

Characteristics of **Nutrient Removal** in Vertical Membrane Bioreactors

Prof. Hang-Sik Shin

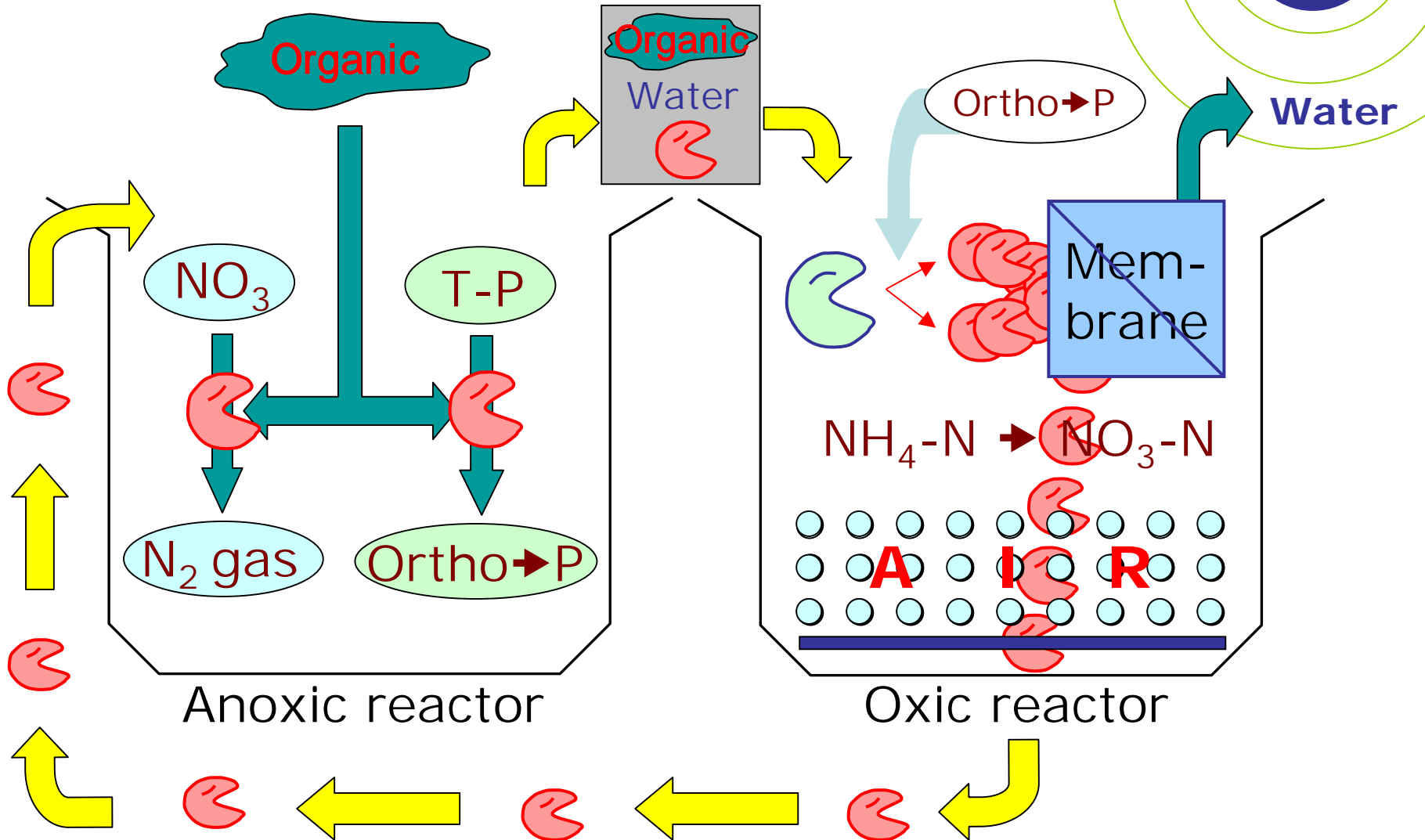
Dept. of Civil and Environmental Engineering
Korea Advanced Institute of Science and Technology



Content

- **Research Background**
- **Operating factors** for vertical MBR
- **Nutrient removal** in vertical MBR
- **Remediation of fouling** in vertical MBR
- **Conclusions**

Mechanisms of membrane bioreactors

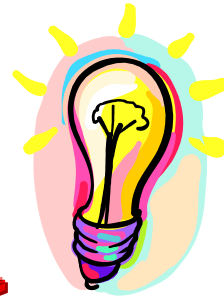


Research Objectives and Scope



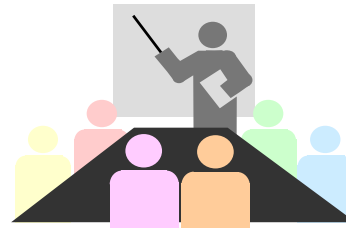
Operating factors

- Hydraulic retention time
- Internal recycle rate
- C/N ratio



Membrane fouling

- Characterization
- Dynamic membrane
- Remediation



Novel MBR

(Anoxic/Oxic vertical)

Nutrient removal

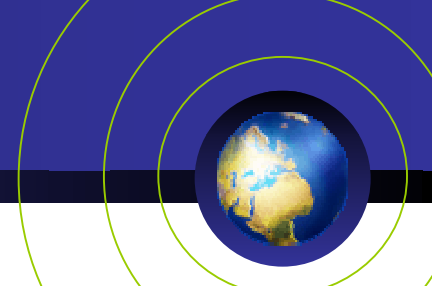
- Various carbon source
- EBPR activity
- Population dynamics

Modelling

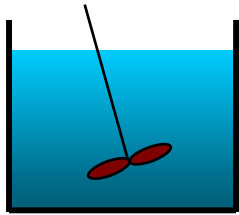
- Kinetic study
- Sludge production
- EPS accumulation

Operating factors in vertical MBR

Objective and Scope

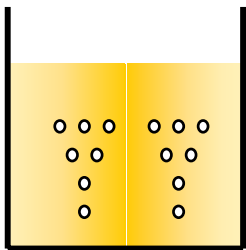


Anoxic tank



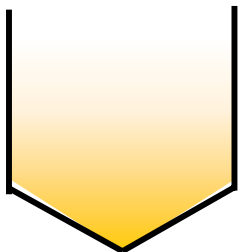
- Denitrification
- Phosphorus release

Aerobic tank

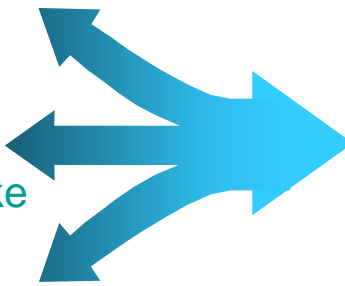


- Nitrification
- Organic oxidation
- Phosphorus uptake

Settling tank



- Liquid/solid separation



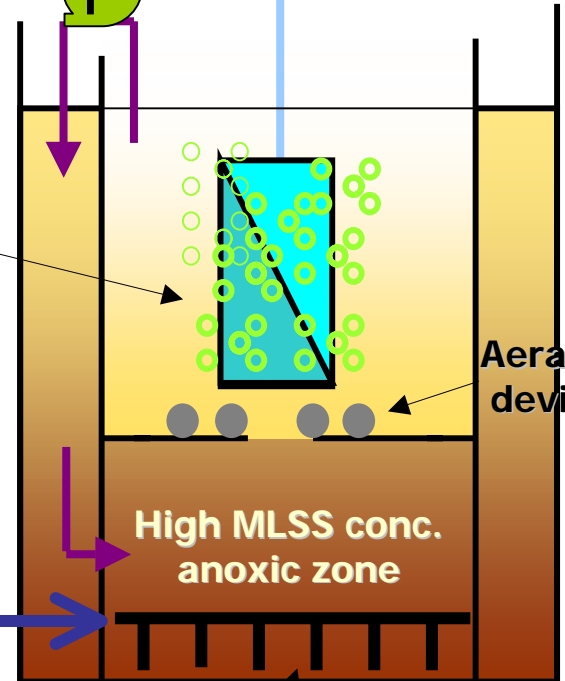
Aerobic zone

Internal recycle

Effluent

Influent

Distribution devices



Test phases

Phase	Internal recycle rate	TCOD/T-N ratio	HRT	Operation period
1	3Q	10	12 hrs	1-120 days
2	4Q			121-150 days
3	5Q			151-180 days
4	4Q	8	12 hrs	181-210 days
5		6		211- 240 days
6		4		241-270 days
7	4Q	10	10 hrs	271-300 days
8			8 hrs	301-330 days
9			6 hrs	331-360 days

[Q is the influent flow rate]

Characteristics of the membrane used

Category	Characteristic
Membrane material	<u>Hydrophilic poly-tetrafluoroethylene (PTFE)</u>
Nominal pore size	0.45 μm
Module type	Hollow fiber
Intensity	5 kg/cm
Outer/Inner diameter	2/1 mm
Maximum temperature	95°C
Operation range of pH	0 - 14

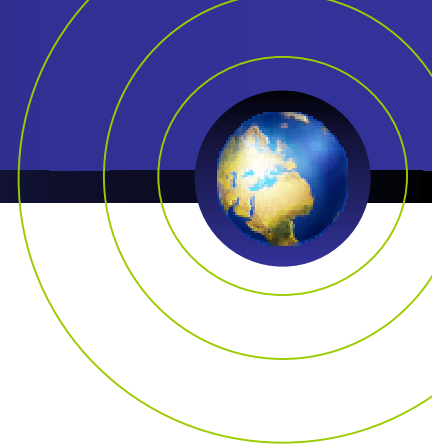
Summary of Results



- I.R. (3Q → 4Q → 5Q): T-N= 68 → 83%, T-P= 51 → 80%
- C/N ratio (4 → 10): T-N= 55 → 80%, T-P= 38 → 76%
: Phosphorus removal is more dependent on the content of organics than nitrogen
- HRT (12 → 6 hrs): at least 8 hrs HRT was needed
- Desirable operating conditions; internal recycle rate = 4Q, HRT > 8 hrs
- Sludge production = 1 - 6% of the CASP

Nutrient removal in vertical MBR

Objective and Scope



Scale	Reactor	Substrate
<u>Laboratory</u>	MBR1	Sodium acetate
Ax (12L) + Ox (20L)	MBR2	Propionic acid
	MBR3	Glucose

Scale	Substrate
<u>Pilot</u> Ax (500L) + Ox (833L)	Municipal wastewater

Nutrient removal

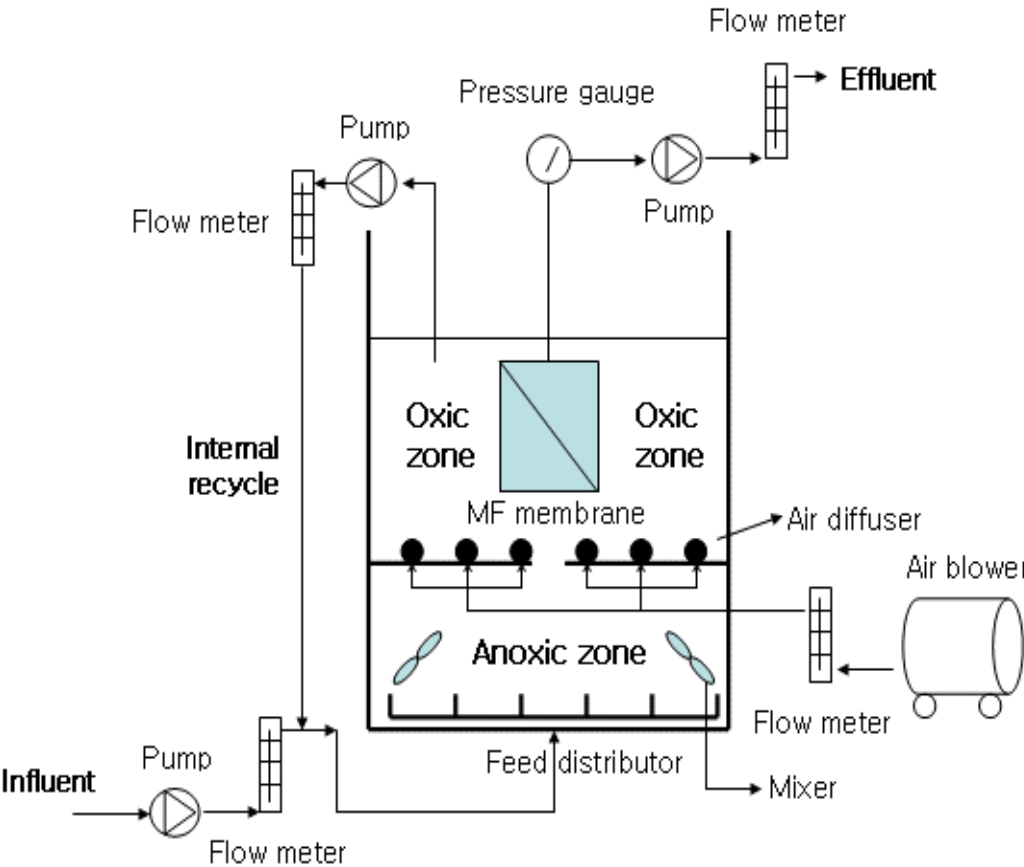
EBPR activity

[EBPR= Enhanced Biological Phosphorus Removal]

Materials and Methods



Characteristics of laboratory-scale MBRs



Item	Ax	Ox
Capacity	96 L/day	
Internal recycle rate	400%	
SRT(d)	30	
Volume (L)	12	20
HRT (hr)	3	5
MLSS (g/L)	5.7	2.2
ORP (mV)	-147	+257

[MLSS= mixed liquor suspended solid]

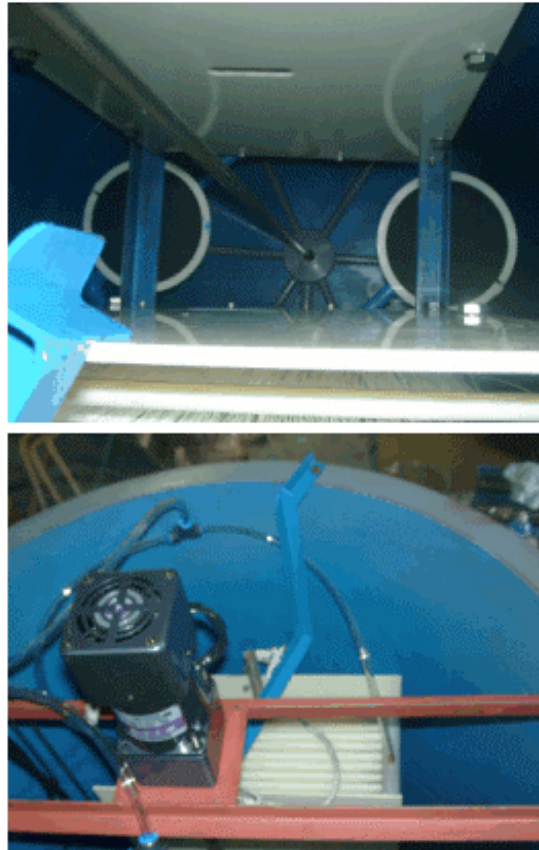
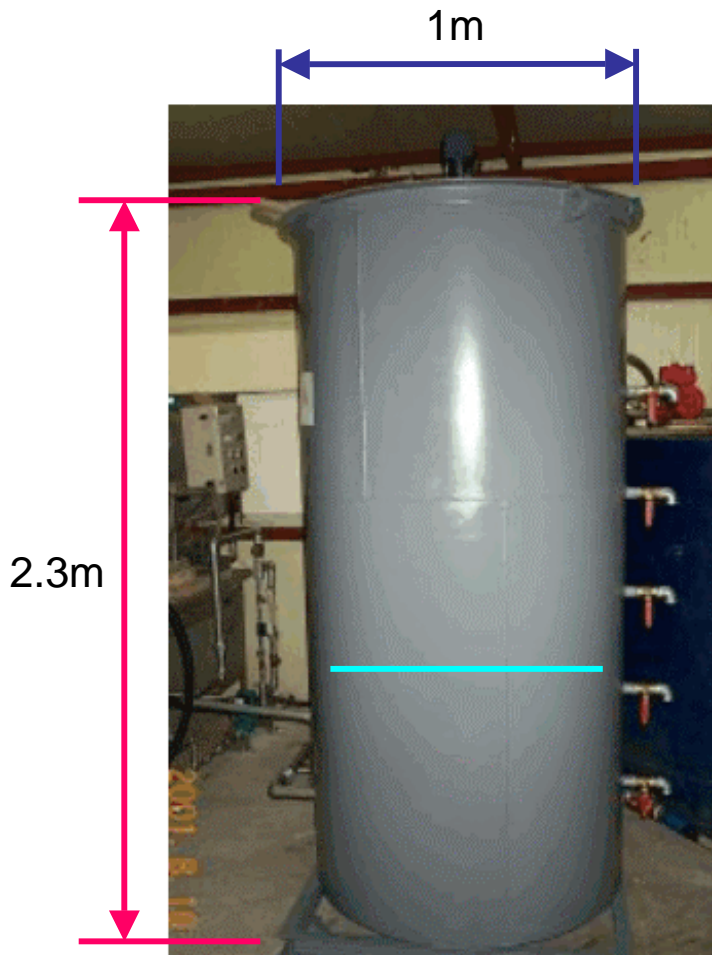
Characteristics of synthetic wastewater

Compound	MBR1	MBR2	MBR3
<u>Organic matter</u>	<u>Sodium acetate</u>	<u>Propionic acid</u>	<u>Glucose</u>
Chemical formula	$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	$\text{CH}_3\text{CH}_2\text{COOH}$	$\text{C}_6\text{H}_{12}\text{O}_6$
Molecular weight	136.1 g/mol	74.1 g/mol	180.0 g/mol
COD value per mol	64 g COD/mol	96 g COD/mol	192 g COD/mol
For <u>C/N ratio 10</u> as COD	300 mg/l	300 mg/l	300 mg/l
For <u>C/N ratio 5</u> as COD	150 mg/l	150 mg/l	150 mg/l
<u>Nitrogen and Phosphorus</u>			
(NH ₄) ₂ SO ₄	30 mg/l	30 mg/l	30 mg/l
KH ₂ PO ₄	6 mg/l	6 mg/l	6 mg/l

Experimental conditions for lab-scale MBRs

Phase	C/N ratio	Internal recycle rate	HRT	Operation period
1	10	<u>400%</u>	<u>8 hours</u>	1-150 days
2	5			151-300 days
3	5 (influent) + 5 (CFW)			301-420 days

Characteristics of a pilot-scale MBR



Item	Ax	Ox
Capacity	4 m ³ /day	
Internal recycle rate	400%	
SRT(d)	60	
Volume (L)	500	833
HRT (hr)	3	5
MLSS (g/L)	8.68	4.21
ORP (mV)	-153	+274



Experimental conditions for a pilot-scale MBR

Phase	HRT	C/N ratio	Operation period	Remark
1A	10 hrs	5.5	1 - 28 days	Accumulation period
1B	10 hrs	5.5	29 - 68 days	Set-up of an internal barrier
2	8 hrs	5.5	69 - 360 days	Temperature effect
3	6 hrs	5.5	361 - 480 days	-
4	4 hrs	5.5	481 - 600 days	-
5	8 hrs	6.8	601 - 630 days	<u>Addition of CFW (0.43 %)</u>
6	8 hrs	8.2	631 - 660 days	<u>Addition of CFW (0.86 %)</u>

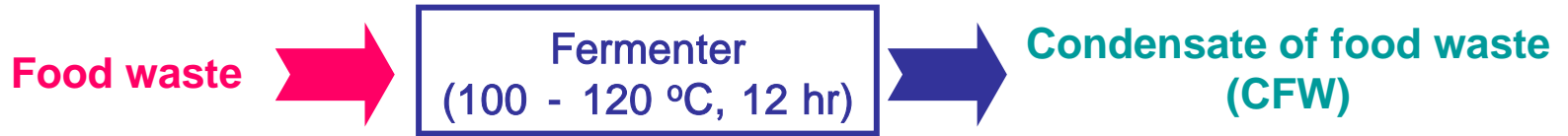


Characteristics of municipal wastewater

Constituents		Concentration
COD	Total	232 ± 41 mg/l
	Soluble	161 ± 25 mg/l
SS	Total	220 ± 52 mg/l
	Volatile	110 ± 30 mg/l
Nitrogen	Total	42 ± 5 mg/l
	NH ₃ -N	27 ± 3 mg/l
	NO ₃ -N	Not detected
Phosphorus	Total	3.2 ± 0.4 mg/l
	Soluble	1.9 ± 0.4 mg/l
VFAs		Not detected
Initial pH		7.3 ± 0.1

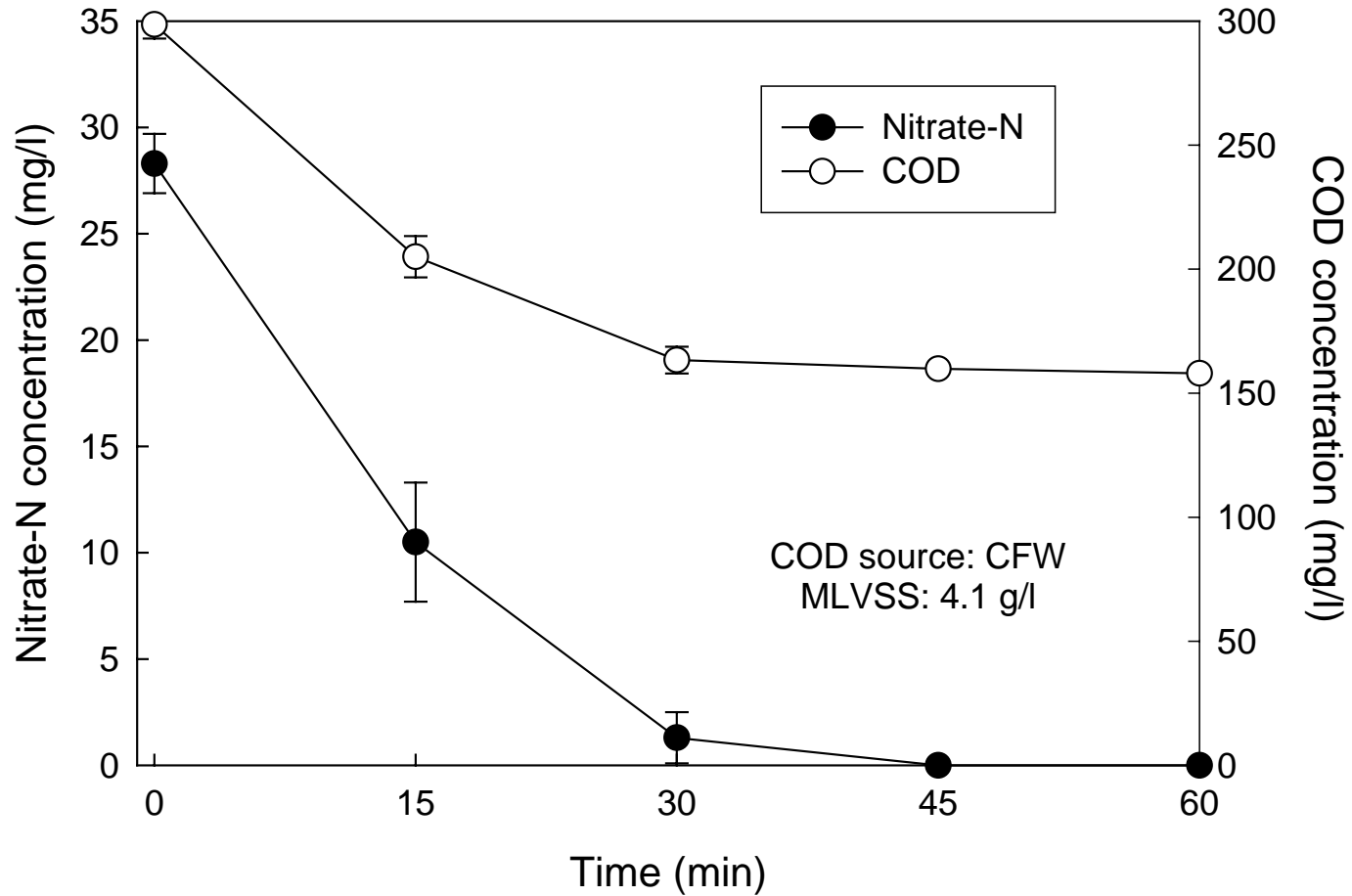
Total COD/Total N = 5.5 → insufficient for nutrient removal

Characteristics of external carbon source



Constituents		Concentration
COD	Total	<u>13,200 ± 260 mg/l</u>
VFAs	as COD	<u>5,100 ± 58 mg/l</u>
SS	Total	Not detected
	Volatile	Not detected
Nitrogen	Total	83 ± 26 mg/l
	NH ₄ -N	55 ± 18 mg/l
Phosphorus	Total	36 ± 15 mg/l
	Soluble	15 ± 9 mg/l
Salt concentration		450 ± 63 mg/l
Initial pH		4.0 ± 0.1

Nitrogen removal potential of the CFW



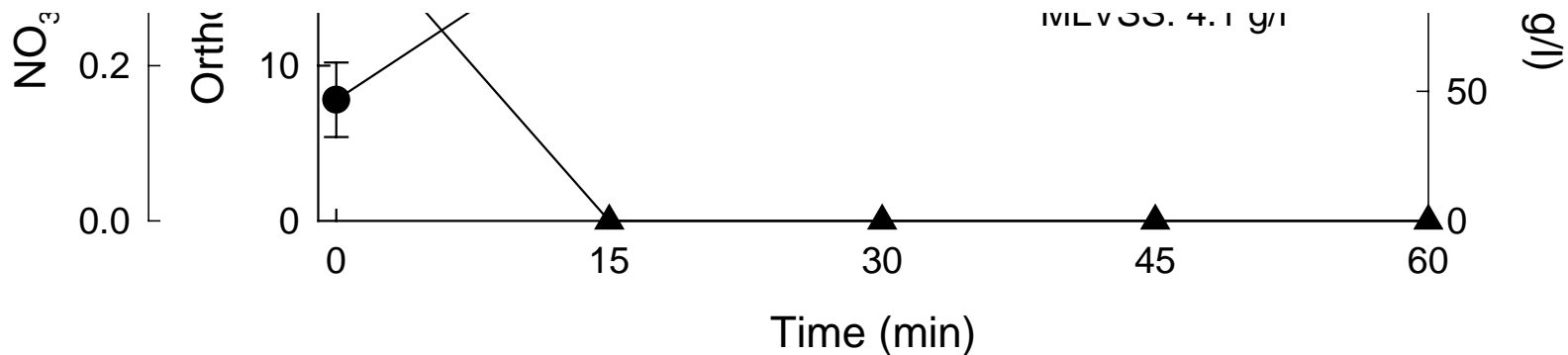
Carbon source	Denitrification yield (mg NO ₃ -N/mg COD)	Reference
Acetate	0.27	Akunna <i>et al.</i> , 1993
	0.28	Lee <i>et al.</i> , 1996
Methanol	0.25	Lee <i>et al.</i> , 1996
Glucose	0.18	Akunna <i>et al.</i> , 1993
CFW	0.20	*This study

Carbon source	Specific denitrification rate (mg N/g VSS/hr)	Reference
Acetate	2.0	Nyberg <i>et al.</i> , 1992
	2.5	Gerber <i>et al.</i> , 1987
	3.4	Isaacs <i>et al.</i> , 1995
	12	Hallin <i>et al.</i> , 1998
	49	Lee <i>et al.</i> , 1996
Propionate	1.7	Gerber <i>et al.</i> , 1987
	3	Hallin <i>et al.</i> , 1998
Methanol	1.0	Nyberg <i>et al.</i> , 1992
	1.3	Gerber <i>et al.</i> , 1987
	7	Hallin <i>et al.</i> , 1998
	29	Lee <i>et al.</i> , 1996
Glucose	1.1	Gerber <i>et al.</i> , 1987
	1.8	Hallin <i>et al.</i> , 1998
CFW	13	*This study

Phosphorus release potential of the CFW



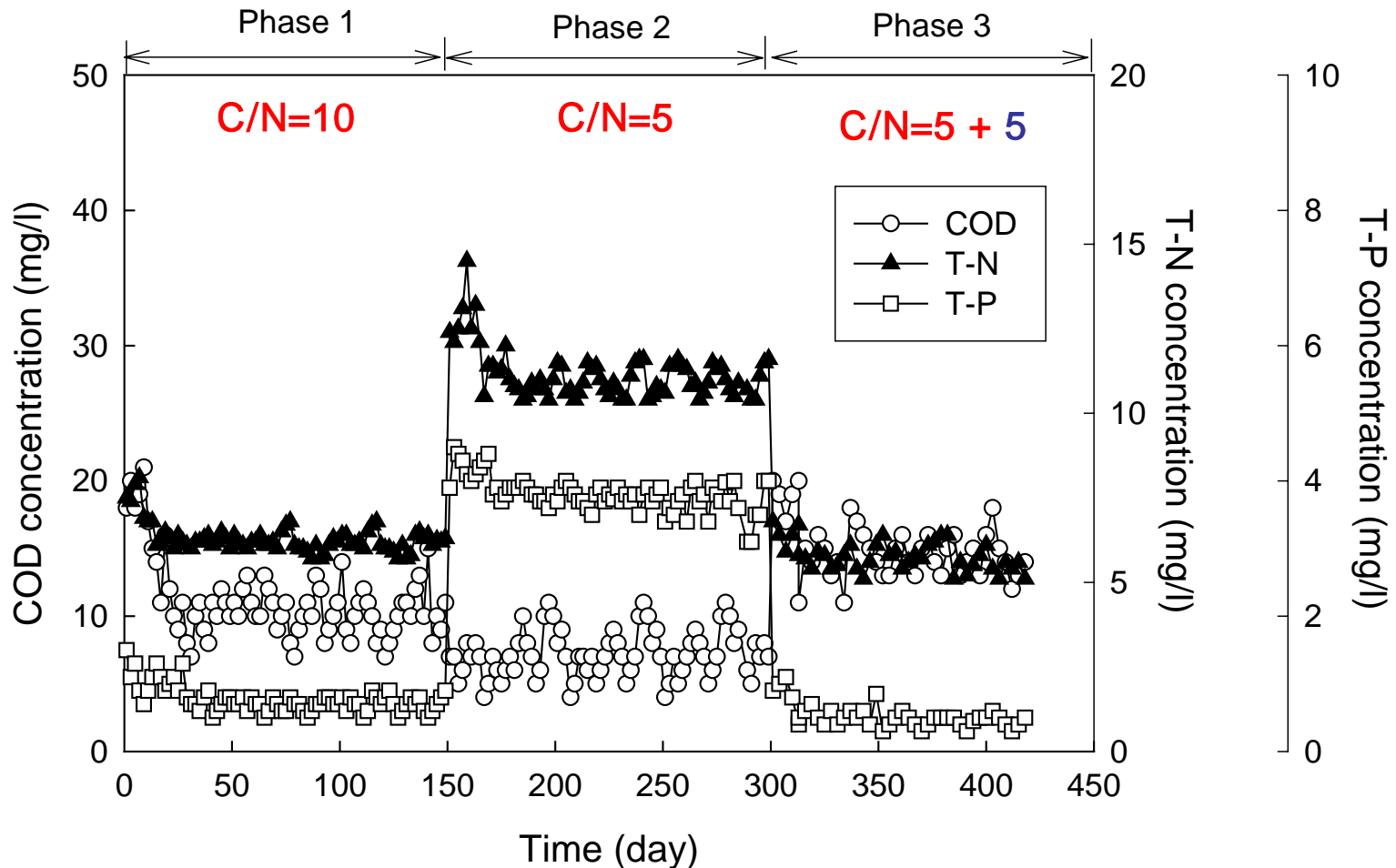
Carbon source	P release yield (mg P/mg COD)	Reference
Acetate	0.47	Isaacs <i>et al.</i> , 1995
	0.50	Wentzel <i>et al.</i> , 1992
VFAs	0.70	Danesh <i>et al.</i> , 1997
Propionic acid	0.15	Chen <i>et al.</i> , 2004
Glucose	0.26	Jeon <i>et al.</i> , 2000
CFW	0.38	*This study



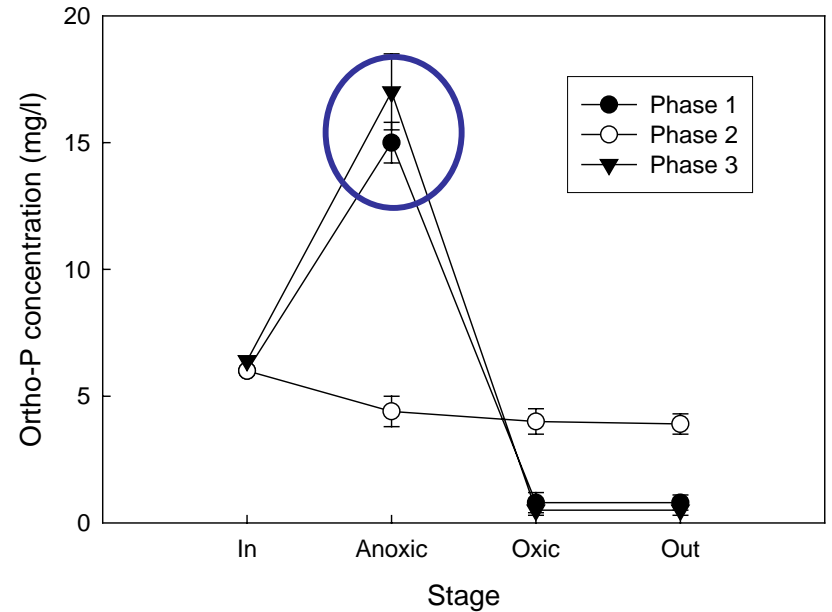
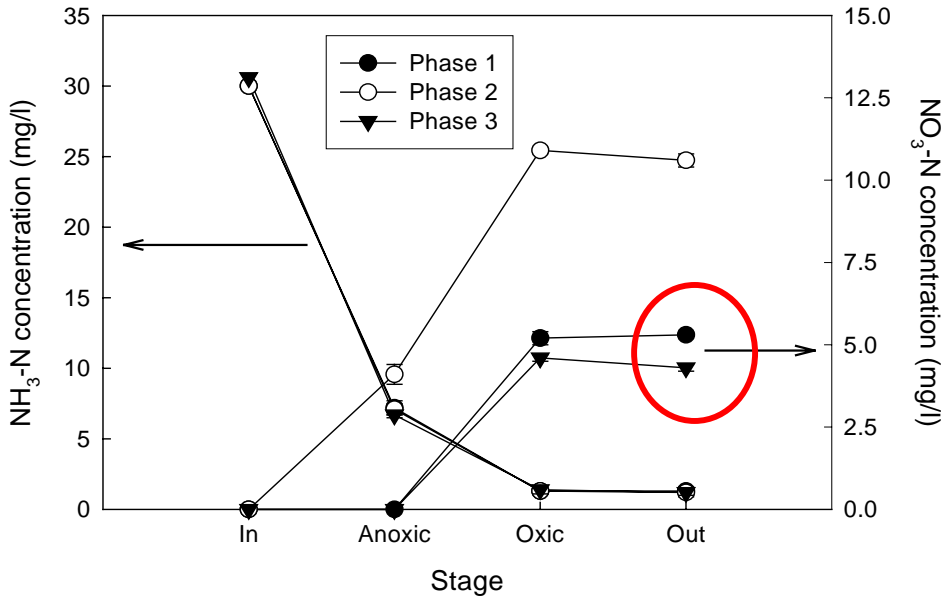
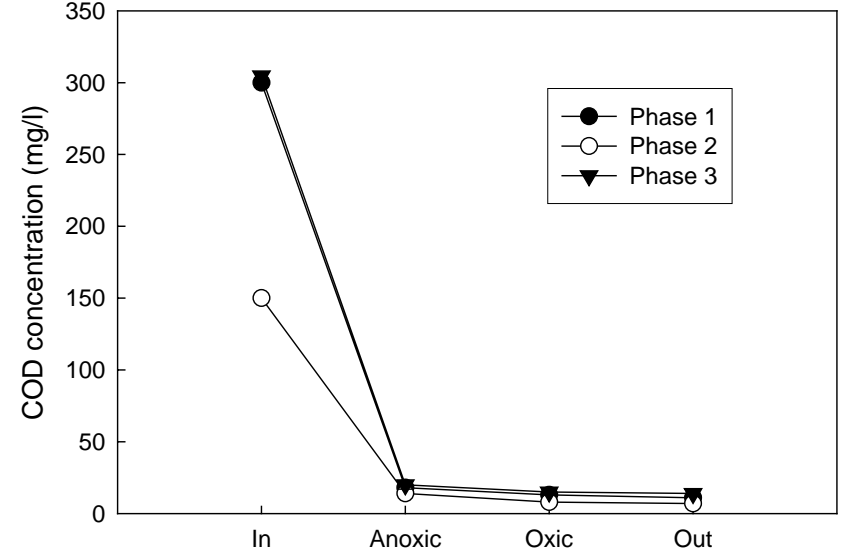
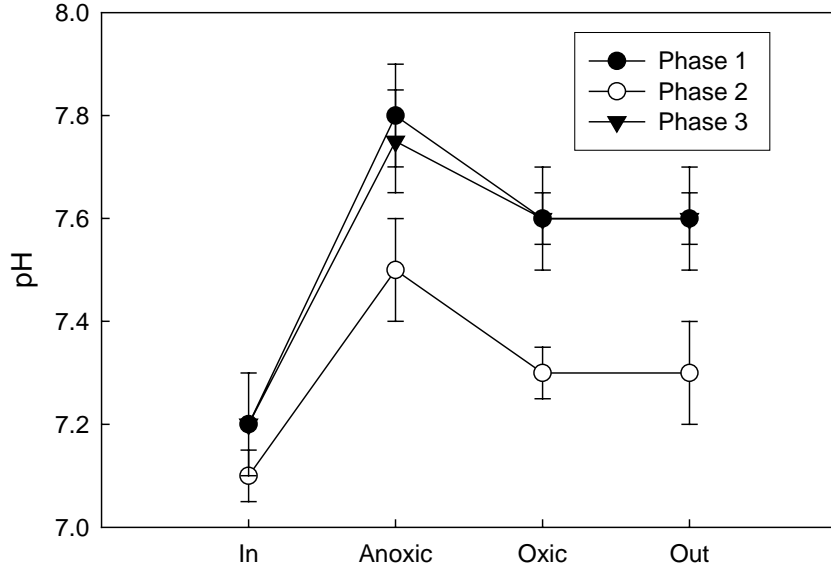
Results and Discussion









Effluent quality of lab-scale MBR fed with sodium acetate















Behaviors of pH and pollutants in the reactor



Removal efficiencies of organics and nutrients

Item	Phase 1			Phase 2			Phase 3		
	COD	T-N	T-P	COD	T-N	T-P	COD	T-N	T-P
Sodium acetate									
In (mg/l)	300	30	6	150	30	6	304.7	30.6	6.4
Avg. out (mg/l)	11.0	6.3	0.8	7.2	11.2	3.9	15.0	5.8	0.5
Std.	2.9	0.4	0.2	1.7	0.7	0.3	2.2	0.4	0.2
Removal (%)	96			95			95		

Item	Phase 1			Phase 2			Phase 3		
	COD	T-N	T-P	COD	T-N	T-P	COD	T-N	T-P
Propionic acid									
In (mg/l)	300	30	6	150	30	6	304.7	30.6	6.4
Avg. out (mg/l)	8	6.6	1.0	6	11.8	4.0	11	5.5	0.4
Std.	2.3	0.5	0.3	1.4	0.4	0.3	1.3	0.4	0.1
Removal (%)	97			96			96		

Item	Phase 1			Phase 2			Phase 3		
	COD	T-N	T-P	COD	T-N	T-P	COD	T-N	T-P
Glucose									
In (mg/l)	300	30	6	150	30	6	304.7	30.6	6.4
Avg. out (mg/l)	6	5.8	1.3	5	11.2	3.8	9	6.1	1.2
Std.	0.4	0.6	0.2	0.9	2.7	0.2	1.9	0.6	0.2
Removal (%)	98			97			97		

[Avg: average; Std: standard deviation]

Characteristics of EBPR activity with various substrates

Experimental conditions for assessment of EBPR activity

Test	Sludge origin			
	Remark	MBR1	MBR2	MBR3
1	Operating condition of the MBR		C/N=10	
	Carbon source	Sodium acetate	Propionic acid	Glucose
	COD concentration	100 mg/l		
2	Operating condition of the MBR		Phase 2 C/N=5	
	Carbon source	Sodium acetate	Propionic acid	Glucose
	COD concentration	100 mg/l		
3	Operating condition of the MBR		C/N=5+5	
	Carbon source	Sodium acetate	Propionic acid	Glucose
	COD concentration	100 mg/l		
4	Operating condition of the MBR		C/N=5+5	
	Carbon source	Sodium acetate + [redacted]	Propionic acid + [redacted]	Glucose + [redacted]
	COD concentration	50 mg/l + 50 mg/l	50 mg/l + 50 mg/l	50 mg/l + 50 mg/l

[CFW= Condensate of Food Waste]

Results of the assessment of EBPR activity with various substrates

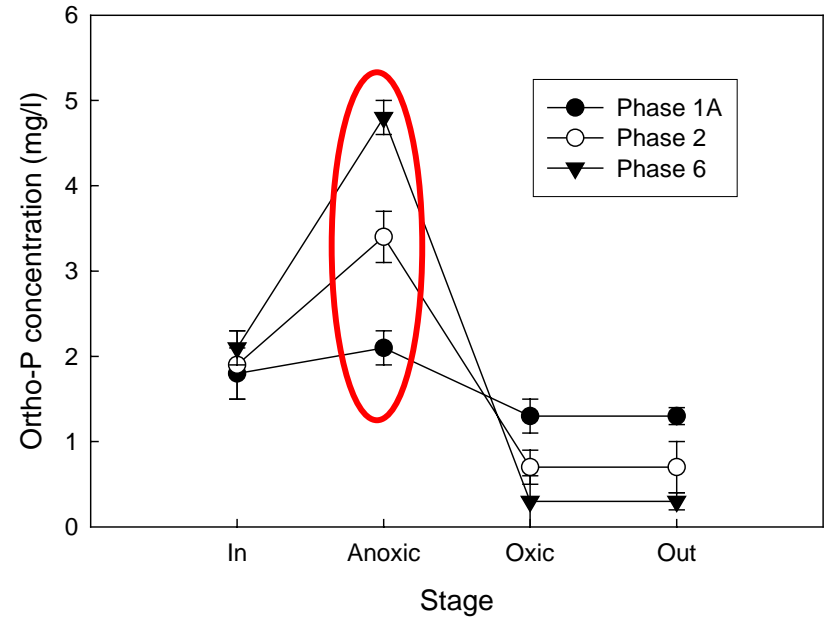
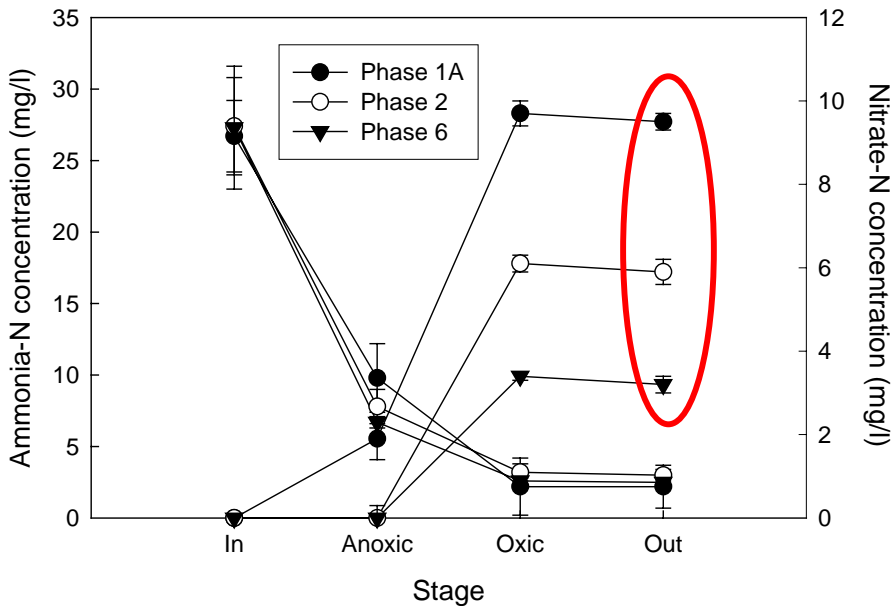
Batch test	P release (mg P/g VSS)			P uptake (mg P/g VSS)		
	Acetate	Propionic acid	Glucose	Acetate	Propionic acid	Glucose
1	8	6	4	10	7	5
2	5	3	2	6	3	2
3	13	9	7	15	11	7
4	15	16	11	17	16	13

Removal efficiencies of nutrients

HRT	Total nitrogen					Total phosphorus				
	In (mg/l)		Out (mg/l)		Re (%)	In (mg/l)		Out (mg/l)		Re (%)
	Avg	Std	Avg	Std		Avg	Std	Avg	Std	
10 hr	41.8	3.9	13.2	1.4		3.1	0.4	1.3	0.2	
10 hr	40.7	4.4	9.8	1.8		3.1	0.4	0.7	0.1	
8 hr	41.4	4.4	10.6	2.6		3.2	0.4	0.7	0.2	
6 hr	42.4	4.8	12.3	1.8	71	3.2	0.5	1.1	0.2	66
4 hr	41.6	4.9	15.7	1.8	62	3.1	0.4	1.8	0.3	42
8 hr +CFW 0.43%	40.5	5.1	9.8	2.2	76	3.2	0.3	0.4	0.1	88
8 hr +CFW 0.86%	43.5	4.6	8.1	1.0		3.3	0.4	0.3	0.1	

[Avg: average; Std: standard deviation; Re: removal efficiency]

Behaviors of nitrogen and phosphorus in the pilot-scale reactor



- Phase 1A = 10 hr HRT w/o internal barrier
- Phase 2 = 8 hr HRT
- Phase 6 = 8 hr HRT + CFW 0.86%

Removal efficiencies of nutrients at various temperatures

- HRT=8 hrs

Phase 2	Ammonia-N					Nitrate-N					Total phosphorus				
	In (mg/l)		Out (mg/l)		Re (%)	In (mg/l)		Out (mg/l)		Re (%)	In (mg/l)		Out (mg/l)		Re (%)
	Avg	Std	Avg	Std		Avg	Std	Avg	Std		Avg	Std	Avg	Std	
17 °C	27.5	3.1	5.2	0.4	81	0	-	5.1	2.0	-	3.2	0.4	0.7	0.1	78
25 °C	27.4	3.1	4.2	0.7	85	0	-	5.4	2.5	-	3.2	0.2	0.7	0.1	78
19 °C	27.8	3.2	3.9	0.5	88	0	-	6.0	2.1	-	3.2	0.5	0.6	0.1	81
13 °C	26.8	2.9	5.7	0.2	79	0	-	7.8	1.3	-	3.0	0.4	0.7	0.1	77

[Avg: average; Std: standard deviation; Re: removal efficiency]

Photographs of the formation of dynamic membranes

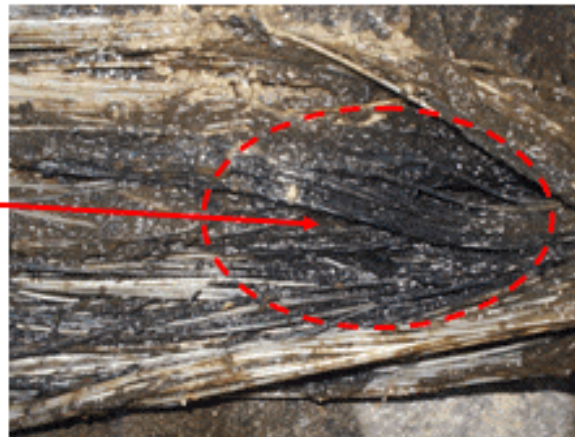
Before use



After use



Inner side
(Black)



Outer side
(Brown)

The role of dynamic membrane in removal of pollutants

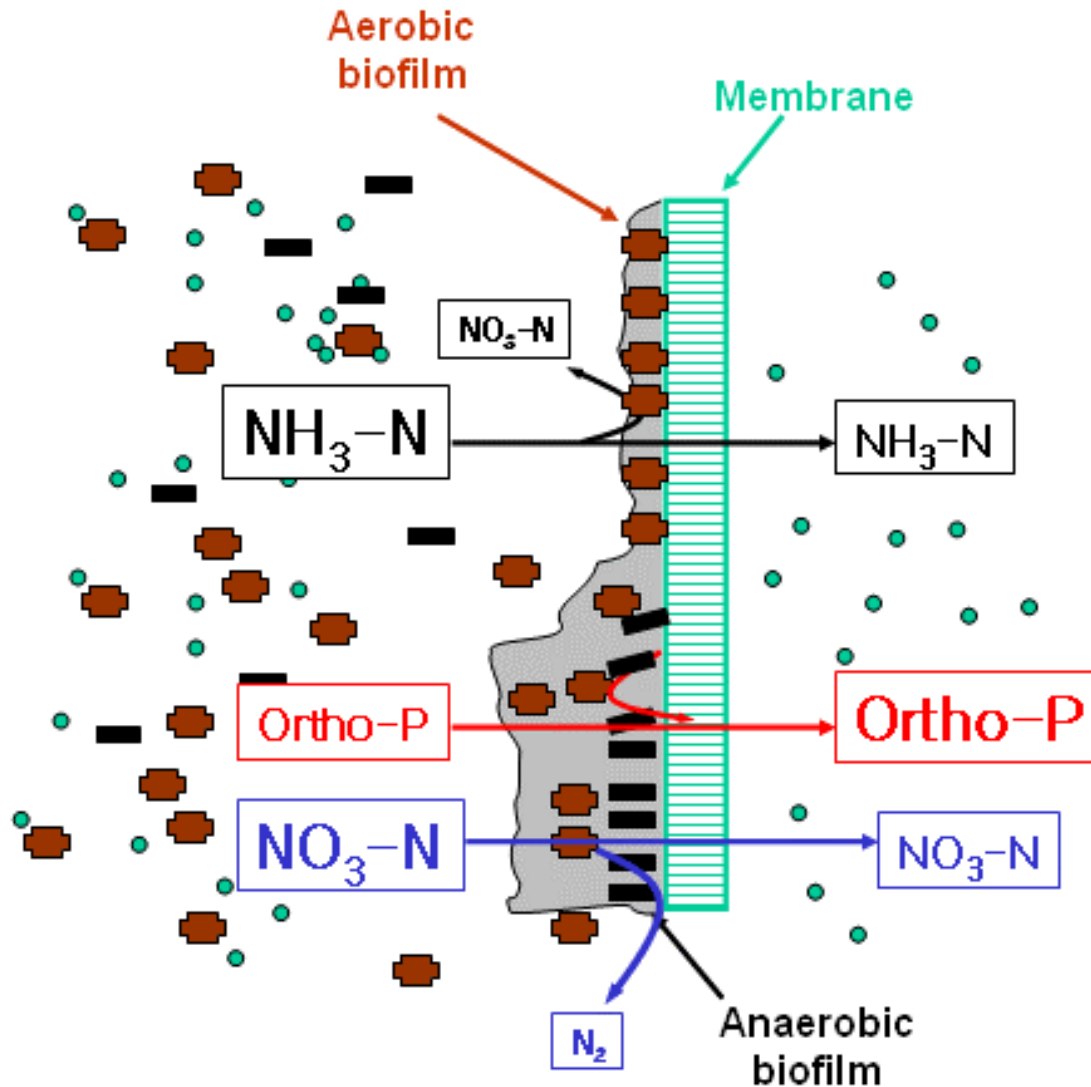
Phase	[Redacted]			[Redacted]			[Redacted]			[Redacted]		
	Ox	Eff	Re	Ox	Eff	Re	Ox	Eff	Re	Ox	Eff	Re
	(mg/l)		(%)	(mg/l)		(%)	(mg/l)		(%)	(mg/l)		(%)
1B	7.0	6.1	13	3.4	3.1	9	4.9	4.7	4	0.70	0.73	-4
2	9.5	8.7	8	3.2	3.0	6	6.1	5.8	5	0.71	0.74	-4
3	12.4	11.6	6	2.8	2.7	4	7.5	7.3	3	1.20	1.24	-3
4	14.2	13.1	8	6.5	6.3	3	9.3	9.0	3	1.89	1.93	-2
5	13.4	12.7	5	2.7	2.6	4	5.2	5.0	4	0.40	0.42	-5
6	13.5	12.7	5	2.6	2.5	4	3.4	3.2	3	0.31	0.32	-6

[Ox = oxitic zone; Eff = effluent; Re = removal efficiency]

Experimental conditions



Schematic diagram of dynamic membranes



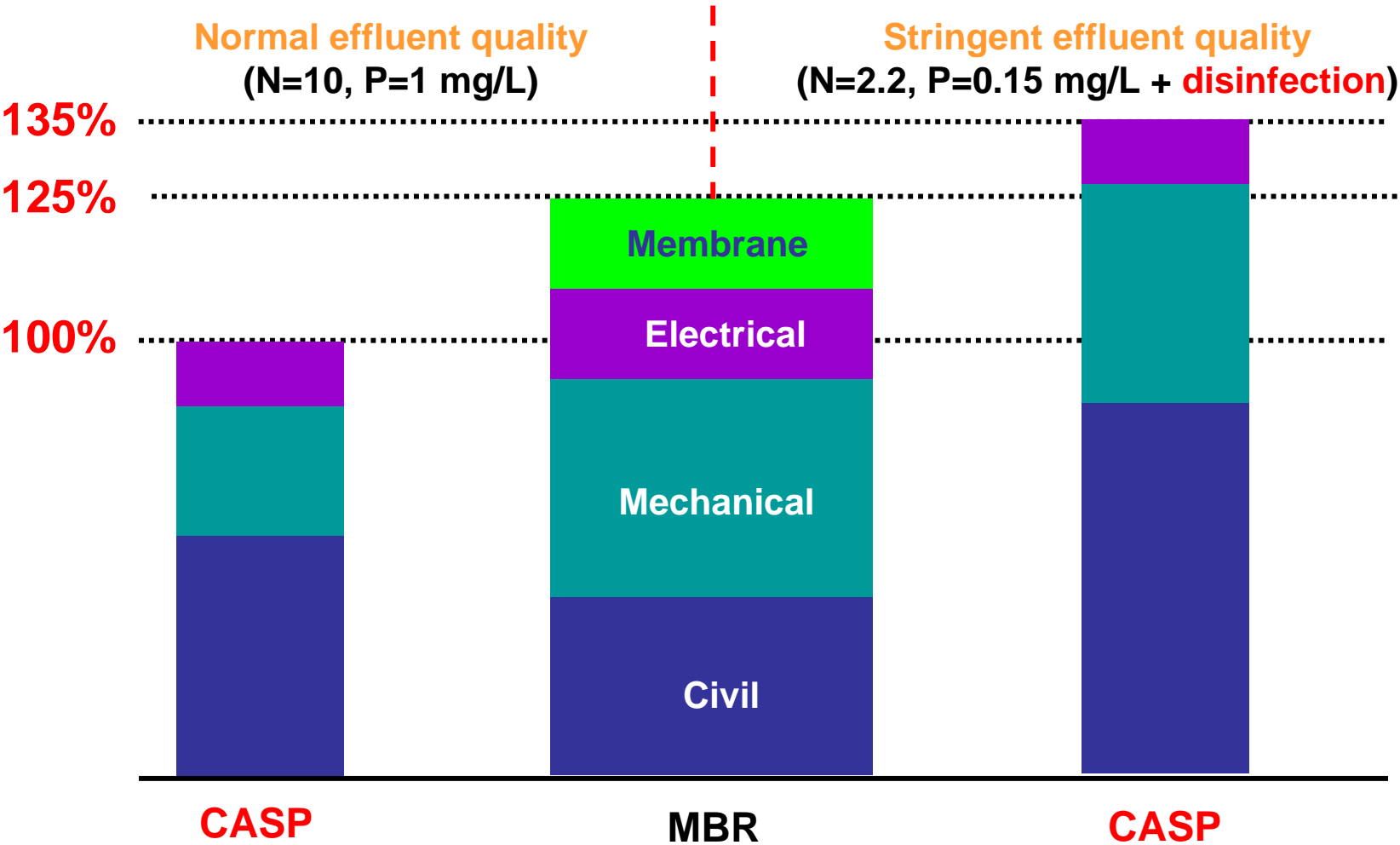
Reuse potential of the effluent in the pilot-scale vertical MBR

Category	Item (Unit)	^a Drinking water standards	^b WHO guidelines	^c MBR effluent quality
Microorganism	Total colony counts (CFU/ml)	100		Not detected
	Total coliforms (CFU/100ml)	0	0	Not detected
Health-related inorganic matters	Lead (mg/l)	0.05	0.01	Not detected
	Fluoride (mg/l)	1.5	1.5	Not detected
	Arsenic (mg/l)	0.05	0.01	Not detected
	Selenium (mg/l)	0.01		Not detected
	Mercury (mg/l)	0.001	1.0	Not detected
	Cyanide (mg/l)	0.01	0.07	Not detected
	Ammonium-N (mg/l)	0.5	0.91	Not detected
	Hexachromium (mg/l)	0.05	0.05	Not detected
	Nitrate-N (mg/l)	10	10.3	5.9
	Cadmium (mg/l)	0.01		Not detected
Boron (mg/l)	0.3		Not detected	
Health-related organic matters	Diazinon (mg/l)	0.02		Not detected
	Malathion (mg/l)	0.25		Not detected
	Parathion (mg/l)	0.06		Not detected
	Fenitrothion (mg/l)	0.04		Not detected
	Cabaryl (mg/l)	0.07		Not detected
	Total trihalomethanes (mg/l)	0.1		Not detected
	Chloroform (mg/l)	0.08		Not detected
	Phenol (mg/l)	0.005	0.001	Not detected
	1,1,1-Trichloroethane (mg/l)	0.1		Not detected
	Tetrachloroethylene (mg/l)	0.01		Not detected
	Trichloroethylene (mg/l)	0.03		Not detected
	Dichloromethane (mg/l)	0.02		Not detected
	Benzene (mg/l)	0.01		Not detected
	Toluene (mg/l)	0.7		Not detected
	Ethylbenzene (mg/l)	0.3		Not detected
	Xylene (mg/l)	0.5		Not detected
1,1-Dichloroethylene (mg/l)	0.03		Not detected	
Tetrachlorocarbon (mg/l)	0.002		Not detected	
Aesthetic-related components	Hardness (mg/l)	300		78
	Permanganate consumption (mg/l)	10		3.5
	Odor	Not abnormal	Acceptable	Acceptable
	Taste	Not abnormal	Acceptable	Acceptable
	Copper (mg/l)	1		Not detected
	Color (color unit)	5	15	2
	Detergent (mg/l)	0.5		0.2
	pH	5.8-8.5	7.0-8.5	7.3
	Zinc (mg/l)	1		0.04
	Chloride (mg/l)	250	200	18
	Total solids (mg/l)	500		267
	Iron (mg/l)	0.3	0.3	Not detected
	Manganese (mg/l)	0.3	0.5	0.056
	Turbidity (NTU)	1	5	0.18
	Sulfate (mg/l)	200	200	16
Aluminium (mg/l)	0.2		0.02	

[Source: a= MOE, 2002; b=Xing *et al.*, 2001; c= average concentrations in phase 2]

Comparison of capital costs

For a 2,500 m³/d treatment plant



[Source: The STOWA, 2002]

Summary of Results



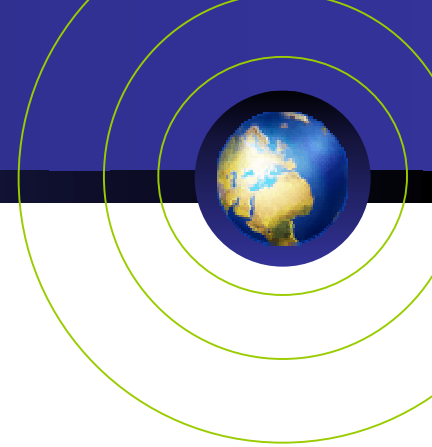
- Condensate of food waste (CFW)
 - **great potential** as a carbon source for nutrient removal !
- In the lab-scale vertical MBRs (acetate, propionic acid, glucose),
 - Average removal efficiency of nitrogen was **about 80%**
 - Removal efficiencies of phosphorus decreased in order of **acetate** (87%), **propionic acid** (83%), and **glucose** (78%) at C/N = 10
 - **Addition of the CFW** (50% of COD) → improved nitrogen and phosphorus removal efficiencies by 2 - 4% and 4 - 11%, respectively.
- Assessment of EBPR activity (batch test)
 - P release/uptake activity; **acetate** > **propionic acid** > **glucose**
 - **several kinds of PHAs** were detected inside the cells

- In the pilot-scale MBR treating municipal wastewater,
 - Average removal efficiency of total COD, T-N, and T-P
 - 96%, 74%, and 78%, respectively at 8 hr HRT and C/N = 5.5
 - As the CFW was supplemented (0.86%), T-N and T-P removal efficiencies increased to 81% and 91%, respectively.
 - At differing temperature (13 - 25 °C),
 - Nitrification efficiency = 79 - 81%
 - Phosphorus removal efficiency = 77 - 81%
 - Additional removal by the formation of dynamic membranes
 - Organics (8%), nitrification (5%) and denitrification (4%)
 - The effluent quality could satisfy the current drinking water standards except for ammonia-N.

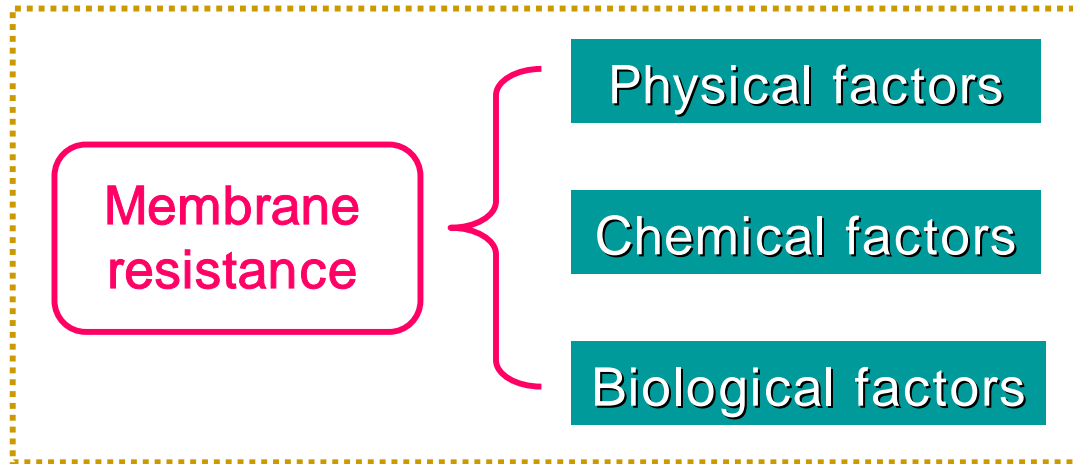
- Analysis of population dynamics
 - As C/N ratio decreased, the number of microbial species decreased
 - Species of the beta subclass or Proteobacteria are considered to play an important role in EBPR.
 - When the CFW was added, *Geothrix fermentans* appeared.

Remediation of **membrane fouling** in a vertical MBR

Objective and Scope



Characteristics of membrane fouling



Lab-scale (glucose)

Ax/Ox vertical MBR



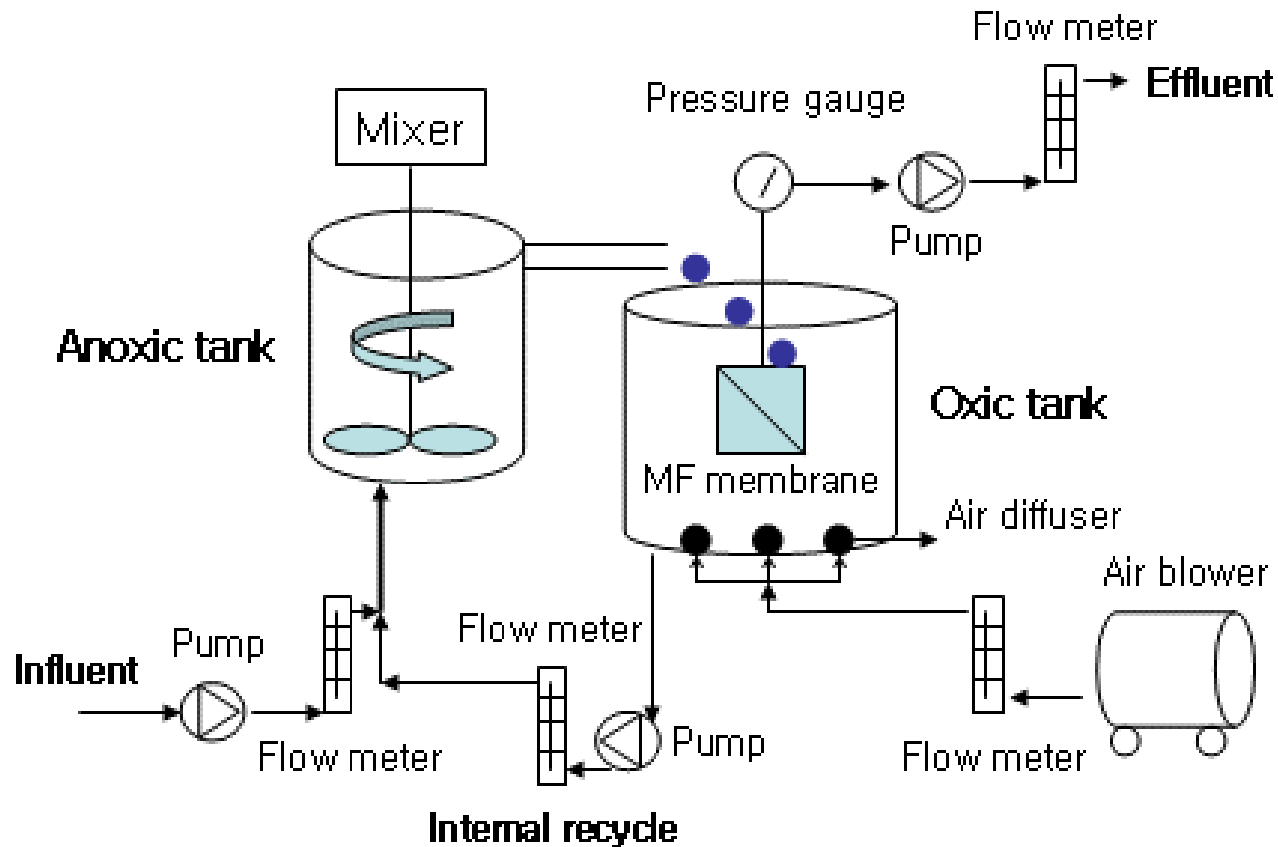
Ax/Ox series MBR



Pilot-scale (sewage)

Ax/Ox vertical MBR

Ax/Ox series MBR



Operating conditions: lab-scale MBRs

Parameter	Ax/Ox series MBR		Ax/Ox vertical MBR	
	Anoxic zone	Oxic zone	Anoxic zone	Oxic zone
SRT	30 days		30 days	
HRT	3 hours	5 hours	3 hours	5 hours
Working volume	6 l	10 l	12 l	20 l
Permeate flux	6.2 L/m ² /h		6.2 L/m ² /h	
Operation mode	Suction (8 min) + Idle (2 min)		Suction (8 min) + Idle (2 min)	
Internal recycle rate	400%		400%	
Average MLSS	4.34 g/l	4.61 g/l	5.68 g/l	2.21 g/l
ORP	-63 mV	+314 mV	-147 mV	+257 mV

- Organic source = glucose
- COD : N : P = 160 : 40 : 6

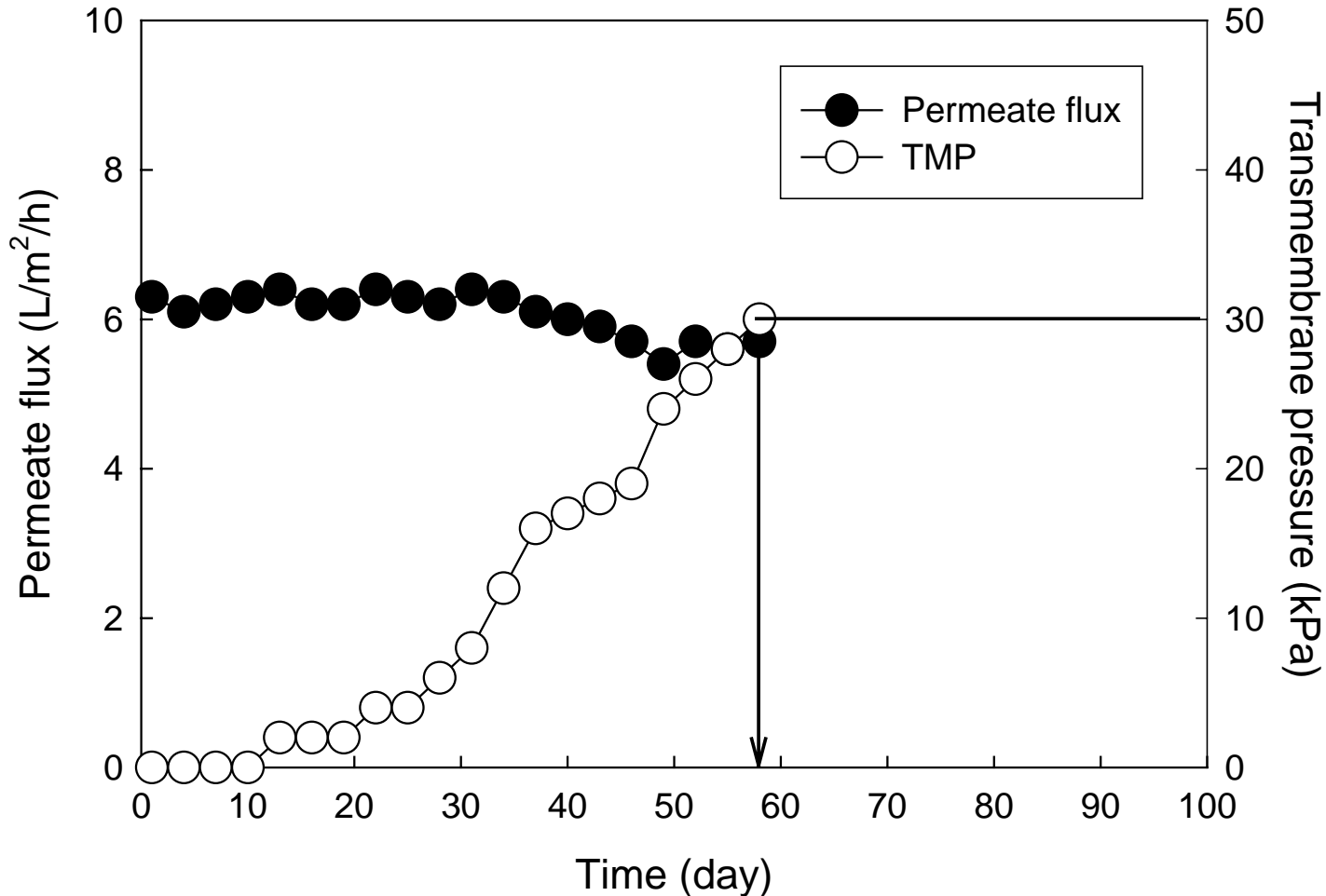
Operating conditions: pilot-scale vertical MBR



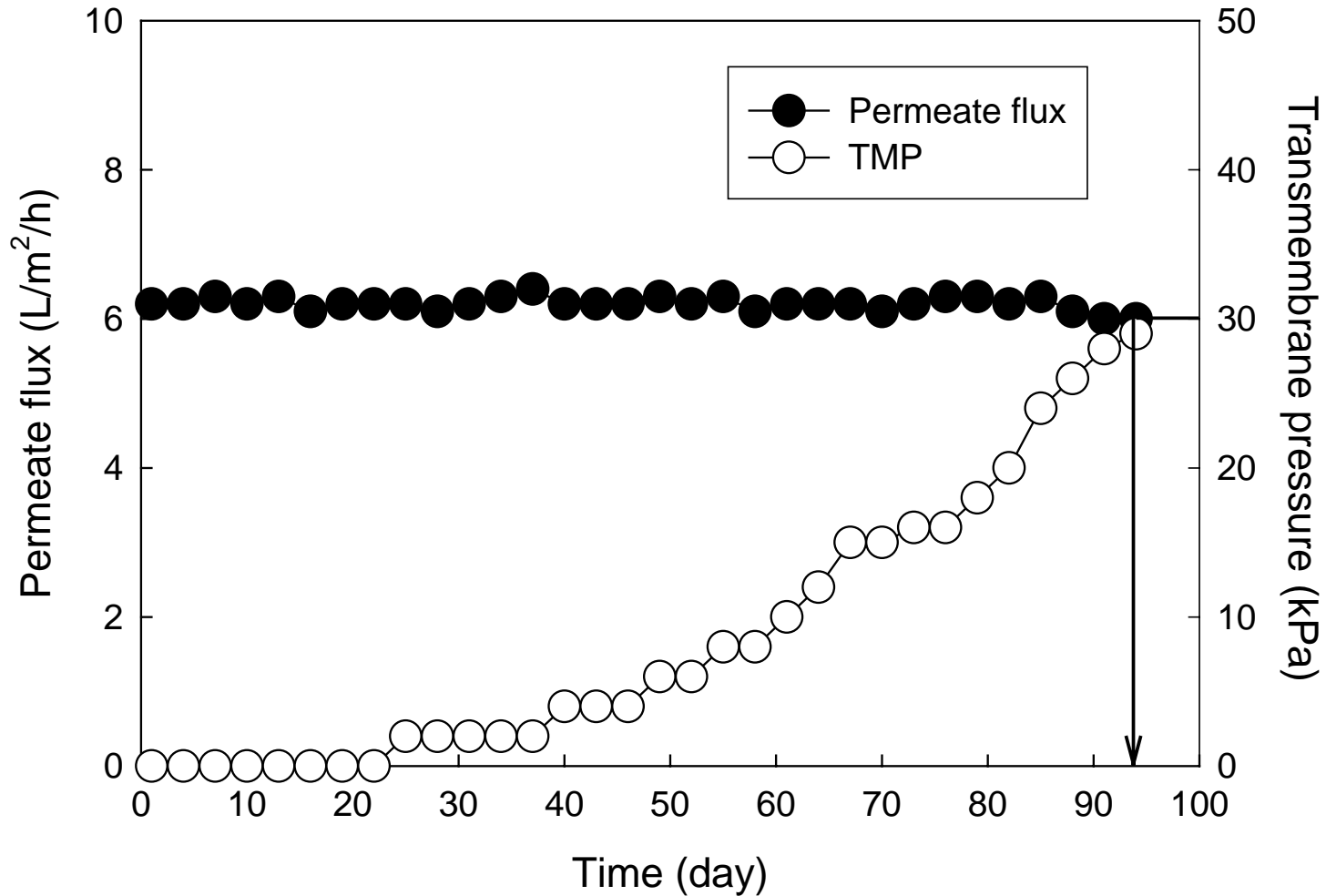
Results and Discussion



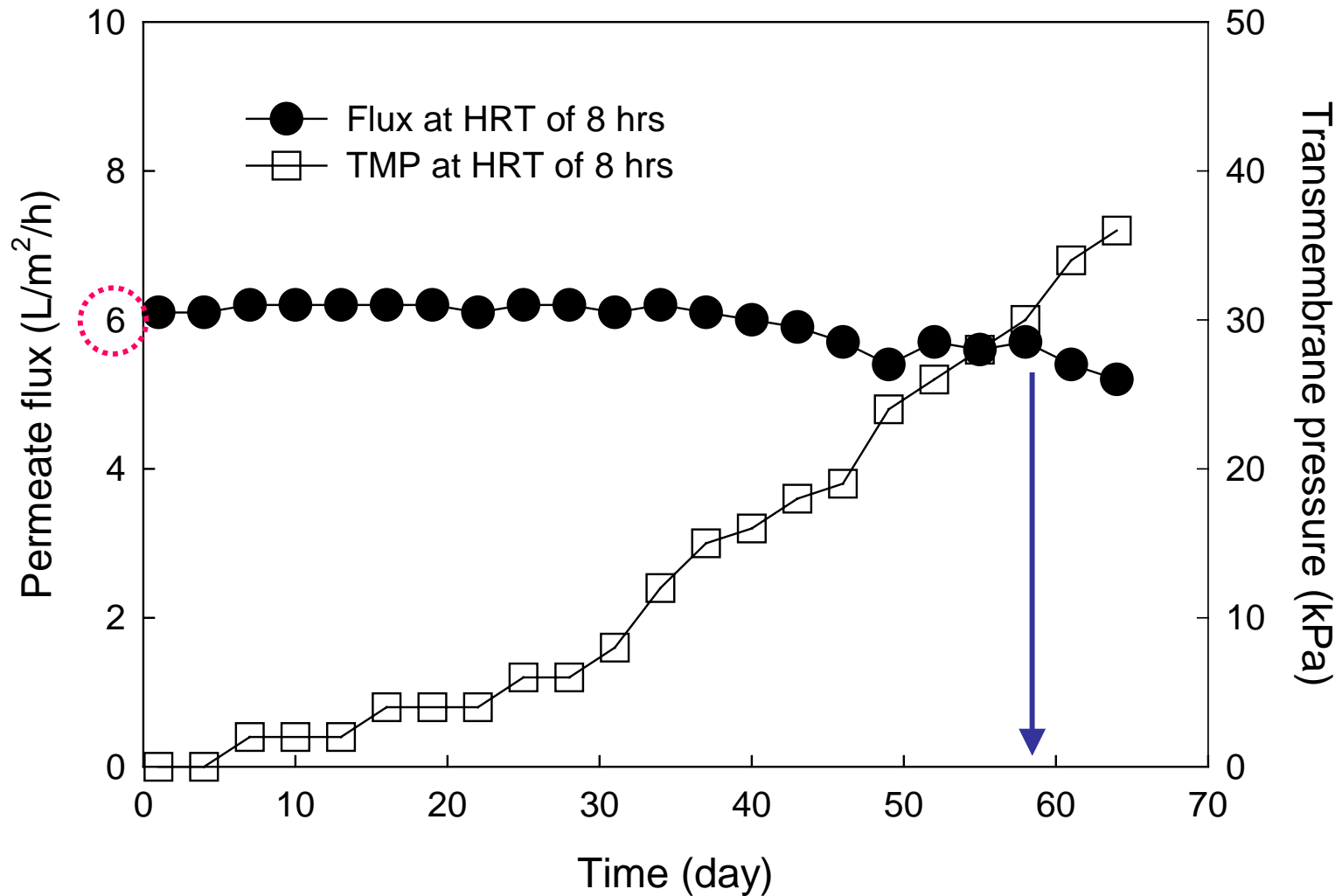
Variations of flux and TMP in the XXXXXX MBR



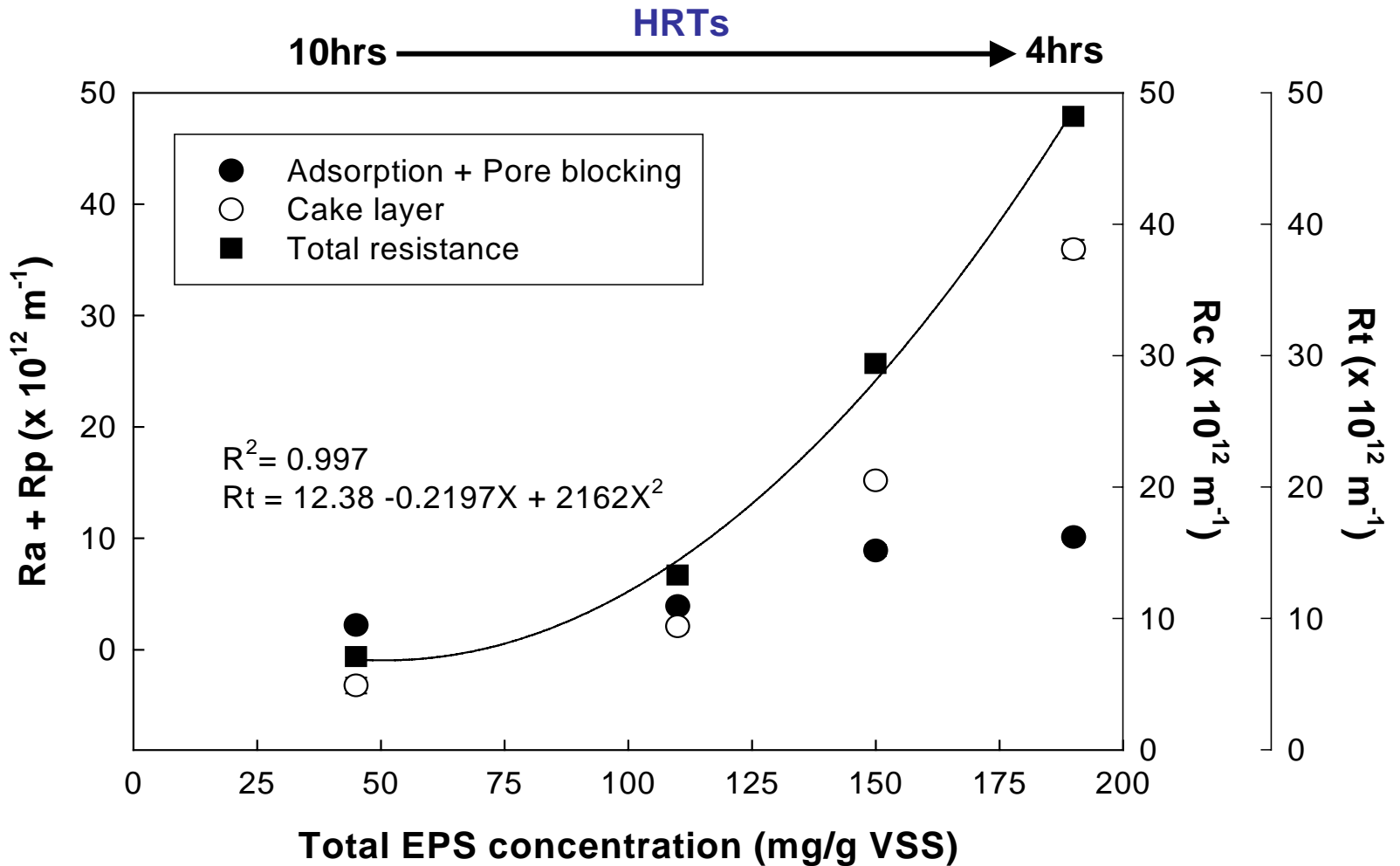
Variations of flux and TMP in the [redacted] MBR



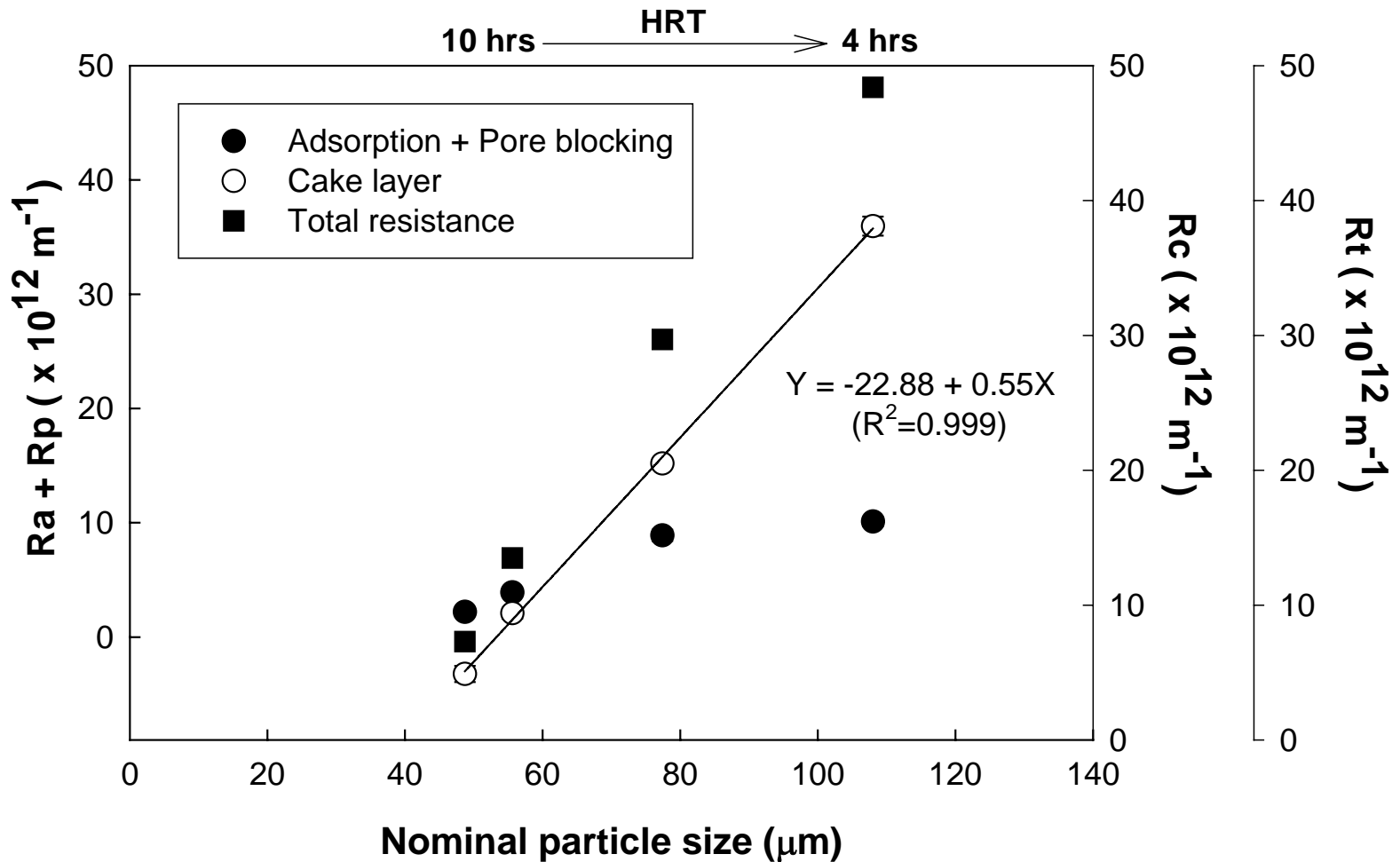
Variations of flux and TMP in the pilot-scale vertical MBR



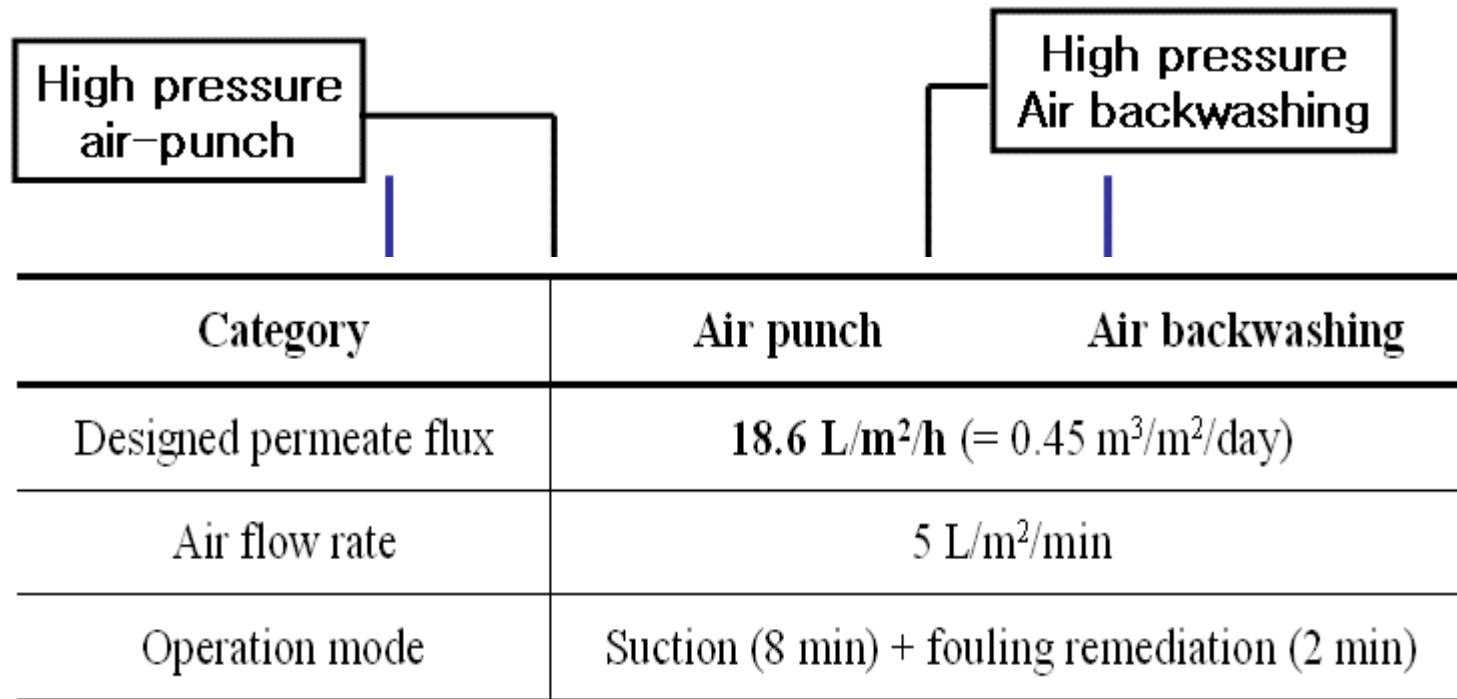
Effect of EPS concentration on fouling at various HRTs



Effect of particle size on fouling at various HRTs

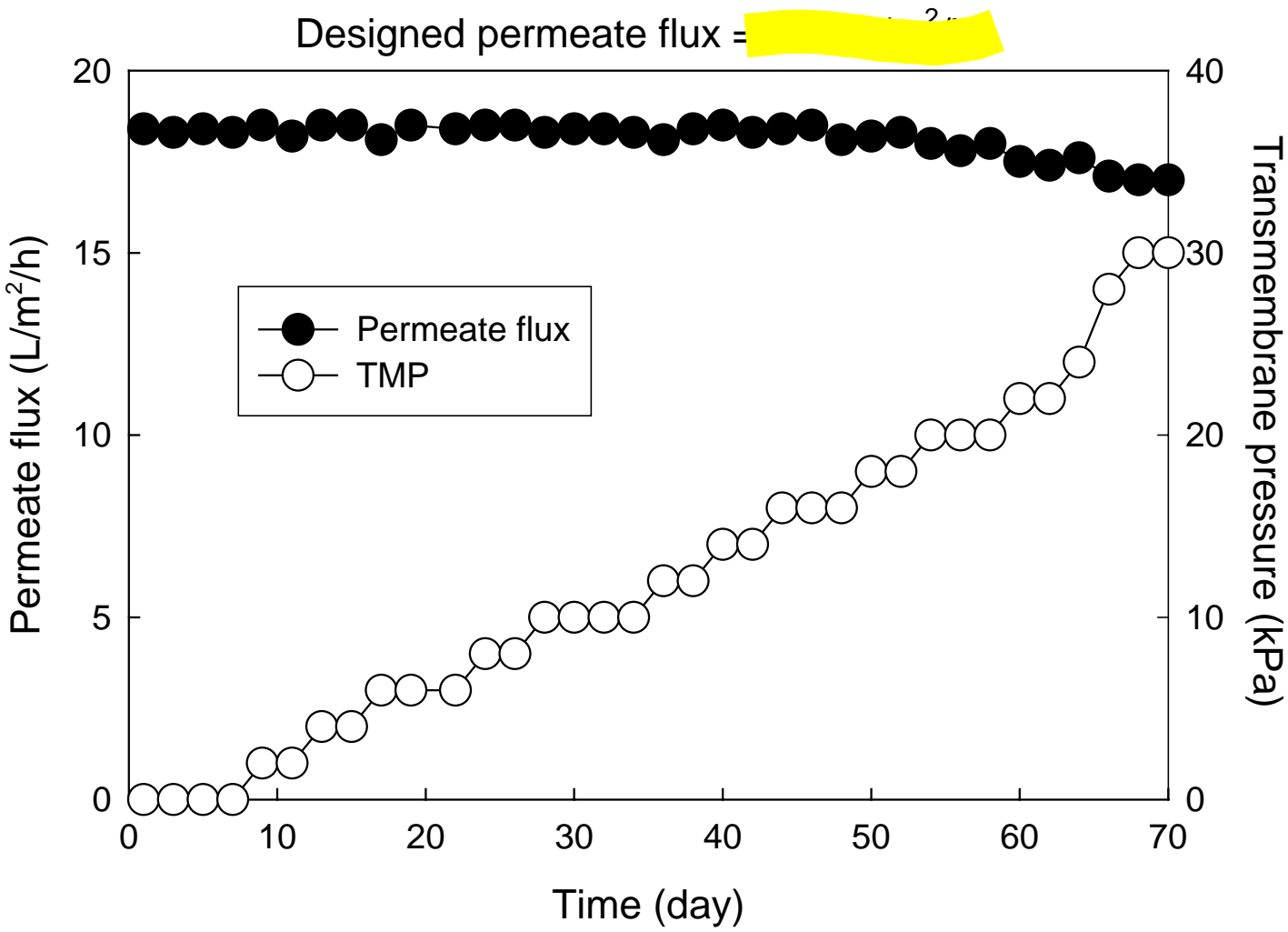


Schematic diagrams of fouling remediation techniques

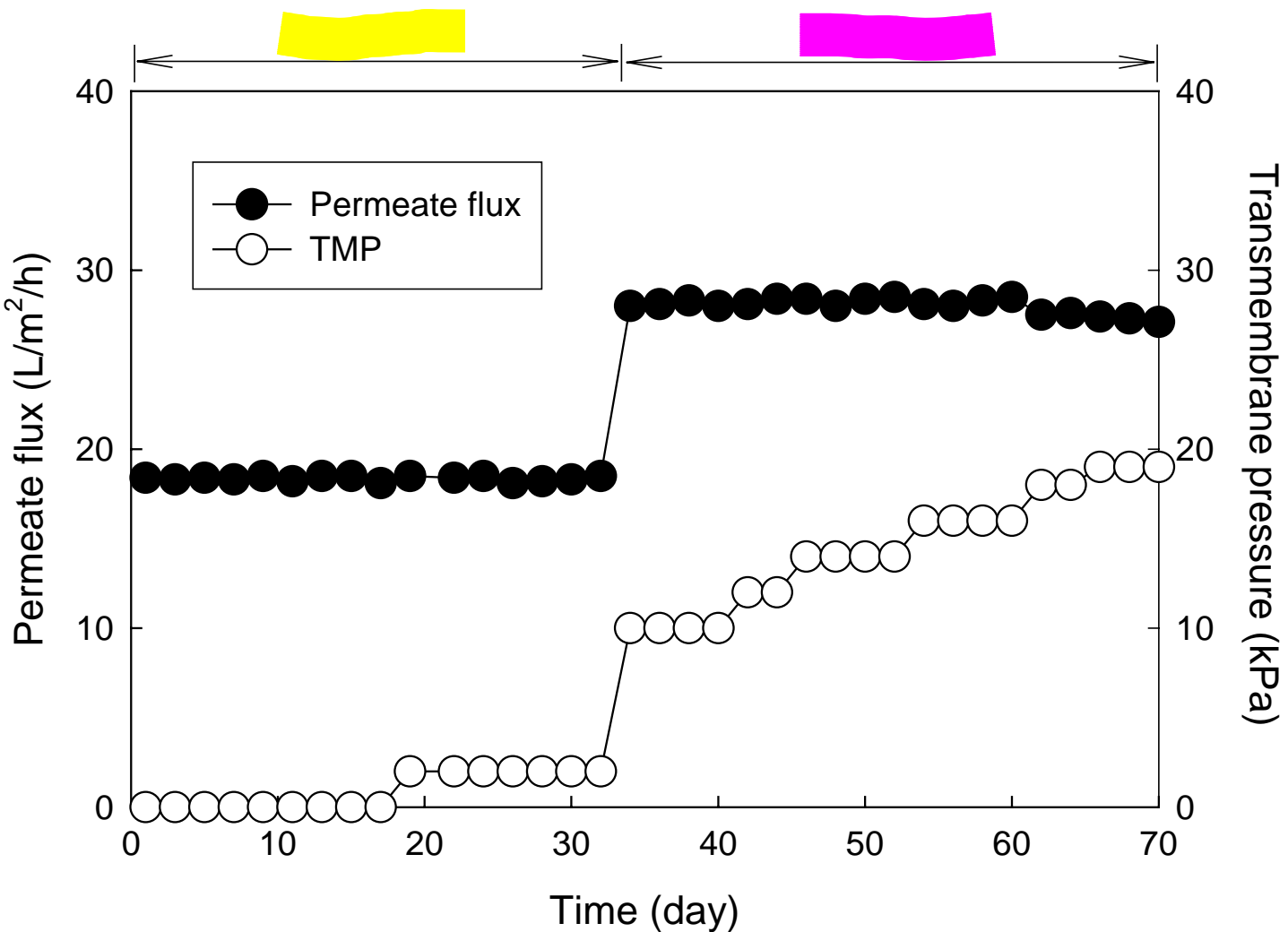


Membrane bioreactor

Fouling remediation by outside air supply



Fouling remediation by inside air supply

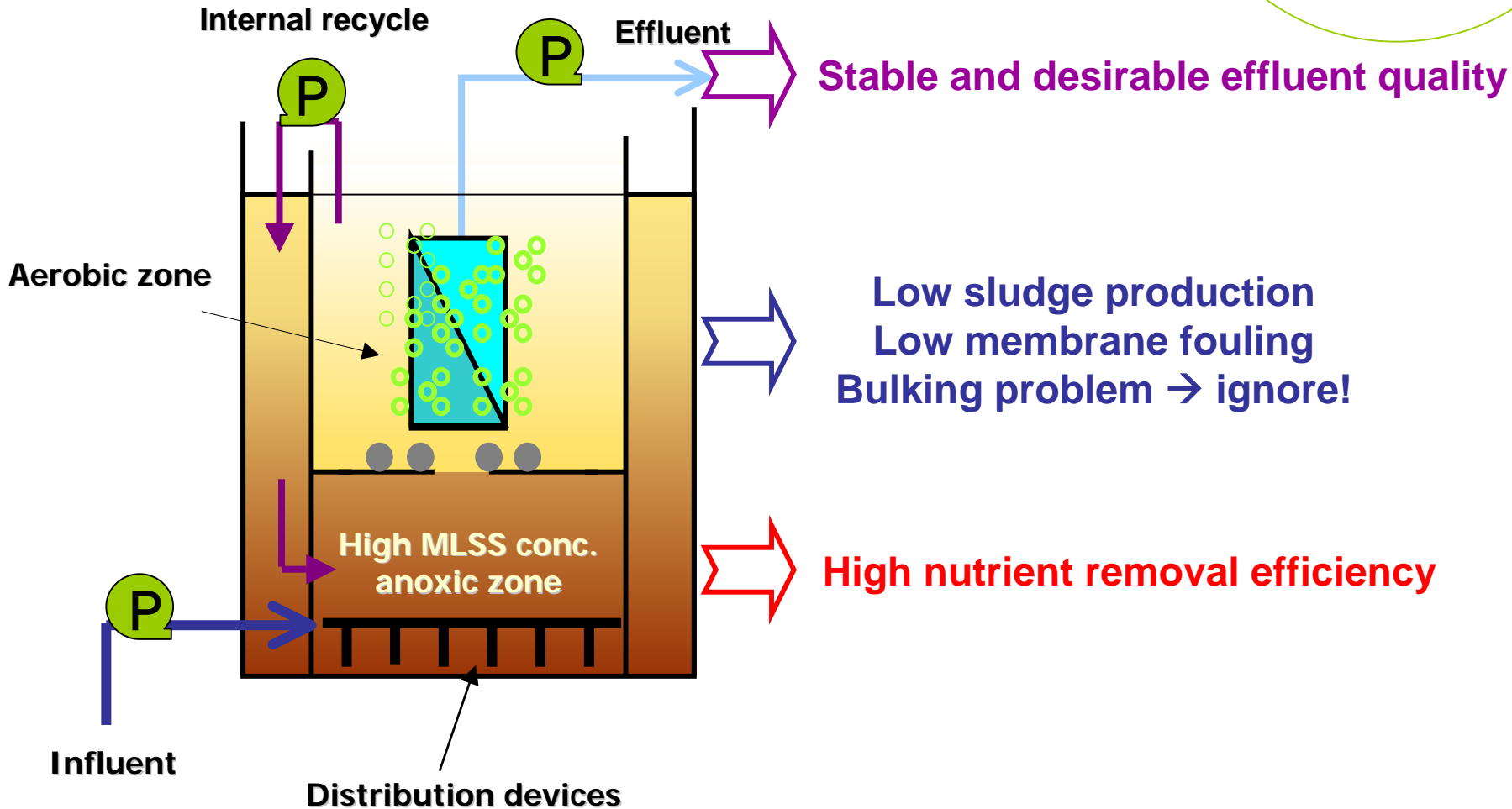
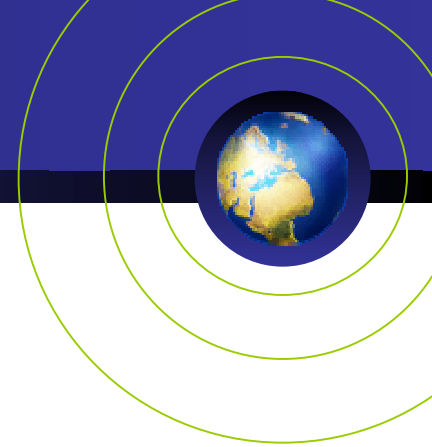


Summary of Results



1. Series MBR vs. Vertical MBR (SRT = 30 days)
 - Vertical-type MBR; relatively low **MLSS concentration** (EPS and viscosity) → reduce membrane fouling !
 - Cake layer resistance was about **60-70%** of the total resistance
2. Lab-scale vs. Pilot-scale vertical MBR
 - Pilot-scale showed relatively **higher** values of EPS and viscosity, **smaller** particle size → **severe fouling** !
 - In pilot-scale MBR (HRT=10 → 8 → 6 → 4 hrs);
 - **EPS content** and **particle size** increased
 - **Cake layer resistance** appeared to be the controlling factor of the total resistance
3. Fouling remediation
 - The **inside** air supply was more efficient than the outside air supply

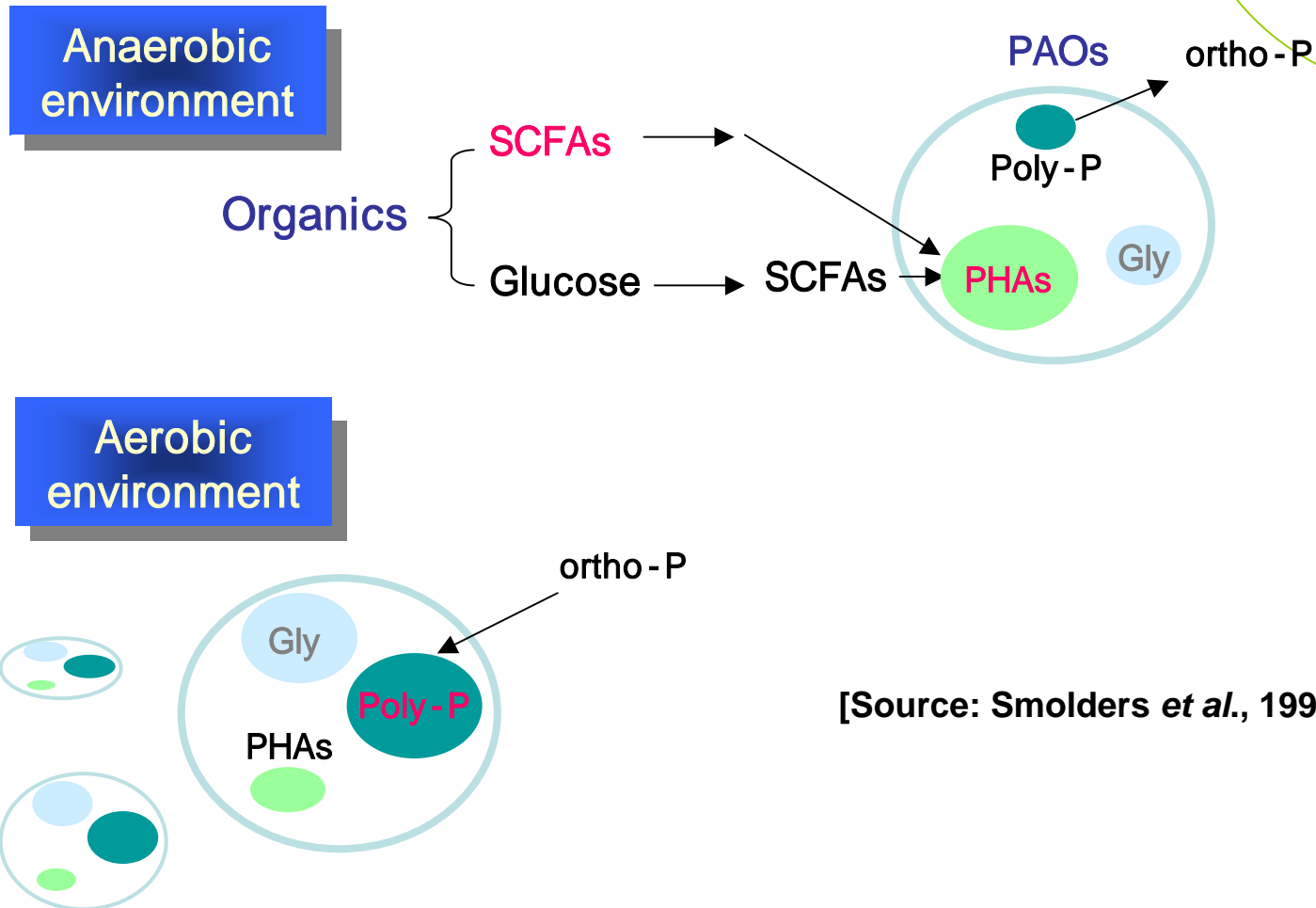
Final Conclusions



THANK YOU!

QUESTION?

Enhanced Biological Phosphorus Removal (EBPR)



[Source: Smolders *et al.*, 1995]