Available online at www.sciencedirect.com
ScienceDirect
Journal of Chromatography A, 1190 (2008) 253–262
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of household chemicals using gas chromatography and liquid chromatography with tandem mass spectrometry

Rebecca A. Trenholm [a,*], Brett J. Vanderford [a], Jörg E. Drewes [b], Shane A. Snyder [a]

[a] *Applied Research and Development Center (ARDC), Water Quality Research and Development Division, Southern Nevada Water Authority, 1350 Richard Bunker Road, Henderson, NV 89015, USA*
[b] *Advanced Water Technology Center (AQWATEC), Environmental Science and Engineering Division, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA*

Received 20 November 2007; received in revised form 1 February 2008; accepted 7 February 2008
Available online 14 February 2008

Abstract

A method has been developed for the determination of 24 household high production volume (HPV) chemicals in municipal wastewater systems using solid-phase extraction (SPE) and analyses using both gas chromatography and liquid chromatography, each with tandem mass spectrometry (GC–MS/MS and LC–MS/MS). Target compounds include pesticides, antioxidants, fragrances, plasticizers, preservatives and personal care products. Method reporting limits ranged from 0.1 to 100 ng/L in water and recoveries for most compounds were between 54 and 112%. Household HPVs were consistently detected in raw sewage entering three full-scale wastewater treatment plants. Compounds such as vanillin, DEET, benzophenone, 3-indolebutyric acid, bisphenol A, triclosan and triclocarban were detected in all wastewater influent and effluent samples, but were significantly lower in the effluent. Many of the remaining compounds were detected in the influent, but below detection in effluent samples. Menthol and phenoxyethanol had the highest observed concentrations in influent samples ranging from 1.5 to 13 μg/L for menthol, and 8.8 to 22 μg/L for phenoxyethanol. MGK-11, methylresorcinol, trifluralin, hexabromododecane, acriflavin and atrazine were not detected in any samples. The method described here detects a broad range of HPV chemicals with great sensitivity and selectivity.

Keywords: Household chemicals; High production volume (HPV) chemicals; Solid phase extraction; Gas chromatography; Liquid chromatography; Tandem mass spectrometry

1. Introduction

Households regularly use products containing organic compounds that ultimately enter municipal wastewater systems and may not be completely eliminated during water treatment. Of the total number of consumer product chemicals the United States Environmental Protection Agency (EPA) has identified, approximately 500 are considered high production volume (HPV) chemicals [1]. Chemicals considered to be HPV in the United States are those that are manufactured in or imported into the U.S. in amounts equal to or greater than one million pounds per year. The EPA estimates that there are more than 15,000 HPV chemicals manufactured or imported into the U.S., of which 3000 are organic chemicals (excluding polymers) [1]. Approximately 43% of the 3000 organic HPV chemicals have never been evaluated for toxicity or environmental impact considering six hazardous endpoints set by the United Nations Environmental Program (UNEP) in the Screening Information Data Set (SIDS) [1,2].

The great interest in trace organic pollutants has lead to an increased awareness of trace contaminants including HPV chemicals. The lack of information both on the safety of HPV chemicals and other organic compounds used in household products is posing a challenge for the water industry. Based on previous research and method development in the determination of trace pharmaceuticals, suspected endocrine disruptors and personal care products [3–5], this study developed a similar analytical approach to determine select HPV household chemicals (Table 1) in raw sewage and treated wastewater effluents.

A comprehensive list of household chemicals was initially derived from a database offered by the National Institutes of Health's (NIH) National Library of Medicine (NLM) [6]. From

* Corresponding author. Tel.: +1 702 856 3658; fax: +1 702 856 3647.
E-mail address: beck.trenholm@snwa.com (R.A. Trenholm).

0021-9673/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2008.02.032

Table 1
Target compounds, use and structures

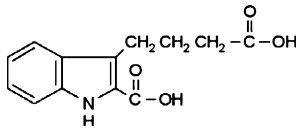
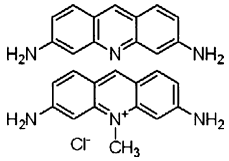
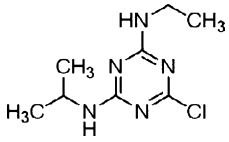
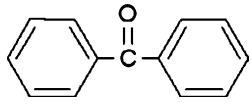
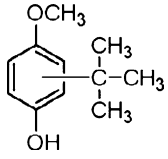
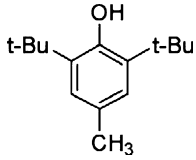
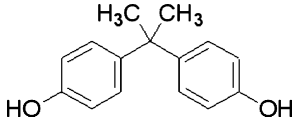
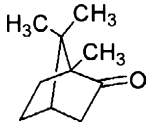
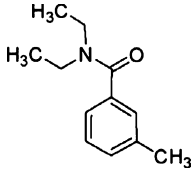
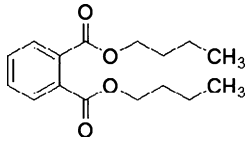
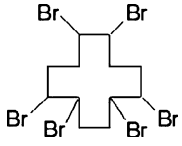
Compound	Use/tier	Structure
3-Indolebutyric acid	Plant growth regulator, root stimulator	
Acriflavine	Topical antiseptic	
Atrazine	Herbicide	
Benzophenone	UV blocker, flavor agent, fragrance	
BHA (butylated hydroxy anisole)	Antioxidant	
BHT (butylated hydroxy toluene)	Antioxidant	
Bisphenol A	Plasticizer	
Camphor	Fragrance, antipruritic, flavor agent	
DEET	Mosquito repellant	
Dibutyl phthalate	Plasticizer	
Hexabromododecane	Flame retardant	

Table 1 (*Continued*)

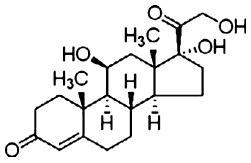
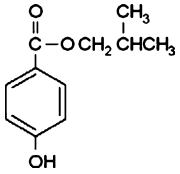
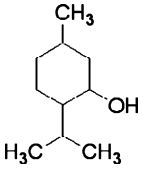
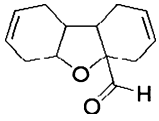
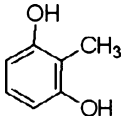
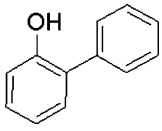
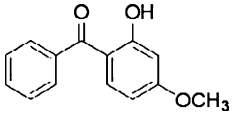
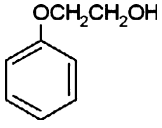
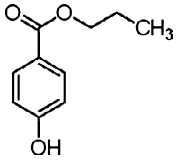
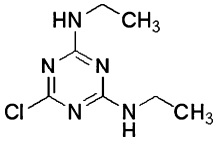
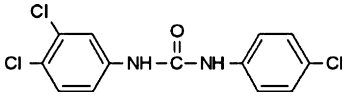
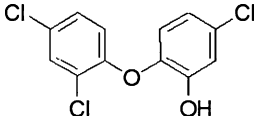
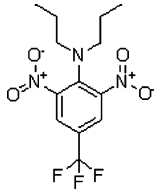
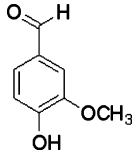
Compound	Use/tier	Structure
Hydrocortisone	Anti-inflammatory	
Isobutylparaben	Preservative	
Menthol	Antipruritic, flavor agent, fragrance, pesticide	
MGK-11	Insect repellent	
Methylresorcinol	Hair dye	
o-Phenylphenol	Germicide	
Oxybenzone	UV blocker	
Phenoxyethanol	Preservative	
Propylparaben	Preservative	
Simazine	Herbicide	
Triclocarban	Antibacterial	
Triclosan	Antibacterial	

Table 1 (*Continued*)

Compound	Use/tier	Structure
Trifluralin	Herbicide	
Vanillin	Flavor agent, fragrance	

this database, approximately 720 organic and inorganic compounds were identified that fall within eight commodities: (1) auto products, (2) inside the home, (3) pesticides, (4) home maintenance, (5) personal care/use, (6) pet care, (7) arts and crafts, and (8) landscape/yard. However, only organic compounds were targeted in this study. The following databases were then used to evaluate production volumes of the identified compounds:

(1) International Council of Chemical Associations (ICCA) HPV Working List of chemicals which includes chemicals considered HPV by various governments or industries (i.e., North America, Europe, or Japan) [7].
(2) United States EPA's Toxic Substances Control Act Inventory Update Rule (TSCA IUR) database, which provides information on organic chemicals that are manufactured in, or imported into, the United States in amounts equal to or exceeding 10,000 pounds per year [8].
(3) European Chemical Substances Information System database (ESIS) which reports on chemicals being produced or imported in quantity of at least 1000 metric tons (equivalent of 2.2 million pounds) per year in the European Union (EU) [9].

The selection of compounds identified for further study and determination were based on production volumes, environmental relevance and feasibility for analytical quantification. The initial selection of chemicals included only those compounds listed in the EPA's Inventory Update Rule (IUR) database [8] with yearly production volumes greater than one million pounds per year and which are likely present in domestic wastewater due to their physicochemical properties (i.e., moderate to high water solubility, low volatilization potential) and reported environmental fate. Triclocarban was integrated into the target compound list because triclocarban can function as a model for emerging contaminants for which only a limited amount of data were available at the time of study initiation [10,11]. The final selection of compounds targeted in this study is summarized in Table 1. Samples were extracted by solid-phase extractions (SPE) and analyzed using GC–MS/MS and LC–MS/MS. The research method described here encompasses a unique collection and wide range of HPV household chemicals, which was applied as a screening method to determine their occurrence in wastewater influent and effluent samples. Preliminary results, based off of a limited upon sampling events, suggest that many of the HPV chemicals were removed through the wastewater treatment processes evaluated.

2. Experimental

2.1. Chemicals and reagents

All standards and reagents used were of the highest purity commercially available. All standards were obtained from Sigma–Aldrich (St. Louis, MO) except MGK-11 and trifluralin from Riedel-de Haën (Seelze, Germany); atrazine and simazine from Ultra Scientific (North Kingstown, RI); butylated hydroxytoluene-d_{24} from C/D/N Isotopes (Quebec, Canada); and [$^{13}C_6$]-vanillin, [$^{13}C_6$]-α-BHC, [$^{13}C_6$]-*o*-phenylphenol, [$^{13}C_{12}$]-bisphenol A, [$^{13}C_3$]-simazine, [$^{13}C_3$]-atrazine, [$^{13}C_{12}$]-triclosan, DDD-d_8 and dibutyl phthalate-d_4 from Cambridge Isotope Laboratories (Andover, MA). All solvents were of the highest purity available and were obtained from Burdick and Jackson (Muskegon, MI), except formic acid and methyl-*t*-butyl ether (MTBE) from EM Science (Gibbstown, NJ) and ammonium acetate from J.T. Baker (Phillipsburg, NJ).

2.2. Sample collection and preservation

Full-scale monitoring for this study was carried out at three wastewater treatment facilities serving a major metropolitan area located in the western United States. During full-scale occurrence monitoring, WWTP influents (sewage), as well as treated and disinfected effluent samples, were collected as composites over a 24-h period. Samples were collected using existing dedicated facility autosamplers employed for quality and compliance purposes. Samples were collected directly into a single, 10-L glass container housed in a refrigerated cabinet. All samples were filtered onsite through 90 mm glass fiber (GF/F) filters (Whatman, England) and then collected in 1-L pre-cleaned, silanized amber glass bottles (Eagle-Picher, Miami, OK). Each bottle contained 1 g sodium azide for preservation and 1 mL of 50 μg ascorbic acid solution to quench any residual chlorine.

Sample bottles were kept cold while transporting back to the laboratory. Once received, samples were stored at 4 °C until extraction. All samples were extracted within 14 days of collection. Typically a 500 mL aliquot was used for each separate SPE method corresponding to GC–MS/MS or LC–MS/MS analysis. For some influent and tertiary treated samples, only a 50–100 mL aliquot of sample was used to help minimize matrix interferences for LC–MS/MS analysis.

2.3. Solid-phase extraction for GC–MS/MS

Five hundred milliliters samples were extracted in batches of six using 200 mg hydrophilic–lipophilic balance (HLB) glass SPE cartridges from Waters Corp. (Milliford, MA). All extractions were performed using an Autotrace automated SPE system (Caliper Life Sciences, Hopkington, MA). The HLB cartridges were sequentially preconditioned with 5 mL dichloromethane (DCM), 5 mL MTBE, 5 mL methanol, and 5 mL reagent water (Barnstead Nanopure). Samples were spiked with 0.25 μg of surrogate standards [$^{13}C_6$]-*o*-phenylphenol, BHT-d_{24}, dibutyl phthalate-d_4 and 1.0 μg of [$^{13}C_6$]-vanillin. Samples were loaded onto SPE cartridges at 15 mL/min. After sample loading, the SPE cartridges were rinsed with 5 mL reagent water and dried using nitrogen for 30 min. The SPE cartridges were eluted with 5 mL of 10/90 (v/v) methanol/MTBE followed by 5 mL of DCM. The combined eluents were collected in a 15 mL calibrated glass vial (Caliper Life Sciences, Hopkington, MA) and concentrated with a gentle stream of nitrogen to 5 mL using a TurboVap (Caliper Life Sciences). The extract was dried over 1 g of sodium sulfate and transferred to another 15 mL calibrated glass vial. The sodium sulfate was rinsed twice with 1 mL of DCM and combined with the sample extract. The combined extract was concentrated to 2 mL with a gentle stream of nitrogen. At this point 1 mL of *iso*-octane was added, vortexed, and further concentrated to less than 0.5 mL, at which time 0.125 μg of internal standards ([$^{13}C_6$]-α-BHC, [$^{13}C_{12}$]-methoxychlor and DDD-d_8) were added and the final volume adjusted to 500 μL with *iso*-octane.

2.4. Solid-phase extraction for LC–MS/MS

SPE for LC–MS/MS was the same as the GC–MS/MS SPE method, except for the following differences. The HLB cartridges were sequentially preconditioned with 5 mL MTBE, 5 mL methanol, and 5 mL reagent water. Samples were spiked with 0.02 μg of surrogate standards [$^{13}C_6$]-triclosan, [$^{13}C_6$]-simazine, [$^{13}C_6$]-atrazine, and 0.1 μg [$^{13}C_6$]-bisphenol A and [$^{13}C_6$]-*o*-phenylphenol. The SPE cartridges were eluted with 5 mL methanol followed by 5 mL of 10/90 (v/v) methanol/MTBE. The combined eluent was collected in a 15 mL calibrated glass vial and concentrated with a gentle stream of nitrogen to 500 μL.

2.5. Gas chromatography–mass spectrometry

A Varian (Walnut Creek, CA) CP-3800 Gas Chromatograph equipped with a CP-8400 autosampler was used for all analyses. The injector (Varian 1177) was operated in splitless mode with a Siltek™ deactivated glass liner with glass frit (Restek, Bellefonte, PA). An injection volume of 2 μL was used for all analyses. Analytes were separated on a 30 m × 0.25 mm ID × 0.25 μm DB5-MS column (J & W, Agilent, Palo Alto, CA) using 1.0 mL/min helium flow and an initial pressure pulse of 45 psi for 0.85 min. The temperature program was as follows: 90 °C, hold for 2.0 min; 90–280 °C at 7 °C/min, hold for 2.0 min; 280–315 °C at 50 °C/min, hold for 5.16 min. The injector and transfer line temperatures were at 280 °C.

Mass spectrometry was performed using a Varian 2200 ion trap mass spectrometer (Walnut Creek, CA) set at 200 °C. All analyses were performed using multiple reaction monitoring (MRM) in positive electron impact mode. For most analytes, two mass transitions were monitored. One transition was used for quantitation while the second transition was used for confirmation. Mass transitions are listed in Table 2. Vanillin and benzophenone did not have an abundant second mass transition; therefore only one transition was used. Vanillin was quantified using the sum of two product ions for improved sensitivity. An example chromatogram is shown in Fig. 1.

Table 2
GC–MS/MS and LC–MS/MS target compounds and mass transitions

Compound	Precursor ions (*m/z*)	Product ions (*m/z*)
GC–MS/MS EI positive		
Camphor	95 (108)	67 (93)
Menthol	95 (123)	67 (81)
Phenoxyethanol	138 (94)	94 (66)
Methylresorcinol	124 (95)	95 (77)
Vanillin	151	108 + 123
BHA	165 (180)	137 (165)
BHT	205 (220)	177 (205)
o-Phenylphenol	170 (141)	141 (115)
DEET	190 (119)	145 (91)
MGK-11	175 (97)	97 (79)
Benzophenone	105	77
Trifluralin	306 (264)	264 (206)
Dibutyl phthalate	149 (223)	121 (149)
Hexabromododecane	239 (319)	157 (237)
LC–MS/MS ESI positive		
Acriflavine	210	193 (166)
Hydrocortisone	363	120 (91)
Simazine	202	132 (104)
Atrazine	216	173 (103)
DEET	192	118 (91)
Oxybenzone	229	150 (104)
LC–MS/MS ESI negative		
3-Indolebutyric acid	202	157 (115)
Bisphenol A	227	211 (132)
Propylparaben	179	92 (135)
o-Phenylphenol	169	114 (141)
Isobutylparaben	193	92 (135)
BHA	179	163 (149)
Triclocarban	313	159 (125)
Triclosan	287	35 (241)

() Confirmation precursor/product ions.

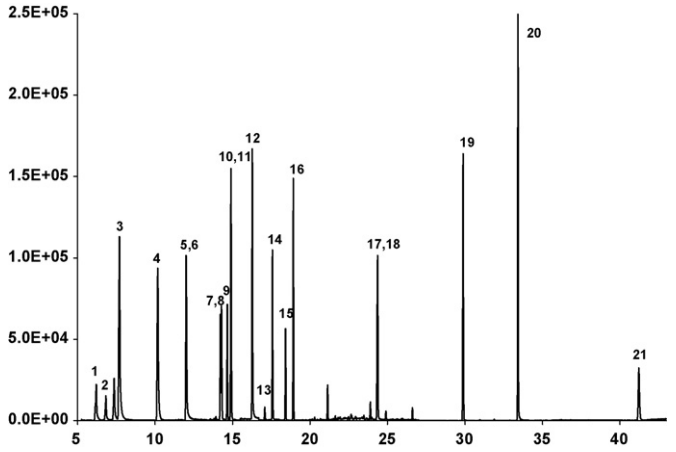


Fig. 1. GC–MS/MS TIC chromatogram of 200 μg/L standard. Key: (1) camphor, (2) menthol, (3) phenoxyethanol, (4) *m*-resorcinol, (5) vanillin, (6) $^{13}C_6$-vanillin, (7) BHA, (8) BHT-d_{24}, (9) BHT, (10) *o*-phenylphenol, (11) $^{13}C_6$-*o*-phenylphenol, (12) DEET, (13) MGK-11, (14) benzophenone, (15) trifluralin, (16) $^{13}C_6$-alpha-BHC, (17) dibutyl phthalate-d_4, (18) dibutyl phthalate, (19) DDD-d_8, (20)) $^{13}C_{12}$-methoxychlor, (21) cholecalciferol, (22) hexabromodecane.

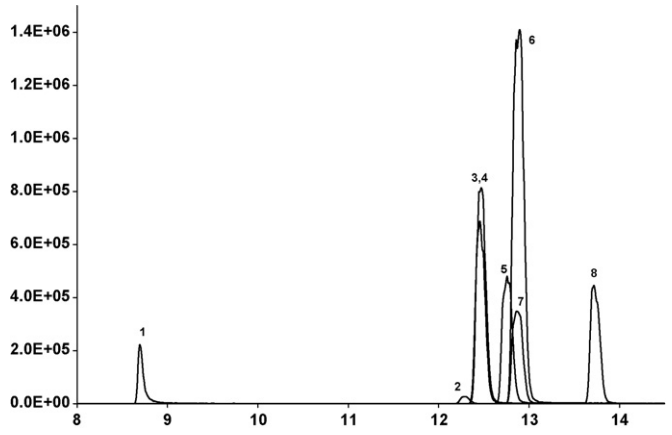


Fig. 2. LC–MS/MS ESI positive chromatogram. Key: (1) acriflavine, (2) hydrocortisone, (3) simazine, (4) $^{13}C_3$-simazine, (5) oxybenzone, (6) atrazine, (7) $^{13}C_3$-atrazine, (8) DEET.

2.6. Liquid chromatography–mass spectrometry

An Agilent G1312A binary pump (Palo Alto, CA) and an HTC-PAL autosampler (CTC Analytics, Zwingen, Switzerland) were used for all analyses. Analytes were separated using a Synergi Max-RP (Phenomenex, Torrance, CA) reverse phase column (250 mm × 4.6 mm). Electrospray ionization (ESI) was used for LC–MS/MS analysis in both positive and negative modes with each mode requiring a different mobile phase for optimal ionization. For ESI positive a dual eluent system composed of 0.1% formic acid in water (A) and 100% methanol (B) was used. A flow rate of 700 μL/min was used with a gradient as follows: 5% B held for 0.5 min, increased linearly to 100% B by 8.5 min, and held at 100% B for 6.5 min. After each run, the column was equilibrated for 9.0 min with 5% B. This resulted in a total analysis time of 24 min. ESI negative mode used a dual eluent system composing of 100 mM ammonium acetate in water (A) and 100% methanol (B). A flow rate of 700 μL/min was used with a gradient as follows: 5% B held for 0.5 min, increased linearly to 100% B by 8.5 min, and held at 100% B for 8.5 min. After each run, the column was equilibrated for 9.0 min with 5% B. This resulted in a total analysis time of 26 min. An injection volume of 10 μL was used for all analyses.

Mass spectrometry was performed using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA). All analyses were performed using MRM with electrospray ionization in both positive and negative modes. ESI positive and negative mass transitions are listed in Table 2. Source-dependent parameters for both modes are listed in Table 3. Example chromatograms of each ionization mode are shown in Figs. 2 and 3.

Table 3
LC–MS/MS source-dependent parameters

	ESI positive	ESI negative
Collision gas (psig)	8	10
Curtain gas (psig)	10	18
Ion source Gas 1–nebulizer gas (psig)	50	50
Ion source Gas 2–turbo gas (psig)	50	50
Ionspray voltage (V)	5500	−4500
Temperature (°C)	600	500
Probe *X*-axis position (mm)	5	5
Probe *Y*-axis position (mm)	5	5
Entrance potential (V)	10	10

2.7. Calibration and recoveries

Method reporting limits (MRLs) were determined based on a signal-to-noise ratio greater than 10 (Table 4). A working stock solution for GC–MS/MS compounds was prepared in methylene chloride at concentrations ranging from 10 to 40 mg/L. This stock solution was diluted to appropriate concentrations in methanol for SPE spiking and diluted into *iso*-octane for calibration standards. For LC–MS/MS compounds, a working

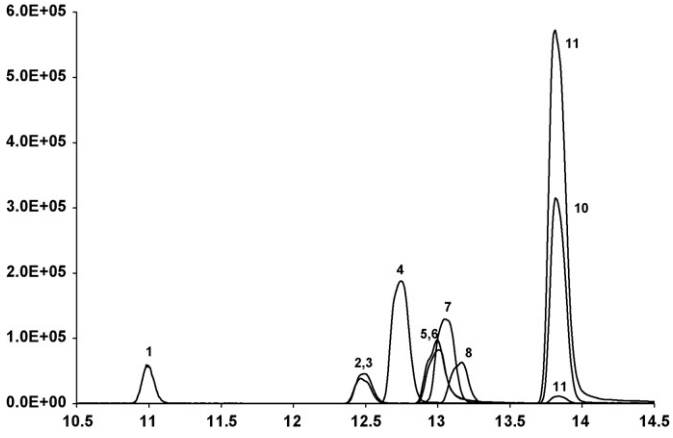


Fig. 3. LC–MS/MS ESI negative chromatogram. Key: (1) 3-indolebutyric acid, (2) bisphenol A, (3) $^{13}C_{12}$-bisphenol A, (4) propylparaben, (5) *o*-phenylphenol, (6) $^{13}C_6$-*o*-phenylphenol, (7) isobutylparaben, (8) BHA, (9) triclocarban, (10) triclosan, (11) $^{13}C_{12}$-triclosan.

Table 4
Method reporting limits (MRLs), calibration range, average percent recovery matrix spikes, relative standard deviation (RSD) or relative percent difference (RPD)

Compound	MRL (ng/L)	Calibration range (μg/L)	Average percent recovery DI water matrix spike	RSD (%)	Average percent recovery surface water matrix spike	RPD (%)	Average percent recovery WWTP effluent matrix spike	RPD (%)
GC–MS/MS			$n=7$		$n=2$		$n=2$	
Camphor	50	50–1000	70	12	76	20	81	10
Menthol	50	50–1000	75	9	86	20	105	13
Phenoxyethanol	100	100–2000	77	5	81	2	98	13
Methylresorcinol	100	100–2000	54	22	62	11	45	5
Vanillin	100	100–2000	74	17	54	14	109	24
BHA	25	25–500	75	7	88	3	127	22
BHT	25	25–500	74[a]	6	93	0	111	26
o-Phenylphenol	25	25–500	93	4	95	0	138	10
DEET	25	25–500	78	15	90	11	111	62
MGK-11	25	25–500	75	8	89	6	126	15
Benzophenone	25	25–500	87	3	101	6	163	53
Trifluralin	25	25–500	85	6	97	2	153	14
Dibutyl phthalate	25	25–500	143	23	69	49	74	11
Hexabromododecane	100	100–2000	75	11	95	1	86	15
	MRL (ng/L)	Calibration range (μg/L)	Average percent recovery DI water matrix spike	RSD (%)	Average percent recovery surface water matrix spike	RSD (%)	Average percent recovery WWTP effluent matrix spike	RSD (%)
LC–MS/MS			$n=7$		$n=3$		$n=3$	
Acriflavine	1.0	1.0–100	61	14	70	4	17	3
Hydrocortisone	1.0	1.0–100	89	10	53	6	30	2
Simazine	1.0	1.0–100	73	20	78	4	52	3
Atrazine	1.0	1.0–100	76	19	81	4	54	1
DEET	0.1	0.1–10	70	21	na[b]	na[b]	na[b]	na[b]
3-Indolebutyric acid	1.0	1.0–100	46	59	32	11	13	28
Oxybenzone	1.0	1.0–100	67	12	0	0	12	19
Bisphenol A	10	10–1000	111	6	84	1	70	11
Propylparaben	0.25	0.1–10	112	10	88	2	40	4
o-Phenylphenol	10	10–1000	82	13	115	3	119	3
Isobutylparaben	0.25	0.1–10	110	7	98	5	58	3
BHA	1.0	1.0–100	83	11	105	2	99	5
Triclocarban	0.25	0.1–10	75	7	17	7	na[b]	na[b]
Triclosan	1.0	1.0–100	109	10	64	7	na[b]	na[b]

[a] $n=6$.
[b] na = data not available due to matrix spike not visible above the baseline concentrations already present in the matrices.

Table 5
Compounds detected in blank reagent water, average concentrations and frequency of occurrence ($n = 7$)

Compound	Average concentration (ng/L)	Frequency of occurrence (%)
Dibutyl phthalate	130	100
DEET	0.27	71
Oxybenzone	1.3	43
Propylparaben	0.29	43
Isobutylparaben	0.29	14
Triclocarban	0.17	43
Triclosan	1.6	43

stock solution was prepared in methanol at concentrations ranging from 0.25 to 25 mg/L. This stock solution was diluted to appropriate concentrations in methanol for SPE spiking and calibration standards. Calibration curves for both analytical methods contained at least six points with the lowest point being at or just below the MRL. Calibration ranges are listed in Table 4. Quantitation was performed using internal standard calibration for GC–MS/MS and external standard calibration for LC–MS/MS. Both used linear or quadratic fit, depending on analyte response, with correlation coefficients of 0.990 or higher. Calibration verifications were analyzed at least every six samples to ensure instrument performance. Isotopically labeled surrogate standards were added to samples prior to extraction to monitor the extraction efficiency. Spike recovery tests were conducted in reagent water, surface water, and wastewater effluent. Recoveries and relative standard deviation (RSD) results are provided in Table 4. For matrix spikes in which only duplicate samples were done, a relative percent difference (RPD) was applied. A laboratory blank was extracted along with every batch of samples. Compounds detected in laboratory blanks are listed in Table 5 along with the corresponding average concentration and frequency of detection.

3. Results and discussion

3.1. Target compound selection

The analytical approach developed during this study was intended to encompass a variety of household compounds for occurrence screening, but during method development some original target compounds were excluded for various reasons. One such compound was cholecalciferol, also known as vitamin D3, which was excluded because of instrumental complications. Both the LC–MS/MS and GC–MS/MS exhibited low detector responses for this compound. Other compounds that were excluded due to poor instrument response included FD&C Yellow #5, folic acid, farnesol and avobenzone. A few compounds were found to exhibit good responses and sensitivity in both instrumental methods investigated. These compounds included DEET, BHA and *o*-phenylphenol. These three compounds were analyzed by both methods for data comparison and additional quality control.

3.2. Solid-phase extraction

During SPE development, glass and plastic HLB cartridges were compared. While recoveries were similar between the different cartridges, the use of plastic cartridges resulted in high levels of BHT contamination, which ranged from approximately 1 to 2 μg/L. Background levels of BHT decreased to below 25 ng/L using glass cartridges; therefore, these were chosen for extraction to minimize background contamination.

For the GC–MS/MS compounds various SPE elution solvents were tested. A single elution with 10 mL of DCM was compared with an elution using a combination of 5 mL 10/90 (v/v) methanol/MTBE followed by 5 mL of DCM. Using only DCM for elution resulted in poor recoveries of methylresorcinol (0%), but acceptable recoveries for the other target compounds (data not shown). When 5 mL 10/90 (v/v) methanol/MTBE followed by 5 mL of DCM elution was applied, the recovery of methylresorcinol increased to 54% in reagent water without affecting the other compounds. Therefore, the latter was used for SPE elution of GC–MS/MS compounds.

3.3. Matrix spikes and recoveries

Some compound recoveries in spiked wastewater effluent samples were greater than recoveries in DI and surface waters (i.e., vanillin and BHA). This was likely due to their presence in the unspiked effluent sample. However, environmental levels were slightly below the reporting limit and therefore, because the detection could not be reported, no recovery adjustment could be performed. Dibutyl phthalate exhibited acceptable SPE recoveries, but had detectable and variable background contamination due to the extraction process, resulting in higher RSDs. However, because the background contamination levels were relatively low compared to the environmental levels observed in wastewater influent, it was not excluded from the target compound list. In relation to the other analytes, 3-indolebutyric acid extraction recoveries were not ideal with low recoveries and high RSDs. Because its environmental levels were well above the method reporting limit, it also remained in the method. However, data reported for 3-indolebutyric acid are associated with a higher degree of uncertainty and should be viewed accordingly.

Oxybenzone and triclocarban were promising during method development in reagent water, but exhibited poor recoveries in matrix spikes, therefore, results for oxybenzone and triclocarban should be viewed qualitatively. During method development, extractions were performed at a variety of adjusted pH values (data not shown). It was determined that oxybenzone had increased recoveries at pH less than 7 and poor recoveries above pH 7. The pH of the reagent water typically ranged from 5.0 to 6.5, whereas the surface water and wastewater effluent ranged between pH 7.3 and 8.1, respectively. This agrees with previous research analyzing pharmaceutical residues and personal care products in aqueous samples in which samples were acidified to pH 2 prior to extraction [3]. Triclocarban also exhibited poor recoveries in surface water and wastewater effluent matrix spikes. Previous research has suggested that triclocarban will readily bind to natural organic matter (NOM) and sediment

Table 6
Occurrence of HPV chemicals in sewage and treated wastewater composite samples collected at three WWTPs (ng/L)

	Facility 1				Facility 2			Facility 3	
Collection Date:	Influent 1/25/06	Final Effluent 1/25/06	Influent 7/23/06	Final Effluent 7/23/06	Influent 9/20/05	Tert Effluent 9/20/05	Final Effluent 3/08/06	Tert Effluent 3/14/06	Final Effluent 3/14/06
GC–MS/MS									
Camphor	160	<50	1800	<50	1700	<50	<50	<50	<50
Menthol	3200	<50	13000	<50	15000	<50	<50	<50	<50
Phenoxyethanol	8800	<100	17000	<100	22000	210	<100	140	<100
Methylresorcinol	<100	<100	<100	<100	<100	<100	<100	<100	<100
Vanillin	1600	470	2000	190	2100	230	150	850	290
BHA	52	39	220	<25	230	<25	<25	57	<25
BHT	43	35	410	43	390	26	<25	150	240
o-Phenylphenol	99	<25	550	27	340	<25	<25	<25	<25
DEET	54	120	470	190	600	210	100	250	260
MGK-11	<25	<25	<125	<25	<25	<25	<25	<25	<25
Benzophenone	110	71	1400	65	1200	150	120	63	72
Trifluralin	<25	<25	<25	<25	<25	<25	<25	<25	<25
Dibutyl phthalate	390	180	2400	150	3100	760	210	2300	1300
Hexabromododecane	<100	<100	<500	<100	<100	<100	<100	<100	<100
LC–MS/MS									
Acriflavine	<10	<5.0	<10	<5.0	<5.0	<1.0	<1.0	<1.0	<1.0
Hydrocortisone	280	<5.0	370	38	270	<1.0	<1.0	<1.0	<1.0
Simazine	<10	<5.0	<10	<5.0	<5.0	1.8	<1.0	<1.0	<1.0
Atrazine	<10	<5.0	<10	<5.0	<5.0	<1.0	<1.0	<1.0	<1.0
DEET	59	51	180	110	270	91	82	210	200
Oxybenzone	300	<5.0	2300	13	860	<1.0	<1.0	2.6	1.1
3-Indolebutyric acid	2600	290	1300	170	1300	89	100	270	260
Bisphenol A	220	2600	530	1600	200	170	1900	1200	860
Propylparaben	2000	2.6	760	3.7	1500	0.40	<0.25	0.78	0.26
o-Phenylphenol	420	<50	360	<50	280	<10	<10	22	<10
Isobutylparaben	390	<1.25	83	3.6	300	0.29	<0.25	0.50	0.31
BHA	160	26	190	<5.0	160	<1.0	<1.0	50	3.3
Triclocarban	77	110	49	99	350	18	26	130	130
Triclosan	860	43	770	110	1500	14	3.4	93	18

[10]. Although every precaution was taken to minimize problems associated with matrix suppression during LC–MS/MS analysis, it was also observed that triclocarban was particularly sensitive to ionization suppression. The combination of binding and suppression may have contributed to its poor recoveries. In addition, matrix spike recoveries were difficult to calculate for triclocarban and triclosan in the wastewater effluents because of the elevated environmental levels, making it difficult to accurately calculate the difference in concentration resulting from the spike. This was also the case for DEET in the wastewater effluent and the surface water matrix spikes for LC–MS/MS.

3.4. Occurrence of household chemicals in wastewater systems

Composite samples of raw sewage and treated and disinfected wastewater effluents were collected at three full-scale tertiary WWTPs. All three WWTPs employ activated sludge achieving nitrification/denitrification as the biological treatment step. For disinfection, Facility 1 uses UV, Facility 2 uses chlorination and Facility 3 uses chloramination. Out of the 24 HPV household chemicals targeted in this study, seven compounds (i.e., methylresorcinol, MGK-11, triflualin, hexabromododecane, acriflavine, simazine, and atrazine) were not detected in raw sewage, treated tertiary effluents or final (post disinfection) effluents (Table 6). Pesticides, such as acriflavine, simazine, and atrazine, are applied outside the home with fewer opportunities, except for urban run-off, to enter a sewer system. Trifluralin and hexambromododecane also exhibit highly hydrophobic properties (i.e., $\log K_{ow}$ values exceeding 5.3), which limits their solubility in water. The highest concentrations in raw sewage approaching the low part-per-billion (μg/L) range were detected for phenoxyethanol, a preservative used in many household products, and menthol, a fragrance. Both compounds, however, were reduced to concentration levels close to or below the reporting limits in treated wastewater effluents. Vanillin, DEET, BHT, benzophenone, dibutyl phthalate, 3-indolebutyric acid, bisphenol A, and triclosan were consistently detected in concentration ranges from several tenths to several hundred parts-per-trillion (ng/L) in treated wastewater effluents. These findings suggest that conventional wastewater treatment plants are capable of removing HPV chemicals with efficiencies varying between 65 and 99%. Although degradation and disinfection by-products may still be present, for the scope of the work presented here, removal is defined as the absence of the parent compound.

4. Conclusions

In this study an analytical approach using GC–MS/MS and LC–MS/MS was developed to determine HPV household chemicals. Twenty-four target analytes were selected from a comprehensive list of approximately 720 compounds identified based on production volumes, environmental relevance and feasibility for analytical quantification. Seven of 24 target household chemicals were not detected in raw sewage. Findings suggest that conventional wastewater treatment plants can partially remove HPV household chemicals but certain compounds are still present in treated effluents at low ng/L-level concentrations.

Acknowledgements

The authors thank the Water Environment Research Foundation (WERF) for its financial, technical, and administrative assistance in funding and managing the project through which this information was derived. The authors also gratefully acknowledge the financial contributions from the WateReuse Foundation (WRF). The comments and views detailed herein may not necessarily reflect the views of WERF or WRF, its officers, directors, affiliates or agents. The research on which this report is based was funded, in part, by the United States Environmental Protection Agency through Cooperative Agreement No. CR827345-01 with WERF. The authors are also grateful to the participating utilities for their technical and administrative support. The authors would like to thank Janie Zeigler for all her assistance in method development and project coordination.

References

[1] United States Environmental Protection Agency (EPA) (2002): Chemical hazard data availability study. www.epa.gov/chemrtk/hazchem.htm (last updated 9-17-2002).
[2] P.J. Landrigan, Disease of the environmental origin in American children: prospects for research and prevention. Testimony before the Committee on Appropriations U.S. House of Representatives. Washington, D.C., 2000.
[3] B.J. Vanderford, R.A. Pearson, D.J. Rexing, S.A. Snyder, Anal. Chem. 75 (2003) 6265.
[4] R.A. Trenholm, B.J. Vanderford, J.C. Holady, D.J. Rexing, S.A. Snyder, Chemosphere (2006) 1990.
[5] B.J. Vanderford, S.A. Snyder, Environ. Sci. Technol. (2006) 7312.
[6] National Institutes of Health & U.S. National Library of Medicine (2004): Medline Plus Drug information. http://www.nlm.nih.gov/medlineplus/druginformation.html (last updated August 2004).
[7] International Council of Chemical Associations (ICCA) (2004): ICCA HPV working list. http://www.cefic.org/activities/hse/mgt/hpv/hpvinit.htm.(last updated June 2004).
[8] United States Environmental Protection Agency (EPA) (2003): Inventory Update Rule. http://www.epa.gov/opptintr/iur (last updated: 12-10-2003).
[9] European Chemicals Bureau (ECB) (2004): European Chemicals Substances Information System (ESIS). http://ecb.jrc.it.
[10] R.U. Halden, D.H. Paull, Environ. Sci. Technol. (2005) 1420.
[11] J. Heidler, A. Sapkota, R.U. Halden, Environ. Sci. Technol. (2006) 3634.