



Emerging Contaminants in the Drinking Water Cycle

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



Office of Research and Development National Exposure Research Laboratory Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy





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











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





Disclaimers and Caveats

- ORD (and Susan) does not promulgate regulations and standards.
- ORD (and Susan) does not monitor compliance.
- ORD (and Susan) does not levy fines.
- Although this work was reviewed by USEPA and approved for publication, it may not necessarily reflect official Agency policy.
- The conclusions and opinions drawn are solely those of the author (Susan) and should not be construed to reflect the views of the Agency.





Intended for educational purposes only. Any resemblance to real persons, living or dead, is purely coincidental. Void where prohibited. Some assembly required. Batteries not included. Contents may settle during shipment. Use only as directed. No other warranty expressed or implied. Do not use while operating a motor vehicle or heavy equipment. Postage will be paid by addressee. Apply only to affected area. May be too intense for some viewers. For recreational use only. Do not disturb. If condition persists, consult your physician. Freshest if eaten before date on carton. Subject to change without notice. Times approximate. Simulated picture. Conditions apply. Postage required if mailed outside the United States. Breaking seal constitutes acceptance of agreement. For off-road use only. As seen on TV. One size fits all. Many suitcases look alike. Colors may, in time, fade. Slippery when wet. For office use only. Drop in any mailbox. Edited for television.





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 Water Source and Finished Water Finished Water Only



╢





Source/ Finished Water Comparisons



	S (n)	F (n)	Wilcoxon <i>p</i> -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 (10⁶ 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







- 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:

 $MOE = (1000 \text{ mg X } 10^6 \text{ ng/mg})/(2 \text{ L X } 65.3 \text{ ng/ L}) = 7,656,968$





Pharmaceutical Detections in Perspective

Compound	Finished Water Maximum Conc	Single Dose (mg)	Volume to Consume Single Dose	Time to Consume Single Dose	Margin of Exposure	Pof
Compound	(ng/ L)	(ing)	(느)	(years)		
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

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



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)



National Exposure Research Laboratory

35

Acetaminophen (MW = 151.17)



National Exposure Research Laboratory

Acetaminophen Chlorination Patterns







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







- 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