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污水处理厂出水中抗雄激素样化合物控制的优先性研究

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摘要: 污水处理厂出水是环境中内分泌干扰物的重要来源之一。针对关注较少的抗雄激素样内分泌干扰物, 在已有研究基础上, 依据抗雄激素样化合物的抗雄激素样活性风险, 建立了污水处理厂出水中抗雄激素样化合物控制的优先性排序方法。在污水处理厂出水中, 共有 147 种疑似抗雄激素样化合物需要关注, 主要为农药类, 约占总数的 60%。抗雄激素样活性风险排名前 10% 的化合物如下: 邻苯二甲酸二丁酯、邻苯二甲酸二己酯、双酚 A、溴螨酯、对叔辛基酚、腐霉利、烯菌酮、氯苯嘧啶醇、烯酰吗啉、杀螟松、十二烷基酚、敌草隆、咯菌酯、2-羟基-4'-甲氧基二苯甲酮、以及邻苯基苯酚。

关键词: 抗雄激素样化合物; 内分泌干扰活性; 生态风险; 污水处理厂

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Control Priority Order of the Environmental Antiandrogens in Effluents of Wastewater Treatment Plants

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Abstract: A major source of endocrine disrupting chemicals (EDCs) into the aquatic environment is the effluents of wastewater treatment plants (WWTPs). In the aquatic ecosystems, much of the EDCs research has concentrated on estrogenic compounds and in this study antiandrogenic compounds were paid attention to. On the basis of antiandrogenic activity risks, the approach to prioritizing antiandrogens in the effluents of WWTPs was constructed. In total, 147 antiandrogens had been reported and nearly 60% of which were pesticides. The developed procedure was applied and the first ten percent antiandrogens were as followed, dibutyl phthalate, di-n-hexyl phthalate, bisphenol A, bromopropylate, 4-t-octylphenol, procymidone, vinclozolin, fenarimol, dimethomorph, fenitrothion, 4-n-dodecylphenol, diuron, fludioxonil, 2-hydroxy-4'-methoxybenzophenone, and o-phenylphenol.

Keywords: environmental antiandrogens; endocrine disrupting activity; ecological risk; wastewater treatment plants

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近年来,环境中普遍存在的内分泌干扰物受到了研究者的广泛关注。尽管内分泌干扰物在水环境中的存在浓度低,通常仅为 $\text{ng} \cdot \text{L}^{-1} \sim \mu\text{g} \cdot \text{L}^{-1}$,属于微量有机污染物,但它们能够在环境相关浓度下对水生生物产生长期的严重危害^[1-2]。目前针对内分泌干扰物的研究,大部分集中在雌激素活性类物质。直到最近几年其他种类的内分泌干扰物才逐渐受到重视,如抗雄激素样物质,它们能够抑制内源雄激素的正常功能,导致雄性生殖器官畸形^[3]、雄性激素分泌降低^[4],造成水生生物的生殖紊乱,对生态环境及人类健康造成潜在的危害^[5-6]。内分泌干扰物的确定需要严格的分类鉴定程序,根据目前已有的相关研究,疑是抗雄激素样化合物种类繁多,包括杀虫剂及其代谢产物(如滴滴伊和某些拟除虫菊酯),杀真菌剂(如烯菌酮、腐霉利),除草剂(如利谷隆、咪鲜胺),遮光剂,药物(如氟他胺、环丙氯地孕酮)以及一些工业化学品(如多氯联苯同系物)^[7]。一些雌激素化合物也具有抗雄激素样活性,如滴滴涕和双酚A等。

抗雄激素样化合物普遍存在于世界各地的水环境中^[8-11]。生活污水是水环境中抗雄激素样化合物的重要来源之一,然而生活污水处理厂并不能完全去除抗雄激素样化合物^[12]。生活污水处理厂出水中的抗雄激素样化合物单独或者与雌激素共同作用能够导致受纳水体中鱼类产生雌性化^[5]。因此,目前亟需确定污水处理厂出水中存在的疑是环境抗雄激素样化合物,在此基础上对其控制的优先性进行排序,从而为抗雄激素样化合物的优先控制清单的制定提供基础资料。针对环境污染物的优先控制筛查方法,研究者开始重点关注其可能造成的环境风险^[13-14]。本研究在已有研究基础上,首先确定污水处理厂出水中可能存在的疑是抗雄激素样化合物种类。之后关注其可能造成的环境风险,建立抗雄激素样化合物控制的优先性排序方法。最后,对污水处理厂出水中抗雄激素样化合物控制的优先性进行排序。

1 方法 (Methods)

1.1 污水处理厂出水中抗雄激素样化合物种类的确定

以“environmental antiandrogen”或“antiandrogenic activity”为关键词在 Web of Science 数据库中检索目前已报道的疑是抗雄激素样化合物,并确定其半数效应浓度 EC_{50} 。之后以“抗雄激素样化合物名称”、“concentration”、“wastewater treatment”为关

键词检索抗雄激素样化合物在全球城市污水处理厂出水中的浓度 G_s 。所有能够检出的抗雄激素样化合物构成本研究的种类名单。

1.2 抗雄激素样化合物控制的优先性排序方法

根据每种抗雄激素样化合物相对于模型化合物氟他胺的活性潜能(RP)以及在污水处理厂出水中的已报道的浓度计算每种抗雄激素样化合物的氟他胺当量抗雄激素样活性(FEQ),如式(1)所示:

$$\text{FEQ} = \text{RP} \times M_f \times \frac{G_s}{M_s} = \frac{\text{EC}_{50f}}{\text{EC}_{50s}} \times M_f \times \frac{G_s}{M_s} \quad (1)$$

其中,FEQ 为氟他胺当量抗雄激素样活性浓度,单位为 $\text{ng} \cdot \text{L}^{-1}$ 。RP 为抗雄激素样化合物相对于氟他胺的抗雄激素样活性潜能。 EC_{50f} 为氟他胺的 EC_{50} ,根据已有报道取 $7.1 \mu\text{mol} \cdot \text{L}^{-1}$ ^[15], EC_{50s} 为待计算物质的半数效应浓度 EC_{50} ,单位为 $\mu\text{mol} \cdot \text{L}^{-1}$ 。 M_f 为氟他胺的相对分子质量,取 276.21。 G_s 单位为 $\text{ng} \cdot \text{L}^{-1}$, M_s 为待计算物质的相对分子质量。

已有研究发现,氟他胺在浓度约为 $0.28 \text{ ng} \cdot \text{L}^{-1}$ 时,就能使三刺鱼产生去雄性化特征^[16],该浓度为体内实验中氟他胺已报道的最低有效应浓度。根据式(2),计算每种抗雄激素样化合物在污水处理厂出水中的抗雄激素样活性指数 i_{AA} :

$$i_{AA} = \lg\left(\frac{\text{FEQ}}{C_{f,MEL}}\right) \quad (2)$$

FEQ 为氟他胺当量抗雄激素样活性浓度, $C_{f,MEL}$ 为氟他胺已报道的最低效应浓度。

当 EC_{50s} 值取参考文献报道中的最小值,出水浓度 G_s 取参考文献报道中的最大值时,抗雄激素样活性指数为极限最大值 $i_{AA,max}$ 。根据名单中化合物的 $i_{AA,max}$,确定控制的优先性。

2 结果与讨论 (Results and discussion)

2.1 污水处理厂出水中抗雄激素样化合物种类

污水处理厂出水中需要关注的疑是抗雄激素样化合物共 147 种,主要为农药,包括杀菌剂、除草剂和杀虫剂,共 88 种,约占总量的 60%。其余包括 16 种阻燃剂、10 种邻苯二甲酸酯类、10 种酚类、6 种紫外线吸收剂、6 种防腐剂、5 种动植物激素、4 种多环麝香等。抗雄激素样活性指数可能大于 2 的化合物如图 1 所示。大部分抗雄激素样化合物相对氟他胺的活性潜能集中在 0~10 之间。它们在不同污水处理厂出水中的浓度变化大,造成了贡献的抗雄激素样活性变化大,甚至相差 1~3 个数量级。详细名单及最大抗雄激素样活性指数 $i_{AA,max}$ 如表 1 所示。

续表1

物质 Chemicals	CAS 号 CAS No.	EC _{50s} /($\mu\text{mol}\cdot\text{L}^{-1}$)	G_s /($\text{ng}\cdot\text{L}^{-1}$)	$i_{\text{AA,max}}$
酚类 Phenols				
双酚 A Bisphenol A (BPA)	80-05-7	2.5, 4.23 ^[27-28]	6 ~ 4 090 ^[19]	4.70
十二烷基酚 4-n-Dodecylphenol	210555-94-5	6, 13 ^[29]	154 ~ 2 210 ^[30]	4.00
4-壬基苯酚 4-n-Nonylphenol	104-40-5	9, 13 ^[27,29]	314 ~ 561 ^[21,31]	3.30
对正辛基苯酚 n-Octylphenol	1806-26-4	46 ^[27]	44.2 ~ 182 ^[25]	2.13
对叔辛基酚 4-t-Octylphenol	140-66-9	2.2, 74 ^[29]	490 ~ 2 100 ^[31]	4.51
己基苯酚 4-n-Hexylphenol	2446-69-7	20 ^[29]	11.9 ^[32]	1.37
正戊基苯酚 4-n-Pentylphenol	14938-35-3	24 ^[29]	<500 ^[33]	<2.95
4-正丙基苯酚 4-n-Propylphenol	645-56-7	66 ^[29]	502 ^[33]	2.60
1-萘酚 1-Naphthol	90-15-3	7.03 ^[34]	120 ~ 170 ^[35]	3.07
紫外线吸收剂类 UV-filters				
2,4,6-三甲基苯甲酰基苯基膦酸乙酯 Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (BP-1)	84434-11-7	1, 5.7 ^[36-37]	n.d. ~ 41 ^[38]	2.96
2,2',4,4'-四羟基二苯甲酮 2,2',4,4'-Tetrahydroxybenzophenone (BP-2)	131-55-5	4.9 ^[39]	1 ~ 14 ^[40]	1.91
2-羟基-4'-甲氧基二苯甲酮 Oxybenzone (BP-3)	131-57-7	4.98, 17.9 ^[38,40]	n.d. ~ 700 ^[38]	3.64
3-(4-甲基苯亚甲基)樟脑 3-(4'-Methylbenzylidene)camphor (4-MBC)	36861-47-9	30 ^[39]	23 ~ 2 700 ^[38]	3.40
2-羟基苯甲酸-3,3,5-三甲基环己酯 Homosalate (HMS)	118-56-9	5.57 ^[41]	8 ~ 9 ^[40]	1.64
3-亚苄基樟脑 Benzylidene camphor (3-BC)	15087-24-8	27.7 ^[39]	n.d. ~ 110 ^[42]	2.07
农药类 Pesticides				
噁菌环胺 Cyprodinil	121552-61-2	28.1 ^[43]	90 ^[44]	2.00
腐霉利 Procyimidone	32809-16-8	0.8 ^[45]	n.d. ~ 5 350 ^[46]	5.21
烯菌灵 Imazalil	73790-28-0	8.3 ^[43]	50 ~ 108 ^[47]	2.49
噁霉胺 Pyrimethanil	53112-28-0	98.6 ^[43]	n.d. ~ 574 ^[48]	2.31
咯菌酯 Fludioxonil	131341-86-1	2.62 ^[43]	80 ~ 430 ^[44]	3.84
环酰菌胺 Fenhexamid	126833-17-8	7.08 ^[43]	<19 ^[49]	<1.80
邻苯基苯酚 o-Phenylphenol	90-43-7	9.57 ^[43]	80 ~ 1 000 ^[44]	3.64
咪酰胺 Prochloraz	67747-09-5	6.03, 7.9 ^[43,50]	22.2 ^[51]	1.84
戊唑醇 Tebuconazole	80443-41-0	8.06 ^[43]	n.d. ~ 691 ^[48]	3.29
烯菌酮 Vinclozolin	50471-44-8	0.3, 0.4 ^[28,50]	11.8 ~ 191 ^[52]	4.20
烯酰吗啉 Dimethomorph	110488-70-5	0.94 ^[43]	n.d. ~ 660 ^[44,53]	4.11
快诺芬* Quinoxifen*	124495-18-7	4.79* ^[54]	20 ^[55]	0.99
乙氧基喹啉* Ethoxyquin*	91-53-2	7.8* ^[56]	6.34 ~ 95.1 ^[57]	1.61
三氯生 Triclosan	3380-34-5	1.47 ^[58]	12 ~ 219 ^[19]	3.56
高效氯氟氰菊酯* Lambda-cyhalothrin*	91465-08-6	1.64* ^[59]	n.d. ~ 1.6 ^[60]	0.19
保棉磷 Azinphos-methyl	86-50-0	7.08 ^[59]	200 ^[61]	2.80
甲基嘧啶磷 Pirimiphos-methyl	29232-93-7	17.1 ^[43]	n.d. ~ 31.2 ^[62]	1.62
o,p'-滴滴涕 1-(o-Chlorophenyl)-1-(p-chlorophenyl)-2,2,2-trichloro ethane (o,p'-DDT)	789-02-6	9.5, 22.2 ^[28,50]	n.d. ~ 1.38 ^[63]	0.46
o,p'-滴滴伊 1-Chloro-2-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (o,p'-DDE)	3424-82-6	1.62, 20.2 ^[28,64]	0.0093 ~ 0.0122 ^[49]	-0.80
滴滴涕 1-Chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene (p,p'-DDT)	50-29-3	3.32, 17.9 ^[28,64]	5.23 ~ 13.5 ^[63]	2.10
丙酯杀螨醇 Chloropropylate	5836-10-2	33.7 ^[28]	-	-
氯二苯乙醇酸盐 Chlorobenzilate	510-15-6	26.8 ^[28]	n.d. ^[65-66]	-
肝氯环氧化物 Heptachlor epoxide	28044-83-9	42 ^[28]	n.d. ~ 131 ^[67]	0.46
三氯希螨醇 Dicofol	115-32-2	11.9 ^[28]	n.d. ^[68-69]	-
p,p'-滴滴滴 1,1-Bis(4-chlorophenyl)-2,2-dichloroethane (p,p'-DDD)	72-54-8	90, 20.4 ^[28,50]	n.d. ~ 2.42 ^[63]	-0.80

续表1

物质 Chemicals	CAS 号 CAS No.	EC _{50s} /($\mu\text{mol}\cdot\text{L}^{-1}$)	G_s /($\text{ng}\cdot\text{L}^{-1}$)	$i_{\text{AA,max}}$
硫丹 II β -Endosulfan	33213-65-9	23.4, 4.9 ^[70-71]	3.65 ~ 243.84 ^[67,72]	2.93
甲氧氯 Methoxychlor	72-43-5	4.43, 7.6 ^[64]	n.d. ~ 115 ^[67]	2.72
反氯丹 trans-Chlordane	5103-74-2	10 ^[70]	0.09 ~ 0.16 ^[73]	-0.57
顺氯丹 cis-Chlordane	5103-71-9	10 ^[70]	0.12 ~ 0.19 ^[73]	-0.50
狄氏剂 Dieldrin	60-57-1	22.8, 7.25 ^[44]	10.4 ~ 36.1 ^[67]	1.96
硫丹 I α -Endosulfan	959-98-8	23.4 ^[70]	n.d. ~ 1 283 ^[67,72]	2.98
毒死蜱 Chlorpyrifos	2921-88-2	11.8, 9.3 ^[49,74]	n.d. ~ 3 ^[62]	0.81
4-氰基四氢吡喃 Chlornitrofen	86-50-0	1.9 ^[28]	n.d. ^[75]	-
甲氧除草醚 Chlormethoxyfen	1836-77-7	0.6 ^[28]	n.d. ^[76]	-
2,4-二氯-4'-硝基二苯醚 Nitrofen	32861-85-1	2.7 ^[28]	200 ~ 300 ^[77]	3.44
氨基 CNP CNP-amino	1836-75-5	5.7 ^[78]	-	-
乙氧氟草醚* Oxyfluorfen*	26306-61-6	0.87* ^[56]	6 ^[79]	1.14
甲羧除草醚* Bifenox*	42874-03-3	3.2* ^[56]	<30 ^[80]	<1.30
三氟羧草醚甲酯* Acifluorfen-methyl*	42576-02-3	8.9* ^[56]	-	-
哌草磷 Piperophos	50594-67-7	1.4 ^[81]	n.d. ^[82]	-
杀螟松 Fenitrothion	24151-93-7	1.6, 2.1 ^[49]	n.d. ~ 780 ^[83]	4.09
莎稗磷* Anilofos*	122-14-5	1.9* ^[56]	n.d. ^[81]	-
苯硫磷 EPN	64249-01-0	6.3 ^[84]	<500 ^[77]	<3.24
丙硫磷* Prothiofos*	2104-64-5	2.2* ^[56]	<200 ^[85-86]	<2.28
对硫磷 Parathion	34643-46-4	0.2 ^[87]	<500 ^[77]	<4.78
甲基对硫磷 Methyl parathion	56-38-2	4.26, 21.1 ^[28,64]	<500 ^[77]	<3.48
甲基立枯磷* Tolclofos-methyl*	298-00-0	2.8* ^[56]	10 ^[88]	0.93
乙硫磷* Ethion*	57018-04-9	3.3* ^[56]	50 ~ 200 ^[77,89]	2.06
抑草磷* Butamifos*	563-12-2	3.3* ^[56]	-	-
伏杀硫磷* Phosalone*	2310-17-0	4.5* ^[56]	<21 ^[49]	<0.96
除线磷* Dichlofenthion*	97-17-6	4.8* ^[56]	11.7 ^[51]	0.75
倍硫磷* Fenthion*	55-38-9	4.9* ^[56]	n.d. ~ 25.6 ^[62]	1.13
杀螟腈* Cyanophos*	2636-26-2	5.5* ^[56]	<200 ^[77]	<2.03
溴苯磷* Leptophos*	21609-90-5	5.7* ^[56]	46 ^[90]	1.15
溴硫磷乙基* Bromophos-ethyl*	4824-78-6	7.4* ^[56]	500 ~ 700 ^[91]	2.24
喹硫磷* Quinalphos*	13593-03-8	7.8* ^[56]	-	-
异丙胺磷* Isofenphos*	25311-71-1	8.7* ^[56]	<300 ^[77]	<1.86
杀螟硫磷* MEP Oxon*	2255-17-6	9.4* ^[56]	-	-
咯菌腈* Flucythrinate*	70124-77-5	6.6* ^[56]	n.d. ^[92]	-
z-噻菌脲 Fenvalerate	51630-58-1	370 ^[93]	34 ~ 349 ^[93]	1.20
氟氯氰菊酯* Cyfluthrin*	68359-37-5	8.4* ^[56]	n.d. ~ 3.9 ^[94]	-0.12
醚菊酯* Etofenprox*	80844-07-1	9.2* ^[56]	-	-
苄氯菊脂 Permethrin	52645-53-1	56.8, 430 ^[34,87]	30 ~ 127 ^[44,60]	1.61
氯氰菊酯 Cypermethrin	86753-92-6	56.8, 420 ^[34,87]	26.7 ~ 183 ^[60,93]	1.74
高效氯氟氰菊酯* Cyhalothrin*	91465-08-6	1.64* ^[59]	n.d. ~ 1.6 ^[60,94]	0.19
溴氰菊酯 Deltamethrin	52918-63-5	5.8, 20 ^[87]	n.d. ~ 2.7 ^[95]	0.81
间苯氧基苯甲酸 3-Phenoxybenzoic acid (3-PBA)	3739-38-6	1 210 ^[34]	220 ^[96]	0.78
甲硫威 Methiocarb	2032-65-7	14.8 ^[43]	10 ^[88]	1.33
禾草丹* Thiobencarb*	28249-77-6	9.4* ^[56]	<20 ^[97]	<0.78

续表1

物质 Chemicals	CAS 号 CAS No.	EC _{50s} /(μmol·L ⁻¹)	G _s /(ng·L ⁻¹)	i _{AA,max}
甲氧嘧草胺* Thenylchlor*	96491-05-3	5.4* [56]	-	-
苯噻草胺* Mefenacet*	73250-68-7	5.6* [56]	-	-
甲草胺* Alachlor*	15972-60-8	9.6* [56]	n.d. ~ 91.3 [62]	1.41
敌草索* Propanil*	709-98-8	1.4* [56]	<11 [97]	<1.23
戊菌隆* Pencycuron*	66063-05-6	1.5* [56]	-	-
利谷隆 Linuron	330-55-2	55, 42 [50,87]	<35 [97]	<1.37
咪鲜胺 Prochloraz	67747-09-5	3.09 [64]	n.d. [44]	-
敌草隆 Diuron	330-54-1	6.83 [64]	40 ~ 1 670 [44]	3.87
溴螨酯* Bromopropylate*	18181-80-1	0.53* [56]	20 ~ 6 000 [98]	4.63
二甲戊乐灵* Pendimethalin*	40487-42-1	1.2* [56]	22 [97]	1.67
联苯三唑醇* Bitertanol*	55179-31-2	2.6* [56]	10 ~ 20 000 [98]	1.72
氟菌唑* Triflumizole*	68694-11-1	3.5* [56]	n.d. [99]	-
溢霉唑* Imazalil*	35554-44-0	4.2* [56]	108 [51]	1.80
2-联苯酚* 2-Phenylphenol*	90-43-7	4.9* [56]	100 [99]	1.94
苄草唑* Pyrazoxyfen*	71561-11-0	5* [56]	-	-
丙环唑 Propiconazole	60207-90-1	7.71 [64]	<500 [99]	3.13
氯苯嘧啶醇 Fenarimol	60168-88-9	11.8, 23.3 [28,64]	40 ~ 8 000 [98]	4.16
甲萘威 Carbaryl	63-25-2	84 [35]	<41 [97]	<1.23
6-乙氧基-2,2,4-三甲基-1,2-二氢化喹啉* Ethoxyquin*	91-53-2	7.8* [56]	n.d. [100]	-
防腐剂类 Parabens				
尼泊金甲酯 Methylparaben	99-76-3	188 [39]	99 ~ 121 [101]	1.82
尼泊金乙酯 Ethylparaben	120-47-8	109 [39]	49 ~ 71 [101]	1.79
尼泊金丙酯 Propylparaben	94-13-3	309 [70]	36 ~ 45 [101]	1.11
尼泊金丁酯 Butylparaben	94-26-8	68 [27]	n.d. [101]	-
尼泊金异丙酯 Isopropylparaben	4191-73-5	42 [29]	n.d. [101]	-
尼泊金异丁酯 Isobutylparaben	4247-2-3	76 [29]	n.d. [101]	-
多环麝香类 Polycyclic musks				
万山麝香 Versalide	88-29-9	3.5 [102]	n.d. [103]	-
粉檀麝香 Phantolide	15323-35-0	2.7 [102]	1 ~ 3.8 [103]	1.47
吐纳麝香 Tonalide	21145-77-7	3.6, 21.4 [39,104]	21.7 ~ 210 [19,105]	1.44
佳乐麝香 Galaxolide	1222-05-5	2.9, 11.1 [39,104]	751 ~ 1 230 [19]	0.76
阻燃剂类 Fire retardants				
2,2',6-三溴联苯醚 BDE-19	147217-73-0	0.06 [106]	n.d. [106-107]	-
2,4,4'-三溴联苯醚 BDE-28	41318-75-6	3.1 [106]	n.d. ~ 0.56 [106-107]	0.50
3,4,5-三溴联苯醚 BDE-38	337513-54-9	1.9 [106]	n.d. [106-107]	-
3,4',5-三溴联苯醚 BDE-39		3.5 [106]	n.d. [106-107]	-
2,2',4,4'-四溴联苯醚 BDE-47	5436-43-1	1 [106]	0.21 ~ 15 [106-107]	2.34
2,2,4,5-四溴联苯醚 BDE-49	243982-82-3	0.67 [106]	n.d. ~ 4 [106-107]	1.94
3,3',4,5'-四溴联苯醚 BDE-79	446254-48-4	2 [106]	n.d. [106-107]	-
2,2',4,4',5-五溴联苯醚 BDE-99	60348-60-9	7.8 [106]	0.03 ~ 11.2 [106-107]	1.09
2,2',4,4',6-五溴联苯醚 BDE-100	189084-64-8	1.64 [106]	0.03 ~ 1.983 [106-107]	0.42
2,2',4,4',5,5'-六溴二苯醚 BDE-153	68631-49-2	13.2 [106]	0.086 ~ 1.6 [106-107]	1.32
2,2',4,4',6,6'-六溴二苯醚 BDE-155	35854-94-5	2 [106]	n.d. ~ 0.18 [106-107]	0.50
2,2',3,4,4',5,6-七溴联苯醚 BDE-181	189084-67-1	3 [106]	n.d. ~ 0.39 [106-107]	0.68

续表1

物质 Chemicals	CAS 号 CAS No.	EC _{50s} /($\mu\text{mol}\cdot\text{L}^{-1}$)	G_s /($\text{ng}\cdot\text{L}^{-1}$)	$i_{\text{AA,max}}$
2,3,3',4,4',5,6-七溴联苯醚 BDE-190	189084-68-2	8.8 ^[106]	0.0039 ^[106]	1.15
α -六溴环十二烷 HBCD alpha	-	3.4 ^[106]	0.41 ^[108]	0.73
β -六溴环十二烷 HBCD beta	-	11.6 ^[106]	0.15 ^[108]	1.27
γ -六溴环十二烷 HBCD gamma	-	3.7 ^[106]	1.4 ^[108]	0.77
动植物激素类 Plant hormone				
黄酮 Flavone	525-82-6	77.62 ^[70]	-	-
雌马酚 Equol	94105-90-5	74.131 ^[70]	520 ^[109]	2.31
染料木素 Genistein	446-72-0	85.1138 ^[70]	1.7~5.623 ^[110-111]	0.24
5,7-二羟基-4'-甲氧基异黄酮 Biochanin A	491-80-5	4.2 ^[70]	1.6~2.3 ^[111]	1.13
其他类 Others				
环丙氯地孕酮 Cyproterone acetate	427-51-0	0.64, 0.12 ^[54,112]	29 ^[113]	3.61
4-羟基苝基丙酮 Raspberry ketone	5471-51-2	252 ^[114]	-	-

注: G_s 表示抗雄激素样化合物在城市污水处理厂出水中的浓度; - 缺乏有效数据, 无法计算; * 相对氟他胺的抗雄激素样潜能通过 EC_{20} 计算, 根据已有研究该值为 $1.64\ \mu\text{mol}\cdot\text{L}^{-1}$ ^[115]。

Note: G_s stands for the concentrations of antiandrogens in the effluents of wastewater treatment plants; - Cannot be calculated; * the relative antiandrogenic potencies were calculated using EC_{20} , which was $1.64\ \mu\text{mol}\cdot\text{L}^{-1}$ ^[115].

表 2 污水处理厂出水中抗雄激素样活性排名前 10% 的化合物

Table 2 The first ten percent antiandrogens with high antiandrogenic activity in the effluents of WWTPs

物质种类 Compound classification	物质名称 Compound	数量 Number
农药类 Pesticides	溴螨酯、腐霉利、烯菌酮、氯苯嘧啶醇、烯酰吗啉、杀螟松、敌草隆、咯菌酯 Bromopropylate, procymidone, vinclozolin, fenarimol, dimethomorph, fenitrothion, diuron, fludioxonil	8
酚类 Phenols	双酚 A、对叔辛基酚、十二烷基酚、邻苯基苯酚 Bisphenol A, 4-t-octylphenol, 4-n-dodecylphenol, o-phenylphenol	4
邻苯二甲酸酯类 Phthalates	邻苯二甲酸二己酯、邻苯二甲酸二丁酯 Dibutyl phthalate, di-n-hexyl phthalate	2
紫外线吸收剂 UV-filters	2-羟基-4'-甲氧基二苯甲酮 2-Hydroxy-4'-methoxybenzophenone	1

3.2 抗雄激素样化合物控制的优先性排序

根据表 1 中最大抗雄激素样活性指数 $i_{\text{AA,max}}$ 对抗雄激素样化合物控制的优先性进行排序, 具体如下表 2 所示。

溴螨酯是一种低毒广谱杀螨剂, 在部分国家或地区应用较广泛。腐霉利属于二甲酰亚胺杀菌剂和杀虫剂, 是最早发现的环境抗雄激素样化合物之一。烯菌酮是最早报道的环境抗雄激素样化合物, 是杀真菌剂。氯苯嘧啶醇是嘧啶杂环类广谱性杀菌剂。烯酰吗啉是杀真菌剂, 农业上主要用来防治真菌对农作物引起的病害。杀螟松属于有机磷系农药, 敌草隆是苯基取代脲类除草剂, 咯菌酯是吡咯类杀菌剂。尽管大部分农药的生物毒性已受到各国研究者

的关注, 但腐霉利、烯酰吗啉仍在 2008 年我国《农业部推荐使用的高效低毒农药品种名单》中, 其由于具有抗雄激素样活性而可能造成的环境风险未受到重视, 亟待进一步关注。双酚 A、对叔辛基酚、十二烷基酚和邻苯基苯酚均是常用的工业原料。双酚 A、对叔辛基酚是环境中极具代表性的雌激素类内分泌干扰物, 污水处理厂出水中低浓度的双酚 A、对叔辛基酚等酚类物质可能产生的抗雄激素样活性风险应受到重点关注。邻苯二甲酸酯类是一类使用普遍的增塑剂, 由于在塑料中以游离状态存在, 极易转移进入环境。以往研究者重点关注邻苯二甲酸酯类的雌激素活性, 由本研究可知, 邻苯二甲酸二己酯和邻苯二甲酸二丁酯 2 种化合物在污水处理厂出水中

的抗雄激素样活性风险亦不容忽视。2-羟基-4'-甲氧基二苯甲酮是二苯甲酮类紫外吸收剂,属于我国化妆品中准用防晒剂。它的广泛使用可能造成的抗雄激素样活性风险应受到重点关注。另外,化合物邻苯二甲酸正丁酯和对硫磷抗雄激素样活性指数可能分别接近6.24和4.78,它们在污水处理厂出水中的抗雄激素样活性风险也应受到重视。

尽管包括抗雄激素样化合物在内的其他类型的内分泌干扰物,近年来逐渐受到重视,但其在污水处理厂中迁移变化的研究仍有限,而且由于受人类活动、气候变化等因素的影响,不同地区抗雄激素样化合物分布会存在差异,从而影响了本研究排序结果的可靠性。因此,在日后对特定地区污水处理厂出水中抗雄激素样化合物的控制时,还应开展针对性的抗雄激素样化合物的识别及浓度迁移变化研究作为补充。

综上所述,污水处理厂出水中需要对邻苯二甲酸二丁酯、邻苯二甲酸二己酯、双酚A、溴螨酯、对叔辛基酚、腐霉利、烯菌酮、氯苯嘧啶醇、烯酰吗啉、杀螟松、十二烷基酚、敌草隆、咯菌酯、2-羟基-4'-甲氧基二苯甲酮、以及邻苯基苯酚等抗雄激素样化合物进行优先控制。但不同地区抗雄激素样化合物分布会存在差异,特定地区污水处理厂出水中抗雄激素样化合物的控制还应开展针对性的识别研究作为补充。

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