Emerging Environmental Contaminants: What’s New

Susan D. Richardson

U.S. Environmental Protection Agency, National Exposure Research Laboratory, Athens, GA
Emerging Contaminants

- Perfluorinated Chemicals (e.g., PFOA and PFOS)
- Pharmaceuticals
- DBPs (including NDMA and nitrosamines)
- Pesticide reaction/degradation products
- Brominated flame retardants (PBDEs)
- Perchlorate
- Nanomaterials
- Sucralose (Splenda !)
- Algal toxins
- Benzotriazoles
- Dioxane
- Sunscreen chemicals (UV filters)
- Gasoline additives
- Naphthenic acids
- Hormones
- Pathogens
Most emerging contaminant research described in this presentation is from EPA's Office of Research & Development's four National Exposure Research Laboratories.
U.S. Contaminant Candidate List (CCL-3)

- More open process (public could submit contaminants)
- Input from EPA-ORD, National Academy of Science’s National Research Council, National Drinking Water Advisory Council, Science Advisory Board
- “Universe” of potential drinking water contaminants considered (7,500)
- Used model to narrow to 560 contaminants
- Used occurrence, toxicity, bioaccumulation, industrial production, and chemical properties to further narrow
- Originally: 11 Microbial contaminants; 95 chemical contaminants
  **Changed now to 12 microbials and 104 chemicals (as a result of SAB review and open comment process)**
- CCL-3 JUST FINALIZED Sept. 25, 2009!

CCL-3: www.epa.gov/safewater/ccl
Microbial Contaminants:

- Adenovirus
- Caliciviruses
- *Campylobacter jejuni*
- Enterovirus
- *Escherichia coli* (O157)
- *Helicobacter pylori*
- Hepatitis A virus
- *Legionella pneumophila*
- *Mycobacterium avium*
- *Naegleria fowleri*
- *Salmonella enterica*
- *Shigella sonnei*
Chemical Contaminants:

- Pesticides & pesticide degradates (e.g., acetochlor ethanesulfonic acid)
- DBPs (5 nitrosamines, formaldehyde, acetaldehyde, benzyl chloride, chlorate, bromochloromethane)
- Industrial chemicals (e.g., solvents and other chemicals)
- Consumer product chemicals (e.g., urethane)
- Food additives (e.g., butylated hydroxy anisole)
- Gasoline additives (e.g., MTBE)
- Explosives (e.g., RDX)
- Inorganics (e.g., cobalt, molybdenum, tellurium, vanadium)
- Algal toxins (anatoxin-a, cylindrospermopsin, microcystin-LR)
- PFOA and PFOS
- Pharmaceuticals and hormones

CCL-3: www.epa.gov/safewater/ccl
Unregulated Contaminants Monitoring Rule (UCMR-2)

- Allows EPA to collect data for unregulated contaminants suspected to be present in drinking water, but that do not have health-based standards under the Safe Drinking Water Act
- Monitors for no more than 30 contaminants every 5 yrs
- All large water treatment plants and a subset of smaller ones monitored
- UCMR-1 (2001-2005): 28 contaminants on list

www.epa.gov/safewater/ucmr/ucmr2
Unregulated Contaminants Monitoring Rule (UCMR-2)

Assessment Monitoring List 1 (common analytical methods)
All plants serving >10,000 people; subset of other plants
• Dimethoate (OP pesticide)
• Terbufos sulfone (OP pesticide degrade)
• 5 Brominated flame retardants (BDE-47, BDE-99, HBB, BFE-153, BDE-100)
• 3 Explosives (1,3-nitrobenzene, TNT, RDX)

Screening Survey List 2 (specialized analytical methods)
All plants serving >100,000 people; subset of other plants
• 3 Parent acetanilide herbicides (acetochlor, alachlor, metolachlor)
• 6 Acetanilide degradates
• 6 Nitrosamines

www.epa.gov/safewater/ucmr/ucmr2
Ambient water quality criteria are levels of individual pollutants, water quality characteristics, or descriptions of conditions of a water body that, if met, should protect the designated use(s) of the water.

Examples: swimming, drinking water, fishing, fish spawning, and navigation

CMC: Criterion maximum concentration (protects against severe acute effects)

CCC: Criterion continuous concentration (protects against longer term effects on survival, growth, and reproduction)
New Water Quality Criteria Under Development

- WQ criteria will set standards for emerging contaminants
- Starting with pharmaceuticals and personal care products
- EE2 -> Trenbolone -> Triclosan
  - These have different modes of action

The Plan:
- Develop this new Water Quality Criteria
- Get states to adopt criteria
- Criteria would be implemented through National Pollutant Discharge Elimination System (NPDES) permits given
PFOS/PFOA

PFOS:
Perfluorooctanesulfonate

PFOA:
Perfluorooctanoic acid

- Used to make soil-, stain-, grease-, and water-resistant coatings that are widely applied to fabrics, carpets, cookware, paper (microwave popcorn bags)
- Persistent, bioaccumulative, toxic (including developmental), ubiquitous contaminant
- PFOA and PFOS now on new CCL-3
- PFOS not manufactured anymore; environmental levels decreasing
- Eight manufacturers to phase out PFOA by 2010

CCL-3: www.epa.gov/safewater/ccl
Ever wonder why grease doesn’t come through paper wrapper?
PFOA

Questions and Concerns

• Why is it in the bloodstream of almost everyone measured?
• Where is it coming from? How is it transported?
• Why is found in biota in the Arctic?
  (Up to 3112 ng/g in polar bears from Arctic—can be at greater levels than PCBs)

Hypothesis: telomer alcohols volatile, transported, oxidized to acid in atmosphere and in the body (Henderson & Smith, *Toxicol. Sci.* 2007, 95(2), 452).

Current work:
- exploring microbial degradation of fluorotelomer polymers
- investigating sources & sinks for PFOA (including sorption)
- large worldwide occurrence study in soils
- investigating source from sewage sludge used as soil improver
- measuring PFCs in fish
PFOA

- Most measurements use LC/ESI-MS/MS or GC/MS/MS
- Can be tricky getting clean backgrounds
Method 537. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

Version 1.0
September 2008

J.A. Shoemaker
US EPA, Office of Research and Development, National Exposure Research Laboratory

P.E. Grimmett
US EPA, Office of Research and Development, National Exposure Research Laboratory

B.K. Boutin
The National Council on Aging, Senior Environmental Employment Program

Available at: www.epa.gov/nerlcwww/ordmeth.htm
Testing prompted by an Associated Press story that revealed trace amounts of pharmaceuticals in drinking water supplies has shown that more Americans are affected by the problem than previously thought — at least 46 million. That's up from 41 million people reported by the AP in March as part of an investigation into the presence of pharmaceuticals in the nation's waterways.
New EPA Method 1694

Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS

December 2007

Available at: www.epa.gov/waterscience/methods/method/files/1694.pdf
Pharmaceuticals

Just included on the CCL-3; will also be included in new Water Quality Criteria

- Potential estrogenic effects on biota
  (e.g., feminization of fish)
- Potential antibiotic resistance
- May affect aquatic organism populations
  (decreased food sources)
- Transformation in drinking water treatment

Recent work:
- Tracing the source of macrolide antibiotics and illicit drugs into the Colorado River Basin (Tammy Jones-Lepp)
- Drinking water: measuring 35 pharmaceuticals and other emerging contaminants in waters from 9 states (so far, levels not a risk for human health effects) (Susan Glassmeyer & USGS researchers)
- Spiking ethinylestradiol in lake in Canada (Jim Lazorchak with researchers from Fisheries and Oceans Canada) (Karen Kidd, Blanchfield, Mills, Palace, Evans)
Lake Havasu, Arizona/California

Slide courtesy of Tammy Jones-Lepp, U.S. EPA, Las Vegas, NV and Doyle Wilson, City of Lake Havasu, AZ

- Colorado River
- North Regional WWTP
- Production Wells Outside Water Service Area
- Monitoring Wells
- Vadose Injection Well Field City Limit
- Lake Havasu
- White Pocket
- Thompson Bay
- Mulberry WWTP
- Island WWTP
- WT
- HCW

WW effluent injected into subsurface
Can migrate to lake
Injected effluent will be recovered for irrigation and possibly domestic use
Emerging Contaminants Analyzed in this Study

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<thead>
<tr>
<th>Pharmaceuticals</th>
<th>EDCs</th>
<th>Steroids</th>
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<td>Atorvastatin</td>
<td>Iopromide</td>
<td>Benzophenone</td>
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<td>Azithromycin</td>
<td>Meprobamate</td>
<td>BHA</td>
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<td>Caffeine</td>
<td>Methamphetamine</td>
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<td>Carbamazepine</td>
<td>MDMA</td>
<td>DEET</td>
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<td>Clarithromycin</td>
<td>Naproxen</td>
<td>Musk ketone</td>
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<td>Primidone</td>
<td>Octylphenol</td>
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<td>Roxithromycin</td>
<td>TCPP</td>
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<tr>
<td>Dilantin</td>
<td>Sulfamethoxazole</td>
<td>Other</td>
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<tr>
<td>Fluoxetine</td>
<td>Triclosan</td>
<td>Estradiol</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>Trimethoprim</td>
<td>Estrone</td>
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<tr>
<td></td>
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<td>Estrinylestradiol</td>
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Other

- Urobilin
- n,n-DMPEA

Slide courtesy of Tammy Jones-Lepp, U.S. EPA, Las Vegas, NV and Doyle Wilson, City of Lake Havasu, AZ
# Horizontal Collector Well and Treated Water Results

<table>
<thead>
<tr>
<th>Compound (ng/l)</th>
<th>HCW</th>
<th>Treated</th>
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<td>Carbamazepine</td>
<td>18.8</td>
<td>14.8</td>
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<td>Dilantin</td>
<td>4.8</td>
<td>4.5</td>
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<td>Meprobamate</td>
<td>1.9</td>
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<td>Primidone</td>
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<td>Sulfamethoxazole</td>
<td>21.5</td>
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**HCW Raw Water**

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<td>May 2008</td>
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<td>August 2008</td>
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**Finished Treated Water**

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*Slide courtesy of Tammy Jones-Lepp, U.S. EPA, Las Vegas, NV and Doyle Wilson, City of Lake Havasu, AZ*
Emerging Contaminants What are They? Or a Paradigm Shift?

An Example of a Whole Lake Ethynylestradiol Dosing Experiment at Canada’s Experimental Lake Area

Jim Lazorchak, U.S. EPA, NERL, Cincinnati, OH

Summary - Fathead Minnow

• Spring 2001 - EE2 additions began
  - Vg gene expression induction in deployed 114 fish in 260 in 24-hrs
    – significant vitellogenin plasma induction after 7 weeks
• Fall 2001 (4 months)
  – proteinaceous accumulation in kidney
  – liver cell size increased
• Spring 2002 (12 months)
  – disorganized testes, immature ovaries
  – decreased spawning aggression, fewer & less-developed eggs
  – reduction in secondary sex characteristics
  – No fish population impacts observed
• Fall 2002 (17 months) - reproductive failure, few age 0 fish
• Spring 2003 (2 years) - only age 2 fish remaining
  – one male found, females with large ovipositors
• 2006 (3 yrs post additions) – Fathead population recovered
Pearl Dace Sex Ratio

K Mills – FW Inst

Year

1999 2000 2001 2002 2003 2004 2005

Male : Female Ratio

0.0 0.2 0.4 0.6 0.8 1.0 1.2

donning started
Formation of 12 iopromide transformation products (TP) detection via HPLC/UV

Slide courtesy of Thomas Ternes, Federal Inst. Hydrology, Koblenz, Germany
Potential aerobic degradation pathway of Iopromide

Reaction products identified using LC/MS/MS and NMR

Source: Schulz et al., ES&T 2009.

Slide courtesy of Thomas Ternes, Federal Inst. Hydrology, Koblenz, Germany
Drinking Water DBPs

• Formed by the reaction of disinfectants with natural organic matter

Concern over possible human health risk:

• Epidemiologic studies: risk of bladder cancer
  some cause cancer in laboratory animals

• Recent concerns about possible reproductive & developmental effects (from epi studies)

• Huge movement toward alternative disinfectants
• Use of UV and membranes increasing dramatically
• By 2025, 70% of drinking water plants expected to use membranes
## DBPs Regulated by the U.S. EPA

<table>
<thead>
<tr>
<th>DBP</th>
<th>MCL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total THMs</td>
<td>80</td>
</tr>
<tr>
<td>5 Haloacetic acids</td>
<td>60</td>
</tr>
<tr>
<td>Bromate</td>
<td>10</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1000</td>
</tr>
</tbody>
</table>

But more than 600 DBPs have been identified

Little known about occurrence & toxicity of unregulated DBPs
Emerging DBPs

- **Halonitromethanes** (up to 3 ppb; highly genotoxic); new *in vivo* effects; increased with *preozonation*

- **Iodo-THMs and Iodo-Acids** (iodo-THMs up to 15 ppb; iodo-acids up to 1.7 ppb; both classes highly cytotoxic or genotoxic); increased with *chloramination*
  
  Richardson et al., *ES&T*, 2008, 42, 8330.

- **Haloamides** (up to 14 ppb; highly genotoxic) may be increased with *chloramination*

- **Halofuranones** (up to 2.4 ppb for total MX analogues; genotoxic, carcinogenic); *chloramination* can also form

- **Haloacetonitriles** (up to 41 ppb; ~10% of THM4; genotoxic, cytotoxic); may be increased with *chloramination*

- **Nitrosamines** (up to 180 ppt; probable human carcinogens); increased with *chloramination*
  
  EPA Method 521: [www.epa.gov/nerlcwww/m_521.pdf](http://www.epa.gov/nerlcwww/m_521.pdf)
Genotoxicity of Iodoacetic acid


IA also caused developmental effects in mouse embryos (Hunter et al., 1995)

New iodo-acid/iodo-THM occurrence study published: Richardson et al., *ES&T*, 2008, 42, 8330. Also reports genotoxicity & cytotoxicity of other iodo-acids and iodo-THMs
Emerging DBPs

- EPA Method 521 for nitrosamines (GC/MS/MS); sub-ng/L detection
- NDMA and other nitrosamines on CCL-3 and UCMR-2
Iodinated X-ray Contrast Media (ICM)

- **Iopamidol**
- **Iopromide**
- **Iohexol**

![Image of X-ray contrast media](image_url)
Iodinated X-Ray Contrast Media Transformation by Chlorine and Chloramines

Iopamidol

GC/EI-MS and GC/NCI-MS used to measure iodo-THMs and iodo-acids
LC/ESI-MS/MS used to measure disappearance of iopamidol
## Iodo-DBP Occurrence Study

<table>
<thead>
<tr>
<th>Plant</th>
<th>Iodide (µg/L)</th>
<th>Sum iodo-acids (µg/L)</th>
<th>Sum iodo-THMs (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant 2</td>
<td>1.0</td>
<td>0.37</td>
<td>4.9</td>
</tr>
<tr>
<td>Plant 4</td>
<td>ND</td>
<td>0.10</td>
<td>1.2</td>
</tr>
<tr>
<td>Plant 11</td>
<td>1.5</td>
<td>0.21</td>
<td>2.3</td>
</tr>
<tr>
<td>Plant 15</td>
<td>ND</td>
<td>0.17</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Detection limit = 0.13 µg/L

Typically, DBPs formed by reaction of disinfectants with NOM and Br/I.
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What about other sources of iodine?
ICM concentrations: rivers, creeks and ground water

## ICM in U.S. Drinking Water Sources (ng/L)

<table>
<thead>
<tr>
<th>Plant</th>
<th>lopamidol</th>
<th>lomeprol</th>
<th>lopromide</th>
<th>lohexol</th>
<th>Diatrizoate</th>
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<tbody>
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<td>ND</td>
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<tr>
<td>Plant 2</td>
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<td>120</td>
<td>93</td>
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<tr>
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<td>ND</td>
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<td>Plant 19</td>
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</table>

Courtesy of Thomas Ternes, Federal Institute of Hydrology, Germany
ICM measured using LC/ESI-MS/MS; DLs = 5-20 ng/L
ICM in U.S. Drinking Water Sources (ng/L)

<table>
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<tr>
<th>Plant</th>
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</table>

Courtesy of Thomas Ternes, Federal Institute of Hydrology, Germany
ICM measured using LC/ESI-MS/MS; DLs = 5-20 ng/L
Pesticide Degradation Products

- May be more environmentally relevant than parent species (and some more toxic than parent)
- Previously overlooked
- Most highly polar; require LC/MS or LC/MS/MS
- Some on the CCL-3:
  - Alachlor ESA & OA
  - Acetochlor ESA & OA
  - Metolachlor ESA & OA

CCL-3: www.epa.gov/safewater/ccl
Perchlorate (ClO$_4^-$)

- On CCL-3
- Contaminant in groundwater, surface water, foods, milk
- Used in solid rocket propellants (rockets, missiles, fireworks); some natural sources (e.g., nitrate)
- Originally found in U.S.
  **now found in many countries
  Present in almost all 350 food and beverage products measured from >50 countries
- Accumulates in plants
- Perchlorate affects thyroid function—which affects normal metabolism, growth, development

CCL-3: www.epa.gov/safewater/ccl
Perchlorate ($\text{ClO}_4^-$)

Recent EPA Methods

- Developed to overcome matrix interferences in high ionic strength waters and to lower detection limits
- EPA Method 314.0: IC-conductivity (MRL 4 µg/L)
- EPA Method 330.0: IC/ESI-MS (MRL 0.02-0.05 µg/L)
- EPA Method 331.0: LC/ESI-MS/MS (MRL 0.02 µg/L)

www.epa.gov/safewater/methods/sourcalt.html
www.epa.gov/nerlcwww/ordmethod.htm

CCL-3: www.epa.gov/safewater/ccl
Polybrominated diphenyl ethers (PBDEs)  
Flame Retardants

on the UCMR-2

www.epa.gov/ogwdw/ucmr

- Found in human samples—worldwide
- Potential adverse developmental effects, cancer
- Global production: 200,000 metric tons (most used in U.S. and Canada)
- Added to plastics, textiles, particularly furniture, consumer electronics
- Environmentally persistent; ubiquitous
- Octa- and penta- phased out in North America in 2004, but deca- still made
- EPA Method 527 (GC/MS; mid-ng/L detection limits)
  www.epa.gov/safewater/methods/analyticalmethods_ogwdw.html
- New method developed at EPA-RTP to measure 9 BDE congeners in dust samples (ASE-SPE cleanup-GC/NCI-MS; Maribel Colon, Walt Weathers et al.)
Algal Toxins

- **Included on the new CCL-3**
  
  (microcystin-LR, anatoxin-a, cylindrospermopsin)

- **EU**: guideline (0.1 µg/L)

- **WHO**: provisional guideline (1.0 µg/L)
  
  for microcystin-LR

- Responsible for large fish kills, poisoning of shellfish, illness in people

**Examples:**

- Microcystins, nodularins, saxitoxins, anatoxins, brevetoxins

- Some found in finished drinking water from Florida (2003)

**CCL-3**: [www.epa.gov/safewater/ccl](http://www.epa.gov/safewater/ccl)
Nanomaterials

• Big new area for research

• New initiative at U.S. EPA to study occurrence, fate, and health effects

• 1-100 nm in size; unique properties

• Examples: Fullerenes (C$_{60}$), zero-valent iron, TiO$_2$, nano-silver, functionalized fullerenes (in hollow spheres, ellipsoids, tubes), quantum dots, metal oxanes

• Already used in many consumer products (cosmetics, sunscreens, clothing, paints, tires, tennis rackets, lubricants, electronics, soaps, shampoos, detergents; zero-valent iron used to remediate groundwater)

• Many more products under development (e.g., medical diagnostics, cancer treatment)
Development of Genomic Indicators of Nanoparticle Exposure in Invertebrates

Helen Poynton, James Lazorchak, Christopher Impellitteri, Joel Allen, Mark Smith, and Katherine Hammer

National Exposure Research Laboratory, National Risk Management Research Laboratory, The McConnell Group

Developing biomarkers of exposure for ZnO and Ag nanoparticles to *D. magna*

EPA-Athens looking at fate & transport of fullerenes
Characterization of Fullerenes with Asymmetric Flow Field-Flow Fractionation (AF4) and LC/APPI-MS

- Aqu/C\textsubscript{60} aggregate ranged in size from 80-260 nm
- Mass of C\textsubscript{60} determined in each fraction by LC/APPI-MS
- Mass balance of 77 ± 5.8 %
- Sizes corroborated by dynamic light scattering in batch mode and transmission electron microscopy
- Use of LC/MS important for specificity—to know which nanoparticles are being measured
Sucralose (Splenda)!

- Artificial sweetener; widely used
- Very stable (can bake with it)
- Large European study (120 samples from 27 countries)
- Up to 1 µg/L in river waters; extremely persistent
- Predominantly in samples from UK, Belgium, the Netherlands, France, Switzerland, Spain, Italy, Norway, Sweden
- SPE-LC/negative ion-ESI-MS/MS method used
- Potential for ecological effects not known
Sucralose (Splenda)!

- Now reported in the United States in marine and coastal waters:

- Up to 118 μg/L in wastewater effluents
  Up to 372 ng/L in Cape Fear River Estuary (NC)
  Up to 67 ng/L in Gulf Stream
  Up to 392 ng/L in Florida Keys

- Persistent in coastal/marine waters
- Deep water levels similar to surface levels
- Significant amount is not degraded microbially; oceanic currents may distribute globally
- GC/MS (with MSTFA derivatization) used
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