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Simultaneous determination of benzotriazoles and ultraviolet filters in ground water, effluent and biosolid samples using gas chromatography–tandem mass spectrometry

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ABSTRACT

A new method using gas chromatography–tandem mass spectrometry (GC–MS/MS) was developed for the determination of four benzotriazoles, i.e. benzotriazole (BT), 5-methylbenzotriazole (5-TTri), 5-chlorobenzotriazole (CBT), 5,6-dimethylbenzotriazole (XTri), and six UV filters, i.e. benzophenone-3 (BP-3), 3-(4-methylbenzylidene)camphor (4-MBC), octyl 4-methoxycinnamate (OMC), 2-(3-t-butyl-2-hydroxy-5-methylphenyl)-5-chloro benzotriazole (UV-326), 2-(2′-hydroxy-5′-octylphenyl)-benzotriazole (UV-329), and octocrylene (OC) in ground water, effluent and biosolid samples. Solid phase extraction (SPE) and pressurized liquid extraction (PLE) were applied as the preconcentration method for water samples (ground water and effluent) and biosolid samples, respectively. The optimized method allowed us to quantify all target compounds with the method detection limits ranging from 0.29 to 11.02 ng/L, 0.5 to 14.1 ng/L and 0.33 to 8.23 ng/g in tap water, effluent and biosolid samples, respectively. The recoveries of the target analytes in tap water, effluent and biosolid samples were 70–150%, 82–127% and 81–133%, respectively. The developed analytical method was applied in the determination of these target compounds in ground water, effluent and biosolid samples collected from Bolivar sewage treatment plants in South Australia. In effluent samples, the target compounds BT, 5-TTri, CBT, XTri and BP-3 tested were detected with the maximum concentration up to 2.2 μg/L for BT. In biosolid samples, eight out of ten compounds tested were found to be present at the concentrations ranging between 18.7 ng/g (5-TTri) and 250 ng/g (4-MBC).

1. Introduction

Benzotriazoles (BTs) including the parent compound benzotriazole (BT) and its derivatives are high production volume chemicals that find broad application in various industrial processes as well as in households, e.g. as a corrosion inhibitor in dishwasher detergents and de-icing/anti-icing fluids, an ultraviolet light stabilizer in plastics, and an antifogging agent in photography. The annual usage of BTs was estimated to be about 9000 tons/year in the United States, and the global usage would be much greater [1]. These chemicals have been detected in effluents [2–4], surface water [2–8] and groundwater [5,9]. They are considered emerging contaminants due to potential adverse effects on aquatic species, microbial community and mammals [10–13]. However, it is reported that the benzotriazole (BT) was quite resistant to microbial degradation [4,14].

Ultraviolet (UV) filters have been commonly used in cosmetic formulation such as sunscreens and skin care products in order to reduce the risk of skin cancer due to overexposure to two types of harmful UV irradiation classified as UV-A and UV-B (280–400 nm wavelength ranges) by blocking UV radiation from 200 to 400 nm wavelengths [15–18]. It is reported that some UV filters such as 4-MBC and OMC could cause adverse effects of hormonal activity (estrogenic, antiestrogenic, androgenic and antiandrogenic) in both vitro and vivo tests [17,19–21]. After use, UV filters enter into the environment due to their incomplete removal in sewage treatment plants or direct discharge. It is essential to develop a sensitive and robust method to analyze these two classes of organic compounds in surface water and ground water, effluent and biosolid samples in order to assess their potential environmental impact.

There have been some reports on the determination of BTs and UV filters in environmental samples using gas chromatography–mass spectrometry (GC–MS) [8,17,22], liquid chromatography–tandem mass spectrometry (LC–MS/MS)

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[2,4,6,23], and two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOF-MS) [24]. Analysis of these organic compounds in the complex environmental samples by GC–MS and LC–MS/MS often experiences matrix effects [25–27]. Gas chromatography–tandem mass spectrometry (GC–MS/MS) has increasingly been applied in the determination of trace organic contaminants due to its extremely high selectivity and sensitivity of multiple reaction monitoring techniques (MRM) in tandem mass spectrometry, and has some advantages such as reduced matrix effects and interferences [28–30]. A summary of the reported analytical methodologies for the determination of BTs and UV filters is presented in Table 1.

Solid phase extraction (SPE) and pressurized liquid extraction (PLE) approaches are the two techniques which have been increasingly used in the extraction of organic compounds in aqueous and solid samples [31–33]. Various SPE cartridges such as C18 and HLB have been applied in the extraction of organic compounds in water samples [2,8,23]. It is known that PLE allows reduction of both extraction time and organic solvent consumption and increases sample throughput. In most of the reported applications of PLE, an exhaustive cleanup of the extracts prior to instrumental analysis is required due to matrix interferences [34,35]. In an attempt to eliminate this time-consumption step, in-cell cleanup could be applied by packing some absorbents such as modified silica, florisil and alumina as well as copper powder together with samples [29,36,37]. Analysis of BTs and UV filters in environmental samples can be improved by combining PLE (or SPE) with GC–MS/MS to reduce matrix interferences. To the best of our knowledge, there has been no report on the simultaneous determination of BTs and UV filters in water and solid samples using GC–MS/MS.

The objective of this study was to develop and validate an analytical method for simultaneous determination of four BTs and six UV filters by using GC–MS/MS technique, after sample pretreatment with SPE for ground water and effluent samples and PLE for biosolid samples. The performance of the overall SPE, PLE and GC–MS/MS method was evaluated in terms of limit of detection (LOD), quantitation (LOQ), repeatability and recovery. In order to obtain optimum recoveries for all target compounds, various SPE extraction parameters (SPE cartridge type, elution solvent and pH) for water samples and PLE operating conditions (extraction solvent, extraction temperature and extraction cycle) for solid samples were optimized. The developed method was applied to screen these selected BTs and UV filters in ground water, effluent and biosolid samples from Bolivar sewage treatment plants in South Australia.

2. Materials and methods

2.1. Chemicals and materials

High purity standards including four benzotriazoles (BTs): benzotriazole (BT, 99%), 5-methylbenzotriazole (5-TTri, 98%), 5-chlorobenzotriazole (CBT, 98%) and 5,6-dimethylbenzotriazole (XTri, 99%), and six UV filters: benzophenone-3 (BP-3, 98%), 3-(4-methylbenzylidene)camphor (4-MBC, 99%), octyl 4-methoxycinnamate (OMC, 95%), 2-(3-t-butyl-2-hydroxy-5-methylphenyl)-5-chloro benzotriazole (UV-326, 97%), 2-(2′-hydroxy-5′-octylphenyl)-benzotriazole (UV-329, 97%), and octocrylene (OC, 97%) and an internal standard benzylcinnamate (IS, 99%) were purchased from Sigma–Aldrich (Seelze, Germany), Wako (Osaka, Japan) and Dr. Ehrenstorfer GmbH (Augsburg, Germany) (Table S1). HPLC-grade methanol, n-hexane, dichloromethane, acetone and acetonitrile were purchased from Merck (Darmstadt, Germany). Anhydrous sodium sulphate (granular, 10–60 mesh, Mallinckrodt Chemicals) and silica gel (60–100 mesh, Sigma–Aldrich (St. Louis, MO, USA)) were baked at

Table 1
Summary of the reported analytical methodologies for the analysis of benzotriazoles and UV filters.

Class	Analyzed compounds	Matrix	Pretreatment method	Detection method	Recovery (%)	LOQs (ng/L)	Observed concentrations (ng/L)	References
Benzotriazoles	BT, 5-TTri, XTri	Municipal wastewater	SPE	LC–MS/MS	97–99	10–25	10–5440	[2]
	BT, 5-TTri, XTri	Municipal wastewater	SPE	LC–MS/MS	97–99	10–30	10000–100000	[3]
	BT, 5-TTri, XTri	Municipal wastewater	SPE	LC–MS/MS	95–113	5–100	nd–22000	[4,6]
	BT, 5-TTri, XTri	Municipal wastewater	SPE	GC × GC-TOF	78–115	31–198	925–17153	[24]
	BT	Groundwater	SPE	GC–MS	–	100 (LOD)	1200–1100000	[39]
	BT, 5-TTri, XTri	Lake water	LLE	GC–MS	–	–	nd–198000	[5]
		River water						
	BT, 5-TTri, XTri, CBT	Tap water	SPE	GC–MS/MS	70–108	10–37	nd	This work
		Municipal wastewater	SPE	GC–MS/MS	77–122	14–47	77–2206	This work
		Biosolid	ASE	GC–MS/MS	66–133	3–14 (ng/g)	nd–21 (ng/g)	This work
UV filters	BP-3, 4-MBC, OMC, OC	Lake water River water	SPE	GC–MS	57–90	10	nd–125	[22]
	BP-3, 4-MBC, OMC, OC	Lake water	SPE	GC–MS	78–129	2 (LOD)	2–35	[17]
		Municipal wastewater	SPE	GC–MS	78–129	10 (LOD)	nd–19000	[17]
		Fish	ASE	GC–MS	93–115	7–380 (ng/g) (LOD)	nd–72 (ng/g)	[17]
	BP-3, 4-MBC, OMC, OC,	Tap water	SPE	GC–MS/MS	71–150	1–19	nd	This work
	UV-326, UV-329	Municipal wastewater	SPE	GC–MS/MS	82–127	1.7–22	<LOQ	This work
		Biosolid	ASE	GC–MS/MS	68–130	1.1–27	32–250 (ng/g)	This work

–: not available; nd: not detected; SPE: solid phase extraction; LLE: liquid–liquid extraction; ASE: accelerate solvent extraction; LOD: method limit of detection; LOQ: method limit of quantitation.

450 °C and stored in a sealed desiccator. Copper powder (40 mesh) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Stock solutions of chemicals (100 mg/L) were prepared in acetone and stored at −20 °C for later use. Working standard solutions were prepared weekly. All glassware was hand-washed with tap water, rinsed with HPLC grade water and methanol and baked at 450 °C for at least 4 h before use.

2.2. Sample collection and preparation

Tap water from the laboratory was used in the method development for groundwater samples due to difficulty in collecting large volume of ground water. Ground water, effluent and biosolid samples were collected from Bolivar sewage treatment plants in Adelaide, South Australia. Effluent reuse is an integral part of the treatment strategy at this sewage treatment plant as it avoids the need for full nutrient removal and provides an alternative water resource for several recycling schemes. The sewage treatment plant serves a population of more than 700,000 and is designed to have dry weather flow of 148.5 ML/d with approximately 75% from domestic sources and 25% from industrial sources. The effluent samples were collected by a 24 h composite sampler and ground water samples collected from an aquifer storage and recovery well at a depth of 300 m below ground within the sewage treatment plant site. Biosolid samples were collected as the composite sludge samples from different sludge treated process (dewatered and dried using a combination of sludge drying lagoons, centrifugation and agitated air drying). The water samples (groundwater and effluent) were collected in 1 L pre-cleaned brown glass bottles, while biosolid samples were collected in 1 L glass jars. Three parallel samples were collected for each sample type. For water samples, about 50 mL of methanol was added to each bottle (1 L) and the pH was adjusted to 2 using 4 M H_2SO_4 in the field. One gram of sodium azide was added to each biosolid sample to suppress microbial activity. All the samples were kept cool during the transport to the laboratory and stored in the dark at 4 °C, and then processed within 48 h. Biosolid samples were freeze-dried, homogenized and passed through a 60 mesh standard sieve. Dried biosolid (1 g) was prepared for each extraction.

2.3. Sample extraction

2.3.1. Water sample extraction

Water samples (1 L each) were filtered through glass fiber filters (Whatman GF/F, 0.7 μm, UK) before SPE. SPE method for water samples was evaluated by testing four SPE cartridges (Oasis HLB 6 mL 500 mg, Supelco ENVI-18 6 mL 500 mg, Starta X-C-33 μm 6 mL 500 mg, Selby Biolab C18 6 mL 500 mg), five elution solvents (methanol, dichloromethane, acetonitrile, methanol/acetonitrile (50:50; v/v), and methanol/dichloromethane (50:50; v/v)), four elution volumes (1× 2 mL, 2× 2 mL, 3× 2 mL and 4× 2 mL for elution solvent methanol/dichloromethane (50:50; v/v)) and two pH values (2 and 7).

The optimized SPE method was described as follows. The SPE cartridges (Oasis HLB 6 mL 500 mg each) were conditioned successively each with 6 mL of DCM, 6 mL of methanol and 6 mL of Milli-Q water. The filtered water samples were passed through the cartridges at a flow rate of 5–10 mL/min. Each sample bottle was rinsed twice with two aliquots of 50 mL of 5% (v/v) methanol in Milli-Q water, which also passed through the cartridge. After loading of water samples, the cartridges were dried under vacuum for 1 h, and the target compounds were eluted from the cartridges using 3× 2 mL of methanol/dichloromethane (50:50; v/v) each. The extracts were dried under a gentle stream of nitrogen and reconstituted in 950 μL of acetone and 50 μL benzylcinnamate (IS, 10 mg/L). Each final extract was then filtered through a 0.22 μm membrane filter into a 2 mL amber glass vial for instrument analysis.

2.3.2. Biosolid sample extraction

The freeze-dried biosolids (1 g each) were weighed into 11 mL capacity stainless-steel cells. Before PLE extraction, the designed volumes of the standard solution of target compounds were spiked into the cells, mixed well and kept in the dark at 4 °C overnight prior to the extraction. Freeze-dried biosolid samples (1.0 g each) were extracted using a pressurized liquid extractor, ASE 300 accelerated solvent extraction system (Dionex, Sunnyvale, CA, USA), equipped with 11 mL capacity stainless-steel cells. The target compounds were divided into two groups, BTs (BT, 5-Tri, CBT and XTri) and UV filters (BP-3, 4-MBC, OMC, UV-326, UV-329 and OC) to be extracted by PLE individually. The extraction method for biosolid samples was developed by optimizing extraction temperatures (90 °C, 100 °C and 120 °C for both two groups), different extraction solvents (methanol/dichloromethane (50:50; v/v), n-hexane/dichloromethane (50:50; v/v) and acetone/dichloromethane (50:50; v/v) for BTs, and methanol/dichloromethane (50:50; v/v), acetone/dichloromethane (50:50; v/v) and n-hexane/dichloromethane (30:70, 50:50 and 70:30; v/v) for UV filters), and two different static time and cycles (5 min 2 cycles and 10 min 1 cycle for both two groups) at a spike concentration of 20 ng/g each.

The optimized PLE methods for BTs and UV filters in biosolid samples were described as follows. Three parallel freeze-dried sludge samples (1.0 g) were put into 11 mL capacity stainless-steel cells; two cellulose filters followed by an in-cell clean-up sorbents were placed at the bottom of each cell. The sorbents used for in-cell clean-up were 1.0 g of sodium sulphate and 1.0 g of silica for the BTs, and 1.0 g of sodium sulphate, 1.0 g of silica and 1.0 g copper powder for the UV filters. After loading of the sorbents and biosolid sample, the remaining volume in the cell was filled with acid washed sand. Then, another cellulose filter was placed on the top. The biosolid samples were extracted with methanol/dichloromethane (50:50; v/v) for BTs, and with n-hexane/dichloromethane (50:50; v/v) for UV filters as the extraction solvent. The operating conditions were given as follows: extraction temperature 100 °C for BTs and 120 °C for UV filters, extraction time 5 min and 2 cycles. Each extract was evaporated to near dryness under a gentle stream of nitrogen, and reconstituted in 950 μL of acetone and 50 μL internal standard (benzylcinnamate, 10 mg/L). Each final extract was then filtered through a 0.22 μm membrane filter into a 2 mL amber glass vial for instrumental analysis.

2.4. GC–MS/MS analysis

Analysis of the target compounds was performed by GC–MS/MS (Agilent 7000A/7890A, USA). One microliter of the reconstituted extract was injected into the gas chromatographic system. The target compounds were separated on a HP-5MS column (30 m × 0.22 mm, 0.25 μm thickness) with helium as carrier gas at a flow rate of 1.656 mL/min. The GC oven temperature was programmed from 80 °C (hold 2 min) to 280 °C (hold 6 min) at a rate of 15 °C/min. The injection port temperature and transfer line temperature were set at 280 °C. Mass spectrometric analyses were performed by tandem MS that operated in electron impact (EI) mode at 70 eV, with the ion source temperature at 230 °C. Quantitation of the target compounds was performed in the multiple reaction monitoring (MRM) mode by recording two pairs of MRM ions per compound. The optimal operating conditions for tandem mass spectrometric analysis of each compound are summarized in

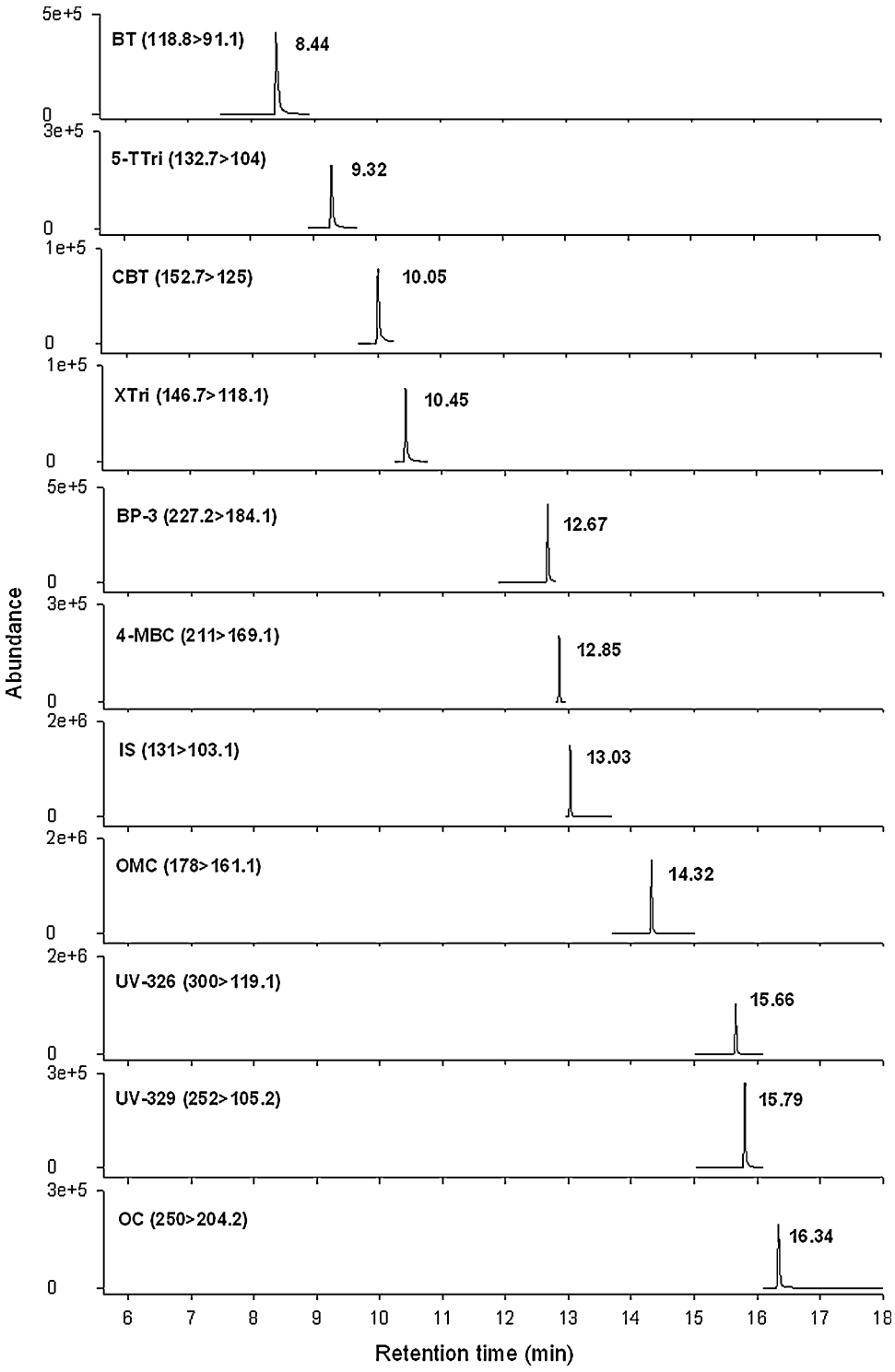

Fig. 1. Extracted ion chromatograms (XIC) of the quantitative ions for benzotriazoles (BTs) and UV filters in neat solvent at a concentration of 1000 μg/L each.

Table S2. Data acquisition was performed by Agilent Mass Hunter (Ver. B.03.01) software.

2.5. Quality control

The target compounds were identified by comparing the retention times (within 2%) and the ratios (within 20%) of the two selected precursor-product ion transitions with those of the standards. Quantification of the target compounds was obtained using the internal standard method. Laboratory blanks were also analyzed along with the samples to assess potential sample contamination. Recovery experiments were done by spiking the standard solutions to tap water, effluent and biosolid samples. The recovery data for each target compound in these matrices were corrected by the corresponding non-spike samples. No target compounds were found in tap water.

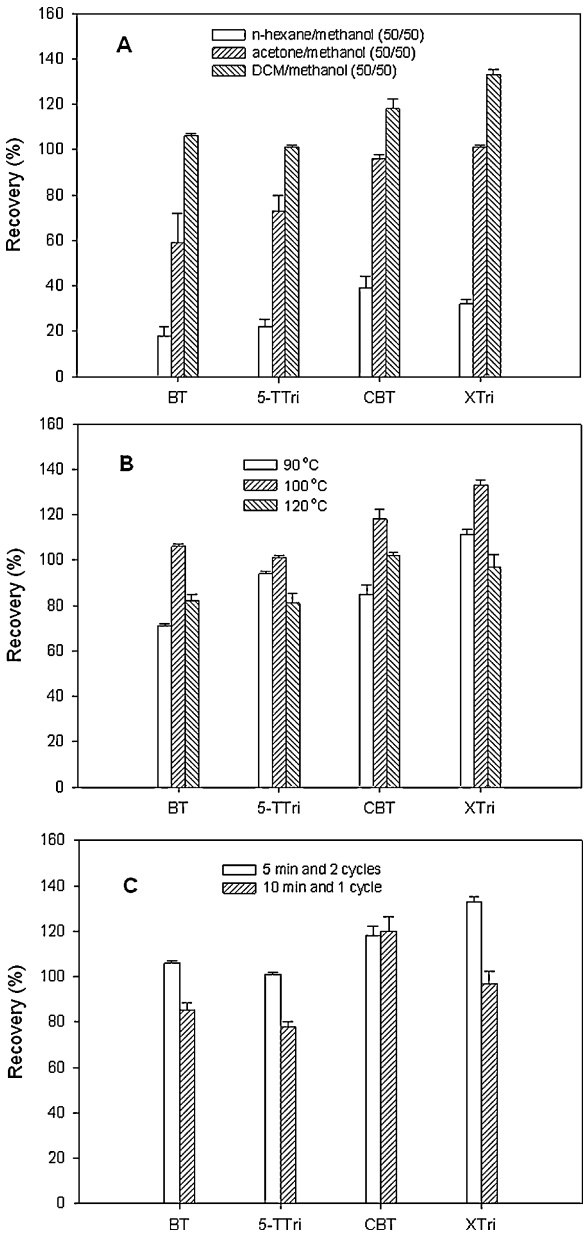

Fig. 2. Effect of the extraction solvents (A), extraction temperatures (B) and extraction cycles (C) on the recoveries (%) of four selected BTs from biosolid samples. Spike level: 20 ng/g (n = 3). DCM: dichloromethane.

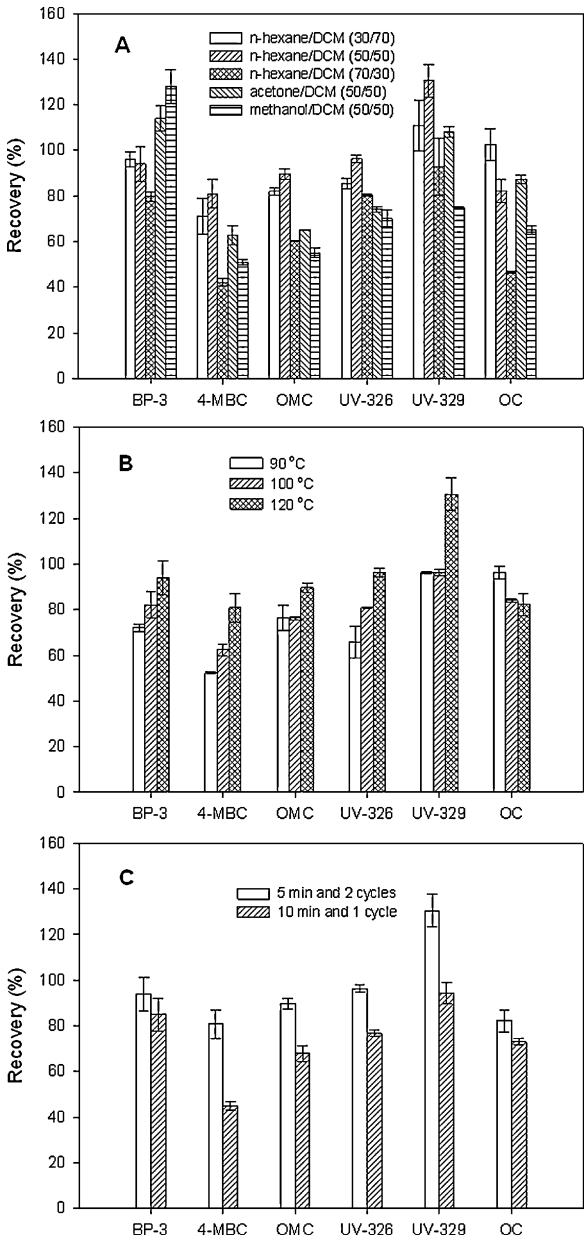

Fig. 3. Effect of the extraction solvents (A), extraction temperatures (B), and extraction cycles (C) on the recoveries (%) of six selected UV filters from biosolid samples. Spike level: 20 ng/g (n = 3); DCM: dichloromethane.

3. Results and discussion

3.1. GC–MS/MS optimization

One instrumental method using GC–MS/MS was developed for the selected BTs and UV filters. Solvents (methanol, dichloromethane and acetone) and oven temperature programs were evaluated to have a better separation and sensitivity for the target compounds. For the UV filters, solvents dichloromethane and acetone were found to produce better peak shape and intensity than methanol. For the BTs, better choices were methanol and acetone. So among the three solvents tested, acetone was finally selected as the solvent to dissolve all target compounds.

Instrumental operating conditions were optimized for each compound (Table S2). The total ion chromatograms (TIC) of the target chemical standards, effluent sample extract and biosolid sample extract, and the extracted ion chromatograms (XIC) of the MRM of each target compound are shown in Fig. S1 and Fig. 1, respectively. All the target compounds were well separated and showed good peak shapes in the MRM chromatograms.

Precision of the instrumental method in terms of repeatability and reproducibility, expressed as the relative standard deviation (RSD) of measured concentrations, were calculated based on the analysis of a standard mixture at a concentration of 50 μg/L for three times within 1 day and within 3 consecutive days, respectively. Repeatability for the target compounds varied from 0.5 to 5.1%, while reproducibility ranged from 0.9 to 9.3%.

3.2. SPE optimization

SPE method for the BTs and UV filters was optimized by testing various factors such as water pH, cartridges, elution solvents and elution volumes at the spike concentration of 500 ng/L each in tap water. Water pH value could affect recoveries of the target

Table 2
Recoveries (%) of the target compounds from tap water by solid-phase extraction with different cartridges. Spike level: 500 ng/L in tap water; elution solvent: methanol/dichloromethane (50/50; v/v), 3× 2 mL.

Compound	Oasis HLB 6 mL 500 mg	Supelco ENVI-18 6 mL 500 mg	Starta X-C-33 μm 6 mL 500 mg	Selby Biolab EC C18 6 mL 500 mg
BT	79 ± 4[a]	34 ± 3	11 ± 5	28 ± 5
5-TTri	108 ± 3	54 ± 2	14 ± 4	54 ± 4
CBT	85 ± 13	65 ± 6	12 ± 6	44 ± 7
XTri	107 ± 2	64 ± 4	14 ± 6	72 ± 5
BP-3	130 ± 1	159 ± 6	74 ± 4	101 ± 1
4-MBC	126 ± 1	86 ± 5	51 ± 2	67 ± 1
OMC	89 ± 3	54 ± 1	44 ± 3	26 ± 8
UV-326	90 ± 5	64 ± 1	43 ± 5	37 ± 2
UV-329	97 ± 4	85 ± 2	37 ± 8	50 ± 2
OC	80 ± 1	49 ± 4	44 ± 6	39 ± 2

[a] Mean ± relative standard deviation [RSD] (%) (n = 3).

compounds using the same HLB cartridge (Table S3). The recoveries for the four BTs were much lower at pH 7 (<50%) than at pH 2 (79–110%). However, the recoveries for the UV filters were not significantly affected by pH except for OMC and OC which had their recoveries of <50% at pH 7 and >70% at pH 2. Therefore, water pH was adjusted to pH 2 prior to SPE of the target compounds.

As shown in Table 2, HLB cartridges gave the best recoveries among the four types of SPE cartridges when using the same elution solvent (methanol/dichloromethane, 3× 2 mL). The target compounds with polar functional groups had better interactions with hydrophilic–lipophilic balanced reversed-phase sorbent in HLB cartridges than C18 or charcoal sorbent in the other cartridges. Elution solvents also had significant influences on the recoveries of the target compounds (Table S4). Elution with methanol, dichloromethane, acetonitrile and methanol/acetonitrile (50:50; v/v) produced recoveries lower than 33% or even 10%. Only elution with 3× 2 mL of methanol/dichloromethane (50:50, v/v) gave satisfactory recoveries (79–130%) for all the target compounds. Therefore, the optimized SPE method for the BTs and UV filters in water samples was described as follows: adjusting water samples to pH 2, extracting the water samples using HLB cartridge, and eluting the target compounds with methanol/dichloromethane (50:50, v/v; 3× 2 mL).

3.3. PLE optimization

PLE method development experiments were performed by spiking 20 ng of each target compound to 1.0 g freeze-dried biosolid sample. Based on the preliminary results, a clean-up step is necessary to avoid the interferences of lipid and sulphur in biosolid samples. Thus a clean-up step was incorporated by using the combination of silica, copper and anhydrous sodium sulphate as the adsorbent to remove interfering components such as sulphur and lipid in the extracts. However, it was found that copper powder led to lower recoveries for the four BTs (<20%), since there might be an interaction between the BTs and copper to form complexes [1]. Therefore, copper powder was only used in extraction of the UV filters in biosolid samples. The final recipes used for the in-cell clean-up of the extracts were given as follows: combination of only 1.0 g silica and 1.0 g anhydrous sodium sulphate for the BTs, and combination of 1.0 g silica, 1.0 g copper powder and 1.0 g anhydrous sodium sulphate for the UV filters.

The influences of extraction solvents, extraction temperatures (90 °C, 100 °C and 120 °C) and extraction static time and cycles (5 min 2 cycles and 10 min 1 cycle) on the extraction yield were also evaluated for the target compounds. The recoveries of the four BTs were below 40% when using n-hexane/dichloromethane (50/50; v/v) as the extracted solvent, whereas the recoveries were >70%, except for BT 59% when using acetone/dichloromethane (50/50; v/v), and ranged between 101 and 133% when using methanol/dichloromethane (50/50; v/v). This suggests that methanol/dichloromethane (50/50; v/v) is the best solvent for extraction of the four BTs (Fig. 2A). The recoveries of the six UV filters were 80–130% when using n-hexane/dichloromethane (50/50; v/v) as the extraction solvent, which is much better than using other solvents (Fig. 3A).

PLE operating conditions such as temperature, time and cycle were also optimized. The best extraction temperature was 100 °C and 120 °C for BTs and UV filters, respectively, as they gave better extraction efficiencies (Figs. 2B and 3B). 2 cycles of each 5 min extraction was found better than 1 cycle of 10 min (Figs. 2C and 3C). Therefore, the optimized PLE method for biosolid samples were: methanol/dichloromethane (50/50; v/v) as the extraction solvent, extraction temperature 100 °C, and 2 cycles of each 5 min for the BTs; and n-hexane/dichloromethane (50/50; v/v) as the extraction solvent, extraction temperature 120 °C, and 2 cycles of each 5 min for the UV filters.

3.4. Matrix effects

Matrix effects were observed in the GC–MS/MS of the target compounds to check if caused signal suppression or enhancement in this study. Matrix effects were evaluated by spiking standard solutions (100 μg/L) into the tap water, effluent and biosolid extract samples. The values of less or greater than 100% indicated signal suppression or enhancement, respectively. The results in Tables 3 and 4 show that matrix components in all of three matrixes had no significant effect on signal responses of the target compounds (matrix effect 75–125%). Only a slight signal enhancement for BP-3 and UV-329 was observed (123% and 125%, respectively).

3.5. Method validation

The recovery test was performed for all target compounds in matrix spiked samples of tap water, effluent and biosolid by using the optimized extraction and instrumental methods. The recoveries ranged between 70% and 120%, except for BP-3 (150% and 130%), 4-MBC (126%) and 5-TTri (122%), BP-3 (124% and 127%) in tap water and effluent samples, respectively (Table 3). For biosolid samples, good recoveries ranging from 66 to 152% were achieved for the target compounds (Table 4).

The limit of detection (LOD) and limit of quantitation (LOQ) for each target compound were calculated based on the signal to noise ratio (SNR) near the target peak. LOD is defined as three times of SNR, and LOQ is ten times of SNR. The LODs for the target analytes in the tap water, effluent and biosolid samples were 0.3–11.0, 0.5–14.1 ng/L and 0.3–8.2 ng/g, respectively (Tables 3 and 4). Higher LODs of the target compounds in the effluent than in the tap water were caused by the elevated chromatographic baseline due to matrix interferences existing in the effluent samples.

Table 3
Recoveries (%), method limits of detection and quantitation of target compounds in tap water and effluent samples for each target compound.

Compound	Tap water				LOD ng/L[a]	LOQ ng/L[a]	Effluent water			LOD ng/L[a]	LOQ ng/L[a]
	100 ng/L	500 ng/L	1000 ng/L	Matrix %			100 ng/L	500 ng/L	Matrix %		
BT	70 ± 4[b]	79 ± 4	80 ± 1	93 ± 3	9.0	30.1	89 ± 5	93 ± 3	94 ± 4	14.1	47.0
5-TTri	86 ± 4	108 ± 3	102 ± 6	101 ± 1	6.6	21.9	118 ± 4	122 ± 5	115 ± 5	9.5	31.7
CBT	81 ± 6	85 ± 13	90 ± 12	90 ± 4	11.0	36.7	92 ± 10	103 ± 10	93 ± 5	13.0	43.3
XTri	88 ± 5	107 ± 2	98 ± 6	98 ± 2	2.9	9.8	77 ± 1	85 ± 4	95 ± 2	4.2	14.0
BP-3	150 ± 19	130 ± 1	117 ± 9	121 ± 3	4.3	14.5	127 ± 5	124 ± 8	119 ± 6	6.5	21.7
4-MBC	83 ± 4	126 ± 1	115 ± 12	101 ± 5	0.3	1.1	88 ± 1	96 ± 12	94 ± 3	0.5	1.7
OMC	79 ± 1	89 ± 3	93 ± 13	96 ± 1	0.3	0.9	82 ± 3	91 ± 13	87 ± 4	0.7	2.3
UV-326	91 ± 4	90 ± 5	102 ± 10	89 ± 3	1.5	4.9	95 ± 2	110 ± 2	95 ± 1	3.3	11.0
UV-329	110 ± 10	97 ± 4	104 ± 11	107 ± 4	5.6	18.6	101 ± 4	97 ± 3	100 ± 2	4.8	16.0
OC	71 ± 1	80 ± 1	75 ± 6	88 ± 2	1.9	6.2	93 ± 2	84 ± 6	92 ± 1	3.4	11.3

[a] LOD: method limit of detection; LOQ: method limit of quantitation.
[b] Mean ± relative standard deviation [RSD] (%) (n = 3).

Table 4
Recoveries (%), method limits of detection and limits of quantitation of target compounds in biosolid samples.

Compound	Spike concentrations[a]				LOD (ng/g)[b]	LOQ (ng/g)[b]
	20 ng/g	50 ng/g	100 ng/g	Matrix %		
BT	106 ± 1	66 ± 8	69 ± 2	79 ± 1	0.9	2.9
5-TTri	101 ± 1	81 ± 8	93 ± 5	92 ± 3	4.1	13.8
CBT	118 ± 4	82 ± 7	110 ± 7	108 ± 4	1.9	6.5
XTri	133 ± 2	103 ± 8	99 ± 4	96 ± 10	3.0	9.9
BP-3	94 ± 13	121 ± 10	130 ± 8	123 ± 5	7.3	24.4
4-MBC	81 ± 11	72 ± 7	68 ± 12	75 ± 1	2.8	9.3
OMC	90 ± 3	76 ± 4	80 ± 2	89 ± 4	0.7	2.4
UV-326	96 ± 1	81 ± 1	87 ± 5	92 ± 4	0.3	1.1
UV-329	131 ± 7	152 ± 2	141 ± 14	125 ± 3	8.2	27.4
OC	82 ± 14	84 ± 16	91 ± 6	90 ± 2	3.6	11.9

[a] Mean ± relative standard deviation [RSD] (%) (n = 3).
[b] LOD: method limit of detection; LOQ: method limit of quantitation.

3.6. Application to environmental samples

The developed method was successfully applied to the analysis of the selected BTs and UV filters in ground water, effluent and biosolid samples from Bolivar sewage treatment plants in South Australia. Four BTs (BT, 5-TTri, CBT and XTri) were detected in effluent water samples and ground water samples; but only one UV filters BP-3 was detected in the effluent water samples with a concentration of 32.7 ng/L (Table 5). The highest concentration of up to 2.2 μg/L was detected for BT in the effluent samples. The rest of target compounds not mentioned here were all below the limit of quantitation in the effluent sample. Detection of the four benzotriazoles in groundwater was expected due to pumping of treated sewage effluent into aquifer for water reuse scheme. Reported concentrations of BT in effluents ranged between 4.6 and 10 μg/L [3,4,7], while the concentrations of BT were detected up to 126 mg/L in airport groundwater [5,9].

In the biosolid samples, all target compounds were detected except for BT and XTri. 4-MBC (a UV filter) was detected at the highest concentration of 250 ng/g in the biosolid sample. A previous investigation has found 4-MBC in stabilized sludge samples from 14 wastewater treatment plants in Switzerland with concentrations ranging between 150 and 4980 ng/g and a mean concentration of 1178 ng/g [38].

Table 5
Concentrations of the target compounds detected in the ground water, effluent and biosolid samples of Bolivar sewage treatment plant, South Australia.

Compound	Ground water (ng/L)	Effluent water (ng/L)	Biosolid (ng/g)
BT	280 ± 17.5	2206 ± 53.2[a]	<LOQ[b]
5-TTri	154 ± 3.2	373 ± 21.1	18.7 ± 1.4
CBT	97.5 ± 1.8	77.2 ± 15.6	21.4 ± 6.8
XTri	114 ± 12.1	103 ± 4.5	<LOQ
BP-3	<LOQ	32.7 ± 1.7	74.0 ± 12.2
4-MBC	<LOQ	<LOQ	250 ± 58.1
OMC	<LOQ	<LOQ	31.9 ± 3.8
UV-326	<LOQ	<LOQ	49.9 ± 7.4
UV-329	<LOQ	<LOQ	122.9 ± 7.1
OC	<LOQ	<LOQ	138.4 ± 24.3

[a] Mean ± standard deviation (n = 3, replicate samples taken at the same sampling time).
[b] <LOQ: below the method limit of quantitation.

4. Conclusion

A robust and sensitive GC–MS/MS method was developed and validated for the analysis of four BTs and six UV filters in tap water, effluent and biosolid samples. Sample pretreatment involves SPE for aqueous samples and PLE for solid samples. The analytical method for the target compounds showed good sensitivity and resolution using MRM mode of GC–MS/MS. Satisfactory recoveries for the target compounds were obtained for the three types of environmental samples. The method was also successfully applied to the determination of these target compounds in the ground water, effluent and biosolid samples collected from a sewage treatment plant in South Australia. The highest concentration of BT reached up to 2.2 μg/L in effluent samples, indicating its persistence of BT in the environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.05.100.

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