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Determination of Alkyl Sulfate Surfactants in Natural Waters

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■ An analytical technique was developed to monitor alkyl sulfate (AS) surfactants in natural water samples and determine AS removal during wastewater treatment. The method utilizes a reverse-phase extraction column followed by strong anionic and cationic exchange column cleanup steps. AS are then derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide with 1% trichloromethylsilane and analyzed by GC/FID as trimethylsilyl ethers. Total AS concentrations in wastewater varied as a function of time and were correlated with expected consumer use patterns of AS-containing products. Flow-weighted average total AS concentrations in influent wastewater were at least 2.4 times lower than expected based on mass balance predictions and were probably due to AS loss during wastewater conveyance. Removal of AS at two trickling filter treatment plants exceeded 90%. AS was not detected in the receiving streams monitored.

Introduction

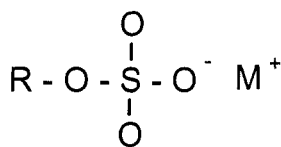
Alkyl sulfates (AS) are anionic surfactants that are currently used in shampoos, bath preparations, cosmetics, medicines, toothpaste, rug shampoos, hard surface cleaners, and light- and heavy-duty laundry applications (1). AS used in consumer products have alkyl chain lengths that range from C₁₂ to C₁₈ (Figure 1) and may contain some methyl or ethyl branching. Total AS use in the United States is ~1.4 × 10⁵ metric tons/year with 9.1 × 10⁴ metric

tons/year used in consumer products (2).

Despite their widespread use, AS are usually measured in environmental samples by nonspecific analytical techniques such as methylene blue active substance (MBAS). This type of analysis measures AS along with other anionic surfactants that contain sulfate or sulfonate functionalities (e.g., linear alkylbenzenesulfonate). The nonspecific methods are also subject to interferences from nonsurfactant organic sulfonates, sulfates, carboxylates, phenols, cationic surfactants, and amines as well as inorganic thiocyanates, cyanates, nitrates, and chlorides (3). Because AS are expected to be a small and variable fraction of the MB active material in natural waters, no correlation between levels of MBAS and AS is anticipated.

Other approaches used to measure AS in product formulations and in water samples include gas chromatography (GC), liquid chromatography (LC), and LC/mass spectrometry (MS). GC techniques involve conversion of AS into a volatile moiety by reaction with a strong acid (HI, HBr) to form an alkyl halide (4, 5). Although this method has been shown suitable for environmental samples (5), the technique does not resolve AS from alkyl-ethoxy sulfate. Because AS do not contain a chromophoric group, LC techniques that have been developed incorporate postcolumn extraction and derivatization steps to gain adequate sensitivity (6, 7). Even though LC methods with postcolumn extraction and derivatization steps can be potentially used for environmental applications, the

ALKYL SULFATE (AS)



R- alkyl chainlength from 12 to 18 carbons

Figure 1. Structure of alkyl sulfate homologs.

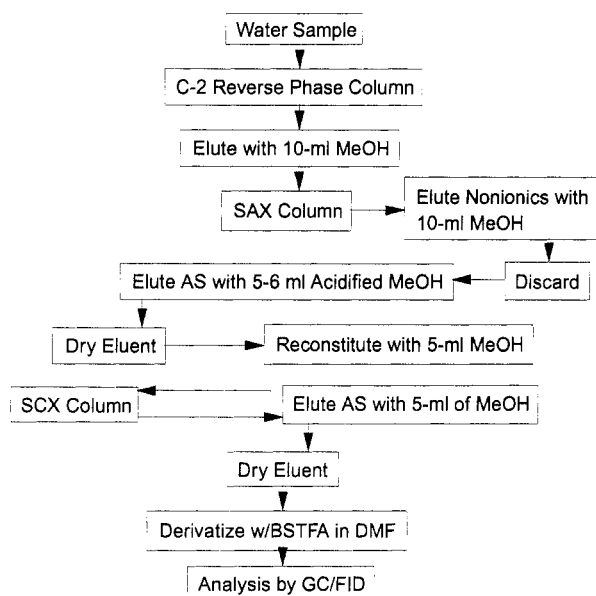


Figure 2. Alkyl sulfate analysis scheme.

methods have not been fully evaluated with respect to positive and negative interferences that may occur in wastewater matrices. Conboy et al. (8) demonstrated that ion spray chromatography/MS provided sensitive detection, molecular weight information, and structural information for alkyl sulfates. Even though this method has great potential for environmental analyses, the method has yet to be fully validated for environmental matrices.

This paper describes a specific GC AS analysis technique and reports results from use of the method to assess AS removal during sewage treatment and determine background levels of AS in streams receiving treated wastewater. Environmental behavior of AS is discussed in light of findings from use of the method.

Experimental Section

A flow chart of the AS analysis procedure is shown in Figure 2. Details of the analytical procedure are provided in the following sections.

Reagents and Apparatus. Reverse-phase (RP) and strong anionic exchange (SAX) columns with 500 mg of packing were obtained from Analytichem (Harbor City, CA). Strong cation exchange (SCX) resin was Bio Rad (Richmond, CA) AG 50W-X8, 50–100 mesh, hydrogen form. HPLC grade methylene chloride and methanol were obtained from Fisher Scientific (West Haven, CT). *N,O*-Bis(trimethylsilyl)trifluoroacetimide (BSTFA) with 1% trichloromethylsilane (TMCS) and derivatization grade dimethylformamide were obtained from Pierce Chemical Co. (Rockford, IL). High-purity water used in this study was produced with the Waters (Milford, MA) Mille-Q system. Reconstituted hard water was made by diluting

0.251 g of NaHCO_3 , 0.185 g of CaSO_4 , 0.185 g of MgSO_4 , and 0.013 g of KCl in 1.9 L of high-purity water. Normal alcohols (C_{12-18}) were obtained from Sigma Chemical Co. (St. Louis, MO) and had stated purities of greater than 98%. Sodium lauryl sulfate (C_{12} AS) was obtained from Gallard Schlessinger Chemical Manufacturing Co. (Long Island, NY) and had a reported purity of 99%. $\text{C}_{13,14,16,17}$ AS were custom synthesized by J. E. Thompson (Procter and Gamble, Miami Valley Laboratories, Ross, OH). Fast atom bombardment mass spectra and IR spectra of the synthesized AS were consistent with expected structures for these compounds. Purities of the AS samples were determined by titrating with a mixed indicator of cationic and anionic complexing dyes in a water-dichloromethane system. The purities of the custom-synthesized AS were as follows: C_{13} , 99%; C_{14} , 78%; C_{16} , 91%; and C_{17} , 85%. Radiolabeled (^{14}C) C_{14} AS and normal alcohol were obtained from Wizard Laboratories (Davis, CA) and had reported radiochemical purities of greater than 96%. Other materials were reagent grade unless otherwise specified.

Extractions were carried out either on a Supelco (Bellefonte, PA) vacuum manifold or in vacuum flasks arranged in series to allow for multiple sample processing. Derivatization reactions were carried out with a Pierce Reacti-Therm heating unit.

Trimethylsilyl ether (TMSE) analyses were done on a Hewlett-Packard (Palo Alto, CA) gas chromatograph equipped with flame ionization detector and Restek (Bellefonte, PA) Rt_x-1 (dimethylpolysiloxane) 60 m \times 0.25 mm, 0.25- μm film thickness bonded-phase capillary column. Chromatographic conditions were as follows: injection, splitless; carrier, H_2 at a linear flow velocity of 40 cm/s; detector gases, N_2 (makeup), 30 mL/min; air, 200–300 mL/min; H_2 , 30 mL/min; injector temperature, 200 $^\circ\text{C}$; detector temperature, 225 $^\circ\text{C}$; initial column temperature 50 $^\circ\text{C}$ for 1 min and then ramped at 10 $^\circ\text{C}/\text{min}$ to 215 $^\circ\text{C}$ and held for 20 min; detector temperature, 225 $^\circ\text{C}$. The minimum TMSE detectable quantity with a 1- μL injection volume was approximately 1 ng for $\text{C}_{12}-\text{C}_{18}$.

^{14}C activity was measured by liquid scintillation spectrometry with a Beckman LS 7800 liquid scintillation spectrometer. Samples were corrected for background and quench.

Sample Collection. Grab samples of untreated wastewater collected prior to entering the treatment plant (influent), treated plant effluent at the discharge pipe (effluent), and effluent receiving stream (river water) were collected at two publicly owned sewage treatment plants (STPs) in the Cincinnati, OH, area for purposes of evaluating the method. The Milford STP located in Clermont County east of Cincinnati is a rotating biological contactor plant. Colerain Heights STP located northwest of Cincinnati in Hamilton County is an activated sludge plant.

Additional sampling at two trickling filter STPs near Cincinnati was conducted to (1) obtain more detailed information on AS removal during wastewater treatment, (2) investigate diurnal influent AS concentrations fluctuations, and (3) further demonstrate the utility of the methodology. To accomplish these objectives, hourly grab samples of influent and effluent were collected for 24–25 h at Shelbyville, IN, and West Union, OH, publicly owned STPs. Single grab samples were also collected above and below the STP outfall in the receiving stream at each of the plants. The treatment plants were selected for sampling on the basis of capacity (West Union, 0.3×10^6 gal/day; Shelbyville, 3×10^6 gal/day), population served (West Union, 3000; Shelbyville, 12 000–16 000), low in-

dustrial contribution, and treatment type (trickling filter).

Grab samples of influent, effluent, and river water were collected by dipping approximately 500 mL from the water stream. Formaldehyde (30% solution) was investigated for use as a sample preservative. Concentrations as high as 5% (v/v) were found to slow but not stop AS loss from samples over a 24-h period. Therefore, samples were extracted immediately after collection to avoid AS loss during sample storage.

Sample Extraction and Derivatization. AS extraction and elution steps were optimized with the use of ^{14}C -labeled C_{14}AS . Labeled C_{14} alcohol was used to demonstrate that alcohols were quantitatively separated from AS during sample preparation.

RP extraction columns were preconditioned prior to extraction by eluting each column with 5 mL of MeOH followed by 5 mL of high-purity water. Samples were passed through the RP column at a flow rate that did not exceed 5 mL/min. Sample volumes used for analysis of the various matrices studied were as follows: 100 mL, influent; 200 mL, effluent and river water. The RP column was then rinsed with 5 mL of high-purity water. The RP column was then fitted on top of a SAX column. AS were eluted onto a SAX column with 10 mL of MeOH. AS are retained by the SAX while nonionic interferences that include alcohols are rinsed from the SAX column with an additional 10-mL MeOH rinse.

AS were eluted from the SAX column with 5–6 mL of acidified MeOH (20% concentrated HCl and 80% MeOH). The SAX column eluent was evaporated to dryness under a stream of nitrogen and by warming slightly (40 °C). The eluent was then reconstituted in 5 mL of MeOH and eluted through an activated SCX column (containing 5 g of resin) with 5 mL of MeOH. The SCX served as an additional extract cleanup step and was used to convert AS to the hydrogen form for derivatization. SCX column activation was accomplished by rinsing with 10 mL of 0.1 N HCl prior to sample application.

The SCX column eluent was evaporated to dryness under a stream of nitrogen and by warming slightly (40 °C). The extract was again evaporated to dryness after addition of 1 mL of MeCl_2 to remove traces of water before derivatization.

The direct derivation of the AS to the corresponding TMSE was accomplished by adding 500 μL of DMF and 500 μL of BSTFA with 1% TMCS to the dried extract. The solvent mixture was then heated at ~ 80 °C for 1 h to complete the derivatization reaction. The likely mechanism for formation of TMSEs from reaction of AS with BSTFA is sulfate ester cleavage and concomitant silylation. Knapp (9) reported a similar mechanism for aromatic sulfate esters. Reaction of BSTFA with alcohols is identical except for the initial cleavage of the sulfate ester group.

The derivatization reaction mixture was analyzed by injecting 1 μL in the GC/FID. TMSE were identified by retention time and quantified by an external calibration technique. There were no differences observed between calibrations obtained from derivatization of normal alcohols versus derivatization of AS following conversion to the hydrogen form, indicating similar derivatization efficiencies. Because the normal alcohols could be derivatized directly without the additional SCX column step, TMSEs derived from alcohols were used for all instrumental calibrations.

Method Validation. C_{17} AS was added to samples collected from the Milford plant as a surrogate spike to evaluate extraction and derivatization efficiency for field

collected samples. C_{17} AS is not used commercially; therefore, measurable concentrations are not expected to be found in wastewater. Analysis of unspiked samples confirmed that C_{17} AS was not present above background levels. At the Colerain Heights plant, $\text{C}_{12,14,16}$ AS were spiked into selected samples to assess performance of the method. In this case, a second sample was analyzed to determine background AS concentrations, which were then subtracted from the concentrations determined for the spiked sample to determine AS recovery from the matrix. The C_{17} or $\text{C}_{12,14,16}$ AS amendments were done immediately after sample collection.

Calculations. Calibration of the GC/FID was done with TMSE derived from normal alcohols. The amount of AS in the samples was calculated with use of the following equation:

$$[\text{AS}] \text{ (ppb)} = \frac{[\text{wt of component } (\mu\text{g})]\text{CF}}{\text{sample volume (L)}} \quad (1)$$

where CF indicates the molar conversion factor from weight of alcohol used in the calibration standard preparation to weight of AS in the sample.

Results and Discussion

Method Evaluation. The performance of the method to measure AS concentrations in natural water samples is dependent on the combined efficiencies of the isolation and derivatization steps. Labeled AS in conjunction with labeled alcohol were used to demonstrate that alcohols were quantitatively separated from AS. Fractionation of AS from alcohols on the SAX column is important because the alcohols present in the sample could be a potential positive interference in the AS determination since both AS and the corresponding alcohol will form the same TMSE when reacted with BSTFA. Results from use of labeled compounds showed that AS were quantitatively extracted and eluted (>90%) from the C_2 RP and SAX columns. Alcohols are quantitatively extracted from water (>90%) on the C_2 RP column but were not quantitatively eluted with MeOH. Alcohols eluted from the RP column were partially retained by the SAX column but were rinsed from the column with a MeOH wash, demonstrating that alcohols were quantitatively separated from AS.

Recovery data for high-purity, hard and river water and influent and effluent amended with AS are summarized in Table I. AS recovery from high-purity water, reconstituted hard water, influent, effluent, and river water was quantitative throughout the range of concentrations tested. Shown in Figure 3 are chromatograms of a TMSE calibration standard derived from normal alcohols, an influent sample without recovery standard added, and an effluent sample.

Utilizing sample volumes of 100–200 mL, a final extract volume of 1 mL, and a 1- μL injection volume, the observed minimum detectable concentration for each AS alkyl chain-length homolog in the matrices examined were 5 $\mu\text{g}/\text{L}$ for river water and effluent and 10 $\mu\text{g}/\text{L}$ for influent.

AS Environmental Levels. AS levels in influent and effluent were measured at Colerain Heights and Milford STPs (Table I) as part of the efforts to validate the method. Additional sampling was conducted at West Union, OH, and Shelbyville, IN, publicly owned STPs to investigate diurnal AS influent concentration fluctuations and determine average AS concentrations in influent and effluent over a 24-h period.

AS homolog concentrations in influent plotted as a function of time for West Union and Shelbyville STPs are illustrated in Figures 4 and 5, respectively. AS homolog

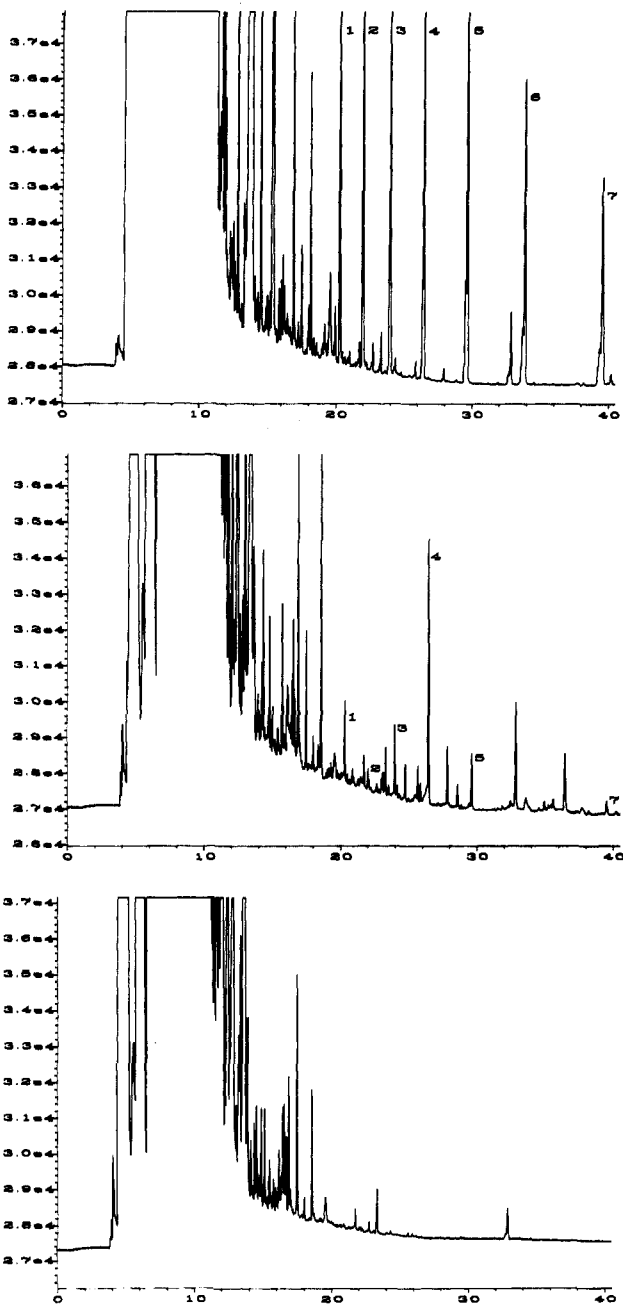


Figure 3. GC/FID chromatograms of (a, top) trimethylsilyl ether (TMSE) standard, (b, middle) influent, and (c, bottom) effluent. Peaks identified are TMSE derived from the following: (1) C₁₂ alkyl sulfate (AS), (2) C₁₃ AS, (3) C₁₄ AS, (4) C₁₅ AS, (5) C₁₆ AS, (6) C₁₇ AS, and (7) C₁₈ AS.

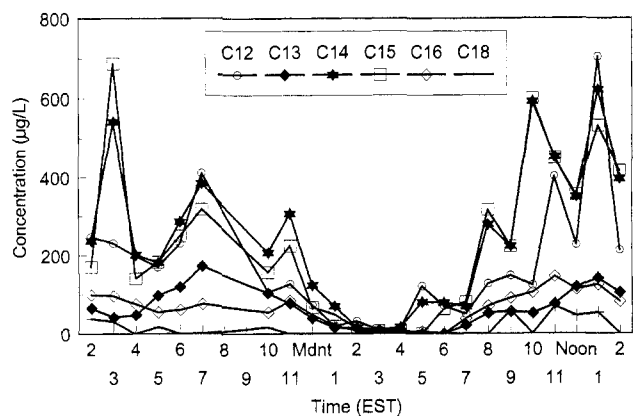


Figure 4. AS homolog concentrations as a function of time in influent collected at the publicly owned wastewater treatment facility in West Union, OH.

Table I. Recovery of Alkyl Sulfate Alkyl Homologs from Reconstituted Hard Water, High-Purity Water, Influent, Effluent, and River Water^a

sample/AS amendment, µg/L	% Recovery ^e			
	C ₁₂	C ₁₄	C ₁₆	C ₁₇
high-purity H ₂ O				
10 (n = 3) ^b	- ^c	119 ± 13	125 ± 8	-
100 (n = 3)	109 ± 4	108 ± 6	108 ± 13	-
400 (n = 3)	89 ± 7	111 ± 2	110 ± 3	-
reconstituted hard H ₂ O				
200 (n = 3)	96 ± 20	87 ± 17	82 ± 6	-
influent, Colerain Hts				
background	180 µg/L	170 µg/L	180 µg/L	ND ^d
400 (n = 3)	114 ± 28 ^d	116 ± 14	91 ± 4	-
influent, Milford				
background	ND	20 µg/L	62 µg/L	ND
100 (n = 2)	-	-	-	92
effluent, Colerain Hts.				
background	ND	ND	ND	ND
100 (n = 2)	70 ± 10	80 ± 1	67 ± 3	-
effluent, Milford				
background	ND	ND	ND	ND
100 (n = 2)	-	-	-	96
river water, Milford				
background	ND	ND	ND	ND
200 (n = 3)	88 ± 7	99 ± 15	-	-
20 (n = 2)	93 ± 7	-	-	-
river water, Colerain Hts.				
background	ND	ND	ND	ND
300 (n = 4)	-	-	-	94 ± 4

^a Spike concentrations are per component. ^b n, number of samples. ^c -, not analyzed. ^d ND, not detected. ^e Recovery data are corrected for background.

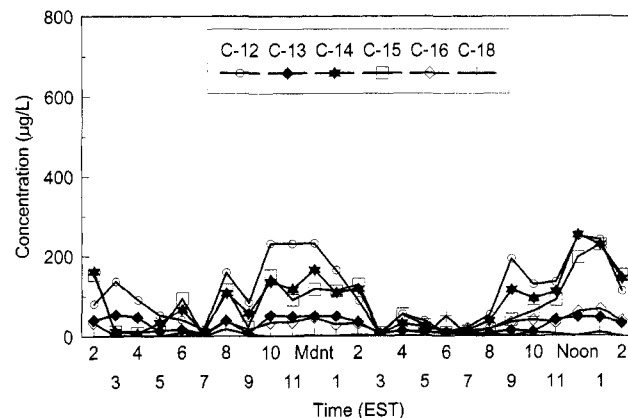


Figure 5. AS homolog concentrations as a function of time in influent collected at the publicly owned wastewater treatment facility in Shelbyville, IN.

concentrations in influent at both plants were found to vary as a function of time and ranged from near the detection level (<10 µg/L) of the method to as high as 700 µg/L. The diurnal variation observed reflects expected consumer use of AS-containing products. For example, lowest AS influent concentrations were measured during late evening and very early morning hours when consumer use of AS-containing products is expected to be low. AS influent concentrations were highest when household activities peak during the morning and early evening hours. High AS concentrations during these times probably reflect use of AS-containing products such as shampoos and laundry and dish-cleaning detergents.

Flow-weighted average total AS influent concentrations based on 24-25 measurements over a 24-h period for West Union and Shelbyville STPs were 755 and 401 µg/L, respectively. The observed AS carbon chain-length dis-

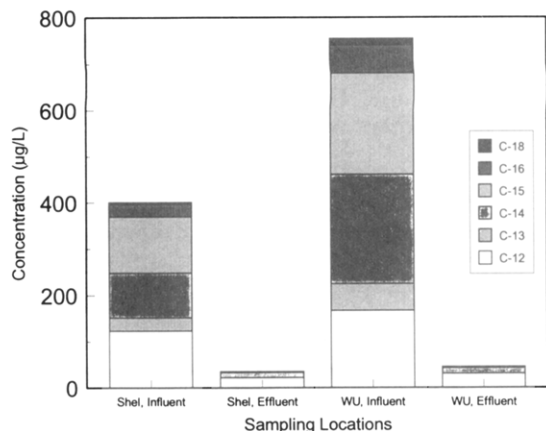


Figure 6. Flow-weighted average AS concentrations in influent and effluent at publicly owned wastewater treatment facilities in Shelbyville, IN, and West Union, OH, calculated from hourly grab samples collected over a 24–25-h period.

tribution for the two locations is shown in Figure 6. Flow-weighted average chain-length distributions reflect use of C₁₂ AS in shampoos and dish-washing applications and the higher chain lengths in laundry and other cleaning product applications.

Total AS influent concentrations were at least a factor of 2.4 times lower than predicted concentrations (1800 µg/L) based on AS use and per capita water use in the United States (10, 11). Previous influent measurements for linear alkylbenzenesulfonate have shown good agreement between predicted and measured concentrations (12, 13). Possible causes for lower than expected influent concentrations may include dilution from industrial sources or storm water, fraction of branched AS in wastewater, or loss of AS during wastewater conveyance. Dilution from industrial sources and storm water runoff was expected to be minimal at both plants, based on conversations with plant operators. In addition, the sampling was coordinated to avoid high-flow conditions that would result from a recent precipitation event. Therefore, it is unlikely that dilution of wastewater from nondomestic sources would result in the lower than expected AS influent concentrations. Because the method as used measured linear AS, the measured values could underestimate the total AS loading. However, the proportion of branched AS in consumer products is low (10–20%), probably does not contribute significantly to total AS loading from domestic use, and would not account for the differences between observed and predicted concentrations. The most likely mechanism that could account for the much lower than expected AS influent concentrations is loss of AS during wastewater conveyance to the sewage treatment plant. AS has been demonstrated to undergo rapid enzymatic hydrolysis to form an alcohol and inorganic sulfate (14). The ubiquitous nature of organisms capable of producing sulfatase is the likely cause of the difficulty we experienced in our attempts to preserve wastewater samples prior to analysis, the rapid loss of AS from wastewater and river water observed by Fendinger et al. (11), and the much lower than expected AS concentrations measured in wastewater.

Effluent AS concentrations at West Union and Shelbyville were attenuated compared to influent concentrations and generally did not vary as a function of time (Figures 7 and 8). Concentrations for individual AS homologs ranged from the detection limit (<5 µg/L) to near 100 µg/L for C₁₂ AS during a single sample period. Total AS flow-weighted average concentrations in treated STP effluent were at least 1 order of magnitude lower than

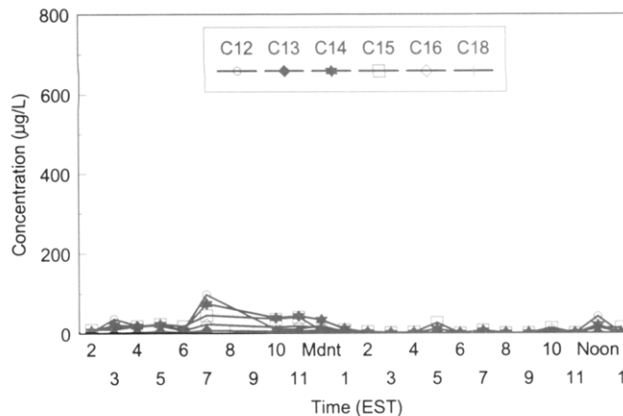


Figure 7. AS homolog concentrations as a function of time in effluent collected at the publicly owned wastewater treatment facility in West Union, OH.

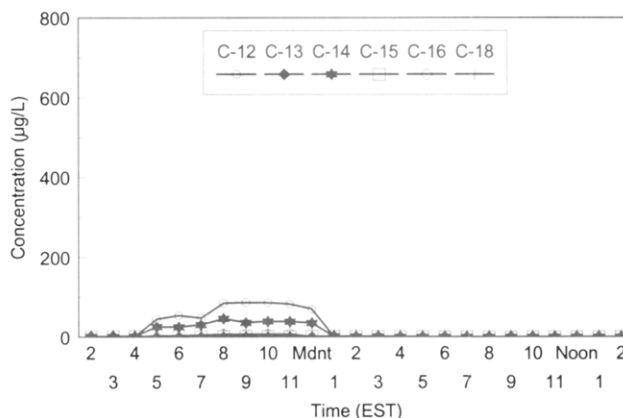


Figure 8. AS homolog concentrations as a function of time in effluent collected at the publicly owned wastewater treatment facility in Shelbyville, IN.

untreated wastewater levels and were 36.2 µg/L at Shelbyville and 46.0 µg/L at West Union (Figure 6). While untreated wastewater AS alkyl chain-length distribution was equally distributed between C_{12,14,15} with lesser amounts of C_{13,16,18}, treated effluent contained predominately C₁₂ AS (Figure 6). Changes in the alkyl distribution between influent and effluent may result from preferential sorption or biodegradation during treatment. Because AS biodegradation is not expected to change dramatically as a function of alkyl chain length (14), shifts in the alkyl distribution probably result from increased removal of longer alkyl chain-length AS homologs because of preferential sorption during treatment. Shifts to lower chain-length homologs in effluent were also observed for LAS by Rapaport and Eckhoff (12) and McAvoy et al. (13). In addition, Marchesi et al. (15) reported that adsorption of linear AS to natural sediments is via a hydrophobic interaction and increases as a function of alkyl chain length.

AS removal, based on flow-weighted average influent and effluent concentrations, was 90% for Shelbyville and 94% for West Union. AS removal at the two plants was similar to BOD removal rates (92–94%). Rapaport and Eckhoff (12) and McEvoy et al. (13) found the trickling filter treatment the least effective treatment type for LAS removal (77% removal compared to 98% removal for activated sludge), with LAS removal correlated with BOD removal. The trickling filter plants sampled in this study had higher BOD removal rates than reported for other trickling filter plants monitored in previous studies (12, 13) and probably had a higher AS removal than would be expected from a larger sampling of treatment plants.

However, AS removal by wastewater treatment should be at least as efficient as LAS removal and also correlate with BOD removal.

AS homolog concentrations in the receiving streams at all the plants monitored were below the detection level (<5 µg/L). Given AS effluent levels and the low dilution of the effluent in the receiving streams sampled, detectable concentrations should be present during some time periods. However, the below detection level concentrations determined in river water grab samples indicate that the half-life of AS in river water is probably very short because of the environmental degradation mechanism for this material (14) and the acclimation of microbial communities in the receiving stream near the treatment plant outfall. For example, White et al. (16) found that 29% of all bacterial isolates from a river produced enzymes capable of AS hydrolysis (alkyl sulfatases).

Conclusions

An analytical method to measure AS in a variety of water samples is described. AS levels in influent were at least 2.4 times lower than predicted based on mass balance calculations and probably result from loss of AS during wastewater conveyance to the sewage treatment plant. Results obtained from use of this method indicate AS removal is similar to BOD removal and was at least 90% at the two trickling filter wastewater treatment plants sampled. AS levels in surface waters that receive treated wastewater were less than the detection limit of the method (<5 µg/L) and reflect the very short half-life of these materials in natural waters.

Registry No. Sodium dodecyl sulfate, 151-21-3; sodium tridecyl sulfate, 3026-63-9; sodium tetradecyl sulfate, 1191-50-0; sodium pentadecyl sulfate, 13393-71-0; sodium hexadecyl sulfate, 1120-01-0; sodium heptadecyl sulfate, 5910-79-2; sodium octadecyl

sulfate, 1120-04-3; water, 7732-18-5.

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