Simultaneous detection of chlorinated polycyclic aromatic hydrocarbons with polycyclic aromatic hydrocarbons by gas chromatography–mass spectrometry

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Abstract Chlorinated polycyclic aromatic hydrocarbons (CIPAHs), including polychlorinated naphthalenes (PCNs), are hazardous and widespread in the environment, but studies of these substances in the wastewater environment are lacking. In this study, five typical PCNs and five typical CIPAHs (other than PCNs) were simultaneously detected along with their parent polycyclic aromatic hydrocarbons in wastewater samples. All these compounds could be analyzed by gas chromatography–electron ionization mass spectrometry in selected ion monitoring mode and separated on a DB-17ms column. Calibration curves were created both in pure solvent and in wastewater matrix samples. The coefficients of determination for most compounds were greater than 0.99, indicating a satisfactory degree of linearity in the complex matrix samples. The influence of the matrix on the true concentrations of the environmental samples was corrected by use of the matrix calibration curve. The recoveries of all compounds were between 58% and 127%, with standard deviations lower than 20%. The method detection and quantification limits were less than 27.6 ng/L and less than 91.9 ng/L respectively in the aqueous phase, and less than 0.18 ng/L and less than 0.61 ng/L respectively in the solid phase of 4-L wastewater samples. This analytical method was successfully used to detect PCNs and CIPAHs in the water from a river receiving

effluent from a wastewater treatment plant. The concentrations of each compound ranged from 3.1 to 29.6 ng/L. This method could also be used for detection of other polycyclic aromatic hydrocarbon derivatives with similar physical and chemical properties in different matrix samples.

Keywords Chlorinated polycyclic aromatic hydrocarbons · Polychlorinated naphthalenes · Solid-phase extraction · Accelerated solvent extraction · Water matrix

Introduction

Chlorinated polycyclic aromatic hydrocarbons (CIPAHs), including polychlorinated naphthalenes (PCNs), are chlorinated derivatives of polycyclic aromatic hydrocarbons (PAHs) that are widespread and persistent in the environment [1]. PCNs are industrially synthesized compounds usually used as dielectric fluids, flame retardants, and fungicides. They might also be formed and released into the environment through waste incineration, copper smelting, and chlorine production [2]. CIPAHs (other than PCNs) can be formed from the photochemical and thermal reaction of PAHs, and discharged into the environment through vehicle exhaust, organic matter incineration, and other industrial activities [3]. Compared with the parent PAHs, some of the chlorinated derivatives are more highly mutagenic [4, 5]. PCNs have been implicated in causing various diseases, such as chloracne, liver damage, X-disease in cattle, and chick edema [2]. Some CIPAHs were found to act as strong mutagens both in the presence and in the absence of metabolic activation, whereas benzo[a]pyrene was found to be the only mutagenically active parent PAH. 9-Chlorofluorene showed higher mutagenic activity than other CIPAHs [6]. Thus, it is necessary to focus on PCNs and

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CIPAHs because of the widespread emission sources and hazardous properties.

In general, PCNs and CIPAHs have been analyzed by high-resolution gas chromatography (HRGC)–high resolution mass spectrometry (HRMS) and gas chromatography (GC)–mass spectrometry (MS). PCNs have been commonly detected by HRGC–HRMS or GC–MS–MS combined with electron ionization (EI) and separated with a nonpolar fused-silica capillary column such as an Agilent DB-5 column (60 m $\times$ 0.25-mm inner diameter, 0.25- μ m film thickness) [2, 7–9]. They have also been analyzed with a GC–MS system equipped with an electron capture negative ion detector and a nonpolar column. The instrument detection limits (IDLs) ranged between 0.0068 and 1.07 ng per sample [10]. GC–EI–MS can be used to determine PCNs. For example, a more polar column, DB-1701 (30 m $\times$ 0.25-mm inner diameter, 0.25- μ m film thickness), connected to a DB-5 column was used for separation and identification of the individual congeners [11]. For CIPAHs, analysis was performed by HRGC–EI–HRMS with a DB-5 column [11, 12] and liquid chromatography–mass spectrometry [13]. CIPAHs, oxygenated PAHs (OPAHs), and PAHs were separated by high-performance liquid chromatography (HPLC) and analyzed by GC–EI–MS with a nonpolar column, SE-54 or DB-5 [14, 15]. For both CIPAHs and PAHs, the isolation was performed with a two-dimensional HPLC system and they were selectively analyzed by GC–MS with chemical ionization in negative ion detection mode [16]. CIPAHs and PAHs were simultaneously determined by GC–ion trap EI–MS and separated on a nonpolar column, Rxi-5MS (30 m $\times$ 0.25-mm inner diameter, $\times$ 0.25- μ m film thickness) [17]. CIPAHs and PAHs were also determined by GC–EI–MS with an Rxi-5MS column. However, the injector temperatures and the column oven temperature programs were different for CIPAHs and PAHs [18]. Studies have also focused on PCNs, CIPAHs, and PAHs. The analysis of PCNs and CIPAHs was performed by HRGC–EI–HRMS with a DB-5ms column, whereas, PAHs were analyzed by GC–MS [19]. Thus, detection of PCNs, CIPAHs, and PAHs with the same instrument and the same procedure could be difficult with the present analytical methods. So, in this study, we intended to develop a method that simultaneous detects PCNs and CIPAHs with PAHs, OPAHs, methyl PAHs (MPAHs), and nitrated PAHs (NPAHs) [20].

Many studies have focused on the determination of these compounds in the atmosphere, soil, sediment, and biota environments, but only a few studies have been conducted in a water environment. CIPAHs, which can be formed during chlorination, have been detected in tap water. The concentrations of 1-chloronaphthalene (1-CN), dichloronaphthalene, 9-chlorophenanthrene (9-CIPhe), 3-chlorofluoranthene, and 1-chloropyrene ranged from 0.03 to 35 ng/L [12, 17]. 9-CIPhe was demonstrated to be a main chlorinated PAH by-product when the pH was less than 4 during chlorination

[14, 15]. The concentrations of PCNs were found to be relatively high in surface water and groundwater. The concentrations of 1-CN, 2-chloronaphthalene (2-CN), 1,4-dichloronaphthalene (DCN), 2,3,6,7-tetrachloronaphthalene, and octachloronaphthalene (OCN) ranged from 0.1 to 542 ng/L in a river used for source water [2]. In groundwater, the total PCN concentrations were higher levels, ranging from less than 0.5 to 79 μ g/L, with 2,3,6,7-tetrachloronaphthalene as the major congener in the group [21]. The concentrations of 1-CN and dichloronaphthalene were 0.01–1.0 μ g/L in the upper aquifer layer and 0.09–750 μ g/L in the lower layer [22]. Thus, it is clear that the pollution levels of PCNs and CIPAHs differ a great deal in different water matrixes and places. However, previous studies seldom focused on wastewater. Therefore, it is essential to give more attention to these types of pollutants in wastewater systems.

Because of the different lipophilicity of the compounds, the lower molecular ring number PAH chlorinated derivatives are preferentially found in water, whereas the higher molecular ring number derivatives preferentially exist in sediment [1]. Therefore, this study focused on the chlorinated derivatives of lower molecular ring number PAHs, including the PCNs and two to three ring CIPAHs. The aim of this study was to optimize and validate a method for simultaneous determination of the lower molecular ring number chlorinated PAHs along with the parent PAHs and some other types of PAH derivatives in water matrix samples. In the future, both contamination by PCNs and CIPAHs in a water environment and the transformation of PAHs to their chlorinated derivatives during chlorine disinfection water treatment processes could be detected with this method.

Method and materials

Standards and chemicals

Five PCN standards—1-CN (in solid form, 95.5%), 2-CN (100 μ g/mL in methanol), DCN (solid, 99.4%), 1,2,3,4-tetrachloronaphthalene (TeCN; solid, 100%), and OCN (100 μ g/mL in methanol)—were purchased from AccuStandard (USA). Five CIPAH standards—9-chloro-9H-fluorene (9-ClFluo; 50 μ g/mL in isooctane), 9-CIPhe (50 μ g/mL in isooctane), 2-chloroanthracene (2-ClAnt; 50 μ g/mL in isooctane), 1-chloroanthraquinone (1-ClAQ; solid, 98%), 9,10-dichloroanthracene (9,10-DCIAnt; solid, 96%)—were purchased from Chiron (Norway). The 16 US EPA priority PAHs, four MPAHs, four OPAHs, and five NPAHs (see Table S1) were the same as in a previous study [20]. Internal standards, including 2-fluorobiphenyl (solid, purity greater than 96%) and decachlorobiphenyl (PCB209) were obtained from Aldrich (UK).

Hexane (Fisher Scientific, USA), dichloromethane (J.T.Baker, USA), methanol (Fisher Scientific, USA) and acetone (Dikma Technologies, USA) were HPLC grade solvents. Silica gel (0.06–0.2 mm) and alumina (100–200 mesh) for chromatography were purchased from Acro Organics (USA). Before use, silica gel and alumina were baked at 180 and 250 °C respectively for 12 h, and then deactivated with 3% redistilled water, and kept in hexane until use. Analytical grade anhydrous sodium sulfate (Tianjin, China) was baked at 450 °C for 5 h before use.

Sampling

Five real wastewater samples were collected from a river receiving wastewater treatment effluent in Beijing in April and November, 2015 respectively. The 4-L water samples were filtered through glass microfiber filters (Whatman GF/F, 142-mm diameter, 0.7- μ m pore size). The aqueous-phase samples were stored at 4 °C and extracted within 2 days. The solid-phase samples (suspended particulates) were stored in a refrigerator at -20 °C, and freeze-dried before analysis.

Pretreatment procedure

Aqueous-phase samples were extracted with C_{18} columns (500 mg, 6 mL, Supelco) by the solid-phase extraction (SPE) method. Before use, the columns were activated with 5 mL dichloromethane, 5 mL methanol, and 5 mL pure water successively. After 4 L water extraction, the contents of the C_{18} columns were eluted with 10 mL dichloromethane and 5 mL hexane continuously. Solid-phase samples were extracted by the accelerated solvent extraction (ASE300, Donex) method with 1:1 dichloromethane–acetone. The extraction temperature was 120 °C, and the pressure was 1500 psi. The step was repeated twice. The extracts from both SPE and accelerated solvent extraction were concentrated and the solvent was changed to hexane. Then, the silica gel–alumina packed columns (12-cm silica gel, 6-cm alumina, and 2-cm sodium sulfate) were used for purification of the complex matrix samples. The eluted fractions were concentrated to 0.5 mL, and internal standards were added before instrumental analysis.

GC–MS analysis

An Agilent 7890A gas chromatograph equipped with a 5795C mass detector with an electron impact source was used for detection of the targets. A DB-17ms fused-silica capillary column (30 m length $\times$ 0.25-mm diameter $\times$ 0.25- μ m film thickness) was used for separation of the compounds. Samples (1 μ L) were injected in splitless mode. The carrier gas was helium. The injector and

source temperatures were kept at 280 and 290 °C respectively. The temperature program was as follows: 60 °C (held for 1 min), heated to 110 °C at a rate of 20 °C/min, and heated to 290 °C at 3 °C/min (held for 20 min).

A mixed standard (1000 μ g/L) was first analyzed in full-scan mode (m/z 50–500) for the identification of the quantification ion, confirmation ion, and retention time of each compound. For the selected ion monitoring (SIM) mode, the chromatogram was divided into several retention time windows on the basis of the results with the full-scan mode. For each compound, quantification and confirmation ions were used for qualitative analysis and quantification ions were used for quantitative analysis (Table S1).

Method characterization

Seven-point calibration curves were established in pure solvent and 4 L wastewater samples on the basis of the internal standard method. The calibration concentrations ranged from 10 to 1000 μ g/L. The 10, 20, 50, 100, 200, 500, and 1000 μ g/L standards were added to the pure solvent and 4 L wastewater matrix samples. The concentrations for the calibration curve, C_{cal} , in the wastewater matrix samples were calculated as follows:

$$C_{cal} = C_{tot} - C_{sam},$$

where C_{tot} is the concentration measured in the spiked wastewater samples and C_{sam} is the concentration measured in the nonspiked wastewater samples.

The recoveries were determined for the extraction procedure, the purification procedure, and the whole procedure in the wastewater matrix samples. The method detection limits (MDLs) and method quantification limits (MQLs) were calculated on the basis of three times and ten times the signal-to-noise ratio respectively.

Results and discussion

On the basis of the method we developed previously [20], five typical PCNs and five typical CIPAHs were adopted as the target compounds.

GC–MS method development

The GC–MS chromatograms for the 39 substituted PAHs and PAHs and the two internal standards are shown in Fig. 1. The results show that the five PCNs and five CIPAHs could be detected simultaneously along with the 16 PAHs, 4 MPAHs, 4 OPAHs, and 5 NPAHs by GC–EI–MS in SIM mode and with a DB-17ms column.

Abundance

Fig. 1 Gas chromatography–mass spectrometry chromatogram for 23 substituted polycyclic aromatic hydrocarbons, 16 polycyclic aromatic hydrocarbons, and two internal standards. 1 naphthalene, 2 2-methylnaphthalene, 3 2-fluorobiphenyl, 4 2-chloronaphthalene, 5 2,6-dimethylnaphthalene, 6 1-chloronaphthalene, 7 acenaphthylene, 8 acenaphthene, 9 1,4-dichloronaphthalene, 10 fluorene, 11 9-chloro-9H-fluorene, 12 9-fluorenone, 13 phenanthrene, 14 anthracene, 15 1,2,3,4-tetrachloronaphthalene, 16 3,6-dimethylphenanthrene, 17 9-chlorophenanthrene, 18 2-chloroanthracene, 19 anthraquinone, 20

fluoranthene, 21 2-methylantraquinone, 22 pyrene, 23 2-nitrofluorene, 24 9-nitroanthracene, 25 9,10-dichloroanthracene, 26 1-methylfluoranthene, 27 1-chloroanthraquinone, 28 benz[a]anthracene, 29 chrysene, 30 3-nitrofluoranthene, 31 benz[a]anthracene-7,12-dione, 32 1-nitropyrene, 33 decachlorobiphenyl, 34 octachloronaphthalene, 35 benzo[b]fluoranthene, 36 benzo[k]fluoranthene, 37 7-nitrobenz[a]anthracene, 38 benzo[a]pyrene, 39 indeno[1,2,3-*cd*]pyrene, 40 dibenz[a,h]anthracene, 41 benzo[g,h,i]perylene, SIM selected ion monitoring

However, some peaks overlapped in the chromatogram when separated by the DB-17ms column, such as peaks 4, 5, and 6 (corresponding to 2-CN, 2,6-dimethylnaphthalene, and 1-CN) and peaks 21, 22, and 23 (corresponding to 2-methylantraquinone, pyrene and 2-nitrofluorene). With SIM mode, when ions 162, 156, 222, 202, and 211 were extracted, the six compounds could be cleanly separated.

It has also been reported that PCNs and CIPAHs could be determined with a DB-5ms column [7, 11, 15]. So we compared the DB-5ms column with the DB-17ms column to evaluate the IDLs (Table 1). For most of the compounds, especially the higher molecular weight ones, the IDLs were two to three times lower when the DB-17ms column was used than when the DB-5ms column was used. For the other compounds, when the DB-17ms column was used, the IDLs were similar to or a little lower than those obtained with the DB-5ms column. This might be due to the different polarities of the two columns. The responses (peak areas) of PCNs and CIPAHs were higher with the more polar DB-17ms column. The instrument noise values were similar with the DB-17ms and DB-5ms columns. Thus, the higher response and similar noise resulted in lower IDLs. As a result, the DB-17ms column was better than the DB-5ms column for determining the five PCNs and five CIPAHs from the aspect of the IDLs.

Extraction

Solid-phase extraction

The target compounds in the aqueous-phase samples were extracted with the C₁₈ columns. The details of the extraction procedure are given in “Pretreatment procedure.” The

Table 1 Instrument detection limits obtained with the DB-17ms and DB-5ms columns

Compound	IDL (ng)	
	DB-17ms	DB-5ms
2-Chloronaphthalene	1.5	1.5
1-Chloronaphthalene	1.5	2.0
1,4-Dichloronaphthalene	0.5	0.5
1,2,3,4-Tetrachloronaphthalene	0.5	1.0
Octachloronaphthalene	1.0	3.0
9-Chloro-9H-fluorene	3.0	2.0
9-Chlorophenanthrene	0.5	0.5
2-Chloroanthracene	0.5	1.0
9,10-Dichloroanthracene	0.5	1.0
1-Chloroanthraquinone	2.5	5.0

IDL instrument detection limit

C₁₈ column can not only extract the target compounds but can also purify environmental samples for which the matrix is not very complicated, such as tap water.

The recoveries of the ten compounds ranged from 46% to 113% (Fig. 2). For PCNs, the recoveries of 1-CN and 2CN were between 46% and 48%, and the recovery of DCN was 72%, lower than the US EPA recommended recovery standard (80–120%), while the recoveries of TeCN and OCN were 99% and 108% respectively, meeting the standard. The volatility of the compounds decreased with increasing chlorine numbers [23, 24]. Similar results were obtained by Pizzini et al. [8]. The evacuation step during the SPE procedure might accelerate the volatilization of the low chlorine number PCNs, resulting in the lower recoveries of 2-CN, 1-CN, and DCN. For CIPAHs, the recovery of 9-ClFluo was 65%, whereas the recoveries of the other four CIPAHs were between 109% and 113%.

All the compound recoveries were tested in triplicate. The standard deviations for each compound were between 4% and 18%, indicating an acceptable repeatability for the SPE method. Thus, although the recoveries of 2-CN, 1-CN, DCN, and 9-ClFluo were lower than the US EPA standards, the concentrations of these compounds could be corrected with the repeatable recovery values in the real samples. In the complex matrix samples, the lower recoveries could be compensated for by use of the matrix calibration curve, described in “Matrix effect.”

Fig. 2 Recoveries of five polychlorinated naphthalenes (PCNs) and five chlorinated polycyclic aromatic hydrocarbons (CIPAHs) during the solid-phase extraction procedure. 2-CN 2-chloronaphthalene, 1-CN 1-chloronaphthalene, D-CN 1,4-dichloronaphthalene, TeCN 1,2,3,4-tetrachloronaphthalene, OCN octachloronaphthalene, 9-ClFluo 9-chloro-9H-fluorene, 9-ClPhe 9-chlorophenanthrene, 2-ClAnt 2-chloroanthracene, 9,10-DClAnt 9,10-dichloroanthracene, 1-ClAQ 1-chloroanthraquinone

Accelerated solvent extraction

The target compounds in solid-phase samples were extracted by accelerated solvent extraction. The recoveries of most of the target compounds were between 80% and 105%, except for OCN (180%) and 9-ClFluo (62%) (Fig. 3). The repeatability of the method was satisfactory. The standard deviations for the compounds were between 2% and 8%. Similarly to in the SPE procedure, although the recovery of OCN was higher and that of 9-ClFluo was lower, the concentrations in the real samples could be corrected with use of the recoveries or the matrix calibration curve.

Purification

Considering the different polarities of the target compounds, different solvents were used for elution during the silica gel–alumina purification procedure. Fraction 1 was 10 mL hexane, fraction 2 was 70 mL 3:7 dichloromethane and hexane, fraction 3 was 60 mL 1:1 dichloromethane and hexane, and fraction 4 was 60 mL 7:3 dichloromethane and hexane. All the compounds except 1-ClAQ were eluted in fraction 2, similarly to the PAHs, MPAHs and NPAHs [20]. Because of its higher polarity, 1-ClAQ was mainly found in fractions 3 and 4, similarly to 9-Fluorenone, anthraquinone, and 2-methylanthraquinone [20]. The recoveries of all the compounds ranged from 69% to 103% (Fig. 4). The standard deviations ranged from 7% to 15%.

As a result, the five PCNs and five CIPAHs could be simultaneously extracted and purified with the 16 PAHs, 4 MPAHs, 4 OPAHs, and 5 NPAHs [20].

Fig. 3 Recoveries of five PCNs and five CIPAHs during the accelerated solvent extraction procedure

Fig. 4 Recoveries of five PCNs and five CIPAHs in different fractions during the purification procedure. F2 fraction 2, F3 fraction 3, F4 fraction 4

Matrix effect

The linearity range, coefficient of determination (R^2), and slope of the calibration curve for the target compounds in

the solvent and 4 L wastewater matrix samples were determined (Table 2). The linearity ranges for the target compounds were between 10 and 1000 $\mu\text{g/L}$ and between 50 and 1000 $\mu\text{g/L}$ for different compounds. On the basis of the linearity range for the target compounds, the linearity ranges for the 4 L spiking samples were between 1.25 and 125 ng/L and between 25 and 125 ng/L . The R^2 values of the target compounds in the solvent samples were all greater than 0.99. The R^2 values of most (more than 80%) of the compounds in the spiked wastewater samples were greater 0.99, and the R^2 values of the other compounds ranged from 0.97 to 0.98. The concentrations of 9-ClFluo could not be determined in the wastewater matrix samples because of the overlap of its peak with an unknown peak from the matrix.

The ratio between the wastewater slope and the solvent slope was calculated. Generally speaking, the slopes of the calibration curves for all the compounds in the wastewater aqueous-phase spiked samples (0.00002–0.0019) were lower than those in the solvent samples (0.0002–0.0037), which corresponded to the loss of the compounds during the pretreatment procedure. Some of the slopes for the wastewater solid-phase spiked samples

Table 2 Linearity range, coefficient of determination (R^2), and slope of the calibration curve for target compounds in solvent and 4-L spiked wastewater matrix samples and recoveries in wastewater calculated with the matrix calibration curves

Phase	Compound	Linearity range		R^2		Slope		Recovery in wastewater (%)
		Solvent ($\mu\text{g/L}$)	Wastewater (ng/L)	Solvent	Wastewater	Solvent	Wastewater	
Aqueous	2-Chloronaphthalene	10-1000	6.25-125	0.99	1.00	0.0012	0.0003	94 ± 13
	1-Chloronaphthalene	10-1000	6.25-125	0.99	1.00	0.0012	0.0002	118 ± 16
	1,4-Dichloronaphthalene	10-1000	2.5-125	0.99	0.99	0.0042	0.0015	83 ± 11
	1,2,3,4-Tetrachloronaphthalene	10-1000	2.5-125	1.00	0.99	0.0037	0.0017	82 ± 13
	Octachloronaphthalene	50-1000	25-125	0.99	0.97	0.0002	0.00002	101 ± 20
	9-Chloro-9H-fluorene	50-1000	- ^a	0.99	- ^a	0.0005	- ^a	- ^a
	9-Chlorophenanthrene	10-1000	6.25-125	1.00	1.00	0.0035	0.0019	93 ± 9
	2-Chloroanthracene	20-1000	6.25-125	0.99	0.98	0.0023	0.0016	58 ± 11
	9,10-Dichloroanthracene	20-1000	2.5-125	0.99	0.99	0.0021	0.0008	75 ± 3
	1-Chloroanthraquinone	50-1000	25-125	0.99	0.98	0.0006	0.0002	127 ± 20
Solid	2-Chloronaphthalene	10-1000	6.25-125	0.99	0.99	0.0012	0.0009	101 ± 17
	1-Chloronaphthalene	10-1000	6.25-125	0.99	0.99	0.0012	0.0007	107 ± 17
	1,4-Dichloronaphthalene	10-1000	2.5-125	1.00	0.99	0.0042	0.0029	99 ± 16
	1,2,3,4-Tetrachloronaphthalene	10-1000	2.5-125	1.00	0.99	0.0037	0.0035	90 ± 11
	Octachloronaphthalene	50-1000	2.5-125	0.99	1.00	0.0002	0.0004	77 ± 12
	9-Chloro-9H-fluorene	50-1000	- ^a	0.99	- ^a	0.0005	- ^a	- ^a
	9-Chlorophenanthrene	10-1000	6.25-125	1.00	1.00	0.0035	0.0035	108 ± 13
	2-Chloroanthracene	20-1000	1.25-125	0.99	1.00	0.0023	0.0036	87 ± 19
	9,10-Dichloroanthracene	20-1000	1.25-125	0.99	1.00	0.0021	0.0031	107 ± 19
	1-Chloroanthraquinone	50-1000	1.25-125	0.99	0.99	0.0006	0.001	116 ± 12

^a Not determined because of the overlap of the peak with an unknown peak in the matrix

Table 3 Method detection and quantification limits, and laboratory background concentrations of polychlorinated naphthalenes and chlorinated polycyclic aromatic hydrocarbons

Compound	Aqueous phase			Solid phase		
	MDL (ng/L)	MQL (ng/L)	Background (ng/L)	MDL (ng/L)	MQL (ng/L)	Background (ng/L)
2-Chloronaphthalene	0.74	2.45	ND	0.10	0.33	1.0
1-Chloronaphthalene	1.62	5.41	ND	0.18	0.61	ND
1,4-Dichloronaphthalene	0.10	0.34	<MQL	0.04	0.12	0.5
1,2,3,4-Tetrachloronaphthalene	0.07	0.24	ND	0.02	0.07	ND
Octachloronaphthalene	27.6	91.9	ND	0.01	0.04	ND
9-Chloro-9H-fluorene	^a	^a	^a	^a	^a	^a
9-Chlorophenanthrene	0.05	0.17	0.4	0.02	0.07	ND
2-Chloroanthracene	0.05	0.15	ND	0.01	0.05	ND
9,10-Dichloroanthracene	0.21	0.69	ND	0.02	0.05	ND
1-Chloroanthraquinone	0.84	2.78	ND	0.04	0.15	<MQL

MDL method detection limit, MQL method quantification limit, ND not detected

^a Not determined because of the overlap of the peak with an unknown peak in the matrix

were higher than those for the solvent (OCN and most CIPAHs), which might have resulted from the enhanced signal in the complex matrix samples. The intercept for all the calibration curves was set as 0. Thus, the ratios should be correlated to the recoveries of the compounds. Our results showed that the ratios between the wastewater slope and the solvent slope had a good linear correlation with the recoveries calculated with the solvent calibration curve ($R^2 = 0.92$) (Table S2). In addition, the coefficients of determination for the matrix calibration were satisfactory. Therefore, the matrix calibration curve could be used to calculate the concentration in the real water samples. In this way, the influence of the matrix [25] on the true concentration in the real samples could be corrected.

Method performance

Recoveries for the pretreatment procedure

The recoveries of the nine compounds (except 9-ClFluo) calculated with the matrix calibration curve in the wastewater matrix samples were almost all between 75% and 118%, except for 2-ClAnt (58%) and 1-ClAQ (127%) in the aqueous phase (Table 2). Five different spiking concentrations were used for recovery determination in the matrix samples. The standard deviations of the compounds were lower than 20%, indicating an acceptable stability. The recoveries for each compound did not significantly differ from 100% (one-sample t test, $P > 0.05$). Thus, the calibration curve for the spiked

Table 4 Detection rates and concentrations of polychlorinated naphthalenes and chlorinated polycyclic aromatic hydrocarbons in five real wastewater samples

Compound	Detection rate (%)		Concentration (ng/L)	
	Aqueous	Solid	Aqueous	Solid
2-Chloronaphthalene	100	100	13.4-29.9	11.2-16.9
1-Chloronaphthalene	0	0	ND	ND
1,4-Dichloronaphthalene	100	100	3.2-8.3	3.9-4.7
1,2,3,4-Tetrachloronaphthalene	0	0	ND	ND
Octachloronaphthalene	0	0	ND	ND
9-Chloro-9H-fluorene	^a	^a	^a	^a
9-Chlorophenanthrene	100	100	7.3-8.3	3.4-4.5
2-Chloroanthracene	100	80	7.7-9.9	ND to 4.3
9,10-Dichloroanthracene	30	0	ND to 11.8	ND
1-Chloroanthraquinone	100	100	23.3-30.4	4.2-5.3

ND not detected

^a Not determined because of the overlap of the peak with an unknown peak in the matrix

matrix samples discussed in the previous section could be used regardless of the influence of the matrix effect.

MDLs, MQLs, and laboratory background conditions

The MDLs and MQLs in the aqueous-phase samples were 0.05–27.6 ng/L and 0.15–91.9 ng/L respectively. In the solid-phase samples, the MDLs and MQLs ranged from 0.01 to 0.18 ng/L and from 0.04 to 0.61 ng/L respectively (Table 3).

In the aqueous phase, only the concentration of 9-CIPhe in blank samples (deionized water) was above the MQL, 0.4 ng/L. In the solid phase, the laboratory background concentrations of 2-CN and DCN were 1.0 and 0.5 ng/L respectively, and those of the other compounds were below the MQLs (Table 3).

Fig. 5 a Concentrations of PCNs and CIPAHs in April and November. b Distribution of PCNs and CIPAHs in aqueous-phase and solid-phase samples

Application of the method to real water samples

The five PCNs and five CIPAHs in five water samples from a river receiving wastewater treatment plant effluent were measured. 2-CN, DCN, 9-CIPhe, and 1-ClAQ were detected at a rate of 100% both in the aqueous-phase and in the solid-phase samples, whereas 1-CN, TeCN, and OCN were not found in the aqueous-phase and solid-phase samples. The concentration ranges of each compound are listed in Table 4.

The average concentrations of the detectable compounds ranged from 3.8 to 29.6 ng/L in the aqueous-phase samples and from 3.1 ng/L to 14.1 in the solid-phase samples (Fig. 5a). Compared with those in April, the concentrations of the CIPAHs (2-ClAnt, 9,10-DCIAnt, and 1-ClAQ) were higher in November, possibly resulting from a higher emission of CIPAHs in the heating season (November) than the nonheating season (April). However, the concentrations of the PCNs (2-CN and DCN) were higher in April than in November.

From comparison of the contributions of each compound in the aqueous-phase and solid-phase samples, the detectable PCNs and CIPAHs were more prone to exist in the aqueous samples (more than 50%). (Fig. 5b). The log K_{ow} values of the ten compounds were all greater than 3.0. The lower concentration in the solid-phase samples might have resulted from the low content of particulates in the wastewater samples.

Conclusion

The simultaneous detection of five typical PCNs and five typical CIPAHs was accomplished along with the 16 priority PAHs, 4 MPAHs, 4 OPAHs, and 5 NPAHs during the same pretreatment and instrumental analysis procedure. The recoveries of the five PCNs and five CIPAHs during the extraction procedure ranged from 46% to 180%. The standard deviations were lower than 18% for each compound, indicating good stability. For the purification procedure, the recoveries of the 10 compounds were between 69% and 103%, with standard deviations lower than 15%.

With this method, the true concentrations in the real aqueous-phase and solid-phase samples could be calculated with use of the matrix calibration curve, correcting the lower or higher recoveries. The recoveries of all the compounds were between 58% and 127%, with standard deviations lower than 20%. The MDLs and MQLs were less than 27.6 ng/L and less than 91.9 ng/L respectively in aqueous-phase samples, and less than 0.18 ng/L and less than 0.61 ng/L respectively in solid-phase samples.

This method was successfully used to detect the ten PCNs and CIPAHs in the water from a river receiving wastewater treatment plant effluent in Beijing. 2-CN, DCN, 9-CIPhe, 2-ClAnt, 9,10-DCIAnt, and 1-ClAQ were detected. In future

studies, other substituted PAHs with properties similar to those of the target compounds could be added for simultaneous detection after confirmation of their separation with the instrument and column, and calculation of the coefficient of determination of the matrix calibration curve.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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