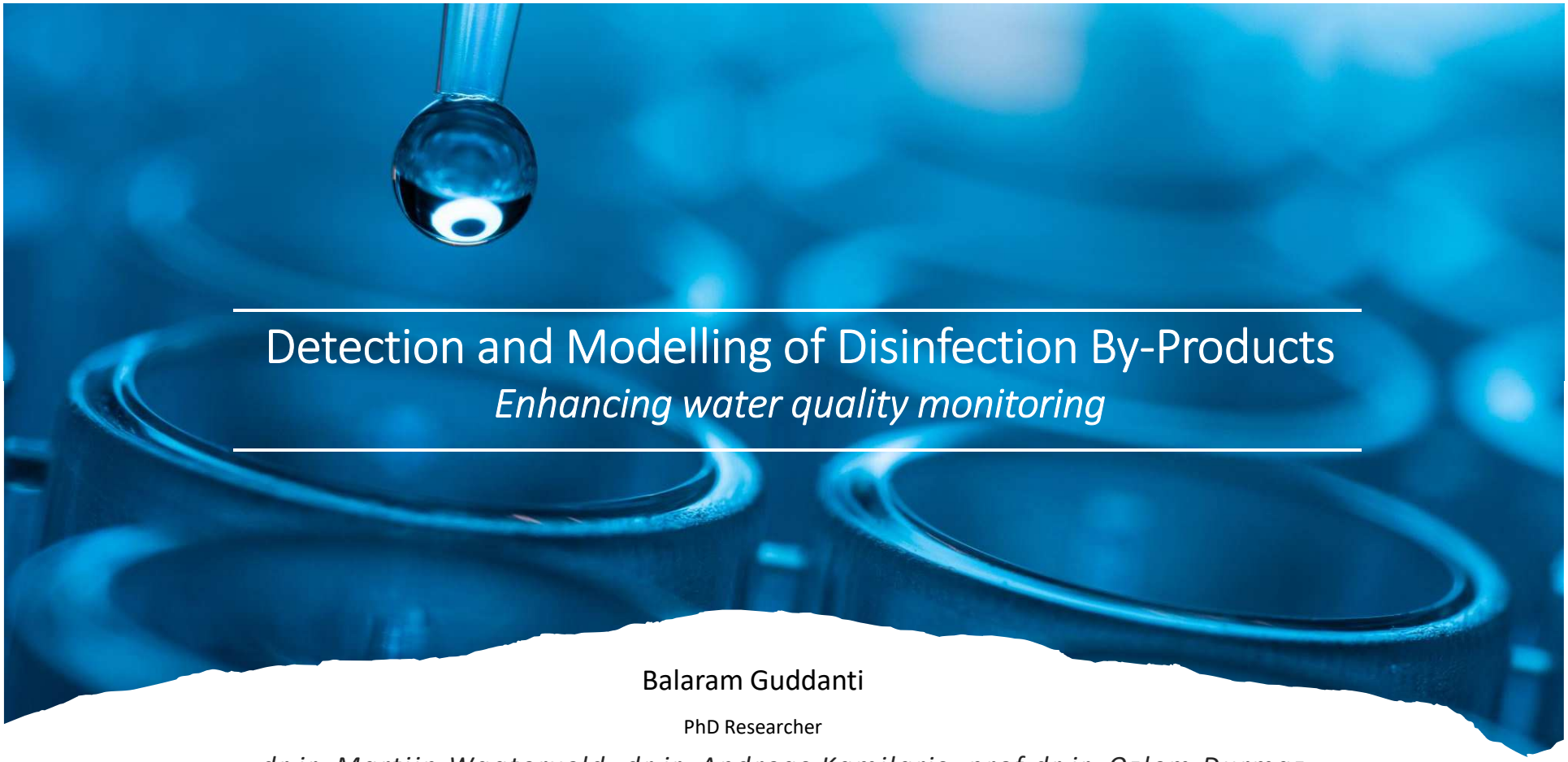

Detection and Modelling of Disinfection By-Products

Enhancing water quality monitoring

Balaram Guddanti

PhD Researcher

dr.ir. Martijn Wagterveld, dr.ir. Andreas Kamilaris, prof.dr.ir. Ozlem Durmaz

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03 December 2024

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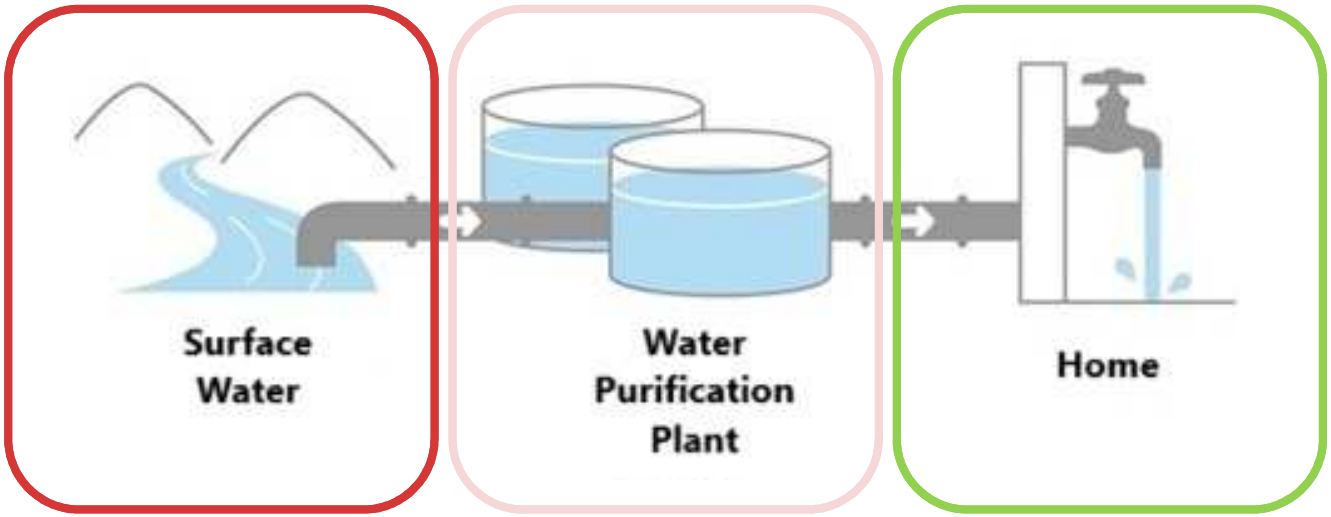
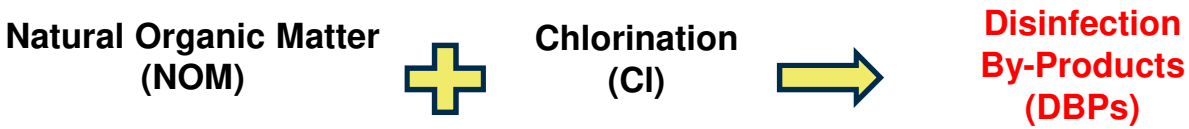
Introduction



Natural Organic Matter (NOM) + Chlorination (Cl) → Disinfection By-Products (DBPs)

Carcinogenic


Natural Organic Matter
(NOM)
Chlorination
(Cl)
Disinfection
By-Products
(DBPs)

Natural Organic Matter (NOM) + **Chlorination (Cl)** → **Disinfection By-Products (DBPs)**

Trihalomethanes(THM)
Haloacetic acids(HAA)
Haloacetonitriles(HAN)
Oxyhalides

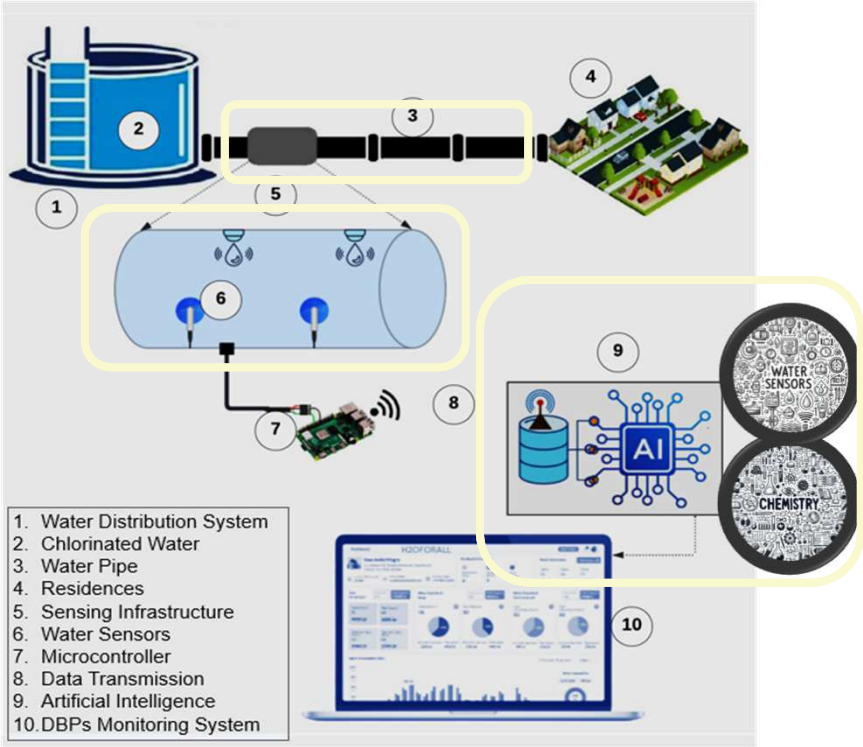
← Lab Sampling
Chromatography
Spectroscopy

Challenges

- Time Consuming
- No samples across pipe distribution
- Not real-time
- Multiple sample analysis
- Expensive Instruments
- Geographical variation in NOM content

Research Question

How can auxiliary sensing reliably detect and monitor Disinfection By-Products in the chlorinated drinking water distribution systems using probabilistic models?



Phase 1
Rate of change of WQP influencing the formation of DBPs

Phase 2
Probabilistic model to detect the concentration of DBPs

Phase 3
Strategic placement of the sensing device

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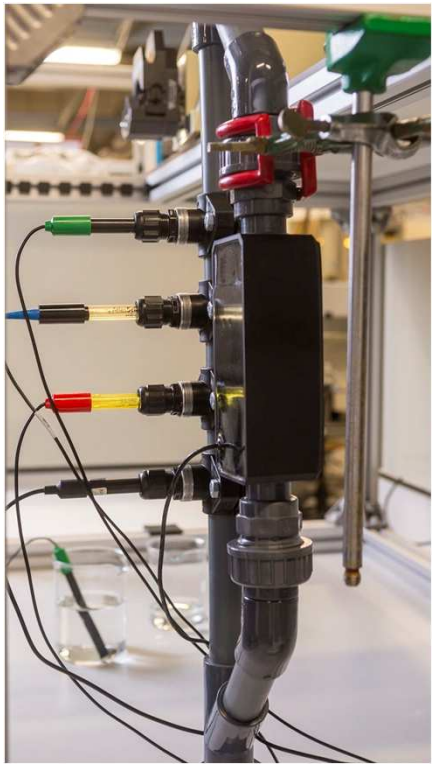
Phase 1
Rate of change of WQP influencing the formation of DBPs

Water Quality Parameters

- Chlorine dosage [Source]
- Natural Organic Matter (NOM) – [TOC & DOC]
- Residence Time
- Temperature
- pH
- Dissolved Oxygen (DO)
- Conductivity
- Oxidation-reduction potential (ORP)
- Water Flow Rate



- Presence of Natural Organic Matter (NOM) in water, which interacts with chlorine, emerged as the foremost factor in DBP formation.

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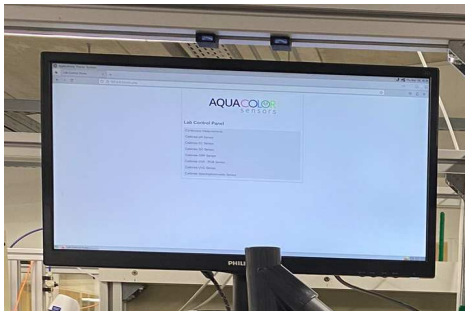
Phase 1
Rate of change of WQP influencing the formation of DBPs

Sensing Device



Probes
Temp., pH, conductivity, ORP, DO

Transmission measurements
280, 400, 461, 520, 641 nm (Future: UV-VIS/fluorescence)

Connectivity
4G connectivity through a SIM card, ethernet

EasyMeasure with AquaColor Sensors
(https://www.aquacolorsensors.nl/nieuws)

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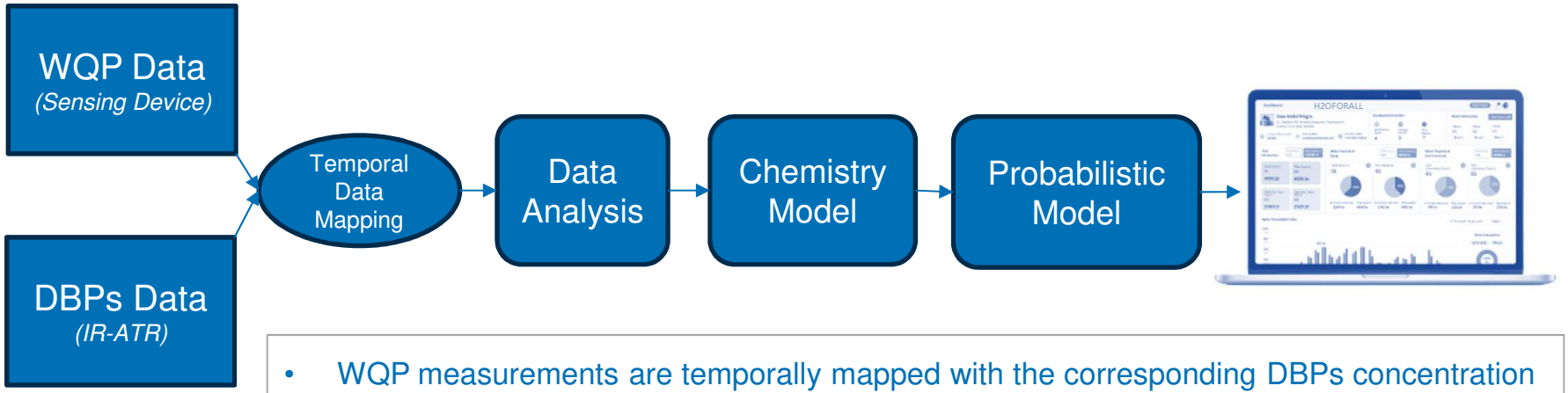
Phase 2
Probabilistic model to detect the concentration of DBPs

Approach



- WQP measurements are temporally mapped with the corresponding DBPs concentration and analysed.
- A chemistry model will be built to assess the rate of reactions in DBPs formation understanding the NOM functional groups.
- A multi-target regression model will be designed on the outcome of the chemistry model.

Phase 2
Probabilistic model to detect the concentration of DBPs

Data set creation

Laboratory Experiments

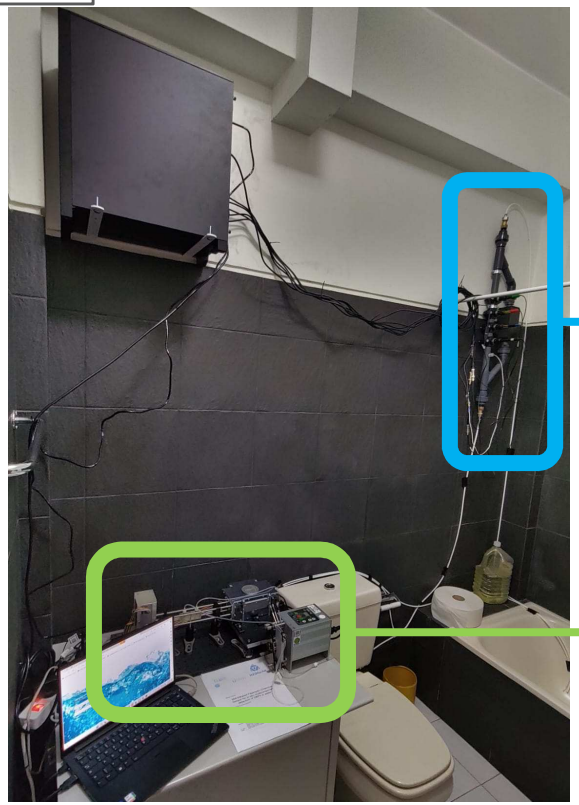
- Designed lab experiment for collecting large data sets with all possible parameters.
- Implementing controlled environment conditions (replicating Coimbra) for data variability.
- Installation of two sensing devices.

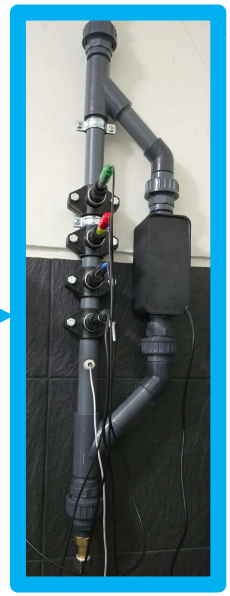
Pilot Location

- Deployment of one sensing device at the pilot location (Arzila) to collect WQPs data
- Mapping DBPs ground truth collected from the IR-ATR device

Phase 2
Probabilistic model to detect the concentration of DBPs

Pilot Location – Data set creation





Water Quality Parameters data from auxiliary sensor (WETSUS & UT)

DBPs concentration data from IR-ATR (UULM)

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Phase 2
Probabilistic model to detect the concentration of DBPs

Probabilistic Models

Data captured from Pilot Location
120 instances

Sensing Device *(Independent Variables)*
- Temperature
- pH
- Conductivity
- Dissolved Oxygen
- Oxidation Reduction Potential

IR-ATR from UULM *(Dependent Variables)*
- THMs
  - **BDCM**
  - DBCM
- HAAs
  - **DBAA**
  - MBAA
  - MCAA
  - TCAA
- HANs
  - **DBAN**
  - DCAN

Machine Learning Models
(Regression)
- Linear Regression
- Decision Trees
- Random Forest
- K Nearest Neighbors

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Phase 2
Probabilistic model to detect the concentration of DBPs

Results

THM - BDCM

HAA - DBAA

HAN - DBAN

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Current Status

- The sensing device is tested successfully for data collection in laboratory environment.
- Deployed auxiliary sensing device at pilot site (Arzila, Portugal)
- Data transfer to central server is tested and functional.

Next steps:

- Laboratory experiments (controlled parameters) for data collection.
- Building chemical and probabilistic models.

THANK YOU

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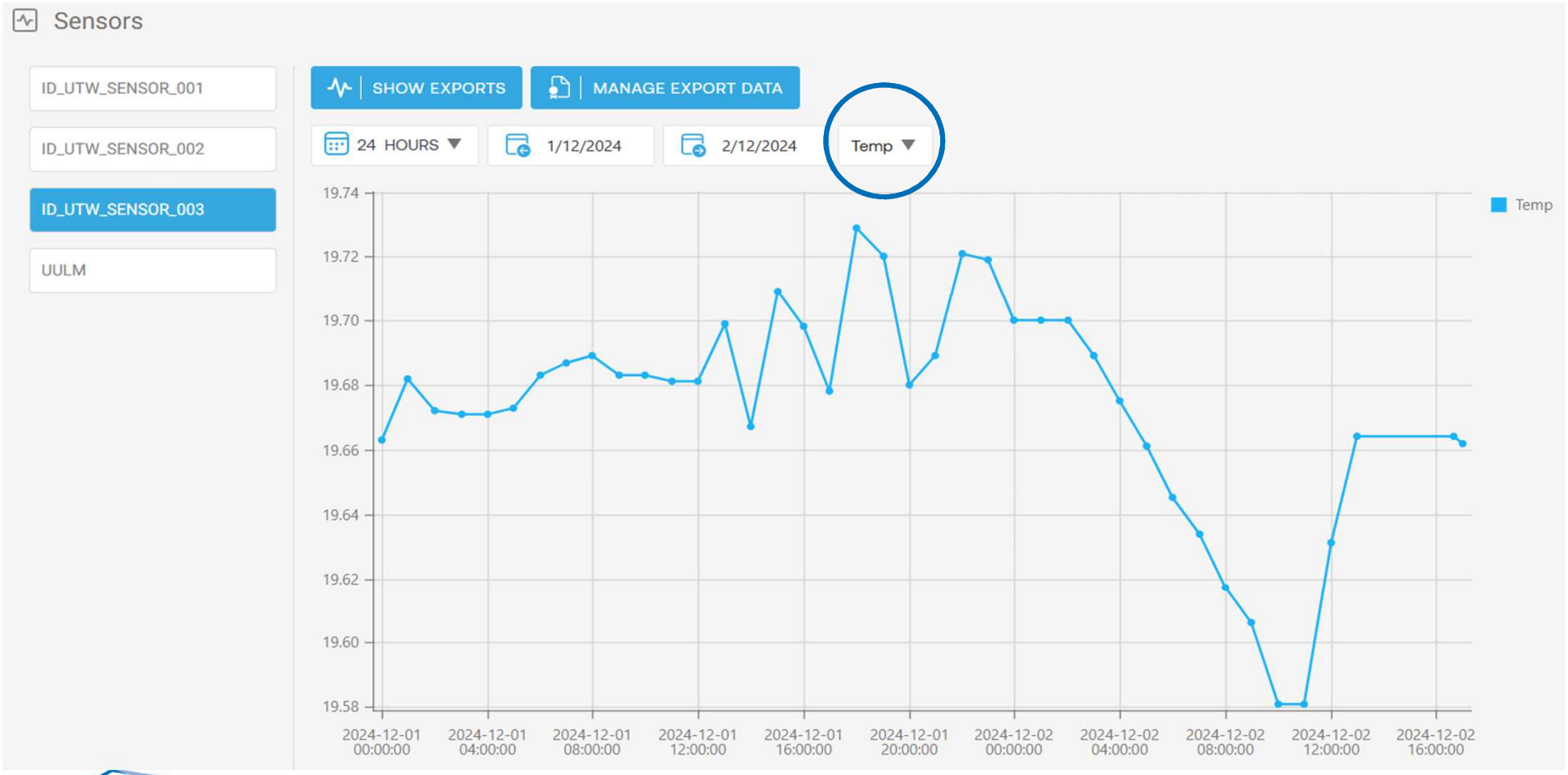
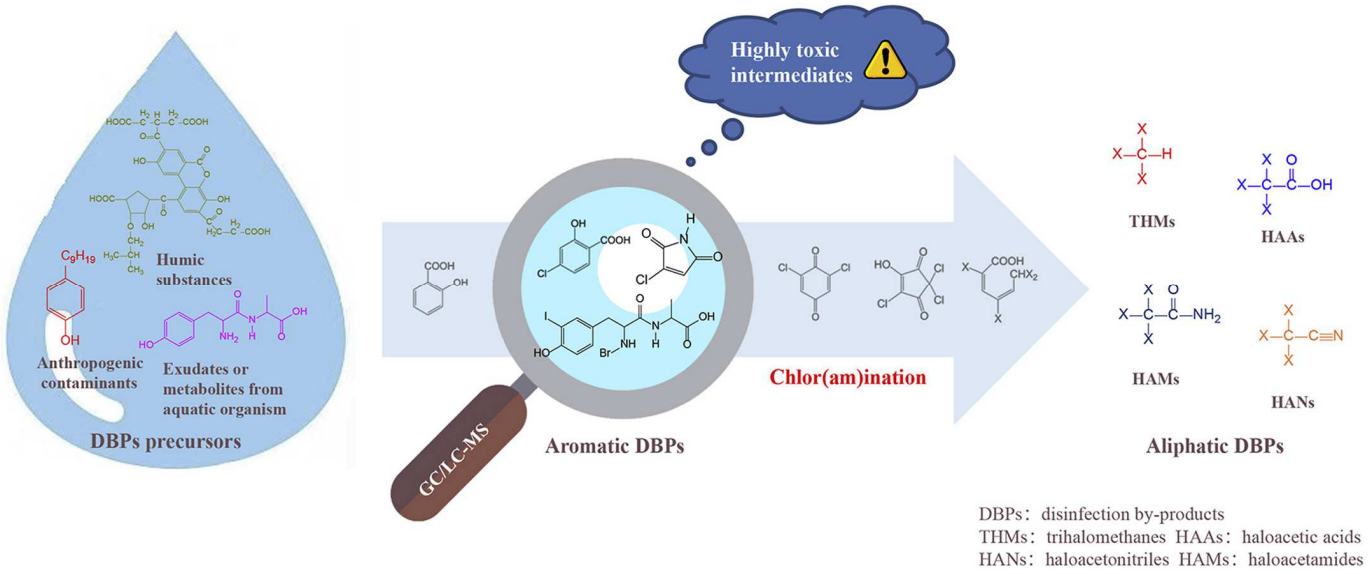
Name of the DBP family	Name of the Compound	Regulations
Trihalomethanes (THM)	Chloroform (CF)	*EU: 100 µg/L* *US-EPA: 70 µg/L*
	Dibromochloromethane (DBCM)	*US-EPA: 60 µg/L*
	Bromodichloromethane (BDCM)	*US-EPA: 45 µg/L*
	Bromoform (BF)	*US-EPA: 6 µg/L*
Haloacetic acid (HAA)	Dichloroacetic acid (DCAA)	*US-EPA: 60 µg/L*
	Trichloroacetic acid (TCAA)	*US-EPA: 20 µg/L*
	Monochloroacetic acid (MCAA)	*US-EPA: 70 µg/L*
	Monobromoacetic acid (MBAA)	*US-EPA: 60 µg/L (Family)*
	Dibromoacetic acid (DBAA)	*US-EPA: 60 µg/L (Family)*
Haloacetonitriles (HANs)	2-Dichloroacetonitrile (DCAN) (C2HCl2N)	*WHO: 20 µg/L* *US-EPA: 6 µg/L*
	2,2-Dibromoacetonitrile (DBAN) (C2HBr2N)	*WHO: 70 µg/L* *US-EPA: 20 µg/L*
Oxyhalide compounds	Bromate	*US-EPA: 10 µg/L*
	Chlorate	*WHO: 700 mg/L* *US-EPA: 100 µg/L*
	Chlorite	*WHO: 700 mg/L* *US-EPA: 1000 µg/L*


Sensors
ID_UTW_SENSOR_001
ID_UTW_SENSOR_002
ID_UTW_SENSOR_003
UULM
SHOW EXPORTS
MANAGE EXPORT DATA
24 HOURS
1/12/2024
2/12/2024
Temp
Temp
19.74
19.72
19.70
19.68
19.66
19.64
19.62
19.60
19.58
2024-12-01 00:00:00
2024-12-01 04:00:00
2024-12-01 08:00:00
2024-12-01 12:00:00
2024-12-01 16:00:00
2024-12-01 20:00:00
2024-12-02 00:00:00
2024-12-02 04:00:00
2024-12-02 08:00:00
2024-12-02 12:00:00
2024-12-02 16:00:00

NOM Functional Groups

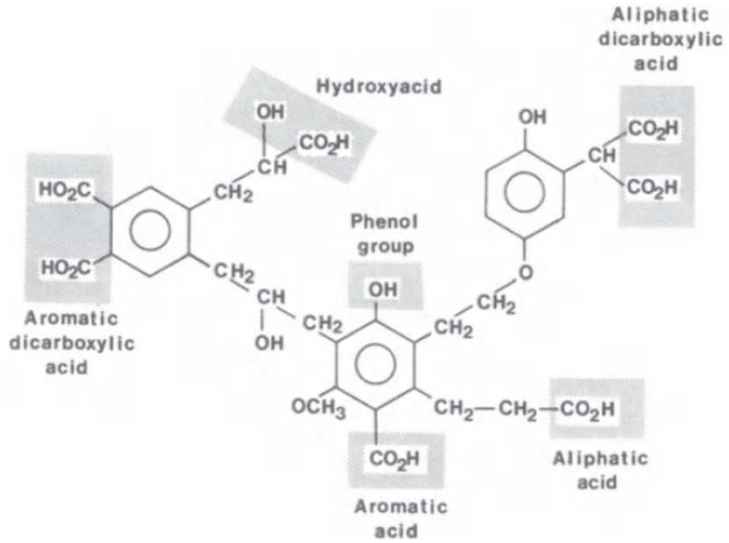
- The composition of functional groups (at varying proportions) within NOM could offer further insights into DBP formation.



DBPs: disinfection by-products
THMs: trihalomethanes HAAs: haloacetic acids
HANs: haloacetonitriles HAMs: haloacetamides

NOM Functional Groups

- The NOM may contain various functional groups within its carbon chain.



NOM functional groups

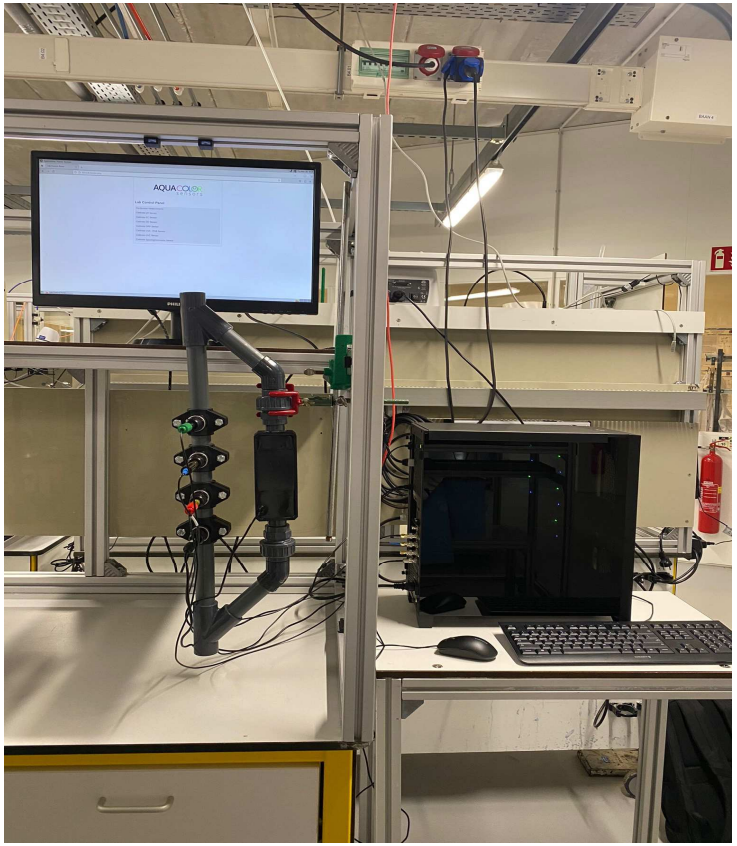
- Carbonyl
- Carboxyl
- Aromatic
- Acetal
- Heteroaliphatic
- Aliphatic

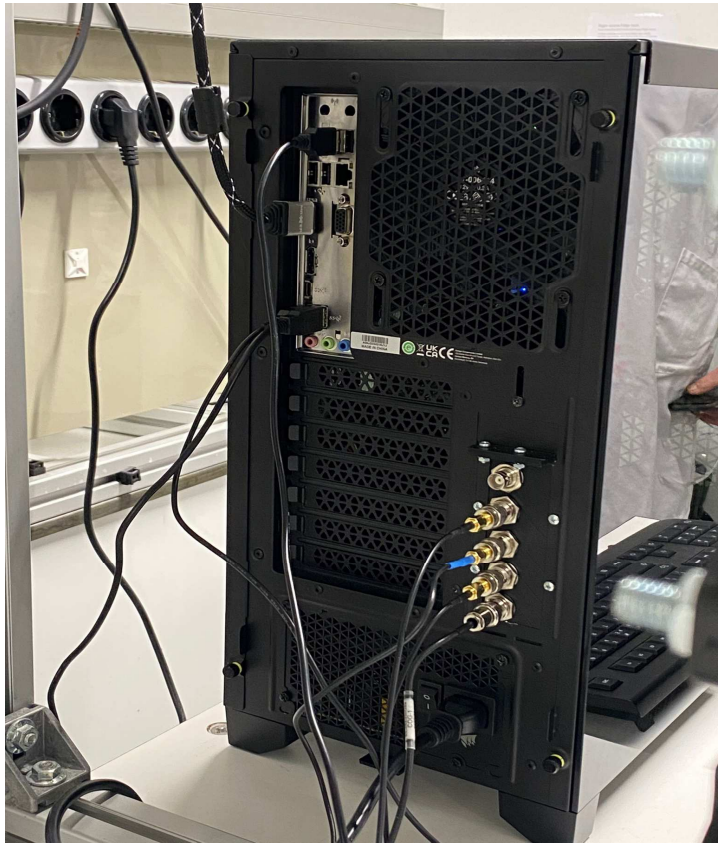
Function group	Corresponding DBPs	Proportion
acyl chlorides	2. chloro-5-oxo-3-hexenediacyl chloride; 4-Methoxybenzoyl-chloride; 4-Methoxybenzoyl-chloride; 2-(6-methyl-3,6-dihydro-1,2-dioxin-3-yl)acetyl chloride; Benzyloxy carbonochloridate;3-(2-Chloro-2-oxo-acetyl)Benzoyl chloride; 3,4-Dihydroxy-5-(2-hydroxyethoxy)benzoyl chloride	0.76%
hydroperoxides	bromo(hydroperoxy)methane	0.13%
dioxins	4-(2-Chloroethyl)-1,2-Dioxine	0.13%
ethers	3-bromophenol methyl ether; 2,3-dibromo-1,4,5-trimethoxybenzene; (3-Chlorobenzo)-1,3-dioxole; Dibromo-trimethoxybenzene; 2,4-Dibromo-1-methoxybenzene	0.63%
hydrocarbons	Benzene;toluene; n-Undecane (n-C11); cyclododecane;naphthalene; 1-methylnaphthalene; 1,2-Bis(1-methylethenyl)-benzene	0.88%
imidazoles	Dibromoimidazole; 4,5-Dibromo-1-methyl-1H-imidazole; 2,4,5-Tribromo-1-methylimidazole	0.38%
pyrans	2-Chloro-3-hydroxy-6-(hydroxymethyl)pyran-4-one	0.13%
pyrazoles	3,4,5-Tribromo-1H-pyrazole	0.13%
pyridines	X72; X105; X86; 5,6,7-trichlorooxazolo[4,5-b]pyridin-2(3H)-one	0.50%
pyrroles	2,3,5-Tribromopyrrole	0.13%
sulfones	Dibromo[(Dibromomethylsulfanyl)oxy]methane	0.13%
triazoles	3. Chloromethyl-2H-benzotriazole; 5-Chloromethyl-1H-benzotriazole; 4-Chloromethyl-1H-benzotriazole	0.38%
oxadiazoles	5-(bromomethyl)-3-chloro-1,2,4-oxadiazole	0.13%

NOM - Identification

Nature	Functionality Group	Structure	Technique
Acidic	Carboxylic acid	R-C02H	Titration
	Enolic hydrogen	R-CH=CH-OH	NMR, IR
	Phenolic OH	Ar-OH	UV/VIS, GC-MS
	Quinone	Ar=O	HPLC, GC-MS
Neutral	Alcoholic OH	R-CH2-0H	GC, IR
	Ether	R-CH2-0-CH2-R	GC-MS, NMR
	Ketone	R-C=O(-R)	IR, NMR
	Aldehyde	R-C=O(-H)	GC-MS
	Ester	R-C=O(-OR)	GC-MS, DNPH derivatization /HPLC
	lactone	R-C=O(-OR)	GC-MS, HPLC
Basic	Amine	R-CH2-NH2	NMR, GC-MS
	Amide	R-C=O(-NH-R)	IR, NMR

- GC-MS, HPLC, IR/Raman are the most straightforward approaches.
- Except NMR, all the techniques are possible in WETSUS.





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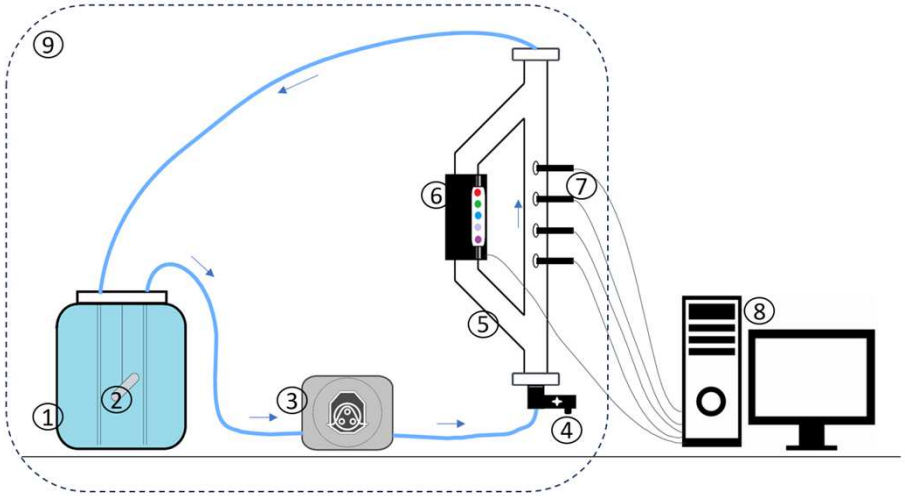
Lab Experiment – Data set creation



1. Water source 2L
2. Magnetic stirrer
3. Peristaltic Pump
4. Sampling outlet
5. Sensing device
6. Optical Sensors (R, G, B, UVA & UVC)
7. Water Quality Parameters (pH, EC, ORP, DO, Temperature)
8. Processing Unit
9. Controlled environment

Controlled Environment	
Chlorine	*[0.1, 2.5] mg/L*
Temperature	*[10, 18, 25] C*
pH	*[6 - 9]*
Flow rate	*10 L/hour*
**NOM	*[100, 250] µM*

****NOM from IHSS**
(https://humic-substances.org/)
Standard HA - Suwannee River III
Standard HA - Leonardite
Standard FA - Suwannee River II

- The DBPs concentrations are detected from collected samples (4) for ground truth.

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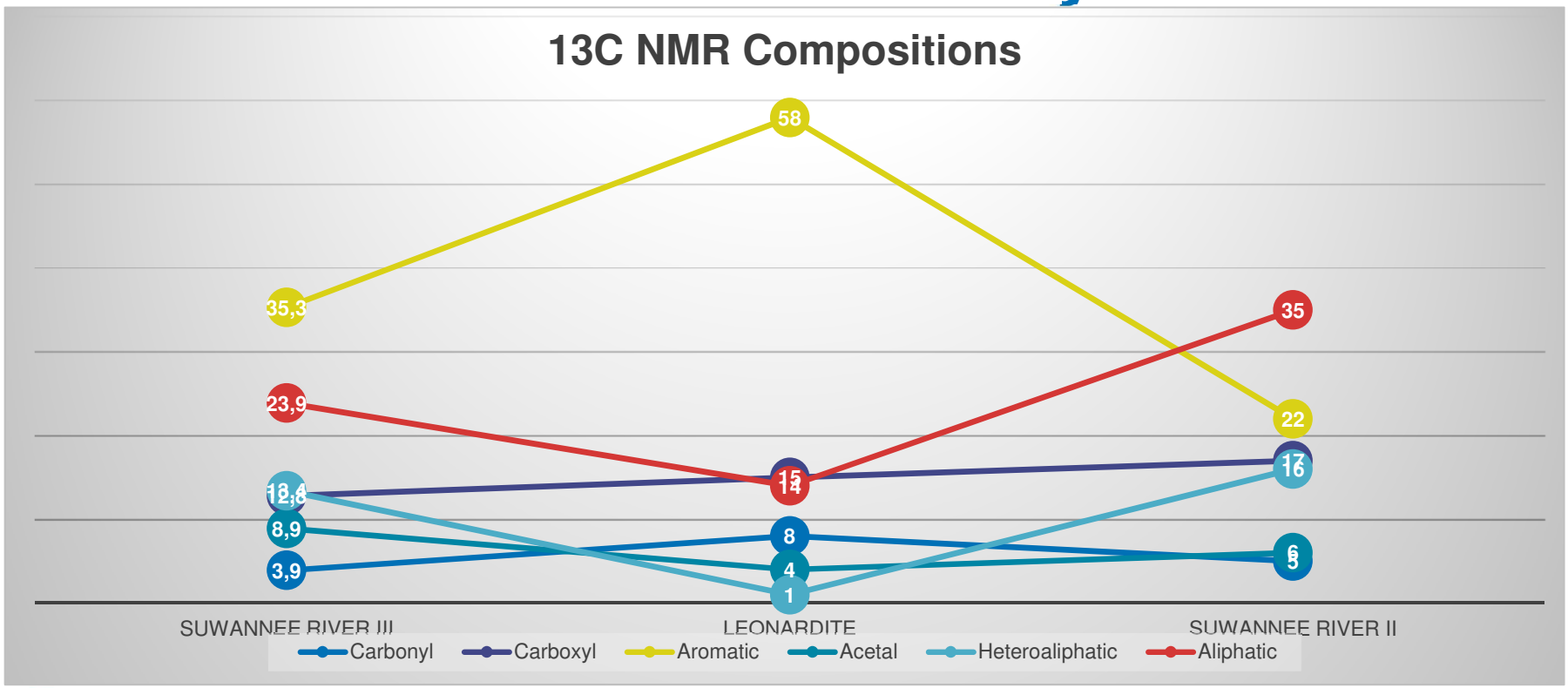
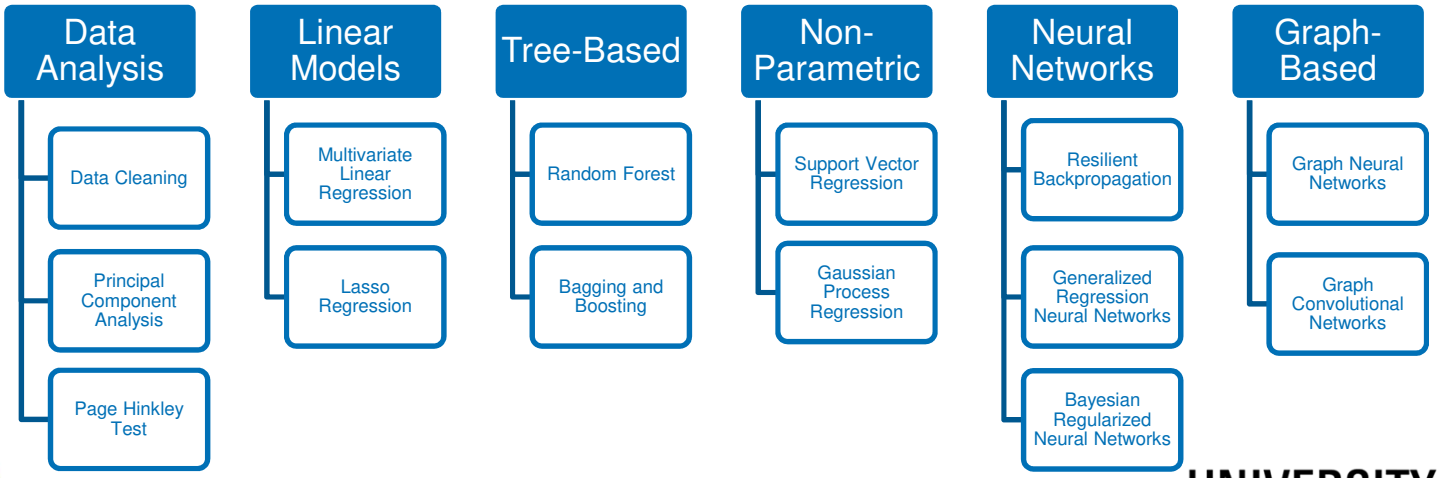
NOM - 13C NMR Analysis



Analytical Techniques

The concentration of the DBPs in the water can be predicted using the probabilistic models mentioned below. The regression models are preferred as the regulatory rules are based on the acceptable level of concentration of the DBPs in drinking water.



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Implemented AI Techniques

Model Type	Model Names
Linear Models	Multivariate Linear Regression (MLR)
	Lasso Regression
	Principal Component Regression (PCR)
Neural Networks	Resilient Backpropagation (RPROP)
	Generalized Regression NN (GRNN)
	Bayesian Regularized NN (BRNN)
Tree-Based	Random Forest (RF)
	Bagging
	Boosting
Non-Parametric	Support Vector Regression (SVR)
	Gaussian Process Regression (GPR)

Evaluation Metric : Mean Square Error (MSE)

Best Performing Models
- DCAN - SVR
- CPK - GPR
- TCP - SVR

Analysis
- For DCAN and TCP

83-90 % of error reduction with SVR compared to PCR/MLR

- For CPK

67 % of error reduction with GPR.

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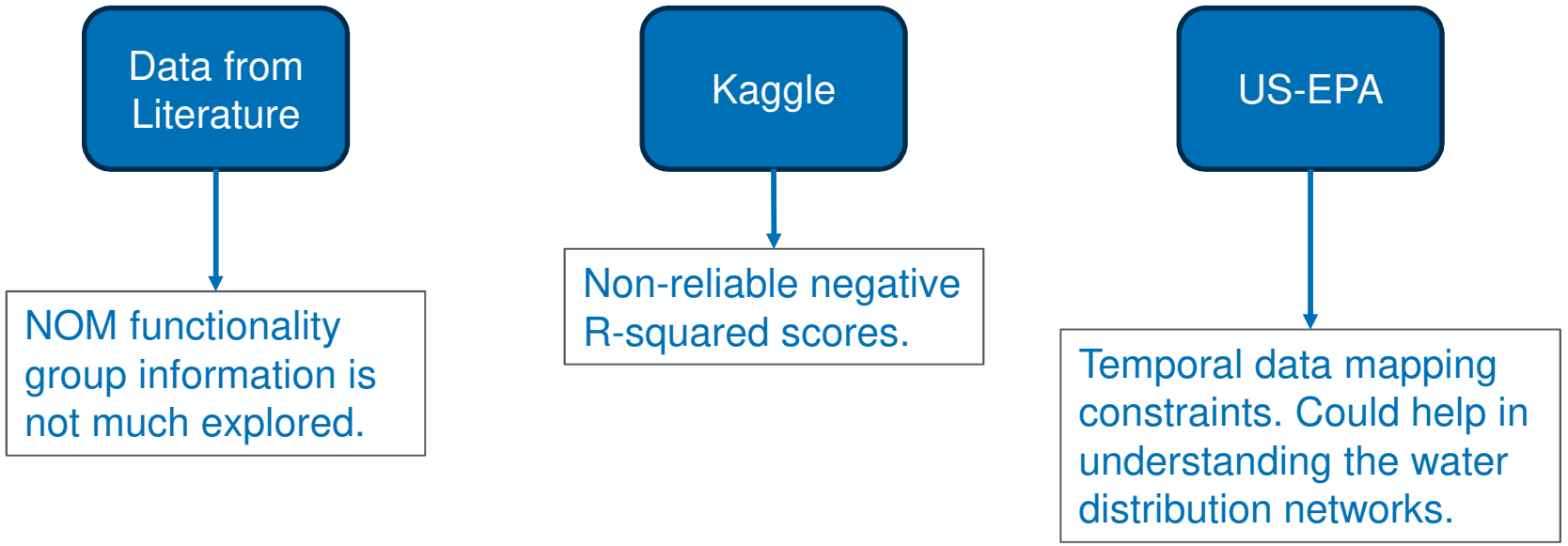
Available public data sets



***So, the data set creation strategies are implemented.**

References

Susana Y. Kimura, Amy A. Cuthbertson, Jonathan D. Byer, Susan D. Richardson, "The DBP exposome: Development of a new method to simultaneously quantify priority disinfection by-products and comprehensively identify unknowns", Water Research, Volume 148, 2019, Pages 324-333, ISSN 0043-1354, https://doi.org/10.1016/j.watres.2018.10.057.
(https://www.sciencedirect.com/science/article/pii/S0043135418308546)