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Trace analysis of mono-, di-, tri-substituted polyfluoroalkyl phosphates and perfluorinated phosphonic acids in sewage sludge by high performance liquid chromatography tandem mass spectrometry

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ABSTRACT

A new method using ultrasonic extraction and solid phase extraction (SPE) clean-up pretreatments was developed for the analysis of mono-, di- and tri-substituted polyfluoroalkyl phosphates (abbreviated as mono-PAPs, di-PAPs and tri-PAPs) and perfluorinated phosphonic acids (PFPA) in sludge from wastewater treatment plants (WWTPs). For the ultrasonic extraction of three mono-PAPs, three di-PAPs and three PFPA in sludge samples, a mixture of tetrahydrofuran/acetic acid (1:1, v/v) was found to be the most suitable extraction solvent. The subsequently optimized clean-up and enrichment procedures were carried out with weak anion exchange (WAX) cartridges in-line coupled with graphitized carbon black (ENVI-Carb) tubes. Two tri-PAPs were ultrasonically extracted by acetonitrile/tetrahydrofuran (1:1, v/v) and cleaned by mixed-mode anion exchange (MAX) in-line coupled with ENVI-Carb cartridges. The analytes were analyzed by optimized high performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS) method either in negative or positive ionization mode. The method quantification limits (MQLs) of the 11 analytes in sludge ranged from 0.6 to 5.1 ng/g, meanwhile the total recoveries of the pretreatment varied from 24% (6:2 mono-PAP) to 107% (PFDP). The method was successfully applied to analyze 16 sewage sludge samples collected from seven provinces in China, and two mono-PAPs were identified with concentrations ranging from < MQLs to 10.7 ng/g.

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1. Introduction

Due to good surface tension properties and thermal stability, poly- and perfluorinated alkyl substances (PFASs) are widely used in a variety of consumer products and industrial applications such as fire fighting foams [1], insecticides [2], textile coatings, paper packaging materials [3] and as polymerization aids in fluoropolymer manufacturing processes [4]. The ubiquitous presence of PFASs in water, air, sediment, wildlife and human [5–11] has triggered an increasing health concern on these chemicals, especially perfluoroalkyl sulfonic acids (PFSA) and perfluoroalkyl carboxylic acids (PFCA), due to their bioaccumulative properties [12], persistence, long-range transport potential [13] and toxic effects [14,15]. Besides major contribution from direct source emissions, many polyfluorinated precursors such as fluorotelomer alcohols, perfluorinated sulfonamides, perfluorooctane sulfonyl fluoride and polyfluorinated iodine alkanes could be transformed into related perfluorinated acids and also contribute to the global distribution of PFSA and PFCA [16–22].

Polyfluoroalkyl phosphates (PAPs) belong to a group of hydrophobic phosphates that are mainly mono-, di- and tri-substituted by partially fluorinated alkyl chains (abbreviated as mono-PAPs, di-PAPs and tri-PAPs). Commercial products usually consist of different fluoroalkyl chain length mixtures (typically C8–C12) and were reported to be primarily used in food-contact paper industries in recent years to replace the previously phased-out leveling and wetting agents [23–25]. Under certain conditions, PAPs could migrate into food from its contact paper and thus might be another potential exposure pathway of PFASs to humans [24]. Perfluorinated phosphonic acids (PFPA) are another group of fluoroalkyl mono-substituted phosphonate derivative but are structurally different in that the perfluorinated carbon tail is directly attached to the phosphonate unit. The PFPA are commonly used as pesticides, lubricant and anti-foaming agents in textile industry [26]. Di-PAPs and perfluorooctyl phosphonic acid (PFOPA) have been reported to be present in the environment such as drinking water and sewage sludge, and even in human serum [27,28]. Furthermore, recent studies have shown that PAPs and PFPA could be bio-transformed into relevant PFCA in activated sludge and in biota such as rat and juvenile rainbow trout [29–31].

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Similar to other hydrophobic substances, most PAPs and PFPAs could be associated with suspended particulate matters and sedimentary sludge [32], and reliable analytical methods to monitor their environmental concentrations and fate in solid matrices are therefore important. However, trace analytical methods for the determination of PAPs and PFPAs in the environment are still limited, especially for complex environmental matrices. Deon et al. were the first to use an ion-pairing based liquid–liquid extraction method to extract di-PAPs and PFCAs from sludge and paper fiber samples with di-PAP recoveries ranging from 38% to 53% [27]. However, the analyte instrument analysis of the method might be vulnerable to matrix interferences due to the lack of clean-up procedures in the sample pretreatment processes. Solid phase extraction (SPE) method is commonly used pretreatment strategy for the analysis of various kinds of PFASs homologs from different complex environmental matrices such as soil, sediment and sludge [33,34]. And optimized solvent–mixture extraction prior to the SPE protocol were also reported to be able to further expand the SPE application scope to maximize extract efficiencies of different PFCA and PFFA homologs from complex food and sludge matrices [28,35]. To the best of our knowledge, there are currently few reports on simultaneous extraction of different kinds of PAPs and PFPAs in sewage sludge by optimizing the solvent extraction procedures.

In this study, a simple and efficient method was developed for the trace analysis of eight PAPs and three PFPAs from sludge samples by comparing a variety of solvent extraction strategies. Weak anion exchange (WAX), mixed-mode anion exchange (MAX), weak cation exchange (WCX) and graphitized carbon black (ENVI-Carb) SPE adsorbents were further optimized in the subsequent enrichment and clean-up procedures. Finally this method was applied to the analysis of PAPs and PFPAs in 16 sludge samples collected from different WWTPs in China.

2. Experimental

2.1. Chemicals and reagents

Analyte name, structure and other relevant data are shown in Table 1. All mono-, di-, tri-substituted and mass-labeled PAPs (6:2 mono-PAP, 8:2 mono-PAP, 10:2 mono-PAP, 6:2 di-PAP, 8:2 di-PAP, 10:2 di-PAP, 6:2 tri-PAP, 8:2 tri-PAP and 6:2 di-PAP-d4) were obtained from Chiron AS (Trondheim, Norway). PFPAs standards (PFHxPA, PFOPA, PFDPA) and the internal standard Cl-PFHxPA were supplied by Wellington Laboratories Inc. (Guelph, Ontario, Canada). The purity for all the target analytes were >99% except for di-PAPs (>94%). Stock standard solutions (50 µg/mL) were individually prepared in methanol and intermediate solutions were weekly prepared from the stock standard solutions by appropriate methanol dilution. Oasis WAX (6 cm³, 150 mg), MAX (6 cm³, 150 mg) and WCX (6 cm³, 150 mg) SPE cartridges were purchased from Waters (Milford, MA, USA), and ENVI-Carb (6 cm³, 250 mg) cartridges were from Supelco (Bellefonte, PA, USA). All solvents were of HPLC grade. Tetrahydrofuran (THF), methanol (MeOH) and acetonitrile (ACN) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water (18.3 MΩ cm) was generated by a Milli-Q purification system (Millipore, Billerica, MA, USA). Acetic acid (HAc) was from Mallinckrodt (Phillipsburg, NJ, USA). Formic acid and ammonia solutions (NH₄OH, 28–30%) were from Dikma (Richmond Hill, ON, Canada) and Alfa Aesar (Ward Hill, MA, USA), respectively.

2.2. Sample collection and preparation

Sixteen sludge samples were collected from different WWTPs in seven provinces in China in February 2011. Approximately

500 g of freshly digested sludge was collected at the dewatering process, packed in aluminum foil, sealed in polypropylene bag, and immediately express-delivered to our lab. All sludge samples were freeze-dried, homogenized, sieved through a stainless steel 100-mesh sieve and then stored in –20 °C until analysis. Detailed information on the sampling location, treatment processing volume and WWTP treatment type is given in the supplementary data (Table S1).

2.3. Sample extraction

The 11 analytes were extracted by two different solvent extraction strategies as follows. For mono-, di-PAPs and PFPAs, an aliquot of 0.3 g sample was placed into a 15 mL polypropylene centrifuge tube and was extracted by 5 mL of THF/HAc (1:1, v/v) in a 50 °C ultrasonic water bath for 20 min. The HAc was a diluted ultrapure water solution with concentration of 1 mol/L (1 M). Supernatant extract was decanted after the centrifuge tube was centrifuged at 4500 rpm for 5 min. The extraction procedure was repeated for 3 times and the extract was combined and then diluted to 100 mL by ultrapure water for the subsequent sample clean-up process. For the analysis of tri-PAPs, the extraction procedure was quite similar except that ACN/THF (1:1, v/v) was used as extraction solvent. Disposable polypropylene tubes, bottles and pipettes were used thoroughly to prevent analyte adsorption and contamination from glassware.

2.4. Sample clean-up and enrichment

Different SPE adsorbents are often specifically chosen to enrich analytes and remove matrix interferences in sample extracts. In this study, WAX cartridge in-line coupled with ENVI-Carb was selected for the elimination of interferences as well as recovery optimization of the mono-, di-PAPs and PFPAs. Before use, the WAX cartridges were preconditioned by 5 mL MeOH containing 5% NH₄OH, 5 mL MeOH and 5 mL ultrapure water in sequence. Diluted extracts from the ultrasonic extraction procedure were passed through the cartridges at a flow rate of 1–2 drops/s. After loading, the cartridges were washed with 5 mL of HAc at pH=4 and 20 mL of ACN/THF (1:1, v/v) mixture to maximize matrix interferent elimination. The cartridges were then dried under vacuum for 10 min and centrifuged at 4500 rpm for 10 min. After that the WAX cartridges were coupled to the 5 mL MeOH preconditioned ENVI-Carb tubes via polyethylene (PE) adapter caps. Elution of 3 × 3 mL MTBE/MeOH (90:10, v/v) containing 5% NH₄OH was applied to ensure maximum recoveries of the target compounds. The eluate was concentrated under nitrogen flow to a final volume of 1 mL for instrument quantification analysis. Before injection, 6:2 di-PAP-d4 and Cl-PFHxPA were added into the final eluates as internal standards for di-PAPs and PFPAs, respectively.

For ultrasonic extracts of tri-PAPs, the subsequent clean-up and enrichment procedures were conducted with MAX in-line coupled with ENVI-Carb adsorbents. The MAX cartridges were preconditioned by 5 mL MeOH containing 2% formic acid, 5 mL MeOH and 5 mL ultrapure water. The diluted extracts were passed through the conditioned cartridges at a flow rate of 1–2 drops/s. After loading, the cartridges were washed with 5 mL of ultrapure water containing 5% NH₄OH and 30 mL of MeOH/H₂O (1:1, v/v) mixture. The cartridges were then dried, centrifuged, and coupled to the 5 mL MeOH preconditioned ENVI-Carb tubes via PE adapter caps. The target compounds were finally eluted with 3 × 3 mL of MTBE/MeOH (90:10, v/v) containing 2% formic acid, and concentrated under nitrogen flow to a final volume of 1 mL.

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