LINEAR
ALKYLBENZENE
SULFONATE

SDA
THE SOAP AND DETERGENT ASSOCIATION
This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on linear alkylbenzene sulfonate (LAS); and 2) conclusions drawn from a risk assessment of LAS in the United States. Although focused on conditions in the U.S., data from other parts of the world that are relevant to a U.S. assessment are included in the monograph. The monograph is written for a technical audience, but not necessarily one familiar with environmental risk assessment.

The monograph is formatted into five sections. The first section describes LAS, its chemical structure and U.S. consumption volumes. The second section describes the function of LAS in cleaning products. The third section describes its fate and exposure concentrations in the environment. The fourth section presents environmental effects information. The fifth section presents a comparison of exposure and effects concentrations in the framework of an environmental risk assessment.

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INGREDIENT IDENTIFICATION

Chemical Description
Linear alkylbenzene sulfonate is an anionic surfactant (surface active agent) which was introduced in 1964 as a more readily biodegradable replacement for highly branched alkylbenzene sulfonate (ABS). LAS is a mixture of closely related isomers and homologs, each containing an aromatic ring which has been sulfonated at the para position and which is attached to a linear alkyl chain at any position except the terminal carbons. LAS used in U.S. detergents and household cleaners is generally in the form of the sodium salt of the sulfonic acid and the alkyl chain length averages 12. LAS is predominantly made from a mixture of C_{10} to C_{14} linear alkylbenzenes. The sulfonate group gives LAS water solubility, while the linear hydrocarbon chain makes the molecule compatible with oil and grease.

Common synonyms for LAS are linear alkylbenzene-sulfonate acid sodium salt, sodium straight chain alkylbenzenesulfonate, LAS sodium salt and dodecylbenzenesulfonic acid sodium salt. Chemical Abstract Service (CAS) numbers for LAS sodium salt mixtures are 68411-30-3 for sodium (C_{10}-C_{13}) alkylbenzenesulfonate acid, which can contain more than one alkyl substituent per benzene ring; 68608-87-7 for sodium mono(C_{6}-C_{12})-alkylbenzenesulfonic acid; 68953-95-7 for sodium mono(C_{9}-C_{12})-alkylbenzenesulfonic acid; and 68081-81-2 for sodium mono(C_{10}-C_{16})-alkylbenzenesulfonic acid.

U.S. Consumption
U.S. consumption of LAS has been between 800 million and 913 million pounds from 1987 to 1991 (Modler, 1993). The distribution of LAS usage in 1991 was 70% for laundry detergents, 15% for dishwashing liquids, 3.5% for other household uses and 12% for non-household applications (Modler, 1993).

INGREDIENT FUNCTION

LAS is an anionic surfactant that lowers the surface tension of water, enabling soils and stains to loosen and release from fabrics and surfaces. LAS provides excellent removal of soils and particulates like clay. LAS has excellent foaming characteristics important to the consumer acceptance of detergents.

LAS is the primary cleaning agent used in many liquid and powder laundry detergents and specialty household cleaners at concentrations up to 30 percent of the total formulation.

If LAS is not used in detergents and specialty household cleaners, another surfactant must be added to provide effective soil and stain removal.

ENVIRONMENTAL FATE AND EXPOSURE

Fate
The primary route of LAS release to the environment is disposal of spent laundry and cleaning solutions into municipal or on-site waste treatment systems.

Prior to the use of LAS, branched surfactants used in detergents biodegraded slowly, leaving a foaming residue in many wastewater treatment plants and receiving waters. Conversion of detergent formulations to LAS in the mid-1960s eliminated the foaming problem, because LAS undergoes rapid biodegradation. Biodegradation is the most important process for degradation of LAS. Chemical degradation, photodegradation and hydrolysis are not important mechanisms for environmental transformation of LAS.

LAS readily undergoes primary and ultimate biodegradation under a wide variety of wastewater treatment processes (McAvoy, Eckhoff and Rapaport, 1993; Rapaport and Eckhoff, 1990; Painter and Zabel, 1989; Takada and Ishiwatari, 1987; Berna, Ferrer, Moreno, Prats and Bevia, 1989; Nielsen and Huddleston, 1981). The well-known biodegradation pathway involves oxidation of carbon atoms of the alkyl side chain to form transient, less toxic sulfophenyl carboxylate intermediates, followed by cleavage of the aromatic ring and ultimate mineralization to carbon dioxide, water and inorganic sulfate. The biodegradation pathways for LAS have been reviewed (Schöberl, 1989), and the extensive literature on biodegradation of LAS has been summarized (Swisher, 1987).

Traces of LAS and LAS biodegradation intermediates in effluents from municipal wastewater treatment facilities continue to biodegrade in receiving water environments. A recent Mississippi River monitoring study by the United States Geological Survey (U.S.G.S.) found LAS only at or immediately below point source discharges. LAS was detected only at low levels, with the highest concentration found being approximately 0.005 mg/L immediately below point discharges (Tabor Jr., Barber II and Runnells, 1993). LAS biodegradation rates are similar whether it is sorbed to sediment or dissolved in the aqueous phase. This conclusion is based on laboratory studies and monitoring data (Larson, Rothgeb, Shimp, Ward and Ventullo, 1993). Recent monitoring studies from the Mississippi River (Tabor Jr. et al., 1993) and from 50 sites in the U.S. (McAvoy et al., 1993) confirm that LAS is not accumulating in river waters or sediments.
LAS is very water soluble. The partition coefficient from water onto solids is greatly influenced by the type of soil, sediment or sludge (Urano, Saito and Murata, 1984; Matthijs and De Henau, 1985; Hand and Williams, 1987; Litz, Doering, Thiele and Blume, 1987; Di Toro, Dodge and Hand, 1990; Hand, Rapaport and Pittinger, 1990; Orth, Powell, Kutey and Kimerle, 1995). The partition coefficient for LAS ranges from 3 to 26,000 (Hand et al., 1987). Sorption is affected by alkyl chain length and phenyl isomer position. Sorption increases with alkyl chain length, which is evidenced by the enrichment of longer alkyl chain length LAS homologs on wastewater sludges leaving municipal wastewater facilities (McAvoy et al., 1993; Takada et al., 1987; Matthijs et al., 1985). The external isomers, such as the 2-sulfophenyl isomer, have adsorption coefficients approximately twice as great as that for the internal isomers (Hand et al., 1987), such as the 5-sulfophenyl isomers. However, the external isomers are not enriched on wastewater sludge, which indicates that biodegradation rather than absorption is the major removal mechanism for these isomers. Sulfophenyl carboxylate biodegradation intermediates from LAS are also highly water soluble and, therefore, do not partition significantly from water onto sediments or soils. LAS is not sufficiently volatile to have significant partitioning from water into air.

Treatability

A recent monitoring study of 50 U.S. sewage treatment plants showed LAS removals of 99.3% in activated sludge, 98.0% in oxidation ditches and 98.5% in lagoon treatment systems (McAvoy et al., 1993). Rotating biological contactor plants removed 96% of LAS and the less effective trickling filter treatment plants removed an average of 77% of the LAS, which was comparable to the level of trickling filter BOD removal. When coupled with other processes, such as sand filtration, removals approaching those of activated sludge plants were obtained with trickling filters. Separate studies have shown complete removal of LAS in on-site treatment systems such as septic tank systems (McAvoy, White, Moore and Rapaport, 1994).

A significant portion of sewage sludge is disposed onto land as fertilizer and soil conditioner. Biodegradation half-lives for LAS in sewage sludge applied to soil range from 5 to 33 days (Berna et al., 1989; Knaebel, Federle and Vestal, 1990; Waters, Holt and Matthijs, 1989; Holt, Matthijs and Waters, 1989). LAS and its biodegradation intermediates continue to biodegrade in sludge-amended soil. In a separate experiment, radiolabeled LAS was applied to two soil types, mixed with digested sludge and the fate of the radiolabeled LAS and intermediates was followed for 76 and 106 days, respectively. In both soils, LAS was rapidly and extensively mineralized and no potential for groundwater contamination was indicated. Furthermore, these tests showed that LAS had no effect on growth of radishes, beans and potatoes in soils amended with sewage (Figge and Schöberl, 1989).

Exposure

Aquatic

In the recent 50-site monitoring study which focused on low dilution (worst case) streams, the receiving water concentrations of LAS averaged 0.044 mg/L and the LAS alkyl chain length averaged 11.9 carbon units (McAvoy et al., 1993). Samples were collected downstream of the wastewater treatment facilities at a point where complete mixing had occurred. The LAS concentrations ranged from less than 0.01 mg/L to 0.33 mg/L. The highest concentration observed was from an irrigation canal which offered virtually no dilution. These results should be compared to more typical values that are observed in the environment when samples are collected along river systems without focusing on low dilution rivers immediately below outfalls. For example, the predicted 90th percentile concentrations for over 500,000 U.S. river miles were less than or equal to 4 ug/L under average flow conditions (Rapaport, Larsen, McAvoy, Nielsen and Trehy, 1992). The recently completed U.S.G.S. monitoring study found that LAS rarely occurred at concentrations greater than 0.005 mg/L in the Mississippi River (Tabor Jr. et al., 1993). Other recent monitoring studies for LAS have found similar results for rivers in Europe, with reported concentrations from 0.01 mg/L to 0.09 mg/L (Matthijs and De Henau, 1987).

Sediment

Concentrations of LAS in sediment are dependent on the type of sediment (Urano et al., 1984; Matthijs et al., 1985; Hand et al., 1987; Litz et al., 1987; Di Toro et al., 1990; Hand et al., 1990; Orth et al., 1992) and proximity to effluents containing residual LAS (Larson et al., 1993; Shimp, 1989). LAS concentrations in the immediate vicinity of sewage outfalls from trickling filters have been reported as high as 567 mg/kg in Japan (Takada et al., 1987) and in the U.S. as high as 340 mg/kg (McAvoy et al., 1993). Concentrations in the sediment rapidly decrease as the distance from the source increases due to continued biodegradation in the river sediment (Larson et al., 1993) and in estuaries (Shimp, 1989). Sediments are enriched in the longer chain length and internal isomers relative to the water column (Tabor Jr. et al., 1993; Urano et al., 1984; Matthijs et al., 1985; Hand et al., 1987). Since this shift is predicted by the adsorption coefficients for LAS, the absorbed LAS appears to have been in equilibrium with LAS in the water column.

LAS concentrations in Mississippi River sediments were reported for 37 sediment samples and ranged from less than 0.01 mg/kg to 5 mg/kg (Tabor Jr. et al., 1993)
where sampling was not targeted for sites near outfalls with minimal dilution. At sites which were targeted for low dilution and activated sludge treated wastewater was released to streams (McAvoy et al., 1993), the sediment concentrations ranged from 0.3 mg/kg to 3.8 mg/kg (average 1.1 mg/kg), while sediments downstream of trickling filters into low dilution streams ranged from 0.2 mg/kg to 340 mg/kg (average 174 mg/kg).

**Terrestrial**

LAS biodegrades rapidly in aerobic biodegradation units employed in wastewater treatment (Berna et al., 1989), but is slow to biodegrade in anaerobic digesters. Concentrations of LAS in anaerobically digested sludge from several countries have been reported from 0.1-3% (McAvoy et al., 1993; Berna et al., 1989; McEvoy and Giger, 1985; Painter and Zabel, 1988). Typically, sludges from wastewater treatment facilities are disposed of at landfills or by incineration or on agricultural lands. An understanding of the fate of the LAS applied to agricultural land as a result of disposal of anaerobically treated sludge on the soil and LAS's impact on terrestrial plants is important.

Four groups of researchers have studied the fate of LAS in sludge amended soils. In one study 51 fields on 24 farms in the U.K. (Thames Water Authority region) were sampled in 1987. The LAS concentrations in 42 sites which had received sludge prior to 1987 were generally less than 1 mg/kg but ranged from <0.2 to 2.5 mg/kg. Samples taken within a few days after sludge addition showed LAS concentrations in the range from <0.2 to 66.4 mg/kg. The rate of biodegradation of LAS in the fields to which sludge had been applied was monitored and half-lives for LAS biodegradation were observed to be 7 to 22 days (Waters et al., 1989; Holt et al., 1989). Since crops are typically planted at least a month (about 2 half-lives) after sewage sludge is added, crop exposure is limited and concentrations in the soil further decrease during the growing season.

Additional studies on grapevine and vegetable soils (Berna et al., 1989) on a test plot where LAS had been repeatedly applied over 10 years (Giger, Alder, Brunner, Marcocini and Siegrist, 1989) and on four amended soils in Europe (De Henau, Matthijs and Hopping, 1986) demonstrate that LAS applied to soils via sewage sludge biodegrades quickly.

**Environmental Effects**

**Aquatic**

Over 400 toxicity tests have been conducted with LAS on a wide range of fresh and saltwater fish, invertebrates and algae (BKH Consulting Engineers, 1993). Acute toxicity of LAS to most fish and invertebrates is in the 0.5 mg/L to 20 mg/L range (Kimerle, 1989). The aquatic toxicity of LAS to algae has a greater spread of responses, with 90% of the species having an EC_{50} between 0.1 mg/L and 100 mg/L (Kimerle, 1989). The alkyl chain length affects the acute toxicity of LAS. The EC_{50} for the different chain lengths of LAS to *Daphnia magna* were found to be 0.68, 2.6, 5.9, 21.2 and 27.6 mg/L for the C_{14}, C_{13}, C_{12}, C_{11} and C_{10} LAS homologs, respectively (Maki and Bishop, 1979). A similar toxicity dependence on chain length for LAS to fathead minnow, goldfish, bluegill and killi fish has also been observed (Divo, 1974; Kimerle and Swisher, 1977; Macek and Sleight, 1977; Holman and Macek, 1980; Wakabayashi, Kikuchi, Ioue, Kawahara and Koido, 1975; Arthur D. Little, Inc., 1991; Lewis, 1991).

The no-observed effect concentrations (NOEC) determined from longer term aquatic toxicity tests which are carried out over the full life cycle of the test organism are available for LAS. These tests have been carried out for various commercially available LAS samples and for model LAS samples. This information permits estimation of the effect of chain length on chronic toxicity. In Figure 1 the plot of the Ln (NOEC) versus chain length is shown for *Daphnia magna*.

![Figure 1. Ln of NOEC values from chronic toxicity for *Daphnia magna* versus average chain length of LAS test material (BKH Consulting Engineers, 1993).](image)

The graphical presentation of the data and trend analysis allows estimation of the best fit for experimental data and avoids single data point experimental variability. The NOEC to *Daphnia magna* can be estimated to be approximately 1 mg/L or greater for LAS with an average chain length shorter than 12. The NOEC for LAS with an average chain length of 11.8 has been reported to be in the range from 1.3 mg/L to 3.3 mg/L (Lewis, 1991). Similarly, data from 11 chronic aquatic toxicity tests are available for fathead minnow and 2 for rainbow trout. From the chronic toxicity test data for fathead minnow and rainbow trout, a plot of the Ln (NOECs) values versus chain length is shown in Figure 2. The data indicate that NOECs for the...
fathead minnow are greater than 1 mg/L for LAS samples with alkyl chain lengths less than or equal to 11.7 carbons. Not enough data are available to estimate LAS alkyl chain lengths on chronic toxicities to other species (BKH Consulting Engineers, 1993).

The toxicity of LAS in sediments has been tested with several species. The NOEC was reported to be \( \text{Branchiura sowerbyi} \) (freshwater bivalve) in a 180-day chronic test; \( \geq 750 \text{ mg/kg} \) (initial dose) to \( \text{Anodonta cygnea} \) (freshwater bivalve) in an 80-day chronic test; and \( >281 \text{ mg/kg} \) to \( \text{Mytilus galloprovincialis} \) (saltwater bivalve) (Bressan, Brunetti, Castellato, Fava, Giro, Marin, Negrisolo, Tallandini, Thomann, Tosoni, Turchetto and Campesan, 1989). The first effect concentration was not determined.

The chronic no-effect concentration of LAS to \( \text{Chironomus riparius} \) (midge) was determined to be \( 319 \text{ mg/kg} \) and the first effect concentration was determined to be \( 993 \text{ mg/kg} \) (Pittinger, Woltering and Masters, 1989).

Absorption of LAS to sediment greatly lowers the toxicity. The degree to which the toxicity is decreased is related to the unique adsorption coefficient for LAS to each sediment exposed (Orth et al., 1992).

### Terrestrial

Since bacteria, plants and earthworms live in the soil, these biological systems were exposed to LAS in an attempt to measure its potential negative effects on the soil. LAS slows nitrification in soils by approximately 10% at 100 mg/kg (Vandomi and Federico, 1973). The 21-day EC\(_{50}\) for LAS to sorghum, sunflower and mung beans was determined to be 167, 289 and 316 mg/kg, respectively (Mieure, Waters, Holt and Matthijs, 1990). In order to simulate the typical agricultural application, soil was mixed with digested sludge dosed with LAS and held for 14 days. Then seeds from yellow nutsedge, barnyard grass, grain sorghum, wheat, corn, soybean, morning glory, cocklebur and velvetleaf were exposed to the sludge amended soil. There was no significant effect on germination or growth at concentrations up to 407 mg/kg (Mieure et al., 1990).

### Sediment

The toxicity of LAS in sediments has been tested with several species. The NOEC was reported to be \( >26 \text{ mg/kg} \) for \( \text{Branchiura sowerbyi} \) (freshwater bivalve) in a 180-day chronic test; \( >750 \text{ mg/kg} \) (initial dose) to \( \text{Anodonta cygnea} \) (freshwater bivalve) in an 80-day chronic test; and

![Figure 2. Ln of NOEC values from chronic toxicity tests for fathead minnow (open boxes) and rainbow trout (solid boxes) versus average chain length of LAS test material (BKH Consulting Engineers, 1993).](image)

LAS chronic toxicity is also influenced by the phenyl isomer content. The external isomers of LAS, such as the 2-(sulfophenyl) dodecane, are more toxic than the internal isomers, such as 6-(sulfophenyl) dodecane (Divo, 1974). LAS that exists in the environment has been changed by preferential biodegradation of the more toxic external isomers and by a combination of preferential absorption and biodegradation of the more toxic longer chain length homologs of LAS (Tabor Jr. et al., 1993; Lewis, 1991; Trehy, Gledhill and Orth, 1990). These factors result in the reduction of toxicity of LAS (Divo, 1974; Kimerle et al., 1977; Brown, Abram and Collins, 1978; Moreno and Ferrer, 1991; Swisher, Gledhill, Kimerle and Taulii, 1976). Toxicity is estimated to be reduced by a factor of 2 to 3 (Trehy and Kimerle, 1993; Mieure, Trehy and Kimerle, 1993).

A field stream study has demonstrated that the NOEC for LAS in “real world” conditions is \( >0.36 \text{ mg/L} \) (Fairchild, Dwyer, La Point, Burch and Ingersoll, 1993). In this study, at the U.S. Department of Interior’s outdoor experimental streams, it was demonstrated that an LAS blend with an average alkyl chain length of 11.9 carbons at a concentration of 0.36 mg/L had no detrimental impact on the survival of fathead minnows, or \( \text{Hyallela aztice} \), benthic invertebrate community dynamics, penphyton growth or detrital leaf processing (Fairchild et al., 1993).

### Aquatic

LAS concentrations in samples collected immediately below the outfalls in the low dilution streams in the 50-site monitoring study (Mcavoy et al., 1993) did not exceed the NOEC determined in the U.S. Department of the Interior field stream study (Fairchild et al., 1993). The highest concentration measured at the 50 sites was 0.33 mg/L, which is less than the NOEC of \( >0.36 \text{ mg/L} \). The maximum LAS value observed in the U.S.G.S. Mississippi River monitoring study was approximately 0.005 mg/L (Tabor et al., 1993), which is at least 72 times less than the NOEC of \( >0.36 \text{ mg/L} \) determined by Fairchild et al., 1993.

Field studies incorporate the mitigation of toxicity due to adsorption of LAS to particulates and biomass materials suspended in the water. This is one of the reasons field NOECs are higher than NOECs determined in laboratory studies. The Department of the Interior field stream study did not include mitigation due to preferential biodegrada-
tion of the LAS external isomers (which are more toxic but more rapidly biodegradable) because of the short residence time in the stream. Field study data from flowing streams which do not allow time for preferential biodegradation of the various LAS isomers are still conservative of the NOEC for LAS in the environment by a factor of 2 or more (Trehy et al., 1993; Mieure, Trehy and Kimerle, 1993). A comparison of the reported chronic toxicity data and measured environmental levels in rivers demonstrates that substantial margins of safety exist for LAS (Lewis, 1991).

**Sediment**
The results from the U.S.G.S. study (Tabor et al., 1993) indicate that LAS concentrations in the sediment are more than five times lower than the lowest NOEC reported for the most sensitive species tested (Bressan et al., 1989). The data indicate that LAS is not impacting sediment organisms in the Mississippi River in spite of the large wastewater input and the lack of secondary treatment by several large metropolitan cities along the river. Similarly, for activated sludge sites with low dilution streams and at sites where the sewage effluent is the only source of water for the stream (McAvoy et al., 1993), LAS concentrations in the sediment are below the lowest NOEC of >26 mg/kg (Bressan et al., 1989).

A comparison of the no-effect concentrations for LAS in sediment versus the measured concentrations in the environment indicates that environmental concentrations of LAS in sediments do not exceed NOECs (McAvoy et al., 1993; Bressan et al., 1989). LAS concentrations in sediments below activated sludge treatment facilities are 10 to 100 times lower than NOECs. Even where higher LAS concentrations in sediments are sometimes detected below trickling filter treatment facilities, these elevated concentrations are unlikely to be harmful due to the low interstitial water concentrations of LAS (Orth et al., 1995).

**Terrestrial**
The 14-day EC<sub>50</sub> to earthworms, Eisenia fetida and Lumbricus terrestris, was determined to be greater than the highest tested concentration of 1333 mg/kg for both species. The NOEC was 235 mg/kg and 613 mg/kg to Eisenia fetida and Lumbricus terrestris, respectively (Mieure et al., 1990). Comparing the lowest NOEC (235 mg/kg for earthworms, 167 mg/kg for sorghum) with a predicted highest exposure concentration of 66.4 mg/kg after adding sludge indicates that the environmental concentrations are much less than the lowest NOEC (Mieure et al., 1990).

**Conclusion**
The environmental effects and fate of LAS have been thoroughly studied. The environmental risk assessment for LAS is based on an extensive data base, probably more so than for any other chemical, and the risk assessment substantiates the environmental acceptability of LAS use in U.S. detergents and household cleaning products. The comprehensiveness of the studies carried out on LAS provides documentation of the environmental safety of LAS that is rarely available for chemicals in commerce.
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