

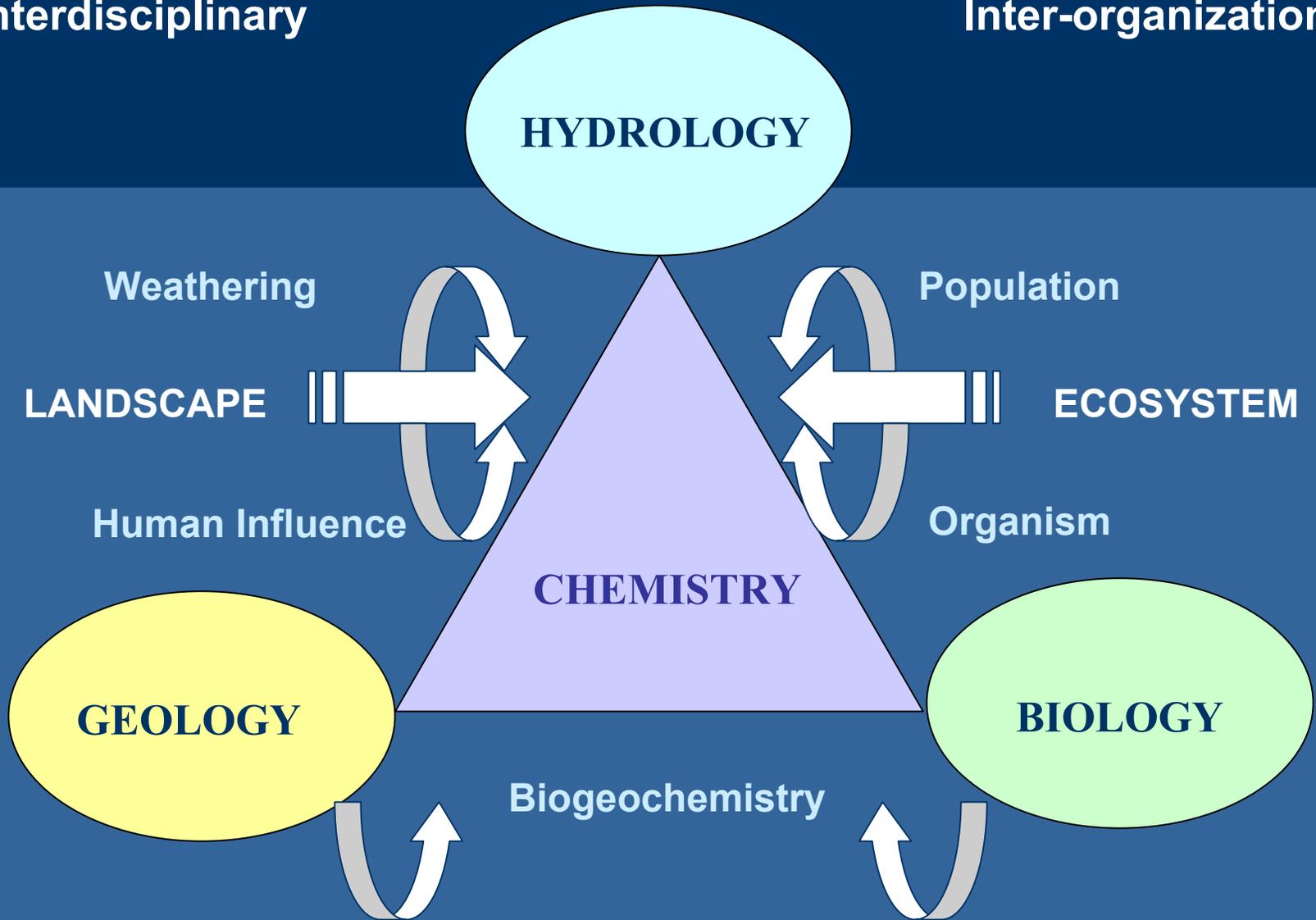
Fate of Endocrine Disrupting Contaminants in WWTPs and Their Impact on Receiving Streams

Larry Barber
U. S. Geological Survey
Boulder, Colorado

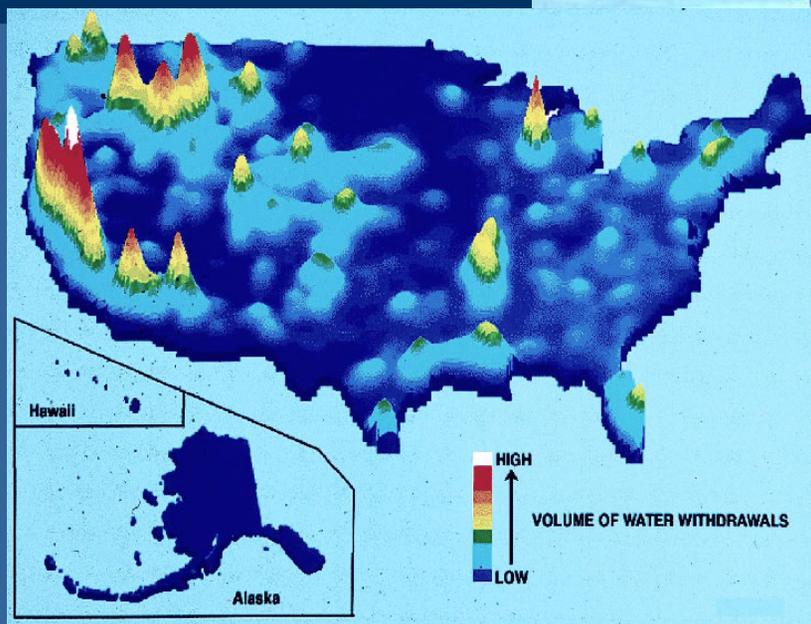


Interdisciplinary

Inter-organizational



Water Reclamation Reuse



Spreading Ponds near Pico Rivera in Los Angeles, California



Intended Reuse

- Direct
- Indirect

Unintended

Consumer Products



Cleaning



Pharmaceutical



Agricultural

Consumer Product Cycle

Active Ingredient
Starting Products
Reaction Pathway

Parent
Degrades
Adjuvants

Parent
Compound

DISCHARGE

Wastewater
Treatment

Water Supply

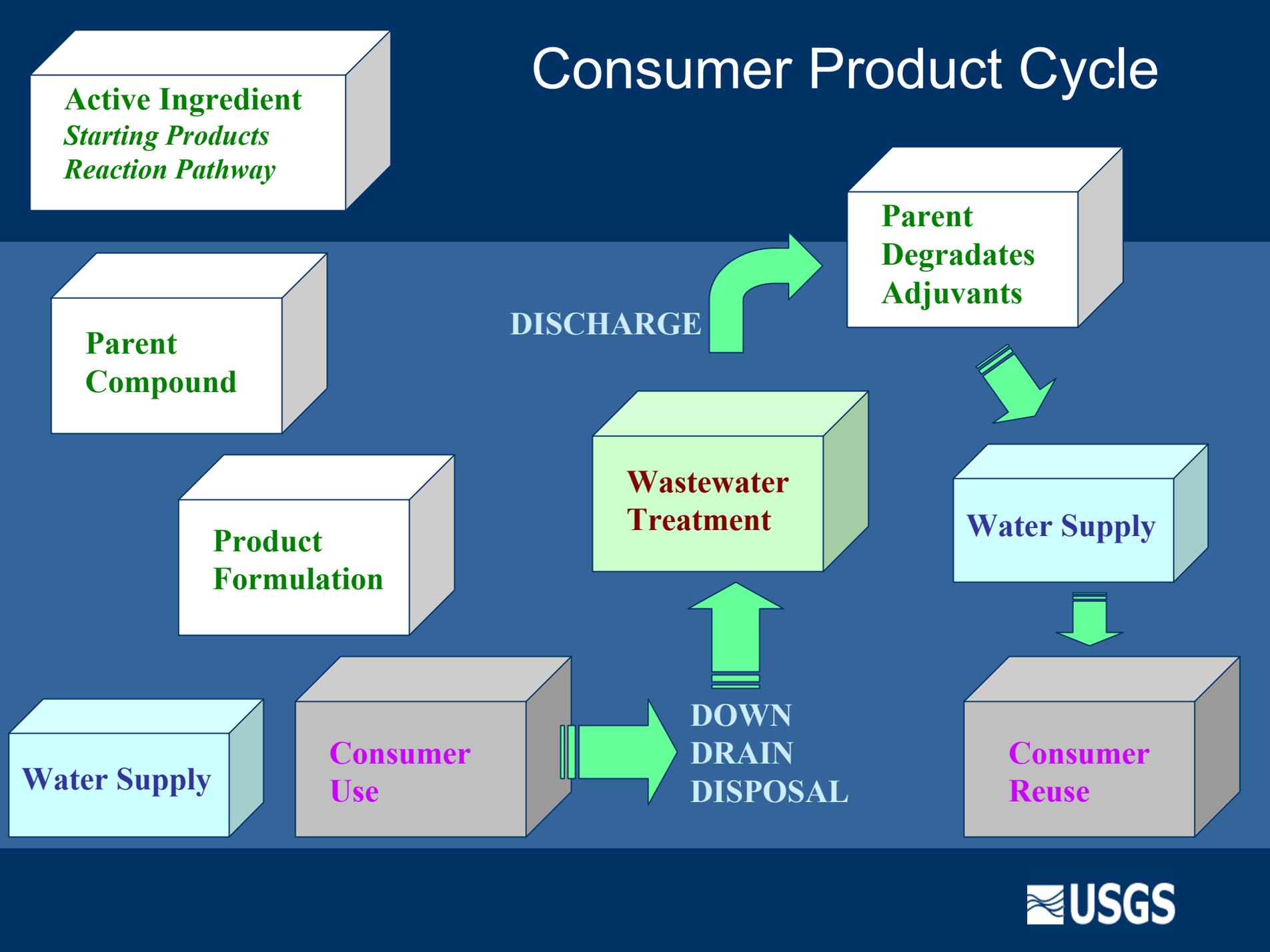
Product
Formulation

Consumer
Reuse

Water Supply

Consumer
Use

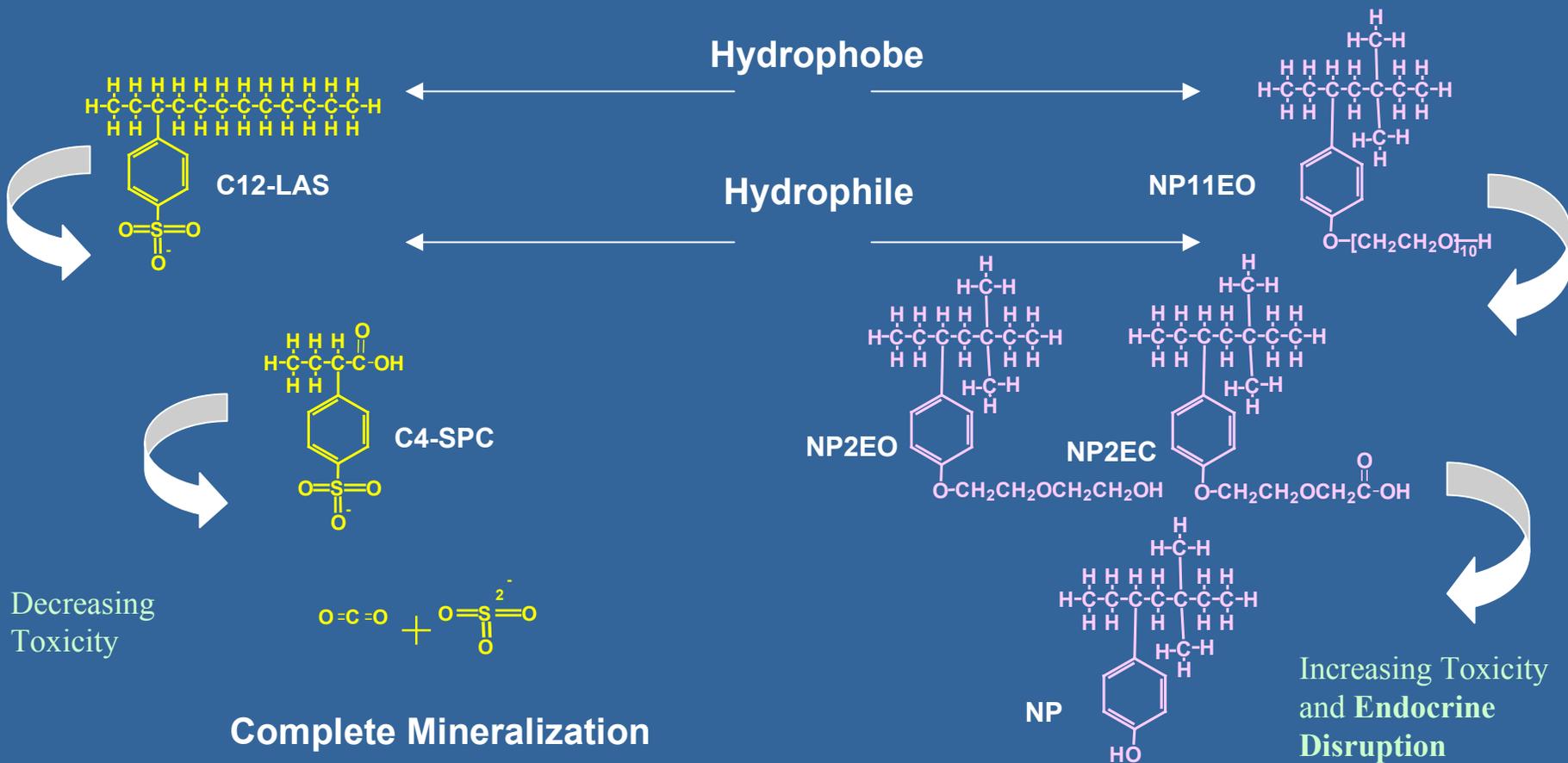
DOWN
DRAIN
DISPOSAL



Aerobic Degradation of Surfactants

Anionic Linearalkylbenzenesulfonate (LAS)

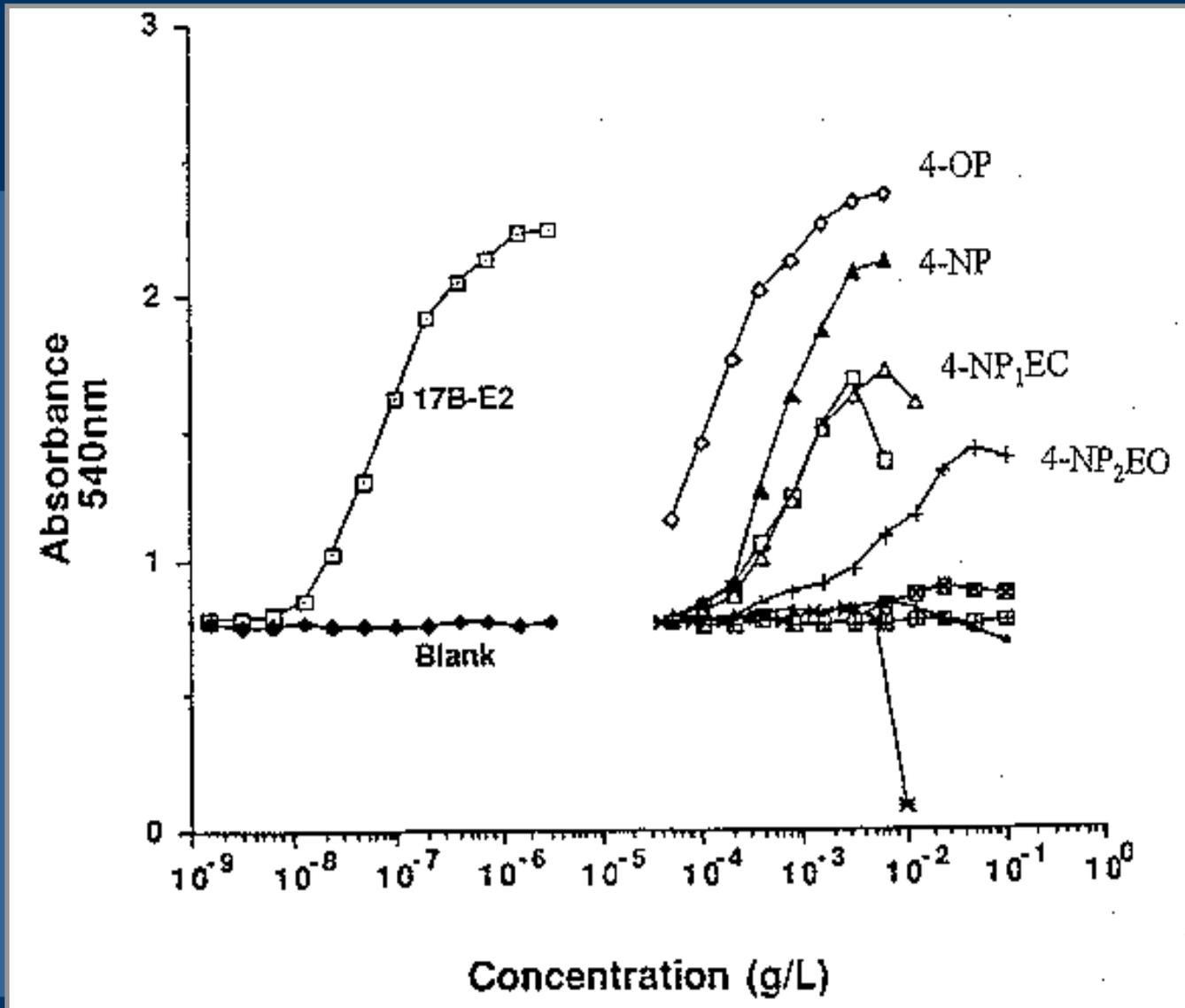
Nonionic Alkylphenolethoxylates (APEO)



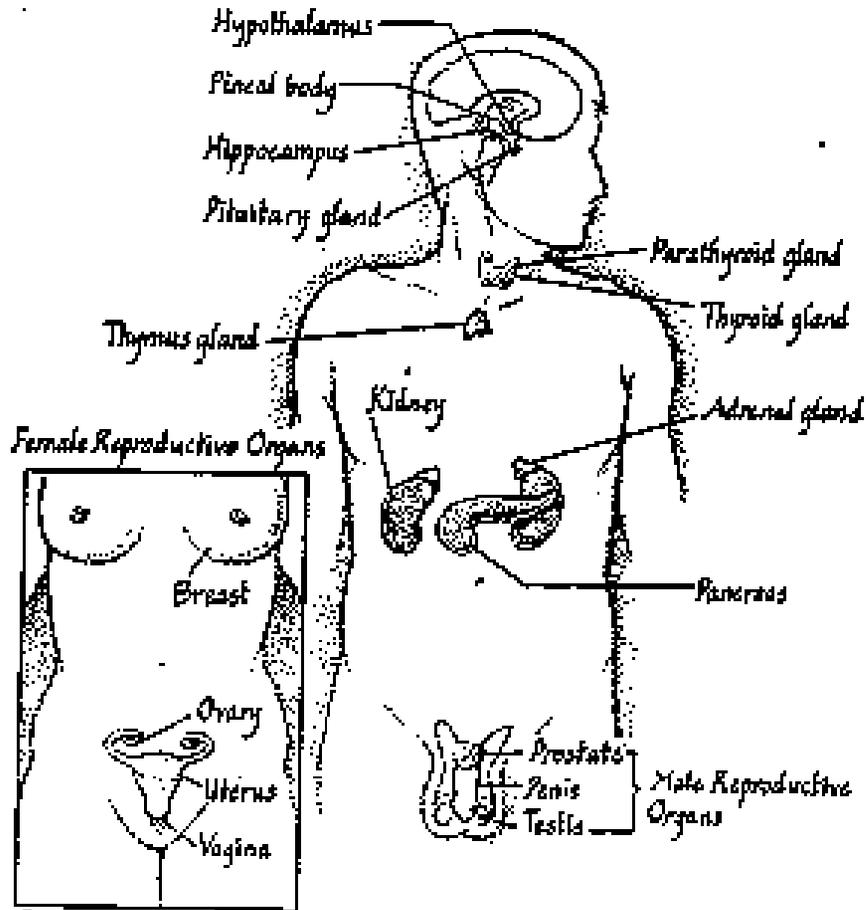
1991 LAS use = 390 million kg (Modler and others, 1993)

1988 APEO use = 200 million kg (Talmidge, 1994)

Endocrine Effects of Alkylphenols



The Human Endocrine System



After Colborn and others, 1996

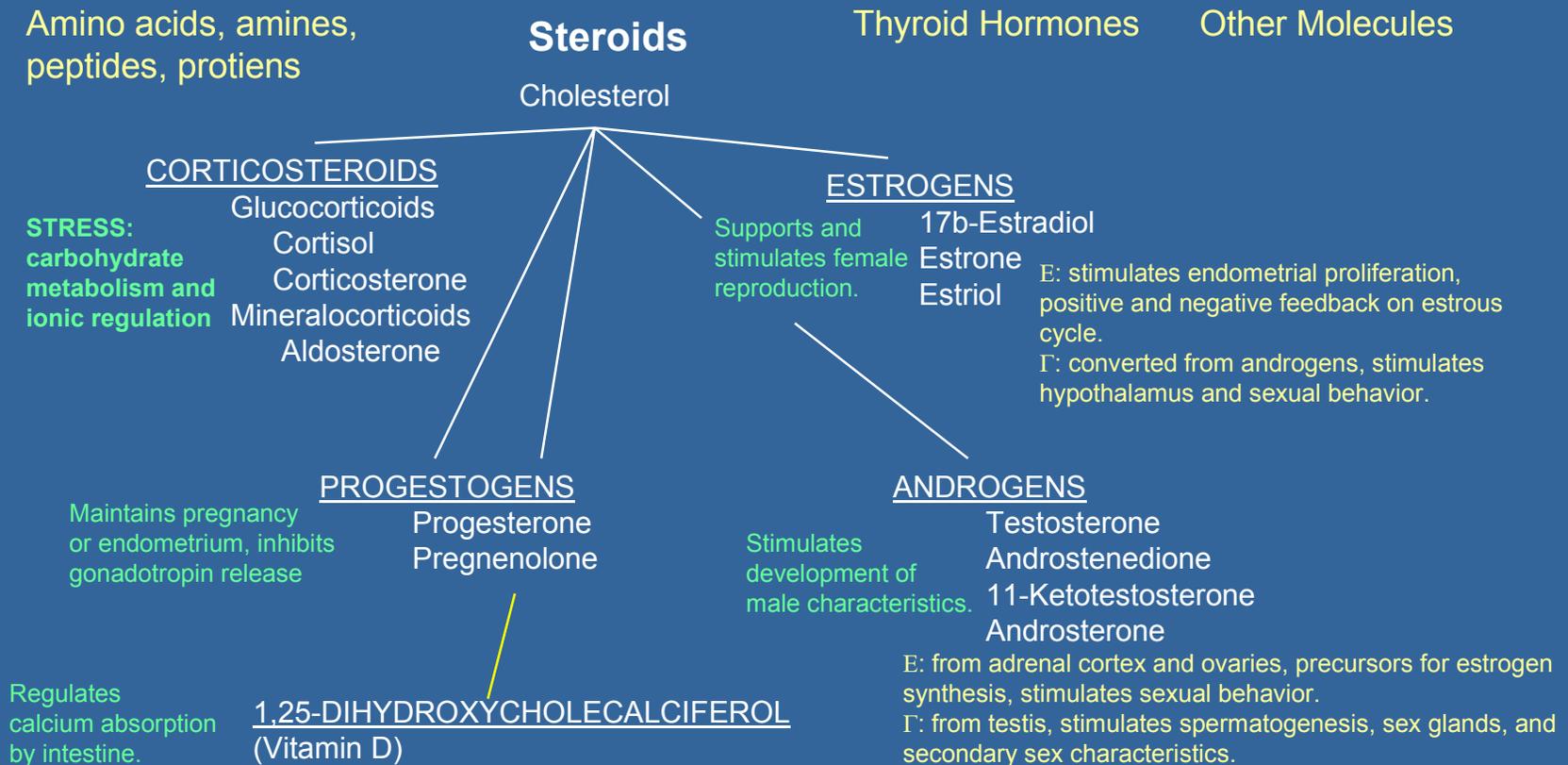
System of glands that produce hormones and corresponding receptors

- Sexual Development
- Reproduction
- Growth
- Metabolism
- Neurological Development
- Cancers

What are hormones?

Chemical regulators, secreted by glands to the blood that effect a change at a target site.

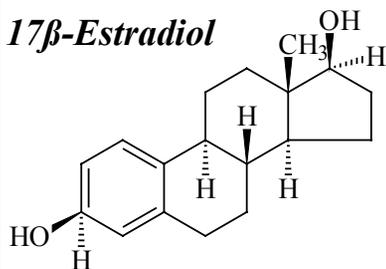
Types of chemical regulators



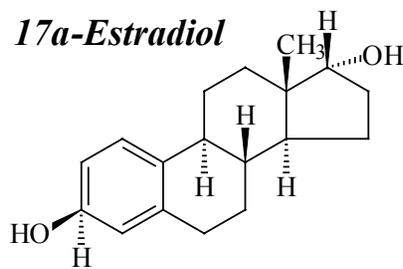
Biogenic and Synthetic Steroidal Hormones

Natural

17 β -Estradiol



17 α -Estradiol



Contraception

10 million use oral contraceptives
88 kg/yr, PEC =

Hormone Replacement Therapy

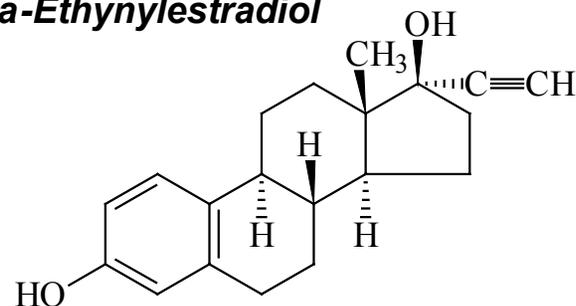
13 million use hormone replacement
1688 kg/yr, PEC =

Biogenic

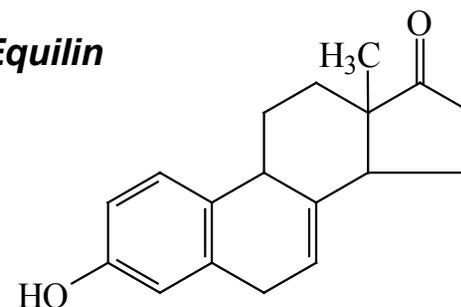
98 million excrete ~0.1 mg/day/person
3577 kg/yr, PEC =

Pharmaceutical

17 α -Ethinylestradiol



Equilin



Premarin - 45 million prescriptions in
2001 = \$2,000,000,000 (C&E News)

Effects of Endocrine Disrupting Chemicals

Ecosystem

Population

Individual reproduction

Secondary behavior and morphology

Primary molecular and biochemical responses

Exposure to potential environmental agents



Emerging Contaminant Reconnaissance

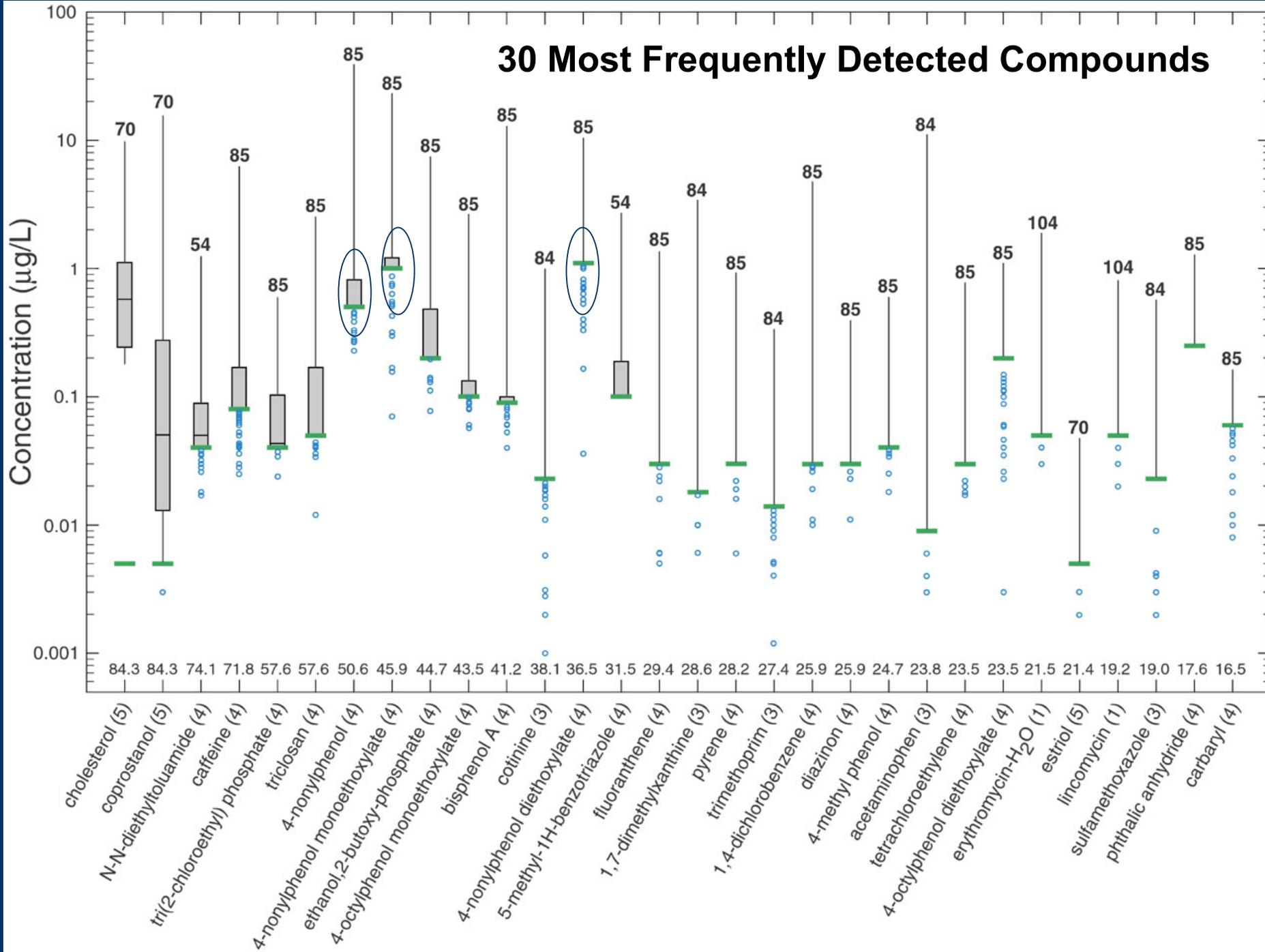
Kolpin and others, 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. Streams, 1999-2000: A national Reconnaissance: ES&T, v. 36.

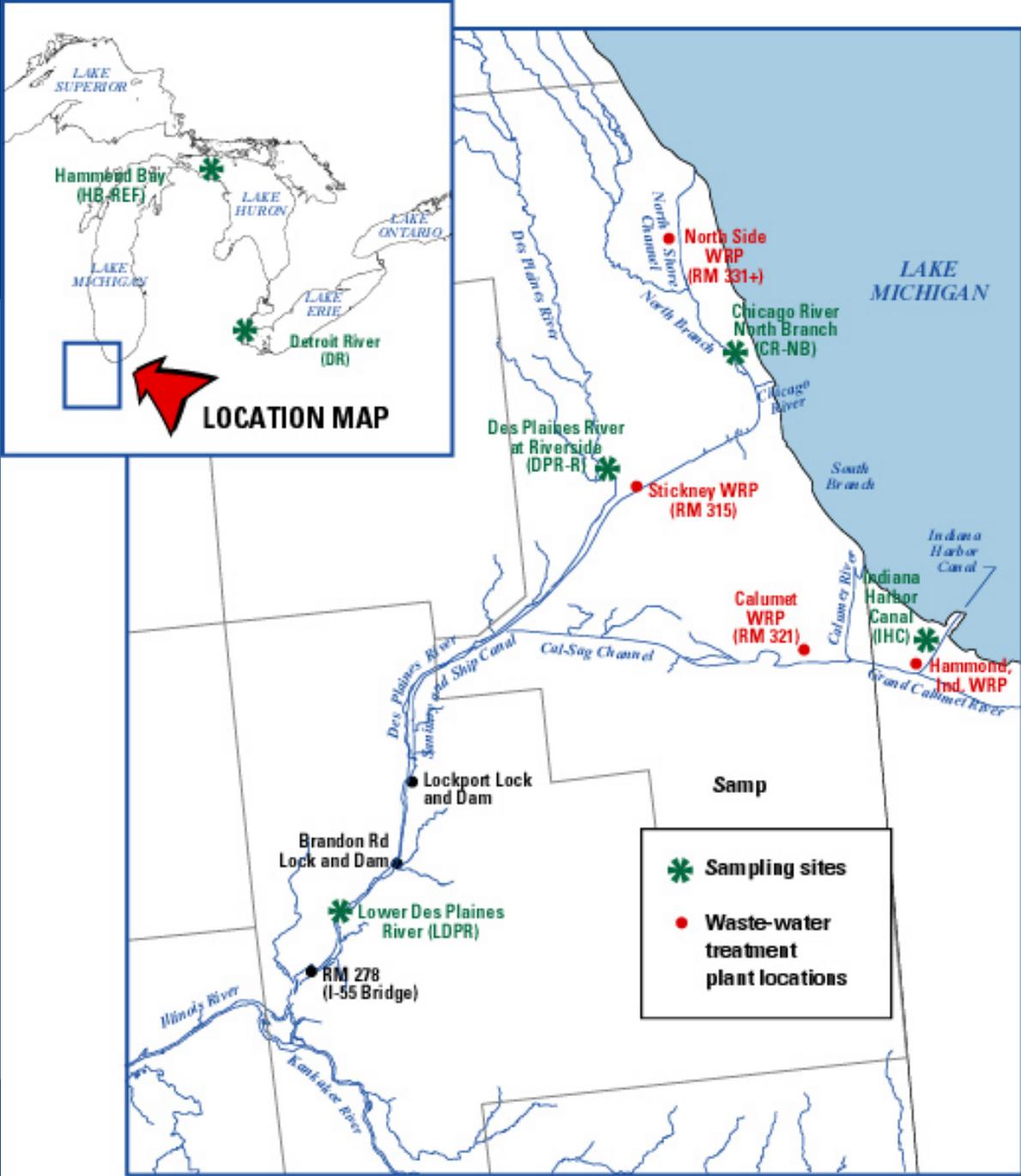


- 139 Streams in 30 States
- 62 Intense AFO Activities
- 52 Intense Urbanization
- 17 Mixed Land Use
- 8 Minimally Developed

- 22 Antibiotics
- 14 Prescription Drugs
- 5 Nonprescription Drugs
- 15 Hormones and Steroids
- 39 Household and Industrial

30 Most Frequently Detected Compounds

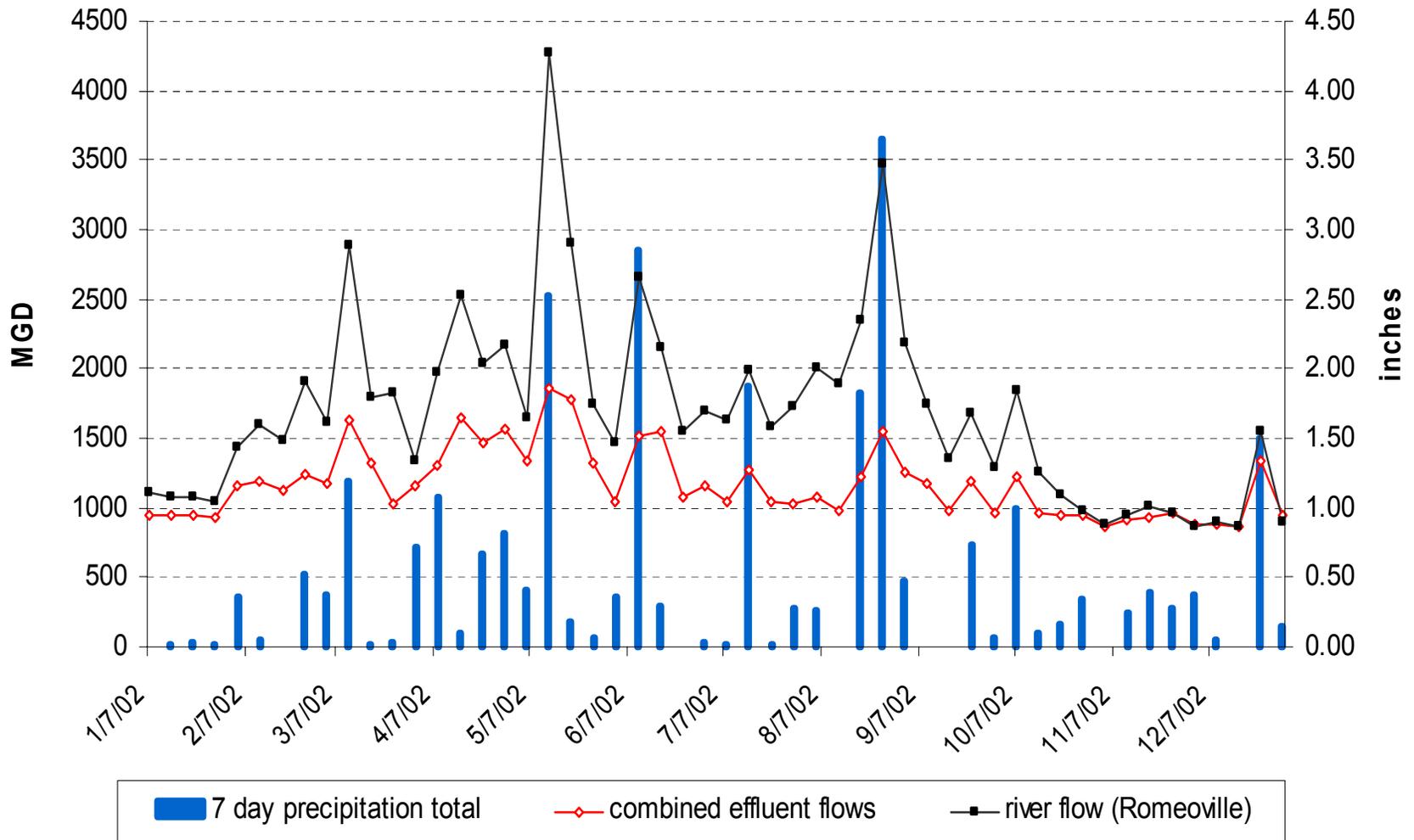




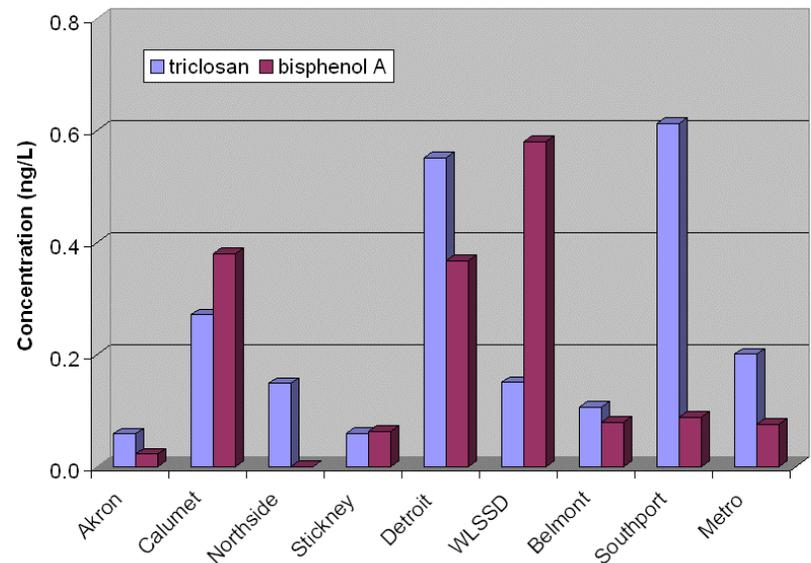
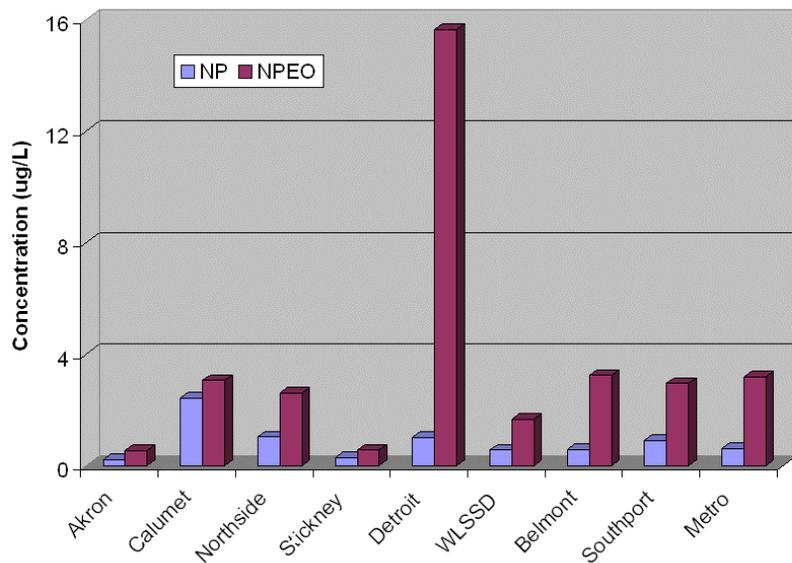
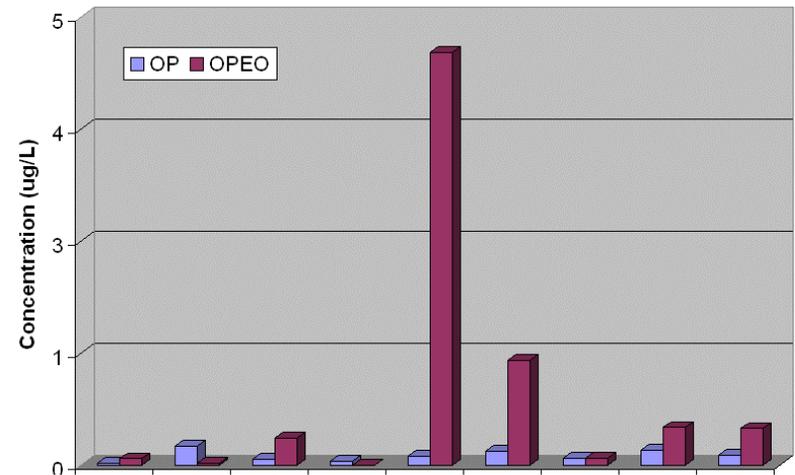
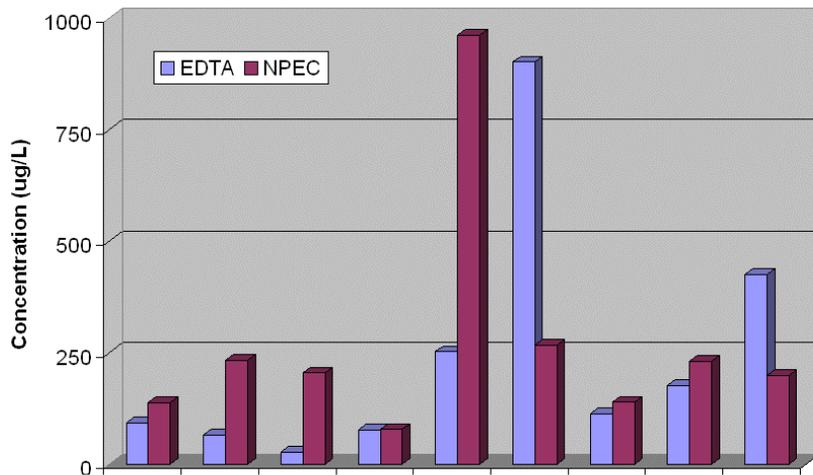
Study Sites

- Akron
- Chicago
- Detroit
- Duluth
- Indianapolis
- Minneapolis
- Calumet River
- Chicago Ship and Sanitary Canal
- Cuyahoga River
- Mississippi River

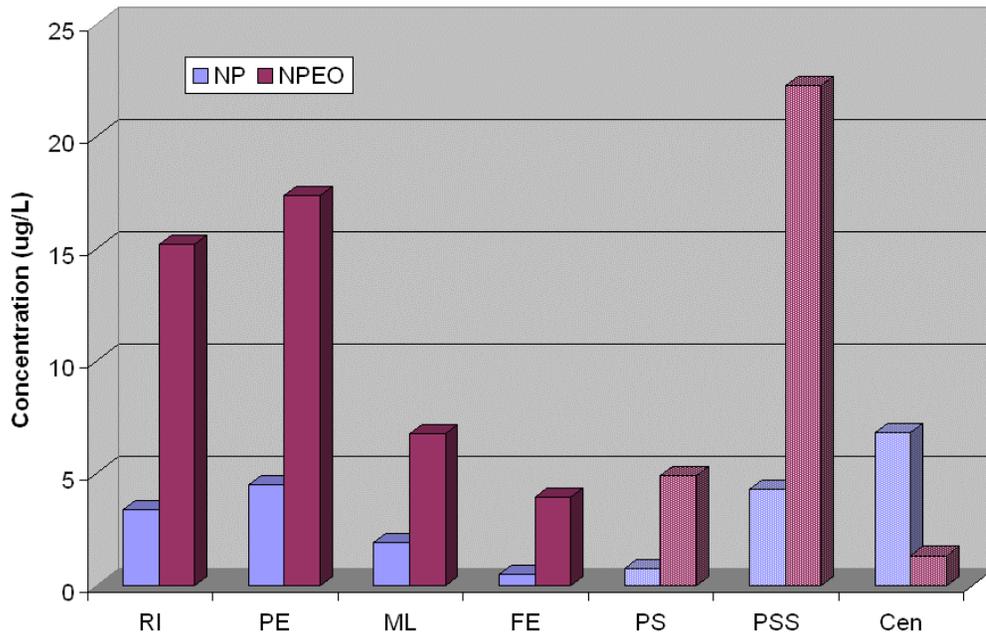
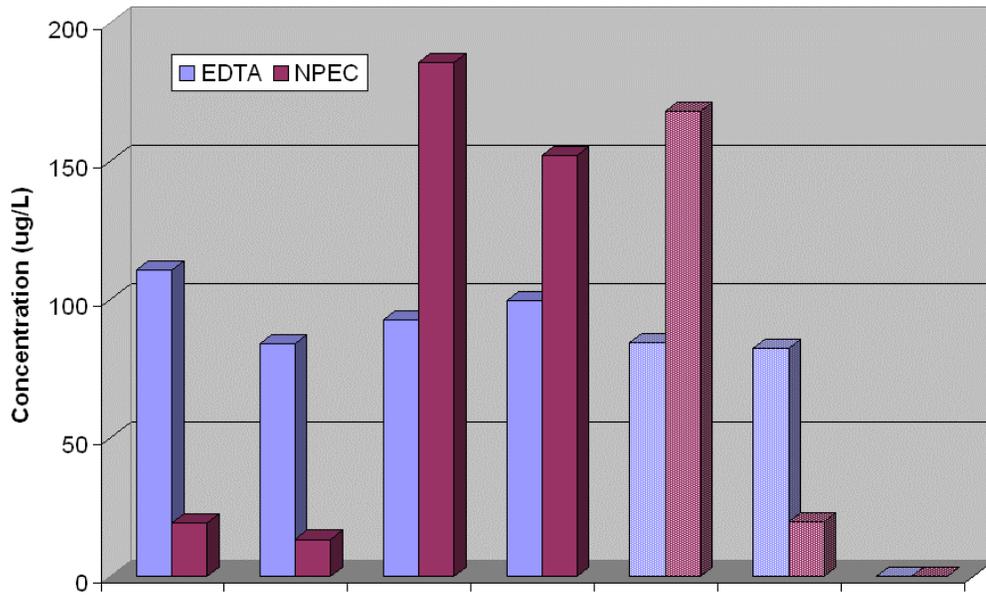
Effluent Contribution to Des Plaines River



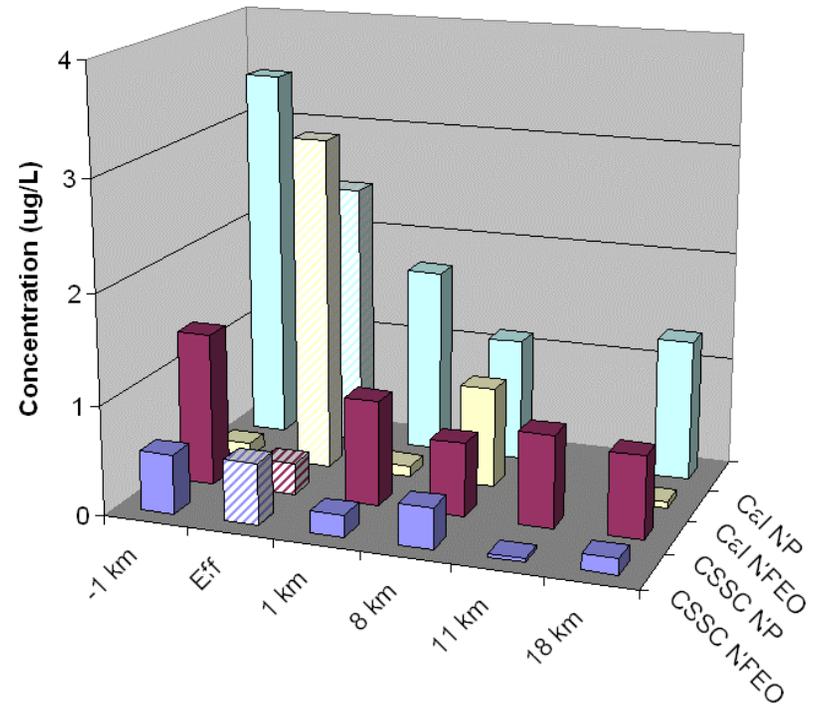
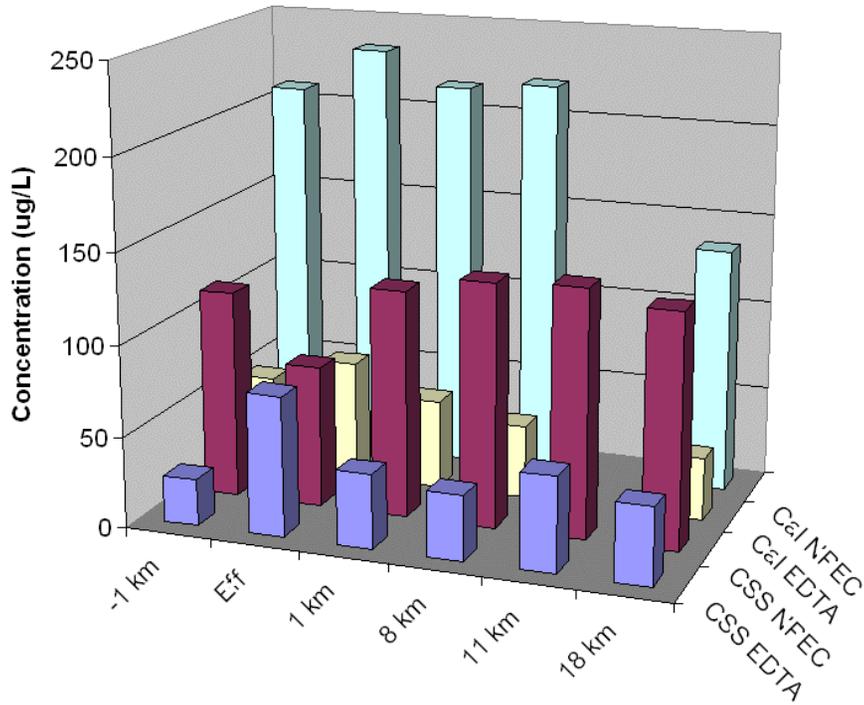
OWCs in WWTP Effluents



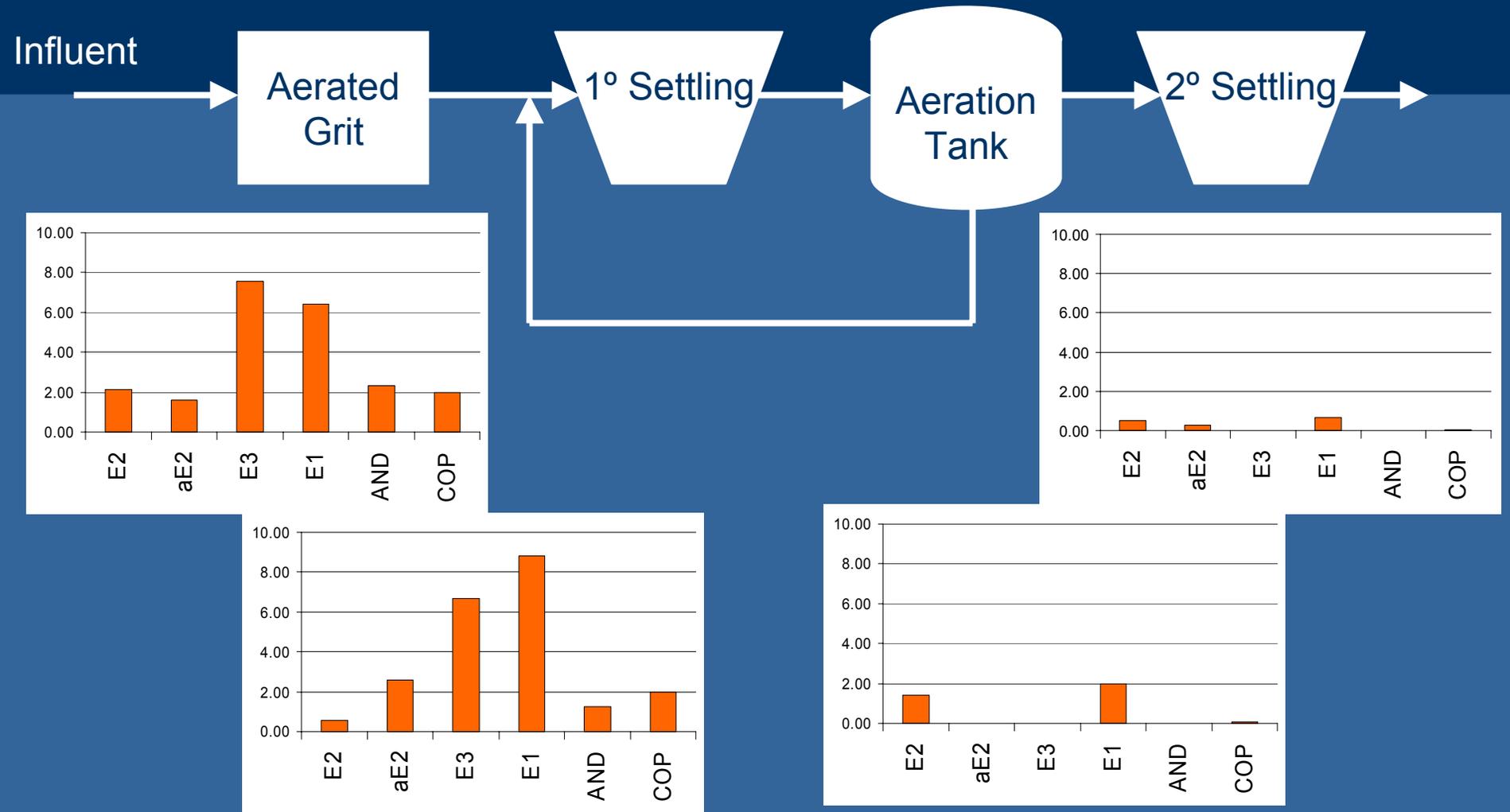
Fate of OWCs in Calumet WRP



OWCs in Chicago Waterways

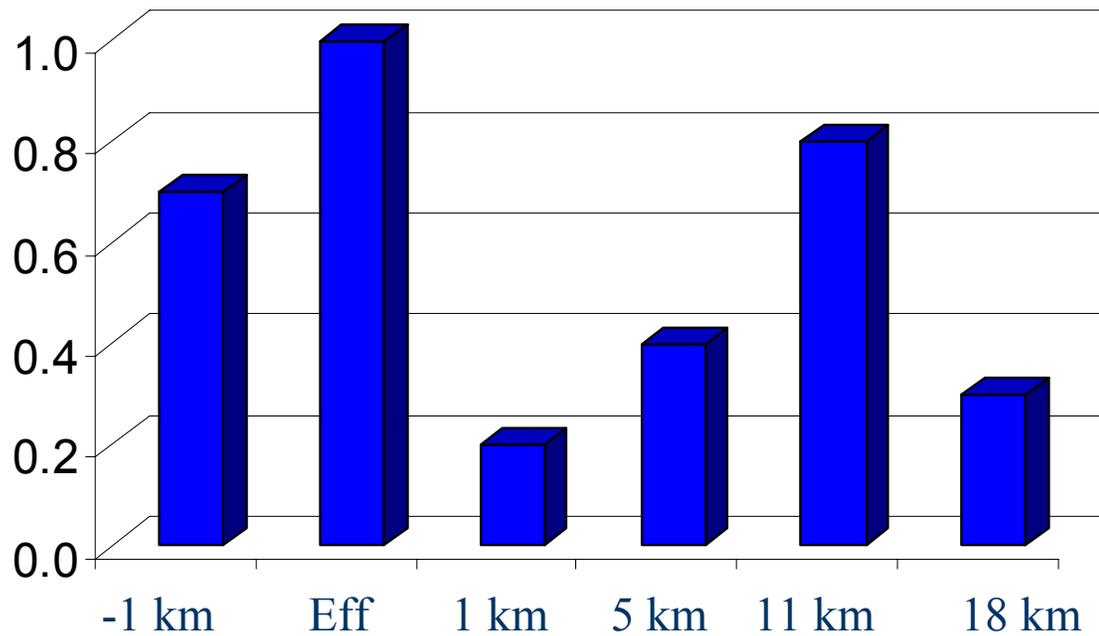


Hormones in CWRP Aqueous Streams



Hormone Occurrence in Cal Sag

17beta-estradiol



Comprehensive Chemical Analysis

1 H Hydrogen 1.0																	2 He Helium 4.0				
3 Li Lithium 6.9	4 Be Beryllium 9.0															5 B Boron 10.8	6 C Carbon 12.0	7 N Nitrogen 14.0	8 O Oxygen 16.0	9 F Fluorine 19.0	10 Ne Neon 20.2
11 Na Sodium 23.0	12 Mg Magnesium 9.0															13 Al Aluminum 27.0	14 Si Silicon 28.1	15 P Phosphorus 31.0	16 S Sulfur 32.1	17 Cl Chlorine 35.5	18 Ar Argon 40.0
19 K Potassium 39.1	20 Ca Calcium 40.2	21 Sc Scandium 45.0	22 Ti Titanium 47.9	23 V Vanadium 50.9	24 Cr Chromium 52.0	25 Mn Manganese 54.9	26 Fe Iron 55.9	27 Co Cobalt 58.9	28 Ni Nickel 58.7	29 Cu Copper 63.5	30 Zn Zinc 65.4	31 Ga Gallium 69.7	32 Ge Germanium 72.6	33 As Arsenic 74.9	34 Se Selenium 79.0	35 Br Bromine 79.9	36 Kr Krypton 83.8				
37 Rb Rubidium 85.5	38 Sr Strontium 87.6	39 Y Yttrium 88.9	40 Zr Zirconium 91.2	41 Nb Niobium 92.9	42 Mo Molybdenum 95.9	43 Tc Technetium 99	44 Ru Ruthenium 101.0	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3				
55 Cs Caesium 132.9	56 Ba Barium 137.4	57-71 Lanthanides	72 Hf Hafnium 178.5	73 Ta Tantalum 181.0	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium 210.0	85 At Astatine 210.0	86 Rn Radon 222.0				
87 Fr Francium 223.0	88 Ra Radium 226.0	89-103 Actinides	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 262	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Uun Ununnilium 272												

Types of Elements Key:

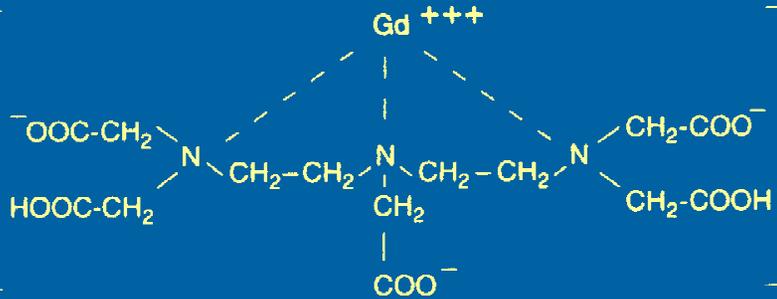
- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanides
- Actinides
- Poor metals
- Semi-metals
- Non-metals
- Noble gases

57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium 147.0	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
89 Ac Actinium 132.9	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium 237.0	94 Pu Plutonium 242.0	95 Am Americium 243.0	96 Cm Curium 247.0	97 Bk Berkelium 247.0	98 Cf Californium 251.0	99 Es Einsteinium 254.0	100 Fm Fermium 253.0	101 Md Mendelevium 258.0	102 No Nobelium 254.0	103 Lr Lawrencium 257.0

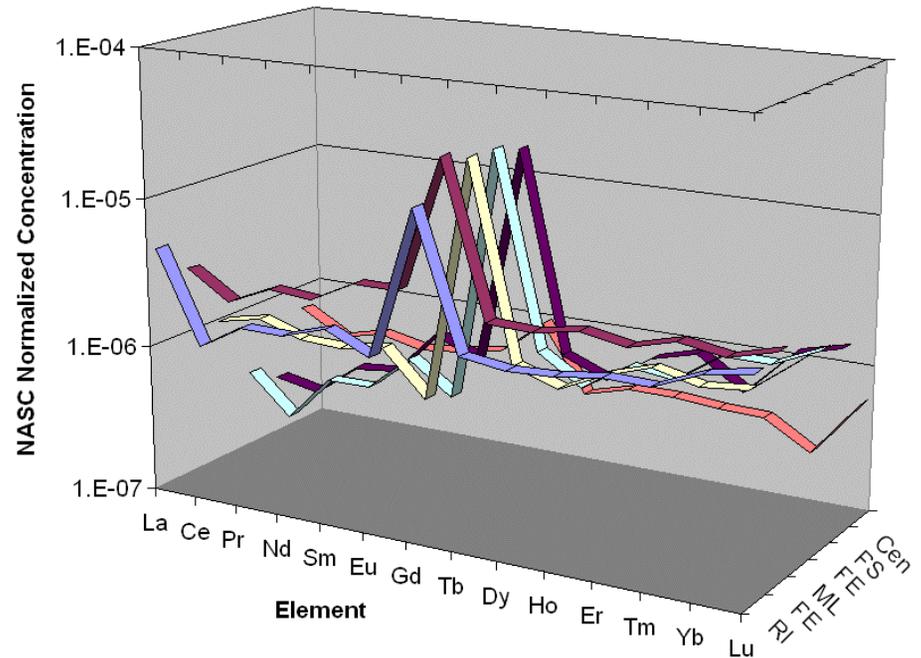
Rare Earth Element Distributions

The Gadolinium Anomaly

Gadolinium complex of diethylenetriamine pentaacetic acid



MRI Contrast Agent



Verplanck and others, 2005, Aqueous stability of gadolinium in surface waters receiving sewage treatment plant effluent, Boulder Creek, Colorado: Environ. Sci. Technol., v. 39

The Link to Biology?

All life depends on water

Molecular, Cellular, and Developmental



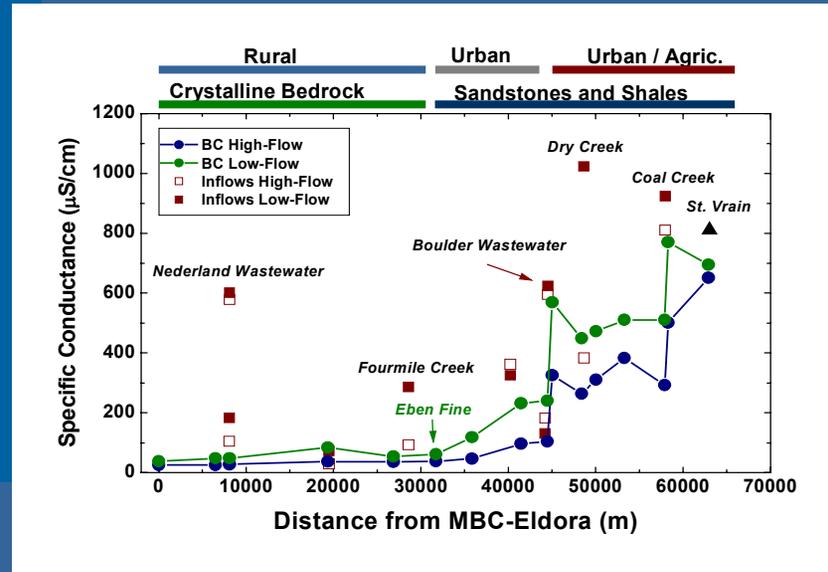
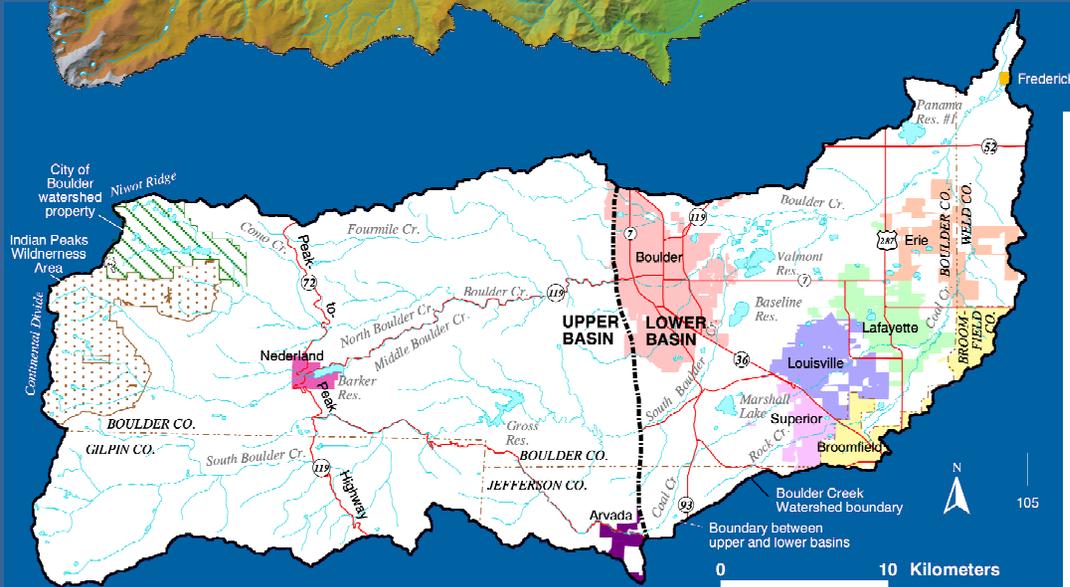
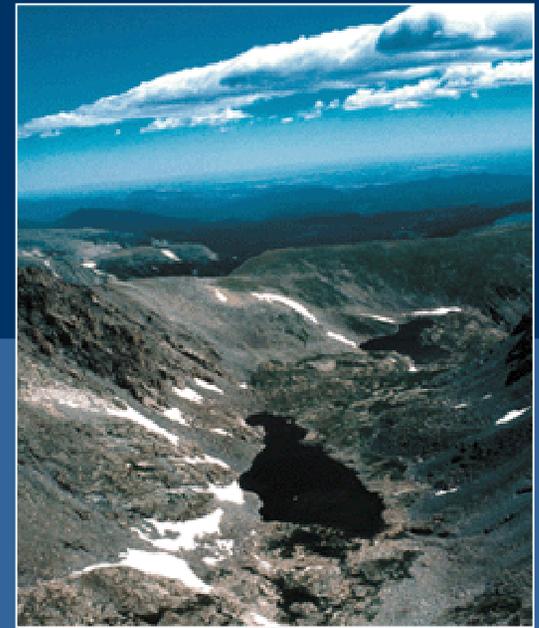
in vitro

in vivo



Environmental, Population, and Organismic

Boulder Creek Watershed

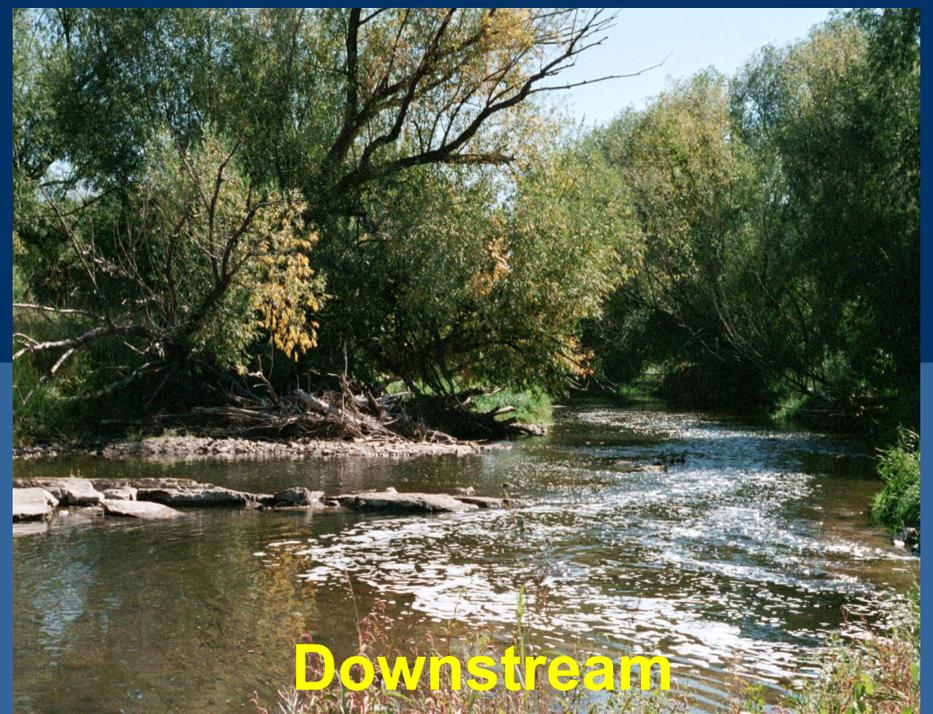


Barber and others, 2006, Chemical loading into surface water along a hydrological, biogeochemical, and land use gradient - A holistic watershed approach: Environ. Sci. Technol., v. 40,



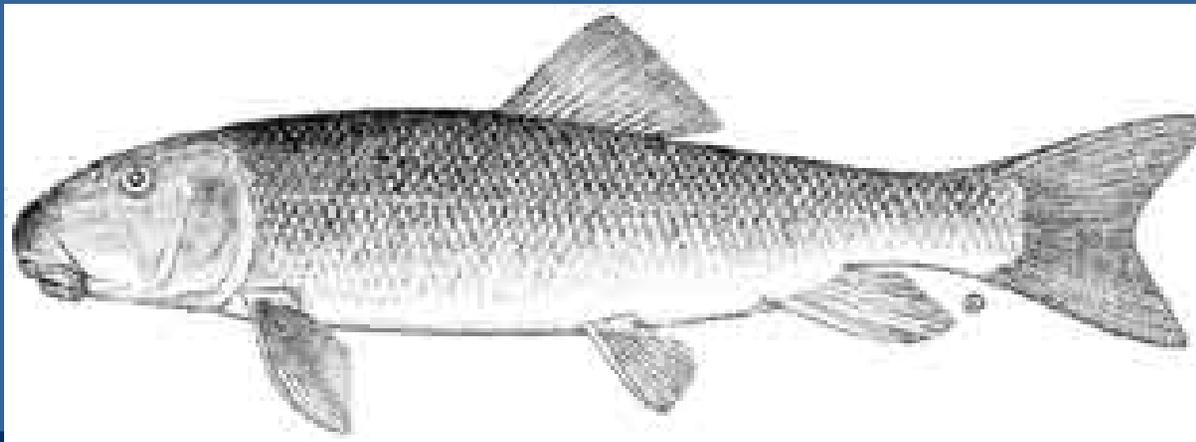


Reference



Downstream

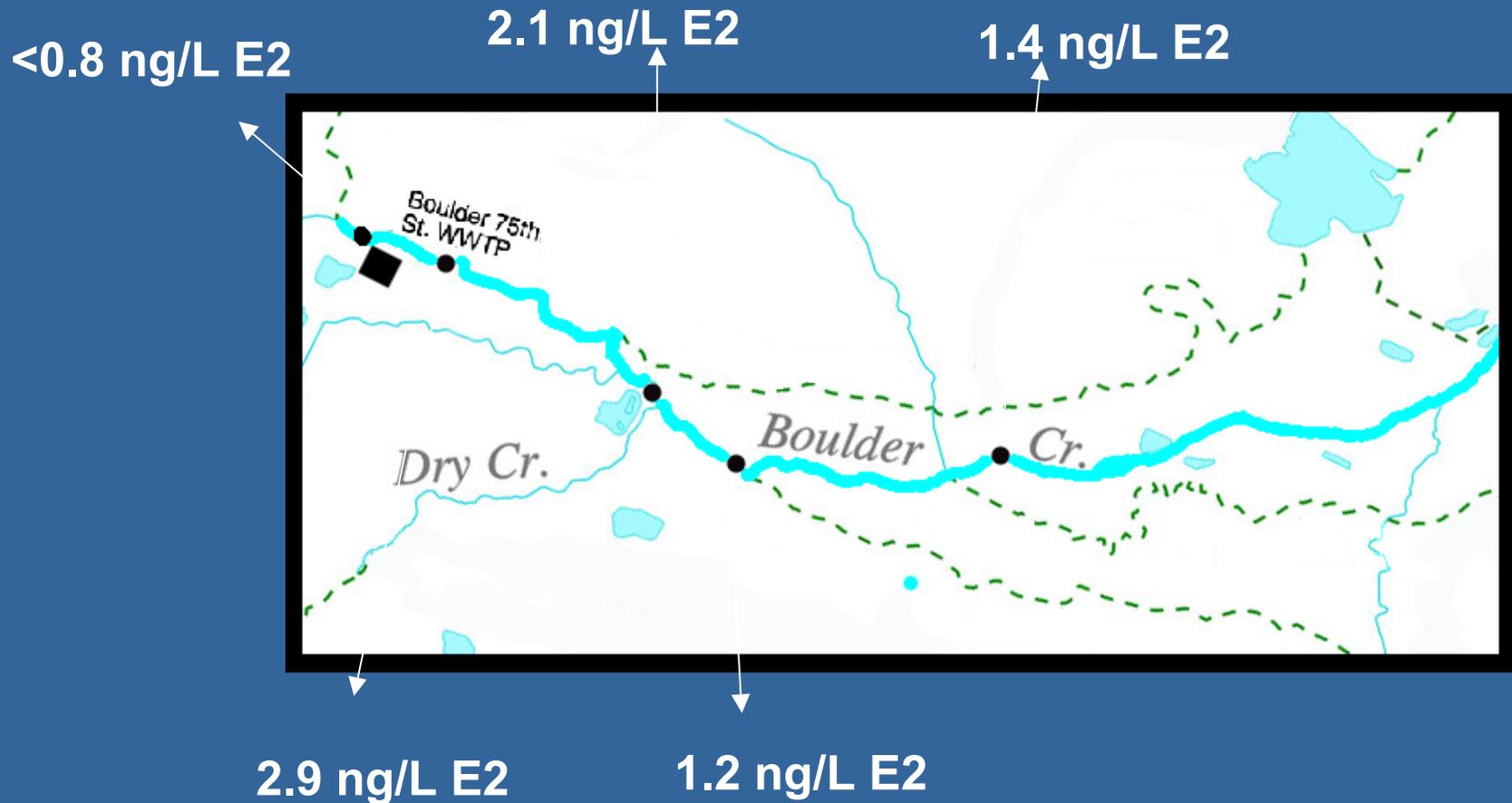
Evidence of Reproductive Disruption in Boulder Creek



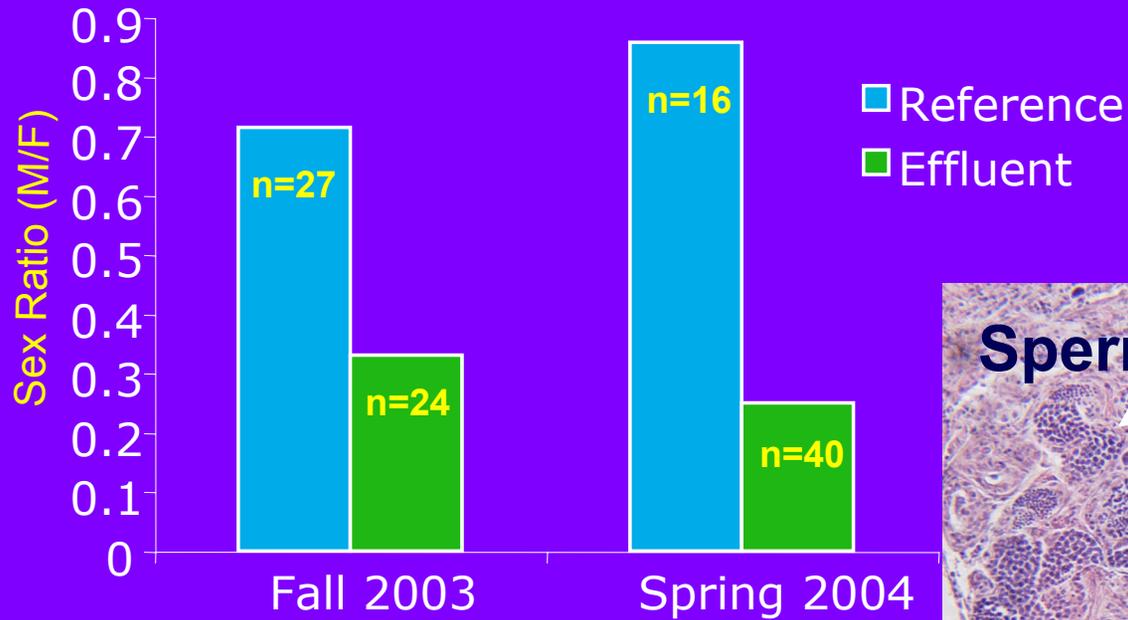
White Sucker (*Catostomus commersoni*)



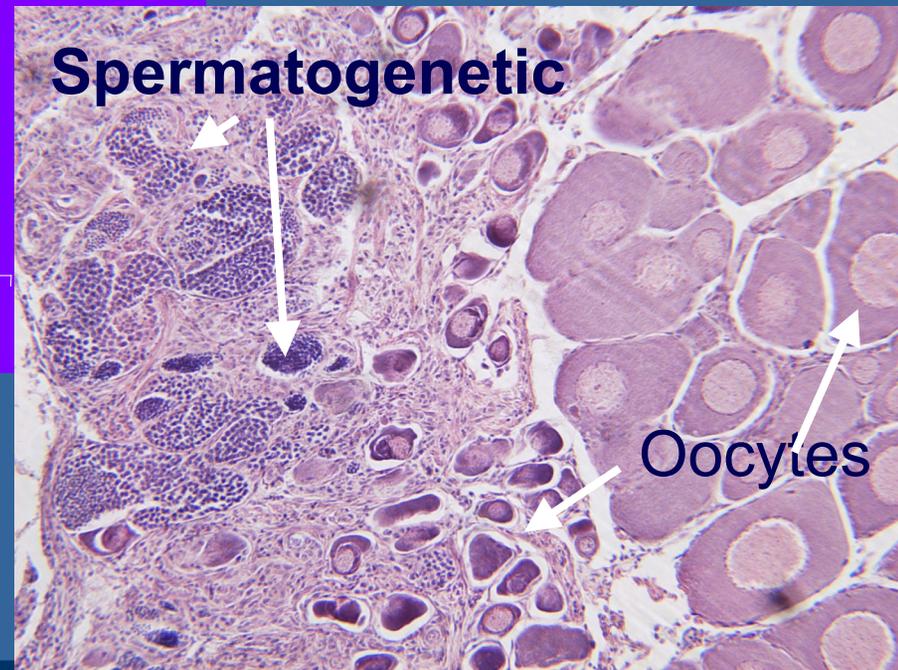
Estradiol in Boulder Creek



Shift in Sex Ratio



Intersex in Downstream Fish



Mobile Exposure Laboratory

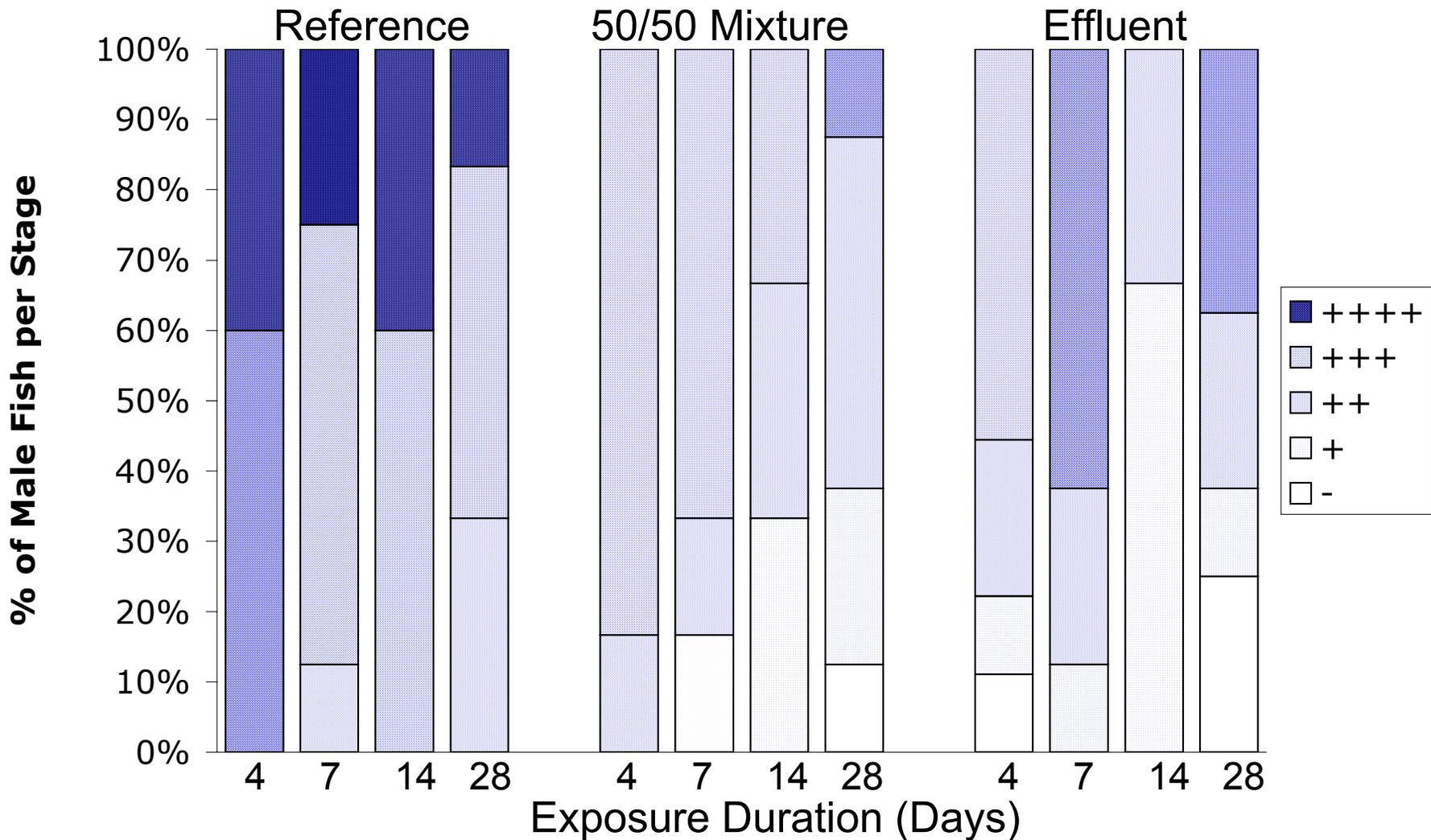


Exposure Conditions

- 5 adult males per tank
- equal length and weight
- temperature = $21^{\circ}\text{C} \pm 1$
- photoperiod 16:8 L:D
- fed frozen brine shrimp
- Flow = 200 mL/min
- Aeration



Effluent Inhibits Spermatogenesis



“Lessons from Endocrine Disruption and Their Application to Other Issues Concerning Trace Organics in the Aquatic Environment “

Sumpter and Johnson, 2005, ES&T, v. 39

- Pay attention to unusual biological observations.
- What is normal?
- One animal's poison may not be another's.
- Potency is a key factor.
- Degradation products may bite!
- Beware of continual exposure to low concentrations and mixtures.
- Beware of nontraditional pollutants from unexpected sources.
- Acute toxicity tests may not be very helpful.
- Central role played by sewage treatment.
- Hydrology will tell you where to look!