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Use of on-site bioreactors to estimate the biotransformation rate of *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) during activated sludge treatment

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HIGHLIGHTS

- We measured the biotransformation of *N*-EtFOSE, a fluorinated repellent.
- We installed on-site activated sludge bioreactors at a wastewater treatment plant.
- *N*-EtFOSAA was detected as the sole biotransformation product.
- *N*-EtFOSE biotransformed with a rate constant of $k = 2.0$ and 2.4 L g^{-1} VSS day^{-1}.

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ABSTRACT

Accurate rates are needed for models that predict the fate of xenobiotic chemicals and impact of inhibitors at full-scale wastewater treatment plants. On-site rates for aerobic biotransformation of *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), a fluorinated repellent, were determined by continuously pumping mixed liquor from an aeration basin into two well-mixed acrylic bioreactors (4-L) operated in parallel. Known masses of *N*-EtFOSE and bromide were continuously added to the reactors. Reactor effluents were then monitored for bromide, *N*-EtFOSE, and metabolites of *N*-EtFOSE. Of the six transformation products reported in batch studies, only *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA) was detected in the effluents. Bromide addition to the reactors enabled rate estimates despite variations in flow rate. Pseudo-second order rate coefficients for the *N*-EtFOSE biotransformation to *N*-EtFOSAA, predicted using a dynamic model of the reactor system, were $k = 2.0$ and 2.4 L g^{-1} VSS d^{-1} for the two reactors, which are slower than the rates previously obtained using batch reactors. Given the relatively slow rate of *N*-EtFOSE transformation, its sorption and volatilization may be important in wastewater processes. The methodology used in this study should be suitable for similar on-site rate assessments with other contaminants or inhibitors.

1. Introduction

Fluorinated sulfonamides, used for more than 40 years as repellent coatings on paper, textiles, carpeting, and food packaging (Butenhoff et al., 2006), contribute to the worldwide dispersal of fluorinated compounds. The environmental fate of fluorinated sulfonamides depends on whether they are released in wastewater, the atmosphere, or in solid form. Previous work has suggested that they may be transported in the atmosphere, chemically transformed to stable, less volatile species, and deposited (D'Eon et al., 2006; Stock et al., 2007; Young et al., 2007; Ahrens, 2011). It remains to be determined, however, to what extent fluorinated sulfonamides discharged in wastewater are biotransformed, transported to the atmosphere, or removed by sorption to solids at wastewater treatment plants (WWTPs). A key piece of information needed for this determination is the biotransformation rate. In this study, we describe a method for estimating the *in situ* biotransformation rate of the fluorinated sulfonamide repellent *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) using an on-site flow-through bioreactor. The methodology developed could be applied to other trace contaminants or inhibitory agents.

In previous batch studies, *N*-EtFOSE biotransformed in activated sludge via pseudo-second order kinetics to form six products, including *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA) and, ultimately, perfluorooctane sulfonate (PFOS) (Rhoads

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et al., 2008). Biotransformation of *N*-EtFOSE to *N*-EtFOSAA was rapid but subsequent products transformed slowly relative to the hydraulic retention time of a WWTP, so *N*-EtFOSAA was the predicted biotransformation product in WWTP effluent. Nonetheless, the concentration of PFOS appears to increase during activated sludge treatment, suggesting a PFOS source is present in wastewater (Sinclair and Kannan, 2006; Xiao et al., 2012). While *N*-EtFOSE is toxic itself (Case et al., 2001), its fate is of interest primarily because the final end product PFOS is toxic, persistent, and bioaccumulative (Newsted et al., 2005; Houde et al., 2006; Conder et al., 2008).

During the manufacturing of textiles and paper, plants discharge wastewater containing *N*-EtFOSE and related perfluorosulfonamides to WWTPs for activated sludge treatment (USEPA, 2000). *N*-EtFOSAA, the first stable oxidation product of *N*-EtFOSE has been detected in wastewater, activated sludge, and human blood (Higgins et al., 2005; Schultz et al., 2006; Calafat et al., 2007; Kato et al., 2009). The question remains, however, as to the fate of perfluorosulfonamides during wastewater treatment, where biotransformation, stripping, and sorption all occur simultaneously. Fate prediction requires accurate rate constants for all three processes. *N*-EtFOSE stripping may be significant because of its volatility and the high aeration rates typically used during activated sludge treatment (Rhoads et al., 2008; Dreyer et al., 2009). *N*-EtFOSE, PFOS, and other fluorinated compounds have been detected in the air near wastewater treatment plants (Ahrens et al., 2011). *N*-EtFOSE has also been detected in both outdoor and indoor air (Shoeib et al., 2005, 2010; Loewen et al., 2008; Goosey and Harrad, 2011). Fluorinated sulfonamides are hydrophobic and may sorb to solids (Arp et al., 2006; Higgins and Luthy, 2006). In activated sludge, higher concentrations have been reported in solids compared to the aqueous phase Once discharged to the environment, fluorinated sulfonamides can transform into perfluorinated carboxylic acids, such as perfluorooctanoic acid (PFOA), via indirect photolysis in natural waters or via atmospheric reaction with hydroxyl radicals (D'Eon et al., 2006; Plumlee et al., 2009).

Attempts to explain the global distribution of perfluoroalkyl compounds using global fate models have been hindered by the lack of reliable transformation data. Armitage et al. (2009) used an overall *N*-EtFOSE to PFOS conversion rate of 1–4.5%, which assumes that all *N*-EtFOSE is transformed atmospherically and ignores biotransformation. Prevedouros et al. (2006) assumed that 0.5–1% of emitted *N*-EtFOSE converts to PFOA. These simplified assumptions do not capture the complexity of phase changes, biotransformation, and atmospheric transformations.

Existing *N*-EtFOSE biotransformation rate data can be questioned on the grounds that they do not simulate on-site conditions. Determining biotransformation rates has been especially difficult for fluorochemicals because of the challenges in analyzing and achieving mass balances for this group of contaminants. In two previous studies, *N*-EtFOSE biotransformation was measured in batch microcosms containing activated sludge diluted with mineral medium (Lange, 2000; Boulanger et al., 2005). Subsequent batch studies were performed with undiluted activated sludge (Rhoads et al., 2008). Common biotransformation test protocols also use batch systems, including the Organisation for the Economic Co-operation and Development Test 314 (OECD, 2008), ASTM Test E1720-01 (ASTM, 2008), and the USEPA test for aerobic aquatic biodegradation (USEPA, 1998). The kinetic data obtained from such systems is unlikely to capture the physiological state of microbial biomass in a continuous-flow aeration basin. The concentrations of electron donors and acceptors decrease with time in a batch system, but remain relatively constant in mixed continuous-flow systems. The nutrients provided in batch media may also select for a different microbial community compared to the activated sludge inoculum, and the new microbial community may differ in enzymatic activity and rates of biotransformation. To overcome such limitations, Temmink and Klapwijk (2003) developed a "by-pass" test, in which a continuous-flow reactor circulated sludge from a pilot-scale (490 L) aeration basin.

The current study uses the by-pass strategy to estimate the kinetics of *N*-EtFOSE transformation in WWTPs. An improved version of the by-pass test was developed using activated sludge withdrawn from the aeration basin of a full-scale municipal WWTP to approximate *in situ* kinetics. The system simulates activated sludge treatment by continuously maintaining activated sludge and dissolved oxygen levels that match those of the full-scale aeration basin. To our knowledge, this study is the first to measure the biotransformation rate of a trace organic contaminant using a by-pass test in a full-scale activated sludge bioreactor. This method could be extended to test transformation rates of other chemicals or to test the impact of reactor conditions on transformation rates.

2. Materials and methods

2.1. Reactor setup

The sources and purities of the eight fluorochemicals used in this study have been given previously (Rhoads et al., 2008). Two independent experimental setups, each consisting of one acrylic bioreactor (total volume = 5 L; working liquid volume = 4 L), mixer, peristaltic pump, and syringe pump (Fig. 1) were installed at the Palo Alto Water Quality Control Plant (PAWQCP). The peristaltic pumps drew activated sludge directly from the PAWQCP aeration basin to each bioreactor. The pumps were controlled by a timer and set at a flow rate of 5 mL min^{-1} to match the hydraulic detention time, 13 h, of the full-scale basin. The sludge flow rate was measured directly by measuring the effluent volume over an approximately 30-min period. The reactor effluent overflowed into a Y tube that separated the slurry effluent from the gas effluent. Pure oxygen was supplied from a tank to the reactor headspace at a minimal flow rate (<50 mL min^{-1}) to minimize fluorochemical volatilization and maintain the dissolved oxygen concentration in the range of 1.2–4.5 mg L^{-1}. The gas effluent from each reactor was filtered through two C18 solid phase extraction cartridges (Alltech, Deerfield, IL; 0.6 g medium) in series. Cartridges were preconditioned with 10 mL methanol and air-dried before use. Viton® tubing was used to carry activated sludge and Tygon tubing to carry oxygen.

N-EtFOSE was delivered via syringe pump in 50:50 water:methanol solution along with a sodium bromide tracer (Christianson et al., 2011). The delivery rate of *N*-EtFOSE, as measured in the lab-

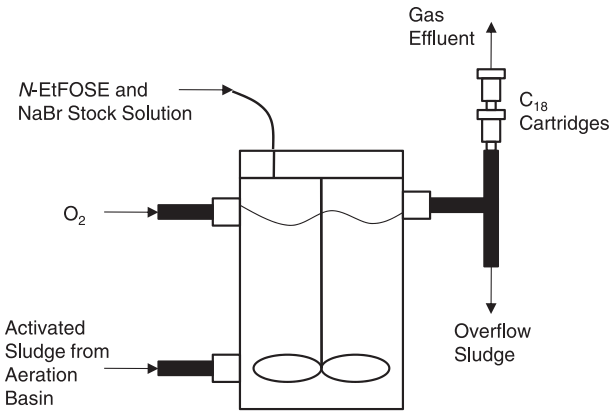

Fig. 1. Flow-through bioreactor.