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Validation and determination of nine PFCS in surface water and sediment samples using UPLC-QTOF-MS

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Abstract In this study, an analytical method for the routine determination of nine perfluorinated compounds (PFCs), using ultra performance liquid chromatography coupled to a quadrupole time-of-flight mass spectrometer (UPLC-QTOF-MS), was developed, validated, and used for their assay in surface water and sediments. The method yielded good linearity with a correlation coefficient (R^2) ranging between 0.991 and 0.999 for all the compounds investigated. Limits of detection (LOD) ranged between 0.02 and 0.08 ng/l, while the limit of quantification (LOQ) ranged from 0.065 to 0.261 ng/l. Recovery studies were carried out in replicate assays, and percentage recoveries ranged between 56 and 112% for the nine perfluorinated compounds investigated. The method was applied to determine levels of perfluorooctanoic acid (PFOA) and PFOS in surface water and sediment samples collected along the Plankenburg River in Stellenbosch, South Africa. Samples were pre-treated, extracted, and cleaned up via offline solid-phase extraction (SPE) procedures, using hydrophilic-lipophilic balance (HLB) C-18 cartridges. Levels of PFOA and PFOS found in surface water ranged between (12.8 ± 4.24 and 62.62 ± 4.86 ng/l) and (<LOD and 3.8 ng/l), respectively, while levels measured in corresponding sediment samples ranged between 0.14–0.33 ng/g (PFOA) and <LOD and 0.7 ± 0.013 ng/g (PFOS). Concentrations of PFOA and PFOS were suspected to be associated with anthropogenic activities in the vicinity of the sampling areas.

Keywords Surface water · Sediment · Perfluorinated compounds · UPLC-QTOF-MS

Introduction

Perfluorinated compounds (PFCs) belong to a class of chemicals referred to as organofluorines. The unique physicochemical properties of PFCs such as lipophobicity and hydrophobicity are responsible for their many industrial and domestic applications. These include oil- and dirt-resistant surface coatings for fabrics and carpets, applications in the pulp and paper industry and the mining industry, fire-fighting foams, oil-well surfactants, floor varnishing, and insecticide formulations (Ahrens et al. 2015; Giesy and Kannan 2002; Post et al. 2012). Enormous use of domestic and industrial PFC-containing applications/substances has been reported as the major source of

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occurrence and distribution of PFCs in various environmental matrices (Prevedouros et al. 2006; Perra et al. 2013).

PFCs have low vapor pressure in the atmosphere. They are soluble in polar solvents, moderately soluble in water, and easily adsorbed onto solids (such as soils and sediments) (Barton et al. 2007). Thus, environmental matrices have been identified as potential sinks for various organic contaminants, including perflurooctanoic acid (PFOA) and PFOS (Chen et al. 2016). A number of reports have established the global presence of PFCs in various environment matrices (surface water, wastewater, wildlife) and in human tissues (Perra et al. 2013; Giesy and Kannan 2002; Post et al. 2012). Tieyu Wang et al. (2015) reviewed the sources and multimedia distribution of PFCs in China and found higher levels of PFCs in sediment and water samples from industrial and urbanized areas than in samples from remote areas. Levels of PFOS obtained from the Yangtze river in China ranged between 72.9 and 536.7 ng/g in sediment samples and 144 and 703 ng/l in corresponding water samples (Pan and You 2010). PFCs were also detected in surface water and sediment samples collected from marine reserves of the Tuscan Archipelago National Park (Italy). PFOA and PFOS were detected at low concentrations, ranging between 0.25 and 1.50 ng/g dry weight sediment samples (Perra et al. 2013). PFOS have also been reported to bio accumulate in fish, seafood, fowl, meat, serum, fruits, vegetables, eggs, and milk and dairy products (Trudel et al. 2008; Benford et al. 2008; Shoeib et al. 2016; Olsen et al. 2003).

Elevated levels of PFOA and PFOS in the environment could lead to critical environmental and health implications in both human and ecological systems (Ericson et al. 2009; Olsen et al. 2003; Fromme et al. 2007). Adverse health risks such as hepatotoxicity, developmental toxicity, immune toxicity, neurotoxicity, endocrine toxicity, gene toxicity, and tumorigenic potential, among others, have been associated with the presence of PFCs released into the environment (Rand and Mabury 2017; Tarafdar and Sinha 2018; Wang et al. 2017). Concerns have been raised by various international environmental organizations and scientists globally about the contributions of PFOA and PFOS to the perturbation of environmental quality, as well as about the threat they pose to both human and environmental health. Human exposure to PFOA and PFOS was identified as occurring through various routes such as ingestion, dermal exposure, and inhalation (Noorlander et al. 2011; Zhang et al. 2010).

As a result of the environmental and health risks associated with elevated levels of fluorinated compounds in various environment components, PFOA and PFOS and their precursors were included as priority contaminants in Annex B of the Stockholm convention on persistent organic pollutants (POPs) (Wang et al. 2009). Recently, PFOS and its salts were included in the list of prioritized hazardous chemicals for environmental management published by the Chinese Ministry of Environment Protection, although a statutory threshold limit is yet to be specified in that country (SAW 2015). Consequently, some developed nations including the USA, Sweden, and Canada have placed restrictions on the use of certain fluoralkyl compounds. Although standard regulations pertaining to these compounds are yet to be established, statutory threshold limits published by the United States Environmental Protection Agency (USEPA) for PFOA and PFOS in drinking water were 400 and 200 ng/l, respectively (USEPA 2009). A European Union (EU) water framework directive specifies an environmental quality standard of no more than 0.65 ng/l for PFOS (Loos et al. 2009).

Few studies are available on the levels of PFCs in Africa, including South Africa; hence, there is no expectation of a reduction in the levels of PFCs in the environment in the near future. This is due of the lack of facilities for the recovery from different matrices and quantitation of these compounds. It is therefore necessary to develop a reliable, accurate, efficient, and sensitive protocol for determination of the concentration of PFCs in various environmental matrices such as surface water and sediment. Some regulatory bodies such as the International Organization for Standardization (ISO) and USEPA, along with a few leading scientists, have published standard operational procedure for the determination of PFCs in environmental and biological matrices (Jahnke and Berger 2009; Berger and Haukås 2005; Hu and Yu 2010). Subsequent studies focused on improving the qualitative and quantitative determination of PFOA and PFOS using a number of techniques, including those of liquid chromatography-mass spectrometry (LC-MS) (Lim et al. 2011; Wille et al. 2010a). There are, however, some limitations associated with some of the methods for determining the concentrations of PFCs in environmental samples. This includes excessive time-consumption and matrix-

induced ionization disturbances as a result of the ion source of the mass spectrometer. For instance, liquid chromatography tandem mass spectrometer could suffer from sensitivity loss due to low fragmentation yields for some perfluorinated alkyl substances during ionization (Wang et al. 2013). A study by Schwanz et al. (2016) reported that quantification and identification of PFCs could be achieved by liquid chromatography (LC) mass spectroscopy (MS) coupled with quadrupole time-of-flight (QTOF) electrospray ionization (ESI).

Many river systems such as the Plankenburg river receive domestic and industrial discharges including various chemical products from domestic waste, electronic waste, fire fighting chemicals, pharmaceutical products, and petrochemicals from their immediate surroundings (Daso et al. 2013; Paulse et al. 2009). However, the presence and levels of many of these contaminants including the PFCs have not been evaluated and characterized. It is, therefore, imperative, that the status of PFOA and PFOS and other PFCs be determined and characterized in different environmental matrices. This will be a basis for assessing the health implications if found at elevated levels. There is a need for routine determination of PFCs in different environmental matrices in order to promote human and environmental health.

In this study, an analytical method for routine qualitative and quantitative analysis of PFCs using UPLC-QTOF-MS was developed, validated, and used for their assay of nine PFCs in surface water and sediment samples collected from the Plankenburg River, Stellenbosch, South Africa.

Materials and methods

Chemicals and reagents

All the chemicals and reagents used in this study were HPLC grade (> 99.99%). Heptadecafluorooctanesulfonic acid (PFOS) was purchased from Fluka Analytical (USA); PFOA, perflouoroheptanoic acid (PFHpA), perfloro(2-ethoxyethane) sulfonic acid (PFBS), and perfluoropentanoic acid (PFPeA) from Alfa Aesar, USA; perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) from Sigma-Aldrich, Germany. Mass-labeled internal standards (IS) [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were obtained from Wellington Laboratories (Guelph, ON). Standard reference material (SRM) sediment was purchased from (Sigma-Aldrich, Germany). Milli-Q water was obtained through the synthesis of distilled water by the Milli-Q synthesis system integral with LC-Pack polisher from Merck Millipore, USA. Membrane syringe filters 0.45-μm polyethersulphone (Sigma-Aldrich, Germany).

Preparation of standard solutions

Standard stock solutions of the nine individual perfluorinated compounds were prepared at a concentration of 1000 ng/l in 100% methanol (LC-MS Ultra Chroma-solv, Sigma-Aldrich, Germany) and stored at 4 °C in the dark before use. A cocktail mixture of the standard solutions was prepared from individual stock solutions with methanol. All the working standard solutions used for calibration and recovery studies were freshly prepared and stored at 4 °C before use.

Mobile phase

Mobile phase solution used for ultra performance liquid chromatography quadruple time-of-flight mass spectroscopic (UPLC-QTOF-MS) analysis was prepared in Milli-Q water and methanol with 2-mM ammonium acetate (Merck Millipore, USA), as mobile phase A and B, respectively. The addition of ammonium acetate to the solutions served as buffer ionization enhancement of the perflourinated compounds during analysis. Buffered water and methanol solutions were passed through a 0.22-μm nylon filter to remove particulate impurity before use as a mobile phase in the UPLC-QTOF-MS system.

Sample collection, preparation, and pre-treatment

Twenty-eight (28) samples were collected in all: 16 water samples and 12 sediment samples, four water samples, and two sediment samples from each of the selected sampling points (A-Upstream, B-industrial area, C-informal settlement, D-Downstream) within longitude (18.51065 E and 18.832514 E) and latitude (− 33.938634S and − 33.893813S) (Fig. 1), during August, 2014.

Water samples were collected in 500 ml polypropylene (PP) bottles with caps washed and rinsed with distilled water and methanol. All samples were collected

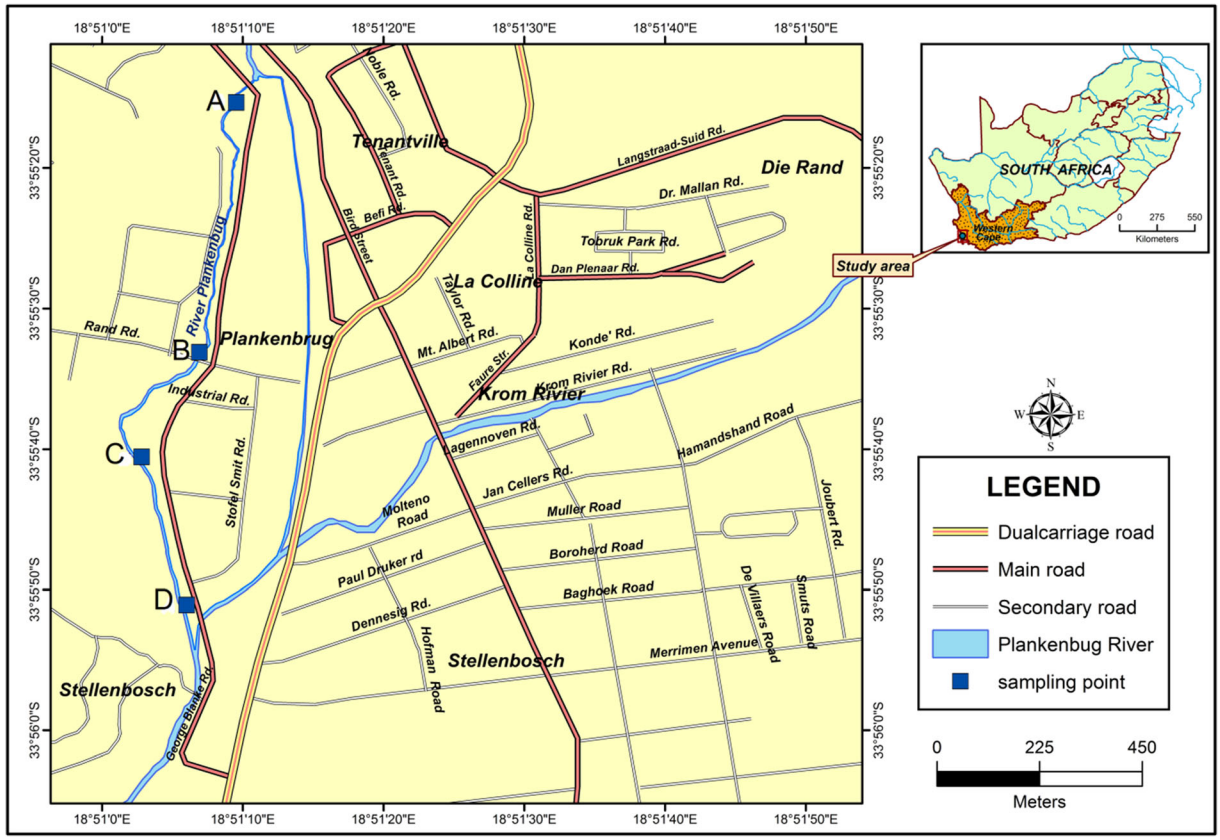

Fig. 1 Map showing the sampling site Plankenburg River Stellenbosch, Cape Town. Point A: agricultural area (upstream), point B: close to informal settlement, point C: close proximity to industrial facility, and point D: educational and recreational facility (downstream)

in triplicate and immediately stored in an ice chest at 4 °C in the field before being transferred to the refrigerator in the laboratory for further processing. Water samples were filtered by passing through 0.45-μm polyethersulphone membrane syringe filters (Sigma-Aldrich, Germany) to remove possible debris and particles before the extraction procedure.

Sediment samples were collected at the same sampling points in aluminum foil pre-treated with methanol and stored in an ice chest at 4 °C in the field before being transferred to the laboratory. Subsequently, sediment samples were air dried and sieved using an 500-μm aperture before the extraction procedure (Higgins and Luthy 2006; Pan and You 2010).

Solid-phase extraction procedure

Extraction of PFCs in the water sample was carried out using a solid-phase extraction (SPE) hydrophilic-lipophilic balance (HLB)-cartridge (0.5 g, 12 cm^3). The SPE columns were conditioned by running 10 ml of 100% methanol, followed by 5 ml of Milli-Q water through the cartridges at a constant flow rate depending on the gravity. The ^{13}C-labeled internal standards [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were added into Milli-Q water before the extraction procedure. Simulated wastewater was filtered using 0.45-μm polyethersulphone membrane syringe filters and allowed to flow through the pre-conditioned cartridges. The target analytes were recovered from the cartridges in 5-ml absolute methanol through the SPE cartridges, eluents were collected into a 50-ml polypropylene (PP) tube and the process repeated thrice (Llorca et al. 2009).

Composite sediment samples were sieved through a 250-μm aperture from which about 3 g were carefully weighed into 15-ml centrifuge tubes. ^{13}C-labeled internal standards [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were added into the Nalgene tubes before the extraction procedure. Ten milliliters of 1% acetic acid was added into a tube, shaken on the vortex homogenizer for 30 min, and heated in a sonication bath for 20 min at 55 °C. It

was then centrifuged at 10000 rpm for 5 min. The resultant eluent was decanted into a clean 50-ml tube. This procedure was repeated with 3.5 ml of 9:1 (*v*/*v*) methanol and 1% acetic acid twice, while the final extraction was carried out with 10 ml of 1% acetic acid into a 50-ml polypropylene (PP) tube, to make 27-ml eluent, this method was adapted from the literature with modifications (So et al. 2007) and (Hu and Yu 2010). Recovered extract from water and sediment was concentrated under a high purity N_2 gas stream to dryness, reconstituted with 1 ml with absolute methanol, and transferred into 2-ml vials for instrumental analysis using UPLC-QTOF-MS. A schematic diagram showing the experimental protocol for water and sediment analyses is shown in Fig. 2.

Ultra performance liquid chromatography quadrupole time-of-flight separations

Sample identification and quantitation of perfluorinated compounds were performed in UPLC-QTOF-MS (Acquity UPLC system—Waters Corporation, Milford, MA, USA). Samples were injected at a flow rate of 0.3 μl/min into the guard column (5-mm long, 4.6-mm internal diameter) before passing into the reverse phase C-18 column (4.6-μm particle size, 150-mm length, 5.0-mm internal diameters) supplied by Sigma-Aldrich, Germany. The target analytes were ionized and separated with 2 mm of ammonium acetate in Milli-Q water as mobile phase A, while 2 mM of ammonium acetate in methanol as mobile phase B. The binary gradient was set at 55% of B for 4 min and increased to 9% at 4 min. The solvent system returned to original concentration in the ninth minute of the run, and the column was allowed to equilibrate for 2 min at 55% mobile phase B. The total run time for the analysis was 11 min, with a good and quick separation time for the nine perfluorinated compounds. The mass spectrometer was coupled with (QTOF) quadrupole time–of-flight and operated in negative ion mode ESI. The full scan ranges between *m*/*z* (100–1000) molecular weight, and the quantification of compounds of interest was achieved by extraction of the mass chromatogram from full scan recording of the cone voltage and mass to charge value obtained.

The standard reference solution was injected simultaneously during the analysis into the liquid chromatography mass spectroscopy system at a constant flow rate of 3 μl/min. Mass-to-charge ratio (*m*/*z*) of the reference solution was within the range of 119.0363 to 998.0164 of 2.5 mm (Hexakis 1H, 1H, 3H-tetrafluoropropoxy)

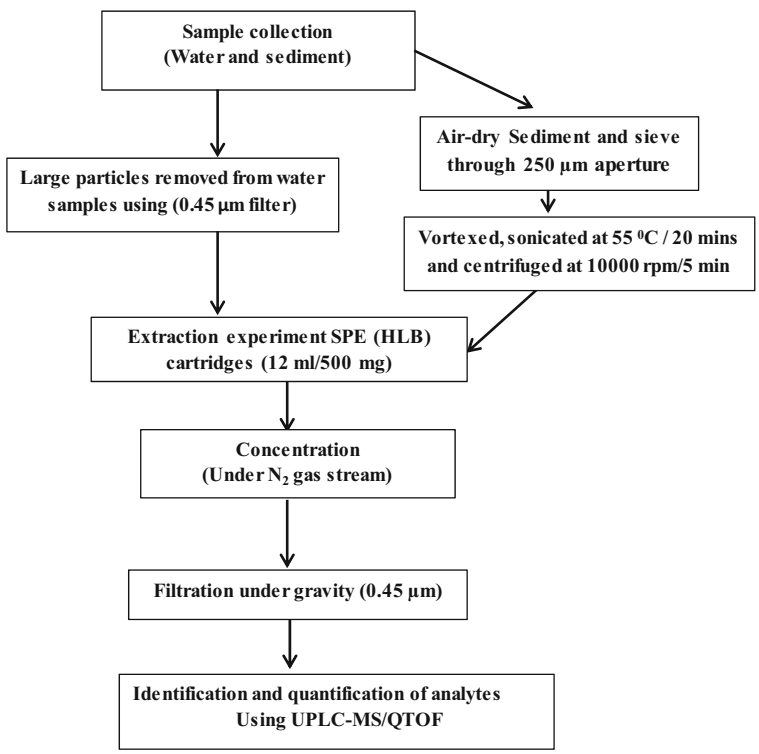

Fig. 2 Schematic diagram showing the experimental protocol for water and sediment analyses

phosphine 97.0% purity, and 100% acetonitrile (99.9% HPLC grade). This enabled the accurate measurement of the masses of ions within the range of standard reference to be detected, while the resulting chromatogram and spectra were recorded for qualitative identification and quantification of the analytes. This instrument was supported by the Masslynx 4.1, SCN803 software. The optimization parameters used in the mass spectrometer parameters for time of flight (TOF) are listed in Table 1.

Method validation

The analytical method was validated with reference to analytical parameters such as linearity, selectivity, sensitivity, accuracy, and precision. This method is adapted from standard procedures published by Fiori and Andrisano (2014), Hu and Yu (2010), Swartz and Krull (1997), and EFSA (2008); criteria established by the European Commission; and methods published in previous works (Loos et al. 2009; Jahnke and Berger 2009).

Linearity, limit of determination (LOD), and limit of quantification (LOQ) were evaluated and statistically calculated. The instrumental response was based on a signal-to-noise ratio of three, and the linear range was determined by replicated injections of a diluted series of cocktails of all the nine perflourinated compounds. Calibration graphs for the investigated compounds and correlation coefficient (R^2) were determined. The instrumental response was based on the signal-to-noise ratio of three, and the linear range was also determined by replicated injections of dilution series of cocktail of all the nine perflourinated compounds. Triplicate injections of blank (55:45) % of 2 mM of ammonium acetate in methanol and Milli-Q water gave values 10 times lower than the LOD. The LOQ was achieved with an average of three standard deviations within a series of five standards runs for 3 days for the validation of the experiment (Martín et al. 2016).

Recovery studies for the determination of all the analytes were achieved using spiked cocktail mixtures (concentrations 125, 250, and 500 ng/l) of the nine PFCs in Milli-Q water, surface water, and sediment samples were subjected to SPE extraction process. The estimation of recoveries after the extraction was determined relative to the initial concentrations. The effect of matrix interference was evaluated by recovery studies. Recovery studies were conducted with the standard mixture of the nine PFCs (PFBS, PFPeA, PFHpA, PFOA, PFOS, PFNA, PFDA, PFUnDA, PFDoDA). Prior to the instrumental evaluation of the concentrations added, the prepared samples and procedural blank samples were allowed to pass through clean-up procedures which accounted for matrix effect and the percentage recovery of the added known concentrations calculated.

Table 1 UPLC-QTOF-MS instrumental parameters

TOF parameters	Values		
Mass spectrometer	Operated in (negative mode) ESI		
Drying gas temperature	250 °C		
Cone gas	0 l/h		
Nebulizer gas	600 l/h		
Capillary voltage	3200 V		
Cone voltage	30 V		
Q-TOF premium acquisition rate	0.15 s inter scan delay		
Drying gas	Argon gas		
Collision gas pressure	5.3×1^{-5} Torr		
Binary gradient	Time (min)	% A	% B
		45	55
	4	10	90
	8	10	90
	9	45	55
	11	45	55
Instrument supported by	Masslynx 4.1 SCN803 software		

Quality assurance and quality control procedure

Instrument contamination was avoided by strict adherence to laboratory ethics. Methanol was used to rinse all laboratory wares before use. Analysis of each of the investigated compounds was done in triplicate and variations were noted. Blank and SRM determination were carried out to establish the contribution of the analytical signals, which include the effect of mobile phase solvent, instrumental response, and possible human error. ^{13}C labeled internal standards for PFOA and PFOS were used for quantification by isotope dilution to enhance quality assurance. Standards mixture containing nine PFCs, PFPeA, PFBS, PFHpA, PFOA PFOS, PFNA, PFDA, PFUnDA, PFDoDA including ^{13}C labeled standards, were injected into the instrument before analysis to check for instrumental variability of the analysis. The method detection limit (LOD) and the LOQ of the

instrument were obtained by the signal-to-noise ratios of 3:1 for LOD and 10:1 for LOQ (Opeolu et al. 2010).

Results and discussion

Method optimization and validation

Analytical protocols for the determination of PFCs in environmental matrices (surface water and sediment) as recommended by the USEPA (2009) and International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH) guideline standard procedures for the method validation were used (Jain and Basniwal 2013).

Mobile phase optimization

Mixed solvents consisting of Milli-Q water (solvent A) and methanol (solvent B) buffered to pH 6 was used as mobile phases. Mobile phase buffering was achieved by the addition of ammonium acetate 2 mM to both solvents. The pH of Milli-Q water and methanol was optimized at a slightly acidic solution of pH 6, in order to enhance the ionization of PFCs during elution into the mass spectrometer. These steps are similar to those of a previous study reported by Berger and Haukas (2005).

Identification and quantification of ions using UPLC-QTOF-MS

Separation of analytes was achieved using a C18-HPLC column (Supelco, Sigma-Aldrich, Germany). Compounds were identified on the basis of their retention time, the ratio of the precursor ions, and the product ion based on the standards used. They were quantified on the basis of peak areas in the chromatogram of the individual analytes, and this took into account the signal-to-noise ratio of a 3:1 minimum (Wille et al. 2010b). The chromatogram of the individual compounds is presented in Fig. 3. While, the mass spectral data for the nine target compounds are presented in the supplementary information (Figure S1).

The ionization of PFCs was achieved with QTOF/MS operated in dual electrospray ionization (ESI) interphase. The identification of target compounds was achieved using their abundance ion ratio and mass transition within the specified tolerance limits. The chromatograms of the mixture of the nine analytes are shown in Fig. 4.

Identification of PFOA and PFOS in surface water samples showing the peaks and the corresponding chromatograms is illustrated in Fig. 5. The parent ions [M^-] for the investigated compounds were observed in negative mode polarity. The precursor ions for PFOA and PFOS were m/z 499 and 364, respectively. The estimation of signal-to-noise ratios for the peaks which were more than 10 times above the blank for all the target compounds was achieved in the multiple reaction modes (MRM), transition of PFOS m/z 499 ($C_8F_{17}SO_3^-$ to m/z 99 score of 88.77%), and the PFOA transition of the precursor ion 412 ($C_7F_{15}COO$-) to 369 is consistent to that reported by Moody et al. (2001), for PFOS, m/z 499 to 99 and PFOA 413 m/z to 369 m/z. Table 2 presents the retention time and other properties of the nine PFCs.

Method validation and optimization

Due to the complexity of the interactions of contaminants and their solubility differences in different environmental samples, liquid chromatographic-mass spectrometric (LC-MS) method is amenable to matrix effect, which results in differences in response to separation process. The developed method was therefore validated for linearity, specificity, precision and accuracy, LOD and LOQ, and analyte recovery using ICH guidelines (Jain and Basniwal 2013).

Linearity and instrumental and method response

A point calibration curve using gradient concentrations of working standards was used to obtain a line of best fit. The responses for concentrations ranged between 31.25 and 500 ng/l for all the target compounds are presented in Table 3. The regression line of best fit compared the relationship between the concentrations and the peak area of the analytes and was used for quantitation of the target analyte (external calibration). Linearity was achieved over the concentration range with a correlation coefficient (R^2) greater than (>0.99) for all the compounds, demonstrating good linearity and suitability for quantitative analysis (Table 3). Calibration plots of the nine PFCs are presented in the Fig. 6. The LODs ranged between 0.008 and 0.064 ng/l and LOQ ranged between 0.026 and 0.195 ng/l for water and LODs ranged between 0.007 and 0.09 ng/l and LOQ ranged between 0.022 and 0.270 ng/l for sediment. These values (0.06–

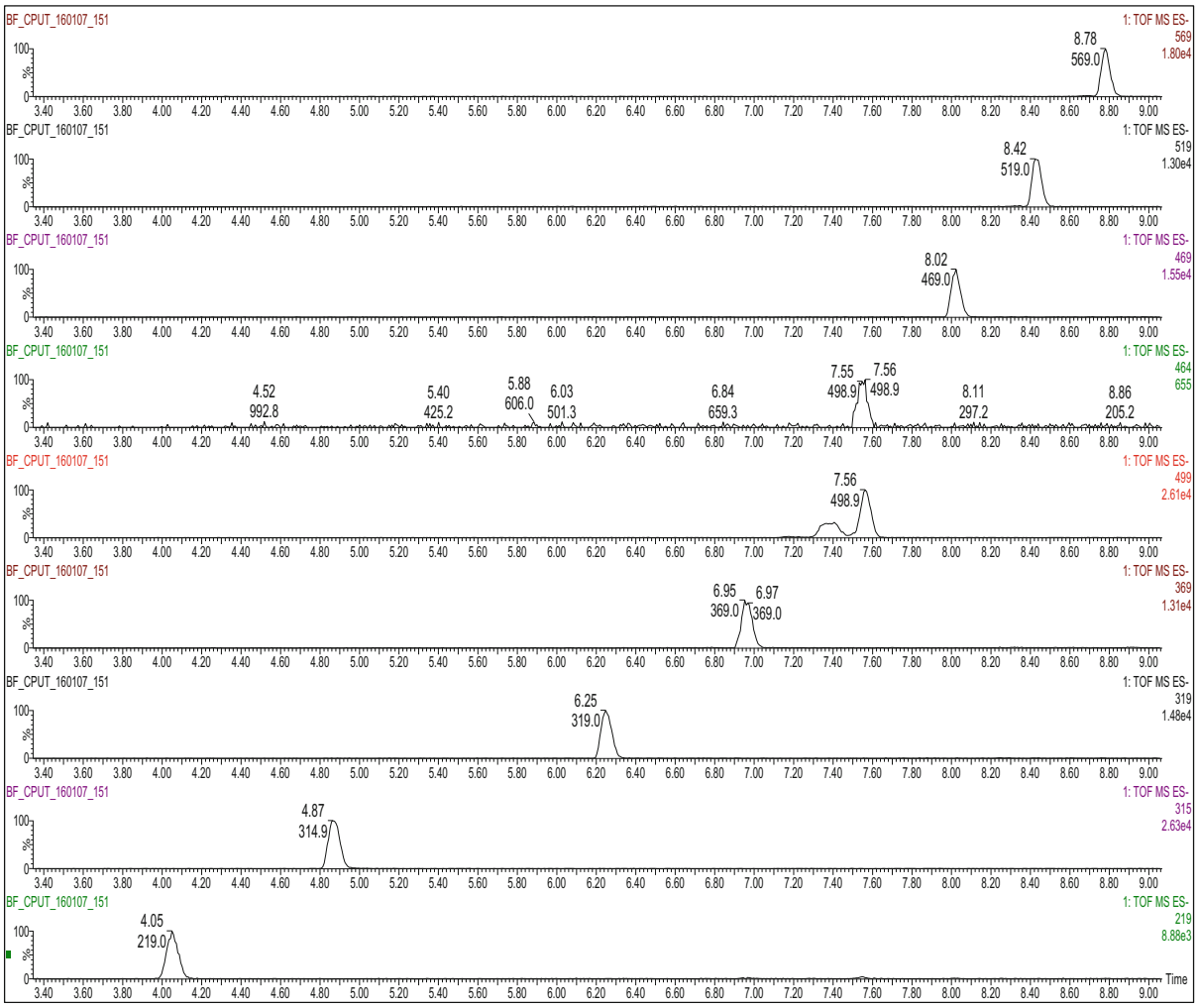

Fig. 3 Chromatogram showing the peaks of the nine individual PFCs

1000 ng/l) were consistent with those obtained by Lin et al. (2016), using LC-ESI-MS/MS methods for analysis of PFSAs. Wang et al. (2016) also reported LODs and LOQs ranging between 0.01 and 0.08 and 0.06 and 0.22 ng/l, respectively, for perfluoroalkyl substances in water.

Precision and accuracy

In order to validate the data obtained using this method, the assessment of the accuracy of the instrument was performed by the injection of blank samples after every 10 injections. Blank injections established that the levels of target analytes were below LOQ. The blank responses relative to the standards are presented in the supplementary information (Figure S2). The degree of precision was represented as relative standard deviation (RSD). Simulated wastewater samples were spiked with considerable low concentration of target analytes at a constant concentration to test for the reproducibility and repeatability of the method. Optimizations for repeatability, reproducibility of the nine PFCs are presented in Table 4. The results obtained on different days show a similar trend, which suggests that the method is reproducible. Any deviation can only be attributed to method uncertainty rather than day-to-day variation and is probably due to the degradation effect. The repeatability test confirmed that the intraday precision was consistent for all compounds, meaning that there were no significant differences ($p > 0.05$) in the results obtained during different periods of the day.

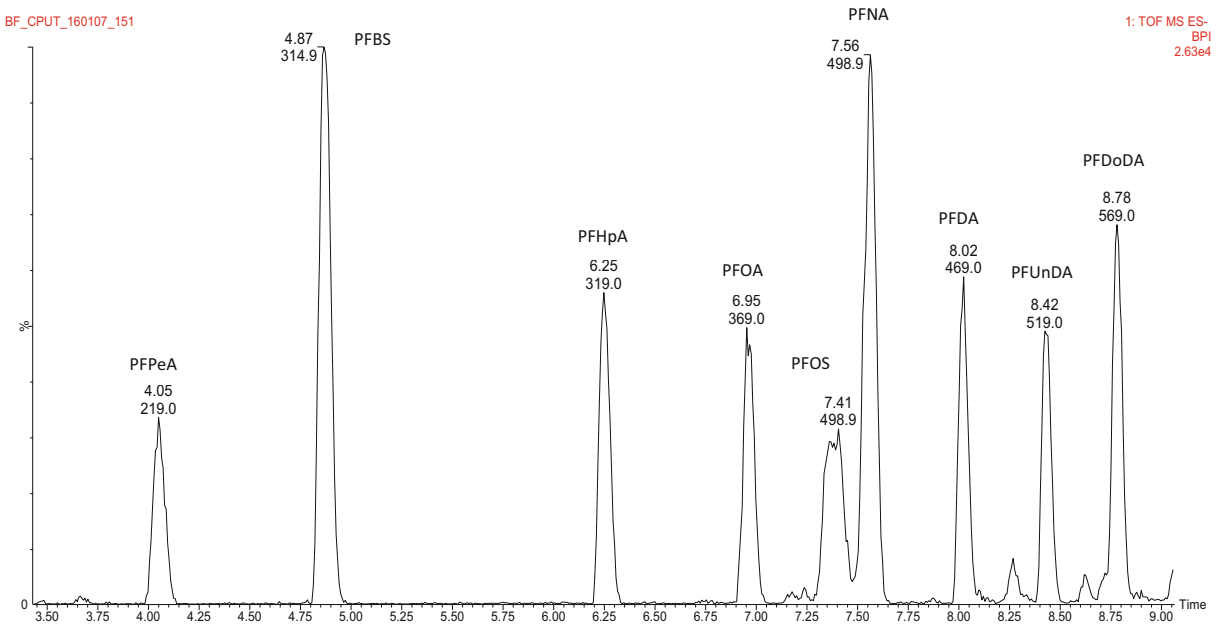

Fig. 4 Chromatogram showing the cocktail of nine PFCs

Recovery studies for PFCs

The recoveries of the tested compounds were from Milli-Q water, surface water, and sediment samples using HLB cartridges for clean-up. The recoveries for Milli-Q water were 78.5 ± 16.5% (PFBS), 93.1 ± 7.2% (PFPeA), 94.4 ± 8.5% (PFHpA), 93.1 ± 11.4% (PFOA), 90.6 ± 13.3% (PFOS), 92.0 ± 6.0% (PFNA), 87.3 ± 8.8% (PFDA), 90.0 ± 12.1% (PFUnDA), and 126.5 ± 14.6% for PFDoDA for 500 ng/l. Meanwhile, percentage recoveries from surface water at 500 ng/l ranged between 67.84 ± 5.24 and 80.56 ± 2.83 spiked of PFCs. Percentage recoveries for sediment at same concentration spiked were lowered ranged between 56.21 ± 4.0 and 69.86 ± 8.63. Percentage recoveries obtained from spiked Milli-Q water gave good recoveries. Low percentage recoveries from ambient surface water and sediment samples could be associated with interferences from environmental matrices. Sediment samples gave the least recoveries due to the complexities of impurities in the sample matrices. Percentage recoveries from spiked Milli-Q water, surface water, and sediment samples for the investigated compounds are presented in Table 5. Results from optimized recovery studies were presented in the supplementary information Table S1, S2, and S3.

Previous study using a combination of HLB with Sep-Pack tubes for extraction of polyfluorinated alkyl substances (PFAS) in wastewater gave recoveries of 89.2–98.0% (Hu and Yu 2010). The non-polar interaction between the compound's C-F bonding and the polar characteristics of the synthetic polystyrene bed of SPE-HLB cartridges favors longer retention time of PFCs, while allowing the passage of interfering matrices (So et al. 2007). Recovery study showed that there was a higher percentage recovery of long-chain (C-F > 9) PFCs than short-chain (C-F < 8) PFCs, similar to the observation of Weinberg et al. (2011).

Concentration levels of PFCs in surface water and sediment samples

The levels of selected PFCs were investigated in surface water and sediment samples using the validated method. The PFCs were identified and quantified by comparing the MS-Transition, retention time, and product ion scans with those of the standard calibration. Their levels were variable in both the surface water and sediment samples (Table 6).

The measured PFCs generally occurred at trace level in the surface waters (<LOD and 77.6 ± 13.64 ng/l) at nearly all sampling locations and in the sediment samples (<LOD and 0.86 ± 0.02 ng/g) at all sampling points. The highest concentrations of ΣPFCs (186.4 ng/l) in surface water were observed at point B, followed by ΣPFCs (128.40 ng/l) at point D, while minimum levels

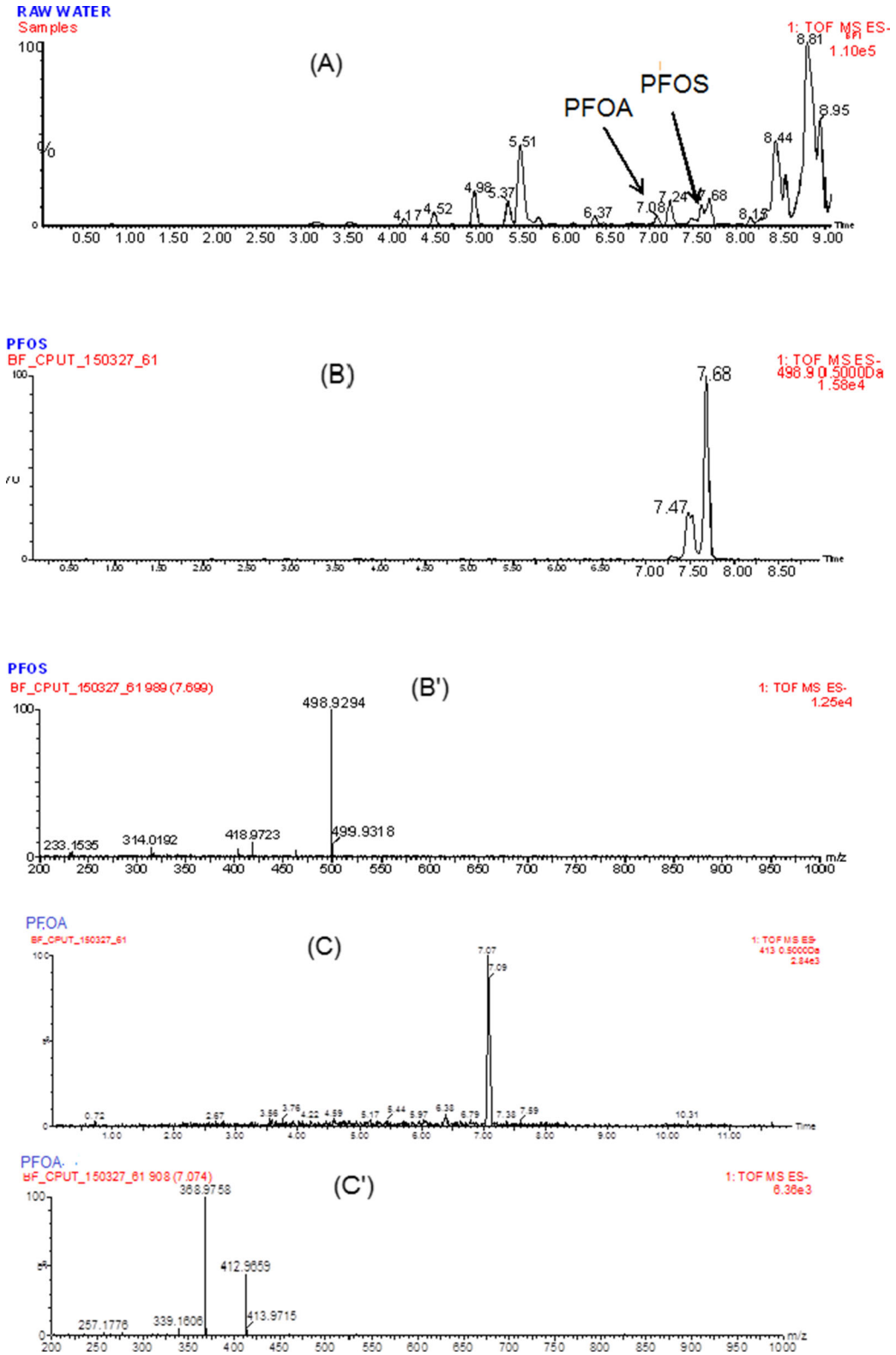

Fig. 5 Chromatogram showing **a** peaks of PFOA and PFOS in raw water sample, **b** chromatogram of PFOS, **b′** mass spectrometry (MS) PFOS, **c** chromatogram of PFOA, and **c′** mass spectrometry (MS) PFOA

Table 2 Precursors ion (*m*/*z*), MS/mass transition (*m*/*z*), and species of nine PFCs

PFCs	RT	Molecular formula	Molecular weight	Species	Precursor ion (*m*/*z*)	Product ion (*m*/*z*)	Collision energy CE (V)	Score (%)
PFPeA	4.05	C_4F_9COOH	264.05	$(M\text{-}H)^-$	262.97	219/197	− 12/− 9	76.88
PFBS	4.87	$C_4F_9SO_3^-$	316.10	$(M + SO_3)^-$	298.84	80/99	− 55/− 36	94.70
PFHpA	6.25	$C_6F_{13}COOH$	364.06	$(M\text{-}H)^-$	362.96	319/169	− 16/− 25	82.76
PFOA	6.95	$C_7F_{17}COOH$	414.07	$(M\text{-}H)^-$	412.96	369/169	− 14/− 25	93.93
PFOS	7.41, 7.55	$C_8F_{17}SO_3^-$	500.13	$(M + SO_3)^-$	498.93	99/80	− 65/− 126	88.77
PFNA	7.56	$C_8F_{17}COOH$	464.08	$(M\text{-}H)^-$	462.96	419/219	− 14/− 26	91.69
PFDA	8.02	$C_9F_{19}COOH$	514.09	$(M\text{-}H)^-$	512.96	469/219	− 20/− 25	90.89
PFUnDA	8.42	$C_{10}F_{21}COOH$	564.09	$(M\text{-}H)^-$	562.95	519/269	− 20/− 30	90.87
PFDoDA	8.78	$C_{11}F_{23}COOH$	614.10	$(M\text{-}H)^-$	612.97	569/319	− 11/− 28	92.25

were measured at point C with ΣPFCs (62.30 ng/l). The highest concentration of ΣPFCs (2.12 ng/g) in sediment samples was measured at point B (informal settlement), followed by samples from point A with ΣPFCs (1.79 ng/g), and the minimum concentrations were measure downstream at point D ΣPFCs (1.49 ng/g).

PFOS level in sediment at point B was 0.104 ng/g, while it was not detected (<LOD) in water at point D. On the other hand, the PFOA measured in sediment samples at points B and D were 0.33 and 0.14 ng/g, respectively. The results obtained in this study are consistent with levels of selected PFCs previously identified in Cape Town rivers, where levels of PFOA and PFOS were up to 314 and 182 ng/l for Diep River; 390 and 47 ng/l for Salt River, and 146 and 23 ng/l for Eerste River, respectively (Mudumbi et al. 2014). Also, levels of PFOS were reported varied between 14.4 and 2610 ng/g in sediment samples collected from water treatment plants elsewhere (Higgins et al. 2005). In another study, concentrations of PFOA (278 ng/g) and PFOS (5383 ng/g) were measured in sediment samples collected from wastewater treatment plants in South China (Guo et al. 2010). Lower concentrations of PFOA (1.03 ng/g) and PFOS (0.29 ng/g dw) were reported in the Dalio river system in northeast China (Bao et al. 2009). A study conducted by Moody et al. (2001) reported levels of PFOA 62 ng/l and 196 ng/g in water and sediment samples, respectively. Another study conducted by Lein et al. (2008) measured the levels of PFOS in

Table 3 Calibration, linearity, and instrumental and method response

Compounds	Range (ng/l)	R/time (min)	Calibration equation	R^2	Water		Sediment	
					LOD (ng/l)	LOQ (ng/l)	LOD (ng/l)	LOQ (ng/l)
PFBS	31.25–500	5.01	$y = 6284.4x - 39.70$	0.999	0.008	0.026	0.007	0.022
PFPeA	31.25–500	4.17	$y = 481.7x - 18.93$	0.994	0.051	0.154	0.012	0.036
PFHpA	31.25–500	6.37	$y = 744.09x - 17.61$	0.999	0.057	0.172	0.015	0.045
PFOA	31.25–500	7.07	$y = 932.95x - 15.29$	0.998	0.035	0.108	0.021	0.063
PFOS	31.25–500	7.47, 7.68	$y = 1175.6x + 1.30$	0.999	0.064	0.195	0.017	0.051
PFNA	31.25–500	7.66	$y = 730.02x + 9.99$	0.991	0.013	0.04	0.047	0.141
PFDA	31.25–500	8.15	$y = 1212.1x + 9.94$	0.997	0.02	0.062	0.090	0.270
PFUnDA	31.25–500	8.56	$y = 1314.6x - 4.39$	0.997	0.022	0.068	0.011	0.033
PFDoDA	31.25–500	8.95	$y = 1735.7x - 8.74$	0.998	0.021	0.065	0.011	0.033

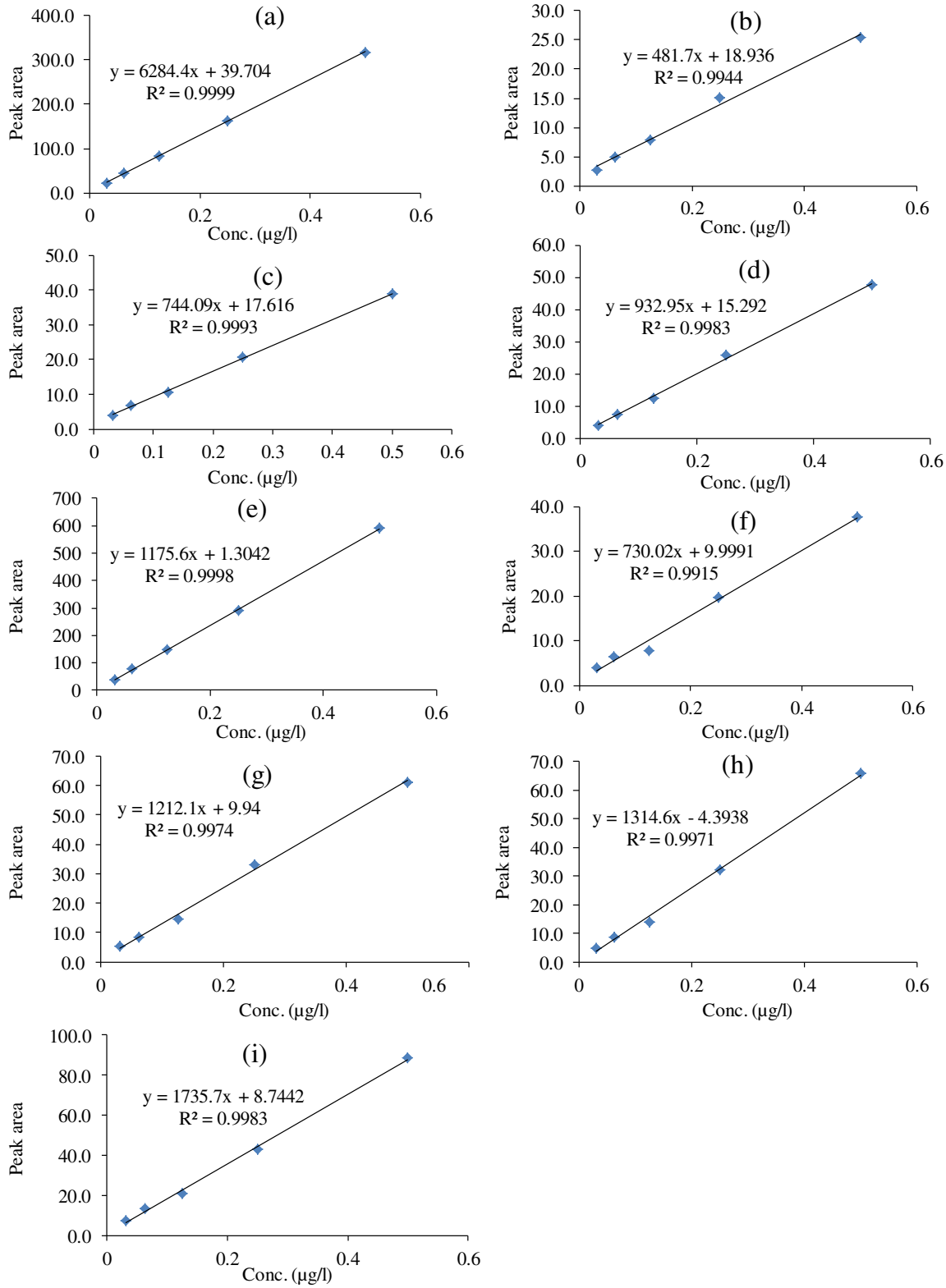

Fig. 6 Calibration plots of nine PFCs: PFBS (**a**), PFPeA (**b**), PFHpA (**c**), PFOA (**d**), PFOS (**e**), PFNA (**f**), PFDA (**g**), PFUnDA (**h**), PFDoDA (**i**)

Table 4 Repeatability, reproducibility, and mean (±SD) relative standard deviation for the nine PFCs (ng/l) standard response

Compounds	Repeatability			Mean + RSD	Reproducibility			Mean + SD
	x-time	y-time	z-time		x-day	y-day	z-day	
PFBS	13.09	12.71	12.43	12.74 ± 0.33	12.65	12.43	12.19	12.42 ± 0.23
PFBA	11.43	10.96	10.59	10.99 ± 0.42	10.63	10.59	10.25	10.49 ± 0.21
PFHpA	55.11	53.28	51.9	53.43 ± 1.61	52.71	51.9	50.3	51.64 ± 1.23
PFOA	16.35	16.03	15.49	15.96 ± 0.43	15.69	15.49	15.03	15.40 ± 0.39
PFOS	8.95	8.53	8.8	8.76 ± 0.21	8.67	8.8	8.47	8.65 ± 0.17
PFNA	13.49	13.08	12.99	13.19 ± 0.27	13.1	12.99	12.5	12.86 ± 0.32
PFDA	18.65	18.56	17.89	18.37 ± 0.42	17.9	17.89	17.43	17.74 ± 0.27
PFUnDA	23.04	22.53	22.2	22.59 ± 0.42	22.21	22.00	22.2	22.14 ± 0.12
PFDoDA	12.16	11.83	11.61	11.87 ± 0.28	11.59	11.61	11.42	11.54 ± 0.10

surface water ranged from 0.1 to 6700 ng/l, with corresponding values for PFOA that ranged from 0.4 to 123 ng/l. Levels of PFOA and PFOS measured in surface water samples in this study were below the USEPA threshold limit of200 ng/l for PFOA and 400 ng/l for PFOS in potable water (USEPA 2009). The concentrations of target compounds obtained in this study are consistent with similar reports elsewhere pertaining to surface water and sediments (Lein et al. 2008).

Statistical analysis using two-way analysis of variance (ANOVA) univariate test showed that levels of PFCs in the sediment samples were significantly higher ($F = 22.94$, $p < 0.05$) than levels in corresponding surface water samples. Two-way ANOVA using multivariate test showed that sampling points had significant effects ($p < 0.05$) on concentrations of PFCs measured in both water and sediment samples (supplementary information TS7, TS8, and TS9). There is positive correlation ($p < 0.01$) between the levels of PFCs measured in samples obtained from points B and C; which implies that the sources of PFC in the water may be of same origin. The concentrations of PFCs detected in both surface water and sediment samples downstream were higher than those upstream as shown in (Fig. 7). This might be due to enhanced sorption of the measured PFCs at the sampling points. Statistical analysis also revealed that data obtained showed significant positive correlation ($p < 0.01$) among PFSAs (PFOS and PFBS) in both surface water and sediment samples. Perfluorinated compounds with carbon chain (≤ 8) such as PFBS, PFPeA, PFHpA, and PFOA were mostly detected at higher concentrations in water and sediment samples at all sampling points. This observation is consistent with a previous study reported by Naile et al. (2016). The occurrence of PFCs could be attributed to their high stability and hydrophobicity, which are induced by increased C-F linkage in the PFCs (Wilhelm et al. 2010). The levels of PFCs measured were suspected to be largely associated with human activities and anthropogenic inputs such as domestic waste from informal human settlement, industrial activities, and agricultural practices.

Conclusion

This study describes a routine analytical method using UPLC-QTOF-MS for the determination of PFCs in environmental matrices (surface water and sediment samples). Extraction and clean-up were achieved using hydrophobic and lipophilic balance (HLB) solid-phase extraction (SPE). The method was validated and used for the determination of PFCs in surface water and sediment samples. Detection of all perfluorinated compounds of interest was achieved in less than 9 min analytical run time. This study also offers a robust and selective method for the determination of the target analytes. Reproducibility and repeatability tests established the stability and resilience of the method for routine application in determining the presence of PFCs. The fragmentation pattern of the compounds obtained in the mass spectrometry enables a clear identification of the target analytes. Application of this

Table 5 Mean values (±SD; $n = 3$) for the recovery of target compounds in spiked Milli-Q water, surface water, and sediment samples

Compounds	Percentage recoveries								
	(125 ng/l)		(125 ng/g)	(250 ng/l)		(250 ng/g)	(250 ng/l)		(250 ng/g)
	Milli-Q water	Surface water	Sediment	Milli-Q water	Surface water	Sediment	Milli-Q water	Surface water	Sediment
PFBS	54.4 ± 10.01	42.58 ± 1.65	41.06 ± 7.17	74.50 ± 2.90	71.04 ± 1.7	57.20 ± 2.83	78.50 ± 16.5	78.66 ± 3.23	56.21 ± 4.07
PFPeA	61.6 ± 6.90	51.2 ± 2.90	48.26 ± 6.64	78.13 ± 1.23	71.46 ± 1.2	59.06 ± 2.01	93.12 ± 7.24	75.68 ± 2.51	62.26 ± 2.66
PFHpA	56.4 ± 12.53	50.13 ± 1.23	45.28 ± 3.85	72.60 ± 4.27	68.26 ± 1.4	60.40 ± 1.65	94.40 ± 8.52	68.0 ± 7.63	64.66 ± 7.32
PFOA	57.0 ± 7.46	53.33 ± 1.21	47.44 ± 1.86	76.60 ± 2.45	68.66 ± 2.4	59.33 ± 2.82	93.13 ± 11.48	72.45 ± 7.56	62.60 ± 4.04
PFOS	56.8 ± 2.11	60.75 ± 1.9	54.82 ± 4.42	77.70 ± 2.29	75.33 ± 1.6	62.00 ± 1.44	90.60 ± 13.35	68.32 ± 13.51	60.00 ± 3.75
PFNA	52.2 ± 12.77	57.84 ± 0.76	54.98 ± 3.52	78.53 ± 6.04	74.0 ± 13.8	59.86 ± 0.83	92.01 ± 6.02	70.19 ± 5.50	69.86 ± 8.62
PFDA	61.8 ± 3.25	52.02 ± 2.14	48.90 ± 4.73	75.31 ± 1.23	70.38 ± 2.2	61.21 ± 2.13	87.30 ± 8.82	80.56 ± 2.82	62.53 ± 4.31
PFUnDA	56.2 ± 11.49	61.12 ± 1.28	58.82 ± 1.88	74.13 ± 2.27	69.06 ± 2.2	60.13 ± 1.89	90.00 ± 12.11	67.84 ± 5.28	62.46 ± 3.85
PFDoDA	66.4 ± 7.22	66.69 ± 3.60	61.2 ± 3.95	73.20 ± 2.63	69.46 ± 0.6	61.20 ± 3.17	126.52 ± 14.67	72.42 ± 5.76	60.20 ± 3.24

Table 6 Levels of PFCs in surface water (ng/l ± SD) and sediment (ng/g ± SD) samples in Plankenburg River

Compounds	PKA (upstream)		PKB (informal settlement)		PKC (industrial effluent)		PKD (downstream)		Validation		
										(LOD)	
	sediment	Surface water	sediment	Surface water	Sediment	Surface water	Sediment	Surface water	Blank	Sediment	Water
PFBS	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	ND	0.0074	< 0.080
PFBA	0.127 ± 0.21	10.2 ± 1.20	0.86 ± 0.02	28.4 ± 7.09	0.16 ± 0.0	20.8 ± 5.22	0.15 ± 0.11	23.2 ± 6.96	ND	0.012	< 0.051
PFHpA	0.105 ± 0.12	22.2 ± 4.10	0.201 ± 0.01	77.6 ± 13.64	0.81 ± 0.67	10.5 ± 3.42	0.243 ± 0.17	74.8 ± 14.77	ND	0.015	< 0.057
PFOA	0.32 ± 0.02	62 ± 6.41	0.33 ± 0.01	12.8 ± 4.24	0.24 ± 0.02	19.6 ± 9.16	0.14 ± 0.08	15.8 ± 7.15	ND	0.021	< 0.035
PFOS	0.7 ± 0.013	LOQ	0.104 ± 0.05	12.4 ± 3.59	0.53 ± 0.01	3.8 ± 2.24	LOQ	LOQ	ND	0.017	< 0.064
PFNA	0.55 ± 0.07	LOQ	0.34 ± 0.02	LOQ	LOQ	LOQ	0.82 ± 0.016	LOQ	ND	0.047	< 0.064
PFDA	LOQ	LOQ	0.18 ± 0.03	25.0 ± 11.87	LOQ	7.6 ± 3.11	LOQ	LOQ	ND	0.09	< 0.020
PFUnDA	LOQ	21.6 ± 0.02	0.10 ± 0.02	32.0 ± 4.21	LOQ	LOQ	0.147 ± 0.18	14.6 ± 6.83	ND	0.011	< 0.022
PFDoDA	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	ND	0.011	< 0.021
ΣPFCs	1.79	117.34	2.12	186.40	1.58	62.30	1.47	128.40			

Concentration = mean ± SD. Plankenburg River Point PKA, PKB, PKC, and PKD

ND non-detected, *LOD* limit of detection, *LOQ* limit of quantification

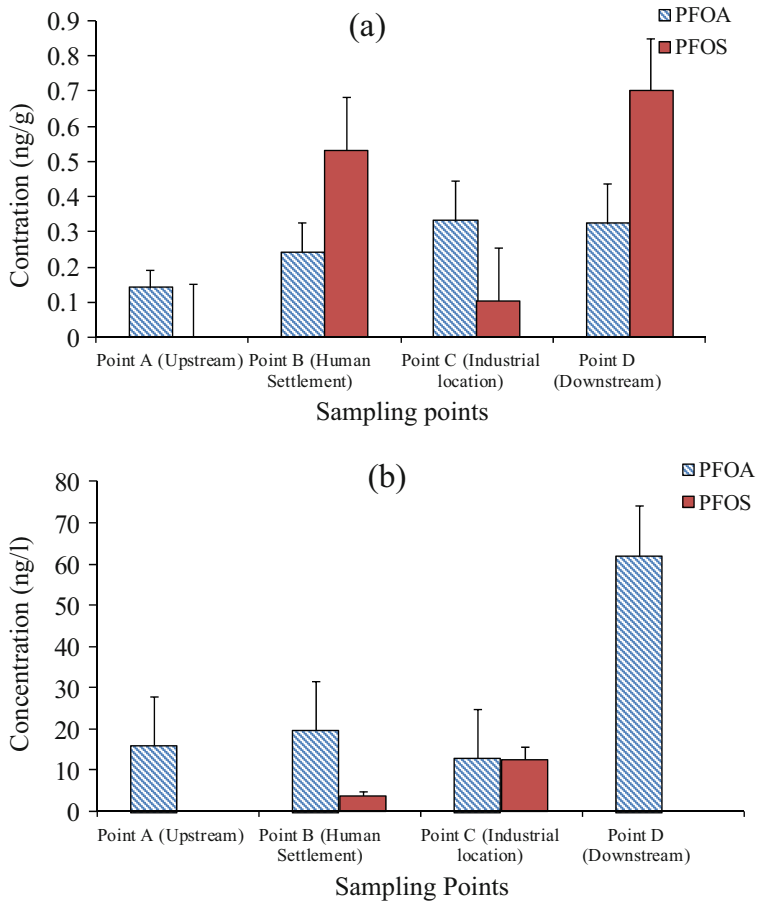

Fig. 7 Levels of PFOA and PFOS (**a**) sediment samples; (**b**) surface water samples collected from Plankenburg River. Point A: agricultural area (upstream), point B: close to informal settlement, point C: close proximity to industrial facility, and point D: close to educational and recreational facilities (downstream)

method for the determination of PFCs (including PFOA and PFOS) in the environmental matrices (surface water and sediment samples) yielded satisfactory recovery results. Higher concentrations of PFOA and PFOS were detected in sampling locations close to human activities than in other sampling locations, which suggests that human activities could have contributed to the presence of PFCs in the environment. Examples of such human activities include improper solid waste management practices, poor sewage disposal, and poor drainage systems, all prominent features visible in the vicinity of the river. In addition, untreated effluents from industrial activities, from poor housekeeping at the recreational facilities, and from agricultural activities may also have contributed significantly to the contamination of the water body. On the other hand, low concentrations of PFCs in the river system might be influenced by the intrusion and dilution of contaminants from other sources. Hence, this method is suitable for identification and quantification of PFCs in environmental samples in the future.

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