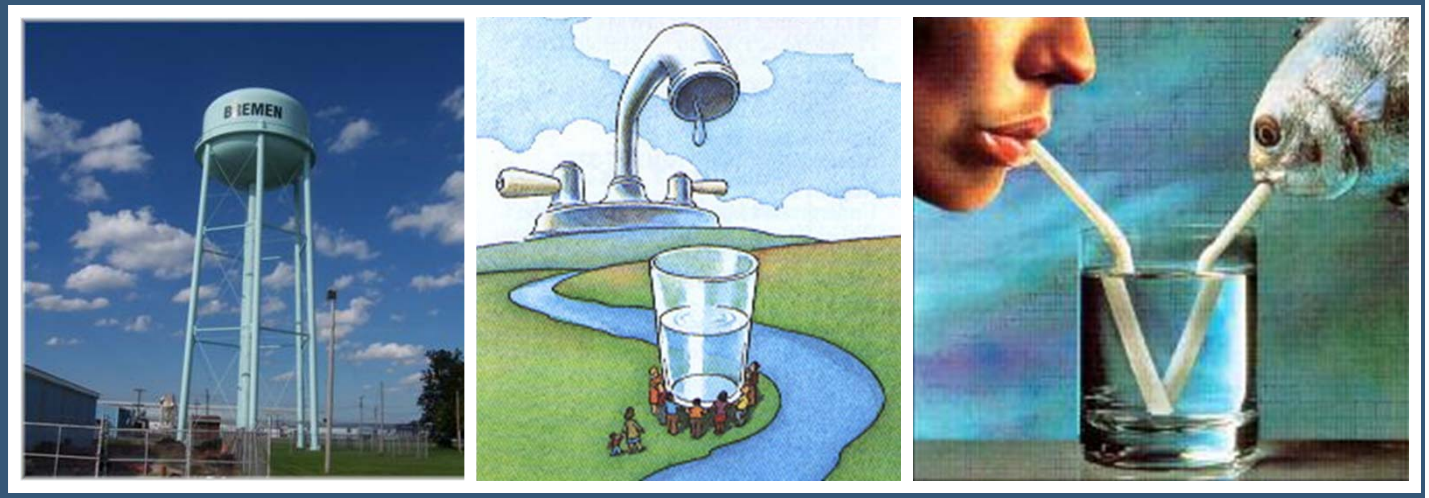
EPA
United States
Environmental Protection
Agency

Wastewater Derived Contaminants of Emerging Concern in the Drinking Water Cycle

Susan Glassmeyer and Jay L. Garland



Office of Research and Development
National Exposure Research Laboratory

EPA United States Environmental Protection Agency

USGS science for a changing world

Disclaimers and Caveats

- ORD (and Jay) does not promulgate regulations and standards.
- ORD (and Jay) does not monitor compliance.
- ORD (and Jay) 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 (Jay) and should not be construed to reflect the views of the Agency.

EPA United States Environmental Protection Agency

USGS science for a changing world

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.

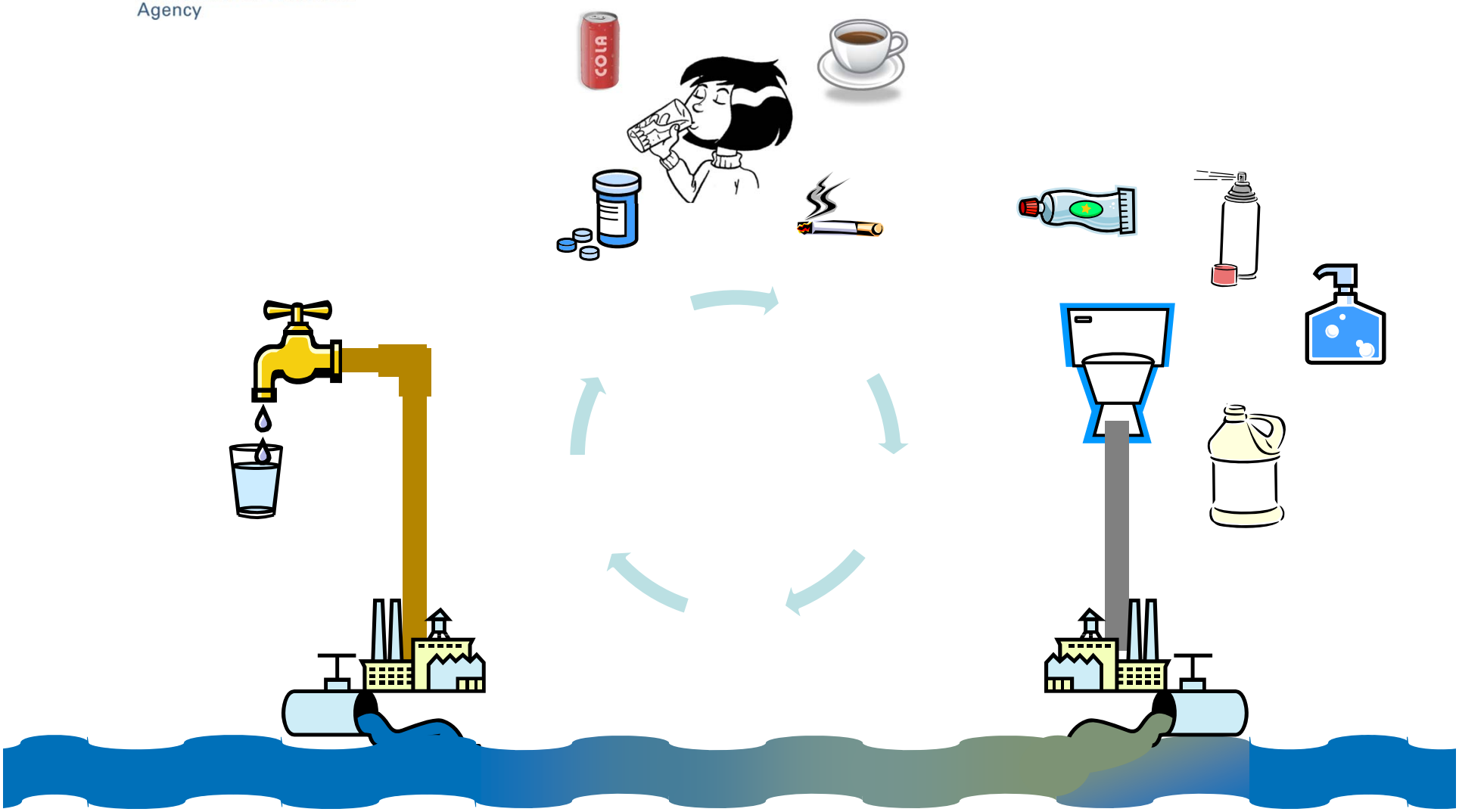
Co-Authors

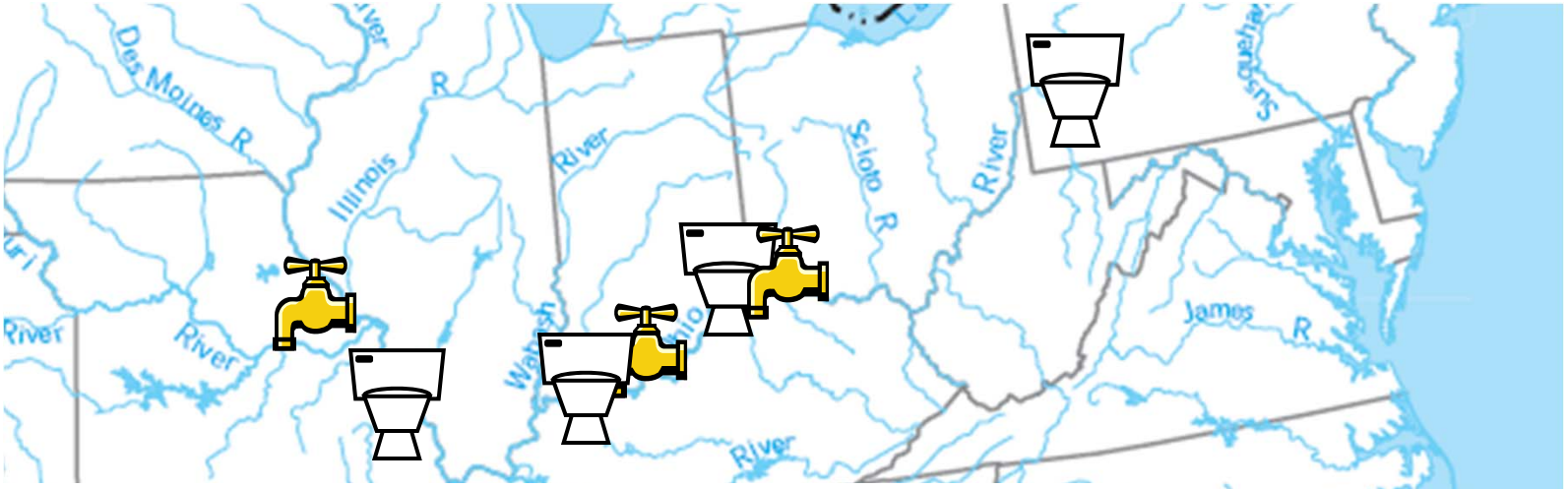
- Susan Glassmeyer
- Edward Furlong
- Dana Kolpin
- Angela Batt
- Bob Benson
- Scott Boone
- Octavia Conerly
- Maura Donohue
- Dawn King
- Mitch Kostich
- Heath Mash
- Stacy Pfaller
- Kathleen Schenck
- Jane Ellen Simmons
- Eunice Varughese
- Stephen Vesper
- Eric Villegas
- Vickie Wilson

Overview of Presentation

- Introduction to CECs
- National study of CECs in Source/Treated Drinking Water
  - Quality Assurance/ Quality Control (QA/QC)
  - Detection Frequency
  - Concentration Trends
- Perfluorinated compounds (PFCs)
- Mycobacteria

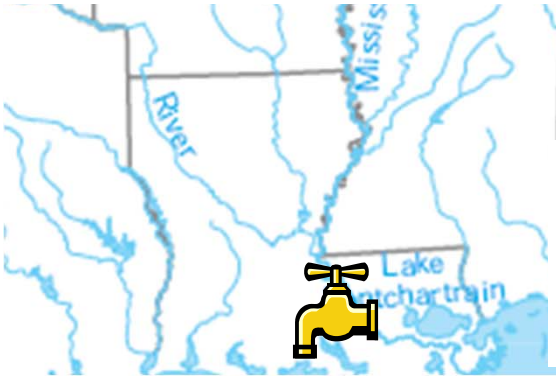
CECs and the Water Cycle





1980 USEPA survey found 20 communities (>7 million people) with drinking water source water containing 2.3-16% wastewater during average flow

(EPA-600/2-80-044)



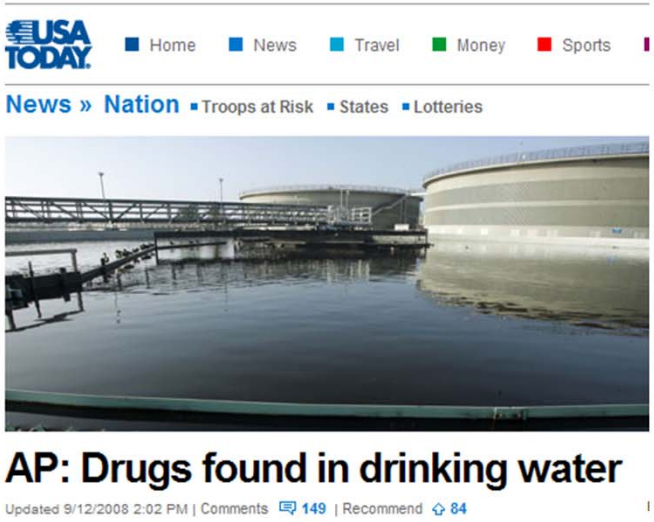
"The best wine is the oldest, the best water the newest."

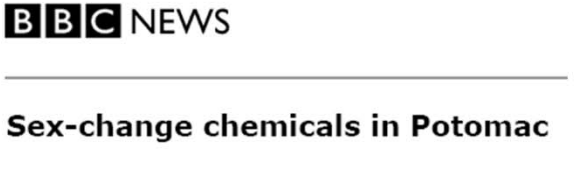
—William Blake (1757-1827)

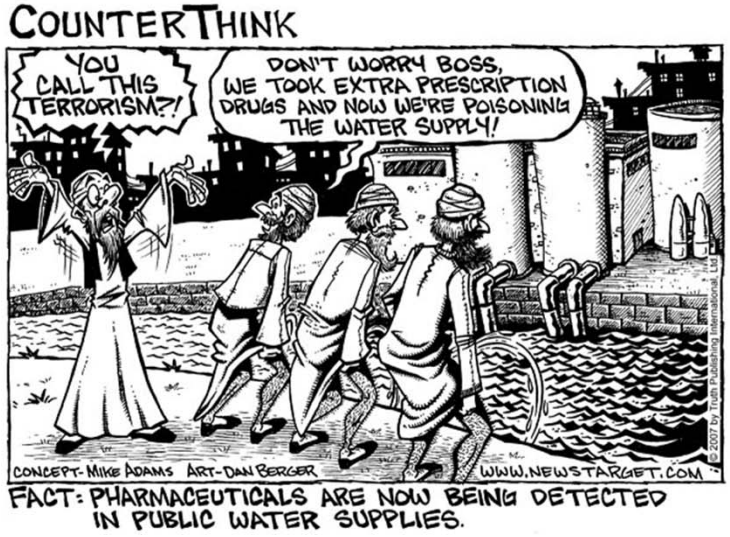
Public Awareness of CECs

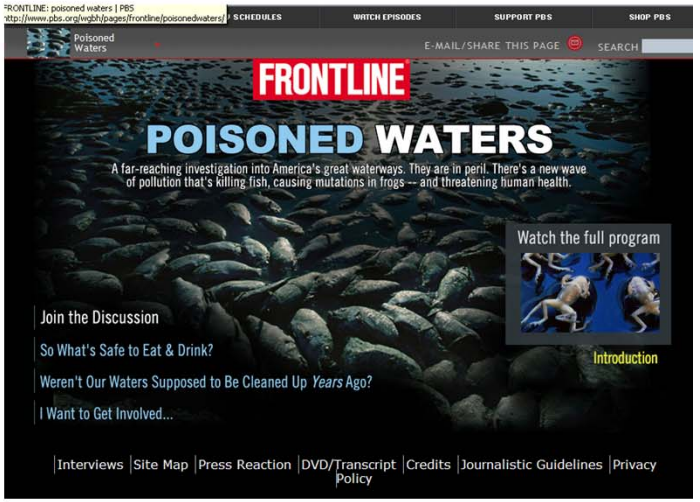
EPA United States Environmental Protection Agency

USGS science for a changing world



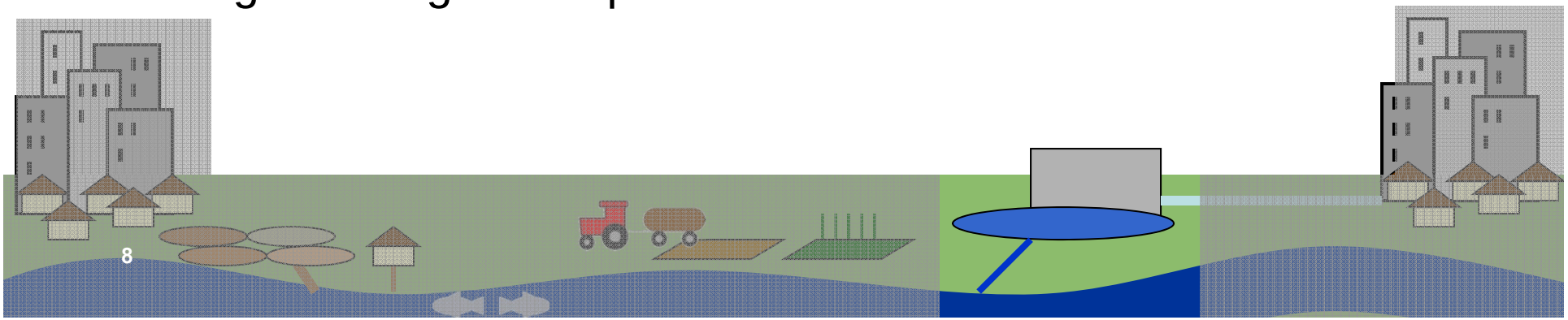






CECs in Untreated and Treated Drinking Water

- Source and treated drinking water pairs from 25 locations
- 249 chemical and microbial analytes
- 52 compounds by 2, 3 or 4 different methods (305 measurements in total)
- Duplicate, laboratory fortified matrix (spike) and field blank collected at each location
- ~ 70% of analyses were QA/QC samples
- Bioassay for estrogenic activity
- Human health margin of exposure assessment
- Ecological margin of exposure assessment

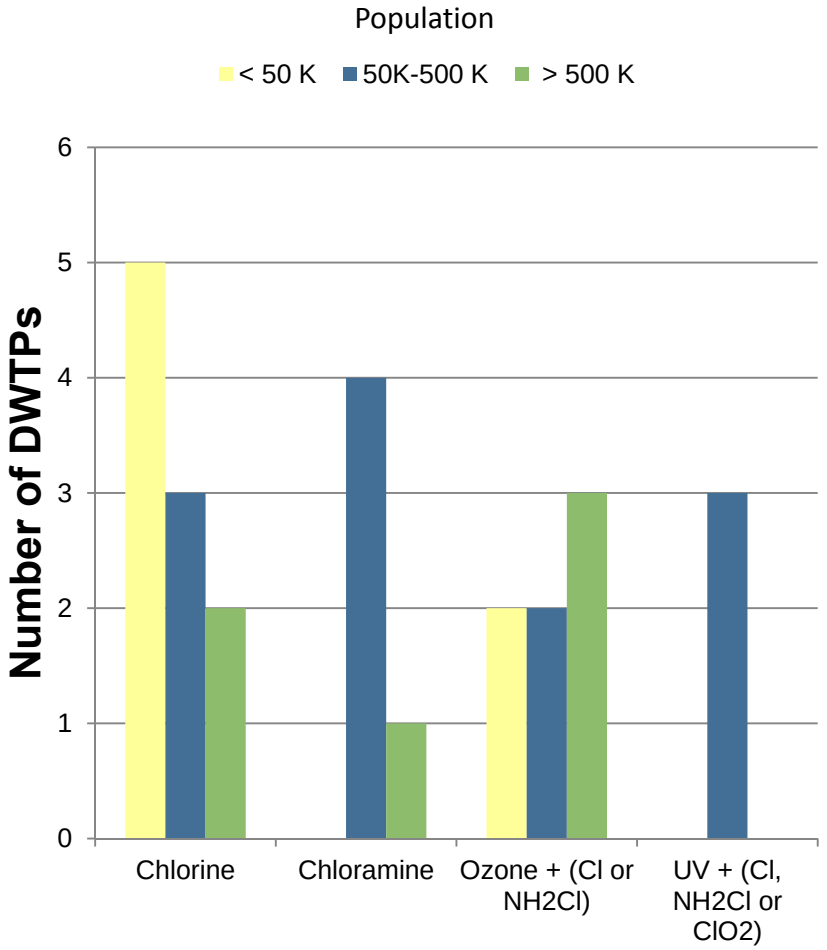


Phase II- 249 Analytes

- 112 prescription and nonprescription pharmaceuticals and their metabolites
- 40 metallic and nonmetallic trace elements
- 17 perfluorinated compounds
- 11 industrial chemicals
- 10 fragrances
- 9 polycyclic aromatic hydrocarbons
- 9 hormones
- 8 pesticides
- 7 detergent-related chemicals
- 5 household chemicals
- 5 viruses
- 4 bacteria
- 4 plant and animal sterols
- 3 phosphorous-based flame retardants
- 3 fungi
- 2 protozoa

Phase II Location Information

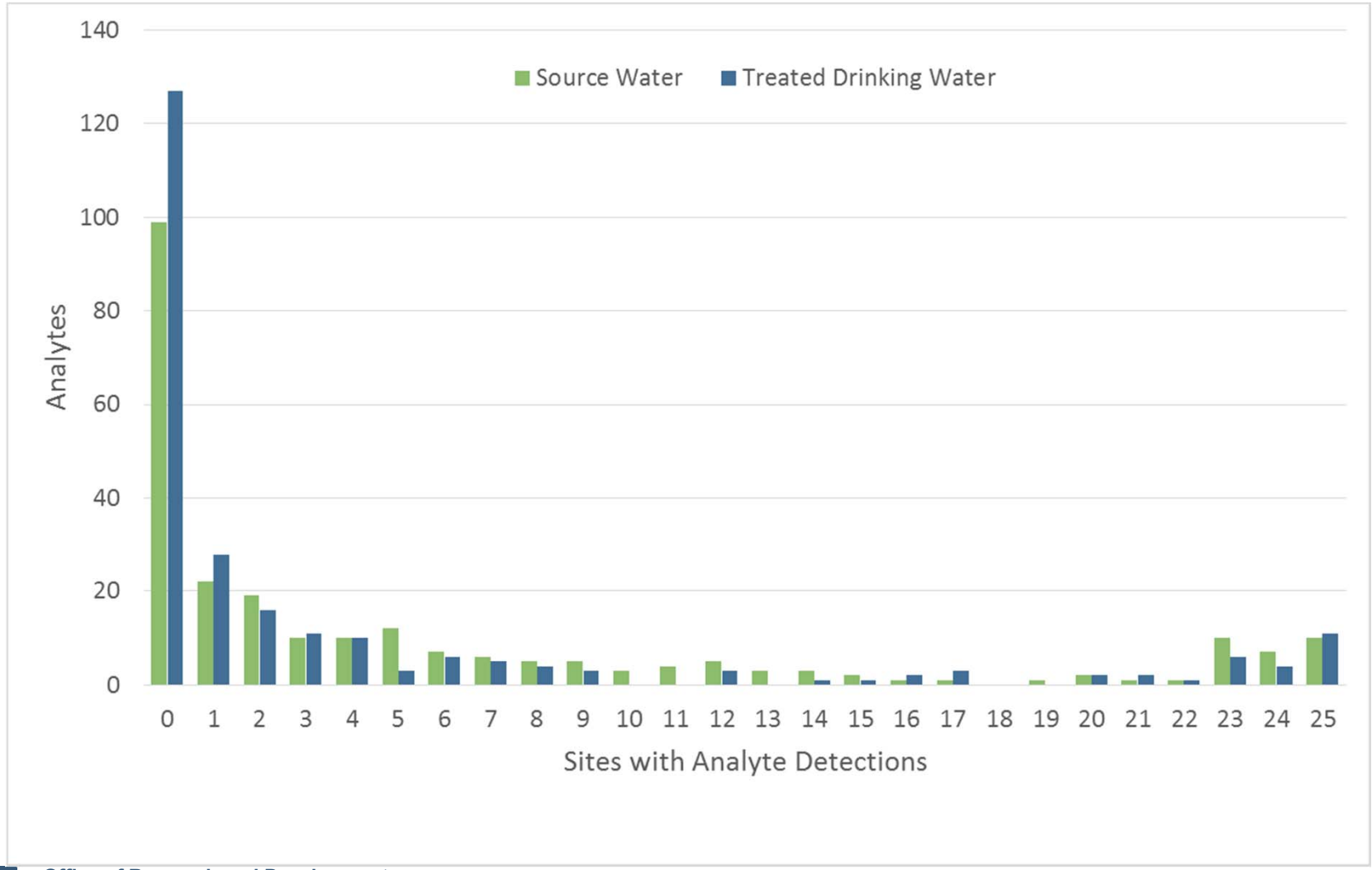
Number of Phase II sampling sites in each USEPA Region



A Note about QA/QC

- Analyte was considered as a QUALITATIVE detection if
  - Detection was above the instrument detection limit but below the lowest concentration minimal reporting limit (LCMRL) or reporting limit (RL)
  - Associated laboratory fortified matrix (LFM aka matrix spike) was > 150% recovery, suggesting matrix enhancement
  - Analyst expertise not confident in quantified detection
- Analyte was CENSORED if
  - Individual detection censored if concentration not greater than three times associated laboratory and field blanks
  - All analyte detections censored if LFMs and laboratory fortified blanks (LFB; aka lab spikes) did not have a median recovery greater than 50 %

Qualitative Frequency of Detection



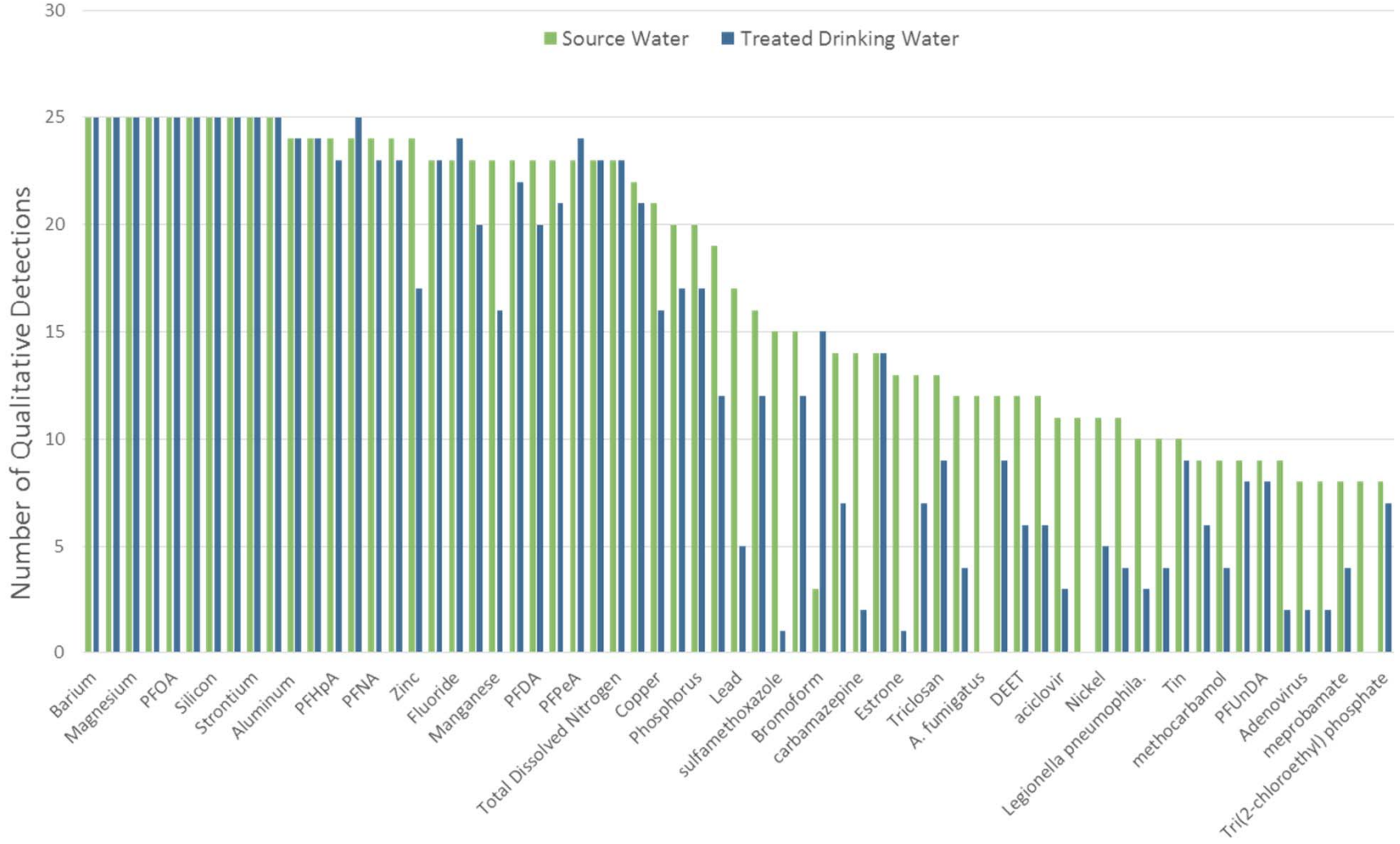
Common (Qual n ≥ 8) Source Water CECs

- Barium
- Calcium
- Magnesium
- PFBS
- PFOA
- Potassium
- Silicon
- Sodium
- Strontium
- Sulfur
- Aluminum
- Nitrate
- PFHpA
- PFHxA
- PFNA
- PFOS
- Zinc
- Chloride
- Fluoride
- Iron
- Manganese
- PFBA
- PFDA
- PFHxS
- PFPeA
- Sulfate
- Total Dissolved Nitrogen
- Atrazine
- Copper
- Phosphate
- Phosphorus
- Bromide
- Lead
- Ammonia
- Sulfamethoxazole
- Uranium
- Arsenic
- Carbamazepine
- Lithium
- Estrone
- Metoprolol
- Triclosan
- 3,4,4'-Trichloro carbanalide
- *A. fumigatus*
- Benzotriazole methyl-1H
- N,N-diethyl-meta-toluamide (DEET)
- Nitrite
- Aciclovir
- *Giardia*
- Nickel
- Vanadium
- *Legionella pneumophila*
- Metformin
- Tin
- Galaxolide (HHCB)
- Methocarbamol
- Metolachlor
- PFUnDA
- Tri(2-butoxyethyl) phosphate
- Adenovirus
- Caffeine
- Meprobamate
- Tramadol
- Tri(2-chloroethyl) phosphate

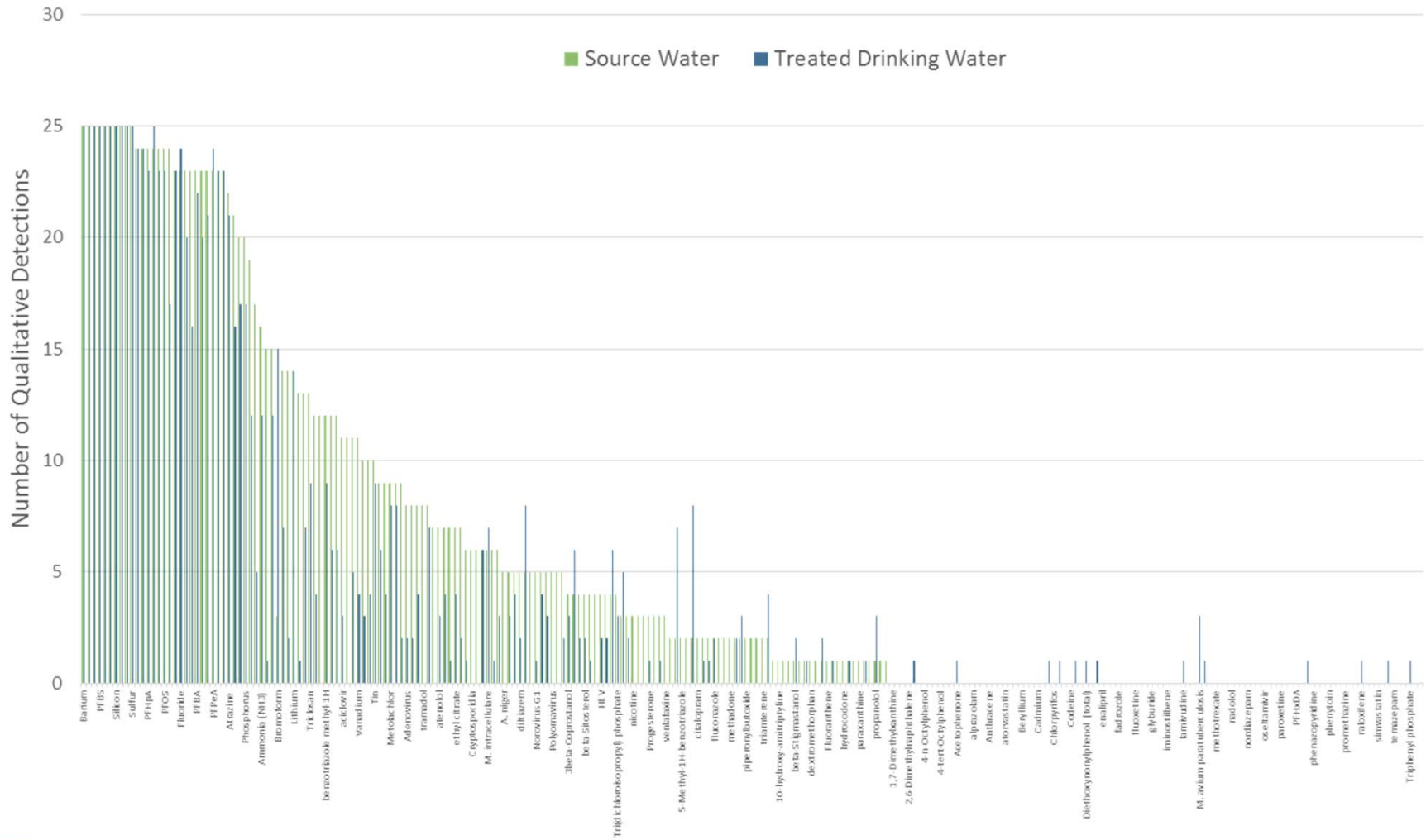
Common (Qual n ≥ 8) Treated Water CECs

- Barium
- Calcium
- Magnesium
- PFBS
- PFHxA
- PFOA
- Potassium
- Silicon
- Sodium
- Strontium
- Sulfur
- Aluminum
- Fluoride
- Nitrate
- PFPeA
- Chloride
- PFHpA
- PFNA
- PFOS
- Sulfate
- Total Dissolved Nitrogen
- PFBA
- Atrazine
- PFHxS
- Iron
- PFDA
- Phosphate
- Phosphorus
- Zinc
- Copper
- Manganese
- Bromoform
- Lithium
- Ammonia
- Bromide
- Uranium
- Benzotriazole methyl-1H
- Tin
- Triclosan
- Chlorate
- Isophorone
- Metolachlor
- PFUnDA

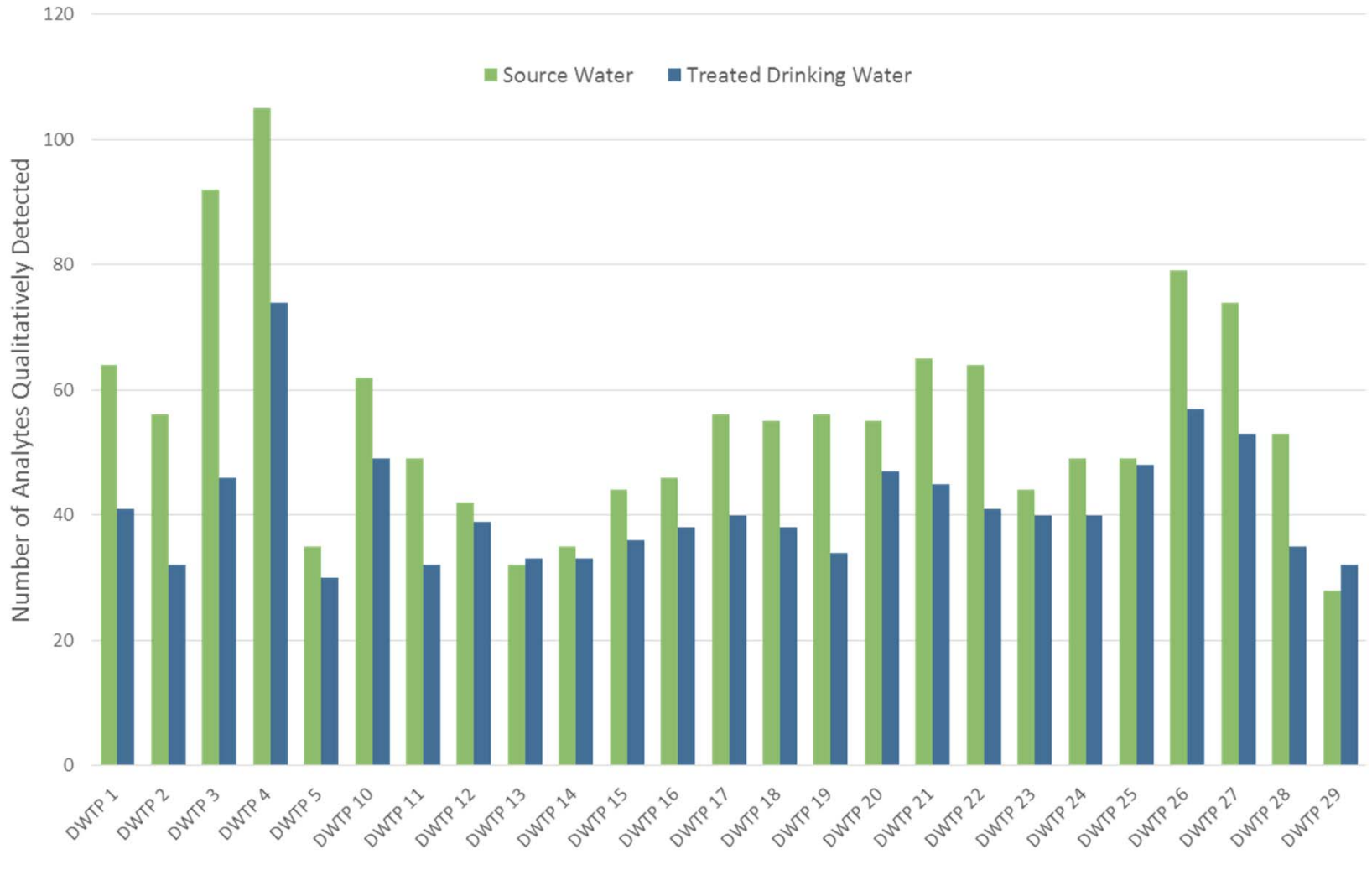
Qualitative Frequency of Detection



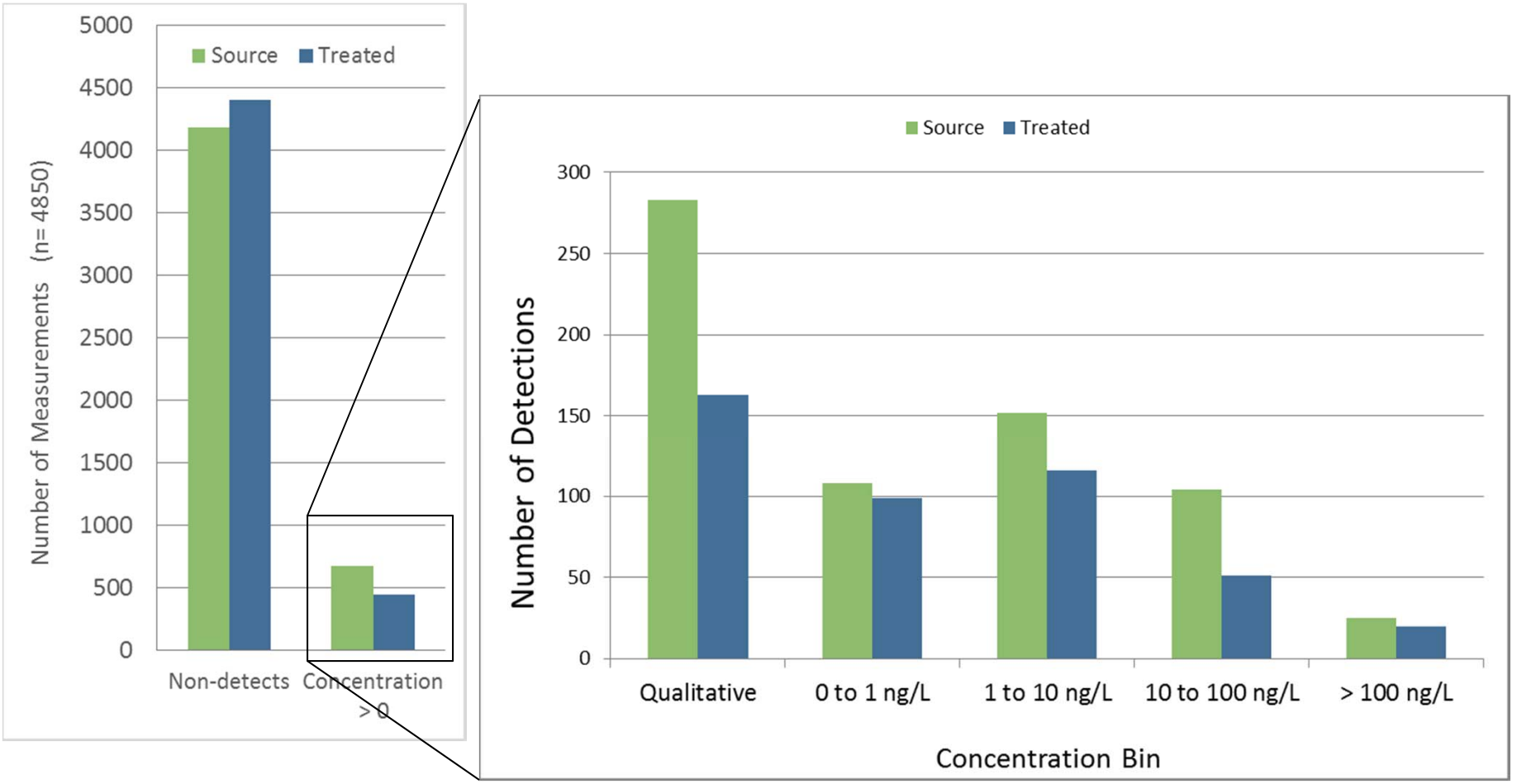
Qualitative Frequency of Detection



Detections by Location

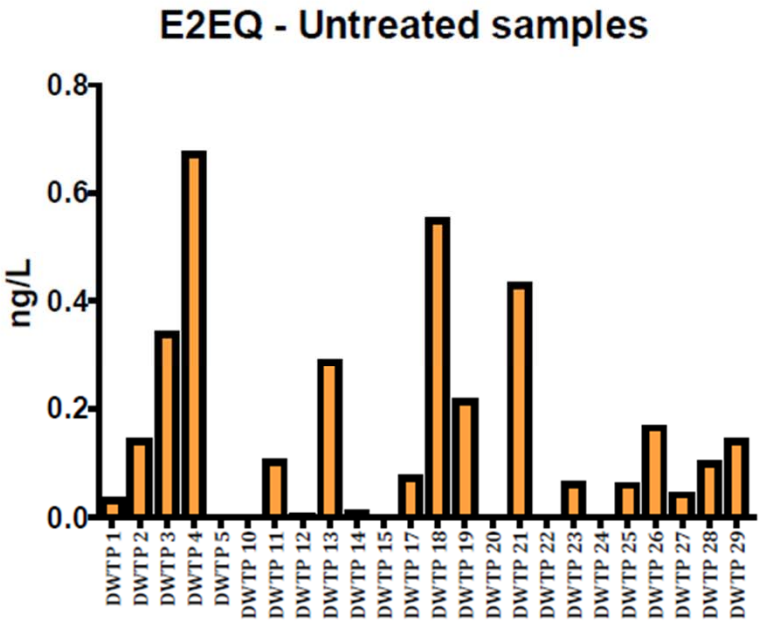


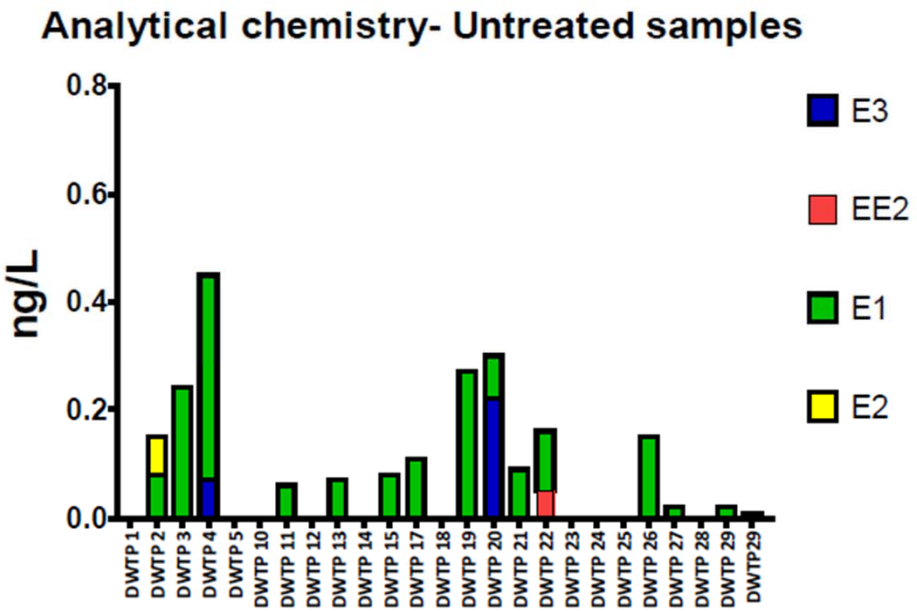
Organic Chemicals Concentration Ranges



Comparison of Measured Concentrations to Bioassay

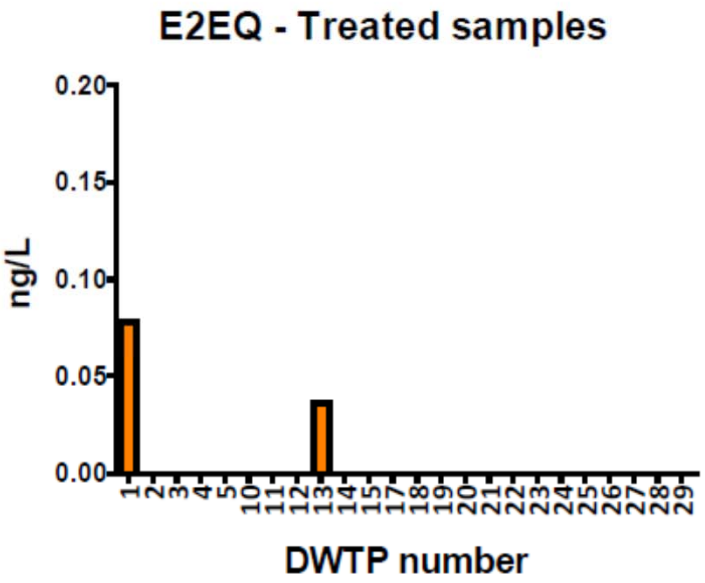
Source water (Untreated water) samples

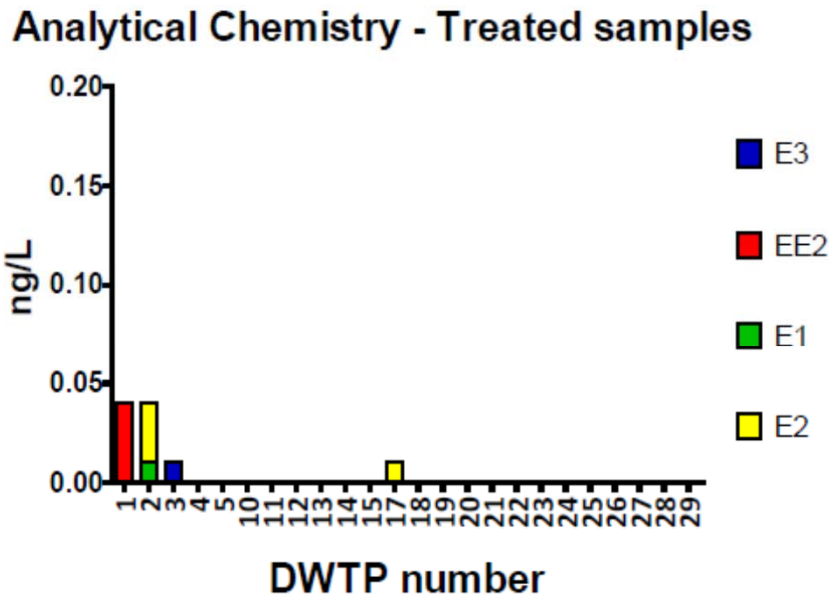




Comparison of Measured Concentrations to Bioassay

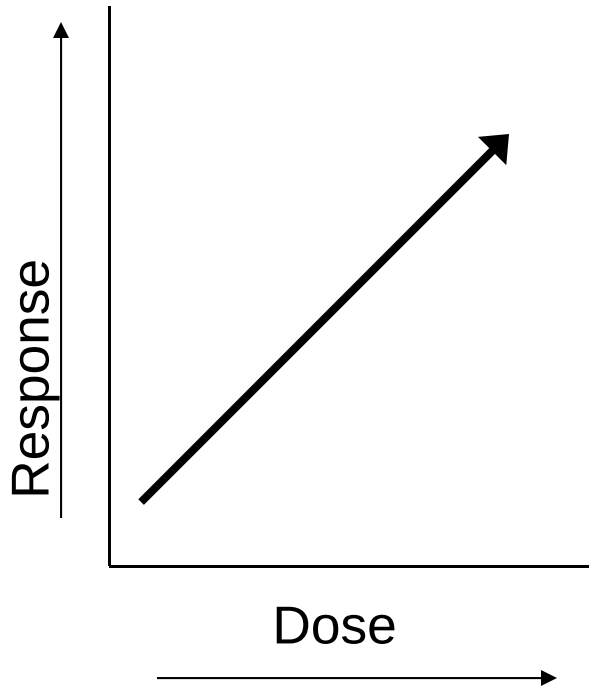
Treated samples



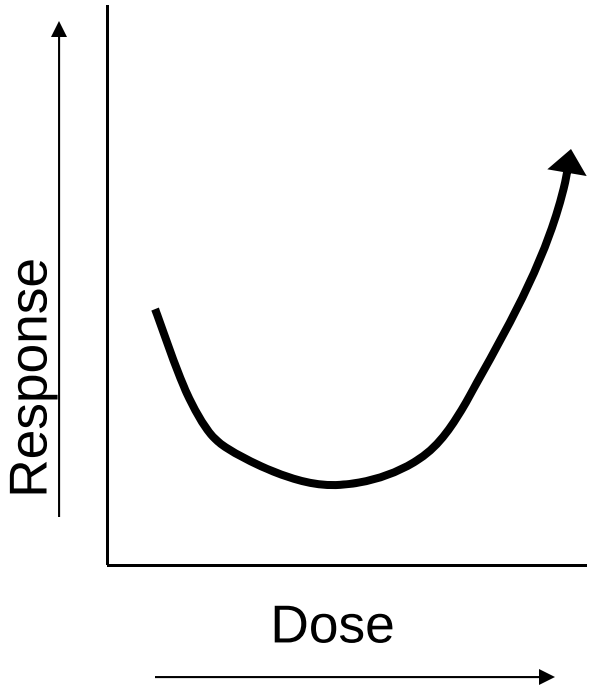


Dose-Response Curves

Monotonic



Non-Monotonic



Examples of Non-Monotonic Dose Response Curves

United States Environmental Protection Agency

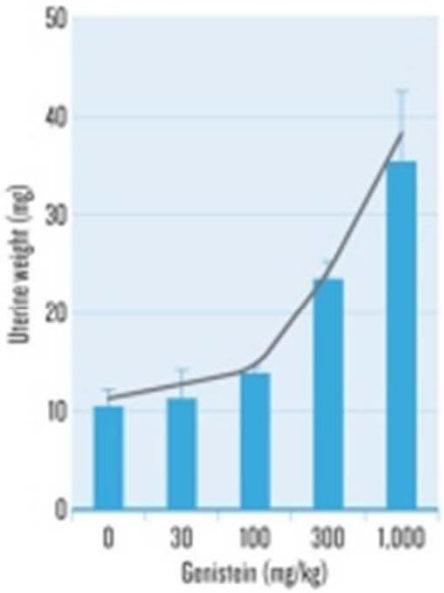
USGS science for a changing world

CURIOUS CURVES

Researchers have found that many endocrine-disrupting chemicals do not generate the standard monotonic dose-response curves seen for other types of compound.

MONOTONIC CURVE

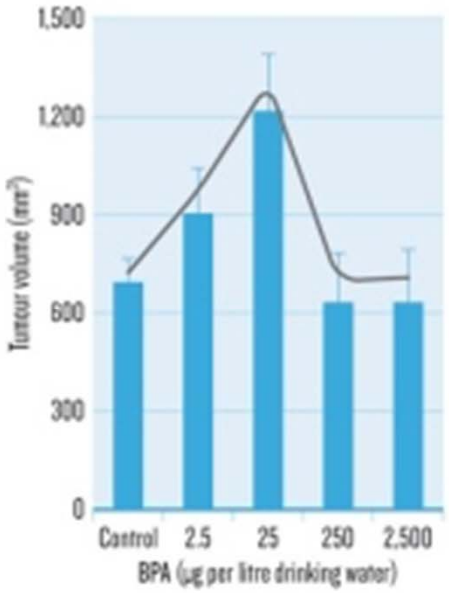
In some cases, dose and response increase together. The plant oestrogen genistein, for instance, causes the mouse uterus to increase in weight.



SOURCE: Ohto, R. *et al. J. Toxicol. Sci.* **37**, 879–889 (2012)

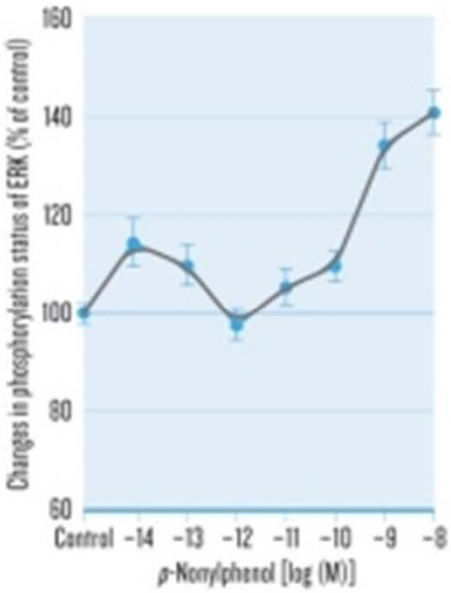
NON-MONOTONIC CURVES

Mice exposed to moderate doses of bisphenol A develop the largest tumours. Moderate and high doses are thought to induce tumour-cell proliferation, but high doses also trigger cell death.



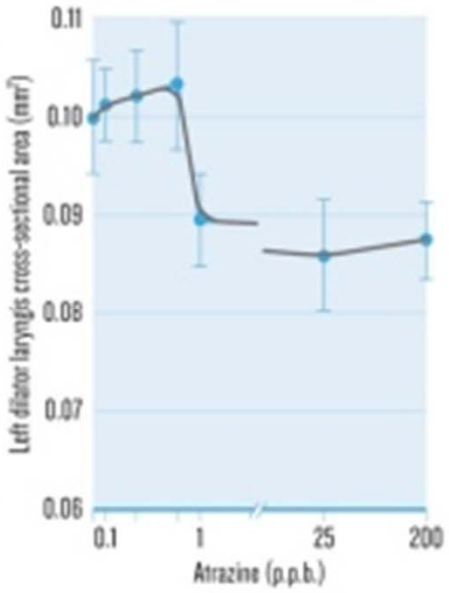
SOURCE: Jenkins, S. *et al. Environ. Health Perspect.* **119**, 1604–1609 (2011)

The oestrogen mimic *p*-nonylphenol stimulates the ERK cell-signalling pathway at low and high doses. Interactions with hormone receptors and other membrane proteins explain the complex shape of the curve.



SOURCE: Bulayeva, N. N. & Watson, C. S. *Environ. Health Perspect.* **112**, 1481–1487 (2004)

Above a certain dose, the herbicide atrazine causes the larynx muscle to shrink in male frogs. But the effect does not increase at higher doses.

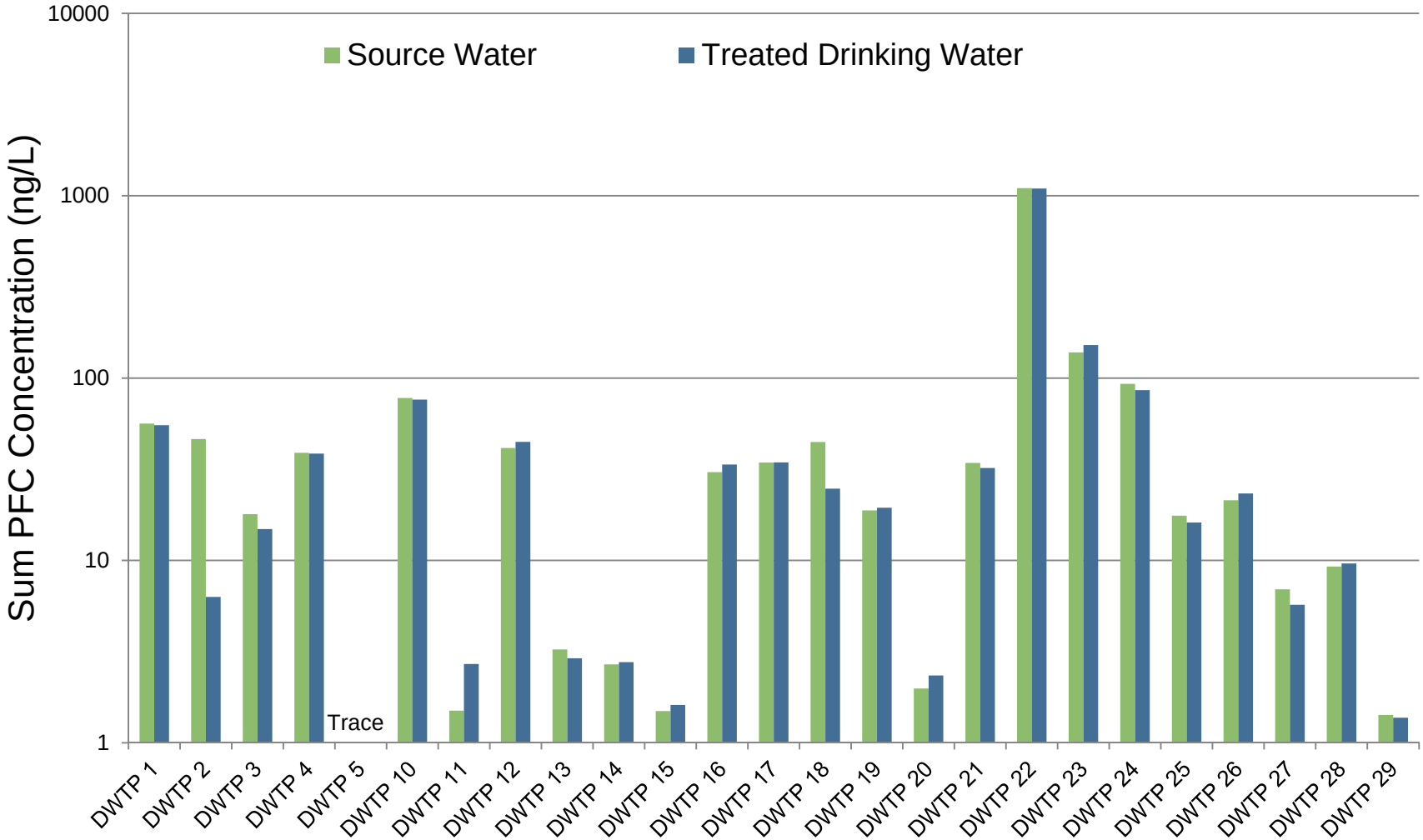


SOURCE: Hayes, T. A. *et al. Proc. Natl Acad. Sci. USA* **99**, 5476–5480 (2002).

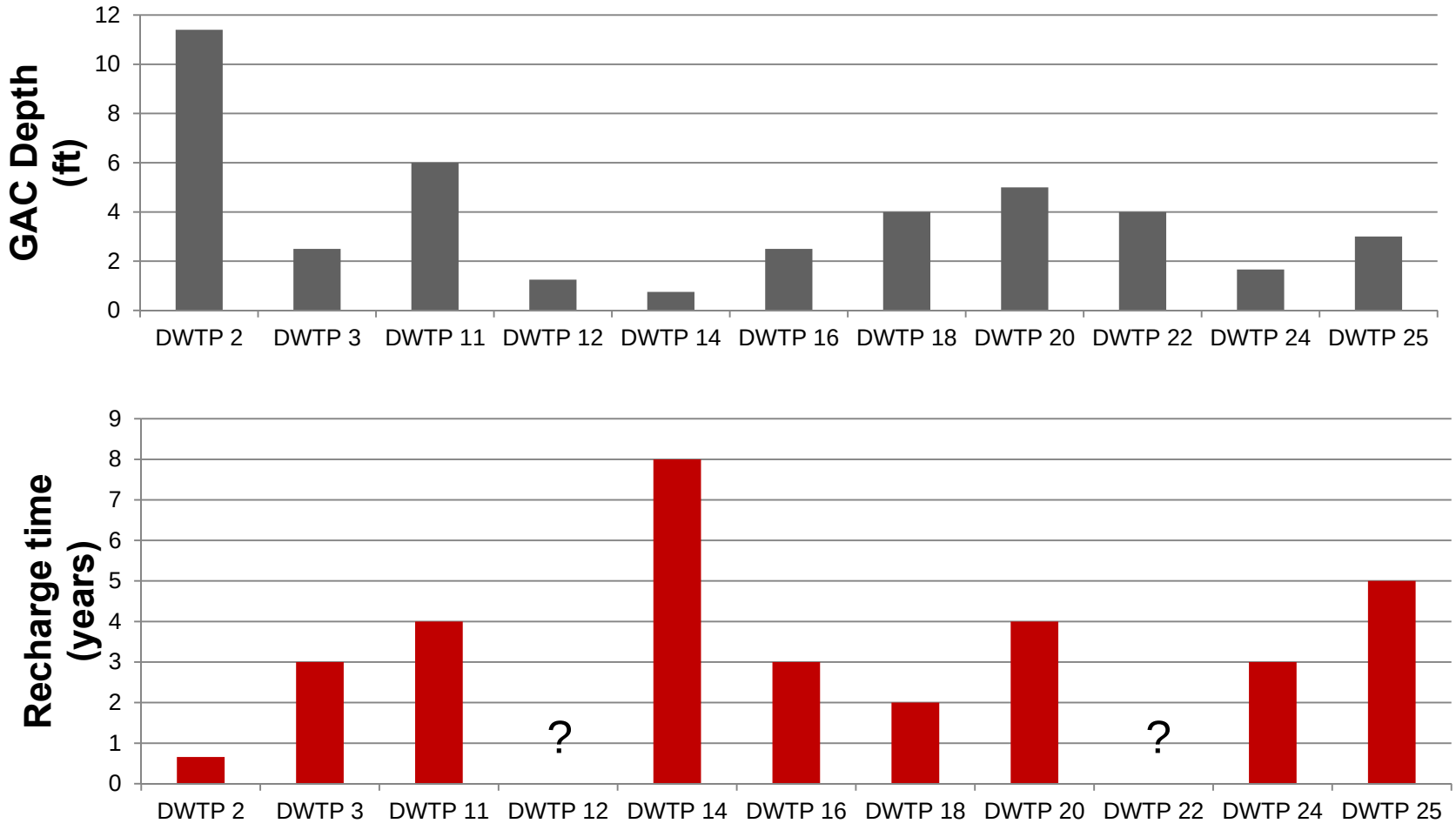
Office of Research and Development
National Exposure Research Laboratory

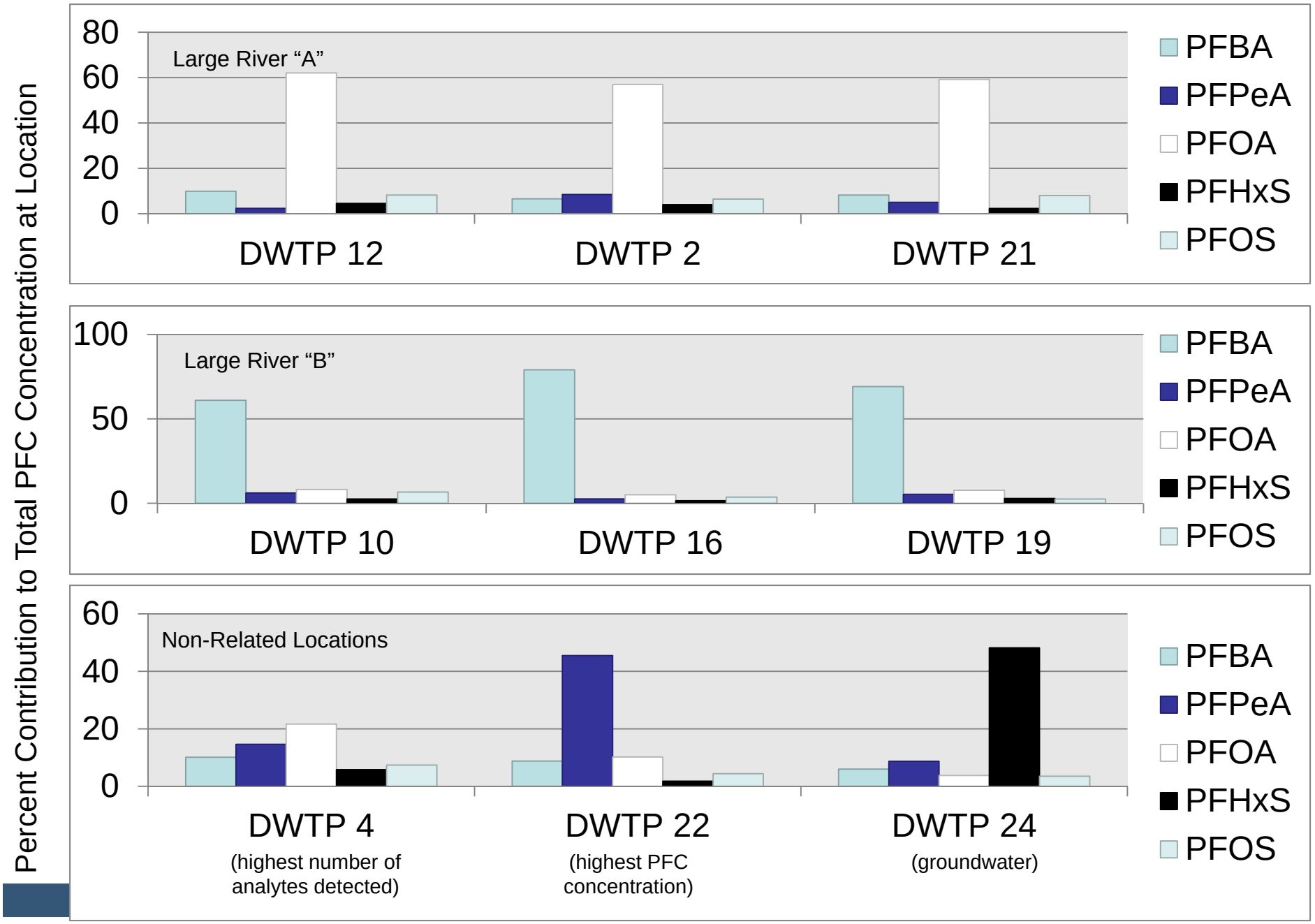
Fagin, Nature 2012

PFC Concentration Trends

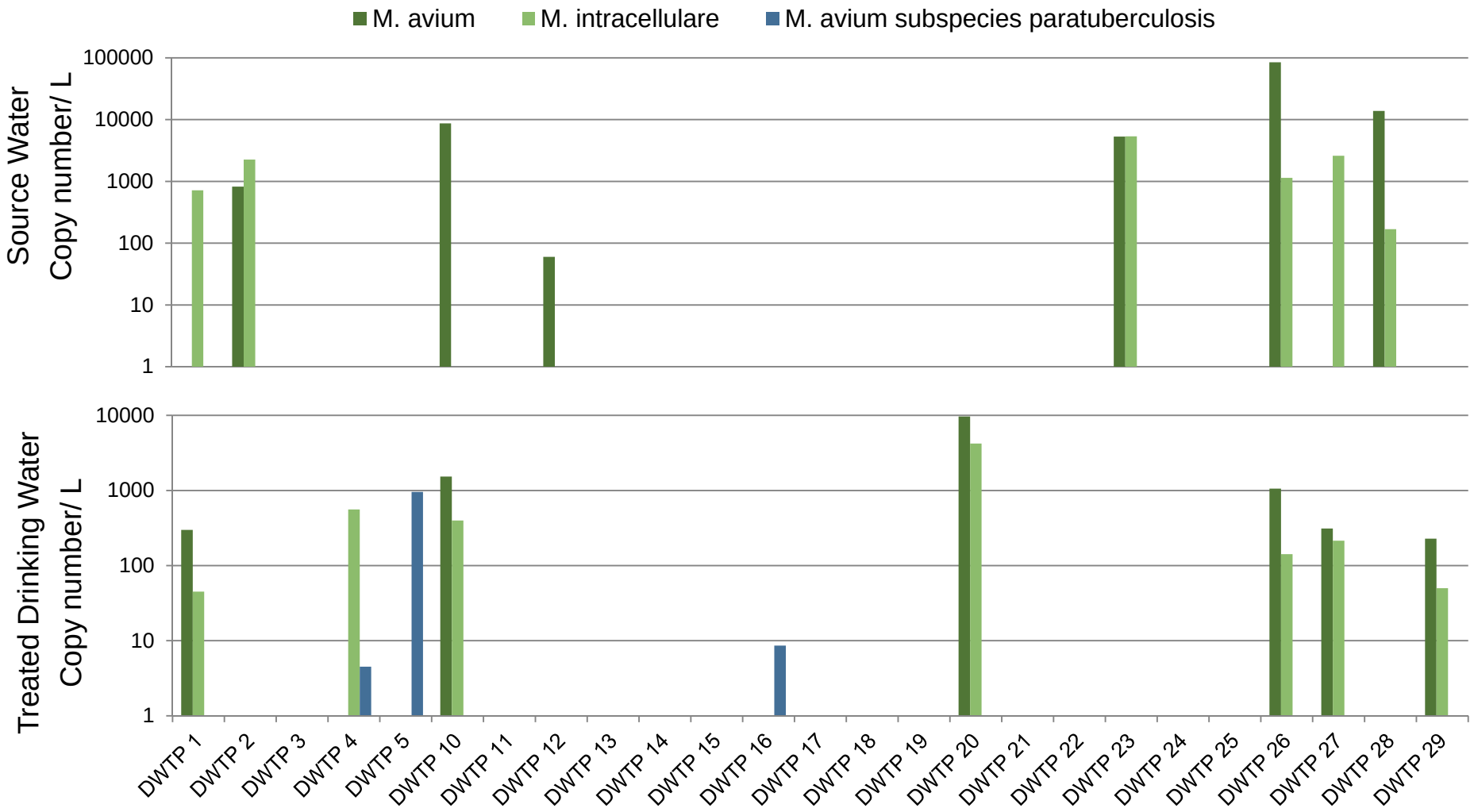


Granular Activated Carbon




Percent Contribution to Total PFC Concentration at Location
80
60
40
20
0
Large River "A"
DWTP 12
DWTP 2
DWTP 21
PFBA
PFPeA
PFOA
PFHxS
PFOS
100
50
0
Large River "B"
DWTP 10
DWTP 16
DWTP 19
PFBA
PFPeA
PFOA
PFHxS
PFOS
60
40
20
0
Non-Related Locations
DWTP 4
(highest number of analytes detected)
DWTP 22
(highest PFC concentration)
DWTP 24
(groundwater)
PFBA
PFPeA
PFOA
PFHxS
PFOS

Mycobacteria



Take Home Messages

- There is no such thing as too much QA/QC.
- Of the 249 analytes measured, 99 were never detected in the source water samples; 127 were never detected in the treated drinking water samples.
- Most of the concentrations of detected organic chemicals were <10 ng/L.
- More research is needed on the toxicity associated with environmentally relevant concentrations of CECs.
- PFC removal during drinking water treatment appears to be related to GAC depth and recharge rate.
- QPCR has enhanced mycobacteria analysis, and demonstrates that it is present in distribution system prior to premise plumbing.

Acknowledgements

- The participating drinking water treatment plants!
- Funded through IA DW14922330

- Contact- glassmeyer.susan@epa.gov; 513-569-7526

EPA United States Environmental Protection Agency

USGS science for a changing world

Safe Drinking Water Act (SDWA)

- Protect the public's health by regulating the drinking water supply.
- 1996 amendments included provisions to enhance source water protection in addition to regulating finished drinking water.
- 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 finalized October 2009, listing 116 contaminants (12 microbial and 104 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
    - UCMR3 was finalized May 2012, Sampling period January 2013- December 2015
    - Phase II has 15 UCMR contaminants in the analyte list

EPA United States Environmental Protection Agency

USGS science for a changing world

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.

UCMR v. Phase II PFC Methods

Criteria	UCMR	Phase II
Intended Use	Potentially Regulatory	Research
Analytes	PFBS, PFHpA, PFHxS, PFNA, PFOS, PFOA	UCMR list + PFBA, PFPeA, PFHxA, PFDA, PFUnDA, PFDoDA, PFTrDa, PFTeDA, PFHxDA, PFOcDA. PFDS
Detection Limit	MRL 10-90 ng/L	LCMRL 0.032-0.56 ng/L

UCMR v. Phase II Data

Analyte	UCMR*			Phase II		
	# Samples	# Detections > MRL	# > Reference Conc**.	# Samples	# Detections > LCMRL	# > Reference Conc.**
PFOS	7411	44	4	25	20	0
PFOA	7411	55	0	25	19	0
PFNA	7411	5	--	25	22	--
PFHxS	7411	29	--	25	21	--
PFHpA	7411	31	--	25	23	--
PFBS	7411	1	--	25	24	--

*Preliminary UCMR 3 data from
http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/upload/epa815s14001.pdf

** Reference Concentrations PFOS 200 ng/L PFOA 400 ng/L