

Removal and environmental exposure of alcohol ethoxylates in US sewage treatment

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Abstract

Alcohol ethoxylates (AE) are a common nonionic surfactant employed in consumer and industrial detergents worldwide. Commercial AE are typically complex mixtures composed of >100 homologous compounds with varying alkyl chain lengths and varying numbers of ethylene oxide (EO) units. Recent improvements in analytical methodology have enabled accurate measurement of the entire AE mixture in sewage treatment plant (STP) influents and effluents, including alkyl chain lengths from 12 to 18 carbons with a range of ethoxylation from 0 to 18 EO units. These improved analytical methods were used to measure AE concentrations at nine sites representative of sewage treatment processes and geographical locations. These new data will make possible a more accurate assessment of environmental risk for AE in the United States. The results indicate that all AE homologues are effectively removed (>99%) in the most common treatment types. Individual STP total AE effluent concentrations ranged from a low of 0.92 µg/L for activated sludge to a high of 15.6 µg/L for a trickling filter process. For the purpose of representing a national average distribution, an average-flow-weighted wastewater treatment plant effluent concentration was determined for each AE component. The total-flow-weighted average AE effluent concentration was 3.64 µg/L.

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1. Introduction

Alcohol ethoxylates (AE) are an important group of nonionic surfactants. In 2003, 453 million pounds of AE were used in North America (SRI, 2004). AE comprises a complex mixture of homologues that vary in alkyl chain length and degree of ethoxylation. The AE mixture can be represented by the molecular formula $\text{CH}_3(\text{CH}_2)_n(\text{OCH}_2\text{CH}_2)_y\text{OH}$, where n is 11–15, 17 and y is 0–18. The distribution of the number of ethoxylate groups (OCH_2CH_2) is referred to as the “ethoxymer distribution.”

AE have been the subject of several environmental monitoring exercises in the United States, as well as Europe. These studies were limited by the available analytical methodologies. Several of these studies quantified AE as an alkyl bromide derivative and had to assumed ethoxymer distribution to obtain environmental AE concentrations (Fendinger et al., 1995; McAvoy et al., 1998). In other studies, mass spectrometric detection depended upon ion adducts to impart a positive charge to the neutral AE. Consequently, these analyses were insensitive to ethoxymers below 3 EO units (Evans et al., 1997; Matthijs et al., 1999). Analytical methodologies have become increasingly sophisticated with numerous advance in sensitivity, selectivity, and range of analytes (Dunphy et al.,

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Table 1
Description of wastewater treatment plants (WWTP) monitored in this study

Location	Type	% Industrial influent (estimated)	Designed flow MGD	Approximate flow MGD	Population served (1000s)	Sampling dates
San Benito, TX	LA	5	2.16	1.3	26	Mar 23–25, 1999
Rockaway Valley, NJ	OD	11	12	10.5	73.9	Jun 8–10, 1999
St Clairsville, OH	RBC	0	3.5	0.55	5	Jun 15–17, 1999
Oskaloosa, IA	TF	0	1.45	0.75	5	Aug 16–17, 1999
Sedalia, MO	TF	10	2.5	1	10	Aug 23–25, 1999
Rose Hill, KA	LA	0	0.5	0.36	3.4	Sep 21–23, 1999
Lodi, CA	AS	<2	8.5	6.3	57	Oct 18–20, 1999
Durham, OR	AS(1)	7.5	56	25	160	Oct 25–27, 1999
Opelika, AL	OD	2	1.1	0.7	6.75	Dec 7–9, 1999

Note: MGD—million gallons per day; LA—lagoon; OD—oxidation ditch with surface brush aeration, no primary settling; RBC—rotating biological contactor, with primary settling; TF—trickling filter, with primary settling; AS—conventional activated sludge system, with diffused air and primary settling; AS(1)—conventional activated sludge system, with diffused air, primary settling, biological nutrient removal, alum coagulation, and sand filtration.

2001). A new monitoring study of US municipal wastewater treatment plants (WWTP) was initiated using improved analytical methodology to overcome the limitations of the previous monitoring efforts and enable improved environmental risk assessment of AE.

All AE components do not have equivalent aquatic toxicity and the “fingerprint” or distribution of AE homologues is a critical factor in an environmental risk assessment (Boeije et al., 2005; Belanger et al., 2005). Acquiring the relevant AE environmental composition information to enable accurate risk assessment in the continental United States was a key objective in this study.

The generation of new exposure data was needed to properly renormalize aquatic toxicity studies of AE under laboratory conditions (Belanger et al., 2005; Boeije et al., 2005). This paper presents a synthesis of the new monitoring in the United States including influent levels to sewage treatment and the influence of sewage treatment type on effluent AE distribution and removal.

2. Materials and methods

2.1. Wastewater treatment plant (WWTP) selection and description

WWTPs were selected to provide diversity across geographical location and treatment type. In addition, the WWTPs sampled had influents containing $\leq 10\%$ industrial wastewater and were operating within designed capacity. Selected sites are representative of the five most common WWTP types found in the United States; (Tchobanoglous and Burton, 1991); activated sludge (AS), oxidized ditch (OD), trickling filter (TF), rotating biological contactor (RBC), and lagoon (LA). Descriptions of the WWTP facilities are summarized in Table 1.

The plants in the study were located in nine principal drainage basins in the United States (Fig. 1). The distribution of sampling sites gives the study national significance. The WWTPs were judged to be operating within expected ranges based upon data obtained directly from the treatment plant records. These data included the removal of biological oxygen demand (BOD) and suspended solids (SS).

2.2. Sample collection and preservation

Twenty-four-hour composite samples of influent and effluent were collected from each of the WWTPs using an ISCO automatic sampler (Los Angeles, California). Twenty-four-hour composite samples of primary effluent were also collected at the WWTPs with a primary settling process. Primary effluent enters the main treatment process and its composition is useful in developing and refining sewage treatment models, but does not reflect environmental discharge. In all cases composite samples were collected for each of 3-days and the daily samples were further composited, based on WWTP flow, to form a 3 day, flow-based composite of each sample type. The hourly samples were preserved with 3% formaldehyde solution (37%,v/v) at the time of collection.

2.3. Sample preparation

All sample preparation and analysis work was conducted at Midwest Research Institute (MRI), located in Kansas City, MO, and is described in detail elsewhere (Dunphy et al., 2001). Briefly, AE is isolated using a series of solid phase extractions (SPE). The water samples are extracted with a C2 SPE cartridge (Varian Mega Bond Elut 2 gram Part No. 1225-6056) and then eluted through strong cation (SCX) and anion (SAX) exchange SPE (Varian Part No. 1425-6019 and 1425-6021) for clean up.

Following the SPE process, the AE is derivitized with 2-fluoro-*N*-methylpyridinium *p*-toluenesulfonate (Fluka

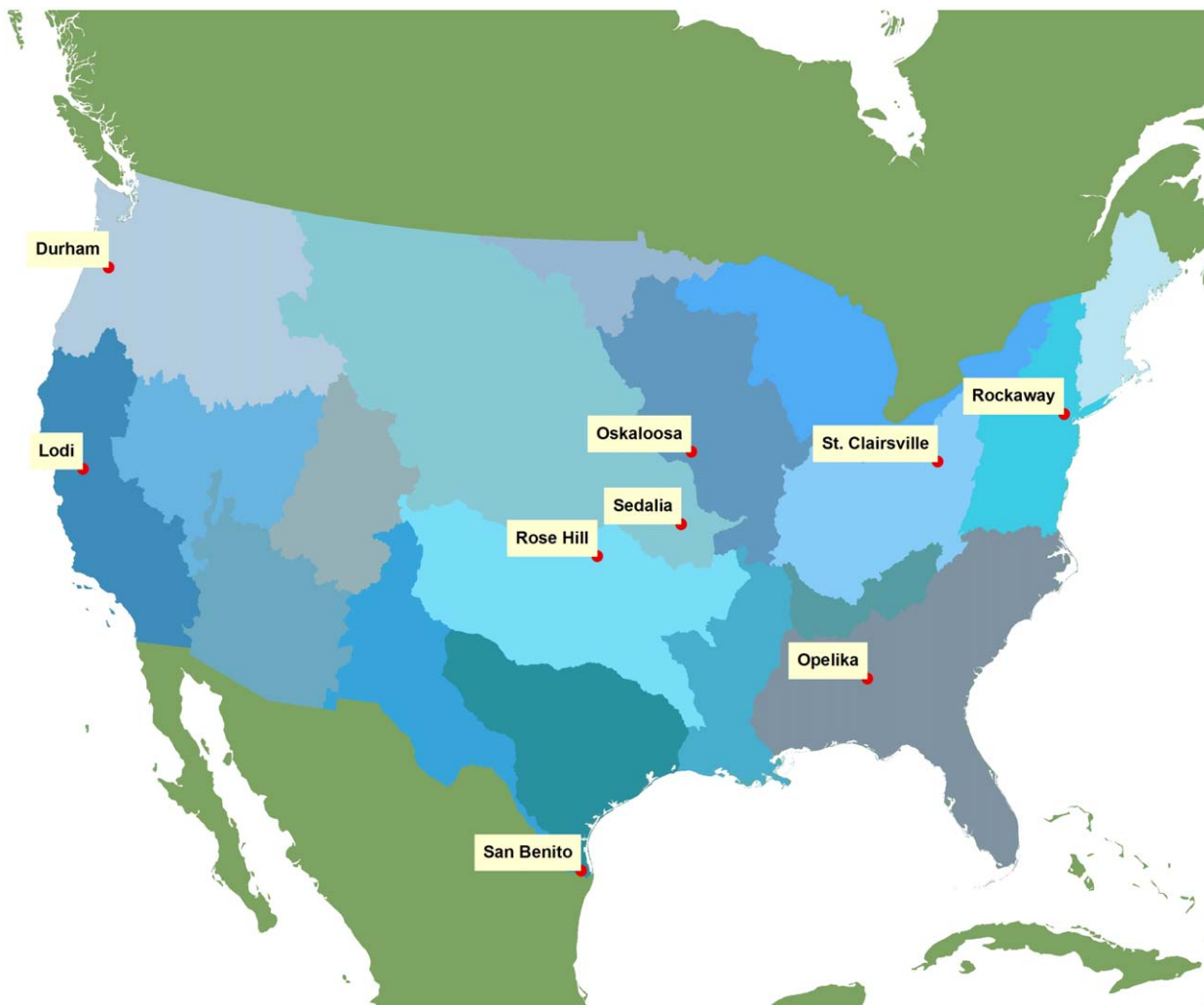


Fig. 1. Map of the United States showing WWTP sampling site locations.

Chemical) to a permanent cation for analysis by HPLC/MS (Quirke et al., 1994). Sample volume was adjusted to enable a single HPLC/MS method to cover a wide range of AE concentrations. Low effluent levels required the extraction of 4-L sample volumes, while 10 ml of influent samples was processed. In some cases, the SPE cartridges clogged before the entire 4-L effluent sample could be processed and smaller sample volumes were used for Rosehill, Kansas (0.4 L), Opelika, Alabama (2.9 L), Durham, Oregon (1.2 L), and San Benito, Texas (0.5 L). Clogging of the SPE cartridge was worst with the Rosehill effluent and a 2:1 dilution with deionized water was needed to facilitate the SPE process. Influent samples contained a high-level of suspended solids and were diluted 1:5 with deionized water prior to extraction. A 50-ml aliquot of the diluted influent (equivalent to a 10-ml volume of the original sample) was processed.

Since water will hinder the derivatization reaction, the C2 SPE cartridges were dried after sample extraction by pulling air through a blank C2 SPE cartridge and then through the sample SPE cartridge.

2.4. HPLC/MS analysis

Chemical analysis was performed on a Micromass Quattro Triple Quadrupole tandem mass spectrometer (Manchester, UK) equipped with an electrospray source operated in the positive ion mode (ESI⁺). The liquid chromatograph used was an HP 1090 (Agilent) equipped with a variable volume autosampler. The HPLC column used was a 10 cm × 2.1 mm SupelcoGel TPR-100. The mobile phase consisted of water/acetonitrile with 0.01 M formic acid. The gradient started at 60/40 water/acetonitrile and was held for 5 min, then ramped from 5 to 25 min up to 10/90 water/acetonitrile, and ramped again from 25 to 30 min to 100% acetonitrile. A final step consisted of 15 min at the initial mobile phase composition to re-equilibrate prior to the next injection. Flow from the analytical column at 0.2 ml/min was sent to the electrospray probe.

Selected ion mass chromatograms of an AE standard are shown in Fig. 2 to illustrate the orthogonal separation of alkyl chain length by RP-HPLC and the ethoxymers by mass-to-charge ratio (m/e). A deuterated internal standard

(D₂₇-C₁₃E₉), prepared by Shell Development (Houston, Texas), was added to the samples prior to derivatization. The peak area ratio of analyte homologue to the internal standard homologue with the same number of EO groups was used to measure the concentration of each AE component separately, 114 in total.

The signal-to-noise ratio (S/N), and consequently the limit of quantitation (LOQ, S/N = 10) and limit of detection (LOD, S/N = 3), was dependent upon the chemical background and varied with the sample matrix. When possible, accurate estimates were obtained by splitting samples and spiking one aliquot with 5 µg/L NEODOL 25-9 (C_{12–15}EO₉) from Shell

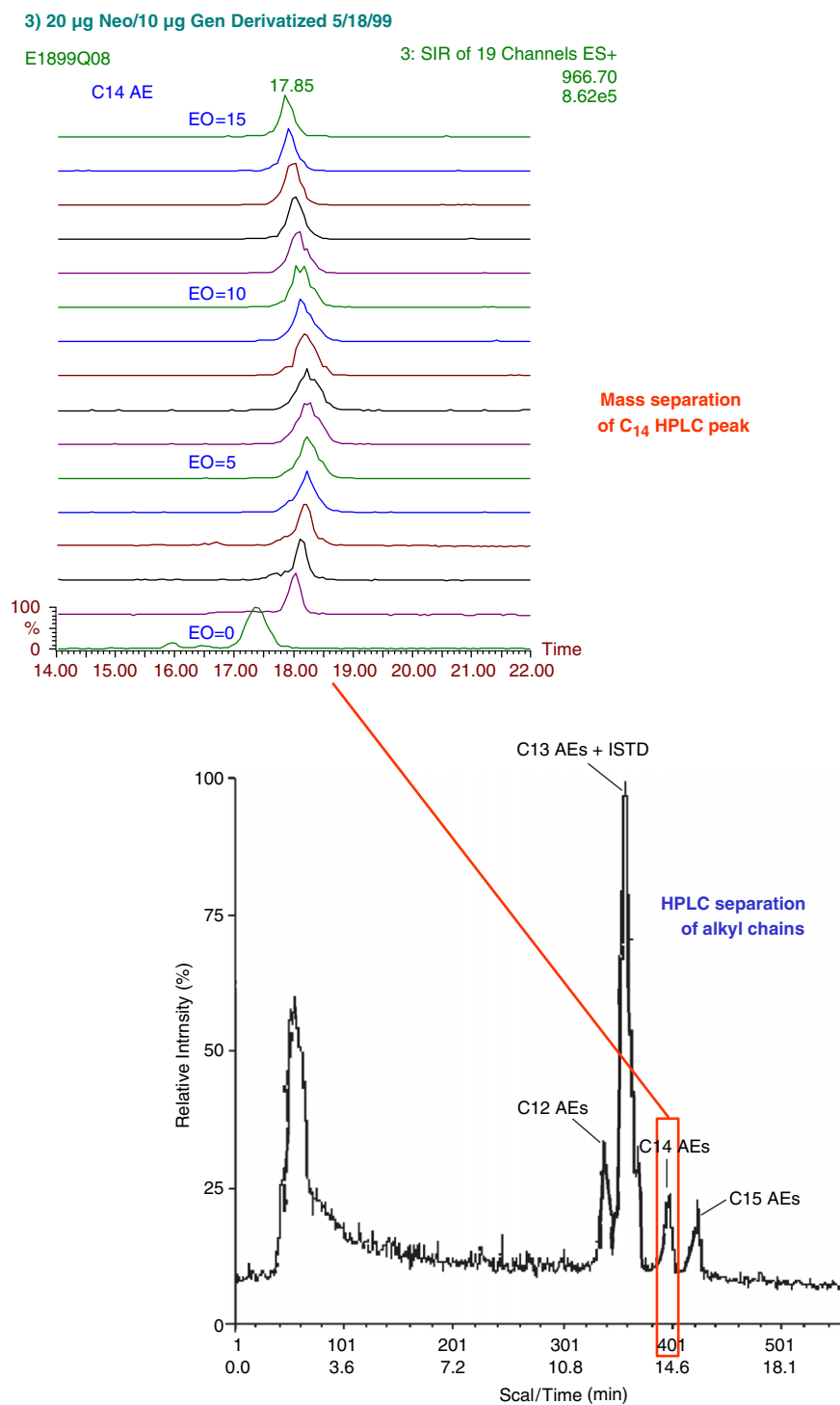


Fig. 2. Mass chromatograms of a derivatized AE standard solution. Lower panel is a total ion current (TIC) mass chromatogram showing separation of AE by alkyl chain length using HPLC. The upper panel displays the mass separation of the C₁₄ ethoxymers, up to 15 EO units.

Development Company, Houston, Texas, and 2.5 µg/L GEN-APOL (C_{16,18}EO₁₃), obtained from Clariant GmbH. Spiking was done for all final effluent samples, with the exception of Rockaway Valley, San Benito, and St. Clairsville. LOQ values for effluent samples ranged from 0.001 to 0.3 µg/L depending upon the matrix and AE homologue. For the purposes of this study, values below the LOD were set to zero, with one exception. Average weighted effluent concentrations (Tables 2 and 3) were calculated using one-half the LOD value for each specific homologue and sample, as determined by spiking with standard reference materials. Measured concentrations below the LOD were set to zero for the three sites where accurate LODs were not determined by spiking.

2.5. Data analysis methods

The entire data set of 114 analytes for 26 samples is too large for inclusion in this paper. For the purposes of discussion

Table 2

Effluent weighted average concentrations of AE homologues (all WWTP, values in µg/L). These values were calculated using one-half the LOD for homologues below the LOD

EO	C12	C13	C14	C15	C16	C18
0	0.270	0.039	0.161	0.070	0.288	0.657
1	0.013	0.050	0.010	0.005	0.001	0.002
2	0.015	0.010	0.012	0.041	0.001	0.022
3	0.016	0.013	0.011	0.006	0.003	0.004
4	0.014	0.014	0.012	0.006	0.002	0.009
5	0.011	0.023	0.012	0.004	0.004	0.007
6	0.011	0.018	0.016	0.008	0.004	0.008
7	0.009	0.009	0.018	0.003	0.006	0.020
8	0.013	0.012	0.023	0.006	0.011	0.027
9	0.013	0.019	0.023	0.014	0.009	0.078
10	0.010	0.011	0.021	0.009	0.009	0.083
11	0.009	0.013	0.018	0.009	0.014	0.083
12	0.013	0.012	0.023	0.015	0.024	0.042
13	0.020	0.013	0.021	0.011	0.021	0.082
14	0.008	0.006	0.013	0.053	0.016	0.170
15	0.010	0.007	0.013	0.015	0.015	0.182
16	0.009	0.005	0.009	0.009	0.009	0.055
17	0.007	0.004	0.007	0.010	0.005	0.035
18	0.007	0.022	0.051	0.027	0.005	0.057

Table 3

Summary of flow weighted average total grouped effluent concentrations

AE homologue group	Average weighted effluent concentration (µg/L)
Short FA C _{12–15} E ₀	0.54
Long FA C _{16,18} E ₀	0.94
Short CL AE C _{12–15} E _{0–18}	1.57
Ethoxylated short CL C _{12–15} E _{1–18}	1.03
Ethoxylated all CLs C _{12–18} E _{1–18}	2.15
Total AE C _{12–18} E _{0–18}	3.64

the data have been summarized in a more concise form, where concentrations are summed for subsets of the entire AE population. These groups include all components (C_{12–16,18}EO_{0–18}), short-alkyl-chain materials (C_{12–15}EO_{0–18}), short-chain fatty alcohols (C_{12–15}EO₀), long-chain fatty alcohols (C_{16,18}EO₀), and only ethoxylated materials (excludes fatty alcohols). Analysis and discussion of AE homologue distributions (Section 3.2) and flow-weighted averages (Section 3.3) incorporate the concentration values for individual homologues.

Removal values were calculated from the measured influent and effluent concentrations for each AE subset using the equation:

$$\% \text{ removal} = [(C_i - C_e)/C_i] \times 100, \quad (1)$$

where C_i and C_e are the concentrations (µg/L) of the AE subset in the influent and effluent, respectively.

A detailed description of the multivariate analysis (MVA) techniques and software (SIMCA P 10.5, Umetrics AB, Sweden) used in this study is available elsewhere (Erikson et al., 2004). A nonsupervised classification by principal component analysis (PCA) and a supervised technique, partial least-squares discriminant analysis (PLS-DA), were applied to the individual measured homologue concentrations. For the purposes of the following analysis and discussion, all homologues below LOQ were considered as “0” values and “normalized” data are the homologue concentrations expressed as a percentage of the total AE concentration for a given sample. This effectively removes absolute concentration as a variable in the MVA and focuses the analysis on the differences in AE component distribution,

$$X_{\text{norm}} = (X_i / \sum X_{i,\dots,n})100, \quad (2)$$

where the normalized value for a given component (X_{norm}) is equal to the concentration of that component (X_i) divided by the sum of all AE homologue concentrations for that sample (X_{i,\dots,n}) multiplied by 100.

In PCA, a multidimensional data matrix, consisting of many observations (samples) and multiple variables (AE homologue concentrations), was reduced to a low-dimensional model defined by principal components (PC), which approximate the data. Each component accounts for the maximum amount of variability remaining in the data and is orthogonal to the other subsequent PCs. There is no sample classification imposed on the PCA model; thus it is “unsupervised,” and any patterns that emerge are strictly due to the data. In addition to the statistical normalization previously described, the data were preprocessed by unit variant scaling and mean centering prior to PCA (Jackson, 1991).

Partial least-squares projection to latent surfaces (PLS) provides several model diagnostics that are useful in understanding the data set. Here, two data matrices, X (AE homologue concentration) and Y (sample classification, such as influent, effluent, or WWTP type), are related to each other by a linear multivariate model. PLS is also a projection method and the model components are orthogonal to each other. The PLS components are drawn in the X data space, but also correlate with the one-dimensional Y vector (the Y data matrix has only a single variable, which is the assigned sample class). The geometric projection of the X data points to the model

components provides a scores value, which is useful for model visualization in a scatter plot. A model diagnostic that is useful for data interpretation is the scores contribution (MacGregor

and Kourti, 1995). This parameter identifies which *X* variables are contributing to the difference in score values between observations. In our case, score contributions were used to

Table 4

Levels of biological oxygen demand (BOD) and suspended solids (SS) for WWTP influents and effluents during period of wastewater sample collection

Location	Type	BOD (mg/L)			Suspended solids (mg/L)		
		Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
Durham, Oregon	AS	196	3	98.5	242	0.7	99.7
Lodi, California	AS	273	3.2	98.8	288	3.6	98.6
Opelika, Alabama	OD	197	2	98.9	163	4.0	97.5
Rockaway Valley, New Jersey	OD	193	6.5	96.6	371	5.5	98.5
San Benito, Texas	LA	150	18.8	87.5	160	16.7	89.6
Rose Hill, Kansas	LA	257	23.5	90.9	122	47.3	61.2
St. Clairsville, Ohio	RBC	114	6.2	94.6	144	3.4	97.6
Oskaloosa, Iowa	TF	63	3.9	93.8%	77	1.8	97.7%
Sedalia, Missouri	TF	265	30.0	88.7%	185	28.7	84.5%

Table 5

Concentrations ($\mu\text{g/L}$) of AE sub groups in wastewater samples. Measured values below the LOD were set to zero. Note that “average” in this context refers to the simple arithmetic mean of collected samples, not weighted by % contribution to effluent flow in the US

WWTP type	Location	Sample	Short FA	Long FA	Short AE	Short ethoxy	All ethoxy	Total AE
			C _{12–15} E ₀	C _{16–18} E ₀	C _{12–15} E _{0–18}	C _{12–15} E _{1–18}	C _{12–18} E _{1–18}	C _{12–18} E _{0–18}
LA	San Benito	Influent	297	92.7	634	338	1470	1860
		Effluent	1.98	2.44	3.1	1.12	5.9	10.3
		% Removal	99.3	97.4	99.5	99.7	99.6	99.4
	Rosehill, KS	Influent	67.5	35.4	256	189	208	311
		Effluent	1.09	2.2	1.83	0.74	5.13	8.42
		% Removal	98.4	93.8	99.3	99.6	97.5	97.3
OD	Rockaway Valley, NJ	Influent	249	181	1360	1110	1190	1620
		Effluent	0.74	0.78	4.04	3.3	3.92	5.44
		% Removal	99.7	99.6	99.7	99.7	99.7	99.7
	Opelika, AL	Influent	702	394	1320	617	617	1713
		Effluent	0.31	0.45	0.72	0.41	0.53	1.29
		% Removal	100	99.9	99.9	99.9	99.9	99.9
TF	Oskaloosa, IA	Influent	499	354	2030	1530	1820	2670
		Effluent	1.97	2.3	8.23	5.69	7.31	11.6
		% Removal	99.6	99.4	99.6	99.6	99.6	99.6
	Sedalia, MO	Influent	532	315	2160	1630	1870	2717
		Effluent	4.92	8.56	6.79	1.87	2.15	15.6
		% Removal	99.1	97.3	99.7	99.9	99.9	99.4
AS	Lodi, CA	Influent	205	169	415	210	286	660
		Effluent	0.22	0.35	0.4	0.88	0.35	0.92
		% Removal	99.9	99.8	99.9	99.6	99.9	99.9
	Durham, OR	Influent	92.9	133	503	410	497	723
		Effluent	0.22	0.6	0.28	0.06	1.04	1.86
		% Removal	99.8	99.5	99.9	100	99.8	99.7
RBC	St. Clairsville, OH	Influent	157	77.3	569	412	1260	1490
		Effluent	0.06	0.07	3.17	3.1	4.1	4.23
		% Removal	100	99.9	99.4	99.2	99.7	99.7
Average	All Sites	Influent	311	195	1030	716	1020	1530
		Effluent	1.28	1.97	3.47	2.19	3.97	7.22
		% Removal	99.6	99.0	99.7	99.7	99.6	99.5

Note: FA—fatty alcohol (EO = 0); CL—chain length; long—carbon chain length of 16 and 18; short—carbon chain length of 12 to 15; ethoxy—ethoxylates only (no fatty alcohol).

determine which AE homologues (X variable) are the most important in differentiating between the sample classes (Y). Thus, differences in AE composition due to geographic location and transformations occurring during the treatment process can easily be identified.

Site-specific removals, influent concentrations, and effluent concentrations were also summarized as regional averages by extrapolating subsets of data for each specific treatment type. Rapaport (1988) developed a US national wastewater treatment plant model (GRIDs) to estimate removals for each treatment type on a flow-weighted basis. The underlying data consist of site-specific values for thousands of facilities that were subsequently updated by the USEPA NEEDs survey (USEPA, 1997). These data were used to calculate national flow-weighted percentages, including those monitored in this study. Mean concentration per homologue for each treatment type in the study was determined, multiplied by the appropriate percentage flow for that type, and then summed across all treatment types to provide the average national concentration per homologue.

3. Results and discussion

3.1. Removal by WWTP

All of the WWTPs in this study were judged to be operating within their specific design ranges. BOD and SS removals through the treatment process were above 95% for AS and OD plants and close to 95% for the RBC site (Table 4). The two lagoon facilities showed BOD removals of 90.9 and 87.5%. Lagoon (LA) removals of S.S. were 89.6% and 61.2%. This apparently low removal of SS was largely due to the detritus originating from the vegetation growing in the lagoon and not a measure of the removal of solids that were present in the influent. The trickling filter (TF) plants showed an average removal of 91% for both BOD and SS.

All the WWTPs in this study were effective in removing >99% of total AE, with the single exception

of a 97.3% value for a lagoon (Rosehill, Kansas) (Table 5). It should be noted that influent concentrations were low for this facility and the final effluent concentrations were actually less than the comparable lagoon (San Benito, Texas), which was 99.4% effective at removing AE. The subgroup with the lowest removal percentage (average 99.0%) was the C16 and C18 fatty alcohols. As removal of suspended solids increases, so does the removal of these long-chain fatty alcohols (Fig. 3). This relationship indicates that the relatively hydrophobic fatty alcohol fraction is highly associated with the particulate matter and removal of suspended solid is an important mechanism for removal of fatty alcohol in wastewater treatment. Additional experimental evidence for this phenomenon is provided by Van Compernelle et al. (2005).

3.2. AE homologue distributions

Total AE concentration, without homologue distribution, is insufficient for rigorous environmental risk assessment. The relative distribution of the AE components is a critical factor that links laboratory toxicity values with the monitoring information in an environmental risk assessment. Insights concerning the environmental fate of AE can also be gained when homologue

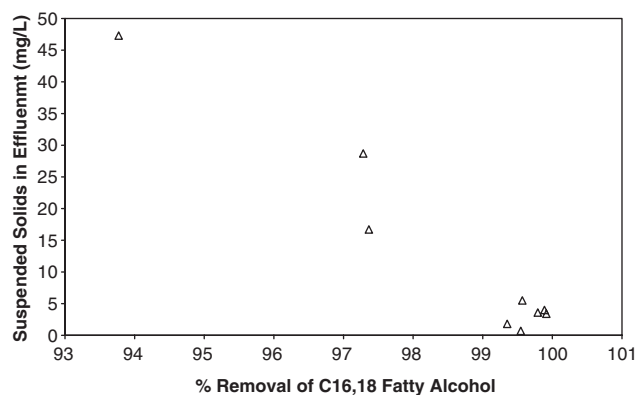


Fig. 3. Plot showing the dependence of C_{16,18} fatty alcohol removal (x -axis) upon the level of suspended solids in effluent (y -axis).

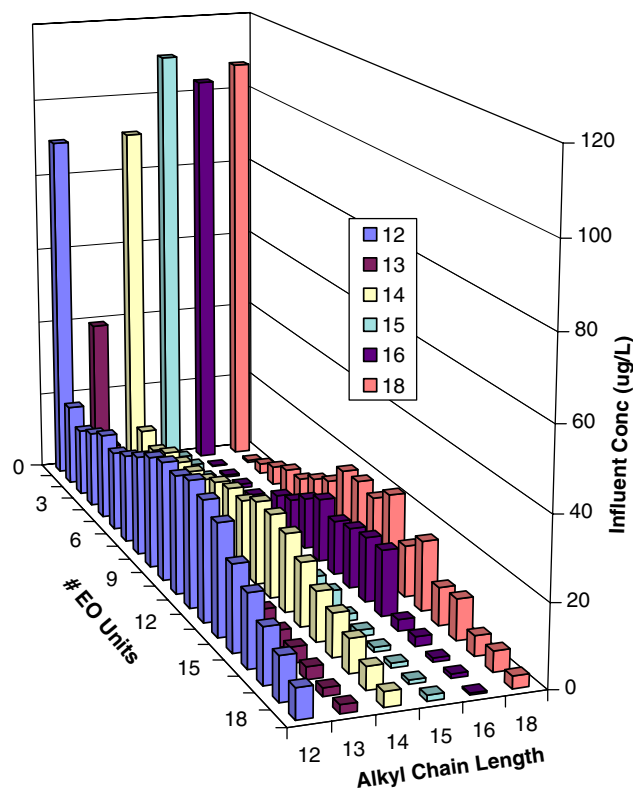


Fig. 4. Average influent concentrations ($\mu\text{g/L}$) for all AE homologues measured at the nine study sites.

distributions are known for both influent and effluent. AE homologue concentrations can be averaged across all influent (Fig. 4) and effluent samples (Fig. 5) to illustrate the relative change in AE composition after

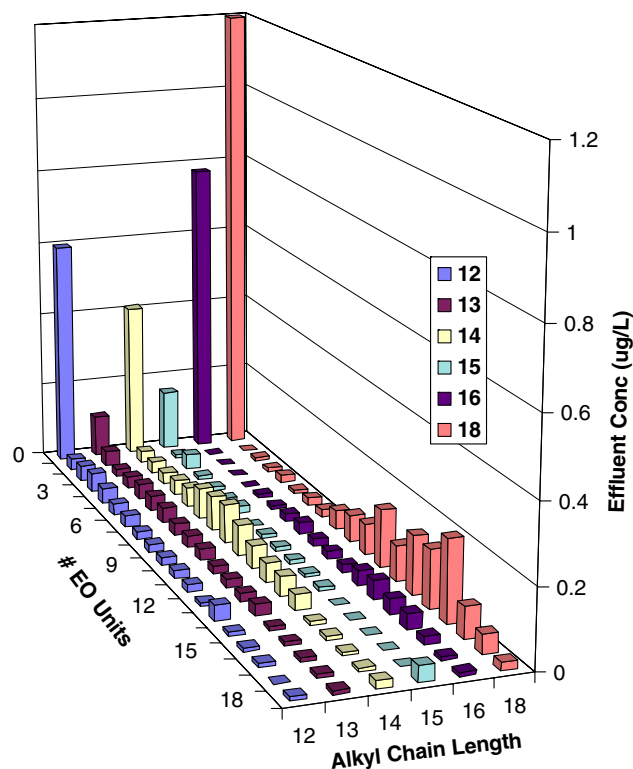


Fig. 5. Average effluent concentrations ($\mu\text{g/L}$) for all AE homologues measured at the nine study sites.

waste water treatment. MVA techniques were used to identify the key factors involved in these transformations.

A PCA of effluent compositions for the short-chain subset of C12–15 AE is shown in Fig. 6. Based on the PCA scores, there is more variability among the RBC, and TF biofilm-based WWTP processes, with the RBC plant being the most different. Effluents from the LA, OD, and AS WWTPs were closely associated in the PCA model as pairs, based on treatment type. This result is somewhat surprising, because samples were collected at different sites and at different times. A PLS-DA model of the data (not shown) gives the same scores pattern as the PCA model. Contributions for the first PLS component indicate that the RBC effluent has a composition enriched in higher ethoxylates relative to the average of all treatment types.

PLS-DA of all AE homologues in influent versus effluent samples collected at nonbiofilm treatment types (OD, LA, AS) was done to determine AE compositional changes upon treatment. The resulting PLS-DA scores plot shows that the first component accounts for most of the differences between influent and effluent composition and illustrates that there are significant changes in the overall AE distribution during the treatment process (Fig. 7). This two-component model has an R^2 value of 0.934 for the Y variable, which is classification as influent or effluent.

There is considerable variability in the influent compositions, as the first component accounts for only 30% of the variability in the data set. This is not

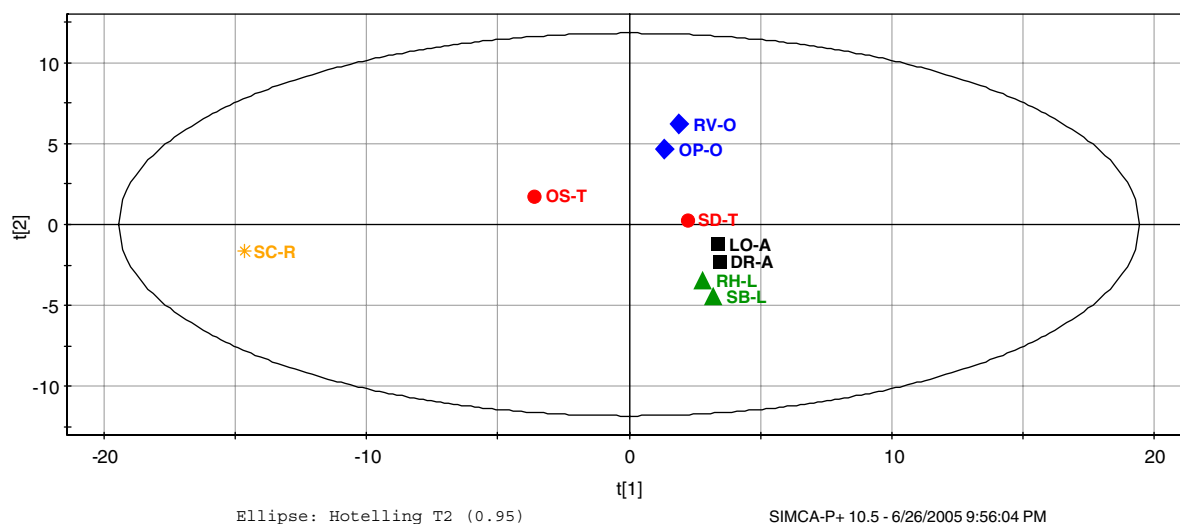


Fig. 6. PCA scores plot of short-alkyl-chain AE, C_{12–15}, in WWTP effluents, showing classification by treatment type. Despite the variability imposed by sampling at different dates and WWTP sites, the oxidation ditch (OD) ♦, activated sludge (AS) ■, and lagoon (LA) ▲ treatments are closely associated as pairs. The biofilm treatments (RBC—* SC-R and TF —● at Oscaloosa OS-T) effluents showed the greatest difference in relative composition versus other effluents. A description of the individual sites is summarized in Table 1.

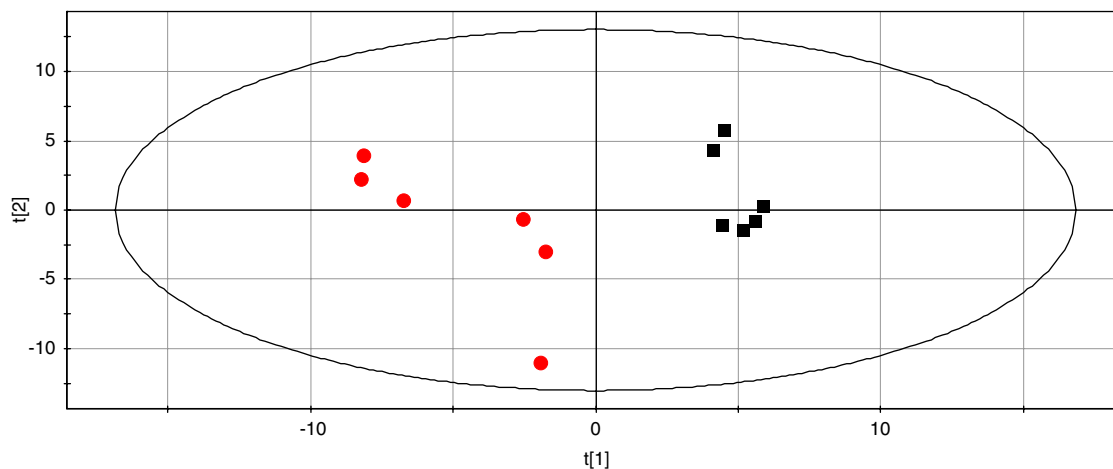


Fig. 7. PLS-DA scores plot for the normalized data set of influent (red circles) and effluent (black squares) samples. The biofilm based treatment types (RBC, TF) were excluded. The first component (t_1) clearly separates the two classes, indicating that AE composition is significantly altered during the treatment process.

Table 6
PLS-DA scores contribution of influent vs effluent AE distributions for non-biofilm treatment types (LA, OD, AS)

EO	C12	C13	C14	C15	C16	C18
0	(1.22)	(0.01)	0.87	1.55	0.98	(2.31)
1	1.54	(0.25)	2.38	1.53	0.02	0.15
2	2.56	0.04	0.67	(0.35)	0.29	(0.25)
3	2.41	0.07	1.56	2.00	1.21	0.53
4	1.98	(0.03)	0.11	1.75	0.16	0.37
5	2.23	(0.09)	(0.09)	1.56	(0.09)	0.47
6	1.76	(0.10)	(0.32)	1.38	(0.33)	0.35
7	2.21	0.01	(0.34)	1.26	(0.67)	0.38
8	1.81	0.01	(0.43)	0.17	(1.35)	0.14
9	2.43	0.87	(0.18)	1.13	(0.58)	(0.12)
10	2.30	1.72	0.02	1.02	(0.37)	(0.19)
11	2.52	1.88	0.63	0.88	(0.23)	(0.37)
12	2.20	2.14	1.68	0.75	(0.58)	(0.18)
13	2.28	2.03	1.64	0.58	(0.61)	(0.51)
14	1.93	1.20	2.03	0.57	(1.14)	(0.98)
15	1.89	1.09	1.88	0.46	(0.86)	(0.79)
16	1.84	0.37	1.06	0.46	(1.06)	(0.88)
17	1.83	na	1.06	0.46	(0.07)	(0.12)
18	0.45	(0.34)	(0.26)	(0.29)	(0.27)	(0.03)

Note: na—not used in PLS-DA model due to low variance across samples.

Values in **(bold)** are negative and indicate the homologues that are characteristic of effluent compositions. Positive values, without parentheses, indicate components that are more effectively removed in the WWTP and are characteristic of untreated wastewater. Negative values for C12 fatty alcohol and some lower EO C13 and C14 homologues might be attributed to these components being degradation products of higher ethoxymers and indicative of an overall decrease in average EO value.

unexpected given the measured variation in laundry product type and usage across the United States (Dyer and Caprara, 1997). A PLS-DA score contribution value is a model diagnostic that describes the impor-

Table 7
Distribution of wastewater treatment plant types in the United States (from USEPA, 1996). AS, OD, TF, RBC and LA refer to activated sludge, oxidation ditch, trickling filter, rotating biological contactor, and lagoon, respectively

Treatment type	AS	OD	TF	RBC	LA
Percent total flow in the US	80.6	3.1	7.1	2.0	6.3
Percent total facilities in the US	39.6	8.3	9.5	3.1	37.7

tance of each homologue in differentiating between influent and effluent (Table 6). Here, a positive value indicates that the component is highly associated with the influent composition, while a negative value describes a homologue whose proportion increases in effluent samples. It might be possible to utilize the ratio of effluent-dominant components ($C_{16,18}$) divided by influent-dominant components (short-chain homologues) to differentiate treated versus untreated sources in environmental surface waters. However, it should be noted that the average % removal is still $\geq 98\%$ for all the individual C16,18 homologues and $> 99\%$ for most.

3.3. Flow-weighting effluent concentrations for environmental risk assessment

In evaluating effluent concentrations and removals of chemicals in different treatment types, it is important to understand the relative contribution of each treatment type to the total wastewater flow and the occurrence of each type facility (Table 7). Effluent concentration values for each AE component are weighted using the percent total flow for each treatment type to give an

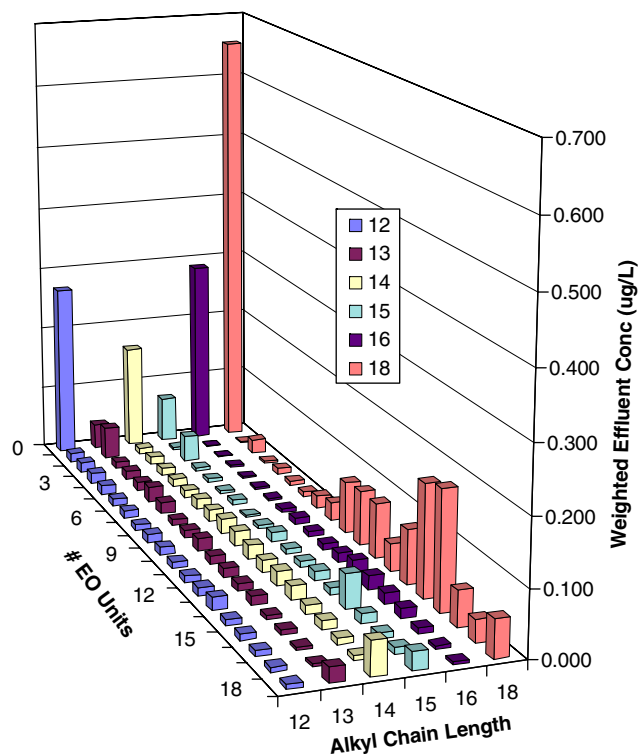


Fig. 8. AE concentrations in effluent weighted by treatment type (volume treated) in United States Plotted values are given in Table 6.

overall weighted AE concentration in US WWTP effluents. These values are summarized by individual homologues and are useful to consider as the national average concentrations for use in environmental risk assessment (Table 2, Fig. 8). A summary of these flow-weighted average concentrations by compound group is provided in Table 3. These weighted AE concentrations are skewed toward the dominant AS treatment type and reflect the effectiveness of this process. As stated in Methods, these values were calculated using one-half LOD values for homologues that were below the LOD.

4. Conclusions

New analytical methodology is capable of measuring all AE components at sub-part per billion ($\mu\text{g/L}$ or ppb) concentrations in environmental matrices. Monitoring WWTP processes in the United States with these state-of-the-art techniques shows that removal of AE is as high (>99%) as previously thought. AE composition in effluents is significantly different from the incoming sewage. This makes the traditional risk assessment using down-the-drain usage volumes difficult and highlights the importance of environmental monitoring. This study found a higher proportion of low ethoxymers and fatty

alcohol components in effluents than previously known. These AE components possess a greater toxicity potential than the higher ethoxymers, which must be accounted for in a risk assessment. Actual exposure from effluent is low and in stream removal processes will reduce exposure further. The least efficient WWTP processes (TF and RBC) are in decline in the United States, which indicates that treatment efficiency will improve in the future. Furthermore, these bio-film-based plants are most often used to treat only low-volume influent streams.

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