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Emerging Contaminants in the Drinking Water Cycle

Susan T. Glassmeyer, Ph.D.
United States Environmental Protection Agency, Cincinnati, OH

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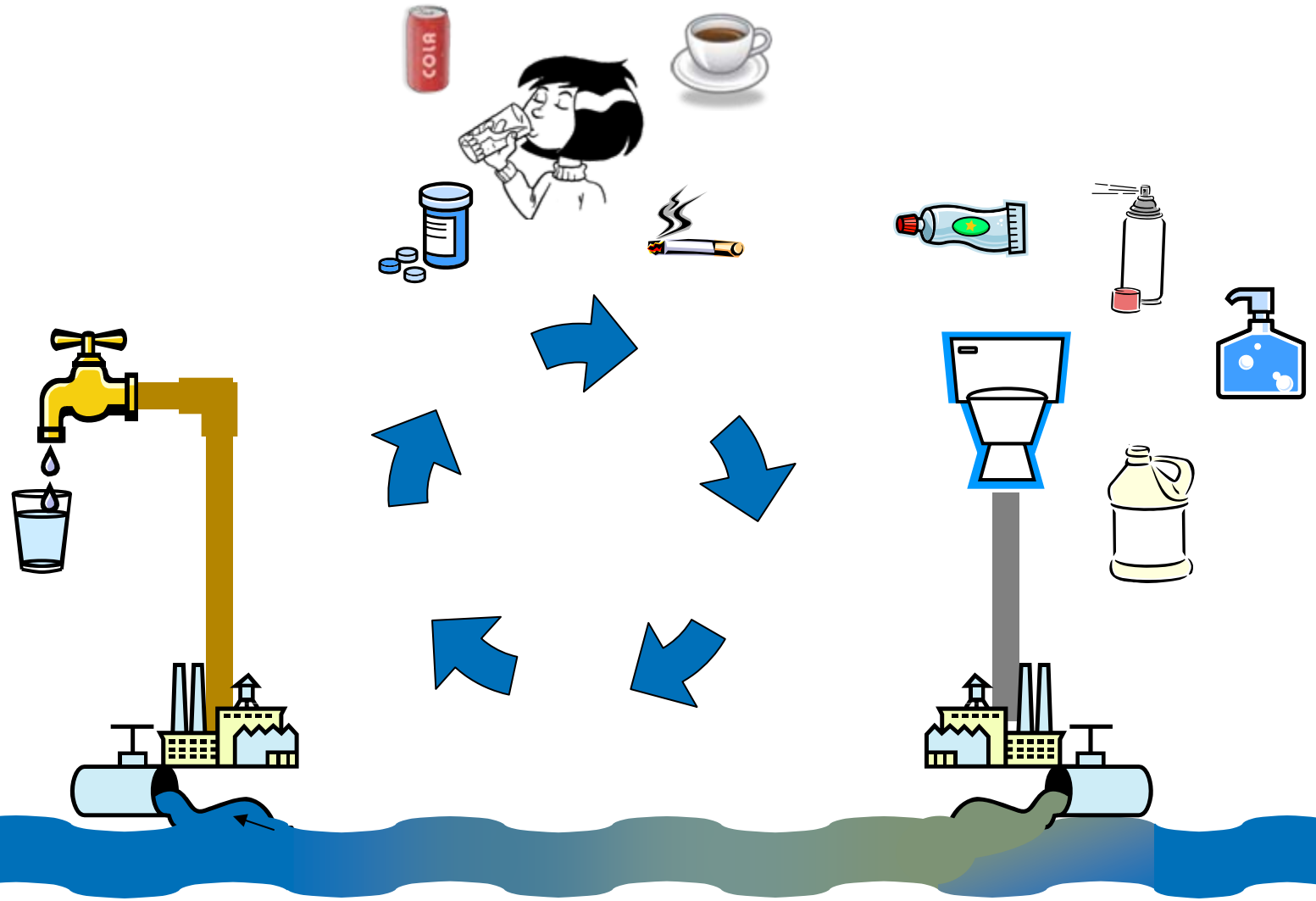
Office of Research and Development
National Exposure Research Laboratory

Presentation Outline

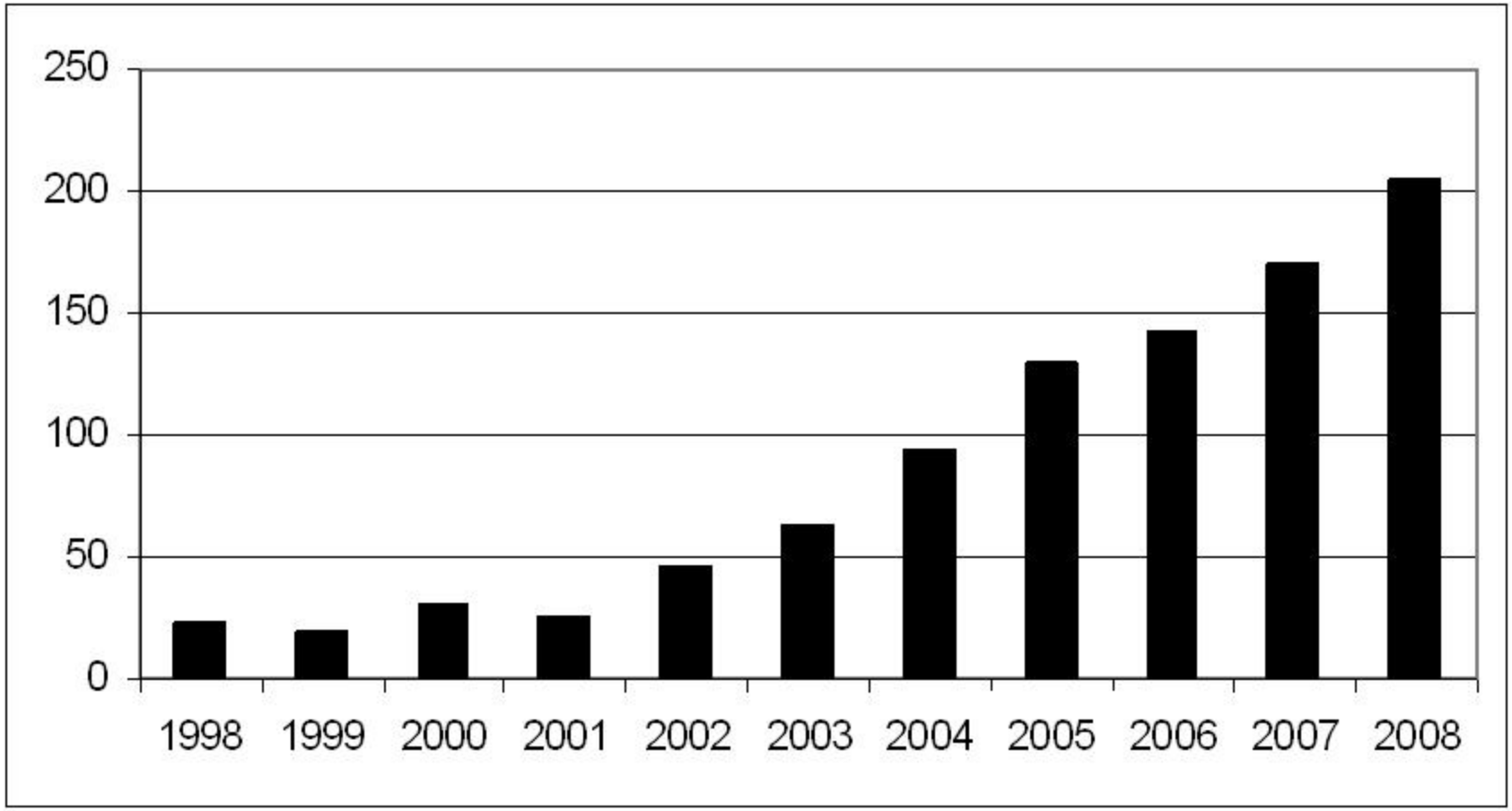
USEPA and USGS Research

- Wastewater treatment plant (WWTP) effluents and downstream surface waters
- Groundwater down gradient from WW lagoon
- Source and finished water from a drinking water treatment plant (DWTP)
- Chlorination laboratory studies

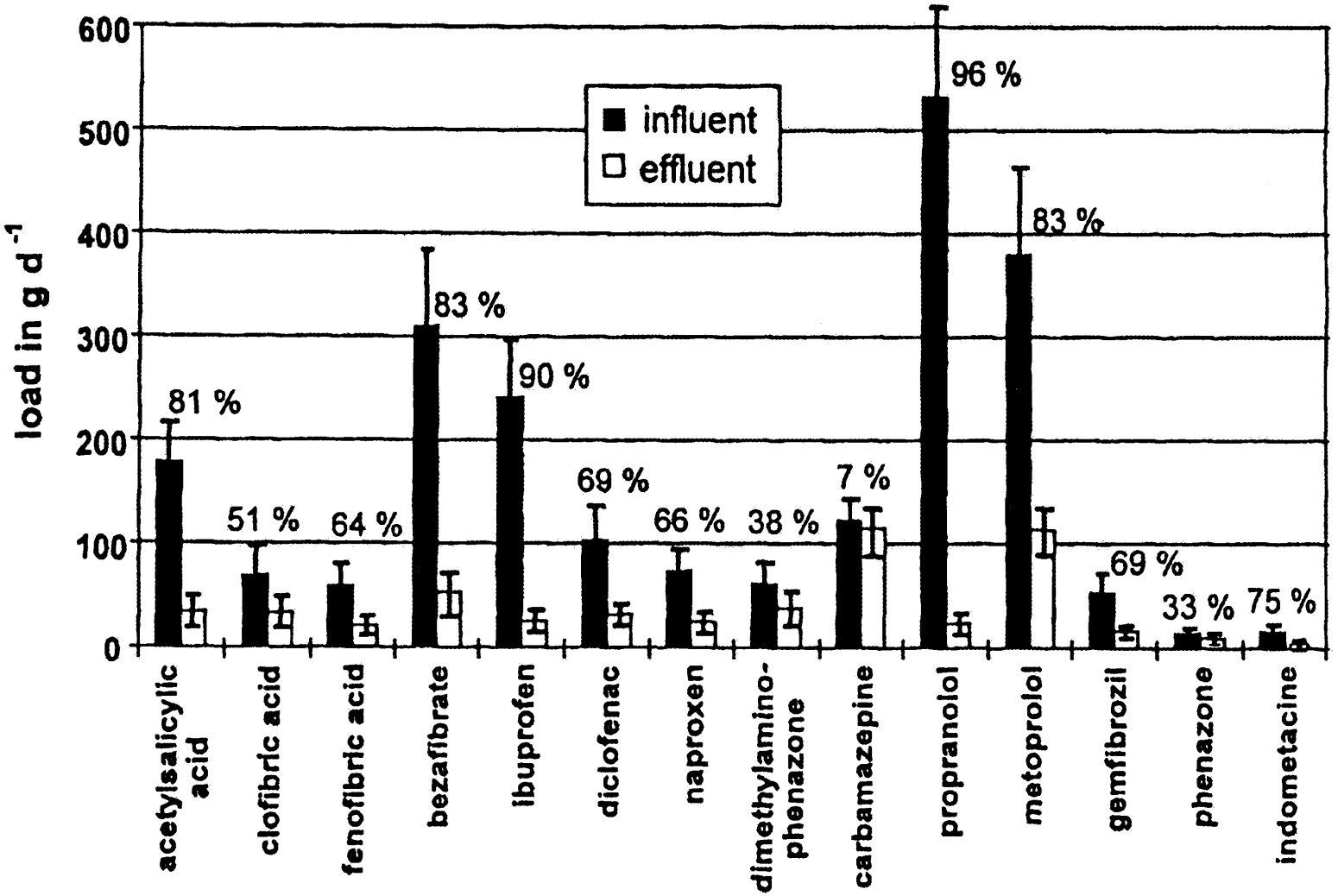
Water Cycle



Pharmaceutical Literature Citations

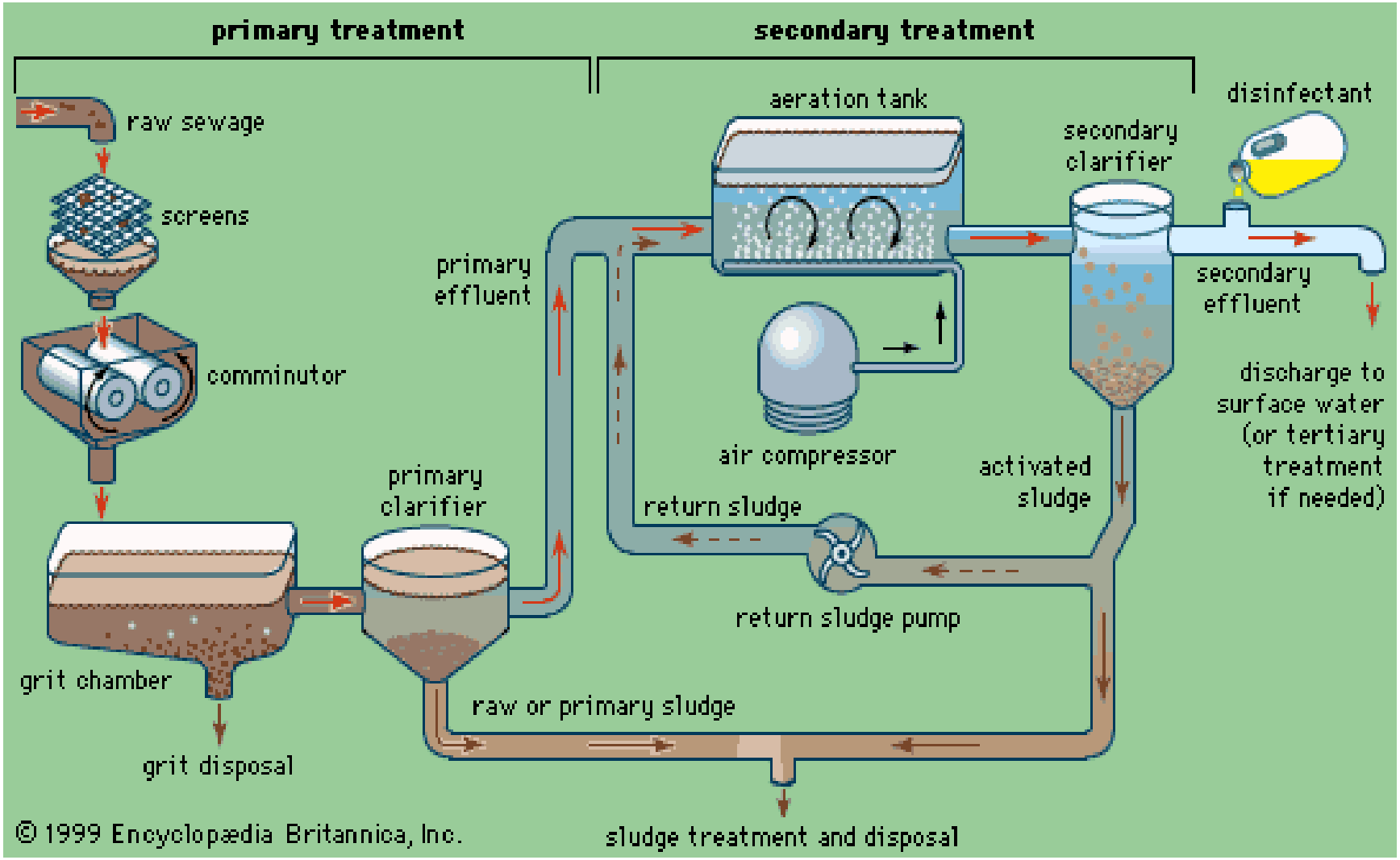


Pharmaceutical Elimination from a Sewage Treatment Plant



From: Ternes, T.A. **1998** Occurrence of Drugs in German Sewage Treatment Plants and Rivers. *Water Research* 32:3245-3260.

Sewage Treatment



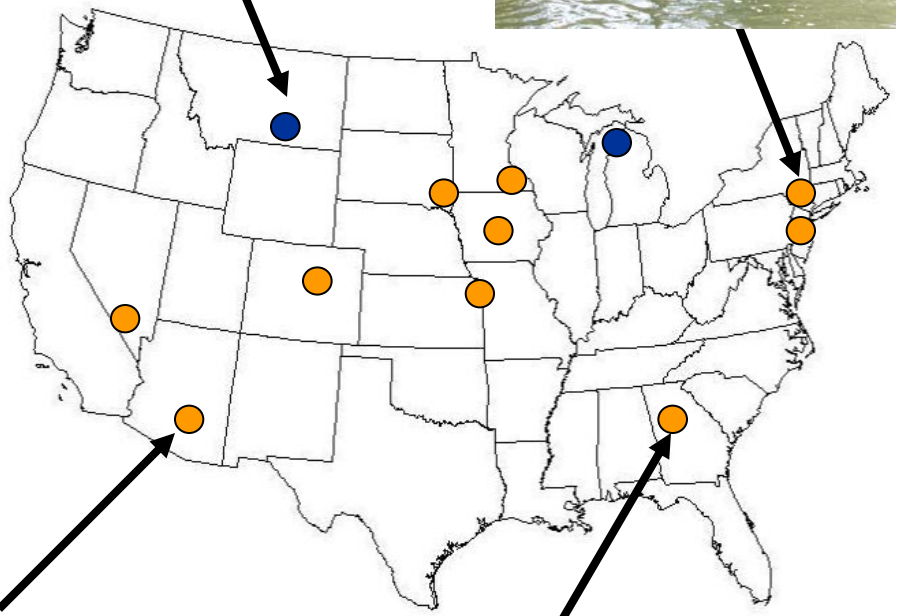
From: www.britannica.com

So, what is happening to ECs during wastewater treatment?

1. Sorbed to particulate matter- removed as sludge
2. Chlorinated during disinfection process
3. Destroyed (oxidized) during disinfection process
4. Degradation not related to disinfection (microbial, photolysis, etc)
5. Nothing- they pass through the system

WWTP Effluent Study - 2002

- Focus on wastewater treatment plants
  - One Upstream
  - One Effluent
  - Two Downstream
- Two Background Locations



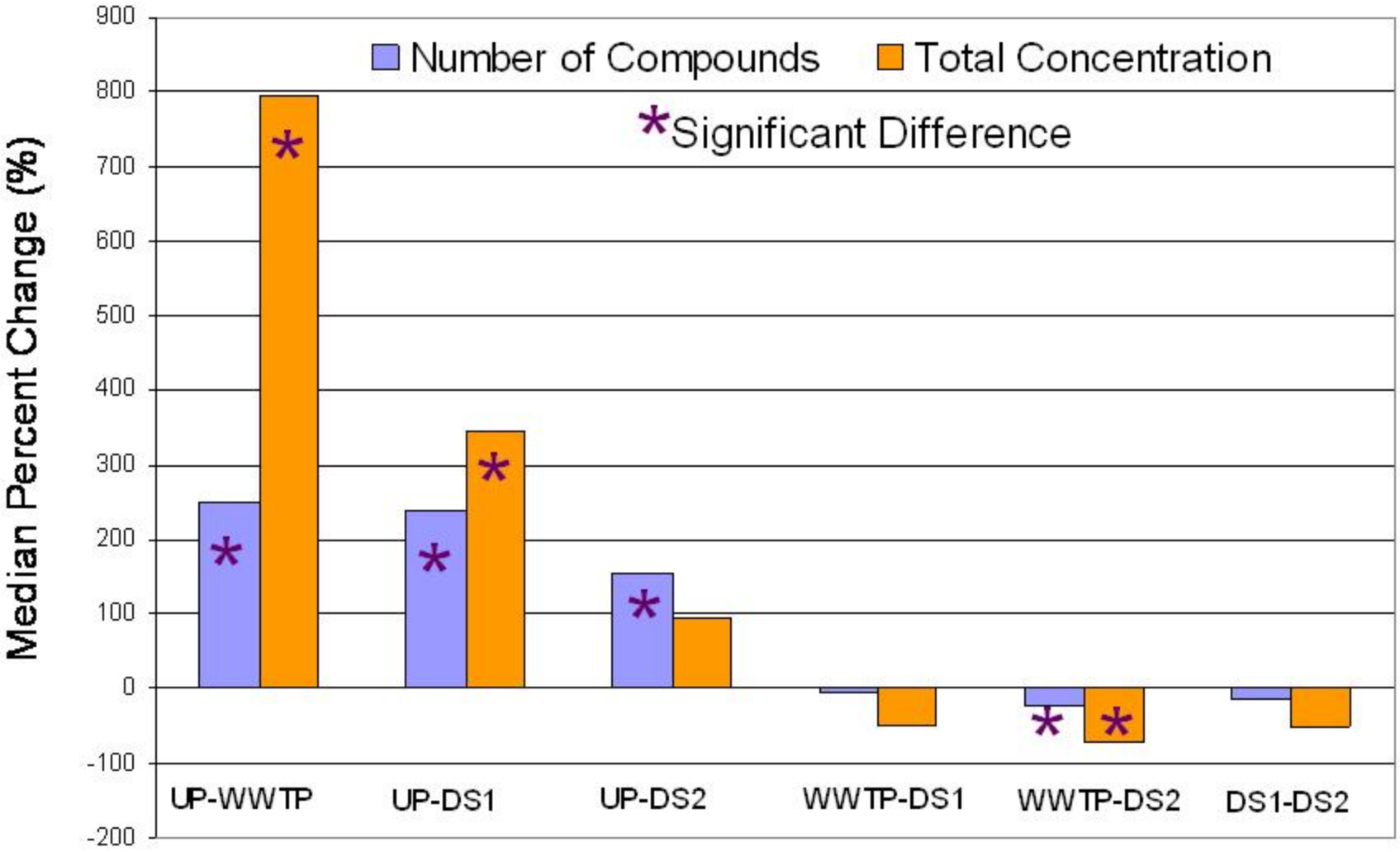
USGS Chemical Methods

- Pharmaceutical Method
  - SPE, LC/MS-ESI(+)
- Wastewater Method
  - liquid/liquid or SPE, GC/MS
- Antibiotic Method
  - SPE, LC/MS-ESI(+) or LC/MS/MS-ESI(+)

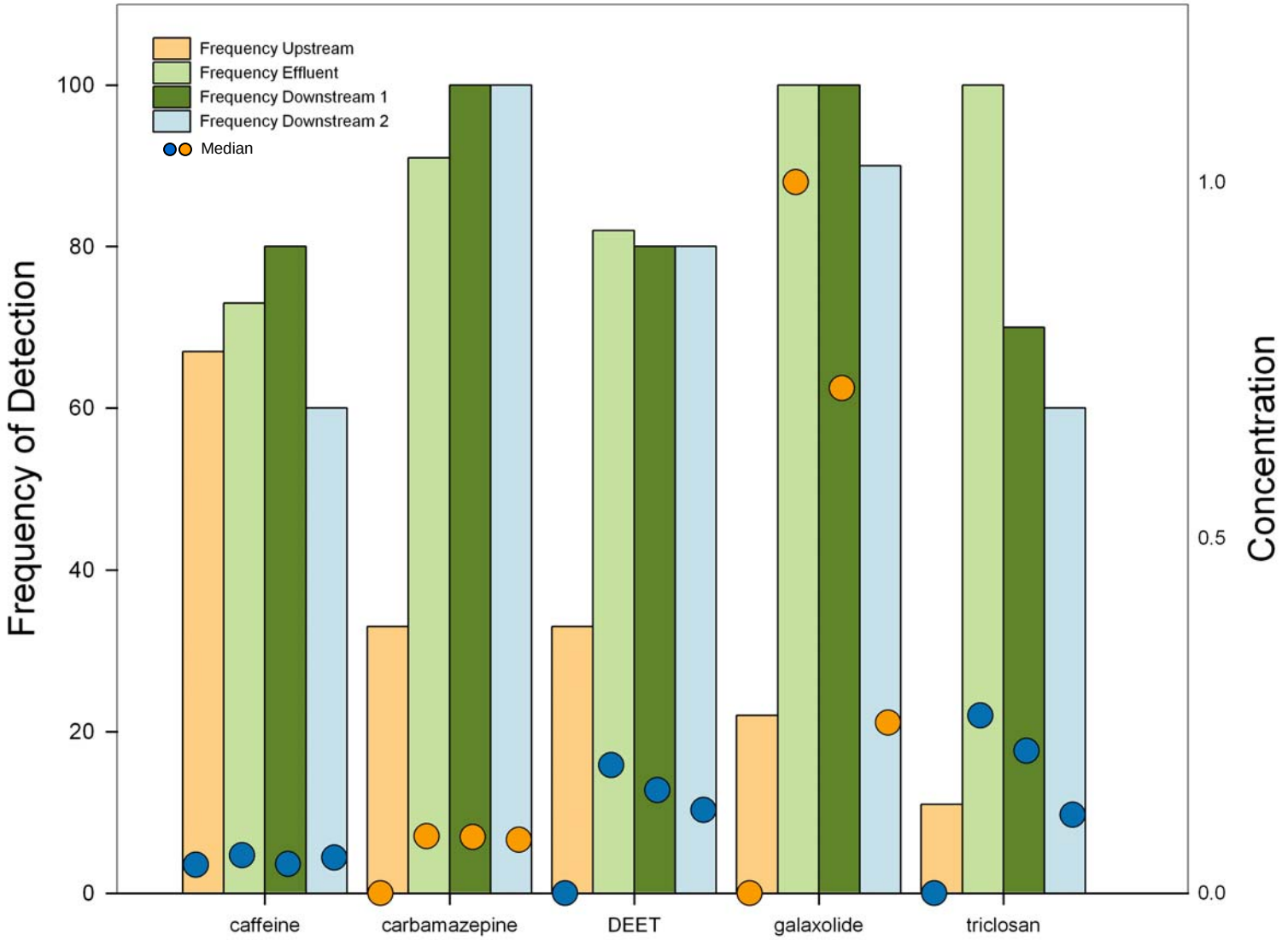
WWTP Effluent Study Results

- 78 out of 110 chemicals were found in at least one sample.
- 6 chemicals were found in at least 75 % of the samples.
- Median numbers of detections by sample type: Upstream, 10; WWTP effluent, 35; 1st Downstream, 32; 2nd Downstream, 24.
- Downstream persistence of the chemicals varied.
- “Transport of Chemical and Microbial Compounds from Known Wastewater Discharges: Potential for Use as Indicators of Human Fecal Contamination” *ES&T* 2005, 39, 5157-5169.

Instream Variability

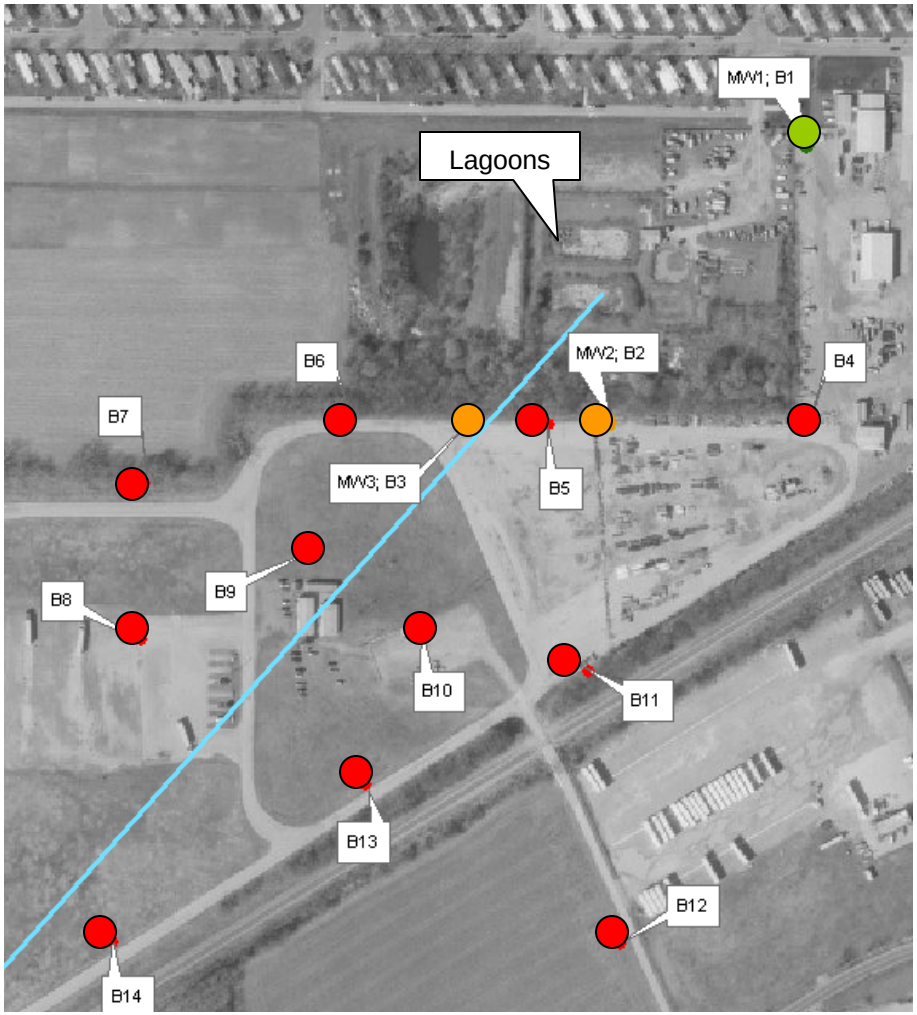


Frequency and Concentration Comparison



OEPA Groundwater Study- 2005-2006

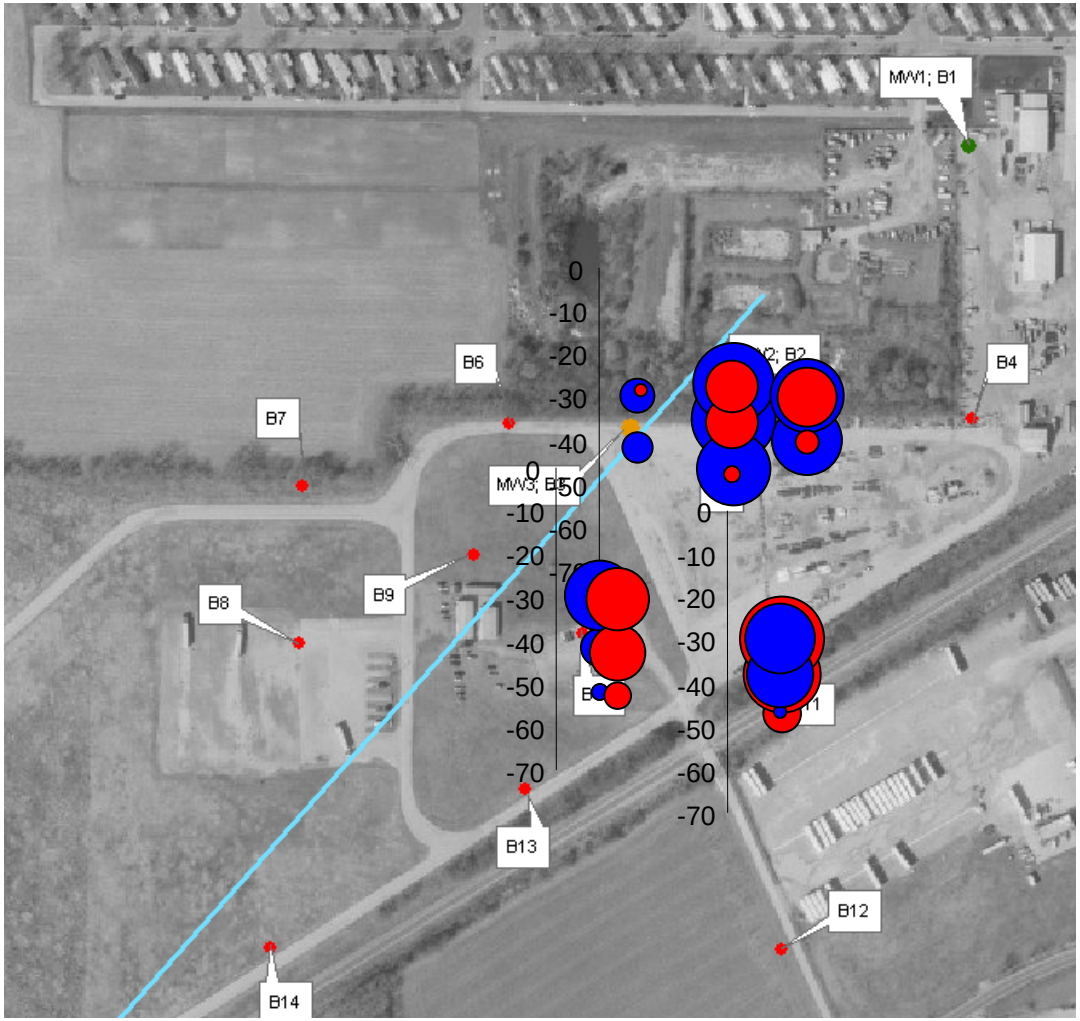
- Two different sampling regimes
  - Boreholes- single measurement at multiple depths
  - Monitoring Wells (MW)- single depth, measured five times over 14 months using pharmaceutical method



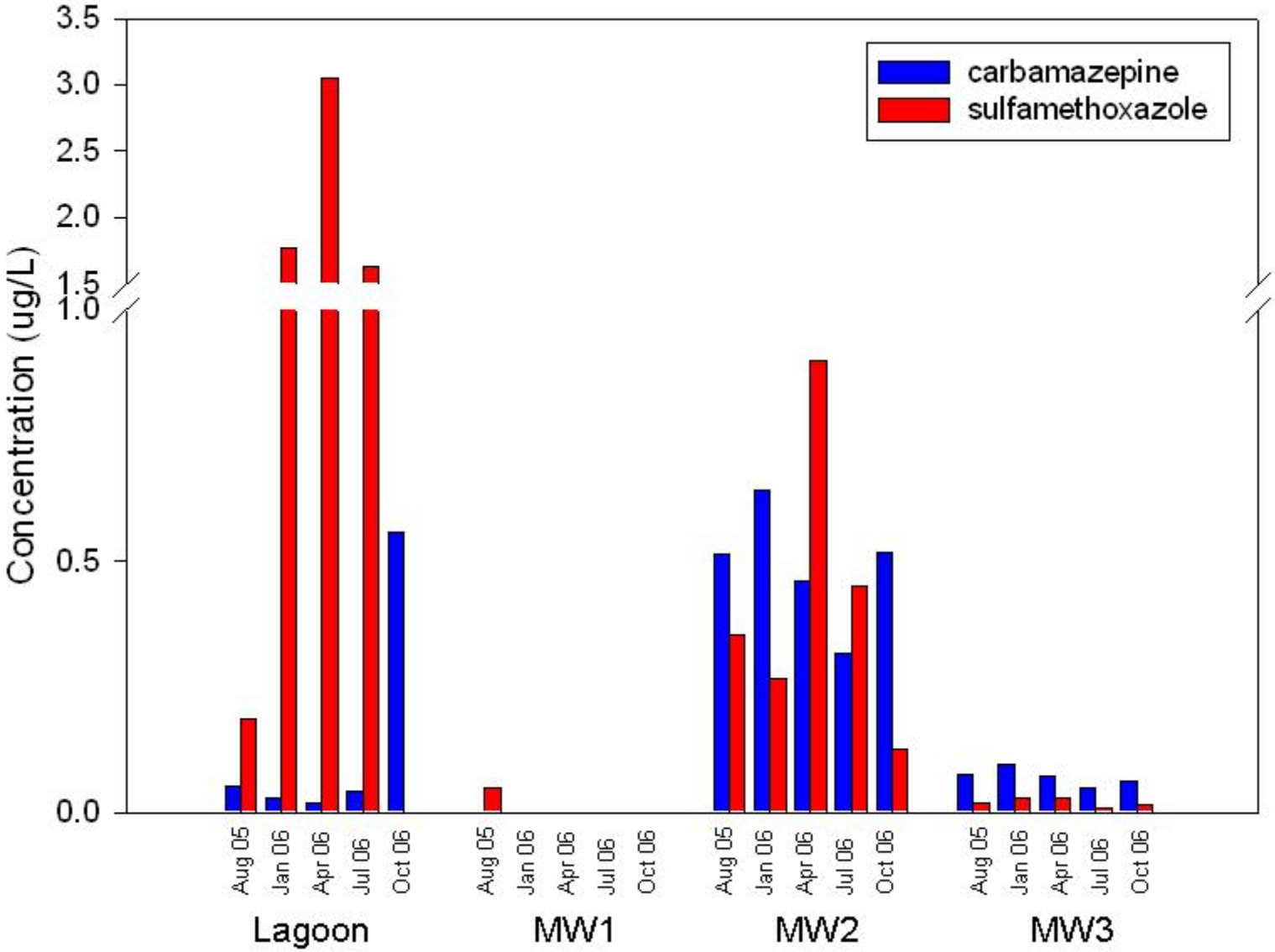
Groundwater Results Overview

- 12 out of 16 pharmaceuticals detected at least once in lagoon samples
- Six pharmaceuticals detected at least once in the MWs and boreholes
- Carbamazepine and sulfamethoxazole most commonly detected

Carbamazepine and Sulfamethoxazole in Boreholes



Groundwater Monitoring Wells



We have just seen ECs in wastewater and surface and ground waters…
what about drinking water?

Safe Drinking Water Act 101

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- ORD (and Susan) does not monitor compliance.
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Safe Drinking Water Act (SDWA)

- Protect the public's health by regulating the drinking water supply
- Rivers, lakes, stream, reservoirs, springs, and ground waters– any potential source of drinking water– are covered.
- Applies to all public water systems that have at least 15 service connections or serve at least 25 people per day for 60 days of the year. Over 160,000!

How are chemicals regulated under SDWA?

- USEPA identifies contaminants that occur, or may occur, in drinking water with a frequency and at levels that pose a threat to public health.
  - Contaminant Candidate List (CCL)
    - CCL3 released February 2008, listing 104 contaminants (11 microbial and 93 chemical)
    - Every five years, must decide to regulate (or not) at least five contaminants
  - Unregulated Contaminant Monitoring Regulation (UCMR)
    - Limited to 30 contaminants in any five year cycle
    - UCMR2 was finalized December 2006- sampling 2008

What is the drinking water regulation decision making process?

When making a “determination” to regulate, the law requires that three areas are considered:

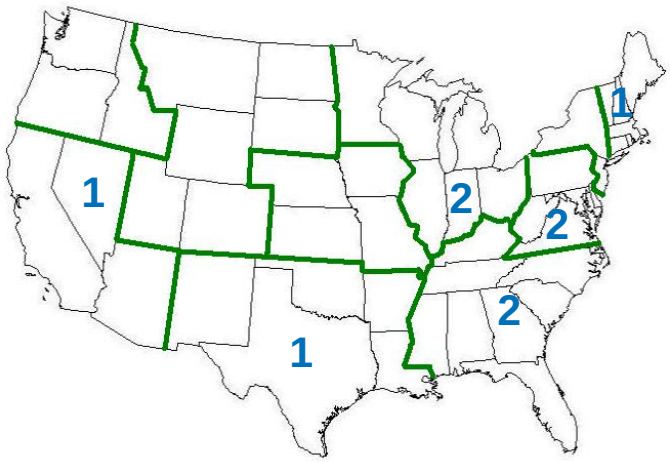
- projected adverse health effects from the contaminant,
- the extent of occurrence of the contaminant in drinking water, and
- whether regulation of the contaminant would present a “meaningful opportunity” for reducing risks to health.

Currently, public interest on emerging contaminants in drinking water is high…

…but the drinking water regulation process is only equipped to evaluate a finite number of chemicals every 5 years

- Literally 1000s of chemicals are considered ECs.
- Very little data on the presence of these chemicals in finished drinking water.
- There is a need to triage which ECs are frequently found and therefore *may* need to be more fully investigated under the SDWA.

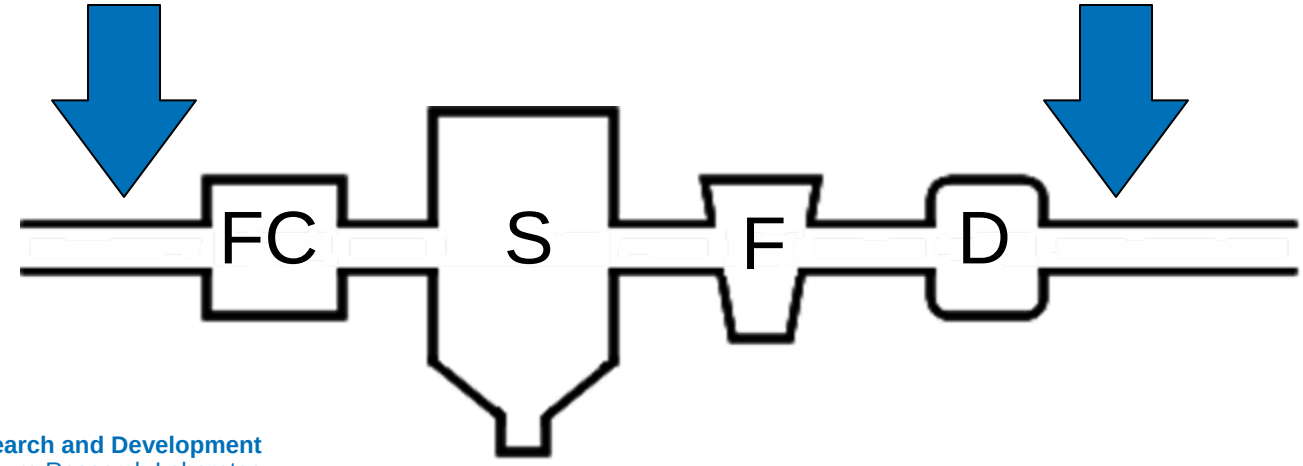
Drinking Water - 2007



- Nine DWTPs (one site sampled twice, n = 10)
- Source water had known or suspected wastewater contributions
- One groundwater
- Five used conventional treatment (coagulation, clarification, filtration, and chlorination)
- Three used advanced treatments (ozone, UV, carbon filtration)

Sampling Design

- Paired source and finished water samples, collected taking the resonance time of the plant into account.
- Locations sampled only once.
- Included high percentage of QA/QC samples (25% spike, 25% duplicate, field blank from every location)



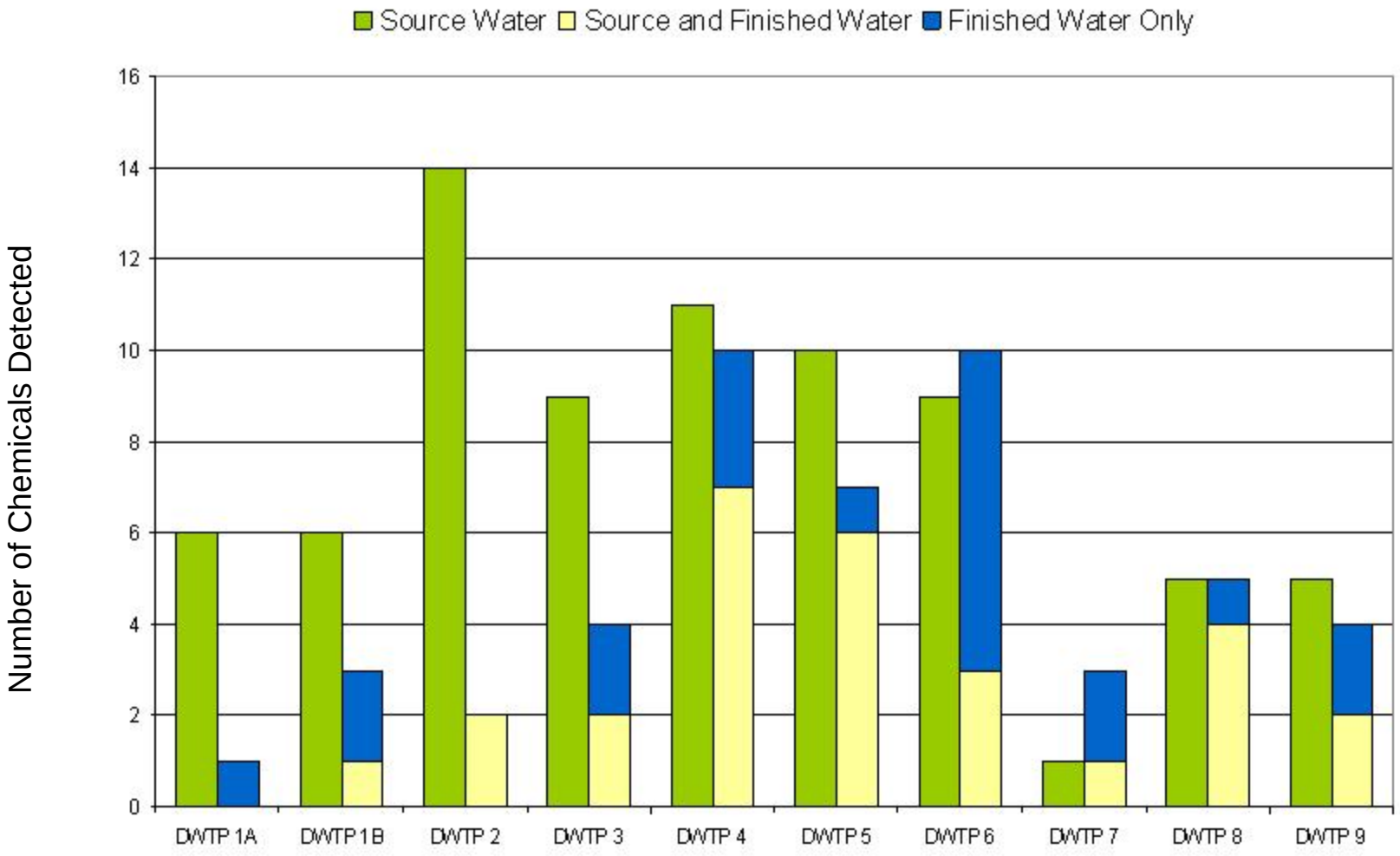
USGS Methods Used

- Pharmaceutical Method (SH 2080)
  - LC/MS
  - 13 Chemicals
- Wastewater Method (SH 1433)
  - GC/MS
  - 60 Chemicals
- New Antidepressant Method
  - LC/MS/MS
  - 10 Chemicals

84 Chemicals

- 18 prescription pharmaceuticals
- 6 nonprescription pharmaceuticals
- 15 industrial chemicals
- 10 fragrances
- 9 polycyclic aromatic hydrocarbons
- 7 pesticides
- 7 detergent metabolites
- 5 household chemicals
- 4 sterols
- 3 flame retardants

Site Specific Detections



Source/ Finished Water Comparisons

	S (n)	F (n)	Wilcoxon *p*-values (based on paired conc)
bupropion	**8**	**4**	**0.148**
venlafaxine	**8**	**nd**	***0.008***
caffeine	**6**	**2**	**0.078**
tri(2-chloroethyl)phosphate	**6**	**2**	***0.031***
carbamazepine	**7**	**6**	**0.406**
sulfamethoxazole	**5**	**1**	**0.436**
tributylphosphate	**4**	**1**	**0.625**
citalopram	**3**	**nd**	**0.250**
sertraline	**3**	**nd**	**0.250**

Comparison of Detections to Dose

- Acetaminophen
- Single dose 1000 mg
- Maximum detected concentration in finished water 65.3 ng/L (Kinney et al *ET&C* 2006)

- To calculate the number of liters to consume single dose
  - 1000 mg X (1L/ 65.3 ng) X (10^6 ng/mg) = 15,313,936 L

- Assuming 2 L drinking water consumption per day
  - 15,313,936 L X (1 day/2 L) X (1 year/ 365 days) = 20,978 years

Margin of Exposure

- What is safe?
- Pomati (*ES&T* 2007) has provided the most conservative guideline.
- Divide lowest recommended therapeutic dose (LRTD) by
  - 10 for intrahuman viability
  - 10 for LRTD not being a no effect level
  - 10 for endocrine active and cytotoxic compounds
  - 10 for extrapolation of animal data to humans
  - 10 for the presence of mixtures in the environment
- MOE > 100,000 (or an environmental concentration < 10^{-5} of LRTD) should be protective of human health

For acetaminophen:

MOE = (1000 mg X 10^6 ng/mg)/ (2 L X 65.3 ng/ L) = 7,656,968

Pharmaceutical Detections in Perspective

Compound	Finished Water Maximum Conc (ng/ L)	Single Dose (mg)	Volume to Consume Single Dose (L)	Time to Consume Single Dose (years)	Margin of Exposure (MOE)	Ref
Caffeine	119	100	840,336	1151	420,168	2
Carbamazepine	258	200	775,194	1062	387,597	2
Codeine	58.7	10	170,358	233	85,179	1
Fluoxetine	5.4	10	1,851,852	2537	925,926	1
Sulfamethoxazole	59.2	1000	16,891,892	23,140	8,445,946	1
Warfarin	73.4	2	27,248	37	13,624	1

[1]Kinney et al *Environmental Toxicology and Chemistry*, 2006.
[2]Stackelberg et al *Science of the Total Environment*, 2006

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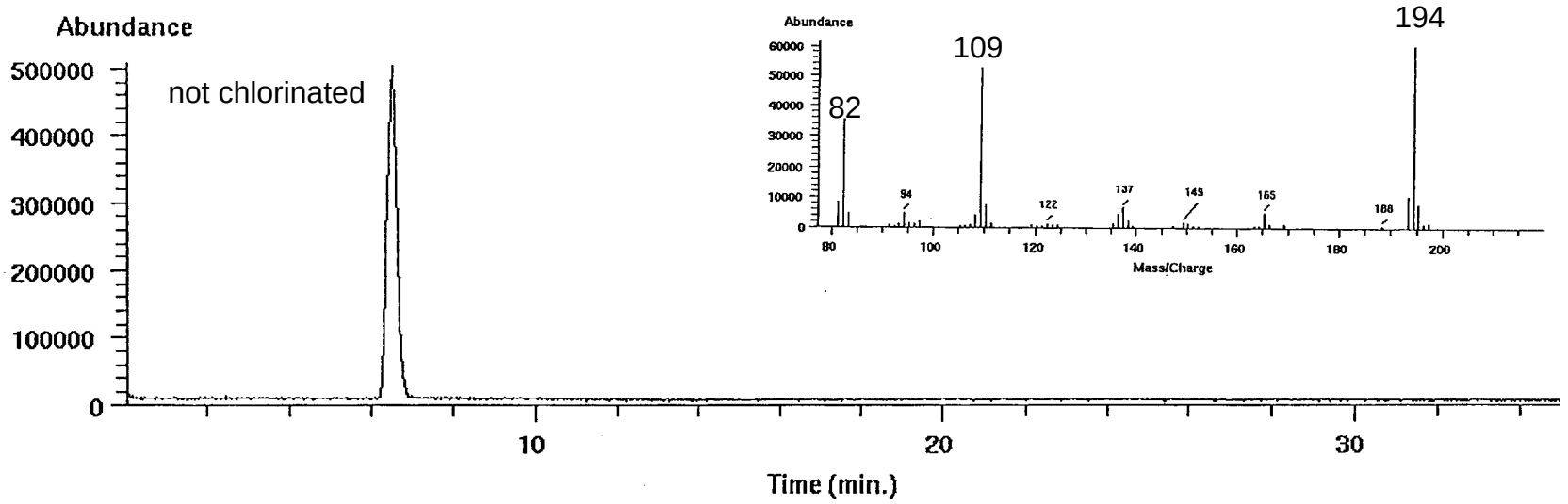
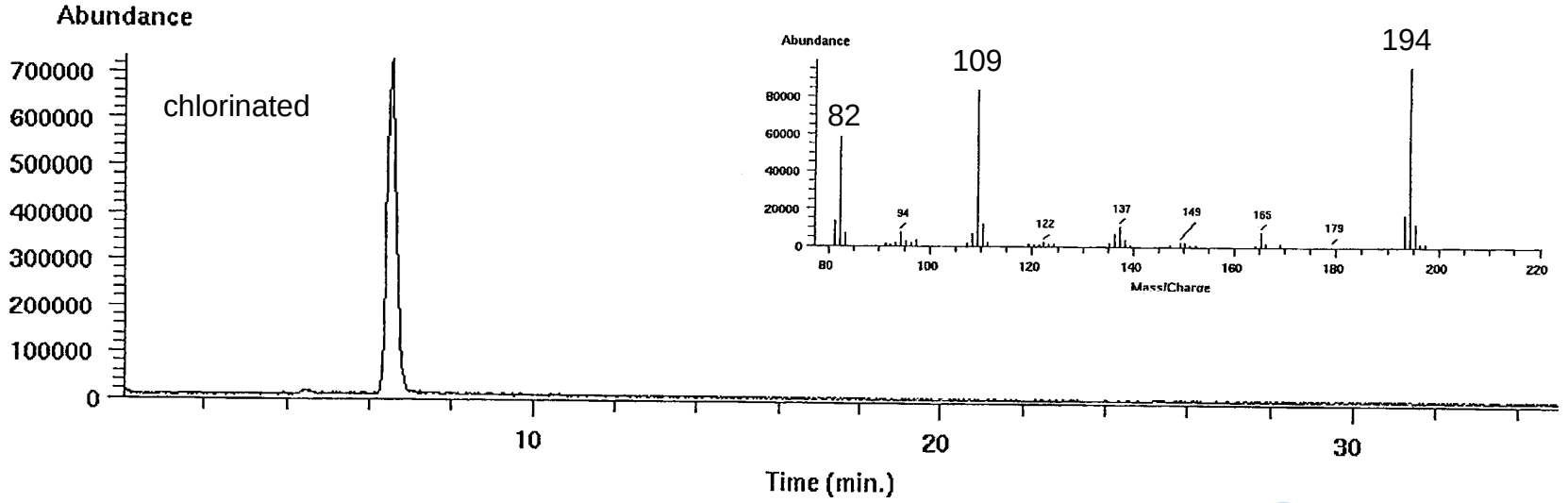
Laboratory Chlorination Studies

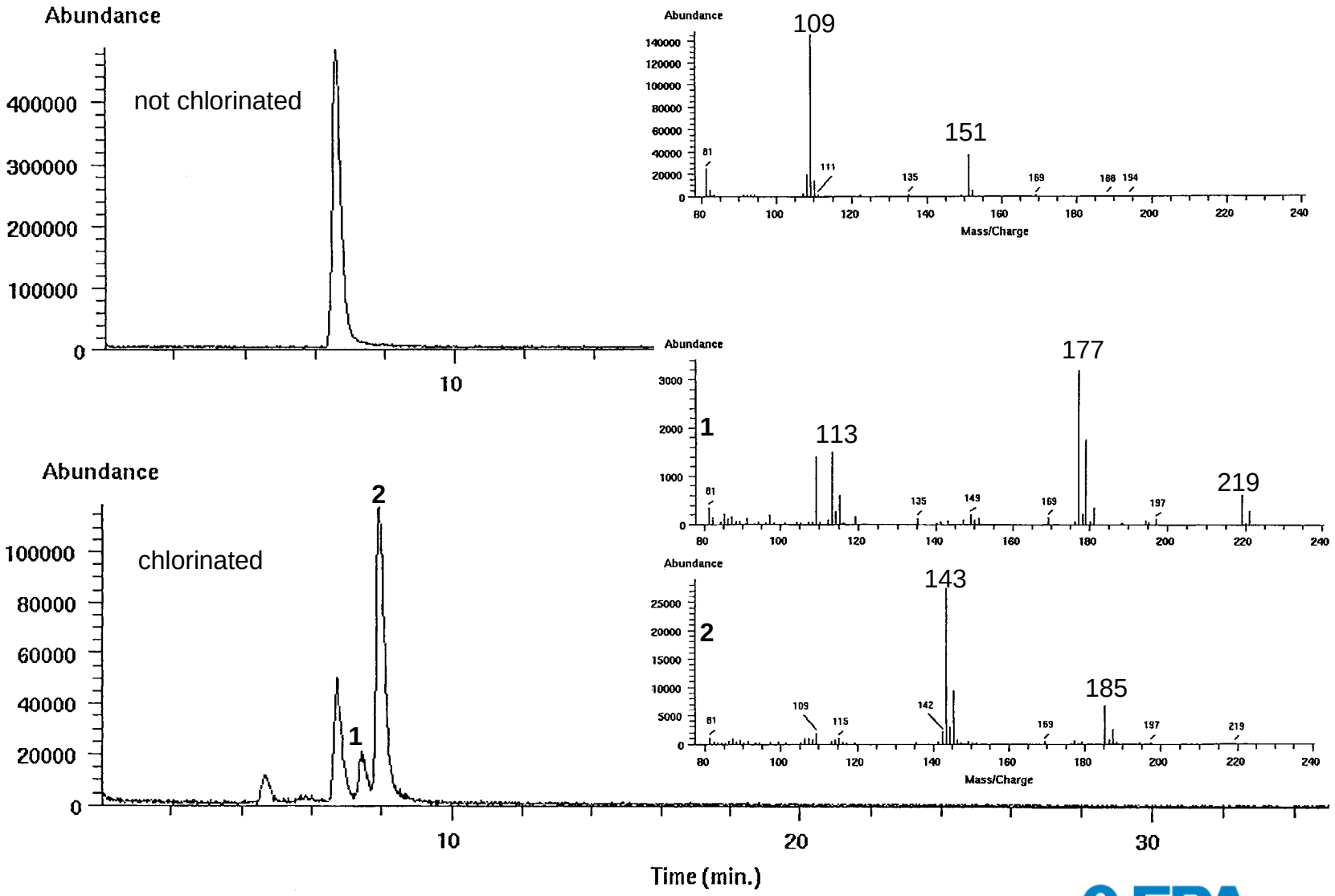
- Paired solutions of 14 pharmaceuticals analyzed using liquid chromatography particle beam mass spectrometry
  - Control, analyzed immediately and after 48 hours
  - Chlorinated sample analyzed after 48 hours
- "Effects of chlorination on the persistence of pharmaceuticals in the environment", *Bulletin of Environmental Contamination and Toxicology*, **2005**, *74*, 24-31

Caffeine (MW= 194.19)

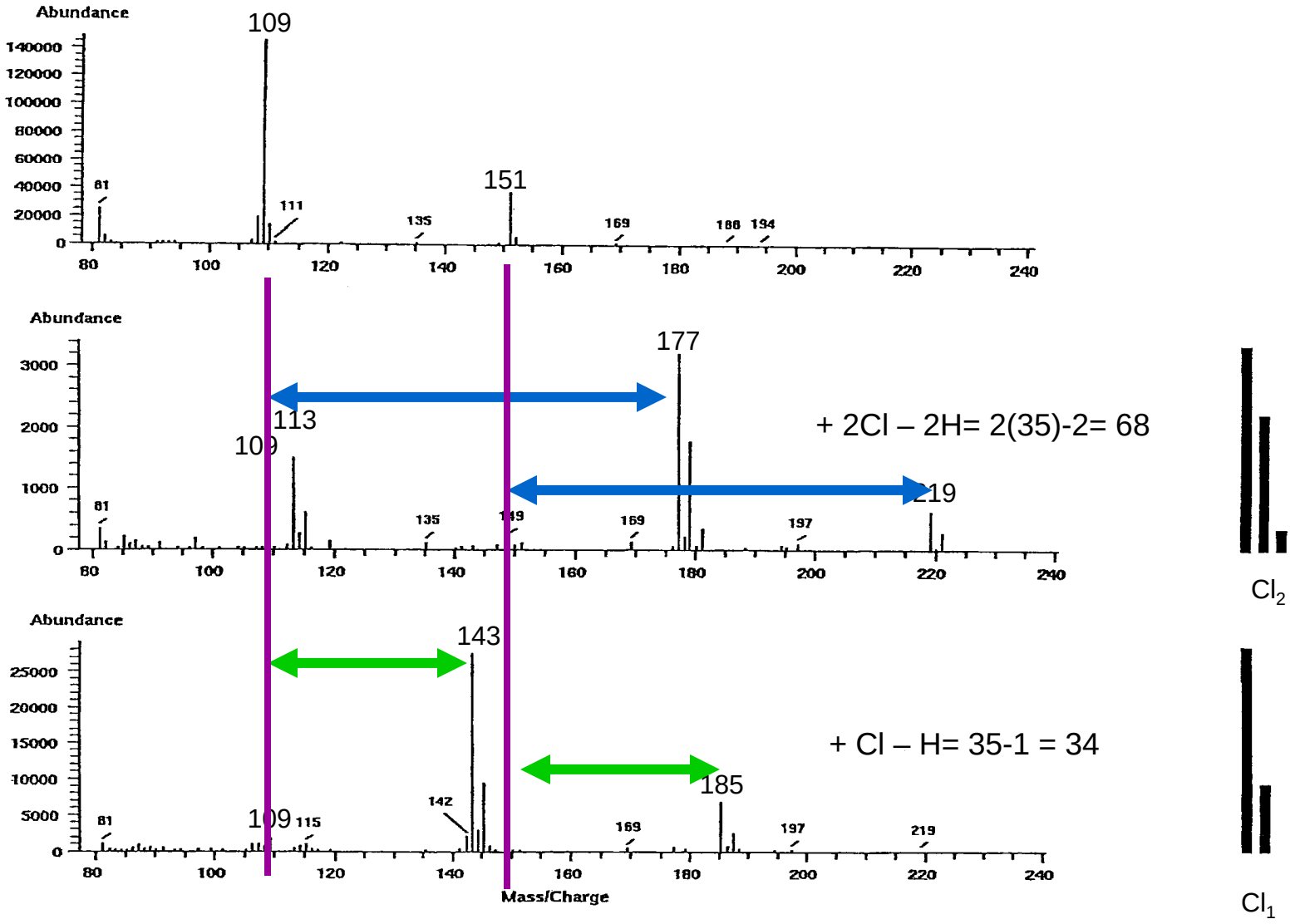




Acetaminophen (MW = 151.17)



Acetaminophen Chlorination Patterns



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Laboratory Chlorination Summary

No Change	Chlorinated	Oxidized
aspirin	acetaminophen	amoxicillin
aspartame	gemfibrozil	cephalexin
caffeine		cimetidine
cotinine		diltiazem
1,7-dimethylxanthine		trimethoprim
6α-methyl-17α-hydroxy progesterone acetate		warfarin

Take Home Messages

- Emerging contaminants are present in household wastewater, and are not entirely removed during wastewater treatment.
- Chlorination can produce chlorinated disinfection byproducts of the ECs.
- Treatment “removal” may just be transformation.
- The chemicals present in treated wastewater can persist and travel through surface and ground waters.
- Natural processes, such as photodegradation, hydrolysis and sorption, work to remove ECs from the water column.
- Concentrations of pharmaceuticals present in finished drinking water are much lower than the typical daily dose.

Collaborators

- Co-PIs: Edward Furlong and Dana Kolpin, USGS

- Groundwater: Christopher Kenah et al., OEPA
- Chlorination Study: Jody Shoemaker, USEPA/NERL