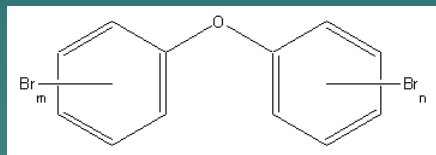


Emerging ~~Pollutants~~ Contaminants Substances of Concern

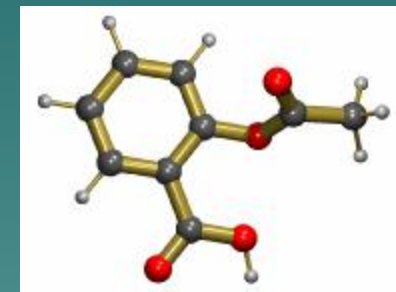
David Whiting and Tim Fitzpatrick
Bureau of Laboratories, Dept. of Environmental Protection

EPOCs



HAAs

PPCP



PIEs

POPs

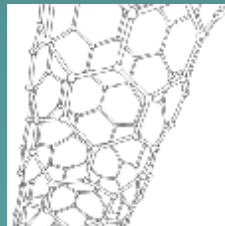
ECOCs

ESOC

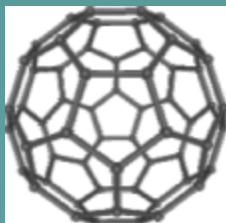
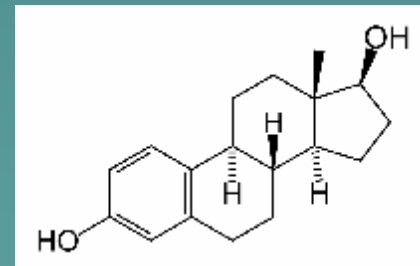
PhACs

OWCs

NanoMats



EDC



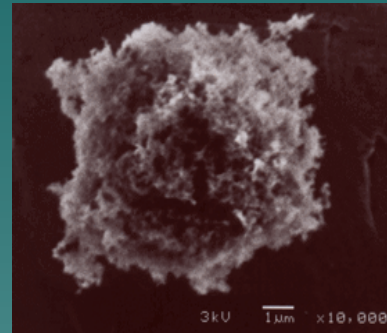
Nanoparticles

EMC

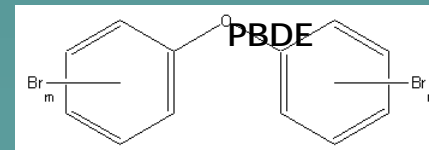
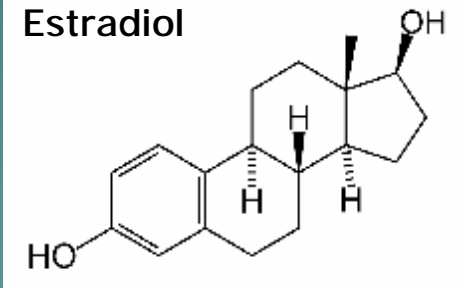
Microconstituents

More Appropriately Termed Emerging Substances of Concern

- u Not all of these substances can accurately be described as contaminants or pollutants
- u Some of these substances are found naturally in our surface waters
- u Others are natural substances that are concentrated by anthropogenic activities
- u And still others are man-made chemicals that do not occur in nature



D.M. Smith, University of Denver



Emerging Substances of Concern

- u Global Organic Contaminants
- u Pharmaceuticals and Personal Care Products
- u Endocrine Modulating Chemicals
- u Nanoparticles
- u Industrial Chemicals (new and recently recognized)
- u Biological Metabolites and Toxins

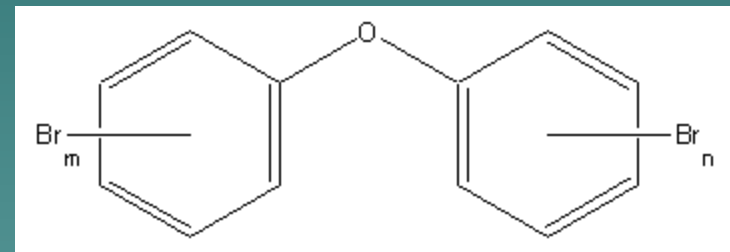
Global Organic Contaminants

- Flame Retardants and their impurities
 - ↳ polybrominated diphenyl ethers (PBDEs)
 - polybrominated biphenyls (PBBs)
 - polybrominated dibenzo-*p*-dioxins (PBDDs)
 - polybrominated dibenzofurans (PBDFs)
 - ↳ Hexabromocyclododecanes (HBCDs)
- Perfluorinated Compounds
 - ↳ Perfluorooctane sulfonates (PFOS)
 - ↳ Perfluorooctanoic Acid (PFOA)
- Siloxanes

Global Organic Contaminants

u PBDEs

- Flame retardants added to wide variety of household and consumer products
- Are not covalently bound to substrate to which they are applied, so they are easy to liberate
- PBBs, PBDDs, PBDFs can be found as impurities in PBDE formulations and created during incineration or pyrolysis of PBDE containing materials



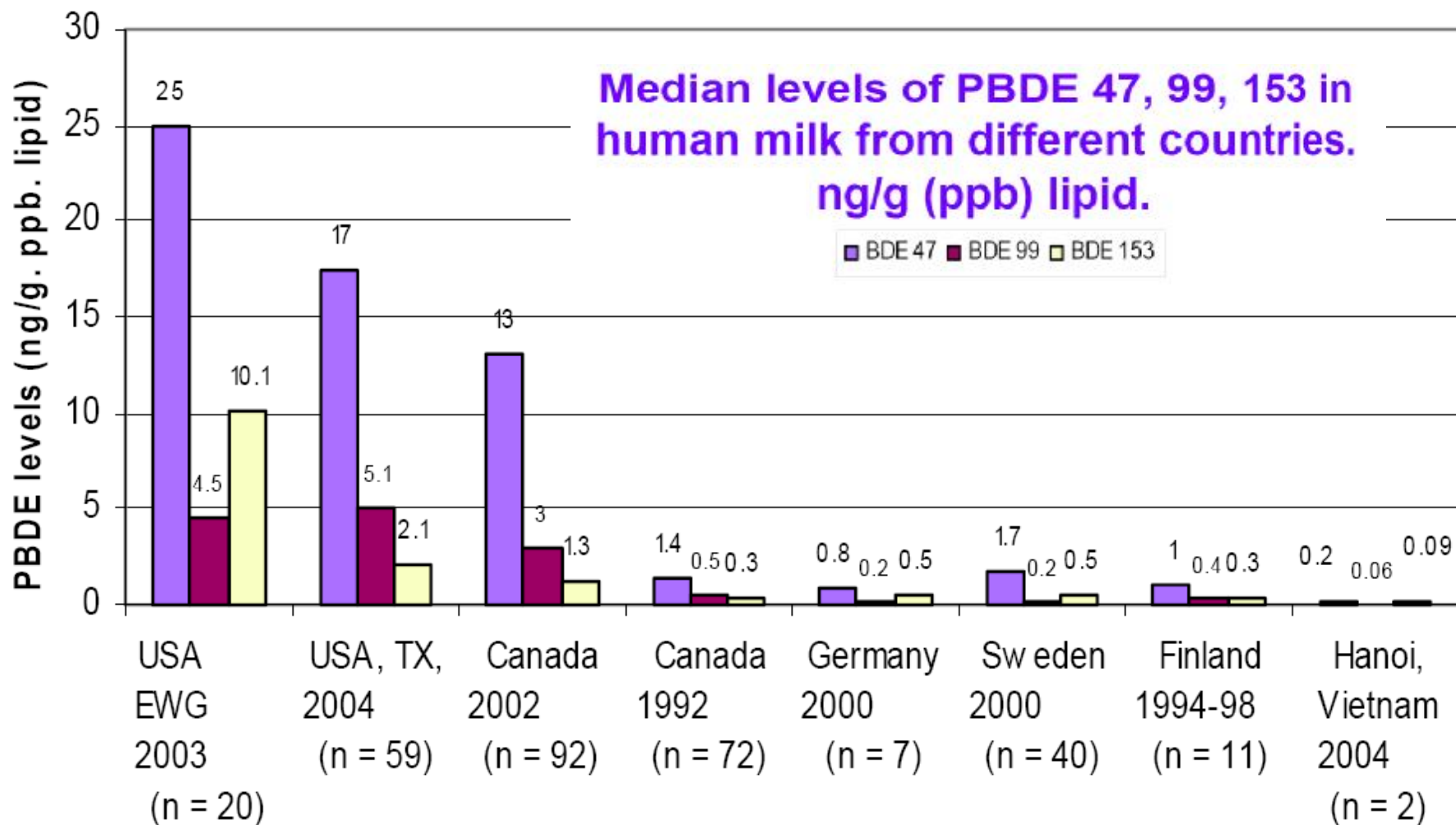
PBDEs Properties

(Burnbaum, L. NEERL/US EPA)

- u Low Solubility ($< 1 \text{ ug/kg}$)
- u High Log K_{ow} (> 5)
- u Persistence
 - t 1/2 Atmospheric > 2 days
 - Water > 2 mos
 - Soil, sediment > 6 mos

PBDEs

- u Tissue burdens (animal and human) doubling every 2-5 years
- u Lower weight congeners absorbed more easily
- u Lower weight congeners more toxic
 - PeBDE >> OBDE > DBDE
 - Higher weight congeners can degrade into more toxic lower weight congeners
- u BAF > 5,000:1
- u BMF ranged 3:1 to 85:1 in sharks and dolphins from Florida study



PBDEs

- u Non-point and point source issue
- u Primary release is to atmosphere not water
- u Global transportation of released PBDEs and other organic contaminants (increasing concentrations in polar bears)
- u Approaching potential effect concentrations in wild Osprey (Henry, C. et al. 2006. PBDE and HBCD Flame Retardants in Eggs of Osprey and Double-crested Cormorants from Washington and Oregon, 2002-2004. Poster at 2006 Annual SETAC meeting, Montreal, QC)
- u Potential (currently unknown) effects from PBDDs and PBDFs;

PBDE Effects

- u Kestrel pipping and hatching success reduced at concentrations $>10\mu\text{g/g}$ (air cell injected), but not chickens or ducks
- u Chicken liver EROD activity increased in 1, 10, and $20\mu\text{g/g}$ treatments, but not kestrels or ducks (USGS, 2006. Comparative Toxicity of Polybrominated Flame Retardants in Avian Embryos. Poster at 2006 SETAC Meeting)
- u Crustaceans very sensitive to PBDEs. 5-day EC_{50} as low as $1.2\mu\text{g/L}$ for larval development in the pelagic calanoid copepod, *Acartia tonsa*

(<http://www2.er.dtu.dk/publications/fulltext/2005/MR2005-012.pdf>)

PBDE Effects

u Adult Mammalian Toxicity

- Hepatic enzyme induction and toxicity
 - u DBDE is a hepatocarcinogen (high dose)
- Endocrine Modulator
 - u Thyroid
 - u Estrogen/anti-androgen
- Developmental and Reproductive effects
 - u Penta/Octa BDE 99
 - Delayed puberty, sex organ changes, decreased sperm counts
- Neurotoxicity
 - u Penta/BDE47, 99, 203, 206
 - Deficits in sensory, motor, and cognitive function

Pharmaceuticals and Personal Care Products (PPCPs)

- u Basically all prescription and over-the-counter drugs
- u Diagnostic agents
- u Dietary Supplements
- u Fragrances, soaps, conditioners, sunscreens, cosmetics...
- u Caffeine
- u Nicotine

PPCPs

- u Most diverse “category” of Emerging Substances of Concern; Many are water soluble;
- u Most common route into the environment is through wastewater (municipal and septic drainage) and land application of sewage sludge and manure, and landfill leachate
- u To state the obvious, the most common route to humans is through ingestion and topically (although the dose is often unintended – drinking water, breast milk)
- u WWTP treatment may or may not be effective at removing the compounds from the effluent depending upon the treatment and chemical

PPCPs

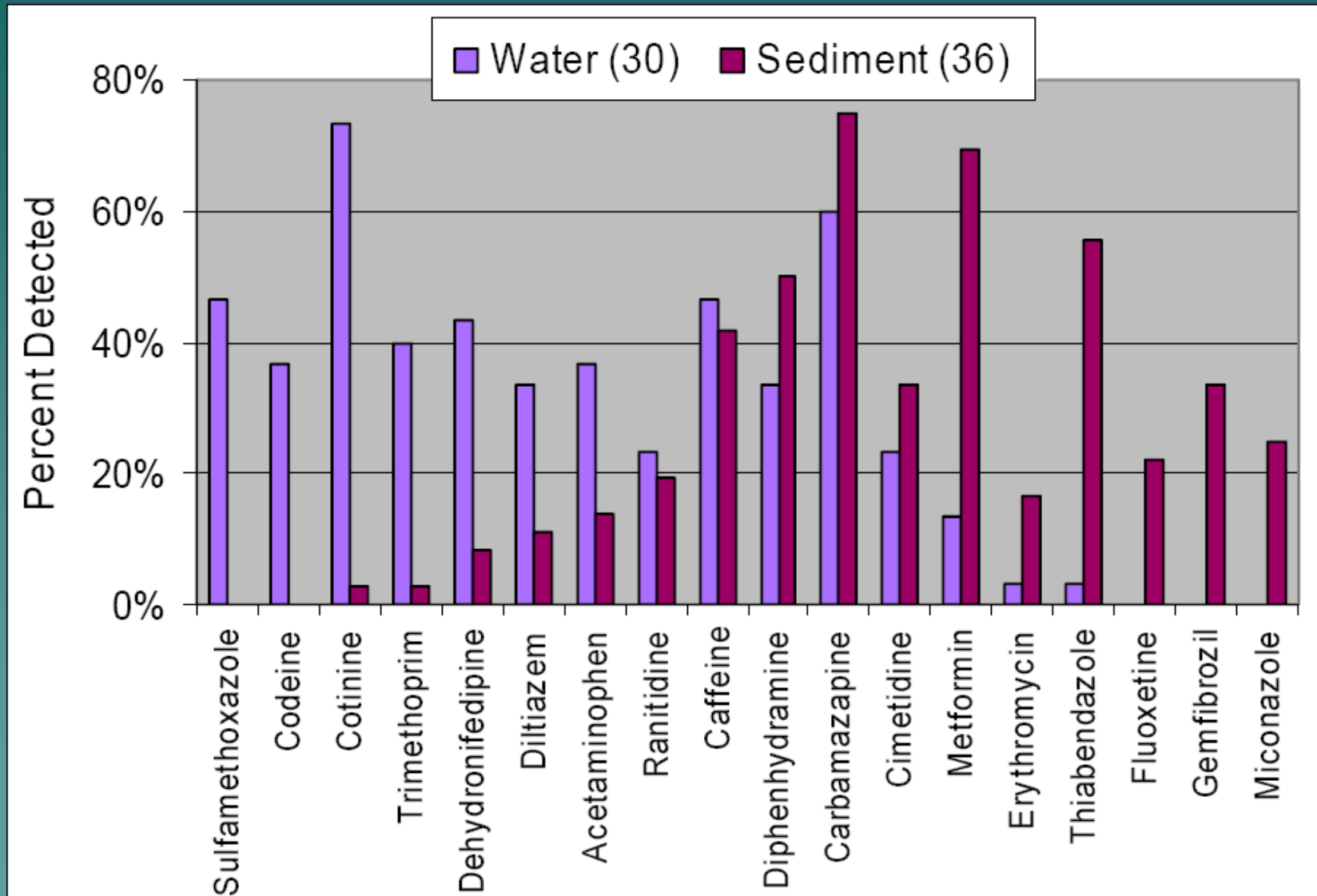
- u Receiving water concentrations are typically in the ng/L to low $\mu\text{g/L}$ range
- u Common pain relievers are usually the PPCP found in the highest concentrations
- u Some PPCPs can induce estrogenic effects in biological receptors, however most research to date suggests that such effects are not likely at current environmental concentrations
- u However, most tests have been on single compounds
- u Usually occur as mixtures

PPCP/EMC

- u USGS study on the fate and effects of PPCP's in a WWTP discharging into Boulder Creek, Boulder Creek, CO.
- u Venlafaxine (Effexor), the most abundance anti-depressant found
- u Concentrations varied significantly with time of day and day of week
- u 1:4 sex ratio in white sucker population in Boulder Creek

Boulder Creek

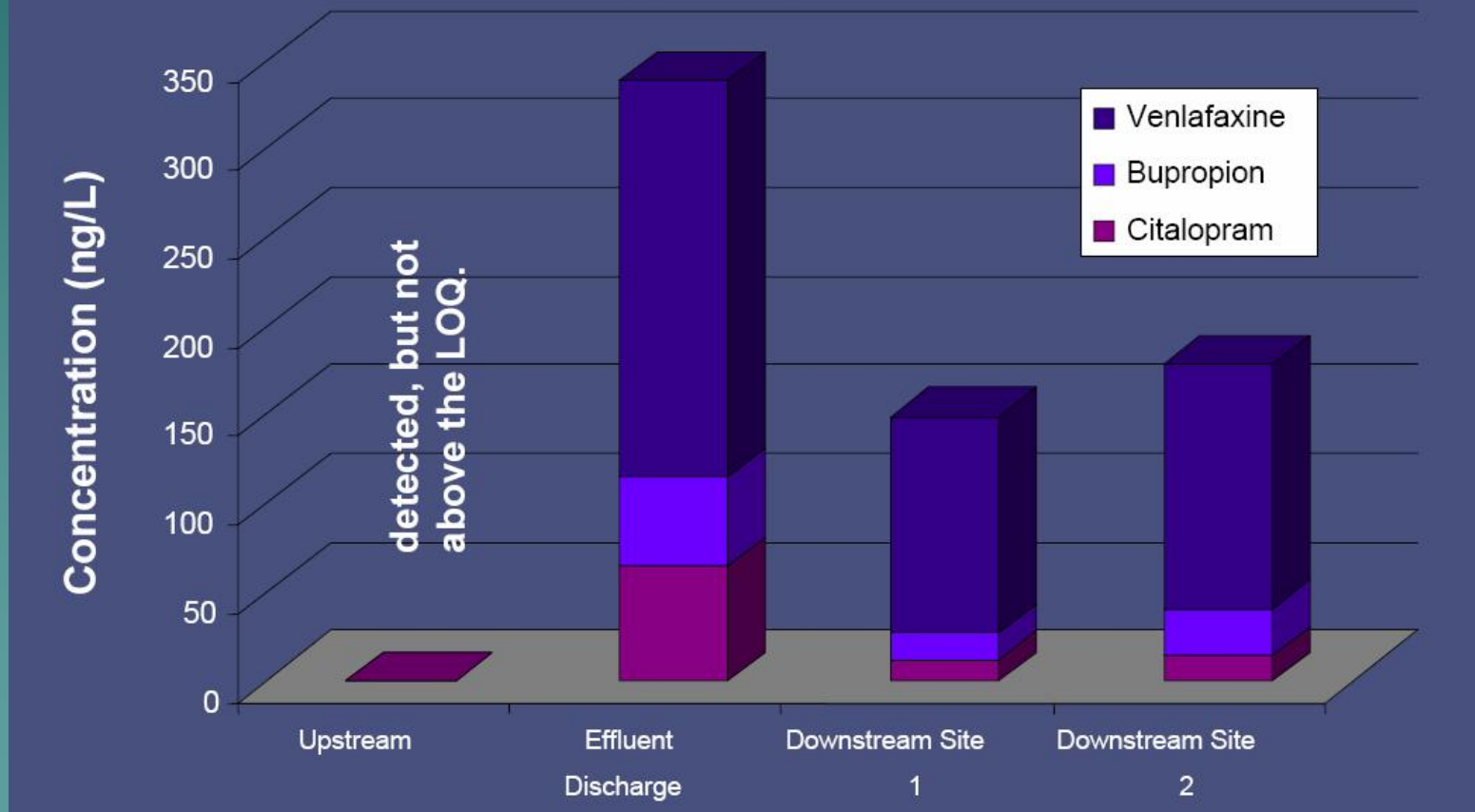
USGS Work in Boulder Creek, Boulder Creek, CO



Boulder Creek

USGS Work in Boulder Creek, Boulder Creek, CO

Antidepressants in Boulder Creek "Major Players"

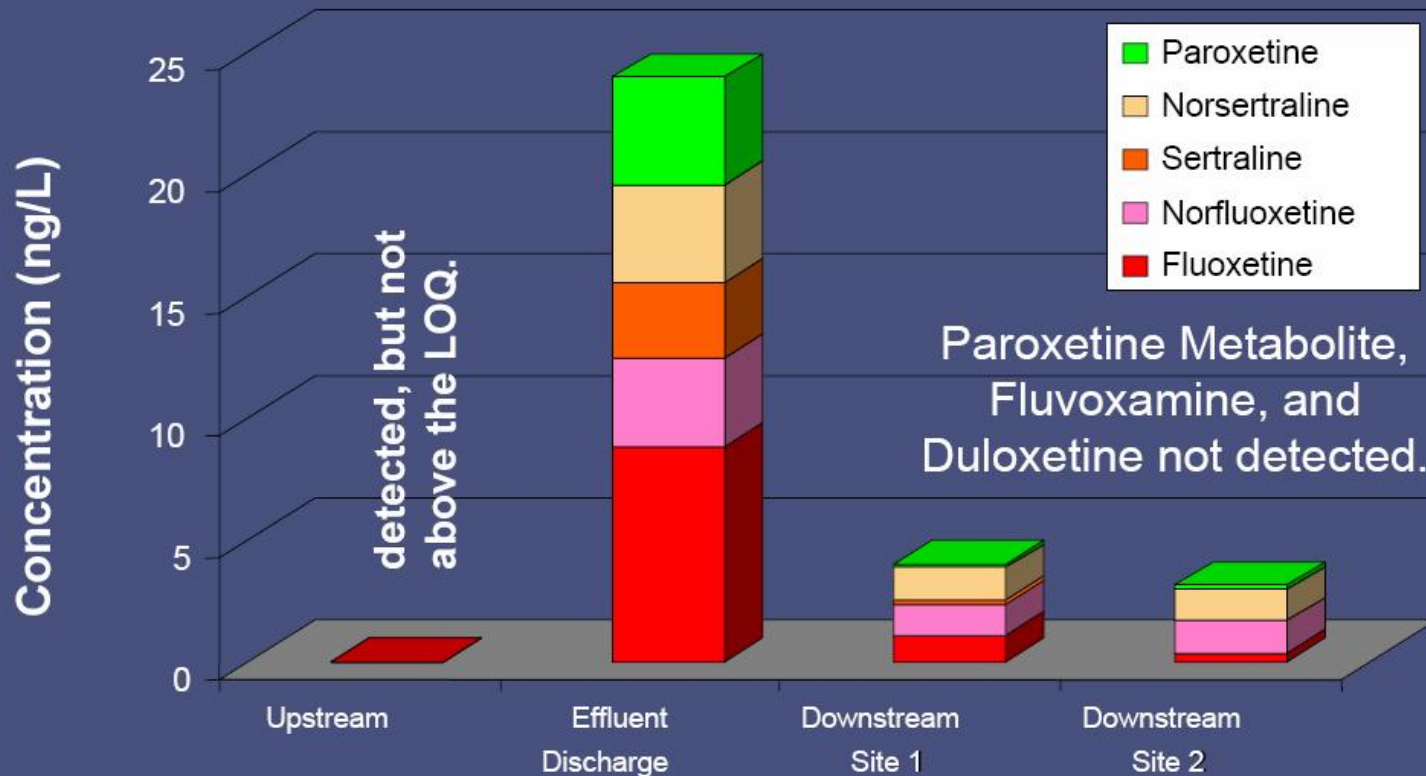


Boulder Creek

USGS Work in Boulder Creek, Boulder Creek, CO

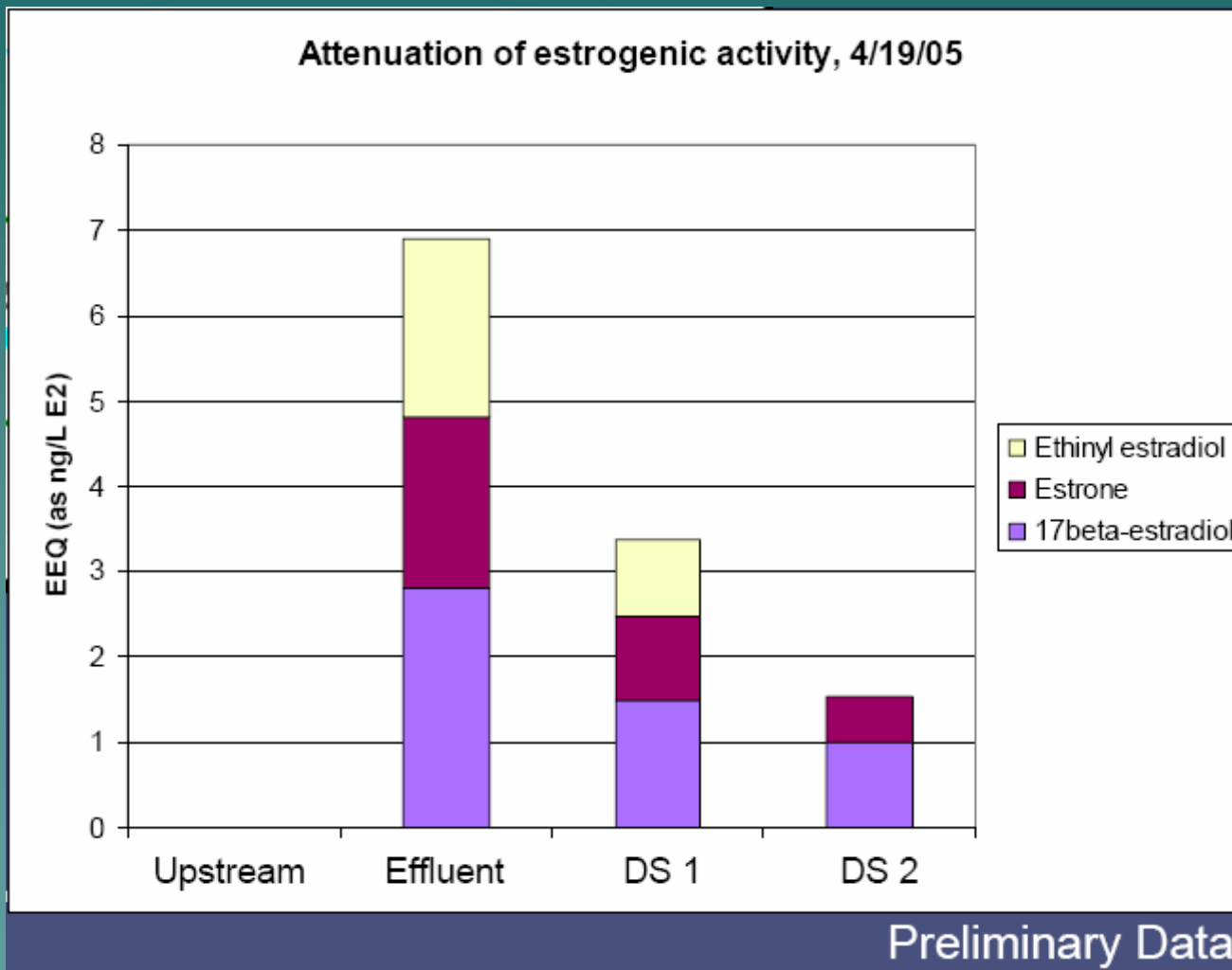
Antidepressants in Boulder Creek

“Minor Players”



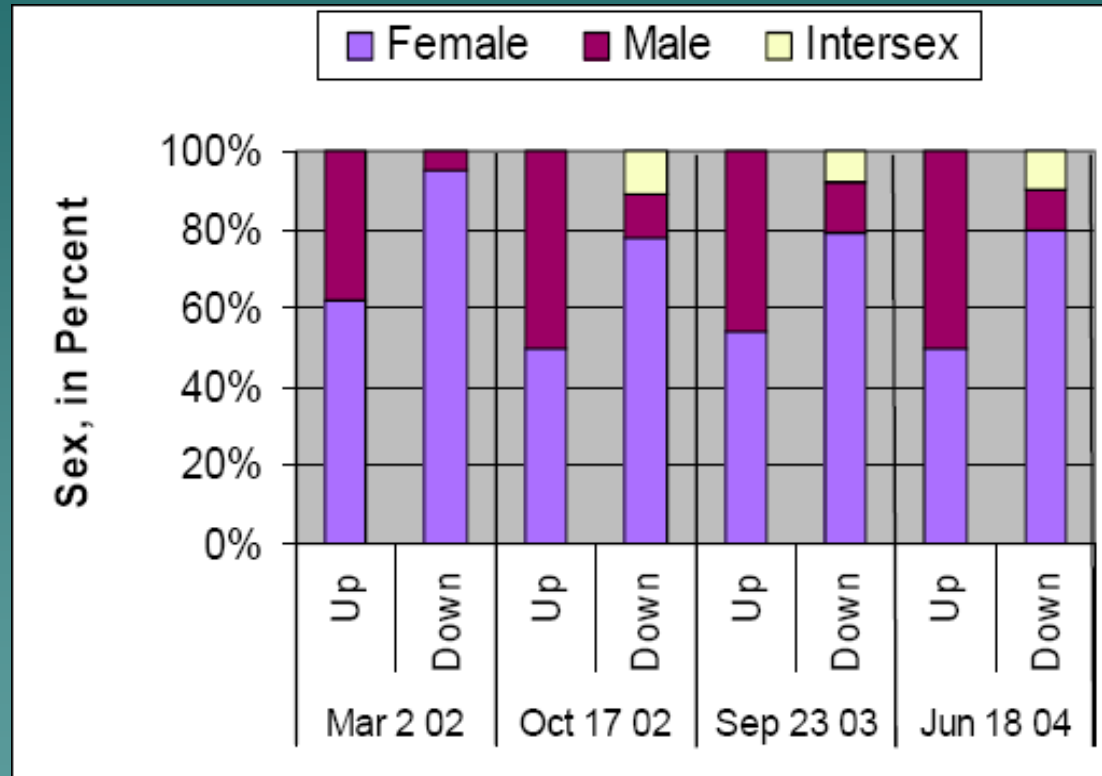
Boulder Creek

USGS Work in Boulder Creek, Boulder Creek, CO



Boulder Creek

USGS Work in Boulder Creek, Boulder Creek, CO



Endocrine Modulating Chemicals

- u EMCs typically categorized as
 - Natural or synthetic hormones
 - Industrial chemicals
 - Pesticides

Endocrine Modulating Chemicals

Modulating is a better descriptor than Disrupting

- u Natural and synthetic hormones
- u Surfactants
- u Pesticides
- u TBT
- u PCBs
- u Dioxins

Natural and Synthetic Hormone EMCs

- u Phytoestrogens – produced by many plants
- u Natural hormones
 - 17 β –estradiol (E2)
 - estrone (E1)
 - Estriol (E3)
- u Estrogen regulating pharmaceuticals
 - Synthetic estrogen ethinylestradiol (EE2)

Natural and Synthetic Hormone EMCs

- u Estrogens readily degradable under aerobic conditions ($T_{1/2}$ 4-10 hours)
- u Slow degradation under anaerobic conditions
- u Both conjugated and de-conjugated forms must be quantified
- u Conjugated estrogens (having a glucuronide or sulfate group attached) are formed as the body eliminates estrogens and are not estrogenically active
- u These conjugated estrogens can be de-conjugated in WWTP systems

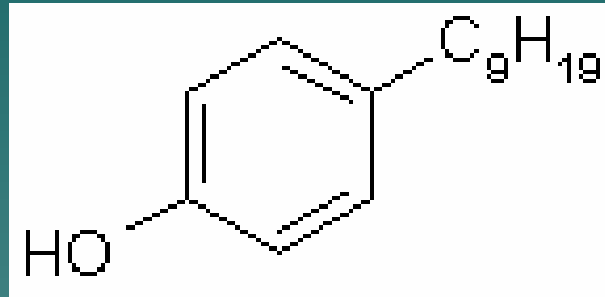
Industrial EMCs

- u Phthalates – plasticizers
- u Nonylphenol and alkylphenol ethoxylates – surfactants, anti-foaming agents and plasticizers or UV stabilizers in plastics
- u Bisphenol A – ingredient in lacquers used to treat cans used for food goods
- u PCBs
- u Dioxins
- u PBDEs – flame retardants
- u Parabens – preservatives used in cosmetics and antibacterial toothpastes

Nonylphenols

- u Commonly used surfactant in US e.g., nonylphenol ethoxylate
- u Banned in Europe
- u Estrogenic (1/10,000 of EE)
- u Persistent in the environment
- u Bioaccumulate
- u Relatively high Log K_{ow} (3.8 to 4.8)
- u Occur in relatively high concentrations (100s of mg/kg dry weight in sediments)

Nonylphenols



- u Proposed EPA WQC
 - FW CMC 27.9 µg/L
 - FW CCC 65.9 µg/L
 - SW CMC 6.7 µg/L
 - SW CCC 1.4 µg/L

List of Potential Pesticide EMCs

Acephate
Acetochlor
Alachlor
Aldicarb
Aldrin
Amitrol
Atrazine
Benomyl
Beta-HCH
Bifenthrin
Bioallethrin
Bromoxynil
Carbaryl
Carbendazim
Carbofuran
Chlordane
Chlordecone
Chlorfenvinphos
Cyathrin
Cyanazine
Cypermethrin

2,4-D
2,4-DB
DDT
Delta HCH
Deltamethrin
Demeton-s-methyl
Dialifos
Diazinon
Dichlorvos
Dicofol
Dieldrin
Dimethoate
Diuron
Endosulfan
Endrin
Etridiazole
Fenarimol
Fentin acetate
Fenitrothion
Fenothrin
Fenoxycarb
Fenvalerate
Fluavinate

HCB
HCH
Heptachlor
Ioxynil
Iprodione
Lindane
Linuron
Malathion
Mancozeb
Maneb
Metam sodium
Methomyl
Methoxychlor
Methyl bromide
Metiram
Metribuzin
Mevinphos
Mirex
Nitrofen
Oxychlordane
Parathion ethyl
Parathion methyl
Pentachlorophenol

Permethrin
Phosphamidon
Photomirex
Picloram
Piperonyl butoxide
Prochloraz
Procymidone
Prometryn
Propanil
Resmethrin
Simazine
2,4,5-T
Tebutryn
Thiram
Toxaphene
Triadimefon
Triadimenol
Tributyltin
Trichlorfon
Trifluralin
Triphenyltin
Vinclazolin
Zineb
Ziram

EMCs

- u EMCs can affect three aspects of Endocrine function
 - Neural input to the endocrine system
 - Hormonal modulation of the nervous system
 - Regulation of hormone and receptor biosynthesis, secretion, and metabolism

Environmental Effects of EMCs

- u Difficult to quantify due to low concentrations and chemical mixtures
- u Can be confounded in field and laboratory experiments by parasites in the test subjects that can alter endocrine pathways (daphnids and amphipods)
- u Widely varying sensitivities amongst wildlife receptors
- u Effects can be reversible

Environmental Effects of EMCs

- u Feminization of fish, birds, reptiles has been reported at environmentally relevant concentrations
- u Intersex Males (males with ova present in their testes) observed in amphibians and fish
- u Gynandromorphism in daphids
- u Abnormal development in fish and birds
- u Biomarkers for exposure do not translate into quantifiable adverse effects

Human Health Effects of EMCs

- u Very little data on human health effects from EMCs from food or drinking water
- u Studies showing reduced sperm counts and increased cancer confounded by life-style choices

Nanoparticles

NanoMats

- u Fullerenes (a.k.a. buckyballs)
- u Nanotubes
- u Quantum dots
- u Nanopowders (metal oxides)
- u Natural particles (e.g., soot)

Nanoparticles

- u Natural and manmade structures in the 1 to 100 nm size range
- u Used in nanotherapeutic pharmaceuticals, drug delivery, cosmetics, energy storage products, fabrics, lubricants, even golf balls
- u Potential use in contaminated site clean up

Nanoparticles

- u Toxicity of most nanotechnology products has not been determined
- u Potential mechanisms of aquatic toxicity from the particles themselves are
 - Ingestion
 - Physical disruption
 - Gill irritation

Gaining Perspective

u Unregulated ≠ Little Risk;

Old Pollutant – New Concern;
vs.

New Pollutant – Unknown Issues;

PPCPs are not new pollutants but are newly identified in waters due to improved analytical techniques.

u Highest Propensity for Adverse Effects

PBT – persistent, bioaccumulative toxicants

- u Possess structural stability (long ½-life)
- u Lipophilic (bioaccumulative)
- u Cause acute or chronic toxicity

Persistence vs. Pseudo-Persistence

Resistance to chemical transformation (detoxification) is typically used to evaluate the persistence of substances;

Continual release of a substance to a media (such as a waterbody) can compounds a 'pseudo-persistent' presence;

Re-Assessing Toxicity

- u Substances may 'elicit' toxicity without being inherently toxic
 - u e.g., by acting as vectors to ferry other toxicants (nanoparticles) or as indirect stressors by altering pathogen resistance (antibiotics);
- u Delayed onset toxicity can mask environmental effects;
- u Real-World exposure includes additive and synergistic effects of multiple stressors;

Substances of Greatest Concern

u High Use Endocrine Disruptors

- u Some PPCPs;
- u Alkylphenols and alkylphenol ethoxylates;
- u Hormones/Steroids (feedlot operations)

u Persistent Bioaccumulative Compounds

- u Polybrominated diphenyl ethers and associated adulterants;
- u Others???

EPA's Stated Strategy

1. Literature Forensics - Assess usage, environmental exposure and prevalence, persistence, bioaccumulation and toxicity;
2. Rank substances by risk based on above considerations;
3. Evaluate measurement methodologies;
4. Engage research to fill gaps in knowledge;
5. Monitor highest ranked candidates (for occurrence and ecological effects);
6. Develop regulation and treatment technology as necessary;

EPA Analytical Method Development

- u Method 1614 – High resolution Isotope Dilution GC/MS for PBDEs (2003);
- u Collaboration with ASTM for development of GC/MS method for nonylphenol and ethoxylates;
- u Draft Method 1694 – LC/MS/MS for 37 PPCPs;
- u Draft Method 1698 – GCMS for 21 steroids and hormones;
- u Draft Method 1699 – High resolution GC/MS for 77 pesticides and metabolites and 8 herbicides;

B/Labs Analytical Capability

- u Analytical technology for environmental chemical measurements of many ESOC is generally adequate (lack high resolution GC/MS technology);
- u Biomarker techniques would need development;
- u Staff resources and methodological development currently inadequate to support ESOC monitoring;