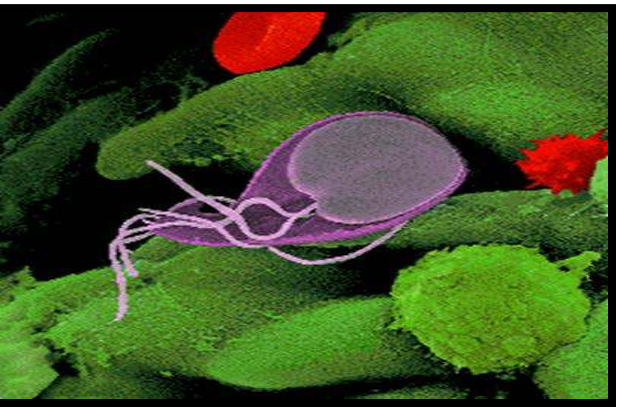
Drinking Water Contaminants:
The Next Generation of Water Safety



ISLI Annual Meeting, San Diego, California – 24th January 2016

Shane Snyder, Ph.D.

Professor: University of Arizona

Visiting Professor: NUS

Editor in Chief: Chemosphere

“We forget that the water cycle and the life cycle are one.”

Jacques Cousteau
1910 - 1997

Energy and Environment

Researchers find unsafe levels of industrial chemicals in drinking water of 6 million Americans

The Washington Post

Charges against 3 in Flint water crisis 'only the beginning'

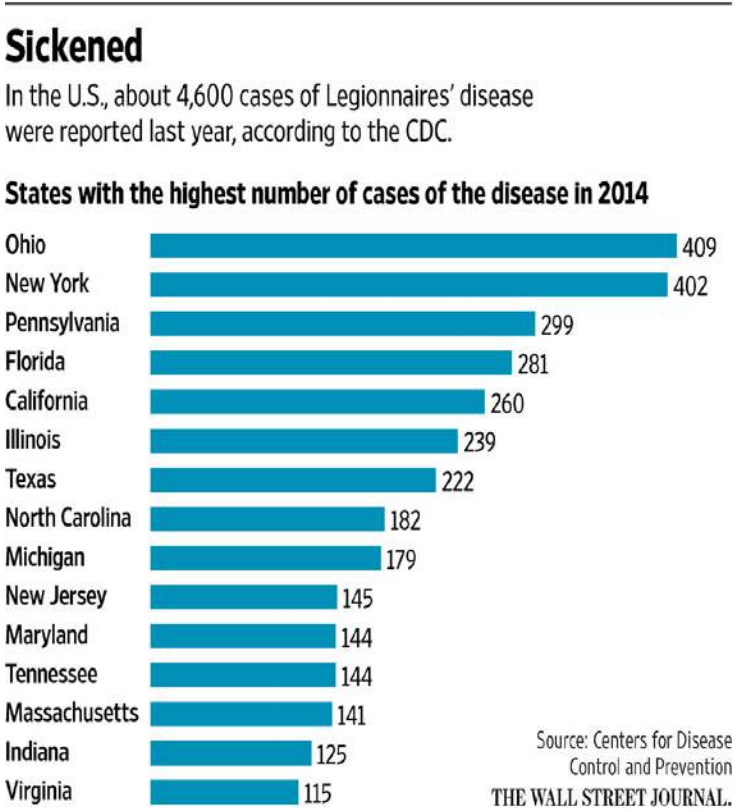
Wed April 20, 2016

CNN

THE WALL STREET JOURNAL.

By CORINNE RAMEY
Aug. 4, 2015 8:46 p.m. ET

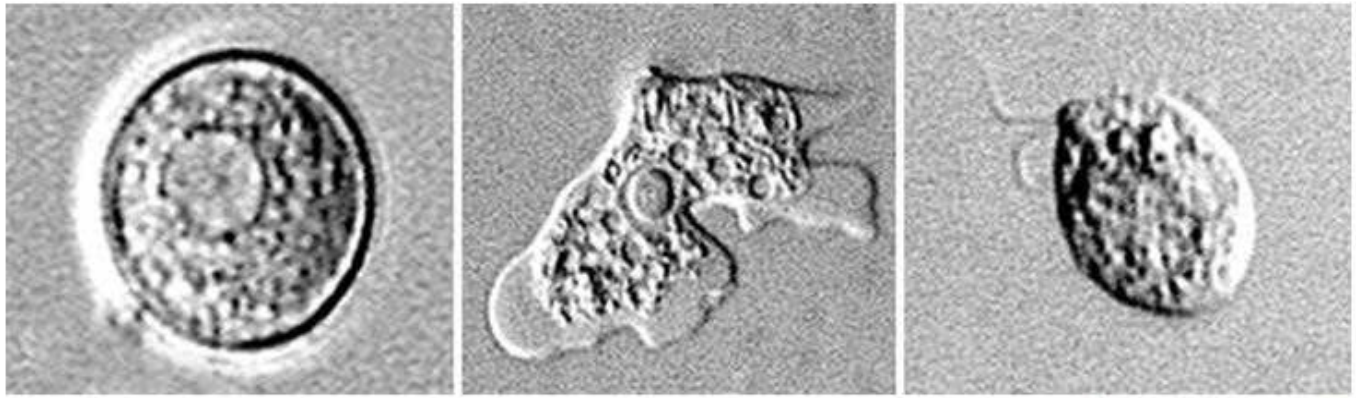
NEW YORK—An outbreak of Legionnaires' disease in the Bronx has killed seven people and sickened more than 80 others, the largest outbreak of the bacterial infection in New York City's history and one of the biggest in the U.S. in recent years.



Deadly brain amoeba infects US tap water for the first time

Maggie Fox , NBC News

Sep. 16, 2013 at 4:35 PM ET



Centers for Disease Control and Prevention

The CDC says it's found Naegleria fowleri, an almost always deadly amoeba, in a U.S. drinking water supply for the first time.

A deadly brain amoeba that's killed two boys this year has been found in a U.S. drinking water supply system for the first time, officials said Monday -- in a New Orleans-area system.

October 20, 2006

LAS VEGAS SUN

Chemicals cause changes in fish and raise concerns for humans

By Launce Rake <lrake@lasvegassun.com>

Las Vegas Sun

There's something wrong with the fish.

It's been confounding scientists for years: Male fish are developing female sexual characteristi
Mead and other freshwater sources around the country.

On Thursday, the U.S. Geological Survey released a four-page summary of more than a decad
studies linking wastewater chemicals to those changes.

Water tainted by traces of discarded drugs could upset the delicate dynamics of the marine environment, scientists say.
Bent Christensen, The Associated Press

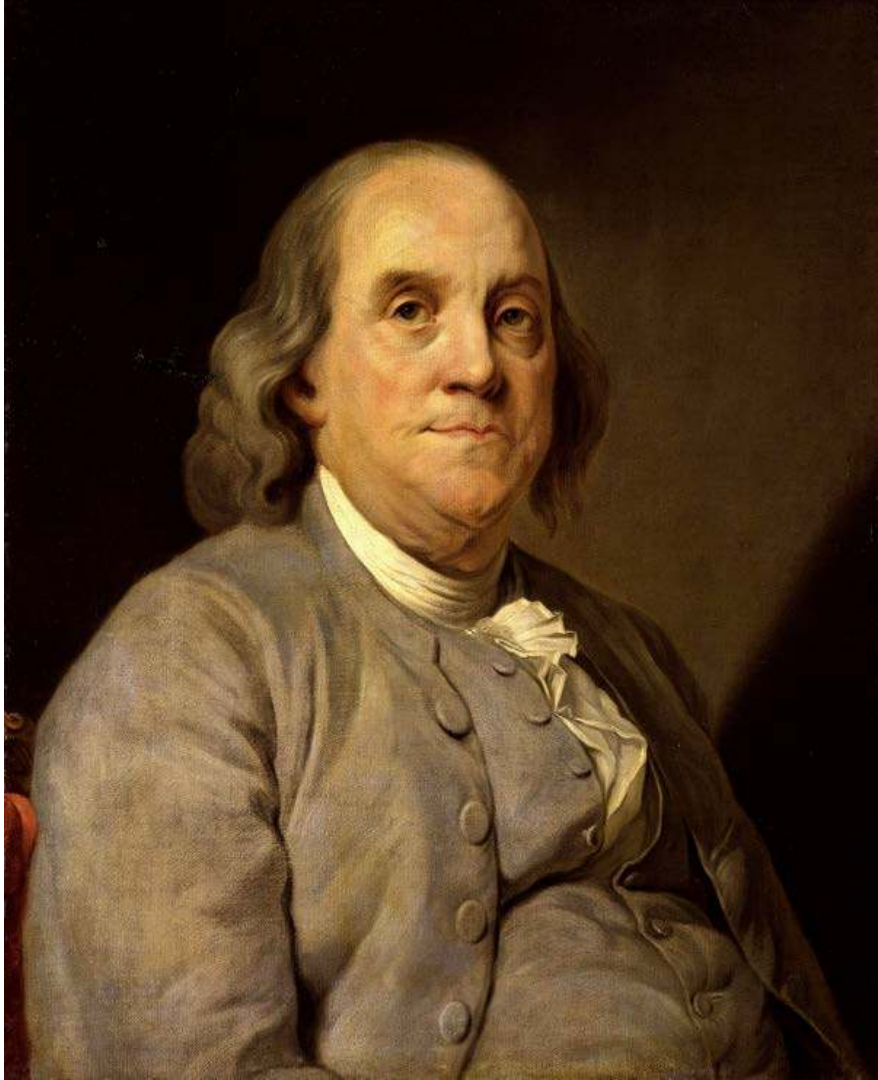
Fish on drugs more likely to drop out of schools, study says

By Brady Dennis *The Washington Post*

What happens to a fish on drugs?

“When the well is dry we know the value of water."

Benjamin Franklin
(1706-1790)

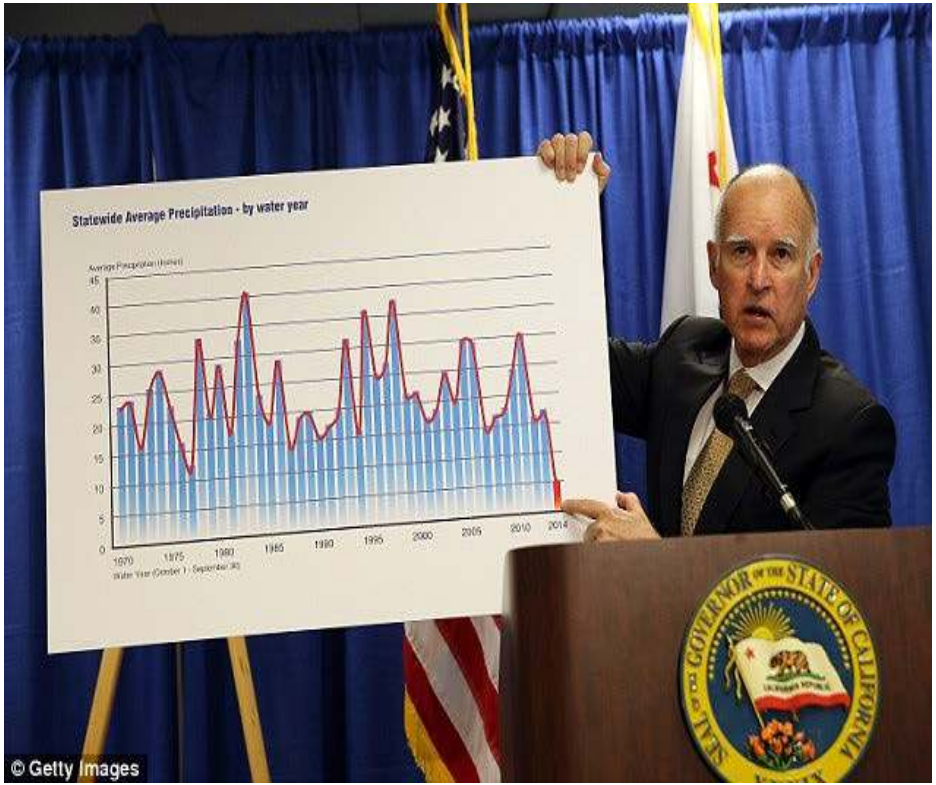


Water Scarce US Cities

10. Orlando
9. Atlanta
8. Tucson
7. Las Vegas
6. Fort Worth
5. San Francisco
4. San Antonio
3. Phoenix
2. Houston
1. Los Angeles

Source: http://247wallst.com/2010/10/29/the-ten-great-american-cities-that-are-dying-of-thirst/3/

Potable Water Reuse



OCT 08 2013

OFFICE OF THE GOVERNOR

To the Members of the California State Senate:

I am signing SB 322 which requires the Department of Public Health in consultation with the State Water Resources Control Board, to investigate the feasibility of developing uniform water recycling criteria for direct potable reuse by September 2016.

This information is past due. In an effort to enhance the use of recycled water, I have proposed the consolidation of the management of the drinking water program and all other water quality programs, including recycled water, under the State Water Board.

I am directing the Water Board to ensure that this work is completed expeditiously. The 3-year time frame mandated in this bill is too slow. California needs more high quality water and recycling is key to getting there.

Sincerely,

Edmund G. Brown Jr.

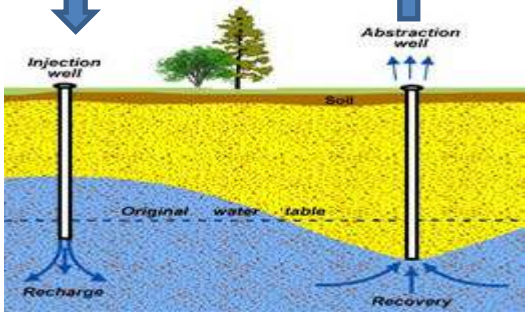
Potable Water Reuse

Alternate Sources of Water to Augment Supplies

"Drought-Proof Resource"

Direct water reuse

Indirect water reuse



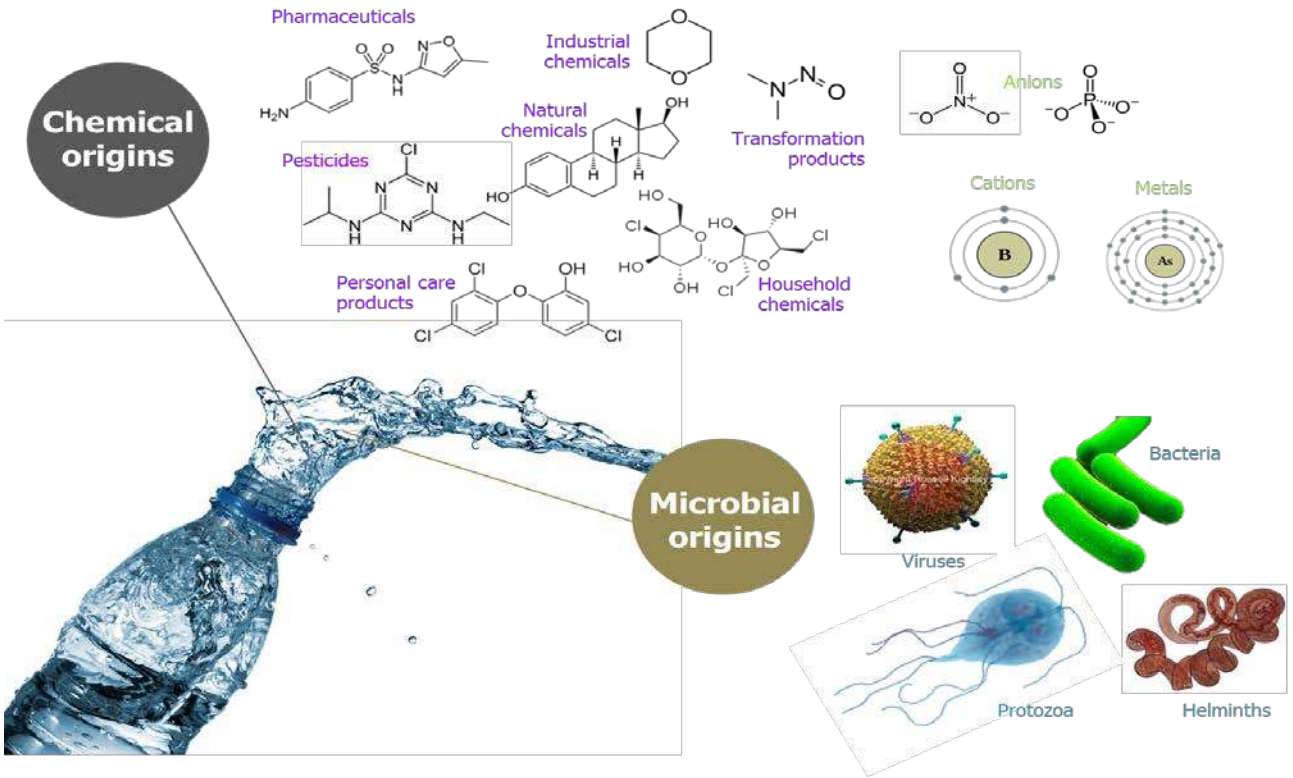
Scientific Perception

Public Perception

“Every policy had to bend to the knees of our water survival”

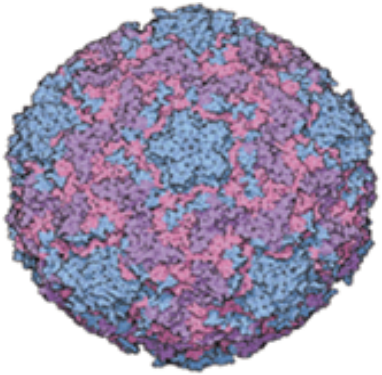
Lee Kuan Yew
(1923-2013)

Potential Contaminants



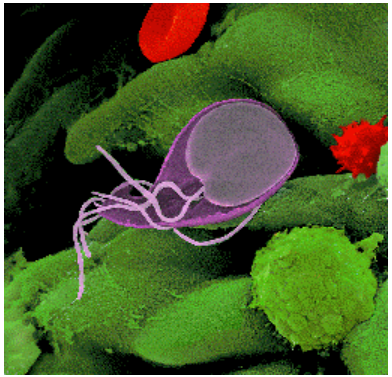
Biologicals are ACUTE Risks

Viruses

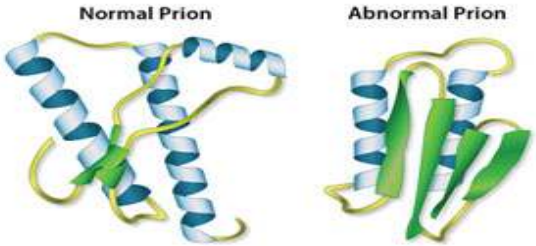


Bacteria

Parasites



Prions



Chemicals are CHRONIC Risks

Organic and Inorganic

Volatile and non-volatile

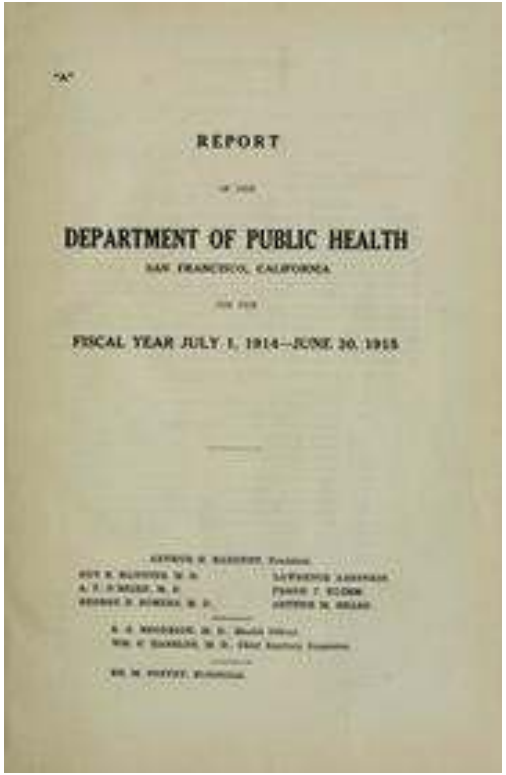
Metals and Salts

1899 – US Rivers and Harbors Act

Required Permit to Discharge Refuge into Navigable Waters or Tributaries.

Also required permit to build dam or alter waterway flow.

1914 & 1962 – Public Health Service

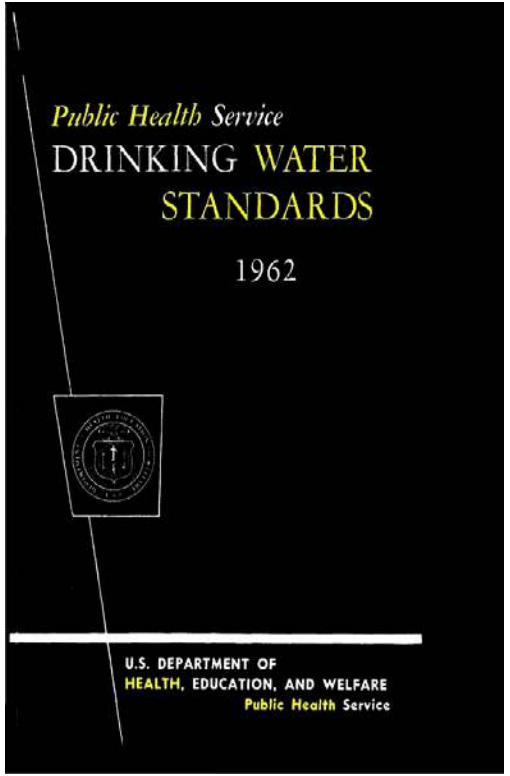

REPORT

DEPARTMENT OF PUBLIC HEALTH

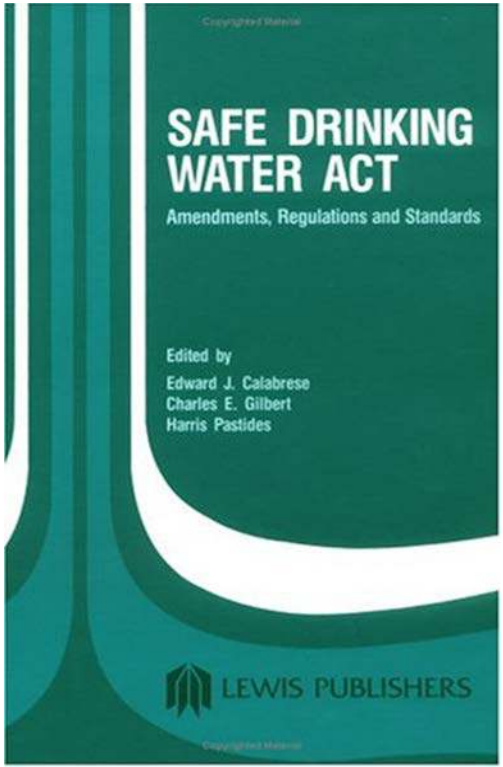
SAN FRANCISCO, CALIFORNIA

FISCAL YEAR JULY 1, 1914—JUNE 30, 1915

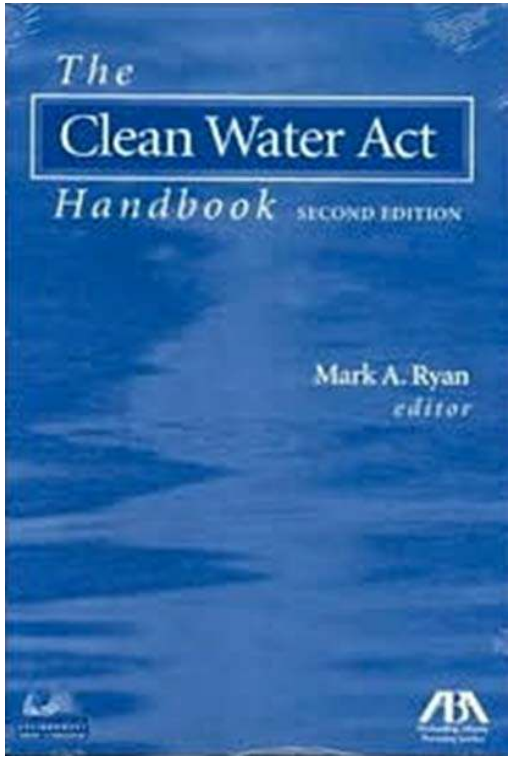
- Monitored coliform bacteria in water
- Metals added in 1925
- Distribution system added in 1942
- Significantly re-written in 1962

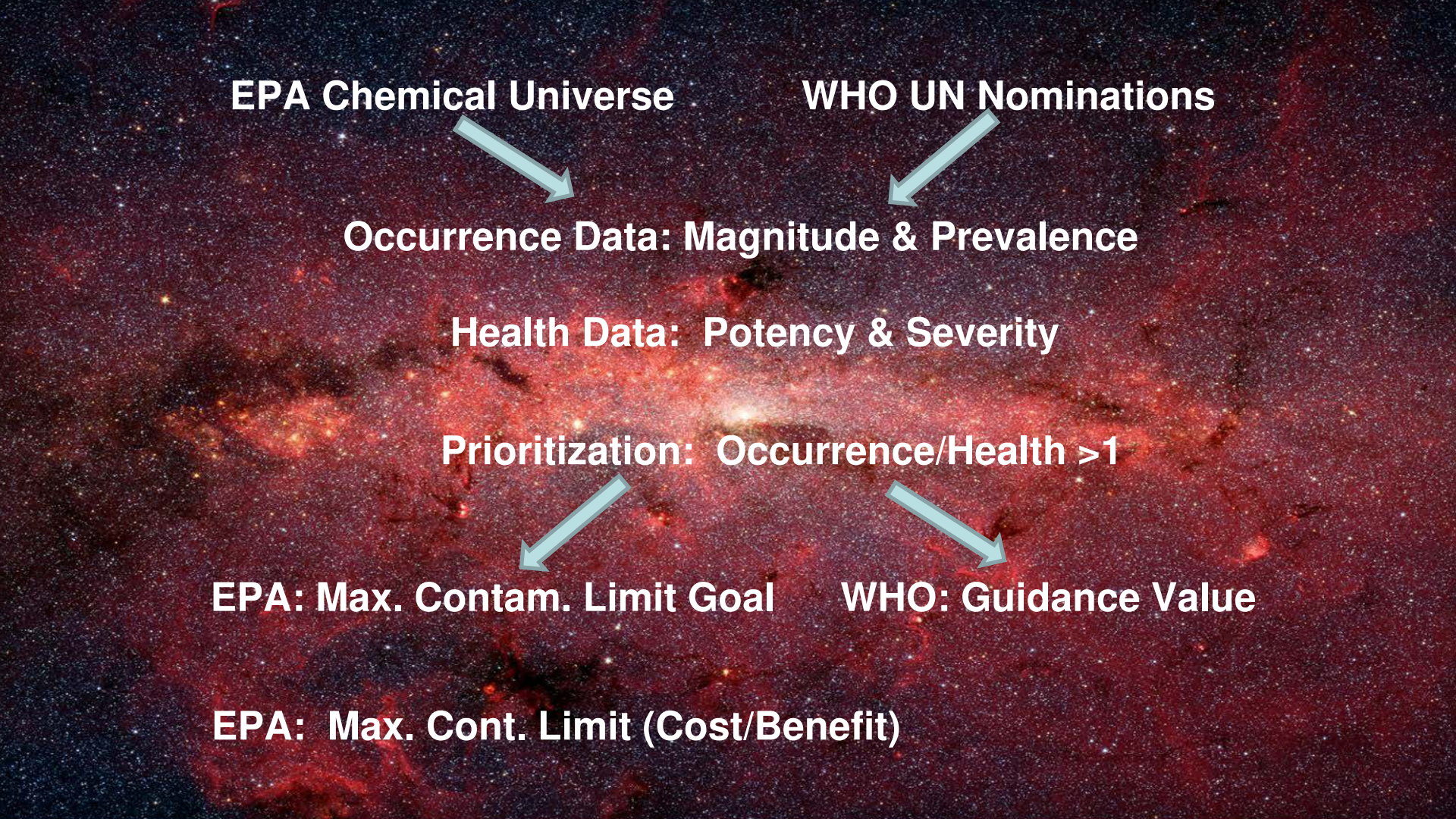


Safe Drinking Water and Clean Water Acts



- **EPA Enforced Regulations (often enforced by states)**
- **SDWA 1972**
  - **MCLs & MCLGs**
- **CWA 1977**
  - **Discharge permits**
  - **Ambient WQ**



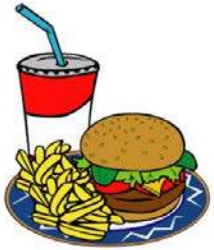

EPA Chemical Universe
WHO UN Nominations
Occurrence Data: Magnitude & Prevalence
Health Data: Potency & Severity
Prioritization: Occurrence/Health >1
EPA: Max. Contam. Limit Goal
WHO: Guidance Value
EPA: Max. Cont. Limit (Cost/Benefit)

Conventional Chemical Paradigm

Uncertainty/Safety Factors (30 – 3,000)

2L/Day

70 Kg



80% Other sources

Magnitude of Potential Occurrence

What was the first synthetic chemical industrially produced?

Mauve – 1856 by Perkin (by accident)

What was the first synthetic pharmaceutical industrially produced?

Aspirin – 1899 by Bayer, Germany

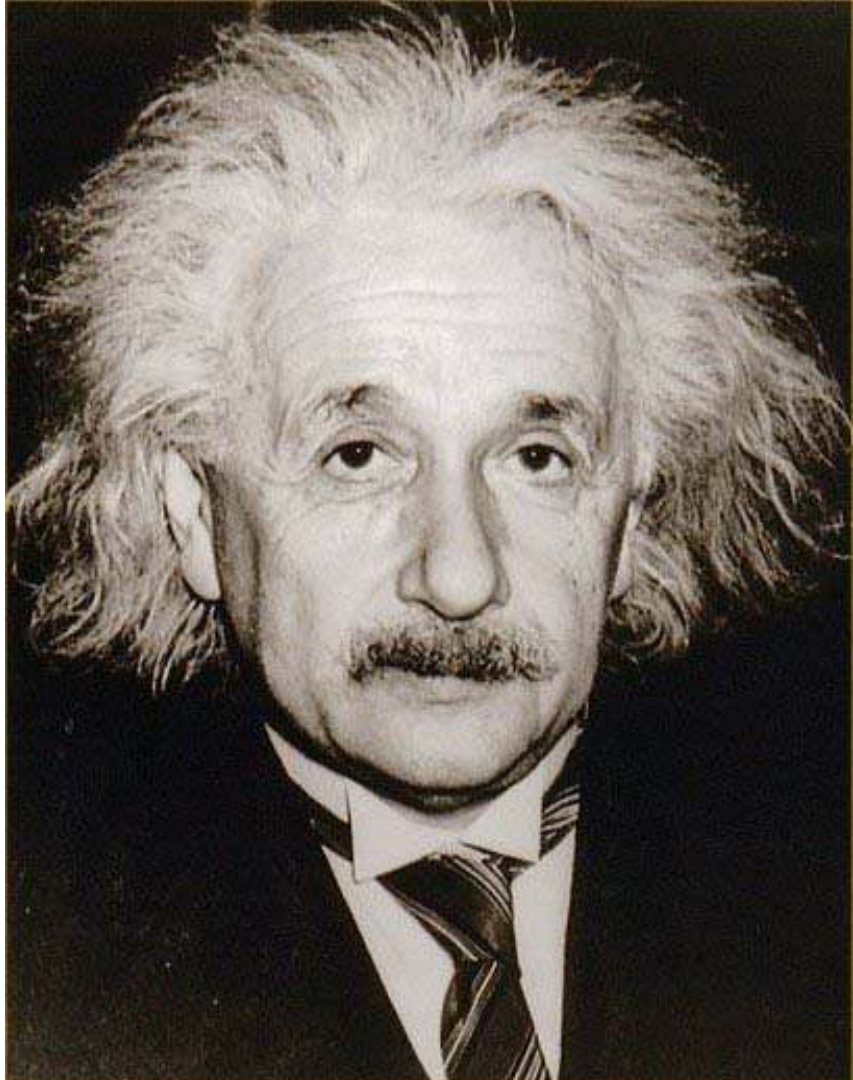
How many chemicals are known/registered?

We can detect anything/anywhere!

But are we looking for the right things?

“Not everything that can be counted counts, and not everything that counts can be counted.”

Albert Einstein
(1879-1955)



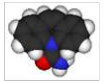
Comprehensive Screening

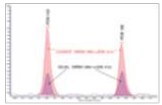
Targeted quantification

Analysis of a small set of predefined target compounds

Standards → Isolation and separation of analytes from matrix → Identification by RT & MS → Calculation of surrogate recoveries → Comparison to target peak areas → Quantification of specific compounds in a sample

Samples →





LC-MS Triple Quad

Polar and moderately polar compounds

GC-MS Triple Quad

Volatile and semi-volatile compounds

ICP-MS

Metals and targeted organic complexes

IC-MS

Anions, cations, oxyhalides

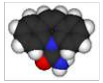
Comprehensive Screening

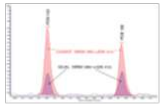
Targeted quantification

Analysis of a small set of predefined target compounds

Standards → Isolation and separation of analytes from matrix → Identification by RT & MS → Calculation of surrogate recoveries → Comparison to target peak areas → Quantification of specific compounds in a sample

Samples





LC-MS Triple Quad

Polar and moderately polar compounds

GC-MS Triple Quad

Volatile and semi-volatile compounds

ICP-MS

Metals and targeted organic complexes

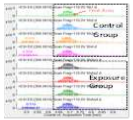
IC-MS

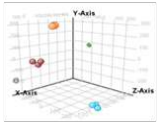
Anions, cations, oxyhalides

Non-targeted screening

Characterization of broader/unknown compounds

Sample → QTOF analysis and sample comparisons → Data alignment and analysis → Validation with MS/MS from standards → Compound profile in a sample





LC-MS QTOF

Polar and moderately polar compounds

GC-MS QTOF

Volatile and semi-volatile compounds

Cell Bioassay

Quantifiable cellular responses from mixtures isolated from biological samples

LC/GC-ICP-MS

Untargeted organic-halogens/ metals

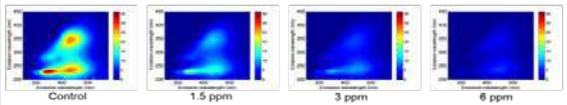
Comprehensive Testing Strategy

Tier 1

Bulk Water Characteristics (Surrogates)

On-line & off-line analysis

- General parameters (pH, temp, conductivity, turbidity, TSS)
- Organic parameters (TOC/DOC, UV254, fluorescence)
- Inorganic parameters (NO_3, NO_2, anion/cation, oxidant residuals)
- ***Near real-time performance***

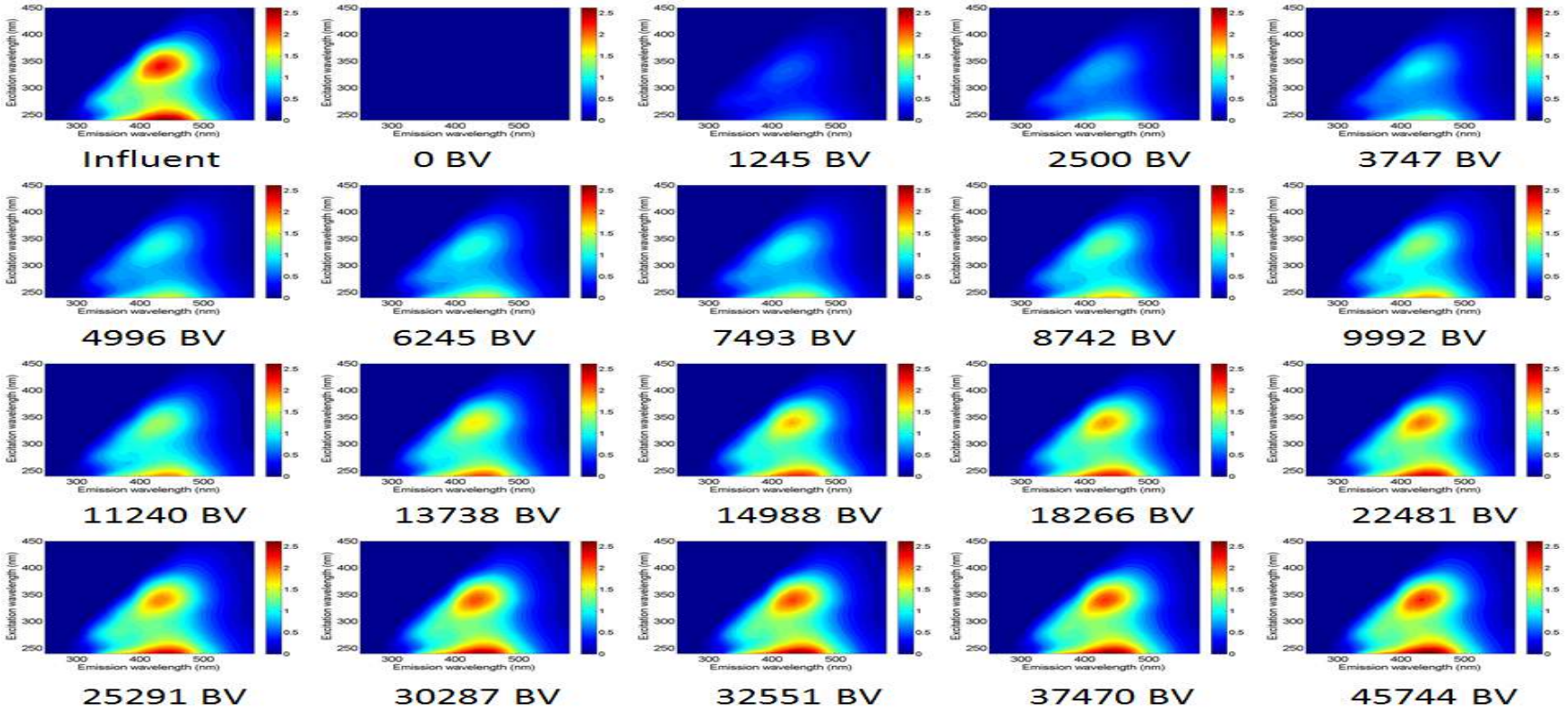


ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/CECpanel/CECMonitoringInCARecycledWater_FinalReport.pdf

SURROGATES

Granular Activated Carbon

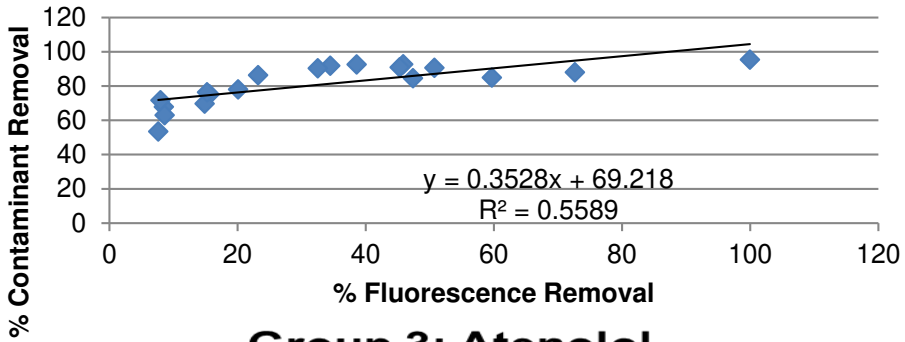
Application of fluorescence as surrogate for water quality



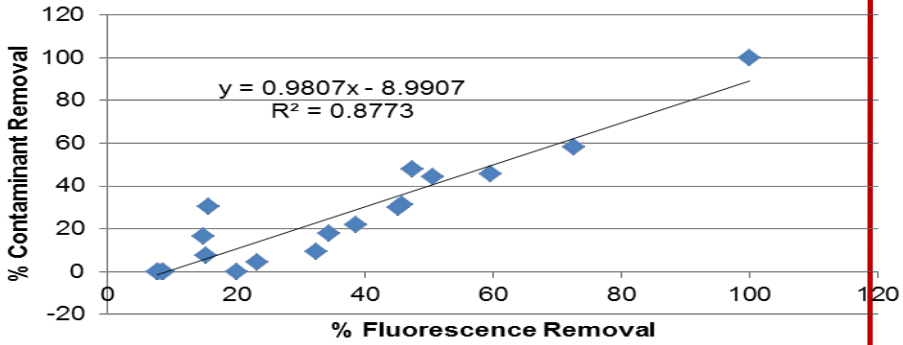
Anumol T, Sgroi M, Park M, Roccaro P, Snyder SA. ***Water Res.*** 2015 (76):76-87.

Fluorescence Correlation

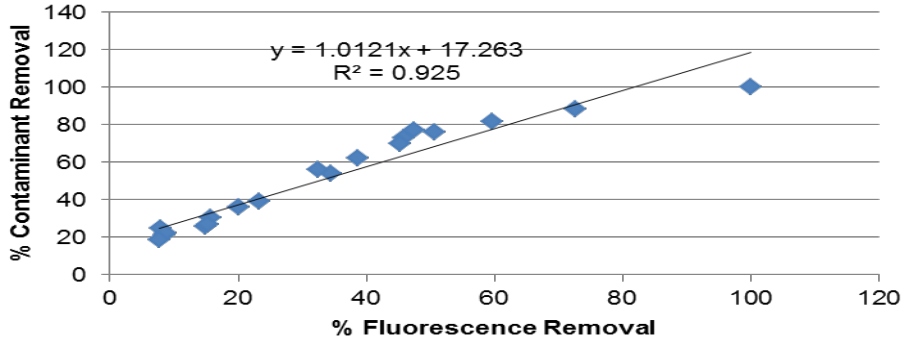
Group 1: Triclocarban



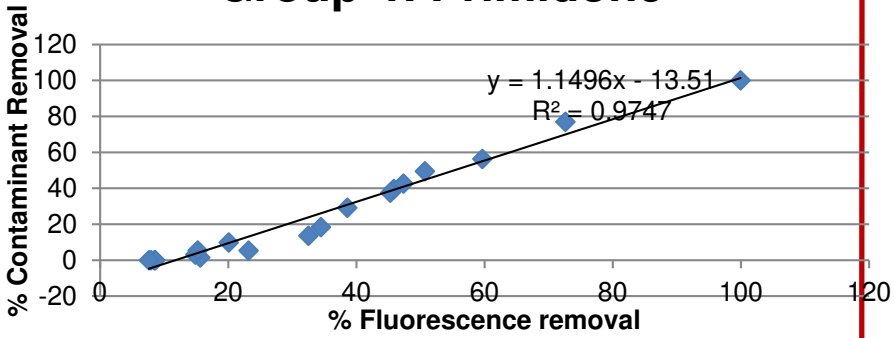
Group 2: PFOA



Group 3: Atenolol

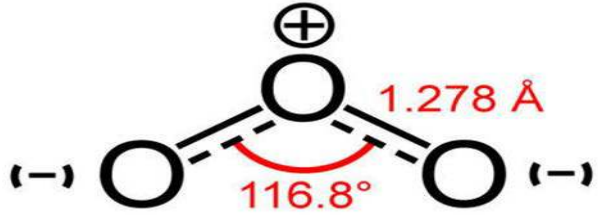


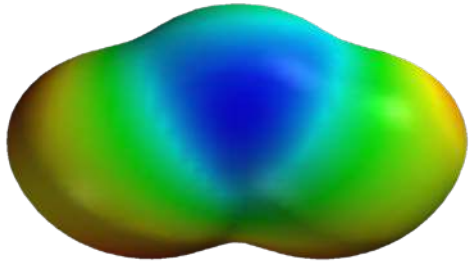
Group 4: Primidone



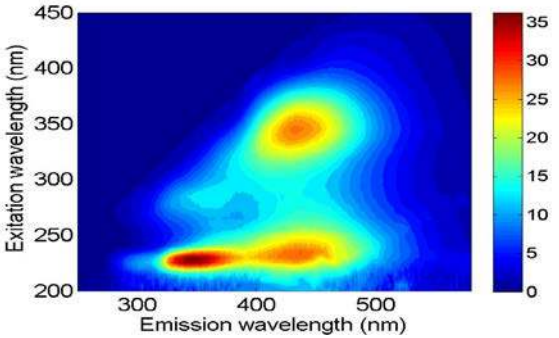
Anumol T, Sgroi M, Park M, Roccaro P, Snyder SA. ***Water Res.*** 2015 (76):76-87.

Ozonation Example

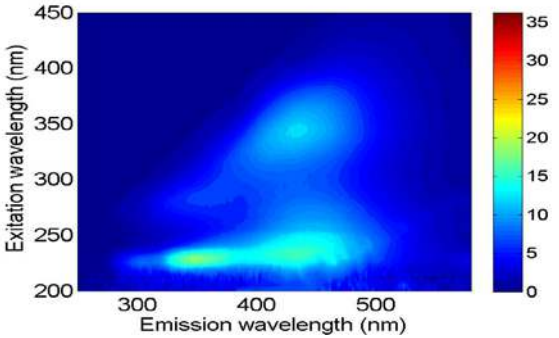




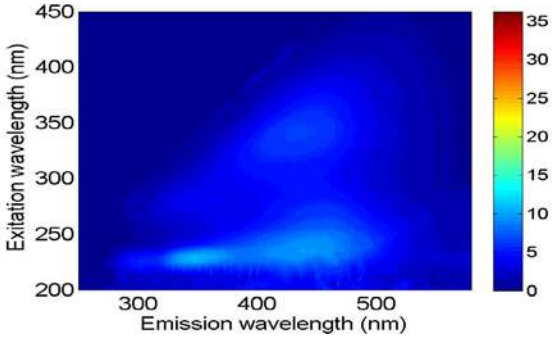
Fluorescence Surrogate Response



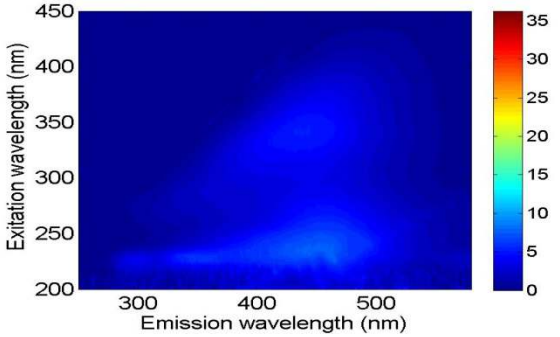
Control



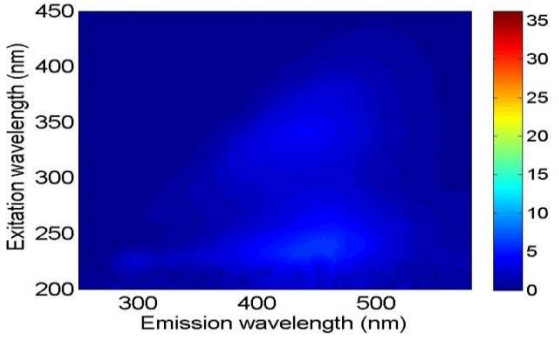
1.5 ppm



3 ppm



4.5 ppm



6 ppm

Merel S, Anumol T, Park M, Snyder SA. *J. Hazard. Mater.* 2015 282:75-85

Surrogates

Environmental Science
Water Research & Technology

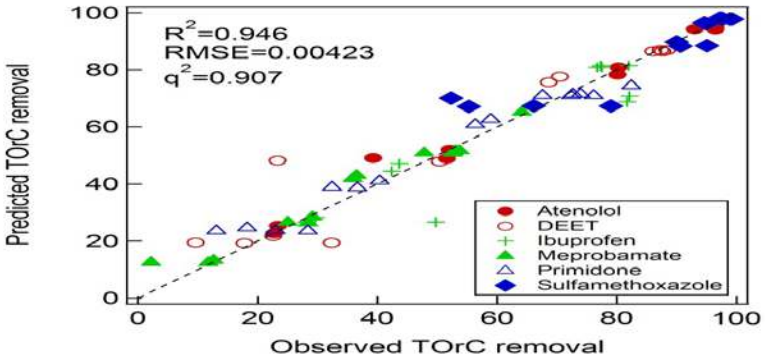
PAPER

Cite this: *Environ. Sci.: Water Res. Technol.*, 2015, **1**, 699

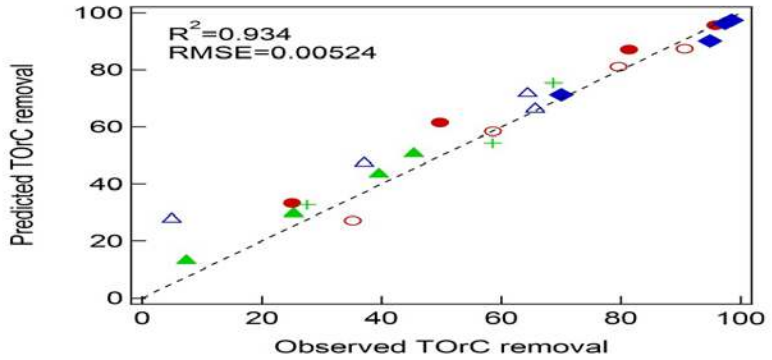
Modeling approaches to predict removal of trace organic compounds by ozone oxidation in potable reuse applications†

Minkyu Park,[a] Tarun Anumol[ab] and Shane A. Snyder*[ac]

PC-ANN: Generation/Training step



PC-ANN: External validation



On-Line/Real-Time Sensor Network

INDICATORS

Indicator Example – Secondary Treatment

Faster Transformation

Higher sorption

Sorption (log K_d)	Biotransformation (K_b, L/g-d)		
	Recalcitrant <0.1	Moderate Slow 0.1-10	Rapid >10
Low <2.5	Carbamazepine Meprobamate Primidone Sucralose	DEET Sulfamethoxazole Gemfibrozil Iopromide	Acetaminophen Naproxen Ibuprofen Atenolol
Sorptive 2.5-3	TCPP	Cimetidine Trimethoprim	Benzophenone Diphenhydramine Bisphenol A
Effective >3	Triclocarban		Triclosan Fluoxetine

WERF CEC4R08 – Tanja Rauch-Williams *et al.* 2013

Targeted Indicator Analysis

Conventional SPE Method

1 L sample

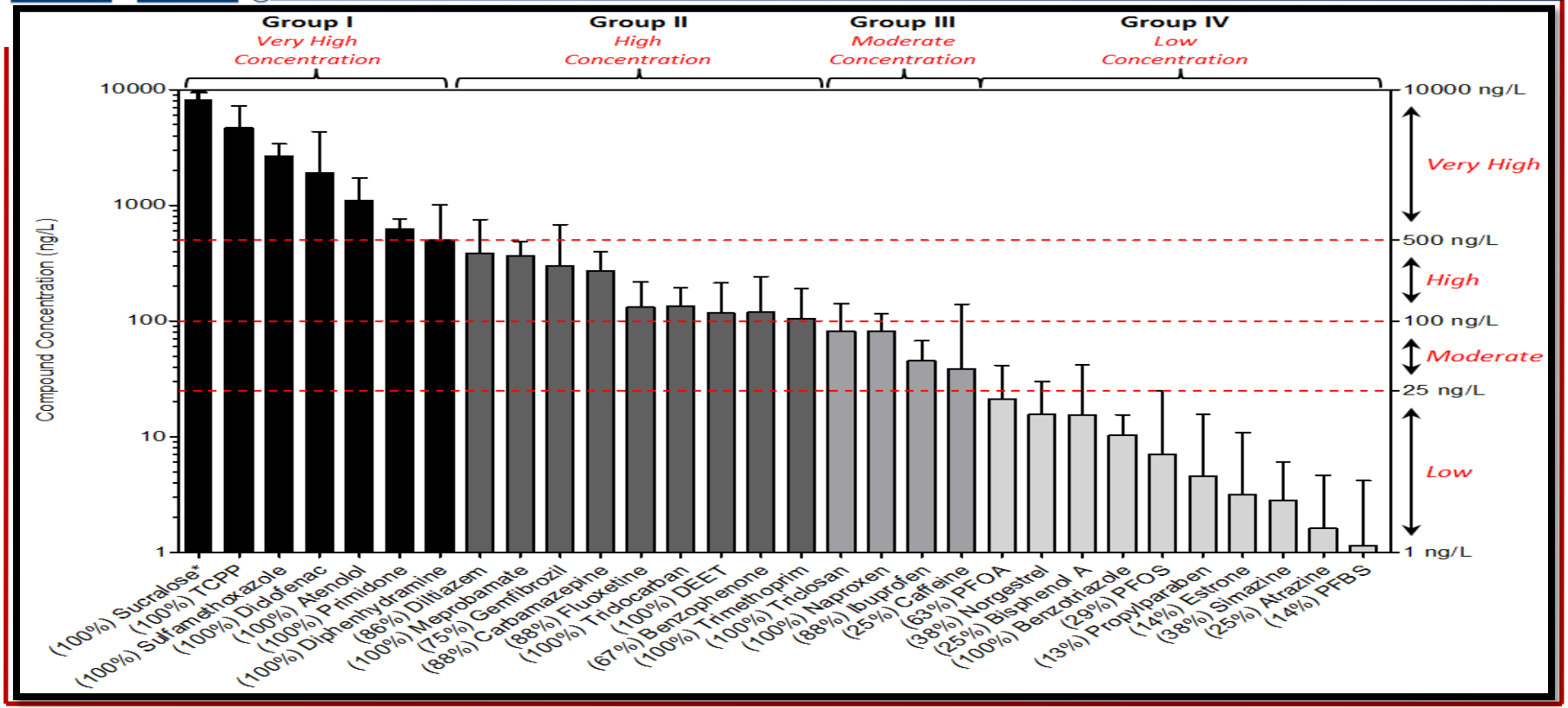
Online SPE Method

1.5 mL sample

Direct Injection Method

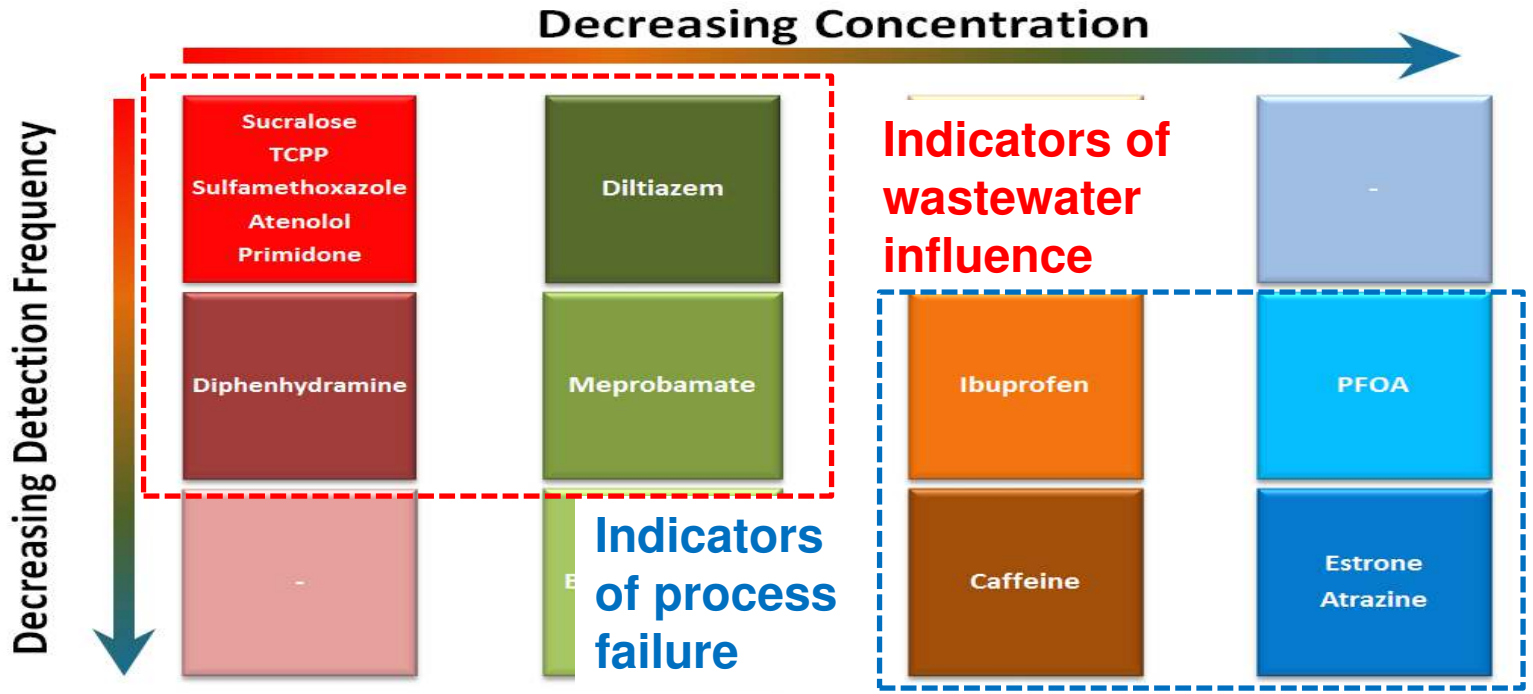
0.1 mL sample

Indicator Occurrence



Merel S, Anumol T, Park M, **Snyder SA.** *J. Hazardous Materials.* 2015 282:75-85.

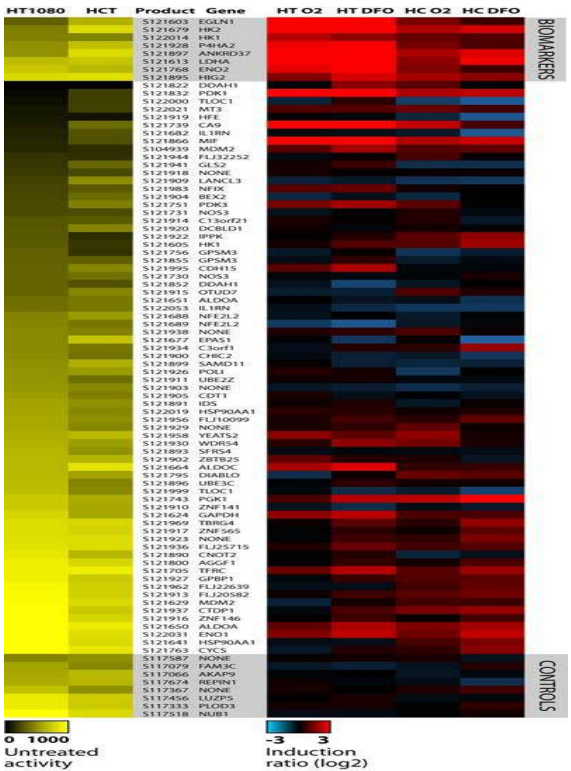
Indicator Priority List

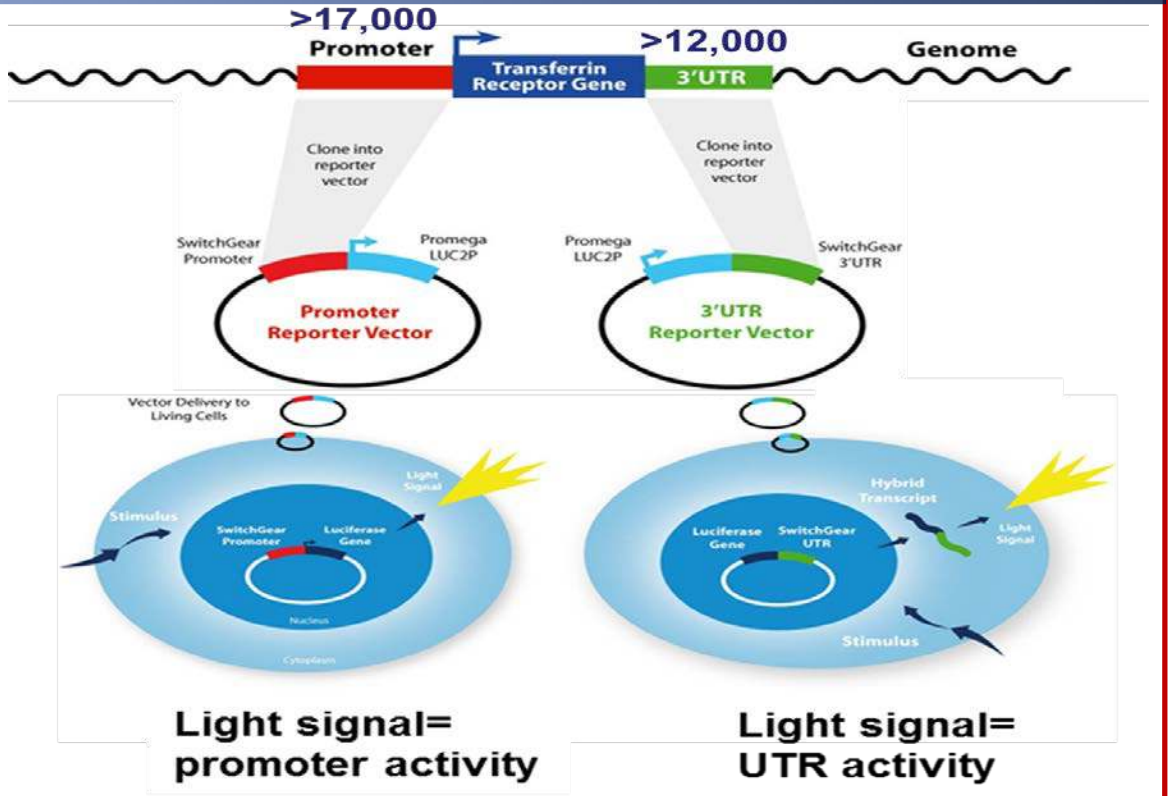


BIOASSAYS & NON-TARGETED ANAYSIS (NTA)

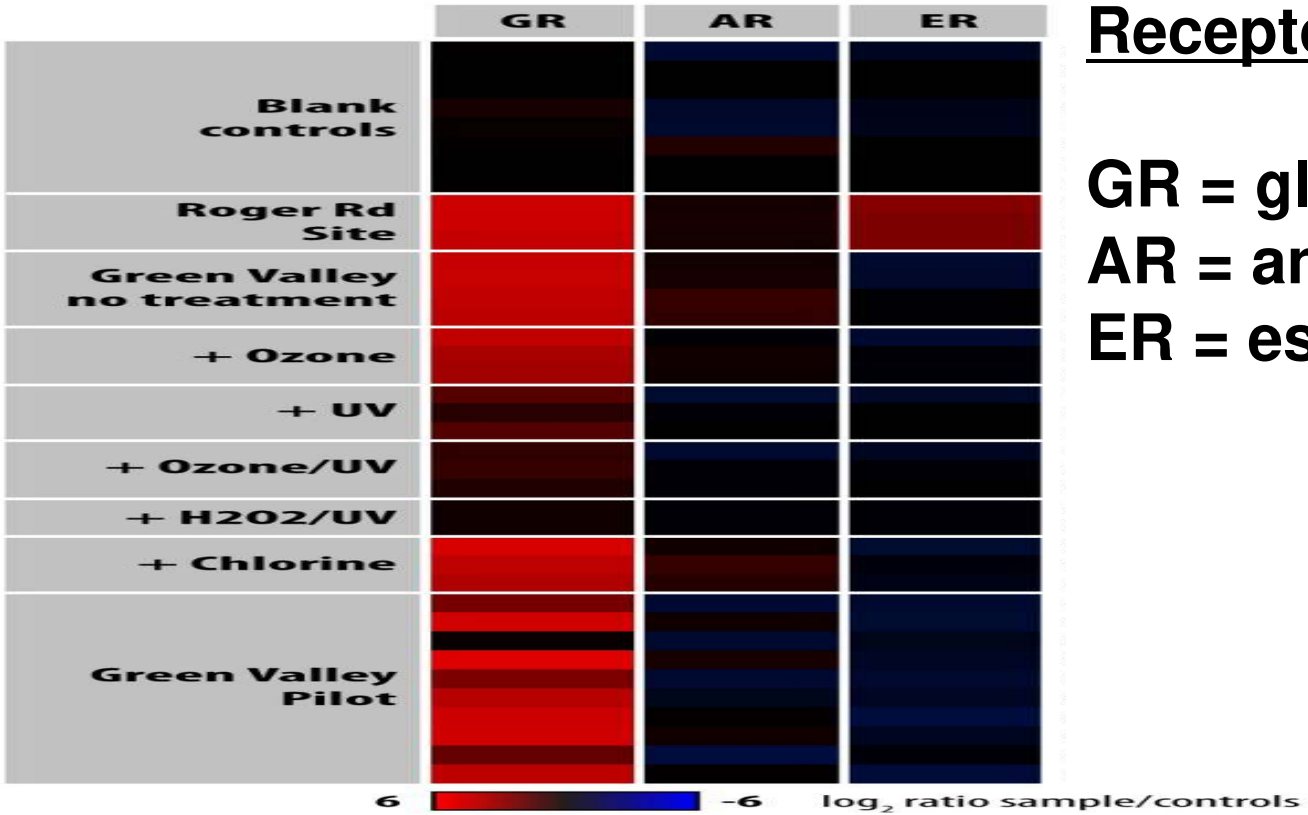
Jia, A.; Wu, S.; Daniels, K. D.; Snyder, S. A., Balancing the Budget: Accounting for Glucocorticoid Bioactivity and Fate during Water Treatment. *Environ. Sci. Technol.* **2016**.

Transient Transfection Assay





Initial Recycled Water Screening



Receptors:

GR = glucocorticoid
AR = androgen
ER = estrogen

Glucocorticoids Among Most Widely Used Drugs

Amount prescribed in UK (2006)

Class	Prescribed (kg)
Estrogens	480
Androgens	307
Progestogens	1705
Glucocorticoids	4368

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http://www.tandfonline.com/loi/bher20

Pharmaceuticals in the Aquatic Environment: Steroids and Anti-Steroids as High Priorities for Research

Tamsin J. Runnalls [a] , Luigi Margiotta-Casaluci [a] , Subramaniam Kugathas [a] & John P. Sumpter [a]
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Published online: 15 Dec 2010.

Medicare drugs USA (2013)

TOP 10 MEDICARE TRADITIONAL THERAPY DRUGS
RANKED BY 2013 PMPY SPEND

RANK	DRUG NAME	THERAPY CLASS
1	Nexium® (esomeprazole magnesium)	Ulcer Disease
2	Lantus® (insulin glargine)	Diabetes
3	Crestor® (rosuvastatin)	High Blood Cholesterol
4	Advair Diskus® (fluticasone propionate / salmeterol)	Asthma
5	Spiriva® HandiHaler® (tiotropium)	COPD
6	Abilify® (aripiprazole)	Mental / Neurological Disorders
7	Cymbalta® (duloxetine)	Depression
8	Namenda® (memantine)	Mental / Neurological Disorders
9	Januvia® (sitagliptin)	Diabetes
10	atorvastatin	High Blood Cholesterol

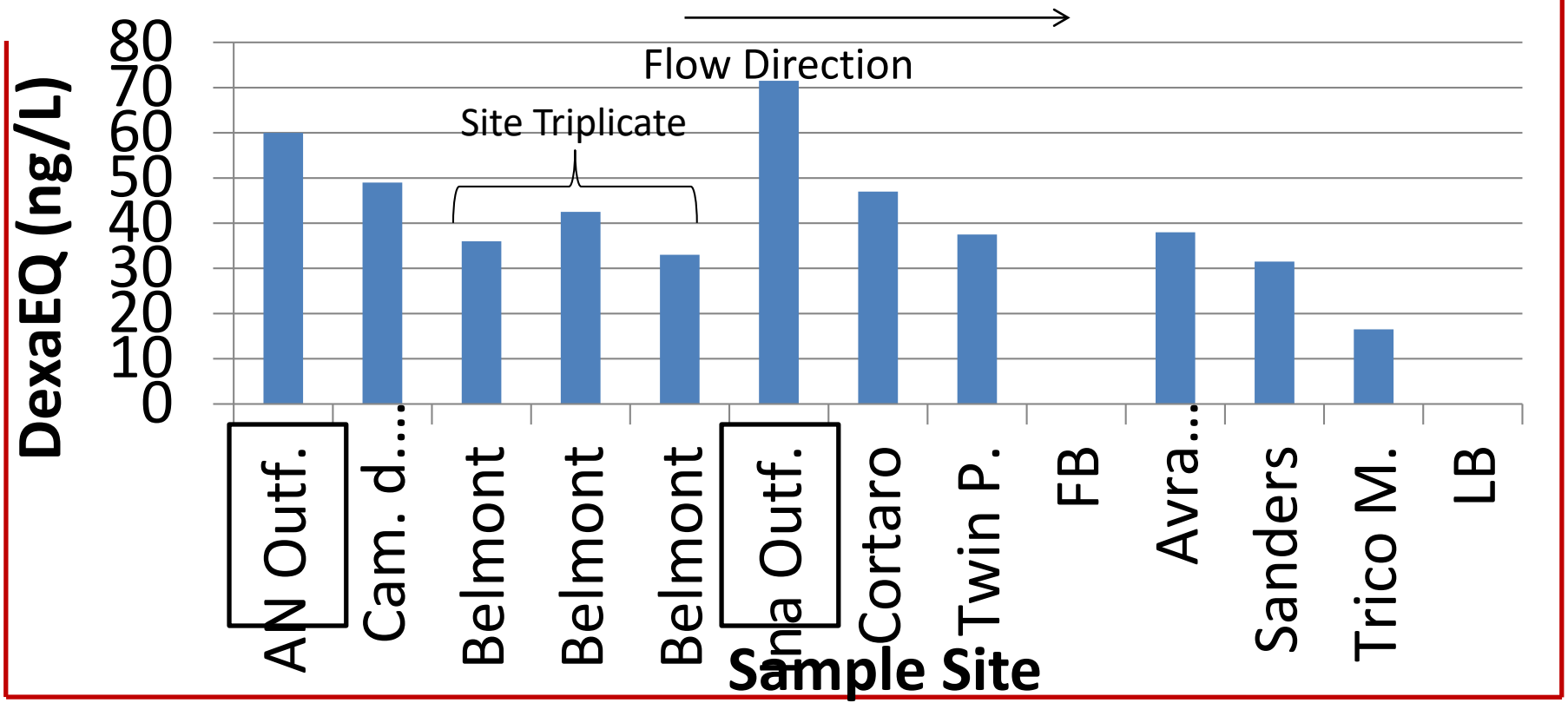
Source: The 2013 Drug Trend Report, Express Scripts Lab.

Over-the-counter (OTC) approved (2014)

Fluticasone propionate (Flonase)
Triamcinolone acetonide (Nasacort)

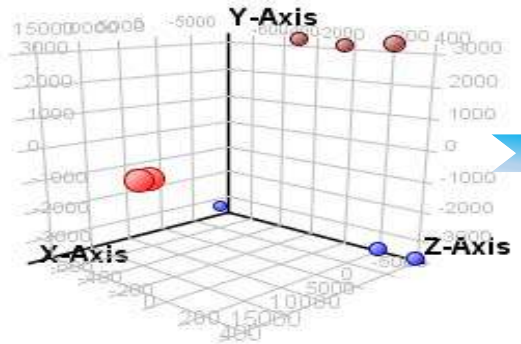
Santa Cruz River Sampling Sites

GR Cellular Activity

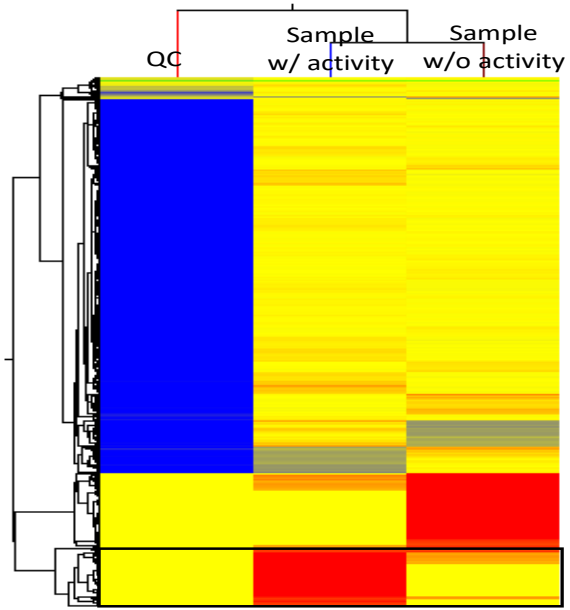


Structural Determination (QTOF)

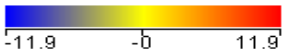
Principal Component Analysis



QC
Sample w/ activity
Sample w/o activity

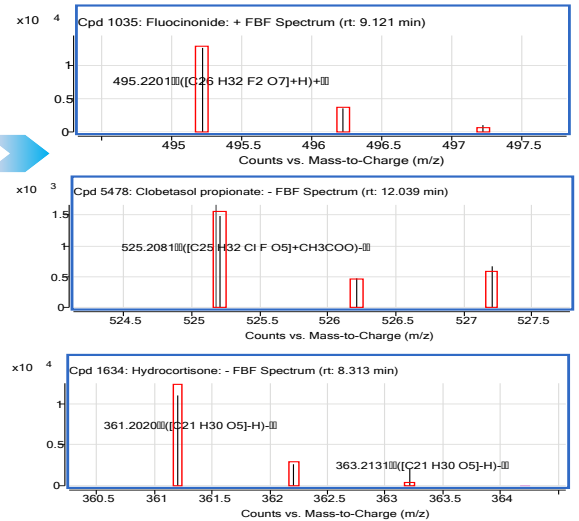


Color by normalized abundance

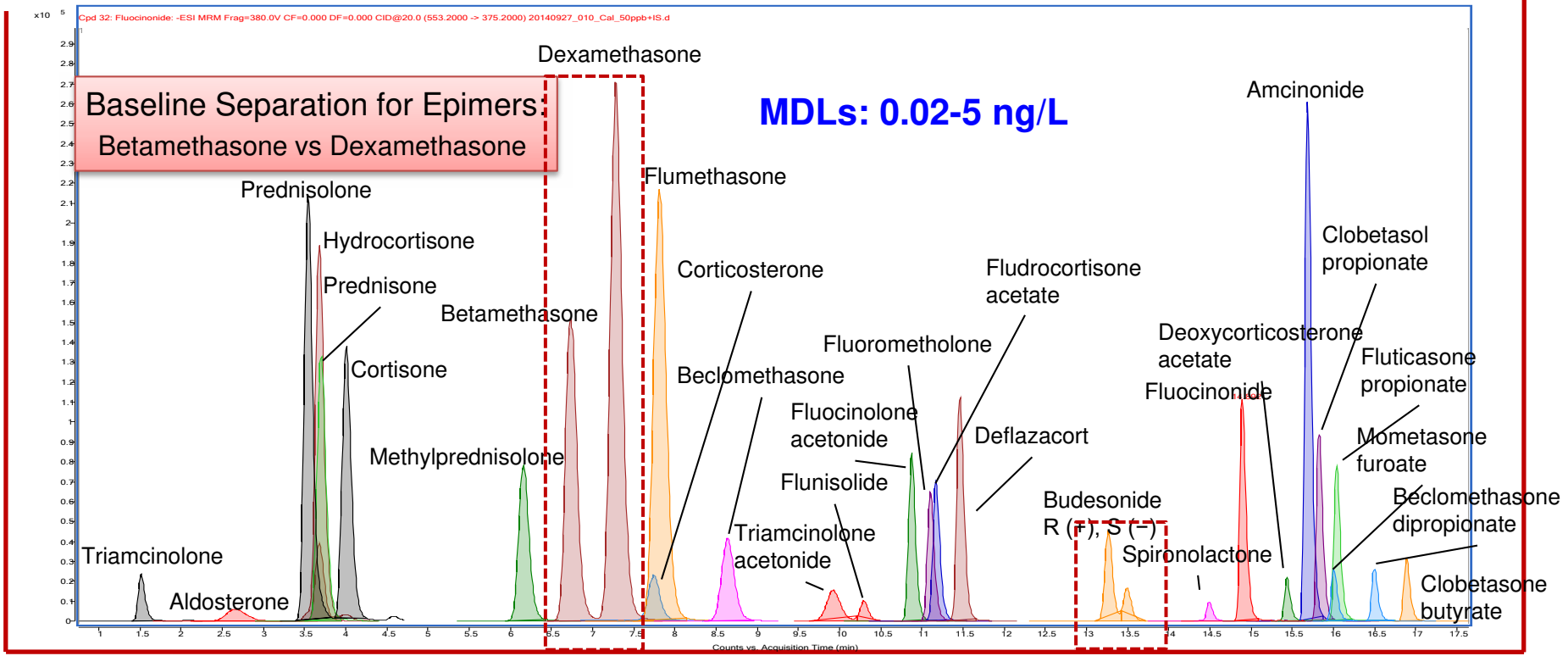


Datadase Search &

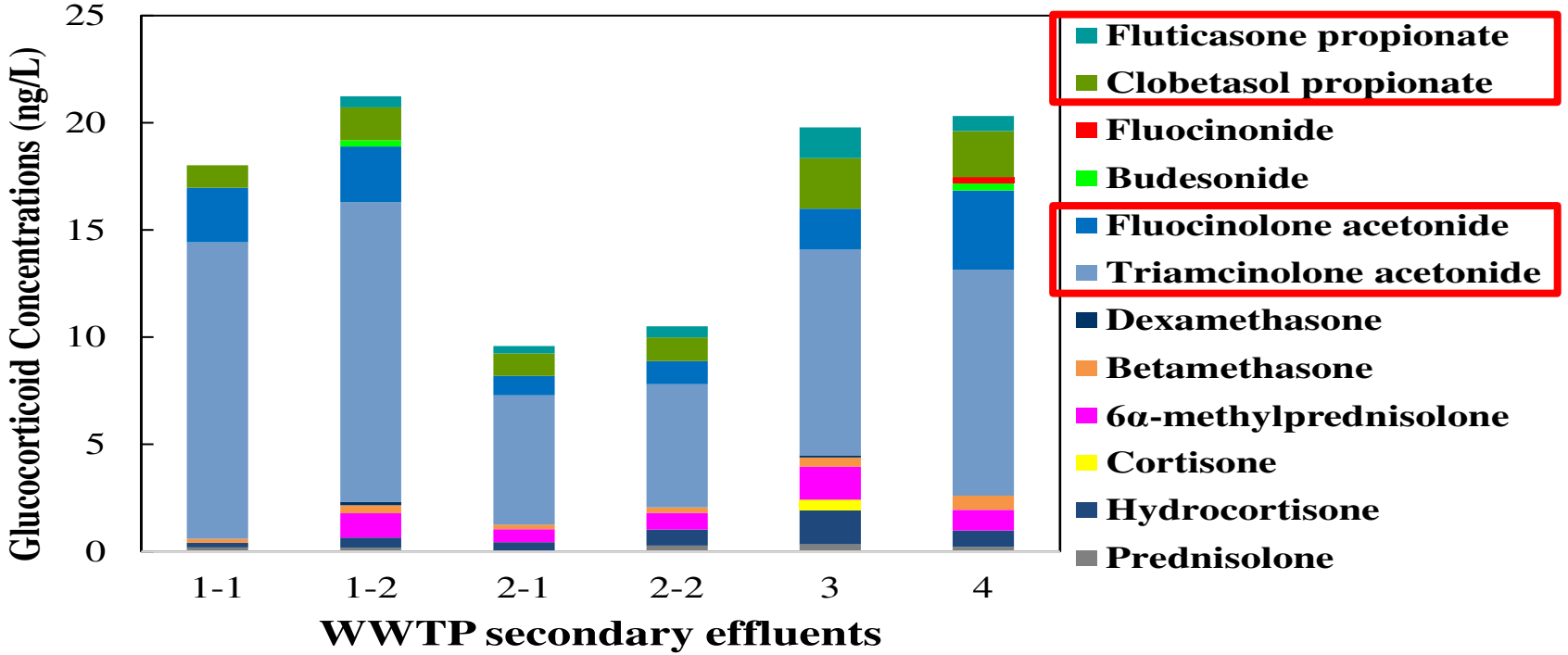
Compounds Identification



Targeted Analysis (LC-MS/MS)

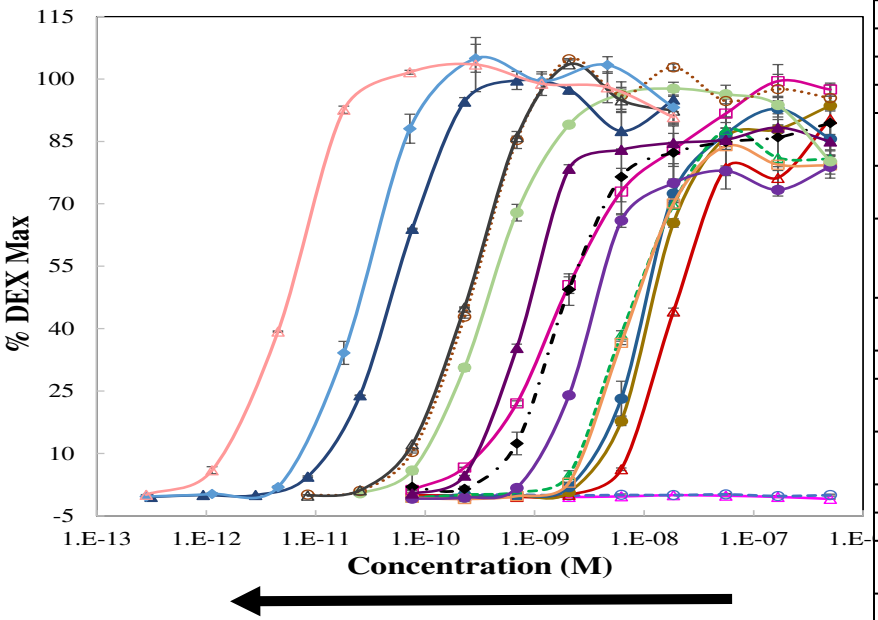


Glucocorticoid Concentrations in WWTP Effluents



9.6-21.2 ng/L, much higher occurrence levels than estrogens at same sites

Relative Potency of GR agonists



GCs	EC_{50} (nM)	REP
Prednisone	>500	<0.004
Cortisone	>500	<0.004
Prednisolone	17.7	0.101
Triamcinolone	11.8	0.152
Fludrocortisone acetate	9.67	0.185
Hydrocortisone	6.81	0.264
6α-methylprednisolone	6.79	0.264
Betamethasone	2.83	0.634
Fluocinonide	1.89	0.948
Dexamethasone	1.79	1.000
Triamcinolone acetonide	0.79	2.265
Flumethasone	0.36	5.032
Budesonide	0.26	6.895
Fluocinolone acetonide	0.24	7.398
Clobetasol propionate	0.048	37.04
Fluticasone propionate	0.025	70.88
GCs mixed standard	0.005	329

Most synthetic GCs have much higher activity than natural GCs

Balancing the GC Budget

WWTP Effluents

In Vitro GR Bioassay

Occurrence

Reclamation Treatment

Chemical Analyses

27 agonists

Attenuation

- Chlorination
- Ozone
- UV
- Membrane

Chemical Concentrations (Chemi-EQ)

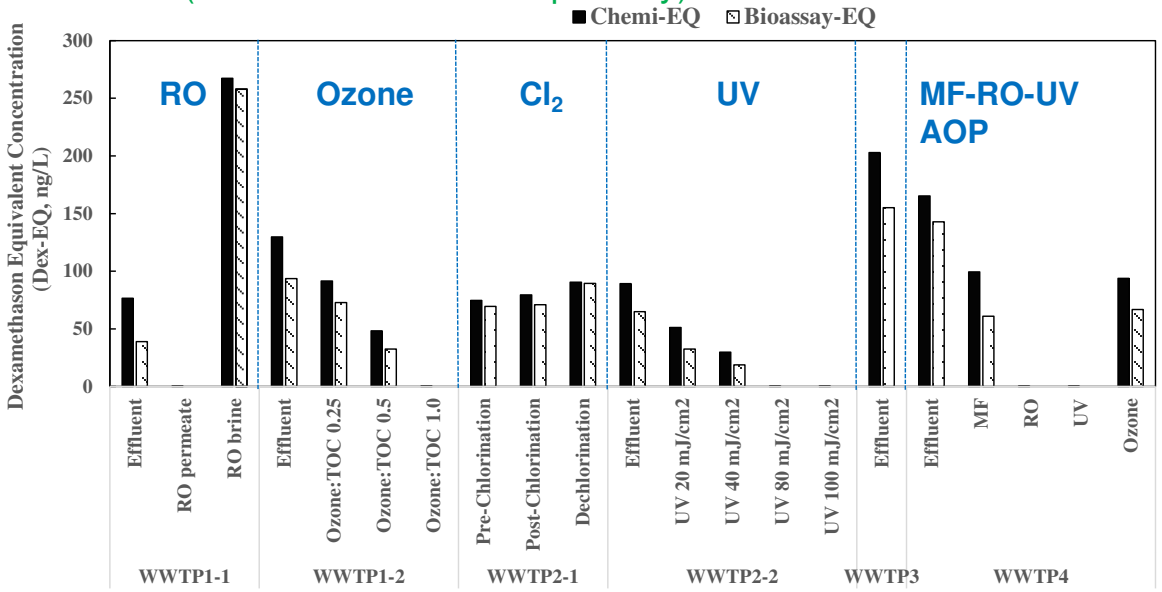
Sample Bioactivity (Bioassay-EQ)

Treatment Efficacy

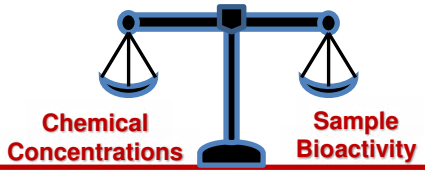
Monitoring Prioritization

Mass-Activity Balance Achieved

Chemi-EQ=Sum(concentration*relative potency)



The quantitated GRs can explain the observed biological GR activity.



“All truths are easy to understand once they are discovered; the point is to discover them..”

Galileo Galilei
(1564-1642)

Acknowledgements

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