CITIZENS' WATER ADVISORY COMMITTEE
(CWAC)
Technical/Planning and Policy Subcommittee

Wednesday, October 28, 2015, 12:00 p.m.
Director's Conference Room
Tucson Water, 3rd Floor
310 W. Alameda Street, Tucson, Arizona

Legal Action Report

1. Roll Call/Call to Order

The meeting was called to order by Subcommittee Chair, Mark Murphy, at 12:00 p.m. Those present and absent were:

Present:

Mark Murphy	Chairperson-Representative, Mayor
Brian Wong	Representative, City Manager
Chuck Freitas	Representative, City Manager
Placido dos Santos	Representative, City Manager

Absent:

Mitch Basefsky	Representative, City Manager
Kelly Lee	Representative, Ward 6

Tucson Water Staff Present:

Melodee Loyer	Water Administrator
Pat Eisenberg	Water Administrator
Wally Wilson	Chief Hydrologist
Daniel Quintanar	Project Manager
Johanna Hernandez	Staff Assistant

Others Present:

Chris Avery	City of Tucson, Assistant City Attorney
Shane Snyder, Ph.D.	University of Arizona
Jessica Ahlstrom	University of Arizona

2. Announcements – No action taken.

3. Call to Audience – No action taken.

4. Review & Approval of September 23, 2015 Legal Action Report and Meeting Minutes – Member Freitas motioned to approve the Legal Action Report and Meeting Minutes of September 23, 2015. Member Wong seconded. Motion passed unanimously by a voice-vote of 4-0.

5. The Impact of Emerging Contaminants on Water Sustainability – Dr. Shane Snyder presented a PowerPoint on the Impact of Emerging Contaminants on Water Sustainability. Dr. Snyder's work focuses on potable water reuse, and he works with these programs both locally and in Singapore. An important consideration in monitoring contaminants is that there is always something in the water to find, finding it is dependent upon technology and the focus of research. Locally, water quality and water reliability is much higher than other places in the world; as a result, water may be taken for granted and under-valued. Changes in circumstances, like drought conditions, are compelling factors driving the development of new water resources. Potable water reuse, desalination, and cloud seeding are methods to mitigate

changes. Local methods of CAP delivery, wetlands, and recharge draw attention worldwide as mitigation methods. One third of wastewater is discharged into the ocean and lost for reuse. Future legislation may limit the ability to discharge the water, requiring reuse. Dr. Snyder emphasized, we have the technology. Natural infiltration treatment systems and advanced treatments provide methods for IPR and DPR. Research shows that the cost of treatment of wastewater is more cost effective than importing water. Public perception surrounding the reuse of water is one of the largest obstacles. Perception is a result of a "yuck" factor related to wastewater, as well as the research showing trace amounts of residual synthetic chemicals in the wastewater. Human cells were used to test the endocrine disruption of fish in Las Vegas, linking it to trace amounts of birth control in the waste water. These trace amounts of contaminants are a chronic issue for wastewater reuse. Research should consider that any chemical used can be found in the water, focus should be on health-relevant contaminants, performance indicators, and surrogates. Wastewater should be screened, tested with a tiered strategy, and treated. An example of ozonation treatment was covered in depth. Treatment processes generally form by-products as a result of treatment. Around 70% of those by-products are of an unknown nature and that makes it difficult to regulate both the original contaminant treated for, and the newly formed by-product. Bioassays are used to determine the safety of the contaminants as it relates to human exposure through water. Researchers are currently debating the use of human cells when testing for the effects of exposure to contaminates. A brief discussion was held on contaminates found in local water treatment plants and in monitoring wells along the Santa Cruz. The question of emerging contaminants is being asked around the world. Regulations will remain in place and enforced for specified contaminants; current questions surround unregulated contaminants. The testing of unregulated contaminants is intended to help prioritize the monitoring and possible future regulation of emerging contaminants. Discussion was held on the impact of the presence of multiple contaminants at once, as opposed to the effects of single contaminants independent of the presence of any others.

6. **Future Meetings/Agenda Items –** See projected agenda for further information.

7. **Adjournment –** Meeting adjourned at 1:08 p.m.

The Impact Of Emerging Contaminants On Water Sustainability

Tucson Water CWAC: 28th October 2015

Shane Snyder, Ph.D.

Professor & Co-Director
University of Arizona

Visiting Professor
National U. of Singapore

Senior Research Specialist

Armando Durazo: UCLA

Post-Doctoral Associates

Ai Jia: Peking University

Hye-Weon Yu: GIST Korea

Christiane Hoppe: Colorado SM

Ph.D. Students

Shimin Wu: Peking University

Minkyu Park: GIST Korea

Sheena Young: Johns Hopkins U.

Kevin Daniels: Northern Arizona U.

Mauricius Santos: UTFPR Brazil

Byron Hempel: U. Kentucky

M.S. Students

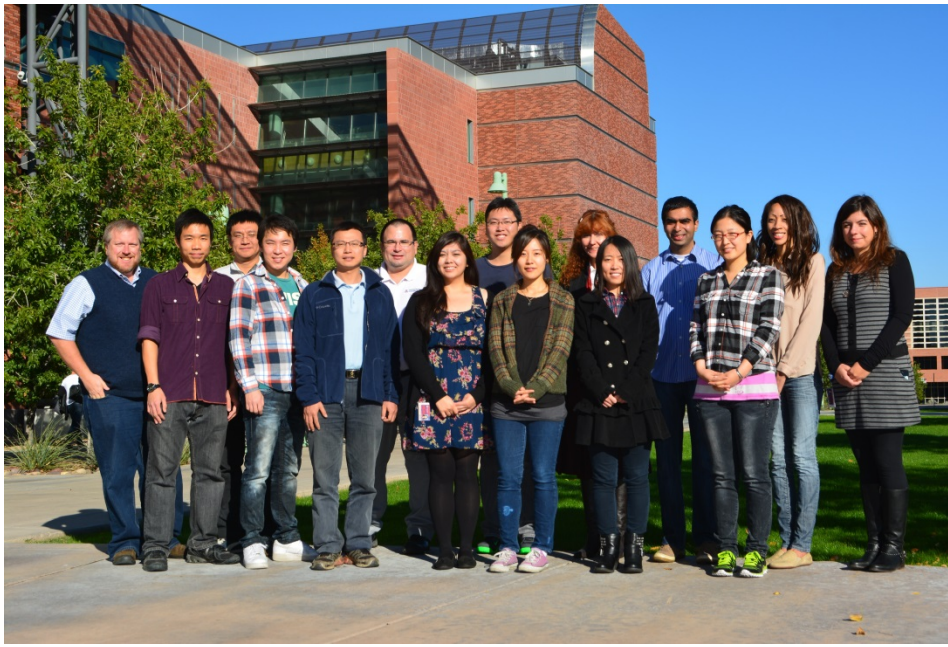
Weikang Ji: China Agricultural U.

Norma Villagomez-Marquez: UNC

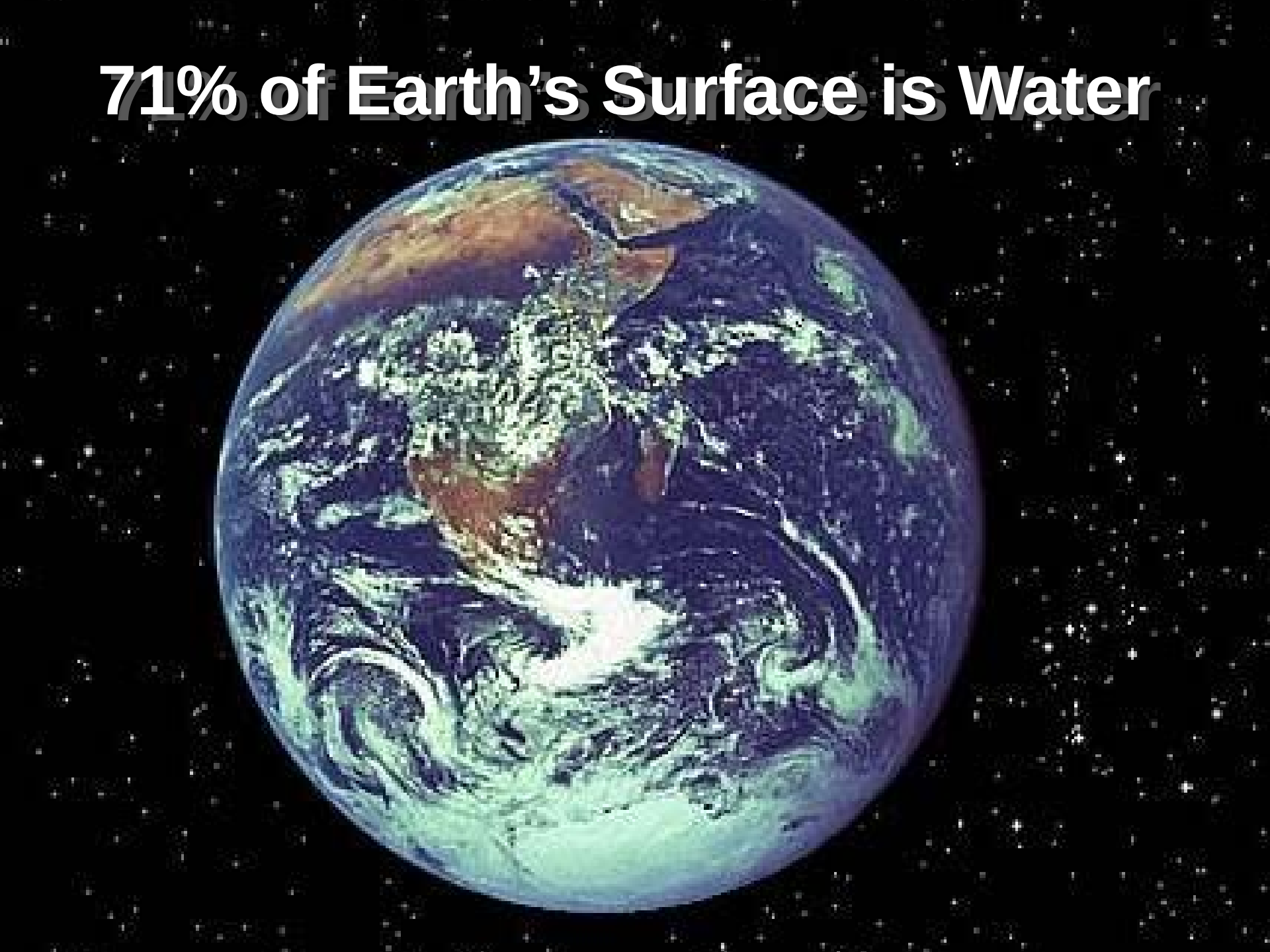
Mojtaba Azadi: Sharif UT

Tharun Murali: SASTRA U

snyderlab.arizona.edu

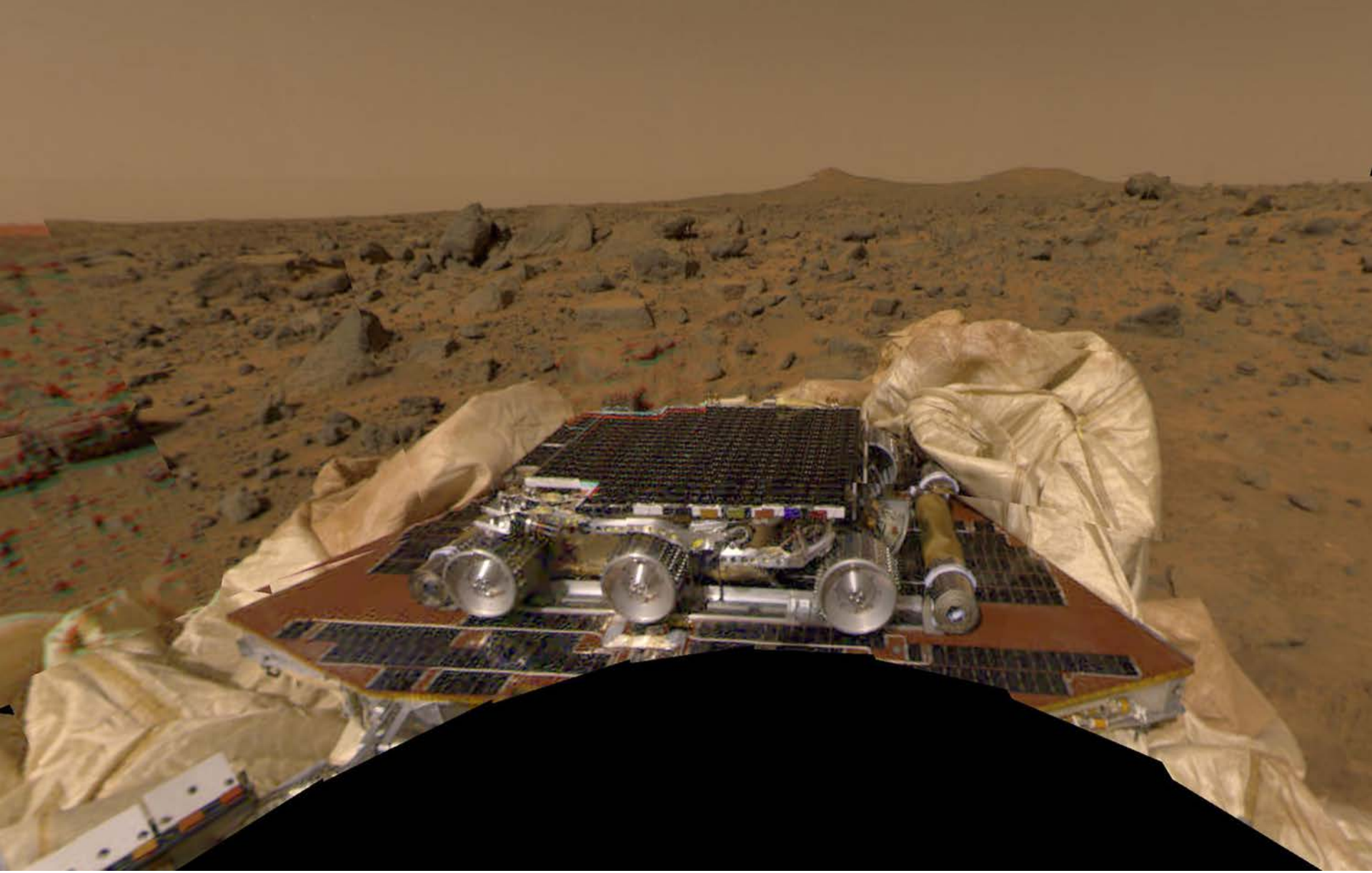


71% of Earth's Surface is Water



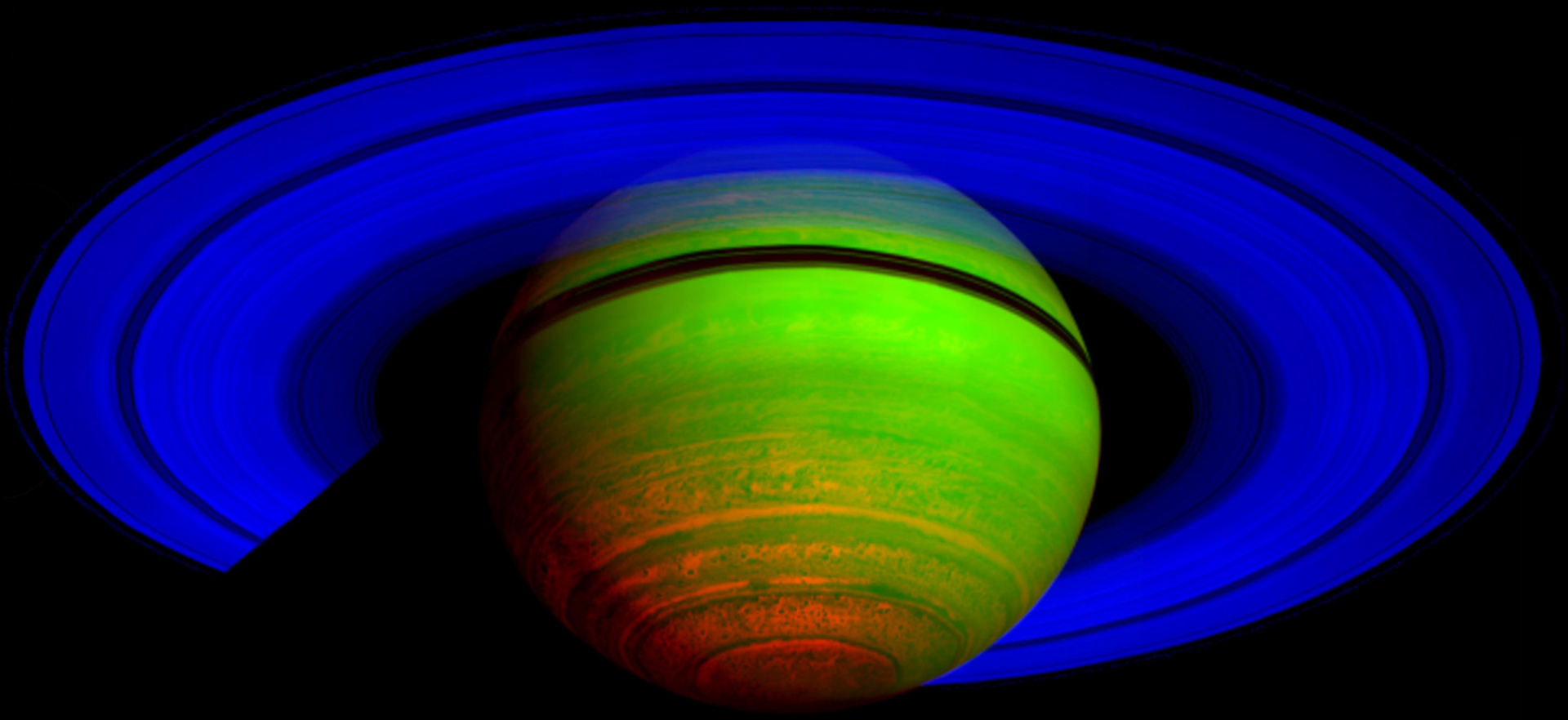
Signs of Water Found on 5 Alien Planets by Hubble Telescope

By Mike Wall, Senior Writer | December 03, 2013 02:54pm ET



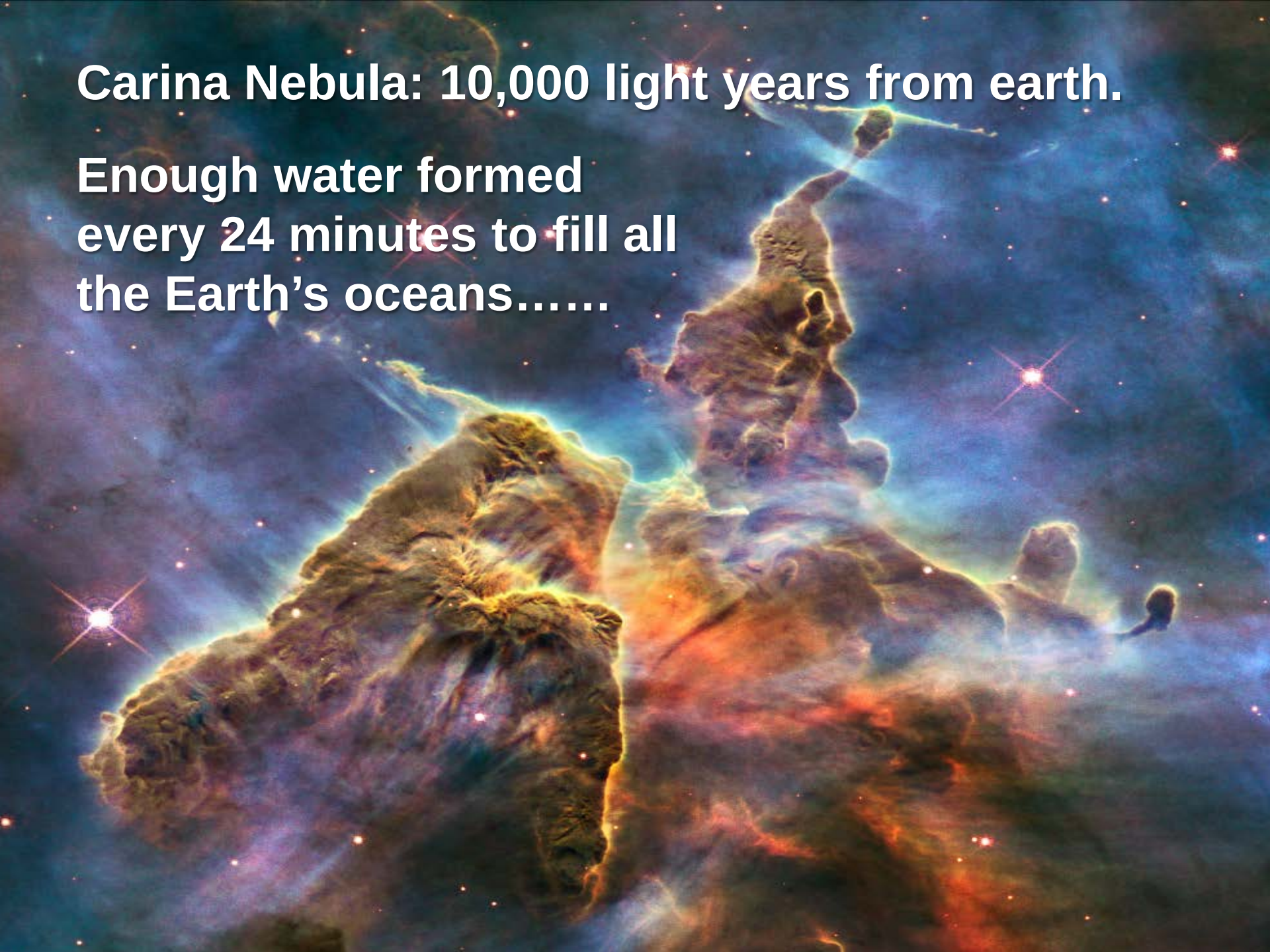
Peter Smith (University of Arizona) Principal Investigator:
The Imager for Mars Pathfinder – “Selfie” after touchdown

Robert Brown (University of Arizona) Principle Investigator, Visual and Infrared Mapping Spectrometer (VIMS) on NASA's Cassini spacecraft



Cassini's visual and infrared mapping spectrometer in the near-infrared reflection of sunlight indicates temperature and atmospheric conditions (dots are storm cells)

University of Arizona Skycenter Telescope
Whirlpool Galaxy = 23,000,000 light years from Earth

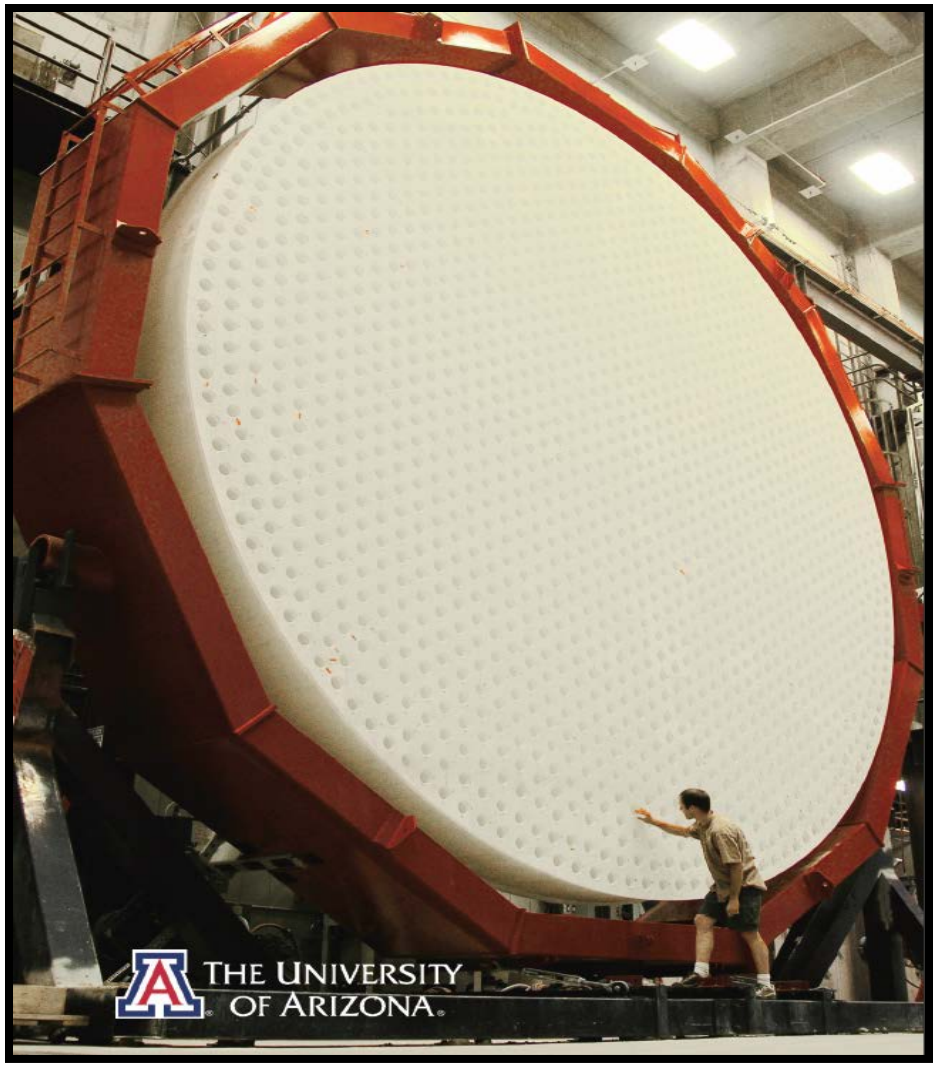

Carina Nebula: 10,000 light years from earth.
Enough water formed every 24 minutes to fill all the Earth's oceans……

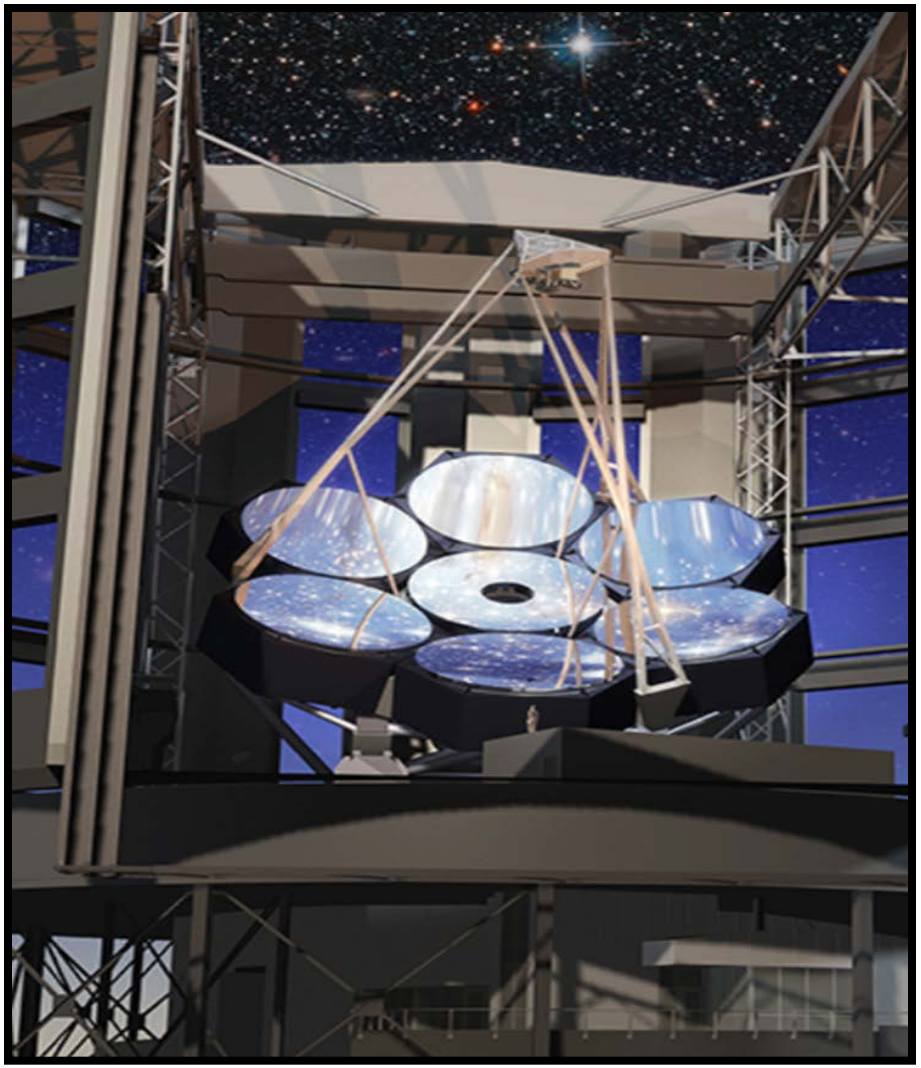
“Non-detectable” region of space… until 1990’s

Hubble made the non-detectable, detectable…

Hundreds of thousands new galaxies discovered, some more than 10 billion light years from Earth.

We can detect anything, anywhere…





We can detect anything, anywhere…

But are we looking for the right things?

WATER TANK
HAND CART
HA 2526

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

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

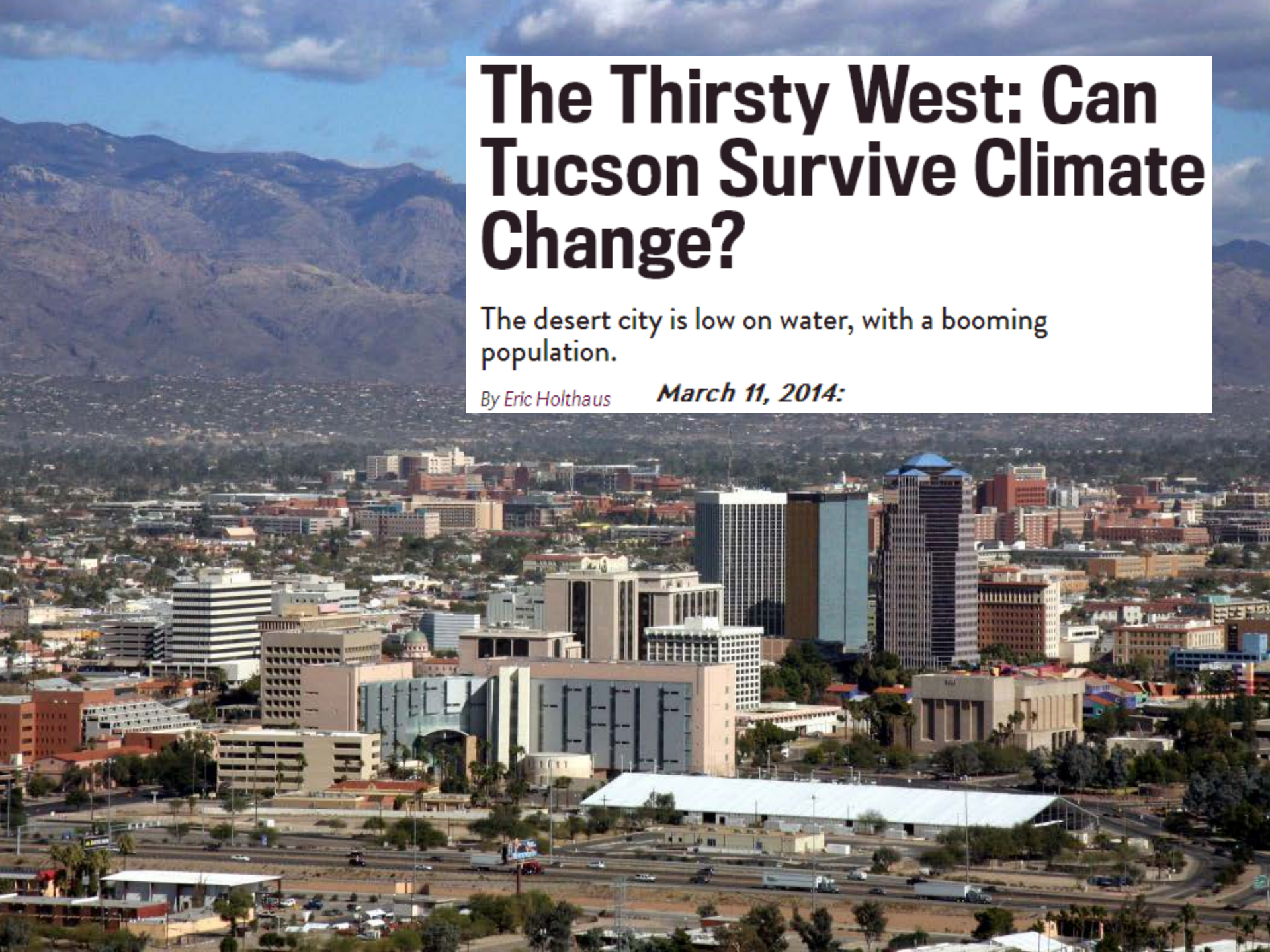
PETALING JAYA, Feb 19 — The water reserve continues to drop, causing concern that rationing could take place soon if the hot spell continues.

FROM THE PRINT EDITION THE MALAY MAIL

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:***

Tucson, other cities could be hit by CAP shortage much sooner than expected

JUNE 15, 2014 12:00 AM • BY TONY DAVIS

For the first time, the state agency that operates the multibillion-dollar Central Arizona Project warns that water shortages could hit Tucson and Phoenix as soon as five years from now.

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

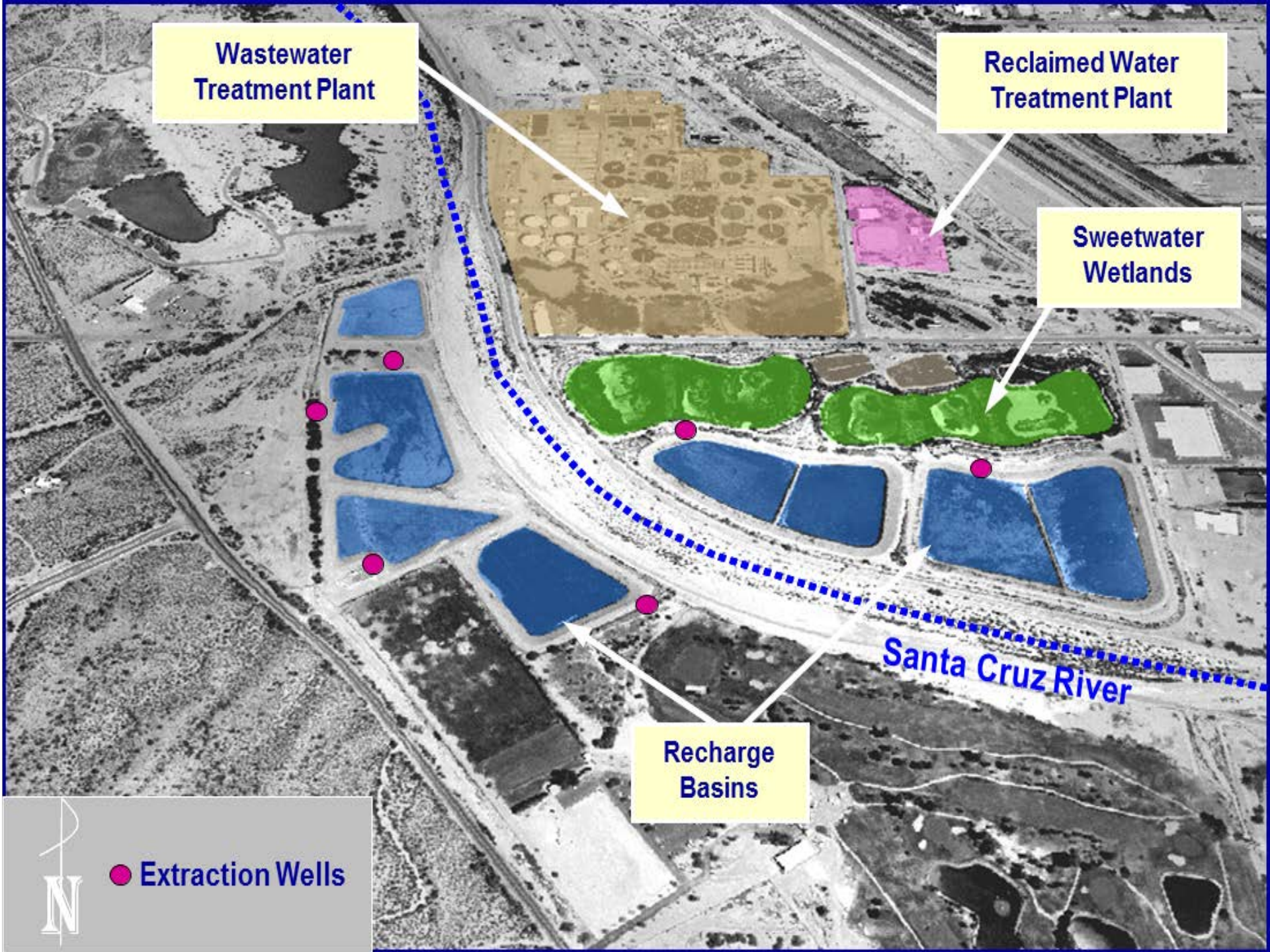
The New York Times

By MICHAEL WINES JUNE 17, 2014

Lake Mead sinks to a record low

By HENRY BREAN LAS VEGAS REVIEW-JOURNAL

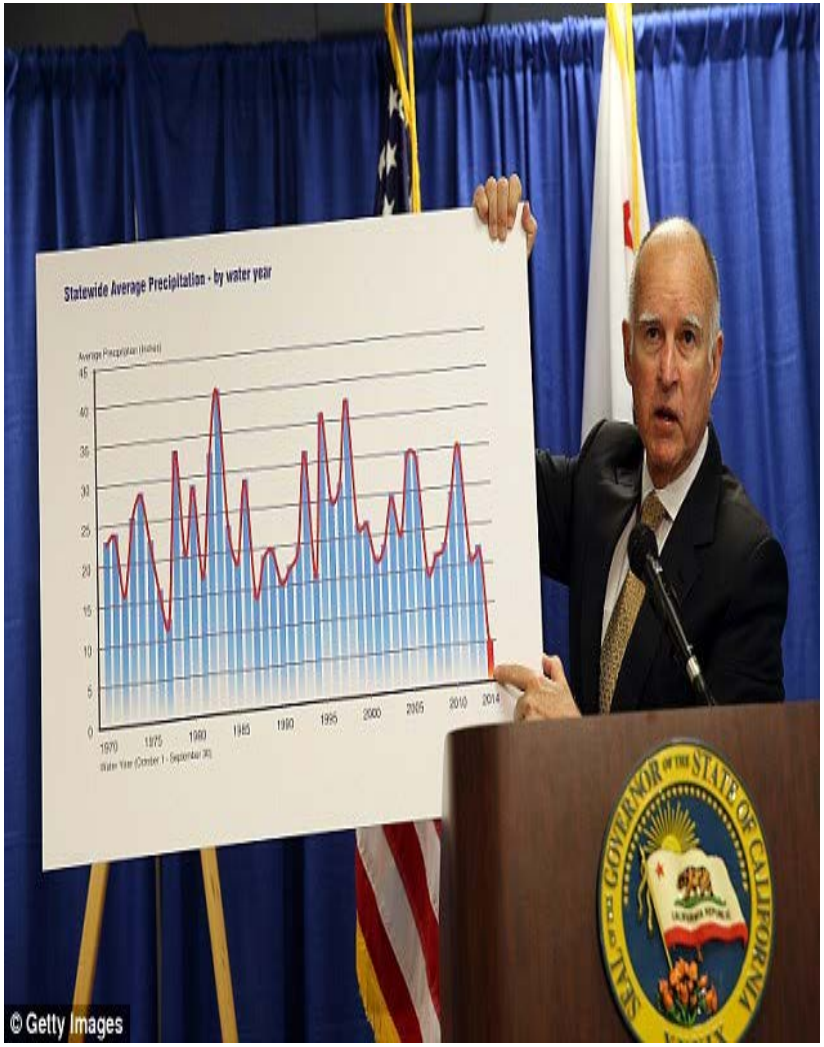
July 10, 2014


Wastewater Treatment Plant
Reclaimed Water Treatment Plant
Sweetwater Wetlands
Santa Cruz River
Recharge Basins
Extraction Wells
N

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.

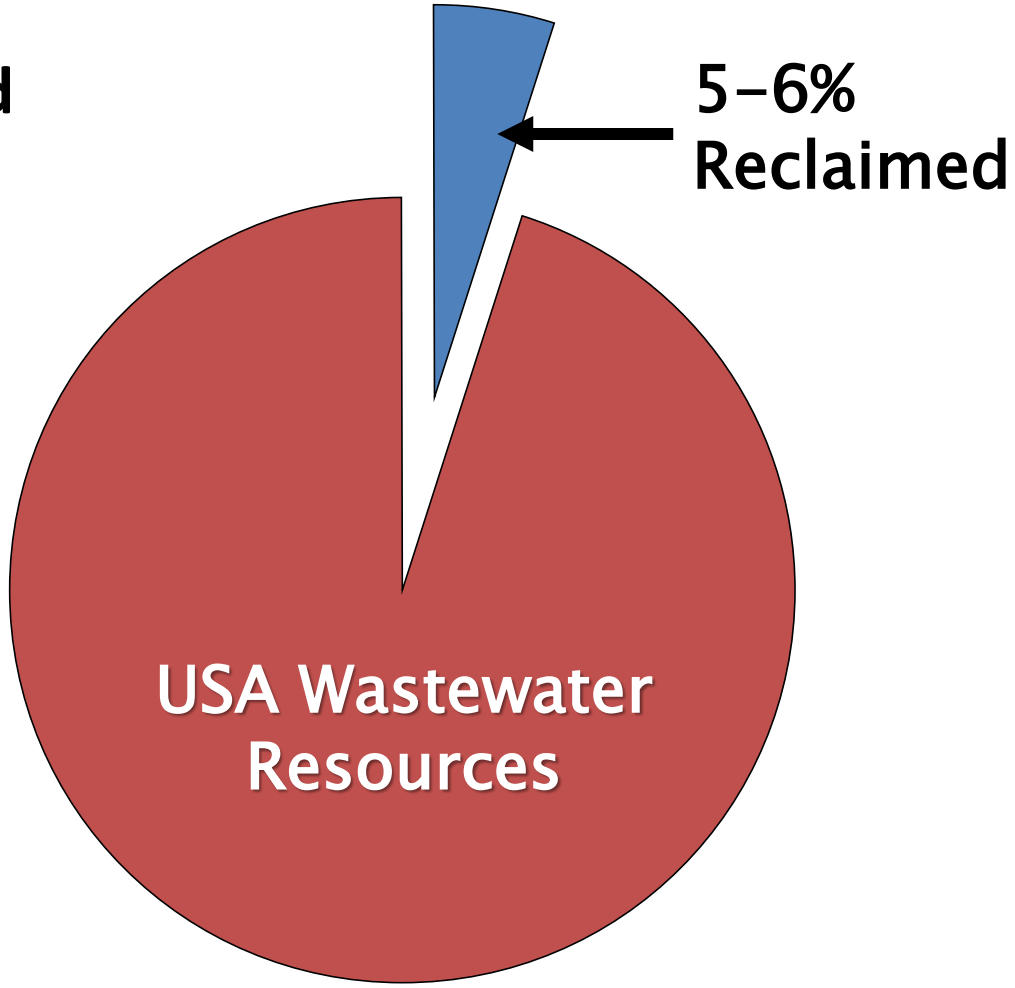
I am directing the Water Board to ensure that this work is completed expeditiously. The 3-year time frame mandated in this bill is too slow. California needs more high quality water and recycling is key to getting there.

Sincerely,

Edmund G. Brown Jr.

Potential for Water Reuse

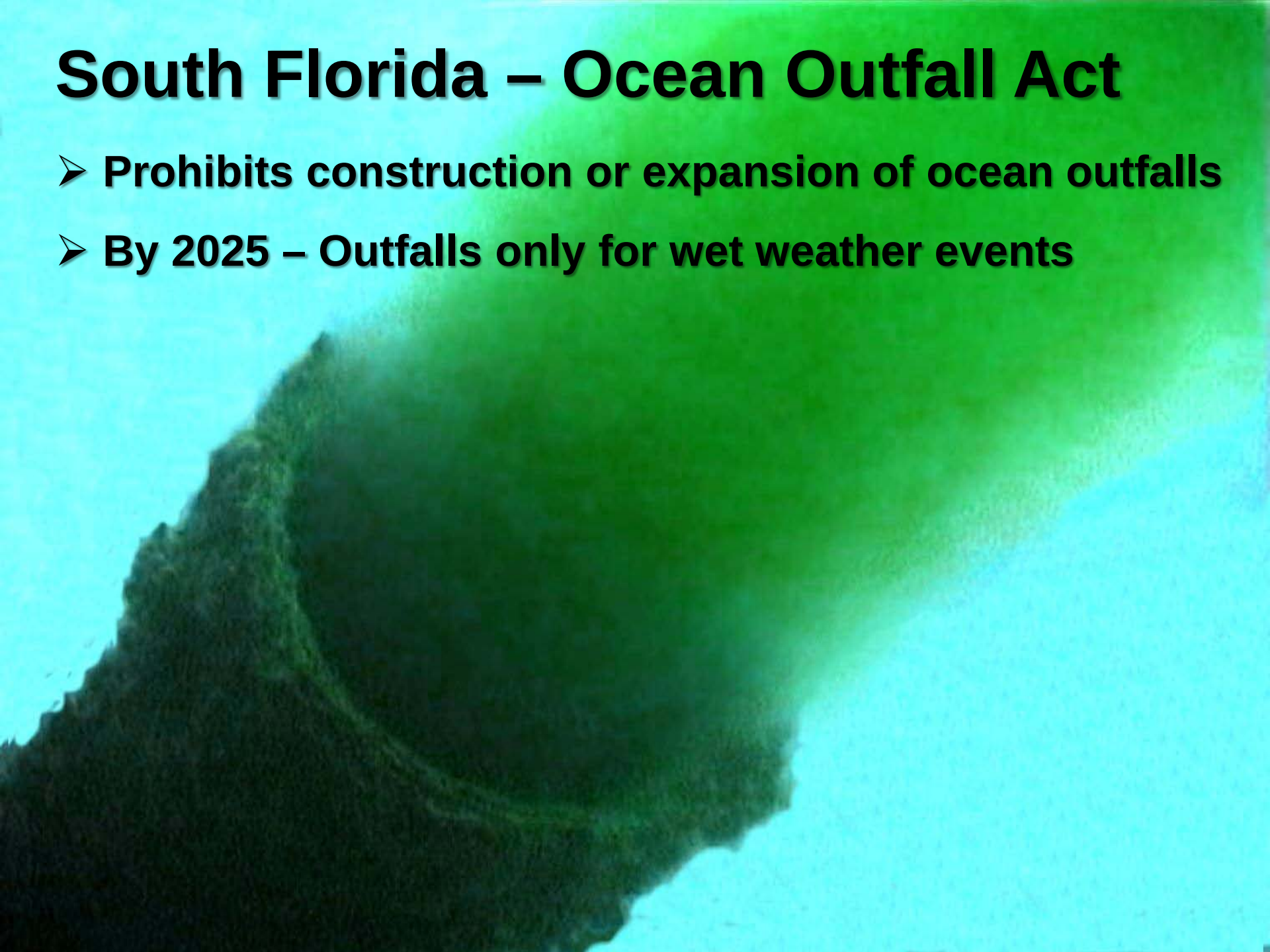
- **About 5-6% of US wastewater is reused**
  - **1/3rd of all US wastewater discharged to oceans**
- **California is mandating increased reuse**
- **Arizona, Florida and Texas also high growth**



Source: Wade Miller – WateReuse Association

South Florida – Ocean Outfall Act

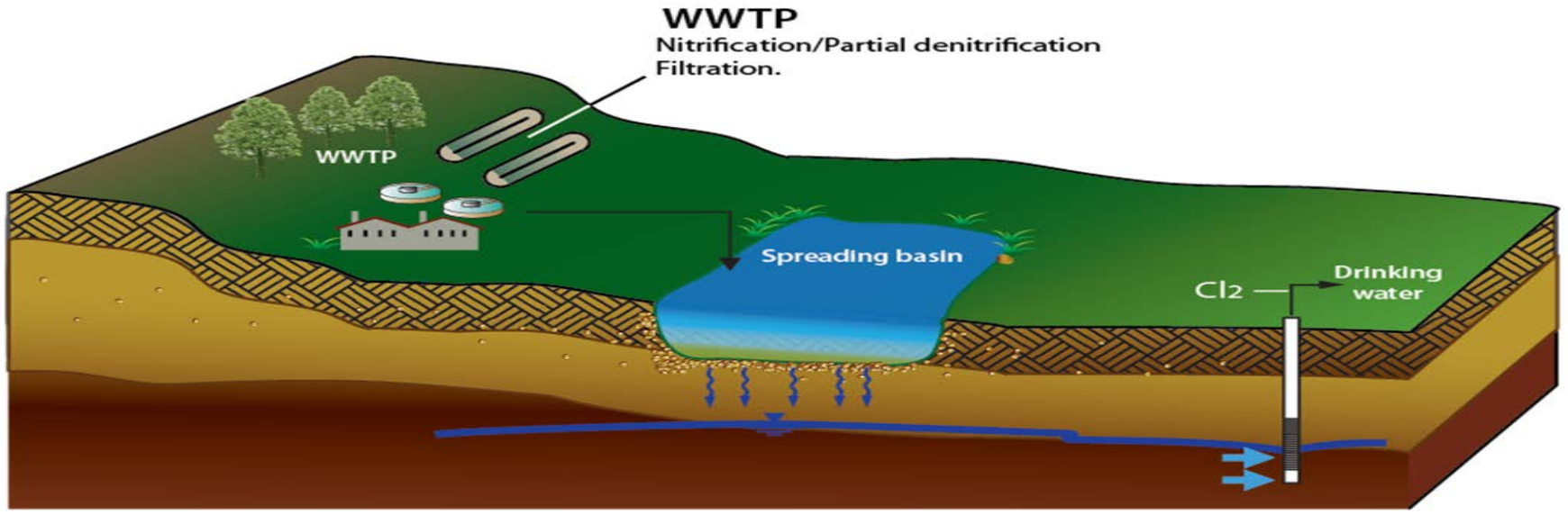
- Prohibits construction or expansion of ocean outfalls
- By 2025 – Outfalls only for wet weather events



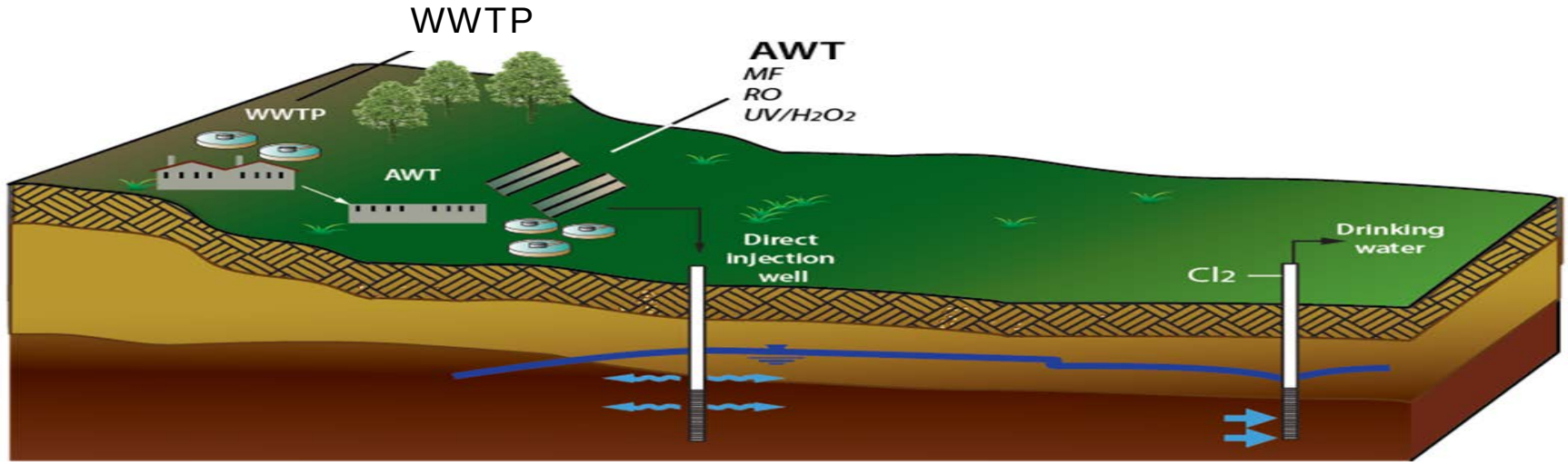
We Have the Technology

Simply a matter of safety, cost, and reliability…

Water Reuse – Natural Systems



Water Reuse – Advanced Treat.



Water Reuse – Direct Potable

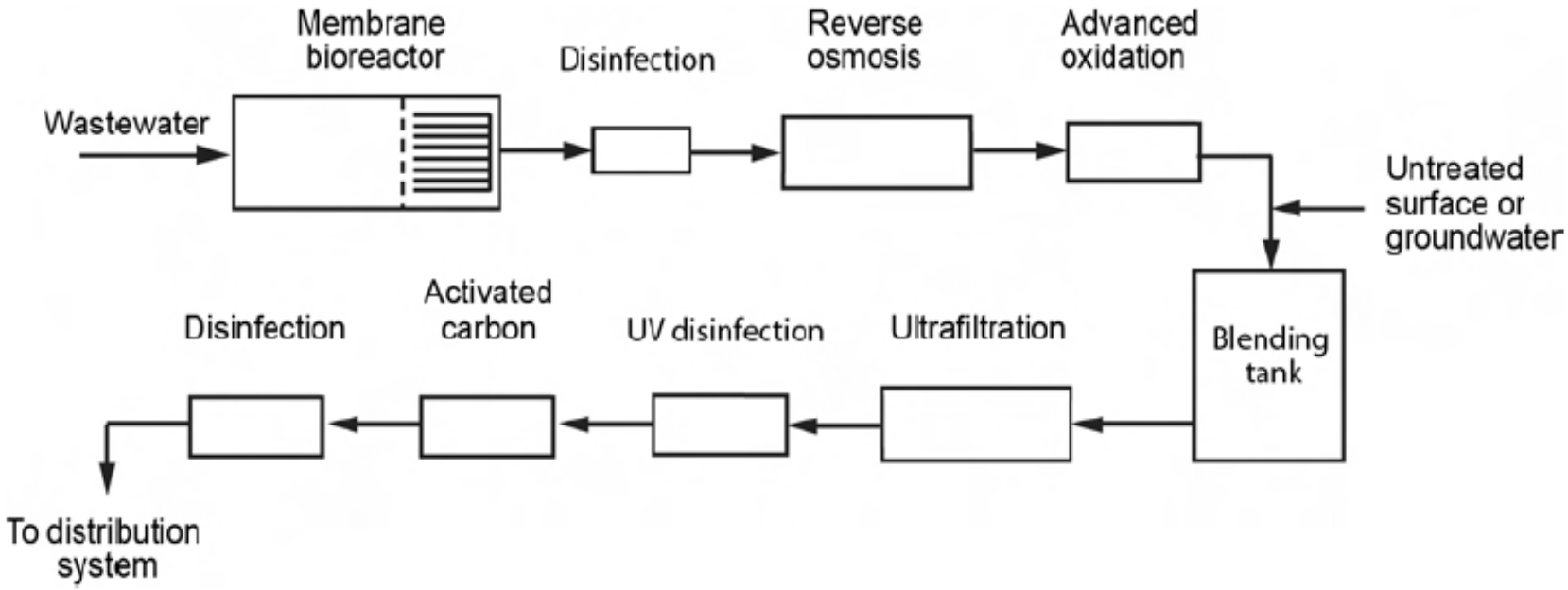
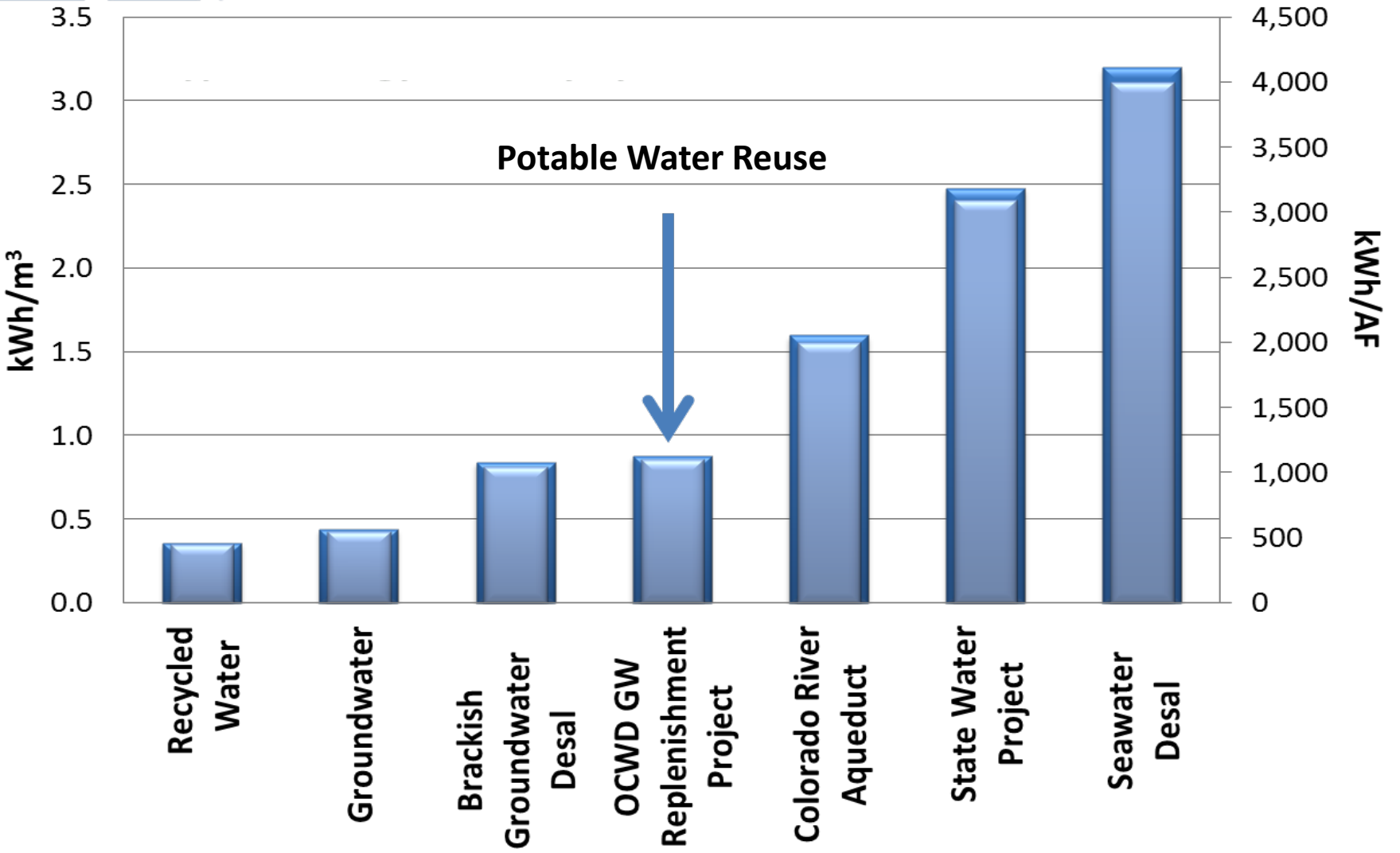


Figure 3-7

Schematic of Cloudcroft, NM DPR treatment process flow diagram (Adapted from Livingston, 2008).

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

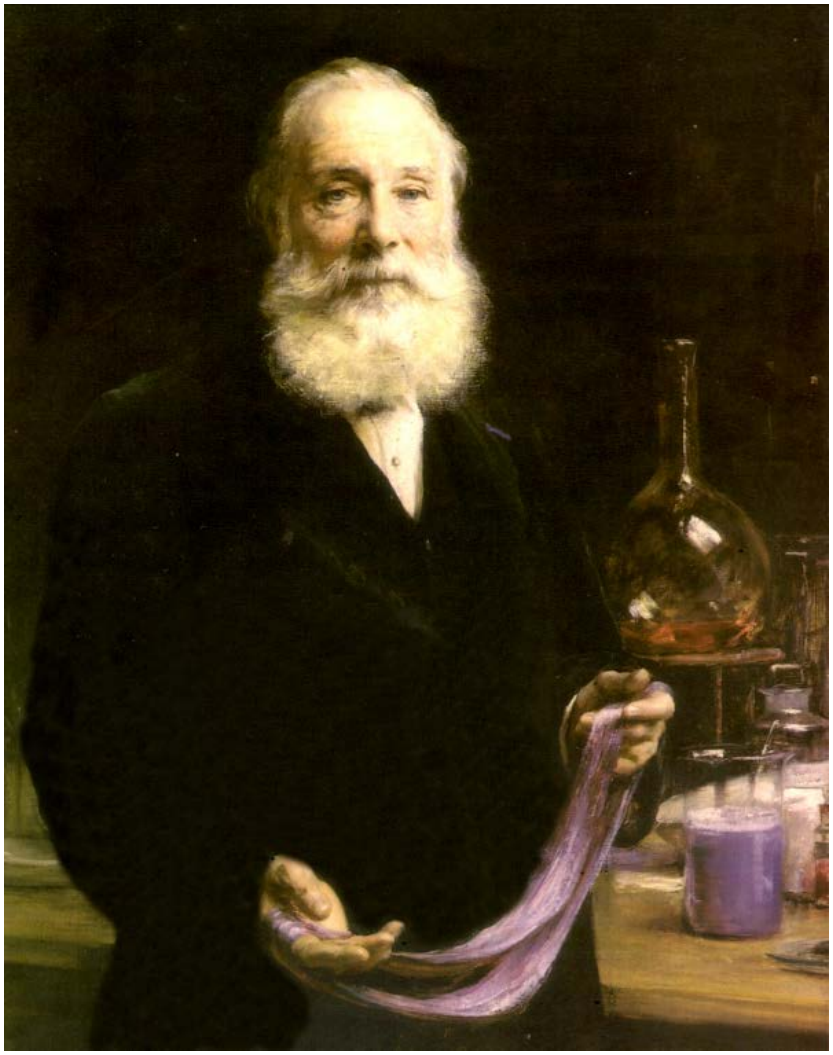
Source: http://www.hcn.org/issues/354/17227

When does waste water become “water”?

What is the “fingerprint”?

1850's: Coal-Tar Byproduct

1856 – Perkin Synthesizes Mauve



1860's – Cancer & Medicines

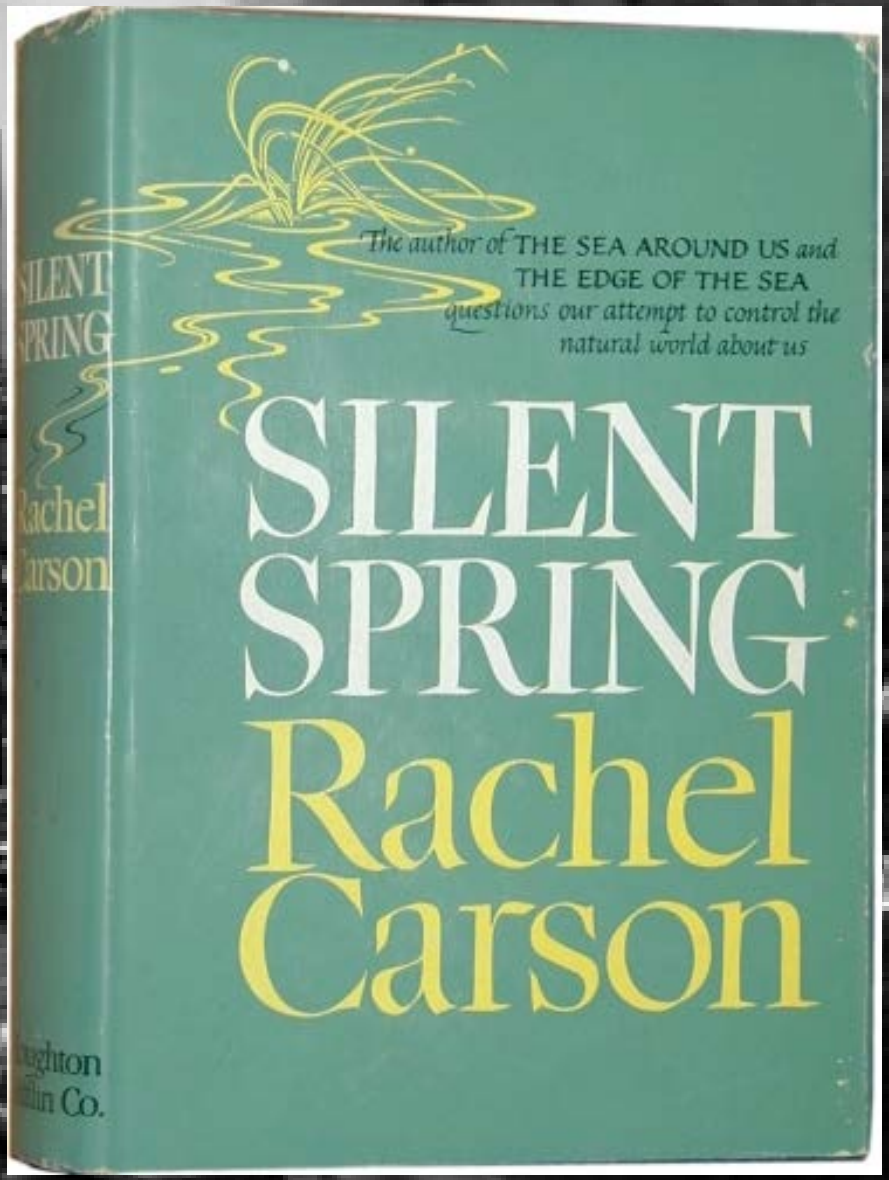
1899 – Industrial “Aspirin”

Early 1900's – Malachite Green

1939 – Discovery of DDT as Pesticide

1948 – Paul Müller Nobel Prize

Cuyahoga River, Ohio – USA 1969

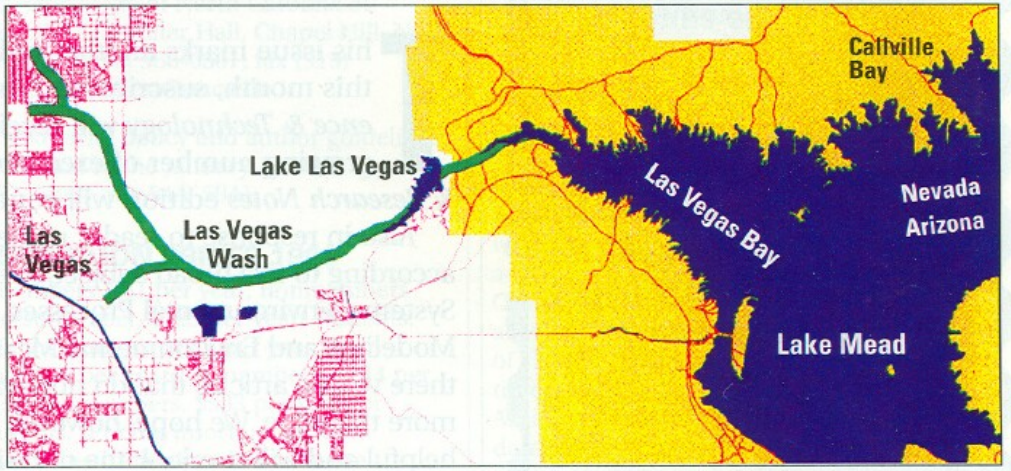


SOUTHERN NEVADA WATER AUTHORITY PUTS A POSITIVE SPIN ON REPORTS THAT A ROCKET FUEL CHEMICAL WAS DETECTED IN LAKE MEAD AND LOCAL WELLS...
PUT A TIGER IN YOUR TANK!
DRINK LAS VEGAS WATER!
FILL UP TODAY
OUTDOOR SIGNS
Jim Day 97
LAS VEGAS REVIEW-JOURNAL
ddy@lvrj.com.

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

Resource

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

MAY 1999

- *Bad Medicine*
- *Grease Relief*
- *Giving Barn Waste the Treat*
- *Biotrickling Filter*
- *1999 ASAE/CSAE-SCGR Annu International Meeting*

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.

Winter 2003 , Volume 2, Issue 4

On Tap

Drinking Water News
For America's Small Communities

NATIONAL DRINKING WATER CLEARINGHOUSE

They're in the water
They make fish change sex

Endocrine Disruptors

What are they doing to you?

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?

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.

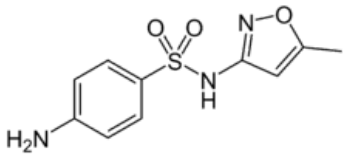
It's been confounding scientists for years: Male fish are developing female sexual characteristics in Lake Mead and other freshwater sources around the country.

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.

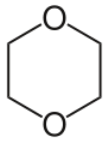
Contaminants potentially detectable in sewage

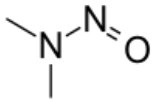
Chemical origins

Pharmaceuticals



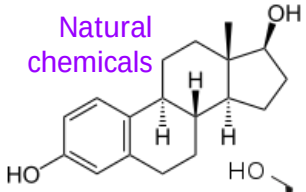
Industrial chemicals



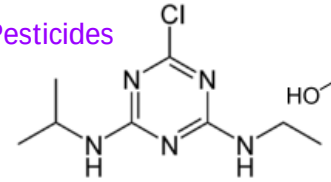


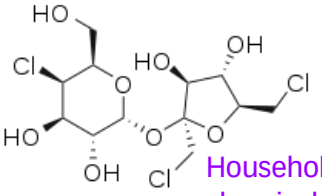
Transformation products

Natural chemicals



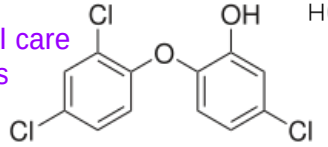
Pesticides



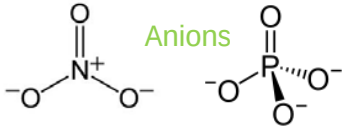


Household chemicals

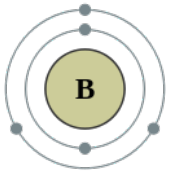
Personal care products



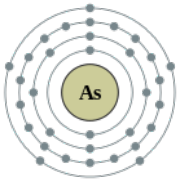
Anions



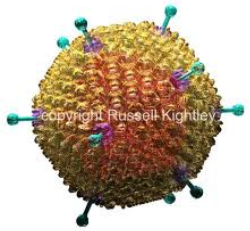
Cations



Metals

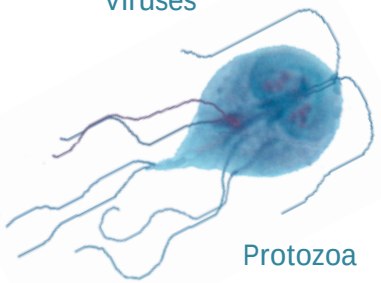


Microbial origins



Viruses

Bacteria

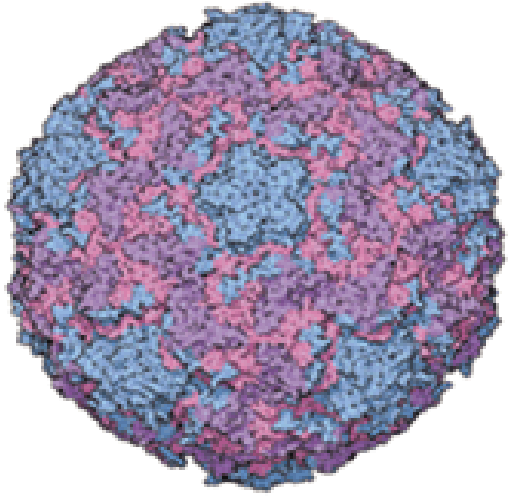


Protozoa

Helminths

Biologicals are ACUTE Risks

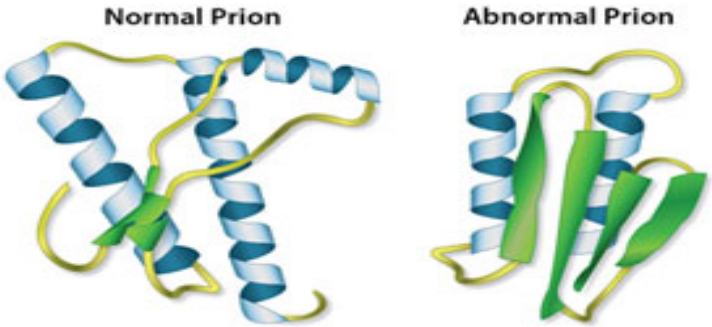
Viruses



Bacteria

Parasites

Prions



Chemicals are CHRONIC Risks

Organic and Inorganic

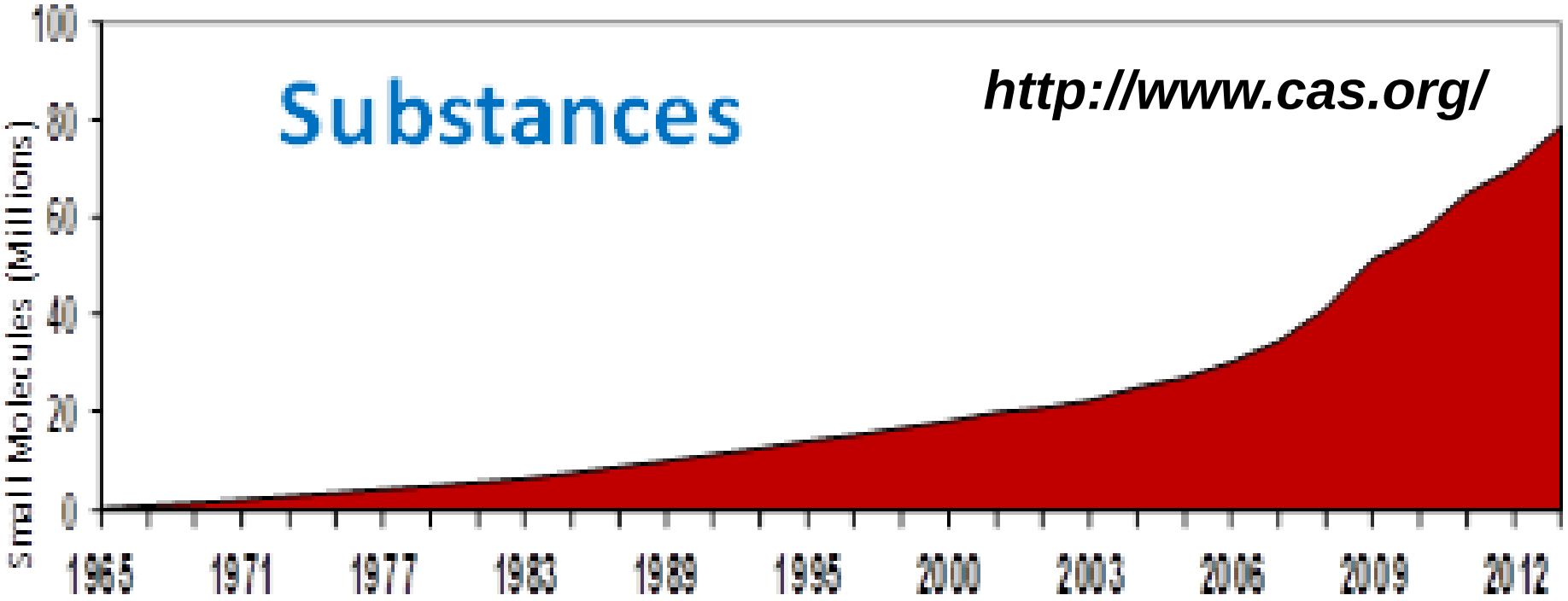
Volatile and non-volatile

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.

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

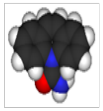
Comprehensive Screening

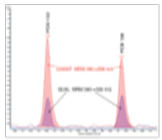
Targeted quantification

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 → Quantification of specific compounds in a sample

Samples → Isolation and separation of analytes from matrix





Comparison to target peak areas → Quantification of specific compounds in a sample

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

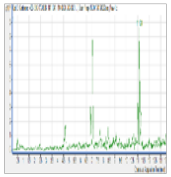
IC-MS

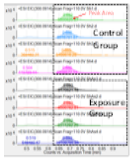
Anions, cations, oxyhalides

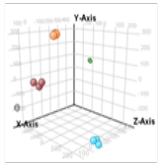
Non-targeted screening

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

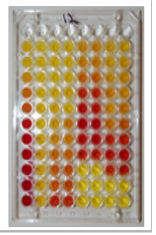
Polar and moderately polar compounds

GC-MS QTOF

Volatile and semi-volatile compounds

Cell Bioassay

Quantifiable cellular responses from mixtures isolated from biological samples



LC/GC-ICP-MS

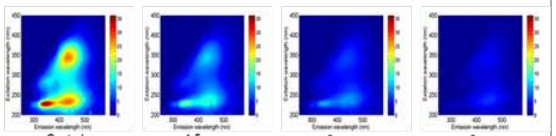
Untargeted organic-halogens/ metals

Tiered Recycled Water Testing Strategy

Tier 1
Bulk water characteristics (Surrogates)

On-line & off-line analysis

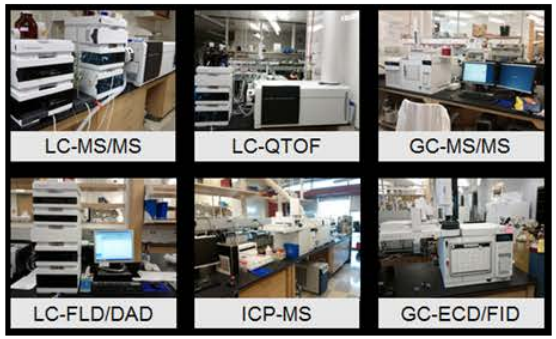
- General parameters (pH, temperature, conductivity, turbidity, TSS)
- Organic parameters (TOC/DOC, UV254, fluorescence)
- Inorganic parameters (Chlorine, NO_3, NO_2, anion and cation)
- Microbial parameters (Total cell counts)



Tier 2
Chemical & microbial Contaminants (Indicators)

Instrument-based chemical analysis

- TOrCs: Trace organic compounds
- Inorganic compounds

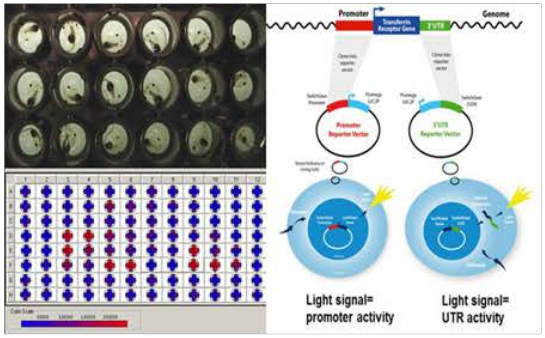


Microbiological analysis

Tier 3
Bioassay

Water toxicity test

- AMES II: Mutagenicity
- Glucocorticoid receptor (GR) assay: endocrine disruption effect
- Umu assay: Genotoxicity



Basic Categories of Treatment

Separation

Biological

Oxidation

Indicator Example – Secondary WWTP

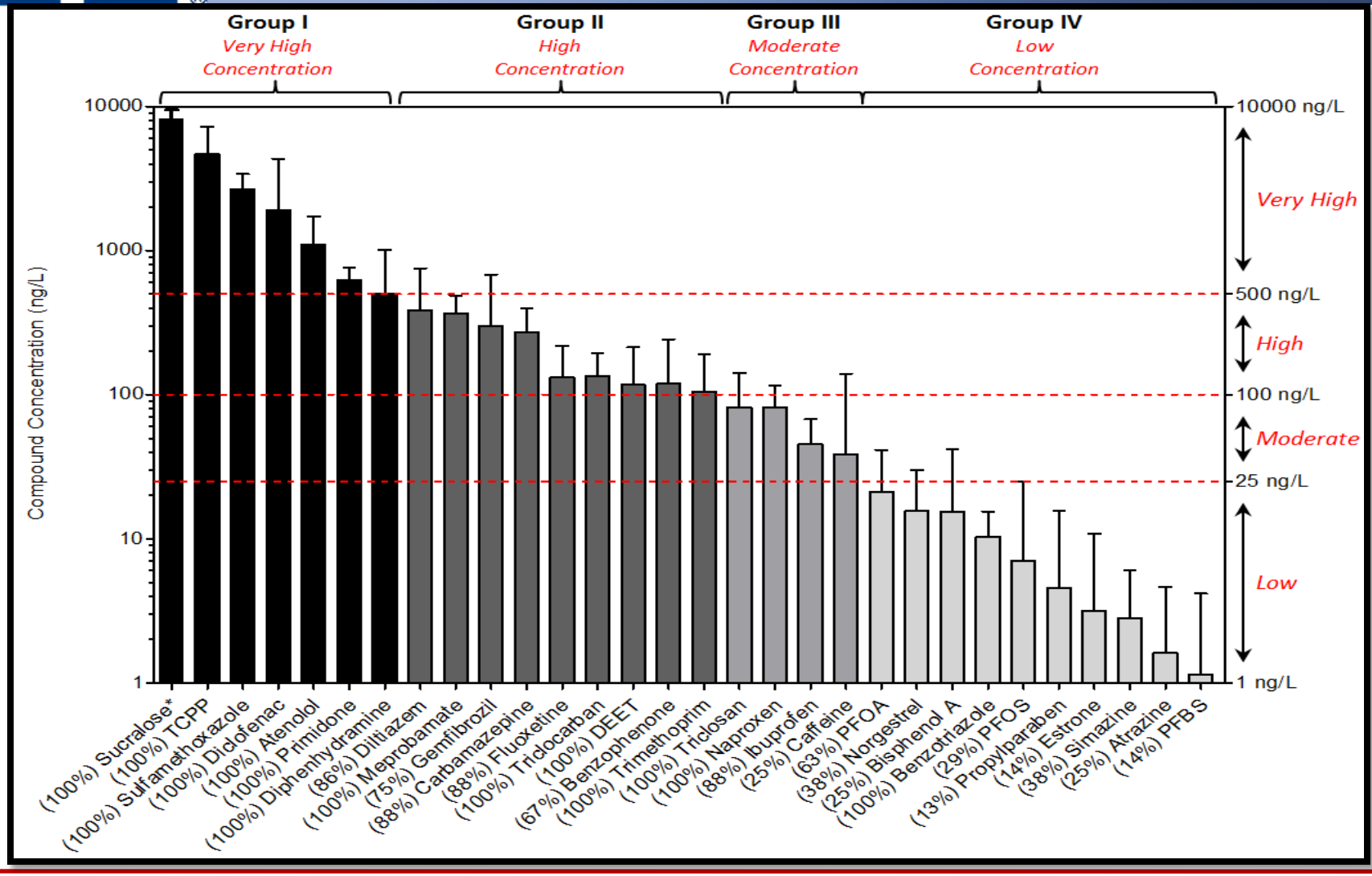
Faster transformation during secondary treatment

Higher sorption during secondary treatment

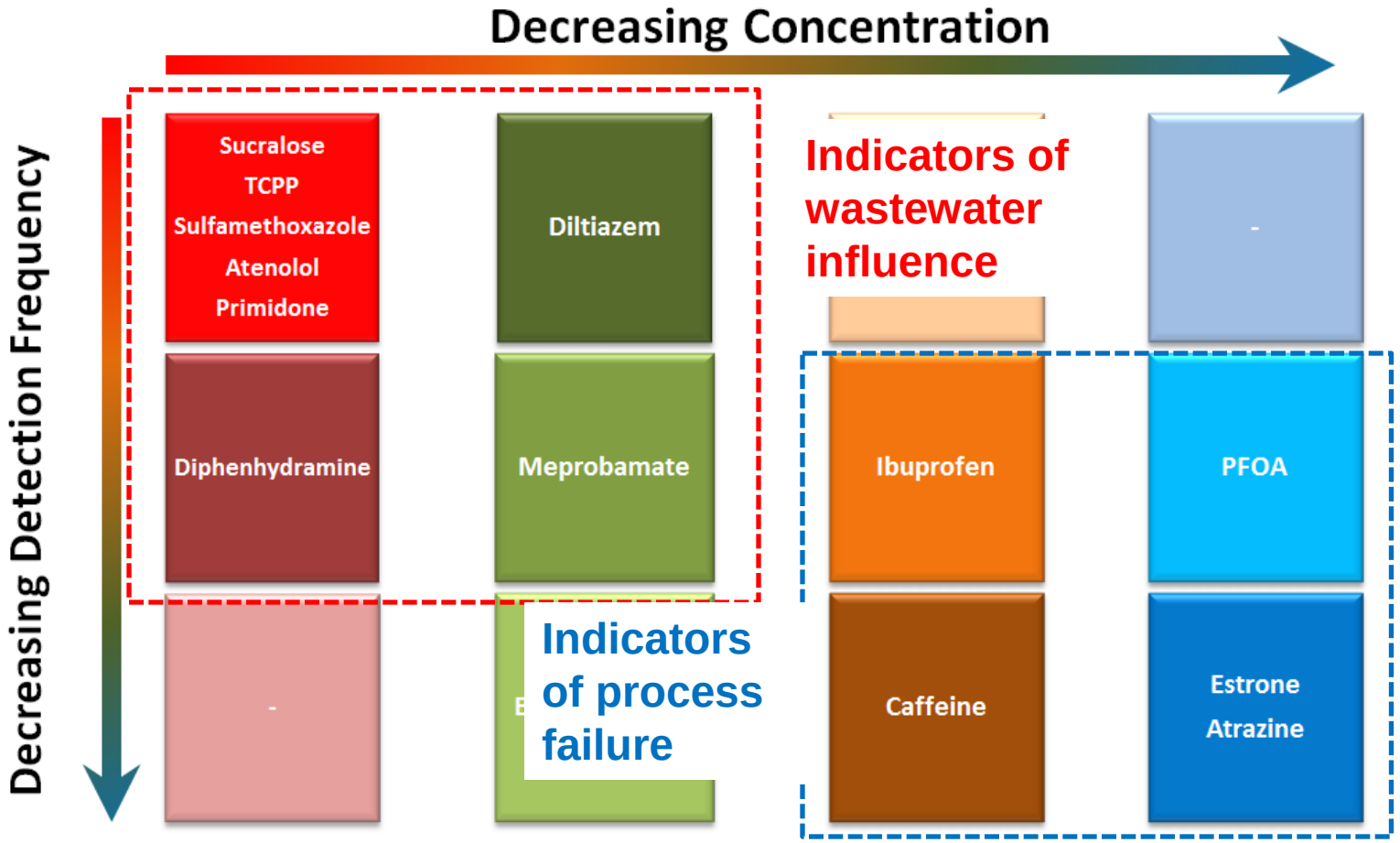
Sorption ($\log K_d$)	Biotransformation (K_b, L/g-d)		
	Recalcitrant <0.1	**Moderate Slow 0.1-10**	**Rapid >10**
Low <2.5	Carbamazepine Meprobamate Primidone TCEP Sucralose	DEET Sulfamethoxazole Gemfibrozil Iopromide	Acetaminophen Caffeine Naproxen Ibuprofen Atenolol
Sorptive 2.5-3	TCPP	Cimetidine Trimethoprim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

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

Indicator Occurence



Indicator List

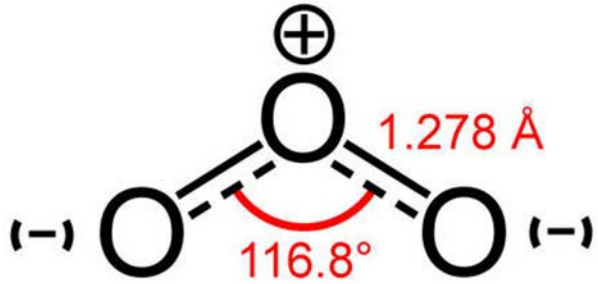


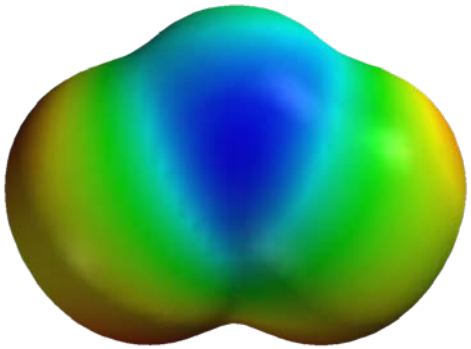
Contaminants in CAP water

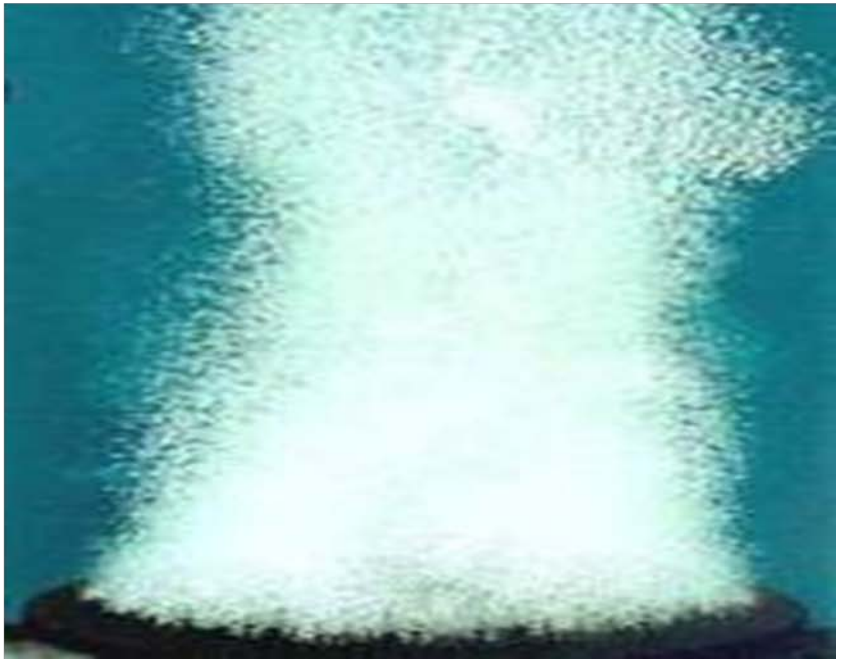
Compound	Conc. (ng/L)	Compound	Conc. (ng/L)	Compound	Conc. (ng/L)
Atenolol	<18	**PFOA**	<1.7	**TCEP**	<110
Caffeine	<12	**Norgestrel**	<33	**TCPP**	<110
Trimethoprim	<6.1	**Benzophenone**	<16	**DEET**	<6.7
Primidone	<27	**Ibuprofen**	<3.2	**Bisphenol A**	<83
Meprobamate	<29	**PFOS**	<2.7	**Testosterone**	<44
Sulfamethoxazole	<11	**Gemfibrozil**	<2.8	**Naproxen**	<4.4
Prednisone	<44	**Triclocarban**	9.0	**Iohexol**	<55
Diphenhydramine	<13	**Triclosan**	<7.1	**Iopromide**	<22
Simazine	<3.6	**Acesulfame**	104	**Dexamethasone**	<14
Ditiazem	<8.5	**Sucralose**	516	**Atrazine**	<3.6
Carbamezapine	<14	**Clofibric Acid**	<9.9		

Collected on Jan. 22th, 2014

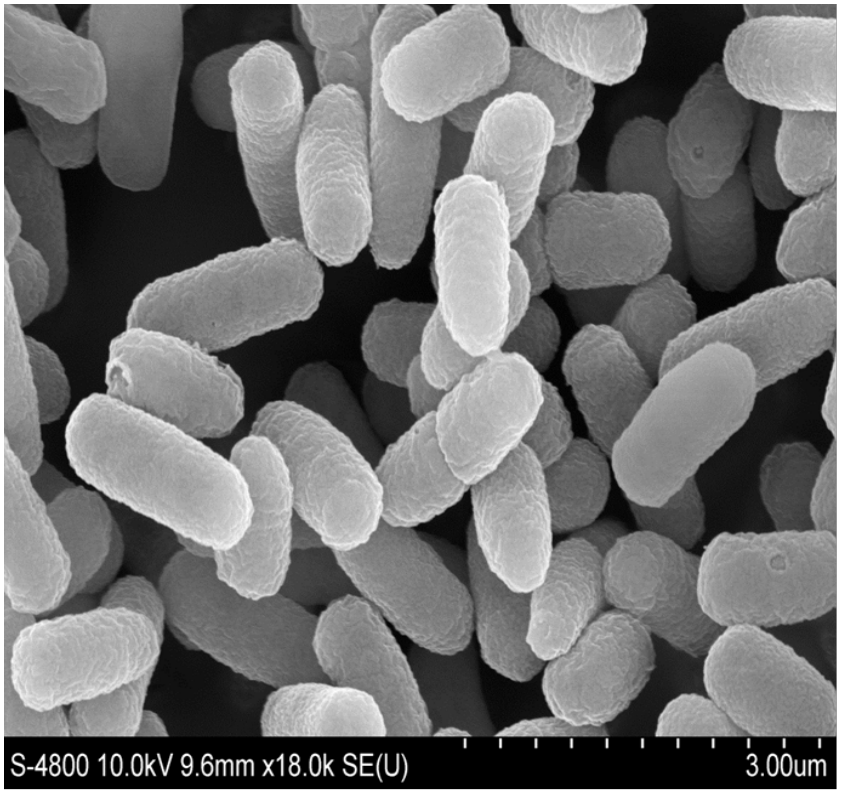
Ozonation Example



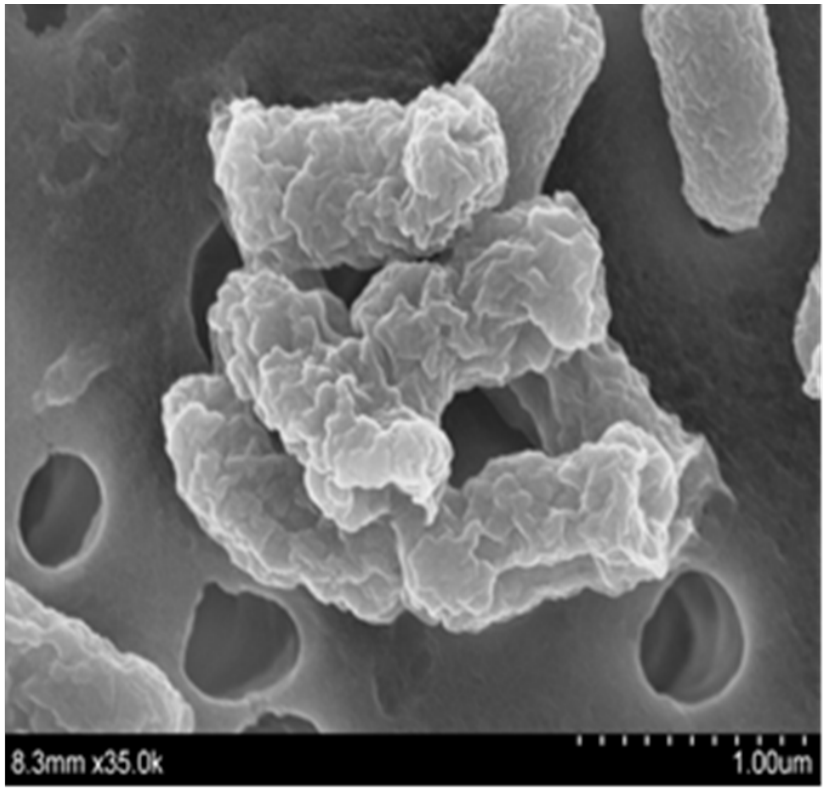




Disinfection



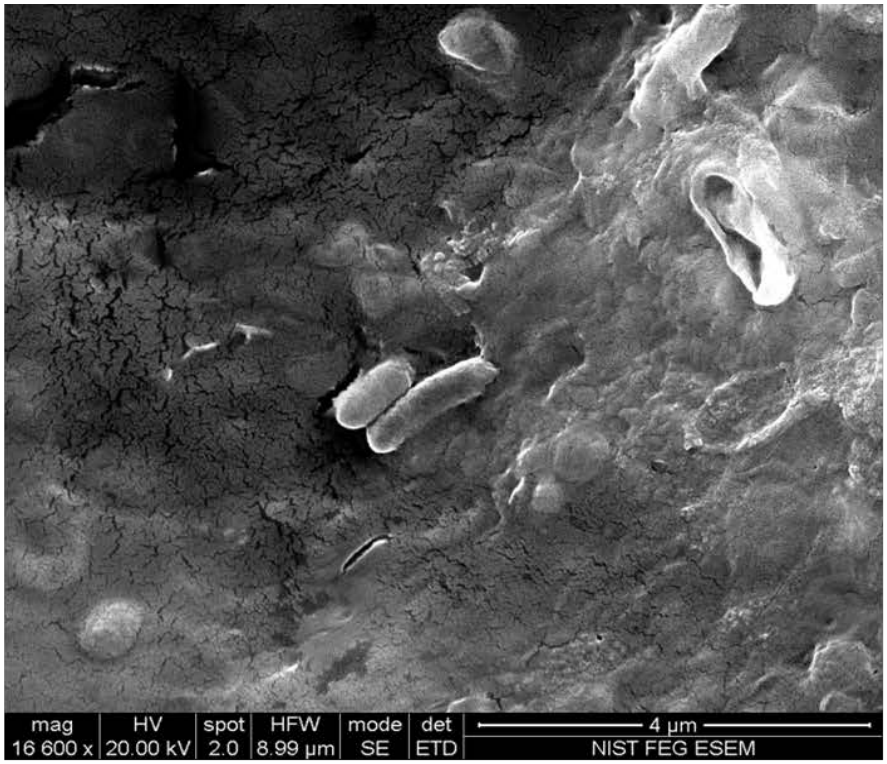
E. Coli - Healthy



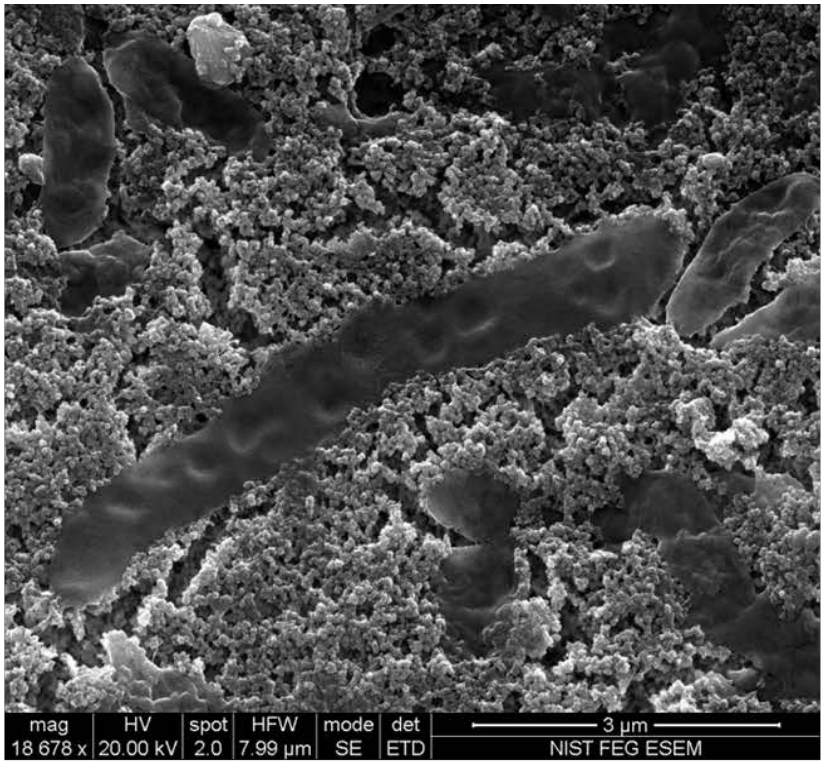
Post-AOP

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



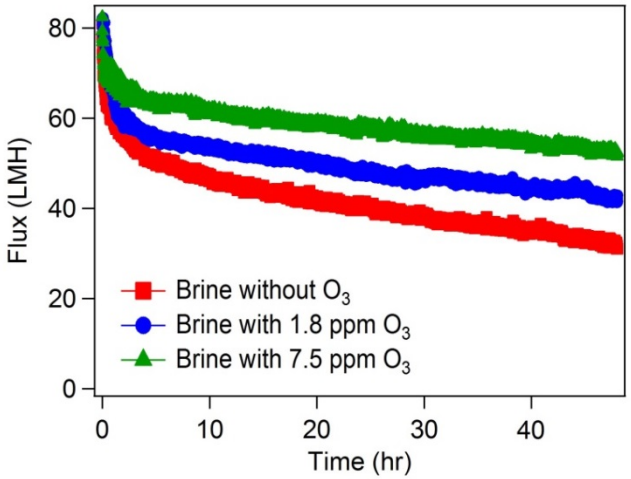
MBR-Ozone-RO (3 mg/L)

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.

Membrane Fouling with CAP

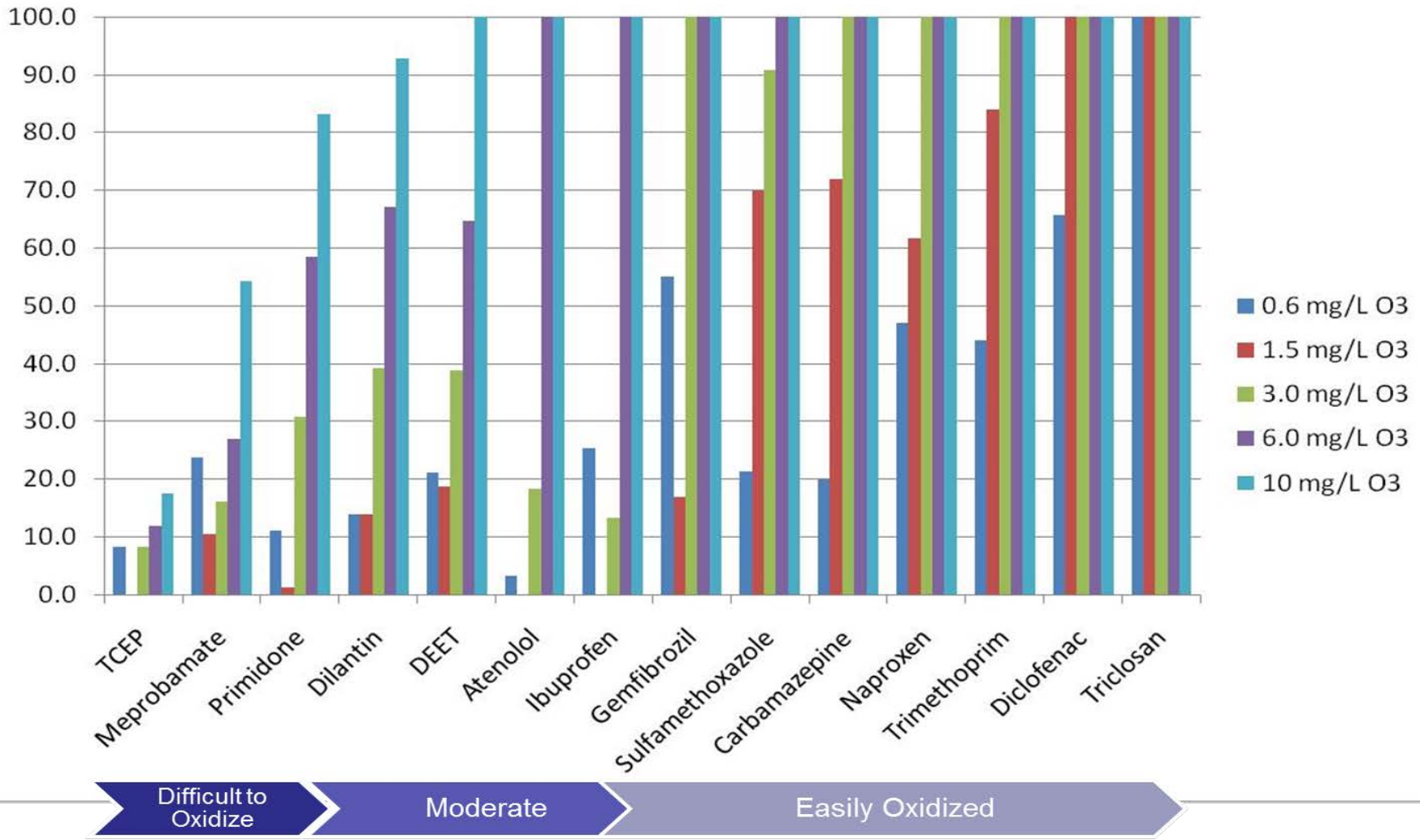
- Brine from NF membrane filtration using CAP water as feed water with 85% recovery was ozonated to recover more water from the NF membrane by reducing organic fouling.

< Ozone generator >



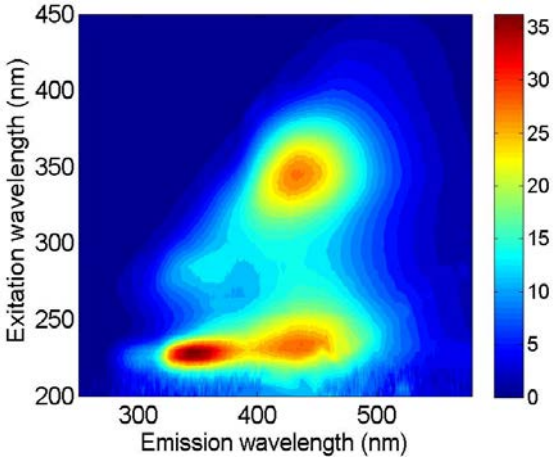
< Fouling test for CAP brine from NF membrane system. >

Indicator Oxidation

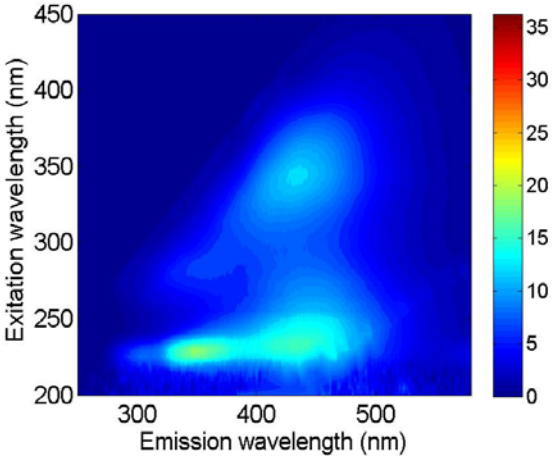


Pisarenko, AN et al.. *Water Res.* **2012,** *46* (2), 316-326.

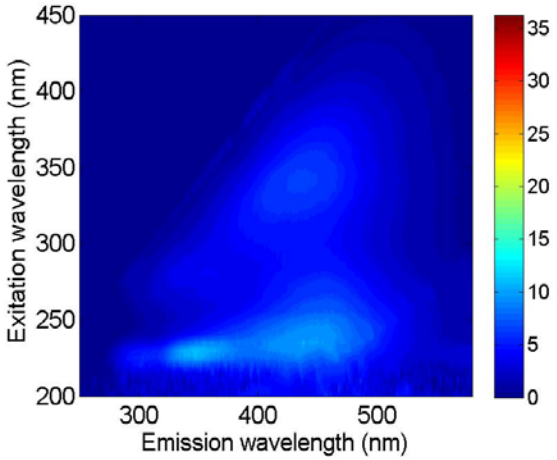
Fluorescence Surrogate Response



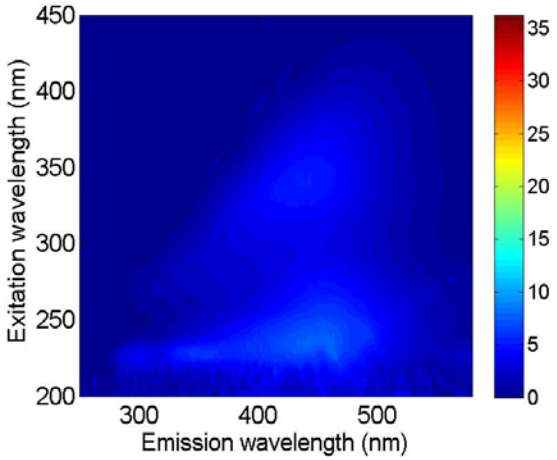
Control



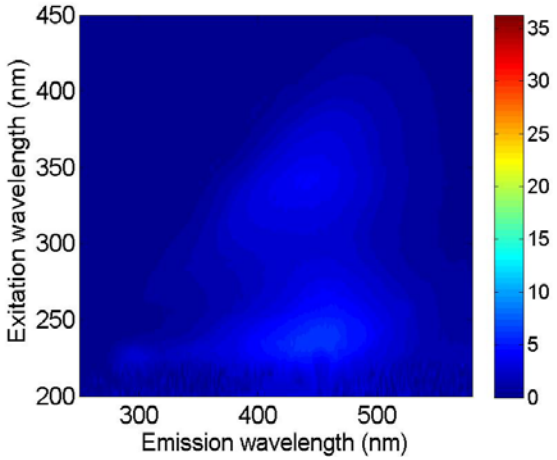
1.5 ppm



3 ppm

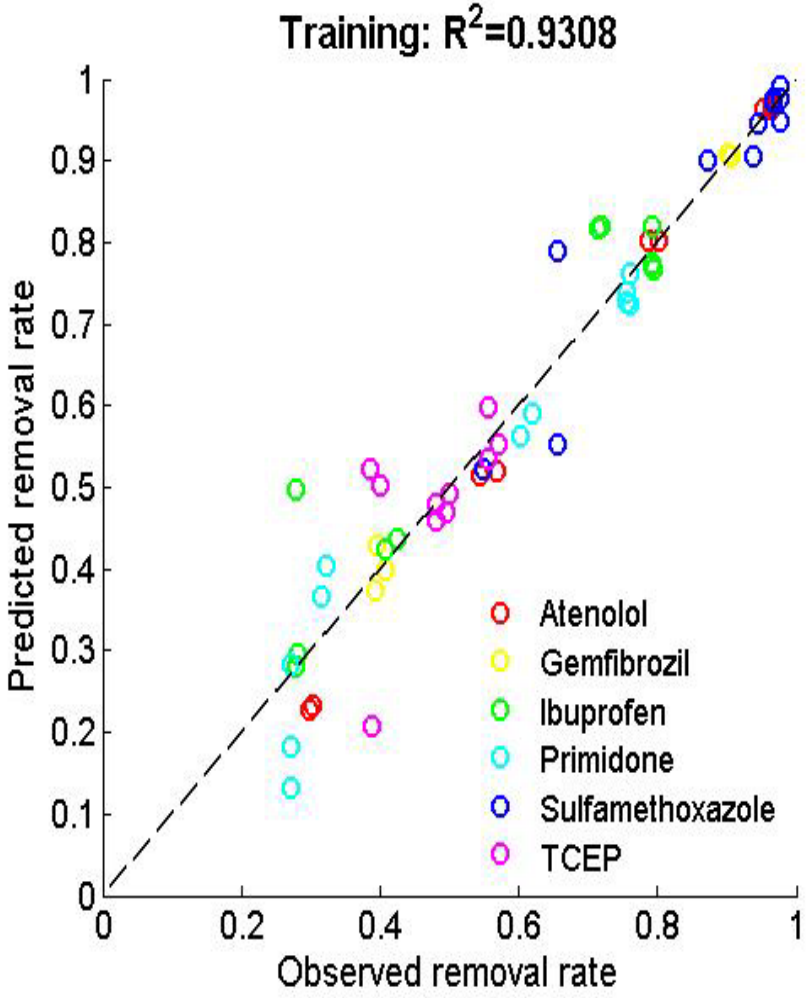


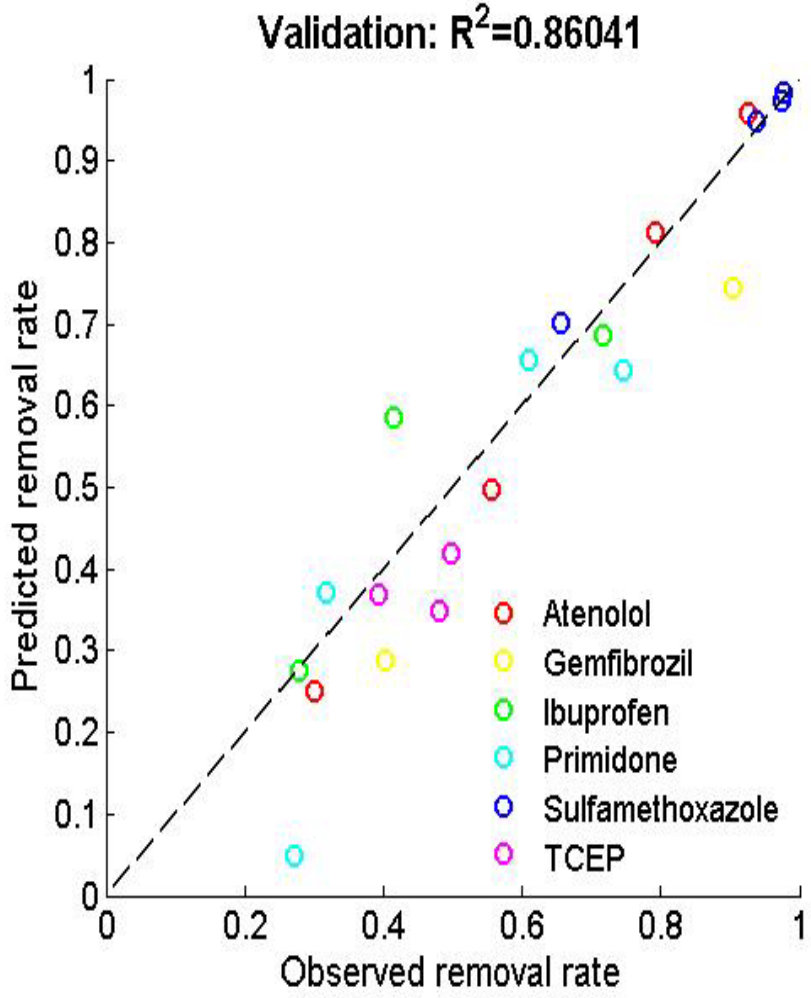
4.5 ppm



6 ppm

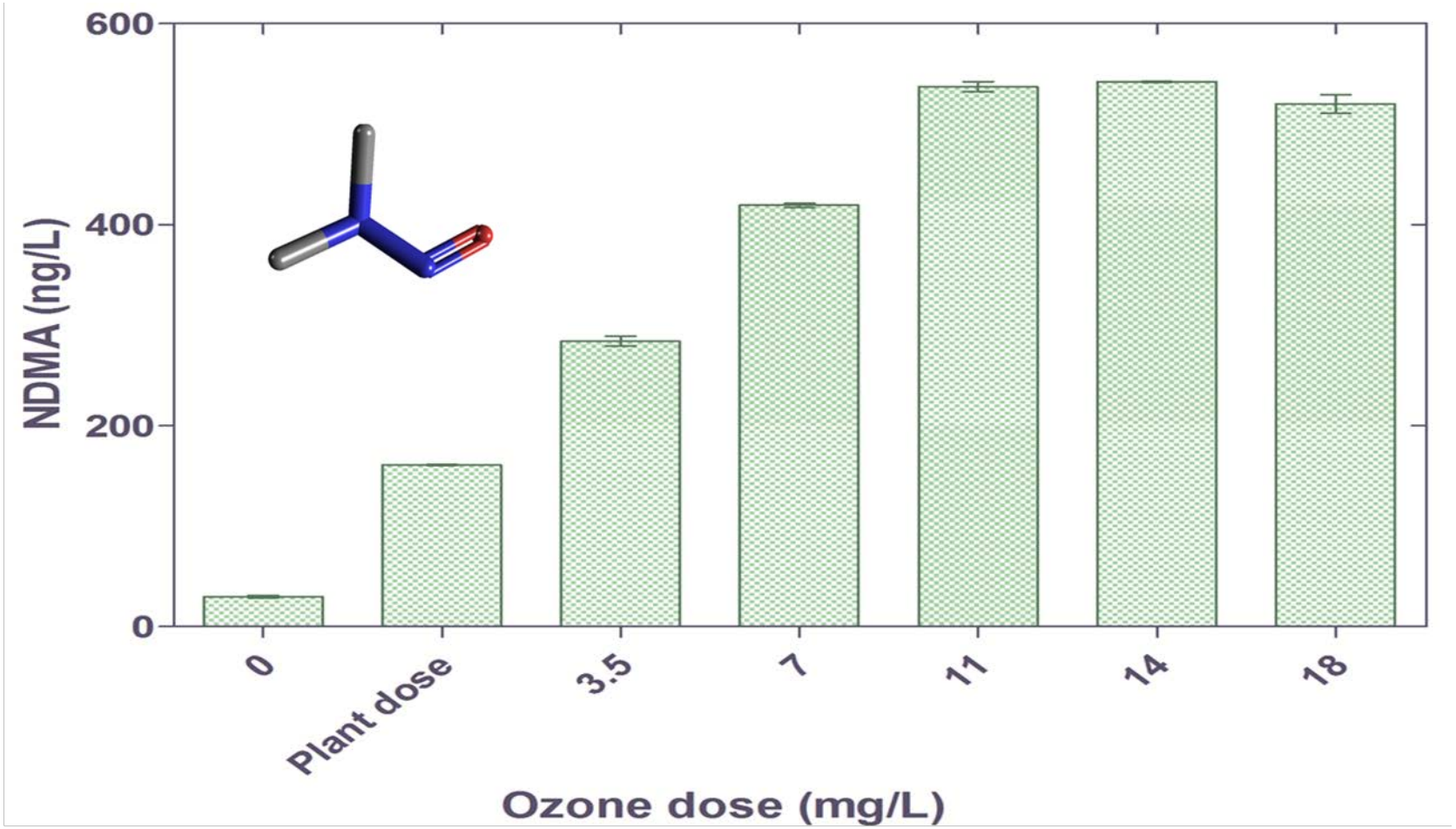
ANN Modeling for Ozone





Park M, Anumol T, Snyder SA. *Water Research & Technology* **2015,** *1*, 699-708

NDMA-FP with Ozone



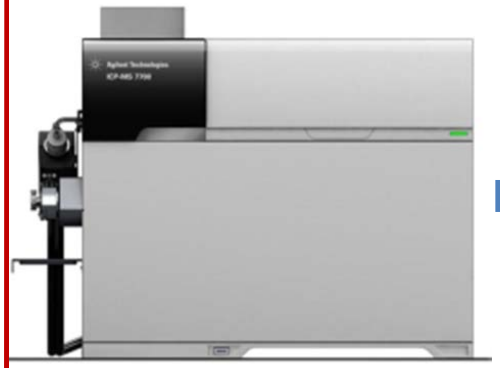
Sgroi, M.; Roccaro, P.; Oelker, G. L.; **Snyder, S. A.**, *ES&T* **2014,** *48* (17), 10308-10315.

GC-ICP-MS

Advantages:

- **No water present → little/no oxide interferences**
- **No evaporative cooling of plasma → lower RF forward power**
- **Lower RF power → fewer Ar-based ions ($^{40}Ar^+$, $^{38}Ar^{40}Ar^+$, $^{38}Ar^{40}ArH^+$, etc.)**

∴ **Interference-free analysis without collision gas**

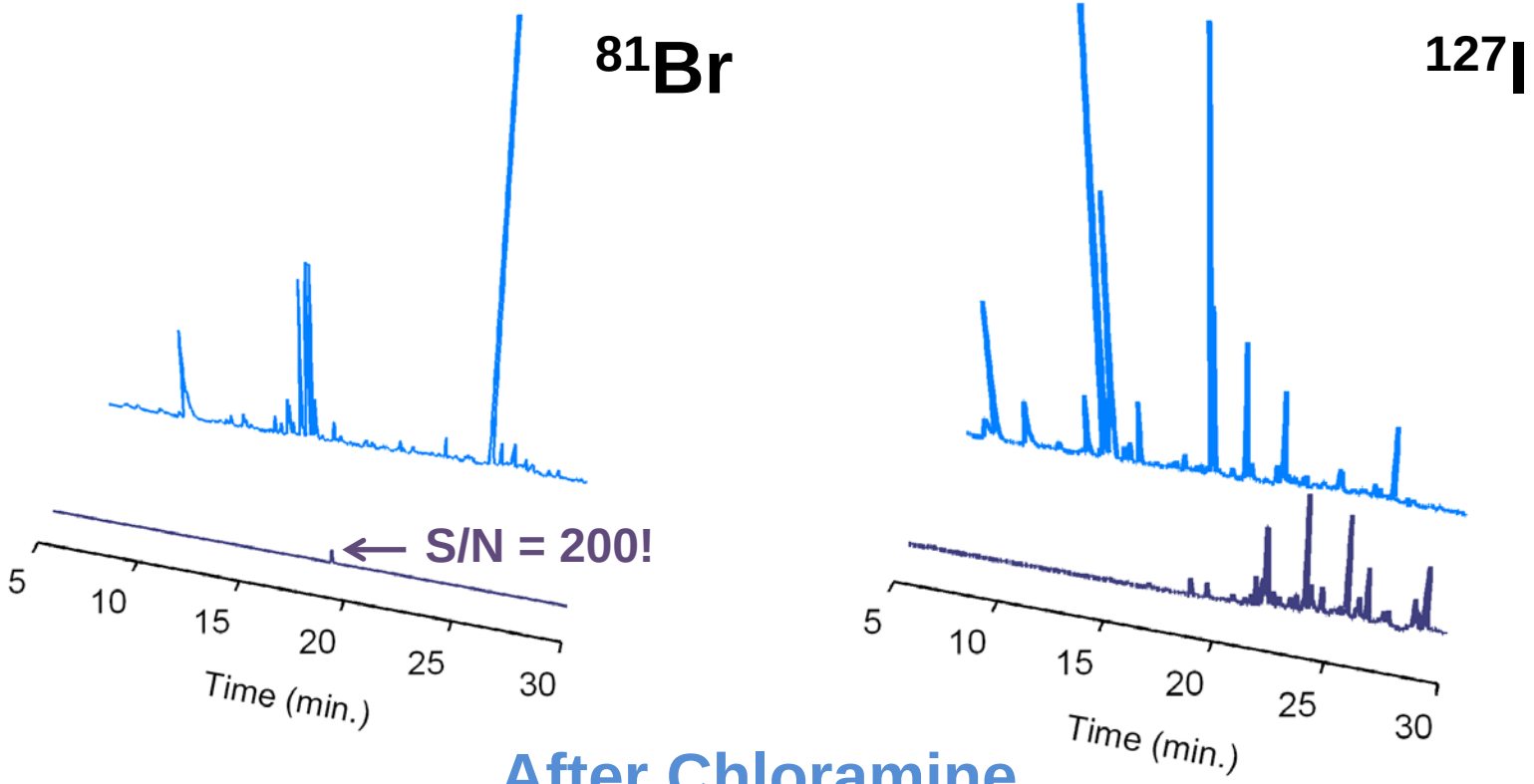


Model 7900 ICP-MS

Model 7890B GC

GC-ICP-MS

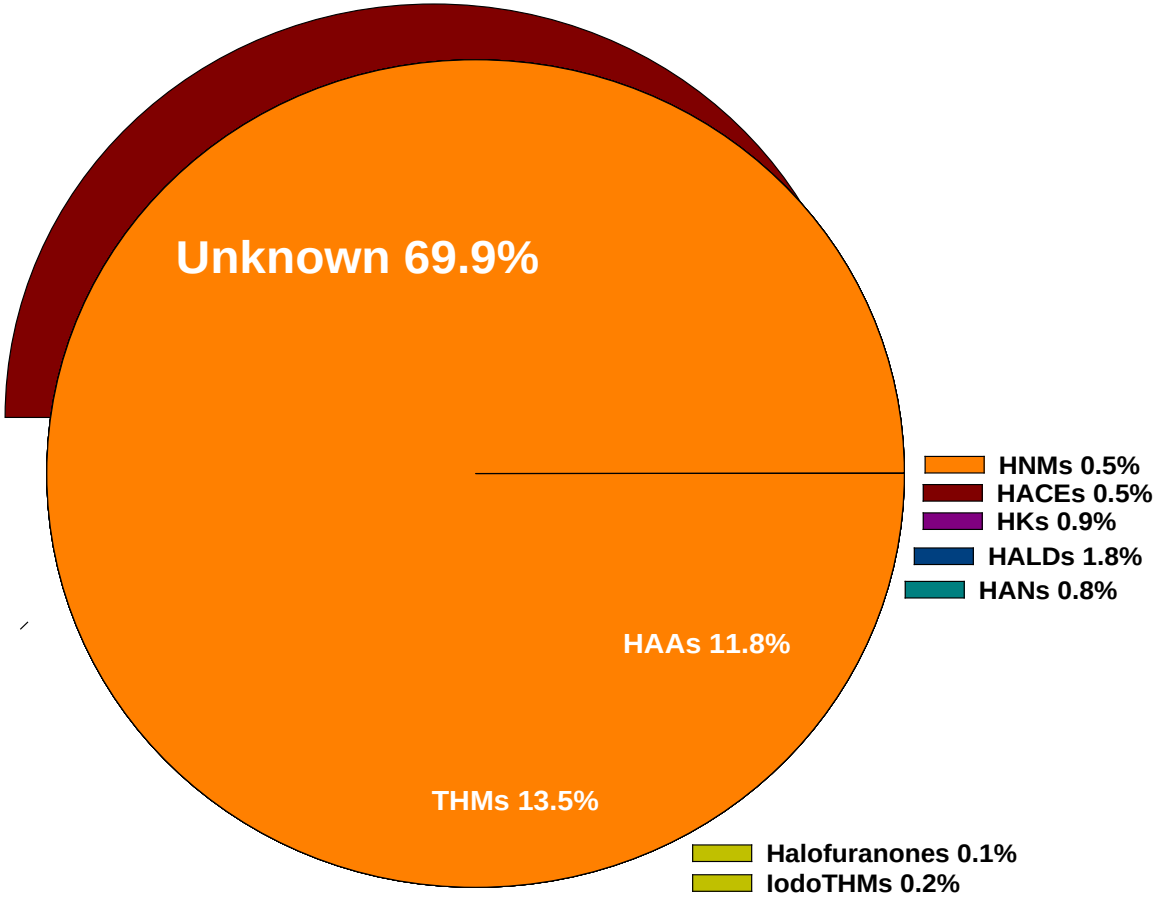
Effects of Chloramination



After Chloramine

Before Chloramine

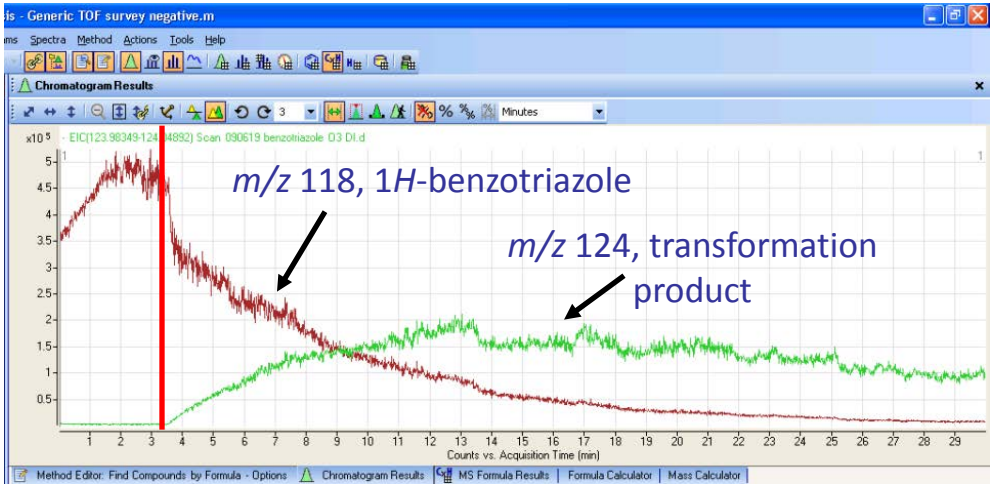
Most DBPs Not Identified

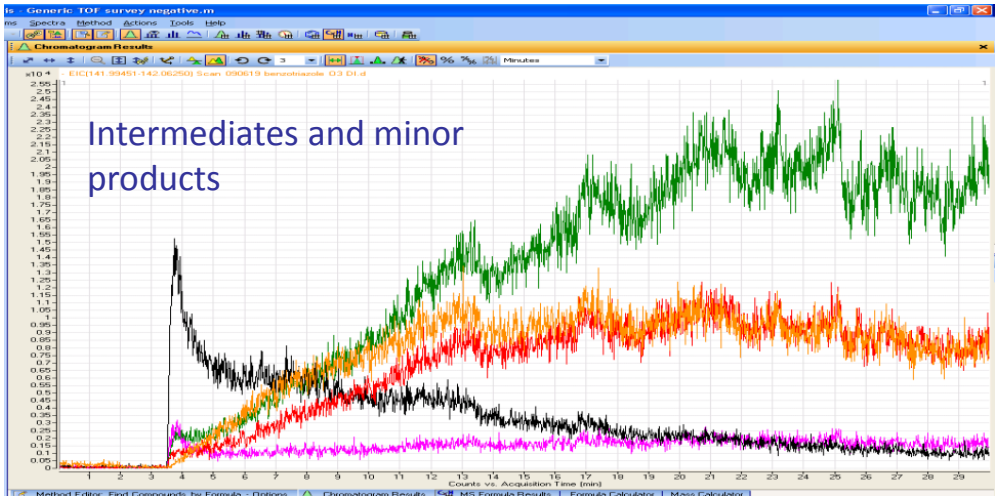


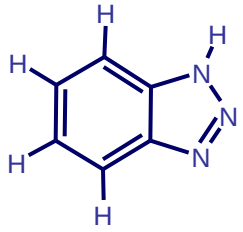
Nationwide Occurrence Study, Krasner et al., *Environ. Sci. Technol*. 2006, *40*, 7175-7185.

LC-QTOF (Agilent 6540)

Benzotriazole Transformation Products

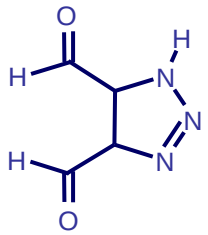






1*H*-benzotriazole

O_3/ ·OH



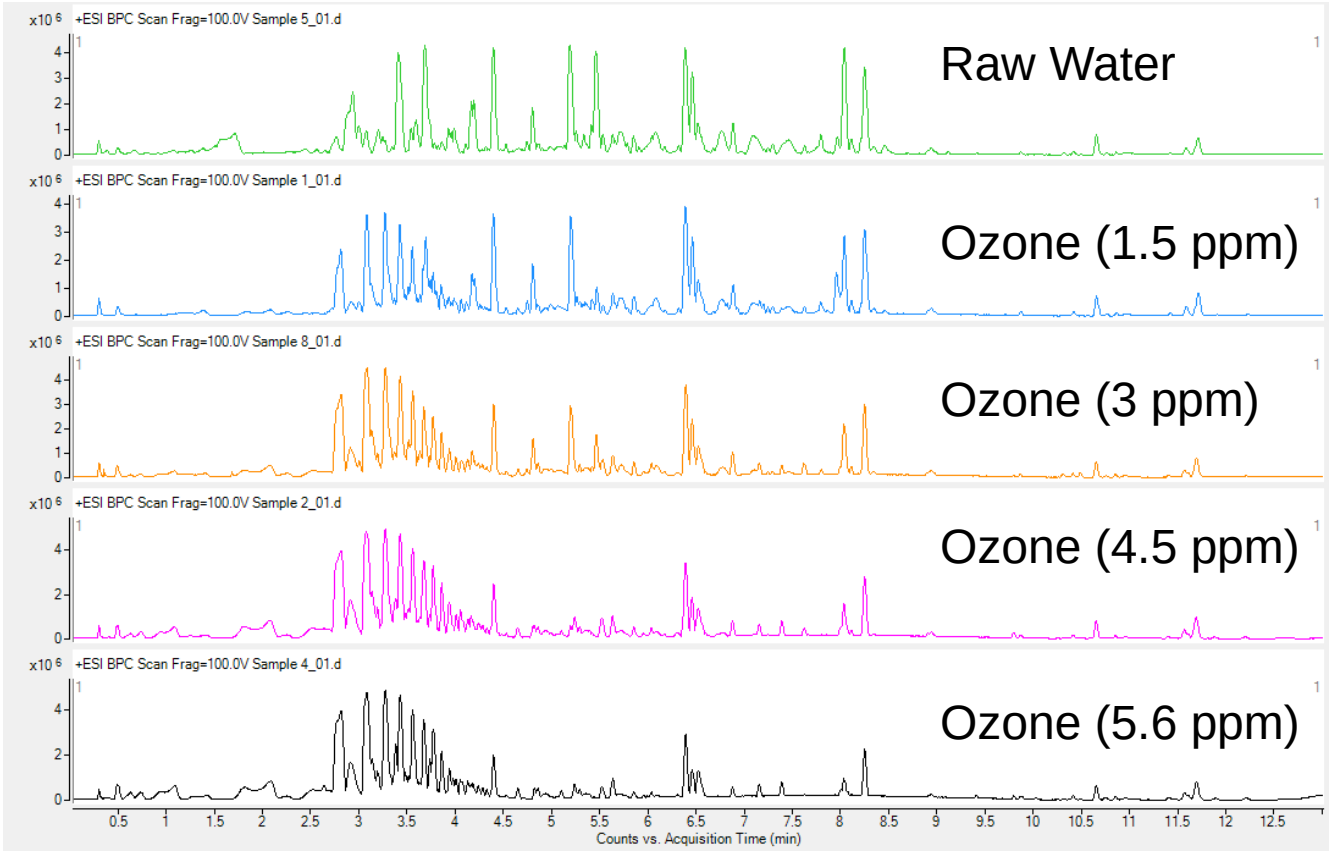
***m/z* 124.01522 (meas.)**
***m/z* 124.01525 (calc.)**
$C_4H_3N_3O_2$

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

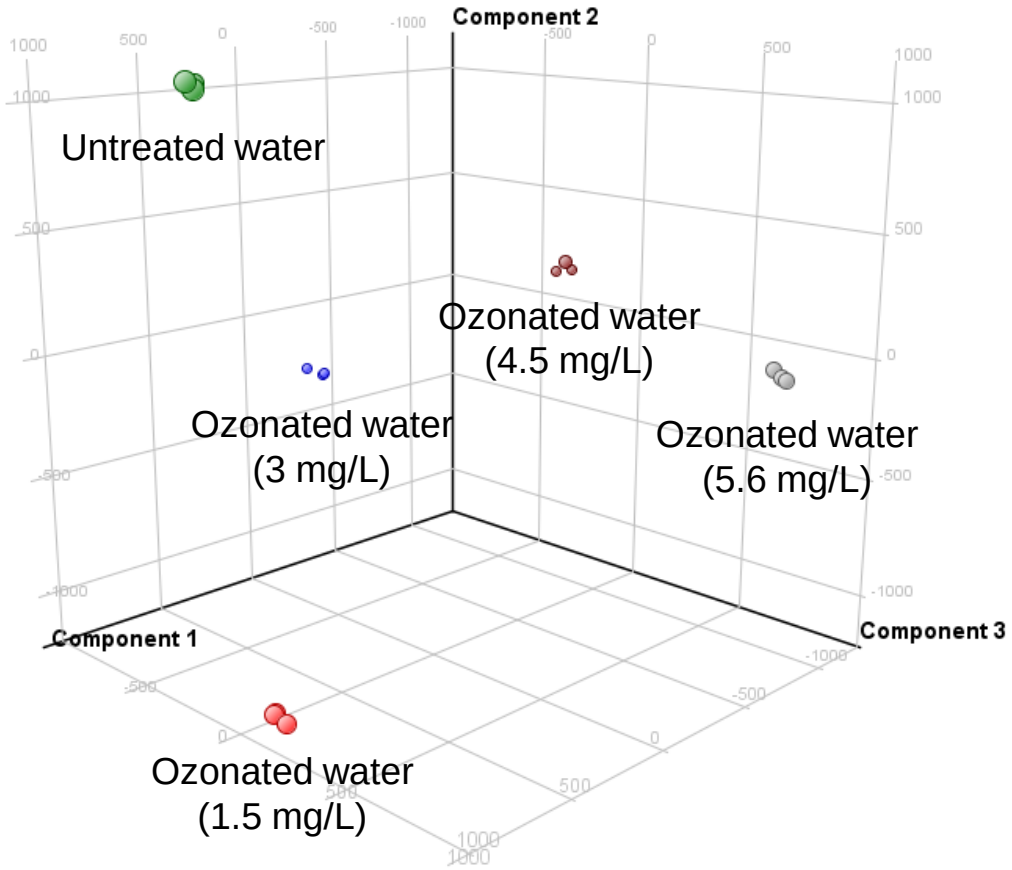
Extraction of Molecular Features Reveals thousands of compounds in each chromatogram

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

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.

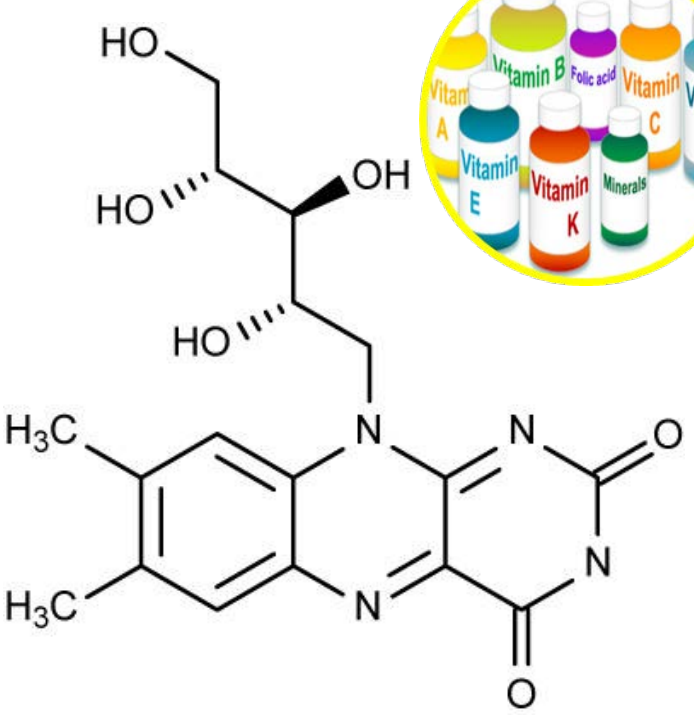
All of the wells are located downstream of the local sewage treatment plant, which releases its treated sewage water into a riverbed.

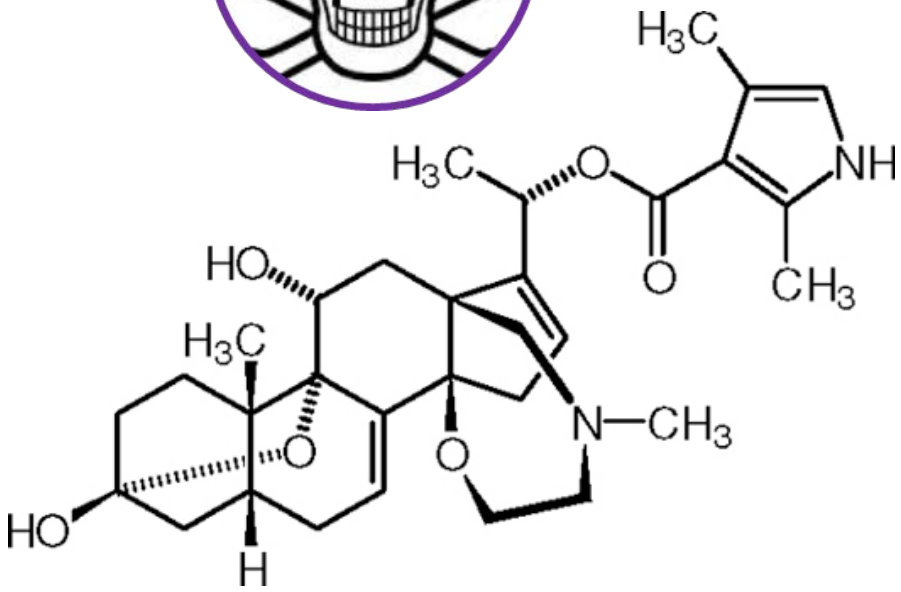
When tested, some of Flagstaff's drinking water wells downstream of the Rio de Flag wastewater treatment plant have also shown tiny traces of other pharmaceuticals and hormones, which have an ability to influence growth in amphibians.”

IS IT SAFE?

History of Bioassays

Safe or Not Safe?

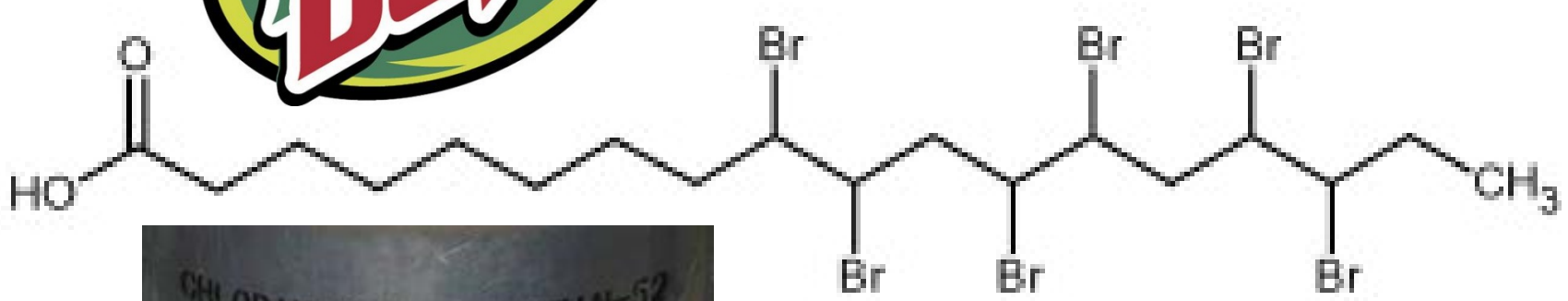


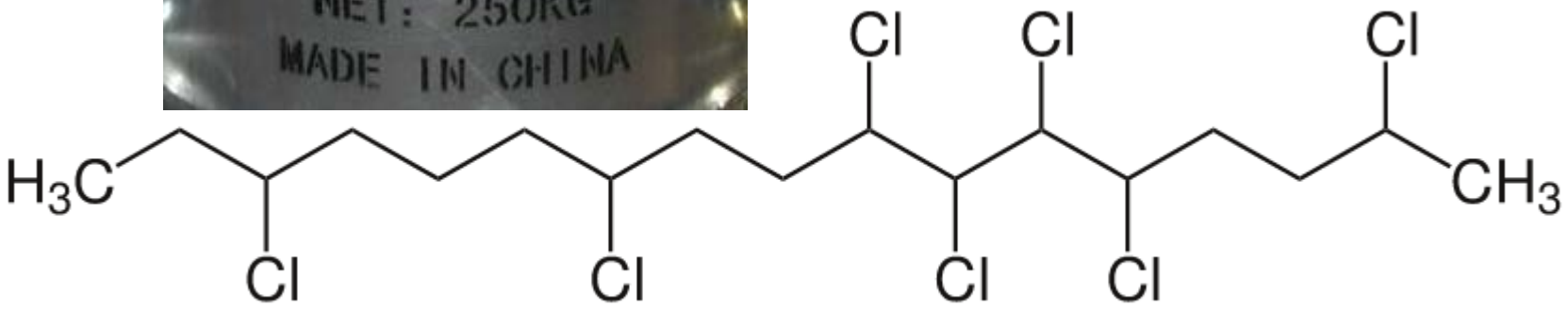


Vitamin B2

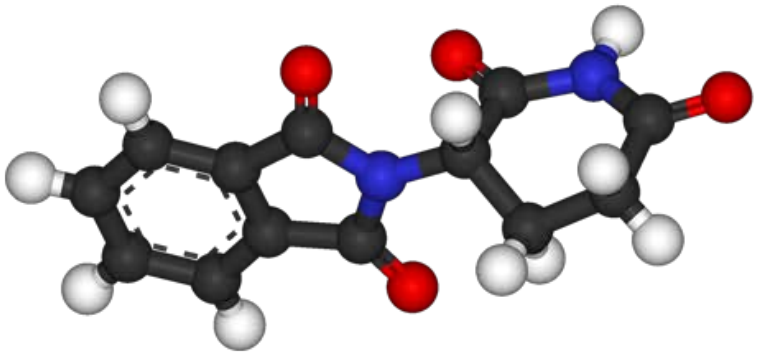
Batrachotoxin

Safe or Not Safe?

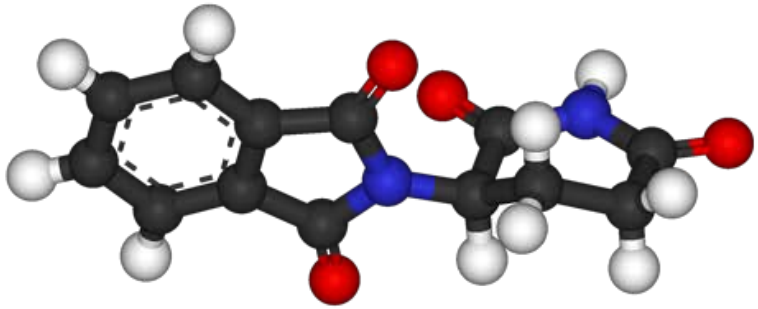




Safe or Not Safe?



(*S*)-thalidomide

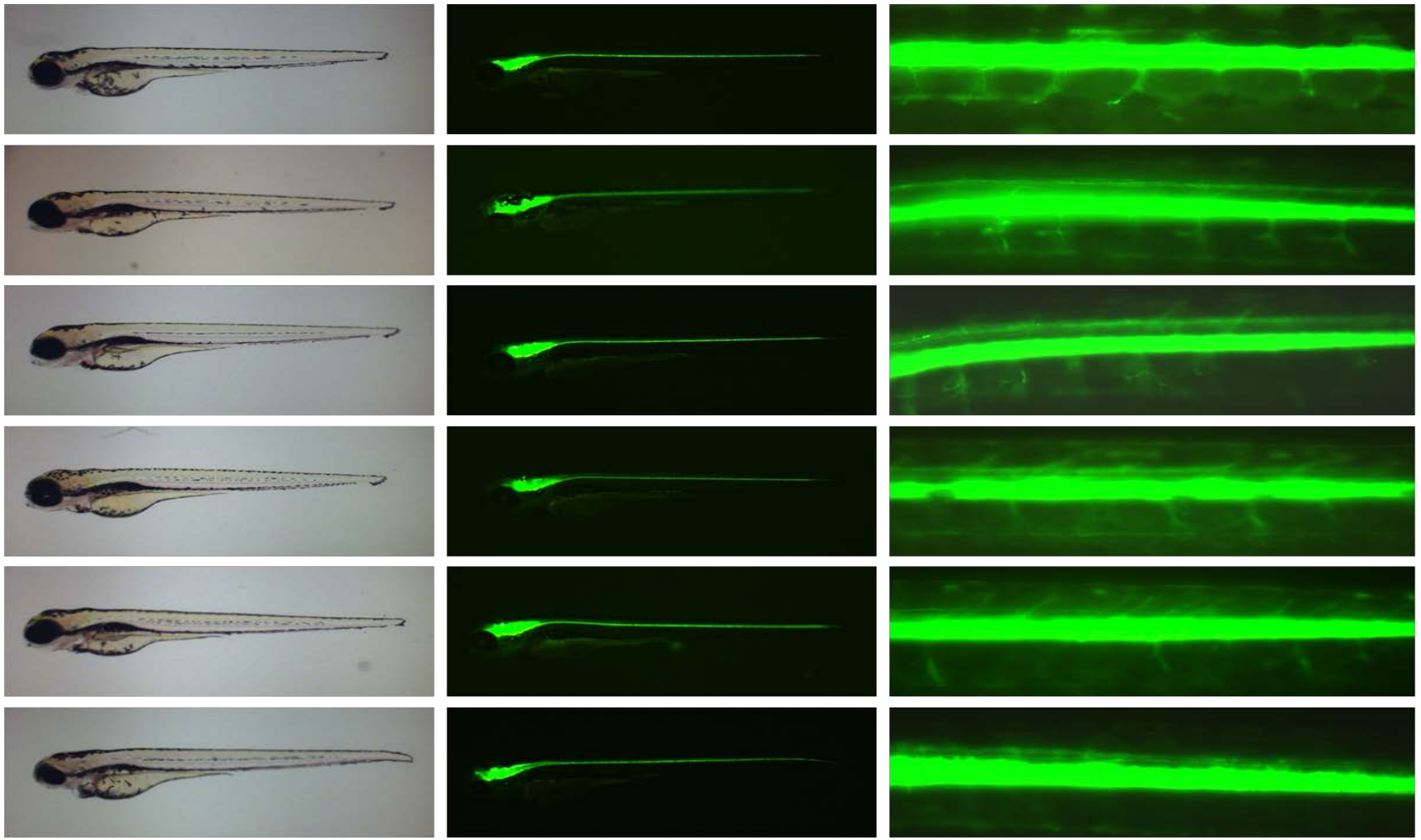


(*R*)-thalidomide

Animal Bioassays

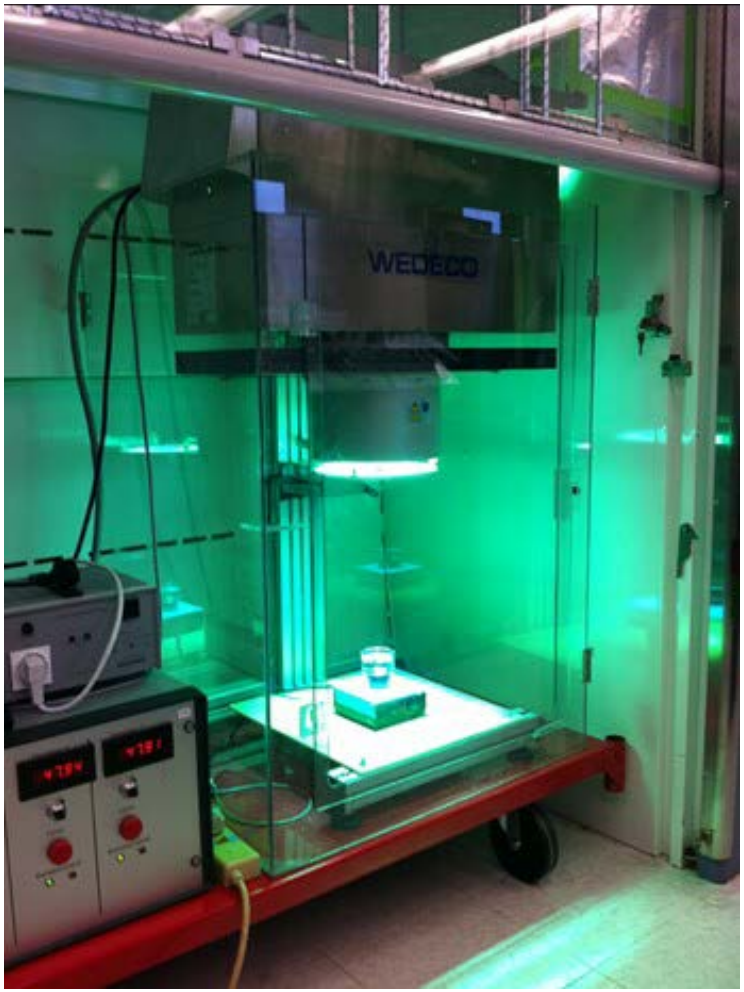
Some assays are available as on-line monitors

Embryonic Assays



Cellular Bioassays

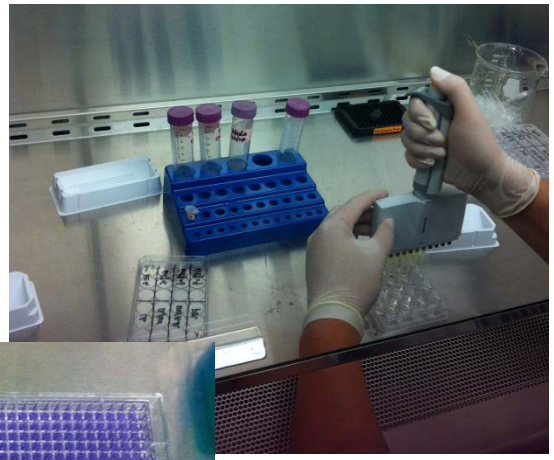
UV Transformation Products



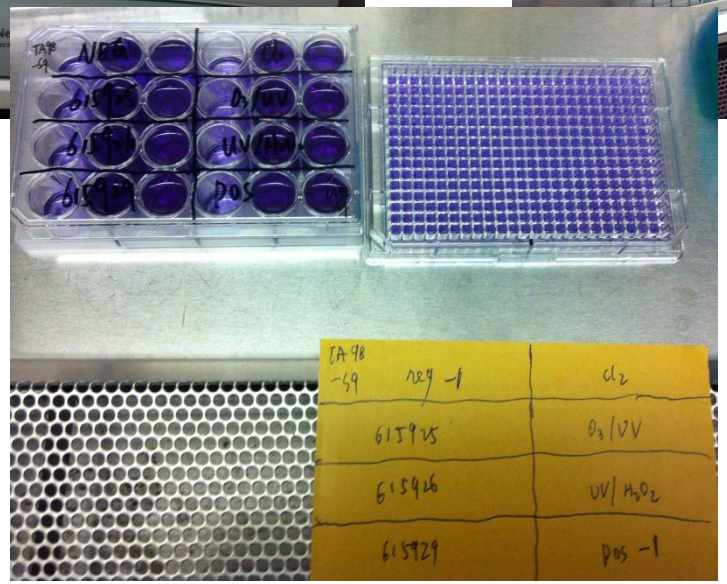
AMESII test

1. Overnight culture

2. Transfer to 24-well plates

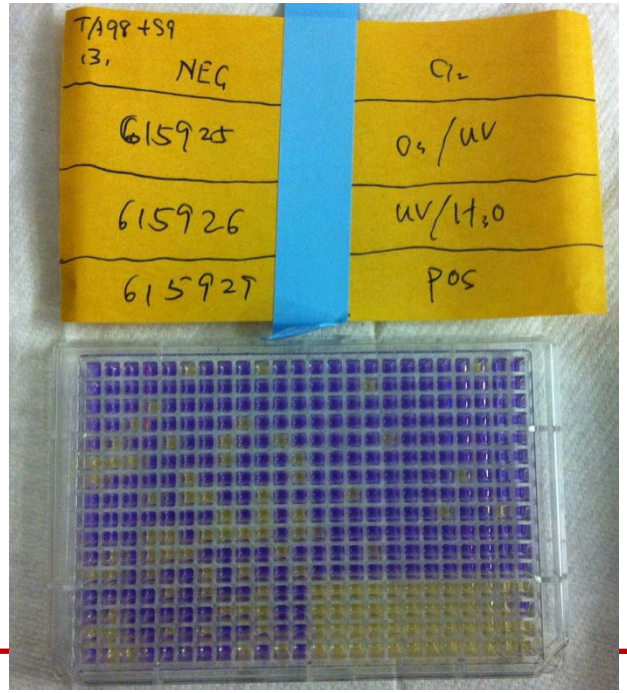


Sample (in DMSO)
S9
Bacteria
Exposure media

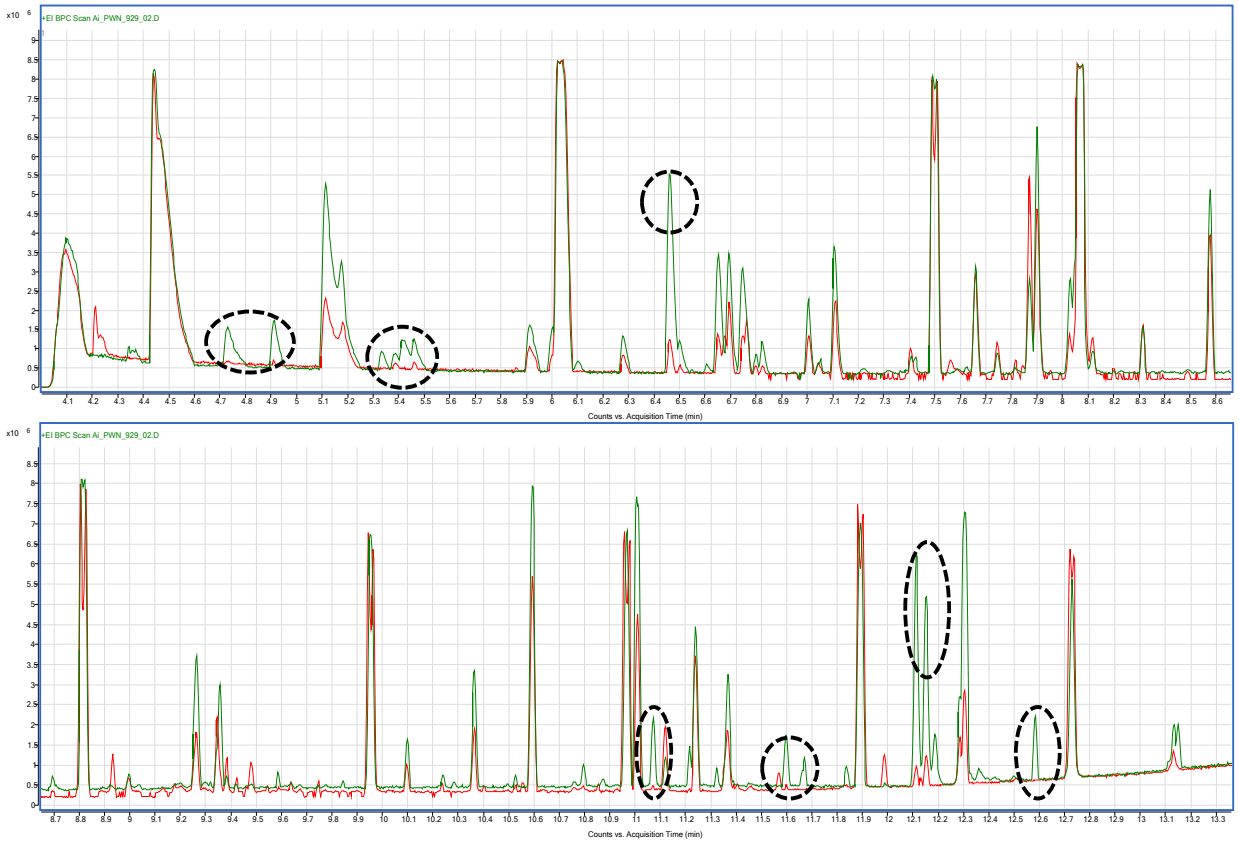


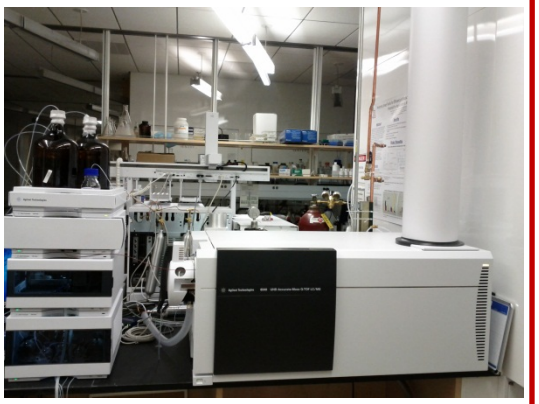
3. Add indicator media, transfer to 384-well plates

4. After 48h, check the results

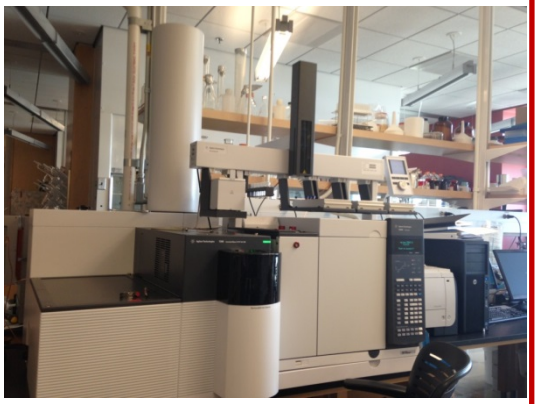


Discovery of New DBPs





LC-QTOF

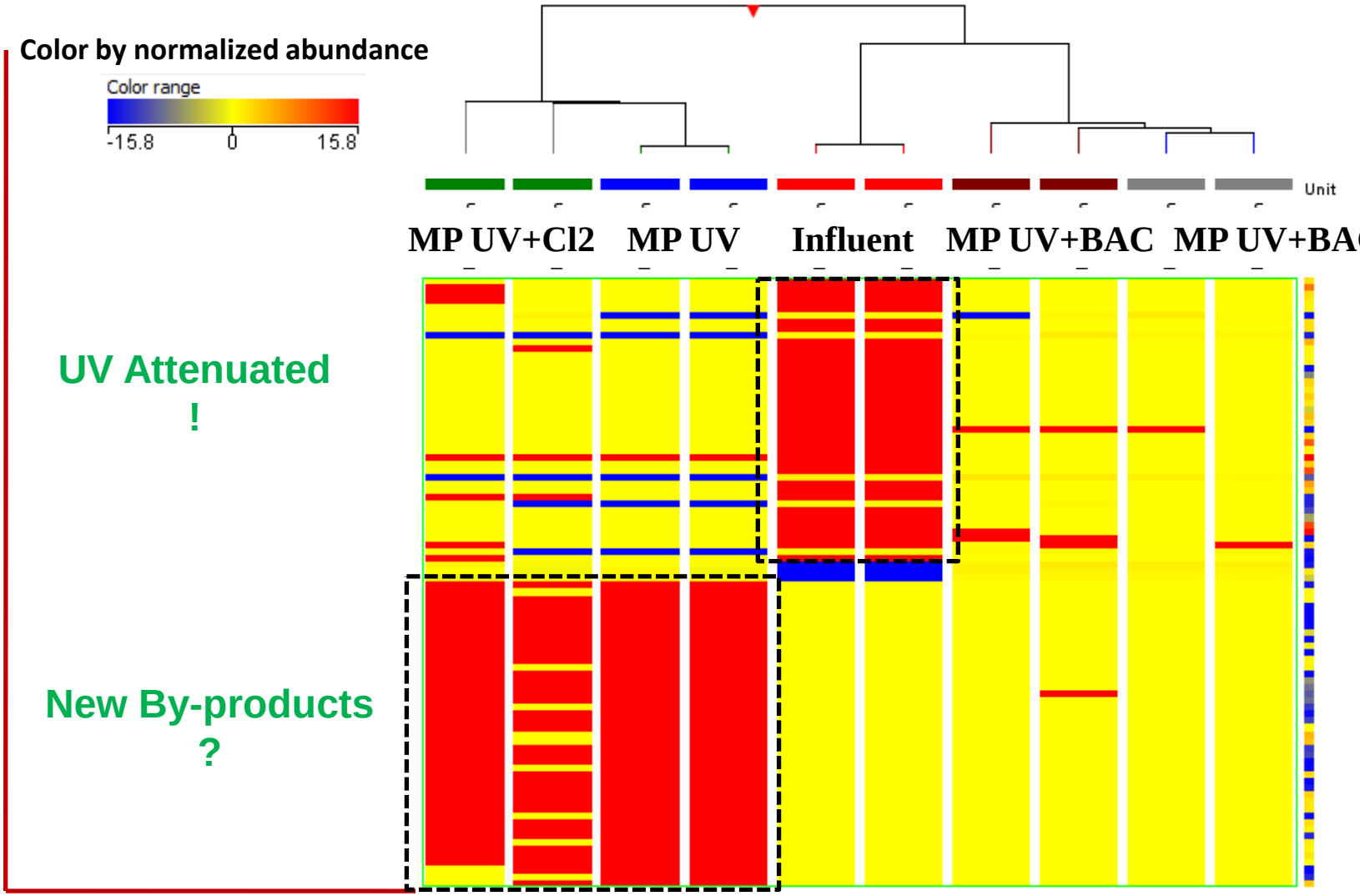


GC-QTOF

Red = Before MP UV

Green = After MP UV

Discovery of Novel UV Transformation Products

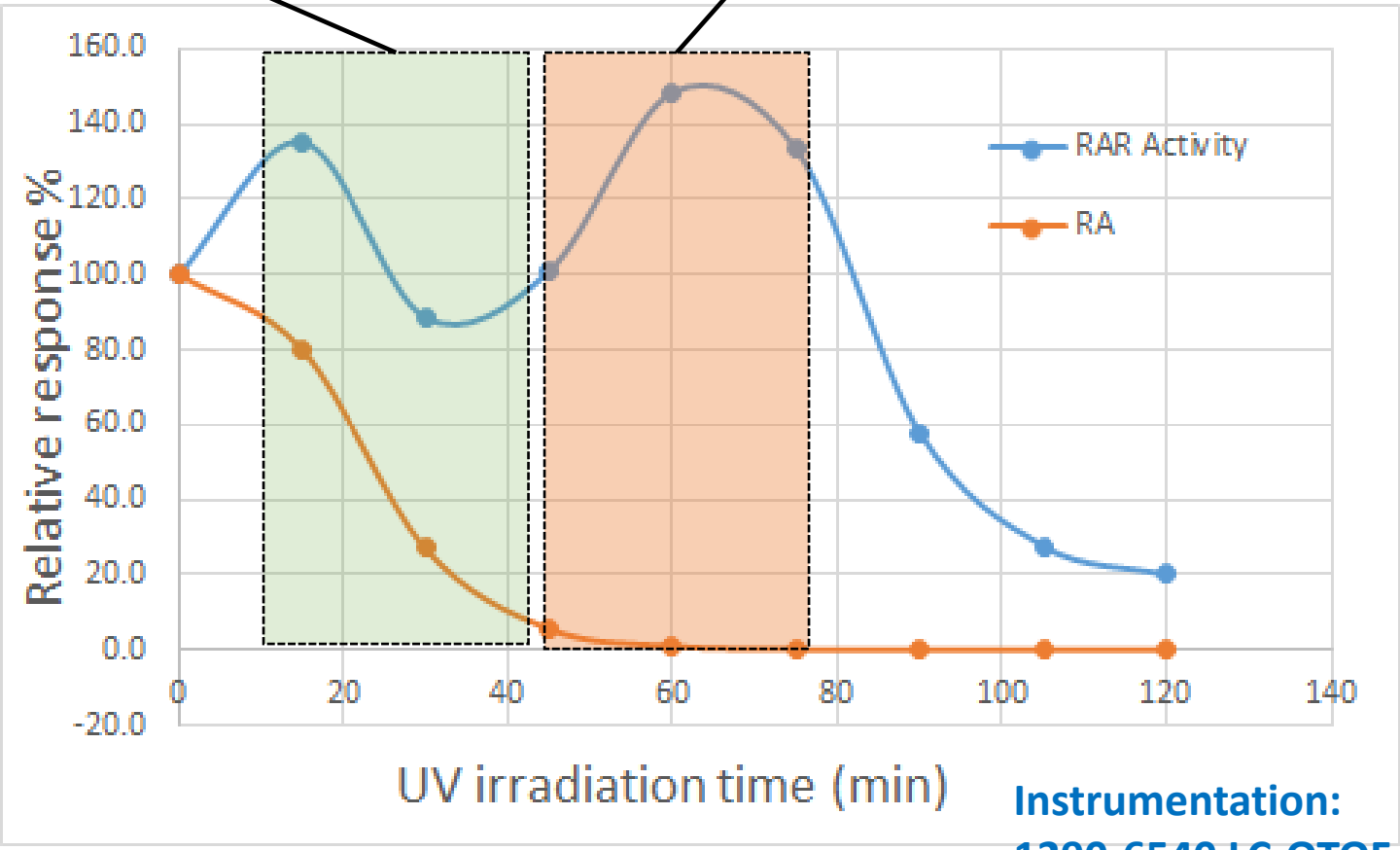


Software: Agilent Mass Profiler Professional (MPP)

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

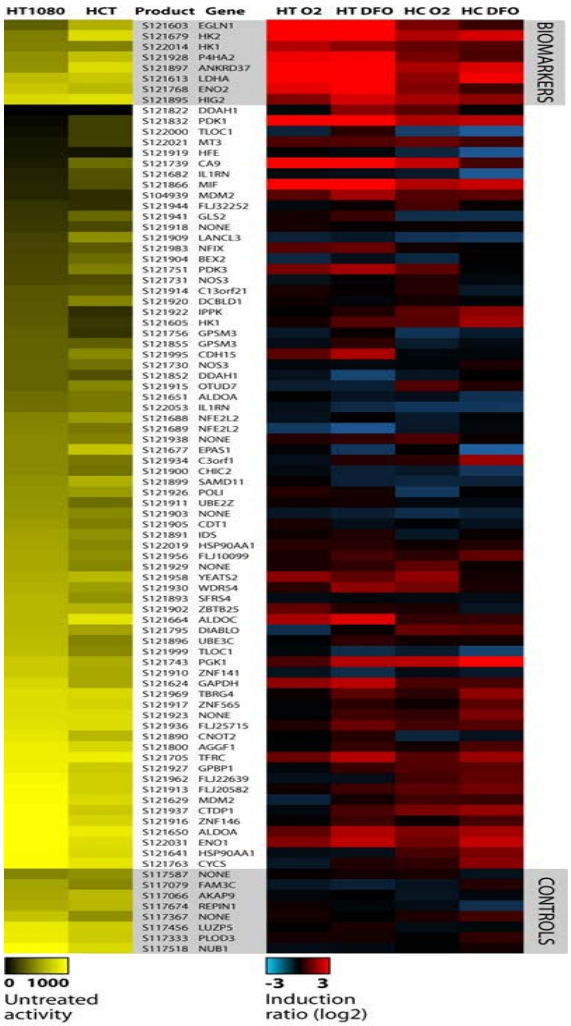
The mixture effect of RA+oxo-RA+OH-RA

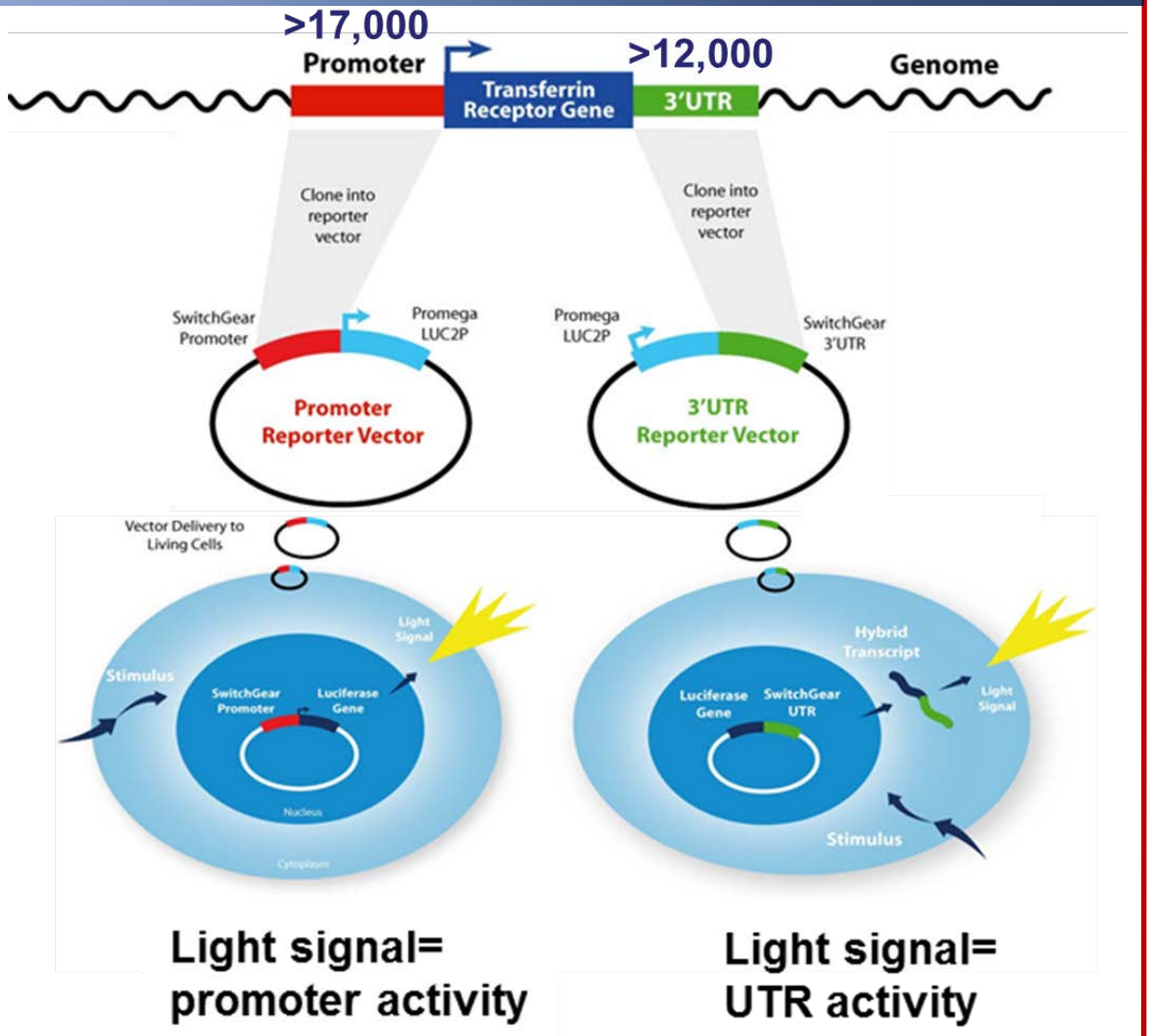
Remains unknown, under further investigation in QTOF and MPP



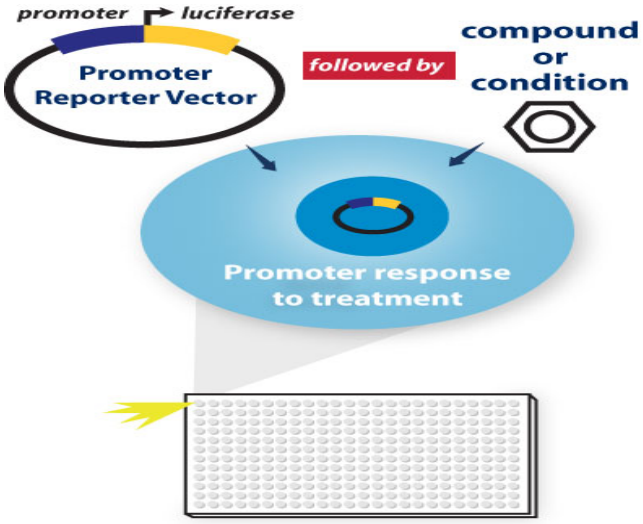
Instrumentation:
1290-6540 LC-QTOF (Agilent)

Cellular Bioassays





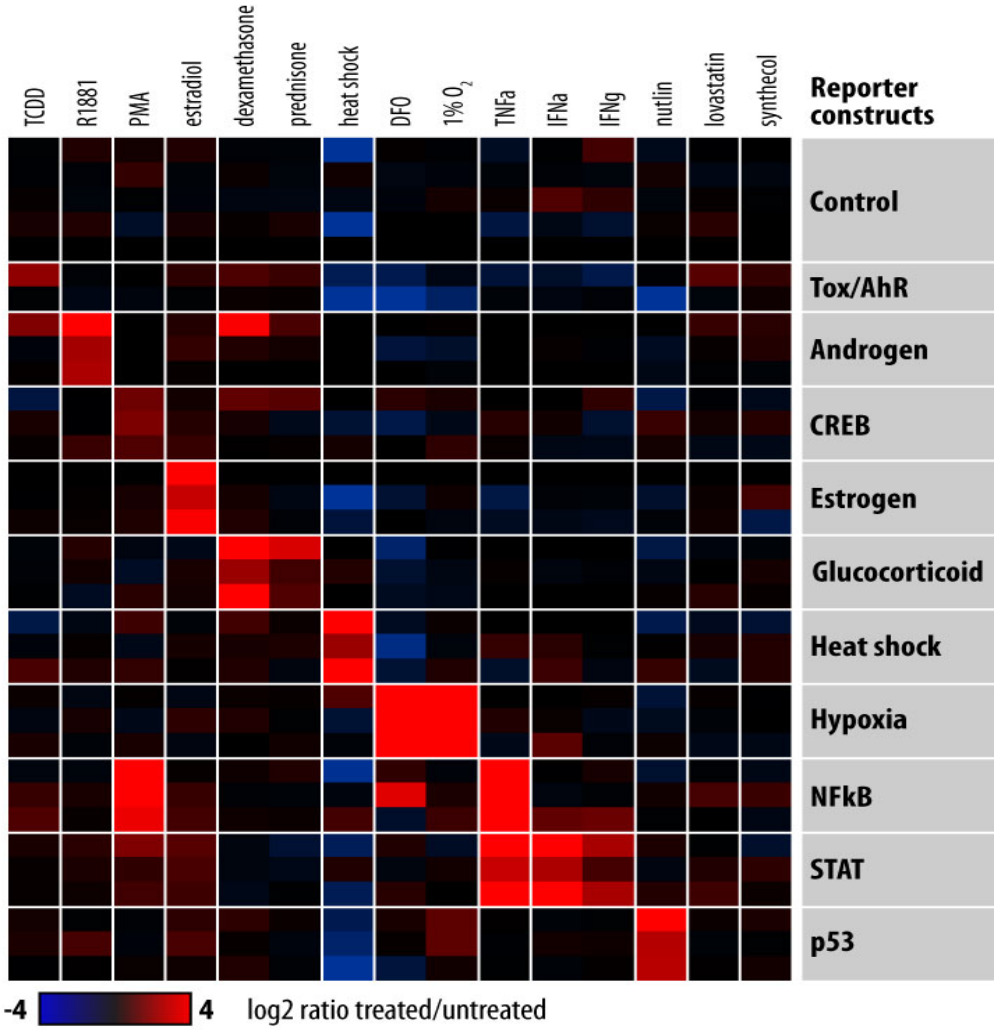
Cellular Bioassays



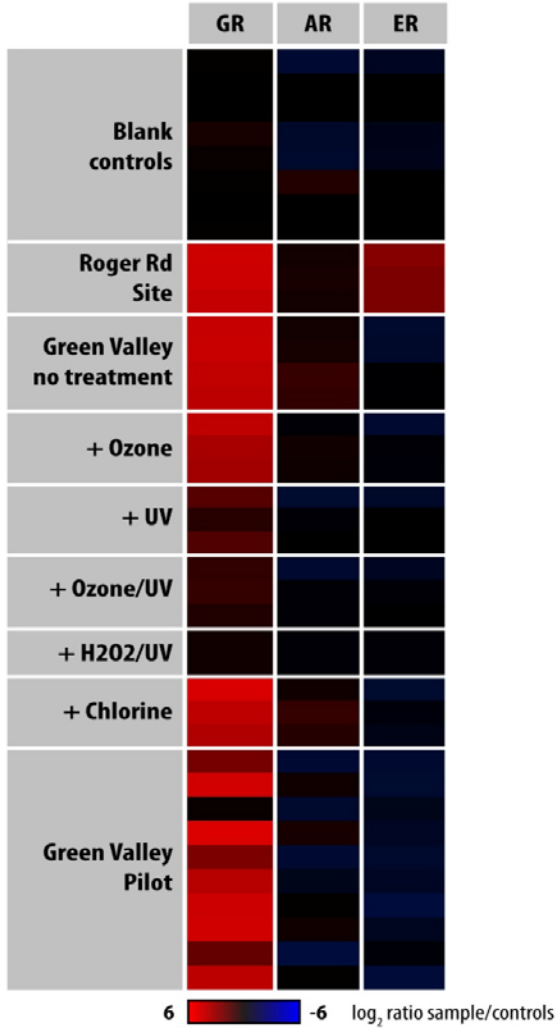
Pathway Profiling Panel
48 promoters and controls

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



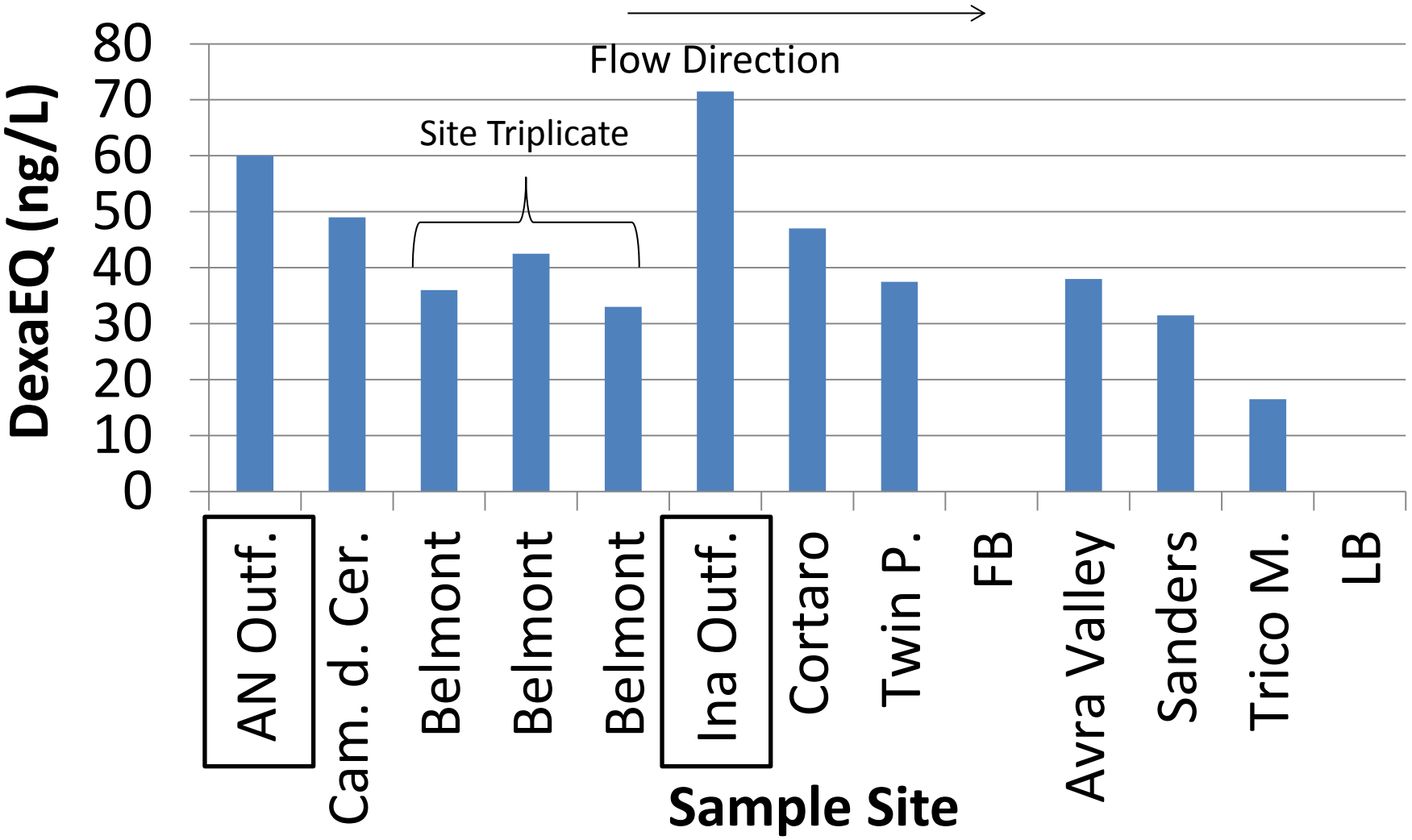
- WWTP effluent had elevated glucocorticoid (GR) activity
- UV processes are most effective at removing GR activity
  - Agonist appears to be UV sensitive (↑ quantum yield)
  - Guides structural elucidation (i.e., NDMA)
- Chlorine and ozone poor for attenuating GR activity
- Antagonistic ER and AR activity

Glucocorticoids

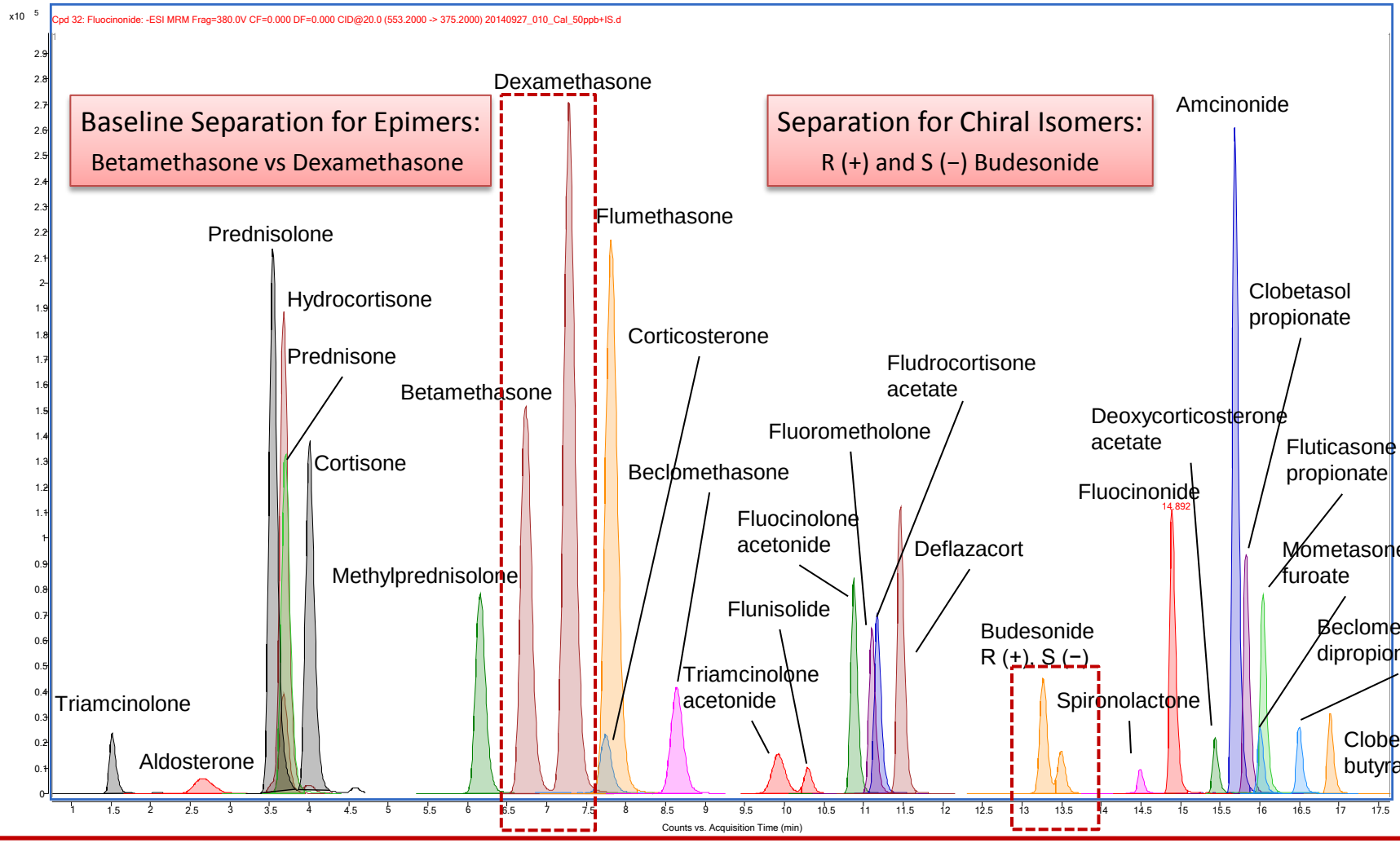
- Natural & Synthetic
- Used for allergies, skin problems, asthma, and arthritis
- Used as veterinary growth promoters

Santa Cruz River Sampling Sites

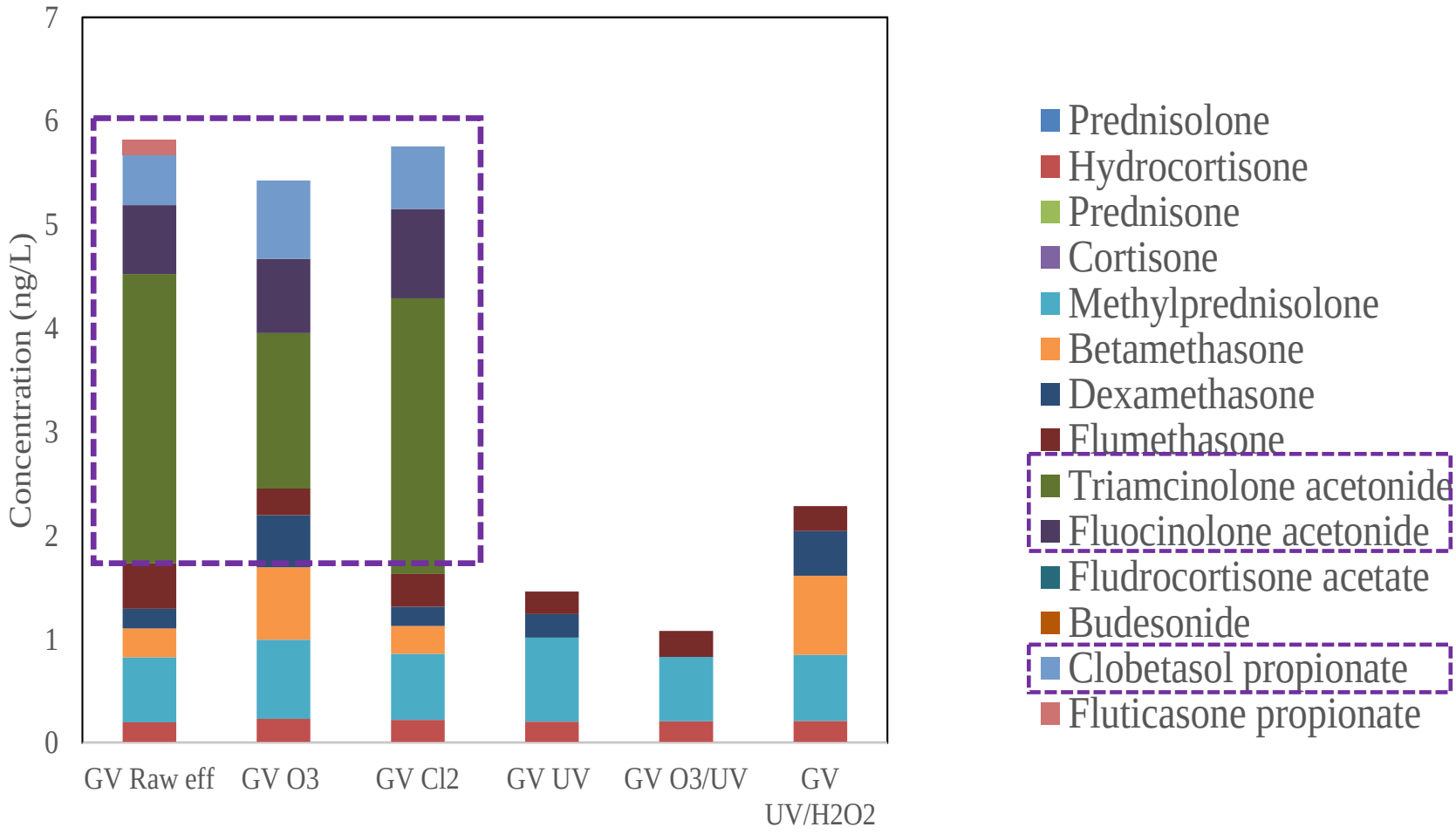
GR Cellular Activity



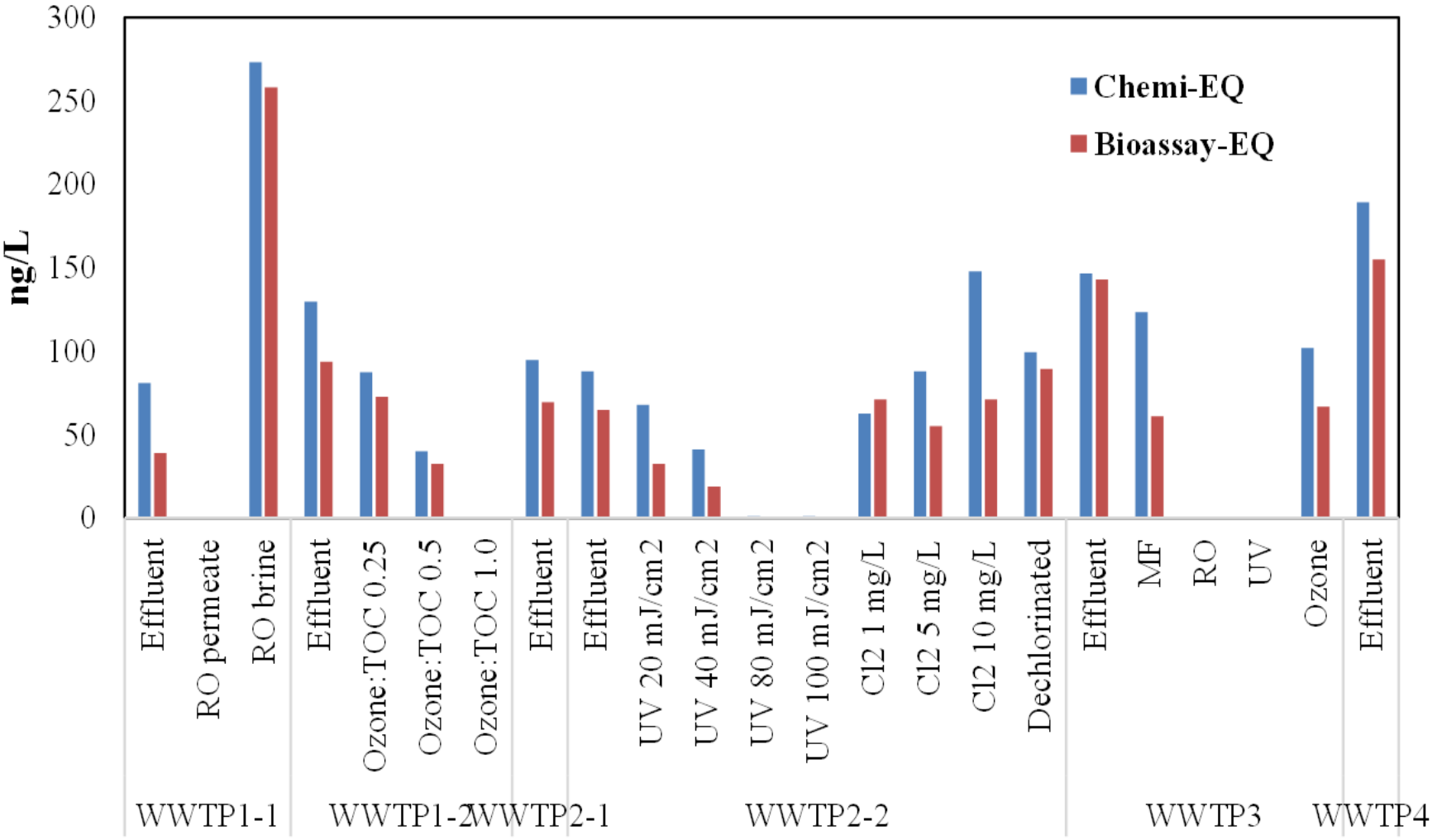
GR Mass Spectrometric Analysis



Distribution of GRs

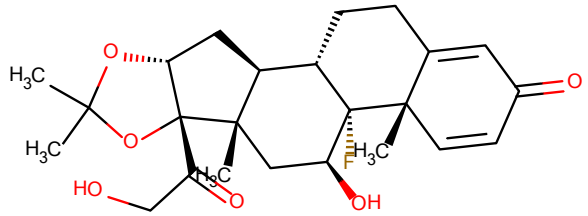


Distribution of GRs

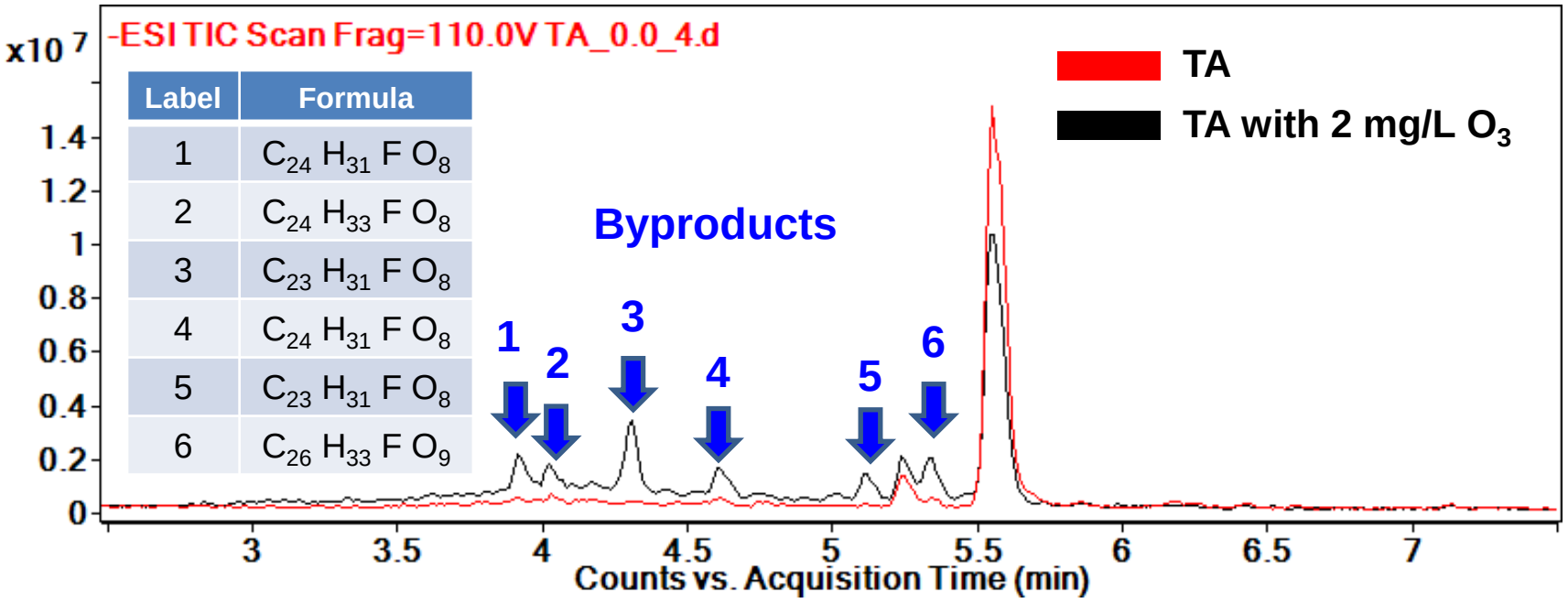


Ozone GR byproducts

Triamcinolone acetonide

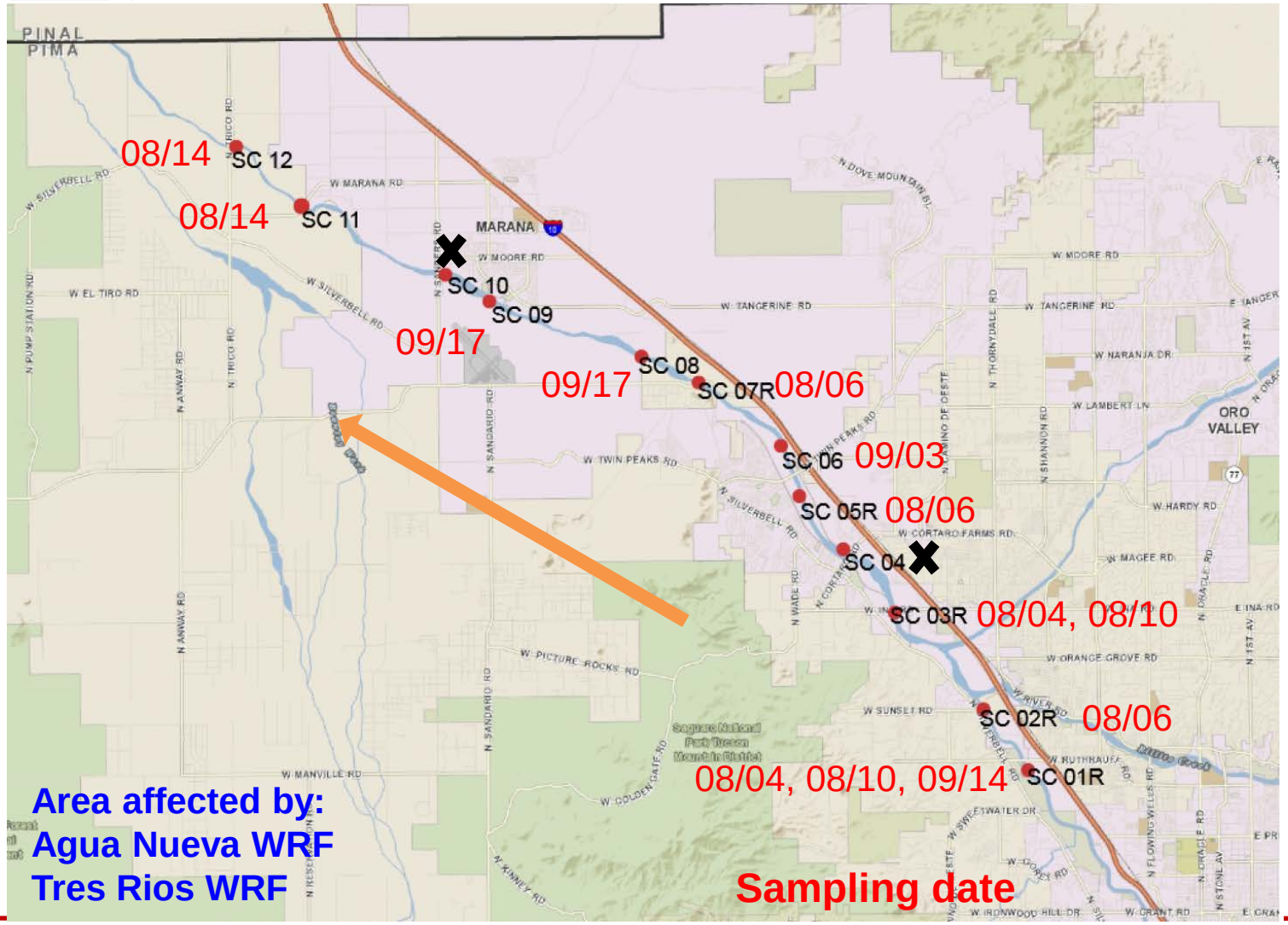


$C_{24}\ H_{31}\ F\ O_6$



Label	Formula
1	$C_{24}\ H_{31}\ F\ O_8$
2	$C_{24}\ H_{33}\ F\ O_8$
3	$C_{23}\ H_{31}\ F\ O_8$
4	$C_{24}\ H_{31}\ F\ O_8$
5	$C_{23}\ H_{31}\ F\ O_8$
6	$C_{26}\ H_{33}\ F\ O_9$

Sampling location



Tests Conducted

- Total organic matter (TOC)
- UV absorbance at 254 nm
- Excitation-emission matrices (EEMs)
- Hormones (ER, AR, GR, PR)
- Contaminants of emerging concern (CECs)

Sample Preparation

1L sample

20 mL

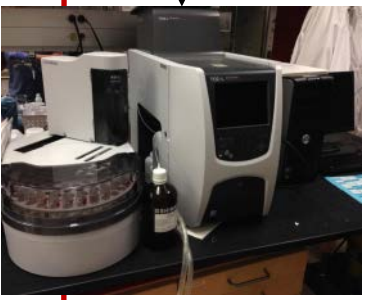
20 mL

20 mL

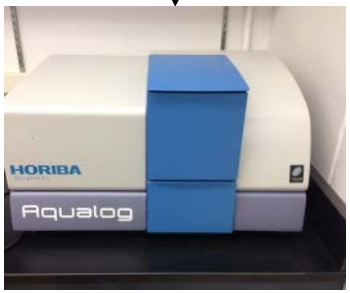
spiked with
isotope surrogates

500 mL

400 mL



TOC Analysis



UV, EEM
Analysis

Online SPE
Direct Injection

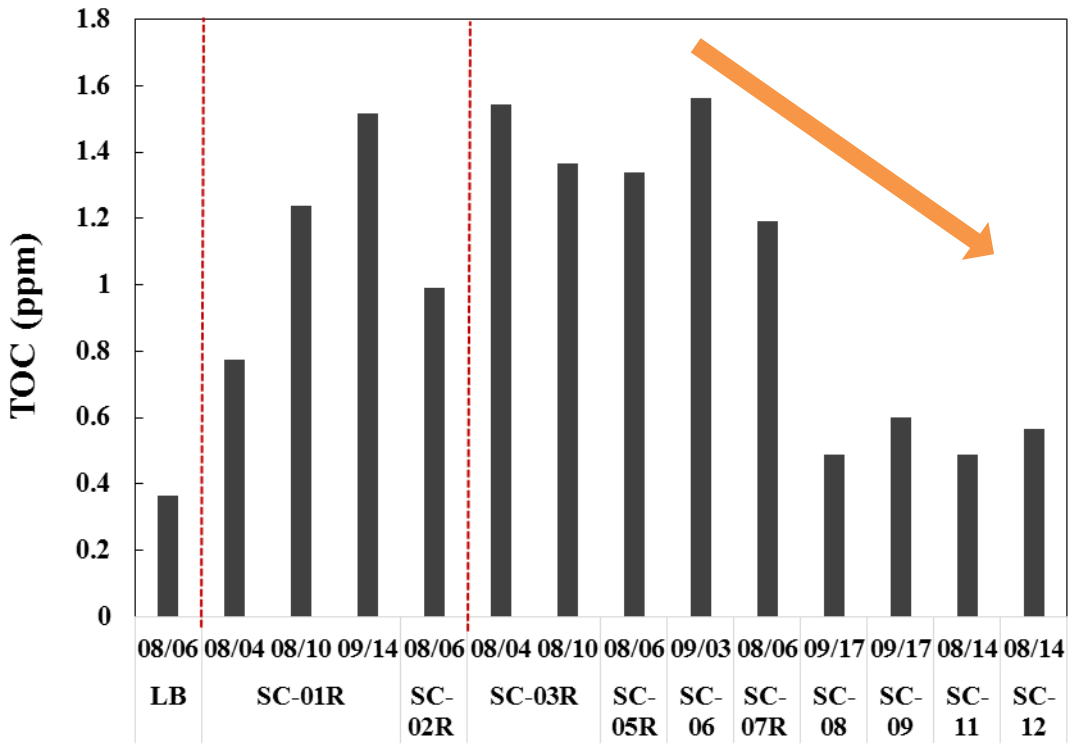
Offline SPE

HLB SPE

LC-QQQ
Chemical Analysis
(CECs, hormones)

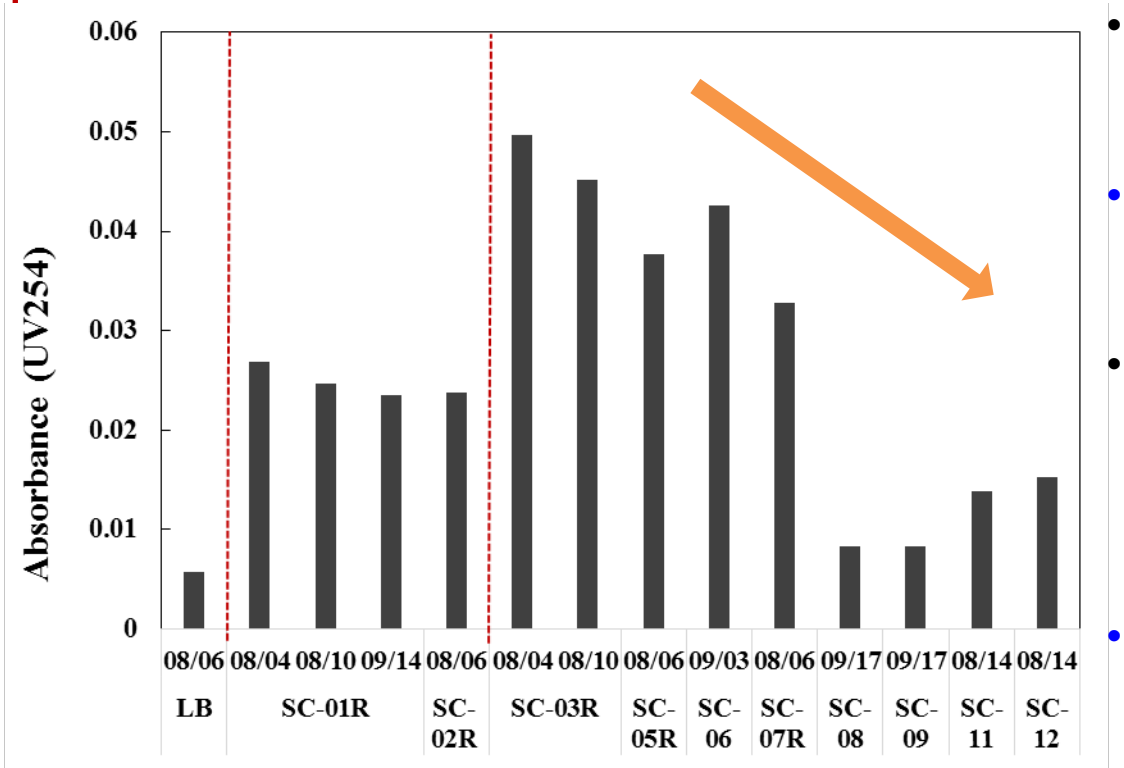
Potential
QTOF/bioassay
Analysis

Results: TOC



- **LB**: lab prepared Milli-Q water, go through all analytical procedures as samples.
- **SC01, SC02**: Agua Nueva WRF affected wells.
- **SC03-SC12**: Tres Rios WRF affected wells.
- Upstream wells have the highest TOC (1.19-1.54 ppm).
- In down stream wells (SC08-SC12), the TOC concentration decrease to 0.49-0.59 ppm, which are slightly higher than blank sample (0.36 ppm).
- TOC varied largely between three sampling events for SC-01R (0.8, 1.2, 1.5 ppm); while it was close in SC-03R (1.4-1.5 ppm).

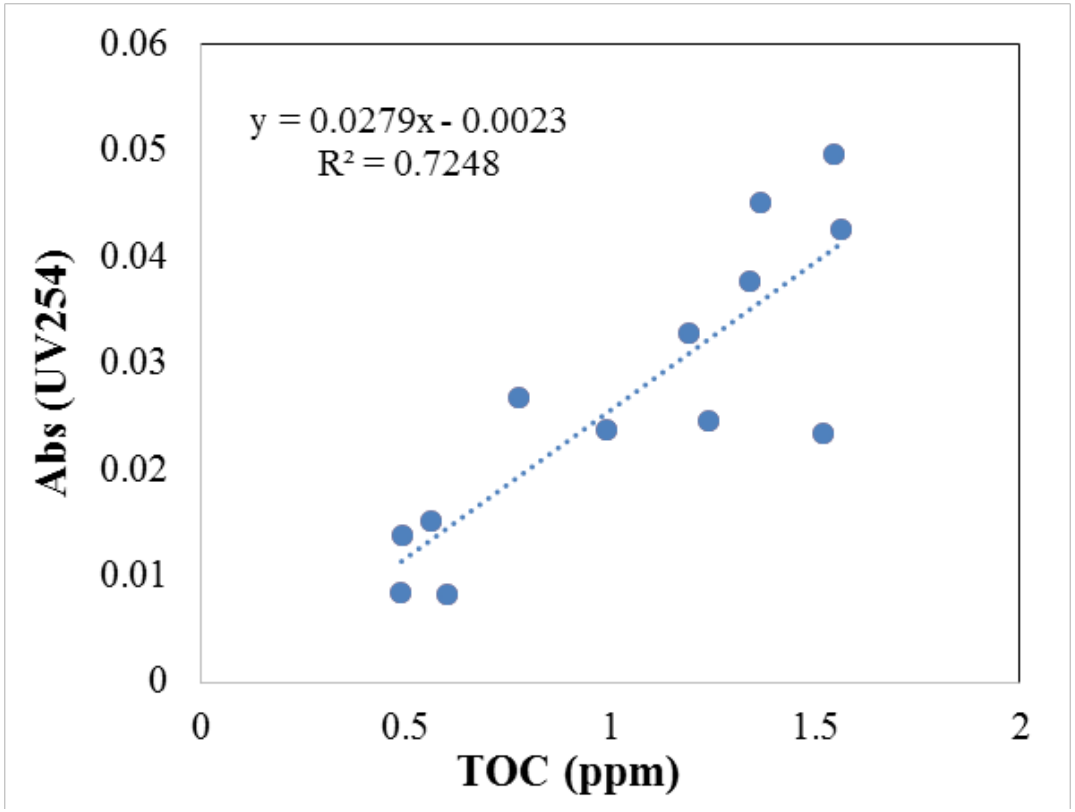
Results: UV_{254nm} absorbance



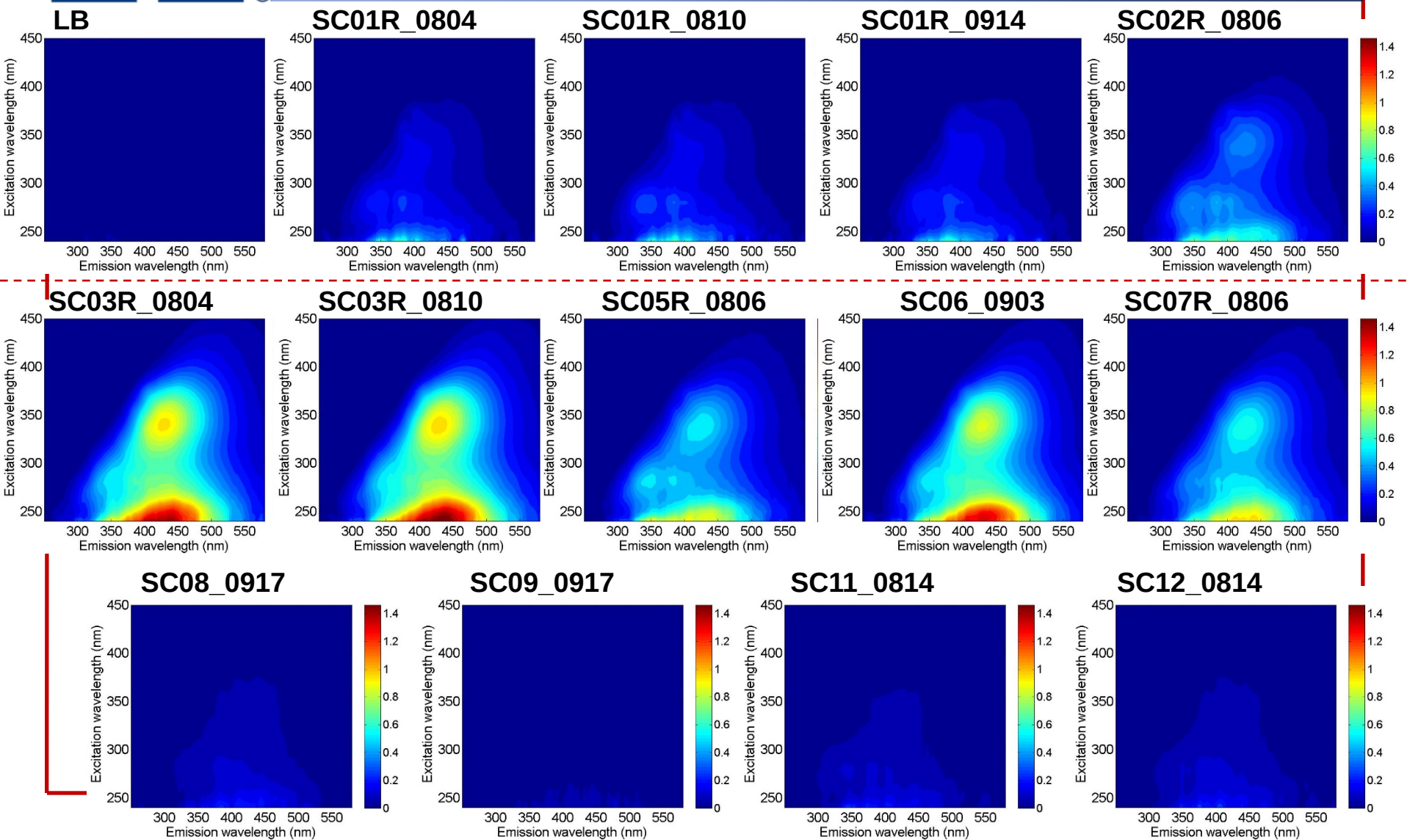
- Upstream wells from Tres Rios WRF have the highest UV absorbance (0.038-0.050).
- Agua Nueva WRF affected wells have lower UV absorbance (0.024-0.027).
- In down stream wells (SC08-SC12), the UV absorbance decrease to 0.008-0.015, which are slightly higher than blank (0.006).
- UV absorbance was consistent between different sampling events for both of SC-01R and SC-03R.

TOC vs. UV_{254nm} absorbance

Positive correlation was observed between sample TOC and UV254 absorbance values.



Results: EEMs



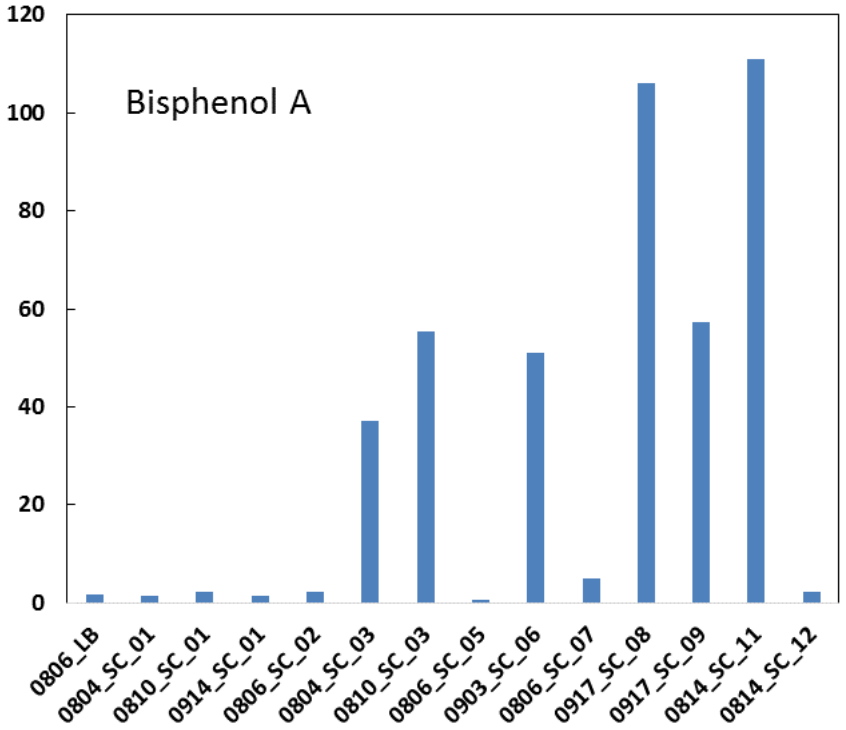
Results: EEMs

- EEMs of all the samples were scaled based on the maximum fluorescence intensity from SC-03R.
- EEMs results showed the same trend as UV_{254} absorbance: Tres Rios WRF affected wells showed higher fluorescent organic matter than Agua Nueva WRF related wells, which is different with the TOC results. Decreasing trend were all observed in the downstream wells.

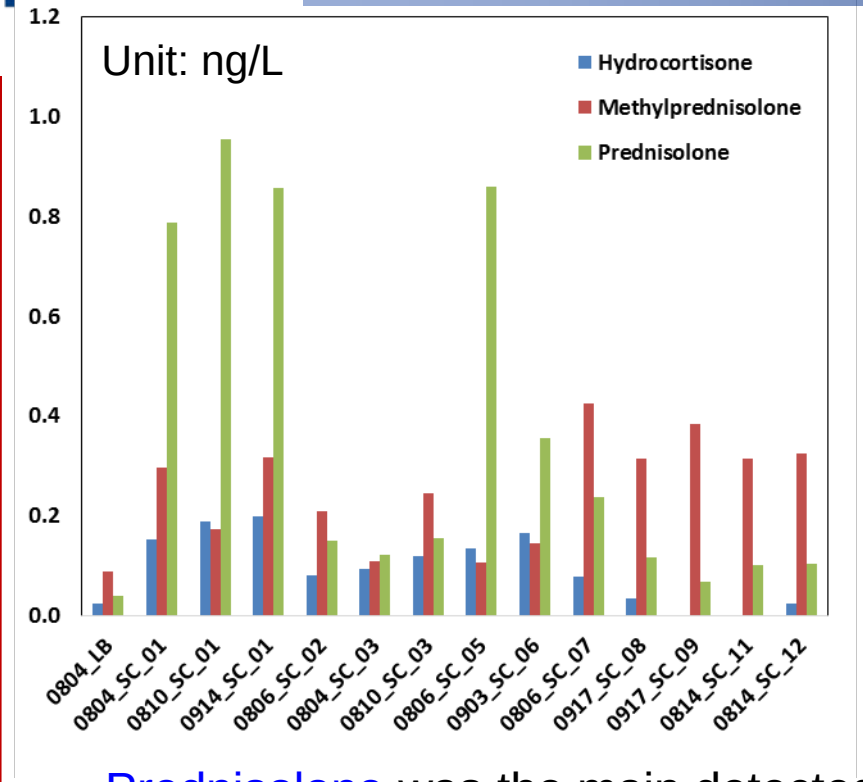
Results: Hormones

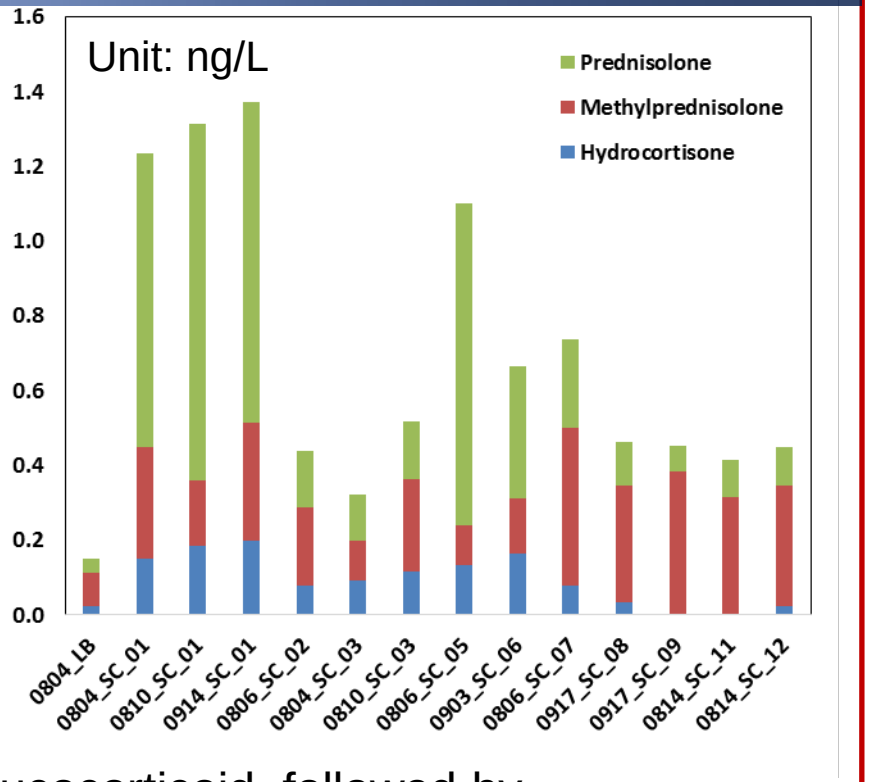
Estrogens

- Five target compounds:
  - Estrone (E1), 17α-Estradiol(αE2), 17β-Estradiol (βE2), Estriol (E3), 17α-Ethynylestradiol (E2), Bisphenol A (BPA).
- E1 was detected in 5 of 14 samples; BPA was detected in all samples. Other analytes were below method detection limits (MDL).
- BPA was detected mainly in Tres Rios WRF affected wells; the highest concentration was observed in downstream wells (111 ng/L).



The occurrence of glucocorticoids





- Prednisolone was the main detected glucocorticoid, followed by methylprednisolone, and hydrocortisone.
- SC-01R and SC-05R showed the highest glucocorticoid contamination.
- The concentrations of prednisolone and hydrocortisone decrease in downstream wells, while it is not obvious for methylprednisolone.

Results: CECs

- 37 targeted CECs:

Acesulfame	Ditiazem	PFBA	Simazine
Atenolol	Fluoxetine	PFBS	Sucralose
Atrazine	Gemfibrozil	PFHpA	Sulfamethoxazole
Benzotriazole	Hydrochlorothiazide	PFHxA	TCEP
Caffeine	Ibuprofen	PFOA	TCPP
Carbamezapine	Iohexol	PFOS	Triclocarban
Clofibric Acid	Iopamidol	Primidone	Triclosan
DEET	Iopromide	Propranolol	Trimethoprim
Diclofenac	Meprobamate	Propylparaben	
Diphenhydramine	Naproxene		

- 34 CECs were detected in more than one sample, except diphenhydramine, ditiazem, and fluoxetine, with the highest concentration at 37.4 ppb (sucralose).

Results: CECs

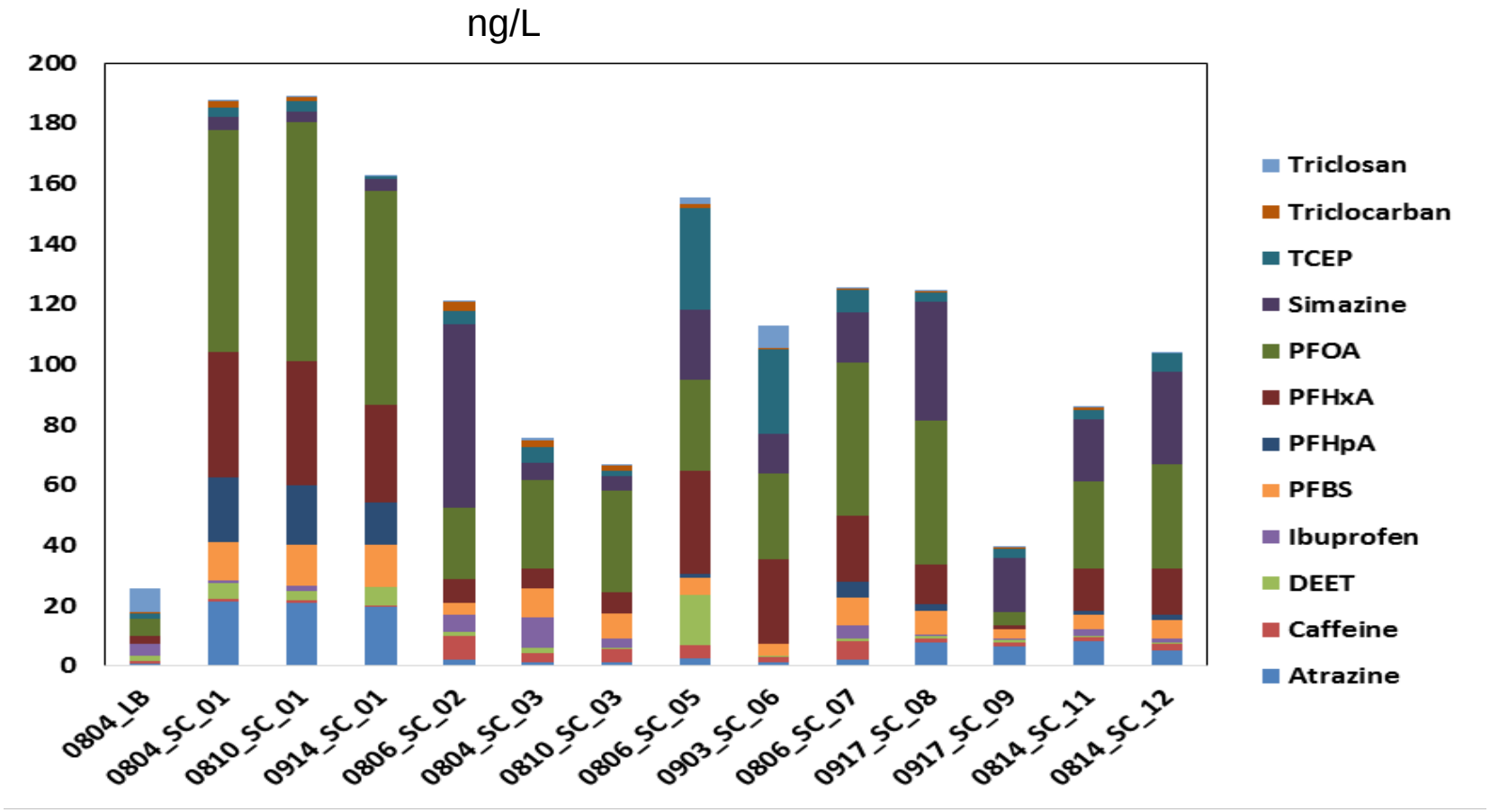
Compound detection summary

13 well samples, unit ng/L

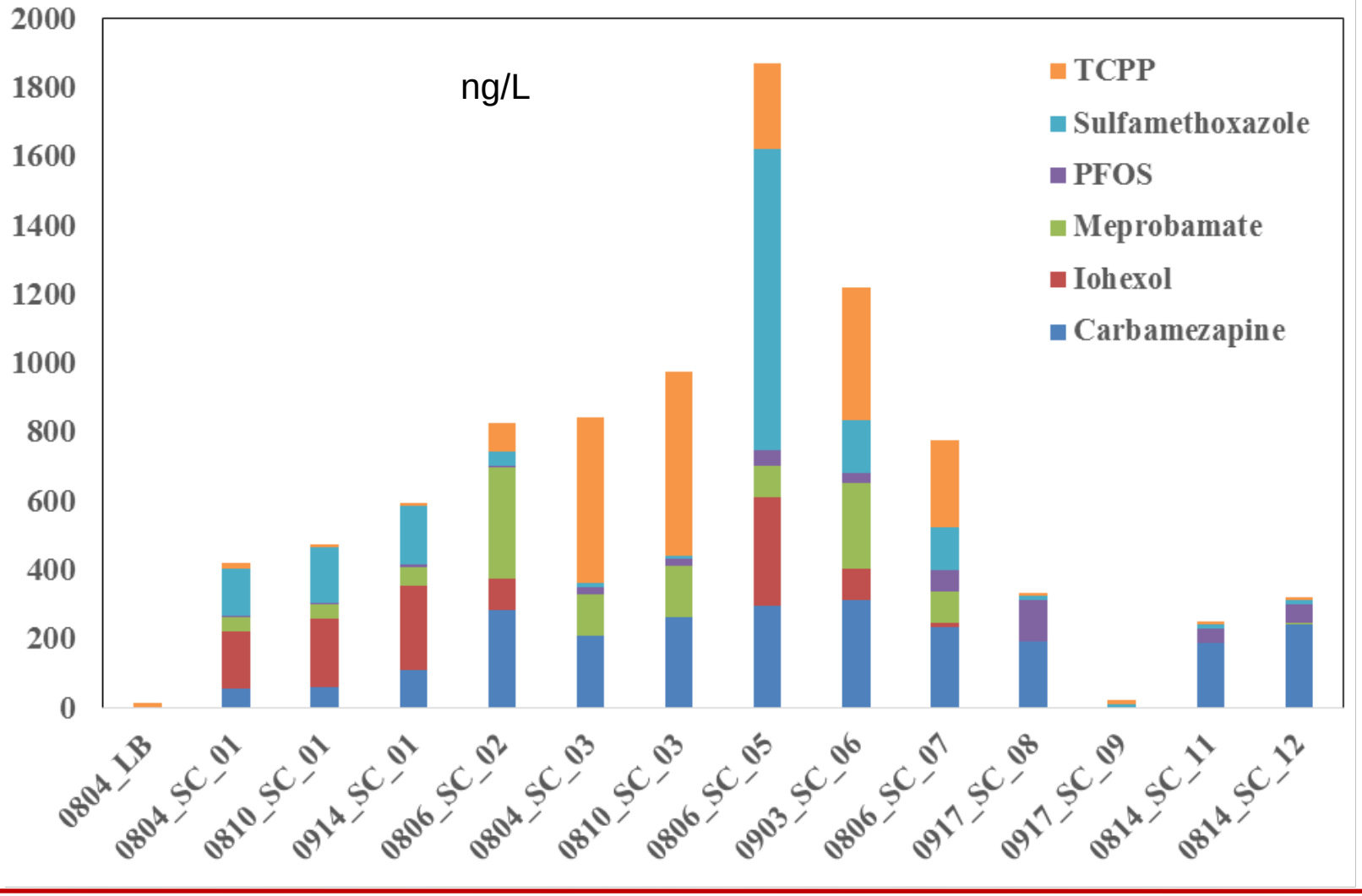
Compound	Frequency	min	max	median	Compound	Frequency	min	max	median
Atrazine	13	1.14	21.5	5.20	Meprobamate	11	1.11	326	89.7
Benzotriazole	13	14.7	31000	1010	Ibuprofen	10	0.49	10.0	1.84
Caffeine	13	0.60	7.74	1.63	PFBA	10	12.7	69.6	23.0
Carbamezapine	13	0.61	315	210	PFHpA	8	1.09	21.6	3.66
DEET	13	0.48	16.7	0.96	Iohexol	7	13.8	313	167
PFBS	13	2.96	13.6	7.84	Iopromide	7	4.55	66.4	16.1
PFHxA	13	1.16	41.3	15.5	Trimethoprim	6	0.32	0.73	0.45
PFOA	13	4.50	79.1	33.7	Naproxene	5	0.44	6.88	0.72
PFOS	13	3.01	119	23.7	Atenolol	4	0.59	1.31	0.91
Primidone	13	3.24	292	65.5	Clofibric Acid	3	2.56	37.9	3.40
Simazine	13	3.66	60.8	16.9	Propylparaben	3	1.98	84.9	4.87
Sucralose	13	27.6	37400	10200	Diclofenac	2	2.40	15.1	8.75
Sulfamethoxazole	13	7.04	875.0	39.6	Hydrochlorothiazide	2	34.2	37.8	36.0
TCEP	13	1.10	33.7	3.22	Gemfibrozil	1	26.1	26.1	26.1
TCPP	13	6.69	531	17.5	Propranolol	1	12.5	12.5	12.5
Triclocarban	13	0.14	2.70	0.66	Diphenhydramine	0	-	-	-
Triclosan	13	0.33	7.17	0.59	Ditiazem	0	-	-	-
Acesulfame	12	111	24100	623	Fluoxetine	0	-	-	-
Iopamidol	12	249	19200	4505					

22 CECs were detected in more than 10 well samples

Results: “Resilient CECs”



Results: “Attenuated” CECs



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

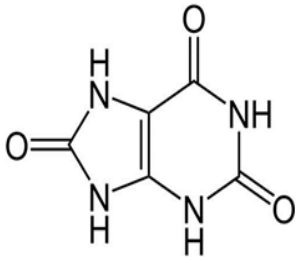
Using *in vitro* and *in silico* testing in primary human cell systems, scientists reported in the May issue of the journal Nature Biotechnology bioactivity profiles for 776 unique and diverse chemicals with potential for human exposure. The use of a human-relevant system may provide a rapid and accurate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

"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."

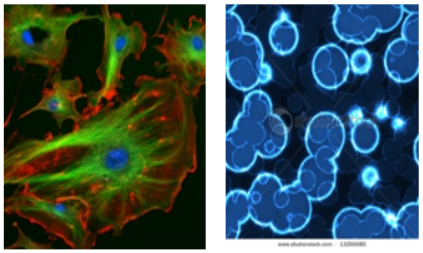
Today, Tomorrow, and Beyond

Toxicology 2012
Where are we now?

High Throughput Screening (Tox21C)

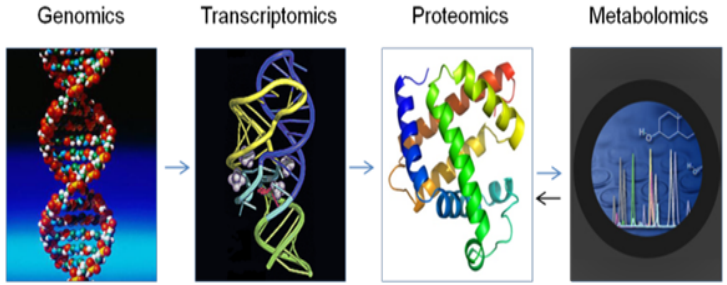


Chemical Characterization

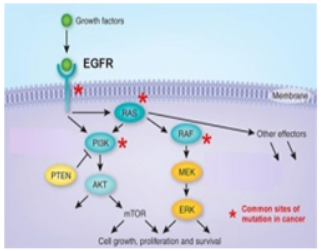


In vitro Assays

Toxicology 2013-2015
A PPP for Integrated Systems Tox



Integrated systems toxicology: Systems analysis of pathways, dose-response, IVIVE



Map Pathways

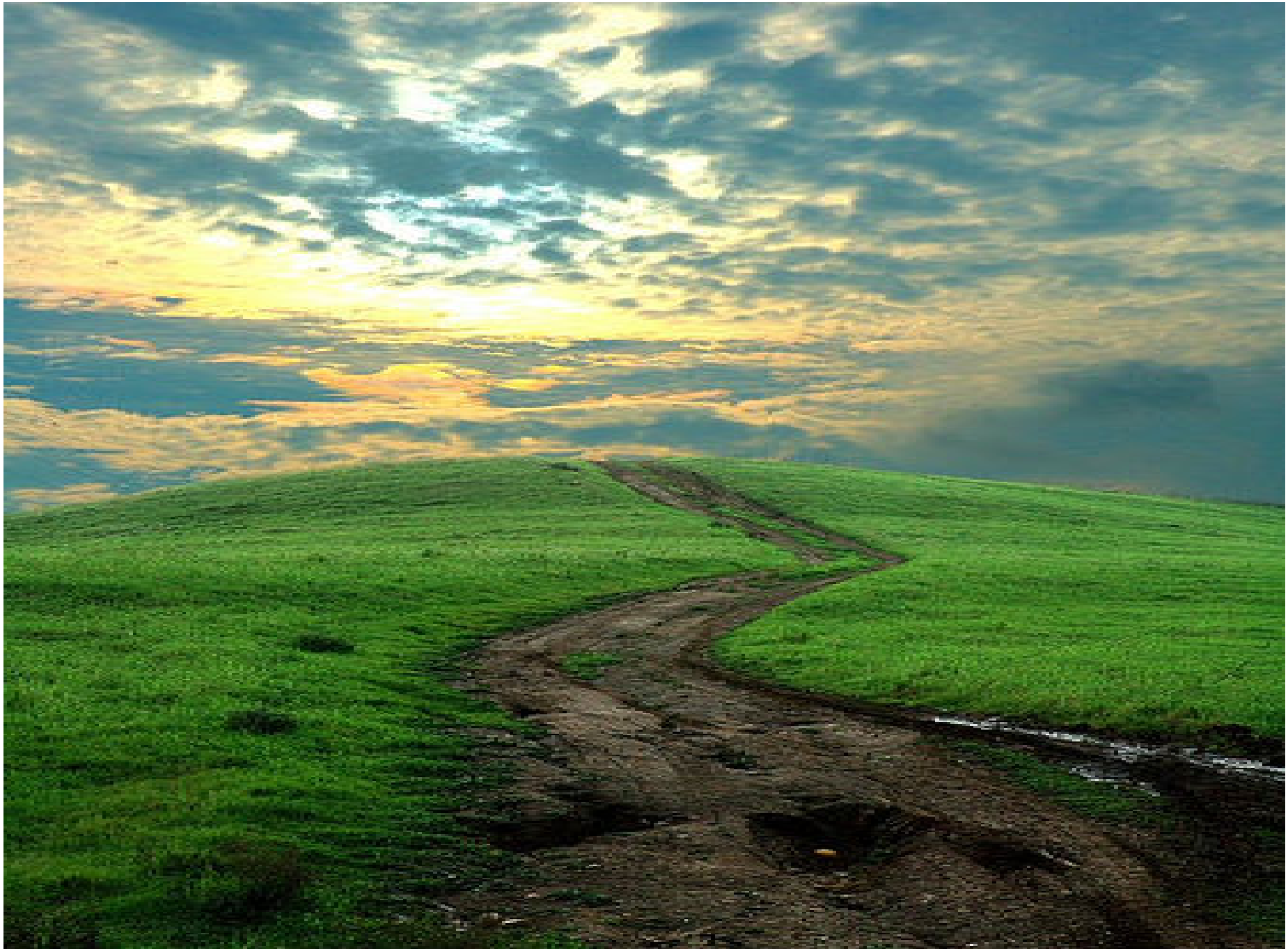
Establish Knowledgebase

2016 and Beyond
What will PPP enable?

Human Health Risk Assessments

Predictive, Pre-Clinical Toxicology; Enhanced Drug Safety

Sustainable Toxicology Testing Architecture



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Acknowledgements

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Citizens' Water Advisory Committee
Technical Planning, Policy Subcommittee
Projected Agenda

Meeting Date/Agenda Items	Materials Deadline
November 18, 2015 • FICO Infrastructure and Plans – Tim Campbell • Risk Communication – Dr. Marti Lindsey	November 13, 2015
December 16, 2015 • Cogeneration • 2016 Meeting Schedule	December 11, 2015
January 27, 2016 • Subsidence in Tucson and Avra Basins • WMG – Tools for Evaluation of RWH Benefits (TBD)	January 22, 2016
February 24, 2016 • Reclaimed Water System	February 19, 2016
March 23, 2016 • Reclaimed Plant	March 18, 2016

Future Agenda Items without a Date:
None