



# 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 polyfluoroalkyl phosphates (PAPs) were achieved with a Waters ACUITY UPLC BEH C8 column using a mixture of methanol/water containing 0.1% NH<sub>4</sub>OH 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.

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## 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 polyfluoroalkyl 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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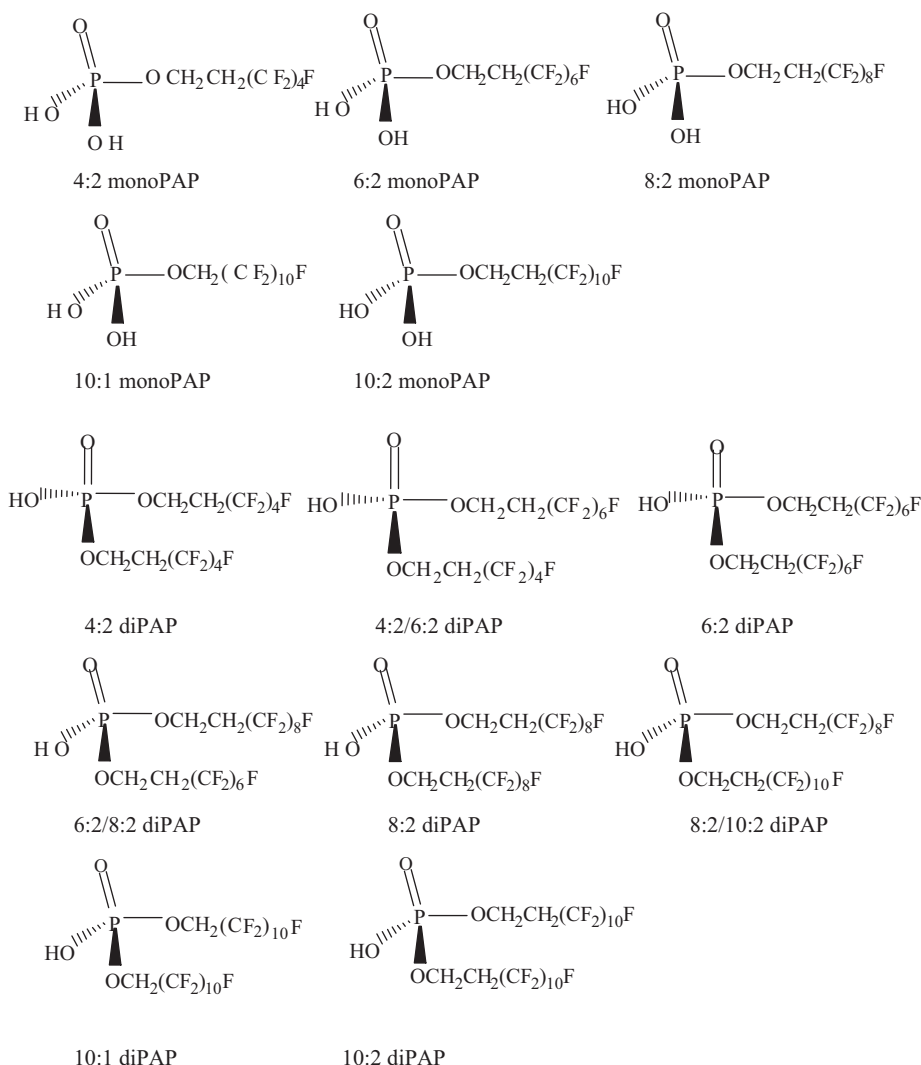


Fig. 1. Chemical structures of monosubstituted polyfluoroalkyl phosphates (monoPAPs) and disubstituted polyfluoroalkyl phosphates (diPAPs).

## 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) and 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<sup>®</sup> C18 (6 mL, 1 g), Oasis<sup>®</sup>HLB (6 cm<sup>3</sup>, 200 mg, 30 μm), and Oasis WAX (6 cm<sup>3</sup>, 150 mg, 30 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA); Sep-Pak<sup>®</sup> 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<sub>4</sub>OH, 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

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