



# National Rivers and Streams Assessment: Fish Tissue Contaminants



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**OW** - Leanne Stahl, Ellen Tarquinio  
**Region 5** – Sarah Lehmann

Region 5 SWiMS Meeting, February 11, 2009

**GLEC c/o OW**– Dennis McCauley  
**Tetra Tech c/o OW**- Blaine Snyder



Office of Research and Development  
National Exposure Research Laboratory (NERL), Ecological Exposure Research Division (EERD), Molecular Indicators Research Branch (MIRB)



## Office of Water - National Rivers and Streams Assessment – NRSA

<http://www.epa.gov/owow/riverssurvey/>



### What is the National Rivers and Streams Assessment?

The National Rivers and Streams Assessment (NRSA) is a statistical survey of flowing waters of the U.S. This survey is designed to:

- Assess the condition of the Nation’s rivers and streams;
- Help build state and tribal capacity for monitoring and assessment;
- Promote collaboration across jurisdictional boundaries;
- Establish a baseline to evaluate progress; and
- Evaluate changes in condition since the 2004 Wadeable Streams Assessment.



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### What key questions will the National Rivers and Streams Assessment address?

EPA will collaborate with State and Tribal partners to answer three key questions of the NRSA:

1. What percent of the Nation's rivers and streams are in good, fair, and poor condition for key indicators of ecological health and human influence?
2. What is the relative importance of key stressors such as nutrients and pathogens? .
3. What are the trends in stream condition since the Wadeable Streams Assessment?

2



## ORD/OW National Rivers and Streams Assessment: Fish Tissue Contaminants



### Objectives:

- Assess the extent of fish tissue contamination by legacy contaminants across U.S. rivers and streams.
- Assess extent of select contaminants of emerging concern in urban rivers.

### Approach:

- In 2008-2009, fish collected by states, tribes and other collaborators from 1200 boatable streams, including a representative subset of 183 urban river sites
- ORD will analyze fish fillets at all 1200 sites for 22 organochlorine pesticides, 20 congeners of PCBs, 6 congeners of PBDEs, mercury, selenium, % lipids, and % moisture.

3



## ORD/OW NRSA – Fish Tissue Contaminants Approach Cont.

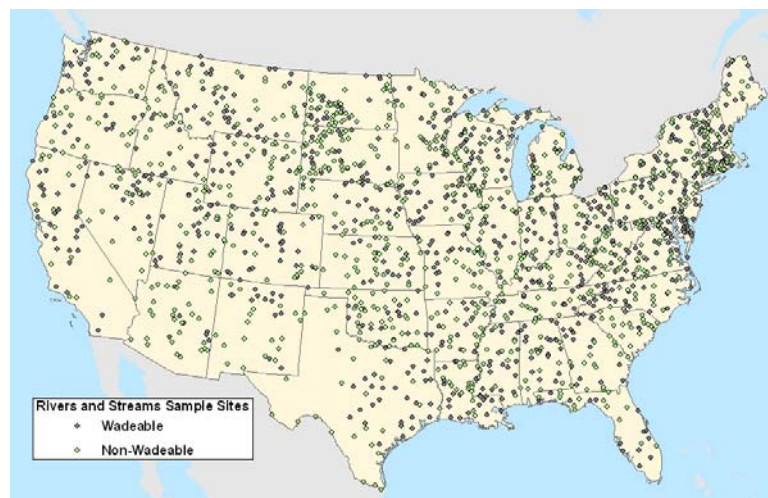
For the 183 Urban river sites ORD will analyze water and fish fillets for the occurrence and extent of selected contaminants of emerging concern (CEC):

- 54 pharmaceuticals
- 4 synthetic musk compounds and two of the nitromusk metabolites
- Under collateral agreements with ORD, NRSA samples from 15 urban sites on the Lower Mississippi River will be analyzed for perfluorinated compounds (PFOS/PFOA).
- In addition, **whole-fish** samples from all 57 urban and non-urban sites on the Lower Mississippi River will be analyzed for the same legacy compounds as the fillets. This will permit an important comparison between human and wildlife exposures to contaminants in the river.

4



## NRSA Map of Wadeable and Non-Wadeable Sites (Fish Tissue Contaminants only on non-wadeable)



5



# Collaborators NRSA Fish Tissue Project

## Office of Water

NRSA Lead – Ellen Tarquinio  
NRSA Fish Tissue Coordinator – Leanne Stahl  
NRSA Regional Contact – Sarah Lehmann

## Office of Air and Radiation Support

Funding for Mercury analyses – David Schmeltz

## Office of Water Support

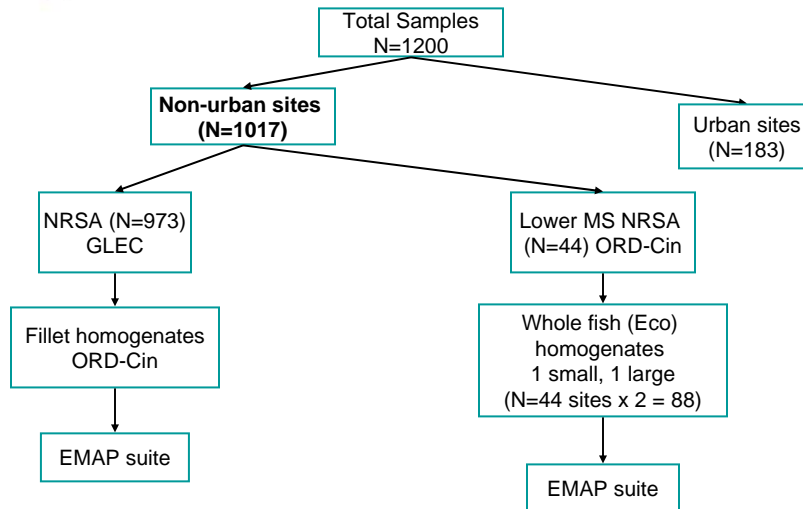
Fish Fillet and Homogenization for Non Urban Rivers- GLEC - Dennis McCauley  
Sample coordination – Tetra Tech - Blaine Synder

## ORD

Fish Tissue Contaminant Lead – Jim Lazorchak, NERL-Cincinnati  
Lead EMAP Great Rivers Lower Mississippi – Dave Bolgrien, NHEERL-Duluth  
EMAP GRE Lower Mississippi Sample Coordination – Terri Jicha, NHEERL-Duluth  
Urban Rivers Active Pharmaceutical Ingredients (APIs) Lead Analyst – Angela Batt, NERL-Cincinnati  
Legacy Contaminants and PBDE Analyses – Ervin O'Bryan, Geri Ahlers, Dan Tettenhorst, Amy Parks, Jayme Grimm, Dynamac Corp c/o NERL-Cincinnati  
Synthetic Musk Compounds – Lantis Osemwengie, NERL-Las Vegas  
PFCs – Lower Mississippi 15 Urban Sites Water - Shoji Nakayama NERL RTP/NRMRL and Marc Mills, ORD NRMRL-Cincinnati  
PFCs – Lower Mississippi 15 Urban Sites Fish Tissue – Amy Delinsky, Mark Strynar, Andy Lindstrom, NERL-RTP  
Data Analyses – Karen Blocksom, NERL-Cincinnati, and Steve Paulsen, NHEERL-Corvallis  
QA Lead – Margie Vazquez, NERL-Cincinnati



## Sample Analysis Flowchart





## Analytes to be Measured on Fish from All NRSA Sites

### 22 Organochlorine pesticides:

Aldrin	Endosulfan I
Alpha BHC	Endosulfan II
Gamma BHC	Endrin
Alpha Chlordane	Heptachlor
Gamma Chlordane	Heptachlor epoxide
2,4'-DDD	Hexachlorobenzene
4,4'-DDD	Mirex
2,4'-DDE	cis-Nonachlor
4,4'-DDE	trans-Nonachlor
2,4'-DDT	Oxychlordane
4,4'-DDT	
Dieldrin	

\*Reporting Limits: 1 ug/kg wet wt all analytes

8



## Analytes to be Measured on Fish from All NRSA Sites (cont'd)

### 21 PCB Congeners:

2,4'-dichlorobiphenyl (PCB #8)	2,2',4,4',5,5'-hexachlorobiphenyl (PCB #153)
2,2',5-trichlorobiphenyl (PCB #18)	3,3',4,4',5,5',5-hexachlorobiphenyl (PCB #169)
2,4,4'-trichlorobiphenyl (PCB #28)	2,2',3,3',4,4',5-heptachlorobiphenyl (PCB #170)
2,2',3,5'-tetrachlorobiphenyl (PCB #44)	2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB #180)
2,2',5,5'-tetrachlorobiphenyl (PCB #52)	2,2',3,4',5,5',6-heptachlorobiphenyl (PCB #187)
2,3',4,4'-tetrachlorobiphenyl (PCB #66)	2,2',3,3',4,4',5,6-octachlorobiphenyl (PCB #195)
3,3',4,4'-tetrachlorobiphenyl (PCB #77)	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (PCB #206)
2,2',4,5,5'-pentachlorobiphenyl (PCB #101)	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (PCB #209)
2,3,3',4,4'-pentachlorobiphenyl (PCB #105)	
2,3',4,4',5-pentachlorobiphenyl (PCB #118)	
3,3',4,4',5-pentachlorobiphenyl (PCB #126)	
2,2',3,3',4,4'-hexachlorobiphenyl (PCB #128)	
2,2',3,4,4',5'-hexachlorobiphenyl (PCB #138)	

9

Reporting Limits: 1 ug/kg wet wt all analytes



## Analytes to be Measured on Fish from All NRSA Sites (cont'd)

**Mercury:** Direct Mercury Analyzer by Milestone  
Reporting Limit: 0.005 ug/g wet wt

**Selenium:** ICP-MS

**Moisture:** Karl Fisher Titration

**Lipids:** Gravimetric method

10



## Analytes to be Measured on Fish from All NRSA Sites (cont'd)

### Flame retardants - 8 PBDE Congeners:

2,2',4,4'-tetrabromodiphenyl ether (PBDE #47)

2,3',4,4'-tetrabromodiphenyl ether (PBDE #66)

2,2'4,4'5-pentabromodiphenyl ether (PBDE #99)

2,2'4,4'6-pentabromodiphenyl ether (PBDE #100)

2,2'3,4,4'5'-hexabromodiphenyl ether (PBDE #138)

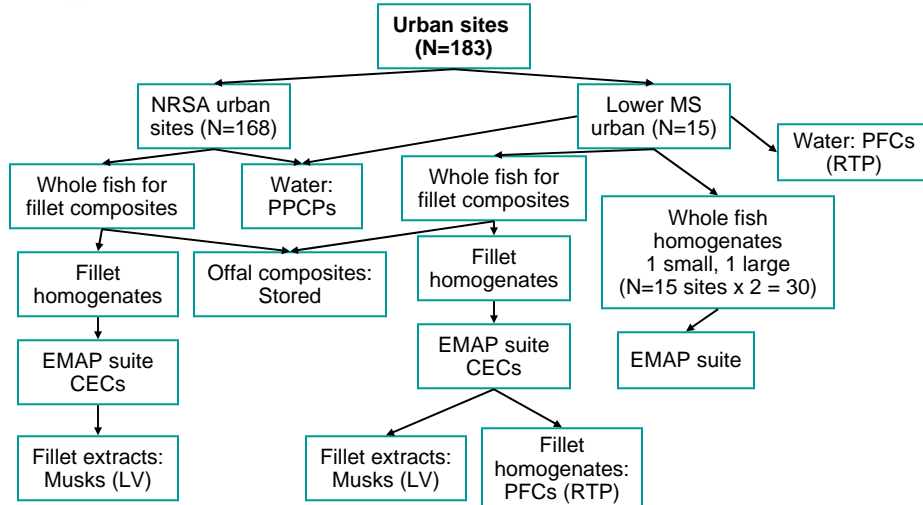
2,2',4,4',5,5'-hexabromodiphenyl ether (PBDE #153)

2,2'4,4'5,6'-hexabromodiphenyl ether (PBDE #154)

2,2',3,4,4',5',6 -heptabromodiphenyl ether (PBDE #183)

11

### Sample Analysis Flowchart (cont'd)



12

### CECs - 54 Pharmaceuticals to be Measured on Water and Fish Fillets Collected from 183 NRSA Urban Sites (PI: Dr. Angela Batt ORD/NERL-Cincinnati)

#### Basic APIs 1 - antidepressants, antibiotics

1. cimetidine
2. ranitidine
3. trimethoprim
4. sulfamethoxazole
5. 10-hydroxy-amitriptyline
6. promethazine
7. paroxetine
8. alprazolam
9. amitriptyline
10. benztropine
11. norfluoxetine
12. fluoxetine
13. desmethylsertraline
14. sertraline

#### Basic APIs 2 - cardiovascular drugs, pain medications

15. albuterol
16. atenolol
17. clonidine
18. oxycodone
19. amphetamine
20. hydrocodone
21. triamterene
22. metoprolol
23. enalapril
24. propranolol
25. desmethyldiltiazem
26. diltiazem
27. norverapamil
28. verapamil
29. propoxyphene
30. amlodipine

Modified from - Analysis of Ecologically Relevant Pharmaceuticals in Wastewater and Surface Water using Selective Solid Phase Extraction and UPLC/MS/MS Angela L. Batt\*, Mitch S. Kostich, and James M. Lazorchak, 2008 ACS

13



## CECs 54 Pharmaceuticals (cont'd)

(PI: Dr. Angela Batt ORD/NERL-Cincinnati)

### Neutral APIs

31. acetaminophen
32. prednisone
33. prednisolone
34. hydrocortisone
35. carbamazepine
36. betamethasone
37. methylprednisolone
38. norethindrone
39. testosterone
40. valsartan
41. fluocinonide
42. atorvastatin
43. fluticasone
44. progesterone
45. simvastatin

### Acidic APIs

46. theophylline
47. hydrochlorothiazide
48. 2-hydroxy-ibuprofen
49. Furosemide
50. warfarin
51. glipizide
52. ibuprofen
53. gemfibrozil
54. glyburide

14



## CECs – Synthetic Musks to be Analyzed on Fish Fillets Collected at 183 Urban Sites

(PI: Dr. Lantis Osemwengie – ORD/NERL-Las Vegas)

- Synthetic musk compounds are:
  - Additives in cosmetics, Shampoo, detergents, and cigarettes.
  - Suspected hormone disruptors.
  - Prevent cells from excreting toxins in animal study.
  - Bioconcentrate in fish tissue.

Source: Environmental Working Group: Human Toxome Project  
[http://www.ewg.org/sites/humantoxome/chemicals/chemical\\_classes.php?class=Polycyclic+Musks](http://www.ewg.org/sites/humantoxome/chemicals/chemical_classes.php?class=Polycyclic+Musks)

- Two polycyclic musk compounds - Galaxolide and Tonalide;
- Two Nitro musk compounds - Musk Xylene, and Musk Ketone;
- Two Nitro musk compound metabolites - 4-Amino Musk Xylene and Amino musk ketone.

15



## CECs –Perfluorinated Compounds (PFC) in Fish Fillets 15 Lower Mississippi

### Urban Sites (Amy Delinsky, Mark Strynar, Andrew Lindstrom) Water Analyses 15 Urban Sites (Shoji Nakayama, Marc Mills)

Name	Acronym	Formula
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
<b>Perfluorooctane sulfonate</b>	<b>PFOS</b>	<b><math>C_8F_{17}SO_3^-</math></b>
Perfluorohexanoic acid	PFHxA	$C_6F_{11}COOH$
Perfluoroheptanoic acid	PFHpA	$C_7F_{13}COOH$
<b>Perfluorooctanoic acid</b>	<b>PFOA</b>	<b><math>C_8F_{15}COOH</math></b>
Perfluorononanoic acid	PFNA	$C_9F_{17}COOH$
Perfluorodecanoic acid	PFDA	$C_{10}F_{19}COOH$
Perfluroundecanoic acid	PFUnA	$C_{11}F_{21}COOH$
Perfluorododecanoic acid	PFDoA	$C_{12}F_{23}COOH$

Modified from - Perfluorinated Compounds in Whole Fish Homogenates from the Ohio, Missouri, and Upper Mississippi Rivers, USA. 2009, Xibiao Ye, Mark J. Strynar, Shoji Nakayama, Jerry Varns, Larry Helfant, James Lazorchak and Andrew B. Lindstrom. ES&T 16



### Plans for Data Analysis

- Estimate extent of occurrence of each legacy contaminant in fish tissue for rivers of the U.S. and of emerging contaminants in urban rivers.
- Estimate extent of rivers with legacy contaminants above human health cancer screening values in NRSA rivers.
- Estimate extent of Lower Mississippi River with legacy contaminants above wildlife risk values.
- Determine extent and magnitude of occurrence of PPCPs and musks in urban rivers.

17



## Current Plans for Outputs

- 1) Paper on the results of PPCPs found in water of urban streams of the United States - Winter 2010
- 2) Paper on the analytical chemistry methods to assess pharmaceuticals in fish tissue - Winter 2010
- 3) Paper on the extent of PPCPs found in fish of urban rivers of the United States - Spring/Summer 2010
- 4) Paper on the extent of musks found in fish of urban rivers of the United States - Spring/Summer 2010
- 5) Paper on the extent of PFCs found in water and fish at urban sites in the Lower Mississippi River Spring/Summer 2010
- 6) Paper on the extent of tissue contamination in rivers and streams of the United States - Fall/Winter 2010/2011
- 7) Full Report (OST) on the extent of PPCPs found in water and fish from urban streams of the United States- Sept 2011
- 8) Chapter in the EPA NRSA Report on fish tissue contamination including both legacy and emerging contaminants - Sept 2011