as a Senior Fisheries Scientist for 9 years and on NOAA's Sea Grant as a Marine Agent for 5 years. Dr. Lowery has 65 publications on fish and shellfish species, marine and estuarine biogeography, eutrophication and hydrodynamic modeling, analytical chemistry, comparative biochemistry and physiology, and mercury in seafood. For the past 9 years, Dr. Lowery has been involved in NOAA's intra-agency and inter-agency efforts to address the seafood safety aspects of the mercury in seafood issue.

Abstract

The Synoptic Survey of Total Mercury in Recreational Finfish of the Gulf of Mexico evaluated selected finfish as potential "indicator" species for their efficacy to identify mercury (Hg) hot spots in marine and estuarine waters. The metric used for the basis of the evaluation was the total Hg concentration in the meat of the fish, versus fish length. In all, 1,660 individual fish were sampled and analyzed (1,076 estuarine fish, 385 reef fish, and 190 pelagic fish). For estuarine waters, spotted seatrout and hardhead catfish are recommended for further evaluation as "indicator" species. Tampa Bay's spotted seatrout and sand seatrout appeared to have elevated total Hg concentrations versus length relationships compared to the other three estuaries sampled (Mobile Bay, Matagorda Bay, and Galveston Bay). Mobile Bay's hardhead catfish appeared to have elevated total Hg concentrations versus length relationships compared to the other three estuaries sampled (Tampa Bay, Matagorda Bay, and Galveston Bay). There was no difference identified between the total Hg concentration versus length relationships of fish from Gulf rigs off the Louisiana Coast and Gulf reefs off the Florida Coast; however, additional sampling for Cobia, blackfin tuna, little tunny, yellowfin tuna, and gag grouper is necessary to complete the comparison. The pelagic fish samples did not identify a difference between the total Hg concentrations versus length relationships of fish from Southern Texas versus Southern Florida. Again, additional sampling is necessary to complete the comparison. Scatter plots and regressions on 23 recreational finfish are presented in this report. Protocols used to complete this survey are also provided.

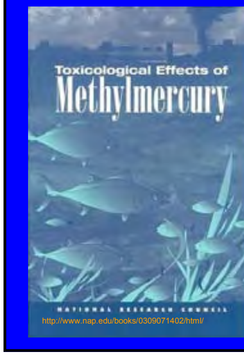
Synoptic Survey of Mercury in Recreational Fish of the Gulf of Mexico

National Forum on Contaminants in Fish
July 23-26, 2007

Portland ME

Tony Lowery, Ph.D
NOAA Fisheries
National Seafood Inspection Laboratory
Pascagoula, MS

National Academies of Science study circa July 2000 concludes that low levels of methylmercury intake can be harmful to developing fetuses, indicating limitations on seafood intake necessary.



NEWS

EPA's Gulf of Mexico Program completes its compilation of mercury in fisheries species of the Gulf of Mexico earlier in 2000. Some are above FDA limit of 1 ppm mercury.

A Survey of the Occurrence of Mercury in the Fishery Resources of the Gulf of Mexico

http://www.epa.gov/gmpo

January 2000

MOBILE REGISTER
Seafood riddled with mercury
By BEN RAINES
Staff Reporter
7/22/01 Tests commissioned by Register find that some popular Gulf fish contain levels exceeding federal safety standards, yet no consumption warnings have been issued for these species

MOBILE REGISTER
Mercury levels alarm scientists
New testing finds dangerously high readings in regular seafood eaters along the Gulf Coast
By BEN RAINES
Staff Reporter
11/18/01

MOBILE REGISTER
Fish contamination is Gulfwide problem
By BEN RAINES
Staff Reporter
11/04/01
A new round of fish testing by the Mobile Register provides hard evidence that mercury contamination is a Gulfwide problem not limited to fish from the Mobile area.

MOBILE REGISTER
Doctor links ailments to consumption of mercury laden fish
Internal medicine specialist and her patients say they see direct relationship between fish consumption, high mercury levels and bizarre ailments
10/20/02
By BEN RAINES
Staff Reporter

MOBILE REGISTER
Experts can't say which fish are safe
05/22/02
By BEN RAINES
Staff Reporter
Federal scientists told some 300 delegates to Mobile's Mercury Forum that many of the Gulf Coast's most important commercial and recreational fish species have never been tested for mercury, and there's no way to know whether eating them endangers people's health.

MOBILE REGISTER
'Ideal' mercury study yet to be done
05/19/02
By BEN RAINES
Staff Reporter
A growing number of scientists agree that despite millions of dollars spent on studies, no one has ruled out the possibility that mercury pollution at the Gulf of Mexico's 4,000 oil rigs is contaminating the sea life.

2001 Gulf States Marine Fisheries Commission and various Federal & State elected officials request federal assistance in resolving the Mercury in Gulf Seafood Issue.

NOAA Technical Report NMFS SSRF-721
National Marine Fisheries Service Survey of Trace Elements in the Fishery Resource
R. A. Hall, E. G. Zook, and G. M. Meaburn
March 1978

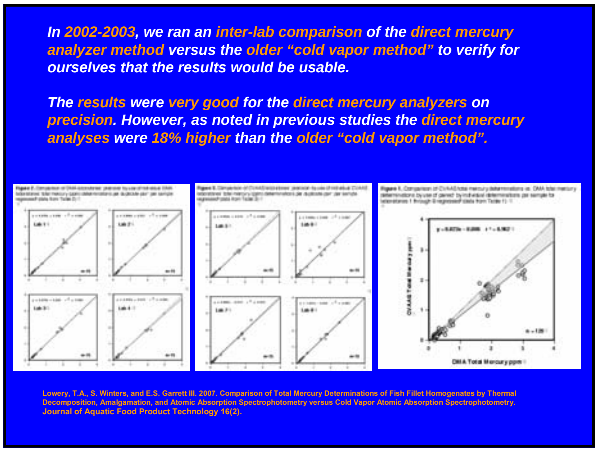
MOBILE REGISTER
Mercury testing planned in Gulf
National Marine Fisheries Service announces that it will begin monitoring fish for toxic metal this year
By BEN RAINES
Staff Reporter
03/22/02

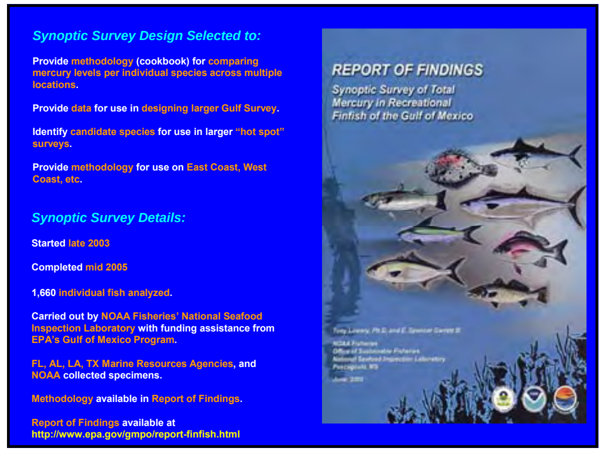
Recent Development of Direct Mercury Analyzers made large scale mercury in seafood species surveys possible.

EPA
U.S. EPA Methods
EPA Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
Method 7473 is designated for the determination of mercury in solids, aqueous samples, and digestion solutions, in both the laboratory and field environments. Integration of thermal decomposition, sample preparation, and atomic absorption detection reduces the total analysis time of most samples to less than five minutes, in either the laboratory or field setting.

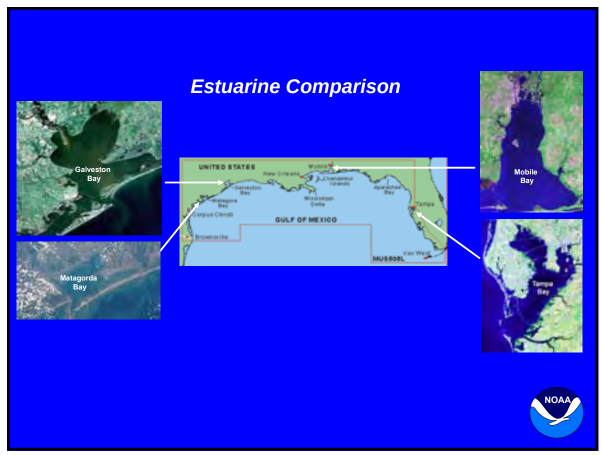
Research just completed using this methodology on fish flesh tissues by EPA Las Vegas Laboratory (Tom Hinners et al.).

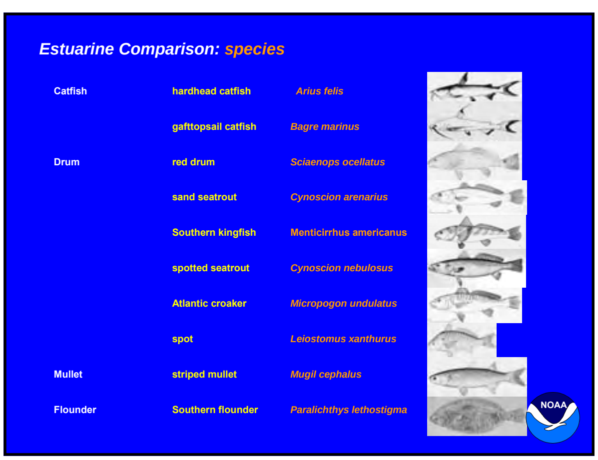
Cizdziel, J.V., T.A Hinners, and E.M Heithmar . 2002. Determination of total mercury in fish tissues using combustion atomic absorption spectrometry with gold amalgamation. Water, Air, and Soil Pollution. 135: 355-370.

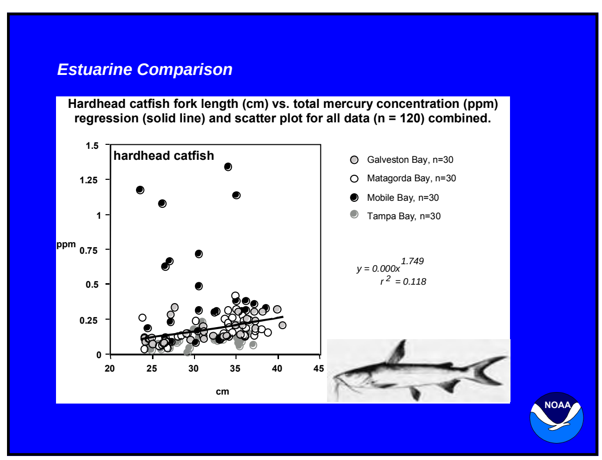

In 2002-2003, we ran an inter-lab comparison of the direct mercury analyzer method versus the older "cold vapor method" to verify for ourselves that the results would be usable.
The results were very good for the direct mercury analyzers on precision. However, as noted in previous studies the direct mercury analyses were 18% higher than the older "cold vapor method".
Lowery, T.A., S. Winters, and E.S. Garrett III. 2007. Comparison of Total Mercury Determinations of Fish Fillet Homogenates by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry versus Cold Vapor Atomic Absorption Spectrophotometry. Journal of Aquatic Food Product Technology 16(2).

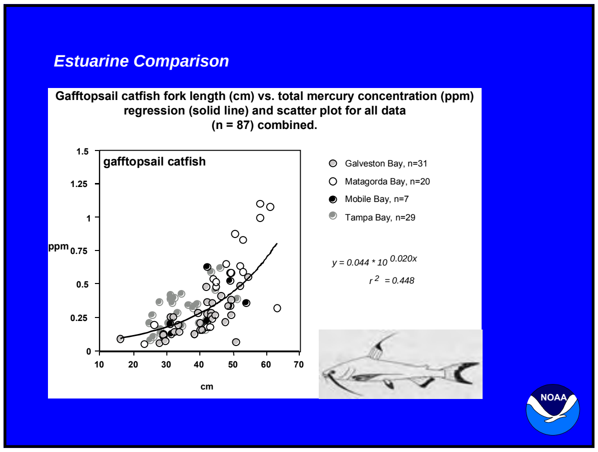

Synoptic Survey Design Selected to:
Provide methodology (cookbook) for comparing mercury levels per individual species across multiple locations.
Provide data for use in designing larger Gulf Survey.
Identify candidate species for use in larger "hot spot" surveys.
Provide methodology for use on East Coast, West Coast, etc.
Synoptic Survey Details:
Started late 2003
Completed mid 2005
1,660 individual fish analyzed.
Carried out by NOAA Fisheries' National Seafood Inspection Laboratory with funding assistance from EPA's Gulf of Mexico Program.
FL, AL, LA, TX Marine Resources Agencies, and NOAA collected specimens.
Methodology available in Report of Findings.
Report of Findings available at http://www.epa.gov/gmpo/report-finfish.html
REPORT OF FINDINGS
Synoptic Survey of Total Mercury in Recreational Finfish of the Gulf of Mexico

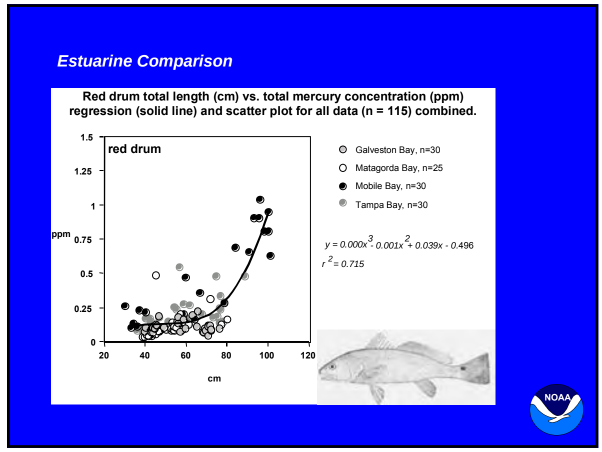

NOAA NOS Status & Trends Mussel Watch Program
Average Mercury Concentrations in Oysters
Average Mercury Concentrations: 1993-2002
NOAA

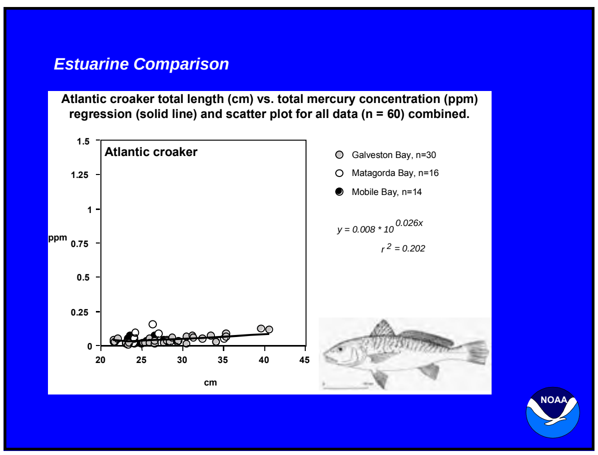

Estuarine Comparison
Galveston Bay
Matagorda Bay
Mobile Bay
Tampa Bay
UNITED STATES
GULF OF MEXICO
NOAA

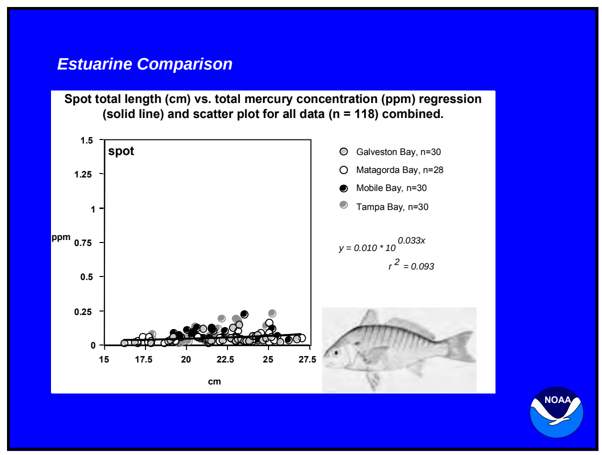

Estuarine Comparison: species
Catfish
hardhead catfish
Arius felis
gafftopsail catfish
Bagre marinus
Drum
red drum
Sciaenops ocellatus
sand seatrout
Cynoscion arenarius
Southern kingfish
Menticirrhus americanus
spotted seatrout
Cynoscion nebulosus
Atlantic croaker
Micropogon undulatus
spot
Leiostomus xanthurus
Mullet
striped mullet
Mugil cephalus
Flounder
Southern flounder
Paralichthys lethostigma
NOAA

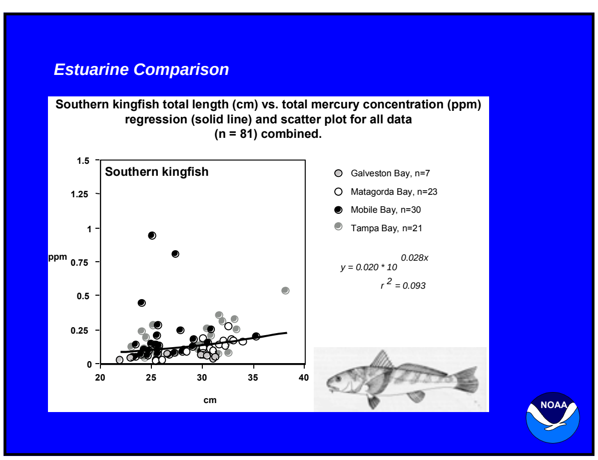

Estuarine Comparison
Hardhead catfish fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 120) combined.
hardhead catfish
ppm
1.5
1.25
1
0.75
0.5
0.25
0
20
25
30
35
40
45
cm
Galveston Bay, n=30
Matagorda Bay, n=30
Mobile Bay, n=30
Tampa Bay, n=30
y = 0.000x^1.749
r^2 = 0.118
NOAA

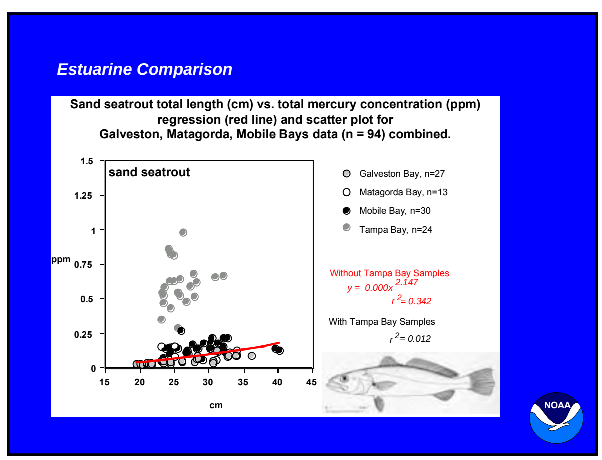

Estuarine Comparison
Gafftopsail catfish fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 87) combined.
gafftopsail catfish
Galveston Bay, n=31
Matagorda Bay, n=20
Mobile Bay, n=7
Tampa Bay, n=29
y = 0.044 * 10 0.020x
r 2 = 0.448
ppm
cm
NOAA

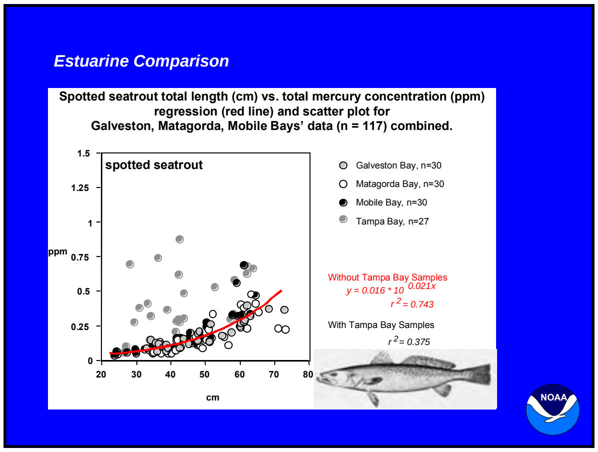

Estuarine Comparison
Red drum total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 115) combined.
red drum
Galveston Bay, n=30
Matagorda Bay, n=25
Mobile Bay, n=30
Tampa Bay, n=30
y = 0.000x 3 - 0.001x 2 + 0.039x - 0.496
r 2 = 0.715
ppm
cm
NOAA

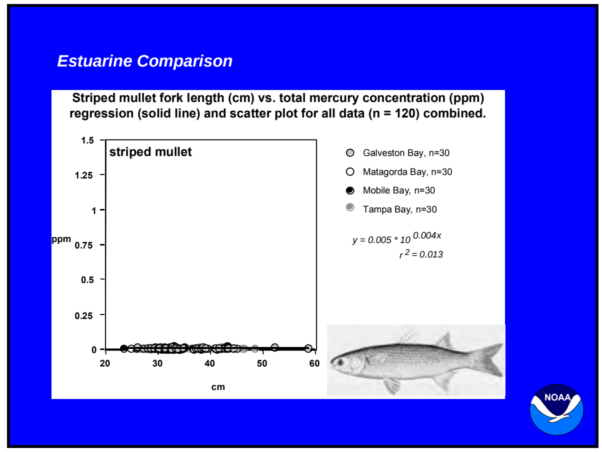

Estuarine Comparison
Atlantic croaker total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 60) combined.
Atlantic croaker
Galveston Bay, n=30
Matagorda Bay, n=16
Mobile Bay, n=14
y = 0.008 * 10 0.026x
r 2 = 0.202
ppm
cm
NOAA

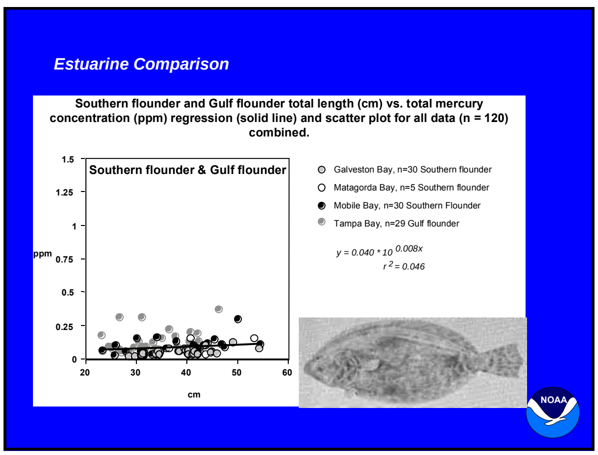

Estuarine Comparison
Spot total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 118) combined.
spot
Galveston Bay, n=30
Matagorda Bay, n=28
Mobile Bay, n=30
Tampa Bay, n=30
y = 0.010 * 10 0.033x
r 2 = 0.093
ppm
cm
NOAA

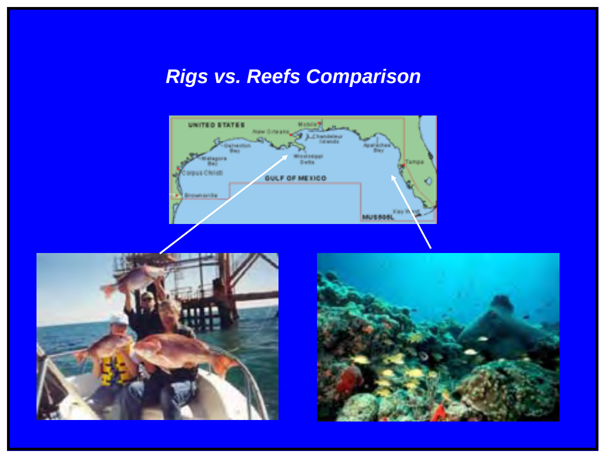

Estuarine Comparison
Southern kingfish total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 81) combined.
Southern kingfish
Galveston Bay, n=7
Matagorda Bay, n=23
Mobile Bay, n=30
Tampa Bay, n=21
y = 0.020 * 10 0.028x
r 2 = 0.093
ppm
cm
NOAA

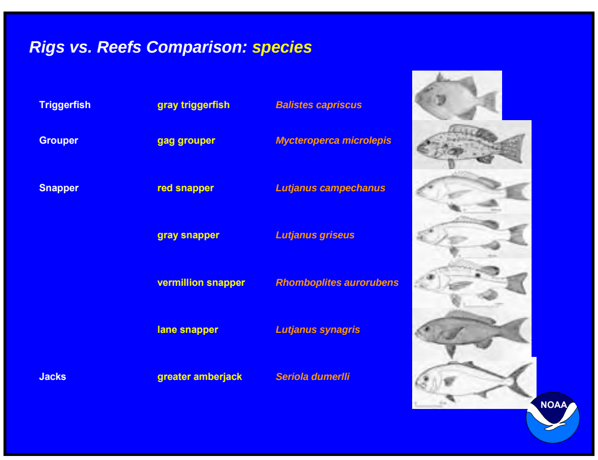

Estuarine Comparison
Sand seatrout total length (cm) vs. total mercury concentration (ppm) regression (red line) and scatter plot for Galveston, Matagorda, Mobile Bays data (n = 94) combined.
sand seatrout
Galveston Bay, n=27
Matagorda Bay, n=13
Mobile Bay, n=30
Tampa Bay, n=24
Without Tampa Bay Samples
y = 0.000x 2.147
r 2 = 0.342
With Tampa Bay Samples
r 2 = 0.012
ppm
cm
NOAA

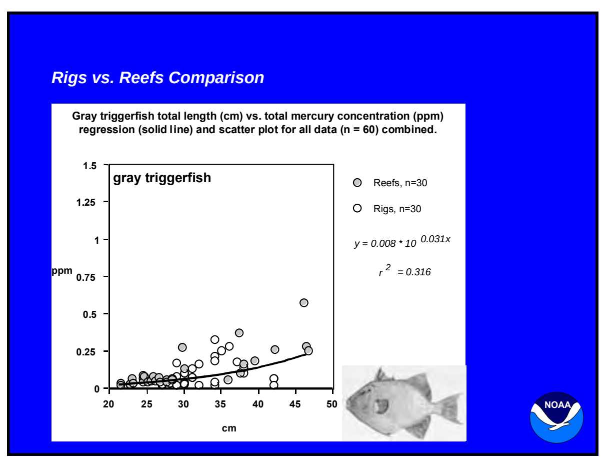

Estuarine Comparison
Spotted seatrout total length (cm) vs. total mercury concentration (ppm) regression (red line) and scatter plot for Galveston, Matagorda, Mobile Bays' data (n = 117) combined.
spotted seatrout
ppm
cm
Galveston Bay, n=30
Matagorda Bay, n=30
Mobile Bay, n=30
Tampa Bay, n=27
Without Tampa Bay Samples
$y = 0.016 * 10^{0.021x}$
$r^2 = 0.743$
With Tampa Bay Samples
$r^2 = 0.375$
NOAA

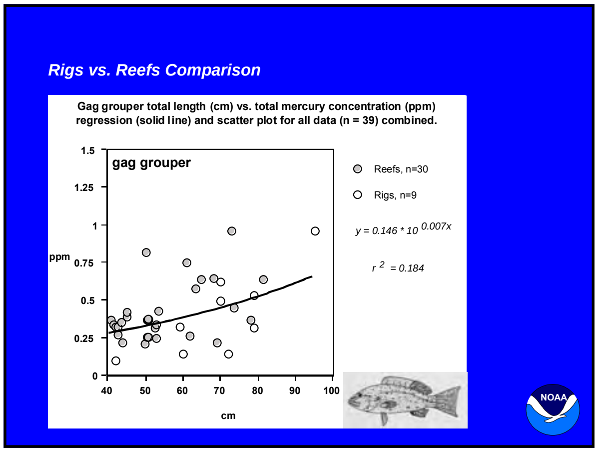

Estuarine Comparison
Striped mullet fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 120) combined.
striped mullet
ppm
cm
Galveston Bay, n=30
Matagorda Bay, n=30
Mobile Bay, n=30
Tampa Bay, n=30
$y = 0.005 * 10^{0.004x}$
$r^2 = 0.013$
NOAA

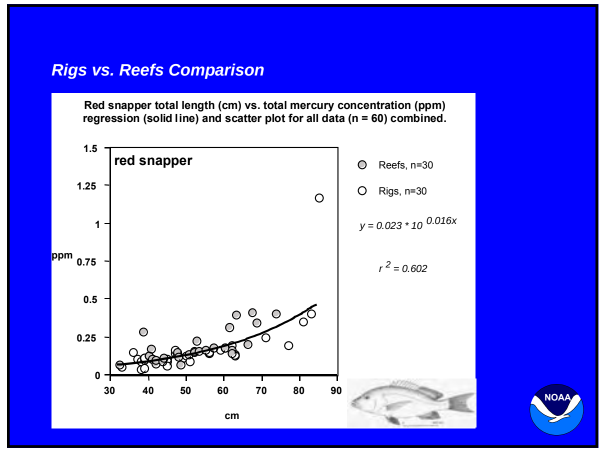

Estuarine Comparison
Southern flounder and Gulf flounder total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 120) combined.
Southern flounder & Gulf flounder
ppm
cm
Galveston Bay, n=30 Southern flounder
Matagorda Bay, n=5 Southern flounder
Mobile Bay, n=30 Southern Flounder
Tampa Bay, n=29 Gulf flounder
$y = 0.040 * 10^{0.008x}$
$r^2 = 0.046$
NOAA

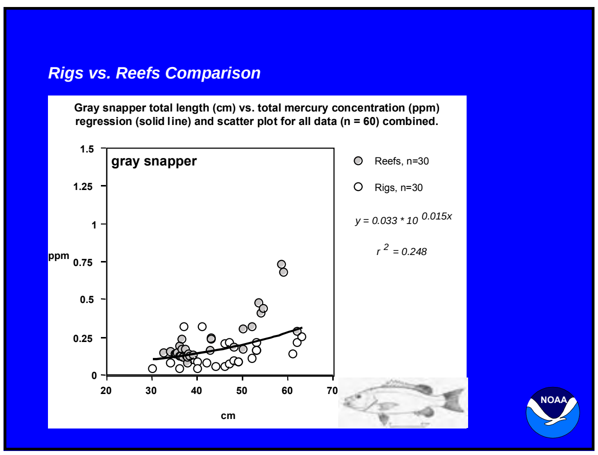

Rigs vs. Reefs Comparison
UNITED STATES
GULF OF MEXICO

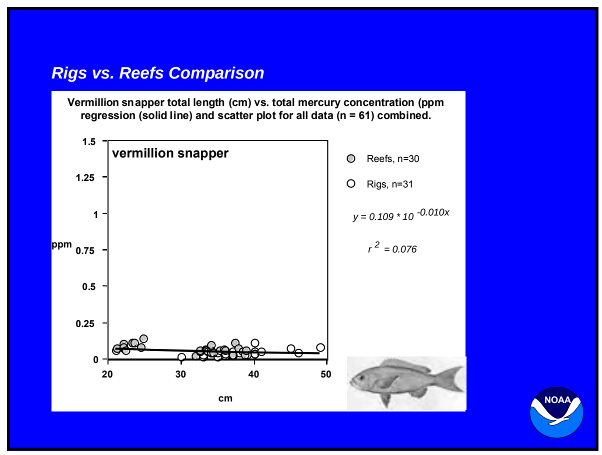

Rigs vs. Reefs Comparison: species
Triggerfish | gray triggerfish | Balistes capriscus
Grouper | gag grouper | Mycteroperca microlepis
Snapper | red snapper | Lutjanus campechanus
gray snapper | Lutjanus griseus
vermillion snapper | Rhomboplites aurorubens
lane snapper | Lutjanus synagris
Jacks | greater amberjack | Seriola dumerlli
NOAA

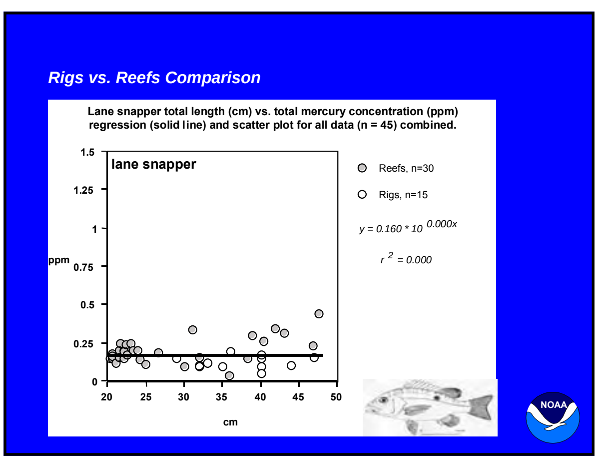

Rigs vs. Reefs Comparison
Gray triggerfish total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 60) combined.
gray triggerfish
ppm
cm
Reefs, n=30
Rigs, n=30
$y = 0.008 * 10^{0.031x}$
$r^2 = 0.316$
NOAA

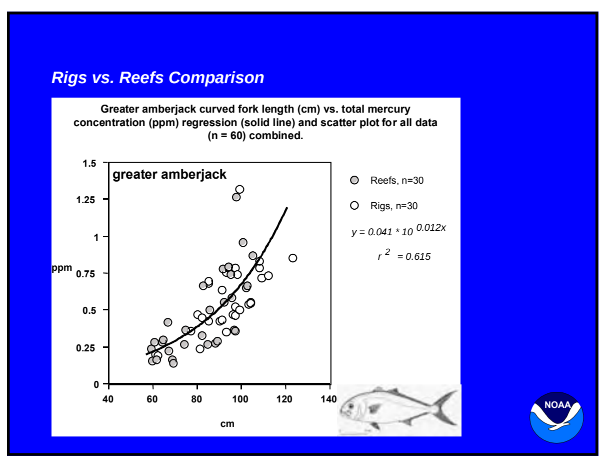

Rigs vs. Reefs Comparison
Gag grouper total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 39) combined.
gag grouper
Reefs, n=30
Rigs, n=9
y = 0.146 * 10 0.007x
r 2 = 0.184
ppm
cm
NOAA

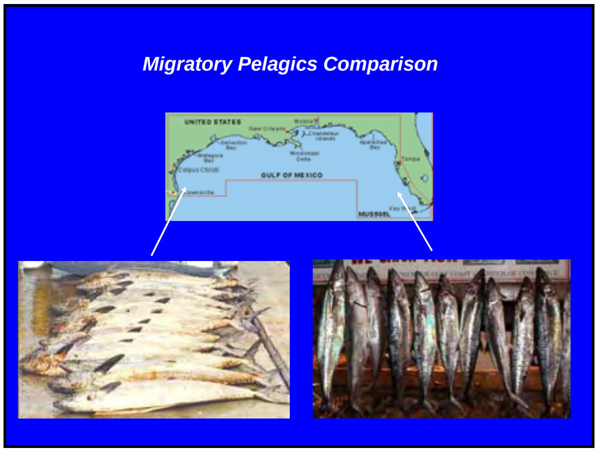

Rigs vs. Reefs Comparison
Red snapper total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 60) combined.
red snapper
Reefs, n=30
Rigs, n=30
y = 0.023 * 10 0.016x
r 2 = 0.602
ppm
cm
NOAA

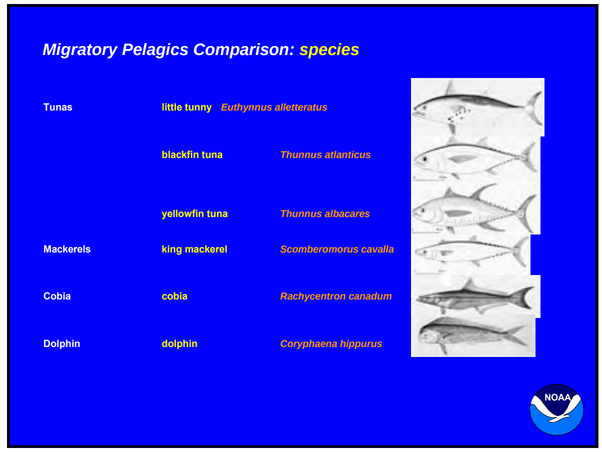

Rigs vs. Reefs Comparison
Gray snapper total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 60) combined.
gray snapper
Reefs, n=30
Rigs, n=30
y = 0.033 * 10 0.015x
r 2 = 0.248
ppm
cm
NOAA

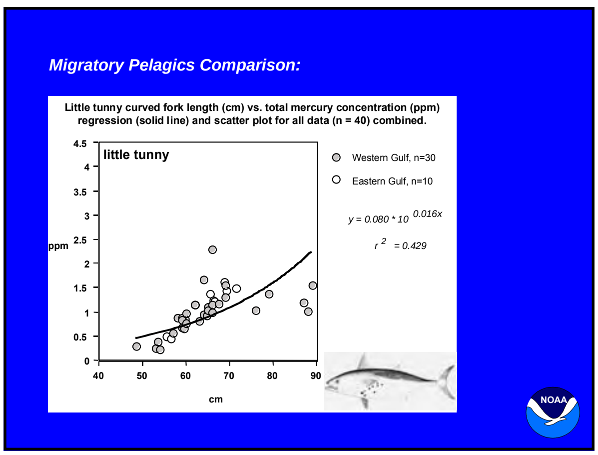

Rigs vs. Reefs Comparison
Vermillion snapper total length (cm) vs. total mercury concentration (ppm regression (solid line) and scatter plot for all data (n = 61) combined.
vermillion snapper
Reefs, n=30
Rigs, n=31
y = 0.109 * 10 -0.010x
r 2 = 0.076
ppm
cm
NOAA

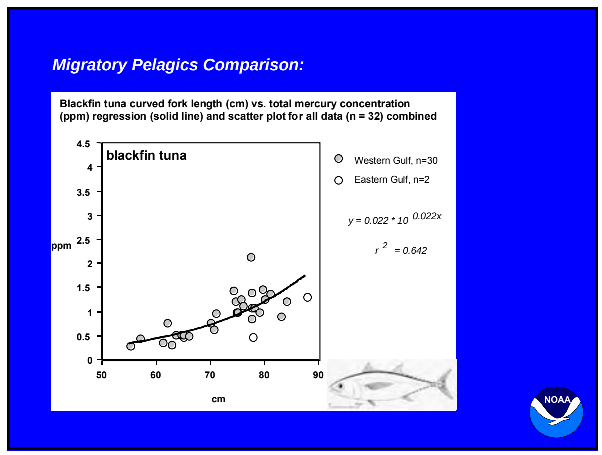

Rigs vs. Reefs Comparison
Lane snapper total length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 45) combined.
lane snapper
Reefs, n=30
Rigs, n=15
y = 0.160 * 10 0.000x
r 2 = 0.000
ppm
cm
NOAA

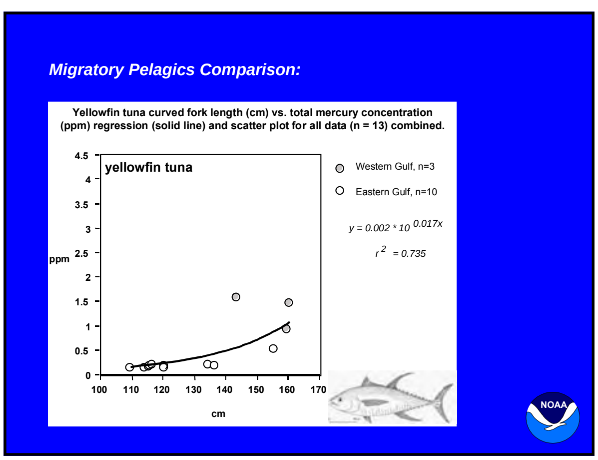

Rigs vs. Reefs Comparison
Greater amberjack curved fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 60) combined.
greater amberjack
Reefs, n=30
Rigs, n=30
y = 0.041 * 10 0.012x
r 2 = 0.615
ppm
cm
NOAA

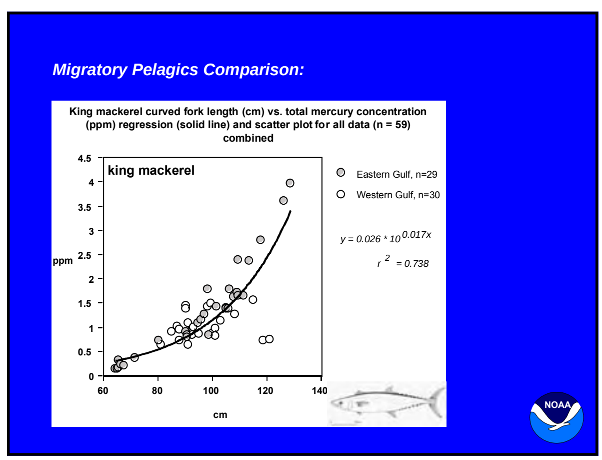

Migratory Pelagics Comparison
UNITED STATES
GULF OF MEXICO

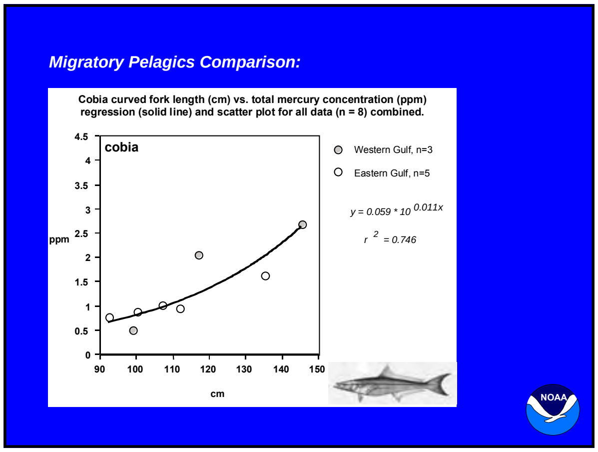

Migratory Pelagics Comparison: species
Tunas little tunny Euthynnus alletteratus
blackfin tuna Thunnus atlanticus
yellowfin tuna Thunnus albacares
Mackerels king mackerel Scomberomorus cavalla
Cobia cobia Rachycentron canadum
Dolphin dolphin Coryphaena hippurus
NOAA

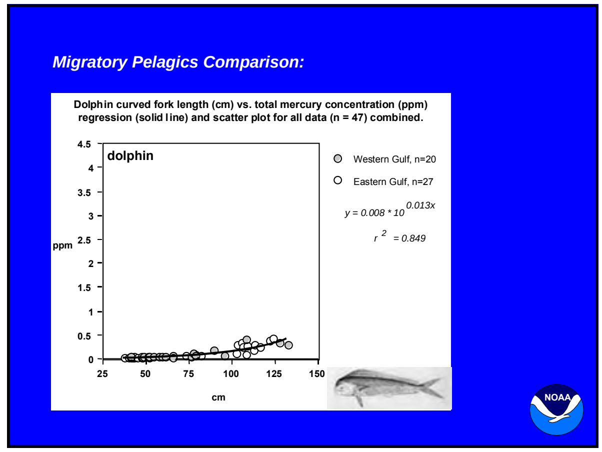

Migratory Pelagics Comparison:
Little tunny curved fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 40) combined.
little tunny
Western Gulf, n=30
Eastern Gulf, n=10
y = 0.080 * 10 0.016x
r 2 = 0.429
ppm
cm
NOAA


Migratory Pelagics Comparison:
Blackfin tuna curved fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 32) combined
blackfin tuna
Western Gulf, n=30
Eastern Gulf, n=2
y = 0.022 * 10 0.022x
r 2 = 0.642
ppm
cm
NOAA


Migratory Pelagics Comparison:
Yellowfin tuna curved fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 13) combined.
yellowfin tuna
Western Gulf, n=3
Eastern Gulf, n=10
y = 0.002 * 10 0.017x
r 2 = 0.735
ppm
cm
NOAA


Migratory Pelagics Comparison:
King mackerel curved fork length (cm) vs. total mercury concentration (ppm) regression (solid line) and scatter plot for all data (n = 59) combined
king mackerel
Eastern Gulf, n=29
Western Gulf, n=30
y = 0.026 * 10 0.017x
r 2 = 0.738
ppm
cm
NOAA





Acknowledgements

This survey was a multi-agency State and Federal collaboration. NOAA FisheriesÕ(aka National Marine Fisheries ServiceÕs) National Seafood Inspection Laboratory designed the survey, coordinated the funding & sampling, carried out the mercury analyses, and conducted the data analyses. EPAÕs Gulf of Mexico Program provided funding in the form of an interagency agreement which was used to fund most of the sampling in the field. The Gulf States Marine Fisheries Sampling Programs provided the field sampling in the estuaries, rigs & reefs, and pelagics. Texas Sea Grant provided field sampling for pelagics. NMFS Pascagoula Fisheries Laboratory provided field sampling for rig, reef, and pelagic species.

E. Spencer Garrett III, NOAA FisheriesÕNational Seafood Inspection Laboratory conceived the survey.

Tony Lowery, NOAA FisheriesÕNational Seafood Inspection Laboratory designed, coordinated, analyzed data, and generated the first draft of the report of findings for the survey.

Al Rainosek, NOAA FisheriesÕNational Seafood Inspection Laboratory statistical analyses & review.

Kenneth Powell, NOAA FisheriesÕNational Seafood Inspection Laboratory for field sampling coordination and chemical analyses.

Steve Winters, NOAA FisheriesÕNational Seafood Inspection Laboratory for chemical analyses coordination.

Phan Nguyen, NOAA FisheriesÕNational Seafood Inspection Laboratory for chemical analyses.

Ginny Steele, NOAA FisheriesÕNational Seafood Inspection Laboratory for sample management.

Lori Robinson, NOAA FisheriesÕNational Seafood Inspection Laboratory for data entry coordination.

John Tennyson, NOAA FisheriesÕNational Seafood Inspection Laboratory for QA coordination.

Kit Doncaster, National Marine Fisheries Service for sampling Southern TX Migratory Pelagic Species species.

Tim Bonner & students, TX State University, San Marcos for sampling Southern TX Migratory Pelagic Species species.

Drew Hopper & Kendall Falana, National Marine Fisheries Service for provision of Central Gulf reconnaissance samples.

Fred Kopfler, Jim Gittano, & Bryon Griffith, EPAÕs Gulf of Mexico Program (EPA-COMP) for providing EPA-NOAA interagency coordination for DW13945924 and funding.

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Randy Pausina & Jason Adriance, Louisiana Dept. of Wildlife and Fisheries for sampling LA oil rigs species.

Steve Heath, Mark VanHoose, & John Mareska, Alabama Dept. Conservation & Natural Resources for sampling Mobile Bay species.

Mark Fisher, Bill Balboa, James Shuler, Rebecca Hensley, & Glen Sutton, Texas Parks and Wildlife for sampling Matagorda Bay & Galveston Bay estuarine species.

Bob McMichael, Gregory Onorato, Florida Fish and Wildlife Conservation Commission for sampling Tampa Bay estuarine species.

Joseph OÕHop & Kelley Kowal, Florida Fish and Wildlife Conservation Commission for sampling FL Natural Reefs species & Southern FL Migratory Pelagic species.

Kevin Rademacher & Lisa Jones, National Marine Fisheries Service for sampling Southern FL Migratory Pelagic species.

Tony Reisinger, Texas Sea Grant Marine Extension Sevice for sampling Southern TX Migratory Pelagic Species species.

Questions and Answers

Q. How did the methods used in this study compare to studies looking at filet data?

A. As long as the filet homogenate was consistent, the results should be uniform. We avoided the bone and/or fatty areas of the fish.

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Report on EPA's National Lake Fish Tissue Survey

Leanne Stahl, Office of Science and Technology, Office of Water, U.S. EPA

Biosketch

Ms. Leanne Stahl is an Environmental Scientist in EPA's Office of Science and Technology within the Office of Water. She received a B.S. degree in Biological Oceanography from the University of Washington in Seattle and completed graduate courses in Fisheries. For 6 years, she worked on fisheries research projects at the University of Washington before joining the federal service. Ms. Stahl began her federal career at NOAA by managing coastal monitoring programs before moving to EPA in 1990. Since 1999, she has served as Program Manager of the National Study of Chemical Residues in Lake Fish Tissue, and she is currently managing the EPA Pilot Study of Pharmaceuticals and Personal Care Products in Fish Tissue.

Abstract

The National Study of Chemical Residues in Lake Fish Tissue (or National Lake Fish Tissue Study) is one of a series of statistically based national environmental surveys conducted by the U.S. Environmental Protection Agency (EPA) since the late 1990s. It is a national screening-level survey of chemical residues in fish tissue from lakes and reservoirs in the contiguous United States, excluding the Laurentian Great Lakes and Great Salt Lake. Two features make this study unique: it is the first national freshwater fish contamination survey with sampling sites selected according to a statistical design and it includes the largest set of chemicals studied in fish. From October 1999 through November 2003, EPA and a large network of State, Tribal, and other federal partners collected fish composite samples from 500 lakes and reservoirs in the lower 48 states. Sampling teams collected two five-fish composites at each site: a predator
(e.g., bass or trout) and a bottom-dweller (e.g., carp or catfish). Predator fillets and bottom-dweller whole bodies were analyzed for 268 persistent, bioaccumulative, and toxic (PBT) chemicals, including mercury (Hg), arsenic, dioxins and furans, all 209 polychlorinated biphenyl (PCB) congeners, 46 pesticides, and 40 semivolatile organic compounds.

Results from the National Lake Fish Tissue Study indicate that Hg, PCBs, and dioxins and furans are widely distributed in lakes and reservoirs in the lower 48 states. Hg and PCBs were detected in 100% of the fish samples collected from the 500 sampling sites over a 4-year period. Dioxins and furans were detected in 81% of the predator fillet and 99% of the bottom-dweller whole-body samples. The five most commonly detected chemicals occurred in this order of decreasing prevalence: Hg, PCBs, dioxins and furans, DDT, and chlordane. Forty-three of the target chemicals were not detected in any samples, including 9 organophosphate pesticides and 33 semivolatile organic chemicals.

The National Lake Fish Tissue Study final report will be ready for release in fall 2007. It contains national estimates of the median concentrations for the full suite of target chemicals in lake fish and statistically derived estimates of the percentage of lakes and reservoirs with fish tissue concentrations that exceed EPA's tissue-based water quality criterion for Hg and risk-based human health screening values for the other four commonly detected chemicals.

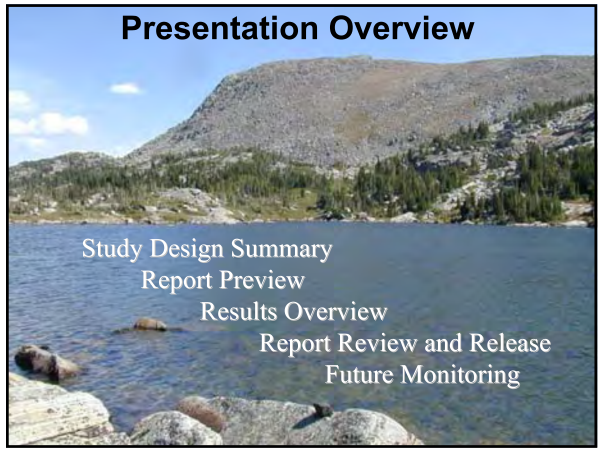
* NOTE: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

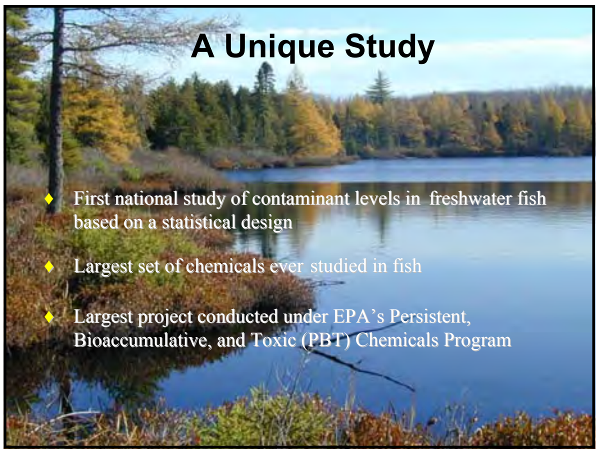
Report on EPA's National Lake Fish Tissue Survey

2007 National Fish Forum

July 23, 2007

Leanne Stahl
Program Manager
Office of Water/
Office of Science & Technology





Objective

- *The objective of the National Lake Fish Tissue Study is to estimate the national distribution of the mean levels of selected persistent, bioaccumulative, and toxic chemical residues in fish tissue from lakes and reservoirs in the contiguous United States.*
- Study results will
  - Provide the first national estimates of median concentrations of PBT chemicals in fish tissue.
  - Define a national baseline for assessing progress of pollution control activities.

4

Sampling Design

- Random selection of lakes and reservoirs in 4 national annual statistical subsets
- 500 lakes and reservoirs in the lower 48 states sampled over 4 years (2000-2003)
- Exclusion of Great Lakes due to existing monitoring programs
- Lake criteria
  - Permanent water body with permanent fish population
  - Minimum surface area of one hectare (~2.5 acres)
  - 1000 square meters of open, unvegetated water
  - Depth of at least one meter

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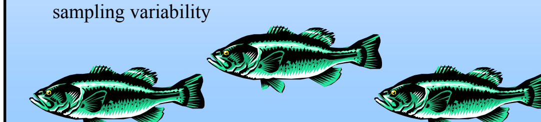
Sampling Design

- Six size categories of lakes ranging from 1 hectare to > 5000 hectares with varying probabilities for each size category
- Two fish composites per site (predators and bottom dwellers) with 5 adult fish per composite
- Preparation of 560 g of tissue for analysis
- Collection of replicate samples from 10% of the lakes to estimate sampling variability



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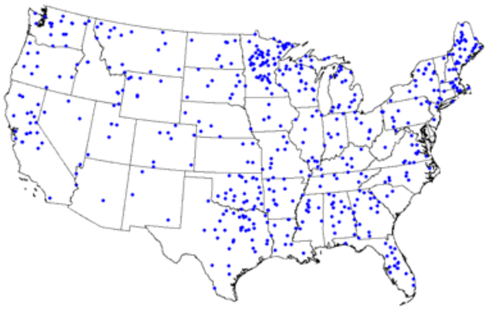
500 Sampling Locations



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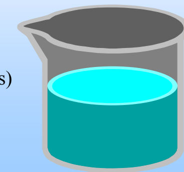
Target Chemicals

- Fish tissue analyzed for 268 chemicals, including PCB congeners and breakdown products.
  - 2 metals (Hg and As [5 forms])
  - 17 dioxins/furans
  - 159 PCB congener measurements
  - 46 pesticides
  - 40 semivolatile organics (e.g., PAHs)
- PBDE analysis added for Year 4 samples only.



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Key Milestones

ACTIVITY	DATE
Produce study design document	June 1999
Complete sample collection	November 2003
Distribute final year of analytical data	April 2005
Release all raw data to the public	October 2005
Develop draft final report	January 2007
Initiate external peer review of report	June 2007

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Final Report Framework

- The National Lake Fish Tissue Study draft report is a 238-page document that includes 9 appendices.
- The main body of the report contains four chapters.
  - **Chapter 1:** Introduction
  - **Chapter 2:** Summary of study design and sample collection/analysis approach
  - **Chapter 3:** Presentation of study results
  - **Chapter 4:** Conclusions and recommendations

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Essential Results Information

The following information is critical for interpreting the results:

- Predator and bottom-dwelling species did not occur together at every sampling site.
  - The target lake was sampled if either composite type occurred.
  - 486 predator composites and 395 bottom-dweller composites were collected from the 500 sampling sites.
- Results from each composite type comprise nationally representative samples, but differences in occurrence define different sampled populations.
  - Predator results can be extrapolated to 76,559 lakes.
  - Bottom-dweller results can be extrapolated to 46,190 lakes.
- Developing national estimates of tissue concentrations requires use of sample weights due to the unequal probability design.

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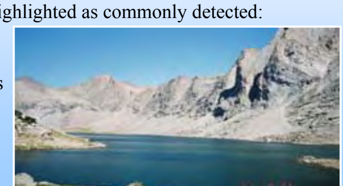
Reporting the Results

- Analytical results are presented in three tiers:
  - Non-detected chemicals
  - Rarely-detected chemicals
  - Commonly-detected chemicals
- Five chemicals are highlighted as commonly detected:
  - Mercury
  - PCBs
  - Dioxins and furans
  - Total DDT
  - Chlordane



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Chemical Detections

CHEMICAL	PREDATORS	BOTTOM DWELLERS
Mercury	100%	100%
PCBs	100%	100%
Dioxins/furans	81%	99%
Total DDT	78%	98%
Chlordane	20%	50%

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2006 Fish Advisories

CHEMICAL	NO. OF ADVISORIES	LAKE ACRES UNDER ADVISORY
Mercury	3,080	14,177,175
PCBs	1,023	4,699,936
Dioxins	125	38,181
DDT	84	827,612
Chlordane	105	847,771

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Percentile Tables

Tissue Concentration Estimates for Predators (Fillets)

Chemical	Number of Samples	Number of Detects	Maximum Concentration	Units	5th Percentile	10th Percentile	25th Percentile	50th Percentile	75th Percentile	90th Percentile	95th Percentile
PCB 84	486	449	2320	ppt	< MDL	< MDL	0.97	3.02	10.01	31.61	85.04
PCB 85 + PCB 116 + PCB 117	486	485	7980	ppt	2.84	3.81	8.76	17.97	64.98	179.65	300.95
PCB 86 + PCB 87 + PCB 97 + PCB 108 + PCB 119 + PCB 125	486	476	18900	ppt	1.96	6.86	14.89	37.03	126.15	418.07	660.55
PCB 88 + PCB 91	486	469	4770	ppt	< MDL	0.77	1.72	4.33	14.31	73.43	113.10
PCB 89	486	121	22.3	ppt	< MDL	< MDL	< MDL	< MDL	< MDL	0.76	1.26
PCB 90 + PCB 101 + PCB 113	486	484	36500	ppt	10.30	15.72	38.92	80.10	262.84	884.10	1420.95
PCB 92	486	481	8620	ppt	1.83	2.94	6.99	15.23	54.77	187.79	303.98

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Tissue Concentrations

Chemicals	Predators (ppb)		Bottom Dwellers (ppb)	
	Median	Maximum	Median	Maximum
Mercury	285	6605	69	596
PCBs	2	705	14	1266
Dioxins/furans	6×10^{-6}	8×10^{-3}	4×10^{-4}	2.4×10^{-2}
DDT	1.5	1481	13	1761
Chlordane	<MDL	100	2	378

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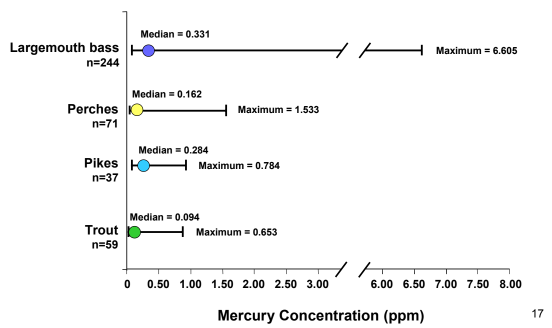
Mercury Median Concentrations



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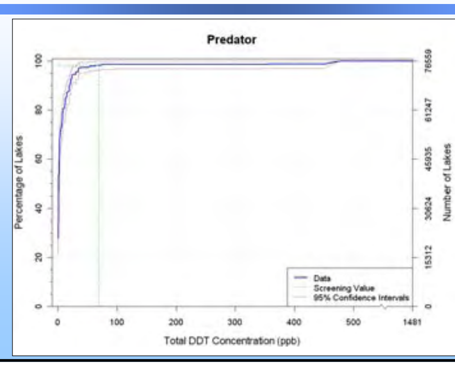
Cumulative Density Functions



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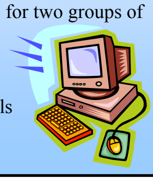
Sampling Variability

- Results from standard and replicate samples were compared using a tiered approach.
  - **Tier 1:** Agreement between paired sample results using detection limits
  - **Tier 2:** Comparison of tissue concentrations when at least one paired result was > MDL
- There was perfect agreement in detections for two groups of sample pairs:
  - All mercury results for the 70 predator and the 52 bottom-dweller sample pairs
  - The full set of 43 non-detected chemicals



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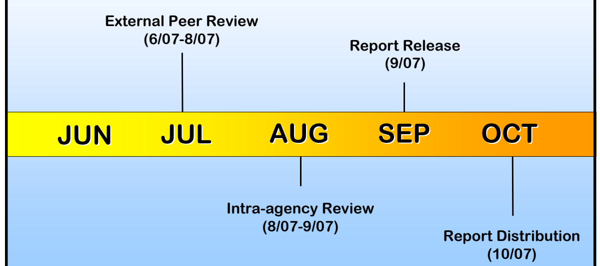
Report Review and Distribution



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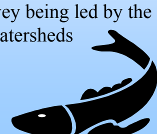
Future Direction

- Shift in monitoring focus to prevalent and emerging contaminants in fish
  - Complete EPA Pilot Study of Pharmaceuticals and Personal Care Products (PPCPs) in Fish Tissue
  - Analyze National Lake Fish Tissue archived samples for emerging contaminants
  - Participate in the Large Rivers Survey being led by the Office of Wetlands, Oceans, and Watersheds





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Questions and Answers

Q. Did the National Lake Fish Tissue Study select whole bodies to look at human health issues?

A. We analyzed whole bodies for the purposes of evaluating aquatic life and human health.

Q. Can you extrapolate data to give the lake condition of individual lakes? Could the lakes data be extrapolated for all 76,000 lakes? Which lakes?

A. We can evaluate the condition of the set of lakes that meet all five criteria. Exceptions include lakes that were not accessible (private property and remote area lakes). We developed Cumulative Distribution Functions for all the data, and we have confidence intervals to look at the extrapolated lakes.

Q. Is there a plan to mine these data further?

A. I am not aware of any additional analyses taking place but we are hoping to create more data in the future.

EPA Pilot Study on Pharmaceuticals and Personal Care Products (PPCPs) in Fish Tissue:

PPCPs as Emerging Contaminants

John Wathen, Office of Science and Technology, Office of Water, U.S. EPA

EPA PPCP Fish Pilot Study

Leanne Stahl, Office of Science and Technology, Office of Water, U.S. EPA

Biosketches

Mr. John Wathen is the Acting Chief of Fish, Shellfish, Beaches, and Outreach Branch (FSBOB) in the Standards and Health Protection Division of the Office of Science and Technology in EPA's Office of Water. Mr. Wathen received his B.A. degree in Geology from Northeastern University and an M.S. degree in Earth Sciences from the University of New Hampshire. He worked as a consulting hydrogeologist for 15 years. In this capacity, he conducted landfill siting and closure investigations, industrial site remediation, and water source protection studies, primarily in northern New England. In 2000, he entered the public sector as Director of the Southern Maine Regional Office of the Maine Department of Environmental Protection, and he held this position until joining EPA in 2005. EPA's Beaches Environmental Assessment and Coastal Health (BEACH) Act monitoring and advisory program and fish research and advisory programs are housed in the branch he currently manages. Mr. Wathen is a Maine-certified Geologist and a Certified Ground Water Professional.

Ms. Leanne Stahl is an Environmental Scientist in EPA's Office of Science and Technology within the Office of Water. She received a B.S. degree in Biological Oceanography from the University of Washington in Seattle and completed graduate courses in Fisheries. For 6 years, she worked on fisheries research projects at the University of Washington before joining the federal service. Ms. Stahl began her federal career at NOAA by managing coastal monitoring programs before moving to EPA in 1990. Since 1999, she has served as Program Manager of the National Study of Chemical Residues in Lake Fish Tissue, and she is currently managing the EPA Pilot Study of Pharmaceuticals and Personal Care Products in Fish Tissue.

Abstract

Pharmaceuticals and personal care products (PPCPs) are a sub-class of a broader group of emerging contaminants. These potential contaminants are currently the subject of scientific study and evaluation at the U.S. Environmental Protection Agency (EPA) and elsewhere both in terms of occurrence in a range of media and for ecological and human health effects resulting from their presence in surface water. This presentation describes the context of PPCPs relative to other compounds, in terms of basic mechanisms of occurrence and exposure pathways, and their place in the regulatory structure. It also serves as an introduction to a more detailed description of the EPA PPCP Fish Tissue Pilot Study which follows.

EPA's Office of Science and Technology within the Office of Water is conducting three studies to investigate the occurrence of PPCPs in various media. One of these studies is the EPA Pilot Study of PPCPs in Fish Tissue. This study involved collecting fish from five effluent-dominated streams and one reference site in different areas of the country during the summer and fall of 2006. An analytical laboratory at Baylor University is analyzing composites of fish fillets and livers for 34 PPCPs. Results from the study should be available in winter 2008. For more information about this study, refer to the poster abstract "EPA Pilot Study of PPCPs in Fish Tissue."

PPCPs as Emerging Contaminants

John B. Wathen, C.G.
Fish Shellfish Beaches and Outreach Branch (FSBOB)
Standards and Health Protection Division
Office of Science and Technology
Office of Water
U.S. Environmental Protection Agency
Washington, DC

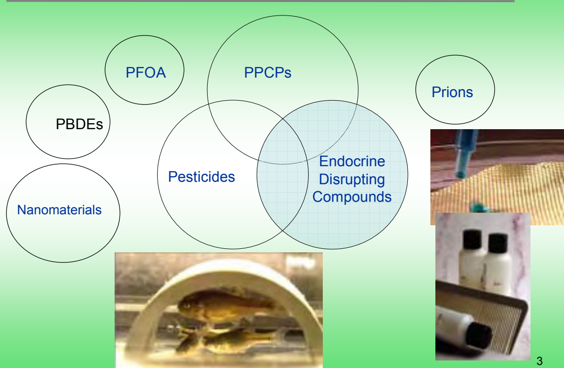
2007 Fish Forum
Portland, Maine
July 23, 2007

Overview

- OW effort to assess the presence of a broader range of compounds in surface water
- EPA regulatory framework related to emerging contaminants
- EPA Activities and Research Plans
- Other observations about the occurrence of environmental contaminants in water

2

*Emerging Contaminants of Potential Concern in Water**



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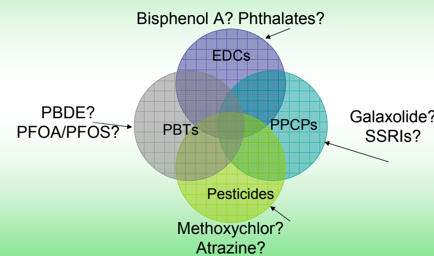
*Not an exhaustive list.

Context of PPCPs

Among Contaminants of Potential Concern



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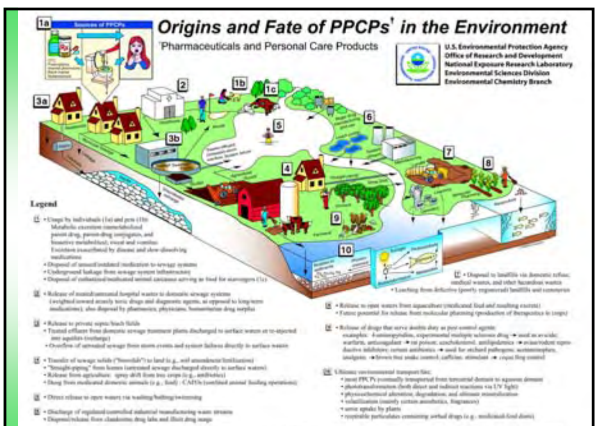
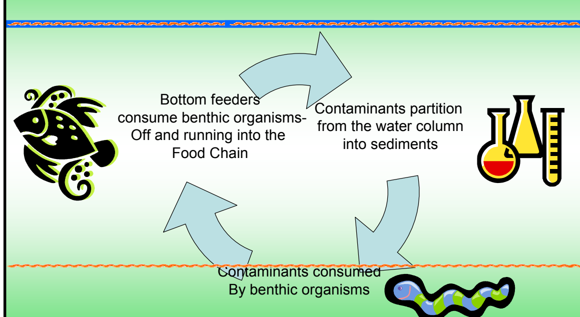


Available: http://www.epa.gov/nerlesd1/chemistry/pharma/image/drawing.pdf

Water column/sediment/fish interaction



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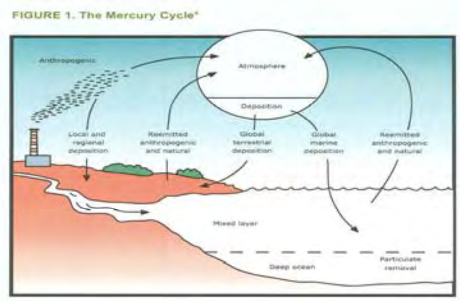
One cycle among many…



From EPA Mercury Roadmap, July 2006

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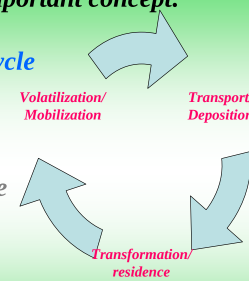
Cycles are an important concept:

- Hydrologic Cycle
- Carbon Cycle
- Mercury Cycle
- P-O-P Cycle



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Ecological Effects: List of EDCs/ Pharmaceuticals Tested at Duluth-ORD

Chemical	MOA	Nominal Concentrations	Spawning Ratio
Methoxychlor	ER Agonist	0.5 and 5 μg/L	4/2
Methyltestosterone (12-d exposure due to mortality)	AR Agonist	0.2 and 2 mg/L	4/2
β-Trenbolone	AR Agonist	0.005, 0.05, 0.5, 5, and 50 μg/L	4/2
α-Trenbolone	AR Agonist	0.003, 0.01, 0.03, and 0.1 μg/L	1/1
Vinclozolin	AR Antagonist	200 and 700 μg/L	1/1
Flutamide	AR Antagonist	50 and 500 μg/L	4/2
Fadrozole	Aromatase Inhibitor	2, 10, and 50 μg/L	4/2
PFOS (14 d exposure at 1.0 mg/L due to mortality)	Aromatase Inhibitor	0.03, 0.1, 0.3 and 1.0 mg/L	1/1
Prometon	Aromatase Inhibitor	15, 50, 250, and 1250 μg/L	1/1
Fenarimol	Aromatase Inhibitor, ER Agonist, AR Antagonist	0.1 and 1.0 mg/L	1/1
Prochloraz	Aromatase Inhibitor, AR/ER Antagonist	0.03, 0.1, and 0.3 mg/L	1/1

9

After: Lazorchak, 2007

Legislative Authorities for Water

- **Clean Water Act (1977)**
  - Sets water quality criteria and guidelines and technology-based standards for ambient water
  - **Sets fishable/swimable standard for U.S. Waters**

- **Safe Drinking Water Act (1974), amended 1986, 1996**
  - Requires EPA to set maximum levels for contaminants in water delivered to users of public water systems.

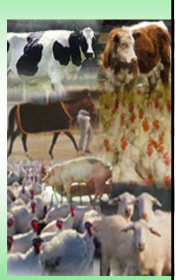
10

EPA Statutory Framework

A. Clean Water Act

- Effluent Guidelines for the regulation of point sources
- Combined Animal Feeding Operations Rule
- **Human Health and Aquatic Life Criteria**

(including new Hg fish tissue criterion)



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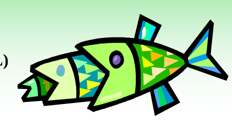
Statutory Framework (Cont'd)

B.Safe Drinking Water Act (SDWA)
- **Six Year Review**
- **Health Advisories**
- **Contaminant Candidate List (CCL)**



C. Resource Conservation and Recovery Act (RCRA)
- **Universal Waste Rule**

D. Toxic Substances Control Act (TSCA)
- **High Production Volume Chemical List**
- **PMN Reviews**

E. Food Quality Protection Act & FIFRA
- **Endocrine Disruptors Screening Program**
- **New Pesticide Registration**
- **Pesticide Re-Registration and Registration Review**

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EPA Research and Studies

- **Office of Research and Development**
  - STAR Grants Program
  - Research targeted at development of new chemical analysis methods, improved waste treatment, aquatic effects and new approaches for prioritizing chemicals for monitoring
  - Endocrine Disruptors Research Program
- **Office of Water (OST)**
  - **Fish Tissue Study**
  - POTW Study
  - Biosolids Survey

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Next Steps

- For OW, other compounds, other settings as resources permit
- Collaborate with Federal/non-Federal partners in targeting research and testing to fill data gaps to support criteria development/ regulatory action

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EPA PPCP Fish Pilot Study

Obtaining data on emerging contaminants is a priority for EPA.

- Recent research indicates that PPCPs occur widely in surface water, sediment, and municipal effluent.
- Limited data are available on accumulation of PPCPs in fish.

In 2006, OST initiated the EPA Pilot Study of PPCPs in Fish Tissue to investigate PPCP occurrence in fish tissue.

Several collaborators are contributing to this project, including:

- Baylor University Center for Reservoir and Aquatic Systems
- EPA Great Lakes National Program Office
- Metropolitan Water Reclamation District of Greater Chicago
- New Mexico Environment Department

1

Study Design

The targeted study design involved the following components:

- Sampling fish from five effluent-dominated streams and one reference site in various parts of the country
- Collecting six composites containing three or four adult fish of the same resident species in the vicinity of WWTP discharges
- Freezing and shipping whole fish to an analytical laboratory at Baylor University
- Analyzing fillet and liver tissue samples from each fish composite
  - 24 pharmaceutical compounds using a liquid chromatography-tandem mass spectrometry (LC-MS/MS) method
  - 10 personal care products using a gas chromatography-tandem mass spectrometry (GC-MS/MS) method

2

Site Selection Criteria

EPA identified five priority sites using the following selection criteria:

- Effluent-dominated stream segments near WWTP discharges
- WWTP discharges subject to different levels of treatment
- Urban/suburban areas with high population densities
- Geographic areas with a larger percentage of elderly residents
- Availability of sufficient numbers and sizes of fish

3

Fish Samples

State	Sampling Locations	Date	Species	No. of Fish
AZ	Salt River, Phoenix	Nov. 2006	Common carp	18
FL	Little Econlockhatchee River, Orlando	Oct. 2006	Bowfin	17
IL	North Shore Channel, Chicago	Sep. 2006	Largemouth bass	24
NM	East Fork Gila River (*Reference Site*)	Nov. 2006	Sonora sucker	24
PA	Taylor Run, West Chester	Aug. 2006	White sucker	24
TX	Trinity River, Dallas	Oct. 2006	Smallmouth buffalo	18

4

Target Chemicals

EPA is analyzing fillet and liver tissue samples for 24 pharmaceutical compounds and 10 personal care products.

Pharmaceuticals

- 3 analgesics
- 1 anti-acid reflux
- 6 antibiotics
- 1 anticoagulant
- 3 antidepressants
- 1 anti-fungal agent
- 1 antihistamine
- 4 anti-hypertension
- 1 antilipemic
- 1 anti-seizure
- 1 antispasmodic
- 1 stimulant

Personal Care Products

- 1 antimicrobial compound
- 3 fragrances/musks
- 1 insecticide
- 3 surfactants
- 2 UV filtering compounds

5

For More Information…

Visit the following posters during the reception and poster session:

- EPA Pilot Study of PPCPs in Fish Tissue
  - Leanne Stahl, et al.
- Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River
  - Elizabeth Murphy, et al.

6

Questions and Answers

Q. *How did you go about attempting to set data quality objectives for the analytical processes? How confident were you that you could achieve those objectives?*

A. We used the same level of quality assurance as used in the National Lake Fish Tissue Study. An analytical chemist at Tetra Tech worked to define the data quality objectives and to collaborate with the lab involved.

Polybrominated Diphenyl Ethers (PBDEs) in Fish from the Delaware River Drainage Basin

Richard Greene, Delaware Department of Natural Resources and Environmental Control

Biosketch

Dr. Rick Greene (Ph.D.) heads the State of Delaware's Fish Contaminant Monitoring and Advisory Program. He has more than 20 years of experience in toxics monitoring, modeling, assessment and control. He received a master's degree in Environmental Engineering from the University of Delaware, where he is currently completing his Ph.D. He is among a select few who has attended all Fish Forums to date.

Abstract

Polybrominated diphenyl ethers (PBDEs) are a group of organohalogen chemicals that were introduced into commerce approximately 30 years ago as flame retardants. They have been used in thousands of products to prevent fires, including polyurethane foam in furniture and seating, textiles and fabrics, printed circuit boards, and coatings on electrical wire. Not long after their introduction into the marketplace, PBDEs began showing up in environmental samples. At present, they have been documented in human blood and milk; terrestrial and aquatic mammals; fish, birds, plants, air, soil, aquatic sediments; and water all over the globe, often showing an exponential increase over time. PBDEs, similar to polychlorinated biphenyls (PCBs) and dioxins and furans, are complex mixtures of congeners with a wide range of physical and chemical properties. Although a substantial amount of information has been generated on PBDEs during the last decade, PBDEs are still considered an "emerging contaminant" because they are not routinely monitored, their fate and transport is not fully understood, and consensus has not been reached concerning their toxicity.

This presentation summarizes the data that have been collected by the States of Delaware and New Jersey, the Academy of Natural Sciences, and the Delaware River Basin Commission on PBDEs in fish collected from the Delaware River Drainage Basin and near-coastal waters. From September 2003 through October 2006, a total of 149 fish samples that represented 18 different species were collected and analyzed for PBDEs. PBDEs were detected in all samples, ranging from a minimum of 0.07 ng/g (ppb) ww fillet to a maximum of 407.9 ng/g ww fillet with a mean of 31.6 ng/g and a median of 9.2 ng/g. PBDEs in fish collected from the Delaware River Drainage Basin are placed into broader perspective through comparison to data collected elsewhere in the United States and abroad. Furthermore, the results of a preliminary risk assessment are presented to provide yet another perspective on the Delaware River data. Finally, future actions regarding PBDE monitoring in the Delaware River Drainage are suggested.

Polybrominated Diphenyl Ethers (PBDEs) in Fish from the Delaware River Drainage Basin

National Forum on Contaminants in Fish
July 23, 2007

Rick Greene
Delaware DNREC

Acknowledgements

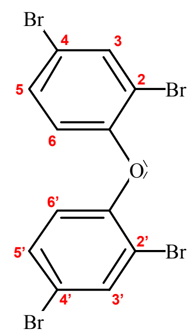
- Collaborators:
  - Gary Buchanan and Bruce Ruppel, NJDEP
  - Jeff Ashley, Phil U and ANS
  - Tom Fikslin and Greg Cavallo, DRBC
- Supplemental Data:
  - Ron Hites, Indiana University (salmon data)
  - Sonya Lunder, EWG (SF Bay striped bass data)
- Mapping:
  - Dave Wolanski, DNREC

Presentation Topics

- **PBDE basics (structure, properties, uses, and distribution)**
- Sample results
- Comparison to other results
- Preliminary risk calcs
- Summary
- Future direction

PBDE Structure & Properties

2,2',4,4'-Tetrabromodiphenyl Ether (BDE-47)



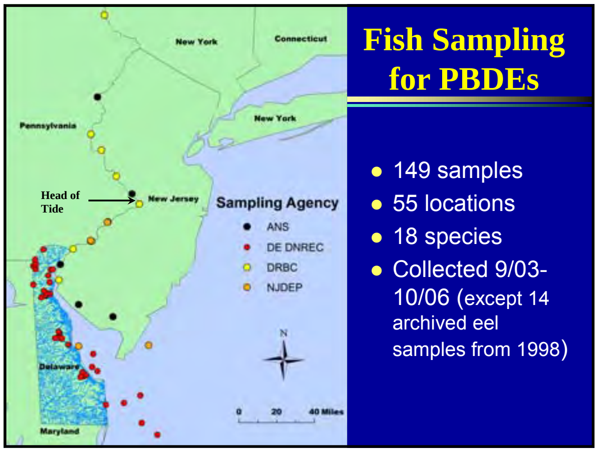
- Organohalogens
- $C_{12}H_{10-x}Br_xO$ (X=1-10) 209 possible congeners
- Hydrophobic, (leads to increased partitioning into organic phases).
- P-C properties vary with # and position of bromines: experimental data sparse but growing

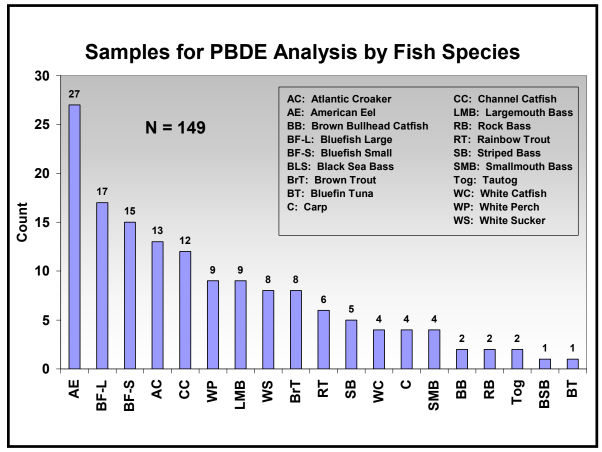
Uses and Distribution

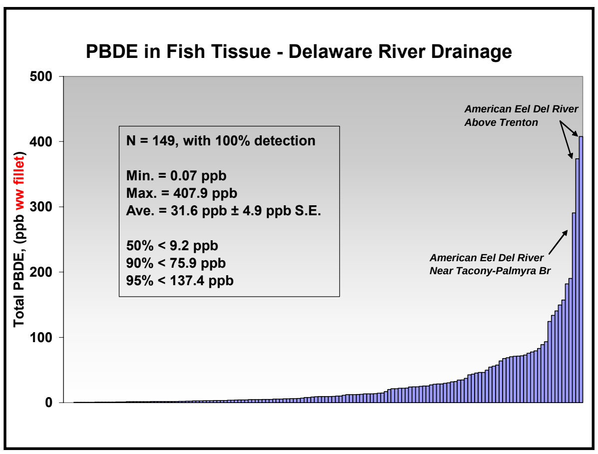
- Introduced ~30 yrs ago. 'Emerging contaminant'?
- In 1000s of consumer products as flame retardants (e.g., foam in seating, textiles, circuit boards, wire coating, etc.).
- Widely distributed in the global environment (people, bears, whales, fish, algae, air, water, ww, sludge, soil, sediment, & house dust). Increasing US trends; falling European trends.
- Manufacturing bans.

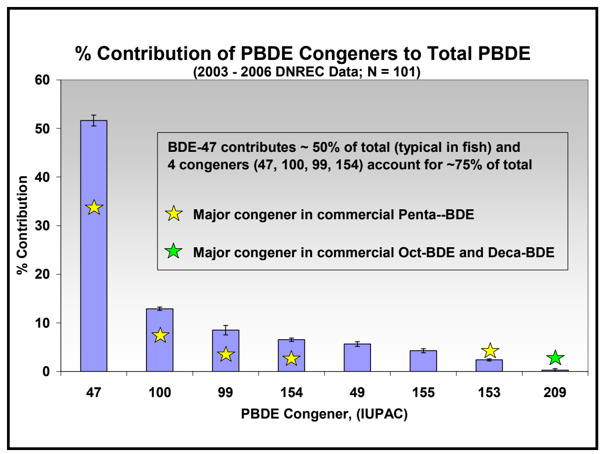
Topics

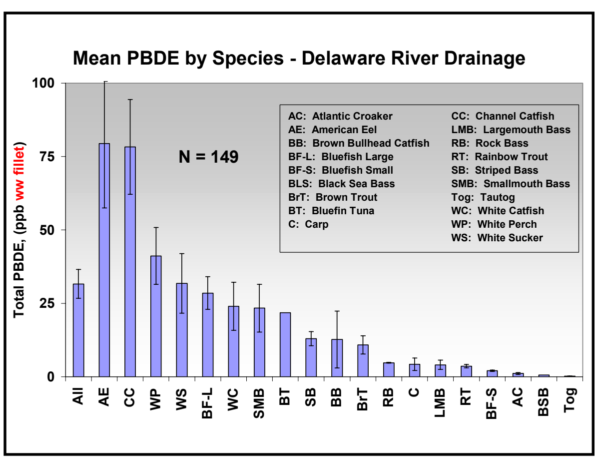
- PBDE basics (structure, properties, uses, and distribution)
- **Sample results**
- Comparison to other results
- Preliminary risk calcs
- Summary
- Future direction

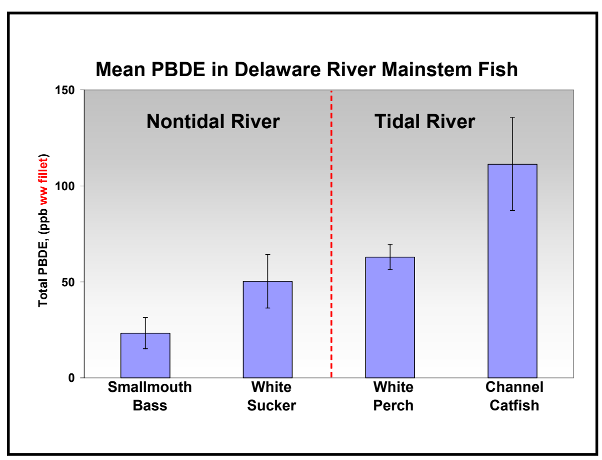

Fish Sampling for PBDEs
149 samples
55 locations
18 species
Collected 9/03-10/06 (except 14 archived eel samples from 1998)
Sampling Agency
ANS
DE DNREC
DRBC
NJDEP
New York
Connecticut
Pennsylvania
New Jersey
Head of Tide
Delaware
Maryland
N
0 20 40 Miles

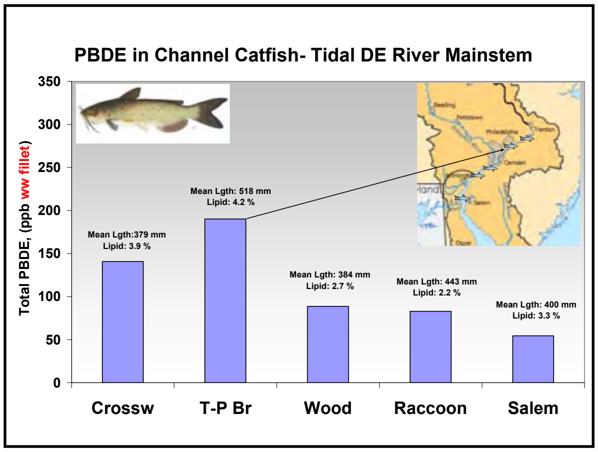

Samples for PBDE Analysis by Fish Species
N = 149
Count
AC: Atlantic Croaker
AE: American Eel
BB: Brown Bullhead Catfish
BF-L: Bluefish Large
BF-S: Bluefish Small
BLS: Black Sea Bass
BrT: Brown Trout
BT: Bluefin Tuna
C: Carp
CC: Channel Catfish
LMB: Largemouth Bass
RB: Rock Bass
RT: Rainbow Trout
SB: Striped Bass
SMB: Smallmouth Bass
Tog: Tautog
WC: White Catfish
WP: White Perch
WS: White Sucker
AE 27, BF-L 17, BF-S 15, AC 13, CC 12, WP 9, LMB 9, WS 8, BrT 8, RT 6, SB 5, WC 4, C 4, SMB 4, BB 2, RB 2, Tog 2, BSB 1, BT 1

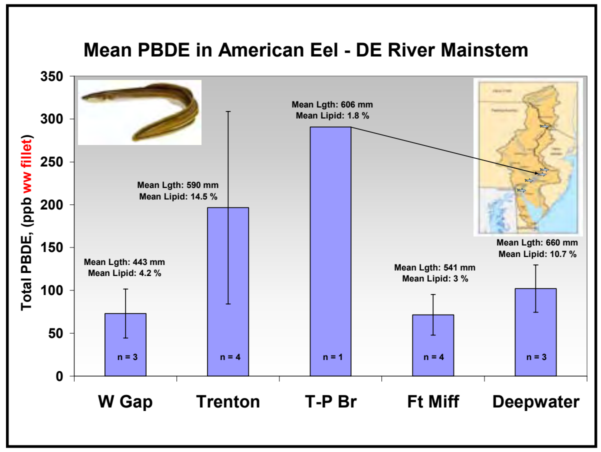

PBDE in Fish Tissue - Delaware River Drainage
Total PBDE, (ppb ww fillet)
N = 149, with 100% detection
Min. = 0.07 ppb
Max. = 407.9 ppb
Ave. = 31.6 ppb ± 4.9 ppb S.E.
50% < 9.2 ppb
90% < 75.9 ppb
95% < 137.4 ppb
American Eel Del River Above Trenton
American Eel Del River Near Tacony-Palmyra Br

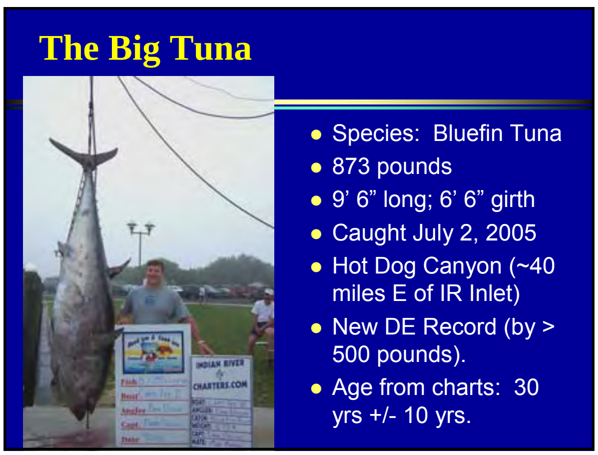

% Contribution of PBDE Congeners to Total PBDE
(2003 - 2006 DNREC Data; N = 101)
% Contribution
BDE-47 contributes ~ 50% of total (typical in fish) and 4 congeners (47, 100, 99, 154) account for ~75% of total
Major congener in commercial Penta--BDE
Major congener in commercial Oct-BDE and Deca-BDE
47 100 99 154 49 155 153 209
PBDE Congener, (IUPAC)

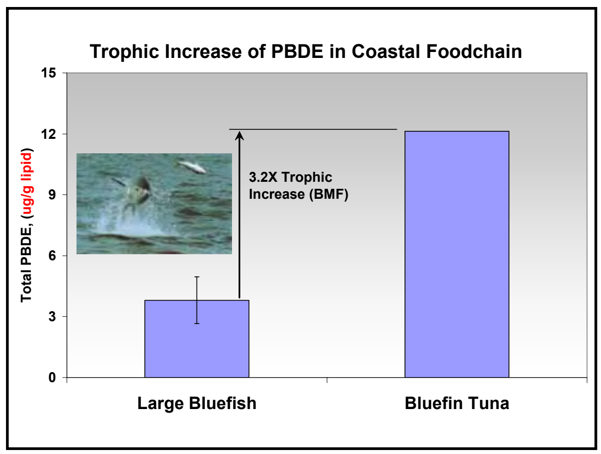

Mean PBDE by Species - Delaware River Drainage
Total PBDE, (ppb ww fillet)
N = 149
AC: Atlantic Croaker
AE: American Eel
BB: Brown Bullhead Catfish
BF-L: Bluefish Large
BF-S: Bluefish Small
BLS: Black Sea Bass
BrT: Brown Trout
BT: Bluefin Tuna
C: Carp
CC: Channel Catfish
LMB: Largemouth Bass
RB: Rock Bass
RT: Rainbow Trout
SB: Striped Bass
SMB: Smallmouth Bass
Tog: Tautog
WC: White Catfish
WP: White Perch
WS: White Sucker
All AE CC WP WS BF-L WC SMB BT SB BB BrT RB C LMB RT BF-S AC BSB Tog

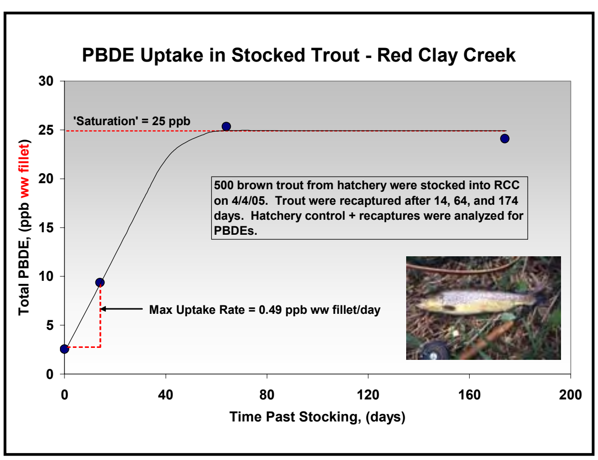

Mean PBDE in Delaware River Mainstem Fish
Total PBDE, (ppb ww fillet)
Nontidal River
Tidal River
Smallmouth Bass
White Sucker
White Perch
Channel Catfish

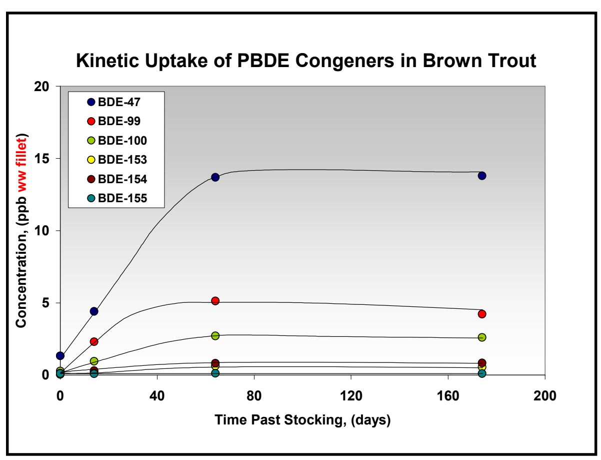

PBDE in Channel Catfish- Tidal DE River Mainstem
Total PBDE, (ppb ww fillet)
Mean Lgth:379 mm
Lipid: 3.9 %
Mean Lgth: 518 mm
Lipid: 4.2 %
Mean Lgth: 384 mm
Lipid: 2.7 %
Mean Lgth: 443 mm
Lipid: 2.2 %
Mean Lgth: 400 mm
Lipid: 3.3 %
Crossw
T-P Br
Wood
Raccoon
Salem

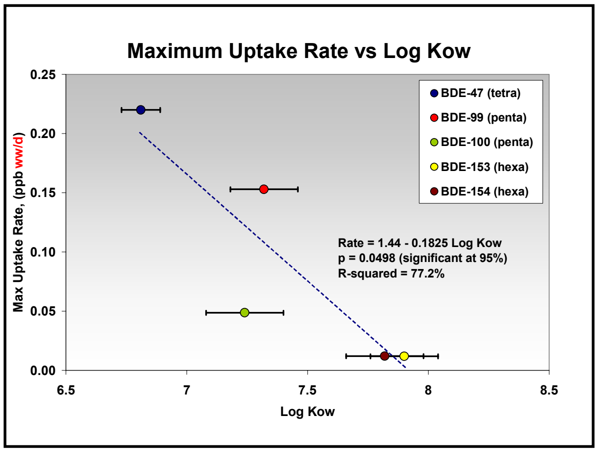

Mean PBDE in American Eel - DE River Mainstem
Total PBDE, (ppb ww fillet)
Mean Lgth: 443 mm
Mean Lipid: 4.2 %
Mean Lgth: 590 mm
Mean Lipid: 14.5 %
Mean Lgth: 606 mm
Mean Lipid: 1.8 %
Mean Lgth: 541 mm
Mean Lipid: 3 %
Mean Lgth: 660 mm
Mean Lipid: 10.7 %
n = 3
n = 4
n = 1
n = 4
n = 3
W Gap
Trenton
T-P Br
Ft Miff
Deepwater


The Big Tuna
Species: Bluefin Tuna
873 pounds
9' 6" long; 6' 6" girth
Caught July 2, 2005
Hot Dog Canyon (~40 miles E of IR Inlet)
New DE Record (by > 500 pounds).
Age from charts: 30 yrs +/- 10 yrs.


Trophic Increase of PBDE in Coastal Foodchain
Total PBDE, (ug/g lipid)
3.2X Trophic
Increase (BMF)
Large Bluefish
Bluefin Tuna

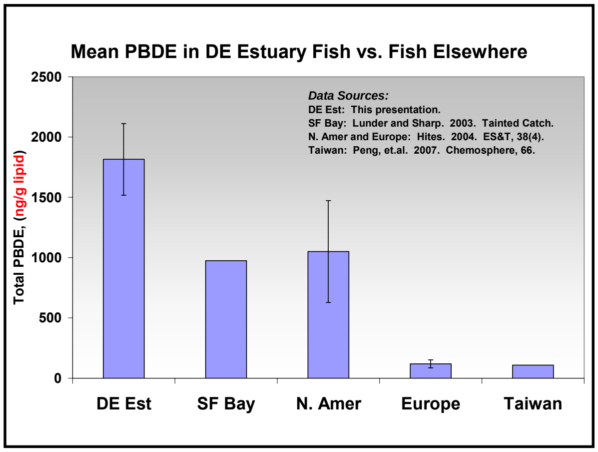

PBDE Uptake in Stocked Trout - Red Clay Creek
Total PBDE, (ppb ww fillet)
'Saturation' = 25 ppb
500 brown trout from hatchery were stocked into RCC on 4/4/05. Trout were recaptured after 14, 64, and 174 days. Hatchery control + recaptures were analyzed for PBDEs.
Max Uptake Rate = 0.49 ppb ww fillet/day
Time Past Stocking, (days)

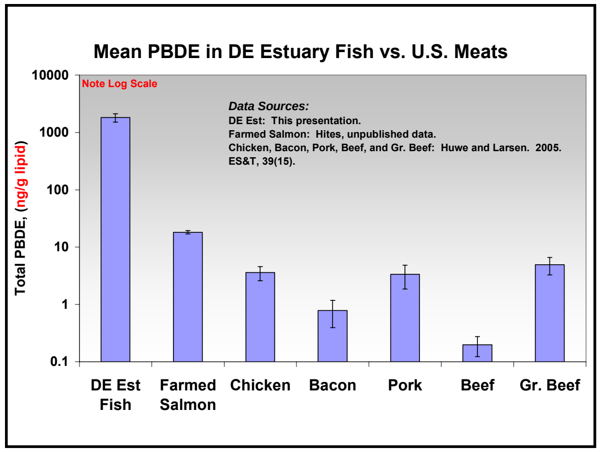

Kinetic Uptake of PBDE Congeners in Brown Trout
BDE-47
BDE-99
BDE-100
BDE-153
BDE-154
BDE-155
Concentration, (ppb ww fillet)
Time Past Stocking, (days)

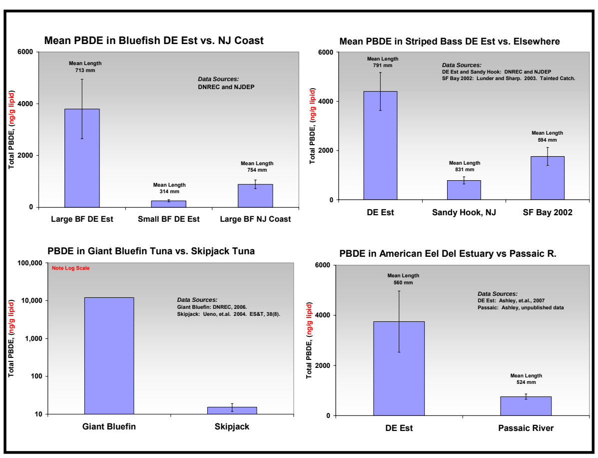


Topics

- PBDE basics (structure, properties, uses, and distribution)
- Sample results
- **Comparison to other results**
- Preliminary risk calcs
- Summary
- Future direction

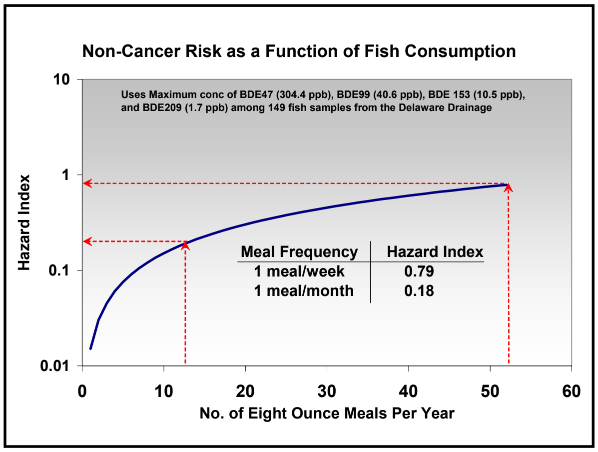


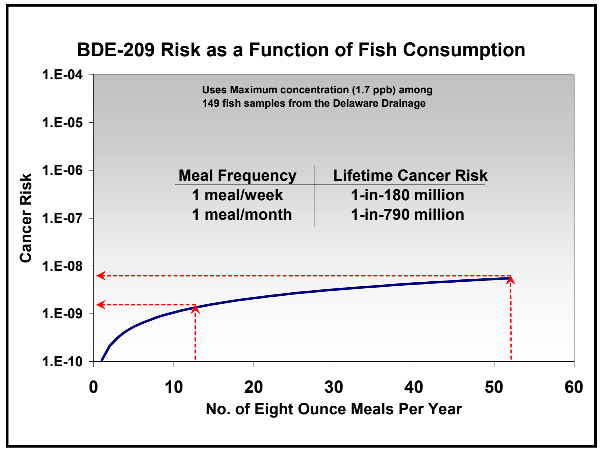




Topics

- PBDE basics (structure, properties, uses, and distribution)
- Sample description and results
- Comparison to other results
- **Preliminary risk calcs**
- Summary
- Future direction





Summary

- Total PBDE in DE Estuary fish: 0.07 – 407.9 ppb ww fillet with mean = 31.6 ppb and median = 9.2 ppb.
- % Contribution: BDE-47 >> 100 > 99 > 154 > 49 > 155 > 153 > 209, with BDE-47 contributing ~50% of total.
- Fish from tidal waters more contaminated than non-tidal and bottom fish more contaminated than pelagic species.
- Uptake in stocked trout is congener-specific and decreases as K_{ow} increases.
- BMF = 3.2 between large bluefish and giant bluefin tuna.
- Total PBDE in DE Estuary fish is greater, on ave., than in fish elsewhere. DE Estuary fish >> other U.S. meats.
- Nevertheless, health risk appears relatively low. Good!

Future

- Prepare journal article.
- Scale back monitoring.
- Revisit selected sites/species in future to assess longer term trends.
- Continue to collaborate/share data.
- Track the literature.

Thank You

Questions and Answers

Q. *Cumulative exposure to PBDEs may stem from other sources such as house dust. Have you taken this into account when issuing fish advisories? (Michigan)*

A. PBDEs are considered "emerging contaminants" because we don't fully understand all of the exposure pathways. A good risk assessment does properly consider all routes of exposure, but we have not completed the assessment.

Q. *Do you know of anyone performing histology on eels?*

A. The majority of the eel data was generated by Jeff Ashley of National Academy of Sciences.

Q. *Have you looked at consumption of multiple fish species to see if varying human exposure levels are found (Mahaffey)?*

A. We are currently working with maximum concentration levels to develop a recommended dosage, but looking at consumption of multiple species may be the next step.

Q. *It appears that PBDE-47 is dwarfing other congeners. Does that have to do with a low partition coefficient, or is it because of its breakdown from deca and octa congeners? Are temporal data available? (Ginsberg)*

A. PBDE-47 is probably most abundant due to a low partition coefficient. PBDE-47 is more mobile and less "sticky." With regard to temporal data, there are some archived data samples, but most of the results are a snapshot. We anticipate looking toward historical analyses.

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Distribution of PBDE Flame Retardants in Fish and Water from Washington Rivers and Lakes

Dale Norton, Washington State Department of Ecology

Biosketch

Mr. Dale Norton received his B.S. degree in Marine Resources from Huxley College of Environmental Studies at Western Washington University in 1980. Since then, he has worked at the Washington State Department of Ecology, where he serves as Lead Scientist on a wide variety of environmental research and monitoring programs. During the last 20 years his work has focused on toxic contaminations issues (fish tissue, sediments, and water) in marine and freshwater aquatic systems. He currently manages the Toxics Studies Unit (TSU) in the Environmental Assessment Program, which oversees activities such as the Washington State Toxics Monitoring Program, total maximum daily loads (TMDLs) for toxic pollutants, and PBT monitoring.

Abstract

The Washington State Department of Ecology analyzed polybrominated diphenyl ether (PBDE) flame retardants in freshwater fish and water samples collected statewide during 2005 and 2006. This was performed in response to concerns about increasing PBDE levels in the environment and the potential for adverse human health effects from fish consumption. The goal was to establish baseline conditions that could be used to evaluate the effectiveness of the *Washington State PBDE Chemical Action Plan* and other efforts to reduce PBDE inputs to the environment.

Data were obtained on concentrations of PBDE-47, -49, -66, -71, -99, -100, -138, -153, -154, -183, -184, -190, and -209 in approximately 120 fish fillet samples, 23 whole fish samples, and 16 water samples, representing 32 waterbodies. The results were used to evaluate the environmental distribution and accumulation of PBDEs in Washington rivers and lakes.

Total PBDE concentrations appear to be <10 µg/Kg (parts per billion, wet weight) in fish fillets from most Washington rivers and lakes. Certain fish species from several large waterbodies—Palouse River, Columbia River, Lake Washington, Snohomish River, Cowlitz River, and Snake River—have total PBDE concentrations in the 10–200 µg/Kg range. PBDEs in fish from watersheds with minimal human disturbance are at or below the limit of detection. High PBDE levels are found throughout the Spokane River, exceeding 1,000 µg/Kg in some cases.

Distribution of PBDE Flame Retardants in Fish and Water from Washington Rivers and Lakes

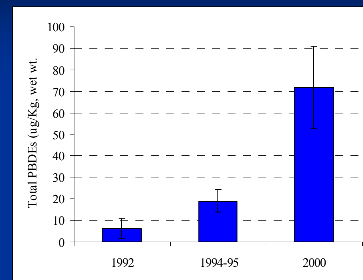
Art Johnson, K. Seiders, C. Deligeannis, K. Kinney, P. Sandvik, B. Era-Miller, D. Alkire, and D. Norton

Washington State Department of Ecology

Environmental Assessment Program

National Forum on Contaminants in Fish 2007
Portland, Maine

Upper Columbia River Whitefish

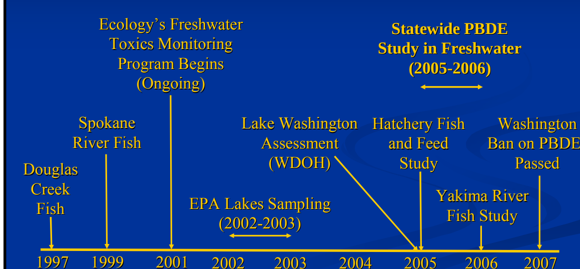


Total PBDE concentrations in Columbia River Mountain Whitefish collected at Genelle, British Columbia (muscle tissue data in Rayne et al., 2003).

Douglas Creek Trout

Displaced Pectoral Fins (Both on one side)

Timeline of PBDE Studies on Freshwater Fish in Washington



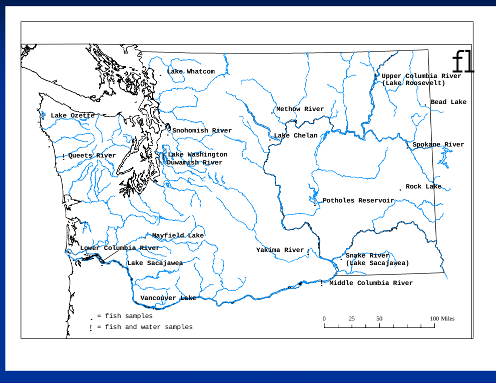
Ecology PBDE Study Goals

- Measure PBDE concentrations in resident freshwater fish fillets from 20 water bodies statewide (benchmark)
- Measure PBDE concentrations in water column at 10 of the fish collection sites.
- Assess seasonal changes in PBDE levels at six of the water sampling sites.
- Evaluate spatial, species, and temporal patterns in the environmental distribution and accumulation of PBDEs.

Study Overview

- Sampling conducted 2005-06
- Resident freshwater fish (20 sites)
- Passive samplers for water (10 sites)
  - Semi-permeable membrane devices (SPMD)
  - Deployed for one month in Fall (10 sites) and Spring (6 sites)
- Analyzed for 13 PBDE congeners

Sampling Sites



Site Information

Waterbody	Fish Samples	Water Samples	County	Drainage Area (sq. miles)	Predominant Land Use
Rivers and Impoundments					
Spokane River	x	x†	Spokane	5,200	urban
Lower Columbia River	x	x†	Cowlitz	256,900	urban
Snohomish River	x		Snohomish	1,720	urban
Duwamish River	x	x†	King	483	urban
Snake River	x		Walla Walla	108,500	agriculture
Yakima River	x	x†	Benton	6,120	agriculture
Middle Columbia River	x	x	Benton	2,214,000	agriculture
Upper Columbia River	x	x	Stevens	64,500	forested
Methow River**	x		Okanogan	1,772	forested
Queets River**	x	x†	Jefferson	143	forested
Lakes					
Lake Washington	x	x†	King	472	urban
Vancouver Lake	x		Clark	39	urban
Lake Sacajawea	x		Cowlitz	6	urban
Lake Chelan	x		Chelan	924	agriculture
Rock Lake	x		Whitman	523	agriculture
Potholes Reservoir	x	x	Grant	4,551	agriculture
Lake Whatcom	x		Whatcom	56	forested
Mayfield Lake	x		Cowlitz	1,400	forested
Bead Lake**	x		Pend Oreille	9	forested
Lake Ozette**	x	x	Clallam	78	forested

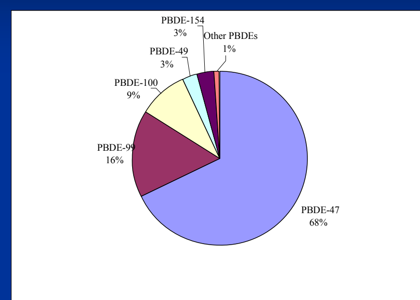
†= Spring and Fall Collection **= Background Site

Summary of PBDE Concentrations in Composite Fish Fillets

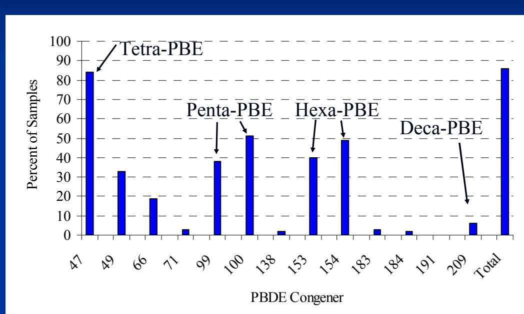
(ug/kg, wet = parts per billion)

PBDE	N	Mean	Minimum	Maximum
47	63	22	0.17	443
49	60	1.3	0.14	13
66	36	1.0	0.29	14
71	63	<0.45	<0.21	0.22
99	63	17	0.15	449
100	63	5.1	0.17	111
138	63	<0.90	0.25	<1.0
153	63	1.1	0.10	17
154	63	0.88	0.11	11
183	63	<0.88	0.25	<1.0
184	60	<0.91	0.21	<1.0
191	60	<0.91	<0.42	<1.0
209	63	<5.3	0.26	<6.2
Total PBDEs	63	35	ND	1,059

Average Contribution of Individual Congeners to Total PBDE's

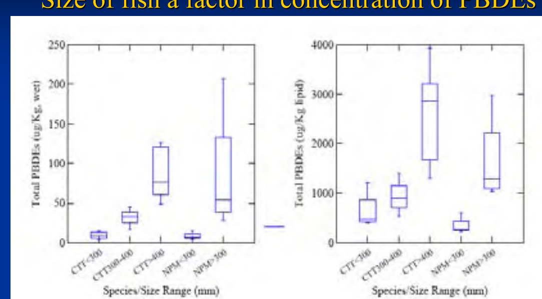


Detection Frequency by Congener in Fish Tissue Fillets



PBDEs vs Length

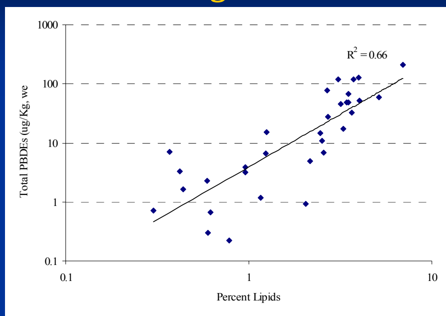
Size of fish a factor in concentration of PBDEs



Lake Washington Data from WDOH

CTT= Cutthroat Trout; NPM= Northern Pikeminnow

PBDE's vs Lipids in Lake Washington Fillets

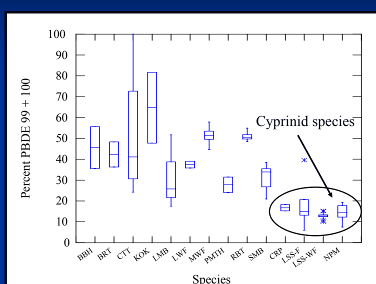


WDOE, 2005 unpublished data

Comparison of Fillets vs Whole Fish (ug/kg, wet)

Location/Species	Fillet	Whole
Spokane River		
Mountain Whitefish	1222	4110
Rainbow Trout	560	1773
Bridgelip Suckers	76	374
Lower Columbia River		
Northern Pikeminnow	17	56
Yakima River		
Smallmouth Bass	8	36

Species Differences



Cyprinid Species Codes

CRP= common carp

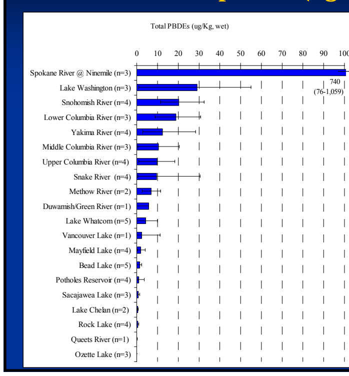
LSS-F= large scale sucker fillet

LSS-WF= large scale suckers whole

NPM= northern pike minnow

Members of minnow family (carp, suckers and pikeminnow) show ability to de-brominate penta-BDEs (-99 and -100)

Ranking by Mean Concentrations in Fillet Composites (ug/kg, wet)



Spokane River= 740
Lake Washington= 29

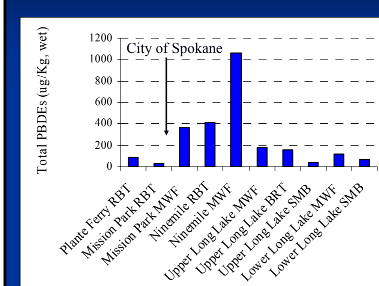
Lower Columbia River= 19

Upper Columbia River= 10

Lake Ozette= Not Detected

Spokane River Collection Sites

PBDEs in Spokane River Fish Fillets

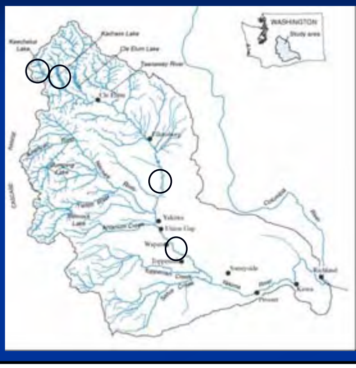


Spokane River

- PBDEs elevated at Idaho Border
- Increase moving downstream-peak at below City of Spokane (Nine mile)
- Decrease downstream of Nine Mile

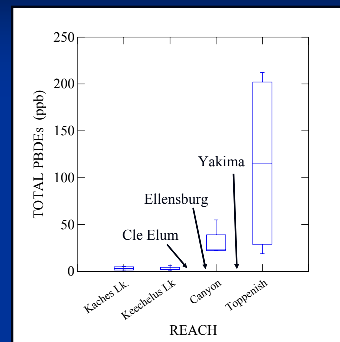
RBT= Rainbow Trout; MWF= Mountain Whitefish; BRT= Brook Trout; SMB= Small Mouth Bass

Yakima River PBDE Fish Sites

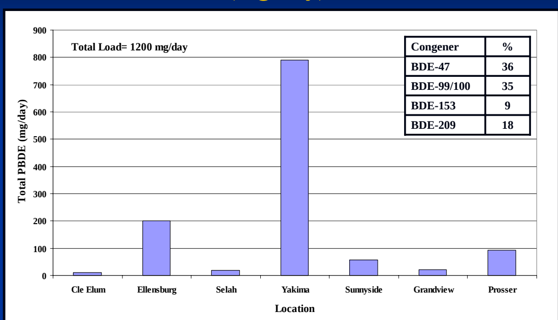


Fish Collection Sites
- Keechelus Lake
- Kachess Lake
- Yakima Canyon
- Wapato-Toppenish

Yakima River Total PBDEs in Fish Fillets



Total PBDEs in Municipal Effluent (mg/day)



Comparison of Washington and North America Data on Fish

Total PBDE's (ug/kg, lipid normalize)

Statistic	Ecology 2005-06 Statewide Study	Major North American Rivers and Lakes (Hites, 2004)
N=	63	281
Mean	1090	1050
Geometric Mean	72	308
Minimum	ND	12
Maximum	29,700	7,200

Water Results from SPMDs

	Total PBDEs pg/l	
	Fall Aug-Sept 05	Spring Mar-Apr 06
Spokane River @ Ninemile	**926**	**146**
Lower Columbia River	21	57
Lake Washington	1	80
Yakima River	3	40
Upper Columbia River	16	NA
Duwamish River	ND	NA
Middle Columbia River	50	NA
Potholes Reservoir	9	NA
Ozette Lake	4	NA
Queets River	12	8

Bioaccumulation Factors for Selected PBDE's Calculated from Fish Fillet and SPMD Data

BAFs on order of 10^4 to 10^5

		PBDEs						
Species	N=	47	49	99	100	153	154	Total
Northern pikeminnow (<300mm)	3	3.0E+05	NA	ND	1.1E+05	ND	6.5E+04	2.0E+05
Northern pikeminnow (>300mm)	4	2.9E+06	NA	ND	1.5E+06	ND	7.9E+05	2.1E+06
Cutthroat (<400 mm)	4	2.3E+05	NA	1.1E+05	1.1E+05	ND	6.9E+04	2.2E+05
Cutthroat (>400 mm)	7	2.3E+06	NA	6.9E+05	1.2E+06	ND	6.4E+05	2.1E+06
Rainbow trout	3	6.2E+05	3.9E+05	1.0E+06	1.0E+06	8.2E+05	5.1E+05	7.8E+05
Smallmouth bass	1	5.6E+05	1.6E+05	9.5E+04	1.9E+05	ND	9.9E+04	4.0E+05
Peamouth	1	3.5E+05	3.5E+05	ND	ND	2.2E+05	1.3E+05	4.1E+05
Common carp	2	9.5E+05	ND	ND	1.2E+06	ND	1.4E+05	7.5E+05
Largescale sucker	3	1.3E+06	2.4E+05	ND	1.3E+06	3.7E+05	5.0E+05	1.2E+06
Mountain whitefish	3	1.5E+06	7.9E+05	2.7E+06	2.8E+06	1.8E+06	1.1E+06	2.0E+06
	Mean =	1.0E+06	3.3E+05	9.2E+05	9.7E+05	6.7E+05	3.7E+05	9.5E+05
	Minimum =	2.3E+05	7.1E+04	9.5E+04	1.1E+05	1.3E+05	6.5E+04	2.0E+05
	Maximum =	2.9E+06	7.9E+05	2.7E+06	2.8E+06	1.8E+06	1.1E+06	2.1E+06

ND = Not detected in fish and/or water samples
NA = Not analyzed in fish and/or water samples

Summary of Findings

- **Total PBDE levels in fish fillets are <10ug/kg, wet in most Washington Lakes and Rivers**
- **Mean concentration of total PBDE's 35ug/kg,wet**
- **Rivers have much higher levels then lakes**
- **Higher concentrations seen in water bodies impacted by urbanization (i.e. Spokane R., Yakima R., Lake Washington)**
- **Spokane River is high compared to both state and national data (up to 1222ug/kg in fillet and 4110ug/kg in whole fish)**

Summary of Findings

- **Concentrations of PBDE's are related to both size of fish and lipid content**
- **Certain species in the minnow family (carp, suckers and pike minnow) have ability to de-brominate penta-BDE's**
- **Bioaccumulation factors on the order of 10^4 to 10^5**

Reports and Data Online

Ecology Publications Page
http://www.ecy.wa.gov/pubs.shtm

Johnson, A., K. Seiders, C. Deligeannis, K. Kinney, P. Sandvik, B. Era-Miller and D. Alkire, 2006. ***PBDE Flame Retardants in Washington Rivers and Lakes: Concentrations in Fish and Water, 2005-06.*** WA. St. Dept. of Ecology Olympia, WA. Pub.# 06-03-027

Electronic Data Availability
http://www.ecy.wa.gov/eim/
Environmental Information Management System

Questions and Answers

Q. *Is it correct that all PBDE congeners except deca congeners have been banned in the United States?*

A. In general, PBDEs in the United States have been voluntarily phased out. We are working on identifying suitable replacement chemicals for PBDEs.

Q. *If deca congeners continue to be used, are you familiar with any studies on debromination?*

A. It is generally believed that deca congeners break down into lower congenated forms.

Q. *Are there any particular locations or species in which you would more often find PBDE-209?*

A. There does not appear to be a pattern for PBDE- 209. We were surprised to see it detected since it is such a large molecule.

Q. *How many samples were collected in total?*

A. There were 123 total fish tissue samples, 15 of which were whole fish. The remaining were filets. Six percent of the samples contained PBDE-209.