

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

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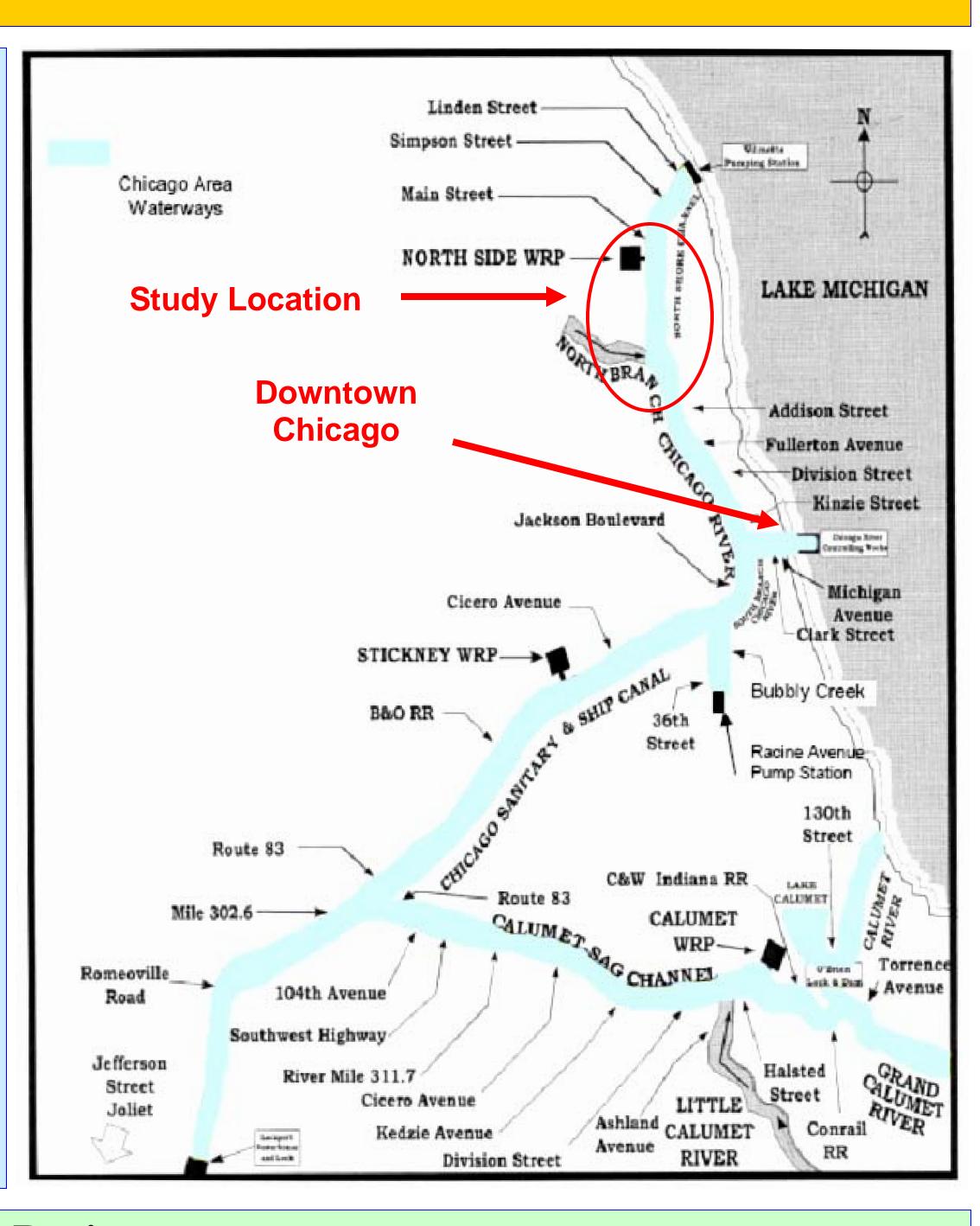
Abstract—U. S. EPA's Great Lakes National Program Office (GLNPO) and U.S. EPA Region 5 have developed a study to supplement and enhance the Office of Water's national pilot project that will investigate the occurrence of PPCPs in fish tissue. The national study will determine the concentrations of 39 PPCPs in composited fish fillets and liver samples from five sites, where waters are dominated by waste water treatment plant (WWTP) effluents, plus one reference site. The Great Lakes site was selected to be the North Shore channel of the Chicago River.

The supplemental study on the North Shore Channel is a collaborative partnership. The four main objectives of the supplemental study are to: (1) determine if there is reproductive impairment to resident fish; (2) estimate whole fish and fillet concentrations of PPCPs, APEs, and hormones; (3) estimate effluent and stream concentrations of PPCPs, APEs, and hormones; and (4) document seasonal differences in concentrations of these compounds in effluent, stream, and fish.

Collaboration

The supplemental study on the North Shore Channel is a collaborative partnership:

- 1. Great Lakes National Program Office, USEPA, Chicago, IL, USA.
- 2. Chicago Regional Laboratory, USEPA, Chicago, IL, USA.
- 3. USGS, Boulder, CO, USA.
- 4. ORD NERL, USEPA, Cincinnati, OH, USA.
- 5. ORD NRMRL, USEPA, Cincinnati, OH, USA.
- 6. Agricultural Research Service, USDA, Beltsville, MD, USA.
- 7. St. Cloud State University, St. Cloud, MN, USA.
- 8. Research and Development, Metropolitan Water Reclamation District of Greater Chicago, Cicero, IL, USA.
- 9. USEPA Office of Water, Washington DC, USA.
- 10. Tetra Tech, Owings Mills, MD, USA.



Study Design

Reproductive impairment was assessed by examining fish gonads for evidence of intersex, analyzing male fish blood for vitellogenin (vtg) - an egg yolk precursor protein expressed only in female fish and is normally dormant in male fish, and examining the livers for abnormalities. Whole fish were homogenized and analyzed for APEs, hormones, and over 100 additional PPCPs. Effluent and stream samples were also analyzed for APEs, hormones, and over 100 additional PPCPs using a variety of methods. The first effluent, stream, and fish sampling event occurred in September and October 2006. The second effluent, stream, and fish sampling event occurred in

2007.





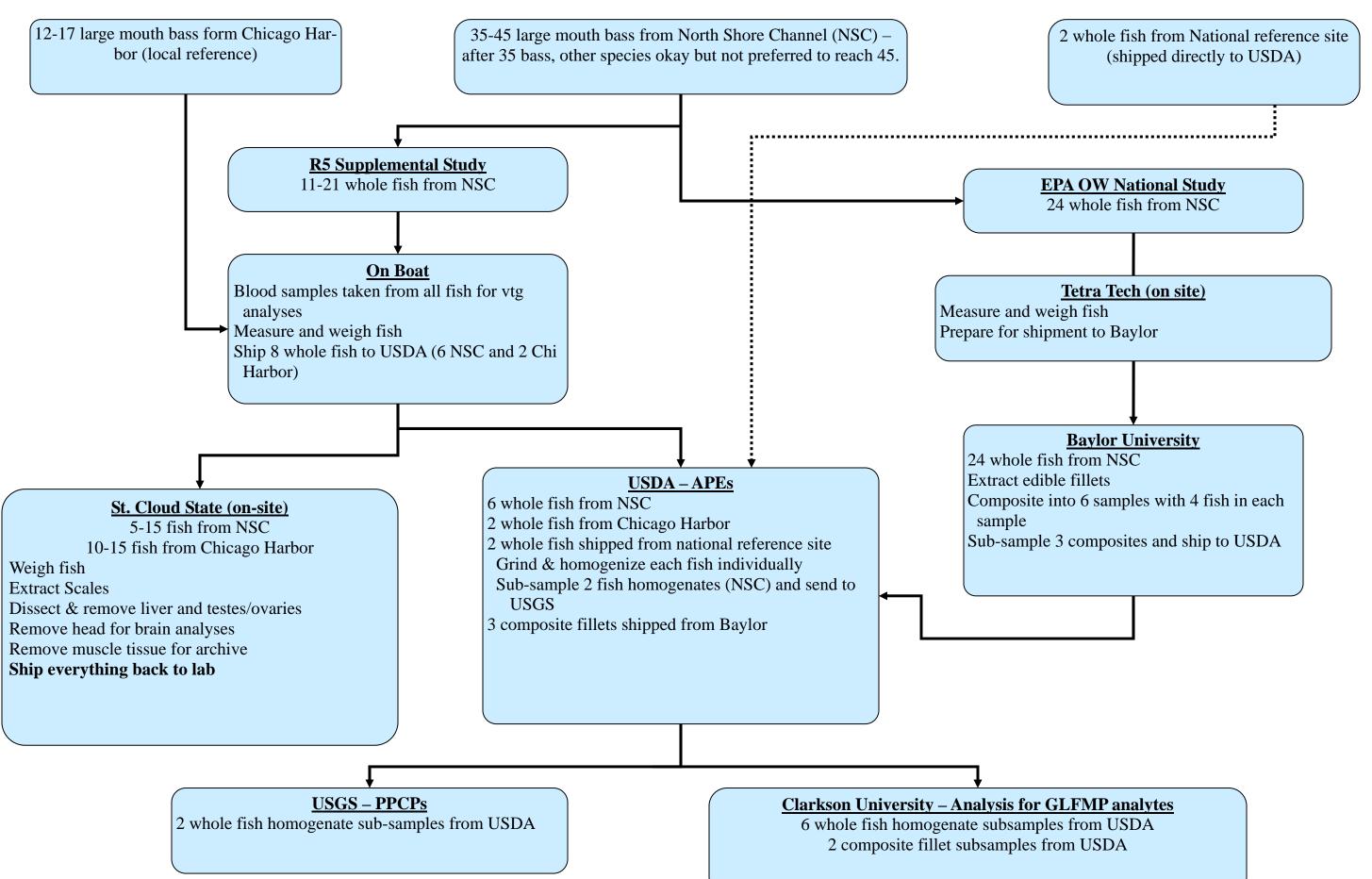








Fish Collection for PPCPs, APEs, and Hormones



Collaborator Roles

Metropolitan Water Reclamation District of Greater Chicago Collected effluent samples from the Northside Waste Water Reclamation Plant for both sampling periods. Conducted general chemistry parameter analysis (including BOD5, CBOD, SS, TOC, etc.) of effluent samples for both sampling periods.

EPA Central Regional Laboratory Analyzed of effluent and stream samples for long chain APEOs and short chain NPECs (NP1EC, NP2EC, NP3-18EO, and OP2-12EO) using a LC/MS method and NP, NP1EO, NP2EO, OP, and BPA using a GC/MS method for both sampling periods.

USGS Boulder and Golden, CO Laboratories Conduct full suite of analyses using OWC 1433 (75 organic waste water contaminants including some personal care products); Pharms 9003 (34 prescription and non-prescription drugs); and Hormones (20 natural and synthetic sex hormones) methods on effluent and stream samples provided by MWRD for both sampling

EPA ORD NERL Conducted analysis of stream and effluent samples for select PPCPs using an alternative LC/MS MS method, spring collection only.

EPA ORD NRMRL Conducted analysis of stream and effluent samples for select hormones using an alternative GC/MS method, spring collection only.

USDA - Environmental Management and Byproduct Utilization Laboratory Conduct APEs analyses on fillet tissue and whole fish collected for both sample periods. Fall collected fish analyzed for alkylphenols and alkylphenol ethoxylates (OP, NP, NP1EO and NP2EO) and Spring collected fish for a larger set of alkylphenols and alkylphenol ethoxylates (OP, OP1EO, NP, NP1EO, NP2EO, and NP3EO).

Saint Cloud State University Conduct vitellogenin (vtg), gonad histopthology, and liver abnormality analyses on fish collected for both sample periods.

Clarkson University Conduct analysis of fillet tissue and whole fish collected for both sample periods. Samples will be analyzed according to EPA GLNPO Great Lakes Fish Monitoring Program (GLFMP) SOPs and methods for the GLFMP routine analyte list (PCBs, OC pesticides, BFRs, Hg, etc.).

Preliminary Results

Estrogenic Effects on Fish Summary of fish sex and occurrence of vitellogenin in Fall 2006 Collection North Shore Channel Outer Chicago Harbor Immature fish (w/ VTG) Male fish (w/ VTG) 5 (60%) 4 (0%) Female fish (w/ VTG) 3 (100%) 5 (100%)

Parameter		Largen	outh Bass		Common Carp					
	E	ffluent	Braidwood		Ef	fluent	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		

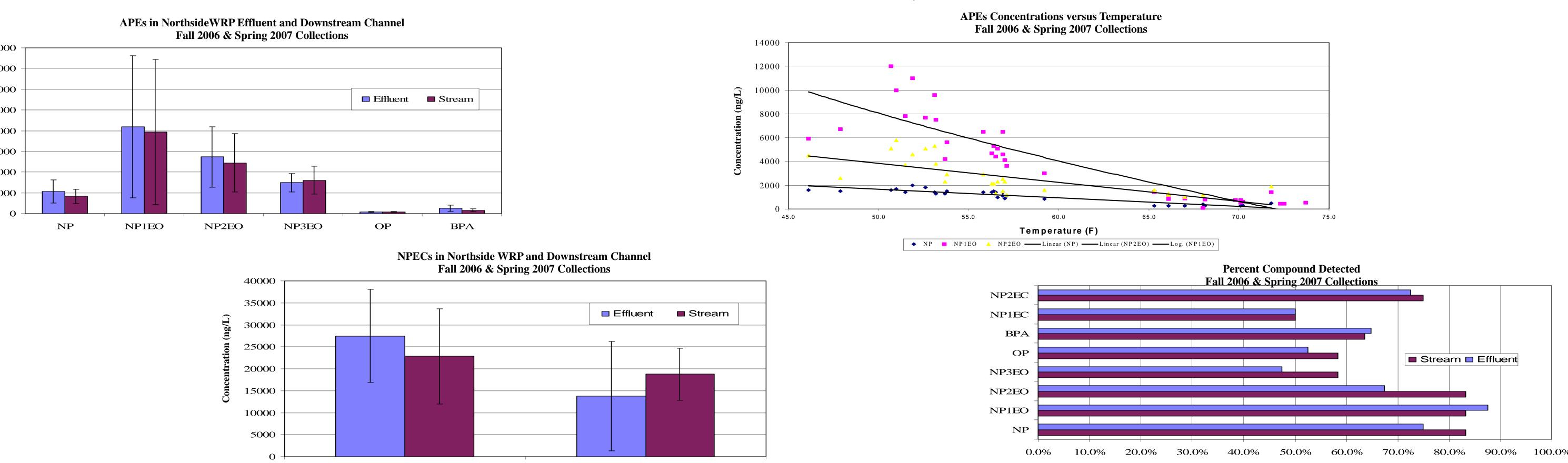
APEs in Whole Fish Analysis

NP Co	oncentratio	ns in Wl	nole Fish f	from the	NSC (ng/g	wet we	ight) Fall 2	006 Colle	ection	
	NP		NP1EO		NP2EO		NP3EO		NP4EO	
	High	Low	High	Low	High	Low	High	Low	High	Low
NSC (n=5)	87	48	736	258	480	205	38	18	12	3.9
Lake Michigan (n=2)	<22.	0	<37	7.0	<8.0	.0 <5.1		1	<2.7	
OPC	oncentratio	ns in W	hole Fish	from the	NSC (ng/g	wet we	ight) Fall 2	2006 Call	ection	

	oncenti atti	0115 111 VV	11016 L 1211	nom me		wet wei	giit) raii 4	ood Conec	.UOII	
	OP		OP1EO		OP2EO		OP3EO		OP4EO	
	High	Low	High	Low	High	Low	High	Low	High	Low
NSC (n=5)	<25	0.0	trace* ((<0.28)	trace* (<4.5)	trace*	(<7.8)	trace*	(<8.8)
Lake Michigan (n=2)	<25	6.0	<23	8.0	<4.	5	<7	7.8	<{	3.8
*Greater than blank but less	than method d	letection lir	nits.							

Source - Clifford P. Rice & Nuria Lozano, Agricultural Research Service, USDA, Beltsville, MD, USA

APEs in Effluent and Stream Analysis





What are Alkylphenol Ethoxylates (APEs)?

• Nonvl & Octvl Phenol Ethoxylates

- High Production Volume Chemicals (~391.5 million lbs/year NPEs and 77 million lbs/yr OPEs used in North America (U.S. & Canada) in 2003)
- <u>Uses</u>—Detergents, wetting agents, dispersants, emulsifiers, solubilizers and
- <u>Industrial applications</u>—Pulp and paper, textiles, coatings, agricultural pesticides lube oils and fuels, metals and plastics

Why are PPCPs and APEs of Concern?

- May be "pseudo-persistent" Chronic exposure May have biological effects
 - Therapeutic design
- May be endocrine disruptors
- Alterations to sexual differentiation - Reproduction and growth impairments
- Behavioral effects

Little known about environn

Estrogenic effects on fish (Fall Collection)—(1) Immature largemouth bass did not coduce plasma vitellogenin. (2) All female largemouth bass produced plasma ellogenin. (3) Most male largemouth bass in the North Shore Channel (3 of 5) oduced vitellogenin at concentrations approaching those found in female gemouth bass at both sites. (4) No difference in vitellogenin concentrations was found between female largemouth bass at the two collections sites. (5) No intesex o other severe pathological conditions were found at either site.

Estrogenic effects on fish (Spring Collection)— (1) Vitellogenin analysis found high plasma vitellogenin concentration in most female fish, as to be expected. (2) Only one male largemouth bass collected in NSC for vitellogenin analysis, cannot ompare to cooling pond. However, the vitellogenin concentration in the NSC argemouth bass was 10X higher than all male largemouth bass collected at the cooling pond. The 9 largemouth bass collected for VTG analysis at the NSC site were a subset of the 33 largemouth bass collected for the U.S. EPA OW study and were chosen randomly. Samples were not chosen with regards to sex, but were chosen according to size and sexual maturity. More females were collected in the ring sampling event than males. (3) Male carp did not exhibit clear trends with most males at both sites having measurable plasma vitellogenin concentrations, although 1,000X below the female fish's mean. (4) Several males at the cooling pond exhibited concentrations of plasma vitellogenin comparable to those of males at the NSC site. (5) No gross –abnormalities of testes or livers in male and female ish of both species were observed. (6) No intesex or other severe pathological conlitions were found at either site. (7) Most fish from the NSC site exhibited greater mounts of fatty tissue in the liver than fish from the cooling pond site. (8) Males at the cooling pond site were generally in an earlier spermatogenic stage than males at the NSC site, which exhibited testes almost entirely filled with mature spermatozoa

APEs in stream and effluent samples—Preliminary results indicate a correlation with temperature. As the temperature of the water decreases, concentration of most APEs increase. However, concentrations of NP do not exceed the toxicity based acute (one-hour average concentration of nonylphenol does not exceed 28 ug/L more than once every three years on the average) or chronic (four-day average concentration of nonylphenol does not exceed 6.6 ug/l more than once every three years on the average) criteria recommendations for nonylphenol designed to protect aquatic life in fresh water.

APEs in Whole Fish—There are currently no criteria for APEs in aquatic life to compare the preliminary results with.

PPCPs in stream and effluent samples and Whole Fish—Results of PPCP analysis in stream, effluent, and whole fish samples are currently not available for the NSC xtension study. There are currently no criteria for PPCPs in aquatic life or for