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Review

SURFACTANTS IN THE ENVIRONMENT

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Surfactants are a diverse group of chemicals that are best known for their wide use in detergents and other cleaning products. After use, residual surfactants are discharged into sewage systems or directly into surface waters, and most of them end up dispersed in different environmental compartments such as soil, water or sediment. The toxic effects of surfactants on various aquatic organisms are well known. In general, surfactants are present in the environment at levels below toxicity and in Croatia below the national limit. Most surfactants are readily biodegradable and their amount is greatly reduced with secondary treatment in wastewater treatment plants. The highest concern is the release of untreated wastewater or wastewater that has undergone primary treatment alone. The discharge of wastewater polluted with massive quantities of surfactants could have serious effects on the ecosystem. Future studies of surfactant toxicities and biodegradation are necessary to withdraw highly toxic and non-biodegradable compounds from commercial use and replace them with more environmentally friendly ones.

KEY WORDS: *biodegradation, detergents, surface-active agents, toxicity, wastewater*

Surfactants (surface-active agents) are a diverse group of chemicals consisting of a polar, water-soluble head group and a nonpolar hydrocarbon tail group, which is not as soluble in water (1). Surfactants are best known for their solubility and cleaning properties which secured them a place among detergents and other cleaning products. Massive quantities of surfactants are being used in households and industry every day, and most end up dispersed in different environmental compartments (soil, water, sediment). More than 4.2 million tonnes of detergent products and 1.2 million tonnes of softener products were used annually in Western Europe ten years ago (2). In the same period the world production of synthetic surfactants was 7.2 million tonnes (3). In 2006, worldwide production of surfactants rose to 12.5 million tonnes (4), and in 2007 over 3 million tonnes were produced in Western Europe alone (5). No doubt these figures will grow with ever growing detergent and cosmetics industry. After use, residual surfactants are discharged into sewage systems or directly into surface waters. They also accumulate in great quantities in wastewater treatment plants. Concentrations of surfactants or their degradation products vary in surface waters, sediments, and soils amended with sludge. For example, the concentrations/mass fractions of one of the most common surfactants, linear alkylbenzene sulphonic acid (LAS), reached up to 1.1 mg L^{-1} in sewage effluents (6) and up to 30.2 g kg^{-1} dry mass of treated sludge (7). Up to 0.4 mg L^{-1} of LAS was measured in surface waters (8). The elevated levels of surfactants in the environment can greatly affect the ecosystem; their toxicity to organisms from mammals to bacteria is well known. The aim of this review was to gather in one place information on all major classes and types of surfactants, their toxicity, behaviour, and fate in the environment.

CHEMISTRY OF SURFACTANTS

When dissolved in water at low concentrations, surfactant molecules exist as monomers (1). At higher concentrations, surfactant molecules aggregate

into micelles, reducing the system's free energy. The threshold concentration at which this occurs is known as the critical micelle concentration (CMC) (9). Nonionic surfactants have lower CMC levels than anionic and cationic surfactants (1). This fundamental ability to form micelles gives surfactants their detergency and solubilisation properties. At concentrations above CMC, surfactants solubilise more hydrophobic organic compounds than would dissolve in water alone. CMC also seems to define surfactant's antibacterial properties. Cella et al. (10) demonstrated that surfactants with lower CMC exhibited higher germicidal activity, whilst Lein and Perrin (11) reported increased protein binding ability with lower CMC. However, as surfactant concentrations in the environment are normally below CMC, this feature is probably not decisive for surfactant ecotoxicity.

Some commonly used surfactants are listed in Table 1, and their chemical structures are presented in Figure 1. Surfactants are generally classified as anionic, cationic, amphoteric, and nonionic, depending on the charge of their head group. The class of surfactant molecule describes its physicochemical properties and application.

Anionic surfactants

Anionics are historically the oldest and the most common type of surfactants. When we think of detergents or common soaps, it is the anionic surfactants that do the washing. The hydrophobic part of the molecule is usually an alkyl chain of various length, alkylphenyl ether or alkylbenzene, and the hydrophilic part is carboxyl, sulphate, sulphonate, or phosphate. Except as detergents, they have successfully been in biotechnological and other industrial processes, including cosmetics industry (12). Anionic surfactants are also used in pharmaceutical formulations to increase the efficiency of the active ingredients by direct binding to the drug (13) or by enhancing adsorption or absorption and the partition of drugs between hydrophobic and hydrophilic compartments in organs and organisms (14). They can also be used to remove petrochemical products from polluted soil. In one study anionic surfactants excelled in the removal of diesel oil adsorbed on various soils (15).

Cationic surfactants

The most common type of cationic surfactants are the quaternary ammonium compounds (QAC). These molecules contain at least one hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom, other alkyl groups such as methyl or benzyl groups acting as substituents. They are widely used in detergents, fabric softeners, and hair conditioners. Long chain QACs are also used as disinfectants due to their antibacterial activity against both Gram-negative and Gram-positive bacteria, as well as against some pathogenic species of fungi and protozoa (16). QACs, in general, are toxic to mammalian cells and are not recommended for systemic application (17), but are acceptable for topical application (mouthwash products, oral antiseptics). There are reports of damaging effects of cationic surfactants on human lymphocytes (18)

Table 1 *Names and abbreviations of the most common classes of surfactants.*

Common name	Abbreviation	Class
Linear alkylbenzene sulphonic acid	LAS	Anionic
Sodium dodecyl sulphate	SDS	
Alkyl sulphate	AS	
Sodium lauryl sulphate	SLS	
Alkyl ethoxysulphate	AES	
Quaternary ammonium compound	QAC	Cationic
Benzalkonium chloride	BAC	
Cetylpyridinium bromide	CPB	
Cetylpyridinium chloride	CPC	
Hexadecyltrimethylammonium bromide	HDTMA	
Amine oxide	AO	Amphoteric
Alkylphenol ethoxylate	APE	Nonionic
Alcohol ethoxylate	AE	
Fatty acid ethoxylate	FAE	

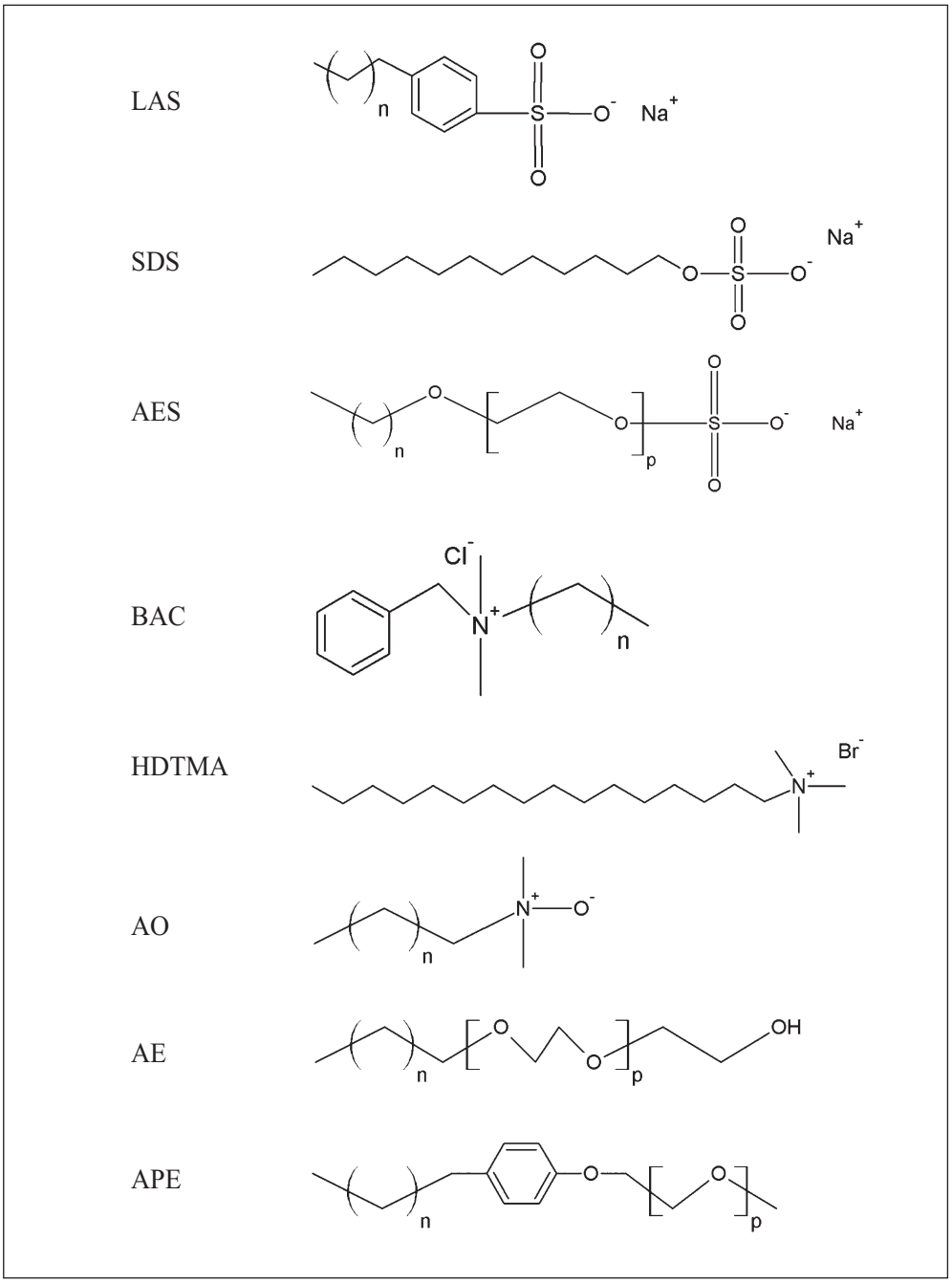

Figure 1 *Chemical structures of some common surfactants (for abbreviations see Table 1)*

and on rabbit corneal epithelial cells (19). These adverse effects are avoided by the use of so-called soft analogues of long chain QACs. These biologically active compounds are readily degraded into non-toxic and biologically inactive products *in vivo*, as well as in the environment. The concept of soft antibacterial agents was proposed over 20 years ago (20), and a number have been synthesised and tested both *in vitro* and *in vivo*. Thorstein et al. (17) synthesised a series of analogues of benzalkonium chloride (BAC) and cetylpyridinium chloride (CPC), which showed satisfactory antibacterial properties and were characterised by good chemical stability and ready non-enzymatic and enzymatic degradation to original, non-toxic building blocks.

Amphoteric surfactants

The behaviour of amphoteric surfactants is dependent on the pH. Their molecules are capable of changing charge from net cationic to anionic from low

to high pH, with zwitterionic behaviour at intermediate pH (21). As newcomers to industrial use, amphoteric surfactants have not been studied much. The best known and studied amphoteric surfactants are amine oxides (AOs). AOs are exothermic, second-order reaction products of tertiary amines and hydrogen peroxide (22). As a rule, AO precursor is a C_{12}-C_{18} alkyldimethyl amine (21) and the nature of tertiary amine may be aliphatic, aromatic, heterocyclic, or alicyclic. AOs were firstly used as substituents for the traditional fatty alkanolamides as foam boosters in dishwashing as their favourable weight/effect ratio offsets its high production cost in this application (23). AOs are also used in textile industry as anti-static agents, in rubber industry as foam stabilisers and polymerisation catalysts, and in deodorant bars as anti-bacterial agents (21). They are skin-compatible and usually used with other surfactants. Due to zwitterionic nature, they are compatible with anionic surfactants and can in fact produce a synergistic effect in such formulations (24). AOs demonstrate low to moderate toxicity; they are non-volatile and easily removed by conventional sewage treatment, and have low potential for bioaccumulation in tissues of terrestrial organisms (24).

Nonionic surfactants

Surface activity of nonionic surfactants derives from a balance between hydrophobic and hydrophilic structures contained in the surfactant molecule. They do not dissociate into ions in the water solution, so the solubility of these substances is provided by their polar head groups. The hydrophobic part of nonionic surfactants is generally an alkylated phenol derivative, fatty acid, or long-chain linear alcohol. The hydrophilic part is generally an ethylene oxide chain of various lengths. With their lack of charge, nonionic surfactants are compatible with both cationic and anionic surfactants. Nonionic surfactants are widely used as emulsifiers, wetting agents, and foam stabilisation agents. They are also successfully used in various biotechnological processes, and to facilitate solubilisation and increase drug carrier stability (25). Nonionic surfactants make part of most pesticide formulations (26). They enhance pesticide performance and pesticides promote or inhibit the photolytic degradation of nonionics (27). As surfactants get in contact with plant species through pesticides, their toxicity has been observed in tobacco (*Nicotiana tabacum*), sugar beet (*Beta vulgaris*), and spiderwort (*Tradescantia albiflora*) (28).

ECOTOXICITY OF SURFACTANTS

Surfactants show a marked biological activity. Anionic surfactants can bind to bioactive macromolecules such as peptides, enzymes, and DNA. Binding to proteins and peptides may change the folding of the polypeptide chain and the surface charge of a molecule. This may modify biological function (12). The primary target site of cationic surfactants is the cytoplasmic (inner) membrane of bacteria. QACs bind to inner membranes and disorganise them via their long alkyl chain (29). Nonionic surfactants exert antimicrobial activity by binding to various proteins and phospholipid membranes. Such binding increases the permeability of membranes and vesicles, causing leakage of low molecular mass compounds. This can result in cell death or damage through loss of ions or amino acids (25).

Concerns about ecotoxicity of surfactants arise from their tremendous exploitation in everyday life. A major proportion of surfactants is degraded in wastewater treatment plants, but some amount ends up in surface waters, soil, or sediment. There is also a concern about surfactant accumulation in the sewage sludge treatment (30). High concentrations of accumulated surfactants can inhibit sewage sludge microorganisms and compromise the way in which a wastewater treatment plant (WWTP) removes pollutants and breaks down sewage. Different types of surfactants have been detected in various levels in sewage effluents, WWTP effluents, surface waters, dry sludge, sludge-amended soils, or sediment (Table 2).

Excessive use of any type of surfactants and their disposal in the environment, especially in aquatic bodies, could seriously affect the ecosystem. For this reason, the amounts of anionic, non-ionic, and cationic surfactants released in sewage and aquatic recipient are monitored and regulated. Table 3 shows Croatian limits of hazardous and other agents in wastewater (31). In general, the concentrations of surfactants allowed in aquatic recipients are below the effective toxicity concentrations to aquatic organisms (Table 4). Dilution in surface waters should minimise toxic effects on aquatic organisms. Cationic surfactants are recognised as the greatest hazard, and their limits are the lowest. Figure 2 shows the toxic effects [half maximal effective concentration (EC_{50}), half maximal inhibitory concentration (IC_{50}), and lethal concentration (LC_{50})] of widely used surfactants in various aquatic species mentioned in this and Ying's review (1).

Table 2 *Levels of different types of surfactants detected in the environment.*

Surfactant	Location	Level	Reference
LAS	Sewage effluent	1090 mg L^{-1}	6
	Treated sludge	30200 mg kg^{-1}	7
	Surface water	0.416 mg L^{-1}	8
	Sediment	(0.01 to 20) mg kg^{-1}	96
AES	Wastewater	(0.24 to 2.85) mg L^{-1}	47
	WWTP effluent	(0.003 to 0.012) mg L^{-1}	47
QAC	Sewage effluent	0.062 mg L^{-1}	70
	Treated sludge	5870 mg kg^{-1}	97
	Sediment	(0.022 to 0.206) mg L^{-1}	98
BAC	Hospital effluent	6 mg L^{-1}	99
APE	Sewage effluent	0.332 mg L^{-1}	1
	Treated sludge	81 mg kg^{-1}	1
AE	WWTP effluent	(0.002 to 0.017) mg L^{-1}	100
		(0.001 to 0.023) mg L^{-1}	51
		(0.001 to 0.016) mg L^{-1}	51
		(0.004 to 0.007) mg L^{-1}	51

Table 3 *Maximum allowed concentrations (MAC) of surfactants in wastewater effluent which can be released in a natural aquatic recipient and sewage system in Croatia*

Class of surfactant	MAC / mg L^{-1}	
	Surface waters	Sewage system
Anionic surfactants	1.0	10.0
Nonionic surfactants	1.0	10.0
Cationic surfactants	0.2	2.0

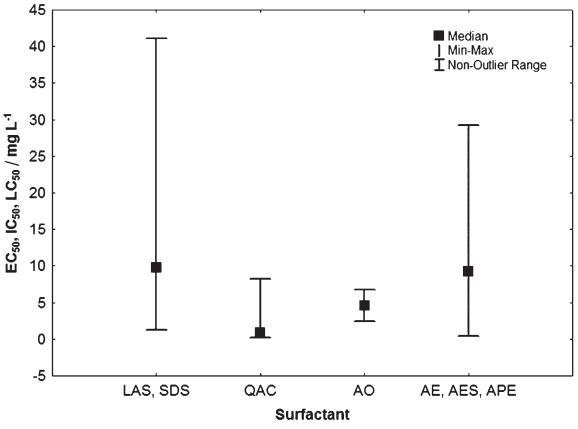

Figure 2 *Collective toxicity (EC_{50}, IC_{50} and LC_{50} in mg L^{-1}) of some widely used surfactants on various aquatic organisms (for abbreviations see Table 1). EC_{50} - half maximal effective concentration; IC_{50} - half maximal inhibitory concentration; LC_{50} - lethal concentration.*

Cationic QACs are the most toxic, but amphoteric AOs are also highly toxic. This class of surfactants has not been identified by Croatian legislation, and deserves the same attention and treatment as cationic surfactants. The amounts of surfactants allowed for release in the sewage system are higher than for aquatic recipients, because sewage is treated in plants and the concentrations of surfactants reduced. Over 90 % of LAS, alkyl sulphate (AS), alcohol ethoxylate (AE) and alcohol ethoxysulphate (AES) are removed with secondary treatment in WWTPs (32). However, primary treatment is not nearly as effective, and these surfactants are identified as toxicants in primary effluent (33).

The toxicity of surfactants to various organisms is well documented (Table 4). Most of the test organisms for surfactant toxicity are aquatic, and include algae, fish, or in a lesser degree bacteria.

Toxicity to bacteria

The data on surfactant toxicity to bacteria (Table 4) are not as abundant as for other aquatic organisms such as invertebrates or fish. Much research is conducted on the toxicity of cationic QACs due to their antimicrobial properties. QACs are widely used as disinfectants in healthcare preparation settings to decontaminate surfaces or disinfect the hands of hospital personnel and to treat patients colonised by *Staphylococcus aureus* (34). There is much concern

that intensive exploitation of these disinfectants may result in bacterial resistance to these agents (35, 36). Bacterial resistance to QACs is likely to occur when sub-lethal concentrations (37) or concentrations below the recommended by the manufacturer (34) are used. Other authors (38) have hypotesised that QACs can exhibit detrimental effect on wastewater treatment through biocidal effect on bacteria inhabiting the activated sludge, which can disorganize the fragile biological balance of such an environment. Amongst the bacterial consortium in effluents of sewage treatment plants receiving QACs, even the bacteria resistant to QAC could be found (39). Negative effects of QACs towards nitrifying bacteria that are required for successful wastewater treatment were found at concentrations of 2 mg L^{-1} (40).

In a study of anionic sodium dodecyl sulphate (SDS) toxicity to various taxa including different species of algae, crustaceans, echinoderms, and fish, the bacterium *Vibrio fischeri* proved to be the most sensitive (41). Tozum-Calgan and Atay-Guneyman (42) reported that both growth and nitrogen fixation of the cyanobacterium *Gloeocapsa* were inhibited in the presence of SDS. Sewage sludge isolates *Acinetobacter johnsonii* and *Oligotropha carboxidovorans* showed 50 % and 20 % viability during treatment with 0.2 mg L^{-1} and 2 mg L^{-1} of SDS, respectively (43). Nonionic Triton X-100 killed *Bacillus subtilis* (44), probably by interaction with the regulatory system which activates autolysis in bacterial cell (45).

Other types of surfactants such as amine oxides and betaines also act against a variety of microorganisms (46).

Toxicity to aquatic plants

Table 4 summarises the toxicity of surfactants to aquatic plants, mostly algae and shows great variability by the type of surfactant and species tested. The algae constitute the first trophic level and are the basic suppliers of oxygen in the water basin. They have been used in water quality assessments as *in-situ* biomonitors (47). The toxic effects of SDS on the duckweed *Lemna minor* depended on the concentration; at lower concentrations, SDS increased its growth rate and inhibited it markedly at higher concentrations (48). Utsunomiya et al. (49) studied the toxic effects of LAS and three QACs on unicellular green alga *Dunaliella sp*. The 24-hour median effective concentrations were 3.5 mg L^{-1} for LAS and 0.79 mg L^{-1}, 1.3 mg L^{-1}, and 18 mg L^{-1} for the three QACs, demonstrating intra-species response variability to the same type of surfactants. Oil dispersant mixtures of anionic and nonionic surfactants displayed toxic effect to brown algae (*Macrocystis pyrifera)* with IC_{50} ranging from 73.0 mg L^{-1} to 95.9 mg L^{-1} (50). Belanger et al. (51) conducted aquatic risk assessment of AE in North America and Europe and collected literature data on chronic toxicity of AE to organisms ranging from algae to fathead minnow. The effective concentrations at 10 % inhibition (EC_{10}) for AEs toxicity to multiple algae species varied from 0.030 mg L^{-1} to 9.791 mg L^{-1}. The authors concluded that the risk from exposure to AE was small, especially considering that exposure was based on undiluted WWTP effluents. With dilution this minimal risk would decline even more.

Toxicity to invertebrates

Invertebrates, especially the water flea, are the most common model organisms used for toxicity testing of chemicals. Warne and Schifko (32) studied acute toxicity of laundry detergent components and their contribution to detergent toxicity in a freshwater cladoceran *Ceriodaphnia dubia* (Table 4). The detergent components included surfactants, enzymes, builders, fabric brighteners, fillers, and colouring agents. The most toxic component was 17 thousand times more toxic than the least toxic component. Surfactants and sodium silicate were the main contributors to the toxicity of detergents. Petersson et al. (2) came to similar conclusions in a toxicity study of Swedish detergents and softener products in *Daphnia magna.* Forty-eight-hour EC_{50} values ranged from 4 mg L^{-1} to 85 mg L^{-1} for 25 detergents and from 15 mg L^{-1} to 166 mg L^{-1} for five softeners. Their toxicity to *D. magna* positively correlated with the concentrations of surfactants used in the product. Hennes-Morgan and Oude (52) found that toxicity ranges for LAS, AES, and alkyl sulphates in *D. magna* were broad and that they overlapped, with EC_{50} ranging roughly between 1 mg L^{-1} and 15 mg L^{-1}. Typical mean EC_{50} of Empicol®, AES-type of surfactant, in freshwater and marine organisms varied between 0.5 mg L^{-1} and 65 mg L^{-1} for algae, and LC_{50} ranged from 0.78 mg L^{-1} to 167.3 mg L^{-1} for invertebrates and from 0.8 mg L^{-1} to 250 mg L^{-1} for fish (Table 4) (47). In a study by Boeije et al. (53), EC_{50} for various non-ionic AEs and AE mixtures in *D. magna* ranged between 0.36 mg L^{-1} and 50.5 mg L^{-1}.

Toxicity to vertebrates

The toxic effects of surfactants to aquatic vertebrates, mostly fish, have also been documented

Table 4 *Toxicity of different types of surfactants against various organisms.*

Organism		Surfactant	Endpoint	Concentration / mg L^{-1}	Reference
Bacteria	*Vibrio fischeri*	SDS	EC_{50} - Luminescence 15 min	2.6	41
	Vibrio fischeri	LAS	EC_{50} - Luminescence 30 min	109.7	101
	Pseudomonas putida	LAS	EC_{50} - Growth inhibition 16 h	33.4	101
	Vibrio fischeri	QAC	EC_{50} - Luminescence 30 min	0.5	101
	Pseudomonas putida	QAC	EC_{50} - Growth inhibition 16 h	6.9	101
	Phosphobacterium phosphoreum	AO	EC_{50} - Luminescence 15 min	2.4	24
	Microcystis aeruginosa	AE	Estimated EC_{10} - Cell density	0.154	51
Algae	*Raphidocelis subcapitata*	SDS	IC_{50} - Cell density 72 h	36.58	102
	Dunaliella sp.	LAS	EC_{50} - 24 h	3.5	1
	Pseudokirchneriella subcapitata	AES	EC_{50} - Cell density 72 h	3.5	103
	Raphidocelis subcapitata	AES	IC_{50} - Cell density 72 h	2.18	102
	Dunaliella sp.	QAC	EC_{50} - 24 h	0.79	1
	Lemna minor	AE	Estimated EC_{10} - Frond count	0.101	51
	Navicula pelliculosa	AE	Estimated EC_{10} - Cell density	0.140	51
Crustaceans	*Artemia salina*	SDS	LC_{50} - Larvae mortality 24 h	41.04	102
	Ceriodaphnia dubia	LAS	EC_{50} - Immobilization 48 h	5.96	32
	Artemia franciscana	AES	LC_{50} - Nauplii mortality 72 h	23.92	47
	Daphnia magna	QAC	EC_{50} - Immobilization 24 h	0.38	24
	Daphnia magna	AO	EC_{50} - Immobilization 48 h	6.8	24
	Ceriodaphnia dubia	AE	EC_{50} - Immobilization 48 h	0.39	32
Gastropod	*Physa acuta*	SDS	LC_{50} - Mortality 24 h	27.2	102
Sea urchin	*Paracentrotus lividus*	SDS	EC_{50} - Fertilization rate	3.2	41
Fish	*Carassius auratus*	LAS	EC_{50} - Immobilization 48 h	5.1	1
	Gammbusia affinis	SDS	EC_{50} - Immobilization 48 h	40.15	1
	Salmo gairdneri	AES	EC_{50} - Immobilization 48 h	10.84	1
	Salmo gairdneri	QAC	EC_{50} - Immobilization 48 h	1.21	1
	Pimephales promelas	AE	NOEC - Survival	4.35	51
Amphibian	*Xenopus laevis*	AES	LC_{50} - 72 h	6750	47

in literature (Table 4). A stream mesocosm study (54) demonstrated that fish and invertebrates were the most responsive to the effects of AE. Fathead minnows were particularly sensitive to AE, with no-observed effect concentration (NOEC) of 0.73 mg L^{-1} for egg production and larval survival. Bluegills were less sensitive with a NOEC for survival and growth of 5.7 mg L^{-1} (54). Nonionic AEs and nonylphenol ethoxylates exhibited acute toxic effects in tadpoles of four Australian and two exotic frogs (55). EC_{50} values ranged between 1.1 mg L^{-1} (mild narcosis) and 12.1 mg L^{-1} (full narcosis) for nonylphenol ethoxylates and between 5.3 mg L^{-1} (mild narcosis) and 25.4 mg L^{-1} (full narcosis) for AEs.

Anionic SDS showed toxic effects in juvenile sea bass (*Dicentrarchus labrax*) (41), with mean EC_{50} of 7.34 mg L^{-1}. The sensitivity of the sea bass was comparable to that of *Tigriopus fulvus* nauplii, and was lower than in marine bacteria, microalgae, or sea urchin.

Another anionic surfactant, dodecylbenzene sodium sulphonate lowered the lipid moieties in the

goblet mucous cells, epithelial cells, and club cells in *Rita rita* catfish. High concentrations of this surfactant also modified fish behaviour (erratic movements, muscle spasms, and body torsion) (12).

Fish seem to take up anionic LAS through gills (56). The concentrations of a few LAS homologues in the liver and internal organs of juvenile rainbow trout increased rapidly, which suggests that they quickly enter systemic circulation. In less perfused tissues, the increase in LAS concentrations was relatively slower. Ferreira-Leach and Hill (57) showed that high amounts of APE can accumulate in a variety of rainbow trout tissues. The study suggested that the APE can rapidly metabolise in fish. The degradation products of APE are octylphenols and nonylphenols and octylphenol residue concentrations were elevated in the bile, faeces, pyloric caeca, liver, and intestine (57). These biodegradation products have attracted a lot of scientific attention because of their oestrogenic effects and the ability to accumulate in aquatic organisms. Octylphenols and nonylphenols can induce vitellogenin production in male fish. Normally, this protein is produced by sexually mature females under the influence of estrogens (58). In this way, octylphenols and nonylphenols can disrupt normal functioning of the fish endocrine system.

Table 5 *Toxicity of sodium dodecyl sulphate (SDS), hexadecyltrimethyl ammonium bromide (HDTMA), cetylpyridinium chloride (CPC) and dodecylpyridinium chloride (DPC) against bacterium* Acinetobacter junii *and yeast* Saccharomyces cerevisiae

Surfactant	EC_{50} / mol L^{-1}	
	A. junii	***S. cerevisiae***
SDS	$5.0x10^{-6}$	$3.0x10^{-4}$
HDTMA	$3.3x10^{-7}$	$4.3x10^{-5}$
CPC	$4.9x10^{-7}$	$3.2x10^{-7}$
DPC	$1.4x10^{-6}$	$6.4x10^{-6}$

EC_{50} - half maximal effective concentration

Toxicity to terrestrial plants

Significant amounts of surfactants can enter soil through sewage sludge increasingly applied as fertilizer. Surfactants are also present in agrochemicals, as they ensure shelf-life stability to agrochemical formulations, bind granules, and disperse, solubilise and wet or emulsify active ingredients.

The toxicity of nonionic surfactants to terrestrial plants was recognised some time ago (59) in a study on the effects of two commercial products (Aqua Gro and Soil-Penetrant) on various plant species (barley, common ryegrass, creeping bentgrass, bluegrass, tall rescue, and common bermuda). Both products were more toxic to plants in solution than in the soil, perhaps because soil adsorption reduced its toxicity. A similar study on the effects of nonionic surfactants on the growth and porosity of barley roots (60) also demonstrated that adsorption of surfactants by soil reduced its toxicity to roots. Moreover, in a water repellent soil, root growth on day 28 was greatly enhanced with an addition of 5000 mg of surfactant per kilogram of soil. In contrast, roots grown in a solution displayed marked sensitivity to surfactant concentrations from 40 mg L^{-1} to 100 mg L^{-1}. Their growth slowed down and the processes in meristematic cells of root tips were inhibited.

Gunther and Pestemer (61) investigated the toxicity of LAS on oat (*Avena sativa*), turnip (*Brassica rapa*), and mustard (*Sinapis alba*) in a sandy loam. Fourteen-day EC_{50} values were similar for all the species, with the lowest EC_{50} of 50 mg kg^{-1} of soil determined for oats. Ying (1) evaluated available terrestrial toxicity data and found that LAS were not highly toxic to terrestrial organisms.

Sorption of surfactants

Sorption on soil or sediment can reduce the toxicity of surfactants in the environment. Traina et al. (62) found that dissolved humic substances reduced the aqueous bioavailability of LAS. Cano et al. (63) found that organic carbon in sediments reduced the toxicity of alkyl-benzene sulphonate (ABS) to *Hyalella azteca*. Adsorption onto insensitive organisms, dead cells in flocs, and inorganic matter in WWTPs could protect susceptible bacteria from the toxic effect of surfactants. This is especially important for cationic surfactants that could act as biocides and have a strong affinity for negatively charged surfaces of particulates in sewage sludge (64). Sorption data can be used to estimate the distribution of a surfactant in different environmental compartments or to estimate its bioavailability. In addition, sorption significantly affects biodegradation of a surfactant (1).

MECHANISM OF TOXICITY

Studies indicate that the toxicity of a single surfactant is highly specific, not only for the type and class of surfactant, but also for the organism tested. Any generalisation or application to similar organisms is highly speculative. Several studies

reported inter-species and intra-species variability in surfactant toxicity. The EC_{50} of anionic AES for *D. magna* varied between 4.2 mg L^{-1} and 72 mg L^{-1} and its LC_{50} for the crustacean *Artemia franciscana* between 19.59 mg L^{-1} and 28.26 mg L^{-1} (47). The same authors observed inter-species variability between algae; EC_{50} varied between 4.86 mg L^{-1} for *Dunaliella salina* and 24.02 mg L^{-1} for *Isochrysis galbana*. The sensitivity of crustaceans to SDS also varied highly; LC_{50} was 9.8 mg L^{-1} for blue crab (*Callinectes sapidus*), 34 mg L^{-1} for grass shrimp, and 48 mg L^{-1} for mysids (65). When the toxicity of one anionic and three cationic QAC-based surfactants to phosphate-accumulating bacterium *Acinetobacter junii* and yeast *Saccharomyces cerevisiae* was investigated (66, 67), the EC_{50} values of different QACs to the same organism differed up to tenfold (*A. junii*) and hundredfold (*S. cerevisiae*). In the study (67) dodecylpyridinium chloride with 12 C atoms in the alkyl chain was less toxic than cetylpyridinium chloride with 16 C atoms in the alkyl chain. The link between the length of the hydrophobic alkyl chain length and the toxicity of pyridinium chlorides to fungi had already been observed before (68). Compounds with a C_6 group exhibited the least toxicity while compounds with a C_{14} group were the most toxic. Beyond this point, *i.e.* with alkyl groups containing 16 and 18 C atoms, the toxicity to the fungi slightly decreased. The same trend was observed for AOs; a pronounced anti-microbial activity increased with chain length, and it peaked with the chain length of approximately C_{14} (39). Garcia et al. (24) showed that the toxicity of AO to daphnia increased with the alkyl chain length. In a study by Verge et al. (69) on toxicity of LAS to *Daphnia magna* both LC_1 and LC_{50} values were lower when LAS with longer alkyl chain were used. Probable reason for toxicity increase with homologue chain length was a greater interaction of the heavier homologues with cell membranes.

A quantitative structure-activity relationship (QSAR) study by Versteeg et al. (70) investigated how structural components of surfactant molecules contribute to toxicity towards rotifer, *Brachionus calyciflorus.* Results demonstrated a relationship between alkyl chain length and toxicity within a surfactant class. Between classes, N-containing amines and quaternary ammonium compounds had greatest toxicity, followed by the nonionic compounds and anionic compounds being the typically least toxic. Calculations suggest that the toxicity of surfactants increases with the length of the alkyl chain within a surfactant class. Hydrophobic interaction forces were also recognised as a factor in surfactant toxicity. QSARs are mathematical relationships between molecular structure descriptors and ecotoxicological effects of these structures (53) and are used to predict physico-chemical properties and toxicity of chemicals in the absence of experimental data. For example, mathematical models for nonionic surfactants use molecule structure parameters such as the length of the alkyl chain or the number of ethoxylated (EO) groups. A study by Boeije et al. (53) on the ecotoxicity of AE mixtures based on substance-specific toxic predictions showed a clear relation between hydrophobicity and ecotoxicity of nonionic AE.

Painter (71) noted that the toxicity of AES with a chain length of less than 16 C atoms tended to decrease with the increasing number of EO groups. Warne et al. (33) found that AE containing eight EO groups was notably more toxic than the AE containing three EO groups. However, Feijtal and Van de Plassche (72) stated that there was no relationship between the carbon chain length or the number of EO groups and acute, subchronic, or chronic toxicity of AE surfactants. Garcia et al. (73) showed that the substitution of a benzyl group for a methyl group increased QAC toxicity to *D. magna* and *Photobacterium phosphoreum*, but did not observe growing toxicity with longer chains. The reason may be lower bioavailability of homologues with the longest chains, as they have lower solubility.

Data linking chemical structure and toxicity are valuable in elucidating how surfactants affect aquatic and other organisms. Knowing which physicochemical properties of a surfactant influence its toxicity could point to surfactants with minimal biological effects. Synthesis of new surfactants could also be guided by these findings. Another property that could help to minimise adverse environmental effects of surfactants is their biodegradability.

BIODEGRADATION OF SURFACTANTS

In the environment, surfactants are primarily degraded through microbial activity, and in sewage treatment plants. Biodegradation mostly depends on surfactant's chemical structure and physicochemical conditions of its environmental medium. Quiroga et al. (74) found that salinity hardly affected decomposition of sodium dodecylbenzene sulphonate in seawater, but that higher temperature increased the degradation

rate. The presence of sediment also enhanced the biodegradaton rate, probably because sediments accumulate both surfactants and bacteria. A study on biodegradation of AS surfactants in water sediments (12) suggests that surfactants adsorb onto the river sediment and stimulate bacteria to attach to them. Primary degradation rate of APE also increased with temperature; 68 % of surfactant was biodegraded at 7 °C and 96 % at 25 °C (75). Light was found to slow down biodegradation of APEs (76).

LAS

Most surfactants are degraded by microbes in the environment. Anionic LAS is degraded by aerobic organisms, which form biofilms (1). However, sewage treatment plants do not completely remove LAS (6), as it may persist under anaerobic conditions (1). LAS is biodegraded through omega-oxidation of the terminal carbon in the alkyl chain, followed by beta-oxidation (77). The resulting mono- and dicarboxyilic sulphophenyl acids are further desulphonated and the aromatic ring cleaved. Omega-oxidation of the alkyl chain and the cleavage of the benzene ring require molecular oxygen. This is why degradation through this pathway is unlikely under anaerobic conditions (78). In a study by Jensen (79), LAS mass fraction in aerobically treated sludge was 100 mg kg^{-1} to 500 mg kg^{-1} dry mass and in anaerobically treated sludge 5 g kg^{-1} to 15 g kg^{-1} dry mass.

Normally, a consortium of several bacterial strains is needed to degrade LAS under aerobic conditions (80). Single bacteria usually have limited ability to degrade the alkyl and cannot cleave the sulphonated aromatic ring of LAS (81). Sigoliot and Nguyen (82) isolated 35 bacterial strains from seawater capable of complete oxidation of LAS. All of the isolates were heterotrophic, strictly aerobic gram-negative bacteria of genera *Alcaligenes*, *Deleya*, *Oceanospirillum*, *Aquaspirillum*, and *Pseudomonas*. The *Oceanospirillum* strains turned out to be absolutely necessary for terminal oxidation of the alkyl chain and its shortening by beta-oxidation. The *Pseudomonas* strains utilised the end-metabolism products of the *Oceanospirillum* and induced aromatic ring cleavage. Benzene ring cleavage is the key step in the mineralisation of LAS, but strains capable of inducing this cleavage exhibited very specific enzymatic activities on a limited number of substrates and were unable to degrade LAS. Abboud et al. (83) found that a consortium of *Acinetobacter calcoaceticus* and *Pantoea agglomerans* can efficiently biodegrade both LAS and AS anionic surfactants. Biodegradation seems to involve cleaving of sulphate ester bonds by enzymes to yield inorganic sulphate and fatty alcohol.

QAC

Cationic surfactants are biologically biodegradable under aerobic conditions at variable rates. In studies of *in situ* soil modification using cationic surfactants, some organisms were able to utilise QACs as a sole carbon and energy source (84).

The degradation pathway for alkyl trimethyl ammonium and alkyl dimethyl ammonium halides is believed to begin with N-dealkylation, followed by N-demethylation (85). The physicochemical properties of QACs can have a decisive role in biodegradation of these compounds in the environment. For example, biodegradability under aerobic conditions generally decreases with the number of non-methyl alkyl groups (1). Substitution of a methyl group with a benzyl group can further decrease QAC biodegradability (73). Thanks to research, non-biodegradable ditallow dimethyl ammonium chloride (DTDMAC), a major cationic surfactant used in fabric softeners for over 30 years, has been replaced with readily biodegradable diethylester dimethyl ammonium chloride (DEEDMAC) (1), which has two ester links between the ethyl and tallow chains. DEEDMAC has confirmed its biodegradability in standard laboratory tests and in environmental media such as sludge, raw sewage, soil, and river water (86). This is a good example how to put laboratory biodegradation studies to use in every day life.

AO

AO surfactants are readily biodegradable under aerobic and anaerobic conditions (21). Garcia et al. (24) tested the biodegradability of C_{12}-AO, C_{14}-AO, and cocoamido-AO in aerobic and anaerobic conditions. The tested surfactants proved readily biodegradable and easily mineralised in aerobic aquatic environments. Under anaerobic conditions cocoamido-AO was readily biodegradable even at levels as high as 80 mg g^{-1} of dry sludge, whereas other AOs exhibited neglible biotransformation in anaerobic digesters.

Two possibilities are considered for the initial enzymatic attack of fatty amine oxides: already mentioned omega-oxidation of terminal carbon, which requires molecular oxygen, or fission of the C-N bond, mechanism already spotted in QACs and

dodecyldimethylamine. The latter is considered as a general mechanism to gain access to the alkyl chain (24).

APE, AE, and AES

Generally, nonionic surfactants are readily biodegradable under aerobic conditions. APE degradation, however, is limited under anaerobic conditions. In anaerobically digested sludge, the mass fractions of APE were between 900 mg kg^{-1} and 1100 mg kg^{-1} and in aerobically digested sludge 0.3 mg kg^{-1} (87). The biodegradation of APE starts with shortening of the EO chain, followed by oxidation of the resulting short chain, which mainly yields alkylphenoxy ethoxy acetic acid and alkylphenoxy acetic acid. Oxidation of the EO chain and co-oxidation of the alkyl chain have been proposed as the alternative pathways for degradation of AEs (88). The primary pathway of aerobic biodegradation is believed to start with central fission of the AE molecule (the cleaving of the ether bond between alkyl and ethoxy chains) leading to the formation of free fatty alcohol (FFA) and polyethylene glycol (PEG) (89). The same initial breakdown occurs with anionic AES, producing fatty alcohol, ethoxylated alcohol, or ethylene glycol sulphate of various lengths (47). The initial cleaving of the ether bond is followed by omega- or beta-oxidation of the terminal carbon of the alkyl chain, and by hydrolytic shortening of the terminal carbon of the polyethoxylic chain in AE (90). In AES it is followed by stepwise oxidation, cleaving of two carbon units, and desulphation (47). However, the primary attack on the ether bond is very unlikely with anaerobic bacteria. Anaerobic biodegradation of AE starts with the cleaving of the terminal EO unit, releasing acetaldehyde stepwise, and shortening of the ethoxy chain until the lipophilic moiety is obtained (91).

RISK ASSESSMENTS

Risk assessment studies gather fate, exposure, and effects data for certain surfactants in order to asses the risk they pose to environment or human health. We do not intend to go into the intricacies of risk assessment methodology in this text, but will show available risk assessment results for major groups of surfactants from Human & Environmental Risk Assessment on Ingredients of Household Cleaning Products (HERA project) (92) and other literature.

LAS, AES, AS and AE

The HERA report concluded that the ecotoxicological parameters for LAS have been sufficiently characterised, and that the ecological risk of LAS is low. The same was reported for AES; there is - no cause for concern for any of the environmental compartments; for AS the same; and judging by the analysis of surface water, sediment, sewage treatment facilities, and soil for AE, - there is no cause for concern in the European Union. The predicted environmental concentrations (PEC) for LAS, AES, and AE are about 50 to 100 times lower than the predicted no-effect concentrations (PNEC), and the risks for the aquatic compartment are low (93). Belanger et al. (51) found low levels of risk for AE in the aquatic environments of Europe and North America. According to a risk assessment for LAS in sludge-amended soils (92), current LAS use does not pose a risk to terrestrial organisms such as plants and invertebrates.

QAC

Risk assessment data for QACs are limited. In 2006, Grillitsch et al. (94) screened a wide array of Austrian surface waters and wastewater effluents for BAC and dialkyldimethylammonium chlorides with different alkyl chain lengths. Their ecotoxicological characterisation was based on microbiotests for a set of representative aquatic organisms and a literature review. They could not exclude the risk posed by QAC to sensitive aquatic organisms. They warned that the database available for QAC environmental risk assessment was still fragmentary and revealed considerable deficiencies in the reproducibility of results reported in literature (95).

CONCLUSIONS

Elevated concentrations of surfactants and their degradation products may affect organisms in the environment. However, further toxicity studies of LAS, AES, AS, or AE types of surfactants are probably not necessary. Although these surfactants seem to be mostly toxic to aquatic organisms, their levels in the environment are below toxic. In addition, there is more than one risk assessment study that finds these compounds as “low risk level” or of “no concern” for the environment. More effort should be made to elucidate the toxic effects of QAC and

AO types of surfactants. These compounds can be highly toxic to some aquatic organisms, but the their ecotoxicity profile is still incomplete. More data could help to produce a trustworthy risk assessment for for these two types. More information is also needed about the APE type of surfactants, because of their biodegradation products octylphenols and nonylphenols, which act as oestrogen in fish and accumulate in aquatic organisms.

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Sažetak

SURFAKTANTI U OKOLIŠU

Surfaktanti ili površinski aktivne tvari raznolika su skupina molekula najpoznatijih po uporabi u sastavu deterdženata i ostalih sredstava za pranje i čišćenje. Nakon uporabe u kućanstvu ili industriji, surfaktanti se ispuštaju u kanalizacijski sustav ili izravno u površinske vode te većina surfaktanata završi raspršena u vodi, sedimentu ili tlu. Toksični utjecaj surfaktanata na vodne organizme dobro je istražen i opisan u literaturi. U većini slučajeva surfaktanti su u okolišu prisutni u koncentracijama nižim od toksične te nižim od maksimalne koncentracije dopuštene hrvatskim zakonskim odredbama. Većina surfaktanata klasificirana je kao biološki razgradiva i njihova se koncentracija znatno smanjuje biološkom obradom otpadne vode pa je najveći rizik za okoliš ispuštanje prethodno pročišćene ili nepročišćene otpadne vode. Takva otpadna voda opterećena visokim koncentracijama surfaktanata može nepovoljno utjecati na okoliš. Potrebno je proučavati toksičnost i biološku razgradnju surfaktanata u svrhu uklanjanja visoko štetnih i biološki nerazgradljivih surfaktanata iz komercijalne uporabe te njihovu zamjenu tvarima manje štetnim za okoliš.

KLJUČNE RIJEČI: *biodegradacija, deterdženti, otpadne vode, površinski aktivne tvari, toksičnost*

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