Emerging Contaminants: Organic Chemical Occurrences in Raw and Finished Drinking Water

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September 9, 2008

Emerging Contaminants

- Non-regulated chemicals, naturally occurring or synthetic, that have become recognized as occurring in water resources and may potentially pose a risk to human health or the environment
- Improvements in analytical methods has increased our ability to detect the occurrence of chemicals in very minute quantities.
- Very little is known about the health impact of these chemicals, but they are widespread, persistent in the environment and tend to bioaccumulate.
- Effects of a mixture of these chemicals unknown

Emerging Contaminants

- Over 30,000,000 organic and inorganic chemicals have been registered
- More than 5,000,000 in the last two years alone
- 13,000,000 are commercially available
  - Pharmaceuticals and Personal Care Products (PPCP)
  - Pesticides
  - Endocrine (hormonal) disrupting chemicals
  - Flame Retardants
  - Nanoparticles (widely distributed, many different uses, smaller than individual cells)
  - Prions – infectious proteins, in waste water, not inactivated by chlorine, cause fatal brain disease in animals/humans

Organic Chemicals in Drinking Water

- Pesticide occurrences
  - **USGS Open-File 01-456: Pesticides in Selected Water-Supply Reservoirs and Finished Water, 1999-2000**
  - **USGS Scientific Invest Rpt 2008-5027: Pesticide Occurrence and Distribution in the Lower Clackamas River Basin, Oregon, 2000-2005**
  - USGS Water-Resources Invest Rpt 97-4268: Distribution of Dissolved Pesticides…in the Willamette…Basin, 1996
  - USGS Water-Resources Invest Rpt 97-4082B: Quality of Shallow Groundwater in…the Willamette Basin, 1993-95
- Pharmaceuticals and Personal Care Products
  - **AWWA 2005 Webcast: Endocrine Disrupters, Pharmaceuticals and Personal Care Products**
  - **http://www.epa.gov/ppcp/**

Pesticides in Drinking Water

- Pilot project by USGS and EPA in 1999
- Samples collected of both raw and finished water prior to distribution system
- Focus was on surface water bodies
  - Primarily reservoirs
  - High vulnerability to pesticide activity in reservoir
- Tested for 178 pesticides (herbicides and insecticides)

Sample Site Characteristics

- States involved: CA, IN, OH, OK, LA, MO, SC, SD, NY, NC, PA, and TX
- Watershed Area: 3,300 to 784,000 mi^2
- Landuse: Usually Ag and Forest > Forest or Ag > Urban
- Ag generally mixture of pasture and row crop
- Treatment methods varied, e.g., in chemical additives and type of filtration
- Sampling quarterly, w/semi-weekly during high-use time of May to September

Occurrence Data

- Of 178 pesticides/degradation products, 108 were detected at least once in raw or finished water
- Occurrence data similar to that of the Willamette River and shallow groundwater studies
- Widely used herbicides, e.g., atrazine, simazine, etc., were most common: 36 to 96% of raw water samples; 19 to 96% of finished water
- Most common insecticides in raw water: Diazinon and chlorpyrofos at 35% and 5% of samples, respectively

Raw Water versus Finished Water (Conventional Treatment)

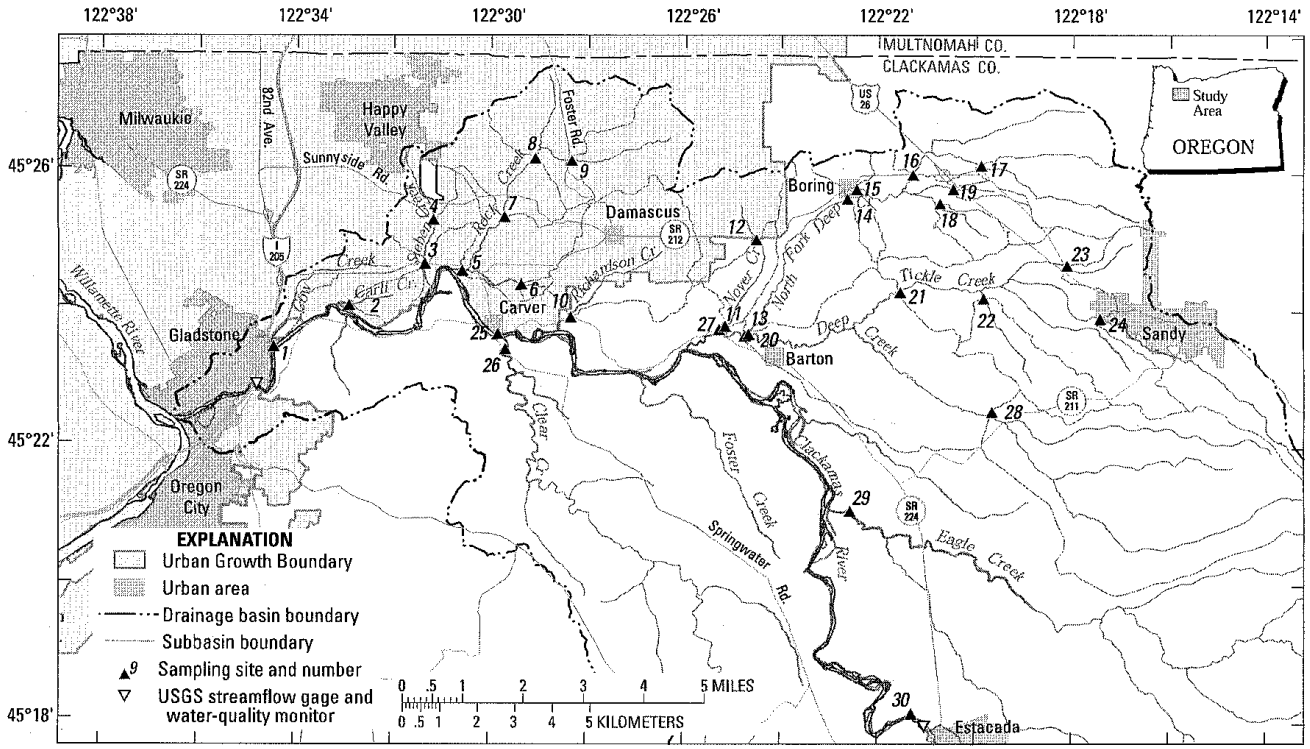
Raw Water (323)				Finished Water (228)		
Chemical	**# Detects**	**%**	**95th %***	**# Detects**	**%**	**95th %***
Atrazine	**311**	**96.3**	**0.516**	**218**	**95.6**	**1.40**
Simazine	**293**	**90.7**	**0.028**	**192**	**84.2**	**0.385**
Metolachlor	**288**	**89.2**	**0.033**	**198**	**86.8**	**0.336**
Prometon	**241**	**74.6**	**0.138**	**145**	**63.6**	**0.067**
Cyanazine	**145**	**44.9**	**0.007**	**96**	**42.1**	**0.128**
Diazinon	**114**	**35.3**	**0.002**	**0**	**0**	**0**
Alachlor	**87**	**26.9**	**0.002**	**51**	**22.4**	**0.027**
Metribuzin	**47**	**14.6**	**0.004**	**0**	**0**	**0**
Dacthal	**16**	**5.0**	**0.002**	**8**	**3.5**	**<0.004**
Terbacil	**7**	**2.2**	**0.008**	**0**	**0**	**0**

* ug/L Underlined = Regulated by SDWA

Pesticide Occurrence in Clackamas River Basin

- 119 water samples analyzed for 86-198 dissolved pesticides (there are 11,000 pesticide products registered in Oregon)
- Pre- and post-treatment samples from one of the four WTPs along lower river
- 63 pesticide compounds detected
  - 33 herbicides
  - 15 insecticides
  - 6 fungicides
  - 9 pesticide degradation products
- Tributary (8) sampling primarily during storm events
- WTP (1 of 5) sampling at regular intervals: 1 storm event

Clackamas River Sample Sites



Base modified from U.S. Geological Survey and Metro RLIS data sets (1:24,000)
Oregon Lambert projection, North American Datum 1983

Figure 1. Locations of sampling sites in the lower Clackamas River basin, Oregon, 2000–2005.

Clackamas Pesticide Sampling Results

- Pesticides detected in lower basin tributaries and from the main stem of the river
- Atrazine, simazine most common in waters tested (50% of samples)
- Glyphosate, triclopyr, 2,4-D and metolachlor also occur
- Below human health standards, but several exceeded the EPA and DEQ aquatic-life benchmarks, e.g., fish and benthic invertebrates

Clackamas Pesticide Sampling Results

- Finished water: 60% of samples (9 of 15)
  - 10 herbicides: diuron, simazine
  - Also, 1 insecticide, 1 fungicide, 1 insect repellent, and 2 pesticide degradation products
- 0-2 pesticides detected in most finished water samples; 6-9 detected during 2 storm events
- All detects below human health standards

Sources of Pesticides

- Tributaries drain basins containing nurseries, pasture, agricultural, rural and residential land
- Most of the 51 current-use pesticides have multiple uses, i.e., are not specific to one land use
  - 94% used on crops
  - 92% used by nurseries
  - 57% lawns and landscaping in urban areas
  - 49% on golf courses
  - 45% along roads and right-of-ways
  - 7% on forestland
- Glyphosate among most common detected (roundup, rodeo, accord); household, Ag, Forest

Newspaper Headlines
March 10, 2008

- **"Pharmaceuticals Lurking in U.S. Drinking Water"**
- **"Water Superintendent Does Not See A Problem With Pharmaceuticals in City Water"**
- "Drugs in Your Water?"

Associated Press and Related Articles

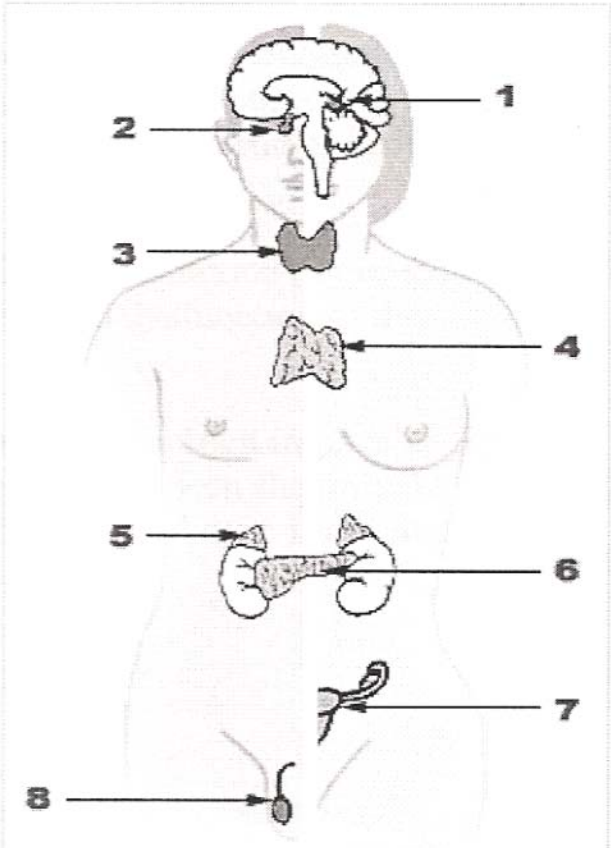
- AP survey of 62 large water providers and independent researchers
  - PPCPs in 24 systems, serving ~41 million people
  - Antibiotics, anti-convulsants, mood stabilizers and sex hormones
  - Detections at very low levels (ppb-ppt)
- Portland: acetaminophen (tylenol), ibuprofen, caffeine, and sulfamethoxazxole (antibiotic)
- Most detections occur, or are at higher levels, downstream from WWTPs

Pharmaceuticals and Personal Care Products (PPCPs)

- Thousands of diverse chemical compounds: used by people, pets, and livestock
  - 50,000,000 lbs/annually, half used in agriculture: growth promotion
- Virtually constant loading into the environment
- Includes prescription and over-the-counter substances
  - Antibiotics, steroids, synthetic hormones
  - Therapeutic drugs, herbal remedies
  - Cosmetics, fragrances, shampoos, sun screen additives
  - Veterinary drugs
  - Feed additives: nutritional, antibiotics (using subtherapeutic levels leads to lower animal care costs in large-scale confined operations)
- Prescription drug use has increased by ~12% since 2003

Endocrine Disrupters

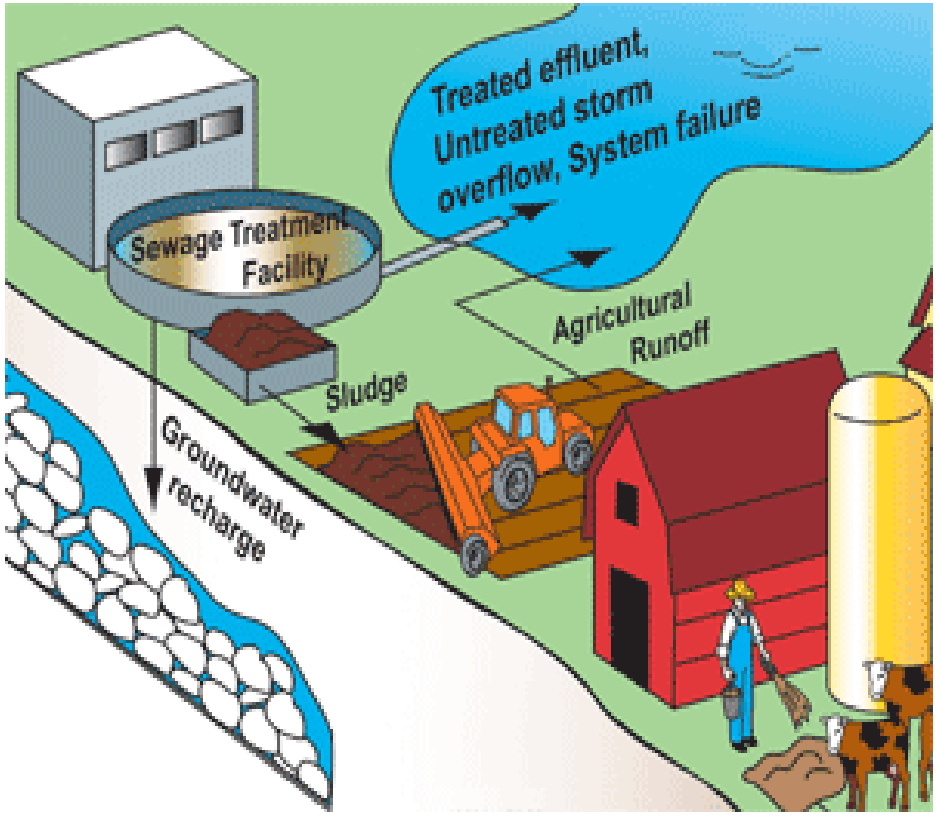
- Chemicals that interfere with glands and hormones that regulate biological processes
- Glands communicate with organs in the body by sending hormones through blood vessels
- Controls development, reproduction, immune system, organ function, metabolism, mood, etc.



Major endocrine glands. (Male left, female on the right.) **1.** Pineal gland **2.** Pituitary gland **3.** Thyroid gland **4.** Thymus **5.** Adrenal gland **6.** Pancreas **7.** Ovary **8.** Testes

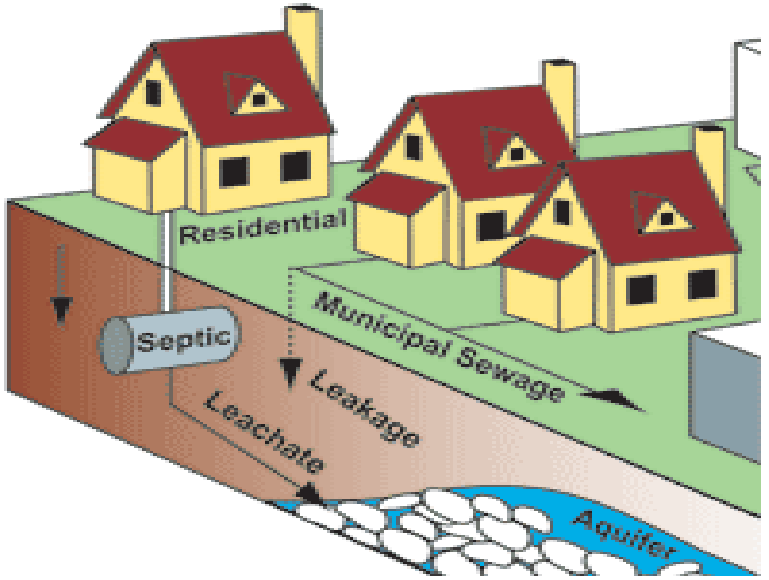
Source of PPCPs

- Agriculture: Feed supplements, Animal waste,
- Veterinary drug use, especially antibiotics and steroids
- Municiple sewage treatment plants
- Land application of sludge

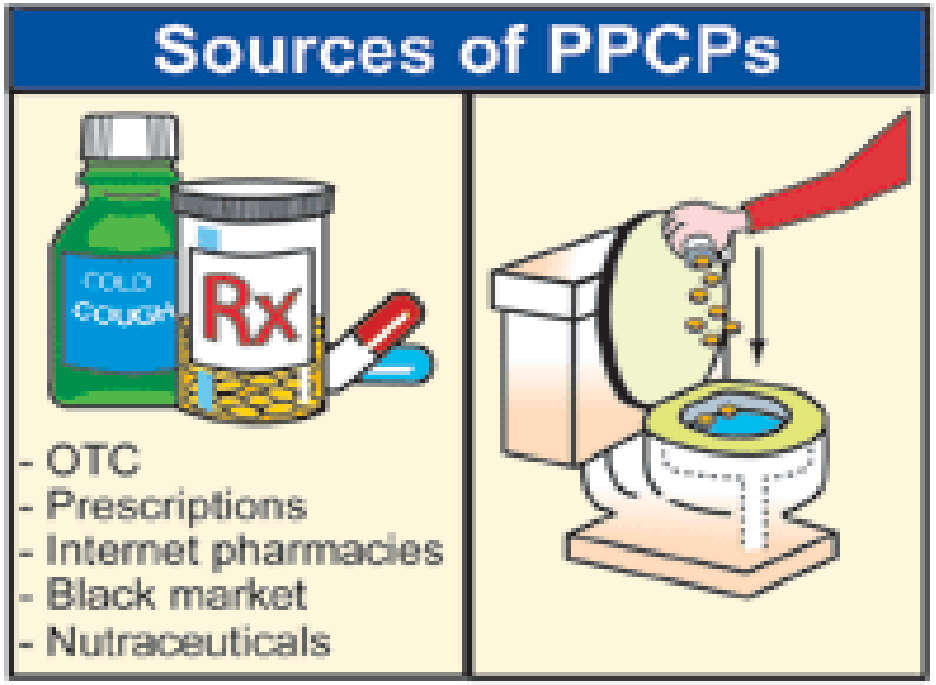


PPCPs Not Fully Metabolized by the Body

- Excreted as active metabolites or parent substances
- Pathway between homes and septic or municipal sewage facilities.



Improper Disposal of Pharmaceuticals



Discarding unused drugs and personal care products down the toilet is a common but poor disposal method.

Disposal of Drugs
Federal Guidelines

- Take unused, unneeded, or expired prescription drugs out of their original containers and throw them in the trash.
- Mixing prescription drugs with an undesirable substance, such as used coffee grounds or kitty litter, and putting them in impermeable, non-descript containers, such as empty cans or sealable bags, will further ensure the drugs are not diverted.
- Flush prescription drugs down the toilet *only* if the label or accompanying patient information specifically instructs doing so.

Fate and Transport of PPPCs

- How do these chemicals move into groundwater:
- Generally must travel though unsaturated zone
  - Open spaces not completely filled with water
- In laboratory column experiments
  - Simulated unsaturated zone
  - Artificial loading of contaminant in representative solution

Chemical Characteristics

- Research needed, preliminary data only
- Sorption characteristics:
  - Attachment to “solids”, e.g., organic matter
  - Bind up contaminant in soil, enhance is surface water
- Retardation of contaminants (V_w/V_c):
  - One study found values from 1.8 to 4.8
- Microbial transformation:
  - Biodegradation, e.g., organic compounds => CO_2
- Persistence (residence time): Length of time for compound to break down.

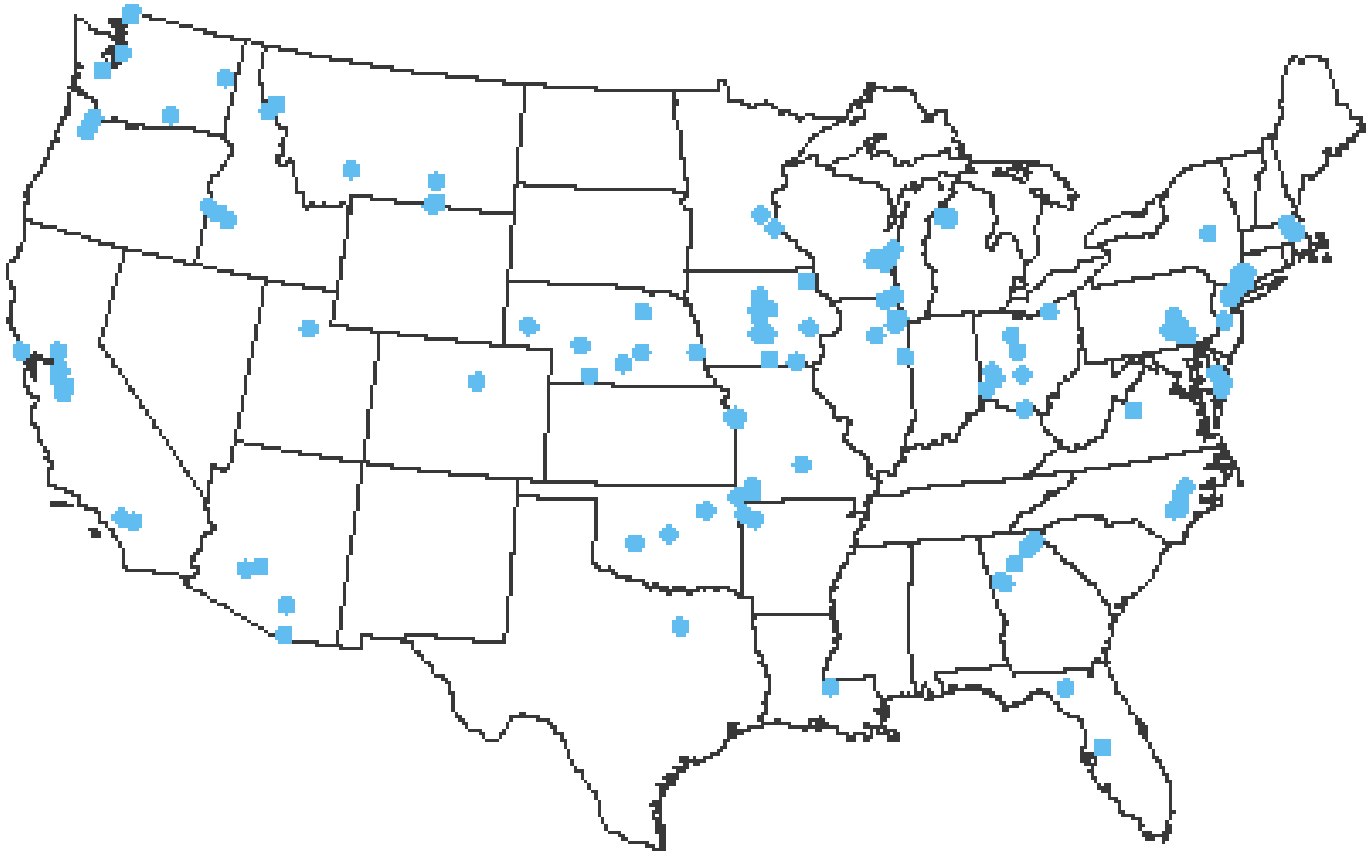
PPCPs: Health Effects

- Found in very low concentrations (ppb – ppt)
- Drinking one gallon/day of water containing 1ppb of a pharmaceutical would be equivalent to:
  - 1 Valium or 1 Ritalin in 3.5 years
  - One Benadryl in 14.5 years
  - One Children's Tylenol in 58 years
- Concern that long-term exposure may cause subtle effects that could accumulate over time through generations
- Hormones work in body at very low concentrations and affect sexual development
- Prevalent use of antibiotics producing "super bugs", i.e., resistant to current medication
- Aquatic Organisms: constant/multi-generational exposure

PPCPs: Health Effects

- Lack of definitive information regarding long-term health effects. **<u>However:</u>**
  - Combination of chemicals: One-third of samples in a reconnaissance study in which PPCPs were detected, contained more than 10 individual chemicals
  - Evidence of impact on wildlife, e.g., fish, plankton, in ppt range
  - Similar concentrations of pesticides have demonstrated impact
  - Impact of constant exposure to a mixture of low-level chemicals
- Target vs. non-Target organisms
- Detection levels
  - Research Methods: ppt
  - Drinking Water Methods: ppb

USGS Reconnaissance Study 1999-2000: 139 Streams



Characteristics of Basins

- 24 streams in 19 states (earlier pesticide occurrence review)
- 14 streams from basins with intense animal production
  - Hogs (2)
  - Poultry (6)
  - Dairy or Beef cattle (4)
  - Mixed-animal production (2)
- 9 urban basins: Denver, Dallas, Minneapolis, and Salt Lake City
- One mixed basin: Mississippi River in Louisiana

PPCPs in 1999-2000 Reconnaissance Study

	Surface Water (139)	Groundwater (47)	Drinking Water (74)
Non-Drugs	**81%**	**15%**	**64%**
Antibiotics	**48%**	**26%**	**26%**
Pharmaceuticals	**32%**	**6%**	**23%**
Metabolites	**69%**	**43%**	**19%**
DEET	**74%**	**35%**	**19%**
Caffeine	**71%**	**11%**	**54%**

Treatment Effectiveness

- Major source is from wastewater treatment plant effluent discharged to surface water
- Surface water treatment, study evaluated
  - Conventional/Direct filtration
  - Slow sand
  - Variety of coagulants/conditioners
- Limited ability to remove these chemicals

Effectiveness of Conventional Treatment

Chemical (Use)	Raw Water (ng/L)	% of samples found in	Finished Water (ng/L)	% of samples found in
DEET (1)	10.8	100	10.9	94.4
TCEP (2)	21.9	94.4	9.9	88.9
Caffeine (3)	26.6	94.4	27.7	83.3
Ibuprofen (4)	7.3	83.3	10.4	77.8
Atrazine (5)	153.8	77.8	117.8	72.2
Meprobromate (6)	6.8	66.7	5.7	66.7
Dilanton (7)	4.1	88.9	3.3	61.1
Iopromide (8)	13.8	61.1	9.0	55.6
Carbamazapine (7)	5.7	88.9	4.1	44.4
Gemfibrozil (9)	6.1	61.1	5.2	22.2
Estrone (10)	1.4	5.6	1.2	11.1
Acetominophen (4)	3.6	22.2	1.1	5.6
Ethromycin-H2O (11)	2.7	44.4	2.6	5.6
Sulfamethoxazole (11)	17.8	83.3	2.1	5.6
Naproxen (12)	5.6	61.1	1.0	5.6

Ranking of Treatment Methods Removal of PPCPs

1. Reverse Osmosis (RO)
2. Nanofiltration
3. Advanced Oxidation (AOP)
4. Granular Activated Carbon (GAC)
5. Ozone
6. Chlorine
7. Micro/Ultrafiltration
8. UV

Responsibility of water system?

- SDWA does not require additional sampling for these chemicals nor does it require systems to inform their customers of detections of unregulated chemicals
- Drinking Water Program recommends that water systems do inform customers
  - Better to tell them than for them to find out through other routes
  - Absent other information, public will reach its own conclusions
- Recommendations:
  - Water meets drinking water standards
  - Concentrations are minute
  - Studies are under way, however there is no known human health effects
  - Customers can choose to install simple carbon filters

From Candidate Contaminant List (CCL) to Regulation

- SDWA regulates more than 90 contaminants
- EPA must periodically publish a CCL of contaminants to potentially regulate
- Current list is CCL3:
  - 93 chemicals, 11 microbiological
  - EPA evaluated ~7,500 chemicals and microbes
- List is evaluated for potential health impacts and overall benefit of establishing regulation

Future Regulation by SDWA?

- Does the contaminant adversely affect public health?
  - Toxicology
- Is the contaminant likely to occur in PWSs at a frequency to pose a threat to public health?
  - Evidence of environmental impact
  - Monitoring
  - Laboratory analytical capabilities?
- Will regulation of the contaminant provide a meaningful opportunity for health risk reduction?
- Regulation in the near future not likely


I'M NOT FEELING WELL. I'M GOING TO RUN OVER TO THE PHARMACY.
LAS VEGAS SUN 2008 KING FEATURES SYNDICATE
MIKE SMITH