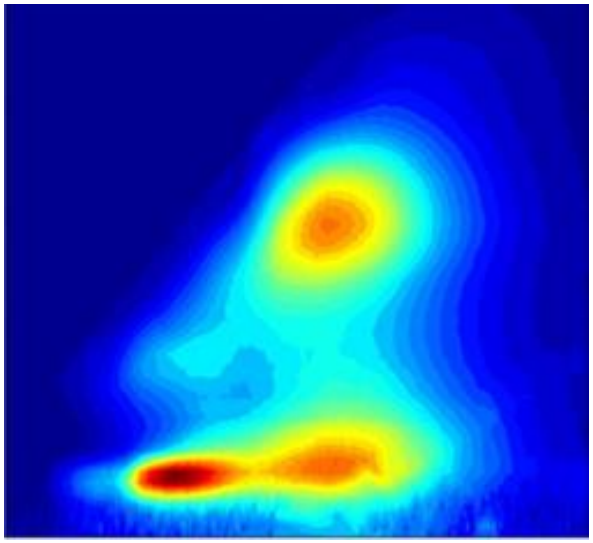
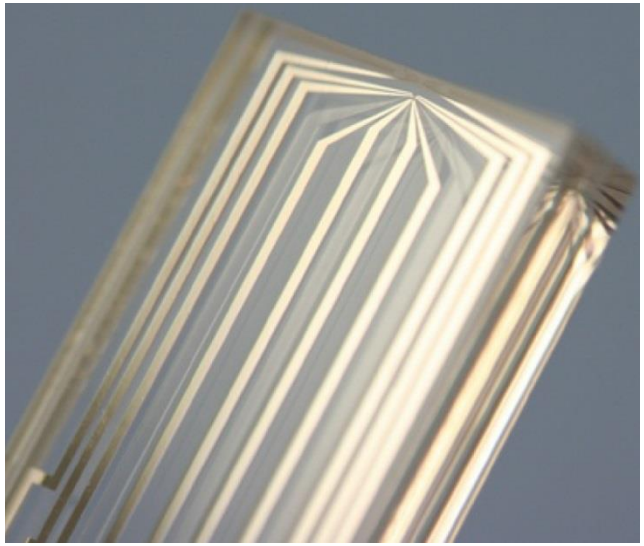
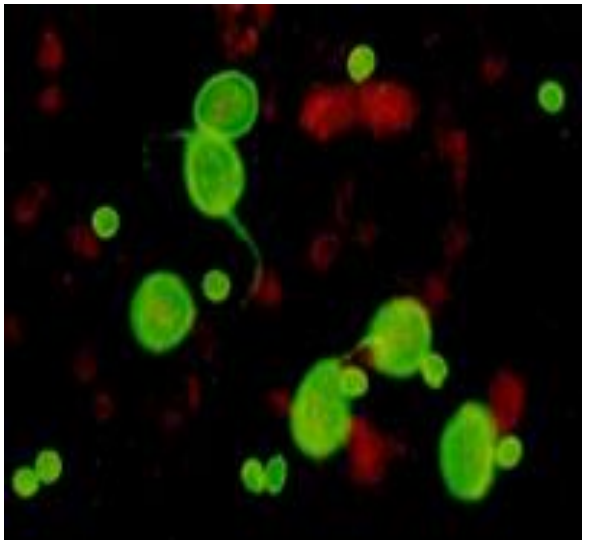
Advances in Water and Wastewater Metrology







Shane Snyder, Ph.D.
Professor & Co-Director

Ian Pepper, Ph.D.
Professor & Co-Director

azengineering

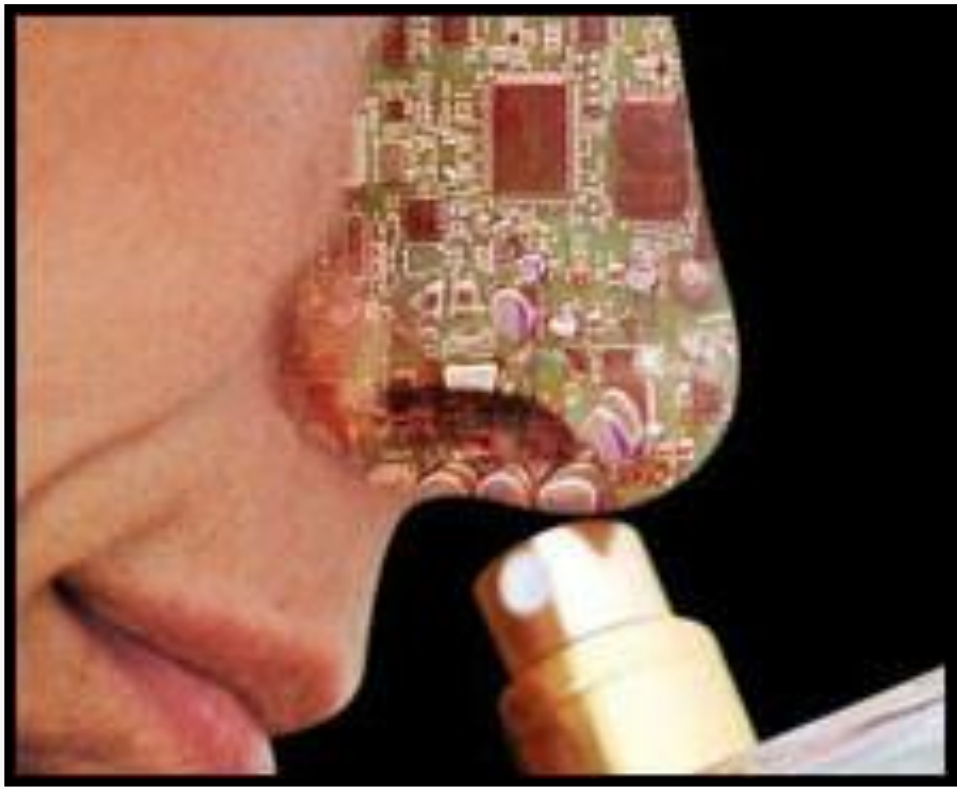
WEST CENTER
WATER & ENERGY SUSTAINABLE TECHNOLOGY

Industries that Rely on Sensors

I. Transportation and Military (aircraft, trains, guidance)

II. Medical and Health-Care (diagnostics, drug delivery)

III. Security and Enforcement (TSA, DEA, EPA)



Sensor Applications for Water

I. Ensuring water quality and treatment integrity (RO credit)

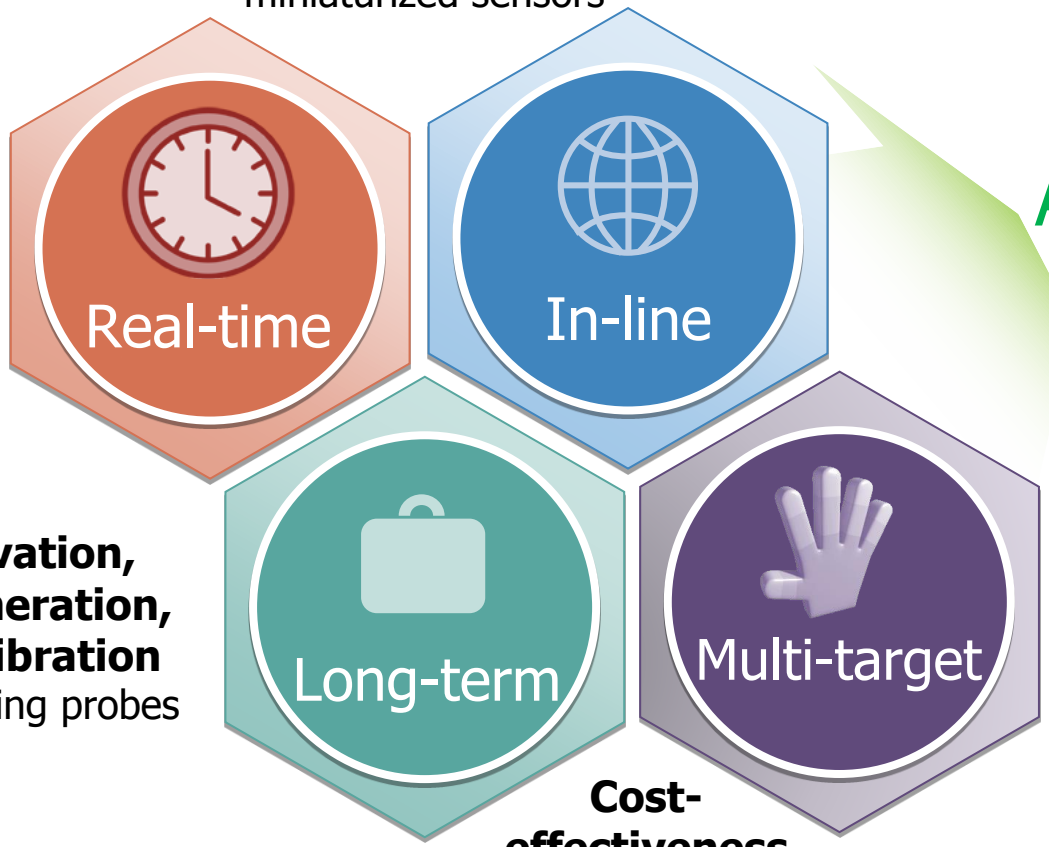
II. Optimization of chemical dosing & mixing (cost savings)

III. Speed & automation (potable reuse, carbon regen.)

The Ideal Sensors

High-throughput
by distribution of
miniaturized sensors

Integration
from sample
pretreatment and
concentration to
sensing system



Practical
Application

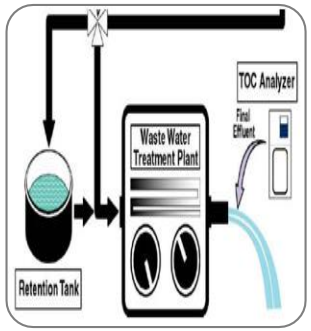
**Activation,
Regeneration,
& Calibration**
Of sensing probes

**Cost-
effectiveness**

Physical/Chemical sensor

A device that transforms **chemical information**, ranging from the concentration of a specific sample component to total composition analysis, **into an analytically useful signal**

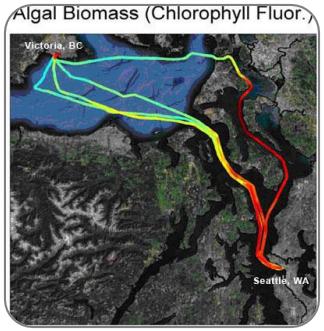
- Organic carbon sensor



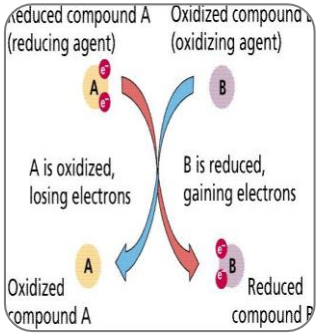
- Ion-selective electrode

- UV/VIS spectrometer

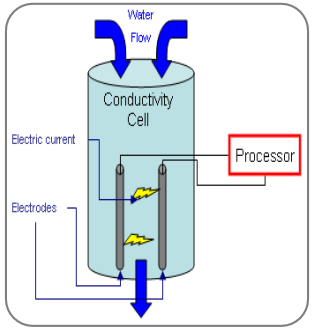
- Fluorometer



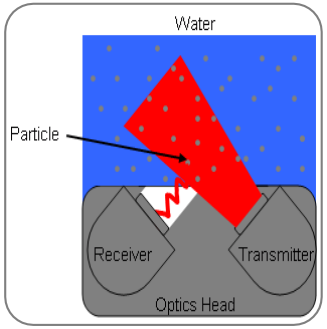
- ORP meter



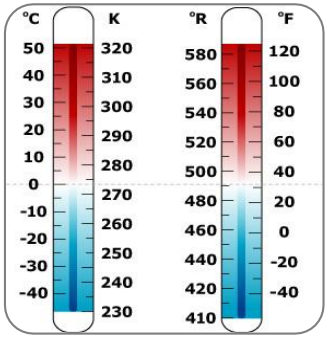
- Conductivity



- Turbidity

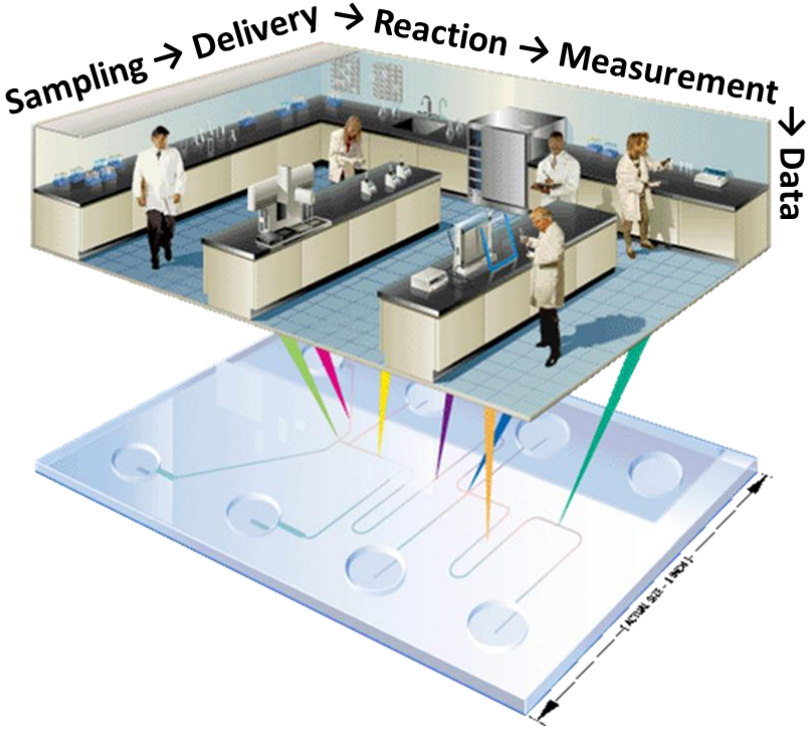


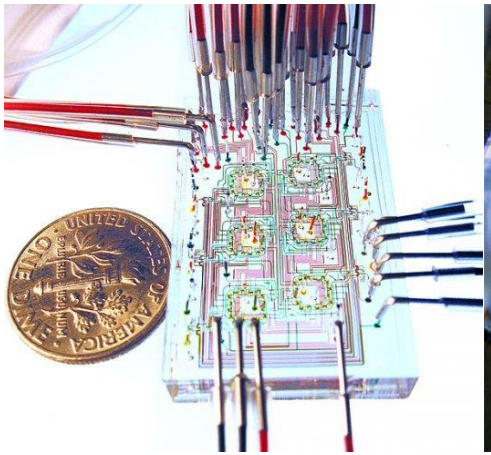
- Temperature



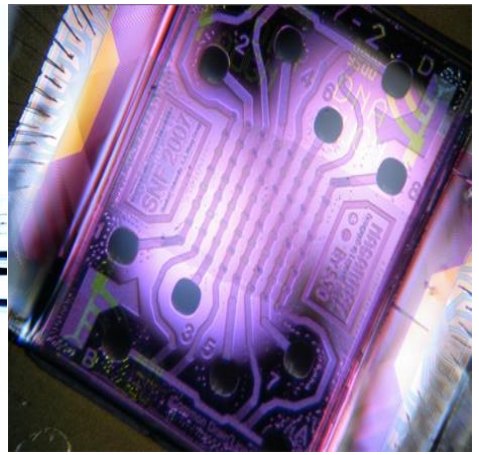
Lab-on-a-chip (LOC)

A microfluidic device that integrates one or several **laboratory functions**, such as sampling, mixing, reaction, and separation **into a small single chip** (only millimeters to a few square centimeters in size)





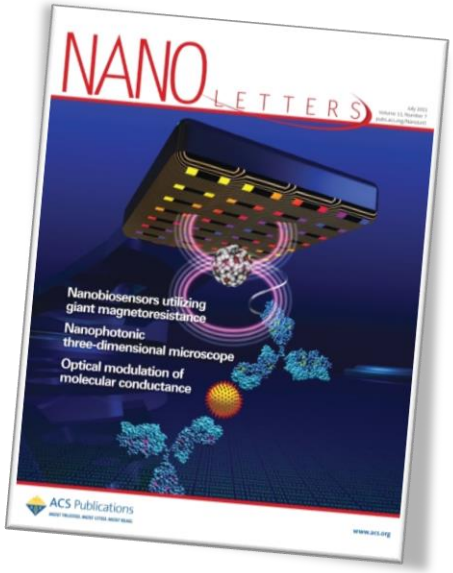
www.popsci.com

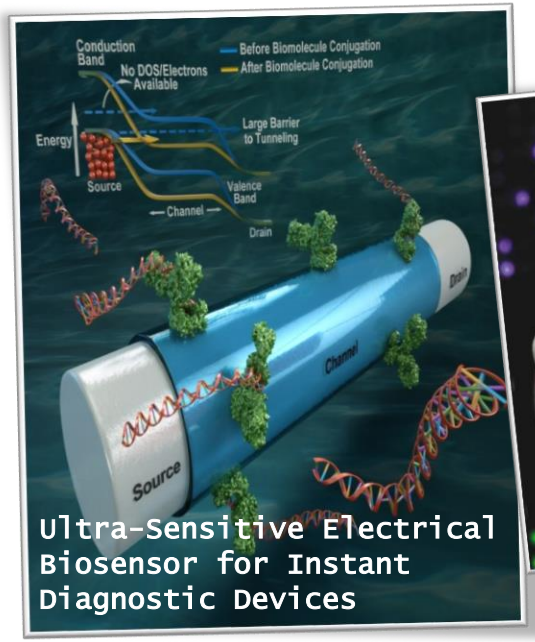


scopeblog.stanford.edu

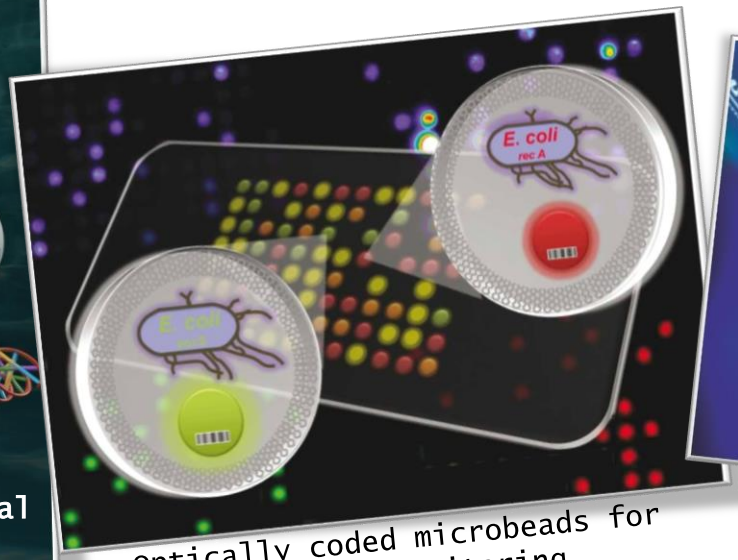
Biosensor

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


Can treatment make this drinkable???

NRC Report on Reuse (2012)

USA TODAY

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

Report: Drinking wastewater preferable to wasting it

Council touts it as potable after treatment

By Wendy Koch
USA TODAY

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

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

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

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

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

By Mark Greenberg for USA TODAY

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

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

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

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

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

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

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

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

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

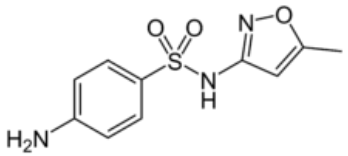
"…distinction between *indirect* and *direct* potable reuse is not scientifically meaningful…"


新newWater
A PRODUCT OF PUB

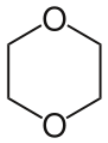
Contaminants potentially detectable in sewage

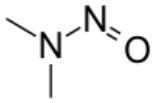
Chemical origins

Pharmaceuticals



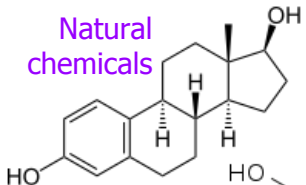
Industrial chemicals



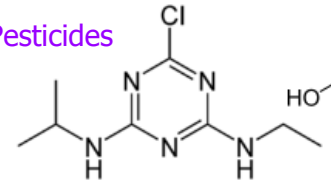


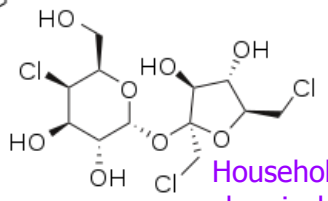
Transformation products

Natural chemicals



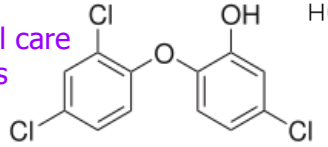
Pesticides



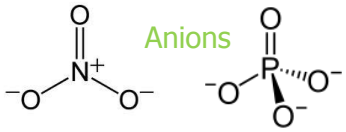


Household chemicals

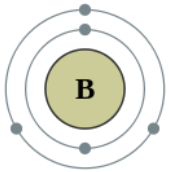
Personal care products



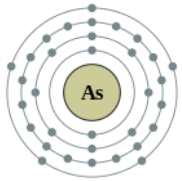
Anions



Cations



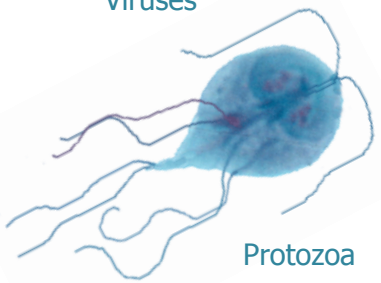
Metals



Microbial origins

Viruses

Bacteria

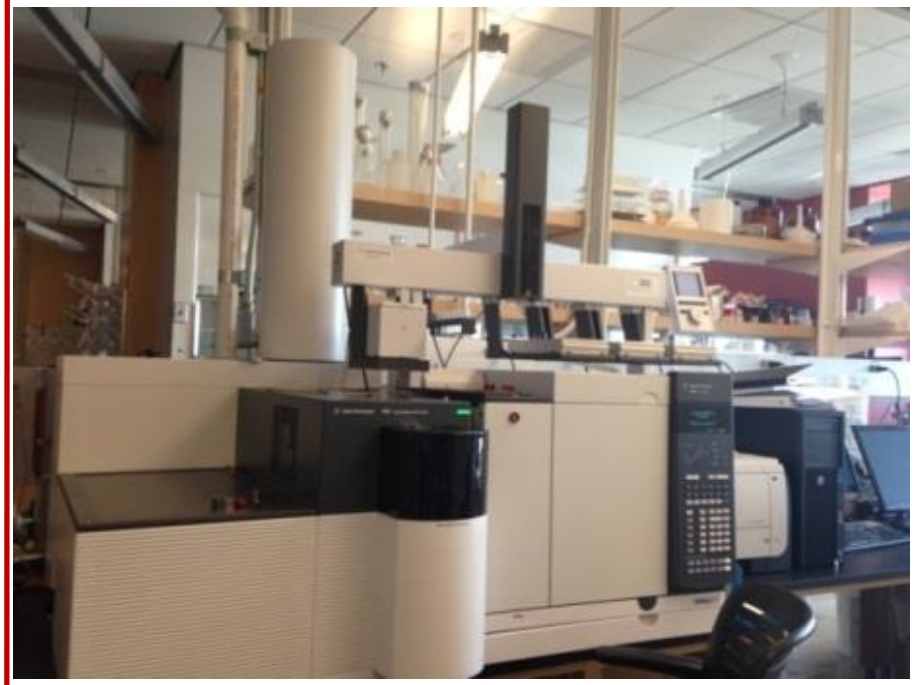


Protozoa

Helminths

Instrumentation:
What's in the Water and What's Changing?

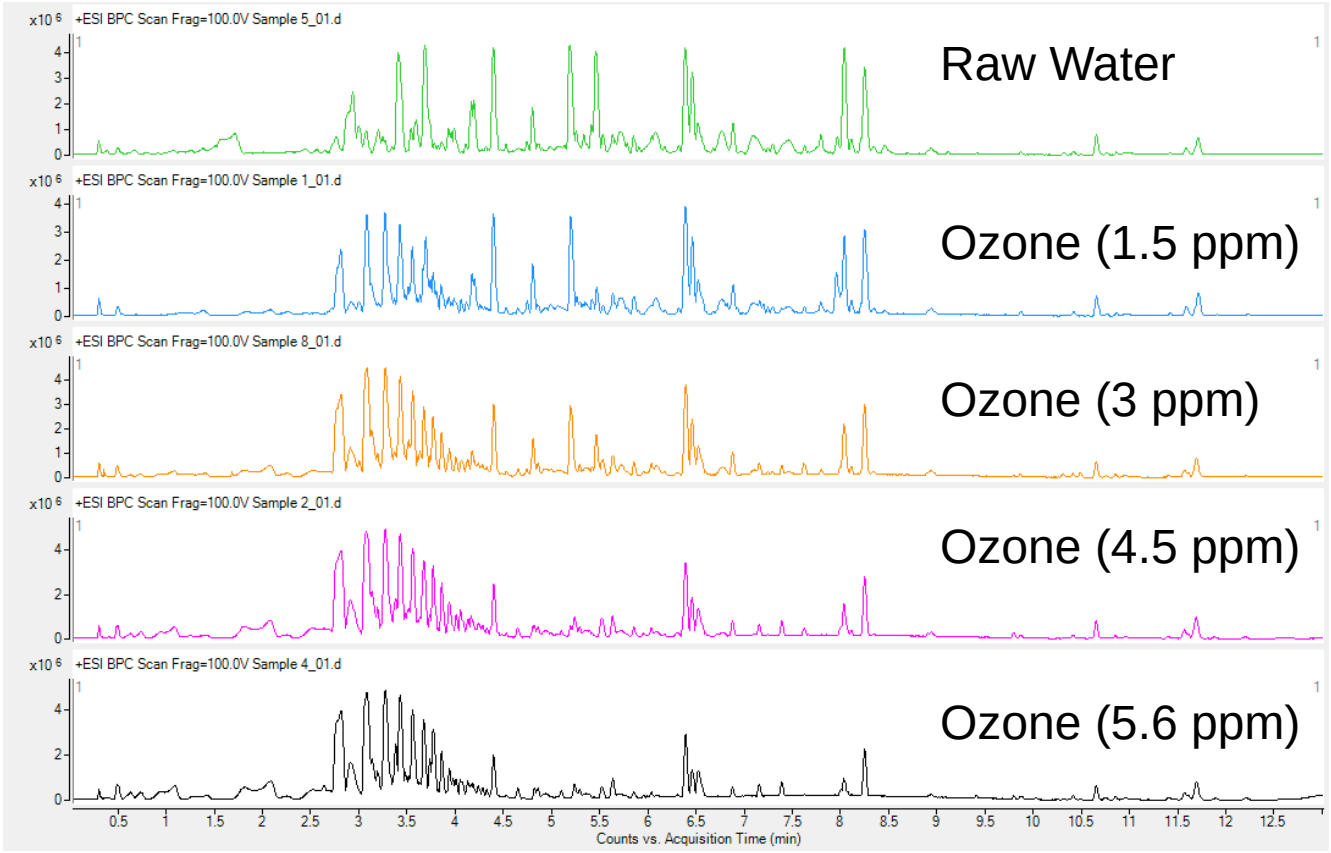
Agilent 7200 GC-QTOF



Agilent 6540 LC-QTOF

WATER TREATMENT & ANALYSIS OF UNKNOWNS

Searching for unknown in water



Chromatograms Very Similar

Extraction of Molecular Features Reveals Almost 1,000 compounds in each chromatogram

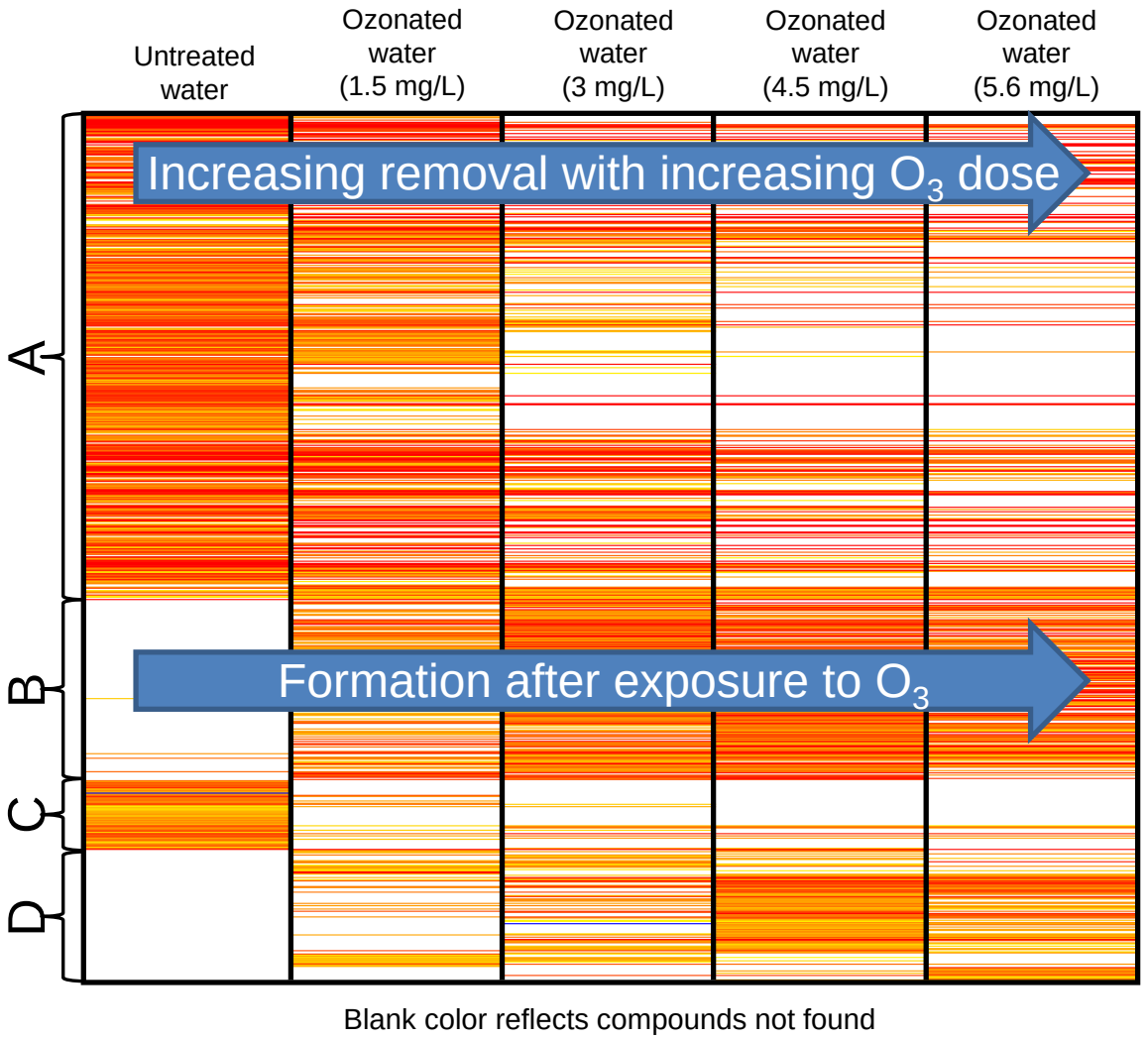
Further Data Processing Requires Statistical Software

WATER TREATMENT & ANALYSIS OF UNKNOWNS

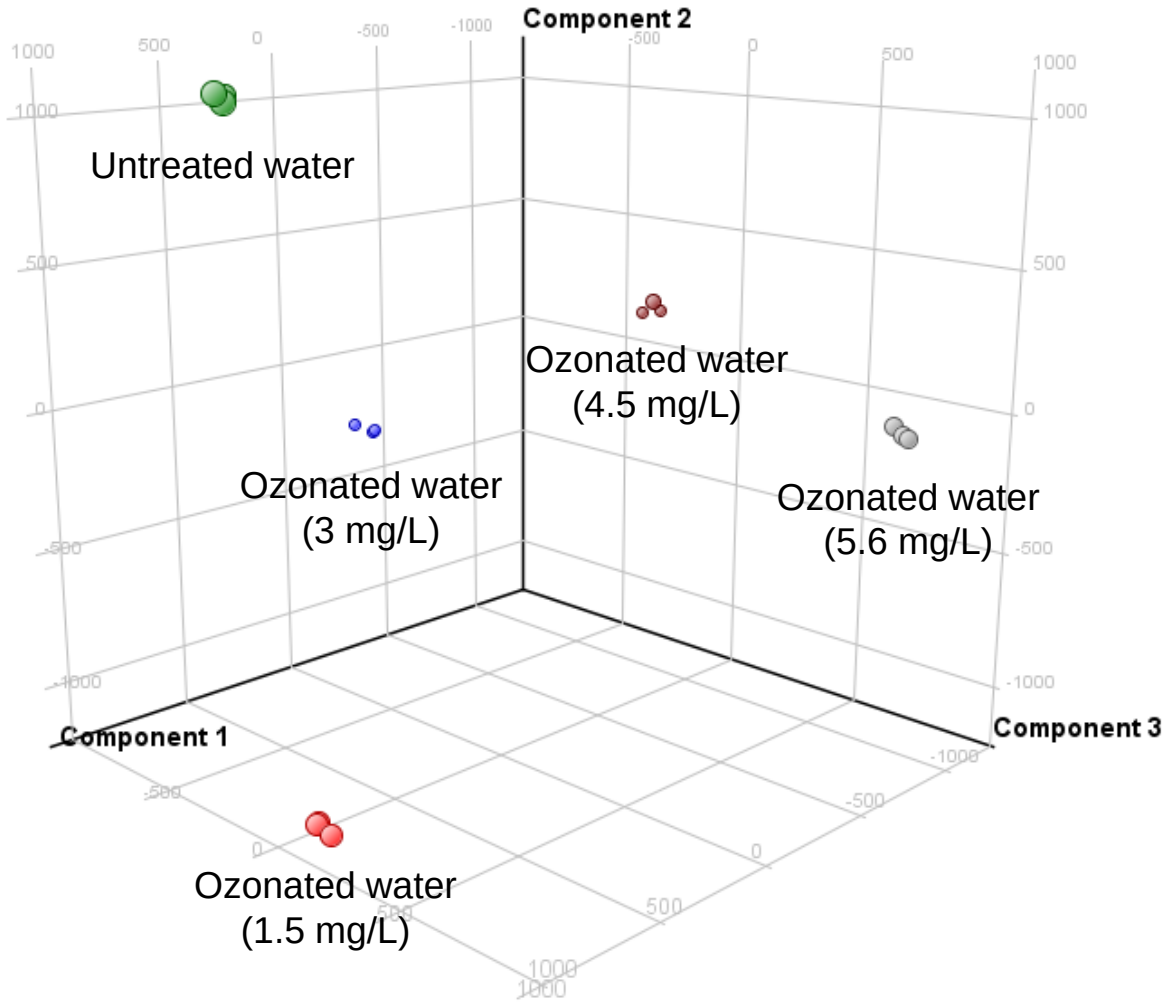
Although chromatograms were all similar for the analyst, clear differences appear on the heatmap

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

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



WATER TREATMENT & ANALYSIS OF UNKNOWNS

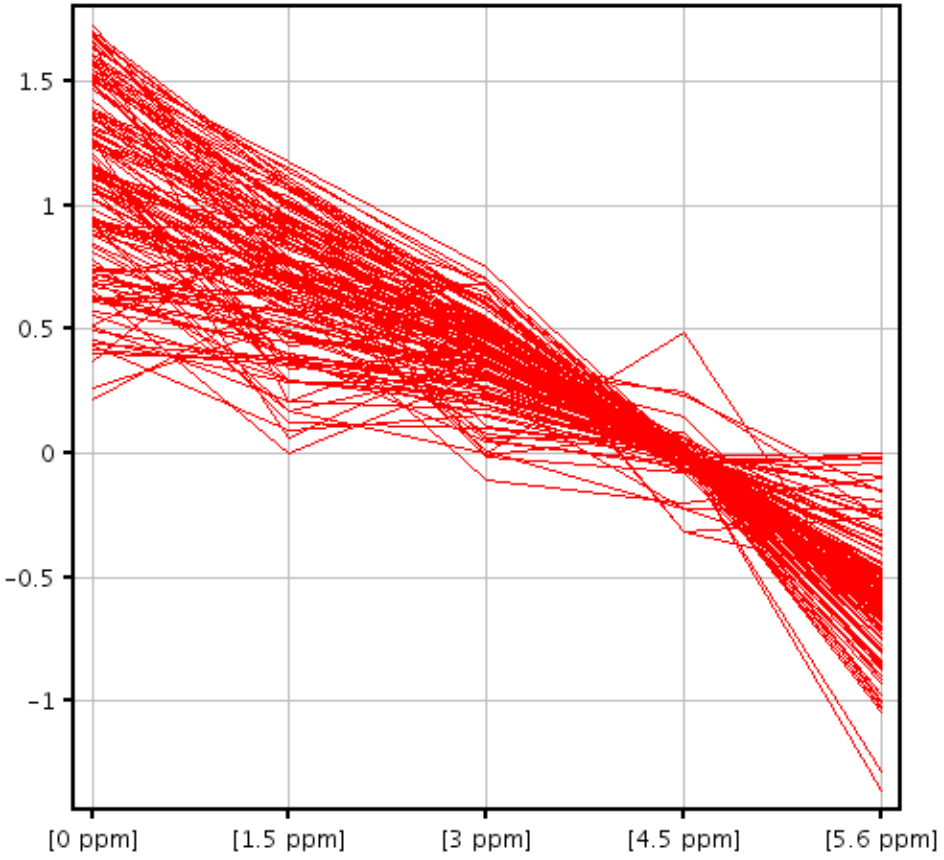


Although chromatograms looked very similar and identified more than 1000 compounds –

Statistical software identifies unique compound clusters within the complex spectra

Monitoring Ozonation Through LC-QTOF Analysis

Cluster unknown compounds around routinely analyzed PPCPs



Cluster around DEET

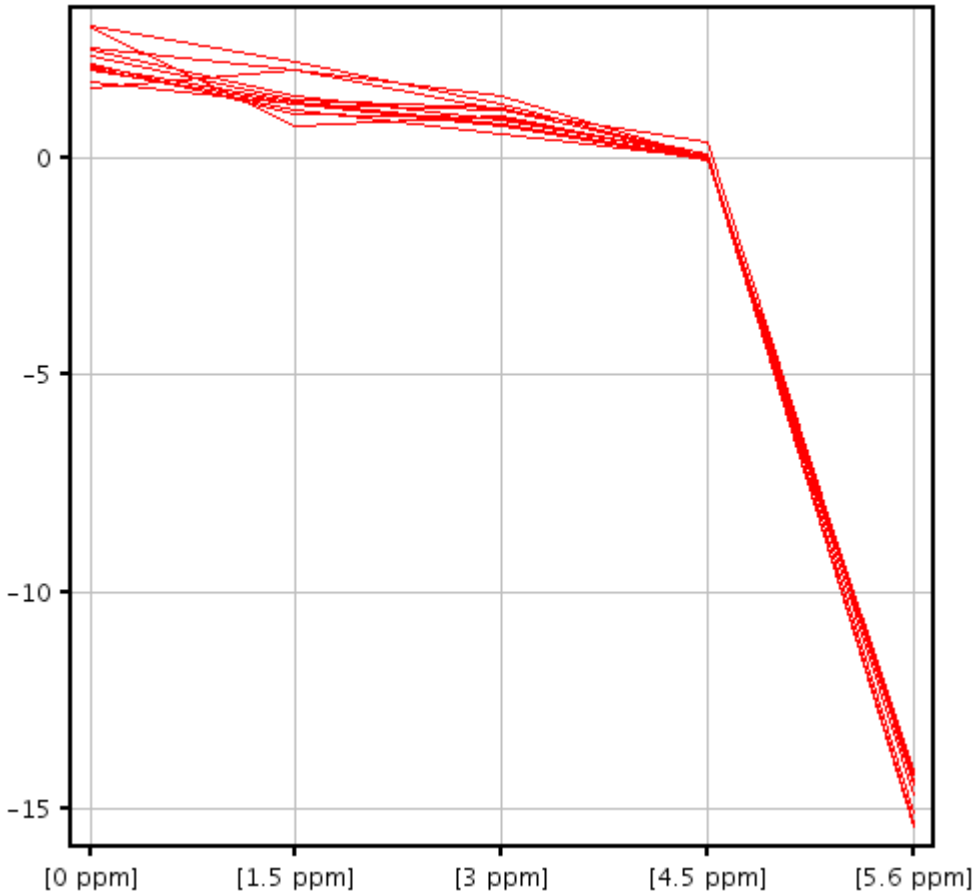
Compounds with progressive attenuation with increasing ozone dose

Overall moderate attenuation

Cluster includes 130 compounds

Monitoring Ozonation Through LC-QTOF Analysis

Cluster unknown compounds around routinely analyzed PPCPs

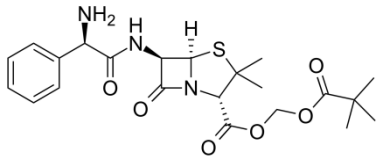


Cluster around Fluoxetine

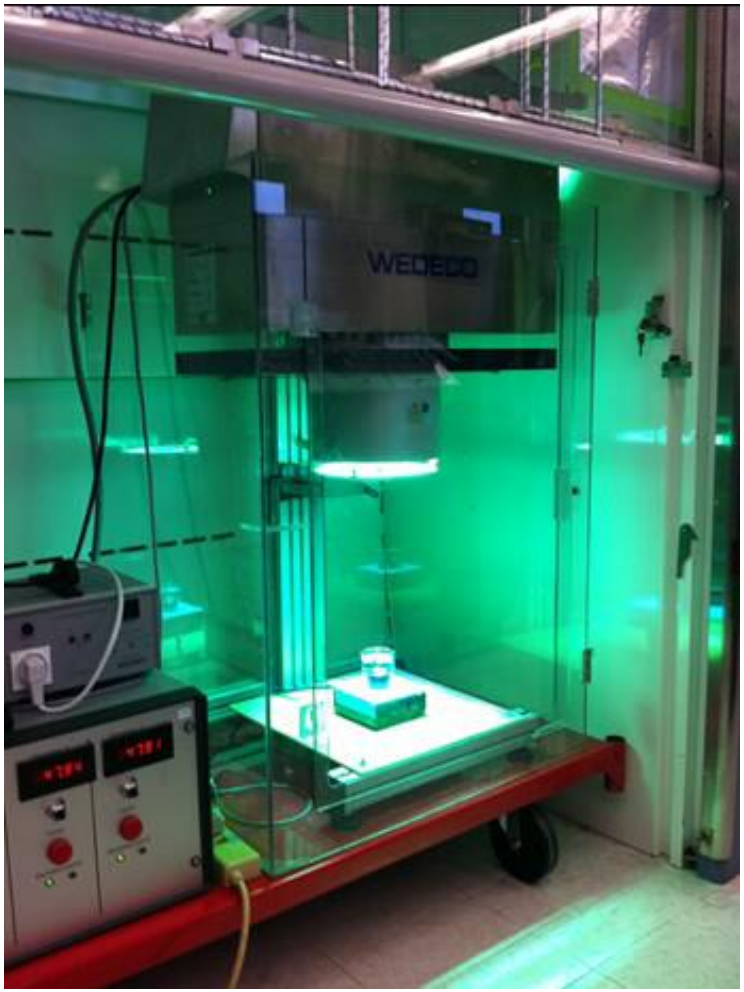
Compounds removed only with the highest ozone dose

Overall strong attenuation

Cluster include 11 compounds Including one identified as the prodrug pivampicillin

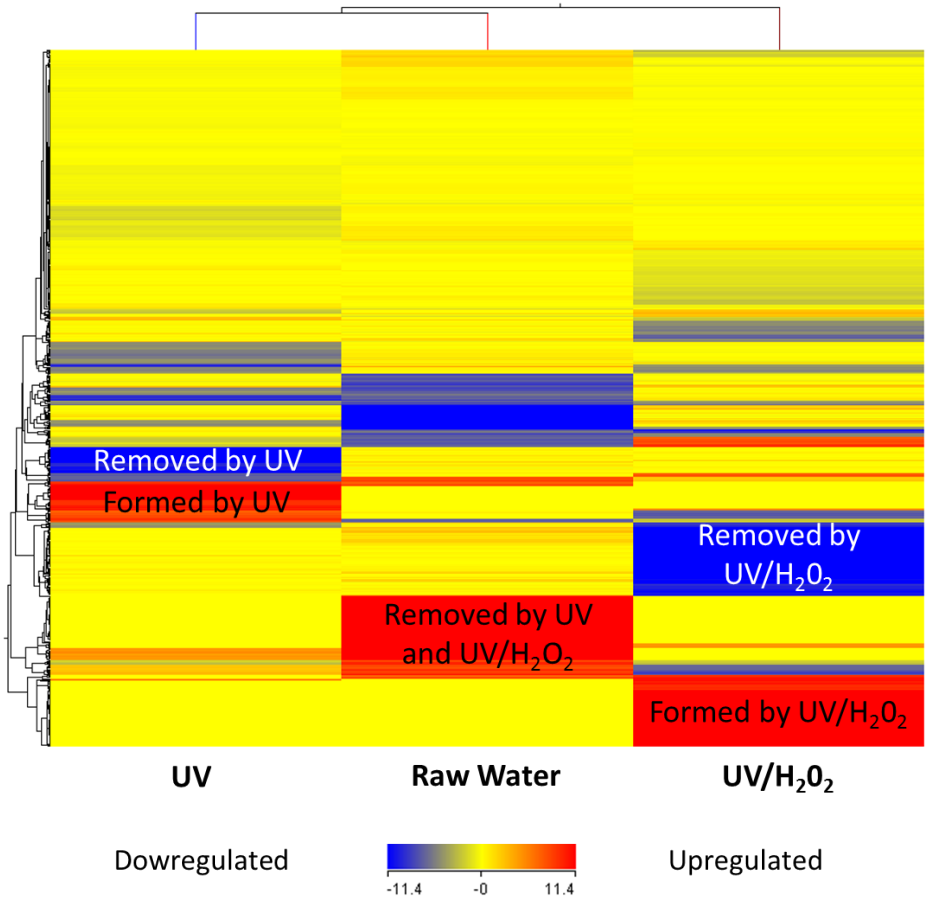


UV Transformation Products



ANALYSIS OF UNKNOWNS WITH QTOF

Searching for unknown in water



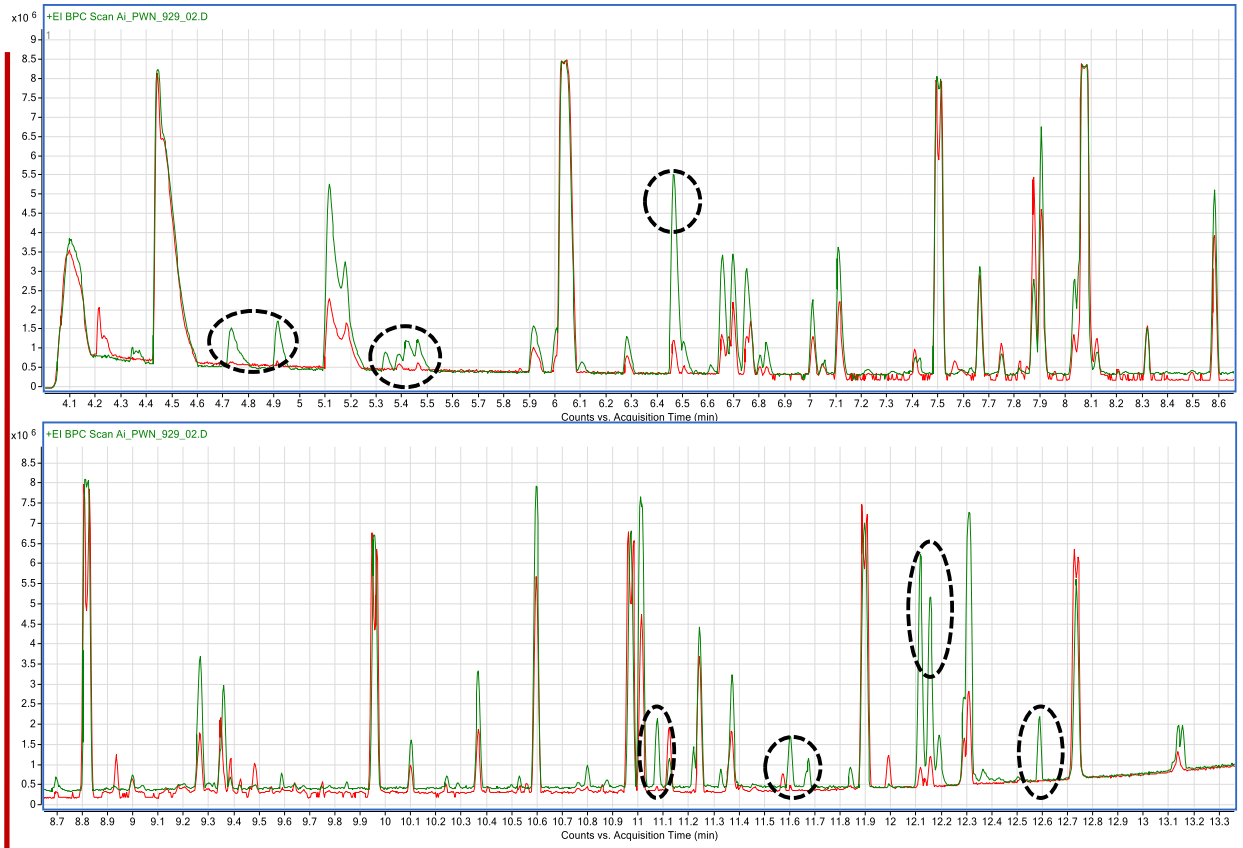
Data Processing in Mass Profiler

Heat Maps

Link samples and/or compounds as in a phylogenetic tree
Here, water treated by UV is closer to the raw water than water treated by UV/H_2O_2

Also compares the abundance of the compounds in each type of water
The heat map shows clusters of compounds formed or removed by each treatment

New mutagenic DBPs detected!



LC-QTOF

GC-QTOF

We can detect anything/anywhere!

But are we looking for the right things?

Indicators and Surrogates

Health-relevant chemicals

Potential health risks at levels at/near occurrence

Performance indicator chemicals

Provide information on treatment efficacy and/or represent broader classes

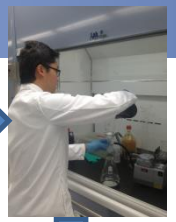
Surrogates

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

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

Recent SPE-LC/MS-MS





Sample collection

Filtration (for wastewater analysis)

Surrogate addition

Extraction (SPE)

Evaporation

Analysis

Online SPE Method

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

Application Note

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Sheher Bano Mohsin
Agilent Technologies, Inc.
Schaumburg, IL
USA

Kolpin et al., USGS (2002)	Vanderford & Snyder (2006)	Anumol & Snyder (2013)
		
		
		

Number of Samples per Day

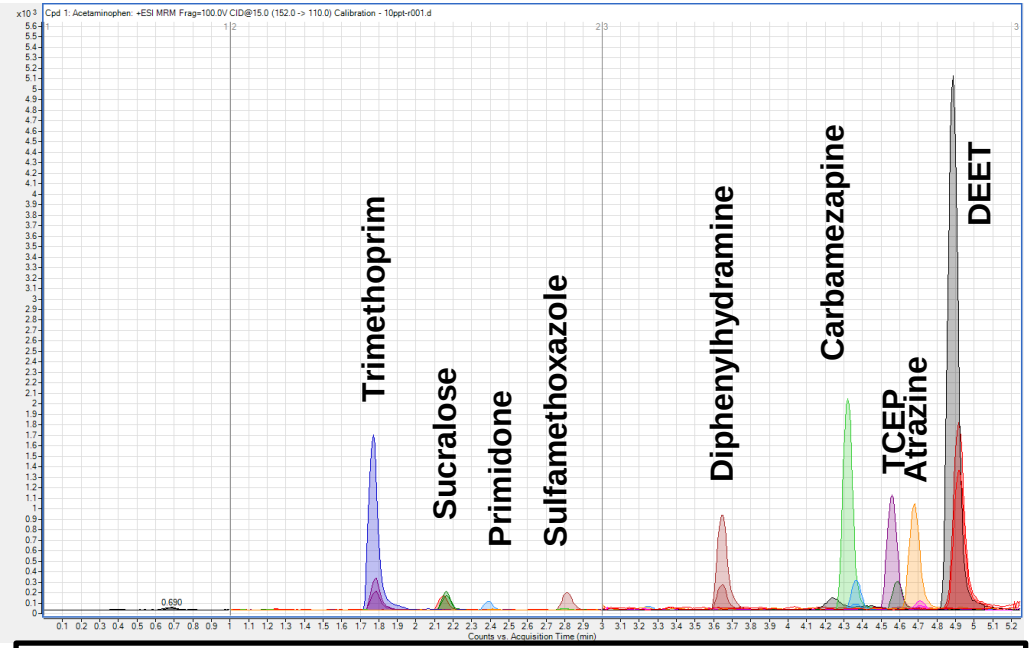
Kolpin et al., USGS (2002)	Vanderford & Snyder (2006)	Anumol & Snyder (2013)
		
1	**4**	**96**

NEWEST - Direct H_2O Injection

- Direct measurement from water w/50 uL injection
- Detection of CECs ≈ 10 ng/L

Advantages:

- **No extraction**
- **Reduced probability of errors**
- **Large savings in standards, solvents & consumables**
- **Enormous time & labor savings**



Column	ZORBAX Eclipse Plus C18 2.1 × 50 mm, 1.8µm
Mobile Phase	A 0.1% Acetic acid B 0.1% Acetic Acid in MeOH
Flow Rate	0.8 mL/min
Gradient	t0 = 5% t1.5 = 5% t6 = 95% B t8 = 100%B (Percent B)

Still not fast enough…

Battling Water Scarcity: Direct Potable Reuse Poised as Future of Water Recycling

Evaluating the Potential for Direct Potable Reuse in Texas

By Sarah Fister Gale

Every drop of water or wastewater back to p

Project Summary

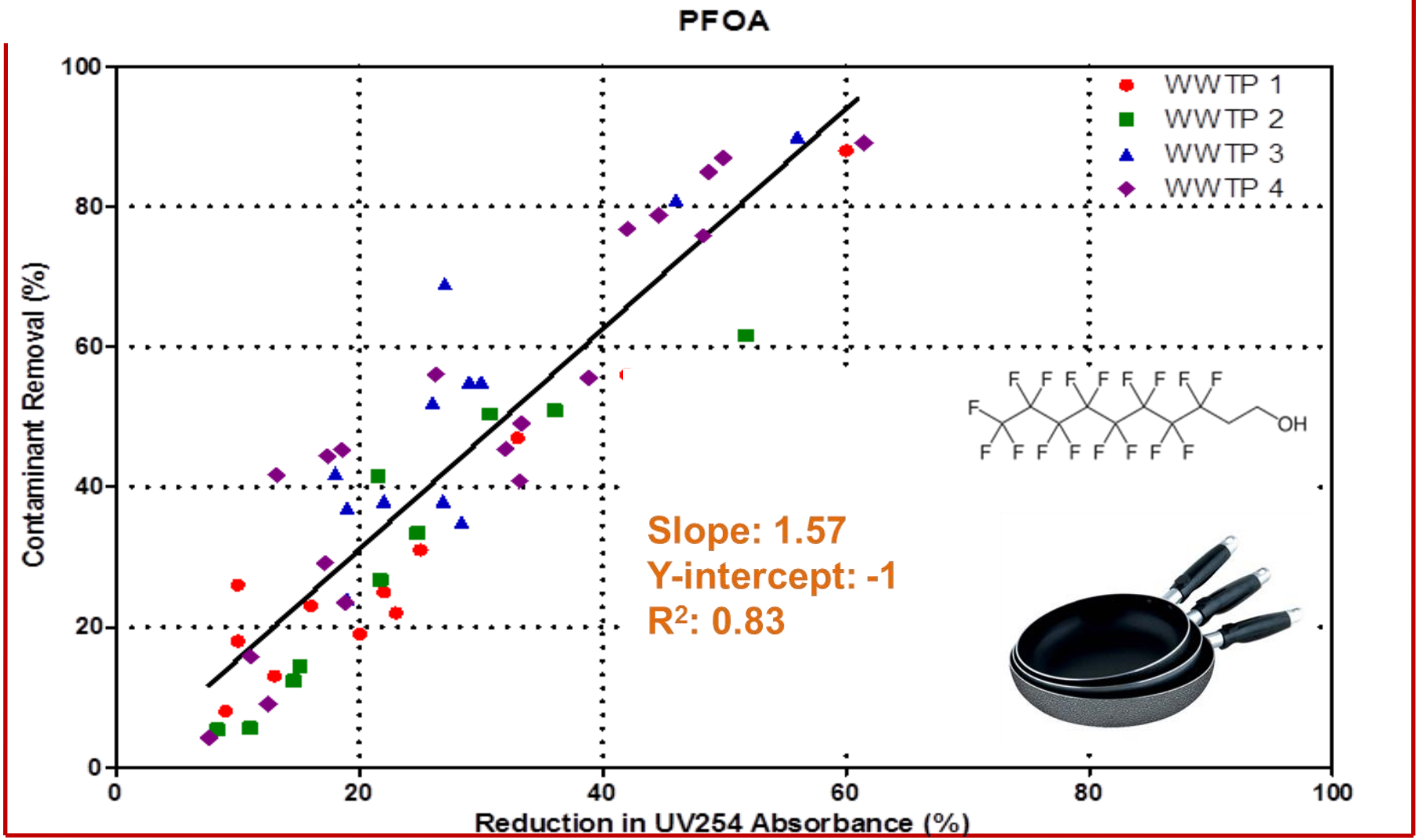
The goal of this project is to develop a resource document that provides scientific and technical information for the implementation of direct potable reuse projects in Texas.

NO WINDING RIVER

Houston considers using its own toilet water as drinking water rather than relying on Dallas flushes

Granular Activated Carbon

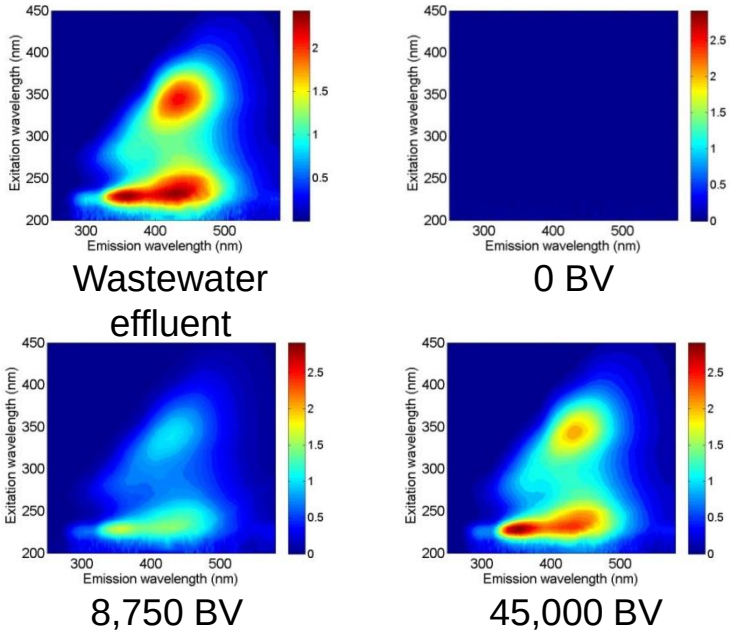
Application of UVA as surrogate for GAC breakthrough



Application of Fluorescence indexes as surrogates for water quality

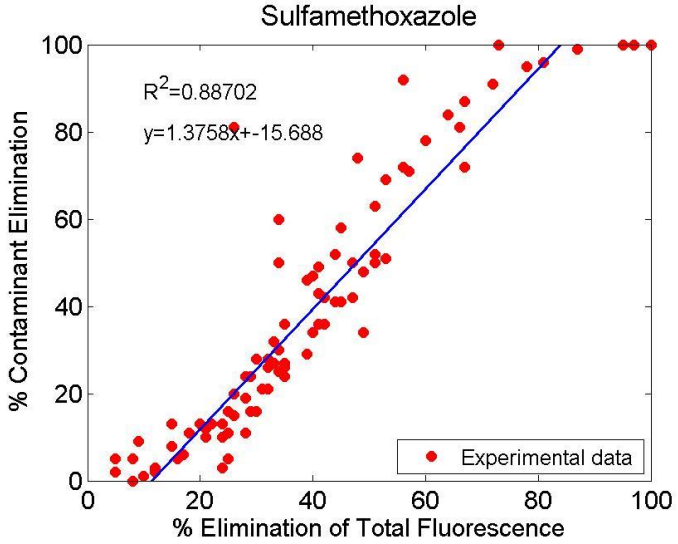
Application of fluorescence indices as surrogates for water quality

- Specific Ex/Em pair or total fluorescence (summation of regional integrations) shows correlation with trace organic removal in GAC process.



Wastewater effluent | 0 BV | 8,750 BV | 45,000 BV

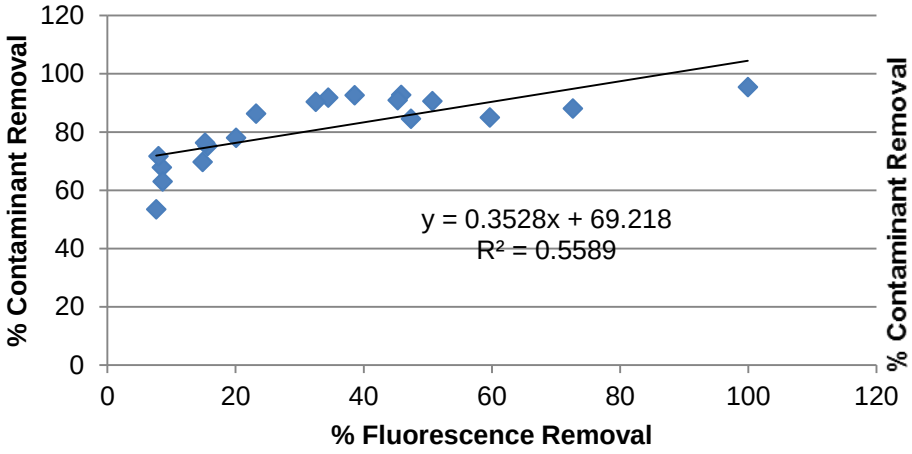
< Excitation-emission matrices of wastewater effluent on GAC treatment >



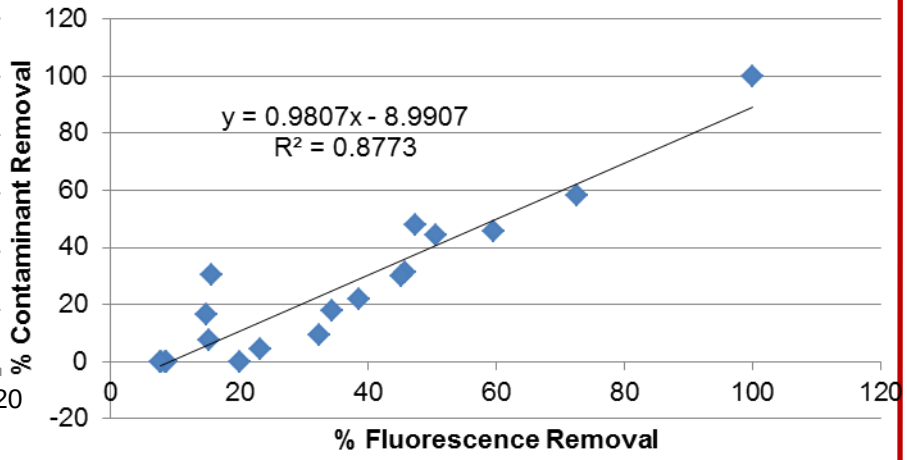
< Correlation of sulfamethoxazole removal and total fluorescence removal by GAC>

Fluorescence Excitation/Emission Pairs

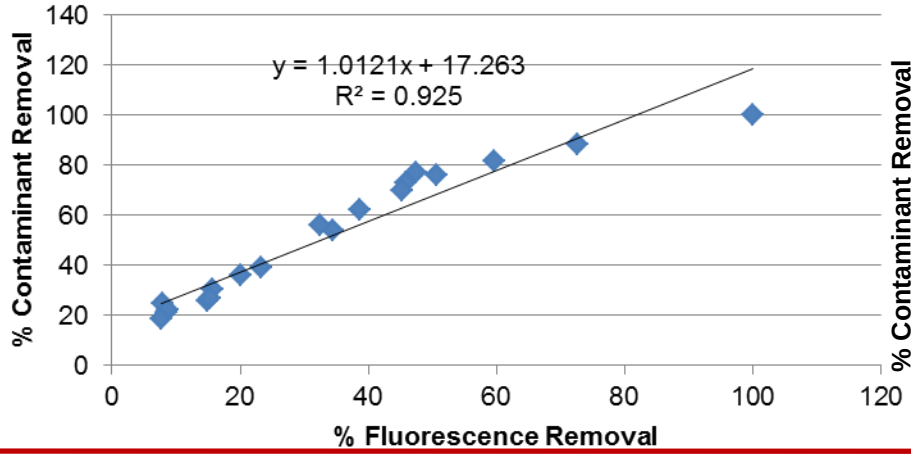
Group 1: Triclocarban



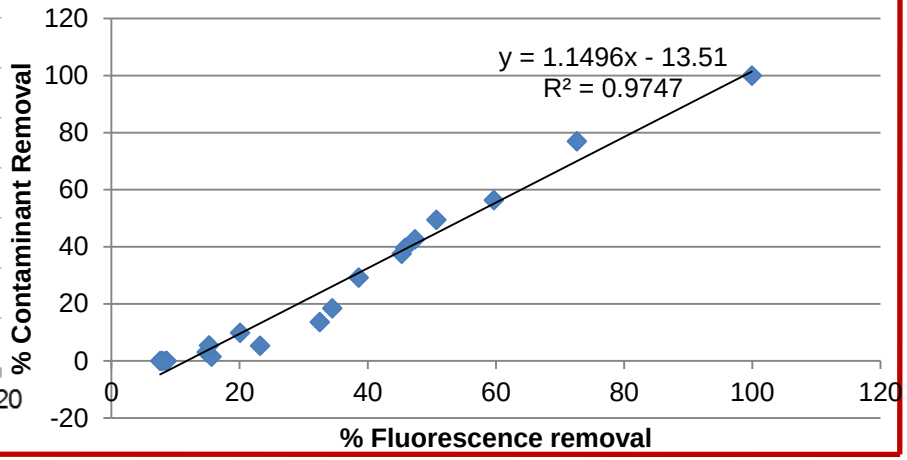
Group 2: PFOA



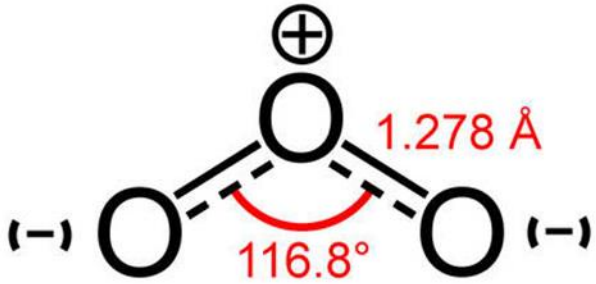
Group 3: Atenolol

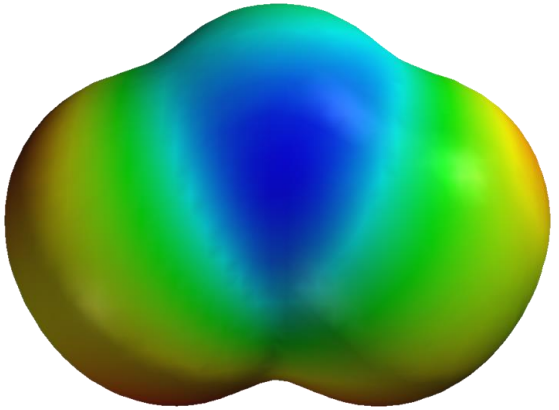


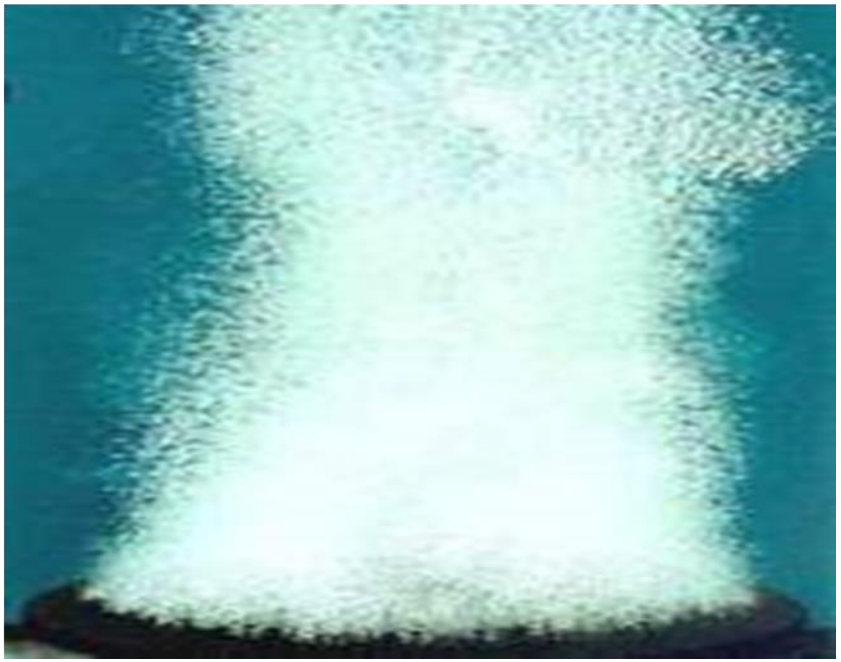
Group 4: Primidone



Ozonation







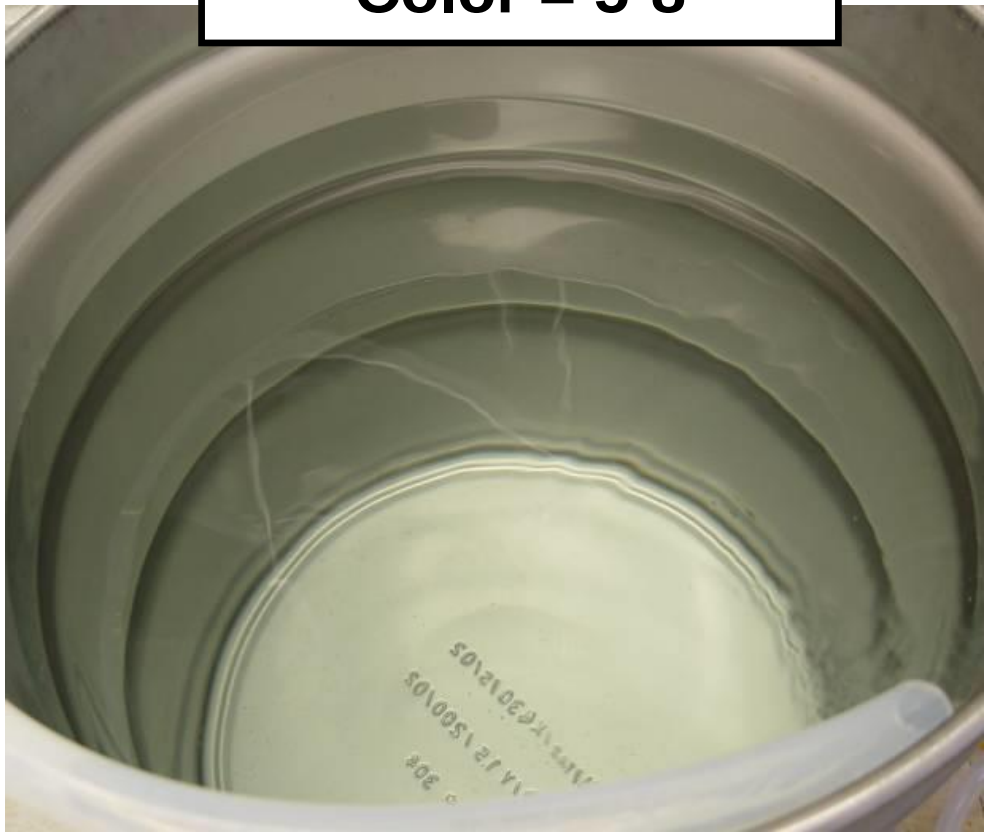
Ozone – Surrogate Development

Before Ozonation

Color = 24

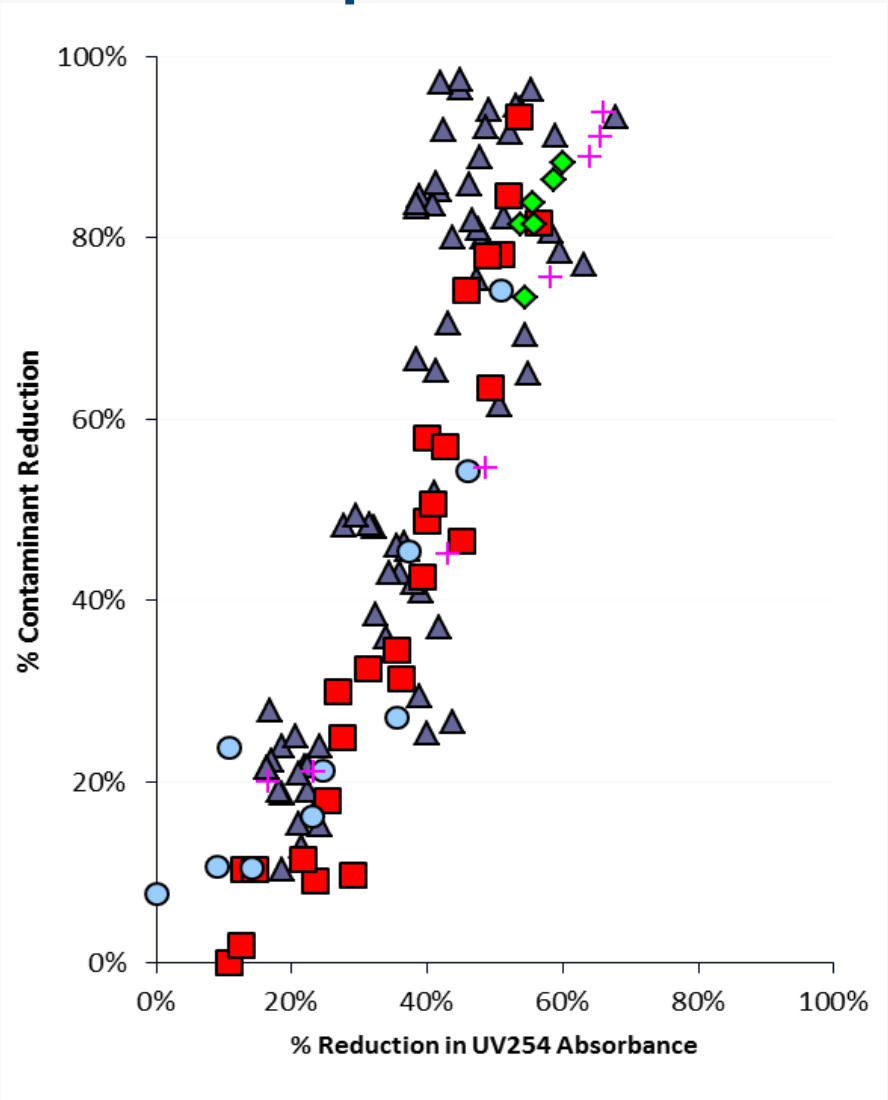
After Ozonation

Color = 5-8

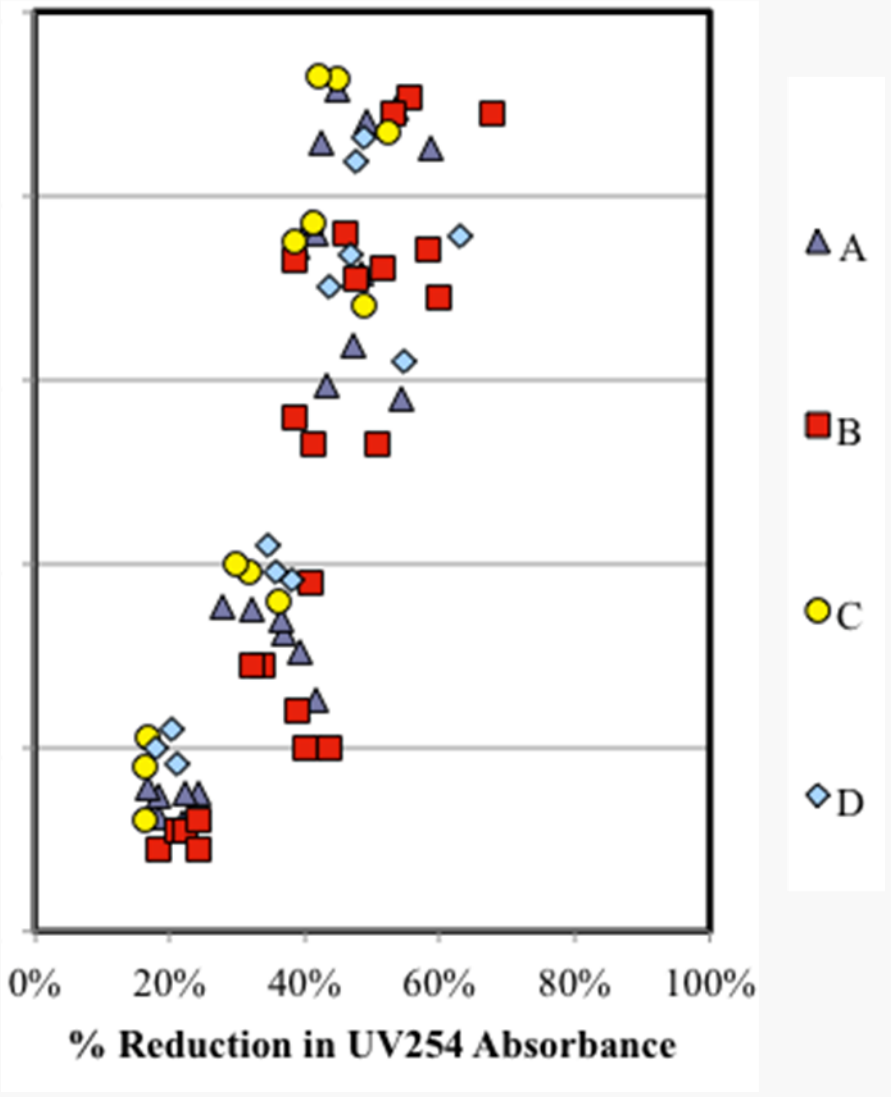


Correlation to UV_{254} Removal (Wert et al, ES&T 2009)

Meprobamate

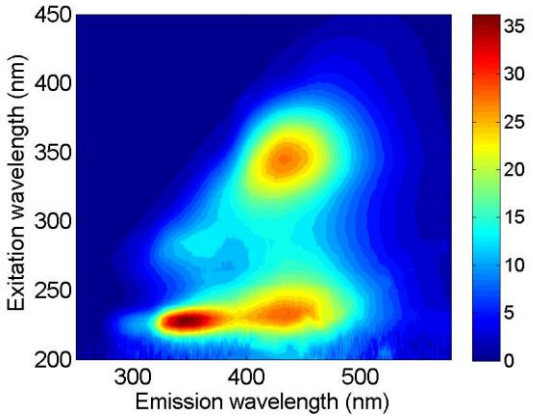


Atrazine

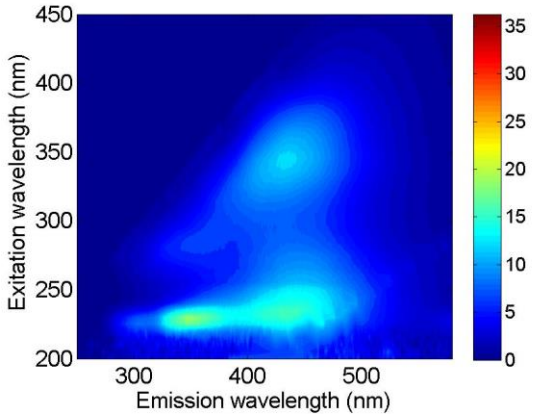


Application of Fluorescence indexes as surrogates for water quality

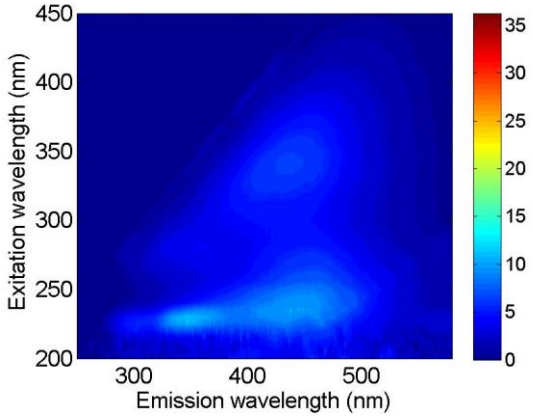
Wastewater Effluent on Ozone treatment



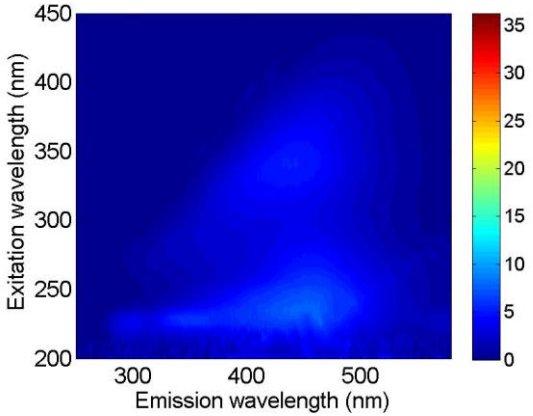
Control



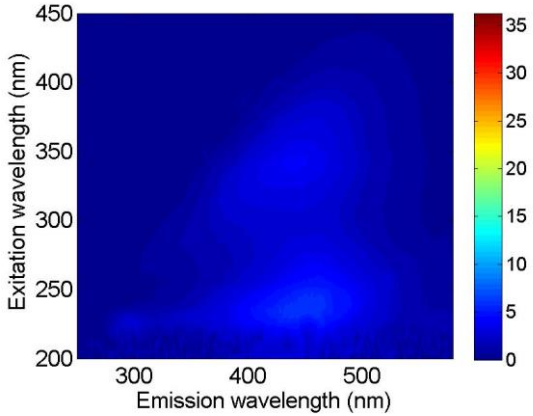
1.5 ppm



3 ppm



4.5 ppm

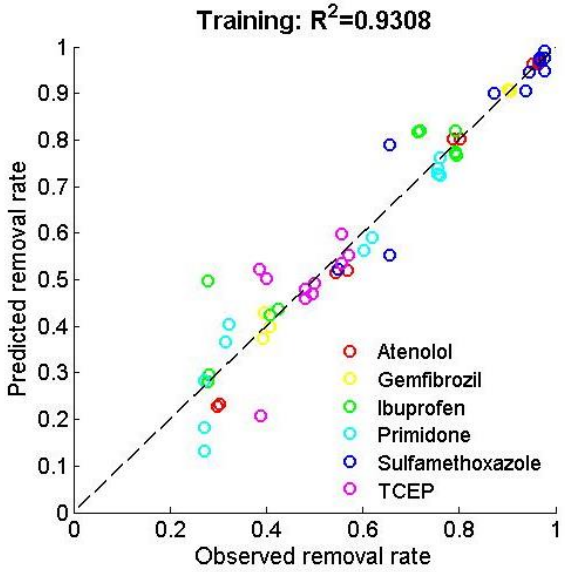


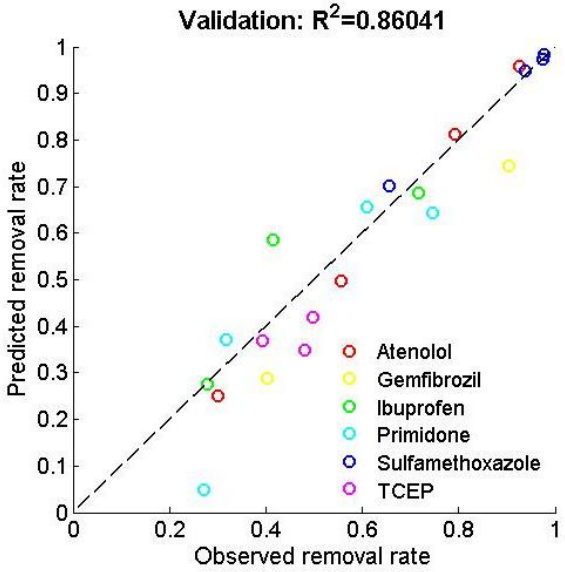
6 ppm

Modeling to predict TOrCs removal

ANN modeling for O_3 process

- Artificial neural network (ANN) modeling was implemented to predict TOrCs removal rate in a wastewater secondary effluent (GV) collected over three-year period (five sampling events)
- Benefit of the developed model is the predictability of TOrCs removal regardless of temporal variation by using ozone doses and a bulk water quality parameter (TOC).

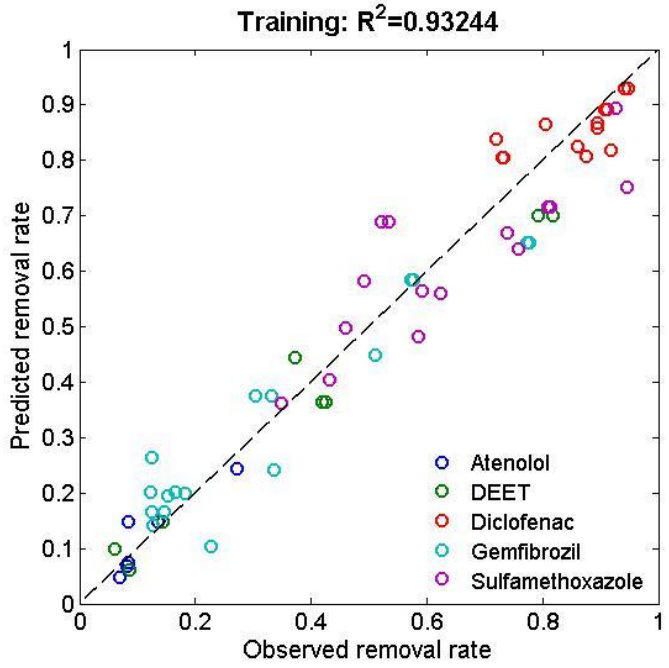


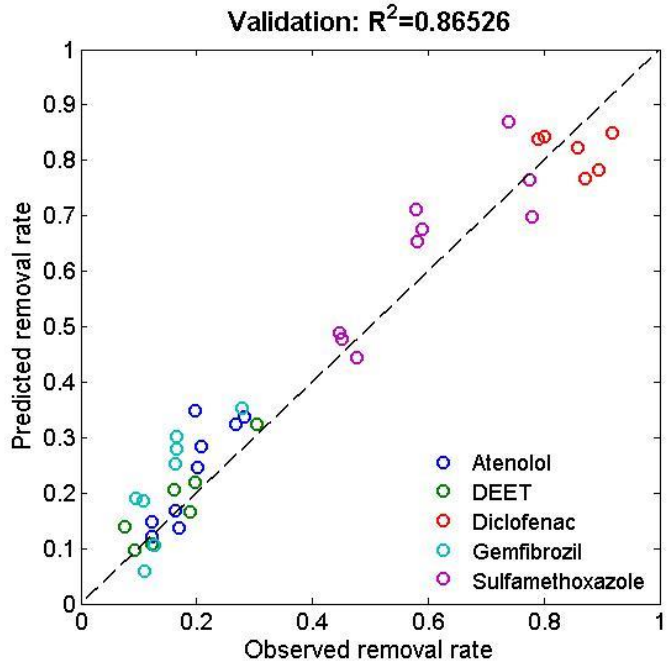


Modeling to predict TOrCs removal

ANN modeling for UV/H_2O_2 process

- In the similar vein, ANN modeling approach also provides successful prediction on TOrCS removal by UV/H_2O_2 process regardless of temporal variation.





WRRF 11-01 Sensor Evaluation

WRRF 11-01 Evaluation of On-line Sensors

Water Village

Feed water tank

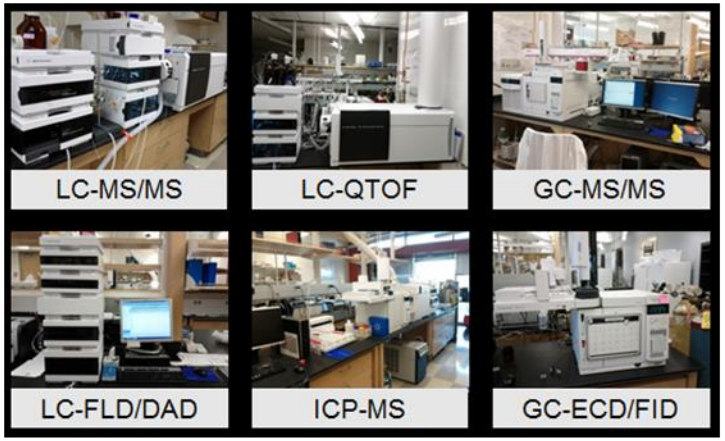
Water treatment unit process

Manifold

- SCADA system (supervisory control and data acquisition)

- **Surrogate sensor**
  - General (pH, temperature, conductivity, turbidity)
  - Organic (UVA/UVT, TOC, DOC, Fluorescence)
  - Inorganic (Chlorine, NO3)
  - Microbial (Total cell count, toxicity)

- **Chemical & microbial contaminants (Indicators)**



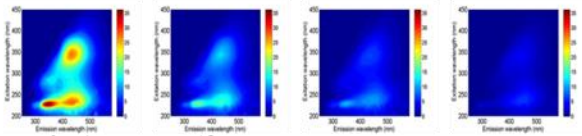
- **Bioassay for water toxicity test**

Project scope

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

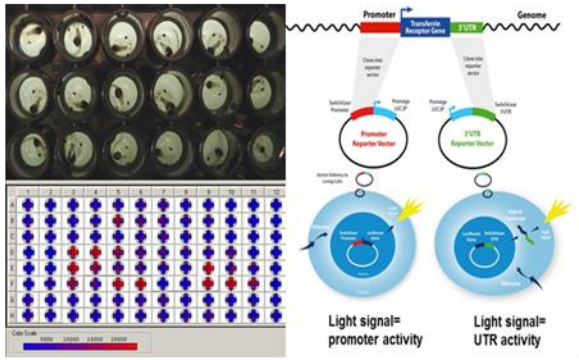
- TOrCs: Trace organic compounds
- Inorganic compounds

Microbiological analysis

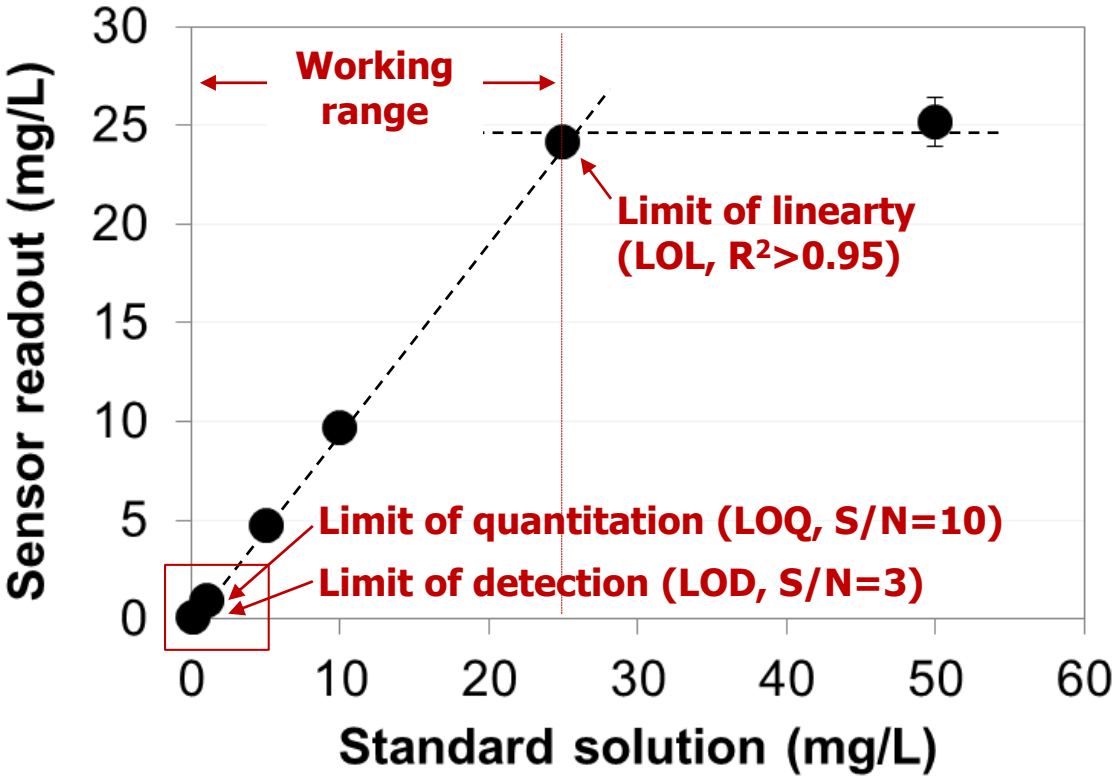
Tier 3
Bioassay

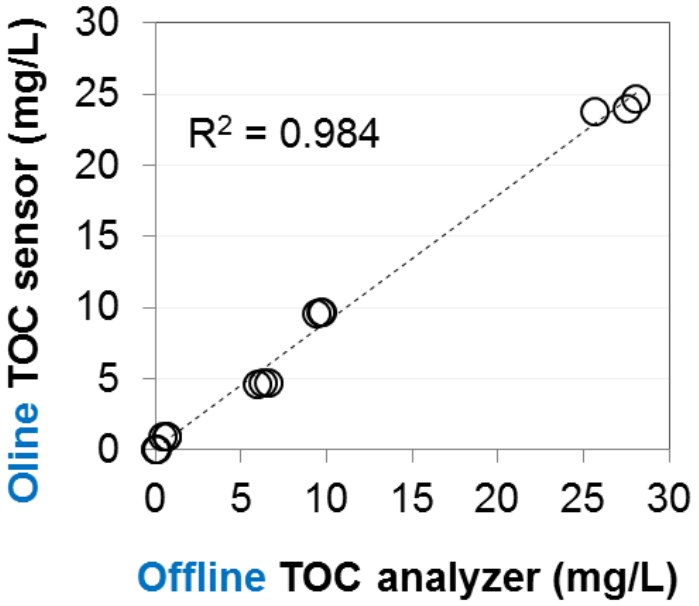
Water toxicity test

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



Evaluation of sensor performance





Sensor performance

(1) Limit of detection (LOD)
(2) Working range
- Limit of quantitation (LOQ)
- Limit of linearity (LOL)

(3) Response time
(4) Accuracy (%Recovery)
(5) Precision (%RSD)
(6) Correlation coefficient to reference method (R^2)

Secondary WWTP Evaluation

SCADA system
(supervisory control and data acquisition)

- **Surrogate sensor**

Tank 1
2nd treated effluent (Green Valley)

Tank 2
DI water

Static mixer

Pump

Manifold

General (pH, temperature, conductivity, turbidity)

HACH GuardianBlue Event Monitor | scientific MicroTol3 Turbidity Analyzer | s::can Spectro::lyser

Organic (UVA/UVT, TOC, DOC, Fluorescence)

REALTECH Real UVT Online | GE Sievers 5310C On-Line TOC Analyzer | HACH GuardianBlue Event Monitor | xylem NiCaVis 705 IQ | s::can Spectro::lyser | WET Labs SAFire

Inorganic (Chlorine, NO3)

HACH GuardianBlue Event Monitor | xylem NiCaVis 705 IQ | s::can Spectro::lyser

Microbial (Total cell count, toxicity)

JMAR BioSentry | Instant BioScan BioScan (RMS-W) | microLAN ToxControl Toxicity Analyzer

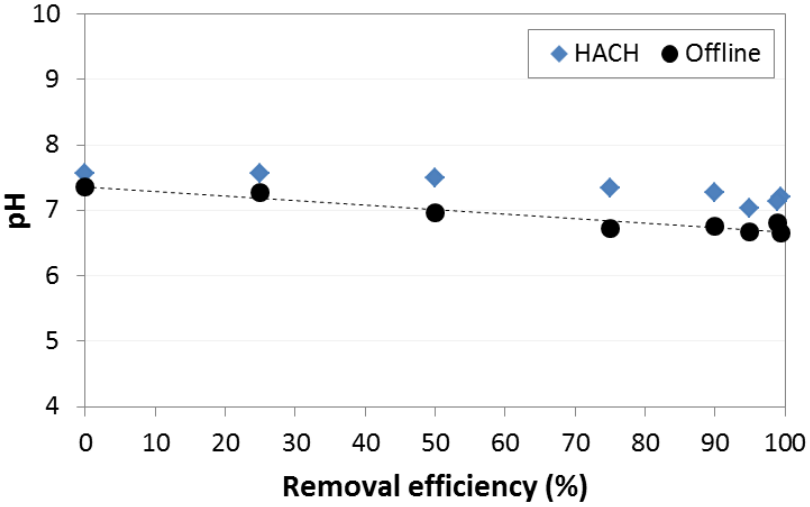
Synthetic water sample

GV (%)	DI (%)
0	100
0.5	99.5
1	99
5	95
10	90
25	75
50	50
75	25
100	0

On-Line vs. Off-Line: General parameters

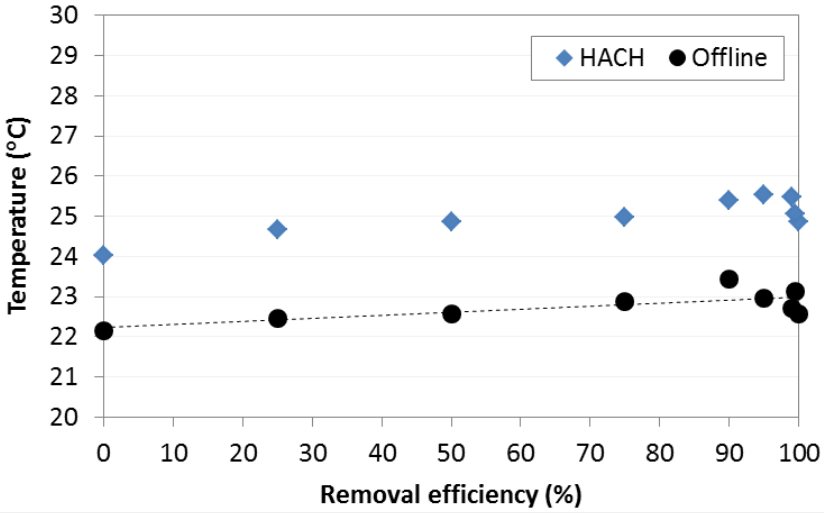
pH

GuardianBlue Event Monitor



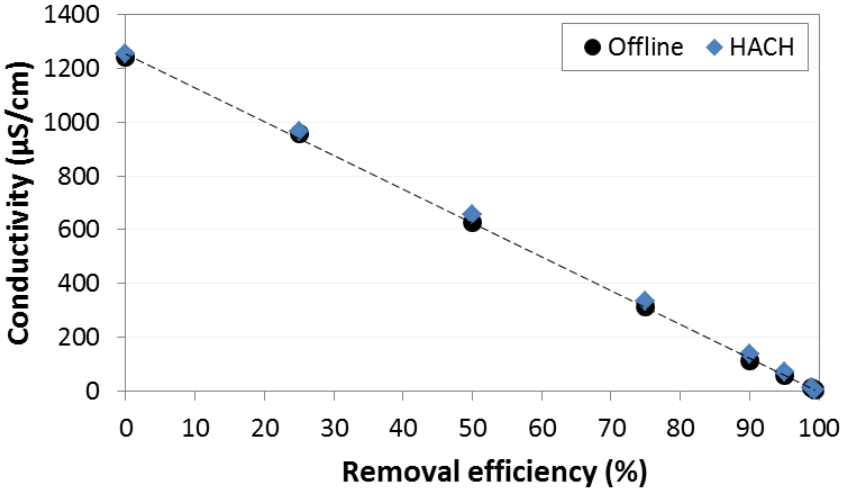
Temperature

GuardianBlue Event Monitor



Conductivity

GuardianBlue Event Monitor

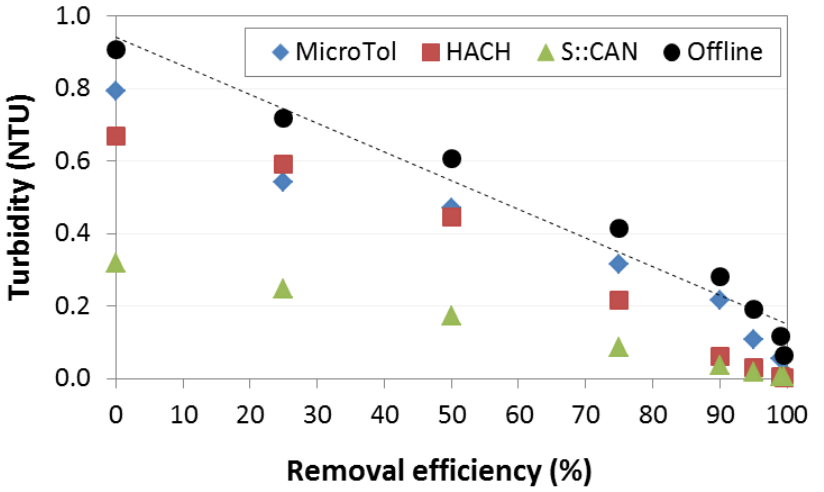


Turbidity

GuardianBlue Event Monitor

MicroTol3 Turbidity Analyzer

Spectro::lyser

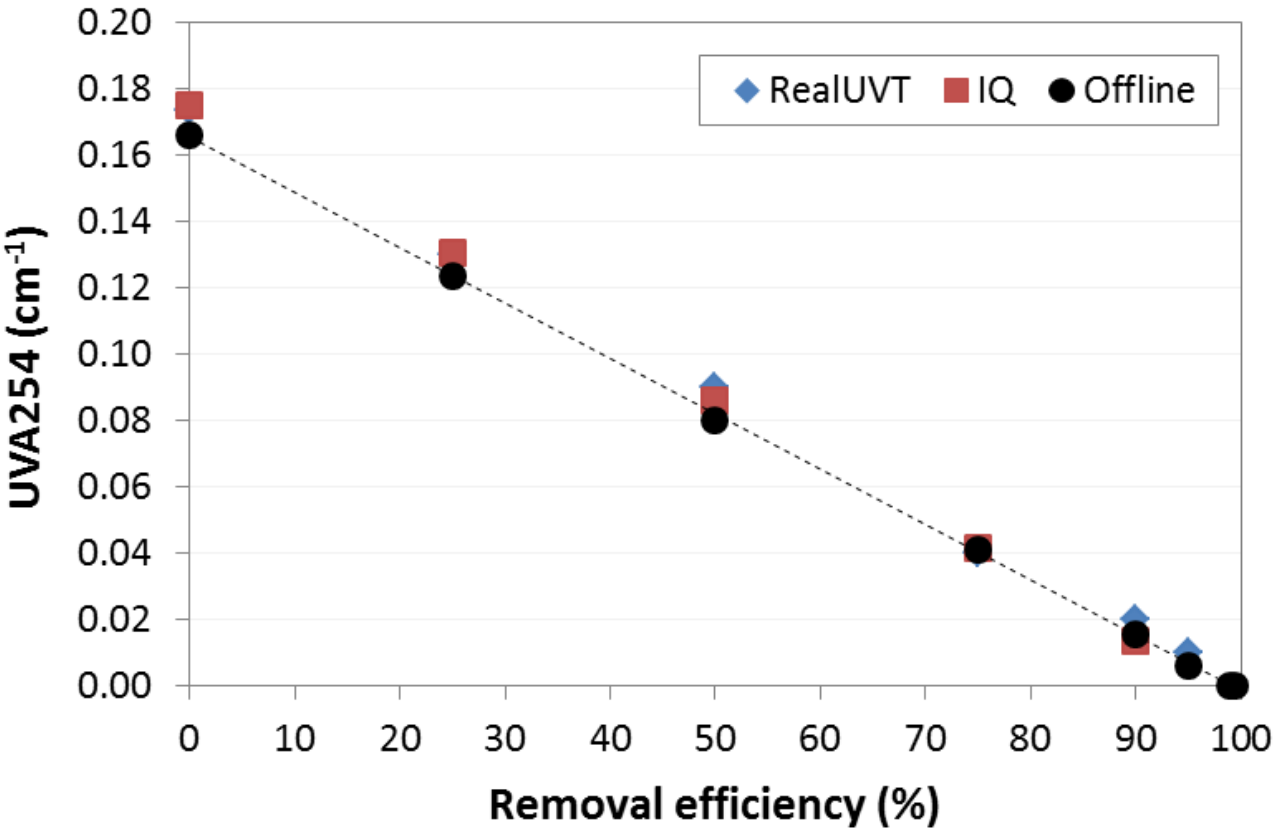


Sensor feasibility test: Organic parameters

Real UVT Online | xylem NiCaVis 705 IQ

UV absorbance & UV transmittance (λ=254 nm)

$UVA = 2 - \log_{10}UVT$



R^2 (Online/Offline data)

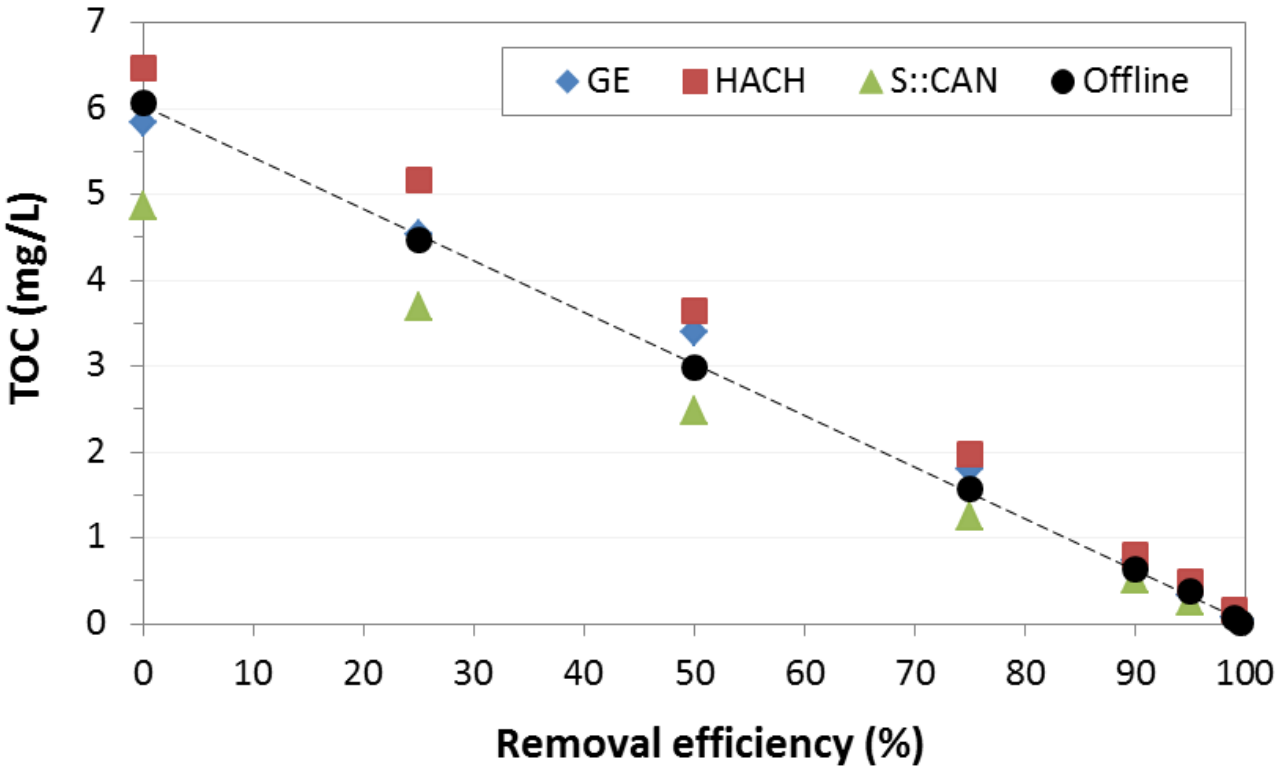
RealUVT	0.99
IQ	0.99

- **UVA**: Reactive or aromatic organic matter which has double bonded ring structures and is typically the most problematic form of organics in water
- **UVT**: - a measure of how much UV light is able to penetrate through a water sample
  - used with UV disinfection systems to aid in the calculation of UV dose

Sensor feasibility test: Organic parameters

Sievers 5310C On-Line TOC Analyzer | GuardianBlue Event Monitor | s::can Spectro::lyser

TOC (Total Organic Carbon)

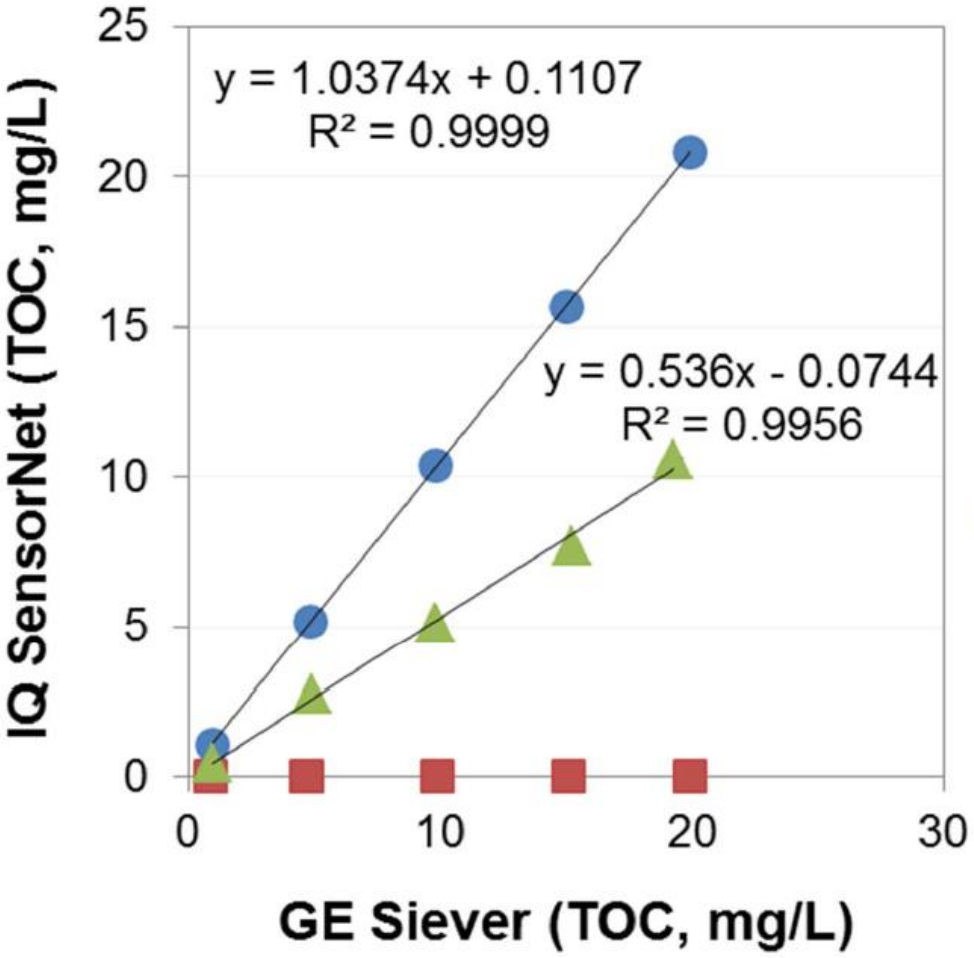


R^2 (Online/Offline data)

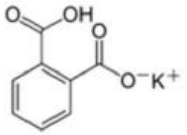
GE	0.99
HACH	0.98
S::CAN	0.95

- TOC indicates the level of organics in water by measuring the total carbon content and so gives a good overall level of all organics

Limitation of optical-based TOC sensor

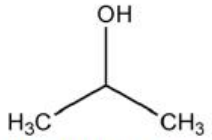


● UV absorbing C



Potassium hydrogen phthalate

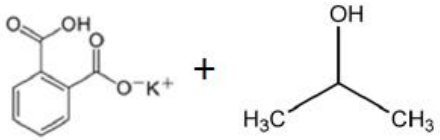
■ non-UV absorbing C



Isopropyl alcohol

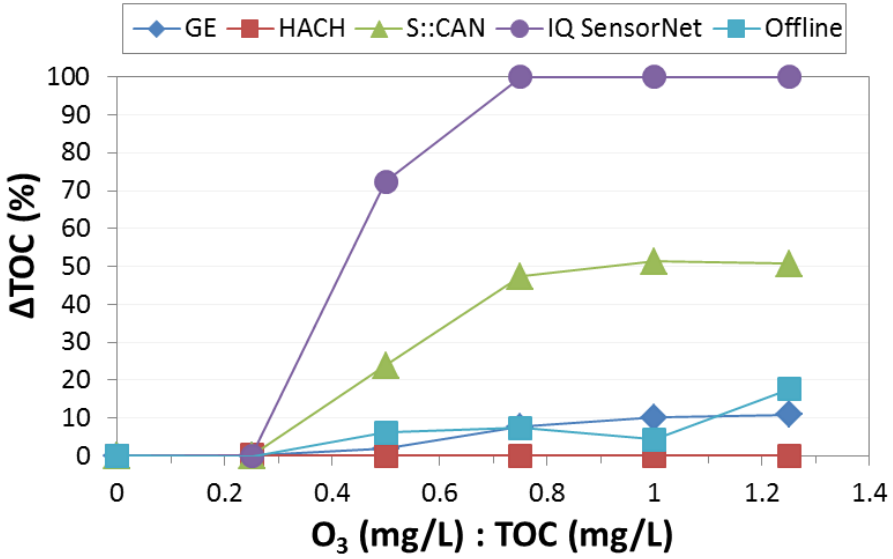
(Carbonyl compound, Aliphatic amines and amino acid, Aliphatic acid, Alcohol, Carbohydrate, Sugar etc.)

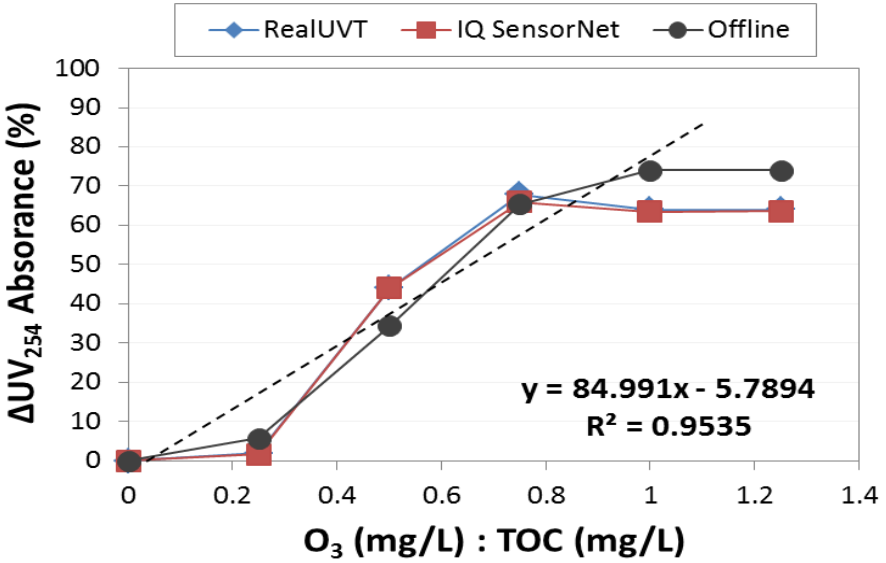
▲ UV absorbing C + non-UV absorbing C (1:1)

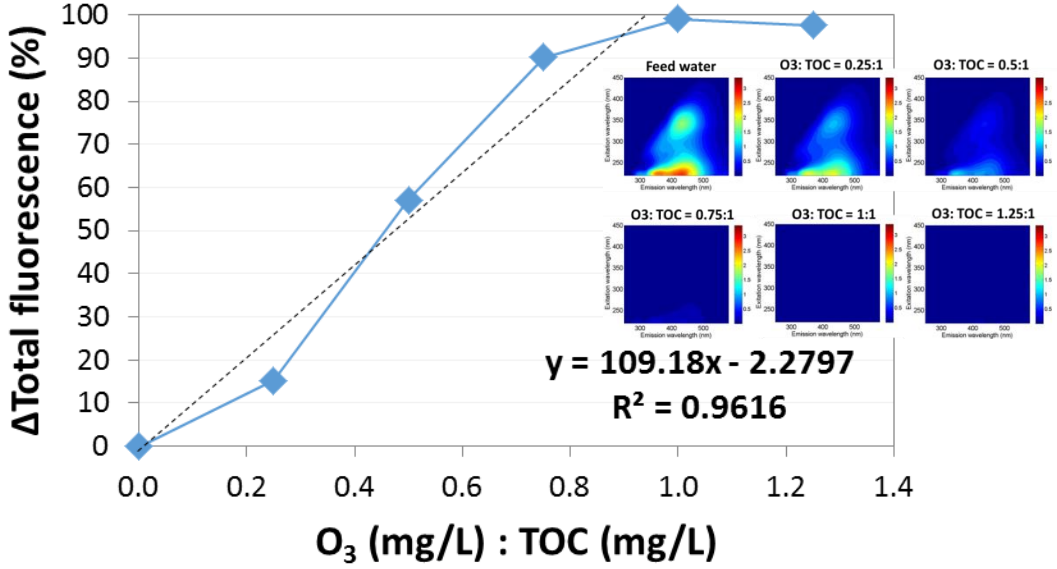


Online sensor-based monitoring of surrogate parameters during O_3 AOP

- **Effect of O_3 dose on oxidation efficacy of organic contaminants to evaluate process performance**







- **Surrogate parameter for oxidation of organic contaminants**

(1) TOC: **Not good**

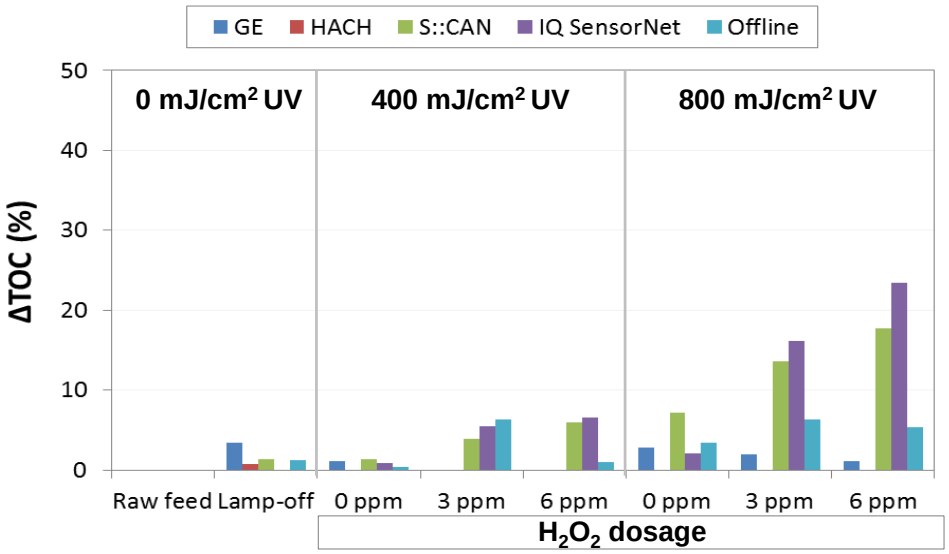
- Due to transformation of organic molecules from large to small not mineralization
- Optical-based TOC sensors are not suitable due to exaggerated decrease of UV-absorbing molecules by ozonation

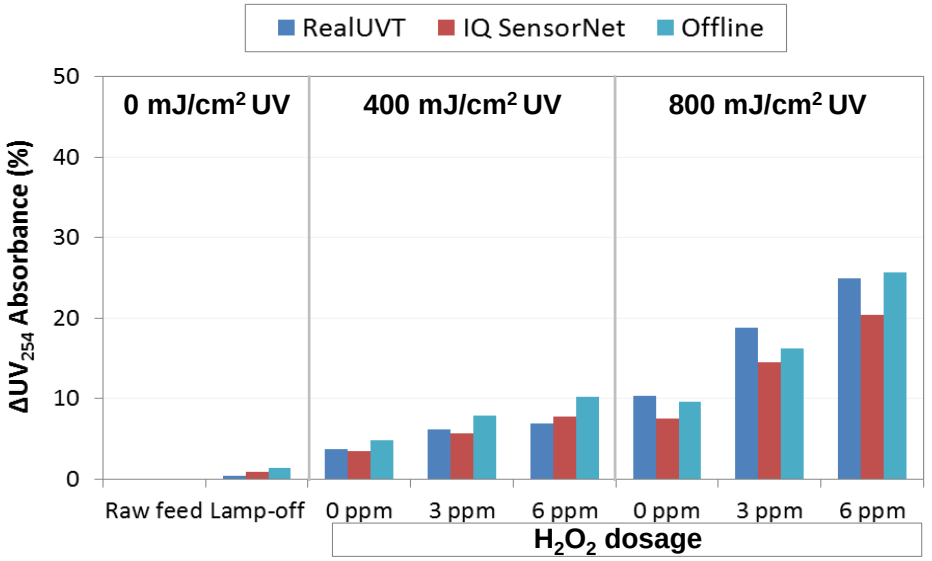
(2) UV_{254} ABS & Total FL: **Good**

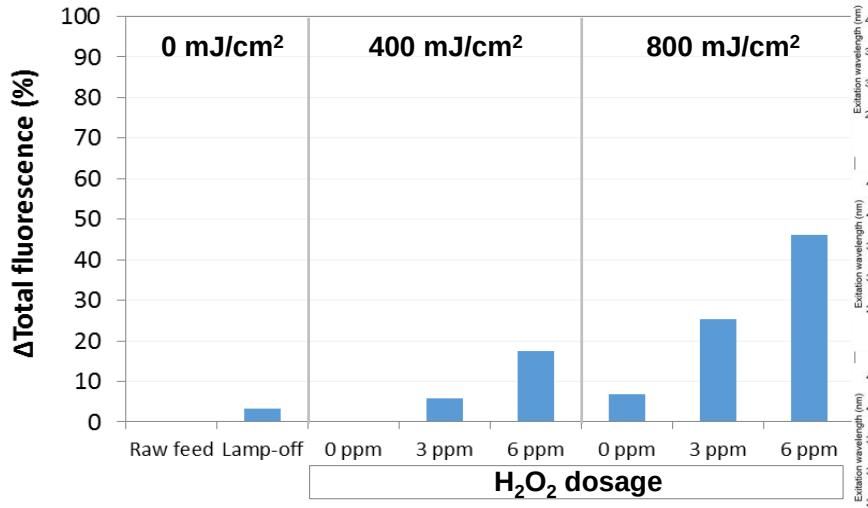
- Response to oxidative capability for O_3 dosage

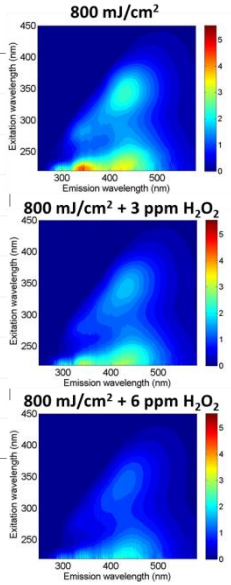
Online sensor-based monitoring of surrogate parameters during UV/H_2O_2 AOP

- **Effect of UV dose and H_2O_2 dosage on oxidation efficacy of organic contaminants to evaluate process performance**









- **Surrogate parameter for oxidation of organic contaminants**

(1) TOC: Not good

- Due to transformation of organic molecules from large to small not mineralization

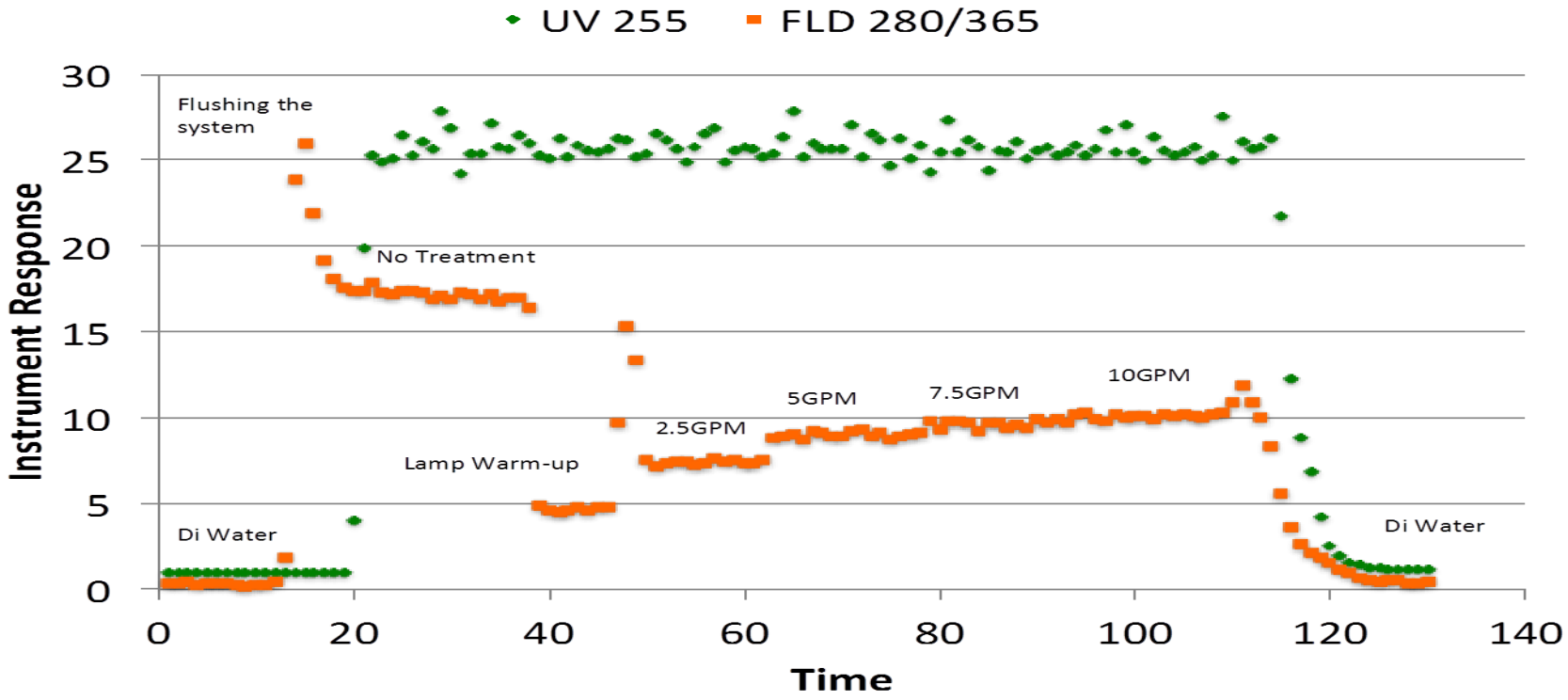
(2) UV_{254} ABS & Total FL: Good

- For evaluating process performance including normal and failure mode (UV lamp-off)
- Response to oxidative capability for both UV dose & H_2O_2 dosage

Fluorescence online sensor

SAFire (WetLabs)

- 6 excitation wavelengths (228, 265, 280, 313, 326 and 365 nm)
- 16 emission wavelengths (269, 300, 313, 326, 340, 350, 351, 365, 380, 400, 420, 430, 450, 460, 485 and 500 nm)
- Utilized as a **surrogate sensor characterizing and quantifying the types of dissolved organic matter (DOM)**

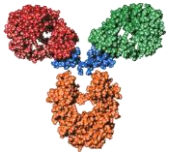


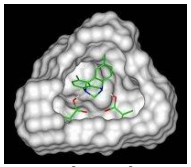

FUTURE
PAST

Biosensors

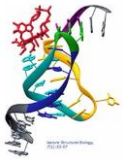
Biorecognition elements


DNA

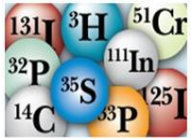

Antibody


Molecular imprinted polymer (MIP)


Enzyme

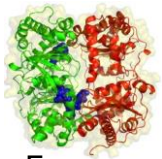

Aptamer

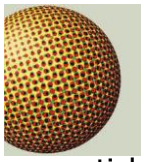
Labels



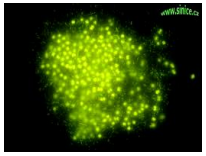
Radioactive isotope

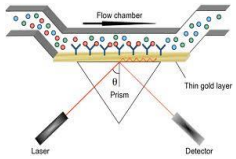

Organic dye


Enzyme

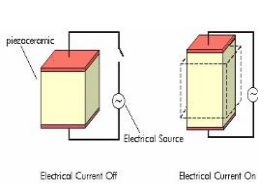

Nanoparticle

Transduction methods

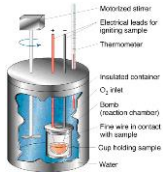

Optical



SPR



Piezoelectric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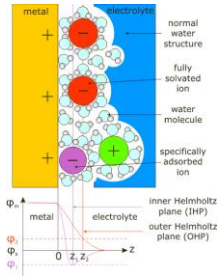
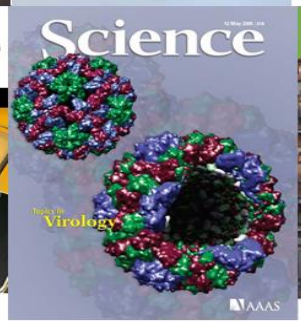


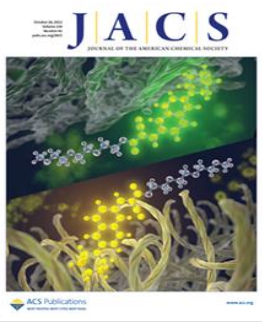
Electrochemical

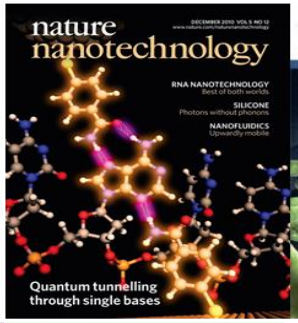
The possibilities are endless!

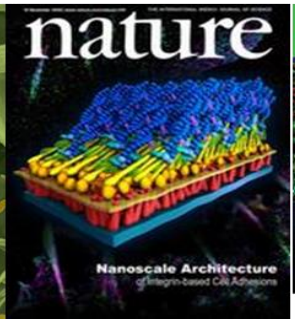
Sensor Performance

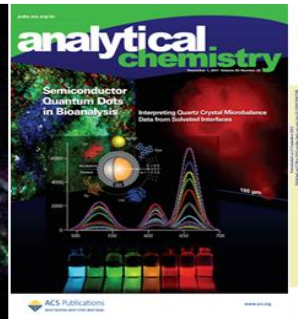
Sensors are
at the forefront of a
multidisciplinary science
that marries
the biological world and
the electronic world

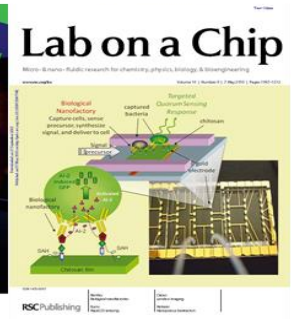






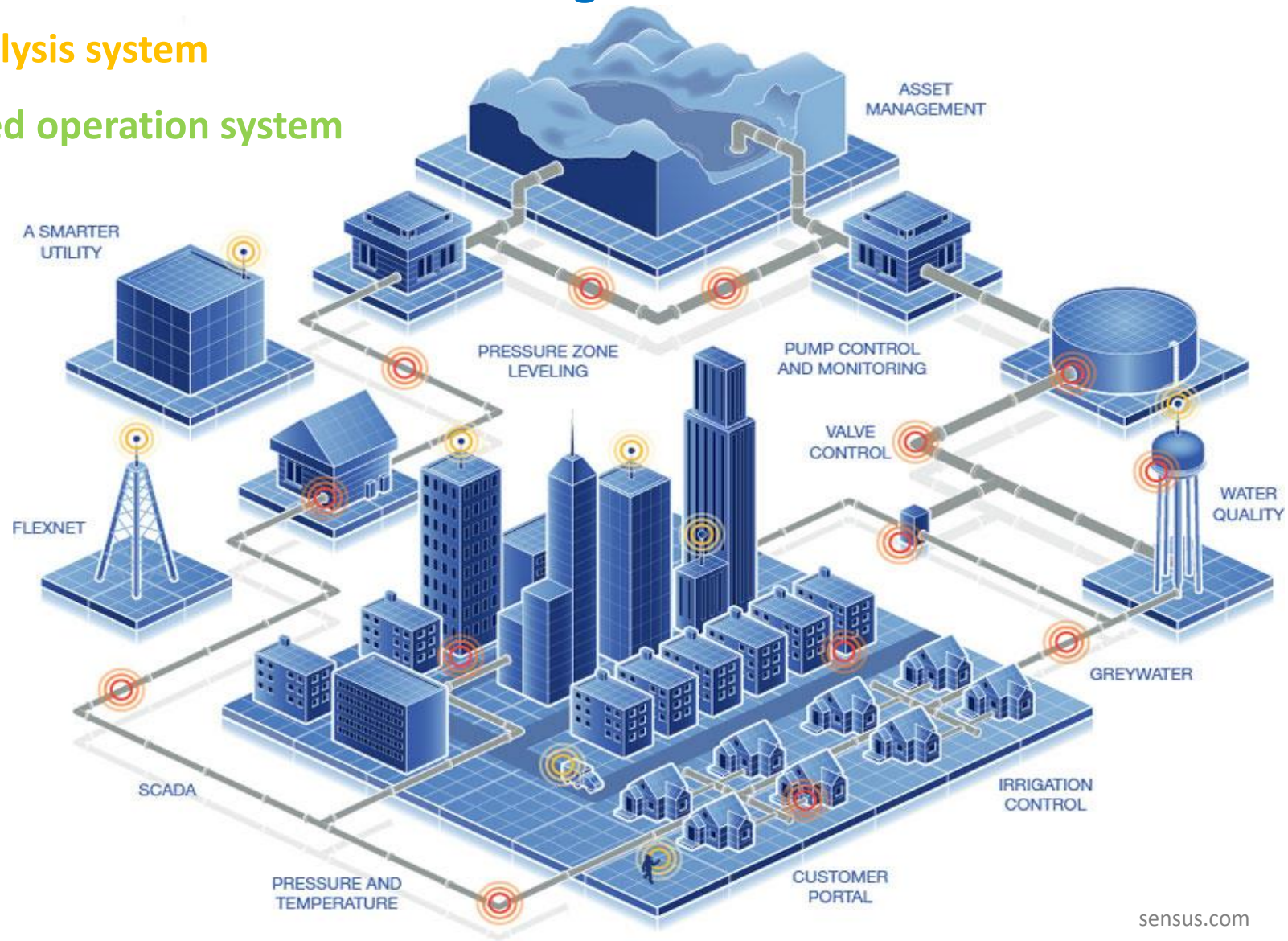






Smart Water Grid

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



Acknowledgements

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