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Simultaneous determination of mono- and disubstituted polyfluoroalkyl phosphates in drinking water by liquid chromatography–electrospray tandem mass spectrometry

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ABSTRACT

A sensitive liquid chromatography–electrospray tandem mass spectrometry method was established for the simultaneous determination of five monosubstituted polyfluoroalkyl phosphates (monoPAPs) and eight disubstituted polyfluoroalkyl phosphates (diPAPs) in drinking water. Complete separation and good retention for 13 polyfluoroalkyls phosphates (PAPs) were achieved with a Waters ACUITY UPLC BEH C8 column using a mixture of methanol/water containing 0.1% NH_4OH as the mobile phases. Extraction of drinking water samples was performed on weak anion exchange (WAX) cartridges, and the recoveries of target compounds were from 65 to 110%. The limits of quantization (LOQs) for 13 analytes were in the range of 0.4–40 ng/L. This method was applied to analyze the PAPs in drinking water samples from three cities in China. Of the 13 PAPs, six PAPs including 6:2 monoPAP (13.0 ng/L), 8:2 monoPAP (3.6 ng/L), 10:1 monoPAP (4.3–70.3 ng/L), 10:2 monoPAP (1.4–5.6 ng/L), 8:2 diPAP (0.10 ng/L), and 10:1 diPAP (0.8–3.8 ng/L) were detected.

1. Introduction

Perfluorinated compounds (PFCs) have been received increasing attention due to their global occurrence in environmental media (air, water, and sediment), wildlife, and human serum [1–7]. Besides the direct inputs of PFCs from production facilities, indirect sources from some precursors have been reported to be responsible for their widespread occurrence [8]. The chemicals which have been reported to be the potential precursors of PFCs include fluorotelomer alcohols (FTOHs) [9], perfluorinated sulfonamides [10] and polyfluoroalkyls phosphates (PAPs) [11].

Of these potential precursors, PAPs are of particular concern. PAPs are a mixture of various fluoroalkyl chain lengths as well as the mono- and disubstituted polyfluoroalkyl phosphates (monoPAPs and diPAPs), and primarily used in food-contact paper products and as leveling and wetting agents [12–14]. The diPAPs have been detected in human sera at 1.9–4.5 μg/L using LC–MS/MS analysis [15], which could contribute to human exposure of perfluorocarboxylates (PFCAs) since PAPs have been proved to be metabolized to perfluorocarboxylates (PFCAs) in an *in vivo* metabolism experiment [11]. While there is little information on the sources and exposure pathways of PAPs, diPAPs have also been detected in WWTP sludge at concentrations ranging from 47 to 200 ng/g [15], and therefore diPAPs could be discharged into drinking water source and residual in drinking water as exemplified by the increased PFCs concentrations at downstream drinking water facilities due to discharging from WWTP [16,17]. Drinking water is one of the human exposure routine to pollutants, but there is no report on the occurrences of monoPAPs and diPAPs in drinking water due to the lack of analytical method. Thus, there is a need for developing a sensitive and reliable method for simultaneously analyzing the broad number of these compounds with various fluoroalkyl chain lengths including both diPAPs and monoPAPs in water matrices in order to further properly estimate human exposure and assess their risks.

In this study, we developed a solid-phase extraction (SPE) method which can simultaneously concentrate 5 monoPAPs (4:2 monoPAP, 6:2 monoPAP, 8:2 monoPAP, 10:1 monoPAP and 10:2 monoPAP) and 8 diPAPs (4:2 diPAP, 4:2/6:2 diPAP, 6:2 diPAP, 6:2/8:2 diPAP, 8:2 diPAP, 8:2/10:2 diPAP, 10:1 diPAP and 10:2 diPAP), and improved the LC–MS–MS method for simultaneously analyzing 13 target PAPs with high sensitivity and separation efficiency. Finally, this method was applied to the analysis of these compounds in the drinking water samples.

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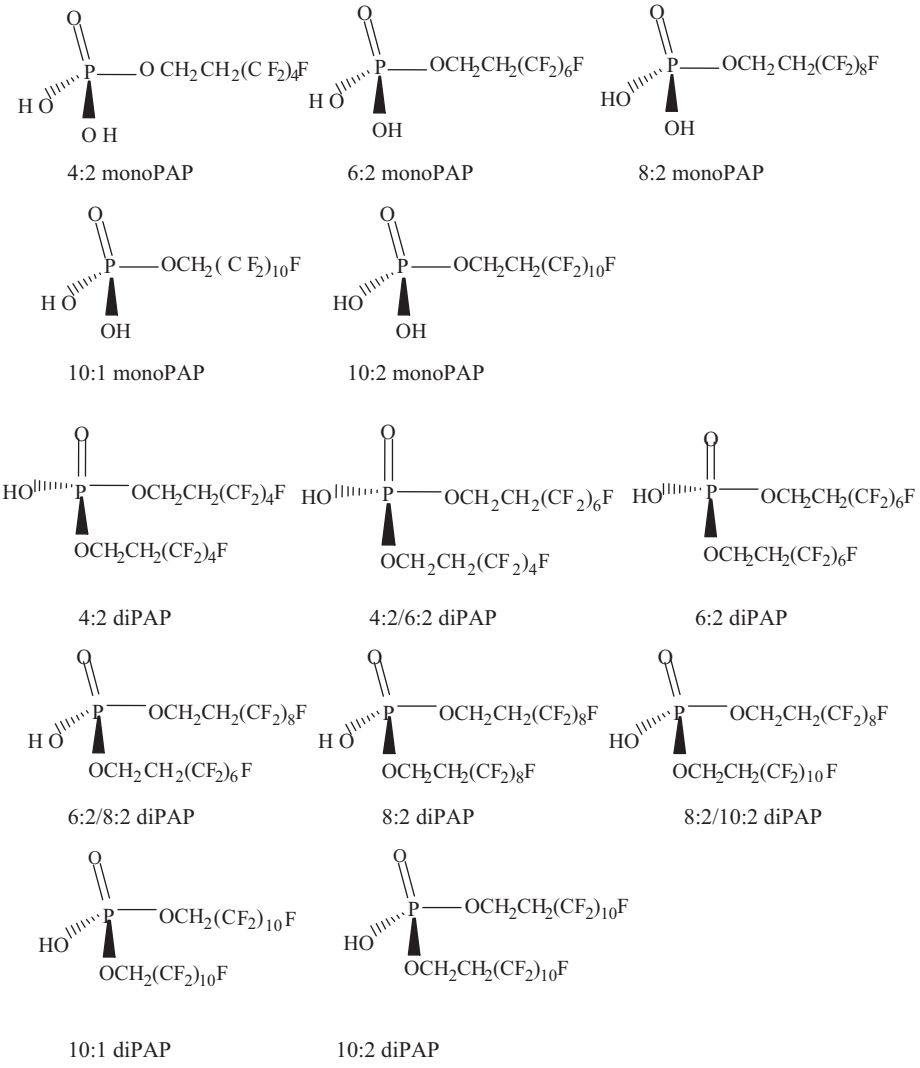

Fig. 1. Chemical structures of monosubstituted polyfluoroalkyl phosphates (monoPAPs) and disubstituted polyfluoroalkyl phosphates (diPAPs).

2. Experimental

2.1. Chemicals and reagents

The structures of thirteen target PAPs including 4:2, 6:2, 8:2, 10:1 and 10:2 monosubstituted polyfluoroalkyl phosphate (monoPAP), 4:2, 4:2/6:2, 6:2, 6:2/8:2, 8:2, 8:2/10:2, 10:1 and 10:2 disubstituted polyfluoroalkyl phosphate (diPAP) are shown in Fig. 1. These chemicals were all synthesized as described by D'eon and Mabury [11]. The purity for 4:2 monoPAP, 6:2 monoPAP, 8:2 monoPAP, 10:2 monoPAP, 4:2 diPAP, 6:2 diPAP, 8:2 diPAP, and 4:2/6:2 diPAP was >95%, the 10:1 diPAP, 10:2 diPAP, 6:2/8:2 diPAP, 8:2/10:2 diPAP was >85% pure, and 10:1 monoPAP was 80% pure. All chemicals, 4:2, 6:2, 8:2, 10:1, 10:2 fluorotelomer alcohol (FTOH) and the triethylamine (TEA), which were used for synthesizing the 13 PAPs, and internal standards M2-8:2 monoPAP and M4-8:2 diPAP were obtained from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Sep-Pak® C18 (6 mL, 1 g), Oasis®HLB (6 cm^3, 200 mg, 30 μm), and Oasis WAX (6 cm^3, 150 mg, 30 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA); Sep-Pak® C8 (6 mL, 1 g) cartridges were purchased from Agilent Technologies (Palo Alto, CA). Formic acid (FA, HPLC grade) was from Dima Technology TNC (Ontario, USA); ammonia solution (28–30%, HPLC grade) was from Alfa Aesar (Massachusetts, USA), and methanol (HPLC grade) was purchased from Fisher Chemicals (New Jersey, USA). Water obtained by a Milli-Q Synthesis water purification system (Millipore, Bedford, MA, USA) was used throughout the study.

2.2. Sample collection

Drinking water samples from three cities in China were collected on March 2010. Two samples were collected from Plant 1 and Plant 2 in Beijing, two samples were from Plant 3 and Plant 4 in Haerbin, and two samples were from Plant 5 and Plant 6 in Haikou. The water samples were collected in 500 mL polypropylene bottles, which were previously washed with methanol and distilled water 3 times. Each sample of 500 mL was extracted by WAX cartridges on the same day after they were centrifuged at the rotational speed of 9000 revolutions per minute (rpm) for 10 min.

2.3. Sample preparation and extraction

WAX cartridges were used to enrich the trace PAPs in environment. WAX cartridges were conditioned by passage of 6 mL of methanol containing 0.5% NH_4OH, followed by 6 mL of methanol and 6 mL of ultrapure water. The water samples (500 mL) containing 25% methanol (v/v) were passed through the conditioned WAX cartridges at a flow rate of 1–2 drops/s. The cartridges were then dried under a flow of nitrogen. Then 6 mL of methanol containing

Table 1
Optimized instrumental and MRM conditions of polyfluoroalkyl phosphates and their products.

Compound	Dwell time (s)	Precursor ion	Cone voltage (V)	Product ion	Collision energy (eV)
4:2 monoPAP	0.05	343	20	79	40
				97	15
6:2 monoPAP	0.05	443	20	79	60
				97	20
8:2 monoPAP	0.05	543	25	79	50
				97	25
10:1 monoPAP	0.05	628	40	79	35
				609	20
10:2 monoPAP	0.05	643	30	79	60
				97	25
4:2 diPAP	0.05	589	30	97	25
				343	16
4:2/6:2 diPAP	0.05	689	35	97	35
				443	18
6:2 diPAP	0.05	789	30	79	50
				97	35
6:2/8:2 diPAP	0.1	889	40	79	55
				97	45
8:2 diPAP	0.1	989	40	79	60
				97	30
8:2/10:2 diPAP	0.2	1089	55	79	50
				97	45
10:1 diPAP	0.05	1161	75	1121	50
				1141	50
10:2 diPAP	0.05	1189	50	79	65
				97	45

0.5% NH_4OH was used to elute the analytes from WAX cartridges. The extracts were dried under a gentle nitrogen stream and redissolved with 0.5 mL of methanol for UPLC–MS/MS analysis.

2.4. Liquid chromatography and mass spectrometry

Analysis of PAPs was performed using a Waters ACQUITY UPLC™ system (Waters, Milford, MA, USA). All PAPs were separated using a Waters ACQUITY UPLC BEH C8 column (1.7 μm; 2.1 mm × 100 mm). The column was maintained at 40 °C, and a flow rate and the injection volume were 0.2 mL/min and 5 μL, respectively. Methanol (A) and ultrapure water containing 0.1% NH_4OH (v/v) (B) were used as mobile phases. The gradient was increased from initial 20% to 50% of solvent A linearly within 2 min. After it was increased to 80% at 3 min, the mobile phase A was increased gently to 95% at 7 min, and then increased to 100% over 1 min and kept for 4 min, followed by a decrease to initial conditions of 20% A and held for 3 min to allow for equilibration.

Mass spectrometry was performed using a Waters Micromass Quattro Premier XE (triple-quadrapole) detector operated with an electrospray ionization source (Micromass, Manchester, UK) in a negative ion mode. The optimized parameters were as follows: source temperature, 110 °C; desolvation temperature, 350 °C; capillary voltage, 2.50 kV; desolvation gas flow, 800 L/h; cone gas flow, 50 L/h; and multiplier, 650 V. Finally, the data acquisition was performed in the multiple-reaction monitoring (MRM) mode, and time-segmented scanning in seven functions was used based on the chromatographic separation of target compounds to maximize sensitivity of detection. The precursor ions for all PAPs were $[M-H]^-$, the major product ion of 10:1 monoPAP was $[PO_3]^-$ (79 *m/z*), and the products ion of the other PAPs was $[H_2PO_4]^-$ (97 *m/z*). MS/MS parameters for the analytes including their precursors and product ions, cone voltage, and collision energy were summarized in Table 1.

2.5. Quantitation

Identification of the target PAPs was accomplished by comparing the retention time (within 2%) and the signal ratio (within 20%) of two selected product ions with the standards. Seven point calibration curves were constructed for the standard solutions in a concentration range between 0.04 and 200 μg/L for quantification. Instrumental detection limits (IDLs) were estimated using a method based on the linear regression ($3s_{x/y}/b$, $s_{x/y}$ indicated the standard deviation of the *y*-residuals and *b* indicate the slope of the calibration curve). The limits of detection (LODs) and limits of quantization (LOQs) were calculated based on the peak-to-peak noise of the baseline near the analyte peak obtained by analyzing field samples and on a minimal value of signal-to-noise of 3 and 10, respectively.

To avoid sample contamination, all equipments were washed with methanol, and laboratory blanks were analyzed to assess potential sample contamination. Recoveries of target compounds were analyzed by spiking standard solution to the distilled water and drinking water samples ($n = 3$). Analyte addition was made with the criterion of at least three times the original concentration that was determined prior to the fortification experiment.

3. Results and discussion

3.1. Optimization of chromatographic separation conditions

The mobile phase composition was studied to achieve optimum conditions for LC separation and ESI sensitivity. A GeminiNX C18 column has been used to separate diPAPs and monoPAPs using methanol/water or methanol/water containing 0.5% FA (v/v) as mobile phases [15,16]. However, while we used a UPLC BEH C18 column for analyzing the two groups of chemicals under similar mobile phase condition, peaks of monoPAPs were obviously tailed as shown in Fig. 2(a and b). To optimize the chromatographic conditions, the effects of pH in aqueous mobile phase on the separation of PAPs were investigated. Water containing 0.5% formic acid (pH = 2.3), water containing 0.1% formic acid (pH = 2.81), water (pH = 7), water containing 0.1% NH_4OH (pH = 10.47) and water containing 0.5% NH_4OH (pH = 10.72) were compared to select proper pH value. It was found that water containing 0.1% NH_4OH as the aqueous mobile phase not only increased the signal intensity of PAPs, but also reduced the tailings of monoPAPs. Distinguishable

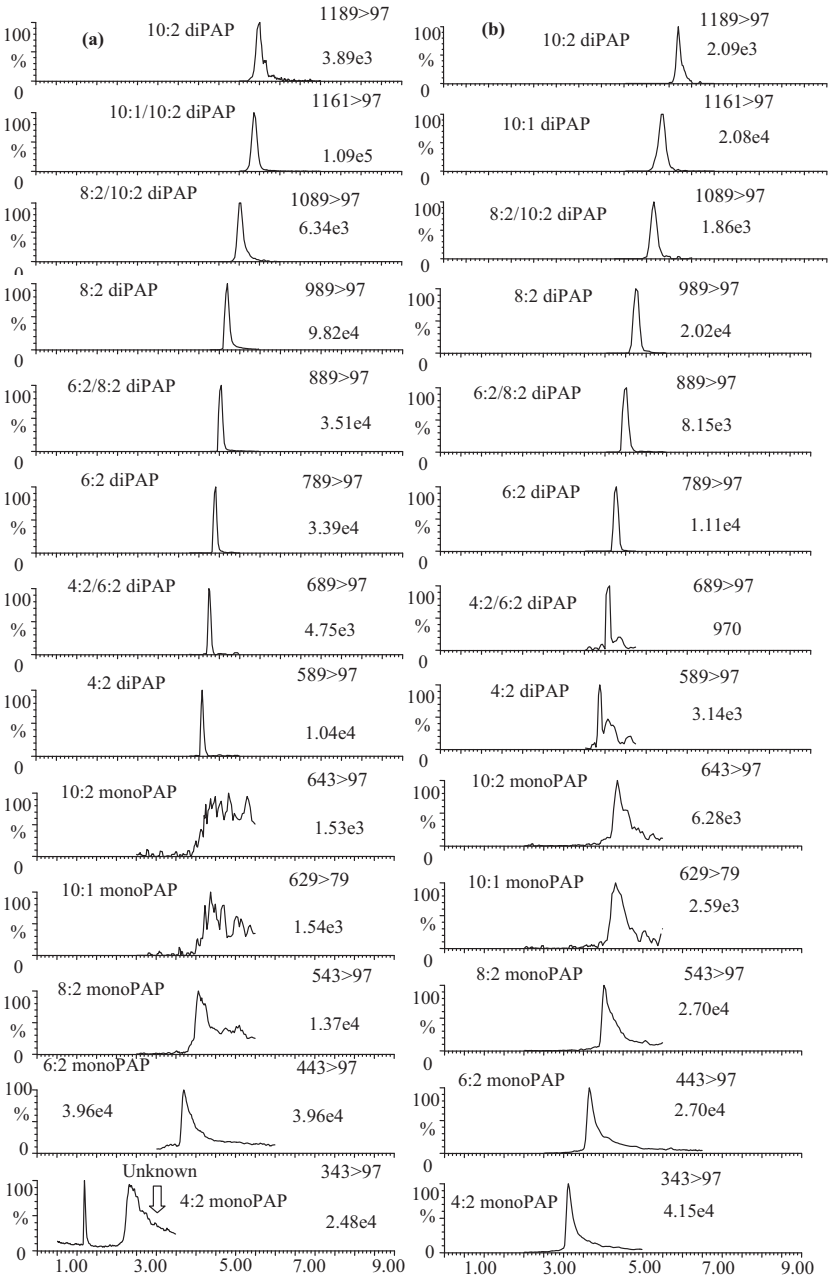

Fig. 2. LC–MS/MS MRM chromatograms of polyfluoroalkyl phosphates (PAPs) under different chromatographic conditions: (a) mobile phase: methanol/water, 100 mm C18 column; (b) mobile phase: methanol containing 0.5% formic acid (FA) (v/v)/water containing 0.5% FA (v/v), 100 mm C18 column; (c) mobile phase: methanol/water containing 0.1% NH_4OH (v/v), 100 mm C18 column; (d) mobile phase: methanol/water containing 0.1% NH_4OH (v/v), 100 mm C8 column.

peaks for all monoPAPs were achieved as shown in Fig. 2(c). This may be due to the fact that the dissociation of PAPs was increased, and therefore the retention of monoPAPs on analytical column becomes weak when using water containing NH_4OH as aqueous mobile phase in PAPs analysis. It is interesting that under such conditions, the intensity of analytes in mass spectrometry was also improved. Thus, methanol/water containing 0.1% NH_4OH were used as the mobile phases in this study.

Considering the slight tailing of peak for 10:2 monoPAP when using UPLC BEH C18 column, we also made an attempt to using a UPLC BEH C8 column to analyze the target chemicals. Comparing to UPLC BEH C18 column, UPLC BEH C8 improved the peak shape of monoPAPs especially 10:2 monoPAP and 10:1 PAP (Fig. 2(d)), meanwhile, UPLC BEH C8 column produced a 1–4-fold increase in the signal intensity for all monoPAP except for 6:2 monoPAP (0.6 fold). The improvement may be due to the fact that the longer C18 chains extended during the later organic period of the gradient and therefore the long-chain 10:1 monoPAP and 10:2 monoPAP were captured, and therefore eluted difficultly in UPLC BEH C18 column. The instrumental detection limits (IDLs) were in the range of 0.04 (8:2 diPAP)–12 (4:2 monoPAP) pg, which were lower than those reported in a previous paper. In that study, the IDLs of 4:2 monoPAP, 6:2 monoPAP, 8:2 monoPAP, 10:2 monoPAP and 6:2 diPAP were 117, 57.5, 20.5, 51.5 and 100 pg, respectively [15]. Thus, UPLC BEH C8 column was finally selected in this study from the view of sensitivity and separation.

3.2. SPE method development

No studies have reported the application of solid-phase extraction on the analytical procedure of PAPs in water samples. In the present study, recoveries of PAPs spiked onto C18, C8, HLB

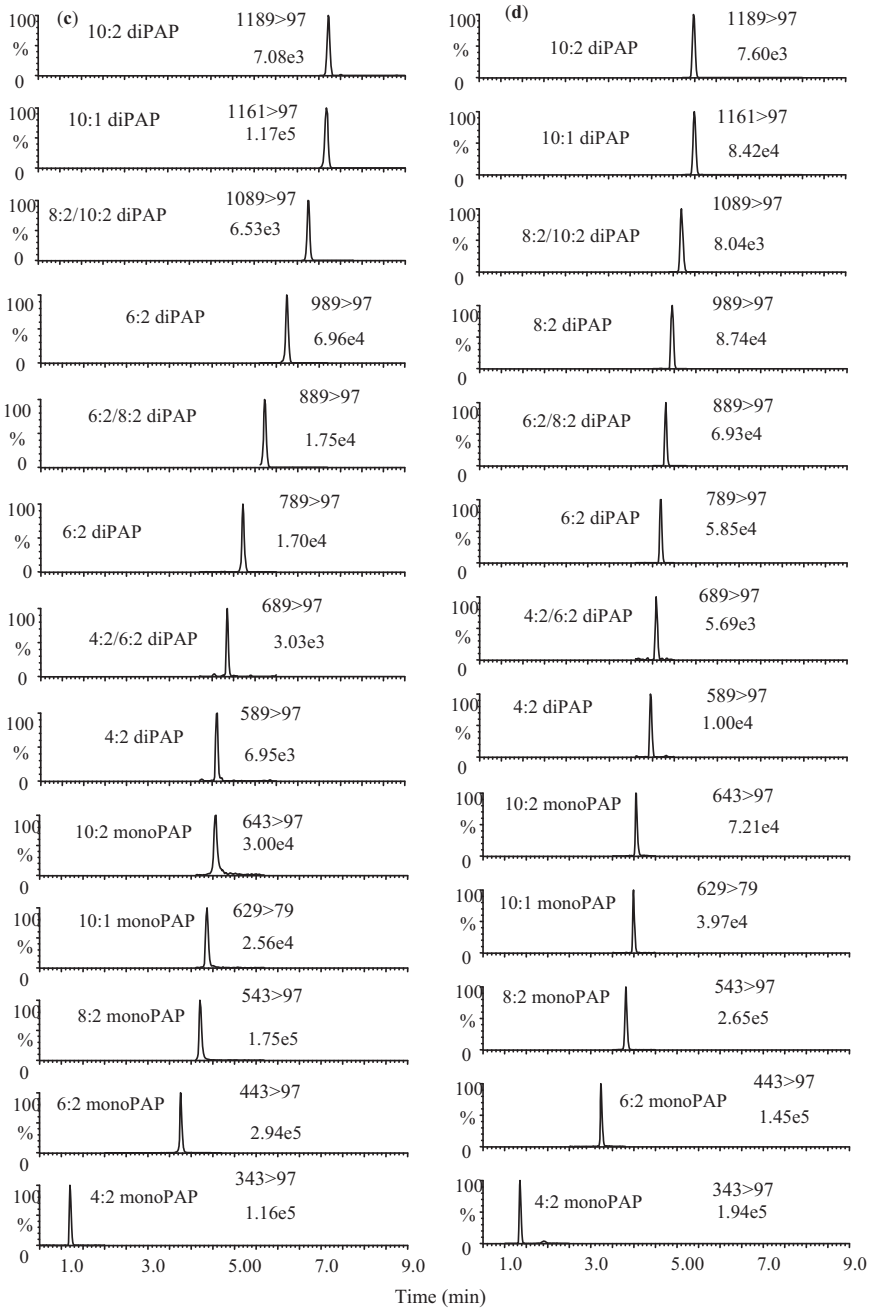

Fig. 2. (*Continued*).

and WAX cartridges were compared to select proper cartridges. Both mono- and diPAPs were eluted from C8, C18, and HLB cartridges by methanol (6 mL) and from WAX cartridges by methanol containing 0.5% NH_4OH (6 mL), respectively. Table 3 shows the detail recoveries of all PAPs through different SPE cartridges. Recoveries of target compounds at 50 ng/L by C18 and C8 cartridges were generally <50%, except for 4:2 diPAP (120%, 100%) and 4:2/6:2 diPAP (76%, 62%). When using HLB cartridges, the recoveries (>85%) of diPAPs were largely improved, while those of 5 monoPAPs except for 6:2 monoPAP (80%) were less than 40%. In order to improve the recoveries of monoPAPs, we further examined a weak anion exchange and reversed-phase sorbent, WAX. The average recoveries of PAPs were between 80 and 114% ($n = 3$) except for 10:1 monoPAP (50%) and 10:2 monoPAP (33%), which was better than those through C18, C8 and HLB cartridges.

Such sub-optimal recoveries for 10:1 monoPAP and 10:2 monoPAP were possibly due to sorption of target compounds to the polypropylene containers, poor retention by WAX, or inefficient elution of extractive procedure. Sorption of target analytes to polypropylene containers was assessed by extracting the containers with methanol after loading of cartridges with water spiked with target chemicals. However, no residual 10:1 monoPAP and 10:2 monoPAP were observed, indicating that sorption of target analytes to containers was not the reason for the low recoveries. For assessing the retention ability of WAX, tandem WAX cartridges were tried to extract the two monoPAPs. The recoveries from the first WAX cartridges were 49% and 32%, and there was no retention on the second WAX cartridges, indicating that 10:1 and 10:2 monoPAP should be retained completely by the first WAX cartridge. Therefore, inefficient elution should be the only reason responsible for the low recoveries and then we tried to weaken the sorption of

Table 2
Instrument detection limits (IDLs, μg/L), recoveries (%, $n = 3$), limits of determination (LODs, ng/L) and limits of quantization (LOQs, ng/L) in distilled and drinking water.

Compound	IDL (μg/L)	Recovery (%) ± RSD (%)		LOD(ng/L)		LOQ(ng/L)	
		Distilled water[a]	Drinking water[a]	Distilled water	Drinking water	Distilled water	Drinking water
4:2 monoPAP	2.3	93 ± 4	73 ± 2	4.1	12	14	40
6:2 monoPAP	1.4	98 ± 4	75 ± 10	2.2	4.0	7.4	13
8:2 monoPAP	0.5	94 ± 4	95 ± 13	0.5	1.4	1.7	4.6
10:1 monoPAP	0.7	79 ± 6	90 ± 10	1.0	0.8	3.4	2.7
10:2 monoPAP	0.2	57 ± 11	65 ± 7	0.3	0.4	1.0	1.2
4:2 diPAP	0.2	120 ± 8	110 ± 5	0.4	0.3	1.4	0.9
4:2/6:2 diPAP	0.1	115 ± 5	80 ± 4	0.2	0.2	0.8	0.4
6:2 diPAP	0.05	80 ± 14	78 ± 10	0.04	0.05	0.1	0.2
6:2/8:2 diPAP	0.05	69 ± 2	85 ± 12	0.2	0.3	0.8	0.8
8:2 diPAP	0.05	75 ± 5	104 ± 2	0.05	0.05	0.1	0.1
8:2/10:2 diPAP	0.05	70 ± 9	82 ± 9	0.4	0.4	1.2	1.3
10:1 diPAP	0.2	80 ± 6	91 ± 10	0.2	0.2	0.8	1.0
10:2 diPAP	0.05	73 ± 0	80 ± 5	0.15	0.2	0.9	0.8

[a] The spiked levels 23, 46, 115 ng/L for 6:2 monoPAP; 20, 40, 100 ng/L for 8:2 monoPAP and 10:1 monoPAP; 20, 40, 80 ng/L for 10:2 monoPAP; 11, 22, 44 ng/L for 4:2 diPAP; 6, 12, 25 ng/L for 4:2/6:2 diPAP; 22, 55, 111 ng/L for 6:2 diPAP; 12, 25, 63 ng/Lfor 6:2/8:2 diPAP; 19, 38, 77 ng/L for 8:2 diPAP; 4, 12, 24 ng/L for 8:2/10:2 diPAP; 10, 20, 40 ng/L for 10:1 diPAP; 5, 10, 20 ng/L for 4:2 monoPAP and 10:2 diPAP.

these two monoPAPs to cartridges by adding methanol into water samples, and different percentages of methanol (0%, 25% and 40%) in water samples were examined. The recoveries of monoPAPs were improved by increasing the percentage of methanol in water sample, while the recoveries of most diPAPs become poor (Fig. 3). At 25% methanol in water samples, the recoveries of 10:1 and 10:2 monoPAPs were improved to 79% and 57%, respectively, and the recoveries of the other target analytes can be improved to be around 75%. Thus, we selected 25% methanol for further studies.

The recoveries in distilled and drinking water samples are shown in Table 2. As shown in Table 2, the recoveries for all the target analytes in the distilled and drinking water at three spiked concentration levels were 57–120% and 65–110%, respectively, with a relative standard error less than 13%.

3.3. Quantification and method validation

While isotopically labeled standards for each PAP are preferable for determination of chemicals in environmental samples, we only commercially obtained M2-8:2 monoPAP and M4-8:2 diPAP. In this study, M2-8:2 monoPAP and M4-8:2 diPAP were used as the internal standard for analysis of monoPAPs and diPAPs, respectively. Calibration curves were constructed for each PAP from 0.04 to 201 μg/L (the standard concentration levels for 4:2 monoPAP were at 1.0, 2.0 4.1, 16, 32, 64, and 129 μg/L, for 6:2 monoPAP were at 0.75, 2.3, 9.0, 18, 36, 72, and 115 μg/L, for 8:2 monoPAP were at 0.38, 0.99, 4.0, 15, 31, 62, 124 μg/L, for 10:1 monoPAP were at 0.11, 0.5, 3.8, 15, 30, 60, and 121 μg/L, for 10:2 monoPAP were at 0.09, 0.2, 6.9, 14, 27, 44, and 110 μg/L, for 4:2 diPAP were at 0.11, 0.94, 1.9, 7.4, 29, 94, and 118 μg/L, for 4:2/6:2 diPAP were at 0.10, 2.5, 13, 25, 50, 100, and 201 μg/L, for 6:2 diPAP were at 0.05, 0.56, 2.2, 8.7, 35, 70, and 139 μg/L, for 6:2/8:2 diPAP were at 0.05, 0.19, 2.5, 9.8, 20, 63, and 158 μg/L, for 8:2 diPAP were at 0.05, 0.12, 1.9, 7.5, 30, 60, and 120 μg/L, for 8:2/10:2 diPAP were at 0.05, 0.2, 1.9, 7.7, 30, 61, 122 μg/L, for 10:1 diPAP were at 0.18, 0.87, 1.7, 11, 27, 55, and 111 μg/L, for 10:2 diPAP were at 0.04, 0.16, 2.5, 8.0, 20, 40, 80, 160 μg/L), and calibration graphs were linear with good correlation coefficients ($r^2 > 0.99$). The intra- and inter-day precisions were calculated by the relative standard deviations (RSDs) at three concentration levels for each PAP within the linear ranges. The intra-day RSDs ($n = 5$) were below 15%. The inter-day RSDs were calculated by a 15-day period replicated analysis, and was generally lower than 12%. The LODs of PAPs were in the range of 0.05 ng/L (6:2 diPAP and 8:2 diPAP)-12 ng/L (4:2 monoPAP), and their LOQs ($n = 3$) were in the range of 0.1 ng/L (8:2 diPAP)-40 ng/L (4:2 monoPAP).

Since matrix effect is a general problem in the LC–MS/MS analysis, we evaluated the extent of signal suppression/enhancement in LC-ESI/MS/MS detection by spiking standards of PAPs to the extracts of drinking water. The signal suppression/enhancement for each analyte was then calculated using the percentage of signal intensity in a sample matrix versus the signal of the same

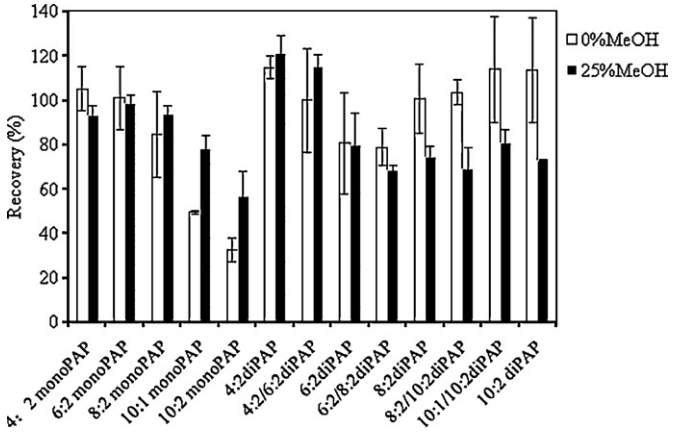

Fig. 3. Effects of methanol content in water samples on the recoveries of monosubstituted polyfluoroalkyl phosphates (monoPAPs) and disubstituted polyfluoroalkyl phosphates (diPAPs) through oasis WAX.

Table 3
Recoveries of monosubstituted polyfluoroalkyl phosphates (monoPAPs) and disubstituted polyfluoroalkyl phosphates (diPAPs) through different SPE cartridges.

Compound	Recovery (%) ± RSD (%)[a]			
	WAX	HLB	C18	C8
4:2 monoPAP	105 ± 10	34 ± 5	25 ± 9	1 ± 0
6:2 monoPAP	101 ± 14	124 ± 4	23 ± 2	12 ± 2
8:2 monoPAP	85 ± 20	30 ± 3	9 ± 2	7 ± 1
10:1 monoPAP	50 ± 1	24 ± 1	3 ± 1	2 ± 1
10:2 monoPAP	33 ± 5	19 ± 3	2 ± 1	2 ± 1
4:2 diPAP	114 ± 5	103 ± 5	122 ± 23	100 ± 20
4:2/6:2 diPAP	100 ± 23	94 ± 6	76 ± 13	63 ± 19
6:2 diPAP	81 ± 22	91 ± 1	43 ± 4	35 ± 13
6:2/8:2 diPAP	80 ± 8	92 ± 2	27 ± 1	33 ± 5
8:2 diPAP	101 ± 15	93 ± 1	19 ± 1	19 ± 3
8:2/10:2 diPAP	104 ± 6	86 ± 4	27 ± 1	22 ± 8
10:1 diPAP	114 ± 23	97 ± 2	36 ± 2	37 ± 13
10:2 diPAP	113 ± 23	87 ± 2	42 ± 17	42 ± 17

[a] Spiked concentration was 50 ng/L for each PAP.

Table 4
Concentrations (ng/L) of polyfluoroalkyl phosphates (PAPs) detected in water plants of China.

Compound	Concentrations (ng/L) [mean ±RSD (%), $n = 3$]					
	Beijing		Haerbin		Haikou	
	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
4:2 monoPAP	–[a]					–
6:2 monoPAP	–		13.0 ± 1.4			–
8:2 monoPAP	–		3.6 ± 1.5			–
10:1 monoPAP	70.3 ± 1.8	10.0 ± 1.3	7.2 ± 0.4	7.2 ± 2.1		4.3 ± 1.1
10:2 monoPAP	5.6 ± 1.3	1.8 ± 0.7		3.0 ± 0.9	1.4 ± 1.1	–
4:2 diPAP	–					–
4:2/6:2 diPAP	–					–
6:2 diPAP	–					–
6:2/8:2 diPAP	–					–
8:2 diPAP	–		0.10 ± 0.05	0.10 ± 0.05		–
8:2/10:2 diPAP	–					–
10:1 diPAP	0.8 ± 1.2		1.4 ± 0.7	3.8 ± 1.6		1.5 ± 1.0
10:2 diPAP	–					–
Total	76.7	11.8	25.3	14.1	1.4	5.8

[a] Under the method determination limit.

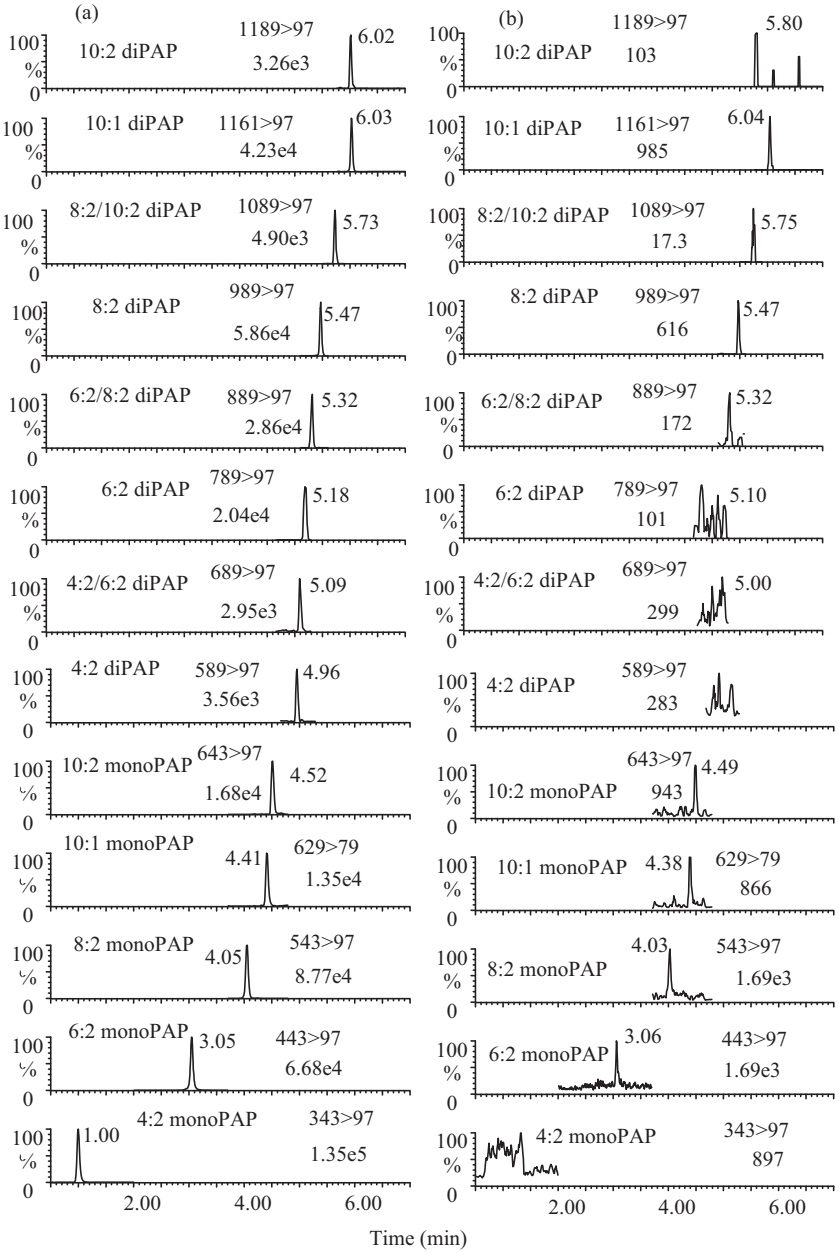

Fig. 4. LC–MS/MS MRM chromatograms of analytes detected in standard solution (a) and drinking water sample (b).

concentration in the pure solvent (methanol). The results showed that less than 20% of signal suppression/enhancement for all target analytes observed in the drinking water. We tested procedural blanks to check for procedural contamination, and no target compounds were detected in the final extracts of procedural blanks.

3.4. Environmental samples

The method developed in this study was applied to the analysis of 13 target PAPs in the drinking water collected from six water supply plants in China. Of the 13 analytes, six PAPs including 6:2 monoPAP, 8:2 monoPAP, 10:1 monoPAP, 10:2 monoPAP, 8:2 diPAP and 10:1 diPAP were detected. Fig. 4 shows the typical chromatograms of PAPs in a drinking water sample. The highest total concentration (76.7 ng/L) and lowest concentration (1.4 ng/L) of PAPs were found in the drinking water samples from Plant 1 in Beijing and Plant 5 in Haikou (Table 4). The highest detection frequency among six PAPs was 10:1 monoPAP. It is interesting that 10:1 monoPAP was the predominant congener in Beijing, accounting for 91% of total PAPs in Plant 1 and 85% in Plant 2. Overall, concentration and composition of PAPs were dependent on sampling location.

4. Conclusions

A UPLC–MS/MS method with high sensitivity and separation efficiencies was established for analyzing 13 polyfluoroalkyl phosphates in drinking water using solid-phase extraction and liquid chromatography–electrospray tandem mass spectrometry. This was the first time to report the method and occurrence of PAPs in drinking water samples. The developed method provided a tool to detect 13 PAPs in drinking water, which will aid the further research of their environmental fates and transport, especially for understanding their contribution to PFCs exposure.

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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.2012.01.004.

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