國立臺灣大學公共衛生學院環境衛生研究所

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Master Thesis

以固相萃取搭配極致液相層析/串聯式質譜儀分析水中全氟碳化合物、鄰苯二甲酸酯、壬基酚與雙酚 A

Determination of Perfluoroalkyl Substances, Phthalate Esters, Nonylphenol, and Bisphenol A in Water by Solid-Phase Extraction and UPLC-MS/MS

陳則穎

Ze-Ying Chen

指導教授: 陳家揚 博士

Advisor: Chia-Yang Chen, Ph.D.

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本論文係陳則穎（R04844007）在國立臺灣大學環境衛生研究所完成之碩士學位論文，於民國 106 年 7 月 31 日承下列考試委員審查通過及口試及格，特此證明

口試委員：陳宗揚（簽名）

（指導教授）

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陳鑫昌

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We, the undersigned, hereby recommended that the thesis entitle, Determination of Perfluoroalkyl Substances, Phthalate Esters, Nonylphenol, and Bisphenol A in Water by Solid-Phase Extraction and UPLC-MS/MS, submitted by Ze-Ying Chen, be accepted as fulfilling the thesis requirement for the degree of Master of Science in Public Health

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Hsin-Chang Chen

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中文摘要

全氟碳化合物、鄰苯二甲酸酯、壬基酚與雙酚 A 普遍存在於環境中，這些物質被廣泛的使用於日常消費性產品，如防水衣物塗料、油漆、塑膠產品、清潔劑及食品容器。許多研究指出，這些物質具有肝毒性、發展毒性與生殖毒性。除此之外，這些物質也都屬於內分泌干擾物質，具有影響人體賀爾蒙系統的性質。此四類物質主要藉由水在環境中傳播，因此就有需要監測此四類物質於環境水體中的濃度。本研究將探討 10 種全氟碳化合物 (PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, and PFOS)、6 種鄰苯二甲酸酯 (DEP, BBP, DEHP, DNOP, DINP and DIDP)、壬基酚、雙酚 A 於水中的濃度。此研究將以極致液相層析搭配串聯式質譜儀進行分析，並以固相萃取做為樣本前處理方法。水樣在分析前會先以 30 μL 88%甲酸酸化至 pH 3。固相萃取吸附劑在操作前依序以 5 mL 異丙醇、甲醇及 Milli-Q 水進行活化，以 5 mL/min 通過 100 mL 水樣後，以 0.6 mL 10%甲醇/90% Milli-Q 水清洗吸附劑兩次，之後氮氣吹淨 45 秒。最後依序使用 2 mL 甲醇、2 mL 異丙醇，以流速 1 mL/min 各沖提兩次，並全部收集。萃取溶液濃縮至 1.0 mL 後以 0.22 μm 尼龍過濾器過濾，並再次濃縮至近乾，最後以 100 μL 甲醇回溶並上機分析。實驗結果顯示，6 種鄰苯二甲酸酯的基質效應介於 88%到 116%之間。全氟碳化物方面，PFBA, PFNA, PFDA, PFUnDA, PFDoDA 的基質效應介於 77%到 85%之間，PFPeA, PFHxA, PFOA, PFHxS, PFOS 的基質效應分別為 64%、33%、55%、60%、10%。壬基酚與雙酚 A 的基質效應則為 79%與 93%。

關鍵字: 全氟碳化合物、鄰苯二甲酸酯、壬基酚、雙酚 A、固相萃取、極致液相層析/串聯式質譜儀

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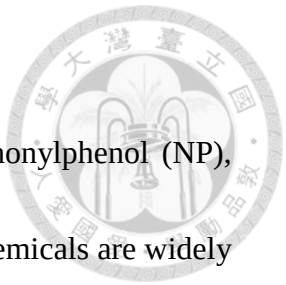

Abstract

Perfluoroalkyl substances (PFASs), phthalate esters (PAEs), nonylphenol (NP), and bisphenol A (BPA) are ubiquitous in the environment. These chemicals are widely used in consumer products, such as protective coatings for textiles, paint, plastic products, detergents, and food containers. Many studies show that these compounds have hepatotoxicity, reproductive toxicity, and developmental toxicity, and they are endocrine-disrupting compounds, which means they can alter the function of our hormone system. Water is the primary way for these chemicals to spread in the environment. Thus, it is necessary to monitor these compounds in the water. This study will determine 10 PFASs (PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, and PFOS), 6 PAEs (DEP, BBP, DEHP, DNOP, DINP, and DIDP), nonylphenol, and bisphenol A in river water with ultra-high performance liquid chromatography/tandem mass spectrometry. Solid-phase extraction (SPE) with HLB cartridges will be chosen as sample preparation method. Water samples were acidified to pH 3 by adding 30 μL of 88% formic acid before SPE. In SPE procedures, the cartridgess were conditioned with 5 mL of isopropyl alcohol, 5 mL of methanol and 5 mL Milli-Q water sequentially. After loading 100 mL water samples at the flow rate of 5 mL/min, the cartridges were washed with 0.6 mL of MeOH/Milli-Q water (1:9, v/v) twice, then dried with nitrogen gas (N_2) for 45 seconds. Elution was

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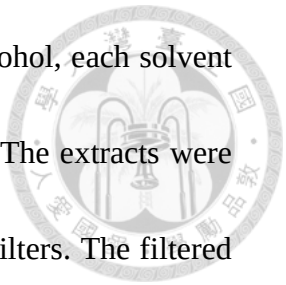

conducted by 2 mL of methanol followed by 2 mL of isopropyl alcohol, each solvent eluted at flow rate of 1 mL/min twice, and was collected together. The extracts were concentrated to 1.0 mL, and were filtrated through 0.22 μm nylon filters. The filtered extracts were concentrated to barely dried, and then were reconstituted with 100 μL of methanol prior to instrumental analysis. The results showed that the matrix effect factors of six PAEs were 88%-116%. In PFASs, the matrix effect factors of PFBA, PFNA, PFDA, PFUnDA and PFDoDA were 77%-85%, and PFPeA, PFHxA, PFOA, PFHxS and PFOS were 64%, 33%, 55%, 60% and 10%, respectively. Matrix effects of nonylphenol and BPA were 79% and 93%, respectively.

Keywords: Perfluoroalkyl substances, phthalate esters, nonylphenol, bisphenol A, solid-phase extraction, UPLC-MS/MS

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Chapter 1. Introduction

1.1 Perfluoroalkyl substances

Perfluoroalkyl substances (PFASs) are chemically stable and surface-active, and are widely used in consumer and industrial products, such as in protective coatings for carpets, textiles, leather, paper, paints, adhesives, in fire-fighting foams, as specialty surfactants in cosmetics, electronics and medical use.[1, 2] Because of the high energy of carbon-fluorine (C-F) bonding, PFASs are resistant to hydrolysis, photolysis, microbial degradation and metabolism by vertebrates.[1-3] PFASs are reported to have hepatotoxicity, developmental toxicity, immunotoxicity, teratogenicity, carcinogenic potency, neurotoxicity and endocrine disrupting.[1, 4] PFASs are very soluble in water, and the processing of drinking water and sewage treatment is ineffective in removing these chemicals, so they have become a concern as contaminants in drinking water.[1, 5] Perfluorooctanoic acid (PFOA) and perfluooctane sulfonate (PFOS) have been found to be the representative PFASs in the environment and in biota.[3] PFOA ranged from 0.6 to 1270 ng/L in river water globally, and PFOS ranged from non-detected (N.D.) to 25 ng/L worldwide.[2, 4, 5] PFOA could be detected at about 56 μg/L in river near fluorochemical manufacturing facilities.[2] The half-lives of PFOA and PFOS are estimated to be longer than 92 and 41 years in 25℃ water.[1, 3] When rodent dams exposed to PFOS at the level of 10

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mg/kg b.w. throughout pregnancy, the neonates became moribund and died soon; on the case of PFOS at the level of 5 mg/kg b.w., over 95% of the neonates did not survive the first day of postnatal. When expose level was 3 mg/kg b.w., survival increased to 50%.[6] United States Environmental Protection Agency (USEPA) sets of PFOA and PFOS in drinking water at 0.4 and 0.2 μg/L, respectively. European Food Safety Authority (EFSA) sets a tolerable daily intake (TDI) of 150 ng/kg b.w./day for PFOS and 1500 ng/kg b.w./day for PFOA.[1] PFASs have attracted public attention because they are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful.[2, 3, 5, 7] These chemicals are primarily emitted to water and accumulate in surface water. Water is the reservoir and the most important transport medium in the environment.[2] Thus, it is necessary to monitor the concentration of PFASs in the environmental water bodies.

1.2 Phthalate esters

Phthalate esters (PAEs) are colorless sticky liquids and are widely used as plasticizers for polyvinyl chloride production. They are common additive in paints, lubricants, food packaging, cosmetics, toys, personal care products, medical devices, and pesticide.[8-17] PAEs are not chemically bonded to the polymer materials, so they are easily released during manufacturing, storage, usage, and disposal.[8-11, 15] Several studies showed that PAEs have teratogenicity, mutagenicity, carcinogenicity,

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reproductive toxicity, and are reported as endocrine disrupting compounds (EDCs) which induce thyroid-disrupting effects and children growth-disrupting effects.[8-11, 13-16] Among PAEs, di(2-ethylhexyl) phthalate (DEHP) is reported as the most abundant phthalate in surface water, which ranged from N.D. to 197 μg/L worldwide, and World Health Organization (WHO) recommend the level at 8 μg/L in drinking water for DEHP.[8-10, 14, 15] Due to the intensive use of PAEs, they are ubiquitous in the environment, such as air, water, soil and sediment, and freshwater is the primary way for PAEs to disperse in the environment.[10, 11, 13] Urbanization and more use of personal care products in summers increase the discharge of PAEs to the environment.[9, 10] Because of the intensive usage and adverse health effects to human, PAEs have received more and more public attention.[11, 16] PAEs has been observed in different water ranging from 0.08 to 9.78 μg/L.[14] Hence, it is important to monitor PAEs concentration in the water.

1.3 Nonylphenol and bisphenol A

Alkylphenol ethoxylates like nonylphenol ethoxylate (NPEO) are widely used as nonionic surfactants for detergents, pesticides, production of pulp and paper, paints emulsifiers, and antioxidants.[17-21] Nonylphenol (NP) is a degradation product from NPEO, which was found in contaminated water in high concentration.[22, 23] Bisphenol A (BPA) is the material of polycarbonate oligomers and epoxy resins, and

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is widely used in flame retardants, food containers and thermal paper.[18-22, 24-27] Both NP and BPA are feminizing compounds or EDCs, which can interfere with the normal function of hormone system, such as binding to the estrogen receptors and acting competitively to natural hormones.[19-21, 23, 24, 28, 29] NP is reported that may have effects on body weight and reproductive organ weight in rats, and have effects of decreasing sperm counts, reproductive disorders and breast cancer in humans.[24, 28, 29] Some studies showed that BPA alters mammary gland morphogenesis, and has adverse reproductive and carcinogenic effects in mice, and causes cardiovascular disease, neuro-behavioral disorders and reproductive impairment.[26, 29] BPA is more degradable than NP, however, its massive production and continuous emission make it present in water.[18, 25] The concentration of NP and BPA ranged from tens ng/L to ten μg/L in surface water.[18, 25] NP and BPA are found widely in the environment in recent years, and traditional wastewater treatment plants cannot remove these compounds completely, which means these chemicals will be released to water.[22, 25, 28] Because of the widespread and adverse health effects, BPA and NP have been included in Drinking Water Contaminant Candidate List by the Taiwan Environmental Protection Agency, and USEPA set the acceptable daily intake (ADI) of BPA at 0.05 mg/kg b.w./day.[22, 27] With more and more public attention, there is a need monitor these compounds in

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the environment.

1.4 Analytical Methods

Quantification and identification of these compounds may be affected by complex environment compounds in water, hence, sample preparation is needed to enrich analytes and reduce interferences.[25, 30] Common sample preparation includes liquid-liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME).[30-34] LLE is used for many years as a routine method.[33] LLE is time-consuming and needs large amount of organic solvents, which is harmful to environment.[32] SPE is a fast, simple, more complete extraction, and uses less organic solvents than LLE.[26, 32] Besides, SPE has the possibility of automation.[30] As a result, this study chose SPE as sample preparation method.

Liquid chromatography (LC) coupled to different detectors is one of the most common determination techniques.[34] Tandem mass spectrometry (MS/MS) is the main tool for trace analysis, because the good sensitivity and good selectivity it offers even in low concentration.[23, 34] Thus, liquid chromatography coupled with tandem mass spectrometry was used in this study.

1.5 Objectives

This study aims to establish a method to detect 10 PFASs, six PAEs, NP and BPA in water (Table 1, page 29), which these chemicals have been used intensively, and

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there are no safe substitutes for them. Water is the primary way for these pollutants to spread in the environment, and wastewater treatment cannot eliminate them completely, so it is necessary to monitor these chemicals in the environment. Methods detecting these chemicals simultaneously are limited, and thus this study focused on developing the method that detects these compounds simultaneously.

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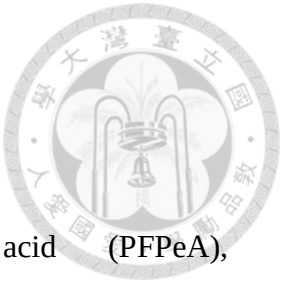
Chapter 2. Methods



2.1 Standards and Reagents

Perfluorobutanoic acid (PFBA), perfluopentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic aid (PFUnDA), perfluorododecanic acid (PFDoDA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluoro-*n*-[$^{13}C_4$]butanoic acid ($^{13}C_4$-PFBA), perfluoro-*n*-[3,4,5-$^{13}C_3$]pentanoic acid ($^{13}C_3$-PFPeA), perfluoro-*n*-[1,2,3,4,6-$^{13}C_5$]hexanoic acid ($^{13}C_5$-PFHxA), perfluoro-*n*-[$^{13}C_8$]octanoic acid ($^{13}C_8$-PFOA), perfluoro-*n*-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid ($^{13}C_7$-PFUnDA), sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate ($^{18}O_2$-PFHxS) and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate ($^{13}C_4$-PFOS) were purchased from Wellington Laboratories (Ontario, Canada; purity > 98%, 50 ± 2.5 μg/mL in methanol). Diethyl phthalate (DEP), butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), (purity > 99%, 100 μg/mL in methanol), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), nonylphenol (NP) (tech mix, 100 μg/mL in methanol), and bisphenol A (BPA) (purity > 99%, 10 mg/mL in methanol) were obtained from AccuStandard (New Haven, CT, USA). Diethyl phthalate-D_4 (DEP-D_4), benzyl butyl phthalate-D_4 (BBP-D_4), bis(2-ethylhexyl)

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phthalate-D_4 (DEHP-D_4) (purity > 98%, 100 μg/mL in nonane), di-*n*-octyl phthalate-D_4 (DNOP-D_4) (purity > 98%, 100 mg), 4-*n*-nonylphenol-$^{13}C_6$ (4-*n*-NP-$^{13}C_6$) (purity > 98%, 100 μg/mL in methanol), and bisphenol A-D_{16} (BPA-$^2D_{16}$) (purity > 98%, 100 μg/mL in acetonitrile) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Diisononyl phthalate-D_4 (DINP-D_4), and diisodecyl phthalate-D_4 (DIDP-D_4) (purity > 99%, 5 mg) were bought from Toronto Research Chemicals (Toronto, ON, Canada).

Formic acid (ACS. Reagent, 88%), HPLC-grade isopropyl alcohol, acetone, methanol, and LC/MS grade methanol (MeOH) were purchased from J.T. Baker (Philipsburg, NJ, USA). Milli-Q water was from a Milli-Q integral water purification system (Merck Millipore, Darmstadt, Germany).

Solid state standards were dissolved in MeOH as stock solution, and the concentration were as follow: DNOP-D_4 at 50 mg/mL; DINP-D_4 and DIDP-$^2D_4$ at 1 mg/mL. All the commercialized standards and stock solutions were stored at 4℃.

2.2 Sample preparation

100-mL river water samples were acidified to pH 3 by adding 30 μL of 88% formic acid and were spiked with 50 μL of internal standards in MeOH (200 ng/mL), then were shaken at 130 rpm for 30 minutes by orbital shaker. After shaking, water samples were filtrated through 90-mm MeOH-washed glass fiber filters (0.5 μm,

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ADVANTEC, Tokyo, Japan), then were extracted with Oasis HLB cartridges (200 mg, 6 mL; Waters, Milford, MA, USA).

The SPE was performed on SmartPrep Automated Cartridge Extractor II (Horizon Technology, Salem, NH, USA). The cartridges were conditioned with 2 mL isopropyl alcohol, 2 mL MeOH and 2 mL Milli-Q water at the flow rate of 5 mL/min sequentially. After loading the samples at 5 mL/min, the cartridges were washed with 0.6 mL MeOH/Milli-Q water (1:9, v/v) twice, then were dried with nitrogen for 45 seconds. The cartridges were eluted with 2 mL MeOH twice, followed by 2 mL isopropyl alcohol twice, and the elution solvents were collected together. The eluents were concentrated to 1 mL at 50℃ with a SpeedVac concentrator (Thermo Savant SPD 1010, Waltham, MA, USA). The residues were filtrated through 25-mm MeOH -washed nylon syringe filters (pore size 0.22 μm), and were concentrated to barely dried, and then were reconstituted with 100 μL of MeOH prior to instrumental analysis.

2.3 Instrumental analysis

Analytes were detected by a Waters Quattro Premier XE triple-quadrupole mass spectrometer with multiple reaction monitoring (MRM) mode (Waters, Milford, MA, USA). 10 PFASs, NP and BPA were ionized by negative electrospray ionization mode (ESI–), and six PAEs were ionized by positive electrospray ionization mode (ESI+).

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The most two abundant product ions of each analyte were detected for quantification and confirmation, respectively, except for PFBA and PFPeA, which only had one stable product ion to be observed. (Table 2, page 32) The MS/MS parameters included capillary voltage, extractor voltage, ion source temperature, desolvation temperature, cone gas flow, desolvation gas flow and collision cell pressure. The MS/MS parameters for 10 PFASs were as follows: capillary voltage 3.2 kV, extractor voltage 4 V, ion source temperature 120℃, desolvation temperature 500℃, cone gas flow 100 L/hr, desolvation gas flow 1200 L/hr, and collision cell pressure 3.22×10^{-3} mbar. The MS/MS parameters for NP and BPA were as follows: capillary voltage 3.0 kV, extractor voltage 5 V, source temperature 120℃, desolvation temperature 500℃, cone gas flow 50 L/hr, desolvation gas flow 1100 L/hr, and collision cell pressure 3.6×10^{-3} mbar. The MS/MS parameters for 6 PAEs were 2 kV, 4 V, 120℃, 500℃, 150 L/hr, 900 L/hr, and 3.22×10^{-3} for capillary voltage, extractor voltage, source temperature, desolvation temperature, cone gas flow, desolvation gas flow and collision cell pressure, respectively. (Table 3, page 34)

Separation was performed on a Waters ACQUITY UPLC system. 10 PFASs, NP and BPA were separated on a BEH C_{18} column (50 × 2.1 mm, 1.7 μm; Waters), and the mobile phase was composed of (A) 10-mM *N*-methylmorpholine$_{(aq)}$ (pH 9.6) and (B) MeOH. The flow rate was 0.4 mL/min, and the oven temperature was 55℃. The

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chromatographic gradient started from 5% of B for 0.5 min, and then increased to 90% in 5 min, and was held for 0.2 min. The gradient turned back to initial composition in 0.3 min, and was held for 2 min for equilibrium. The total run time was 7.5 min. As for NP and BPA, the flow rate was 0.5 mL/min, and the oven temperature was 55℃. The chromatographic gradient started from 40% of B for 0.5 min, and then increased to 95% of B in 2 min, and was held for 0.5 min. The gradient turned back to initial composition in 0.5 min, and was held for 1.5 min to equilibrium. Six PAEs were separated on an Ascentis Express F5 column (30 × 2.1 mm, 2.0 μm; Supelco. St. Louis, Missouri, USA), and the mobile phase consisted of (A) 5-mM ammonium acetate$_{(aq)}$ (pH 6.5) and (B) MeOH. The flow rate was 0.65 mL/min, and the column oven was 35℃. The chromatographic gradient began from 40% of B for 0.5 min, then increased to 70% in 2 min. The gradient continued to increase to 80% of B in 2 min, then to 95% in 0.1 minutes. After holding at 95% of B for 1 min, the gradient went back to the initial composition in 0.3 minu, and was held for 1.7 min for column re-equilibrium. The total run time took 7.6 minutes. The temperature of autosampler chamber was set at 4℃ in both separation scenario. (Table 4, page 35) All the analytes were separated well, and the peak widths were from 4.8 seconds (DIDP) to 12 seconds (PFDoDA). (Figure 1 and Figure 2, page 26 and page 27)

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2.4 Quality assurance and quality control

Deactivated (silanized) glass vials and inserts (Waters) were used to prevent the analytes from adsorbing on the glass surface. All the glassware was washed with Milli-Q, and was rinsed by acetone and MeOH sequentially. Then it was covered with aluminum foil and was dried in the hood.

An isolator column (Waters) was installed in the UPLC to prevent the potential interference from the UPLC system and the mobile phase. A reagent blank (Milli-Q water), two Milli-Q water spiked samples, one sample spike, and duplicate sample were analyzed with other real samples together in each batch.

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Chapter 3. Results and discussion

3.1 Optimization of solid-phase extraction

The conditions of SPE were optimized by using Oasis PRiME HLB μElution Plate (3 mg, Waters). After optimization, the procedures were scaled up to disks (Horizon).

The pH of water samples affected the retention of analytes on the adsorbents. When water samples were neutral, DNOP, DINP, DIDP, PFBA, PFPeA and PFHxA were not totally retained, which were 86%, 87%, 71%, 33%, 21% and 60% retention on the sorbents, respectively. With the acidification to pH 3 by 88% formic acid, almost all the analytes were 100% retained on the sorbents, except for PFBA (82%). As a result, water samples was acidified before SPE. (Table 5, page 36)

10-40% of MeOH/Milli-Q water were tested as wash solvents. Short-chain perfluorinated carboxylic acids including PFBA, PFPeA, PFHxA and PFOA, and DEP, were washed out 1-34% by 40% MeOH /Milli-Q water. 10% MeOH/Milli-Q water only washed out little PFBA (16%) and PFPeA (2.6%). Consequently 10% MeOH/Milli-Q water was used as wash solvent in SPE. (Table 6, page 37)

MeOH was tested as elution solvent on μElution Plate first. All the analytes had good elution (73%-166%) except for long-chain perfluorinated carboxylic acids like PFUnDA and PFDoDA, which had poor elution that were 45% and 36%, respectively.

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0.1% ammonium hydroxide in MeOH was chosen to test, and offered better elution on long-chain perfluorinated carboxylic acids (43-80%). A solvent mixture, MeOH/acetone (1:1, v/v), was tested, and had elution which was 52-225% for all analytes. The elution of DPE, BBP, DEHP, and DNOP were 181%, 116%, 124%, and 154%, respectively, and DINP and DIDP were 225%. In PFASs, the elution of PFBA was 88%, and C_5-C_{10} perfluorinated carboxylic acids were 107%-141%. The elution of C_{11} and C_{12} perfluorinated carboxylic acids were 68% and 52%, respectively. PFHxS, PFOS, NP and BPA were 137%, 133% 138%, and 166%, respectively. Aside from the solvent mixture of MeOH/acetone (1:1, v/v), acetone only was also tested on elution, and the elution was 22-375%. The elution of six PAEs ranged from 196% to 375%. C_4-C_9 perfluorinated carboxylic acids were 65%-101%. PFDA, PFUnDA, and PFDoDA were 49%, 29%, and 22%, respectively. The elution were 100%, 97%, 151%, and 181% for PFHxS, PFOS, NP, and BPA, respectively. The extremely high elution of the analytes may came backgrounds that washed out by acetone in the experiments. With the better elution, the solvent mixture of MeOH/acetone (1:1, v/v) was chosen as the elution solvent, and the procedures were scaled up to the disks. (Table 7, page 38)

The disk type (HLB, medium capacity; Horizon) SPE was performed on SPE-DEX 4790 (Horizon). The elution on the disks was N.D. to 97% when 10 mL

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solvent mixture of MeOH/acetone (1:1, v/v) were used as elution solvent. Only DEP (97%), BPA (78%), and PFPeA (57%) had better elution, and the elution of rest analytes were not greater than 20%. 10 mL MeOH followed by 10 mL solvent mixture of MeOH/acetone (1:1, v/v) were tested to improve the elution, and offered the elution ranged from N.D. to 97%. In this test, the results were similar with the previous results, only DEP (97%), BPA (71%), PFPeA (63%), and PFHxA (32%) had better elution, and the elution of rest analytes were not greater than 14%. 10 mL MeOH followed by 10 mL mixture of MeOH/dichloromethane (DCM)(1:1, v/v) and 10 mL MeOH followed by 10 mL DCM were tested as elution solvents on the disks, and the recoveries were 1-102% and 1-115%, respectively. In these two tests, long-chain PAEs such as DEHP, DNOP, DINP, and DIDP had poor elution, and elution of these compounds in the two tests were not greater than 11%. DEP had good elution, which were 102% and 103% in the two tests. In PFASs, long-chain perfluorinated carboxylic acids (C_{10}-C_{12}) and NP had poor elution, which were not greater than 11%. The elution of PFNA were 19% and 27% in these two tests, respectively. (Table 8, page 39)

Due to the poor elution on disks, SPE was conducted on HLB cartridges instead. 0.5 mL/min, 1.0 mL/min and 5.0 mL/min were chosen as tested elution flow rates, and the test elution solvents were 1mL MeOH followed by 1 mL solvent mixture of

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MeOH/acetone (1:1, v/v). The results showed that 1.0 mL/min was the best choice of elution flow rate, which offered the recoveries ranged from N.D. to 81%. At the flow rate of 1 mL/min, the elution of all analytes ranged from 20% to 81%, and PFBA, PFPeA, PFHxA, PFOA, and BPA were even greater than 70%, except for DNOP, DIDP, PFUnDA, and PFDoDA, which were not greater than 5%. At the flow rate of 0.5 mL/min, the elution of DEP and DEHP were 45% and 15%, respectively, and the rest PAEs were not greater than 5%. In PFASs, the elution of PFBA, PFPeA, PFHxA, PFOA, PFNA, and BPA were all greater than 40%, but lower than 80%. PFDA, PFUnDA, PFDoDA, and NP were not greater than 18%. At the flow rate of 5 mL/min, the elution of DEP, PFBA, PFPeA, PFHxA, and BPA were 81%, 72%, 78%, 25%, and 48%, respectively, and the rest analytes were not greater than 3%. (Table 9, page 40)

The elution solvent combination of 1 mL MeOH and 1 mL ethyl acetate, and 1 mL MeOH and 1 mL isopropyl alcohol were tested to improve the elution of analytes on cartridges. The elution of MeOH and ethyl acetate were 4%-115%. In six PAEs, the elution of DNOP and DIDP were 3.8% and 7.0%, DEP and BBP were 19%, and DEHP and DINP were 34% and 33%, respectively. In PFASs, the elution of C_4-C_9 perfluorinated carboxylic acids ranged from 63% to 87%, and C_{10}-C_{12} perfluorinated carboxylic acids were 39%, 15%, and 5%, respectively. The elution of rest analytes, PFHxS, PFOS, NP, and BPA, were 65%, 41%, 18%, and 115%, respectively. The

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elution of the solvent combination of MeOH and isopropyl alcohol was 6.9%-127%. In PAEs, the elution of DNOP and DIDP were 6.9% and 12%, DEP and BBP were 11% and 26%, and DEHP and DINP were 97% and 80%, respectively. In PFASs, the elution of C_4-C_9 perfluorinated carboxylic acids ranged from 79% to 102%, and C_{10}-C_{12} perfluorinated carboxylic acids were 59%, 32%, and 16%, respectively. The elution were 79%, 69%, 37%, and 127% for PFHxS, PFOS, NP, and BPA, respectively. With the better elution, the combination of MeOH and isopropyl alcohol was used as the elution solvents on SPE for further optimization. (Table 10, page 41)

Different elution volume of solvent and soak time were tested as following combinations:

I. 1 mL MeOH×2, soak 20 seconds; 1 mL isopropyl alcohol×2, soak 20 seconds.

II. 2 mL MeOH×2, soak 20 seconds; 2 mL isopropyl alcohol×2, soak 20 seconds.

III. 1 mL MeOH×2, soak 45 seconds; 1 mL isopropyl alcohol×2, soak 45 seconds.

IV. 2 mL MeOH×2, soak 45 seconds; 2 mL isopropyl alcohol×2, soak 45 seconds.

The results demonstrated that 2 mL per portion and soak 20 seconds offered the best elution in different combination of volume of solvents and soak time. In PAEs, the elution of DEP, BBP, DNOP, and DIDP were 20%, 52%, 24%, and 42%, respectively. DEHP and DINP were 386% and 277%, respectively. The pretty high elution of DEHP and DINP may cause by backgrounds that were washed out by

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isopropyl alcohol in experiments. In PFASs, the elution of C_4-C_{10} perfluorinated carboxylic acids ranged from 75% to 120%, and PFUnDA and PFDoDA were 67% and 59%, respectively. The elution of PFHxS, PFOS, NP, and BPA were 55%, 21%, 22%, and 73%, respectively. When the volumes of solvents were increased, the elution of PFUnDA and PFDoDA were better than the volumes that were not increased. In the combinations of larger volumes, the elution of PFUnDA were 67% and 49%, and PFDoDA were 59% and 33%, respectively. As for the combination of smaller volumes, PFUnDA were 32% and 22%, and PFDoDA were 16% and 9.1%, respectively. As a result, the combination of 2 mL per portion and soak 20 seconds was used on elution of SPE. (Table 11, page 42)

3.2 Identification and quantification

The instrumental detection limits (IDLs) and the instrumental quantification limits (IQL) were determined by analyzing the low concentration chemical standards in MeOH. IDLs were calculated as the signal-to-noise ratio (S/N) of confirmatory ions equals to 3, and IQLs were calculated as S/N of quantification ions equals to 10, respectively. If the IQLs were lower than the IDLs, the IQLs were reported as the same values of the IDLs. The IDLs were 0.36-3.58 pg, 0.20-7.20 pg, 2.09 pg and 4.02 pg for PFASs, PAEs, NP and BPA, respectively. The IQLs of PFASs, PAEs, NP and BPA were 0.67-11.9 pg, 0.52-7.20 pg, 2.09 pg, and 7.30 pg, respectively. The linear

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ranges of BBP, PFOA, PFNA, PFDA, PFUnDA, PFDoDA and PFHxS were 0.5 to 1000 ng/mL, and PFBA was 5 to 1000 ng/mL. The linear ranges of rest compounds were 1 to 1000 ng/mL. (Table 12, page 43)

3.3 Matrix effect

Five concentration levels were post-spiked to extracts from non-spiked river water, and there were triplicate at each level. The five spiked levels of analytes were 20, 50, 100, 200, and 500 ng/mL, respectively. Linear regression was applied to establish regression curve, and the x-axis and the y-axis of the regression were the spiked concentration of analytes and the peak areas of analytes, respectively. Matrix effect factors were calculated as the slope ratio of regression curve from post-spiked samples to the chemical standards in MeOH. Matrix effect factors of all analytes were 10% to 116%. In six PAEs, the matrix effect factors ranged from 87% to 116%, which meant that there was no obvious matrix effect. The matrix effect factors of DEP, DNOP, DINP, and DIDP were greater than 100%, which were 116%, 107%, 110%, and 105%, respectively. As for the other two PAEs, BBP and DEHP, the matrix effect factors were the same 88%. In PFASs, matrix effects factors of PFOS, PFHxA, PFOA, PFHxS, and PFPeA were all lower than 70%, which were 10%, 33%, 55%, 60%, and 64%, respectively. The matrix effect factors lower than 70% represented obvious matrix effects in these analytes, and the performance of the analytes in extracts were

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worse than the analytes in MeOH. The matrix effect factors of rest PFASs (C_4 and C_9-C_{12} carboxylic acids) ranged from 77% to 85%, and matrix effect factors were 79% and 93% for NP and BPA, respectively. (Figure 3, page 28)

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Chapter 4. Conclusion

After optimization of SPE, this multi-residue assay may be a feasible method that detects 10 PFASs, six PAEs, NP, and bisphenol A in river water. Based on matrix effect, this method is suitable for detecting six PAEs, because the matrix effect factors of six PAEs are 88%-116%, representing no obvious matrix effects in these analytes. In PFASs, the matrix effect of PFPeA, PFHxA, PFOA, PFHxS, and PFOS are 64%, 33%, 55%, 60%, and 10%, respectively. This results showed that there were serious matrix effects in these compounds. The matrix effect factors of other PFASs, NP, and BPA are 77%-93%, and it meant the matrix effects were not obvious in these analyte.

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Figures

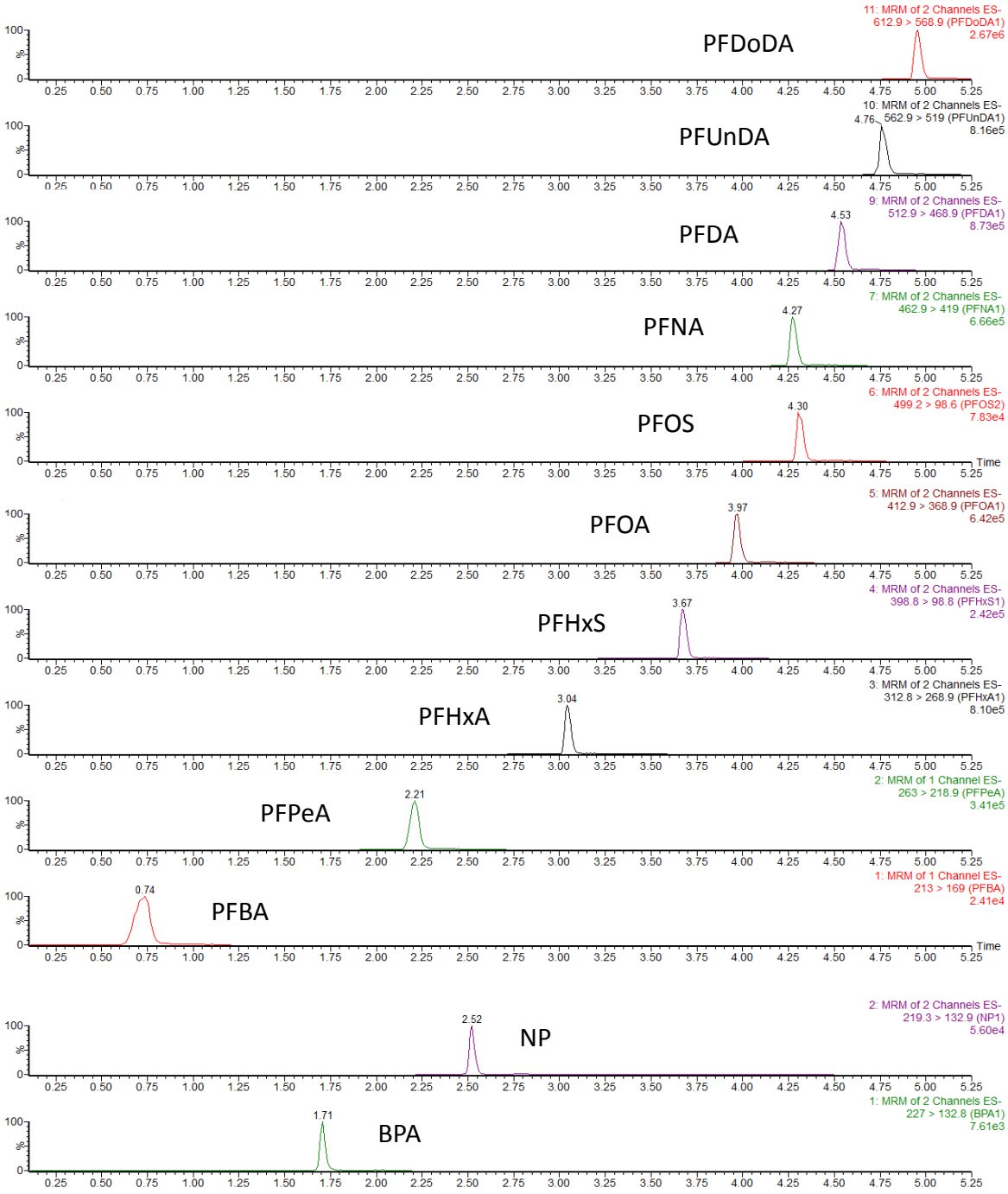

Figure 1. Chromatograms of 10 PFASs, NP, and BPA in MeOH (500 ng/mL, injection 4 μL)

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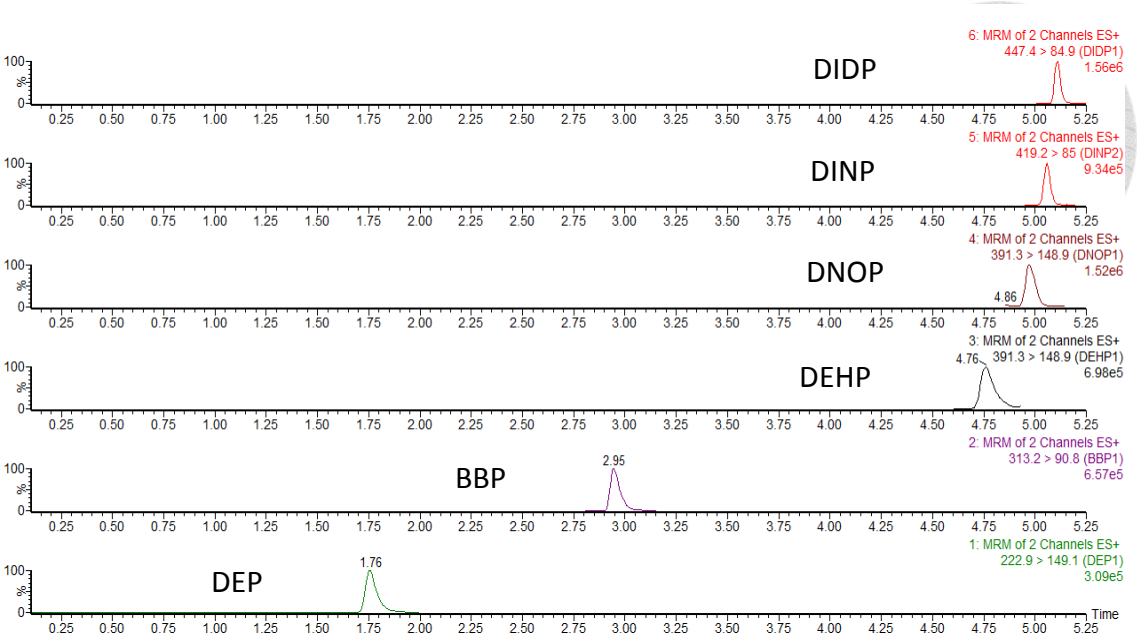

Figure 2. Chromatograms of six phthalate esters in MeOH (500 ng/mL, injection 4 μL)

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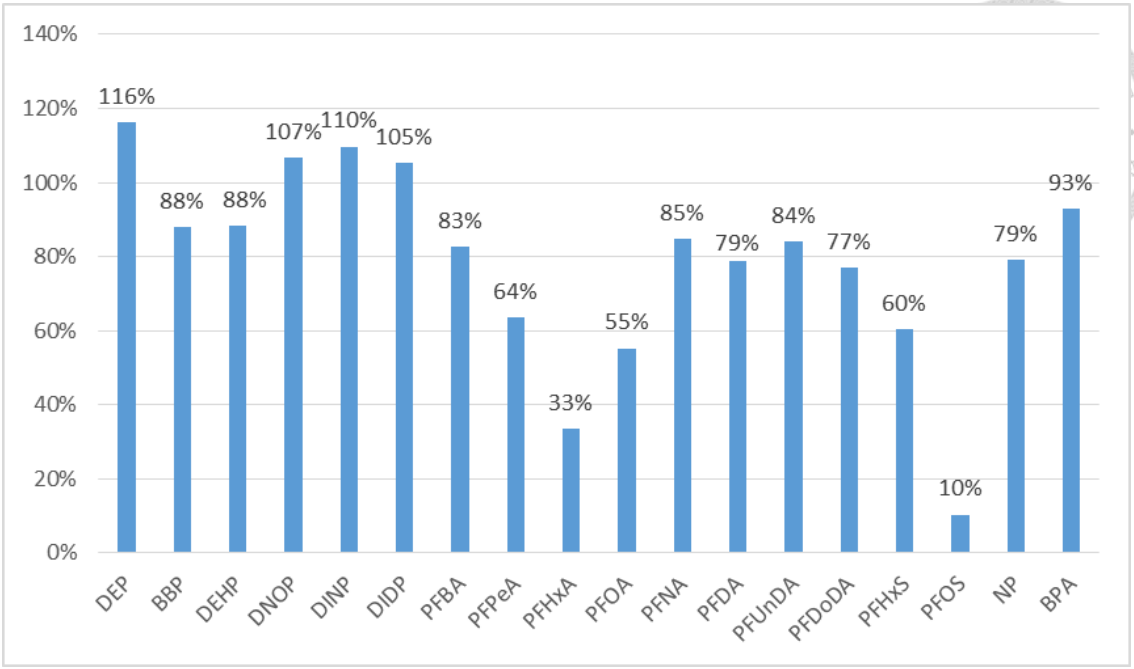

Figure 3. Matrix effect factors of analytes

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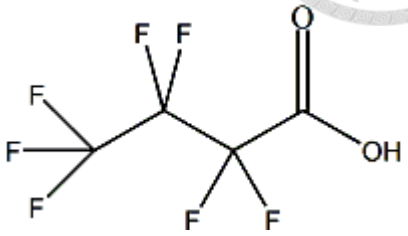
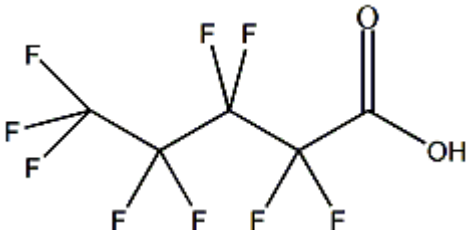
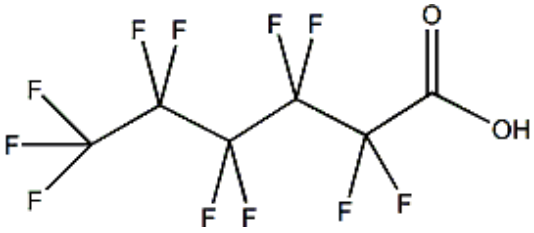
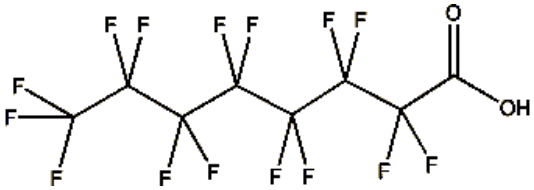
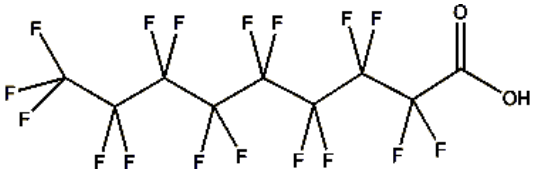
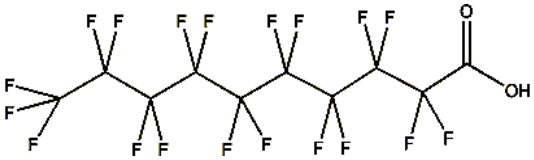
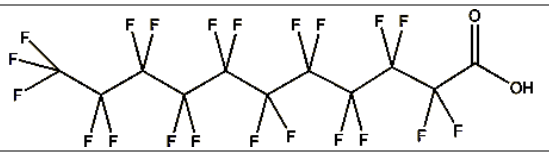
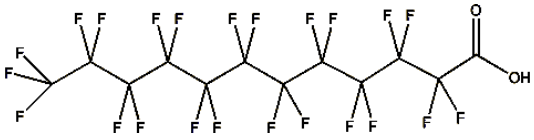
Tables

Table 1. Molecular weights and structures of analytes

Compounds	Molecular Weight	Structure
Perfluoroalkyl substances		
Perfluorobutanoic acid (PFBA)	214.0	
Perfluoropentanoic acid (PFPeA)	264.0	
Perfluorohexanoic aicd (PFHxA)	313.8	
Perfluorooctanoic acid (PFOA)	413.9	
Perfluorononanoic acid (PFNA)	463.9	
Perfluorodecanoic acid (PFDA)	513.9	
Perfluoroundecanoic acid (PFUnDA)	563.9	
Perfluorododecanoic acid (PFDoDA)	613.6	

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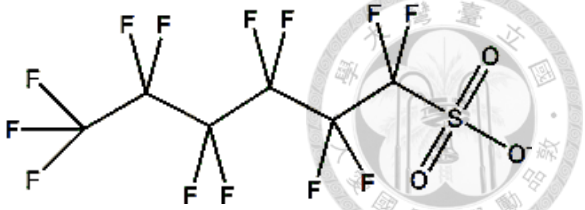
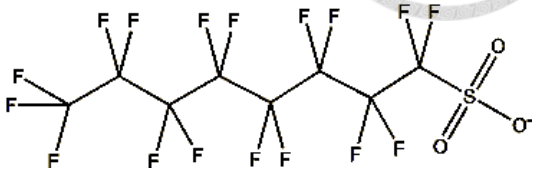
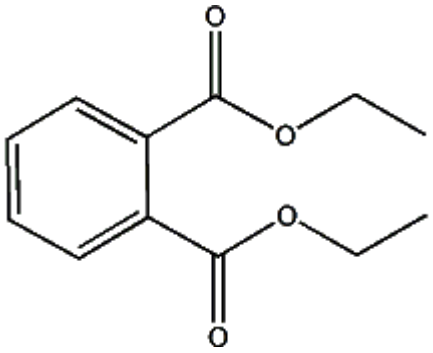
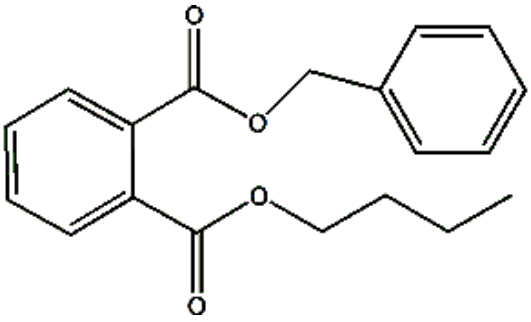
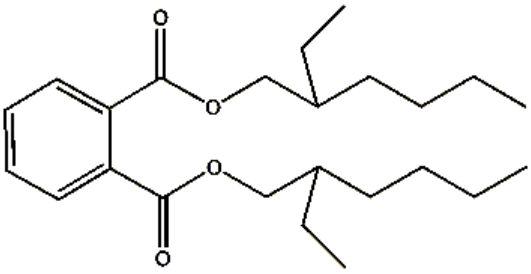
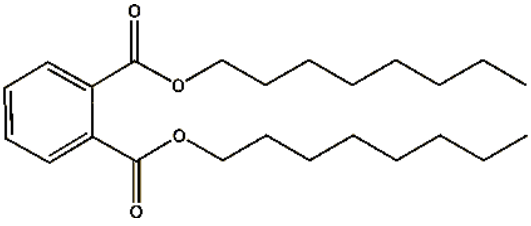
Perfluorohexane sulfonate (PFHxS)	399.8	
Perfluorooctane sulfonate (PFOS)	499.8	
Phthalate esters		
Diethyl phthalate (DEP)	222.2	
Benzyl butyl phthalate (BBP)	312.3	
Di(2-ethylhexyl) phthalate (DEHP)	390.5	
Di-*n*-octyl phthalate (DNOP)	390.5	

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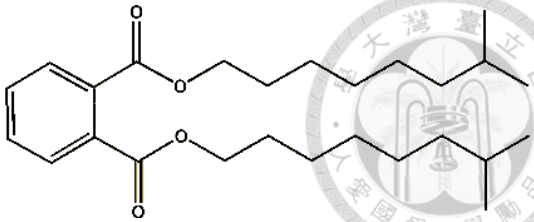
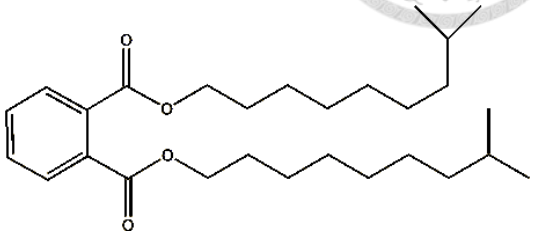
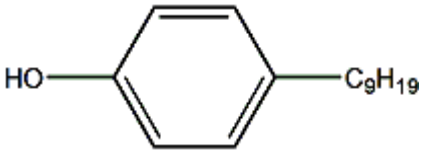
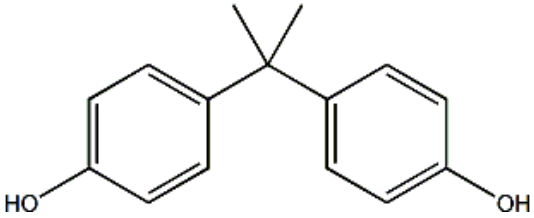
Diisononyl phthalate (DINP)	418.6	
Diisodecyl phthalate (DIDP)	446.7	
Nonylphenol and bisphenol A		
Nonylphenol (NP)	220.2	
Bisphenol A (BPA)	228.1	

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Table 2. MS/MS parameters

Compounds	Cone voltage (V)	Ion transition (collision voltage, V)
PFBA	12	(-)213.0 > 169.0 (7)
$^{13}C_4$-PFBA	12	(-)217.1 > 172.0 (7)
PFPeA	15	(-)263.0 > 218.9 (10)
$^{13}C_3$-PFPeA	15	(-)265.9 > 221.9 (3)
PFHxA	12	(-)312.8 > 118.8 (18)
	12	(-)312.8 > 268.9 (12)
$^{13}C_5$-PFHxA	11	(-)317.8 > 272.9 (17)
PFOA	13	(-)412.9 > 168.8 (18)
	13	(-)412.9 > 368.9 (10)
$^{13}C_8$-PFOA	13	(-)420.9 > 375.9 (10)
PFNA	20	(-)462.9 > 218.9 (14)
	20	(-)462.9 > 419.0 (12)
PFDA	20	(-)512.9 > 218.9 (16)
	20	(-)512.9 > 468.9 (11)
PFUnDA	18	(-)562.9 > 268.9 (16)
	18	(-)562.9 > 519.0 (13)
$^{13}C_7$-PFUnDA	17	(-)569.9 > 524.9 (13)
PFDoDA	20	(-)612.9 > 319.0 (17)
	20	(-)612.9 > 568.9 (14)
PFHxS	47	(-)398.8 > 79.8 (31)
	47	(-)398.8 > 98.8 (31)
$^{18}O_2$-PFHxS	22	(-)402.0 > 83.9 (31)
PFOS	68	(-)499.2 > 79.6 (42)
	68	(-)499.2 > 98.6 (40)
$^{13}C_4$-PFOS	18	(-)502.9 > 79.9 (42)
DEP	15	(+)222.9 > 149.1 (17)
	15	(+)222.9 > 177.0 (8)
DEP-D_4	10	(+)227.1 > 152.9 (17)
BBP	20	(+)313.2 > 90.8 (17)
	20	(+)313.2 > 148.8 (12)
BBP-D_4	17	(+)317.2 > 90.9 (20)
DEHP	20	(+)391.3 > 148.9 (23)
	20	(+)391.3 > 166.9 (12)
DEHP-D_4	20	(+)395.3 > 152.9 (25)

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Compounds	Cone voltage (V)	Ion transition (collision voltage, V)
DNOP	23	(+)391.3 > 148.9 (15)
	23	(+)391.3 > 261.2 (8)
DNOP-D_4	22	(+)395.4 > 153.2 (15)
DINP	23	(+)419.2 > 85.0 (17)
	23	(+)419.2 > 127.0 (10)
DINP-D_4	25	(+)423.3 > 70.9 (18)
DIDP	27	(+)447.4 > 84.9 (15)
	27	(+)447.4 > 141.0 (10)
DIDP-D_4	25	(+)451.3 > 153.0 (20)
NP	39	(-)219.3 > 132.9 (31)
	39	(-)219.3 > 147.0 (31)
4-*n*-NP-$^{13}C_6$	35	(-)225.1 > 111.8 (20)
BPA	35	(-)227.0 > 132.8 (30)
	35	(-)227.0 > 211.0 (30)
BPA-D_{16}	35	(-)241.0 > 141.9 (25)

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Table 3. MS parameters

Parameters	PFASs	NP and BPA	Phthalate esters
Ionization mode	ESI–	ESI–	ESI+
Capillary voltage (kV)	3.2	3.0	2
Extractor voltage (V)	4	5	4
Source temperature (℃)	120	120	120
Desolvation temperature (℃)	500	500	500
Cone gas flow (L/hr)	100	50	150
Desolvation gas flow (L/hr)	1200	1100	900
Collision cell pressure (mbar)	3.22×10^{-3}	3.6×10^{-3}	3.22×10^{-3}

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Table 4. UPLC conditions

Compounds	**PFASs**			**NP and BPA**		
Column	Waters BEH C_{18} column (50 × 2.1 mm, 1.7 μm)					
Oven temperature (℃)	55					
Flow rate (mL/min)	0.4			0.5		
Injection volume (μL)	4			6		
Mobile phase	A: 10-mM *N*-methylmorpholine$_{(aq)}$ pH 9.6 B: MeOH					
Gradient	Time (min)	A (%)	B (%)	Time (min)	A (%)	B (%)
	Initial	95	5	Initial	60	40
	0.5	95	5	0.5	60	40
	5.0	10	90	2.0	5	95
	5.2	10	90	2.5	5	95
	5.5	95	5	3.0	60	40
	7.5	95	5	4.5	60	40

Compounds	**Phthalate esters**	
Column	Ascentis Express F5 column (30 × 2.1 mm, 2.0 μm)	
Oven temperature (℃)	35	
Flow rate (mL/min)	0.65	
Injection volume (μL)	4	
Mobile phase	A: 5-mM ammonium acetate$_{(aq)}$ pH 6.5 B: MeOH	
Gradient (min)	A (%)	B (%)
Initial	60	40
0.5	60	40
2.5	30	70
4.5	20	80
4.6	5	95
5.6	5	95
5.9	60	40
7.6	60	40

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Table 5. Retention (%) of analytes at different pH on μElution plates (N = 3)

Compounds	pH 3	pH 7
	Mean (%RSD)	Mean (%RSD)
DEP	99 (4.9%)	98 (16%)
DEHP	100 (0.0%)	95 (38%)
DNOP	100 (0.0%)	86 (18%)
DINP	100 (0.0%)	87 (15%)
DIDP	100 (0.0%)	71 (0.9%)
PFBA	82 (3.5%)	33 (5.7%)
PFPeA	100 (25%)	21 (4.5%)
PFHxA	100 (0.0%)	60 (13%)
PFOA	100 (0.0%)	99 (38%)
PFHxS	100 (0.0%)	99 (53%)

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Table 6. Loss (%) of analytes on different composition of MeOH/water wash solvents on μElution plates (N = 3)

Compounds	10% MeOH*	20% MeOH	30% MeOH	40% MeOH
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	0.0 (0.0%)	0.0 (0.0%)	0.0 (0.0%)	4.2 (14%)
PFBA	16 (4.7%)	22 (23%)	27 (24%)	34 (2.8%)
PFPeA	2.6 (14%)	8.8 (36%)	15 (19%)	21 (4.8%)
PFHxA	0.0 (0.0%)	0.0 (0.0%)	0.9 (15%)	5.2 (8.2%)
PFOA	0.0 (0.0%)	0.0 (0.0%)	0.0 (0.0%)	1.0 (13%)

* MeOH: methanol

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Table 7. Recoveries (%) of analytes on different elution solvents on μElution Plate (N = 3)

Compounds	MeOH*	0.1% $NH_4OH_{(aq)}$ in MeOH	MeOH/Acetone (1/1, v/v)	Acetone	MeOH, MeOH/DCM** (1:1, v/v)	MeOH, DCM
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	150 (13%)	165 (3.0%)	181 (25%)	313 (28%)	103 (11%)	238 (4.9%)
BBP	92 (20%)	61 (2.7%)	116 (27%)	203 (30%)	52 (11%)	118 (6.8%)
DEHP	104 (29%)	103 (6.2%)	124 (34%)	196 (41%)	3.8 (6.7%)	9.7 (14%)
DNOP	127 (31%)	86 (3.6%)	154 (39%)	251 (43%)	2.1 (6.1%)	6.9 (10%)
DINP	193 (32%)	112 (3.9%)	225 (39%)	361 (39%)	10 (23%)	17 (12%)
DIDP	184 (35%)	104 (3.1%)	225 (44%)	375 (49%)	20 (5.5%)	44 (11%)
PFBA	63 (10%)	65 (5.5%)	88 (7.2%)	80 (19%)	0.0 (0.0%)	0.0 (0.0%)
PFPeA	97 (11%)	111 (5.4%)	139 (8.0%)	101 (26%)	3.5 (26%)	3.0 (68%)
PFHxA	100 (11%)	89 (4.6%)	141 (8.0%)	84 (31%)	84 (5.1%)	105 (13%)
PFOA	94 (14%)	102 (4.0%)	135 (6.5%)	67 (33%)	146 (7.8%)	176 (7.6%)
PFNA	90 (16%)	91 (5.6%)	130 (4.4%)	65 (33%)	146 (7.4%)	179 (6.2%)
PFDA	70 (17%)	80 (3.3%)	107 (5.2%)	49 (35%)	134 (6.4%)	167 (7.5%)
PFUnDA	45 (14%)	64 (5.0%)	68 (6.1%)	29 (33%)	144 (5.2%)	181 (6.7%)
PFDoDA	36 (13%)	43 (6.7%)	52 (7.3%)	22.2 (31%)	89 (5.6%)	119 (5.2%)
PFHxS	89 (11%)	123 (4.2%)	137 (6.2%)	100 (36%)	135 (6.0%)	162 (8.9%)
PFOS	85 (17%)	70 (3.9%)	133 (4.5%)	97 (37%)	131 (6.5%)	151 (9.2%)
NP	93 (13%)	119 (3.3%)	138 (7.1%)	151 (34%)	49 (16%)	108 (52%)
BPA	126 (15%)	128 (6.1%)	166 (10%)	181 (28%)	130 (6.0%)	108 (11%)

* MeOH: methanol

** DCM: dichloromethane

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Table 8. Recoveries (%) of analytes on different elution solvents on SPE disks (N = 3)

Compounds	MeOH/Acetone	MeOH, MeOH/Acetone	MeOH, MeOH/DCM	MeOH, DCM
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	97 (8.1%)	97 (11%)	102 (16%)	103 (15%)
BBP	5.4 (5.6%)	9.7 (108%)	22 (40%)	34 (10%)
DEHP	6.5 (20%)	0.6 (0.0%)	11 (73%)	7.7 (75%)
DNOP	2.7 (19%)	1.9 (32%)	3.4 (58%)	4.7 (0.0%)
DINP	6.1 (24%)	1.8 (65%)	6.3 (60%)	2.9 (62%)
DIDP	1.1 (119%)	0.9 (74%)	5.1 (89%)	3.4 (50%)
PFBA	20 (16%)	14 (21%)	15 (6.8%)	11 (7.0%)
PFPeA	57 (15%)	63 (11%)	63 (11%)	63 (11%)
PFHxA	16 (21%)	32 (43%)	67 (22%)	79 (7.1%)
PFOA	1.1 (23%)	1.7 (70%)	34 (51%)	44 (1.9%)
PFNA	1.0 (27%)	1.3 (21%)	19 (53%)	27 (5.5%)
PFDA	0.5 (111%)	0.4 (31%)	6.7 (57%)	11 (5.9%)
PFUnDA	0.8 (0.0%)	0.3 (0.0%)	2.1 (65%)	3.6 (4.9%)
PFDoDA	0.1 (0.0%)	0.2 (0.0%)	0.8 (49%)	1.4 (27%)
PFHxS	1.1 (13%)	3.5 (110%)	42 (56%)	53 (7.7%)
PFOS	1.5 (33%)	2.3 (27%)	25 (58%)	30 (19%)
NP	1.0 (37%)	0.9 (101%)	1.7 (0.0%)	2.0 (0.0%)
BPA	78 (6.2%)	71 (20%)	99 (25%)	115 (4.2%)

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Table 9. Recoveries (%) of analytes on different elution flow rate (mL/min) on SPE cartridges (N = 3)

Compounds	0.5	1.0	5.0
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	45 (19%)	28 (25%)	81 (2%)
BBP	2.8 (111%)	51 (55%)	0.1 (16%)
DEHP	15 (16%)	55 (51%)	2.7 (31%)
DNOP	0.0 (84%)	0.3 (141%)	0.0 (0.0%)
DINP	4.3 (36%)	14 (53%)	0.0 (0.0%)
DIDP	0.6 (27%)	1.8 (68%)	0.0 (0.0%)
PFBA	76 (18%)	81 (7.2%)	72 (3.8%)
PFPeA	75 (21%)	77 (9.1%)	78 (2.4%)
PFHxA	71 (27%)	75 (12%)	25 (8.8%)
PFOA	63 (38%)	72 (14%)	1.9 (4.4%)
PFNA	41 (47%)	53 (15%)	1.1 (10%)
PFDA	18 (65%)	22 (20%)	0.3 (36%)
PFUnDA	4.6 (94%)	5.4 (32%)	0.0 (0.0%)
PFDoDA	1.1 (106%)	1.3 (54%)	0.0 (0.0%)
PFHxS	43 (58%)	55 (17%)	2.2 (5.9%)
PFOS	16 (82%)	21 (19%)	0.0 (0.0%)
NP	10 (52%)	22 (49%)	0.0 (0.0%)
BPA	53 (47%)	73 (30%)	48 (10%)

* Elution solvents: 1 mL MeOH followed by 1 mL MeOH/acetone (1:1, v/v), each solvent eluted twice

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Table 10. Recoveries (%) of analytes on different elution solvents on cartridges (N = 3)

Compounds	MeOH, MeOH/Acetone	MeOH, Ethyl acetate	MeOH, Isopropyl alcohol
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	28 (25%)	19 (36%)	11 (21%)
BBP	51 (55%)	19 (28%)	26 (29%)
DEHP	55 (51%)	34 (36%)	97 (24%)
DNOP	0.3 (141%)	3.8 (14%)	6.9 (25%)
DINP	14 (53%)	33 (28%)	80 (9.0%)
DIDP	1.8 (68%)	7.0 (17%)	12 (18%)
PFBA	81 (7.2%)	79 (3.8%)	79 (28%)
PFPeA	77 (9.1%)	86 (2.1%)	102 (3.0%)
PFHxA	75 (12%)	87 (1.7%)	88 (36%)
PFOA	72 (14%)	78 (7.6%)	82 (32%)
PFNA	53 (15%)	63 (9.0%)	79 (32%)
PFDA	22 (20%)	39 (16%)	59 (31%)
PFUnDA	5.4 (32%)	15 (25%)	32 (23%)
PFDoDA	1.3 (54%)	4.6 (31%)	16 (15%)
PFHxS	55 (17%)	65 (5.6%)	79 (32%)
PFOS	21 (19%)	41 (16%)	69 (30%)
NP	22 (49%)	18 (8.2%)	37 (102%)
BPA	73 (30%)	115 (13%)	127 (11%)

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Table 11. Recoveries (%) of analytes on different volumes of elution solvents and soak time (N = 3)

Compounds	1 mL/portion 20 seconds	2 mL/portion 20 seconds	1 mL/portion 45 seconds	2 mL/portion 45 seconds
	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)	Mean (%RSD)
DEP	11 (21%)	20 (36%)	11 (33%)	17 (51%)
BBP	26 (29%)	52 (2.8%)	18 (22%)	37 (32%)
DEHP	97 (24%)	386 (32%)	64 (31%)	211 (40%)
DNOP	6.9 (25%)	24 (16%)	4.8 (32%)	11 (32%)
DINP	80 (9.0%)	277 (16%)	43 (61%)	79 (16%)
DIDP	12 (18%)	42 (5.9%)	7.3 (33%)	16 (29%)
PFBA	79 (28%)	81 (17%)	90 (7.9%)	79 (20%)
PFPeA	102 (3.0%)	120 (17%)	129 (7.1%)	113 (21%)
PFHxA	88 (36%)	79 (20%)	86 (6.3%)	73 (22%)
PFOA	82 (32%)	83 (20%)	90 (5.2%)	81 (21%)
PFNA	79 (32%)	82 (18%)	79 (6.8%)	76 (19%)
PFDA	59 (31%)	75 (20%)	53 (8.8%)	64 (20%)
PFUnDA	32 (23%)	67 (21%)	22 (26%)	49 (26%)
PFDoDA	16 (15%)	59 (17%)	9.1 (55%)	33 (48%)
PFHxS	79 (32%)	83 (18%)	86 (6.2%)	78 (22%)
PFOS	69 (30%)	77.0 (20%)	51 (11%)	62 (25%)
NP	37 (102%)	150 (74%)	4.2 (15%)	24 (41%)
BPA	127 (11%)	96.9 (8%)	64 (16%)	63 (30%)

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Table 12. IDLs, IQLs, linear ranges and r^2 of calibration curves

Compounds	IDL (pg)	IQL (pg)	Linear range (ng/mL)	r^2
DEP	2.84	3.89	1-1000	0.997
BBP	0.20	0.52	0.5-1000	0.997
DEHP	3.86	8.33	1-1000	0.996
DNOP	7.20	7.20	1-1000	0.995
DINP	2.82	4.09	1-1000	0.995
DIDP	0.87	2.63	1-1000	0.997
PFBA	3.58	11.9	5-1000	0.998
PFPeA	0.86	2.88	1-1000	0.997
PFHxA	0.81	2.69	1-1000	0.999
PFOA	0.90	1.95	0.5-1000	0.998
PFNA	1.48	1.48	0.5-1000	0.995
PFDA	1.20	1.66	0.5-1000	0.996
PFUnDA	0.68	1.54	0.5-1000	0.997
PFDoDA	0.72	0.72	0.5-1000	0.996
PFHxS	0.36	0.67	0.5-1000	0.999
PFOS	0.73	3.96	1-1000	0.994
NP	2.09	2.09	1-1000	0.999
BPA	4.02	7.30	1-1000	0.999

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