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

Things I plan to talk about…

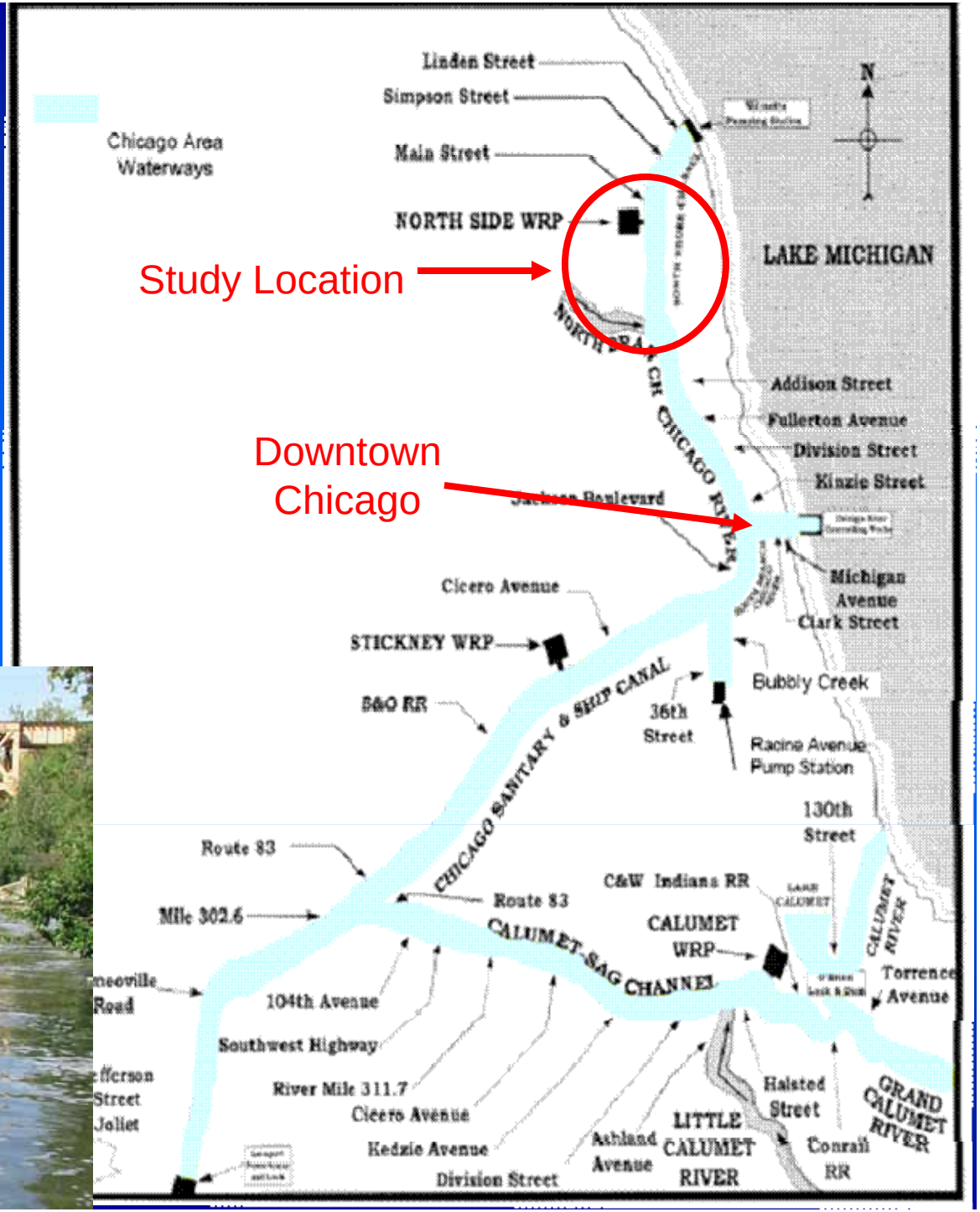
- Objectives of study
- **Study location**

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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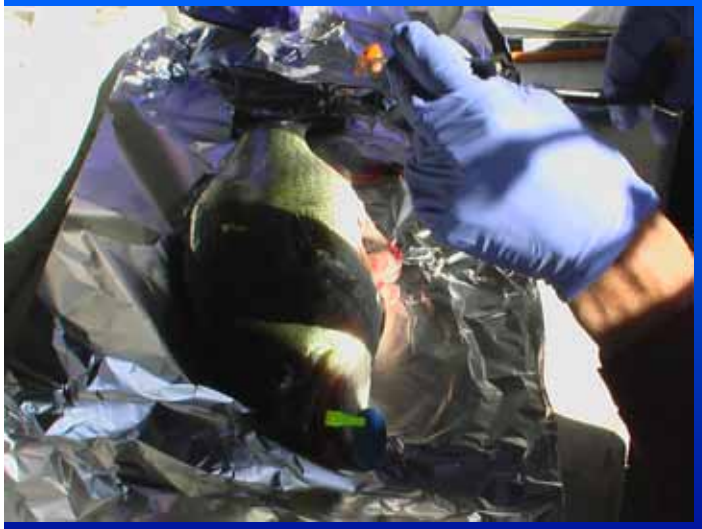
- **Study design**

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 (Sprng 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

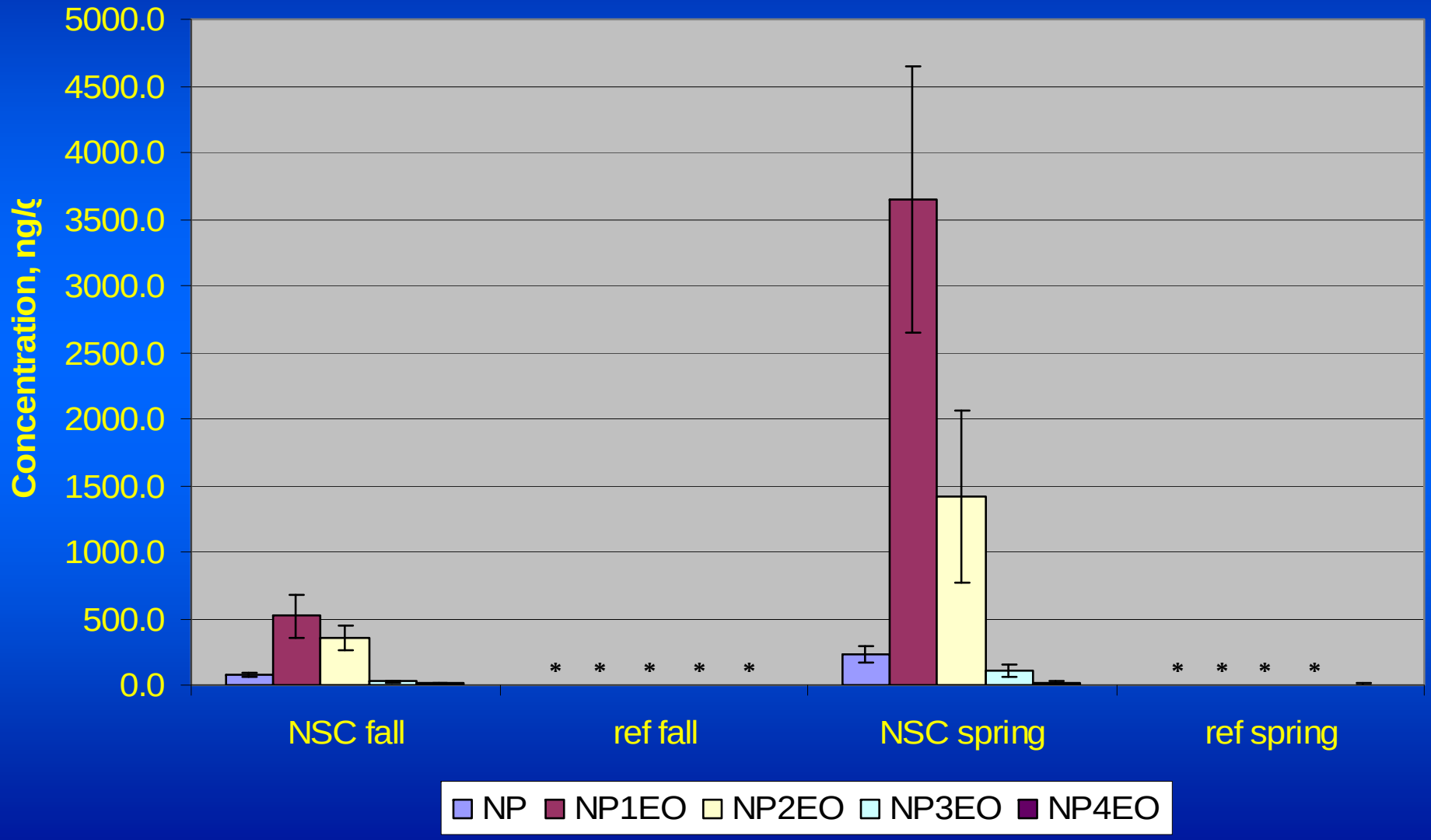
Summary of fish sex and occurrence of vitellogenin in Fall 2006 Collection

	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 ± standard error) Spring 2007

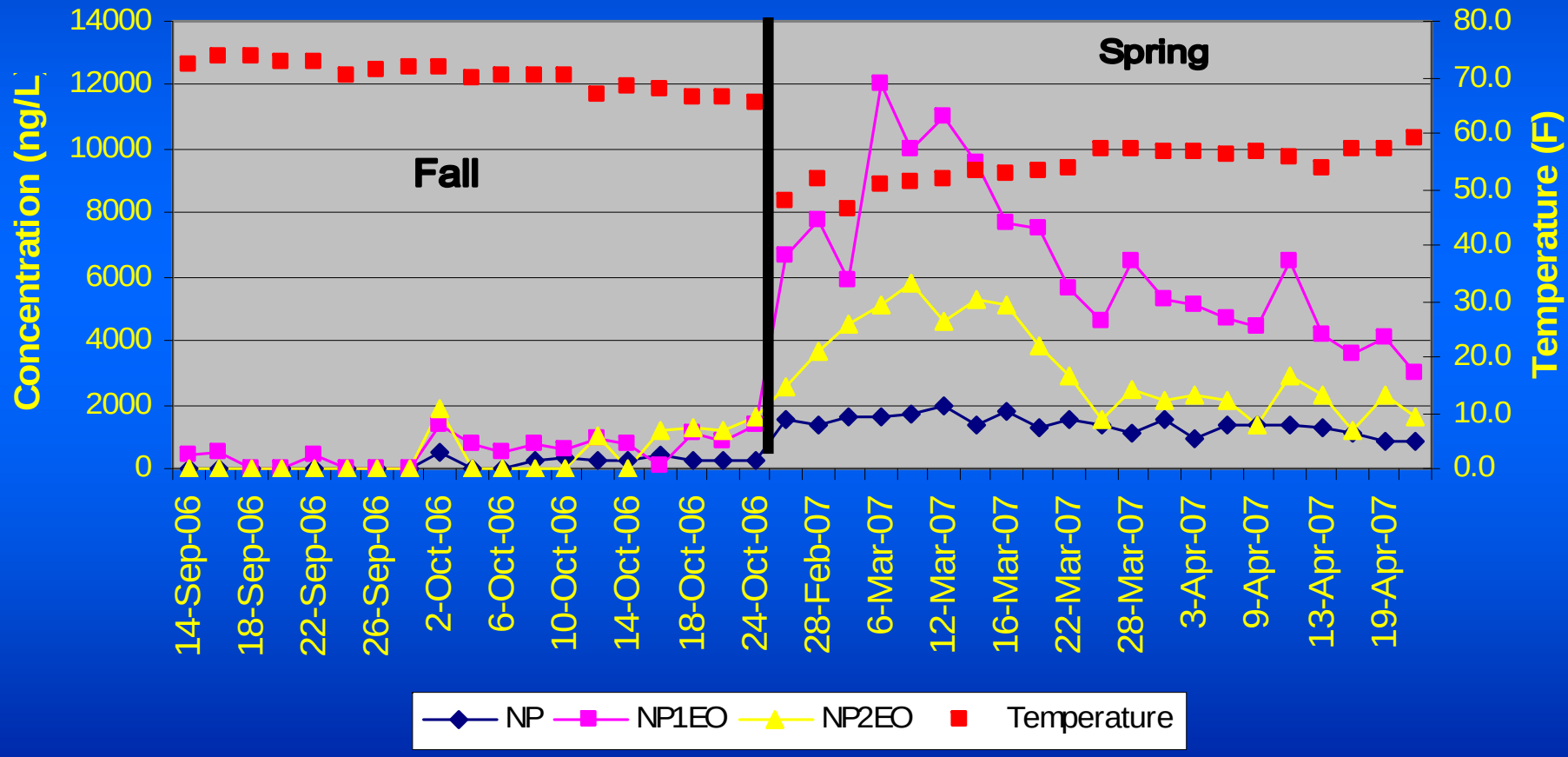
Parameter	Largemouth Bass				Common Carp			
	Effluent		Braidwood		Effluent		Braidwood	
	Male	Female	Male	Female	Male	Female	Male	Female
Sample size	1	8	8	4	9	5	11	2
Weight (g)	1050	949±64	998±110	941±114	3176±466	3518±779	2222±207	1889±874
VTG (µg/mL)	3.3	7±1.8	0.08±0.05	9.3±5.1	38±17	38900±9334	29±12	48350±31950

NPEs in Large Mouth Bass

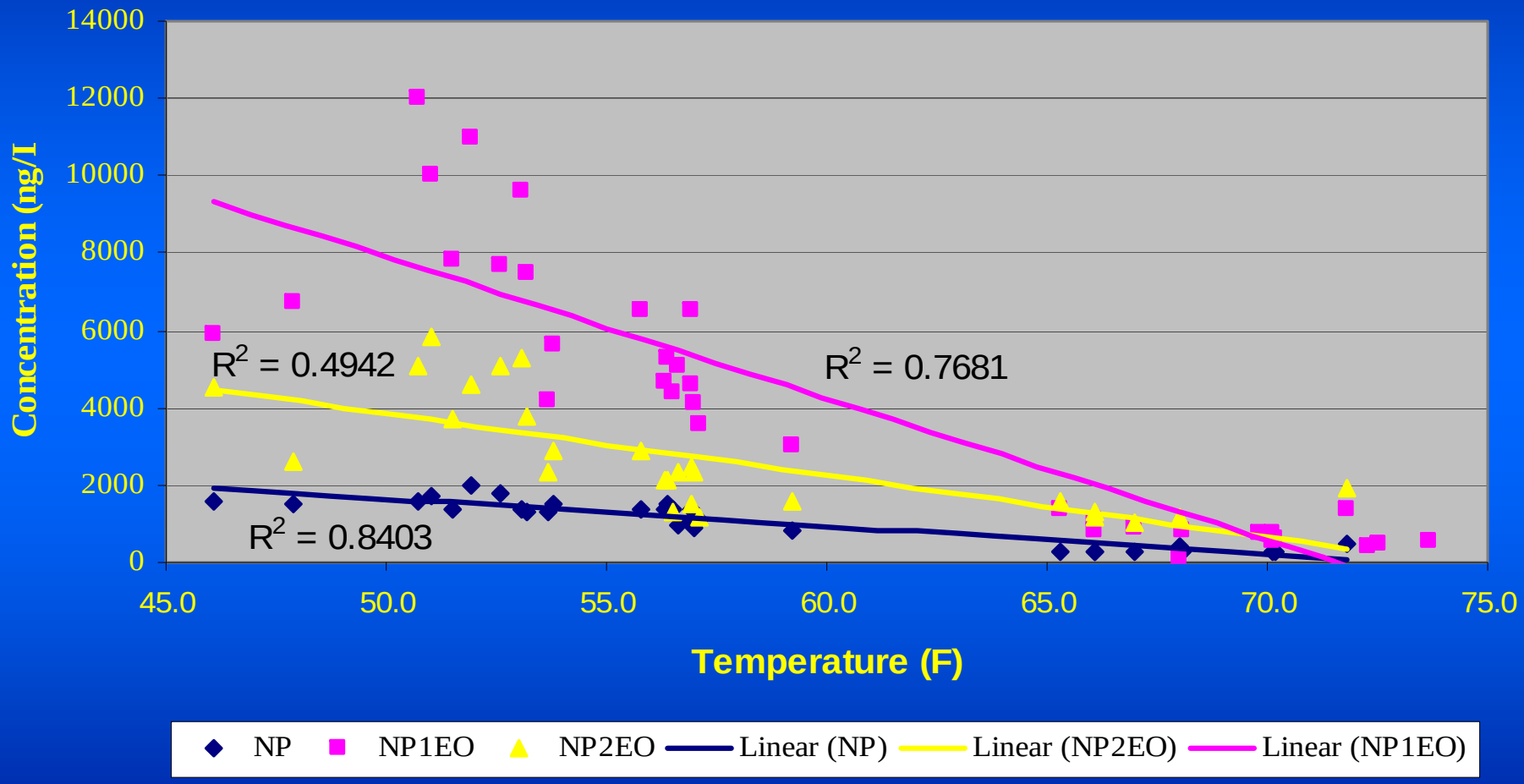


* Below MDL

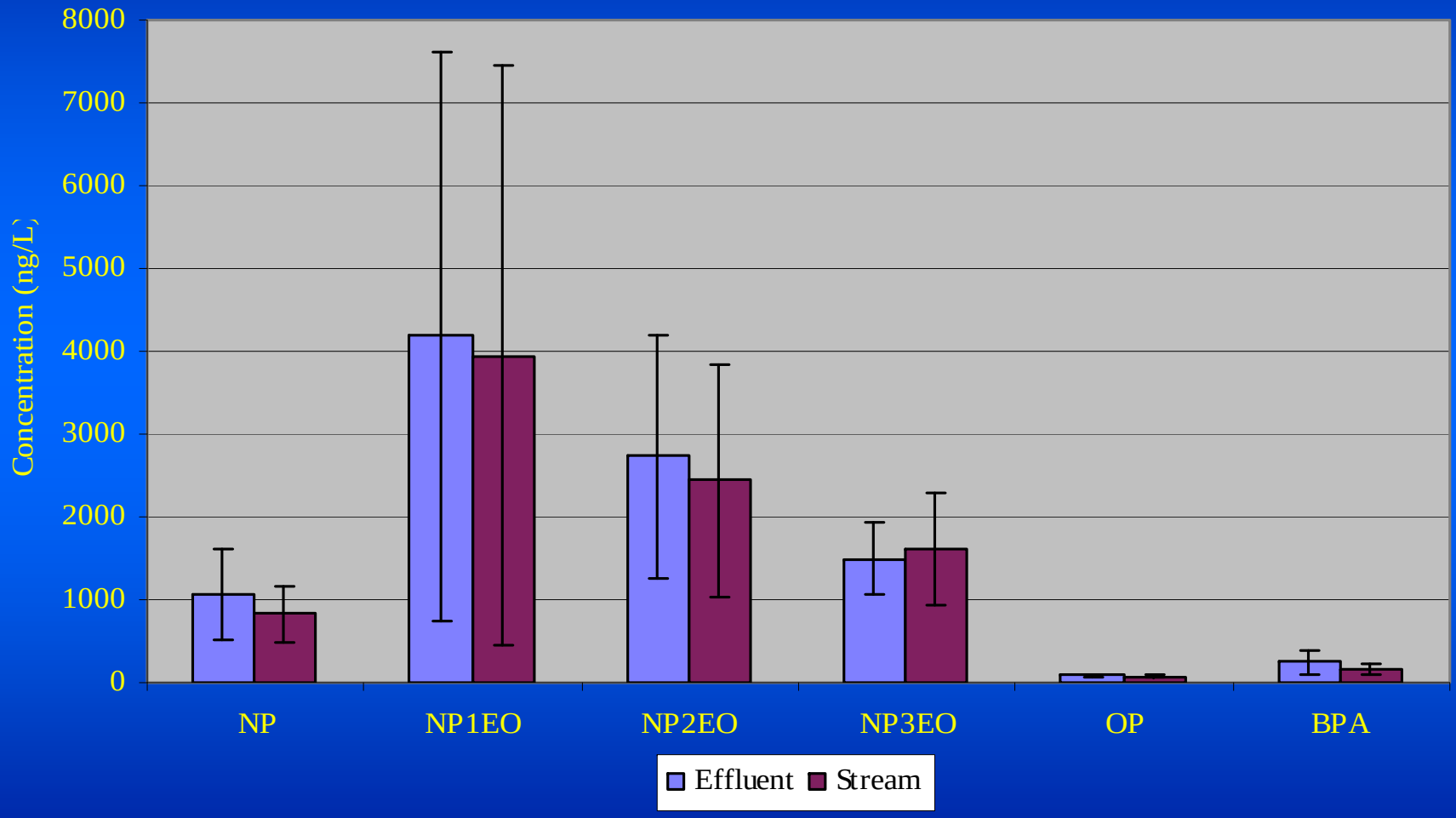
Nonylphenol and Nonylphenol Ethoxylates in Northside WRP Effluent



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 is effluent, stream and fish
  - PPCPs in effluent, stream and fish

Thank You!

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