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## Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity

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### Abstract:

Perfluorinated surfactants are used in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon-fuel fires. Virtually nothing is known about the occurrence of perfluorinated surfactants in the environment, in particular, at fire-training areas and emergency response sites where AFFF entered groundwater without prior treatment. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater collected from fire-training facilities located on Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL. The carboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by gas chromatography/mass spectrometry. Perfluorocarboxylates containing six to eight carbons were detected in groundwater collected from the two field sites with total concentrations ranging from 125 to 7090  $\mu\text{g/L}$ . The detection of perfluorocarboxylates at field sites after 7-10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by fire-fighting activity.

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What is significance of findings?  
is this a bad thing?

Test site is trng ground.

Significance is it was Funded  
by EPA. Indicates their  
getting interested in AFFF.

# Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity

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Perfluorinated surfactants are used in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon-fuel fires. Virtually nothing is known about the occurrence of perfluorinated surfactants in the environment, in particular, at fire-training areas and emergency response sites where AFFF entered groundwater without prior treatment. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater collected from fire-training facilities located on Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL. The carboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by gas chromatography/mass spectrometry. Perfluorocarboxylates containing six to eight carbons were detected in groundwater collected from the two field sites with total concentrations ranging from 125 to 7090  $\mu\text{g/L}$ . The detection of perfluorocarboxylates at field sites after 7–10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by fire-fighting activity.

## Introduction

Aqueous film forming foams (AFFF) are complex mixtures of surfactants and other components used to extinguish hydrocarbon-fuel fires that occur at fire-training sites as well as in emergency situations. Aqueous film forming foams have been commercially available for fire-fighting applications since their development by the United States Navy and 3M Co. in the mid-1960s (1). At fire-training areas that routinely used AFFF mixtures and military emergency response sites, AFFF-laden wastewater that entered surface water and groundwater without treatment has led to groundwater and soil contamination. For example, perfluorinated compounds were tentatively identified in groundwater impacted by fire-training activities at Tyndall Air Force Base (2). Unfortunately, definitive identifications of the perfluorinated compounds were not reported.

Commercial AFFF mixtures are proprietary in nature and typically contain fluorinated and nonfluorinated surfactants (1, 3–5). Due to the proprietary nature of AFFF formulations, the chemical structures of the actual perfluorinated surfactants used in commercial AFFFs are not known outside the companies that manufacture them (5). Moreover, the analysis of anionic perfluorinated surfactants that are known to occur

in AFFF formulations (6) is problematic because the surfactants are nonvolatile and may not contain chromophores. As a result, analytical methods for AFFF formulation components are lacking, and therefore it is difficult to assess their occurrence, fate, and transport in AFFF-contaminated groundwater. Because perfluorinated surfactants co-occur with other pollutants (e.g. fuel components, solvents, etc.) in groundwater, it is important to determine if perfluorinated surfactants affect the transport and biodegradation of other contaminants. Free and emulsified oil, fuel, and AFFF components were shown to adversely affect activated sludge processes (6, 7) and the performance of anaerobic sludge digestors (8) in wastewater treatment facilities. For this reason, perfluorinated surfactants may have an adverse effect on groundwater microbial populations and their ability to degrade co-contaminants present in AFFF-contaminated groundwater.

In addition to fluorinated surfactants use in fire-fighting foams, they are also utilized in herbicides and insecticides, cosmetics, greases and lubricants, and adhesives (3). Fluorinated carboxylic acids of industrial significance include perfluorooctanoic acid (PFC8) and perfluorodecanoic acid (PFC10) (9). There is concern regarding the potential toxicity of perfluorinated carboxylic acids. An *in vivo* study of rat liver response to PFC10 indicated the rapid onset of a low-level hepatotoxicity but no detectable damage to the DNA (10). Perfluorodecanoic acid and PFC8 have been found to inhibit gap junction intercellular communication in rat liver epithelial cells (11) and may be involved in tumor promotion (9).

In this paper, we describe the isolation, identification and quantification of perfluorinated carboxylates in groundwater impacted by fire-training activities at Naval Air Station (NAS) Fallon, NV, and Tyndall Air Force Base, FL. The development of analytical methods is necessary before investigating the occurrence and distribution of perfluorinated surfactants in AFFF-contaminated groundwater and their effect on co-contaminant transport and biodegradation.

## Experimental Section

**Standards and Reagents.** Standards of PFC8 (98%), perfluorodecanoic acid (PFC12) (95%), and the internal standard, 2-chlorolepidine (99%), were purchased from Aldrich Chemical (Milwaukee, WI). Methyl iodide (neat) was used as purchased from Aldrich Chemical.

**Field Sites and Sample Collection.** From the mid-1950s to 1988, the crash crew training area at NAS Fallon, NV (Figure 1a), was used to conduct fire-training activities, which consisted of flooding a fire pit with flammable liquids, igniting the fluids, and subsequently extinguishing the fire with fire-fighting agents including AFFF (12). For a typical training exercise, approximately 75–100 L of AFFF concentrate were diluted with 1200–3200 L of water according to specifications (3% or 6% solution) and subsequently employed. During the years of activity at the NAS Fallon site, training exercises occurred on a weekly to monthly basis. At the NAS Fallon site, groundwater samples were collected from four monitoring wells located within a 120 m radius of the fire pit where the water table is located between 2 and 3 m below the land surface.

The Tyndall Air Force Base Fire-Training Area FT-23 was used from 1980 to 1992 for similar activities (Figure 1b) (13). Four groundwater samples were obtained from wells surrounding the fire-training area; the water table is located between 1 and 2 m below the land surface. All samples were collected in high-density polyethylene brown bottles because

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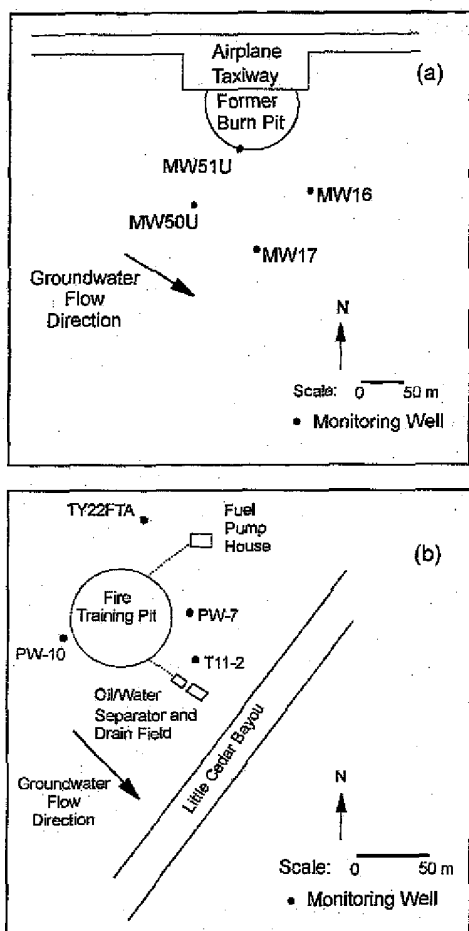


FIGURE 1. Map of (a) Naval Air Station Fallon and (b) Tyndall Air Force Base field sites indicating location of groundwater wells and direction of regional groundwater flow.

perfluorinated carboxylates adsorb to glass (14). Samples were shipped on ice without preservation and stored at 4 °C prior to analysis.

**Solid-Phase Extraction and Derivatization.** Samples (55–200 mL) were extracted through 25 mm strong anion exchange (SAX) disks in a manner similar to that described by Field and Reed (15) with the exception that the SAX disks were pretreated prior to use to remove interfering disk impurities. Pretreatment consisted of soaking the disks in 12 mM HCl/acetonitrile for 2 days after which the disks were soaked in pure acetonitrile for several hours. Just prior to use, the disks were rinsed with a minimum of 350 mL of deionized water in order to sufficiently rinse the HCl from the disks and wet them prior to passing groundwater samples through them. Samples (55–200 mL) were passed through the disks under full vacuum, and the disks were then allowed to dry. The disks containing the exchanged analytes were placed in a 2 mL autosampler vial together with 1 mL of acetonitrile, 51.2 µg of internal standard, and 100 µL of methyl iodide. When heated at 80 °C for 1 h, the acids were simultaneously eluted from the disk and derivatized to their methyl esters.

**Spike and Recovery.** Spike and recovery experiments were performed to determine the precision and accuracy of the SAX disk extraction and in-vial elution method. A set of experiments was performed on groundwater samples from NAS Fallon MW 50U and MW 17 that had been previously

determined to contain neither PFC8 nor PFC12 above detection. Duplicate groundwater samples from wells MW 50U and MW 17 were spiked to contain a final concentration of 1240 µg/L of PFC8 and 560 µg/L of PFC12.

Standard addition analyses were performed with NAS Fallon groundwater samples that contained measurable quantities of PFC8; the samples did not contain PFC12 above detection. Known amounts of PFC8 were added to samples to give a final concentration twice that of the background concentration. For example, groundwater from MW 51U and MW 16, which contained background concentrations of 6570 and 460 µg/L, respectively, were spiked to give final concentrations of 12900 and 1000 µg/L of PFC8, respectively. Each sample also was spiked with 56.4 µg of PFC12. To determine the detection limit of the method, single samples of groundwater that contained no perfluorinated carboxylates above detection were spiked to give a range of final PFC8 concentrations from 18 to 54 µg/L.

**Gas Chromatography/Mass Spectrometry.** Extracts were analyzed using a Hewlett-Packard Model 5890 Series II Plus gas chromatograph (GC) equipped with a 30 m × 0.32 mm × 4.00 µm SPB-1 SULFUR column (Supelco Inc., Bellefonte, PA). An injection volume of 1 µL was used under splitless conditions with an injector temperature of 200 °C. The GC oven temperature was initially held for 6 min at 60 °C, increased by 6 °C/min to 190 °C, increased further by 30 °C/min to 270 °C, and then held for 5 min.

Quantification of perfluorocarboxylate methyl esters was performed using a Hewlett-Packard Model 5972 mass selective detector operated in electron impact (EI) mode (70 eV). The mass selective detector was operated in full scan (50–450 amu) mode and in selected ion monitoring (SIM) mode using a dwell time of 100 ms for each ion. The scanning mode was used for qualitative identification while SIM mode was used for quantification. The ions of  $m/z$  131 [ $C_3F_5$ ]<sup>+</sup>,  $m/z$  169 [ $C_3F_7$ ]<sup>+</sup>, and  $m/z$  219 [ $C_4F_9$ ]<sup>+</sup>, which are characteristic fragments of perfluorocarbons (16–18), were used to identify and quantify the methyl esters of perfluorohexanoic acid (PFC6), perfluoroheptanoic acid (PFC7), PFC8, and PFC12. The internal standard, 2-chlorolepidine, was quantified with the ions at  $m/z$  177 and  $m/z$  115.

The identification of perfluorocarboxylate methyl esters was confirmed by electron capture negative ionization (ECNI) GC/MS, which gave unique molecular ions for each of the perfluorinated carboxylate methyl esters (e.g.  $m/z$  328 for PFC6,  $m/z$  378 for PFC7,  $m/z$  428 for PFC8, and  $m/z$  628 for PFC12). These measurements were performed with a Varian 3400 gas chromatograph interfaced with a Finnigan Model 4023 mass spectrometer. Methane was used as the reagent gas, and the mass spectrometer was operated in full scan mode (100–650 amu). The gas chromatograph was operated with a column and temperature program identical to that used for the EI GC/MS.

Initially, samples prepared in deionized water were used as the matrix for constructing calibration curves, and standard recoveries were low. However, when samples prepared in tap water, which contains inorganic cations and anions, were used as the matrix for constructing calibration curves, quantitative recovery of standards was obtained. It is proposed that the 350 mL of deionized water does not sufficiently rinse the disks of residual HCl and tap water is required to completely rinse the disks and obtain quantitative recovery of standards. Therefore, calibration curves for quantification of PFC8 were constructed by passing 100 mL of tap water samples that had been spiked with 3.6–1080 µg of PFC8 through 25 mm SAX disks and derivatizing the acids to their methyl esters using the in-vial elution and derivatization technique. The calibration curve for PFC12 was constructed in a similar manner by adding 7.5–113 µg of PFC12 standard to 100 mL of tap water. For all quantitation

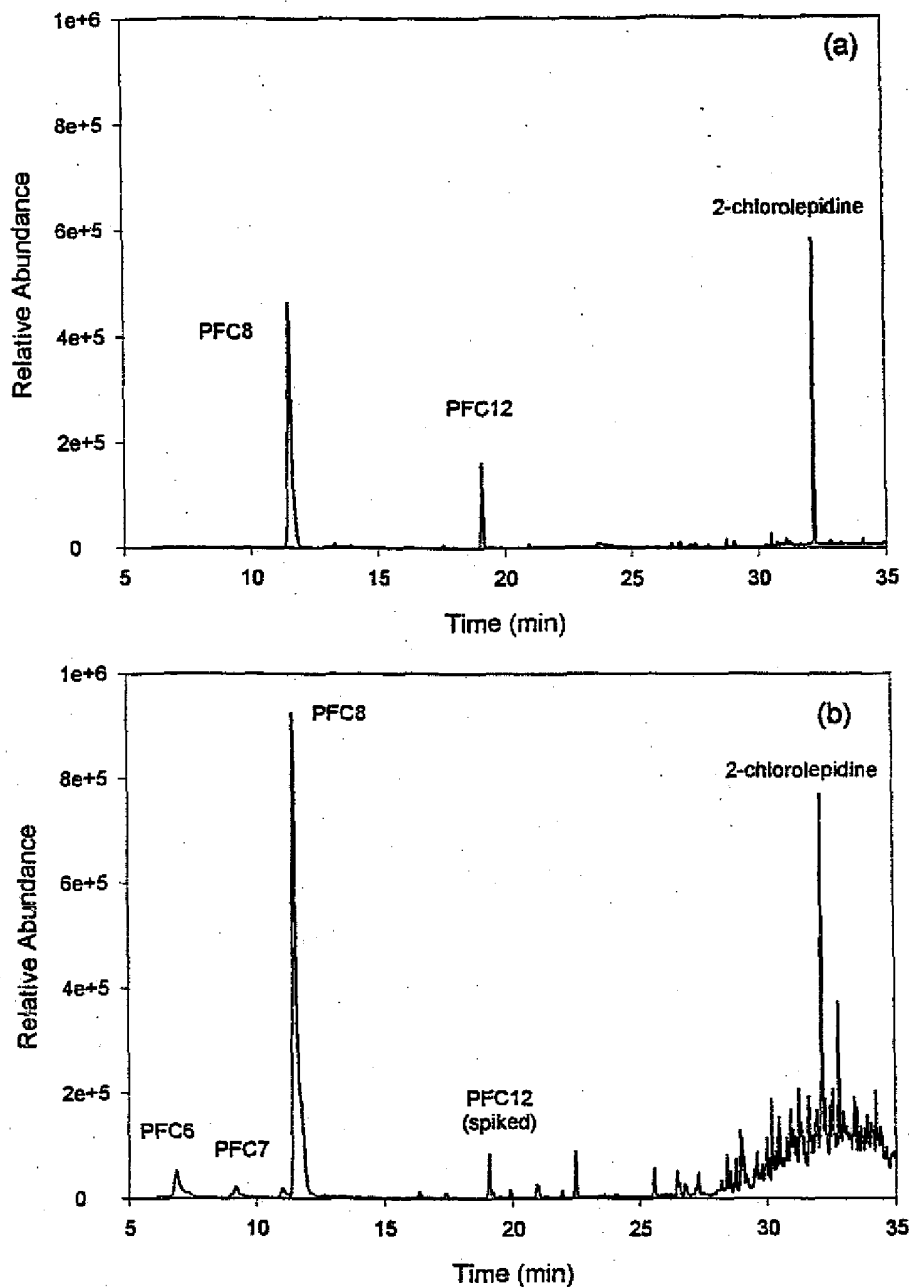


FIGURE 2. (a) Typical EI GC/MS chromatogram of PFC8 and PFC12 standards and (b) perfluorinated carboxylates, including PFC5, PFC7, PFC8, and PFC12 (spiked) in Naval Air Station Fallon groundwater.

standards, a total of 51.2  $\mu\text{g}$  of the 2-chlorolepidine internal standard was added to the autosampler vial just prior to the addition of methyl iodide. Both calibration curves were linear with  $r^2$  typically greater than 0.99. Quantification of PFC6 and PFC7 was performed assuming a response factor equal to an equimolar amount of PFC8.

## Results and Discussion

**Gas Chromatography/Mass Spectrometry.** A film thickness of 4  $\mu\text{m}$  (30 m  $\times$  0.32 mm SPB-1 SULFUR; Supelco, Bellefonte, PA) was necessary to obtain sufficient retention times for the methyl esters of PFC8 and PFC12 to allow for the separation and quantification (Figure 2a). Initial attempts to separate and quantify the perfluorinated carboxylate methyl esters on a thin film (0.25  $\mu\text{m}$ ), 30 m  $\times$  0.25 mm DB-1 (J&W Scientific,

Folsom, CA) column were unsuccessful regardless of the initial column temperature. Note that the stationary phases in the SPB-1 SULFUR and DB-1 columns are comparable. A standard of perfluorobutyric acid was not observed under any of the described GC conditions; it is most likely that an initial oven temperature less than 40  $^{\circ}\text{C}$  would be required.

The EI mass spectra of methyl PFC8 (Figure 3a) and PFC12 indicate characteristic perfluorocarbon fragmentation (16, 17) in which the major ions (e.g., 69, 119, 169, 219, etc.) differ by 50 amu, which corresponds to the mass of  $\text{CF}_2$ . Molecular ions were not observed for any of the perfluorinated carboxylate methyl esters under EI conditions; however, molecular ions  $[\text{M}]^-$  were observed under ECNI conditions. For example  $m/z$  428 (in Figure 3b) corresponds to the molecular ion of methyl PFC8.

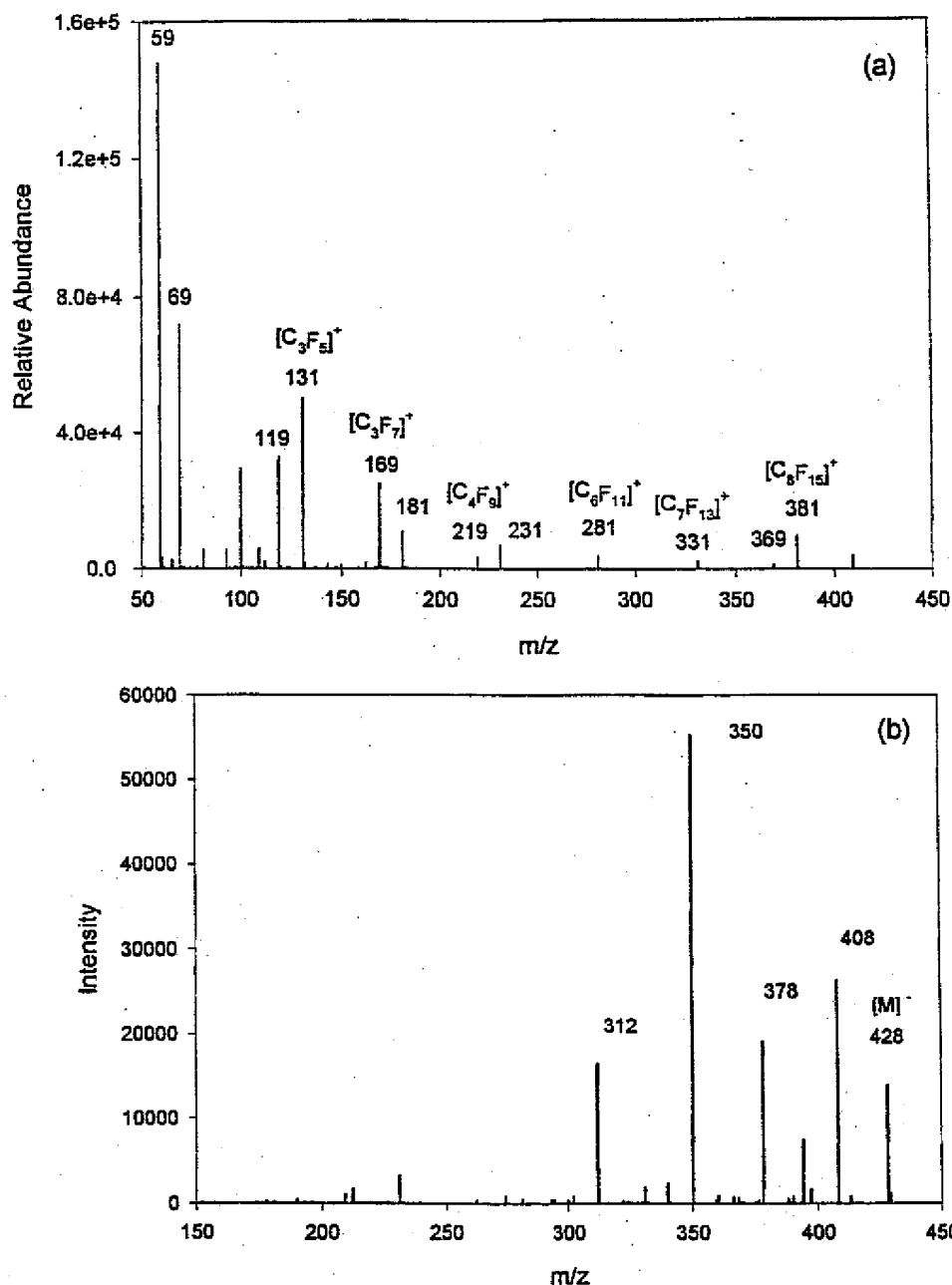


FIGURE 3. (a) EI mass spectrum of methyl PFC8. (b) ECNI mass spectrum of methyl PFC8.

**Solid-Phase Extraction.** Prior to developing a solid-phase extraction method, initial experiments were conducted using diazomethane as the derivatization reagent. When perfluorinated carboxylates were derivatized using ethanol-based diazomethane, multiple peaks corresponding to methyl and ethyl esters were detected (unpublished data). Because EI GC/MS did not produce molecular ions, ECNI GC/MS was used to verify the formation of both methyl and ethyl esters. Consequently, if ethanol-based diazomethane was used for derivatization in conjunction with EI GC/MS, multiple peaks in a chromatogram could be erroneously interpreted as a greater number of perfluorinated compounds than are actually present. In contrast, only the methyl ester was obtained when butyl carbitol (2-(2-butoxyethoxy)ethanol) was used to prepare the diazomethane reagent. However, because of the hazards associated with the use of diazo-

methane and the time-consuming nature of diazomethane derivatization, an alternative method was desired.

Derivatization of the perfluorocarboxylates by solid-phase extraction and the in-vial elution and derivatization technique gave only a single peak that corresponded to the methyl ester of each perfluorinated carboxylate standard; the identification of each methyl ester was confirmed by ECNI GC/MS. In addition, the solid-phase extraction approach combined the steps of isolation and derivatization, which greatly simplified the procedure and eliminated the use of diazomethane.

Six replicate analyses of blank 25 mm SAX disks that had not been prerinsed with 12 mM HCl/acetonitrile prior to use, yielded an average of  $21 \pm 1 \mu\text{g}$  (4.8% relative standard deviation (RSD)) of PFC8 per disk. No other perfluorinated carboxylates were present in the disks above the detection limit. The PFC8 is associated with the Teflon matrix and not

**TABLE 1. Recovery of PFC8 and PFC12 Spiked into Groundwater Samples from Naval Air Station Fallon<sup>a</sup>**

| sample                         | % recovery      |       |
|--------------------------------|-----------------|-------|
|                                | PFC8            | PFC12 |
| NAS Fallon MW 51U <sup>b</sup> | 83 <sup>c</sup> | 35    |
| NAS Fallon MW 16               | 90 <sup>d</sup> | 85    |
| NAS Fallon MW 50U              | 73              | 77    |
| NAS Fallon MW 17               | 74              | 88    |

<sup>a</sup> Duplicate samples were analyzed. Sample volume was 100 mL unless otherwise noted. <sup>b</sup> Sample volume was 55 mL. <sup>c</sup> Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 6,570 µg/L. <sup>d</sup> Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 460 µg/L.

the embedded anion exchange particles (unpublished data). The background PFC8 was successfully removed by rinsing the disks prior to use with 12 mM HCl/acetonitrile followed by 350 mL of deionized water. It should be noted that benzoic acid and ethylhexylphthalic acid are also present in the disks as artifacts and are removed by the HCl/acetonitrile prerinse step.

**Accuracy, Precision, and Detection Limits.** The recoveries of PFC8 from blank groundwater samples obtained from NAS Fallon wells MW 50U and MW 17 were 73 and 74%, respectively, while the recoveries of PFC12 were 77 and 88%, respectively (Table 1). Because detectable levels of PFC8 occurred in groundwater from MW 51U and MW 16, standard addition experiments were performed to determine the recoveries of PFC8. The recoveries of the PFC8 spiked into MW 51U and MW 16 groundwater to give a final concentration double that of the background concentration were 83 and 90%, respectively (Table 1). The recoveries of PFC12 from MW 51U and MW 16 groundwater, which did not contain background concentrations of PFC12, were 35 and 85%, respectively (Table 1). Although the recovery of PFC8 (83%) differs significantly from that of PFC12 (35%) in groundwater from MW 51U, the recoveries of PFC8 and PFC12 were nearly equivalent for the other groundwater samples. Monitoring well 51U is located closest to the fire pit where AFFF agents were applied to burning mixtures of fuels and solvents. Due to its proximity to the fire pit, the groundwater from MW 51U most likely contains the greatest diversity of inorganic and organic constituents, which may adversely affect PFC12 recoveries relative to that of PFC8. Therefore, although the original intent was to use the PFC12 as a surrogate standard because it did not occur in the groundwater samples, PFC12 appears more sensitive to matrix interferences compared to PFC8 so that it is an inappropriate choice for a surrogate standard. For this reason, all subsequent quantification was based on the 2-chlorolepidine internal standard.

The precision, indicated by the RSD, calculated from five replicate analyses each of groundwater from NAS Fallon MW 16 and Tyndall AFB T11-2 ranged from 3.7 to 14% (Table 2). The detection and quantitation limit of the method was defined as those concentrations of PFC8 needed to produce a signal-to-noise (S/N) of 3:1 and 10:1, respectively. The detection and quantitation limits for PFC8 were 18 and 36 µg/L, respectively.

**Application to Groundwater Samples.** Four groundwater samples from both NAS Fallon and Tyndall AFB were analyzed for perfluorinated carboxylates. Chromatograms obtained by EI GC/MS indicated the presence of multiple perfluorinated compounds all having characteristic perfluorocarbon fragmentation (Figure 2b). Analysis by ECNI GC/MS established the identification of PFC6, PFC7 and PFC8 in groundwater obtained from wells MW 51U and MW 16 from NAS Fallon. The molecular ions [M]<sup>-</sup> for methyl PFC6 (*m/z* 328) and methyl PFC7 (*m/z* 378) were observed for peaks eluting 4.7 and 2.3 min before that of PFC8 (Figure 4a,b). The ECNI mass spectrum for methyl PFC8 in MW 51U was similar to that of the PFC8 standard (Figure 2b).

The groundwater samples from NAS Fallon MW 51U and MW 16 had total perfluorinated carboxylate concentrations of 7090 and 540 µg/L, respectively (Table 2). The PFC6 detected in NAS Fallon groundwater samples from MW 51U and MW 16 comprised 5.2% and 11%, respectively, of the total perfluorocarboxylates detected. The PFC7 was 2.1% and 3.3% respectively, of the total perfluorinated carboxylates detected in these wells. The dominant perfluorinated carboxylate, PFC8, accounted for 93% and 85%, respectively, of the total perfluorocarboxylate concentration.

The highest concentrations of perfluorocarboxylates were observed in groundwater collected from NAS Fallon MW 51U, which is the well located closest to the fire-training pit (Figure 1a). Monitoring well 16, which is located downgradient of MW 51U and the fire-training pit, had lower but detectable concentrations of perfluorocarboxylates. Groundwater from MW 50U and MW 17, which are located off gradient from the fire-training pit, contained no detectable perfluorinated carboxylates. Over the approximate 100 m distance between MW 51U and MW 16, the concentrations of the perfluorinated carboxylates decreased with increasing number of carbons. For example, the concentration of PFC6 decreased 85% over the 100 m compared to decreases of 88% and 93% for PFC7 and PFC8, respectively.

The groundwater samples from Tyndall AFB PW-10, PW-07, and T11-2 contained total perfluorinated carboxylate concentrations of 298, 159, and 124 µg/L, respectively (Table 2). The compositions of Tyndall AFB groundwater collected from the three wells ranged from 46 to 52% for PFC6, from 13 to 15% for PFC7 and from 34 to 40% for PFC8. In contrast to the groundwater samples from NAS Fallon, the dominant perfluorinated carboxylate in Tyndall AFB groundwater was PFC6.

**TABLE 2. Concentrations of Perfluorinated Carboxylates in Groundwater Samples from Naval Air Station Fallon and Tyndall Air Force Base<sup>a,b</sup>**

| sample              | n | PFC6 (µg/L)    | PFC7 (µg/L)                | PFC8 (µg/L)       | total (µg/L)      |
|---------------------|---|----------------|----------------------------|-------------------|-------------------|
| NAS Fallon MW 51U   | 3 | 372 ± 4 (1.1%) | 149 ± 5 (3.4%)             | 6570 ± 150 (2.3%) | 7090 ± 160 (2.3%) |
| NAS Fallon MW 16    | 5 | 57 ± 8 (14%)   | 18 ± 2 (11%) <sup>c</sup>  | 460 ± 20 (4.3%)   | 540 ± 20 (3.7%)   |
| NAS Fallon MW 50U   | 3 | nd             | nd                         | nd                | nd                |
| NAS Fallon MW 17    | 3 | nd             | nd                         | nd                | nd                |
| Tyndall AFB PW-10   | 2 | 144            | 38                         | 116               | 298               |
| Tyndall AFB PW-07   | 2 | 73             | 22 <sup>c</sup>            | 64                | 159               |
| Tyndall AFB T11-2   | 5 | 64 ± 4 (6.3%)  | 19 ± 1 (5.3%) <sup>c</sup> | 42 ± 2 (4.8%)     | 124 ± 8 (6.5%)    |
| Tyndall AFB TY22FTA | 2 | nd             | nd                         | nd                | nd                |

<sup>a</sup> The relative standard deviation is given in parentheses. <sup>b</sup> nd: not detected above the detection limit. <sup>c</sup> The reported value is near the detection limit (S/N ≤ 3) and less than the quantitation limit (S/N ≤ 10). The value has been included in the reported total concentration.

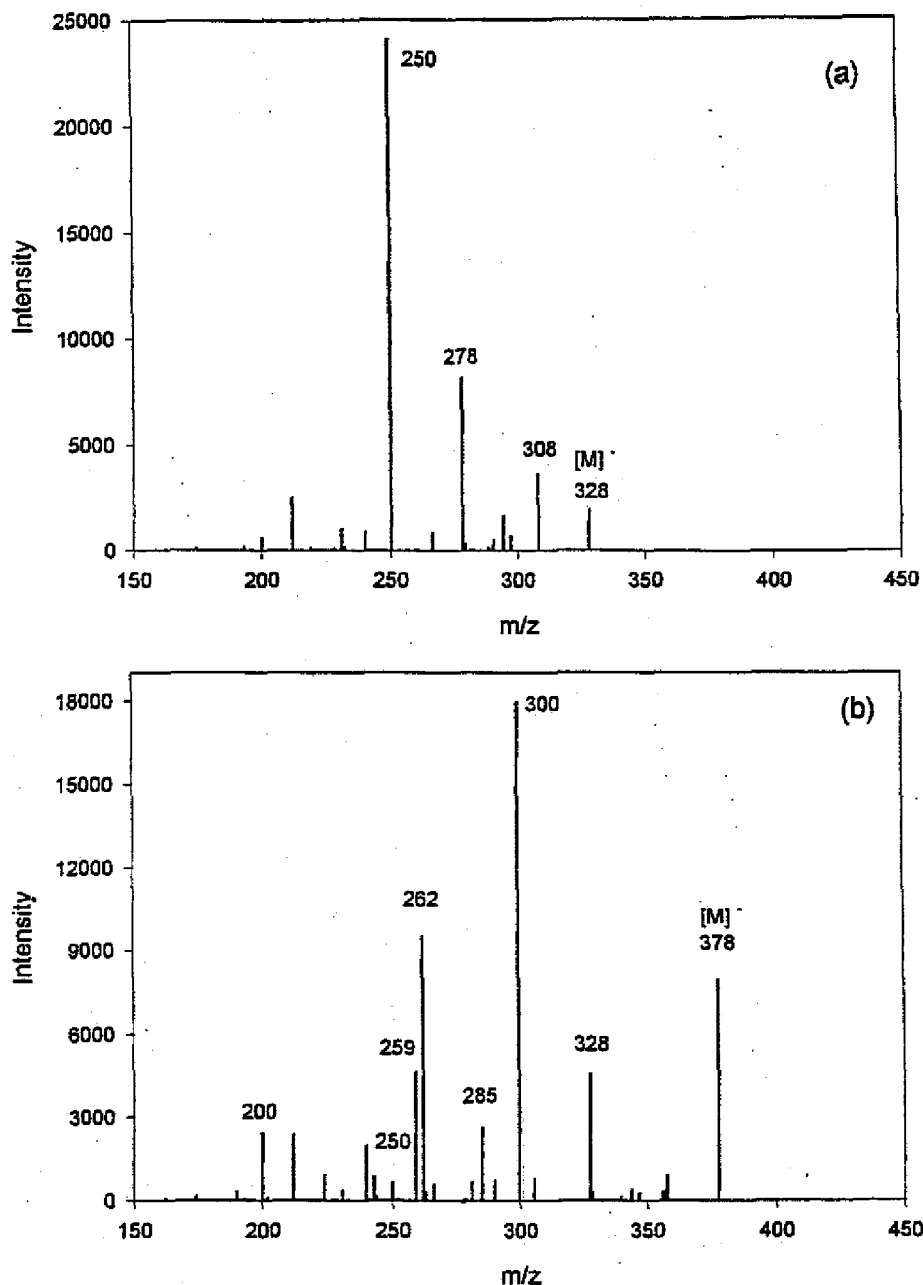


FIGURE 4. ECNI mass spectra of (a) methyl PFC6 and (b) methyl PFC7.

The highest concentrations of perfluorocarboxylates among the groundwater samples from Tyndall AFB were observed in PW-10 and PW-07, which are the two wells located closest to the fire-training pit (Figure 1b). Monitoring well T11-2, which is located downgradient of the fire-training pit, had lower but detectable groundwater concentrations of perfluorocarboxylates. The groundwater collected from a well located north of the fire-training pit, TY22FTA, contained no perfluorinated carboxylates above the detection limit (18  $\mu\text{g/L}$ ).

It is not surprising to observe a suite of perfluorinated carboxylates since the raw materials used in the synthesis of perfluorinated organic compounds are mixtures (3, 19). Different ratios of PFC6, PFC7, and PFC8 may result from the use of different AFFF formulations at the two fire-training areas. The observed homologous series consisting of even and odd number perfluorinated carboxylates is indicative of

the electrochemical fluorination process used by 3M Co. (3). Other fluorination processes, such as telomerization, produce only even number homologues (3). Because of the proprietary nature of AFFFs, it is not known if perfluorinated carboxylates are present as one of the major surface active agents in AFFF formulations or as unreacted starting materials used in the synthesis of the principal perfluorinated surfactants used in AFFF formulations. In addition, the carboxylates may be combustion, biological, or nonbiological degradation products of the principal perfluorinated components in AFFF mixtures. Unfortunately, the exact source and history of AFFF applications at the two field sites are unknown, and therefore, the relationship between the observed perfluorocarboxylate ratios and that of the original AFFF mixtures is unknown.

To the best of our knowledge, very little is known regarding the transport and fate of perfluorocarboxylates in groundwater. Adsorption to sludge at wastewater treatment facilities

is considered a significant process for the removal of perfluorinated surfactants during treatment (3). However, detection of perfluorinated carboxylates at the NAS Fallon and Tyndall AFB sites, which have not been used since 1988 and 1992, respectively, is consistent with the view that biodegradation of the long chain perfluorocarbon hydrophobe is unlikely (6, 9, 19). The recalcitrant nature of perfluorinated compounds is attributed in part to the rigidity of the perfluorocarbon chain (9, 20) as well as the strength of the carbon-fluorine bond (3, 9, 21).

To the best of our knowledge this is the first definitive identification of perfluorinated carboxylates in groundwater impacted by fire-fighting activity. Further work is needed to determine if additional perfluorinated components are present, such as perfluorooctane sulfonic acid, which is thought to be one of the principle components in some commercial AFFF formulations. In addition, it is of interest to relate the occurrence and distribution of perfluorinated compounds to other site characterization parameters such as dissolved organic carbon, inorganic constituents, and the distribution of co-contaminants and to understand the potential influence of perfluorinated compounds on the biotransformation and transport of other co-contaminants.

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