Micropollutants: The Singapore Experience

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Water Quality Department

5 Nov 2019

PUB SINGAPORE'S NATIONAL WATER AGENCY

Country Information

Land Area: 724.2 km^2 (279.6 mi^2)
Population: 5.7million
Average Annual Rainfall: 2,330mm (92 inches)
Average Water Demand: 430 $m_i$gd (516.4 mgd / 1585 acre-foot/day)

We Are PUB, We Are Water

Ministry of the Environment and Water Resources
SINGAPORE

"To ensure a clean sustainable environment, and supply of water and safe food for Singapore."

National Environment Agency
Safeguard • Nurture • Cherish

"To ensure a clean and sustainable environment for Singapore, together with our partners and the community"

- Clean Land
- Clean Air

Singapore Food Agency

"To ensure and secure a supply of safe food."

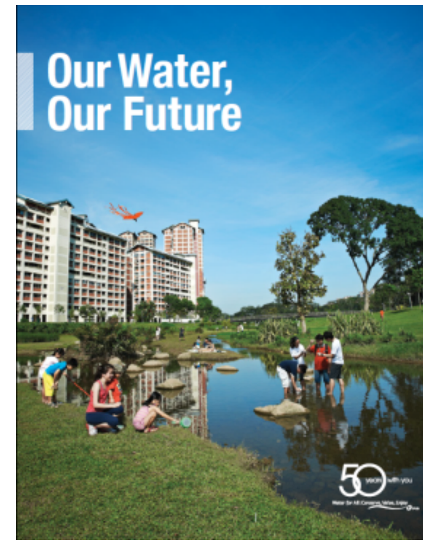
- Safe Food
- Public Health

PUB SINGAPORE'S NATIONAL WATER AGENCY

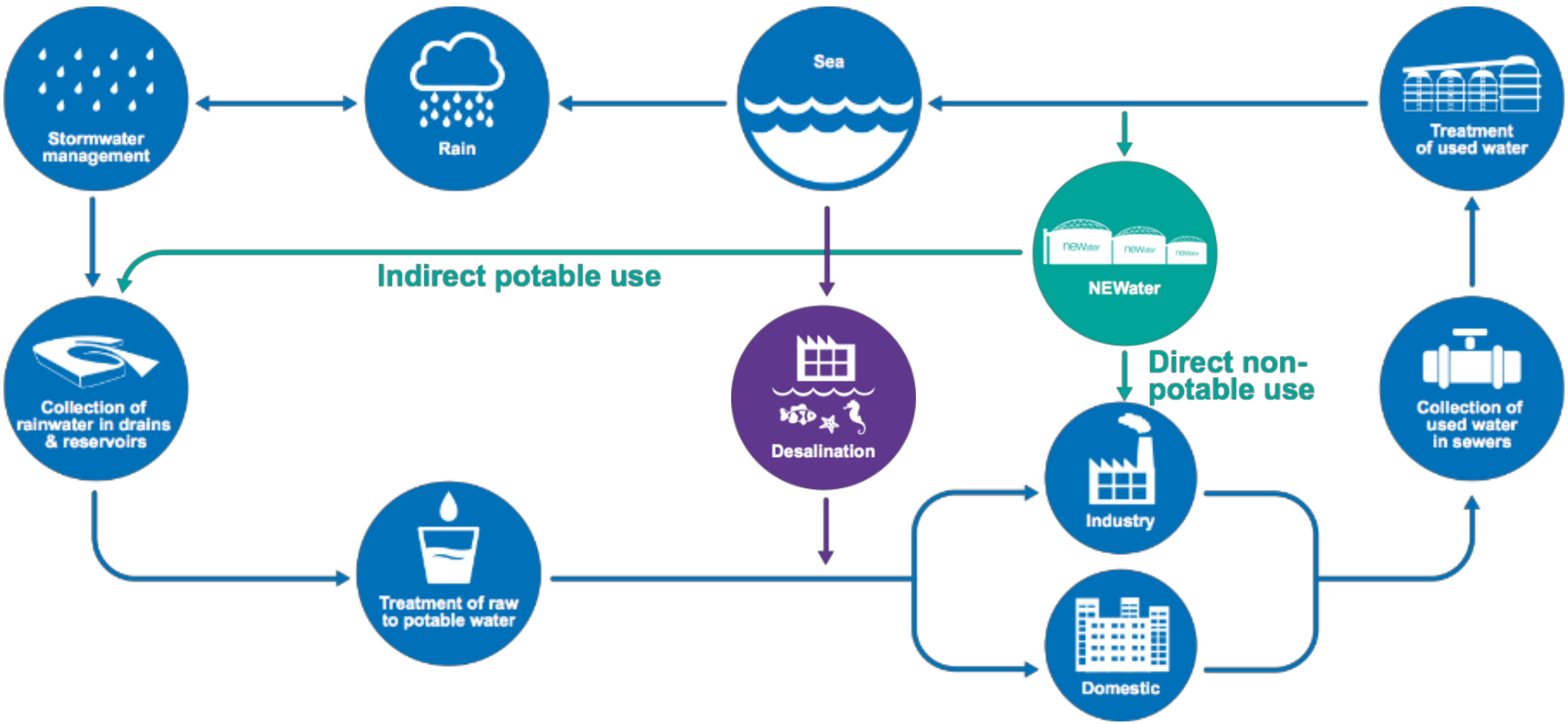
"Supply Good Water. Reclaim Used Water. Tame Storm Water."

- Clean Water

A Statutory Board constituted under the Public Utilities Act 2001 to provide integrated water supply, sewerage and drainage services



PUB manages the complete water cycle



Presentation Outline

- Research findings on micropollutants in water reclamation plant in Singapore
- PUB’s approach on micropollutants management

Occurrence & Removal of Emerging Contaminants by Conventional Activated Sludge (CAS) and Membrane Bioreactor (MBR) Systems

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Dr You Luhua

Department of Civil & Environmental Engineering

E2S2-CREATE

NUS Environmental Research Institute (NERI)

Objectives

- Investigate the occurrence of ECs in raw wastewater and treated effluent.
- Evaluate the removal of ECs in a full-scale biological wastewater treatment plant using different treatment systems, i.e. conventional activated sludge (CAS) and membrane bioreactor (MBR).

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Occurrence and removal of pharmaceuticals, hormones, personal care products, and endocrine disrupters in a full-scale water reclamation plant

CrossMark

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Target Emerging Contaminants

The selection of target ECs was based on at least one of the following criteria:

- High consumption in the world.
- Widespread occurrence in urban wastewater/ treated effluent all over the world as reported in the literature.
- Potential risk to human health and aquatic ecosystems.
- The analytical capability of the laboratory.

Target Emerging Contaminants

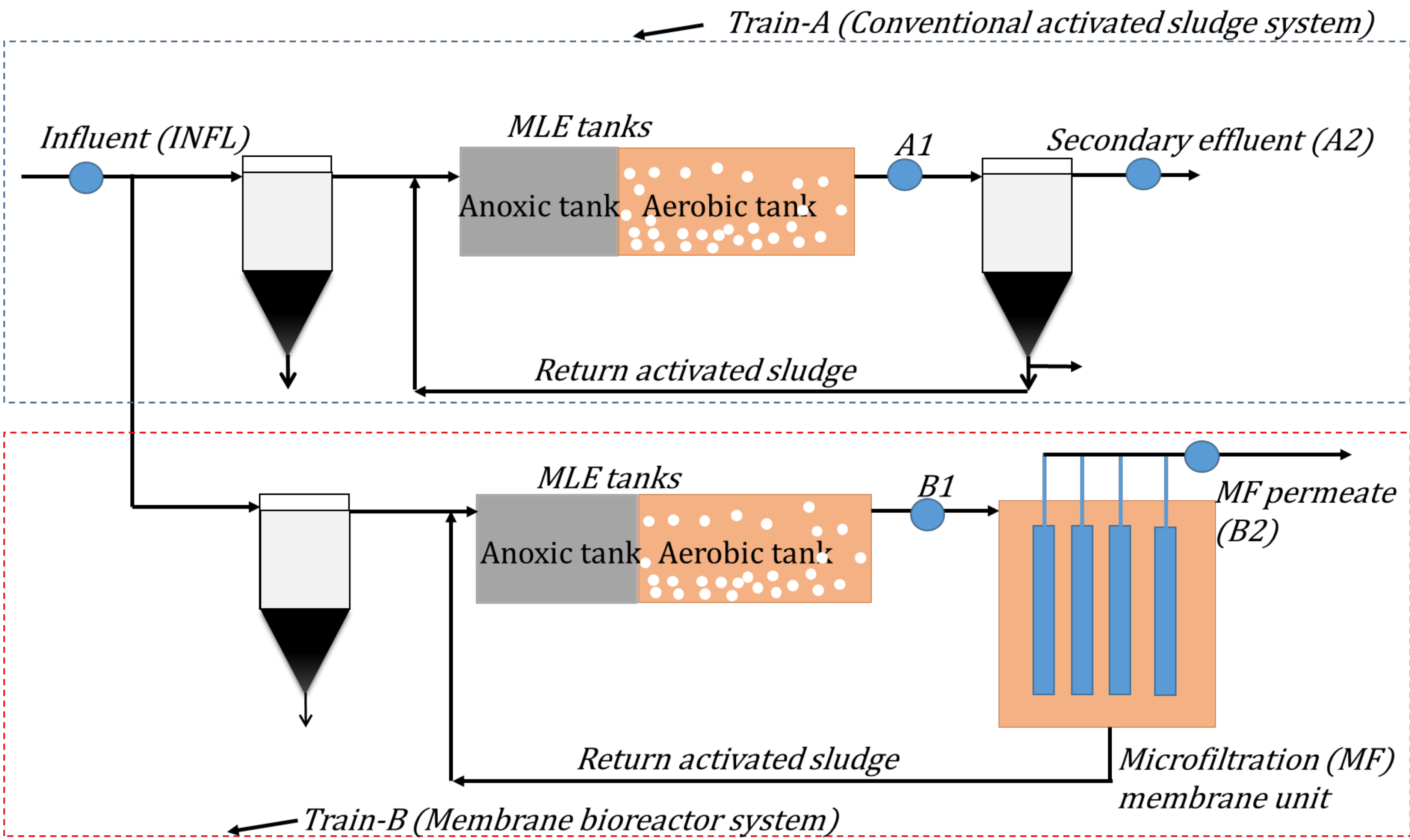
Antibiotics & Antimicrobials

	Class	Target ECs	Abbr.		Class	Target ECs	Abb
1	**β-lactams**	Ceftazidime	CFZ	**12**	**Sulfonamides**	Sulfamethazine	SMZ
2		Meropenem	MER	**13**	**Reductase inhibitor**	Trimethoprim	TMP
3		Amoxicillin	AMX	**14**	**Tetracycline family**	Tetracycline	TET
4	**Quinolones**	Ciprofloxacin	CIPX	**15**		Minocycline	MIN
5	**Lincosamides**	Lincomycin	LIN	**16**		Chlortetracycline	CTC
6		Clindamycin	CLI	**17**		Oxytetracycline	OXY
7	**Macrolides**	Erythromycin	ERYC	**18**	**Antiseptics**	Triclosan	TCS
8		Azithromycin	AZT	**19**		Triclocarban	TCC
9		Clarithromycin	CLAR	**20**	**Glycopeptide**	Vancomycin	VCM
10		Tylosin	TYL	**21**	**Amphenicol**	Chloramphenicol	CAP
11	**Sulfonamides**	Sulfamethox-azole	SMX				

Other ECs

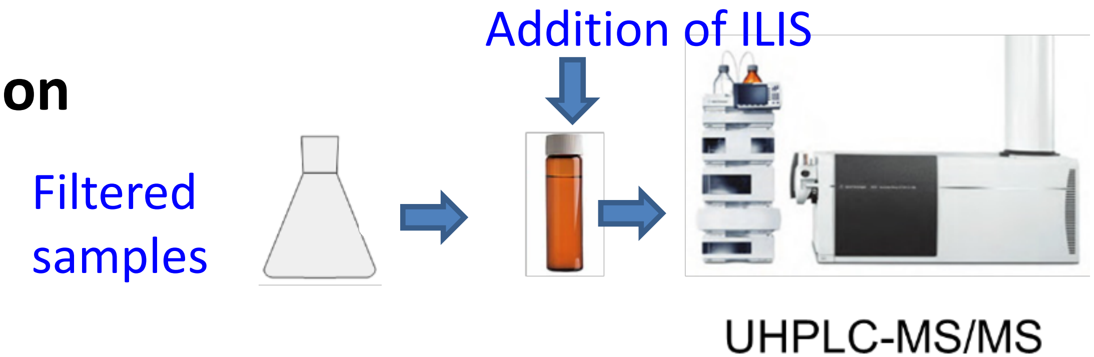
No	Class	Target ECs	Abbr.		Class	Target ECs	Abbr.
22	**NSAIDs**	Acetaminophen	ACT	36	**Hormones**	Estrone	E1
23		Ibuprofen	IBP	37		Estriol	E3
24		Naproxen	NPX	38		Cortisone	C2
25		Ketoprofen	KEP	15		Corticosterone	C1
26		Fenoprofen	FEP	39	**UV-filters**	4-MBC	4-MBC
27		Indomethacin	IDM	40		Octocrylene	OCT
28		Salicylic acid	SA	41		Oxybenzone	OXB
29		Diclofenac	DCF	42	**Anti-itching**	Crotamiton	CTMT
30	**Lipid regulator**	Clofibric acid	CA	43	**Repellent**	Diethyltoluamide	DEET
31		Gemfibrozil	GFZ	44	**Artificial sweetener**	Acesulfame	ACE
32	**Anti-convulsant**	Carbamazepine	CBZ	45		Sucralose	SUC
33		Gabapentin	GBP	46		Cyclamate	CYC
34	**Anti-psychotic**	Sulpiride	SUL	47		Saccharin	SAC
35	**β-blockers**	Atenolol	ATN	48			
				49	**X-ray contrast agents**	Iohexol	IOH
				50		Iopromidol	IOP
				51	**Plasticizer**	Bisphenol A	BPA

Schematic diagram of Water Reclamation Plant

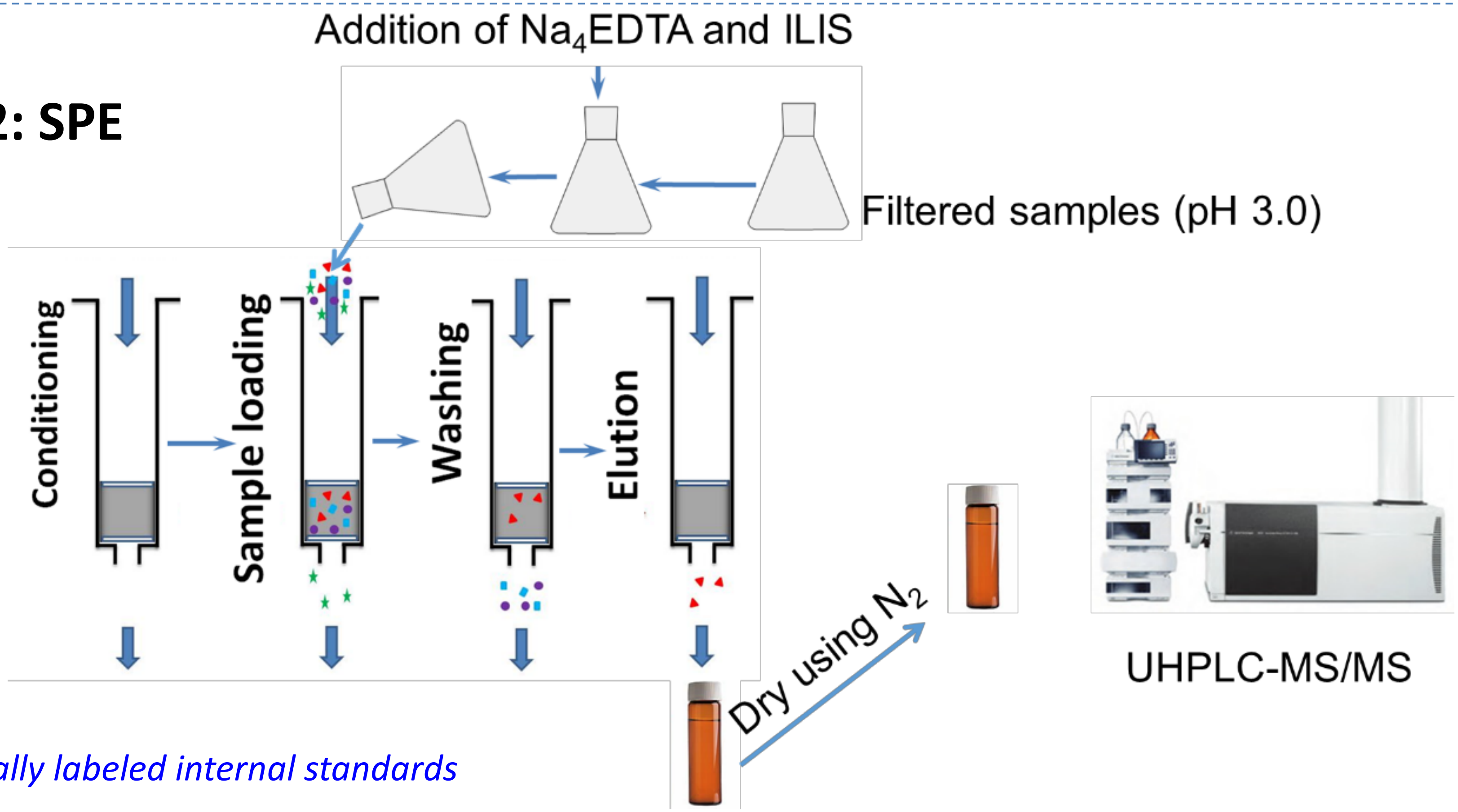


Methods

Method 1: Direct injection



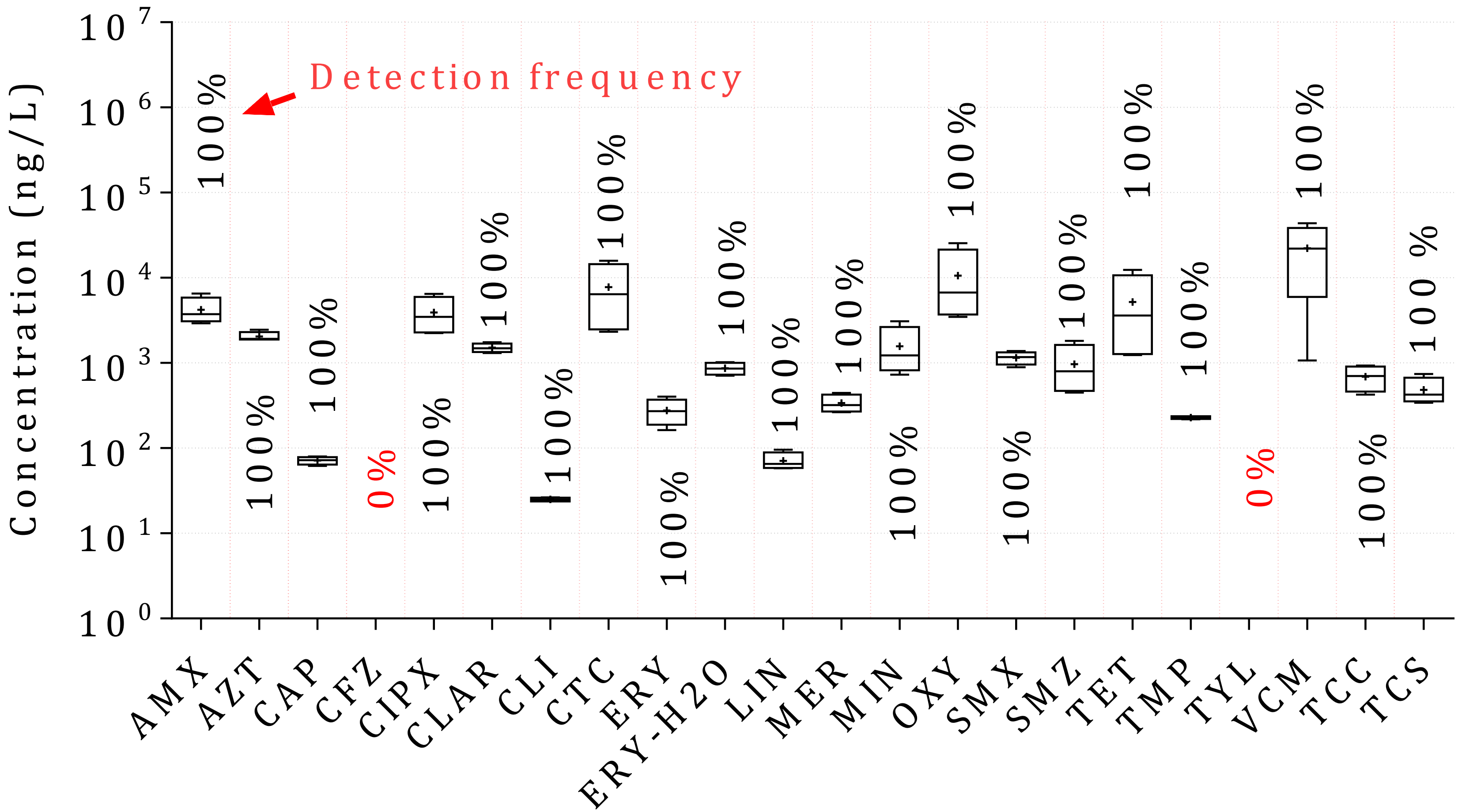
Method 2: SPE



ILIS: isotopically labeled internal standards

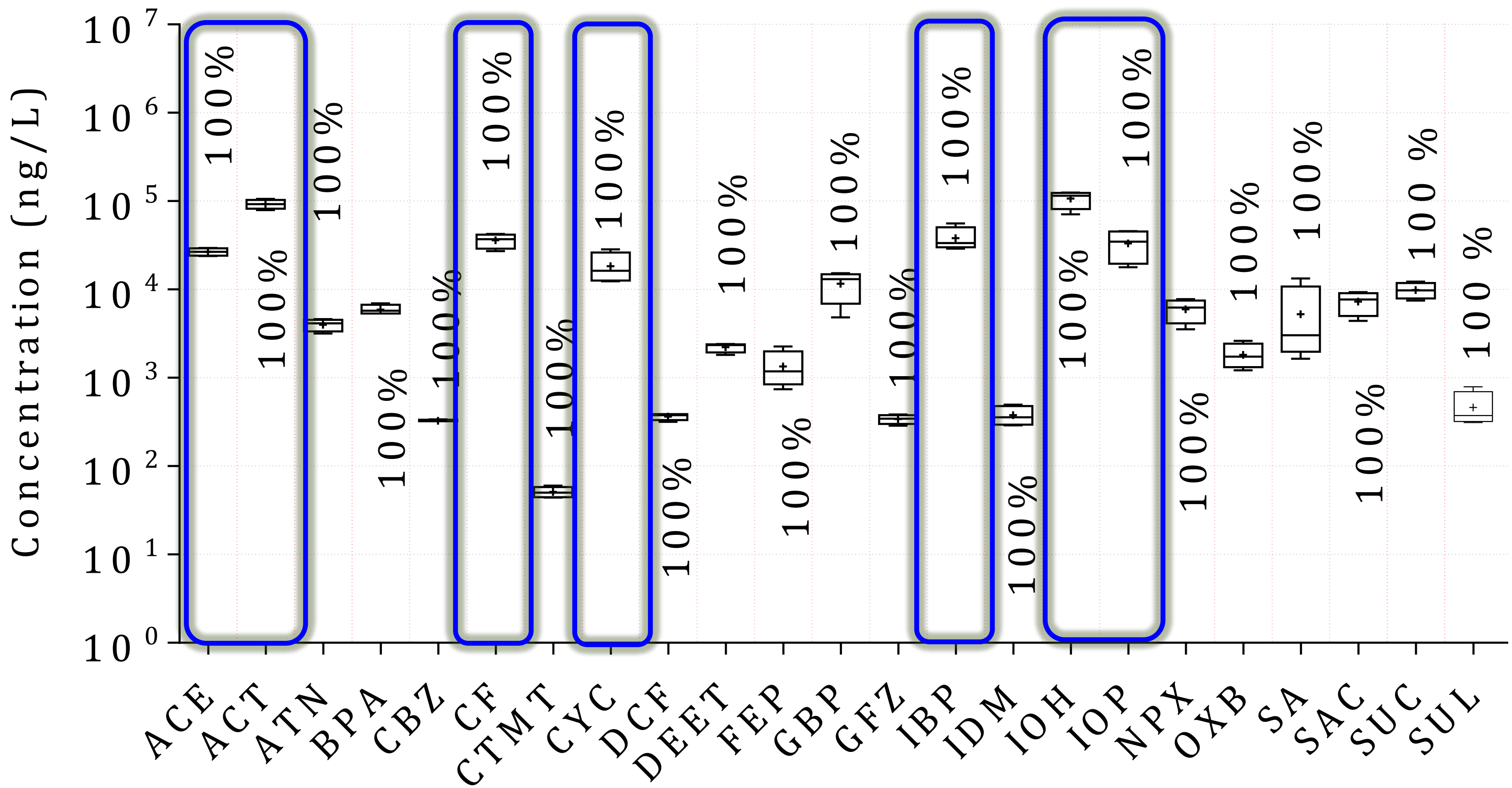
Occurrence of Emerging Contaminants in Raw Wastewater

Antibiotics/Antimicrobials in Raw Influent



- High variability in antibiotics
- All antibiotics, except CFZ and TYL, were detected in raw influent
- β-lactams, macrolides, sulfonamides, fluoroquinolone, and tetracyclines, were detected in raw influent > 1000 ng/L.

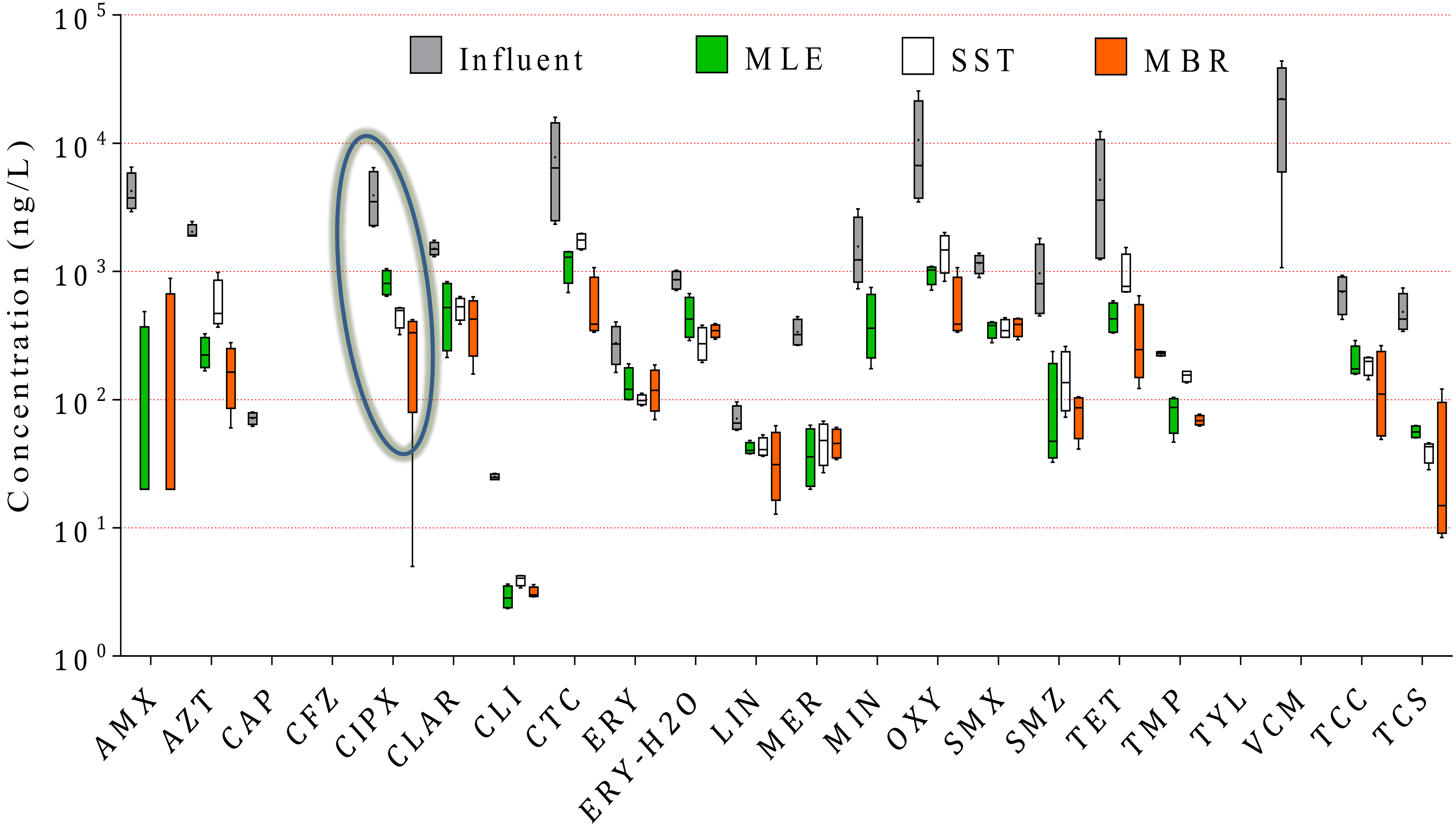
PPCPs, ASs and EDCs in Raw Influent



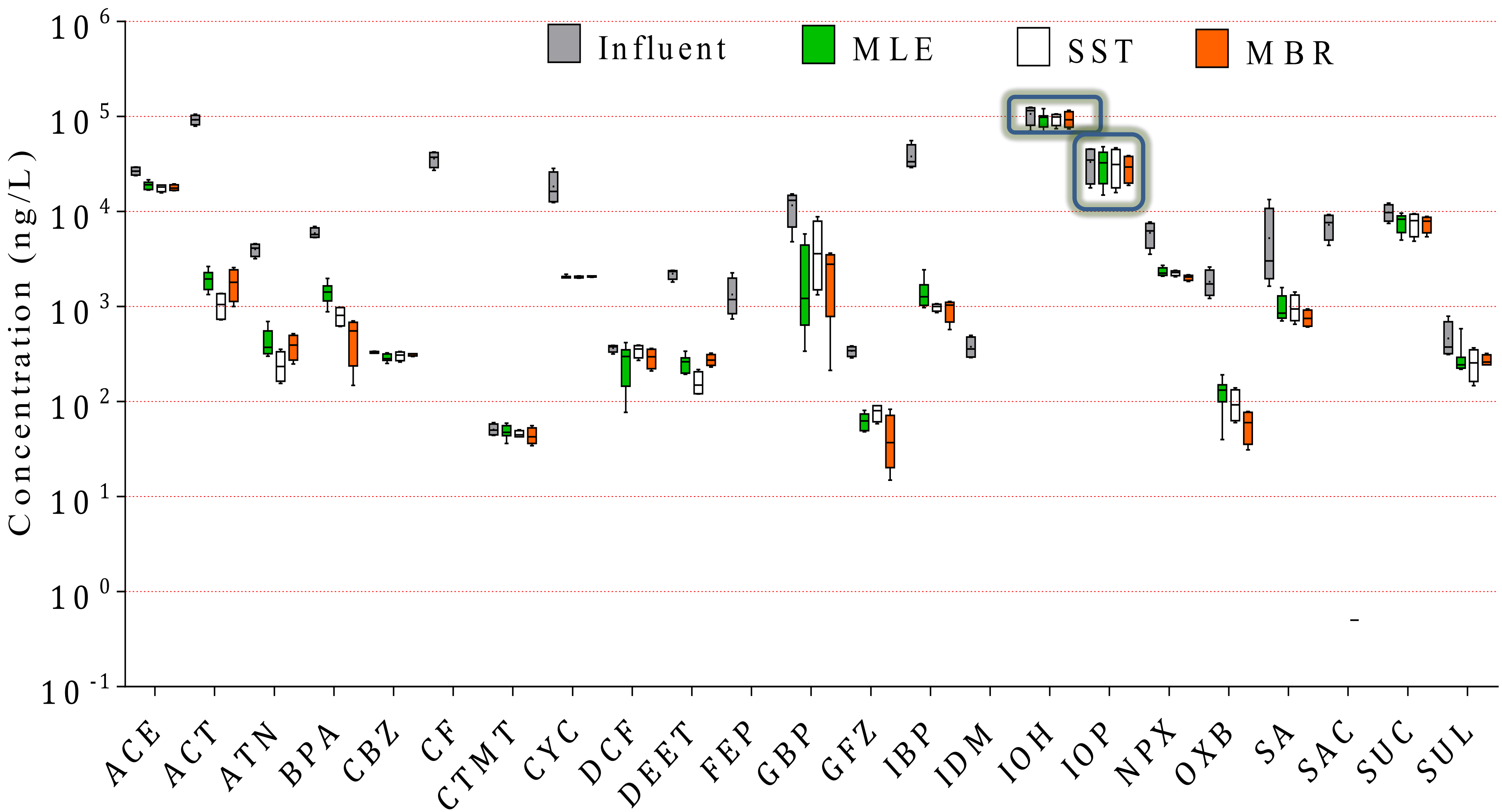
- All target PPCPs, EDCs, and ASs (except hormones: E1, E3, C1, C2 and OCT) were present in raw influent
- Concentrations of PPCPs, EDCs, and ASs varied substantially, from several tens to upper hundred thousands ng/L, depending upon compound and sampling date
- NSAIDs, X-ray contrast media (IOH and IOP), β-blocker (ATN), ASs (ACE, CYC, SAC, and SUC) were the most abundant compounds and caffeine (CF)

Occurrence of Emerging Contaminants in Treated Wastewater

Antibiotics/antimicrobials



PPCPs, ASs and EDCs



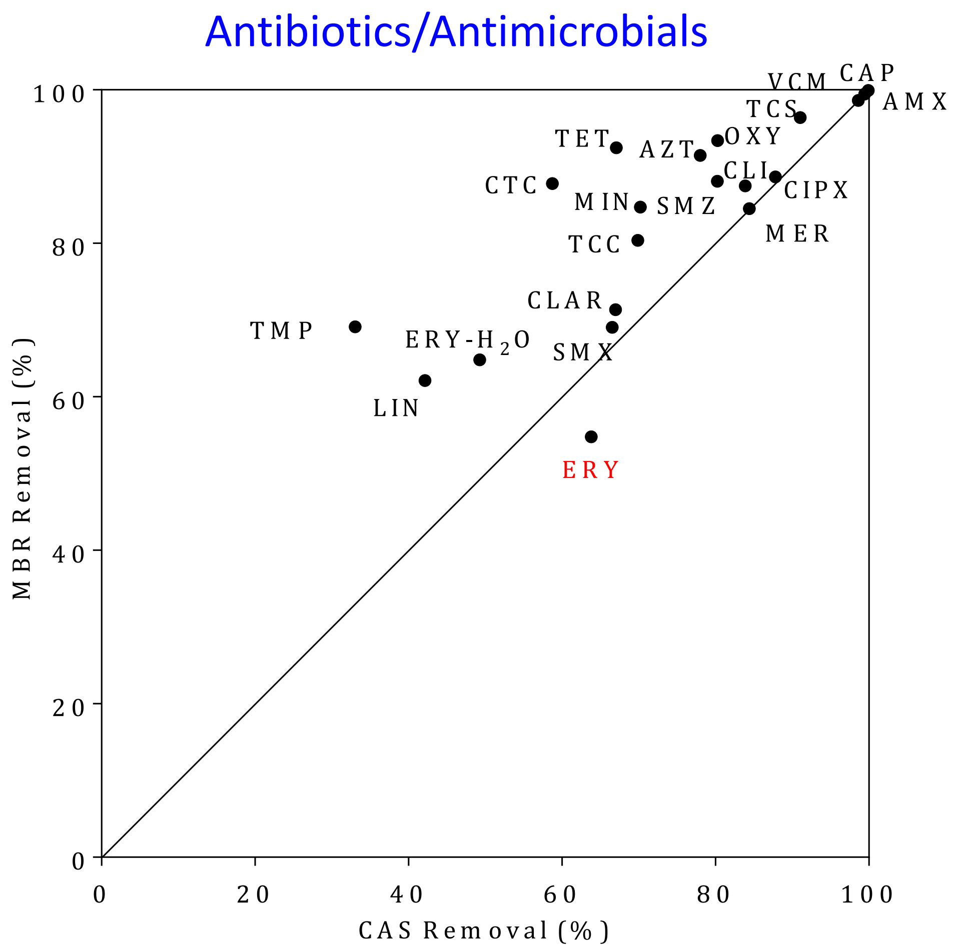
Removal of Antibiotics by CAS & MBR Systems

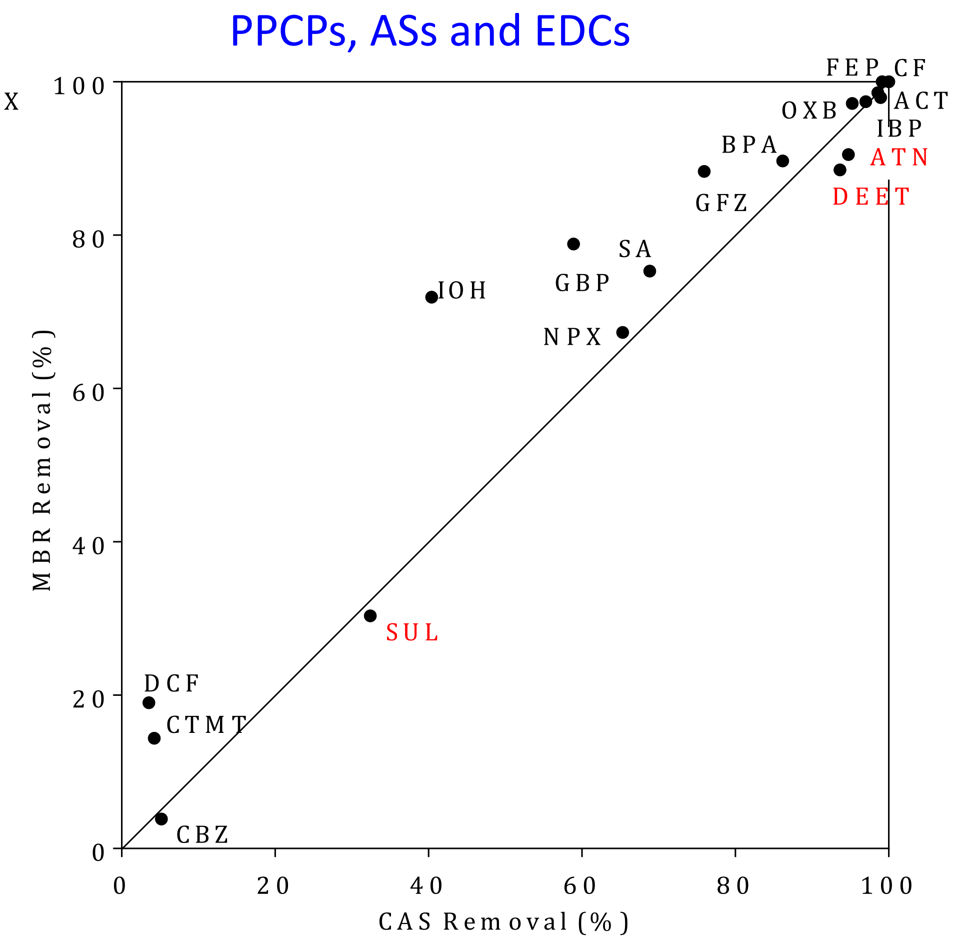
Target ECs	% Removal by CAS system (n = 4)			% Removal by MBR system (n = 4)		
	Range (%)	Median (%)	Mean±SD (%)	Range (%)	Median (%)	Mean ± SD (%)
MER	80.7–92.6	84.4	85.5 ± 5.0	81–92.3	84.5	85.6 ± 4.9
AMX	99.3–99.7	99.5	99.5 ± 0.2	69.9–99.7	99.5	92.1 ± 14.8
CIPX	76.6–92.4	87.8	86.2 ± 6.8	84.9–99.9	88.6	90.5 ± 6.8
LIN	8.1–56.1	42.1	37.1 ± 21	-8.1–79.3	62.1	48.8 ± 38.8
CLI	83.6–85.7	83.9	84.3 ± 1.0	85.8–88.9	87.5	87.4 ± 1.3
ERY	31.4–77.7	63.8	59.2 ± 19.7	26.6–74.9	54.8	52.3 ± 19.8
ERY-H_2O	35–64.7	49.3	49.6 ± 13.8	49.9–67.7	64.8	60.6 ± 10.5
AZT	48.8–80.9	78.0	71.4 ± 15.3	88.6–96.8	91.4	90.1 ± 3.4
CLAR	51.3–73.8	67.0	64.8 ± 10.1	57.8–89.3	71.3	72.4 ± 13.8
SMX	62.8–77.7	66.6	68.4 ± 4.5	54–74.9	69.0	66.8 ± 8.9
SMZ	52.2–96	80.3	76.9 ± 19	78.4–96.2	88.1	87.7 ± 9.6
TMP	23.8–42.2	33.1	33.0 ± 7.8	67.7–73.3	69.1	69.8 ± 2.4
TET	44.3–87.6	67.1	66.5 ± 23.4	83.3–95.5	92.4	90.9 ± 5.6
MIN	44.8–86.9	70.2	68.1 ± 20.8	70.1–86.9	84.7	81.6 ± 7.8
CTC	31.4–88	58.8	59.2 ± 31.6	84–97.8	87.9	89.4 ± 6.1
OXY	54.6–93.9	80.3	77.3 ± 16.8	89.3–96.3	93.4	93.1 ± 3.5
TCS	87.4–94.2	91.1	90.9 ± 3.6	83.8–97.6	96.4	93.5 ± 6.6
TCC	51.1–84.7	69.9	68.9 ± 14.9	67.9–93.5	80.4	86.6 ± 12.3
VCM	96.6–99.9	99.9	99.1 ± 1.7	97.2–99.9	99.9	99.3 ± 1.4
CAP	98.4–98.8	98.6	98.6 ± 0.2	98.4–98.8	98.6	98.6 ± 0.2

Removal of PPCPs & EDCs by CAS & MBR Systems

Target ECs	Removal by CAS system (n = 4)			Removal by MBR system (n = 4)		
	Removal range (%)	Median (%)	Mean ± SD (%)	Removal range (%)	Median (%)	Mean ± SD (%)
ACT	98.3–99.2	98.9	98.9 ± 0.4	97.4–98.9	97.9	98.0 ± 0.7
ATN	88.9–96	94.8	93.6 ± 3.3	83.7–94.6	90.5	89.8 ± 4.5
BPA	81.9–90.6	86.2	86.2 ± 4.0	88.3–97.9	89.7	91.4 ± 4.4
CBZ	-0.2–19.1	5.2	7.3 ± 8.9	1.9–7.7	3.9	4.3 ± 2.9
CF	100	100	100	100	100	100
CTMT	0.4–28.8	4.3	9.4 ± 13.1	6.8–22.1	14.4	14.4 ± 6.9
DCF	-16.9–28.5	3.6	4.7 ± 19.7	-4.7–44.4	19.0	19.4 ± 22.3
DEET	88–95	93.7	92.6 ± 3.2	82.1–90.1	88.5	87.3 ± 3.5
FFP	98.6–99.6	99.1	99.1 ± 0.4	100	100	100
GBP	-8.3–91.3	58.9	50.2 ± 46.7	76.2–95.6	78.8	82.4 ± 9.0
GFZ	74.9–82.5	76	77.3 ± 3.5	78.5–95.5	88.3	87.7 ± 7.1
IBP	96.9–98.2	97	97.3 ± 0.6	96.7–98.1	97.4	97.4 ± 0.8
IDM	98.3–99	98.6	98.6 ± 03	98.3–99	98.6	98.6 ± 03
IOH	7.3–70.3	40.4	40.8 ± 29.8	65.9–79.2	71.9	72.2 ± 6.2
IOP	-53.7–44.8	-16	-10.2 ± 45.4	-80.7–53.4	38.5	12.4 ± 63
NPX	36.5–68.9	65.3	59.0 ± 15.1	48.3–72.2	67.3	63.8 ± 10.8
OXB	92.5–95.7	95.3	94.7 ± 1.5	95.6–97.5	97.2	96.9 ± 0.9
SA	12.9–95.1	68.9	61.47 ± 34.6	42.2–95.4	75.3	72.1 ± 22.1
SUL	9.5–73.5	32.4	37.0 ± 31.5	20.6–59.3	30.4	35.2 ± 18.5

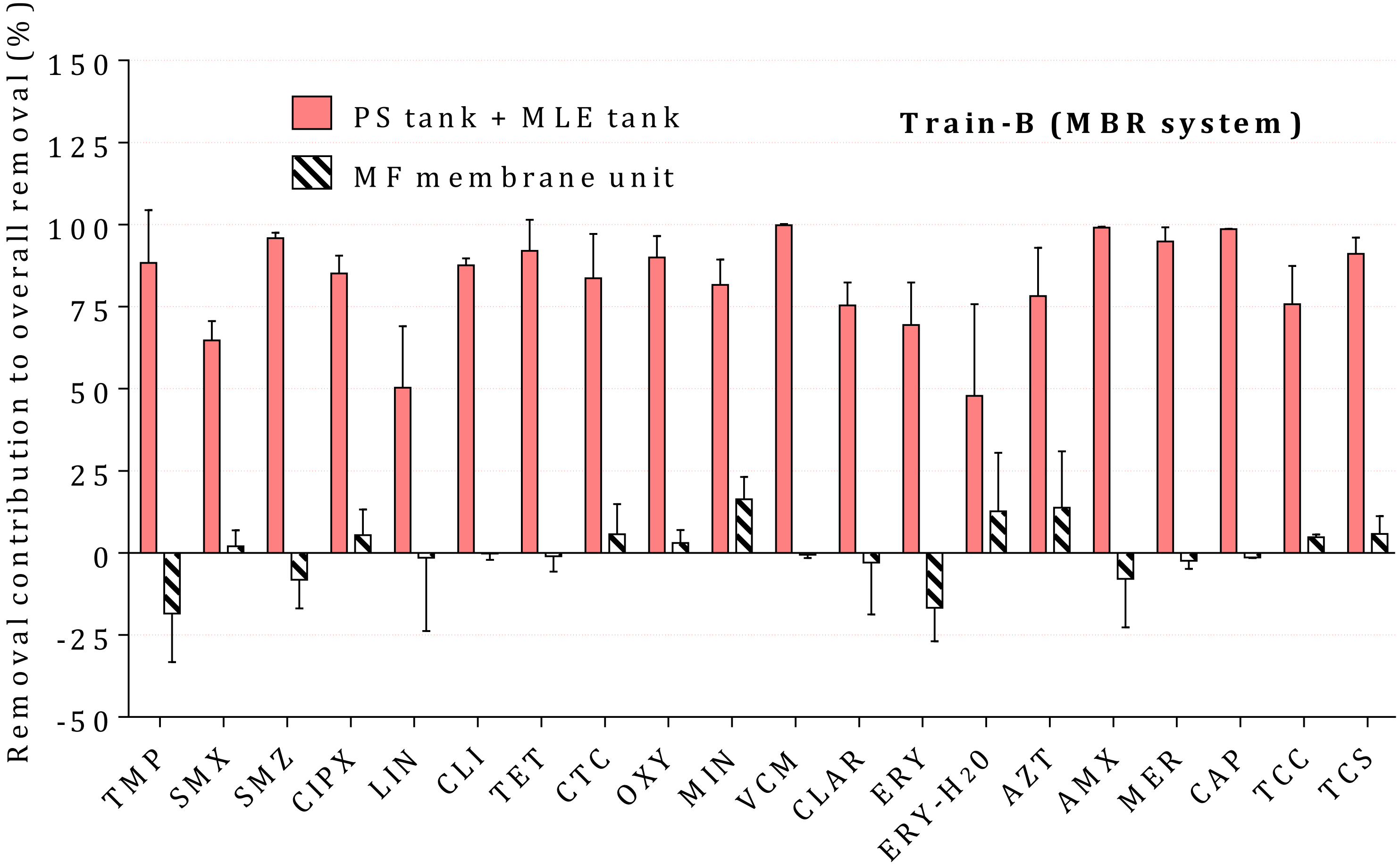
Comparison Between CAS and MBR





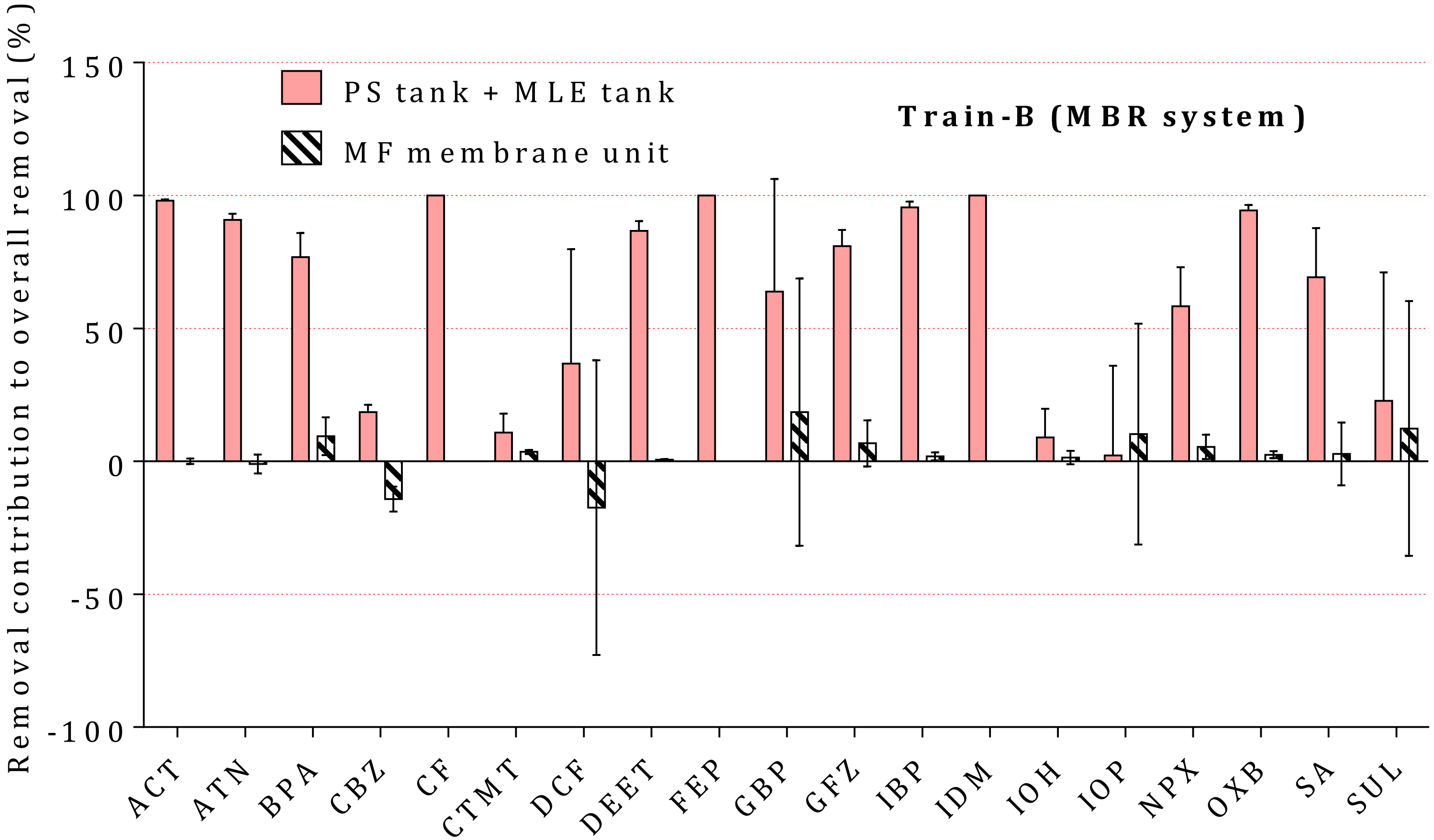
- MBR generally showed higher removal efficiencies than CAS
- For labile compounds (e.g. beta-lactams, VCM, CIPX, CAP, ACT, IBP, CF, and FEP) or poorly biodegradable compounds (CBZ and SUL), there was no significant difference between CAS and MBR.

Role of MF Membrane Unit in Overall Removal for MBR system (Antibiotics)



- The treatment in PS and MLE tanks appeared to be the most important processes for removal of all antibiotics and antimicrobials.
- More than 75% of most antibiotics was removed after treatment in [PS + MLE] tanks.

Role of MF Membrane Unit in Overall Removal for MBR System (PPCP, AS, EDC)



- A significantly higher removal efficiency was observed in [PS+MLE] tanks compared to MF membrane unit for majority of PPCPs & EDCs.
- [PS+MLE] tanks played a key role in the elimination of PPCPs & EDCs in MBR system.

Comparison of Antibiotics Removal with Literature

Target compound	Removal efficiencies observed in this study		Removal efficiencies reported in the literature	
	Removal range (%)	Median (%)	Removal range (%)	Median (%)
MER	81–92.3	84.5	Not reported	Not reported
AMX	69.9–99.7	99.5	49.7–100	99.5
CIPX	84.9–99.9	88.6	<0–100	88
LIN	-8.1–79.3	62.1	<0–100	29
CLI	85.8–88.9	87.5	<0–88.9	83.9
ERY	26.6–74.9	54.8	Not reported	Not reported
ERY-H_2O	49.9–67.7	64.8	<0–100	44.5
AZT	88.6–96.8	91.4	<0–99	63
CLAR	57.8–89.3	71.3	<0–99	42
SMX	54–74.9	69.0	<0–99	69.3
SMZ	78.4–96.2	88.1	<0–96.2	77.1
TMP	67.7–73.3	69.1	<0–99	57
TET	83.3–95.5	92.4	34–97	86.7
MIN	70.1–86.9	84.7	Not reported	Not reported
CTC	84–97.8	87.9	Not reported	Not reported
OXY	89.3–96.3	93.4	80.4–97.9	90.2
TCS	83.8–97.6	96.4	<0–100	92
TCC	67.9–93.5	80.4	<0–99	75.4
VCM	97.2–99.9	99.9	Not reported	Not reported
CAP	98.4–98.8	98.6	11.8–73.8	Not reported

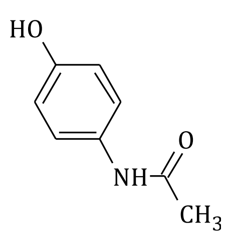
Comparison of PPCPs Removal with Literature

Target compound	Removal efficiencies observed in this study		Removal efficiencies reported in the literature	
	Removal range (%)	Median (%)	Removal range (%)	Median (%)
ACT	97.4–98.9	97.9	<0–100	99
ATN	83.7–94.6	90.5	<0–97	67
BPA	88.3–97.9	89.7	32–100	95.2
CBZ	1.9–7.7	3.9	<0–83	1
CF	100	100	84–100	100
CTMT	6.8–22.1	14.4	0–70	50
DCF	-4.7–44.4	19.0	<0–98	58.5
DEET	82.1–90.1	88.5	27–100	95.3
FEP	100	100	100	99.6
GBP	76.2–95.6	78.8	6.4–78	80
GFZ	78.5–95.5	88.3	0–100	81.3
IBP	96.7–98.1	97.4	<0–100	98.2
IDM	98.3–99	98.6	7–100	98.4
IOH	65.9–79.2	71.9	<0–90	11.5
IOP	-80.7–53.4	38.5	<0–33.4	18.7
NPX	48.3–72.2	67.3	<0–100	91.5
OXB	95.6–97.5	97.2	92.5–97.5	95.7
SA	42.2–95.4	75.3	12.9–100	95.7
SUL	20.6–59.3	30.4	<0–100	30

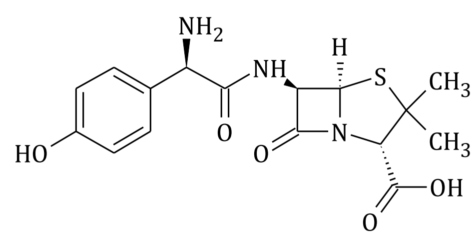
Relationship between Molecular Features & Removal Efficiencies

Excellent removal (>90%) was observed for ECs with at least one of the following characteristics:

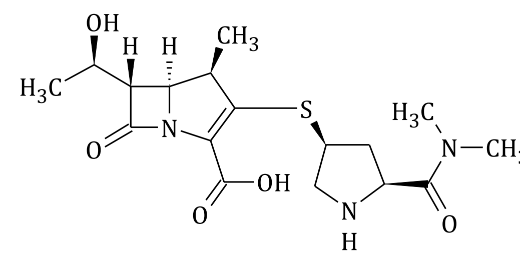
- Log D_{ow} > 3.0 (e.g. TCS, and OXB)
- Presence of electron donating groups, such as phenolic (–OH), methoxy (–O–CH_3), phenoxy (–O–C_6H_5), pseudo-peptide group (–NH–CO–R), alkyl and/or phenyl groups, or lactam rings (AMX, MER, ACT, ATN, CF, FEP, and IBP)



ACT



AMX



MER

- Mainly exist as cations/zwitterions at environmental pH (AMX and ATN).

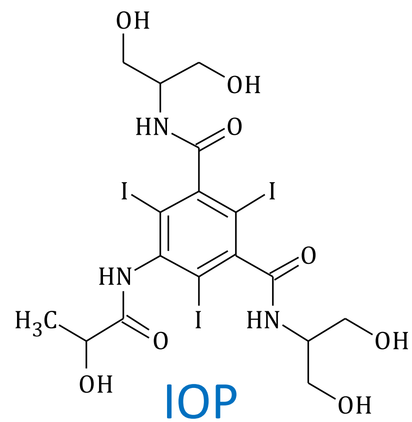
Relationship between Molecular Features & Removal Efficiencies

High removal (70–90 %) was frequently observed for:

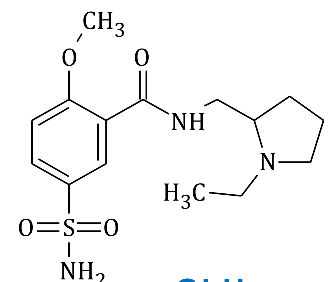
- $1.0 < \text{Log } D_{ow} < 3.0$.
- Presence of electron donating groups (e.g. BPA and GFZ).
- Exist as cations/zwitterions at env. pH (e.g. AZT, CLAR, CIPX, ERY, TET, MIN, OXY, and TCC).

Low removal (< 30 %) was frequently observed for:

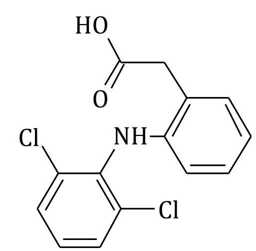
- $\text{Log } D_{ow} < 3.0$
- Absence of electron donating groups and/or presence of strong electron withdrawing groups (e.g. CBZ, DCE, IOP and SUL)
- Exist mainly as anions at env. pH (e.g. DCF, IOP)



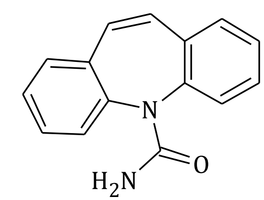
IOP



SUL



DCF



CBZ

Conclusions

Removal Efficiencies

- Excellent (>90%): AMX, MER, ACT, ATN, CF, FEP, TCS, OXB
- High (70-90%): TCC, AZT,CLAR,CIPX, ERY, TET, MIN, OXY, BPA, and GFZ.
- Low (<30%): CBZ, CTMT, DCF, IOP, and SUL.

Comparison of CAS and MBR

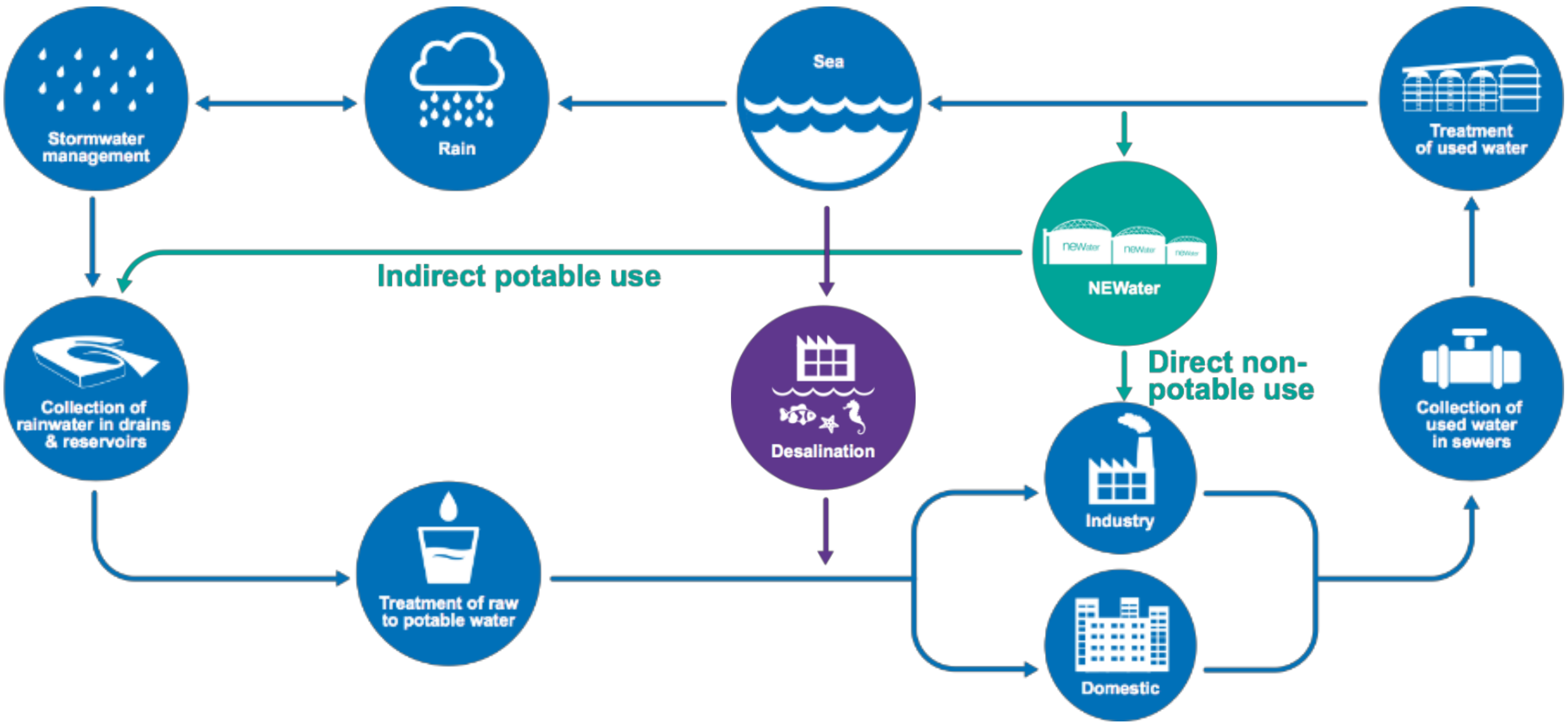
- MBR more stable, higher removal efficiencies

Mechanisms

- Enhanced removal: electron-donating groups/cations
- Poor removal: electron- withdrawing groups/anions

PUB's Approach on the Issue of Micropollutants/ Emerging Contaminants (ECs)

PUB manages the complete water cycle



CHALLENGES WITH ECs

- There are thousands of pharmaceutical and personal care products which are used on day to day basis.
- Most of them ends up in the wastewater.
- Depending on the demographic and changing disease spectrum their consumption changes.
- It varies to population to population, country to country.
- There is no single water treatment process which can remove all the ECs at one go.

ARE ECs REALY A CONCERN?

- **More ECs are detected today due to the increasingly sensitive analytical technology that allows identification and quantification of minute concentrations.**

- **The highest concentration of any pharmaceutical detected in U.S. drinking water is approximately 5,000,000 times lower than the therapeutic dose, which is orders of magnitude lower than the level that would pose a public health threat.**

  - ✓ Dr. Shane Snyder’s comments, while briefing United States Senate Subcommittee on Transportation Safety, Infrastructure Security and Water Quality on 15 Apr 2008.

- **Decisions or regulations should be made based on protection of public health and not the ability to find contaminants.**

ARE ECs REALY A CONCERN?

- **The 2011 World Health Organization (WHO) report on Pharmaceuticals in Drinking Water concluded that development of formal health-based guideline values for pharmaceuticals in drinking water is not necessary.**
  - ✓ The report assessed that if pharmaceuticals do present in drinking water, the concentrations are well below 50 ng/L (part per trillion) which are several orders of magnitude (more than 1000-fold) below the minimum therapeutic dose and largely below the acceptable daily intake (ADI) with respect to health impact. The substantial margin of safety for these individual compounds suggests that impacts on human health are very unlikely at current levels of exposure in drinking water for countries with pharmaceuticals detected in the water supplies.

STATE OF AFFAIRS OF ECs IN SINGAPORE - 1

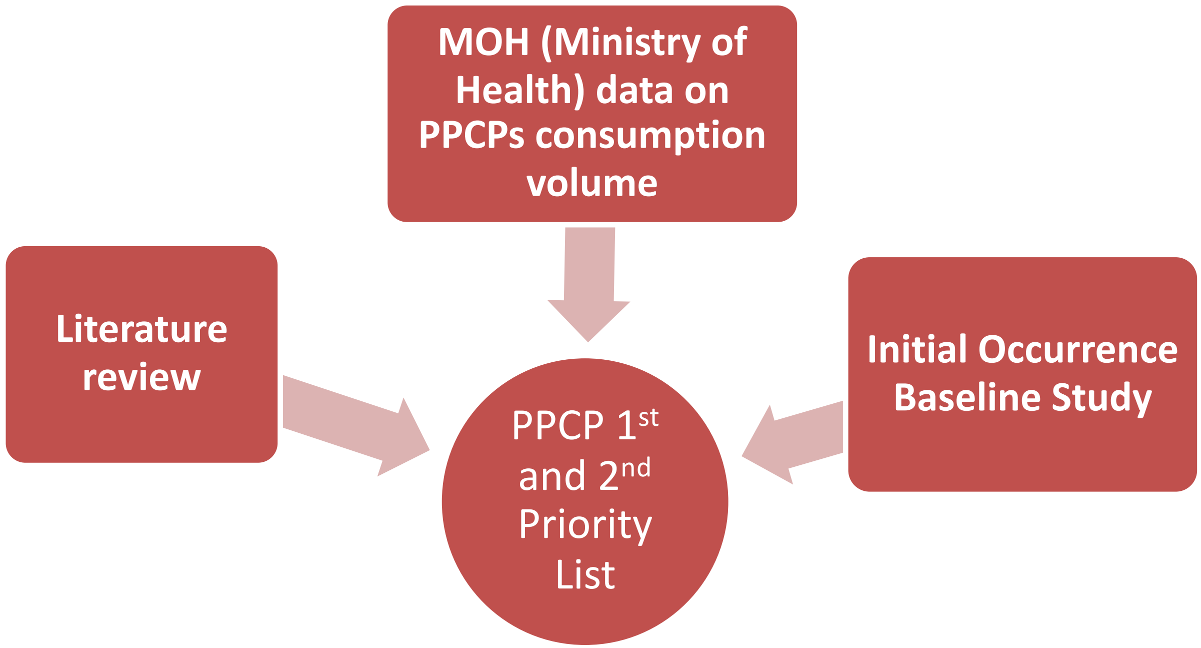
- PUB has been monitoring ECs in water since 2008.
- To include ECs in monitoring regime, ECs are prioritized based on local consumption, detection, treatability, toxicity etc.
- PUB priority list based on 5 criteria based on literature information, local consumption data and initial baseline occurrence study.
- The local consumption changes due to demographic and disease spectrum changes with time. Hence, a periodic review of the local consumption data carried out every year.
- PUB priority list is reviewed every year to check if there is any changes in the base criteria.

6 CRITERIA FOR PRIORITIZING ECs

S/N	Criterion	Reasoning
1.	**Consumption**	Consumption is directly related to the probability of occurrence in environment, as long as there is no special mechanism of elimination during the process.
2.	**Regulation**	Wastewater Utilities and drinking water supplies are obliged to fulfil any regulation. Most of the PPCPs are unregulated.
3.	**Physicochemical properties**	Physiochemical properties (such as polarity, water solubility, chemical reactivity) determine the behaviour of the PPCP in the environment as well as during drinking water/ wastewater treatment (based on sorption, degradation etc.). Thus contribute significantly while prioritizing.
4.	**Human toxicity/ Eco-toxicity**	Toxicological data reveals the impact human and environment.
5.	**Degradability/ Persistence**	Degradation of a compound during wastewater treatment or in environment can significantly decrease environmental relevance of the compound.
6.	**Resistance to Treatment**	PPCPs are difficult to remove during water treatment processes are of high relevance. Henceforth resistance to treatment (drinking / wastewater treatment) is very relevant.

Ref: *Development of an International Priority List of Pharmaceuticals relevant for the Water cycle*, GWRC, **2008**

PUB’S PRIORITY LIST



DECIDING FACTORS FOR PRIORITY LIST

- **Basis for of the PPCP's in 1st priority list**
- ✓ Analgesics (Acetaminophen, Salicylic acid, Ketoprofen, Diclofenac, Ibuprofen, Naproxen) were infrequently detected (in low ppt) in our urban waters. They are also highly consumed in Singapore. Some of them are over the counter drugs.
- ✓ Gemfibrozil (lipid lowering agent), Carbamazepine (anti epileptic drug) and Trimethoprim (antibiotic drug) are detected in our wastewaters (high ppt). They are among the highly consumed drugs in Singapore.
- ✓ DEET (N,N′ - Diethyl-meta-toluamide) has been reported to be present worldwide at trace levels.
- ✓ Though EDCs are not detected in any of our waters, they are selected based on their high endocrine disrupting impact on the marine ecosystem.

DECIDING FACTORS FOR PRIORITY LIST

- **Basis for of the PPCP’s in 2nd priority list**
- ✓ Compounds which were sometimes detected in our waste waters (initial occurrence baseline study) and were reported to be top consumed drugs in Singapore.
- ✓ Artificial sweeteners were listed in a separate category as tracers.

PUB'S PRIORITY LIST

Top Priority (Routine Monitoring in SAMP)	2nd Priority List		Chemical Tracers (Routine Monitoring in SAMP)
Diclofenac	Norfloxacin	Demethyl Diazepam	Acesulfame
Gemfibrozil	Erythromycin	Diazepam	Aspartame
Ibuprofen	Atenolol	Furosemide	Cyclamate
Naproxen	Bezafibrate	Oleandomycin	Saccharin
Ketoprofen	Amoxycillin	Oxytetracycline	Sucralose
Acetaminophen	Clarithromycin	Tilmicosin	
Salicylic Acid	Cyclophosphamide	Tylosin	
Carbamazepine	Clofibric Acid	Simvastatin	
17α- Ethinylestradiol	Hydrochlorothiazide	Clotrimazole	
17β- Estradiol	Lincomycin	Enalapril	
Estrone	Ofloxacin	Fluoxetine	
DEET	Sulfamethoxazole	Salbutamol	
Bisphenol A	Trimethoprim		

ECs MANAGEMENT IN SINGAPORE

- Island wide sewer rehabilitation programme has been completed
  - ✓ Significantly reduces Point Source contamination from sewer leaks
- Anthropogenic contamination cannot be completely eliminated
  - ✓ Most of the PUB's water treatment plants are equipped with Ozone/BAC treatment process or in the process of upgrading
  - ✓ New treatment process like Advanced Oxidation Processes (AOP) are rigorously tested in pilot plants, which if required will be implemented in future

STATE OF AFFAIRS OF ECs IN SINGAPORE - 2

- Most ECs are not detected in Singapore Waters. If detected they are the concentrations were minute in part per trillion (ng/L) levels, which are many orders of magnitude lower than the guidelines values (Reference: Australian Drinking Water Guideline Values, 2008)
- Used water in Singapore is discharged into sewers and there is a clear segregation of surface storm water drainage and sewerage system.
- The treated used water effluent is either discharged directly into the surrounding sea or delivered to NEWater factories at which the reverse osmosis process would effectively remove the ECs. Similarly, ECs would also be removed by the reverse osmosis process of the seawater desalination plants.

CONCLUSION

- ECs are not a concern in Singapore waters.
- An efficient monitoring regime has been put in place for detection and analysis of ECs in Singapore waters.
- Water Quality Department in PUB is equipped with latest instruments for detection and analysis of ECs.
- PUB periodically updates its EC priority list based on latest consumption data.
- AOPs are tested for treatment and removal of ECs in water, for future concern, if any.

Thank You

PUB SINGAPORE'S NATIONAL WATER AGENCY