

INVESTIGATION OF AN ONSITE WASTEWATER TREATMENT SYSTEM IN SANDY SOIL: SITE CHARACTERIZATION AND FATE OF ANIONIC AND NONIONIC SURFACTANTS

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Abstract—This study reports on the fate of linear alkylbenzene sulfonate (LAS), alcohol ethoxylate (AE), and alcohol ether sulfate (AES) surfactants in a home septic system near Jacksonville (FL, USA) that has been used since 1976. The drainfield at this site resides in fine sand (<6% silt and clay) with an unsaturated zone that ranges from 0 to 1.3 m. During the wettest times of the year, it is likely that effluent from the septic system passes directly into the groundwater without exposure to an unsaturated zone of soil. Groundwater was collected during two sampling events, representing seasonal high and low groundwater table levels, and analyzed for the surfactants LAS, AES, and AE. During the wet season, the unsaturated zone was approximately 0.01 m beneath the drainfield. During the dry season, the unsaturated zone was about 0.4 m below the drainfield. Alcohol ethoxylate was not detected in any groundwater samples during either sampling. Alcohol ether sulfate was not found in the dry season sampling, but traces of AES had migrated downgradient about 4.7 m horizontally and 1.8 m vertically in the wet season. Linear alkylbenzene sulfonate was detected in some dry season samples and had moved downgradient some 11.7 m horizontally and 3.7 m vertically in the wet season. These observations demonstrate that these surfactants were removed to a great extent; otherwise, they would have traveled more than 260 m downgradient, which is the calculated distance that a conservative tracer like bromide would have moved downgradient over the life of the system. The most likely removal mechanisms for these surfactants were biodegradation and sorption. Therefore, this study indicates that LAS, AES, and AES are readily removed from groundwater in soils below septic system drainfields even in situations with minimal unsaturated soil zones.

Keywords-Groundwater Surfactants Fate Septic systems Soil

INTRODUCTION

On-site wastewater treatment systems (OWTS) serve approximately 25% of the U.S. population and about 37% of new development. Over 25 million U.S. households use OWTS, predominantly septic systems, for wastewater treatment, making them one of the largest sources of effluent discharge to groundwater [1].

As wastewater progresses through a conventional OWTS and into the groundwater, the fate and transport of a given wastewater constituent is determined largely by the characteristics of the soil and groundwater in this subsurface environment, including physical, chemical, and biological characteristics [2]. Impacts of OWTS to ground and surface water quality under certain conditions have been well documented [3–10]. However, most OWTS investigations have focused on constituents such as nitrogen, phosphorous, fecal bacteria, and viruses. Less information is available in the literature regarding the fate and transport of household cleaning and personal care product ingredients discharged to OWTS.

The most widely used surfactants in North America are LAS, AE, and AES. Annual consumption in North America during 2000 for LAS, AE, and AES was estimated at 400,000, 256,000, and 370,000 metric tons, respectively [11]. Details

of the chemical structures for commercial grades of these three surfactants are shown in Table 1. Since these surfactants are used primarily in cleaning and personal care products, their usual route of disposal is down the drain to publicly owned treatment works (POTWs) or OWTS, resulting in their wide dispersal. Although the excellent environmental safety profiles of these surfactants (including their high removals in POTWs) are well documented [12,13], little information exists concerning their fate beneath the drainfields of septic systems. One exception is a series of articles reporting on a comprehensive study of a home OWTS in Ontario, Canada, that provided information on the fate and transport of LAS. As part of this work, LAS was shown to be effectively removed within 5 cm of soil below the drainfield [14-18]. It was also demonstrated that the remaining LAS residues were removed in the unsaturated zone soil so that LAS levels in the aquifer were below the detection limit of 10 μ g/L.

In order to better understand the fate of these surfactants used in household cleaning and personal care products discharged to OWTS, an extensive study of a septic system serving an individual home near Jacksonville (FL, USA) was conducted. This home was selected because it reflected a situation typical in Florida where subtropical weather conditions prevail and septic systems exist in fine sandy soils close to the water table. During the wettest times of the year, it is likely that effluent from the septic system will pass directly into the

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Table 1. Surfactants monitored in the on-site wastewater treatment system effluent and groundwater

Surfactant	Structure	x ^a	y ^a	x + y
Linear alkylbenzene sulfonate (LAS)	$CH_{3}(CH_{2})_{x}CH(CH_{2})_{y}CH_{3}$ $\downarrow \qquad \qquad$	-	-	7 - 11
Alcohol ethoxylate (AE)	CH3(CH2)xO(CH2CH2O)yH	11 - 14	0 - 20	-
Alcohol ether sulfate (AES) ^b	$CH_3(CH_2)_xO(CH_2CH_2O)_ySO_3$	11 - 14	0 - 4	-

^a Common values for commercial-grade materials.

^b Approximately 20 to 50% of the mixture has y = 0 and thus represents an alkyl sulfate component.

groundwater. The first phase of this study involved a detailed characterization of the site, including the home, OWTS, site geology, soils, and groundwater characteristics. This was followed by an evaluation of the fate and transport of three major surfactants found in the household wastewater discharged after septic system treatment. Specific chemical measurements were made for LAS, AE, and AES in septic tank effluents and groundwater during the seasonal high and low groundwater table levels.

SITE DESCRIPTION

The residence utilized for this investigation was a threebedroom, two-bathroom home constructed in 1976. During this study, the house had four residents consisting of two adults and two children. The home had a dishwasher and washing machine but no garbage disposal or water softener. The wastewater from the home flowed into a septic tank with a capacity of 3,400 L. The septic tank effluent (STE) flowed by gravity through the infiltration system that covered 19.5 m² and was approximately 0.6 m below ground surface (BGS). This system consisted of three 0.6×0.6 -m gravel-filled trenches that contained a 10-cm-diameter polyvinyl chloride perforated pipe. The home was in a 200-unit subdivision that was located approximately 800 m east of the St. Johns River in St. Johns County, south of Jacksonville. A plan view of the home's OWTS is shown in Figure 1.

The Jacksonville study site is located in the physiographic area referred to as the Coastal Lowlands [19]. The topography of the lowlands is controlled by a series of marine terraces. Elevations at the site range from 3 to 5 m above mean sea level. Surface drainage in the area is primarily through the St. Johns River and its tributaries.

The climate is subtropical and is characterized by warm, humid summers and mild, dry winters with occasional frost between November and February. Average annual rainfall is approximately 137 cm. Rainfall is seasonal, with the majority falling during the months of June through September [20].

St. Johns County is underlain by two major geologic units of differing lithologies [21]. The uppermost unit consists of clastic sediments including poorly to moderately consolidated sand, clay, and shell. This overlies a thick sequence of limestone and dolomite, commonly referred to as the Floridan aquifer. The top of the limestone of the Floridan aquifer is encountered at approximately 122 m below mean sea level.

Surface soils throughout the subdivision were derived from sandy marine sediments. The site is underlain with Adamsville fine sand [20]. The Adamsville series is classified as a somewhat poorly drained sandy soil with rapid permeability. The water table is typically at 51 to 102 cm BGS for approximately two to six months of the year and greater than 102 cm BGS for the rest of the year. The typical Adamsville profile has a fine sand texture throughout. Limitations for a conventional septic system drainfield are classified as severe because of wetness and poor filtration.

MATERIALS AND METHODS

Soils characterization

Subsurface characteristics of the site were determined from the exploratory soil borings taken to a depth of 15 m BGS during monitoring well and piezometer construction. Representative soil samples were taken from the borings at various depths with a split-spoon sampler. Particle size analyses were conducted according to accepted methods [22].

Additional soil samples were collected in the immediate vicinity of the drainfield to delineate various soil parameters that affect contaminant transport. Soil core samples were collected at three locations below and downgradient of the drainfield using a stainless-steel soil recovery auger with polycarbonate sample liners. Soil core 1 (SC-1) was a composite sample of unsaturated soil collected from locations along the infiltrative surface of trench 1 (directly below the trench) approximately 71 to 91 cm BGS. Soil core 2 (SC-2) was a composite sample from the same boreholes as SC-1, but the cores were taken from the saturated zone below SC-1 from 122 to 142 cm BGS. Soil core 3 (SC-3) was a composite sample of the soil approximately 4.6 m downgradient (southwest) of trench 1 between TW-4 and TW-5 (see Fig. 1). The SC-3 sample was taken from the same relative elevation as SC-2 (122-142 cm BGS) and was also in the saturated zone at the time of sampling. These samples were analyzed for bulk density, porosity, water content, and saturated hydraulic conductivity according to standard methods [22].



Fig. 1. Diagram of septic tank site showing monitoring wells, sampling sites, and groundwater flow.

Groundwater hydrology

This investigation included measurements of groundwater elevation and flow direction. Subsequent aquifer testing was used to identify groundwater monitoring points in downgradient locations likely to be impacted by advective transport of septic system effluent constituents.

Shallow groundwater monitoring wells were installed via a hand auger. The wells consisted of a 5-cm-diameter polyvinyl chloride pipe with a 60-cm slotted well screen attached at the bottom. Monitoring wells were installed to a depth just below the water table and were used to determine water table elevations and the general direction of groundwater flow. Three pairs of nested piezometer sets were also installed at the site to determine if a vertical component of flow was present. Each nested piezometer set consisted of two 5-cm-diameter polyvinyl chloride wells with 60-cm screen length, installed side by side with a hollow-stem auger drill rig. One well was installed to a depth of 15 m and the other to a depth of 1.5 m BGS. Differences in water elevation in these side-by-side wells indicated vertical groundwater flow, and these data were used to determine whether the vertical flow component was great enough to cause the contaminant plume to be transported into a deeper zone.

Water table elevation data were obtained to determine the thickness of the unsaturated soil beneath the bottom of the infiltration system. Monitoring well W-5 was installed between the trenches of the OWTS infiltration system for this purpose. A remote data-sensing water level indicator was installed adjacent to W-5 to automatically record water table elevations at 6-h intervals. A data-logging rain gauge was installed at the site to measure and record precipitation events. This automation allowed for a more detailed evaluation of water table

fluctuations and unsaturated zone thickness below the OWTS in response to rainfall.

Slug testing was performed on several monitoring wells at the site to obtain estimates of the saturated hydraulic conductivity in the shallow water table zone. The slug tests were performed by rapidly removing a large slug of water from the well casing and measuring the rate of rise of water back into the well. Slug tests were performed in wells W-5, SW-7, and SW-9 (see Fig. 1). Data from these tests were used to calculate saturated hydraulic conductivity using the method of Bouwer and Rich [23,24].

Groundwater transport monitoring

In addition to the permanent monitoring wells described here, a network of discrete sample points was installed downgradient of the drainfield using the direct push method [25]. Two types of stainless-steel miniature wellpoint probes were used to obtain groundwater samples at the site. The first probe unit utilized a push-pull wellpoint attached to Teflon[®] tubing (0.95-cm i.d.). The Teflon tubing was inserted through 1.27cm-i.d. stainless-steel tubing that was then pushed or driven into the saturated zone to the desired sample depth. The groundwater samples were obtained from this device by opening the wellpoint with a slight upward pull and then pumping samples to the surface through the Teflon tubing using a peristaltic pump. The entire probe system could then be pulled from the ground and installed at a new sample location. This system allowed collection of groundwater samples from 10 to 15 different locations in a day and was especially useful for initial identification of the contaminant plume. The second direct push probe was similar to the first, except that a miniature stainless-steel wellpoint attached to Teflon tubing was left in the ground after pulling the probe system out.

A system of 30 direct push, stainless-steel miniature wellpoints was installed in January 1993 at 13 surface locations. Sampling points TW-1 through TW-6 were installed at three depths (1.8, 3.7, and 6.1 m BGS); TW-7 through TW-9 were added with wellpoints at 1.8 and 6.1 m BGS (see Fig. 1). One sample point of TW-10 through TW-12 at 1.8 m BGS and an upgradient background well BW-1 had wellpoints at 1.5, 3.1 and 4.6 m BGS. Groundwater samples were taken from these wellpoints in January 1993, preserved with 1% (v/v) formalin (37% formaldehyde solution), and analyzed for chloride (Cl⁻), methylene blue active substance (MBAS), and six other parameters according to standard methods [26].

Twenty-two additional miniature stainless-steel wellpoints were installed in August 1993. These wellpoints included sample points TW-13 through TW-18 with wellpoints at 1.8, 3.7, and 6.1 m BGS, wellpoints at 3.7 m BGS in TW-7 through TW-9, and a wellpoint at 6.1 m BGS in BW-1. Thirty-three more miniature stainless-steel wellpoints were added in February 1995. These new sample points were TW-19 through TW-25 with wellpoints at the typical 1.8, 3.7, and 6.1 m BGS and TW-26 through TW-28 with wellpoints at 1.8, 3.7, 6.1, and 9.1 m BGS. Figure 1 shows the sample locations at the site after February 1995.

Bromide tracer testing

A groundwater tracer test was conducted to determine groundwater velocities, verify groundwater flow direction, quantify the effects of dilution, and obtain more accurate hydraulic conductivity values of the saturated soils. Bromide was selected as the tracer because it is highly mobile in groundwater and is not typically present in septic tank effluent to any great extent. Bromide was added by flushing 8 kg of sodium bromide down the household toilet on May 9, 1995. Bromide ion concentrations were then measured in samples from the septic tank effluent and shallow groundwater wellpoint network using a bromide ion-selective electrode in the field. This information was used to calculate groundwater transport characteristics at the site.

Septic tank effluent characterization

A septic tank effluent sampling basin was installed between the septic tank and the infiltration system. Grab samples were obtained by pumping STE from the basin through a dedicated Teflon tubing line with a peristaltic pump. Twelve STE samples were taken from August 1993 through May 1995. The STE samples were preserved and analyzed according to standard methods [26] for the following parameters: biochemical oxygen demand (BOD), total organic carbon (TOC), MBAS, chloride, ammonia nitrogen (NH₃-N), nitrate nitrogen (NO₃-N), and total phosphorous (TP).

Nine STE samples taken from August 1993 through May 1995 were analyzed for LAS. Single grab samples taken in November 1993 and May 1995 were analyzed for AE and AES. Septic tank effluent quantity was estimated using water meters installed at various locations on the home water system. Interior water use was then used as an estimate of wastewater flow to the septic tank.

Groundwater sampling procedures for surfactant analysis

A peristaltic pump with Teflon tubing was utilized to pump groundwater samples from the wellpoints directly into amber glass bottles. Pump tubing was replaced between each sampling event. Each wellpoint had dedicated Teflon tubing attached to the desired depths. Prior to filling the sample bottles, several liters of groundwater were pumped from the wellpoints to purge the system of stagnant water. Samples were preserved with 8% (v/v) formalin (37% formaldehyde solution) and shipped immediately to the analytical laboratories for specific surfactant analysis. Samples were also prepared and assayed for the same parameters as was done with the STE [26]. Two sampling events for analysis of LAS, AE, and AES were performed. The first was from November 3 to 5, 1993 (wet season). Since November is part of the wet season, the unsaturated soil thickness was very small (0.01 m) at the time of sampling. Nineteen sampling locations with 52 wellpoints were available for sampling. Fifty of these wellpoints were sampled and analyzed for MBAS and LAS. Both AE and AES analyses were done on 15 and 21 samples, respectively. The selection of wellpoints to sample and analyze for the surfactants was based on MBAS results from the January 1993 sampling event. Results of MBAS were used because methylene blue responds to LAS and AES in water samples. Furthermore, it was assumed that AE would be in samples that showed LAS and AES.

The second sampling event was from May 8 to 12, 1995 (dry season). Even though this sampling event was in the middle of the dry season, the unsaturated soil thickness was only 0.4 m. By this time period, the monitoring system had been expanded to 29 sample locations with 85 permanent stainless-steel wellpoints at depths from 1.5 to 9.1 m BGS. Of these wellpoints, 57 were analyzed for MBAS and LAS, 20 for AE, and 21 for AES. The selection of these wellpoints was based on the results from the November 1993 sampling event.

LAS analysis

Concentrations of commercial LAS (C10-C14) were determined in STE and groundwater samples using a procedure similar to the method of Castles et al. [27]. The sample was acidified and spiked with a C₉ LAS homolog (prepared by Sasol North America, Houston, TX, USA) as an internal standard. An aliquot of the sample was passed through a C_2 solidphase extraction (SPE) cartridge (Varian, Harbor City, CA, USA), and the cartridge was rinsed with a 70:30 (v/v) water: methanol. Linear alkylbenzene sulfonate was eluted with methanol and then passed through a strong anion exchange (SAX) cartridge (Varian). The SAX cartridge was rinsed with 2% acetic acid in methanol, which was followed by 5 ml of methanol. The LAS was eluted with 1:1 (v/v) 2-N hydrochloric acid (HCl) and methanol. The SAX cartridge eluate was evaporated to dryness, and a C15 LAS homolog (prepared by Sasol North America) was added as an internal standard. The dried eluate was reconstituted in a solution of 1:1 (v/v) water and methanol and 0.25 mM sodium dodecyl sulfate. All solvents were high-performance liquid chromatography grade, and the water was Nanopure (Macalaster Bicknell, New Haven, CT, USA [18 milliohms]).

Linear alkylbenzene sulfonate was analyzed by high-performance liquid chromatography similar to the method of Castles et al. [27]. The method was isocratic, using a 45:55 (v/v) tetrahydrofuran and 0.1-M NaClO₄ (in water) eluent. Detection was with ultraviolet fluorescence, which was optimized for detection of LAS (225 nm for excitation and 290 nm for emission). The limit of quantitation was 10 μ g/L.

Septic tank effluent and groundwater samples were spiked with a commercial-type LAS with an average alkyl chain length of 11.4 carbons. Septic tank effluent samples were spiked in the field with 1 to 30 mg/L and in the laboratory with 3 and 30 mg/L LAS. Field spikes were done at 0.1 to 5.0 mg/L LAS in groundwater samples. Some spiking of groundwater samples was done after the samples were taken to the laboratory at 0.1 to 1.0 mg/L LAS. Spikes were done in the field and the laboratory to determine the effects of sample manipulations and storage on the efficiency of the analytical method to detect LAS. Procedural blanks were included in all analyses.

AE analysis

Alcohol ethoxylate isolation, concentration, and analyses were done using three different procedures for groundwater samples from the November 1993 sampling event, septic tank effluent samples from the August 1993 sampling event, and groundwater and septic tank effluent samples from the May 1995 sampling campaign. Different procedures were used because the AE analytical technology was improving during this time period.

Sample preparation for the November 1993 sampling event was similar to the methods of Evans et al. [28]. A C₈ SPE cartridge was used to isolate the AE. The AE samples were passed through a preconditioned C₈ column (methanol followed by deionized water). Following rinses of 0.001 N HCl (to remove excess formaldehyde), AE was eluted with methanol and isopropyl alcohol (2:1, v/v). Solvents were removed by evaporation, and AE was resuspended in methanol:water (1:1, v/v). Alcohol ethoxylate analysis was done in a manner similar to that described in Dorn et al. [29]. This method separated and quantified the AE by high-performance liquid chromatography with evaporative light scattering detection. Results were reported as total AE, and the detection limit was approximately 10 μ g/L. Selected groundwater samples from November 1993 were spiked in the field with 100 μ g/L deuterated C₁₃EO₉ alcohol ethoxylate.

Septic tank effluent samples from August 1993 were prepared and analyzed by a methodology similar to that described in Evans et al. [28]. Sample preparation used a C₈ SPE cartridge as described previously. Alcohol ethoxylate analysis and quantitation were done by reverse-phase thermospray liquid chromatography/mass spectroscopy (LC/MS) using deuterated $C_{13}EO_9$ alcohol ethoxylate as an internal standard (injected before MS analysis). Results were reported as total AE, and the detection limit was approximately 10 µg/L. Selected STE samples were spiked with 10 mg/L Neodol[®] 25-9 alcohol ethoxylate (Shell Chemical, Houston, TX, USA).

Groundwater and septic tank effluent samples from the May 1995 sampling campaign were prepared and analyzed in a manner similar to the methods of Evans et al. [30]. Samples were prepared by passing them through a C₈ SPE cartridge, which was preconditioned with methanol, followed by isopropanol, and finally deionized water. Alcohol ethoxylate was eluted with methanol followed by isopropanol (2:1, v/v). Solvents were removed by evaporation, and the AE was resuspended in methanol. Alcohol ethoxylate analysis and quantitation were done by electrospray LC/MS using deuterated $C_{13}EO_9$ alcohol ethoxylate as an internal standard. Results were reported as total AE, and the detection limit was approximately 5 µg/L. In addition, groundwater samples from this sampling event were spiked in the field (100 µg/L) and in the laboratory (10.3 µg/L) with Neodol 25-9 alcohol ethoxylate.

The results for all three sets of samples were reported as total AE, which is a sum of all the ethoxymers $(C_{12-15}EO_{2-18})$.

AES analysis

The STE and groundwater samples for AES analysis were first passed through a preconditioned C_2 SPE column for surfactant isolation. Surfactants were eluted from the SPE cartridge with methanol:ethyl acetate (1:1, v/v) followed by methanol. Separation of anionic and nonionic surfactants was performed using a SAX column. After elution with 2.4 M HCl in methanol, the anionic surfactants were dried, derivatized with HBr (33% in glacial acetic acid) at 10°C for 4 h, cooled to room temperature, resuspended in water, and extracted three times with methylene chloride.

Alkyl bromide analysis was accomplished with a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a Hewlett-Packard 5971 mass selective detector (Palo Alto, CA, USA). Chromatographic conditions were as follows: column— HP-1 (dimethylpolysiloxane) or HP-5 (5% diphenyl, 95% dimethylpolysiloxane); 30 m \times 0.25 mm, 0.25-µm film thickness bonded-phase capillary column; carrier gas—helium; heat linear flow velocity of 40 cm/s; injection—splitless; injector temperature—280°C; GC temperature—50°C for 1 min and increased at 10°C/min to 280°C and held for 2 min. Mass detection was done at 280°C.

The total AES concentrations were calculated from the masses of alkyl bromides as measured by GC/MSD. The average number of moles of EO for AES was assumed to be 1.7 as determined by LC/MS during another study [31]. The method did not distinguish between alkyl bromides from AES or alkyl sulfates (AS). The quantitation limit was 10 μ g/L. Groundwater samples were spiked in the field with approximately 100 μ g/L of a deuterated C₁₃ AS.

Table 2. Summary of soil data from cores

	Sample identification			
Soil parameter	SC-1 ^a	SC-2 ^b	SC-3°	
Bulk density (g/cm^3)	1.43	1.54	1.53	
Water content (% wt)	23.60	26.00	42.30 30.10	
Saturated hydraulic con- ductivity (cm/d)	324.00	410.00	514.00	

^a Soil core 1 (SC-1) was a composite sample of unsaturated soil directly below trench 1 (see the *Materials and Methods* section).

^b Soil core 2 (SC-2) was a composite sample from boreholes of SC-1 but taken from the saturated zone (see the *Materials and Methods* section).

^c Soil core 3 (SC-3) was composite sample about 4.6 m downgradient of trench 1 (see *Materials and Methods* section).

RESULTS AND DISCUSSION

Soil characteristics

Particle size analyses indicated that soil samples were of fine sand texture. Approximately 85 to 97% by weight of the soil samples obtained were composed of fine sand, while the percentage of silts and clays (fines) ranged from 0.9 to 6.0%. Percentages of medium sand were generally less than 5% with the exception of soil samples obtained at approximately 8.2 to 9.8 m BGS that contained approximately 10% medium sand. Physical characteristics of the soil from the site are presented in Table 2.

Groundwater hydrology

Water level measurements indicated that the groundwater flow at the site was south-southwest toward the St. Johns River. Figure 1 shows the location of piezometers, monitoring wells, and relative groundwater elevation contours calculated from data collected in February 1995. The horizontal groundwater elevation gradient measured during the wet sampling period ranged from 0.0029 m/m (November 5, 1993) to 0.0043 m/m (February 20, 1995) and was 0.0016 m/m during the dry season (June 29, 1995). A vertical downward gradient that ranged from 0 to 0.008 m/m was observed at the southwest corner piezometers, indicating a potential for horizontal and downward groundwater flow at the site.

The water table would fall through the dry season and rise during the rainy season (Fig. 2). For example, a 20-cm rainfall event in 1995 caused a 0.6-m rise in the water table. The unsaturated soil thickness ranged from 0 to 1.26 m BGS. The



Fig. 2. Relative groundwater elevations and 7-d cumulative precipitation at study site. Note the rapid response of water table to precipitation.

top of the unsaturated zone was routinely within 0.3 m of the infiltrative surface of the drainfield, and occasionally the measured groundwater levels were higher than the infiltrative surface of the drainfield. For example, on October 17, 1994, the water table was 0.15 m above the infiltrative surface.

The saturated hydraulic conductivity estimated from the slug tests ranged from 212 cm/d at SW-9 to 282 cm/d at well W-5.

Bromide transport

Bromide began to exit the septic tank shortly after input; the first STE sample taken 30 min after input contained >600 mg/L bromide. The peak bromide concentration (2,000 mg/L) in the STE was measured approximately 54 h after input. Four subsequent bromide samplings were conducted with the pushpull sampler as well as the permanent sample points to determine where the bromide plume was located. The bromide infiltrated along the length of trench 1, but it moved more quickly in the area farther from the septic tank. This would likely be the case if a biomat had developed in the near-tank area, as biomats have been shown to slow effluent infiltration into unsaturated zones [32,33]. After 150 d, the bromide plume had extended past TW-4, TW-5, and TW-6 and had moved approximately 7 m downgradient of trench 1 (Fig. 3).

These bromide data were based on groundwater samples taken 1.8 m BGS. Vertical profile samples showed that the peak bromide concentrations were at 1.8 to 2.4 m BGS and that the shallow sample data used to delineate the plume shown in Figure 3 were the highest bromide concentrations.

Average groundwater seepage velocities were calculated from the bromide groundwater data (Fig. 3). These velocities were based on the distance of the highest bromide concentration downgradient from trench 1 and the time of travel. The velocity calculations are very consistent and indicate a relatively uniform average seepage velocity of approximately 0.04 m/d downgradient.

The bromide tracer data also provided the opportunity to more accurately estimate the average, in situ hydraulic conductivity of the shallow water table soils at this site. The travel time of the bromide peak between two points downgradient is related to the saturated hydraulic conductivity of the soil through which it travels since bromide is an inert compound that moves readily with groundwater flow [34]. The saturated hydraulic conductivity was estimated to be 257 cm/d by applying the relationship between the seepage velocity and the saturated hydraulic conductivity described in the Darcy equation. This value for the saturated hydraulic conductivity is lower than those determined on soil cores in the laboratory (Table 2); however, it agrees well with the saturated hydraulic conductivity values determined with the slug test. The differences observed between the saturated hydraulic conductivity values determined in the laboratory with core samples and the field values are probably due to two factors: The act of extracting a core sample from the field disturbs the soil and changes the soil's physical characteristics, and the results from the cores reflect a very small portion of the actual field situation. These results illustrate the importance of determining transport parameters in the field prior to predicting or modeling contaminant transport.

Surfactant analysis

Results of surfactant analysis described earlier (LAS, AE, and AES) were corrected on the basis of field spike recoveries. Recoveries from field spikes of LAS into STE (1–30 mg/L)



Fig. 3. Groundwater bromide concentrations (mg/L) following addition to the septic tank.

ranged from 80 to 103% with a mean of 87% and a standard deviation of 8%. Two laboratory spikes of STE with LAS at 3 and 30 mg/L were recovered at 107 and 108%. Groundwater samples (1993 and 1995) spiked in the field with LAS from 0.1 to 5.0 mg/L showed recoveries ranging from 40 to 170% with a mean of 100% and a standard deviation of 33%. Laboratory spikes of groundwater (1993 and 1995) with LAS from 0.1 to 1.0 mg/L had a range of recovery from 70 to 121% with a mean of 94% and a standard deviation of 14%. The greatest variability in the recoveries was noted with the 0.1-mg/L spike.

The recoveries for the field spikes of 100 µg/L deuterated $C_{13}EO_9$ alcohol ethoxylate into the groundwater samples taken in November 1993 ranged from 62 to 100% with a mean of 95% and a standard deviation of 19%. Recoveries for field spikes of Neodol 25-9 alcohol ethoxylate into groundwater (1995) of 100 μ g/L ranged from 23 to 48% with a mean of 34% and a standard deviation of 10%. Neodol 25-9 alcohol ethoxylate was recovered more efficiently from spikes of 10.3 μ g/L into groundwater (1995) done in the laboratory with a mean of 60% and a standard deviation of 4%. The recovery of Neodol 25-9 alcohol ethoxylate from 10-mg/L spikes into STE (1993) ranged from 98 to 172% with a mean of 135% and a standard deviation of 37%. For AES analysis, field spikes of 100 μ g/L of a deuterated C₁₃ AS into groundwater (1993 and 1995) was recovered with a range of 58 to 130% with a mean of 99% and a standard deviation of 26%.

STE monitoring

The soil and groundwater conditions at this single home septic system near Jacksonville represent a worst case for demonstrating the treatment of the organic load (including surfactants) coming from STE. In contrast to this system was the septic system in Canada that always has an unsaturated soil zone of at least 2 m and showed removal of LAS within 5 cm of the soil beneath the drainfield [14-18]. The opportunities for the STE in the Florida system to be exposed to unsaturated soil are diminished. The septic system drainfield is placed in sand with a high water table, which results in an unsaturated soil treatment zone from 0 to 1.3 m. Many times, the STE passes directly into the groundwater without exposure to an unsaturated zone. In order to follow the fate of key STE components, including major surfactants that are used in cleaning products, it was necessary to first determine the concentrations of these and other key components in the STE. Results from these analyses are detailed in Table 3. Values for the parameters measured were typically in the range of previously reported STE measurements by Sherman et al. [35]. The concentrations of BOD₅, MBAS, and nitrogen were on the high end of the range reported in the literature.

Average removal of key components after passing through the infiltration surface was estimated by comparing concentrations in groundwater samples (taken just below the infiltration surface and 0.4 m unsaturated soil, locations TW-19, TW-20, and TW-21) to the STE concentrations. The results from May 1995 (dry season) are summarized in Table 4. The organic load from STE as measured by TOC was about 91 mg/L with the surfactants accounting for approximately 13% of this TOC. The surfactants showed a higher level of removal (>96%) across the aerobic infiltration surface than the TOC (90%). After exposure to the infiltration surface, the surfactants' contribution was reduced to <4% of the STE organic load, which would pass to the groundwater. Ammonium ion was converted to nitrate as the septic tank effluent passed through the highly active biomass at the infiltration surface. The large variability in the ammonium-to-nitrate ratio in the closest downgradient samples suggests that pockets of anaerobic conditions may have been present in the immediate subsurface soil environment. Chloride and total phosphorus concentrations do not appear to be significantly reduced by exposure to the biomass.

Table 3. Septic tank effluent quality; samples from August 1993 to May 1995

		G: 1 1		Range	
Parameter	Mean	deviation	N^{a}	Min	Max
Methylene blue active substances (MBAS)					
(mg/L)	23.8	6.3	12	15	32
Linear alkylbenzene sulfonate (LAS) (mg/L)	14.6	2.8	9	9.5	18.1
Alcohol ether sulfate (AES) (mg/L)	4.8	NA ^b	2	4.13	5.47
Alcohol ethoxylate (AE) (mg/L)	0.64	0.18	8	0.44	0.94
Total organic carbon (TOC) (mg/L)	90.7	47.0	12	42	190
Biochemical oxygen demand (BOD ₅) (mg/L)	217	93	12	160	419
Chloride (Cl ⁻) (mg/L)	54.6	8.0	11	41	65
Total phosphorous (TP) (mg/L)	8.4	1.1	12	6.9	10.0
Ammonia-nitrogen (NH_3-N) (mg/L)	62.0	10.0	12	48	86
Nitrate-nitrogen $(NO_3^ N)$ (mg/L)	0.03	0.02	12	0.01	0.07

^a Number of samples analyzed.

^b NA = not applicable.

Groundwater monitoring

Since the groundwater seepage velocity was 0.04 m/d and the house had been in use since 1976, the water-soluble components of the STE that were passed to the groundwater should have traveled more than 260 m downgradient from the drainfield. If retardation by sorption and removal due to biodegradation were occurring, it would be expected that STE components should be removed from the groundwater within 260 m. In order to test this prediction, it was necessary to determine the concentrations of key STE components in the contaminant plume downgradient of the drainfield.

Visual presentation of the LAS, MBAS, nitrogen species, and total phosphorous groundwater data are shown as concentration contours in Figures 4 and 5. Figure 6 illustrates the vertical and horizontal migration of LAS through the groundwater by showing LAS concentrations along the centerline of the plume. The location of the centerline is shown in Figure

Table 4. Concentrations of components (May 1995) just below drainfield and average removals compared to septic tank effluent (STE) concentrations (see Table 3)

	Component concn. (mg/L) ^b					
-		G(1 1		Range		D 1a
Component ^a	Mean	deviation	N^{d}	Min.	Max.	(%)
MBAS	0.76	0.85	3	0.06	1.7	96.8
LAS	< 0.55	>0.82	3	< 0.1	1.5	>96.2
AES	ND ^e	NA^{f}	3	NA	NA	>99.8
AE	ND	NA	2	NA	NA	>99.1
TOC	9.0	2.6	3	7.5	12.0	90.1
Cl-	32.0	12.1	3	23	46	41.0
TP	8.8	4.8	3	3.3	12.0	0
NH_4^+-N	31.8	30.4	3	0.3	61.0	NA
$NO_3^ N$	<3.2	>5.4	3	< 0.01	9.4	NA

^a For descriptions of abbreviations, see Table 3.

^b Values of 1.8 m wellpoints from sampling locations. TW-19, TW-20, and TW-21 that are the closest downgradient points (see Fig. 1).

° % Removal

 $= \frac{(\text{mean concn. in STE}) - (\text{mean concn. in samples})}{\text{mean concn. in STE}} \times 100.$

^d Number of samples analyzed.

 e ND = not detectable for AE (<5 $\mu g/L$), for LAS and AES < limit of quantitation (10 $\mu g/L$).

f NA = not applicable.





Fig. 4. Contours of (A) linear alkylbenzene sulfonate (LAS) plume (1.8 m below ground surface [BGS]) and the centerline of the plume cross section and (B) contours of methylene blue active substance (MBAS) plume (1.8 m BGS) from sampling in 1993 and 1995. Concentrations in mg/L.



Fig. 5. Contours of (A) NH₃-N plume, (B) contours of NO $_{3}$ -N plume, and (C) contours of total phosphorous plume (1.8 m) from 1993 and 1995 sampling. Concentrations in mg/L. BGS = below ground surface.





Distance along centerline of plume (cross section) (m)

Fig. 6. Vertical distribution of linear alkylbenzene sulfonate (LAS) along the centerline of the plume (cross section) from sampling in 1993 (A) and 1995 (B).

4A. The MBAS and LAS concentration contours (Fig. 4) are very similar. This is an expected result since LAS is a major component of the soluble chemicals detected by MBAS. Total organic carbon concentrations were reduced to the levels seen in the background well (3–5 mg/L) in samples \geq 22 m downgradient from the drainfield.

The ammonia and nitrate contours (Fig. 5) indicate that the concentration of dissolved oxygen in the groundwater varies with time and space, which apparently resulted in anoxic conditions in certain locations where denitrification may have occurred. Consequently, variation in the ammonia-to-nitrate ratio in groundwater samples was observed. These conditions may also have reduced the rate of LAS removal. The total phosphorous concentration contours are very similar between the high and low water table sampling events.

The septic tank drainfield system was extremely effective at removing AE and AES. Even in the worst-case sampling regime (November 1993), nondetectable levels (<5 µg/L) of AE were measured, and only 3 of 21 samples analyzed for AES were greater than the quantitation level of 10 µg/L. Samples at 1.7 and 4.7 m downgradient of the drainfield showed 18 and 13 µg/L of AES, respectively. The other sample was directly beneath the drainfield and had an AES concentration of 13 µg/L. During the dry season sampling event, no detectable levels of AE or AES were found in any groundwater samples (<0.2 m downgradient of drainage field).

Linear alkylbenzene sulfonate was found to migrate in the groundwater with detectable levels as far as 11.7 m horizontally (Fig. 4) and 3.7 m vertically (Fig. 6) from the drainfield during the wet season. As reflected in Figure 4, the LAS plume was smaller during the dry season. The concentrations of LAS in the plume dramatically decreased during the dry season, when more unsaturated soil was available for rapid removal of the surfactant. These data suggest that LAS is being removed from the groundwater environment because it should have migrated some 260 m downgradient of the drainfield by 1995 as predicted by the seepage velocity if no removal mechanisms were present. The most reasonable removal mechanisms for LAS are biodegradation and adsorption. Research by Doi et al. [36] demonstrated that the subsurface soils at this site have the potential for adsorbing and mineralizing LAS. Also, chloride monitoring data show that dilution of surfactants by groundwater in the main portion of the plume was insignificant. For example, during the January 1993 sampling, the mean chloride concentration at the 1.7-m-BGS depth in downgradient sample locations TW-1 through TW-12 (see Fig. 1) was 58 mg/L, which compares to a mean of about 55 mg/L in the STE.

CONCLUSIONS

The soil and groundwater conditions at a single home septic system near Jacksonville represent a worst case for demonstrating the treatment of septic tank effluent. Despite these adverse circumstances, the septic treatment system (aerobic infiltration surface/unsaturated soil and saturated soil) effectively removes STE components. Most of the treatment occurs at the infiltration surface since about 90% of the STE organic load (TOC), >96% of LAS, and >99% of AE and AES were removed when a 0.4-m unsaturated zone existed. The remaining 10% of the STE total organic carbon was reduced to background concentrations after moving 22 m downgradient of the drainfield. Under the worst conditions, when very little (0.01 m) or no unsaturated treatment zone is present, LAS and AES surfactant residues were detected in the groundwater; AE was not detected. Alcohol ether sulfate was not detected beyond 4.7 m horizontally and 1.8 m vertically downgradient from the drainfield. Linear alkylbenzene sulfonate was detected only up to 11.7 m horizontally and 3.7 m vertically from the drainfield during the wet season. Since it was possible for the surfactants to have migrated as much as 260 m if they had moved uninhibited with the wastewater plume, it is clear that removal was occurring. The most likely removal mechanisms for these surfactants are biodegradation and sorption.

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