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苯甲酮及苯并三唑类紫外吸收剂的检测方法及残留现状*

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摘 要 苯甲酮和苯并三唑类物质是应用广泛的紫外吸收剂,主要用于防止紫外辐射对人体皮肤和高分子材料的损害.随着温室效应和臭氧层破坏的加剧,紫外吸收剂的使用量日益增加,近年来,苯甲酮和苯并三唑类物质的内分泌干扰特性和对人体健康的潜在影响引起了广泛关注.本文系统地综述了苯甲酮及苯并三唑类紫外吸收剂的检测方法及环境残留的最新研究现状.目前,环境样品的预处理方法多采用固相萃取法,根据不同化合物极性大小,选择使用气相或液相色谱串联质谱进行检测.研究表明,苯甲酮和苯并三唑类物质在城市污水厂进出水和活性污泥中含量较高,地表水、地下水、土壤、底泥及生物体均能检测到此类物质的残留,土壤、底泥及生物样品中苯甲酮和苯并三唑类物质的浓度在 ng·g^{-1}到 μg·g^{-1}(干重)之间.同时,本文对苯甲酮及苯并三唑类物质在城市污水处理系统中的去除途径、多介质环境中的归趋、人体暴露及其风险评价等方面的研究趋势进行了展望.

关键词 甲酮, 苯并三唑, 紫外吸收剂, 检测方法, 环境残留.

Detection method and occurrence of benzophenone and benzotriazole UV-filters in environment

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Abstract: Benzophenones and benzotriazoles are widely used as ultraviolet absorbents to protect human skin and polymer material against UV radiation. Their applications have been increasing due to the intensification of the greenhouse effect and ozone depletion. In the past decade, benzophenones and benzotriazoles have attracted wide attention due to their endocrine disruption effects and potential threat to human health. This review mainly summarized the analytical methods and occurrence of benzophenones and benzotriazoles in environment. According to literature, most of environmental samples were treated by solid phase extraction, and benzophenones and benzotriazoles were analyzed by gas chromatography or liquid chromatography tandem mass spectrometry. The results indicated that concentrations of benzophenones and benzotriazoles were relatively high in municipal wastewater and sludge samples. Furthermore, they were also detected in surface water, soil, sediment and biota samples with the concentrations from ng·g^{-1} to μg·g^{-1} (dry weight). Finally, hot research topics (the removal pathways in municipal wastewater treatment plants,

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environmental behaviors and fates, toxic effect, human exposure and risk assessment of benzophenones and benzotriazoles) were pointed out in future studies.

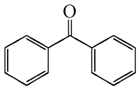
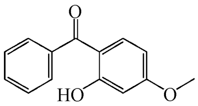
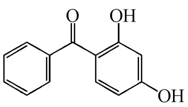
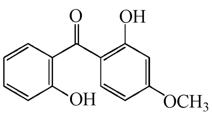
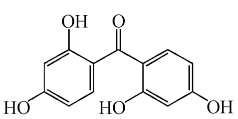
Keywords: benzophenone, benzotriazole, UV-filters, analytical method, occurrence.

近年来,全球温室效应不断加剧,臭氧层破坏愈加严重,导致大量紫外线穿透大气层到达地面.在太阳光辐射中,紫外线辐射区的谱区范围为200—400 nm,其能量约占太阳辐射总量的8%[1].大量照射紫外线可导致皮肤损伤,同时也可导致光敏性材料分解.紫外线吸收剂是一种光稳定剂,能吸收阳光及荧光光源中的紫外线部分,而本身又不发生变化.目前,我国紫外吸收剂的生产能力在万吨以上,由于光稳定剂应用市场前景较好,“十二五”期间,国内光稳定剂年产量平均增幅为30%[2].苯并三唑类紫外线吸收剂在300—385 nm内有较高的吸光指数,其吸收光谱接近于理想吸收剂的要求,这类化合物在50 MED(最小红斑剂量)的阳光下照射,光降解低于0.3%,能够大幅度减少光降解产物对皮肤的刺激[3].苯甲酮类紫外线吸收剂因价格低廉而被广泛应用,其分子结构中内氢键越稳定,开环所需的能量越多,吸收紫外线的能力就越强,因此传递给高分子材料的能量就越少,光稳定性就越佳.目前紫外吸收剂在化妆品、润肤霜、沐浴液、喷发定型剂、毛发染料以及洗发香波等日用品中应用广泛,据文献报道,苯并三唑类物质在洗洁精中的使用量为每次0.09—27.8 mg[4],紫外吸收剂还可以用于除冰或防冻剂[5-10],作为缓蚀剂加入到除冰液中,例如发动机冷却剂、飞机除冰剂或防冻液等[10-13],苯并三唑及其衍生物还可以用于汽车防冻剂、刹车油、金属切削液、工业冷凝系统[14]等方面,苯甲酮类还可以应用于农药、调味品、食品包装等方面[15-16].这两类化合物在人们使用其产品的过程中被间接地释放到自然环境中,对生态环境和人体健康可能造成危害.

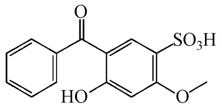
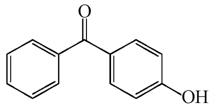
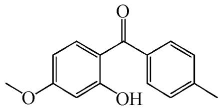
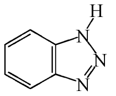
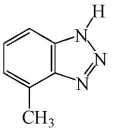
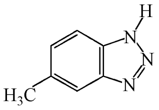
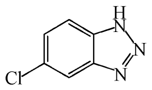
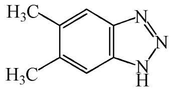
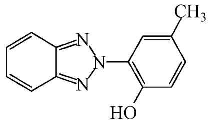
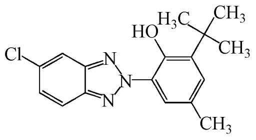
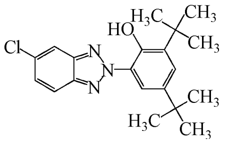
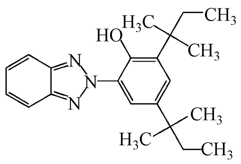
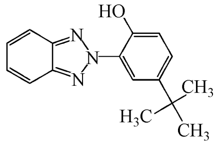
Daughton和Ternes等第一次对紫外吸收剂的研究现状进行了综述[17],随后关于紫外吸收剂的转化产物[18]及其在生物体内的残留[19],化妆品[20]、人体样品[21]以及各环境介质[17]中紫外吸收剂的检测方法,以及个别紫外吸收剂在水环境中的毒性[22]等方面的研究也有了相关概述.但是,现有研究通常只针对个别紫外吸收剂或者某种类型的环境样品,缺少较为全面的系统综述.本文综述了所有已发表的关于苯甲酮及苯并三唑类物质的检测方法和环境残留的文章,所涉及的苯甲酮及苯并三唑类紫外吸收剂的主要化合物的理化性质及分子结构图如表1所示.

表1 苯甲酮、苯并三唑类物质的相关信息

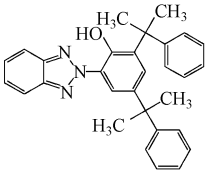
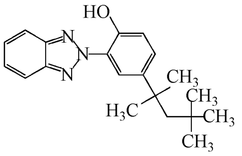
Table 1 Physicochemical properties and structures of target compounds

分析物 Compounds	结构图 Structure	CAS/MF/MW	$\lg K_{ow}{}^a/\lg K_{oc}{}^b/\lg K_{oa}{}^c/\lg BCF^d$
Benzophenone (BP)		CAS: 119-61-9 MF: $C_{13}H_{10}O$ MW: 182.22	$\lg K_{ow}=3.15$, $\lg K_{oc}=3.06$, $\lg K_{oa}=7.28$, $\lg BCF=1.18$
2-hydroxy-4-methoxybenzophenone (BP-3)		CAS: 131-57-7 MF: $C_{14}H_{12}O_3$ MW: 228.25	$\lg K_{ow}=3.52$, $\lg K_{oc}=2.98$, $\lg K_{oa}=10.00$, $\lg BCF=1.58$
2,4-dihydroxybenzophenone(BP-1)		CAS: 131-56-6 MF: $C_{13}H_{10}O_3$ MW: 214.22	$\lg K_{ow}=2.96$, $\lg K_{oc}=3.28$, $\lg K_{oa}=11.93$, $\lg BCF=1.04$
2,2′-dihydroxy-4-methoxybenzophenone (BP-8)		CAS: 131-53-3 MF: $C_{14}H_{12}O_4$ MW: 244.25	$\lg K_{ow}=3.82$, $\lg K_{oc}=3.10$, $\lg K_{oa}=10.91$, $\lg BCF=1.60$
2,2′,4,4′-tetrahydroxybenzophenone (BP-2)		CAS: 131-55-5 MF: $C_{13}H_{10}O_5$ MW: 246.22	$\lg K_{ow}=2.78$, $\lg K_{oc}=3.51$, $\lg K_{oa}=16.61$, $\lg BCF=0.92$

续表1

分析物 Compounds	结构图 Structure	CAS/MF/MW	lg K_{ow} ^{a}/lg K_{oc} ^{b}/lg K_{oa} ^{c}/lg BCF^{d}
2-hydroxy-4-methoxy-5-sulfonylbenzophenone(BP-4)		CAS: 4065-45-6 MF: $C_{14}H_{12}O_6S$ MW: 308.31	lg K_{ow} = 0.37, lg K_{oc} = 1.83, lg K_{oa} = 12.91, lg BCF = 0.50
4-hydroxybenzophenone(4-OH-BP)		CAS: 1137-42-4 MF: $C_{13}H_{10}O_2$ MW: 198.22	lg K_{ow} = 2.67, lg K_{oc} = 3.16, lg K_{oa} = 11.15, lg BCF = 1.11
2-hydroxy-4-methoxy-4′-methylbenzophenone(BP-10)		CAS: 1641-17-4 MF: $C_{15}H_{14}O_3$ MW: 242.27	lg K_{ow} = 4.07, lg K_{oc} = 3.19, lg K_{oa} = 10.24, lg BCF = 1.77
1H-benzotriazole(BTri)		CAS: 95-14-7 MF: $C_6H_5N_3$ MW: 119.13	lg K_{ow} = 1.17, lg K_{oc} = 1.72, lg K_{oa} = 6.66, lg BCF = 0.62
4-methybenzotriazole(4-TTri)		CAS: 29878-31-7 MF: $C_7H_7N_3$ MW: 133.15	lg K_{ow} = 1.71, lg K_{oc} = 1.94, lg K_{oa} = 6.89, lg BCF = 0.80
5-methybenzotriazole(5-TTri)		CAS: 136-85-6 MF: $C_7H_7N_3$ MW: 133.15	lg K_{ow} = 1.71, lg K_{oc} = 1.93, lg K_{oa} = 6.89, lg BCF = 0.80
5-chlorobenzotriazole(CBT)		CAS: 94-97-3 MF: $C_6H_4ClN_3$ MW: 153.57	lg K_{ow} = 1.81, lg K_{oc} = 1.93, lg K_{oa} = 7.16, lg BCF = 0.86
5,6-dimethylbenzotriazole(XTri)		CAS: 4184-79-6 MF: $C_8H_9N_3$ MW: 147.18	lg K_{ow} = 2.26, lg K_{oc} = 2.14, lg K_{oa} = 7.40, lg BCF = 1.16
2-(5-Methyl-2-hydroxyphenyl) benzotriazole(UV-P)		CAS: 2240-22-4 MF: $C_{13}H_{11}N_3O$ MW: 225.25	lg K_{ow} = 3.00, lg K_{oc} = 5.00, lg K_{oa} = 15.91, lg BCF = 2.62
2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole(UV-326)		CAS: 3896-11-5 MF: $C_{17}H_{18}ClN_3O$ MW: 315.81	lg K_{ow} = 5.55, lg K_{oc} = 4.64, lg K_{oa} = 16.87, lg BCF = 3.11
2,4-di-t-butyl-6-(5-chloro-2Hbenzotriazole-2-yl)phenol(UV-327)		CAS: 3864-99-1 MF: $C_{20}H_{24}ClN_3O$ MW: 357.89	lg K_{ow} = 6.91, lg K_{oc} = 5.28, lg K_{oa} = 17.86, lg BCF = 4.01
2-(2H-Benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)phenol(UV-328)		CAS: 25973-55-1 MF: $C_{22}H_{29}N_3O$ MW: 351.50	lg K_{ow} = 7.25, lg K_{oc} = 5.65, lg K_{oa} = 17.82, lg BCF = 3.78
2-(5-t-butyl-2-hydroxyphenyl) benzotriazole(UV-PS)		CAS: 3147-76-0 MF: $C_{16}H_{17}N_3O$ MW: 267.33	lg K_{ow} = 4.36, lg K_{oc} = 4.22, lg K_{oa} = 15.59, lg BCF = 2.54

续表1

分析物 Compounds	结构图 Structure	CAS/MF/MW	lg K_{ow} ^{a}/lg K_{oc} ^{b}/lg K_{oa} ^{c}/lg BCF^d
2-[3,5-bis(1-methyl-1-phenylethyl-2-hydroxyphenyl]benzotriazole(UV-234)		CAS：70321-86-7 MF：$C_{30}H_{29}N_3O$ MW：447.58	lg K_{ow} = 7.67，lg K_{oc} = 7.79， lg K_{oa} = 20.92，lg BCF = 3.57
2-(2-Hydroxy-5-tertoctylphenyl)-2H-benzotriazole(UV-329)		CAS：3147-75-9 MF：$C_{20}H_{25}N_3O$ MW：323.43	lg K_{ow} = 6.21，lg K_{oc} = 5.11， lg K_{oa} = 16.95，lg BCF = 3.77

注：MF：分子式；MW：分子量；K_{ow}：辛醇-水分配系数；K_{oc}：底泥-水分配系数；K_{oa}：辛醇-空气分配系数；BCF：生物富集系数. a：来源于 EPI Suite，KOWWIN v.-1.68. b：来源于 EPI Suite，KOCWIN，MCl Method. c：来源于 EPI Suite，KOAWIN v.-1.10. d：来源于 EPI Suite.

1　检测方法(Detection method of benzophenone and benzotriazole UV-filters)

1.1　样品预处理

1.1.1　液体样品预处理

固相萃取(Solid phase extraction,SPE)是应用最广泛的预处理方法,条件优化主要包括固相萃取柱类型、样品流速、pH 值、有机相的比例等.固相萃取柱类型是影响回收率的重要因素,选取固相萃取柱时应考虑吸附剂的特性和目标物的物理化学性质,样品流速影响分析时间,pH 影响物质的形态及其在萃取柱上的吸附,有机相的比例可以改善目标物在器皿上的吸附损失.聚合物反相吸附剂可用于紫外吸收剂的样品处理[23],紫外吸收剂具有一定的极性,多数情况下用中间极性溶剂如二氯甲烷[24]或乙酸乙酯[25]作为萃取剂.Liu 等[26]检测地下水、污水中苯并三唑类物质时,选择的萃取条件为 Oasis HLB、甲醇/二氯甲烷溶液(50/50,V/V)、pH = 2 等.Montesdeoca-Esponda[27]、Liu 等[28]用 on-line SPE 和 off-line SPE 两种方法检测了海水、污水中苯并三唑类物质,结果显示,on-line SPE 方法简单、灵敏、校正曲线线性范围宽、精密度高,适用于水环境中多种苯并三唑物质的同时分析检测.Liu 等[28]选择的萃取优化条件为 Polar Advantage Ⅱ固相萃取柱、样品流速 2 mL·min^{-1}、pH = 6、甲醇比例为 30%等,在最优条件下所得的定量限(Limit of quantitation,LOQ)较低(0.21—2.17 ng·L^{-1}),可用于河水或污水厂中苯并三唑类物质的常规分析.Montesdeoca-Esponda 等[27]采用 on-line SPE 和 off-line SPE 与 HPLC-MS/MS 相结合的方法,可降低方法检出限、缩短实验时间,适用于水环境中苯并三唑类物质检测.

固相微萃取(Solid phase microextraction,SPME)方法是在 SPE 的基础上发展起来的,该方法具有有机溶剂用量少、检测速度快、基质效应小等优点,但是相对于常用的 SPE 方法来说,SPME 的灵敏度和精确度较差[17].萃取时间、洗脱时间、洗脱溶剂、盐度以及 pH 等均可对 SPME 的效果产生影响.Li 等[29]分析河水中苯甲酮类紫外吸收剂时选择的最优条件为萃取时间 60 min、洗脱时间 10 min、洗脱溶剂甲醇、盐度 200 mg·mL^{-1} NaCl,pH 不做调节.

人体尿液中苯甲酮和苯并三唑类吸收剂的样品处理多用液-液萃取(Liquid-liquid extraction,LLE)方法[30-31].影响 LLE 的选择性和回收率的主要因素为溶剂极性、溶液 pH、提取方法、溶剂回收方法等.Wang 等[30]采用 LLE 方法处理 500 μL 人体尿液时,加入 50 μL 代标和缓冲液后,用 3 mL 乙酸乙酯振荡萃取 3 次,离心、浓缩后进仪器分析,测得苯甲酮类物质的 LOQ 为 0.07—0.20 ng·L^{-1}.

分散液液微萃取(Dispersive liquid-liquid microextraction,DLLME)是一种用磁性粒子回收萃取剂的方法.2006 年由 Rezaee 等首次报道[32],是一种简单有效的萃取技术,可以摒弃传统的离心分离技术或特定的仪器设备,对于萃取条件的优化主要包括涡流时间、萃取溶剂体积、解吸溶剂、磁粒子质量、pH、离子强度等.Zhang 等[33]检测分析苯甲酮等紫外吸收剂时选择的萃取条件为:涡流旋转时间 4 min、萃取溶剂为 30 μL 正辛醇、50 μL 乙腈解析 1 min、35 mg 磁粒子、pH = 6.7、未加入盐,并在此条件下分析了其

可测线性范围（0.067—6.7 mg·mL^{-1}）、MDLs（0.7—12.3 ng·L^{-1}）、精密度（$R^2>0.99$）、富集因子（64—110）等相关参数.

搅拌棒吸附萃取（Stir bar sorption extraction，SBSE）溶剂使用量少，具有环境友好性，优化条件主要有样品体积、萃取时间、温度、pH值、离子强度等. Montesdeoca-Esponda等[34]采用此方法检测海水、污水中的苯并三唑类紫外吸收剂时选择的最优条件是：不加盐、样品体积为25 mL、pH值为5、萃取温度为40 ℃，时间为120 min，解吸温度为60 ℃，时间为20 min，并加入1.5 mL乙腈.

1.1.2　固体样品预处理

Jeon等[35]分析土壤样品时，取甲醇振荡萃取干燥后的土壤样品，加入1 mL浓度为5%的NaCl离心后蒸发浓缩，振荡离心后置于-30 ℃环境下，然后将有机层转移到离心管中，并干燥浓缩，测得BP的方法检出限（Method detection limits，MDLs）为100 ng·kg^{-1}，平均回收率为115%. Wang等[36]采用固相萃取柱处理大气灰尘样品时，首先在室温下使样品与代标平衡30 min后，加入甲醇/水溶液（5∶3，V/V）振荡萃取60 min，离心5 min，用5+3 mL甲醇/水萃取后浓缩至4 mL，浓度为0.2%甲酸/超纯水溶液（pH=2.5）稀释至10 mL，Oasis MCX柱萃取和甲醇/水溶液（20∶80，V/V）洗脱，测得苯并三唑类物质的LOQ为0.5 ng·g^{-1}，回收率范围为44%—113%. Peng等[37]将生物样品冷冻干燥、研磨、加入内标后用甲醇超声振荡萃取3次，融入乙酸乙酯/环已烷（50/50，V/V）溶液中，样品经去油脂后，用乙酸乙酯/环已烷（50/50，V/V）进行洗脱，样品浓缩后用已烷进一步硅胶净化，紫外吸收剂用二氯甲烷/乙酸乙酯（50/50，V/V）溶液从硅胶柱上洗脱，样品浓缩后进仪器分析，测得BP-3的回收率为88.3%—102.0%，LOQ为0.08 ng·g^{-1}.

加速溶剂萃取（Accelerated solvent extraction，ASE）是一种对固态或半固态样品进行处理的方法，可用于污泥或土壤样品的处理. Ruan等[38]分析了市政污泥中苯并三唑类紫外吸收剂的含量，LOQ为0.15—0.77 ng·g^{-1}，平均回收率为93%.

1.2　仪器分析

随着使用量的与日俱增，人们对于紫外吸收剂在环境中的残留及其对人体健康的影响展开了大量的研究，GC-MS[7, 39-40]、GC-MS/MS[6,41]、LC-MS/MS[42-45]等分析检测仪器已经应用于苯并三唑、苯甲酮的定性和定量研究.

1.2.1　GC-MS

Sulej等[7]将Agilent仪器（GC：7980A；MS：5975C）的进样口温度设为260 ℃，分析时间约为19 min（升温范围为70—275 ℃），检测飞机场地表水中的BTri、4-TTri和5-TTri，MDLs范围为0.3—10 ng·L^{-1}，回收率为68—102%. Kiss等[13]将Agilent仪器（GC：6890N；MS：5973）的进样口温度设为280 ℃，升温范围为80—300 ℃，检测河水中的BTri和5-TTri，MDLs为8—12 ng·L^{-1}，回收率为62%和70%. Poiger等[46]将VG Tribrid仪器的分析时间设为30 min（升温范围为70—280 ℃），检测湖水和河水中的BP-3，LOQ为10 ng·L^{-1}，回收率为57%—90%. Balmer等[47]将VG Tribrid仪器的进样口温度设为280 ℃，分析时间约30 min（升温范围为70—280 ℃），湖水和污水的MDLs分别为2 ng·L^{-1}和10 ng·L^{-1}，回收率为78%—129%. Breedveld等[48]开发的仪器分析方法针对地下水及飞机场地表水中BTri的MDLs为100 ng·L^{-1}.

1.2.2　GC-MS/MS

与GC-MS相比，GC-MS/MS在选择性和灵敏度等方面都有很大的提高. Liu等[5,26]将Agilent仪器（GC：7000A；MS：7890A）进样口温度设为280 ℃，分析时间为22 min（升温范围80—280 ℃），测得污水中BP-3的MDLs为3.2—6.5 ng·L^{-1}，回收率为119%—133%；BTri、5-TTri、CBT及XTri在污水中的MDLs为4.2—16.3 ng·L^{-1}，回收率为77%—122%，在自来水中的MDLs相对较低，为2.9—11.0 ng·L^{-1}，回收率为70%—108%；污水中UV-326和UV-329的MDLs为3.3—5.6 ng·L^{-1}，回收率为95%—110%. Jover等[41]对GC×GC的优化时发现，衍生化的作用很小，由于选择离子的质荷比小，共洗脱现象不可避免，因此分析复杂混合物时使用GC×GC和TOF-MS检测器Agilent HP 6890N，可以节省样品处理时间，并且实现了4-TTri和5-TTri的分离，但是，即使提高GC×GC的分辨率，也不能完全避免共洗脱现象，在检测市政污水中的BTri、5-TTri、4-TTri及XTri时所得MDLs较高，为48—112 ng·L^{-1}，回收率为78%—115%. Da Silva等[25]将仪器（GC：Varian CP-3800；MS：Saturn 2000离子肼）进样口温度设为300 ℃，分析时间

22 min(升温范围为 60—300 ℃),测得污水、加氯水和河水中 BP-3 和 BP-10 的 MDLs 分别为 7.6 ng·L^{-1}和 10.0 ng·L^{-1},回收率为 85%—105%.

1.2.3 LC-MS/MS

高效液相色谱法是应用最广泛的紫外吸收剂检测方发,通常,随着保留时间的增加,4-TTri 和 5-TTri 的峰会加宽,因此液相色谱法不能将两者完全分离,而以两者的加和(TTR)作为结果[14, 49].Weiss 等[14]用 Agilent 1100 HPLC 系统分析时,选用的流动相为水/甲醇 80/20(A)和 10/90(B)以及 0.1%的甲酸进行梯度洗脱,离子源温度 120 ℃,去溶剂化温度 220 ℃,由于灵敏度高可以直接进样,地表水中 BTri、5-TTri、4-TTri 及 XTri 的 LOQ 为 10—25 ng·L^{-1},回收率为 95%—113%.Giger 等[49]采用 Agilent 1100 HPLC 系统,甲醇/水/甲酸(70/30/0.4)作为流动相对目标物进行梯度洗脱,分析时间为 5 min,湖水中 BTri 和 TTR 的 MDLs 分别为 8 ng·L^{-1}和 3 ng·L^{-1},回收率为 99%和 97%.近年来,超高效液相色谱(Ultra-performance liquid chromatography,UPLC)逐渐发展起来,UPLC 具有进样量少、分析时间短、分辨率高、基质效应少、对窄而锋利的色谱峰更灵敏等优点.由于 on-line SPE-HPLC-MS/MS 检出限低、使用方便,应用于水环境的检测时 MDLs、LOQ 和回收率均优于 off-line SPE-HPLC-MS/MS.Liu 等[28]采用 on-line SPE-HPLC-MS/MS 方法时,选择甲醇/水作为流动相,离子源温度为 110 ℃,MDLs 和 LOQ 分别为信噪比的 3 倍和 10 倍,测得 UV-P、UV-PS、UV-329 等 9 种紫外吸收剂在污水中的 MDLs 范围为 0.28—2.17 ng·L^{-1},回收率范围为 76%—114%,在河水中 9 种目标物的 MDLs 范围为 0.21—1.53 ng·L^{-1},回收率范围为 78%—110%. Montesdeoca-Esponda 等[27]采用甲醇(0.1%的甲酸调节 pH 为 2.5)为流动相,源温度为120 ℃,由于 on-line SPE 的富集系数(500)明显高于 off-line SPE 的富集系数(50),所以 on-line SPE 的 MDLs(0.6—4.1 ng·L^{-1})和 LOQ(2.1—14 ng·L^{-1})均低于 off-line SPE 的 MDLs(4.9—15 ng·L^{-1})和 LOQ(16—51 ng·L^{-1}),回收率分别为 58%—94%和 56%—89%.Loos 等[50-51]方法的 MDLs 较低,仅为 1 ng·L^{-1};而用 SBSE 预处理方法的 MDLs 较高,范围为 14.8 ng·L^{-1}—55.1 ng·L^{-1},回收率较低,为 18.%—92.2%%;采用 DLLME 预处理方法的 MDLs 更高,达 40 ng·L^{-1}—2200 ng·L^{-1},回收率为 67.4%—86.1%[42];HPLC-UV 方法测得湖水中 BP 的 MDLs 为 800 ng·L^{-1},回收率为 64.3%—73.5%[33];HPLC-MS/MS方法测得地表水中 BP-1、BP-3、BP-4 及 BP-8 的 MDLs 为 0.03—0.11 ng·L^{-1},回收率为 98%—105%[52].

综上所述,水环境中 BTri、TTR、CBT 和 XTri 的检测,HPLC-MS/MS 方法的 MDLs 较高,为 40—100 ng·L^{-1},GC-MS/MS 方法的 MDLs 为 4.2—16.3 ng·L^{-1};BTri 和 TTR 的检测过程中,LC-MS/MS 方法的 MDLs 为 1—8 ng·L^{-1},GC-MS 的 MDLs 为 0.3—12 ng·L^{-1};UV-326 和 UV-329 的检测过程中,on-line SPE-HPLC-MS/MS 方法的 MDLs 最低(UV-326:1.23-2.6 ng·L^{-1},UV-329:0.9—2.08 ng·L^{-1}),其次是 GC-MS/MS方法(UV-326:3.3—4.1 ng·L^{-1},UV-329:4.8—5.6 ng·L^{-1}),off-line SPE-HPLC-MS/MS 的 MDLs 为 14—15 ng·L^{-1}(UV-326)和 9.4—9.7 ng·L^{-1}(UV-329),Montesdeoca-Esponda[34]的 SBSE-HPLC-MS/MS(UV-326:41.7—55.1 ng·L^{-1},UV-329:14.8—19.1 ng·L^{-1})的 MDLs 最高;BP-3 的检测过程中,HPLC-MS/MS 的 MDLs 最低;虽然 SBSE、DLLME 等方法具有环境友好性,但是在 MDLs 及回收率方面不及 SPE 方法.

2 环境残留(Occurrence of benzophenone and benzotriazole UV-filters in environment)

目前,由于紫外吸收剂的广泛使用,在水体、底泥和土壤、生物体、甚至人体样本中都能够检测到紫外吸收剂的存在.由于污水厂的常规工艺对于紫外吸收剂的去除不完全,污水厂出水以及污水排放受体中都已检测到了苯甲酮和苯并三唑类物质的存在[5-6, 50-51, 53-61],污水厂出水已经成为地表水体中苯甲酮和苯并三唑类物质一个重要的污染源.另外,在地表水体的沉积物[62-64]、污水淤渣[60]等介质中也有苯甲酮和苯并三唑类物质的残留.

2.1 水环境中的残留

由于紫外吸收剂的大量使用,在皮肤和衣物清洗过程中、污水厂出水排放等过程中苯甲酮及苯并三唑类物质的残留物或代谢物就会直接或间接地进入到水环境中[65],进入城市污水管网系统,进而进入污水处理厂.常规的污水处理工艺不能够完全去除某些有毒物质,这些物质会随地表径流进入到土壤、

地表水当中,甚至进入到作为饮用水源地的地下水当中[66-73].苯并三唑类物质是继 EDTA(Ethylenediaminetetraacetic acid, 乙二胺四乙酸)、NTA(Nitrilotriacetic acid, 氨三乙酸)、LAS(Linear alkylbenzene sulfonates, 线性烷基苯磺酸盐)之后的第四大水体污染物[74],并且在水环境中不进行生物降解和光氧化降解,具有持久性、迁移性、生物累积性等特性,它们能够随着水生生物或陆生生物的食物链或食物网传递,成为环境污染物,但是关于此类物质潜在的不利影响、作用方式和毒理学效应等方面的研究较少[75-76].Cancilla 等[66]首次报道了靠近飞机场的地下水中含有苯并三唑类物质,柏林某污水处理厂中未处理的废水中苯并三唑的平均浓度为 12 μg·L^{-1}[11],Asimakopoulos 等[77]对希腊雅典的某污水厂进行了系统的研究,并计算了进水、出水以及污泥中苯并三唑类物质在悬浮颗粒相和溶解相中的分配.生物固相吸附和污泥累积对于苯并三唑类物质的去除效果并不明显[67],Liu 等[78]在好氧和厌氧处理过程中检测到了 3 种苯并三唑类物质的生物转化产物,说明在污水处理过程中,生物转化可以去除苯并三唑类紫外吸收剂.

BP-1 和 BP-3 是应用较为广泛的紫外吸收剂,由图 1 和图 2 中可知,不同水环境中都能够检测到两种紫外吸收剂,如污水、地表水(海水、河水、湖水、池塘等)和地下水等.对于紫外吸收剂在水环境中的残留,检出率较高的有 BTri、TTR、XTri、BP-3、BP-1、BP-4 和 BP-8 等.苯并三唑类物质主要检出于污水中,而苯甲酮多检出于地表水和海水中,在污水中的含量最高.BP-3 是水环境中检测最多的苯甲酮类紫外吸收剂,而且含量也最高,某污水厂中的最高浓度为 7800 ng·L^{-1}[47], BP-3 在海水中的浓度要高于地表水,分别为 17—5429 ng·L^{-1}和<2—550 ng·L^{-1}.Tsui 等[52]发现,我国香港海水中 BP-3 的浓度最高,台湾地区某污水厂中 BP-8 的浓度为 9.8—10.1 ng·L^{-1}[79],在人烟稀少的南极地区也检测到了较高浓度的紫外吸收剂[80],人们休闲娱乐用水如泳池中紫外吸收剂的含量也较高[81],由图 1 可知,地表水中 BP-4 的最高浓度要高于其他苯甲酮类物质的浓度,为 862 ng·L^{-1}[82].

BTri 在污水中的浓度最高,西班牙巴塞罗那某污水厂中的浓度高达 36200 ng·L^{-1}[57],地表水和地下水中 BTri 的含量也较高,分别为 38—3400 ng·L^{-1}和<10—1032 ng·L^{-1},海水中 BTri 的浓度最低,仅为 1.7—40 ng·L^{-1}[61].BTri 在水环境中的残留报道较多的是欧洲地区,并且浓度较高.TTR 的含量也较高,与 BTri 类似,污水中浓度最高,范围为<60—17153 ng·L^{-1},其次是地表水和地下水,分别为 25—2140 ng·L^{-1}和<10—154 ng·L^{-1}.XTri 的浓度小于 BTri 和 TTR,污水中浓度最高,范围为 13—1682 ng·L^{-1},但与 BTri 和 TTR 不同的是,地下水的浓度略高于地表水,分别为<10—114 ng·L^{-1}和<10 ng·L^{-1}.

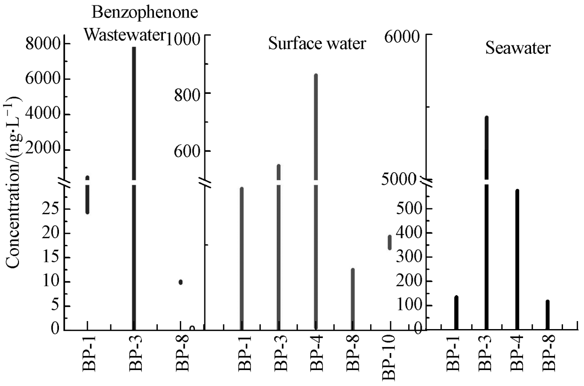


图 1　苯甲酮类紫外吸收剂在全球水环境中的残留范围（图中的上下限分别为所报道的最大值与最小值）

Fig.1　Concentration range of benzophenone UV-Filters in water worldwide

(The upper and lower bounds of the graph are the maximum and the minimum of the reported values)

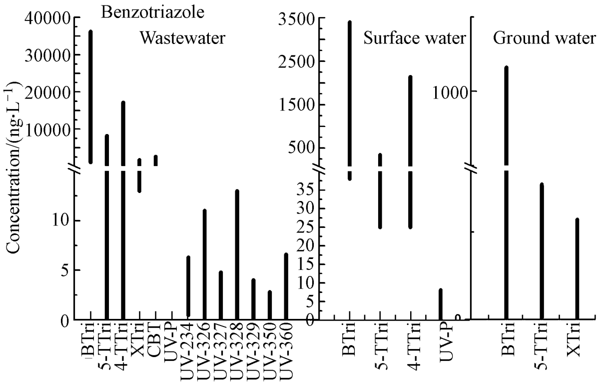


图 2　苯并三唑类紫外吸收剂在水环境中的残留（图中的上下限分别为所报道的最大值与最小值）

Fig.2　Concentration range of benzotriazole UV-Filters in water worldwide

(The upper and lower bounds of the graph are the maximum and the minimum of the reported values)

2.2　底泥和土壤中的残留

文献综述表明,水环境中紫外吸收剂的残留的报道较多,但是关于紫外吸收剂在底泥和土壤中的残留的文献却较少.当 $\lg K_{ow} \geq 4$ 时,土壤和底泥中的紫外吸收剂多是疏水的,当 $\lg K_{oc} = 5.5$ 时,表明它们与基质之间的结合力非常强,足以使它们吸附在土壤/沉积物中[17].Amine 等[83]认为在当河流流量较小

时,紫外吸收剂在底泥中的检出浓度较高,如旱季时各种紫外吸收剂的使用量增加,进而导致环境中紫外吸收剂的浓度较高.Gago-Ferrero 等[84]通过对土壤中紫外吸收剂与总有机碳的相关性分析发现,两者之间并没有直接的相关性.Jeon 等[35]在住宅区、公园、商业区及工业区土壤中检出了较高浓度的紫外吸收剂,分别为 820—16550 ng·g^{-1}-dw(BP)、730—3880 ng·g^{-1}-dw(BP-3)、500—4170 ng·g^{-1}-dw(BP-8)、1060—4910 ng·g^{-1}-dw(4-OH-BP),而 Sánchez-Brunete 等[85]在农业土壤中检测到的 BP-1 和 BP-6 的浓度分别为 5.7 ng·g^{-1} dw 和 0.6 ng·g^{-1} dw.

图 3 和图 4 为各个国家底泥和土壤中苯甲酮及苯并三唑类紫外吸收剂的残留情况,在各国已报道的文献中,中国市政污泥中 UV-328 的浓度远高于其他物质[38,60],美国河底污泥中 UV-PS、UV-326 及 UV-327 的浓度分别为 ND(Not detected,未检出)、5.88 ng·g^{-1} dw 和 0.31 ng·g^{-1} dw[60],澳大利亚市政污泥中 UV-329 和UV-326的残留为 27—272 ng·g^{-1} dw 和 48—114 ng·g^{-1} dw[5],均低于中国.韩国土壤底泥中的 BP、BP-3、BP-1、BP-8 及 4-OH-BP 的浓度远高于其他地区[5, 35, 60, 84, 86],可能与韩国化妆品行业较繁荣有关,其他苯甲酮类紫外吸收剂在各国检出的浓度都很低[35, 60, 84-85].澳大利亚市政污泥中检出的 BTri、5-TTri、CBT 和 XTri 的浓度分别为 75—219 ng·g^{-1} dw、68—125 ng·g^{-1} dw、53—114 ng·g^{-1} dw 和 56—121 ng·g^{-1} dw,高于中国和美国.

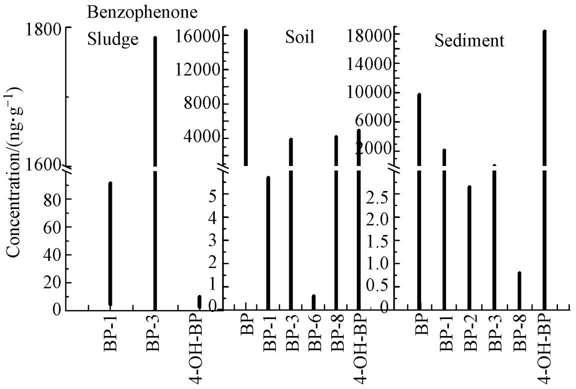


图 3　苯甲酮类紫外吸收剂在全球底泥和土壤中的残留范围

(图中的上下限分别为所报道的最大值与最小值)

Fig.3　Concentration range of benzophenone UV-Filters in sediment and soil worldwide

(The upper and lower bounds of the graph are the maximum and the minimum of the reported values)

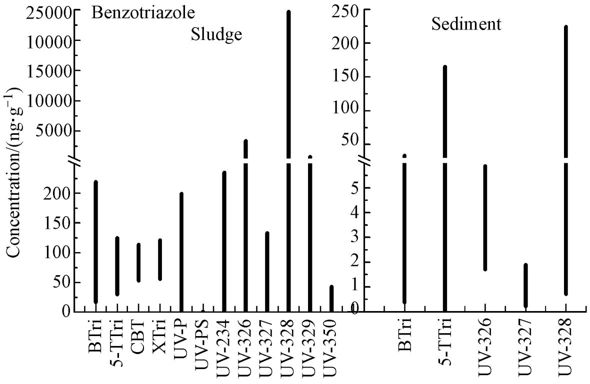


图 4　苯并三唑类紫外吸收剂在全球底泥和污泥中的残留范围

(图中的上下限分别为所报道的最大值与最小值)

Fig.4　Concentration range of benzotriazole UV-Filters in sediment and sludge worldwide

(The upper and lower bounds of the graph are the maximum and the minimum of the reported values)

2.3　生物体内的残留

关于生物体中紫外吸收剂的残留,近年来已有广泛的研究.Peng 等[37]研究比较了中国野生鱼与养殖鱼中紫外吸收剂的含量,发现 BP-3 在两者中的浓度均相对较低,挪威的野生鱼中 BP-3 含量较高[87],Tsai 等[88]对台湾地区不同种类野生鱼中紫外吸收剂的检测发现, BP-3、BP-1、BP-8 的浓度相近,新西兰生物体内检出的 BP-3 浓度为 108 ng·g^{-1} dw(蛤蚌)、8.6 ng·g^{-1} dw(海胆)、14.1 ng·g^{-1} dw(鱼片)和 41.0 ng·g^{-1} dw(鱼肝),BP-1 未检出[80].由统计结果知,BP-3 检出率最高,几乎所有的生物体内都能够检测到 BP-3 的存在.图 5 为苯甲酮及苯并三唑类紫外吸收剂在各个国家生物体内的检出情况,BP-3 浓度最高,为 1037 ng·g^{-1},其次为 UV-329 及 UV-326[26, 37, 87-88].

2.4　室内灰尘残留

Wang 等[36]采集了美国、中国、日本及韩国 158 个室内灰尘样品,首次分析了室内灰尘中的苯甲酮及苯并三唑类物质,发现所有样品中均有苯甲酮和苯并三唑类紫外吸收剂检出,韩国苯并三唑的平均浓度最高,为 87.1 ng·g^{-1},其次是美国(36.2 ng·g^{-1})和日本(33.7 ng·g^{-1}),中国的检出浓度最低,仅为 19.3 ng·g^{-1},但是浓度最高的灰尘样品(1980 ng·g^{-1})来自中国;苯甲酮类物质的检出浓度分别为 612 ng·g^{-1}(美国)、176 ng·g^{-1}(韩国)、138 ng·g^{-1}(日本)和 78.6 ng·g^{-1}(中国),BP-3 在 5 种苯甲酮物质

中所占比重最高,约为 60%—70%;农村家庭的室内灰尘中苯甲酮和苯并三唑类物质的检出浓度均低于城镇家庭和城镇办公室,由于苯甲酮和苯并三唑的应用不同,使得苯并三唑在办公室中的浓度高于家庭中灰尘的浓度,而苯甲酮在家庭灰尘中的浓度高于办公室中的浓度.

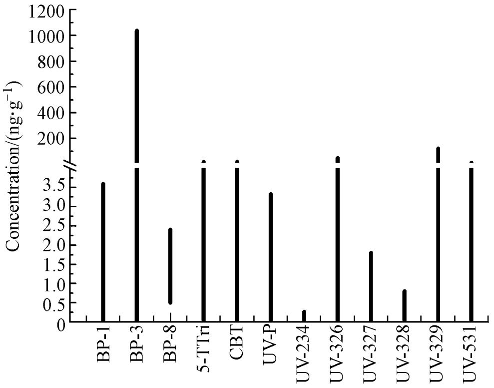


图 5　紫外吸收剂在全球生物体内的残留范围

(图中的上下限分别为所报道的最大值与最小值)

Fig.5　Concentration range of benzophenone and benzotriazole UV-Filters in biota worldwide

(The upper and lower bounds of the graph are the maximum and the minimum of the reported values)

3　人体暴露(Human exposure)

苯甲酮类紫外吸收剂是一种内分泌干扰物质,具有明显的雌激素特性[15,89],紫外吸收剂暴露与致癌、性发育异常以及异常行为的发生有明显的关系[90-92].研究表明,BP-3 在人体内具有雌激素特性[15, 93-94]和抗雄性激素特性[95-96],并且大约 10%的含量就能够进入到人体内循环[97],苯甲酮类紫外吸收剂还具有遗传毒性[98-101].此外,苯甲酮类物质由于亲脂性而具有生物累积性,Hany 等[102]对母乳的检测分析证明了苯甲酮类物质的累积特性.苯甲酮类紫外吸收剂之间能够相互转化,通常转化后的产物干扰性能会比转化前更强[103],如 BP-3 在生物体内可转化为 BP-1 和 BP-8[103-106],且 BP-1 的内分泌干扰性更强[105, 107-109],其他苯甲酮类的衍生物如 BP-2、4-OH-BP 也是 BP-3 的代谢产物,在人体尿液中已经被检出[30, 110].已有研究表明,苯并三唑衍生物对细菌具有致突变性,并且对植物具有毒性[6],5-TTri 对水生生物的急性毒性较低,EC_{50}(半数致死浓度)为 4.25 $mg·L^{-1}$[68].

由于紫外吸收剂应用于不同种类的产品中,因而增加了人们对于此类物质的暴露风险,个人护理品(Personal care products, PCPs)中紫外吸收剂的检测分析可以为紫外吸收剂的风险评估提供数据支持,Manová 等[111]对 PCPs 的检测分析表明昂贵名牌产品中紫外吸收剂的含量更高,并且经常使用的化妆品中与防晒化妆品中紫外吸收剂的含量相差无几.Zhang 等[112]分析了人体血液和尿液中的苯甲酮类物质的含量,并且分析了性别、年龄、地域以及生活方式等方面的影响.Zhang 等[112]首次报道了 5 种苯甲酮类物质在中国儿童、成年人以及孕妇体内的残留及暴露,BP-3 和 BP-1 的暴露量低于美国人,BP-3 在女性当中的暴露量要高于男性,BP-3 和 4-OH-BP 能够由血液进入尿液中,并可以经胎盘由母体进入到胎儿体内.Asimakopoulos 等[31]通过对人体尿液中 BP-1、BP-2、BP-8、4-OH-BP、2,3,4-OH-BP 的检测分析发现,4-OH-BP 和 2,3,4-OH-BP 具有近似的检出率,表明在人体内这两种代谢产物的转化是呈比例的,但是 4-OH-BP 的浓度略高于 2,3,4-OH-BP,苯甲酮类物质在人体内的总体浓度在性别上没有明显的区别,5 种苯甲酮类物质平均摄入量为 28.9 $\mu g·kg^{-1}bw·d^{-1}$.Wang 等[36]计算了苯甲酮和苯并三唑类物质通过室内灰尘的摄入量,发现苯并三唑在韩国儿童及成年人的摄入量(0.19 $ng·kg^{-1}$-bw·day^{-1})要高于日本儿童(0.10 $ng·kg^{-1}$-bw·d^{-1})和美国儿童(0.08 $ng·kg^{-1}$-bw·day^{-1}),中国儿童的摄入量最低,为 0.01 $ng·kg^{-1}$-bw·d^{-1},苯甲酮摄入量较高的是美国居民,为 1.60 $ng·kg^{-1}$-bw·d^{-1}(儿童)和 0.25 $ng·kg^{-1}$-bw·d^{-1}(成年人),苯甲酮通过灰尘暴露的贡献值小于 0.1%,对比实验数据发现,对苯甲酮和苯并三唑类物质来说,儿童的摄入量均高于成年人的摄入量.Asimakopoulos 等[113]第一次分析了人体尿液中的苯并三唑和苯并噻唑类物质,测得苯并三唑物质的浓度分别为<LOQ—5.67 $ng·L^{-1}$(BTri)、<LOQ—3.37 $ng·L^{-1}$(TTR)和<LOQ—3.69 $ng·L^{-1}$(XTri).Gao 等[110]测得的 BP-3、4-OH-BP、BP-1、BP-2、

BP-8 等的平均浓度分别为 2.34、0.15、0.56、0.09、0.02 ng·mL^{-1}，并计算出每种物质的日排泄量分别为 27.2、2.24、5.86、0.76、0.30 ng·kg^{-1}-bw·d^{-1}.

4 问题及未来研究趋势（Problems and future research trends）

（1）文献调研表明，污水处理厂排水是环境中紫外吸收剂的主要污染来源，关于污水处理过程中紫外吸收剂的去除机制的研究尚处于起步阶段，在污水处理系统的水力停留时间里该类紫外吸收剂是否发生生物降解，降解途径是什么，生物降解率是多少，挥发、吸附与沉降速率这些基本问题的研究还刚刚开始，还不能深刻认识该类污染物的环境归趋.

（2）关于紫外吸收剂在污水处理系统中的归趋研究还需要深入探讨.污水处理系统是紫外吸收剂的重要环境归趋，深入研究污水处理系统中紫外吸收剂的环境行为，可为开展新兴污染物筛查和进一步评价水体风险提供基础数据.

（3）需要构建模拟此类紫外吸收剂在污水处理过程中行为的模型.评价有机污染物在污水处理系统中的化学行为时，应该采取合适的计算方法还原或预测有机污染物的迁移转化过程，即通过建立数学模型描述其迁移分配过程，对于新兴污染物的风险评估和采取有效的防控措施是非常必要的，目前需通过构建模型模拟紫外吸收剂在污水处理过程中的归趋.

（4）苯甲酮及苯并三唑类物质在环境中的高残留量可能会危及淡水生态系统，但是关于苯并三唑类物质的作用方式、潜在影响以及毒理学效应等方面的研究相对较少，并且苯甲酮及苯并三唑类物质在环境中的代谢产物可能具有更大的危害性，未来应该引起关注.

（5）已有研究表明，苯甲酮和苯并三唑类物质广泛存在于多种环境介质中，但是，大气或灰尘中苯甲酮和苯并三唑类物质的污染水平研究报道较少，呼吸是人体暴露的主要途径之一，了解大气和灰尘中苯甲酮和苯并三唑类物质的含量对于计算人体内此类物质的暴露水平具有重要的参考价值.此外，苯甲酮和苯并三唑类物质在人体内的代谢过程及其对人体健康的危害等问题的研究尚不清晰，此类物质在人体内的健康风险评价研究尚处于起步阶段，未来有必要展开深入系统地研究，以保证人们在日常生活中有效的防范和规避此类物质的暴露.

参考文献（References）

[1] 孙海云，杨叶. 紫外吸收剂及其在皮革化学品上的应用[J]. 皮革与化工，2014，31(5)：10-15.
SUN H Y, YANG Y. The UV absorber and its application in leather chemicals[J]. Leather and Chemicals, 2014, 31(5): 10-15(in Chinese).

[2] 光稳定剂和抗氧化剂确立四大目标[EB/OL]. [2015-6-25]. http://www.fengguangchem.com/html/hydt/20111201/65.html.
Four major targets of light stabilizers and antioxidants[EB/OL]. [2015-6-25]. http://www.fengguangchem.com/html/hydt/20111201/65.html(in Chinese).

[3] 李宇. 可聚合型苯并三唑类紫外线吸收剂的合成[D]. 大连：大连理工大学硕士学位论文，2007.
LI Y. Synthesis of polymerizable benzotriazole ultraviolet stabilizers[D]. Dalian: Master Degree Thesis of Dalian University of Technology, 2007(in Chinese).

[4] JANNA H, SCRIMSHAW M D, WILLIAMS R J, et al. From dishwasher to tap? Xenobiotic substances benzotriazole and tolyltriazole in the environment[J]. Environmental Science & Technology, 2011, 45(9): 3858-3864.

[5] LIU Y S, YING G G, SHAREEF A, et al. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant[J]. Environmental Pollution, 2012, 165: 225-232.

[6] LA FARRE M, PÉREZ S, KANTIANI L, et al. Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment[J]. TrAC Trends in Analytical Chemistry, 2008, 27(11): 991-1007.

[7] SULEJ A M, POLKOWSKA Ż, ASTEL A, et al. Analytical procedures for the determination of fuel combustion products, anti-corrosive compounds, and de-icing compounds in airport runoff water samples[J]. Talanta, 2013, 117: 158-167.

[8] CORNELL J S, PILLARD D A, HERNANDEZ M T. Comparative measures of the toxicity of component chemicals in aircraft deicing fluid[J]. Environmental Toxicology and Chemistry, 2000, 19(6): 1465-1472.

[9] JIA Y, AAGAARD P, BREEDVELD G D. Sorption of triazoles to soil and iron minerals[J]. Chemosphere, 2007, 67(2): 250-258.

[10] VAN LEERDAM J A, HOGENBOOM A C, VAN DER KOOI M M, et al. Determination of polar 1H-benzotriazoles and benzothiazoles in water by solid-phase extraction and liquid chromatography LTQ FT Orbitrap mass spectrometry[J]. International Journal of Mass Spectrometry, 2009, 282(3): 99-107.

[11] WEISS S, JAKOBS J, REEMTSMA T. Discharge of three benzotriazole corrosion inhibitors with municipal wastewater and improvements by membrane bioreactor treatment and ozonation[J]. Environmental Science & Technology, 2006, 40(23): 7193-7199.

[12] SWITZENBAUM M S, VELTMAN S, MERICAS D, et al. Best management practices for airport deicing stormwater[J]. Chemosphere, 2001, 43(8): 1051-1062.

[13] KISS A, FRIES E. Occurrence of benzotriazoles in the rivers Main, Hengstbach, and Hegbach (Germany)[J]. Environmental Science and Pollution Research, 2009, 16(6): 702-710.

[14] WEISS S, REEMTSMA T. Determination of benzotriazole corrosion inhibitors from aqueous environmental samples by liquid chromatography-electrospray ionization-tandem mass spectrometry[J]. Analytical Chemistry, 2005, 77(22): 7415-7420.

[15] SUZUKI T, KITAMURA S, KHOTA R, et al. Estrogenic and antiandrogenic activities of 17 benzophenone derivatives used as UV stabilizers and sunscreens[J]. Toxicology and Applied Pharmacology, 2005, 203(1): 9-17.

[16] ZENKER A, SCHMUTZ H, FENT K. Simultaneous trace determination of nine organic UV-absorbing compounds (UV filters) in environmental samples[J]. Journal of Chromatography A, 2008, 1202(1): 64-74.

[17] DAUGHTON C G, TERNES T A. Pharmaceuticals and personal care products in the environment: Agents of subtle change? [J]. Environmental Health Perspectives, 1999, 107(Suppl 6): 907.

[18] SANTOS A J M, MIRANDA M S, DA SILVA J C E. The degradation products of UV filters in aqueous and chlorinated aqueous solutions [J]. Water Research, 2012, 46(10): 3167-3176.

[19] GAGO-FERRERO P, DÍAZ-CRUZ M S, BARCELÓ D. An overview of UV-absorbing compounds (organic UV filters) in aquatic biota[J]. Analytical and Bioanalytical Chemistry, 2012, 404(9): 2597-2610.

[20] SALVADOR A, CHISVERT A. Sunscreen analysis: A critical survey on UV filters determination[J]. AnalyTica Chimica Acta, 2005, 537 (1): 1-14.

[21] JIMÉNEZ-DÍAZ I, ZAFRA-GÓMEZ A, BALLESTEROS O, et al. Analytical methods for the determination of personal care products in human samples: An overview[J]. Talanta, 2014, 129: 448-458.

[22] BRAUSCH J M, RAND G M. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity[J]. Chemosphere, 2011, 82(11): 1518-1532.

[23] ARUKWE A, EGGEN T, MÖDER M. Solid waste deposits as a significant source of contaminants of emerging concern to the aquatic and terrestrial environments—A developing country case study from Owerri, Nigeria[J]. Science of the Total Environment, 2012, 438: 94-102.

[24] TASHIRO Y, KAMEDA Y. Concentration of organic sun-blocking agents in seawater of beaches and coral reefs of Okinawa Island, Japan [J]. MarinE Pollution Bulletin, 2013, 77(1): 333-340.

[25] DA SILVA C P, EMÍDIO E S, DE MARCHI M R R. Method validation using weighted linear regression models for quantification of UV filters in water samples[J]. Talanta, 2015, 131: 221-227.

[26] LIU Y S, YING G G, SHAREEF A, et al. Simultaneous determination of benzotriazoles and ultraviolet filters in ground water, effluent and biosolid samples using gas chromatography-tandem mass spectrometry[J]. Journal of Chromatography A, 2011, 1218(31): 5328-5335.

[27] Montesdeoca-Esponda S, Sosa-Ferrera Z, Santana-Rodríguez J J. On-line solid-phase extraction coupled to ultra-performance liquid chromatography with tandem mass spectrometry detection for the determination of benzotriazole UV stabilizers in coastal marine and wastewater samples[J]. Analytical and Bioanalytical Chemistry, 2012, 403(3): 867-876.

[28] LIU R, RUAN T, WANG T, et al. Determination of nine benzotriazole UV stabilizers in environmental water samples by automated on-line solid phase extraction coupled with high-performance liquid chromatography-tandem mass spectrometry[J]. Talanta, 2014, 120: 158-166.

[29] LI J, MA L, TANG M, et al. C 12-Ag wire as solid-phase microextraction fiber for determination of benzophenone ultraviolet filters in river water[J]. Journal of Chromatography A, 2013, 1298: 1-8.

[30] WANG L, KANNAN K. Characteristic profiles of benzonphenone-3 and its derivatives in urine of children and adults from the United States and China[J]. Environmental Science & Technology, 2013, 47(21): 12532-12538.

[31] ASIMAKOPOULOS A G, THOMAIDIS N S, KANNAN K. Widespread occurrence of bisphenol A diglycidyl ethers, *p*-hydroxybenzoic acid esters (parabens), benzophenone type-UV filters, triclosan, and triclocarban in human urine from Athens, Greece[J]. Science of the Total Environment, 2014, 470: 1243-1249.

[32] REZAEE M, ASSADI Y, HOSSEINI M R M, et al. Determination of organic compounds in water using dispersive liquid-liquid microextraction[J]. Journal of Chromatography A, 2006, 1116(1): 1-9.

[33] ZHANG T, GUO J-F, BAI L, et al. Retrieval of the extraction solvent by magnetic particles for dispersive liquid-liquid microextraction of UV filters[J]. Journal of Liquid Chromatography & Related Technologies, 2015, 38(1): 104-110.

[34] MONTESDEOCA-ESPONDA S, del Toro-Moreno A, Sosa-Ferrera Z, et al. Development of a sensitive determination method for benzotriazole UV stabilizers in enviromental water samples with stir bar sorption extraction and liquid desorption prior to ultra-high performance liquid chromatography with tandem mass spectrometry[J]. Journal of Separation Science, 2013, 36(13): 2168-2175.

[35] JEON H K, CHUNG Y, RYU J C. Simultaneous determination of benzophenone-type UV filters in water and soil by gas chromatography-mass spectrometry[J]. Journal of Chromatography A, 2006, 1131(1): 192-202.

[36] WANG L, ASIMAKOPOULOS A G, MOON H B, et al. Benzotriazole, benzothiazole, and benzophenone compounds in indoor dust from the United States and East Asian countries[J]. Environmental Science & Technology, 2013, 47(9): 4752-4759.

[37] PENG X, JIN J, WANG C, et al. Multi-target determination of organic ultraviolet absorbents in organism tissues by ultrasonic assisted extraction and ultra-high performance liquid chromatography-tandem mass spectrometry[J]. Journal of Chromatography A, 2015, 1384: 97-106.

[38] RUAN T, LIU R, FU Q, et al. Concentrations and composition profiles of benzotriazole UV stabilizers in municipal sewage sludge in China [J]. Environmental Science & Technology, 2012, 46(4): 2071-2079.

[39] DOMÍNGUEZ C, REYES-CONTRERAS C, BAYONA J M. Determination of benzothiazoles and benzotriazoles by using ionic liquid stationary phases in gas chromatography mass spectrometry. Application to their characterization in wastewaters [J]. Journal of Chromatography A, 2012, 1230: 117-122.

[40] VOUTSA D, HARTMANN P, SCHAFFNER C, et al. Benzotriazoles, alkylphenols and bisphenol A in municipal wastewaters and in the Glatt River, Switzerland[J]. Environmental Science and Pollution Research, 2006, 13(5): 333-341.

[41] JOVER E, MATAMOROS V, BAYONA J M. Characterization of benzothiazoles, benzotriazoles and benzosulfonamides in aqueous matrixes by solid-phase extraction followed by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry[J]. Journal of Chromatography A, 2009, 1216(18): 4013-4019.

[42] PENA M T, VECINO-BELLO X, CASAIS M C, et al. Optimization of a dispersive liquid-liquid microextraction method for the analysis of benzotriazoles and benzothiazoles in water samples[J]. Analytical and Bioanalytical Chemistry, 2012, 402(4): 1679-1695.

[43] CARPINTEIRO I, ABUIN B, RAMIL M, et al. Simultaneous determination of benzotriazole and benzothiazole derivatives in aqueous matrices by mixed-mode solid-phase extraction followed by liquid chromatography-tandem mass spectrometry [J]. Analytical and Bioanalytical Chemistry, 2012, 402(7): 2471-2478.

[44] MCNEILL K, CANCILLA D. Detection of triazole deicing additives in soil samples from airports with low, mid, and large volume aircraft deicing activities[J]. Bulletin of Environmental Contamination and Toxicology, 2009, 82(3): 265-269.

[45] REEMTSMA T. Determination of 2-substituted benzothiazoles of industrial use from water by liquid chromatography/electrospray ionization tandem mass spectrometry[J]. Rapid Communications in Mass Spectrometry, 2000, 14(17): 1612-1618.

[46] POIGER T, BUSER H R, BALMER M E, et al. Occurrence of UV filter compounds from sunscreens in surface waters: regional mass balance in two Swiss lakes[J]. Chemosphere, 2004, 55(7): 951-963.

[47] BALMER M E, BUSER H R, MÜLLER M D, et al. Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes[J]. Environmental Science & Technology, 2005, 39(4): 953-962.

[48] BREEDVELD G D, ROSETH R, SPARREVIK M, et al. Persistence of the de-icing additive benzotriazole at an abandoned airport[J]. Water, Air and Soil Pollution: Focus, 2003, 3(3): 91-101.

[49] GIGER W, SCHAFFNER C, KOHLER H P E. Benzotriazole and tolyltriazole as aquatic contaminants. 1. Input and occurrence in rivers and lakes[J]. Environmental Science & Technology, 2006, 40(23): 7186-7192.

[50] LOOS R, GAWLIK B M, LOCORO G, et al. EU-wide survey of polar organic persistent pollutants in European river waters[J]. Environmental Pollution, 2009, 157(2): 561-568.

[51] LOOS R, LOCORO G, CONTINI S. Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS 2 analysis[J]. Water Research, 2010, 44(7): 2325-2335.

[52] TSUI M M, LEUNG H, WAI T C, et al. Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries[J]. Water Research, 2014, 67: 55-65.

[53] BLASCO C, PICÓ Y. Prospects for combining chemical and biological methods for integrated environmental assessment[J]. TrAC Trends in Analytical Chemistry, 2009, 28(6): 745-757.

[54] CÉSPEDES R, LACORTE S, GINEBREDA A, et al. Chemical monitoring and occurrence of alkylphenols, alkylphenol ethoxylates, alcohol ethoxylates, phthalates and benzothiazoles in sewage treatment plants and receiving waters along the Ter River basin (Catalonia, NE Spain)[J]. Analytical and Bioanalytical Chemistry, 2006, 385(6): 992-1000.

[55] KLOEPFER A, JEKEL M, REEMTSMA T. Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants[J]. Environmental Science & Technology, 2005, 39(10): 3792-3798.

[56] LOOS R, LOCORO G, COMERO S, et al. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water[J]. Water Research, 2010, 44(14): 4115-4126.

[57] MATAMOROS V, JOVER E, BAYONA J. Occurrence and fate of benzothiazoles and benzotriazoles in constructed wetlands[J]. 2010, 61(1): 191-198.

[58] MüLLER A, WEISS S C, BEIßWENGER J, et al. Identification of ozonation by-products of 4-and 5-methyl-1H-benzotriazole during the treatment of surface water to drinking water[J]. Water Research, 2012, 46(3): 679-690.

[59] REEMTSMA T, MIEHE U, DUENNBIER U, et al. Polar pollutants in municipal wastewater and the water cycle: occurrence and removal of benzotriazoles[J]. Water Research, 2010, 44(2): 596-604.

[60] ZHANG Z, REN N, LI Y F, et al. Determination of benzotriazole and benzophenone UV filters in sediment and sewage sludge[J]. Environmental Science & Technology, 2011, 45(9): 3909-3916.

[61] WOLSCHKE H, XIE Z, MÖLLER A, et al. Occurrence, distribution and fluxes of benzotriazoles along the German large river basins into the North Sea[J]. Water Research, 2011, 45(18): 6259-6266.

[62] NAKATA H, MURATA S, FILATREAU J. Occurrence and concentrations of benzotriazole UV stabilizers in marine organisms and sediments from the Ariake Sea, Japan[J]. Environmental Science & Technology, 2009, 43(18): 6920-6926.

[63] REDDY C M, QUINN J G, KING J W. Free and bound benzotriazoles in marine and freshwater sediments[J]. Environmental Science & Technology, 2000, 34(6): 973-979.

[64] KAMEDA Y, KIMURA K, MIYAZAKI M. Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes[J]. Environmental Pollution, 2011, 159(6): 1570-1576.

[65] LIU Q, CHEN Z, WEI D, et al. Acute toxicity formation potential of benzophenone-type UV filters in chlorination disinfection process[J]. Journal of Environmental Sciences, 2014, 26(2): 440-447.

[66] CANCILLA D A, MARTINEZ J, VAN AGGELEN G C. Detection of aircraft deicing/antiicing fluid additives in a perched water monitoring well at an international airport[J]. Environmental Science & Technology, 1998, 32(23): 3834-3835.

[67] SULEJ A M, POLKOWSKA Ż, NAMIEŚNIK J. Pollutants in airport runoff waters[J]. Critical Reviews in environmental Science and Technology, 2012, 42(16): 1691-1734.

[68] CANCILLA D A, BAIRD J C, GEIS S W, et al. Studies of the environmental fate and effect of aircraft deicing fluids: Detection of 5-methyl-1H-benzotriazole in the fathead minnow (*Pimephales promelas*)[J]. Environmental Toxicology and Chemistry, 2003, 22(1): 134-140.

[69] CORSI S R, HARWELL G R, GEIS S W, et al. Impacts of aircraft deicer and anti-icer runoff on receiving waters from Dallas/Fort worth International Airport, Texas, USA[J]. Environmental Toxicology and Chemistry, 2006, 25(11): 2890-2900.

[70] GRANT S B, REKHI N V, PISE N R, et al. A review of the contaminants and toxicity associated with particles in stormwater runoff[J]. Terminology, 2003, 2: 2.

[71] SULEJ A M, POLKOWSKA Ż, NAMIEŚNIK J. Analysis of airport runoff waters[J]. Critical Reviews in Analytical Chemistry, 2011, 41(3): 190-213.

[72] FRENCH H, VAN DER ZEE S, LEIJNSE A. Transport and degradation of propyleneglycol and potassium acetate in the unsaturated zone[J]. Journal of Contaminant Hydrology, 2001, 49(1): 23-48.

[73] STRONG-GUNDERSON J M, WHEELIS S, CARROLL S, et al. Degradation of high concentrations of glycols, antifreeze, and deicing fluids: Oak Ridge National Lab[C]. International in situ and on-site bioreclamation symposium, San Diego, CA, United States, 1995.

[74] SCHAEFER A, RENNER R, THACKER P D. Snowbanks harbor aircraft deicer toxics| News Briefs: Standards for fly ashNew tool to fight mercuryWood-burning's sooty priceGuarding wetlands| Chloramine's effect on lead in drinking water|" Catch-22" makes it tough to get the lead out| Oysters and clams clean up dirty water| Perspective: Hidden ties[J]. Environmental Science & Technology, 2006, 40(10): 3128-3134.

[75] FENT K, CHEW G, LI J, et al. Benzotriazole UV-stabilizers and benzotriazole: Antiandrogenic activity in vitro and activation of aryl hydrocarbon receptor pathway in zebrafish eleuthero-embryos[J]. Science of the Total Environment, 2014, 482: 125-136.

[76] HART D, DAVIS L, ERICKSON L, et al. Sorption and partitioning parameters of benzotriazole compounds[J]. Microchemical Journal, 2004, 77(1): 9-17.

[77] ASIMAKOPOULOS A G, AJIBOLA A, KANNAN K, et al. Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece[J]. Science of the Total Environment, 2013, 452: 163-171.

[78] LIU Y S, YING G G, SHAREEF A, et al. Biodegradation of three selected benzotriazoles under aerobic and anaerobic conditions[J]. Water Research, 2011, 45(16): 5005-5014.

[79] WU J W, CHEN H C, DING W H. Ultrasound-assisted dispersive liquid-liquid microextraction plus simultaneous silylation for rapid determination of salicylate and benzophenone-type ultraviolet filters in aqueous samples[J]. Journal of Chromatography A, 2013, 1302: 20-27.

[80] EMNET P, GAW S, NORTHCOTT G, et al. Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base[J]. Environmental Research, 2015, 136: 331-342.

[81] GRABICOVA K, FEDOROVA G, BURKINA V, et al. Presence of UV filters in surface water and the effects of phenylbenzimidazole sulfonic acid on rainbow trout (*Oncorhynchus mykiss*) following a chronic toxicity test[J]. Ecotoxicology and Environmental Safety, 2013, 96: 41-47.

[82] GAGO-FERRERO P, MASTROIANNI N, DíAZ-CRUZ M S, et al. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry[J]. Journal of Chromatography A, 2013, 1294: 106-116.

[83] AMINE H, GOMEZ E, HALWANI J, et al. UV filters, ethylhexyl methoxycinnamate, octocrylene and ethylhexyl dimethyl PABA from untreated wastewater in sediment from eastern Mediterranean river transition and coastal zones[J]. Marine Pollution Bulletin, 2012, 64(11): 2435-2442.

[84] GAGO-FERRERO P, DíAZ-CRUZ M S, BARCELó D. Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV filters and their degradation products in sediments[J]. Analytical and Bioanalytical Chemistry, 2011, 400(7): 2195-2204.

[85] SáNCHEZ-BRUNETE C, MIGUEL E, ALBERO B, et al. Analysis of salicylate and benzophenone-type UV filters in soils and sediments by simultaneous extraction cleanup and gas chromatography-mass spectrometry[J]. Journal of Chromatography A, 2011, 1218(28): 4291-4298.

[86] BARóN E, GAGO-FERRERO P, GORGA M, et al. Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from South America[J]. Chemosphere, 2013, 92(3): 309-316.

[87] LANGFORD K H, REID M J, FJELD E, et al. Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway[J]. Environment International, 2015, 80: 1-7.

[88] TSAI D Y, CHEN C L, DING W H. Optimization of matrix solid-phase dispersion for the rapid determination of salicylate and benzophenone-type UV absorbing substances in marketed fish[J]. Food Chemistry, 2014, 154: 211-216.

[89] OISHI S. Effects of propyl paraben on the male reproductive system[J]. Food and Chemical Toxicology, 2002, 40(12): 1807-1813.

[90] KANG K S, CHE J H, RYU D Y, et al. Decreased sperm number and motile activity on the F1 offspring maternally exposed to butyl

p-hydroxybenzoic acid (butyl paraben)[J]. Journal of Veterinary Medical Science, 2002, 64(3): 227-235.

[91] WEISBROD C J, KUNZ P Y, ZENKER A K, et al. Effects of the UV filter benzophenone-2 on reproduction in fish[J]. Toxicology and Applied Pharmacology, 2007, 225(3): 255-266.

[92] RHODES M, BUCHER J, PECKHAM J, et al. Carcinogenesis studies of benzophenone in rats and mice[J]. Food and Chemical Toxicology, 2007, 45(5): 843-851.

[93] FENT K, KUNZ P Y, GOMEZ E. UV filters in the aquatic environment induce hormonal effects and affect fertility and reproduction in fish [J]. CHIMIA International Journal for Chemistry, 2008, 62(5): 368-375.

[94] SCHLUMPF M, COTTON B, CONSCIENCE M, et al. In vitro and in vivo estrogenicity of UV screens[J]. Environmental Health Perspectives, 2001, 109(3): 239.

[95] MA R, COTTON B, LICHTENSTEIGER W, et al. UV filters with antagonistic action at androgen receptors in the MDA-kb2 cell transcriptional-activation assay[J]. Toxicological Sciences, 2003, 74(1): 43-50.

[96] SCHREURS R H, SONNEVELD E, JANSEN J H, et al. Interaction of polycyclic musks and UV filters with the estrogen receptor (ER), androgen receptor (AR), and progesterone receptor (PR) in reporter gene bioassays[J]. Toxicological Sciences, 2005, 83(2): 264-272.

[97] JIANG R, ROBERTS M, COLLINS D, et al. Absorption of sunscreens across human skin: an evaluation of commercial products for children and adults[J]. British Journal of Clinical Pharmacology, 1999, 48: 635-637.

[98] MORTELMANS K, HAWORTH S, LAWLOR T, et al. Salmonella mutagenicity tests: Ⅱ. Results from the testing of 270 chemicals[J]. Environmental Mutagenesis, 1986, 8(S7): 56-119.

[99] FLUCK E R, POIRIER L A, RUELIUS H W. Evaluation of a DNA polymerase-deficient mutant of E. coli for the rapid detection of carcinogens[J]. Chemico-biological Interactions, 1976, 15(3): 219-231.

[100] ZEIGER E, ANDERSON B, HAWORTH S, et al. Salmonella mutagenicity tests: Ⅲ. Results from the testing of 255 chemicals[J]. Environmental Mutagenesis, 1987, 9(S9): 61-109.

[101] JEON H K, SARMA S N, KIM Y J, et al. Forward gene mutation assay of seven benzophenone-type UV filters using L5178Y mouse lymphoma cell[J]. Mol Cell Toxicol, 2007, 3(1): 23-30.

[102] HANY J, NAGEL R. Nachweis von UV-filtersubstanzen in muttermilch[J]. Deutsche Lebensmittel-Rundschau, 1995, 91(11): 341-345.

[103] JEON H-K, SARMA S N, KIM Y J, et al. Toxicokinetics and metabolisms of benzophenone-type UV filters in rats[J]. Toxicology, 2008, 248(2): 89-95.

[104] KASICHAYANULA S, HOUSE J D, WANG T, et al. Simultaneous analysis of insect repellent DEET, sunscreen oxybenzone and five relevant metabolites by reversed-phase HPLC with UV detection: Application to an in vivo study in a piglet model[J]. Journal of Chromatography B, 2005, 822(1): 271-277.

[105] NAKAGAWA Y, SUZUKI T. Metabolism of 2-hydroxy-4-methoxybenzophenone in isolated rat hepatocytes and xenoestrogenic effects of its metabolites on MCF-7 human breast cancer cells[J]. Chemico-Biological Interactions, 2002, 139(2): 115-128.

[106] OKEREKE C S, ABDEL-RHAMAN M S, FRIEDMAN M A. Disposition of benzophenone-3 after dermal administration in male rats[J]. Toxicology Letters, 1994, 73(2): 113-122.

[107] KAWAMURA Y, OGAWA Y, NISHIMURA T, et al. Estrogenic activities of UV stabilizers used in food contact plastics and benzophenone derivatives tested by the yeast two-hybrid assay[J]. Journal of Health Science, 2003, 49(3): 205-212.

[108] TAKATORI S, KITAGAWA Y, ODA H, et al. Estrogenicity of metabolites of benzophenone derivatives examined by a yeast two-hybrid assay[J]. Journal of Health Science, 2003, 49(2): 91-98.

[109] MOROHOSHI K, YAMAMOTO H, KAMATA R, et al. Estrogenic activity of 37 components of commercial sunscreen lotions evaluated by *in vitro* assays[J]. Toxicology in Vitro, 2005, 19(4): 457-469.

[110] GAO C-J, LIU L-Y, MA W L, et al. Benzonphenone-type UV filters in urine of Chinese young adults: Concentration, source and exposure[J]. Environmental Pollution, 2015, 203: 1-6.

[111] MANOVá E, VON GOETZ N, HAURI U, et al. Organic UV filters in personal care products in Switzerland: A survey of occurrence and concentrations[J]. International Journal of Hygiene and Environmental Health, 2013, 216(4): 508-514.

[112] ZHANG T, SUN H, QIN X, et al. Benzophenone-type UV filters in urine and blood from children, adults, and pregnant women in China: partitioning between blood and urine as well as maternal and fetal cord blood[J]. Science of the Total Environment, 2013, 461: 49-55.

[113] ASIMAKOPOULOS A G, BLETSOU A A, WU Q, et al. Determination of benzotriazoles and benzothiazoles in human urine by liquid chromatography-tandem mass spectrometry[J]. Analytical Chemistry, 2012, 85(1): 441-448.