Fate of low molecular weight dissolved organic matters in reclaimed water treatment systems

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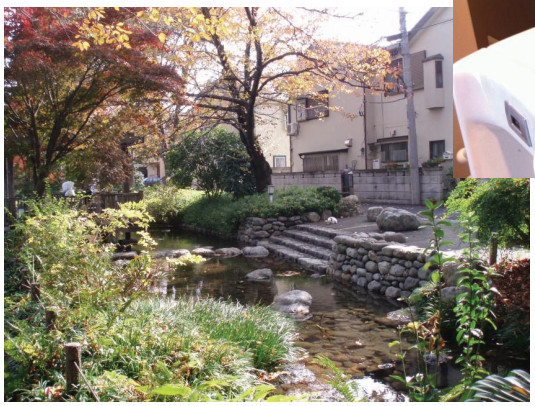
Reclaimed Water in Urban Region

Tachikawa-city, Tokyo



Parking Area on a Highway

Dissolved Organic Matter (DOM) in Reclaimed Water

Problems/concerns related to DOM in reclaimed water

Water Reclamation Plant | Distribution pipes | Points of use | Water Environments

- Membrane fouling[1]
- EOPs[2]
- Formation of Disinfection byproducts (DBPs)
- Microbial regrowth& biofilm[3]
- Pathogen?[4]
- Fate of DBPs

[1]Xu et al., 2010; ,[2]Yang et al., 2011; [3]Thayanukul et al.,2013; [4]Jjemba et al.,2010

Guideline of Reclaimed Water Quality

Ministry of Land, Infrastructure, Transport, and Tourism, 2005

	Toilet Flushing	Water Sprinkling	Landscape Irrigation	Recreational Use
Turbidity (degree)	<2			
pH	5.8-8.6			
Appearance & Odor	pleasant			
Color (degree)	-	-	40	10
E. coli (CFU/100mL)	ND	ND	(T. coli, 1000)	ND
Residual chlorine (mg/L)	Free: 0.1< or Combined: 0.4<	Free: 0.1< or Combined: 0.4< (Optional)	-	Free: 0.1< or Combined: 0.4< (Optional)

To expand reclaimed water application, more comprehensive water quality information is necessary.

Objectives

- Characterize DOM in Reclaimed Water
  - DBPs and their precursors
- Evaluate BOM removal/production in Reclaimed Water Treatment Processes
  - ozonation, activated carbon, sand filtration, chlorination
- Identify the BOM molecules and the fate in the processes

Sampling at Water Reclamation Plant

- Receiving **secondary effluent** (Activated sludge process) from municipal wastewater treatment plant
- Average reclaimed water production: 800 m^3/d

Secondary effluent

Sampling Point

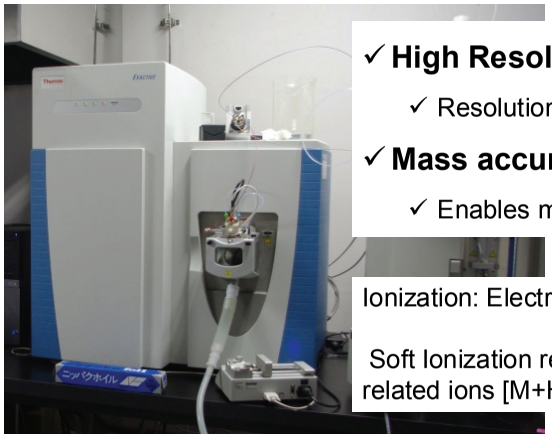
Biofiltration
- Removal of remaining biodegradable organic matters

Ozonation
- Removal of color and odor
- 4.5 g O_3/m^3 water

Chlorination
- Disinfection
- NaOCl (6 mg/L as Cl_2) to achieve 1 mg/L of total chlorine

Reclaimed water

Orbitrap Mass Spectrometer



✓ **High Resolving Power** : ~ 100,000
- ✓ Resolution in complex samples

✓ **Mass accuracy:** < 2 ppm
- ✓ Enables molecular formula identification

Ionization: Electron Spray Ionization (ESI)

Soft Ionization results in producing molecule-related ions $[M+H]^+$, $[M-H]^-$

"Exactive" (Thermo Scientific)

Unknown Screening Analysis of DOM

Filtration → SPE → Orbitrap-MS → Post analysis

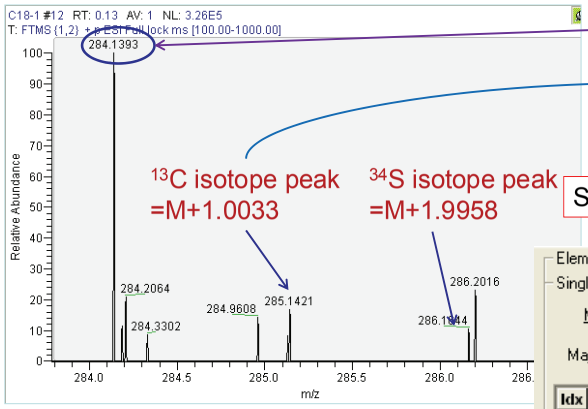
~500mL
0.7 µm + 0.45 µm Glass-fiber filter

Bond Elut PPL (Varian)
Stylene-Divinylbenzene polymer
Hydrophilic ~ Hydrophobic

Polarity: Negative ion mode
m/z range: 100-1,000
Low MW Organic matters

Molecular formula identification ("Xcalibur", Thermo Scientific)

Molecular formula determination



m/z=284.1393

mono valence

M=284.1393

^{13}C isotope peak =M+1.0033

^{34}S isotope peak =M+1.9958

Set mass accuracy = 5 ppm

Elemental composition

Single mass

Mass: 284.1392822

Max. results 400 Calculate

Idx	Formula	RDB	Delta pp
1	$C_{16}H_{18}O_2N_3$	9.5	-0.250
2	$C_8H_{22}O_4N_6S$	0.5	2.044
3	$C_{17}H_{20}NNa_2$	7.5	2.522

Compute molecular formula within M±5 ppm

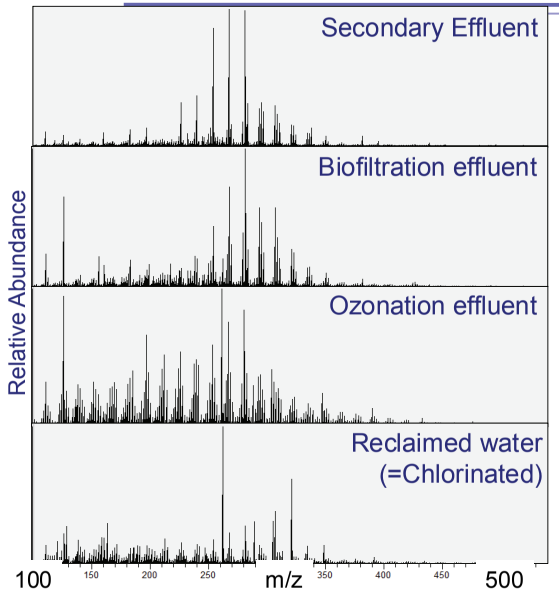
Refer to $^{13}C/^{12}C$ ratio, ^{34}S Isotope peak

Narrow down mass error down to 1.5 ppm

Determination

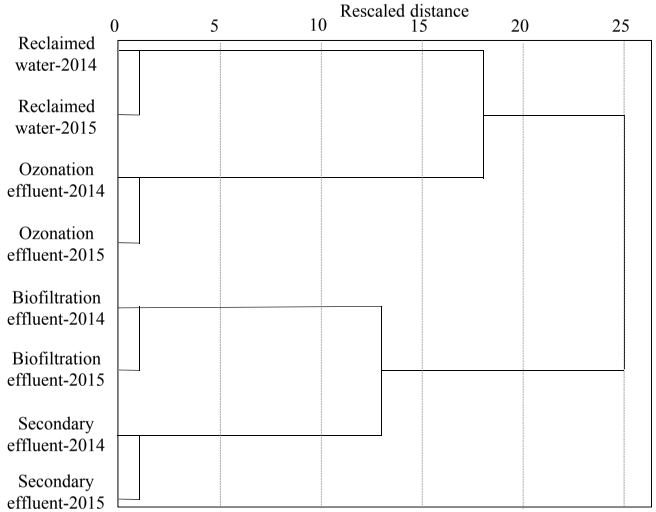
$C_{16}H_{18}O_2N_3$

Mass Spectra



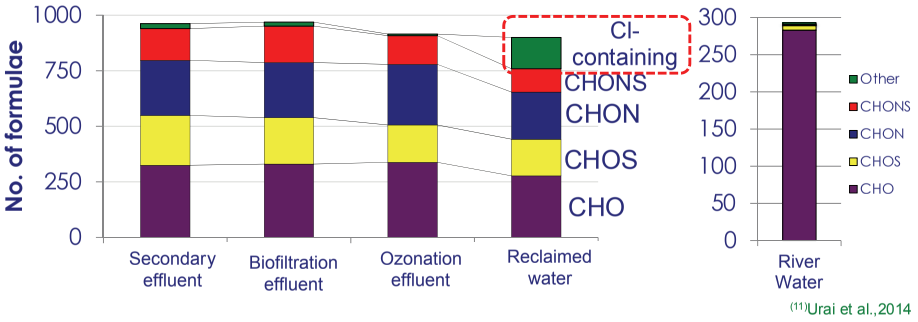
- DOC recovery by PPL SPE cartridge was 55% on average
- Intense peaks – observed in m/z 100-500 (or 100-500 Da)

Cluster analysis of mass spectra



Elemental Compositions

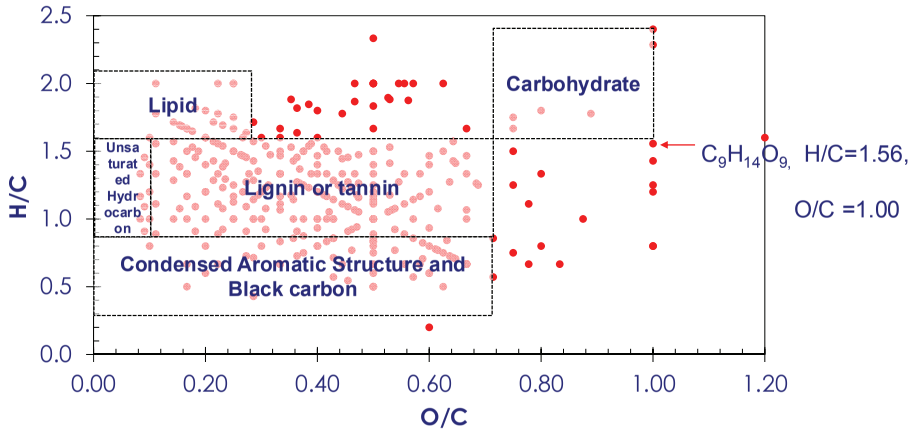
- In total, 2,078 formulae were identified



(11)Urai et al.,2014

- Elemental compositions of wastewater – more complex compared to river NOM
- After chlorination, 133 chlorine-containing formulae – additionally detected

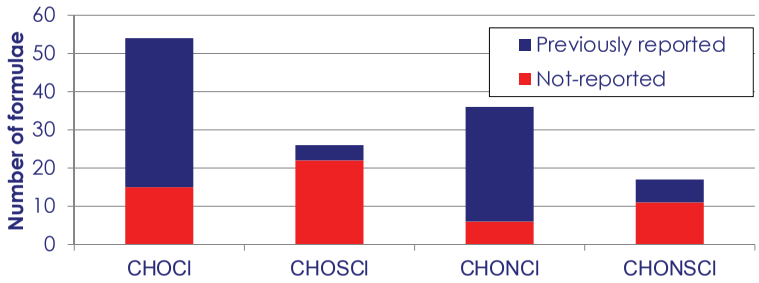
Van Krevelen Diagram of CHO formulae in Secondary Effluent



- Most of CHO formulae found in regions of lignin or tannin[13-14] and condensed aromatic structure compounds
  - Originated from NOM

[13]Ohno et al., 2010 and [14]Kim et al., 2006

Chlorinated DBPs in Reclaimed Water

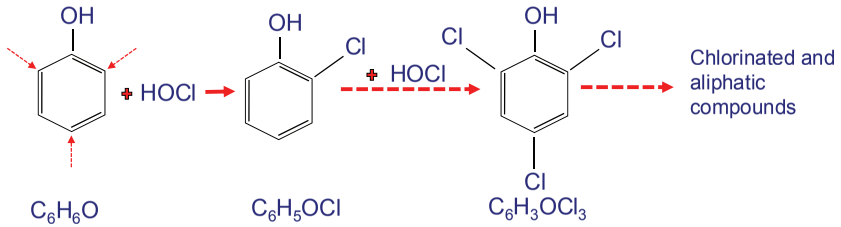


- Known DBP, including dichloroacetic acid ($C_2H_2O_2Cl_2$) and Trichloroacetic acid ($C_2HO_2Cl_3$) – detected
- No compounds for 39/133 formulae were listed on **ChemSpider Databases** (contains >30,000,000 compounds)

Tracking Precursors of Chlorinated DBPs

Electrophilic substitution

- Most predominant reaction at wastewater treatment condition[16]



- The reaction results in molecule with +1 Cl and -1 H

We may track their putative precursors from chlorinated formulae

[16]Deborde et al., 2008

Putative Precursors and DBPs after Chlorination

Putative precursor			Chlorinated DBPs	
m/z (error in ppm)	Chemical formula	Present in	m/z (error in ppm)	Chemical formula
161.0239 (2.95)	$C_9H_6O_3$	All processes	194.9857 (1.31)	$C_9H_5O_3Cl$
195.0660 (1.24)	$C_{10}H_{12}O_4$	All processes	229.0271 (0.92)	$C_{10}H_{11}O_4Cl$
229.0717 (0.92)	$C_{10}H_{14}O_6$	All processes	296.9938 (0.05)	$C_{10}H_{12}O_6Cl_2$
241.0718 (0.18)	$C_{11}H_{14}O_6$	All processes	308.9942 (1.23)	$C_{11}H_{12}O_6Cl_2$
179.0710 (2.05)	$C_{10}H_{12}O_3$	Raw, Bf and Oz	213.0323 (0.44)	$C_{10}H_{11}O_3Cl$
213.0403 (0.56)	$C_9H_{10}O_6$	Bf,Oz and Rm	280.9626 (0.34)	$C_9H_8O_6Cl_2$
207.0660 (1.17)	$C_{11}H_{12}O_4$	Oz and Rm	241.0275 (0.89)	$C_{11}H_{11}O_4Cl$
243.0512 (0.61)	$C_{10}H_{12}O_7$	Oz and Rm	310.9734 (1.27)	$C_{10}H_{10}O_7Cl_2$

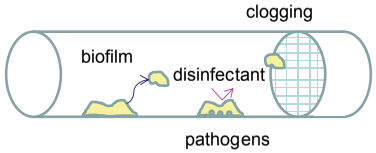
- 8 DBP precursors were identified by assuming electrophilic substitution
- Putative precursors originate not only in secondary effluent but also treatment processes

Biodegradable Organic Matter in RW

Bacterial Regrowth after chlorination

Growth of chlorine-tolerant microorganisms

by using their growth substrates



To suppress the regrowth,

☹ Increase chlorine dose

☺ Reduce biodegradable organic matters (BOM)

⇩

Develop methods to characterize BOM in RW

Method developed to evaluate BOM

Extend Assimilable Organic Carbon (AOC) method

1. Isolate bacterial strains

Reclaimed Water, Process water from 7 RWTPs

⇩

R2A media
25 ºC, 7 days

⇩

Isolate morphologically different colonies (198 strains obtained)

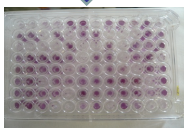
⇩ rRNA gene sequencing

34 phylogenetically distinctive strains

2. Evaluate substrate spectra

34 isolates

⇩



BIOLOG GN2 Microplate™

Test 95 organic matters

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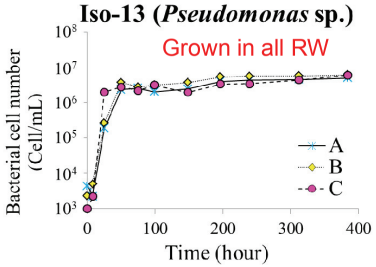
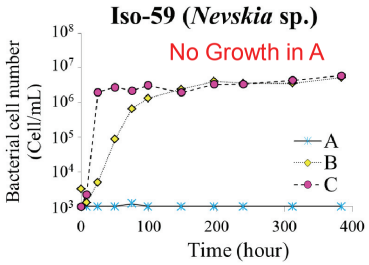
Cluster analysis of the patterns

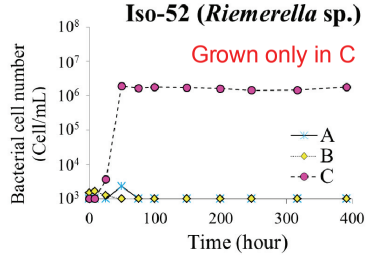
(Thayanukul et al., 2013b)

Method developed to evaluate BOM (contd)

3. Growth pattern in RW







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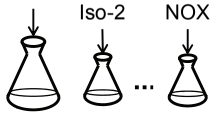
Through steps 1-3, we screened 9 bacterial strains to be used for BOM evaluation

(Thayanukul et al., 2013b)

Bacterial Growth Fingerprint (BGF)

Step1 Inoculation

Iso-1 Iso-2 NOX



Inoculate 10^3 cells/mL of the isolates individually

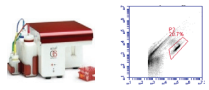
	Name	Phylogeny
9 isolates from RWTP	Iso-1	*Sphingomonas yabuuchiae* strain W211
	Iso-2	*Acidovorax* sp. CNE29
	Iso-3	*Herminiimonas saxobsidens* strain AA
	Iso-4	*Pseudomonas* sp. Iyh1B
	Iso-5	*Nevskia ramose*
	Iso-6	*Mycobacterium* sp. 18GUW
	Iso-7	*Microbacterium* sp. 5BCO-S1.1
	Iso-8	*Pedobacter* sp. BR-9
	Iso-9	*Riemerella* sp. IPDH98/90
Strains used for AOC	P17	*Pseudomonas fluorescens* P17
	NOX	*Aquaspirillum* sp. NOX

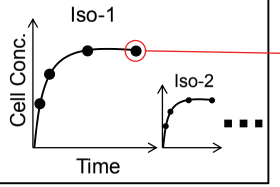
Step2 Incubation, enumeration

Incubate at 20 ºC for 10 days

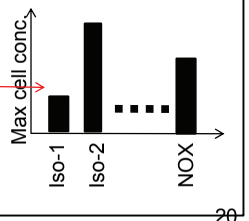
Flow Cytometer

Total cell counts by staining with SYBR® Green I





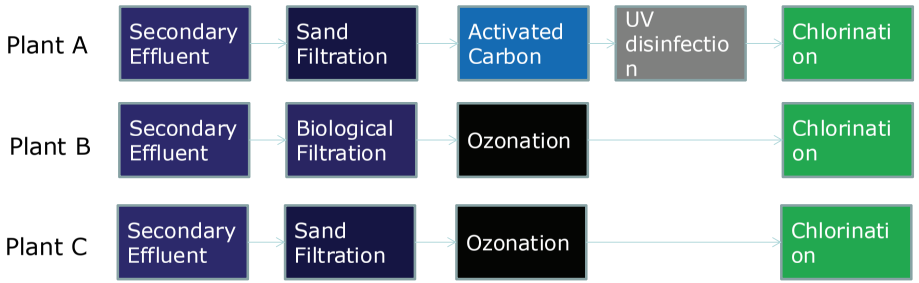
Step3 Max Growth



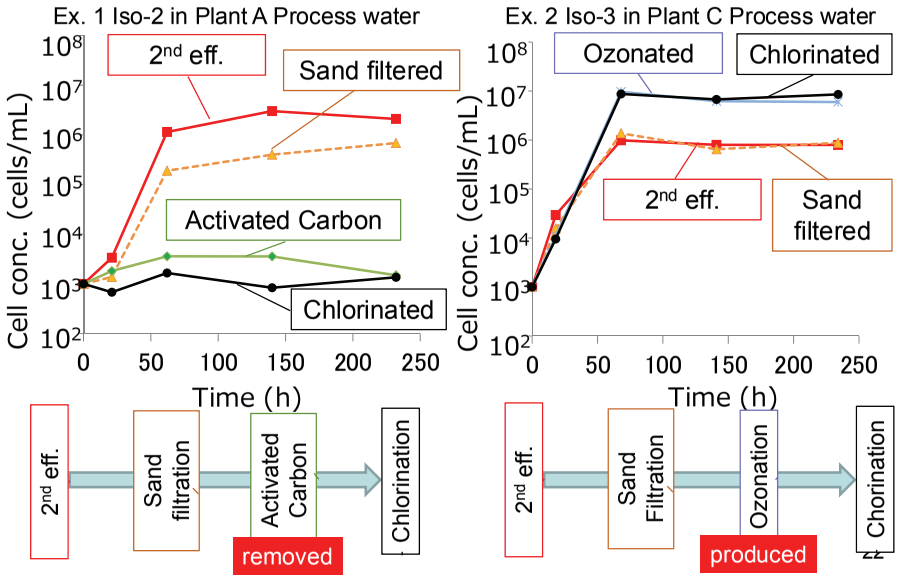
(Thayanukul et al., submitted.)

Reclaimed water samples

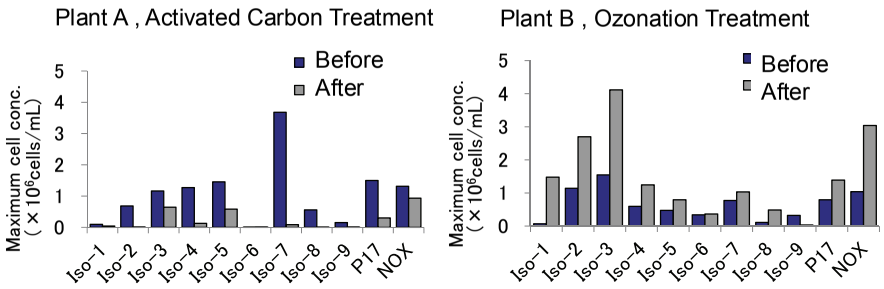
Reclaimed water treatment facilities in domestic wastewater treatment plants near Tokyo, Japan.



Growth of BGF strains in process water



Process Evaluation by BGF



Activated carbon removed substrate for all 11 strains

Ozonation produced substrate for all except for Iso-9

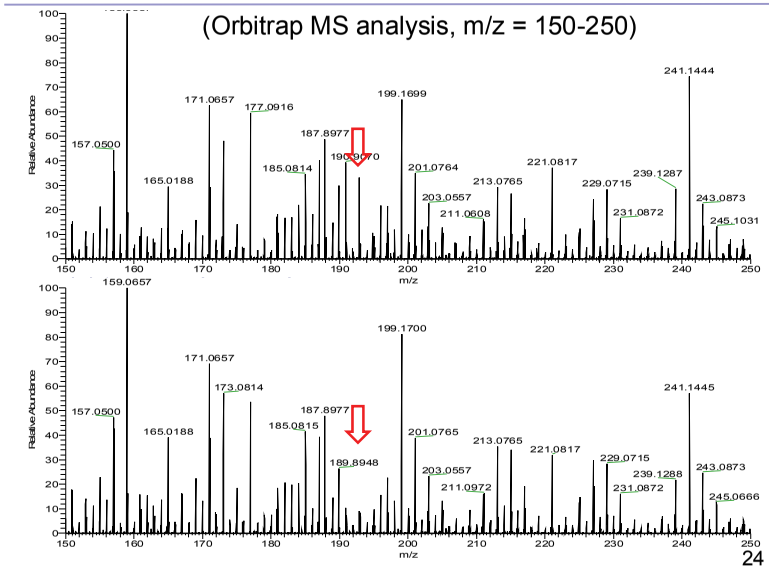
BGF successfully evaluated the BOM change in the reclaimed water treatment processes

What are the BOMs utilized by the strains?

Which OM is used for the growth?

Mass spectrum before the growth

Mass spectrum after the growth



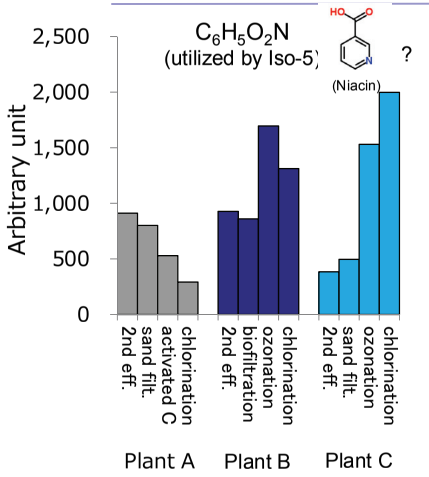
BOM consumed by BGF strains

MW	Formula	Isolates (Iso-1~9)									AOC	
		1	2	3	4	5	6	7	8	9	P17	NOX
119.0363	$C_7 H_5 O N$								○			
123.0313	$C_6 H_5 O_2 N$					○						
123.0676	$C_7 H_9 O N$	○	○	○	○	○	○	○	○	○		○
131.0939	$C_6 H_{13} O_2 N$								○			
147.0314	$C_8 H_5 O_2 N$	○										
165.0420	$C_8 H_7 O_3 N$								○			
191.0578	$C_{10} H_9 O_3 N$	○	○	○	○	○	○	○	○	○		○
211.9422	$C_8 H_4 O S_3$											○
214.0507	$C_8 H_{11} O_3 N_2 P$				○							
237.0634	$C_{11} H_{11} O_5 N$				○	○	○			○	○	
259.0426	$C_{12} H_9 O_2 N_3 S$	○	○	○	○	○	○	○	○	○	○	○
264.1725	$C_{16} H_{24} O_3$				○							
278.0283	$C_{10} H_{14} O_5 S_2$											○
282.0926	$C_{14} H_{18} O_4 S$		○		○			○			○	
327.2775	$C_{19} H_{37} O_3 N$		○	○	○	○	○	○	○	○	○	○
515.2910	$C_{26} H_{45} O_7 N S$			○	○	○	○	○	○	○	○	○

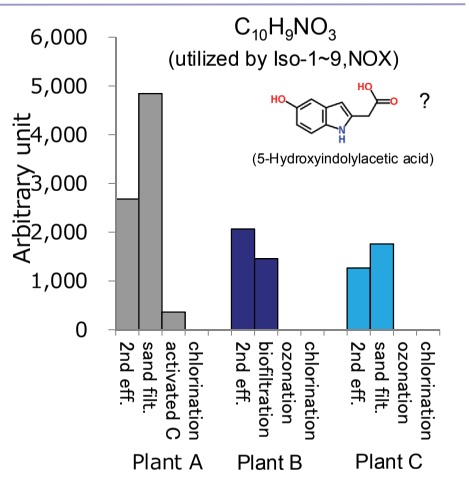
7 compounds out of 16 were not utilized by conventional AOC strains

⇒BGF method can capture wide variety of BOM

Fate of BOM substances in the process



Removed by activated carbon, Produced by ozonation
May cause regrowth



Removed by ozonation and activated carbon

Summary

- Ozonation substantially altered DOM composition
- Yet to be known DBP and their precursors can be found by the unknown screening analysis
- BOM removal/production in Reclaimed Water Treatment Processes can be described by Bacterial Growth Fingerprint (BGF) method
- BOM molecules were identified and the fate in the processes were illustrated

Reference

- Urai, M., Kasuga, I., Kurisu, F. and Furumai, H. (2014) Molecular Characterization of Dissolved Organic Matter in Various Urban Water by Using Orbitrap Fourier Transform Mass Spectrometry. *Water Science & Technology: Water Supply* ***14(4), 547-553.***
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- Thayanukul, P., Kurisu, F., Kasuga, I. and Furumai, H. (2013) Evaluation of Microbial Regrowth Potential by Assimilable Organic Carbon in Various Reclaimed Water and Distribution Systems. *Water Research* ***47(1), 225-232.***