A high throughout semi-quantification method for screening organic contaminants in river sediments

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ABSTRACT

A high throughput semi-quantification method for screening nearly 900 organic contaminants (OCs) in river sediments has been developed. For most OCs tested, concentrations calculated from the proposed semi-quantification method deviated from actual values by a factor of 4. The overall recovery tests indicated that most OCs can be successfully extracted from sediments with recovery rates from 84.1 to 128.6%. To demonstrate the effectiveness of our method towards OC quantification, we screened OCs from sediments collected from the Haihe River basin. Seventy unregulated OCs (including pesticides, flame retardants, PPCPs, etc.) were identified and quantified at concentrations up to 2600 ng/g from 24 sediment samples. From these results, it is confirmed that the developed method is a useful way to fulfill a comprehensive analysis of OCs in sediments and would be valuable for the identification and prioritization of priority pollutants in watershed management.

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1. Introduction

Large number of organic chemicals have been produced and released into the environment worldwide and the number is increasing (Bu et al., 2013). Adverse ecological and human health effects have been observed for these organic contaminants (OCs) (Long et al., 1995; Sharpe, 2001; Feron et al., 2002; Sharpe and Irvine, 2004). It is thus of fundamental importance to determine OC concentrations in various environmental matrices which is essential for causation validation in dose-effect analysis. However, the number of environmentally monitored OCs is limited and is not enough to assess ecological and human health risks posed by OCs in general. Currently, analytical methods (Kolpin et al., 2002) required to assess OC contamination levels are time-consuming and costly. Hence high throughput screening of samples offers attractive prospects for environmental managers.

Several methods for comprehensive analysis of OCs in the environment have been reported. For example, Gómez et al. (2009)

introduced a novel method for simultaneous analysis of 934 OCs in water. Kadokami et al. (2005) developed a comprehensive screening method for nearly 700 OCs in environmental samples and applied to nearly 1000 OCs recently (Kadokami et al., 2012). In our previous studies, a broad spectrum of 50 phenols were screened using retention time locking (RTL) technology and deconvolution reporting software (DRS) (Zhong et al., 2010). Further, we established a qualitative screening method for 1093 contaminants in water and applied it for OC screening in water of the Danjiangkou reservoir (Bu et al., 2014). Our previous methods are sufficient for qualitative screening, but are insufficient for quantitative analysis. Previously a single random internal standard was used to quantify all OCs (Kadokami et al., 2005, 2012) and the accuracy of quantitative analysis was seldom reported. This may lead to bias in quantification results as response factors (RFs) of chemicals differ on mass selective detector (MSD).

In the present study, a set of quantification internal standards (QISs) was proposed to estimate concentrations of 847 OCs in river sediments. All 847 OCs were selected from our previous database (Bu et al., 2014) by excluding OCs that can be routinely monitored (e.g. polycyclic aromatic hydrocarbons). To facilitate this process, sample extraction and clean-up procedures were optimized for OC analysis in river sediments; then the accuracy of semi-quantification was evaluated using QISs; and finally the

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effectiveness our new method was validated. The overall goal of this study is to develop a novel high throughput, semi-quantification method for OC screening in river sediments.

2. Materials and methods

2.1. The database

Our database contains 847 OCs that are relevant to China, including current in-use and legacy pesticides, traditional persistent organic pollutants such as co-planar polychlorinated biphenyls (PCBs), emerging contaminants such as pharmaceuticals and personal care products (PPCPs), fire retardants, and new persistent organic pollutants (e.g. chlordecone and pentachlorobenzene). All of which are suitable for analysis by gas chromatography-mass selective detector (GC-MSD) (Pang et al., 2006).

2.2. Chemicals and materials

All solvents were HPLC grade (J.T. Baker, Phillipsburg, NJ, USA). QISs were purchased from AccuStandard Inc. (New Haven, Connecticut, USA). Acidic alumina (2 g, 6 mL), basic alumina (2 g, 6 mL), neutral alumina (2 g, 6 mL), silica (500 mg, 6 mL) and Florisil (500 mg, 6 mL) cartridges were obtained from Supelco (Bellefonte, Pennsylvania, USA). All glassware was washed with acetone and water, soaked overnight in concentrated sulfuric acid containing 5% $K_2Cr_2O_4$ solution, washed with distilled water and baked at 550–600 °C for five hours.

2.3. Analytical procedure

OCs were extracted from freeze-dried sediments (5 g) with dichloromethane/acetone (1:1, v/v) using an accelerated solvent extraction (ASE, Dionex ASE350, Dionex, Sunnyvale, California, USA) system, at 130 °C and 1500 psi, with two extraction cycles. The static time for each cycle was 5 min and the cell was flushed with 100% of the cell volume at the end of the extraction. The extracts were cleaned-up by the gel permeation chromatography (GPC), followed by solid phase extraction (SPE) with the adsorption chromatography.

GPC clean-up was conducted on a Bio-Beads SX3 column (Bio-Rad Laboratories, Hercules, California, USA) using the following conditions: mobile phase, cyclohexane/ethyl acetate (1:1, v:v); flow rate, 4.7 ml/min; detection wavelength, 254 nm; commenced collection time, 9 min; stopped collection time, 17 min. Thereafter, the solvent was changed to hexane in approximately 1 ml. The hexane concentrate was applied to SPE with a Florisil cartridge, which was pre-conditioned by using 6 ml of methanol and 6 ml of hexane. The cartridge was eluted by 5 ml of mixture of dichloromethane/acetone (1:1, v:v). The cleaned extracts were evaporated under a gentle stream of nitrogen and analyzed by GC-MSD.

2.4. GC-MSD analysis

An Agilent 6890N-5975D GC-MSD (Agilent Technologies, Santa Clara, California, USA) with a DB-5 capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, Agilent J&W Scientific) was used for sample analysis. High purity helium (99.9999%) was used as the carrier gas. RTL, data acquisition and processing were performed using Agilent MSD ChemStation Software (Version E.0200.493). Retention time of fluoranthene was locked at 20.839 min during analysis by adjusting the column pressure. The oven temperature was held at 70 °C for 2 min, raised to 150 °C at 25 °C/min, then raised to 200 °C at 3 °C/min, then raised to 280 °C at 8 °C/min and held at 280 °C for 15 min. The inlet and

MS transfer line temperatures were both set at 250 °C, and the ion source temperature was 230 °C. MSD was operated in full scan mode from m/z 50 to 700.

All data were analyzed using DRS. A positive identification was confirmed when the following criteria were met: the automated mass spectral deconvolution and identification system match values were higher than 60% and the retention time differences between the expected and observed values were less than 10 s. The extracted spectrum was also reverse-matched with the National Institute of Standards and Technology library. Quantification was conducted by comparing their peak areas of identified contaminants to the respective QISs.

2.5. Collection of river sediments

Sediment samples used for performance validation were collected at 24 sites (Fig. S1) from different zones of the Haihe River basin using a grab sampler. All samples were immediately transported to the laboratory and stored at –20 °C until analysis.

3. Results and discussion

3.1. Optimization of sample pretreatment

Although several extraction methods have been reported for solid samples, such as soxhlet extraction and ultrasonic extraction, ASE was chosen in the present study due to high extraction efficiency of various OCs from different matrices (Bandh et al., 2000; Ding and Fann, 2000; Windal et al., 2000; Li et al., 2007). Dichloromethane and acetone were used as extraction solvents because they are suitable for a wide range of OCs (Kadokami et al., 2012).

In clean-up procedure, GPC combined with SPE was employed. GPC is generally used to separate smaller molecules from the larger ones, and can be used to purify a broad range of analytes, both polar and non-polar (USEPA, 1994). The commenced collection time is optimized by using coin oil (as the marker of interfering substances) and tralomethrin (as the marker of high molecular weight targets). Strong response was found between 5 and 9.2 min, with peak at 7.1 min corresponding to coin oil. Tralomethrin was eluted between 9.5 and 13.5 min, with peak value at 11.9 min. Therefore commenced collection time was chosen at 9 min. To determine the stopped collection time, elution curves of four PCBs (PCB-28, PCB-41, PCB-138 and PCB-209, representing contaminants with different molecular weights) were profiled in Fig. S2. All selected PCBs started to elute at 11 min. PCB-209 and PCB-138, which have greater molecular weights, completely eluted within 11–15 min, while complete elution of PCB-41 and PCB-28 falls between 11 and 16 min. To validate the stopped collection time, 2,4-dichlorophenol (with molecular weight of 163) was used as the marker of low molecular weight targets and was completely eluted at 16 min on GPC column. From above results, we conservatively inferred that all target contaminants eluted from GPC columns between 9 and 17 min. Good recoveries (91.8–106.3%) were obtained for all four PCBs. Therefore GPC clean-up condition has been decided to be: clean-up column, Bio-Beads SX3 (300 mm × 25 mm i.d.); mobile phase, cyclohexane/ethyl acetate (1:1, v/v); flow rate, 4.7 ml/min; detection wavelength, 254 nm; the commenced collection time, 9 min; the stopped collection time, 17 min; the collection volume, 37.6 ml.

For adsorption chromatography, five widely used adsorbents were tested, including silica, Florisil, acid alumina, neutral alumina and basic alumina. The detailed optimization procedure was described in SI-1. For each adsorbent, elution solvents were optimized for 74 OCs (Table S1). Considering the wide spectrum of OCs analyzed using this method, we performed a principal component analysis, which offers an integrative indicator for OC recovery. In

addition, enhanced OC recovery was observed by increasing polarity and/or amounts of elution solvents for each adsorbent (Fig. S3, Tables S2 and S3), which was in accordance with previous observations (Ahn et al., 2007; Turlington and McDow, 2010). However, pronounced matrix effects were observed for polar elution solvents. Therefore minimal amount of elution solvents with adequate polarity that produces 60% or higher OC recovery was used. Elution condition was determined to be: 7 ml of dichloromethane/acetone (9:1, v:v) for silica; 5 ml of dichloromethane/acetone (1:1, v:v) for Florisil; 5 ml of dichloromethane/acetone (1:1, v:v) for acid alumina; 5 ml of dichloromethane/methanol (9:1, v:v) for neutral alumina; and 5 ml of dichloromethane/methanol (9:1, v:v) for basic alumina.

Although elution patterns are similar for all five adsorbents (Tables S2 and S3), Florisil eluent has shown least turbidity (Fig. S4).

From these results, the clean-up chromatography for OCs in river sediments was decided to be a combination of GPC and Florisil SPE. Although matrix effect may not be completely avoided by our optimized clean-up method, it is acceptable for high throughput screening of OCs with a broad range of physio-chemical properties.

3.2. Accuracy of semi-quantification

In this study, all 847 OCs screened were categorized into 14 groups according to their chemical properties by which QIS was assigned (Table S4).

The accuracy of semi-quantification was tested by analyzing a standard solution containing 1 µg/mL of selected OCs. The ratios of measured to theoretical concentrations (M/Ts) of different OCs were calculated and listed in Table 1. For most OCs tested, the calculated

Table 1

The selected OCs for method development, with their chemical abstract service registration number (CAS No.), chemical class, physio-chemical properties, M/Ts in different samples, and recoveries using the high throughput analytical method presented.

CAS no.	Contaminant	Chemical class	Physio-chemical property ^a			M/T			Recovery, % ⁱ	
			MW	Log <i>K</i> _{ow}	<i>S</i> _w , mg/L	Standard solution 1 µg/ml	Spiked sample 100 ng/g	Spiked sample 50 ng/g	Average	RSD
51218452	Metolachlor	Amides	283.8	3.13	530		0.51	0.70		
67129082	Metazachlor	Amides	277.76	2.13	430		0.32	0.23		
99309	Dichloran	Anilines	207.02	2.8	7		0.87 ^c	1.1 ^d		
40487421	Pendimethalin	Anilines	281.31	5.18	0.3		3.4 ^e			
63252	Carbaryl	Carbamates	201.23	2.36	110	5.4	6.4	6.7	118	11.9
1563662	Carbofuran	Carbamates	221.16	2.32	320	6.7	7.1	6.8	106	3.51
16655826	3-Hydroxycarbofuran	Carbamates	237.26	0.76	6207		0.74	1.3		
1928376	2,4,5-T methyl ester	Methyl Esters	269.51	3.55	17.16	2.6	3.6	2.8	135	4.68
1928387	2,4-D methyl ester	Methyl Esters	235.07	2.9	258	3.3	3.8	2.1	113	4.76
2436739	MCPA methyl ester	Methyl Esters	214.65	2.81	147.4	4.1	4.0	2.2	96.7	8.35
4841207	Fenoprop methyl ester	Methyl Esters	283.54	3.97	6.278	4.1	4.8	4.4	117	4.55
18625122	2,4-DB methyl ester	Methyl Esters	263.12	3.89	9.599	5.7	6.7	5.8	118	19.0
23844566	Mecoprop methyl ester	Methyl Esters	228.67			4.7	4.5	4.2	95.8	7.22
57153170	Dichloroprop methyl ester	Methyl Esters	249.09			5.7	6.2	6.0	110	9.89
57153181	MCPB methyl ester	Methyl Esters	242.7			6.4	6.9	5.6	108	3.59
60515	Dimethoate	OPPs	229.25	0.28	23300	0.48	0.82	0.65	171	13.3
62737	Dichlorvos	OPPs	220.98	1.43	8000	2.8	0.84	0.62	29.7	20.4
470906	Chlorfenvinphos	OPPs	359.58	3.81	124	0.68	0.15	0.15	22.7	11.8
2921882	Dursban	OPPs	350.59	4.96	1.12	0.83	0.81	0.77	98.5	9.47
13593038	Quinalphos	OPPs	298.3	4.44	22	1.1	1.1	1.2	93.6	11.5
23560590	Heptenophos	OPPs	250.62	2.32	2500	0.79	0.96	0.82	121	8.81
24017478	Triazophos	OPPs	313.31	3.34	39	0.69	0.54	0.37	77.9	7.49
90153	1-Naphthalenol	Phenols	144.17	2.85	866	0.22	0.092		41.5	21.4
51630581	Fenvalerate	Pyrethroids	419.91	6.2	0.024	15	11 ^e	9.2 ^f	75.3	17.5
52315078	Cypermethrin	Pyrethroids	416.31	6.6	0.004	5.6	7.3 ^e	6.9 ^f	131	17.7
52918635	Deltamethrin	Pyrethroids	505.21	6.2	0.002	10	13 ^e	10 ^f	136	12.3
68359375	Cyfluthrin	Pyrethroids	434.3	5.95	0.003	8.2	11 ^e	8.8 ^f	139	1.22
79538322	cis-Tefluthrin	Pyrethroids	418.74	6.5	0.02	0.41 ^b	0.66 ^c	0.62 ^d	162	3.07
122349	Simazine	Triazines	201.66	2.18	6.2	0.43 ^b	0.39 ^g	0.37 ^h	90.7	10.1
886500	Terbutryn	Triazines	241.36	3.74	25	0.78	0.61	0.66	78.5	20.5
1014693	Desmetryn	Triazines	213.3	2.38	580	0.69	0.63	0.59	92.1	21.0
1912249	Atrazine	Triazines	215.69	2.61	34.7	0.95	0.52 ^g	0.60 ^h	54.7	18.6
5915413	Terbutylazine	Triazines	229.71	3.21	8.5		0.94	0.92		
6190654	Desethyl atrazine	Triazines	187.63	1.51	3200		0.11	0.12		
7286693	Sebutylazin	Triazines	229.71	3.31	45.64		1.1	1.2		
7287196	Prometryn	Triazines	241.36	3.51	33	0.71	0.64	0.67	89.7	22.3
21087649	Metribuzin	Triazines	214.29	1.7	1050	0.44	0.44	0.34	98.8	13.1
51235042	Hexazinone	Triazines	252.32	1.85	33,000		1.1	0.96		
3060897	Metobromuron	Ureas	259.1	2.38	330		1.0	1.2		
18691979	Methabenzthiazuron	Ureas	221.28	2.64	59		0.093			

Abbreviations: OPPs, organophosphorus pesticides; MW, molecular weight; *K*_{ow}, octanol–water partition coefficients; *S*_w, solubility; RSD, relative standard derivation.

^a Six duplicates were analyzed for each spike level. Physio-chemical properties were estimated using the EPISuite software package.

^b The concentration was 0.2 µg/mL.

^c The spiked concentration was 40 ng/g.

^d The spiked concentration was 20 ng/g.

^e The spiked concentration was 200 ng/g.

^f The spiked concentration was 100 ng/g.

^g The spiked concentration was 240 ng/g.

^h The spiked concentration was 120 ng/g.

ⁱ Recovery was calculated according to samples spiked at 100 ng/g level.

concentrations usually differed from actual measurements by a factor of 4. However our estimates imposed uncertainty in factors of 5–10 for two exceptional cases: pyrethroids and carbamates.

The over- or under-estimated concentrations by our QISs are due to different RFs between targets and the respective QIS on MSD. In electron ionization mode, RFs of OCs were affected by ion transmission, fractional ion abundance, ionization cross section, and compound molecular weights (Sauter et al., 1986). And these are exactly factors considered in the selection of QISs in our study. The M/T ratios showed that RFs of tested OCs were comparable to their respective QIS, which was in agreement with Sauter et al. (1983). They reported comparable RFs between chemicals within the same chemical class. Lundgren et al. (2004) determined RFs of 87 polychlorinated dibenzofurans and found that the maximum to minimum RF ratio was close to 2 for all homologues. All these results demonstrated the potential of using QISs to semi-quantify concentrations of large number of OCs in the high throughput screening analysis.

3.3. Overall recovery tests

The overall recovery tests were run to confirm the performance of our proposed method. Sediment with a high organic matter (40.3 g/kg) was spiked by a series of OCs (from nine chemical classes with varying properties) at two concentration levels in a 100 ml container. The container was capped immediately and hand shaken for at least 10 min after spiking. The prepared spiked samples were stored at room temperature at dark for at least 10 days before extraction.

The recovery rates of tested OCs are listed in Table 1. Acceptable recovery rates were obtained, on average, for the whole analytical procedure. The M/Ts of OCs in the spiked samples and in the standard solution were comparable (Table 1), indicating the satisfactory recoveries. The average recoveries for methyl esters, pyrethroids, triazines and organophosphorus pesticides (OPPs) were 111.6%, 128.6%, 84.1% and 87.8%, respectively. The procedure can, therefore, be used to determine a series of OCs with varying properties. Lower recoveries were found for some OPPs due to the loss during the evaporation steps (Barranco et al., 2003), the width of the GPC fractionating window (Navarro et al., 2006), and/or matrix effects. In addition, OPPs are prone to thermal degradation during analysis. Albeit this, overall recoveries of the tested OCs ranged from 84.1 to 128.6% (Table 1), indicating that the developed screening method can analyze most OCs included in our database.

3.4. Application to actual sediments

In order to confirm the effectiveness of our high throughput method, we analyzed 24 sediment samples collected from the Haihe River basin. Seventy OCs were identified from sediment samples, and 17 OCs were detected in more than 25% of sampling sites (Tables 2 and S5).

In general, OC concentrations increased from west to east of the Haihe River basin, such trend can be explained by the intensive agricultural and industrial activities in the corresponding area. Bird repellents 9,10-anthraquinone and biphenyl (a microbiocide) were detected in all sediment samples, with concentrations of 2.3–180 ng/g and 3.8–44 ng/g, respectively. Benzophenone, benzyl

Table 2
Semi-quantitative concentrations of OCs in river sediments collected from the Haihe River basin.

CAS no.	Contaminant	Usage	Frequency (n = 24)	Concentration level, ng/g				
				West (n = 5)	East (n = 6)	Center (n = 6)	North (n = 5)	South (n = 2)
84651	9,10-Anthraquinone	Bird repellent	100%	36 (26–69) ^a	52 (2.8–180)	12 (2.3–23)	21 (5.1–53)	13 (11–16)
92524	Biphenyl	Microbiocide	100%	16 (6.6–31)	14 (4.2–44)	13 (6.5–29)	12 (5.5–20)	4.0 (3.8–4.2)
119619	Benzophenone	Radiation-sensitizing agent	83%	4.5 (n.d–6.8)	49 (10–180)	15 (n.d–28)	11 (2.3–22)	2.9 (2.0–3.7)
120514	Benzyl benzoate	Insect repellent	79%	4.9 (n.d–7.4)	7.2 (n.d–10)	4.2 (0.98–8.9)	13 (4.2–21)	n.d.
2941551	Ethiolate	Herbicide	79%	0.75 (n.d–1.0)	870 (n.d–2600)	5.1 (n.d–8.2)	4.0 (1.4–9.2)	1.7 (1.1–2.3)
1918112	Terbutol	Herbicide	75%	720 (260–1500)	1400 (n.d–2100)	580 (n.d–970)	330 (n.d–470)	28 (24–32)
14214325	Difenoxuron	Herbicide	75%	11 (n.d–13)	14 (n.d–238)	260 (10–1500)	44 (0.36–170)	n.d.
122394	Diphenylamine	Fungicide and plant growth regulator	67%	140 (28–240)	90 (n.d–150)	52 (n.d–100)	56 (n.d–100)	18 (n.d–18)
126738	Tributyl phosphate	Flame retardant	63%	71 (n.d–74)	89 (n.d–110)	52 (n.d–91)	180 (61–260)	n.d.
106467	p-Dichlorobenzene	Insect repellent	58%	0.84 (n.d–1.2)	1.2 (n.d–1.7)	1.4 (n.d–2.1)	1.2 (n.d–1.5)	n.d.
90437	o-Phenylphenol	Disinfectant	42%	16 (9.0–22)	19 (n.d–33)	— (n.d–10)	n.d.	n.d.
52857	Famphur	Insect repellent	38%	44 (n.d–74)	98 (n.d–280)	19 (n.d–20)	1.1 (n.d–1.1)	n.d.
85416	Phthalimide	Flopel degradation product	33%	n.d.	27 (n.d–42)	— (n.d–4.8)	2.4 (n.d–2.7)	6.0 (5.4–6.6)
58082	Caffeine	Stimulant	33%	4.6 (n.d–6.0)	— (n.d–2.4)	2.6 (n.d–3.5)	— (n.d–2.5)	n.d.
95761	3,4-Dichloroaniline	Diuron degradation product	29%	n.d.	53 (n.d–64)	n.d.	n.d.	190 (0.45–360)
115968	Tris (2-chloroethyl) phosphate	Flame retardant	29%	3.5 (n.d–10)	— (n.d–6.2)	3.5 (n.d–7.0)	n.d.	n.d.
119904	o-Dianisidine	Raw material in production of dyes	29%	7.4 (n.d–15)	53 (n.d–100)	— (n.d–0.43)	n.d.	n.d.

^a Concentration range.

benzoate, ethiolate, terbutol and difenoxuron were found in almost all of the sediments at concentrations up to 2600 ng/g. Two flame retardants (tributyl phosphate and tris (2-chloroethyl) phosphate) and two PPCPs (the disinfectant *o*-phenylphenol and the stimulant caffeine) were detected in more than 30% of the samples at concentrations up to 260 ng/g (flame retardants) and 33 ng/g (PPCPs), respectively. Pesticide degradation products, such as phthalimide, which are generally omitted by target analysis, were also identified (Table 2). A notable result was the detection of *o*-dianisidine, which is a possible human carcinogen, in both the eastern and western zones of the Haihe River basin.

To our knowledge, few newly identified OCs have been reported in previous studies of the Haihe River basin. Heeb et al. (2012) screened 268 micro-pollutants in water samples from the Haihe River system. Caffeine and a diuron metabolite were identified, which is consistent to our results. In addition we have detected prometon, dicamba, and metribuzin, which were absent from Heeb's report. The difference could be due to deviation in sampling sites and matrices. The performance of our high throughput semi-quantification method clearly demonstrates its viability for OC screening in sediments. From which OC contamination mapping that is important for environmental managers can be generated.

4. Conclusions

A high throughput screening method was developed for screening of large number of OCs in river sediments. Under optimized conditions, this method can simultaneously estimate concentrations of at least 847 OCs. Tests of semi-quantification method demonstrated satisfying accuracy for OC quantification. Recovery tests indicate that most OCs can be successfully extracted from sediments, with recovery rates ranging from 84.1 to 128.6%. This method was applied to screen OCs in sediments collected from the Haihe River basin. Seventy unregulated OCs (including pesticides, flame retardants, PPCPs, etc.) in 24 sediment samples were identified and quantified at concentration up to 2600 ng/g. Our high throughput semi-quantification method offers a framework for screening and semi-quantification of a broad range of OCs in sediments, making it possible to identify and quantify unknown OCs. The method presented here will be valuable for both identification and prioritization of priority pollutants in watershed management.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2014.05.009>.

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