

**LAS: Aquatic Toxicity  
and Biodegradation**

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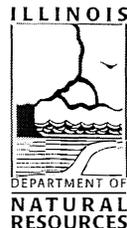
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TN 93-029

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Printed March 1993



*Illinois Department of Energy and Natural Resources*

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Research supported by  
U.S. Army Construction Engineering Research Laboratory

Printed March 1993

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This report was prepared as part of the effort under contract to the U.S. Army Construction Engineering Research Laboratory (contract no. DACA88-90-D-0041-35). The information in this article has not been subject to review by CERL or the Department of Energy and Natural Resources. The material included is a survey of existing literature and does not necessarily reflect the views of either agency and no official endorsement should be inferred.

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## Abstract

The US Army Corps of Engineers has experienced numerous problems with bacterial die-off at wastewater treatment plants experiencing loads from aircraft cleaning operations. The logical conclusion reached in investigations of these facilities is that the cleaners, and more specifically, the surfactants in the cleaners, are adversely impacting treatment plant operations. This review represents a further step in the pursuit of a solution to that problem.

The purpose of this review is to investigate the toxicity to aquatic organisms and the environmental stability of the most widely used surfactant, linear alkylbenzene sulfonate (LAS). Toxicity data specific for LAS to bacteria in treatment plants are extremely limited, however, data on toxicity of LAS to a variety of organisms in other aquatic environments are available. Further, considerable data exists on the biodegradation of LAS in treatment systems and natural waters. This review presents the current scientific understanding of the toxicological effects of LAS and its environmental stability. From this base of information, it should be possible to infer potential effects of LAS-based surfactants on wastewater treatment plant bacterial populations.

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## I. Introduction

The intent of this paper is to describe the toxicity of linear alkylbenzene sulfonates (LAS) to bacteria in wastewater treatment processes. Toxicity data specific for LAS to bacteria in treatment plants are extremely limited, however data on the toxicity of LAS in other aquatic environments are available and are reported here. Using data from other aquatic systems to predict what may occur in a treatment facility has some obvious limitations. Nonetheless, those data may offer valuable insight into the following discussion of the factors involved in toxicity of LAS, including the biodegradability and species specificity.

After soap, LAS is the most widely used raw material in laundry and cleaning detergents for household, industrial and institutional formulations (Berna et al. 1991). The main benefit of LAS in these products is its cleaning power which comes from its good wetting, rolling-up, emulsifying, dispersing, and foaming characteristics, as well as its ability to reduce surface tension (Fisher and Marsh, 1983). LAS is currently produced and used in over 100 countries with approximately  $2 \times 10^6$  tons consumed worldwide in 1989 (Berna et al., 1991). Interestingly, the attempts to correlate LAS consumption based on sales data to LAS consumption based on environmental monitoring data shows large discrepancies. These discrepancies are most often due to biodegradation in sewers and washing machines (Painter and Zabel, 1989; Giger et al., 1987).

Surfactants were first discovered in the late 1930s, but it wasn't until the 1950s that they came into widespread use. ABS (alkylbenzene sulfonate), a branched alkyl chain surfactant, was the first surfactant used commercially. ABS does not completely biodegrade in wastewater treatment processes, causing the effluents to foam as they enter natural waters. The problems relating to this excessive foaming made ABS use aesthetically unpleasant (Swisher, 1987). LAS was developed in the early 1960s as improved technologies

allowed production of straight alkyl chain surfactants. These linear chains biodegrade easier and quicker than branched chains and cause minimal problems with wastewater treatment. When the Soap and Detergent Association made the switch from ABS to LAS in 1965, the foaming problem was eliminated. The newly adopted LAS proved to be more acutely toxic to some aquatic organisms (fish). However, this acute toxicity was offset by the rapid degradation of LAS during sewage treatment (Painter and Zabel, 1989).

In terms of environmental impact, LAS has been and continues to be one of the most intensely investigated synthetic chemicals (Giger et al., 1989). When LAS was introduced in 1965, environmental issues had moved into the worldwide consciousness. The foaming characteristics of surfactants were under close scrutiny and the environmental acceptability of this compound was a sensitive issue. LAS would be produced in large quantities and would reach the environment through direct disposal as well as in the effluents of treatment plants. Human health safety issues as well as the impact of the LAS on the aquatic and terrestrial environments had to be addressed. Resulting investigations have led to the conclusion that LAS exhibits no detrimental impact in sewage treatment facilities or their effluents (Brown, 1977; Huber et al., 1989; Kimerle, 1989).

Toxicity is a major consideration in assessing the environmental acceptability of a material. As a class, surfactants exhibit significant toxicity (Sivak et al., 1982), with fish being one of the most highly susceptible to the toxic effects. Other aquatic species are comparably sensitive with tolerance increasing in the lower, less organized life forms (Swisher, 1987). Terrestrial animals are much less sensitive than aquatic organisms.

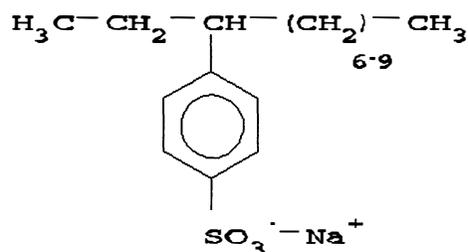
Structural characteristics such as carbon chain length and alkyl group position, as well as many environmental factors can influence the range in toxicity of chemicals entering an aquatic ecosystem. The characteristics of the ecosystem into which the LAS is deposited,

such as temperature and water hardness can affect toxicity. Different biotic species, as well as the life stage and nutritional status of the each individual species tested, vary in toxic response to LAS. This paper will address these factors of LAS toxicity.

Disposal of LAS is usually 'down the drain' so the primary mode of environmental entry is as a component of domestic/municipal wastewater. The percentage of LAS treated is as high as 50-75% of total LAS used in most industrialized countries, and as low as 5-30% in less developed areas. In areas where no waste treatment is available, disposal involves direct discharge to the surface or subsurface waters or soil (Swisher, 1987).

## II. Chemical Characteristics

A surfactant is composed of a strongly hydrophilic group and a strongly hydrophobic group combined in the same molecule. The hydrophobic group usually consists of an 8 to 20 carbon atom chain, whereas the hydrophilic end consists of either an anionic (sulfonate, sulfate, or carboxylate), cationic (quaternary ammonium), or nonionic (polyoxyethylene, sucrose or polypeptide) group (Swisher, 1970). Linear alkylbenzene sulfonate is a blend of homologs of varying carbon chain lengths with a terminal methyl group and a sulphonated benzene ring (see Figure 1). In different isomers the aromatic ring resides on different carbons along a particular chain length (Schöberl, 1989).



**Figure 1**  
Structural formula of LAS (C<sub>10-13</sub>)

It is the surface characteristics and micelle formation properties which give surfactants their widespread applications. The surface action occurs because of the hydrophobic and hydrophilic groups on the surfactant molecule. The behavior of the molecules in aqueous solution is such that the hydrophilic group tends to associate with the water, and the hydrophobic group tends to be repelled by the water. This causes the molecules to concentrate at the surfaces or boundaries of a solution rather than in the bulk solution. At the air-water interface this action lowers the surface tension of the water and promotes dispersion and emulsification as droplets or bubbles. Similar phenomena occur at liquid-liquid and liquid-solid interfaces.

Micelle formation is also characteristic of surfactants. This is the aggregation of surfactant molecules into larger oriented groups called micelles. Micelle formation occurs above a critical concentration of surfactant molecules, referred to as the critical micelle concentration. Surfactant molecule orientation within the micelle is with the hydrophobic groups clustered together and the hydrophilic groups extending outward into the bulk solution (Swisher, 1987). Micelles may facilitate the solubilization of water insoluble organic materials in water as the organic solute is molecularly dispersed in the internal region of the micelle as in a quasi-solution. Swisher (1987) found no relationship between micelle formation and biodegradation. Normally, the surfactant concentrations found in wastewater treatment plants are well below the critical micelle concentration.

### III. Biodegradation

#### A. Overview

There is extensive literature on the biodegradation of LAS during wastewater treatment (Kimerle, 1989). Selected biodegradation findings are reported herein to describe the breakdown of LAS in treatment processes, and the subsequent loss of toxicity.

Biodegradation can be defined as the destruction of chemical compounds by living organisms (Swisher, 1989). Bacteria are the principal organisms which degrade surfactants. There are two types of biodegradation- primary and ultimate. The loss of parent analytical response and of toxic properties of a compound constitutes primary degradation (De Henau et al., 1989). Primary degradation of surfactants is accomplished when the foaming processes are no longer evident in the mixture (Swisher, 1970). Ultimate biodegradation, also referred to as mineralization, is achieved with complete conversion of a compound to CO<sub>2</sub>, water and other inorganic compounds. The concept of 'environmentally acceptable' biodegradation is used to describe an incomplete degradation yielding end-products which are totally acceptable to the environment in which they are discharged (Swisher, 1989).

Biodegradability is not an absolute parameter, but is defined by the design of the experiment to assess the type of degradation occurring. The Organization for Economic Cooperation and Development (OECD) 'screening test procedure' is referred to as the 'die-away' test. For this test, the surfactant is held in dilute aqueous solution in the presence of bacteria, with no other organic substrate added. The extent of degradation is assessed over a specified time period. This type of test is a simplistic type, mimicking what may occur in natural waters. The more rigorous OECD 'confirmatory test procedure' requires the mixing of the surfactant with a synthetic sewage, and treating this mixture in a bench scale model

of sewage treatment. This test defines biodegradability in terms of removal during sewage treatment, although the percentage biodegradation figures obtained for LAS from the two procedures are quite similar (Brown, 1977).

#### B. Metabolic pathway

The most common metabolic pathway for surfactant biodegradation is the beta-oxidation sequence, the pathway for fatty acid metabolism in all organisms. The low specificity of the enzymes of this pathway allows the degradation of a wide variety of compounds that either occur naturally, such as fats and hydrocarbons, or are man-made, as in the case of surfactants. The beta-oxidation of the alkyl chain is initiated by oxidation of the terminal methyl carbon to a carboxylate group followed by a progressive removal of two carbon units as acetyl-CoA. This process continues in stepwise fashion until the alkyl chain has only 4-5 remaining carbons (Fisher and Marsh, 1983). Following the beta oxidation, oxidative splitting of the benzene ring begins, which involves the incorporation of molecular oxygen into the ring. Desulfonation follows which results in the formation of sulphophenyl alcohol and sulphophenyl aldehyde (Schöberl, 1989). These intermediate breakdown products biodegrade rapidly and completely to CO<sub>2</sub>, water and innocuous mineral salts under typical aerobic freshwater conditions (Painter and Zabel, 1989).

Biodegradation is the major mechanism by which the toxicity of LAS is reduced in natural and sewage treatment systems. LAS has been shown to rapidly undergo primary degradation which implies a loss of toxicity to aquatic organisms (De Henau, et al., 1989). Kimerle (1977) had earlier shown that loss of aquatic toxicity of LAS occurred more rapidly than loss of surfactant properties, as measured by the Methylene Blue Active Substances

(MBAS) test (APHA, 1992). He attributed this drop in toxicity to the rapid biodegradation of the more toxic LAS molecular components.

Chemical characteristics which influence the rate of biodegradation of LAS include the alkyl chain length, the phenyl group position on the carbon chain, and the sulfonate position on the benzene ring. The rate of biodegradability of C<sub>6</sub>-C<sub>14</sub> linear alkyl chains increases with chain length. However, at chain lengths of C<sub>18</sub> and above, degradability decreases markedly due to low solubility in water (Swisher et al., 1977). Schöberl (1989) studied the biodegradation rates of different LAS homologs and concluded that those most rapidly biodegraded have the sulphophenyl group furthest from the methyl ends of the molecule. This phenomenon is referred to as the distance factor (Fisher and Marsh, 1983). Although individual homologs and isomers differ considerably in bacteriostatic action and speed of biodegradation these differences are averaged and become minimal in commercial LAS blends comprising the various isomers of the C<sub>10</sub> to C<sub>13</sub> homologs (Swisher, 1981).

### C. Biodegradation in the Environment

Biodegradation is the major mechanism in reducing the toxicity of LAS. LAS has been shown to rapidly undergo primary degradation which implies a loss of toxicity to aquatic organisms (De Henau et al., 1989). Kimerle (1977) also showed that the aquatic toxicity of LAS drops rapidly with exposure time.

LAS degradation/removal in activated sludge sewage treatment facilities is usually very high (97-99%). This removal is due to two parallel effects: biodegradation and adsorption/precipitation. (Berna et al., 1991). Precipitation/adsorption can remove as much as 10-20% of the total LAS load in treatment plants in the primary settling basin. Where water hardness is high, LAS precipitation increases. Differences in concentrations of LAS in

final effluents can be explained by differences in treatment processes, water hardness and secondary treatment time from facility to facility. No high concentrations of LAS have been found in sludges from sewage treatment plants operating mainly with aerobic digestion, which effectively biodegrades the LAS (Berna et al., 1989).

DeHanau et al. (1989) in a study of treatment plant biodegradation found that primary settling could remove 32-33% of the influent LAS. Only 11-17% of the influent LAS could be accounted for in the precipitated LAS, so 17-21% was apparently biodegraded in the primary settler. Biodegradation in the aerator following the primary settler was essentially complete, with 97.2-97.8% of the LAS entering the reactor being degraded.

#### IV. Environmental Toxicity

##### A. Overview

Regardless of how rapidly a material biodegrades it is expedient to have some understanding of its toxicological properties. Toxicity of chemicals are studied with two effects in mind, the acute (or short term) toxicity and the chronic (lifetime) effect. Acute toxicity is reported as the median lethal concentration,  $LC_{50}$ , the concentration which kills 50% of the population in a specific time period. Another common value reported for acute toxicity is the  $EC_{50}$  value. This refers to the effect concentration that reduces the chosen study parameter 50% relative to the control population. Common effect parameters include growth, photosynthesis, morphology, and light diffusion. For measuring chronic toxicity, exposure effects are reported for either the first observed effect concentration (FOEC) or the no observed effect concentration (NOEC). These concentrations are reported with respect to parameters (i.e. growth, morphology) as for the  $EC_{50}$ .

Kimerle (1989) in a review of the LAS aquatic and terrestrial toxicological databases evaluated the hazards of LAS. The decision on the safety of LAS was made by comparing the determined toxicity concentration ( $LC_{50}$ ) for a species in a specific environment, to the actual concentrations of LAS in that environment. For example, if the  $LC_{50}$  of LAS to rainbow trout is 0.36mg/L, but the actual concentration of LAS in river water is  $3\mu\text{g/L}$ , there is not enough LAS in the river to cause a problem. The wider the margin between concentration data and acute toxicity data the safer the chemical is in the ecosystem. Kimerle found a greater than 10-fold margin for most organisms in aquatic and terrestrial environments.

#### B. Fish

The toxicity to fish swimming in water containing LAS at low ppm concentrations is very pronounced. The toxicity is not due to ingestion, but rather to exposure of gill tissues to the surfactant (Swisher, 1987). Maki (1979) reported the respiratory rate of bluegills was first altered at concentrations of 0.39 to 2.20mg/L of LAS. Zaccone et al. (1985) reported separation of gill lamellae in catfish at 1.5 to 2.5mg/L.

In a study of the fate of LAS in marine and estuarine environments, Stalmans et al. (1991) found that LAS is mineralized at realistic concentrations under marine conditions. The 96 h  $LC_{50}$  for LAS was roughly 1mg/L for cod, 1.5mg/L for flounder and 1 to 5mg/L for plaice. In a test of LAS toxicity to goldfish, Tsai and McKee, (1977) reported a 96 hour  $LC_{50}$  of 6.17mg/l to 7.6mg/L. Misra et al. (1987) showed the FOEC in skin morphology at 0.005mg/L in the *Cirrhina mrigala*, a grouper type fish, after 30 days of exposure.

Brown et al. (1978) compared the toxicity of treated and untreated sewage effluent spiked with LAS to rainbow trout. The comparison was intended to show that the biodegradation of LAS in a sewage treatment plant reduced the toxicity. The untreated

effluent was prepared by dissolving 30mg/L of LAS in a prepared detergent-free sewage. The treated effluent was made by spiking the detergent-free sewage with LAS at an initial concentration of 30mg/L. The activated sludge units were allowed to operate, with the concentration of LAS added in increasing doses at 3-day intervals until it reached 150mg/L. The MBAS concentration was measured daily until it reached a constant value. The effluent was then collected and trout were exposed to this effluent under constant flow conditions to determine the toxicity. The 96 hour LC<sub>50</sub> to rainbow trout was 0.3mg/L for the untreated surfactant and 30mg/L for the sewage treated effluent. The treatment process had reduced the toxicity of the surfactant.

Chronic toxicities of LAS to fish are most often based on toxicity to fathead minnows (Lewis, 1991). The first effect levels for LAS exceed 0.1mg/L in most cases for the fathead minnow ( Macek and Sleight, 1977, Holman and Macek, 1980). The NOEC values for C<sub>13</sub>LAS and C<sub>11,8</sub>LAS were 0.15 and 0.90mg/L, respectively (Maki, 1979). Pickering and Thatcher (1970) reported 0.63mg/L as the NOEC concentration for fathead minnow.

The greater toxicity of the higher alkyl chain length LAS blends observed by Maki (1979) has been concurred by Kimerle and Swisher, 1977; Macek and Sleight, 1977 and Holman and Macek, 1980. Macek and Sleight (1977) reported an effect of chain length on fathead minnow 96-h LC<sub>50</sub> values ranging from 0.5mg/L for C<sub>14</sub> to 100mg/L for C<sub>10</sub>. The FOEC (hatching) ranged from 0.05 to 14.0mg/L for C<sub>14</sub> LAS, and from 14 to 28mg/L for C<sub>10</sub>LAS.

### C. Invertebrates

The most common invertebrate toxicity test species for surfactants has been *Daphnia magna*. The effect concentrations for this species and LAS have ranged from 0.005 to >

10.0mg/L, with the more typically reported values exceeding 0.1mg/L (Lewis, 1990). In six 21-day chronic toxicity (survival) tests the FOEC was 1.7 to 3.4mg/L, and the NOEC ranged from 1.3 to 3.3mg/L. The 21-day LC<sub>50</sub> value ranged from 2.2 to 4.7mg/L. Kimerle (1989) reported NOEC values for *D. magna* ranging from 0.1mg/L for C<sub>14</sub>LAS to 9.8mg/L for C<sub>10</sub>LAS. In that same study the author reported an NOEC value of 3.0mg/L for *Ceriodaphnia dubia*. Lundahl (1974) found that toxicity to *Daphnia* decreased in conjunction with the surfactant content in a 'die-away' biodegradation study of LAS and other surfactants. Lewis et al. (1989) tested chronic toxicity of treated municipal effluent to *C. dubia*. They diluted effluent with river water and tested 5 dilutions from 60 to 100% effluent. After 3-days exposure the survival rate was 80-100% for all but the 100% effluent. In this study they also found that fathead minnows were considerably less sensitive than *C. dubia*. Masters et al. (1991) found NOEC for *C. dubia* ranging from <0.32 to 0.89mg/L.

Maki and Bishop (1979) developed acute toxicity tests to compare existing acute toxicity data for fish and *Daphnia*. An increase in toxicity of approximately one order of magnitude for each additional 2 carbons between C<sub>10</sub> and C<sub>14</sub> was noted for LAS. The acute toxicity measured as the 48 hour LC<sub>50</sub> value was 29.5mg/L for C<sub>10</sub> to 0.11mg/L at C<sub>16</sub>. They noted that the acute toxicity values for bluegill and *Daphnia* were analogous.

Ankley and Burkhard (1992) conducted a partial toxicity identification evaluation (TIE) with publicly owned treatment works (POTW) effluent that received no secondary treatment. Their approach involved exposing *C. dubia* to varied dilutions of effluents. The observed effects showed a range in toxicity to *C. dubia* from LC<sub>50</sub> with a 13% effluent sample, to a no effect response with a 100% effluent sample. In order to determine the cause of the effluent toxicity they spiked the effluent with LAS and determined that LC<sub>50</sub> for LAS was 4.62mg/L

for *C. dubia*. They were able to show that LAS was a contributing factor in the toxicity of the effluent.

The LAS effect concentrations for other invertebrate species are similar to those observed for daphnids. Pittinger et al. (1989) reported the NOEC at 3.19mg/g and the LOEC (lowest observed effect concentration) at 9.93mg/g for the midge *Chironomus riparius*. Similarly, Bressan et al. (1989) exposed benthic marine organisms to sediment-sorbed LAS and reported LC<sub>50</sub> values from 0.25 to 200mg/Kg of sediment.

In a study involving LAS toxicity to a variety of marine organisms Stalmans et al. (1991) found in chronic toxicity tests with marine mysid shrimp the NOEC for C<sub>11,7</sub> LAS was 0.38mg/L. They compared the lowest toxicity concentration reported in the literature (0.025mg/L) with the actual concentration of LAS in the North Sea (0.001mg/L) and showed that the safety margin between these was larger than 25-fold. They also showed that LAS levels decrease more rapidly than expected on the basis of simple dilution in sea water, implying degradation.

Berth et al. (1989) found that chronic effects, based on changes in fertilization, egg development and larval growth in clams, oysters and mussels have occurred at concentrations of LAS higher than 0.025mg/L. Huber et al. (1989) reported that 5.0mg/L LAS adversely affected cyclopod egg production and developmental stages after 8 weeks exposure in model ponds.

#### D. Microorganisms

Hršák et al. (1977) studied changes in a mixed bacterial population during a continuous flow biodegradation test. The *Pseudomonas* and *Alcaligenes* species bacterial cultures were isolated from a wastewater treatment facility. A commercial blend of LAS was used at two

concentrations, 20 and 50mg/L. The flow rates of the apparatus used for the test were 10, 20 and 40 ml/hour. The results showed that a balanced biodegradation rate could be attained under all conditions, but the steady state was more rapidly achieved at low flow rates and low LAS concentrations. At high LAS concentrations the ratio of members in the mixed bacterial population was disturbed and the degradation oscillated initially. Under those conditions the *Pseudomonas* species were enriched suggesting a bacteriocidal effect of LAS on *Alcaligenes* species.

Sánchez Leal et al. (1991) used the Microtox™ test (*Photobacterium phosphoreum*) to determine the effect of the LAS degradation rate on the toxicity of LAS to bacteria. They tested a commercial detergent slurry containing 65% LAS to determine if the toxicity of LAS was affected during the degradation. Initially LAS showed toxicity, with an EC<sub>50</sub> of 1.04mg/L, but continued degradation completely eliminated the toxic effects after 4 days. The authors also used the OECD 'die-away' test which showed that 50% of the LAS is removed after 4 days with removal increasing to 100% after 8 days.

Algae vary considerably in their response to LAS (Gledhill, 1974). Effect levels have varied at least an order of magnitude in several reported studies (Yamane et al., 1984; Lewis and Hamm, 1986; Chawla, 1988). The difference in response of *Microcystis aeruginosa* and *Selenastrum capricornutum* to LAS was three orders of magnitude (Lewis and Hamm, 1986). This study was a 5 month *in situ* photosynthetic response of lake phytoplankton. The 4-day growth EC<sub>50</sub> response varied from 116.0mg/L to 1.4mg/L for these different algae, with the green algae *S. capricornutum* being the less sensitive species. In a separate study, the first reduction in growth of an enclosed phytoplankton community occurred at 108mg/L LAS (Lewis, 1986).

In a 3-day growth study with 3 types of freshwater algae, EC<sub>50</sub> values between 10 and 100mg/L (72 h) were recorded by Yamane et al., (1984). The *Gymnodinium breve* marine alga (red tide organism) is unusually sensitive to LAS, more so than freshwater species, with reported EC<sub>50</sub> (growth) concentrations of 0.003 to 0.025mg/L (Hitchcock and Martin, 1977). Stalmans et al. (1991) reported an EC<sub>50</sub> growth concentration varying from 0.025mg/L to 0.125mg/L for the red tide organism. In the same study, other algae showed EC<sub>50</sub> effects at 0.2, 2.4 and >10mg/L LAS.

Lewis, in his recent review of toxicity of surfactants to algae (1990), notes three general trends. Foremost is the fact that current scientific conclusions about the effects of surfactants on algae, cultured under laboratory conditions, are based largely on the results for a few freshwater species. Secondly, the toxicity of most surfactants is less when determined for natural algal communities under natural conditions. Lastly, the toxicities of cationic surfactants are greater than those of other surfactants, LAS included.

The mode of LAS toxicity in algae is that the LAS denatures and binds protein in the cell wall and consequently alters membrane permeability to nutrients and chemicals. Algal cell walls differ between species and the thickness and chemical composition of the cell wall influences the degree of surfactant invasion. Generally the extent of toxicity is reduced with increasing cell wall thickness (Lewis, 1990).

#### E. Effects of Environmental Variables on Toxicity

Many environmental characteristics can effect the toxicity of contaminants entering aquatic ecosystems. Biotic factors such as type of organism, life stage and nutritional status can effect toxicity. Also temperature, water hardness and dissolved oxygen, which change seasonally, can have mitigating effects on chemical toxicity.

Mixture toxicity trends are described generally as synergistic, antagonistic or additive. If the mixture effect is greater than that expected based on the effects of the single components tested individually, synergism has occurred. If the mixture toxicity is less, antagonism is the result. Addition is indicated if the mixture toxicity is equivalent to the combined toxicities of the individual mixture components. The toxicity trends observed for mixtures containing surfactants and either a pesticide or a metal have been mixture specific. Mixtures containing oil and surfactants have been consistently synergistic (Lavie et al., 1984).

Attempts to predict environmental risk from laboratory toxicity tests conducted with mixtures containing surfactants are largely futile, because the possible combinations of these chemicals are too numerous and the time scale of the various exposure conditions too difficult to duplicate in laboratory tests. Tests with effluents are more realistic, but still lack applicability due to their small scale and site specific application (Lewis, 1992).

Versteeg and Woltering (1990) reported that the addition of a detergent manufacturing plant effluent to municipal sewage plant influent did not increase the toxicity of the resulting effluent after activated sludge treatment.

Tsai and McKee (1977) showed differing effects when LAS was mixed with copper and chloramines and exposed to goldfish. When LAS and copper were in equal ratios, or the LAS was higher (2:1) the toxicity was similar to LAS alone, suggesting the toxicity was additive. At higher concentrations of copper (LAS to copper; 1:2) the effect was synergistic. The same effects were noted for the Cu, chloramine and LAS mixture. At higher concentrations of copper or chloramines the toxicities were synergistic, while at lower concentrations the effects were additive.

Interpretation of the effect of water hardness (concentration of calcium carbonate,  $\text{CaCO}_3$ ) on LAS toxicity must consider whether a commercial product or its specific

ingredients were tested. Henderson et al. (1959) reported that detergent products were two times more toxic to fathead minnows in hard water than in soft. This was not true for several individual surfactants in these products. Kikuchi et al. (1986) reported that the toxicity of soap decreased with increasing water hardness, but the toxicity of the soaps' primary ingredient, LAS, to killifish increased with  $\text{Ca}^{2+}$  concentration. It has also been found that the toxicity of surfactants is a function of both the organism culture history and the test water hardness (Maki and Bishop, 1979). LAS was significantly more toxic to a daphnid tested in soft water when the test organisms were cultured for the test in hard water.

The water temperature effect is inconclusive. Studies investigating the effects of water temperature between 6 to 25°C on the toxicity of LAS, showed that increasing temperature increased the toxicity (Lewis, 1992). Hokanson and Smith, (1971) for example, reported the toxicity of LAS to bluegill increased at 25°C relative to 15°C. The toxicity of LAS to goldfish and bluegill was greater at 17°C than at 6°C (Swedmark et al., 1971). Contradicting this trend, a diatom was more sensitive to LAS at 15°C than 25°C (Nyberg, 1976).

The observed effects of suspended solids on the toxic response caused by other types of surfactants (cationic and nonionics) has not been observed for LAS (Lewis, 1992). Maki and Bishop (1979) reported that the effect of the addition of 50mg/L of bentonite on the toxicity of  $\text{C}_{14}$ LAS and  $\text{C}_{18}$ LAS to *D. magna* was slight and they observed even less effect for  $\text{C}_{11}$ LAS. Hokanson and Smith (1971) reported the acute toxicity of LAS to bluegill was not affected by the addition of 200mg/L of bentonite.

Venezia et al. (1980) found that increasing salinity increased the toxicity of LAS to marine copepods. Hokansson and Smith (1971) reported that decreasing dissolved oxygen increased the toxicity of LAS to bluegill.

Lewis and Hamm (1986) monitored the effects of LAS on phytoplankton photosynthesis in a 5 month test in lake water. The EC<sub>50</sub> values varied 80-fold during this period. It was concluded that the differences in effect levels were due to seasonal changes in water temperature and phytoplankton interactions.

## V. Conclusion

The published literature on the toxicity of LAS to aquatic organisms is extensive, as evidenced in this review. LAS has been studied for over 25 years, and many investigators have ruled out the possibility of risk to aquatic ecosystems. The concentrations of LAS found in natural settings offers a sufficient ecotoxicological safety margin for aquatic and terrestrial organisms.

Most of the literature that deals with microbial interactions with LAS focuses on biodegradation. LAS biodegradation can occur in many natural settings, but most degradation occurs in sewage treatment facilities. The basic axiom of a sewage treatment facility is biodegradation of waste by a consortium of bacteria. With regard to degradation at sewage treatment facilities, there is no consistent type of influent or bacterial population used from one facility to the next. POTW efficiency also varies, and in any particular facility the conditions will differ from day to day, not only for the treatment of LAS but also for all sewage components. The evaluations of numerous data have established that more than 95% of LAS is removed in sewage treatment facilities. It seems highly unlikely that LAS is the direct cause of breakdown in the bacterial workings of a POTW. There are, however, extenuating circumstances that could conceivably cause a disruption in the workings of a POTW, such as influent mixture effects, and assorted changes in environmental conditions.

LAS can be found in POTW's worldwide. These systems continue to function, therefore LAS from normal domestic and commercial sources would not likely be the direct cause of the malfunctioning of a sewage treatment facility. However, it is conceivable that shock loads of LAS could cause a decrease in bacterial levels as Hršak et al. (1977) described in their study of mixed bacterial populations and LAS biodegradation. Historically LAS toxicity to microbial communities in sewage treatment facilities has not been a concern. Due to this lack of interest there is a noticeable shortage of published literature on microbial toxicity of LAS. This lack of concern combined with the obvious efforts to establish the toxicity to other organisms, leads one to the conclusion that LAS is an environmentally acceptable compound.

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