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Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge

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Perfluorochemicals (PFCs) are the subject of increasingly intense environmental research. Despite their detection both in biota and in aqueous systems, little attention has been paid to the possible presence of this class of compounds in solid environmental matrixes. The limited available data indicate that some PFCs such as perfluorooctane sulfonate (PFOS) may strongly sorb to solids, and sewage sludge is widely suspected as a major sink of PFCs entering municipal waste streams. A quantitative analytical method was developed that consists of liquid solvent extraction of the analytes from sediments and sludge, cleanup via solid-phase extraction, and injection of the extracts with internal standards into a high-performance liquid chromatography (HPLC) system coupled to a tandem mass spectrometer (LC/MS/MS). The limits of detections of the method were analyte and matrix dependent, but ranged from 0.7 to 2.2 ng/g and 0.041 to 0.246 ng/g (dry weight) for sludge and sediment, respectively. A demonstration of the method was performed by conducting a limited survey of domestic sludge and sediments. The concentration of PFCs in domestic sludge ranged from 5 to 152 ng/g for total perfluorocarboxylates and 55 to 3370 ng/g for total perfluoroalkyl sulfonyl-based chemicals. Data from a survey of San Francisco Bay Area sediments suggest widespread occurrence of PFCs in sediments at the low ng/g to sub-ng/g level. Furthermore, substances that may be transformed to PFOS, such as 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) and 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA), are present in both sediments and sludge at levels often exceeding PFOS.

Introduction

Produced and used widely over the last half-century, perfluorochemicals (PFCs) are being detected in wildlife (*1*−*4*) and humans (*5*−*8*) around the globe. These compounds and their derivatives (Figure 1) have been used in a wide variety of industrial, commercial, and consumer applications, including coatings for textiles and paper packaging products (*9*), fire fighting foams (*10*), insecticides (*11*), and as polymerization aids in the manufacturing of fluoropolymers (*12*). Some PFCs are extremely resistant to biological and chemical degradation (*13*) and many exhibit toxicological effects in laboratory animals (*14*). Despite a recent voluntary phase-out of one perfluoroalkyl sulfonyl-based product line (*15*), some PFCs such as perfluorooctanoic acid (PFOA) are still in use, and degradation of fluorotelomer alcohols (FTOHs) may provide an additional source of PFOA and related chemicals (*16, 17*). Although a preliminary understanding of the global dissemination of PFCs is beginning to emerge (*18*), much less is known about the ultimate environmental fate and cycling of this emerging class of chemical contaminants. In particular, very little is known about the potential for sorption of these chemicals to environmental solids. If PFCs do strongly sorb to solids, this may have important implications with respect to long-term retention and release of these chemicals to the environment.

The important role of sediments in the environmental fate of hydrophobic organic contaminants has long been recognized (*19*). Hydrophobic contaminants such as polychlorinated biphenyls (PCBs) are expected to partition from the water column into organic-matter-rich sediments. The sorption of linear alkylbenzene sulfonate surfactants, which exhibit both hydrophobic and hydrophilic functionalities, has been reported for sediments (*20*), yet it is unknown whether the factors controlling the sorption of these surfactants also govern the sorption of anionic PFCs to environmental solids. Given that within organisms, some PFCs appear to associate with specific proteins rather than accumulate in the lipids (*21*), and that PFCs exhibit both hydrophobic and lipophobic characteristics, it is unlikely that a simple hydrophobic partitioning paradigm is applicable to this class of chemicals. Some investigators report minimal losses of PFOS and PFOA in rivers due to volatilization or sorption to sediments (*22*), while other data suggest sorption of PFOS to sediments and sludge (*23*). Additional studies of aquatic foodwebs indicate different PFC profiles in benthic-dwelling organisms as compared to organisms with limited sediment exposures (*2, 24*), and elevated levels of PFCs such as PFOS for organisms linked to inshore, benthic foodwebs as opposed to offshore, pelagic foodwebs (*25*). However, before an accurate conceptual model of the movement of PFCs into aquatic foodwebs can be developed, the relative importance of sediments as a potential source of PFCs to the foodweb must be evaluated.

Two major suspected sources of PFCs to the natural environment are releases through aqueous industrial and residential wastestreams. Whereas the former is well-documented for a fluorochemical manufacturing facility (*22*), to date, evidence of the latter is limited to a small subset of PFCs (*26*). However, determining the levels of PFCs present in the effluents of industrial or municipal wastewater treatment plants (WWTPs) only reveals the potential for direct releases to receiving water bodies and does not account for releases from the solid wastes (biosolids) co-generated at these plants. For strongly sorbing chemicals, the sludge produced by a WWTP may contain high concentrations and constitute the dominant mass flow through the plant. For persistent and toxic chemicals, the disposal of biosolids results in potential human and ecological risks, particularly if the biosolids are land-applied (*27*). Data collected by 3M Co. indicate the presence of PFOS in nearly all WWTP biosolids sampled (*26*), while others did not detect PFOS or other PFCs in sludge (*28*).

To date, the majority of analyses of PFCs in nonaqueous media such as biota rely on ion-pair extraction (*1, 6, 29*).

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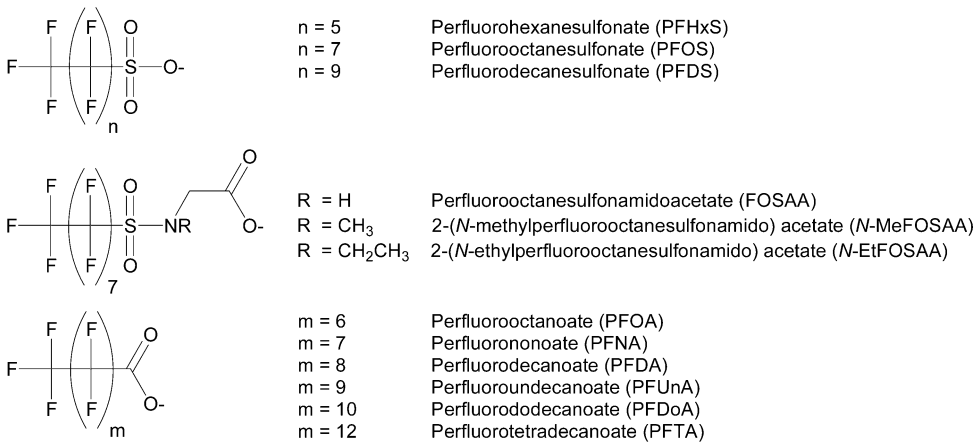

FIGURE 1. Perfluorochemicals detected in sediments and sludge.

This extraction procedure is suitable for analysis of relatively homogeneous matrixes such as serum and biological tissue and it is most often employed when quantitation is based on extractions of standards spiked into samples similar to those of interest. In such cases, calibration curves based on extractions from a similar sample matrix not only account for the method's potential losses of analyte (due to poor extraction and/or recovery during cleanup), but also account for any ionization effects (e.g., ion suppression) that may affect the accuracy of the LC/MS/MS analysis. For this reason, investigators attempt to match the sample matrix as closely as possible with a similar matrix (e.g., using calf serum to quantify PFCs in human sera) (*8*). For heterogeneous matrixes such as sludge and sediment, this matrix-matched calibration curve approach is limited by the variability in the quantity and composition of the organic material present in the samples. This material, when extracted, can lead to differing degrees of ion suppression from sample to sample (unpublished data).

The goal of this study was to develop an analytical method to detect and accurately quantify anionic PFCs in sediments and sewage sludge, and to demonstrate the method's applicability by conducting limited surveys of these media. An extraction and cleanup method consisting of liquid solvent extraction followed by cleanup and concentration via solid phase extraction was developed for the analysis of anionic PFCs in sediments and sludge. This method, which does not rely on matrix-matched calibration curves, is both broadly applicable and sensitive for the determination of PFCs in sediments and sewage sludge.

Experimental Section

Standards and Reagents. Standards of perfluorooctanoic acid (PFOA, 96%), perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUnA, 95%), perfluorododecanoic acid (PFDoA, 95%), perfluorotetradecanoic acid (PFTA, 97%), and ammonium perfluorodecanesulfonate (PFDS, 25%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Perfluorononanoic acid (PFNA, 97%) and potassium perfluorooctanesulfonate (PFOS, 98%) were purchased from Fluka through Sigma-Aldrich (St. Louis, MO). The potassium salt of perfluorohexanesulfonate (PFHxS, 97%) as well as 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA, 54%), 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA, 100%), and perfluorooctanesulfonamidoacetate (FOSAA, 99.6%) were provided by 3M Co. (St. Paul, MN). The internal standards perfluoro(2-ethoxyethane)-sulfonic acid (PFEES, 97%), [1,2-$^{13}C_2$]perfluorooctanoic acid ([$^{13}C_2$]PFOA, 97.5%), and 2-perfluorooctyl[1,2-$^{13}C_2$]ethanoic acid (MFOEA, 98%) were purchased from Oakwood Research Chemicals (West Columbia, SC), Perkin-Elmer Life Sciences (Boston, MA), and Wellington Laboratories (Guelph, ON), respectively. Optima grade methanol was purchased from Fisher Scientific (Pittsburgh, PA), ammonium hydroxide was obtained from Sigma-Aldrich, and ammonium acetate and glacial acetic acid were from Mallinckrodt (Phillipsburg, NJ). Standard Reference Material 2781 (Domestic Sludge) was purchased from the National Institute of Standards and Technology (Gaithersburg, MD), and was used as received.

FIGURE 2. Locations of San Francisco Bay Area sampling sites.

Sample Collection and Preparation. In March 2004, surficial sediments (top 1−5 cm) from the outlets of various rivers and creeks in the San Francisco Bay Area (Figure 2) were collected in duplicate in 50-mL polypropylene tubes and were stored on ice for transport to the laboratory. Additional sediments from the Palo Alto Mudflats and Hayward, CA, as well as those from Baltimore, MD and Corvallis, OR, were collected between April of 2002 and June 2004. Upon arrival at the laboratory, samples were frozen (−15 °C) until extraction. Digested sludge samples from eight WWTPs and primary settled solids from three WWTPs were collected from February 1998 through June 2004 in polypropylene jars or bottles and were also transported on ice and frozen (−15 °C) until analysis. All WWTPs included in this study received at least 50% domestic waste. Additional information regarding the WWTPs included in this study is available as Supporting Information. Prior to extraction, all samples were thawed to room temperature and air-dried.

Sediment samples were ground and homogenized with a mortar and pestle; sludge samples were ground and homogenized in a solvent-rinsed coffee grinder. When necessary, air-dry sediments were passed through a 2.36-mm sieve to remove pebbles and debris. The air-dry to oven-dry mass conversion factors were measured in triplicate for each sediment and sludge after drying aliquots of the sediment and sludge overnight at 105 °C and 103 °C, respectively.

Sample Extraction. A simple and efficient extraction method was developed allowing for quantitative recovery of anionic PFCs from sediments and sludges. The method employed an acetic acid wash followed by repeated extractions of the acidified sediment using a solvent mixture of 90:10 (v/v) methanol and 1% acetic acid in Milli-Q water (MilliPore, Billerica, MA). The wash and extractions were performed in a heated (60 °C) sonication bath (Branson 2510 ultrasonic cleaner; Danbury, CT). Homogenized, air-dried sediment (1 g) was transferred to a 50-mL polypropylene vial, to which 10 mL of a 1% acetic acid solution was added. Each vial was vortexed, placed in the preheated sonication bath, and sonicated for 15 min. After sonication, the vials were removed from the heated bath, centrifuged at 3000 rpm (1500 relative centrifugal force) for 2 min, and the acetic acid solution was decanted into a second 50-mL polypropylene vial. An aliquot of the methanol/acetic acid extraction solvent mixture (2.5 mL) was then added to the original vial and the vial was again vortexed and sonicated for 15 min at 60 °C before centrifuging and decanting the extract. This process of acetic acid washing followed by methanol/acetic acid extraction was repeated, and a final 10-mL acetic acid wash was performed. For each sample, all washes and extracts were combined. Sludge was extracted using the same procedures with a few minor modifications: 100 mg of homogenized air-dry sludge was extracted in three sequential wash/extraction cycles and each cycle consisted of a 7.5-mL 1% acetic acid wash followed by 1.7 mL of methanol/acetic acid extraction solvent. In addition, sludge samples were centrifuged for 10 min before decanting. To reduce solid phase extraction (SPE) cartridge clogging during the subsequent cleanup step, the final vials containing sludge extracts and washes were centrifuged an additional 1 h. For both sediments and sludge, the total volume of extract and washes was approximately 35 mL.

Sample Cleanup. To concentrate the extracts and to remove the acetic acid, salts, and potential matrix interferences, each sediment and sludge extract was passed through a 500-mg C18 SPE cartridge (Alltech Associates; Deerfield, IL). Each cartridge was first conditioned with 10 mL of methanol followed by 10 mL of 1% acetic acid. The samples were then loaded at a flow rate of 1−2 mL/min onto SPE cartridges that were mounted on a vacuum manifold. After loading, the SPE cartridges were rinsed with 10 mL of Milli-Q water before being allowed to dry under vacuum for at least 2 h prior to elution. PFCs were eluted from the cartridge with 4 mL of methanol and collected in 1:1 (v/v) methanol/acetone-washed graduated glass 15-mL tubes. The eluent was concentrated under nitrogen to 2 mL and transferred to 10-mL glass vials. The graduated glass tube was then rinsed with 800 μL of methanol. After combining the rinse with the eluent, an additional 1200 μL of 0.01% aqueous ammonium hydroxide solution was added. To reduce matrix interferences and bring the samples into the appropriate range for LC/MS/MS analysis, sludge extracts were further diluted to 10 mL by adding 6 mL of a 70:30 (v/v) methanol/ aqueous ammonium hydroxide (0.01%) solution. The extracts were then stored at 4 °C until analysis. Immediately prior to LC/MS/MS analysis, a 500-μL aliquot of extract was transferred to a 2-mL glass autosampler vial, and 50 μL of 20−50 ng/mL aqueous internal standard mixture containing PFEES, [$^{13}C_2$]-PFOA, and MFOEA was added.

Determination of Method Accuracy and Precision. The accuracy of the method was evaluated using sequential extraction experiments, standard additions, and spike/recovery experiments. Each experiment was performed to evaluate different components of the method's accuracy. First, to evaluate whether the method's extraction procedure was capable of completely removing the analyte from the solid matrixes, sequential extraction experiments were performed. Sequential (exhaustive) extractions of both unspiked (native) sludge and sediment spiked at 10 ng/g and aged for 60 days were conducted by extracting these samples and analyzing each extraction step separately. The sequential extraction profiles generated were then used to determine whether the concentrations of PFCs present in the extract accurately reflected the concentrations present on the environmental solids.

To determine the accuracy of the LC/MS/MS analysis step, standard addition experiments were performed for a subset of sediments and sludges. Because these experiments were performed with cleaned-up sample extract, they only reflect the accuracy of the LC/MS/MS analysis step and account for any matrix-induced ion suppression or enhancement. Standard additions were performed by removing three to five 900-μL aliquots of each cleaned-up sample extract and adding 100 μL of standard (with increasing concentrations of analyte) to each aliquot immediately prior to LC/MS/MS analysis. By dividing the intercept of the resulting standard addition curve by the slope, the concentration of analyte present in the unspiked extract was determined. These values were then compared to the concentrations determined using the internal standard-normalized calibration curves. Though full standard addition experiments were only performed for a subset of samples, single-point standard additions (hereafter referred to as extract spikes) were performed for all samples. Preparing extract spikes for all samples is particularly important when the extracted matrix is expected to vary significantly from sample to sample. These extract spikes were prepared by adding 100 μL of standard to 900 μL of extract, and then calculating the recovery of the spike after correcting for the concentration present in the unspiked extract (as determined using an internal standard-normalized calibration curve).

To evaluate the accuracy of the method as a whole, spike/recovery experiments were performed for sediment, digested sludge, and primary sludge. For sediments, the recovery of analyte spiked at 10 ng/g onto dried sediments immediately prior to extraction (extraction spike/recovery) was determined. Extraction spike/recovery experiments with primary and digested sludges used spikes ranging from 100 to 1000 ng/g. The effect of aging the sediments was evaluated by spiking analyte (at 10 ng/g) onto dried sediment reconstituted in Milli-Q water and aging the spiked sediment for 60 days prior to drying and extraction. Aging experiments were not conducted for sludge. All extraction recoveries determined for both sediments and sludges accounted for the presence of some PFCs detected in the unspiked sediment and sludge. Finally, the precision of the entire method was determined by extracting and analyzing each sludge and sediment sample in triplicate, and calculating the relative standard deviation (RSD) of the analyses.

Analysis of PFCs via HPLC/MS/MS. Extracts were analyzed via LC/MS/MS under conditions similar to those previously reported (*22*). Chromatography was performed using an aqueous ammonium acetate (2 mM) and methanol gradient delivered at a flow rate of 250 μL/min by a Shimadzu LC system (LC10ADvp pumps controlled by an SCL10Avp controller, Columbia, MD). Samples and standards were injected (20 μL) by a Shimadzu SIL10ADvp autosampler onto a 40 mm × 2.1 mm Targa Sprite C18 column (5-μm pore size, Higgins Analytical, Mountain View, CA) equipped with a C18

TABLE 1. Mass Transitions Monitored and Method Validation Parameters

analyte	transition monitored (*m/z*) (primary)[a] (secondary)[b]	Sediment Method Validation Parameters: % recovery (SD) of extraction spike[c]	% recovery (SD) of aged spike[c,d]	sediment LOD (ng/g)[e]	Sludge Method Validation Parameters: % recovery (SD) from digested sludge[f]	% recovery (SD) from primary sludge[f]	estimated sludge LOD (ng/g)[g]
PFHxS	(399>99) (399>80)	85 (2)	56 (6)	0.041	79 (2)	37 (5)	2.2
PFOS	(499>99) (499>80)	81 (7)	87 (2)	0.109	87 (3)	79 (2)	0.9
PFDS	(599>99) (599>80)	79 (3)	79 (2)	0.042	63 (2)	76 (2)	1.0
FOSAA	(556>498) (556>78)	78 (3)	93 (6)	0.107	83 (3)	88 (1)	1.1
N-MeFOSAA	(570>419) (570>483)	73 (2)	72 (5)	0.122	77 (3)	72 (4)	0.8
N-EtFOSAA	(584>419) (584>526)	73 (3)	69 (1)	0.109	72 (3)	82 (2)	0.6
PFOA	(413>369) (413>169)	94 (4)	88 (1)	0.011	80 (2)	71 (3)	1.0
PFNA	(463>419) (463>219)	98 (3)	88 (1)	0.054	91 (2)	98 (4)	1.9
PFDA	(513>469) (513>219)	94 (2)	89 (1)	0.049	82 (1)	88 (2)	0.7
PFUnA	(563>519) (563>269)	82 (1)	83 (1)	0.246	72 (3)	86 (5)	2.1
PFDoA	(613>569) (613>319)	80 (2)	61 (2)	0.170	46 (2)	53 (2)	1.4
PFTA	(713>669) (713>169)	74 (2)	69 (1)	0.088	41 (3)	62 (3)	0.6

[a] Used for quantitation. [b] Used for confirmation. [c] Recoveries based on four replicate analyses spiked at 10 ng/g. [d] Sediments aged for 60 days prior to extraction. [e] Based on nine replicate analyses. [f] Recoveries based on four replicate analyses spiked at 100−1000 ng/g. [g] Based on seven replicate analyses.

Guard Column (Higgins Analytical). Initial eluent conditions were 5% methanol. The percent methanol was increased to 60% at 0.75 min, ramped to 100% over 10 min, held at 100% for 1.5 min, and reverted to 5% at 12.5 min.

A Sciex API 3000 triple quadrupole mass spectrometer (MDS Sciex, Ontario) operating in negative electrospray ionization multiple reaction monitoring (MRM) mode was employed for sample analysis. Two MRM transitions (Table 1) were acquired for all analytes and a dwell time of 80 ms was used for each transition. To maintain adequate peak resolution and monitor two transitions for each analyte without loss of sensitivity, each sample was injected twice, with data collected for the perfluorocarboxylates (PFCAs) and the perfluoroalkyl sulfonyl-based chemicals (PFASs) separately. Optimal instrumental source parameters were determined and are as follows: ionspray voltage −2800 V, curtain gas flow 8 arbitrary units (au), nebulizer gas flow 14 au, turbo gas flow 8 au, collision gas flow 12 au, and source temperature 425 °C. Zero air provided by a Parker-Balston 76-818 Zero Air Generator (Haverhill, MA) was used for the nebulizer and drier gas, and nitrogen (provided by a Parker-Balston N2-4000 generator) was used as the curtain and collision gas.

Quantitation and Confirmation. For all analytes, quantitation was performed using an inverse weighted ($1/X$) internal standard calibration curve with calibration standards prepared in 70:30 methanol/aqueous ammonium hydroxide (0.01%). A mixed stock standard solution was prepared containing all analytes and this solution was corrected for standard purities (values expressed reflect the anionic species of each analyte). An 8−12 point calibration curve spanning the 0.01−50 pg/μL range was performed at the beginning and end of every sample batch. Solvent blanks used to monitor instrument background and calibration verification standards used to monitor the validity of the calibration during the sample run were run after every six sediment samples and after every four sludge samples. For each analyte, all active points in the calibration curve were calculated to be within 30% of their actual values and the coefficient of determination (R^2) was greater than 0.99 for all calibration curves. In addition, calibration verification standards during the sample runs were consistently within 20% of the expected values. The internal standards selected for this study were PFEES, [$^{13}C_2$]PFOA, and MFOEA and were analyte-dependent: PFEES was selected for PFHxS, PFOS, and PFDS; [$^{13}C_2$]-PFOA was selected for the PFCAs; and MFOEA was selected for FOSAA, *N*-MeFOSAA, and *N*-EtFOSAA. Confirmation was performed by quantitating on both transitions for each analyte (Table 1). For samples where both transitions were above the limits of quantitation, the calculated values from the two transitions were in very good agreement (average ratio of 1.00, range of 0.71 to 1.36).

Determination of Limits of Detection and Quantitation. For sediments, the limit of detection (LOD) for each analyte was calculated from nine replicate spikes using the procedure outlined in 40 CFR 136 Appendix B. The LOD, defined as the mass of analyte needed to yield a signal-to-noise (S/N) ratio of 3:1 when added to blank sediment extract, where the noise is calculated as 3× the standard deviation of the background signal. For sludges, the inability to identify blank samples for each analyte required the LODs to be estimated from seven replicate analyses of a low-concentration sample fortified with PFHxS, FOSAA, PFUnA, PFDoA, and PFTA, which were found to be in low abundance in this sample. The relative standard deviations (RSDs) from these replicate analyses were then applied to the mass of analyte in a standard needed to produce a S/N ratio between 5 and 20, and the corresponding sludge concentration was calculated. For both sediments and sludge, the limit of quantitation (LOQ) was defined as the higher of either the concentration in a standard yielding a S/N ratio of 10:1 or the lowest calibration standard calculated to be within 30% of its actual value (typically 0.04−

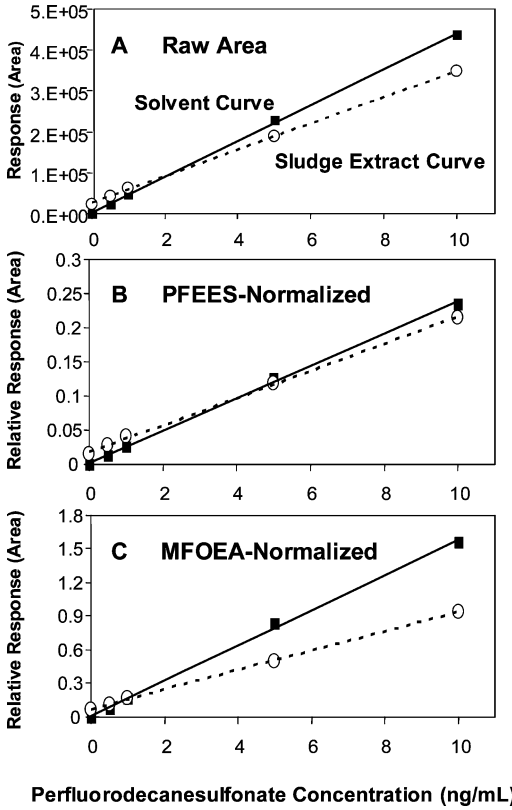

FIGURE 3. Appropriate selection of internal standards for perfluorodecane sulfonate (PFDS). PFDS was spiked into clean solvent (■, solid lines) and into digested sludge extract (○, dashed lines). (A) Absolute response for PFDS, (B) perfluor (2-theoxyethane)sulfonic acid (PFEES)-normalized PFDS response, and (C) 2-perfluorooctyl-[1,2-$^{13}C_2$]ethanoic acid (MFOEA)-normalized response.

0.4 ng/g for sediment and 1−10 ng/g for sludge). In addition, for certain problem analytes routinely detected as instrument background, such as PFOA, the LOQ was required to produce a signal with at least twice the area of the highest solvent blank (typically less than the 0.025 pg/μL calibration standard for PFOA). Mean sample responses ($n = 3$) corresponding to concentrations less than the calculated sediment LODs and estimated sludge LODs were reported as nondetections (n.d.), whereas concentrations above the LODs but less than the LOQs were reported as less than the LOQ (i.e., <3 ng/g). For calculation of multiple sample means and total concentrations, all nondetections were treated as zero and all concentrations greater than the LOD but less than the LOQ were arbitrarily given a value of the LOD or one-half the LOQ, whichever was greater.

Results and Discussion

Matrix Interferences and Selection of Internal Standards. As noted previously (*30*) and as confirmed in this study, the analysis of complex environmental samples such as sediment and sludge by electrospray LC/MS/MS can be significantly hampered by ionization effects induced by coeluting components present in the sample extracts. Therefore, it was necessary to evaluate these matrix interferences and confirm that the internal standards selected for this study were appropriate. Standard addition curves built in the extract of interest were compared to calibration curves constructed in the solvent, as illustrated in Figure 3. To evaluate signal suppression, the slope of the extract curve was then compared to the slope of the solvent curve, and the extent of signal suppression (or enhancement) was evaluated. Signal suppression results in the slope of the extract curve being smaller than that of the solvent curve (Figure 3A), while appropriately selected internal standards can partially correct for this suppression (Figure 3B). Extract spikes were also used to evaluate the appropriateness of the internal standards selected. For example, the low average extract spike recovery for PFDoA (65%) relative to PFOA (97%) in sludge extract suggests that [$^{13}C_2$]PFOA was not as suitable an internal standard for some of the longer chain carboxylates which eluted significantly later, as shown in Figure 4. PFEES functioned extremely well as an internal standard for PFHxS, PFOS, and PFDS despite large differences in retention times (Figures 3B and 4), while MFOEA, which eluted much closer to PFDS than PFEES, did not function well as an internal standard for PFDS (Figure 3C), as evidenced by the relative slopes of internal standard-normalized calibration curves when compared to the solvent curves. MFOEA functioned relatively well for FOSAA, *N*-MeFOSAA, and *N*-EtFOSAA as evidenced by average extract spike recoveries of 94, 88, and 94% for sludge, respectively. These data indicate that chemical similarities influencing the ionization process as well as elution time may be important when choosing internal standards for this particular class of compounds.

Method Accuracy and Precision. Sequential extraction experiments of both aged sediment and native sludge indicated that only two and three extractions were necessary to extract >95% of the total mass of the analytes from sediment and sludge, respectively (Figure 5). In addition, the concentrations estimated via standard addition for a subset of sediments and sludge (data not shown) were in good agreement with concentrations determined using the internal standard-normalized calibration curve. For example, the concentrations of PFOS and *N*-EtFOSAA in WWTP 11 DS were 486 ng/g and 329 ng/g, respectively, when determined using standard additions, and 444 ng/g and 335 ng/g, when determined using the internal standard-normalized calibration curves. Extract spikes, which provided an indication as to the accuracy of the LC/MS/MS analysis for each sample, were consistently greater than 70% for nearly all analytes in both sediments and sludges (data not shown). As discussed previously, the major exceptions were the longer chain carboxylates such as PFDoA and PFTA, which tended to show lower extract spike recoveries. Sediment extracts generally showed more consistent matrix effects, with average extract spike recoveries (for all sediment samples) ranging from a low of 86% (±13% SD) for PFTA to a high of 99% (±8% SD) for PFNA. In sludge, these recoveries ranged from 65% (±17% SD) to 109% (±14% SD) for PFDoA and PFOS, respectively (data not shown). Sediment extracts for which multiple analytes had extract spike recoveries less than 70% were diluted (2-fold) and reanalyzed. This dilution step yielded marginal improvements in extract spike recoveries, suggesting that substantial dilutions (i.e., 10-fold) would be necessary to significantly reduce matrix interferences. Further dilutions were not performed for sludge extracts, as the concentrations observed for the analytes with substantial ion suppression (i.e., PFDoA, PFTA) were already near the limits of quantitation.

Recoveries of the method as a whole ranged from 73 to 98% and 56 to 93% for dry sediment spiked immediately prior to extraction and reconstituted wet sediment spiked before aging for 60 days, respectively (Table 1). Analyte losses may have occurred due to inefficient extraction from the environmental solids, insufficient retention and/or elution during the SPE cleanup, and suppression of signal due to matrix interferences during LC/MS/MS analysis. Previous attempts to extract shorter chain PFCs from aqueous matrixes via C18 SPE have demonstrated poor recoveries of these analytes, even from purely aqueous systems (*31*). Thus, insufficient retention during the SPE cleanup is likely responsible for the low recoveries of two analytes not included in this study: perfluoroheptanoic acid (PFHepA) which

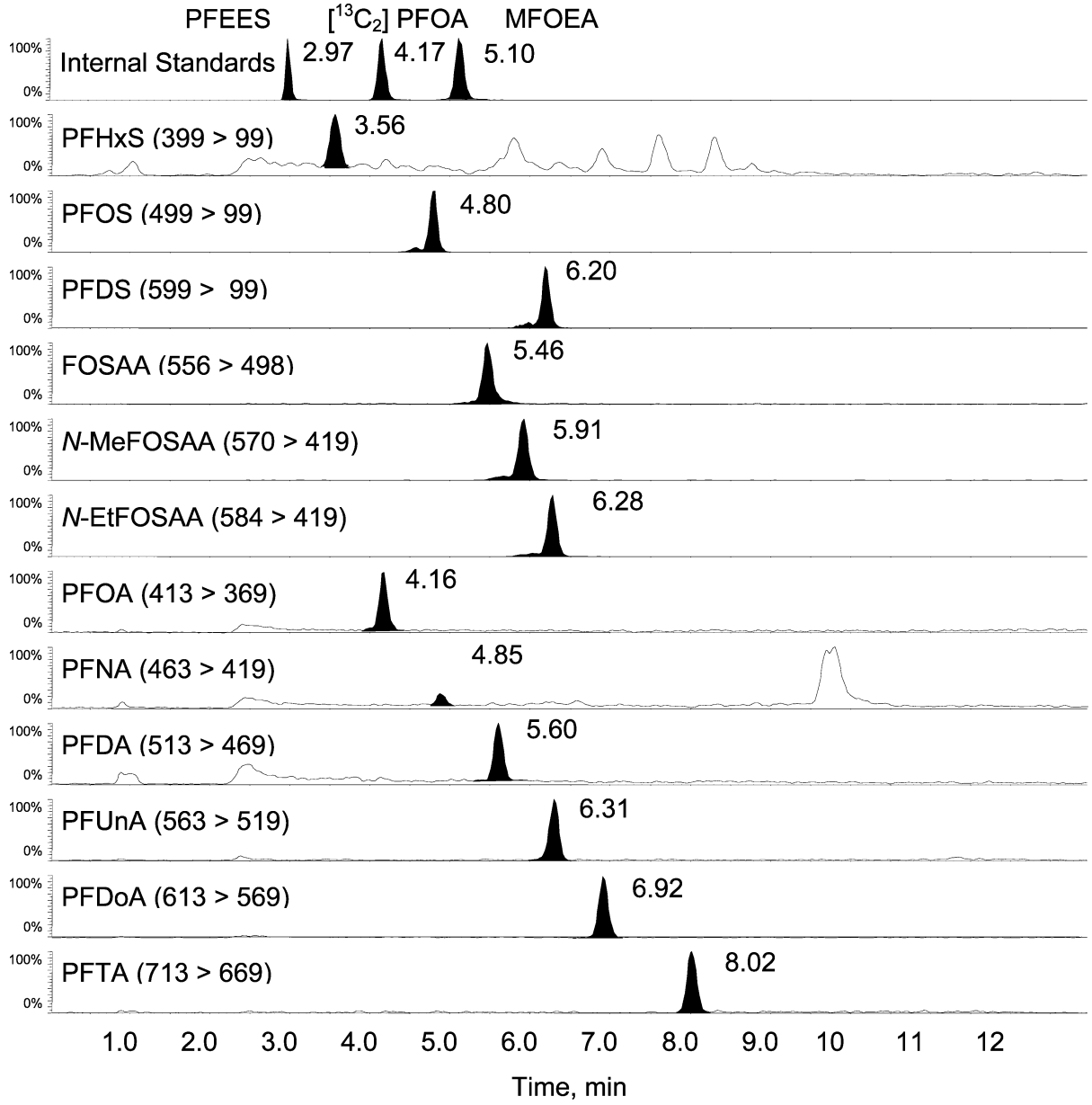

FIGURE 4. Typical chromatogram for sludge extract containing PFCs (WWTP 1 DS1).

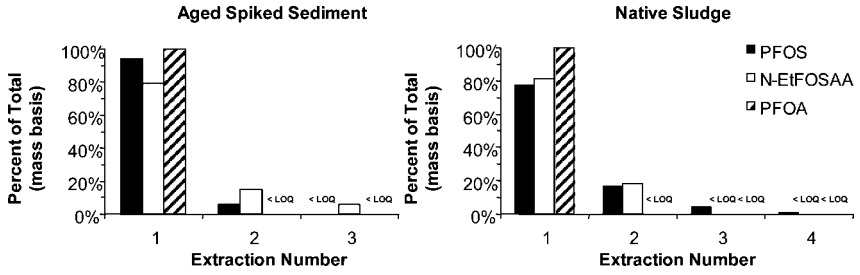

FIGURE 5. Sequential extraction profiles of sludge and sediment for example analytes. Sediments were spiked to 10 ng/g and aged for 60 days prior to extraction. Percentages listed are the average of duplicate sediment extractions. Native sludge (WWTP 1 DS1) contained approximately 2610, 235, and 5.56 ng/g of PFOS, *N*-EtFOSAA, and PFOA, respectively. Note that the method described in this study included two extractions for sediment and three extractions for sludge, which recovered analytes to below the limit of quantitation (LOQ).

demonstrated very low recovery (~20%), and perfluorobutane sulfonate (PFBS) which was entirely lost. Recoveries of analyte spiked onto digested and primary sludge immediately prior to extraction were generally good, with greater than 70% recovery for most analytes (Table 1). Method precision was analyte and matrix dependent, but was generally good with 81% of quantifiable sludge samples and 68% of quantifiable sediment samples having relative standard deviations less than 20% for triplicate analyses (Tables 2 and 3).

Potential Method Limitation. Despite the fact that extract spikes were performed for each sample, the concentrations listed in Tables 2 and 3 were not corrected for the recovery of the extract spikes. Such corrections, while potentially increasing the accuracy of the values reported, would have

TABLE 2. Concentrations (ng/g) of PFCs in Sludge[a]

sample[b]	PFHxS	PFOS	PFDS	FOSAA	*N*-MeFOSAA	*N*-EtFOSAA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	ΣPFAS[c]	ΣPFOS[d]	ΣPFCA[e]	ΣPFC	ΣPFOS ΣPFCA
WWTP 1 DS1	3.18 (60)	2610 (1)	426 (1)	14.5 (10)	79.4 (11)	235 (3)	5.56 (28)	n.d.	2.52 (10)	5.38 (41)	5.64 (16)	<3	3370	2900	21	3390	140
WWTP 1 DS2	n.d.	167 (12)	91.0 (2)	7.19 (11)	108 (3)	78.8 (3)	<11	6.94 (12)	4.36 (2)	n.d.	4.81 (5)	<3	452	335	23	474	15
WWTP 2 DS	n.d.	139 (4)	31.9 (5)	<6	47.6 (13)	61.3 (1)	<6	<3	4.55 (3)	7.07 (39)	3.93 (24)	<3	283	236	22	305	11
WWTP 6 ADS	n.d.	62.8 (9)	27.1 (7)	26.9 (6)	154 (1)	179 (1)	29.4 (4)	4.39 (12)	72.6 (7)	<11	32.7 (4)	7.77 (7)	450	375	152	602	2.5
WWTP 7 DS	n.d.	14.4 (10)	24.4 (8)	5.25 (25)	43.0 (3)	76.4 (2)	<11	n.d.	7.43 (12)	n.d.	n.d.	n.d.	163	122	13	176	9.4
WWTP 8 DS	n.d.	77.3 (5)	38.7 (16)	3.32 (17)	68.6 (9)	109 (7)	<11	n.d.	7.81 (10)	n.d.	<3	n.d.	297	234	15	312	16
WWTP 10 DS	n.d.	66.6 (6)	79.0 (4)	<3	30.9 (5)	80.2 (7)	n.d.	n.d.	4.58 (6)	n.d.	n.d.	n.d.	258	164	5	263	33
WWTP 11 DS	n.d.	444 (7)	58.4 (6)	62.1 (7)	126 (3)	335 (6)	8.22 (13)	3.25 (36)	10.5 (13)	7.87 (17)	6.51 (13)	<3	1030	895	38	1070	24
WWTP 12 DS	n.d.	22.6 (11)	29.4 (3)	6.20 (40)	56.9 (15)	151 (4)	13.3 (19)	n.d.	4.33 (9)	6.93 (38)	3.85 (29)	<3	266	207	30	296	6.9
SRM 2781[f]	n.d.	251 (5)	350 (2)	9.79 (49)	87.4 (11)	544 (2)	10.8 (5)	n.d.	4.84 (1)	8.58 (14)	3.49 (34)	<3	1240	801	29	1270	28
WWTP 1 PS2	n.d.	28.9 (6)	17.3 (16)	n.d.	<6	<11	5.20 (57)	10.3 (96)	<3	n.d.	n.d.	n.d.	55	36	17	73	2.1
WWTP 5 PS	<3	38.2 (20)	11.0 (18)	n.d.	<6	34.4 (10)	6.30 (12)	n.d.	<3	n.d.	n.d.	<3	89	70	9	97	7.8
WWTP 12 PS	n.d.	30.9 (12)	n.d.	<6	<26	21.3 (11)	n.d.	n.d.	1.16 (47)	5.34 (67)	<3	<3	68	63	10	78	6.3

[a] Values in parentheses are % relative standard deviations (RSDs; $n = 3$). Concentrations are mass analyte per unit mass oven-dry sludge. n.d. = not detected. [b] DS denotes anaerobically digested sludge, PS denotes primary sludge. ADS denotes sludge treated using autothermal thermophilic aerobic digestion. [c] Total of [PFHxS] + [PFOS] + [PFDS] + [FOSAA] + [*N*-MeFOSAA] + [*N*-EtFOSAA]. [d] Total of [PFOS] + [FOSAA]×499/556 + [*N*-MeFOSAA]×499/570 + [*N*-EtFOSAA]×499/584. [e] Total of [PFOA] + [PFNA] + [PFDA] + [PFUnA] + [PFDoA] + [PFTA]. [f] Standard Reference Material 2781, National Institute of Standards and Technology "Domestic Sludge," originating from Denver, CO. Collected September 1990.

TABLE 3. Concentrations (ng/g) of PFCs in Sediments[a]

site	PFHxS	PFOS	PFDS	FOSAA	*N*-MeFOSAA	*N*-EtFOSAA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	ΣPFAS[b]	ΣPFOS[c]	ΣPFCA[d]	ΣPFC	ΣPFOS ΣPFCA
Bolinas Lagoon	n.d.	0.379 (31)	n.d.	0.121 (20)	0.373 (34)	n.d.	0.290 (13)	n.d.	0.204 (12)	n.d.	0.227 (26)	0.160 (8)	0.873	0.811	0.881	1.75	0.9
Hayward Marsh	<0.2	1.72 (3)	<0.4	n.d.	0.125 (23)	0.307 (19)	0.625 (19)	n.d.	0.335 (26)	n.d.	n.d.	0.309 (30)	2.45	2.09	1.27	3.72	1.7
Kirby Park	<0.2	0.201 (8)	n.d.	n.d.	n.d.	n.d.	<0.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.301	0.201	0.050	0.351	4.0
Lagunitas Creek	n.d.	n.d.	n.d.	0.153 (14)	0.199 (30)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.352	0.312	0.000	0.352	n.c.
Palo Alto Mudflats	n.d.	1.47 (3)	0.279 (9)	n.d.	0.199 (23)	0.765 (6)	0.136 (8)	n.d.	0.084 (6)	n.d.	n.d.	n.d.	2.71	2.30	0.220	2.93	10.5
Petaluma River	n.d.	1.24 (2)	0.158 (5)	<0.12	0.327 (44)	0.340 (5)	0.229 (27)	<0.12	0.162 (9)	n.d.	n.d.	n.d.	2.17	1.92	0.451	2.62	4.2
Salinas River	n.d.	1.30 (3)	1.47 (4)	0.289 (4)	1.04 (6)	1.43 (2)	0.168 (10)	<0.12	0.240 (7)	n.d.	0.365 (6)	0.151 (11)	5.53	3.69	0.984	6.51	3.8
San Francisquito Creek	n.d.	3.07 (3)	0.576 (3)	0.254 (0.3)	0.610 (3)	0.958 (8)	0.251 (15)	n.d.	0.220 (7)	n.d.	0.283 (18)	0.155 (11)	5.47	4.65	0.909	6.38	5.1
San Lorenzo River	n.d.	n.d.	n.d.	n.d.	0.141 (38)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.141	0.124	0.00	0.141	n.c.
San Pedro Creek	n.d.	0.248 (6)	<0.12	n.d.	0.209 (30)	n.d.	0.268 (26)	n.d.	0.199 (30)	n.d.	n.d.	<0.12	0.517	0.430	0.555	1.07	0.8
Soquel Creek	n.d.	n.d.	<0.12	n.d.	n.d.	n.d.	0.277 (12)	n.d.	0.194 (17)	n.d.	n.d.	n.d.	0.060	0.00	0.471	0.531	0.0
Waddell Creek	n.d.	n.d.	<0.12	n.d.	n.d.	n.d.	0.227 (35)	n.d.	0.156 (34)	n.d.	n.d.	n.d.	0.060	0.00	0.383	0.443	0.0
Yosemite Slough	<0.2	0.288 (26)	n.d.	n.d.	n.d.	n.d.	0.272 (28)	n.d.	0.203 (22)	n.d.	n.d.	0.435 (42)	0.388	0.288	0.910	1.30	0.3
WWTP 5 Outfall	n.d.	3.76 (5)	2.70 (3)	1.12 (2)	1.67 (31)	3.94 (2)	0.388 (10)	0.194 (3)	1.11 (3)	0.337 (3)	0.584 (5)	0.201 (6)	13.2	9.60	2.81	16.0	3.4
Baltimore Inner Harbor, MD	0.072 (24)	0.846 (3)	0.980 (9)	n.d.	0.465 (10)	1.06 (8)	0.390 (6)	0.237 (6)	0.751 (8)	0.396 (6)	0.556 (8)	0.206 (10)	3.42	2.37	2.54	5.96	0.9
Gwynn's Run, MD	n.d.	n.d.	0.202 (22)	n.d.	0.247 (45)	<0.24	0.186 (18)	n.d.	0.122 (20)	n.d.	n.d.	<0.12	0.569	0.319	0.396	0.965	0.8
Willamette River, OR	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.184 (37)	n.d.	0.144 (37)	n.d.	n.d.	n.d.	0.000	0.00	0.328	0.328	0.0

[a] Values in parentheses are % RSDs ($n = 3$). Concentrations are mass analyte per unit mass oven-dry sediment. n.d. = not detected. n.c. = not calculable. [b] Total of [PFHxS] + [PFOS] + [PFDS] + [FOSAA] + [*N*-MeFOSAA] + [*N*-EtFOSAA]. [c] Total of [PFOS] + [FOSAA]×499/556 + [*N*-MeFOSAA]×499/570 + [*N*-EtFOSAA]×499/584. [d] Total of [PFOA] + [PFNA] + [PFDA] + [PFUnA] + [PFDoA] + [PFTA].

minimal effects for most of the analytes included in this study as evidenced by the relatively high extract spike recoveries. Because correction factors were not applied, the recoveries reported in Table 1 reflect all potential losses of signal previously discussed, including ion suppression not accounted for by the internal standards. The data in Table 1 suggest that aging may lower the recovery from sediments of some analytes, particularly PFDoA and PFTA. However, this is not due to poor extraction, as examination of the extract spike recoveries for PFDoA and PFTA for the aged samples reveals that lower recoveries were primarily due to increased ion suppression. For example, if the PFDoA sediment recoveries listed in Table 1 are corrected for ion suppression, the two values become essentially equivalent [e.g., 87% (±7% SD) for recovery of the extraction spike vs 98% (±8% SD) for recovery of aged spike]. Similar effects also aid in explaining some of the low recoveries observed for sludge: with the exception of PFHxS extracted from primary sludge, extract spike-corrected recoveries from sludge were between 71% and 119% (data not shown). Applying extract spike correction factors would have had the largest impact on the longer chain carboxylates (i.e., PFDoA and PFTA) in sludge. For these reasons, the development of stable isotope-labeled longer chain PFCAs is needed if better accuracy is desired for these analytes, particularly for matrixes such as sludge.

Concentrations in Sludge. Total PFC concentrations in digested sludge ranged from 176 to 3390 ng/g (Table 2). An example chromatogram is provided in Figure 4. PFOS, PFDS, FOSAA, *N*-MeFOSAA, *N*-EtFOSAA, and PFDA were detected in every digested sludge sample. *N*-EtFOSAA was the dominant analyte in 6 of the 10 digested sludge samples, while PFOS was dominant in 4. The highest PFOS sludge concentration was observed in WWTP 1 DS1, collected in February 1998. This same WWTP, when sampled six years later (i.e., WWTP 1 DS2), showed substantially lower PFOS levels, as well as lower levels of PFDS and *N*-EtFOSAA. The two highest concentrations reported for total PFCs (ΣPFCs) were WWTP 1 DS1 and SRM 2781, with both sludges collected prior to the phase-out of PFOS and other perfluorooctane sulfonyl fluoride-based chemicals by 3M in 2002 (*32*). These data may represent a trend of decreasing ΣPFCs following the PFOS phase-out. When the data set is limited to recent (post-2002) digested sludges, mean PFOS and ΣPFCs levels of 124 ng/g (112% RSD, $n = 8$) and 436 ng/g (65% RSD) are calculated. These preliminary estimations of ΣPFCs in post-phase-out U. S. domestic WWTP sludges suggest that PFCs are present at levels lower than typical levels of PCBs in digested sludge (e.g., 500−1000 ng/g) (*33*), and much lower than polybrominated diphenyl ethers (PBDEs; e.g., 1800−2500 ng/g) (*34*).

Domestic sources of the perfluoroalkyl sulfonyl-based chemicals (PFASs) observed in this study remain unclear. Whereas PFOS may be present as unreacted residual in consumer products such as clothing and surface-treatment products (*9*), preliminary results suggest PFOS, *N*-EtFOSAA, and FOSAA may also be formed during the biotransformation of *N*-ethyl-*N*-(2-hydroxyethyl) perfluorooctanesulfonamide (*N*-EtFOSE) (*35*). However, given the presence of both PFOS and *N*-EtFOSAA in primary sludge, it is unlikely that degradation of precursors such as *N*-EtFOSE within the WWTP is entirely responsible for the observed levels of these chemicals in the digested sludge. Other potential sources include degradation within the sewage transmission lines or metabolism in humans, as these chemicals have been observed as metabolic products of *N*-EtFOSE (*36*). The potential for direct releases of *N*-EtFOSAA is also likely, as this chemical was itself used in aftermarket/consumer applications and as a performance chemical surfactant (*37*).

Total perfluorocarboxylates (ΣPFCAs) levels in sludge were consistently lower than the total levels of perfluoroalkylsulfonyl-based chemicals (ΣPFASs). In addition, despite the fact that the even-chain length PFCAs (e.g., PFOA, PFDA, PFDoA) were more frequently detected than the odd-chain length PFCAs (PFNA, PFUnA), no clear trend of either odd-numbered or even-numbered PFCAs being dominant was observed in the digested sludge as has been observed in biota from the Canadian Arctic (*1*). Although digested sludge from WWTP 6 was clearly dominated by the even chain-length PFCAs, this pattern was not as evident in the PFCA profiles of the other digested sludges. An even-chain length dominated PFCA pattern would be consistent with the biodegradation of fluorotelomer alcohols (FTOHs), which have been shown to yield predominantly even-chain-length PFCAs when degraded under aerobic conditions (*38*). Given their potential to form even-chain-length PFCAs, it is possible that the aerobic biodegradation of FTOHs is a potential source of the even-chain-length PFCAs observed in this study. In particular, this may explain the elevated concentrations of PFCAs (ΣPFCAs of 153 ng/g vs mean of 34.8 ng/g in digested sludge) observed in WWTP 6, which was the only sludge analyzed in this study to have undergone aerobic digestion, rather than anaerobic digestion. Characterization of the isomeric composition of the PFCAs, as has been performed for PFCAs detected in polar bears (*39*), could aid in determining whether FTOHs are the source of these chemicals in domestic sludge. In addition, the biotransformation of FTOHs as a source of the even-chain-length PFCAs may also be supported by the generally lower levels of ΣPFCAs in primary sludge, but given the high variability of the levels observed, such conclusions must remain tentative. Other potential sources include industrial sources, consumer products containing residuals, and releases of PFC-containing aqueous film-forming foam (AFFF) from fire-fighting activity and training.

Concentrations in Sediments. The levels of PFCs observed in sediments were substantially lower than those measured in sludge, but tended to follow the same general trends. Though no single analyte was detected in every sediment, PFOS, PFDS, *N*-MeFOSAA, *N*-EtFOSAA, PFOA, and PFDA were the most commonly detected PFCs, as listed in Table 3. However, unlike sludge, sediment PFCAs showed a dominance of even chain-lengths, with the odd-chain-length PFCAs quantifiable in only two sediments. While the calculated sediment LOD for PFUnA was elevated relative to the other PFCA sediment LODs (Table 1), the PFNA sediment LOD was comparable to the PFDA LOD and yet PFNA was detected much less frequently than PFDA. This suggests that any bias due to the elevated PFUnA sediment LOD is negligible and that the dominance of the even-chain-length PFCAs is not an artifact of the analytical method. As discussed with sludge, an even-chain-length dominance pattern would be expected if the source of the PFCAs was the biodegradation of FTOHs (*38*).

The levels of PFCs in sediments were also different from the levels in sludge in that the ΣPFASs were not always significantly higher than the ΣPFCAs. For four sediments, predominantly those in which PFASs were not detected or were detected below the LOQ, ΣPFCAs were significantly higher ($p < 0.05$) than ΣPFASs. Three sediments showed comparable levels of ΣPFASs and ΣPFCAs, while the remaining all showed higher levels of ΣPFASs than ΣPFCAs. Another useful metric is to compare the ΣPFCAs to only PFOS and chemicals that may be transformed to PFOS (i.e., total PFOS-equivalents; ΣPFOS). For sediments with detectable levels of PFCAs, the ratios of ΣPFOS to the ΣPFCAs ranged from zero (when no PFOS-equivalents were detected) to 10.5, with a median of 0.9 (Table 3). Though a direct comparison is not possible due to differences in analytes monitored, these ratios are somewhat consistent with those observed in wildlife (*1,2*), but generally lower than those observed in sludge (Table 2).

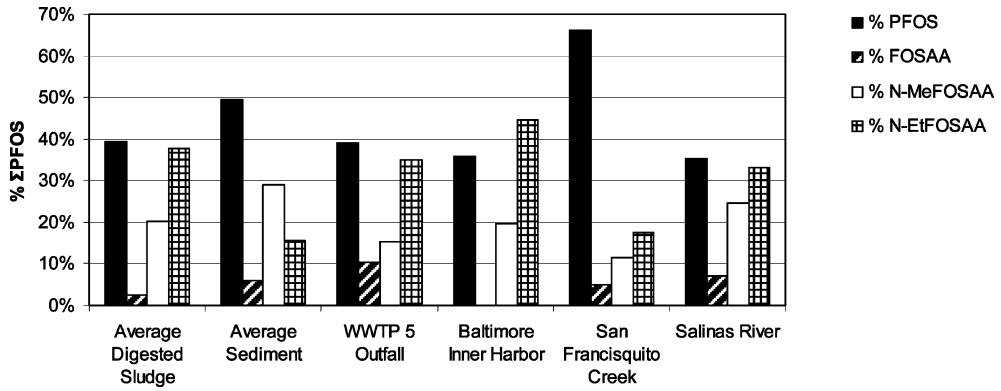

FIGURE 6. Relative contributions to total PFOS equivalents (ΣPFOS) of PFOS, FOSAA, *N*-MeFOSAA, and *N*-EtFOSAA for average digested sludge ($n = 10$), average sediment ($n = 17$), and select sediments high in ΣPFCs.

For sludge, the ratio ranged from 2.1 to 140, with a median of 11. Given that both classes of chemicals are likely recalcitrant, these differences may suggest different relative inputs to these environments, with perhaps proportionally more PFOS-based chemicals entering the sludge from domestic wastewater. Alternatively, this difference may reflect the fact that intermediates in the FTOH degradation pathway were not quantified in this study. These intermediates, once released to the environment, may undergo further degradation to PFCAs and therefore lower the ΣPFOS/ΣPFCA ratio in sediments. A slightly higher abundance of PFCAs relative to ΣPFOS in sediments is consistent with the observation that elevated PFOA levels in Lake Ontario biota may indicate a benthic contamination source signature (*2*). Further investigations into how sediment PFC profiles are or are not reflected in sediment-dwelling organisms should help elucidate the role of sediments in the movement of PFCs into foodwebs.

The high levels of PFCs present in sediment adjacent to the WWTP 5 outfall are not surprising given the presence of these PFCs in sludge and in the effluent from this plant (*40*). In addition, both the Salinas River and San Francisquito Creek had significantly higher ($p < 0.01$) levels of ΣPFCs when compared to other San Francisco Bay Area sediments. These sites also have had elevated levels of nutrients and fecal indicator bacteria (*41*), suggesting that these locations may be impacted by domestic sewage, a potential source of PFCs. While San Francisquito Creek does not currently receive direct discharges from any WWTP, periodic releases of sewage to the creek from sewer overflows have occurred (*42*). The Salinas River receives WWTP effluent from at least one municipality, though this discharge occurs approximately 200 km from the sampling site. Sediment from Baltimore Inner Harbor, a location with a history of polluted sediments, contained only moderate levels of PFCs, and yet was equal to the WWTP 5 outfall with respect to the number of quantifiable PFCs. Sediments from San Francisco Bay showed significantly higher ($p < 0.01$) levels of PFOS when compared to other local sediments (Figure 2, Table 3). Possible explanations for the elevated PFOS levels in Bay sediments include the presence of multiple point sources within the Bay (e.g., WWTP outfalls) and hydrodynamic factors limiting the dilution of Bay water. Additional sampling of San Francisco Bay sediments would be required to evaluate spatial variability within the Bay and determine whether WWTP outfall locations can explain the sediment PFOS or PFC distributions within the Bay.

Relative Contributions to Total PFOS. While this study is the first to report the presence of PFCs such as PFOS and PFOA in sediment and sludge, it also differs from many previous reports on perfluorooctane-based chemicals in the environment in that PFOS was not always the dominant chemical detected. Many of the first monitoring efforts for PFCs in the environment sought only to detect and quantify the presence of PFOS and/or PFOA, and only recently have PFOS precursors been included in the list of analytes monitored. Specifically, perfluorooctanesulfonamide (FOSA), which can be metabolically transformed to PFOS (*36*), has been detected in arctic wildlife and in the Lake Ontario foodweb, but only occasionally at levels exceeding those of PFOS (*1, 2*). Other investigations into PFOS and PFOS precursors indicate PFOS concentrations in human sera typically exceed *N*-EtFOSAA and *N*-MeFOSAA concentrations (two PFOS precursors measured in this study) by 1−2 orders of magnitude (*5, 8*). In a recent examination of water from Lake Erie and Lake Ontario, PFOS, FOSA, FOSAA, and *N*-EtFOSAA were all detected, though PFOS exceeded all PFOS precursors in all samples (*43*). However, unlike human sera, PFOS levels generally exceeded *N*-EtFOSAA levels by less than 1 order of magnitude. For some samples, the concentration of *N*-EtFOSAA was nearly one-third the concentration of PFOS.

In this study, unlike previous studies, levels of PFOS precursors such as *N*-MeFOSAA and *N*-EtFOSAA were comparable to, and in several cases exceeded, the levels of PFOS. This was particularly true for sludge, where between 2 and 36% and 7−62% of the total PFOS equivalents were *N*-MeFOSAA and *N*-EtFOSAA, respectively. When combined, these two analytes, on average, constituted 58% of the ΣPFOS in digested sludge (Figure 6). For sediments, the relative contributions were much more variable, though, on average, PFOS only accounted for 50% of the ΣPFOS. These data strongly suggest that despite the relatively low levels detected in human sera, *N*-MeFOSAA and *N*-EtFOSAA may account for a significant fraction of the ΣPFOS in the environment, and thus, as noted previously (*2*), should be included in future environmental monitoring efforts. In addition, while these two analytes can potentially be biologically transformed to PFOS, their presence in sediments and particularly in WWTP sludge suggests that these chemicals may be relatively stable intermediates. This suggestion is supported by the observation that *N*-EtFOSAA is not readily biotransformed in rat livers (*36*). Further investigations into the potential for biotransformation and sorption of these PFCs will be needed to determine whether the higher levels of PFOS in the Great Lakes, relative to *N*-EtFOSAA, can be explained by microbial transformations and/or equilibrium partitioning.

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Supporting Information Available

Information on the wastewater treatment plants included in this study (population served, source of waste, geographic region, and sampling date). This material is available free of charge via the Internet at http://pubs.acs.org.

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