

Results of the EPA Pilot Study of Pharmaceuticals and Personal Care Products in Fish Tissue a.k.a

**Occurrence of pharmaceuticals and personal care
products (PPCPs) in fish:
Results of a national pilot study in the U.S.**

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EPA PPCP Fish Pilot Study

Obtaining data on pharmaceuticals as contaminants of emerging concern is a priority for EPA.

- Recent research indicates that pharmaceuticals occur widely in surface water, sediment, and municipal effluent.
- Limited data are available on accumulation of pharmaceuticals in fish.
- Designed to be biologically active, affect specific receptors.

Personal Care Products are a separate but related issue

- Different properties, not designed to be biologically active
- Produced and discharged in very large quantities





EPA PPCP Fish Pilot Study

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

Several collaborators contributed 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





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
- Sample preparation include the preparation of both fillet and liver tissue samples
- Analyzing fillet and liver tissue samples from each fish composite for 24 pharmaceutical compounds
- Analyzing fillet tissue samples (only) for 12 personal care products





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



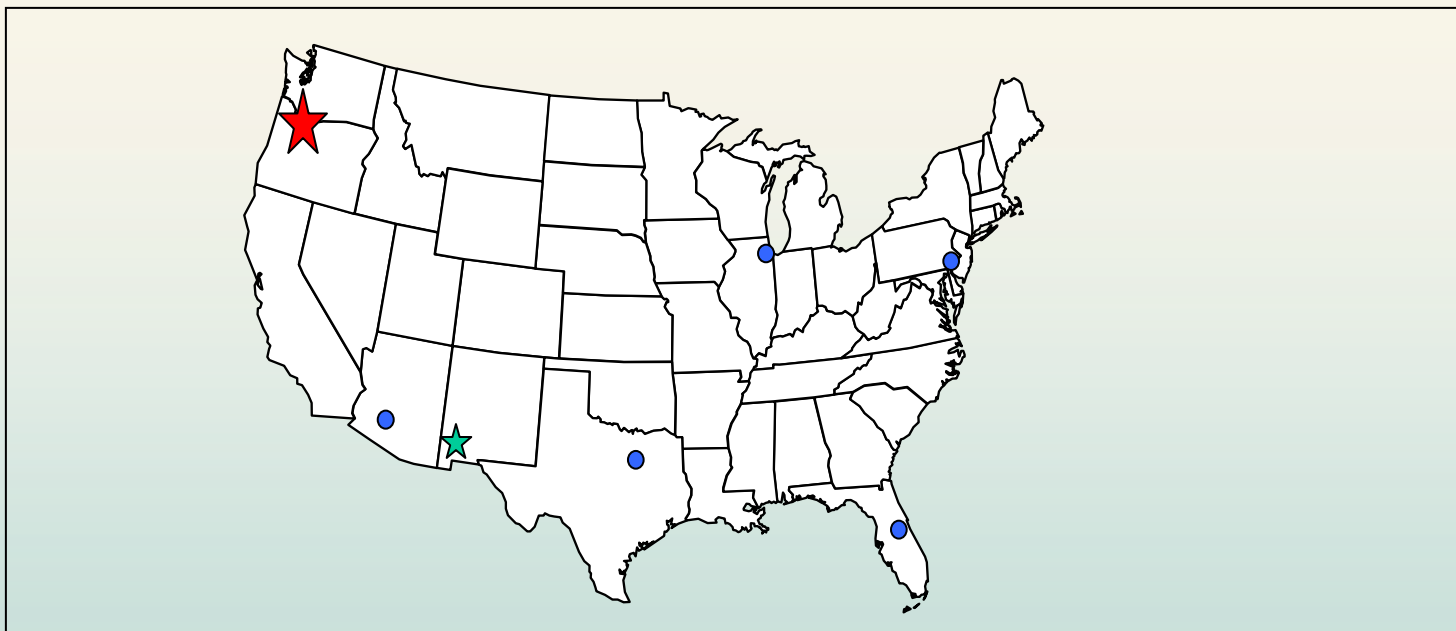


Sampling Sites

State	River, Location	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 (<i>Reference Site</i>)	Nov. 2006	Sonora sucker	24
PA	Taylor Run, West Chester	Aug. 2006	White sucker	24
TX	Trinity River, Dallas	Oct. 2006	Smallmouth buffalo	18



Sampling Sites



Portland! *Not a sampling site*





Target Chemicals

EPA analyzed fillet and liver tissue samples for 24 pharmaceutical compounds and 12 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
- 5 fragrances/musks
- 1 insect repellent
- 3 surfactants
- 2 UV filtering compounds





Analytical Methods

Baylor employed different methods for the two classes of compounds

Pharmaceuticals

- Pharmaceutical analyses were performed using HPLC-MS/MS (Ramirez et al., 2007)
- Tissue and Liver Samples analyzed

Personal Care Products

- Personal Care Products analyses employed GC-MS/MS (Mottaleb et al., 2008)
- Fillet tissue only





Pharmaceutical Chemicals

Not Detected in Fillet and Liver Tissue

<u>Chemical</u>	<u>Use</u>	<u>Chemical</u>	<u>Use</u>
Acetaminophen	Analgesic	Metoprolol	Anti-hypertension
Atenolol	Anti-hypertension	Miconazole	Anti-fungal
Caffeine	Stimulant	Propranolol	Anti-hypertension
Cimetidine	Anti-acid reflux	Sulfamethoxazole	Antibiotic
Codeine	Analgesic	Thiabendazole	Anti-fungal
Erythromycin	Antibiotic	Warfarin	Anticoagulant
Ibuprofen	Analgesic	Tylosin	Antibiotic
Lincomycin	Antibiotic	1,7-dimethylxanthine	Antispasmodic
Trimethoprim	Antibiotic		





Pharmaceuticals detected

Antidepressants: Fluoxetine, Norfluoxetine, Sertraline

Antihistamine: Diphenhydramine

Anti-Hypertension: Diltiazem

Antilipemic: Gemfibrozil

Anti-seizure: Carbamazepine

Difficult analyses- issues with matrix spike and matrix spike duplicate over-recovery.





Pharmaceuticals detected

In **fillet** tissue, mean/max

Central Nervous System compounds:

	<u>Chicago</u>	<u>Phoenix</u>	<u>W. Chester</u>
Norfluoxetine	3.2/3.2	4.0 /4.8	3.9/5.0
Sertraline	nd	5.0/6.5	11/19
Carbamazepine	2.3/3.1	nd	nd

Units: ng/g ww (ppb)

Note: Means are of detections only





Pharmaceuticals detected

In **fillet** tissue, mean/max

Other pharmaceutical compounds:

	<u>Chicago</u>	<u>Phoenix</u>	<u>W. Chester</u>
Diphenhydramine	1.4/1.7	1.2/1.4	1.7/2.5
Diltiazem	0.13/0.2	nd	0.15/0.2

ng/g ww (ppb)





Pharmaceuticals detected

In **liver** tissue, mean/ max

Central Nervous System compounds:

	<u>Chicago</u>	<u>Phoenix</u>	<u>W. Chester</u>
Fluoxetine	19/23	nd	70/80
Norfluoxetine	73/130	33/44	38/48
Sertraline	84/149	71/105	381/545
Carbamazepine	6/8	nd	nd

ng/g ww (ppb)





Pharmaceuticals detected

In **liver** tissue, mean/ max

Central Nervous System compounds:

	<u>Dallas</u>	<u>Orlando</u>	<u>MDL</u>
Fluoxetine	nd	nd	12.41
Norfluoxetine	37/48	57/78	15.31
Sertraline	27/28	--/21	17.29
Carbamazepine	nd	nd	1.86

ng/g ww (ppb)





Pharmaceuticals detected

In **liver** tissue, mean/max

Other pharmaceutical compounds:

ng/g ww (ppb)	<u>Chicago</u>	<u>Phoenix</u>	<u>W. Chester</u>
Diphenhydramine	7/10	7/11.1	10/11
Diltiazem	0.7/0.9	0.3/0.4	0.7/0.8
Gemfibrozil	nd	70/90	27.1/27.3
		<u>Dallas</u>	
Diphenhydramine		0.5/0.9	





Personal Care Products

- Determined only in **fillet** tissue
- Major lipid interference in GC/MS method
- Galaxolide detected in all samples at all locations (*except* Orlando (5/6))
- Tonalide detected in all samples at all locations (*except* Orlando (1/6))



Personal Care Products

Concentration in **fillet** tissue (mean/max)

<u>Location</u>	<u>Galaxolide</u>	<u>Tonalide</u>
Chicago	1,300/1,800	160/230
Dallas	800/1,800	70/150
Orlando	100/300	--/21
Phoenix	1,800/2,100	240/290
West Cester	1,800/2,000	60/70

ng/g ww (ppb)





Personal Care Products

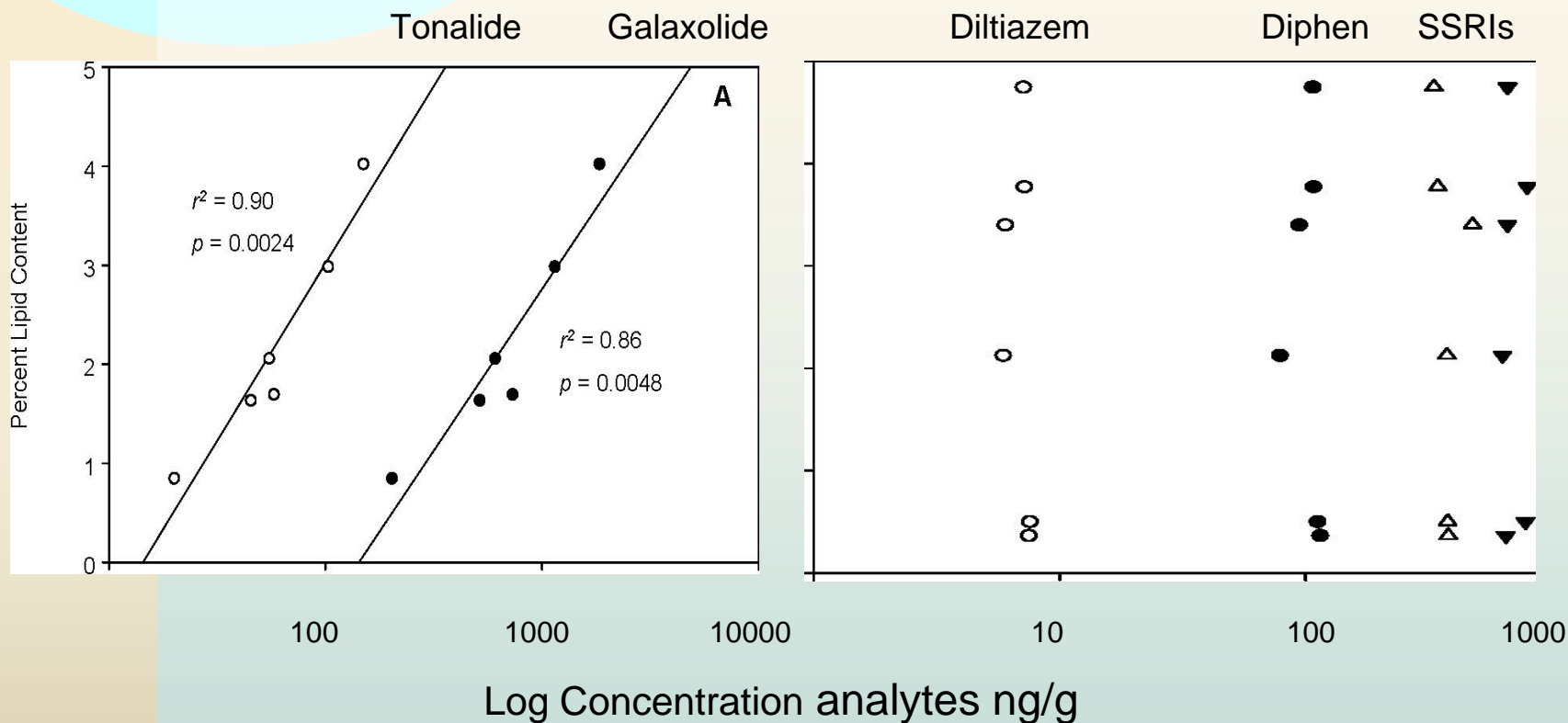
Compounds NOT detected in fish tissue

<u>Compound</u>	<u>MDL (ng/g)</u>
4-methylbenzylidene-camphor (4MBC)	120.5
Benzophenone	16.4
Celestolide	17.7
m-Toluamide	5.1
Musk Ketone	321.2
Musk Xylene	397.1
Nonylphenol	9.7
Octocrylene	36
Octylphenol	8.2
Triclosan	37.8





Lipids and polar/nonpolar compounds





Type of treatment at Study Facilities

<u>Facility</u>	<u>%Effluent</u>	<u>Type Treatment</u>
Phoenix Az	100	Advanced Treatment I, Nutrient removal
Orlando FL	64	Advanced Treatment II, Nutrient removal
Chicago	100	Advanced Treatment I, Nutrient removal
West Chester PA	36-86	Advanced Treatment I, Nutrient removal
Dallas	100	Advanced Treatment II, Nutrient removal





Conclusions

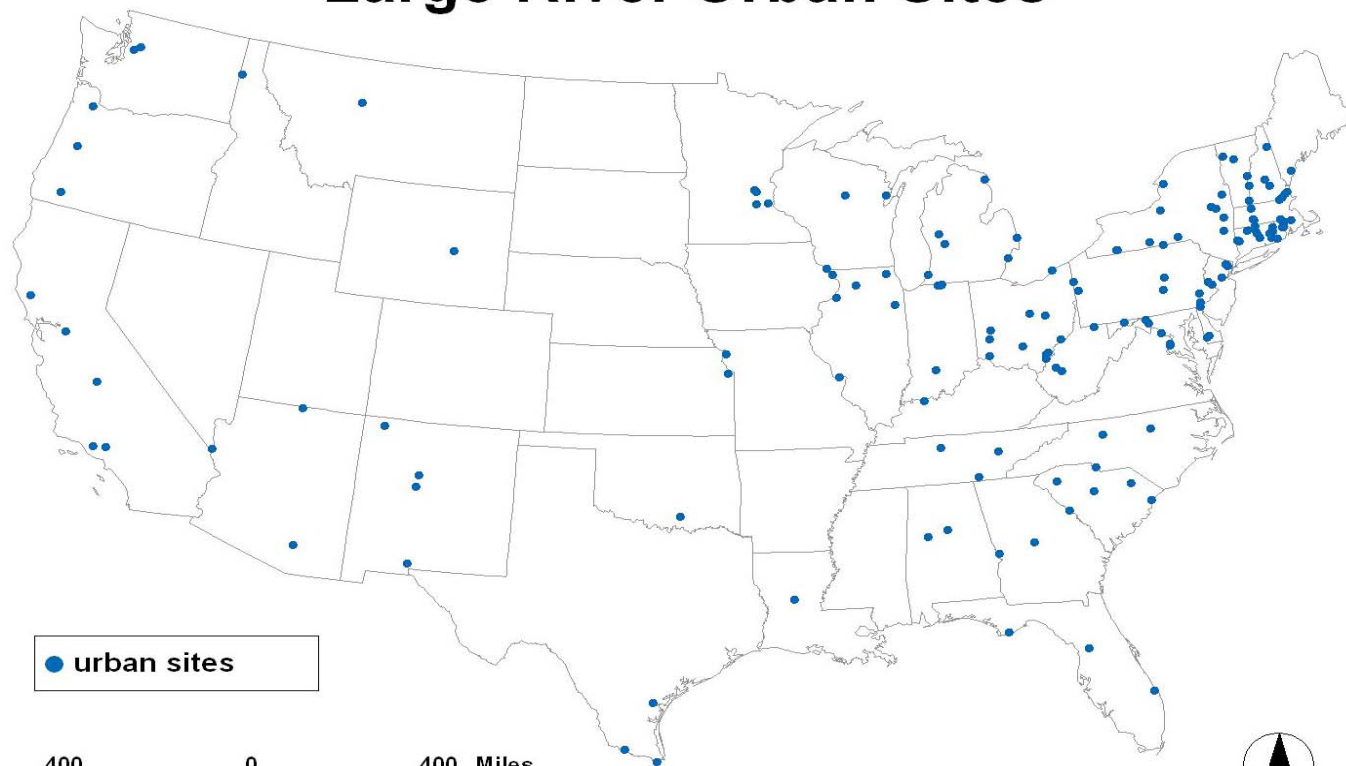
- ➡ Pharmaceuticals and personal care products are imparted to fish tissue from wastewater- compound/class specific
- ➡ Level of treatment matters
- ➡ Extent of occurrence is unknown





What's next...

National Rivers & Streams Assessment Large River Urban Sites





National Rivers and Streams Assessment

- ➡ Pharmaceuticals, limited personal care products, and perfluorinated compounds (PFOS/PFOA, etc.) determined in fish from 154 urban sites out of 900 sites sampled
- ➡ Sampling being conducted 2008-2009





Questions

- ☞ Can you smell galaxolide in fish at 2 ppm?
- ☞ Do you have any questions?

Additional information:

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<http://www.epa.gov/waterscience/ppcp/>

