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CHRONIC AND SUBLETHAL TOXICITIES OF SURFACTANTS TO AQUATIC ANIMALS: A REVIEW AND RISK ASSESSMENT

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Abstract—Surfactants are one of the major components (10–18%) of detergent and household cleaning products and are used in high volumes. Several are commonly found in natural waters and consequently, their impact on the environment has been, and continues to be, discussed in the U.S.A., Western Europe and Japan. The chronic and sublethal toxicities of commercially important surfactants to aquatic animal life have not been summarized in the available scientific literature. Based on the summary provided here scientific understanding of the chronic and sublethal toxicities of cationic surfactants is less than that for the other surfactant groups. Chronic toxicity of anionic and nonionic surfactants occurs at concentrations usually greater than 0.1 mg/l. Effects of these same surfactants on several behavioral and physiological parameters range from 0.002 to 40.0 mg/l. The available toxicity data base is largely comprised of laboratory-derived toxicity data for a few surfactants, predominantly LAS, and single freshwater planktonic species such as *Daphnia magna* and the fathead minnow and a benthic midge. Community effect levels have been reported only for linear alkylbenzene sulfonate (LAS) and effects on single freshwater and saltwater test species and on natural biotic communities are largely unknown for many commercially important surfactants. Based on a comparison of the reported chronic toxicity data and measured environmental levels in rivers, the aquatic safety of the anionic LAS is indicated, more so than for any other surfactant. Safety assessments for other major surfactants in saltwater and freshwater should be considered preliminary and limited until validated with corresponding exposure measurements and additional laboratory and field-derived chronic toxicity data for animal test species.

Key words—surfactants, chronic toxicity, review, risk assessment, environmental concentrations

INTRODUCTION

Surfactants are synthetic organic chemicals used in high volumes in detergents, personal care and household cleaning products. These compounds usually comprise 10–18% of granular and liquid detergents and are the largest ingredient of the 20–25 compounds used in these products (Höglund, 1976; Richtler and Knaut, 1988). Surfactants are used also by the oil, textile, food and mining industries. Although there are many surfactant types, linear alkylbenzene sulfonates, alkyl sulfates, alkyl ether sulfates, alkyl ethoxylates, alkyl phenol ethoxylates and quaternary ammonium halide compounds are common in commercial detergent applications (Richtler and Knaut, 1988). Approximately 15 million tons of soap and synthetic surfactants were used worldwide in 1987 (Berth and Jeschke, 1989). Surfactants, due to their widespread use, have been measured at various concentrations in river water, drinking water, sediments and sludge-amended soils (Sivak *et al.*, 1982; McEnvoy and Giger, 1985; DeHenau *et al.*, 1986; Giger *et al.*, 1987; Brunner *et al.*, 1988; Ventura *et al.*, 1989). As a result of their presence primarily in river water, the environmental effects and fate of anionic and cationic surfactants have been discussed at various international seminars and symposia (German Chemical Society, 1982; Richtler and Knaut, 1988; Ruchay, 1989) and have been reviewed by regulatory agencies primarily in Western Europe and Japan where dilution of the receiving water and sewage treatment are less than in the U.S.A.

The toxicities of surfactants to aquatic life have been summarized previously in the scientific literature (Abel, 1974; A. D. Little Co., 1977, 1981; Koskova and Kozlovskaya, 1978; Margaritis and Creese, 1979; Sivak *et al.*, 1982; Lewis and Suprenant, 1983; Lewis and Wee, 1983; Cooper, 1988). Environmental assessments based on these reviews, however, are outdated considering the constant development of new surfactants and reformulation of existing surfactant components in detergent products. In addition, the previously summarized data typically are limited to acute toxicity values for a few surfactants, primarily the anionic and, to a lesser extent, nonionic forms. Many reviews contain few or no chronic and sublethal toxicity data while others do not consider cationic surfactants.

A comprehensive and current summary of the chronic and sublethal effects of surfactants to aquatic animals is needed, since contemporary environmental safety assessments, particularly the toxicity assessment phase, are based on chronic toxicity information. In addition, the need to evaluate the role of sublethal effects in the safety assessment process has been identified as one of the key future research priorities in the environmental risk assessment process (Society of Environmental Toxicology and Chemistry, 1987). The first phase in gaining an insight into this role is to understand the data base. Therefore, a summary of the chronic and sublethal toxic concentrations for surfactants would be helpful in consolidating the data base, providing an overview of their potential environmental impact based on chronic effects and indicating the priority for future research. This review represents a comprehensive summary of these effects for commercially important surfactants and freshwater and saltwater animal life.

METHODS

Structures of several representative surfactants for which chronic toxicity data have been reported appear in Fig. 1. The test methods used to determine the toxicity of these and other surfactants have not been consistent; the test species, test durations, effect parameters, the test compound and analytical confirmation of the test concentrations are several experimental variables that have differed. The analytical verification of the test concentrations, an important consideration, was not a common occurrence in the reviewed studies. Therefore, the results summarized in the tables, unless noted, are based on nominal concentrations. Chronic toxicity tests typically include life cycle, partial life cycle and early life stage tests (Stephan *et al.*, 1985). In many cases the types of studies reviewed here did not represent these categories and consequently in a strict sense do not represent chronic toxicity data as commonly accepted by the scientific community. However, for simplicity, data generated in tests exceeding normal acute test durations of 48 h for invertebrates and 96 h for fish were included as "chronic toxicity" data.

The amount of detail possible in a summary paper of this type is limited. Additional detail concerning experimental technique and, in some cases, additional toxicity data can be found in the reviewed papers.

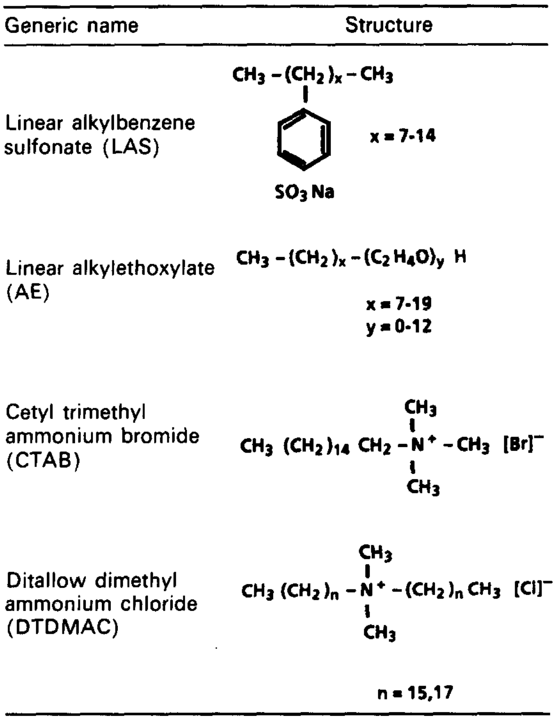

Fig. 1. Structures of representative surfactants commonly used in commercial detergent and softener products.

RESULTS

Chronic Toxicity

Invertebrates

Daphnia magna has been the most common test species (Table 1). The effect concentrations for this species and LAS (linear alkylbenzene sulfonate), the predominant test compound, have ranged from 0.005 to >10.0 mg/l; however, the more typically reported chronic effect concentrations exceed 0.1 mg/l (Fig. 2). Values less than 0.1 mg/l are few and the 0.005 mg/l effect value for *D. magna* reported by Lal *et al.* (1984) should be considered an outlier. LAS has been used for 25 years in granular and liquid detergent products, shampoos, soaps, shaving creams and industrial cleaners. Based on data from Taylor (1985), the first effect concentration range (geometric mean of NOEC and LOEC) for six 21-d chronic toxicity tests conducted with *D. magna* and $C_{11.8}$ LAS, an approximate alkyl chain length blend commonly used in commercial products, was 1.7–3.4 mg/l. The no observed effect concentrations for these studies ranged from 1.3 to 3.3 mg/l and the 21-d LC_{50} values, 2.2 to 4.7 mg/l. Kimerle (1989) reported NOEC values for *D. magna* and several LAS homologues that ranged from 0.1 mg/l (C_{14} homologue) to 9.8 mg/l (C_{10} homologue). The NOEC value for a $C_{11.7}$ LAS blend and *Ceriodaphnia* was 3.0 mg/l. Masters *et al.* (1991) reported that the first effect concentrations for *Ceriodaphnia* and $C_{11.8}$ LAS were <0.32 and 0.89 mg/l.

The effect concentrations for LAS and other invertebrate species are similar to those observed for daphnids. Effect concentrations were between 0.2 and 0.4 mg/l for *Gammarus* exposed to LAS (Arthur, 1970). Pittinger *et al.* (1989) reported that the NOEC for the midge was 319 μg/g and the LOEC (lowest observed effect concentration) was 993 μg/g based on sediment-adsorbed LAS concentrations. Likewise, Bressan *et al.* (1989), reported the relatively low toxic nature of sediment-adsorbed LAS to other freshwater and marine benthic organisms.

The toxicities of other anionic surfactants, based on limited data appears to be similar to that for LAS (Table 1). For example, first-effect concentrations for alkyl sulfate (AS) compounds were reported between 0.25 and 1.46 mg/l for flatworms and oyster and clam larvae (Hidu, 1965; Patzner and Adam, 1979) and a NOEC of 0.27 mg/l was reported for *D. magna* and an alkyl ethoxy sulfate (Maki, 1979a).

The chronic effects of several nonionic alkyl ethoxylates (AE) and the cationic ditallow dimethyl ammonium chloride (DTDMAC) to *D. magna* occur between 0.1 to 1.0 mg/l. Maki (1979a), for example,

Table 1. Reported chronic toxicities of surfactants to invertebrates

Surfactants	First effect concentration (mg/l)	Test species	Test duration	Effect	Reference
Anionic					
$C_{11.8}$LAS[1]	1.7–3.4[2]	*Daphnia magna*	21 d	Survival Reproduction	Taylor (1985)
LAS	>10.0 (NOEC)	*Daphnia magna*	21 d	Reproduction	Canton and Slooff (1982)
$C_{11.8}$ LAS	1.18 (NOEC)*	*Daphnia magna*	21 d	Reproduction	Maki (1979a)
C_{13}LAS	0.57 (NOEC)*				
AES[3]	0.27 (NOEC)*				
AS[4]	0.25	Flatworms: *Dugesia gonocephala* *Notoplana humilis*	30 d	Regeneration	Patzner and Adam (1979)
LAS	0.2–0.4* 0.4–1.0* >4.4*	*Gammarus pseudolimnaeus* *Campeloma decisum* (snail) *Physa integra* (snail)	6–15 wk	Growth, reproduction	Arthur (1970)
LAS	0.05–0.10	Oyster (*Crassostrea virginica*)	10 d	Larval growth, egg development	Calabrese and Davis (1967)
$C_{11.8}$ LAS	<0.32, 0.89	*Ceriodaphnia dubia*	7 d	Reproduction	Masters *et al.* (1991)
LAS (C_{10}–C_{14} homologues)	0.1–9.8 (NOEC range)	*D. magna*	ND	Reproduction	Kimerle (1989)
$C_{11.7}$ LAS	3.0 (NOEC)	*Ceriodaphnia* sp.	ND	Reproduction	Kimerle (1989)
$C_{13.1}$ LAS	0.04 (NOEC)	Mysid shrimp (*Mysidopsis bahia*)	ND	ND	Kimerle (1989)
$C_{11.4}$ LAS	0.4 (NOEC)				
ABS[5]	0.55–5.8 0.14–1.63	Clams (*Mercenaria mercenaria*) Oysters (*C. virginica*)	14 d	Larval growth and development	Hidu (1965)
AS	0.47–1.46 0.37–1.46	*M. mercenaria* *C. virginica*	14	Larval growth and development	Hidu (1965)
$C_{11.8}$ LAS	993 SC[6]* 15.2 IW[7] 1.69 OW[8] 3.72 NS[9]	Midge (*Chironomus riparius*)	24 d	Emergence	Pittinger *et al.* (1989)
LAS	0.05	Mussel (*Mytilus edulis*)	10 d	Fertilization, larval growth	Granmo (1972)
Nonionic					
$C_{12\text{-}13}$ $AE_{6.5}$[10]	0.24 (NOEC)*	*D. magna*	21 d	Reproduction	Maki (1979a)
$C_{14\text{-}15}$ AE_7	0.24 (NOEC)*				
$C_{14\text{-}15}$ AE_7	0.17, 0.70	*C. dubia*	7 d	Reproduction	Masters *et al.* (1991)
Laurox-9	1.0	*D. magna*	30 d	Reproduction	Shcherban (1980)
$C_{13\text{-}15}$ AE_{10}	0.25–0.50	*D. gonocephala* *N. humilis*	30 d	Regeneration	Patzner and Adam (1979)
TAE_{10}	<0.1–20	*M. edulis*	5 mth	Fertilization, spawning	Granmo and Jorgensen (1975)
Alkyl polyether alcohol	1.75–2.5 1.6–2.5	*M. mercenaria* *C. virginica*	14 d	Larval growth and development	Hidu (1965)
Iso-octyl phenoxy polyethoxy ethanol	0.77–2.5 0.86–1.0	*M. mercenaria* *C. virginica*	14 d	Larval growth and development	Hidu (1965)
APE[11]	2.4	*M. edulis*	14 d	Larval growth and development	Hidu (1965)
Cationic					
TMAC[12]	0.065 (NOEC)*	*D. magna*	ND	ND	Pittinger *et al.* (1989)
TMAC	0.17, 0.35	*C. dubia*	7 d	Reproduction	Masters *et al.* (1991)
DTDMAC[13]	0.38–0.76*	*D. magna*	21 d	Reproduction	Lewis and Wee (1983)
DSDMAC[14]	2708 SC[6]* 0.18 IW[7] 0.41 OW[8] 1.02 NS[9]	*C. riparius*	24 d	Emergence	Pittinger *et al.* (1989)
TMAC	>3084 SC[6]* >2.3 IW[7] >0.9 OW[8] 0.62 NS[9]	*C. riparius*	24 d	Emergence	Pittinger *et al.* (1989)
Lauryl pyridinium chloride	0.009–0.05 0.05–0.09	*M. mercenaria* *C. virginica*	14 d	Larval growth and development	Hidu (1965)
Ethyl dimethyl benzyl ammonium chloride	0.25–1.27 0.10–0.49	*M. mercenaria* *C. virginica*	14 d	Larval growth and development	Hidu (1965)

[1]LAS = linear alkylbenzene sulfonate. [2]Range of first effect levels for six studies. [3]AES = alkyl ethoxy sulfate. [4]AS = alkyl sulfate. [5]ABS = alkylbenzene sulfonate. [6]Sediment concentration LOEC in μg/g. [7]Interstitial water concentration LOEC in mg/l. [8]Overlying water concentration LOEC in mg/l. [9]LOEC in study with no sediment. [10]AE = alkyl ethoxylate. [11]APE = alkylphenol ethoxylate. [12]TMAC = dodecyl trimethyl ammonium chloride. [13]DTDMAC = ditallow dimethyl ammonium chloride. [14]DSDMAC = distearyl dimethyl ammonium chloride. NOEC = no observed effect concentration. *Value based on measured concentrations. ND = no data.

reported a NOEC of 0.24 mg/l for two nonionic alkyl ethoxylates. The first effect concentrations of an AE for *Ceriodaphnia* were 0.17 and 0.70 mg/l in tests of 7 days duration (Masters *et al.*, 1991). Lewis and Wee (1983) reported that the first effect level for DTDMAC was between 0.38 (NOEC) and 0.76 mg/l

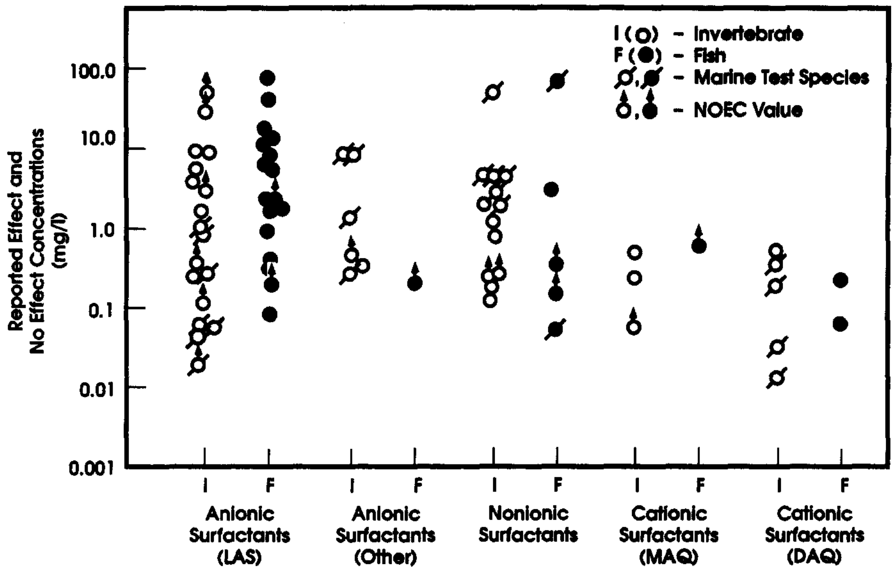

Fig. 2. Reported effect and no effect levels for surfactants. MAQ = monoalkyl quaternary ammonium salts; DAQ = dialkyl quaternary ammonium salts.

(LOEC) for a study conducted in river water. DTDMAC is used primarily as softening agent in fabric softeners and as an anti-static agent on drier sheets. This same cationic compound adsorbed to sediment was toxic to early life stages of midge only at very high level concentrations (Pittinger *et al.*, 1989). Lee (1986) found that the safety margin for the midge and sediment-bound DTDMAC ranged from 17 to 105 based on two partial life-cycle tests.

A NOEC of 0.065 mg/l has been reported for *D. magna* and a monoalkyl quaternary ammonium compound, TMAC (Pittinger *et al.*, 1989). The first effect concentrations derived from two tests using a similar compound for *Ceriodaphnia* were 0.17 and 0.35 mg/l (Masters *et al.*, 1991).

The chronic effect concentrations for surfactants and marine organisms have been reported primarily for clams, oysters and mussels. Effects of LAS on oysters and mussels based on changes in fertilization, egg development and larval growth have occurred at concentrations generally exceeding 0.025 mg/l (Calabrese and Davis, 1967; Granmo and Jorgensen, 1975). The first effect levels for several nonionic compounds on clam and oyster larvae were between 0.8 and 2.5 mg/l (Hidu, 1965) and at concentrations less than 0.1 mg/l for an alkyl ethoxylate (Granmo and Jorgensen, 1975). Threshold values of 0.010 and 0.050 mg/l LAS have been reported for oysters and sponges (Berth *et al.*, 1988). The NOEC values for the mysid shrimp and two LAS blends, $C_{11.4}$ and $C_{13.1}$, were 0.4 and 0.04 mg/l, respectively (Kimerle, 1989). Hidu (1965) reported the effects of two cationic compounds on clam and oyster larvae and the lowest first effect concentration was 0.0085 mg/l. Overall, the cationic surfactants were the most toxic of the surfactants tested in that study.

Fish

The reported chronic toxicities for surfactants and fish are based largely on the response of fathead minnows to various blends and homologues of the anionic LAS (Table 2; Fig. 2). The first effect levels for LAS exceed 0.1 mg/l in most cases for the fathead minnow (Macek and Sleight, 1977; Holman and Macek, 1980), and for other fish species (Vailati *et al.*, 1975; Canton and Slooff, 1982; McKim *et al.*, 1975; Chattopadhyay and Konar, 1986a). Holman and Macek (1980) for example, reported NOEC values of 0.11–5.1 mg/l and LOEC values of 0.25–8.4 mg/l for fathead minnows in life cycle and early life stage tests using several LAS blends. The NOEC values for C_{13} LAS and $C_{11.8}$ LAS and the fathead minnow were 0.15 and 0.90 mg/l, respectively (Maki, 1979a). The greater toxicity of the higher alkyl chainlength LAS blends observed by Maki (1979a) has been reported elsewhere (Kimerle and Swisher, 1977; Macek and Sleight, 1977; Holman and Macek, 1980). The first effect concentration of a C_{14} LAS homologue was between 0.05 and 0.10 mg/l for the fathead minnow relative to 14.0–28.0 mg/l for a C_{10} LAS homologue (Macek and Sleight, 1977).

Relatively few chronic toxicity values have been reported for nonionic and cationic surfactants and fish (Table 2; Fig. 2). The NOEC values for two nonionic alkyl ethoxylates were 0.18 and 0.32 mg/l, respectively (Maki, 1979a) whereas a nonionic oil dispersant was toxic at 0.05 mg/l to one marine flatfish but not another (Yasunaga, 1976). Chattopadhyay and Konar (1986b) reported that fecundity of *Tilapia* was reduced after exposure to 3.98 mg/l nonionic surfactant. Only two toxicity reports were found for cationic surfactants, Lewis and Wee (1983) reported that the first effect concentration for

Table 2. Reported chronic toxicities of surfactants to fish

Surfactant	First effect concentration (mg/l)	Test species	Test duration	Effect	Reference
Anionic					
$C_{11.8}$ LAS	0.90 (NOEC)*	Fathead minnow	28 d	Hatching, growth, larval survival	Maki (1979a)
C_{13} LAS	0.15 (NOEC)*				
AES	0.10 (NOEC)*				
$C_{11.2}$ LAS	5.1–8.4*	Fathead minnow	Complete life cycle, partial life cycle	Hatching, growth, larval survival	Holman and Macek (1980)
$C_{11.7}$ LAS	0.48–0.49*				
$C_{13.3}$ LAS	0.11–0.25*				
LAS	0.63–1.2[1]	Fathead minnow	28 wk	Survival	Pickering and Thatcher (1970)
C_{10} LAS	14.0–28.0	Fathead minnow	28 d	Survival, hatching	Macek and Sleight (1977)
C_{11} LAS	7.2–14.5				
C_{12} LAS	1.08–2.45				
C_{13} LAS	0.12–0.28				
C_{14} LAS	0.05–0.10				
LAS	3.2 (NOEC)	*Poecilia reticulata*	28 d	Immobility	Canton and Slooff (1982)
LAS	0.05–0.50	Marine flatfish (*Limanda yokohamae*, *Paralichtys olivaceus*)	30 d	Hatching	Yasunaga (1976)
LAS	2.0–5.0	Fathead minnow	30 d	—	Swisher *et al.* (1978)
LAS	0.25–1.10	*Tilapia mossambica*	90 d	Fecundity, maturity	Chattopadhyay Konar (1986a)
LAS	4–10	Bluegill	6 d	Fertilization, hatching	Hokanson and Smith (1971)
LAS	0.5–1.1*	Fathead minnow	30 d	Standing crop	McKim *et al.* (1975)
	<0.3*	White sucker			
	0.5–1.2*	Northern pike			
	2.3–5.8*	Smallmouth bass			
Nonionic					
C_{12-13} AE	0.32 (NOEC)*	Fathead minnow	28 d	Growth, hatching, larval survival	Maki (1979a)
C_{14-15} AE	0.18 (NOEC)*				
Oil dispersant	10–50	*Limanda yokohamae*,	10 d	Hatching	Yasunaga (1976)
	0.05	*Paralichtys olivaceus*			
Oleyl-cetyl alcohol Ethylene oxide condensate	<3.98	*Tilapia mossambica*	90 d	Fecundity, maturity	Chattopadhyah and Konar (1986b)
Cationic					
DTDMAC	0.05–0.09[1]*	Fathead minnow	28 d	Growth, hatching	Lewis and Wee (1983)
	0.23–0.45[2]*				
TMAC	0.46 (NOEC)*	Fathead minnow	ND	ND	Pittinger *et al.* (1989)

[1] Test conducted in laboratory water.
[2] Test conducted in river water.
*Value based on measured test concentrations.
ND = no data.

DTDMAC was between 0.05 (NOEC) and 0.09 mg/l (LOEC) for fathead minnows exposed in laboratory water and between 0.23 (NOEC) and 0.45 mg/l (LOEC) in river water. The NOEC for C_{12} trimethyl ammonium chloride and the fathead minnow was 0.46 mg/l (Pittinger *et al.*, 1989).

Sublethal Toxicity

Physiological responses

The majority of reports describe the effects of anionic surfactants on several physiological processes of fish during exposures of 15 min to 30 days (Table 3). Effects on olfaction, respiration and gill physiology were more frequently monitored than other parameters and effects occurred at concentrations that exceed 0.1 mg/l in most cases. For example, changes in adrenergic control mechanisms and vasodilation in salmon gills were noted at LAS concentrations of 0.6 mg/l or greater (Bolis and Rankin, 1978, 1980). The respiratory rate of bluegills was first altered at concentrations ranging from 0.39 to 2.20 mg/l for several anionic surfactants (Maki, 1979b). The low effect concentrations of 0.005 and 0.015 mg/l were reported for LAS based on changes in gill and skin morphology after 30 days of exposure (Misra *et al.*, 1985, 1987).

Sutterlin *et al.* (1971), in a comprehensive study, tested many surfactants for their stimulatory and blocking effectiveness on the olfactory epithelium of Atlantic salmon. Blocking effects were noted at 1 mg/l for several of the cationic surfactants and the anionic alkylbenzene sulfonate. No blocking effect was noted for the nonionic surfactants. Overall, the effects were reversible in many cases. Maciorowski *et al.* (1977) also reported that the effects of an anionic surfactant on intestinal damage to clams was reversible. The no observed effect concentrations based on the respiratory rate of bluegill were 0.54 and > 1.56 mg/l for two alkyl ethoxylates (Maki, 1979b).

The physiological effect concentrations of anionic surfactants on species other than fish have ranged from 0.015 to 3.0 mg/l (Table 3). Moffett and Grosch (1967), for example, reported that 1–3 mg/l LAS caused developmental abnormalities in several marine invertebrates whereas 0.015 mg/l ABS reduced calcium uptake in a snail after 72 h exposure (Misra *et al.*, 1984).

Behavioral responses

The avoidance reaction by fish has been one of the more commonly monitored effect parameters in behavioral studies with surfactants. Avoidance of several anionic surfactants by a variety of fish species has been observed at concentrations ranging from 0.002 to 0.40 mg/l (Table 4). The concentration resulting in a 65% avoidance ratio by the Ayu for several anionic surfactants was 0.002–0.011 mg/l (Tatuskawa and Hidaka, 1978) whereas avoidance reactions of another fish species, the Medaka, for similar compounds ranged from 0.007 to 0.027 mg/l (Hidaka *et al.*, 1984). Other responses such as swimming activity and feeding behavior are affected at higher concentrations. The effects of LAS on these characteristics for trout, goldfish, cod and carp have occurred at concentrations between 0.2 and 5.0 mg/l (Marchetti, 1968; Swedmark *et al.*, 1976; Saboureau and Lesel, 1977; Walzak *et al.*, 1983). For example, the swimming activity of trout was altered at 0.2–0.4 mg/l LAS (Saboureau and Lesel, 1977) and that of carp at 5 mg/l after 125 d exposure (Walczak *et al.*, 1983).

The reported behavioral effect concentrations for nonionic surfactants have ranged from 0.002 to 40.0 mg/l (Table 4). Höglund (1976) reported that cod avoided a tallow alkyl ethoxylate and a nonylphenol compound at 0.002 mg/l. The avoidance responses however, were erratic in many cases. Swedmark *et al.* (1971), in a comprehensive study, reported the effects of a variety of surfactants including several nonionic compounds on several characteristics of marine fish and invertebrates. Effect levels exceeded 0.5 mg/l in all cases based on changes in swimming activity, shell closures, byssal activity, locomotion and burrowing. Byssal activity and growth of mussels were affected by 0.056 mg/l of a nonylphenolic compound (Granmo *et al.*, 1989). The behavioral effects of cationic surfactants on aquatic life have not been reported.

Table 3. Sublethal responses (physiological/histopathological) to surfactants as reported in the literature

Surfactants	Effect concentration (mg/l)	Test species	Effect	Reference
Anionic				
$C_{11.8}$ LAS	2.2	Bluegill	Respiration	Maki (1979b)
C_{13} LAS	<0.39			
AES	0.39			
ABS LAS	0.5	Yellow bullhead	Chemoreception of taste buds	Bardach *et al.* (1965)
ABS	1.0	Atlantic salmon	Olfaction	Sutterlin *et al.* (1971)
SLS[1] NaC_{12} AS	0.1	Whitefish	Depressed olfactory response	Hara and Thompson (1978)
LAS	1.5–2.5	Catfish	Separation of gill lamellae	Zaccone *et al.* (1985)
LAS	1.0	Brown trout European eel	Noradrenaline response in gills	Bolis and Rankin (1980)
LAS	0.6–0.3	Pacific salmon	Gill vasodilation	Bolis and Rankin (1978)
LAS	1.0	Rainbow trout	Skin degeneration	Pohla-Gubo and Adam (1982)
LAS	0.005	*Cirrhina mrigala*	Gill morphology	Misra *et al.* (1985)
LAS	1–3	Sea urchin (*Arbacia*) Starfish (*Asterias*) Sponge (*Spicula*) Annelid (*Chaetopteris*) Tunicate (*Molgula*)	Developmental abnormalities	Moffett and Grosch (1967)
$NaC_{12}AS$	0.67–1.04	Pacific oyster (*Crassostrea gigas*)	Abnormal development	Cardwell *et al.* (1978)
$NaC_{12}AS$	28	Sea urchin (3 spp)	Inhibition of micromere formation	Tanaka (1976)
LAS	0.005	*Cirrhina mrigala*	Skin morphology	Misra *et al.* (1987)
SLS	0.61	Snail (*Limnaea peregra*)	Shell dry weight	Tarazona and Nunez (1987)
ABS	0.015	Snail (*Limnaea vulgaris*)	^{45}Calcium uptake	Misra *et al.* (1984)
LTBS[2]	1.0	Clam (*Pisidium casertanum*)	Intestinal damage	Maciorowski *et al.* (1977)
LAS	3.5	Rainbow trout	Gill uptake of cadmuim	Pärt *et al.* (1985)
Nonionic				
C_{14-15} AE_6	0.54	Bluegill	Respiration	Maki (1979b)
C_{12-13} AE	>1.56	Bluegill		
Several nonionic surfactants	>10	Atlantic salmon	Olfaction	Sutterlin *et al.* (1971)
Cationic				
Several quaternary ammonium and imidazolinium salts	1.0	Atlantic salmon	Olfaction	Sutterlin *et al.* (1971)

[1] SLS = sodium lauryl sulfate.
[2] LTBS = linear tridecyl benzene sulfonate.

DISCUSSION

Data overview

Overall, most of the toxicity data available in the scientific literature is for anionic surfactants (Fig. 2). More specifically, the chronic and sublethal toxicity data base available to the scientific community is limited to a few commercially important surfactants, primarily various blends of LAS (1987 consumption in U.S.A., Japan and Western Europe = 984,000 MT) and to a lesser extent the nonionic alkyl ethoxylates (467,000 MT) and the cationic DTDMAC. Toxicity data for high-volume anionic surfactants other than LAS such as the alkyl sulfates (236,000 MT) and the alkyl ethoxysulfates (350,000 MT) are fewer. The usage values are from Richtler and Knaut (1988). The relative absence of chronic toxicity data for fish is most noticeable, particularly for several major anionic surfactants and cationic dialkyl and monoalkyl quaternary ammonium halide compounds. The U.S.A. and Western Europe consumption of cationics in 1987 was 190,000 and 150,000 MT, respectively (Roes and de Groot, 1988).

The reported chronic toxicity results summarized here are based largely on the response of laboratory cultured single species exposed under controlled laboratory conditions usually for 21 days duration or less. Effects of most surfactants on structural and

Table 4. Sublethal responses (behavioral) to surfactants as reported in the literature

Surfactant	Effect concentration (mg/l)	Test species	Effect	Reference
Anionic				
LAS	0.002	Ayu (*Plecoglossus altivelis*)	Avoidance	Tatuskawa and Hidaka (1978)
AS	0.008			
ABS	0.011			
LAS	0.014	Medaka (*Oryzias latipes*)	Avoidance	Hidaka *et al.* (1984)
AS	0.007			
AES	0.025, 0.027			
ABS	0.014			
ABS	0.001	Rainbow trout	Avoidance	Sprague (1968)
ABS	0.02	Cod (*Gadus morrhua*)	Avoidance	Höglund (1976)
LAS	0.002			
LAS	0.02	Arctic charr (*Salvelinus alpinus*)	Chemoattraction, locomotor activity	Olsén and Höglund (1985)
LAS	5.0	Carp	Swimming pattern, appetite	Walczak *et al.* (1983)
LAS	>0.015	*Cirrhina migola*	Schooling pattern	Lal *et al.* (1984)
C_{10-15} LAS	0.2–0.4	Rainbow trout	Swimming endurance	Saboureau and Lesel (1977)
C_{12}, C_{14} LAS	3.2–4.7	Goldfish (*Carasssus auratus*)	Swimming activity	Marchetti (1965)
ABS	10.0	Flagfish (*Jordanella floridae*)	Feeding behavior	Foster *et al.* (1966)
LAS	0.5	Cod (*G. morrhua*)	Swimming activity	Swedmark *et al.* (1971)
ABS	>1.0	*G. morrhua*	Swimming activity	
LAS	10.0	Mussel (*Mytilus edulis*)	Byssal thread formation, Aductor muscle closing	
Nonionic				
C_9 APE_{10}	2–4	Cod, mussel	Swimming activity, avoidance	Swedmark *et al.* (1976)
TAE EO(10)	0.5	*G. morrhua*	Swimming activity	Swedmark *et al.* (1971)
NP EO(10)[1]	>1.0	*G. morrhua*	Swimming activity	Swedmark *et al.* (1971)
NP EO(10)	5.0	*M. edulis*	Byssal thread formation, Adductor muscle closing	Swedmark *et al.* (1971)
NP EO(10)	2.0	Cockle (*Astarte montagui*) Cockle (*Cardium edule*)	Burrowing	Swedmark *et al.* (1971)
	5.0	*Crangon crangon*	Burrowing	
	20.0	Decapod (*Leander adspersus*)	Locomotion	
	40.0	Hermit crab (*Eupagurus bernhardus*) Shore crab (*Carcinus maenas*)	Locomotion	
	5.0	Barnacle (*Balanus balanoides*)	Cirral activity	
APE[2]	5–6	Rainbow trout	Swimming activity	A. D. Little Co. (1977)
C_9 APE_{10}	2.0	*G. morrhua*	Swimming activity, bysal activity	Swedmark *et al.* (1976)
NP[3]	0.002			
TAE-EO(10)	0.002	*G. morrhua*	Avoidance	Höglund (1976)
NP-EO(10)	0.002			
4-NP	0.056	*M. edulis*	Byssal activity, growth	Granmo *et al.* (1989)
Oleyl-cetyl alcohol-ethylene oxide condensate	<3.98	*Tilapia mossambica*	Feeding	Chattopadhyay and Konar (1986b)

[1] Nonylphenol ethoxylate.
[2] Alkylphenol ethoxylate.
[3] Nonylphenol.

functional aspects of natural animal communities are unknown. Only a few studies have been reported describing the "long-term" effects of surfactants on natural zooplankton and invertebrate communities and these studies were conducted with LAS. Chattopadhyay and Konar (1985) reported that ostracods, rotifers and chironomids, in outdoor vats were adversely affected after 90 d exposure to 0.38–1.10 mg/l LAS based on the active ingredient. Zooplankton were reduced significantly at 0.51 and 1.10 mg/l. Huber *et al.* (1987) reported that 5 mg/l LAS adversely affected cyclopod egg production and developmental stages after 8 weeks exposure in model pond ecosystems. Egg production occurred at 3.5 mg/l LAS. Cladocera and phytoplankton were affected only after exposure to 10.0 mg/l. Ladle *et al.* (1989) found that sediment-bound LAS concentrations of 1–40 μg/g had no impact on the invertebrate diversity in a stream survey conducted above and below a municipal discharge. The effects of LAS in combination with a petroleum refinery effluent were investigated on phytoplankton, zooplankton and benthic organisms in outdoor ponds (Panigrahi and Konar, 1986). Combinations of 1 mg/l LAS with 0.4–13% effluent were toxic to zooplankton.

The range of reported chronic toxicity values for surfactants and aquatic animals is wide which can be attributed in part to the differences in experimental conditions. It is obvious that the toxicities of surfactants vary widely even within the same surfactant class (Fig. 2). Furthermore, toxicities of surfactants can vary with the chemical structure such as for LAS where the toxicity varies with the length of the alkyl chainlength (Kimerle and Swisher, 1977) and for the nonionic ethoxylated surfactants where toxicity varies with the length of the ethoxylate chainlength (Sivak *et al.*, 1982; Hall *et al.*, 1990). The range of effect and no effect concentrations based on the studies reviewed in this summary for fish was 0.05–28.0 mg/l (anionic surfactants), 0.05–50.0 mg/l (nonionic) and 0.05–0.46 mg/l (cationic). The range for invertebrates is 0.04–> 10.0 mg/l (anionic), < 0.1–20.0 mg/l (nonionic) and 0.009–1.27 mg/l (cationic). In previous surfactant toxicity reviews, chronic effect levels for aquatic animals were reported to range from 0.11 to 2.0 mg/l for alkyl ethoxylates (A. D. Little, Co., 1981) and to be as low as 0.1 mg/l for several major surfactants (Sivak *et al.*, 1982). Lewis and Suprenant (1983) reported that the acute toxicities of anionic, nonionic and cationic surfactants to aquatic invertebrates range, respectively, from 0.11 to 92.0, 0.21 to 500.0 and 0.08 to 2800.0 mg/l.

Sublethal effects data predominate for LAS and, with the exception of fish avoidance responses, the effect levels typically exceed 0.1 mg/l. The effect concentrations for nonionic surfactants, with a few exceptions, exceed 0.5 mg/l. Reported sublethal responses for cationic surfactants are too few to indicate a data trend.

Risk assessment

A relatively complete toxicity evaluation of a compound needs to include data for several test organisms (algae, invertebrate, fish) representing the trophic levels contained in the planktonic and benthic habitats of the environment (freshwater and saltwater) to which the compound is discharged. In addition, current measured environmental concentrations of the specific compound are needed since they would reflect recent usage rates, biodegradation and in-stream removal mechanisms and consequently provide the most realistic exposure scenario. Rarely are these data available for most chemical compounds and, with the exception of LAS and to a lesser extent for DTDMAC, this is true for most commercially important surfactants.

A brief description of the aquatic safety of representatives of the three major surfactant groups (LAS, alkyl ethoxylates, DTDMAC) follow based on the published data base and the generalized procedure of comparing laboratory-derived toxicity data with measured environmental concentrations.

Toxicity. The reported chronic effect concentrations have usually exceeded 0.1 mg/l for the various LAS blends, the alkyl ethoxylates (AE) and, in fewer cases, for DTDMAC (Fig. 2). These surfactants have been the more commonly tested and are commercially important representatives of the major surfactant groups used in detergent and softener products. The effect concentrations for the AE compounds, reviewed for this summary, were between 0.1 and 1.0 mg/l in all but one case and over 80% and 40% of the effect and no effect values for LAS exceeded 0.1 mg/l and 1.0 mg/l, respectively. The trend for DTDMAC is less clear due to the limited data base but results from standard toxicity tests with two commonly used test species have indicated an effect range of 0.1 to 1.0 mg/l when conducted in river water.

Exposure. Reported measured concentrations of specific surfactants in the environment have not been common until recently. The use of FAB mass spectrometry (Ventura *et al.*, 1989) and other analytical methodologies (Kikuchi *et al.*, 1989) will likely increase the availability of these data in the future. Currently, most reported environmental concentrations for surfactants are for LAS and the cationic DTDMAC in rivers receiving activated sludge treated municipal effluents (Table 5). Under these circumstances, and for the selected papers reviewed here, LAS concentrations in rivers have ranged from 0.0008 to 3.3 mg/l. Kimerle (1989) reported that although LAS concentrations of 0.001–10 mg/l have been reported for freshwater and marine waters, 85% of the values are between 0.01 and 0.1 mg/l, and 70% are between 0.01 and 0.05 mg/l. Concentrations of DTDMAC in various rivers have ranged from 0.001 to 0.092 mg/l. The reported values for LAS and DTDMAC, with few exceptions, are based on

Table 5. Measured environmental levels of surfactants as reported in the selected literature. Values, unless noted, represent range (mg/l)

Surfactant	Concentration (mg/l)	Location	Reference
Anionic			
ABS	BD[1]–0.54	Malaysia rivers and estuaries	Ludwig and Sekaran (1988)
AES	0.008	Ohio River	Woltering *et al.* (1987)
LAS	0.01–3.3	Major U.S. rivers	A. D. Little Co. (1977)
LAS	0.01–0.27	Unamed U.S. river	Osburn (1986)
LAS	0.04 (0.008–0.17)	U.K. rivers	Gilbert and Kleiser (1986)
LAS	0.0008–0.030	Tokyo Bay	Kikuchi *et al.* (1986)
LAS	0.28 (0.08–0.61)	German rivers	Topping and Waters (1982)
LAS	0.04–0.59	Town River, Mass.	Lewis and Wee (1983)
LAS	0.04 (0.01–0.09)	German rivers	Matthijs and de Henau (1987)
LAS	0–0.26	Seawater	Martinez *et al.* (1989)
	0–0.34	Ebro River	
LAS	0.01–0.04	Eight U.S. rivers	Hennes and Rapaport (1989)
	0.01–0.09	Eleven European rivers	
Nonionic			
Alcohol ethoxylates	0.01–1.0	Several European rivers	A.D. Little Co. (1977)
Cationic			
DTDMAC	0.004–0.092	Rhine River Basin	Kappeler (1982)
DTDMAC	0.013–0.037	U.S. river	Wee (1984)
DTDMAC	0.033 (0.001–0.092)	Rapid Creek, S.D.	Lewis and Wee (1983)
DTDMAC	0.017 (0.009–0.028)	Blackstone River, Mass.	Lewis and Wee (1983)
DTDMAC	0.024 (0.012–0.040)	Otter River, Mass.	Lewis and Wee (1983)
DTDMAC	<0.002	Millers River, Mass.	Lewis and Wee (1983)
DSDMAC	0.008 (0.002–0.016)	German river	Topping and Waters (1982)
	0.014 (0.009–0.02)	U.K. river	
C_{12-18} MAQ[2]	BD–0.012	31 European and U.S. rivers	Woltering *et al.* (1987)

[1] BD = below detection.

[2] MAQ = monoalkyl quaternary ammonium salt.

chemical-specific methodologies. In contrast, routine analytical methods for specific nonionic surfactants have not been reported. A. D. Little Co. (1977) summarized the reported concentrations of nonionic surfactants in several European rivers. The range of concentrations was 0.01–1.0 mg/l which represented total "nonionic substance". It was reported in the A. D. Little Co. review that no reports of nonionic surfactant levels in the U.S.A. were found.

Toxicity–exposure comparison. In most cases, a safety margin is indicated based on the comparison of the more commonly observed toxicity values (>0.1 mg/l) and exposure data for LAS. The significance of the infrequent overlap in the exposure and effects data for LAS is unknown but should not be a major concern due to the site-specific and sometimes non-specific nature of the measured environmental concentrations and to most field-derived toxicity results that show LAS to be relatively nontoxic to natural animal communities (Chattopadhyay and Konar, 1985; Huber *et al.*, 1987). It appears that DTDMAC is not an obvious environmental hazard based on the available data. However, this conclusion is less technically supported than is that for LAS. Effects on saltwater environments and on natural freshwater animal communities are key unknowns that need to be determined before the environmental safety of this and other similar cationic compounds can be confidently assumed. Measured concentrations of specific AE compounds in the environment are needed to confirm the predicted safety of these nonionic surfactants.

The environmental impacts of LAS and DTDMAC have been discussed by the international scientific community (German Chemical Society, 1982; Ruchay, 1982). In addition, LAS has been reported to be environmentally safe in a variety of reports (Gledhill, 1974; Sivak *et al.*, 1982; A. D. Little Co., 1981; Gilbert and Pettigrew, 1984; DeHenau *et al.*, 1986; Huber, 1989; Kimerle, 1989; Martinez *et al.*, 1989). Of these papers, Kimerle's is the most thorough evaluation of the subject. The environmental data base for LAS is the most extensive of any surfactant (Kikuchi *et al.*, 1986; Huber, 1989) and a review of the data summarized in this report for planktonic and benthic animal life and for aquatic vegetation (Lewis, 1991) supports the aquatic safety of this compound more so than for any other surfactant. A detailed discussion of the environmental safety of LAS can be found in *Tensides Surfactants Detergents* (Vol. 26, No.2).

Risk assessments for the softener active DTDMAC based on laboratory toxicity data (Lewis and Wee, 1983) and on laboratory and field-derived data for algae and phytoplankton (Lewis and Hamm, 1986; Lewis, 1991) predict the likelihood of safety in freshwater. It can be stated with more certainty that DTDMAC adsorbed to sediment is probably non-toxic to freshwater benthic life. Lee (1986) and Pittinger *et al.* (1989), have reported the non-toxic nature of sediment bound cationic compounds to midge. In contrast, Lahl and Zeschmer (1986) recommended that cationic surfactants as well as a variety of other detergent ingredients not be included in "environmentally safe" detergent products. Several Western European countries are debating DTDMAC "bans". Published reports for other cationic surfactants are either uncertain on safety primarily due to the lack of field and exposure data (Cooper, 1988) or predict safety based on the available data (Woltering *et al.*, 1987). Detailed safety assessments for most nonionic surfactants have not been reported, but the safety of alkyl ethoxylates has been concluded (Kravetz *et al.*, 1986; Shell Chemical Co.). In contrast, nonylphenol based ethoxylates, a major class of industrial surfactants, and their biodegeneration by-products are toxic and recalcitrant (Brunner *et al.*, 1988) and their environmental safety is highly questionable.

Overall, the data summary and brief risk assessment presented here shows that a comprehensive effect and exposure data base exists for aquatic animal life and LAS but that comparable information for other surfactants is either unknown or unreported. Therefore, safety evaluations for most surfactants in freshwater and more so in saltwater environments should be considered limited and preliminary in nature since they are based largely on toxicity and exposure predictions in need of validation. With this in mind, continued generation of environmental effects and exposure data for LAS should be of low priority when compared to the obvious need for these data for other widely used surfactants.

Sublethal effects

The utility of behavioral and physiological effects data in estimating an environmental impact is unknown in most cases (Rand, 1985) and has been rated below the value of chronic test results (Macek *et al.*, 1978). This lack of predictive value is attributable to a variety of factors including lack of established methodologies, incomplete understanding of the physiology of aquatic organisms and the current inability to relate biophysiological and behavioral changes to the health and survival of the organism. It is obvious that avoidance responses are a sensitive effect parameter when compared to the other effect parameters reported for surfactants. However, their predictive capability for estimating chronic effects is limited due to a lack of field validation and also to the lack of a statistical correlation of avoidance concentrations and chronically toxic levels (Giattina and Garton, 1983; Smith and Bailey, 1989). Furthermore, in several reports the sublethal effects were reversible (Maciorowski *et al.*, 1977; Olsen and Hoglund, 1985). The utility of sublethal effects data in the safety assessment process will increase in the future as their environmental relevance is investigated. When this occurs, priority should be assigned to determining these effects for the cationic surfactants.

OVERVIEW AND RECOMMENDATIONS

Historically, the effects of the anionic ABS (alkylbenzene sulfonate) and LAS have been the primary focus of scientific investigations concerning surfactant environmental safety. The importance of the nonionic and cationic surfactants to the detergent industry has increased during the past 15 years. Consequently, their use in toxicity tests has increased, but the cationic surfactants still do not receive the attention they deserve. The reported toxicity data base for surfactants is dominated by data for freshwater species which reflects, in part, the availability of standard test methods and suitable culture techniques. This contrasts the lack of standard methods and culture techniques for marine species which have been available only until recently. Consequently, the toxicities of surfactants on saltwater life have been and continue to be largely estimated from effects derived on freshwater life. Since this practice is not technically sound, in most cases, toxicity data for saltwater species are needed. Based on the data in this review and that reported earlier for algae (Lewis, 1991) the chronic toxicities of surfactants for freshwater aquatic plants are better understood, particularly on natural communities, than are those for animal life. With the exception of cationic surfactants, algae are not sensitive to surfactants. It even appears that the toxicitity of the cationic surfactants observed in the laboratory for single algal species is less for natural phytoplankton communities although additional supporting data for periphyton communities are needed. Overall, future investigations concerning the environmental safety of surfactants should center on understanding their chronic toxicities to animal life.

Animal test species have exhibited a moderate degree of sensitivity to several major anionic and nonionic surfactants but at concentrations typically exceeding, where available, measured environmental concentrations. The few available effect and no effect levels for cationic surfactants appear to occur at lower concentrations than those for many anionic and nonionic surfactants but a definitive trend cannot be identified at this time due to the limited nature of the data base.

Commonly used surfactants for which a limited chronic toxicity data base exists include the alkyl sulfates (anionic), alkyl ethoxylate sulfates (anionic) and several of the monoalkyl and dialkyl quaternary ammonium salts (cationic). Of these compounds it would be expected, based on the available information for aquatic animal and plant life, that the toxicities of the anionic compounds would likely parallel those for LAS and be relatively nontoxic. However, the use of alkyl sulfates and alkyl ethoxylate sulfate in commercial products is substantial and increasing, and selected chronic toxicity determinations with these surfactants would determine if their toxicities are comparable to LAS. The key scientific need for nonionic surfactants is to determine the environmental concentrations in freshwater and saltwater environments of the major alkyl ethoxylates and compare these to the available toxicity data base. This need for a realistic exposure analysis includes most other surfactants as well. The use of the nonionic alkylphenol exthoxylates, particularly several of the nonylphenol ethoxylates is decreasing due in part, to their environmental toxicity and legislative action in Western Europe to ban their use (Richtler and Knaut, 1988). Therefore, they should be of a low priority from a research perspective. The toxicity data base for cationic surfactants needs to be expanded. The chronic toxicity tests needed for these surfactants are chemical-specific but would include baseline toxicity studies with saltwater and freshwater laboratory fish and invertebrates, tests investigating physiological and behavioral effects, and of greater priority, those determining effect levels for natural freshwater and saltwater animal assemblages.

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