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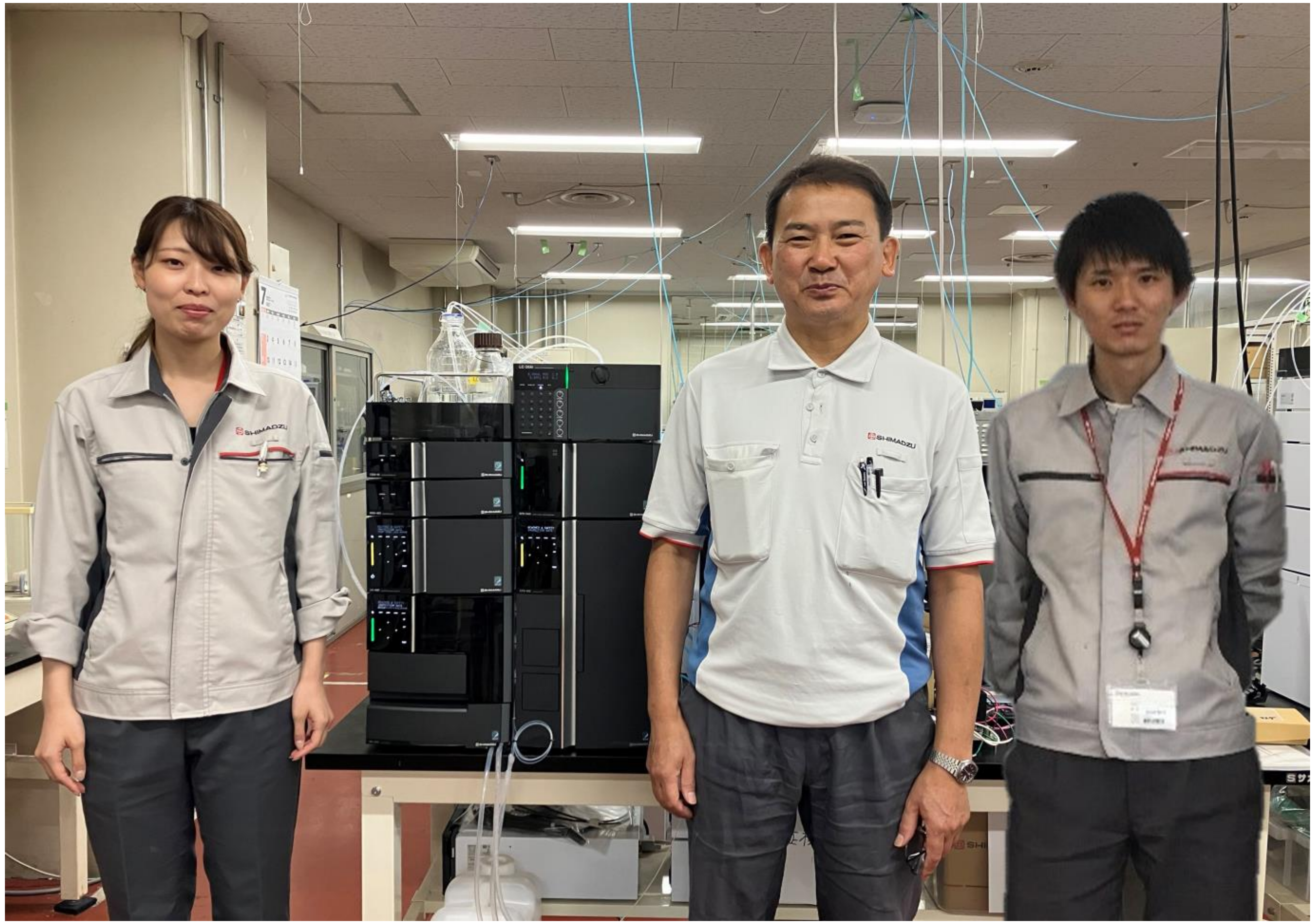
A New Light Into the Characterization of Organic Matter

Ruth Marfil-Vega, PhD

August 3rd, 2023

Team



Maiko Kaji, Masahito Yahata, Kazuma Maeda
(left to right)

Today's presentation

1. NOM and TOC
2. SEC-TOC
3. Results
4. Take-home messages
5. Q&A

Characterization of NOM – Why it is important

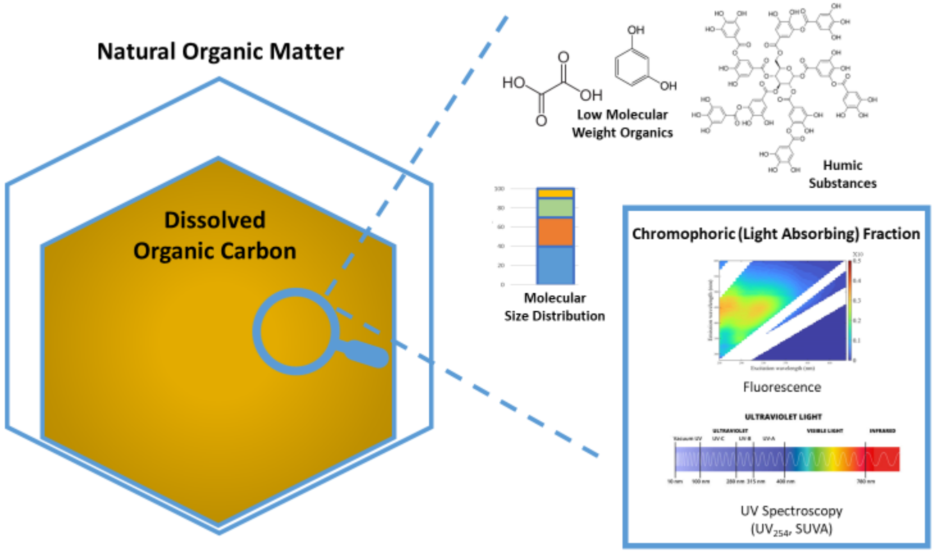


Figure by Donald Ryan

Opflow

Features

Operators Need to Know About Organic Contaminants

Hunter Adams, David Hanigan, Ruth Marfil-Vega, Donald Ryan, Daniel Mccurry, Olya Keen, Steve Ash, Mark Southard

First published: 08 July 2023 | https://doi.org/10.1002/opfl.1840

Reasons to monitor Natural Organic Matter (NOM):

1. Understand:
   a) Disinfection Byproducts (DBPs) formation
   b) Changes in water quality and treatment performance
2. Meet regulation (based on Total Organic Carbon (TOC) concentration)

Increased relevance with the broader implementation of water reclamation

Total Organic Carbon Analysis

	Is TOC analysis enough to characterize NOM?	Additional info
DBPs formation	NO	TOC correlates with formation (in wastewater), but not with specific fingerprint
Understanding changes	NO	TOC does not provide specific information of fate from different fractions of NOM
Meet regulation	YES	--

Other parameters commonly used to characterize NOM:
SUVA254, FEEM, Adsorbable Organic Carbon

TOC analysis – Instrumentation: Examples

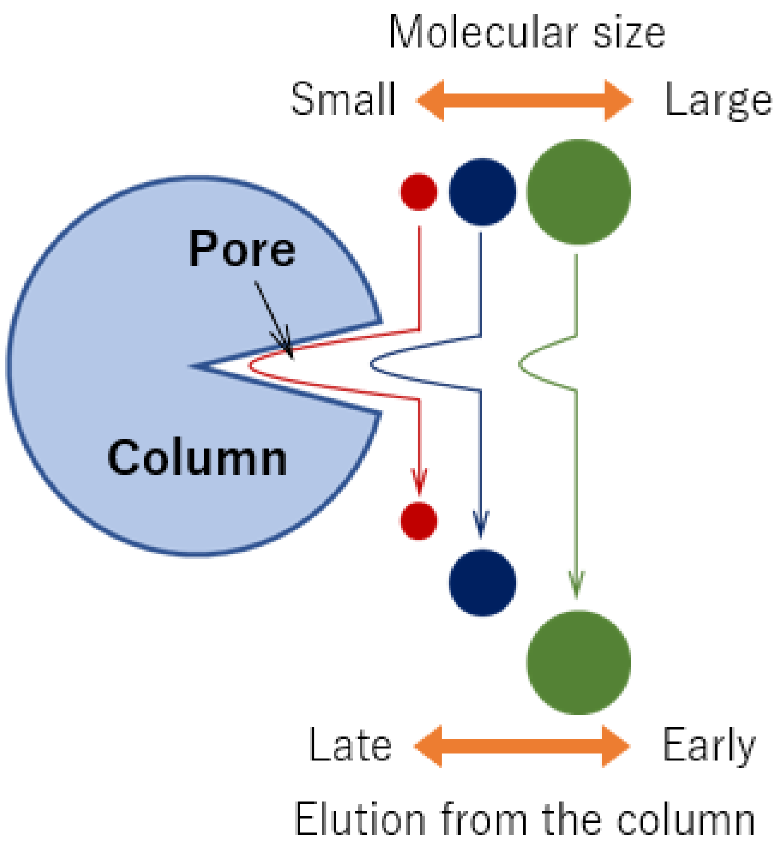
Common: Sum parameter based on detection of carbon dioxide by the NDIR

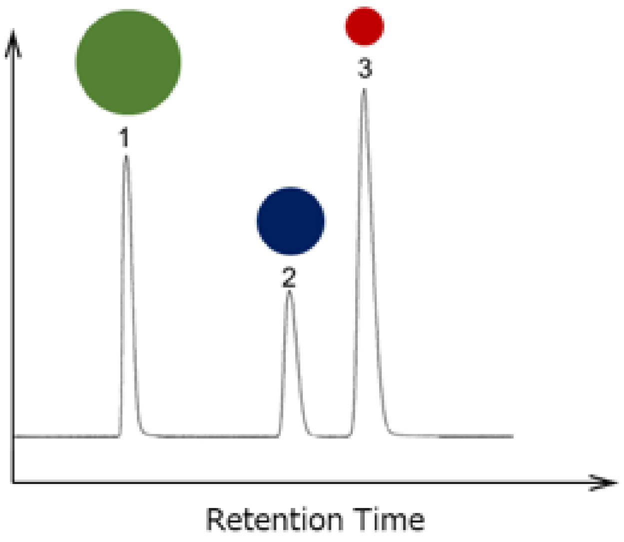
High temperature combustion catalytic oxidation

Simultaneous TOC and TN analysis
with the TN-module

Wet oxidation (persulfate)

Size Exclusion Chromatography (SEC)



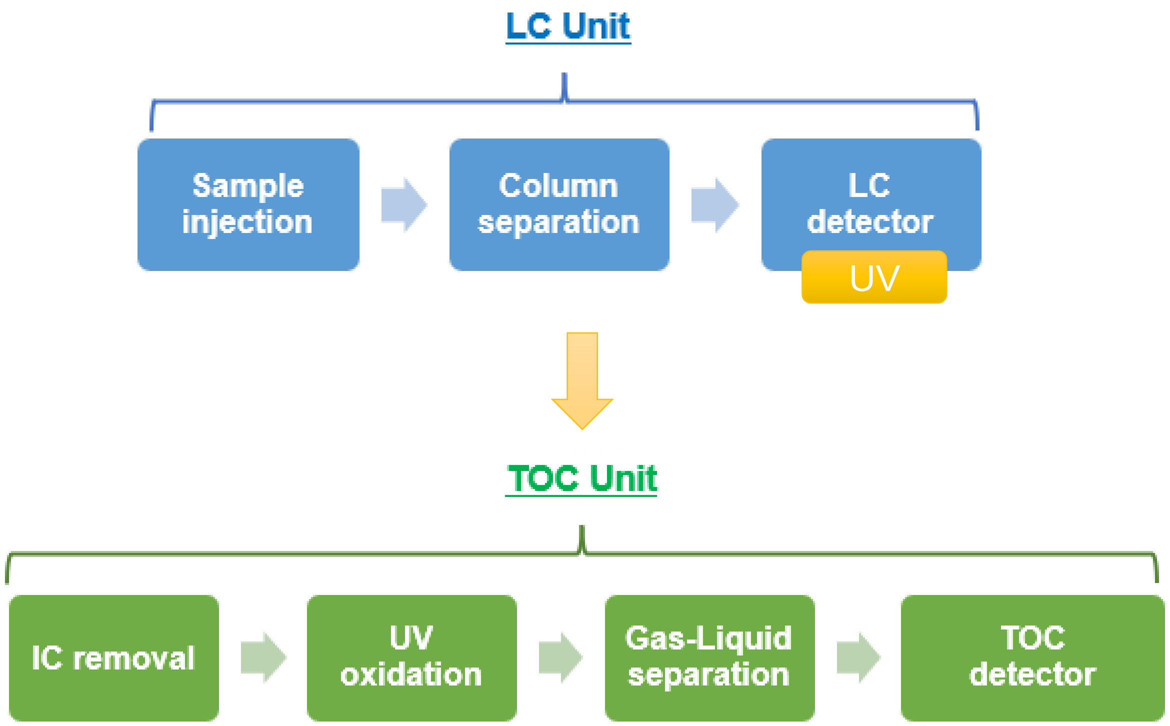


NOM components get separated by molecular weight with SEC

SEC-TOC

Output from SEC-TOC: Chromatogram of TOC

Measuring Range (TOC)	0～25 ppm
Limit of Detection (TOC)	5 ppb

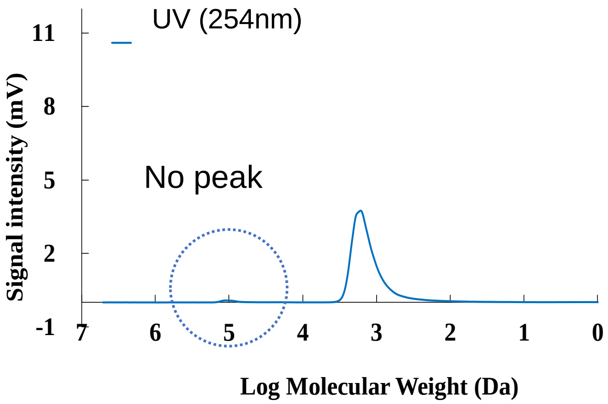


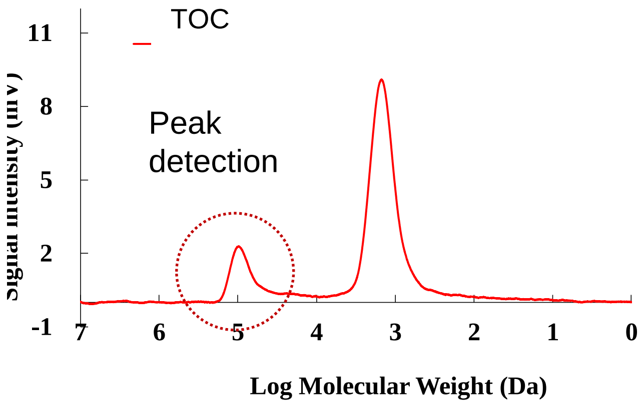
Fluorescence Detector - optional

SEC-TOC - Benefits

- SEC-TOC provides a quantitative measurement to characterize unknown samples.
- The use of two detectors in-line (UV or fluoresce and TOC detector) provides additional lines of evidence for characterizing the samples.

Example of SEC-TOC analysis of Lake Biwa (Japan) water





Results - Chromatography

Gel Filtration Calibration Kit LMW / HMW – Cytiva
LMW：6.5k ~ 2000k
HMW：43k ~ 2000k

Table 1. Characteristics of Gel Filtration Calibration Kit LMW

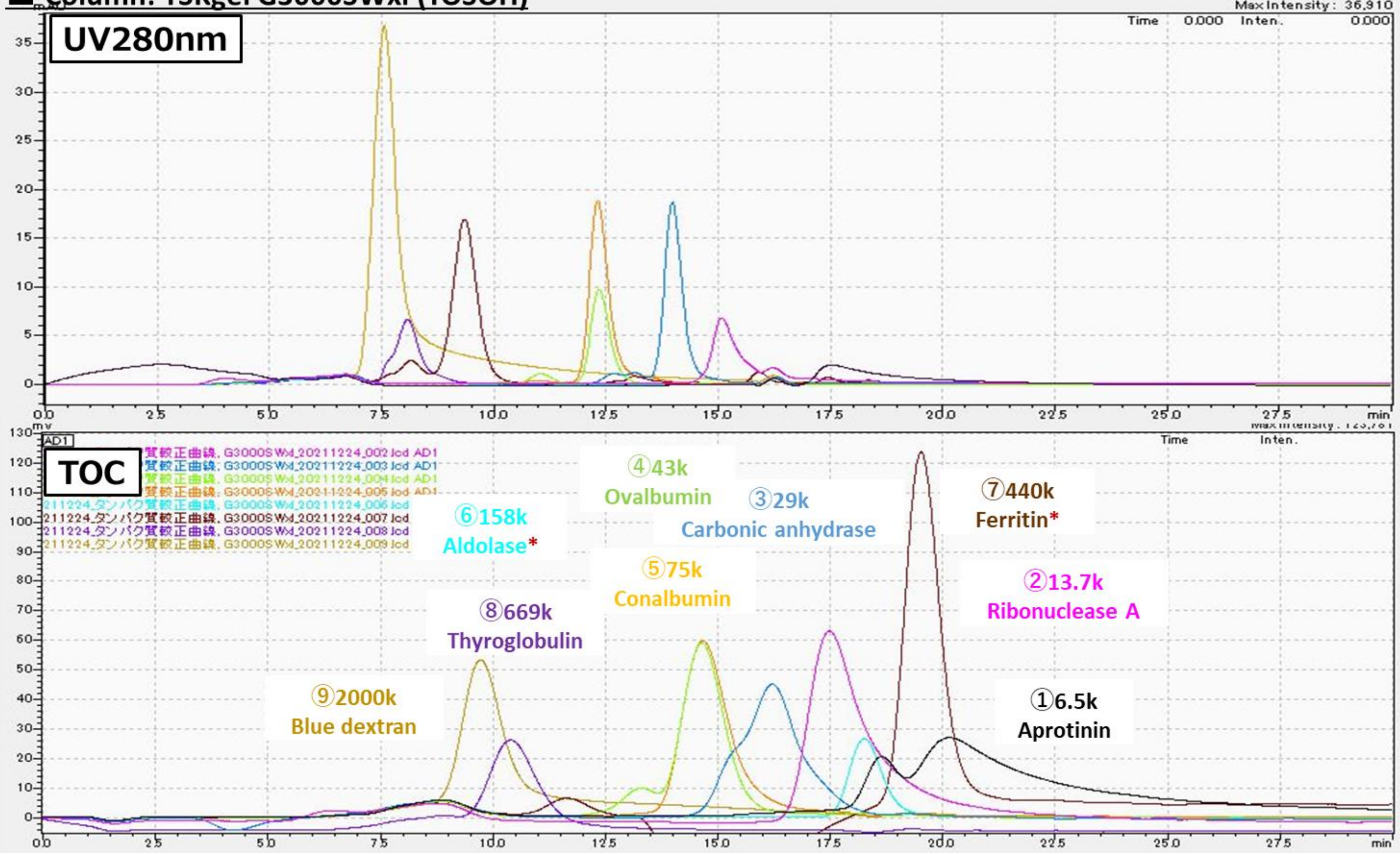
Protein (weight per vial)	Molecular weight (M_r)	Source
Aprotinin (10 mg)	6500	Bovine lung
Ribonuclease A (50 mg)	13 700	Bovine pancreas
Carbonic anhydrase (15 mg)	29 000	Bovine erythrocytes
Ovalbumin (50 mg)	43 000	Hen egg
Conalbumin (50 mg)	75 000	Chicken egg white
Blue dextran 2000 (50 mg)	2 000 000	

Table 2. Characteristics of Gel Filtration Calibration Kit HMW

Protein (weight per vial)	Molecular weight (M_r)	Source
Ovalbumin (50 mg)	43 000	Hen egg
Conalbumin (50 mg)	75 000	Chicken egg white
Aldolase* (50 mg)	158 000	Rabbit muscle
Ferritin* (15 mg)	440 000	Horse spleen
Thyroglobulin (50 mg)	669 000	Bovine thyroid
Blue dextran 2000 (50 mg)	2 000 000	

* These proteins are supplied mixed with sucrose or mannitol to maintain stability and aid their solubility.

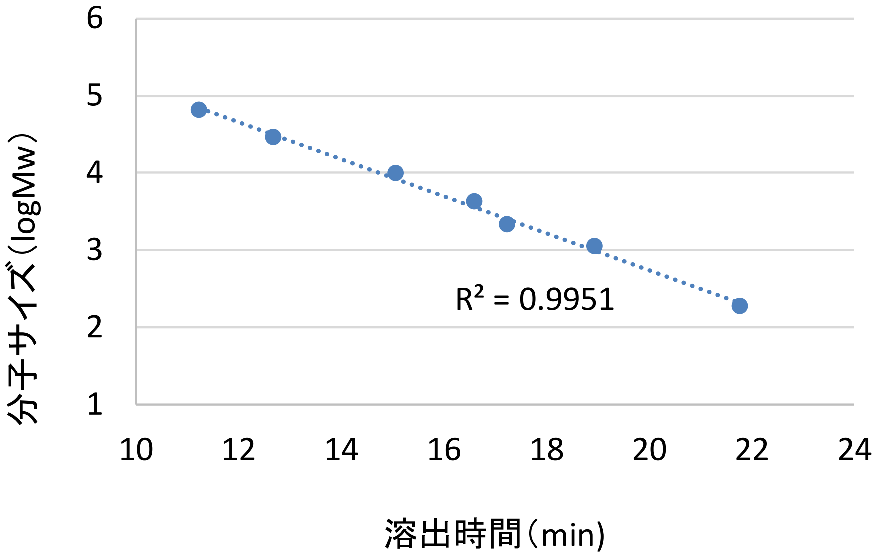
■ Column: TSKgel G3000SWxl (TOSOH)



Injection Volume：250 μL

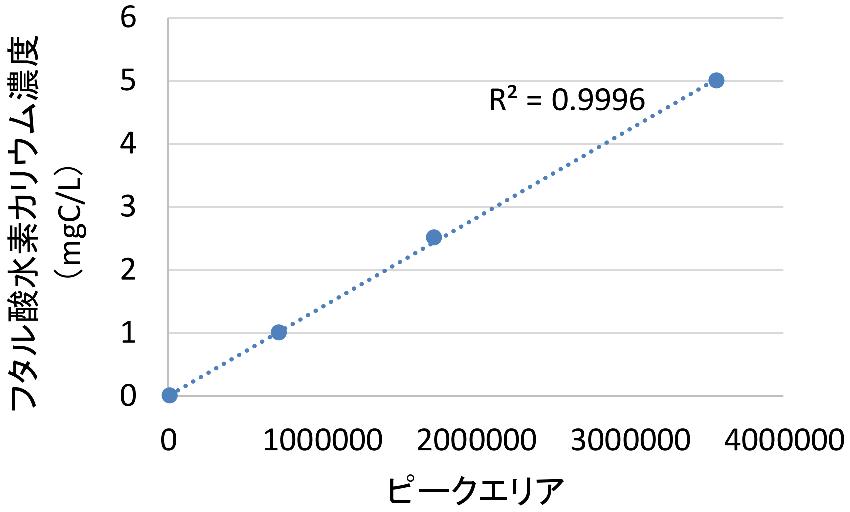
Results – Calibration *(in collaboration with NIES)*

Size Calibration by PSS



PSS（Poly Styrene Sulfonate Salt）
Linear range: 184～64k Da
PSS is suitable for measuring molecular size of DOM from water

TOC Calibration by KHP



KHP calibration linear range: 1～5 mg C/L
Limit of detection（S/N = 3）: 17 µg C/L

Results – Comparison TOC and SEC-TOC *(in collaboration with NIES)*

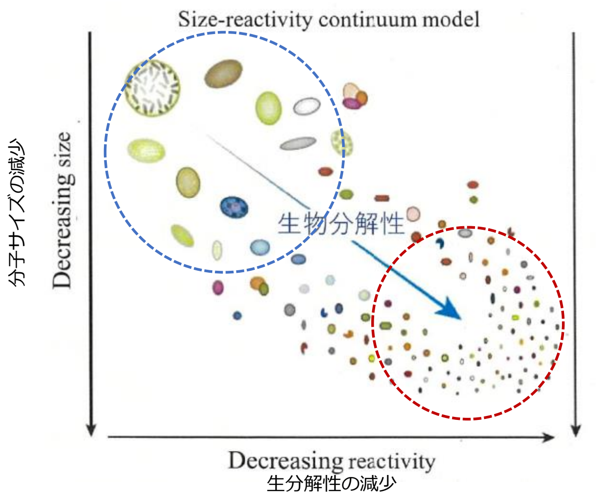
Table 2. DOC concentration and carbon recovery rate of seawater samples before and after desalination. Values in parentheses indicate the standard deviation for triplicate samples. HPSEC = high-performance size exclusion chromatography.

	DOC concentration (mgC L^{-1})				
	Combustion catalytic oxidation				
Sample name	Raw	Desalted	HPSEC system Desalted	Carbon recovery rate (%)	DOC ratio of HPSEC system/Combustion catalytic oxidation
Tokyo Bay	1.66	1.46 (0.10)	1.38 (0.06)	88	0.92
Kashima Port	1.18	1.06 (0.11)	0.92 (0.04)	90	0.87
Cape Inubo	1.13	0.87 (0.03)	0.80 (0.02)	77	0.94

Shimotori et al (2016) doi: 10.1002/lom3.10118

Comparable results TOC vs SEC-TOC

Study of Source Water



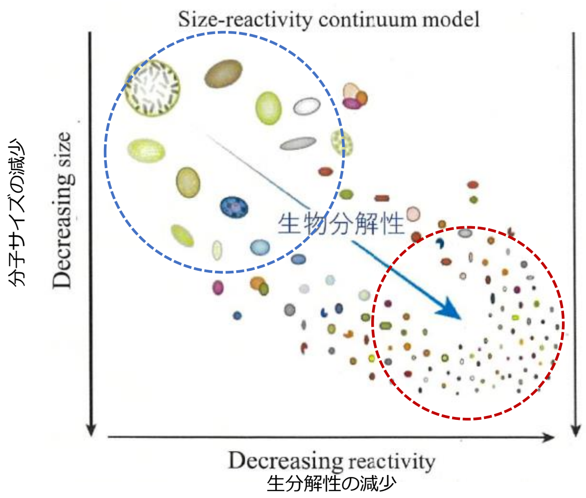
【Easily decomposable DOM】
（Molecular size：**large**,
Biodegradability：**high**）

Carbon source for bacteria:
Amino acids, proteins, sugars, etc.

【Persistent DOM
（Molecular size：**small**,
Biodegradability：**low**）

Carbon storage and water contaminants

Study of Source Water *(in collaboration with NIES)*



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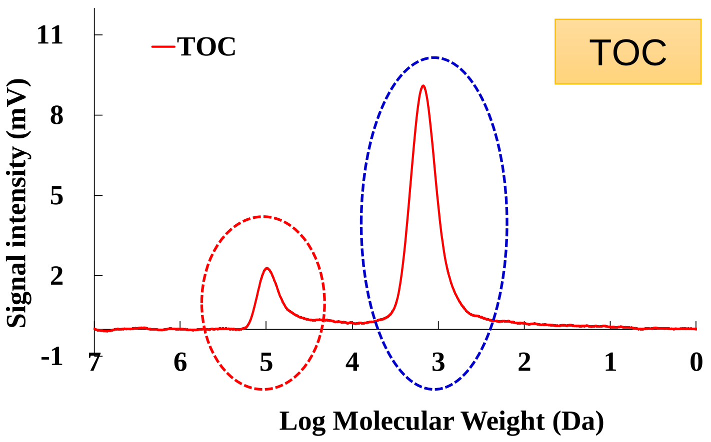
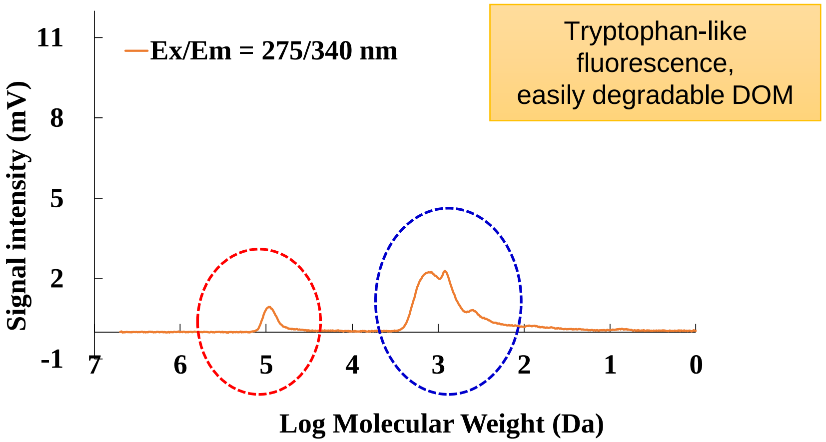
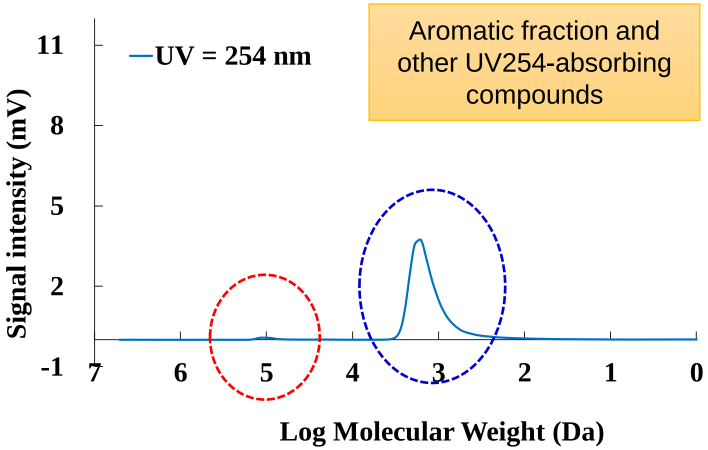
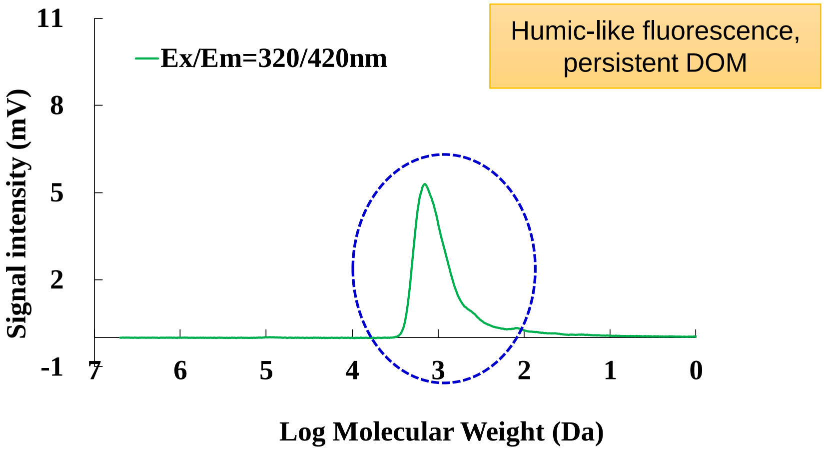
Carbon storage and water contaminants

Water Source - Lake Biwa (Japan)



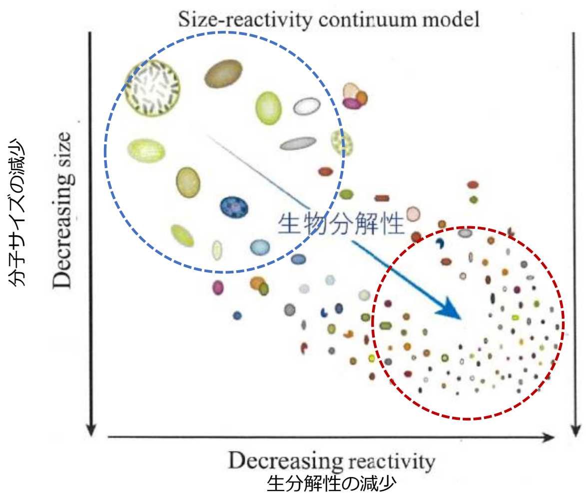






Study of Source Water

Fluctuations of water quality were evaluated



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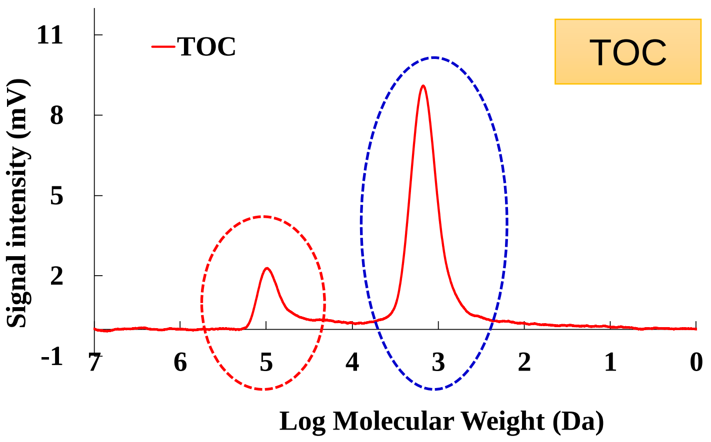

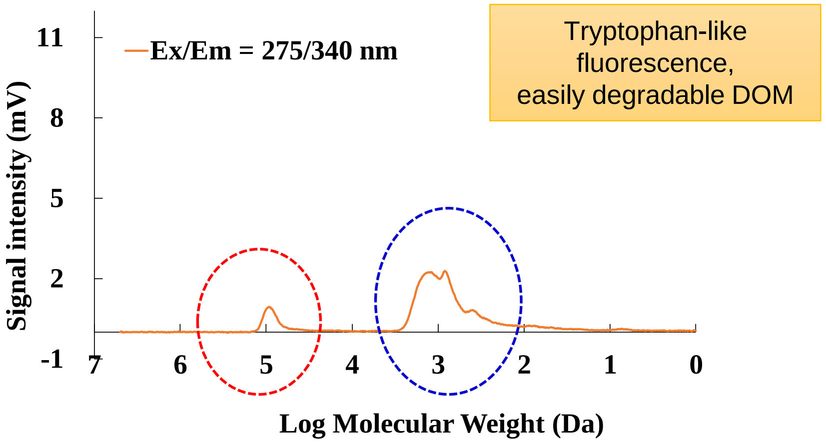

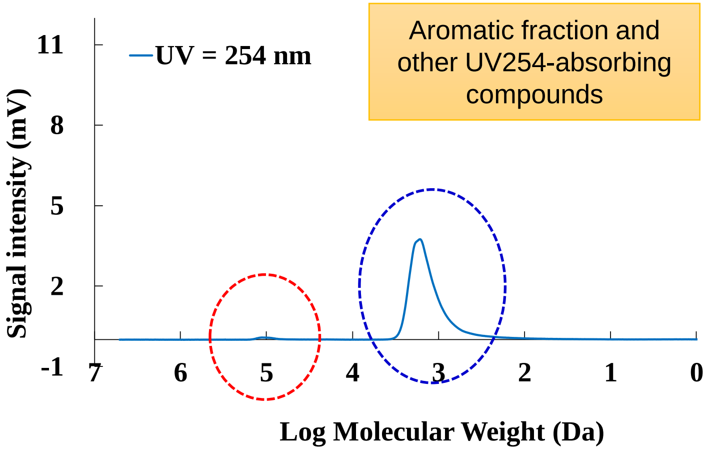

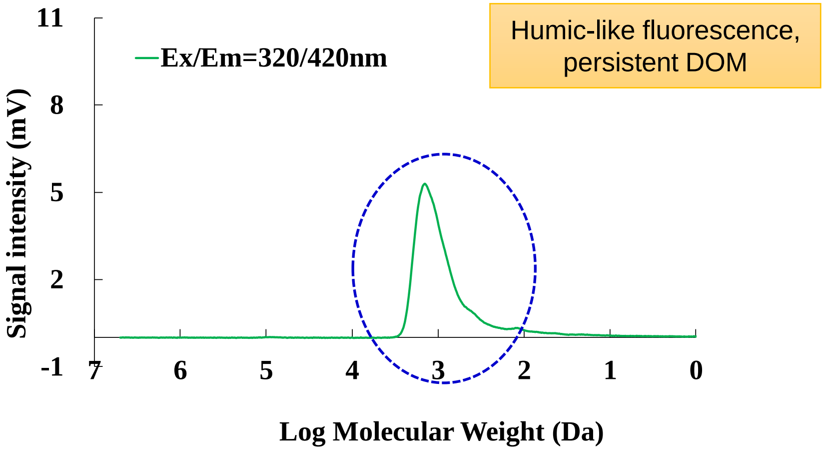

Evaluation of treatment performance

- Drinking water treatment plants traditionally relied on physicochemical processes
- Biofiltration has been widely implemented in drinking water treatment
- Treatment technologies used in water reclamation rely on membranes filtration, ozonation, and biofiltration

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Performance depends on NOM composition

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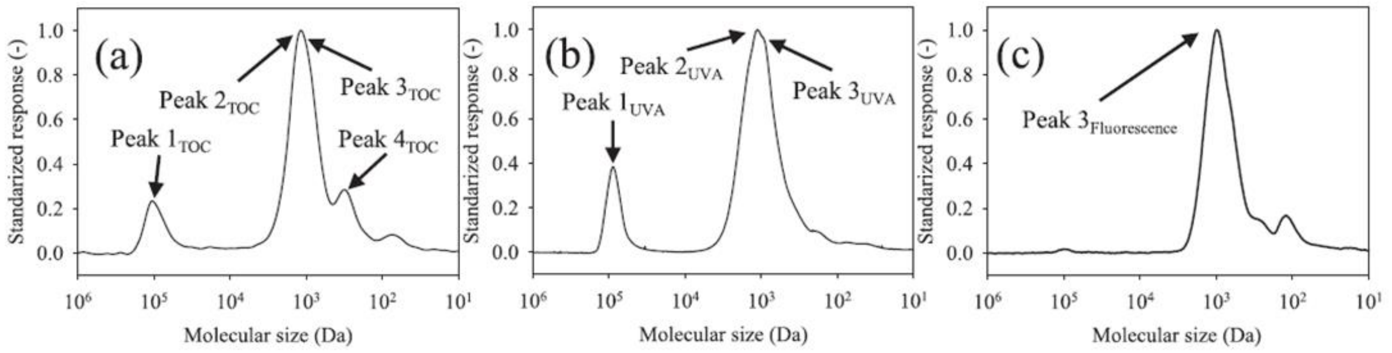


Fig. 2. Size exclusion chromatograms of the WWTP influent (June 2017), detected by (a) TOC, (b) UVA (254 nm), and (c) fluorescence (excitation/emission of 340/430 nm).

FEEM data (c) acquired with a benchtop fluorescence spectrophotometer

Komatsu et al (2020) https://doi.org/10.1016/j.watres.2019.115459

Evaluation of treatment performance

Table 1
Data on influent, effluent, and removal/reduction percentages during WWTP.

		Basic parameters			EEM-PARAFAC				
		DOC (mgC/L)	UV_{254} (mAbs/cm)	SUVA (mAbs·L)/(mgC·cm)	Comp. 1 (Score)	Comp. 2 (Score)	Comp. 3 (Score)	Comp. 4 (Score)	Comp. 5 (Score)
October 2016	Influent	27.2	282	10.4	1.22	0.51	1.66	0.66	3.00
	Effluent	5.9	79.5	13.4	0.14	0.40	0.83	0.64	1.50
	Removal/reduction %	78%	72%	–	88%	22%	50%	3%	50%
March 2017	Influent	19.1	455	23.9	1.80	0.57	1.48	0.74	2.92
	Effluent	4.5	98.2	21.9	0.16	0.39	0.71	0.64	1.75
	Removal/reduction %	76%	78%	–	91%	31%	52%	14%	40%
June 2017	Influent	14.3	457	31.9	1.28	0.65	1.60	1.12	3.39
	Effluent	4.3	97.6	22.7	0.19	0.45	0.84	0.84	1.60
	Removal/reduction %	70%	79%	–	85%	31%	47%	25%	53%
August 2017	Influent	17.9	370	20.6	1.27	0.54	1.47	0.88	1.75
	Effluent	4.1	89.3	22.0	0.17	0.44	0.77	0.77	0.97
	Removal/reduction %	77%	76%	–	87%	20%	48%	13%	44%

		HPLC-SEC					
		TOC detection			UVA detection		
		Peak 1 (Area)	Peak 2 (Area)	Peak 3 (and 4) (Area)	Peak 1 (Area)	Peak 2 (Area)	Peak 3 (Area)
October 2016	Influent	1283004	7586154	20809968	49662	5013606	4894044
	Effluent	220724	2686482	2496860	28804	3463460	1735356
	Removal/reduction %	83%	65%	88%	42%	31%	65%
March 2017	Influent	–	–	–	–	–	–
	Effluent	–	–	–	–	–	–
	Removal/reduction %	–	–	–	–	–	–
June 2017	Influent	2567490	7327640	10655250	1486370	5508675	4433625
	Effluent	275133	3093937	2439484	65697	3048592	2335802
	Removal/reduction %	89%	58%	77%	96%	45%	47%
Aug. 2017	Influent	3077034	6629784	13187802	2962674	4662972	6954942
	Effluent	207181	3225615	3108931	36568	2537282	3619719
	Removal/reduction %	93%	51%	76%	99%	46%	48%

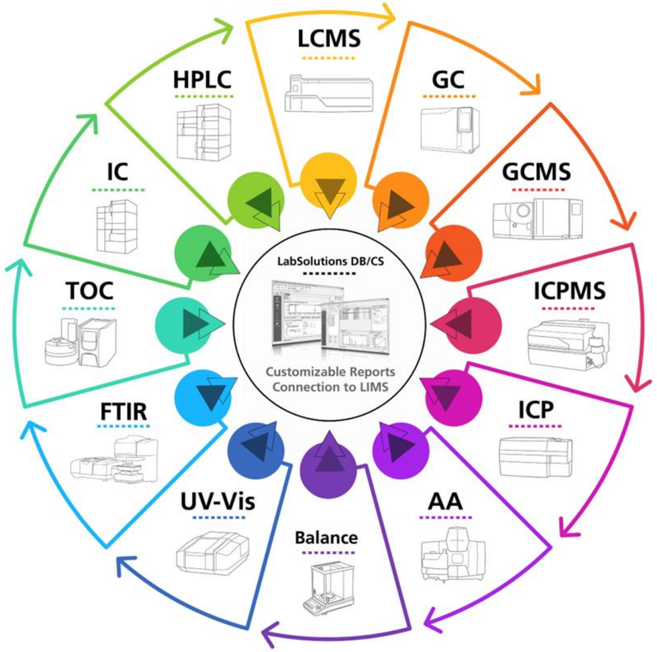
Component	Description
C1	Protein-like, derived from tryptophan
C2	Microbial, fulvic-like, and observed in wastewater samples Decomposed by photo-irradiation
C3	Humic-like with terrestrial origin; present in all freshwater samples
C4	Humic-like, observed in wetland samples Decomposes biologically after photodegradation
C5	Might be specific to sewage samples Information on this component is scarce

DOC and UV254 provided insights of overall removal; FEEM added information about removal of specific NOM fractions

SEC-TOC (with UV detection) allowed for investigating the removal selectivity of each treatment step

Take-Home Messages

- There is an increasing need for investigating the specific composition of NOM in environmental waters and during water treatment as the implementation of water reclamation grows
- A combination of in-line detectors is a suitable alternative to perform this work (e.g., TOC with UV or fluorescence). SEC adds the benefit of the chromatographic separation of NOMs components before the detectors
- Examples shared demonstrated the use of SEC-TOC for the study of source water quality and treatment performance. Limit of detection of TOC: 5 ppb.



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