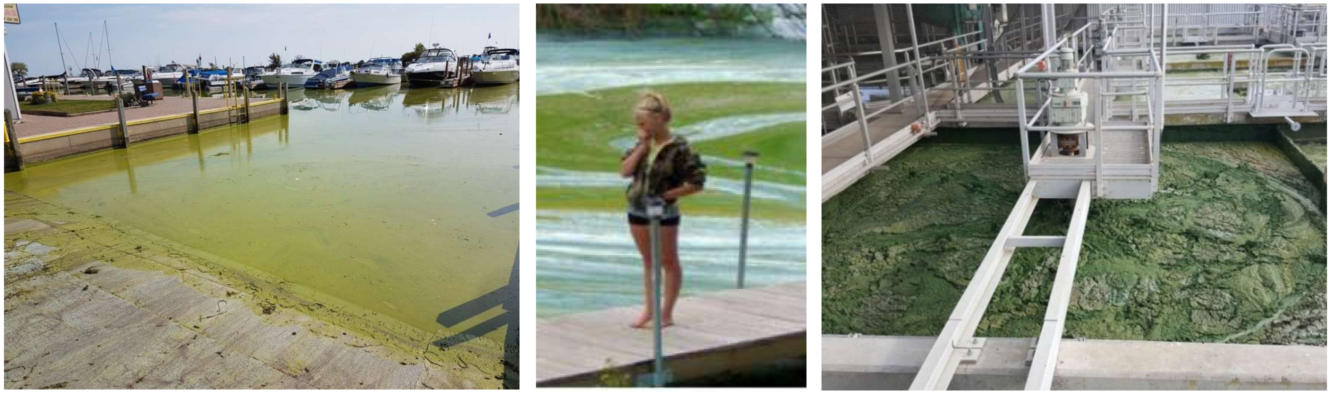
Investigating water advanced treatment processes for removal of taste and odour compounds: Focus algae

Arash Zamyadi, Ph.D.
Water Research Australia and Department of Chemical Engineering,
Faculty of Engineering and Information Technology,
The University of Melbourne



Training School “AOPs for water T&O”
5-9 Sep 2022, Athens, Greece

A bit about me – employment:

2019 – Present

- Senior Lecturer, School of Chemical Engineering, The University of Melbourne, Melbourne, Australia
- Scientist, Walter and Eliza Hall Institute of Medical Research (WEHI), Melbourne, Australia
- Research Manager, Water Research Australia Limited (WaterRA), Melbourne (hosted by Melbourne Water), Australia

2017 – 2019

Assistant Professor, Civil, Geological and Mining Department, Polytechnique Montréal, Montreal, Canada

2014 – 2017

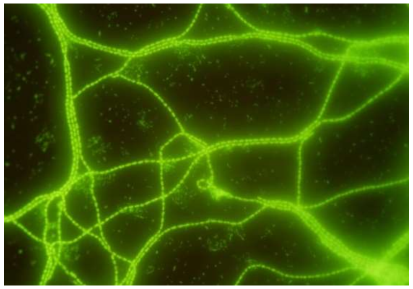
Senior Research Associate, Water Research Centre, The University of New South Wales, Sydney, Australia

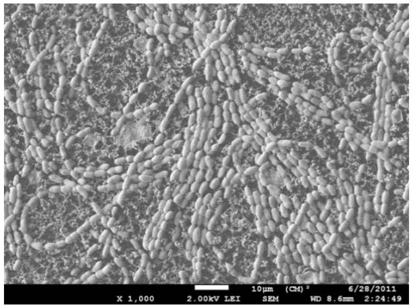
2012 – 2014

Natural Sciences and Engineering Research Council of Canada (NSERC) Postdoctoral Fellow, Drinking Water Research Group, Civil Engineering Department, University of Toronto, Toronto, Canada

Graduated PhD: 2011 – 2012

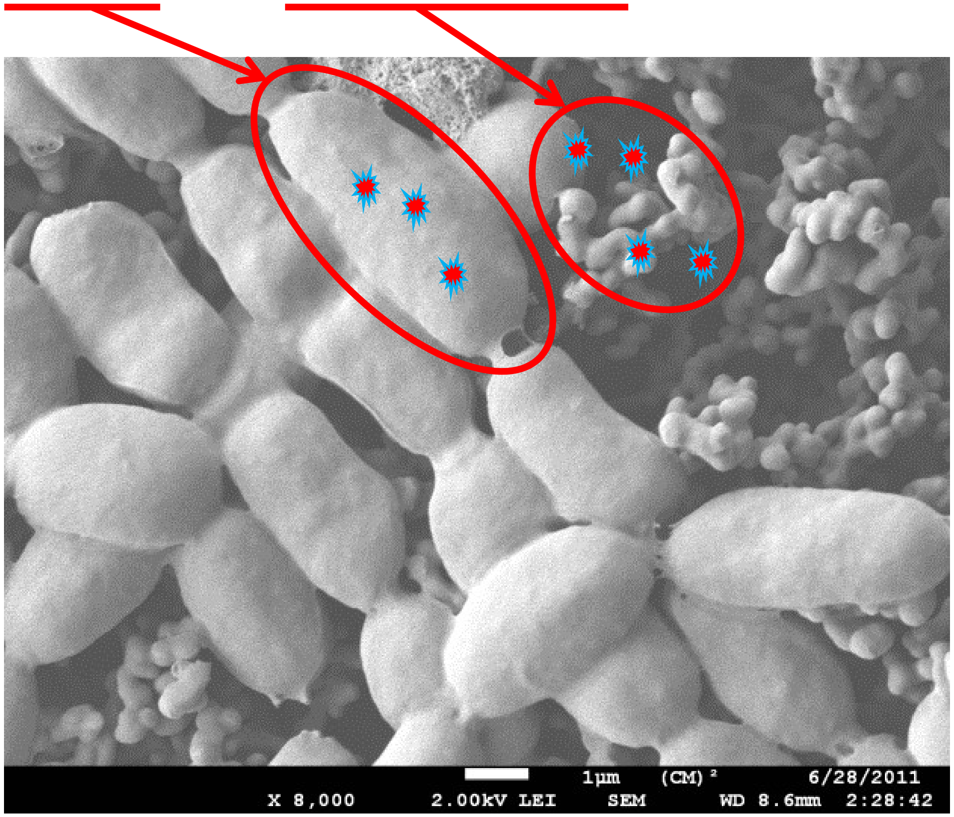
Principal Investigator and Project Manager, Civil, Geological & Mining Department, Polytechnique Montréal, Montreal, Canada





Cell Identification/Integrity & Release

Intra- and extracellular compounds



BIOGENIC T&O IN DRINKING WATER

- In Australia, most T&O events are caused by microbes in source water
- Cyanobacteria produce 100s of T&O compounds
    - ○ We only monitor geosmin and MIB
        - ○ Human detection 7 ng/L; no Cl2
        - ○ Major cause of customer complaints & distrust
    - ○ Responsible for Earth/Musty odour
- Most T&O events remain undetected and untreated
    - ○ Consumer complaints and loss of trust
    - ○ How can we do better?

EPA- Water Is Worth It
4 hrs ·

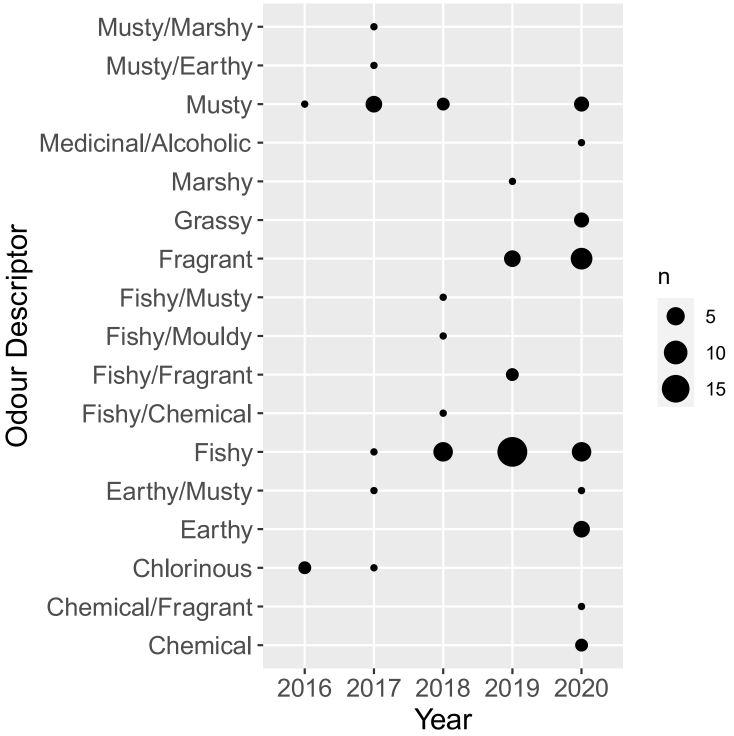
When algal blooms take over a water body, they can produce extremely dangerous toxins that can sicken or kill people and animals. http://ow.ly/z00H301Ic7V

Clean Water or Green Water? EPA
http://www2.epa.gov/nutrientpollution/harmful-algal-blooms

If you see water that is:
discolored
foamy
scummy
has mats of algae
smells musty

Avoid contact or rinse off immediately in fresh water.

When in doubt, stay out!



Biogenic T&O in an Australia city
(Ref: Dr B Tamburic, UNSW)

ALGAL BLOOM AND T&O MONITORING PATHWAYS

Sample Multiple Locations in waterbody

Chlorophyll and Phycocyanin probes help justify when a trip to the field is required.

FlowCam Cyano: identify organisms, plus count, and concentration.

Toxin Path

qPCR

Dip Sticks

Thermo LC-MS/MS

T&O Path

Thermo GC-MS/ECD to quantify MIB/Geosmin

Monitoring of Benthic Cyanobacteria

Benthic cyanobacteria can be a significant source of cyanotoxins and T&O compounds[3]. However, only 20% of utility respondents include benthic monitoring in their routine sampling. Benthic cyanobacteria may explain instances where metabolites are detected in a water supply without visible evidence of a bloom. Figure 8 illustrates benthic cyanobacteria in surface water sources and corresponding sampling methods. Figure 9 presents a decision tree to evaluate potential risks related to benthic cyanobacteria.

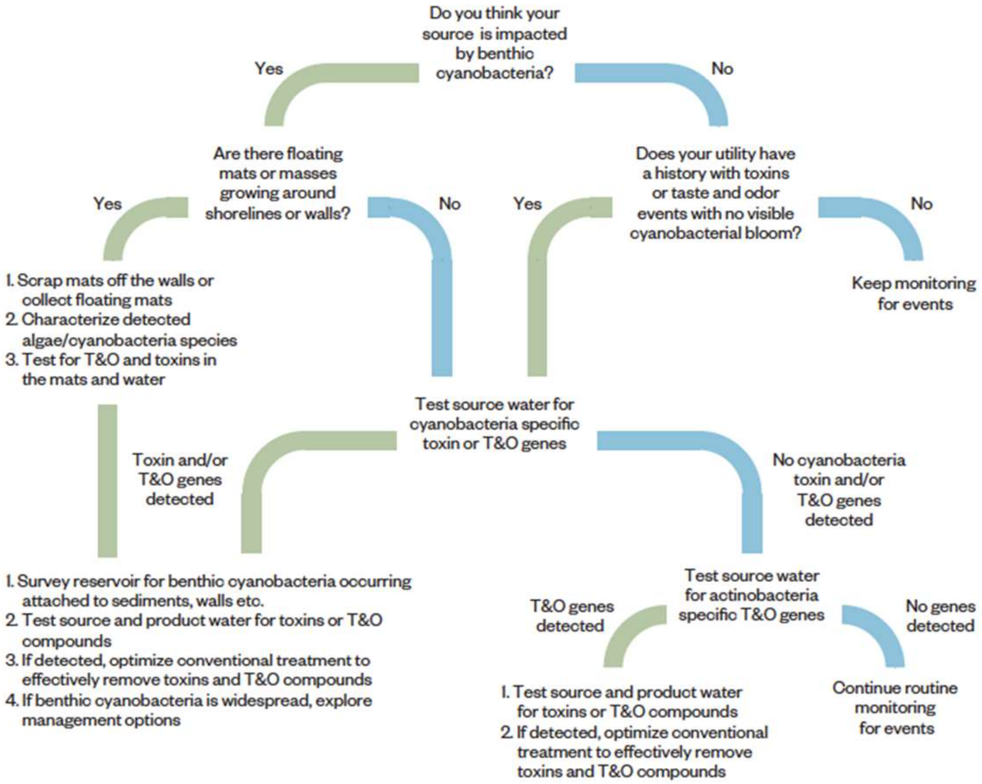
Deploying artificial substrates e.g., wood, PVC, and tile in reservoirs and allowing for biofilm development.

Scrapping biofilm from rocks or reservoir walls.

Collecting sediment core samples in the reservoir.

Raking the sediment.

Figure 8. Summary of benthic cyanobacteria sources and available sampling methods.



Do you think your source is impacted by benthic cyanobacteria?

Yes → Are there floating mats or masses growing around shorelines or walls?

- Yes →
  1. Scrap mats off the walls or collect floating mats
  2. Characterize detected algae/cyanobacteria species
  3. Test for T&O and toxins in the mats and water
- No → Test source water for cyanobacteria specific toxin or T&O genes

No → Does your utility have a history with toxins or taste and odor events with no visible cyanobacterial bloom?

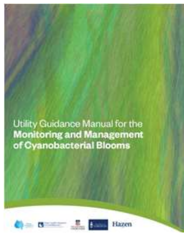
- Yes → Test source water for cyanobacteria specific toxin or T&O genes
- No → Keep monitoring for events

Test source water for cyanobacteria specific toxin or T&O genes

- Toxin and/or T&O genes detected →
  1. Survey reservoir for benthic cyanobacteria occurring attached to sediments, walls etc.
  2. Test source and product water for toxins or T&O compounds
  3. If detected, optimize conventional treatment to effectively remove toxins and T&O compounds
  4. If benthic cyanobacteria is widespread, explore management options
- No cyanobacteria toxin and/or T&O genes detected → Test source water for actinobacteria specific T&O genes
  - T&O genes detected →
    1. Test source and product water for toxins or T&O compounds
    2. If detected, optimize conventional treatment to effectively remove toxins and T&O compounds
  - No genes detected → Continue routine monitoring for events

Figure 9. Decision tree on determining issues with benthic cyanobacteria at the drinking water source

Gaget et. al (2021) "Benthic cyanobacteria: a utility-centered field study"; Under review



Utility Guidance Manual for the Monitoring and Management of Cyanobacterial Blooms

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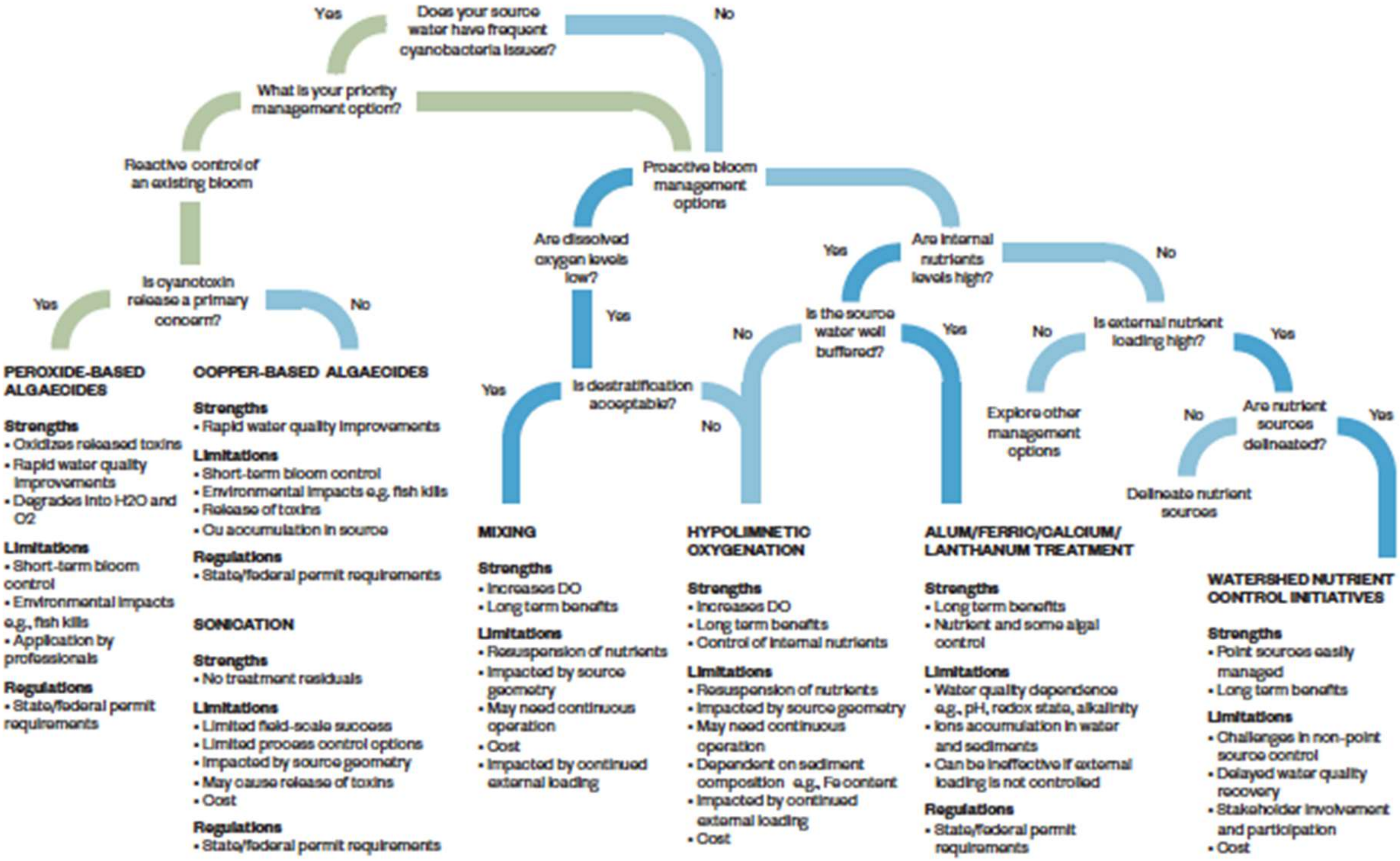
[3] Gaget, V., Almuhtaram, H., Kibuye, F. A., Hobson, P., Zamyadi, A., Brookes, J. D., Trends in production of benthic secondary metabolites across different climates-In preparation



Does your source water have frequent cyanobacteria issues?

Yes

No

What is your priority management option?

Reactive control of an existing bloom

Proactive bloom management options

Is cyanotoxin release a primary concern?

Yes

No

Are dissolved oxygen levels low?

Yes

Is destratification acceptable?

Yes

No

Are internal nutrients levels high?

Yes

No

Is the source water well buffered?

No

Yes

Is external nutrient loading high?

No

Explore other management options

Yes

Are nutrient sources delineated?

No

Delineate nutrient sources

Yes

PEROXIDE-BASED ALGAECIDES

Strengths
- Oxidizes released toxins
- Rapid water quality improvements
- Degrades into H2O and O2

Limitations
- Short-term bloom control
- Environmental impacts e.g., fish kills
- Application by professionals

Regulations
- State/federal permit requirements

COPPER-BASED ALGAECIDES

Strengths
- Rapid water quality improvements

Limitations
- Short-term bloom control
- Environmental impacts e.g. fish kills
- Release of toxins
- Cu accumulation in source

Regulations
- State/federal permit requirements

SONICATION

Strengths
- No treatment residuals

Limitations
- Limited field-scale success
- Limited process control options
- Impacted by source geometry
- May cause release of toxins
- Cost

Regulations
- State/federal permit requirements

MIXING

Strengths
- Increases DO
- Long term benefits

Limitations
- Resuspension of nutrients
- Impacted by source geometry
- May need continuous operation
- Cost
- Impacted by continued external loading

HYPOLIMNETIC OXYGENATION

Strengths
- Increases DO
- Long term benefits
- Control of internal nutrients

Limitations
- Resuspension of nutrients
- Impacted by source geometry
- May need continuous operation
- Dependent on sediment composition e.g., Fe content
- Impacted by continued external loading
- Cost

ALUM/FERRIC/CALCIUM/ LANTHANUM TREATMENT

Strengths
- Long term benefits
- Nutrient and some algal control

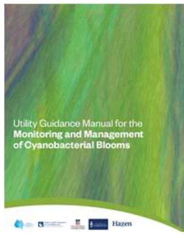
Limitations
- Water quality dependence e.g., pH, redox state, alkalinity
- Ions accumulation in water and sediments
- Can be ineffective if external loading is not controlled

Regulations
- State/federal permit requirements

WATERSHED NUTRIENT CONTROL INITIATIVES

Strengths
- Point sources easily managed
- Long term benefits

Limitations
- Challenges in non-point source control
- Delayed water quality recovery
- Stakeholder involvement and participation
- Cost



Protocols for algal bloom management
Source mitigation using sonication

intelligent water networks

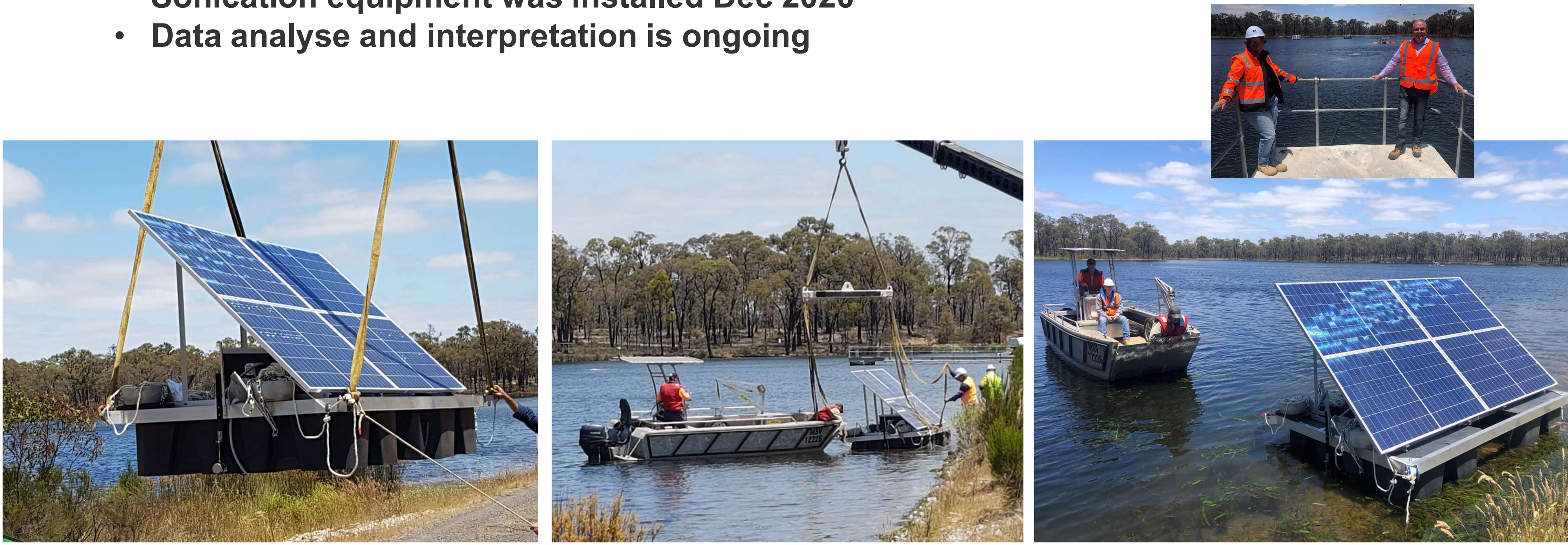
VICTORIA State Government | Environment, Land, Water and Planning

CENTRAL HIGHLANDS WATER

VEOLIA

Trial package for Intelligent Water Network (IWN) & Veolia:

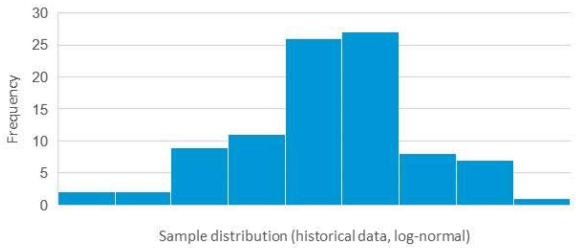
- Trialling of non-chemical dosing for cyanobacteria mitigation at the source
- Developed the sampling protocol to collect systematic algal and cyanobacterial, and water quality data
- Sonication equipment was installed Dec 2020
- Data analyse and interpretation is ongoing

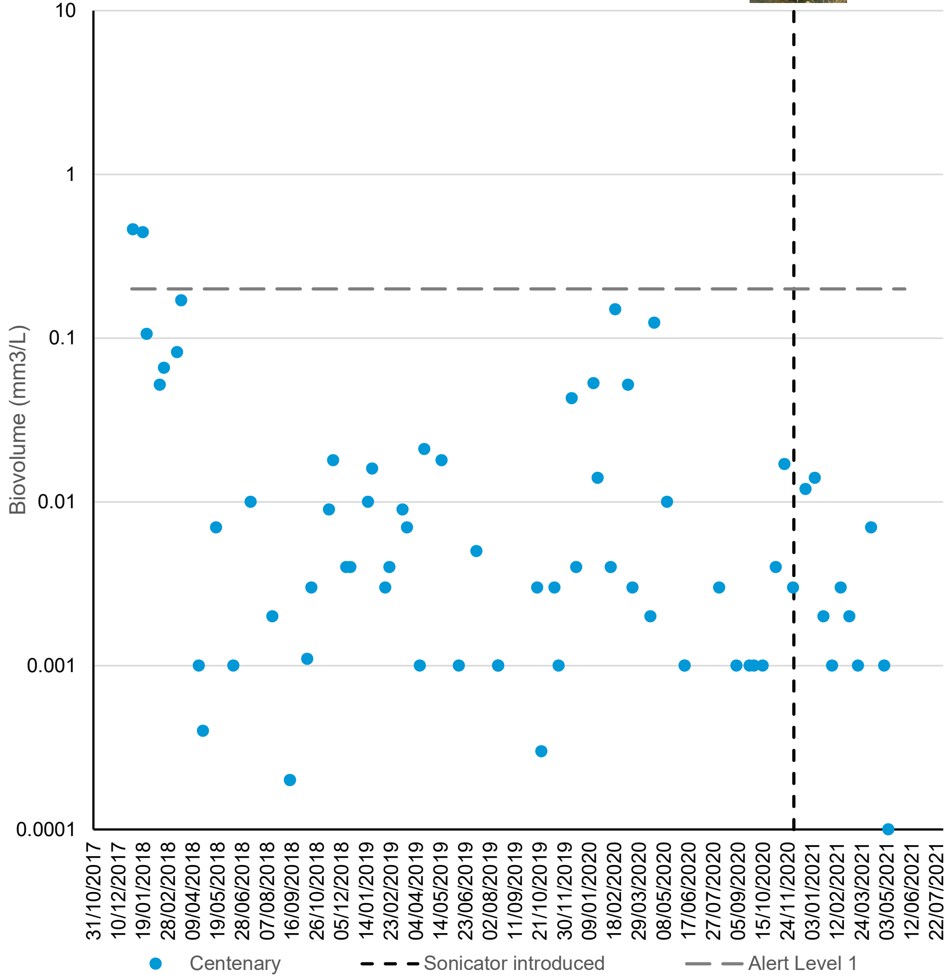


Source mitigation using sonication

Total Cyanobacteria Biovolumes – Statistical Observations

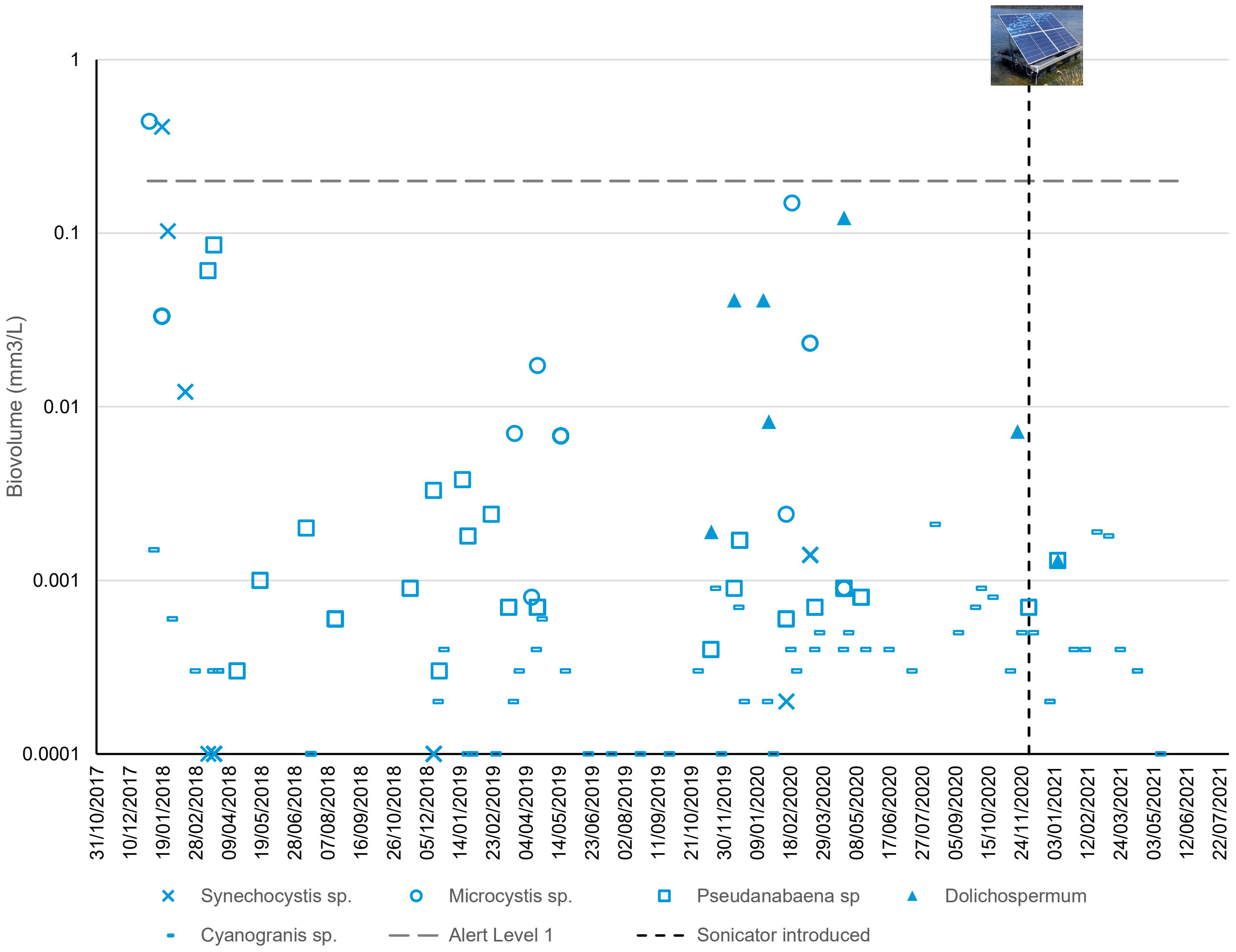
- **Preliminary analysis (Log-normal distribution)**
    - **Practicality of controls?**
    - **Data from only 1 bloom season**
    - **Testing is lower during non-bloom periods**
- Centenary Reservoir Walkway
    - Historical distribution (n=56) compared to post-sonicator distribution (n=10)
    - Statistically significant difference observed
- Water treatment plant intake stream
    - Historical (n=94) and post-sonicator (n=20)
    - Statistically significant difference observed



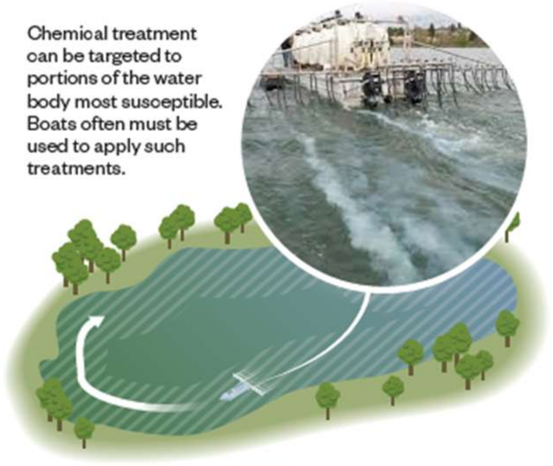


Dominant Cyanobacteria Species Biovolumes – Centenary Reservoir

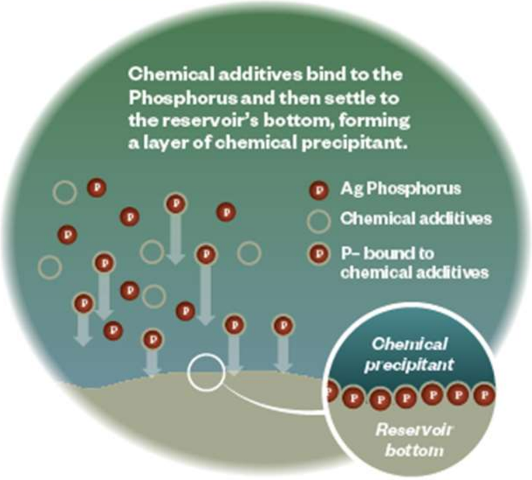
- Disruptions in dominant species observed after sonicator installation
- *Microcystis sp.* undetected in 2020/2021 bloom season
- *Cyanogranis sp.* and *Anathece sp.* dominant in recent blooms

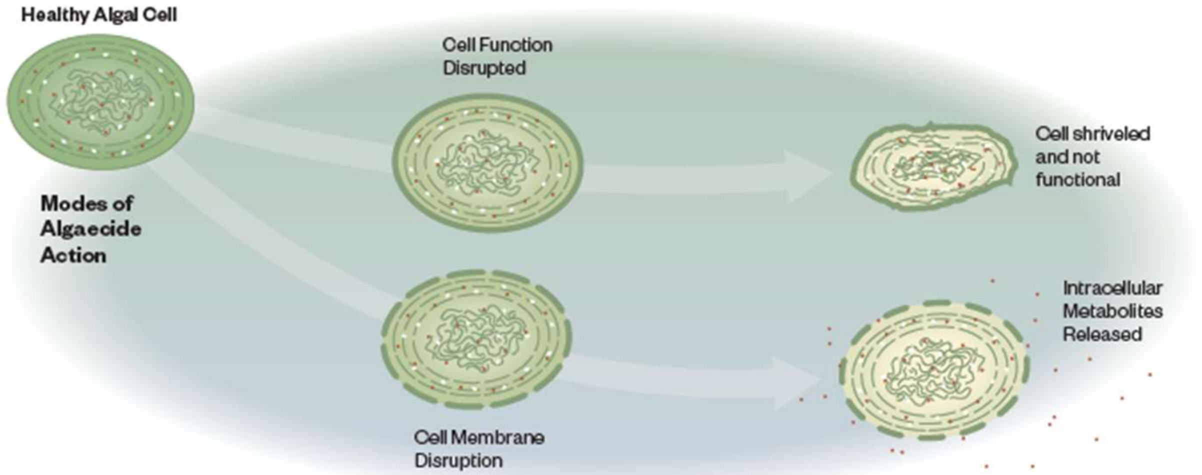


CHEMICAL CONTROL STRATEGIES



Chemical treatment methods consist of algaecides and nutrient sequestering chemicals frequently are applied by boat. Copper and peroxide-based algaecides damage cellular integrity and cause cell death (Figure 11), limiting bloom expansion in a drinking water source. Nutrient sequestering additives such as alum, polyaluminum chloride (PACl), iron salts, and bentonite clays bind P in the water column, creating nutrient limited conditions that inhibit cyanobacteria growth. A detailed review of chemical methods is available^4.





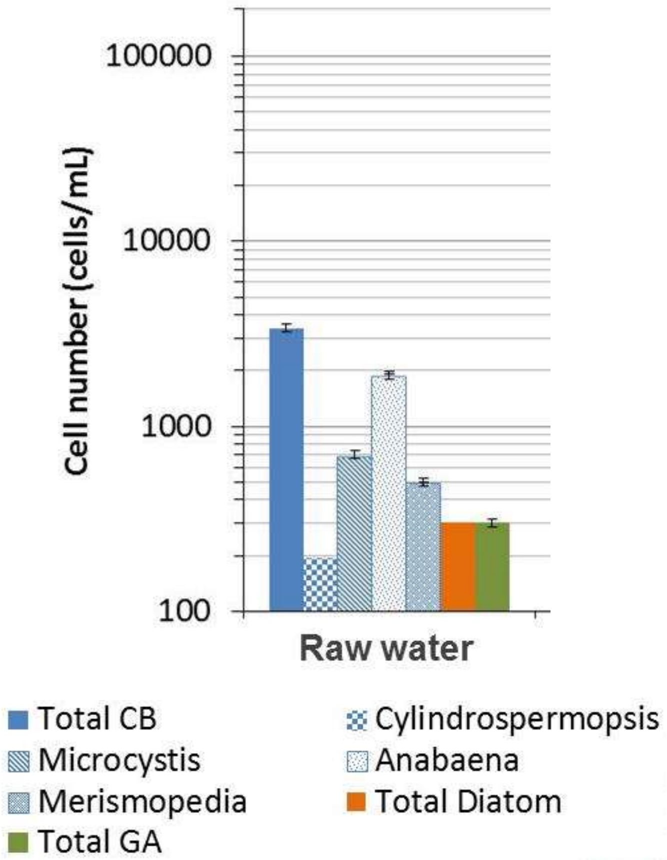
K.E. Greenstein, A. Zamyadi, C.M. Glover, C. Adams, E. Rosenfeldt, E.C. Wert (2020) Delayed Release of Intracellular Microcystin Following Partial Oxidation of Cultured and Naturally Occurring Cyanobacteria. Toxins, 12(5), 335.

A. Zamyadi, K. E. Greenstein, C. M. Glover, C. Adams, E. Rosenfeldt, E. C. Wert (2020) Impact of hydrogen peroxide and copper sulfate on the delayed release of microcystin. Water, 12(4).

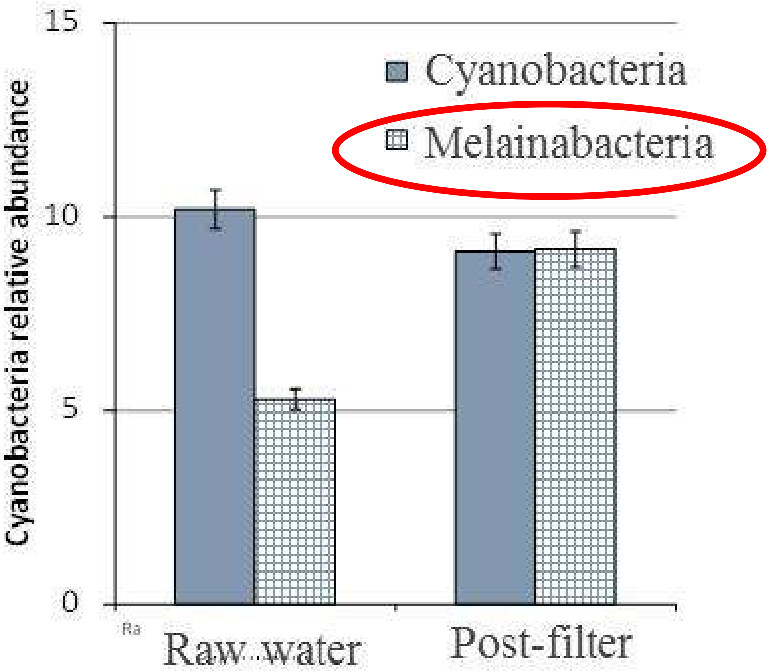
Kibuye et. al (2021) "A critical review on operation and performance of source water control strategies for cyanobacterial blooms: Part I-chemical control methods"

TREATMENT ISSUES/UNKNOWNS?

Identified organisms using macroscopic taxonomy



Extra info obtained by genomics



Water Research 152 (2019) 96–105

Contents lists available at ScienceDirect

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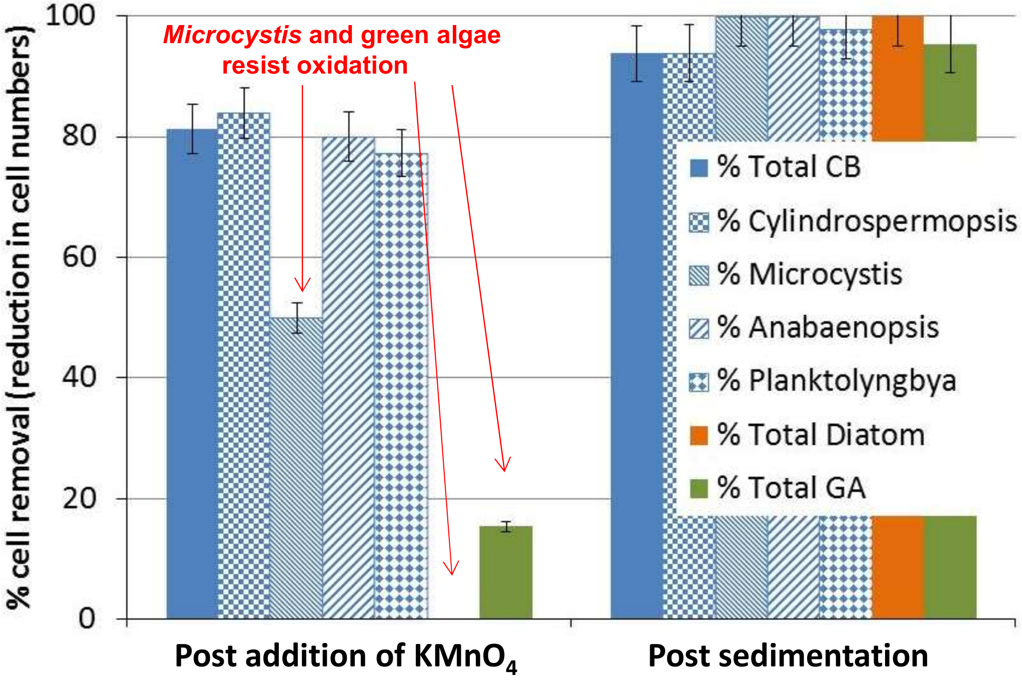
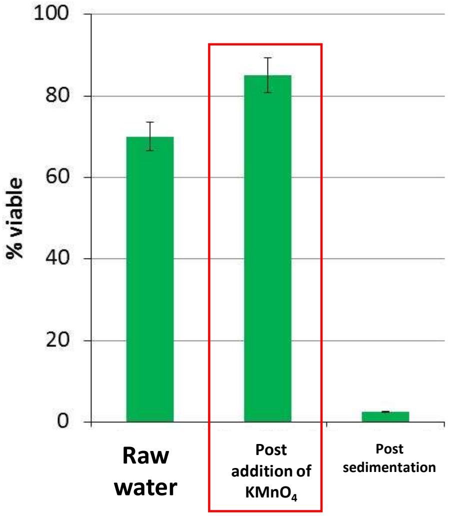
Sampling results: Pre-oxidation using pre-$KMnO_4$:

% cell removal & total MIB

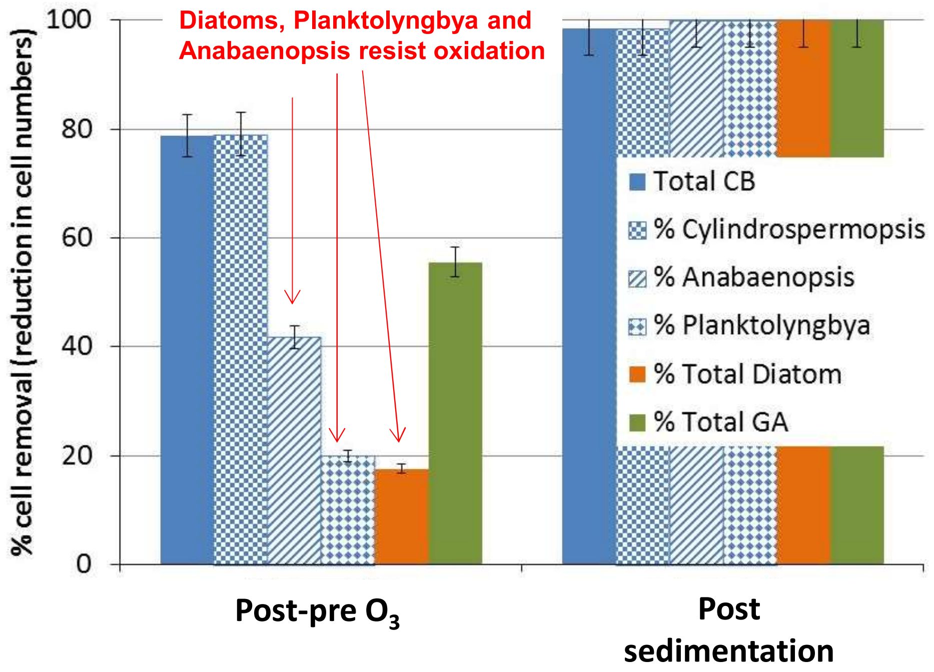

Microcystis and green algae resist oxidation


High removal rate but the remaining were healthy cells

	Raw water	Raw water + KMnO4	Surface of sedimentation tank	Filtered water	Finished water
MIB (ng/L) :	**12.6**	**12.9**	**6.6**	**6.4**	**6.8**

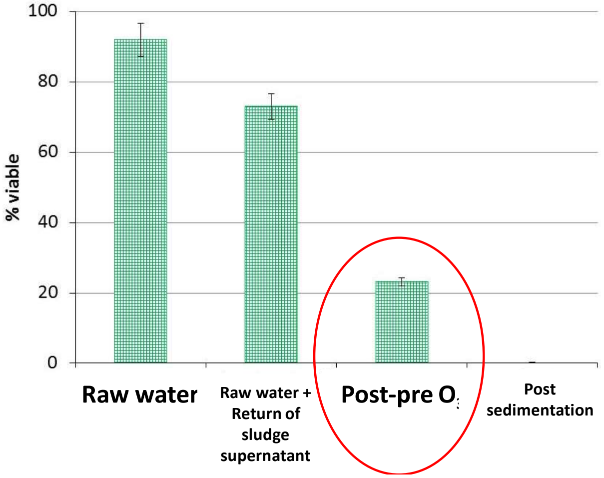
Sampling results: Pre-oxidation using pre-O_3

% cell removal & total geosmin



Diatoms, Planktolyngbya and Anabaenopsis resist oxidation

High removal rate & the remaining were damaged cells



Geosmin (ng/L) :

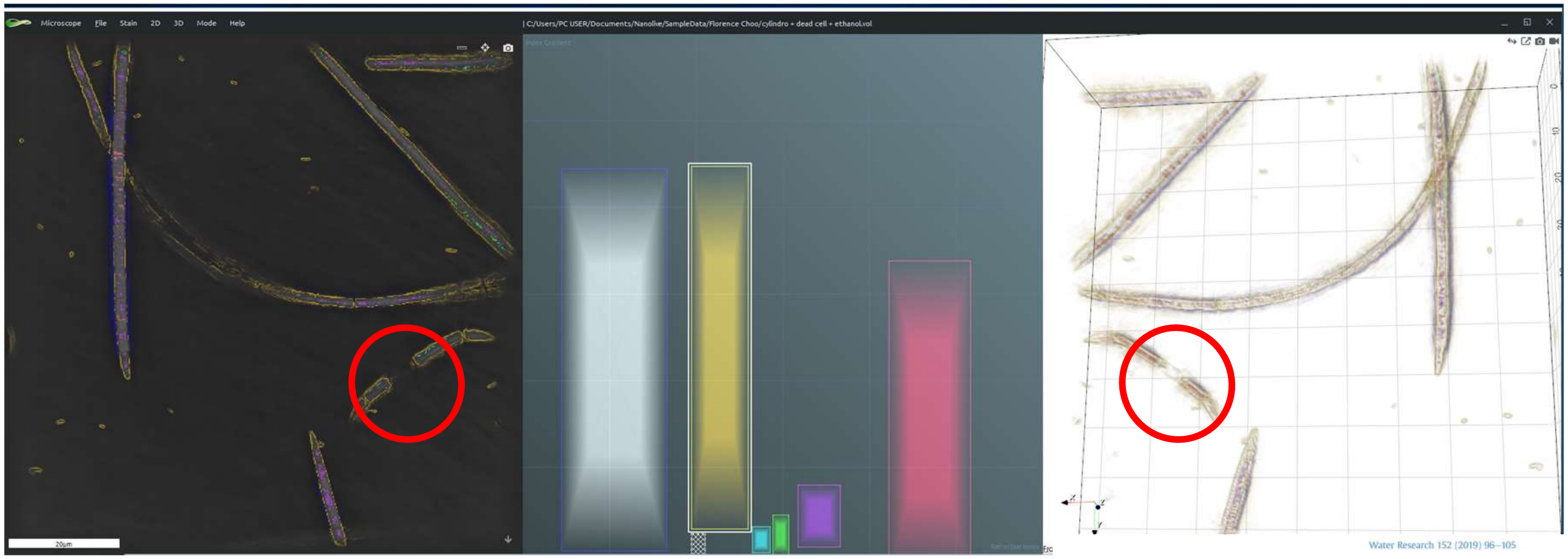
Raw water	Return of sludge recovery supernatant	Post pre-ozonation	Surface of sedimentation tank	Filtered water	Post interozonation and BAC	Finished water
15.9	15.1	8.7	7.6	BDL	BDL	BDL

Accumulation of geosmin in sludge: 20.6 ng/L

OXIDATION – UNKNOWNS?

Understand the phenomena governing cell wall damage & release of intracellular metabolites during oxidation:

Fate of Cylindrospermopsis cells post ozonation



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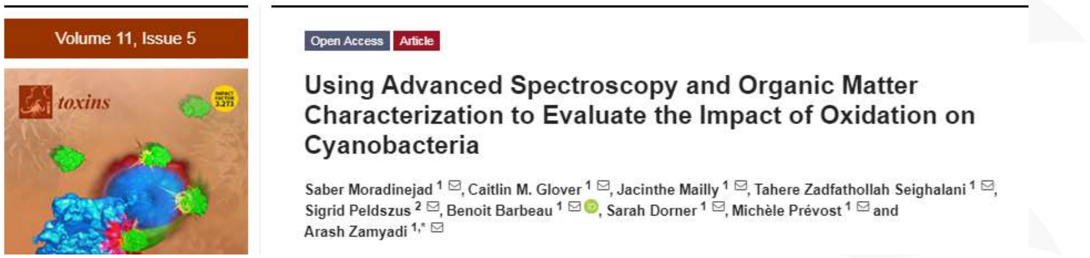
Flowcytometry confirmed complete cells damaged but not at the same level!

Understanding oxidation:

Understand the phenomena governing oxidation of cells, biomarker indicating toxin production, triggers of toxicity, release of intracellular metabolites



Volume 11, Issue 5

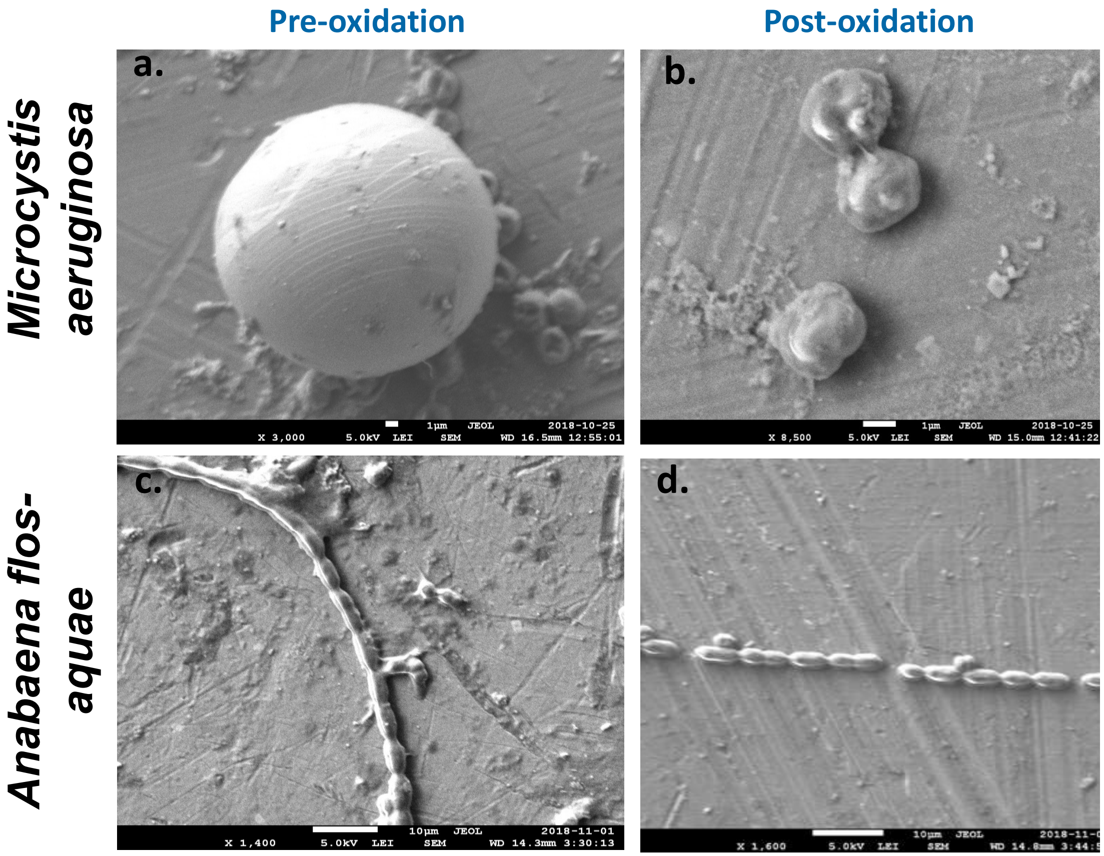
toxins

Open Access Article

Using Advanced Spectroscopy and Organic Matter Characterization to Evaluate the Impact of Oxidation on Cyanobacteria

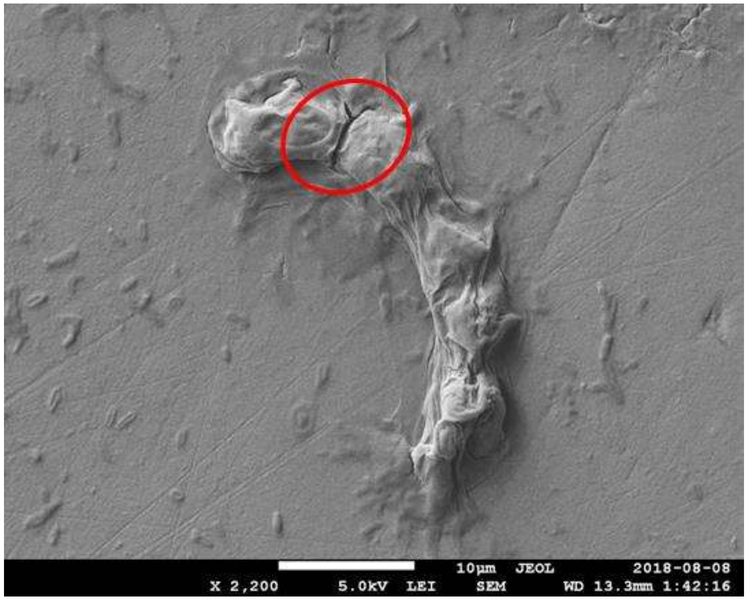
Saber Moradinejad [1], Caitlin M. Glover [1], Jacinthe Mailly [1], Tahere Zadfathollah Seighalani [1], Sigrid Peldszus [2], Benoit Barbeau [1], Sarah Dorner [1], Michèle Prévost [1] and Arash Zamyadi [1,*]

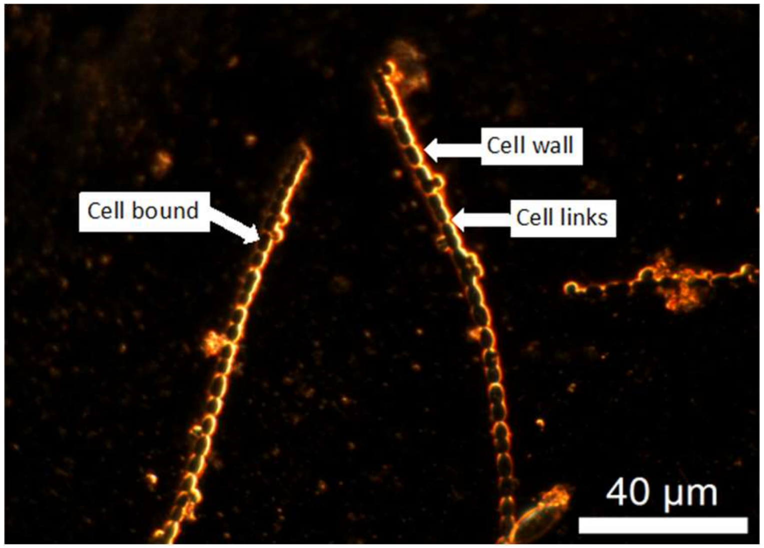
Chlorination for maximum dose-contact time (CT) 120 mg.min/L and ozonation for maximum dose-contact time (CT) 50 mg.min/L



Understanding oxidation:

Enhanced Darkfield Microscopy with Hyperspectral Imaging (EDM/HSI) allows for spectra (400–1000 nm) to be generated from a specific pixel (containing a cell component of interest)





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[1] BGA Innovation Hub and Civil, Mineral and Mining Engineering Department, Polytechnique Montréal, Montréal, QC H3T 1J4, Canada

[2] Department of Civil & Environmental Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

* Author to whom correspondence should be addressed.

Toxins **2019**, *11*(5), 278; https://doi.org/10.3390/toxins11050278

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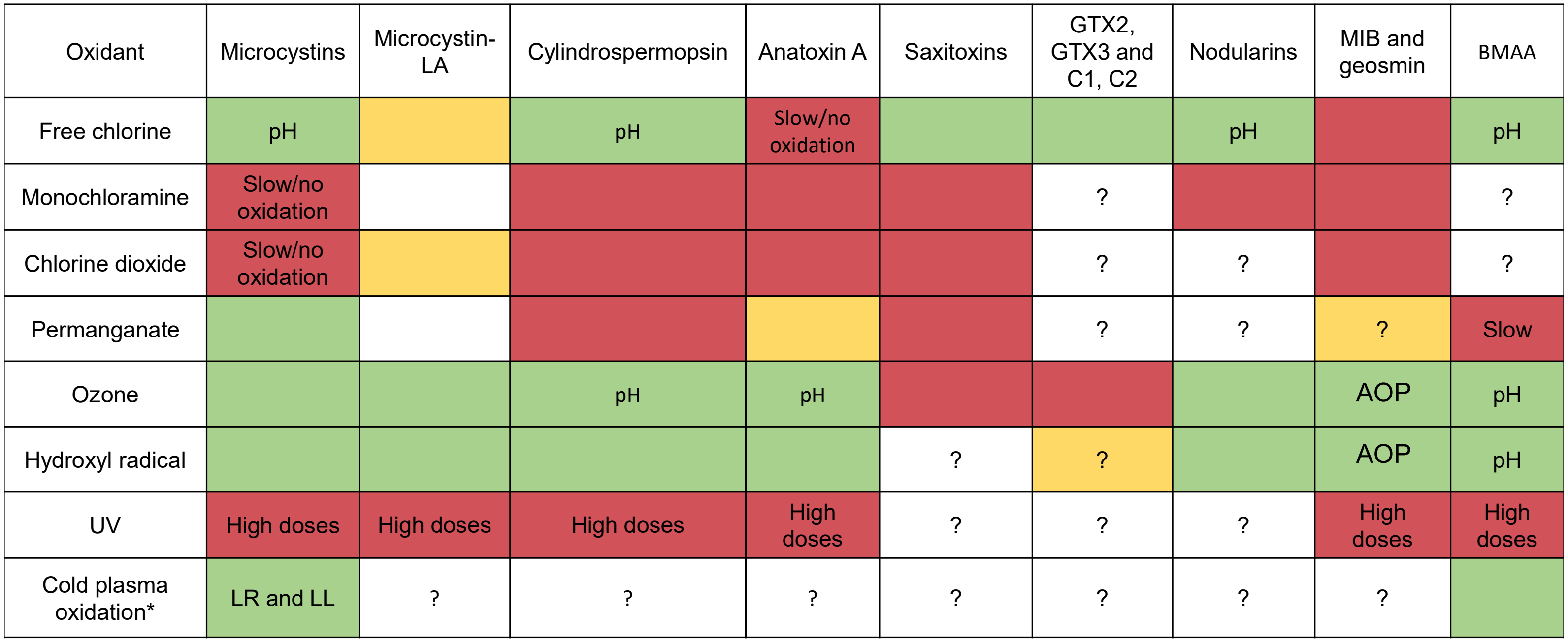
(This article belongs to the Collection Toxicological Challenges of Aquatic Toxins)

OXIDATION?

WRF4692 - #WRFCyanoToxinOxid:

Release of Intracellular Cyanotoxins During Oxidation of Naturally Occurring and Lab Cultured Cyanobacteria



Oxidant	Microcystins	Microcystin-LA	Cylindrospermopsin	Anatoxin A	Saxitoxins	GTX2, GTX3 and C1, C2	Nodularins	MIB and geosmin	BMAA
Free chlorine	🟩 pH	🟨	🟩 pH	🟥 Slow/no oxidation	🟩	🟩	🟩 pH	🟥	🟩 pH
Monochloramine	🟥 Slow/no oxidation		🟥	🟥	🟥	?	🟥	🟥	?
Chlorine dioxide	🟥 Slow/no oxidation	🟨	🟥	🟥	🟥	?	?	🟥	?
Permanganate	🟩		🟥	🟨	🟥	?	?	🟨 ?	🟥 Slow
Ozone	🟩	🟩	🟩 pH	🟩 pH	🟥	🟥	🟩	🟩 AOP	🟩 pH
Hydroxyl radical	🟩	🟩	🟩	🟩	?	🟨 ?	🟩	🟩 AOP	🟩 pH
UV	🟥 High doses	🟥 High doses	🟥 High doses	🟥 High doses	?	?	?	🟥 High doses	🟥 High doses
Cold plasma oxidation*	🟩 LR and LL	?	?	?	?	?	?	?	🟩

*Treatment technology currently at bench-scale.

AOP: a method to produce…

OH$^\bullet$ (hydroxyl radical)

- very powerful and fast (nanoseconds)

Other radicals ($O_2^{\bullet -}$, $Cl^\bullet$, $SO_4^{\bullet -}$, etc.)

Some methods for AOPs

Ozone-based
  - $O_3 + H_2O_2$, O_3 + UV

UV-based
  - UV + H_2O_2, UV+Cl2, UV + TiO_2, vacuum UV

Others
  - $H_2O_2 + Fe^{2+}$ at low pH (Fenton process)

Drawback: $$

Purposes

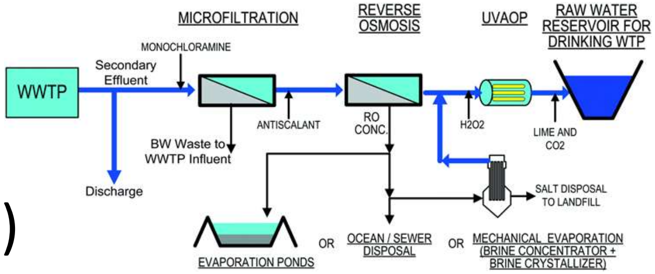
Micropollutants

- surface waters (e.g. pesticides), groundwaters (e.g. solvents), wastewaters (e.g. dyes)

Taste and odour compounds in surface waters

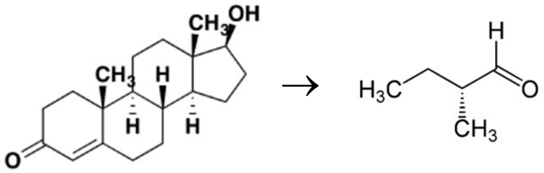
Multibarrier approach

- potable reuse
  (e.g. MF + RO + UV/H_2O_2)



AOP products

Large, complex organic + $OH^{\bullet}$
→ smaller, oxidized organic



Impractically high AOP dose → CO_2 (mineralization)

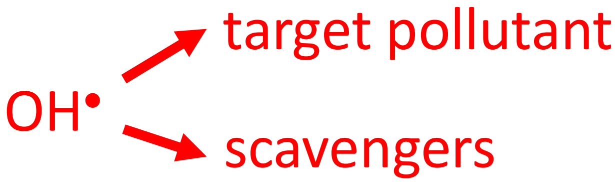
Possibility for undesirable transformation products
e.g. trichloroethylene + AOP → vinyl chloride

Research shows only rare instances of
Toxic parent + AOP → toxic byproduct
e.g. WRF project 4241 (Linden and von Gunten)

Water quality considerations

- UV absorbance/transmittance of water
  - Blocks photons
  - Put UV-AOP downstream of other treatment

- Low scavenging potential
  - TOC (k ≈ $5X10^8\ M^{-1}s^{-1}$)
  - HCO_3^- (k ≈ $1.5X10^7\ M^{-1}s^{-1}$); CO_3^{2-} (k ≈ $4X10^8\ M^{-1}s^{-1}$)



$OH^\bullet$

target pollutant

scavengers

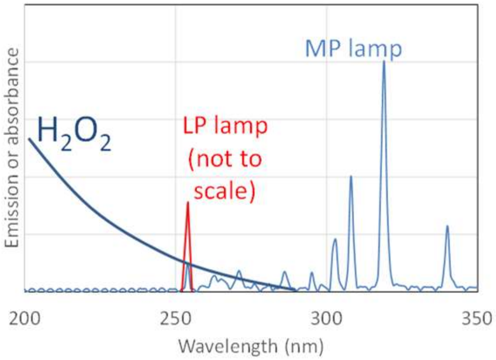
Water quality considerations

- Good oxidant/activator: absorbs photons well & has high quantum yield
  - H_2O_2 "decent" for absorbing photons, QY=1.1
- pH
  - AOP often better at low pH (less CO_3^{2-}; more HCO_3^{-})
- Temperature
  - ↑ temperature leads to small ↑ $OH^{\bullet}$ reaction rates

Types of UV-AOPs: UV/H_2O_2

- Most common
  - H_2O_2 inexpensive, relatively operator friendly
- Theoretically, LP more efficient than MP UV
  - Reactor design can affect this
- UV dose ≈ 500-1000 mJ/cm^2

  H_2O_2 dose ≈ 5-10 mg/L
- Economics: often use
  high UV dose, minimize H_2O_2

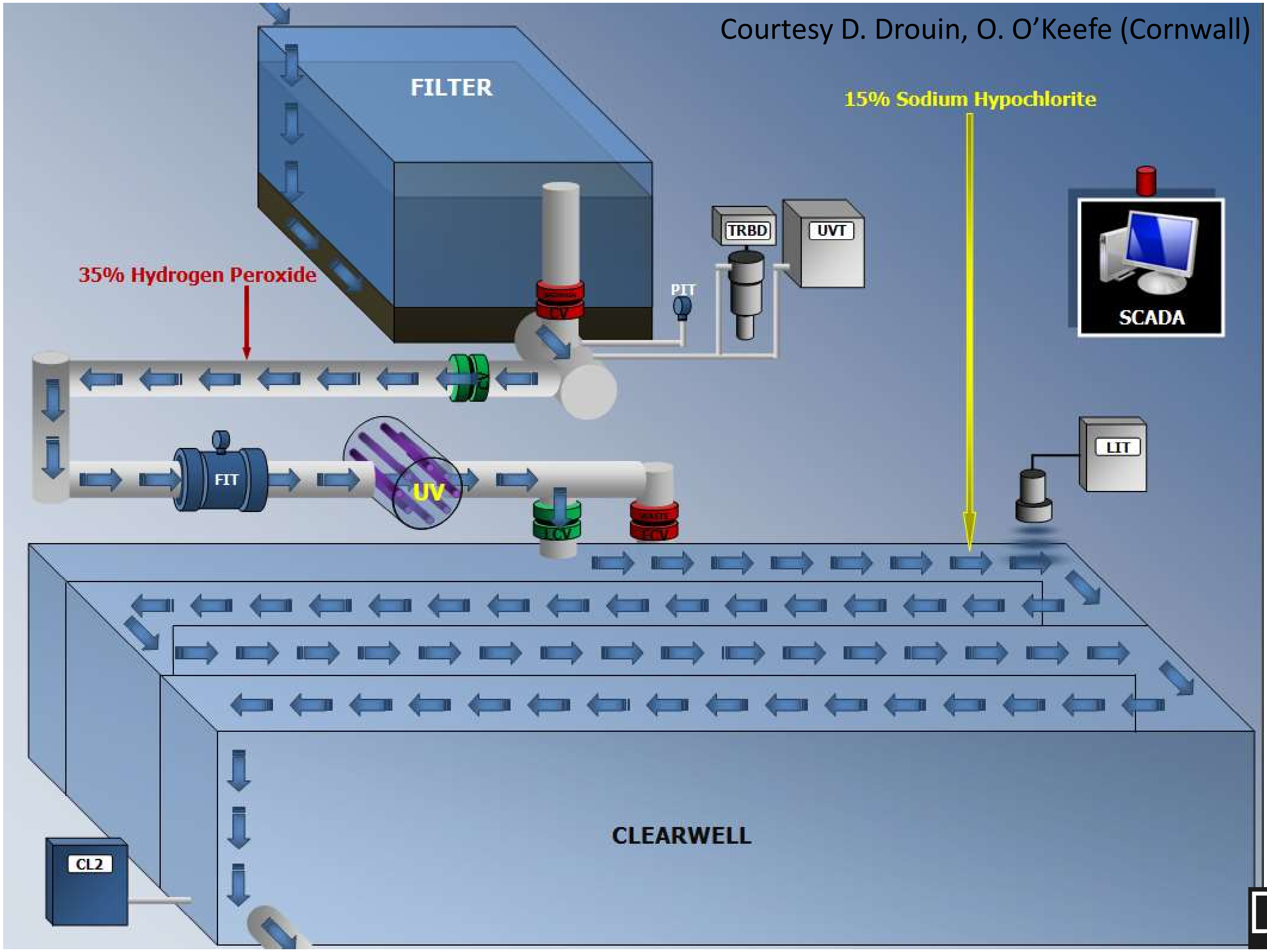



3
4
5
6
7
8
TROJANUVSWIFT
TROJANUVSWIFT


O'BRIEN
1 TONNE CAPACITY
EXIT
TROJANUVSWIFT
UV BASICS
FUTURE AOUV REACTOR
UV DRAIN

UV/H_2O_2 for seasonal geosmin

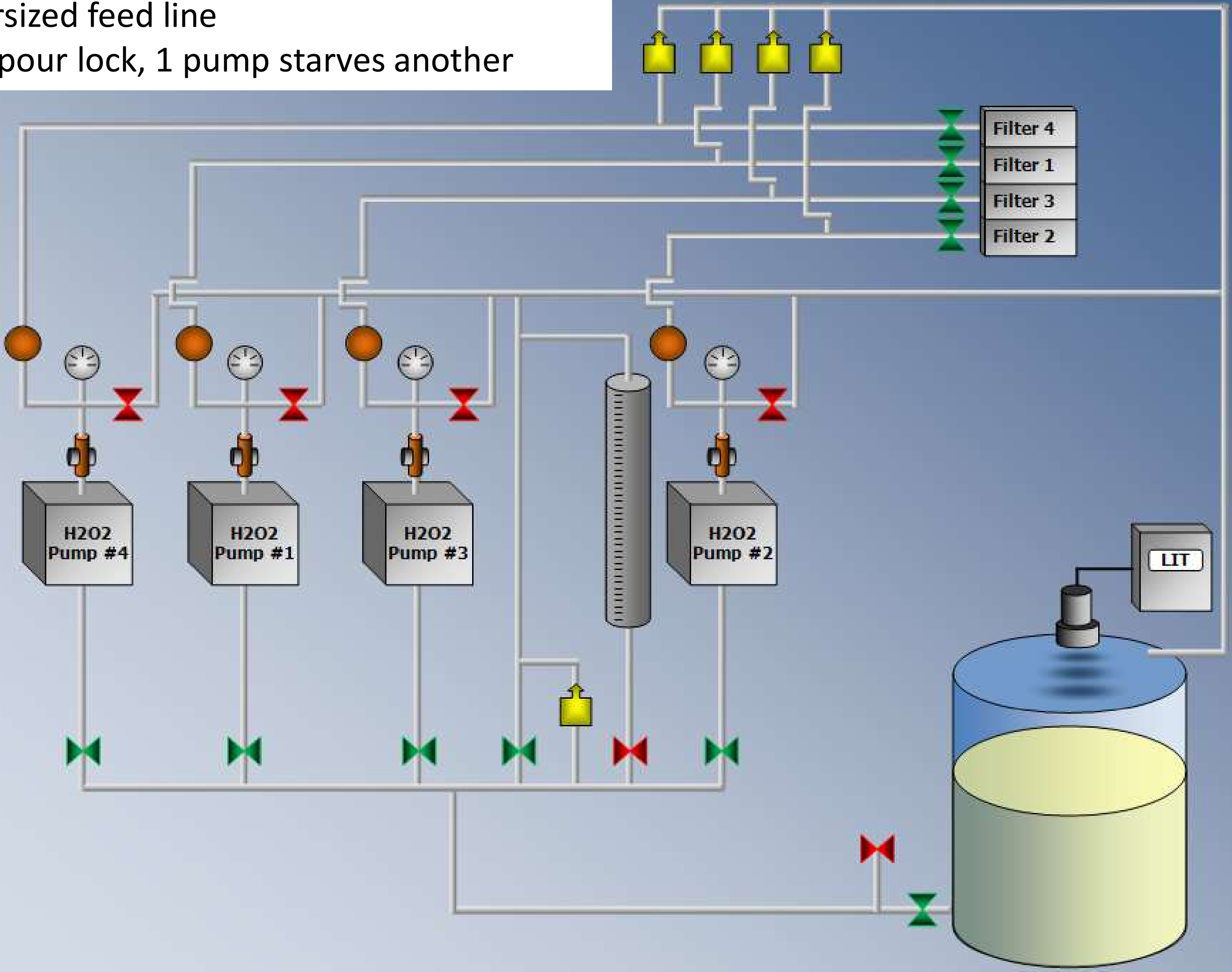
DWRG
DRINKING WATER RESEARCH GROUP

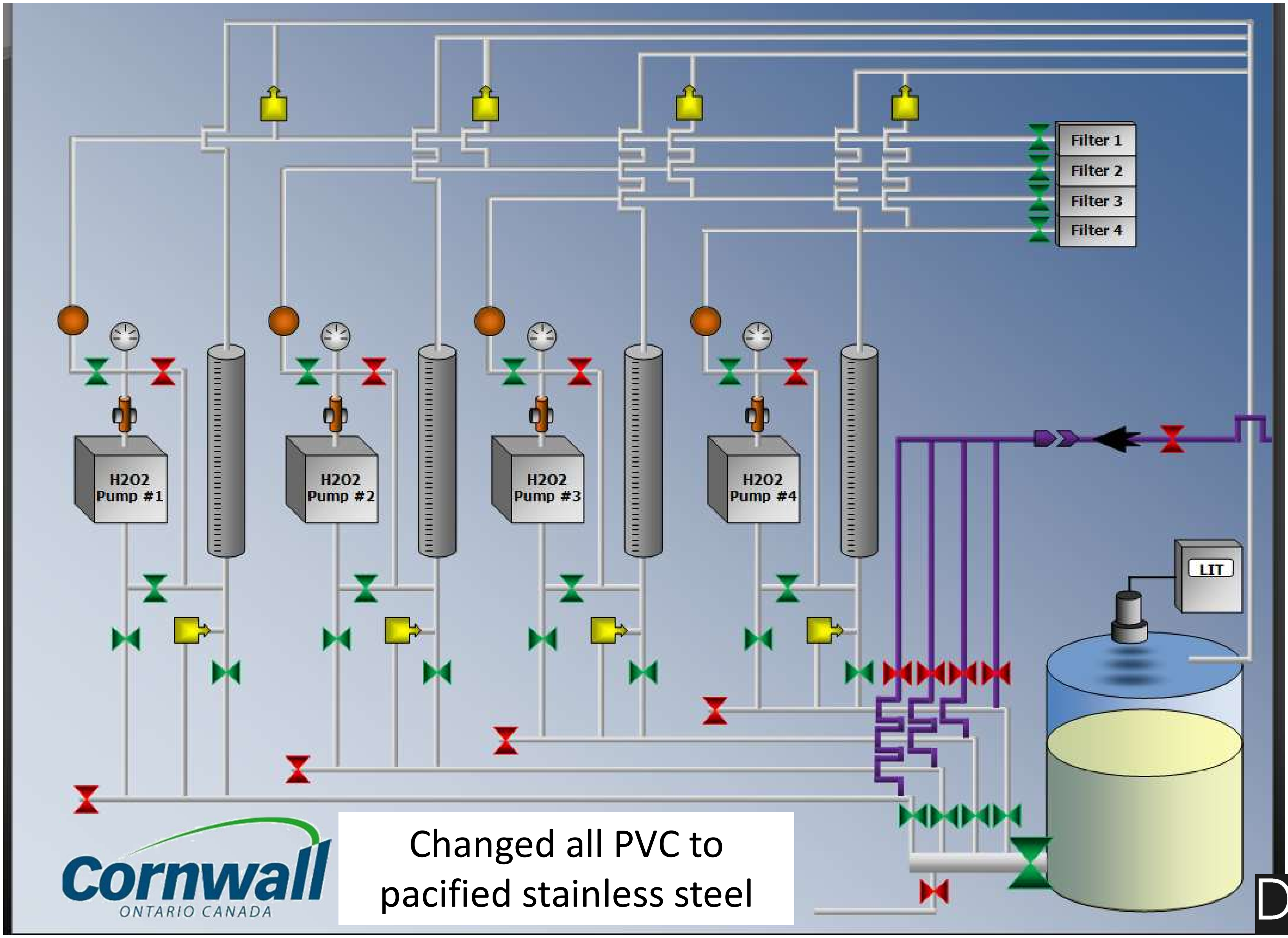


Courtesy D. Drouin, O. O'Keefe (Cornwall)

Couldn't isolate 1 pump
Undersized feed line
= vapour lock, 1 pump starves another

Courtesy D. Drouin, O. O'Keefe (Cornwall)





Changed all PVC to pacified stainless steel

DWRG
DRINKING WATER RESEARCH GROUP

H_2O_2 Quenching (for drinking water)

Only about 5-10% of H_2O_2 undergoes photolysis during UV+H_2O_2 AOP

$$H_2O_2 + \text{chlorine} \rightarrow O_2, Cl^-, H_2O$$

Must remove H_2O_2 for chlorine 2^o disinfection

- Can quench H_2O_2 with Cl_2 itself
  - Need to know how much H_2O_2 survives UV

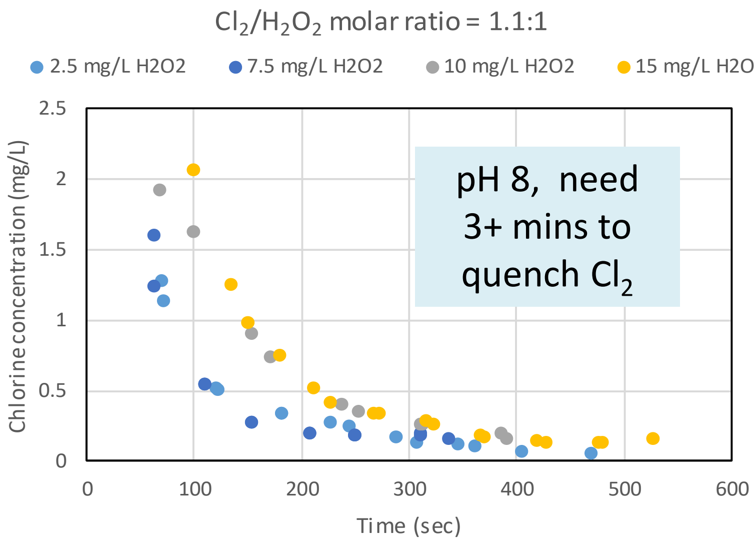
- H_2O_2 monitors can lack some accuracy
- Variable destruction across UV reactors

Reaction stoichiometry

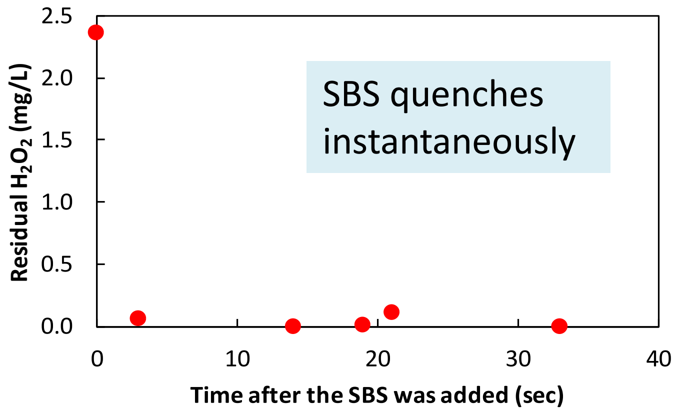
2.1 mg/L Cl_2 : 1 mg/L H_2O_2

- a 0.2 mg/L error in H_2O_2 leads to 0.4 mg/L error in Cl_2
- Also, the reaction is not instantaneous

Study on quenching H_2O_2 using Cl_2 gas or sodium bisulfite (SBS)


Cl_2/H_2O_2 molar ratio = 1.1:1

pH 8, need 3+ mins to quench Cl_2

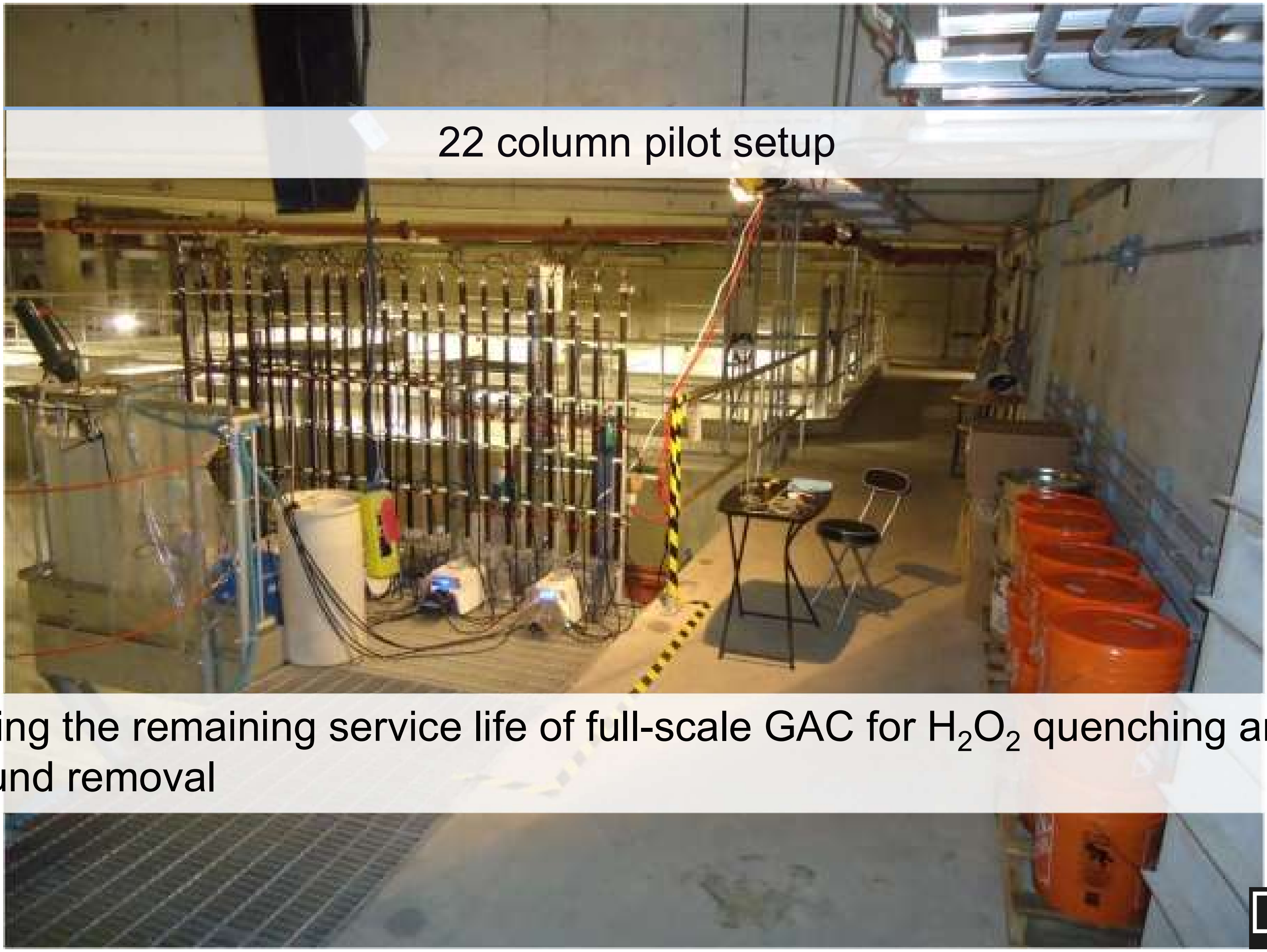

SBS quenches instantaneously

Quenching H_2O_2 with Cl_2: summary

- Conceptually elegant
- Not instantaneous
- Can be hard to control Cl_2 dose due to poor H_2O_2 monitors; reaction time
- Probably NOT a good idea for small, automated plants

H_2O_2 quenching with GAC

Pass water with H_2O_2 through GAC bed

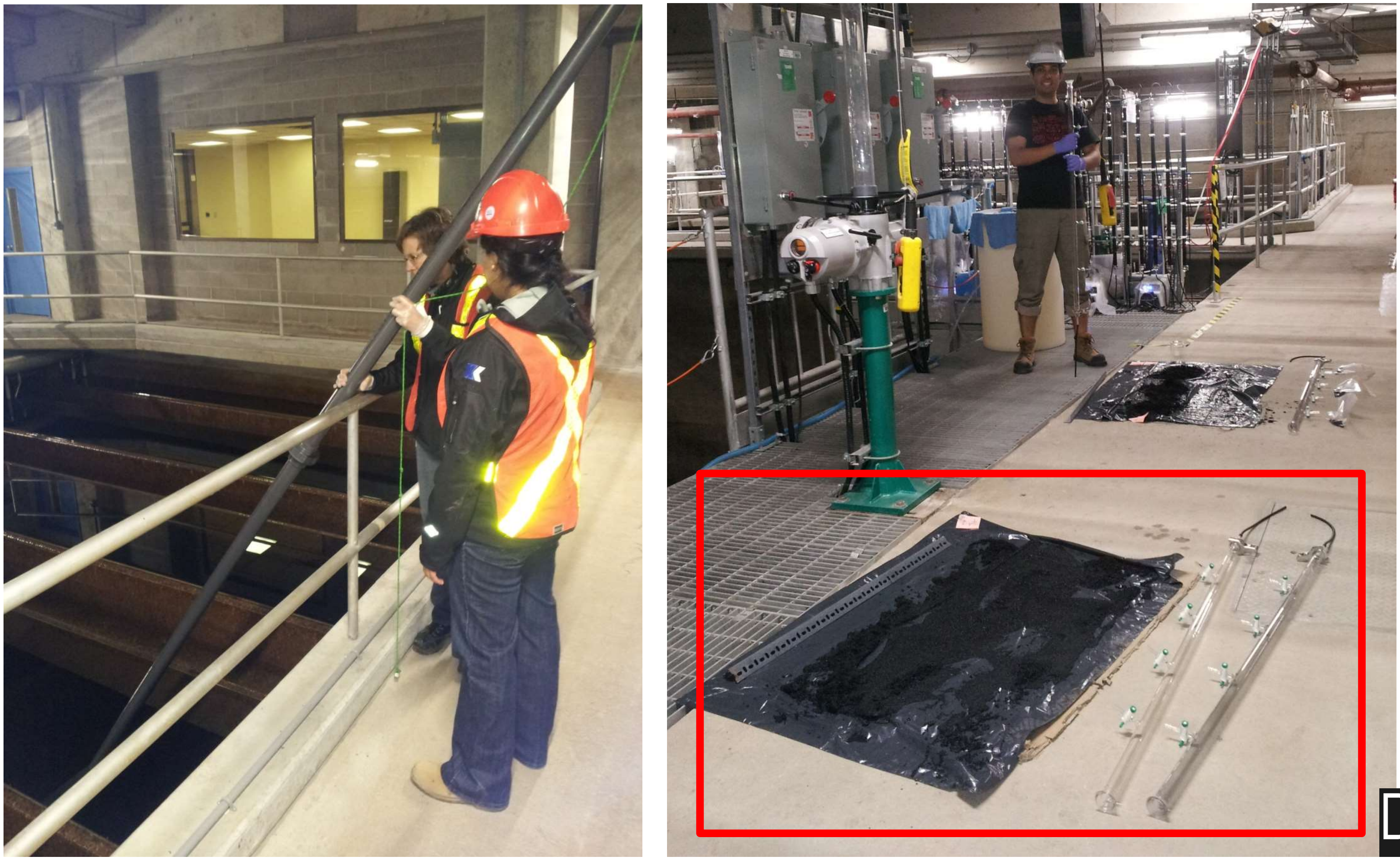


22 column pilot setup

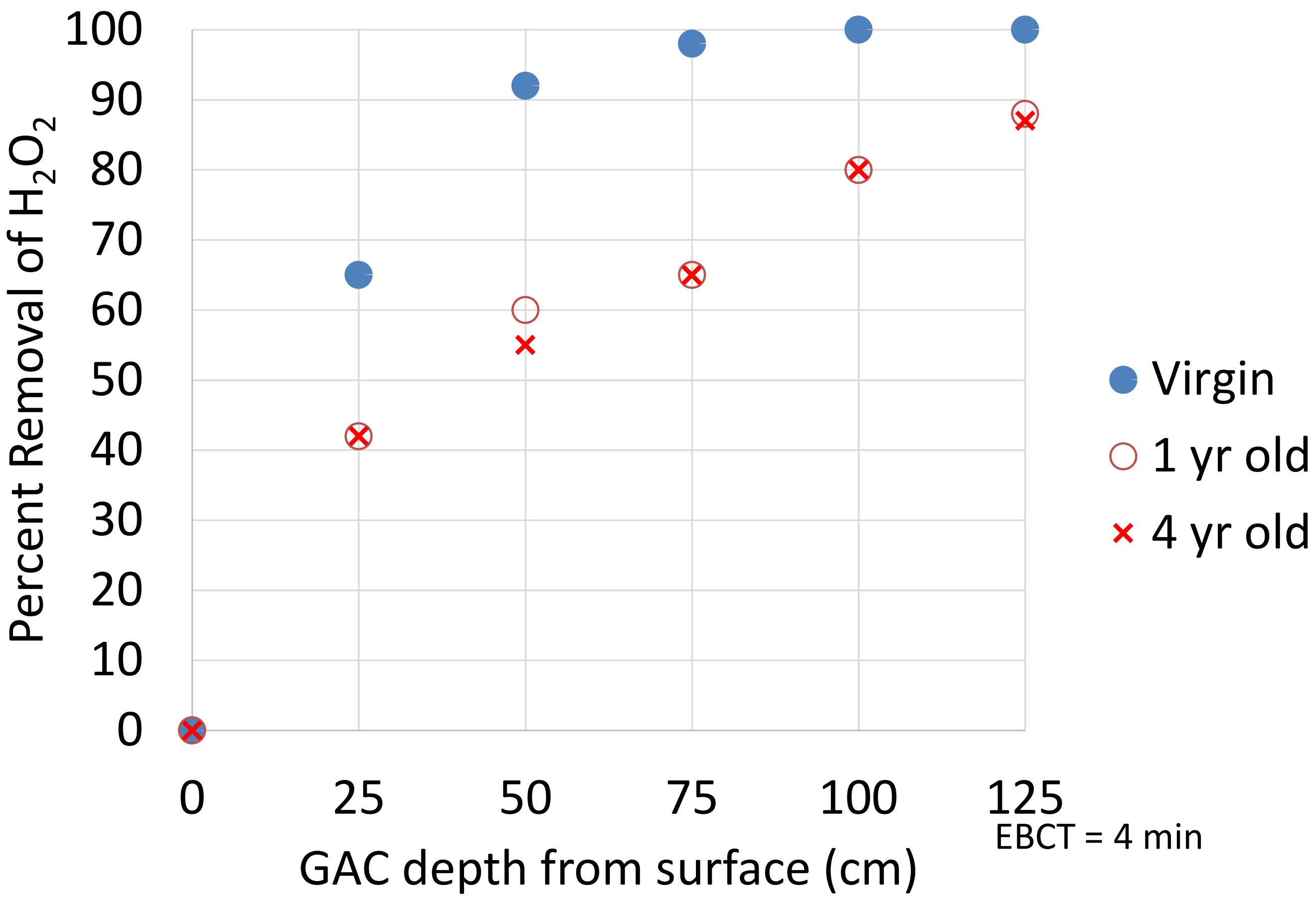
Assessing the remaining service life of full-scale GAC for H_2O_2 quenching and T&O compound removal

22 Column Pilot Set-up

Colum preparation: GAC sampling from the full-scale contactors



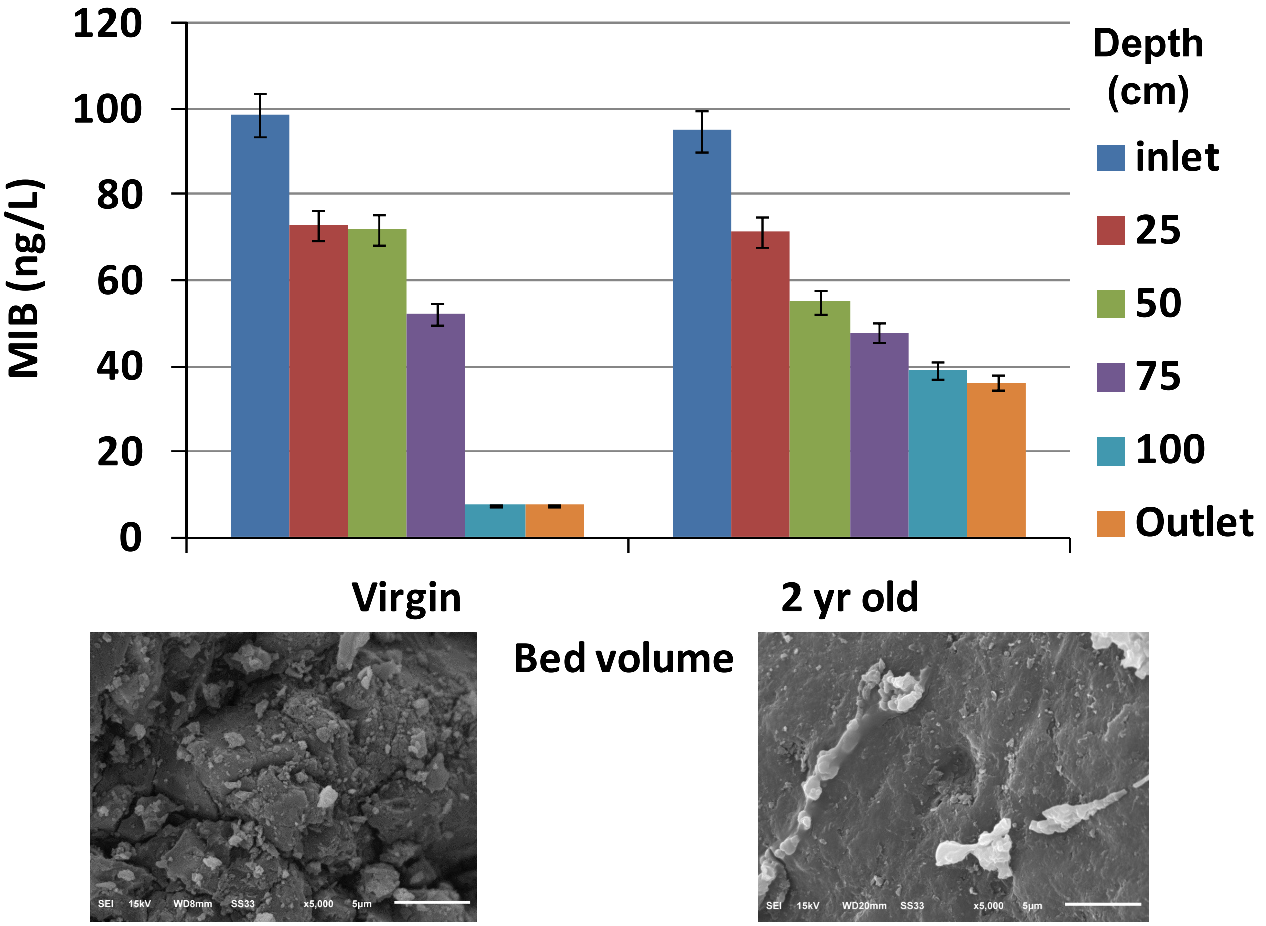
H_2O_2 quenching with GAC



EBCT = 4 min

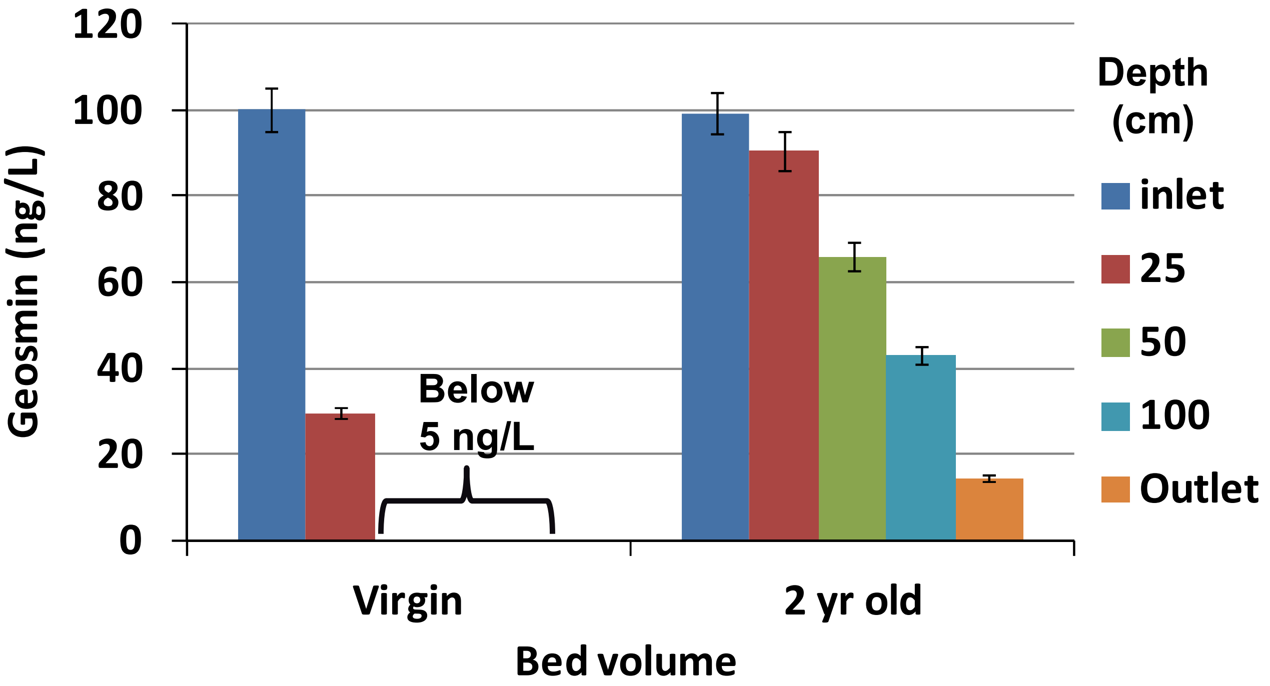
Application of GAC for removal MIB

MIB removal using full-scale & virgin centaur GAC
(similar results for 1 year old GAC and geosmin)

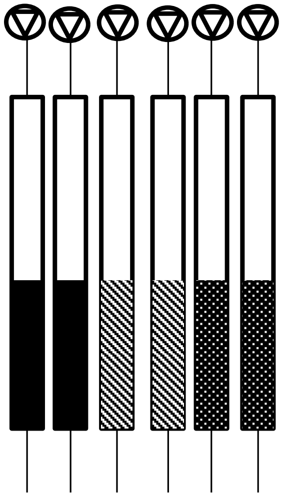


DWRG
DRINKING WATER RESEARCH GROUP

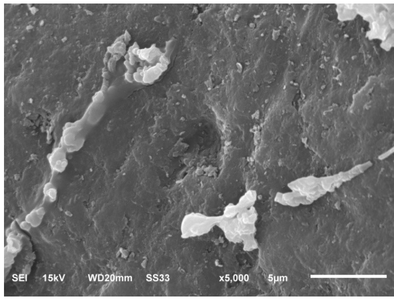
Geosmin Removal Using Full-scale & Virgin Centaur GAC

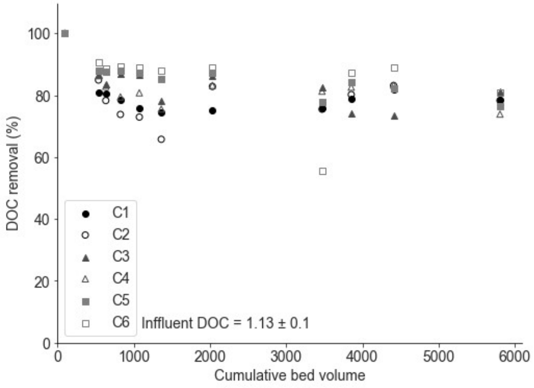


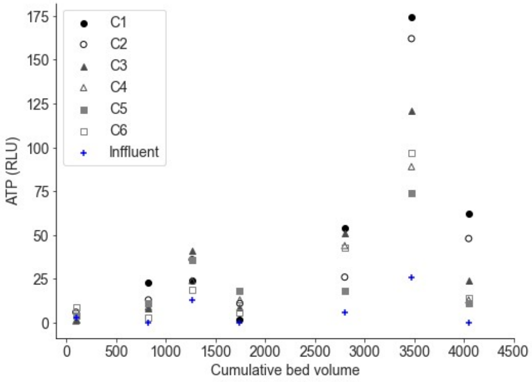
Understating BAC



- DOC
- ATP
- DO
- Nitrate
- T&O
- pH
- Temperature





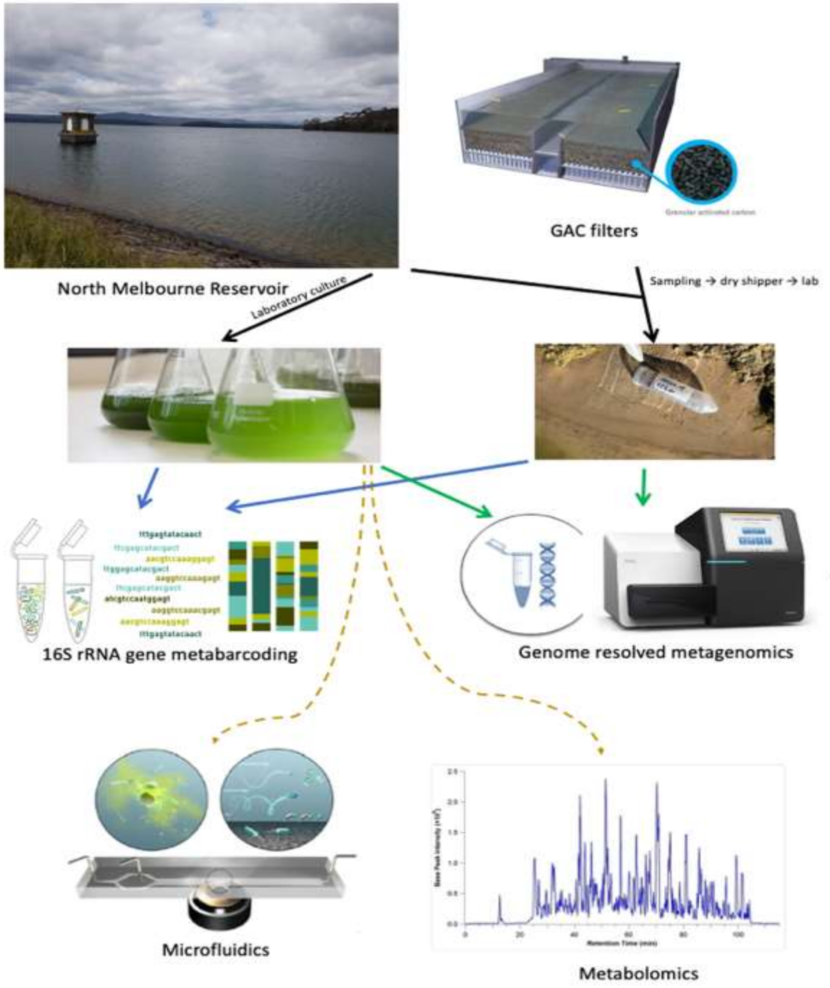


Rafael Paulino, PhD candidate at UNSW

Ongoing work: Understating BAC

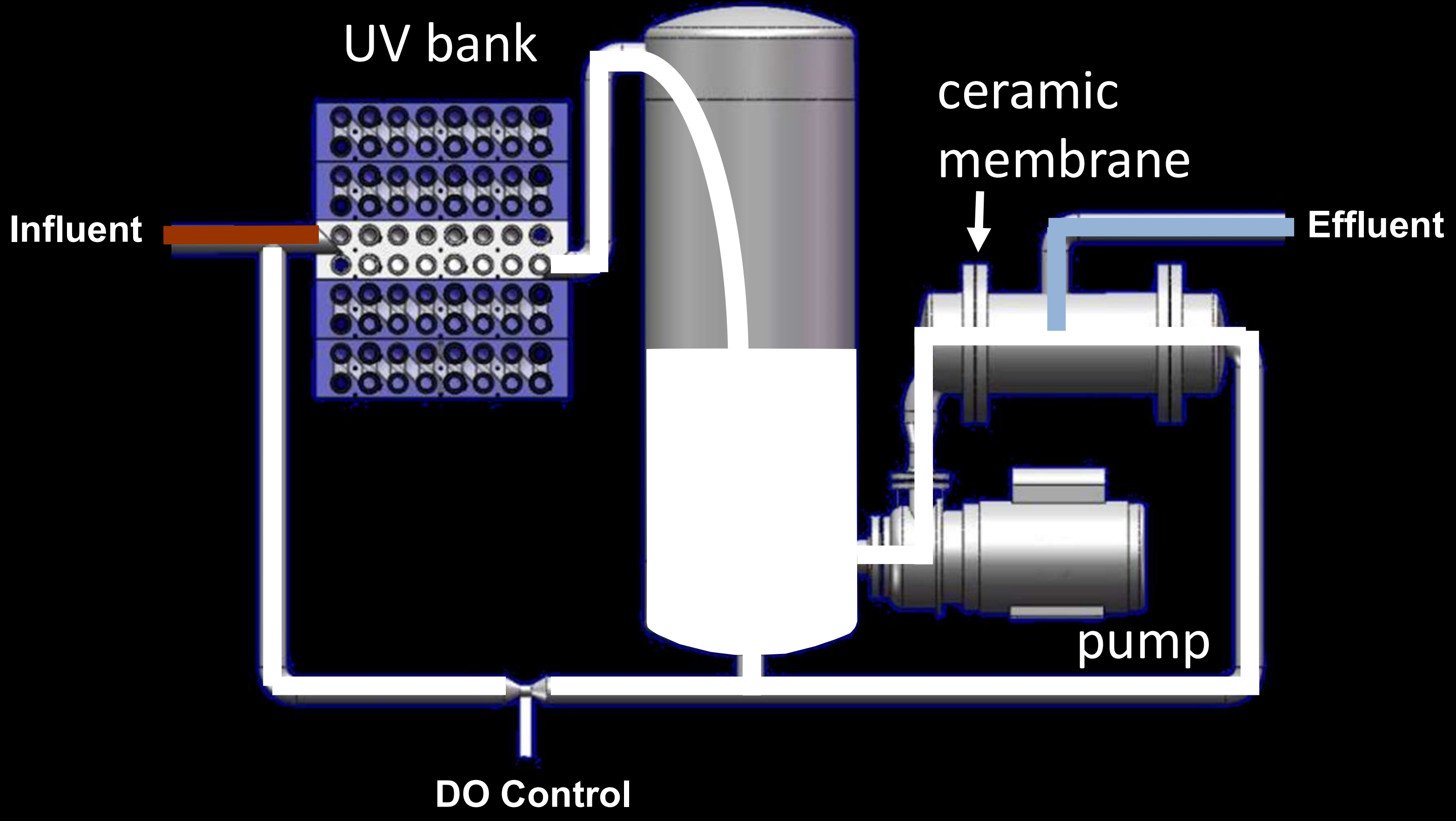
Assessment package for Melbourne Water:

- **Identity potential functions of cyanobacteria in the reservoir, as well as the BAC biofilm communities with focus on stagnation**
  - PhD student at University of Melbourne funded by an ARC Discovery Gant
  - Supervisors: Linda Blackall, Dug Romney, Arash Zamyadi (Melbourne), Jillian Banfield (University of California Berkeley)



Types of UV-AOPs: UV-TiO_2

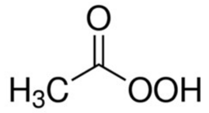
Courtesy Purifics

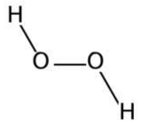


Courtesy Purifics

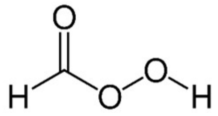
Other types of UV-AOPs

- UV + peracetic acid (PAA) → $OH^{\bullet}$
  - PAA is a disinfectant/oxidant (wastewater)

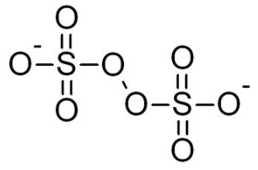




- UV + performic acid (PFA) → $OH^{\bullet}$



- UV + persulfate → $SO_4^{\bullet -}$ + $OH^{\bullet}$

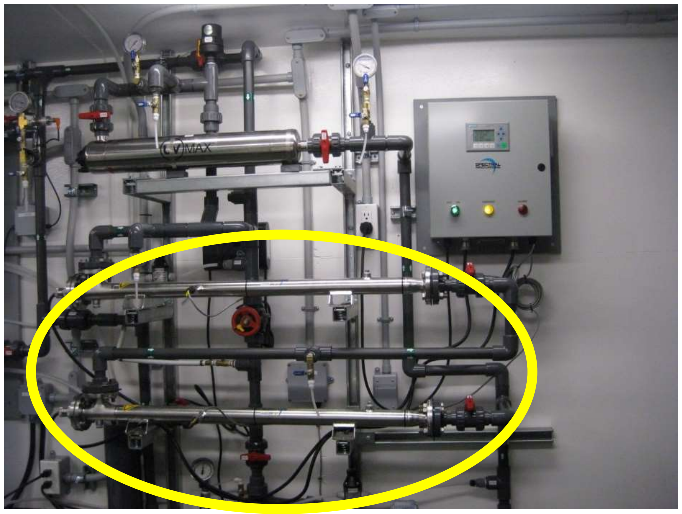


- UV + Fe(III) at pH 3 (photofenton)

Other types of UV-AOPs

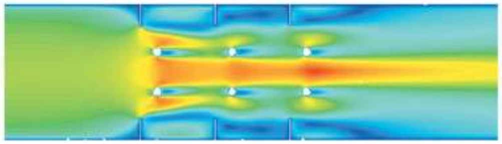
- Vacuum UV
  - UV at 185 nm: normal lamp, special quartz that allows 185 nm light through
  - $UV + H_2O \rightarrow OH^{\bullet}$

Courtesy Prof. M. Mohseni, UBC



UV-AOP Reactor Design and Regulation

- Much simpler than UV drinking water disinfection
  - You can *measure* effluent quality (e.g. T&O, 1,4-dioxane)
- Major vendors have models to ensure adequate dose based on worst-case:
  - Scavenging potential, UVT, flow rate, pH, UV power, etc.



UV-AOP Reactor Design and Regulation

- Drinking water: combined AOP + disinfection
  - Can do both, but likely a compromised design:

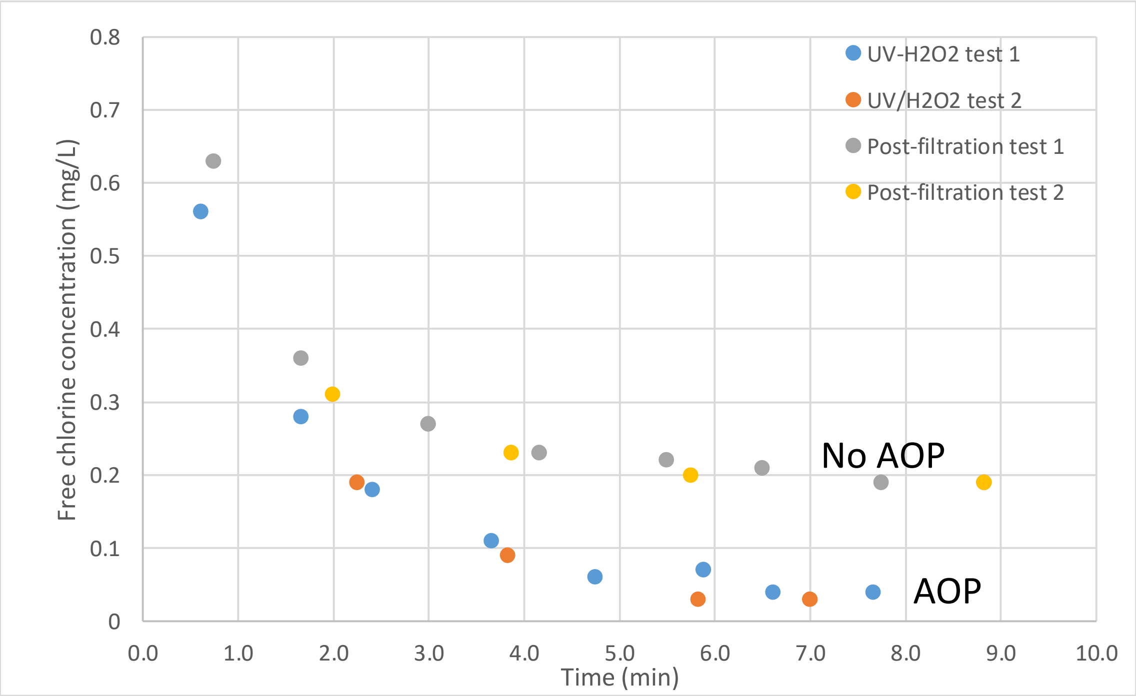
    best disinfection reactor ≠ best AOP reactor
    (different optimum lamp spacing, etc.)
  - Often turn lamps on/off for disinfection vs. AOP
    - e.g. 4 lamps for disinfection, 16 for AOP
  - Regulators likely(?) to give full disinfection credit when operating at AOP doses

AOP DBPs (Drinking Water)

- UV-H_2O_2 may form some biodegradable organic carbon
  - usually less than when using ozone
- Some experience that UV-AOP may lead to slightly higher distribution system THMs, HAAs, and more chlorine demand

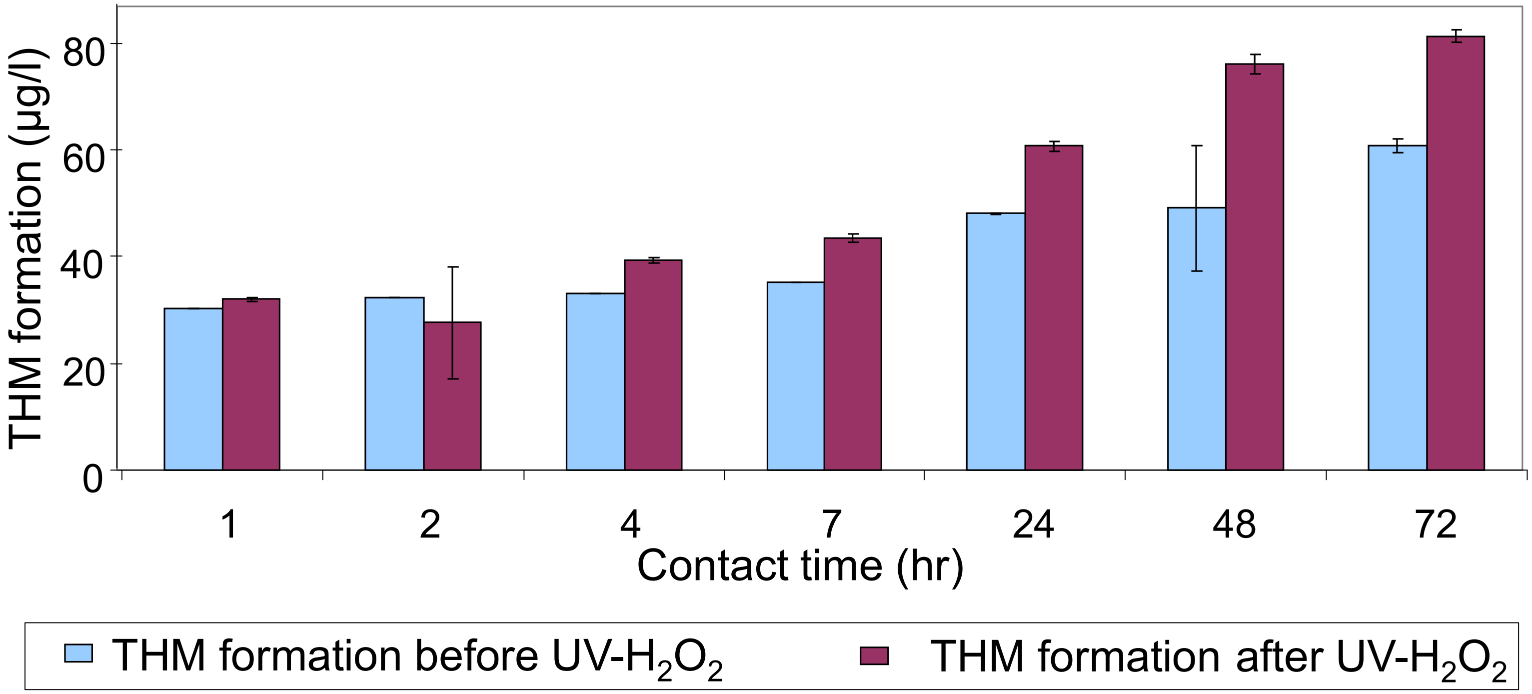
Case study:

Effect of UV-H_2O_2 on Cl_2 residual at Cornwall



THM formation following UV/H_2O_2

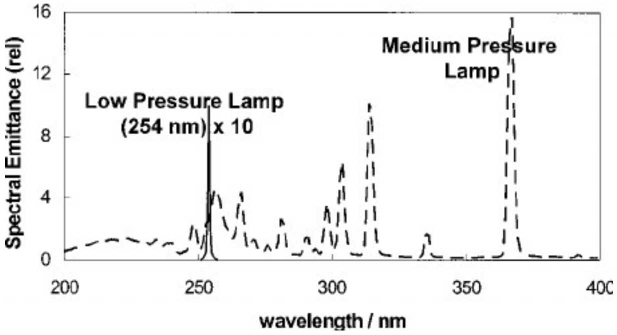
Simulated distribution system tests on post-filter water, before/after UV-H_2O_2 turned on.

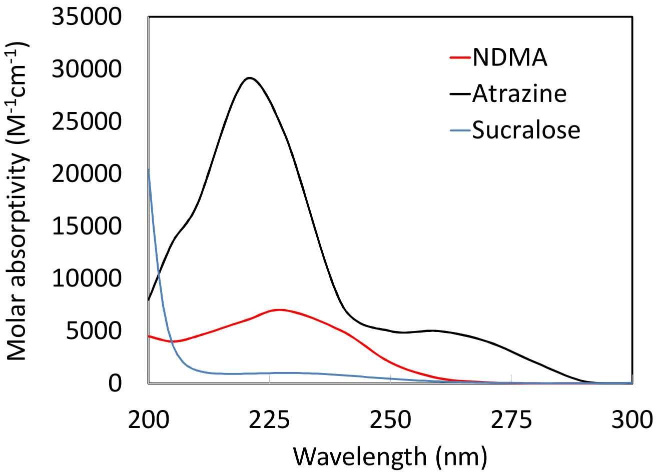


UV Photolysis vs. UV AOP

Intense UV light (alone) can destroy some contaminants, to some extent

- e.g. NDMA, atrazine,…





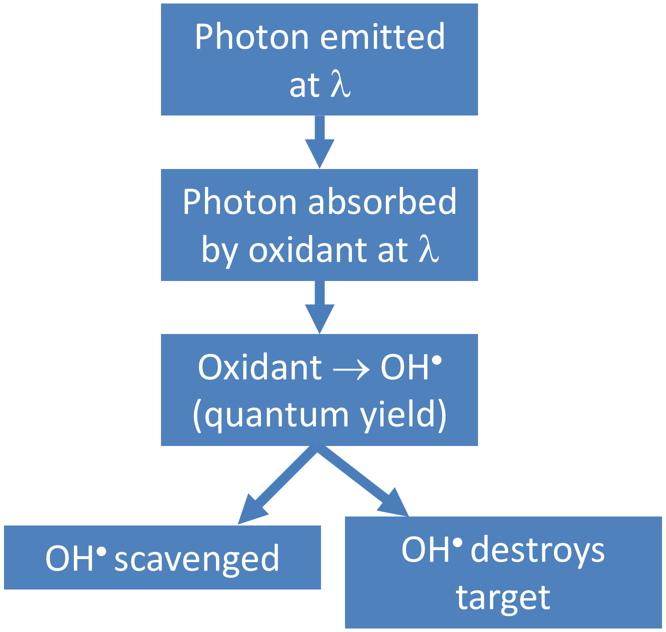
Theoretical time to quench 90% of 2.5 mg/L H_2O_2 with 5 mg/L Cl_2

pH	Time
6	20 minutes
7	2 minutes
7.5	40 seconds
8	10 seconds
8.5	4 seconds

Downstream Cl_2 analyzer to control Cl_2 must account for this

Note: monochloramine + H_2O_2 slow (3 days for 90% reaction)

How AOPs work



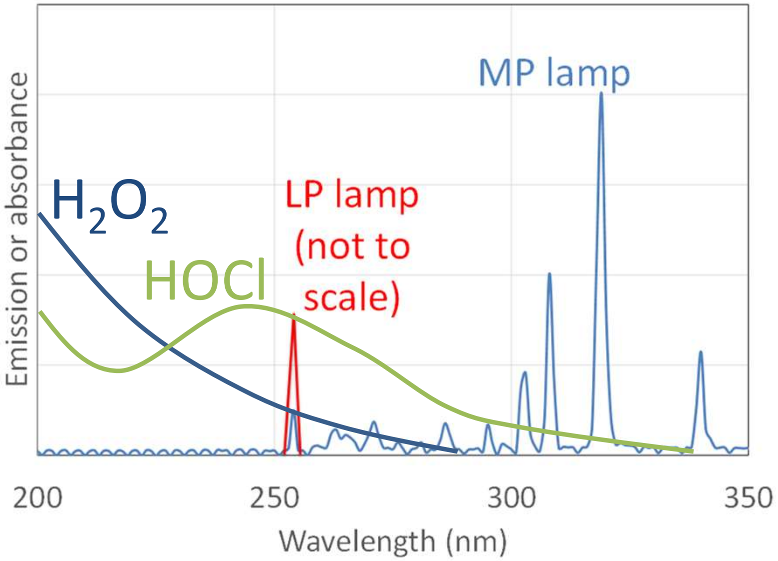
Photon emitted at λ

Photon absorbed by oxidant at λ

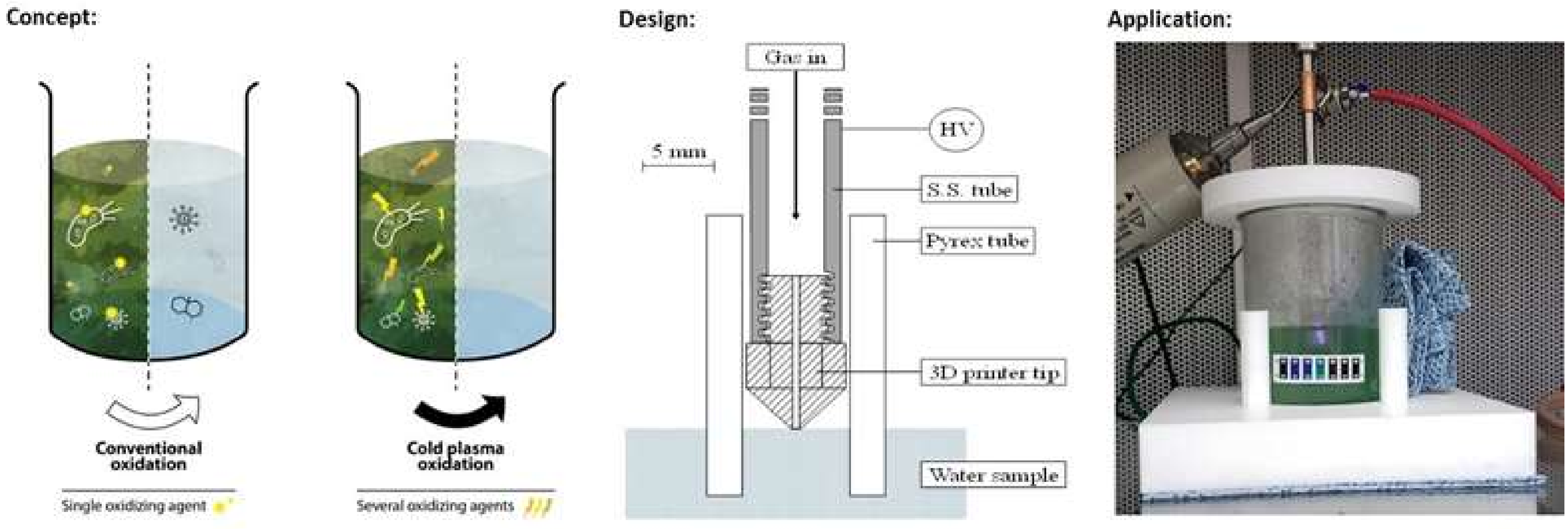
Oxidant → $OH^\bullet$ (quantum yield)

$OH^\bullet$ scavenged

$OH^\bullet$ destroys target



What if we oxidize them all together:



B. Nisol, S. Watson, Y. Leblanc, S. Moradinejad, M. R. Wertheimer, A. Zamyadi (2019) Cold plasma oxidation of harmful algae and associated metabolite BMAA toxin in aqueous suspension. Plasma Processes and Polymers, 16(2). https://doi.org/10.1002/ppap.201800137S

Hydrogen Circular Economy: Viability, Scalability, & Risk For Water Industry

Water Research AUSTRALIA

THE UNIVERSITY OF MELBOURNE

MONASH University

THE UNIVERSITY OF QUEENSLAND AUSTRALIA

Introduction

Integration of sustainable hydrogen (H_2) production with capture of associated greenhouse gases & carbon, & local use of co-products:

- facilitate an emerging circular economy,
- help the water industry to achieve net zero carbon emissions,
- supply chain security for water treatment chemicals.

In particular, green hydrogen & co-products such as O_2, O_3 and H_2O_2 are essential within an emerging circular economy:

- sustainable fuels,
- chemical synthesis feedstocks,
- oxidising agents for AOP.

H2

VICTORIAN
RENEWABLE
HYDROGEN
INDUSTRY
DEVELOPMENT
PLAN

VICTORIA
State
Government

WATER SERVICES
ASSOCIATION OF AUSTRALIA

WATER

FUELLING THE PATH
TO A HYDROGEN FUTURE

THE ROLE OF THE URBAN WATER
INDUSTRY IN AUSTRALIA
AND NEW ZEALAND'S
RENEWABLE ENERGY FUTURE

H2

Introduction

Wastewater treatment plants produce large quantities of recycled water & biogas, providing co-location opportunities for hydrogen production and alternative reuse prospects:

- Water source concerns for sustainable hydrogen,
- Reinforces circular economy principles of wastewater as a valuable resource,
- Avoids potentially harmful wastewater discharges to the environment,
- Reduces capital expenses by using existing infrastructure, land, & supply chains.
- + recycled-water-based drought schemes may have potential for hydrogen production during non-drought periods.

Challenge

While hydrogen production opportunities may add significant value to WWTP operations:

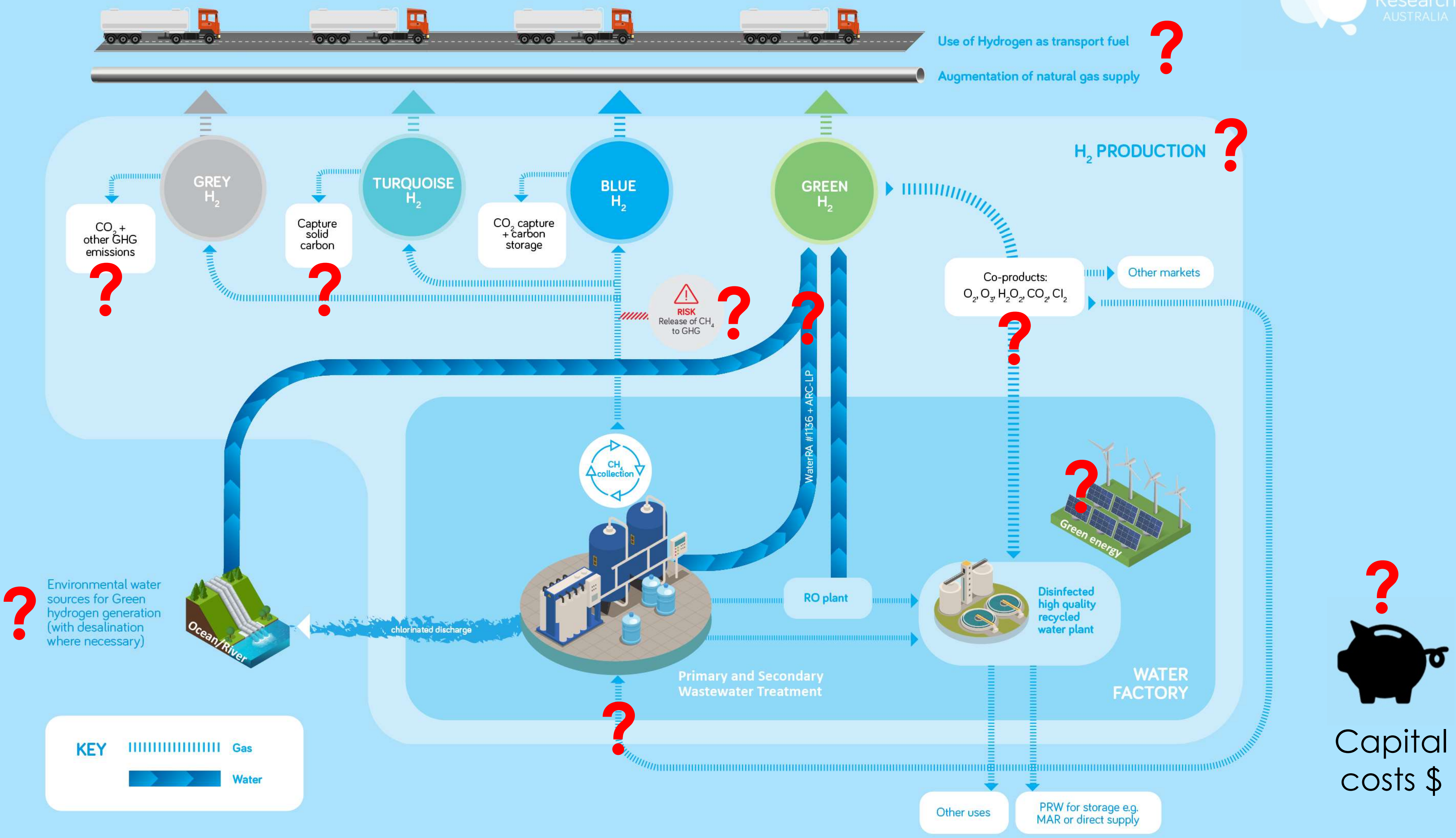
- Associated risks
- Viability?
- Scalability?
- Urban and regional perspectives?
- Value proposition of a hydrogen circular economy to water industry stakeholders?

Objective

- Understand these concerns and provide site-specific guidance to prospective utilities aiming to address technical considerations of feasibility, scalability and viability
- Formulate a decision tree to support utility decision-making and risk assessment.

Conceptual model of how the water industry can drive a circular economy

Water Research AUSTRALIA



Use of Hydrogen as transport fuel ?

Augmentation of natural gas supply

H_2 PRODUCTION ?

GREY H_2

TURQUOISE H_2

BLUE H_2

GREEN H_2

CO_2 + other GHG emissions ?

Capture solid carbon ?

CO_2 capture + carbon storage

RISK Release of CH_4 to GHG ?

?

WaterRA #1136 + ARC-LP

Co-products: O_2, O_3, H_2O_2, CO_2, Cl_2 ?

Other markets

CH_4 collection

Green energy ?

Environmental water sources for Green hydrogen generation (with desalination where necessary) ?

Ocean/River

chlorinated discharge

Primary and Secondary Wastewater Treatment

?

RO plant

Disinfected high quality recycled water plant

WATER FACTORY

Other uses

PRW for storage e.g. MAR or direct supply

KEY

- IIIIIIIIIIIIIIII Gas
- ▬ Water

?

Capital costs $

Economic viability

Understand the economic viability of hydrogen production:

- Projected future demands for hydrogen & associated supply chain
  - The global hydrogen industry is expected to increase 40% by 2030, with Australia aiming to become a leading exporter of hydrogen, with potential export values of $5.7bn by 2040.
  - To accelerate the development of a hydrogen economy and transition to a decarbonised future, we need to produce “clean” hydrogen at under AU$2.00 per kilogram.

Economic viability

Understand the economic viability of hydrogen co-products:

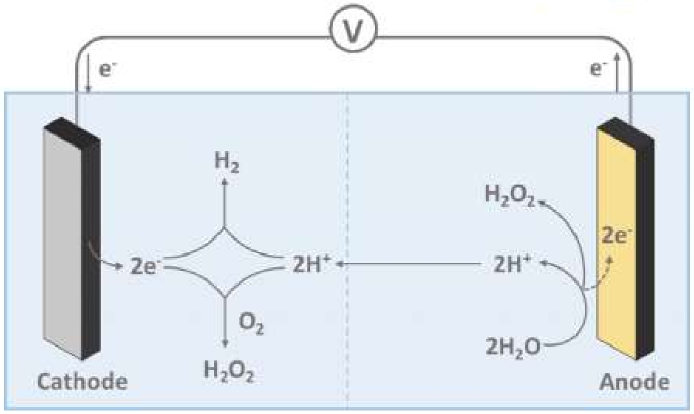
- Projected future demands for co-products: O_3
    - The global O_3 market size was valued at USD $ 880 million in 2016 and is expected to grow at a compound annual growth rate (CAGR) of 7.4% from 2017 to 2023.
    - O_3 generators predominantly use air as the feed, but when oxygen is used, more ozone can be generated at lower energy consumption.
- Projected future demands for co-products: H_2O_2
    - Use in water industry; food, paper and pulp; chemical manufacturing; pharmaceutical & health; disinfectant products.
    - The global hydrogen peroxide market size was valued at USD 1.44 billion in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 5.7% from 2020 to 2028.
        - *Can production of co-products offset the production cost of H_2, bringing the cost of H_2 production down to the targeted $2/kg?*

Technical viability

The technical viability of recycled-water-based hydrogen production also presents many research questions:

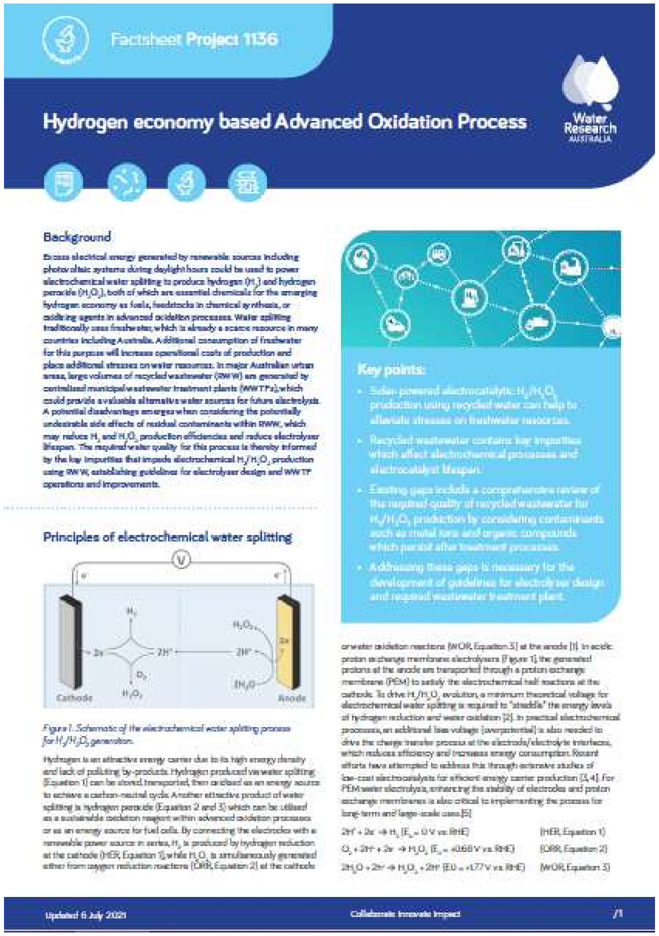
- Performance of electrolysers (which split water into hydrogen and oxygen in the presence of a catalyst)
    - low pH conditions ideal for hydrogen reduction
- Volumes of (recycled) water required
- Optimal operating conditions
- Impacts of contaminants in wastewater:
    - organic compounds
    - metal ions
    - nutrients
    - inorganic debris

Principles of electrochemical water splitting



Technical viability: WaterRA factsheet

https://www.waterra.com.au/_r11390/media/system/attrib/file/2690/WaterRA_FS_1136_HydrogenEconomy.pdf



Factsheet Project 1136

Hydrogen economy based Advanced Oxidation Process

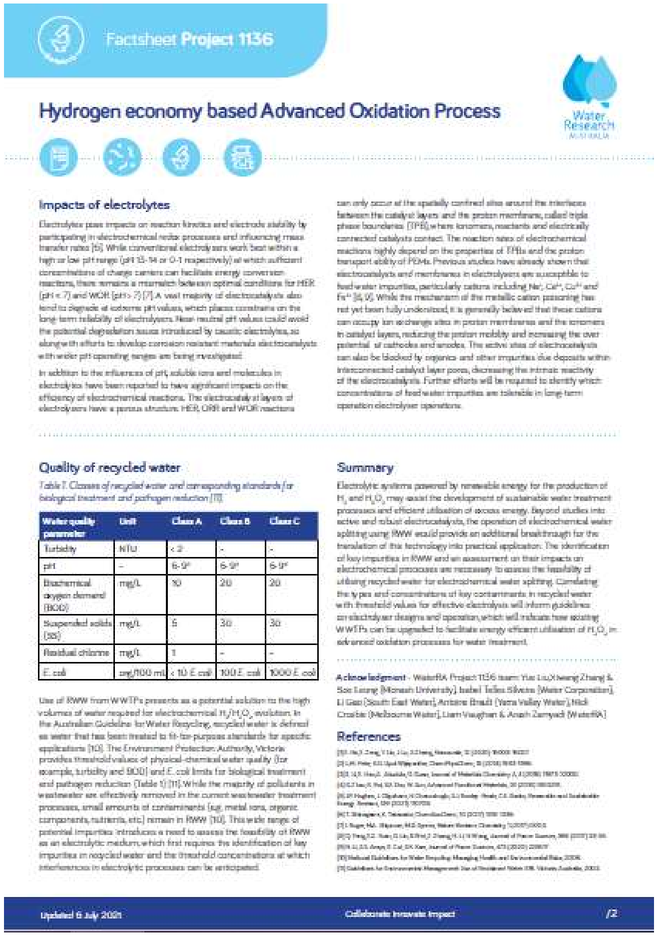
Background

Principles of electrochemical water splitting

Figure 1. Schematic of the electrochemical water splitting process for H_2/H_2O_2 generation.

Key points:

Updated 6 July 2021 Collaborate Innovate Impact /1



Factsheet Project 1136

Hydrogen economy based Advanced Oxidation Process

Impacts of electrolytes

Quality of recycled water

Table 1. Classes of recycled water and corresponding standards for biological treatment and pathogen reduction [11].

Water quality parameter	Unit	Class A	Class B	Class C
Turbidity	NTU	< 2	-	-
pH	-	6-9*	6-9*	6-9*
Biochemical oxygen demand (BOD)	mg/L	10	20	20
Suspended solids (SS)	mg/L	5	30	30
Residual chlorine	mg/L	1	-	-
E. coli	org/100 mL	< 10 *E. coli*	100 *E. coli*	1000 *E. coli*

Summary

References

Updated 6 July 2021 Collaborate Innovate Impact /2

Technical viability

3-year ARC linkage project: Sustainable Hydrogen Production from Used Water

Objectives

1. To gain an in-depth understanding of how existing electrolysers perform in the presence of water impurities, and develop guidelines for designing water electrolysers with high tolerance of water
2. To identify the water quality gap between the treated water from existing WWTPs and the required feed water for water electrolysis, and provide recommendations for WWTPs operation and potential upgrading;
3. To evaluate the technical feasibility of utilising the co-products from waster electrolysis in wastewater treatment, and develop frameworks for the integration between wastewater treatment and water electrolysis.

Project partners & funding model

Water Research Australia

WaterRA water industry consortium:

Yarra Valley Water

South East Water

Water Corporation

Melbourne Water

Barwon Water

Energy sector:
Leverage 1$:6$

GRAPHENEX

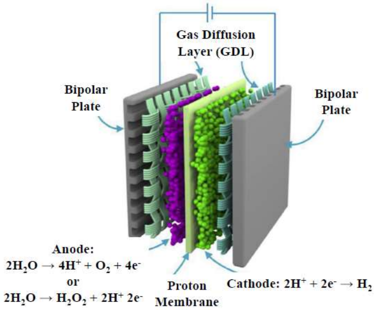
Academic research:

The University of Queensland Australia

Monash University

Academic research:
Leverage 1$:11$

Australian Government
Australian Research Council



Technical viability: ***Impacts of impurities*** *& mitigation strategies*

	TYPES	MECHANISMS	PERFORMANCE
Failure of exchange membranes	• Mechanical damage, e.g. cracks, pores • Membrane degradation • Active site occupation	• O_2 permeation • Low conductivity	Activity decay
Electrode catalyst damage	• Dissolution/corrosion of catalysts • Poisoned by impurities • Agglomeration of catalysts • Passivation of catalysts/supports	• Changes in chemical/ structural features	

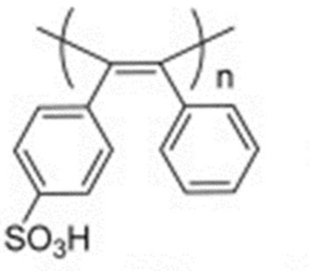
Water Research Australia · The University of Queensland Australia · Monash University

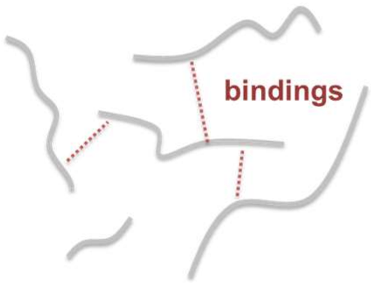
Technical viability: ***Impacts of impurities*** *& mitigation strategies*

Exchange membranes

- Developing tough polymer
- Engineering methods (e.g. refreshing the electrolyte)
- Hybridization with binder ionomers

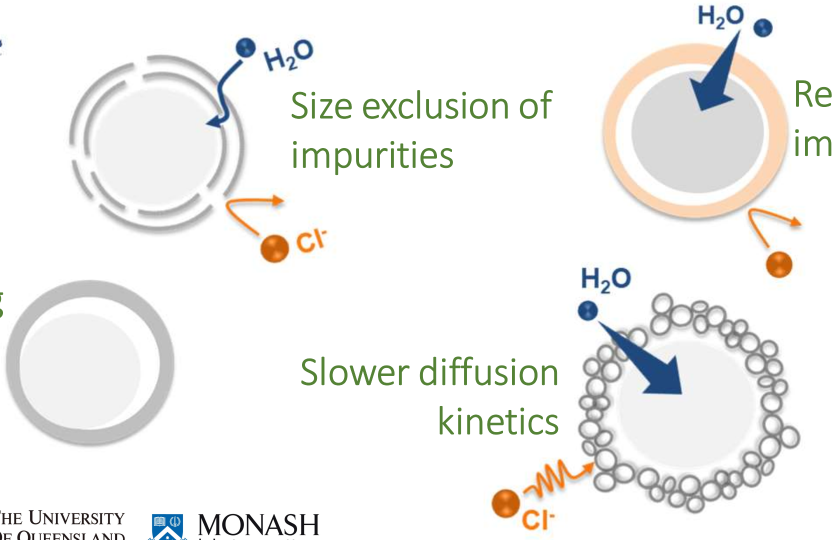
Hydrocarbon polymer





Perfluorosulfonic acid ionomers

Electrode catalysts



- Developing active & robust catalysts
- Post-treatment (e.g., acidic washing)
- Introducing protective shells

Technical viability

- Volumes of water required: Theoretically 9kg of H_2O to produce 1 kg H_2. At scale: estimated to be up to 90 kg electrolyser cooling
- Energy consumed for hydrogen production

Manufacturer	Technology Name	Operating Pressure	Hydrogen Flowrate	Energy Consumption	Operating Range	Water Consumption	Power	Electrical Efficiency
Manufacturer 1	HOGEN S10	13.8 bar_g	0.265 Nm^3/hr - 0.57kg/d	74 kWh/kg H_2	0-100%	9.9 L/kg H_2	1.1 kW	-
	HOGEN S20		0.53 Nm^3/hr - 1.14 kg/d				2.2 kW	-
	HOGEN S40		1.05 Nm^3/hr - 2.27 kg/d				4.3 kW	-
	H2	15 bar_g / 30 bar_g option	2 Nm^3/hr	81 kWh/kg H_2	0-100%	10.2 L/kg H_2	8.1 kW	-
	H4		4 Nm^3/hr	78 kWh/kg H_2			16.1 kW	-
	H6		6 Nm^3/hr	76 kWh/kg H_2			23.7 kW	-
Manufacturer 2	ME 100/350	15 - 30 bar_g	15-46.3 Nm^3/hr	55 kWh/kg H_2	32-100%	14.4 L/kg H_2	225 kW	73%
	ME 450/1400	15 - 30 bar_g	42-210 Nm^3/hr	53 kWh/kg H_2	20-100%	13.8 L/kg H_2	1 MW	74%
	HCS 2MW	15 - 30 bar_g	420 Nm^3/hr	<53 kWh/kg H_2	20-100%	16 L/kg H_2	2 MW	>74%
	HCS 4MW	15 - 30 bar_g	840 Nm^3/hr			17 L/kg H_2	4MW	
	HCS 10MW	15 - 30 bar_g	2100 Nm^3/hr			18 L/kg H_2	10MW	
	S30/10	0 - 20 bar_g	0.22 Nm^3/hr	-	-	29 kg/hr	1 kW	78%
	S30/30	0 - 20 bar_g	0.66 Nm^3/hr	-	-	87 kg/hr	3 kW	
	S30/50	0 - 20 bar_g	1.10 Nm^3/hr	-	-	145 kg/hr	5 kW	
Manufacturer 3	HyLYZER 200	30 bar_g	200 Nm^3/hr	<55 kWh/kg H_2	5 - 100%	9 L/kg H_2	-	-
	HyLYZER 250		250 Nm^3/hr					
	HyLYZER 400		400 Nm^3/hr	<54 kWh/kg H_2				
	HyLYZER 500		500 Nm^3/hr					
	HyLYZER 1000		1000 Nm^3/hr	<51 kWh/kg H_2	5 - 125%			
Manufacturer 4	SILYZER 200	35 bar	225 Nm^3/h	-	-	17 L/kg H_2	1.25 MW	60-65%
	SILYZER 300	-	1300 kg/hr	-	0-100%	10 L/kg H_2	~70 MW	>75.5 %

Scalability of production processes

- The scalability of production processes is also a key concern:
    - Regional utilities: many plants distributed across a large geographic area.
- The risks associated with utility involvement in a hydrogen circular economy are also poorly defined:
    - Core business of a water utility?
- From a sustainability perspective a key potential risk is the allocation of water for hydrogen production in regions where water resource availability is subject to extreme variability due to climate change.
    - In this context, how can we not only secure water for electrolysis but continue to meet accessibility and affordability for other uses?

Scalability:

WaterRA water
industry consortium

SCALING GREEN
HYDROGEN CRC

Water “core partnership” workshop May 6th 2022 (online) - Themes:

- Water sources and their social licence;
- Technology needs for water reuse and beneficial co-products;
- Co-location opportunities (including renewable energy generation) and Integrated planning.

Contact me to join the workshop:
arash.zamyadi@waterra.com.au

Water
Research
AUSTRALIA

CASE STUDY #3

FUELLING THE FUTURE

PROJECT:
Assessing hydrogen production viability and scalability

REGION:
Australia-wide

Hydrogen production can add significant value to water operations, but the risks are poorly defined.

Dr Arash Zamyadi, Karen Rouse and Liam Vaughan

Integration of sustainable hydrogen production with the capture of associated greenhouse gases and carbon has the potential to facilitate an emerging circular economy. This could help the water industry achieve net zero carbon emissions and supply chain security for water treatment chemicals.

Co-products such as oxygen, ozone and hydrogen peroxide are essential within a circular economy as sustainable fuels, chemical synthesis feedstocks, or as oxidising agents for advanced treatment processes.

Wastewater treatment plants (WWTPs) produce large quantities of recycled water and biogas, providing co-location opportunities for hydrogen production and alternative reuse prospects. This mitigates water source concerns for sustainable hydrogen, while reinforcing circular economy principles of wastewater as a valuable resource.

The co-location of hydrogen production at existing WWTPs may reduce capital expenses by using existing infrastructure, land, and supply chains. Additionally, established recycled-water-based drought schemes may have potential for hydrogen production during non-drought periods.

While hydrogen production opportunities could add significant value to WWTP operations, the associated risks yet to be understood, along with the viability and scalability from both urban and regional perspectives.

Due to these uncertainties, the value proposition of a hydrogen circular economy remains ambiguous. Further studies are required to address concerns and provide site-specific guidance to prospective utilities – such as a current research project by Water Research Australia – which aims to address technical considerations of feasibility, scalability and viability to support utility decision-making and risk assessment.

KEY CONSIDERATIONS

To understand the economic viability of hydrogen production, projected future demands for hydrogen and associated supply chain impacts must be defined. Capital costs present a significant barrier to entry, so a viability assessment must also consider the inherent value to prospective hydrogen producers of the secure water source, WWTP access to transport infrastructure, and land availability – including for renewable energy generation.

The technical viability of recycled-water-based hydrogen production also presents many research questions, such as the volumes of recycled water required, optimal operating conditions, and the impacts of contaminants contained in wastewater. While WWTP processes effectively remove most contaminants, some persist, such as organic compounds, metal ions, nutrients, and inorganic debris, which could affect the performance of electrochemical reactions integral to hydrogen production.

Performance of electrolysers improves when contaminants cause extreme pH values. But the low pH conditions ideal for hydrogen reduction are inconsistent with the high pH conditions optimal for water oxidation. This mismatch introduces process challenges which are further complicated by the degradation of electrocatalysts induced by extreme pH conditions. Further efforts are therefore necessary to investigate corrosion resistant catalysts and the operation of electrochemical water splitting under neutral conditions.

SCALABILITY AND RISK

The scalability of production processes is a key concern, particularly for regional utilities that have many smaller WWTPs distributed across a large geographic area. The risks of utility involvement in a hydrogen circular economy are also not defined. From a sustainability perspective, a key risk is the allocation of water for hydrogen production in regions where water resource availability is variable due to climate change.

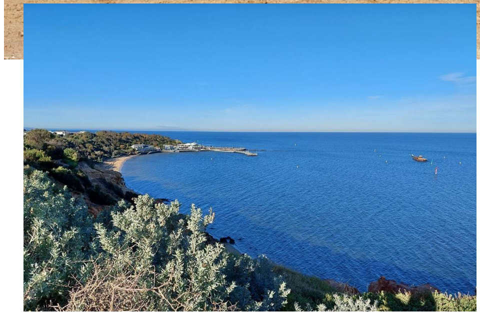
Despite these knowledge gaps, the gains of integrating hydrogen and oxidant production look promising, with adaptation of novel technologies for water reuse having the potential to facilitate a significant improvement in the sustainability and resilience of water treatment processes. ♦

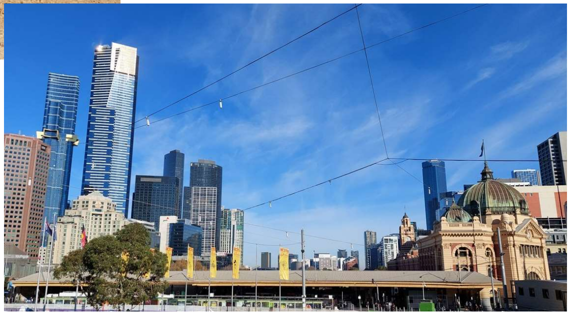
> “*The co-location of hydrogen production at existing wastewater treatment plants may reduce capital expenses by using existing infrastructure, land, and supply chains.*
>
> **Water Research Australia**

WHO ARE WE?

Water Research Australia is an independent, leading hub for collaborative research that is member-driven and funded. We are dedicated to healthy communities and a healthy planet – delivering innovation and capability building that supports public health and safeguards the sustainability of our water resources. To view more information about our Whole Water – water/energy/nutrient circular economy research, visit bit.ly/waterra_whole-water

Discover more: **awa.asn.au**





Enjoying a bit of beach life here in Melbourne, Australia ☺

Thank you and please contact me to co-design interesting project!

Arash Zamyadi, Ph.D.
WaterRA Senior Research Manager (hosted by Melbourne Water) & Senior Lecturer
Chemical Engineering | Faculty of Engineering and Information Technology
The University of Melbourne, Victoria 3010 Australia

T: +61 4 3773 1414 **E: arash.zamyadi@unimelb.edu.au / arash.zamyadi@waterra.com.au**

https://findanexpert.unimelb.edu.au/profile/862353-arash-zamyadi

Training School “AOPs for water T&O”
5-9 Sep 2022, Athens, Greece