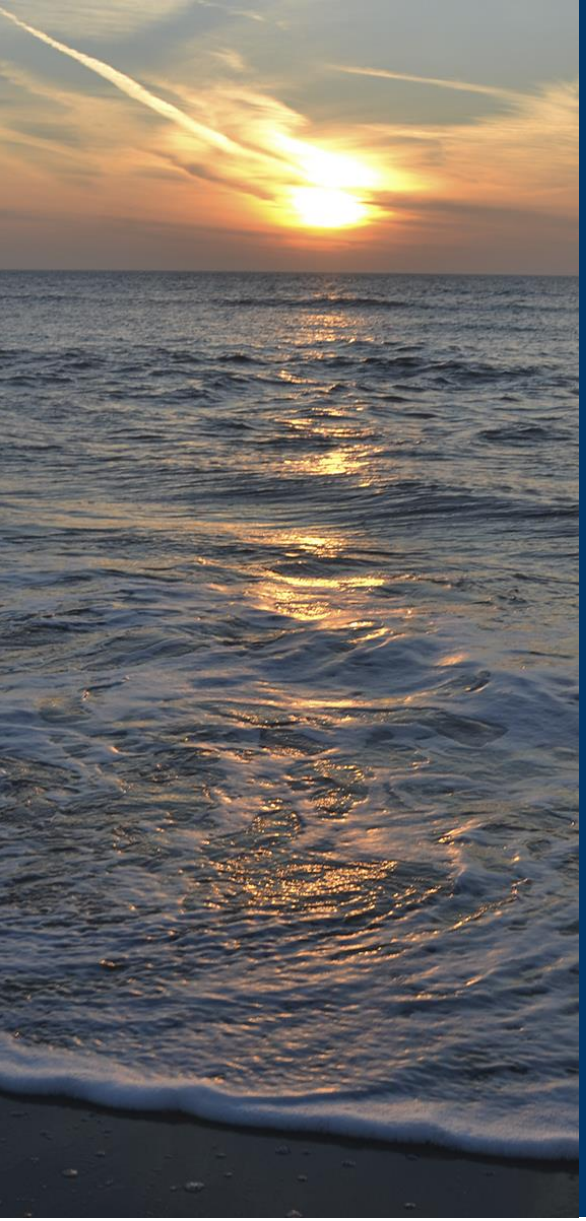


Risk Assessment of Disinfection By-Product Formation

Henry MACKEOWN – *PhD student, Lille 1 University*

Supervisor – Professor Baghdad OUDDANE, *Lille 1 University*

Co-supervisor – University Lecturer Justine CRIQUET, *Lille 1 University*

Interreg 2 Seas Mers Zeeën DOC2C's European Regional Development Fund

Risk assessment of Disinfection By-Product formation

Outline

I. Context

II. Research interest

III. Literature Review

IV. Development of analytical methods

V. First results

VI. Upcoming work

Interreg 2 Seas Mers Zeeën DOC2C's European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

I. Context

Minimising Disinfection By-Products

- Strategy information and local specificities for partners and observers for Organic Matter treatment" (Irene Caltran, Delft)
  - DBP minimisation as one of the main reasons for improving DOC removal

Improving **D**issolved **O**rganic **C**arbon **removal** to **reduce** **D**isinfection **B**y-**P**roduct formation

Developing a **risk assessment** of **DBP formation** in the 2 seas area, looking at the **benefits** of **DOC removal** on DBP formation and speciation

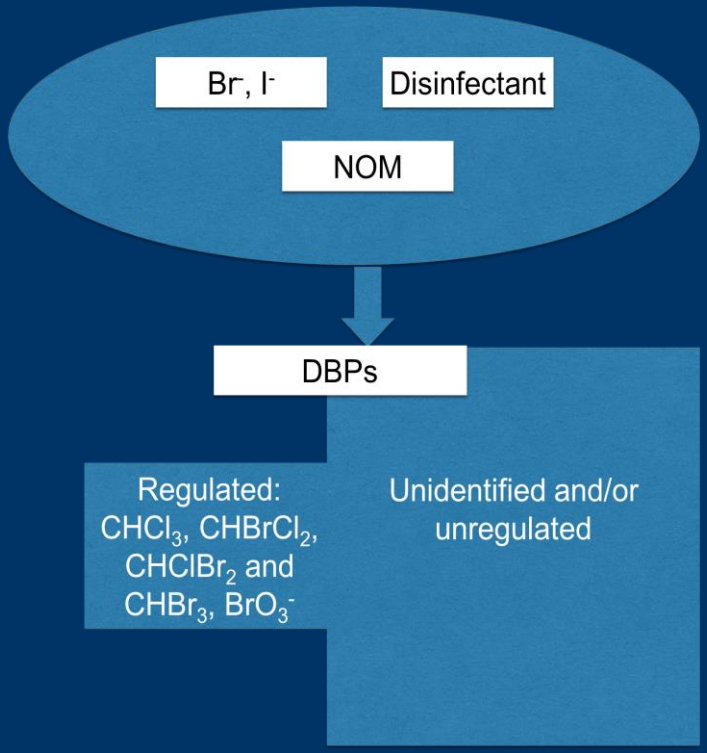
I. Context

Disinfection By-Product characterization

- Oxidation of Natural Organic Matter by a disinfectant
- $HOCl/ClO^- + NOM \rightarrow Cl\text{-}DBPs$

- $HOCl/ClO^- + Br^- \rightarrow HOBr/BrO^- + Cl^-$
- $HOCl/ClO^- + I^- \rightarrow HOI/IO^- + Cl^-$

- $HOBr/BrO^- + NOM \rightarrow Br\text{-}DBPs$
- $HOI/IO^- + NOM \rightarrow I\text{-}DBPs$



Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

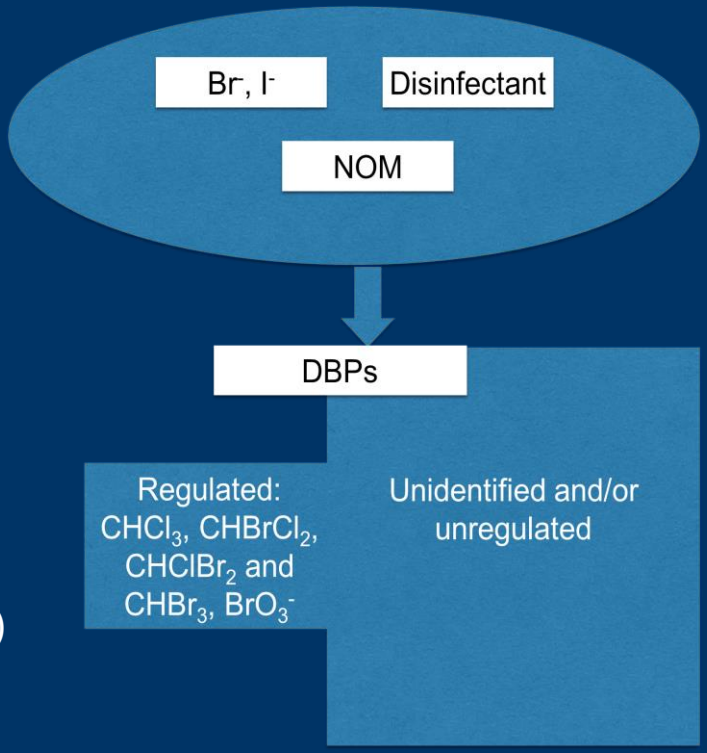
I. Context

Disinfection By-Product regulations

- Sum of 4 Trihalomethanes: 100 µg/L (EU), 80 µg/L (US), 250 µg/L (Australia)

- Sum of 5 Haloacetic Acids: 60 µg/L (US)
- Several chlorophenols and chloroacetic acids (Australia)

- Bromate : 10 µg/L (EU and US), 80 µg/L (Australia)
- Chlorite: 1 mg/L (US), 800 µg/L (Australia)



Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

I. Context

Emerging Disinfection By-Products, a growing concern

- Over 800 compounds
- Some of the emerging classes (haloacetonitriles, haloacetamides) are more toxic than regulated DBPs
- Iodinated-DBPs > Brominated DBPs > Chlorinated-DBPs
- Not regulated, nor widely measured

➢ Study of THMs as well as several other DBPs

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

II. Research interest

Study plan

Literature review

- DBPs analytical methods by HS-GC/MS
- Iodine and bromine analysis by ICP-MS

Method development

- Calibration curve
- Limits of quantification
- Precision
- Repeatability

Future experiments

- Analysis of water samples from partners
- Study of the DBP formation potential

Result exploitation

Relating the results:

- with the characterization of NOM
- with the treatment steps

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

II. Research interest

List of compounds

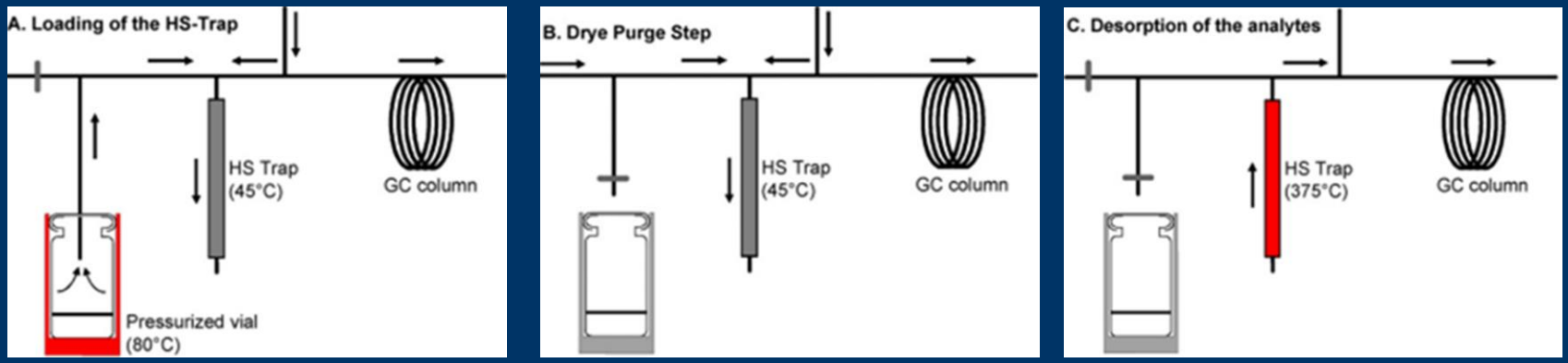
Trihalomethanes	Haloacetic Acids	Other compounds

• **Regulated**
  • Chloroform
  • Bromoform
  • Bromodichloromethane
  • Dibromochloromethane
 	
• **Iodinated**
  • Iodoform
  • Dichloroiodomethane
  • Bromodiiodomethane
  • Dibromoiodomethane
  • Chlorodiiodomethane
	• **HAA5**
	  • Monochloroacetic acid
	  • Dichloroacetic acid
	  • Trichloroacetic acid
	  • Monobromoacetic acid
	  • Dibromoacetic acid
	
	• Iodoacetic acid
		• **Haloacetonitriles**
		  • Iodoacetonitrile
		  • Bromoacetonitrile
		  • Chloroacetonitrile
		
		• **Haloacetamides**
		  • 2-chloroacetamide
		  • 2-bromoacetamide
		  • 2,2-dichloroacetamide
		  • 2,2,2-trichloroacetamide

II. Research interest

Disinfection By-Product analysis by Headspace-Trap GC/MS

- Less toxic solvents and lower limits of detection



Principle of sample preparation
with headspace trap (Schulz K. et al. 2007)

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

III. Literature review

Important parameters to consider for HS-Trap GC/MS methods

Important parameters		Optimum conditions			
		THMs	HAAs	HANs	HAcAMs
Sample preparation	pH	2-9	5.2-7.1	2.6-5.6	4-7
	Organic modifier	none	n-pentane	MTBE/none	MTBE
	Derivatisation reagent	0	DMS + TBA–HSO4	0	0
HS-trap settings	Equilibration time (min)	10-30	20	20	NR
	Equilibration temp (°C)	60	60	80	NR
	Trap Desorb temp (°C)	200-250	]180-230[for SPME	NR	NR

III. Literature review

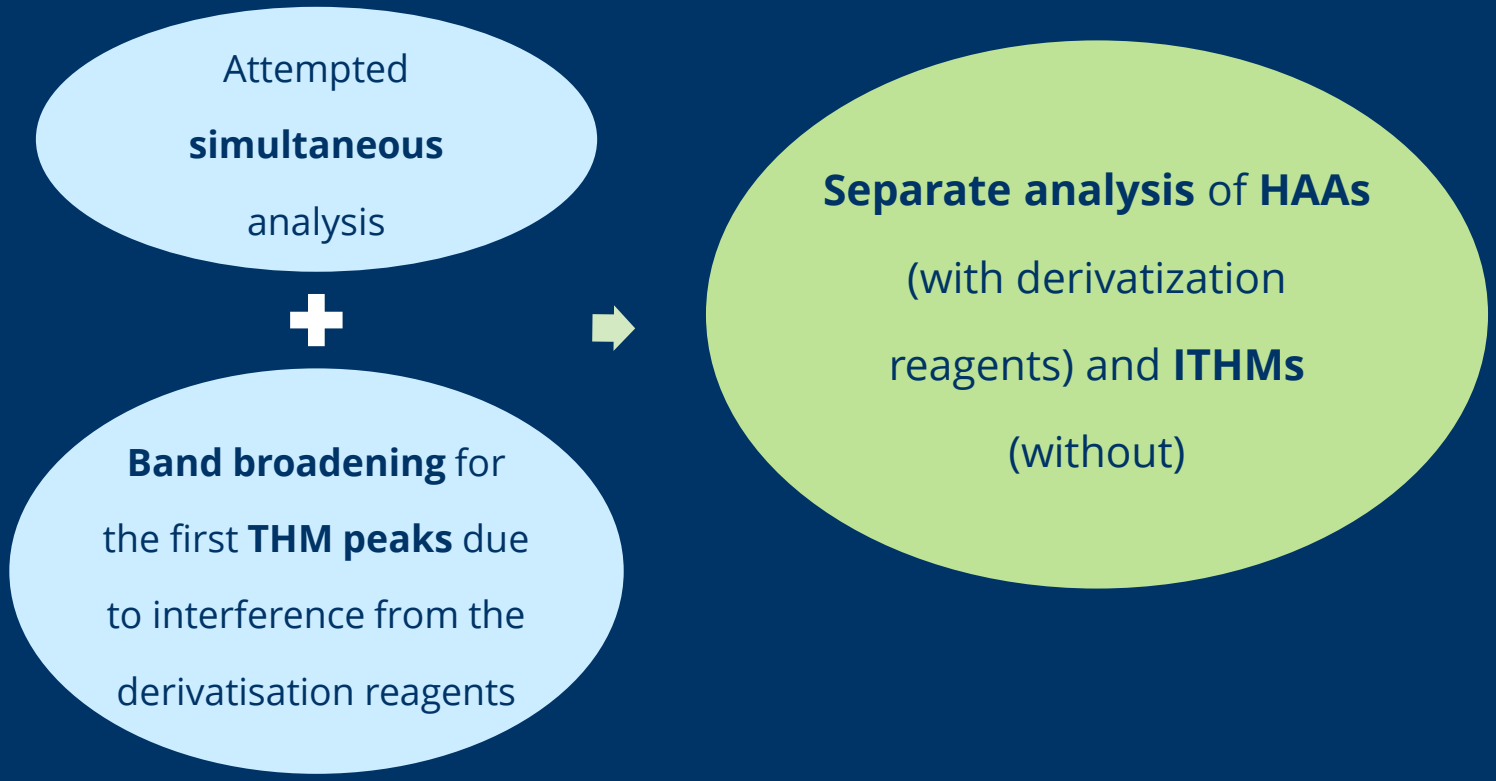
Existing Headspace methods for simultaneous analysis

- Trihalomethanes and Haloacetic acids
  - Headspace method (*Cardador et al. 2015*)
- Haloacetonitriles and Trihalomethanes
  - Headspace methods (*Antoniou et al. 2006; Montesinos and Gallego 2013; Luo et al. 2014*)
- Haloacetonitriles and Haloacetamides
  - Liquid/Liquid extraction (*Bond et al. 2015*)

Interreg 2 Seas Mers Zeeën DOC2C's European Regional Development Fund
PWNT Water Technology
South West Water
Provincie Noord-Holland
De Watergroep Water. Vandaag en morgen
Université de Lille
TU Delft

IV. Development of analytical methods

1. Analysis of HAAs and ITHMs separately



Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

IV. Development of analytical methods

2. Analysis of Haloacetonitriles and Haloacetamides

Haloacetamides L/L extraction with an organic solvent

+

Haloacetonitriles by HS techniques with/without a small amount of an organic solvent

→

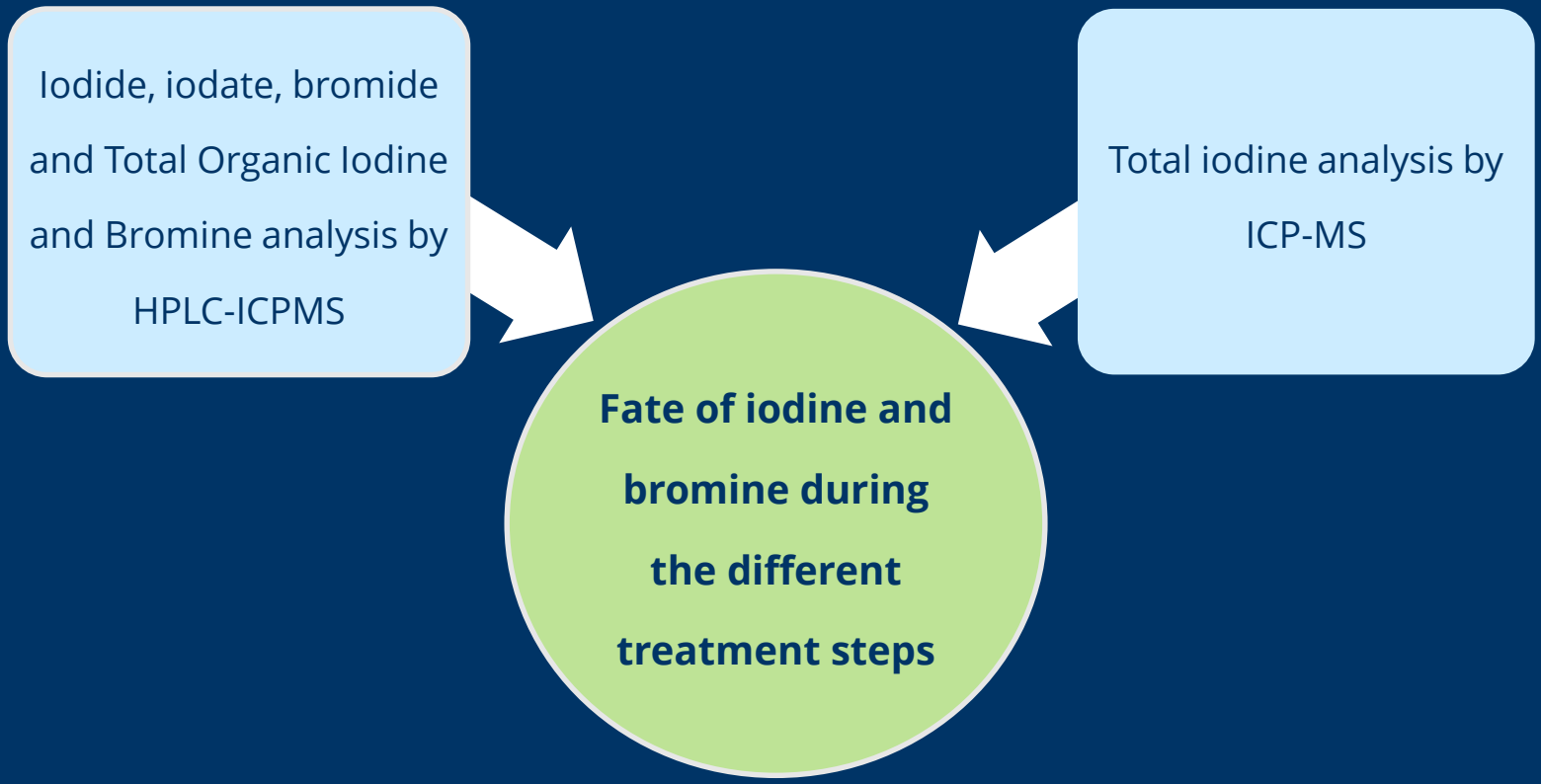
1) Analysis **with the ITHMs**

2) If not possible, analysis of the remaining compounds **separately** with an organic solvent

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

IV. Development of analytical methods

3. Other analytical methods



Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

V. First results

1. Initial Headspace instrument problems

Compatibility issue

leading to difficulties controlling the pressure

- Direct connection
- Splitless injection

Leaking headspace

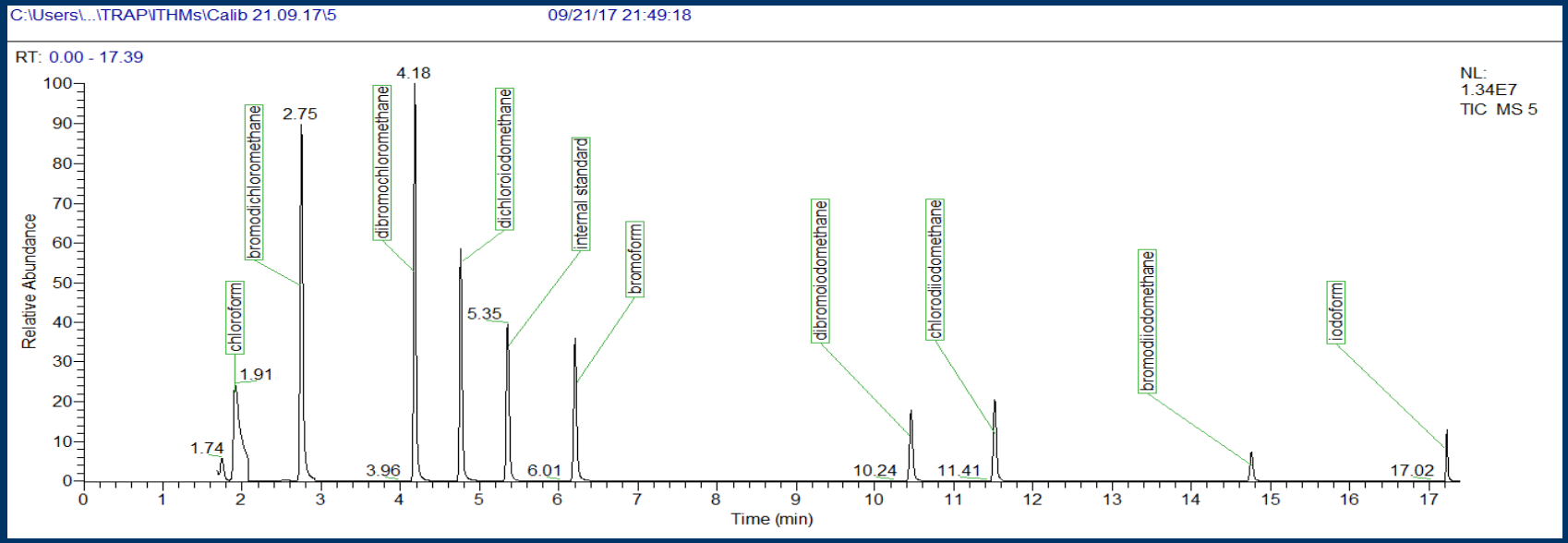
leading to pre-injection and double peaks

- Repairs by Perkin Elmer

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

V. First results

2. Separate analysis of ITHMs



- Good peaks except for chloroform
- Matrix issue for chloroform
- RSD < 10% for 5 standards at 5 µg/L
- LOQ < 50 ng/L

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT Water Technology
South West Water
Provincie Noord-Holland
De Watergroep Water. Vandaag en morgen
Université de Lille
TU Delft

VI. Upcoming work

Other analytical methods

- Analysis of Haloacetic Acids, Haloacetonitriles and Haloacetamides
- Analysis of iodide, iodate, bromide and Total Organic Iodine and Bromine
- Analysis of real water samples to study the DBP formation potential (by testing disinfection scenarios)

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

VI. Upcoming work

Analysis of real samples

- 2 samples:
  - Raw water
  - Non-chlorinated treated water samples
- 1 L bottles filled to the rim

- Start: November 2017

➢ ***To determine the best treatment to reduce DBP formation potential***

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
South West Water
Provincie Noord-Holland
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

Thank you for your attention

References

- Antoniou C. et al. 2006. 'Determination of Chlorinated Volatile Organic Compounds in Water and Municipal Wastewater Using Headspace–solid Phase Microextraction–gas Chromatography'. Journal of Chromatography A 1132 (1–2): 310–14.
- Bichsel Y. 2000. Behavior of Iodine Species in Oxidative Processes During Drinking Water Treatment.
- Bond T. et al. 2015. 'Nitrogenous Disinfection Byproducts in English Drinking Water Supply Systems: Occurrence, Bromine Substitution and Correlation Analysis'. Water Research 85: 85–94.
- Luo, Qian, Xichao Chen, Zi Wei, Xiong Xu, Donghong Wang, and Zijian Wang. 2014. 'Simultaneous and High-Throughput Analysis of Iodo-Trihalomethanes, Haloacetonitriles, and Halonitromethanes in Drinking Water Using Solid-Phase Microextraction/Gas Chromatography-Mass Spectrometry: An Optimization of Sample Preparation'. Journal of Chromatography A 1365: 45–53.
- Montesinos Isabel and Mercedes Gallego. 2013. 'Speciation of Common Volatile Halogenated Disinfection By-Products in Tap Water under Different Oxidising Agents'. Journal of Chromatography A 1310: 113–20.
- Richardson S. D. et al. 2007. 'Occurrence, Genotoxicity, and Carcinogenicity of Regulated and Emerging Disinfection by-Products in Drinking Water: A Review and Roadmap for Research'. Mutation Research 636 (1-3).

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund