#### ABUNDANCE, SCARCITY AND INNOVATION: A WATER QUALITY TRIPARTITE ALLIANCE CENTRED ON NOM

#### By Prof Thabo T.I Nkambule 21 February 2022



#### Define tomorrow.



Innovatively addressing current and emerging issues relating to water scarcity and water quality

iNanoWS is a research institute at Unisa's College of Science Engineering and Technology

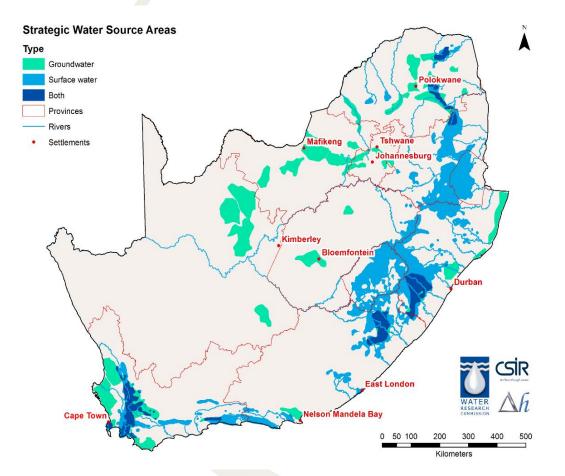


"The strength of a family, like the strength of an army, lies in its loyalty to each other." – Mario Puzo

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dida

### **SURFACE & GROUNDWATER SOURCES**



	SA	Africa	Global (continents)
Mean annual precipitation (mm)	465	670	718
Evaporation loss (%)	91%	83%	64%
Mean annual runoff (mm)	40	114	266

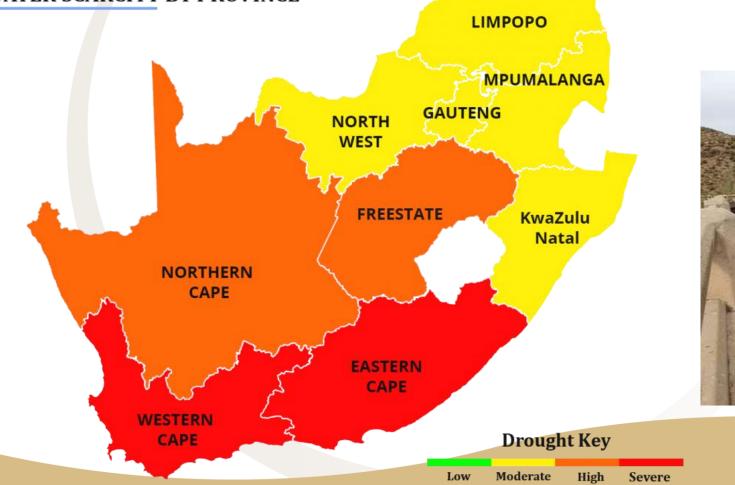
#### Water source areas

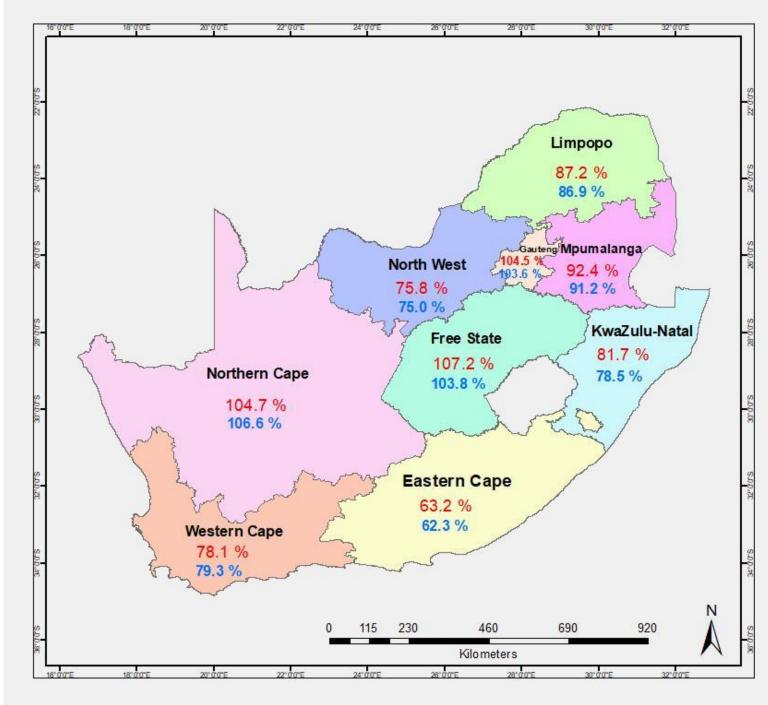
 22 water source areas on 8% of land providing 50% of our surface run-off

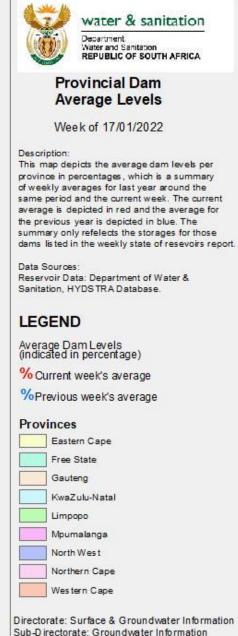
## NATIONAL VULNERABILITY: WATER SERVICES CHALLANGES

#### SOUTH AFRICA

#### WATER SCARCITY BY PROVINCE



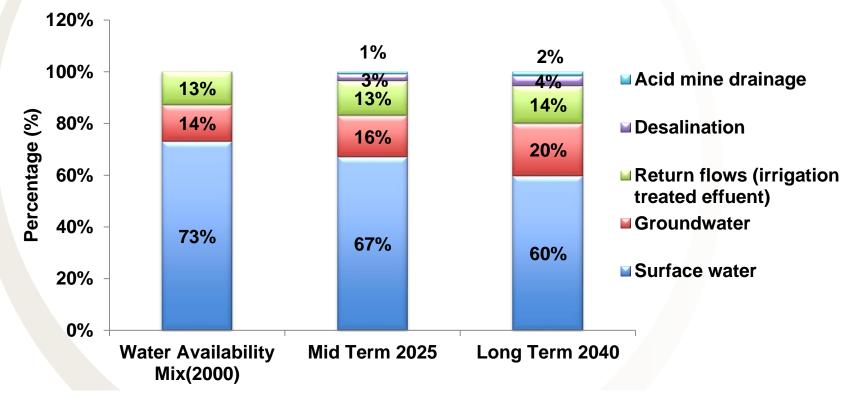




## PARADIGM SHIFT IN WATER SUPPLY

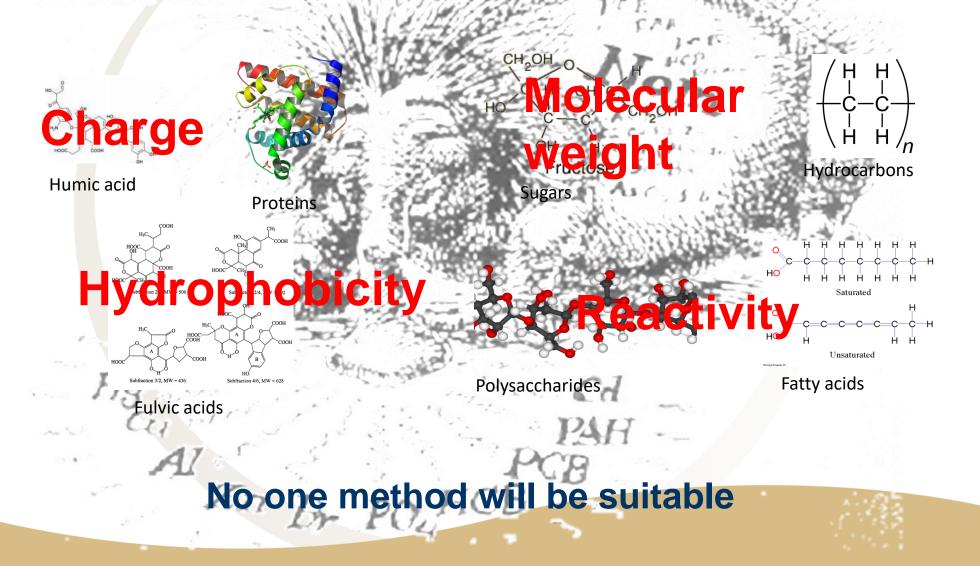
As per National Water & Sanitation Master Plan

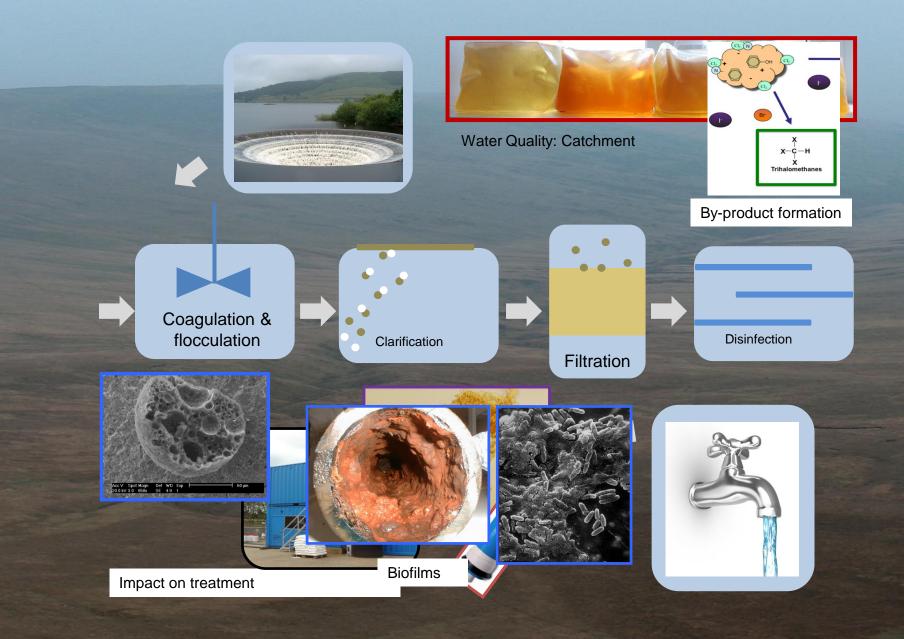
# <u>Supply</u>: water mix approach with progressively increased use of unconventional water sourceS



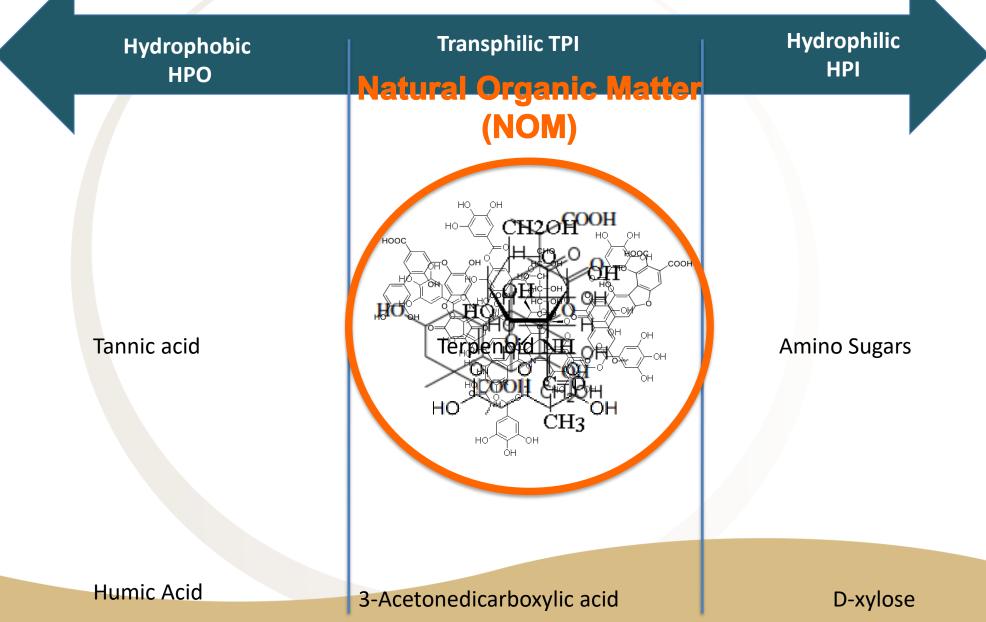
**KEY MESSAGE:** Percentage usage of unconventional sources (such as groundwater, reuse, desalination, etc.), is progressively increased with time, while reliance on the oversubscribed surface water decreases. Improved water security = adaptation

### NOM- AN IMPOSSIBLY COMPLEX MATRIX THAT VARIES TEMPORALLY AND SPATIALLY

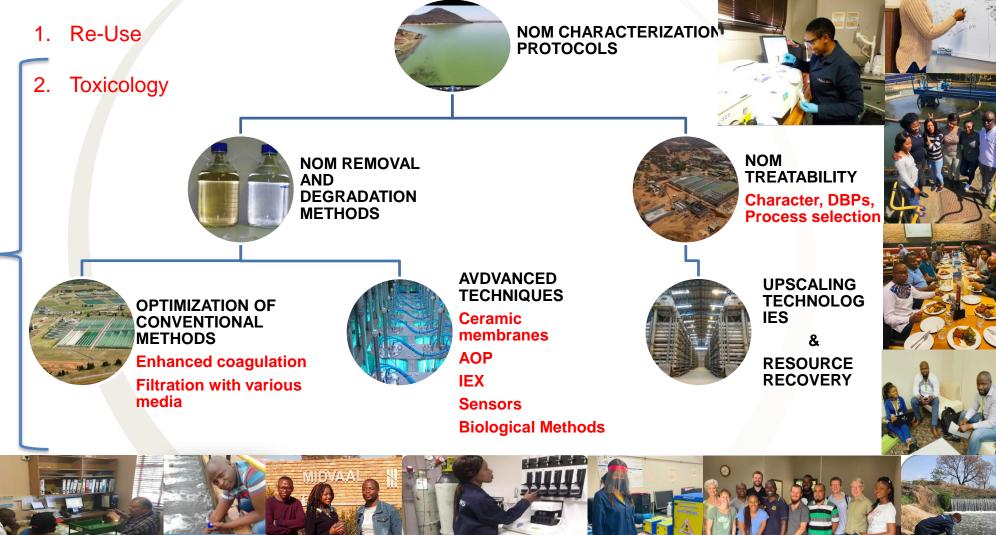




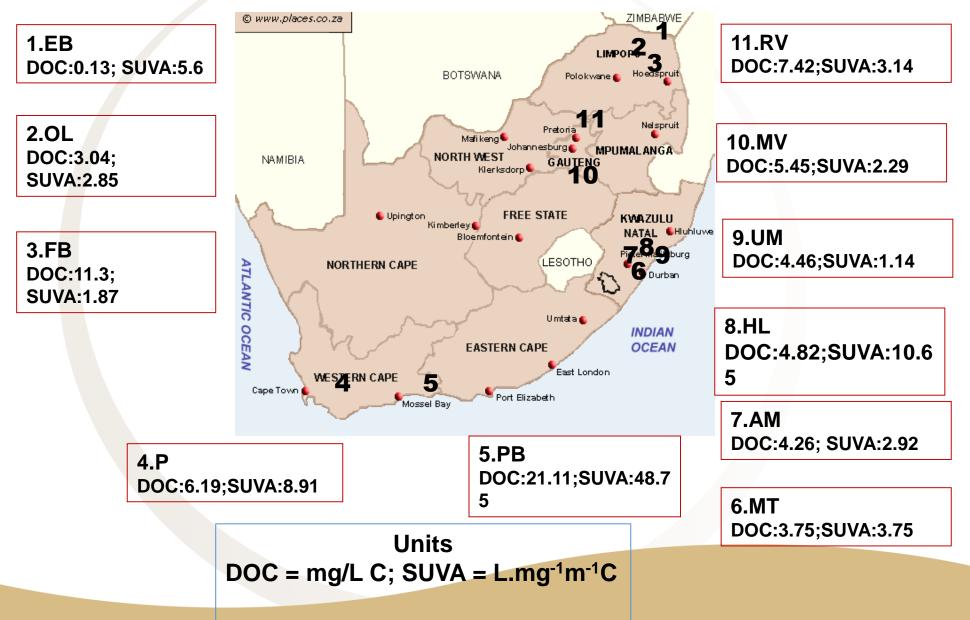
### **NOM IN THE ENVIRONMENT**



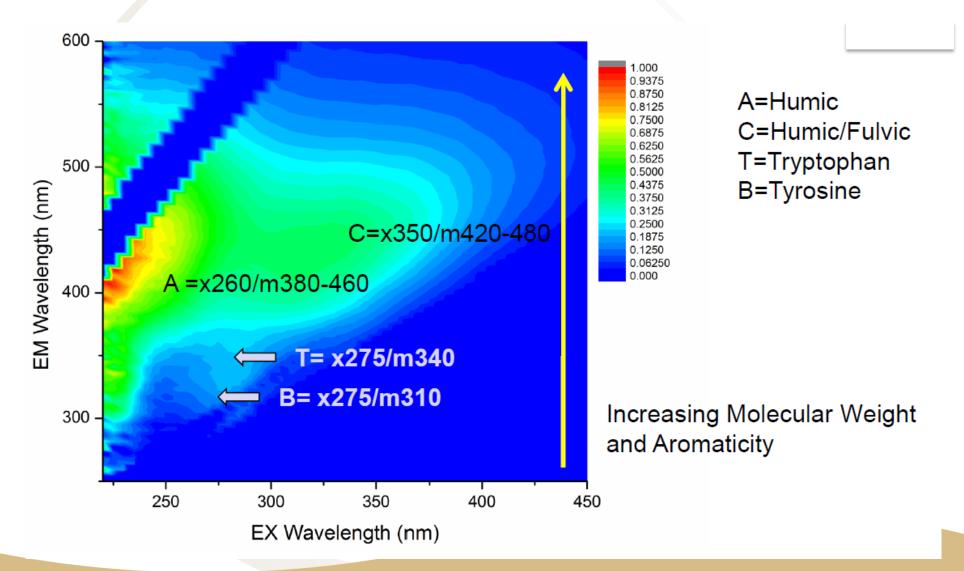
## OUR APPROACH: URBAN WATER CYCLE AND WATER TREATMENT TECHNOLOGIES



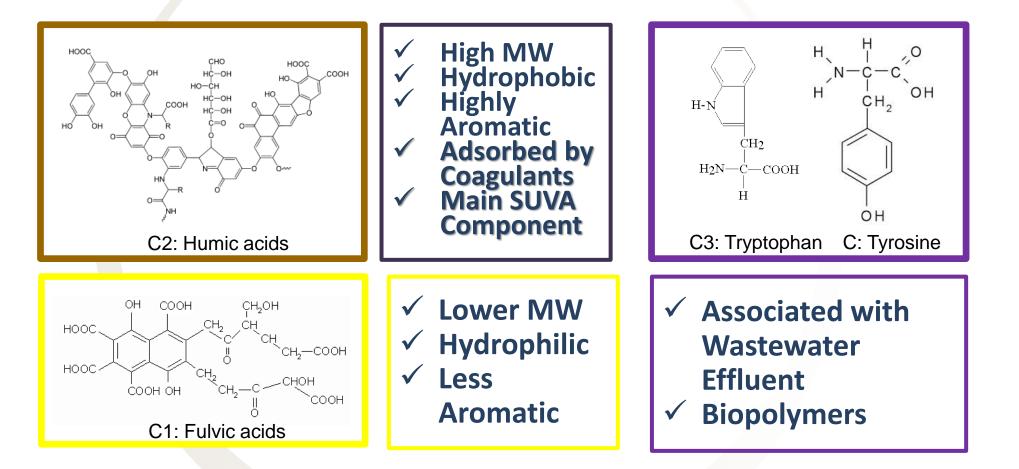
### **SAMPLING - NOM CHARACTER**



## **TYPICAL RAW SURFACE WATER FEEM**



### **COLORED DISSOLVED ORGANIC MATTER (CDOM)**



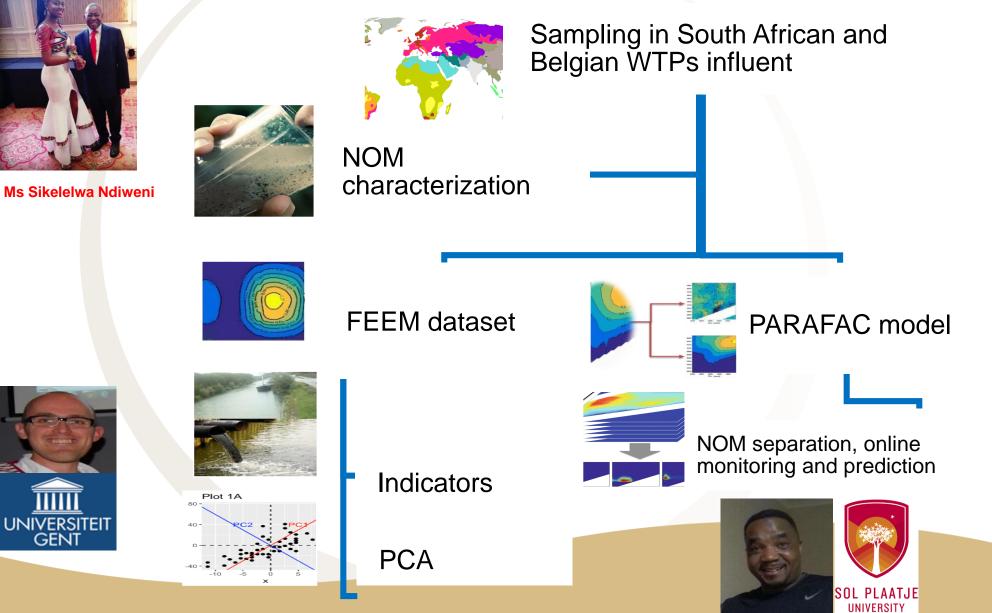
### **FEED STREAM ANALYSIS**

- □ Identify: -Type/class/Character
- □ Fractionate into various Fractions
- Determine the treatability Influence of each





#### THREE-DIMENSIONAL CORRELATION BETWEEN NOM AND ITS HETEROGENEOUS ADSORPTION BEHAVIOR ON ACTIVATED CARBON USING EEM-PARAFAC



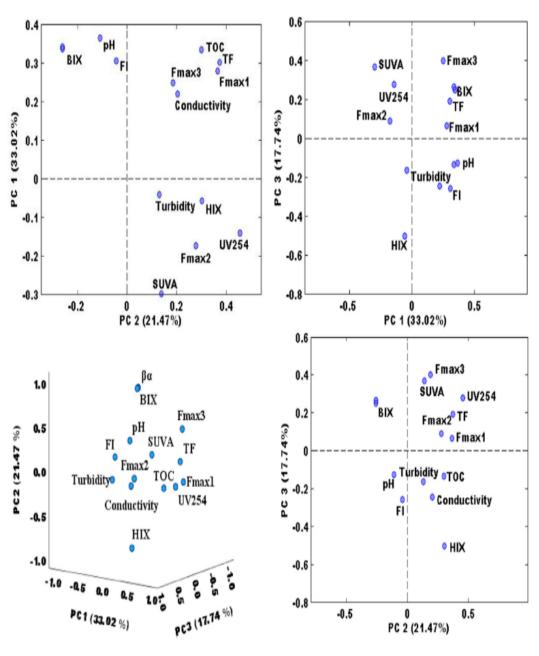


Figure 4. Principal component analysis for WTPs in South Africa and Belgium.

ENVIRONMENTAL TECHNOLOGY https://doi.org/10.1080/09593330.2019.1575920

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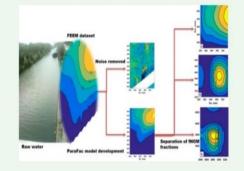
#### Assessing the impact of environmental activities on natural organic matter in South Africa and Belgium

Sikelelwa N. Ndiweni <sup>3</sup><sup>a</sup>, Michael Chys <sup>b</sup>, Nhamo Chaukura <sup>a</sup>, Stijn W. H. Van Hulle <sup>b</sup> and Thabo T. I. Nkambule <sup>a</sup>

<sup>a</sup>Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa; <sup>b</sup>LIWET, Department of Green Chemistry and Technology, Ghent University, Kortrijk, Belgium

#### ABSTRACT

The presence and persistence of natural organic matter (NOM) in drinking water treatment plants (WTPs) requires a robust and rapid monitoring method. Measurement and monitoring of NOM fractions using current technology is time-consuming and expensive. This study uses fluorescence measurements in combination with Parallel Factor (ParaFac) analysis to characterize NOM fractions. This was achieved through: (1) determining the origin and composition of NOM fractions using fluorescence index (FI), humification index, biological index, and freshness index, and (2) using multivariate analysis to reveal key parameters and hidden NOM fraction characteristics influenced by seasonal changes and environmental activities. The ParaFac model revealed that the NOM fractions for Belgium plants are mainly hydrophobic acids, aromatic proteins, biological activity, humic acid-like, and fulvic acid-like moieties. The NOM fractions in South African plants were mainly aromatic protein, humic acid-like, fulvic acid-like, tryptophanlike, and protein-like moieties. For Belgium plants in spring Fl >1.7, indicating high microbial sources, whereas FI < 1.3 for South African plants, signifying terrestrial sources of NOM. On the one hand, the first principal component (PC1) interpreted 33.02% of the total variance, and is a measure of fluorescent NOM relative concentration. On the other hand, the PC2 interpreted 21.47% and contains most of the information on humification, freshness, and biological indicators, while PC3 interpreted 17.74% and contains information on the origin and variation in environmental conditions. These results will assist in developing a method for online monitoring of NOM fractions in water sources based on environment activities and spectral measurements.



Received 18 December 2018 Accepted 23 January 2019

**ARTICLE HISTORY** 

#### KEYWORDS

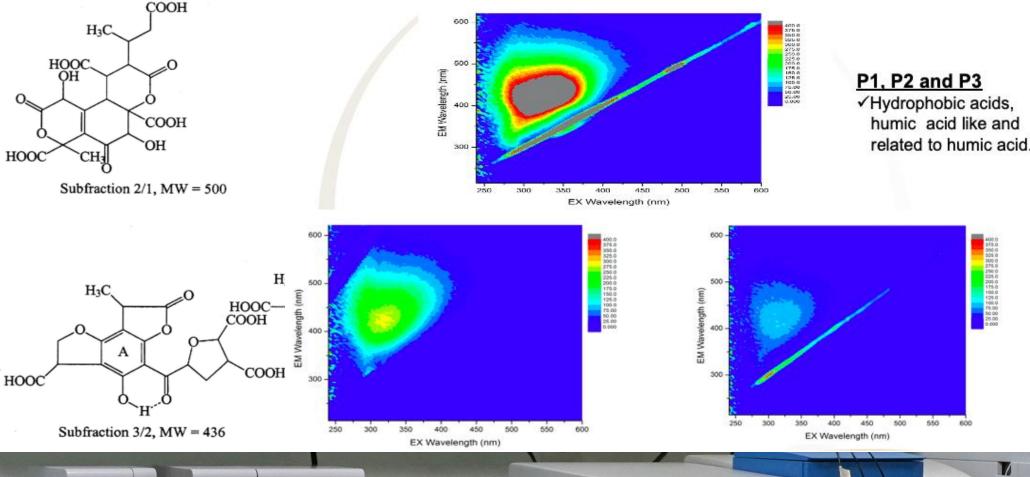
Fluorescence excitationemission matrix; fluorescence index; natural organic matter; parallel factor (ParaFac) analysis; principal component analysis

#### WHAT ARE THE RESEARCH QUESTIONS AND RESEARCH GAPS?

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### WHAT IS THE PROPERTY OF INFLUENCE?





### WHAT SHOULD AN IDEAL MEASUREMENT OF DOC TELL ME?

#### TREATABILITY

Is it removed by (different) treatment processes?

 Bulk DOC removal
 Specific fractions of DOC removed/untreated PROCESS IMPACTS

Will it influence the performance of other processes?

Delicate Floc

- Membrane fouling
- Competition for Binding sites

#### DOWNSTREAM REACTIVITY

What is the downstream influence of DOC in treated water?

DBPs
Biostability of water

Taste & odour

PREDICTION BASED ON MODELS

> Can it be measured online?

Control systems

Diagnostic tools

### TO DEVELOP A RAPID TOOL TO IDENTIFY NOM TREATMENT LIMITS ACHIEVABLE BY ANY METHOD



- Rapid
- Robust
- Portable
- > Inexpensive

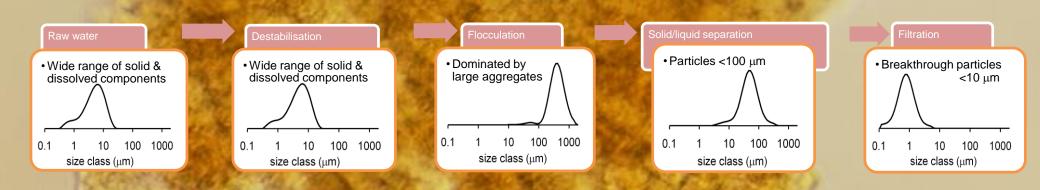


## **UNDERSTANDING NOM TREATABILITY**

#### High [DBP's], membrane fouling, higher coagulant and disinfectant dosages

High

[NOM]



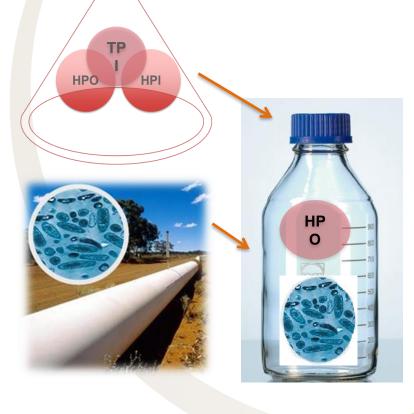




### **BIODEGRADABILITY OF NOM**



## Investigate biodegradability of NOM



#### Simultaneously measure:

- Organic carbon available to bacteria in each fraction (BDOC method)
- Bacterial growth

#### Identify:

- Problematic NOM fraction (abundant bacterial growth)
   Develop:
  - Characterization technique

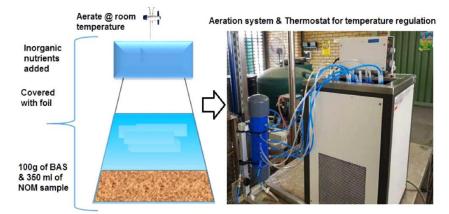






NOM sample NaOH NaOH C18 NH<sub>2</sub> CN Tpi fraction Hpo Hp fraction fraction

Fig. 2. A set-up of the SPE cartridges during m-PRAM method [7].



Daily measurement of DOC and UV254

BDOC = DOC (Initial) - DOC (Final)

Fig. 3. The biodegradable dissolved organic carbon (BDOC) set-up.

#### Journal of Water Process Engineering 36 (2020) 101332

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/jwpe

Quantification of biodegradable natural organic matter (NOM) fractions and its impact on bacterial regrowth in a South African Water Treatment Plant



Sifiso P. Sambo<sup>1,2</sup>, Savia S. Marais<sup>1</sup>, Titus A.M. Msagati<sup>2</sup>, Bhekie B. Mamba<sup>2</sup>, Thabo T.I. Nkambule<sup>2,\*</sup>

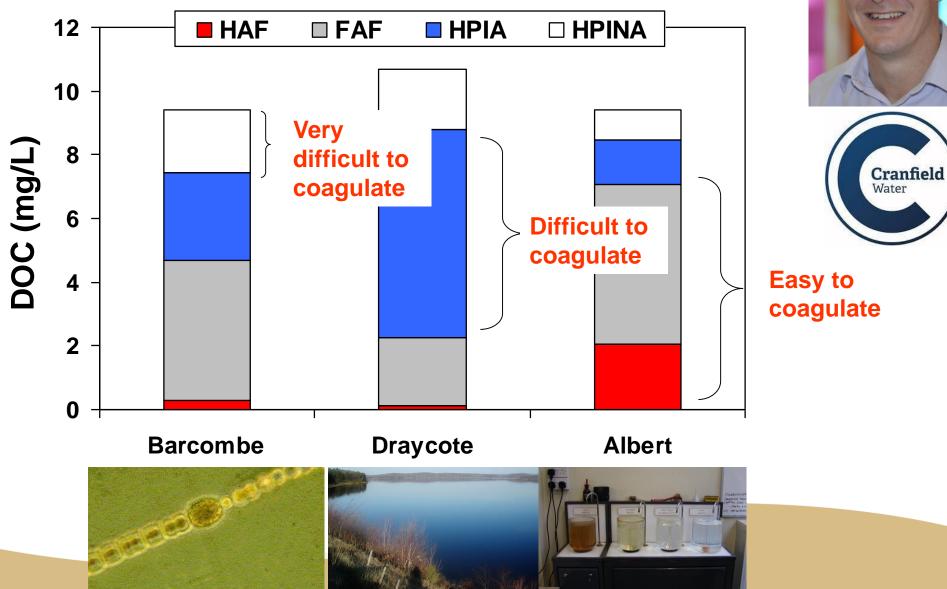
<sup>1</sup> Rand Water, Process Technology Department, PO Box 3526, Vereeniging 1930, South Africa

<sup>2</sup> Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida Campus, 1709, Johannesburg, South Africa

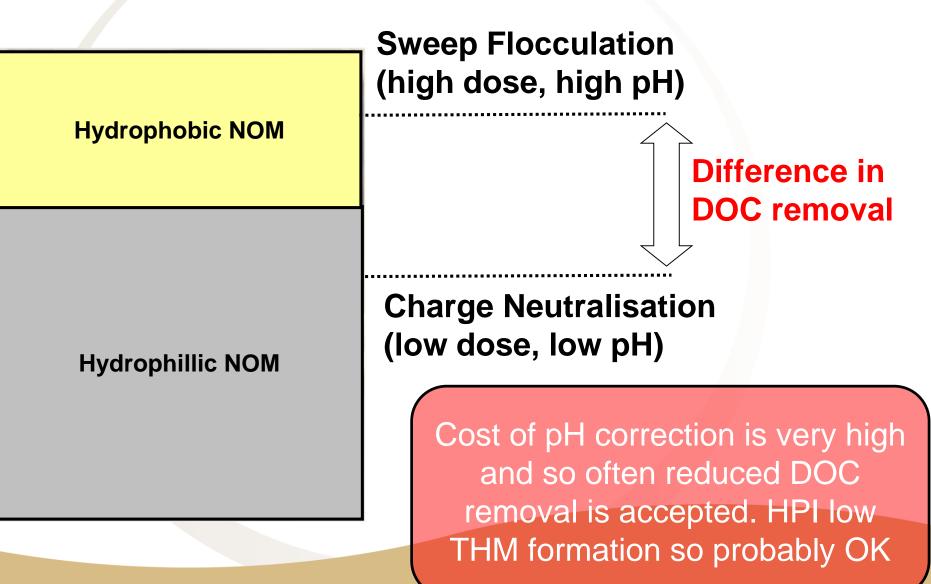
S.P. Sambo, et al.

Journal of Water Process Engineering 36 (2020) 101332

### SO WHAT ARE THE PROPERTIES OF NOM



### LOW COLOUR, MODERATELY HARD WATER

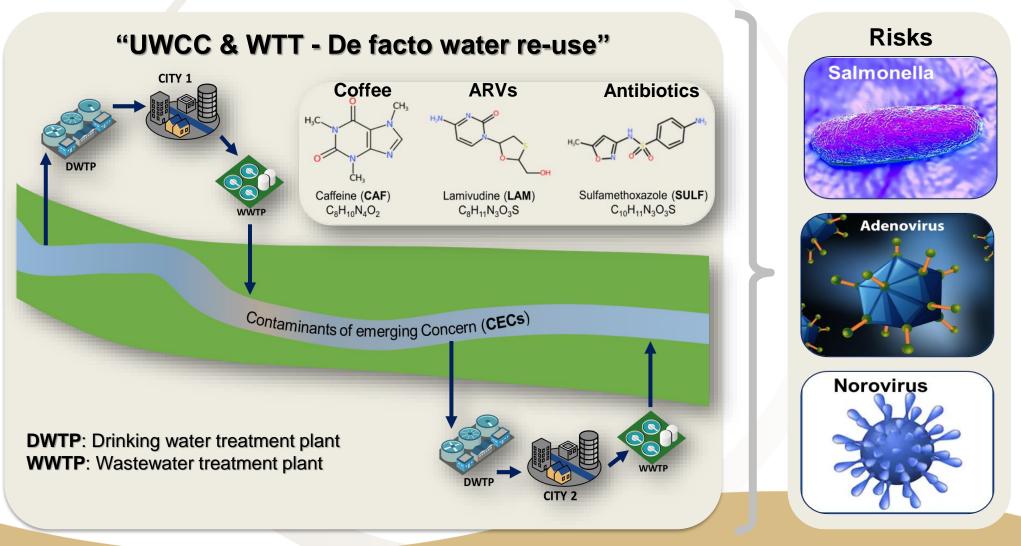


#### UNDERSTAND AND CONTROL THE IMPACT OF DOM IN ENGINEERING SYSTEMS

 $\mathcal{C}_{\mathcal{I}}$ 

11

### URBAN WATER CYCLE AND WATER TREATMENT TECHNOLOGIES



### COMPETITION FOR BINDING SITES ON ADSORBANTS (PORE BLOCKAGE)

action remaining

0.3



PERGAMON

CARBON

Carbon 40 (2002) 2147-2156

Simultaneous adsorption of MIB and NOM onto activated carbon II. Competitive effects

G. Newcombe<sup>a,\*</sup>, J. Morrison<sup>a</sup>, C. Hepplewhite<sup>a</sup>, D.R.U. Knappe<sup>b</sup>

\*Australian Water Quality Centre, A Partner in the CRC for Water Quality and Treatment, Private Mail Bag, Salisbury, SA 5108, Australia
\*Department of Civil Engineering, North Carolina State University, Campus Box 7908, Raleigh, NC 27695-7908, USA Received 24 June 2001; accepted 10 February 2002

Abstract

The adsorption of an odour compound common in drinking water, 2-methylisoborneol (MIB), was studied on six activated carbons in the presence of six well-characterised natural organic matter (NOM) solutions. It was found that, although the carbons and the NOM solutions had a wide range of characteristics, the major competitive mechanism was the same in all cases. The low-molecular-weight NOM compounds were the most competitive, participating in direct competition with MIB for adsorption sites. Equivalent background compound calculations indicated a relatively low concentration of directly competing compounds in the NOM. Some evidence of pore blockage and/or restriction was also seen, with microporous carbons being the most affected by low-molecular-weight NOM and mesoporous carbons impacted by the higher-molecularweight compounds.

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Keywords: A. Activated carbon; D. adsorption properties, Surface properties

Humic acid as a model for natural organic matter (NOM) in the removal of odorants from water by cyclodextrin polyurethanes

#### BB Mamba\*, RW Krause, TJ Malefetse, SP Sithole and TI Nkambule

Department of Chemical Technology, University of Johannesburg, PO Box 17011, Johannesburg, South Africa

#### Abstract

Current practices in some water-treatment facilities have reported that natural organic matter (NOM) blocks the adsorption sites of activated carbon resulting in lower geosmin and 2-methylisoborneol (2-MIB) removal. Humic acid has been reported to compete with geosmin and 2-MIB is important for potable-water treatment by water supply companies and municipalities. We have previously demonstrated that cyclodextrin polyurethanes are capable of removing a number of organic pollutants from water, but are not able to reduce the levels of NOM significantly. We wished to determine if the polymers would selectively remove geosmin and 2-MIB is obtained from this study indicate that the presence of NOM. Humic acid was chosen as a model for NOM since NOM constitutes about 70% of humic acid. Results obtained from this study indicate that the presence of lumic acids at different concentrations could not affect the removal of geosmin and 2-MIB when cyclodextrin polymers were used since 90% removal was achieved. However the UV-Vis analysis showed a low removal of humic acids (3 to 20%).

Keywords: cyclodextrin polymers, geosmin, 2-methylisoborneol (2-MIB), humic acids

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-D---HP

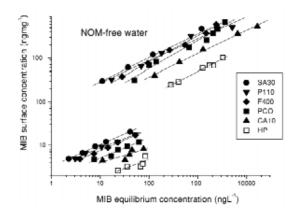
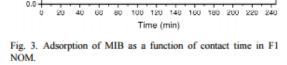
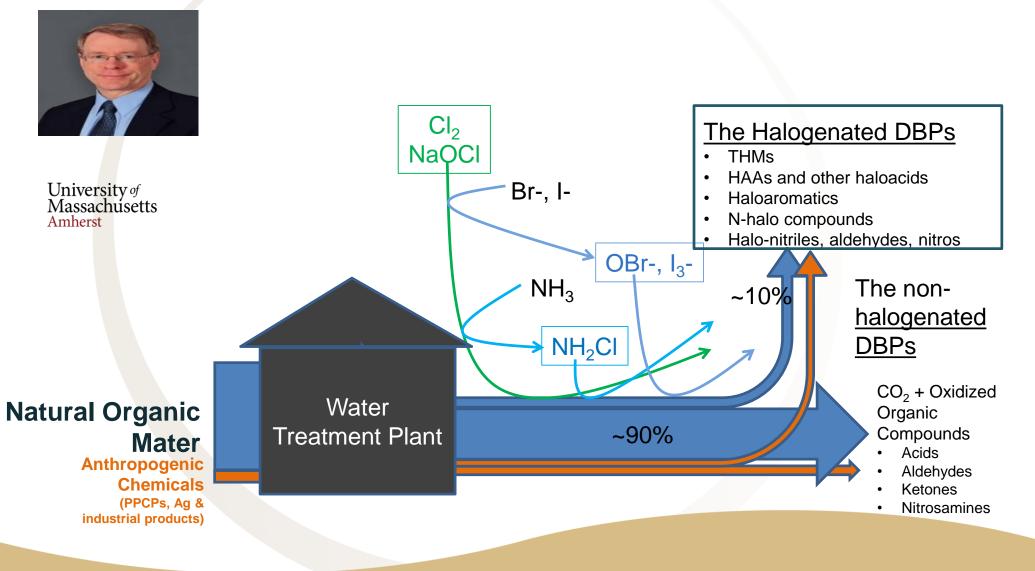


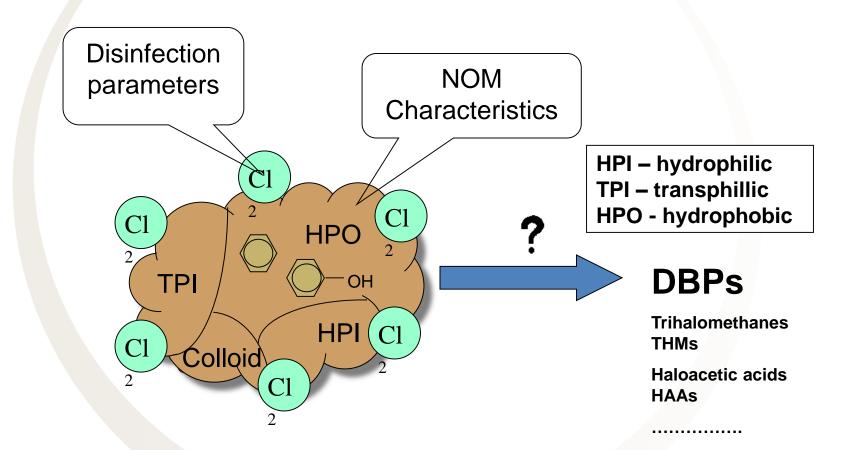
Fig. 1. Adsorption isotherms of MIB onto six activated carbons in the presence and absence of competing NOM.



## **NOM AND DBP CONTROL**



**FORMATION OF DBPS** 



### NOM FRACTION IN TREATED WATER & DBP RELATIONSHIP

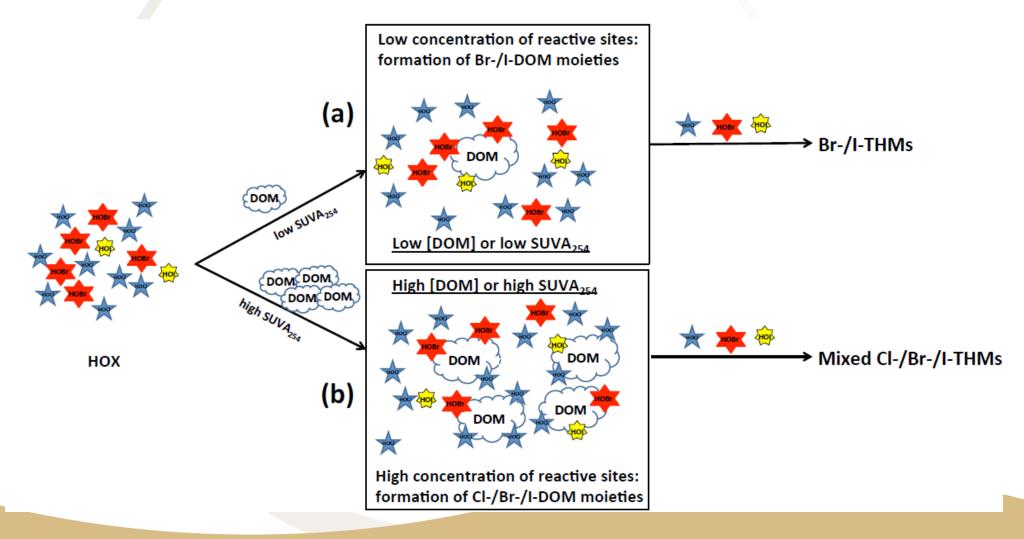
HPI – present in greater proportions after disinfection

TPI – variable & different from stage to stage

HPO – very reactive & variable (thus easy to remove)

Use fractionation to identify "problematic" NOM fraction thus informing choice of treatment methods Apply alternative combination regimes or specific treatment technologies

#### IMPORTANCE OF DOM REACTIVITY ON THE INCORPORATION OF Br AND I IN DBPs PRODUCED DURING CHLORINATION AND CHLORAMINATION

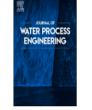




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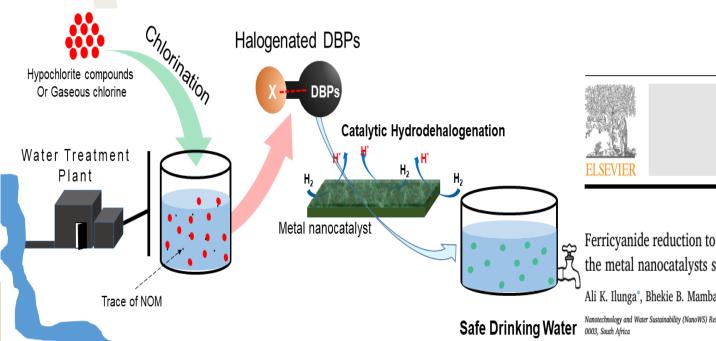
#### Nanocatalysts and Disinfection **By-Products Degradation** "Nano-DBPs"



Catalytic hydrodehalogenation of halogenated disinfection byproducts for clean drinking water production: A review

Ali K. Ilunga<sup>\*</sup>, Bhekie B. Mamba, Thabo T.I. Nkambule

Institute for Nanotechnology and Water Sustainability (iNanoWS), University of South Africa, UNISA Science Campus, Florida (Johannesburg), P.O. Box 392, Pretoria 0003, South Africa





Dr Ali lunga

Chemical Engineering Journal 398 (2020) 125623

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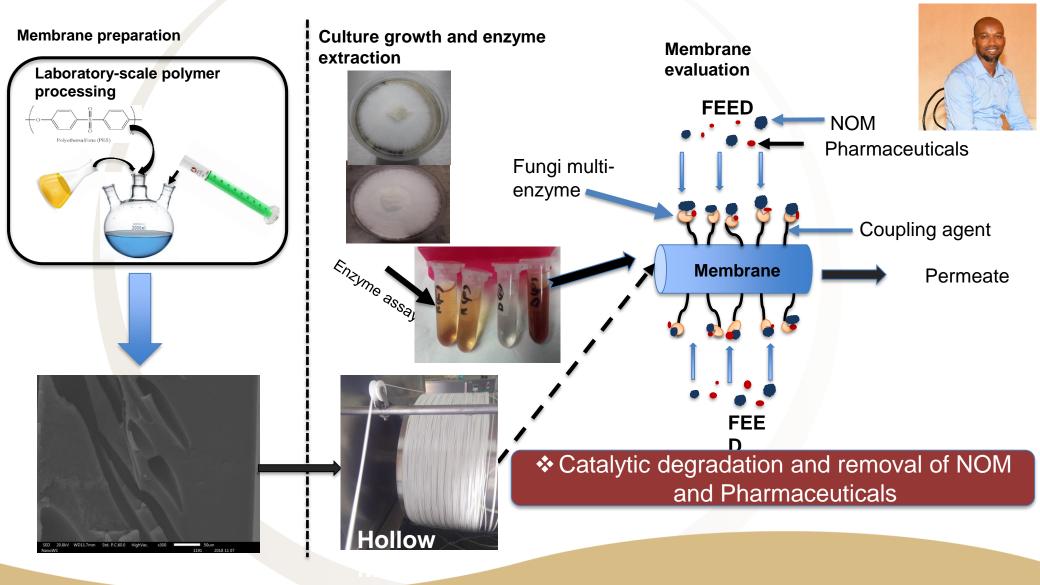
Ferricyanide reduction to elucidate kinetic and electrochemical activities on the metal nanocatalysts surface

Ali K. Ilunga\*, Bhekie B. Mamba, Thabo T.I. Nkambule

Nanotechnology and Water Sustainability (NanoWS) Research Unit, University of South Africa, UNISA Science Campus, Florida (Johannesburg), P.O. Box 392, Pretoria

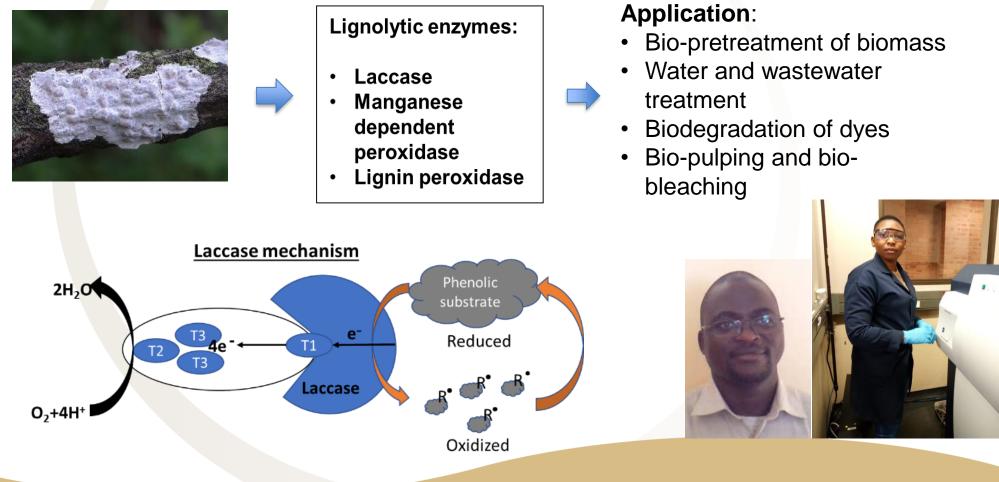


#### **HIGH-PERFORMANCE MEMBRANES FOR NOM REMOVAL**



### LACCASE-COATED POLYETHERSULFONE MEMBRANES FOR ORGANIC MATTER REMOVAL

#### White rot fungi



LACCASE-COATED POLYETHERSULFONE MEMBRANES FOR ORGANIC MATTER REMOVAL

#### Fungal isolation and enzyme extraction



Membran

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Laccase-coated polyethersulfone membranes for organic matter degradation and removal

Document Type : Research Pape

Johannesburg, South Africa

#### Authors Machawe Mota Sal © 1; Phumille P Mamba <sup>2</sup>; Henry J Ogola <sup>2</sup>; Titus AM Msagati <sup>2</sup>; Bhekie B Mamba <sup>2</sup>; Thabo Ti Nikambule <sup>2</sup> I institute for Nanotechnology and Water Sustainability. College of Science, Engineering and Technology, University of South Africa,

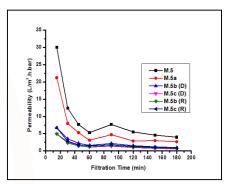
<sup>1</sup> Institute for Nanotechnology and water Sustainability, College of Science, Engineering and rectinology, University of South Africa. <sup>2</sup> Institute for Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa.

10.22079/JMSR.2021.139576.1418





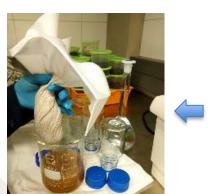




Fungal collection



**Enzyme purification** 

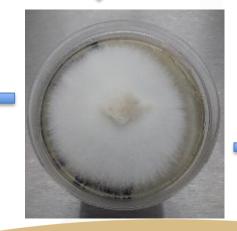


Enzyme extraction



**Plating and culturing** 

Fermentation



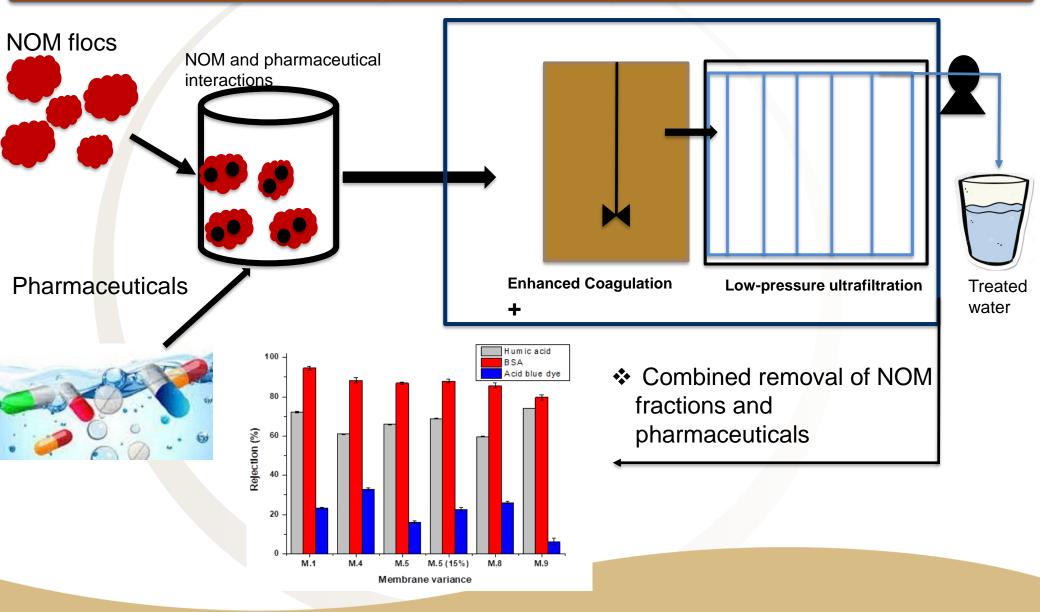
**Pure fungal culturing** 

#### **Isolates screening**





### Hybrid system development



## THE MONITORING AND REMOVAL OF EMP'S AND NOM THROUGH HIGH FLUX UF MEMBRANES

Part of projects	Method	Findings
Removal of EMPs through alum coagulation-flocculation	<ul> <li>10 min rapid mix at 200 rpm</li> <li>10 min slow mix at 20 rpm</li> <li>10 min settling</li> </ul>	<ul> <li>Humic acid fraction of NOM interacts better with EMPs</li> <li>Water with high DOC and ionic strength is more suitable for EMP removal</li> </ul>
Membrane preparation and coagulation-ultrafiltration hybrid system	<ul> <li>Polymer dissolving at 60°C</li> <li>Casting at 150µm thickness</li> <li>Immersing in non-solvent solution</li> <li>Flux at 3 bar and rejection of DOM</li> <li>Membrane filtration post coagulation-flocculation.</li> </ul>	<ul> <li>Rapid phase inversion produces highly permeable membranes</li> <li>Hybrid system enhances removal of NOM</li> </ul>
80 Caffeine Naproxen Carbamazepine Sulfamethoxazole 75 ppm 125 ppm 250 ppm 250 ppm 175 ppm 175 ppm 175 ppm 175 ppm 175 ppm 175 ppm	30 25 20 20 20 5 10 5 10 5 10 5 10 5 10 5 10 5 10 5 10 10 5 10 10 5 10 10 10 10 10 10 10 10 10 10	BO BO BO BO BO BSA: Bovine Serum Albumin HZ: Hazelmere raw water Rand: Rand raw water And raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water Rand: Rand raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water Rand: Rand raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water Rand: Rand raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water Rand: Rand raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water BSA: Bovine Serum Albumin HZ: Hazelmere raw water HA FA BSA HZW RW
Florida lake raw water	Humic acid synthetic water	Water type

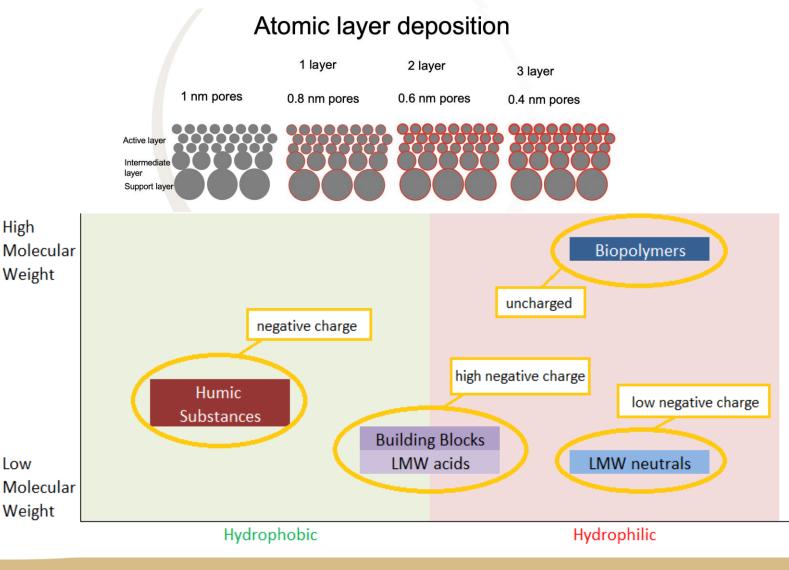
## UNLOCKING THE POTENTIAL APPLICATION OF SOUTH AFRICAN CLAYS TO THE WATER TREATMENT INDUSTRY

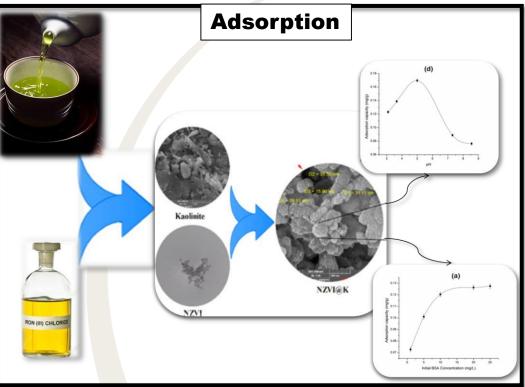




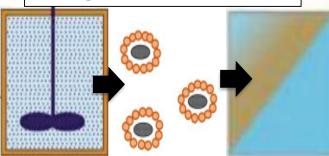
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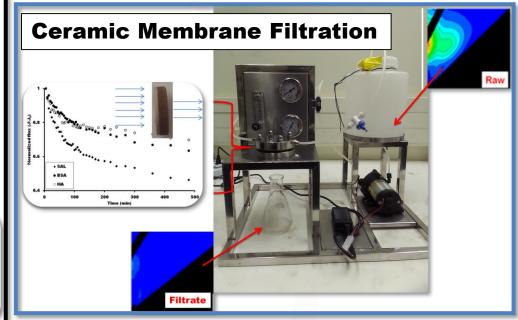


#### Integrated processes



**Coagulation – Adsorption - Membrane** 

## **FOR COMMUNICATION**

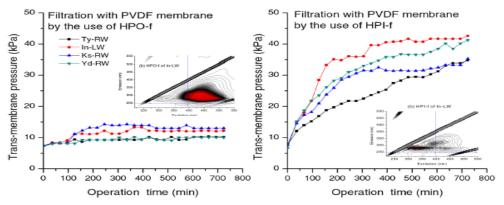


- 1. Removal of natural organic matter fractions by low cost adsorptive asymmetric ceramic membrane functionalized with *in situ* phytogenic nanoscale zero valent iron **(In Preparation)**
- 2. Characterization and performance low cost ceramic membrane functionalized with *in situ* phytogenic nanoscale zero valent iron for efficient Fenton degradation and filtration of natural organic matter fractions (In Preparation)



## WHICH NOM FRACTION(S) IS RESPONSIBLE FOR MF & UF MEMBRANE FOULING?

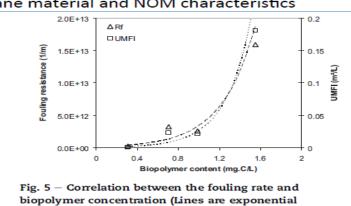
#### **River Water**



#### Extend of irreversible fouling from HPI depends on Membrane material and NOM characteristics

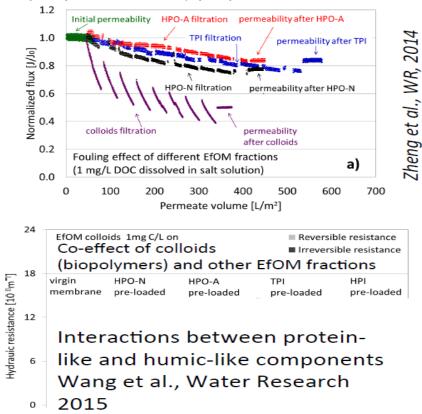
Filloux et al., WR 2012 Treated Secondary Effluent

correlations).



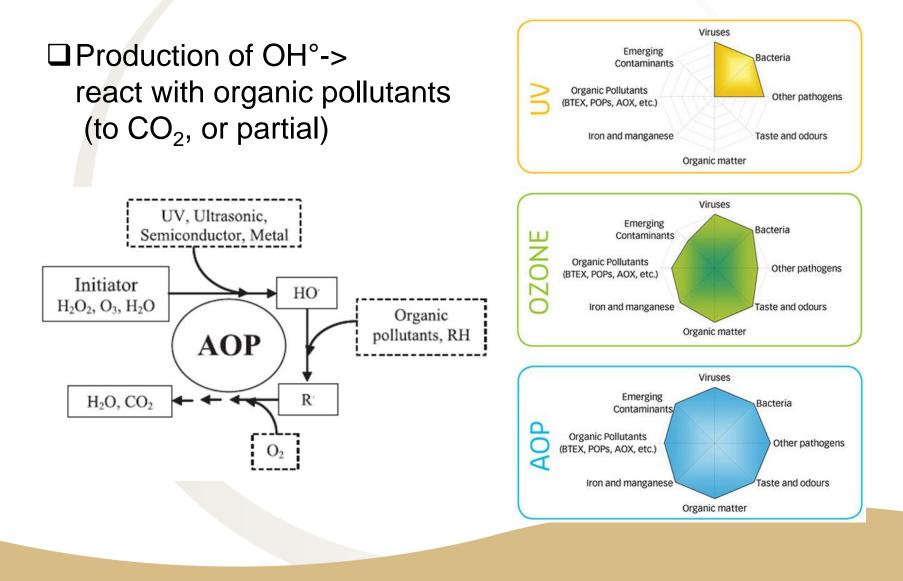
#### **Treated Wastewater**

Capillary UF membranes (hydrophilized PES, MWCO 150 kDa)



Humic substances play a major role in irreversible fouling (Filloux et al., submitted)

## **EXPLORING AOP FOR NOM REMOVAL**



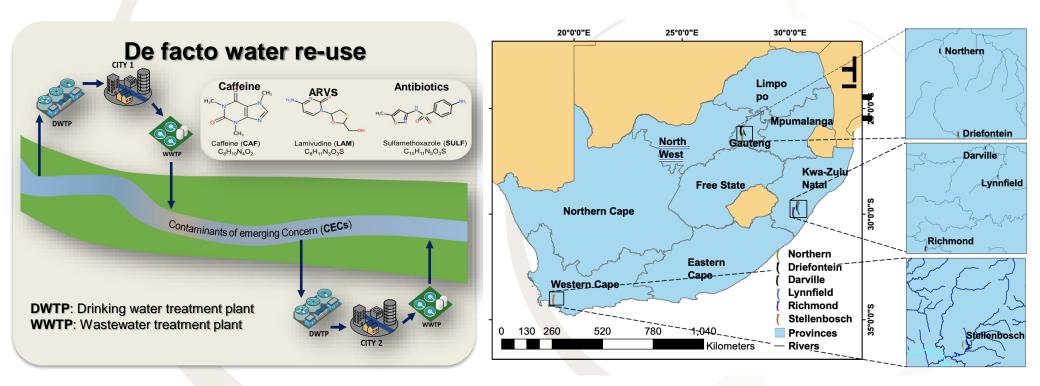


## ULTRASONIC-ASSISTED SYNTHESIS OF BINARY NANOCOMPOSITES FOR PHOTOCATALYTIC WATER TREATMENT (JULY 2018-AUGUST 2021)

<u>AIM:</u> To design and prepare visible light active photocatalysts using ultrasoundassisted synthesis for the abatement of emerging pollutants in water



## DETERMINING THE EXTENT OF DE FACTO WATER RE-USE IN SOUTH AFRICA: THE CASE OF CITIES IN GAUTENG, WESTERN CAPE AND KWA-ZULU NATAL PROVINCE



## **SAMPLING AREAS**



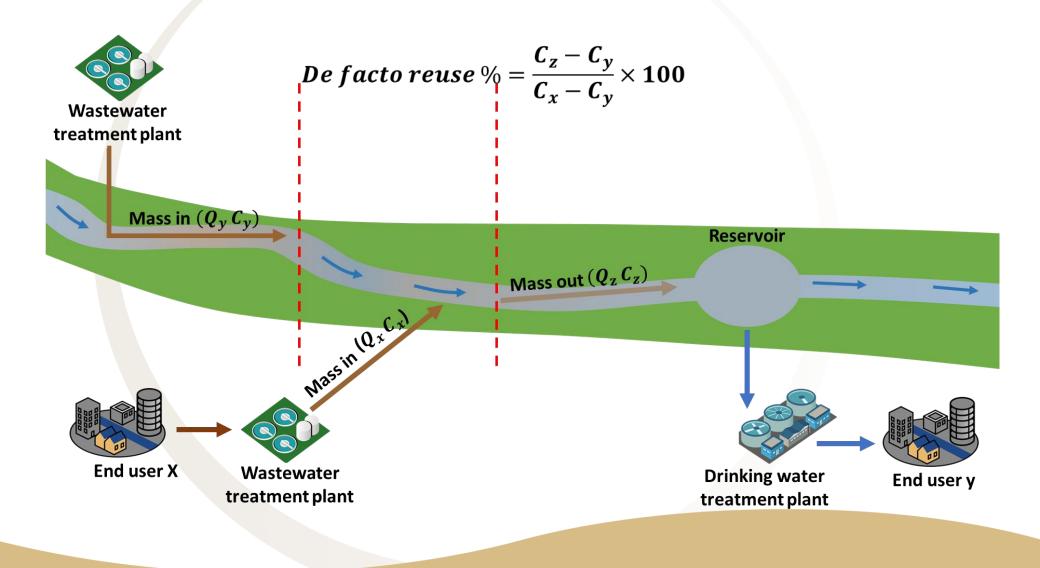
### Wastewater effluent



### Downstream



**Calculation model for wastewater tracers** 



## DE FACTO WATER RE-USE: LESSONS LEARNED

© IWA Publishing 2020 225 Water Practice & Technology Vol 15 No 2 doi: 10.2166/wpt.2020.021

The status and quantification of de facto water reuse in South Africa – a review

Umhle U. Swana<sup>a</sup>, Usisipho Feleni<sup>a</sup>, Tshepo J. Malefetse<sup>b</sup>, Bhekie B. Mamba MA<sup>a</sup>, Peter Schmitz<sup>c</sup> and Thabo T. I. Nkambule<sup>a</sup>.\*

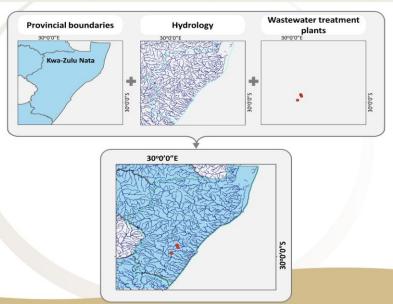
<sup>a</sup> Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida Campus, Johannesburg 1709, South Africa

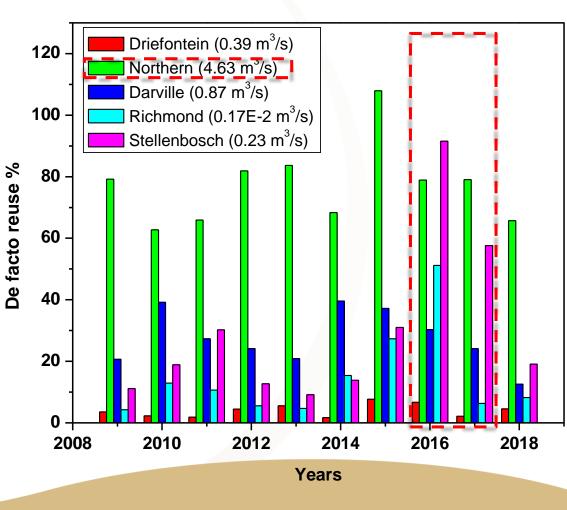
<sup>b</sup>Mintek, Randburg 2125, South Africa

<sup>c</sup> Department of Geography, University of South Africa, Florida Campus, Johannesburg 1709, South Africa

\*Corresponding author. E-mail: nkambtt@unisa.ac.za

#### Data incorporation to ArcMap 10.6.1 (GIS soft ware)





## ELECTROCHEMICAL DETECTION AND DEGRADATION OF NOM IN WATER

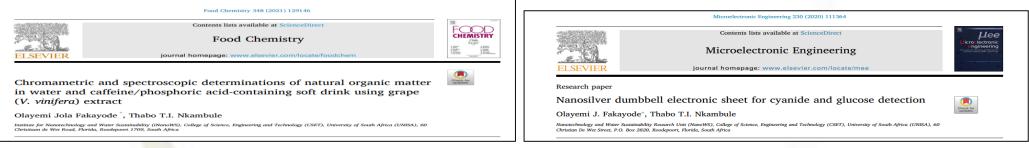
Dr Olayemi Fakayode

### Materials and Methodology

Hydrotherma Metastable crystallization hierarchical precipitation Non-solvent phase separation - similar to membrane casting using water as non-solvent. **Electrochemical Galvanization** 5.0KV LED Light ' Copper(II)oxide plastics Humic acid

## SUSTAINABLE MATERIALS AS SENSORS/DEGRADING TOOLS FOR NOM







# **KEY POINTS TO REMEMBER**

- **1.** NOM is a complex, heterogeneous mixture, but not hopelessly complex
  - Faster progress can be made by treating it as such
  - Categorize based on underlying structural features rather than methods of extraction
  - Recognize the distinction between microstructure and macrostructure

## 2. Sources set the stage

- Terrestrial  $\rightarrow$  Atmospheric
- Aquatic Anthropogenic (EfOM, etc.)
- 3. Processes change the outcome
  - Natural Systems
    - Aerobic degradation & Anoxia (sediments)
  - Engineered Systems (Treatment topic for another day)

## 4. Innovation and adaptability

- New and emerging trends
- Costs (effectiveness vs performance)
- Abundace, scarcity and Innovation

**Role of Climate Change?** 



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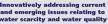


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and emerging issues relating to water scarcity and water quality

