RECWET Symposium: "Behavior of micropollutants in urban water systems“
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Characterizing NOM and Unknown DBPs in Drinking Water Treatment Processes using FTICR MS

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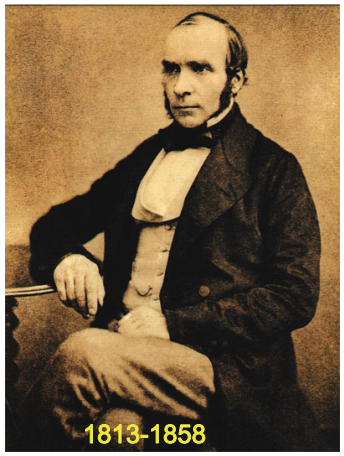
Outline

1. Background: NOM and DBPs
2. Brief Introduction of FT-ICR MS
3. Transformation of NOM during Chlorination with and without Bromide
4. Characterizing NOM and DBPs in Water Treatment Processes
5. On-going Work

Dr. John Snow and Cholera in London

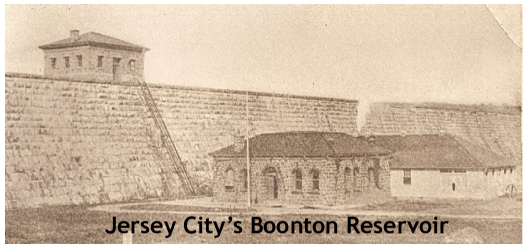
- Characterizing “the acute problem”
- Cholera
  - 1852-1860: The third cholera pandemic
  - Snow showed the role of water in disease transmission in a cholera outbreak in London in 1854



Dr. Snow was the first person to reveal that drinking water could cause epidemic problems.

John L. Leal and Chlorination

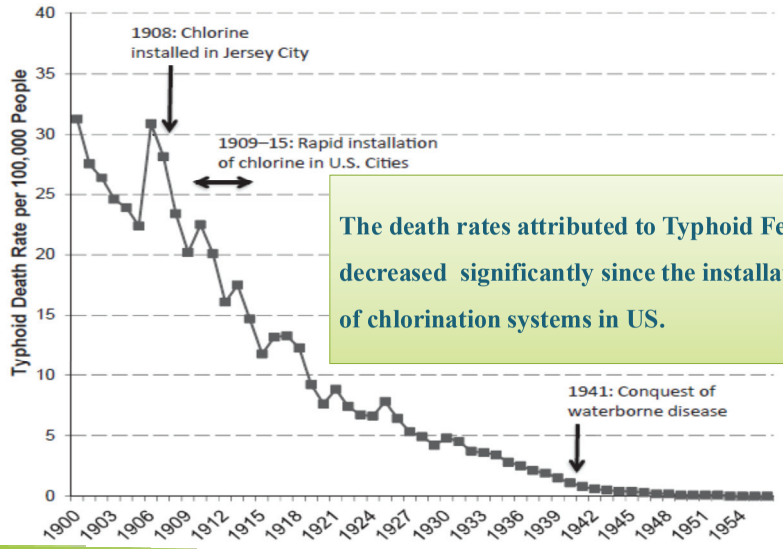
- Provide “pure and wholesome” water
  - Leal studied the effectiveness of chlorine on disinfection of drinking water.
  - Leal hired George Fuller to construct a chlorination plant at Boonton Reservoir using calcium hypochlorite (1908)



1858-1914

Dr. Leal was the first person to demonstrate that chlorination could provide safe drinking water.

Success Story for Water Supply in US

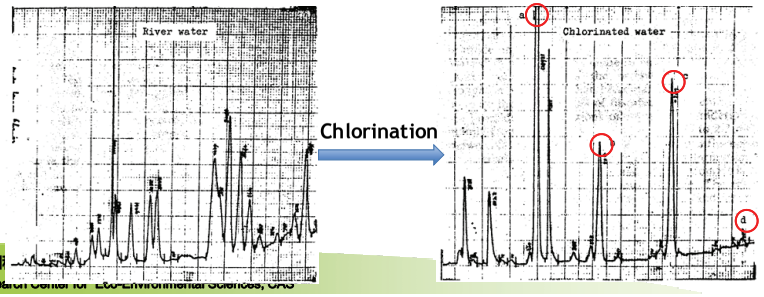


The death rates attributed to Typhoid Fever decreased significantly since the installation of chlorination systems in US.

John Rook and DBPs

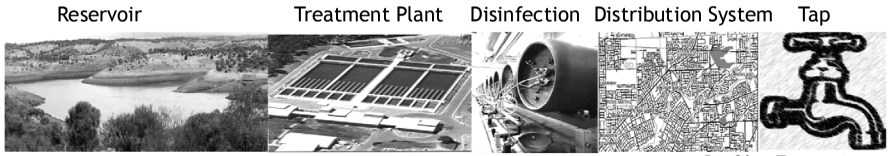
- Chlorine: "the chronic problem"
  - Brought headspace analysis from the beer industry to drinking water
  - Found trihalomethanes (THMs) in finished water in 1974
  - Deduced that they were formed as byproducts of chlorination
  - Proposed chemical pathways

1921-2010



Natural Organic Matter (NOM) as DBPs Precursor

- **A mixture of degradation and repolymerization products from aquatic and terrestrial organisms which is heterogeneous with respect to structure and reactivity.**
- **Affect drinking water production from source to tap**

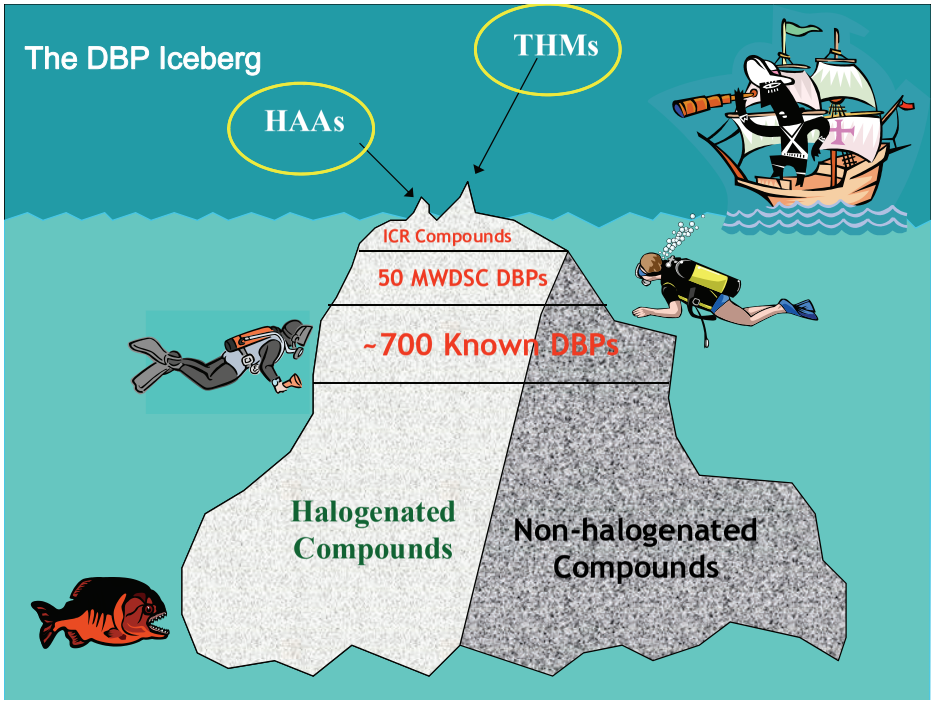


Raw Water Quality — Treatment Performance — Disinfectant Demand, DBP — Biofilm Formation, Bacterial Regrowth, Discoloured Water

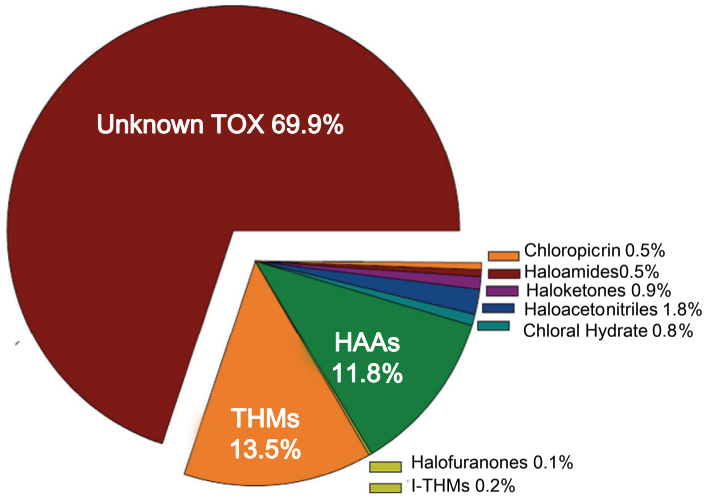
Epidemiology

- **Bladder Cancer**
  - **DBPs linked to ~10,000 US cases every year**
- **Other Cancers**
  - **Rectal, colon**
- **Reproductive and developmental effects**
  - **Neural tube defects**
  - **Miscarriages and low birth weight**
  - **Cleft palate**
- **Others**
  - **Kidney and spleen disorders, etc.**

Epidemiology is not supported by Toxicology of known DBPs!



TOX: Known and Unknown



Challenge in Analysis of Unknown DBPs

- Compositions may be very complex because of the extremely complex precursors (NOM)
- Standards are not available
- Concentrations may be very low
- May be too polar, insufficiently volatile and not suited to GC/MS

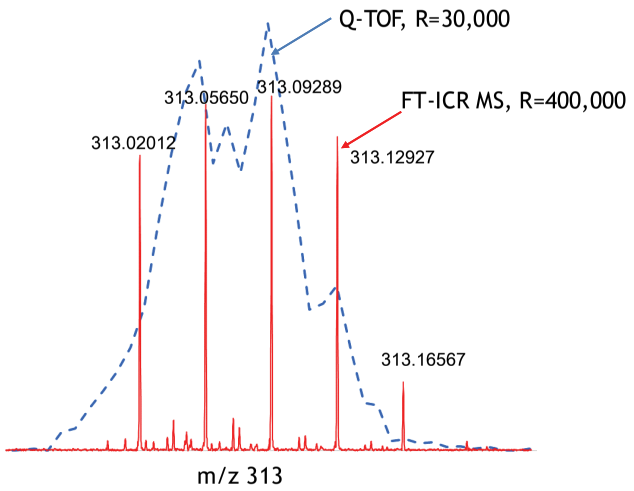
- **Technique suitable for the analysis of polar compounds with high resolution and sensitivity**

Fourier Transform Ion Cyclotron Resonance Mass Spectrometer

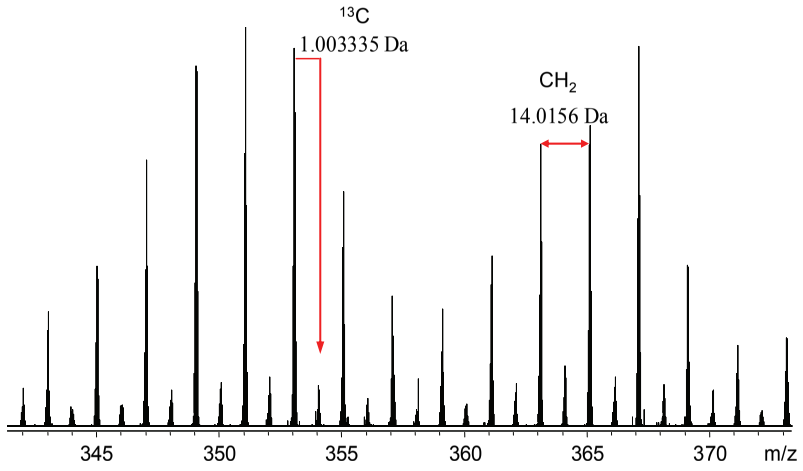
Bruker Solarix FTICR MS

Thermo LTQ-FTMS

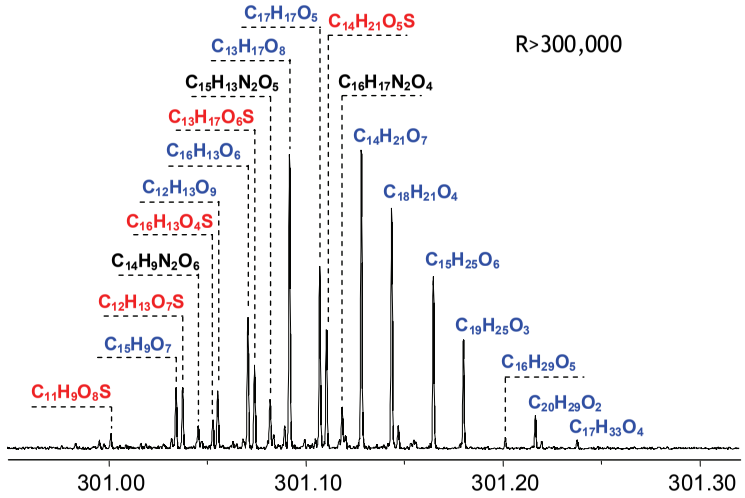
What is FT-ICR MS?



Typical mass spacing patterns for NOM



ESI FT-ICR mass spectra expanded at nominal mass 301



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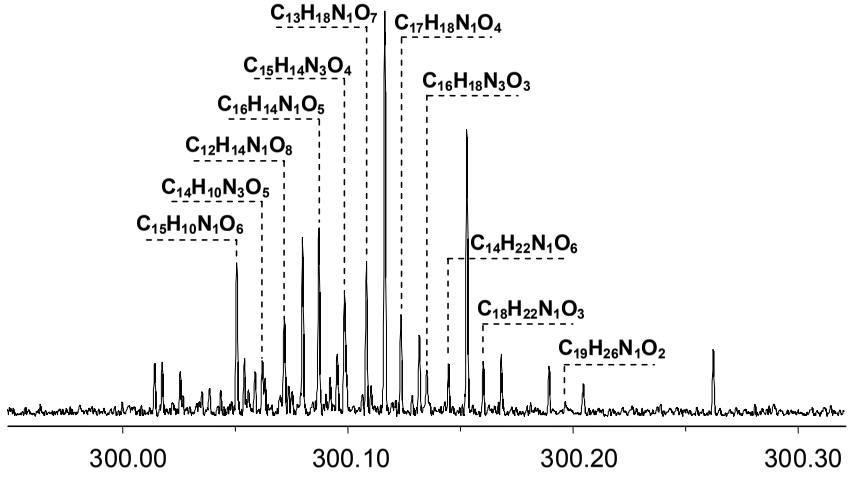
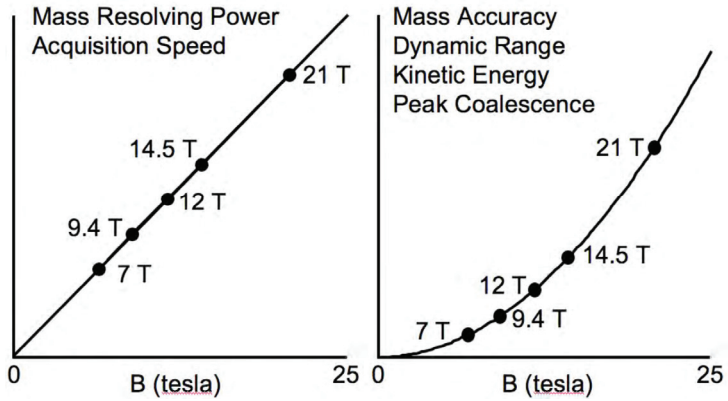


- all key parameters of FTICR mass spectrometry performance improve linearly or quadratically with increased magnetic field



21T FT-ICR MS

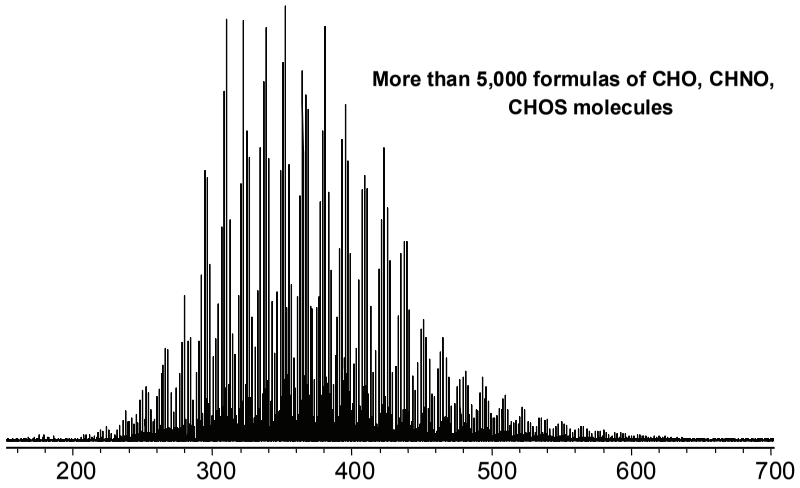
Transformation of NOM during Chlorination without Bromide

Methods

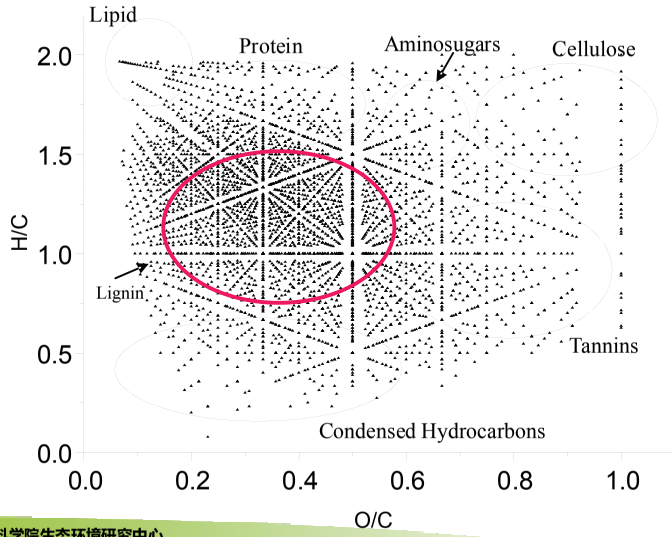
- Chlorination
  - 1L Source water, Cl_2 20mg/L, pH 7.0, 20°C, 5 day
- Solid Phase Extraction

- FT-ICR MS
  - Bruker Apex Ultra 9.4T

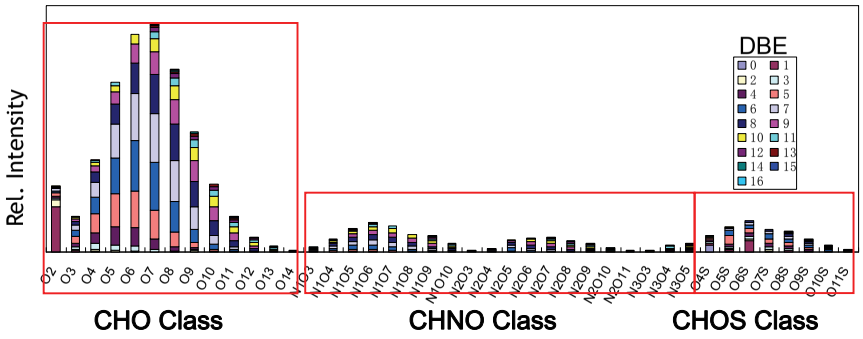
Broadband negative-ion ESI FT-ICR mass spectra of source water NOM



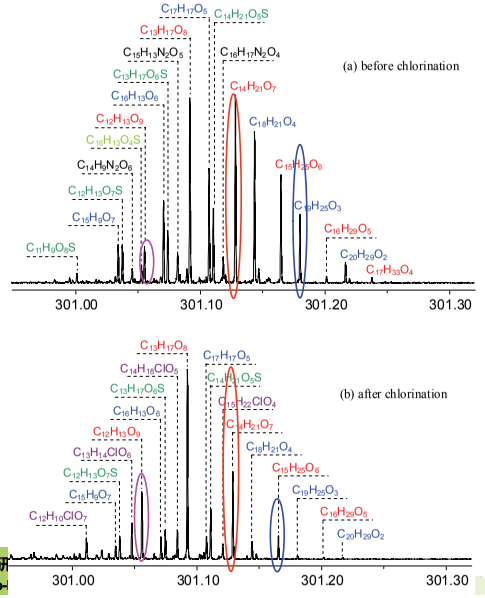
The van Krevelen Diagram of Source Water NOM



Molecular Classes and DBE analysis for Source Water NOM



Change of NOM Compositions during Chlorination



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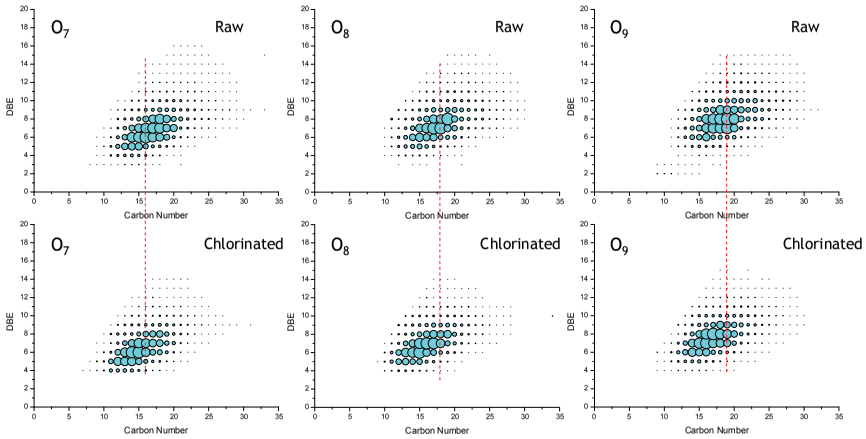
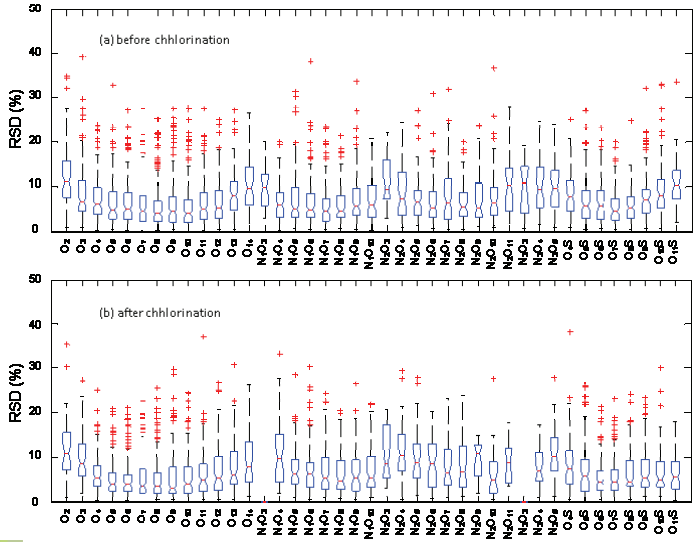
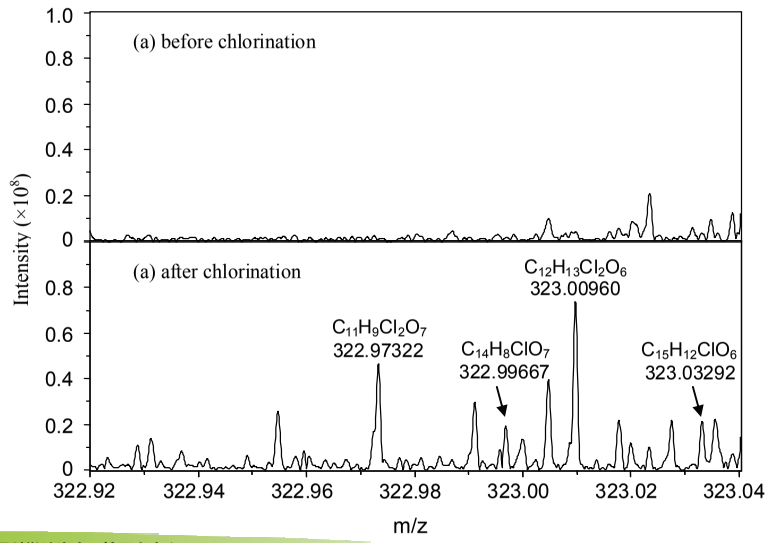


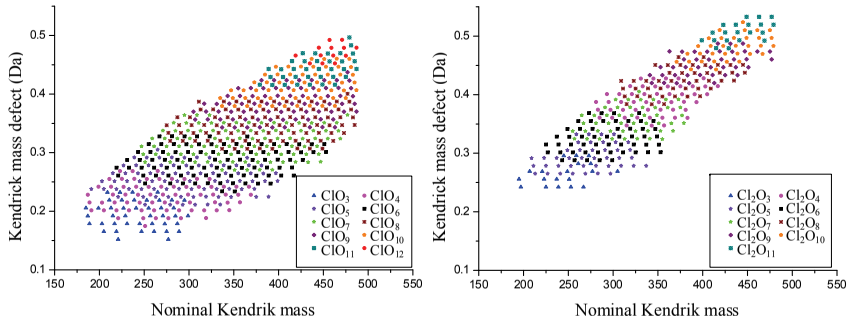
Boxplots of RSDs for each molecular class (a) before chlorination and (b) after chlorination



Newly Formed Chlorine-containing DBPS



CH_2-based Kendrick Mass Analysis of DBPS



Transformation of NOM during Chlorination with Bromide

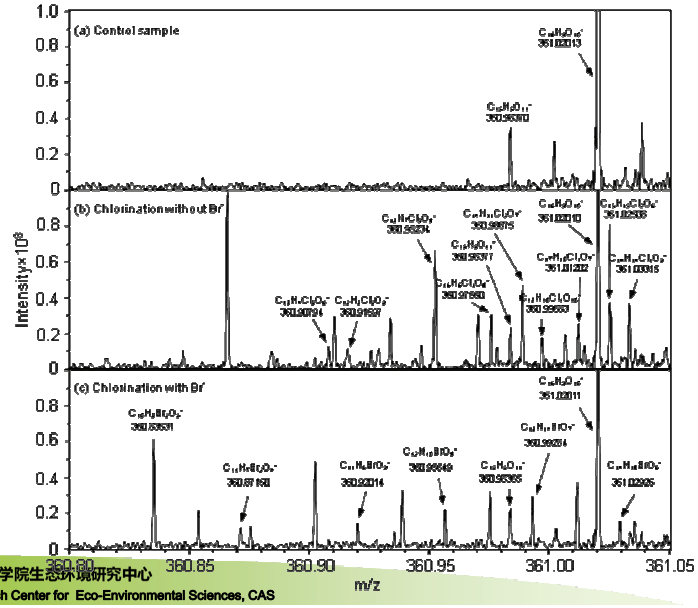
Experiments

- Chlorination

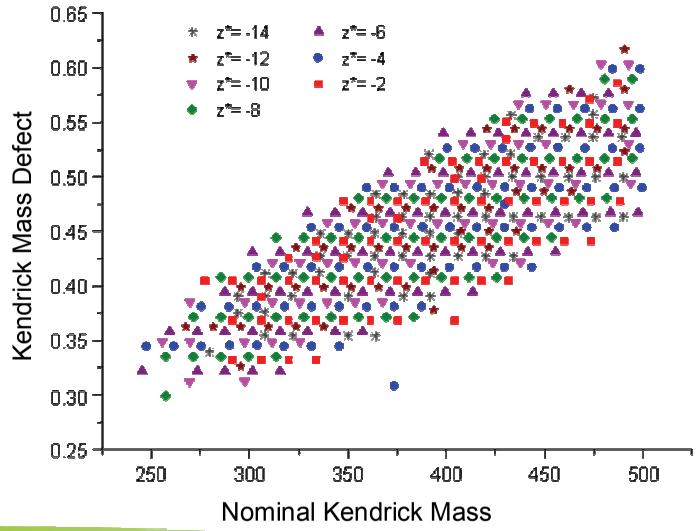
Sample name	Components	Chlorination	SPE
SRFA control	3.0 mg/L SRFA as C, 90.0 mg/L $NaHCO_3$, and 2.0 mg/L NaBr as Br^-	Chlorination was not applied. Stored at 20 °C in darkness for 5day.	applied
SRFA chlorination control	3.0 mg/L SRFA as C, 90.0 mg/L $NaHCO_3$	Chlorinated in sealed 1-L amber glass bottles with chlorine dose of 5.0 mg/L as Cl_2 at 20 °C in darkness for 5day	applied
SRFA chlorination with Br-	3.0 mg/L SRFA as C, 90.0 mg/L $NaHCO_3$, and 2.0 mg/L NaBr as Br^-	Chlorinated in sealed 1-L amber glass bottles with chlorine dose of 5.0 mg/L as Cl_2 at 20 °C in darkness for 5day	applied

- Solid Phase Extraction
- FT-ICR MS
  - Bruker Apex Ultra 9.4T

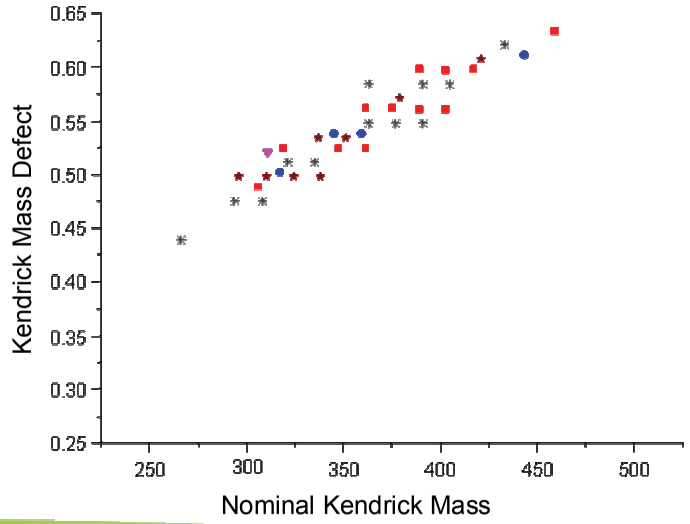
Newly Formed Brominated DBPs



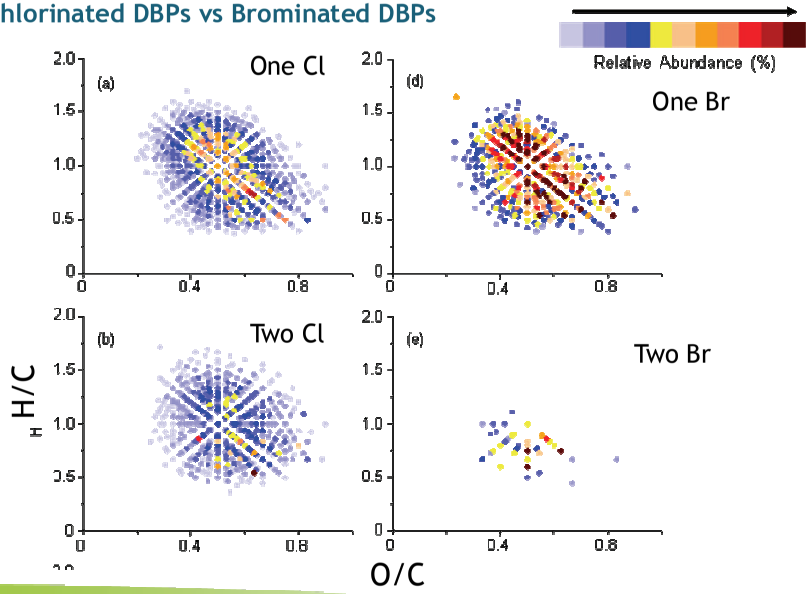
Newly Formed Brominated DBPs



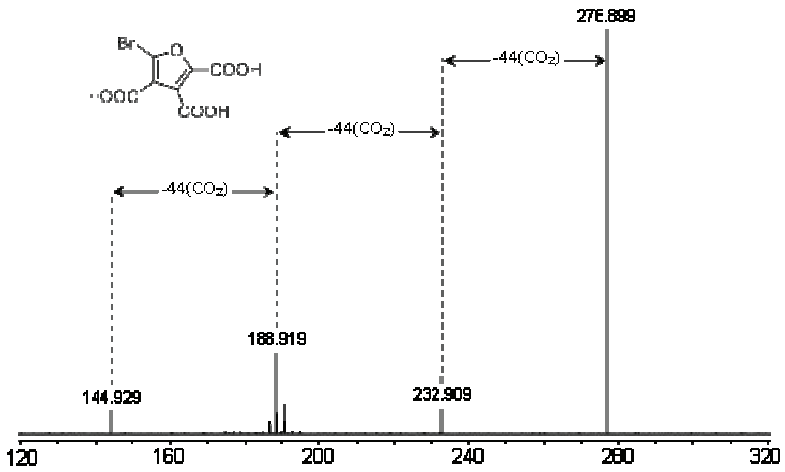
Newly Formed Brominated DBPs



Chlorinated DBPs vs Brominated DBPs

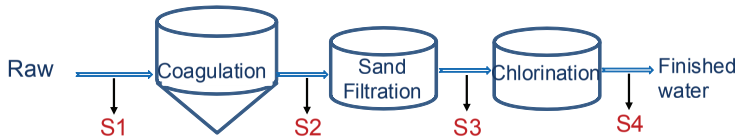


In-cell CID fragmentation spectra of Brominated DBPs



Characterizing NOM and DBPs in Water Treatment Processes

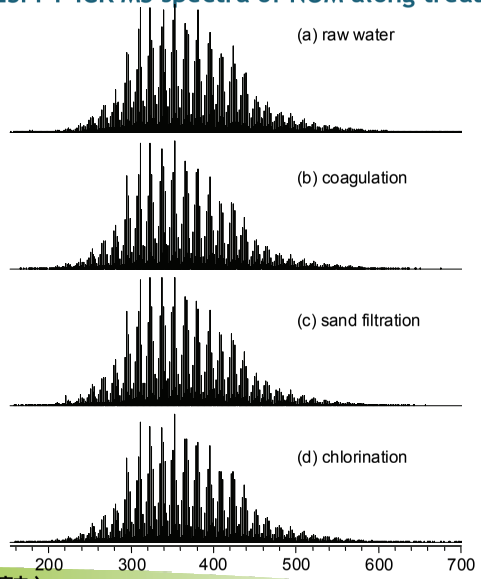
Sampling point in a conventional treatment waterworks



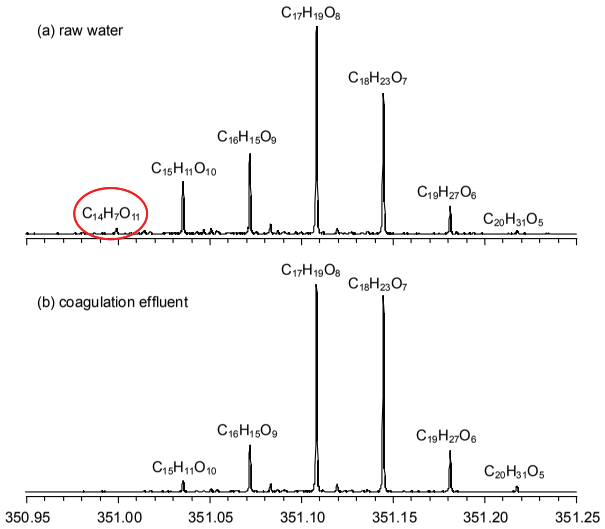
Solid Phase Extraction

FT-ICR MS Analysis

Negative-ion ESI FT-ICR MS spectra of NOM along treatment train



Change of NOM Compositions during Coagulation



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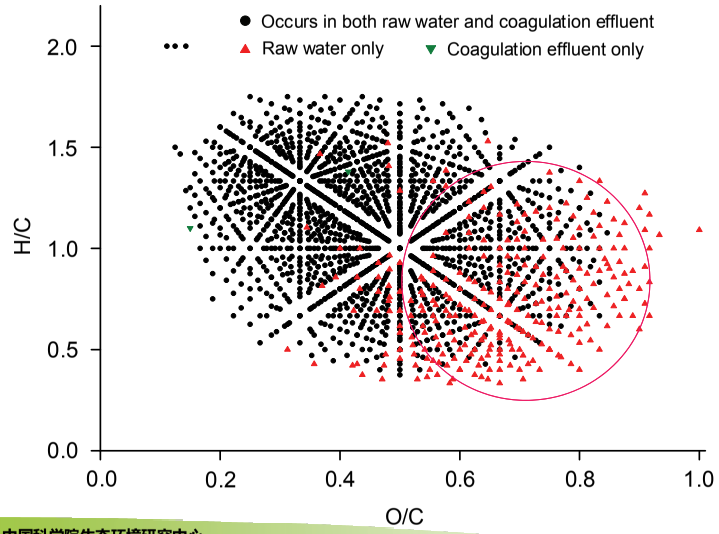
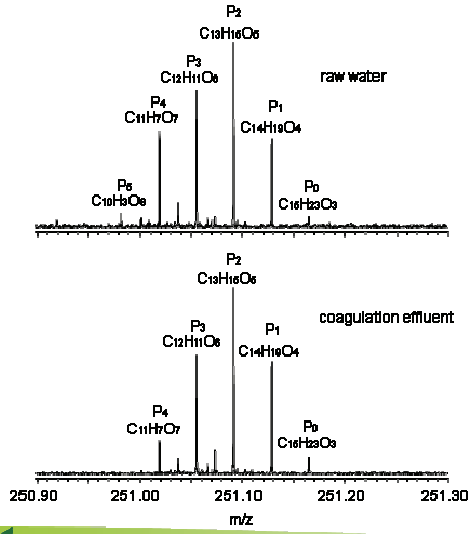
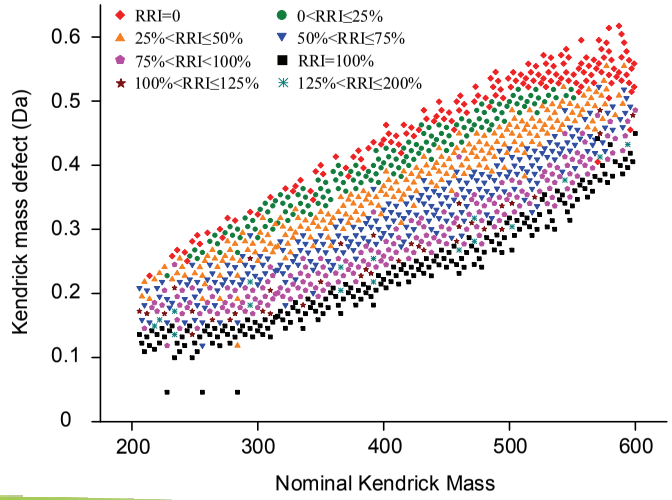


Relative reactive index (RRI)

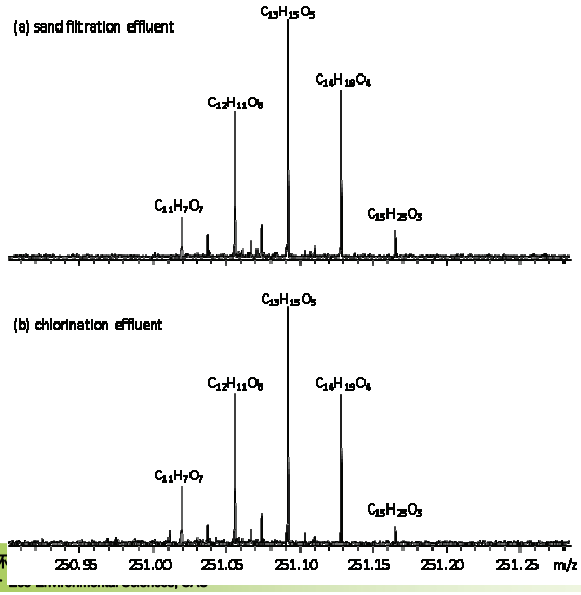


$$RRI_{P_i} = \frac{P_{i(after)}/P_{0(after)}}{P_{i(before)}/P_{0(before)}}$$

Change of NOM Compositions during Coagulation



Change of NOM Compositions during Chlorination



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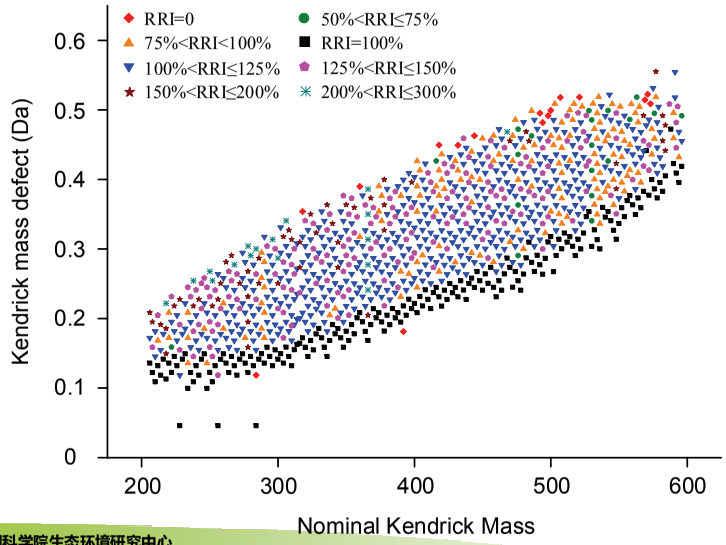

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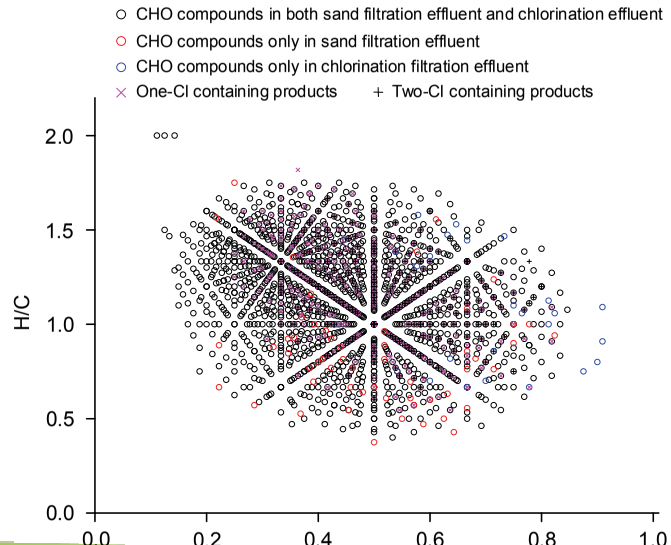

Thanks for the invitation by Prof. Furumai and Prof. Kurisu

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