

US EPA ARCHIVE DOCUMENT

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

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- Other collaborators
 - ◆ USGS National Water Quality Laboratory in Golden, CO
 - ◆ U.S. EPA Office of Water – John Wathen and Leanne Stahl
 - ◆ 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 who helped to collect fish and effluent samples



Things I plan to talk about...

- Objectives of study
- Study location
- Study design
- Preliminary results



Objectives of Study

- 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 effluent and stream concentrations of PPCPs, APEs, hormones, and general chemistry
 - Estimate whole fish concentrations of PPCPs, APEs, and hormones; and
 - Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.
- Strengthen collaborative ventures



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- **Study location**

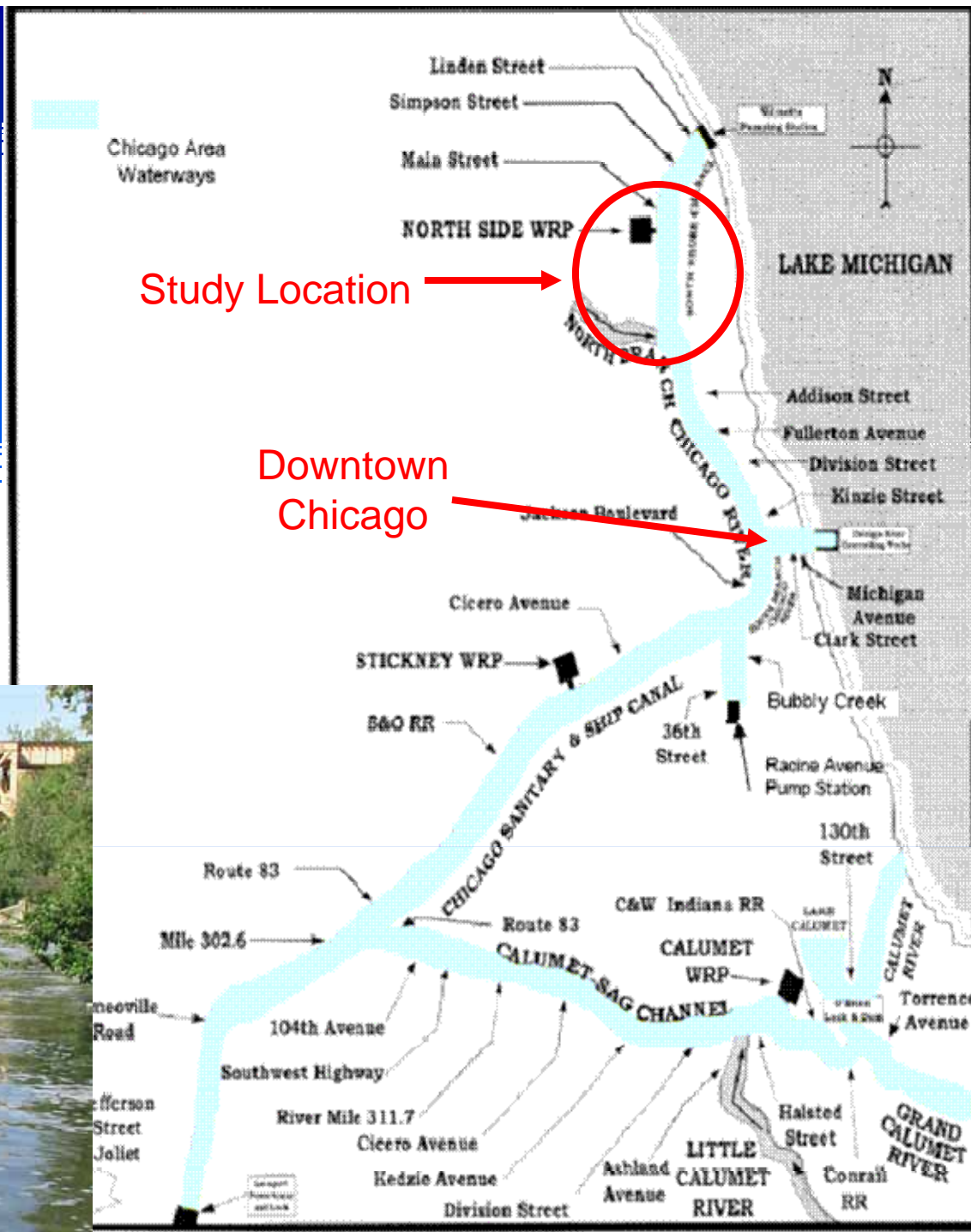


North Side WRP

- 333 MGD
- Serves 1.3 million people
- Secondary treatment
- Sludge pumped to another WRP

North Shore Channel

- Man-made (early 1900s)
- Effluent dominated
- Recreational fishery





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Study Design – Objective 1



- Determine reproductive impairment
 - Analyze fish blood for vitellogenin (vtg)
 - Perform mRNA analyses for vtg in livers
 - Examine livers for abnormalities
 - Examine fish gonads for imposex and abnormalities (histopathology)
 - Examine fish brains for abnormalities
- Large mouth bass and common carp
 - Sexually mature fish
- Local reference sites analyzed for control
 - Lake Michigan and Braidwood cooling pond
- Collaborative partners
 - St. Cloud State University
 - ORD Cincinnati



Study Design – Objective 2

- Estimate effluent and stream concentrations of PPCPs and Hormones



- USGS Boulder and Golden, CO, Labs – Conduct weekly analysis of stream and effluent samples using OWC 1433 (75 organic waste water contaminants including some personal care products); Pharma 9003 (34 prescription and non-prescription drugs); and hormones method (20 natural and synthetic sex hormones)
- EPA ORD NERL – Conduct weekly analysis of stream and effluent samples for 56 pharmaceuticals and metabolites using SPE and UPLC/MS/MS (Spring only)
- EPA ORD NRMRL – Conduct weekly analysis of stream and effluent samples for 8 hormones using SPE and GC/MS (Spring only)





Study Design – Objective 2 (cont.)

- Estimate effluent and stream concentrations of APEs and general chemistry
 - EPA Central Regional Laboratory (CRL) – Analyze of 2-3 effluent samples per week and weekly stream samples for long chain APEOs (NP3-18EO and OP2-12EO) and NP1EC and NP2EC using direct injection LC/MS; and NP, NP1EO, NP2EO, OP, and BPA using CLLE and GC/MS.
 - MWRD – Analyze 2-3 effluent samples per week and a stream sample for general chemical parameters (e.g. N-NH₃, BOD, SS, etc.)





Study Design – Objective 3



- Estimate whole fish concentrations of PPCPs, APEs, and hormones (sexually mature fish)
 - USDA - Conduct analyses on whole fish homogenates and fillet tissue for alkylphenols and alkylphenol ethoxylates (NP, NP1-4EO, OP, OP1-4EO).
 - ◆ 6 large mouth bass from NSC and 3 large mouth bass from reference site
 - ◆ 3 fillet composite samples from National Fish Tissue study
 - ◆ 3 small mouth bass from national reference location (New Mexico)
 - USGS - Conduct analysis of whole fish homogenates using OWC 1433 (75 organic waste water contaminants including some personal care products) and hormones method (20 natural and synthetic sex hormones)
 - ◆ 3 large mouth bass from NSC and 3 large mouth bass from reference site
 - Clarkson University - Conduct analysis of whole fish homogenates for PCBs, OC pesticides, BFRs, Hg, and dioxins.
 - ◆ 6 large mouth bass from NSC and 3 large mouth bass from reference site



Study Design – Objective 4

- Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.
 - Fall 2006 campaign
 - ◆ Effluent and stream samples collected from September to October
 - ◆ 24 large mouth bass collected for National Fish Tissue study
 - ◆ 12 large mouth bass collected for this study
 - ◆ 9 large mouth bass collected from local reference site (Lk Michigan)
 - Spring 2007 campaign
 - ◆ Effluent & stream samples collected from February to April
 - ◆ 24 large mouth bass collected for National Fish Tissue study
 - ◆ 9 large mouth bass & 14 common carp collected for this study
 - ◆ 12 large mouth bass, 13 carp and 2 catfish from Braidwood



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- **Preliminary results**



Estrogenic Effects on Fish

Fall 2006

Summary of fish sex and occurrence of vitellogenin in Fall 2006 Collection

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

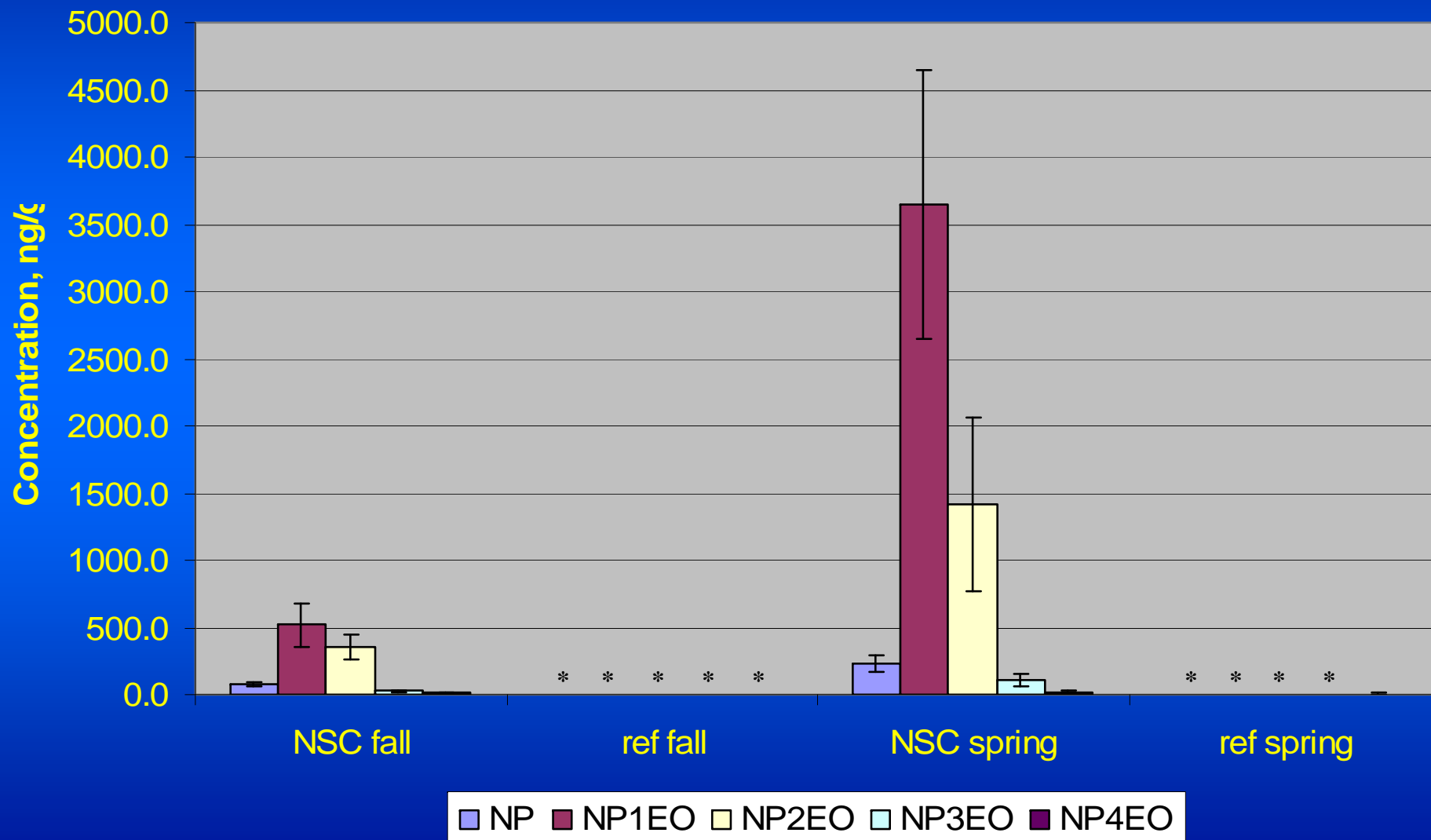


Estrogenic Effects on Fish

(values mean \pm standard error) Spring 2007

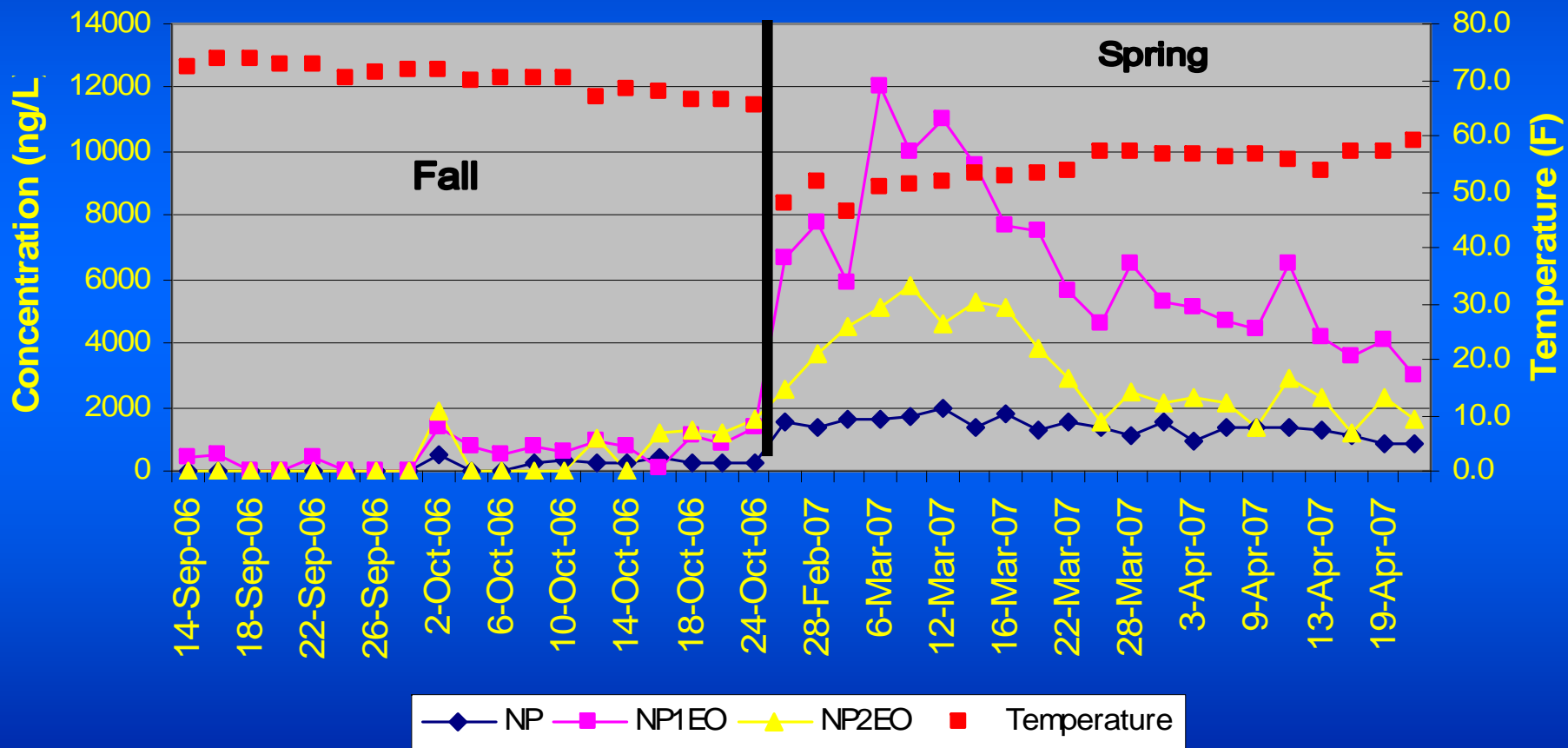
Parameter	Largemouth Bass				Common Carp			
	Effluent		Braidwood		Effluent		Braidwood	
	Male	Female	Male	Female	Male	Female	Male	Female
Sample size	1	8	8	4	9	5	11	2
Weight (g)	1050	949 \pm 64	998 \pm 1 10	941 \pm 11 4	3176 \pm 4 66	3518 \pm 77 9	2222 \pm 207	1889 \pm 874
VTG (μ g/mL)	3.3	7 \pm 1.8	0.08 \pm 0.05	9.3 \pm 5.1	38 \pm 17	38900 \pm 9 334	29 \pm 12	48350 \pm 31 950

NPEs in Large Mouth Bass

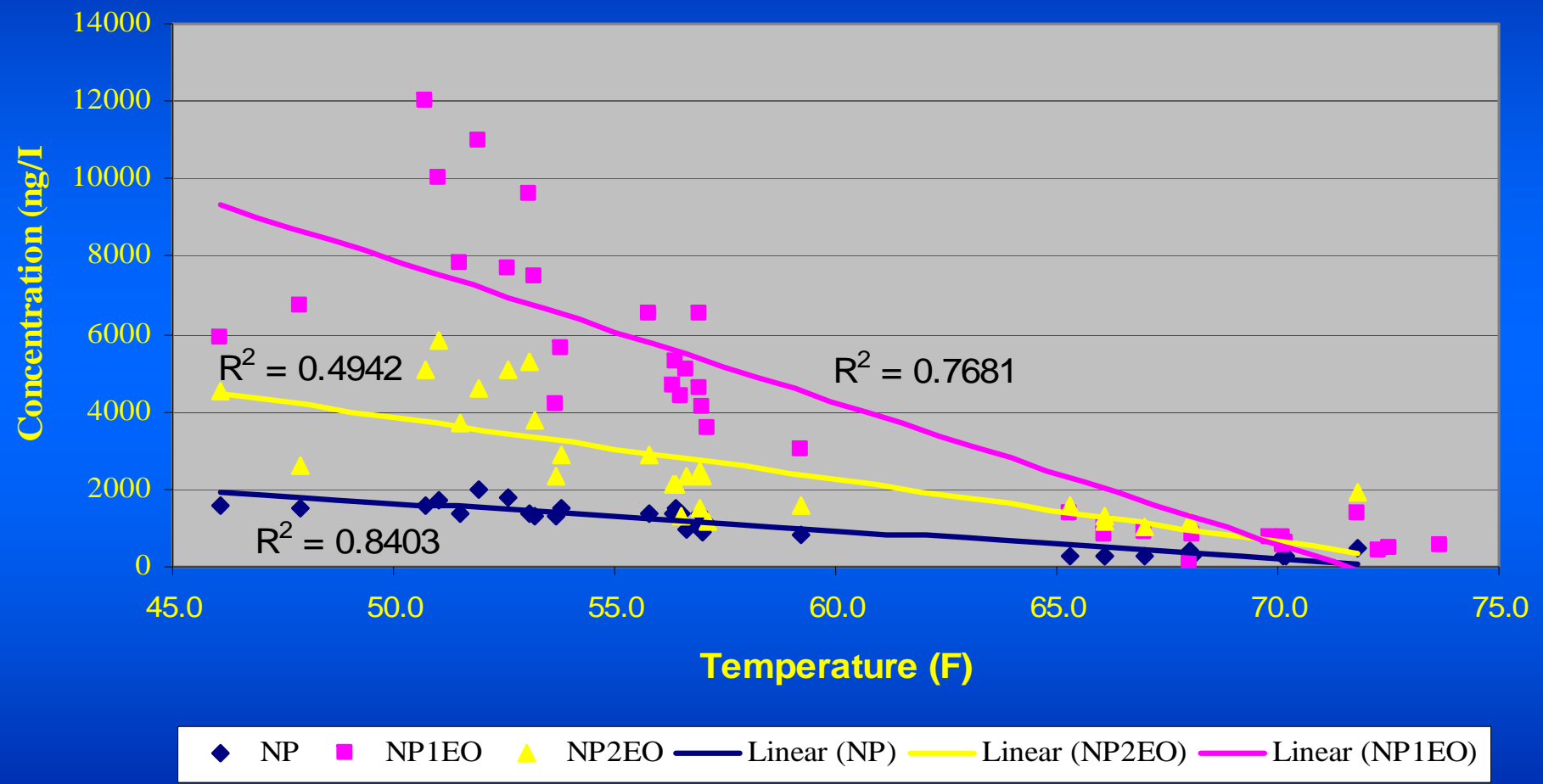


* Below MDL

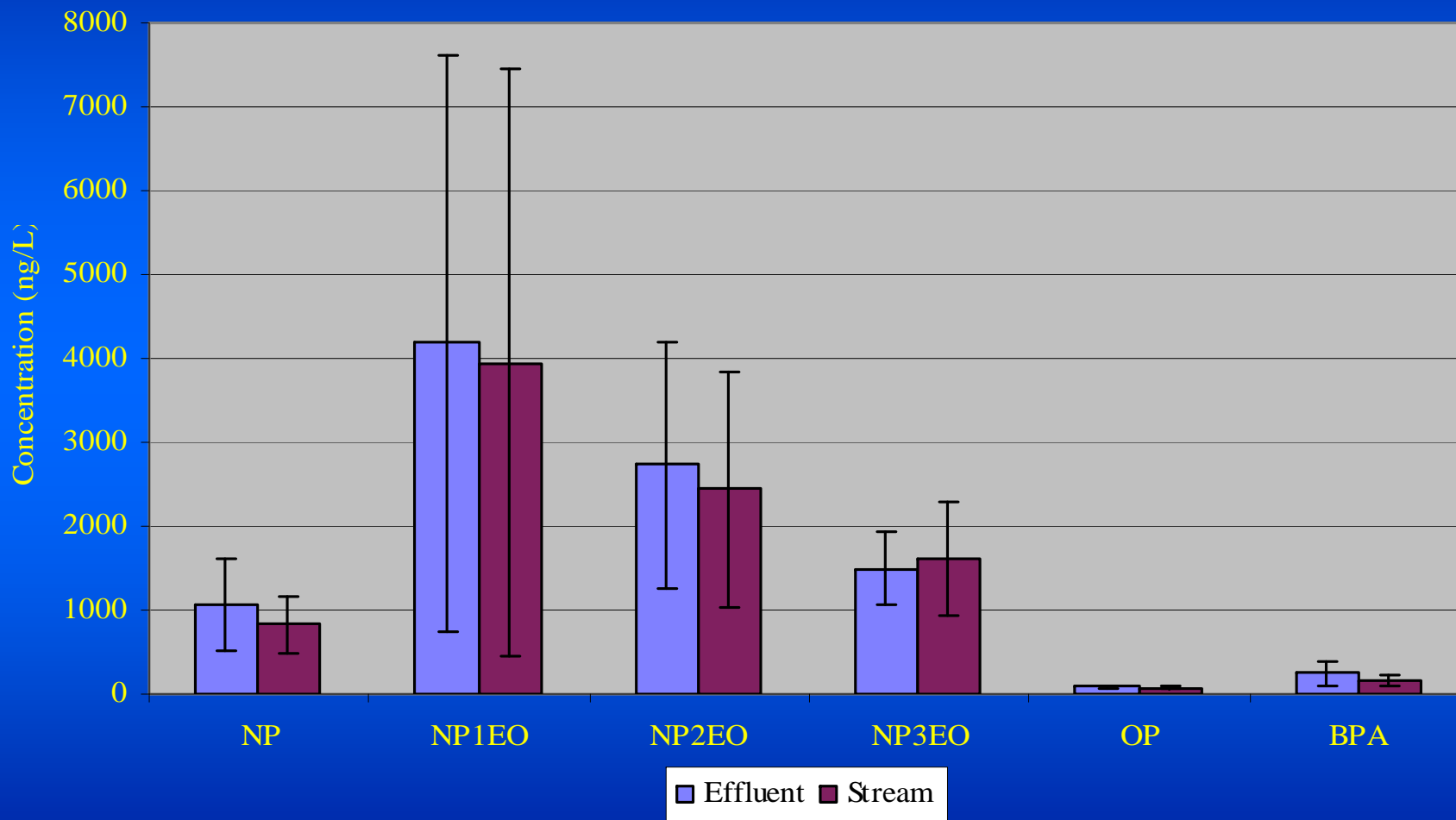
Nonylphenol and Nonylphenol Ethoxylates in Northside WRP Effluent



APEs Concentrations versus Temperature Fall 2006 & Spring 2007 Collections



APEs in Northside WRP Effluent and Downstream Channel Fall 2006 & Spring 2007 Collections





Bioconcentration Factor (BCF) for NPEs

- BCF = Concentration in fish / Concentration in water
 - ◆ NP = 130-230
 - ◆ NP1EO = 450-630
 - ◆ NP2EO = 200-480
 - ◆ NP3EO = 40-60
- These values agree reasonably well with the values published on common carp by Mitchelmore and Rice 2006.
 - ◆ NP = 280
 - ◆ NP1EO = 1713
 - ◆ NP2EO = 693



Pharmaceuticals in Effluent and Stream Samples

Pharmaceuticals present at high ppt to ppb

- Lisinopril
- Valsartan
- Hydrochlorothiazide
- Ibuprofen-2-hydroxy
- Gemfibrozil

Pharmaceuticals present at mid ppt

- Atenolol
- Metoprol
- Diltiazem
- Ciprofloxacin
- Trimethoprim
- Carbamazepine
- Furosemide
- ibuprofen

Pharmaceuticals not detected

- Clonidine
- Oxycodone
- Propoxyphene
- Amitriptyline-10-OH
- Alprazolam
- Liothyronine
- Levothyroxine
- Acetaminophen
- Prednisone, Prednisolone, Betamethasone, Methylprednisolone
- Norethindrone
- Testosterone
- Fluocinonide
- Fluticasone
- Progesterone
- Simvastatin
- Theophylline
- Warfarin
- Glipizide
- Hydrocortisone
- glyburide



Summary and Next Steps

- Collaboration is KEY!
- Estrogenic effects present
 - ◆ What is the significance?
- Fish tissue concentrations vary along with effluent and stream concentrations
 - ◆ Similar BCFs in fall and spring
- Wastewater effluent is a soup of 1000s of compounds
- Much more data to come
 - ◆ Hormones in effluent, stream and fish
 - ◆ PPCPs in effluent, stream and fish



Thank You!

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