Aerobic Biotransformation and Fate of *N*-Ethyl Perfluorooctane Sulfonamidoethanol (*N*-EtFOSE) in Activated Sludge

KURT R. RHOADS,
ELISABETH M.-L. JANSSEN,
RICHARD G. LUTHY, AND
CRAIG S. CRIDDLE*

Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305

Received November 13, 2007. Revised manuscript received January 27, 2008. Accepted January 29, 2008.

Processes affecting the fate of perfluorinated organics are of increasing concern due to the global dispersal, persistence, and bioaccumulation of these contaminants. The volatile compound *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) and its phosphate esters have been used in protective surface coatings. In this report, we describe the fate of *N*-EtFOSE in aerobic batch assays. These assays were performed using undiluted activated sludge in serum bottles that were sealed to prevent the escape of *N*-EtFOSE and volatile transformation products. Separate assays were performed with *N*-EtFOSE and reported transformation products. *N*-EtFOSE degraded to *N*-ethyl perfluorooctane sulfonamido acetic acid (*N*-EtFOSAA) with an observed first-order rate of 0.99 $\pm$ 0.08 day^{-1} and a pseudosecond order rate of 0.26 $\pm$ 0.02 L/mg VSS day^{-1}. *N*-EtFOSAA underwent further transformation at a slower rate (0.093 $\pm$ 0.012 day^{-1}) to *N*-ethylperfluorooctane sulfonamide (N-EtFOSA). N-EtFOSA then transformed to perfluorooctane sulfonamide (FOSA). FOSA transformed to perfluorooctane sulfinate (PFOSI), and PFOSI transformed to perfluorooctane sulfonate (PFOS). Perfluorooctanoic acid (PFOA) was not detected as a transformation product of any compound. Using the measured rate of *N*-EtFOSE biotransformation and literature values for phase partitioning and mass transfer in aeration basins, we modeled the fate of *N*-EtFOSE in a typical activated sludge aeration basin open to the atmosphere. The model predicts that 76% of the *N*-EtFOSE is stripped into the atmosphere, 5% sorbs to waste solids, 13% undergoes transformation to *N*-EtFOSAA, and 6% is discharged in the wastewater effluent.

Introduction

Over the past decade, concerns regarding perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) have increased due to their worldwide detection (*1*) and environmental stability (*2, 3*). Such compounds have been found in humans (*4–6*) and wildlife, even in remote regions such as the high Arctic (*7, 8*). PFCAs and PFSAs have low p K_a values and high water solubility values (*9*) and are, therefore, not expected to be transported from manufacturing sites via atmospheric pathways. Consequently, researchers have proposed two mechanisms to explain their detection in places distant from their manufacture and use: (1) transport via ocean currents (*10*), and (2) transport via volatile precursors that are oxidized atmospherically (*8*).

One of the potential precursors of PFSAs and PFCAs is *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), a volatile compound present by itself and attached to phosphate esters in protective paper coatings (*11*). The only producer of *N*-EtFOSE in the United States, 3M, halted production in 2002 (*12*); however, it is still detected in North American atmospheric samples (*13, 14*). There is also evidence that perfluorinated sulfonamides such as *N*-EtFOSE are oxidized in the atmosphere to PFCAs and PFSAs (*15*). Because of its volatility (dimensionless Henry's constant H_{cc} = 0.79 (*16*)), *N*-EtFOSE has likely been discharged to the atmosphere during its production and during application of *N*-EtFOSE-containing products. *N*-EtFOSE could also be transferred to the atmosphere during aeration when it enters wastewater treatment plants (WWTPs) or is generated within the activated sludge aeration basin by hydrolysis of monomers. However, the fate of *N*-EtFOSE in WWTPs is complicated by solids interactions and the fact that it biotransforms (*17*).

It is also currently unknown how much the biotransformation of sulfonamides such as *N*-EtFOSE and *N*-MeFOSE (*N*-methyl perfluorooctane sulfonamidoethanol) contributes to the burden of PFCAs and PFSAs. Several studies have shown that mass flows of PFCAs and PFSAs increase in WWTPs, indicating biological transformation of precursors (*18–20*). However, there is lack of consensus regarding the sources, identity, and relative importance of these precursors. Schultz et al. (*19*) found increases of *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA), a potential *N*-EtFOSE metabolite, during activated sludge treatment. In two reports produced for 3M, Lange (*17, 21*) found that *N*-EtFOSE transformed to a PFCA, perfluorooctanoic acid (PFOA), and a PFSA, perfluorooctane sulfonate (PFOS), in a mixed microbial culture. However, in a subsequent biotransformation study of *N*-EtFOSE performed under similar conditions by Boulanger et al. (*22*), neither PFOA nor PFOS were detected.

In order to predict the fate of *N*-EtFOSE in WWTPs, the transformation products and kinetics must be known. Previous studies relied upon batch activated sludge assays in which the activated sludge was diluted approximately 10-fold. Dilution decreases biomass concentration and slows biotransformation, allowing abiotic transformations to assume a greater relative significance. Prior studies also entailed addition of a substrate to stimulate microbial activity. This step stimulates growth of those organisms that can consume the substrate, and large biomass increases can occur if initial biomass concentrations are low and the substrate is added at high levels. Consequently, transformation kinetics derived from such studies are not useful for prediction of fate in activated sludge systems.

In an initial study by Lange (*17*), *N*-EtFOSE was 90% transformed to seven products. At the end of the 35-day study, PFOS and PFOA were detected at a ratio of 11.5:1. A reaction pathway was proposed involving sequential side chain oxidation, dealkylation, and deamination with simultaneous formation of the end products PFOS and PFOA via different mechanisms. In a subsequent study, Lange (*21*) performed separate biotransformation experiments lasting 18 days using each identified *N*-EtFOSE product. Three oxidation and/or dealkylation products of *N*-EtFOSE did not significantly

* Corresponding author phone: 650-723-9032; fax: 650-725-3164; e-mail: criddle@stanford.edu.

10.1021/es702866c CCC: $40.75
Published on Web 03/07/2008

TABLE 1. MRM Transitions Monitored, Internal Standards, And Method Recovery Data

analyte	% recovery ± SD of sludge spike[a]	quantitation transition monitored (*m/z*)	confirmation transition monitored (*m/z*)	internal standard	internal standard transition monitored (*m/z*)
N-EtFOSE	98 ± 6	630 > 59	none	[D_9] *N*-EtFOSE	639 > 59
N-EtFOSAA	98 ± 3	584 > 419	584 > 526	[D_5] *N*-EtFOSAA	589 > 419
FOSAA	98 ± 5	556 > 498	556 > 78	[$^{13}C_2$] PFDA	513 > 469
FOSA	119 ± 6	498 > 78	498 > 64	[D_5] *N*-EtFOSAA	589 > 419
N-EtFOSA	83 ± 13	526 > 169	526 > 219	[D_5] *N*-EtFOSA	531 > 169
PFOSI	90 ± 6	483 > 219	483 > 83	[$^{18}O_2$] PFOS	503 > 84
PFOA	109 ± 7	413 > 369	413 > 169	[$^{13}C_2$] PFOA	415 > 370
PFOS	94 ± 4	499 > 99	499 > 80	[$^{18}O_2$] PFOS	503 > 84

[a] Recoveries based on four replicate autoclaved sludge samples spiked at 100 μg/L.

biodegrade, despite the fact that they appear to be important links in the transformation pathway. Toxicity and limited bioavailability were invoked as possible explanations. By contrast, Boulanger et al. (*22*) identified only two products accounting for 28% of the transformed *N*-EtFOSE. Possible explanations would include differences in the length of the incubation period, microbial communities, or extraction methods.

To evaluate the pathway and rates of *N*-EtFOSE transformation in WWTPs, we assayed the fate of *N*-EtFOSE and that of all its previously identified transformation products. Our assays used undiluted activated sludge, and our analysis used new extraction and cleanup methods adapted from Powley et al. (*23*). The kinetics obtained, together with estimated values for partition coefficients, have allowed us to model the fate of *N*-EtFOSE in activated sludge aeration basins.

Materials and Methods

Chemicals and Standards. The test compounds *N*-EtFOSE (97.7%), *N*-EtFOSAA (54%), *N*-ethylperfluorooctane sulfonamide (*N*-EtFOSA, 95%), perfluorooctane sulfonamido acetate (FOSAA, 99.6%), perfluorooctane sulfonamide (FOSA, 98.94%), and potassium perfluorooctane sulfinate (PFOSI, 100%) were provided by 3 M Co. (St. Paul, MN). The impurities in *N*-EtFOSAA were identified by the supplier as predominately water, ethanol and 2-butoxyethanol, with trace amounts of C5–C7 PFCAs. Potassium perfluorooctane sulfonate (PFOS, 98%) and perfluorooctanoic acid (PFOA, 98%) were purchased from Fluka through Sigma-Aldrich (St. Louis, MO) and Aldrich Chemical Co. (Milwaukee, WI), respectively. The internal standards [D_9] *N*-EtFOSE, [D_5] *N*-EtFOSAA, [D_5] *N*-EtFOSA, [$^{13}C_2$] perfluorodecanoic acid (PFDA), and [$^{13}C_2$] PFOA were purchased from Wellington Laboratories (Guelph, ON, Canada); [$^{18}O_2$] PFOS was obtained from RTI International (Research Triangle Park, NC). All internal standards had purities greater than 98%. Optima grade methanol was purchased from Fisher Scientific (Pittsburgh, PA). Ammonium acetate and glacial acetic acid were obtained from Mallinckrodt (Phillipsburg, NJ).

Microcosm Setup. Fresh aerobic activated sludge (volatile suspended solids 3.8 g/L) was obtained from the aeration basin at the Palo Alto Regional Water Quality Control Plant (Palo Alto, CA). Aliquots (75 mL) of the activated sludge were transferred into 120 mL glass serum bottles. Half of the bottles were autoclaved to serve as controls. Ten microliters of methanol stock solution containing the desired test compound was added to achieve a final concentration of 100 μg per L sludge. This initial concentration was ~100 fold higher than background concentrations of the perfluorochemicals in the activated sludge, but lower than the solubility limit of *N*-EtFOSE (150 μg/L (*24*)). The resulting methanol concentration in each microcosm was 105 mg/L (158 mg COD/L). The headspace of each microcosm was flushed with pure oxygen, and the flasks were immediately sealed with butyl rubber stoppers. Active and control microcosms were incubated at 30 °C on a shaker (175 rpm). On days 0, 1, 3, 6, and 10, triplicate samples were sacrificed for analysis. The oxygen concentration of the sacrificed samples was measured at each sampling point by injecting 250 μL headspace into a Series 580 TCD gas chromatograph (GOW-MAC Instrument Company, Bridgewater, NJ). Twenty milliliters of pure oxygen was added to the remaining, unsampled microcosms on days three and six to maintain aerobic conditions. Immediately after sacrifice, the headspace of each microcosm was sampled as previously described (*3*) by drawing 10 mL of headspace through a C18 solid phase extraction cartridge (Alltech, Deerfield, IL; 0.6 g medium, preconditioned with 10 mL methanol, and air-dried before use). After headspace analysis, sacrificed microcosms were frozen at −80 °C and the entire contents were lyophilized.

Extraction and Cleanup. The lyophilized contents were transferred to a 50 mL polypropylene tube. The glass serum bottle and rubber stopper were rinsed with 20 mL methanol and added to the solids. The tube containing the solids and methanol was sonicated for 20 min at 60 °C and centrifuged at 3600 rpm for 15 min. The resulting extract was poured into a new 50 mL tube and diluted with methanol to 20 mL. Extracts were purified using a dispersed sorbent (ENVI-Carb), as previously described (*23*). Purified extracts were diluted 1/10 with methanol and again 3/5 with 0.01% aqueous ammonium hydroxide solution. Immediately prior to analysis, a 500 μL aliquot was transferred to a glass autosampler vial with 50 μL of 11 μg/L 50:50 (water:methanol) internal standard solution. Solid phase extraction cartridges from headspace sampling were eluted with 10 mL methanol, which was then diluted 3/5 with 0.01% aqueous ammonium hydroxide solution and prepared for analysis the same as the sludge extracts. Spiked recovery data were obtained by spiking autoclaved sludge microcosms with a 10 μL of mixed methanol stock containing all analytes, shaking for one day at 30 °C on a shaker, lyophilizing, and proceeding with extraction and analysis identically to other samples (Table 1).

Sample Analysis via HPLC/MS/MS. All samples were analyzed on a Shimadzu HPLC system (Columbia, MD) coupled to a Sciex API 3000 triple quadrupole mass spectrometer (MDS Sciex, Ontario) operating in negative electrospray ionization multiple reaction monitoring (MRM) mode. Chromatography was performed using an aqueous ammonium acetate (2 mM) and methanol gradient delivered at a flow rate of 300 μL/min. The eluent was initially 35% methanol, ramped to 100% methanol over 7.5 min, held at 100% for 2.5 min, and restored to 35% at 10 min (total run time 13 min). The sample injection volume was 30 μL, and the column used was a Targa Sprite C18 (5-μm pore size Higgins Analytical, Mountain View, CA) equipped with a C18 guard column (Higgins Analytical). Quantification was achieved using a 10-point inverse weighted (1/X) standard calibration curve spanning 0.05–100 μg/L. The limit of

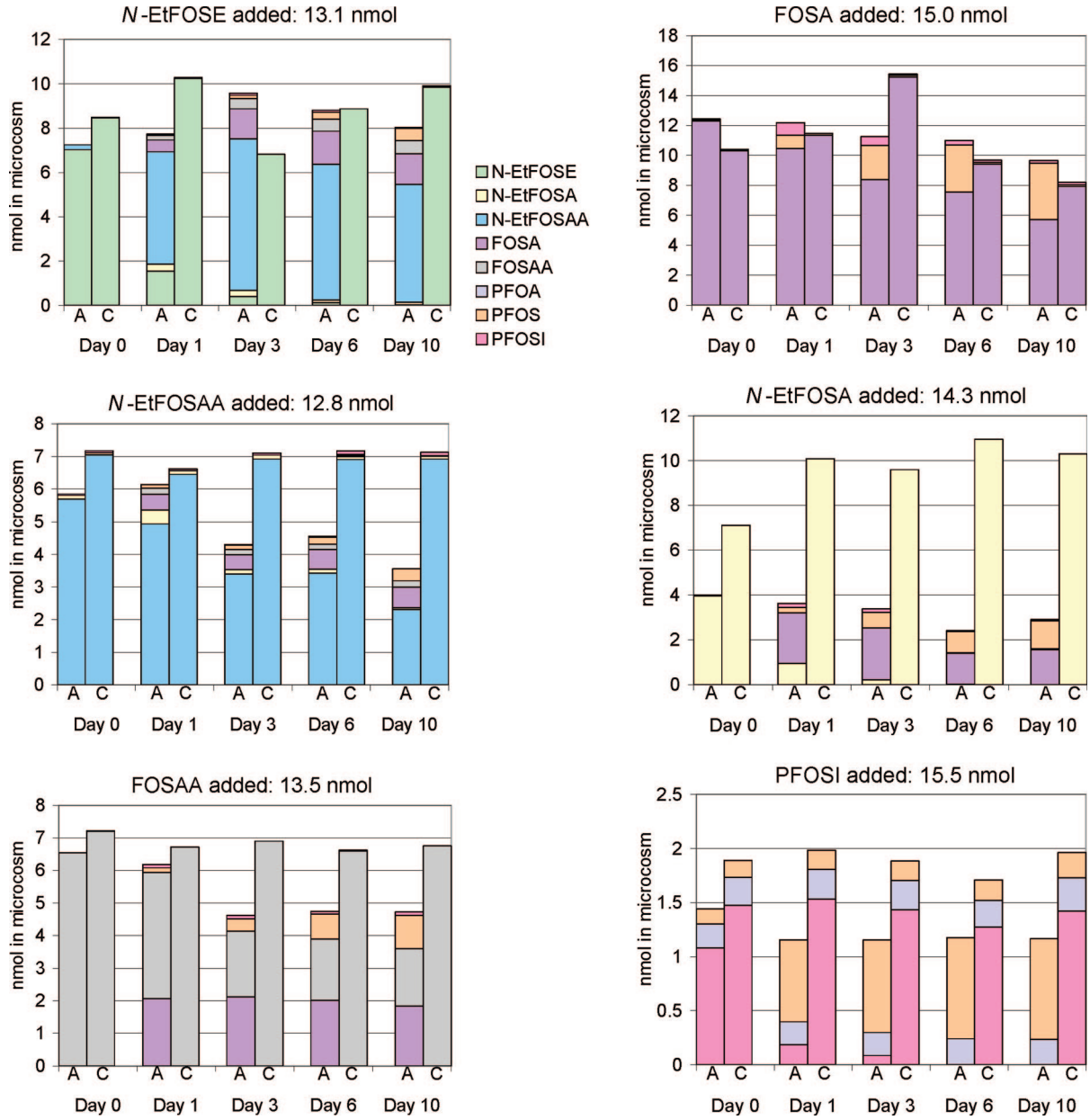

FIGURE 1. Average moles detected after incubation of specified compound in activated sludge (n = 3). Initial spike concentration 100 μg/L. *A* = active microcosms. *C* = autoclaved control microcosms. Statistics provided in Supporting Information (Table S1).

quantification (LOQ) was defined as the standard concentration yielding a S/N of at least 10 or the lowest standard concentration calculated to be within 30% of its actual value, whichever was higher. In most cases, the LOQ was 0.1 μg/L in vial, which corresponds to 49–69 pmol in the microcosm. Additional analytical parameters and quality control procedures were the same as described previously (*25*).

Determination of Rate Constants and Phase Partitioning Behavior. The observed first-order reaction rate, k_{obs}, was calculated for each reactant from the slope of the regression line passing through a plot of ln (M/M_0) vs t, where M is the total mass present at time t and M_0 is the initial mass at time zero. The observed first-order reaction rate, k_{obs}, is related to the first order aqueous phase reaction rate, k, by the expression

$$\frac{dM}{dt} = k_{obs}M = kC_{aq}V_{aq} \quad (1)$$

where C_{aq} is the concentration in the aqueous phase, and V_{aq} is the volume of the aqueous phase. If M is assumed to be the sum of the masses of the reactant in the gas, aqueous, and solid phases, k can be calculated from the following expression:

$$k = k_{obs}\frac{H_{cc}V_g + V_{aq} + K_dX_vV_{aq}}{V_{aq}} \quad (2)$$

where H_{cc} is the Henry's constant, V_g is the volume of the gas phase, K_d is the sludge-water distribution coefficient, and X_v is the volatile suspended solids concentration of the sludge.

The value used for log K_d of *N*-EtFOSE was 4.6 L/g. It was estimated from its octanol–water distribution coefficient (K_{ow}) using the relationship developed by Matter-Muller et al. (*26*). A log K_{ow} value of 4.89 (unitless) was estimated for *N*-EtFOSE from the value previously determined for *N*-MeFOSE (*27*), adjusted to account for the additional CH_2 group (*28*). Use of K_{ow} to predict K_d may introduce error because the Matter-Muller relationship was not calibrated using polar compounds (*29*). Therefore, this model should be updated as better solids partitioning data become available.

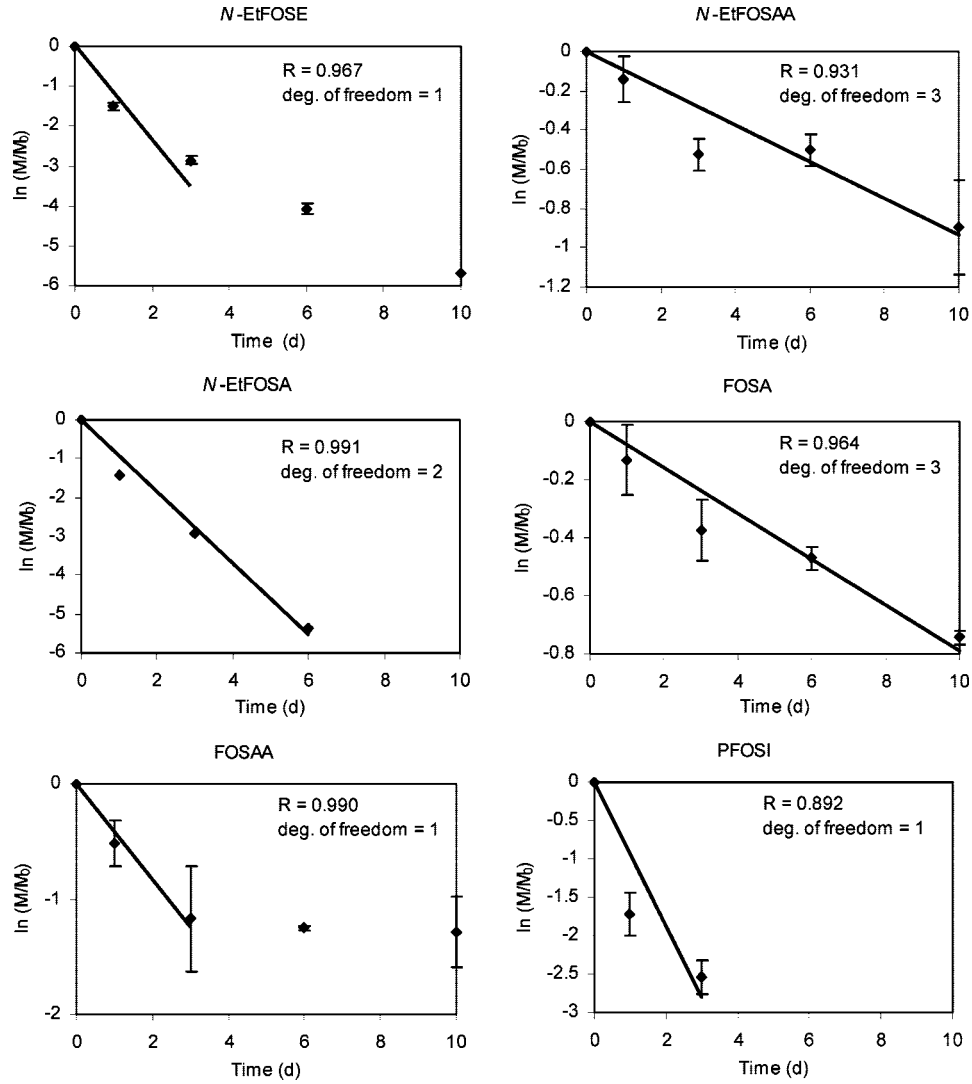

FIGURE 2. Scatter plots to determine of first-order rate constants. Error bars represent ± one standard deviation (n = 3). Standard deviations not available for N-EtFOSA because one replicate was lost during analysis.

TABLE 2. Observed Rate Constants, k_{obs}, and Half Lives in Activated Sludge at 30 °C (mean ± standard deviation)

test compound	first-order rate constant (day^{-1})	half life (days)	pseudo-second order rate constant (L/g VSS day^{-1})
N-EtFOSE	0.99 ± 0.08	0.71 ± 0.05	0.26 ± 0.02
N-EtFOSAA	0.093 ± 0.012	7.5 ± 1.0	0.025 ± 0.003
FOSAA	0.41 ± 0.15	1.89 ± 0.79	0.11 ± 0.04
FOSA	0.075 ± 0.003	9.2 ± 0.3	0.020 ± 0.001
N-EtFOSA	0.92[a]	0.75[a]	0.24[a]
PFOSI	0.95 ± 0.07	0.73 ± 0.054	0.25 ± 0.02

[a] One replicate was destroyed during analysis so the average is based on duplicate samples, and no standard deviation is available.

Results and Discussion

Serum Bottle Assays. No compounds were detected in any of the headspace samples filtered with C18 cartridges. This method has been previously used to measure *N*-EtFOSE in pure water samples, however the concentration of analytes in the headspace above sludge in the current study was below the detection limit due to solids partitioning. A phase partitioning analysis predicts that 2.6% of the total *N*-EtFOSE exists in the gas phase at equilibrium. All amounts reported are for lyophilized sludge extracts.

The parent compound *N*-EtFOSE decreased from an initial 7.0 ± 0.6 nmol/bottle to 0.024 ± 0.042 nmol/bottle after 10 days in aerobic sludge (Figure 1). A table of complete results with statistical information is included in the Supporting Information (Table S1). The observed first-order rate constant for the disappearance of *N*-EtFOSE calculated from the linear portion (days 0–3) of the regression in Figure 2 (R = 0.967, degrees of freedom = 1) is k_{obs} = 0.99 ± 0.08 day^{-1}, corresponding to a half-life of 0.71 ± 0.06 days (Table 2). The aqueous rate constant for *N*-EtFOSE is k = 17.5 ± 1.3 day^{-1} or 5.0 ± 0.4 L/g VSS day^{-1}. The primary metabolite was *N*-EtFOSAA, which increased from an initial mass of 0.22 ± 0.00 nmol/bottle to a maximum mass of 6.8 ± 0.3 nmol/bottle at day 3 before decreasing to 5.3 ± 0.8 nmol/bottle at day 10. The relatively slow transformation of *N*-EtFOSAA (k_{obs} = 0.093 ± 0.012 day^{-1}) compared to *N*-EtFOSE may explain its high concentration in domestic sludge, which often exceeds that of PFOS (*25*). The fact that *N*-EtFOSAA was detected in time zero samples after spiking with *N*-EtFOSE and freezing the samples is consistent with fast oxidation of *N*-EtFOSE through an aldehyde intermediate (Figure 3). *N*-EtFOSA, FOSA, FOSAA, and PFOSI all first appear from *N*-EtFOSE at day 1. The last compound to appear is PFOS at day 3, indicating that multiple transformations steps are necessary for its production. PFOS is extremely stable, and previous studies have shown that it is not transformed in

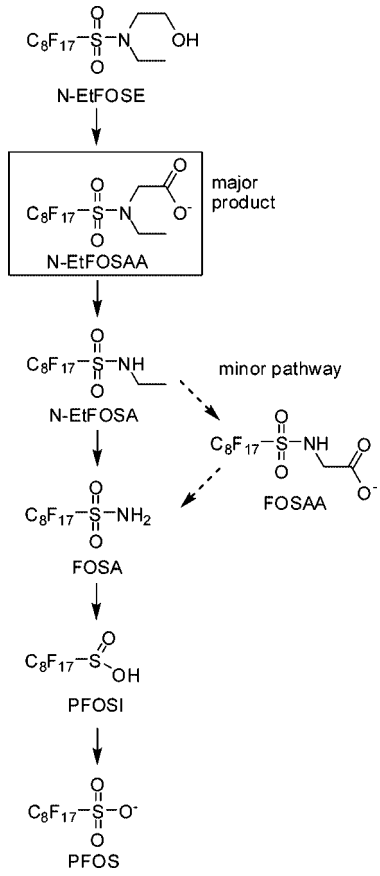

FIGURE 3. Proposed transformation pathway of *N*-EtFOSE in activated sludge.

microbial cultures (*2*). It was detected as the terminal transformation product of all six compounds tested in this study. Lange detected PFOA (*17*), and postulated that it was a product of PFOSI hydrolysis. We detected contaminant PFOA in all PFOSI incubations (active and control), but its concentration did not increase over time.

In our assays, only 21% of the added *N*-EtFOSE remained after one day, and FOSAA, FOSA, and PFOS were detected at that time. Boulanger et al. (*22*) detected only *N*-EtFOSAA and PFOSI as *N*-EtFOSE products and did not detect FOSAA, FOSA, or PFOS. Given that 40% of the initial *N*-EtFOSE remained in their samples after four days, it is possible that their incubations lacked a factor (sufficient incubation time, biomass, oxygen, etc.) required for transformation of *N*-EtFOSAA and accumulation of products.

A mass balance is provided in Table S1. *N*-EtFOSE disappeared in the activated sludge, but appreciable removal did not occur in autoclaved sludge controls, implicating microbial transformation as the removal mechanism. For those samples spiked with *N*-EtFOSE, the total moles of analytes was 7.3–9.6 nmol/bottle for active microcosms and 6.8–10.3 nmol/bottle for control microcosms. On day 10, the sum of moles of *N*-EtFOSE and its transformation products was 111% of the sum of moles on day 0. For samples spiked with *N*-EtFOSE transformation products, however, the sum of the moles of added compound and products ranged from 61 to 81%. The incomplete mole balance for samples spiked with transformation products of *N*-EtFOSE suggests that unidentified transformation products were formed, and/or that one or more of the *N*-EtFOSE transformation products binds irreversibly to biomass, making it resistant to extraction and quantification. Data for samples spiked with *N*-EtFOSA support the latter hypothesis. Despite the addition of equal amounts of *N*-EtFOSA to active and control samples, the number of moles measured on day zero in active incubations was 3.9 ± 2.0 nmol/bottle, while the amount measured in autoclaved controls was 7.1 ± 1.6 nmol/bottle, suggesting fast and irreversible binding of *N*-EtFOSA to live cells. This trend continued for all other sampling points. Similarly, Lange (*21*) found only 31% of the original *N*-EtFOSA remaining in culture incubations after 18 days and detected no products. He hypothesized that the loss was due to volatilization since the bottles were open. Given that our assays were performed in sealed bottles, the more likely removal mechanism is binding to biomass.

PFOA was detected at 0.21−0.31 nmol/bottle in both active and control incubations spiked with PFOSI but since concentrations remained constant over time, this detection is most likely due to contamination of the PFOSI starting material. Further testing confirmed that PFOA is present in the PFOSI starting material (data not shown). PFOA was not detected in microcosms spiked with any of the other compounds, except one replicate in a control microcosm spiked with N-EtFOSAA. Therefore, the effects of this impurity appear limited. The only biotransformation product from PFOSI was PFOS, which was also detected in autoclaved controls but the concentration of PFOS did not increase with time.

Pathway. The proposed pathway in Figure 3 is based upon the observed transformation products from batch incubations. Our pathway agrees with that of Lange (*17*), except in two details: (1) production of PFOA (reported by Lange, but not observed here), and (2) the pathway for FOSA production. Lange proposed oxidation of *N*-EtFOSA to FOSAA followed by dealkylation to FOSA. We found FOSA production in one day from *N*-EtFOSA, with FOSAA production delayed until day 6. The rate of *N*-EtFOSA transformation is higher than the rate of FOSAA transformation, so accumulation of FOSAA should occur if it is a major intermediate. But FOSAA did not accumulate. We therefore surmise that *N*-EtFOSA undergoes direct dealkylation to FOSA, while FOSAA production proceeds at a slower rate.

Transformation Rate Modeling. To test the overall transformation pathway for consistency and to assess the predictive power of individually measured transformation rates, a MATLAB model was developed to model the degradation of *N*-EtFOSE using the first-order rates measured for each individual compound. The starting conditions were set to those at time zero in the *N*-EtFOSE transformation experiment, and all reactions were allowed to occur simultaneously. FOSAA was ignored because it is formed by a minor branching pathway. The model correctly predicted *N*-EtFOSAA as the major product at day 10. It also predicted an increase in *N*-EtFOSAA from days 0–3 and a decrease from days 6–10, replicating the patterns observed in the batch assay of *N*-EtFOSE. At day 10, the predicted quantity of *N*-EtFOSE remaining was 0.0003 nmol, and the amount of PFOS produced was 0.86 nmol. The greater extent of transformation predicted by the model can be attributed to use of a first-order rate for *N*-EtFOSE from data for days 0–3 that is higher than the rate at later time periods. The full model output is provided in the Supporting Information (Table S2).

WWTP Fate Modeling. Using literature values for phase partitioning with the biotransformation kinetics determined in this study, we modeled removal of *N*-EtFOSE in a typical activated sludge WWTP. The model assumed steady-state operation of an open completely mixed aeration basin with forced aeration and a sedimentation tank with sludge recycle as per Barton (*30*). We assumed that no reaction occurs during primary sedimentation or secondary sedimentation. Partitioning of *N*-EtFOSE was modeled using its estimated K_{ow} and Henry's law constant as stated above. Other model inputs were: temperature = 20 °C, aeration basin residence time =

7 h, solids retention time = 10 days, liquid diffusivity = 3.63×10^{-10} m^2/s (estimated by the Wilke and Chang relationship (*31*)), and temperature correlation base for biodegradation rate constant = 1.1. A list of input parameters is available in the Supporting Information (Table S3).

The predicted fraction of *N*-EtFOSE sorbed to waste solids is 5%, and the predicted fraction biotransformed is 13%, with 6% exiting in the plant effluent. Little production of PFOS is predicted. The major transformation product is *N*-EtFOSAA, which sorbs to solids (log K_d = 3.49 (*32*)), but is neither stripped nor biotransformed at a high rate. Consequently, processes affecting waste solids treatment become important. Most importantly, the model predicts that air stripping will remove 76% of *N*-EtFOSE. WWTPs could thus be one source of atmospheric *N*-EtFOSE (*13, 33*), and could contribute to the dispersal and global detection of PFCAs and PFSAs.

Acknowledgments

We thank Melissa Schultz for help obtaining internal standards. We also thank staff of the Palo Alto Regional Water Quality Control Plant for sludge procurement. Funding was provided by the National Science Foundation Division of Bioengineering and Environmental Systems for research (0201955) and instrumentation (0216458). Kurt Rhoads was supported by a U.S. Environmental Protection Agency Science to Achieve Results (STAR) Fellowship.

Supporting Information Available

Complete batch incubation results with statistical information in table format, transformation rate model output, and WWTP fate model input parameters. This material is available free of charge via the Internet at http://pubs.acs/org.

Literature Cited

(1) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.* **2006**, *40*, 3463–3473.

(2) Key, B. D.; Howell, R. D.; Criddle, C. S. Defluorination of organofluorine sulfur compounds by Pseudomonas sp. strain D2. *Environ. Sci. Technol.* **1998**, *32*, 2283–2287.

(3) Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T. Fluorotelomer alcohol biodegradation—direct evidence that perfluorinated carbon chains breakdown. *Environ. Sci. Technol.* **2005**, *39*, 7516–7528.

(4) Calafat, A. M.; Kuklenyik, Z.; Caudill, S. P.; Reidy, J. A.; Needham, L. L. Perfluorochemicals in pooled serum samples from United States residents in 2001 and 2002. *Environ. Sci. Technol.* **2006**, *40*, 2128–2134.

(5) Yeung, L. W. Y.; So, M. K.; Jiang, G. B.; Taniyasu, S.; Yamashita, N.; Song, M. Y.; Wu, Y. N.; Li, J. G.; Giesy, J. P.; Guruge, K. S.; Lam, P. K. S. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. *Environ. Sci. Technol.* **2006**, *40*, 715–720.

(6) Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldous, K. M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ. Sci. Technol.* **2004**, *38*, 4489–4495.

(7) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. Identification of long-chain perfuorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* **2004**, *38*, 373–380.

(8) Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in the Canadian arctic: evidence of atmospheric transport and local contamination. *Environ. Sci. Technol.* **2007**, *41*, 3529–3536.

(9) Kissa, E., *Fluorinated Surfactants, Synthesis, Properties, Applications*; Marcel Dekker: New York, 1994; Vol. 50.

(10) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32–44.

(11) *3M. Fluorochemical Use, Distribution and Release Overview*; U.S. EPA Docket AR-226–0550; St. Paul, MN, 1999.

(12) *3M. Phase-Out Plan for PSOF-Based Products*; U.S. EPA Docket AR-226–0600; St. Paul, MN, 2000.

(13) Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Polyfluorinated telomer alcohols and sulfonamides in the North American troposphere. *Environ. Sci. Technol.* **2004**, *38*, 991–996.

(14) Martin, J. W.; Muir, D. C.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Anal. Chem.* **2002**, *74*, 584–90.

(15) D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric chemistry of *N*-methyl perfluorobutane sulfonamidoethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$: kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40*, 1862–1868.

(16) Hekster F. M., V. P. d., Pinjenburg AMCM, Laane, RWPM. *Perfluoroalkylated Substances - Aquatic Environmental Assessment; Report RIKZ/2002.043*; National Institute for Coastal and Marine Management/RIKZ: Amsterdam, The Netherlands, 2002.

(17) Lange, C. C. *The Aerobic Biodegradation of N-EtFOSE Alcohol by the Microbial Activity Present in Municipal Wastewater Treatment Sludge*; U.S. EPA Docket AR-226–058; 3M Environmental Laboratory: St. Paul, MN, 2000.

(18) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry - Characterization of municipal wastewaters. *Environ. Sci. Technol.* **2006**, *40*, 289–295.

(19) Schultz, M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F.; Field, J. A. Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ. Sci. Technol.* **2006**, *40*, 7350–7357.

(20) Sinclair, E.; Kannan, K. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environ. Sci. Technol.* **2006**, *40*, 1408–1414.

(21) Lange, C. C. *The 18-Day Aerobic Biodegradation Study of Perfluorooctanesulfonyl-Based Chemistries*; U.S. EPA docket AR-226–1030; 3M Environmental Laboratory: St. Paul, MN, 2001.

(22) Boulanger, B.; Vargo, J. D.; Schnoor, J. L.; Hornbuckle, K. C. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. *Environ. Sci. Technol.* **2005**, *39*, 5524–5530.

(23) Powley, C. R.; George, S. W.; Ryan, T. W.; Buck, R. C. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. *Anal. Chem.* **2005**, *77*, 6353–6358.

(24) Hekster, F. M.; Laane, R. W. P. M.; de Voogt, P.; Ware, G. W., Environmental and toxicity effects of perfluoroalkylated substances. In *Reviews of Environmental Contamination and Toxicology*;, Springer-Verlag Inc.: New York, NY, 2003; *Vol 179*, pp 99–121.

(25) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. *Environ. Sci. Technol.* **2005**, *39*, 3946–3956.

(26) Matter-Muller, C.; Gujer, W.; Giger, W.; Stumm, W. Non-biological elimination mechanisms in a biological sewage-treatment plant. *Prog. Water Technol.* **1980**, *12*, 299–314.

(27) *3M. Determination of the Partition Coefficient (n-octanol/water) of T-5874 by High Performance Liquid Chromatography (HPLC)*; NOTOX: 's-Hertogenbosch, The Netherlands, 1994.

(28) William, M. Meylan, P. H. H. Atom/fragment contribution method for estimating octanol-water partition coefficients. *J. Pharm. Sci.* **1995**, *84*, 83–92.

(29) Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. The partition behavior of fluorotelomer alcohols and olefins. *Environ. Sci. Technol.* **2006**, *40*, 3572–3577.

(30) Barton, D. A. Intermedia transport of organic compounds in biological wastewater treatment processes. *Environ. Prog.* **1987**, *6*, 246–255.

(31) Wilke, C. R.; Chang, P. Correlation of diffusion coefficients in dilute solutions. *AIChE J.* **1955**, *1*, 264–270.

(32) Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006**, *40*, 7251–7256.

(33) Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers. *Environ. Sci. Technol.* **2004**, *38*, 1313–1320.

ES702866C