

An Exploration of Emerging Contaminants in the Chicago Waterways: Ongoing Collaborative Research between EPA and the Metropolitan Water Reclamation District

MWRD Research & Development Seminar

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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



Outline of talk

- Background on emerging chemicals of concern
- Collaborative studies
 - Distribution of Chemical Contaminants within a Large Wastewater Treatment Plant and in Downstream Surface Waters (**Calumet**)
 - Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River (**NSC**)
- Conclusions and next steps



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





Personal Care Products



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

Fragrances

Preservatives

Disinfectants/Antiseptics

Sunscreen Agents





What are APEs?

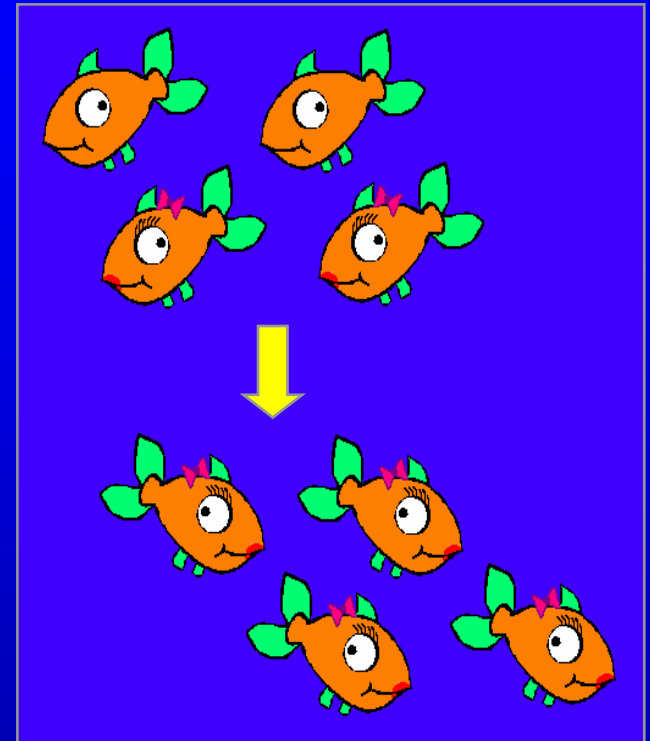
APE = Alkylphenol Ethoxylates (APEs)

- Nonyl & Octyl Phenol Ethoxylates
- High Production Volume Chemical
 - ◆ ~ 391.5 million lbs/year NPEs and 77 million lbs/yr OPEs used in North America (U.S. & Canada) in 2003
- Uses - Detergents, wetting agents, dispersants, emulsifiers, solubilizers and foaming agents
- Industrial applications - Pulp and paper, textiles, coatings, agricultural pesticides, lube oils and fuels, metals and plastics
- Chief concern is NP based compounds.
 - OP is also toxic, and more potent ED but only = 10 – 15% of APEs used



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





Distribution Study at the Calumet WRP

Calumet



Image © 2007 NASA

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Pointer 41°39'58.29" N 87°36'17.12" W

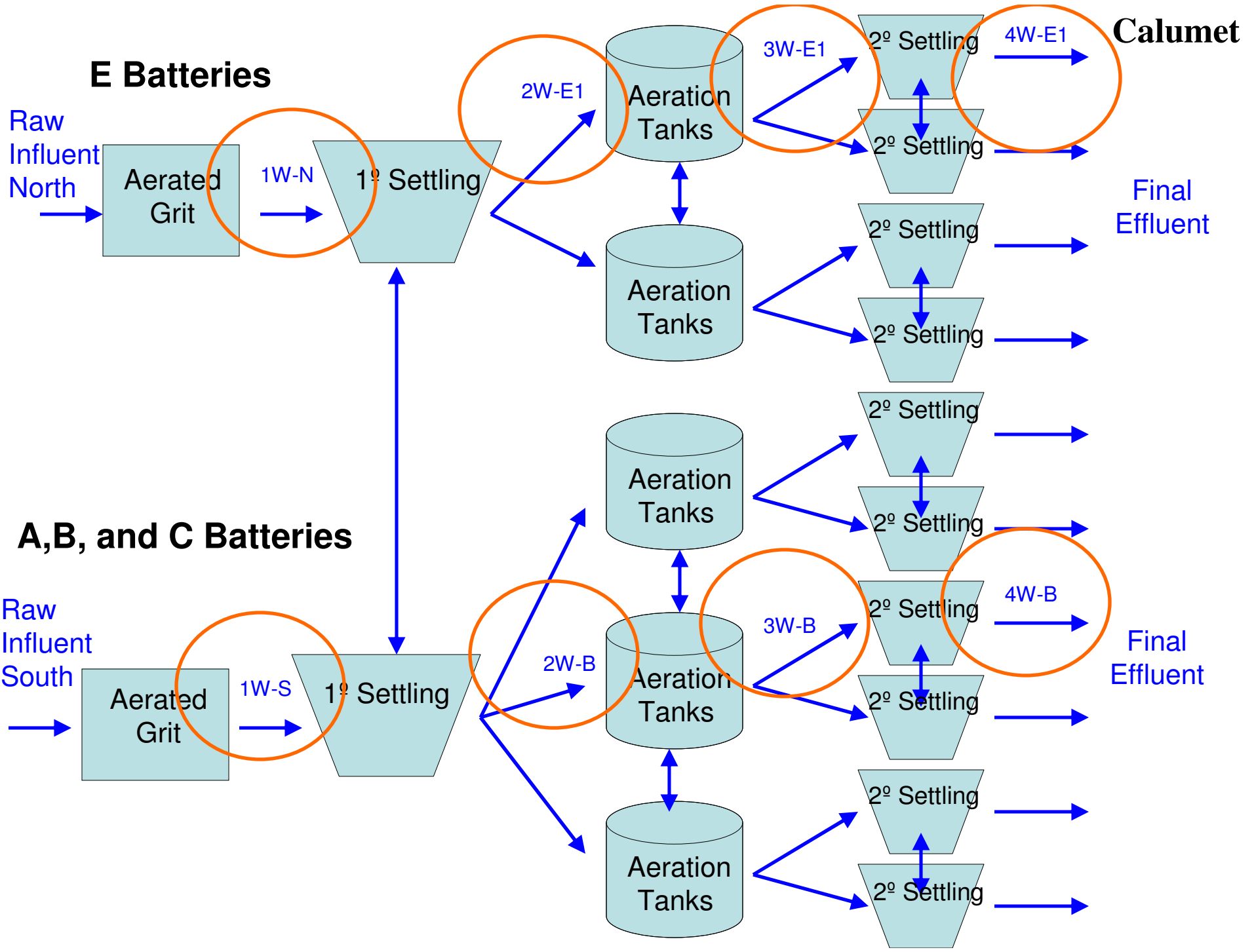
Streaming ||||| 100%

Eye alt 6078 ft



Objective of Distribution Study

- Fate of toxic substances throughout a WWTP
 - ◆ Solid and hydraulic cycles
- Degree of treatment effectiveness across treatment processes
- 3 sampling events
 - ◆ Approximately 11 aqueous and 11 sludge samples per event
 - ◆ Between 140 and 300 analytes per sample
 - ◆ **Over 12,000 data points!**
- Strengthen collaborative ventures

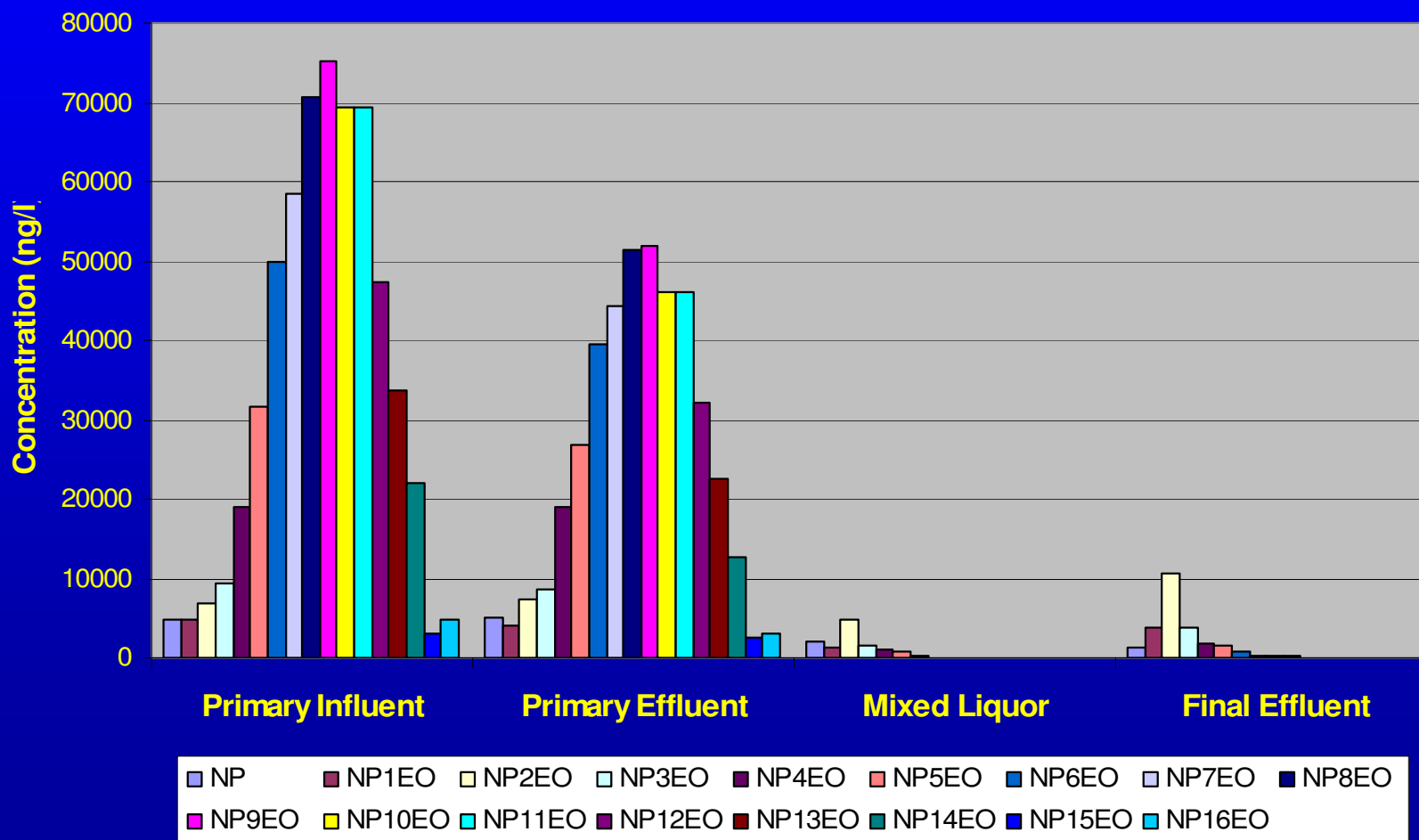




Most action occurs in the aeration tanks!

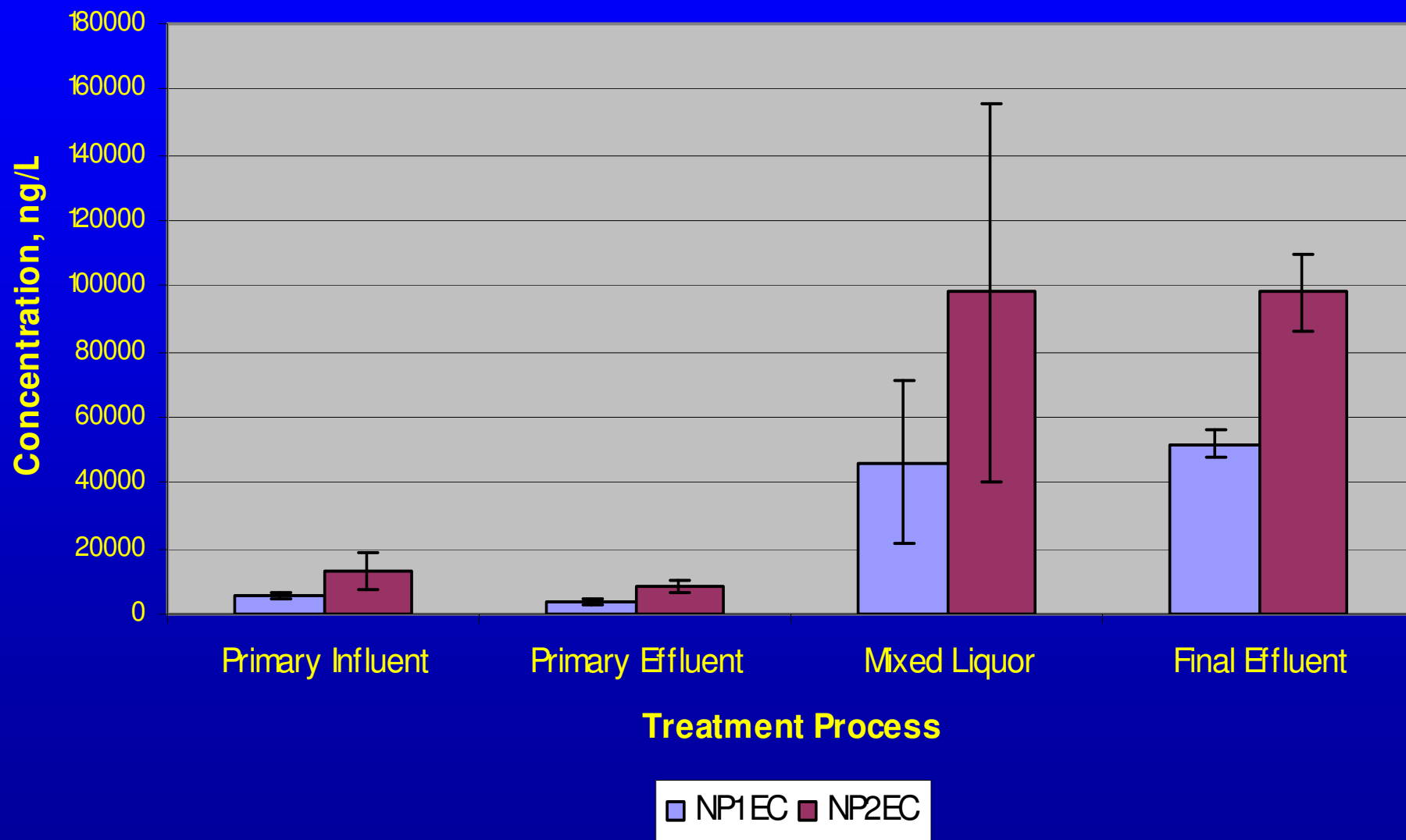
Calumet

Nonylphenol Ethoxylates in the Calumet WRP

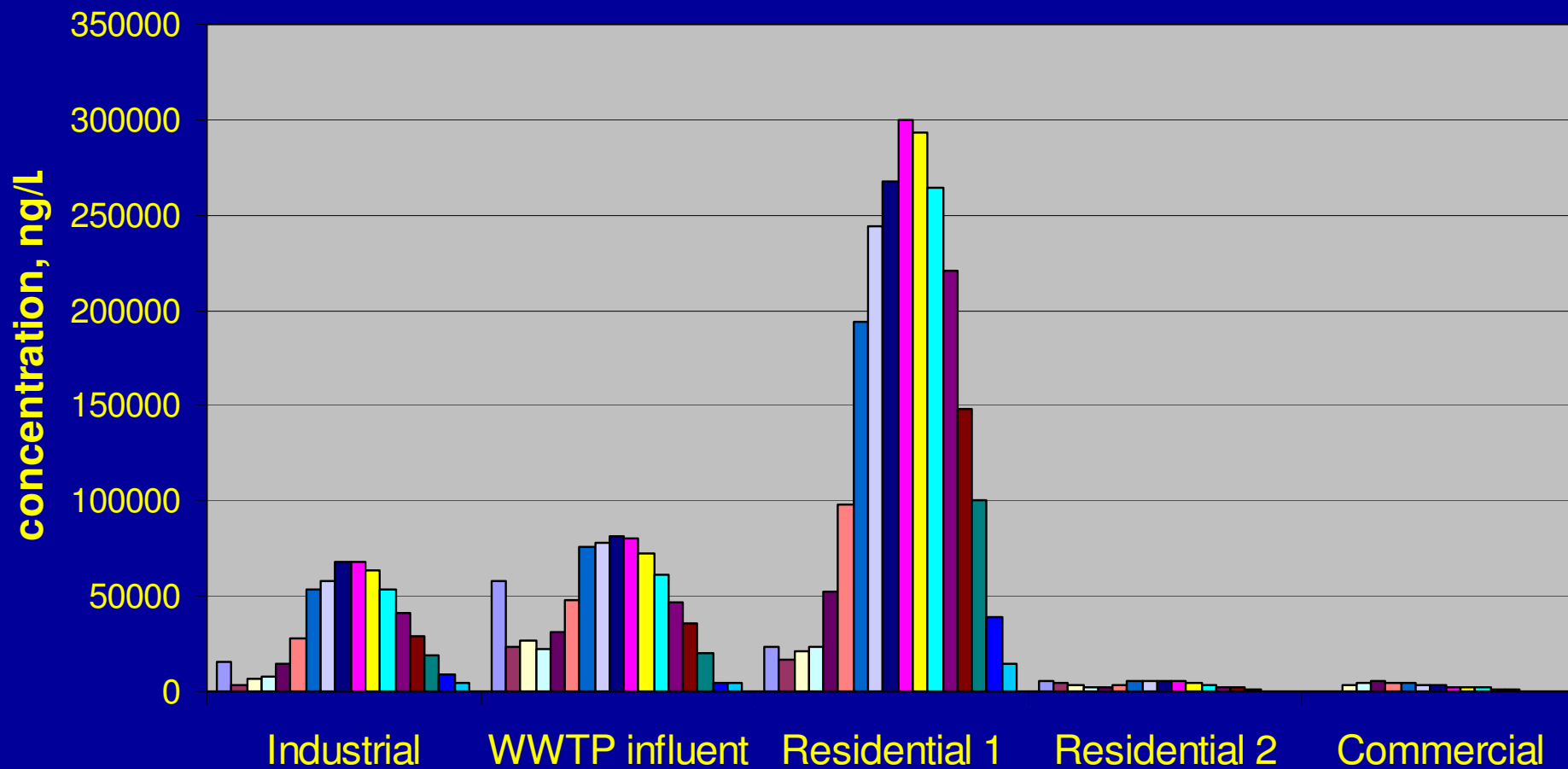




Nonylphenol Carboxylates in the Calumet WRP



Total NP0-16EO Concentrations (dissolved + particulate) in grab sewer samples (May 2005)

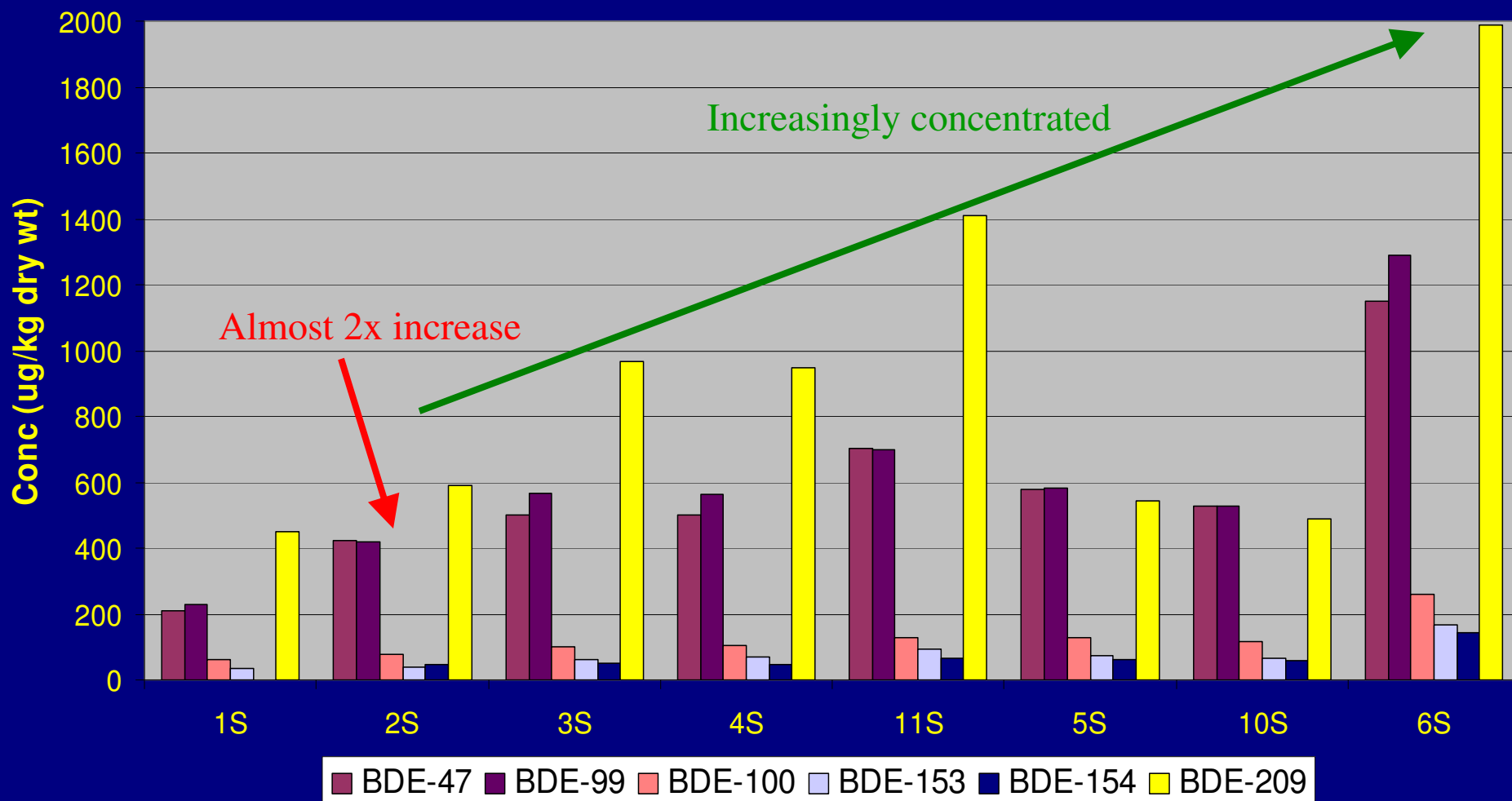


- NP
- NP1EO
- NP2EO
- NP3EO
- NP4EO
- NP5EO
- NP6EO
- NP7EO
- NP8EO
- NP9EO
- NP10EO
- NP11EO
- NP12EO
- NP13EO
- NP14EO
- NP15EO
- NP16EO

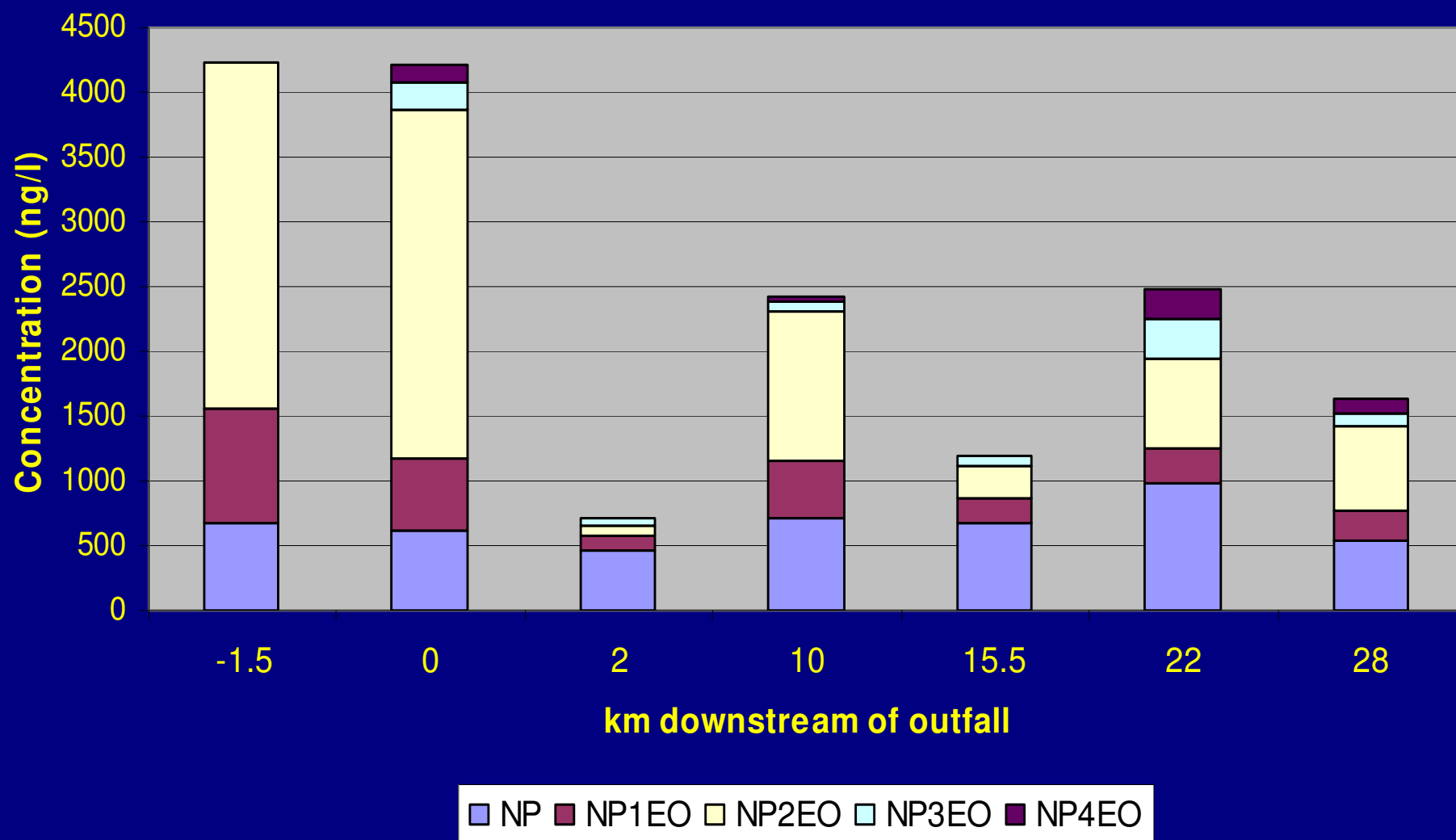


Aeration Tanks are also effective at removing PBTs - due to partitioning

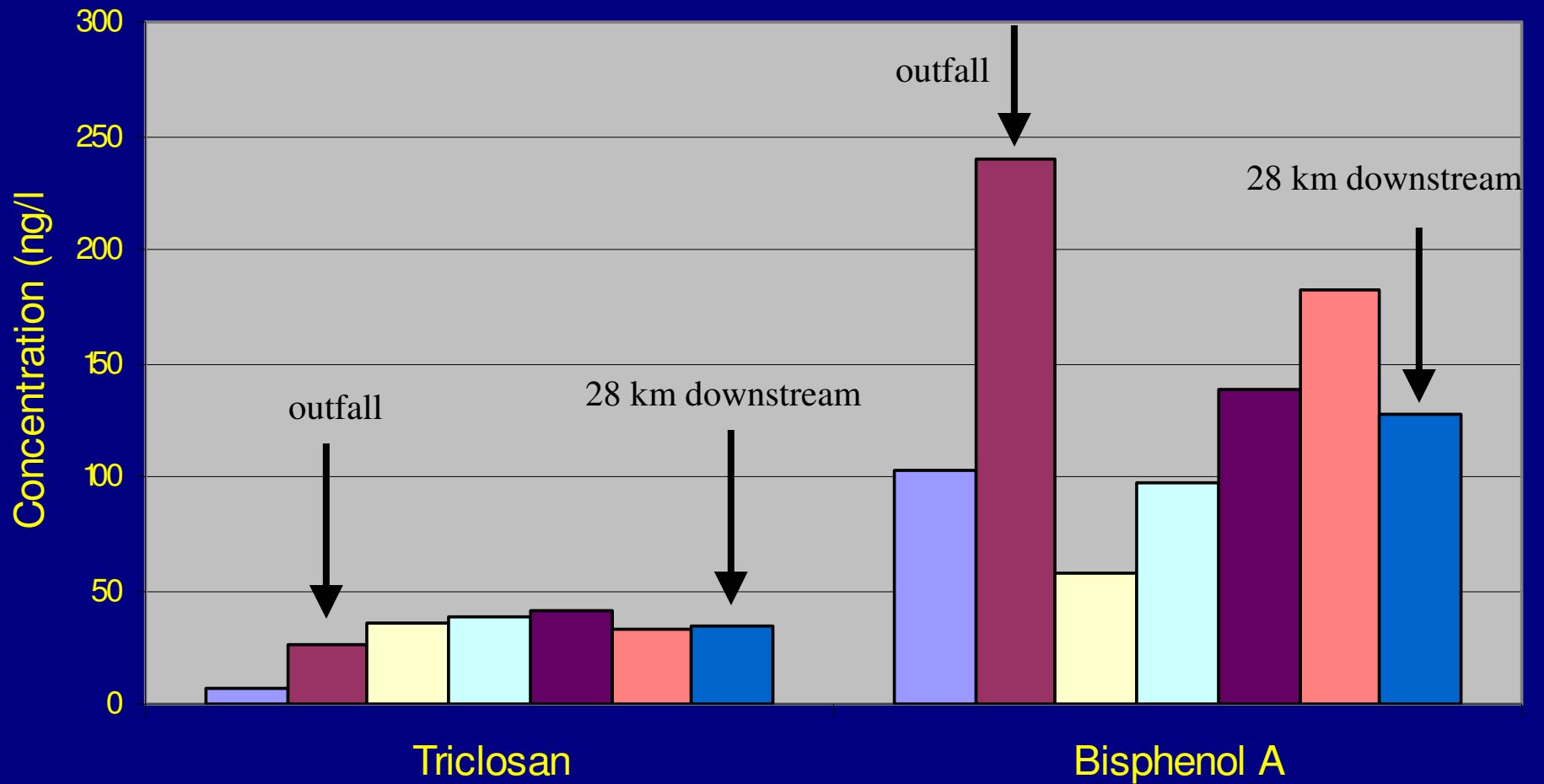
PBDEs in Sludge at CWRP



Nonylphenol and its Ethoxylates in the Cal-Sag Channel

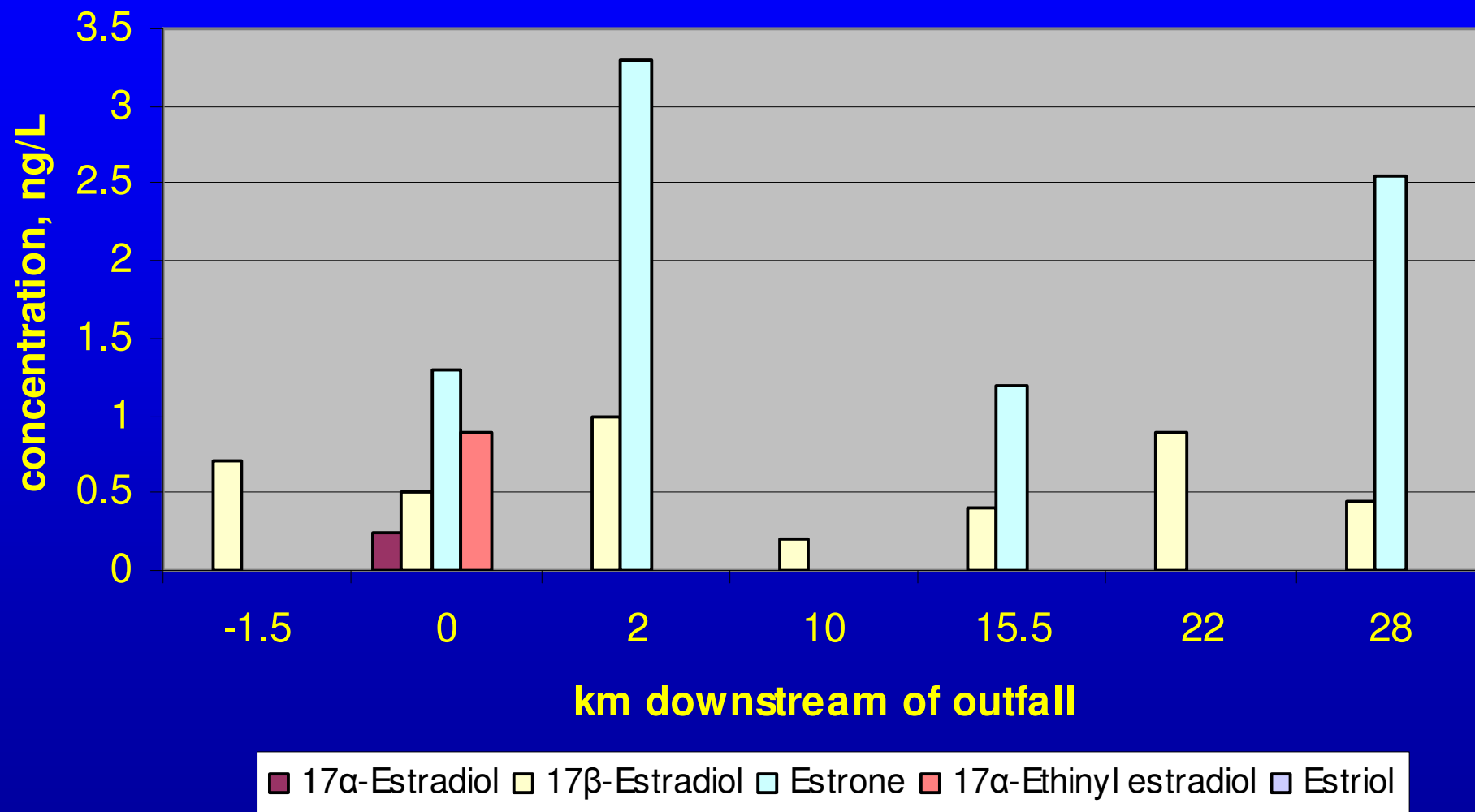


Downstream Persistence in the Cal-Sag





Estrogens in Cal-Sag (August 2005)





Summary of Calumet Distribution Study

Calumet

- Sampling is a HUGE challenge
- Low-level analysis in complex matrices is also a HUGE challenge
- Removal mechanisms can be degradation, partitioning, and/or others
 - ◆ Consider the by-products and additives!
- Many compounds persist well downstream of outfall
 - ◆ What is the significance?



NSC Study Objectives

- Supplemental study to EPA's National Fish Tissue Study
- Strengthen collaborative ventures
- The 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
 - Document seasonal differences in concentrations of these compounds in effluent, stream, and fish.
 - Identify any correlations between common wastewater treatment plant parameters and APEs/hormones in effluent



Collection Location and Time

NCS Pilot Study

North Shore Channel 9-10/2006 & 3-4/2007

Lake Michigan 9/2006

Braidwood Cooling Pond 3/2007

Nat. Pilot Study

● AZ Nov-06

NM Nov-06



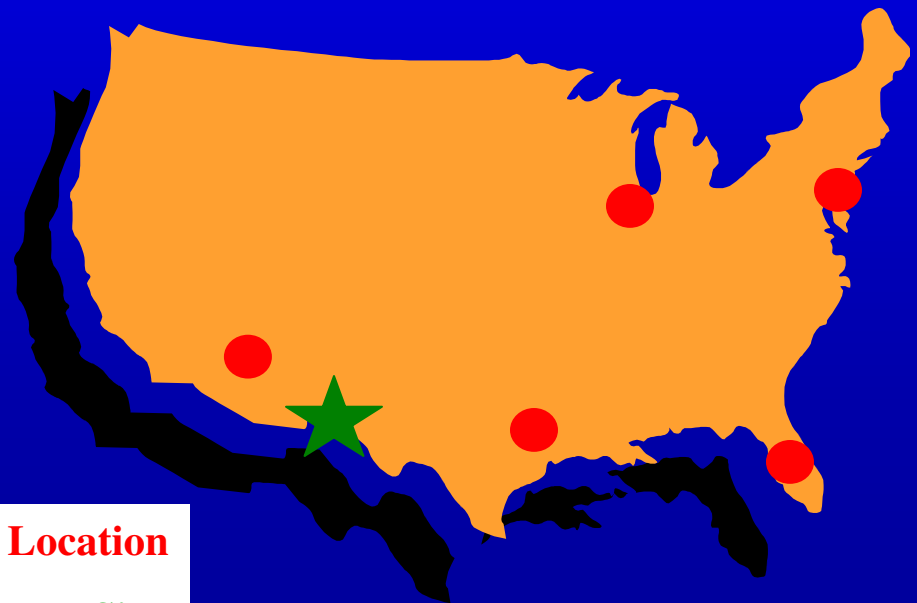
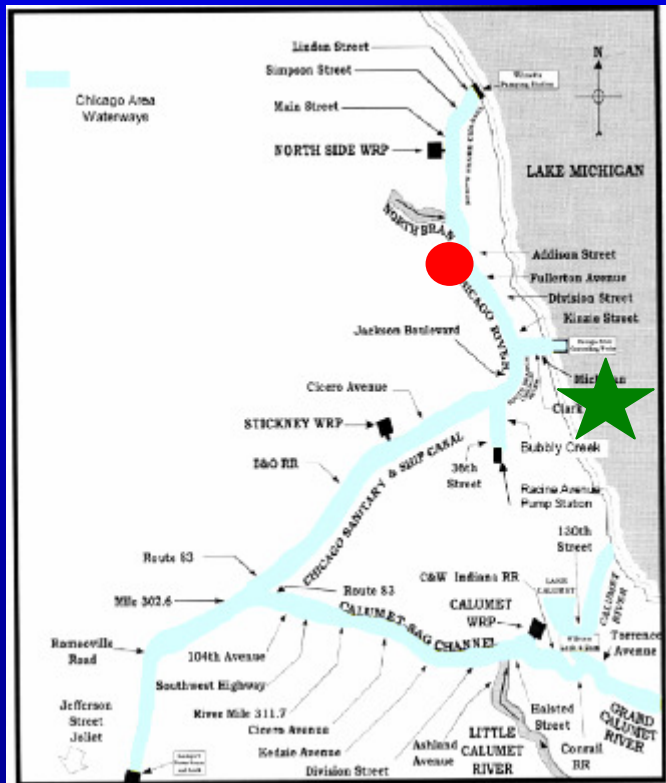
● FL Oct-06

PA Aug-06



● IL Sep-06

TX Oct-06



Study Location

Reference Site



NSC Study Design



- Whole fish collected, processed, and stored from NSC and reference sites in the fall and spring.
- Brain, liver, & gonads taken for histopathology. Blood sampled for VTG. Scales taken for age.
- Effluent & Stream samples collected on same day.
 - MWRD (Northside WRP effluent ; 2-3/week)
 - U.S. EPA (NSC stream; 1/week)
- *Study changes from Fall to Spring*
 - St. Cloud State collected additional species to add statistical power
 - Analysis of livers for mRNA vitellogenin - a better indicator of recent exposure to endocrine disruptors
 - Different reference site used





Chemicals of Concern in Fish

EPA Pilot Study

NP

m-toluamide

musk xylene

octocrylene

celestolide

OP

tonalide

tricolan

4-methylbenzylidene

camphor

1,7-dimethylxanthine

acetaminophen

atenolol

caffeine

cimetidine

codeine

carbamazepine

diltiazem

diphenylhydramine

erythromycin

fluoxetine

gemfibrozil

ibuprofen

lincomycin

metoprolol

micnazole

norfluoxetine

propranolol

sertraline

sulfamethoxazole

thiabendazole

trimethoprim

tylosin

warfarin

galaxolide

NSC Supp. Study

NP

NP1EO

NP2EO

NP3EO

NP4EO

OP

OP1EO

OP2EO

OP3EO

OP4EO

Diethylstilbestrol

17 α -Estradiol

17 β -Estradiol

Estrone

Mestranol

Equilenin

Equilin

17 β -Ethinyl estradiol

Estriol

cis-Androsterone

Epitestosterone

Androstenedione

Dihydrotestosterone

Testosterone

11-Ketotestosterone

19-Norethindrone

Progesterone

3 β -Coprostanol

Cholesterol

and ~75 OWCs

and PCBs, PBDEs,

Hg, organochlorine

pesticides



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)**



Estrogenic Effects on Fish

Fall 2006

NSC

	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



Estrogenic Effects on Fish Spring 2007

NSC

	North Shore Channel		Braidwood Cooling Pond	
	Large Mouth Bass	Common Carp	Large Mouth Bass	Common Carp
Male fish (w/ VTG)	1 (3.3)	9 (38±17)	8 (0.08±05)	11 (29±12)
Female fish (W/VTG)	8 (7±1.8)	5 (38900±9334)	4 (9.3±5.1)	2 (48350±31950)
Total Fish	9	14	12	13

() = Total concentration ($\mu\text{g/mL}$) VTG expressed \pm standard error

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



Estrogenic Effects on Fish

Spring 2007

NSC

- High plasma [VTG] in most female fish, as to be expected.
- **NSC and Braidwood male LMB cannot be compared for VTG analysis.**
- Male carp did not exhibit clear trends .
- [VTG] comparable in several males at both sites.
- **No gross abnormalities of testes or livers**
- **No intersex or other severe pathological conditions were found at either site.**
- NSC fish exhibited greater amounts of fatty tissue in the liver than Braidwood site.
- Males at the cooling pond site were generally in an earlier spermatogenic stage than males at the NSC site.



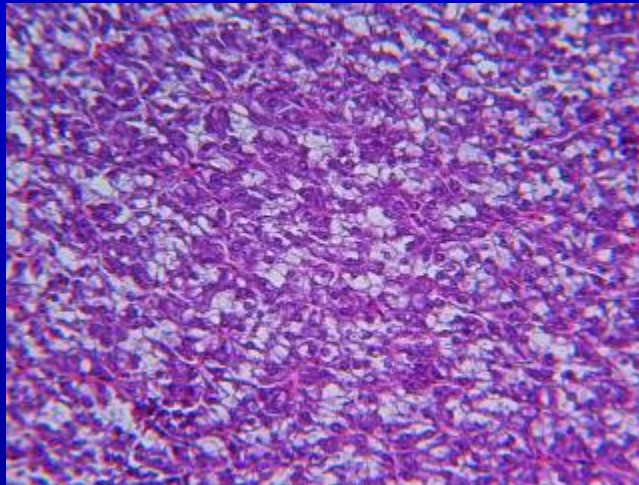
Histopathology - Liver

Fall

- 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

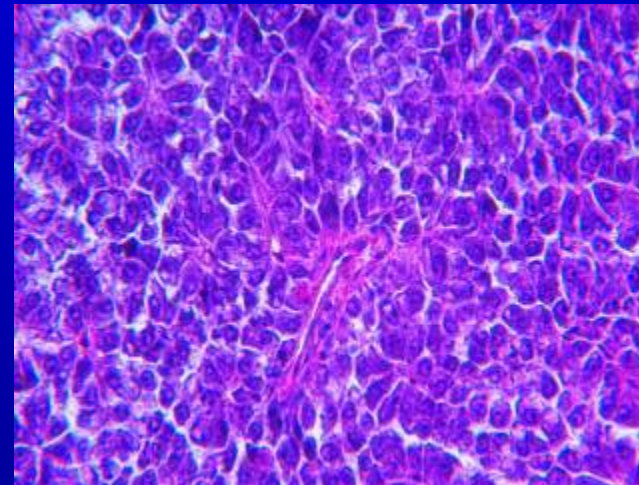
Spring

NSC LMB



Pollutant exposure

Braidwood LMB



Healthy



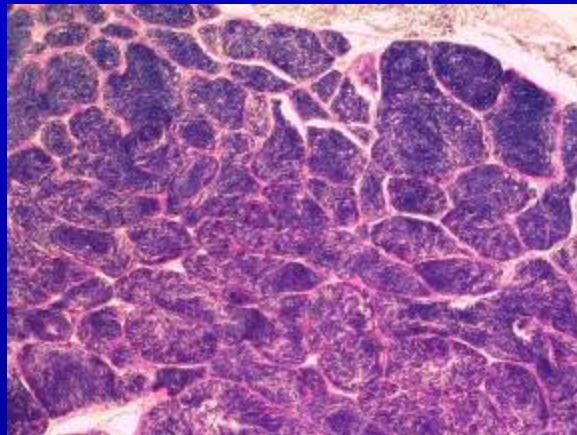
Histopathology - Gonad

Fall

- 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

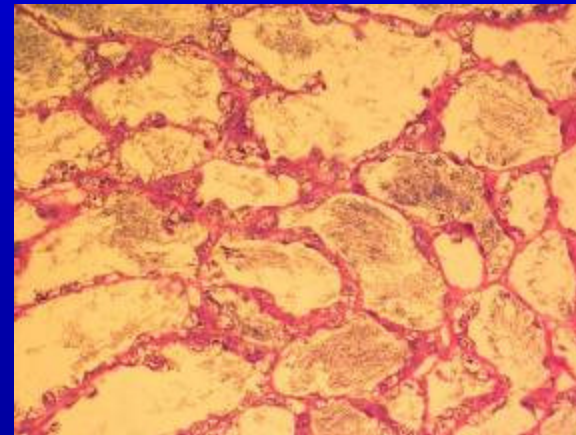
Spring

NSC Carp



Typical Carp Testis Healthy

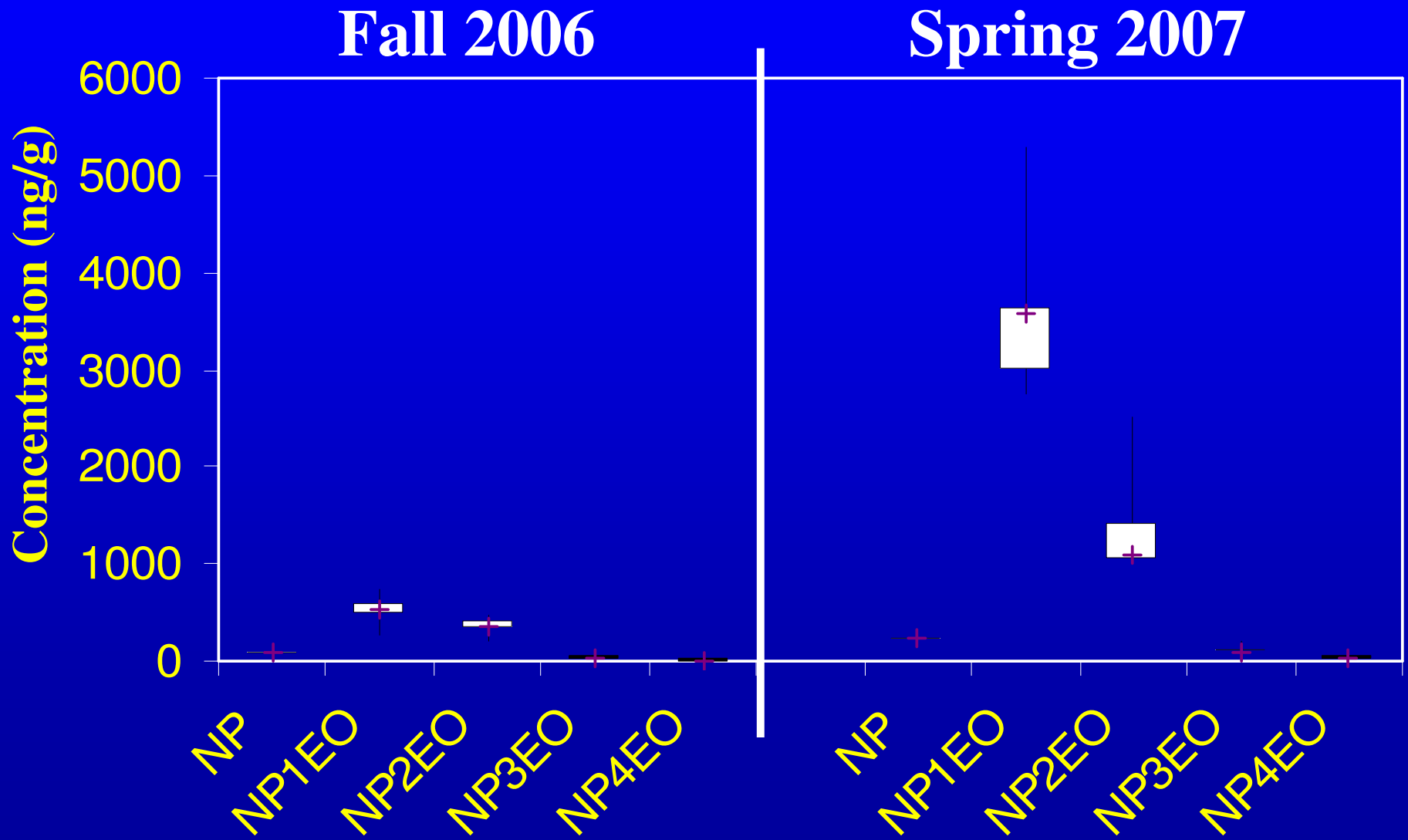
Braidwood LMB



LMB testis, recently spawned



APEs in NSC Large Mouth Bass

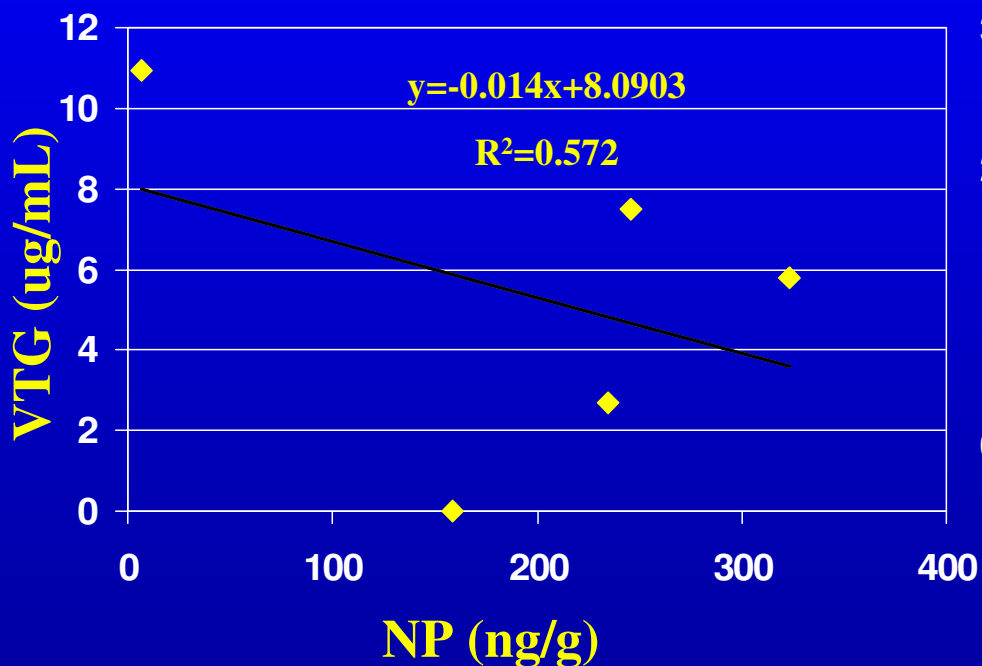


*Clifford P. Rice, Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD

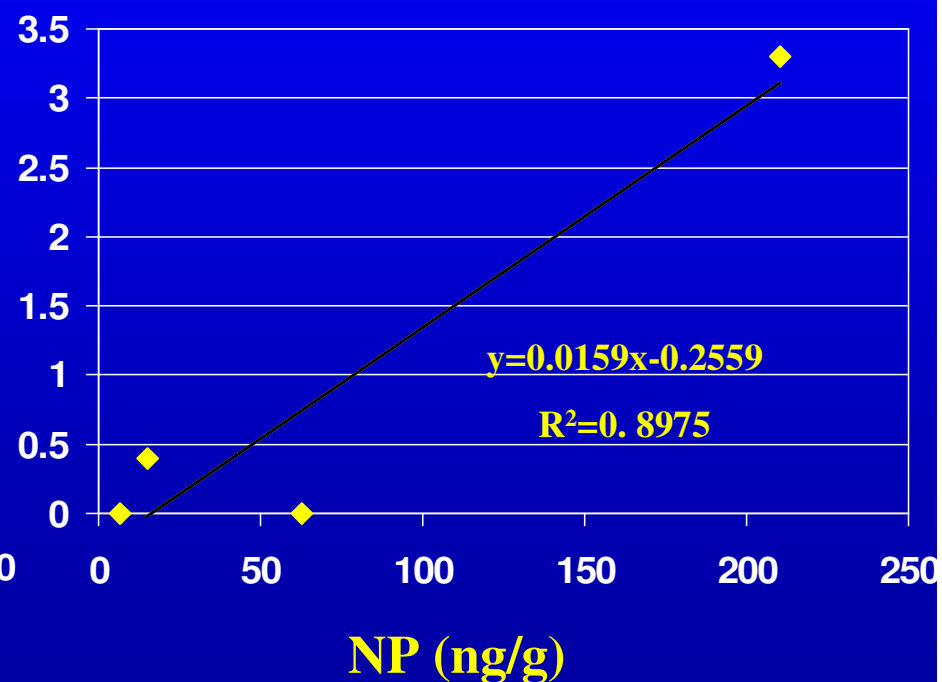


VTG vs. NP in Large Mouth Bass

Female Fish in NSC



Male Fish in Ref. Site and NSC



Correlation Coefficient = **-0.3964**

Correlation Coefficient = **0.9474**

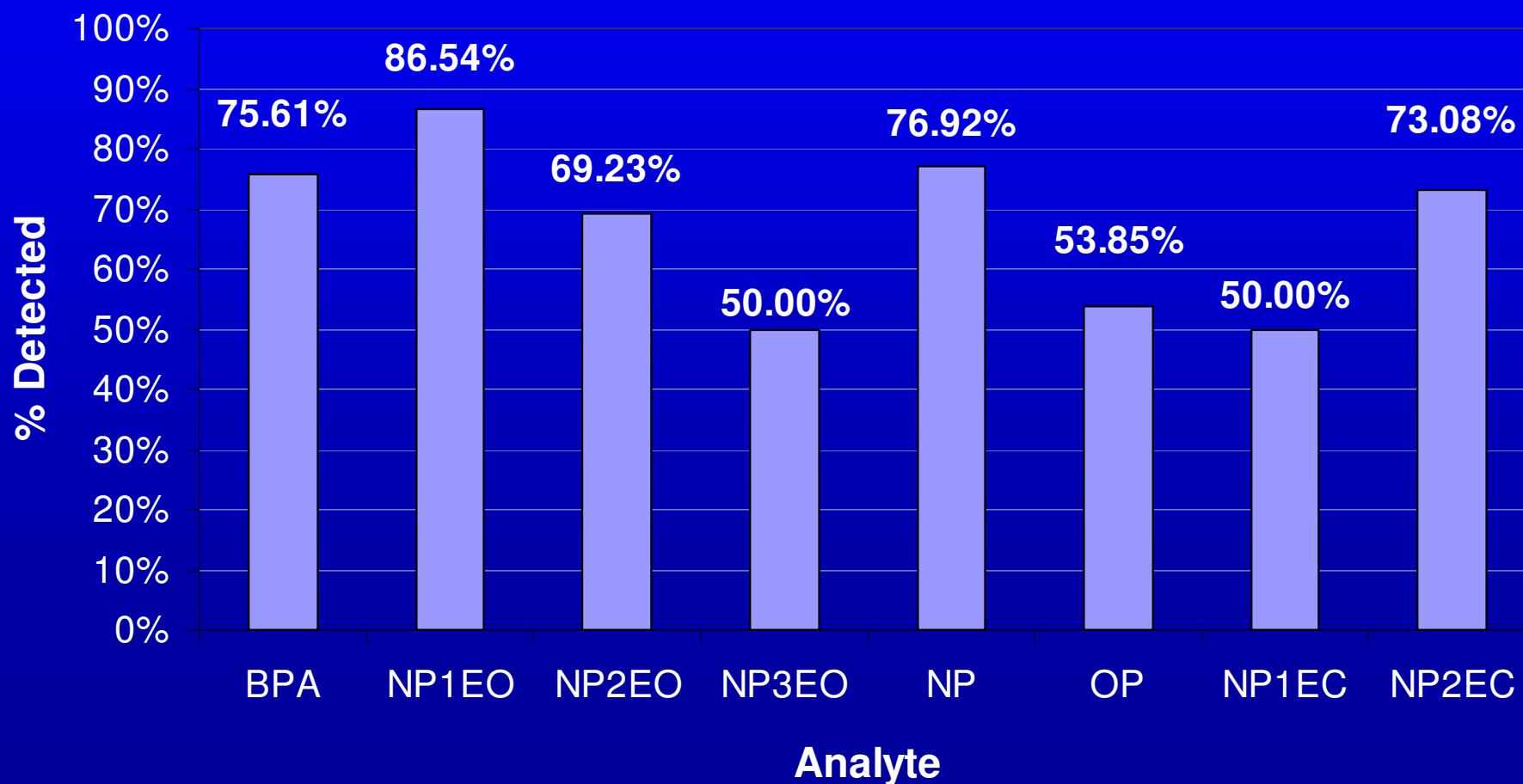


Percent of APEs Detected



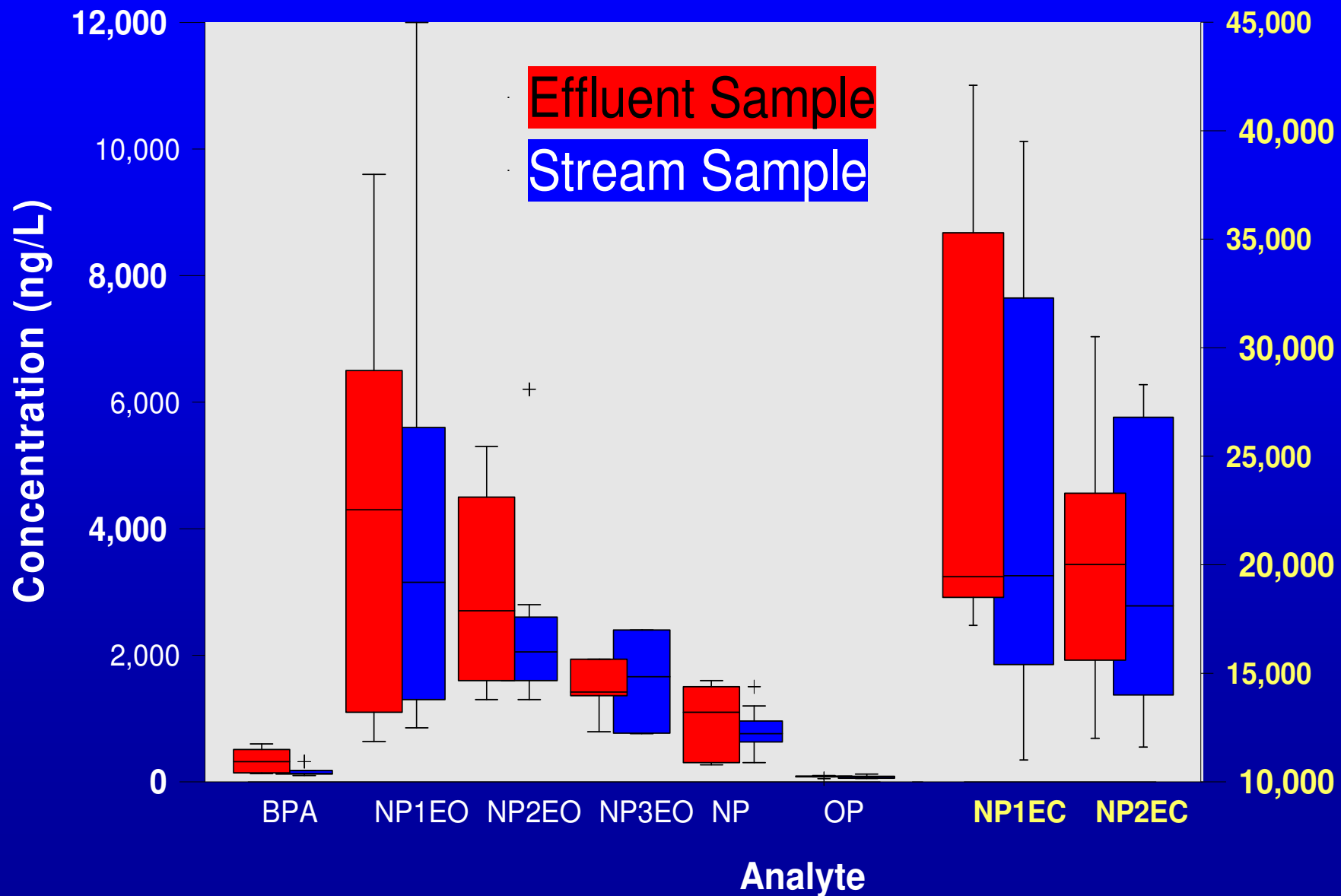
Analyzed for:

BPA, NP, NP1EO-NP18EO, NP1EC, NP2EC, OP, OP2EO-OP12EO



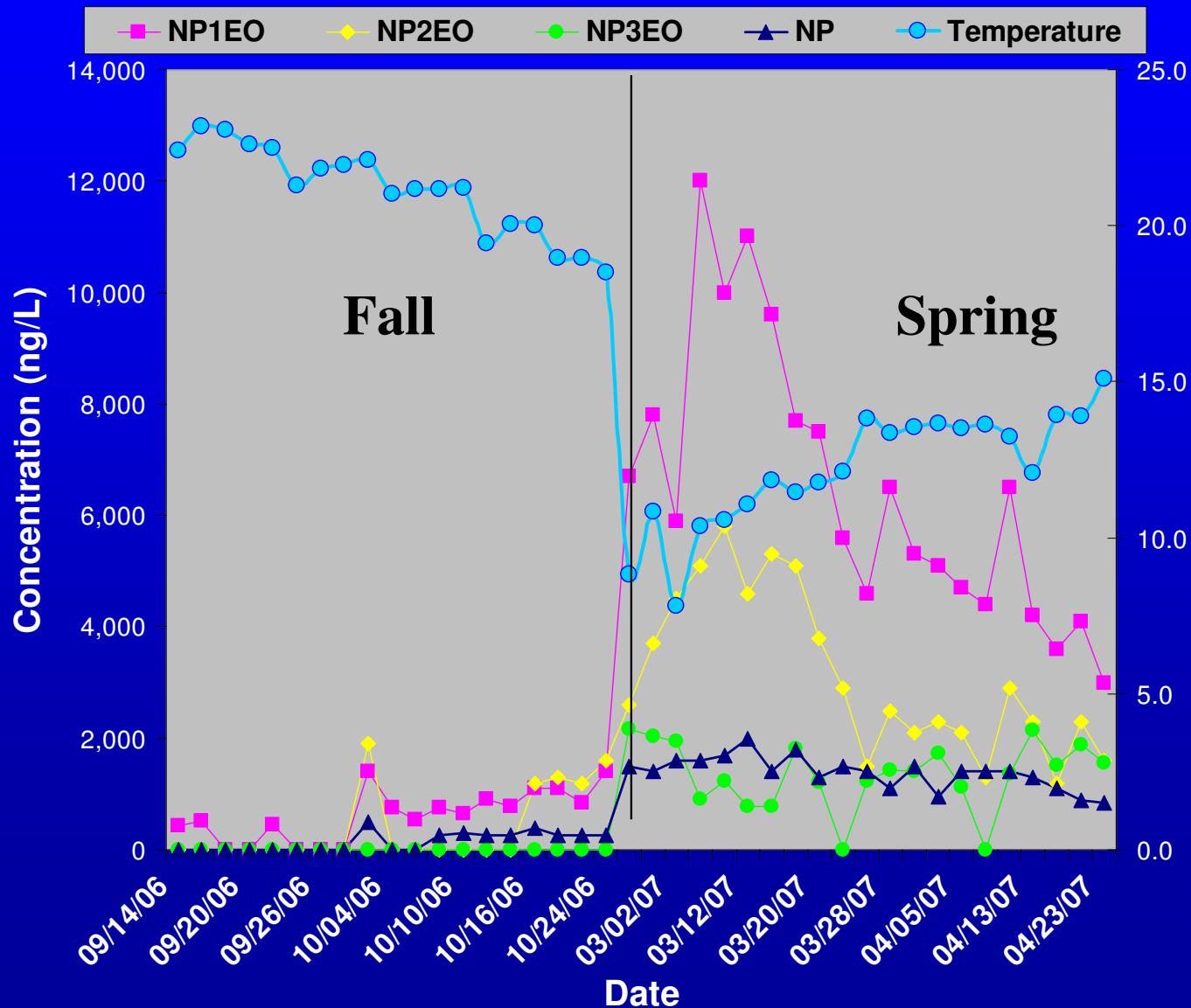


Attenuation





Seasonality of Observed NPE Concentrations

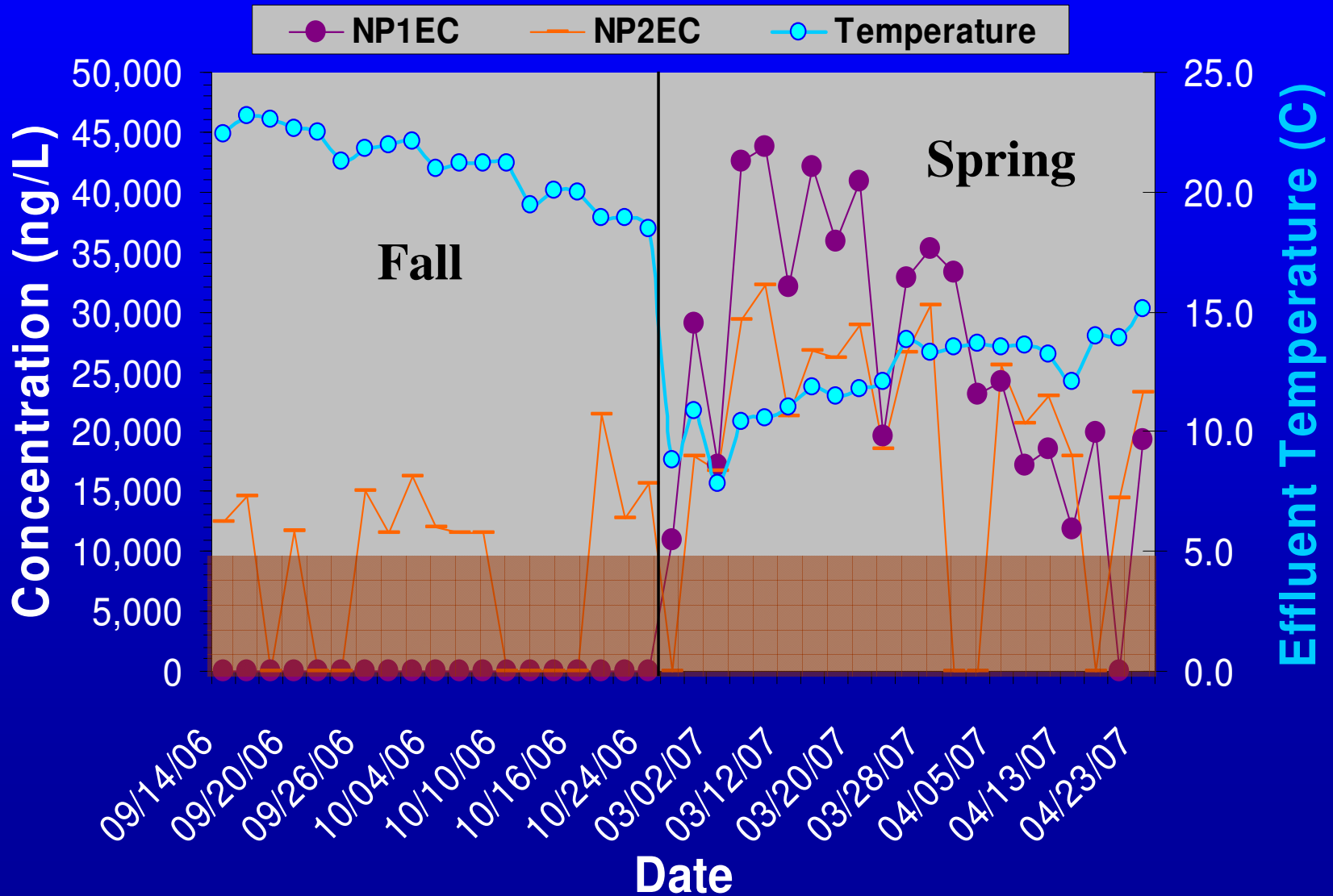


- Conc. ↑ as temps. ↓

- NP levels below toxicity based criteria for aquatic life

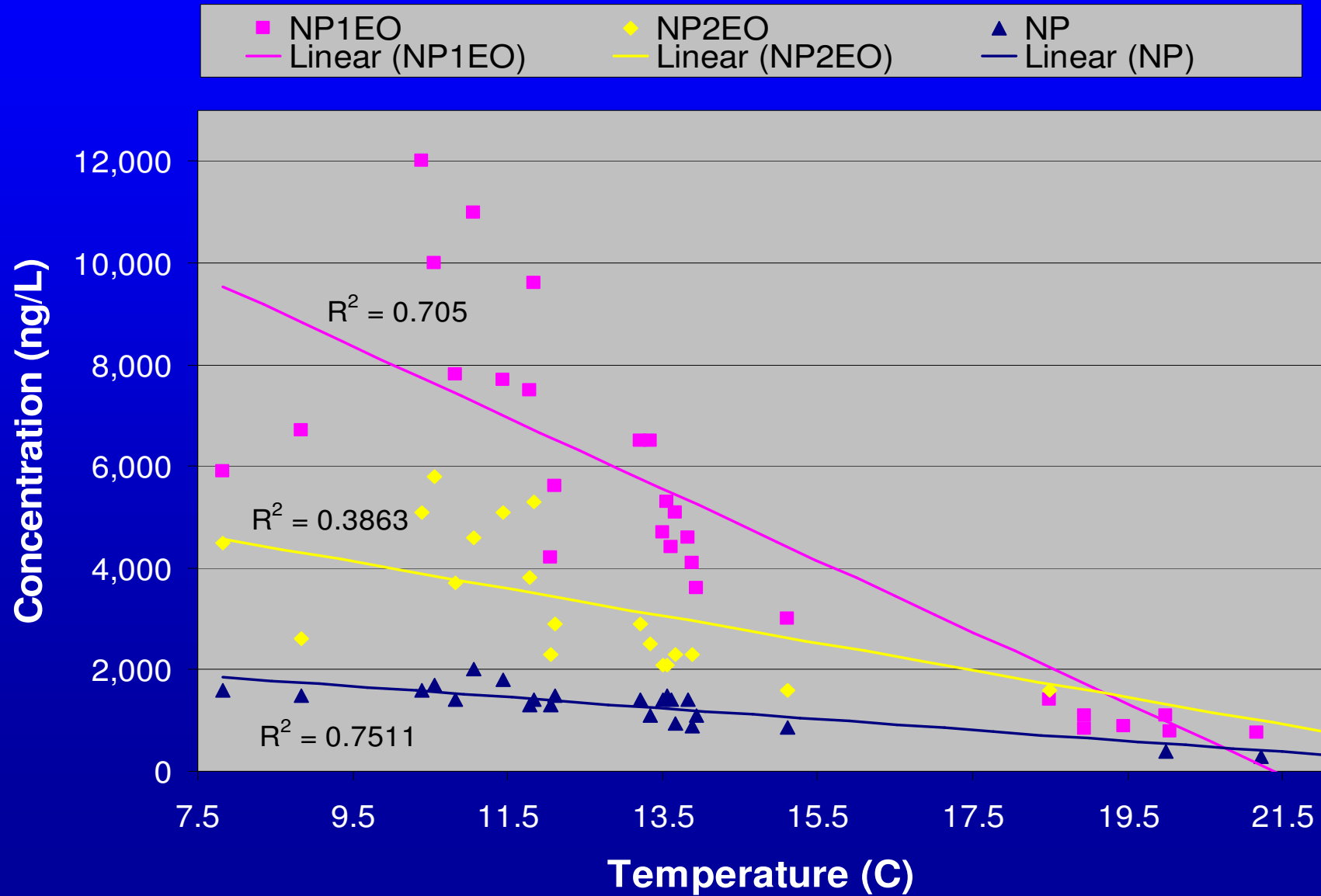


Seasonality of NPEC Concentrations





Correlation with Temperature

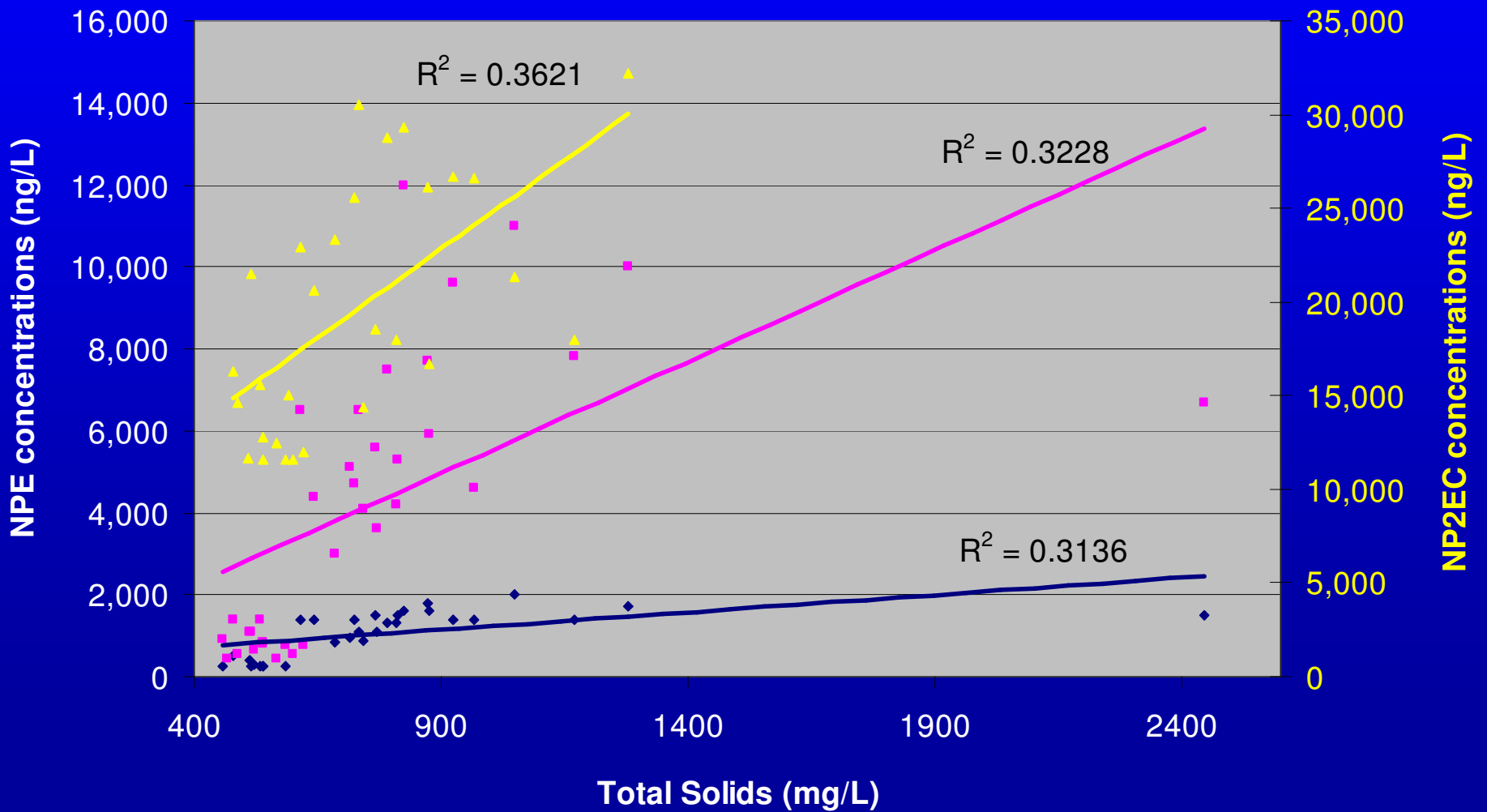




Correlation with treatment plant parameters

NP compounds and Total Solids

◆ NP and TS ■ NP1EO and TS ▲ NP2EC and TS — Linear (NP2EC and TS) — Linear (NP and TS) — Linear (NP1EO and TS)





Pharmaceuticals Present at...

High ppt to ppb levels (> 500 ng/L)

lisinopril
valsartan
hydrochlorothiazide
ibuprofen-2-hydroxy
gemfibrozil

Mid ppt levels (100 - 500 ng/L)

atenolol
metoprolol
diltiazem
furosemide
ciprofloxacin
carbamazepine
trimethoprim
ibuprofen

Low ppt levels (<100 ng/L)

amphetamine
hydrocodone
triamterene
enaliprilat
enalipril
propranolol
diltiazem-desmethyl
verapamil
norverapamil
amlodipine
sulfamethoxazole
promethazine
paroxetine
amitriptyline
benztropine
norfluoxetine
fluoxetine
sertraline-desmethyl
sertraline



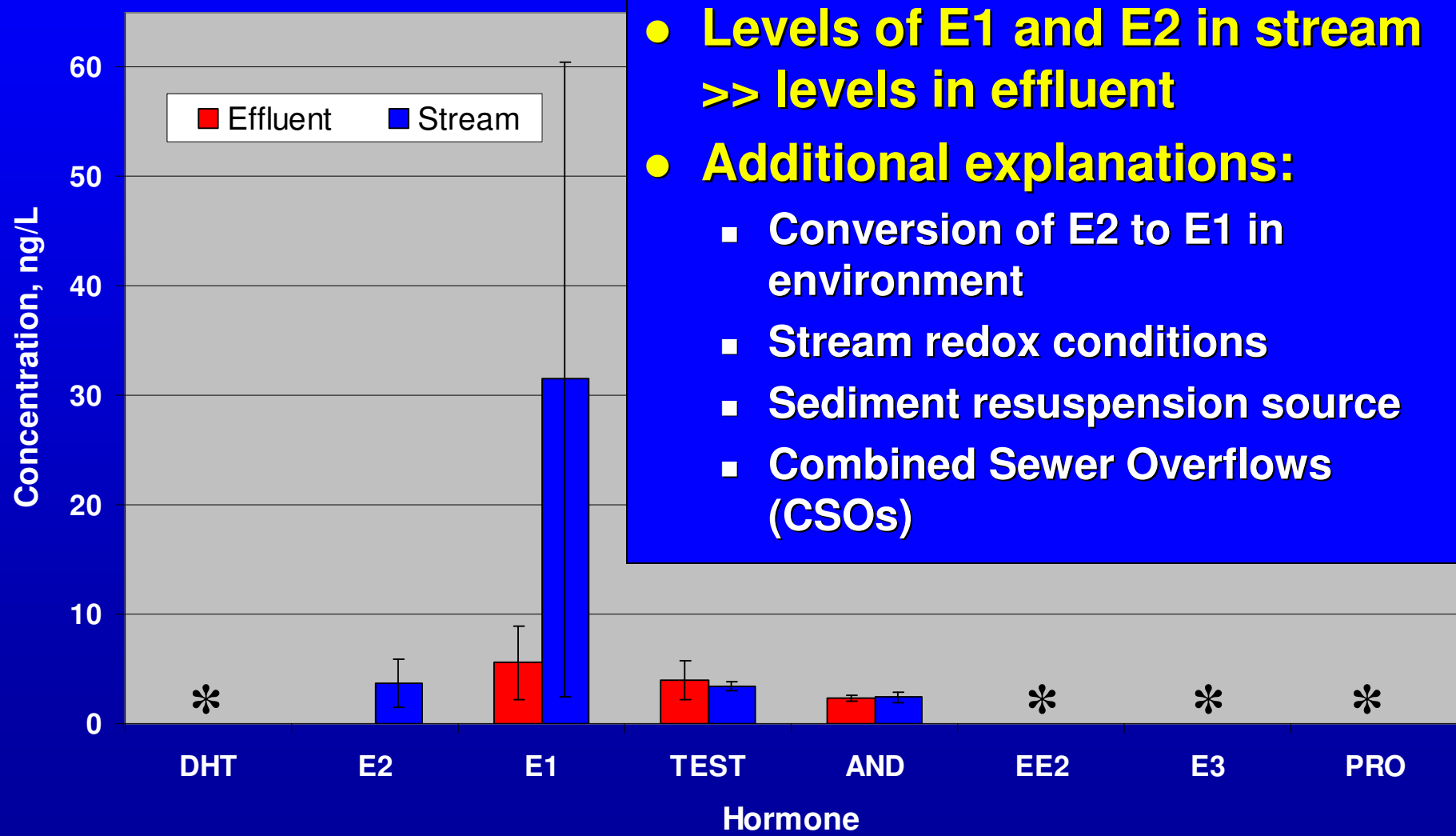
Pharmaceutical Chemicals Detected in EPA Pilot Study & Fillet and Liver Tissue from NSC

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
Diphenyldramine (0.26ppb)	Antihistimine	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



Hormones in Effluent and Stream



- Levels of E1 and E2 in stream >> levels in effluent

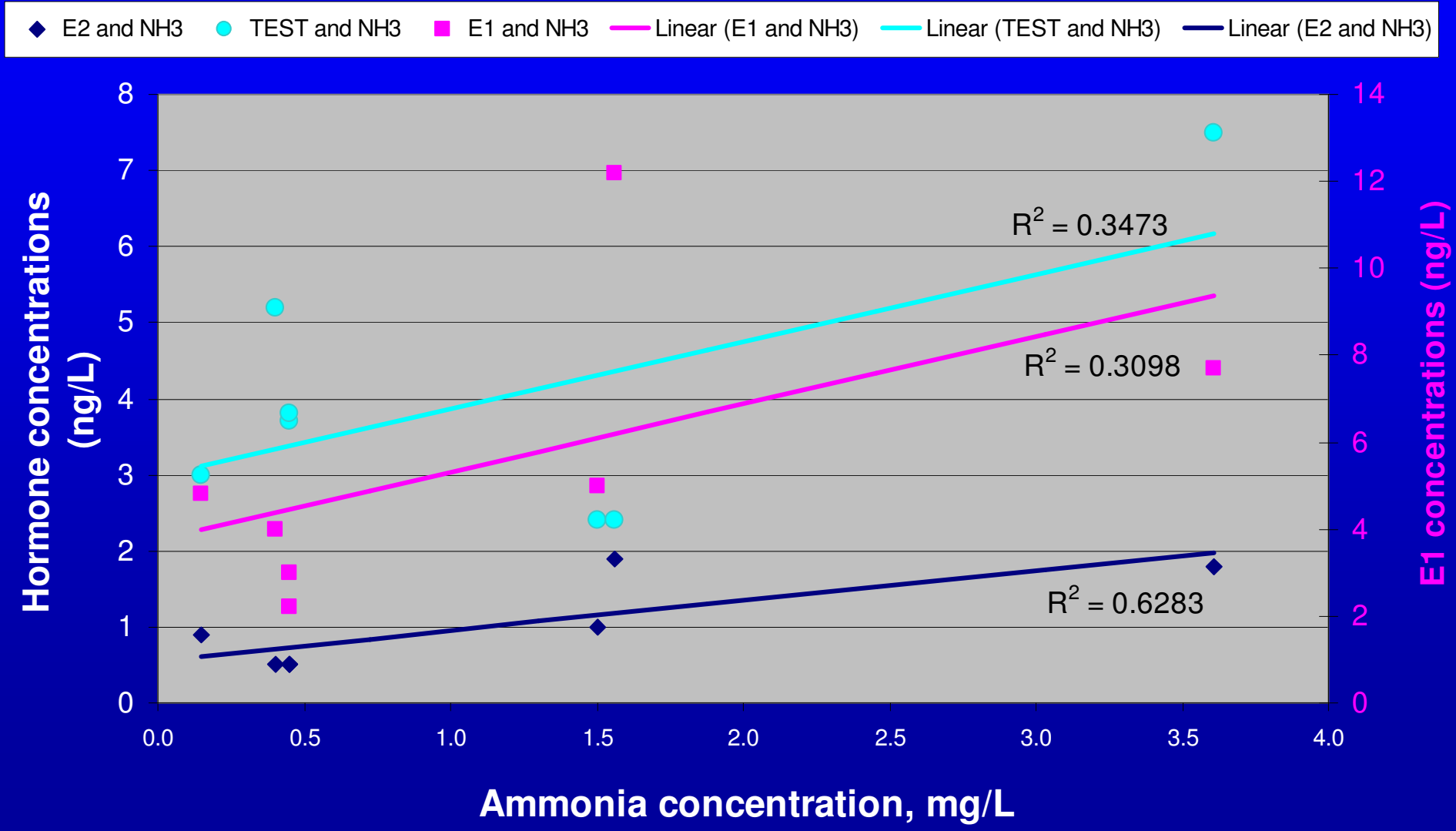
- Additional explanations:

- Conversion of E2 to E1 in environment
- Stream redox conditions
- Sediment resuspension source
- Combined Sewer Overflows (CSOs)

* - below reporting limit of 2 ng/L



Correlation Between Hormones and Ammonia





NSC Study Preliminary Conclusions

- 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.
- Significance of sampling timing and duration
 - ◆ Observed concentrations in fish and effluent 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!**
- Publication on various pieces of the project
 - Estrogenic effects
 - Seasonality of fish tissue and effluent concentrations
- Much more data to come
 - ◆ Hormones in fish
 - ◆ PPCPs fish
 - National Pilot Study
 - Fall and Spring fish samples
 - ◆ Legacy contaminants (that are suspected EDs) in fish
 - ◆ Pharms, OWCs, and extended hormone list in effluent and stream





Questions?



Thank You!

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