Available online at www.sciencedirect.com
SCIENCE DIRECT®
Ecotoxicology and Environmental Safety 64 (2006) 30–41
Ecotoxicology and Environmental Safety
www.elsevier.com/locate/ecoenv

Fate of free and linear alcohol-ethoxylate-derived fatty alcohols in activated sludge

Thomas W. Federle*, Nina R. Itrich

Central Product Safety Department, The Procter & Gamble Co., Miami Valley Innovation Center, P.O. Box 538707, Cincinnati, OH 45253-8707, USA

Received 17 February 2005; received in revised form 2 May 2005; accepted 8 May 2005
Available online 18 July 2005

Abstract

Pure homologues of [1- ^{14}C] C_{12}, C_{14}, and C_{16} alcohols and the linear alcohol ethoxylates, AE [1- ^{14}C alkyl] $C_{13}E_9$ and $C_{16}E_9$ were tested in a batch-activated sludge die-away system to assess their biodegradation kinetics and to predict levels of free alcohol derived from AE biodegradation in treated effluent. First-order rates for primary biodegradation were similar for all alcohols (86–113 h^{-1}) and were used to predict removal under typical treatment conditions. Predicted removals of fatty alcohols ranged from 99.76% to 99.85%, consistent with published field data. During the biodegradation of the AE homologues, lower than expected levels of fatty alcohol based upon the assumption that biodegradation occurs through central fission were observed. Rather than fatty alcohols, the major metabolites were polar materials resulting from *omega* oxidation of the alkyl chain prior to or concurrent with central cleavage. The amounts of free fatty alcohols that were formed from AEs in influent and escape into effluent were negligible due both to their rapid degradation and to the finding that formation of free alcohol through central cleavage is only a minor degradation pathway in activated sludge.

Keywords: Fatty alcohol; Linear alcohol ethoxylate; Surfactant; Biodegradation; Activated sludge; Wastewater treatment; Environmental fate

1. Introduction

Fatty alcohols and fatty-alcohol-derived surfactants are major components of domestic wastewater. In 2002, over 500,000 metric tons of fatty alcohol and fatty-alcohol-based surfactants were consumed in North America. Approximately 67% of this tonnage consisted of alcohol ethoxylates (AE) or sulfated AE, while 15% was composed of alkyl sulfates and 6% was represented by free alcohols. Free fatty alcohols are used extensively in cosmetics, toiletries, and pharmaceutical preparations, while fatty-alcohol-based surfactants are used widely in laundry detergents, hard surface cleaners, and personal cleansing products (Modler et al., 2004).

There is little question that fatty alcohols are rapidly and fully biodegradable. For example, hexadecanol has been shown to be extensively mineralized to carbon dioxide in an OECD 301B ready test and in freshly collected samples of activated sludge, river water, and soil (Federle et al., 1997). Nevertheless, there is little specifically known about the actual rates of this biodegradation in sewage treatment for a range of chain lengths. Rates of biodegradation control the efficiency of removal during treatment and the level of fatty alcohols escaping in effluents. In addition, free fatty alcohols in wastewater are not the only possible source of fatty alcohols in treated effluents. AE and alkyl ethoxy sulfates have been shown to undergo central cleavage leading to the formation of free alcohols (Swisher, 1987). Likewise, the biodegradation of alkyl sulfates initially involves sulfatase reactions that yield free fatty alcohols and sulfate (Thomas and White, 1989). While free fatty alcohols have been measured in wastewater and treated effluents (McAvoy et al., 1998; Morrall et al., 2005; Eadsforth et al., 2005),

*Corresponding author. Fax: +1 513 627 1208.
E-mail address: federle.tw@pg.com (T.W. Federle).

0147-6513/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.ecoenv.2005.05.008

the dynamics of their degradation and formation during wastewater treatment have not been investigated.

The objectives of the work reported in this paper were to: (1) assess the kinetics of fatty alcohol biodegradation in activated sludge as a function of chain length, (2) estimate removal in activated sludge based upon these kinetics, (3) examine the biodegradation of AE in activated sludge with special attention to the formation of free fatty alcohol, and (4) estimate the level of free alcohol derived from this biodegradation that was escaping in activated sludge effluents. Radiolabeled [1- ^{14}C] C_{12}, C_{14}, and C_{16} alcohols and the AE, $C_{13}E_8$, and $C_{16}E_8$, radiolabeled in the alcohol moiety (1- ^{14}C), were dosed at trace levels into freshly collected activated sludge. Disappearance of parent, formation and disappearance of metabolites, uptake into biomass, and mineralization to $^{14}CO_2$ were monitored over time. The resulting kinetic parameters were subsequently used to estimate the fate of free and linear alcohol-ethoxylate-derived fatty alcohols in activated sludge.

2. Materials and methods

2.1. Test materials

The [1- ^{14}C]fatty alcohols, dodecanol, tetradecanol, and hexadecanol, were purchased from American Radiolabeled Chemicals Inc. (ARC, St. Louis, MO). The radiochemical purity for all three materials was $\geqslant$99% based on radio-thin-layer chromatography (Rad-TLC). Specific activities were 295 mCi/g for dodecanol, 257 mCi/g for tetradecanol, and 230 mCi/g for hexadecanol. $C_{13}E_8$ and $C_{16}E_8$ alcohol ethoxylate materials were synthesized at the Procter & Gamble Co. (Cincinnati, OH). [1- ^{14}C]1-bromotridecane or [1- ^{14}C]1-bromohexadecane reacted with octaethyleneglycol to produce AE homologues, which were specifically ^{14}C-labeled in the 1 position of the alkyl moiety. Radiochemical purity was $\geqslant$99% for both materials based upon Rad-TLC, and specific activities were 30 mCi/g for $C_{13}E_8$ and 27.9 mCi/g for $C_{16}E_8$.

2.2. Test overview

Details of the radiolabeled die-away test procedure have been described previously (Federle and Itrich, 1997; Itrich and Federle, 2004). Briefly, a trace concentration of radiolabeled test material was dosed to freshly collected activated sludge in an open test system. Periodically, subsamples were collected, lyophilized, and extracted. The disappearance of parent and progression of metabolite formation and decay were monitored over time by TLC of the extracts with radioactivity detection. Production of $^{14}CO_2$ was determined by comparing total radioactivity in a bioactive treatment compared to that in an abiotic control following acidification using liquid scintillation counting (LSC). Incorporation into biomass was monitored by combustion and LSC analysis of the extracted sludge solids.

2.3. Test system

Activated-sludge-mixed liquor was obtained from Fairfield Wastewater Treatment Plant (Fairfield, OH), which receives predominantly domestic wastewater. The solids level of the mixed-liquor suspended solids was adjusted to 2500 mg/L before use. Two treatments consisting of 1 L each of biologically active sludge and abiotic control sludge were prepared for each test material. The abiotic control was prepared by amending the sludge with 1 g/L mercuric chloride followed by autoclaving for 90 min. The ^{14}C-labeled alcohols were dissolved in methanol, which was diluted with water and dosed into the sludge in 2-L flasks. Fatty alcohols were dosed at a concentration of 0.05 μM and the ^{14}C AEs were dosed at 0.06 μM. With regards to mass, these doses equaled 9.3 μg/L for dodecanol, 10.0 μg/L for tetradecanol, 10.7 μg/L for hexadecanol, 33.0 μg/L for $C_{13}E_8$, and 35.6 μg/L for $C_{16}E_8$. The flasks were continually mixed on a shaker table and incubated at 20 ± 2 °C. Samples were collected for both mineralization and chemical analysis at each sampling interval. In an effort to accurately assess the early events in the biodegradation process, frequent samples were taken during the first 8 h of the test. Subsequent samples were collected after 24 and 48 h.

2.4. Analysis of mineralization

Triplicate 1-mL aliquots of sludge were taken from each treatment, and placed into separate 20-mL glass scintillation vials containing 1 mL of 0.5% HCl. The acidified samples were incubated overnight, mixed with 15 mL of Ultima Gold Scintillation Cocktail (Packard, Meriden, CT), and analyzed by LSC.

2.5. Analysis of parent and metabolites

In the case of fatty alcohols, 25 mL of sludge was collected from each treatment, transferred to a 35-mL screwtopped centrifuge tube, and immediately frozen in a dry ice acetone bath. The frozen samples were stored at −80 °C until lyophilization on a Virtis bench-top Model 3.3-L freeze dryer (Virtis, Gardiner, NY). To recover parent and less polar metabolites, the lyophilized sludge was refluxed with two 5-mL aliquots of methanol at 70 °C for 2 h and subsequently extracted with water to recover more polar intermediates. The methanol extracts were combined, and radioactivity in the methanol and water extracts was determined by LSC. To separate the parent fatty alcohol from its corresponding fatty acid metabolite, the methanol extracts were methylated to convert fatty acids to fatty acid methyl esters prior to TLC analysis. The methanol extracts were dried under nitrogen and refluxed at 100 °C for 2 h with 10:1:1 MeOH:$CHCl_3$:HCl. After cooling, water and chloroform were added to the samples, and the chloroform fraction was recovered and analyzed by Rad-TLC. The solvent extracts were spotted onto prechanneled 60 A Silica Gel 60 TLC plates (Whatman, Clifton, NJ) and developed with petroleum ether:diethyl ether:acetic acid (80:20:1 v:v:v), and the plates were scanned using a Bioscan 200 System (Bioscan, Washington, DC). Due to the very low level of radioactivity recovered in the abiotic water extracts,

the biotic water extracts were assumed to contain only highly polar intermediates and were not further characterized. A similar approach was used for AEs with the following exceptions: 10 mL sludge samples were flash frozen and lyophilized, the initial extraction solvent was 75:25 MeOH:$CHCl_3$, the TLC plates were developed with 90:10:1 $CHCl_3$:MeOH:formic acid, and the extracts were not methylated prior to TLC analysis.

2.6. Analysis of sludge solids for biomass incorporation

The extracted solids were quantitatively transferred to microfuge tubes and centrifuged. The supernatant was decanted, and the solids were combusted in a Packard Sample Oxidizer (Model 307; Hewlett-Packard, Avondale, PA) system and analyzed by LSC.

2.7. Kinetic analyses

The data describing the disappearance of parent were fit to various decay equations using nonlinear regression analysis with Table Curve 2D software, Version 4.0 (Jandel Scientific, San Raefael, CA). Based on statistical considerations and the visual quality of the fit, the two-compartment first-order decay model was used to fit all data. This model has the form

$$y = (Ae^{-k_1 t}) + (Be^{-k_2 t}),$$

where y equals the percentage of parent remaining at time t, A equals the percentage degraded at first-order rate k_1, and B equals the percentage degraded at the first-order rate k_2. Likewise, the mineralization data were fit to a two-compartment first-order production model with the form

$$y = A(1 - e^{-k_1 t}) + B(1 - e^{-k_2 t}),$$

where y equals the percentage of the material mineralized to $^{14}CO_2$ at time t, A equals the percentage $^{14}CO_2$ produced at first-order rate k_1, and B equals the percentage $^{14}CO_2$ produced at the first-order rate k_2.

3. Results

The average recovery of radioactivity from the abiotic controls exceeded 90% for all test compounds (Table 1). The average recovery from the biologically active treatments ranged from 83% to 102%. The lowest average recoveries were obtained with dodecanol and $C_{13}E_8$ alcohol ethoxylate. Table 2 shows the disposition of radioactivity in the test systems at the end of the experiments (48 h). Although the majority of the activity in the fatty alcohol abiotic controls remained as parent, up to 12% of the radioactivity was in the form of transformation products, which extracted into methanol and had chromatographic mobility similar to that of the two major metabolites observed in the biotic treatments. The degradation observed in these treatments was likely due to limited biotic processes that resulted from the incomplete deactivation of the sludge. Less than 0.5% of the radioactivity in the fatty alcohol abiotic controls was recovered in a subsequent water extraction, and 0.6–2.1% remained associated with the extracted solids. In contrast, the amount of radioactivity associated with the solids in the biotic treatments ranged from 17% to 21%, consistent with incorporation of the fatty alcohols into biomass. After 48 h, the level of parent fatty alcohol

Table 1
Percentage of added radioactivity (mean + standard deviation) recovered from abiotic and biologically active (biotic) activated sludge at each sampling ($n = 13$)

Test material	Abiotic	Biotic
$C_{12}OH$	92.3 ± 7.4	85.5 ± 12.9
$C_{14}OH$	97.1 ± 5.8	99.5 ± 6.3
$C_{16}OH$	101.2 ± 5.0	101.6 ± 5.0
$C_{13}E_8$	94.5 ± 5.7	83.0 ± 2.8
$C_{16}E_8$	90.9 ± 5.3	90.6 ± 9.4

Table 2
Final disposition of radioactivity recovered from abiotic and biologically active (biotic) activated sludge after 48 h of incubation

Test material by treatment		Parent (%)	Metabolites[a] (%)	Water extracted (%)	Associated with solids (%)	CO_2 (%)	Total recovery (%)
$C_{12}OH$	Biotic	0.8	5.9	3.5	20.7	73.9	104.8
	Abiotic	78.4	6.7	0.2	0.6	N/A	85.8
$C_{14}OH$	Biotic	1.3	6.3	2.0	21.0	76.7	107.3
	Abiotic	88.6	8.3	0.3	2.1	N/A	99.3
$C_{16}OH$	Biotic	2.6	11.5	2.1	17.1	66.3	99.5
	Abiotic	83.0	11.8	0.5	1.2	N/A	96.5
$C_{13}E_8$	Biotic	0.0	4.8	0.7	10.5	66.4	83.2
	Abiotic	90.4	0.0	N/A	0.7	N/A	91.1
$C_{16}E_8$	Biotic	0.0	6.5	1.8	31.1	58.0	97.3
	Abiotic	89.7	0.0	N/A	5.6	N/A	95.3

[a]Extracted into organic solvent and resolved by TLC.

recovered from the biotic treatments was less than 3%. Six to 12% of the radioactivity was present as methanol-extractable metabolites, and 2.0–3.5% was not extractable into methanol but was recovered in the subsequent water extract. In these treatments, the vast majority of the radioactivity was mineralized (66–77%) or associated with the biosolids (17–21%), consistent with complete biodegradation.

Approximately 90% of the radioactivity in the alcohol ethoxylate abiotic controls was recovered in the form of parent, and no transformation products were observed. The amounts associated with the solids in the abiotic controls were 0.7% for $C_{13}E_8$ and 5.6% for $C_{16}E_8$, compared to 10.5% and 31.1% in the biologically active treatments. No parent and only a low level of metabolites (4.8–5.5%) were recovered from the biotic treatments with the majority of the radioactivity having been mineralized to $^{14}CO_2$ (58–66%).

Fig. 1 shows the Rad-TLC chromatogram of a methanol extract from the $C_{12}OH$ biotic treatment after 30 min. Similar chromatograms were obtained with C_{14} and C_{16} alcohols (not shown). In addition to the parent peak, two other major peaks occur in these chromatograms. The peak to the right of the parent is confirmed to be fatty acid, which was deliberately methylated to its corresponding fatty acid to better resolve it from the parent alcohol. The peak to the left, which is more polar than the alcohol, is unknown. While it was not possible to definitely identify this and other more polar metabolites given their low levels and transient occurrence, it is possible to infer their likely identity based upon their chromatographic behavior and known biochemical pathways. The likely identity for this peak is a fatty alcohol or acid, whose terminal methyl group has undergone *omega* oxidation. It definitely is not a shortened fatty acid since *beta* oxidation would result in the immediate loss of the ^{14}C from the molecule given its 1-C position in the molecule. This metabolite was transient and never accounted for more than 5–8% of the total for any fatty alcohol.

The disappearance of the parent fatty alcohols, formation and disappearance of metabolites, uptake into solids, and formation of $^{14}CO_2$ as a function of time are shown in Fig. 2. Polar metabolites include the polar metabolite recovered in methanol that was just described and uncharacterized polar materials that were too polar to extract into methanol but were subsequently recovered in water. Based upon the location of the label and their polarity, these materials are likely short dicarboxylic acids that were oxidized and shortened from the methyl end by *omega* and *beta* oxidation. Primary biodegradation was very rapid. Only 5% of dodecanol, 7% of tetradecanol, and 32% of hexadecanol remained intact as parent after 1 h. Concurrent with the loss of parent was the instantaneous appearance of fatty acids and polar metabolites, which peaked and

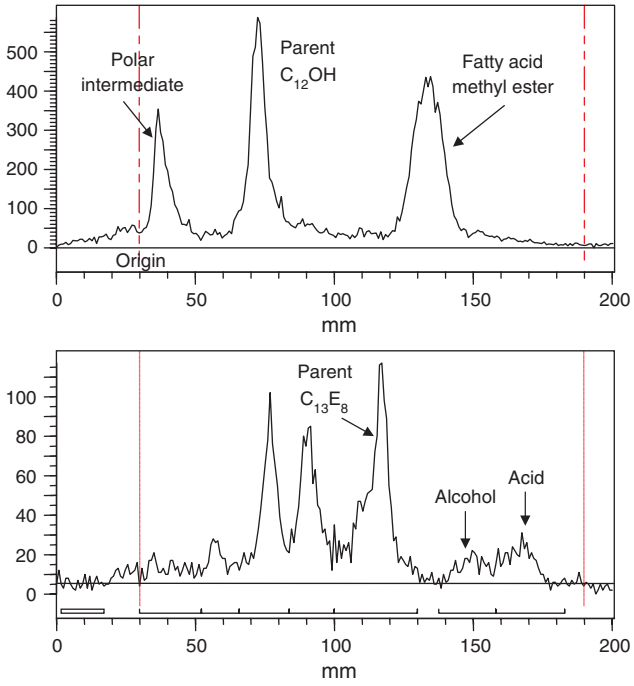

Fig. 1. Rad-TLC chromatograms of organic solvent extracts of bioactive activated sludge incubated with ^{14}C-dodecanol for 30 min (top) and ^{14}C-$C_{13}E_8$ alcohol ethoxylate for 2 min (bottom).

subsequently declined. With increasing fatty alcohol chain length, the ratio of fatty acid compared to the amount of other polar metabolites observed during metabolism increased. In the case of dodecanol, dodecanoic acid reached a maximum level of 7.6% within 0.08 h, while more polar metabolites reached their maximum of 31.7% after 0.02 h. With tetradecanol, tetradecanoic acid reached its maximum level of 18.2% and polar metabolites reached their maximum of 7.7% after 0.08 h. With hexadecanol, hexadecanoic acid reached its maximum of 15.3% after 2 h, while polar metabolites reached their maximum of 7.3% after 1.5 h. The onset of $^{14}CO_2$ production and uptake into solids also occurred concurrently with the disappearance of parent, and its abundance increased as the level of metabolites declined. Mineralization exceeded 32% after 1 h for all fatty alcohols and by 48 h reached 74%, 77%, and 66% for C_{12}, C_{14}, and C_{16} alcohols, respectively. Uptake into biomass estimated by subtracting the level associated with the solids in the abiotic control from the level associated with the solids in the biotic treatment equaled 20.1%, 18.9%, and 15.9% for C_{12}, C_{14}, and C_{16} alcohols, respectively.

A representative Rad-TLC chromatogram for a methanol/chloroform extract from an alcohol ethoxylate biotic sample is also shown in Fig. 1. This specific chromatogram is for a sample from the biologically active $C_{13}E_8$ treatment taken after 2 min. $C_{16}E_8$ (not shown) exhibited a similar R_f value (0.55) for parent and a comparable metabolite pattern. In interpreting the

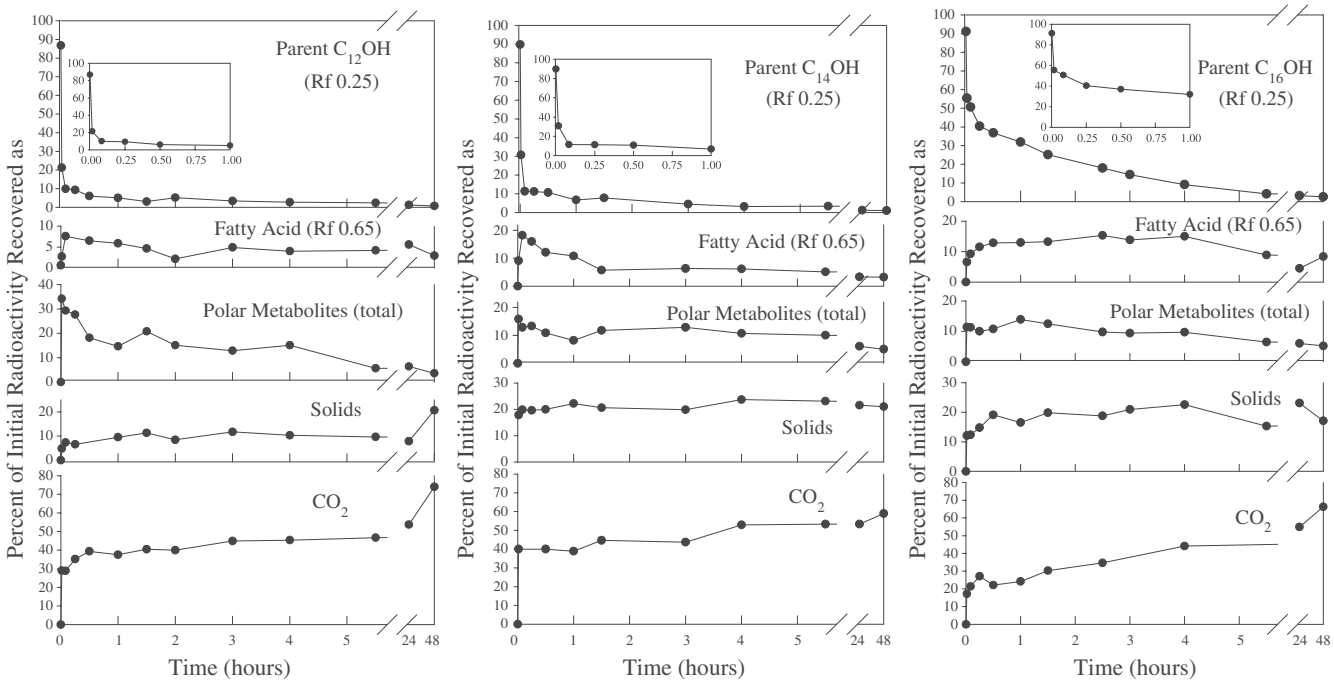

Fig. 2. Percentage of radioactivity present as parent, metabolites, and $^{14}CO_2$ or associated with solids in bioactive activated sludge incubated with [^{14}C]-dodecanol (left), [^{14}C]-tetradecanol (middle), and [^{14}C]-hexadecanol (right) as a function of time.

chromatograms and data for the AE, it should be noted that the extraction and chromatographic conditions differ from those used for the fatty alcohols and the samples were not methylated to better resolve fatty acids, and alcohols. In addition to the parent alcohol ethoxylate peaks, four other major peaks occur in the chromatograms. The peaks to the right of the parent are confirmed to be fatty alcohol and fatty acid. The peaks to the left, which are more polar than the parent, are unknown. Likely identities include fatty alcohol, fatty acid, or otherwise intact AE, which have undergone *omega* oxidation of their opposing methyl ends.

The disappearance of the parent AE, formation and disappearance of metabolites, incorporation into solids, and formation of $^{14}CO_2$ are shown in Fig. 3 as a function of time. In these graphs, polar metabolites include the polar metabolites recovered in methanol/chloroform described above and more polar materials not extracted into methanol/chloroform but subsequently recovered in water. Based upon the location of the label and their polarity, these materials are likely short carboxy alkyl ethoxylates or dicarboxylic acids formed from longer-chain alcohols and acids. Loss of parent $C_{13}E_8$ and $C_{16}E_8$ from the system was very rapid. Less than 5% of both AEs remained intact as parent after 5 min. Concurrent with the loss of parent was the instantaneous appearance of fatty alcohols, fatty acids, and polar metabolites, all of which peaked and subsequently declined. Throughout the experiment, the predominant metabolites were polar materials representing at their peaks 38.6% of $C_{13}E_8$-derived radioactivity at 0.02 h and 47.6% of $C_{16}E_8$-derived radioactivity at 0.08 h. In the case of $C_{13}E_8$, polar metabolites that extracted into methanol chloroform accounted for a maximum of 23.4% of the total radioactivity within 0.08 h, while more polar metabolites recovered in water accounted for a maximum of 21.8% after 0.02 h. With $C_{16}E_8$, metabolites that extracted into methanol/chloroform reached a maximum level of 22.0% within 0.08 h, while more polar metabolites recovered in water reached a maximum of 25.4% after 0.02 h. Fatty alcohol accounted for at most 3.5% and 5.4% of $C_{13}E_8$ and $C_{16}E_8$-derived radioactivity, while the maximum levels of tridecanoic acid and hexadecanoic acid were 2.8% and 2.5%. The onset of $^{14}CO_2$ production occurred concurrently with the disappearance of parent and continued as the level of metabolites declined. Mineralization was rapid, reaching 42% and 39% after 1 h and 66% and 58% after 48 h for $C_{13}E_8$ and $C_{16}E_8$, respectively. Uptake into biomass also began at the same time as disappearance of parent. The level incorporated into biomass, calculated by subtracting the level associated with the solids in the abiotic control from the amount associated with the solids in the biotic treatment, equaled 9.8% for $C_{13}E_8$ and 25.5% for $C_{16}E_8$, after 48 h.

Inspection of the parent decay curves for all the compounds (Figs. 2 and 3) reveals that the disappearance of parent was biphasic with an initial rapid loss followed by a period of slower loss. The deflection point

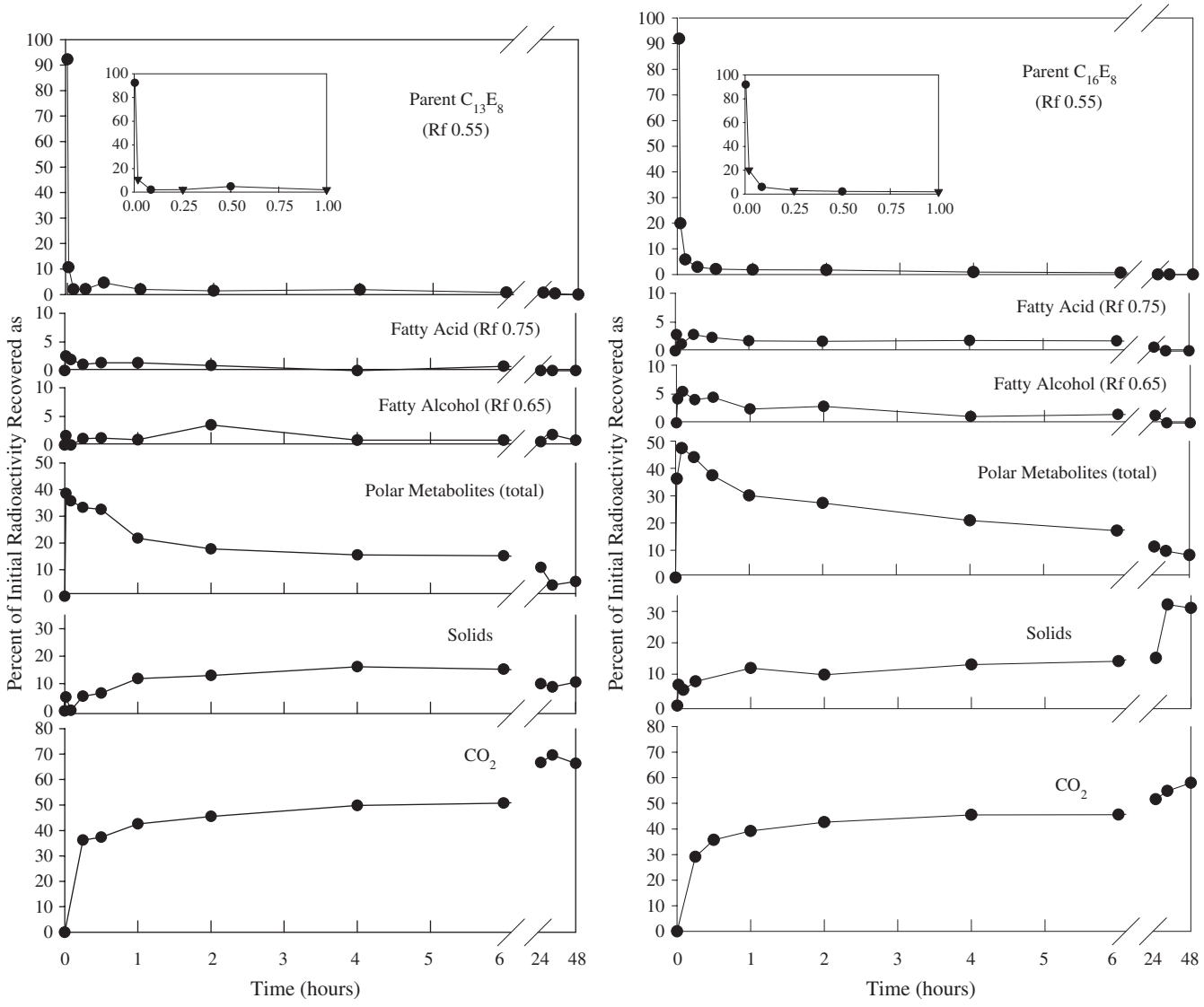

Fig. 3. Percentage of radioactivity present as parent, metabolites, and $^{14}CO_2$ or associated with solids in bioactive activated sludge incubated with ^{14}C–$C_{13}E_8$ (left) and ^{14}C–$C_{16}E_8$ (right) alcohol ethoxylates as a function of time.

varied with test chemical and occurred after 60–97% of the parent had undergone biodegradation. A similar biphasic pattern existed in the $^{14}CO_2$ production curves. The decay and mineralization data were fit to two-compartment models, which describe two pools of material biodegraded at two distinct first-order rates. In the decay model, k_1 describes the rate of biodegradation for a bioavailable pool of the parent material, while k_2 refers to biodegradation of a less bioavailable fraction, which is presumably bound tightly to the sludge solids. The situation with mineralization is more complicated since the pool sizes and mineralization rates not only are related to different environmental forms of parent but also reflect mineralization of metabolites and radioactivity incorporated into biomass. The k_1 for parent is the most relevant for predicting removal of a chemical in an activated sludge system. This rate describes the degradation of the fraction in solution, which is most bioavailable and most likely to escape into the effluent given the low level of sludge solids normally in effluent.

Table 3 shows the kinetic constants describing the loss of parent and production of $^{14}CO_2$ for the different alcohols and AE. In all cases, the initial decay of parent was extremely rapid ($k_1 = 86$–$146\,h^{-1}$), representing half-lives of less than a minute. Given the speed of these reactions and the inability to sample at a correspondingly rapid rate, it is difficult to differentiate materials based upon these rates. With the exception of hexadecanol, the initial rate (k_1) described the loss of the vast majority of the parent (A). Within a chemical class, the fraction of parent (B) decaying at the slower rate (k_2) increased with increasing alkyl chain length. This pattern is consistent with the size of this fraction being a function of sorption to the sludge solids. Increasing

Table 3
Kinetic parameters (estimate + standard error) describing the primary biodegradation and mineralization of fatty alcohols and alcohol ethoxylates based upon two-compartment decay and production models

Test material	r^2	A (%)[a]	k_1 (h^{-1})	B (%)[b]	k_2 (h^{-1})
Decay of parent					
$C_{12}OH$	0.998	81.5 + 1.6	113.1 + 7.5	8.9 + 0.9	0.36 + 0.09
$C_{14}OH$	0.998	81.5 + 1.5	86.5 + 4.5	11.6 + 0.8	0.30 + 0.06
$C_{16}OH$	0.989	41.3 + 3.0	103.4 + 23.2	48.4 + 1.7	0.43 + 0.04
$C_{13}E_8$	0.999	89.3 + 1.7	146.0 + 12.6	2.9 + 1.0	0.21 + 0.41
$C_{16}E_8$	0.999	87.0 + 1.5	105.6 + 5.4	5.1 + 1.1	1.08 + 0.53
Mineralization to $^{14}CO_2$					
$C_{12}OH$	0.996	37.2 + 1.4	11.0 + 3.5	36.5 + 1.7	0.062 + 0.013
$C_{14}OH$	0.998	45.9 + 1.6	3.4 + 0.4	32.1 + 1.6	0.060 + 0.014
$C_{16}OH$	0.987	33.2 + 3.7	1.8 + 0.6	34.4 + 4.2	0.049 + 0.019
$C_{13}E_8$	0.993	38.7 + 1.6	9.3 + 2.6	30.0 + 1.9	0.096 + 0.020
$C_{16}E_8$	0.990	40.1 + 1.3	4.8 + 0.6	17.6 + 1.9	0.061 + 0.023

[a] % of parent degraded or % of total parent converted to CO_2 at first-order rate k_1.
[b] % of parent degraded or % of total parent converted to CO_2 at first-order rate k_2.

alkyl chain length increases hydrophobicity, which would increase partitioning to sludge. This pool was degraded at rates that were more than two orders of magnitude slower than the initial rate. However, if one assumes that this rate describes the loss of sorbed parent, these slow rates are sufficient to prevent significant accumulation in the sludge since a typical sludge residence time (SRT) is more than 40 times the hydraulic residence time (HRT). The slowest observed k_2 of 0.21 h^{-1} represents a half-life of 3.3 h compared to a typical SRT of 240 h. Mineralization rates were more than an order of magnitude slower than the parent decay rates. Within a chemical class, k_1 for mineralization decreased with increasing alkyl chain length, but otherwise the fractions mineralized and k_2 rates for mineralization exhibited no clear patterns as a function of test material.

The first-order rates (k_1) and sorption coefficients from Van Compernolle et al. (2005) were used to estimate removal of the fatty alcohols and AE in the aeration and clarification units of a typical activated sludge treatment plant. The percentage of a material leaving a treatment plant is a function of its first-order biodegradation rate (k_1), its sorption coefficient (K_d), the solids level in the aeration basin ($SS_{reactor}$), the HRT, the solids retention time, and the concentration of solids in the final effluent (SS_{eff}) (Namkung and Rittman, 1987; Itrich and Federle, 2004). The percentages of material entering the influent and leaving as dissolved material in the effluent ($C_{eff(dissolved)}$) were calculated using the equation

$$C_{eff(dissolved)} = \frac{C_{inf}}{1 + k_1\,SS_{reactor}(HRT) + K_d\,SS_{reactor}(HRT/SRT)}, \quad (1)$$

where C_{inf} = influent concentration (100%), $SS_{reactor} = 2.5 \times 10^{-3}$ kg/L, HRT = 6 h, and SRT = 240 h. These HRT, SRT, and $SS_{reactor}$ values are typical values found in the field (Struijs and van de Ment, 1991; Tchobanoglous and Burton, 1991). The percentage of material entering in the influent and sorbed ($C_{eff(sorbed)}$) to effluent solids was calculated from the dissolved material as

$$C_{eff(sorbed)} = C_{eff(dissolved)} K_d\,SS_{eff}. \quad (2)$$

The total percentage in effluent and the percentage removal (R) can then be calculated as

$$C_{eff} = C_{eff(dissolved)} + C_{eff(sorbed)} \quad \text{and} \quad (3)$$

$$R = \frac{C_{inf} - C_{eff}}{C_{inf}} 100. \quad (4)$$

The predicted removal of each material as a function of effluent solids is shown in Table 4. In all cases, removal is predicted to be very high, exceeding 99.76% due to the fast k_1 values. Sorption plays a minor role in removal, but as sorption coefficient increases the effect that the level of effluent solids has on removal increases due to materials leaving the wastewater treatment plant bound to solids. For example, hexadecanol removal is predicted to equal 99.84% with no solids in the effluent but decreases to 99.76% when 20 mg/L of solids are present in the effluent. While this difference appears negligible as it relates to removal, it actually represents a greater than 30% increase in the effluent concentration. Similarly, removal of $C_{16}E_8$ alcohol ethoxylate is predicted to decrease from 99.84% to 99.80% with the presence of 20 mg/L of solids in the effluent, resulting in a 25% increase in the total amount of $C_{16}E_8$ in effluent.

Table 4
Predicted removal of parent fatty alcohol and alcohol ethoxylates from activated sludge as a function of the concentration of effluent solids

Test material	K_d (L/kg)	% Removed as a function of effluent solids[a]		
		0 mg/L	5 mg/L	20 mg/L
$C_{12}OH$	3002[b]	99.85	99.85	99.84
$C_{14}OH$	8486[b]	99.81	99.80	99.77
$C_{16}OH$	23,790[b]	99.84	99.82	99.76
$C_{13}E_8$	1300[c]	99.89	99.89	99.88
$C_{16}E_8$	13,056[c]	99.84	99.83	99.80

[a]Assumes HRT = 6 h, SRT = 240 h, and reactor solids = 2500 mg/L.
[b]Reported in Van Compernolle et al. (2005).
[c]Estimated using QSAR reported in Van Compernolle et al. (2005).

4. Discussion

Primary degradation of free fatty alcohols in activated sludge was extremely rapid. Although the initial decay rates were similar for C_{12}, C_{14}, and C_{16} parent alcohols, the fraction of the total biodegradation defined by this rate differed. In the case of hexadecanol, a much smaller fraction (41% versus >80%) of the material was degraded at this initial rapid rate. Hexadecanol is significantly more sorptive and less soluble than the shorter-chain alcohols. Measured solubility is 4 mg/L for dodecanol, 0.30 mg/L for tetradecanol, and 0.035 mg/L for hexadecanol (Yaws et al., 1997). At the level dosed (~10 μg/L), dodecanol and tetradecanol were at concentrations well below their solubility limits, while hexadecanol was approaching its solubility limit. Hence, hexadecanol's marginal solubility combined with its higher sorption coefficient likely led to higher partitioning to the solids, thereby reducing its bioavailability and altering the shape of its parent decay curve.

Predicted removal of fatty alcohols during typical activated sludge treatment ranged from 99.76% to 99.85% with lower removal in the presence of higher levels of effluent solids. Removal was not greatly affected by chain length beyond the effect of effluent solids. In a recent study, removal of fatty alcohols was examined in different types of wastewater treatment plants including two activated sludge plants (Morrall et al., 2005). Removal was reported for C_{12}–C_{15} fatty alcohols and for longer-chain-length alcohols (C_{16}–C_{18}). Measured removal for the shorter-chain alcohols was 99.89% and 99.76% in the two activated sludge plants, while measured removal of the longer-chain fatty alcohols was 99.79% and 99.54%. Thus, there was reasonable correspondence between predicted removals from laboratory data and field measurements. In another recent study (Wind et al., 2005), a laboratory continuous activated sludge system (CAS) was fed synthetic sewage dosed with a linear AE mixture containing C_{12}–C_{18} fatty alcohols. Mean measured removals for specific alcohols were 98.62% for dodecanol, 99.57% for tetradecanol, and 99.46% for hexadecanol. Mean removal of total fatty alcohol was 99.34%. While removals of fatty alcohols in the CAS were somewhat lower than those predicted from laboratory k_1 and K_d values, it is important to recognize that fatty alcohols in the influent were not the sole source in the effluent since these alcohols could be formed during the biodegradation of AE in the CAS unit. Likewise, free fatty alcohols could be generated from AE, alkyl sulfates, and alcohol ethoxy sulfates in the field. Nevertheless, the small differences between measured and predicted removal in both systems suggest that these alternative sources for fatty alcohol are relatively minor.

Conventional wisdom would dictate that fatty alcohols are oxidized to their corresponding aldehydes, which are further oxidized to their corresponding fatty acids that are ultimately broken down by *beta* oxidation (Rehm and Reiff, 1981). If this were the case with fatty alcohols radiolabeled in the C-1 position, then the initial round of *beta* oxidation would liberate the radiolabel in the form of an acetyl group, which would be quickly mineralized or incorporated into biomass. In addition to fatty acids, larger quantities of polar metabolites were formed in the early stages of the fatty alcohol biodegradation process. These materials can only be products of diterminal oxidation of the alcohols, whereby both *alpha* and *omega* ends of the molecule are oxidized, ultimately leading to the formation of dicarboxylic acids, which can then undergo *beta* oxidation from either end. The generation of *alpha* and *omega* dioic acids has been observed previously during the oxidation of alkanes by a *Corynebacterium* strain (Broadway et al., 1993) and during the oxidation of dodecanoic acid by a *Pseudomonas* strain (Tidswell et al., 1996). This observation of multiple modes of attack should not be surprising given the diversity of the organisms and the high oxidative potential present in activated sludge.

Previous work has examined the effect of alkyl chain length and ethoxylate number on the biodegradation

kinetics of AE in activated sludge using an approach similar to that in this study (Itrich and Federle, 2004). First-order k_1 rates for parent decay varied little as a function of chain length or ethoxylate number for $C_{12}E_6$, $C_{14}E_1$, $C_{14}E_3$, $C_{14}E_6$, and $C_{14}E_9$ and ranged from 61 to 68 h^{-1}. Notably, $C_{16}E_6$ was the exception with a slower k_1 (18 h^{-1}). Primary biodegradation rates in the current study were significantly faster, 146 and 106 h^{-1} for $C_{13}E_8$ and, $C_{16}E_8$, respectively (Table 3). These differences could relate to the different homologues tested or to normal environmental variation. This difference between studies was even more exaggerated for mineralization rates (k_1). Previously, the mineralization k_1 values ranged from 1 to 4 h^{-1}, while in the current study they ranged from 5 to 9 h^{-1}. These differences in rates are explained in part by the position of the radiolabel within the molecules. In the earlier study, the radiolabel was present in the ethoxylate moieties versus the alkyl moieties in the current study. Kravetz et al. (1984) and Steber and Wierich (1985) found that ^{14}C-labeled AEs which were labeled in the alkyl chain exhibited more rapid mineralization than the same materials labeled in their ethoxylate group.

Predicted removal of AE in activated sludge treatment ranged from 99.80% to 99.89% with removal of $C_{13}E_8$ being somewhat higher than that for $C_{16}E_8$, as functions of both its faster degradation and its lower sorption to effluent solids (Table 4). While biodegradation rates were substantially faster than those previously observed (Itrich and Federle, 2004), predicted removals were high in both studies. For example, predicted removal of $C_{14}E_9$ in the previous study assuming 20 mg/L of effluent solids was 99.78%, while predicted removal for $C_{13}E_8$ in the current study is 99.88%. These values can be compared to those observed in a variety of CAS studies. Steber and Wierich (1983) reported >99% removal for a model $C_{18}E_7$ homologue in a CAS system operated with a 3-h HRT and fed real wastewater. Battersby et al. (2001) reported that >99.9% of $C_{12-15}E_3$ and $C_{12-15}E_7$ were removed in a CAS-fed synthetic wastewater, operated with an HRT of 6 h, and based upon high-performance liquid chromatography with fluorescence detection. The AE in the influent of the CAS study conducted by Wind et al. (2005) represented an alcohol ethoxylate mixture, corresponding to that typically found in wastewater, using an HRT of 6 h and synthetic wastewater. In this study, the removal of specific homologues was determined using a new liquid chromatographic/mass spectrometric method that measured all homologues for the first time. Overall mean removal of all homologues was found to equal 99.95%, while specific removals for $C_{13}E_8$ and $C_{16}E_8$ were >99.996% and 99.947%. These removals can be further compared to those measured in the field. McAvoy et al. (1998) used gas chromatography with mass selective detection to measure the total AE concentration in raw influent and effluent from four activated sludge plants and reported removals averaging 99.1 + 0.9%, excluding a single overloaded plant. Notably, removal was inversely correlated with the level of solids in the effluents, consistent with the model predictions. Matthijs et al. (1999) monitored seven municipal treatment plants in the Netherlands and found removal of 99.1% for one plant but 99.7–99.9% for the six other plants. More recently, Morrall et al. (2005) reported removal in two activated sludge plants ranging from 99.68% to 99.89%, depending upon the chain and ethoxylate lengths examined. Overall, there was better correspondence between predicted removals and those measured in the field rather than those measured in CAS studies utilizing synthetic wastewater feed, which exhibited particularly high AE removal values.

Three different pathways have been identified in AE primary biodegradation (Swisher, 1987). In central cleavage, the ether bond connecting the hydrophobe to the ethoxylate chain is broken leading to the formation of fatty alcohol and polyethylene glycol, which are biodegraded independently. Alternatively, the terminal carbon of the alkyl chain can undergo *omega* oxidation, which is followed by inward biodegradation involving *beta* oxidation. Finally, the terminal end of the hydrophile can undergo hydrolytic or oxidative attack. Two important goals in the present study were to evaluate the formation of fatty alcohols during the degradation of AE and to assess the significance of this source of alcohol to levels in treated effluents. These issues were addressed in two ways. First, the formation of fatty alcohols was modeled based upon measured decay rates for AE and fatty alcohols. Second, the formation of fatty alcohol was directly examined during the biodegradation of AEs ^{14}C-labeled in the alkyl chain.

In a batch system, the molar fraction of a parent material present as an intermediate metabolite (C_{met}) as a function of time (t) can be estimated from its rates of formation (k_{form}) and disappearance (k_{loss}) using the following equation:

$$C_{met} = \frac{k_{form}(e^{-k_{form}t} - e^{-k_{loss}t})}{(k_{loss} - k_{form})}. \quad (5)$$

This equation can be used to derive the following, which estimates the molar fraction of parent at steady state in the form of metabolite in an activated sludge reactor as a function of hydraulic retention time

$$C_{reac} = \frac{k_{form}\,HRT}{(1 + k_{loss}\,HRT)(1 + k_{form}\,HRT)}. \quad (6)$$

The fractions of parent in the forms of dissolved (C_{diss}), sorbed (C_{sorb}), and total (C_{Teff}) metabolite in effluent can be further estimated based upon the

Table 5
Predicted concentrations of fatty alcohol derived from alcohol ethoxylates (AE) in activated sludge effluent as a function of the concentration of effluent solids based upon first-order decay rates for AE (k_{form}) and fatty alcohol (k_{loss})

Alcohol ethoxylate	k_{form} (h^{-1})	k_{loss} (h^{-1})	K_d (L/kg) alcohol	Molar fraction of fatty alcohol in effluent as a function of effluent solids			Fatty alcohol (μg) in effluent per mg of AE in influent as a function of effluent solids		
				0 mg/L	5 mg/L	20 mg/L	0 mg/L	5 mg/L	20 mg/L
$C_{12}E_6$	69.2[a]	113	3002[b]	0.00124	0.00126	0.00131	0.51	0.52	0.54
$C_{13}E_8$	146	99.7[c]	1603[d]	0.00152	0.00153	0.00156	0.55	0.55	0.57
$C_{14}E_1$	61.6[a]	86.5	8486[b]	0.00125	0.00131	0.00147	1.04	1.08	1.22
$C_{14}E_3$	70.6[a]	86.5	8486[b]	0.00125	0.00131	0.00147	0.77	0.81	0.91
$C_{14}E_6$	74.0[a]	86.5	8486[b]	0.00125	0.00131	0.00147	0.56	0.59	0.66
$C_{14}E_9$	78.4[a]	86.5	8486[b]	0.00125	0.00131	0.00147	0.44	0.46	0.51
$C_{16}E_6$	17.9[a]	103	23790[b]	0.00063	0.00070	0.00092	0.28	0.32	0.42
$C_{16}E_8$	106	103	23790[b]	0.00063	0.00071	0.00093	0.23	0.26	0.34

Assumes HRT = 6 h, SRT = 240 h, and reactor solids = 2500 mg/L.
[a]Reported in Itrich and Federle (2004).
[b]Reported in Van Compernolle et al. (2005).
[c]Average for C_{12} and C_{14} alcohols.
[d]Estimated using QSAR reported in Van Compernolle et al. (2005).

metabolite's sorption coefficient (K_d)

$$C_{diss} = \frac{C_{reac}}{(1 + K_d\,SS_{reac}(HRT/SRT)}, \quad (7)$$

$$C_{sorb} = C_{diss} K_d\,SS_{eff}, \quad \text{and} \quad (8)$$

$$C_{Teff} = C_{diss} + C_{sorb}, \quad (9)$$

where SS_{reac} equals the level of suspended solids in the reactor and SS_{eff} equals the level of solids in the effluent.

These equations were used to estimate the level of fatty alcohols expected in effluent based upon the assumption that the rate of AE degradation (k_1) is equal to the rate of fatty alcohol formation (k_{form}). This assumption entails the existence of only a single pathway involving central fission to form free fatty alcohol. The AE decay rates were obtained from the current study and from Itrich and Federle (2004). Other assumptions in the calculations include HRT of 6 h, SRT of 240 h and SS_{reac} = 2500 mg/L. The results of the calculations are shown in Table 5. The predicted molar fraction of alcohol ethoxylate converted to fatty alcohol and present in effluent ranged from 0.0006 to 0.0016. When expressed as alcohol in effluent/mg of alcohol ethoxylate in influent, this range was 0.24–1.22 μg depending upon the homologue in question. These predicted levels can be compared to actual measurements of fatty alcohol in various AE CAS studies and to field samples. Battersby et al. (2001) reported less than 2 μg/L of free fatty alcohol in the effluent of CAS systems, which were dosed with 12.5 mg/L of $C_{12-15}E_7$ and 10.7 mg/L of $C_{12-15}E_3$. More recently, Wind et al. (2005) reported a mean of 0.13 μg/L of total fatty alcohol in the effluent of a CAS system dosed with 4 mg/L of an AE mixture approximating the homologue distribution found in wastewater. With regard to field studies, Morrall et al. (2005) reported 0.57 and 0.82 μg/L of total fatty alcohol in the effluents of two activated sludge plants, which had influent AE levels equal to 660 and 720 μg/L. In a survey examining the effluents of 12 activated sludge plants in Europe and another six in Canada, the median levels of total free fatty alcohol were 1.26 in Europe and 0.57 μg/L in Canada (Eadsforth et al., 2005).

Although the model predicts only a small fraction of AE being converted to free fatty alcohol, measured levels of alcohol in CAS and field studies are consistent with the expected removal of fatty alcohols in influent rather than in situ generation of alcohols from AE during treatment. The reason for this over prediction by the model is evident in the results obtained in the die-away studies with the AEs. Based upon the measured decay rates of the AEs and their corresponding alcohols, Eq. (6) would predict that free fatty alcohol would account for more than 40% of the total radioactivity in the early stages of biodegradation. In reality, the maximum level of fatty alcohol observed for both AE homologues tested in this study were less than 5.5% of the total. Instead of fatty alcohols being the major metabolites in the early stages of biodegradation, polar metabolites were predominant. These metabolites are likely to consist of *omega* oxidation products, in which the terminal methyl group of the alkyl chain had been oxidized. Such polar metabolites would dominate only if *omega* oxidation of the chain occurred prior to or concurrent with central cleavage. Patterson et al. (1970) found evidence that AE degradation might involve the simultaneous action of central cleavage and *omega*

oxidation of the hydrophobe. Steber and Wierich (1985) characterized the metabolites formed during the biodegradation of a pure $C_{18}E_7$ AE in activated sludge and found that the major products were polyethylene glycols and acidic polyglycol structures with small residual fragments of the alkyl chain remaining (carboxy alkyl ethoxylates). These findings also led them to conclude that primary degradation involved the simultaneous action of two distinct modes of attack, central fission and *omega* oxidation of the alkyl chain. Itrich and Federle (2004) likewise found evidence for the formation of carboxy alkyl ethoxylates in their die-away studies with ^{14}C-ethoxylate-labeled AEs in activated sludge. Consequently, the model's assumption that the majority of AE is degraded by central fission through alcohol is wrong. Hence, the miniscule levels of fatty alcohol in wastewater effluents are not solely the result of rapid oxidation and mineralization of fatty alcohols but also the involvement of *omega* oxidation in the primary biodegradation of alcohol-derived surfactants such as AE. Rapid *omega* oxidation of the terminal methyl simultaneous with another mode of attack therefore was observed with both fatty alcohols and AEs in this study.

5. Conclusions

Fatty alcohols and AE were rapidly biodegraded in activated sludge. Half-lives for the bulk of all tested materials were less than 1 min. Fatty alcohol degradation involved two pathways: oxidation of the alcohol to a fatty acid, which was *beta* oxidized to form carbon dioxide, and *omega* oxidation of the methyl group to yield dioic acids, which undergo *beta* oxidation from either direction. Based upon the measured biodegradation rates, predicted removal of these materials in activated sludge plants exceeds 99.7%, consistent with measurements from the field. AE biodegradation does not represent a significant source of fatty alcohols in activated sludge effluent. In addition to being rapidly degraded, fatty alcohols were not a major metabolite of AE biodegradation. Rather than undergoing central cleavage as the first step in biodegradation, the majority of AE molecules were oxidized in their terminal methyl groups prior to or concurrent with this central cleavage step.

Acknowledgment

We are grateful to Dr. Drew McAvoy of Procter & Gamble, who helped us derive the equations that were used to estimate the level of metabolites that occur in the reactor and effluent of an activated sludge plant.

References

Battersby, N.S., Sherren, A.J., Bumpus, R.N., Eagle, R., Molade, I.K., 2001. The fate of linear alcohol ethoxylates during activated sludge sewage treatment. Chemosphere 45, 109–121.

Broadway, N.M., Dickinson, M., Ratledge, C., 1993. The enzymology of dicarboxylic acid formation by *Corynebacterium* sp. Strain 7E1C grown on *n*-alkanes. J. Gen. Microbiol. 139, 1337–1344.

Eadsforth, C.V., Sherren, A.J., Selby, M.A., Toy, R., Eckhoff, W.S., McAvoy, D.C., Matthijs, E., 2005. Monitoring of environmental fingerprints of alcohol ethoxylates in Europe and Canada Ecotoxicol. Environ. Saf., this issue, doi:10.1016/j.ecoenv.2005.06.009.

Federle, T.W., Itrich, N.R., 1997. Comprehensive approach for assessing the kinetics of primary and ultimate biodegradation of chemicals in activated sludge: application to linear alkylbenzene sulfonate. Environ. Sci. Technol. 31, 1178–1184.

Federle, T.W., Gasior, S.D., Nuck, B.A., 1997. Extrapolating mineralization rates from the ready CO_2 screening test to activated sludge, river water and soil. Environ. Toxicol. Chem. 16, 127–134.

Itrich, N.R., Federle, T.W., 2004. Effect of ethoxylate number and alkyl chain length on the pahway and kinetics of linear alcohol ethoxylate biodegradation in activated sludge. Environ. Toxicol. Chem. 23, 2790–2798.

Kravetz, L., Chung, H., Guin, K.F., Shebs, W.T., Smith, L.S., 1984. Primary and ultimate biodegradation of an alcohol ethoxylate and a nonylphenol ethoxylate under average winter conditions in the United States. Tenside Det. 21, 1–6.

Matthijs, E., Holt, M.S., Kiewiet, A., Rijs, G.B., 1999. Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylates, alcohol ethoxy sulfate, alcohol sulfate, and soap. Environ. Toxicol. Chem. 18, 2634–2644.

McAvoy, D.C., Dyer, S.D., Fendinger, N.J., Eckhoff, W.S., Lawrence, D.L., Begley, W.M., 1998. Removal of alcohol ethoxylate, alcohol ethoxylate sulfates, and linear alkylbenzene sulfonates in wastewater treatment. Environ. Toxicol. Chem. 17, 1705–1711.

Modler, R.F., Gubler, R., Inoguchi, Y., 2004. Detergent alcohols. In: Chemical Economics Handbook. SRI International Consulting, Menlo Park, pp. 609.500A–609.500S.

Morrall, S.W., Dunphy, J.C., Cano, M.L., Evans, A., McAvoy, D.C., Price, B.P., Eckhoff, W.S., 2005. Removal and environmental exposure of alcohol ethoxylates in US sewage treatment. Ecotoxicol. Environ. Saf. (submitted for this issue).

Namkung, E., Rittman, B.E., 1987. Estimating volatile organic compound emissions from publicly owned treatment works. J. Water Pollut. Control Fed. 59, 670–678.

Patterson, S.J., Scott, C.C., Tucker, K.B., 1970. Nonionic detergent degradation: initial mechanism of the degradation. J. Am. Oil Chem. Soc. 47, 37–41.

Rehm, H.J., Reiff, I., 1981. Mechanisms and occurrence of microbial oxidation of long-chain alkanes. Adv. Biochem. Eng. 19, 175–215.

Steber, J., Wierich, P., 1983. The environmental fate of detergent range fatty alcohol ethoxylates—biodegradation studies with a ^{14}C labeled model surfactant. Tenside Det. 20, 183–187.

Steber, J., Wierich, P., 1985. Metabolites and biodegradation pathways of fatty alcohol ethoxylates in microbial biocenoses of sewage treatment plants. Appl. Environ. Microbiol. 49, 530–537.

Struijs, J.S., van de Ment, D., 1991. A spreadsheet-based box model to predict the fate of xenobiotics in a municipal wastewater treatment plant. Water Res. 25, 891–900.

Swisher, R.D., 1987. Surfactant Biodegradation. Marcel Dekker, New York.

Tchobanoglous, G., Burton, F.L., 1991. Wastewater Engineering: Treatment, Disposal and Reuse, third ed. McGraw-Hill, New York.

Thomas, O.R.T., White, G.F., 1989. Metabolic pathway for the biodegradation of sodium dodecyl sulfate by *Pseudomonas* sp. C12B. Biotechnol. Appl. Biochem. 11, 318–327.

Tidswell, E.C., Russell, N.J., White, G.F., 1996. Ether-bond scission in the biodegradation of alcohol ethoxylate nonionic surfactants by *Pseudomonas* sp. strain SC25A. Microbiology 142, 1123–1131.

van Compernolle, R., McAvoy, D.C., Sherren, R., Wind, T., Cano, M.L., Belanger, S.E., Dorn, P.B., Kerr, K.M., 2005. Predicting the sorption of fatty alcohols and alcohol ethoxylates to effluent and receiving water solids. Ecotoxicol. Environ. Saf. (submitted for this issue).

Wind, T., Stephenson, R.J., Eadsforth, C.V., Sherren, A., Toy, R., 2005. Determination of the fate of alcohol ethoxylate homologues in a laboratory continuous activated sludge unit study. Ecotoxicol. Environ. Saf., this issue, doi:10.1016/j.ecoenv.2005.05.007.

Yaws, C.L., Hopper, J.R., Sheth, S.D., Han, M., Pike, R.W., 1997. Solubility and Henry's law constant for alcohols in water. Waste Manage. 17, 541–547.