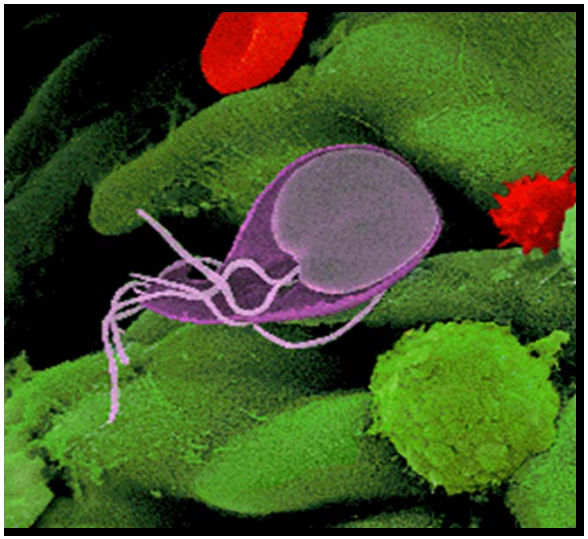
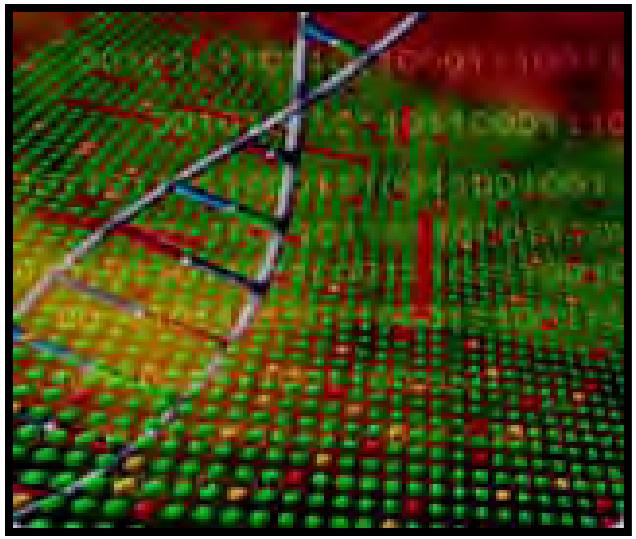
State of Science: Contaminants of Emerging Concern Research


California Water Boards: Recycled Water Research Workshop

27th October 2015 – Costa Mesa

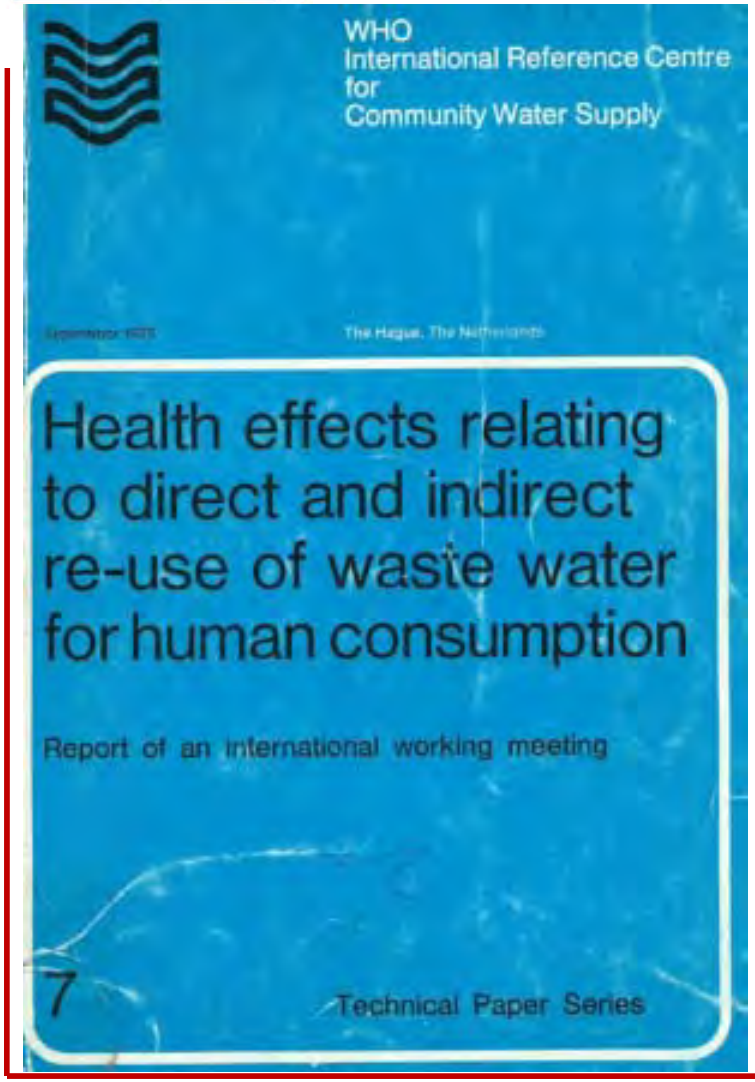
Shane Snyder, Ph.D.

Professor & Co-Director
University of Arizona

Visiting Professor
National U. of Singapore

When does waste water become “water”?

WHO: 1975 Reuse Guidance



1. Bioassays suggested for evaluating mixture toxicity from organic contaminants
2. Development of cytotoxicity tests based on mammalian tissue cultures.
3. Encouraged the development of on-line/continuous monitoring systems.
4. Selection of biotoxicity monitoring systems on their response time and sensitivity to micropollutants.

Facing the Yuck Factor

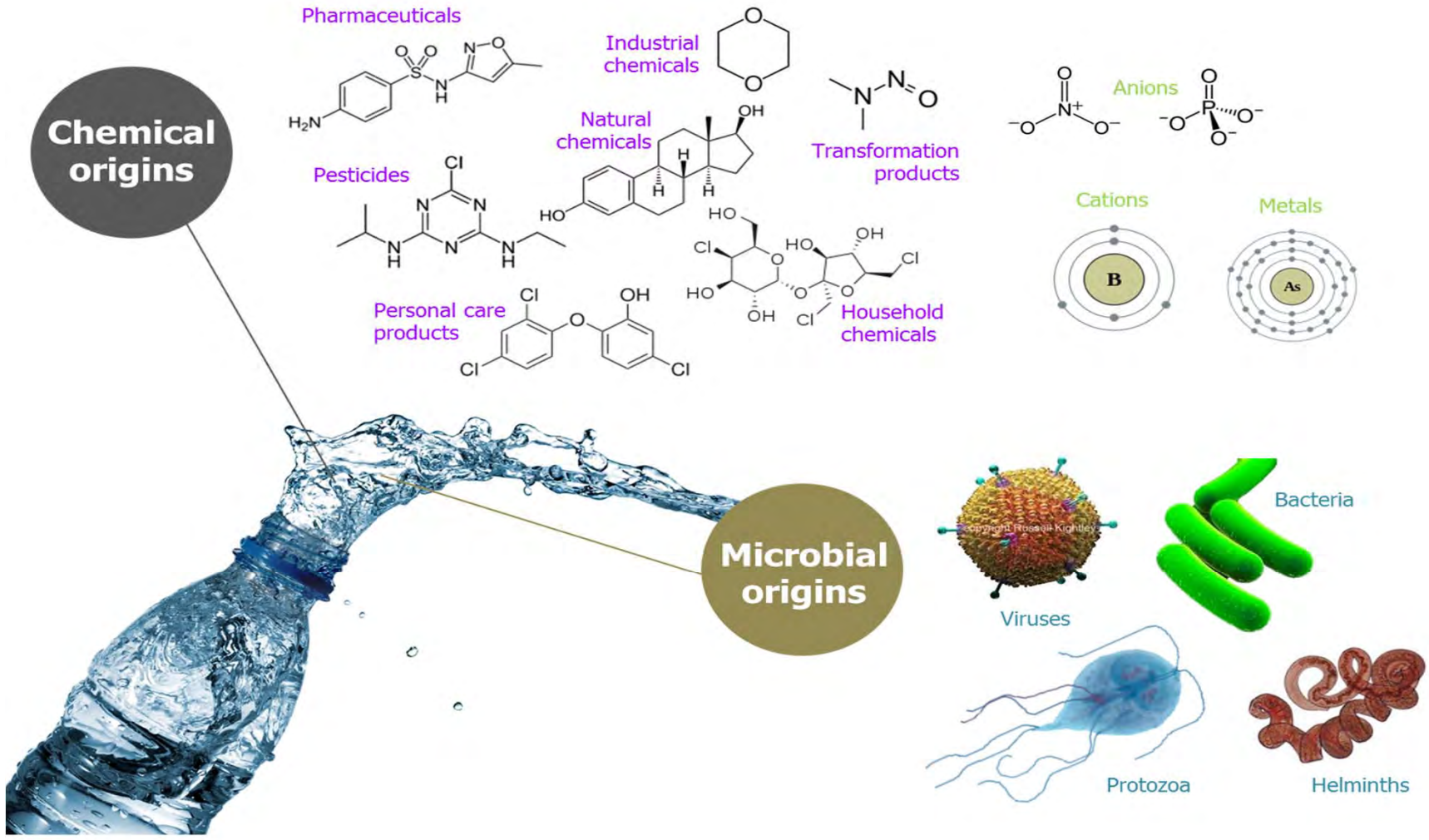
FEATURE ARTICLE - September 17, 2007 *by Peter Friederici*

Facing the yuck factor. PAUL LACHINE

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

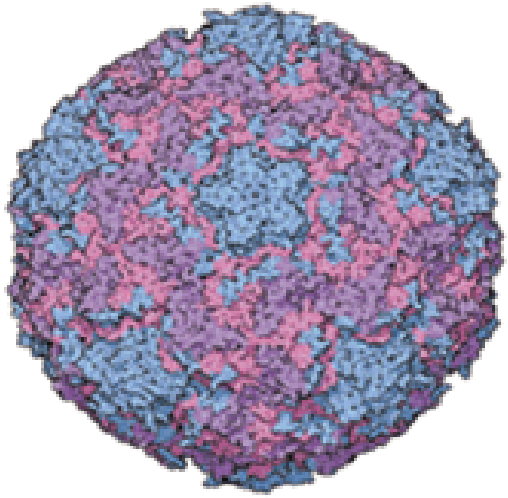
Source: http://www.hcn.org/issues/354/17227

Potential Contaminants



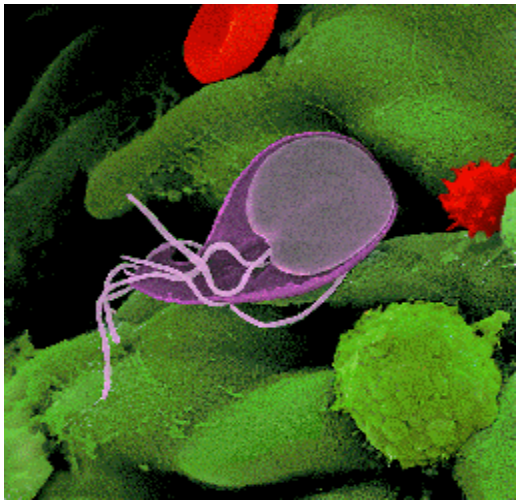
Biologicals are ACUTE Risks

Viruses

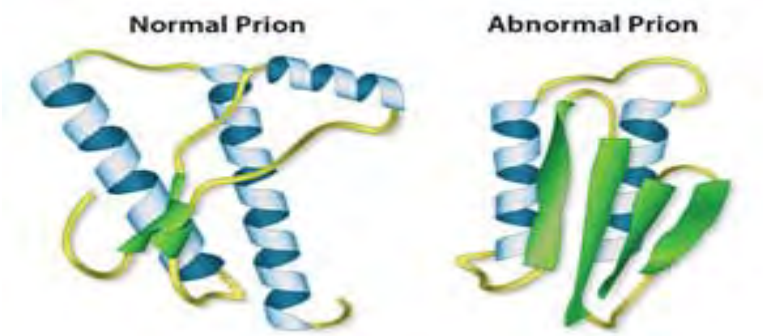


Bacteria

Parasites



Prions



Chemicals are CHRONIC Risks

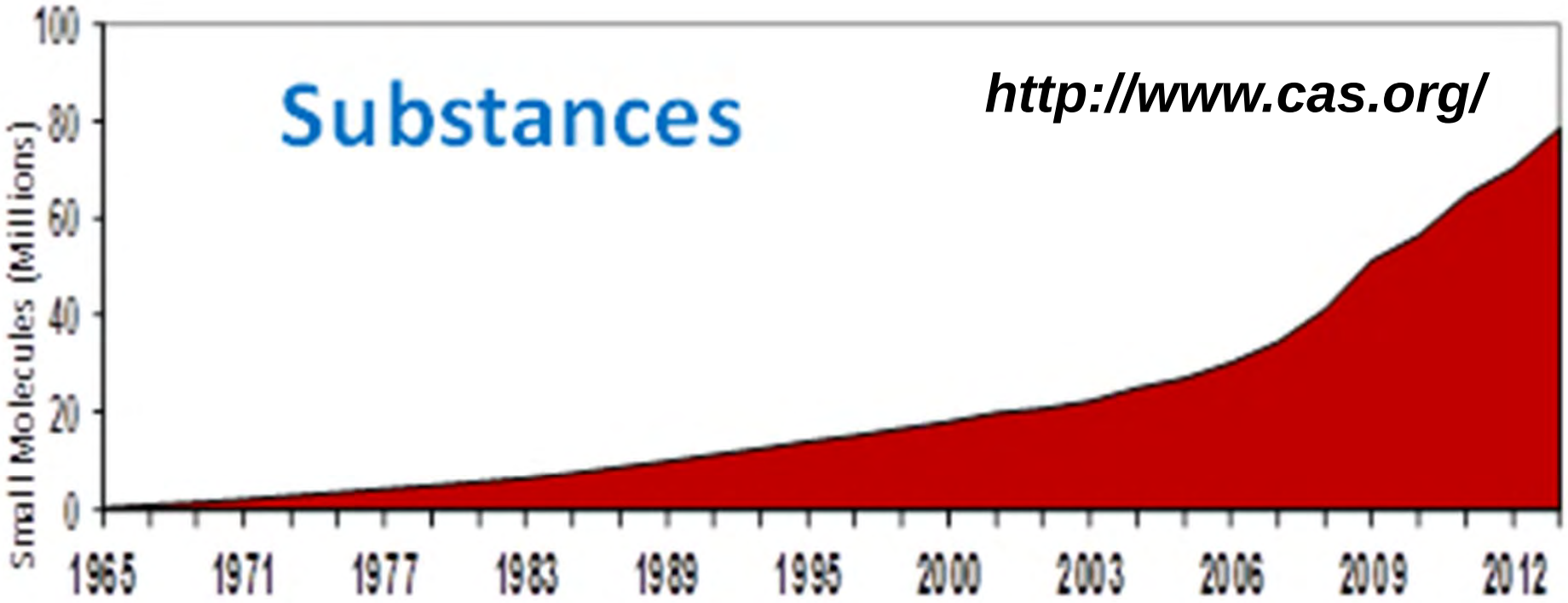
Organic and Inorganic

Volatile and non-volatile

Metals and Salts

89,008,294 ORGANIC AND INORGANIC SUBSTANCES TO DATE

CHEMCATS 65,768,974 Commercially available chemicals



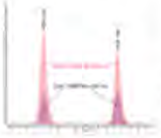
Snyder, S. A., Emerging Chemical Contaminants: Looking for Better Harmony. *J. Am. Water Works Assoc.* **2014,** *106* (8), 38-52.

Comprehensive Screening

Targeted quantification

Analysis of a small set of predefined target compounds

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



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

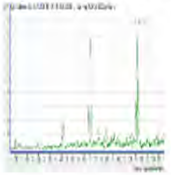
IC-MS

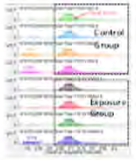
Anions, cations, oxyhalides

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

We can detect anything, anywhere…

But are we looking for the right things?

Expert Panel Input

Surrogates and Indicators

Final Report

Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water

Recommendations of a Science Advisory Panel

Panel Members

Paul Anderson, Nancy Denslow, Jörg E. Drewes (*Chair*), Adam Olivieri, Daniel Schlenk, and Shane Snyder

Convened by the

State Water Resources Control Board

June 25, 2010
Sacramento, California

Designing monitoring programs for chemicals of emerging concern in potable reuse – what to include and what not to include?

J. E. Drewes, P. Anderson, N. Denslow, A. Olivieri, D. Schlenk, S. A. Snyder and K. A. Maruya

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

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

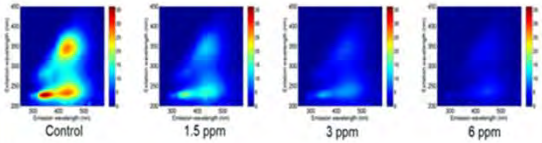
ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/CECpanel/CECMonitoringInCARecycledWater_FinalReport.pdf

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

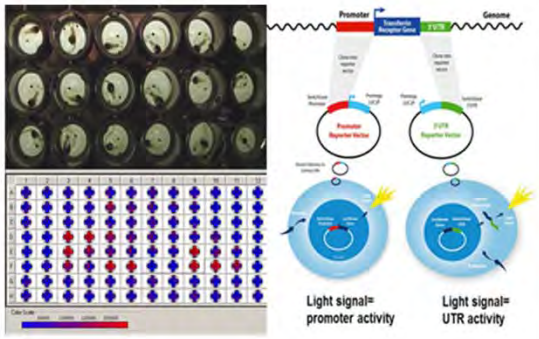
- TOrCs: Trace organic compounds
- Inorganic compounds

Microbiological analysis

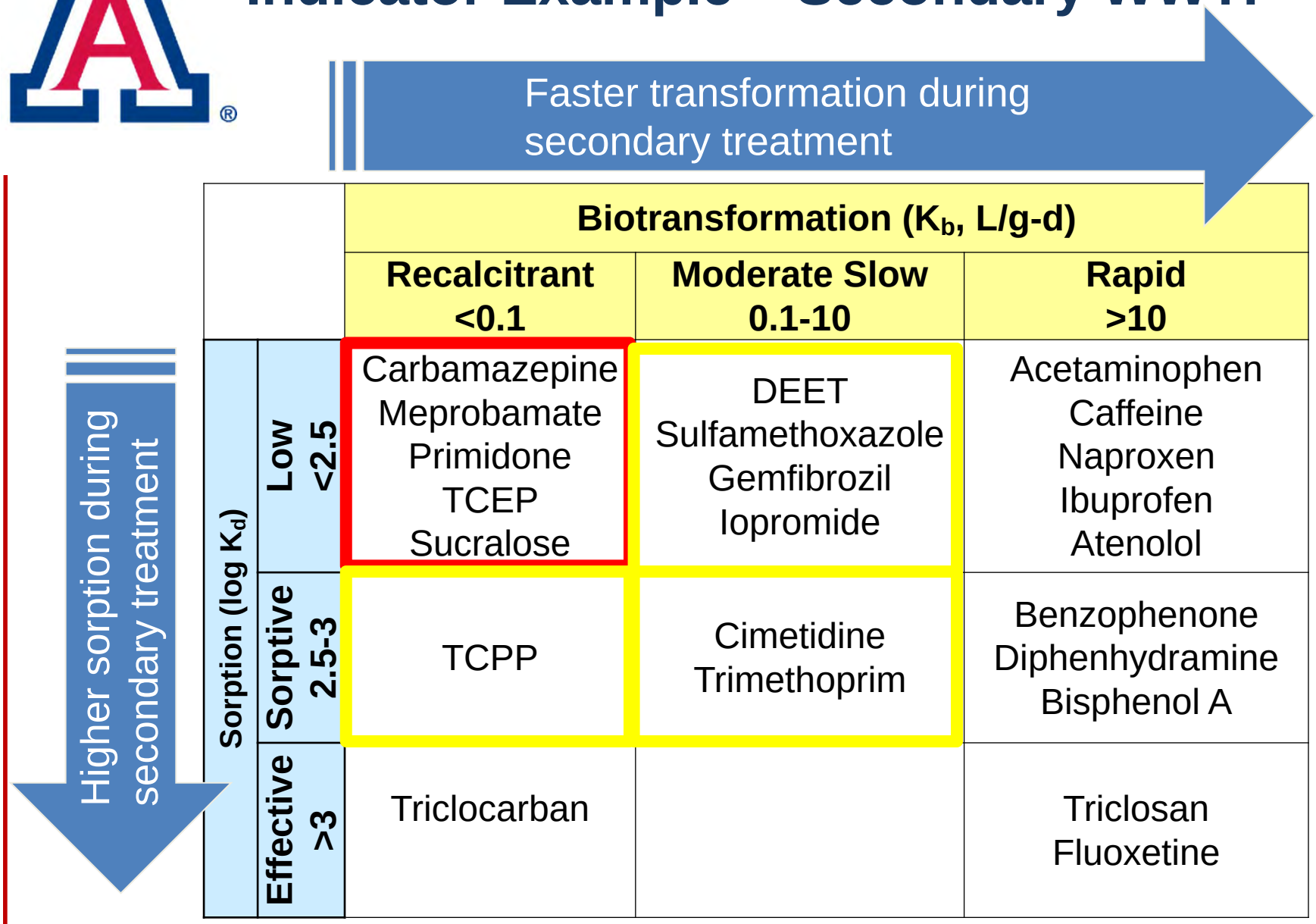
Tier 3
Bioassay

Water toxicity test

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

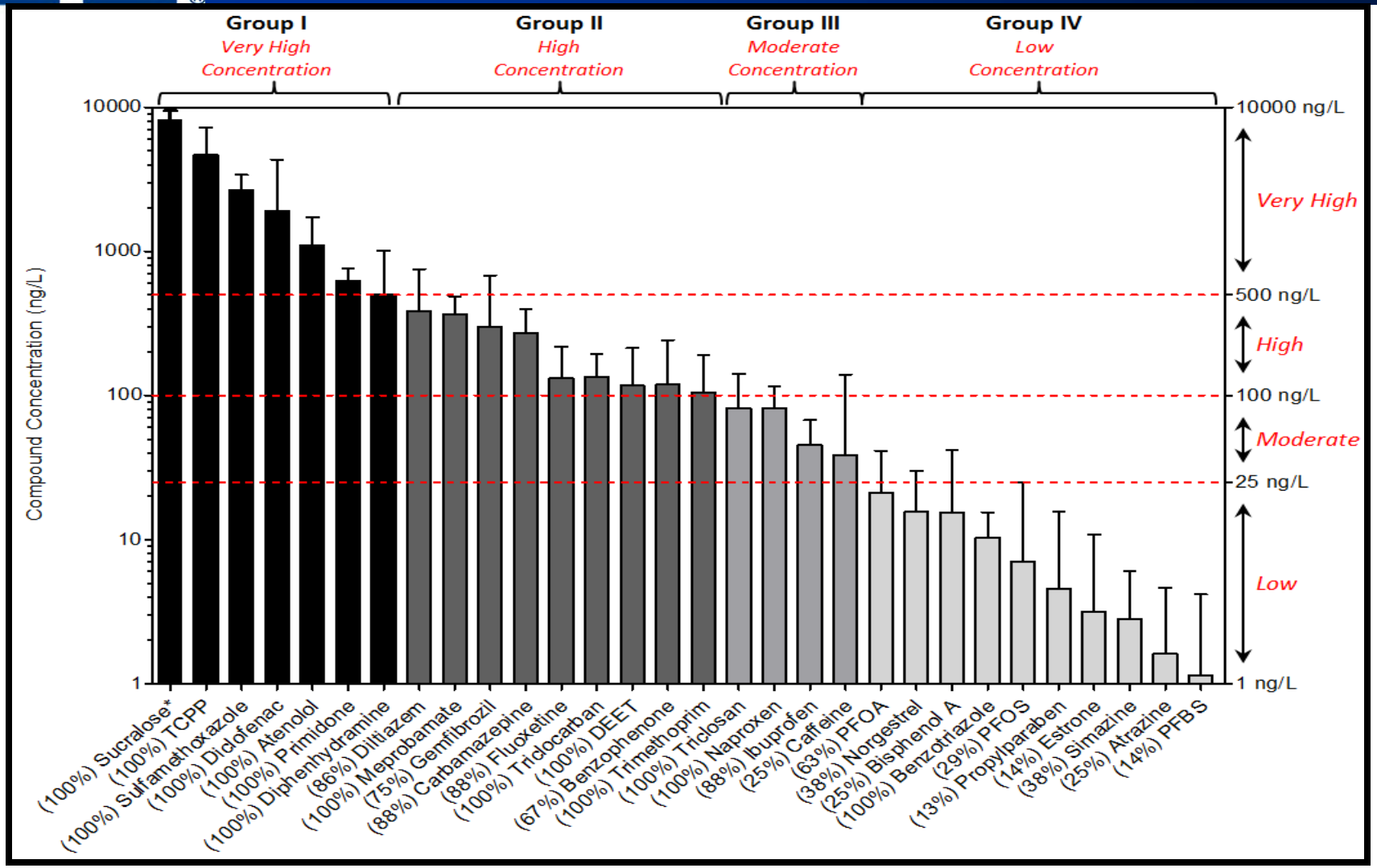


Indicator Example – Secondary WWTP

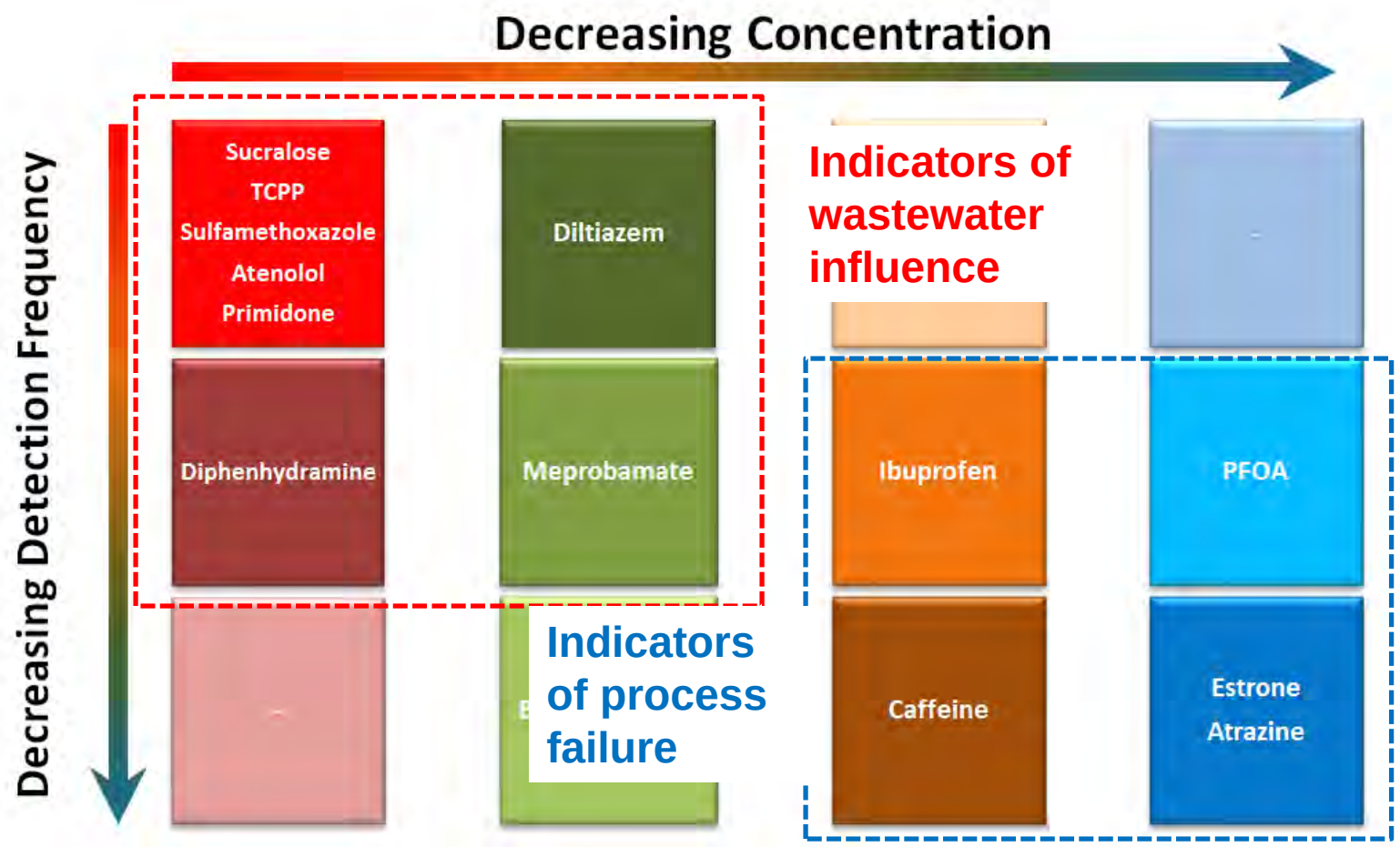


WERF CEC4R08 – Tanja Rauch-Williams *et al.* 2013

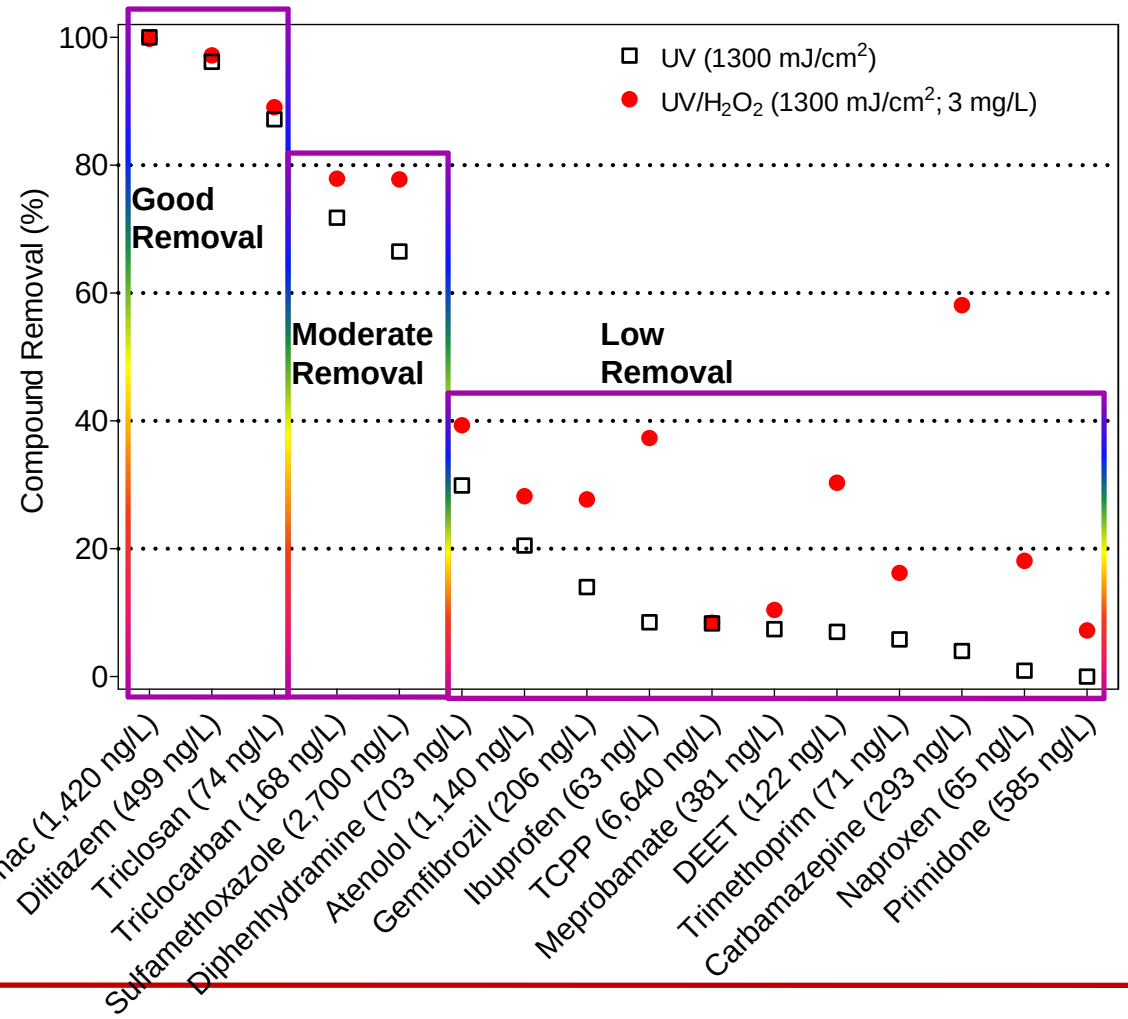
Indicator Occurence



Indicator List

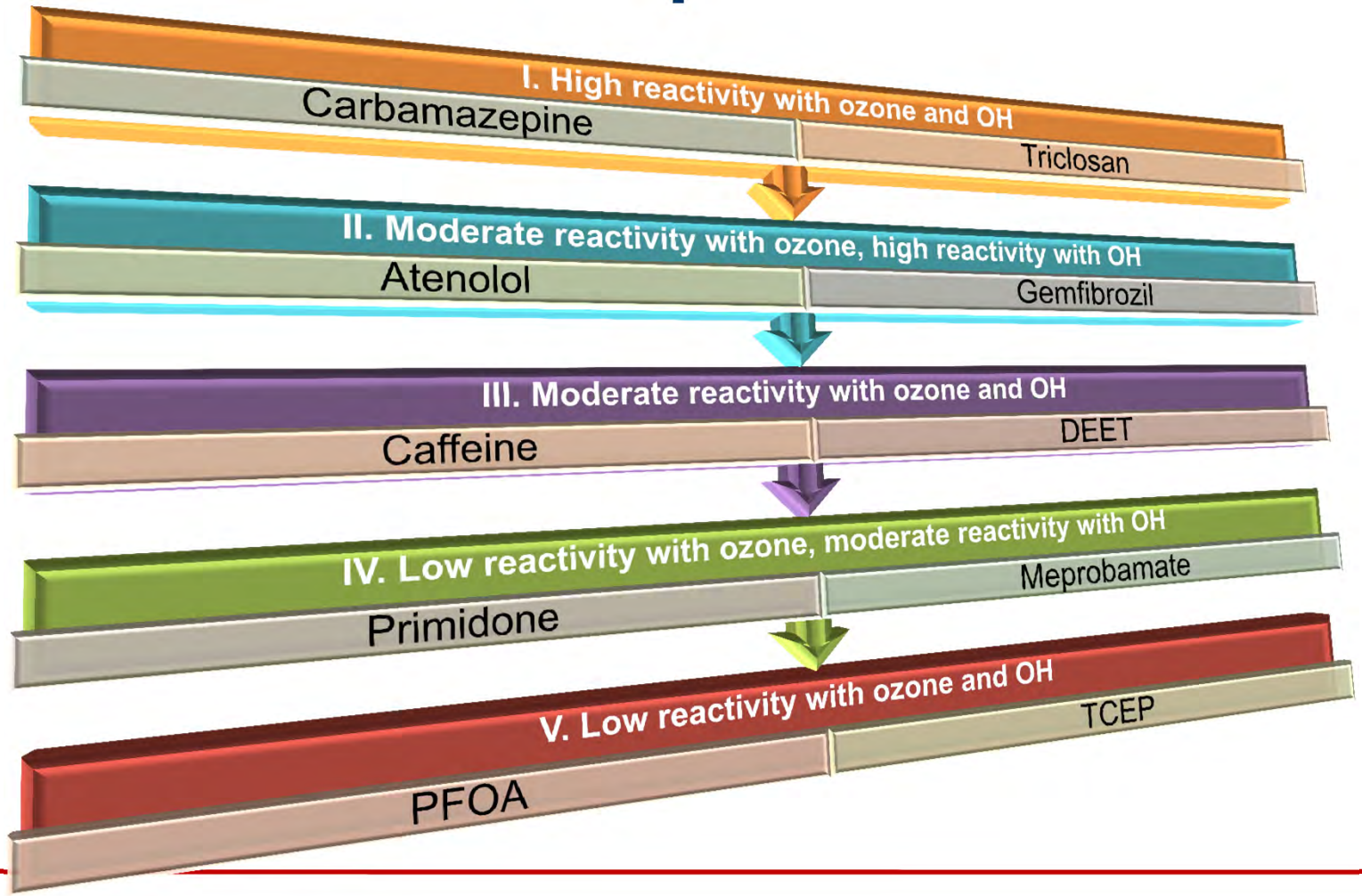


Indicators for Treatment Efficacy



Indicators for Treatment Efficacy

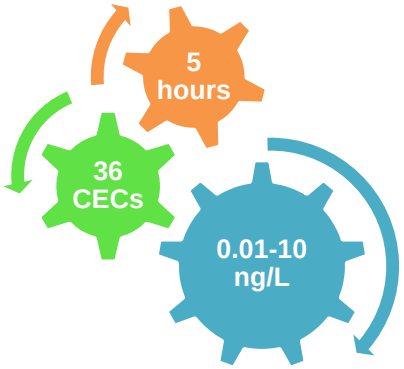
Physical/Chemical Properties



Analysis of Emerging Contaminants in Water

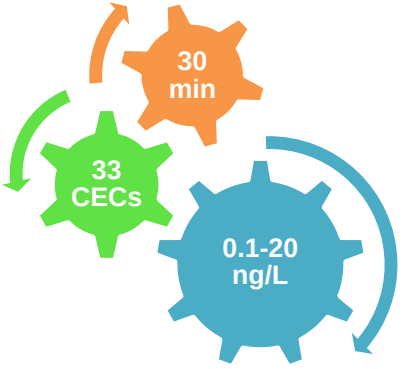
Conventional SPE Method

1 L sample



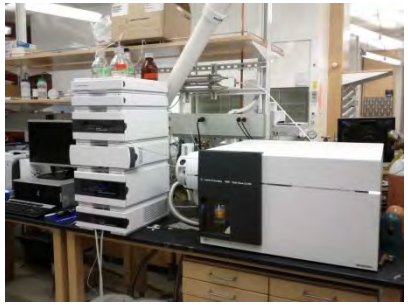
Online SPE Method

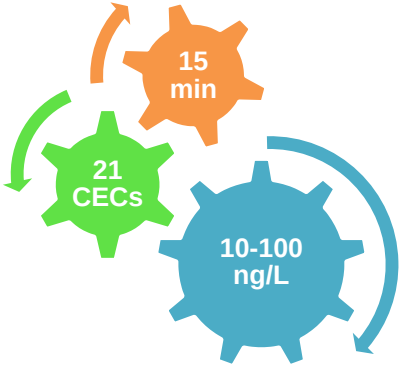
1.5 mL sample



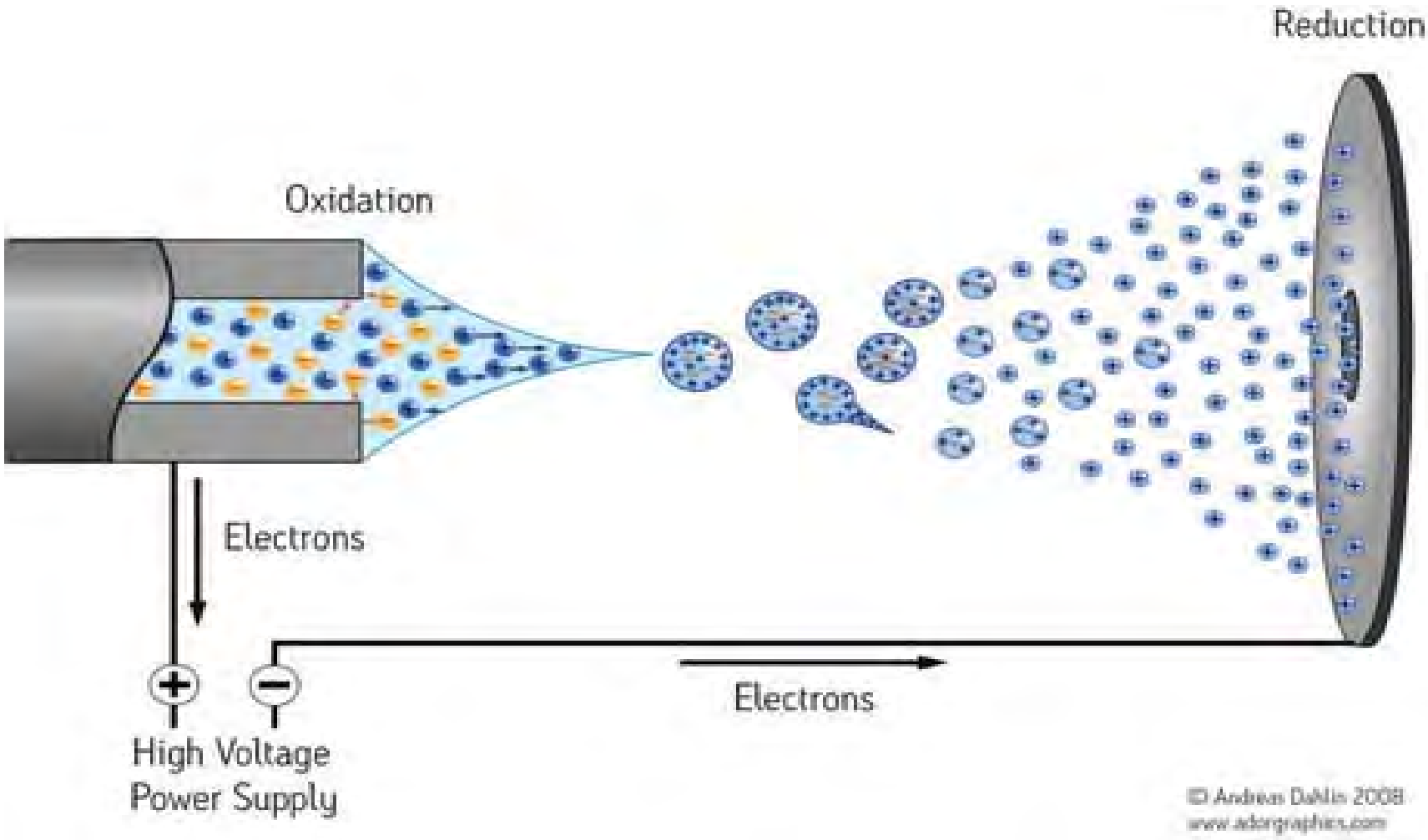
Direct Injection Method

0.1 mL sample

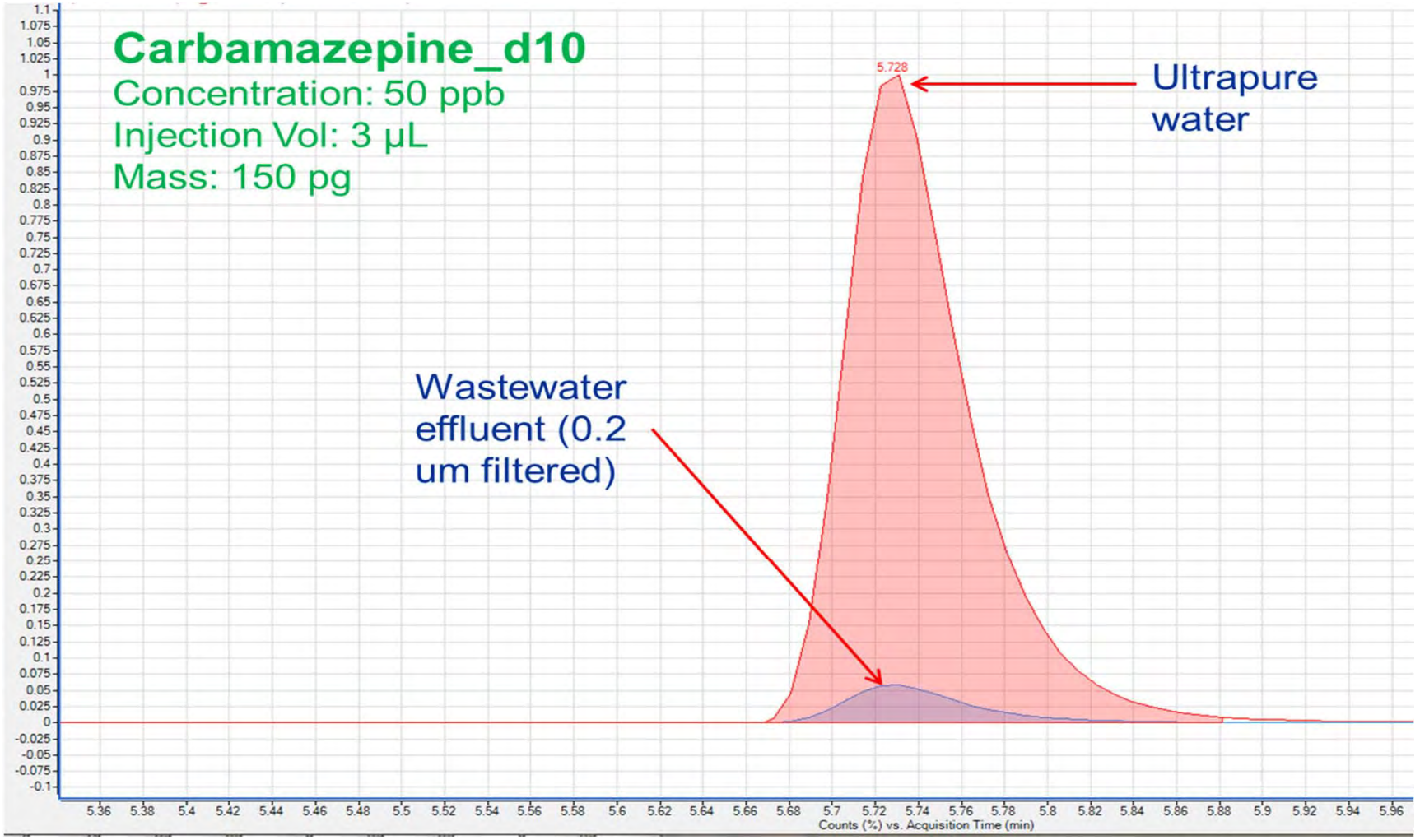




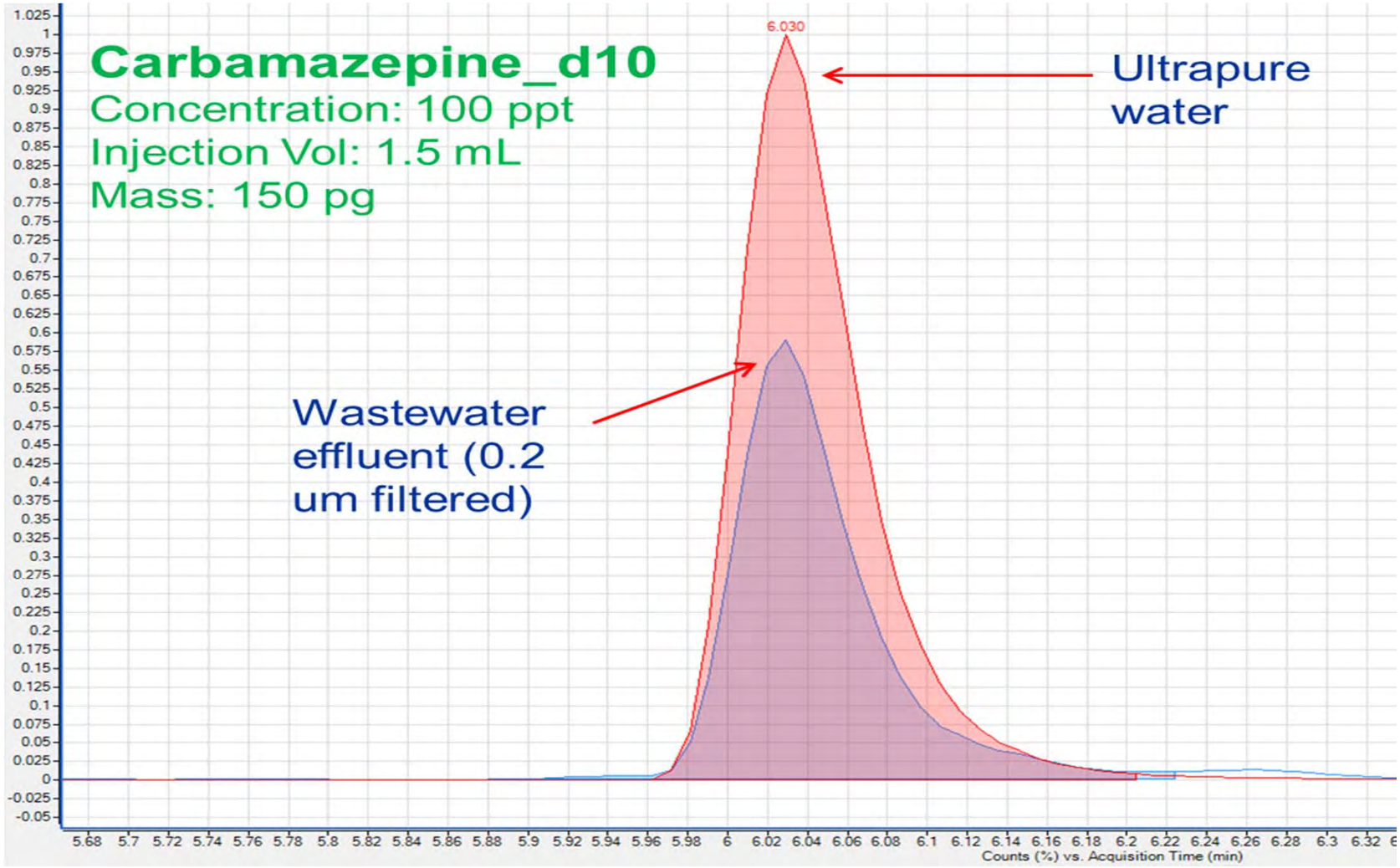
Ion Suppression - Challenge!



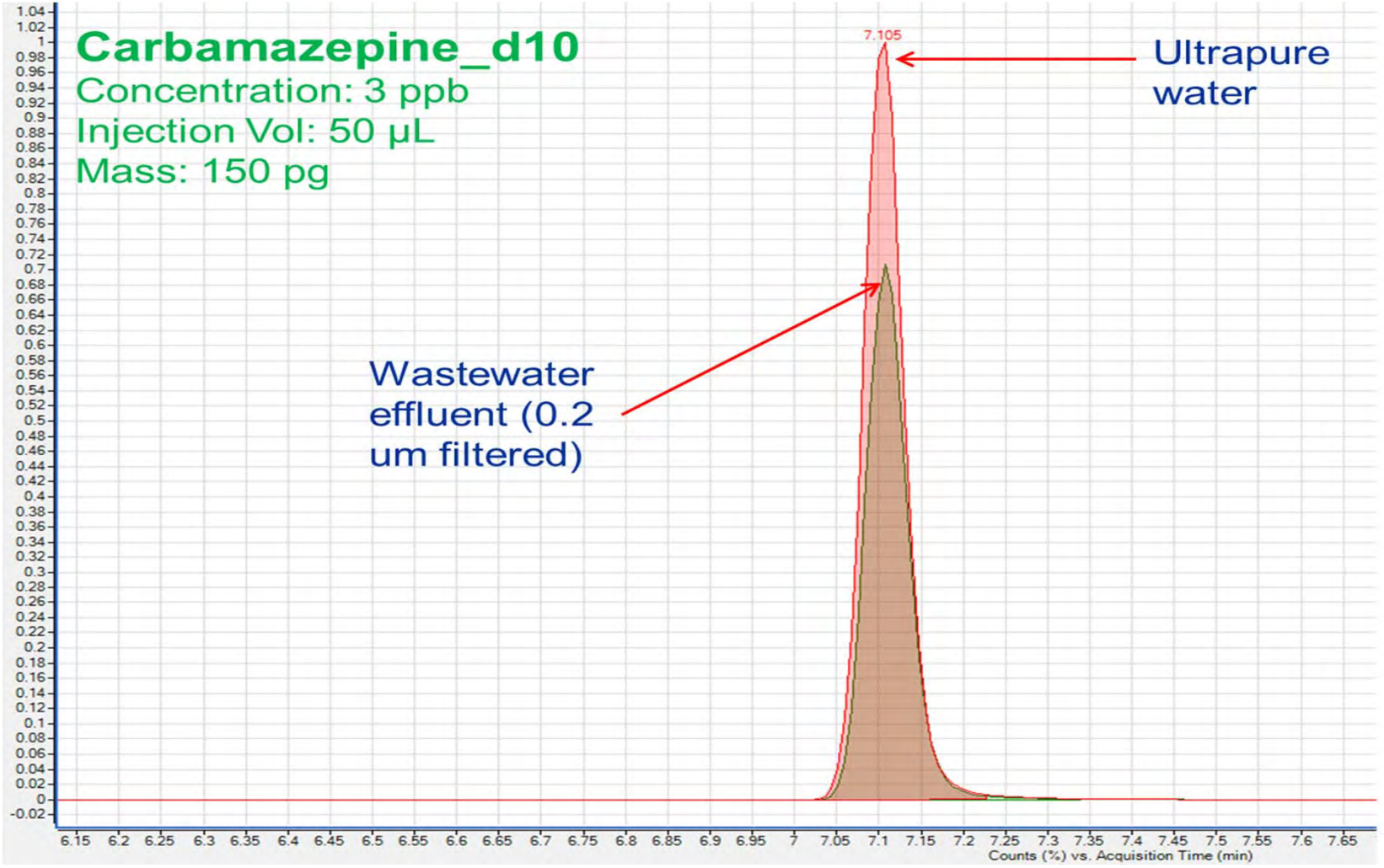
Ion Suppression – Conv. SPE



Ion Suppression - OSPE



Ion Suppression - LVI



Surrogates

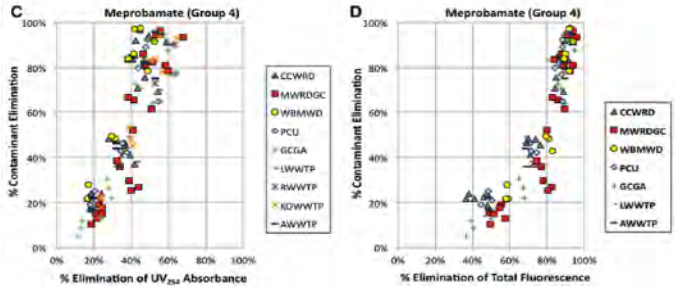
Characterisation of reverse osmosis permeates from municipal recycled water systems using fluorescence spectroscopy: Implications for integrity monitoring

Sachin Singh [a], Rita K. Henderson [a], Andy Baker [b], Richard M. Stuetz [a], Stuart J. Khan [a,*]

[a] UNSW Water Research Centre, School of Civil and Environmental Engineering, University of New South Wales, NSW 2052, Australia
[b] Connected Waters Initiative Research Centre, Water Research Laboratory, University of New South Wales, NSW 2052, Australia

Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation

Daniel Gerrity [a,b,c,], Sujanie Gamage [c], Darryl Jones [d], Gregory V. Korshin [e], Yunho Lee [f,g], Aleksey Pisarenko [c], Rebecca A. Trenholm [c], Urs von Gunten [g,h], Eric C. Wert [c], Shane A. Snyder [d]*



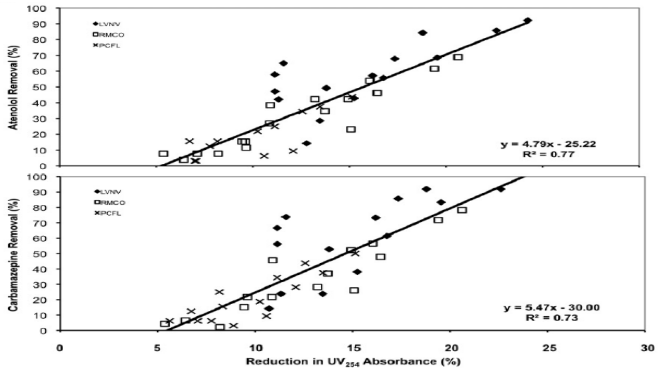
Evaluation of UV/H_2O_2 treatment for the oxidation of pharmaceuticals in wastewater

Fernando L. Rosario-Ortiz, Eric C. Wert, Shane A. Snyder*

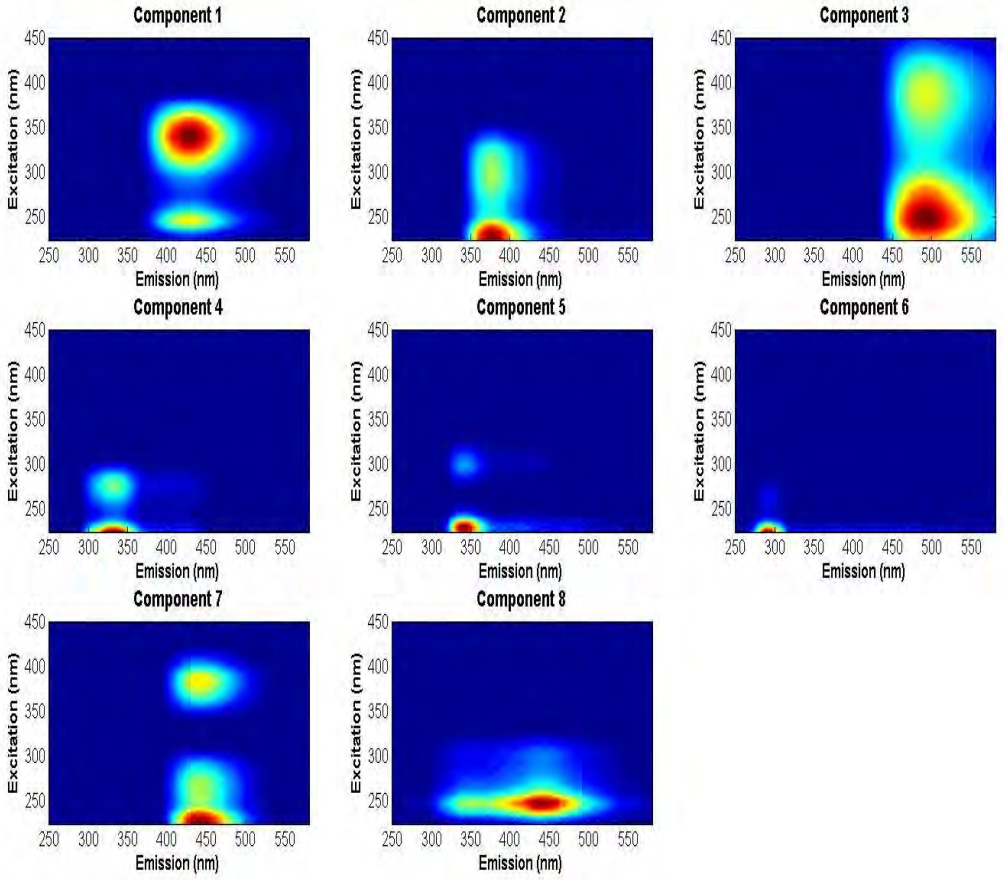
Using Ultraviolet Absorbance and Color To Assess Pharmaceutical Oxidation during Ozonation of Wastewater

ERIC C. WERT,*
FERNANDO L. ROSARIO-ORTIZ, AND
SHANE A. SNYDER

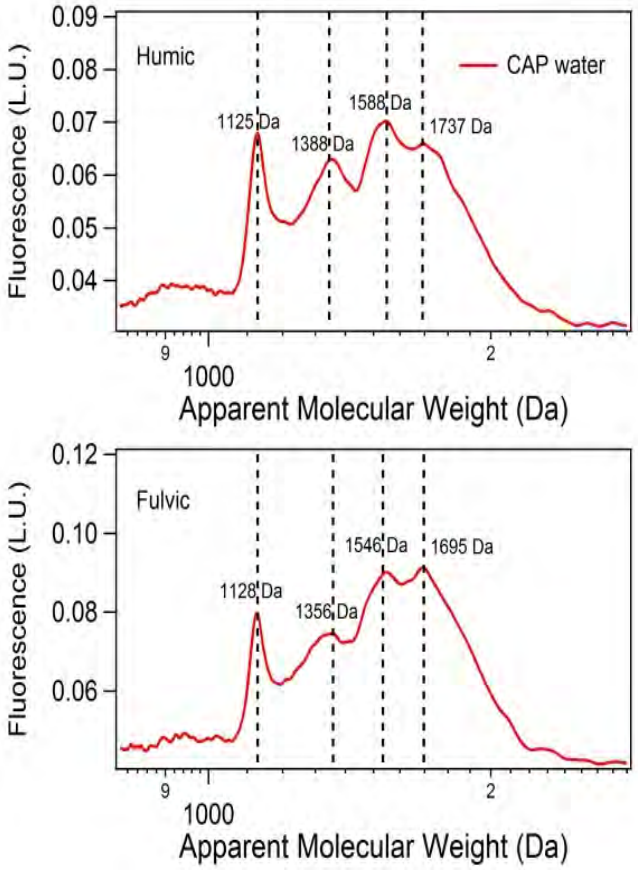
Southern Nevada Water Authority (SNWA), P.O. Box 99955, Las Vegas, Nevada 89193-9955



Surrogates - PARAFAC model



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



< SEC chromatogram of CAP water >

Basic Categories of Treatment

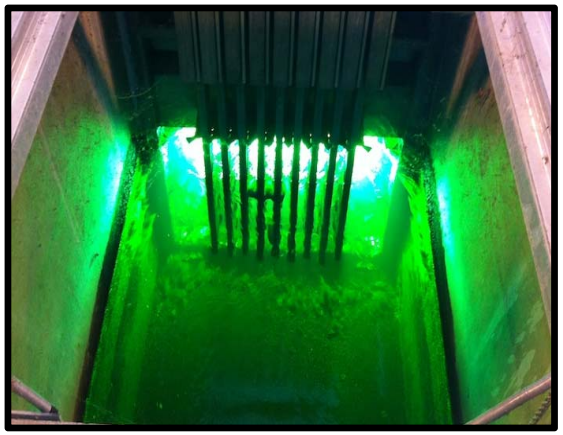
Separation

Biological

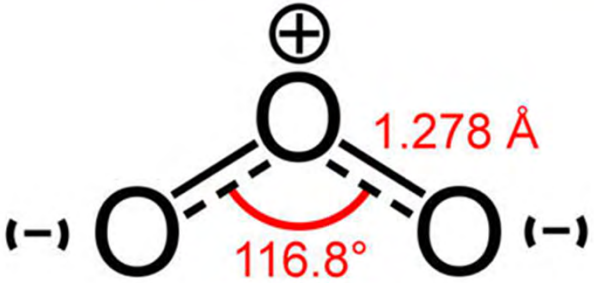
Oxidation

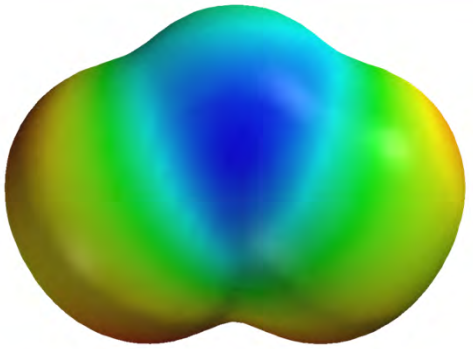
The Multi-Barrier Approach

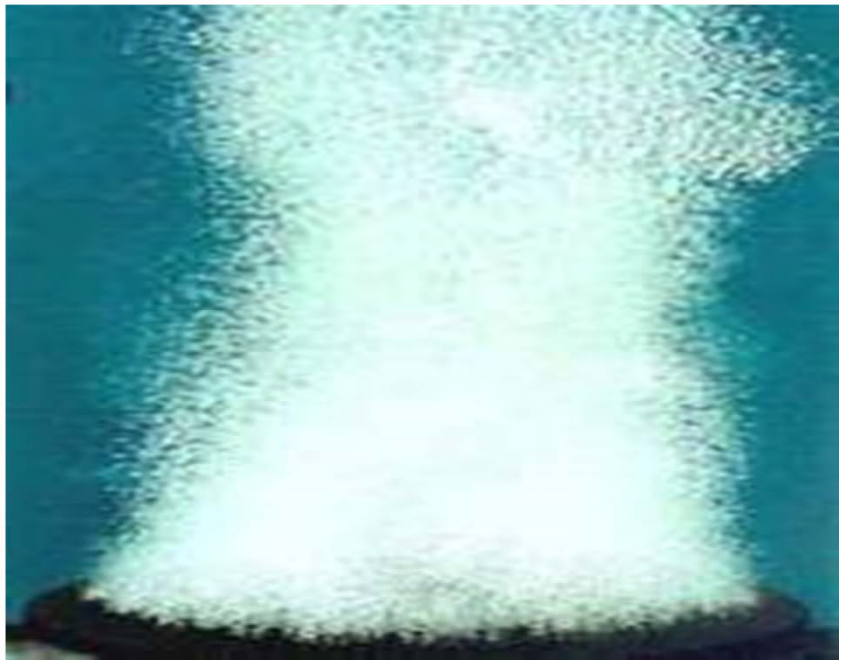
Disinfectant	Bacteria	Viruses	Parasites	DBPs
Free Chlorine	✓	✓	✗	THMs, HAAs
Chloramines	–	✗	✗	NDMA
UV	✓	–	✓	None???
Ozone	✓	✓	–	Bromate, NDMA



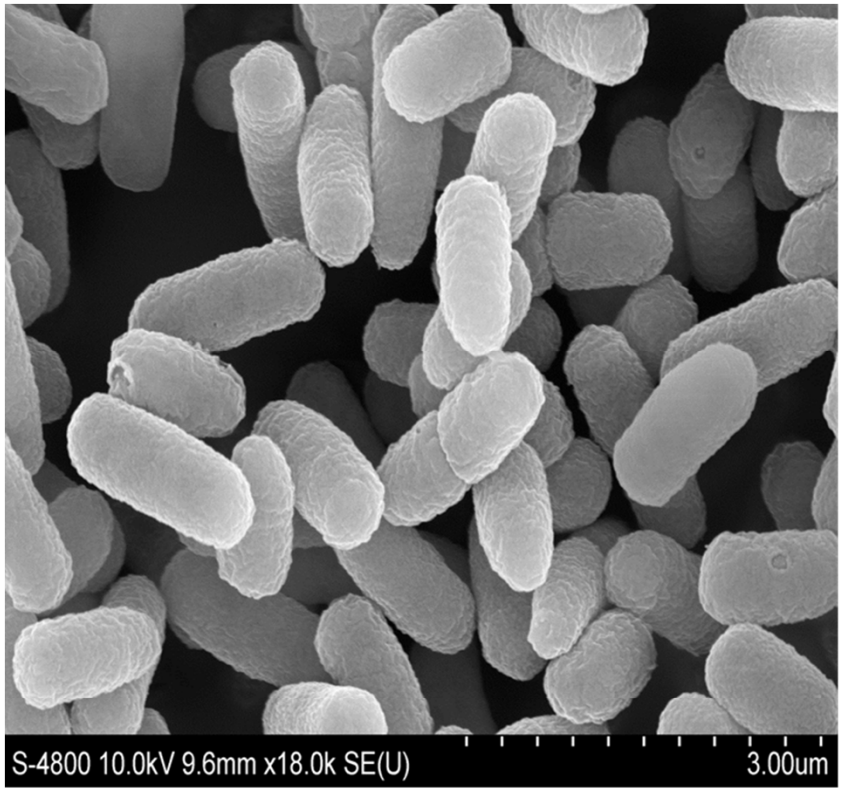
Ozonation Example



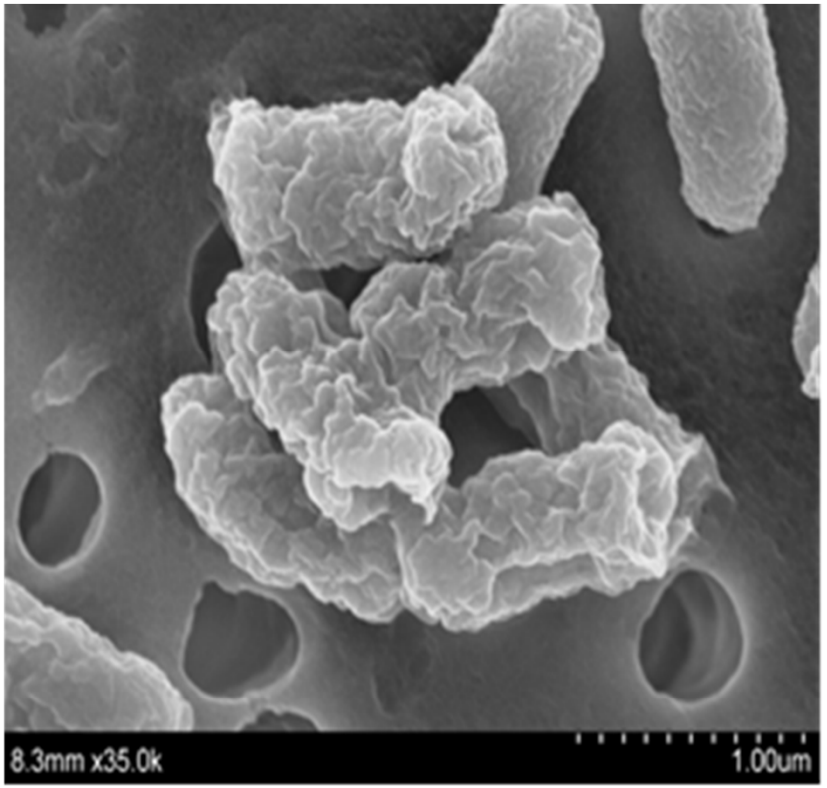




Disinfection



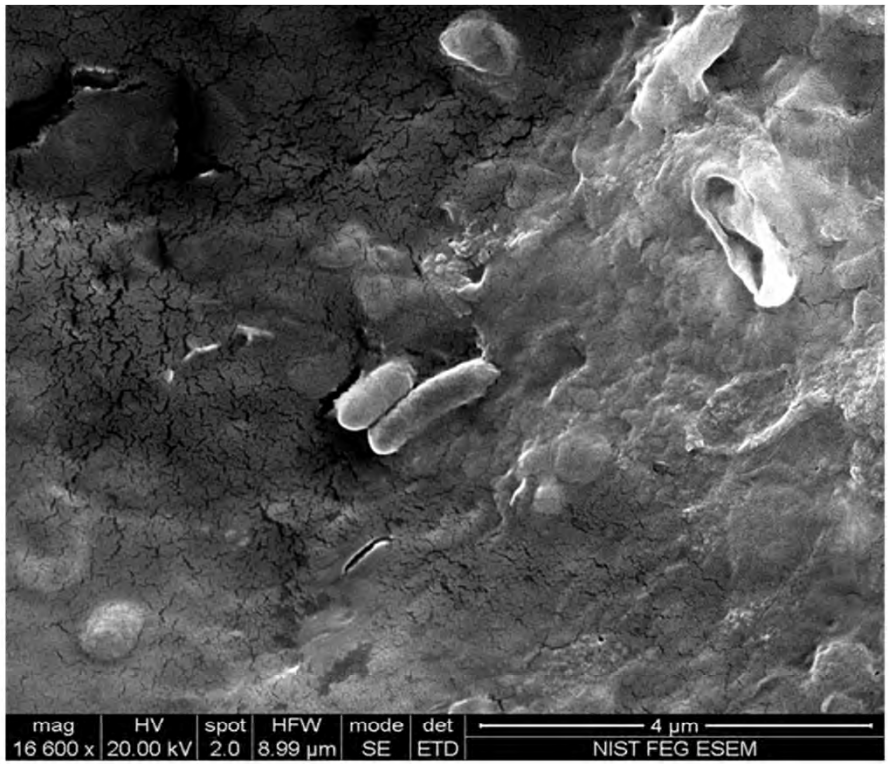
E. Coli - Healthy



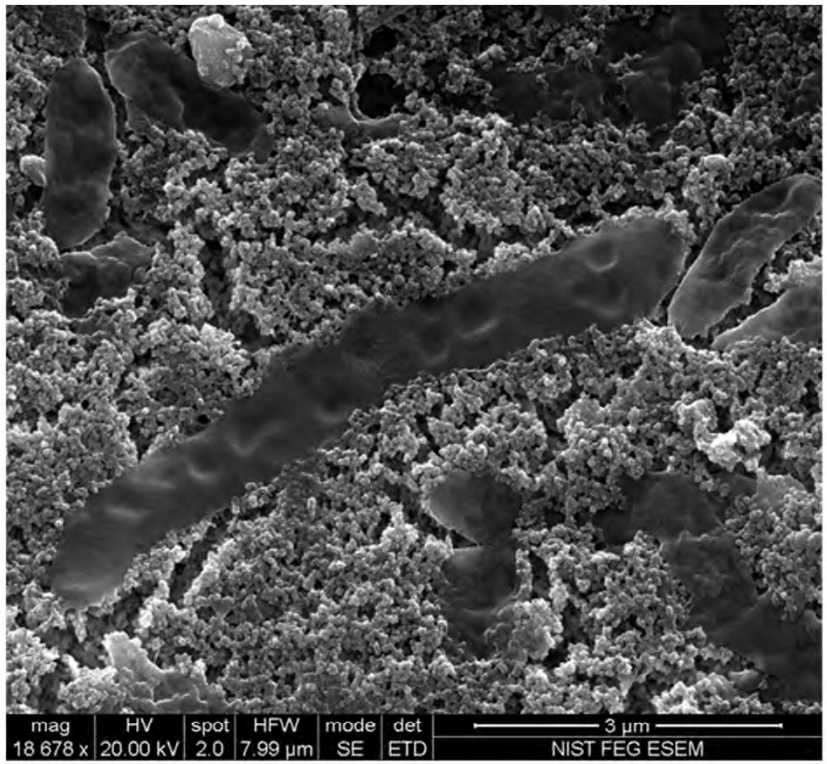
Post-AOP

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



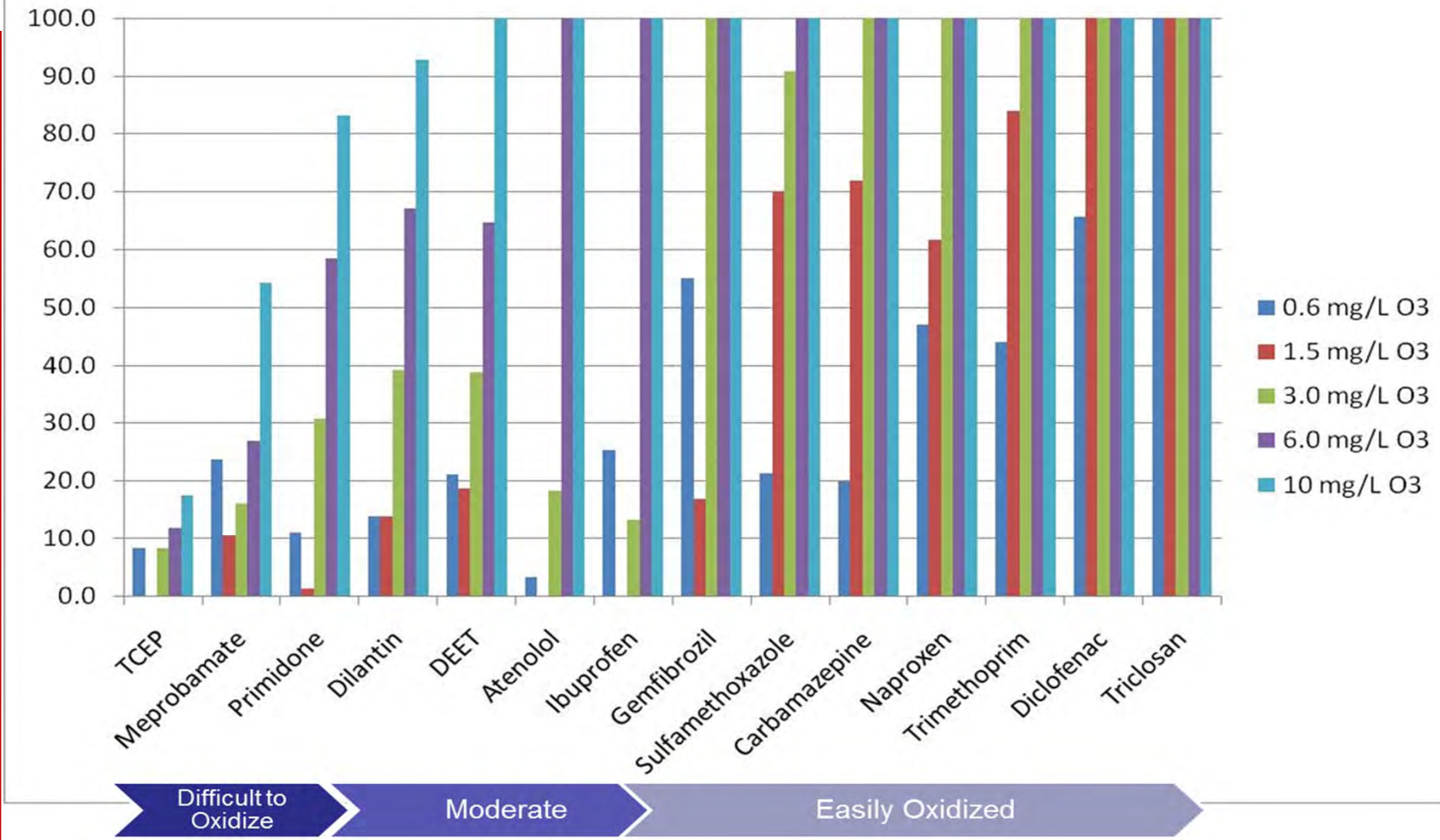
MBR-RO control



MBR-Ozone-RO (3 mg/L)

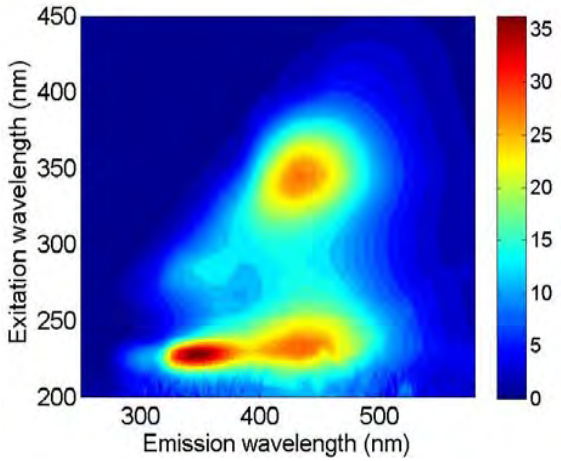
Stanford, B. D.; Pisarenko, A. N.; Holbrook, R. D.; Snyder, S. A., Preozonation Effects on the Reduction of Reverse Osmosis Membrane Fouling in Water Reuse. *Ozone-Sci. Eng.* **2011,** *33* (5), 379-388.

Indicator Oxidation

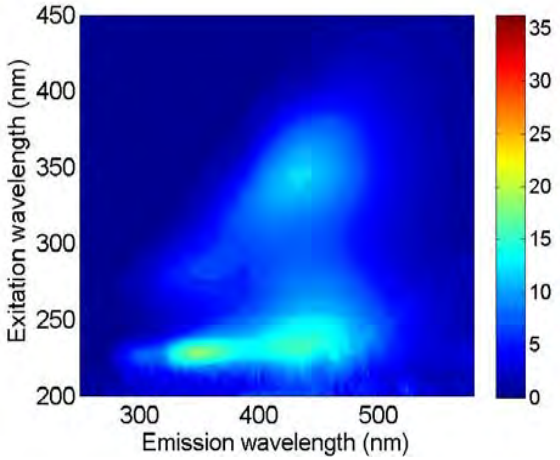


Pisarenko, AN et al.. *Water Res.* **2012,** *46* (2), 316-326.

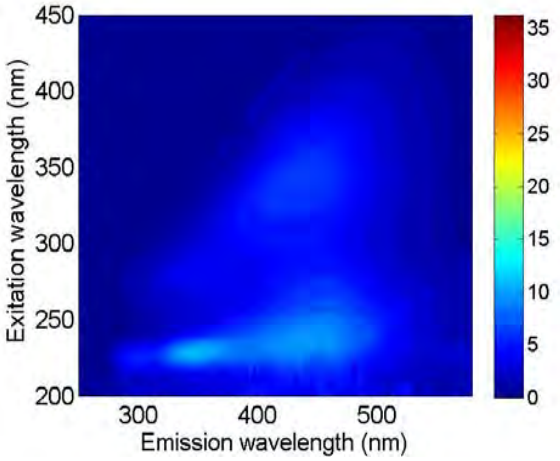
Fluorescence Surrogate Response



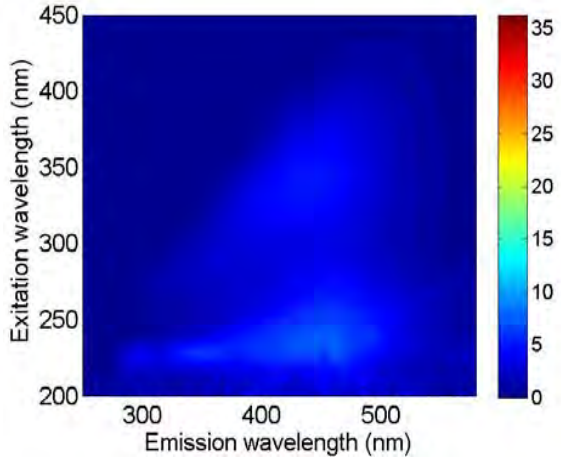
Control



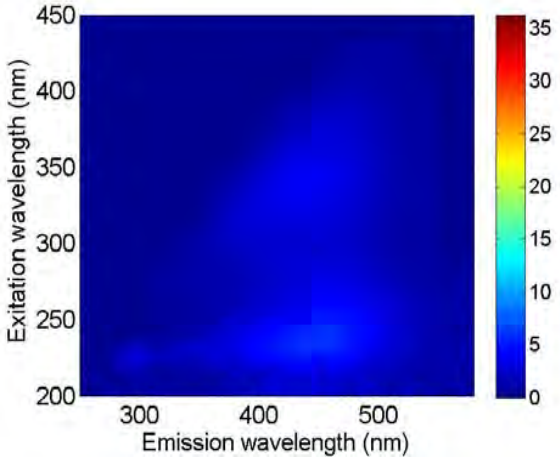
1.5 ppm



3 ppm



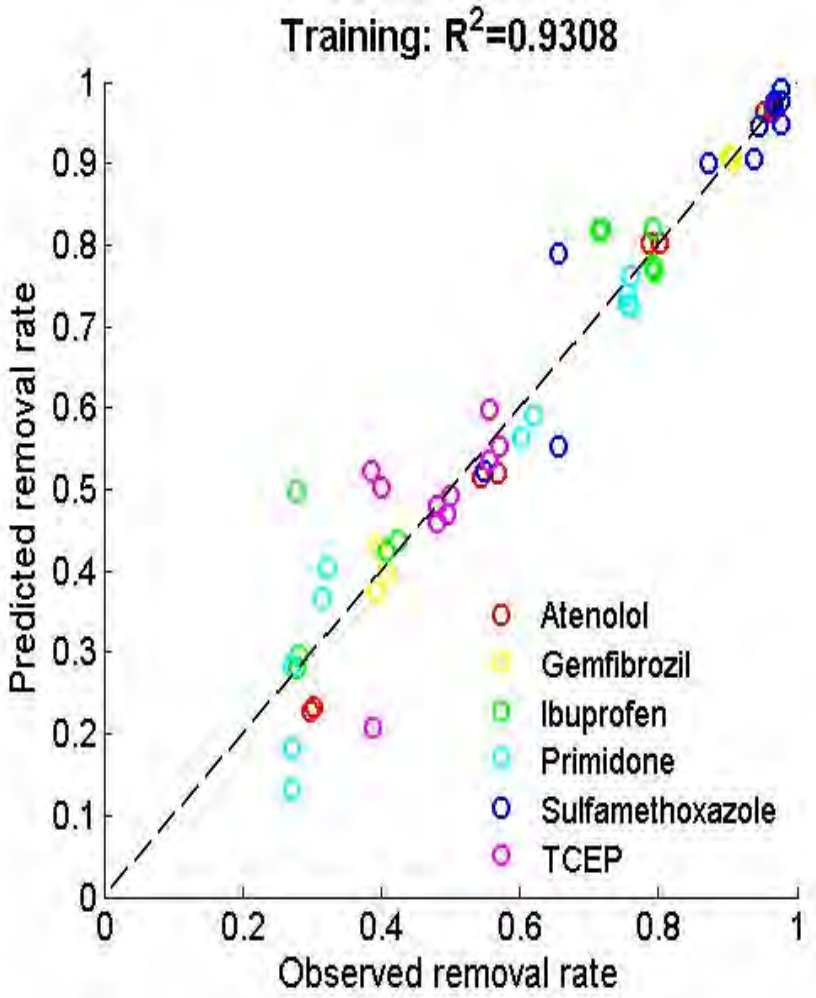
4.5 ppm

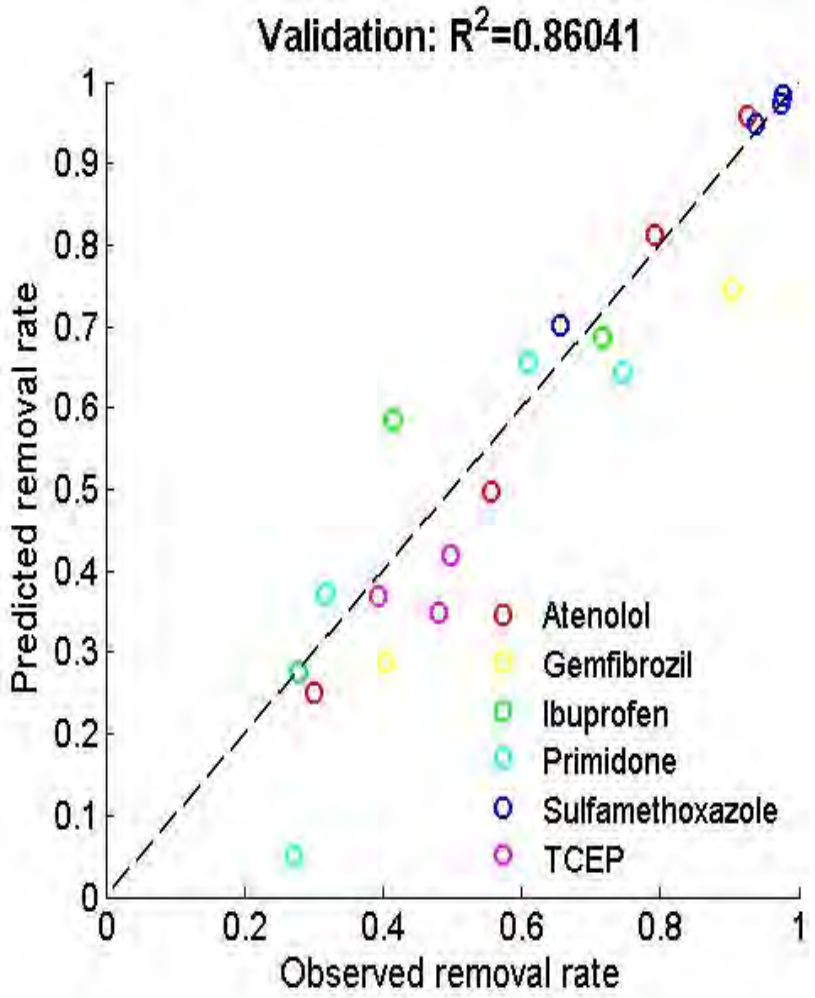


6 ppm

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

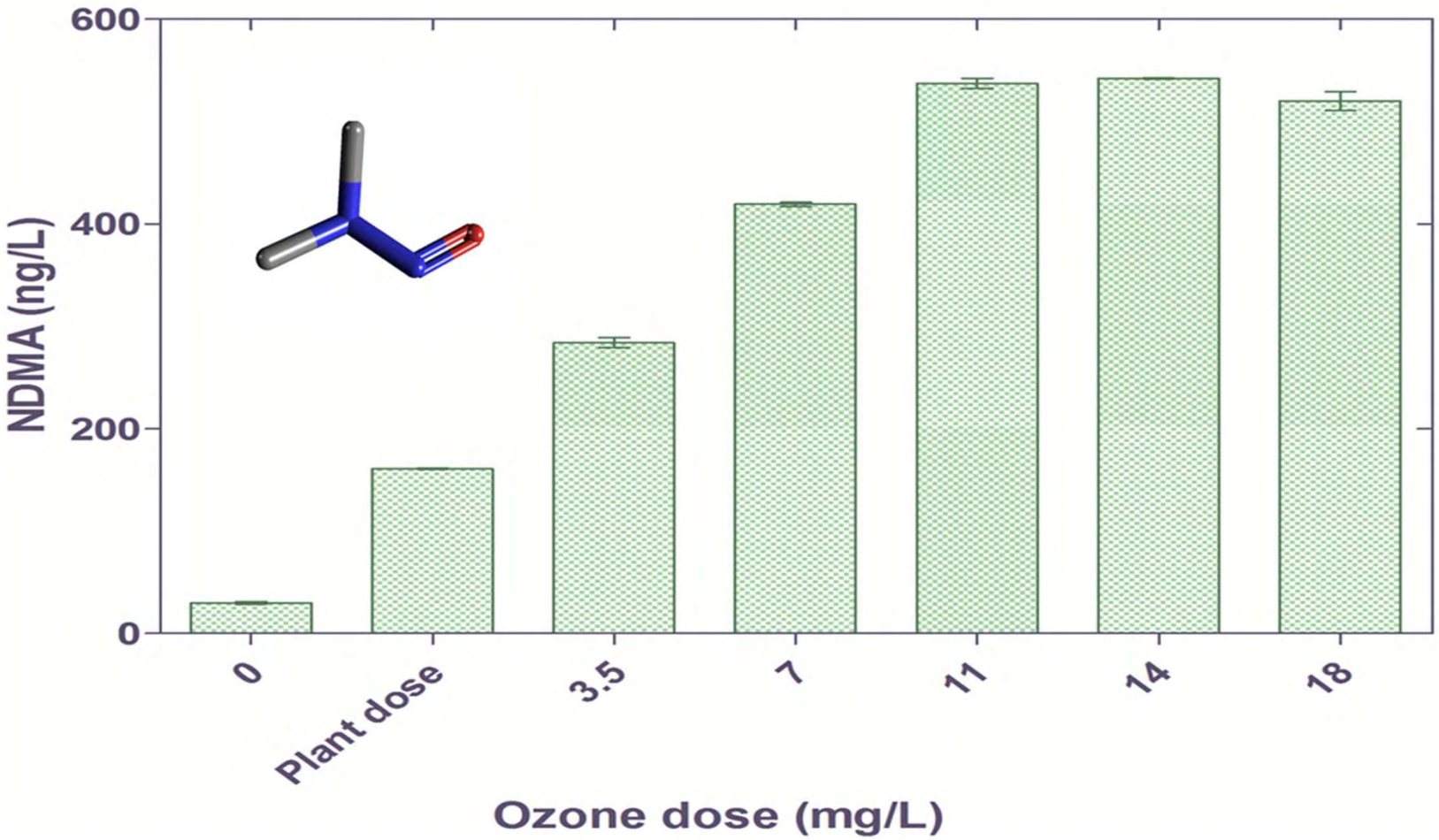
ANN Modeling for Ozone





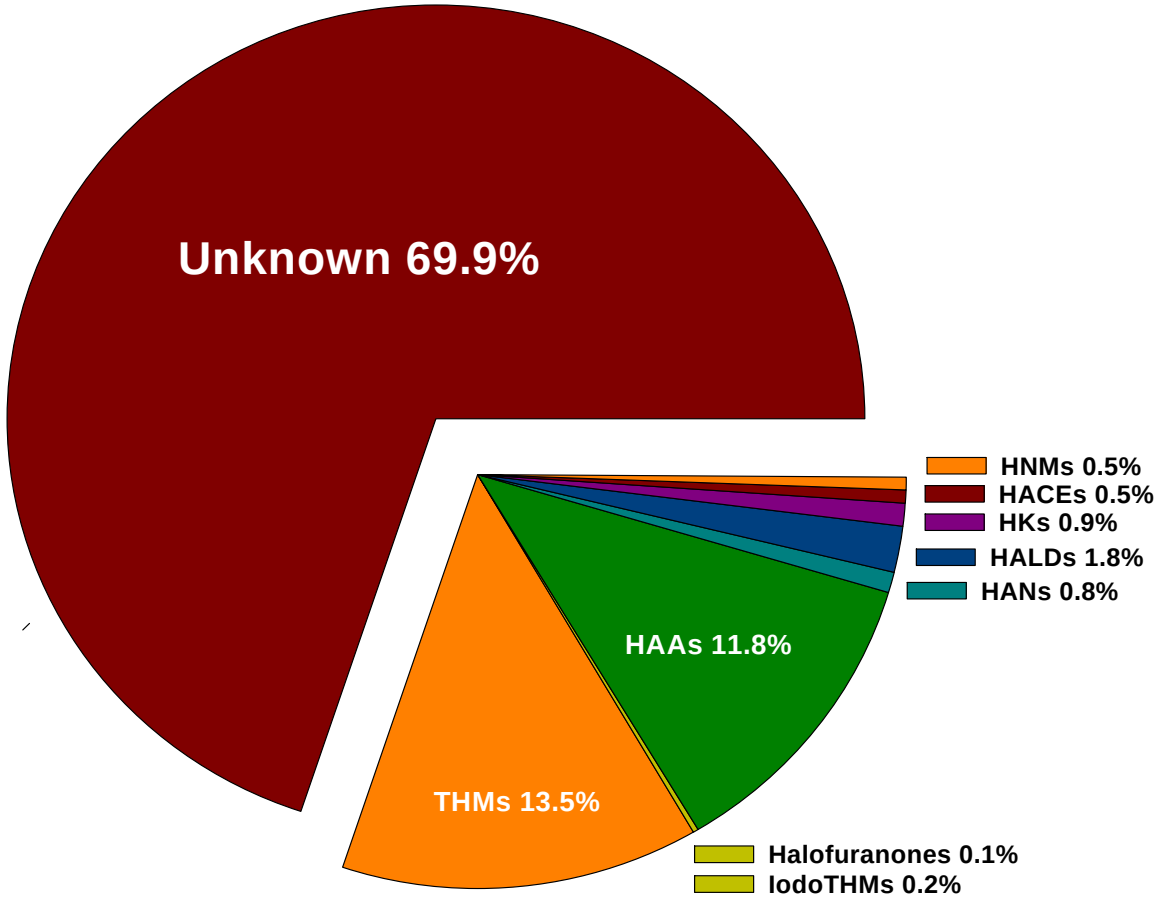
Park M, Anumol T, Snyder SA. *Water Research & Technology* **2015,** *1*, 699-708

NDMA-FP with Ozone



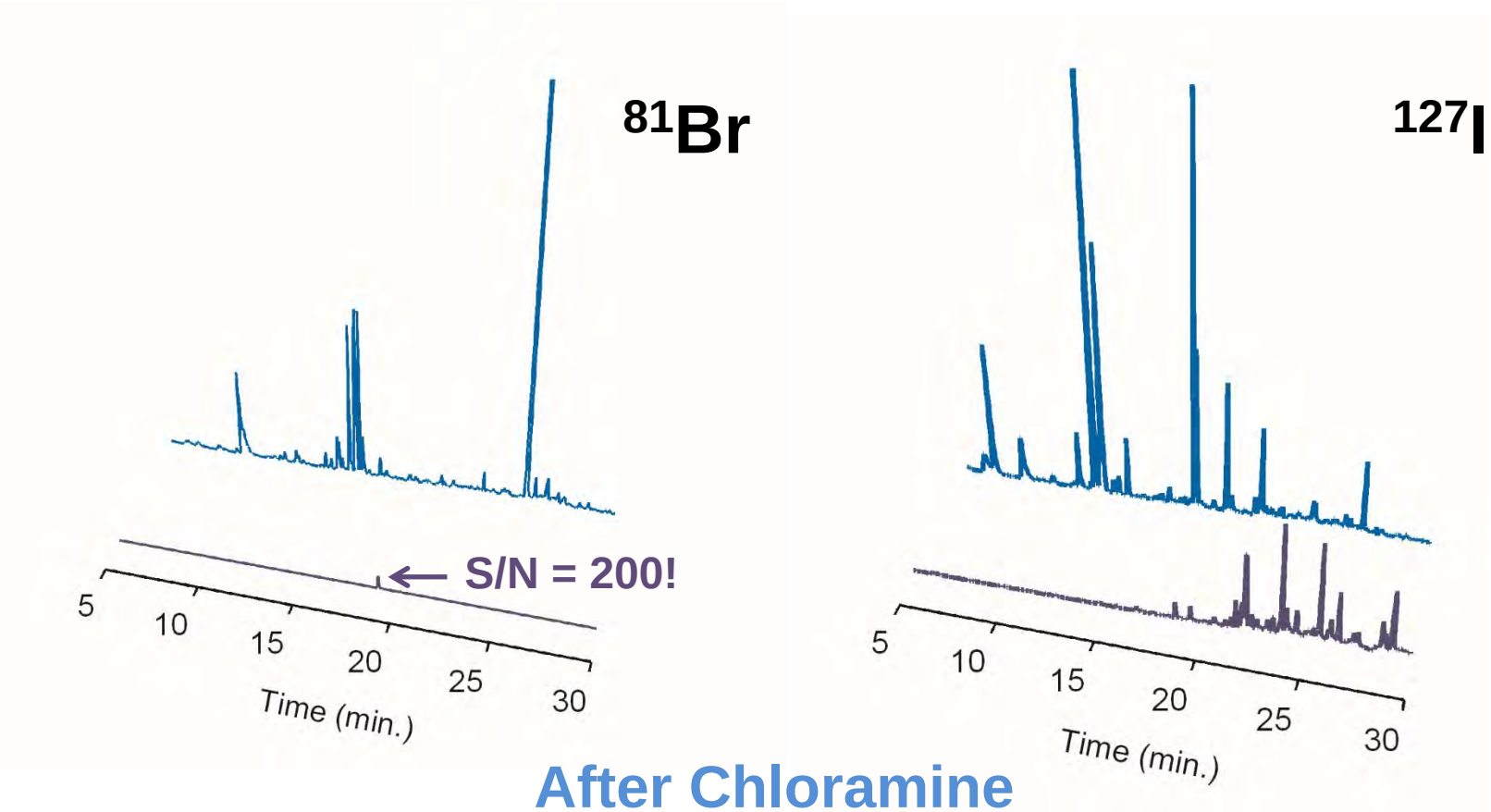
Sgroi, M.; Roccaro, P.; Oelker, G. L.; **Snyder, S. A.**, *ES&T* **2014,** *48* (17), 10308-10315.

Most DBPs Not Identified



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

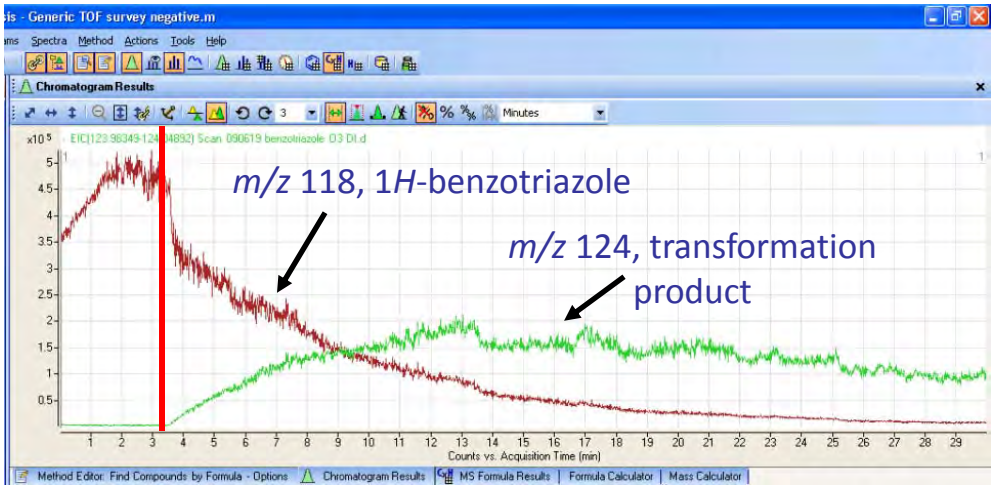
GC-ICP/MS: DBP Formation

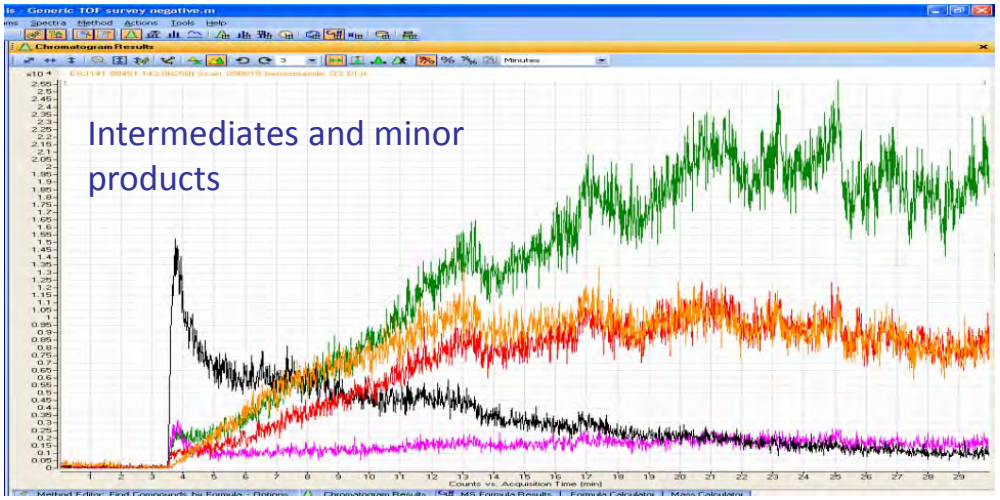


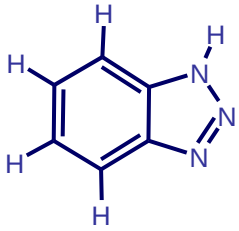
After Chloramine

Before Chloramine

Benzotriazole Transformation Products

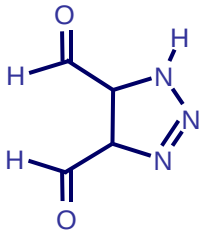






1*H*-benzotriazole

O_3/ ·OH



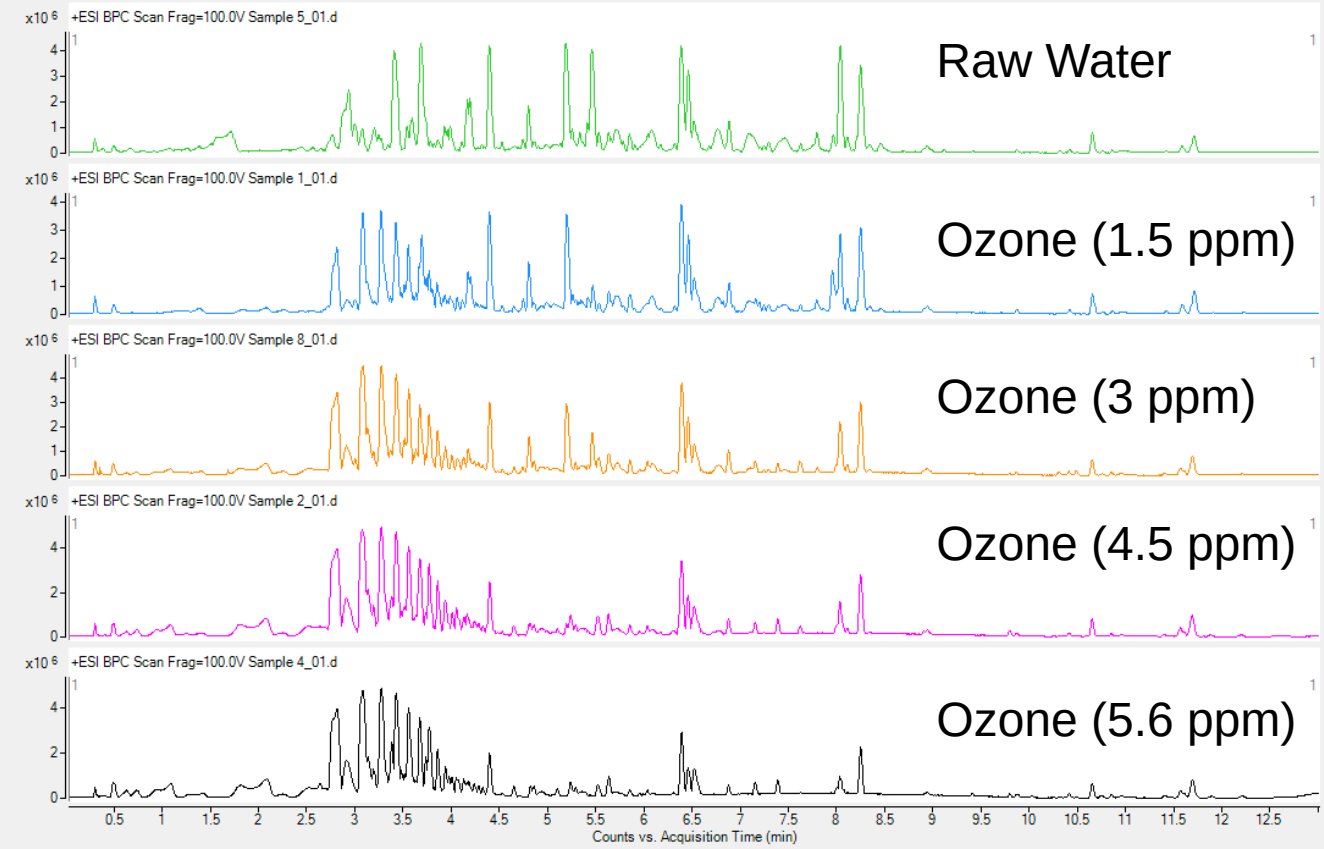
***m/z* 124.01522 (meas.)**
***m/z* 124.01525 (calc.)**
$C_4H_3N_3O_2$

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

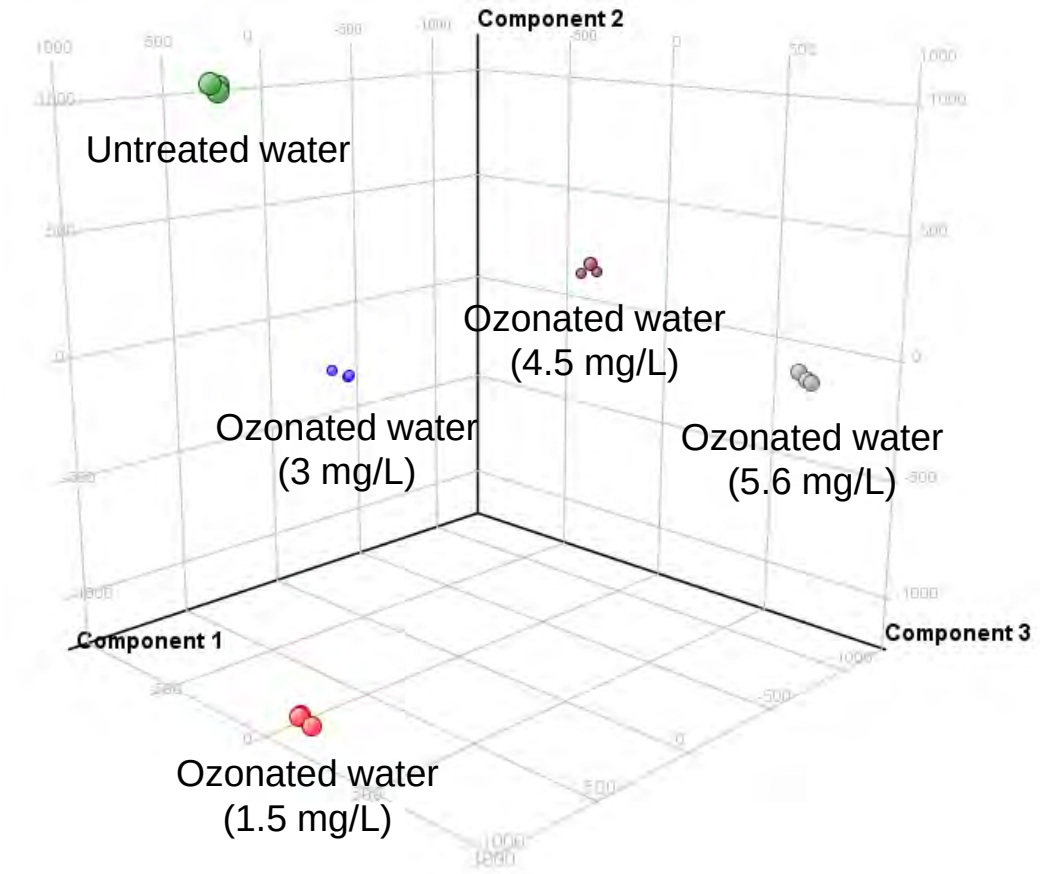
Extraction of Molecular Features Reveals thousands of compounds in each chromatogram

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



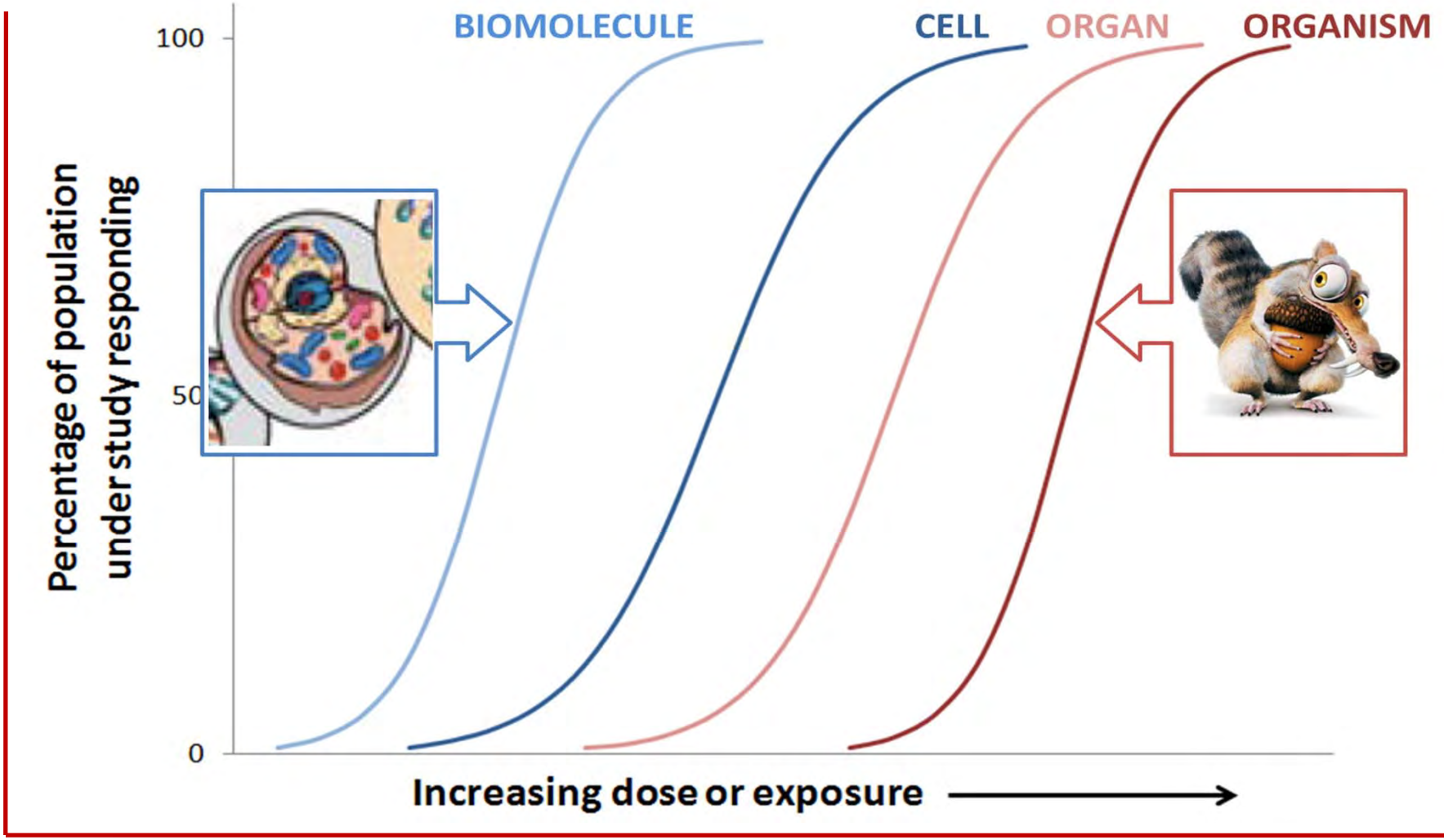
Although chromatograms were all similar for the analyst

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

Relevance?

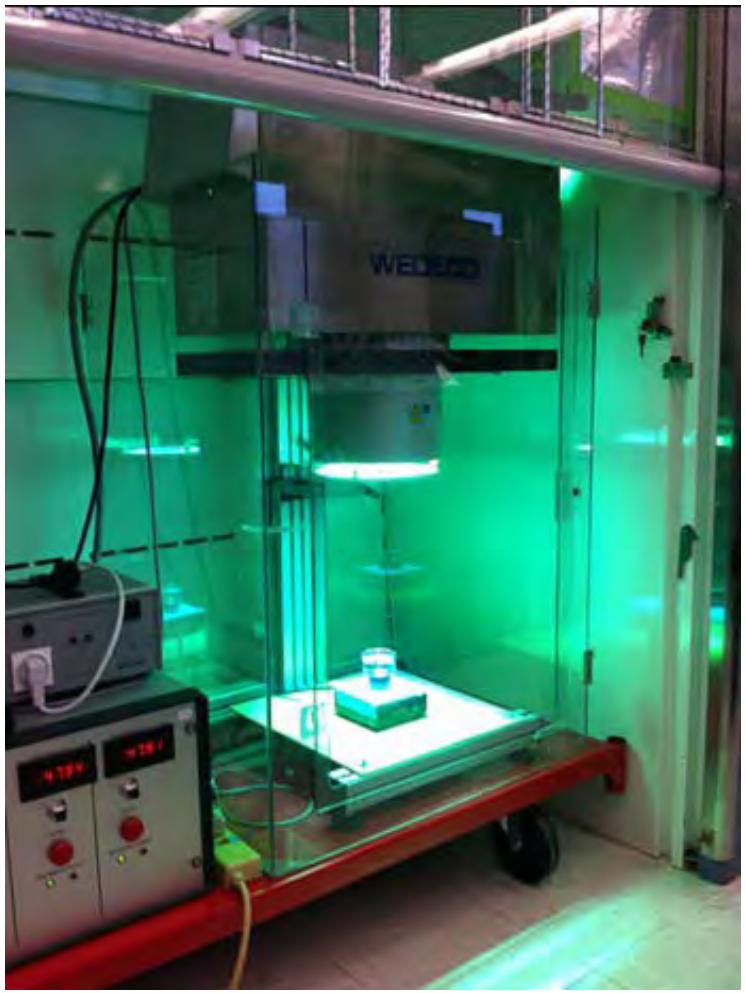
Cells & Metabolomics



Credit: Dr. Fred Leusch – Griffith University, Australia

Cellular Bioassays

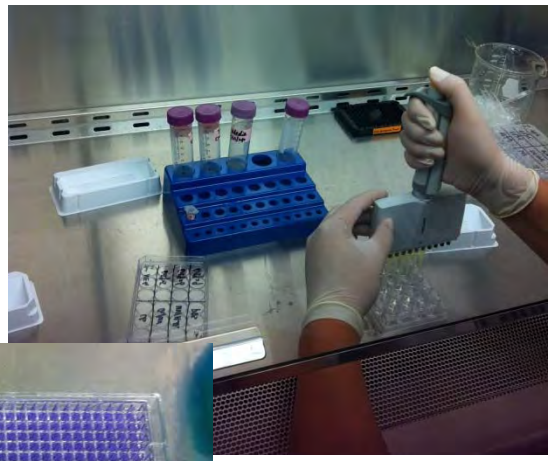
UV Transformation Products



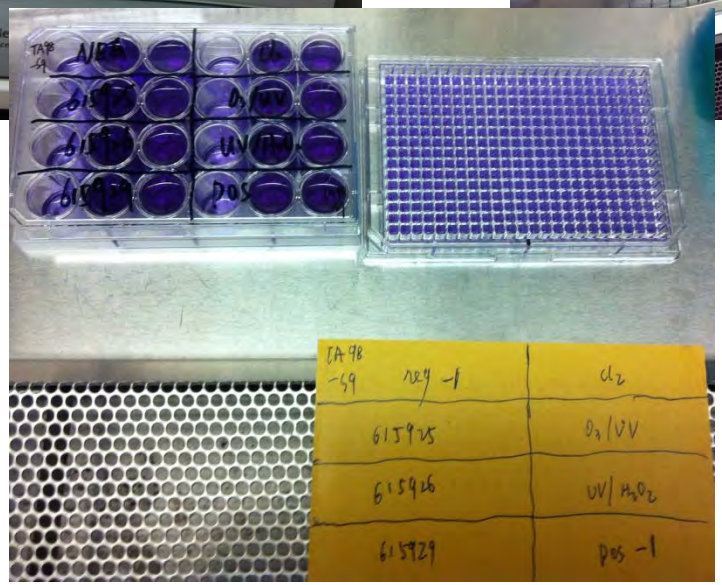
AMESII test

1. Overnight culture

2. Transfer to 24-well plates

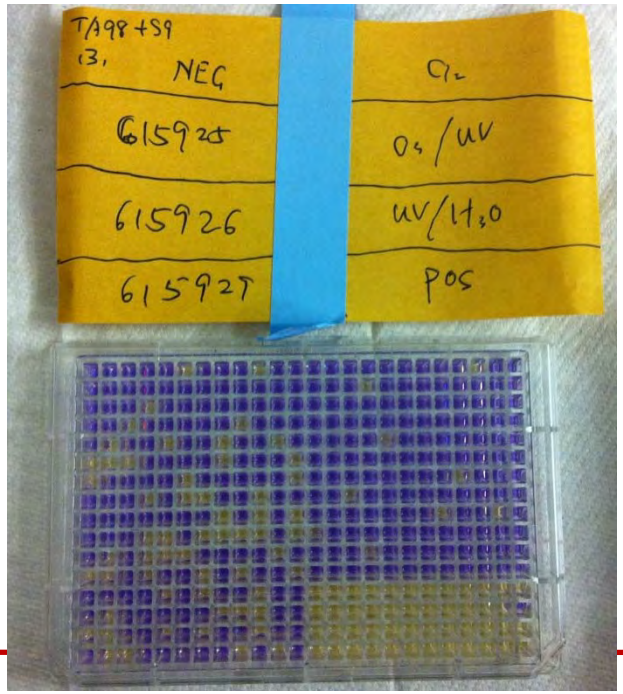


Sample (in DMSO)
S9
Bacteria
Exposure media

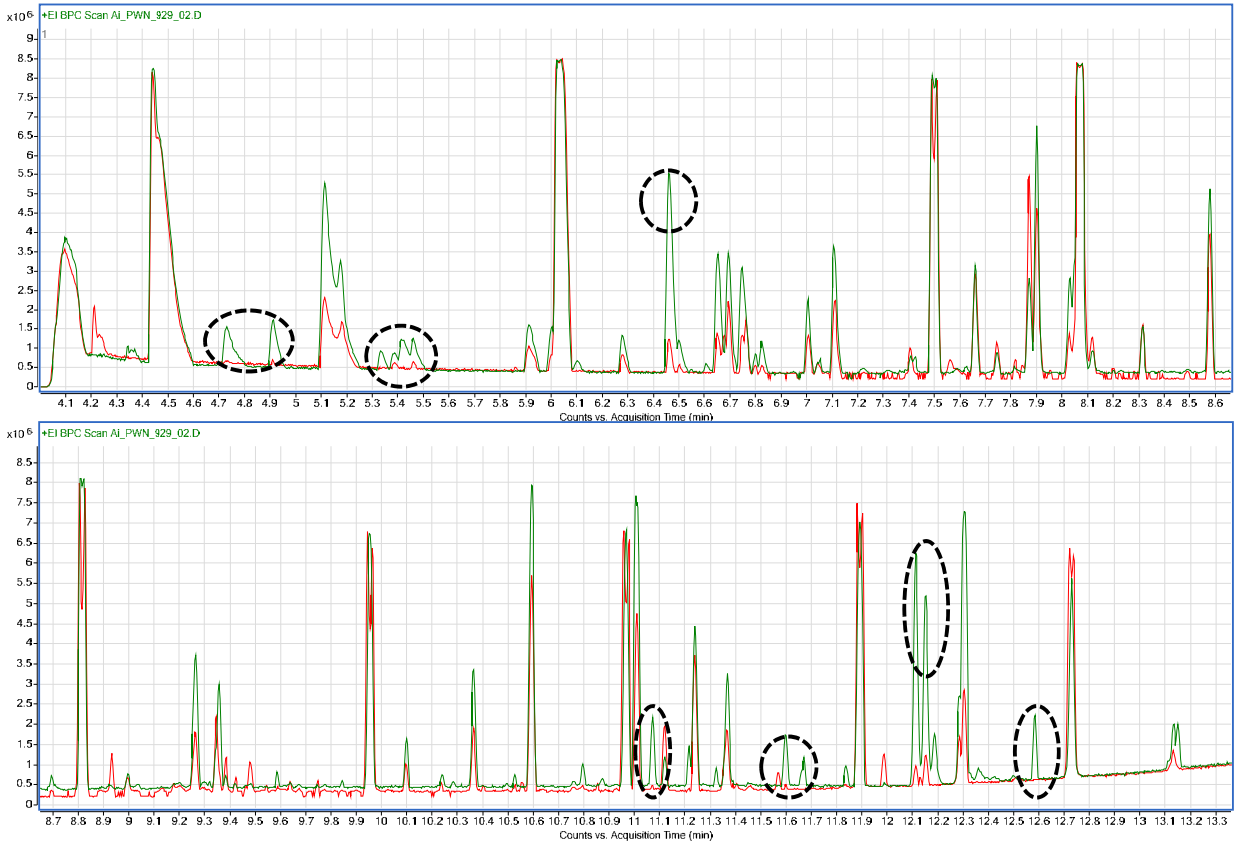


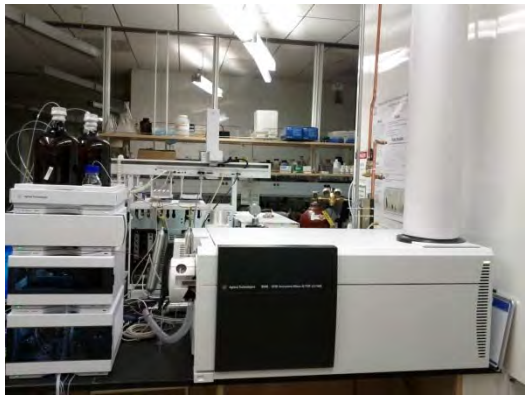
3. Add indicator media, transfer to 384-well plates

4. After 48h, check the results



Discovery of New DBPs





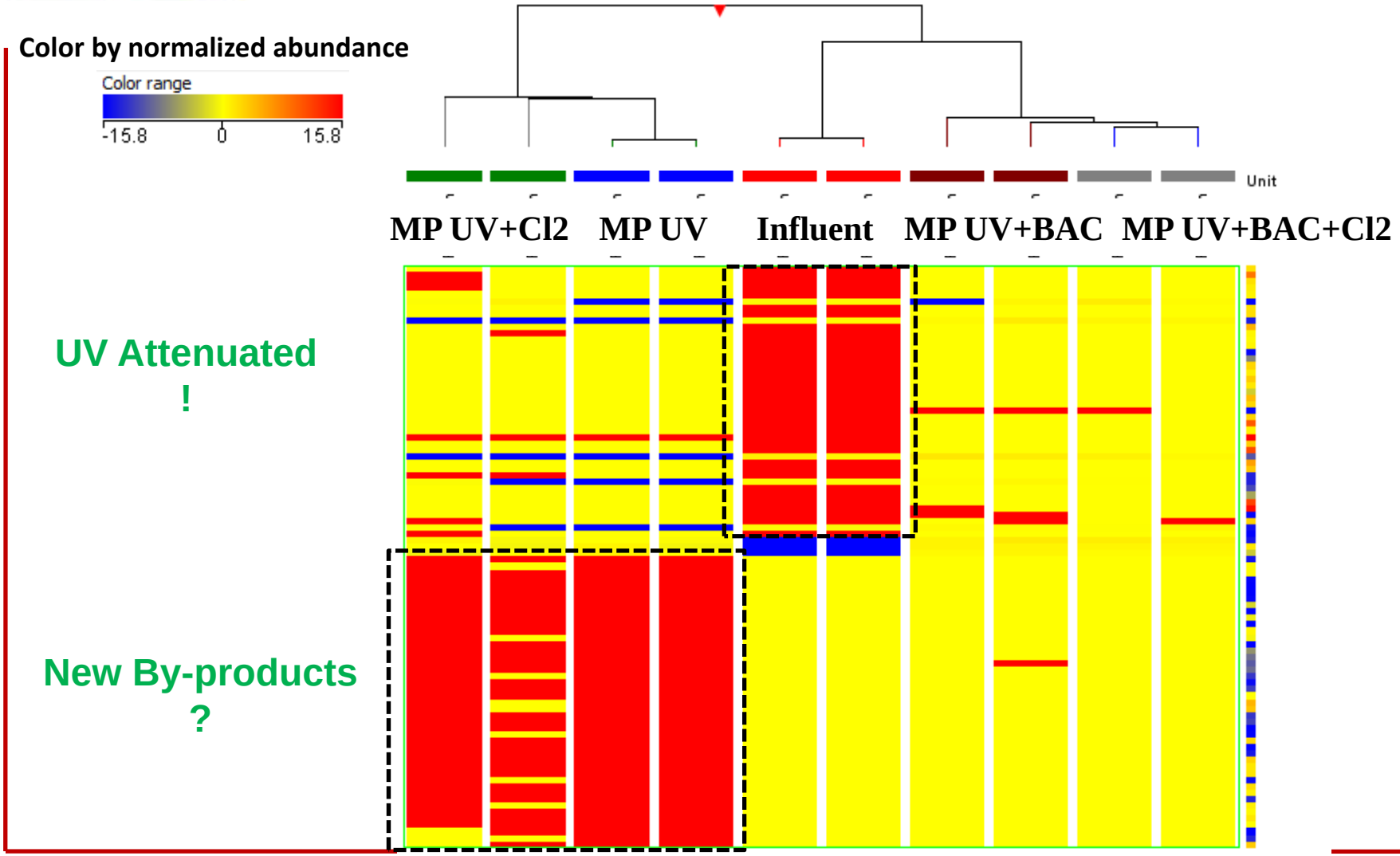
LC-QTOF

GC-QTOF

Red = Before MP UV

Green = After MP UV

Discovery of Novel UV Transformation Products

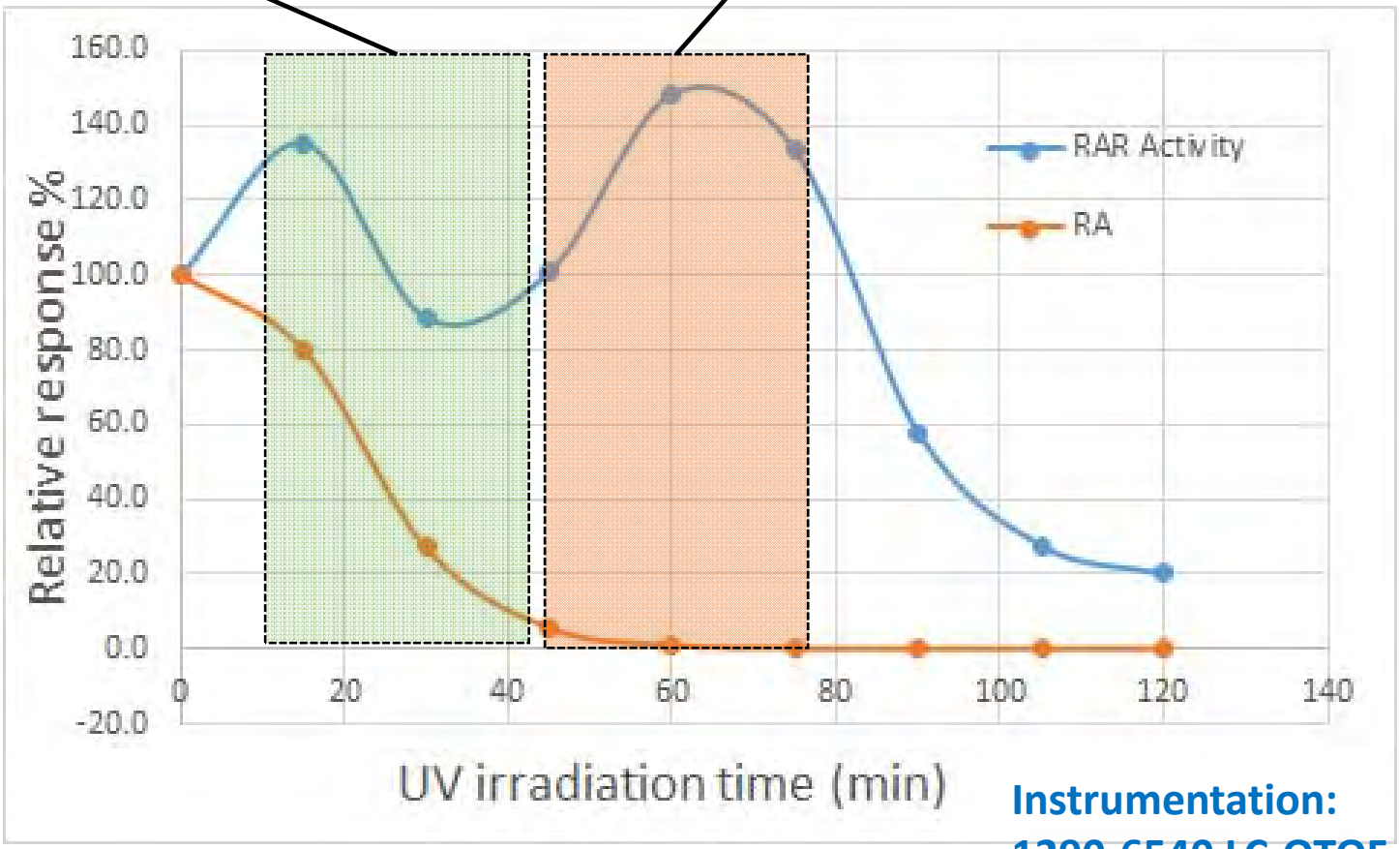


Software: Agilent Mass Profiler Professional (MPP)

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

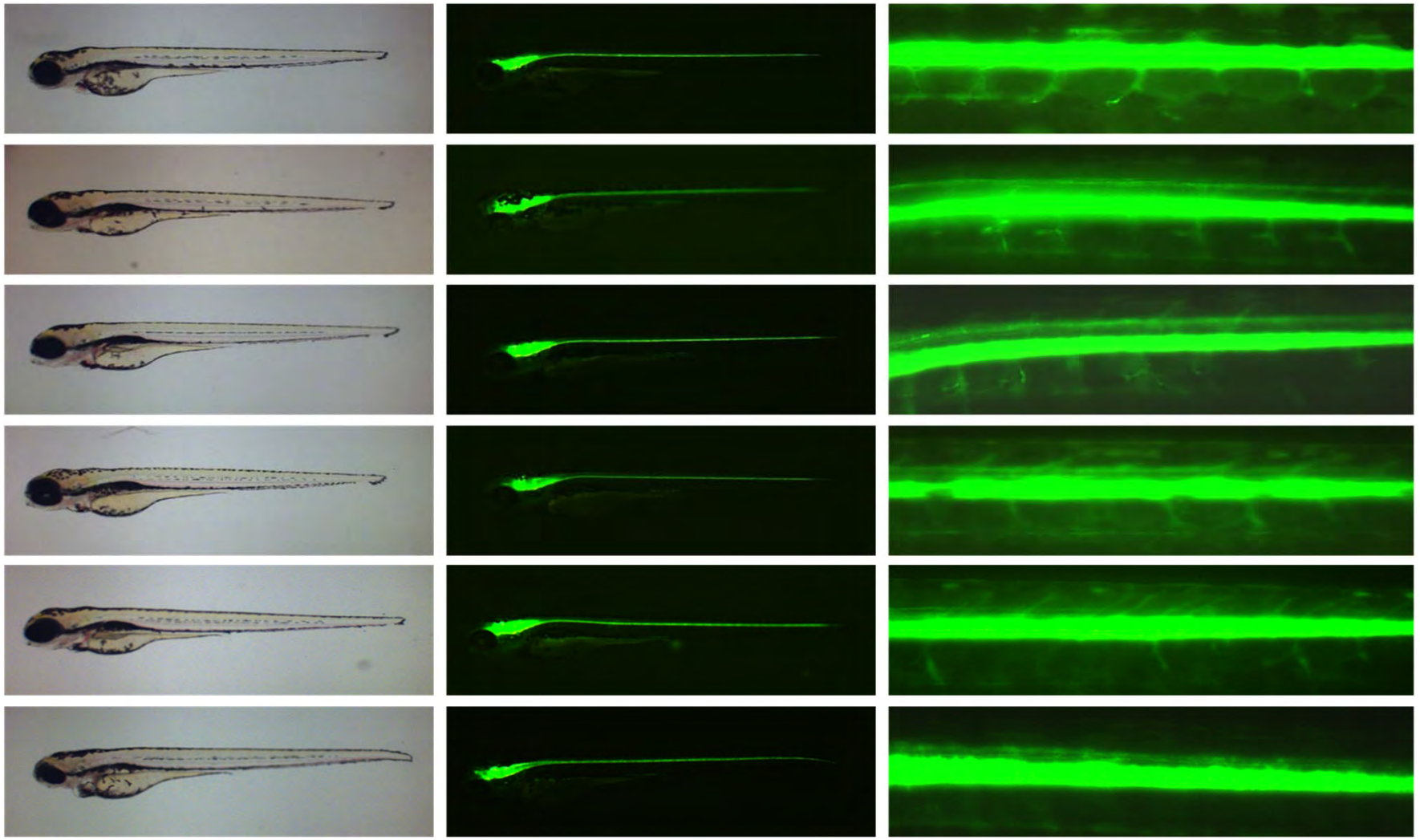
The mixture effect of RA+oxo-RA+OH-RA

Remains unknown, under further investigation in QTOF and MPP



Instrumentation:
1290-6540 LC-QTOF (Agilent)

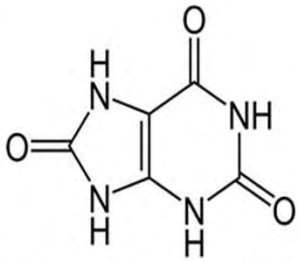
Embryonic Assays



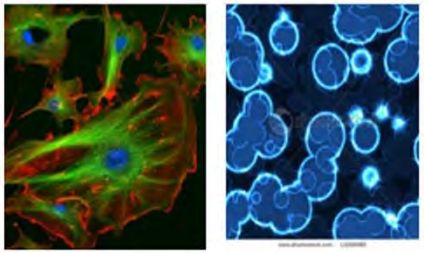
Today, Tomorrow, and Beyond

Toxicology 2012
Where are we now?

High Throughput Screening (Tox21C)



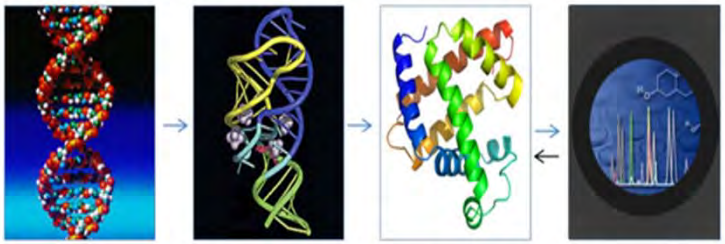
Chemical Characterization



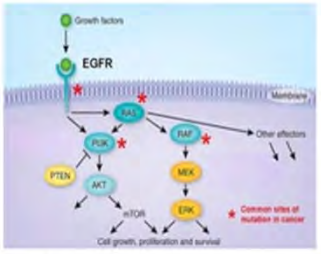
In vitro Assays

Toxicology 2013-2015
A PPP for Integrated Systems Tox

Genomics Transcriptomics Proteomics Metabolomics



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

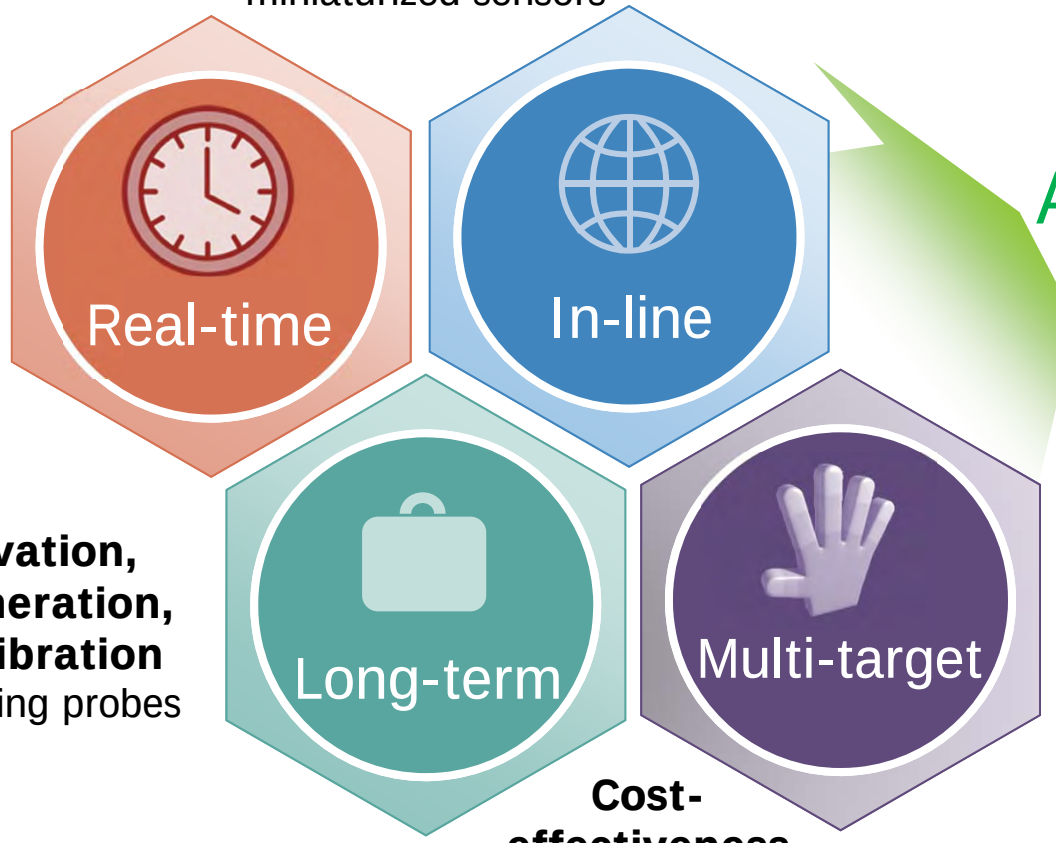

Opportunity
Next Exit

On-Line/Real-Time Sensor Network

The Ideal Sensors

High-throughput
by distribution of
miniaturized sensors

Integration
from sample
pretreatment and
concentration to
sensing system



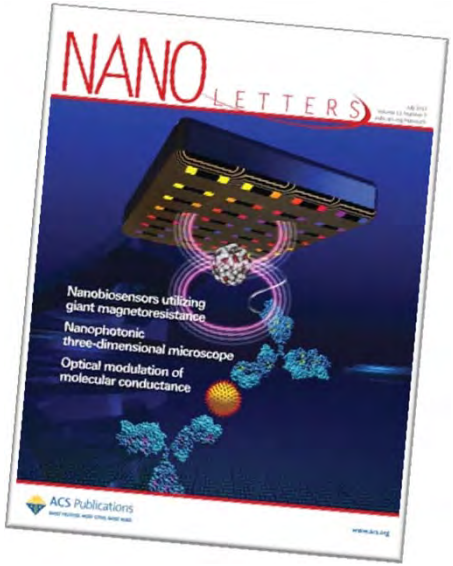
Practical
Application

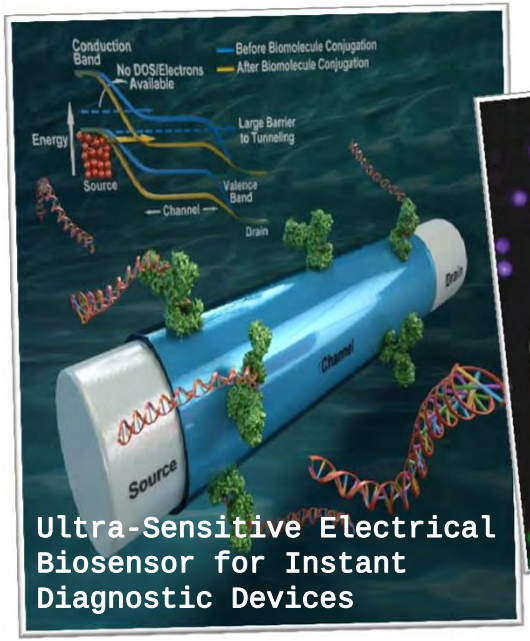
**Activation,
Regeneration,
& Calibration**
Of sensing probes

**Cost-
effectiveness**

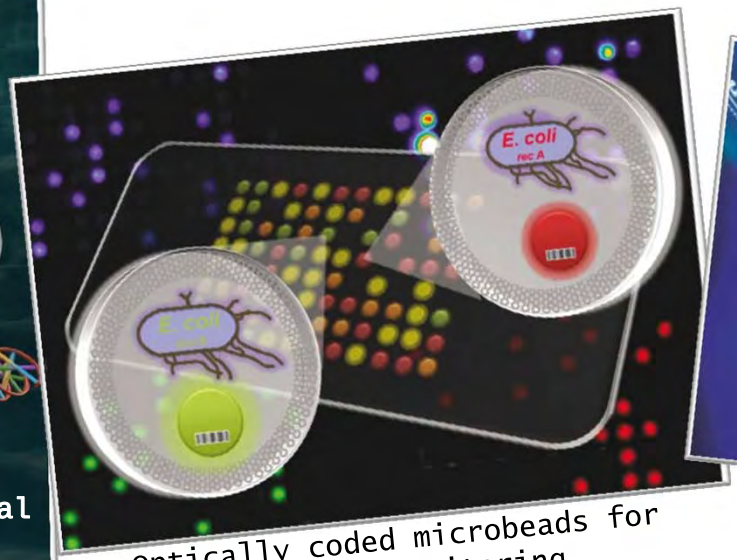
Biosensor

Analytical device that combines a **biological sensing element** with a transducer **to produce a signal** proportional to the analyte concentration





Ultra-Sensitive Electrical Biosensor for Instant Diagnostic Devices

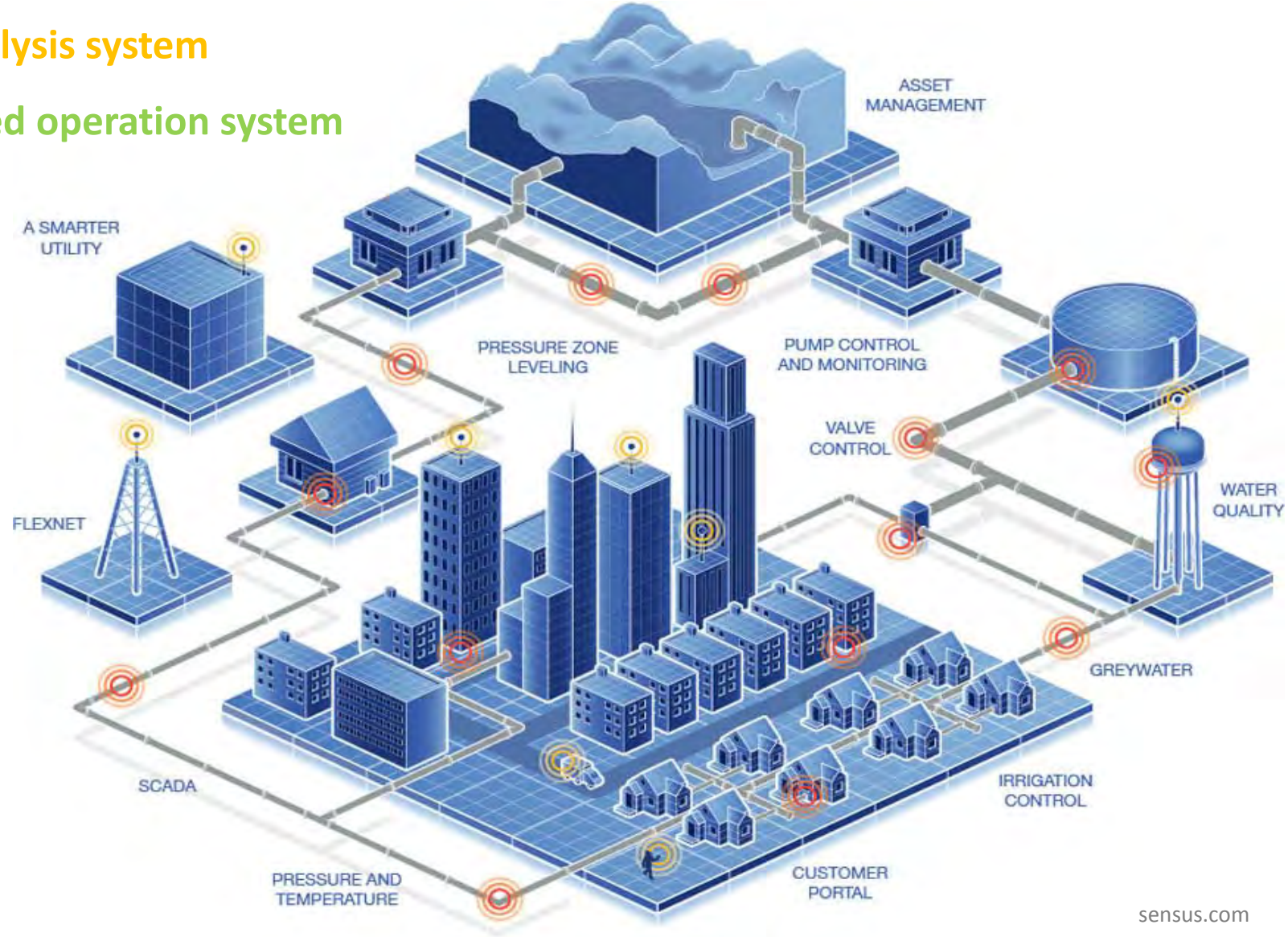


Optically coded microbeads for toxicity monitoring

Diabetes diagnosis

Smart Water Grid

- **High-tech sensor-based monitoring**
- **Data analysis system**
- **Integrated operation system**



sensus.com

Sensors are
at the forefront of a
multidisciplinary science
that marries
the biological world and
the electronic world

The Absolute Certainties

1. More chems will be detected at lower concs.
   a) ~15,000 new chemicals registered/day
   b) Transformation products
2. Current chemical testing paradigm will fail
   a) Does not account for mixtures
   b) Animal testing slow, high doses, unpopular
3. Bioassays will be the way of the future (soon)
   a) Step in the right direction for monitoring
   b) Relatively in expensive and fast
4. Mass spectrometry is great, but…
   a) Only detectable if ionized (and optimized)
   b) Must consider GC, LC, and IC interfaces

Critical Research Needs

1. More validation of S&I approach at full-scale
2. More consideration of sampling bias
   a) Diurnal, location, holding times, etc.
   b) Especially in regard to bioassay methods
3. Rational discussion regarding appropriate detection limits to better optimize methods
4. Screening of RO Brines for initial characterization of contaminant occurrence
   a) ≈5-10x concentration of source water
   b) Passive samplers for bioaccumulation studies and composite samples for hydrophilic contaminants

Acknowledgements

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