化工园区废水中的新污染物：分析方法、风险及挑战

刘则华

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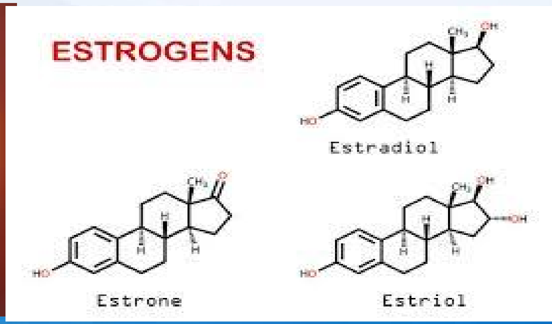

个人教育及研究经历

1997.9-2001.6, 湘潭大学化学工程学院，化学工程 学士

2001.9-2004.6， 北京化工大学生命科学与技术学院，
生物化工 硕士 （剩余污泥减量化的污水处理新工艺研究）

2007.4-2010.3, 日本大阪市立大学， 博士（环境干扰化学物质的分析及其去除机理研究）

2010.11-2012.9, 美国弗吉尼亚理工大学， 博士后（奶牛废水处理及抗生素抗性基因微污染）

2012.11-2013.9, 新加坡南洋理工大学， 研究员 （污泥厌氧发酵产甲烷）

2013.9-现在， 华南理工大学环境与能源学院， 副教授

究基础


刘则华

荣获二〇〇九年度国家优秀自费留学生奖学金，特颁证嘉奖，以资鼓励。

CHINA SCHOLARSHIP COUNCIL

Presents the

2009 Chinese Government Award for Outstanding Self-financed Students Abroad

to

Liu Zehua

Dr. Liu Jinghui
Secretary-General
China Scholarship Council

以色列环境与农业部的项目评审专家（German-Israeli Program in Water Technology).

荣获2009年度国家优秀留学生奖学金。

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国务院办公厅关于印发新污染物治理行动方案的通知

国办发〔2022〕15号

各省、自治区、直辖市人民政府，国务院各部委、各直属机构：

《新污染物治理行动方案》已经国务院同意，现印发给你们，请认真贯彻执行。

15. 强化含特定新污染物废物的收集利用处置。严格落实废药品、废农药以及抗生素生产过程中产生的废母液、废反应基和废培养基等废物的收集利用处置要求。研究制定含特定新污染物废物的检测方法、鉴定技术标准和利用处置污染控制技术规范。（生态环境部、农业农村部等按职责分工负责）

16. 开展新污染物治理试点工程。在长江、黄河等流域和重点饮用水水源地周边，重点河口、重点海湾、重点海水养殖区，京津冀、长三角、珠三角等区域，聚焦石化、涂料、纺织印染、橡胶、农药、医药等行业，选取一批重点企业和工业园区开展新污染物治理试点工程，形成一批有毒有害化学物质绿色替代、新污染物减排以及污水污泥、废液废渣中新污染物治理示范技术。鼓励有条件的地方制定激励政策，推动企业先行先试，减少新污染物的产生和排放。（工业和信息化部、生态环境部等按职责分工负责）

什么是新污染物？

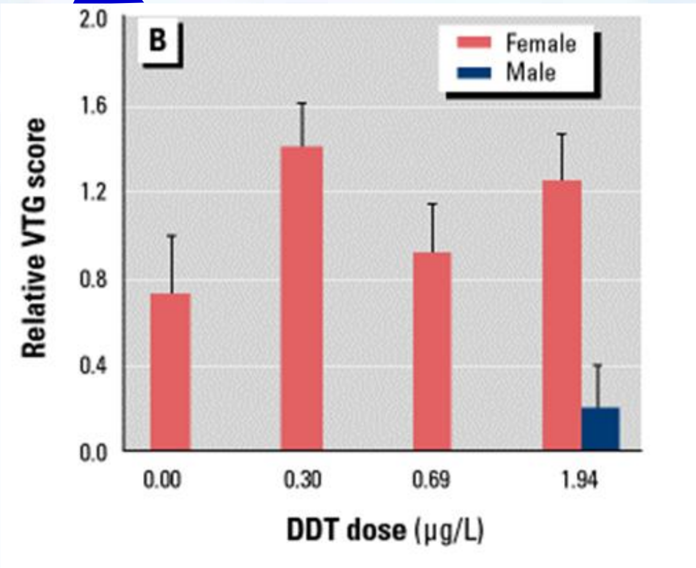
Contaminants of emerging concerns:新关注污染物

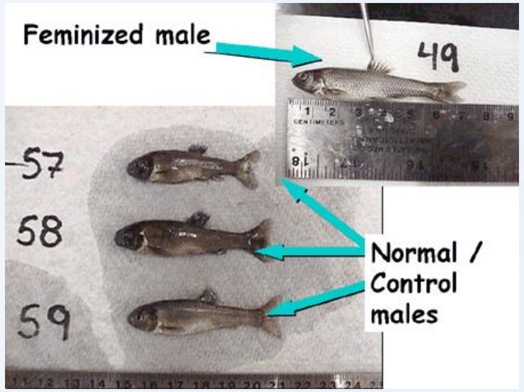
Emerging Contaminants: 新兴污染物

环境危害

新污染物

环境干扰化学物质 （EDCs)





River of Canada

天然雌激素的环境危害(ES&T,1998)

Research

Identification of Estrogenic Chemicals in STW Effluent. 1. Chemical Fractionation and in Vitro Biological Screening

C. DESBROW,[†] E. J. ROUTLEDGE,[*,‡] G. C. BRIGHTY,[§] J. P. SUMPTER,[‡] AND M. WALDOCK[†]

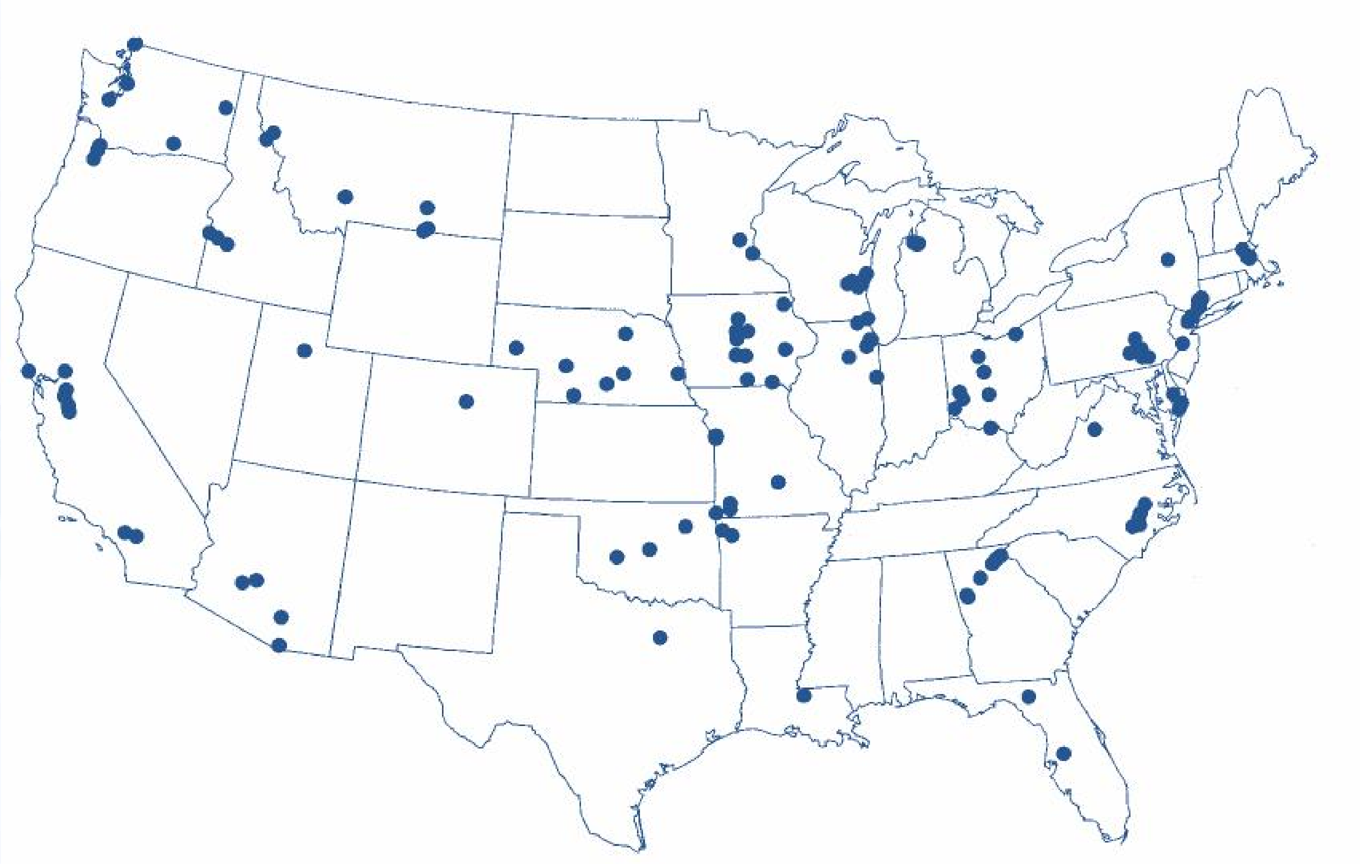
Centre for Environment, Fisheries and Aquaculture Science, Burnham Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex, CMO 8HA, U.K., Department of Biology and Biochemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, U.K., and Environment Agency, National Centre for Ecotoxicology and Hazardous Substances, Hawberry Park, Wallingford, Oxon, OX10 8BD, U.K.

A fractionation system, combined with an in vitro assay for detecting estrogenic activity, was developed in order to isolate and identify the major estrogenic chemicals present in seven sewage-treatment works (STW) effluents,

down products of one group of nonionic surfactants), have been implicated (*1, 2*). STWs receiving domestic and industrial waste release a complex (and ill-defined) mixture of natural and synthetic chemicals into the aquatic environment, due to their partial or complete resistance to biodegradation during the treatment process. Although effluents have been tested for their toxicity to aquatic organisms, usually in order to determine safe discharge levels, few chemicals within an effluent have been tested for toxicity or hormone disrupting activity on an individual basis, either in vivo or in vitro. As it was clearly not practical to identify, quantify, and test all the individual substances present in effluent, a bioassay-directed fractionation procedure was adopted in which STW effluent was chemically separated into fractions of decreasing complexity. Each fraction was analyzed for estrogenic activity using a yeast-based estrogen screen (*3*). Fractions identified as active in the bioassay were separated further until they could be analyzed by gas chromatography−mass spectrometry (GC−MS), leading to identification of the active chemicals. This procedure, through a series of steps involving separation and resolution, simultaneously eliminates inactive compounds and isolates chemicals that are biologically active without using any preconceived ideas about the identity of the compounds responsible for the activity in the mixture.

美国亚洲鲤鱼泛滥

新污染物(Emerging contaminants)



USGS:美国地质勘探局 (139 streams, ~86%)

新污染物种类

新污染物种类

- 环境激素（天然雌激素/雄激素/植物雌激素，合成激素，兴奋剂，双酚A，塑化剂,全氟辛烷磺酸/全氟辛烷酸铵(PFOS/PFOA)等工业化学品等）
- 抗生素（antibiotics)
- 异味化学物质
- 消毒副产物
- 元素污染（重金属）

各国饮用水限制标准

目标物	英文*	CAS	国家或地区							
			中国 (μg/L)	澳大利亚[20] (μg/L)	日本[9] (μg/L)	新加坡[10] (μg/L)	美国[11] (μg/L)	新西兰[13] (μg/L)	欧盟[14] (μg/L)	加拿大[12] (μg/L)
亚硝基二甲胺	NDMA	62-75-9	0.1	0.1	无	0.1	无	无	无	0.04
全氟辛烷磺酸	PFOS	45298-90-6	0.04	0.07	无	无	无	无	无[i]	0.6
全氟辛酸	PFOA	335-67-1	0.08	0.56	无	无	无	无	无[i]	0.2
邻苯二甲酸二（2-乙基）己酯	DEHP	117-81-7	8	10	无	8	6	9	无	无
二（2-乙基己基）己二酸酯	DEHA	103-23-1	400	无限值	无	无	400	无	无	无
邻苯二甲酸二丁酯	DBP	84-74-2	3	无	200	无	无	无	无	无
邻苯二甲酸二乙酯	DEP	84-66-2	300	无	无	无	无	无	无	无
双酚A	**BPA**	**80-05-7**	**10**	**无**	**100**	**无**	**无**	**无**	**2.5**	**无**
邻苯二甲酸丁苄酯	BBP	85-68-7	无	无	500	无	无	无	无	无
雌二醇	E2	50-28-2	无	无	0.08	无	无	无	无	无
炔雌醇	EE2	57-63-6	无	无	0.02	无	无	无	无	无
壬基酚	NP	25154-52-3	无	无	300	无	无	无	无	无

新污染物的分析方法

气相色谱质谱

液相色谱串联质谱

工业废水排放标准

水环境保护

水环境质量标准 | **水污染物排放标准** | 相关标准

· 农药工业水污染物排放标准 GB 21523—2024代替GB 21523—2008	2024-12-01 实施
· 地方水产养殖业水污染物排放控制标准制订技术导则 HJ 1217—2023	2023-03-01 实施
· 电子工业水污染物排放标准 GB 39731-2020	2021-07-01 实施
· 船舶水污染物排放控制标准 GB 3552-2018代替GB 3552-83	2018-07-01 实施
· 石油炼制工业污染物排放标准 GB 31570-2015	2015-07-01 实施
· 再生铜、铝、铅、锌工业污染物排放标准 GB 31574—2015	2015-07-01 实施
· 合成树脂工业污染物排放标准 GB 31572-2015	2015-07-01 实施
· 无机化学工业污染物排放标准 GB 31573-2015	2015-07-01 实施
· 电池工业污染物排放标准 GB 30484-2013	2014-03-01 实施
· 制革及毛皮加工工业水污染物排放标准 GB 30486—2013	2014-03-01 实施
· 合成氨工业水污染物排放标准 GB 13458 - 2013代替GB 13458-2001	2013-07-01 实施

化工园区废水

新污染物排放收费？

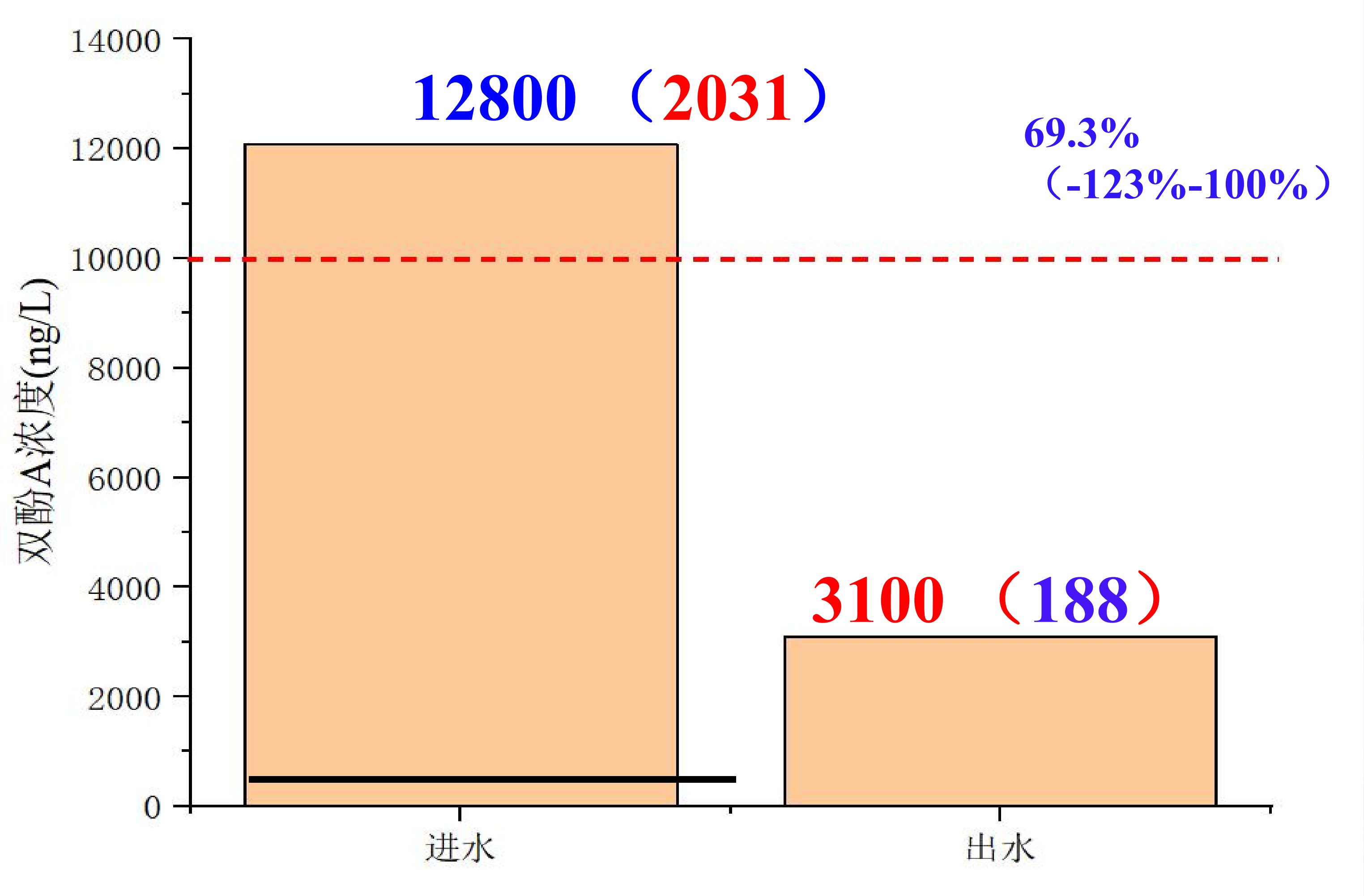
广东省纺织印染厂废水双酚类物质(n=6)

名称	进水(ng/L)		出水(ng/L)		去除率(%)
	平均值	最大值	平均值	最大值	
BPA	164	565	296	2292	-80
BPS	193	734	42	138	78
BPF	245	1702	86	782	65

广东省医药废水双酚类物质(n=17)

名称	进水(ng/L)		出水(ng/L)		去除率(%)
	平均值	最大值	平均值	最大值	
BPA	371	2045	86	570	77
BPS	2	14	3	26	-50
BPF	3	10	9	39	-200

全球144个污水处理厂的调查数据



珠江流域广州段双酚类物质

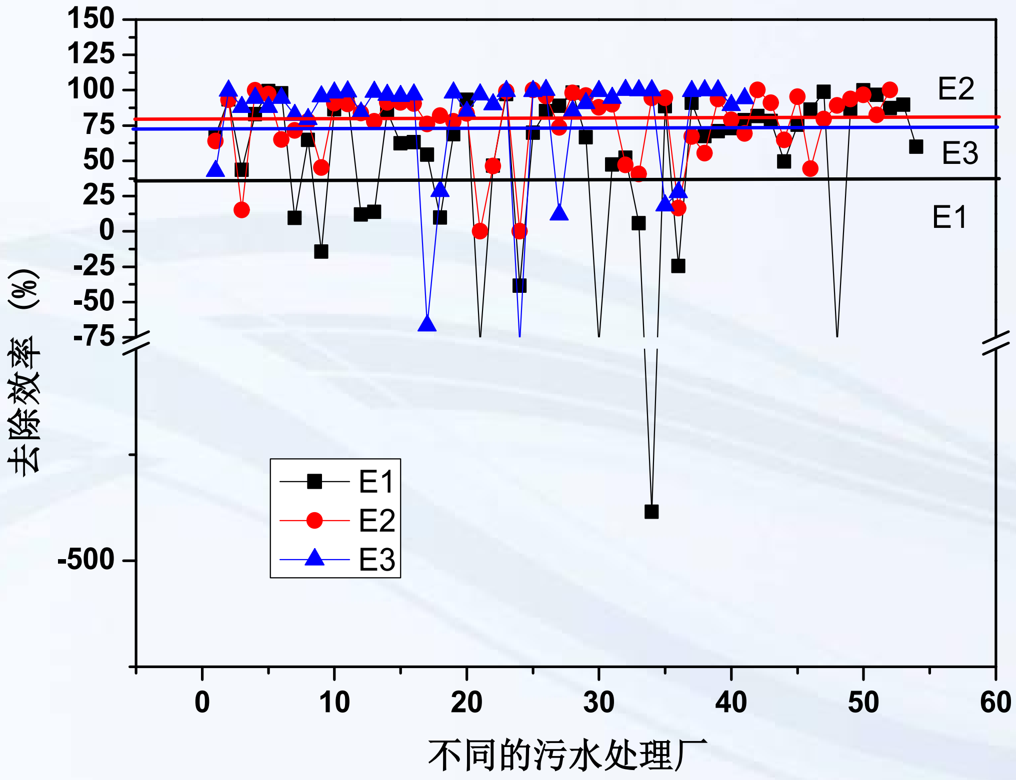
Table 2 Concentrations of target compounds in surface water from the Pearl River*

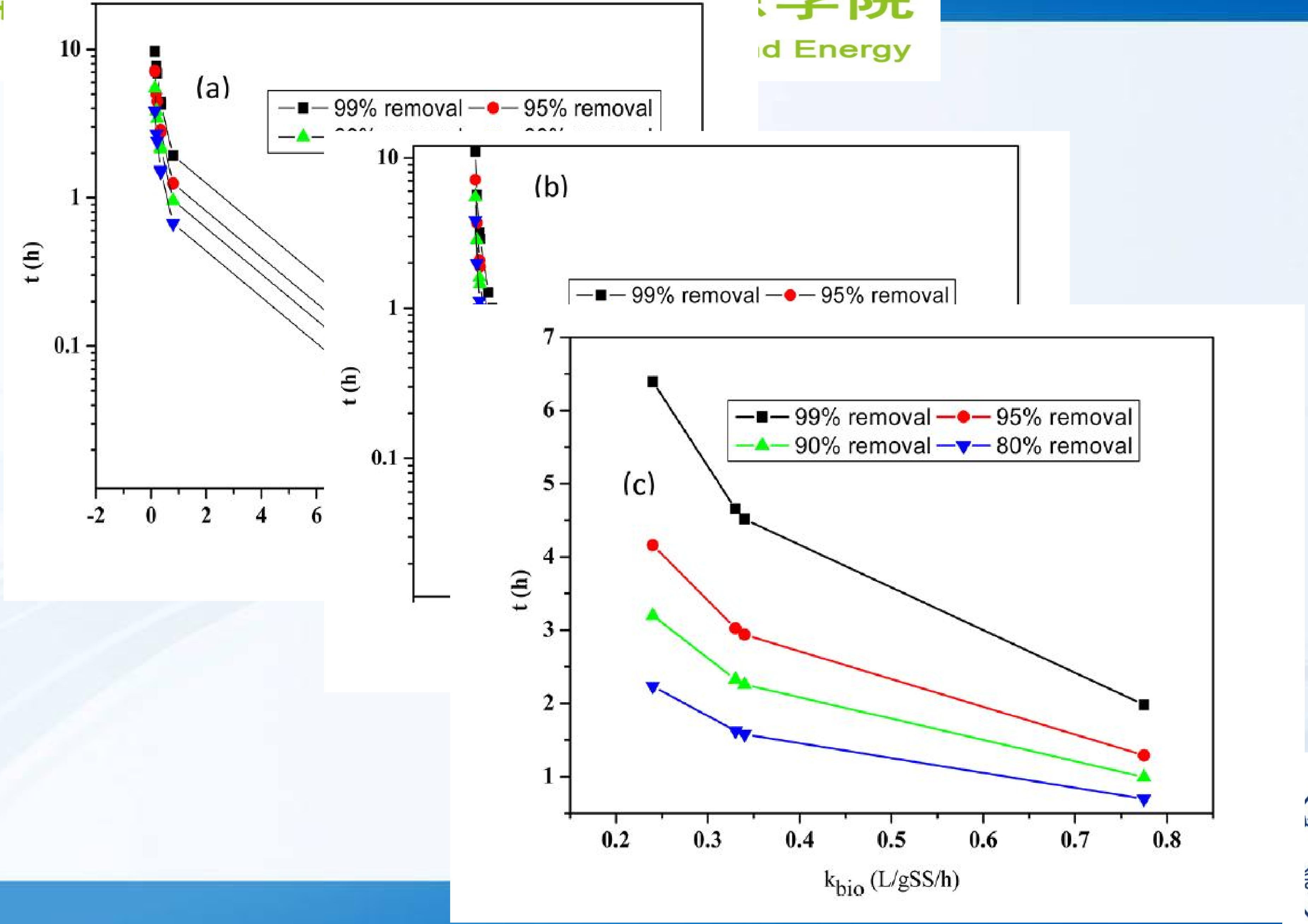
Site	BPA	BPB	BPC	BPE	BPF	BPP	BPS	BPZ	BPAP	BPAF	ΣBPs
S0	29.0±1.1	7.7±0.07	n.d	n.d	8.4±0.2	n.d	29.5±0.9	n.d	n.d	14.1±1.4	89.8
S1	18.9±0.5	n.d	9.0±0.0	n.d	n.d	n.d	n.d	n.d	n.d	9.9±0.2	42.9
S2	13.9±0.4	n.d	9.0±0.0	n.d	n.d	n.d	n.d	n.d	n.d	9.7±0.1	36.6
S3	18.9±0.4	n.d	9.1±0.0	n.d	n.d	n.d	n.d	n.d	n.d	11.2±0.5	48.6
S4	16.9±0.7	7.7±0.0	8.8±0.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	40.1
S5	19.9±0.5	7.6±0.1	9.1±0.1	n.d	9.1±0.1	n.d	n.d	n.d	n.d	25.5±1.3	71.2
S6	39.1±1.1	n.d	n.d	n.d	8.9±0.2	n.d	21.6±0.3	n.d	n.d	9.3±0.5	80.1
S7	28.2±0.3	7.7±0.7	n.d	n.d	9.0±0.3	n.d	24.6±0.6	n.d	n.d	10.3±0.7	81.0
S8	26.1±0.6	n.d	n.d	n.d	9.5±0.1	n.d	12.2±0.0	n.d	n.d	13.5±0.5	64.0
S9	29.1±0.7	n.d	9.0±0.0	n.d	8.7±0.3	n.d	n.d	n.d	n.d	16.3±0.4	70.3
S10	17.1±0.3	7.8±0.2	8.8±0.0	n.d	9.0±0.3	n.d	n.d	n.d	n.d	11.2±0.1	53.8
S11	36.0±0.9	8.7±0.1	9.0±0.0	n.d	11.6±0.3	n.d	115.9±5.8	n.d	n.d	9.1±0.2	194.1
S12	40.0±2.2	8.8±0.1	9.1±0.0	n.d	13.1±0.4	n.d	118.3±7.3	n.d	n.d	9.4±0.8	201.3
S13	64.7±0.7	8.5±0.2	n.d	n.d	12.4±0.3	n.d	124.4±6.2	n.d	n.d	n.d	214.3
S14	41.4±1.7	8.3±0.1	n.d	n.d	10.5±0.28	n.d	57.8±2.7	n.d	n.d	8.6±0.1	127.8
S15	37.8±0.5	8.7±0.2	n.d	n.d	10.0±0.4	n.d	79.8±5.0	n.d	n.d	9.3±0.5	146.8
S16	34.9±2.7	7.6±0.1	n.d	n.d	9.5±0.1	n.d	39.2±3.3	n.d	n.d	8.0±0.1	101.9
S17	31.8±3.0	7.6±0.1	n.d	n.d	9.0±0.1	n.d	28.2±2.5	n.d	n.d	8.5±0.4	87.7
S18	36.3±0.3	n.d	9.4±0.1	n.d	8.6±0.1	n.d	18.7±0.5	8.0±0.3	8.9±0.0	15.4±0.2	107.9
S19	25.8±1.4	n.d	n.d	n.d	9.2±0.1	n.d	24.8±3.2	n.d	n.d	11.3±2.5	73.8
S20	40.5±1.06	7.7±0.0	9.3±0.2	n.d	9.8±0.2	n.d	53.7±2.0	n.d	n.d	123.1±2.8	246.8
S21	52.8±2.2	8.2±0.1	n.d	n.d	9.7±0.2	n.d	48.2±2.1	n.d	n.d	87.5±1.4	211.5
S22	53.1±1.9	n.d	n.d	n.d	9.0±0.2	n.d	31.8±2.5	n.d	n.d	8.8±0.3	103.4
S23	126.0±1.4	n.d	n.d	n.d	9.7±0.5	n.d	110.8±13.2	n.d	n.d	10.1±0.5	261.8
S24	44.7±3.3	n.d	n.d	n.d	9.0±0.2	n.d	23.1±2.0	n.d	n.d	17.0±0.1	93.8
Range	13.9–126.0	0–8.8	0–9.4	0–2.7	0–13.1	0–2.8	0.0–124.4	0–8.0	0–8.9	0–123.1	36.6–261.8
Mean	36.9	4.6	4.3	1.5	8.3	0.2	38.7	0.5	0.65	18.3	114.0
Median	34.9	7.6	1.2	2.7	9.0	0	24.8	0	0	10.1	89.8
SD[a]	22.4	4.0	4.3	1.4	3.4	0.8	40.6	1.6	1.8	27.1	68.0
RSD[C]	60.7%	87.0%	100.0%	93.3%	41.0%	400%	104.9%	320.0%	276.9%	148.1%	59.6%
DF[b]	100	52	44	0	84	0	72	4	4	92	-

Wang et al, Environ Sci Polut Res, 2022, 29:27352

强化去除新污染物工艺？

城市污水处理厂的去除效率




(a)
99% removal
95% removal
10
1
0.1
t (h)
-2
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2
4
6
(b)
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95% removal
10
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(c)
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80% removal
7
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5
4
3
2
1
t (h)
0.2
0.3
0.4
0.5
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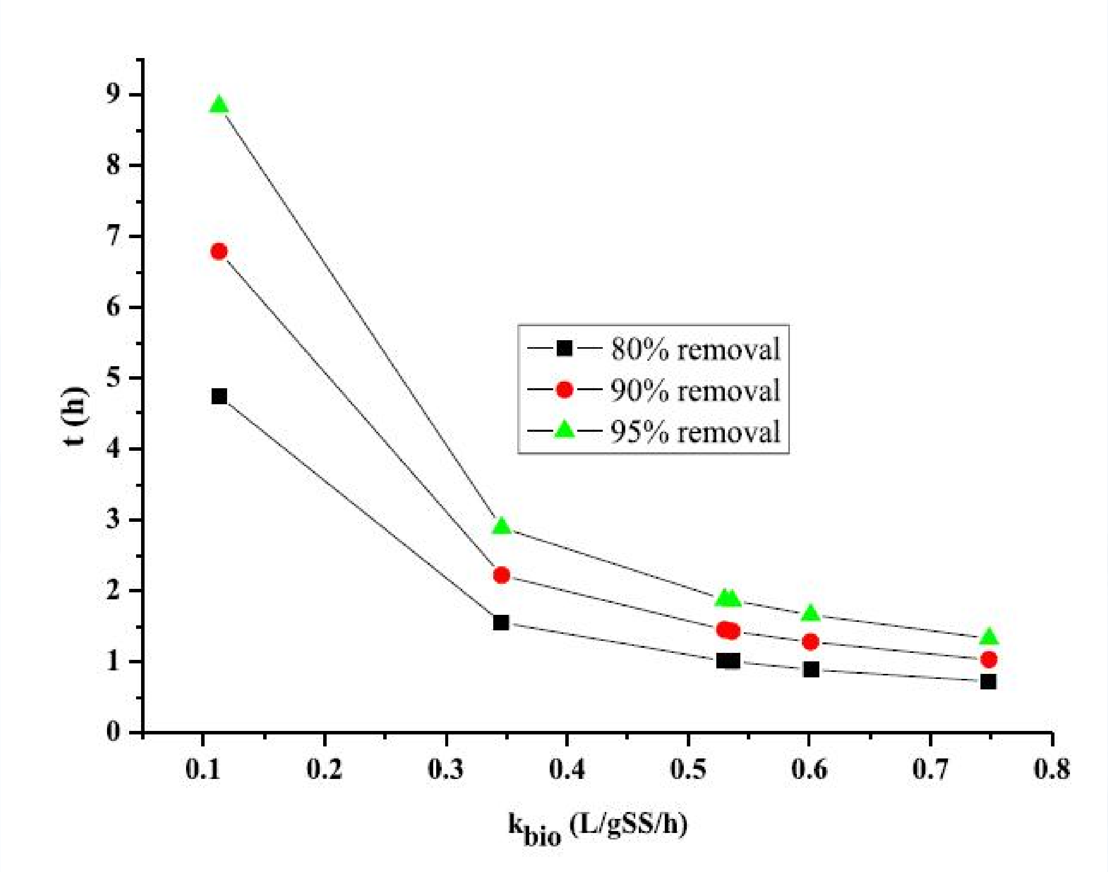
0.8
k_{bio} (L/gSS/h)

双酚A的理论去除效率


9
8
7
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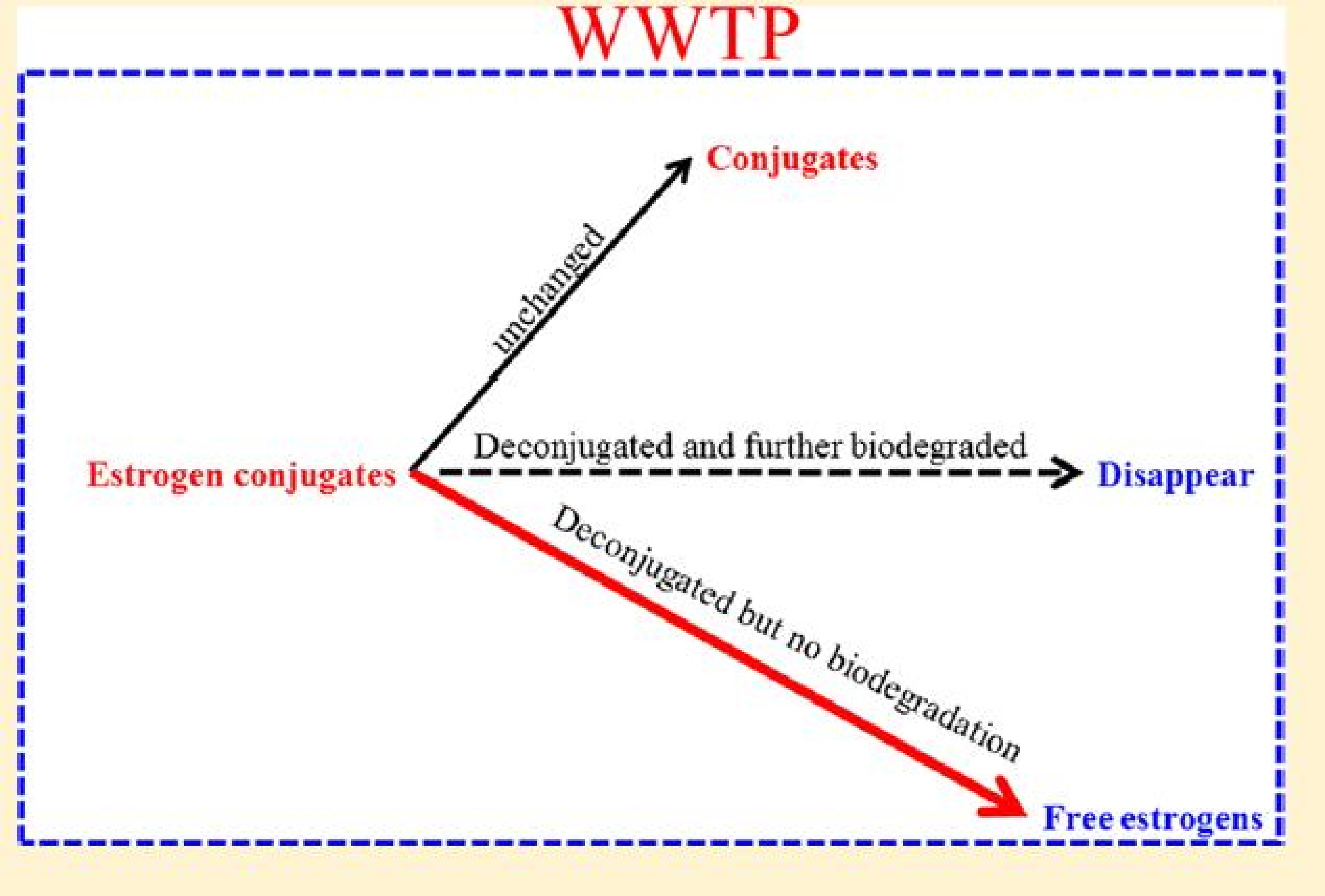
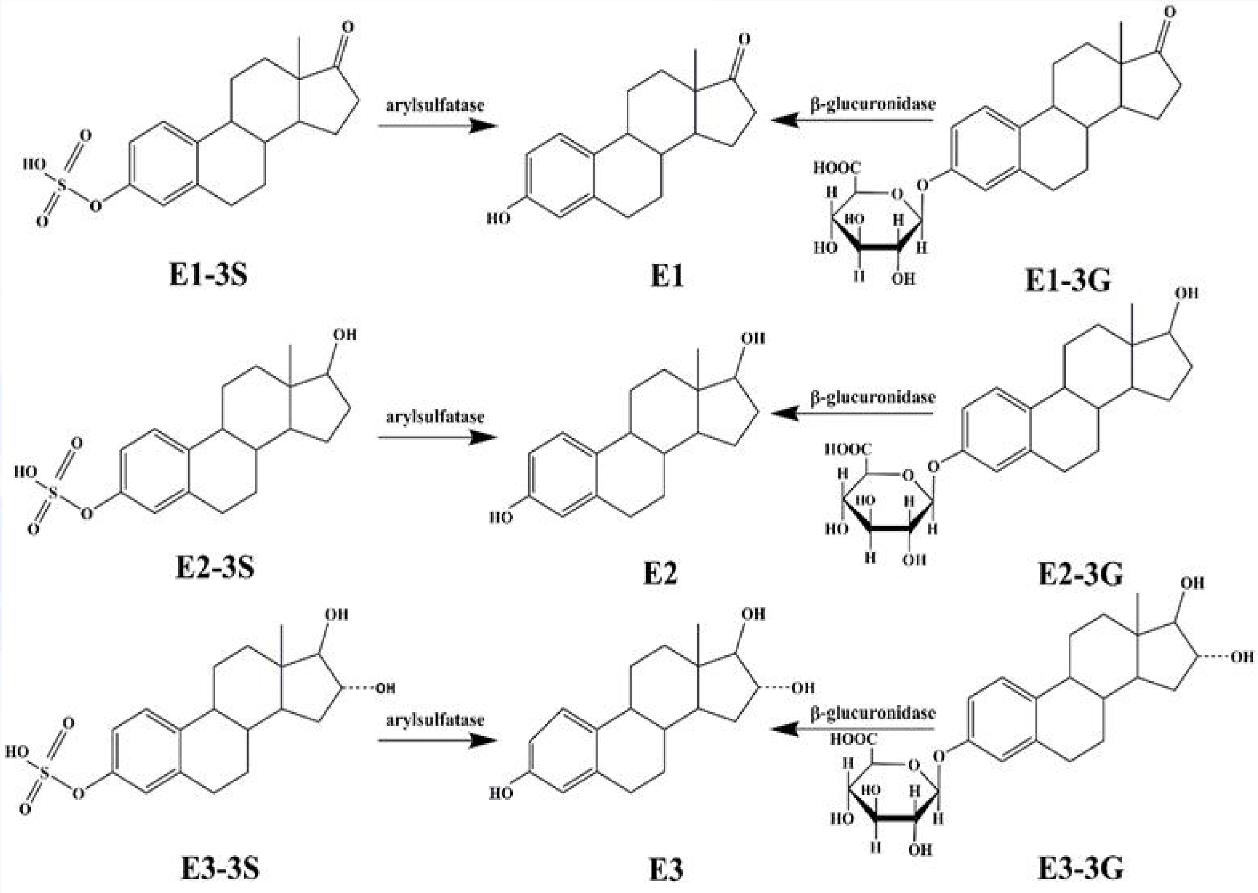
t (h)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
kbio (L/gSS/h)
80% removal
90% removal
95% removal

为什么去除效率为负？



Liu et al., Environmental Science & Technology, 2015, 49:5288-5300

天然雌激素及其结合体

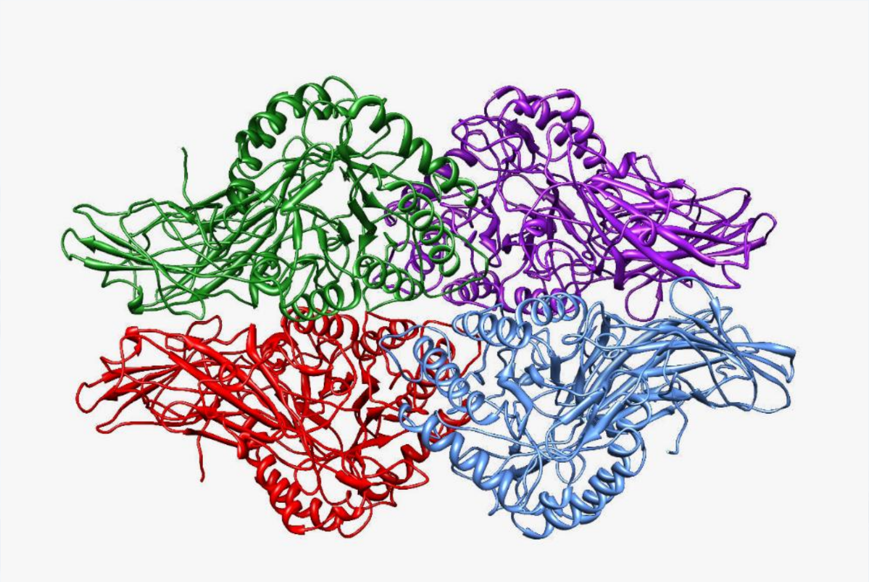

arylsulfatase
β-glucuronidase
E1-3S
E1
E1-3G
E2-3S
E2
E2-3G
E3-3S
E3
E3-3G

硫酸酯酶和β-葡萄糖苷酸酶

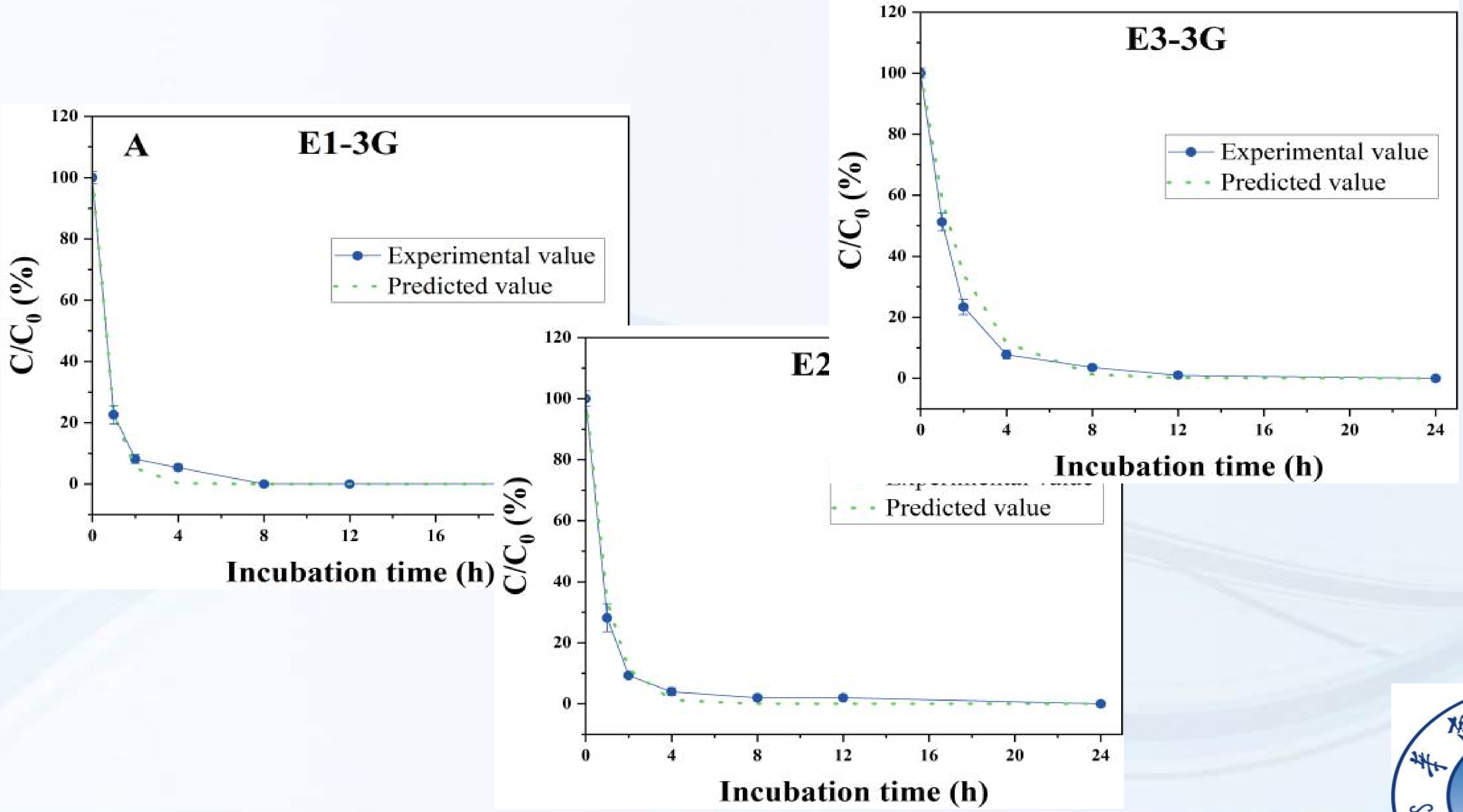
芳香基硫酸酯酶（arylsulfatase）

能将芳香基硫酸酯水解为芳香基化合物和无机硫酸盐的一类酶

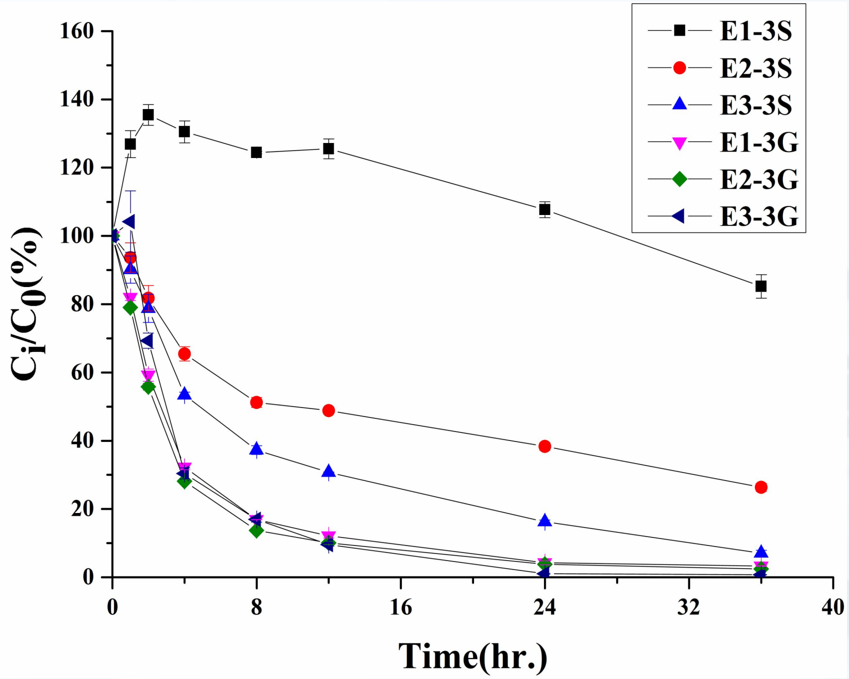
β-葡萄糖醛酸酶(β-glucuronidase)

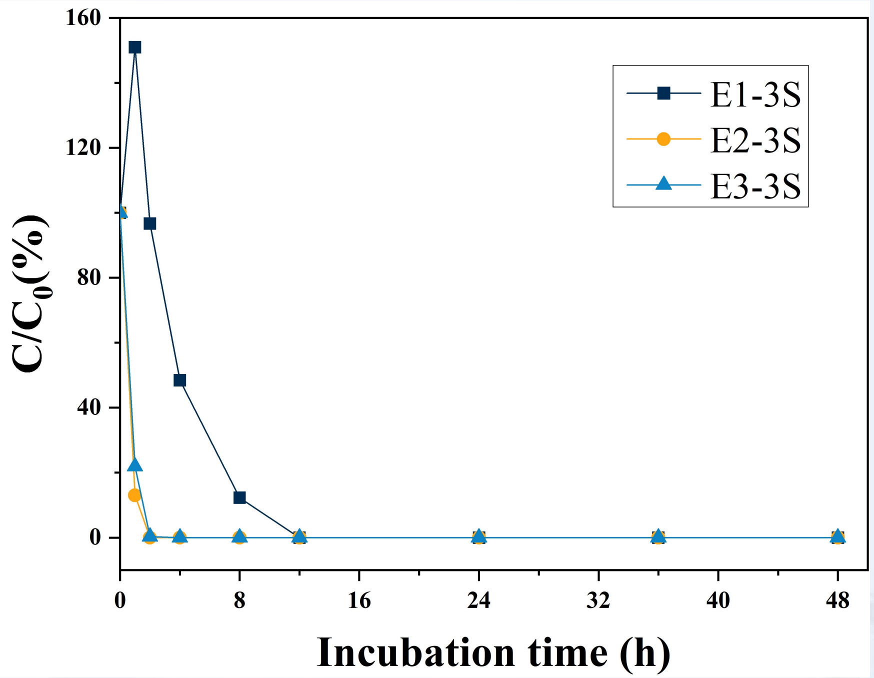


可以将葡萄糖醛酸苷水解为单糖D-葡萄糖醛酸和糖苷配基的一类酶


A
E1-3G
Experimental value
Predicted value
C/C0 (%)
Incubation time (h)
E2
Predicted value
C/C0 (%)
Incubation time (h)
E3-3G
Experimental value
Predicted value
C/C0 (%)
Incubation time (h)

新污染物的强化去除

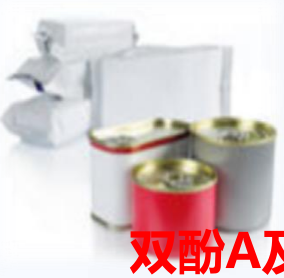


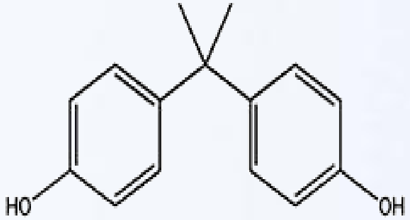


500 ng/L

25 µg/L

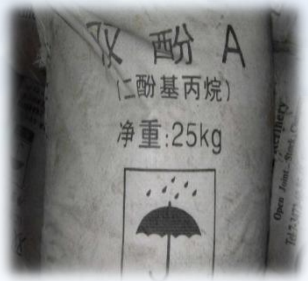
双酚类物质





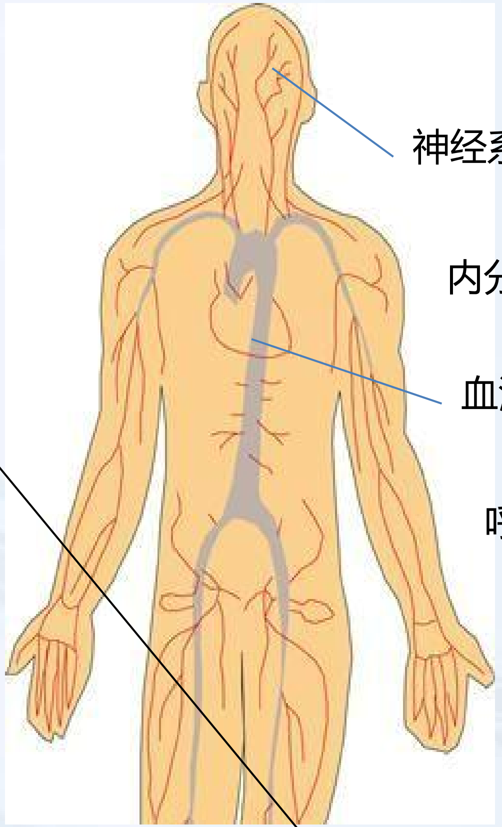
双酚A及其类似物

聚碳酸酯塑料
环氧树脂



工业化学原料

暴露水平计算?
暴露风险评估?
降低暴露风险?

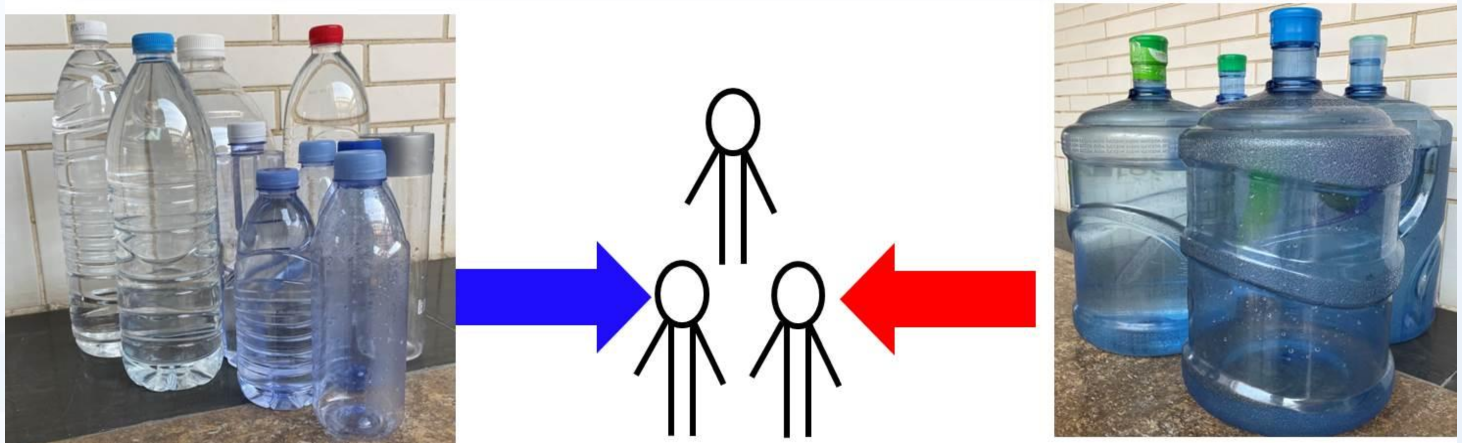


神经系统
内分泌系统
血液循环系统
呼吸系统
生殖系统

内分泌干扰物

瓶装水和桶装水双酚类物质

Bisphenol analogues in bottled water of China



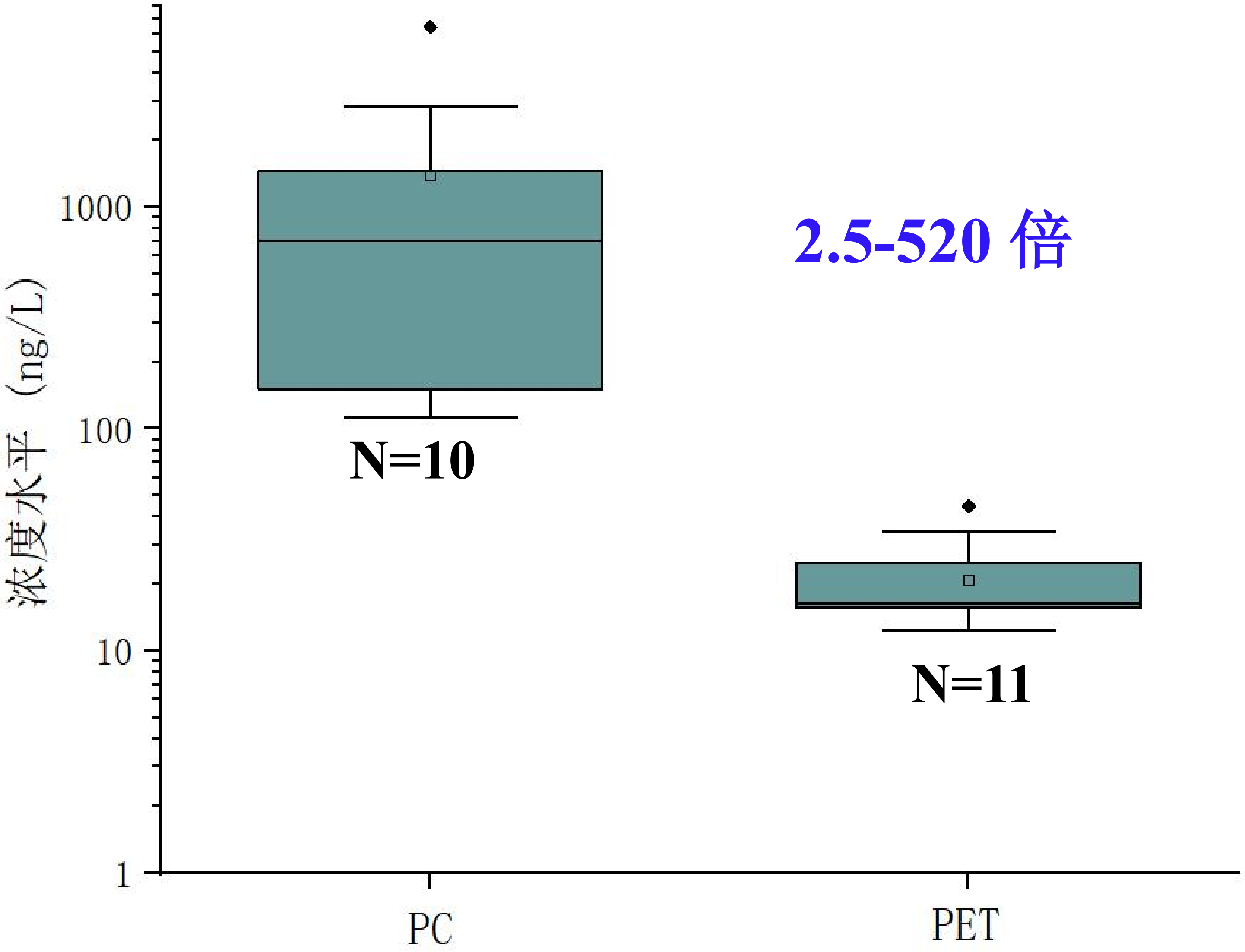
PET bottle

PC bottle

Main findings

- BPA analogues were hardly detected in PET and PC bottled waters
- BPA concentrations in PET bottled waters were low
- BPA concentrations in PC bottled waters were much higher
- PC bottled water likely increase human BPA daily intake
- EEQ of PC bottled water may pose adverse health effects to human

浓度水平



通过瓶装水人体暴露水平

材质	Parameter	BPA	BPE	BPS	BPAP	BPAF
PET	最高浓度 (ng/L)	44.9	7.8	0	0	4.9
	平军浓度(ng/L)	20.8	1.8	0	0	2.2
	日均摄入量(ng/p/d)	41.6-89.8	3.6-15.6	0	0	4.4-9.8
	与欧盟标准相比(%)	0.01-0.03	--[d]	--	--	--
	与人日均暴露相比(%)	1.9-4.0	--	0	0	7.3-16.3
PC	最高浓度 (ng/L)	6452.8	0	10.6	7.4	4.9
	平军浓度(ng/L)	1394.3	0	1.9	1.4	1.0
	日均摄入量(ng/p/d)	2788.6-12905.6	0	3.8-21.2	2.8-14.8	2.0-9.8
	与欧盟标准相比(%)	1.0-4.4	--	--	--	--
	与人日均暴露相比(%)	124.2-574.7	--	0.6-3.5	0.8-4.1	3.3-16.3

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Bisphenol analogues in Chinese bottled water: Quantification and potential risk analysis

Hao Wang [a], Ze-hua Liu [a,b,c,d,*], Zhao Tang [a], Jun Zhang [a], Hua Yin [a], Zhi Dang [a], Ping-xiao Wu [a], Yu Liu [e,f]

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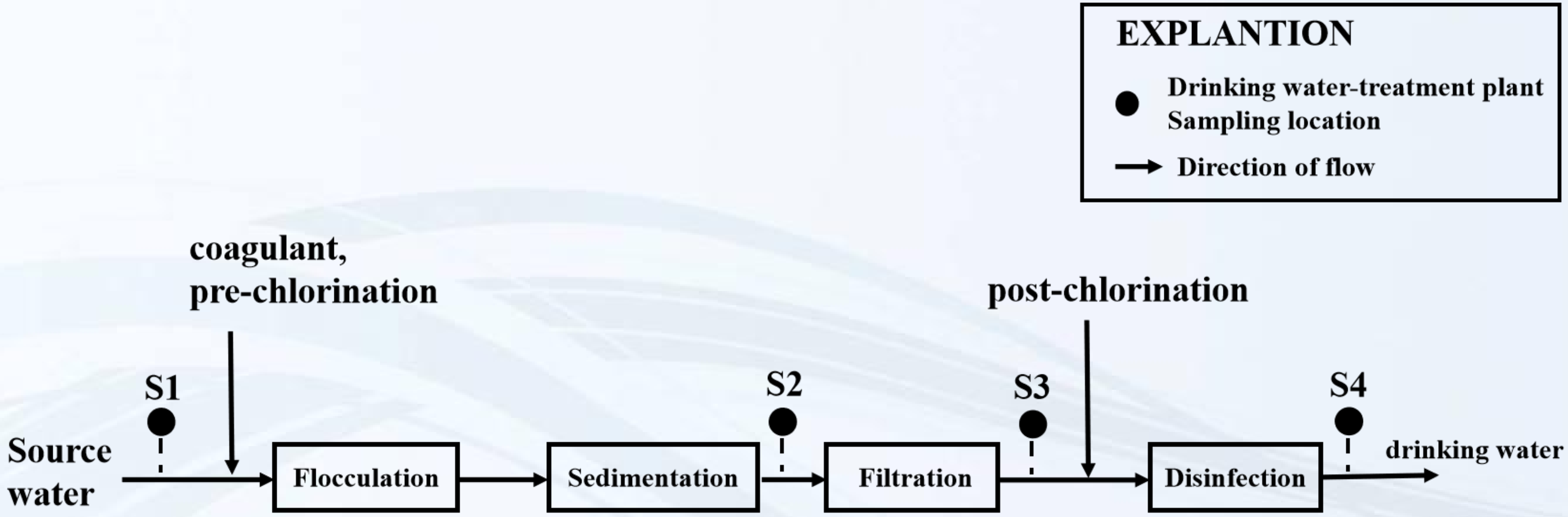
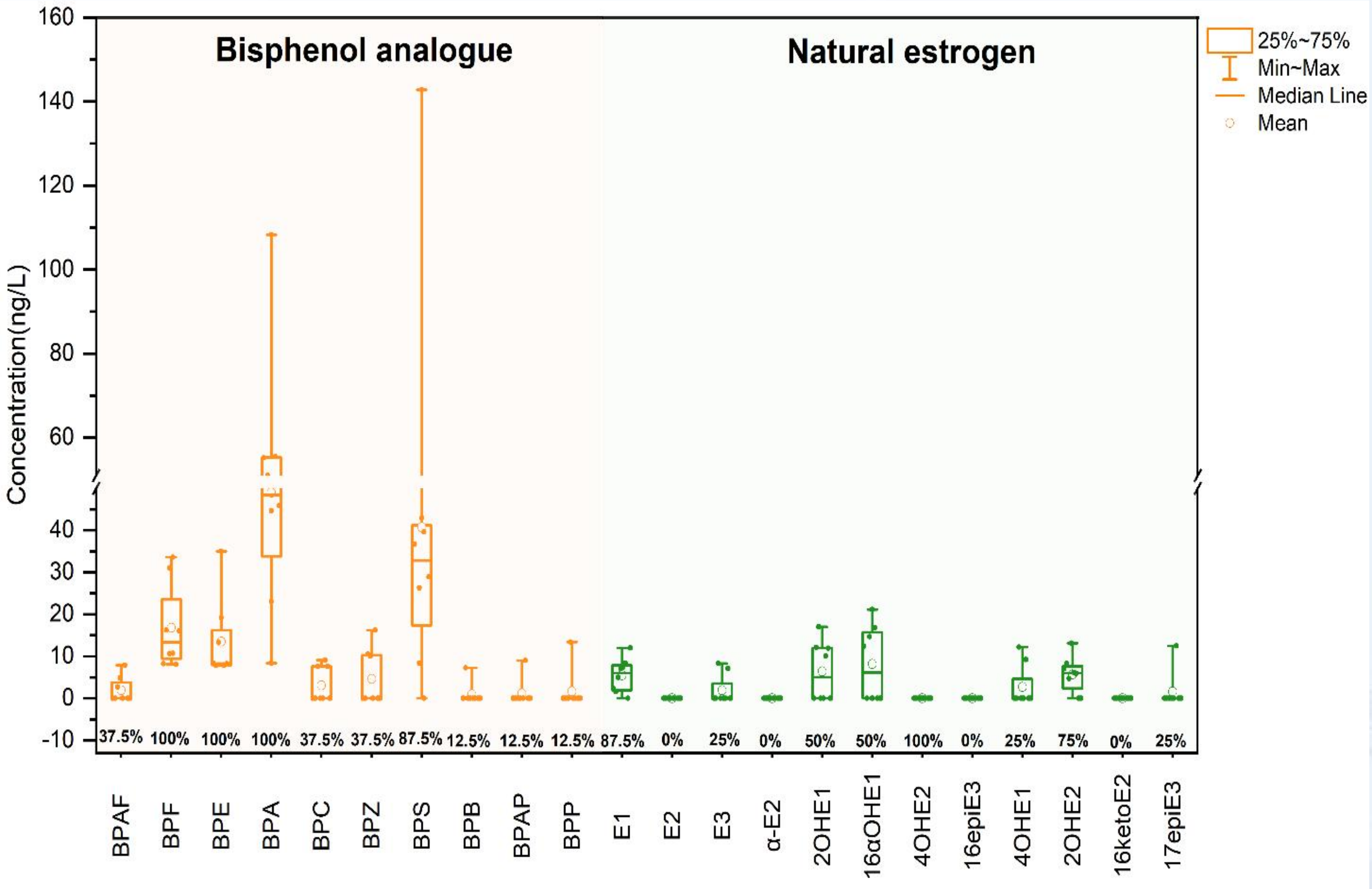
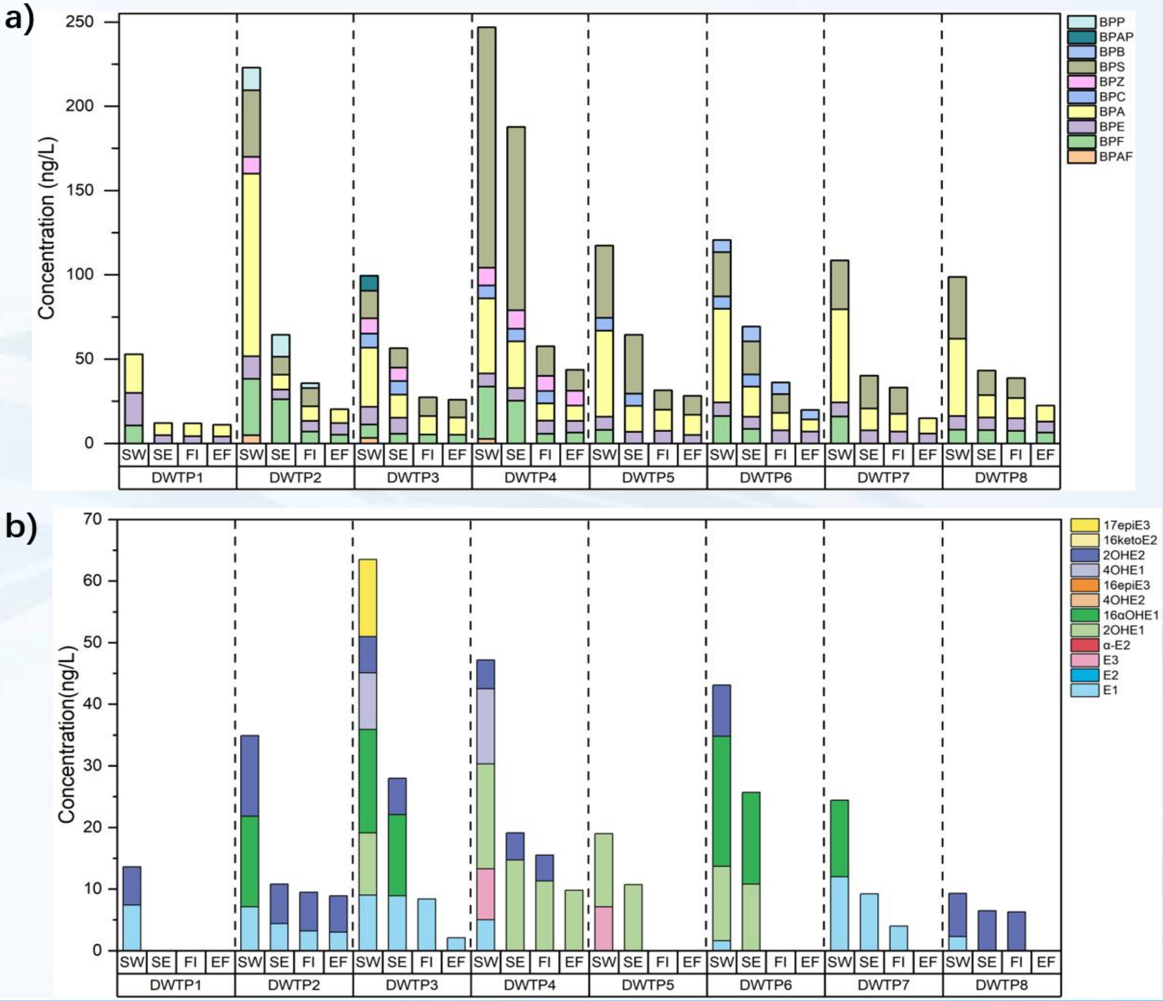
[f] *School of Civil and Engineering, Nanyang Technological University, 639798, Singapore*

自来水处理工艺


EXPLANTION
Drinking water-treatment plant
Sampling location
Direction of flow
coagulant,
pre-chlorination
post-chlorination
S1
S2
S3
S4
Source water
Flocculation
Sedimentation
Filtration
Disinfection
drinking water


Bisphenol analogue
Natural estrogen
Concentration(ng/L)
160
140
120
100
80
60
40
30
20
10
0
-10
25%~75%
Min~Max
Median Line
Mean
37.5%
100%
100%
100%
37.5%
37.5%
87.5%
12.5%
12.5%
12.5%
87.5%
0%
25%
0%
50%
50%
100%
0%
25%
75%
0%
25%
BPAF
BPF
BPE
BPA
BPC
BPZ
BPS
BPB
BPAP
BPP
E1
E2
E3
α-E2
2OHE1
16αOHE1
4OHE2
16epiE3
4OHE1
2OHE2
16ketoE2
17epiE3

各个处理单元的浓度情况



华南理工大学环境与能源学院
School of Environment and Energy

Water Research 243 (2023) 120310

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Water Research

journal homepage: www.elsevier.com/locate/watres

Twelve natural estrogens and ten bisphenol analogues in eight drinking water treatment plants: Analytical method, their occurrence and risk evaluation

Zhao Tang[a], Ze-hua Liu[a,b,c,*], Hao Wang[a], Yi-ping Wan[a], Zhi Dang[a], Peng-ran Guo[d,*], Yu-mei Song[d], Sa Chen[e]

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