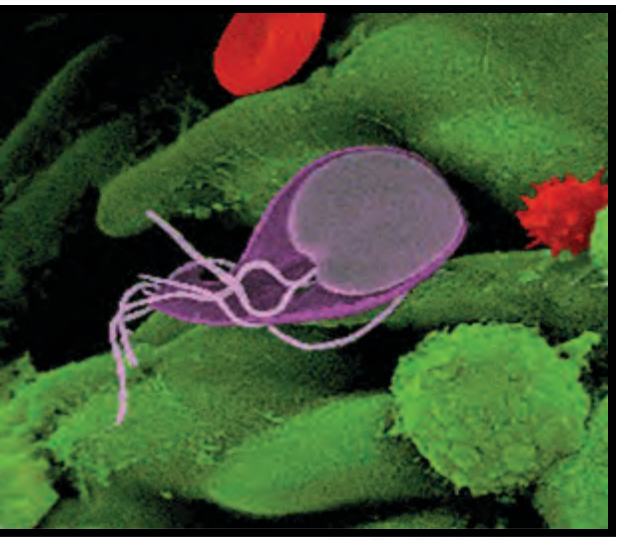
Assessing the Safety of Recycled Water



WRRC Brownbag Lunch Seminar – 20th April 2016

azengineering

Shane Snyder, Ph.D.

Professor & Co-Director

University of Arizona

WEST CENTER

WATER & ENERGY SUSTAINABLE TECHNOLOGY

Acknowledgements

ARIZONA
SNYDER RESEARCH GROUP
PIONEERING RESEARCH REGARDING DETECTION, TREATMENT, AND HEALTH RELEVANCE OF ENVIRONMENTAL CONTAMINANTS

Agilent Technologies

ARIZONA
Water, Environmental, and Energy Solutions

THE UNIVERSITY OF ARIZONA
WEST CENTER
WATER & ENERGY SUSTAINABLE TECHNOLOGY

Research
Office for Research & Discovery

Pima County Regional Wastewater Reclamation Department

Institute of the Environment

THE UNIVERSITY OF ARIZONA
BIO5 Institute
Science | Education | Jobs

BDS BioDetection Systems

THE UNIVERSITY OF ARIZONA

DOW

WEST CENTER

WATER & ENERGY SUSTAINABLE TECHNOLOGY

HACH

CalgonCarbon

http://west.arizona.edu

Regional Wastewater Reclamation Department

Orange County Water District — Since 1933

xylem — Let's Solve Water

NSF

Agilent Technologies

suez environment / United Water

JMAR

THE SANITATION DISTRICTS OF LOS ANGELES COUNTY — www.lacsd.org

TROJAN UV — WATER CONFIDENCE™

WET — Water and Environmental Technology Center

Research Staff

Armando Durazo: UCLA

Shawn Beitel: U. Saskatoon

Christiane Hoppe-Jones: CSM

Post-Doctoral Associates

Hye-Weon Yu: GIST Korea

Ph.D. Students

Shimin Wu: Peking University

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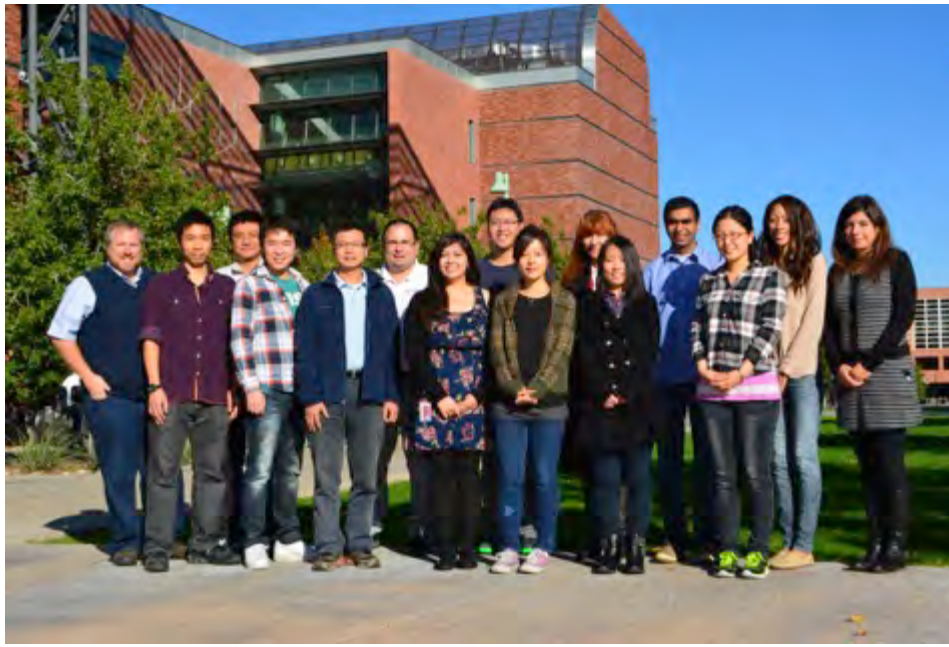
Mojtaba Azadi: Sharif UT

Tharun Murali: SASTRA U

snyderlab.arizona.edu



Pure

1. free from anything of a different, inferior, or contaminating kind; free from extraneous matter: *pure gold; pure water*.

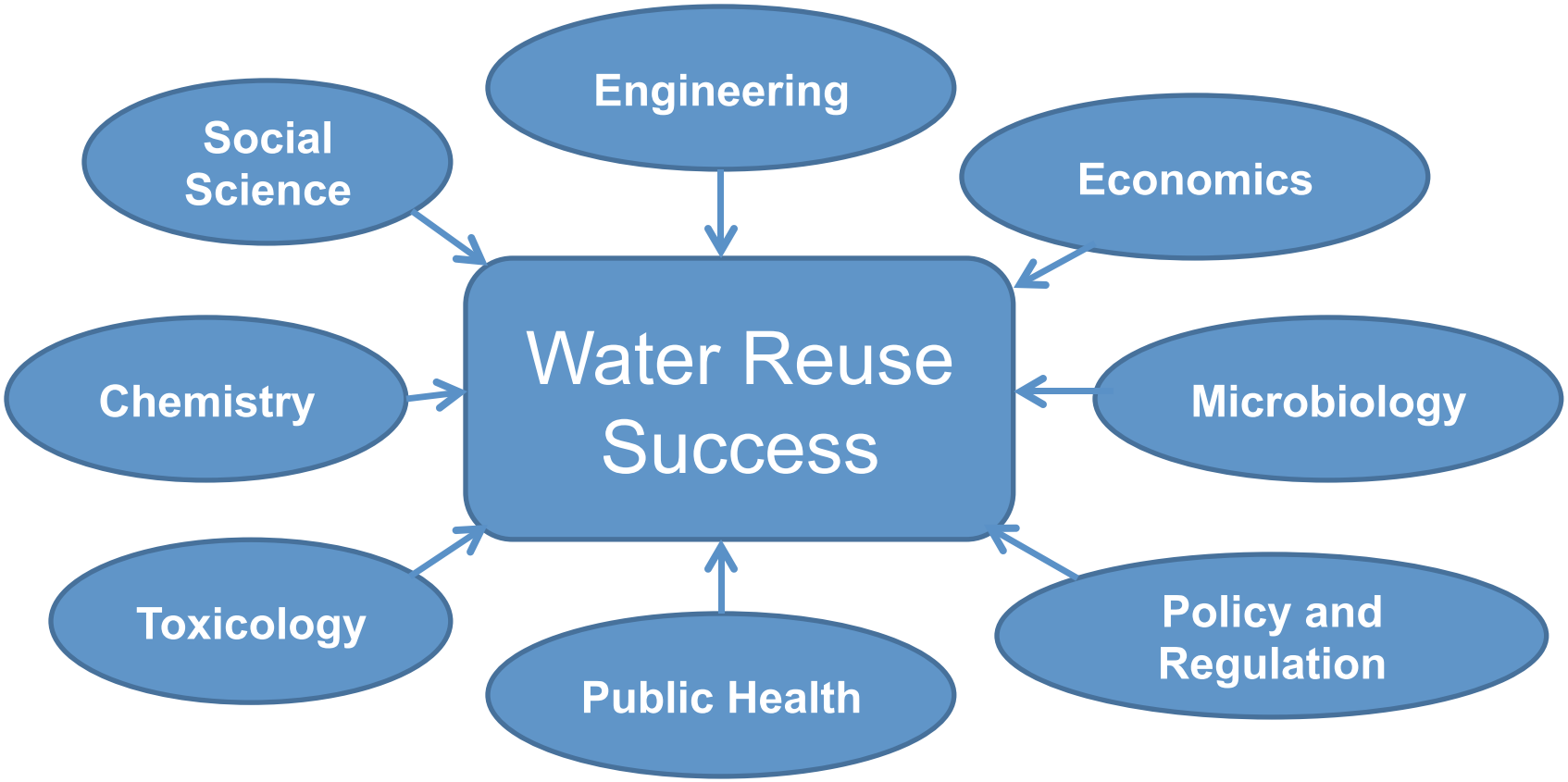
Safe Drinking Water

1. secure from liability to harm, injury, danger, or risk

Risk

1. exposure to the chance of injury or loss

Multi-Disciplinary Aspects



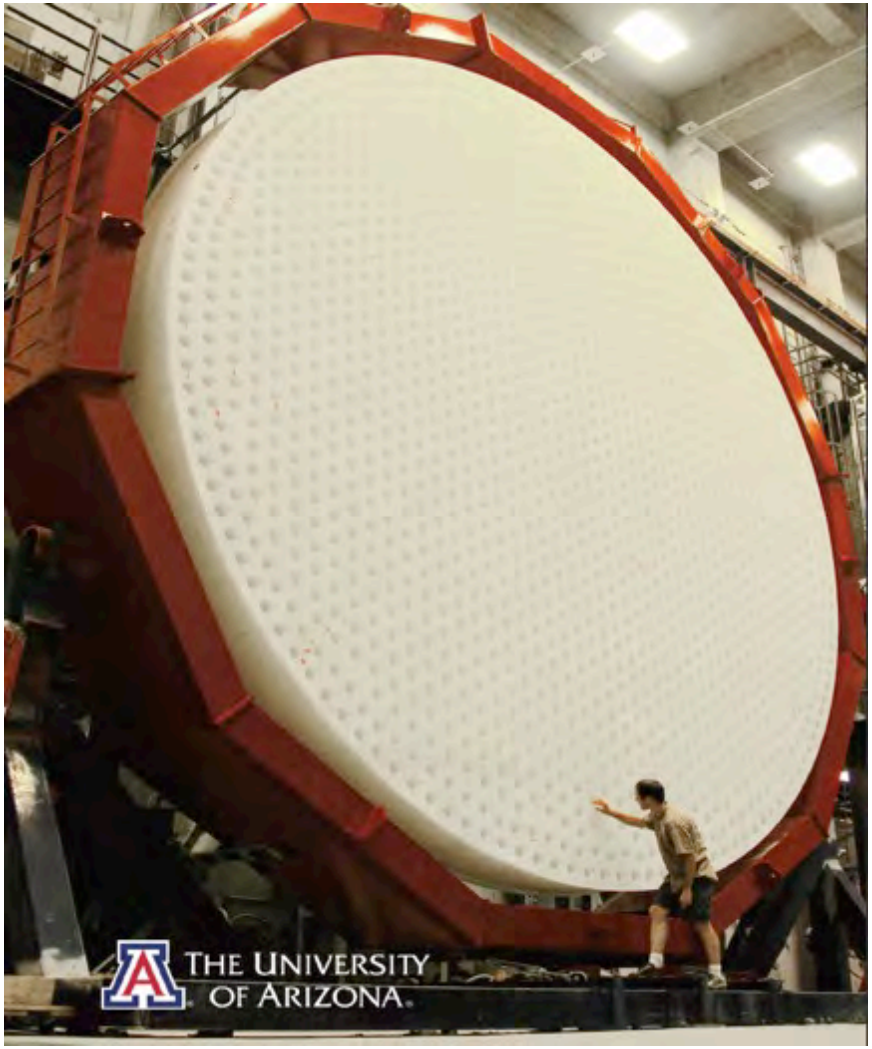
Related Policy Efforts

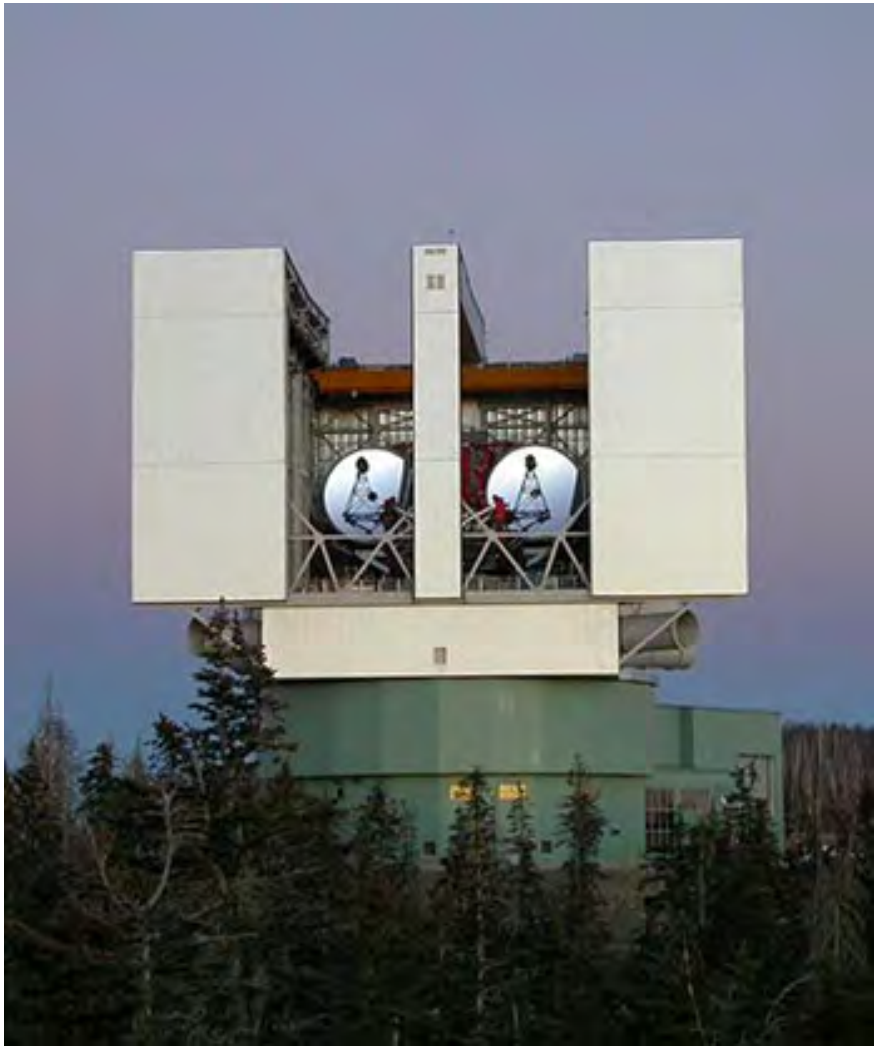
World Health Organization

Grand Challenge

When does waste water become “water”?

We can detect anything, anywhere





We can detect anything/anywhere!

But are we looking for the right things?


WATER TANK
HAND CART
HA 2526

Kuala Lumpur and Singapore receive over 90” rainfall/year.

Cities are 300 Km apart.

February was Singapore's driest month since 1869 *Despite ave. rainfall of 234 cm!*

Singapore Botanical Gardens February 2014

Singapore experiencing record dry spell - and it could get worse: NEA

PUBLISHED ON FEB 25, 2014 7:14 AM

East Coast Park, Singapore, March 2014

Nonetheless, Singapore's public water agency has started a campaign to urge residents to conserve water, as the dry weather **is expected to persist** into March.

Updated: 02/28/2014 18:07 | By Agence France-Presse

Drought forces water rationing on millions of Malaysians

Malaysia said Friday it will expand water rationing in and around its capital, in a move affecting millions as drought continues to scorch a tropical country usually synonymous with torrential rain.

MALAYSIA

Deputy minister: Cloud seeding this week as Selangor water levels plunge

BY FAIZAL NOR IZHAM FEBRUARY 19, 2014

The Sungai Selangor dam could see its water reserve fall further if the heatwave persists. — Picture by Zuraneeza Zulkifli

PETALING JAYA, Feb 19 — The water reserve continues to drop, causing concern that rationing could take place soon if the hot spell continues.

Malaysia

Kuala Lumpur

Sections of Kuala Lumpur ran out of water entirely.

Singapore reservoirs did not drop below 90% capacity.

Only 300 Km apart.

Gambang

District

Endau-Rompin

AH2

50

Kluang

3

Pengo

Pahat

91

5

E22

JOHOR

92

Singapore

Singapore Strait

Batam

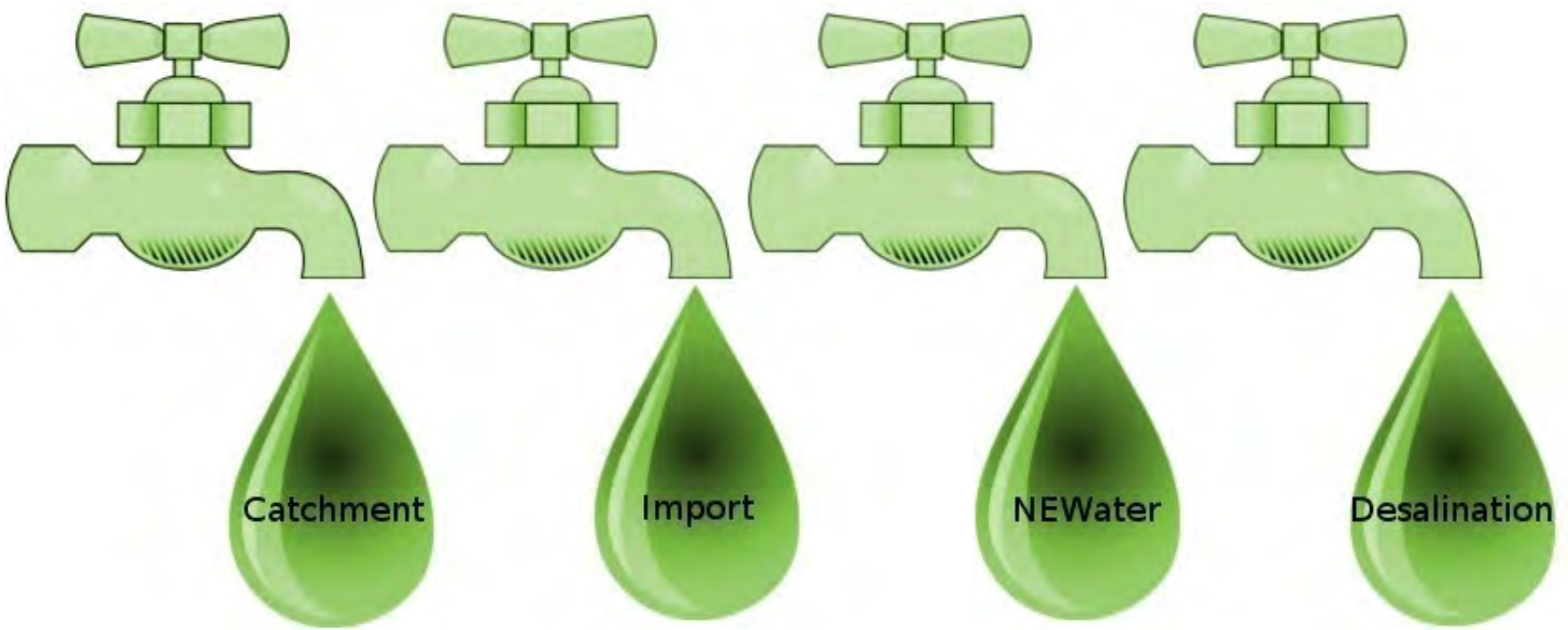
Pulau Bir

Duri

1942 Japanese Threaten Singapore's Water Supply

http://www.singaporetojohor.com/

Four National Taps of Singapore



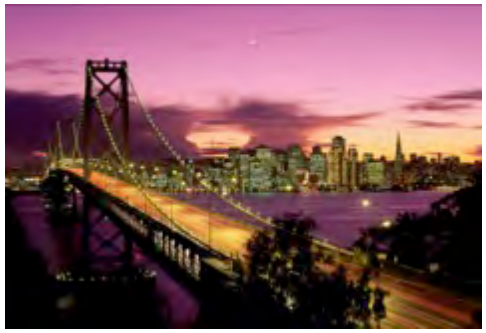
http://www.pub.gov.sg/water/Pages/default.aspx

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/

The Thirsty West: Can Tucson Survive Climate Change?

The desert city is low on water, with a booming population.

By Eric Holthaus ***March 11, 2014:***

Arizona Cities Could Face Cutbacks in Water From Colorado River, Officials Say

The New York Times By MICHAEL WINES JUNE 17, 2014

Apr 18, 2016

LOWER COLORADO WATER SUPPLY REPORT

River Operations

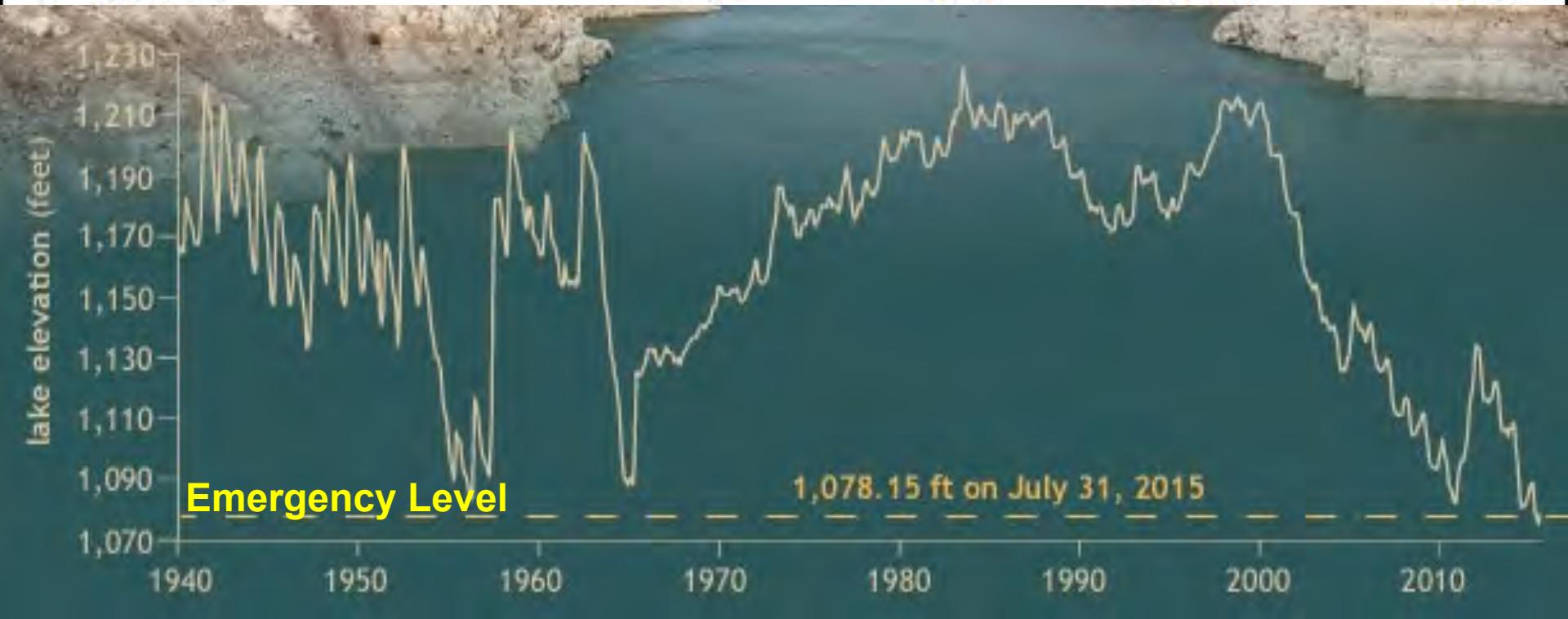
Bureau of Reclamation

Questions: BCOOWaterops@usbr.gov

(702)293-8373

http://www.usbr.gov/lc/region/g4000/weekly.pdf

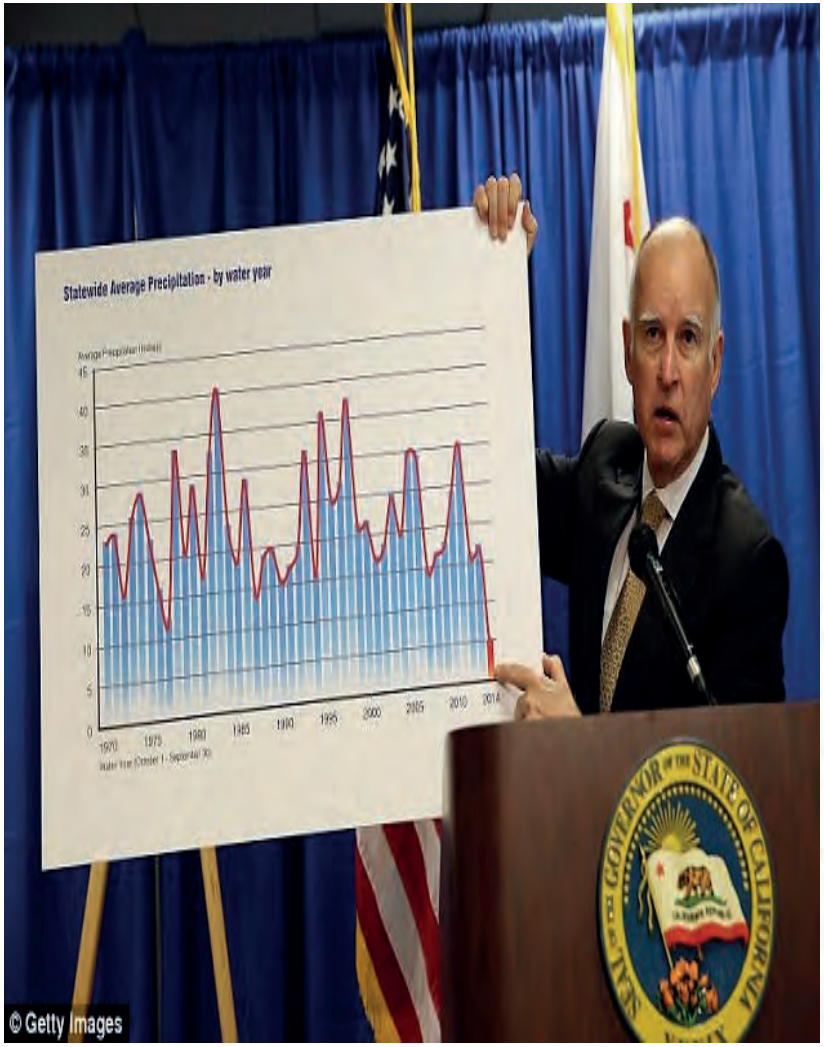
CURRENT STORAGE	PERCENT FULL	Content 1000 ac-ft (kaf)	Elev. (Feet above mean sea level)	7-Day Release (CFS)
LAKE POWELL	45%	10,931	3591.22	11,100
* LAKE MEAD	38%	9,864	1078.22	17,000



California 2011

California 2014

California Water Reuse Future



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.

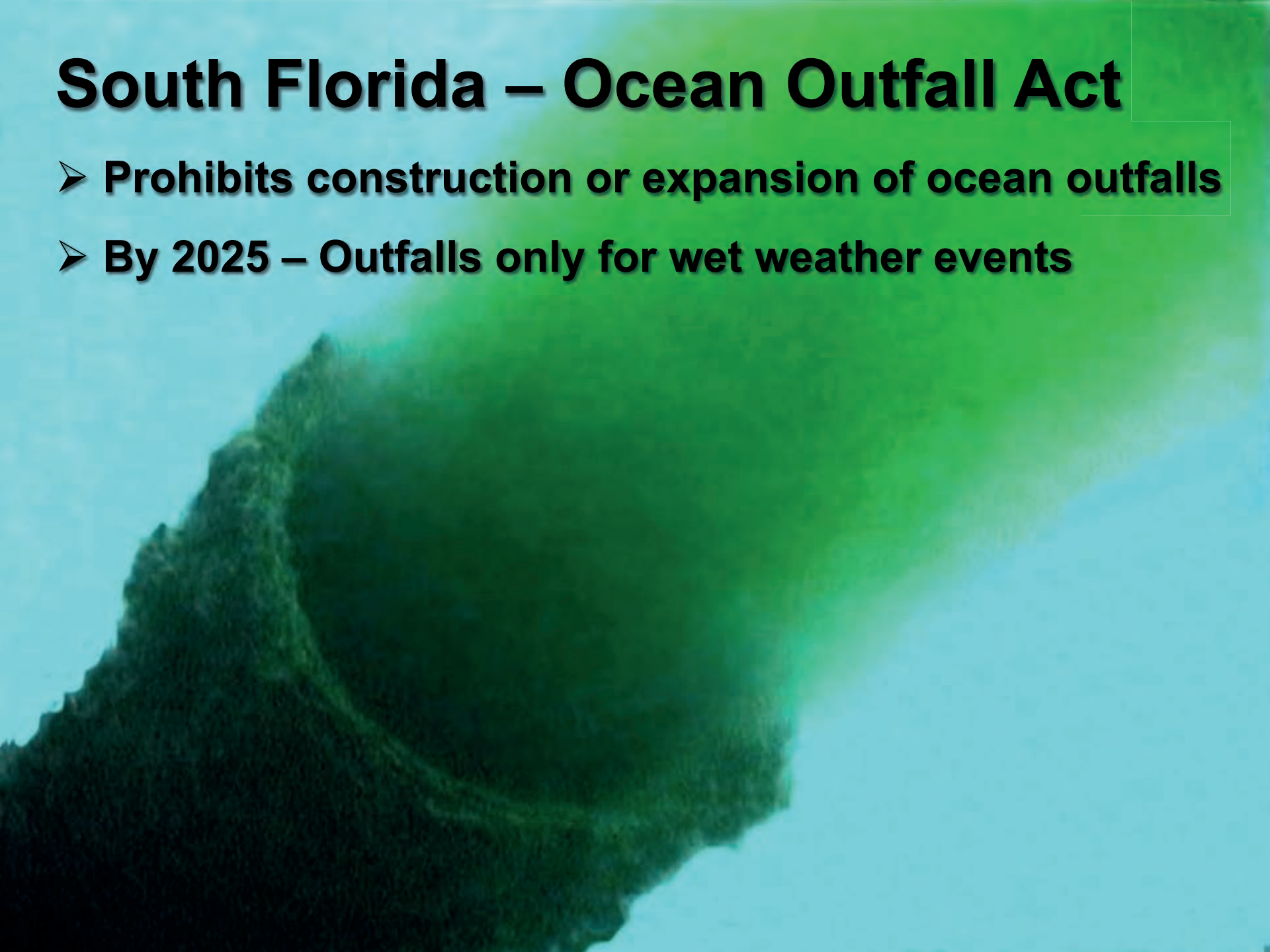
I am directing the Water Board to ensure that this work is completed expeditiously. The 3-year time frame mandated in this bill is too slow. California needs more high quality water and recycling is key to getting there.

Sincerely,

Edmund G. Brown Jr.

South Florida – Ocean Outfall Act

- Prohibits construction or expansion of ocean outfalls
- By 2025 – Outfalls only for wet weather events



We Have the Technology

Simply a matter of safety, cost, and reliability…

Water Reuse

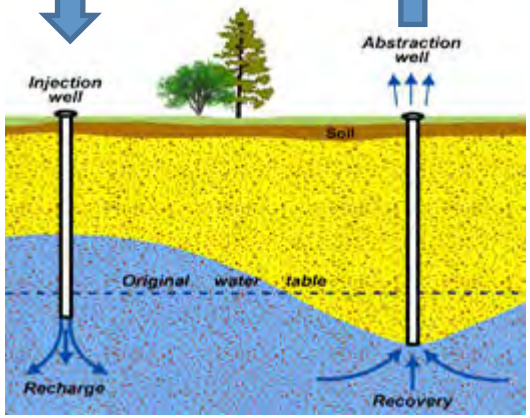
Alternate Sources of Water to Augment Supplies

"Drought-Proof Resource"

Scientific Perception

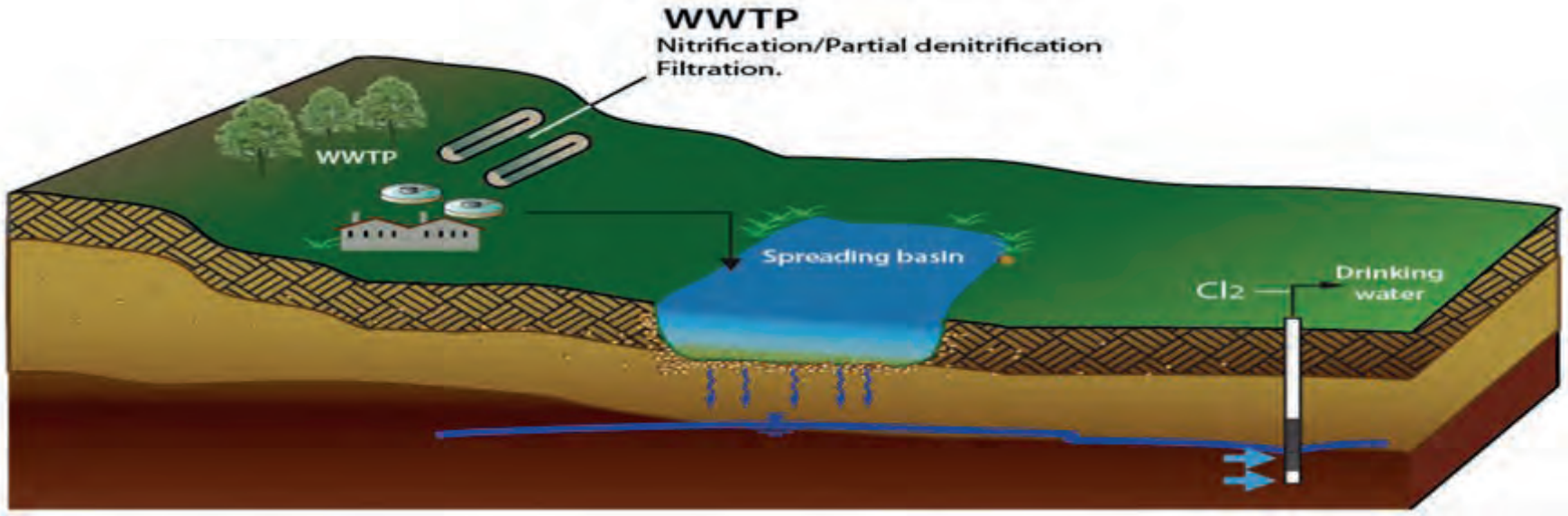
Direct water reuse

Indirect water reuse

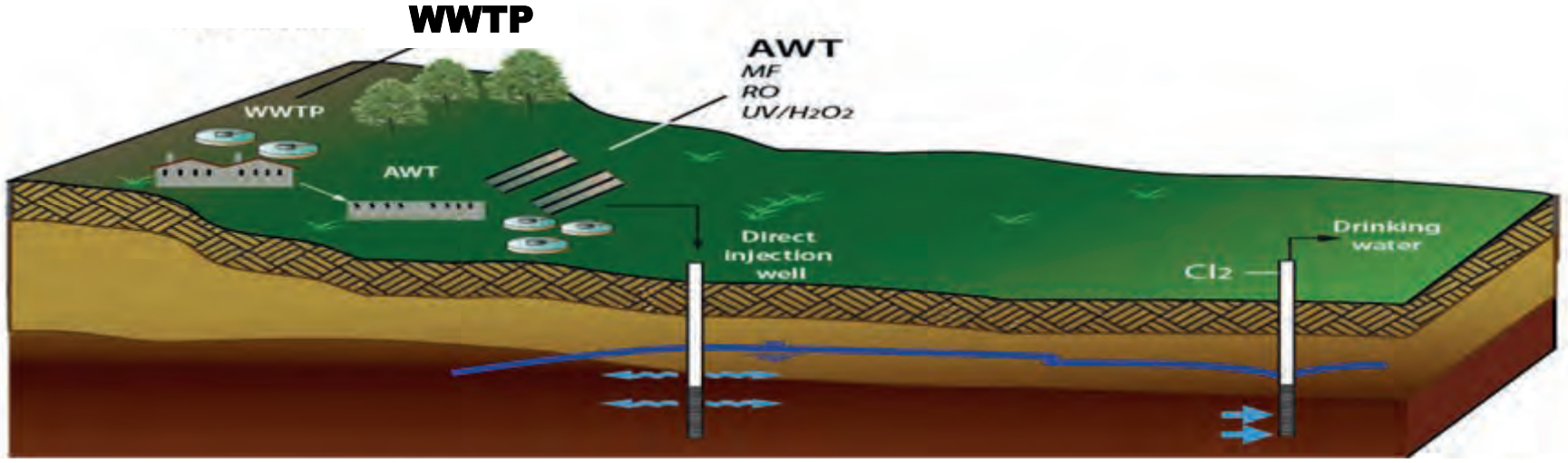


Public Perception

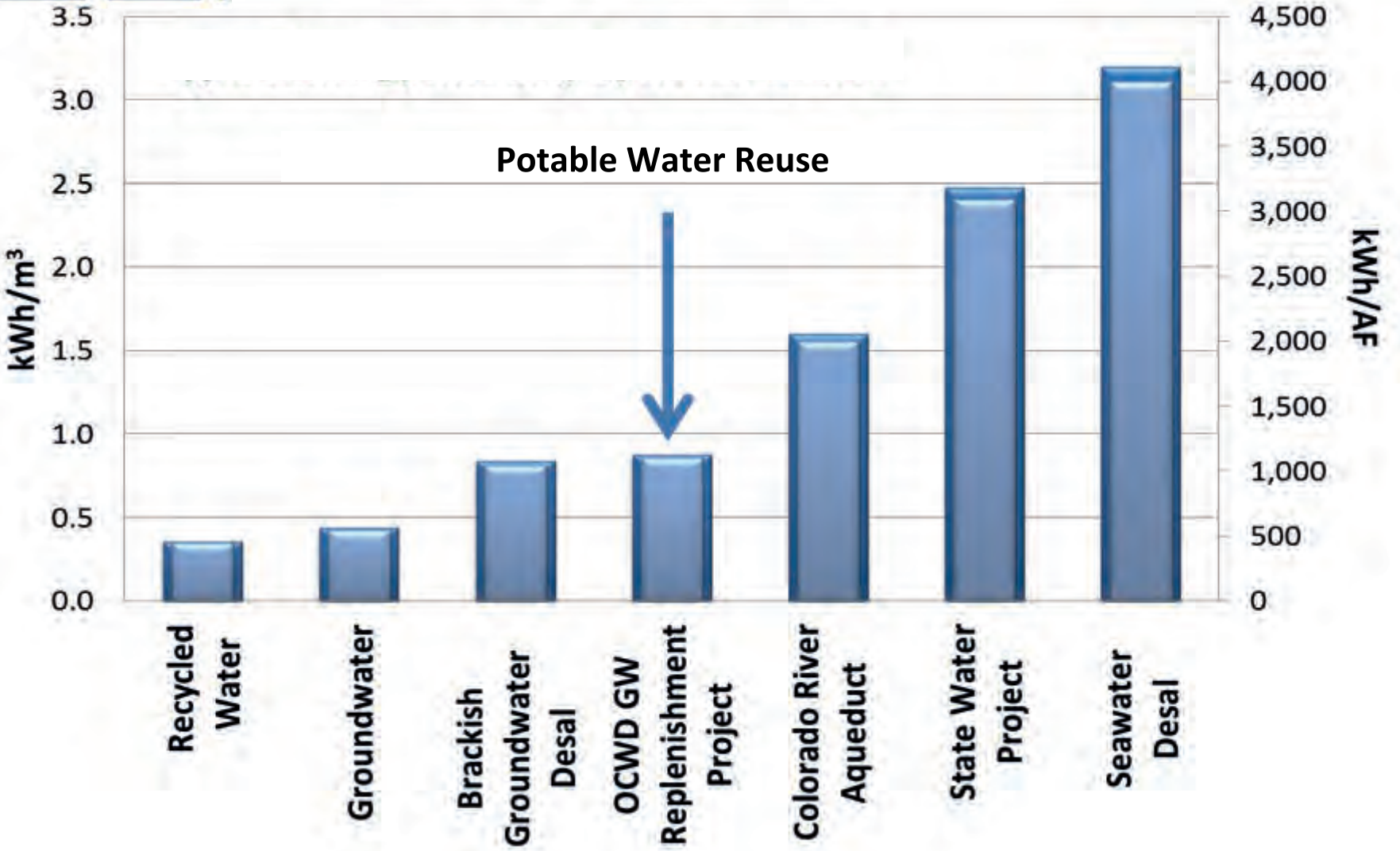
Water Reuse – Natural Systems



Water Reuse – Advanced Treat.



Energy Intensity by Water Source



Source: Pacific Institute analysis regarding SDCWA data

Facing the Yuck Factor

FEATURE ARTICLE - September 17, 2007 *by Peter Friederici*

Facing the yuck factor. PAUL LACHINE

How has the West embraced water recycling? Very (gulp) cautiously

Source: http://www.hcn.org/issues/354/17227

NRC Report on Water Reuse

USA TODAY

THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

Report: Drinking wastewater preferable to wasting it

Council touts it as potable after treatment

By Wendy Koch
USA TODAY

Drinking wastewater? The idea may sound distasteful, but new federally funded research says more Americans are doing so — whether they know it or not — and this reuse will be increasingly necessary as the U.S. population expands.

Treated wastewater poses no greater health risks than existing water supplies and, in some cases, may be even safer to drink, according to a report released Tuesday by the National Research Council, a science advisory group chartered by Congress. "We believe water reuse is a viable option" to deal with growing water scarcity, especially in coastal areas, says Jörg Drewes, an engineering professor at the Colorado School of Mines who contributed to the report.

"This can be done reliably without putting the public at risk," he says, citing technological advances. He says it's a waste not to reuse the nation's wastewater, because almost all of it is treated before discharge. This water includes storm runoff as well as used water from homes, businesses and factories.

Of the 32 billion gallons of wastewater discharged every day in the USA, the report says 12 billion — equal to 6% of total U.S. water use — is sent to an ocean or estuary and is thus a lost resource.

Many communities reuse wastewater for irrigation and industrial purposes. Some — notably Cloudcroft, N.M., and California's Orange County — have treatment facilities to reuse it as drinking water.

Wastewater treatment: Mechanic Phillip Castro does a routine inspection of the systems at a plant in San Antonio.

In many places, the report says, the public does not realize it is drinking water that was treated after being discharged as wastewater somewhere upstream. For example, wastewater discharged into the Trinity River from Dallas/Fort Worth flows south into Lake Livingston, the source for Houston's drinking water.

Despite the growing importance of this "de facto reuse," the report says there has been no systemic analysis of its extent nationwide since a 1980 study by the Environmental Protection Agency.

"There's always someone downstream," says Alan Roberson of the American Water Works Association, a non-profit group dedicated to clean water. He says wastewater reuse is common, so the council's report is important but not surprising.

Roberson says he expects this recycling will continue to increase, especially for irrigation and industrial needs.

He says it will take longer to establish potable uses because of public skittishness about drinking wastewater, however treated.

"We have to do something" to address water scarcity, says Olga Naidenko, a senior scientist at the non-profit Environmental Working Group. She says less than 10% of potable water is used for drinking, cooking, showering or dishwashing.

"We flush it down the toilet, literally," she says. Technologies exist to safely treat the water, she says, although some are expensive.

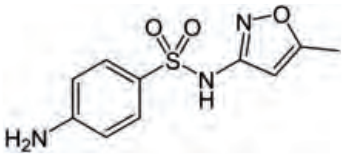
The report says water reuse projects tend to cost more than most water conservation options but less than seawater desalination and other supply alternatives. It calls on the EPA, a co-sponsor of the report, to develop rules that set safe national standards.

"…distinction between *indirect* and *direct* potable reuse is not scientifically meaningful…"

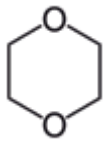
Contaminants potentially detectable in sewage

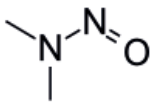
Chemical origins

Pharmaceuticals



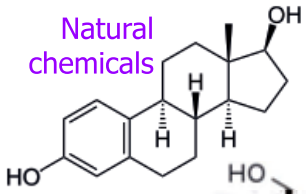
Industrial chemicals



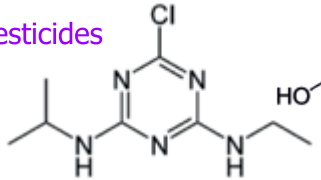


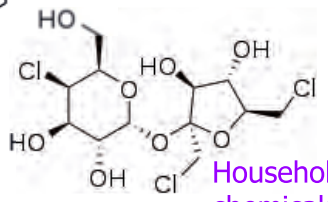
Transformation products

Natural chemicals



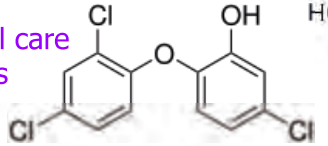
Pesticides

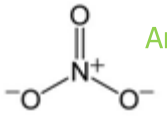




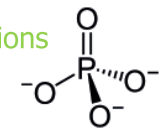
Household chemicals

Personal care products

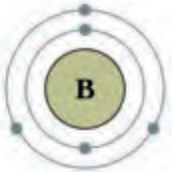




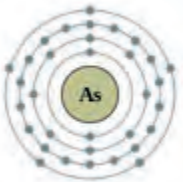
Anions



Cations



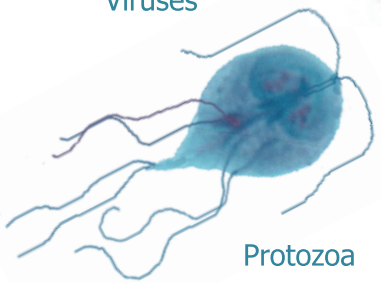
Metals



Microbial origins

Viruses

Bacteria

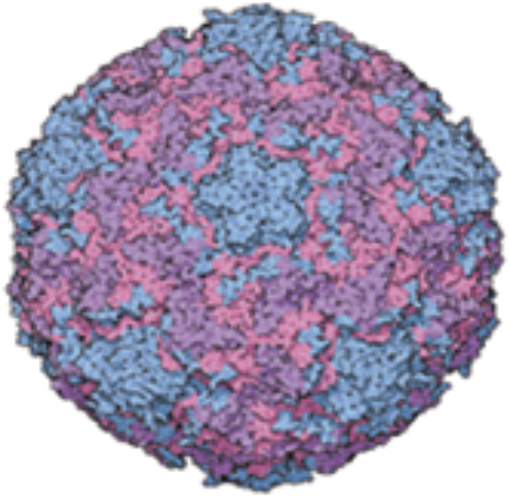


Protozoa

Helminths

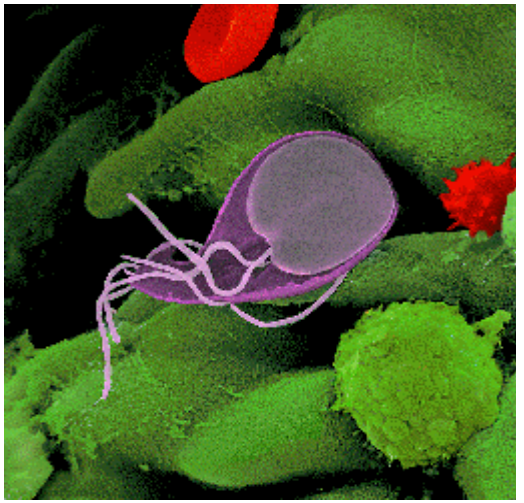
Biologicals are ACUTE Risks

Viruses

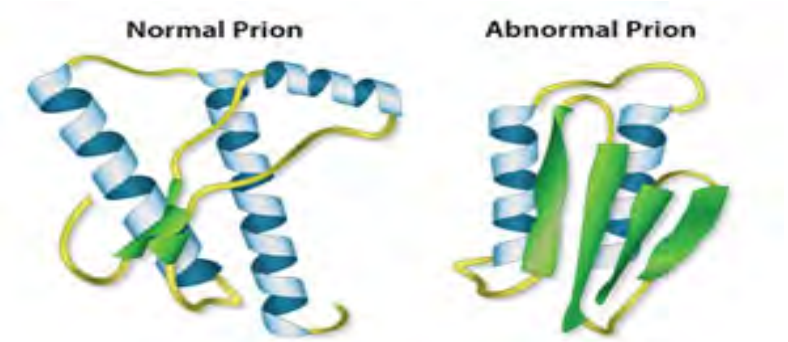


Bacteria

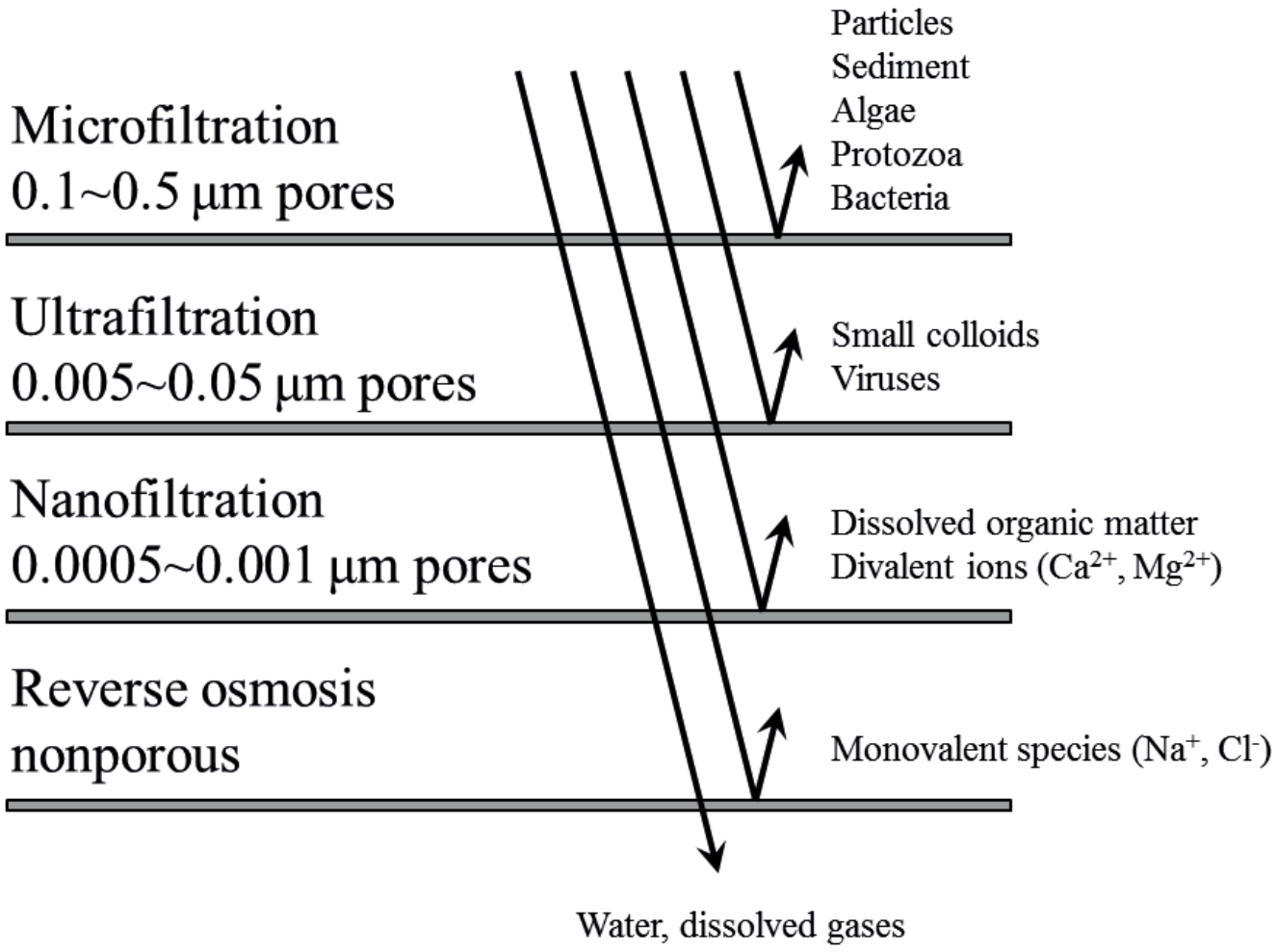
Parasites



Prions



Biologicals are ACUTE Risks



Chemicals are CHRONIC Risks

Organic and Inorganic

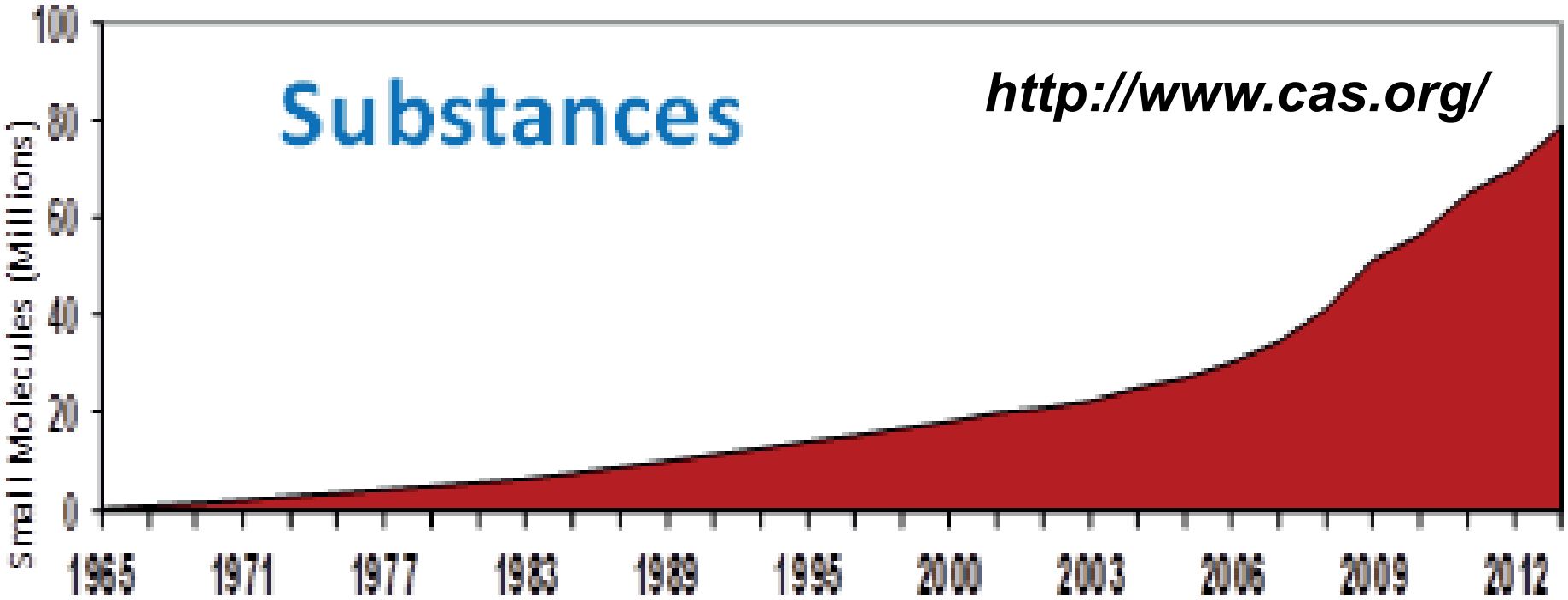
Volatile and non-volatile

Metals and Salts

89,008,294

ORGANIC AND INORGANIC SUBSTANCES TO DATE

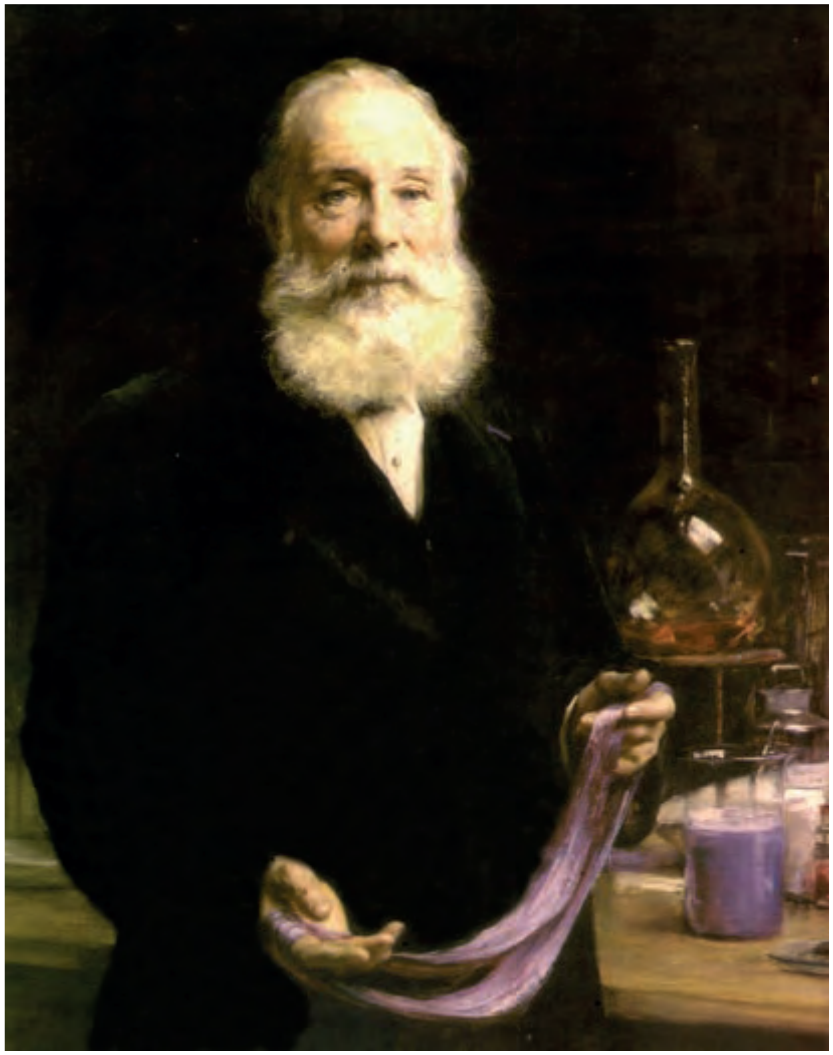
CHEMCATS 65,768,974 Commercially available chemicals



Snyder, S. A., Emerging Chemical Contaminants: Looking for Better Harmony. *J. Am. Water Works Assoc.* **2014,** *106* (8), 38-52.

1850's: Coal-Tar Byproduct

1856 – Perkin Synthesizes Mauve



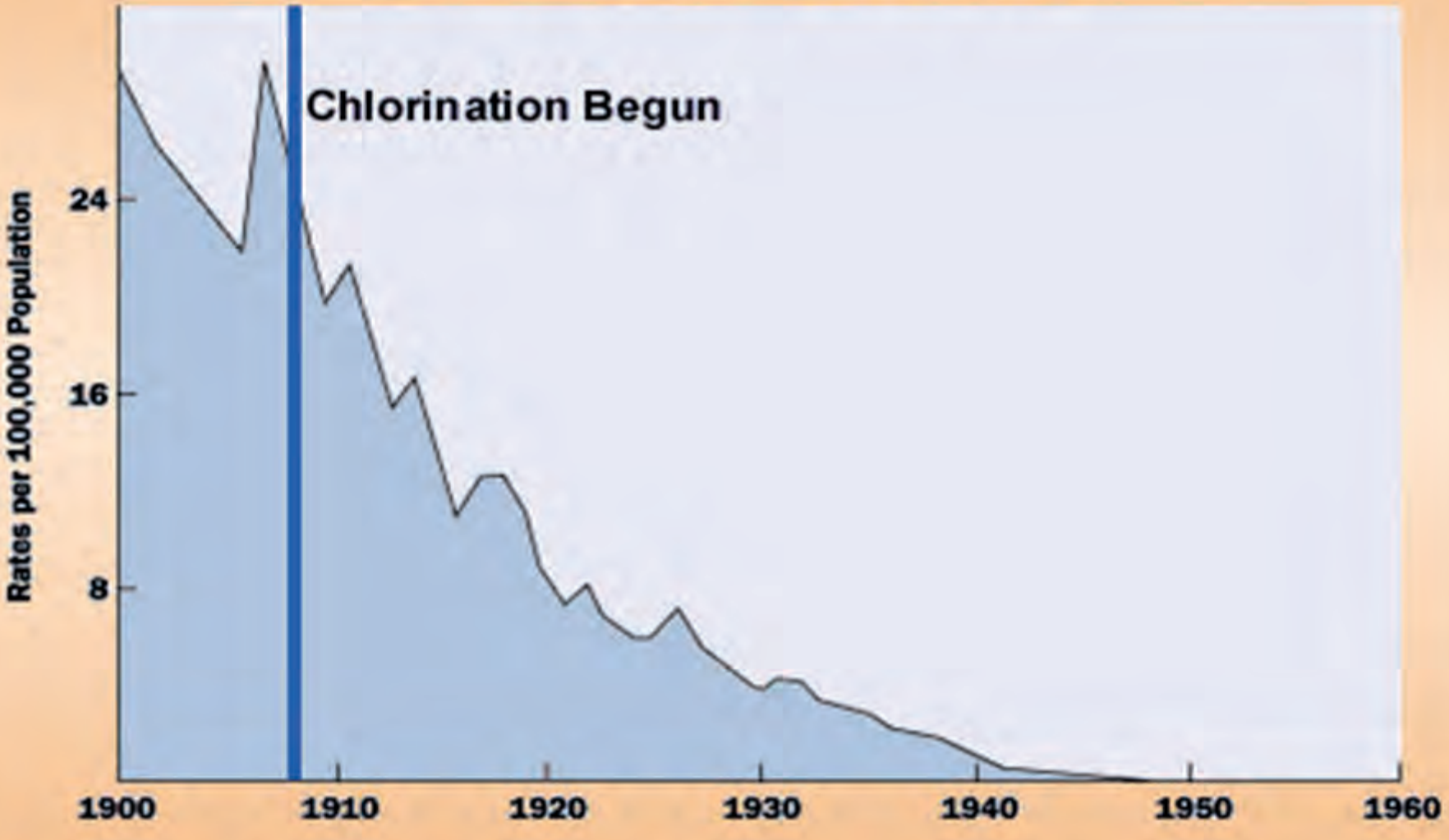
1860's – Cancer & Medicines

1899 – Industrial “Aspirin”

1902 Solid Chlorine & 1906 Ozone

Source: http://alternativewellnessstore.com; http://www.asia.ru/en/ProductInfo/933983.html

Death Rate for Typhoid Fever
United States, 1900-1960



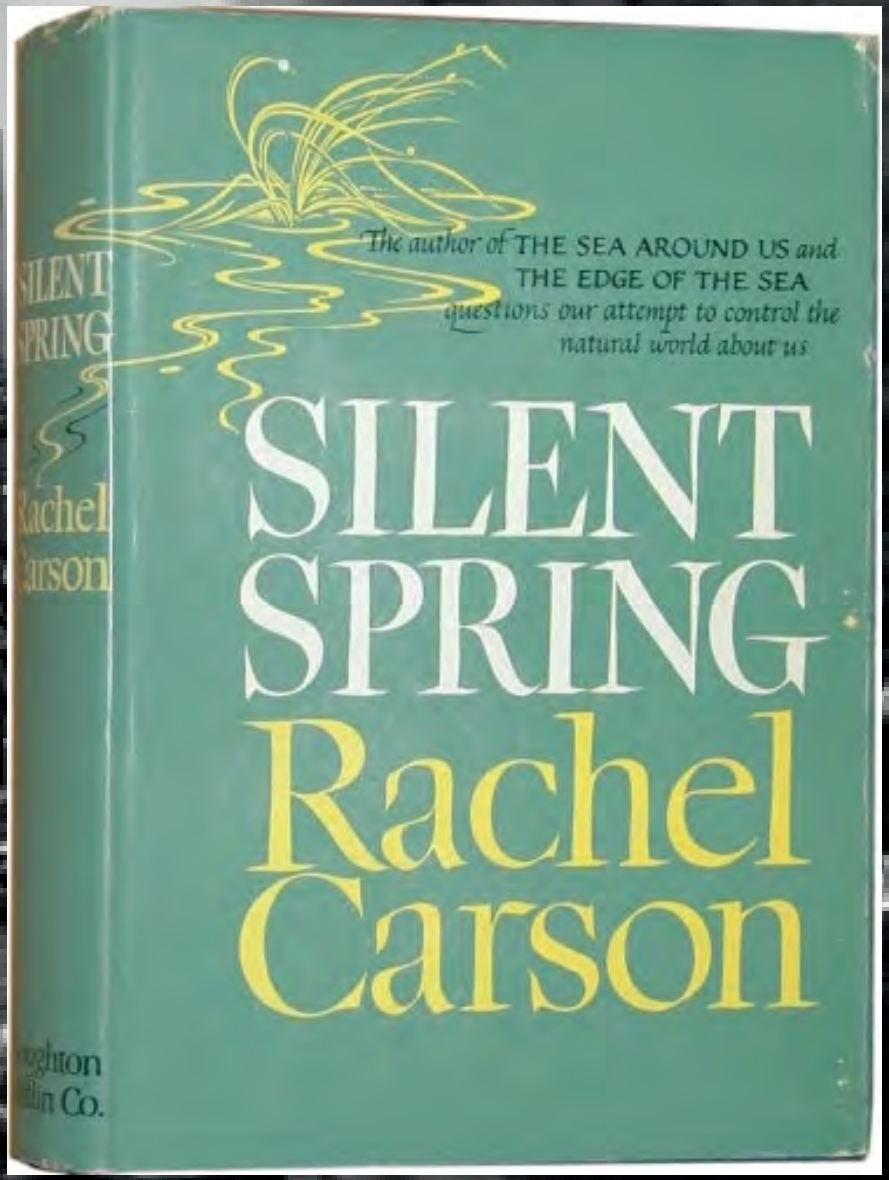
Source: U.S. Centers for Disease Control and Prevention, Summary of Notifiable Diseases, 1997.

Early 1900's – Malachite Green

1939 – Discovery of DDT as Pesticide

1948 – Paul Müller Nobel Prize

Cuyahoga River, Ohio – USA 1969



Background: Milwaukee, Wisconsin 1993

Outbreak of cryptosporidium

- Drinking water contaminated
- 403,000 people ill and approximately 104 deaths
- Cryptosporidium not disinfected by chlorine

Background: Las Vegas, Nevada 1994

1 March 1996 Volume 124 Number 5

Annals of Internal Medicine

Cryptosporidiosis: An Outbreak Associated with Drinking Water Despite State-of-the-Art Water Treatment

Susan T. Goldstein, MD; Dennis D. Juranek, DVM, MSc; Otto Ravenholt, MD, MPH; Allen W. Hightower, MS; Debra G. Martin, RN; June L. Mesnik, BA; Sean D. Griffiths, BA; Angela J. Bryant, BS; Rick R. Reich, BA; and Barbara L. Herwaldt, MD, MPH

cates. In the case–control study, persons who drank any unboiled tap water were four times more likely than persons who drank only bottled water to have had cryptosporidiosis (odds ratio, 4.22 [95% CI, 1.22 to 14.65]; $P = 0.02$).

SOUTHERN NEVADA WATER AUTHORITY PUTS A POSITIVE SPIN ON REPORTS THAT A ROCKET FUEL CHEMICAL WAS DETECTED IN LAKE MEAD AND LOCAL WELLS...

ENVIRONMENTAL NEWS

Human estrogens linked to endocrine disruption

For the first time in North America, high levels of natural and synthetic hormones in municipal wastewater treatment plant effluent have been linked with endocrine disruption in fish. The study by researchers at Michigan State University's Department of Zoology indicates that human hormones, not industrial chemicals, in the effluent caused male fish to produce vitellogenin, a well-accepted indicator of endocrine disruption.

"This is a significant, if not a surprising, result," commented Gary Ankley, an EPA toxicologist who studies endocrine disrupters. The results were similar to findings published last year by U.K. researchers that identified hormones secreted in women's urine as the cause of vitellogenesis in caged fish exposed to sewage effluent in U.K. waters.

High levels of a female protein in male fish found in Lake Mead, Nev., led to a search for the cause in the effluent-dominated waters of the Las Vegas Wash. (Courtesy Shane Snyder, Michigan State University)

the compounds that were likely to act like estrogens in the fish. They also used an innovative method that involves solid-phase extraction and in vitro cellular bioassays to detect endocrine-modulating compounds in complex aqueous mixtures. Of the

the highest level of estrogenic activity in effluent downstream from a small plant (55,000 gal/day) with relatively few treatment processes.

Results from a companion Michigan State study, in which caged fish were exposed to Michigan wastewater effluent, suggest

Resourc

PUBLISHED BY ASAE – THE SOCIETY FOR ENGINEERING IN AGRICULTURAL, FOOD, AND BIOLOGICAL S

MAY 1999

Bad Medicine

Pharmaceuticals taken by humans and animals can end up in waterways

Shane Snyder and Erin Snyder

Pharmaceuticals have improved human health and lengthened the human life span.

But new research is showing that although most medicine taken into the body is absorbed, some of the non-degraded or biologically activated drugs may be excreted as waste. These human-passed drugs ultimately end up in wastewater treatment plants (WWTPs) where they are processed and often released into waterways.

The degree to which these drugs are eliminated by WWTPs depends on the treatment method. Some percentage of the pharmaceuticals passes through WWTPs unaffected and is discharged into lakes or rivers.

Concerns about pharmaceuticals entering natural U.S. waters have surfaced in the past. In 1970, Henry H. Tabak of the U.S. Environmental Protection Agency (EPA) investigated synthetic ovulation-inhibiting hormones in wastewater. He found significant levels of natural and synthetic hormones in WWTP effluent.

"Although a prediction of possible future danger from the accumulation of synthetic steroid compounds in treated wastewater is not possible at present," Tabak said in 1970, "it is certain that if treatment processes are not modified in the future to encourage high conversion rates of these compounds into safe end products, one might predict their accumulation in water courses."

Pinpointing the problem

European scientists recently detected clofibric acid, a drug used to lower blood cholesterol, in high concentrations in lakes and rivers in their countries. As early as 1976, clofibric acid and salicylic acid were discovered in wastewater effluents in the United States.

Pharmaceuticals discharged into U.S. natural waters are at low levels, generally a few parts per trillion (ppt) or less. The U.S. Food and Drug Administration (FDA) suggests that a drug or bioactivated metabolite enter the aquatic environment at levels no greater than 1 part per billion (ppb).

Michigan State University researchers used this equipment to take samples of waste water effluents.

Reports of pharmaceuticals in natural U.S. waters are rare. There have been no reports of pharmaceuticals in drinking water.

But antibiotic-resistant bacteria strains have been detected in Michigan's Detroit River by R.C. Campeau of the University of Detroit Mercy. He believes the bacteria pose "a potential health risk." Similar strains have been reported in Asia and Europe. The problem is magnified by large concentrations of antibiotics used in raising livestock.

Endocrine disruption in the aquatic environment has brought the issue of pharmaceuticals in wastewater effluents to the forefront. Much of the current interest in endocrine disrupting chemicals in wastewater was generated by a finding in the United Kingdom that fish living in water influenced by wastewater effluents showed reproductive abnormalities. These abnormalities were seen infrequently in fish not exposed to wastewater.

In 1996, Hugh Bevans of the U.S. Geological Survey (USGS) in Carson City, Nevada, reported that feral carp captured in a bay of Nevada's Lake Mead, which received large amounts of treated wastewater, showed reproductive abnormalities. No cause has been established for these effects.

In spring 1997, the National Park Service and the Southern Nevada Water Authority (SNWA) contacted the Aquatic Toxicology Laboratory (ATL) at Michigan State University (MSU) regarding the USGS report of endocrine disruption in feral carp. At the time, MSU researchers were developing the Toxicity Identification and Evaluation (TIE) method to screen for estrogenic and anti-estrogenic compounds in effluents and rivers in Michigan.

The method involved extracting 5.3 qt. (5 L) of water *in situ* using solid-phase extraction (SPE) disks. The chemicals trapped on the disks were eluted in the laboratory and the resulting extract was fractionated and tested using analytical techniques.

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?

Testicles Shrinking in Las Vegas Bay

The U.S. Geological Survey, in cooperation with the U.S. Fish and Wildlife Service, recently released a four-page report, "Investigations of the Effects of Synthetic Chemicals on the Endocrine System of Common Carp in Lake Mead, Nevada and Arizona." The report summarizes a number of investigations over the last decade concerning the potential of endocrine disruption in fish in the lake. Water discharged into Lake Mead via Las Vegas Wash includes residential-irrigation runoff, stormwater runoff, subsurface flow, and tertiary treated sewage effluent, collectively carrying a cocktail of chemicals. The characteristics

PNAS | May 22, 2007 | vol. 104 | no. 21 | 8897–8901

Collapse of a fish population after exposure to a synthetic estrogen

Karen A. Kidd*†, Paul J. Blanchfield*, Kenneth H. Mills*, Vince P. Palace*, Robert E. Evans*, James M. Lazorchak‡, and Robert W. Flick‡

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 characteristics in Lake Mead and other freshwater sources around the country.

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

Surrogates and Indicators

Health-relevant CECs

Potential health risks at levels at/ near occurrence

Performance indicator CECs

Provide information on treatment efficacy and/or represent broader classes

Surrogates

Bulk parameters that are indicative of occurrence and/or attenuation of substances/organisms

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

Indicator Example – Secondary WWTP

Faster transformation during secondary treatment

Higher sorption during secondary treatment

		Biotransformation (K_b, L/g-d)		
		Recalcitrant <0.1	**Moderate Slow 0.1-10**	**Rapid >10**
Sorption (log K_d)	**Low <2.5**	Carbamazepine Meprobamate Primidone TCEP Sucralose	DEET Sulfamethoxazole Gemfibrozil Iopromide	Acetaminophen Caffeine 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

100L samples – Circa 1997

Analysis of Emerging Contaminants in Water

Conventional SPE Method

1 L sample

5 hours

Ultra high performance liquid chromatography tandem mass spectrometry for rapid analysis of trace organic contaminants in water

ng/L

Online SPE Method

1.5 mL sample

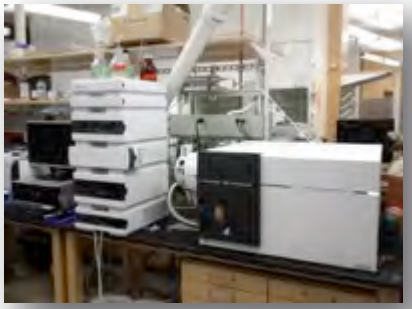
30 min

Sensitive LC/MS Quantitation of Trace Organic Contaminants in Water with Online SPE Enrichment

0.1-20 ng/L

Direct Injection Method

0.1 mL sample



15

Analysis of Trace Organic Contaminants in Water by Direct Injection Using Agilent 6490 LC/MS/MS with Pos/Neg Switching

0.1-100 ng/L

Basic Categories of Treatment

Separation

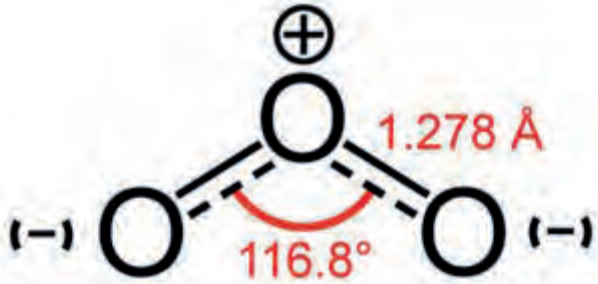
Biological

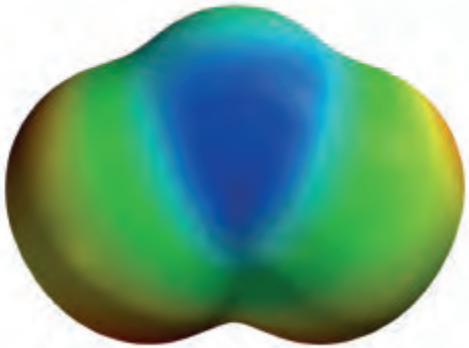
Oxidation

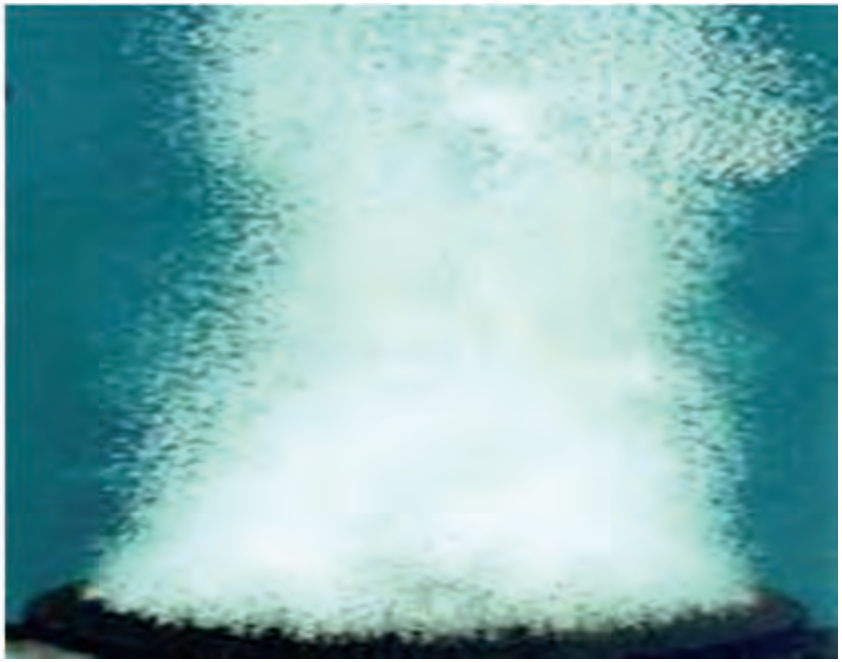
The Multi-Barrier Approach

Disinfectant	Bacteria	Viruses	Parasites	DBPs
Free Chlorine	✓	✓	✗	THMs, HAAs
Chloramines	–	✗	✗	NDMA
UV	✓	–	✓	None???
Ozone	✓	✓	–	Bromate, NDMA

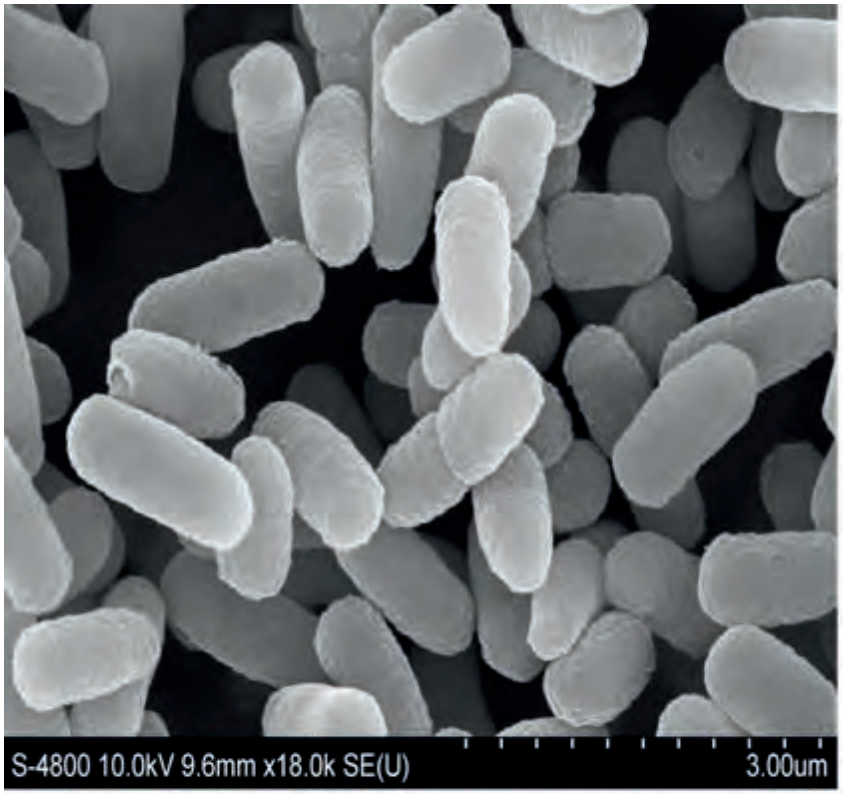
Ozonation Example







Disinfection

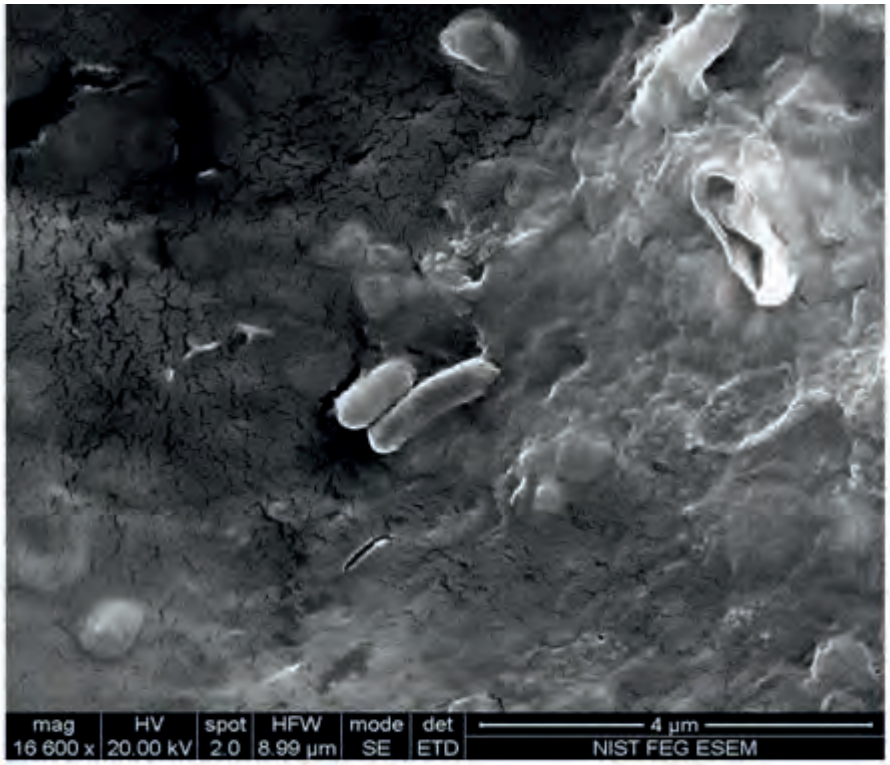


E. Coli - Healthy

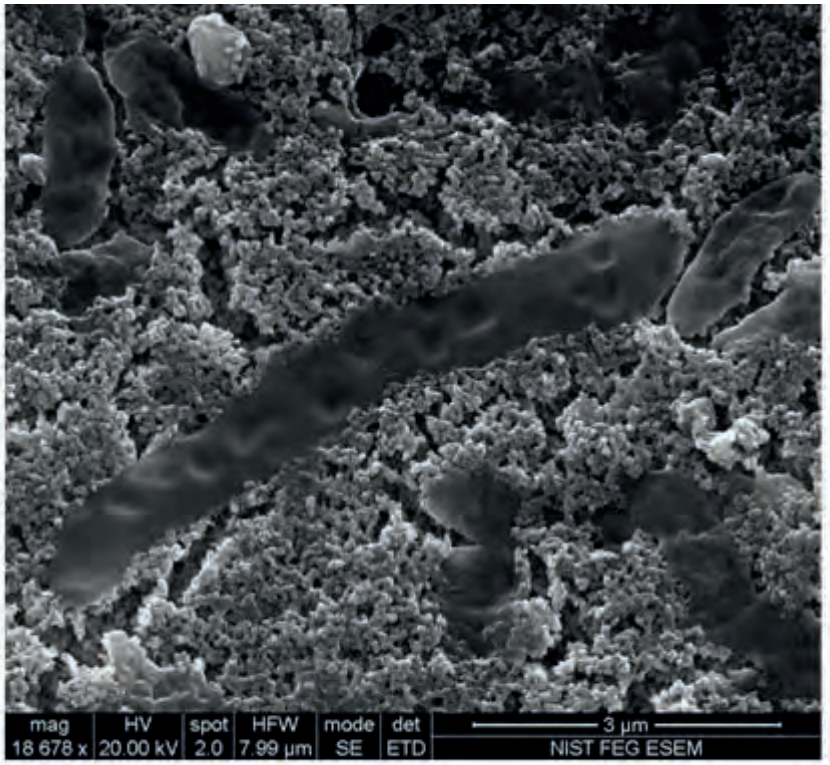
Post-AOP

Sherchan, S. P.; Snyder, S. A.; Gerba, C. P.; Pepper, I. L. *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* **2014,** *49* (4), 397-403.

Membrane Fouling Reduction



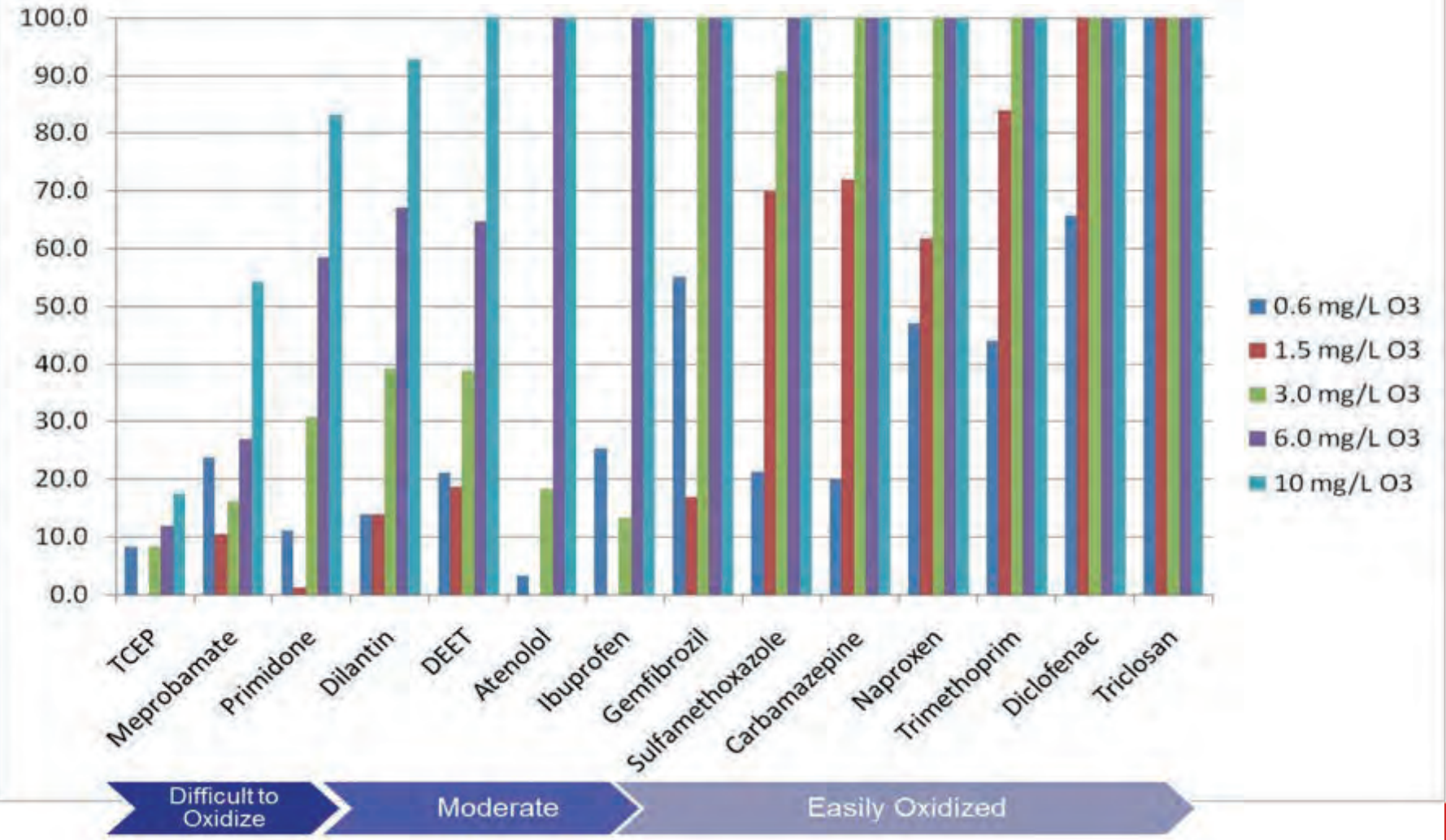
MBR-RO control



MBR-Ozone-RO (3 mg/L)

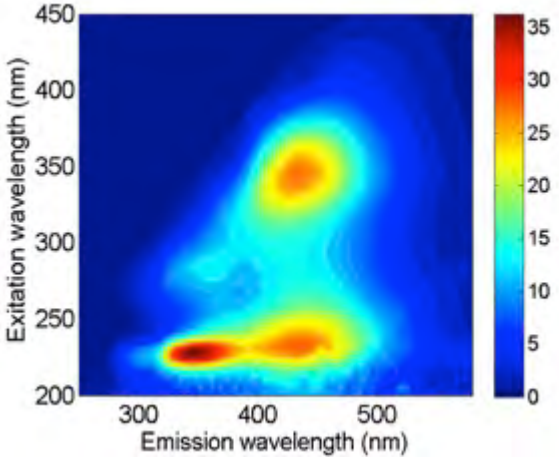
Stanford, B. D.; Pisarenko, A. N.; Holbrook, R. D.; Snyder, S. A., Preozonation Effects on the Reduction of Reverse Osmosis Membrane Fouling in Water Reuse. *Ozone-Sci. Eng.* **2011,** *33* (5), 379-388.

Indicator Oxidation

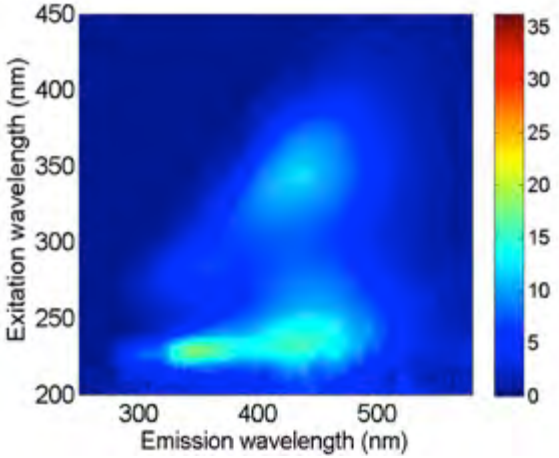


Pisarenko, AN et al.. *Water Res.* **2012,** *46* (2), 316-326.

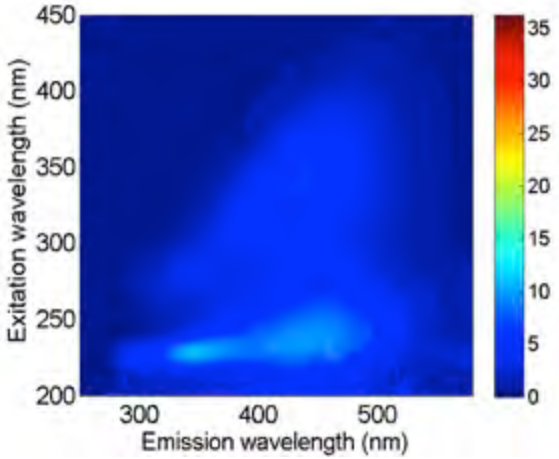
Fluorescence Surrogate Response



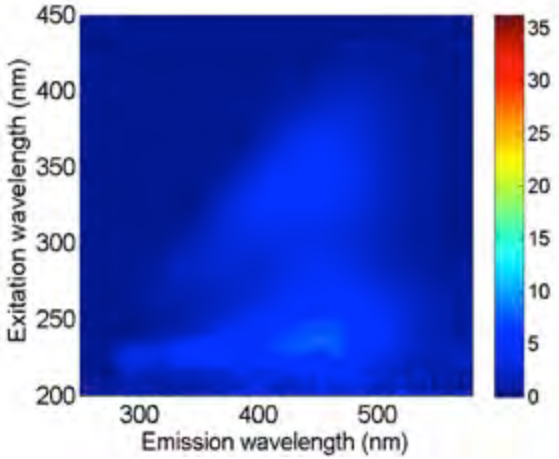
Control



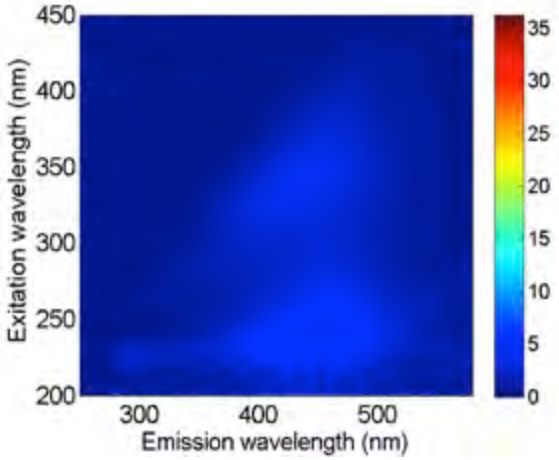
1.5 ppm



3 ppm



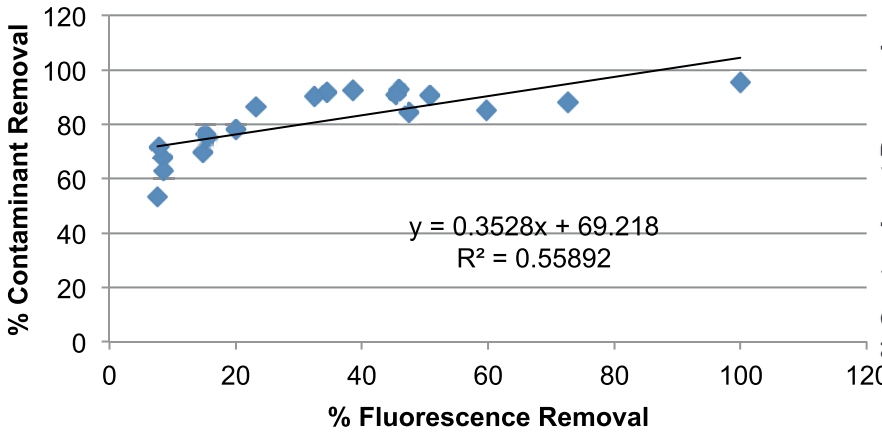
4.5 ppm



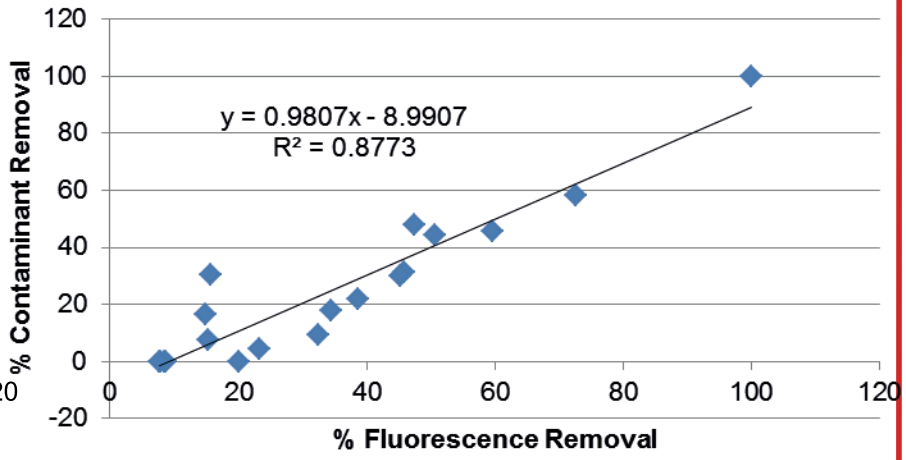
6 ppm

Fluorescence Surrogate Correlation to LC-MS/MS

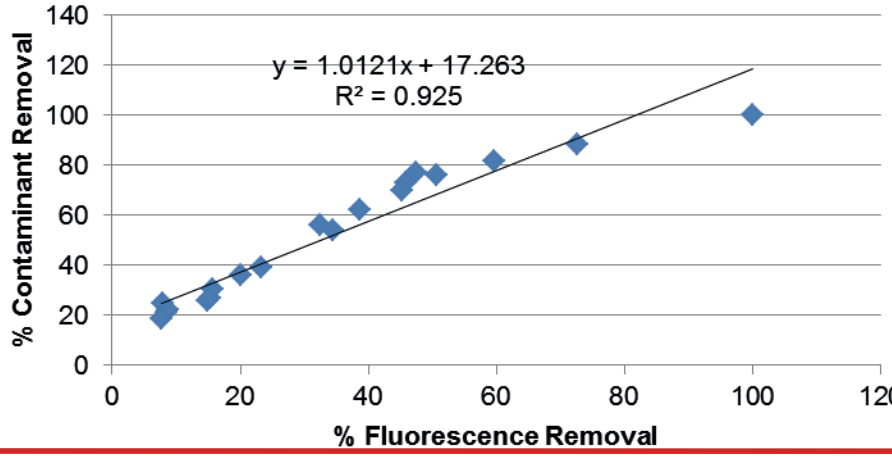
Group 1: Triclocarban



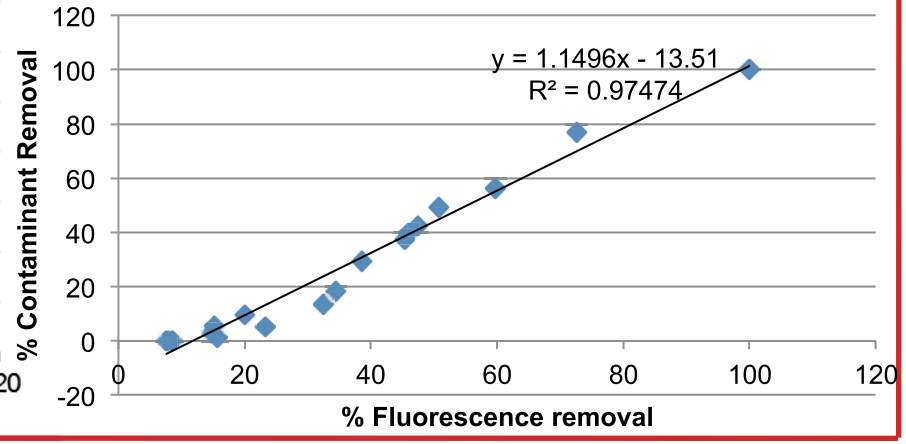
Group 2: PFOA



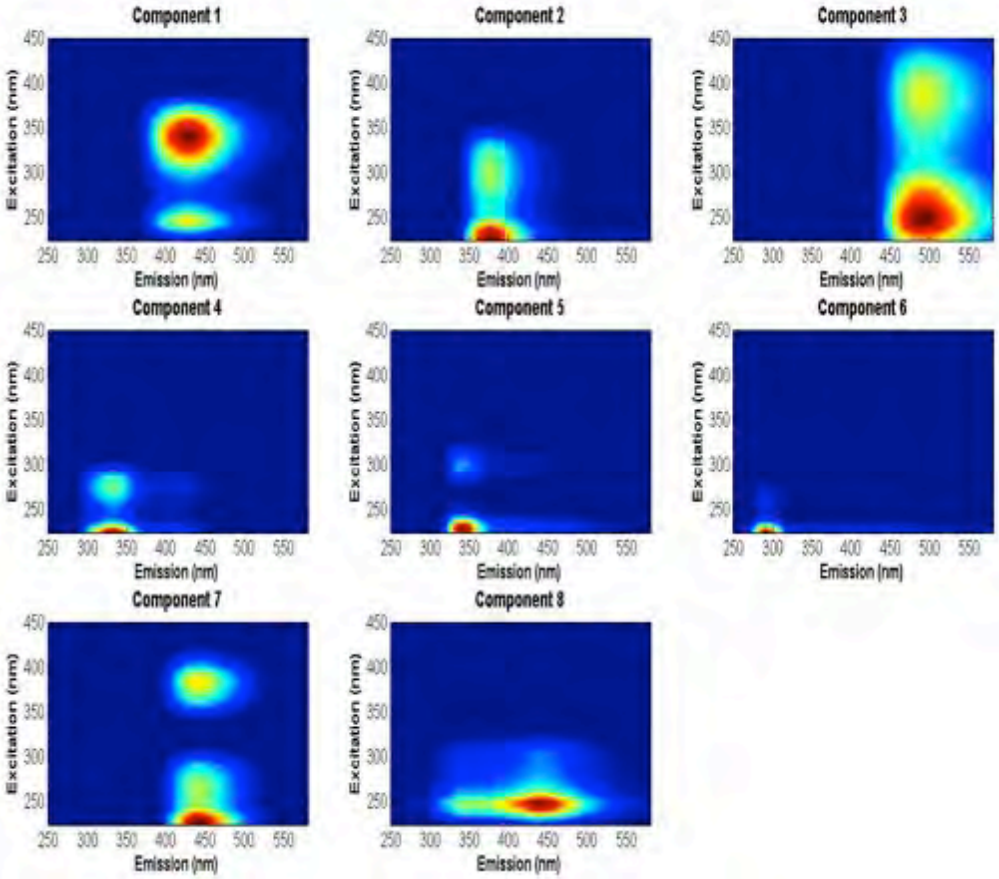
Group 3: Atenolol



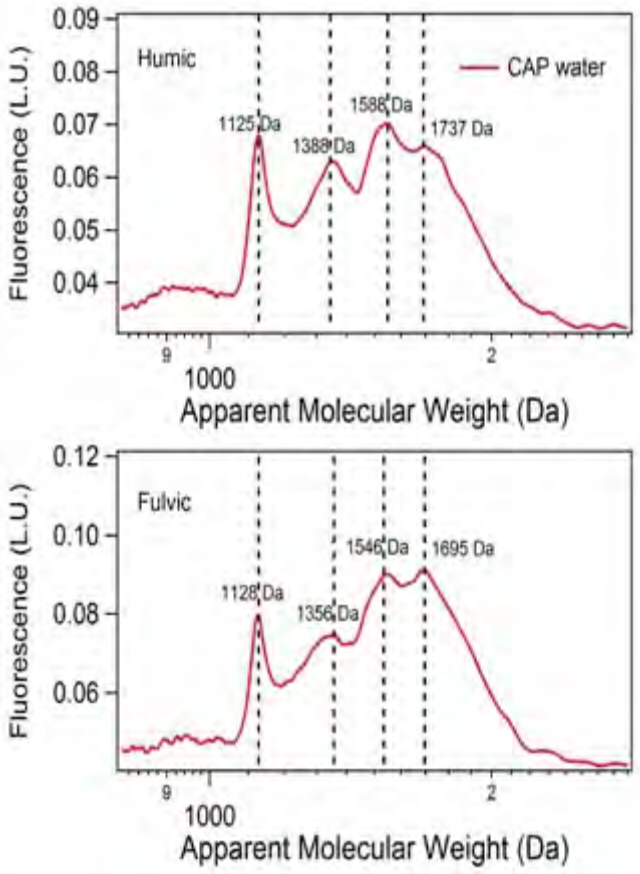
Group 4: Primidone



Use of PARAFAC model

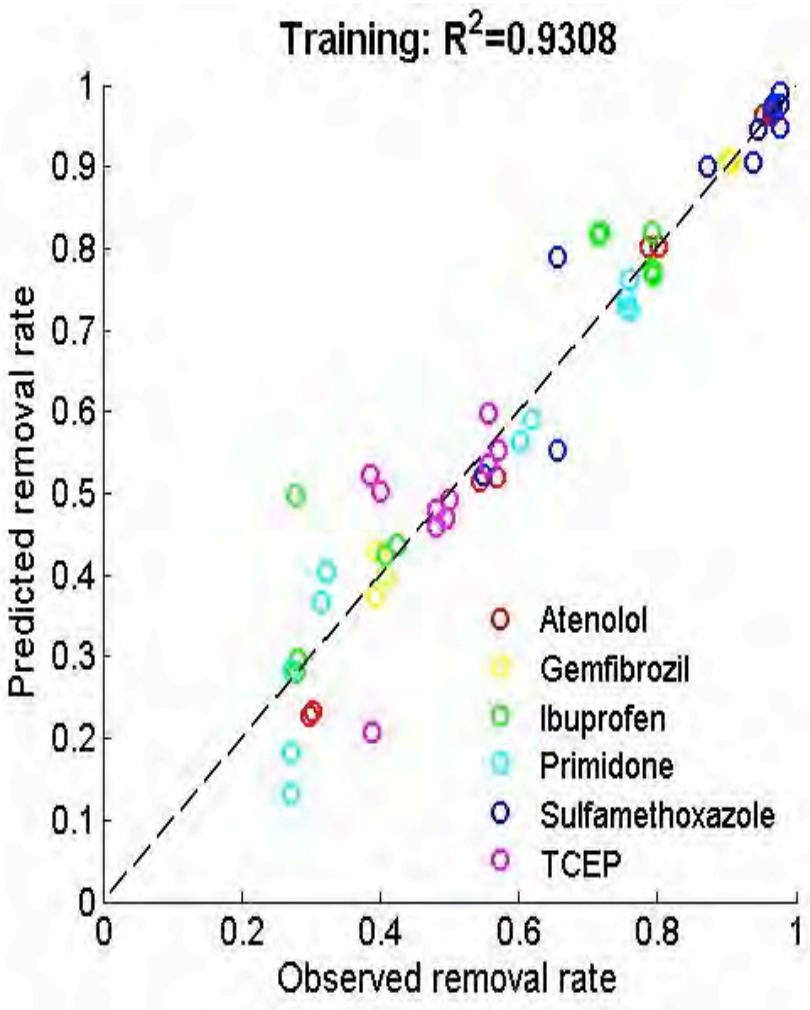


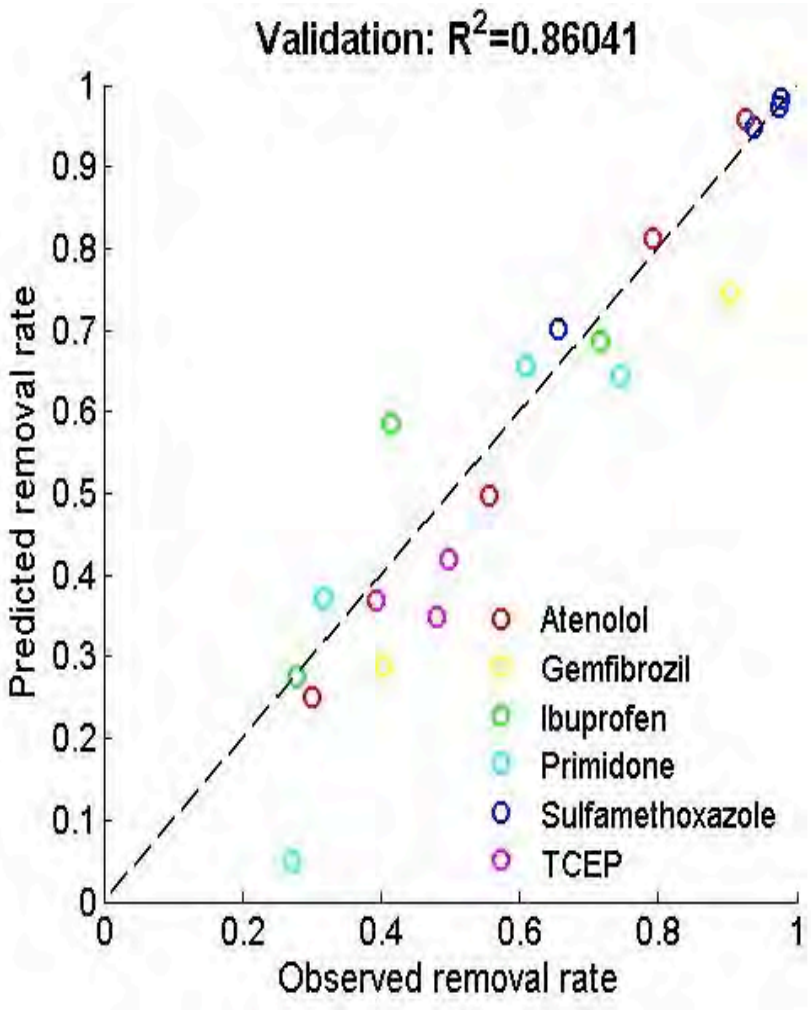
< Eight components of fluorescent organic matters obtained by PARAFAC model >



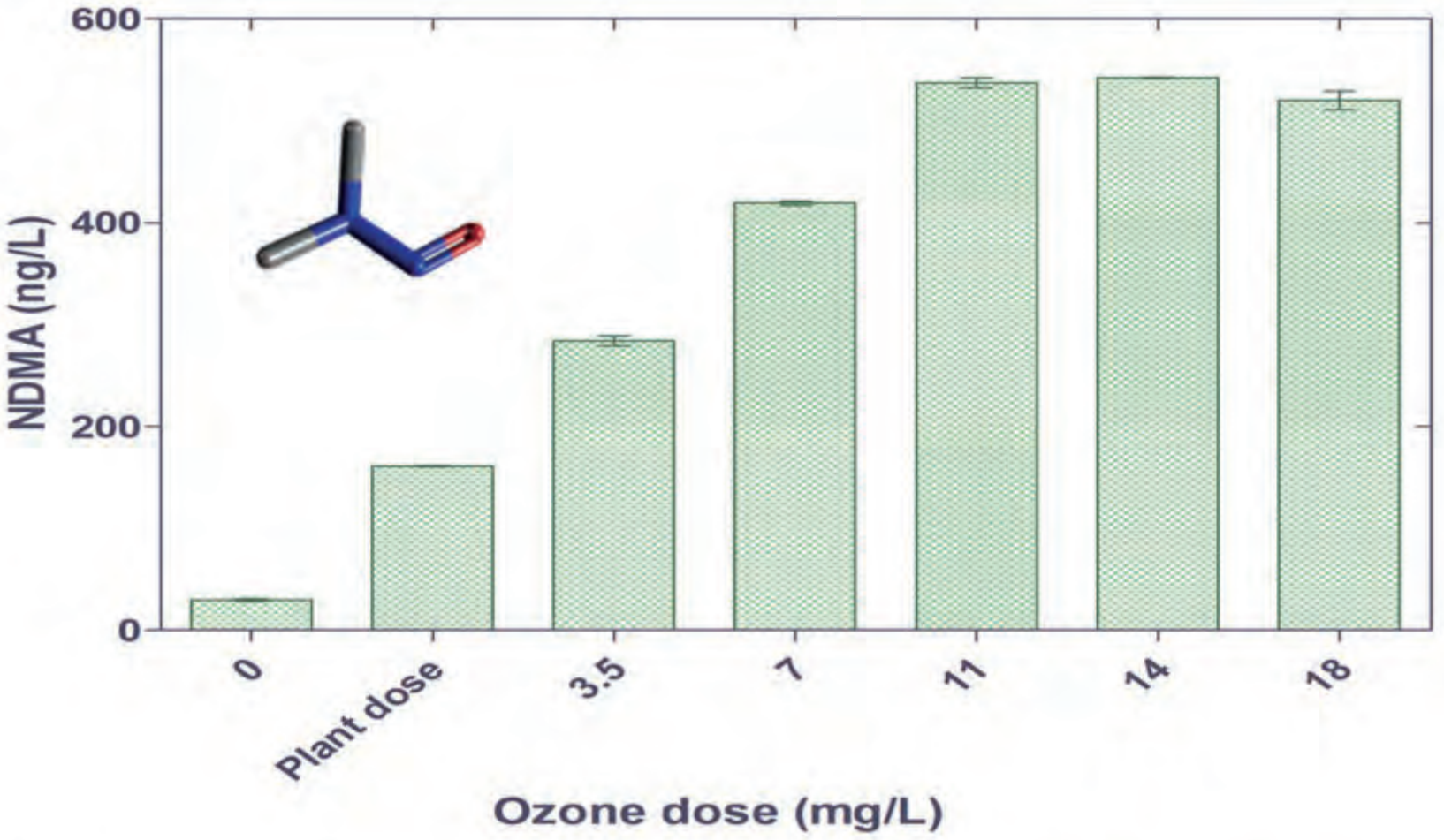
< SEC chromatogram of CAP water >

ANN Modeling for Ozone



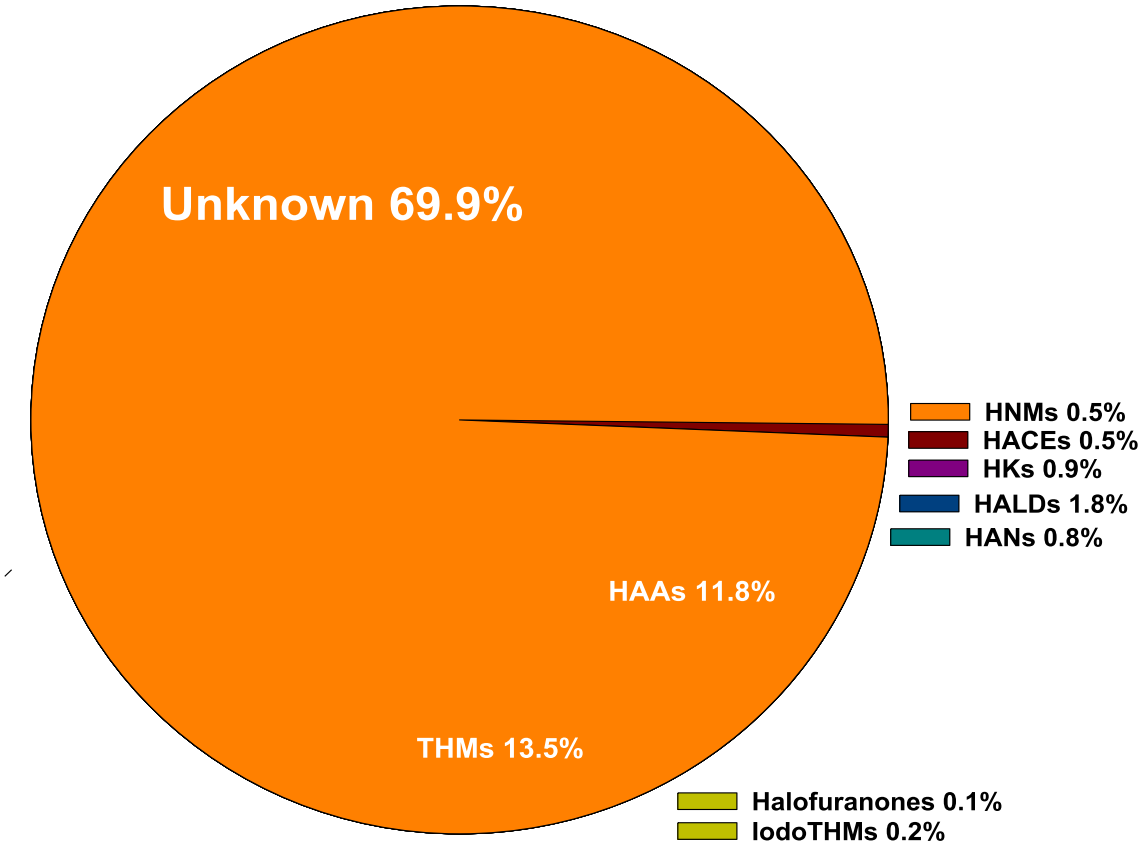


NDMA-FP with Ozone



Sgroi, M.; Roccaro, P.; Oelker, G. L.; **Snyder, S. A.**, *ES&T* **2014,** *48* (17), 10308-10315.

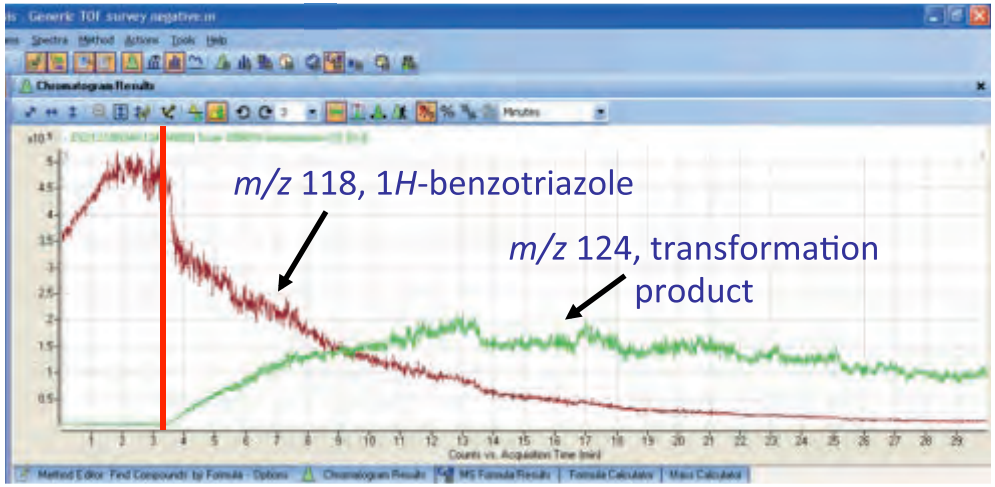
Most DBPs Not Identified

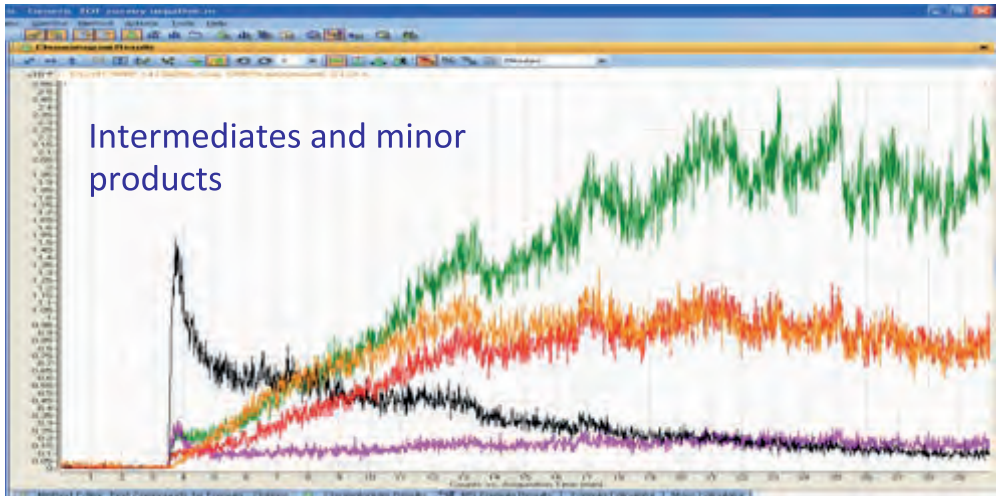


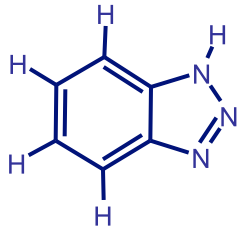
Nationwide Occurrence Study, Krasner et al., *Environ. Sci. Technol*. 2006, *40*, 7175-7185.

LC-QTOF (Agilent 6540)

Benzotriazole Transformation Products

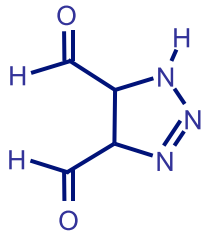






1*H*-benzotriazole

O_3/ ·OH



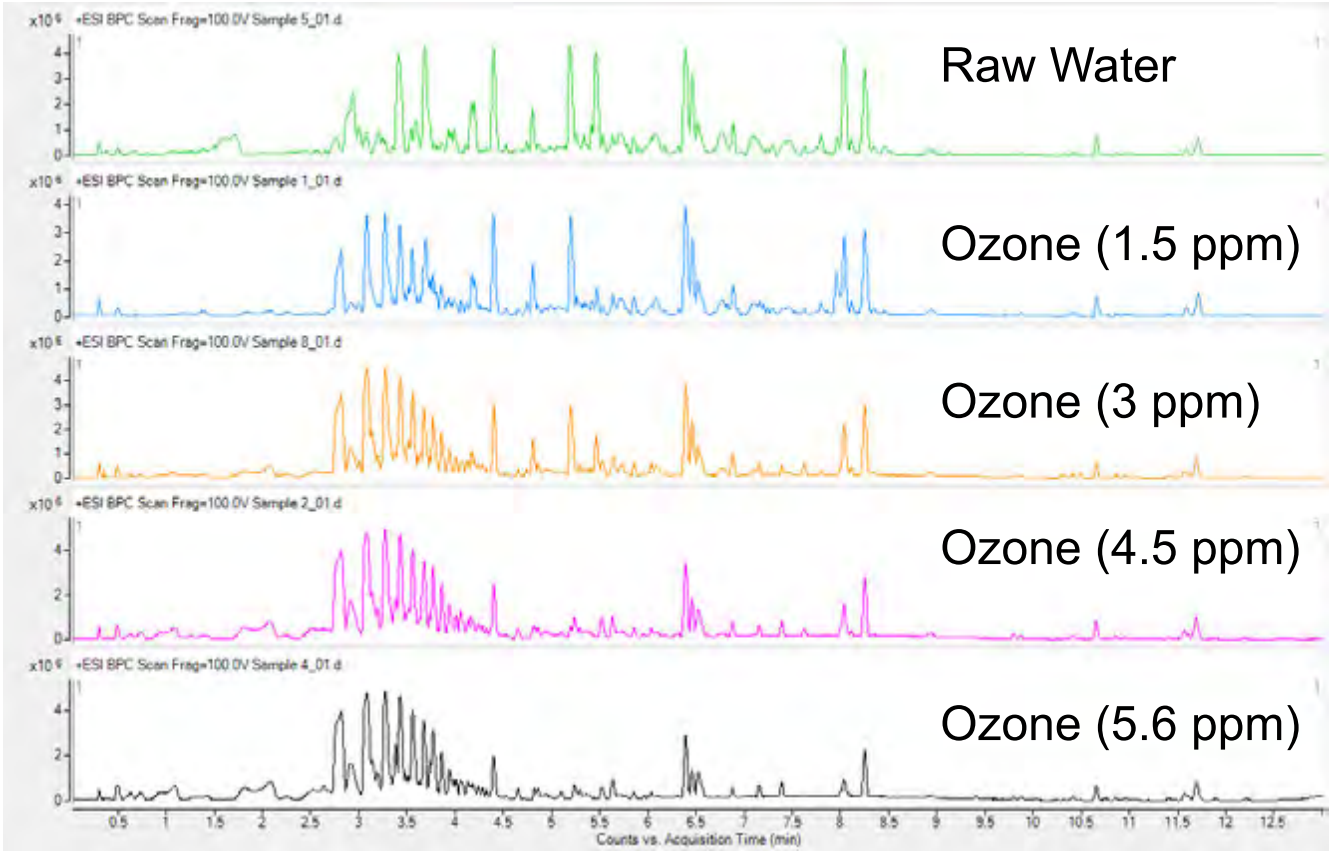
***m/z* 124.01522 (meas.)**
***m/z* 124.01525 (calc.)**
$C_4H_3N_3O_2$

11,2,3-triazole-4,5-dicarbaldehyde

Mawhinney, DB, BJ Vanderford, **SA Snyder**. (2012) *ES&T* 46(13):7102-7111.

OZONE TREATMENT & QTOF ANALYSIS OF UNKNOWNS

Searching for unknown in water



Chromatograms Very Similar

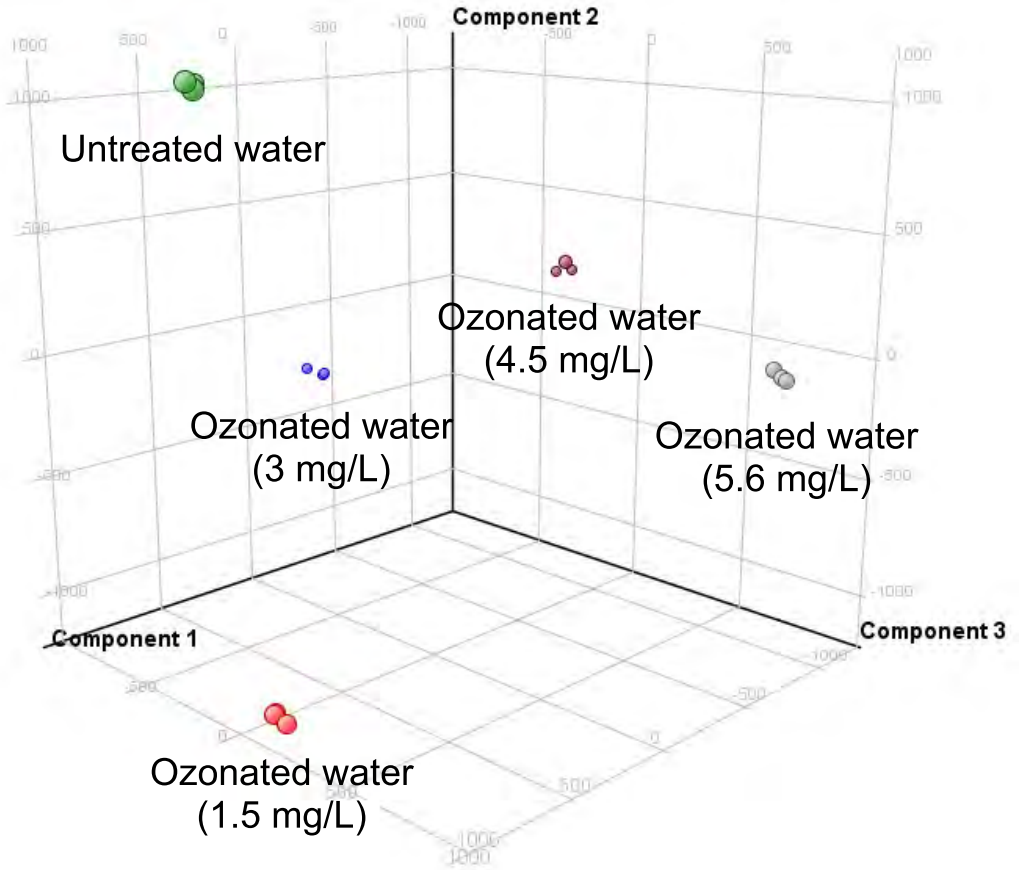
Extraction of Molecular Features Reveals thousands of compounds in each chromatogram

Further Data Processing Requires Specific Software

Merel, S.; Anumol, T.; Park, M.; **Snyder, S. A.**, *J. Hazard. Mater.* 2014 In Press

OZONE TREATMENT & QTOF ANALYSIS OF UNKNOWNS

PCA Plot for Different Ozone Doses



Although chromatograms were all similar for the analyst

Software identifies features able to discriminate the different water quality

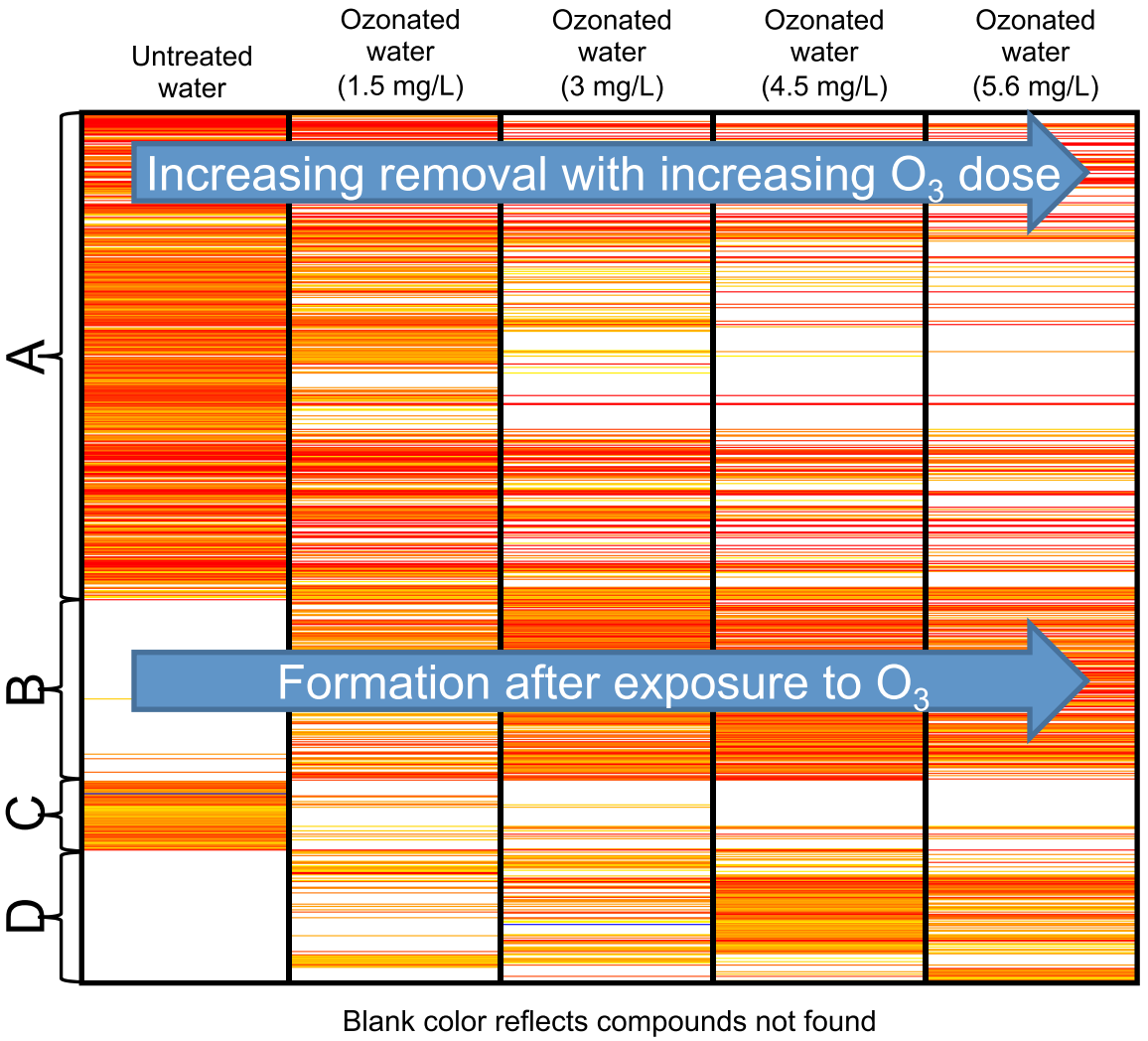
Merel, S.; Anumol, T.; Park, M.; **Snyder, S. A.**, *J. Hazard. Mater.* 2014 In Press

OZONE TREATMENT & QTOF ANALYSIS OF UNKNOWNS

Although chromatograms were all similar for the analyst, clear differences appear on the heatmap

A & C are group of compounds in the raw water but at lower concentration or absent in ozonated water **(removed by ozone)**

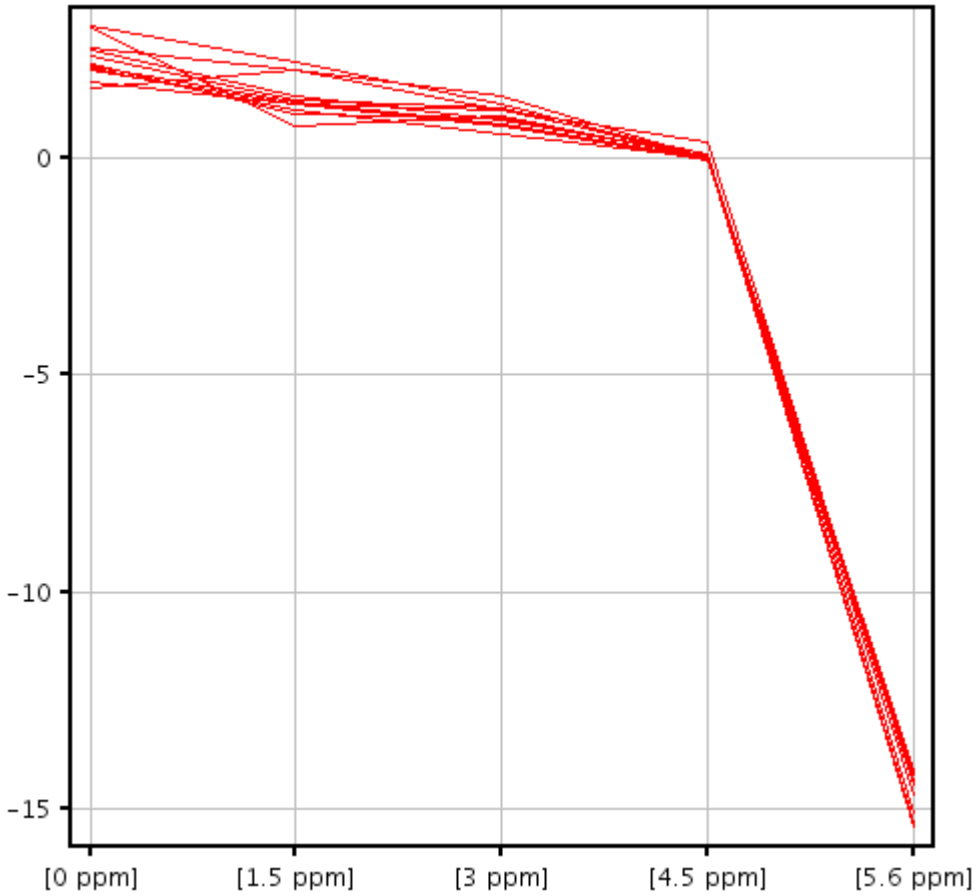
B & D are compounds absent in raw water but present in treated water **(ozone by-products)**



Merel, S.; Anumol, T.; Park, M.; **Snyder, S. A.**, *J. Hazard. Mater.* 2014 In Press

Compound Cluster Analysis with QTOF

Cluster and Trend Analysis

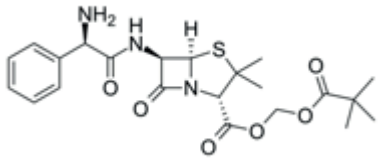


Cluster around Fluoxetine

Compounds removed only with the highest ozone dose

Overall strong attenuation

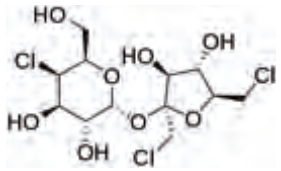
Cluster include 11 compounds Including one identified as the prodrug pivampicillin



Data Mining with QTOF

Forgot to analyze for a compound of interest???

Example of Sucralose



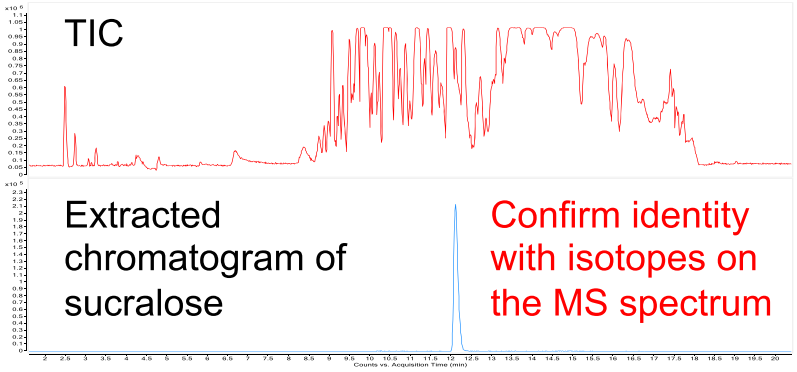
QQQ

- Need to run again the sample
- Need to procure standard
- Need to develop the method if the compound is not on the list of target analytes

QTOF

- No need to reanalyze sample

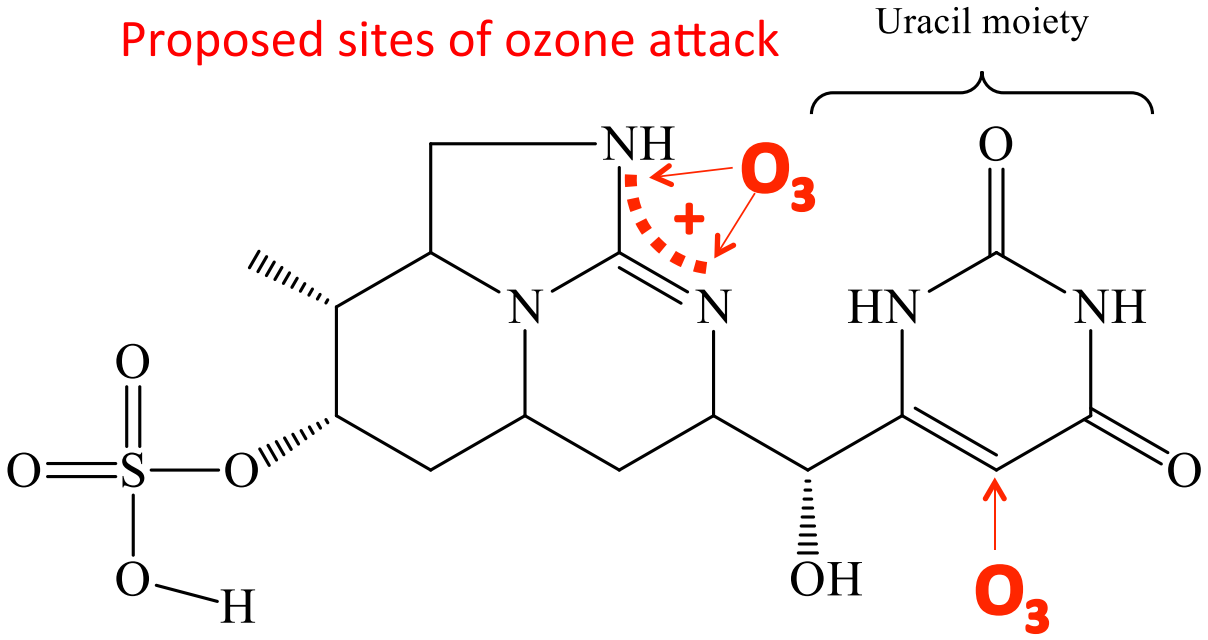
Just extract the exact mass from the total ion chromatogram (Na adduct m/z 419.0038)



Oxidation Products of Algal Blooms

Using Ozone to remove CYN?

Proposed sites of ozone attack



Proposed sites of ozone attack

Cylindrospermopsin (CYN)

Molecular Weight: 415.42

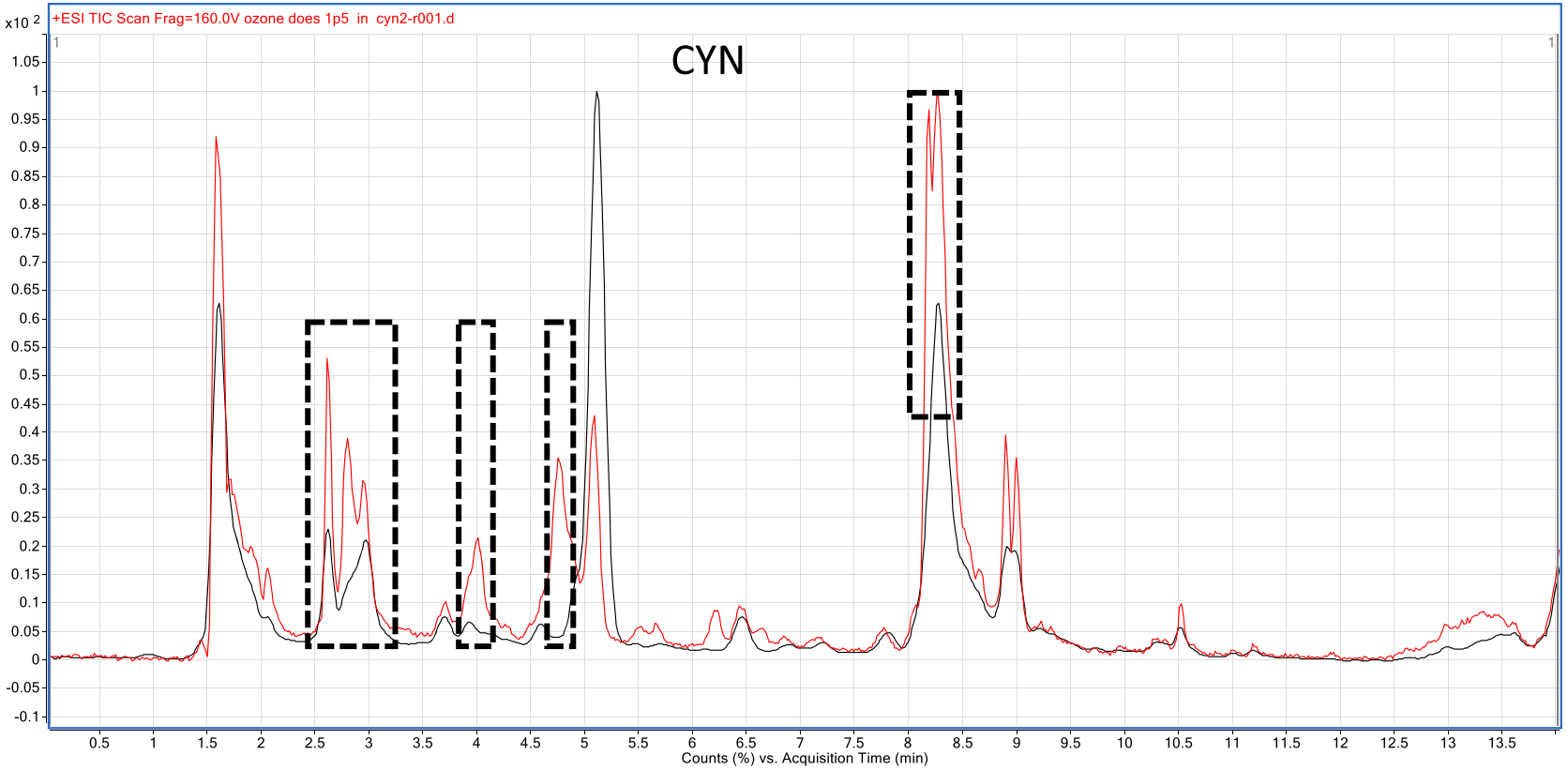
m/z: 416.12

MS Scan on CYN

Instrumentation: 1290-6540 LC-QTOF (Agilent)

QTOF MS Scan: byproducts generated

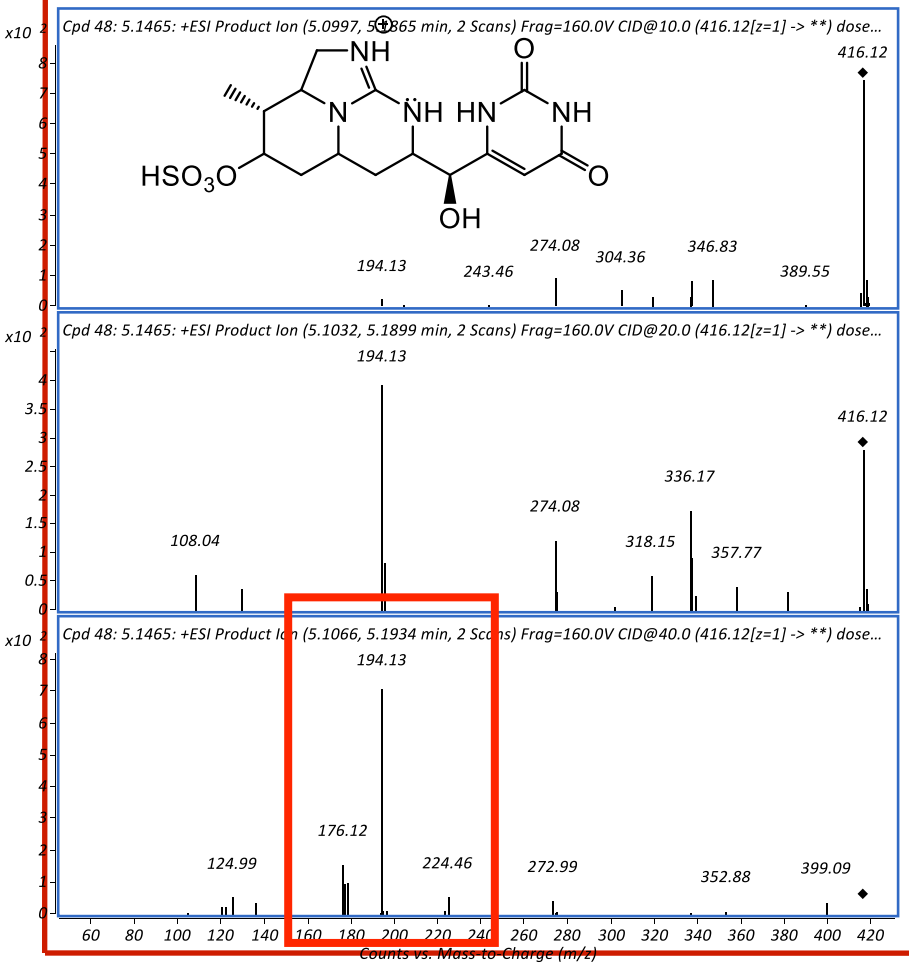
Ozone: 0ppm
Ozone: 1.5ppm

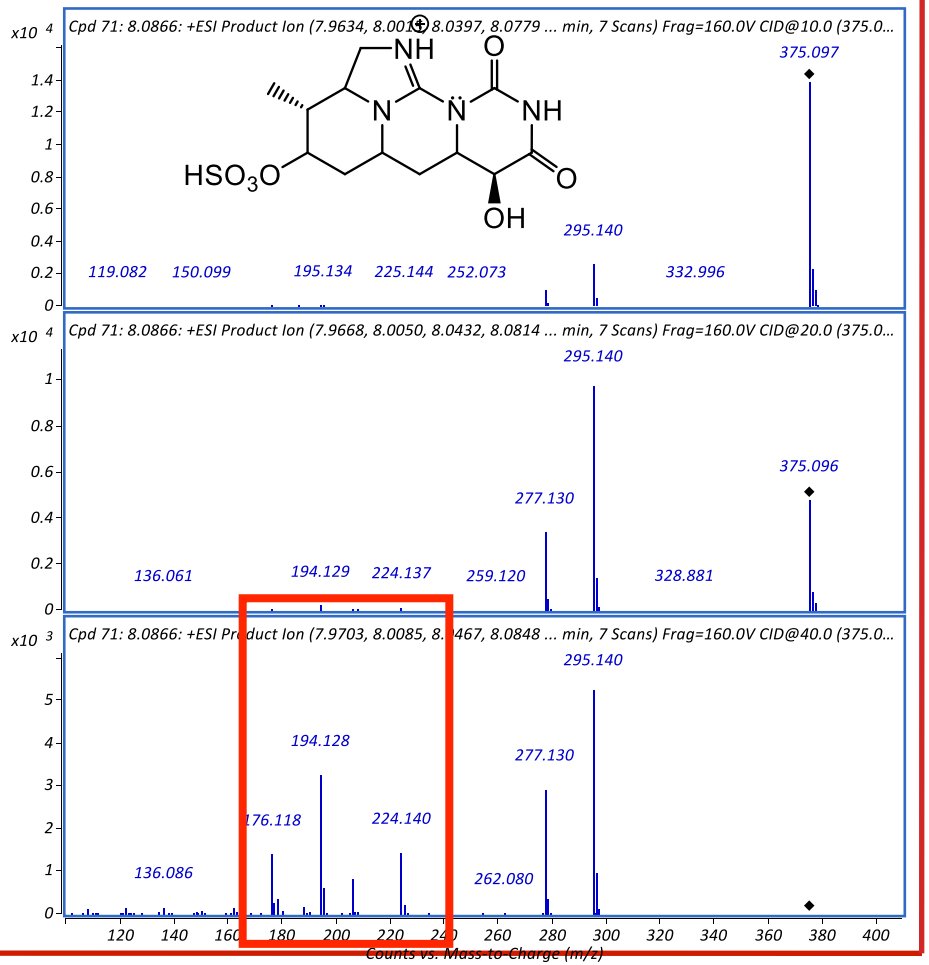


Using the fragments information to judge CYN by-products

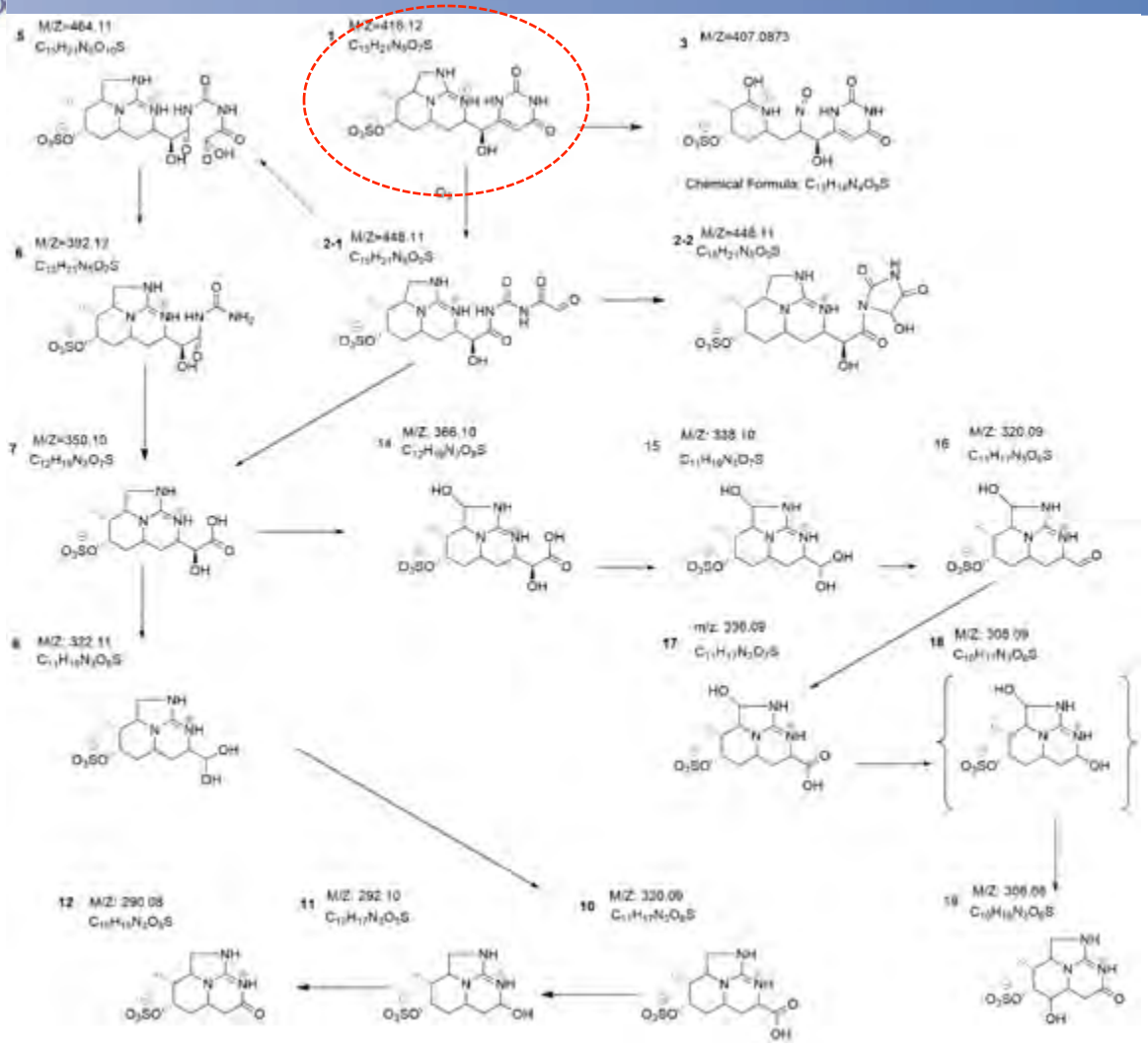
CYN M/Z=416.12

byproduct M/Z=375.10





CYN byproducts generated pathway under O_3



azdailysun.com
Serving Flagstaff and northern Arizona

Is Flag's drinking water at risk?

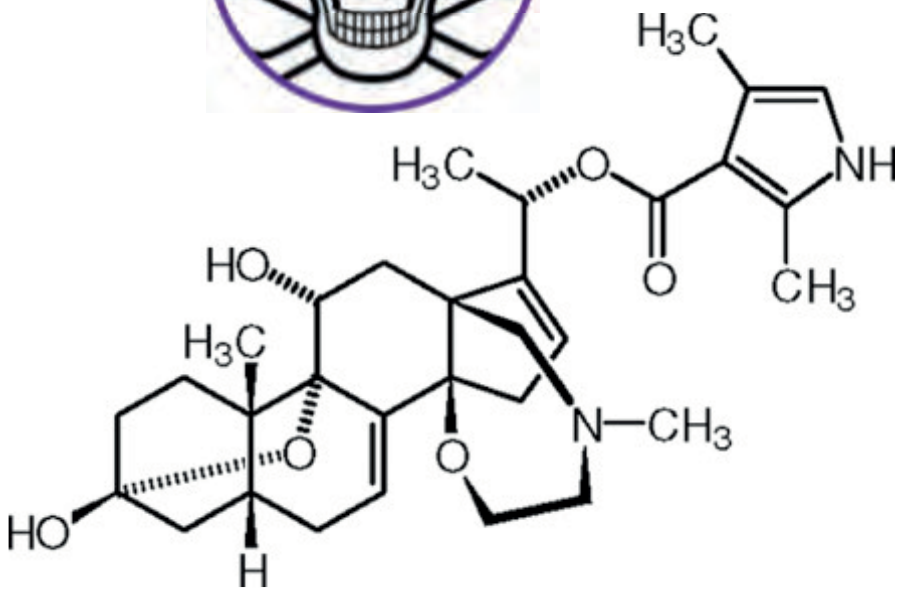
CYNDY COLE Sun Staff Reporter | Posted: Tuesday, October 18, 2011 5:30 am

“About two years ago, very small traces of an antibiotic, an anti-seizure medication and a possible cancer-causing agent appeared in four groundwater wells in northwest Tucson.

All of the wells are located downstream of the local sewage treatment plant, which releases its treated sewage water into a riverbed.

When tested, some of Flagstaff's drinking water wells downstream of the Rio de Flag wastewater treatment plant have also shown tiny traces of other pharmaceuticals and hormones, which have an ability to influence growth in amphibians.”

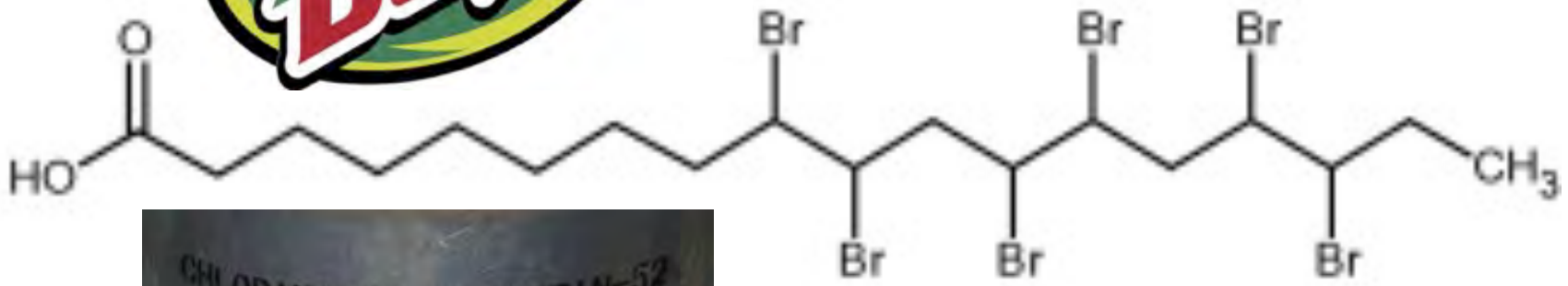
Safe or Not Safe?

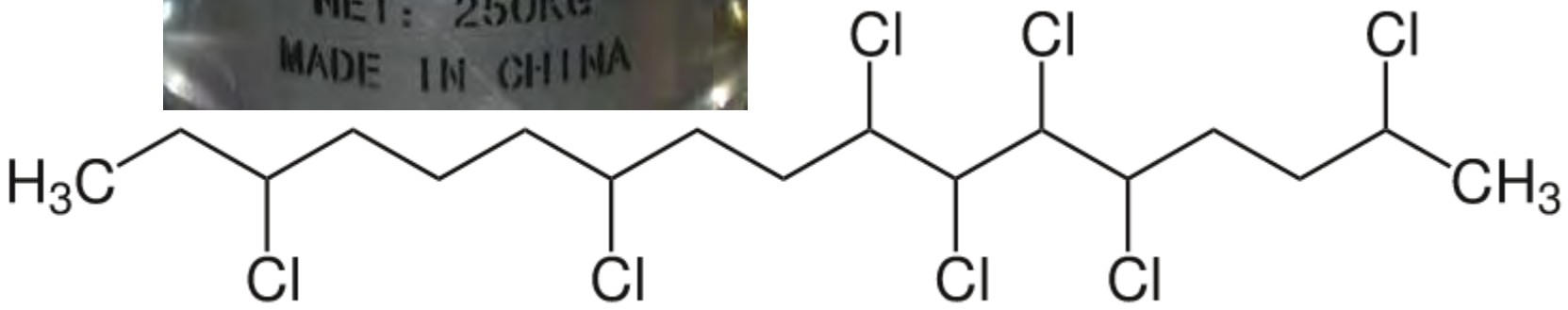


Vitamin B2

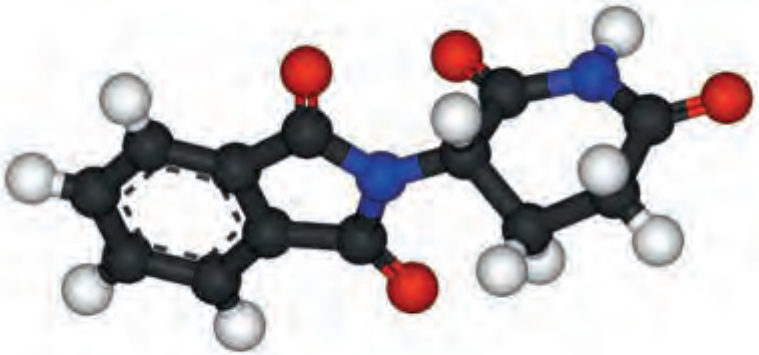
Batrachotoxin

Safe or Not Safe?

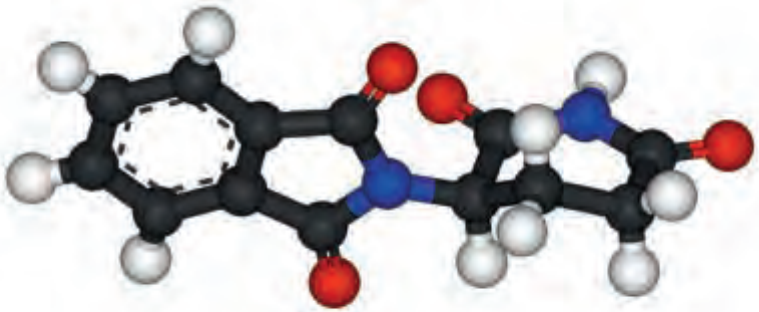




Safe or Not Safe?



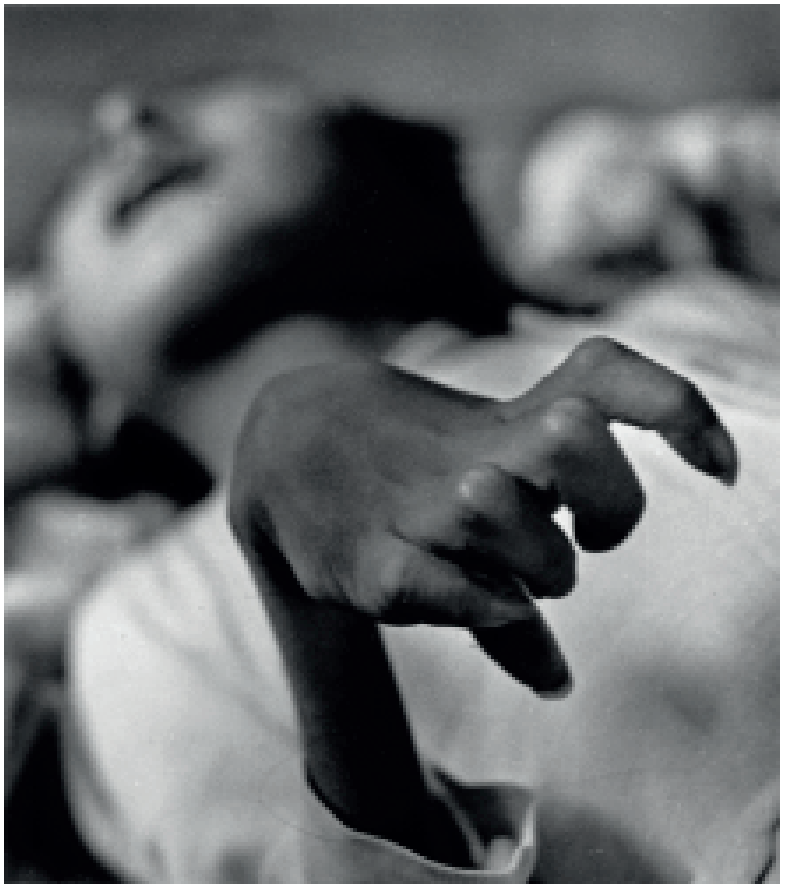
(*S*)-thalidomide



(*R*)-thalidomide

History of Bioassays

Animal Sentinels

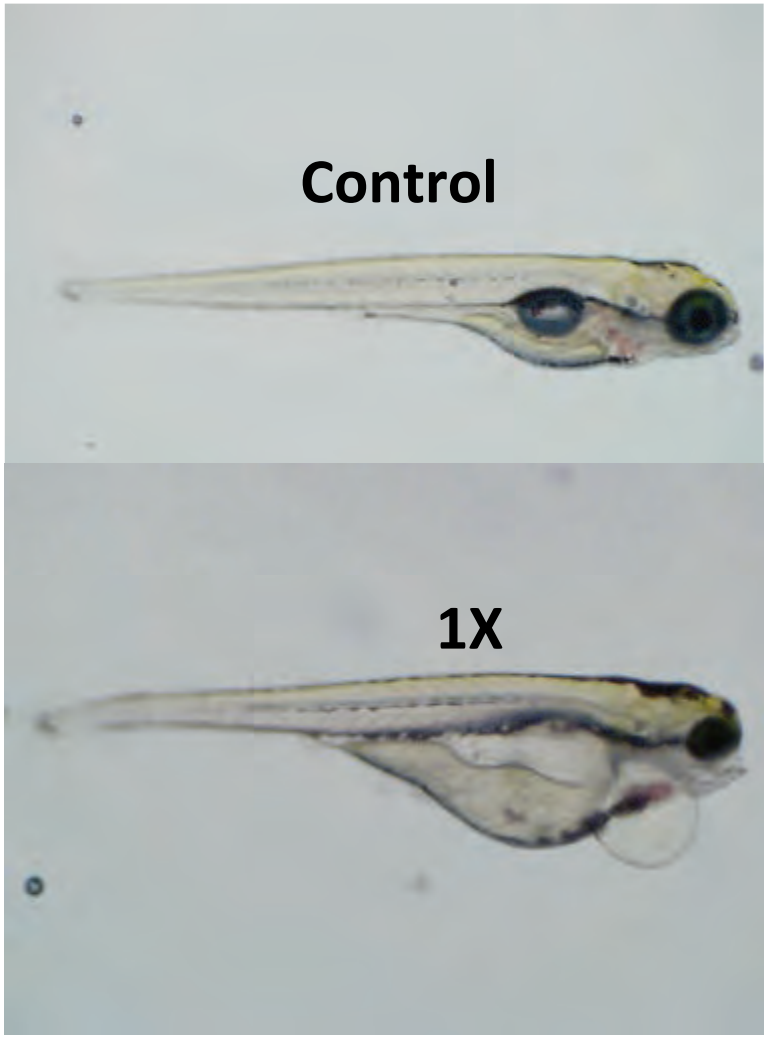


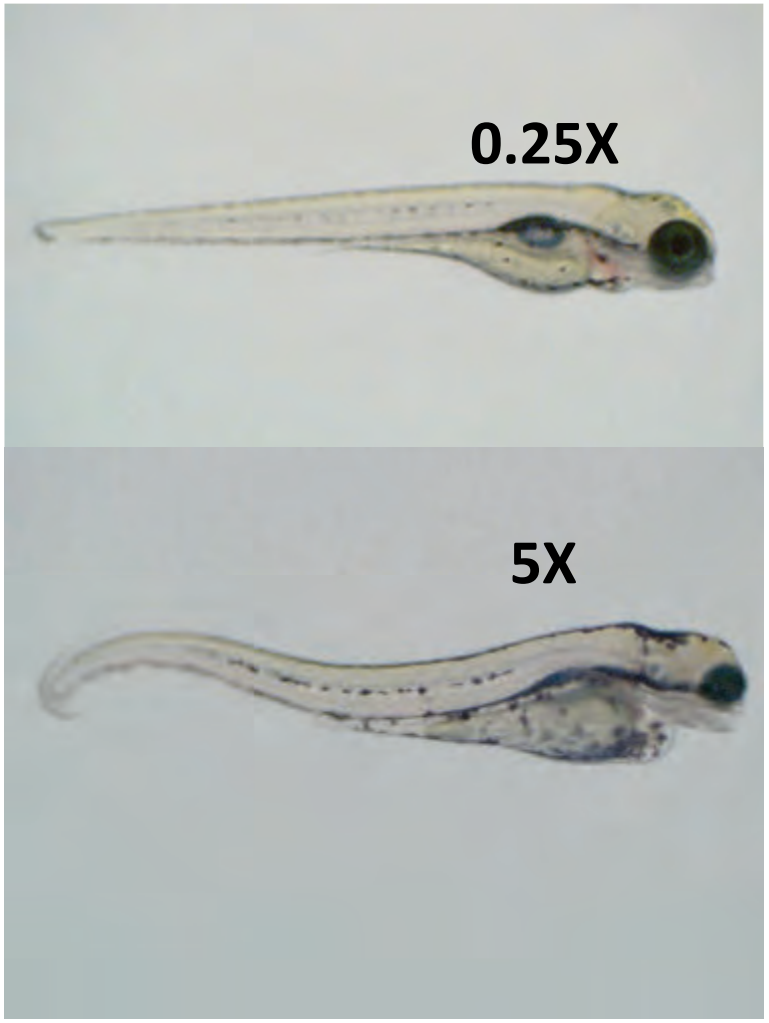
Minamata Disease: Mercury poisoning (Japan 1956)

Animal Bioassays

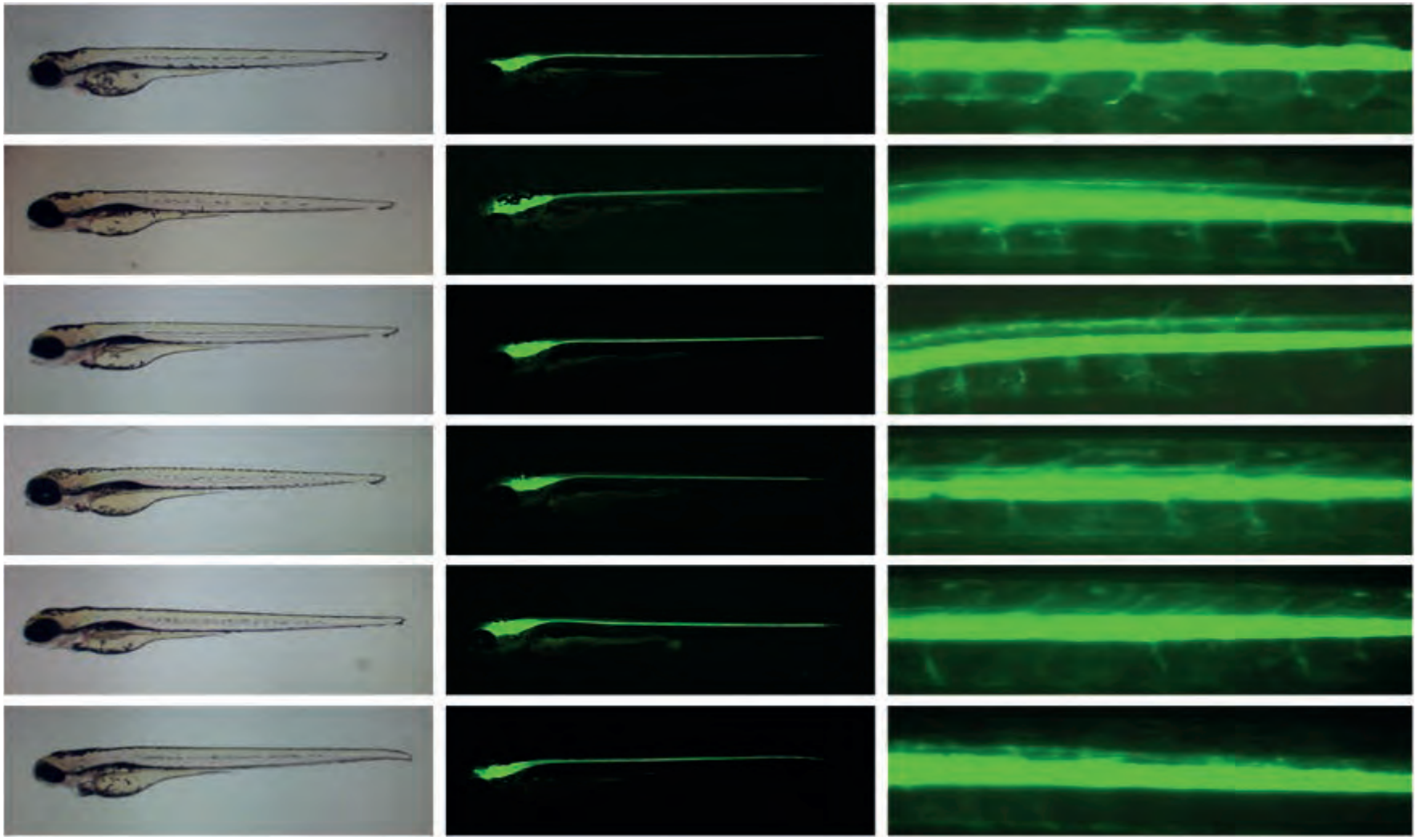
Some assays are available as on-line monitors

Embryonic Assays



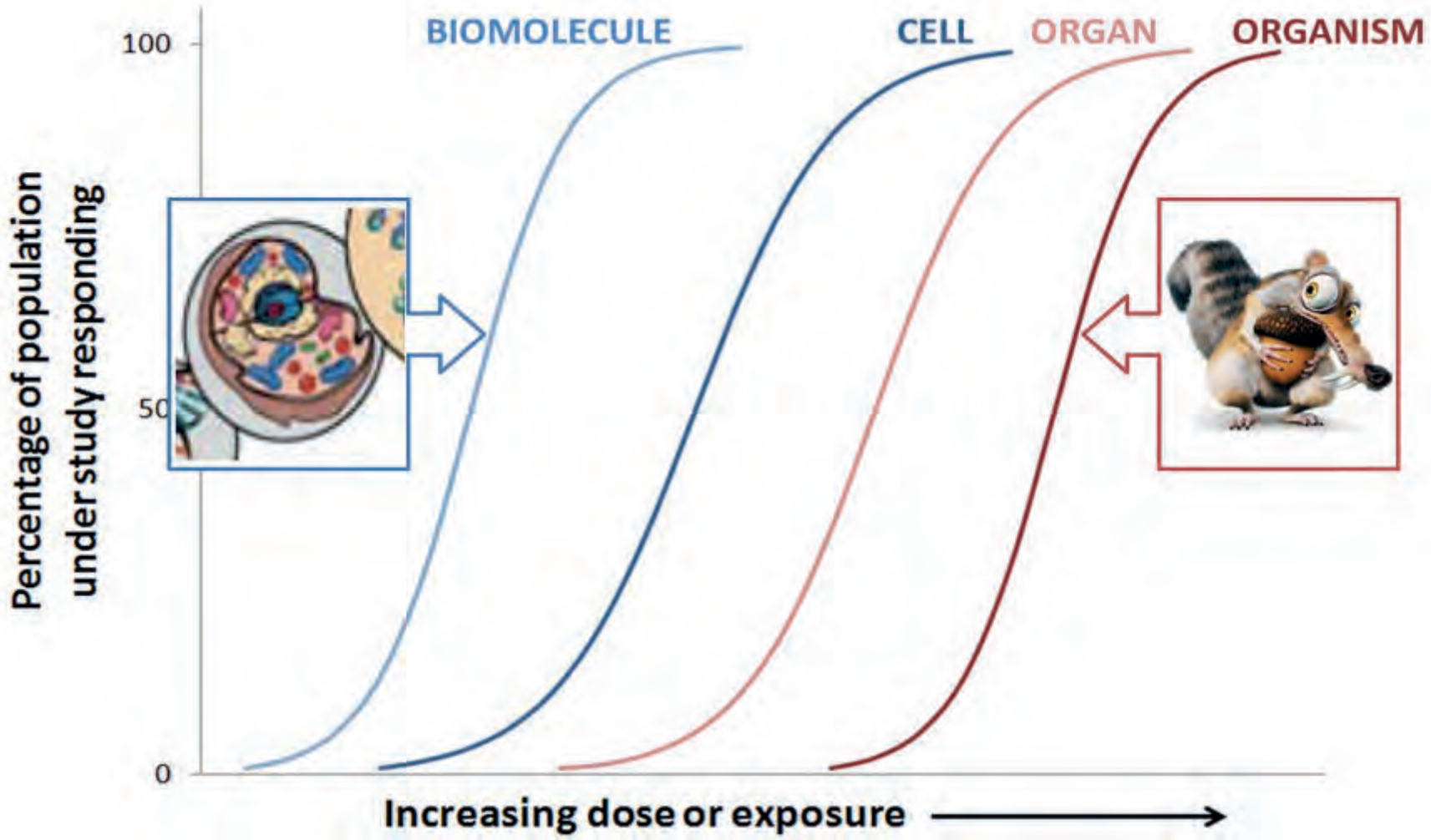


Embryonic Assays



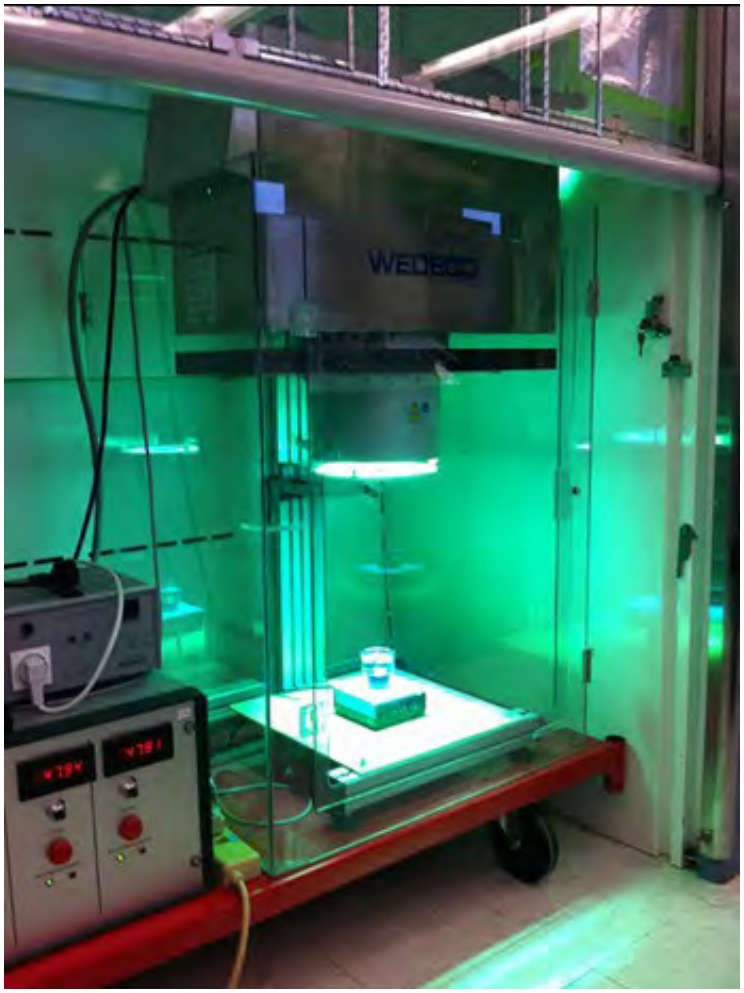
Cellular Bioassays

Cells & Metabolomics



Credit: Dr. Fred Leusch – Griffith University, Australia

UV Transformation Products

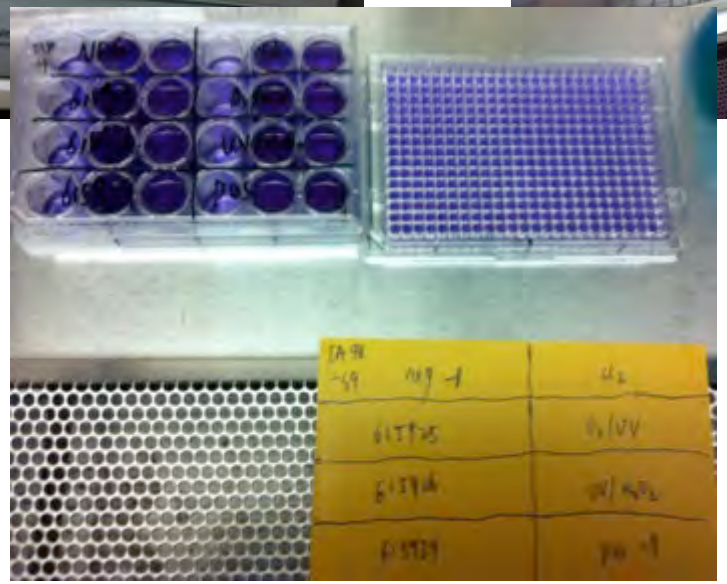


AMESII test

1. Overnight culture

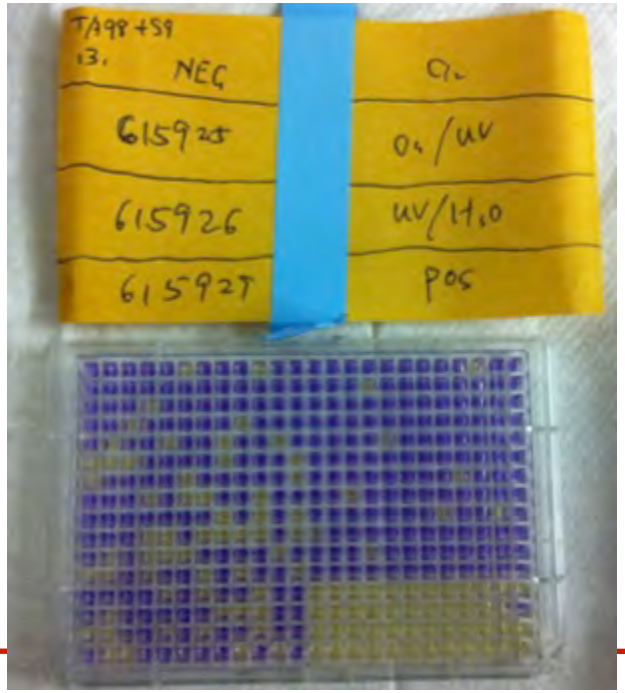
2. Transfer to 24-well plates

Sample (in DMSO)
S9
Bacteria
Exposure media

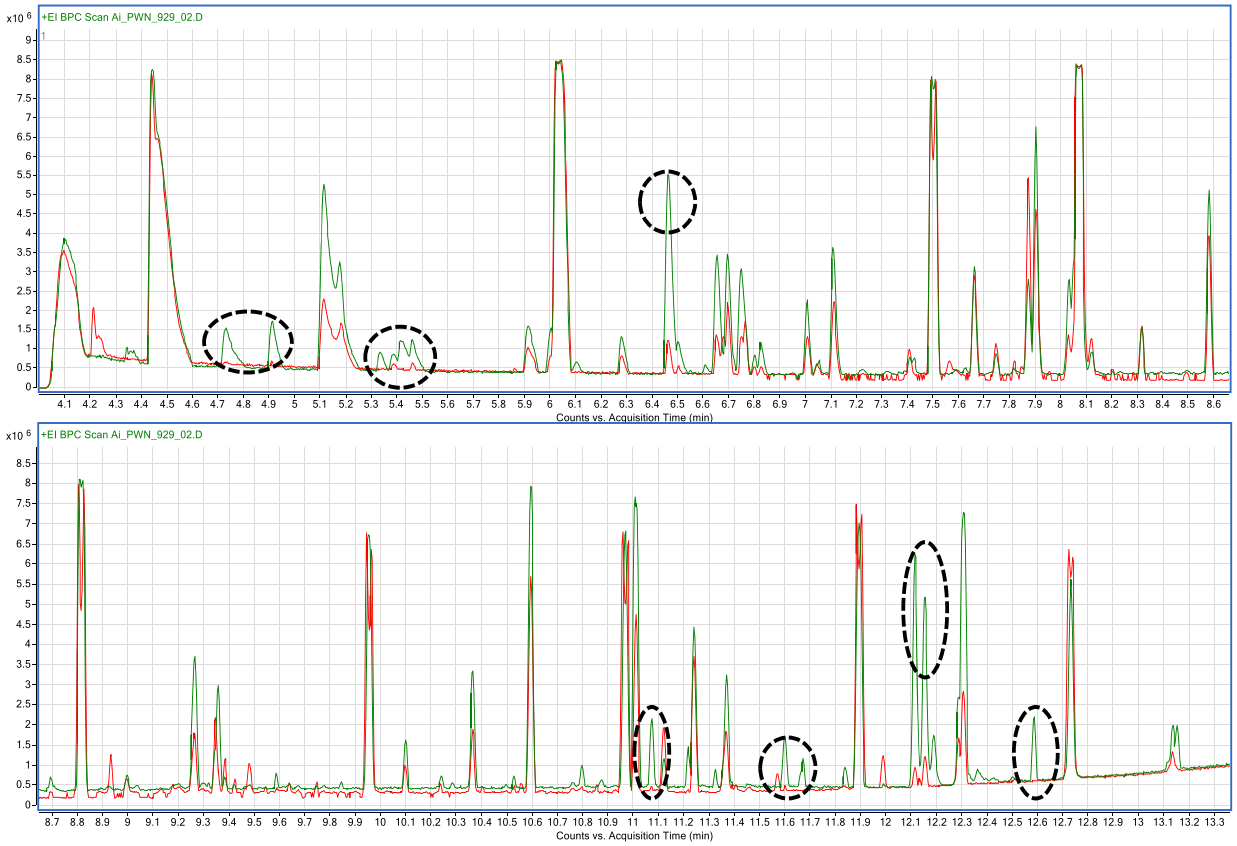


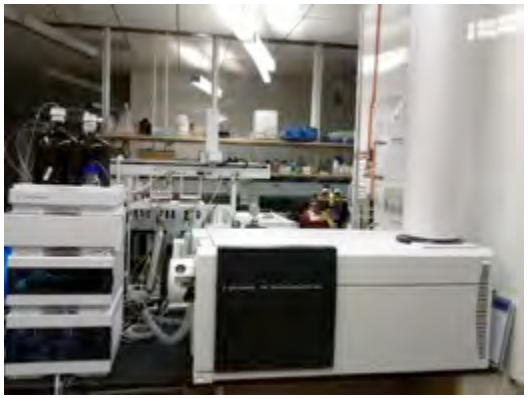
3. Add indicator media, transfer to 384-well plates

4. After 48h, check the results



Discovery of New DBPs





LC-QTOF

GC-QTOF

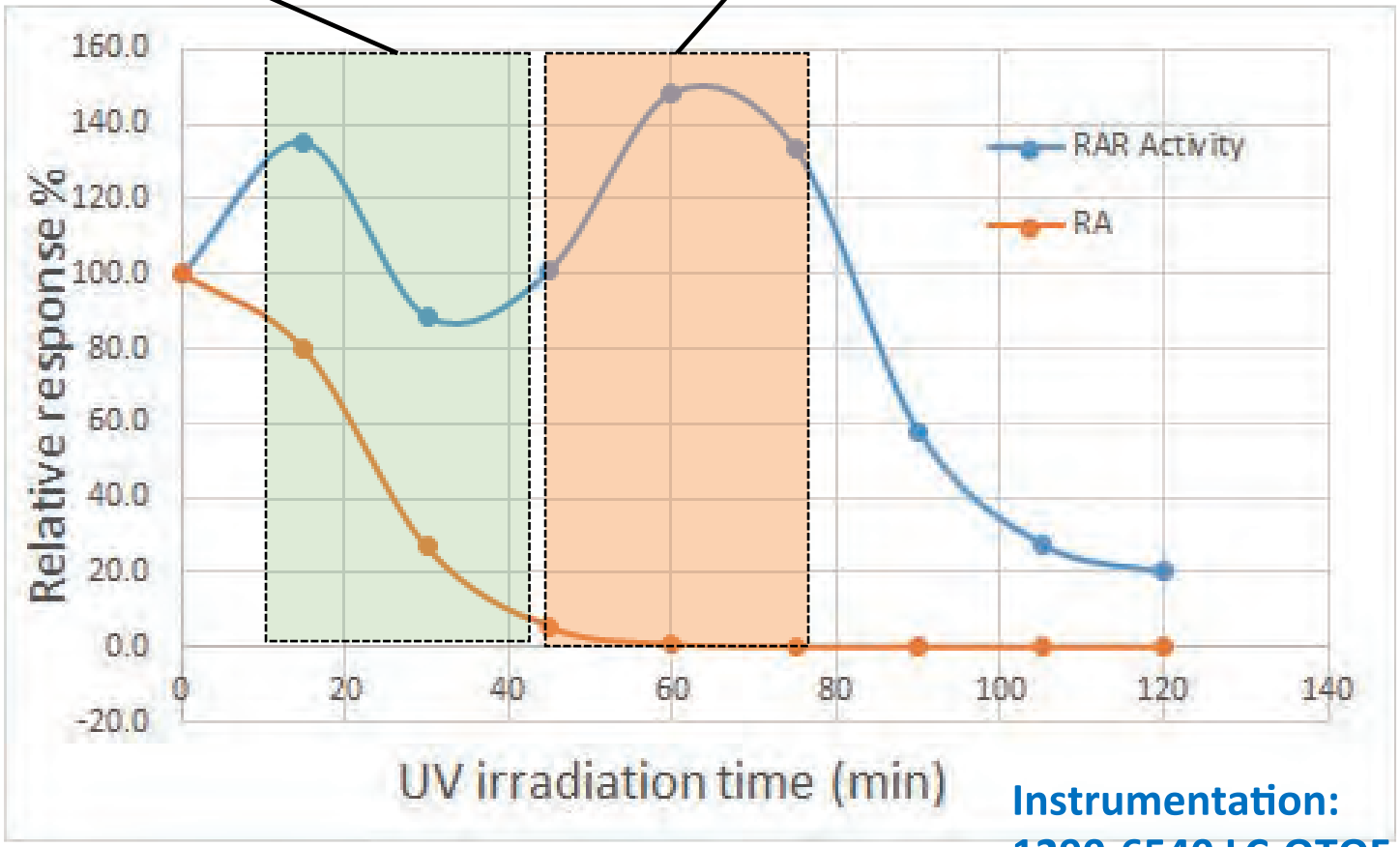
Red = Before MP UV

Green = After MP UV

Products of UV-treated retinoic acid (RA) and their RAR activity

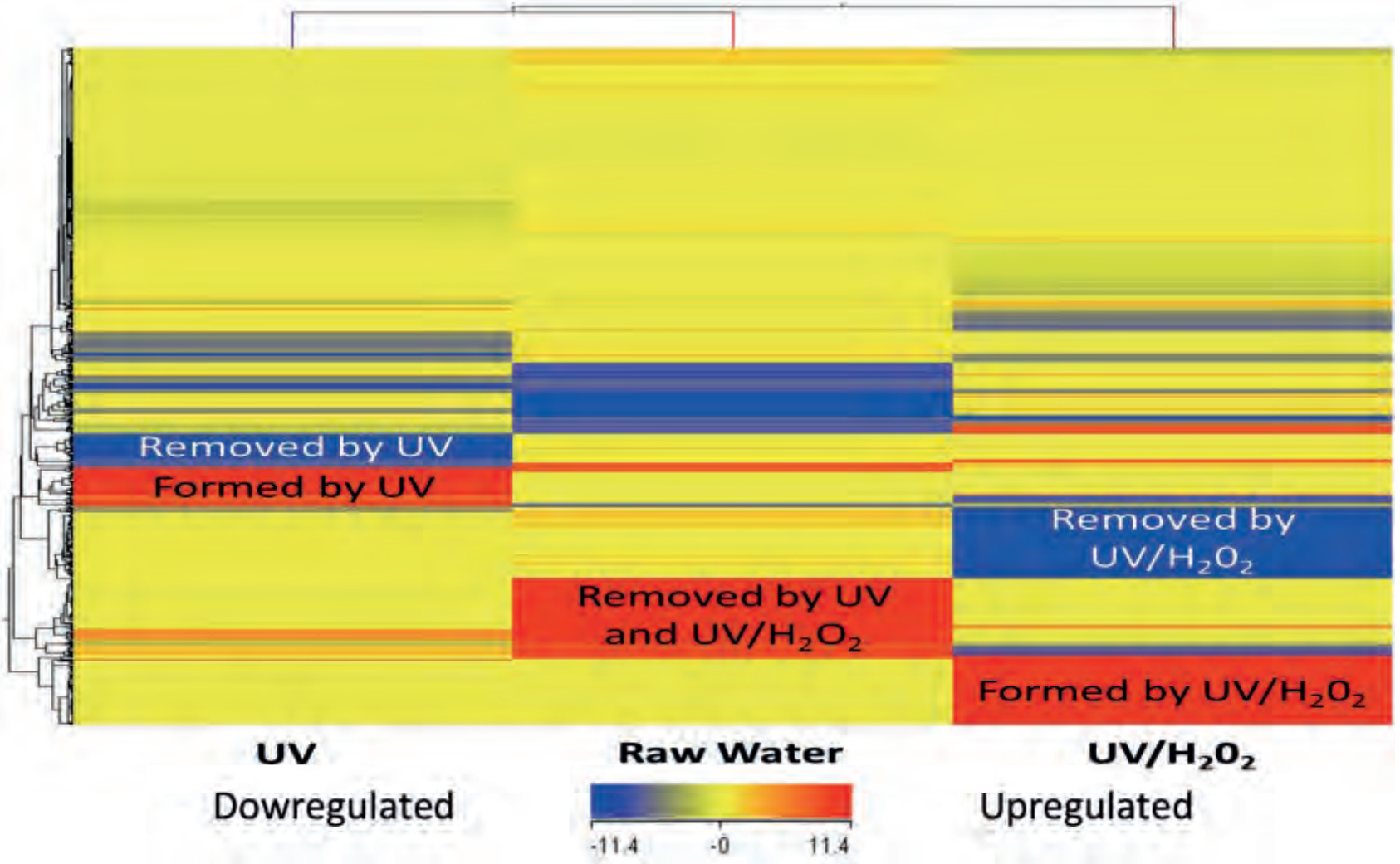
The mixture effect of RA+oxo-RA+OH-RA

Remains unknown, under further investigation in QTOF and MPP

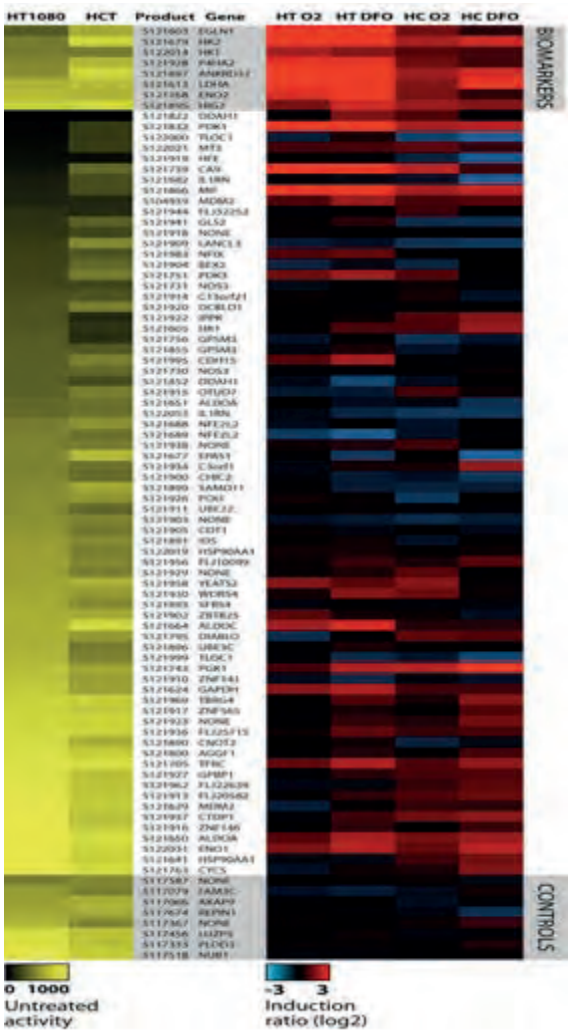


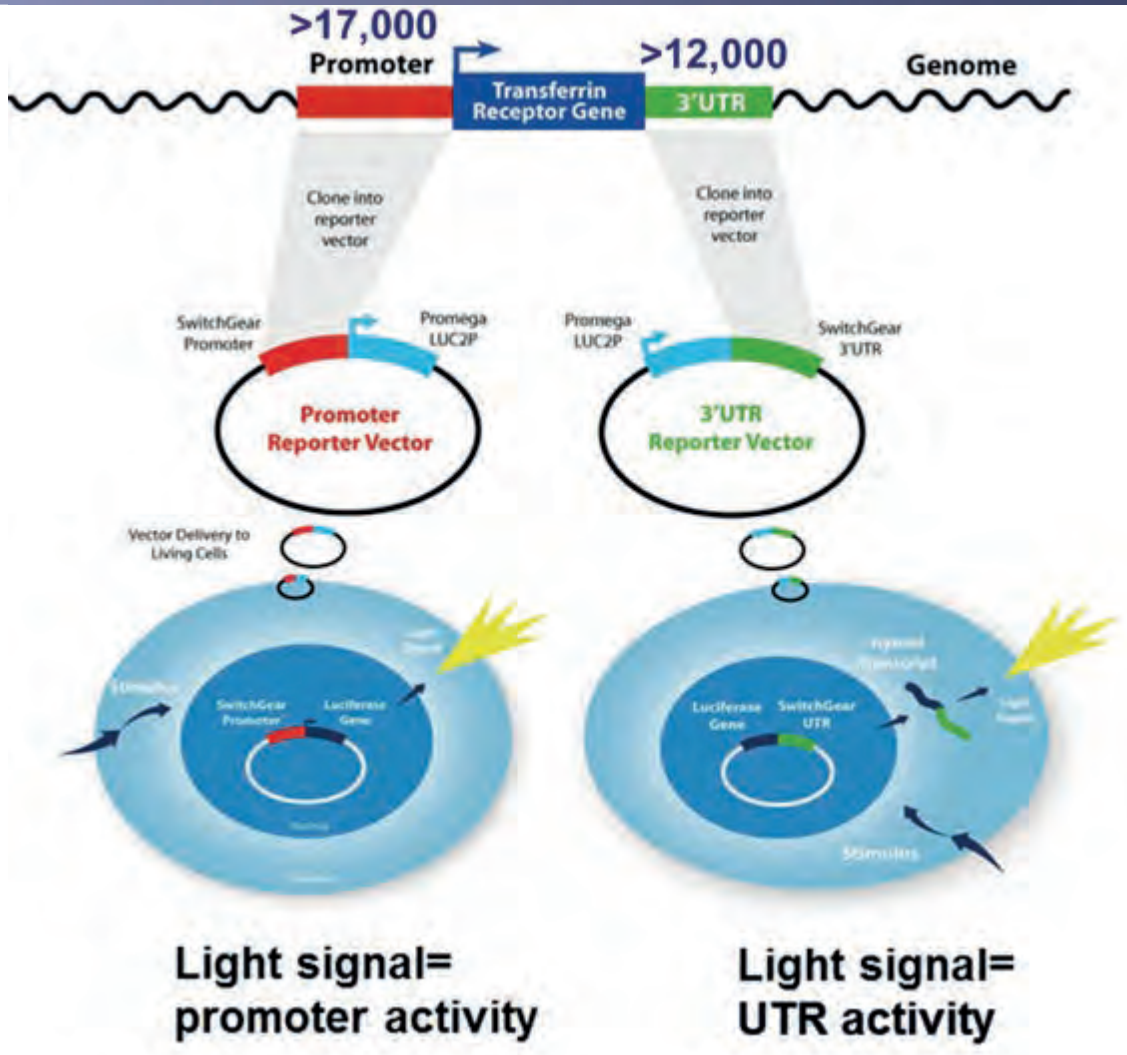
Instrumentation:
1290-6540 LC-QTOF (Agilent)

Discovery of New DBPs

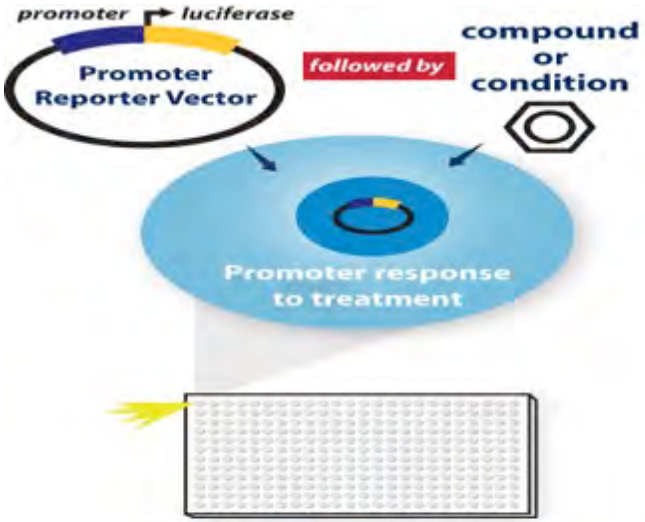


Cellular Bioassays





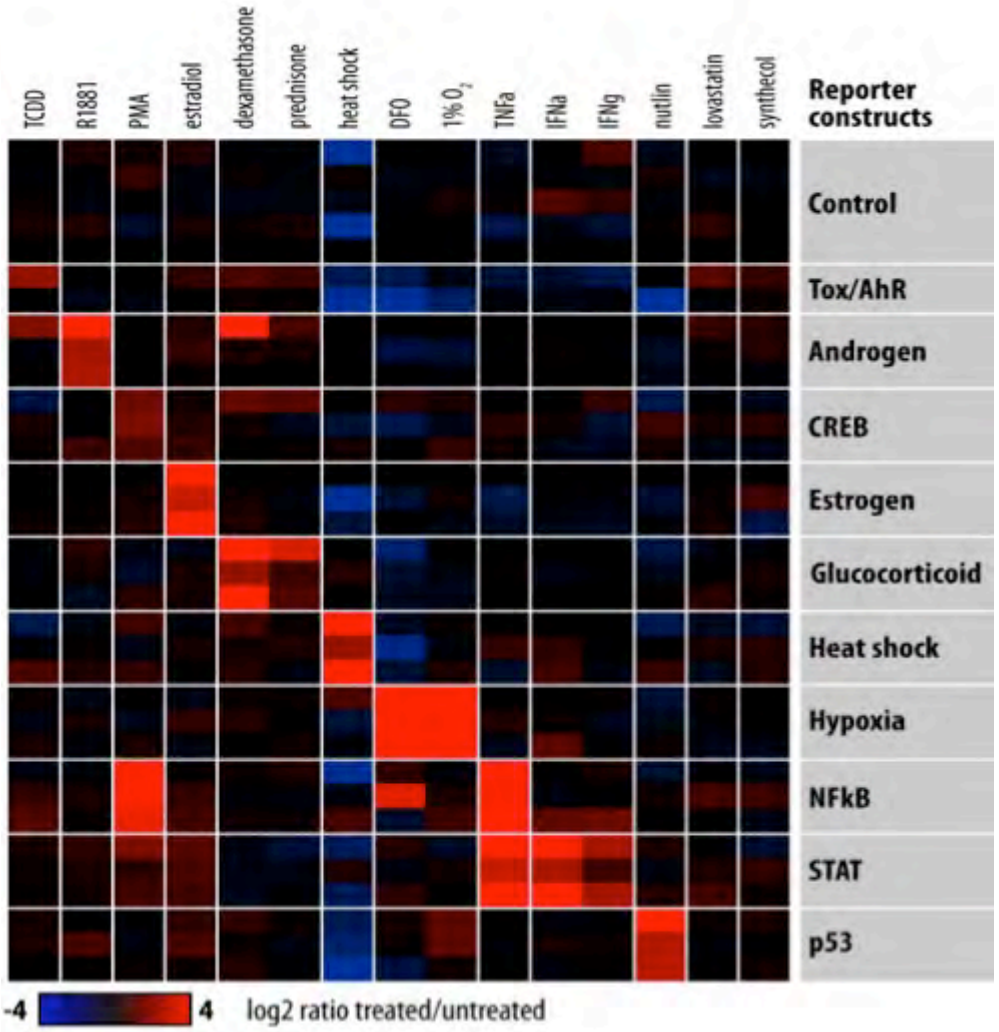
Cellular Bioassays



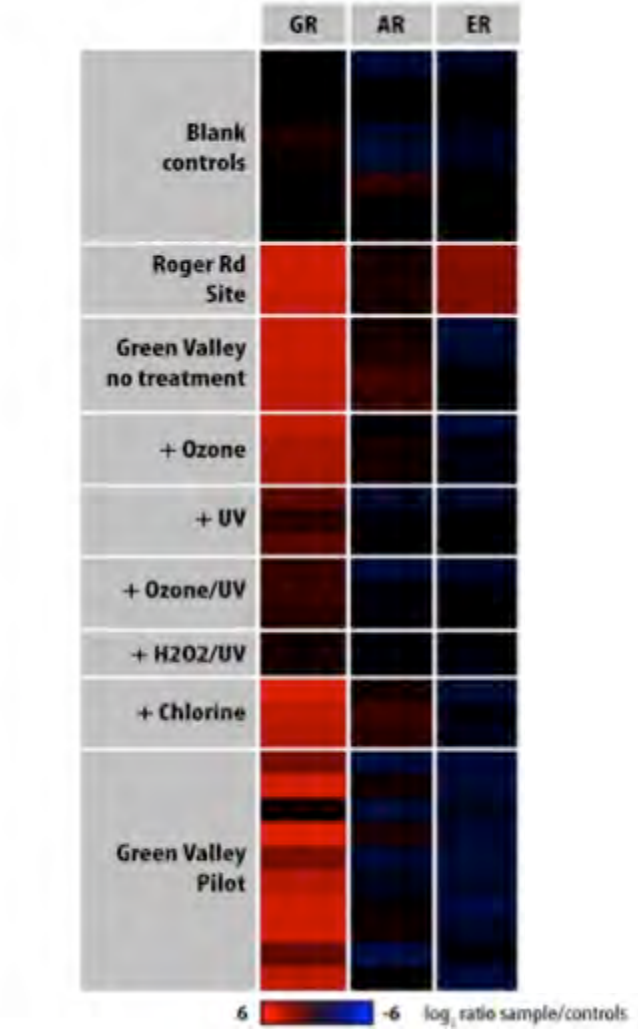
Pathway Profiling Panel
48 promoters and controls

Pathway activity readout for:

HIF1a	Hypoxia
NFkB	Inflammation
CREB	cyclic-AMP
HSF1	Heat shock
p53	DNA damage, apoptosis
STAT	Interferon
SREBP	Cholesterol biosynthesis
ER	Estrogen
AR	Androgen
GR	Glucocorticoid
AhR	Toxicity



Reuse Pilot Plant – O3, UV, Cl



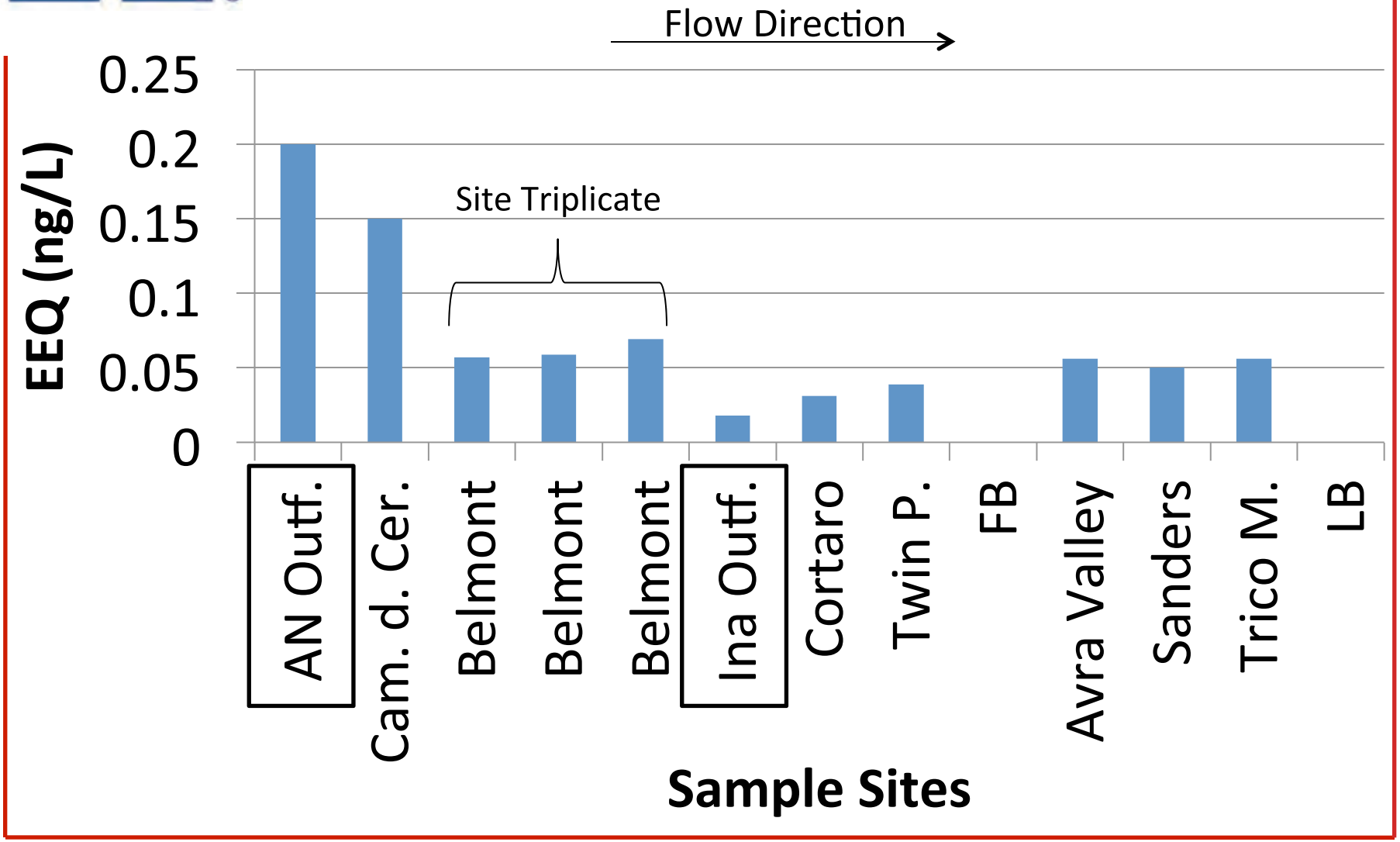
- WWTP effluent had elevated glucocorticoid (GR) activity
- UV processes are most effective at removing GR activity
  - Agonist appears to be UV sensitive (↑ quantum yield)
  - Guides structural elucidation (i.e., NDMA)
- Chlorine and ozone poor for attenuating GR activity
- Antagonistic ER and AR activity

Glucocorticoids

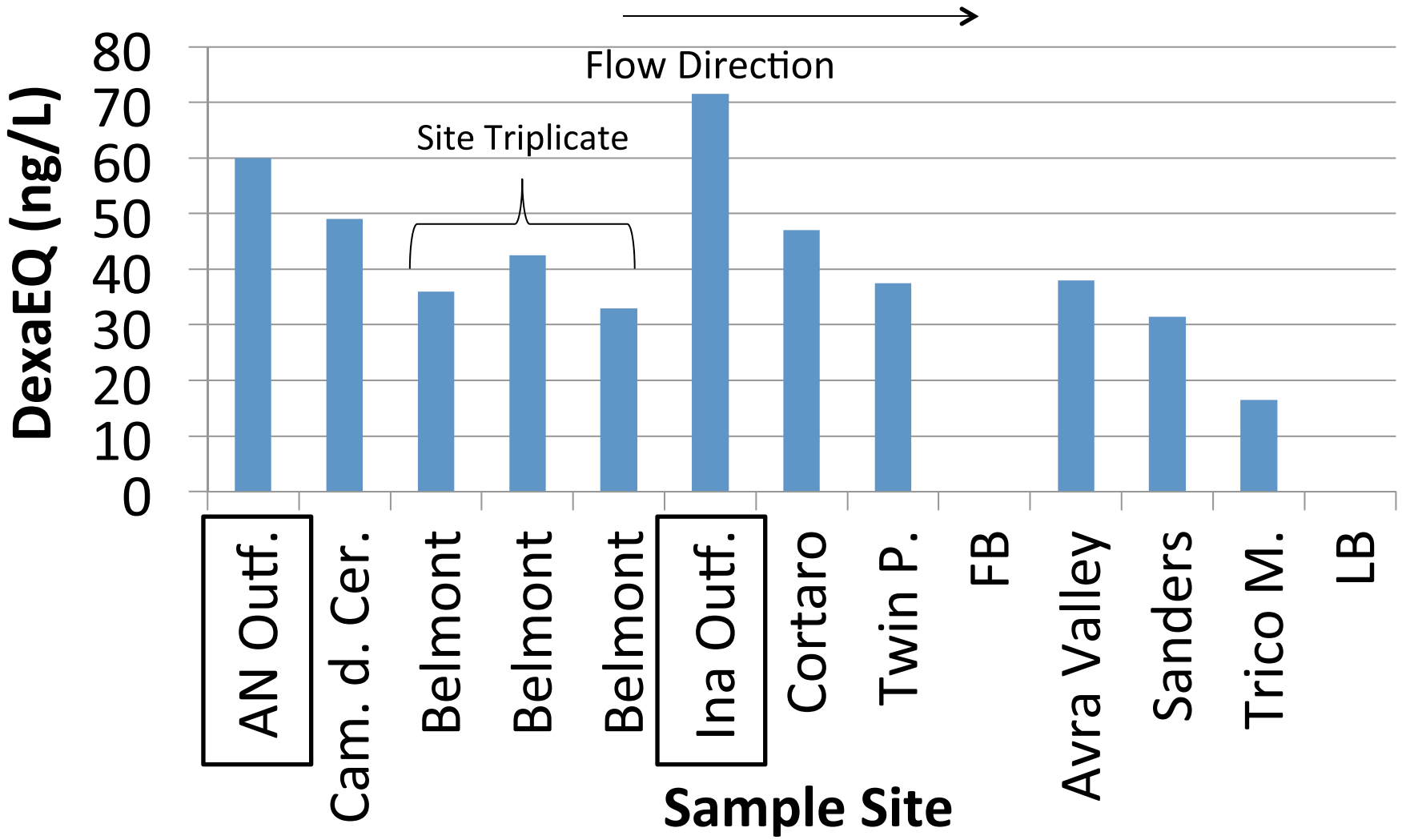
- Natural & Synthetic
- Used for human diseases such as severe allergies, skin problems, asthma, and arthritis
- Used as veterinary medicine to restore muscle strength and as growth promoters to increase muscle size

Santa Cruz River Sampling Sites

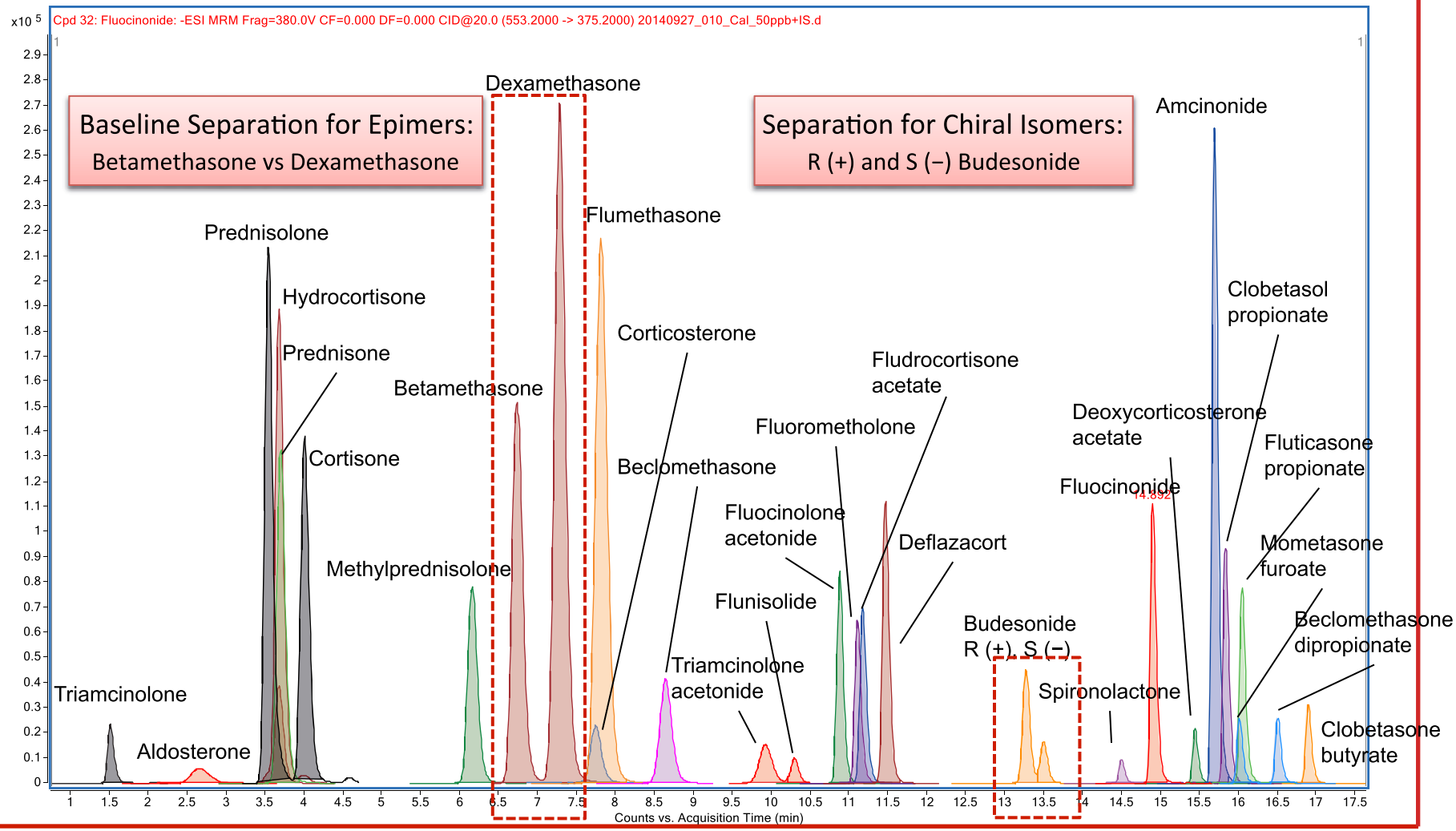
ER Cellular Activity



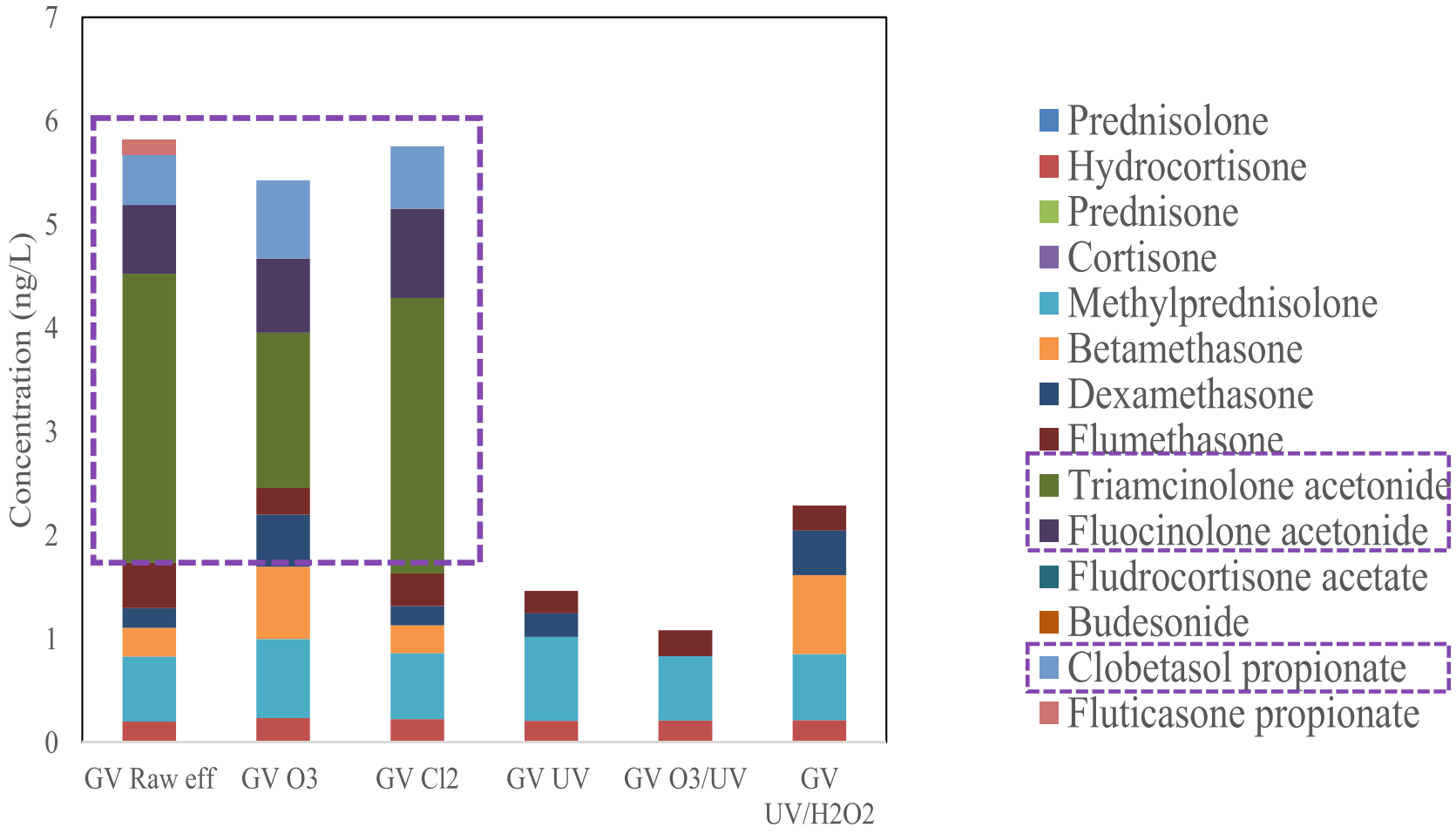
GR Cellular Activity



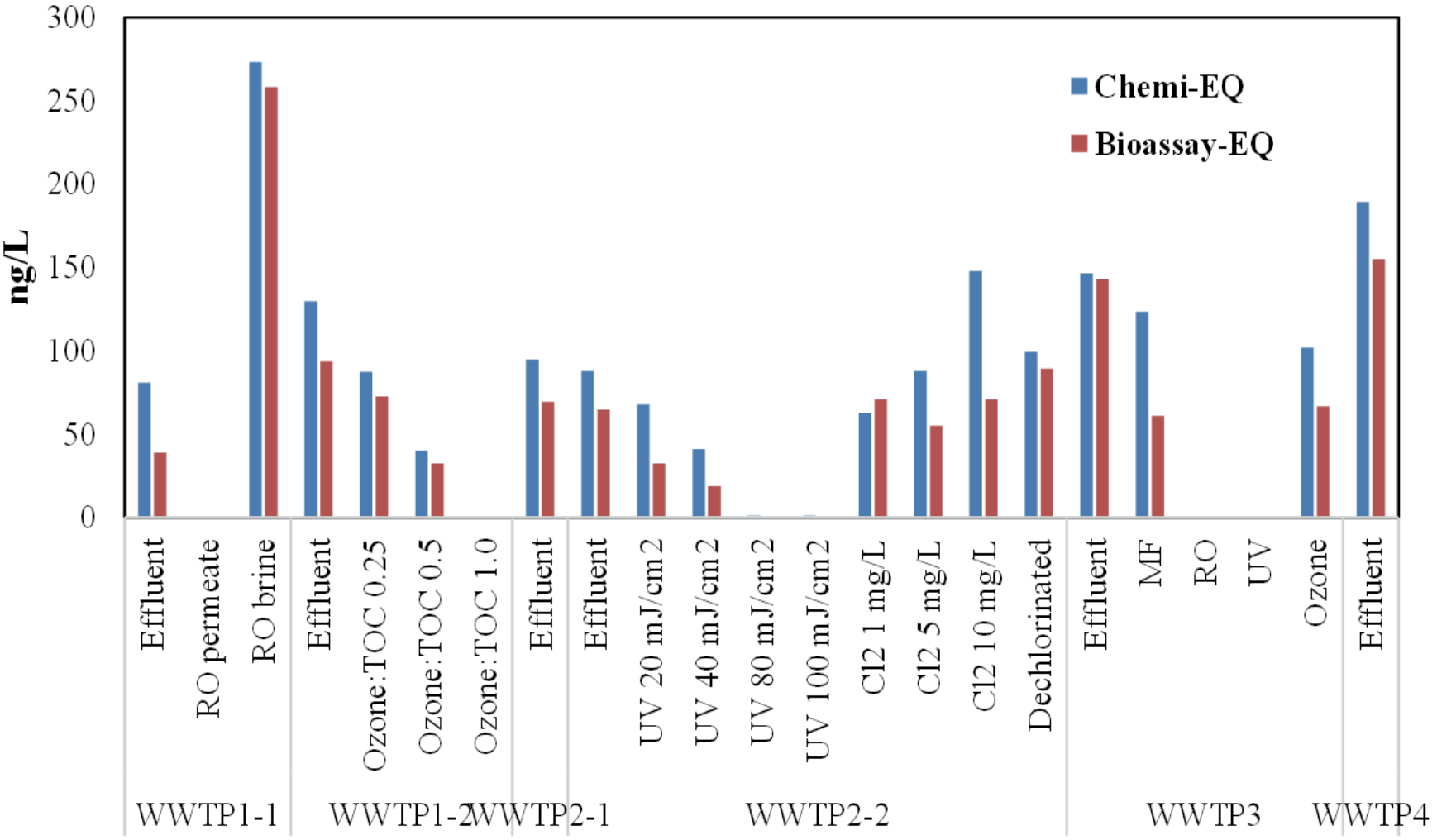
GR Mass Spectrometric Analysis



Distribution of GRs



Distribution of GRs



High-Throughput Assays

A Shift in Paradigm is Imminent

UPDATE
National Toxicology Program
U.S. Department of Health and Human Services

July 2014

Headquartered at the
National Institute of Environmental
Health Sciences • NIH-HHS

High-throughput toxicity screening produces human-relevant results

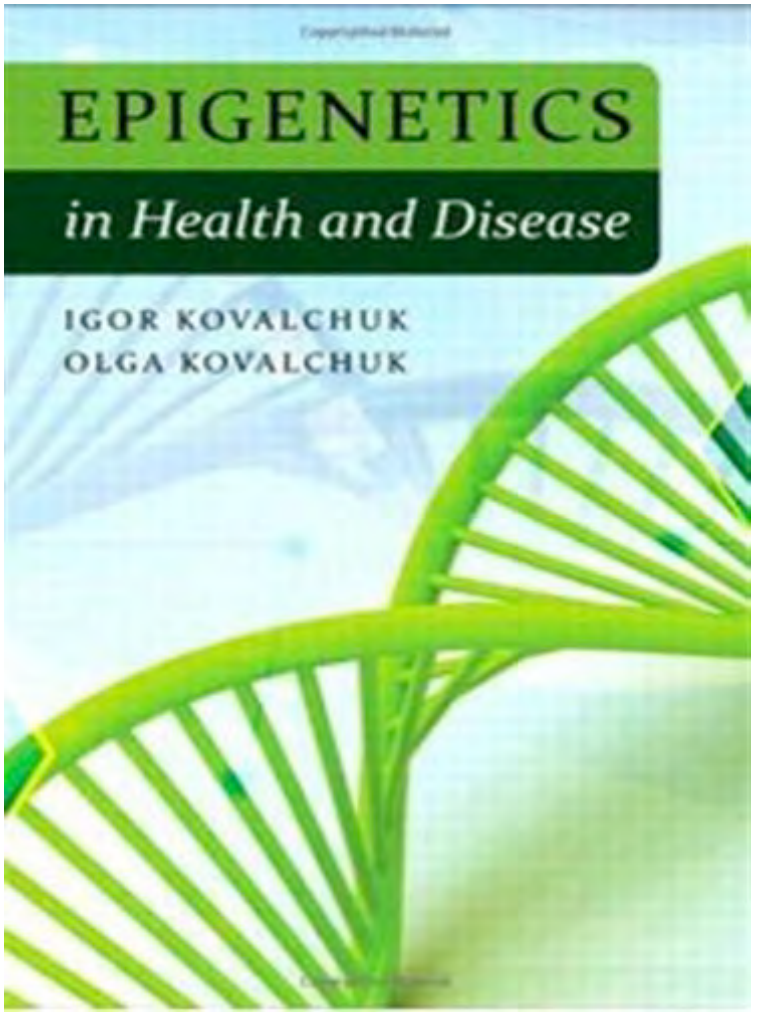
By Thomas Burns Jr., reprinted from Environmental Factor, June 2014

Using *in vitro* and *in silico* testing in primary human cell systems, scientists reported in the May issue of the journal Nature Biotechnology bioactivity profiles for 776 unique and diverse chemicals with potential for human exposure. The use of a human-relevant system may provide a rapid and accurate screening method to prioritize chemicals for further toxicity testing or to identify new pharmaceutical activities.

Tox21

"This is the first data manuscript in the field of high throughput toxicity screening [HTS] on such a large number of chemicals to be published in one of the Nature journals," said Nicole Kleinstreuer, Ph.D., the paper's lead author, who is now a contractor supporting the NTP Interagency Center for the Evaluation of Alternative Toxicological Methods (NICEATM). "It demonstrates the utility of HTS assays that use human primary cells to elucidate mechanisms of action and predict toxicities for a diverse set of chemicals."

Public Concerns Remain



The Multi-barrier Approach to Protecting Public Health

Barrier #1: Risk Prevention	Barrier #2: Risk Management	Barrier #3: Monitoring and Compliance	Barrier #4: Individual Action
• **Source Water** • **Barriers:** Selecting and protecting the best source of supply.	• **Treatment** • **Barriers:** Installing treatment methods, implemented by a certified operator, that will improve the quality of the source water.	• **Storage and Distribution** • **Barriers:** Constructing, operating, and maintaining well engineered storage facilities and distribution systems.	• **Monitoring and Public Information** • **Barriers:** Providing consumers with information on water quality and health effects.

Source: http://www.epa.gov/ogwdw/smallsystems/pdfs/guide_smallsystems_mba_09-06-06.pdf

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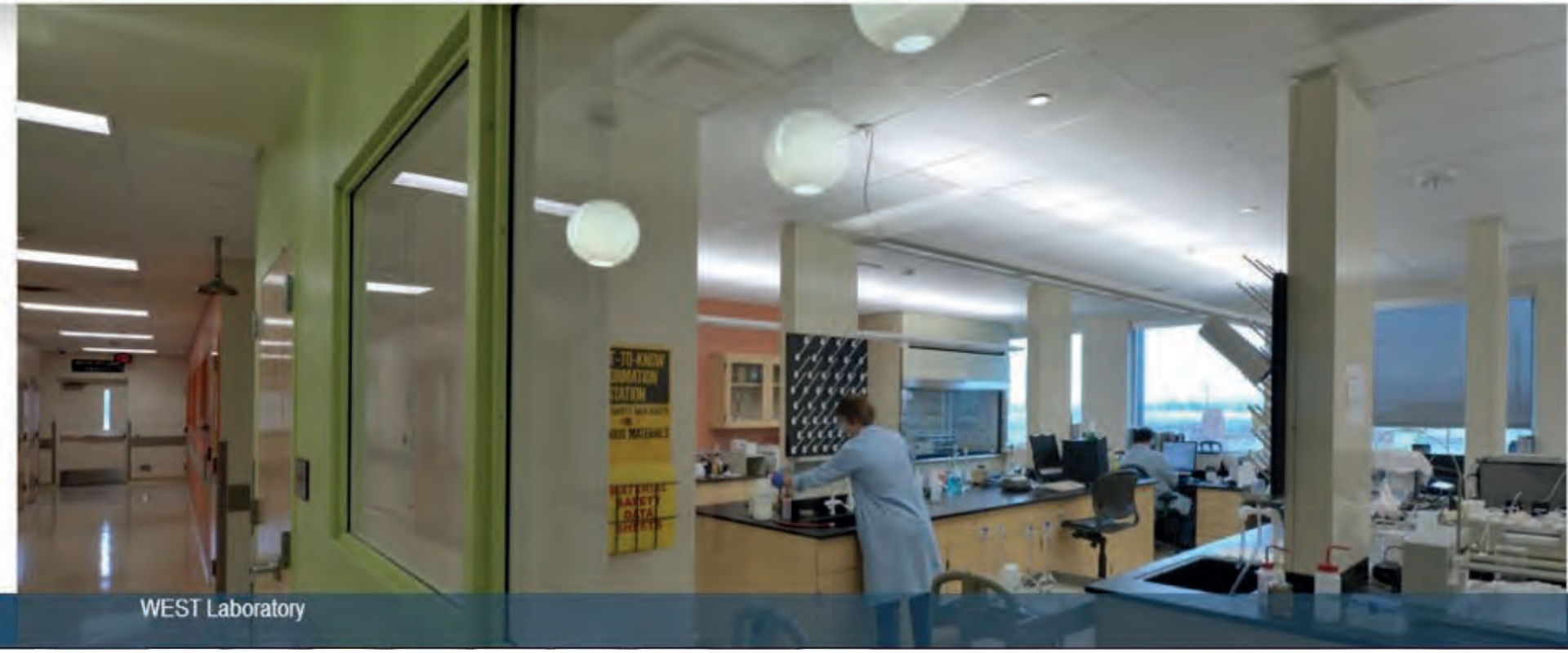
WEST CENTER
WATER & ENERGY SUSTAINABLE TECHNOLOGY

SEARCH

RESEARCH FOR STUDENTS WATER RECLAMATION CAMPUS MEMBER BENEFITS MEMBER GATEWAY



WEST Laboratory

WEST is Inspired by the Challenges

Real-Time Sensor Laboratory

The Absolute Certainties

1. More and more chemicals will be detected at lower and lower levels
   a) ~15,000 new chemicals registered/day
   b) Transformation products
   c) Increasingly more sensitive instruments
2. Current chemical testing paradigm will fail
   a) Does not account for mixtures
   b) Animal testing slow, high doses, unpopular
   c) Unknown transformation products
3. Bioassays will be the way of the future (soon)
   a) WET testing already in place
   b) Prevents the “next perchlorate & NDMA”

Acknowledgements

Contact: snyders2@email.arizona.edu
Visit Us: snyderlab.arizona.edu