

Analytical methods for the determination of persistent ingredients of personal care products in environmental matrices

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Abstract Concern about the environmental fate and potential effects of synthetic organic chemicals used in soaps, lotions, toothpaste, and other personal care products continues to increase. This review describes procedures used for the analysis of five classes of these compounds—synthetic musk fragrances, antimicrobials, ultraviolet filters, insect repellents, and parabens—in water, sediment, sewage sludge, air, and aquatic biota. The primary focus is on sample extraction and preparation methods for these compounds. Instrumental methods commonly used for these compounds are also discussed.

Keywords HHCB · Sunscreen agents · Triclosan · Triclocarban · DEET · Emerging compounds

Introduction

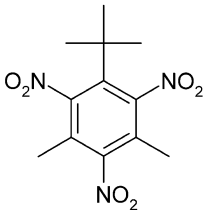
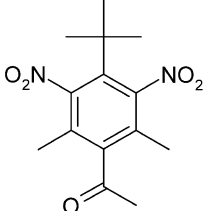
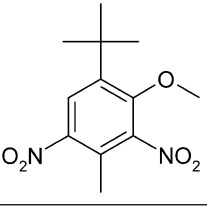
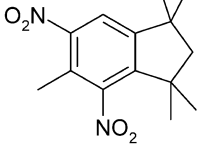
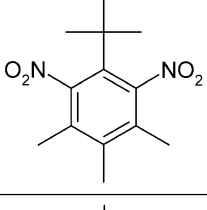
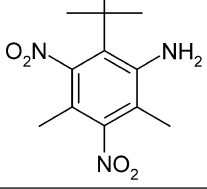
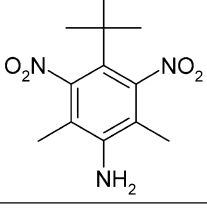
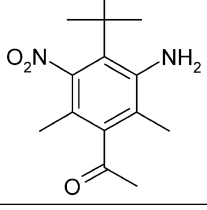
Several personal care product ingredients were among the most commonly detected compounds in the seminal report on organic contaminants in United States' (US) streams published in 2002 by the United States Geological Survey (USGS) [1]. Concern about the environmental fate and potential effects of synthetic organic chemicals used in soaps, lotions, toothpaste, and other personal care products

continues to increase [2–6]. Of particular concern are compounds that are used in large volumes, persist in the environment, bioaccumulate, or have a designed bioactivity. The primary objective of this review is to provide a thorough summary of sample preparation methods published over the last decade (ca. 1995 to 2005) for the routine measurement of five important groups of personal care chemicals in air, water, sediments, aquatic biota, and sewage sludge. These groups are synthetic musk fragrances, antimicrobials, sunscreen agents, insect repellents, and parabens (Tables 1, 2, 3, 4, 5 and 6). Common instrumental analysis techniques are also summarized.

Synthetic musk fragrances are compounds added to scent a variety of personal care products, including deodorant, shampoo, and detergents. There are two types of synthetic musk fragrances: nitro musk fragrances and polycyclic musk fragrances. The nitro musk fragrances were the first to be produced and include musk xylene, musk ketone, musk ambrette, musk moskene, and musk tibetene. In the environment, the nitro substituents can be reduced to form amino metabolites of these compounds. The structures, formula names, CAS registry numbers, and molecular masses of these compounds are listed in Table 1. The polycyclic musk fragrances include 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyrane (HHCB), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI), 5-acetyl-1,1,2,6-tetramethyl-3-*iso*-propylindane (ATII), and 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (DPMI) (structures shown in Table 2). The polycyclic musk fragrances are used in higher quantities than the nitro musk fragrances. HHCB and AHTN are used in the highest quantities and HHCB is on the US Environmental Protection Agency (EPA) High Production Volume (HPV) list [its

Electronic supplementary material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s00216-006-0728-3> and is accessible for authorized users.

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Name	Formula Name	CAS RN	Structure	M.W.
Musk Xylene	2,4,6-trinitro-1,3-dimethyl-5- <i>tert</i> -butylbenzene	81-15-2		297.3
Musk Ketone	4-aceto-3,5-dimethyl-2,6-dinitro- <i>tert</i> -butylbenzene	81-14-1		294.3
Musk Ambrette	4- <i>tert</i> -butyl-3-methoxy-2,6-dinitrotoluene	123-69-3		268.3
Musk Moskene	1,1,3,3,5-pentamethyl-4,6-dinitroindan	116-66-5		278.3
Musk Tibetene	1- <i>tert</i> -butyl-3,4,5-trimethyl-2,6-dinitrobenzene	145-39-1		266.3
2-Amino Musk Xylene	2-amino-4,6-dinitro-1,3-dimethyl-5- <i>tert</i> -butylbenzene	107342-55-2		267.3
4-Amino Musk Xylene	4-amino-2,6-dinitro-1,3-dimethyl-5- <i>tert</i> -butylbenzene	107342-55-6		267.3
2-Amino Musk Ketone	4-aceto-2-amino-3,5-dimethyl-6-nitro- <i>tert</i> -butylbenzene	255393-52-3		264.3

◀ **Table 1** Nitro musk fragrances and metabolites

use and production in the United States is greater than 450,000 kg per year (1 million pounds)]. Recent global usage statistics for these compounds are unavailable. Worldwide production estimates in 1996 for the nitro musk fragrances (mainly musk xylene and musk ketone) and polycyclic musk fragrances (mainly HHCB and AHTN) were 2000 metric tons and 5600 metric tons [7, 8].

The first synthetic musk fragrances detected in the environment were the nitro musk fragrances musk xylene

and musk ketone [9]. The concentrations of these compounds in freshwater fish collected from the Tama River in Tokyo, Japan in 1980 were ≈ 0.2 ng/g and ≈ 0.05 ng/g for musk xylene and musk ketone, respectively. In this first study, an extensive sample extraction and preparation procedure was used followed by analysis using gas chromatography with an electron capture detector (GC-ECD) and gas chromatography with electron impact mass spectrometry (GC/EI-MS). Using similar methods, these compounds were measured for the first time in surface water and wastewater treatment plant effluent, and marine

Table 2 Polycyclic musk fragrances and a metabolite

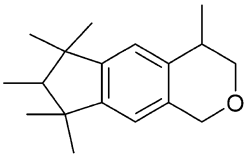
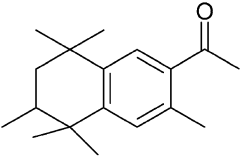
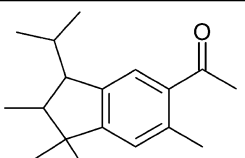
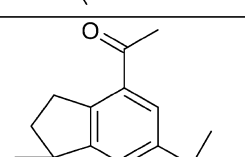
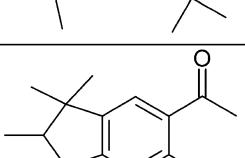
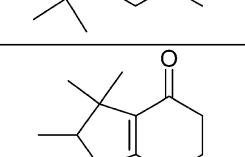
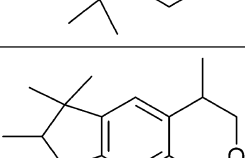
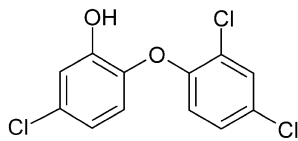
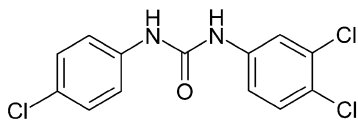
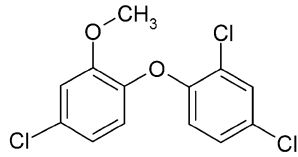
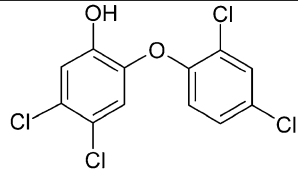
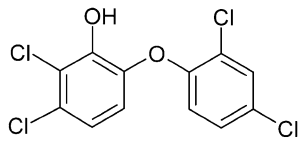
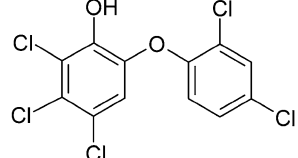
Name (Trade Name)	Formula Name	CAS RN	Structure	M.W.
HHCB (Galaxolide)	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	1222-05-5		258.4
AHTN (Tonalide)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	1506-02-1		258.4
ATII (Traseolide)	5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-indane	68140-48-7		258.4
ADBI (Celestolide)	4-acetyl-1,1-dimethyl-6-tert-butylindane	13171-00-1		244.4
AHMI (Phantolide)	6-acetyl-1,1,2,3,3,5-hexamethylindane	15323-35-0		244.4
DPMI (Cashmeran)	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	33704-61-9		206.3
HHCB-lactone	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[γ]-2-benzopyran-1-one	-		272.4

Table 3 Antimicrobials and metabolites

Name (Trade Name)	Formula Name	CAS RN	Structure	M.W.
Triclosan (e.g., Irgasan DP 300, Microban B)	2,4,4'-trichloro-2'- hydroxydiphenyl ether	3380-34-5		289.5
Triclocarban (e.g., Solubacter)	3,4,4'-trichlorocarbanilide	101-20-2		315.6
Methyl triclosan	2,4,4'-trichloro-2'- methoxydiphenyl ether	4640-01-1		303.6
Tetra(II)closan	2',3,4,4'-tetrachloro-2- hydroxydiphenyl ether	63709-57-9-		324.0
Tetra(III)closan	2',4,4',5-tetrachloro-2- hydroxydiphenyl ether	3380-44-7		324.0
Pentaclosan	2',3,4,4',5-pentachloro-2- hydroxydiphenyl ether	53555-01-4		358.4

shellfish around Tokyo [10]. Rimkus and coworkers have highlighted the published extraction, purification, and analysis methods for musk xylene and musk ketone in fish [11]. In response to reports of a rapid method for the analysis of musk xylene in fish without further purification [12, 13], they stressed the importance of lipid removal prior to analysis by gas chromatography–mass spectrometry (GC/MS). The occurrence and fate of nitro musk fragrances [8] and polycyclic musk fragrances [7, 14] in the aquatic environment has been reviewed recently.

Triclosan and triclocarban (structures shown in Table 3) are antimicrobial compounds used in soap, toothpaste, and other consumer products. The environmentally relevant metabolites of triclosan (methyl triclosan and three chlorinated derivatives) are also included in this review. Kanetoshi and coworkers first identified the potential for

triclosan to form chlorinated products [15]. Triclosan has been measured in human milk samples in Sweden [16] and in environmental matrices in North America and Europe.

Sunscreen agents [ultraviolet (UV) filters] are increasingly added to cosmetics and lotions as protection against harmful UV radiation. These compounds are added to products in relative amounts of 0.1% to 10%. There are currently sixteen different compounds permitted for use as sunscreen agents in the US, fourteen of which are organic compounds [17]. In the European Union, twenty-six different organic compounds are permitted [17]. Several of these compounds show estrogenic activity [18–28]. Salvador and Chisvert recently reviewed methods for the analysis of these compounds in sunscreen cosmetics [29].

Relatively little is known about the occurrence and fate of UV filters in the environment. The hydrophobicity of

Table 4 UV filters (sunscreen agents) and metabolites

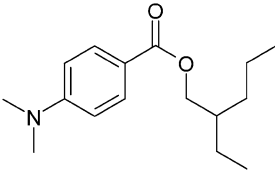
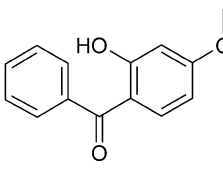
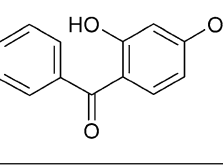
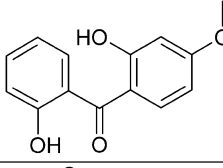
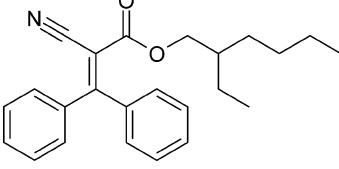
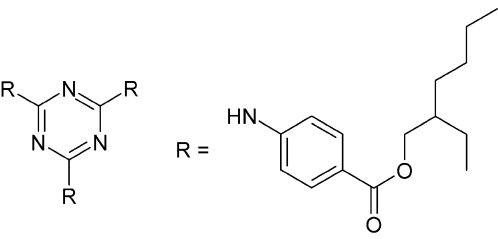
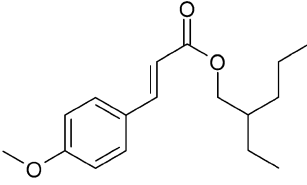
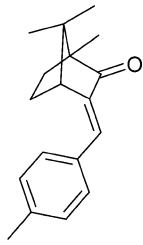
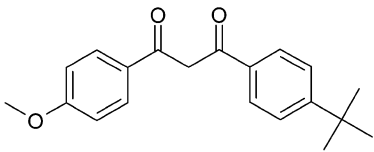
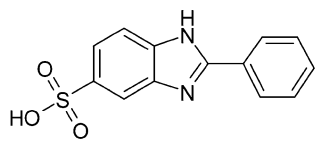
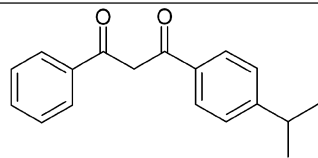
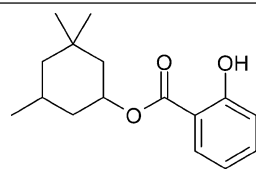
Name [Abbreviation] (Other names, trade names, or notes)	CAS RN(s)	Structure	M.W.
Octyldimethyl- <i>p</i> -aminobenzoic acid [ODPABA] (e.g., Eusolex 6007)	21245-02-3		277.4
Benzophenone-3 [BP-3] (Oxybenzone; e.g., Eusolex 4360)	131-57-7		228.2
2,4-Dihydroxybenzophenone [DHB] (metabolite of benzophenone-3)	131-56-6		214.2
2,2'-Dihydroxy-4-methoxybenzophenone [DHMB] (metabolite of benzophenone-3)	131-53-3		244.2
Octocrylene [OC] (e.g., Eusolex OCR, Uninul 3039)	6197-30-4		361.5
Octyl triazone [OT] (e.g., Uvinul T 150)	88122-99-0 116244-12-3		826.1
Octyl methoxycinnamate [EHMC] (ethylhexyl methoxycinnamate; e.g., Eusolex 2292)	5466-77-3		290.4
4-Methylbenzylidene camphor [4-MBC] (e.g., Eusolex 6300)	36861-47-9		254.4

Table 4 (continued)

Avobenzone [BMDBM] (butyl methoxydibenzoylmethane; e.g., Eusolex 9020)	70356-09-1		310.4
2-Phenylbenzimidazole-5-sulfonic acid [PMDSA] (e.g., Eusolex 232)	27503-81-7		274.3
4-Isopropyl-dibenzoylmethane [4-IDM] (e.g., Eusolex 8020)	63250-25-9		266.3
Homosalate [HS] (3,3,5-trimethylcyclohexyl salicylate; e.g., Eusolex HMS)	118-56-9		262.3

many of these compounds ($\log K_{ow}$ 5–8) indicates the potential for bioaccumulation. Analytical methods for the identification and quantification of ten UV filters and two metabolites shown in Table 4 are reviewed here. The lack of analytical methods for the other UV filters of economic importance is an important limitation on the understanding of the environmental fate of this class of compounds.

Analytical methods for the insect repellents *N,N*-diethyl-*m*-toluamide (DEET, from *N,N*-diethyl-*m*-toluamide) and Bayrepel, and an oxidation product of Bayrepel—Bayrepel-acid—are reviewed (structures shown in Table 5). Of these compounds, the majority of published works is on DEET, which is widely used. An estimated 1.8 million kg was used in the US in 1990 [30]. It is possible that the use of DEET has increased in the US over the last several years due to

Table 5 Insect repellents and a metabolite

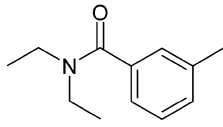
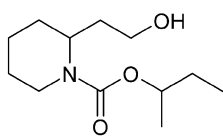
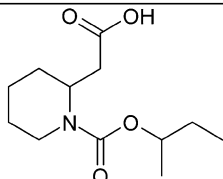
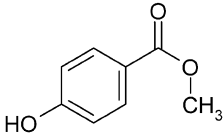
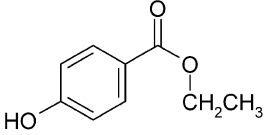
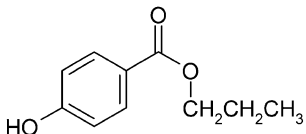
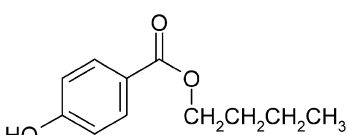
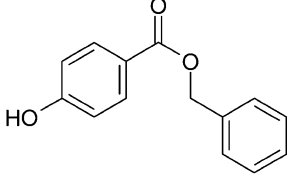
Name (Trade Name)	Formula Name	CAS RN	Structure	M.W.
DEET (e.g., Ultrathon)	<i>N,N</i> -diethyl- <i>m</i> -toluamide	134-62-3		191.3
Bayrepel (e.g., KBR 3023, Bayrepel)	1-methylpropyl 2-(2-hydroxyethyl)-1-piperidinecarboxylate	119515-38-7		229.3
Bayrepel-acid	1-[(1-methylpropoxy)carbonyl]-2-piperidineacetic acid	749864-16-2		243.3

Table 6 Parabens

Name	Formula Name	CAS RN	Structure	M.W.
Methylparaben	4-hydroxybenzoic acid methyl ester	99-76-3		152.2
Ethylparaben	4-hydroxybenzoic acid ethyl ester	120-47-8		166.2
Propylparaben	4-hydroxybenzoic acid propyl ester	94-13-3		180.2
Butylparaben	4-hydroxybenzoic acid butyl ester	94-26-8		194.2
Benzylparaben	4-hydroxybenzoic acid benzyl ester	94-18-8		228.3

concern about the spread of West Nile Virus by mosquitoes. DEET is classified as an indoor, residential-use pesticide by the US EPA. As such, ecological risk assessments are not required. DEET has been detected widely in aquatic systems, but the processes controlling its environmental fate have not been well-studied. From limited toxicity data, DEET is slightly toxic to aquatic invertebrates, fish, and birds [30]. In some places (e.g., Germany) DEET has been phased out. One alternative chemical is Bayrepel.

P-hydroxybenzoic esters (parabens) are the most common preservatives used in personal care products. Parabens are also used as preservatives in pharmaceuticals and food products. This group of compounds includes methylparaben, propylparaben, ethylparaben, butylparaben, and benzylparaben (structures shown in Table 6). Methylparaben and propylparaben are the most widely used parabens and are normally used together due to synergistic preservative effects. Due to their high use and resistance to antimicrobial degradation, it is expected that parabens enter the environment; however, little work has been done

to quantify the distribution and fate of these compounds in the environment. Routledge and coworkers first reported on the estrogenic behavior of parabens in 1998 [31]. The current knowledge about the endocrine activity of these compounds has been summarized recently in two reviews [32, 33]. Parabens have been measured in a variety of consumer products including cosmetics, pharmaceuticals, and food using high-pressure liquid chromatography (HPLC) with UV absorbance detection (HPLC-UV) [34, 35], ion mobility spectrometry [36], and chemiluminescence [37] detection.

General comments on sample preparation methods

Extraction and preparation methods

Several of the sample preparation methods described in here have been reviewed in detail previously. Soxhlet extraction has been a common method for the extraction

of environmental contaminants [38]. The use of pressurized fluid extraction (PFE) for contaminants in environmental and biological matrices has been reviewed recently [39–43]. PFE is also referred to as pressurized liquid extraction (PLE), and by the trade name Accelerated Solvent Extraction (ASE; Dionex; Sunnyvale, CA, USA). Microwave-assisted extraction (MAE) is becoming an important extraction method for environmental samples [44–46]. In addition, there are a variety of solid-phase extraction (SPE) sorbents available for the concentration of contaminants in water. The selection and use of these materials has been reviewed recently [47–49].

Precautions to avoid sample contamination

Due to the ubiquitous use of these compounds, care must be taken to avoid contamination of samples and the laboratory environment. Basic precautions include avoiding the use of products containing these target compounds and the use of gloves for sample handling. Careful cleaning of glassware is important. A typical cleaning procedure involves sonication with a detergent without these chemicals, baking for at least 4 h at 450 °C, and rinsing with acetone and hexane or similar solvents prior to use. High-purity solvents should be used. Also, method blanks should be used to monitor for contamination from the laboratory environment, contaminated solvents, or other sources. The potential for contamination of solvents by musk xylene [50] and UV filters [51, 52] has been discussed.

Synthetic musk fragrances

Sample extraction and preparation

Water

Liquid–liquid extraction (LLE) [1, 53–67], SPE [68–78], solid-phase microextraction (SPME) [79–82], and simultaneous steam-distillation/solvent extraction (SDE) [83] have been used for the analysis of synthetic musk fragrances in various water matrices. These methods are summarized in Table 7.

Filtered and unfiltered wastewater and surface water samples (0.5 L to 100 L) have been extracted using LLE with dichloromethane [1, 56–58], pentane [67], dichloromethane and pentane [61, 62], hexane [55, 59, 60, 63], toluene [65, 66], cyclohexane [82], and petroleum ether [64]. In many instances, particularly for surface water samples, additional extract purification was not performed. The most common purification procedure for these extracts was SPE using silica [64, 67, 82] and alumina [59, 60].

Several SPE sorbents have been used for the analysis of synthetic musk fragrance in water, including C18 [68, 75–78], Absolut NEXUS (Varian; Palo Alto, CA, USA) [73, 74], Bio Beads SM-2 (Bio-Rad Laboratories; Hercules, CA, USA) [71], XAD-2 (Supelco; St. Louis, MO, USA) [72], and XAD-4/XAD-8 [70]. HHCB, AHTN, musk ketone, and musk xylene were among suites of compounds concentrated from water with C18 at ambient pH [75–78] and pH < 3 [68]. Eluents included acetone, dichloromethane and acetone, and dichloromethane and methanol. Polystyrene-divinylbenzene (PS-DVB) copolymers, including XAD-2 [72], XAD-4/XAD-8 [70], and Bio Beads SM-2 [71] have also been used to concentrate synthetic musk fragrances from surface water and wastewater. Large-volume water samples (80–200 L) were used in two of these studies [71, 72]. Absolut NEXUS, a proprietary 1:1 mixture of modified PS-DVB and poly(methyl methacrylate), was also used for the concentration of synthetic musk fragrances and amino metabolites from large-volume (60 L) water samples [73, 74]. Elution from these materials was achieved with hexane/acetone (1:1 VR) [72], methanol and dichloromethane [71], hexane and ethyl acetate [73, 74], and acetone [70]. Some researchers purified extracts prior to analysis using SPE with silica [71–74] and size-exclusion chromatography (SEC) [73, 74].

HHCB, AHTN, ADBI, musk xylene, musk ketone, musk ambrette, musk moskene, and musk tibetene were analyzed in water by direct solid-phase microextraction (DI-SPME) with polydimethylsiloxane (PDMS) (100 μm) [80]. A sorption time of 40 min at room temperature (22 °C) with stirring (1000 rpm) was used. DI-SPME and headspace solid-phase microextraction (HS-SPME) using PDMS (100 μm), PDMS-DVB (65 μm), Carboxen-PDMS (75 μm), and Carbowax-DVB (65 μm ; Supelco) provide adequate recoveries of HHCB, AHTN, ATII, AHMI, ADBI, and DPMI [81]. PDMS-DVB (65 μm) was more efficient than PDMS (30 μm), polyacrylate (PA) (85 μm), and Carboxen-PDMS (75 μm ; Supelco) for DI-SPME of HHCB, AHTN, ADBI, and musk ketone [79]. Using the PDMS-DVB fiber, equilibrium was achieved after 90–120 min at 1250 rpm. Reproducible recoveries were obtained after 45 min with 45–50% recoveries compared to those obtained at equilibrium. Negligible depletion solid-phase microextraction (nd-SPME) [84] was used to measure the dissolved-phase concentration of HHCB and AHTN in wastewater [82].

Semipermeable membrane devices (SPMDs) have been used for passive sampling of synthetic musk fragrances in surface water [70]. The sampling devices were deployed for 3–4 weeks and semiquantitative concentrations were reported (mass/SPMD). HHCB has been sampled from wastewater effluents using another passive, in situ sampler [85] (the polar organic chemical integrative sampler or

Table 7 Analysis of synthetic musk fragrances in water

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
WWTP influent and effluent and surface water	MX, MK, MA, MT, MM, 2-AMX, 4-AMX, 2-AMK	1. Unfiltered sample 2. LLE with Hex 3. Alumina purification 4. Silica purification (WWTP only)	GC-FID GC/EI-MS	SPB 608 NB 54	NR	[59, 60]
Seawater	HHCB, AHTN	1. Unfiltered sample 2. LLE with Pent 3. Dried with sodium sulfate 4. Silica purification	GC/EI- HRMS	MN-52 (25 mm×0.30 mm; 0.50 μm)	66– 87	[67]
Surface water and wastewater	HHCB, AHTN, HHCB-lactone	1. Unfiltered sample 2. LLE with Tol 3. Frozen to remove water	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	75– 100	[65, 66]
Wastewater	All musks (no metabolites)	1. LLE with Hex 2. SEC (Bio Beads SX-3) 3. Silica purification	GC/EI-MS	VR-5MS (30 m×0.25 mm; 0.25 μm)	NR	[63]
Wastewater	HHCB, AHTN	1. Unfiltered sample 2. LLE with CHex 3. Silica purification	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	85– 106	[82]
WWTP influent and effluent	All musks (no metabolites)	1. LLE with PE 2. Dried with sodium sulfate 3. Silica purification	GC/EI-MS GC/NCI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	91– 104	[64]
Activated sludge	All musks and metabolites (except DPMI)	1. Unfiltered sample 2. LLE with Hex 3. SEC (Bio Beads S-X3) 4. Silica purification	GC/MS/M GC/EI-MS GC/NCI-MS GC/PCI-MS	DB-1 (60 m×0.25 mm; 0.25 μm) HP-35MS (30 m×0.25 mm; 0.25 μm)	50– 118	[93, 94]
WWTP effluent	All musks (no metabolites)	1. pH adjusted to 2 2. LLE with DCM	GC/EI-MS	DB-5MS (60 m×0.32 mm; 0.25 μm)	69– 95	[56]
Wastewater, surface water, and drinking water	HHCB, AHTN (and 44 others)	1. Unfiltered sample 2. CLLE with DCM 3. Adjust to pH 2 4. CLLE with DCM	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	NR	[57, 58]
WWTP effluent and surface water	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK	1. SLLE with Pent, DCM, DCM (at pH 2) 2. Dried with sodium sulfate	GC/EI-MS	BPX-5 (30 m×0.25 mm; 0.25 μm)	87– 94	[61, 62]
Surface water	HHCB, AHTN, ADBI, MK, MX	1. LLE with hexane 2. Dried with sodium sulfate 3. Sulfur removed with copper	GC-ECD GC/EI-MS	DB-5 and DB-1701 HT-8	>70	[55]
Leachate from soil/sludge mesocosm studies	HHCB, AHTN DPMI, MX, MK	1. SPE (C18) 2. Eluent: Acet, DCM (sequential)	GC/EI-MS	DB-1701 (30 m×0.25 mm; 0.25 μm)	43– 86	[76]
WWTP influent and effluent	HHCB, AHTN, MX, MK	1. SPE (C18) 2. Eluent: DCM	GC/EI-MS	DB-5MS (30 m×0.25 mm)	79– 143	[77]
Surface water	HHCB, AHTN	1. SPE (C18)	GC/EI-MS	DB-1701	NR	[75]

Table 7 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Groundwater	HHCB, AHTN	2. Eluent: DCM, MeOH (sequential) 1. SPE (C18) 2. Eluent: Acet/Hex (3:17 VR) 3. Silica purification	GC/EI-MS	(30 m×0.25 mm; 0.25 μm) XTI-5 (30 m×0.25 mm; 0.25 μm)	78–82	[89]
WWTP effluent	All musks, 2-AMX, 4-AMX, 2-AMK	1. SPE (Absolut NEXUS) 2. Eluent: EtAc, Hex (sequential) 3. SEC (Envirogel) 4. Silica purification	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	80–97	[73, 74]
Surface water	HHCB, AHTN, ATIL, ADBI, AHMI, DPMI, MX, MK	1. SPE (XAD-2) 2. Resin Soxhlet extracted with Acet/Hex (1:1 VR) 3. Silica purification	GC/EI-MS HP-5MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	NR	[72]
Surface water and wastewater	HHCB, AHTN	1. Unfiltered samples 2. SPE (Bio Beads SM-2) 3. Eluent: MeOH, DCM (sequential) 4. Silica purification	GC/EI-MS	DB-1 (25 m×0.32 mm; 0.25 μm)	81–141	[71]
WWTP effluent	Polycyclic musks	1. HS-SPME (PDMS, PDMS-DVB, CAR-PDMS, or CW-DVB)	GC/EI-MS	VA-5MS (25 m×0.25 mm; 0.25 μm)	NR	[81]
Surface water	HHCB, AHTN, ADBI, MX, MK, MA, MT, MM	1. Unfiltered 2. DS-SPME (PDMS)	GC/EI-MS	HP-5 (25 m × 0.2 mm; 0.33 μm)	NR	[80]
WWTP effluent	Polycyclic musks	1. DS-SPME (PDMS, PDMS-DVB, CAR-PDMS, or CW-DVB)	GC/EI-MS	VA-5MS (25 m× >0.25 mm; 0.25 μm)	NR	[81]
Surface water	HHCB, AHTN, ADBI, MK	1. DS-SPME (PDMS, PDMS-DVB, PA)	GC/EI-MS	HT-8 (25 m×0.22 mm; 0.25 μm)	≤82	[79]
WWTP effluent and surface water	HHCB, AHTN, ATIL, ADBI, AHMI	1. SDE	GC/EI-MS	DB-XLB (30 m×0.25 mm; 0.25 μm)	82–101	[83]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

POCIS [86–88]). These devices were deployed for 54 days followed by recovery of target compounds with methanol and methanol/toluene/dichloromethane (1:1:8 VR).

Sludge

Extraction of synthetic musk fragrances from activated and digested sludge has been accomplished by PFE [63, 64, 76, 77, 89], supercritical fluid extraction (SFE) [64], sonication [89], Soxhlet extraction [65, 66, 90, 91], and LLE [92–94]. HS-SPME has also been used for the determination of synthetic musk fragrances in wet and dry sludge [95]. These methods are summarized in Table 8.

HHCB, AHTN, musk xylene, and musk ketone were among sixteen fragrance chemicals extracted from activated sludge by PFE with dichloromethane [77]. The extraction cells were packed with activated silica at the cell outlet for initial extract purification. The remaining cell volume was packed with a mixture of sludge solids and diatomaceous earth (30–40% mass fraction). The resulting extract was purified using silica columns with elution with dichloromethane. This method was used later for the determination of HHCB, AHTN, musk xylene, musk ketone, and eighteen other fragrance compounds in sludge and sludge-amended soil with minor alterations [76]. All synthetic musk fragrances were extracted from wastewater treatment plant

Table 8 Analysis of synthetic musk fragrances in WWTP sludge, sediments, soil, and dust

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Digested sludge	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK, MA, MM, MT	1. Dried with sodium sulfate 2. Soxhlet extraction with DCM 3. Sulfur removed with copper in flask during extraction 4. Silica/alumina purification (layered) 5. SEC (Bio Beads S-X3) 6. Silica/alumina purification (layered)	GC/EI-MS	HP-5MS (30 m×0.25 mm)	NR	[91]
Finished sludge	HHCB, AHTN, ATII, ADBI, AHMI, DPMI	1. Soxhlet extraction with DCM 2. Sulfur removed with copper in flask during extraction 3. Silica/alumina purification (layered) 4. Silica/alumina purification (layered)	GC/EI-MS	HP-5 (30 m×0.32 mm; 0.25 μm)	58– 109	[90]
Digested sludge	HHCB, AHTN	1. Sample freeze-dried 2. Soxhlet extracted with EtAc 3. Silica purification 4. SEC (Bio Beads SX-3)	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	76– 100	[66]
Activated and digested sludge	HHCB, AHTN	1. Ultrasonic extraction with MeOH and Acet (successive) 2. Extract dissolved in 150 mL H ₂ O 3. SPE (C18) 4. Silica purification	GC/EI-MS	XTI-5 (30 m×0.25 mm; 0.25 μm)	64– 87	[89]
Finished sludge	HHCB, AHTN, ATII, ADBI, AHMI, HHCB-lactone	1. Wet sludge extracted with Hex by stirring 2. Filtered (0.2 μm)	GC/EI-MS	HT-8 (50 m×0.22 mm; 0.25 μm)	79– 108	[92]
Sludge	All musks	1. Air-dried 2. Mixed with celite 3. SFE with Acet/DCM (1:1 VR) 4. Silica purification 5. Sulfur removed with copper	GC/EI-MS GC/NCI-MS	HP-5MS (30 m×0.25 m; 0.25 μm)	87– 97	[64]
Sludge	All musks	1. Air-dried 2. PFE with Acet/Hex (1:1 VR) 3. Silica purification 4. Sulfur removed with copper	GC/EI-MS GC/NCI-MS	HP-5MS (30 m×0.25 m; 0.25 μm)	NR	[64]
WWTP influent solids and activated sludge	HHCB, AHTN, MX, MK	1. Dried with diatomaceous earth 2. PFE with DCM 3. Silica purification at outlet of PFE cell 4. Silica purification	GC/EI-MS	DB-5MS (30 m×0.25 mm)	68– 91	[77]

Table 8 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Finished sludge	All musks (no metabolites)	1. Dried with sodium sulfate 2. PFE with Hex/EtAc (1:1 VR) 3. SEC (Bio Beads SX-3) 4. Silica purification	GC/EI-MS	VR-5MS (30 m×0.25 mm; 0.25 μm)	NR	[63]
Soil amended with finished sludge	HHCB, AHTN, DPMI, MX, MK	1. Dried with diatomaceous earth 2. PFE with DCM 3. Silica purification at outlet of PFE cell	GC/EI-MS	DB-1701 (30 m×0.25 mm; 0.25 μm)	73–91	[76]
Activated and digested sludge	HHCB, AHTN	1. PFE with MeOH 2. Extract dissolved in 1 L H ₂ O 3. SPE (C18) 4. Silica purification	GC/EI-MS	XTI-5 (30 m×0.25 mm; 0.25 μm)	78–109	[89]
Sediment	AHTN, HHCB (and 59 others)	1. PFE with H ₂ O/iPrOH (1:1 VR) 2. PFE with H ₂ O/iPrOH (1:1 VR) 3. Extracts diluted with phosphate buffer (pH 7) 4. SPE (PS-DVB) 5. Eluent: DCM/DE (4:1 VR) 6. Extract passed through Florisil/sodium sulfate (1:4 MF) column	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.50 μm)	77–84	[100]
Suspended sediment	HHCB, AHTN, ADBI, MK, MX	1. Particulate collected with flow through centrifuge 2. Soxhlet extracted with DCM 3. Silica purification 4. Sulfur removed with copper	GC-ECD GC/EI-MS	DB-5 and DB-1701 HT-8	NR	[55]
Suspended sediment	HHCB, AHTN, ADBI, AHMI	1. Particulate collected with flow through centrifuge 2. Dispersion-extraction with Acet, Hex 3. Dried with sodium sulfate 4. Sulfur removed with copper	GC/EI-MS	BPX-5 (30 m×0.25 mm; 0.25 μm)	43–49	[62]
Suspended sediment	HHCB, AHTN	1. Particulate collected on GFF 2. Ultrasonic extraction with DCM, MeOH (sequential)	GC/EI-MS	DB-1701 (30 m×0.25 mm; 0.25 μm)	NR	[75]
Suspended sediment	HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK	1. Particulate collected on GFF 2. GFF Soxhlet extracted with Acet/Hex (1:1 VR) 3. Silica purification	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	NR	[72]
Surficial sediments	HHCB, AHTN, ATII, ADBI, AHMI	1. Sample suspended in 600 mL H ₂ O 2. SDE 3. Sulfur removed with copper	GC/EI-MS	DB-XLB (30 m×0.25 mm; 0.25 μm)	78–96	[83]

Table 8 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Sludge	HHCB, AHTN, ATII, ADBI, AHMI, MX, MK, MM, MT	1. Mixed with water 2. HS-SPME (PA, PDMS, CAR-PDMS, CW-DVB)	GC/EI-MS	VA-5MS (25 m×0.25 mm; 0.25 μm)	NR	[95]
House dust	HHCB, AHTN, ATII, ADBI, AHMI, MK	1. PFE with Hex/DE (19:1 VR)	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	91– 100	[110]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

solids by PFE with hexane/ethyl acetate (1:1 VR) [63]. The resulting extracts were purified by SEC with a Bio Beads S-X column (Bio-Rad Laboratories; Hercules, CA, USA) and hexane/ethyl acetate (1:1 VR) mobile phase. Following SEC, extracts were loaded onto activated silica columns and eluted with ethyl acetate and acetone. All synthetic musk fragrances were extracted by PFE from freeze-dried sludge mixed with sand using acetone/hexane (1:1 VR) [64]. These authors also extracted freeze-dried samples by supercritical fluid extraction using supercritical CO₂. Extracts using both methods were purified using 5% deactivated silica columns. When necessary, sulfur was removed by shaking with activated copper or mercury. AHTN and HHCB were extracted by PFE from freeze-dried sludge samples mixed with quartz sand with methanol [89]. These authors also extracted freeze-dried sludge samples by sonication with methanol and acetone. Sample extracts resulting from both methods were dissolved in water and passed through C18 cartridges. AHTN and HHCB were eluted with methanol. The extracts were further purified using 1.5% deactivated silica columns with elution using hexane/acetone (17:3 VR). This method was also used for the determination of these compounds in 1 L water samples.

HHCB, AHTN, ATII, ADBI, and AHMI were extracted with a suite of polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polychlorinated alkanes (PCAs), and polycyclic aromatic hydrocarbons (PAHs) by Soxhlet extraction with dichloromethane [91]. Sulfur was removed with activated copper added to the Soxhlet collection flask. Extracts were purified using columns packed with 1% deactivated alumina and 5% deactivated silica with elution with dichloromethane/pentane (1:1 VR). Similar methods have been used for the extraction of these compounds and DPMI [90]. Sludge from anaerobic digesters has been Soxhlet-extracted with ethyl acetate for the analysis of HHCB and AHTN [66]. Extracts were purified using silica cartridges and SEC with a Bio Beads SX-3 column.

Liquid sludge samples have been extracted with hexane for the analysis of nitro musk fragrances and their amino metabolites [93, 94] and the polycyclic musk fragrances and HHCB-lactone [92]. Purification for the nitro musk fragrances and amino musk metabolites consisted of SEC with a Bio Beads SC-3 column and cyclohexane/ethyl acetate mobile phase (1:1 VR) followed by a silica column with elution with dichloromethane [93, 94]. For analysis of the polycyclic musk fragrances the extracts were filtered prior to analysis [92]. These methods could be used for the analysis of these compounds in whole water samples with minimal alteration.

Headspace SPME with PA (85 μm), PDMS (100 μm), PDMS-DVB (75 μm), Carboxen-PDMS (75 μm), and Carbowax-PDMS (65 μm) was used for the determination of HHCB, AHTN, ATII, AHMI, ADBI, musk xylene, musk ketone, musk tibetene, and musk moskene from solid and liquid sludge samples [95]. Headspace sampling times of 15 min at 100 °C provided reproducible results with all fibers. The PDMS-DVB fiber provided the lowest detection limits for all compounds. The photodegradation kinetics of musk xylene, musk ketone, musk tibetene, and musk moskene were studied using SPME [96].

Surficial and suspended sediments

Synthetic musk fragrances have been Soxhlet-extracted from suspended sediments collected from surface water using dichloromethane [55, 75] and hexane/acetone [72]. HHCB, AHTN, AHMI, and ADBI were measured in surficial and suspended sediment collected from river water and banks as part of a screening study of organic contaminants in the German Bight [62, 97, 98]. These samples were dispersion-extracted sequentially with acetone, acetone/hexane (1:1 VR), and hexane. HHCB, AHTN, ADBI, musk xylene, and musk ketone were Soxhlet-extracted from surficial sediment with toluene [99]. HHCB, AHTN, ATII, AHMI, and ADBI were

Table 9 Analysis of synthetic musk fragrances in aquatic biota

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Various biota including lobster, fish and bivalves	HHCB, AHTN, MX, MK, 2AMX, 4AMX, 2AMK	1. Dried with sodium sulfate 2. Soxhlet extraction with Hex/Acet (9:1 VR) 3. SEC 4. Silica purification	GC/EI-MS	DB-5 (20 m×0.25 mm; 0.25 μm)	66–85	[105]
Eel muscle tissue	HHCB, AHTN, ATII, ADBI, AHMI	1. Dried with sodium sulfate 2. Soxhlet extraction with EtAc/CHex (50.4:49.6 VR) 3. SEC (Bio Beads S-X3) 4. Silica purification	GC/EI-MS	DB-XLB (30 m×0.25 mm; 0.25 μm)	78–95	[83, 99]
Fish and mammal tissue	HHCB, AHTN	1. Dried with sodium sulfate 2. Soxhlet extraction with DCM/Hex (3:1 VR) 3. SEC (Bio Beads S-X3) 4. Silica purification	GC/EI-MS	DB-5 (30 m×0.25 mm)	85–98	[103]
Eel muscle tissue	MX, MK	1. Dried with sodium sulfate 2. Soxhlet extraction with EtAc/CHex (50.4:49.6 VR) 3. SEC (Bio Beads S-X3) 4. Silica purification	GC-ECD	HP-1 and HP-5 (50 m×0.20 mm; 0.50 μm)	NR	[99]
Marine mammal and shark tissue	HHCB, AHTN, MX, MK, MA	1. Dried with sodium sulfate 2. Soxhlet extraction with DCM/Hex (8:1 VR) 3. SEC (Bio Beads S-X3) 4. Silica purification	GC/EI-MS	DB-1 (30 m×0.25 mm; 0.25 μm)	92–108	[104]
Fish	HHCB, AHTN, HHCB-lactone, MX, MK	1. Dried with sodium sulfate 2. Homogenized with iPrOH, Hex (sequential) 3. SEC (Bio Beads S-X3) 4. Silica purification	GC/EI-MS GC/NCI-MS	DB-5MS (30 m×0.25 mm; 0.20 μm)	NR	[101]
Fish	All musks	1. Dried with sodium sulfate 2. Homogenized with Acet/Pent (1:3 VR) 3. SEC (Bio Beads S-X3) 4. Florisil purification (some samples)	GC/EI- HRMS GC/ EI-MS GC- ECD	DB-5MS (30 m×0.25 mm) HP-5 (30 m×0.25 mm) DB-17 (60 m) and Sil-5CB (50 m)	70–97	[102]
Fish	All musks and 2-AMX, 4-AMX, 2-AMK	1. Homogenized tissue mixed with water, sodium sulfate, and NaOH 2. Closed-loop stripping with musk collection on Absolut NEXUS 3. Analytes eluted with EtAc, Hex (sequential)	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	2–32	[73, 108]
Fish	All musks and 2-AMX, 4-AMX,	1. Dried with diatomaceous earth	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	88–110	[73, 108]

Table 9 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
	2-AMK	2. PFE with Hex/EtAc (1:5 VR) 3. Alumina purification at outlet of PFE cell 4. SEC (Envirogel) 5. Alumina/Strata NH ₂ purification				
Fish mussels, shrimp	MX, MK, MA, MM, MT	1. Extracted with water/Acet/PE 2. SEC 3. Silica purification	GC-ECD	DB-5 (60 m×0.25 mm; 0.25 μm) DB-1701 (60 m×0.25 mm; 0.25 μm)	NR	[106, 107]
Freshwater fish	HHCB, AHTN, ATII, ADBI, AHMI	1. Dried with diatomaceous earth 2. PFE with Hex/EtAc (5:1 VR) 3. Alumina purification at outlet of PFE cell	GC/EI-MS	Supelcowax 10 (30 m×0.20 mm; 0.20 μm)	105	[109]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

extracted from freeze-dried surficial sediment using SDE [83]. HHCB and AHTN and 59 other compounds were extracted from wet sediment by PFE with water/isopropanol

(1:1 VR) followed by water/isopropanol (1:4 VR) [100].

Suspended and surficial sediment extracts have been purified by SPE using silica [55, 62, 72, 97–99], Oasis

Table 10 Analysis of synthetic musk fragrances in air

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Indoor and outdoor air	HHCB, AHTN, ATII, MX, MK	1. Particulate collected on GFF 2. Gas phase collected on PUF 3. GFF or PUF Soxhlet extracted with Hex/DE (9:1 VR) 4. Silica purification	GC/EI-MS GC/NCI-MS	DB-5MS (30 m×0.25 mm; 0.2 μm) Ultra 2 (25 m×0.2 mm; 0.11 μm)	NR	[111, 112]
Outdoor air	HHCB, AHTN, ATII, ADBI, AHMI, DPML, MX, MK	1. Particulate collected on GFF 2. Gas phase collected on XAD-2 3. GFF or XAD-2 Soxhlet extracted with Acet/Hex (1:1 VR) 4. Silica purification	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	NR	[72]
Indoor air	HHCB, AHTN, ATII, ADBI, AHMI, MK	1. Collected on PUF 2. PFE with Hex/DE (19:1 VR)	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	91–100	[110]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

Table 11 Methods for antimicrobials in various water matrices

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Surface water and WWTP effluent	Triclosan and methyl triclosan	1. LLE with Tol 2. Residual water removed by freezing	GC/EI-MS	DB-5MS (15 m×0.25 mm)	88–100	[116, 117]
WWTP influent and effluent	Triclosan (and 3 others)	1. Acidified to pH 2 2. LLE with DCM 3. Frozen to remove water 4. Filtered 5. Derivatized with diazomethane	GC/EI-MS	DB-5MS (60 m×0.32 mm; 0.25 μm)	138	[56]
Wastewater, surface water, and drinking water	Triclosan (and 45 others)	Unfiltered sample CLLE with DCM at ambient pH, pH 2 (sequential)	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	NR	[1, 57, 58]
River and sea water	Triclosan, tetra(II)closan, tetra(III)closan, and pentaclosan	1. pH adjusted to >13 and washed with Hex (river water only) 2. Acidified to pH 2-3 3. LLE with Hex 4. Derivatized with diazomethane	GC/EI-MS	Ultra-2 (30 m×0.25 mm; 0.25 μm)	74–119	[118]
Surface water, treated water, and stormwater	Triclosan (and eight others)	1. Acidified to pH 2 2. SPE (SDB-XC Empore disk) 3. Eluent: MeOH, DCM, MeOH (sequential) 4. Silica purification 5. Derivatized with BSTFA	GC/EI-MS	DB-5MS (25 m×0.25 mm; 0.25 μm)	60	[122, 123]
WWTP effluent	Triclosan (and biphenylol)	1. Acidified to pH 4 2. SPE (Sep-Pak C18 or Isolute Env+ or Oasis HLB) 3. Eluent: MeOH, Acet (sequential)	LC/MS/MS ESI (-)Ion trap	XTerra MS C ₈ (100 mm×2.1 mm; 3.5 μm)	84 (C18) 69 (Env+) 68 (Oasis)	[120]
WWTP effluent	Triclosan (and biphenylol)	1. Acidified to pH 4 2. SPE (Sep-Pak C18 or Isolute Env+ or Oasis HLB) 3. Eluent: MeOH, Acet (sequential)	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	84 (C18) 69 (Env+) 68 (Oasis)	[120]
WWTP effluent	Triclosan (and biphenylol)	1. Acidified to pH 4 2. SPE (Sep-Pak C18 or Isolute Env+ or Oasis HLB) 3. Eluent: MeOH, Acet (sequential)	GC/NCI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	84 (C18)69 (Env+) 68 (Oasis)	[120]
Surface water and WWTP effluent	Triclosan	1. Acidified to pH 3 2. SPE (Oasis HLB) 3. Eluent: EtAc/Acet (1:1 VR) 4. Derivatized with diazomethane	GC/EI-MS	RTX-5MS (30 m×0.25 mm; 0.25 μm)	105	[128–130]
Surface water	Triclosan (and 26 others)	1. Adjusted to pH 2 2. SPE (Oasis HLB) 3. Eluent: MeOH/MTBE (1:9 VR), MeOH (sequential)	LC/ESI-MS/MS	Synergi Max-RP C12 (250 mm×4.6 mm; 4 μm)	79	[135]

Table 11 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Wastewater and seawater	Triclosan (and 13 others)	1. pH adjusted to 7 2. SPE (Oasis HLB) 3. Eluent: Hex, EtAc, MeOH (sequential) 4. Eluted in MeOH 5. Derivatized with MCF	GC/EI-MS	HP5-MS (30 m×0.25 mm; 0.25 μm)	66	[136, 137]
Wastewater and surface water	Triclosan (and seven others)	1. pH adjusted to 7 2. SPE (Oasis HLB) 3. Eluent: EtAc 4. Derivatized with BSTFA	GC/EI-MS	Factor Four-5MS (30 m×0.25 mm; 0.25 μm)	89	[132, 133]
WWTP influent and effluent	Triclosan (and 11 others)	1. Acidified with HCl 2. SPE (Oasis HLB) 3. Eluent: MeOH 4. Derivatized with 1 % TMCS in BSTFA	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	82–89	[126]
Wastewater and surface water	Triclosan (and 14 others)	1. Acidified to pH 2-2.5 2. SPE (Oasis HLB) 3. Eluent: MeOH	LC/ESI-MS/MS	Luna Phenyl-Hexyl (150 mm×2 mm; 3 μm)	43–53	[134]
Wastewater	Triclosan (and dioxins)	1. SPE (Oasis HLB) 2. Eluent: MeOH	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	80	[131]
River water and wastewater	Triclosan (and other chlorophenols)	1. Acidified to pH 2-2.5 2. SPE (Oasis HLB) 3. Eluent: EtAc 4. Silica purification (EtAc) 5. Derivatized with MTBSTFA	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	88–102	[127]
WWTP influent and effluent, raw and finished drinking water, and surface water	Triclocarban	1. SPE (Oasis HLB) 2. Eluent: 10 mmol/L acetic acid in MeOH/Acet (1:1 VR) 3. Filtered	LC/ESI-MS	Ultra IBD (150 mm×2.1 mm; 5 μm)	95–103	[141, 142]
WWTP influent and effluent	Triclosan (10 others)	1. SPE (Oasis MAX) 2. Eluent: MeOH, 2 % formic acid in MeOH (sequential, triclosan eluted in acidic fraction) 3. Compounds were derivatized with 1 % TBDMSCI in MTB-STFA	GC/MS	RTX-5Sil MS (30 m×0.25 mm; 0.25 μm)	87–99	[121]
Surface water	Triclocarban (and sulcofuron and flucofuron)	1. SPE (C18) 2. Eluent: MeOH	LC/ESI-MS/MS	HiChrom HiRPB (250 mm×2.1 mm; 5 μm)	86.3 (pH 7) 50.7 (pH 2)	[140]
Wastewater influent and effluent and surface water	Triclosan (and acidic pharmaceuticals)	1. Acidified to pH< 3 2. SPE (C18) 3. Eluent: Acet 4. Derivatized with MCF	GC/EI-MS	ZB-5 (30 m×0.25 mm; 0.25 μm)	NR	[68, 69]
Wastewater	Triclosan, methyl triclosan, tetra(II) closan, tetra(III) closan, and pentaclosan	1. Acidified to pH<2 and mixed with EtOH 2. SPE (C18 mixed with Florisil; 2:1 MF) 3. Eluent: MeOH, DCM, MeOH (sequential)	GC/EI-MS	DB-5 type (30 m×0.25 mm; 0.25 μm)	65–108	[119]

Table 11 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Surface water	Triclosan and methyl triclosan	4. Silica purification 5. Derivatized with TMSDEA 1. Acidified to pH 2 2. SPE (Bio Beads SM-2) 3. Eluent: MeOH/DCM 4. Derivatized with diazoethane	GC/EI-MS	DB-5 (25 m×0.32 mm)	50–90	[124, 125]
Surface water	Triclosan and methyl triclosan (and 429 others)	1. 80 L unfiltered water sample extracted with XAD-4 and XAD-8 2. XAD-4 and XAD-8 extracted with Acet 3. Acet extract dissolved in water 4. Water extracted with DCM	GC-AED/MS	HP-5MS (24 m×0.25 mm; 0.25 μm)	NR	[70]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

HLB (Waters; Milford, MA, USA) [100], and Florisil (US Silica Company; Berkeley Springs, WV, USA) [100]. Copper has been used to remove sulfur from sediment extracts [55, 83].

Aquatic biota

Synthetic musk fragrances have been extracted from aquatic biota by dispersion–extraction [101, 102], Soxhlet extraction [83, 99, 103–105], cold extraction [106, 107], PFE [73, 108, 109], and closed-loop stripping [73, 108]. These methods are summarized in Table 9.

HHCB, AHTN, ATII, musk xylene, musk ketone, and HHCB-lactone were extracted from fish tissue by dispersion–extraction. Fish tissue was mixed with sodium sulfate and sequentially homogenized with isopropanol and hexane [101]. All synthetic musk fragrances were similarly extracted from fish tissue using ethyl acetate/cyclohexane (1:1 VR) or acetone/pentane (1:3 VR) [102].

A variety of solvent systems have been used for the extraction of synthetic musk fragrances from homogenized biota with a Soxhlet apparatus. Tissue homogenate mixed with sodium sulfate have been extracted with hexane/acetone (9:1 VR) [105], dichloromethane/hexane (3:1 VR) [103], dichloromethane/hexane (8:1 VR) [104], and cyclohexane/ethyl acetate (98.5:100 VR) [83, 99] for 2.5–12 h. Musk xylene, musk ketone, musk ambrette, musk moskene, and musk tibetene were cold-extracted from homogenized fish, mussels, and shrimp with water/acetone/petroleum ether [106, 107].

Fish muscle tissue homogenate was mixed with diatomaceous earth and extracted using PFE with ethyl acetate/hexane (1:5 VR) for the analysis of the polycyclic musk fragrances [109]. Prior to extraction, the PFE cell was packed with the dried fish homogenate and deactivated alumina at the outlet to remove lipids. Additional lipid removal and extract purification was not necessary. This PFE method was later used for the extraction of all synthetic musk fragrances and 2-amino musk ketone, 2-amino musk xylene, and 4-amino musk xylene with ethyl acetate/hexane (5:1 VR) [73, 108]. The higher polarity solvent was likely necessary due to the higher polarity of the nitro musk fragrances and amino musk metabolites relative to the polycyclic musk fragrances. Due to this change in solvent, additional removal of lipids was necessary.

A closed-loop stripping system was developed for the analysis of all synthetic musk fragrances and 2-amino musk ketone, 2-amino musk xylene, and 4-amino musk xylene in fish tissue [73, 108]. A mixture of fish tissue homogenate, water, sodium sulfate, and sodium hydroxide was continually mixed at 50 °C in a closed system for 24 h. Nitrogen was pumped through the system and the target compounds were collected on Absolut NEXUS sorbent in the exhaust gas. The synthetic musk fragrances and amino musk metabolites were recovered from the sorbent with 25 mL ethyl acetate and 25 mL hexane. The recoveries using this system were low (2–32%) but reproducible.

Typically, lipids are removed from extracts by SEC. Lipids cannot be removed destructively with sulfuric acid for the determination of nitro musk fragrances due to the

Table 12 Methods for antimicrobials in sediment, sludge, and aquatic biota

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Marine sediment	Triclosan (and biphenylol)	1. Dried with diatomaceous earth 2. PFE extraction with DCM 3. Silica purification	LC/MS/ MS ESI(-) Ion trap	XTerra MS C ₈ (100 mm × 2.1 mm; 3.5 μm)	100	[120]
Marine sediment	Triclosan (and biphenylol)	1. Dried with diatomaceous earth 2. PFE extraction with DCM 3. Silica purification	GC/EI-MS	HP-5MS (30 m × 0.25 mm; 0.25 μm)	100	[120]
Marine sediment	Triclosan (and biphenylol)	1. Dried with diatomaceous earth 2. PFE extraction with DCM 3. Silica purification	GC/NCI-MS	HP-5MS (30 m × 0.25 mm; 0.25 μm)	100	[120]
Lake sediment	Triclosan	1. Freeze-dried material mixed with sand 2. PFE DCM 3. Silica purification 4. Derivatized with diazomethane	GC/EI-MS/MS Ion trap	RTX-5MS (30 m × 0.25 mm; 0.25 μm)	100	[129]
Marine sediment	Triclosan (and nine others)	1. Lyophilized 2. Soxhlet extraction with DCM, water (sequential) or water, DCM (sequential) 3. LLE of water extract with Hex	GC/EI-MS/MS Ion trap	DB-17MS (30 m × 0.25 mm; 0.15 μm)	98–100	[144, 145]
Marine sediment	Triclosan (and nine others)	1. Lyophilized 2. Microwave-assisted Soxhlet extraction with DCM, water (sequential) or water, DCM (sequential) 3. LLE of water extract with Hex	GC/EI-MS/MS Ion trap	DB-17MS (30 m × 0.25 mm; 0.15 μm)	96–100	[145]
Marine sediment	Triclosan (and nine others)	1. Lyophilized 2. Superheated liquid extraction with DCM, water (sequential) or water, DCM (sequential) 3. LLE of water extract with Hex	GC/EI-MS/MS Ion trap	DB-17MS (30 m × 0.25 mm; 0.15 μm)	102	[144]
Sediment	Triclosan, tetra(II)closan, tetra(III)closan, and pentaclosan	1. Ultrasonic extraction with Acet 2. Centrifuged to remove solids 3. Extract dissolved in water 4. pH adjusted to >13 and washed with Hex (river water only) 5. Acidified to pH 2-3 6. LLE with Hex 7. Derivatized with diazomethane 8. Florisil purification	GC/EI-MS	Ultra-2 (30 m × 0.25 mm; 0.25 μm)	83–117	[118]
River sediment	Methyl triclosan (and 17 others)	1. Extracted with Acet and Hex (sequential) 2. Sulfur removal with activated copper 3. Silica purification and fractionation	GC/EI-MS	SE-54 (45 m × 0.25 mm; 0.25 μm)	35	[98]
Sediment	Triclosan (and 60 others)	1. PFE with water/iPrOH (1:1 VR) 2. PFE with water/iPrOH (1:4 VR) 3. Extracts diluted with phosphate buffer (pH 7) 4. SPE (PSDVB) 5. Eluent: DCM/DE (4:1 VR) 6. Extract passed through Florisil/sodium sulfate (1:4 MF) column	GC/EI-MS	DB-5MS (30 m × 0.25 mm; 0.50 μm)	71–83	[100]
Suspended solids	Triclocarban	1. Extracted with MeOH/Acet 2. Filtered	LC/EI-MS	Ultra IBD (150 mm × 2.1 mm; 5 μm)	NR	[141, 142]

Table 12 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Sludge and sediment	Triclosan (and two others)	1. Lyophilized and sieved 2. MAE with Acet/MeOH (1:1 VR) 3. Centrifuged to remove solids 4. Mixed with NaOH and washed with Hex 5. Acidified to pH 2.5 6. Concentrated on Oasis HLB 7. Silica purification 8. Derivatized with MTBSTFA	GC/EI-MS GC/EI- MS/MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	81.7– 98.9	[146]
WWTP effluent suspended solids	Triclosan (and dioxins)	1. Dried on filter 2. Ultrasonic extraction with EtAc	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	NR	[131]
Sludge	Triclosan (and 6 others)	1. Dried and crushed 2. Derivatized with acetic anhydride and triethylamine 3. SFE 4. Dissolved in PE 5. Washed with 1 % K ₂ CO ₃ 6. Silica purification	GC/EI-MS	HP-5MS (30 m×0.25 mm; 0.25 μm)	NR	[143]
Sludge	Triclosan, methyl triclosan, tetra(II)closan, tetra(III)closan, and pentaclosan	1. Lyophilized 2. SFE (cell packed with silica) 3. Derivatized with TMSDEA	GC/EI-MS	DB-5 type (30 m×0.30 mm; 0.25 μm)	13– 120	[119, 147]
Sludge	Triclosan	1. Lyophilized 2. Soxhlet extraction with EtAc 3. Silica purification 4. SEC purification (Biorad SX-3)	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	94	[117]
Fish	Triclosan, tetra(II)closan, tetra(III)closan, and pentaclosan	1. Homogenized with ACN 2. Centrifuged to remove solids 3. Washed with Hex 4. Dissolved in water 5. pH adjusted to >13 and washed with Hex (river water only) 6. Acidified to pH 2-3 7. LLE with Hex 8. Derivatized with diazomethane 9. Saponification with KOH EtOH solution followed by extraction into Hex 10. Florisil purification	GC/EI-MS	Ultra-2 (30 m×0.25 mm; 0.25 μm)	85– 119	[118]
Fish	Methyl triclosan	1a. Homogenized with sodium sulfate 2a. Column extracted with CHex/DCM or 1b. Homegnized material mixed with diatomaceous earth 2b. PFE with CHex/DCM 3. SEC (EnviroSep-ABC or Biobeads S-X3) purification 4. Silica purification	GC/EI-MS GC/EI- MS/MS	DB-5 (25 m×0.32 mm)	76– 108	[139, 154]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene
NR not reported

simultaneous destruction of the target compounds [11]. SEC phases and solvent systems used for lipid removal in the analysis of synthetic musk fragrances include Bio Beads SX-3 with hexane/dichloromethane (1:1 VR) [103, 104], Bio Beads SX-3 with cyclohexane/ethyl acetate (98.5:100 VR) [83, 99], Bio Beads SX-3 with cyclohexane/ethyl acetate (1:1 VR) [101, 102], and Envirolgel and Phenogel guard column with dichloromethane [73, 108]. Final extract purification has been accomplished primarily with silica and a variety of eluents [83, 99, 101, 103–105, 107]. Florisil [102] and Strata-NH₂/alumina (Strata-NH₂; Phenomenex; Torrance, CA, USA) [73, 108] have also been used.

House dust

HHCB, AHTN, ATII, ADBI, AHMI, and musk xylene were extracted from house dust collected from vacuum cleaner bags with hexane/diethyl ether (19:1 VR) using PFE [110]. Additional purification steps were not performed.

Air

Synthetic musk fragrances have been collected from indoor [110, 111] and outdoor [72, 111, 112] air by active sampling through polyurethane foam (PUF) [110, 112] and XAD-2 resin [72] (Table 10). The outdoor air samples were passed through glass fiber filters prior to the PUF or XAD-2 to collect the particulate phase. The glass fiber filters and PUF or XAD-2 resin were Soxhlet-extracted with hexane/diethyl ether (9:1 VR) [112] or acetone/hexane (1:1 VR) [72]. A sample fractionation was developed using activated silica columns [112]. Extracts were loaded onto the columns in hexane, rinsed with hexane and hexane/ethyl acetate (99:1 VR), and HHCB, AHTN, ATII, musk xylene, and musk ketone eluted in hexane/ethyl acetate (9:1 VR). The PUF used for sampling indoor air was extracted with hexane/diethyl ether (19:1 VR) using PFE [110]. Additional purification steps were not performed.

Detection and quantification

The GC methods used for these compounds are summarized in Tables 7, 8, 9 and 10. Synthetic musk fragrances are most commonly analyzed by GC/EI-MS, but gas chromatography coupled to negative chemical ionization mass spectrometry (GC/NCI-MS) is more sensitive for the nitro musk fragrances. Nitro musk fragrances have also been analyzed by gas chromatography with a flame ionization detector (GC-FID) and GC-ECD. Common GC phases, including 5%-phenyl-methylpolysiloxane and dimethylpolysiloxane, can be used for the separation of these compounds. Separation of the enantiomers of HHCB and AHTN has been reported with a heptakis (6-*O*-*tert*-butyldimethylsilyl-

2,3-di-*O*-methyl)- β -cyclodextrin in 20%–50% OV1701 GC columns [113, 114]. Typical ions monitored for the analysis of synthetic musk fragrances by GC/EI-MS, GC/NCI-MS, and gas chromatography with positive chemical ionization (GC/PCI-MS), as well as high-resolution and ion trap tandem mass spectrometry (MS/MS) methods are summarized in Table S1 of the Electronic Supplementary Material. There has been one report of a method for the analysis of HHCB in wastewater by HPLC-UV [115].

Synthetic musk fragrance standards are commercially available. The amino musk metabolites have been synthesized by the reduction of the parent nitro musk fragrance using a variety of methods [59, 74, 93, 94, 108]. HHCB-lactone has been synthesized from HHCB [114]. Deuterated musk xylene and AHTN standards are commercially available for use as recovery or injection standards. There have been reports of problems with the use of the deuterated AHTN (AHTN-*d*₃) due to the occurrence of proton exchange during sample processing [65, 71]. A variety of other recovery and injection standards have been used for the analysis of synthetic musk fragrances, including pentachloronitrobenzene, deuterated polycyclic aromatic hydrocarbons, and various labeled and unlabeled polychlorinated biphenyls. A summary of common recovery and injection standards used for these compounds is provided in Table S2 of the Electronic Supplementary Material.

Antimicrobials

Sample extraction and preparation

Water

Methods for the extraction of triclosan, triclocarban, and triclosan metabolites are summarized in Table 11. Triclosan has been extracted using LLE from unfiltered surface water and wastewater samples with dichloromethane at pH 2 [56] and toluene at ambient pH [116, 117]. Lipophilic interferences and methyl triclosan were removed from unfiltered river water samples with hexane at pH>13. Triclosan was then extracted with hexane at pH 2–3 [118]. Due to the formation of hydroxide precipitates with the addition of NaOH, the washing step was omitted for seawater samples. Continuous liquid–liquid extraction (CLLE) with dichloromethane at ambient pH and pH 2 has also been used for the extraction of triclosan from unfiltered surface water samples [1, 57, 58].

Triclosan has been extracted from water using various SPE sorbents including C18 [68, 69, 119, 120], Oasis MAX (Waters; Milford, MA, USA) [121], XAD-4/XAD-8 [70], SDB-XC [122, 123], Bio Beads SM-2 [124, 125], Isolute

ENV+ (Biotage; Charlottesville, VA, USA) [120], and Oasis HLB [120, 126–137].

Triclosan and its metabolites methyl triclosan, tetra(II) closan, tetra(III) closan, and pentaclosan were extracted from unfiltered wastewater influent and effluent samples with C18 mixed with Florisil [119]. Prior to extraction, the samples were adjusted to pH < 2 with phosphoric acid. Ethanol was also added to minimize clogging. After extraction, the sorbent was rinsed with ethanol/water (1:4 VR) and ethyl acetate. The closans were recovered with toluene and hexane. Triclosan and several acidic drugs were concentrated from wastewater samples using C18 sorbent [68, 69]. Prior to concentration samples were centrifuged, filtered, and adjusted to pH < 3 with HCl or formic acid. Target compounds were eluted with acetone. Filtered, wastewater samples at pH 4 were processed with C18 cartridges with elution of triclosan with methanol and acetone [120].

Oasis MAX is a mixed-mode sorbent with reversed-phase and anion exchange functionality. Oasis MAX cartridges were used to extract triclosan and twenty other phenolic and acidic compounds from filtered, acidified (pH 3) wastewater samples [121]. Prior to elution the cartridges were washed with a methanol/sodium acetate solution. Triclosan was eluted with other phenols with methanol.

Several PS-DVB copolymers have been used to extract triclosan from water. One advantage of using PS-DVB is that large water volumes can be passed through it before clogging relative to other sorbents. Due to its relatively low selectivity, a second purification step is normally necessary prior to instrumental analysis. PS-DVB copolymers used for triclosan extraction include XAD [70], SDB-XC (3M; St. Paul, MN, USA) [122, 123], and Bio Beads SM-2 [124, 125]. A mixture of XAD-4 and XAD-8 was used to extract a large suite of compounds from 80 L surface water samples [70]. Triclosan and other compounds were eluted with acetone. SDB-XC Empore disks have been used to extract triclosan and ten other compounds associated with wastewater from surface water samples [122, 123]. Prior to extraction samples were filtered and acidified to pH < 2. Compounds were eluted with methanol, dichloromethane, and methanol. Extracts were purified using silica columns using three bed volumes of dichloromethane and methanol for elution. Triclosan and methyl triclosan were extracted from surface water samples after acidification (pH 2) with Bio Beads SM-2 [124, 125]. Methanol/dichloromethane was used as the eluent. These extracts were purified using silica with elution using ethyl acetate/methanol (19:1 VR).

Isolute ENV+ is a chemically modified (hydroxylated) PS-DVB polymeric sorbent. Isolute ENV+ cartridges were used to extract triclosan from filtered wastewater samples at pH 4 [120]. Triclosan was eluted with methanol and acetone.

The most commonly used SPE sorbent for the analysis of triclosan has been the divinylbenzene/*N*-vinylpyrrolidone copolymer Oasis HLB. Triclosan has been efficiently extracted from filtered surface water and wastewater samples ranging in volume from 50 mL to 1 L using 60 mg [127–130, 132–134], 200 mg [120, 126, 131], and 500 mg [135–137] Oasis HLB cartridges. The breakthrough volume for triclosan with Oasis HLB has not been determined, but it is likely much larger than 1 L for 500 mg sorbents as 60 mg cartridges adequately retained triclosan in 1 L water samples [128–130, 132, 133]. Sample volumes are likely limited by sorbent clogging rather than contaminant breakthrough. Triclosan recovery using Oasis HLB appears to be independent of sample pH (for pH range 2–7). Several researchers have extracted at pH 7 to reduce clogging and interferences caused by retention of dissolved organic matter (DOM) [132, 133, 136, 137]. Retention of DOM by a variety of polymeric sorbents is reduced at pH 7 relative to lower pH values [138].

After extraction, potential interferences have been removed from Oasis HLB cartridges with rinses of water [135], methanol/water (1:9 VR) [128–130], methanol/water (1:3 VR) [126], hexane [132, 133]. Eluents for triclosan from Oasis HLB include ethyl acetate, [127, 132, 133], methanol [126, 134, 136, 137], ethyl acetate/acetone (1:1 VR) [128–130], methanol and acetone (sequential) [120, 131], methanol/methyl *tert*-butyl ether (MTBE) (1:9 VR) and methanol (sequential) [135].

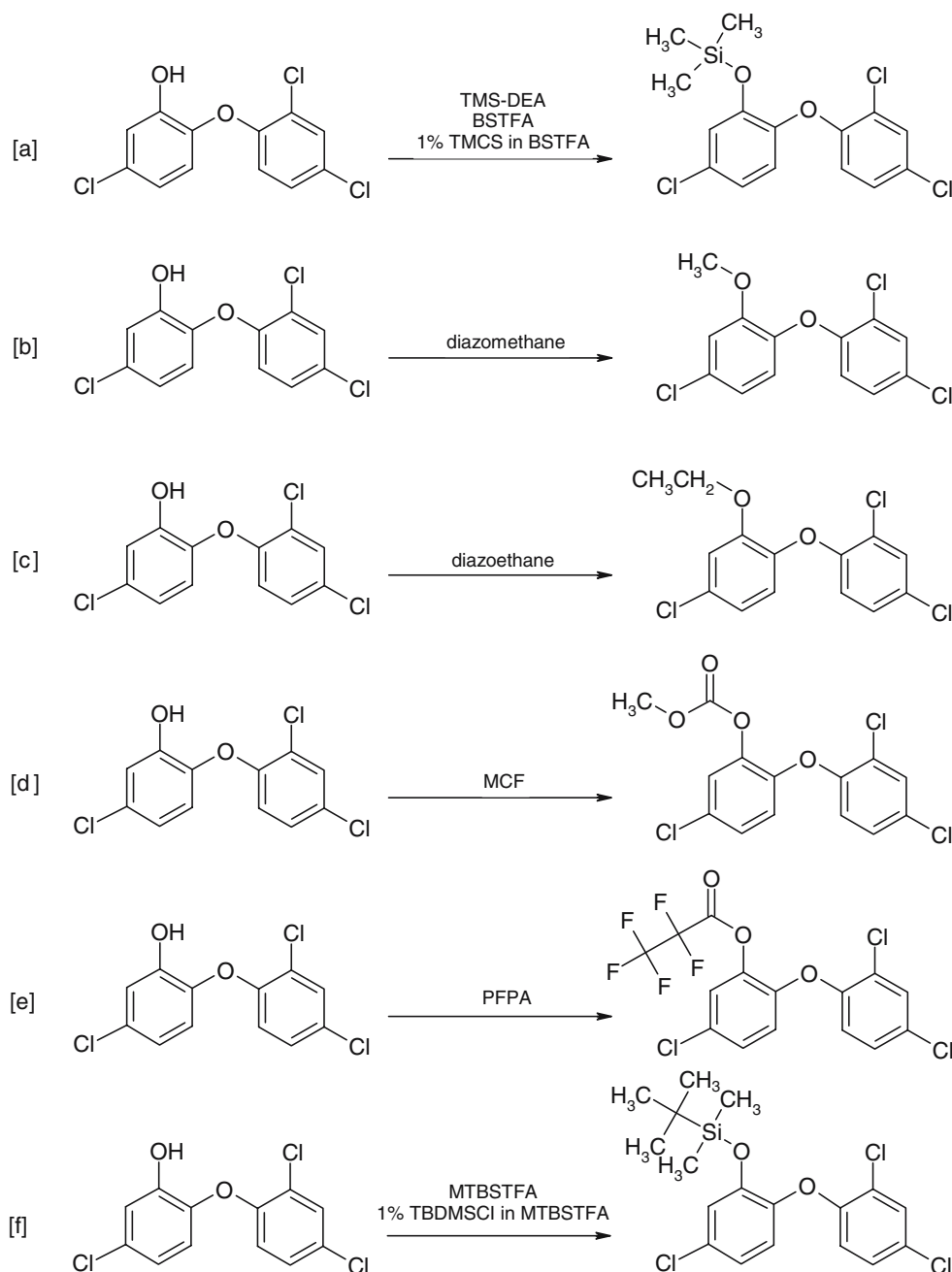
SPMDs have been used for triclosan and methyl triclosan in surface water [70, 124, 125, 139]. The sampling devices were typically deployed for 3–6 weeks and semiquantitative concentrations were reported (mass/SPMD). Triclosan has also been sampled using POCIS [85].

Triclocarban has been extracted from water by LLE [140] and SPE using Oasis HLB [141, 142] and C18 cartridges [140]. Triclocarban was used as a recovery standard for the analysis of the mothproofing compounds sulcofuron and flucofuron in water [140]. These compounds were extracted by LLE with dichloromethane at pH 2 after the addition of NaCl. A separate extraction method involved concentration of these compounds on C18 cartridges at ambient pH with elution with methanol. Triclocarban was concentrated from centrifuged wastewater and surface water samples using Oasis HLB cartridges and eluted with methanol/acetone (1:1 VR) with 10 mmol/L acetic acid [141, 142]. The extracts were filtered prior to analyses. The centrifuged solids were extracted with methanol/acetone (1:1 VR) and filtered prior to analysis.

Sludge and sediments

Several extraction methods have been used for triclosan in sludge and surficial sediments, including dispersion-ex-

Fig. 1 Derivatization of triclosan (and chlorinated triclosan metabolites) with *A* TMS-DEA [119, 147], BSTFA [122, 123, 132, 133], or 1% TMCS in BSTFA [126]; *B* diazomethane [56, 118, 128–130]; *C* diazoethane [124, 125]; *D* MCF [68, 69, 136, 137]; *E* PFPA [121]; and *F* MTBSTFA [127, 146] or 1% TBDMSCI in MTBSTFA [121]



traction [98], supercritical CO₂ extraction [119, 143], Soxhlet extraction [117, 144, 145], PFE [100, 120, 129, 144], microwave-assisted extraction [146], and focused microwave-assisted Soxhlet extraction [145]. These methods are listed in Table 12.

Triclosan was among a suite of compounds quantified during a non-target screening of organic contaminants in sediments [98]. Sediment samples were dispersion-extracted with acetone and hexane (sequential). Sulfur was removed from extracts with activated copper and further purified on silica.

Triclosan and the metabolites methyl triclosan, tetra(II)closan, tetra(III)closan, and pentaclosan were extracted from lyophilized or air-dried sludge using supercritical CO₂ extraction [119, 143].

Freeze-dried sludge samples were Soxhlet-extracted with ethyl acetate for the analysis of triclosan [117]. Extracts were purified using silica cartridges with elution with ethyl acetate and by SEC with a Bio Beads SX-3 column and cyclohexane/ethyl acetate (1:1 VR) mobile phase. Triclosan was among ten compounds extracted from freeze-dried sediment samples by sequential Soxhlet extraction with

Table 13 Methods for UV filters in environmental matrices

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Water	BP-3, DHB, DHBM	1. SPME (DVB)	GC/EI-MS	DB5-MS	42–69	[155]
Water	BP-3	1. SPE (C18, Empore disk) 2. Eluent: DCM	HPLC-UV	Waters Symmetry C8	90–95	[155]
Swimming pool water	ODPABA	1. SPE (C18) 2. Eluent: DCM/EtAc (1:1 VR)	HPLC-UV	Discovery C18 (250 mm×4.6 mm; 5 μm)	98–101	[150]
Surface water	BP-3, 4-MBC, EHMC, BMDDBM	1. KCl added (10 %) 2. Acidified to pH 3 3. SPE (C18, Empore disk) 4. Eluent: EtAc/DCM	HPLC-UV GC/EI-MS	Discovery C18 (250 mm×4.6 mm; 5 μm) DB-5MS (30 mm×0.25 mm; 0.25 μm)	86–99	[151]
Surface water	BP-3, ODPABA	1. DI-SPME (PDMS 100 μm or PA 85 μm)	GC-FID GC/EI-MS	DB-5 (30 mm×0.32 mm; 1 μm) DB-5MS (30 mm×0.25 mm; 0.25 μm)	82–99	[152]
Surface water	BP-3 (and 26 others)	1. Adjusted to pH 2 2. SPE (Oasis HLB) 3. Eluent: MeOH/MTBE (1:9 VR), MeOH (sequential)	LC/ESI-MS/MS	Synergi Max-RP C12 (250 mm×4.6 mm; 4 μm)	68	[135]
Surface water	BP-3, ODPABA	1. HS-SPME (PDMS 100 μm or PA 85 μm)	GC-FID GC/EI-MS	DB-5 (30 mm×0.32 mm; 1 μm) DB-5MS (30 mm×0.25 mm; 0.25 μm)	89–98	[152]
Surface water	BP-3, ODPABA	1. SPE (C18, Empore disk) 2. Eluent: DCM	GC-FID GC/EI-MS	DB-5 (30 mm×0.32 mm; 1 μm) DB-5MS (30 mm×0.25 mm; 0.25 μm)	93–97	[152]
Surface water	PMDSA, BP-3, 4-MBC, BMDDBM, EHMC	1. Samples preserved with 0.05 % TX-114 2. Micelle-mediated extraction with extraction into MeOH or back-extraction into Hex	HPLC-UV GC/EI-MS	Discovery C18 (250 mm×4.6 mm; 5 μm) DB-5MS (30 mm×0.25 mm; 0.25 μm)	95–102	[149]
Surface water and WWTP effluent	4-MBC, BP-3, EHMC, OC	1. SPE (Biobeads SM-2) 2. Eluent: MeOH/DCM 3. Silica purification	GC/EI-MS	SE54 (25 m×0.32 mm; 0.25 μm) or BGB-5 (30 m×0.25 mm; 0.25 μm)	78–129	[154]
Surface water	4-MBC, EHMC, BP-3, OC, BMDDBM	1. SPE (Biobeads SM-2) 2. Eluent: MeOH, DCM (sequential) 3. Silica purification	GC/EI-MS	SE54 (25 m×0.32 mm; 0.25 μm)	42–90	[153]
Surface water	4-MBC, ODPABA, HS, EHMC, BP-3	1. pH adjusted to 7 2. LLE with CHex 3. Dried with sodium sulfate	GC/EI-MS	SE54 (25 m×0.32 mm; 0.25 μm) or BGB-5 (30 m×0.25 mm; 0.25 μm)	72–101	[52]
Fish	4-MBC, BP-3, EHMC, OC (and methyl triclosan)	1a. Homogenized with sodium sulfate 2a. Column extracted with CHex/DCM or 1b. Homogenized material mixed with diatomaceous earth 2b. PFE with CHex/DCM 3. SEC (EnviroSep-ABC or Biobeads S-X3) purification 4. Silica purification	GC/EI-MS	SE54 (25 m×0.32 mm; 0.25 μm) or BGB-5 (30 m×0.25 mm; 0.25 μm)	93–115	[154]
Fish	4-IDM, BMDDBM, 4-MBC, ODPABA, TMCHS, EHMC, BP-3	1. Homogenized with sodium sulfate 2. Soxhlet extracted with PE/EtAc (2:1 VR)	GC/EI-MS	SE-54-CB (50 m×0.25 mm; 0.25 μm)	89–106	[52]

Table 13 (continued)

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Sludge	4-MBC, EHMC, OC, OT	3. SEC (Biobeads SX-3) 4. Derivatized with CH ₃ I/NaH 5. Silica purification 1. Shaker extracted with Pent/Acet (1:1 VR) 2. Dried over sodium sulfate 3. Silica purification	GC/EI-MS HPLC-UV LC/ESI-MS/ MS	DB-5 (60 m× 0.25 mm; 0.25 μm) C18 (250 mm×4.6 mm; 5 μm) C18 (150 mm×0.2 mm; 3 μm)	75– 101	[156]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene

dichloromethane (12 h) and water (12 h) or water (12 h) and dichloromethane (12 h) [144, 145]. The extraction time using the same extraction solvents was reduced using focused microwave-assisted Soxhlet extraction (25 min dichloromethane and 50 min water extractions) [145]. The water extracts from both methods were extracted with hexane for GC analysis. Sediment and sludge samples were analyzed for triclosan and two chlorophenols by microwave-assisted extraction with acetone/methanol (1:1 VR) [146]. Extracts were centrifuged, dissolved in 0.2 mol/L NaOH, and washed with hexane. The resulting aqueous solution was adjusted to pH 2.5 and concentrated on an Oasis HLB cartridge.

Triclosan was extracted from sediments and sludge by PFE with dichloromethane [120, 129]. Extracts were purified by SPE using silica. Triclosan and 60 other compounds were extracted from wet sediment by PFE with water/isopropanol (1:1 VR) followed by water/isopropanol (1:4 VR) [100]. Extracts were collected in vials containing pentane. The extracts were purified using Oasis HLB and Florisil cartridges. Freeze-dried sediment samples mixed with sand were extracted by PFE with dichloromethane and water [144]. The water extract was extracted with hexane for GC analysis. This was the only study reviewed that did not use a commercial Dionex system (ASE) for PFE.

Suspended sediment collected on filters has been extracted by sonication with ethyl acetate for the analysis of triclosan [131].

Aquatic biota

Methyl triclosan was extracted from homogenized fish filets mixed with sodium sulfate by mixing with cyclohexane/dichloromethane (1:1 VR) or from homogenized fish filets mixed with diatomaceous earth by PFE with cyclohexane/dichloromethane (1:1 VR) [139]. Extracts from both methods were purified by SEC with an EnviroSep-ABC column (Phenomenex; Torrance, CA, USA) and dichloromethane/hexane (7:13 VR) mobile phase or Bio Beads SX-3 and dichloromethane/cyclohexane (7:13 VR) mobile phase. Extracts were then passed through 5% deactivated silica with hexane/ethyl acetate (10:1 VR).

Derivatization

Triclosan and its chlorinated metabolites have been transformed to a variety of ether derivatives for analysis by gas chromatography (Fig. 1). *N,N*-diethyltrimethylamine (TMS-DEA) [119, 147], *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) [122, 123, 132, 133] and BSTFA with 1%

Fig. 2 Derivatization of *A* isopropyl-dibenzoylmethane (4-IDM) and *B* avobenzone (BMDBM) with CH₃I/NaH [52]

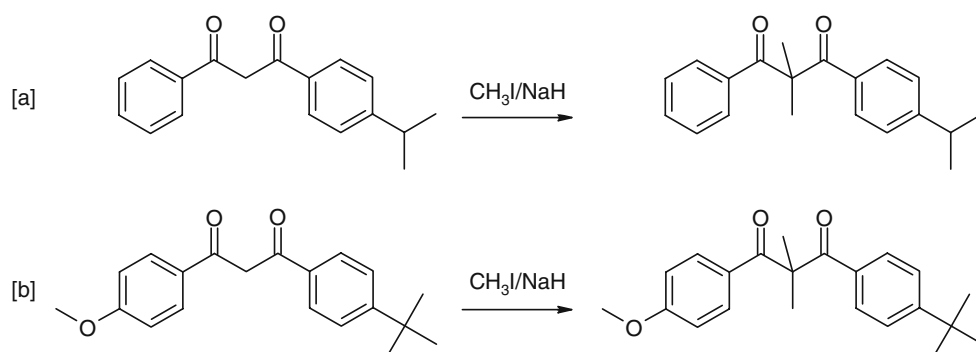


Table 14 Methods for insect repellents in environmental matrices

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Surface water	DEET (and 26 others)	1. Adjusted to pH 2 2. SPE (Oasis HLB) 3. Eluent: MeOH/MTBE (1:9 VR), MeOH (sequential)	LC/ESI-MS/MS	Synergi Max-RP C12 (250 mm×4.6 mm; 4 μm)	81	[135]
Wastewater and seawater	DEET (and 13 others)	1. pH adjusted to 7 2. SPE (Oasis HLB) 3. Eluent: Hex, EtAc, MeOH (sequential)	GC/EI-MS	HP5-MS (30 m × 0.25 mm; 0.25 μm)	82	[136, 137]
Surface water	DEET (and 23 others)	1. pH adjusted to 8.5 2. LLE with DCM	GC/EI-MS	DB-5 (30 m×0.25 mm; 0.25 μm)	84	[158]
Wastewater, surface water, and drinking water	DEET (and 45 others)	1. Unfiltered sample CLLE with DCM at ambient pH, pH 2 (sequential)	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	NR	[1, 57, 58, 159]
Surface water	DEET (and 36 others)	1. On-line SPE (PLRP-S)	LC/APCI-MS/MS	Supelcosil C18 (250 mm×4.6 mm; 5 μm)	NR	[165]
Seawater	DEET (and 7 others)	1. SPE (SDB-1) 2. Eluent: EtAc, Hex/EtAc (4:1 VR), MeOH (sequential)	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.25 μm)	68	[164]
WWTP influent and effluent and surface water	DEET Bayrepel and Bayrepel-acid	1. Adjusted to pH 2 2. SPE (LiChrolute EN/Isolute C18) 3. Eluent: Acet/EtAc (1:1 VR), MeOH (sequential) 4. For GC analysis: Bayperal-acid derivatized with diazomethane	GC/EI-MS LC/ESI-MS	XTI-5 (30 m×0.25 mm; 0.25 μm) Inertsil ODS-2 C18 (250 mm×4.6 mm; 5 μm)	97– 98	[162, 163]
Landfill leachate	DEET (and 21 others)	5. SLLE (Pent at pH 8, DCM at pH 8, DCM at pH 2) (DEET at pH 8)	GC-FID/ ECD GC/ EI-MS	SE-54 (25 m×0.25 mm; 0.25 μm) BPX-5 (30 m×0.22 mm; 0.25 μm)	60	[160]
Surface water	DEET (and 5 others)	1. SPE (Empore disk, C18) 2. Eluent: ACN	FAC/ MEKC	NA	38– 44	[161]
Sediment	DEET (and 60 others)	1. PFE with water/iPrOH (1:1 VR) 2. PFE with water/iPrOH (1:4 VR) 3. Extracts diluted with phosphate buffer (pH 7) 4. SPE (PSDVB) 5. Eluent: DCM/DE (4:1 VR) 6. Extract passed through Florisil/sodium sulfate (1:4 MF) column	GC/EI-MS	DB-5MS (30 m×0.25 mm; 0.50 μm)	57– 76	[100]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene

NR not reported

NA not applicable

trimethylchlorosilane (TMCS) [126] have been used to form triclosan and chlorinated triclosan trimethylsilyl ethers (Fig. 1a). Trislosan has been transformed to methyl triclosan using diazomethane (Fig. 1b) [56, 118, 128–130]. Because methyl triclosan is a natural derivative of triclosan, this

method can overestimate the triclosan concentration. Triclosan concentrations can be determined by difference if the methyl triclosan concentration is determined prior to methylation. A similar alternative has been the use of diazoethane to form ethyl triclosan (Fig. 1c) [124, 125]. A

methoxycarbonyl derivative (Fig. 1d) is formed by reaction with methyl chloroformate (MCF) [68, 69, 136, 137]. A pentafluorinated triclosan derivative (Fig. 1e) can be formed with pentafluoropropionic acid anhydride (PFPA) [121]. Reaction of triclosan with *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) [127, 146] and MTBSTFA with 1% *tert*-butyldimethylchlorosilane (TBDMSCl) [121] forms a *tert*-butyldimethylsilyl triclosan derivative (Fig. 1f).

Detection and quantification

Triclosan has been analyzed by liquid chromatography–mass spectrometry (LC/MS), liquid chromatography–tandem mass spectrometry (LC/MS/MS), and GC/MS with and without derivatization. Lower detection limits are achieved with derivitization using GC/MS and LC/MS provides lower sensitivity than LC/MS/MS. Triclocarban is best analyzed by LC-based methods. Common ions and transitions monitored for these compounds are listed in Table S3 of the Electronic Supplementary Material. Liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS) has been used for the identification of photo-degradation products of triclosan [148].

Labeled triclosan ($^{13}\text{C}_{12}$ -triclosan) is currently available for use as a recovery standard. Other compounds used as recovery and injection standards for triclosan, triclocarban, and metabolites are listed in Table S4 of the Electronic Supplementary Material.

UV filters

Sample extraction and preparation

Water

Methods used for the analysis of UV filters (sunscreen agents) in environmental matrices are summarized in Table 13. Benzophenone-3,4-methylbenzylidene camphor, homosalate, octyldimethyl-*p*-aminobenzoic acid, and octyl methoxycinnamate were analyzed in water samples at pH 7 using LLE with cyclohexane [52]. A suite of PCBs and chlorinated pesticides was also analyzed using this method. Benzophenone-3,4-methylbenzylidene camphor, octyl methoxycinnamate, 2-phenylbenzimidazole-5-sulfonic acid, and avobenzone were extracted from water using micelle-mediated extraction with solvent back-extraction at pH 3 (adjusted with HCl) [149]. NaCl was added after pH adjustment to yield a 0.2 mol/L ionic strength. The surfactant Triton X-114 (A. G. Scientific; San Diego, CA, USA) was added at 0.1%. After mixing (1 min) and resting (15 min) at 60 °C the

samples were centrifuged and cooled. The surfactant phase was then removed and extracted with methanol (for LC analysis) or back-extracted with hexane (for GC analysis).

UV filters have been concentrated from water using several different SPE sorbents, including C18 [150–152], Oasis HLB [135], and Bio Beads SM-2 [153, 154]. C18 cartridges [150, 152] or disks [151] have been used for the concentration of benzophenone-3 [151, 152], octyldimethyl-*p*-aminobenzoic acid [150, 152], avobenzone [151], octyl methoxycinnamate [151], and 4-methylbenzylidene camphor from water. Compounds were eluted with ethyl acetate/dichloromethane (1:1 VR) or dichloromethane after drying C18 under vacuum. Benzophenone-3 was among 27 compounds concentrated from surface water samples at pH 2 using Oasis HLB cartridges [135]. Compounds were eluted using sequential elution with methanol/MTBE (1:9 VR) and methanol. Octyl methoxycinnamate, 4-methylbenzylidene camphor, benzophenone-3, octocrylene, and avobenzone were extracted from surface water and wastewater samples with Bio Beads SM-2 [153, 154]. Compounds were recovered with sequential rinses of methanol and dichloromethane. Extracts have been purified by SPE using silica [153, 154].

SPME has been used for octyldimethyl-*p*-aminobenzoic acid and benzophenone-3 [152, 155] and its metabolites 2,4-dihydroxybenzophenone [155] and 2,2'-dihydroxy-4-methoxybenzophenone [155]. Both DI-SPME and HS-SPME with PDMS (100 μm) and PA (85 μm) provided adequate recoveries for benzophenone-3 and octyldimethyl-*p*-aminobenzoic acid [152]. The recoveries were similar to those provided by SPE using C18 for these compounds. PA (85 μm) and Carbowax-DVB (65 μm) were both adequate for the retention of benzophenone-3, 2,4-dihydroxybenzophenone and 2,2'-dihydroxy-4-methoxybenzophenone for DI-SPME [155]. The retention of benzophenone-3 using PDMS (30 μm) was lower than these other materials, but PDMS is still adequate for benzophenone-3. The retention of 2,4-dihydroxybenzophenone and 2,2'-dihydroxy-4-methoxybenzophenone was much lower with PDMS (30 μm). PA (85 μm) and Carbowax-DVB (65 μm) are better sorbent choices for these compounds.

SPMDs have been used for 4-methylbenzylidene, benzophenone-3, octyl methoxycinnamate, octocrylene, and avobenzone in surface water and wastewater [153, 154]. The sampling devices were typically deployed for 3–6 weeks, and semiquantitative concentrations were reported (mass/SPMD).

Sewage sludge

Wet sewage sludge mixed with NaCl was sequentially extracted with pentane/acetone (1:1 VR), pentane/diethyl

ether (1:1 VR), and diethyl ether/dichloromethane (4:1 VR) by shaking [156]. The resulting extract was purified by SPE using silica. It is likely that this method could also be used for water samples with little modification.

Fish tissue

Benzophenone-3, 4-methylbenzylidene camphor, homosalate, octyldimethyl-*p*-aminobenzoic acid, octyl methoxycinnamate, 4-isopropylidibenzoylmethane and avobenzone were Soxhlet-extracted from fish tissue with petroleum ether/ethyl acetate (2:1 VR) [52]. Prior to extraction the tissue was homogenized and dried with sodium sulfate. Lipids and other potential matrix interferences were removed by SEC (Bio Beads SX-3) with a mobile phase consisting of cyclohexane/acetone (3:1 VR). After SEC, $\text{CH}_3\text{I}/\text{NaH}$ was added to half of the extract to derivatize 4-isopropylidibenzoylmethane and avobenzone (Fig. 2). The other half of the extract was loaded onto a silica column and the UV filters were eluted with hexane/ethyl acetate (91:9 VR). The derivatized extract was also loaded onto a silica column. Petroleum ether was first used to remove lipophilic interferences. The dimethylated 4-isopropylidibenzoylmethane and avobenzone compounds were recovered from the silica column with hexane/ethyl acetate (7:3 VR).

A similar method was used for the determination of 4-methylbenzylidene camphor, benzophenone-3, octyl methoxycinnamate, and octocrylene in fish tissue [154].

Detection and quantification

While LC-based methods dominate the analysis of UV filters in cosmetics [29], most of these compounds detected in the environment are measured with GC-based techniques. All of the compounds reviewed here are amenable to GC except octyl triazone, avobenzone, 4-isopropylidibenzoylmethane, and 2-phenylbenzimidazole-5-sulfonic acid. Derivatives of avobenzone and 4-isopropylidibenzoylmethane were analyzed by GC/MS [52]. 4-Methylbenzylidene camphor, octyl methoxycinnamate, and octocrylene were analyzed by GC/EI-MS using a programmable temperature vaporizing (PTV) inlet, a DB-5 column (Agilent; Palo Alto, CA, USA), and selected ion monitoring (SIM) [156]. Octyl triazone is not amenable to gas chromatography and has been analyzed by HPLC/UV using a C18 column [250 mm×4.6 mm inner diameter (i.d.); 5 μm film thickness] and gradient elution using methanol and water [156]. Enantiomeric separation of 4-methylbenzylidene camphor was achieved with a laboratory-prepared 2,6-bis-(*tert*-butyldimethylsilyl)- γ -cyclodextrin in 70% PS086 GC column [157]. LC/MS/MS with positive

electrospray ionization has been used for the confirmation of octyl triazone [156]. Benzophenone-3 has been analyzed by GC/EI-MS. It has also been quantified by LC/MS/MS with separation using a Synergi Max-RP C12 column (250 mm×4.6 mm i.d.; 4 μm particle size; Phenomenex; Torrance, CA, USA), a gradient solvent program consisting of 0.1% formic acid in water and methanol, and positive electrospray ionization [135].

Recovery standards were not used in the majority of reviewed studies. Benzyl cinnamate [153], $^{13}\text{C}_3$ -caffeine [154], $^{13}\text{C}_6$ -metolachlor [154], and $^{13}\text{C}_{12}$ -PCB 77 [154] have been used as recovery standards for various UV filters. Development of isotopically-labeled compounds for use as recovery standards is an important need for the analysis of UV filters. Common ions monitored for the analysis of UV filters and recovery and injection standards used for these compounds are listed in Tables S5 and S6, respectively, in the Electronic Supplementary Material.

Insect repellents

Sample extraction and preparation

Water

Methods for the analysis of DEET, Bayrepel, and metabolites in water and sediments are summarized in Table 14. DEET has been extracted from surface water LLE with dichloromethane [158] and CLLE with dichloromethane for 3 h at ambient pH and pH 2 [1, 57, 58, 85, 159]. Sequential liquid–liquid extraction (SLLE) with pentane, dichloromethane, and dichloromethane after acidification to pH 2 was used to extract DEET from landfill leachate [53, 160].

Insect repellents have been extracted from water using several SPE phases, including C18 [161], Oasis HLB [135–137], LiChrolute EN/C18 [162, 163], SDB-1 [164]. DEET was eluted from C18 membrane disks with acetonitrile [161]. Sequential elution was used with Oasis HLB cartridges. An initial rinse with hexane to remove lipophilic interferences was followed by elution of DEET with ethyl acetate, and acidic compounds with methanol [136, 137]. DEET was eluted with 26 other compounds from Oasis HLB cartridges using sequential elution with methanol/MTBE (1:9 VR) and methanol [135]. DEET [162], Bayrepel [162, 163], and the metabolite Bayrepel-acid [163] were extracted from wastewater and surface water using a combination of LiChrolute EN (Merck; Darmstadt, Germany) and C18. Bayrepel and DEET were eluted with acetone/ethyl acetate (1:1 VR). Bayrepel-acid was then eluted with methanol. Typical sample volumes in these

studies were 0.5–1 L. DEET was concentrated from 10 L to 20 L seawater using the polymeric styrene-divinylbenzene sorbent SDB-1 (J.T. Baker; Phillipsburg, PA, USA) followed by elution with ethyl acetate and hexane/ethyl acetate (4:1 VR) [164]. DEET has also been sampled with POCIS [85].

DEET appears to be stable in water samples. DEET did not degrade in unpreserved surface water samples stored for 14 days at 4 °C [135]. It was also unaffected by the addition formaldehyde or sulfuric acid used for the preservation of other target analytes [135].

Sediments

PFE with water/isopropanol (1:1 VR) was used to extract DEET from surficial and suspended sediments [100]. The extracts were loaded onto modified PS-DVB, washed with water, and dried under vacuum. Compounds were eluted from the modified PS-DVB and through a sodium sulfate/Florisil cartridge with dichloromethane/diethyl ether (4:1 VR).

Derivatization

Bayrepel-acid was derivatized to its methyl ester with diazomethane (Fig. 3) for GC/MS analysis [163].

Detection and quantification

DEET is typically analyzed by GC/EI-MS using splitless injection, a 5% polyphenylmethylsilicone or similar capillary column, and SIM [1, 57, 58, 85, 100, 136, 137, 158–160, 162, 164]. It has also been quantified by LC/MS/MS with separation using a Synergi Max-RP C12 column (250 mm×4.6 mm i.d.; 4 μm particle size; Phenomenex; Torrance, CA, USA) a gradient solvent program consisting of 0.1% formic acid in water and methanol, and positive electrospray ionization [135]. There has been one report of an online SPE/LC/MS/MS method for DEET [165]. DEET was among 40 different analytes concentrated from 100 mL water samples using PLRP-S columns (10 mm×2 mm i.d.; Polymer Laboratories; Amherst, MA, USA) with online desorption with acetonitrile. Analytes were separated using a Supelcosil LC-18-DB column (250 mm×4.6 mm i.d.; 5 μm particle size; Supelco; St. Louis, MO, USA) and a solvent gradient

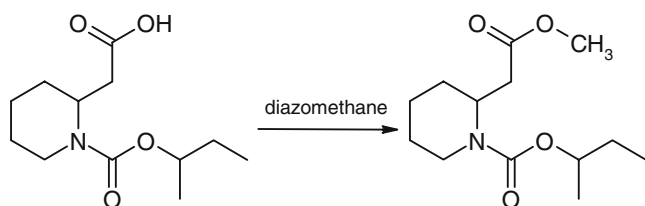


Fig. 3 Derivatization of Bayrepel acid with diazomethane [163]

consisting of methanol/water (5:95 VR) and methanol, each with a glacial acetic acid volume fraction of 3 mL/L followed by positive atmospheric pressure chemical ionization. DEET has also been quantified by field-amplified concentration with micellar electrokinetic chromatography (FAC/MEKC) [161]. Bayrepel was analyzed with DEET by GC/EI-MS [162, 163]. Bayrepel-acid has been analyzed by LC/ESI(-)MS and its methyl derivative by GC/EI-MS [163]. Typical ions monitored for each compound using each type of analysis are listed in Table S7 of the Electronic Supplementary Material.

Isotopically labeled standards for these compounds are not commercially available for use as recovery or injection standards. Compounds that have been used include atrazine-*d*₅ and ¹⁵N₂-caffeine (Table S8 in the Electronic Supplementary Material). It is unclear whether these compounds are good surrogate compounds for insect repellents.

Parabens

Sample extraction, preparation, detection, and quantification

Water

There have been few methods published for parabens in environmental matrices (Table 15). Methylparaben, ethylparaben, propylparaben, and benzylparaben were extracted from filtered water samples with 31 other compounds using Oasis HLB cartridges [166]. LC/ESI(-) MS/MS (ion trap) was used for quantification. Separation was achieved with a C18 HPLC column (C18 Luna; 100 mm×2 mm, 3 μm; Phenomenex; Torrance, CA, USA). The transition from [M-1]⁻ to [M-alkyl-1]⁻ or [M-alkyl-2]⁻ was used for quantification of each compound. These transitions were 151>136, 165>137, 179>137, and 227>136 for methylparaben, ethylparaben, propylparaben, and benzylparaben, respectively. The recovery standard was *d*₂-estradiol. Good recoveries (91.1–104.5%) and reproducibility [relative standard deviation (RSD)<20%] were found in experiments using river water fortified at 10 ng/L, 40 ng/L, and 400 ng/L.

Methylparaben, ethylparaben, propylparaben, and butylparaben were among 21 compounds extracted from WWTP influent and effluent using Oasis MAX cartridges. Prior to extraction, the samples were filtered and acidified to pH 3. After extraction, the Oasis MAX was washed with a methanol/sodium acetate solution, and the analytes were eluted with methanol. Acidic compounds were then eluted with 2% (VF) formic acid in methanol. After extraction, the parabens were derivatized with pentafluoropropionic acid

Table 15 Methods for parabens in environmental matrices

Matrix	Analytes	Extraction and preparation	Analysis method	Column (length × i.d.; film thickness)	Rec. (%)	Ref.
Surface water, WWTP effluent, industrial effluent	Methylparaben, ethylparaben, benzylparaben, propylparaben	1. SPE (Oasis HLB) 2. Eluent: MTBE/ <i>i</i> PrOH (9:1 VR)	LC/MS/MS	Luna C18 (100 mm × 2 mm; 3 μm)	91–104	[166]
WWTP influent and effluent	Methylparaben, propylparaben, ethylparaben, butylparaben	1. Acidified to pH 3 2. SPE (Oasis MAX) 3. Eluent: MeOH 4. Compounds were derivatized with PFPFA	GC/MS	RTX-5Sil MS (30 m × 0.25 mm; 0.25 μm)	87–99	[121]
Indoor air	Methylparaben, ethylparaben, butylparaben	1. 4–14 m ³ air was sampled using XAD-2 resin sandwiched between two PUF plugs 2. PUF plugs were extracted with DCM (shaker) 3. Compounds were derivatized with BSTFA	GC/MS	DB-5MS (60 m × 0.25 mm)	NR	[167]
House dust	Methylparaben, ethylparaben, butylparaben	1. Acidified then extracted with DCM (sonication) 2. Compounds were derivatized with BSTFA	GC/MS	DB-5MS (60 m × 0.25 mm)	NR	[167]

Solvent abbreviations: *Acet* acetone; *ACN* acetonitrile; *CHex* cyclohexane; *DCM* dichloromethane; *DE* diethyl ether; *EtOH* ethanol; *EtAc* ethyl acetate; *Hex* hexane; *iPrOH* isopropanol; *MeOH* methanol; *MTBE* methyl-*tert*-butyl ether; *Pent* pentane; *PE* petroleum ether; *Tol* toluene

anhydride (PFPFA) for GC/EI-MS analysis (Fig. 4). The separation was performed with an Rtx-5Sil column (30 m × 0.25 mm; 0.25 μm; Restek; Bellefonte, PA, USA). The derivatized parabens were quantified using SIM and their [M-alkyl]⁺ ions (*m/z*=267). The closest eluting recovery standard was Bisphenol A-*d*₁₆. Good recoveries (87–99%) and reproducibility (RSD <10%) were found in experiments using distilled water fortified at 0.1 μg/L and 1 μg/L.

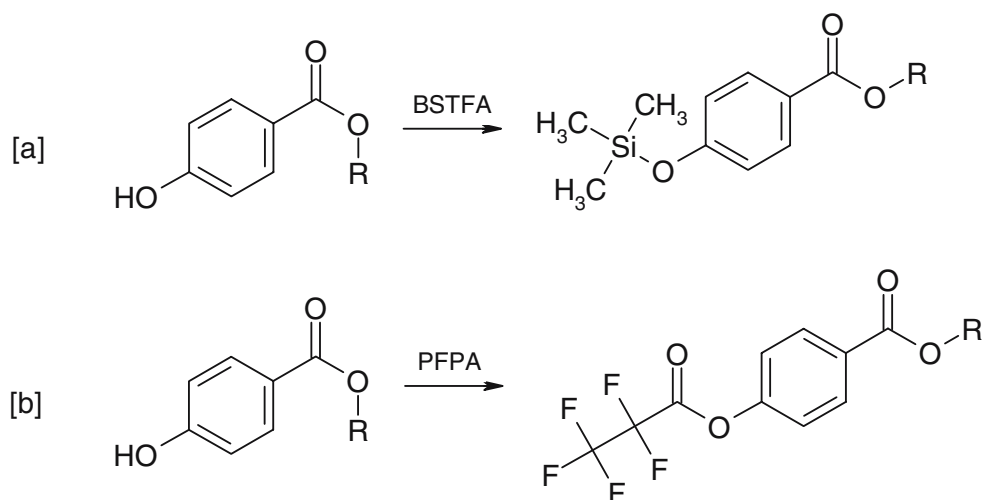
Using the reported detection limits (10 ng/L and 0.2–0.5 ng/L) and correcting for differences in sample volumes

(1 L and 0.5 L), final extract volumes (1 mL and 0.2 mL), and injection volumes (1 μL and 50 μL) between the two methods, the on-column detection limits of the GC/MS and LC/MS/MS methods are similar (10 pg and 10–50 pg, respectively).

Indoor air and house dust

Methylparaben, ethylparaben, and butylparaben were measured in indoor air and house dust using GC/MS after

Fig. 4 Derivatization of parabens with *A* BSTFA [167] and *B* PFPFA [121] for GC analysis



derivatization with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Fig. 4) [167]. These compounds were concentrated from air with XAD-2 resin sandwiched between two PUF plugs. The XAD-2 and PUF sorbents were extracted by shaking with dichloromethane. House dust was extracted by sonication with dichloromethane after acidification. After derivatization, the analytes were quantified by GC/MS (SIM; 30 m×0.25 mm DB-5MS column) using 3,4,5-trichlorophenol as the recovery standard. Additional information about the analysis of parabens is listed in Tables S9 and S10 of the Electronic Supplementary Material.

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Disclaimer Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best for the purpose.

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