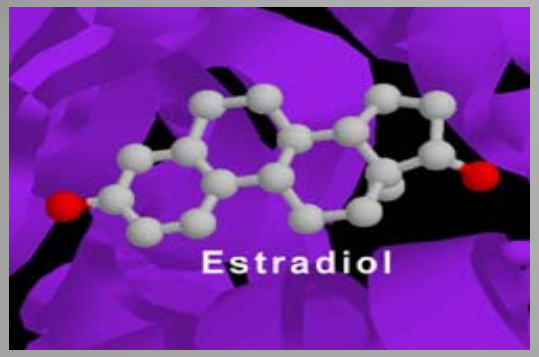
Emerging Contaminants: Ongoing Research and Future Regulatory Challenges

ORSANCO

Biological & Research Programs



Emerging Contaminants

- Pharmaceuticals & Personal Care Products (PPCPs)
- Hormones and Sterols
- Perfluorinated Compounds

Research Committee 2002

- ECs identified as a top research priority
  - Eventually, the Commission will have to make regulatory decisions regarding ECs
  - Don't want to be in the position of being asked what we are doing……and say "*nothing*".
    - Be proactive

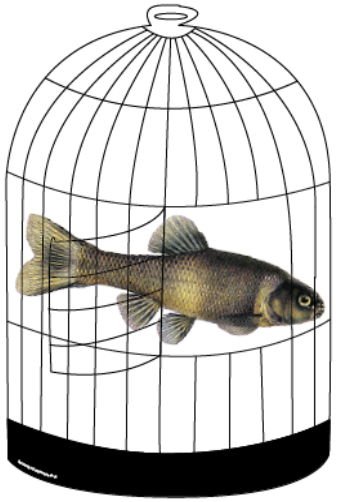
A Few Key Points

- To date, no evidence has been found of human health effects.

- However, scientists are concerned over the lack of fetal exposure studies and studies involving possible effects of complex mixtures and long-term exposure.

A Few Key Points

- <u>Effects on aquatic life is the primary concern</u>
  - Risks for aquatic organisms much greater than humans
    - Continuous exposure
    - Exposure to higher concentration in waste streams from many different sources
    - Possible low dose effects
      - Intersex – classic example
      - Other reproductive effects and anomalies
      - Neurobehavioral
      - Nest guarding
      - Homing during migration (salmon)



Fish replace the canary

ORSANCO's Research Strategy

- Do we find ECs in the Ohio River?
- Are fish and other aquatic organisms showing effects possibly caused by exposure to ECs?
- If YES…
  - Develop a strategy for testing fish health indicators and develop a routine monitoring strategy.

Phase 1

- 2005
  - Document presence of ECs
  - Look for possible fish health effects

Study Design 2005

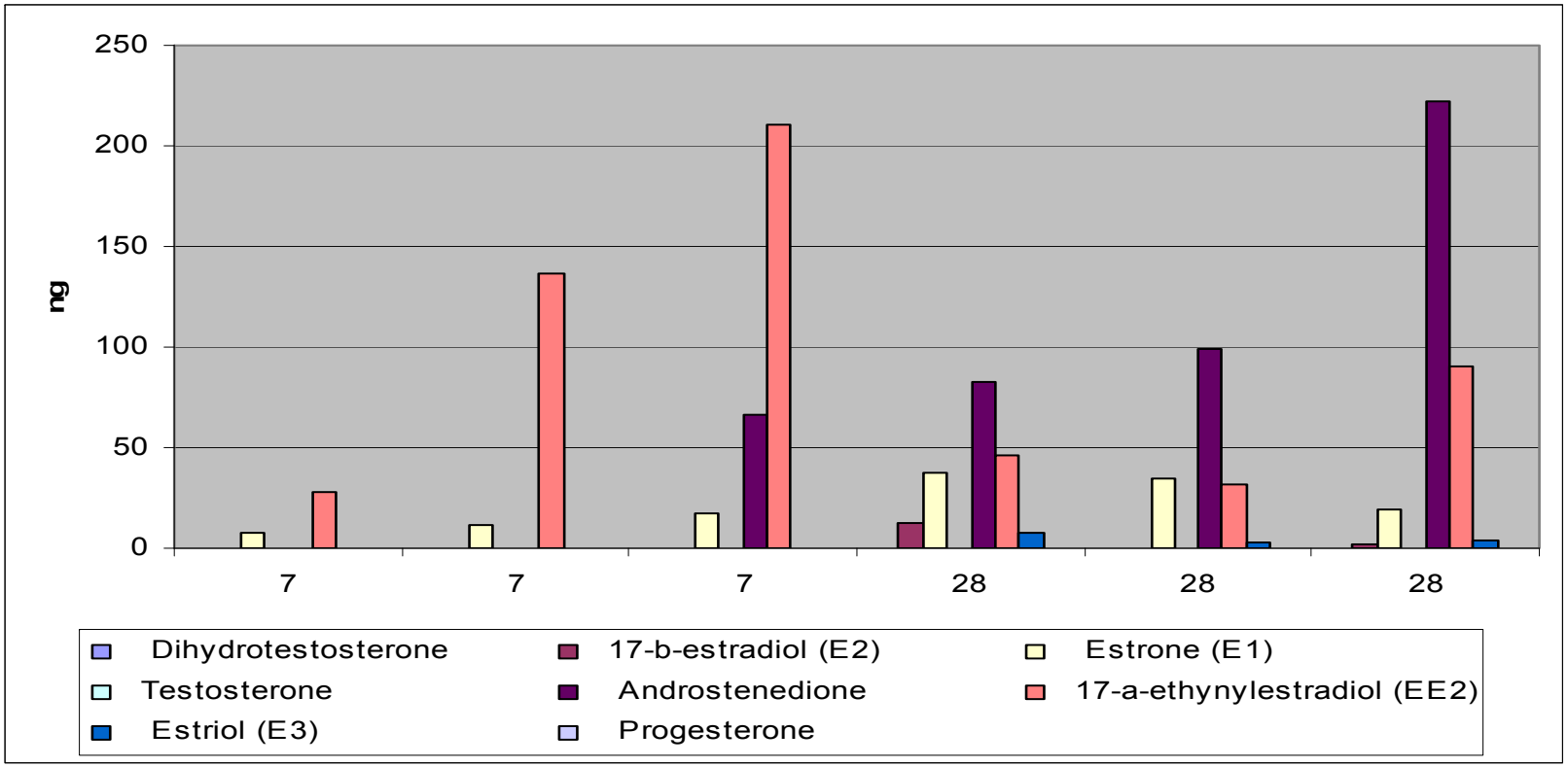
- Collect Grab Samples – Effluent
  - Chemistry
  - In-lab **Vitellogenin** (Vg) gene analysis
    - Vg is an egg yolk precursor protein expressed only in female fish and is normally dormant in male fish.
- Deployments
  - Vg – Caged (♂) Fathead Minnows (*Pimephales promelas)*
  - POCIS/SPMD
- Indigenous Fish
  - Vg
  - Histopathology

Detecting EDCs in the Water Column 2005

- Round 1
  - 5 hormones at upstream reference site
    - Vandalism!
    - No outfall data
- Round 2
  - 2 hormones found
    - Reference and outfall locations
    - Outfall levels only slightly higher
- Results were highly variable and largely insignificant

Detecting EDCs in the Water Column

Wheeling Reference – July 2005
POCIS



Phase 1 – Results

- Hormones found
  - In effluent mixing zones
  - At upstream reference locations
- Fish showed possible signs of health effects
  - No Intersex found!!

Vtg Results Summary

- Laboratory assay using effluent grab sample did not cause gene expression.
- Caged fish results
  - Higher gene expression rates in one of the downstream samples
  - Overall results too variable

Linking EDCs to Adverse Biological Effects

- Fish collected using boat-mounted electrofishing.
- 355 individuals collected (244 submitted)
  - Round 1
    - 35 males (27 with anomalies)
  - Round 2
    - 142 males (108 with anomalies)
    - 67 females (56 with anomalies)
- Livers and gonads removed

Histopath Results

- No intersex found!!
- Other indications that may be due to exposure to EDCs.
  - Ripe males found at the wrong time of the year
  - Increase in spermatagonia
  - Many types of degenerative conditions noted
- Timing Issue?
  - Increase in hybrids due to breakdown in timing isolation mechanism?

Problems Encountered

- $$ – Research isn't cheap
- Sampling platform/logistics
- Vandalism
- Gender identification – difficult
- Gonad identification – difficult
- 'Noisy' results
  - EDCs are much more than PPCPs
  - Complex mixtures

Phase 2

- Quantifying Compounds
  Adding a Spatial Component

Phase 2 – Ongoing

- A more comprehensive look at the occurrence of Emerging Contaminants within the mainstem Ohio River
  - 22 Locations
    - Longitudinal spread
    - Range of potential for occurrence
      - POTW mixing zones
      - Tributaries
      - 'Background' areas
  - 121 Pharmaceutical and Personal Care Compounds
  - Hormones & Sterols
  - Nonylphenol (+)
  - Perfluorinated Compounds (PFCs)
  - Optical Brighteners

Phase 2 – Sampling Locations (22)

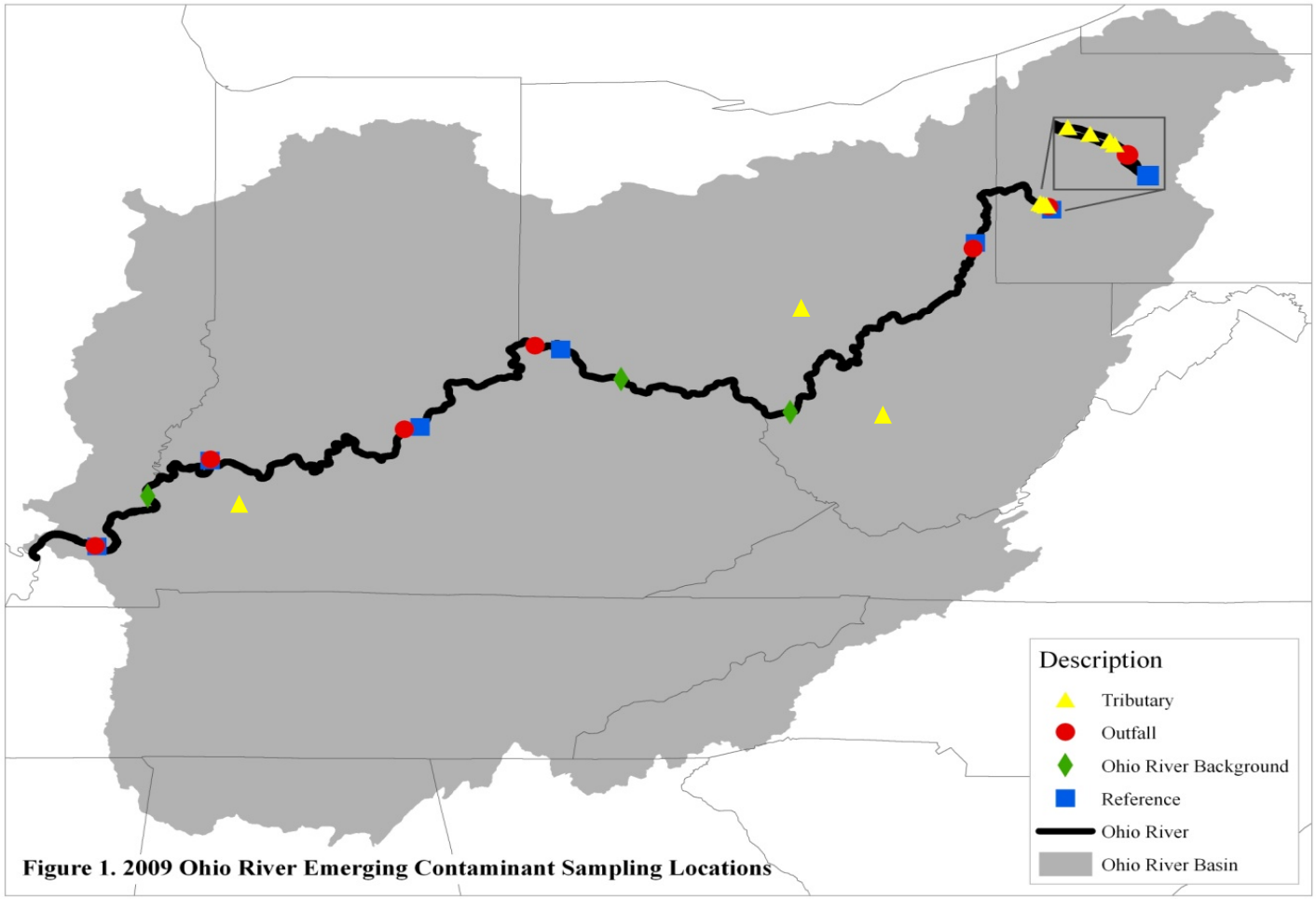


Figure 1. 2009 Ohio River Emerging Contaminant Sampling Locations

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Phase 2 – Objectives

- Document occurrence of ECs within the mainstem Ohio River

- Identify areas of the river with a greater risk potential (to aquatic organisms)
  - Number of contaminants present
  - Levels observed
  - Single chemical 'WERF ranking' (ongoing project)
    - Prioritizing Trace Organic Compounds

Phase 2 – "Partners"

- USEPA NERL – Cincinnati
  - APEOs – NPEOs – Optical Brighteners – PFCs
  - Researchers are national/international experts in the EC field
- AXYS Analytical
  - Developed PPCP methods for EPA (1694; 1698)
- Waters
  - Demonstrating new analytical capabilities
    - 20ml –vs– 2L

Phase 2 – Sampling

Phase 2 – Contaminants 158 Compounds

PPCP-B-POS
Albuterol
Amphetamine
Atenolol
Atorvastatin
Cimetidine
Clonidine
Codeine
Cotinine
Enalapril
Hydrocodone
Metformin
Oxycodone
Ranitidine
Triamterene

PPCP-A-NEG
2-Hydroxy-ibuprofen
Bisphenol A
Furosemide
Gemfibrozil
Glipizide
Glyburide
Hydrochlorothiazide
Ibuprofen
Naproxen
Triclocarban
Triclosan
Warfarin

Phase 2 – Contaminants

PFCs
PFBA
PFBS
PFDA
PFDoA
PFHpA
PFHxA
PFHxS
PFNA
PFOA
PFOS
PFOSA
PFPeA
PFUnA

PPCP-TCYC
4-Epianhydrochlortetracycline [EACTC]
4-Epianhydrotetracycline [EATC]
4-Epichlortetracycline [ECTC]
4-Epioxytetracycline [EOTC]
4-Epitetracycline [ETC]
Anhydrochlortetracycline [ACTC]
Anhydrotetracycline [ATC]
Chlortetracycline [CTC]
Demeclocycline
Doxycycline
Isochlortetracycline [ICTC]
Minocycline
Oxytetracyclin [OTC]
Tetracycline [TC]

Phase 2 – Contaminants

Hormones
17 alpha-Dihydroequilin
17 alpha-Estradiol
17 alpha-Ethinyl-Estradiol
17 beta-Estradiol
Androstenedione
Androsterone
beta-Estradiol 3-benzoate
Desogestrel
Equilenin
Equilin
Estriol
Estrone
Mestranol
Norethindrone
Norgestrel
Progesterone
Testosterone

Sterols
beta Stigmastanol
beta-Sitosterol
Campesterol
Cholestanol
Cholesterol
Coprostanol
Desmosterol
Epicoprostanol
Ergosterol
Stigmasterol

Phase 2 – Contaminants

PPCP-A-POS

PPCP-A-POS
1,7-Dimethylxanthine
Acetaminophen
Azithromycin
Caffeine
Carbadox
Carbamazepine
Cefotaxime
Ciprofloxacin
Clarithromycin
Clinafloxacin
Cloxacillin
Dehydronifedipine
Digoxigenin
Digoxin
Diltiazem
Diphenhydramine
Enrofloxacin
Erythromycin-H2O
Flumequine
Fluoxetine
Lincomycin
Lomefloxacin
Miconazole
Norfloxacin
Norgestimate
Ofloxacin
Ormetoprim
Oxacillin
Oxolinic Acid
Penicillin G
Penicillin V
Roxithromycin
Sarafloxacin
Sulfachloropyridazine
Sulfadiazine
Sulfadimethoxine
Sulfamerazine
Sulfamethazine
Sulfamethizole
Sulfamethoxazole
Sulfanilamide
Sulfathiazole
Thiabendazole
Trimethoprim
Tylosin
Virginiamycin

Phase 2 – Contaminants

PPCP – A-POS-Ex

PPCP-A-POS-Ex
10-hydroxy-amitriptyline
Alprazolam
Amitriptyline
Amlodipine
Benzoylecgonine
Benztropine
Betamethasone
Cocaine
DEET
Desmethyldiltiazem
Diazepam
Fluocinonide
Fluticasone propionate
Hydrocortisone
Meprobamate
Methylprednisolone
Metoprolol
Norfluoxetine
Norverapamil
Paroxetine
Prednisolone
Prednisone
Promethazine
Propoxyphene
Propranolol
Sertraline
Simvastatin
Theophylline
Trenbolone
Trenbolone acetate
Valsartan
Verapamil

Project Status

Results

- Data undergoing internal and external (EPA) QA/QC check
  - Over 7300 pages of QA documentation
- Expected data 'release' – April 2010
- These data only represent a 'snapshot' of EC occurrence
- ORSANCO committees will review/discuss and make recommendations to the Technical Committee

Direction of Future Research

- Phase 3

Phase 3 – Overview

- Use Phase 2 results to identify a 'gradient of (EC) condition'
  - Areas with differing potential for showing biological response
    - Occurrence of ECs
      - Type
      - Concentration
      - *Risk Potential* – ongoing WERF Research Project
- Test various candidate measures of *Fish Health* along the gradient identified
  - Currently seeking *Funding*

Future Challenges

- Budgetary
- Standardization
- Baseline
- Communication

Budgetary Constraint$

- 2009 Study
  - 25 Sites @ $3,120/site (+) shipping
    - $84,000

Standardization

- No EPA approved methods
  - Makes some folks ‘uneasy’
  - EPA *draft* methods are available
    - We used the lab that developed the draft methods

Baseline Information

- New Science
- Few studies available to compare results to and put results into context
  - WERF and others helping to rapidly fill gaps

Communication

- Concept of '*relative risk*' not clear to the general public.
- Emerging Contaminants can be over sensationalized at times.

" Tap water contaminant 'castrates' frogs "

Questions?