

# **Report as of FY2006 for 2006AZ132B: "Perfluorinated Chemicals in Municipal Wastewater Treatment Plants in Arizona"**

## **Publications**

- Dissertations:
  - Ochoa, Valeria, 2006, Processes for the Removal of Perfluorooctane Sulfonate (PFOS) from Semiconductor Effluents, MS Dissertation, Department of Chemical and Environmental Engineering, Univ. of Arizona, Tucson, Arizona.

## **Report Follows**

## **A. Problem and Research Objectives**

### A.1. Statement of critical regional or state water problems

Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and related PFCs are emerging environmental pollutants. These compounds have come under increased scrutiny due to recent reports of their detection in environmental and biological matrices as well as concerns regarding their persistence and toxicity. Recent studies indicate that wastewater treatment plants are point sources of PFCs (Boulanger *et al.*, 2004; Higgins *et al.*, 2005). The fluorochemicals may enter the environment through effluent discharge or land application of biosolids.

Little is known about the fate of PFCs in municipal wastewater treatment systems. Sewage sludge is suspected to be the main sink of perfluorinated compounds in municipal wastewater treatment plants as these compounds are expected to partition into biosolids due to their high bioaccumulation potential. There is presently no data on the occurrence of PFCs in environmental samples nor in municipal wastewater treatment plants (WWTP) in Arizona, yet PFCs are extensively used in the growing semiconductor industry sector in the State, in (forest) fire fighting operations, and in a wide variety of other industrial, commercial and consumer applications. Data regarding the presence of PFCs in municipal wastewaters will be useful to understand the potential role of municipal WWTPs as indirect sources of PFCs emissions. As Arizona's population centers expand and the demand for water increases, reuse of treated wastewater is expected to become more prevalent, which could increase the potential for environmental contamination with PFCs. Information on the occurrence of PFCs in sewage sludge is also of importance for Arizona because biosolids are used as soil amendments throughout the State.

Safe water resources are of strategic importance for Arizona to meet the rapidly increasing demand for potable water. Understanding the occurrence and fate of these emerging pollutants in Arizona's wastewater treatment plants could be critical to protecting our water supplies. Utilities and government agencies will be able to utilize information gained from this study to determine the need for implementing measures to prevent the spread of PFCs in the environment.

### A.2. Background information

PFCs are emerging pollutants that have been used for over the last 50 years in a wide variety of industrial processes and consumer-based products. Among these chemicals, PFOS and PFOA (Figure 1) are the most studied fluorinated alkyl surfactants due to their world-wide distribution, environmental persistence and bioaccumulation potential. Studies show that PFOS has been detected in human blood samples (Olsen *et al.*, 2003; Kannan *et al.*, 2004; Calafat *et al.*, 2006), in wildlife tissues collected worldwide, including biota from pristine areas (Giesy and Kanan, 2001; 2002; Martin *et al.*, 2004a) and in environmental matrices such as sewage sludge (Higgins *et al.*, 2005). In response to these concerns, regulatory agencies in numerous industrialized countries have initiated studies to quantify the use of perfluorinated chemicals, assess their potential risks, and consider regulations restricting or banning their use (Martin *et al.*, 2004b).

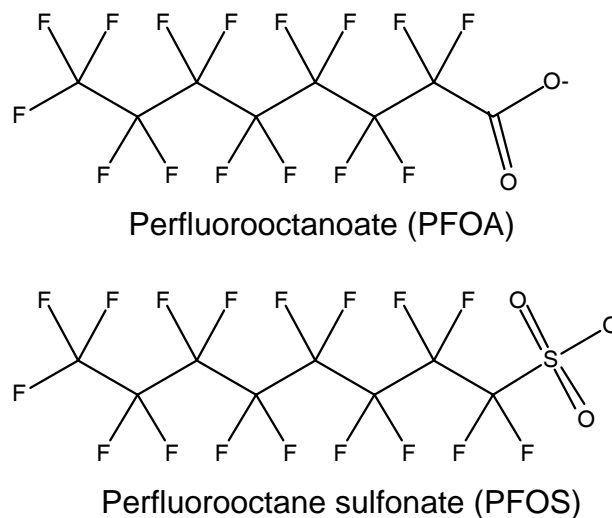
Little is known about the occurrence and fate of perfluorinated compounds in municipal WWTPs. A study conducted by 3M in 2001 revealed that PFOS concentrations in sewage sludge in Alabama, Tennessee, Georgia and Florida were in the range of 58 to 3,120 ng/g (3M, 2001). Higgins *et al* (2005) quantified PFC levels in sewage sludge and in sediments impacted by sewage discharges in California. The survey detected total PFCs levels ranging from 55 to 3,370 ng/g in domestic sludge. Loganathan and coworkers (2006) reported PFOS and PFOA at concentrations of 62 – 990 ng/g in sludge samples obtained from a municipal WWTP in Kentucky.

Research on the fate and transport of PFCs in the environment has been hampered by a lack of analytical capability (Martin *et al.*, 2004b). Compound specific quantitative methods for the analysis of PFCs became first available in the year 2001, when a procedure consisting of liquid solvent extraction, solid-phase extraction cleanup, and analysis by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) was described for the analysis of PFCs in biological matrices (Hansen *et al.*, 2001). Methods for the determination of perfluoroalkylsulfonates and perfluoroalkylcarboxylates in aqueous samples, sludge and sediments by LC-MS/MS have also been described recently (Boulanger *et al.*, 2004; Higgins *et al.*, 2005; Moody *et al.*, 2001). LC-MS/MS is the method of choice for the quantification of PFCs constituents in environmental samples and biological matrices, both because of its sensitivity and selectivity (Martin *et al.*, 2004b; Schultz *et al.*, 2003). Quantitative analysis of perfluoroalkylsulfonate anions in water has been accomplished by direct injection MS, without prior chromatographic separation (Hebert *et al.*, 2002). Direct injection MS is less expensive and time consuming than LC-MS/MS and could offer an interesting alternative for samples that do not cause interfering matrix effects.

### A.3. Objectives

The objective of this study is to conduct a preliminary evaluation of the significance of PFCs in discharges from municipal wastewater treatment plants by: 1) developing analytical methods for the detection and quantification of PFCs in wastewater treatment sludge; 2) assessing PFCs levels in sludge samples obtained from selected municipal wastewater treatment plants; and 3) evaluating the importance of biosorption processes on the fate of fluorinated compounds during biological wastewater treatment.

## **B. Methodology**



**Fig.1.** Chemical structure of the most ubiquitous perfluoro alkyl surfactants in the environment.

## B.1 Chemicals

Perfluorooctane sulfonic acid potassium salt, PFOS (98%), was purchased from SynQuest Laboratories (Alachua, FL). Perfluorobutane sulfonic acid potassium salt or PFBS (98.2%) was kindly provided by the 3M Company (St. Paul, MN). Sodium perfluoro-1-hexane sulfonate, PFHxS (98%), sodium perfluoro-1-decanosulfonate, PFDS (98%) and perfluoro-n-decanoic acid, PFDA (98%) were obtained from Wellington Laboratories (Ontario, Canada). Perfluorooctanoic acid, PFOA (96%) and sodium fluoride (99%) were obtained from Sigma-Aldrich (St. Louis, MO). Solid phase extraction (SPE) cartridges, 3ml, 500 mg ODS-C18 were supplied by Agilent Technologies (New Castle, DE). Methanol (HPLC grade) was purchased from Burdick & Jackson (Muskegon, MI). Acetic acid, glacial (ACS grade) was obtained from EMD chemicals (Gibbstown, NJ). Sulfuric acid (95-98% ACS grade) was purchased from Sigma-Aldrich (St. Louis, MO), acetonitrile (99.8 % HPLC grade) and boric acid (99.5%, ACS grade) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ). All chemicals were used as received.

## B.2. Analytical Methods

C.2.1. Suppressed conductivity ion chromatography quantification. PFOS and related compounds in aqueous samples were analyzed by ion chromatography with suppressed conductivity detection (Dionex ICS-3000 system). The chromatograph was equipped with an autosampler (injection volume 5  $\mu$ l), a pump, a degasser, a guard column and a separation column (Acclaim Polar Advantage II, C18, 4.6mm i.d., 25 cm length) operating at 35°C. A mixture of 20 mM boric acid (pH 8.0) and 95% acetonitrile was used as the mobile phase at a flow rate of 1ml/min. The ratio of boric acid to acetonitrile varied with linear gradient program 0 min: 75:25 v/v to 13.2 min: 45:55 v/v. Blanks were continuously run to assure that the column was clean and that traces of the analyte were not carried over between samples.

The total concentration of perfluorinated compounds in aqueous samples was obtained by linear calibration curves ( $r^2 > 0.99$ ) using known concentrations of PFOS ranging from 0–150 mg/l. The detection limit of PFOS was 0.5 mg/l.

C.2.2. LC-MS/MS: Mass spectrometry analysis was conducted by a method described by Higgins *et al.* (2005). LC-MS/MS measurements were performed on a Magic 2002 (Michrom Biosciences, Inc.) ThermoFisher (Finnigan) LCQ Classic HPLC-MS system. Chromatographic separation was conducted on a MagicMS C18 micobore column (5  $\mu$ m, 200A, 1x150 mm). Two solutions were used as a mobile phase: (A) buffer (10mM NH<sub>4</sub>OAc in H<sub>2</sub>O) and (B) methanol. A gradient program with 5% B to 90% B in 35 min was used to elute the components of the samples with a flow rate of 50  $\mu$ l/min, temperature 40°C and injection volume 25  $\mu$ l. Negative ionization was employed to detect fluorinated sulfonates and carboxylates. Selected ion monitoring (SIM) was used to improve detection limit for the perfluorinated compounds. Standard solutions were run first to determine peak intensity ratios for the selected ions (m/z 399, 413, 499, 513, and 599). A m/z window of +/- 3 around the selected m/z value was used in the SIM experiments. Tandem MS/MS was also applied to get structural information on selected

ions (e.g., on  $m/z$  499,  $\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$ ). He was used as a collision gas and a 35% relative collision energy was applied in the MS/MS experiments. MS/MS spectra were recorded within a mass range of  $m/z$  75-1000 using a scan time of 0.2 s. Blanks samples were used to monitor instrument background and were continuously run after three sludge samples.

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### B.3 Sewage sludge extractions

Sludge extractions were conducted according to the method described by Higgins *et al.* (2005). Anaerobically digested sewage sludge (ADS) from two different municipal wastewater treatment plants in Tucson, Arizona (Ina Road and Roger Road treatment plants), were evaluated in this study. ADS samples were dried in an oven at 70°C overnight and air-dried for 1 day. Samples were ground and homogenized using a mortar and pestle. Homogenized sludge (100 mg) was transferred to a Nalgene bottle and 7.5 ml of 1% acetic acid solution was added. Each sample was vortexed for 10 min and sonicated for 30 min at 60°C. Following sonication, samples were centrifuged (10,000 rpm, 25 min) and the wash was decanted in a second Nalgene flask. A volume of 1.7 ml of a methanol/1% acetic acid (90/10, v/v) solution was added to the original vial to extract PFCs. Before centrifugation, samples were vortexed for 10 min and then sonicated for 30 min at 60°C. The extract was decanted in a third Nalgene flask. This procedure was conducted two more times and all washes and extracts were combined. Ina Road ADS was also extracted using a modified procedure. Briefly, 75 ml of 1% acetic acid solution was added to 6,000 mg of homogenized air-dried sludge followed by 20 ml methanol/1% acetic acid (90/10, v/v) extraction mixture. All wash and extract vials were centrifuged (10,000 rpm, 25 min) to avoid clogging of the SPE column. Each sludge sample was extracted and analyzed in triplicate.

### B.4 Sample cleanup

Solid phase extraction (SPE) was conducted to preconcentrate and cleanup wash and extract samples. SPE cartridges (3 ml, 500 mg ODS-C18, Agilent Technologies, DE) mounted on a vacuum manifold were conditioned with 6 ml MeOH, followed by 6 ml of 1% acetic acid solution. The desired volume of wash or extract was loaded at 1 ml/min. SPE cartridges were rinsed with 4 ml of deionized water and then centrifuged (4,000 rpm, 25 min) prior elution. Analytes were eluted with 4 ml methanol and collected in clean Nalgene flasks. The eluent was concentrated 8-fold under  $\text{N}_2$ . In the second extraction when significant amounts of Ina Road ADS were employed, the sample was loaded in 3 different columns and each column was washed with 20 ml of deionized water. All eluents were combined and finally concentrated 10-30-fold under  $\text{N}_2$ . The extracts were stored at 4°C. Prior to analysis, the samples were diluted 10-fold to reduce matrix interferences and bring concentration in the right LC-MS/MS ranges.

### B.5 Quantification

Selected ion monitoring (SIM) was employed to enhance sensitivity during

quantification. Standards of the perfluorinated compounds were run in parallel to validate the analysis. Since chemical characteristics influence the ionization process, PFDS was used as an internal standard for PFOS. The latter compounds belong to the perfluoroalkyl sulfonate family and chemically are very similar.

Samples were spiked with a known concentration of the internal standard, PFDS, 0.5 mg/l. Peaks were averaged and the areas were calculated by multiplying the height by the peak width at the half-height. Quantification was possible by relating the area of the PFOS peak to the area of the internal standard. The ratio of areas of PFOS and PFDS in an equimolar standard solution was employed to correct for the differences in response factors of the compounds. The precision of the method was determined by analyzing sludge samples in triplicate and calculating the standard deviation.

### B.6 Biosorption assays

Sorption assays were conducted to study the partitioning of PFOS between the aqueous phase and sludge obtained from municipal WWTPs. Three different types of wastewater treatment sludge were employed in this study, anaerobic granular sludge, aerobic activated sludge (RAS) and anaerobically digested sewage sludge (ADS). The anaerobic granular sludge was obtained from an industrial anaerobic reactor treating wastewater from recycle paper manufacturing (Eerbeek, The Netherlands). The samples of RAS and ADS were obtained from the Ina Road municipal WWTP in Tucson, Arizona.

Sorption isotherm experiments were performed in duplicate using Nalgene flasks supplied with aqueous samples containing known concentrations of PFOS (0 to 100 mg/l) in 3 mM phosphate buffer (pH 7.2). In the case of the anaerobic granular sludge, each flask received 100 ml of solution and an amount of sludge that ranged from 0 to 1 gram. For the RAS and ADS samples, the amount of sludge added varied from 0 to 50 ml and the solution volume ranged from 50 to 140 ml. Flasks were shaken in an orbital shaker at 150 rpm overnight at 30°C. Control flasks in which no sludge was added were run in parallel to correct for possible removal of PFOS by other mechanisms than biosorption. Removal of PFOS from solution was determined using suppressed conductivity ion chromatography following centrifugation and filtration of the samples to remove insoluble matter.

The adsorptive capacity of the various wastewater treatment sludge samples over a range of different concentrations was determined by fitting the sorption results to Langmuir and Freundlich models.

The Langmuir isotherm is defined by:

$$C_s = \frac{a \cdot b \cdot C_e}{1 + b \cdot C_e}$$

where  $C_s$  is the concentration of the solute in the solid phase (mg PFOS/g sludge organic matter),  $C_e$  is the equilibrium concentration of the solute in solution (mg PFOS/l),  $a$  and  $b$  are Langmuir adsorption constants;  $a$  represents the maximum achievable surface concentration of the solute and  $b$  is the equilibrium constant for the sorption reaction.

The Freundlich isotherm is defined by:

$$C_s = K_F \cdot C_e^n$$

where  $K_F$  is the Freundlich adsorption constant or capacity factor and  $n$  is the Freundlich exponent. When  $n = 1$ , the isotherm is linear; when  $n < 1$ , the isotherm is concave

downward and when  $n > 1$ , the isotherm is convex upward.

## C. Principal Findings and Significance

### C.1. Analytical methods for the detection and quantification of PFOS and related compounds

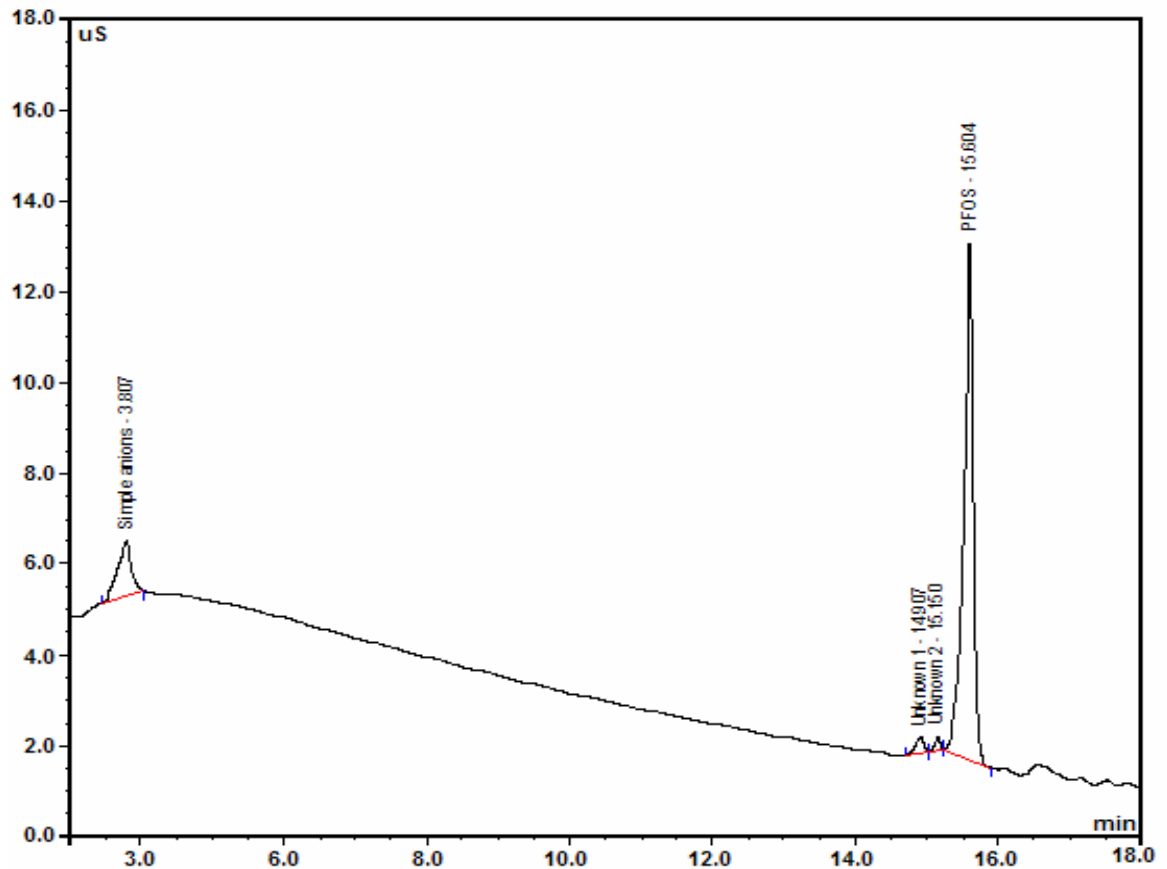
Analytical methods relying on HPLC with suppressed conductivity detection and LC-MS/MS have been successfully developed to monitor PFOS and related compounds in aqueous and solid environmental matrices. The results and discussion will be presented below.

C.1.1. PFC quantification by ion chromatography. An analytical method that relies on suppressed-conductivity ion chromatography has been developed to separate and detect aqueous PFOS and related perfluoroalkyl compounds. Figure 2 shows a chromatogram obtained for a sample containing 12.5 mg/l PFOS. Well resolved peaks and reproducible results were achieved by this chromatography method. The peak at 15.60 min is assigned to PFOS anion and the two little peaks eluting before the major peak at 14.91 min and 15.15 min correspond to PFOS impurities. These impurities have been identified elsewhere as structural isomers of PFOS which are compounds that have the same molecular weight as PFOS but are branched perfluoroalkyl sulfonates (Langlois and Oehme, 2006), by-products with geminal diperfluoromethyl groups and perfluoromethyl substituted compounds (Longanathan *et al.*, 2006).

The quantitative determination of low-ppm concentration of aqueous PFOS was effectively conducted by HPLC suppressed-conductivity ion chromatography as described in the *Materials and Methods* section. A calibration curve for PFOS in aqueous samples is shown in Figure 3. Linear calibration ranges of 0.5 to 100 mg/l PFOS were obtained. The detection limit was 0.5 mg/l PFOS. These results are consistent with those obtained by Hori *et al* (2004) utilizing a different HPLC method in which linear response up to 100 mg/l PFOS and detection limit of 0.66 mg/l PFOS were reported ( Langlois and Oehme, 2006).

The use of a reverse-phase C18 column provided good resolution of perfluorinated alkyl substances. A mixture of PFBS, PFOA and PFOS in a 1:1:1 molar ratio was successfully separated as shown in Figure 4. Standard samples of each fluorinated compound studied were run in parallel to identify the retention times of the various compounds. The peaks eluted based on number of carbons and molecular weight. PFBS, a 4-carbon compound with a molecular weight of 299.1 g/mol, appeared first followed by PFOA, a 8-carbon compound with a molecular weight of 414.1 g/mol, and finally PFOS, a 8-carbon compound with a molecular weight of 499.1 g/mol. The response factors of these perfluorinated compounds were significantly different, namely, 0.099, 0.064, and 0.034, for PFBS, PFOA and PFOS, respectively. The response factor was calculated by dividing the area of analyte by the concentration of the analyte.

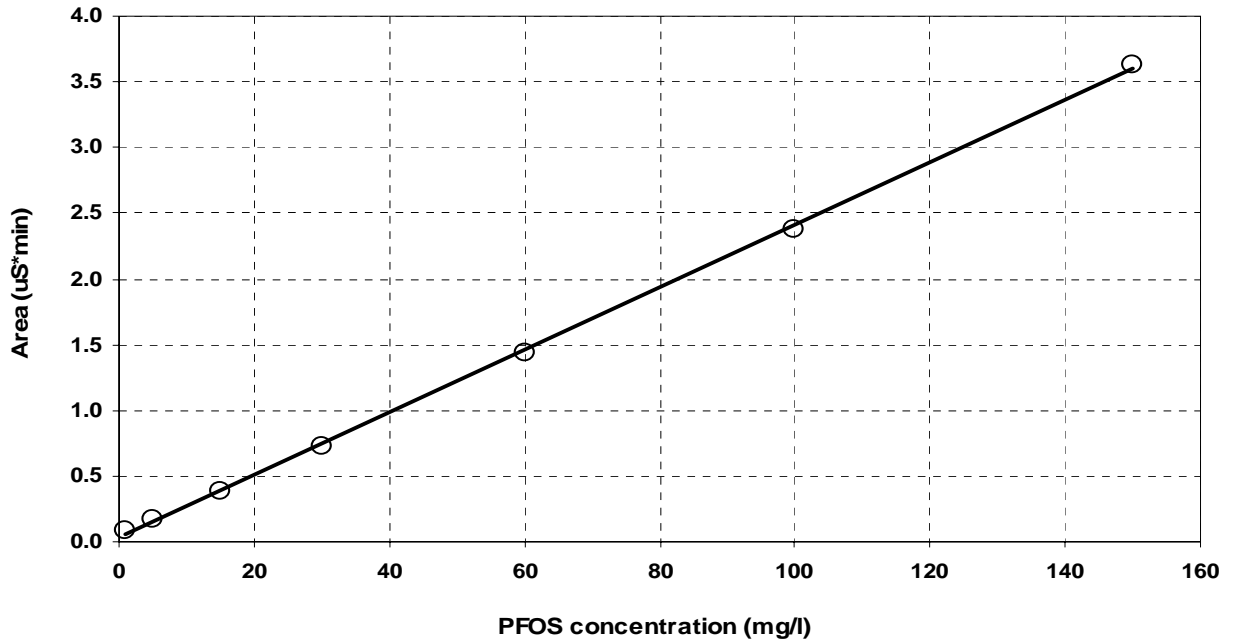
Ion chromatography is a simple, rapid and efficient method for the separation and detection of perfluorinated compounds. This technique is less expensive than LC-MS/MS and could be commonly applied for monitoring low-ppm amounts of ionic perfluorinated compounds on a routine basis in aqueous solutions. An inherent limitation of the technique is its inability to detect non-ionic compounds.



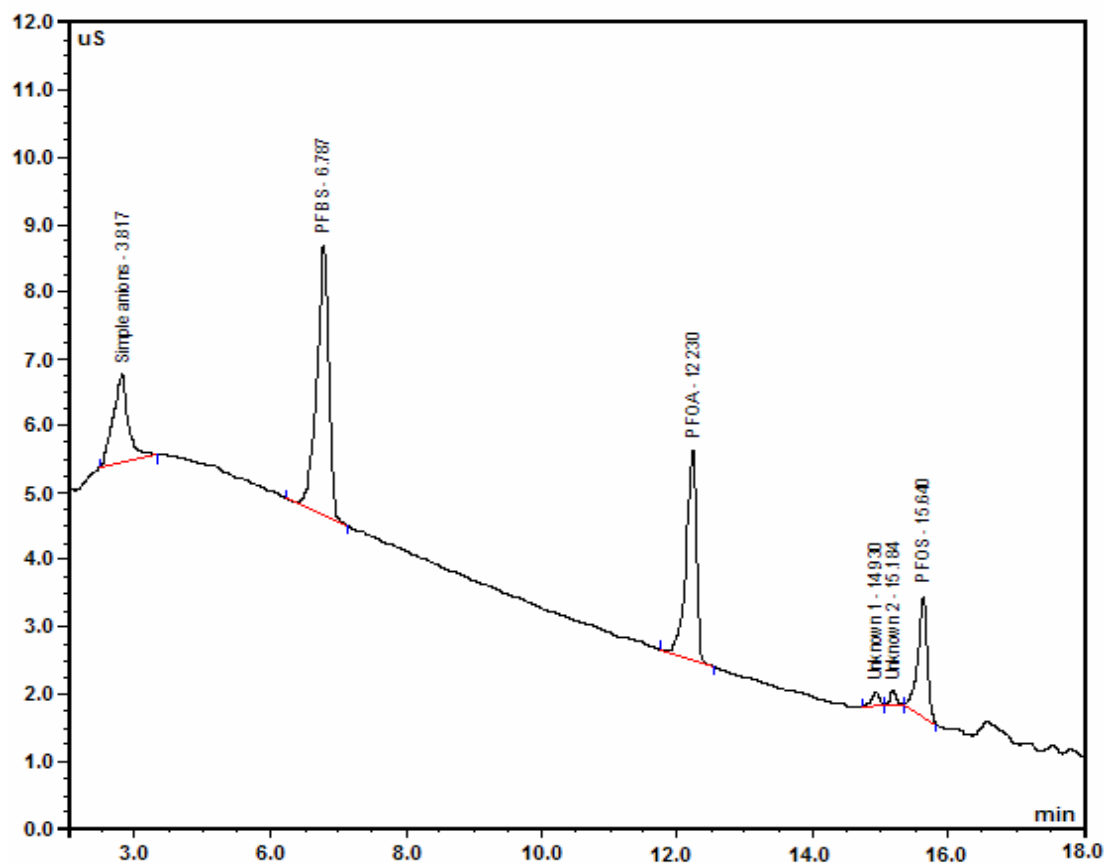
**Fig. 2.** Detection of aqueous perfluorooctane sulfonate (PFOS) using HPLC-suppressed conductivity ion chromatography.



C.1.2. HPLC with electrospray tandem mass spectrometry. A method based on reverse-phased high-performance liquid chromatography with negative electrospray tandem mass spectrometry (LC-MS/MS) described by Higgins *et al* (2005) was employed to detect PFCs in aqueous and solid environmental matrices. Figure 5 shows a chromatogram obtained for a mixed standard solution containing 5 mg/l of PFHXs, PFOA, PFOS, PFDA and PFDS in methanol. The MS/MS spectra of the same mixed standard solution are shown in Figure 6.



**Fig. 3.** Calibration curve of aqueous PFOS by HPLC suppressed-conductivity ion chromatography.



**Fig. 4.** HPLC-suppressed conductivity ion chromatograph of a solution containing PFBS, PFOA and PFOS.

As expected for a reverse-phased C18 column, perfluorinated chemicals were separated based on the perfluoroalkyl chain length. Distinct peaks are evident for the mixed standard solution of the perfluorinated chemicals (Figure 5). PFHXs ( $C_6$ , 399.10 g/mol) eluted first, followed by PFOA ( $C_8$ , 413 g/mol), PFOS ( $C_8$  499.12 g/mol), PFDA ( $C_{10}$ , 514.09 g/mol) and last PFDS ( $C_{10}$  599.13 g/mol). The response factor of perfluorinated compounds was calculated by dividing the peak area by the concentration of the analyte. The response factor of PFHXs, PFOA, PFOS, PFDA and PFDS were calculated to be 15, 21, 32, 14 and 14, respectively. The response factors of perfluorinated sulfonates and carboxylates with chain lengths of 6 and 10 carbons were the same. However, in the case of PFOA and PFOS (8-carbon chain), these values were higher and significantly different among compounds and within their families. The detection limits of the PFCs chemicals evaluated in this study differ among compounds. The estimated detection limit based on a signal-to-noise ratio of 3 was calculated to be 0.05 mg/l for PFOS, PFDA and PFDS as compared to 0.2 mg/l in the case of PFHXs and PFOA.

LC-MS/MS is a valuable technique to analyze PFCs chemicals in aqueous and solid environmental samples. The precision, accuracy and high sensitivity of the

technique make this method ideal for the quantitative determination of PFCs in low-ppb levels ( $\mu\text{g/l}$  range). However, ionization suppression effects and matrix interferences such as coelution of other chemicals present in the samples can compromise the quantitative analysis of environmental samples, sewage sludge.

### C.2. Assessment of PFCs levels in wastewater treatment sludge

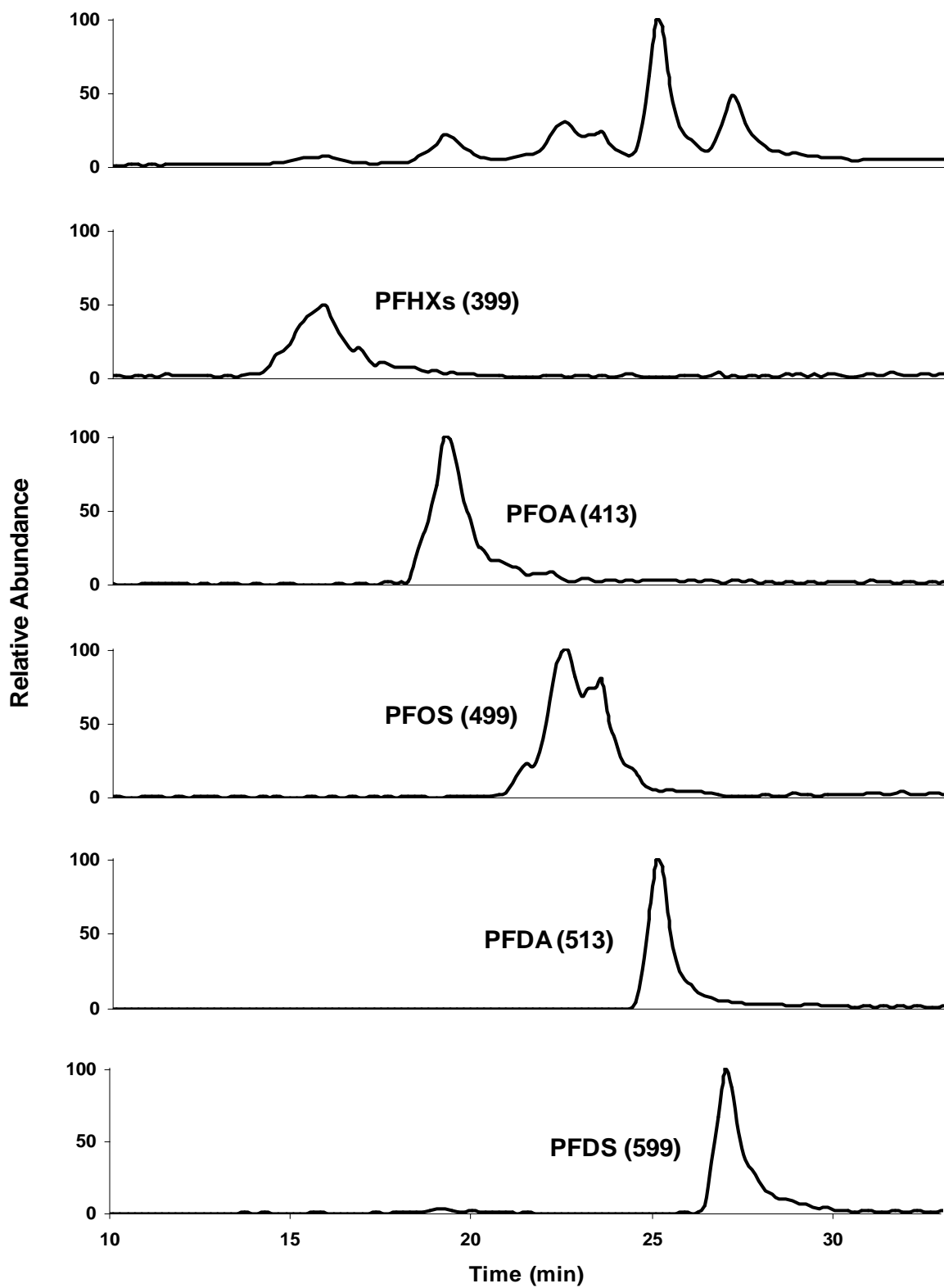
The presence of perfluorinated chemicals in anaerobically digested sewage sludge (ADS) in two different municipal wastewater treatment plants from Tucson, Arizona was evaluated in this study. LC-MS/MS quantification of PFCs in sewage sludge was performed according to the protocol described in the *Materials and Methods* section. Briefly, an acid wash-solvent extraction cycle followed by a SPE sample cleanup and concentration procedure were conducted to assess the levels of PFCs in municipal sludge. Two extractions were carried out, the first one employing 100 mg and a second one using 6,000 mg of dried sewage sludge. In both cases, the wash and the extract were analyzed. In the first extraction, no PFCs were detected, either in the wash or in the extract of ADS from the Ina Road and Roger Road treatment plants, suggesting that the compounds were not present or their concentrations were lower than the detection limits. In the second extraction using 6,000 mg of Ina Road ADS, PFOS was measured in the extract, but PFCs were not detected in the wash. The analytical results obtained in the second extraction are presented below in more detail.

Higgins and collaborators reported that high-molecular weight perfluorinated compounds ( $> 499$  g/mol) are the predominant compounds detected in municipal sewage sludge (Higgins *et al.*, 2005). PFOS, PFDS, FOSAA (perfluorooctanesulfonamidoacetate), *N*-MeFOSAA (2-(*N*-methylperfluorooctanesulfonamido) acetate), *N*-EtFOSAA (2-(*N*-ethylperfluoro-octanesulfonamido) acetate) and PFDA were detected in WWTP discharges in San Francisco Bay Area (Higgins *et al.*, 2005) at concentrations ranging from 176 to 3,390 ng/g. Based on this report, selected ion monitoring (SIM) was employed to analyze PFHXs, PFOA, PFOS, PFDA, *N*-MeFOSAA, *N*-EtFOSSA and PFDS in the extract obtained following extraction of sewage sludge.

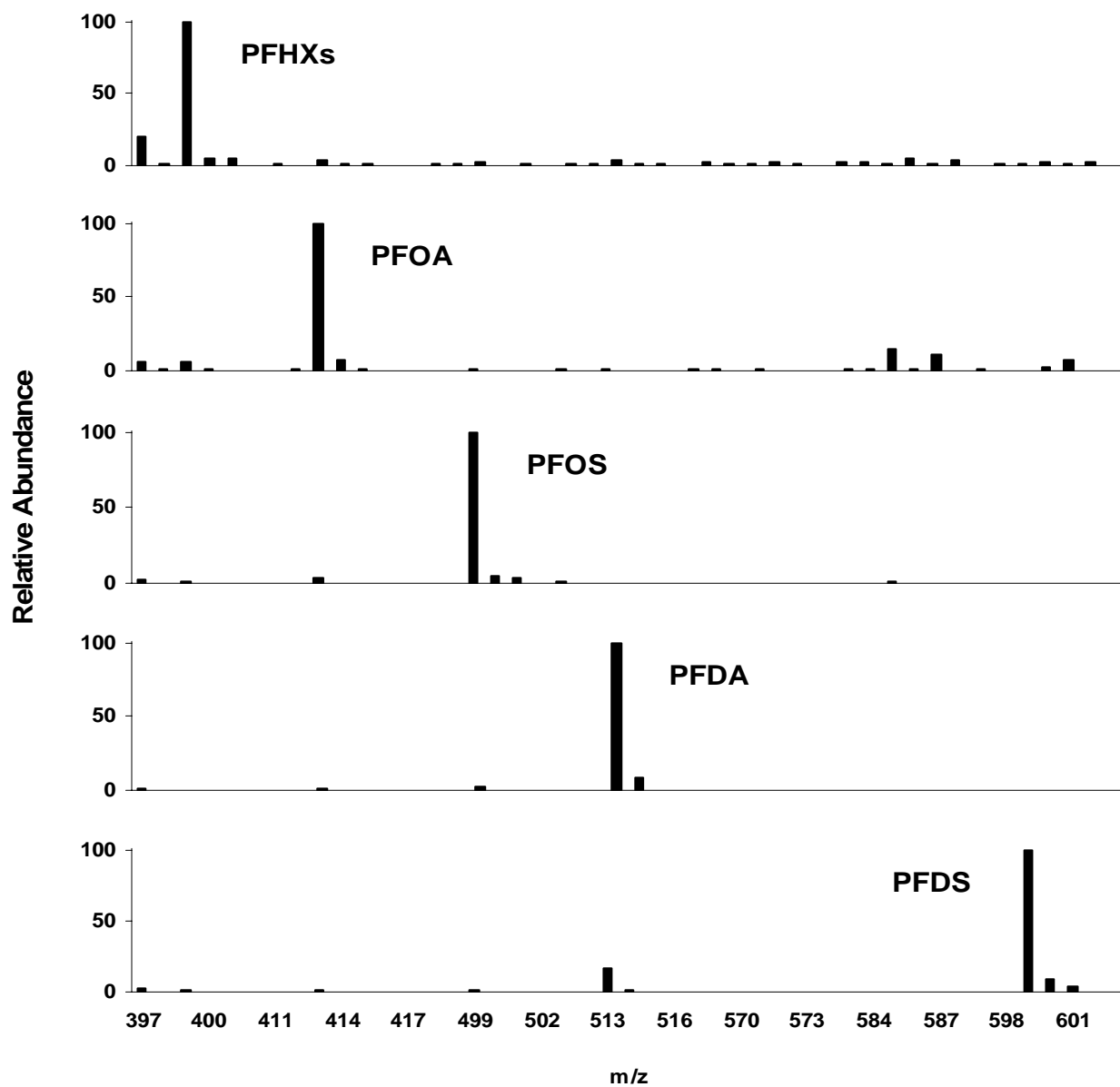
Figure 7 shows a LC-MS chromatogram and MS/MS spectrum obtained under SIM analysis of an extract sample spiked with 0.5 mg PFDS/l. PFOS was the only perfluorinated compound detected under the experimental conditions evaluated in this study. PFOS concentration in Ina Road ADS was  $77 \pm 5$  ng/g sludge dwt. The levels of PFOS determined here are within the range of those determined in related studies around the country (3M, 2001; Loganathan *et al.*, 2006). PFOS appears to be the dominant PFC in sewage sludge samples. Data collected by 3M in 2001 indicated that PFOS concentrations in municipal sludge from Alabama, Tennessee, Georgia and Florida exceed PFOA and FOSA (perfluorooctanesulfonamide) concentrations by one order of magnitude (3M, 2001). In sewage sludge samples from Kentucky, PFOS concentrations were 2 to 5-fold higher than those of PFOA (Loganathan *et al.*, 2006). These results are also consistent with previous work on the presence of perfluorinated chemicals in the environment. In wildlife samples throughout the world, PFOS was the only compound detected (Giesy and Kanan, 2001; 2002; Martin *et al.*, 2004a). PFOS concentrations in

human sera samples from a global study were 2-fold greater than those of PFOA and about one order of magnitude higher than PFHXs concentrations (Kannan *et al.*, 2004).

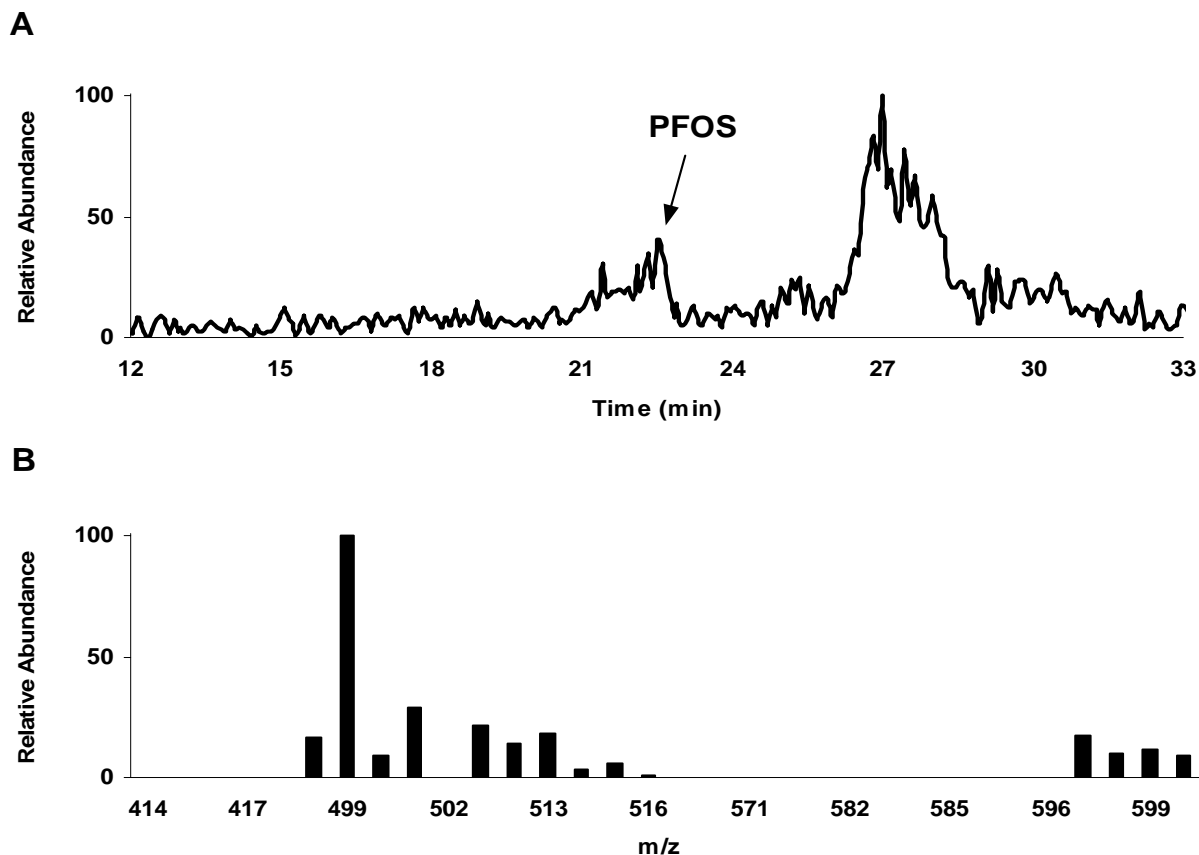
Unlike the results reported by Higgins *et al* (2005), PFOS was the only compound detected in the sewage sludge samples analyzed in this study. This could be attributed to several aspects, inefficient extraction recoveries, inadequate retention or elution times during SPE cleanup, instrument limitations and most likely matrix-derived analyte signal suppression effects (Ferguson *et al.*, 2000; Higgins *et al.*, 2005). In electrospray LC-MS/MS the intensity of an analyte ion signal is a function of both the concentration of the analyte and the total ions present in solution. In heterogeneous matrices such as sewage sludge, the variability and amount of organic matter present can result into suppression effects of the analyte signal (Ferguson *et al.*, 2000). In fact, in the extraction with 6 g of sludge, linear alkylbenzene sulfonates surfactants co-eluted with high molecular weight PFCs (*N*-MeFOSAA, *N*-EtFOSAA and PFDS) in significant concentrations (Figure 7). Therefore, it could be possible that these perfluorinated chemicals might be present however due the matrix interferences they cannot be detected.



*Fig. 5. LC-MS chromatogram of a mixed standard solution containing 5 ppm of PFHXs, PFOA, PFOS, PFDA and PFDS.*



*Fig. 6. Negative ESI/MS spectra of a mixed standard solution containing 5 mg/l of PFHXs, PFOA, PFOS, PFDA and PFDS obtained under SIM analysis.*

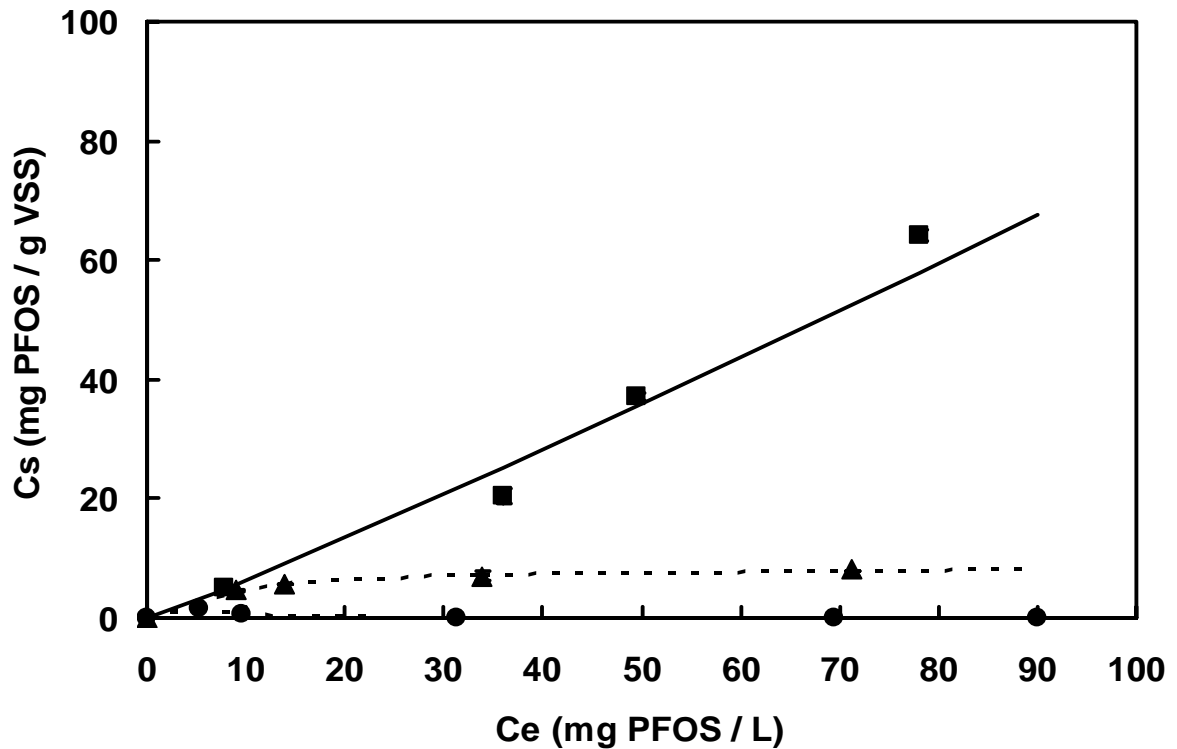


*Fig. 7. SIM analysis of a sewage sludge sample in Ina Road WWTP from Tucson, Arizona. A) Typical LC-MS chromatogram and B) MS/MS spectrum of extract sludge sample spiked with 0.5 mg/l of PFDS.*

### C.3 Adsorption of PFOS onto wastewater treatment sludge

The sorption of PFOS from aqueous solutions onto wastewater treatment sludge was examined in batch experiments at 30°C and pH 7.2 under well defined conditions according to the protocol described in *Materials and Methods* section. Three different types of sludge obtained from industrial wastewater treatments plants, anaerobic granular sludge, aerobic activated sludge (RAS) and anaerobically digested sewage sludge (ADS) were evaluated in this study. The adsorption isotherms obtained for the various sludge tested are shown in Figure 8.

The experimental isotherms obtained show the concentration of PFOS sorbed to the wastewater treatment sludge ( $C_s$ , expressed as mg PFOS per gram sludge organic matter) as a function of the equilibrium concentration of the contaminant in solution ( $C_e$ , in mg PFOS/l). The organic matter content in the sludge was measured as volatile suspended solids (VSS). The VSS content of the anaerobic granular sludge, RAS sludge and ADS were 13.7%, 1.0% and 11.8% based on the weight if the wet sludge, respectively. The isotherms were fit to the Freundlich and Langmuir models (Table 1).



**Fig. 8.** Adsorption isotherms of PFOS onto wastewater treatment sludge. Legend: (■) anaerobic granular sludge, (▲) anaerobic digested sludge (●) activated sludge; (dashed line) experimental data fit to Langmuir model; (solid line) experimental data fit to Freundlich model.

The ADS data fit best to a Langmuir isotherm, whereas the granular anaerobic sludge data fit a linear Freundlich isotherm.

The removal of PFOS by ADS is poor compared to removal by anaerobic granular sludge. Although, at treated effluent concentrations lower than 9 mg PFOS/l, the affinities of ADS sludge and anaerobic granular sludge for PFOS are comparable. The former sludge is estimated to become saturated when the equilibrium concentration of PFOS in the aqueous phase is higher than 14 mg/l, whereas anaerobic granular sludge shows a linear correlation between the sorbed PFOS concentration and all studied equilibrium concentrations in solution

PFOS adsorbed significantly to anaerobic granular sludge, poorly to ADS sludge and it did not adsorb to RAS. Similar adsorptive behavior should be expected for ADS and anaerobic granular sludge, which showed comparable VSS content, if partitioning of PFOS onto the biomass was only governed by the amount of organic matter in the sludge. The very different adsorptive capacities determined suggest that characteristics other than organic matter content must contribute to controlling sorption of the perfluoroalkyl sulfonate to wastewater treatment sludge. Given the dual lipophilic-hydrophobic nature of PFOS, it is unlikely that they obey simple hydrophobic partitioning paradigms. In humans, PFOS and related PFCs appear to associate with proteins rather than lipid



moieties (Jones *et al.*, 2003).

**Table 1.** Langmuir isotherm constants  $a$  (mg PFOS/g sludge-VSS) and  $b$  (l/mg PFOS) and Freundlich isotherm constants  $K_f [(mg\ PFOS/g\ sludge-VSS)(mg\ PFOS/l)^{-n}]$  and  $n$  for the adsorption of PFOS from aqueous solutions onto wastewater treatment sludge.

Sludge	Langmuir isotherm			Freundlich isotherm		
	$a$	$b$	$r^2$	$K_f$	$n$	$r^2$
Anaerobic granular sludge	-181.7	-0.003	0.430	0.5	1.080	0.983
ADS sludge	9.0	0.115	1.000	2.7	0.262	0.930

### ACKNOWLEDGEMENTS

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