Ecological safety in water reuse – precautionary principles and feasible measures

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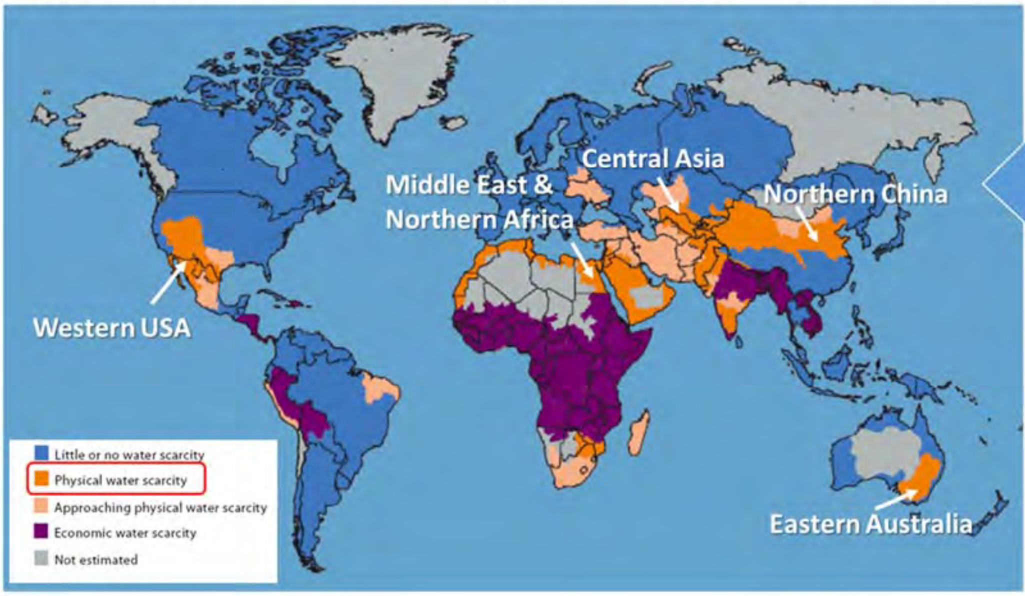
Outline

- Background
- Pollutants in reclaimed water and associated hazards
- Safety evaluation methods for reclaimed water quality
- Bio-toxic characteristics of residual organics
- Biotoxicity reduction by ecological processes
- Consideration on precautionary principle and feasible measures
- Concluding remarks

Background

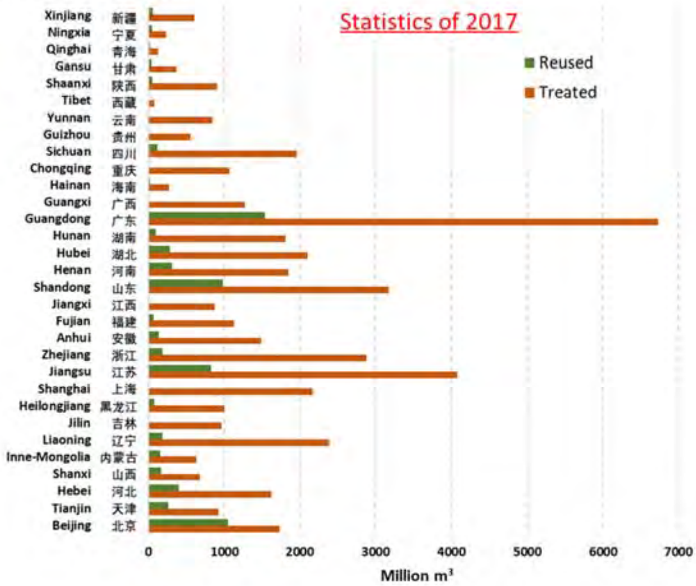
- **Worldwide water scarcity is the driver for water reuse**



- **Physical water scarcity in Central Asia, Middle East & Northern Africa, Western USA and Eastern Australia**
- **Northern China is suffering from serious water shortage**

Background

- **Urban wastewater treatment and reuse in China**

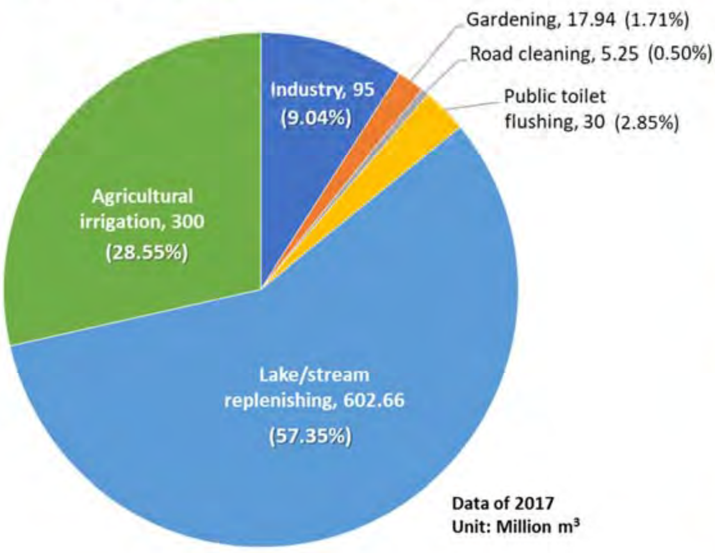


Background

- **Urban wastewater treatment and reuse in China**

Background

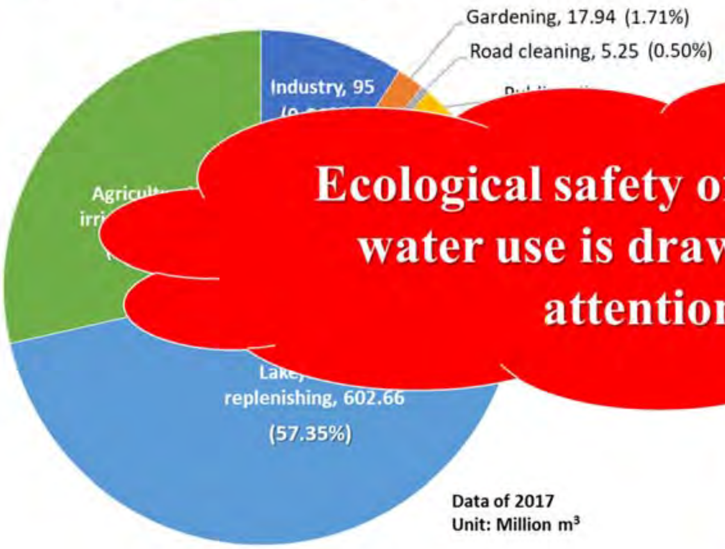
- **Water reuse in Beijing as an example**



- Ecological reuse for replenishing urban lakes and rivers (streams) took more than 57%
- Agricultural irrigation took about 29%
- Municipal reuse including gardening, road cleaning and toilet flushing took about 20%
- Industrial reuse took about 9%

Background

- **Water reuse in Beijing as an example**



Ecological safety of reclaimed water use is drawing wide attention

- Ecological reuse for ... lakes and ... more ... took
- ... reuse including gardening, road cleaning and toilet flushing took about 20%
- Industrial reuse took about 9%

A Special Water Course on "Technological Innovation and Practice of Reclaimed Water Treatment and Application" was held in Beijing with more than 300 participants from China water industries

Safety of water reuse was an important topic

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Pollutants in reclaimed water and associated hazards

Pollutants		Examples	Main sources	Associated hazards	Related types of reuse
Bulk pollutants	Pathogens	Bacteria, Viruses	Domestic	Public health	Various reuse with possible human contact
	Nutrients	N, P	Domestic	Water eutrophication	Water body replenishment
Trace pollutants	Heavy metals	Cd, Hg, Ni, Pb etc.	Industrial	Public health/ Eco-toxicity	Various reuse with possible human contact/ Ecological reuse
	Organic chemicals	EDCs, POPs, PPCPs etc.	Industrial/ Domestic	Public health/ Eco-toxicity	Various reuse with possible human contact/ Ecological reuse

Pollutants in reclaimed water and associated hazards

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	Nutrients				…eplenishment
Trace pollutants	Heavy metals	Cd, Hg, Pb etc.		…lth/ Eco-toxicity	Various reuse with possible human contact/ Ecological reuse
	Organic chemicals	EDCs, POPs, PPCPs etc.	Industrial/ Domestic	Public health/ Eco-toxicity	Various reuse with possible human contact/ Ecological reuse

Attention paid to trace organic chemicals

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Safety evaluation methods for reclaimed water quality

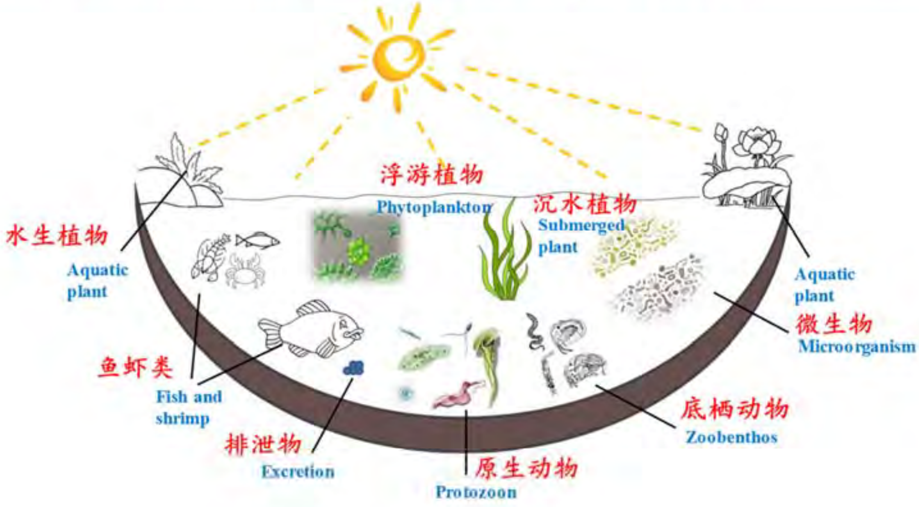
- Evaluation based on water quality standard
  - ✓ Standards referred: water reuse standard, surface water standard etc.
  - ✓ Method of evaluation: Standard-reaching rate

Safety evaluation methods for reclaimed water quality

- Evaluation based on water quality standard
  - ✓ Standards referred: water reuse standard, surface water standard etc.
  - ✓ Method of evaluation: Standard-reaching rate

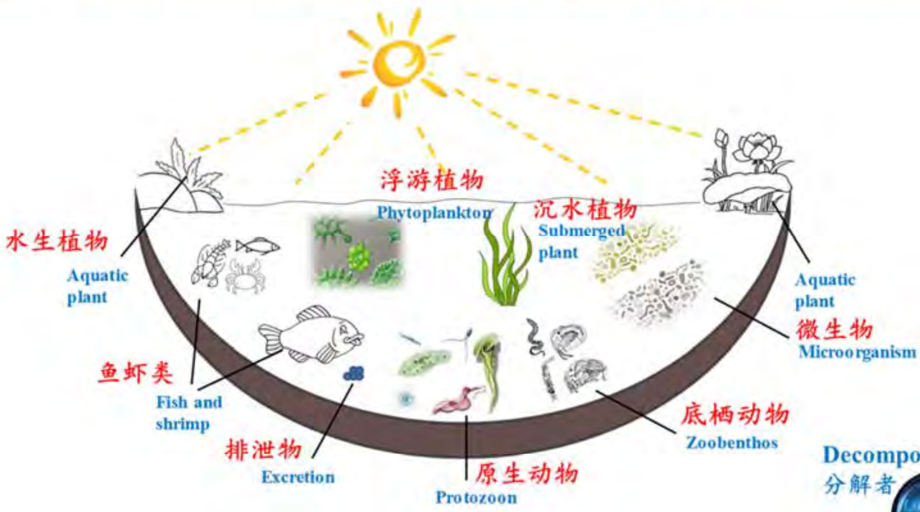
- Evaluation based on biotoxicity
  - ✓ Biotoxicity: Damage to non-human organisms in ecosystem due to exogenous chemicals
  - ✓ Categories of biotoxicity: Phytotoxicity, animal toxicity, genotoxicity etc.

Safety evaluation methods for reclaimed water quality



Organisms in the aquatic ecosystem

Safety evaluation methods for reclaimed water quality



Organisms in the aquatic ecosystem

Biotoxicity tests

Safety evaluation methods for reclaimed water quality

- **Standardized/guided bioassays**

Category 类别	Bioassays 生物毒性检测	ISO	OECD	China	USA	Japan	Germany	UK
Acute toxicity 急性毒性	Alga growth inhibition test 藻类生长抑制试验	Standardized	Guided	Guided	Standardized	Standardized	Standardized	Standardized
	Flea inhibition/lethal test 蚤类运动抑制/致死试验	Standardized	Guided	Standardized	Standardized	Standardized	Standardized	Standardized
	Fish acute toxicity test 鱼类急性毒性试验	Standardized	Guided	Standardized	Standardized	Standardized	Standardized	Standardized
	Luminescent bacteria test 发光细菌试验	Standardized	Not standardized/Guided	Standardized	Standardized	Not standardized/Guided	Standardized	Standardized
	Germination/root growth test 发芽/根生长毒性试验	Not standardized/Guided	Not standardized/Guided	Guided	Standardized	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided
Chronic toxicity 慢性毒性	Flea chronic toxicity test 蚤类慢性毒性(生命周期评价试验)	Standardized	Guided	Not standardized/Guided	Standardized	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided
	Fish chronic toxicity test 鱼类慢性毒性试验	Standardized	Guided	Not standardized/Guided	Standardized	Not standardized/Guided	Standardized	Not standardized/Guided
Genotoxicity 遗传毒性	Bacterial reverse mutation test 细菌回复突变试验	Standardized	Guided	Guided	Standardized	Not standardized/Guided	Standardized	Guided
	SOS/umu test 遗传毒性试验	Standardized	Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Standardized	Not standardized/Guided
	Micronucleus test 微核试验	Standardized	Guided	Guided	Standardized	Not standardized/Guided	Standardized	Standardized
Endocrine interference 内分泌干扰性	Hybrid yeast method 双杂交酵母法	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided
	Fish endocrine interference test 鱼类内分泌干扰性试验	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided	Guided	Not standardized/Guided	Not standardized/Guided	Not standardized/Guided

Standardized
Guided
Not standardized/ Guided

Safety evaluation methods for reclaimed water quality

- **Biotoxicity analyses/evaluation methods used in this study**

Biotoxicity analyses

Luminescent bacteria | Microalgae | SOS/umu

Biotoxicity evaluation

EC_{50}/IR1.5 equivalent BEQ | On quality standard EQS-EBT | On hazardous concentration HC5-EBT

Model prediction

Nonspecific biotoxicity

$$EC_{50,\,CA} = \left(\sum_{i=1}^{n} \frac{p_i}{EC_{50,i}}\right)^{-1} \Rightarrow BEQ_{phenol}\text{-pre} = \frac{EC_{50,\,phenol}}{EC_{50,\,CA}/C_{Total}}$$

Specific biotoxicity

$$RP_i = \frac{EC_{50,diuron}}{EC_{50,i}} \Rightarrow BEQ_{diuron}\text{-pre} = \sum_{i=1}^{n} RP_i \times C_i$$

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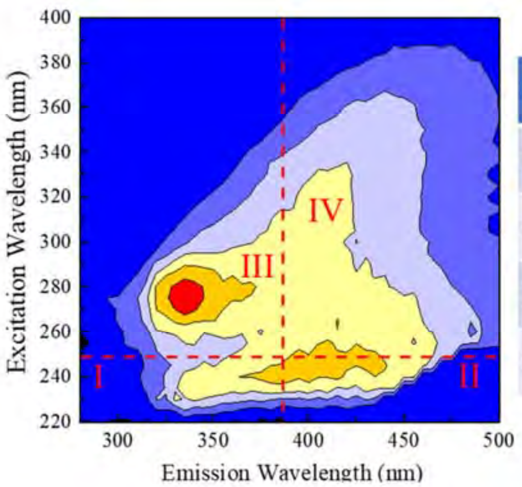
Bio-toxic characteristics of residual organics

- **Dissolved organic matter (DOM)**



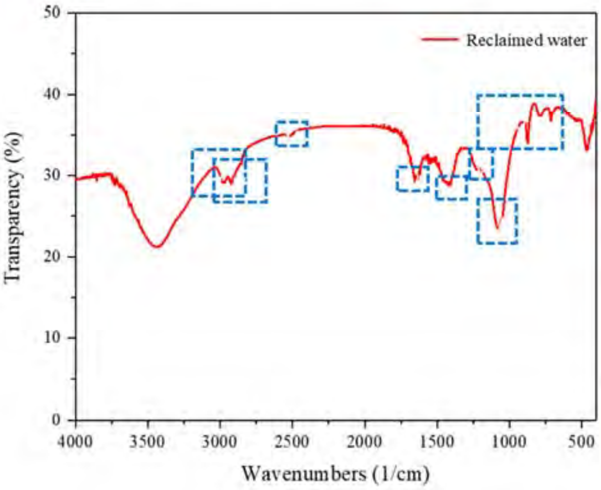
3D fluorescence assay

FIR Region	Excitation (nm)	Emission (nm)	Characteristics	Φi.n ($\times 10^6$ Au·nm^2)
Region I	220-250	280-380	Aromatic protein-like fluorophores	6.5
Region II	220-250	380-500	Fulvic acid-like fluorophores	5.9
Region III	250-400	280-380	Soluble microbial product-like fluorophores	6.0
Region IV	250-400	380-500	Humic acid-like fluorophores	4.8

Different fluorescence absorption characteristics for DOM from sewage and biological byproducts

Bio-toxic characteristics of residual organics

- **Dissolved organic matter (DOM)**



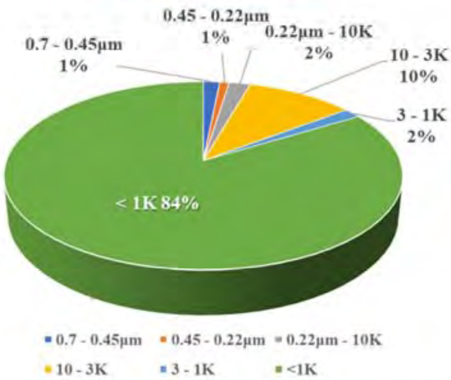
FTIR Analysis

Characteristic peaks 峰归属	Wave number 波数	Organic compounds 化合物来源
Sugar C-OH	3570-3050	Polysaccharides, cellulose 多糖类、纤维素
Antisymmetric methylene CH_2	2925±5	Fats and lipids 脂肪和脂质类
Aliphatic COOH	2700-2500	Fatty acid 脂肪酸
Carbonyl amide C= O	1664	Amino compound, protein 氨基化合物、蛋白质
Phenolic hydroxyl C-O	1400	Phenolic compounds 酚类化合物
Aromatics COOH	1280-1150	Fulvic acid 富里酸
Sugar C-O	1100-1000	Polysaccharides 多糖类
Aromatic acid esters C-O-C	1050-1000	Humic acid 腐殖酸

Bio-toxic characteristics of residual organics

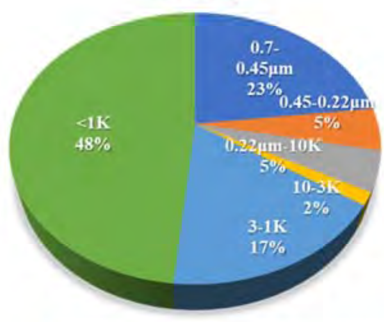
- **MW fractionation of DOM and corresponding non-specific toxicity**

MW fractionation

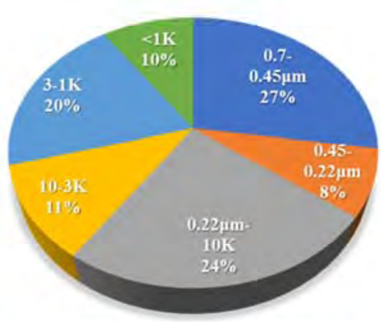


84% of DOM with MW < 1k

Luminescent bacteria toxicity



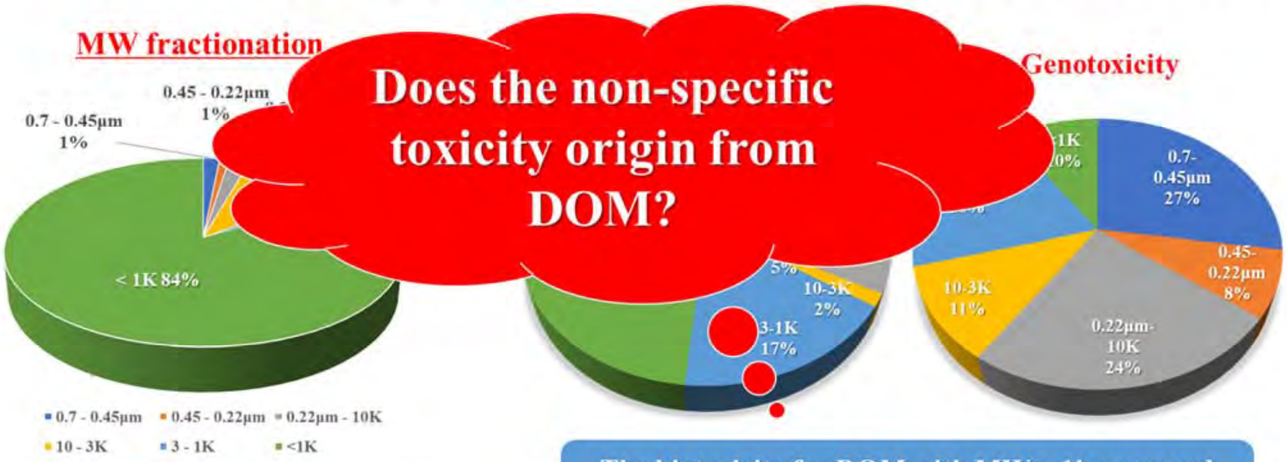
Genotoxicity



The biotoxicity for DOM with MW > 1k appeared much higher than their percent of MW fractionation

Bio-toxic characteristics of residual organics

- **MW fractionation of DOM and corresponding non-specific toxicity**



84% of DOM with MW < 1k

The biotoxicity for DOM with MW > 1k appeared much higher than their percent of MW fractionation

Bio-toxic characteristics of residual organics

- **Trace organic pollutants in WWTP effluent**

Categories	Example	References
Nonpolar compounds-Hydrocarbons	Linear alkylbenzenes C10–C14, petroleum-derived hydrocarbons, etc.	Smital et al. 2011
Medium-polar compounds	Coumarine, indole, etc.	Smital et al. 2011
Surfactants	Alkylphenol polyethoxylates, linear alkylbenzene sulfonates, etc.	Smital et al. 2011
Phenols	phenol, 2-cresol, 3-cresol, 2-chlorophenols, etc.	Zhong et al. 2018
EDCs	17-β-estradiol, estrone, ethinyl estradiol, etc.	Sun et al. 2013; Tang et al. 2014
PPCPs	Caffeine, gemfibrozil, propyphenazone, octocrylene, tonalide, triclosan, etc.	Yoon et al. 2010; Cabeza et al. 2012; Tang et al. 2014
Dioxins	2,3,7,8-Tetrachloro-dibenzo-p-dioxin, etc.	Cabeza et al. 2012
PAHs	Anthracene, naphthalene, pyrene, etc.	Estévez et al. 2012; Ratola et al. 2012
POPs	Dichlorodiphenyltrichloroethane, hexachlorocyclohexanes, etc.	Zhang et al. 2013; Sharma et al. 2014
Pesticides	Atrazine, simazine, terbutryn, etc.	Ratola et al. 2012; Tang et al. 2014
Disinfection by-product	Bromodichloromethane, bromoform, etc.	Leusch et al. 2014
Volatile organic compounds	Hepta-brominated diphenyl ether, 1,2,3-trichlorobenzene, etc.	Estévez et al. 2012; Rodriguez et al. 2012
Flame retardants	Trichloroethyl phosphate, Trichloropropyl phosphate, etc.	Cabeza et al. 2012; Estévez et al. 2012
x-ray contrast media	Diatrizoic acid, lopromide, etc.	Tang et al. 2014
Priority substances	Tributylphosphate	Cabeza et al. 2012; Leusch et al. 2014b

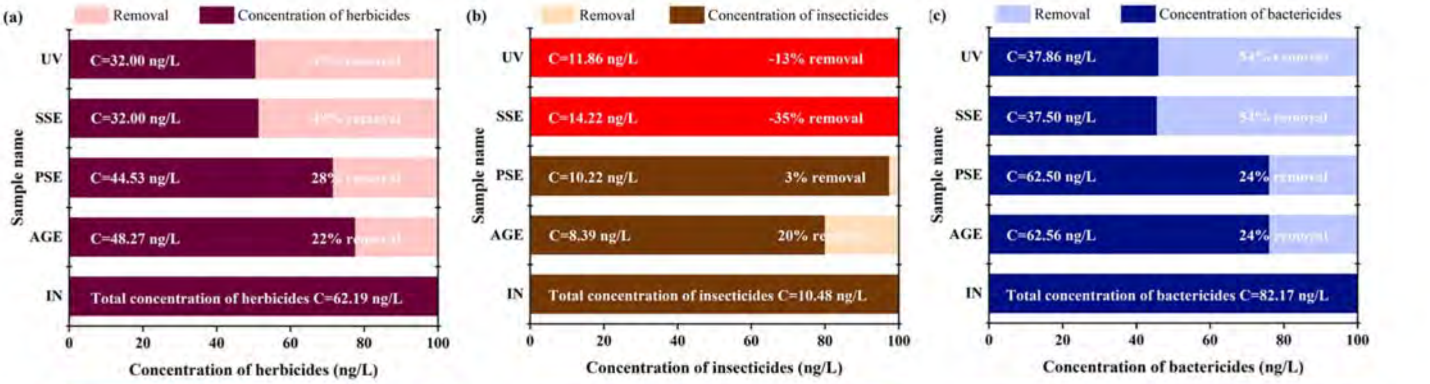
✓ From domestic, industrial and agricultural sources

✓ Mostly as bio-refractory organic compounds

Bio-toxic characteristics of residual organics

- **Micropollutant removal by conventional treatment**

IN: Influent; AGE: Screened; PSE: Primarily settled; SSE: Secondarily settled; UV: UV disinfected



Herbicide: about 50% removal

Pesticide: almost no removal

Bactericide: about 55% removal

Bio-toxic characteristics of residual organics

- **Micropollutant removal by conventional treatment**

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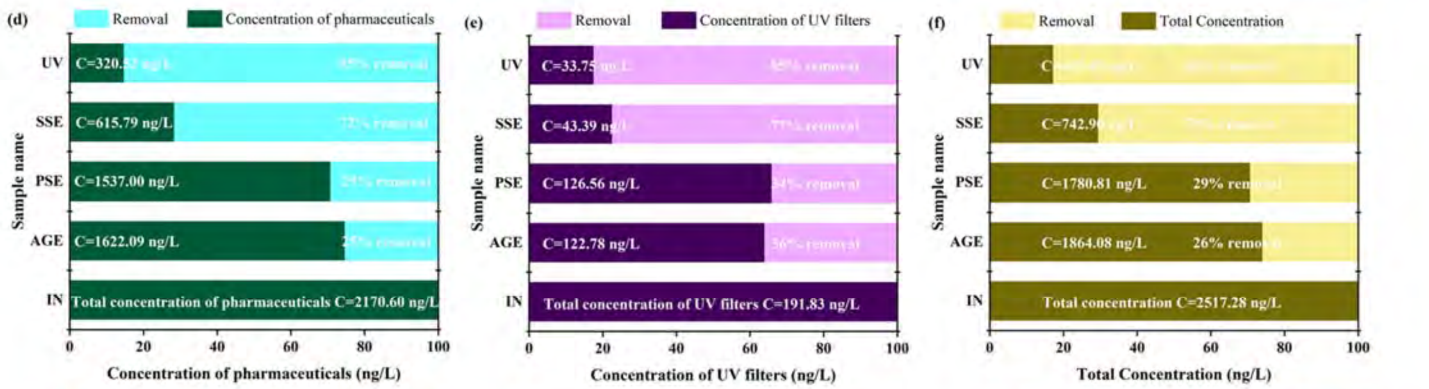


Pharmaceuticals: about 85% removal

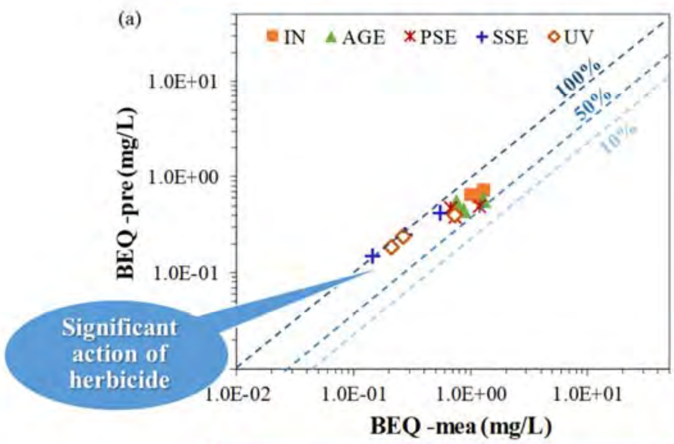
Sunscreen: about 85% removal

Total concentration: about 80% removal

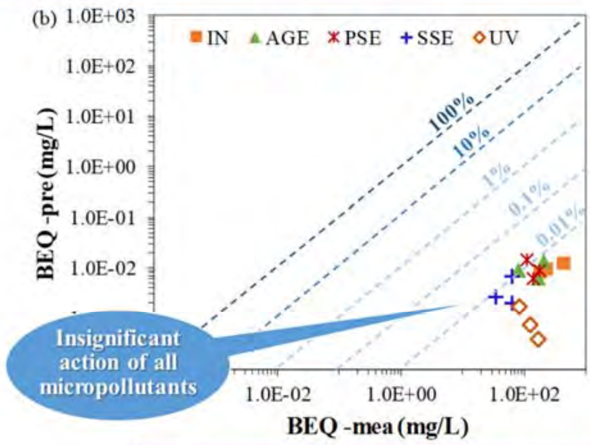
Bio-toxic characteristics of residual organics

- **Biotoxicity reduction by conventional treatment**

IN: Influent; AGE: Screened; PSE: Primarily settled; SSE: Secondarily settled; UV: UV disinfected



Specific photoinhibition toxicity



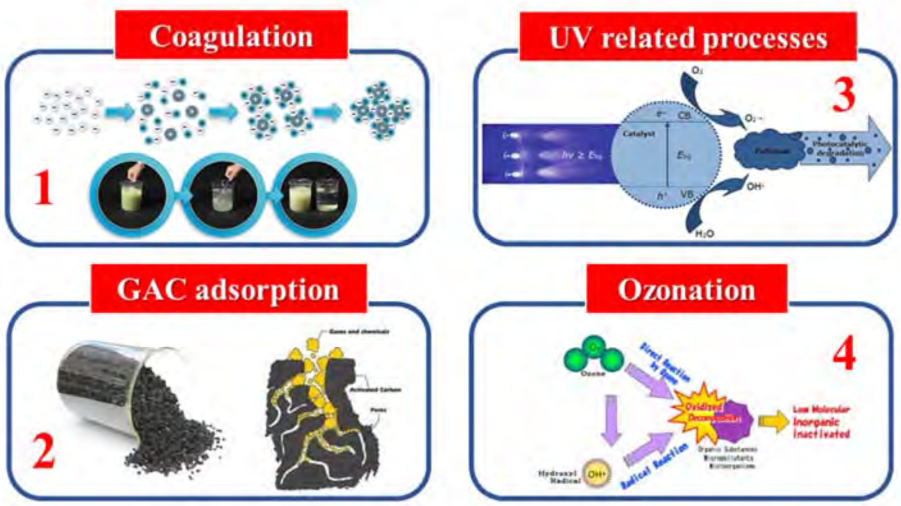
Measurement (BEQ-mea) vs model prediction (BEQ-pre) for 32 micro-pollutants

Nonspecific acute bacterial toxicity

Bio-toxic characteristics of residual organics

- **Micropollutant removal by advanced treatment**

Comparison of four treatment processes



Bio-toxic characteristics of residual organics

- **Micropollutant removal by advanced treatment**

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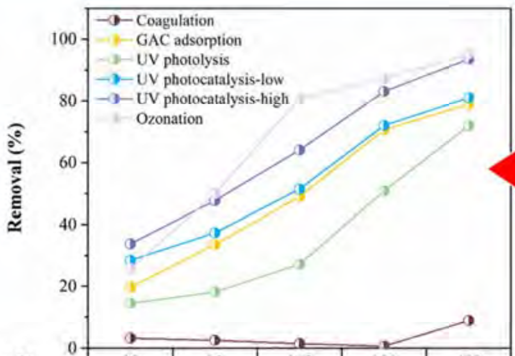


PACl (mg/L)	20	50	100	200	400	Coagulant dose 混凝剂投量
GAC (g/L)	2.5	5	10	20	30	GAC dose 粒状活性炭投量
Time (h)	0.5	1	2	4	8	UV reaction time 紫外光解时间
Dosage (gO3/gDOC)	0.21	0.34	0.71	0.82	1.31	Ozone dose 臭氧投量

Order of Revomal

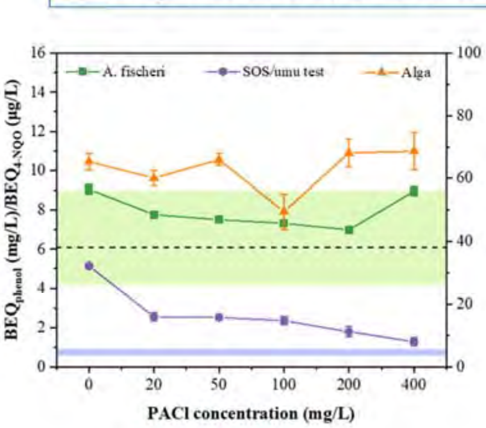
- Ozonation
- UV photocatalysis-high
- UV photocatalysis-low
- GAC adsorption
- UV photolysis
- Coagulation

Bio-toxic characteristics of residual organics

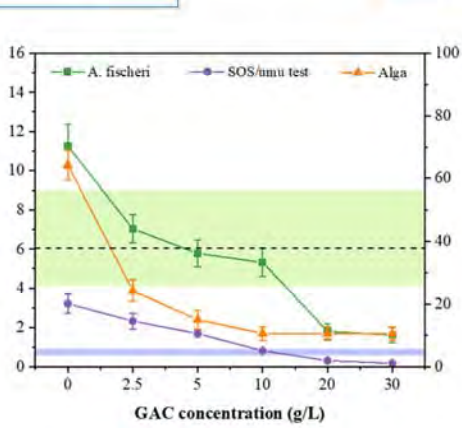
- **Biotoxicity reduction by advanced treatment**

: 95% confidence interval of the HC5-EBT for A. fischeri
: Scope of the HC5-EBT for SOS/umu

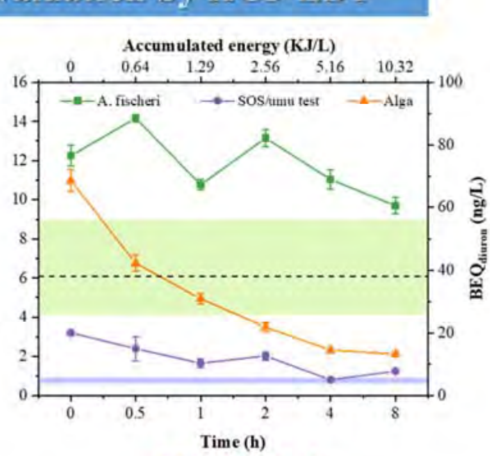
Evaluation by HC5-EBT



Coagulation



GAC adsorption



UV photolysis

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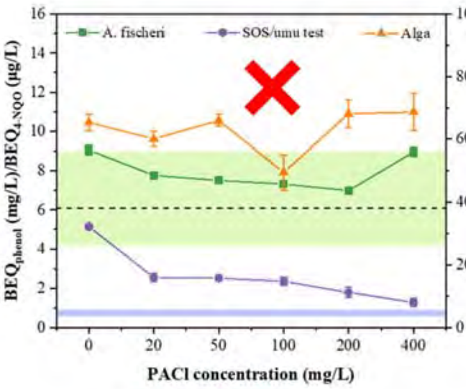

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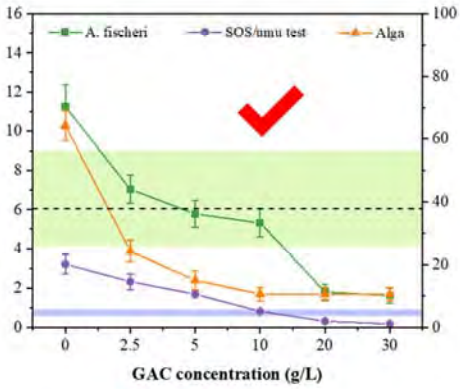

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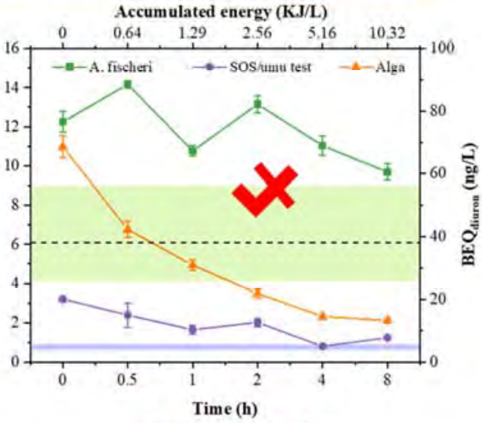

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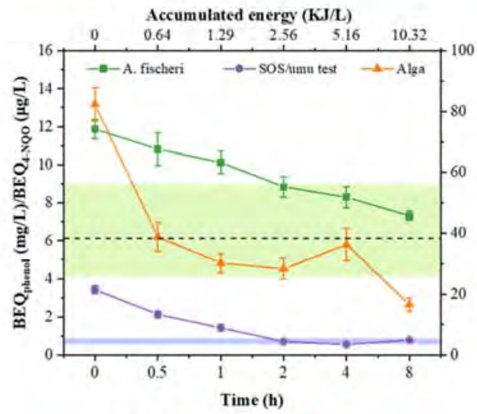
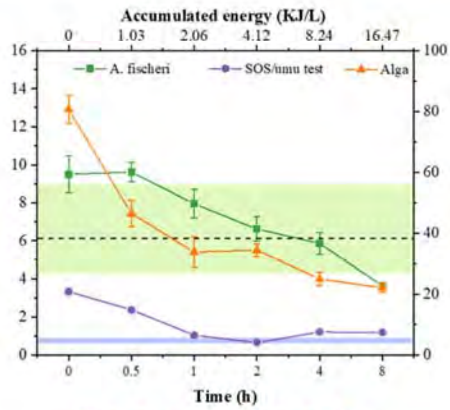
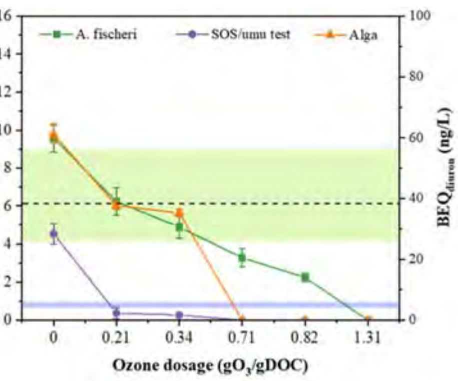


UV photocatalysis-low



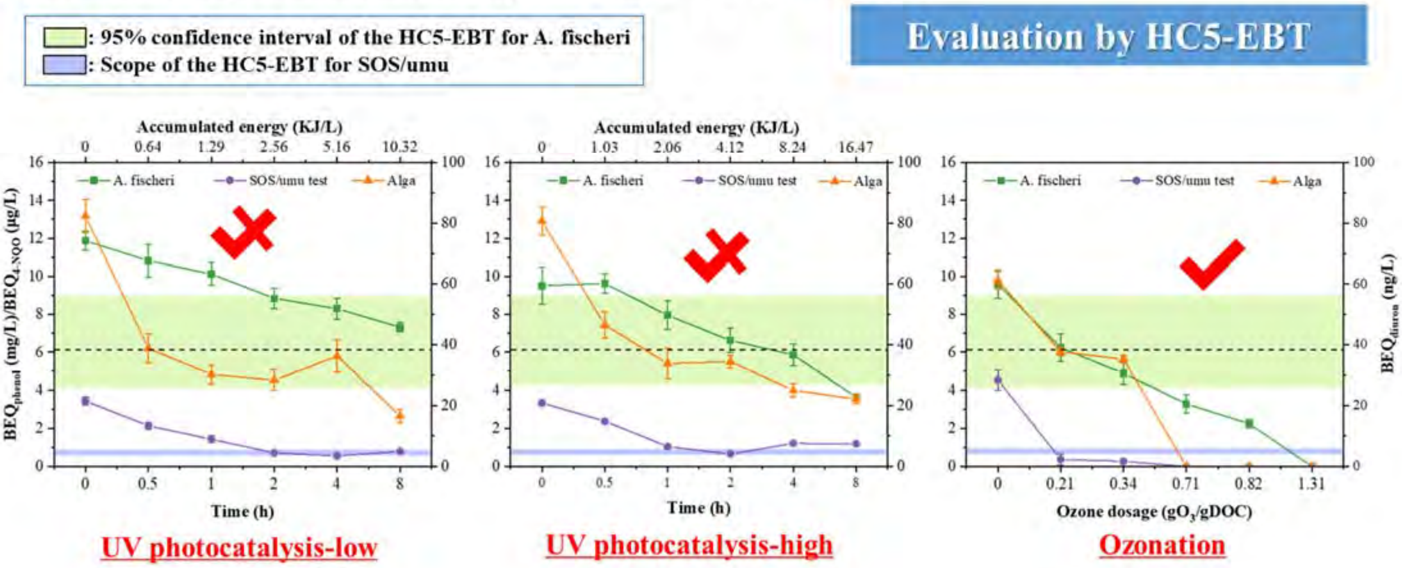
UV photocatalysis-high



Ozonation

Bio-toxic characteristics of residual organics

- **Biotoxicity reduction by advanced treatment**



Bio-toxic characteristics of residual organics

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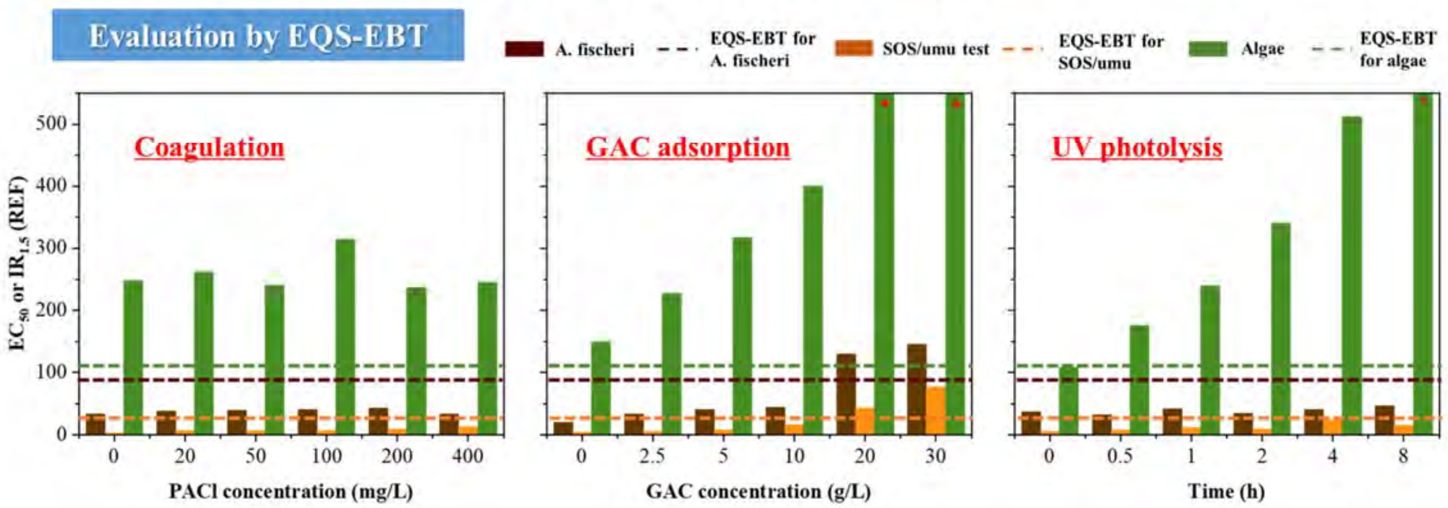

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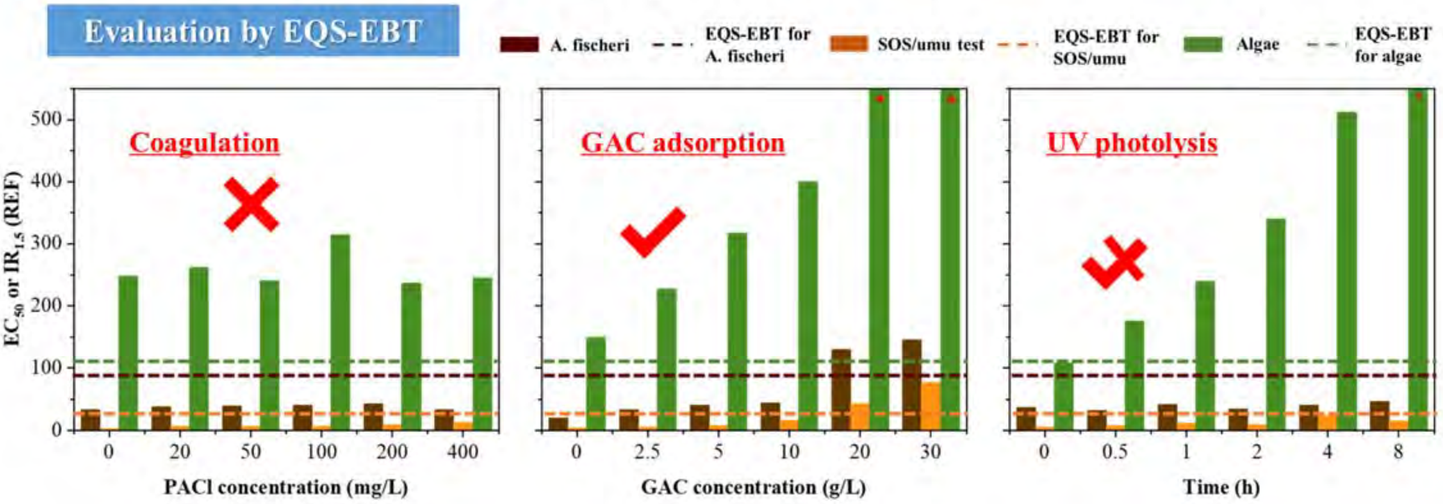

Bio-toxic characteristics of residual organics

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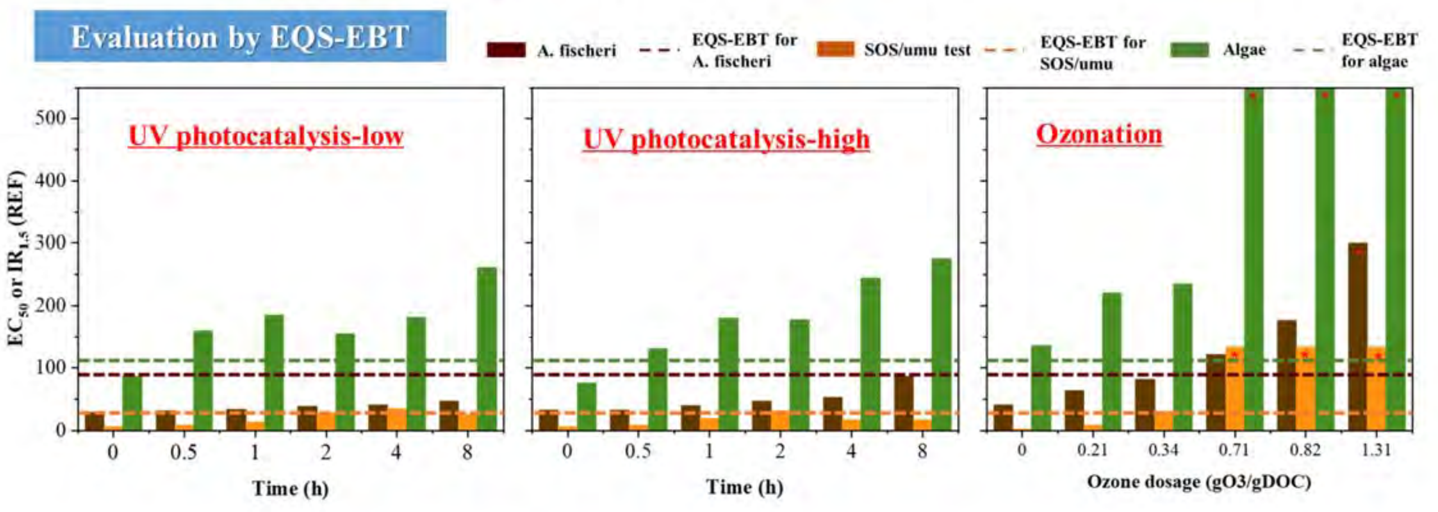
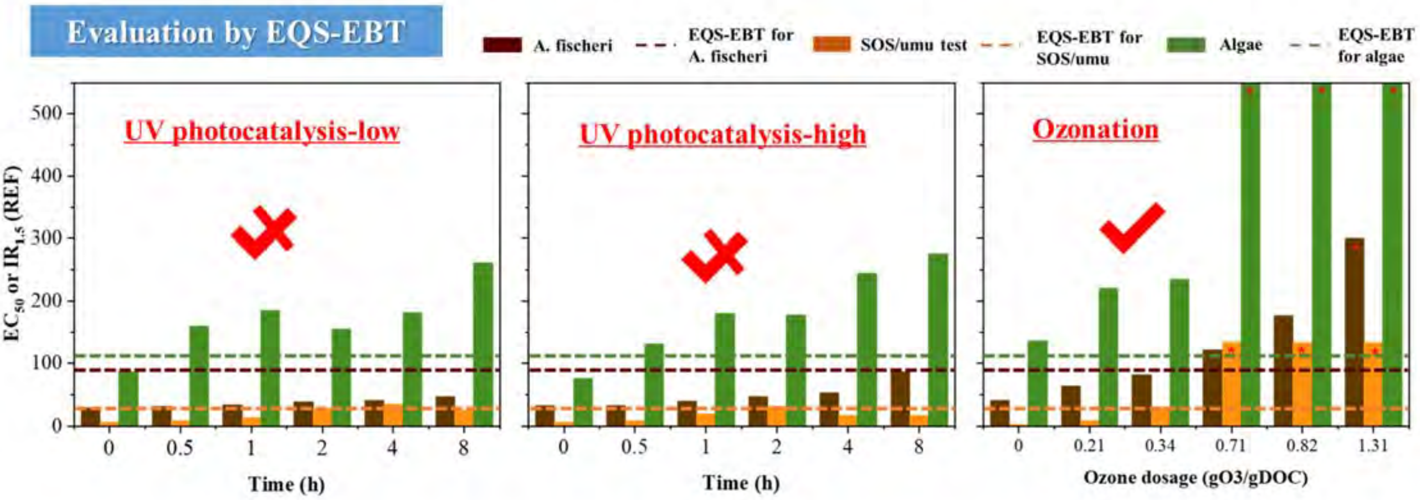


Bio-toxic characteristics of residual organics

- **Biotoxicity reduction by advanced treatment**



Bio-toxic characteristics of residual organics

- **Evaluation of biotoxicity reduction efficiency**

Results comparison

Treatment process	Assessment method	Biouminescece inhibition (Non-specific)	Genotoxicity (Non-specific)	Photosynthesis inhibition (Specific)
Coagulation	EQS-EBT	*Unacceptable*	*Unacceptable*	——
	HC5-EBT	*Unacceptable*	*Unacceptable*	——
GAC adsorption	EQS-EBT	≥20g/L GAC	≥20g/L GAC	——
	HC5-EBT	≥20g/L GAC	≥20g/L GAC	——
UV photolysis	EQS-EBT	*Unacceptable*	*Unacceptable*	≥0.5h UV
	HC5-EBT	*Unacceptable*	*Unacceptable*	——
UV photocatalysis-low	EQS-EBT	*Unacceptable*	4h UV	≥0.5h UV
	HC5-EBT	*Unacceptable*	≥2h UV	——
UV photocatalysis-high	EQS-EBT	*Unacceptable*	2h UV	≥0.5 h UV
	HC5-EBT	8 h UV	2h UV	——
Ozonation	EQS-EBT	≥0.71 gO_3/gDOC	≥0.34 gO_3/gDOC	——
	HC5-EBT	≥0.34 gO_3/gDOC	≥0.34 gO_3/gDOC	——

Bio-toxic characteristics of residual organics

- **Evaluation of biotoxicity reduction efficiency**

Results comparison

Treatment process	Assessment method	Biouminescece inhibition (Non-specific)	Genotoxicity (Non-specific)	Photosynthesis inhibition (Specific)	
Coagulation	EQS-EBT	*Unacceptable*	*Unacceptable*	——	No effect
	HC5-EBT	*Unacceptable*	*Unacceptable*	——	
GAC adsorption	EQS-EBT	≥20g/L GAC	≥20g/L GAC	——	Remarkable effect
	HC5-EBT	≥20g/L GAC	≥20g/L GAC	——	
UV photolysis	EQS-EBT	*Unacceptable*	*Unacceptable*	≥0.5h UV	Effective but uncertain
	HC5-EBT	*Unacceptable*	*Unacceptable*	——	
UV photocatalysis-low	EQS-EBT	*Unacceptable*	4h UV	≥0.5h UV	
	HC5-EBT	*Unacceptable*	≥2h UV	——	
UV photocatalysis-high	EQS-EBT	*Unacceptable*	2h UV	≥0.5 h UV	
	HC5-EBT	8 h UV	2h UV	——	
Ozonation	EQS-EBT	≥0.71 gO_3/gDOC	≥0.34 gO_3/gDOC	——	Remarkable effect
	HC5-EBT	≥0.34 gO_3/gDOC	≥0.34 gO_3/gDOC	——	

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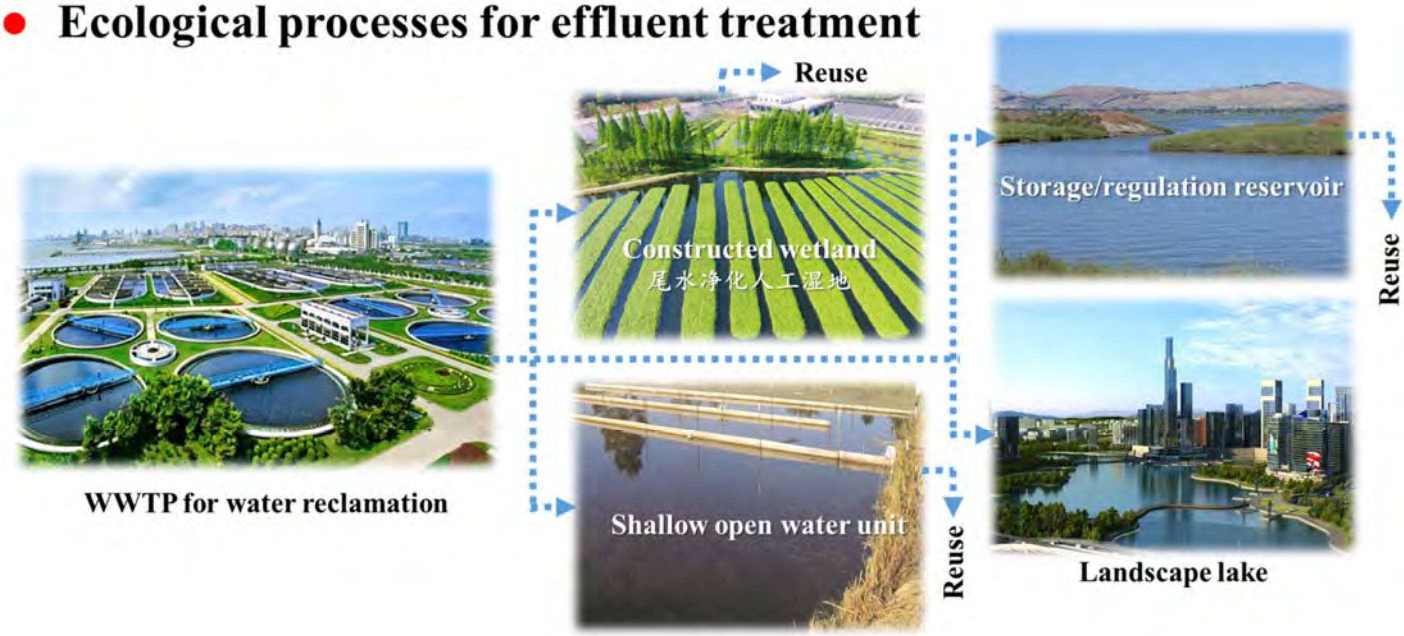
Biotoxicity reduction by ecological processes

- **Ecological processes for effluent treatment**



Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction by shallow water unit**

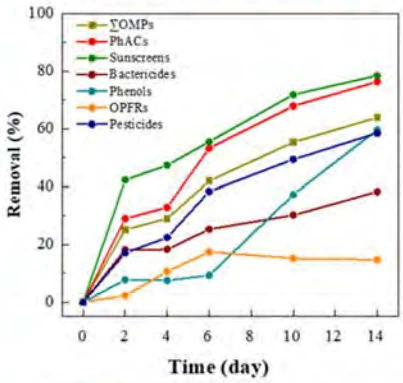
System

Shallow flowing water
(Depth < 0.4 m)

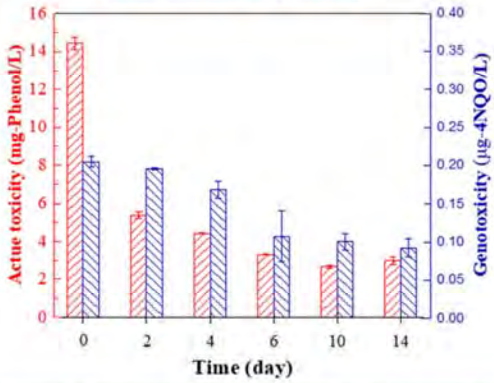
Main actions

- ✓ Natural UV photolysis
- ✓ Other physico-chemical/ecological actions

Micropollutant removal



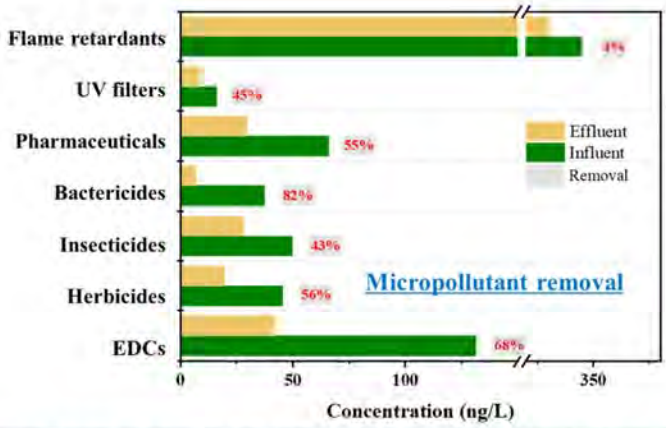
Biotoxicity reduction

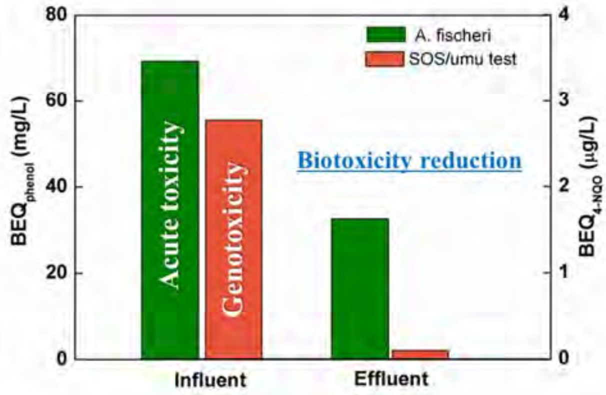


- ✓ 80% pharmaceuticals/sunscreens, and 15-42% agricultural chemicals removal
- ✓ Significant reduction of biotoxicities

Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction by constructed wetland**





✓ Surface flow wetland achieved removals of EDCs(68%), pharmaceuticals (55%) and agricultural chemicals (43-82%)
✓ Remarkable reductions of acute toxicity (50%) and genotoxicity (>95%) were achieved

Biotoxicity reduction by ecological processes

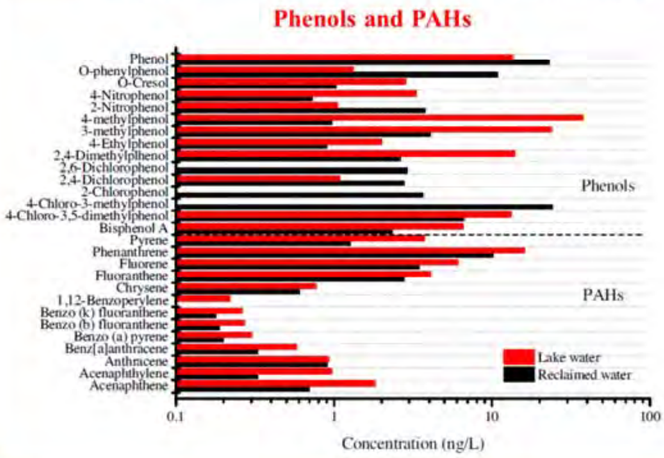
- **Micropollutant removal and biotoxicity reduction in a landscape lake system**

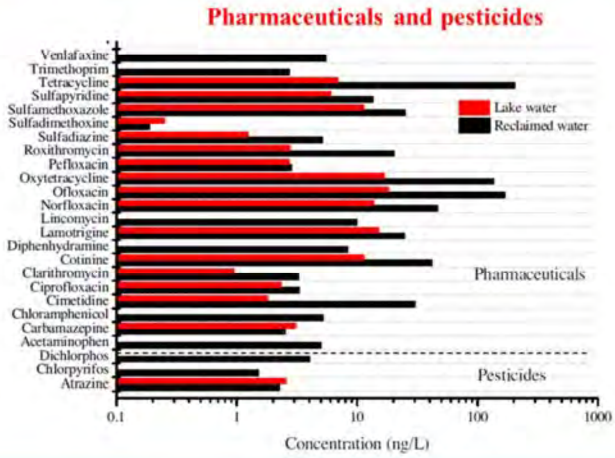
Water reclamation and reuse system

Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction in a landscape lake system**

Micropollutants in reclaimed water and lake water





Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction in a landscape lake system**

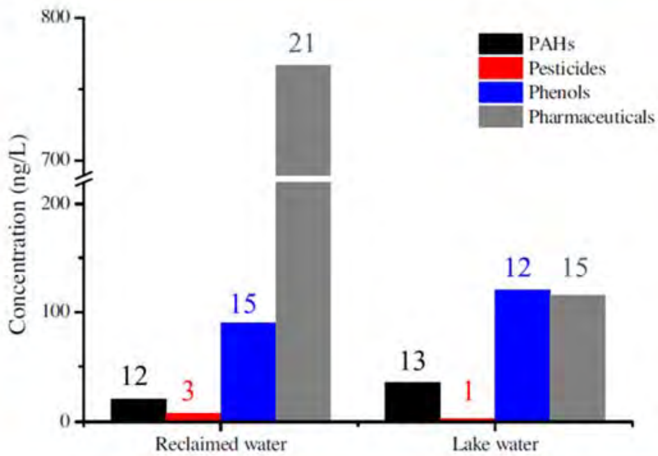
Variation of micropollutant concentrations

- ✔ **PAHs**
  - Detected: RW12, LW 11
  - Concentration: LW > RW
- ✔ **Phenols**
  - Detected: RW15, LW 12
  - Concentration: LW > RW

Possibly due to nonpoint sources

- ✔ **Pesticides**
  - Detected: RW3, LW 1
  - Concentration: LW < RW
- ✔ **Pharmaceuticals**
  - Detected: RW21, LW 15
  - Concentration: LW < RW

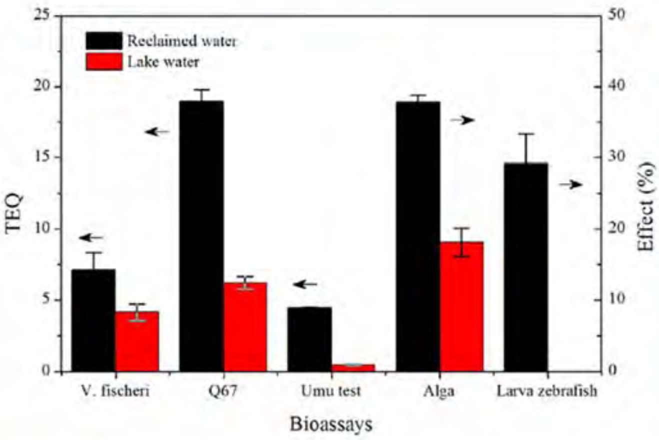
Significant removal in the landscape lake



Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction in a landscape lake system**

Variation of biotoxicity

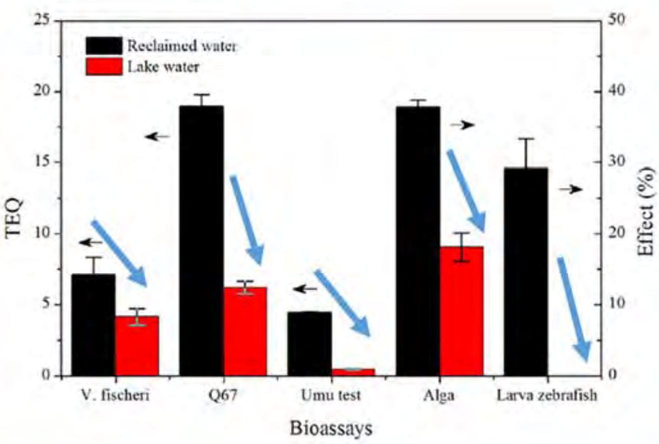


- ✓ **By luminescent bacteria**
  - Reclaimed water: High TEQ
  - Lake water: Remarkable TEQ reduction
- ✓ **Genotoxicity**
  - Reclaimed water: TEQ about 5
  - Lake water: TEQ reduced to less than 0.5
- ✓ **By alga test**
  - Reclaimed water: Toxic effect about 40%
  - Lake water: Toxic effect < 20%
- ✓ **By larva zebrafish test**
  - Reclaimed water: Toxic effect about 30%
  - Lake water: No apparent toxic effect < 20%

Biotoxicity reduction by ecological processes

- **Micropollutant removal and biotoxicity reduction in a landscape lake system**

Variation of biotoxicity



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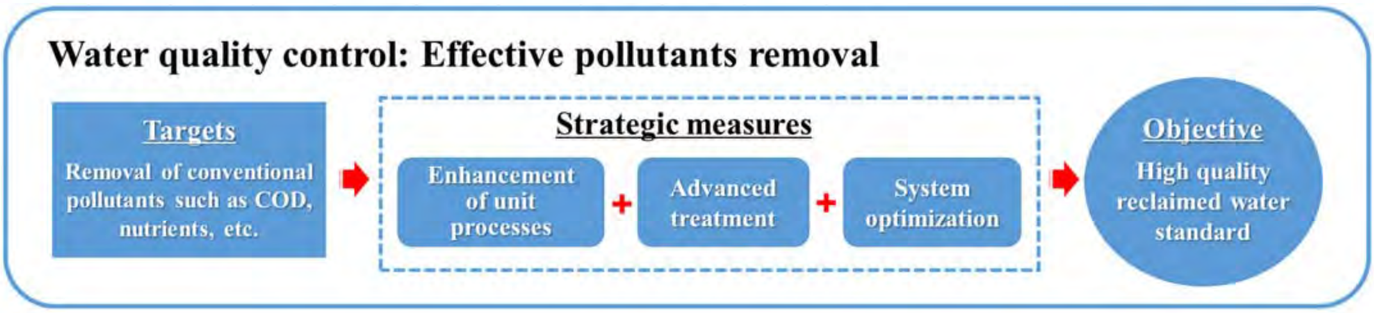
Consideration on precautionary principle and feasible measures



Consideration on precautionary principle and feasible measures

Water quality control: Effective pollutants removal

- **Targets**: Removal of conventional pollutants such as COD, nutrients, etc.
- **Strategic measures**: Enhancement of unit processes + Advanced treatment + System optimization
- **Objective**: High quality reclaimed water standard

Ecological safety control: Micropollutant removal & biotoxicity reduction

- **Targets**: Reduction of specific & non-specific biotoxicities
- **Strategic measures**: Biotoxicity reduction in treatment processes + Biotoxicity reduction through biological processes
- **Objective**: Ecological safety & healthy aquatic environment

Consideration on precautionary principle and feasible measures

Engineering & ecological barriers

Water quality con…

- **Targets**: Removal of con… pollutants such as… nutrients, et…
- **Objective**: High quality reclaimed water standard

Ecological safety control: Micropolluta… removal & biotoxicity reduction

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Concluding remarks

- **Trace organic chemicals and their associated ecotoxicity are drawing wide attention in ecological water reuse**

Concluding remarks

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Concluding remarks

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- Biotoxicity can also be effectively reduced by ecological processes such as wetlands and open storage

Concluding remarks

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- Biotoxicity can also be effectively reduced by ecological processes such as wetlands and open storage
- Setting engineering and ecological barriers is recommendable for safety control in water reuse

Acknowledgement

Thanks to my colleagues' contribution to this work!

Dr. Xiaoyan Ma

Dr. Yucong Zheng

Mr. Yongkun Wang