8th International Symposium on Water Supply Technology, 10-12, June 2009, Kobe

Mechanism and Control of Membrane Fouling in Water Purification

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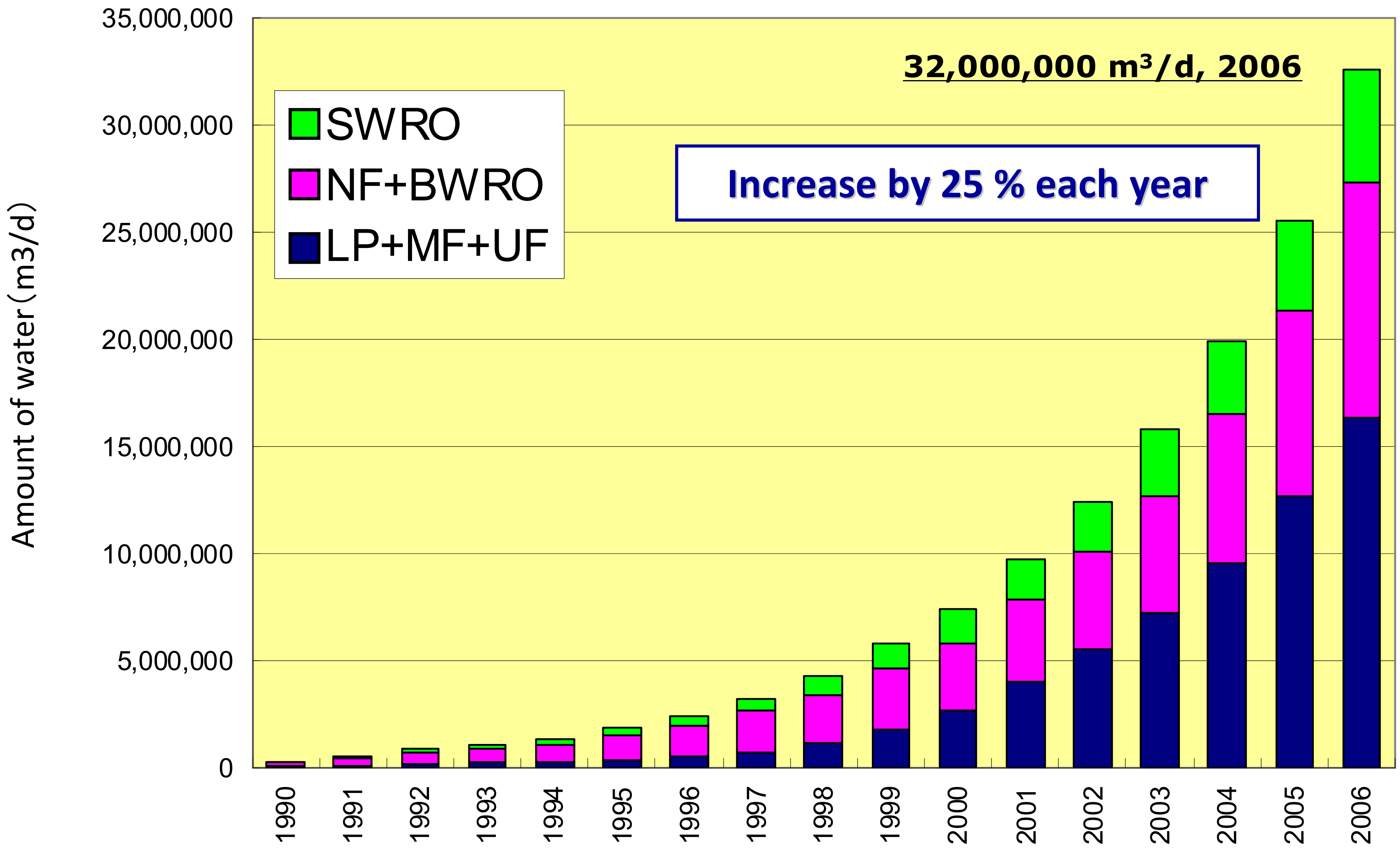
Global amount of water produced by membrane processes



(引用)膜分離技術振興協会: 浄水膜第2版(技報堂出版), p6, 2008.2

配水管内における微粒子の挙動

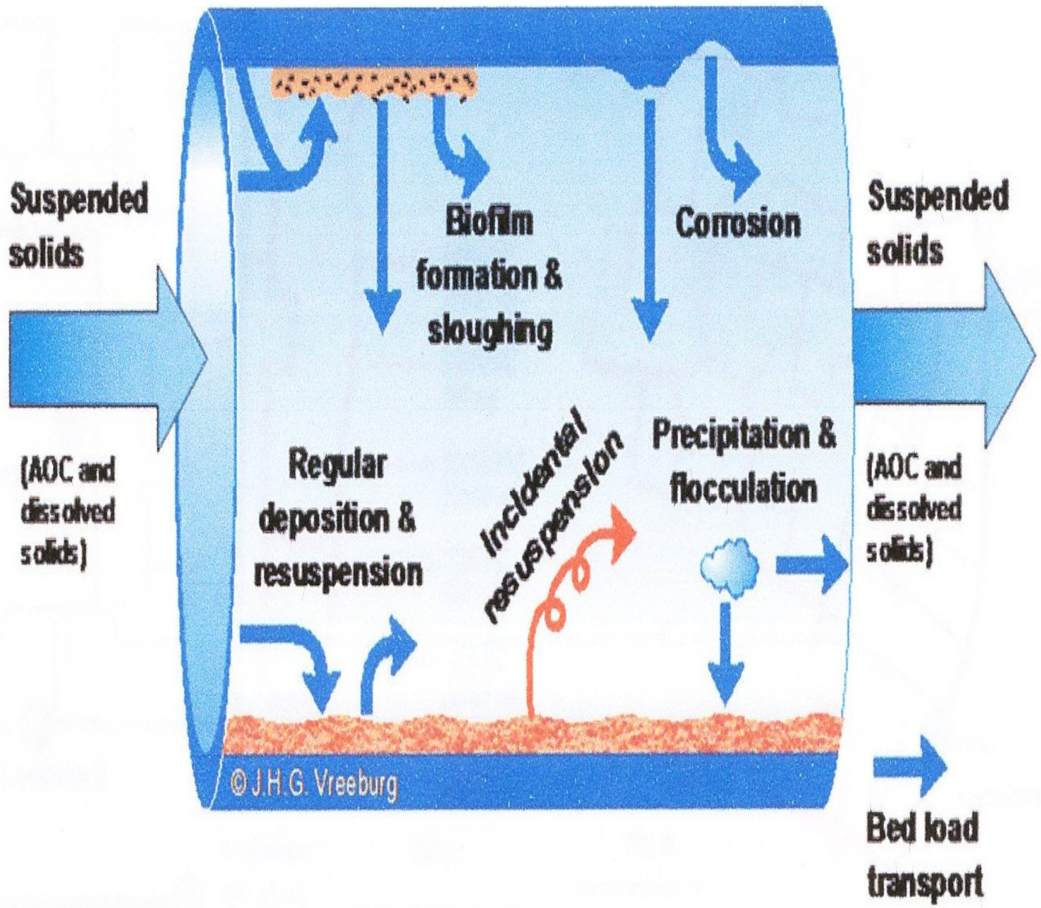
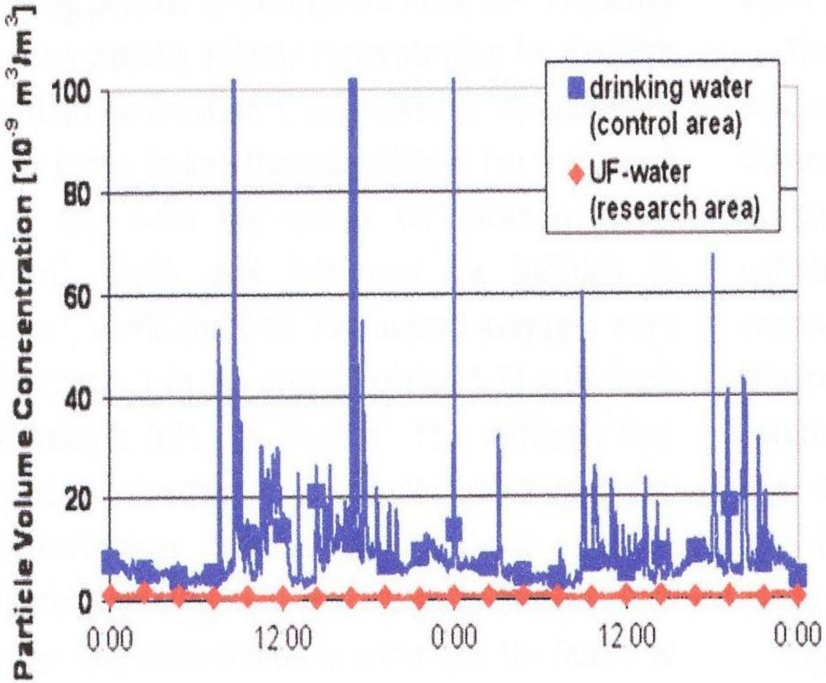


Fig. 1 – Particle related processes in a drinking water distribution system (Vreeburg, 2007).

Pipe cleaning

Sand filtration: Every 0.5 years
Membrane filtration: Every 15 years



Frequency Percentile	Control Area [10^{-9} m^3/m^3]	Research Area [10^{-9} m^3/m^3]
90	16.38	1.09
92	18.84	1.13
94	21.07	1.20
96	25.49	1.28
98	34.02	1.40
99	54.15	1.52
99.5	84.70	1.63

		Cntrl Area	Res Area
Avg	[10^{-9} m^3/m^3]	9.44	0.74
Avg+90	[10^{-9} m^3/m^3]	31.46	1.28
surf+90	[%]	33.3	17.4
Ratio 90/99.5	[-]	0.19	0.67

Fig. 4 – Particle volume concentration at Location 1 for the Control Area and the Research Area (drinking water and UF water) during two representative days in the first measuring period (March–April 2006).

(Vreeburg, et.al, 2008)

Water Purification Processes in Japan

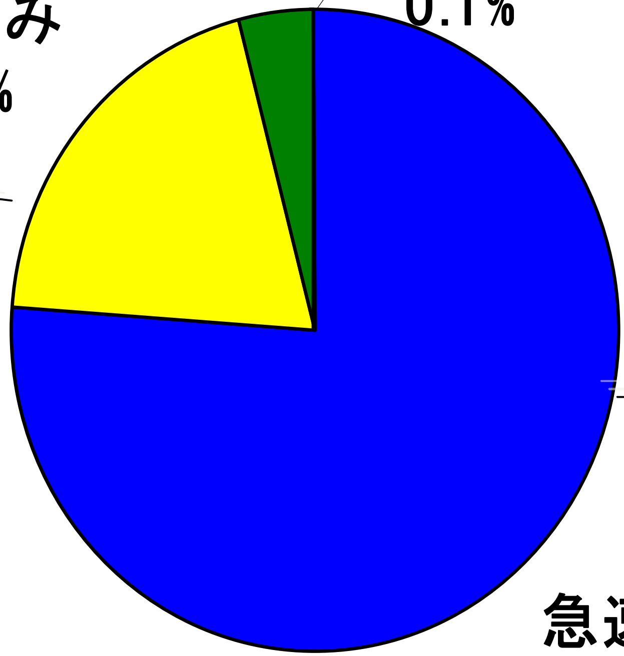
Membrane Filtration:

84×10^4 m^3/day (1.2 %) in 2007

586 plants in 2006
623 plants in 2007

101×10^4 m^3/day (1.5%) in 2009

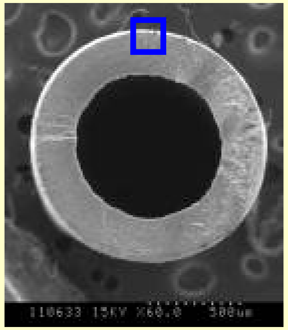
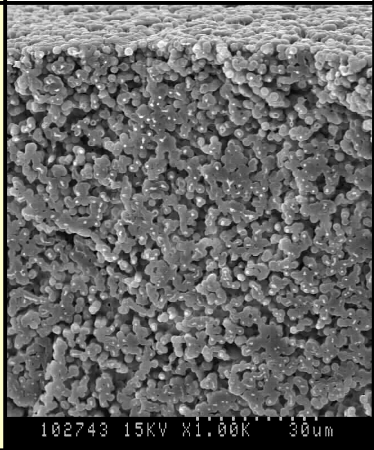
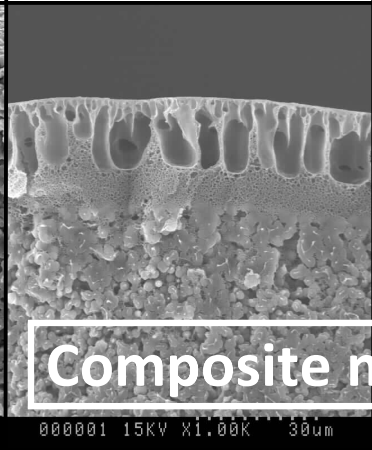
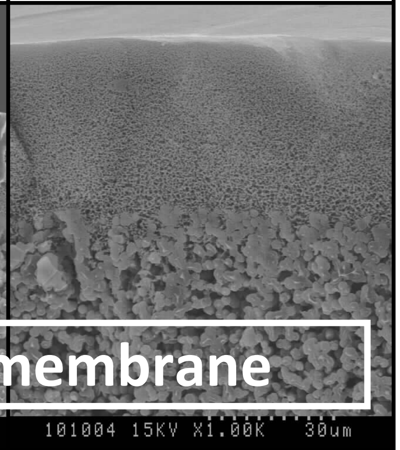
173,000 m^3/d membrane filtration plant under construction in Yokohama city



In 1999

Total production of drinking water:
6900×10^4 m^3/day

Line-up of PVDF hollow fiber membranes (Toray products)

	HFM	HFS	HFU
Pore size or MWCO	0.1 μm	0.02 μm	150*kDa*
Cross section 			
Water source	Ground water	Surface water	Surface water
Pretreatment	None	Coagulation	No Need or Coagulation
Applicable ave. Feed turbidity	~ 0.05 NTU	~ 30 NTU	~ 50 NTU
Applicable Flux	~ 5.0 m/d (208 lmh)	~ 3.0 m/d (125 lmh)	~ 3.0 m/d (125 lmh)

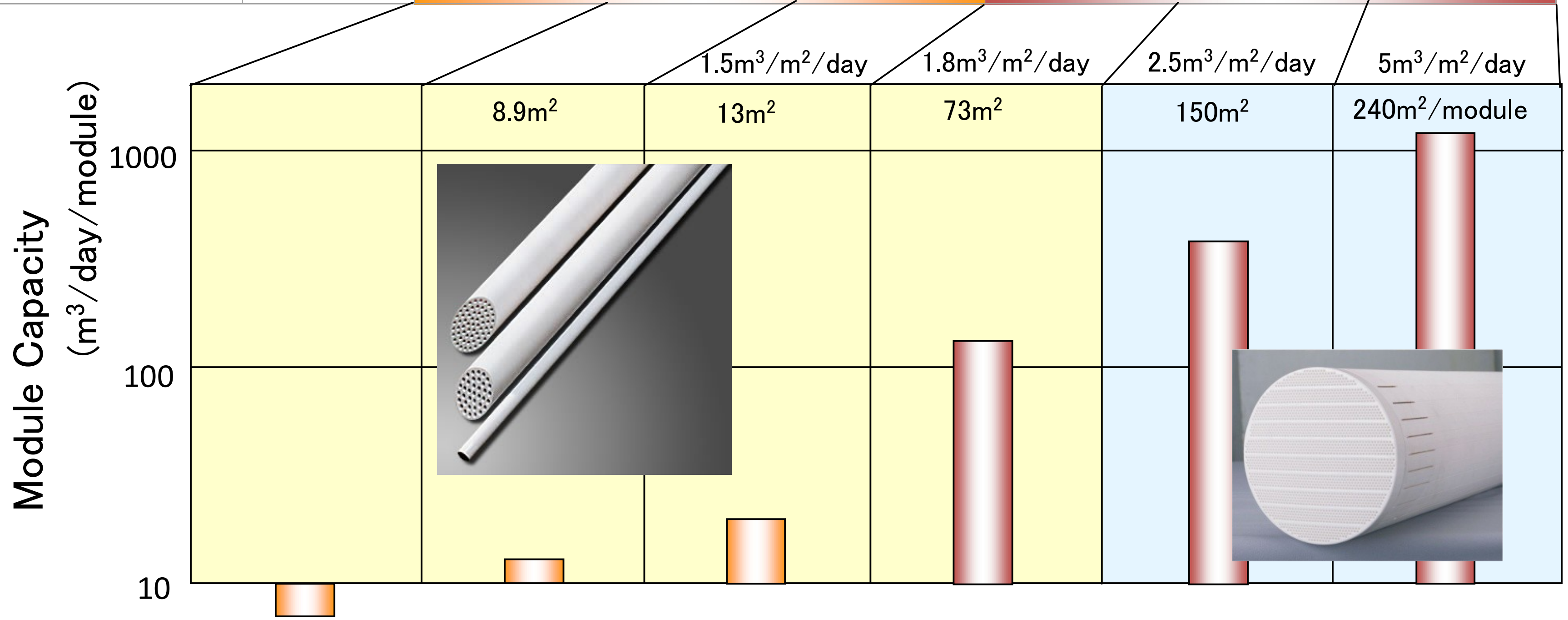
Low fouling layer

Support layer (high flux & high Strength)

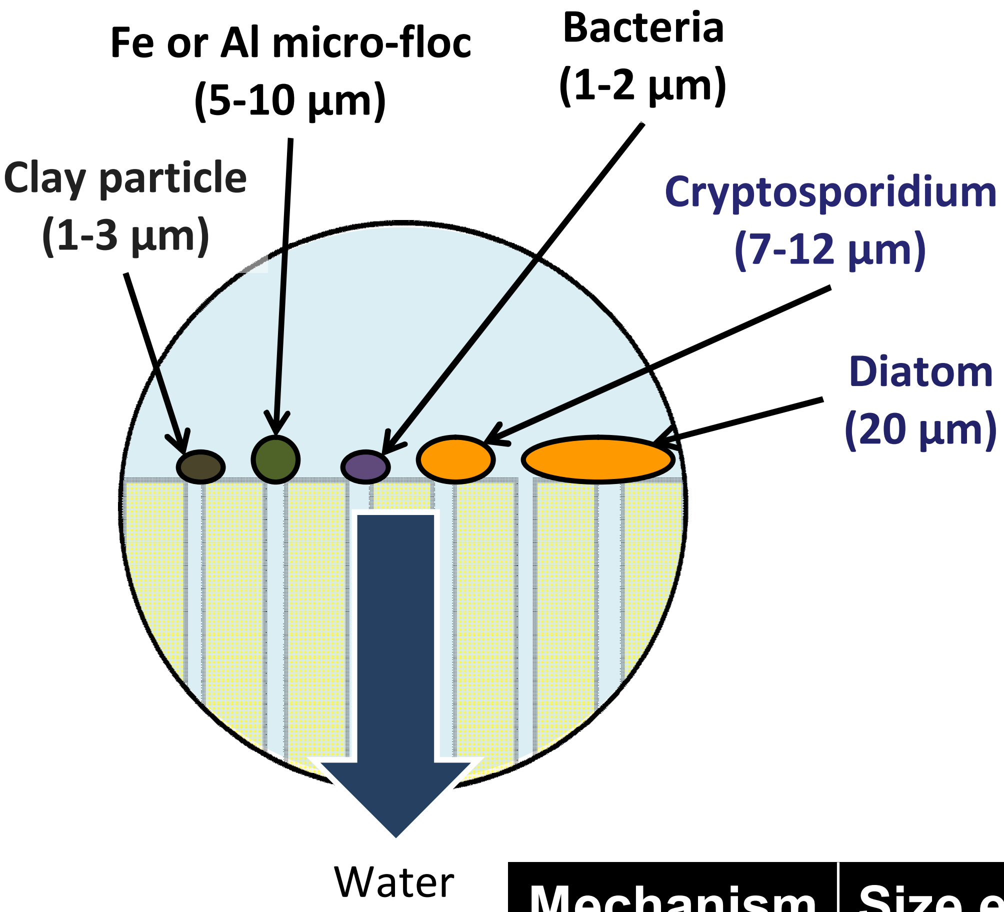
Most Suitable membrane can be selected to meet the feed water quality.

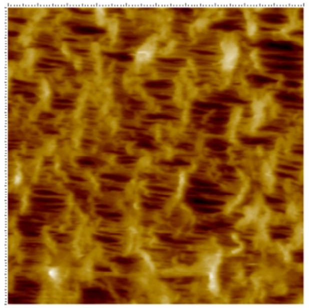
Advance of Monolith Ceramic Membrane

Configuration	unit	Tube	Monolith				
Stage		1985	1988	1990	1994	2001	(2006)
Length	mm	1,000					1,500
Diameter	mm	10	30			180	
Channel Number	—	1	19	37	61	2000	
Channel Diameter	mm	7	4	3	2.5		
Membrane Area	m^2	0.02	0.24	0.35	0.48	15	24
Packing Density	m^2/L	0.25	0.34	0.50	0.63	0.6	0.63
Application	—	Industrial Use			Water Purification		



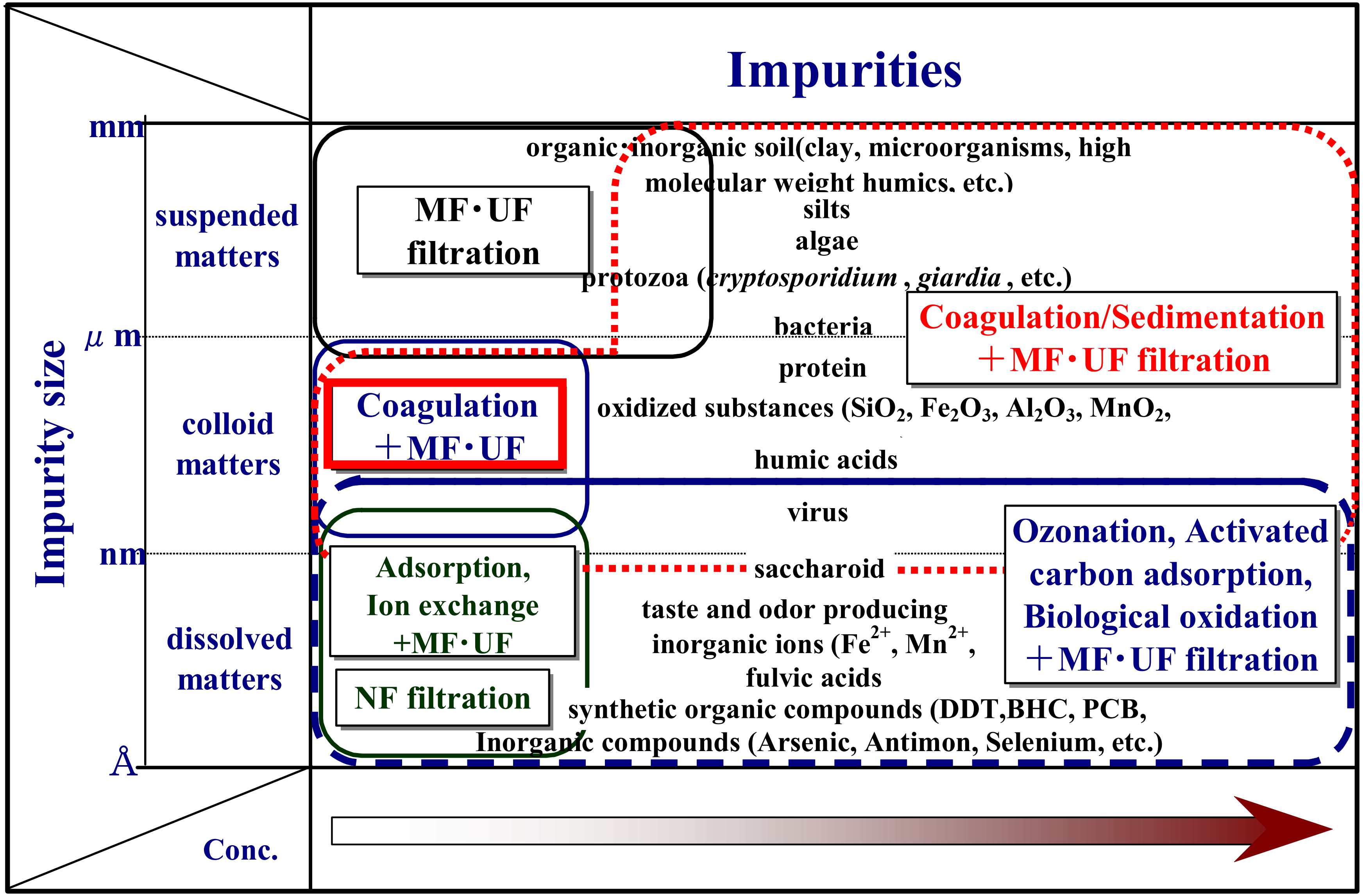
Membrane filtration



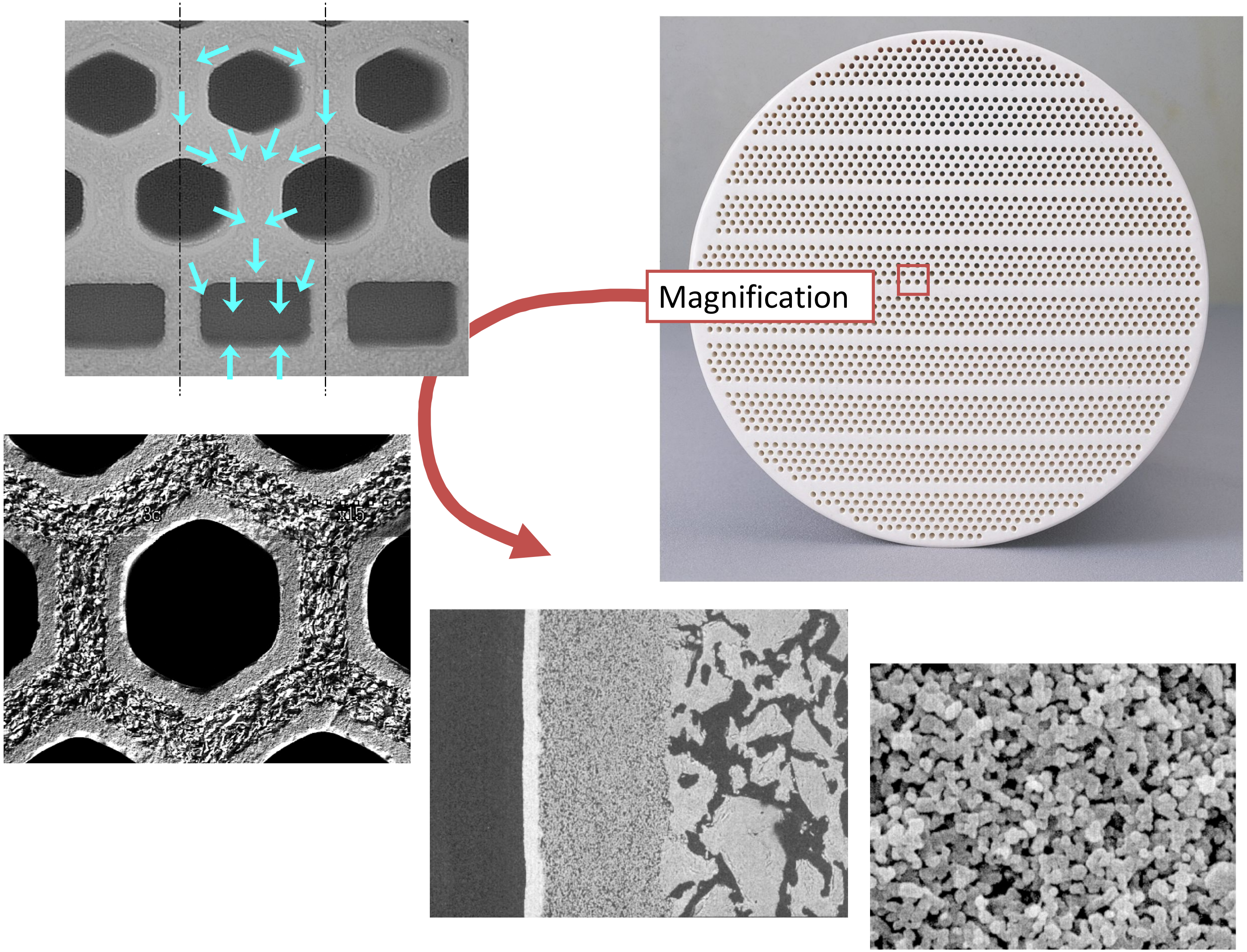


Mechanism	Size exclusion
Advantages	• Strict removal of suspended and colloidal matters • Easy operation without any special skill • Small footprint

Design Matrix of MF/UF Membrane System



Monolith Ceramic Membrane (META Water Product)



Profile of G and GCt Value in Monolith Channel with low κ

Let's consider
"flocculation condition in channel"

Especially, near the membrane surface

G value

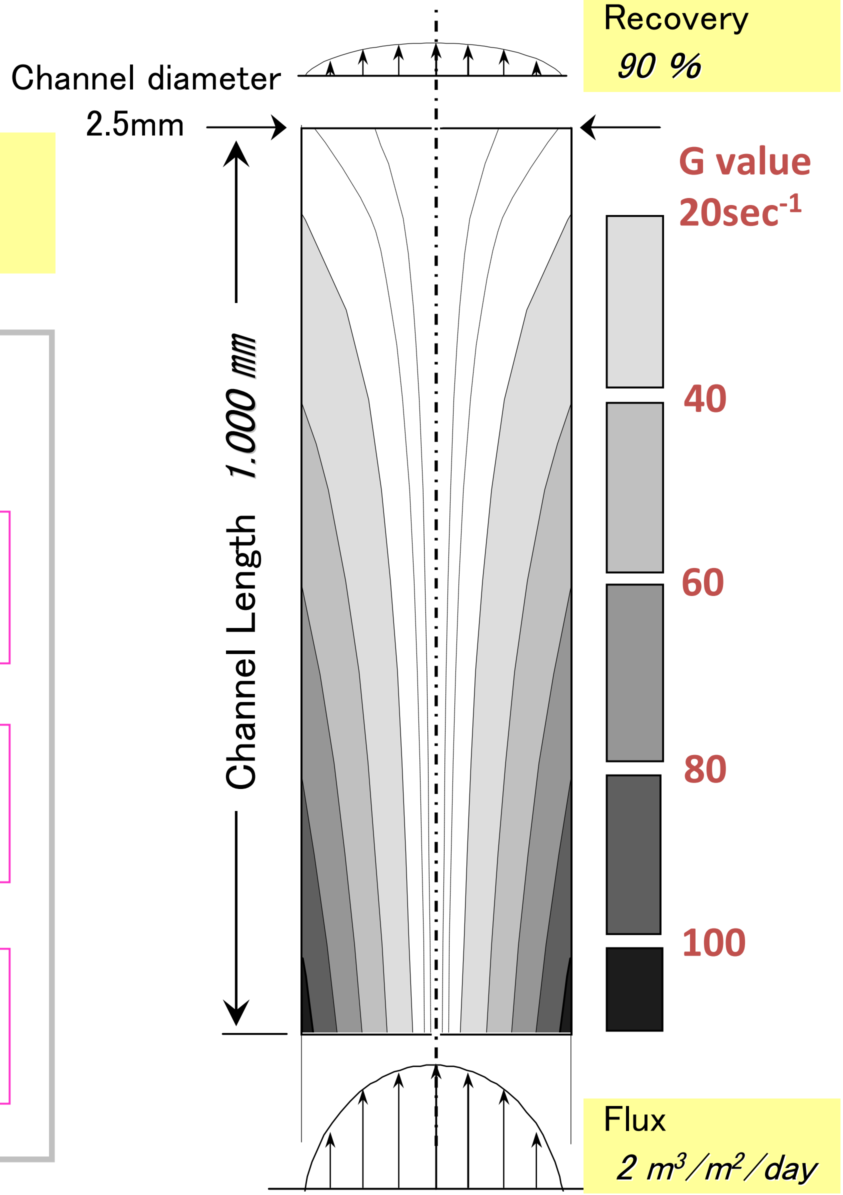
20-100sec^{-1} : desirable value for flocculation

Contact **T**ime

Enough. : Laminar velocity is very low.

Concentration.

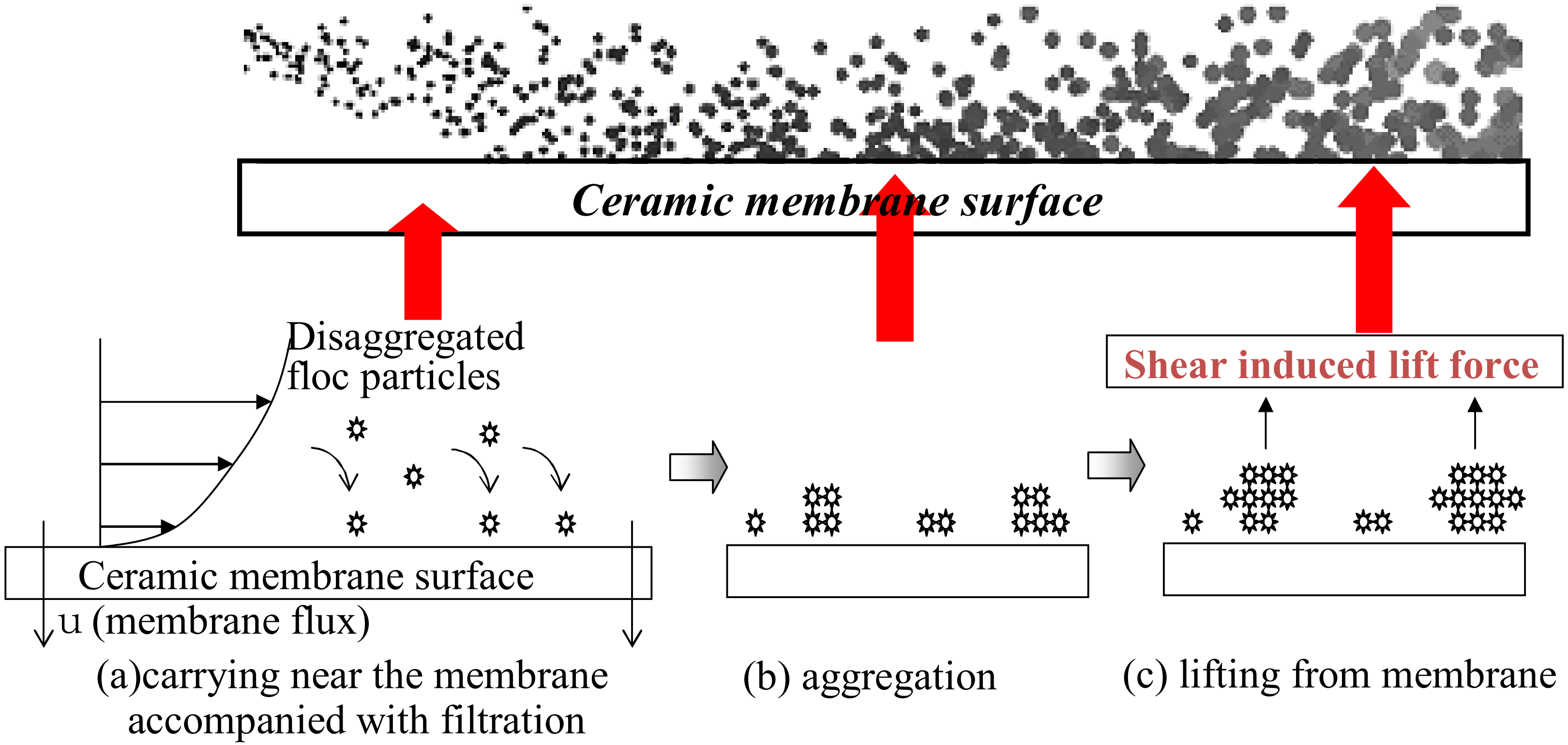
Highly concentrated : accompanied by filtration



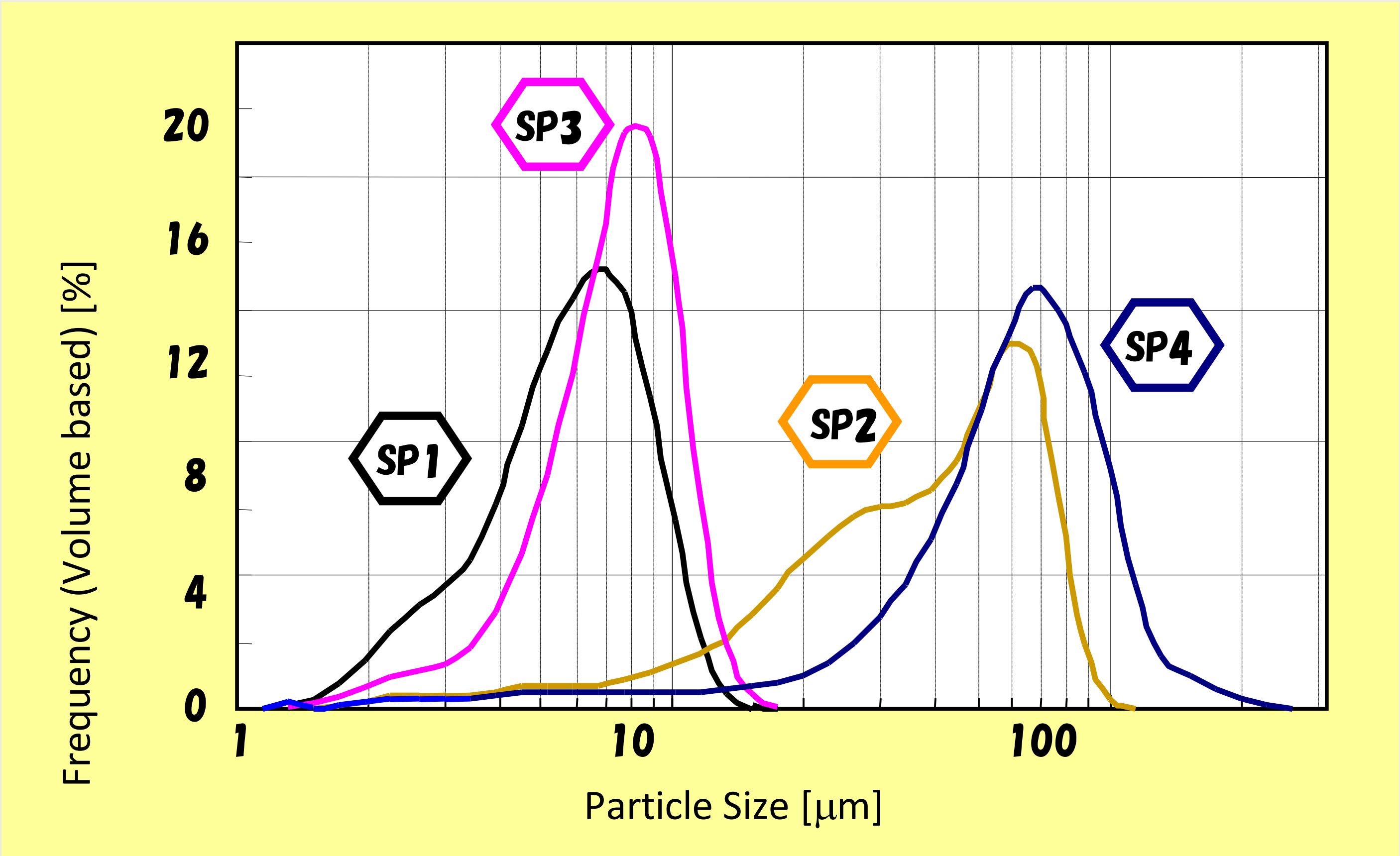
Floc Re-aggregation in Monolith Channel

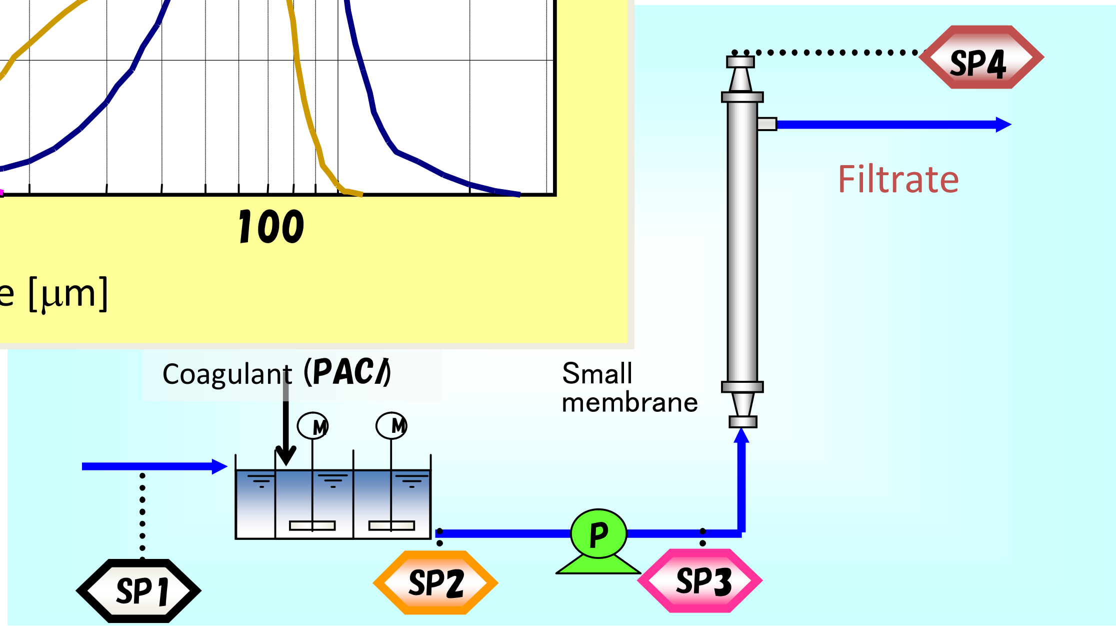
Lateral migration $v_L = u_o^2 \cdot d_p^3 / (32 \cdot \nu \cdot r_o^2)$

Shear-induced Diffusion $v_S = 0.05 \cdot u_o \cdot d_p^2 / (4 \cdot r_o^2)$

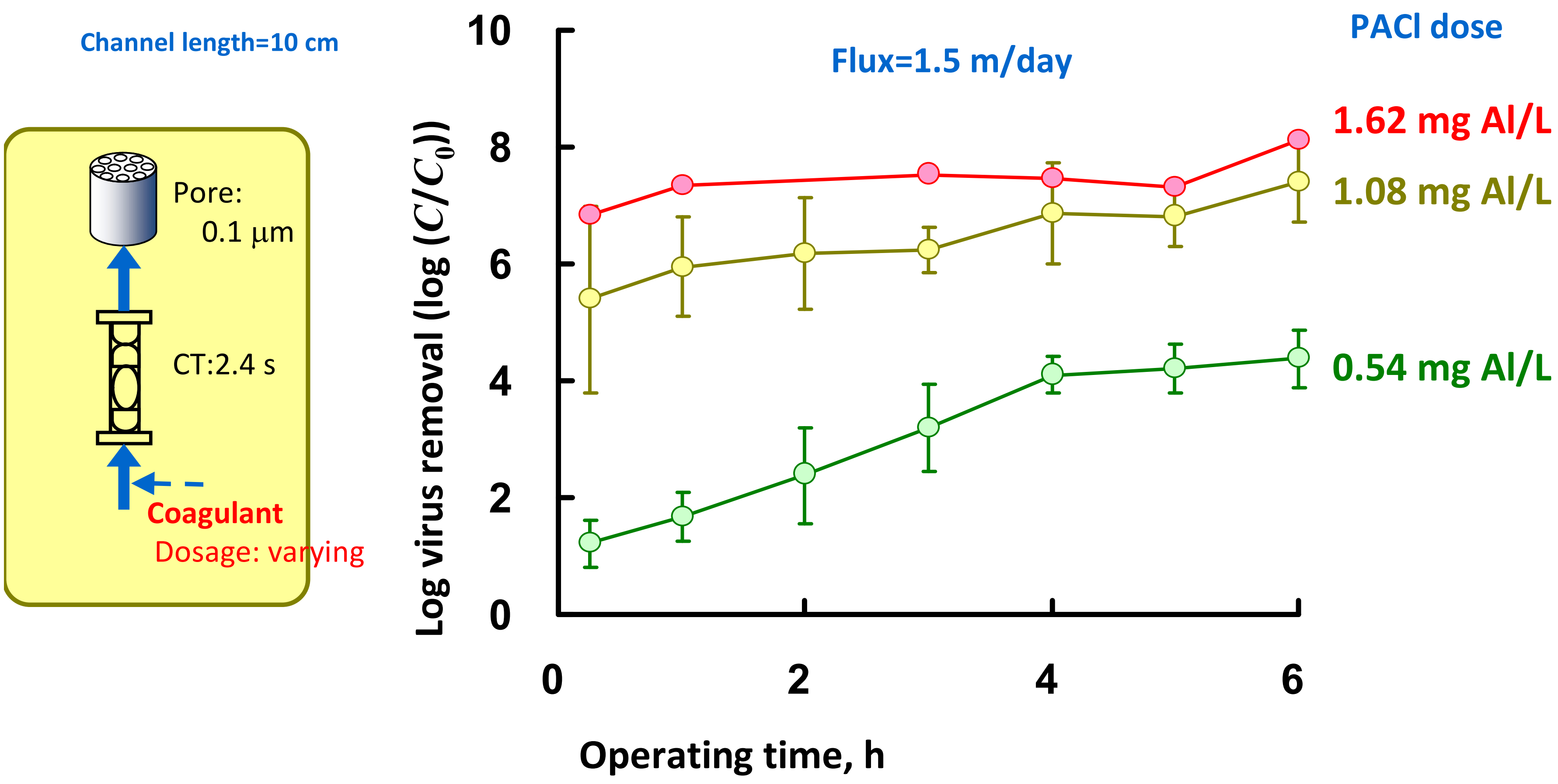


Particle Size in pre-coagulated Monolith Membrane System



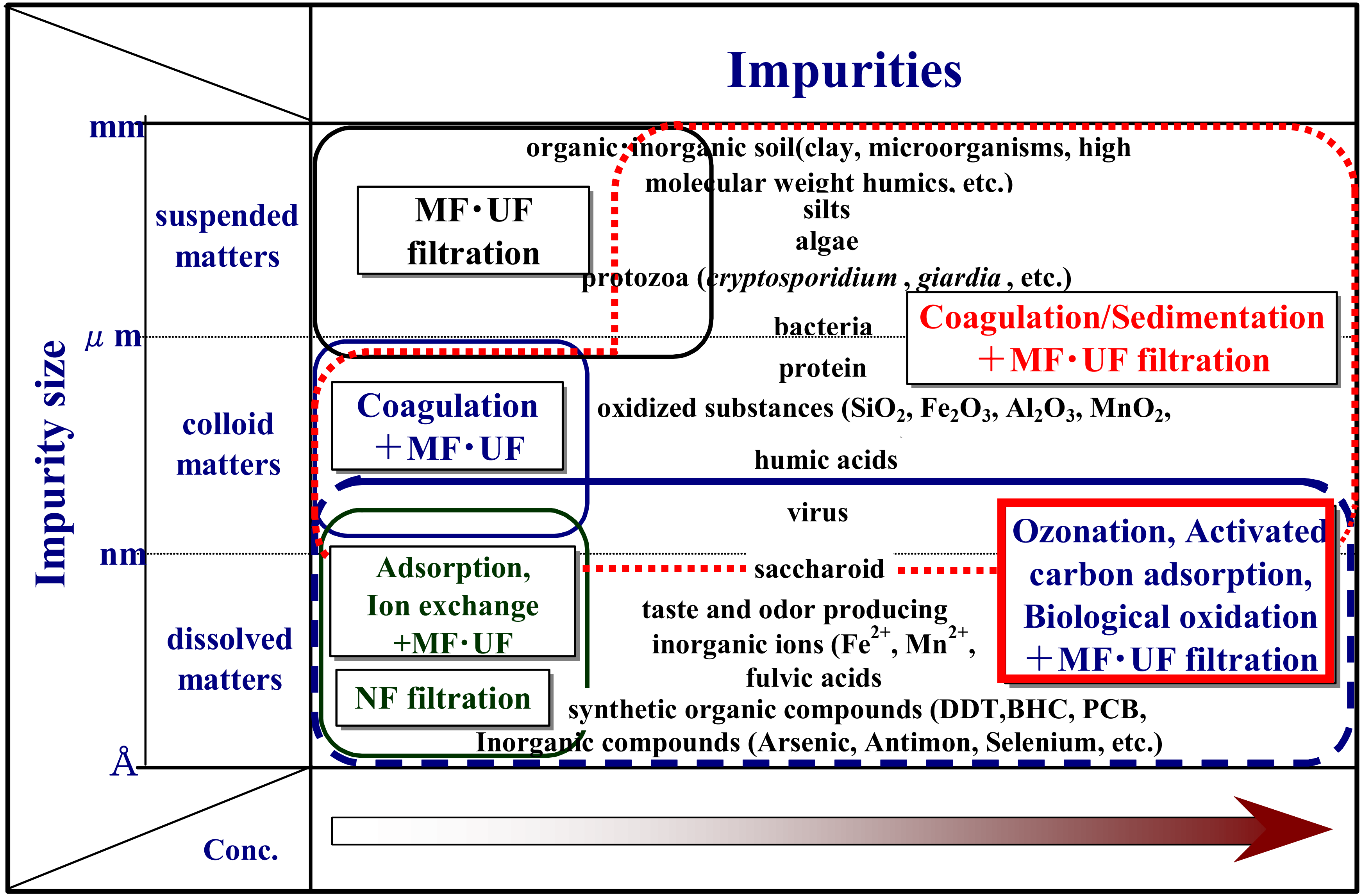


Virus Removal by Coagulation-MF



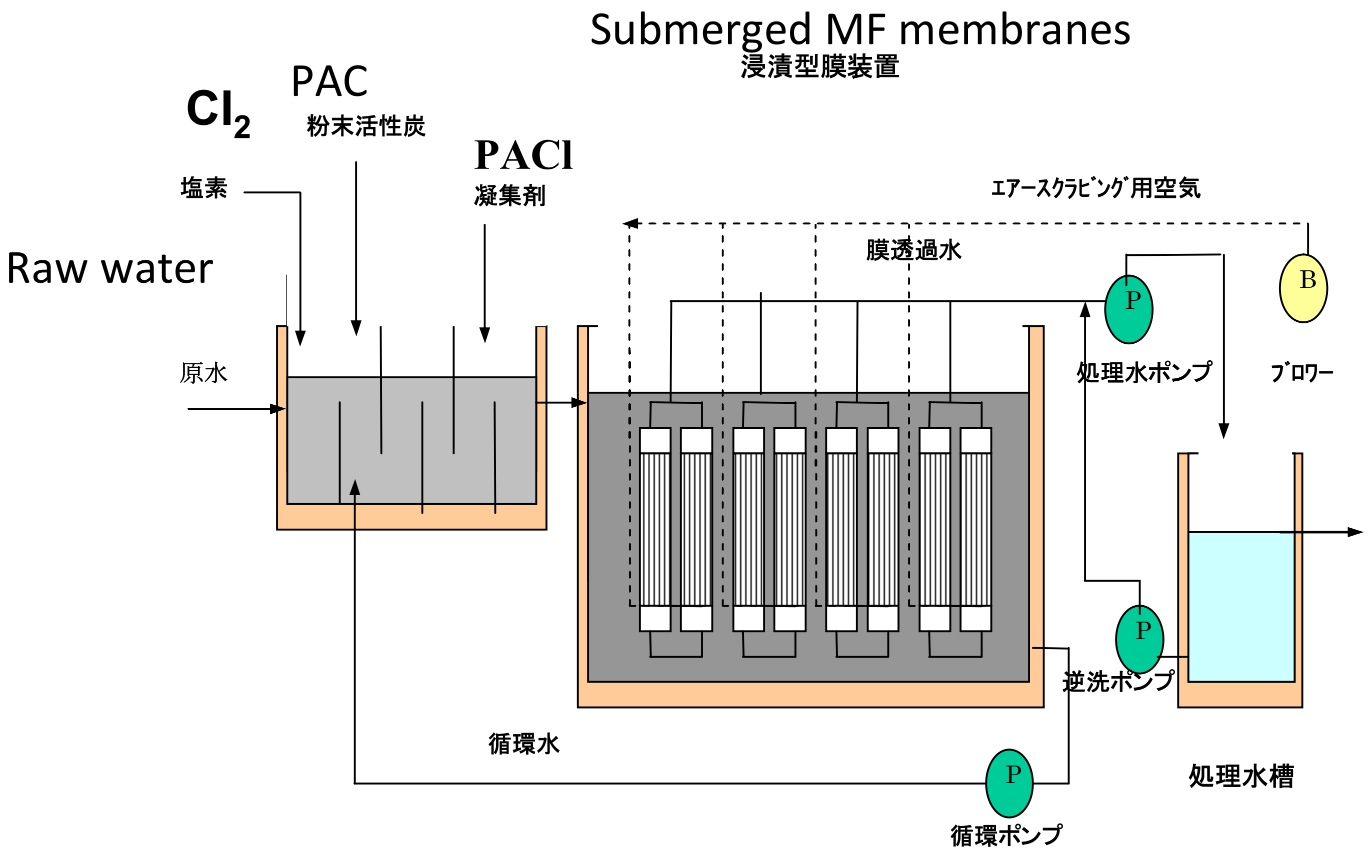
Matsushita, T., Matsui, Y., Shirasaki, N. and Kato, Y., Effect of membrane pore size, coagulation time, and coagulant dose on virus removal by a coagulation-ceramic microfiltration hybrid system, *Proceedings of EDS 6th International Conference on Membranes in Drinking and Industrial Water Production*, L'aquila, Italy, 15-17 November 2004 (Keynote Speech), selected for publication in *Desalination*, **178** (1-3), 21-26, 2005.

Design Matrix of MF/UF Membrane System

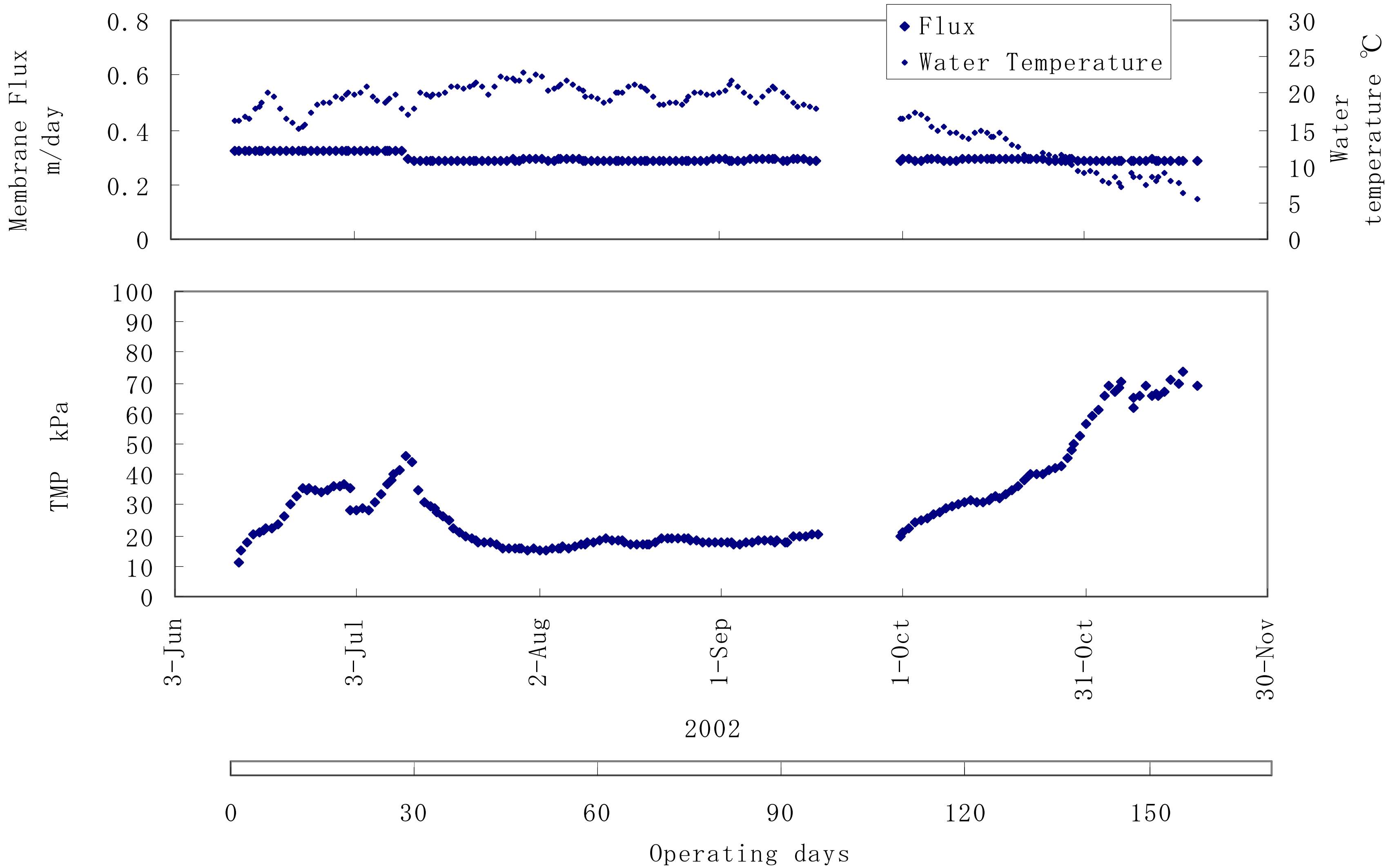


Hybrid Submerged MF membrane system

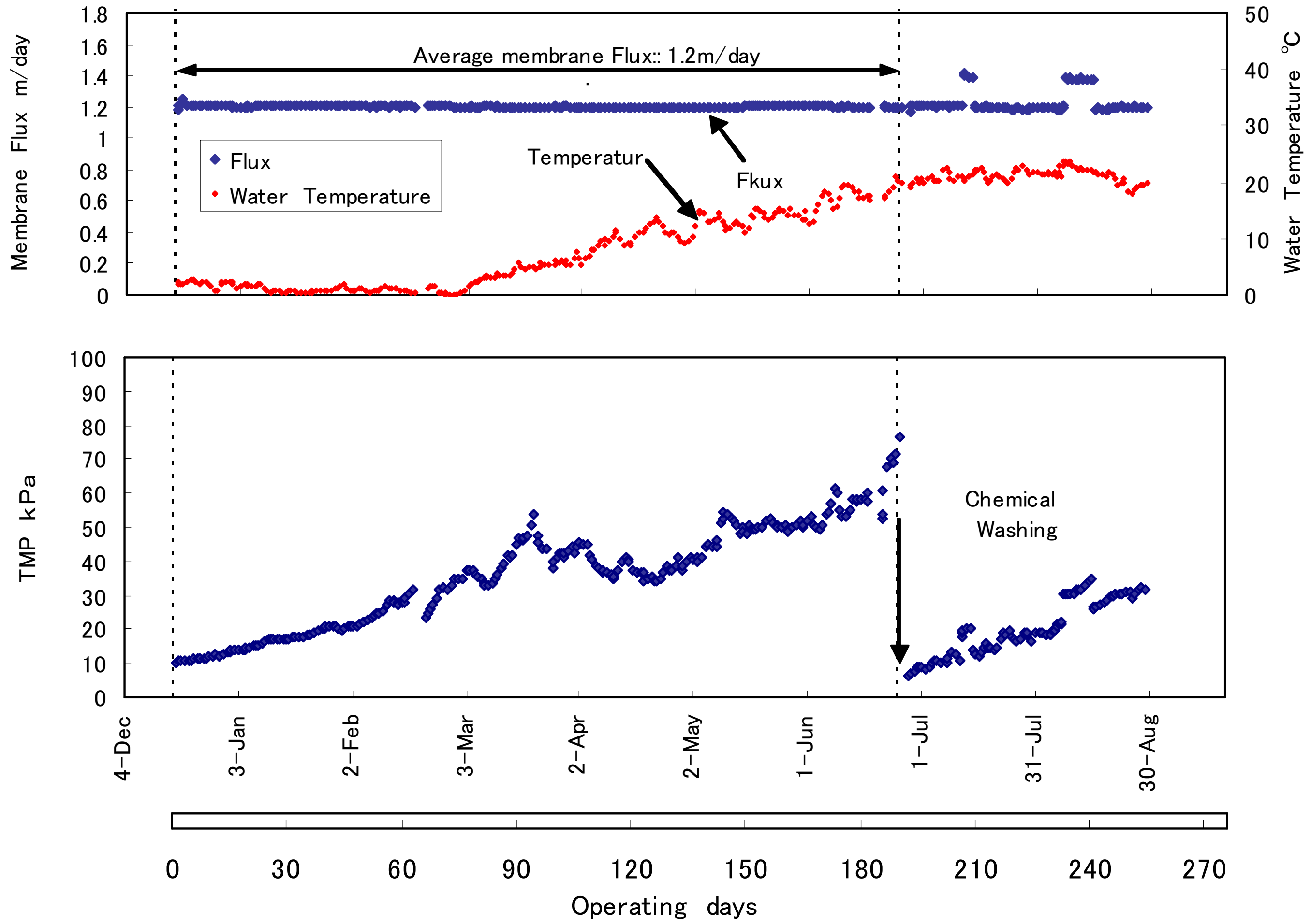
including coagulation, carbon adsorption and biological oxidation



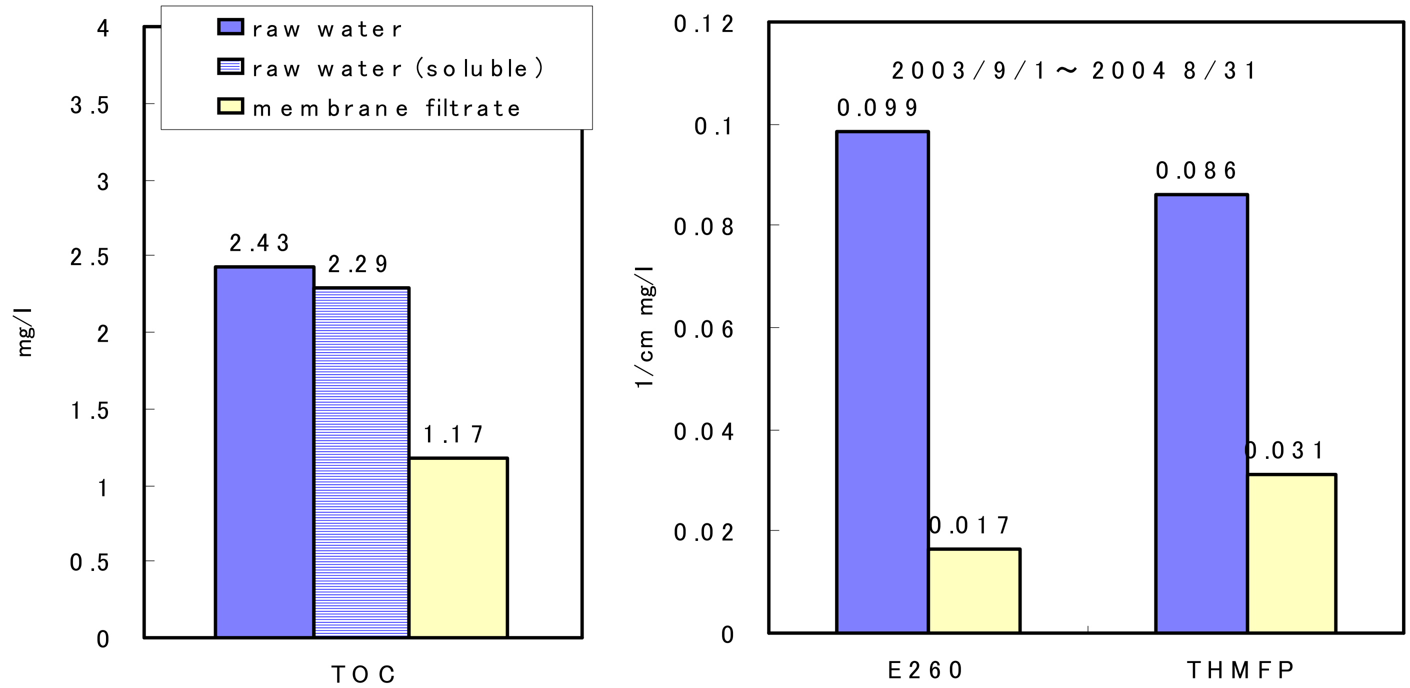
TMP increase for symmetric PTFE MF membrane (pore size=0.1 μ m)



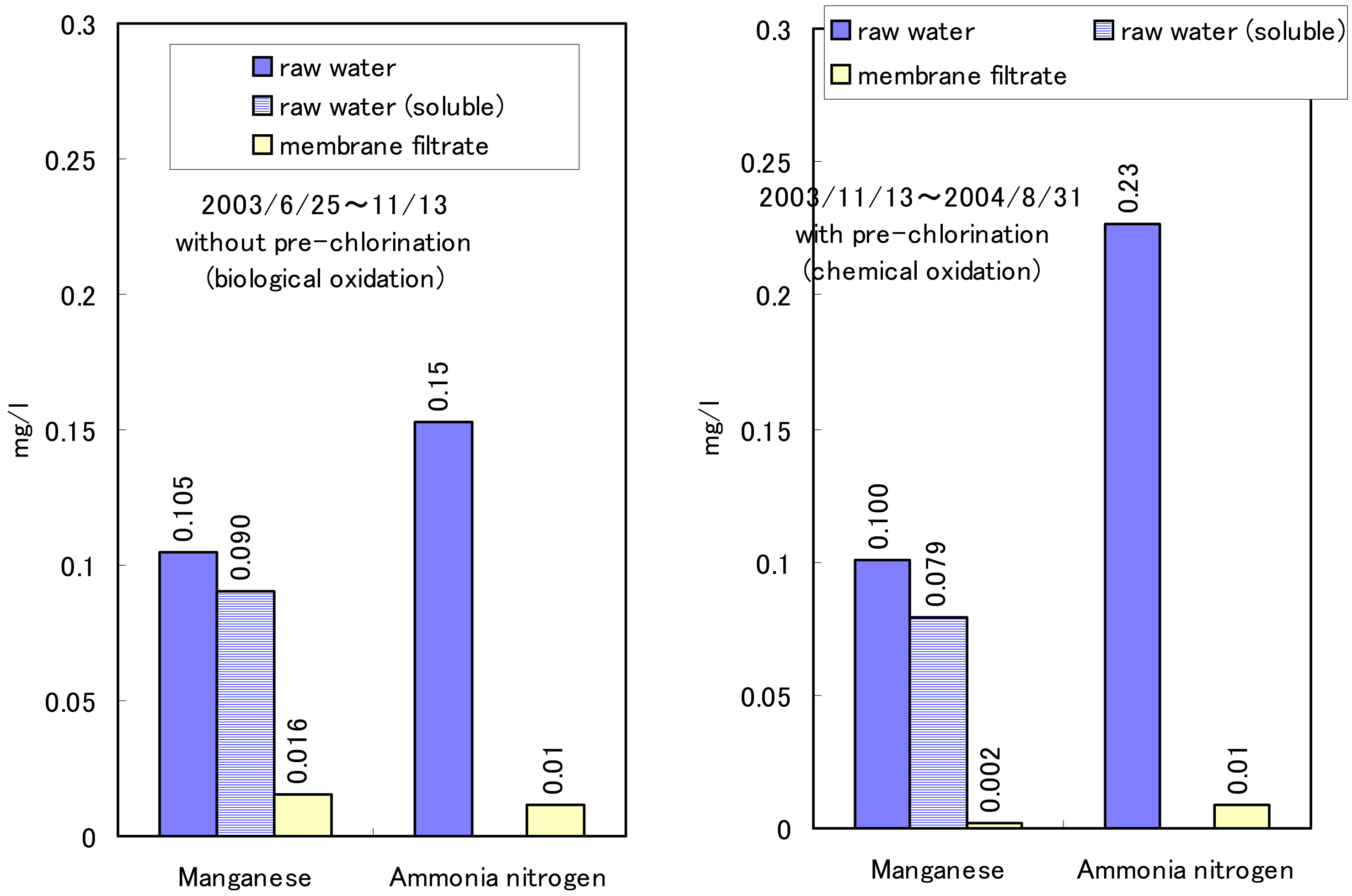
New Composite PTFE membrane with a skin layer of 15 μ m and porosity of about 80 %



Removal Efficiency of TOC, E260, THMFP in Hybrid System



Removal Efficiency of Mn and NH_4-N in Hybrid System



Membrane fouling

Physically reversible fouling
which can be canceled
by physical cleaning

Physically irreversible fouling
which is difficult to be canceled
by physical cleaning
(Canceled by chemical cleaning)

Pre-coagulation
for monolith ceramic MF Membrane

Hybrid system

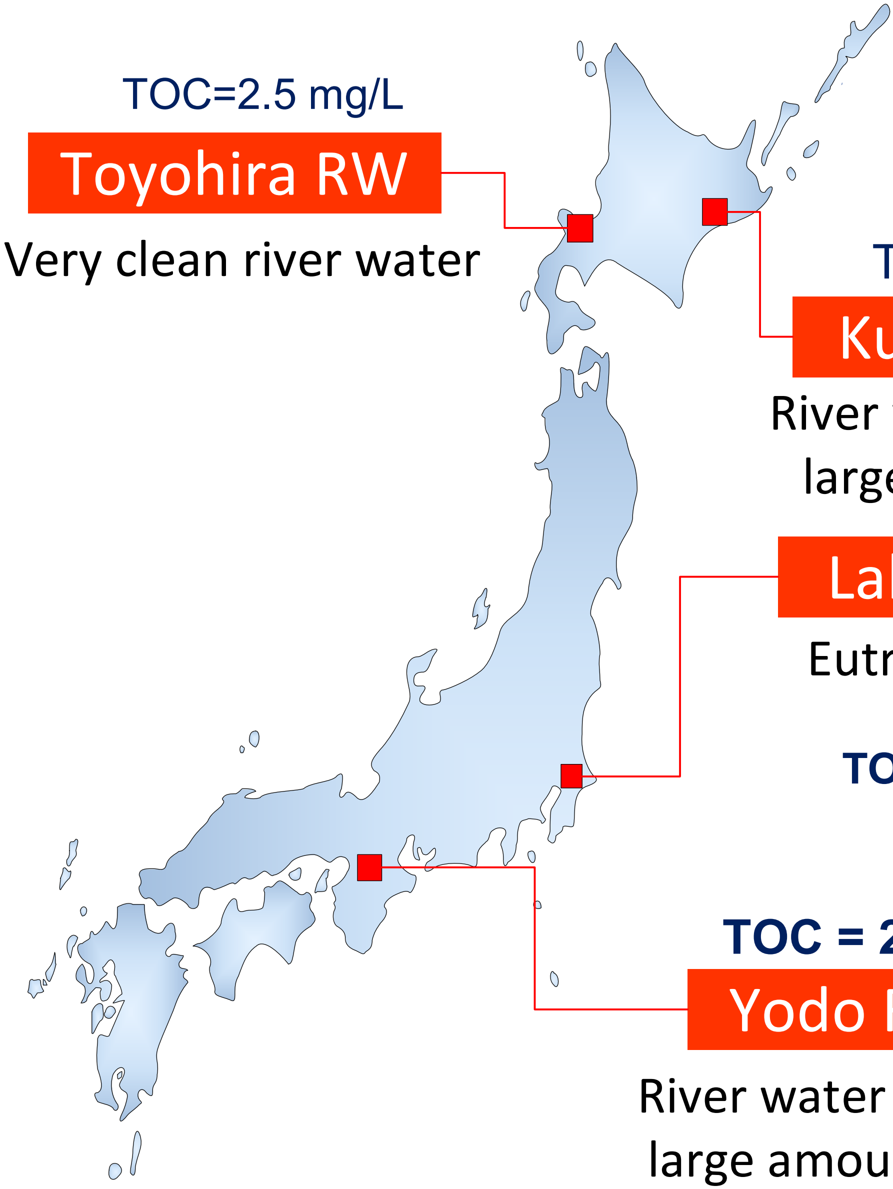
Chemical cleaning will cause **significant problems**

Damage of membrane material
Disposal of chemical reagents…

Control of physically irreversible fouling is important

NOM samples used for fractionation

Four different natural water samples (400L) were used for fractionation



TOC=2.5 mg/L
Toyohira RW
Very clean river water

TOC= 2.8 mg/L
Kushiro RW
River water containing large amount of HA

Lake Inbanuma
Eutrophic lake water
TOC = 5.7 mg/L

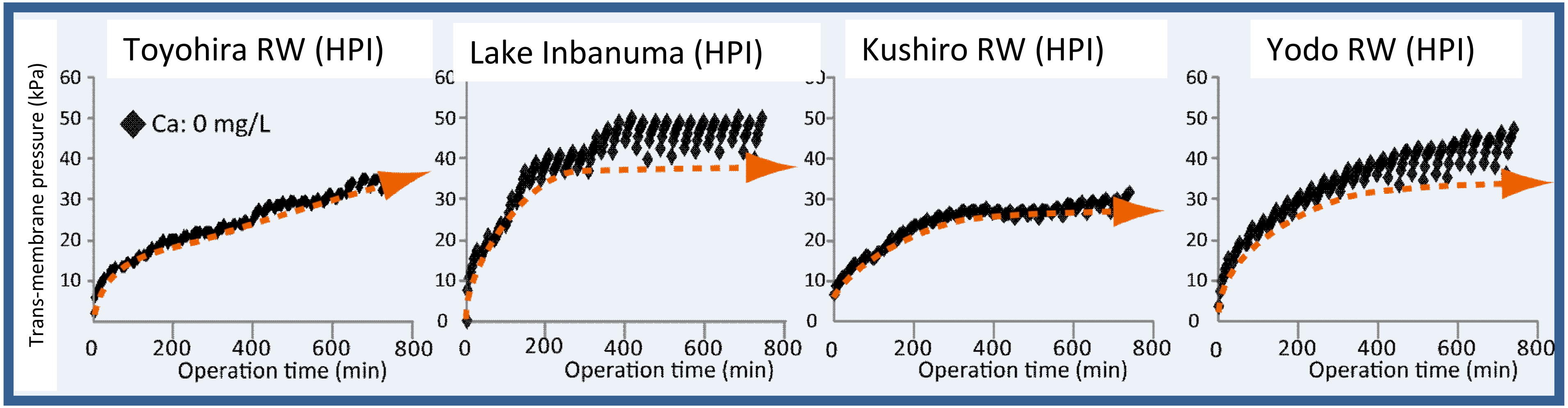
TOC = 2.6 mg/L
Yodo RW
River water containing large amount of EfOM

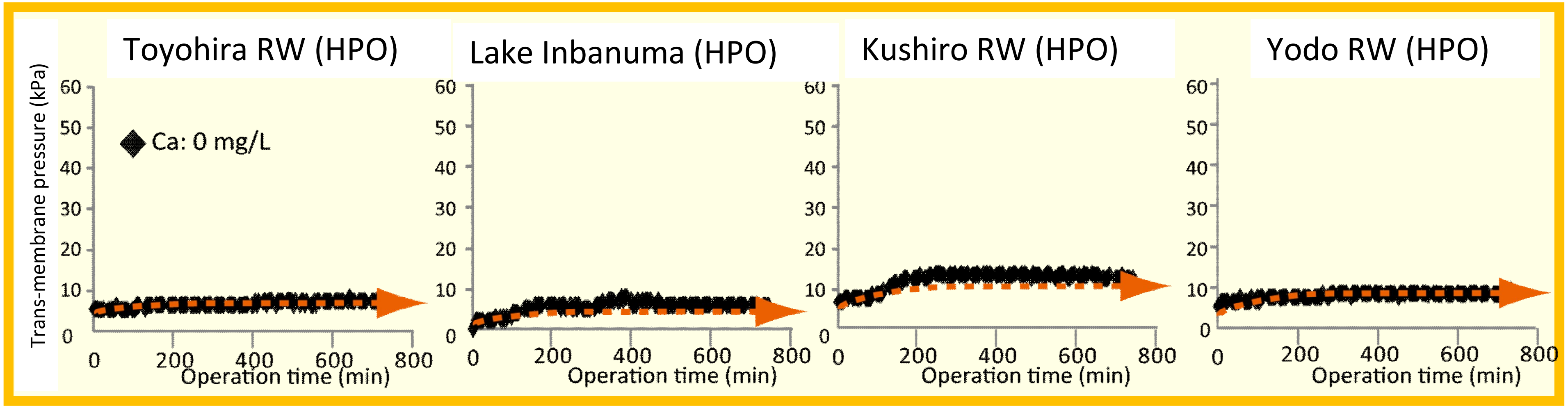
Removal of particles with cartridge filter

Removal of divalent ions with cation exchange resins

Concentration of NOM with RO membrane

Fraction contributing to membrane fouling

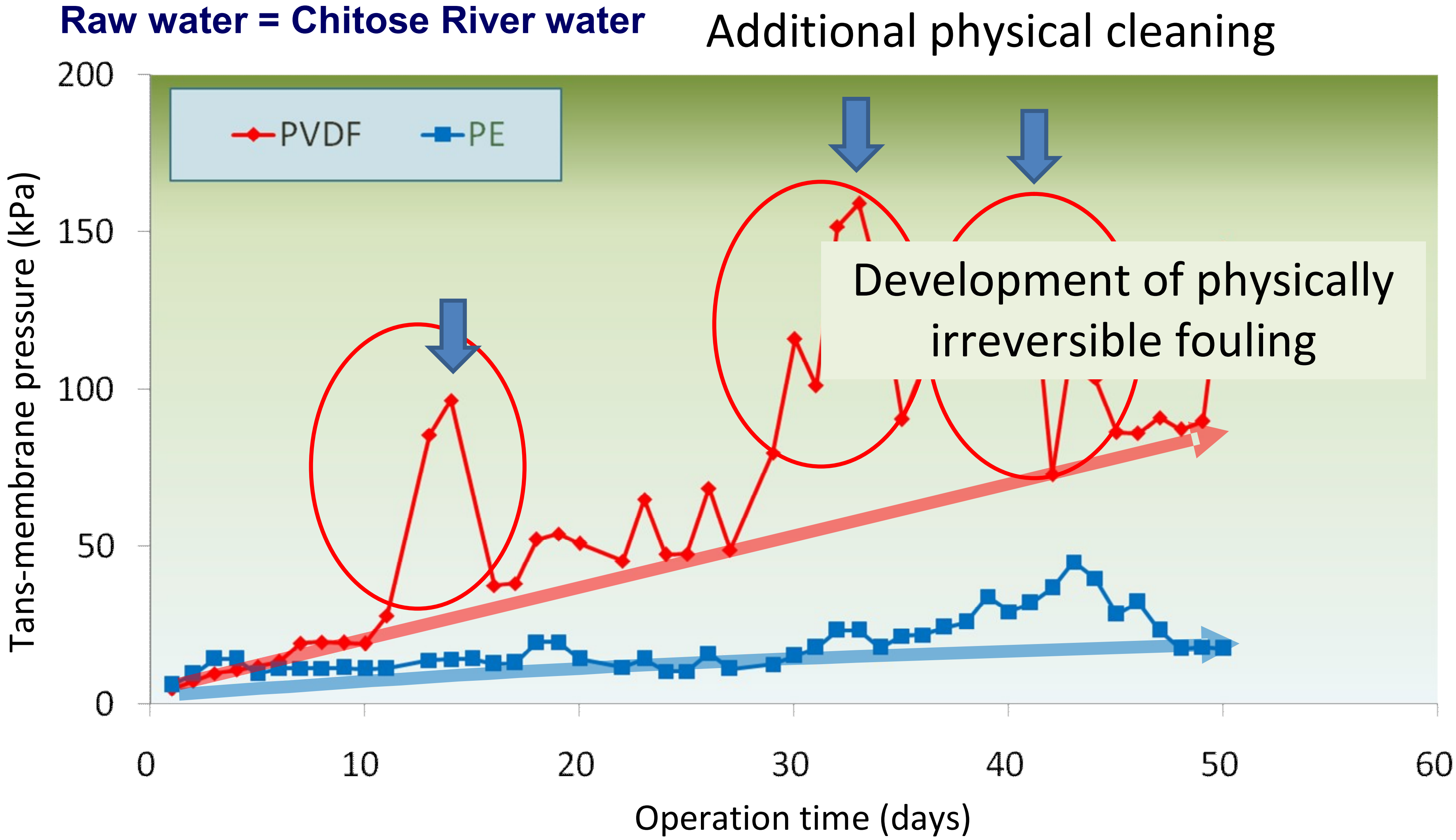




HPI fraction of NOM contributed to the physically irreversible fouling regardless of the types of NOM sources

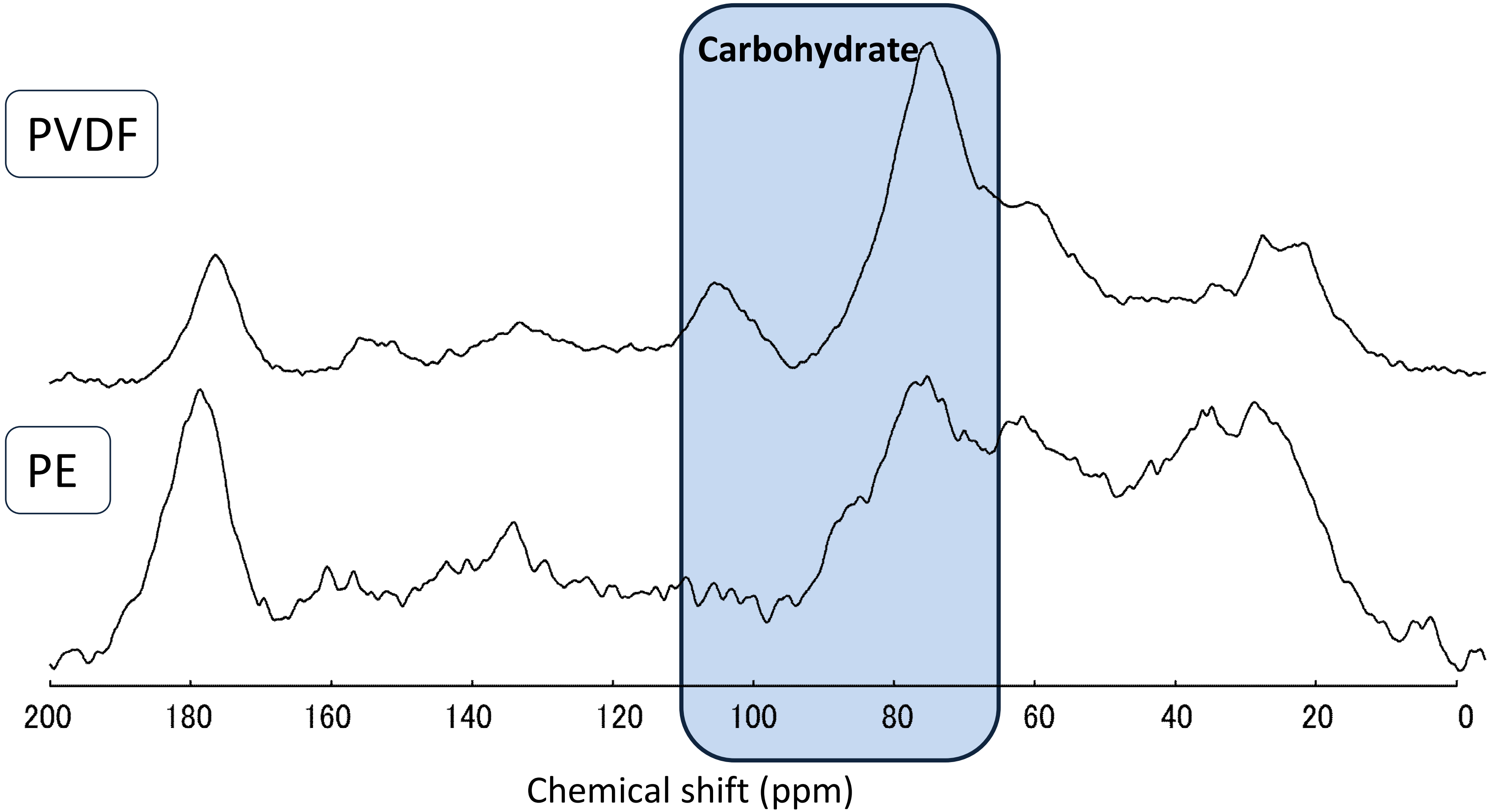
Variation of TMP in two membranes in pilot plant

Raw water = Chitose River water



Rate of accumulation of physically irreversible fouling was fairly different depending on membrane materials

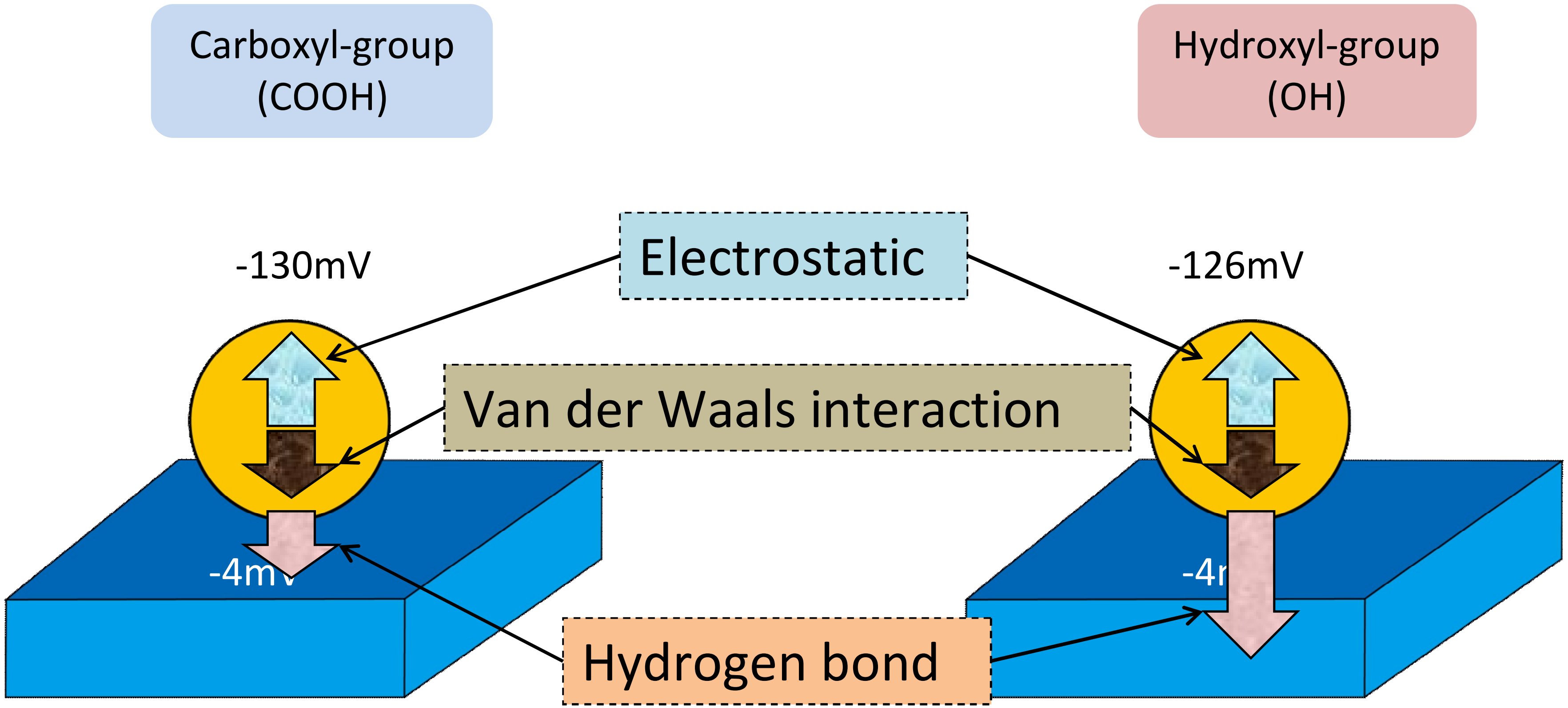
NMR results - Organic matters extracted by NaOH



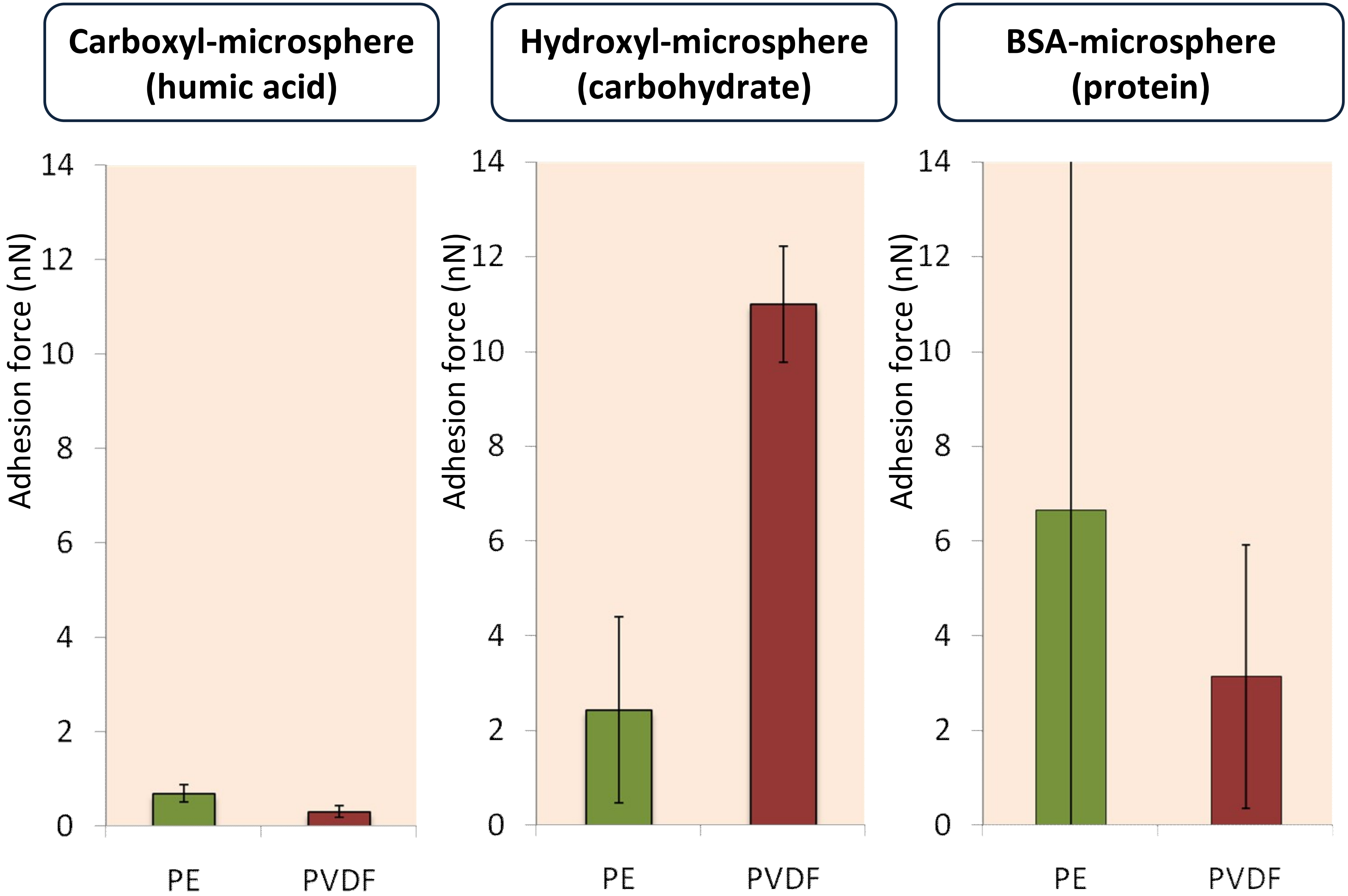
Carbohydrate-like substances mainly contributed to the physically irreversible fouling

Forces exerted on particles

1. Electrostatic repulsion
2. Van der Waals interaction
3. Hydrogen bond



Membrane material vs. adhesion force of foulants



Summary 1 (Continuous Experiments)

1. **Degree of physically irreversible fouling was different (PVDF membrane > PE membrane)**

2. **Carbohydrate-like substances mainly contributed to the development of physically irreversible fouling for both membranes**

3. **HPI fraction of NOM contributed to the physically irreversible fouling regardless of the types of NOM sources**

Summary 2 (Fouling mechanisms)

1. **Hydroxyl groups showed much higher adhesion force than carboxyl groups possibly because the generation of hydrogen bond**

2. **Affinity of hydroxyl group was much higher for PVDF membrane than for PE membrane, possibly due to the high electronegative nature of PVDF**

3. **Significant adhesion force of hydroxyl group was seen even when the membrane was fouled to a large extent**

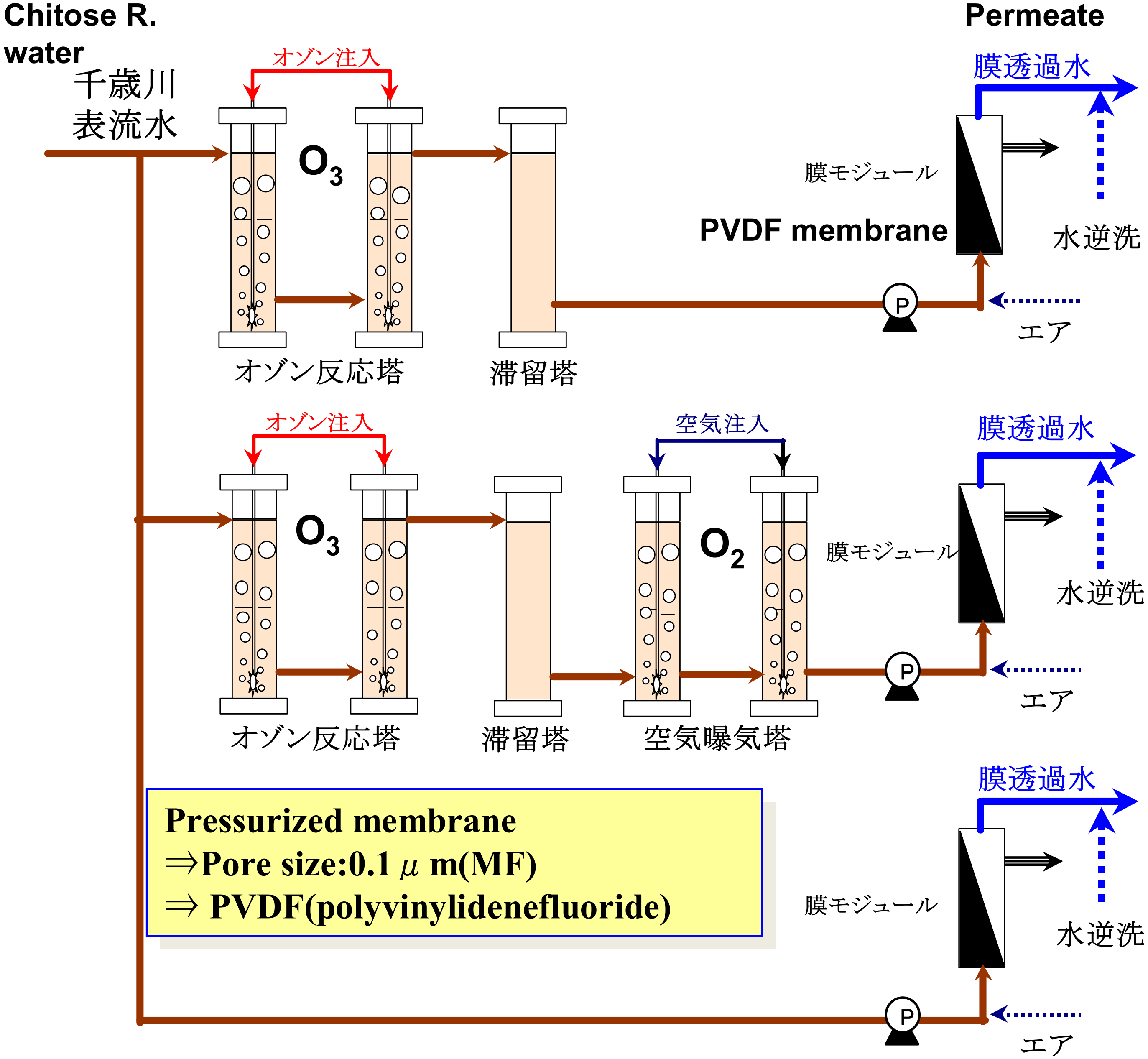
There is a possibility to prevent fouling by using membrane that has low affinity for hydroxyl group

Membrane filtration systems with high flux operation

(1) Pre-ozonation + PVDF membrane

(2) Monolith ceramic membrane with chemically enhanced backwashing

Pre-Ozonation- PVDF MF Membrane System



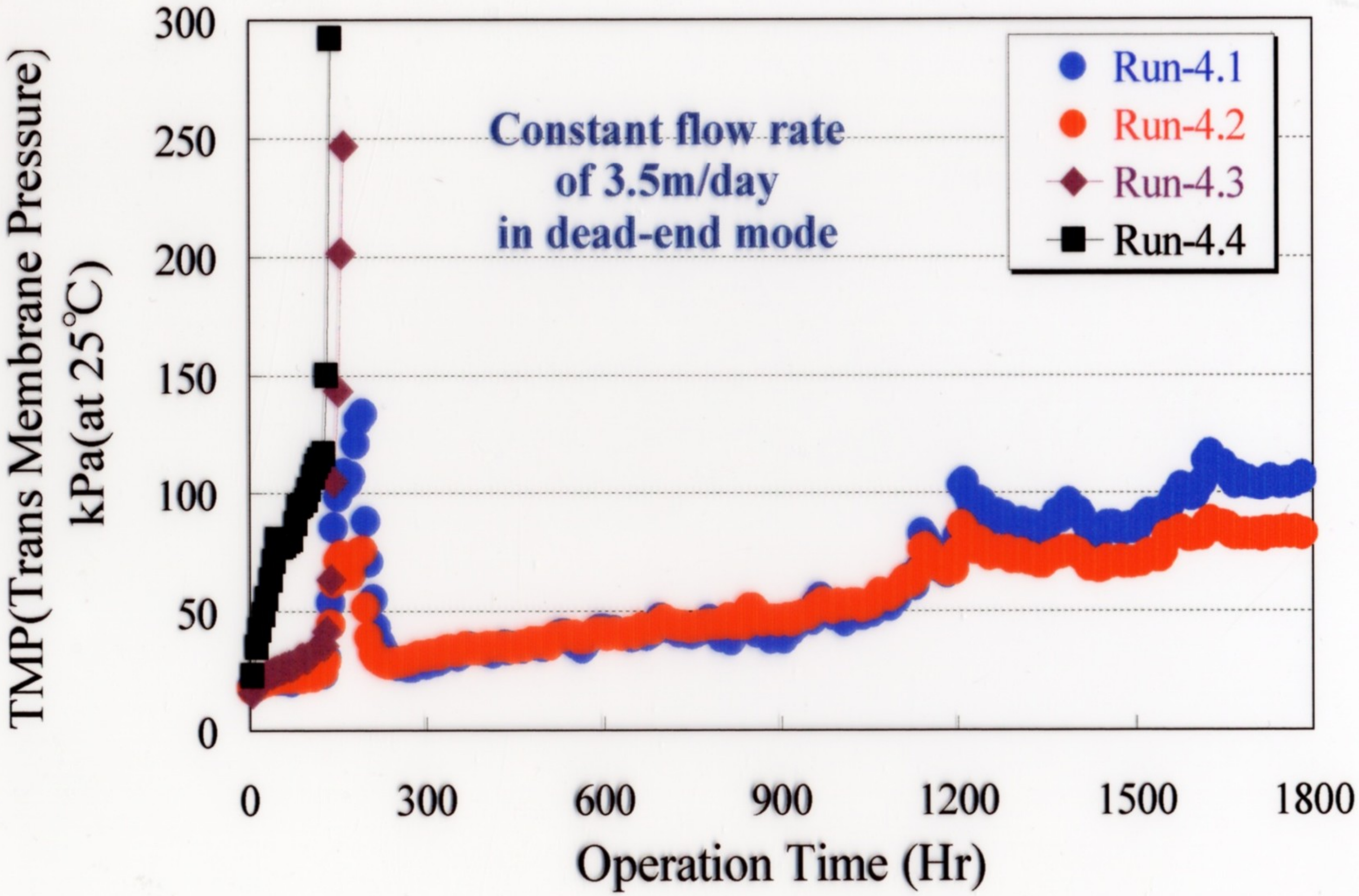
Ozonation－Membrane
Residual O_3
Run－4.1、4.2
Run－5.1、5.2

Ozonation－Membrane
No residual o_3
Run－4.3
Run－5.3

Pressurized membrane
⇒Pore size:0.1 μ m(MF)
⇒ PVDF(polyvinylidenefluoride)

Membrane
Run－4.4
Run－5.4

Trends of TMP in MF membrane system with pre-ozonation



Residual Ozone Conc. (Run-4.1)

- **Raw Water 0～1.34mg/L(0.73 mg/L)**
- **Permeate 0～0.83mg/L(0.31mg/L)**

Residual Ozone Conc. (Run-4.2)

- **Raw Water 0～1.78mg/L(1.14mg/L)**
- **Permeate 0～1.26mg/L(0.61mg/L)**

High Flux Experiment of Monolith Ceramic Membrane Using Acid CEB

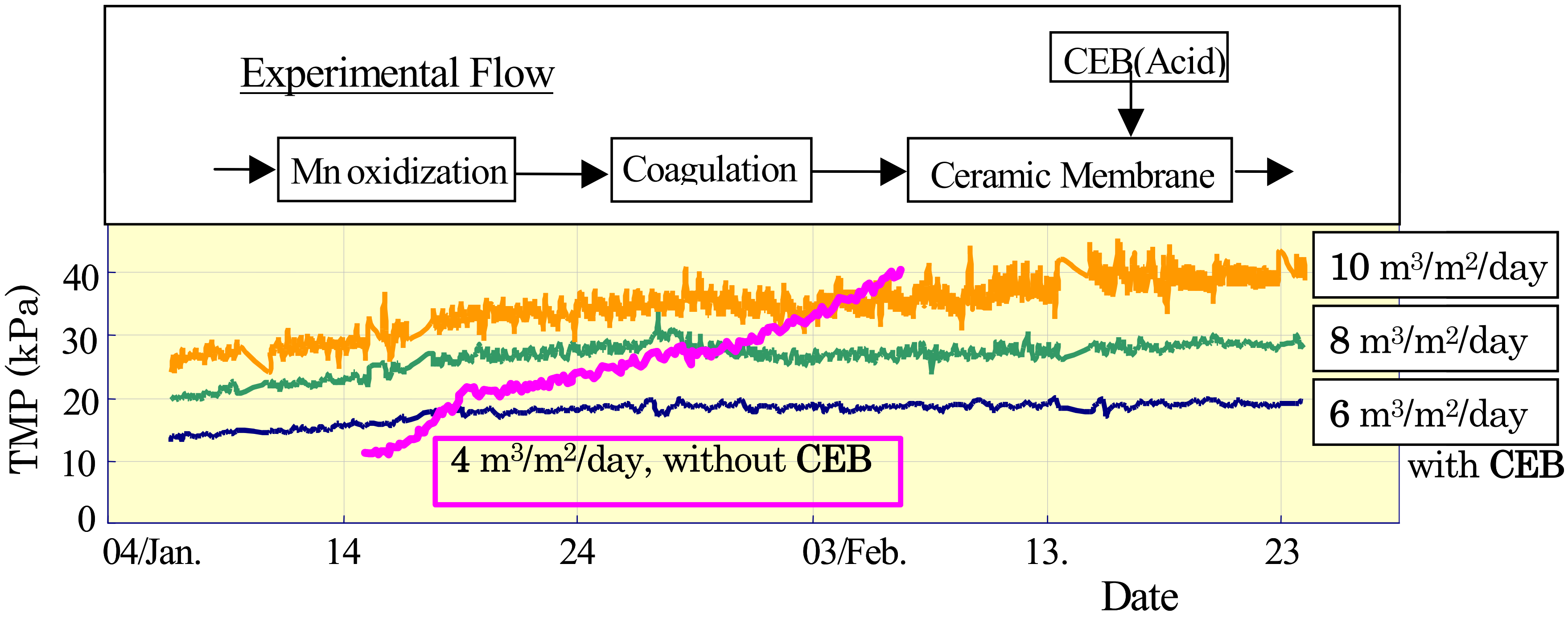


Fig.6 High Flux experiment using acid CEB.

Conclusions

To gain the knowledge about the constituents and mechanisms related to physically irreversible fouling

1: Characteristics of components causing physically irreversible fouling

2: Affinity of carbohydrate-like substances to membrane surface

3: High flux membrane filtration system with pre-Ozonation or CEB