

Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River – A study in 2 parts

Industrial Pretreatment Program Seminar

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Elizabeth Murphy, Todd Nettesheim, Chiara Zaccarino-Crowe (formerly of the) Great Lakes National Program Office, USEPA, Chicago, IL
 Lawrence Zintek, Chicago Regional Laboratory, USEPA, Chicago, IL
 Clifford P. Rice, Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD
 Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN
 James M. Lazorchak, Angela L. Batt, Marc A. Mills, USEPA ORD, Cincinnati, OH
 Larry B. Barber, James L. Gray, USGS, Boulder, CO
 David Lordi, Tom Minarik, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL
 Leanne Stahl, Office of Water, USEPA, Washington DC, USA

Acknowledgments

- Other collaborators
 - Tetra Tech – Blaine Snyder and Jennifer Pitt
 - Baylor University
 - Clarkson University, SUNY-Oswego, SUNY-Fredonia
 - Illinois DNR – Rob Miller and Jim Langbein
 - Exelon Corp – John Petro
- Captains of the MWRD PC-1 boat
- MWRD R&D Laboratory staff
- Countless others at MWRD and GLNPO who helped to collect fish and effluent samples

Objectives

- Supplemental study to EPA's National Fish Tissue Study
- The four main objectives of the supplemental study are to:
 - Determine if there is reproductive impairment to resident fish;
 - Estimate whole fish concentrations of PPCPs, APEs, and hormones; and
 - Estimate effluent and stream concentrations of PPCPs, APEs, and hormones
 - Document seasonal differences in concentrations of these compounds in effluent, stream water, and fish.
- Strengthen collaborative ventures

The NSC Study

Part 1: Concentrations in Fish Tissue and Analysis of Reproductive Impairment

- Determine if there is reproductive impairment to resident fish;
- Estimate whole fish concentrations of PPCPs, APEs, and hormones

Part 2: Concentrations in Effluent and the Receiving Stream

- Estimate effluent and stream concentrations of PPCPs, APEs, and hormones
- Document seasonal differences in concentrations of these compounds in effluent, stream water, and fish.

An AP Investigation: Pharmaceuticals found in Drinking Water - Headlines

- Pharmaceuticals found in drinking water, affecting wildlife and maybe humans
- Pharmaceuticals found in drinking water of 24 major metro areas, 34 say no testing
- Fish, wildlife affected by drug contamination in water
- No standards to handle pharmaceuticals in water
- Tests of Philadelphia's drinking water reveal 56 drugs
- And many more...

http://hosted.ap.org/specials/interactives/pharma_water_site/index.html





Prescription Drugs Found in Tap Water



Pharmaceuticals

- Medicines are produced and used in very large volumes
 - In 2006, over \$274 billion was spent on over 3.7 million scripts
 - Consumption has increased significantly in last 20 years
 - UN projects a 3-fold increase in usage in next 25 years

Personal Care Products

Bath additives, shampoos, skin care products, hair sprays, oral hygiene, soaps, detergents

Fragrances

Preservatives


Disinfectants/Antiseptics

Sunscreen Agents



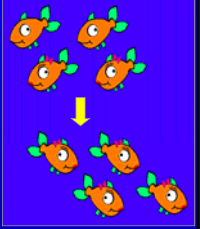
Daughton and Ternes (1999)

What are APEs?



Why are PPCPs (including APEs) of concern?

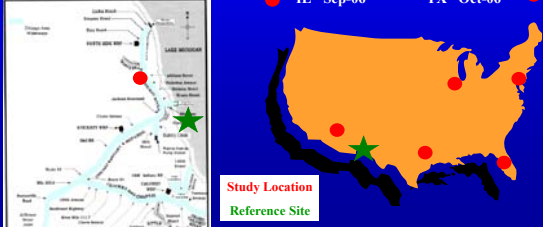
- Produced and used in large volumes
- May be "pseudo-persistent"
 - ◆ Chronic exposure
- May have biological effects
 - ◆ Therapeutic design
 - ◆ Non-target organisms
- May be endocrine disruptors
 - ◆ alterations to sexual differentiation
 - Boulder Creek
 - Potomac River
 - ◆ reproduction and growth impairments
 - ◆ behavioral effects
- Little known about environmental persistence, fate



Part 1: Concentrations in Fish Tissue and Analysis of Reproductive Impairment

Collection Location and Time

NCS Pilot Study		Nat. Pilot Study	
Foster Street Bridge	9/2006 & 3/2007	AZ	Nov-06
Lake Michigan	9/2006	NM	Nov-06
Braidwood Cooling Pond	3/2007	FL	Oct-06
		IL	Sep-06
		PA	Aug-06
		TX	Oct-06



NSC Study Design

- Whole fish collected & analyzed for APEs, hormones, and PPCPs from the NSC and reference sites in the fall and spring.
- Brain, liver, & gonads taken for histopathology. Blood for VTG. Scales taken for age.
- Effluent & Stream samples collected on same day.

Study changes from Fall to Spring

- St. Cloud State collected additional species to add statistical power to study.
- Analysis of livers for mRNA vitellogenin - a better indicator of recent exposure to endocrine disruptors
- Different reference site used

Chemicals of Concern

EPA Pilot Study		NSC Supp. Study	
NP	diltiazem	NP	17β-Ethinyl estradiol
m-toluamide	diphenhydramine	NP1EO	Equilenin
musk xylene	erythromycin	NP2EO	Equilin
octocrylene	fluoxetine	NP3EO	Estriol
celestrolide	gemfibrozil	NP4EO	cis-Androsterone
OP	ibuprofen	OP	Epitestosterone
tonalide	lincomycin	OP1EO	Androstenedione
tricosan	metoprolol	OP2EO	Dihydrotestosterone
4-methylbenzylidene	micnazole	OP3EO	Testosterone
camphor	norfluoxetine	OP4EO	11-Ketotestosterone
1,7-dimethylxanthine	propranolol	Diethylstilbestrol	19-Norethindrone
acetaminophen	sertraline	17α-Estradiol	Progesterone
atenolol	sulfamethoxazole	17β-Estradiol	3β-Coprostanol
caffeine	thiabendazole	Estrone	Cholesterol
cimetidine	trimethoprim	Mestranol	
codeine	tylosin		
carbamazepine	warfarin		
	galaxolide		

Estrogenic Effects on Fish Fall 2006

	North Shore Channel	Outer Chicago Harbor
Immature fish (w/ VTG)	4 (0%)	0 (0%)
Male fish (w/ VTG)	5 (60%)	4 (0%)
Female fish (w/ VTG)	3 (100%)	5 (100%)
Total Fish	12	9

() = % fish expressing VTG

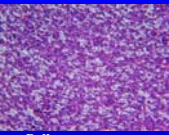
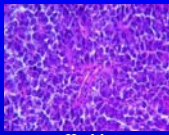
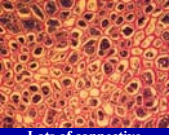
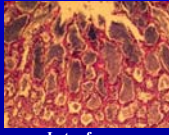
*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN

Histopathology - Fall

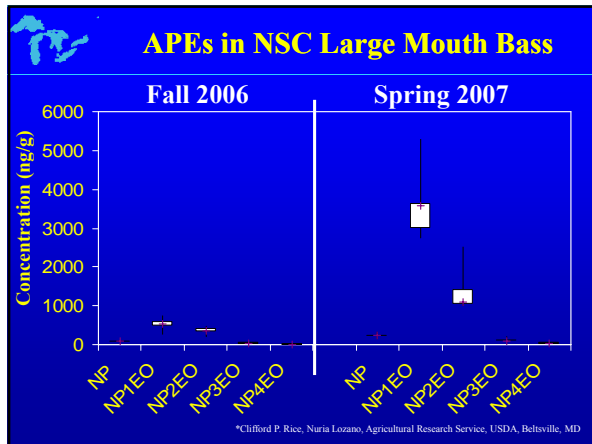
- Liver
 - No clear pattern between males and females or b/w VTG males and those without VTG
 - 76% of mature fish displayed brown inclusions
 - 25% NSC (2 of 8) & 11% LM (1 of 9) contained cysts in livers consistent with parasite infection
- Gonad
 - No observable trends between study sites
 - All female LMB contained all stages of oogenesis in ovaries
 - All male LMB exhibited all stages of spermatogenesis
 - Greater abundance of connective tissue in testis of male LMB from NSC
 - No ovatestis observed in any fish



Histopathology -Spring

Liver	NSC LM Bass	Braidwood LM Bass
		
	Pollutant exposure	Healthy
Gonads		
	Lots of connective tissue & few sperm	Lots of sperm

*Heiko L. Schoenfuss, St. Cloud State University, St. Cloud, MN



- ### Bioconcentration Factor (BCF) for APEs
- **BCF = Concentration in fish / Concentration in water (LMB)**
 - NP = 130-230
 - NP1EO = 450-630
 - NP2EO = 200-480
 - NP3EO = 40-60
 - **These values agree quite well with the values published by Mitchelmore and Rice 2006. (Carp)**
 - NP = 280
 - NP1EO = 1713
 - NP2EO = 693
 - **EPI Suite Calculations of BCFs for APEs**
 - NP = 543.5
 - NP1EO = 87.85
 - NP2EO = 54.01
 - NP3EO = 33.2
 - NP4EO = 20.41

Pharmaceutical Chemicals Detected in EPA Pilot Study & Fillet and Liver Tissue from NSC

Detected Chemicals & Method Detection Limits (MDLs)	Use	National Composites with Detection (N=30)		Detections in NSC (N=6)	
		Fillet	Liver	Fillet	Liver
Carbamazepine (1.86 ppb)	Anti-seizure	6	6	6	6
Diltiazem (0.26ppb)	Anti-hypertension	8	16	5	6
Diphenhydramine (0.26ppb)	Antihistamine	18	23	6	6
Fluoxetine (12.41ppb)	Antidepressant	0	11	0	3
Gemfibrozil (24.82ppb)	Antilipemic	0	8	0	0
Norfluoxetine (15.31ppb)	Fluoxetine metabolite	12	26	2	6
Sertaline (17.29ppb)	Antidepressant	12	23	6	6

*Leanne Stahl, Office of Water, USEPA, Washington DC, USA

- ### EPA Pilot Study Preliminary Conclusions - Pharmaceuticals
- No target pharmaceutical compounds were detected in any of the composites collected at the reference site.
 - Seventeen of the 24 pharmaceutical compounds were not detected in any of the fillet or liver samples from the five sites located on effluent-dominated streams.
 - All seven pharmaceutical compounds detected in the tissue samples occurred in livers while only five were detected in fillets.
 - The pharmaceuticals that occurred most frequently were diphenhydramine, norfluoxetine, and sertraline.
 - Norfluoxetine and sertraline (antidepressants) both occurred in livers at all five sites and in fillets at three and two sites, respectively.
 - Diphenhydramine (antihistamine) occurred in livers at four sites and in fillets at three sites.

- ### EPA Pilot Study Preliminary Conclusions - PPCPs
- No target personal care product chemicals were detected in any of the composite samples collected at the reference site.
 - The PCP results are only for fish fillets. Current analytical techniques for PCPs are subject to interference from fat and other substances found in fish liver.
 - Ten of the 12 personal care product chemicals were not detected in any of the fillet samples from the five sampling locations on effluent-dominated streams.
 - Two personal care product chemicals occurred in fish fillets at all five sites: galaxolide and tonalide, which are both fragrances (musk).
- <http://www.epa.gov/waterscience/ppcp/studies/fish-tissue.html>

- ### NSC Supplemental Study Conclusions for fish
- Some male fish do have measurable levels of VTG, but no intersex or other severe pathological conditions at either site.
 - Loose correlation between APEs concentration and VTG levels in fish.
 - Measured concentrations of NP and OP vary with season.
 - Currently, no criteria for NPEOs in aquatic life.
 - Analytical capability is still a work in progress

Part 2: Concentrations in Effluent and the Receiving Stream

Study Design and Sample Collection

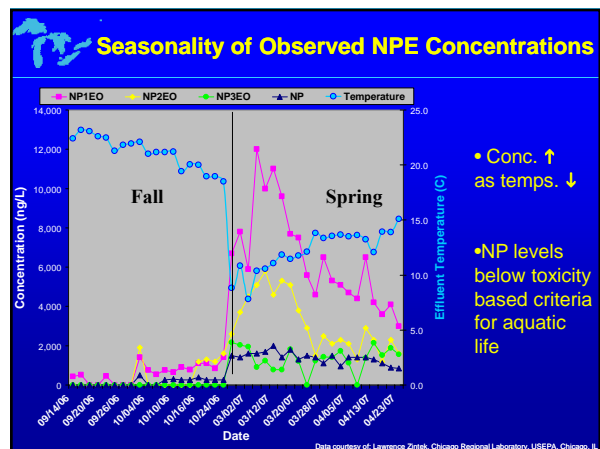
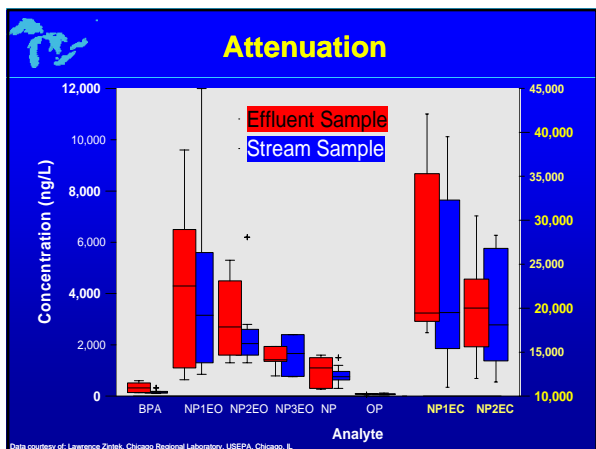
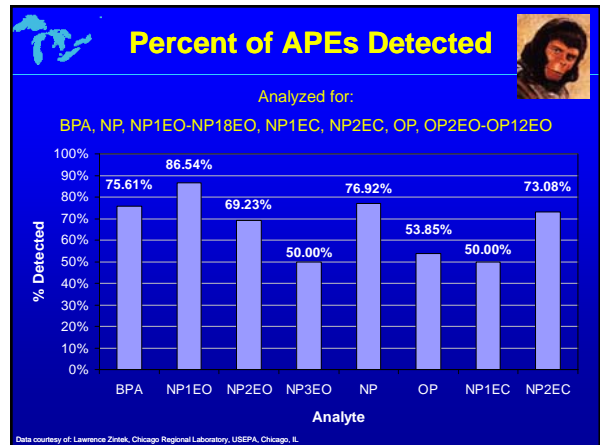
Water collections (Fall and Spring):

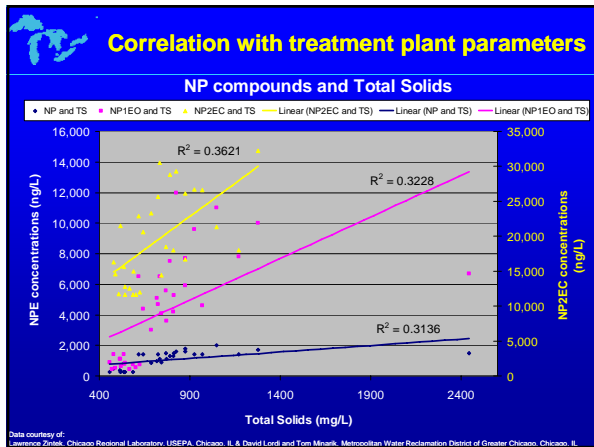
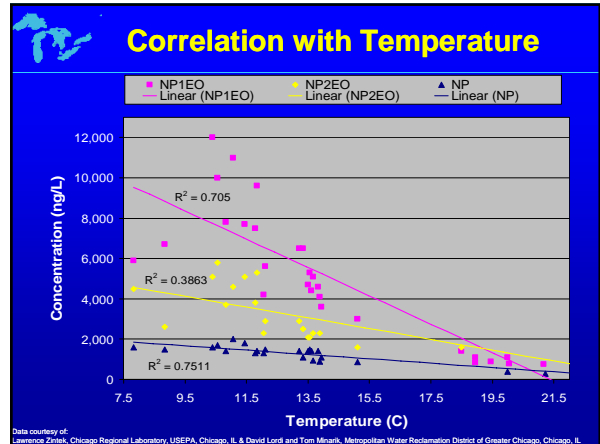
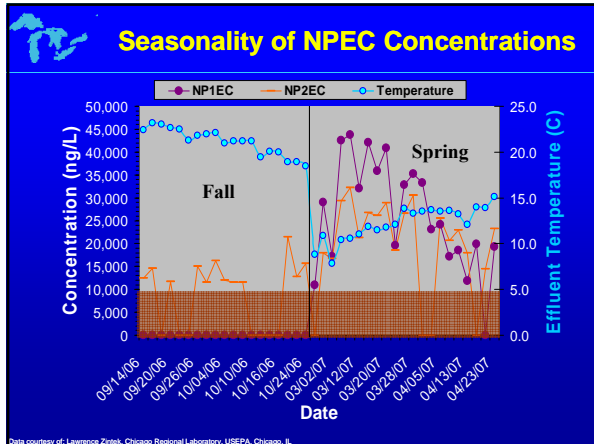
- MWRD (Northside WRP effluent ; 2-3/week)
- U.S. EPA (NSC stream; 1/week)

Study Design and Methods

Water analyzed by a variety of labs

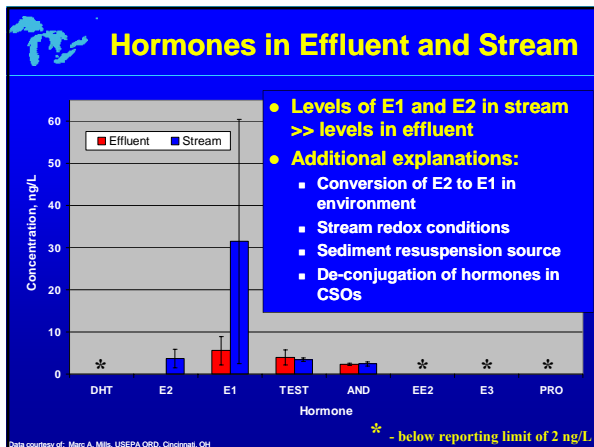
- USGS (CO) (75 organic wastewater contaminants, 34 pharmaceuticals, and 20 hormones)
- MWRD (General chemical parameters of plant effluent)
- U.S. EPA, ORD – NERL (56 pharmaceuticals and metabolites in 2007)
- U.S. EPA, ORD – NRMRL (8 hormones in 2007)
- U.S. EPA, Chicago Regional Laboratory (APEs)






Pharmaceuticals in effluent present at...

High ppt to ppb levels (> 500 ng/L)	Low ppt levels (<100 ng/L)
lisinopril	amphetamine
valsartan	hydrocodone
hydrochlorothiazide	triamterene
ibuprofen-2-hydroxy	enaliprilat
gemfibrozil	enalipril
	propranolol
	diltiazem-desmethyl
	verapamil
	norverapamil
	amlodipine
	sulfamethoxazole
	promethazine
	paroxetine
	amitriptyline
	benztropine
	norfluoxetine
	fluoxetine
	sertraline-desmethyl
	sertraline



NSC Supplemental Study Conclusions for stream and effluent

- Significance of sampling timing and duration
 - Observed concentrations correlated with effluent temperature and other wastewater treatment parameters
- Analytical capabilities and reporting limits a work in progress
 - Many compounds often below MDLs or RLs
- Effluent (and therefore streams) contain a wide mixture of compounds
 - Persistent exposure to aquatic life
- Other possible sources
- Emerging concern that we've just begun to investigate

 **Next Steps**

- Collaboration is **KEY!**
- Publications on various pieces of the project
- Much more data to come
 - ◆ Hormones in fish
 - ◆ PPCPs fish
 - National Pilot Study
 - Fall and Spring fish samples
 - ◆ Legacy contaminants that are suspected EDs
- New EPA site on PPCPs -
<http://www.epa.gov/waterscience/ppcp/>

 **Questions?**



Thank You!

Beth Murphy
U.S. EPA GLNPO
(312) 353-4227
murphy.elizabeth@epa.gov

