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Chronic Toxicities of Surfactants and Detergent Builders to Algae: A Review and Risk Assessment

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Surfactants are high volume chemicals used primarily in detergent products and are found in natural waters. The toxic effects of representative surfactants on aquatic life have been determined and summarized in greater detail for animal test species than for aquatic vegetation. This paper summarizes the chronic toxicity levels for algae, an important trophic level in aquatic ecosystems. Toxic effects have been determined for a few commercially important surfactants and primarily for cultured freshwater algae under the controlled conditions of the laboratory where inhibition, and in some cases, stimulation have been observed. The reported toxicities of surfactants have varied widely over several orders of magnitude and the effect levels are compound and species-specific. Species sensitivity can vary as much as three orders of magnitude to the same surfactant and the effects of different surfactants on the same algal species can vary as much as four orders of magnitude. Therefore, data generalizations and extrapolations are difficult but anionic and nonionic surfactants and detergent builders are relatively non-toxic when compared to various cationic monoalkyl and dialkyl quaternary ammonium salts. Recent toxicity studies conducted in the field monitoring the effects of several surfactants used in commercial products on various structural and functional parameters of natural algal communities have shown toxicity to be less in many cases than that predicted from laboratory tests. Furthermore, the field-derived effect levels typically exceed the reported measured environmental levels of the corresponding surfactants indicating the likelihood of no impact. Additional field studies are needed to substantiate this trend for these and other commercially important surfactants particularly for natural saltwater algal assemblages for which the toxicity data base is unavailable.

INTRODUCTION

Surfactants are large volume chemicals used in detergents, household cleaning and personal care products and, to a lesser extent, in pesticides, herbicides, paints, plastics, and in the mining, oil, and textile industries. Reported volumes of surfactants used annually vary. A comprehensive and recent summary of surfactant use in U.S., Japan, and Western Europe is that reported in the Proceedings of the Second Worlds Surfactant Congress by Bryan, (1988); Richtler and Knaut, (1988); and Roes and de Groot, (1988). Anionic surfactants are the most commonly used of the three major classes in these geographical locations, 1.8×10^6 MT in 1987 (Bryan, 1988) whereas volumes of alkyl ethoxylates and alkylphenol ethoxylates, both important nonionic surfactants, were 4.7×10^5 and 3.9×10^5 MT, respectively in 1987 (Richtler and Knaut, 1988). Approximately, 1.5×10^5 MT of cationic surfactants were used in Western Europe and 1.9×10^5 MT in the U.S. (Roes and de Groot, 1988). Overall, the annual rate of increase in surfactant use is greater for the cationic types (4–5%) than for the remaining classes (2–3%) (Boethling, 1984; Roes and de Groot, 1988).

Surfactants have been reported in natural waters that receive municipal wastes in the U.S., Japan, and Western Europe by among others Matulová, (1964); Nyberg, (1976); Margaritis and Creese, (1979); Fischer, (1980); Sivak *et al.*, (1982); Kikuchi

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et al., (1986); and Tarazona and Nuñez, (1987). Several surfactants and their breakdown products also have been measured to various degrees in drinking water (Crawthorne *et al.*, 1984; Ventura *et al.*, 1989), sewage sludges, sludge-amended soils, and sediments (Waters and Topping, 1982; Takada and Ishiwatari, 1985; McEnvoy and Giger, 1985; DeHenau *et al.*, 1986; Brunner *et al.*, 1988). Surfactants usually enter U.S. rivers as part of a treated municipal effluent; however, in other countries, surfactants enter waterways largely untreated (Yamane *et al.*, 1984). Some surfactants are mostly removed by sewage treatment (Games *et al.*, 1982; Sullivan, 1983; Boethling, 1984; Brown *et al.*, 1986) and biodegradation occurs to various degrees (Sivak *et al.*, 1982; Larson and Vashon, 1983; Larson, 1983; Boethling, 1984; Richtler and Knaut, 1988). Algae are able to degrade some surfactants (Davis and Gloyna, 1969; Swisher, 1970; Ernst *et al.*, 1973; Chawla *et al.*, 1987).

The toxic effects of surfactants on aquatic life have been determined during the past 30 years and the results have been summarized in many reports (Marchetti, 1965; Abel, 1974; Gledhill, 1974; A. D. Little Co., 1977; Margaritis and Creese, 1979; Koskova and Kozlovskaya, 1979; Sivak *et al.*, 1982; Gilbert and Pettigrew, 1984; Kimerle, 1989; Lewis, 1990). Many of these reviews have centered on detailing the laboratory-derived acute toxicities of anionic and, to a lesser extent, nonionic surfactants on animal life. Effects of cationic surfactants as a class have not been discussed in any detail although reports by Lewis and Suprenant, (1983); Lewis and Wee, (1983); Woltering *et al.*, (1987), and Cooper, (1988) summarize some data. Furthermore, the chronic toxicities of surfactants on algae in the previous reviews are absent or limited despite the unique ecological importance of this food chain component and the existence of a relatively abundant although scattered literature. The absence of a reference document may be responsible, in part, for the sometimes lack of consideration of the effects of surfactants on algae in published reviews and hazard assessments (Envirocontrol, 1981; Huber, 1984; Gilbert and Pettigrew, 1984; Cooper, 1988). In addition, algal toxicity data are seldom the focal point of environmental safety considerations discussed for surfactants at international symposia (Anonymous, 1982; Richtler and Knaut, 1988; Roes and de Groot, 1988) and in various environmental legislation (Fischer, 1980; Dinkloh, 1983; Noll, 1987; Fed. Regist., 1988). Therefore, a need exists to summarize and evaluate the current algal toxicity data base for surfactants and detergent builders and to assess their potential for causing an impact in the environment. This paper represents a comprehensive summary of these chronic toxicity data for detergent builders and commercially important surfactants and freshwater and saltwater algae.

METHODS

The chronic toxicities of detergent builders and surfactants representative of the three major classes (anionic, nonionic, and cationic) were considered in this review. Representative structures of commercially important surfactants appear in Fig. 1. A number of standard toxicity test methods using microalgae have been published (OECD, 1984; ISO, 1987; ASTM, 1990). However, these methods were seldom used in the reviewed reports where the objectives included not only attempts to determine environmental safety of surfactants used in detergents and household cleaning products but also to determine the effectiveness of algicides (Fitzgerald *et al.*, 1952; Palmer and Maloney, 1955), controlling red tide organisms (Kutt and Martin, 1974), and deter-

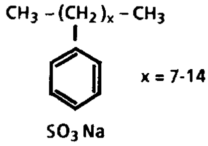
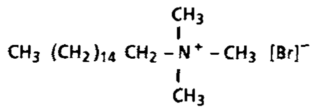
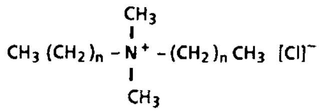
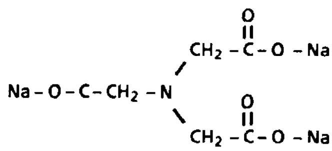
GENERIC NAME	STRUCTURE
Linear Alkylbenzene Sulfonate (LAS)	
Linear Alkylethoxylate (AE)	$CH_3-(CH_2)_x-(C_2H_4O)_y\ H$ x = 7-19 y = 0-12
Cetyl Trimethyl Ammonium Bromide (CTAB)	
Ditallow Dimethyl Ammonium Chloride (DTDMAC)	 n = 15,17
Trisodium Nitriloacetate (NTA)	

FIG. 1. Structures of commercially important surfactants and a detergent builder.

mining bacteriostatic and fungistatic properties of the test compounds (Hueck *et al.*, 1966; Mottley and Griffiths, 1977).

The results in the reviewed studies were reported in various ways. In most cases, the EC_{50}, algistatic, or algicidal effect values were reported. These effect values were usually on the basis of nominal concentrations. The EC_{50} value is that concentration reducing the effect parameter, which is most commonly growth, 50% relative to the control algal population. The algistatic concentration is that concentration of a test compound that totally inhibits algal growth (EC_{100}) but allows the growth to continue when the algae are recultured in fresh medium that does not contain the test chemical. The algicidal concentration is that concentration of chemical which causes cell death such that the test species will not grow when subcultured into a fresh medium that does not contain the test chemical.

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

TOXICITY SUMMARY

Single Species Toxicity Studies

Anionic surfactants. The reported effect concentrations for anionic surfactants range from 0.003 to 4000 mg/liter; however, most effect levels exceed 1.0 mg/liter (Table 1). The exposure periods in the laboratory studies using anionic surfactants have ranged from 30 min to 21 days during which the growth of a green alga or diatom was most frequently monitored. As for most of the surfactants reviewed here, the effect levels are dependent upon the test species, effect parameter, study duration, and surfactant type. The anionic surfactant most frequently used in algal toxicity tests has been the various blends of linear alkylbenzene sulfonate (LAS). This surfactant is used in a variety of cleaning products including liquid and granular detergents. Laboratory-derived EC_{50} values (96 hr) for LAS determined under identical experimental conditions ranged from 1.4 to 116 mg/liter for three freshwater species (Lewis and Hamm, 1986) and 72 h EC_{50} values were between 10 and 100 mg/liter for similar species (Yamane *et al.*, 1984). This trend of relatively low toxicity can be observed as can other anionic surfactants and freshwater algal be observed (Blanck *et al.*, 1984; Chawla *et al.*, 1987).

The few reports available for marine species show *Gymnodinium breve,* a red tide alga, to be unusually sensitive to LAS, moreso than freshwater species, with reported effect levels of 0.003 to 0.025 mg/liter (Kutt and Martin, 1974; Hitchcock and Martin, 1977). However, the sensitivity of other marine species to several anionic surfactants appears to be considerably less; the reported effect levels are between 2 and 54 mg/liter (Ukeles, 1965).

Nonionic surfactants. The reported laboratory-derived toxicities of nonionic surfactants for algae range from 0.003 to 17,784 mg/liter (Table 1). The number of reported toxicity values for these compounds are the fewest in the three surfactant classes. The more frequently tested nonionic surfactants have been the alkyl ethoxylates (AE) and Triton X-compounds. Alkyl ethoxylates are commonly used in shampoos and liquid and granular household detergents. The 96 h EC_{50} values for an AE and three freshwater algal species were between 0.09 and 0.60 mg/liter relative to values of 0.21 and 7.4 mg/liter, respectively, for green and blue-green species exposed to Triton X-100 (Lewis and Hamm, 1986). Yamane *et al.*, (1984) reported EC_{50} values for an AE between 4 and 50 mg/liter, whereas algistatic concentrations (EC100) for a similar compound ranged between 5 and >100 mg/liter (Payne and Hall, 1977). Roederer, (1987) reported algicidal levels of Triton X-compounds between 124 and 17,784 mg/liter, whereas other reported effect levels for Triton X-compounds are between 5 and 15 mg/liter (Nyberg, 1985; 1988). Effects of an AE on *G. breve* were observed at a relatively low level of 0.003 mg/liter (Kutt and Martin, 1974) that is considerably less than effect levels reported for other nonionic surfactants and marine algae, 10 to 100 mg/liter (Ukeles, 1965).

Cationic surfactants. The effects of cationic surfactants have been determined for at least 21 freshwater and 14 saltwater species (Table 1). Most effect levels are between 0.1 and 1.0 mg/liter which are considerably less than those reported for the anionic and nonionic surfactants. The most commonly tested cationic surfactants have been quaternary ammonium halide compounds such as cetyl trimethyl ammonium bromide

(CTAB). The toxicity of CTAB to a variety of algae has been reported in terms of first effect levels and EC_{50} values to be less than 5.0 mg/liter (Nyberg 1976, 1985, 1988), between <0.007 and 0.09 mg/liter (Mottley and Griffiths, 1977; Lewis and Hamm, 1986), and 3 to 5 mg/liter (Walker and Evans, 1978). Another commonly used cationic compound has been ditallow dimethyl ammonium chloride (DTDMAC) which is used in fabric softeners and as an antistatic agent on drier sheets. The 96 h EC_{50} values for this substance have ranged from 0.05 to 0.07 mg/liter for three freshwater species (Lewis and Hamm, 1986).

Ukeles, (1965) reported that the growth of 12 marine species was affected by 0.1 to 10.0 mg/liter lauryl pyridinium chloride. Algicidal and algistatic concentrations for the marine flagellate, *Dunaliella tertiolecta*, and DTDMAC were between 1.0 to 10.0 mg/liter and 0.5 to 1.0 mg/liter, respectively, (Lewis and Wee, 1983). Growth of *G. breve* was stimulated 235% by 0.003 mg/liter of a similar compound (Kutt and Martin, 1977) contrasting the relatively high inhibitory properties of anionic and nonionic surfactants that affect this same species.

Detergent builders. Detergent builders are less toxic to algae than surfactants (Table 1). This is largely on the basis of the toxicity information published for NTA (nitrilotriacetic acid). Effects of this compound on a variety of freshwater algae species have ranged from 1 to 1000 mg/liter. For example, EC_{50} values between 185 and 477 mg/liter were reported by Anderson *et al.*, (1985). The lowest algistatic concentrations for a zeolite compound were between 50 and 100 mg/liter for a diatom and blue-green species (Maki and Macek, 1978). Twenty to 60 mg/liter sodium triphosphate were found toxic (EC_{50}) to several freshwater algae (Yamane *et al.*, 1984).

Other Toxicity Studies

Several studies have reported the toxic effects of surfactants in an effluent matrix after biological treatment. Typically, toxicity of the surfactants was less after the sewage treatment process primarily due to the removal (adsorption, biodegradation) of the surfactant to nontoxic levels. This effect has been shown by Neufahrt *et al.*, (1976) and Camp, (1974) who observed that activated sludge treatment reduced the level of two anionic and one nonionic surfactants to nontoxic levels, to a green alga. Azov *et al.*, (1982) reported that the addition of 30 mg/liter of a nonionic surfactant to a high rate oxidation pond did not significantly reduce the algal concentration in the pond.

The effects of a few surfactants on functional and structural characteristics of natural algal assemblages have been reported and in most cases toxicities were less than those demonstrated under laboratory conditions with the same test compound. Five mg/liter of ABS was found stimulatory (approximately 5%) to river algal photosynthesis relative to concentrations of 25–50 mg/liter which reduced photosynthesis (Hicks and Neuhold, 1966). The *in situ* photosynthetic response of lake phytoplankton exposed to several surfactants varied considerably over a 5 month period (Lewis and Hamm, 1986). The 3 h EC_{50} values for cationic surfactants, for example, ranged from 0.1 to 31.9 mg/liter during this time period. Concentrations of 5 mg/liter and greater of a cationic polyelectrolyte reduced chlorophyll *a* of Nile River algae (Shehata and Nawar, 1979). LAS has been used in several studies. Chattopadhyay and Konar, (1985) reported that LAS concentrations of 0.25 to 1.10 mg/liter reduced photosynthesis of phytoplankton in outdoor vats approximately 40% after 90 days. Huber *et al.*, (1987) in a 2 year study, reported that 5.0 mg/liter LAS adversely affected community composition

TABLE 1

REPORTED EFFECT LEVELS OF SURFACTANTS AND DETERGENT BUILDERS ON ALGAE[1]

Surfactant	Test Species	Effect Parameter	Effect Concentration (mg/l)	Reference
ANIONIC				
Alkyl sulfate	Chlamydomonas gelatinosa Scenedesmus abundans Chlorella saccharophila	21d growth	9-37 (first effect) 111-296 (algicidal)	Matulova, 1964
Alkyl sulfate Alkylbenzene sulfonate	Chlamydomonas sp. Carteria sp. Platymonas sp. Dunaliella euchlora D. primolecta Pyramimonas grossi Chlorella sp. Chlorella stigmatophora Chlorococcum sp. Stichococcus sp. Protococcus sp. Nannochloris sp.	12-14d growth	2 - 54	Ukeles, 1965
Sodium lauryl sulphate	Cladophera glomerata	3d growth	70-100 (inhibition) 125 (algicidal)	Whitton, 1967
Alkylbenzene sulphate			5-30 (inhibition) 15-35 (algicidal)	
Alkylbenzene sulfonate	Nitzschia linearis	120h growth	10.0	Patrick et al., 1968
Linear alkylbenzene sulfonate	Scenedesmus communis Oocystis lacustris	3d growth	1.0 (EC_{50}) 20.0	Huber et al., 1987
Sodium lauryl sulfate	Chlamydomonas dysosmos Chlorella emersonii Kirchneriella contorta Monoraphidium pusillum Scenedesmus obtusiusculus Selenastrum capricornutum Klebsormidium marinum Raphidonema longiseta Bumilleriopsis filiformis Monodus subterraneus Tribonema aequale Synechococcus leopoliensis	14d growth	EC_{100}: 500 (median) 31-4000 (range)	Blanck et al., 1984
$C_{11.6}$ Linear alkylbenzene sulfonate	Selenastrum capricornutum Microcystis aeruginosa Nitzschia fonticola	3d growth	50-100 (EC_{50}) 10-20 20-50	Yamane et al., 1984
Alkyl sulfate	Selenastrum capricornutum		60	
Polyoxyethlene alkyl ether sulfate	Selenastrum capricornutum		65	
Linear alkylbenzene sulfonate	Scenedesmus quadricauda	7-17 d Chlorophyll content, protein synthesis, DNA synthesis, and growth	200-500 (stimulatory) >500 (inhibitory)	Chawla et al., 1986
Linear alkylbenzene sulfonate	Scenedesmus quadricauda	15d oxygen uptake/ evolution, biosynthesis of chlorophyll and morphology	>1000 (inhibitory)	Chawla et al., 1987
Linear alkylbenzene sulfonate	Nostoc muscorum	15d protein content, growth, biomass and heterocyst number	>10 (inhibitory)	Chawla et al., 1988
$C_{13.3}$ Linear alkylbenzene sulfate	Selenastrum capricornutum Microcystis aeruginosa Navicula pelliculosa	4d growth	116.0 (EC_{50}) 5.0 1.4	Lewis and Hamm, 1986
$C_{11.8}$ Linear alkylbenzene sulfonate	Selenastrum capricornutum Microcystis aeruginosa	4d growth	29.0 (EC_{50}) 0.9	
Six Compounds	Selenastrum capricornutum	3w growth	<10 (first effect)	Nyberg, 1988

TABLE 1—*Continued*

Surfactant	Test Species	Effect Parameter	Effect Concentration (mg/l)	Reference
Sodium dodecyl sulfate Sodium deoxycholate	Poterioochromonas malhamensis	3d growth	89 (algicidal) 37 (algicidal)	Roederer, 1987
Mixture of Sodium dodecylbenzene sulfonate, Sodium lauryl ether sulphate and Lauric diethanolamide	Laminaria saccharina	7 min. zoospore motility	50 (first effect)	Pybus, 1973
Linear dodecyl-benzene sulfonate and Linear tridecyl-benzene sulfate	Selenastrum capricornutum	8d growth	10-20 (inhibitory) 5 (stimulatory)	Camp, 1974
C_{12} alkylbenzene sulfonate	Gymnodinium breve	9d growth	69% reduction at 0.003	Kutt and Martin, 1974
Coconut ethoxylate sulfate			87% reduction at 0.003	
Sodium dodecyl sulfate	Nitzschia holsatica	5d growth	15-18 (15°C) 10-12 (25°C)	Nyberg, 1976
Sodium dodecyl sulfate	Nitzschia actinastroides Porphyridium purpureum	5d growth	<5.0 <2.5	Nyberg, 1985
Sodium dodecyl sulfate	Chlamydomonas reinhardi	1-2 w growth	0.17-0.69 (minimum inhibitory concentration)	Mottley and Griffiths, 1977
$C_{11.2}$ Linear alkylbenzene sulfonate	Plectonema boryanum Chlamydomonas reinhardi	growth	20-30 (first effect)	Dhaliwal et al., 1977
C_{13} Linear alkylbenzene sulfonate	Gymnodinium breve	mortality	0.025	Hitchcock & Martin, 1977
Linear alkylbenzene sulfonate	Chlorella vulgaris Microcystis aeruginosa	4d growth	18-32 32-56	Canton and Slooff, 1982
NONIONIC				
Nonylphenol ethoxylate, (E09) Polyoxyethylene cetylalcohol	Selenastrum capricornutum	5d growth	<100 (first effect) <2.5	Nyberg, 1988
Cetyloleyl alcohol (Slovasol 0)	Chlamydomonas gelatinosa Scenedesmus abundans Chlorella saccharophila	21d growth	5 (first effect) 200-450 (algicidal)	Matulova, 1964
Polyether alcohols	12 species (see anionic surfactants)	14d growth	10-1000	Ukeles, 1965
Primary alcohol ethoxylate	Selenastrum capricornutum	8d growth	1.0	Camp, 1974
Coconut ether ethoxylate	Gymnodinium breve	9d growth	0.003 (213% stimulation) 0.050 (33% death)	Kutt and Martin, 1974
Triton X 100	Nitzschia holsatica	5d growth	9 (15°C) 15 (25°C)	Nyberg, 1976
Triton X 100	Nitzschia actinastroides Porphyridium purpureum	5d growth	10-15 5-10	Nyberg, 1985
C_{12-16} $AE_{6.3}$ C_{12-14} $AE_{7.4}$	Selenastrum capricornutum	growth	5.0 (EC_{50}) 3.8	A. D. Little Co., 1977
C_{14-15} AE_6	Selenastrum capricornutum Microcystis aeruginosa Navicula seminulum	5d growth	50 (algistatic) >1000 5-10	Payne and Hall, 1979
Pluronic nonionics (block copolymers of ethylene oxide and prophylene oxide)	Scenedesmus quadricauda	9d, chlorophyll a 5d, photosynthesis, growth	<0.1-10,000 (first effect)	Karpinska - Smulikowska, 1984

TABLE 1—*Continued*

Surfactant	Test Species	Effect Parameter	Effect Concentration (mg/l)	Reference
Alcohol ethoxylate (EO:9)	Selenastrum capricornutum Microcystis aeruginosa Nitzschia fonticola	3d growth	4-8 (EC_{50}) 10-50 5-10	Yamane et al., 1984
Alcohol ethoxylate (EO:4) (EO:9) (EO:13)	Selenastrum capricornutum		2-4 4-8 10	Yamane et al. 1984
Alkylphenol ethoxylates	Selenastrum capricornutum		20-50	
C_{14-15} AE_{6}	Selenastrum capricornutum Microcystis aeruginosa Navicula pelliculosa	4d growth	0.09 (EC_{50}) 0.60 0.28	Lewis and Hamm, 1986
Triton X 100	Selenastrum capricornutum Microcystis aeruginosa		0.21 7.4	
Tritox X 100 Triton X 405	Poterioochromonas malhamensis	72h growth	124 (algicidal) 17, 784 (algicidal)	Roederer, 1987
CATIONIC				
Thirteen imidazoline derivatives and quaternary ammonium compounds	Microcystis aeruginosa Aphanizomenon flosaquae	24h growth	1-10 (algicidal)	Fitzgerald et al., 1952
Methyldodecylbenzyl trimethyl ammonium chloride, Cetyl dimethyl ammonium bromide, Dodecylacetamido dimethyl benzyl ammonium chloride	Cylindrospermum licheniforme Microcystis aeruginosa Scenedesmus obliquus Chlorella variegata Gomphonema parvulum Nitzschia palea Gloeocapsa dimidiata	21d growth	2.0	Palmer and Maloney, 1955
Cetyl pyridinium bromide	Chlamydomonas gelatinosa Scenedesmus abundans Chlorella saccharophila	21d growth	0.10-0.25 (first effect) 2-5 (algicidal)	Matulova, 1965
Lauryl pyridinium chloride	12 species (see anionic surfactants)	12-14d growth	0.1-10.0	Ukeles, 1965
Ditallow dimethyl ammonium chloride	Selenastrum capricornutum Microcystis aeruginosa Navicula pelliculosa	4d growth	0.06 (EC_{50}) 0.05 0.07	Lewis and Hamm, 1986
Cetyl trimethyl ammonium bromide	Selenastrum capricornutum Microcystis aeruginosa		0.09 0.03	
C_{12} trimethyl ammonium chloride	Selenastrum capricornutum Microcystis aeruginosa Navicula pelliculosa		0.19 0.12 0.20	
Saturated imadizolinium compound	Selenastrum capricornutum Microcystis aeruginosa		0.60 0.45	
Unsaturated imadizolinium compound	Selenastrum capricornutum Microcystis aeruginosa		0.30 0.21	
Cetyl trimethyl ammonium bromide Dodecyl trimethyl ammonium chloride	Poterioochromonas malhamensis	72h growth	4.4 (algicidal) 9.0 (algicidal)	Roederer, 1987
Fatty nitrogen compounds (mono, di, tri and poly quaternaries)	Chlorella vulgaris Stigeoclonium sp. Anabaena cylindrica Oscillatoria tenuis	7d growth	0.20->100.0 (algistatic)	Hueck et al., 1966
Ditallow dimethyl ammonium chloride	Gymnodinium breve	9d growth	0.003 (235% stimulation)	Kutt and Martin 1974
Cetyl trimethyl ammonium chloride	Nitzschia holsatica	5d growth	4.0 (15°C) 5.0 (25°C)	Nyberg, 1976

TABLE 1—*Continued*

Surfactant	Test Species	Effect Parameter	Effect Concentration (mg/l)	Reference
Cetyl trimethyl ammonium bromide	Nitzschia actinastroides Porphyridium purpureum	5d growth	<5.0 <2.5	Nyberg, 1985
Cetyl trimethyl ammonium bromide	Selenastrum capricornutum	5d growth	<2.5 (first effect)	Nyberg, 1988
Cetyl trimethyl ammonium bromide	Chlamydomonas reinhardi	1-2w growth	<0.007-0.027 (minimum inhibitory concentrations)	Mottley and Griffiths, 1977
Cetyl trimethyl ammonium bromide, Cetyl pyridinium bromide, Dialkyl dimethyl ammonium chloride, Alkylbenzyl dimethyl ammonium chloride	Chlorella sp.	3-12d growth	1-5 (x 10^{-5}M) (algistatic)	Walker and Evans, 1978
Cationic polyelectrolyte	Scenedesmus sp.	10d growth	1.0 (first effect) 10-20 (algistatic)	Shehata and Nawar, 1979
Ditallow dimethyl ammonium chloride	Selenastrum capricornutum	12d growth	0.23-2.6 (algistatic) 0.5-1.0 (algicidal)	Lewis and Wee, 1983
	Microcystis aeruginosa		0.10-0.32 (algistatic) 0.1-1.0 (algicidal)	
	Navicula seminulum		0.5-10.0 (algistatic) 0.5-10.0 (algicidal)	
	Dunaliella tertiolecta		0.5-1.0 (algistatic) 1.0-10.0 (algicidal)	
DETERGENT BUILDERS				
NTA	Chlorella pyrenoidosa	14d growth	>275	Christie, 1970
NTA	Cyclotella nanna	3d growth	1.0	Erickson et al., 1970
NTA	Dunaliella tertiolecta Isochrysis galbana	5d growth	>10.0	Bressan and Brunetti 1988
NTA	Anabaena flos-aquae	20d growth	>5.0	Sturm and Payne, 1970
NTA	Selenastrum capricornutum	12d growth	>5.0	Payne and Hall, 1979
NTA	Scenedesmus quadricauda	7d growth	>8.3	Brigmann and Kuhn, 1980
NTA	Microcystis aeruginosa Chlorella vulgaris	4d growth	180-320 (EC_{50}) >560-1000	Canton and Slooff, 1982
NTA	Navicula seminulum	4d growth	185-477 (EC_{50})	Anderson et al., 1985
Zeolite	Selenastrum capricornutum Microcystis aeruginosa Navicula seminulum	5d growth	100-1000 (algistatic) 50-100 50-100	Maki and Macek, 1978
Sodium triphosphate	Selenastrum capricornutum Microcystis aeruginosa Navicula seminulum	3d growth	20-60 (EC_{50}) 60 25-600	Yamane et al. 1984

[1] The algistatic concentration is that concentration that totally inhibits algal growth (EC_{100}) but allows growth to continue when the algae are recultured in nutrient media not containing the test compound. The algicidal concentration is that concentration that causes cell death.

of phytoplankton and macrophytes in model ponds. The first effect of three surfactants, which included LAS, on the community composition of an enclosed phytoplankton community occurred between 2.9 and 108 mg/liter in studies of 10 days duration (Lewis, 1986). The first effect of the cationic lauryl trimethyl ammonium chloride occurred between 0.21 and 0.96 mg/liter for periphyton exposed *in situ* for 21 days (Lewis *et al.*, 1986). The periphyton in this same study were less sensitive (first effect = 0.96–9.69 mg/liter) when exposed in the presence of 20 to 30% treated municipal wastewater. The first effects on phytoplankton occurred at 0.03 to 1.99 mg/liter. Whitton, (1967) reported that 125 mg/l of sodium lauryl sulfate was algicidal to natural *Cladophera* communities.

COMPARATIVE SPECIES SENSITIVITY

Algae

The response of different freshwater algae exposed to the same surfactant is species-specific which is a trend reported for other chemicals as well (Bringmann and Kuhn, 1978; Blanck *et al.*, 1984; Wängberg and Blanck, 1988). The literature contains numerous references since 1952 reporting this fact for freshwater species (Palmer and Maloney, 1952) and since at least 1965 for several marine forms (Ukeles, 1965). For example, EC_{100} values for sodium lauryl sulfate and thirteen freshwater species varied from 31 to 4000 mg/liter, over two orders of magnitude (Blanck *et al.*, 1984). Algae vary considerably in their response to LAS as well (Gledhill, 1974); effect levels have varied at least an order of magnitude in several reported studies using this anionic surfactant (Yamane *et al.*, 1984; Lewis and Hamm, 1986; Chawla *et al.*, 1988). The difference in response of *M. aeruginosa* and *S. capricornutum* to LAS, for example, was three orders of magnitude (Lewis and Hamm, 1986). The green alga, *S. capricornutum*, was the least sensitive of the test species in this study as well as in those reported by Yamane *et al.*, (1984) for LAS, and by Maki and Macek, (1978) for a detergent builder. Nyberg (1985) reported the marine red alga, *Porphyridium purpureum*, was more sensitive to anionic and cationic surfactants than was *Nitzschia actinastroides*. In contrast, *P. purpureum* was less sensitive than *N. actinastroides* to the nonionic Triton X.

The interspecific response to the same cationic surfactant is less variable than it is for the other surfactant types. Kappeler, (1982) reported, for example, that the algistatic concentrations for four species of algae (one marine) to DTDMAC were between 0.1 and 1.0 mg/liter. The 96 hr EC_{50} values for C_{12} trimethyl ammonium chloride and three freshwater algae ranged from 0.12 to 0.20 mg/liter (Lewis and Hamm, 1986).

Algae and Animal Test Species

The sensitivities of algae to surfactants have been greater than or at least comparable to those for animal test species in several reported studies. This is demonstrated most clearly for the nonionic and cationic types. For example, the 96h EC_{50} values for an alkyl ethoxylate and three freshwater algal species were between 0.09 and 0.60 mg/liter (Lewis and Hamm, 1986) relative to NOEC values (no observed effect concentrations) of 0.18 and 0.24 mg/liter for a fish and invertebrate exposed to the same compound (Maki, 1979). The same algal species were as sensitive to the cationic DTDMAC (EC_{50} values = 0.05 to 0.07 mg/l) as was the fathead minnow (NOEC = 0.07 mg/l) exposed in a standard 28 day chronic toxicity study (Lewis and Wee, 1983). In addition, green algae have been found to be as or more sensitive than fish are to other cationic compounds (Jacob and Nisbet, 1952, Shehata and Nawar, 1979), and to a nonionic surfactant (Karpínska-Smulikowska, 1984).

Patrick *et al.* (1968) found a diatom more sensitive (120 hr TLm = 10 mg/liter) than either an invertebrate (96 hr TLm = 34.2 mg/liter) or fish (96 hr TLm = 17.4 mg/liter) were to the anionic alkylbenzene sulfonate. In other reports, fish were found more sensitive to LAS than algae were (Maki and Macek, 1981; Canton and Slooff, 1982; Lewis and Hamm, 1986), but daphnids were less sensitive than algae in one case (Canton and Slooff, 1982).

Algae and Other Aquatic Vegetation

Most test species in the reviewed studies were algae, although effects on other aquatic vegetation have been determined. Photosynthesis in the macrophytes *Elodea canadensis*, a *Chara sp.*, and *Myriophyllum spicatum* was reduced 50% after exposure to 1.0 mg/liter LAS (Huber *et al.*, 1987). Degens *et al.*, (1950) reported that effect levels for several anionic surfactants on *Valisneria spiralis* and *Elodea canadensis* exceeded 40 mg/liter. The 7d EC_{50} values for duckweed, *Lemna minor*, and three surfactants ranged from 0.08 mg/liter for the cationic cetyl trimethyl ammonium chloride to 2.7 mg/liter for $C_{11.8}$ LAS (Bishop and Perry, 1981). The sensitivity of *L. minor* was less than that for three freshwater algae exposed to a similar nonionic surfactant but it was comparable to the sensitivities of the algae to the anionic and cationic surfactants (Lewis and Hamm, 1986). Likewise, Walker and Evans (1978) showed no significant difference in response of duckweed (*Spirodela oligorhiza*) and a *Chlorella* species to four quaternary ammonium compounds.

COMPARATIVE TOXICITY

Surfactants

A high degree of chemical specificity in toxicity is evident in the studies reviewed here (Matulova, 1964; Ukeles, 1965; Nyberg, 1976; 1985; 1988; Yamane *et al.*, 1984). The toxicities of different surfactants representing either the same or different classes to the same alga test species have varied over four orders of magnitude (Lewis and Hamm, 1986). The only consistent finding has been that cationic surfactants have a greater effect on algae than either nonionic or anionic surfactants (Table 2). The phy-

TABLE 2

REPORTED EFFECTS OF SURFACTANT GROUPS IN ORDER OF DECREASING TOXICITY TO AQUATIC VEGETATION

Toxicity Order	Test Species	Reference
cationic>anionic>nonionic	three freshwater algae	Matalova, 1964
cationic>nonionic>anionic	marine phytoplankton	Ukeles, 1965
nonionic>anionic	Selenastrum capricornutum	Camp, 1974
anionic>nonionic>cationic	Gymnodium breve	Kutt and Martin, 1974
cationic>anionic>nonionic	Nitzschia holsatica	Nyberg, 1976
cationic>nonionic>anionic	Selenastrum capricornutum	Nyberg, 1988
cationic>nonionic>anionic	Nitzschia actinastroides Porphyridium purpureum	Nyberg, 1985
cationic>anionic	Chlamydomonas reinhardi	Mottley and Griffith, 1977
cationic>nonionic>anionic	Lemna minor (duckweed)	Bishop and Perry, 1982
nonionic>anionic	three freshwater algae	Yamane et al., 1984
cationic>nonionic>anionic	three freshwater algae; natural phytoplankton	Lewis and Hamm, 1986
cationic>nonionic>anionic	natural phytoplankton	Lewis, 1986
cationic>anionic>nonionic	Poterioochromonas malhamensis	Roederer, 1987

totoxic properties of cationic surfactants are well-known and have been reported frequently in the literature (Walker and Evans, 1978; Ernst *et al.*, 1983; Boethling, 1984; Nyberg, 1988). For example, Nyberg (1988) found that cationics were the most toxic of 28 surfactants to *S. capricornutum*, a trend similar to that reported by Ukleles, (1965). This trend has been observed also with duckweed and natural algal assemblages (Bishop and Perry, 1981; Lewis, 1986; Lewis and Hamm, 1986). In contrast, the anionic LAS was more toxic than a cationic surfactant to the marine red tide organism, *G. breve* (Kutt and Martin, 1974).

Surfactants and Other Compounds

Several published reports have compared the toxicities of surfactants to those for other chemicals determined under the same experimental conditions. The results are largely chemical specific but it appears that several cationic surfactants are as toxic as some metals. The minimum inhibitory concentration of a cationic surfactant on *Chlamydomonas* ranged from 7 to 14 mg/liter which was lower than most of the effect levels for 46 growth inhibitors (Mottley and Griffiths, 1977). Bishop and Perry (1981) reported that duckweed is more sensitive to a cationic surfactant than to copper, however, copper was more toxic than the nonionic and anionic surfactants, and diquat was more toxic than all the surfactants. Roederer, (1987) found several anionic, nonionic, and cationic surfactants to be more toxic than lead to a freshwater diatom. Fitzgerald *et al.*, (1952) found that the lethal concentrations for 13 nondetergent compounds range from 0.20 to 20.0 mg/liter relative to 1 to 10 mg/liter for several quaternary ammonium compounds. Zinc was more toxic (0.1 mg/liter) to *Selanastrum* than were anionic and nonionic compounds (1.0–10.0 mg/liter) (Camp, 1974). Sodium lauryl sulfate was reported less toxic than a variety of metals and nonsurfactant compounds (Whitton, 1967; Blanck *et al.*, 1984; Wängberg and Blanck, 1988). Huber *et al.*, (1987) reported that LAS was as toxic as atrazine but less toxic than PCP to three species of macrophytes. In the same study, LAS was less toxic than atrazine and PCP were to two freshwater algae.

STIMULATION

Algal stimulation has been observed at surfactant concentrations usually greater than 2.0 mg/liter (Palmer and Maloney, 1955; Matulova, 1964; Hicks and Neuhold, 1966; Camp, 1974; Nyberg, 1976; 1988; Karpínska-Smulikowska, 1984; Lewis *et al.*, 1986; Chawla *et al.*, 1986). Growth, photosynthesis, biomass, and chlorophyll *a* of natural algal communities and various single species such as *Nitzschia holsatica*, *Chlamydomonas gelatinosa*, and *Scenedesmus quadricauda* have been increased after exposure to various anionic and nonionic surfactants. For example, Matulova, (1964) found 10 and 30 mg/liter of an anionic compound to be stimulatory (approximately 36 to 250% above control) to *Chlamydomonas gelatinosa* after 21 days exposure. Nyberg, (1988) reported that some nonionic nonylphenol ethoxylates at concentrations exceeding 100 mg/liter stimulated the growth of *S. capricornutum*. In contrast to these relatively high stimulatory effect levels, Kutt and Martin, (1974) reported that 0.003 mg/liter nonionic and cationic surfactant stimulated the growth of *G. breve*.

MODE OF TOXICITY

The different effect levels reported for algae and surfactants are due in part to differences in algal physiology. The toxicity mode of surfactants on algae has been reported and discussed in detail by, among others, Hicks and Neuhold, (1966); Nyberg, (1976, 1985, 1988); Ernst *et al.*, (1983); Roederer, (1987); Chawla *et al.*, (1986, 1987, 1988). Generally, surfactants have been observed to denature and bind protein in the cell wall and consequently alter membrane permeability to nutrients and chemicals. Algal cell walls differ in algal species and cell wall thickness and chemical composition influence the severity of the effects. The thicker the cell wall the less likely the impact. High lipid and protein content in the cell wall allows penetration of hydrophobic surfactants. Charged surfactants (anionic and cationic) have been reported to have a greater denaturing effect than neutral compounds (Nyberg, 1976) and it has been reported that the toxic dosage of surfactants is inversely proportional to their ability to reduce surface tension (Bock, 1965).

DISCUSSION

Generalizations

Few generalizations can be made concerning the toxicity of surfactants to algae as reported in the literature. Experimental variables such as the surfactant type, test species, and effect parameters used in the studies have varied considerably. In addition, analytical verification of the exposure concentrations did not usually occur, primarily due to the lack of precise analytical methods such as those recently reported by Osburn, (1982, 1986); Simms *et al.*, (1988); and Ventura *et al.*, (1989). Overall, differences in experimental approach have resulted in part in the wide range of reported effect levels for algae, 0.003 to 17,784 mg/liter. This range of toxic effects encompasses those reported for surfactants and fish, 0.4 to 40.0 mg/liter (Abel, 1974), and for vertebrates and invertebrates, 0.1 mg/liter (Sivak *et al.*, 1982) and 0.005 to 50.0 mg/liter (Lewis, 1990).

Despite the lack of consistency in the experimental approach and wide range of toxicity a few trends are evident. First, the current scientific understanding of the effects of commercially important surfactants on laboratory cultured algae is based largely on the results for a few freshwater species. Second, the toxicity of most surfactants is less when determined for natural algal communities under natural conditions. Third, the toxicities of cationic surfactants are greater than those of the other surfactants and detergent builders on the basis of laboratory and field-derived toxicity results.

Risk Assessment

It is obvious that technically-based risk assessments are performed on a site-specific basis. Therefore, the following brief discussion of this subject provides only a generalized indication of the current exposure–toxicity relationship as reported in the literature.

The current scientific understanding of the levels of surfactants in the aquatic environment is largely limited to concentrations of the anionic LAS and the cationic DTDMAC in rivers receiving treated municipal effluent. Concentrations of these surfactants are listed in detail by Kimerle, (1989); and Lewis, (1990). Several examples of the reported levels in rivers indicate that LAS concentrations have ranged from 0.01 to 0.27 mg/liter (Games, 1983; Gilbert and Pettigrew, 1984; Nyberg, 1985). Kimerle (1989) reported that 85% of the reported LAS concentrations in the environment has been between 0.01 and 0.1 mg/liter. Levels of DTDMAC have ranged from 0.001 to 0.092 mg/liter in several U.S. rivers (Lewis and Wee, 1983) and 0.004 to 0.092 mg/

liter in the Rhine River basin (Kappeler, 1982). Concentrations of 0.01 to 1.0 mg/liter nonionic surfactant have been reported for U.K. rivers (A. D. Little Co., 1977) and 0.01 to 0.05 mg/liter in West German rivers (Nyberg, 1985).

Several of the reported effect concentrations for algae in Table 1 are less than some of the reported measured environmental levels suggesting a potential for impact. It should be noted, however, that the environmental relevance of single species tests with algae is questionable and the tests are considered to have a low predictive value relative to tests conducted under natural conditions (Macek *et al.*, 1978; Blanck *et al.*, 1984; Wängberg and Blanck, 1988). Consequently, results from field studies monitoring effects on natural communities are better indicators of environmental impact. The reported field-derived effect levels derived for the commercially important LAS, alkyl ethoxylates, and DTDMAC exceed the currently measured environmental levels indicating the unlikeliness of an effect of these important surfactants on freshwater algae, particularly phytoplankton. A similar conclusion for these and other commercially important surfactants and saltwater algal assemblages, would need to consider similar effect data which are either unavailable or unreported. It would be expected, however, that based on the comparable sensitivities of the freshwater and the few marine species used in the laboratory toxicity tests that the conservative nature of the laboratory test data for freshwater species and some surfactants would also apply to those surfactants and marine species. This would indicate the likelihood of safety in the marine environment. Nevertheless, this prediction does not diminish the need to conduct field toxicity studies with natural saltwater assemblages to validate this prediction.

Recommendations

Field studies with natural saltwater assemblages and, in some cases, with freshwater periphyton are needed to confirm the conservative nature of the laboratory-derived toxicity data reported to date for several surfactants and primarily natural phytoplankton communities. Priority should be given to determining those effects for cationic surfactants since other surfactants and detergent builders appear to be relatively nontoxic. The field-derived effect levels should be compared to accurate and current measurements of surfactants in the environment (freshwater and saltwater) which would reflect the annual increase in surfactant use and also the constant new formulations and reformulations of surfactants in existing detergent products. Of equal importance is the incorporation of more realistic experimental conditions and the utilization of several phylogenetically different test species in laboratory algal toxicity tests conducted in the future with surfactants. The realistic experimental conditions would include conducting the tests in river water (Shehata and Nawar, 1979; Chattopadhyay and Konar, 1985), utilizing mixtures (Nyberg, 1976; Tsai and McKee, 1978; Margaritis and Creese, 1979; Wong 1985; and Nyberg, 1985; Bressan and Brunetti, 1988), and studying the effects of environmental modifying factors on toxicity (Nyberg, 1976; 1985).

Finally, the laboratory-derived toxicity base for algae and many surfactants is more comprehensive than that for comparable surfactants and aquatic animal test species. Furthermore, the toxicity data base for natural algal communities is more substantial than that for natural aquatic animal communities. Therefore, other than the primary need for toxicity data for natural saltwater algal communities, the scientific focus concerning surfactant environmental safety should center on understanding the surfactant chronic toxicities on freshwater and saltwater animals which have been recently summarized (Lewis, 1990).

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