Emerging ~~Pollutants~~ ~~Contaminants~~ Substances of Concern

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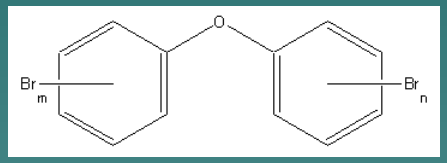
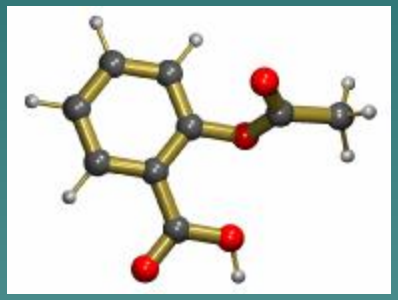
Bureau of Laboratories, Dept. of Environmental Protection

EPOCs



HAAs

PPCP



PIEs

POPs

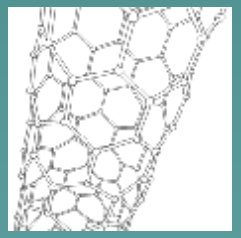
ECOCs

ESOC

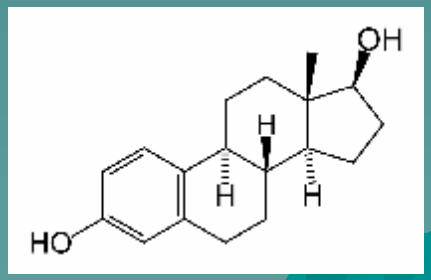
PhACs

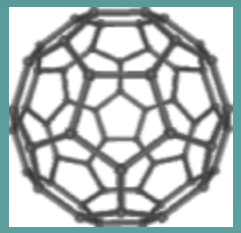
OWCs

NanoMats



EDC





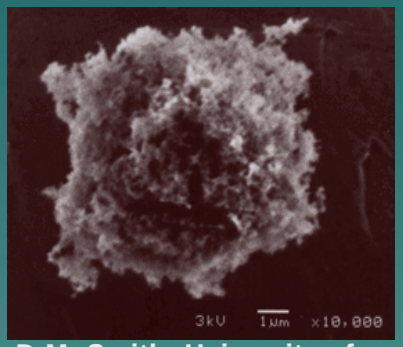
Nanoparticles

EMC

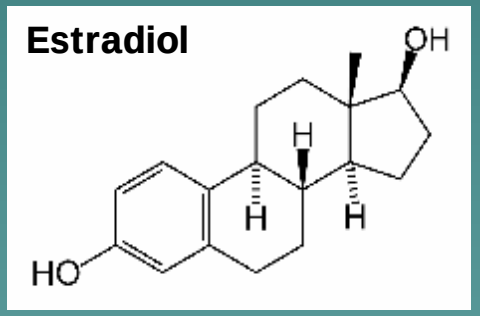
Microconstituents

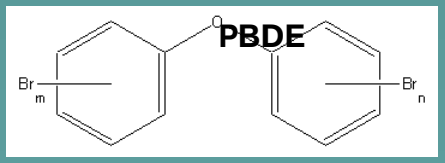
More Appropriately Termed Emerging Substances of Concern

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



D.M. Smith, University of Denver





Emerging Substances of Concern

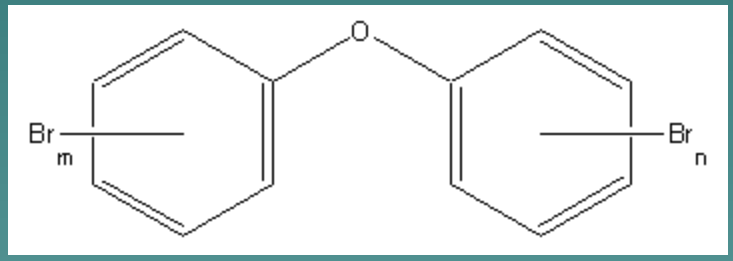
- **Global Organic Contaminants**
- **Pharmaceuticals and Personal Care Products**
- **Endocrine Modulating Chemicals**
- **Nanoparticles**
- **Industrial Chemicals (new and recently recognized)**
- **Biological Metabolites and Toxins**

Global Organic Contaminants

- **Flame Retardants and their impurities**
  - **polybromonated diphenyl ethers (PBDEs)**
    - **polybromonated biphenyls (PBBs)**
    - **polybromonated dibenzo-*p*-dioxins (PBDDs)**
    - **polybromonated dibenzofurans (PBDFs)**
  - **Hexabromocyclododecanes (HBCDs)**
- **Perfluoronated Compounds**
  - **Perfluororoctane sulfonates (PFOS)**
  - **Perfluoroctanoic Acid (PFOA)**
- **Siloxanes**

Global Organic Contaminants

- **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)

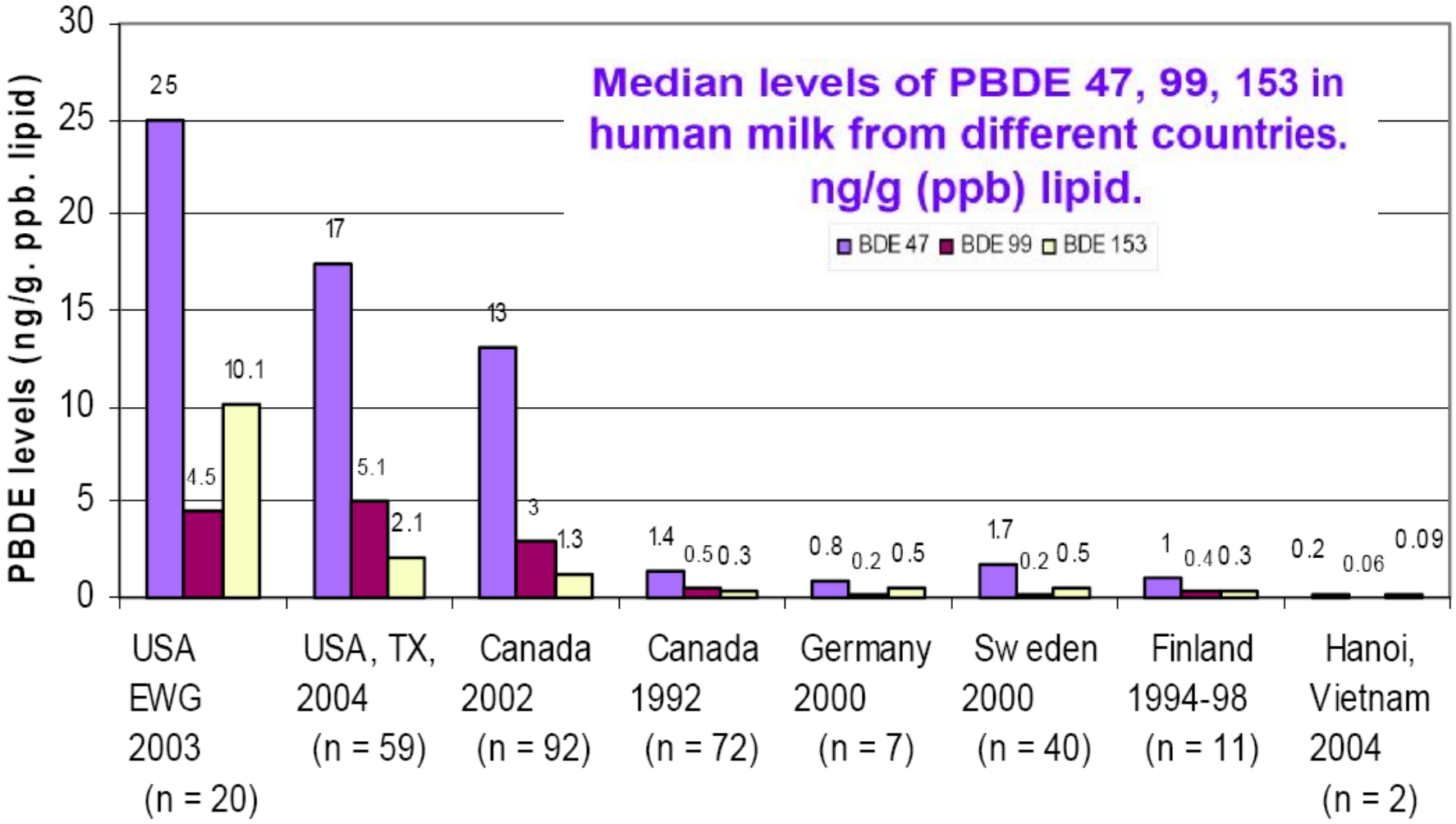
- **Low Solubility (< 1 ug/kg)**
- **High Log K_{ow} (> 5)**
- **Persistence**
  - **t 1/2 Atmospheric >2 days**
  - **Water >2 mos**
  - **Soil, sediment >6 mos**

http://www.hesiglobal.org/NR/rdonlyres/A41C84C0-B32A-493D-911D-32449D97C814/0/10bPBDEpresentation.pdf

PBDEs

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

http://www.hesiglobal.org/NR/rdonlyres/A41C84C0-B32A-493D-911D-32449D97C814/0/10bPBDEpresentation.pdf



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PBDEs

- Non-point and point source issue
- Primary release is to atmosphere not water
- Global transportation of released PBDEs and other organic contaminants (increasing concentrations in polar bears)
- 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)
- Potential (currently unknown) effects from PBDDs and PBDFs;

PBDE Effects

- **Kestrel pipping and hatching success reduced at concentrations >10µg/g (air cell injected), but not chickens or ducks**
- **Chicken liver EROD activity increased in 1, 10, and 20µg/g treatments, but not kestrels or ducks** (USGS, 2006. Comparative Toxicity of Polybrominated Flame Retardants in Avian Embryos. Poster at 2006 SETAC Meeting)
- **Crustaceans very sensitive to PBDEs. 5-day EC_{50} as low as 1.2 µg/L for larval development in the pelagic calanoid copepod, *Acartia tonsa***
  (http://www2.er.dtu.dk/publications/fulltext/2005/MR2005-012.pdf)

PBDE Effects

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

http://epa.gov/waterscience/fish/forum/2005/presentations/Tuesday%20Slides%200920/afternoon/Birmbaum.ppt#275,15,PBDE Toxicity

Pharmaceuticals and Personal Care Products (PPCPs)

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

PPCPs

- Most diverse “category” of Emerging Substances of Concern; Many are water soluble;
- Most common route into the environment is through wastewater (municipal and septic drainage) and land application of sewage sludge and manure, and landfill leachate
- 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)
- WWTP treatment may or may not be effective at removing the compounds from the effluent depending upon the treatment and chemical

PPCPs

- Receiving water concentrations are typically in the ng/L to low µg/L range
- Common pain relievers are usually the PPCP found in the highest concentrations
- 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
- However, most tests have been on single compounds
- Usually occur as mixtures

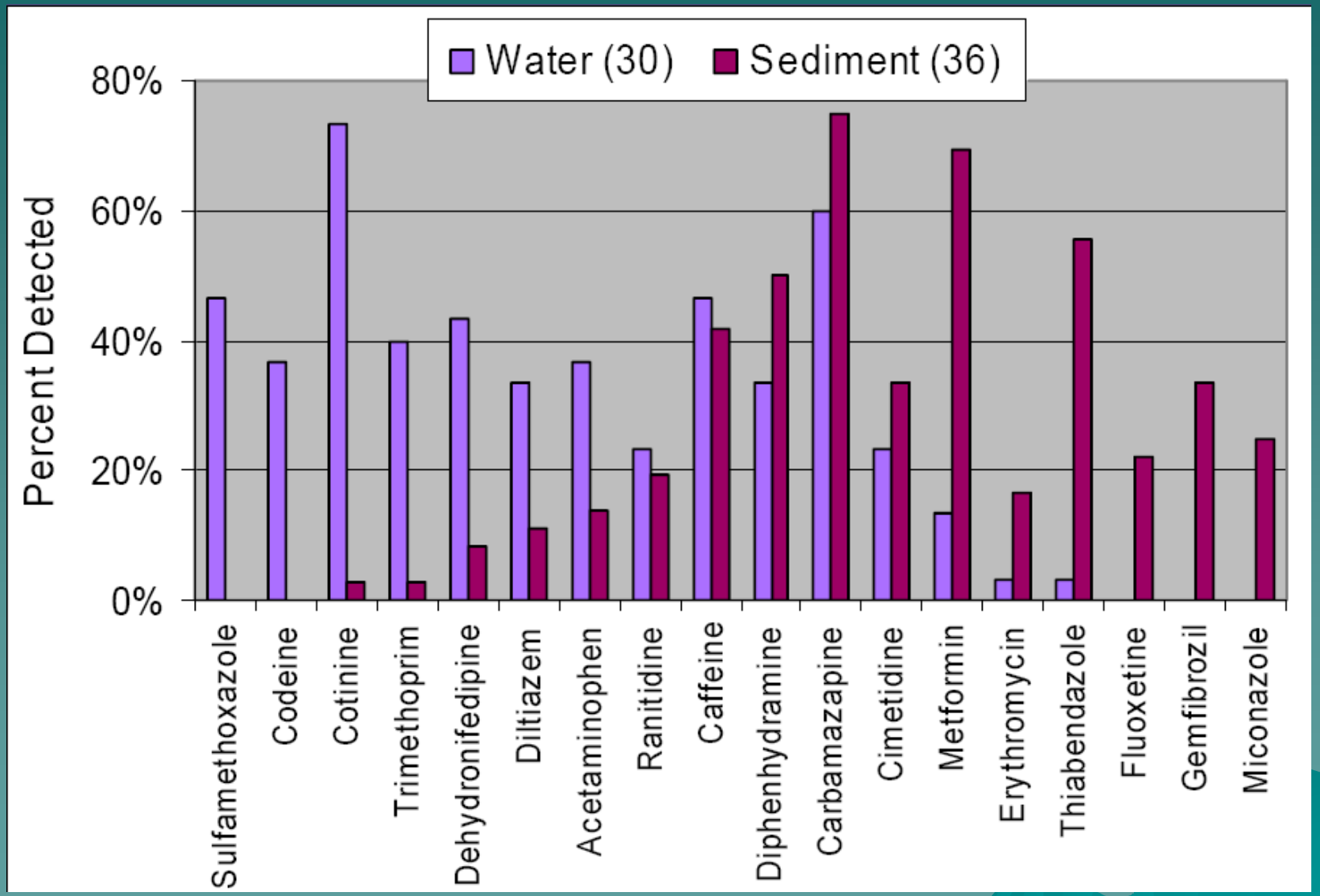
PPCP/EMC

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

Schultz and Furlong . Transport and Fate of Antidepressant Pharmaceuticals in Municipal Wastewater and Receiving Waters. 2006 SETAC Platform Presentation

Boulder Creek

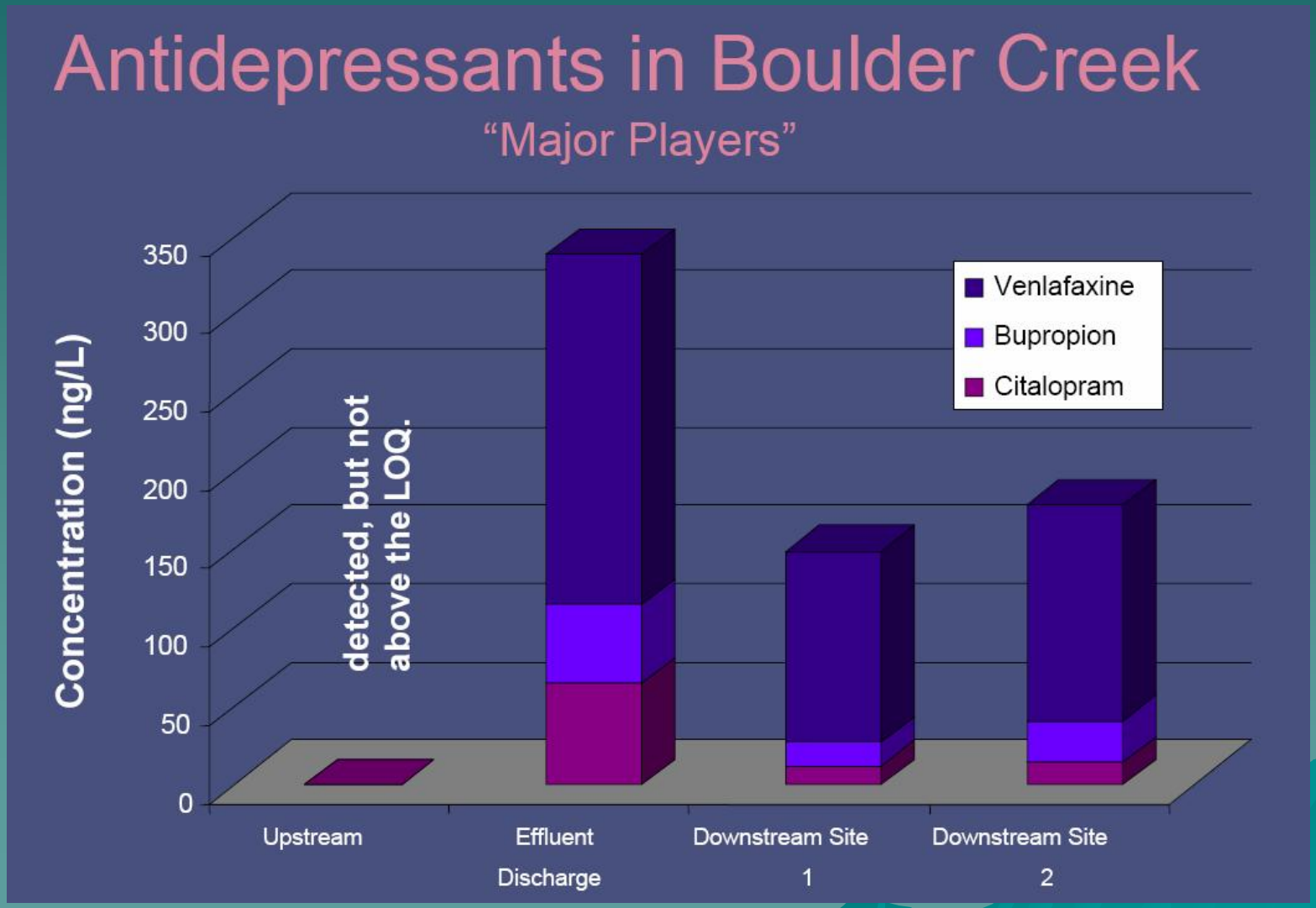
USGS Work in Boulder Creek, Boulder Creek, CO



http://www.state.nj.us/dep/wmm/Buxton%20Emerging%20Contaminants%20For%20Posting.pdf

Boulder Creek

USGS Work in Boulder Creek, Boulder Creek, CO



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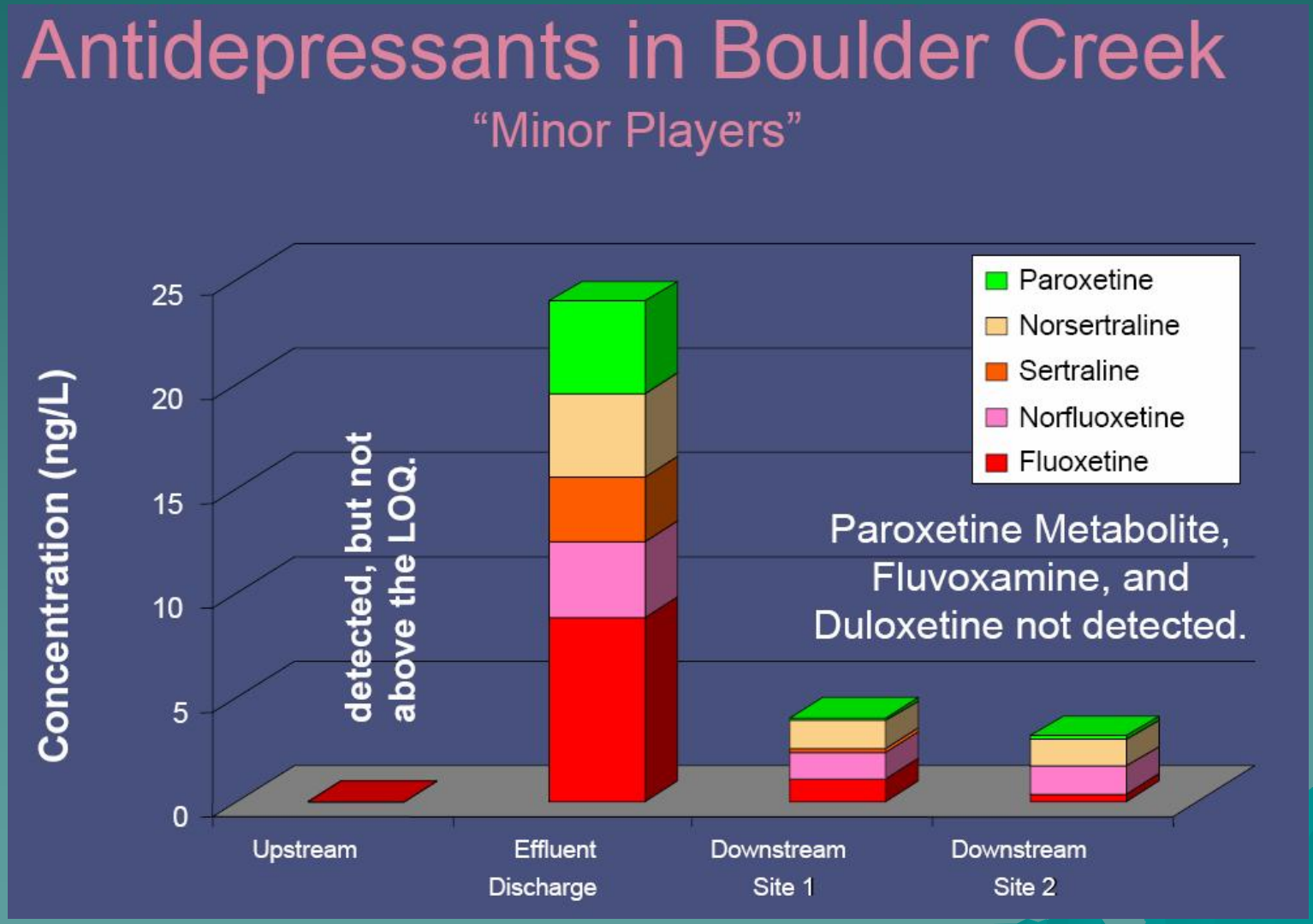

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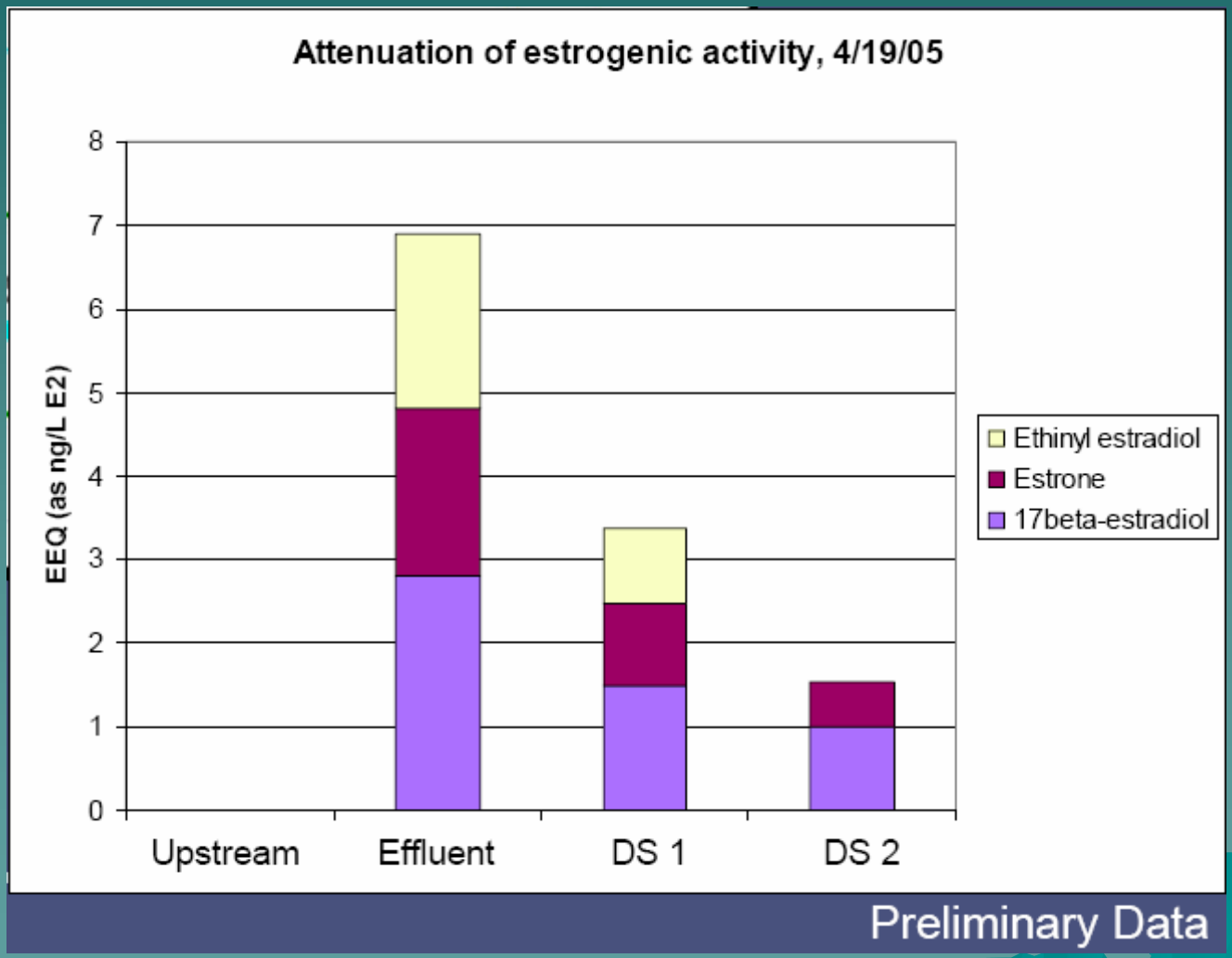

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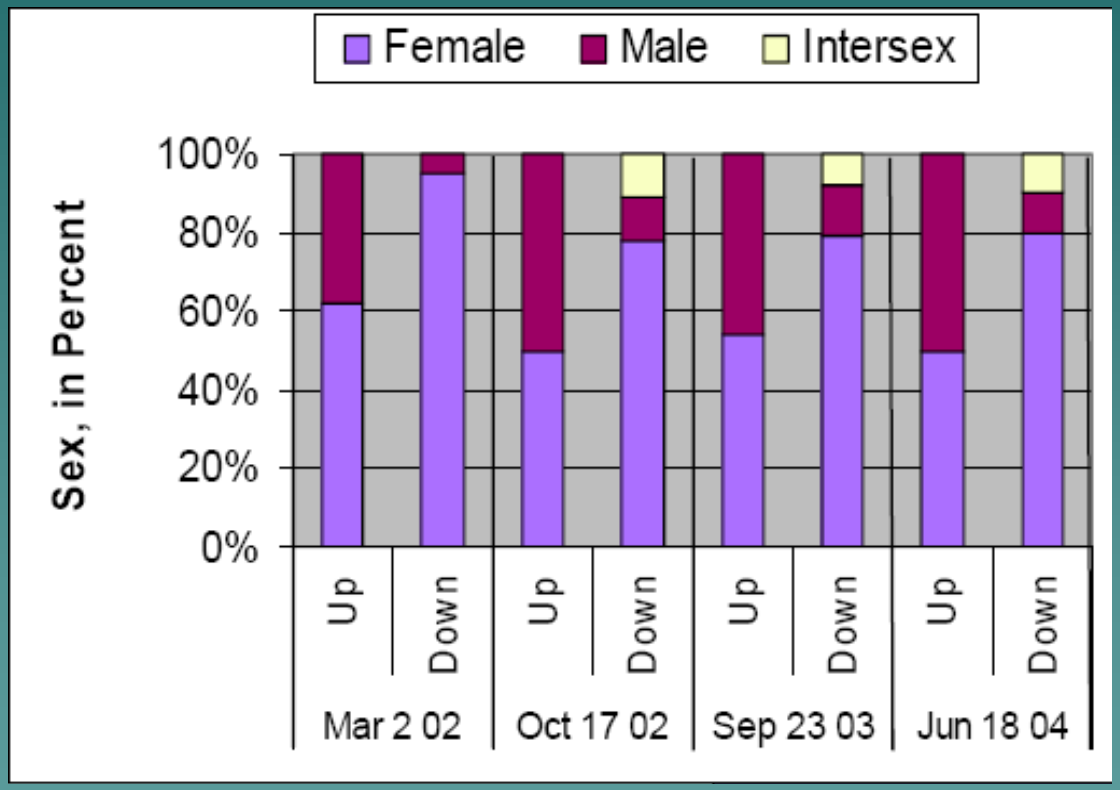

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Endocrine Modulating Chemicals

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

Endocrine Modulating Chemicals

Modulating is a better descriptor than Disrupting

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

Natural and Synthetic Hormone EMCs

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

Natural and Synthetic Hormone EMCs

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

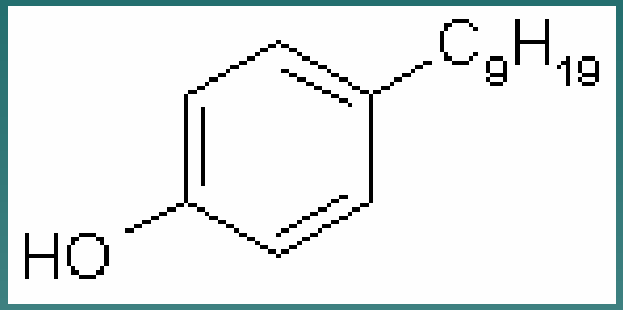
Industrial EMCs

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

Nonylphenols

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

Nonylphenols



- **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
- Cyalothrin
- 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
- Vinclozolin
- Zineb
- Ziram

EMCs

- 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

Chapman, P. 2006. Editorial: Emerging Substances – Emerging Problems. ET&C 25:6, pp. 1445-1447.

Environmental Effects of EMCs

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

Chapman, P. 2006. Editorial: Emerging Substances – Emerging Problems. ET&C 25:6, pp. 1445-1447.

Environmental Effects of EMCs

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

Chapman, P. 2006. Editorial: Emerging Substances – Emerging Problems. ET&C 25:6, pp. 1445-1447.

Human Health Effects of EMCs

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

Chapman, P. 2006. Editorial: Emerging Substances – Emerging Problems. ET&C 25:6, pp. 1445-1447.

Nanoparticles

NanoMats

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

Nanoparticles

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

Nanoparticles

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

Gaining Perspective

- **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.

- **Highest Propensity for Adverse Effects**

  PBT – persistent, bioaccumulative toxicants

  - **Possess structural stability (long ½-life)**
  - **Lipophilic (bioaccumulative)**
  - **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

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

Substances of Greatest Concern

- **High Use Endocrine Disruptors**
  - **Some PPCPs;**
  - **Alkylphenols and alkylphenol ethoxylates;**
  - **Hormones/Steroids (feedlot operations)**
- **Persistent Bioaccumulative Compounds**
  - **Polybrominated diphenyl ethers and associated adulterants;**
  - **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

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

B/Labs Analytical Capability

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