Available online at www.sciencedirect.com

SCIENCE DIRECT®

Environment International 32 (2006) 417 – 431

ENVIRONMENT INTERNATIONAL

www.elsevier.com/locate/envint

Review article

Fate, behavior and effects of surfactants and their degradation products in the environment

Guang-Guo Ying *

CSIRO Land and Water, Adelaide Laboratory, PMB 2, Glen Osmond, SA 5064, Australia

Received 20 January 2005; accepted 26 July 2005

Abstract

Surfactants are widely used in household and industrial products. After use, surfactants as well as their products are mainly discharged into sewage treatment plants and then dispersed into the environment through effluent discharge into surface waters and sludge disposal on lands. Surfactants have different behavior and fate in the environment. Nonionic and cationic surfactants had much higher sorption on soil and sediment than anionic surfactants such as LAS. Most surfactants can be degraded by microbes in the environment although some surfactants such as LAS and DTDMAC as well as alkylphenols may be persistent under anaerobic conditions. LAS were found to degrade in sludge amended soils with a half-lives of 7 to 33 days. Most surfactants are not acutely toxic to organisms at environmental concentrations and aquatic chronic toxicity of surfactants occurred at concentrations usually greater than 0.1 mg/L. However, alkylphenols have shown to be capable of inducing the production of vitellogenin in male fish at a concentration as low as 5 μg/L. More toxicity data are needed to assess the effects on terrestrial organisms such as plants.

Keywords: Surfactants; Behavior; Biodegradation; Toxicity; Water; Soil; Sediment

---

Contents

---

* Fax: +61 8 83038565.
E-mail address: guang-guo.ying@csiro.au.

0160-4120/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envint.2005.07.004

1. Introduction

Surfactants are a diverse group of chemicals that are designed to have cleaning or solubilisation properties. They generally consist of a polar head group (either charged or uncharged), which is well solvated in water, and a nonpolar hydrocarbon tail, which is not easily dissolved in water. Hence, surfactants combine hydrophobic and hydrophilic properties in one molecule. Synthetic surfactants are economically important chemicals. They are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper industries. The world production of synthetic surfactants amounts to 7.2 million tons annually (Di Corcia, 1998).

Surfactants consisted mainly of three types: anionic, nonionic and cationic (Table 1). Linear alkylbenzene sulphonates (LAS), alkyl ethoxy sulphates (AES), alkyl sulphates (AS), alkylphenol ethoxylates (APE), alkyl ethoxylates (AE), and quaternary ammonium compounds (QAC) are the commonly used commercial surfactants. Especially, LAS, APE, and QAC are the most extensively studied surfactants. In the following, we use abbreviations for each class of surfactants, for example, C12EO9 (EO = ethylene oxide unit) having nine EO units and an alkyl chain of 12 carbon atoms, C14LAS having an alkyl chain of 14 carbon atoms, NPE9 or NPEO9 for nonylphenol ethoxylates with 9 EO units.

Table 1
Acronyms of the most widely used surfactants

Class	Common name	Acronym
Anionic surfactants	Linear alkyl benzene sulphonates	LAS
	Secondary alkane sulphonates	SAS
	Alcohol ether sulphates (Alkyl ethoxy sulphates)	AES
	Alcohol sulphates (Alkyl sulphates)	AS
Nonionic surfactants	Alkylphenol ethoxylates	APE (or APEO)
	Nonyl phenol ethoxylates	NPE (or NPEO)
	Octyl phenol ethoxyales	OPE (or OPEO)
	Alcohol ethoxyaltes	AE (or AEO)
Cationic surfactants	Quaternary ammonium-based compounds	QAC
	Alkyl trimethyl ammonium halides	TMAC
	Alkyl dimethyl ammonium halides	DMAC
	Alkyl benzyl dimethyl ammonium halides	BDMAC
	Dialkyl dimethyl ammonium halides	DADMAC
	Dihydrogenated tallow dimethyl ammonium chloride	DHTDMAC or DTDMAC
	Ditallow trimethyl ammonium chloride	DTTMAC
	Diethyl ester dimethyl ammonium chloride	DEEDMAC

Linear alkylbenzene sulphonates (LAS) are the most popularly used synthetic anionic surfactants. It has been extensively used for over 30 years with an estimated global consumption of 2.8 million tons in 1998 (Verge et al., 2000). Commercially available products are very complex mixtures containing homologues with alkyl chains ranging from 10 to 14 carbon units (C10–C14LAS). Furthermore, since the phenyl group may be attached to any internal carbon atom of the alkyl chain, each homologue contains 5–7 positional isomers.

Alkylphenol ethoxylates (APE) constitute a large portion of the nonionic surfactant market. The worldwide production of APEs was estimated at 500,000 tons in 1997 with 80% of nonylphenol ethoxylates (NPE) and 20% of octylphenol ethoxyalyes (OPE) (Renner, 1997). Concern has increased recently about the wide usage of APE because of their relatively stable biodegradation products nonylphenol (NP) and octylphenol (OP). NP and OP have been demonstrated to be toxic to both marine and freshwater species (Comber et al., 1993; McLeese et al., 1981), and to induce estrogenic responses in fish (Jobling and Sumpter, 1993; Purdom et al., 1994).

Quaternary ammonium-based surfactants (QAC) are molecules with at least one hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom, the other alkyl groups being mostly short-chain substituents such as methyl or benzyl groups. The major uses of this group of cationic surfactants are as fabric softeners and antiseptic agents in laundry detergents as well as other industrial uses. The most widely used active ingredient in fabric softeners has been dihydrogenated tallow dimethyl ammonium chloride (DTDMAC) until recently. However, the replacement of DTDMAC by ester cationic surfactants such as diethyl ester dimethyl ammonium chloride (DEEDMAC) has recently begun in Europe (Giolando et al., 1995).

After use, residual surfactants and their degradation products are discharged to sewage treatment plants or directly to surface waters, then dispersed into different environmental compartments. Due to their widespread use and high consumption, surfactants and their degradation products have been detected at various concentrations in surface waters, sediments and sludge-amended soils. In order to assess their environmental risks, we need to understand the distribution, behavior, fate and biological effects of these surfactants in the environment. There have been some detailed research papers and review articles on the occurrence of various surfactants and their degradation products in the environment (e.g., Fendinger et al., 1995;

Table 2
Octanol/water partition coefficients (K_{ow}) and critical micelle concentrations (CMC) of surfactants[a]

Compound	Log K_{ow}	CMC (mM) (distilled water)
C12LAS	1.96	1.1
C13LAS	2.54	0.46
C12SO4	1.60	8.2
C14SO4	Na[b]	2.1
C16SO4	Na	0.52
C12EO3SO4	Na	2.8
C12EO5SO4	Na	1.9
NPEO10	Na	0.094[c]
NPEO12	Na	0.057[d]
NPEO15	Na	0.114[c]
NPEO30	Na	0.206[c]
OPEO9-10	Na	0.24[e]
C14EO7	2.47	0.0095
C12EO4	Na	0.064
C12EO8	Na	0.11
C12EO16	Na	0.25
C18DMAC	2.69	0.0046
C18TMAC	Na	0.4
C16TMAC	1.81	1.6
C12TMAC	Na	20
C8TMAC	Na	220

[a] Adapted from Tolls and Sijm (1995).
[b] Not available.
[c] Kibbey and Hayes (2000).
[d] Brix et al. (2001).
[e] Adeel and Luthy (1995).

Holt et al., 1995; Ahel et al., 1996, 2000; Jensen, 1999; Matthijs et al., 1999; Bruno et al., 2002; Ying et al., 2002; Knepper et al., 2003; Berryman et al., 2004). Different types of surfactants have been detected in sewage effluents with concentrations up to 1090 μg/L for LAS (Holt et al., 1998), up to 332 μg/L for APEs (Snyder et al., 1999), and up to 62 μg/L for DTDMAC (Versteeg et al., 1992). These surfactants were also found in treated sludges at high concentrations of up to 30200 mg/kg dry weight for LAS (Berna et al., 1989), up to 81 mg/kg for APEs (Bruno et al., 2002), and up to 5870 mg/kg for DTDMAC (Fernandez et al., 1996). They have also been reported in surface waters at concentrations of up to 416 μg/L for LAS (Fox et al., 2000), and the degradation products of APE were widely detected in different environmental compartments (air, water, sediment) (Ahel and Giger, 1985; Blackburn and Waldock, 1995; Bennie et al., 1997; Blackburn et al., 1999; Ying et al., 2002; Berryman et al., 2004). This review paper mainly focused on the behavior and fate as well as ecotoxicity of different types of surfactants in the environment.

2. Behavior of surfactants in the environment

2.1. Chemistry of surfactants

A fundamental property of surfactants is their ability to form micelles in solution. This property is due to the presence of both hydrophobic and hydrophilic groups in each surfactant molecule. It is the formation of micelles in solution that gives surfactants their detergency and solubilisation properties. When dissolved in water at low concentration, surfactant molecules exist as monomers. At higher concentrations, the system's free energy can be reduced by the aggregation of the surfactant molecules into clusters (micelles) with the hydrophobic groups located at the center of the cluster and the hydrophilic head groups towards the solvent. The concentration at which this occurs is known as the critical micelle concentration (CMC) (Haigh, 1996). Nonionic surfactants have lower CMC levels than anionic and cationic surfactants (Table 2).

At concentrations above the CMC level, surfactants have the ability of solubilise more of hydrophobic organic compounds than would be dissolve in water alone (Fig. 1). The effectiveness of surfactants in solubilising water insoluble or poorly soluble compounds is dependent on the sorbed compounds, the environmental media and the surfactant (Aronstein et al., 1991). Surfactants may affect the mobility and degradation of hydrophobic organic compounds in soil or sediment (Edwards et al., 1994; Tiehm, 1994). Aronstein et al. (1991) found that the extent of phenanthrene biodegradation was markedly increased at nonionic surfactant concentrations of 10 μg/kg soil in both a mineral and organic soil, despite lack of desorption enhancement in the organic soil. Ying et al. (2005) also found that small percentages (> 1%) of surfactants in water could mobilize triazines in the contaminated soils, which have been stabilized by activated carbon.

In sewage sludge amended soils, there are many other hydrophobic organic compounds except surfactants at high concentrations. These surfactants may interact with those hydrophobic compounds. Kile and Chiou (1989) studied the effect of anionic, cationic and nonionic surfactants on the water solubility of DDT and trichlorobenzene. As would be expected, the solubility was enhanced when the surfactant was present at concentrations greater than the critical micelle concentration. There was also a solubility enhancement at surfactant concentrations less than the CMC levels. However, the studies by Klumpp et al. (1991) and Edwards et al. (1994) found that surfactants below CMC enhanced

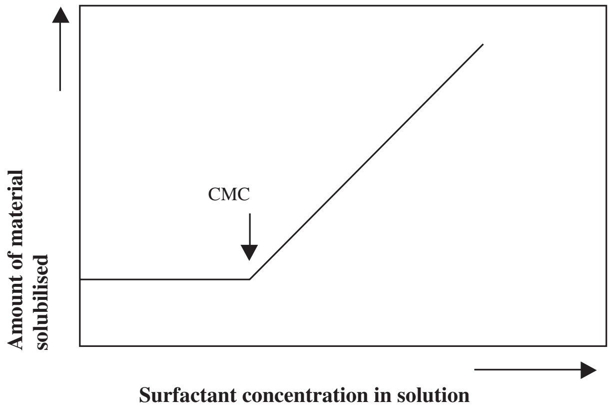

Fig. 1. Solubilisation of an insoluble or poorly soluble material as a function of surfactant concentration.

the sorption uptake of hydrophobic organic pollutants due to the formation of hemimicelles. At higher concentrations, the same surfactants in micellar form remobilized those hydrophobic compounds already adsorbed by solubilisation. The concentration of surfactants required to mobilize contaminants is significantly above those normally found in sewage sludge (Sweetman et al., 1994).

2.2. Sorption of surfactants

Once surfactants enter the environment through sewage discharge into surface water, pesticide application or sludge disposal on land, they undergo many processes such as sorption and degradation. Knowledge of the processes involved in distributing these surfactants among ecosystem compartments is essential to an understanding of their behavior in the environment. Sorption of a surfactant onto sediment/soil depends on many factors including its physiochemical properties, sediment nature and environmental parameters. The information from sorption process of a surfactant can be used to estimate the distribution of the surfactant in different environmental compartments (sediment/soil and water). Sorption data can also be used to estimate the bioavailability of the surfactant. Furthermore, sorption has a significant influence on the degradation of the surfactant in the environment.

Sorption can be described by using sorption isotherms. The commonly used Freundlich equation defines a non-linear relationship between the amount sorbed and the equilibrium solution concentration:

$$S = K_f C^n$$

where S is the concentration of a surfactant sorbed by the solid phase (mg/kg); K_f is the Freundlich sorption coefficient (L/kg); C is the equilibrium solution concentration (mg/L) and n is a power function related to the sorption mechanism. When the value of n is unity, we have the simplest linear isotherm:

$$S = K_d C$$

where K_d is the sorption coefficient (L/kg). The parameter K_d is frequently used to characterise the sorption of a chemical in sediment/soil and is an important parameter governing the partitioning and mobility of the chemical in the environment. Sorption of some chemicals especially those nonpolar compounds closely depends on organic matter in the sediment/soil. Therefore, the organic carbon sorption coefficient (K_{oc}) is often used to describe the sorption of those compounds on sediment/soil.

Due to their chemical features, surfactant molecules may sorb directly onto solid surfaces or may interact with sorbed surfactant molecules. The sorption mechanism is dependent on the nature of the sorbent and the surfactant concentration (Adeel and Luthy, 1995; Brownawell et al., 1997; Fytianos et al., 1998; Ou et al., 1996). At low concentrations, the surfactant molecules may be sorbed to a mineral surface or clean sediment that has very few sorbed surfactant molecules, and sorption may occur mainly due to van der Waals interactions between the hydrophobic and hydrophilic moieties of the surfactant and the surface. There are no significant sorbate–sorbate interactions at the low concentrations. As the surfactant concentration increases, active sorption sites on solid surface become less and less available, and more and more hemimicelles form. At higher concentrations, such sorption may entail the formation of more structured arrangements including the formation of monomer surfactant clusters on the surface or a second layer, for which these arrangements may be governed mainly by interactions between hydrophobic moieties of the surfactant molecules. Therefore, two stage sorption isotherms (Fig. 2) have been reported for nonionic surfactants NPE and AE and anionic LAS although the sorption behavior is different for nonionic and anionic surfactants (Adeel and Luthy, 1995; Brownawell et al., 1997; Fytianos et al., 1998; Ou et al., 1996).

The sorption of LAS on natural soils had two stages: linear and exponentially increasing isotherms (Ou et al., 1996). At low LAS concentration (< 90 μg/mL), the sorption isotherms were linear and K_d ranged from 1.2 to2.0. At high levels (> 90 μg/mL), cooperative sorption was observed and the sorption amount of LAS increased exponentially with the increasing of LAS concentration in solution. This enhanced sorption of LAS on soils was also observed by Fytianos et al. (1998). Under real soil environment or aquatic environment where LAS levels are rather low, the LAS sorption ability of a soil or sediment is very weak.

In contrast, the sorption of a nonionic surfactant reached a maximum on the solid surface when the solution is near or just at the critical micelle concentration of the surfactant. The decreased sorption of nonionic surfactants (APEs and AEs) on sediment at higher concentrations was observed (Adeel and Luthy, 1995; Kibbey and Hayes, 2000). A Langmuir isotherm as described by the following equation provides a reasonable fit to the sorption data

$$S = S_{\max} K_l C / (1 + K_l C)$$

where S is the sorbed concentration of the surfactant on the solid surface (mg/kg), $S_{\max}$ is the maximum sorbed concentration (mg/kg), C is the aqueous phase surfactant

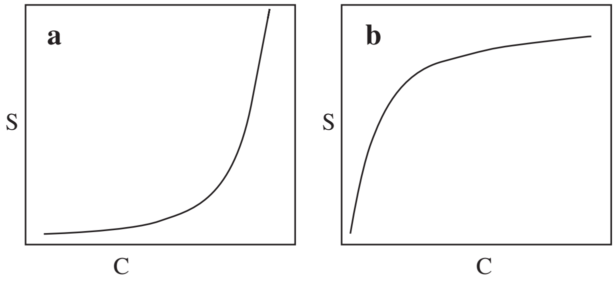

Fig. 2. Sorption isotherms for anionic and nonionic surfactants (a LAS; b APEs and AEs). S is the sorbed surfactant concentration and C is the surfactant concentration in the solution.

Table 3
Sorption coefficients (K_d) of surfactants

Compound	Sorbent	K_d (L/kg)	K_{oc} (L/kg)	Reference[a]
C12LAS	Sable soil (TOC 2.9%)	3.3–45	114–1552	1
	Spinks soil (TOC 1.2%)	3.6–9	300–750	1
	Sarpy soil (TOC 0.6%)	2–3.5	333–583	1
C12LAS	Soil (TOC 0.46–1.08%)	1.2–2.0	185–261	2
C18TMAC	Activated sludge solids	1.8×10^4 4.9×10^4		3
NPEO3	River sediment	1460		4
NPEO10	River sediment	450		4
C15EO9	Sediment (TOC 0.2–2.8%)	350–2100		5
C13EO6	Sediment (TOC 0.76–3.04%)	40–62		6
C13EO3	Sediment (TOC 0.2–2.8%)	110–500		7
C13EO9		110–590		7
C10EO3	Suspended sediment (TOC 11%)	41		8
C10EO5		48		
C10EO8		126		
C12EO3		257		
C12EO5		724		
C12EO8		1230		
C14EO3		2951		
C14EO5		3467		
C14EO8		3548		

[a] References: (1) Orth et al. (1995), (2) Ou et al. (1996), (3) Games and King (1982), (4) John et al. (2000), (5) Cano and Dorn (1996a,b), (6) Brownawell et al. (1997), (7) Cano and Dorn (1996a,b), (8) Kiewiet et al. (1996).

concentration (mg/L), and K_l is the Langmuir constant (L/kg).

Surfactant concentrations in the environment are normally at low concentration range below the critical micelle concentration (CMC) of the surfactant. Surfactant sorption onto environmental sorbents (sediment or soil) is mostly Freundlich type (Brownawell et al., 1997; Cano and Dorn, 1996a,b). Table 3 lists some reported sorption coefficients for some surfactants. Anionic surfactant LAS had much lower K_d values than nonionic surfactants APEs and AEs. However, cationic surfactants tend to adsorb strongly onto sediment/soil (Haigh, 1996). For example, the calculated K_d value was 5000 L/kg for DEEDMAC on sludge (Giolando et al., 1995). Topping and Waters (1982) and Games and King (1982) reported that > 95% of the cationic surfactants were adsorbed on the surface of particulate matter in activated sludge. Sorption coefficients of AEs on suspended sediment increased with increasing alkyl and ethoxylate chain lengths (Kiewiet et al., 1996). The dominant influence of the alkyl chain suggests a hydrophobic sorption mechanism.

Ferguson et al. (2001) investigated the partitioning of APE metabolites to suspended solids in Jamaica Bay, New York, and found that log K_{oc} values did not vary greatly among the APE metabolites and were 5.39 for NP, 5.18 for OP, 5.46 for NPE1, 5.18 for NPE2 and 4.87 for NPE3, respectively. John et al. (2000) measured sorption coefficients (K_d) of NPE3-13 homologues onto native sediment, organic-free sediment, kaolinite, silica, and sewage sludge and found that K_d values for native sediment decreased progressively from 1460 L/kg for NPE3 to 450 L/kg for NPE10, then increased again slightly for higher homologues. In contrast, K_d values for organic-free sediment (230–590 L/kg) or kaolinite (190–490 L/kg) increased steadily from NPE3 to NPE13. Adsorption to sewage sludge was very strong with K_d values ranged from 12,000 to 33,000 L/kg. These data indicated that interactions with organic matter were important in controlling sorption of APs and short ethoxylate APEs. However, as the level of APE ethoxylation increased, association with mineral surfaces became the dominant contributor to APE sorption.

2.3. Bioconcentration of surfactants and their degradation products

When a chemical in sewage effluent is discharged into the environment, it distributes into the different phases such as water, air, sediment and biota, and equilibrium is formed depending on the properties of the chemical and the phases. Therefore, the water to biota transfer is of critical importance because we are principally concerned with adverse effects on biota. The process involving the direct transfer of a chemical from water to biota is described as bioconcentration (Connell, 1988). At equilibrium, bioconcentration is characterised by the bioconcentration factor (BCF), the ratio between the concentration in biota, C_{B}, and the concentration in water, C_{w}, i.e., $\mathrm{BCF}=C_{\mathrm{B}}/C_{\mathrm{w}}$.

Since a surfactant has to be taken up into an organism before it can elicit an effect, the processes and factors influencing uptake are relevant when assessing the environmental risk. Lipophilic compounds are the organics most likely to bioaccumulate. Mackay (1982) has demonstrated that the lipid phase in biota is the dominant phase for their accumulation. Lipophilicity, or hydrophobicity, measured as the octanol to water partition coefficient (K_{ow}) has identified as the driving force for bioconcentration. Bioconcentration increases with increasing K_{ow} value.

2.3.1. LAS

It has been found that longer LAS homologues have higher K_{ow} values (Table 2). LAS are taken up from water via the fish gills rather than skin (Tolls et al., 2000). The concentrations of the selected LAS homologues (C10LAS to C13LAS) in the liver and the internal organs of juvenile rainbow trout increased rapidly demonstrating fast uptake into systemic circulation. The relatively slow increase of LAS concentrations in the less well-perfused tissue pointed to internal redistribution being controlled by perfusion. The bioconcentration factors (BCFs) in rainbow trouts ranged between 1.4 and 372 L/kg. The BCFs in fathead minnows were higher ranging from 6 to 990 L/kg (Tolls et al., 2000). Water hardness was found to influence the aqueous phase behavior of LAS. Increased water hardness can bring higher fluxes of LAS from water into fish.

In the terrestrial environment, BCFs are significantly lower than in the aquatic environment and a bioaccumula-

Table 4
Bioconcentration factor (BCF, wet weight) data for alkylphenols

Species	4-Nonylphenol	4-*t*-Octylphenol	Reference[a]
Ayu fish (field)	21 ± 15	297 ± 194	1
Killifish	167 ± 23	267 ± 62	1
Sticklebacks (field)	1300		2
Salmon	282		3
Fathead minnow	270–350		4
Rainbow trout		471	5

[a] References: (1) Tsuda et al. (2001), (2) Ekelund et al. (1990), (3) McLeese et al. (1981), (4) Naylor (1995), (5) Ferreira-Leach and Hill (2001).

tion of LAS in terrestrial biota is mostly unlikely (Jensen, 1999). Figge and Schöberl (1989) used radiolabelled LAS to estimate uptake by plants in two mesocosm studies. The concentrations of LAS were estimated up to 210 mg/kg in roots of grass, between 106 and 134 mg/kg in roots of radishes and garden beans, and up to 66 mg/kg in potatoes. BCFs were estimated between 2 and 7 for the four plant species based on the initial LAS concentrations of 16 and 27 mg/kg in soil.

2.3.2. Alkylphenols

Alkylphenols (nonylphenols and octylphenols) are the degradation products of a widely used class of nonionic surfactants, i.e., alkylphenol polyethoxylates during wastewater treatment (Giger et al., 1984). Nonylphenol (NP) and octylphenol (OP) have attracted a lot of scientific attention because of their estrogenic effects and ability to bioaccumulate in aquatic organisms. These two chemicals have been widely detected in the environment due to the discharge of sewage effluents into surface waters (Ying et al., 2002). NP has a log K_{ow} of 4.48 and water solubility of 5.4 mg/L whereas OP has a log K_{ow} of 4.12 and water solubility of 12.6 mg/L (Ahel and Giger, 1993a,b). This physiochemical profile indicates that NP and OP may bioaccumulate in aquatic organisms. This has been documented in some species of fish from natural waters and from controlled laboratory exposure (Table 4). The reported bioconcentration factors (BCF values) in whole fish range from 21 to 1300 for 4-NP and 267 to 471 for 4-*t*-OP. The differences in the BCF values of NP and OP among fish species are probably due to their different metabolic abilities, functioning of their gills, etc. (Tsuda et al., 2001).

Alkylphenols can be rapidly metabolized by phase I and II enzymes in fish (Arukwe et al., 2000; Ferreira-Leach and Hill, 2001; Thibaut et al., 1999). Arukwe et al. (2000) studied the in vivo metabolism and organ distribution of 4-*n*-NP in juvenile salmon and found that 4-*n*-NP was mainly metabolized to its corresponding glucuronide conjugate and to a lesser extent to various hydroxylated and oxidated compounds. The half-life of residues in carcass and muscle was between 24 and 48 h after exposure. Similar results were found by Ferreira-Leach and Hill (2001) in a study on bioconcentration and distribution of 4-*t*-OP in juvenile rainbow trout. The concentrations of 4-*t*-OP residues were higher in bile, followed by faeces, pyloric caeca, liver and intestine. In these tissues, the majority of alkylphenol was in the form of two metabolites, which were identified by GC-MS as the glucuronide conjugates of 4-*t*-OP and *t*-octylcatechol. 4-*t*-OP accumulated as the parent compound in fat with a BCF of 1190, and in brain, muscle, skin, bone, gills and eye with BCF values between 100 and 260. This suggests that exposure to water-borne alkylphenols results in rapid conjugation and elimination of the chemical via the liver/bile route, but that high amounts of the parent compound can accumulate in a variety of other fish tissue (Ferreira-Leach and Hill, 2001).

3. Biodegradation of surfactants in the environment

Degradation of surfactants through microbial activity is the primary transformation occurring in the environment. Biodegradation is an important process to treat surfactants in raw sewages in sewage treatment plants, and it also enhances the removal of these surfactants in the environment, thus reducing their impact on biota. During biodegradation, microorganisms can either utilize surfactants as substrates for energy and nutrients or cometabolize the surfactants by microbial metabolic reactions. There are many chemical and environmental factors that affect biodegradation of a surfactant in the environment. The most important influencing factors are chemical structure, and physiochemical conditions of the environmental media. Different classes of surfactants

Table 5
Biodegradability of surfactants in the environment

Surfactant	Aerobic condition	Anaerobic condition
LAS	Degradable [1, 2, 3, 4,5, 6]	Persistent [5, 7]
SAS	Readily degradable [7, 8]	Persistent [7]
Soap	Readily degradable [7, 9]	Readily degradable [7, 9]
Fatty acid esters (FES)	Readily degradable [10, 11]	Persistent [12]
AS	Readily degradable [13, 14]	Degradable [15, 16]
AES	Readily degradable [7]	Degradable [7]
Cationic surfactants (e.g. DTDMAC)	Degradable [17, 18, 19]	Persistent [20]
APE	Degradable [21, 22, 23]	Partially degradable [24]
AE	Readily degradable [25, 26, 27, 28]	Degradable [29, 30, 31]

References: (1) De Wolf and Feijtel (1998), (2) Takada et al. (1994), (3) VanGinkel (1996), (4) Eichhorn et al. (2002), (5) Krueger et al. (1998), (6) Yadav et al. (2001), (7) Scott and Jones (2000), (8) Field et al. (1995), (9) Prats et al. (1999), (10) Gode et al. (1987), (11) Steber and Wierich (1989), (12) Maurer et al. (1965), (13) George (2002), (14) Margesin and Schinner (1998), (15) Feitkenhauer and Meyer (2002a), (16) Feitkenhauer and Meyer (2002b), (17) Games and King (1982), (18) Garcia et al. (2001), (19) Giolando et al. (1995), (20) Garcia et al. (1999), (21) Mann and Boddy (2000), (22) Manzano et al. (1999), (23) Potter et al. (1999), (24) Charles et al. (1996), (25) Marcomini and Pojana (1997), (26) Reznickova et al. (2002), (27) Salanitro et al. (1995), (28) Szymanski et al. (2000), (29) Huber et al. (2000), (30) Mezzanotte et al. (2002), (31) Salanitro and Diaz (1995).

have different degradation behavior in the environment (Table 5). Most of the surfactants can be degraded by microbes in the environment, although some surfactants such as LAS may be persistent under anaerobic conditions.

3.1. Anionic surfactants

3.1.1. LAS

LAS can be degraded by consortia of aerobic microorganisms and attached biofilms in the environment (VanGinkel, 1996; Yadav et al., 2001; Takada et al., 1994). LAS biodegradation intermediates are mono- and dicarboxylic sulfophenyl acids (SPC) that are formed by ω-oxidation of the alkyl chain terminal carbon followed by successive β-oxidation (Di Corcia and Samperi, 1994; Yadav et al., 2001; Navas et al., 1999). A variety of SPCs have been identified having an alkyl chain length of 4 to 13 (Gonzalez-Mazo et al., 1997; Yadav et al., 2001). Then the SPCs are further desuphonated. The ω-oxidation of the alkyl chain and the cleavage of the benzene ring require molecular oxygen, therefore, under anaerobic conditions, degradation via these pathway is unlikely. There is no evidence that LAS can be degraded anaerobically (De Wolf and Feijtel, 1998; Krueger et al., 1998).

Due to the incomplete removal of LAS in sewage treatment plants (Holt et al., 1998), some residues of the surfactant together with its aerobic breakdown intermediates, the sulfophenyl carboxylates (SPC) enter the receiving waters via the discharge of the sewage effluents. Aerobic degradation of LAS in river water is well documented with half-lives less than 3 days (Larson and Payne, 1981). LAS could be primarily biodegraded to more than 99% by natural microbial flora of river water even at 7 °C (Perales et al., 1999). However, in the marine environment, the degradation of LAS and its intermediates SPCs is slower, which is mainly due to the lower microbial activity and their association with Ca^{2+} and Mg^{2+} (Gonzalez-Mazo et al., 1997). In sewage-contaminated groundwater, the rate of LAS biodegradation increased with increasing dissolved oxygen concentrations, but under low oxygen conditions ($<$ 1 mg/L), only a fraction of the LAS mixture biodegraded (Krueger et al., 1998).

Concentrations of LAS in raw sewage sludges are very high due to its widespread usage and strong sorption on sludge during the treatment. Sewage sludge that had been aerobically treated had LAS concentrations of 100–500 mg/kg dry weight, while those anaerobically treated sludge had much higher LAS concentrations ranging from 5000 to 15000 mg/kg dry weight (Jensen, 1999). Of course, the LAS level in sludge also depends on the individual wastewater treatment plant because the input of LAS into a sewage treatment plant and its treatment method and efficiency are different. However, McEvoy and Giger (1985) measured LAS concentrations in sludge before and after anaerobic digestion and found no degradation of LAS occurred during anaerobic treatment. This further substantiates the conclusion that the degradation of LAS under anaerobic conditions is not favoured.

LAS are readily degradable in aerobic soil with a half-life of 7–33 days (Table 6). Once sludge is applied on land, LAS are rapidly metabolized by aerobic bacteria in sludge-amended soil and will not accumulate in soil as demonstrated by field experiments (Berna et al., 1989; Figge and Schöberl, 1989; Holt et al., 1989; Marcomini et al., 1989; Waters et al., 1989). Holt et al. (1989) concluded that degradation of LAS in soil was primarily microbially driven and that soil type, agricultural land use, application method and whether a soil had been ploughed or not had no effect on degradation rates. LAS homologue distribution showed no significant changes post-application suggesting no differential degradation.

3.1.2. AS

Fatty alcohol sulphates (AS) are among the most rapidly biodegradable surfactants. Both primary and ultimate biodegradations are fast and complete in a wide range of test designs (Swisher, 1987; Scott and Jones, 2000). The biodegradation is found to involve the enzymatic cleavage of the sulphate ester bonds to give inorganic sulphate and a fatty alcohol. The alcohol is oxidised to an aldehyde and subsequently to a fatty acid with further oxidation via the β-oxidation pathway, thus achieving ultimate biodegradation (Thomas and White, 1989). This pathway is further confirmed by the identification of alkylsulphatase enzymes, which catalyse the initial desulphation step, and long-chain alcohol dehydrogenases that follow them (White, 1995). Alkylsulphatase-producing strains such as *Pseudomonas* spp. are widely distributed in the environment (White, 1995). Lee et al. (1998) found faster degradation of sodium dodecyl sulfate (SDS) by riverine biofilms. SDS biodegra-

Table 6
Concentrations of LAS in sludge amended soils

Location	Soil concentration post-application (mg/kg)	Monitoring period	Final soil concentration (mg/kg)	Half-life (days)	Reference[a]
Germany	16	76 days	0.19	13	1
Spain	16	90 days	0.3	26	2
Spain	53	170 days	Not reported	33	2
Switzerland	45	12 months	5	9	3
UK	2.6–66.4	5–6 months	< 1	7–22	4, 5

[a] References: (1) Figge and Schöberl (1989), (2) Berna et al. (1989), (3) Marcomini et al. (1989), (4) Waters et al. (1989), (5) Holt et al. (1989).

dation was reported in Antarctic coastal waters with half-lives of 160 to 460 h (George, 2002). AS was readily degraded under anaerobic conditions using municipal digester solids as a source of anaerobic bacteria (Salanitro and Diaz, 1995). Therefore, AS can be readily bioavailable under aerobic and anaerobic conditions and easily degradable both primarily and ultimately. Treatment in a sewage treatment plant can sufficiently remove AS with little possibility to reach the environment by effluent discharge and sludge disposal.

3.2. Cationic surfactants

Quaternary ammonium compounds (QACs) are cationic surfactants used increasingly as fabric softeners or disinfectants. Most uses of QACs lead to their release to wastewater treatment plants. Cationic surfactants sorb strongly onto suspended particulates and sludge, which are predominantly negatively charged. Cationic surfactants are considered biologically degradable under aerobic conditions although the biodegradation for individual surfactant varies. The degradation pathway for alkyl trimethyl ammonium and alkyl dimethyl ammonium halides (TMAC and DMAC) is believed to begin initially by *N*-dealkylation, followed by *N*-demethylation (Nishiyama et al., 1995). Trimethylamine, dimethylamine and methylamine were identified as the intermediates of alkyl trimethyl ammonium salts in activated sludge obtained from a municipal sewage treatment plant (Nishiyama et al., 1995). In this pathway, alkyl trimethyl ammonium salts are initially degraded to trimethylamine by *N*-dealkylation. The trimethylamine is then degraded to dimethylamine, and this intermediate is further degraded to methylamine, which is rarely detected. Long-chain alkyl trimethyl ammonium salts are ultimately biodegradable in activated sludge. Games and King (1982) reported a half-life of 2.5 h for octadecyl trimethyl ammonium chloride (C18TMAC) primary biodegradation in laboratory based activated sludge system.

Cationic surfactants containing a quaternary ammonium (e.g., R_4N^+; where R = alkyl chain and N = quaternary nitrogen) often have a strong biocidal nature (Baleux and Caumette, 1997). The alkyl chain length not only determines the physical–chemical properties of a surfactant, but also may have a decisive role in the fate and effects of these compounds in the environment. Under aerobic conditions, the biodegradability of QACs generally decreases with the number of non-methyl alkyl groups (i.e., $R_4N^+ < R_3MeN^+ < R_2Me_2N^+ < RMe_3N^+ < Me_4N^+$; where Me = methyl radical) (Swisher, 1987). Moreover, substitution of a methyl group in a QAC with a benzyl group can decrease biodegradability further (Swisher, 1987; Garcia et al., 2001). Garcia et al. (2001) reported time to achieve a 50% of primary biodegradation for a series of QAC homologues ranged from 3 to 8 days in the modified OECD screening test and seawater, except for hexadecyl dimethyl ammonium chloride (C16DMAC) (> 15 days). The degradation of these compounds in coastal waters was associated with an increase in bacterioplankton density, suggesting that the degradation takes place because the compound is used as a growth substrate.

In contrast, under anaerobic conditions, QACs showed no or very poor primary biodegradation and no evidence of any extent of ultimate biodegradation was found (Garcia et al., 1999, 2000). Primary biodegradation in sludge under anaerobic conditions was found to range from 19 to 38 for mono-alkyl quaternary ammonium based surfactants and the toxicity to methanogenesis decreased with increasing alkyl chain length (Garcia et al., 1999). No degradation was observed for ditallow dimethyl ammonium chloride (DTDMAC) in anaerobic screening tests (Garcia et al., 2000). Due to its poor biodegradation kinetics, diethyl ester dimethyl ammonium chloride (DEEDMAC) was introduced to replace DTDMAC, the major cationic surfactant used as fabric softener formulations worldwide for over 30 years. DEEDMAC differs structurally from DTDMAC by the inclusion of two ester linkages between the ethyl and tallow chains. These ester linkages allow DEEDMAC to be rapidly and completely degraded in standard laboratory screening tests and a range of environmental media such as sludge, soil and river water with half-lives ranging from 0.8 days to 18 days (Giolando et al., 1995). DEEDMAC can be completely degraded under aerobic and anaerobic conditions, and it has a half-life of around 24 h in raw sewage. Therefore, removal of DEEDMAC during sewage treatment is greater than 99% (Giolando et al., 1995).

3.3. Nonionic surfactants

3.3.1. APE

The biodegradation of APEs in conventional sewage treatment plants is generally believed to start with a shortening of the ethoxylate chain, leading to short-chain APEs containing one or two ethoxylate units. Complete deethoxylation with formation of alkylphenols (APs) has been observed only under anaerobic conditions (Giger et al., 1984). Further transformation proceeds via oxidation of the ethoxylate chain, producing mainly alkylphenoxy ethoxy acetic acid and alkylphenoxy acetic acid (Talmage, 1994). The three most common groups of intermediates reported were as follows: (a) alkylphenols (e.g., NP and OP); (b) short-chain alkylphenol ethoxylates having 1–4 ethoxylate units, with APE2 predominating; (c) a series of ether carboxylates including alkylphenoxy acetic acid (APEC1) and alkylphenoxy ethoxy acetic acid (APEC2). Recalcitrant decarboxylated NPE biotransformation products with the alkyl chain carboxylated (CAPEs) were also detected in a sewage treatment plant effluent (Di Corcia, 1998). Previous investigations showed that APE metabolites degraded more easily under aerobic than under anaerobic conditions (Brunner et al., 1988).

The measured removal rates of NPEs through sewage treatment plants varied from 93 to 99% in the US (Naylor, 1995), from 66% to 99% in Japan (Nasu et al., 2001), from 74 to 98% in Italy (Crescenzi et al., 1995; Di Corcia and Samperi, 1994), and from 47 to 89% in Switzerland (Ahel et al., 1994). This suggests that only partial degradation occurs.

Due to the amphiphilic nature APE and their metabolites show an affinity for particulate surfaces, a significant proportion is observed in sludge. Concentrations of APE ranged from 900 to 1100 mg/kg in anaerobically digested sludge, which are much higher than in aerobically digested sludge (0.3 mg/kg) (Scott and Jones, 2000). APE degradation appears restricted under anaerobic conditions. However, under aerobic conditions, APEs undergo almost complete primary degradation. Jones and Westmoreland (1998) reported 98% reduction of NPEs in composted Australian wool scouring sludge within 100 days.

The primary degradation of NPE9 showed half-lives of 4 days in water and < 10 days in sediments in a river die-away test (Yoshimura, 1986). Manzano et al. (1999) conducted a river die-away test on the biodegradation of a nonylphenol polyethoxylate in river water and found that temperature had a strong influence on the period of acclimation of the microorganisms and on the rate of biodegradation. The percentages of primary biodegradation vary from 68% at 7 °C to 96% at 25 °C and, at all the temperatures studied, metabolites (NPE2, NPE1, NPEC1 and NPEC2) were generated during the biodegradation process which do not totally disappear at the end of the assay (30 days). The mineralisation rates reached in the various assays, ranging from 30% at 7 °C to 70% at 25 °C. Similar results were generated from a static die-away test of NPE in estuarine water in the dark at 28 °C for 183 days (Potter et al., 1999). Primary degradation was complete in 4–24 days with a lag periods between 0 and 12 days. The intermediates detected include NPE2 and NPEC2 with much smaller amounts of NPE1 and NPEC1. But NP was not detected. In the primary biodegradation, light was found to be a retarding factor for biodegradation (Mann and Boddy, 2000).

3.3.2. AE

Fatty alcohol ethoxylates (AE) are easily degradable under aerobic and anaerobic conditions. High primary biodegradation (96±0.5%) was found for AEs in the continuous flow activated sludge test with a high concentration of metabolites free fatty alcohol (FFA) and poly(-ethylene glycols) (PEG) (Szymanski et al., 2000). However, in a static test, a primary degradability of 75–98% in an aqueous environment was achieved in 10 days, without significant accumulation of metabolites PEG (Reznickova et al., 2002). Knaebel et al. (1990) showed AE to be readily biodegraded in a variety of different soil types, suggesting AE will not accumulate in aerobic sludge-amended soils.

The mechanism for aerobic biodegradation of AE was believed to be initiated by the central cleavage of the molecule, leading to the formation of PEG and FFA, followed by ω-, or β-oxidation of the terminal carbon of the alkyl chain, and the hydrolytic shorting of the terminal carbon of the polyethoxylic chain (Marcomini and Pojana, 1997; Reznickova et al., 2002). In contrast to aerobic biodegradation where central prevails, the first step of anaerobic microbial attack on the AE molecule is the cleavage of the terminal ethoxy unit, releasing acetaldehyde stepwise, and shortening the ethoxy chain until the lipophilic moiety is reached (Huber et al., 2000).

4. Biological effects of surfactants and their degradation products

Surfactants entering the environment through the discharge of sewage effluents into surface waters and application sewage sludge on land have the potential to impact the ecosystem owing to their toxicity on organisms in the environment. The toxicity data from laboratory and field studies are essential for us to assess the possible environmental risks from the surfactants.

Table 7
Aquatic toxicity data for anionic surfactants

Chemical	Species	Endpoint	References[a]
C10LAS	*Daphnia magna*	LC50–48 h, 13.9 mg/L	1
C12 LAS		LC50–48 h, 8.1 mg/L	
C14LAS		LC50–48 h, 1.22 mg/L	
C12LAS	*Dunaliella* sp. (green alga)	EC50–24 h, 3.5 mg/L	2
C11–12LAS	*Oncorhynchus mykiss* (rainbow trout fry)	NOEC–54 days, 0.2 mg/L	3
C12LAS (SDBS)	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 3.63 mg/L	4
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 8.81 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 5.1 mg/L	
C12AS (SDS)	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 33.61 mg/L	4
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 40.15 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 38.04 mg/L	
Sodium dodecyl ethoxy sulfate (SDES)	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 10.84 mg/L	4
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 13.64 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 12.35 mg/L	

[a] References: (1) Verge et al. (2000), (2) Utsunomiya et al. (1997), (3) Hofer et al. (1995), (4) Singh et al. (2002).

Table 8
Aquatic toxicity data for cationic surfactants

Chemical	Species	Endpoint	Reference[a]
TMAC	*Dunaliella* sp. (green alga)	EC50–24 h, 0.79 mg/L	1
DADMAC		EC50–24 h, 18 mg/L	
BDMAC		EC50–24 h, 1.3 mg/L	
C16TMAC	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 1.21 mg/L	2
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 8.24 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 3.58 mg/L	
DTDMAC	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 0.74 mg/L	2
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 7.91 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 2.37 mg/L	
DTDMAC	*Daphnia magna*	LC50–48 h, 0.49 mg/L	3
		NOEC–21 days, 0.38 mg/L	
DEEDMAC	*Daphnia magna*	Immobilization LC50–24 h, 14.8 mg/L	4
		Growth NOEC–21 days, 1 mg/L	
	Pimphales promelas (fathead minnow)	Growth NOEC–35 days, 0.68 mg/L	
	Selenastrum capricornutum *(algae)*	Growth inhibition EC50–96 h, 2.9 mg/L	
TMAC	*Daphnia magna*	Immobilization IC50–24 h, 0.13–0.38 mg/L	5
BDMAC	*Daphnia magna*	Immobilization IC50–24 h, 0.13–0.22 mg/L	5

[a] References: (1) Utsunomiya et al. (1997), (2) Singh et al. (2002), (3) Lewis and Wee (1983), (4) Giolando et al. (1995), (5) Garcia et al. (2001).

4.1. Aquatic toxicity

Aquatic toxicity data are widely available for anionic, cationic and nonionic surfactants. Lewis (1991) has summarised the chronic and sublethal toxicities of surfactants to aquatic animals and found that chronic toxicity of anionic and nonionic surfactants occurs at concentrations usually greater than 0.1 mg/L. Tables 7–9 list some recently published toxicity data for the three classes of surfactants on several test organisms (alga, invertebrate, fish) from the literature. Singh et al. (2002) tested seven surfactants for toxicity (immobility EC50-48 h) on six freshwater macrobes and found that cationic surfactants were more toxic than anionic surfactants and anionic surfactants more toxic than nonionic surfactants. Utsunomiya et al. (1997) studied the toxic effects of C12LAS and three quaternary alkylammonium chlorides on unicellar green alga *Dunaliella* sp. by measuring ^{13}C glycerol. The 24-h median effective concentrations (EC50–24 h) were 3.5 mg/L for LAS, 0.79 mg/L for alkyl trimethyl ammonium chloride (TMAC), 18 mg/L for dialkyl dimethyl ammonium chloride (DADMAC) and 1.3 mg/L for alkyl benzyl dimethyl ammonium chloride (BDMAC): the toxic potencies were in the order of TMAC > BDMAC > LAS > DADMAC.

LAS acute toxicity to *D. magna* increases with the alkyl chain or homologue molecular weight probably due to higher interaction of heavier homologues with cell membranes (Verge et al., 2000). It is also found that a very high water hardness (> 2000 mg/L as $CaCO_3$) may be a stress factor giving a much lower LC50–48 h than at lower water hardness and the same LAS concentrations. Although 0.2 mg/L is considered as the no observed effect concentration (NOEC), lamellar gill epithelia of rainbow trout fry hypertrophied and its swimming capacity was reduced after 54 days of exposure (Hofer et al., 1995). Temart et al. (2001) conducted risk assessment of LAS in the North Sea. The LAS concentration range in the estuaries around the North Sea ranged from 1 to 9 μg/L, while in the offshore sites, it is below the detection limit (0.5 μg/L). The predicted no-effect concentrations (PNEC) were 360 and 31 μg/L for freshwater

Table 9
Aquatic toxicity data for nonionic surfactants

Chemical	Species	Endpoint	Reference[a]
C12EO6	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 22.38 mg/L	1
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 29.26 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 28.02 mg/L	
C9–11EO6	Pimphales promelas (fathead minnow)	LC50–10 days, 2.7 mg/L	2
OPEO6	*Salmo gairdneri* (rainbow trout)	Immobilization EC50–48 h, 6.44 mg/L	1
	Gammbusia affinis (mosquito fish)	Immobilization EC50–48 h, 9.65 mg/L	
	Carassius auratus (goldfish)	Immobilization EC50–48 h, 9.24 mg/L	
NPEO8	Australian native frogs	Full narcosis EC50–48 h, 2.8–3.8 mg/L	3
NPEO9	Fathead minnow	LC50–96 h, 4.6 mg/L	4
	Daphnia magna	LC50–48 h, 14 mg/L	
NP	Fathead minnow	LC50–96 h, 0.3 mg/L	4
	Daphnia magna	LC50–48 h, 0.19 mg/L	

[a] References: (1) Singh et al. (2002), (2) Dorn et al. (1997), (3) Mann and Bidwell (2001), (4) Naylor (1995).

and marine pelagic communities, respectively. Given that the maximum expected estuarine and marine concentrations are 3 to > 30 times lower than the PNEC, the risk of LAS to pelagic organisms in these environments is judged to be low.

Although the toxicity of SPC, biodegradation intermediates of LAS are not known with any certainty, Kimerle and Swisher (1977) found that SPC give LC50 values that are 120–240% higher than that of LAS. But no estrogenic effects were observed by Navas et al. (1999) for LAS and SPC by two in vitro assays: the yeast estrogen receptor assay and the vitellogenin assay with cultured trout hepatocytes.

Garcia et al. (2001) carried out acute toxicity tests on *Daphnia magna* and *Photobacterium phosphoreum* for two families of monoalkyl quaternary ammonium surfactants: alkyl trimethyl ammonium and alkyl benzyl dimethyl ammonium halides. The 24-h immobilization EC50 on *D. magna* ranged from 0.13 to 0.38 mg/L for the six cationic surfactants whereas EC50 on *P. phosphorem* ranged from 0.15 to 0.63 mg/L. Although the substitution of a benzyl group for a methyl group increases the toxicity, an incremental difference in toxicity between homologues of different chain length was not observed. This could be attributed to a lower bioavailability of the longest chain homologues due to their decreasing solubility. This assumption is enhanced by the results on *D. magna* for DTDMAC, which is a less soluble compound than QACs tested exhibits a lower toxicity (Roghair et al., 1992). DTDMAC is being replaced by less toxic and easily degradable DEEDMAC. The 21-day growth NOEC values on *D. magna* are 0.38 mg/L for DTDMAC (Lewis and Wee, 1983) and 1.0 mg/L for DEEDMAC (Giolando et al., 1995).

Mann and Bidwell (2001) studied the acute toxicity of NPE and AE to the tadpoles of four Australian and two exotic frogs. All species exhibited non-specific narcosis following exposure to both these surfactants. The 48-h EC50 values for NPE ranged between 1.1 mg/L (mild narcosis) and 12.1 mg/L (full narcosis). The 48-h EC50 values for AE ranged between 5.3 mg/L (mild narcosis) and 25.4 mg/L (full narcosis).

A stream mesocosm study by Dorn et al. (1997) demonstrated that fish and invertebrates were most responsive to the effects of AE. For C9-11EO6, the 10-day lab LC50 value for fathead minnows was found to be 2.7 mg/L compared to a 10-day mesocosm LC50 of 6.4 mg/L. The 30-day mesocosm LC50 value was 5.5 mg/L, which indicates that there is little change after 10 days of exposure to this surfactant. Fathead minnows were particularly sensitive to AE with a NOEC of 0.73 mg/L for egg production and larval survival. Bluegills were less sensitive than fathead minnows, with a NOEC for survival and growth of 5.7 mg/L. The stream mesocosm results for fish and invertebrates were similar to those obtained using laboratory single-species tests.

APEs are found much less acutely toxic than their degradation products (NP and OP) to aquatic organisms (Naylor, 1995). Yoshimura (1986) found that the LC50–48 h value for NPE increased with EO unit chain length, therefore, becoming less toxic. NP showed much more toxic than NPEO9 to aquatic organisms (Yoshimura, 1986; Naylor, 1995).

4.2. Terrestrial toxicity

Sewage sludges are increasingly being applied on agricultural lands as fertilizers for plants. These sludges have been found to contain high concentrations of surfactants as well as other contaminants. The terrestrial environment has become a significant sink for the surfactants. In order to sustainably use sewage sludge, it is therefore necessary to assess the toxicity of those surfactants to the soil-dwelling organisms, especially plants.

The terrestrial toxicity data are quite scattered and they are mainly measured for LAS on plants (Table 10), but limited toxicity also available on soil fauna (Kloepper-Sams et al., 1996; Jensen, 1999). Unilever (1987), as cited from Mieure et al. (1990), studied the effect of LAS on sorghum (*Sorghm bicolour*), sunflower (*Helianthuus annuus*) and mung bean (*Phaseolus aureus*) by the OECD Terrestrial Plant Growth Test (OECD 208). Using test concentrations of 1, 10, 100, 1000 mg/kg LAS in a potting soil, they

Table 10
Terrestrial toxicity data for anionic surfactants (LAS)

Species	Test condition	Endpoint	Reference[a]
Bush beans, radish and grasses	Field tests in sludge amended clay soil	Yield and growth NOEC–76 days, 27 mg/kg	1
Potatoes	Field, sandy soil	Yield and growth NOEC–106 days, 16 mg/kg	1
Ryegrass	Field, two soils	Yield NOEC 500 kg/ha, with necrosis and chlorosis observed	2
Sorghum	Lab, potting compost	Growth EC50–21 days, 167 mg/kg	3, 4
Sunflower		Growth EC50–21 days, 289 mg/kg	
Mung bean		Growth EC50–21 days, 316 mg/kg	
Oats	Lab, sandy loam	Growth EC5–14 days, 50 mg/kg	5
		Growth EC50–14 days, 300 mg/kg	
Turnip		Growth EC5–14 days, 90 mg/kg	
		Growth EC50–14 days, 200 mg/kg	
Mustard		Growth EC5–14 days, 200 mg/kg	
		Growth EC50–14 days, 300 mg/kg	

[a] References: (1) Figge and Schöberl (1989), (2) Litz et al. (1987), (3) Unilever (1987), (4) Mieure et al. (1990), (5) Gunther and Pestemer (1990).

determined the 21-day growth EC50 of 167, 289, and 316 mg/kg for sorghum, sunflower and mung bean, respectively. The highest reported NOEC was 100 mg/kg for the three species. Gunther and Pestemer (1990) performed a series of toxicity tests with LAS on oat (*Avena sativa*), turnip (*Brassica rapa*) and mustard (*Sinapis alba*) in a sandy loam at different concentrations and measured the fresh weight of shoots after 14-day exposure. The lowest 14-day EC5 value was determined for oats (50 mg/kg soil). But its EC50 value was similar to that of turnip or mustard.

Litz et al. (1987) observed considerable short-term acute physiological damage on ryegrass in a field experiment using an application rate of 500 kg/ha, but no reduction in yield was found after harvest. Figge and Schöberl (1989) conducted an extensive study of LAS effects on plants (and potato) using a plant metabolism box. They estimated the field NOEC values to be 16 mg/kg for bush beans, grass and radish and 27 mg/kg for potatoes. From the terrestrial toxicity data available, LAS can be considered as not being highly toxic to terrestrial organisms.

4.3. Endocrine disruption

Some chemicals in the environment can disrupt the normal functioning of endocrine system in wildlife as well as human being; these chemicals are called endocrine disrupting chemicals (EDCs) (Ying and Kookana, 2002). The estrogenic properties of alkylphenols were recognised as early as 1938 (Dodds et al., 1938). The ability of 4-alkylphenols to displace estradiol from the estrogen receptors was reported about 20 years ago (Mueller and Kim, 1978). More recently, the estrogenic activities of alkylphenols have been demonstrated both in vitro (Soto et al., 1991) and in vivo (Jobling et al., 1996). NP and OP have shown to be capable of inducing the production of vitellogenin in male fish, a protein usually only found in sexually mature females under the influence of estrogens (Pedersen et al., 1999). The relative potencies of OP and NP to β-estradiol were measured to be 1×10^{-4} and 1.3×10^{-5} (Gutendorf and Westendorf, 2001). Therefore, alkylphenols (OP and NP) are weak estrogen mimic compounds.

The study by Jobling et al. (1998) showed widespread sexual disruption in wild fish in UK rivers. The lowest observable effect level (LOEL) values were reported to be 5 and 20 μg/L for 4-*t*-OP and 4-NP on rainbow trout, respectively (Jobling et al. (1996). This suggests that in some highly contaminated rivers and estuaries in the UK, levels of alkylphenols are high enough to affect the reproductive health of fish. Hence, alkylphenols may play a significant role in the feminisation of fish in UK rivers.

5. Summary

Surfactants have been found in the aquatic environment at μg/L levels mainly due to their widespread usage and discharge of sewage effluents into surface waters. They are also measured in sludge-amended soils because of the high residual concentrations in sludges. Surfactants have relatively high sorption on sludge, sediment and soil, and their sorption is in the order of: cationic > nonionic > anionic. They are strongly associated with particulates or sediment; therefore, biodegradation of surfactants in sediment is detrimental in determining their fate in the environment.

Surfactants can be degraded under aerobic conditions; however, some of them are persistent under anaerobic conditions, such as LAS and DTDMAC. APEs are partially degraded in the anaerobic environment to form alkylphenols (NP and OP), which are also persistent and have estrogenic activities to organisms such as fish.

Elevated concentrations of surfactants and their degradation products may affect organisms in the environment. The environmental risks posed by surfactants and their degradation products can be assessed based on the comparison of the predicted environmental concentration and the predicted no-effect concentration. But more toxicity data are needed for terrestrial risk assessment of surfactants and their degradation products.

Acknowledgement

The authors would like to thank internal reviewers Drs. D Steve and E Smith (CSIRO Land and Water) for their useful comments.

References

Adeel Z, Luthy RG. Sorption and transport kinetics of a non-ionic surfactant through an aquifer sediment. Environ Sci Technol 1995; 29:1032–42.

Ahel M, Giger W. Determination of alkylphenols and alkylphenol mono- and diethoxylates in environmental samples by high-performance liquid chromatography. Anal Chem 1985;57:1577–83.

Ahel M, Giger W. Aqueous solubility of alkylphenols and alkylphenol polyethoxylates. Chemosphere 1993;26:1461–70.

Ahel M, Giger W. Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. Chemosphere 1993; 26:1471–8.

Ahel M, Giger W, Koch M. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment: I. Occurrence and transformation in sewage treatment. Water Res 1994;28:1131–42.

Ahel M, Schaffner C, Giger W. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment: III. Occurrence and elimination of their persistent metabolites during infiltration of river water to groundwater. Water Res 1996;30:37–46.

Ahel M, Molnar E, Ibric S, Giger W. Estrogenic metabolites of alkylohenol olyethoxylates in secondary sewage effluents and rivers. Water Sci Technol 2000;42(7–8):15–22.

Aronstein BN, Calvillo YM, Alexander M. Effect of surfactants at low concentrations on the desorption and biodegradation of sorbed aromatic compounds in soil. Environ Sci Technol 1991;25:1728–31.

Arukwe A, Goksøyr A, Thibaut R, Cravedi JP. Metabolism and organ distribution of nonylphenol in Atlantic salmon (*Salmo salar*). Mar Environ Res 2000;50:141–5.

Baleux BA, Caumette P. Biodegradation of some cationic surfactants. Water Res 1997;11:833–41.

Bennie DT, Sullivan CA, Lee HB, Peart TE, Maguire RJ. Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St Lawrence river. Sci Total Environ 1997;193:263–75.

Berna JL, Ferrer J, Moreno A, Prats D, Bevia FR. The fate of LAS in the environment. Tenside Surfactants Deterg 1989;26:101–7.

Berryman D, Houde F, DeBlois C, O'Shea M. Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp and paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life. Chemosphere 2004; 56:247–55.

Blackburn MA, Waldock MJ. Concentrations of alkylphenols in rivers and estuaries in England and Wales. Water Res 1995;29:1623–9.

Blackburn MA, Kirby SJ, Waldock MJ. Concentrations of alkylphenol polyethoxylates entering UK estuaries. Mar Pollut Bull 1999; 38(2):109–18.

Brix R, Hvidt S, Carlsen L. Solubility of nonylhenol and nonylphenol ethoxylates On the possible role of micelles. Chemosphere 2001;44:759–63.

Brownawell BJ, Chen H, Zhang W, Westall JC. Sorption of non-ionic surfactants on sediment materials. Environ Sci Technol 1997; 31:1735–41.

Brunner PH, Capri A, Marcomini A, Giger W. Occurrence and behaviour of linear alkylbenze-sulphonates, nonylphenol, nonylphenol mono- and di-ethoxylates in sewage and sewage sludge treatment. Water Res 1988;22:1465–72.

Bruno F, Curini R, Di Corci A, Fochi I, Nazzari M, Samperi R. Determination of surfactants and some of their metabolites in untreated and anaerobically digested sewage sludge by subcritical water extraction followed by liquid chromatography-mass spectrometry. Environ Sci Technol 2002;36:4156–61.

Cano ML, Dorn PB. Sorption of an alcohol ethoxylate surfactant to natural sediments. Environ Toxicol Chem 1996;15(5):684–90.

Cano ML, Dorn PB. Sorption of two model alcohol ethoxylate surfactants to sediments. Chemosphere 1996;33(6):981–94.

Charles W, Ho G, Cord-Ruwisch R. Anaerobic bioflocculation of wool scouring effluent: the influence of non-ionic surfactant on efficiency. Water Sci Technol 1996;34(11):1–8.

Comber MHI, Williams TD, Stewart KM. The effects of nonylphenol on *Daphnia magna*. Water Res 1993;27:273–6.

Connell DW. Bioaccumulation behaviour of persistent organic chemicals with aquatic organisms. Rev Environ Contam Toxicol 1988; 101:117–54.

Crescenzi C, Di Corcia A, Samperi R. Determination of non-ionic polyethoxylate surfactants in environmental waters by liquid chromatography/electrospray mass spectrometry. Anal Chem 1995; 67:1797–804.

De Wolf W, Feijtel T. Terrestrial risk assessment for linear alkylbenzene sulfonate (LAS) in sludge-amended soils. Chemosphere 1998; 36:1319–43.

Di Corcia A. Characterisation of surfactants and their biointermediates by liquid chromatography-mass spectrometry. J Chromatogr, A 1998; 794:165–85.

Di Corcia A, Samperi R. Monitoring aromatic surfactants and their biodegradation intermediates in raw and treated sewages by solid-phase extraction and liquid chromatography. Environ Sci Technol 1994; 28:850–8.

Dodds EC, Goldberg L, Lawson W, Robinson R. Oestrogenic activity of certain synthetic compounds. Nature 1938;1:247–8.

Dorn PB, Rodgers JH, Dubey ST, Gillespie WB, Lizotte RE. An assessment of ecological effects of a C9-11 linear alcohol ethoxylate surfactant in stream mesocosm experiments. Ecotoxicology 1997;6:275–92.

Edwards DA, Adeel Z, Luthy RG. Distribution of non-ionic surfactant and phenanthrene in a sediment/aqueous system. Environ Sci Technol 1994;28:1550–60.

Eichhorn P, Rodrigues SV, Baumann W, Knepper TP. Incomplete degradation of linear alkylbenzene sulfonate surfactants in Brazilian surface waters and pursuit of their pola metabolites in drinking waters. Sci Total Environ 2002;284:123–34.

Ekelund R, Bergman A, Granmo A, Berggren M. Bioaccumulation of 4-nonylphenol in marine animals—a re-evaluation. Environ Pollut 1990;64:107–20.

Feitkenhauer H, Meyer U. Anaerobic digestion of alcohol sulfate (anionic surfactant) rich wastewater-batch experiments: Part I. Influence of the surfactant concentration. Bioresour Technol 2002a;82:115–21.

Feitkenhauer H, Meyer U. Anaerobic digestion of alcohol sulfate (anionic surfactant) rich wastewater-batch experiments: Part II. Influence of the hydrophobic chain length. Bioresour Technol 2002b;82:123–9.

Fendinger NJ, Begley WM, Mcavoy DC, Eckhoff WS. Measurement of alkyl ethoxylate surfactants in natural waters. Environ Sci Technol 1995;29:856–63.

Ferguson PL, Iden CR, Brownwell BJ. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. Environ Sci Technol 2001;35:2428–35.

Fernandez P, Alder AC, Suter MJF, Giger W. Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with postcolumn ion-pair formation. Anal Chem 1996;68:921–9.

Ferreira-Leach AMR, Hill EM. Bioconcentration and distribution of 4-tert-octylphenol residues in tissues of the rainbow trout (*Oncorhynchus mykiss*). Mar Environ Res 2001;51:75–89.

Field JA, Field MA, Poiger T, Siegrist H, Giger W. Fate of secondary alkane sulfonate surfactants during municipal wastewater treatment. Water Res 1995;29:1301–7.

Figge K, Schöberl P. LAS and the application of sewage sludge in agriculture. Tenside Surfactants Deterg 1989;26:122–8.

Fox K, Holt M, Daniel M, Buckland H, Guymer I. Removal of linear alkylbenzene sulfonate from a small Yorkshire stream: contribution to GREAT-ER project. Sci Total Environ 2000;251/252:265–75.

Fytianos K, Voudrias E, Papamichali A. Behaviour and fate of linear alkylbenzene sulfonate in different soils. Chemosphere 1998; 36:2741–6.

Games LM, King JE. Fate and distribution of a quarternary ammonium surfactant, octadecyltromethylammonium chloride (OTAC), in wastewater treatment. Environ Sci Technol 1982;16:483–8.

Garcia MT, Campos E, Sanchez-Leal J, Ribosa I. Effect of the alkyl chain length on the anaerobic biodegradability and toxicity of quaternary ammonium based surfactants. Chemosphere 1999;38:3473–83.

Garcia MT, Campos E, Sanchez-Leal J, Ribosa I. Ananerobic degradation and toxicity of commercial cationic surfactants in anaerobic screening tests. Chemosphere 2000;41:705–10.

Garcia MT, Ribosa I, Guindulain T, Sanchez-Leal J, Vives-Rego J. Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment. Environ Pollut 2001;111:169–75.

George AL. Seasonal factors affecting surfactant biodegradation in Antarctic coastal waters: comparison of a polluted and pristine site. Mar Environ Res 2002;53:403–15.

Giger W, Brunner PH, Schaffner C. 4-Nonylphenol in sewage sludge: accumulation of toxic metabolites from non-ionic surfactants. Science 1984;225:623–5.

Giolando St, Rapaport RA, Larson RJ, Federle TW, Stalmans M, Masscheleyn P. Environmental fate and effects of DEEDMAC: a new rapidly biodegradable cationic surfactant for use in fabric softeners. Chemosphere 1995;30(6):1067–83.

Gode P, Guhl W, Steber J. Environmental compatibility of fatty acid, alpha-sulfomethyl esters. Fat Sci Technol 1987;89:548–52.

Gonzalez-Mazo E, Honing M, Barcelo D, Gomez-Parra A. Monitoring long-chain intermediate products from the degradation of linear alkylbenzene sulfonates in the marine environment by solid-phase extraction followed by liquid chromatography/ion spray mass spectrometry. Environ Sci Technol 1997;31:504–10.

Gunther P, Pestemer W. Phytotoxicity of surfactants to higher plants. In: Hall JE, Sauerbeck DE, Hermit PL, editors. Effects of organic contaminants in sewage sludge on soil fertility, plants and animals; 1990. As cited in Jensen (1999) and Kloepper-Sams et al. (1996).

Gutendorf B, Westendorf J. Comparison of an array of in vitro assays for the assessment of the estrogenic potential of natural and synthetic estrogens, phytoestrogens and xenoestrogens. Toxicology 2001; 166:79–89.

Haigh SD. A review of the interaction of surfactants with organic contaminants in soil. Sci Total Environ 1996;185:161–70.

Hofer R, Jeney Z, Bucher F. Chronic effects of linear alkylbenzene sulfonate (LAS) and ammonia on rainbow trout (*Oncorhynchus mykiss*) fry at water criteria limits. Water Res 1995;29:2725–9.

Holt MS, Matthijs E, Waters J. The concentrations and fate of linear alkylbenzene sulphonate in sludge amended soils. Water Res 1989; 23:749–59.

Holt MS, Waters J, Comber MHI, Armitage R, Morris G, Newbery C. AIS/CESIO Environmental surfactant monitoring programme SDIA sewage treatment pilot study on linear alkylbenzene sulphonate (LAS). Water Res 1995;29:2063–70.

Holt MS, Fox KK, Burford M, Daniel M, Buckland H. UK monitoring study on the removal of linear alkylbenzene sulphonate in trickling filter type sewage treatment plants Contribution to GREAT-ER project #2. Sci Total Environ 1998;210/211:255–69.

Huber M, Meer U, Rys P. Biodegradation mechanisms of linear alcohol ethoxylates under anaerobic conditions. Environ Sci Technol 2000; 34:1737–41.

Jensen J. Fate and effects of linear alkylbenzene sulphonates (LAS) in the terrestrial environment. Sci Total Environ 1999;226:93–111.

Jobling SJ, Sumpter JP. Detergent components in sewage effluent are weakly oestrogenic to fish: an in vitro study suing rainbow trout hepatocytes. Aquat Toxicol 1993;27:361–72.

Jobling S, Sheahan D, Osborne JA, Matthiessen P, Sumpter JP. Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environ Toxicol Chem 1996;15:194–202.

Jobling S, Nolan M, Tyler CR, Brighty G, Sumpter JP. Widespread sexual disruption in wild fish. Environ Sci Technol 1998;32:2498–506.

John DM, House WA, White GF. Environmental fate of nonylphenol ethoxylates: differential adsorption of homologs to components of river sediment. Environ Toxicol Chem 2000;19:293–300.

Jones FW, Westmoreland DJ. Degradation of nonylphenolethoxyaltes during the composting of sludges from wool scour effluents. Environ Sci Technol 1998;32:2623–7.

Kibbey TCG, Hayes KF. Effects of surfactant concentration and sorbent properties on the sorption and transport of ethoxylated non-ionic surfactant mixtures. J Contam Hydrol 2000;41:1–22.

Kiewiet AT, de Beer KGM, Parsons JR, Govers HAJ. Sorption of linear alcohol ethoxylates on suspended sediment. Chemosphere 1996; 32:675–80.

Kile DE, Chiou CT. Water solubility enhancement of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. Environ Sci Technol 1989;23:832–8.

Kimerle RA, Swisher RD. Reduction of aquatic toxicity of linear alkylbenzene sulphonate (LAS) by biodegradation. Water Res 1977; 2:31–7.

Kloepper-Sams P, Torfs F, Feijtel T, Gooch J. Effects assessment for surfactants in sludge-amended soils: a literature review and perspectives for terrestrial risk assessment. Sci Total Environ 1996;185:171–85.

Klumpp E, Heitman H, Schwuger MJ. Interactions in surfactant/pollutant/-soil mineral systems. Tenside Surfactants Deterg 1991;28:441–6.

Knaebel DB, Federle TW, Vestal JR. Mineralisation of linear alkylbenzene sulphonate (LAS) and linear alcohol ethoxylate (LAE) in 11 contrasting soils. Environ Toxicol Chem 1990;9:981–8.

Knepper TP, Barcelo D, De Voogt P, editors. Analysis and fate of surfactants in the aquatic environment. Comprehensive Analytical Chemistry, vol. 40. Amsterdam: Elsevier; 2003.

Krueger CJ, Radakovich KM, Sawyer TE, Barber LB, Smith RL, Field JA. Biodegradation of the surfactant linear alkylbenzenesulfonate in sewage-contaminated groundwater: a comparison of column experiments and field tracer tests. Environ Sci Technol 1998;32:3954–61.

Larson R, Payne A. Fate of the benzene ring of linear alkylbenzene sulfonate in natural waters. Appl Environ Microbiol 1981;41:621–7.

Lee C, Russell NL, White GF. Development and validation of laboratory microcosms for anionic surfactant biodegradation by riverine biofilms. Water Res 1998;32:2291–8.

Lewis MA. Chronic and sublethal toxicities of surfactants to aquatic animals: a review and risk assessment. Water Res 1991;25:101–13.

Lewis M, Wee V. Aquatic safety assessment for cationic surfactants. Environ Toxicol Chem 1983;2:105–8.

Litz N, Doering HW, Thiele M, Blume HP. The behaviour of linear alkylbenzenesulfonate in different soils: a comparison between field and laboratory studies. Ecotoxicol Environ Saf 1987;14:103–16.

Mackay D. Correlation of bioconcentration factors. Environ Sci Technol 1982;16:274–6.

Mann RM, Bidwell JR. The acute toxicity of agricultural surfactants to the tadpoles of four Australian and two exotic frogs. Environ Pollut 2001; 114:195–205.

Mann RM, Boddy MR. Biodegradation of a nonylphenol ethoxylate by the autochthonous microflora in lake water with observations on the influence of light. Chemosphere 2000;41:1361–9.

Manzano MA, Perales JA, Sales D, Quiroga JM. The effect of temperature on the biodegradation of a nonylphenol polyethoxylate in river water. Water Res 1999;33:2593–600.

Marcomini A, Pojana G. Surfactant metabolites in environmental aqueous samples: a liquid chromatographic approach to the routine analysis of alcohol polyethoxylae biointermediates. Analusis 1997;25(7):M35–7.

Marcomini A, Capel PD, Lichtenseiger TH, Brunner PH, Giger W. Behaviour of aromatic surfactants and PCBs in sludge-treated soil and landfills. J Environ Qual 1989;18:523–8.

Margesin R, Schinner F. Biodegradation of the anionic surfactant sodium dodecyl sulfate at low temperatures. Int Biodeterior Biodegrad 1998;41:139–43.

Matthijs E, Holt MS, Kiewiet A, Rijs GBJ. Environmental monitoring for linear e, alcohol sulfate, and alkylbenzene sulfonate, alcohol ethoxylate, alcohol ethoxy sulfate, and soap. Environ Toxicol Chem 1999;18: 2634–44.

Maurer EW, Weil JK, Linfield WM. The biodegradation of esters of α-sulfo fatty acids. J Am Oil Chem Soc 1965;54:582–4.

McEvoy J, Giger W. Accumulation of linear alkyl benzenesulphonate surfactants in sewage sludges. Naturwissenschafen 1985;72:429–31.

McLeese DW, Zitko V, Sergeant DB, Burridge L, Metcalfe CD. Lethality and accumulation of alkylphenols in aquatic fauna. Chemosphere 1981;10:723–30.

Mezzanotte V, Bolzacchini E, Orlandi M, Rozzi A, Rullo S. Anaerobic removal of linear alcohol ethoxylates. Bioresour Technol 2002; 82:151–6.

Mieure JP, Waters J, Holt MS, Matthijs E. Terrestrial safety assessment of linear alkylbenzene sulfonate. Chemosphere 1990;21:251–62.

Mueller GC, Kim UH. Displacement of estradiol from estrogen receptors by simple alkylphenols. Endocrinology 1978;102:1429–35.

Nasu M, Goto M, Kato H, Oshima Y, Tanaka H. Study on endocrine disrupting chemicals in wastewater treatment plants. Water Sci Technol 2001;43(2):101–8.

Navas JM, Gonzalez-Mazo E, Wenzel A, Gomez-Parra A, Segner H. Linear alkylbenzene sulfonates and intermediate products from their degradation are not estrogenic. Mar Pollut Bull 1999;38(10):880–4.

Naylor CG. Environmental fate and safety of nonylphenol ethoxylates. Text Chem Color 1995;27:29–33.

Nishiyama N, Toshima Y, Ikeda Y. Biodegradation of alkyltrimethylammonium salts in activated sludge. Chemosphere 1995;30:593–603.

Orth RG, Powell RL, Kute G, Kimerle RA. Impact of sediment partitioning methods on environmental assessment of surfactants. Environ Toxicol Chem 1995;14:337–43.

Ou Z, Yediler A, He Y, Jia L, Kettrup A, Sun T. Adsorption of linear alkylbenzene sulfonate (LAS) on soils. Chemosphere 1996;32:827–39.

Pedersen SN, Christiansen LB, Pedersen KL, Korsgaard B, Bjerregaard P. In vivo estrogenic activity of branched and linear alkylphenols in rainbow trout (*Oncorhynchus mykiss*). Sci Total Environ 1999; 233:89–96.

Perales JA, Manzano MA, Sales D, Quiroga JA. Biodegradation kinetics of LAS in river water. Int Biodeterior Biodegrad 1999;43:155–60.

Potter TL, Simmons K, Wu J, Sanchez-Olvera M, Kostecki P, Calabrese E. Static die-away of a nonylphenol surfactant in estuarine water samples. Environ Sci Technol 1999;33:113–8.

Prats D, Rodriguez M, Varo P, Moreno A, Ferrer J, Berna JL. Biodegradation of soap in anaerobic digesters and on sludge amended soils. Water Res 1999;33:105–8.

Purdom CE, Hardiman PA, Bye VJ, Eno NC, Tyler CR, Sumpter JP. Estrogenic effects from sewage treatment works. Chem Ecol 1994;8: 275–85.

Renner R. European bans on surfactant trigger transatlantic debate. Environ Sci Technol 1997;31:316A–20A.

Reznickova I, Hoffmann J, Komarek K. Biodegradation of technical mixtures of oxyethylenated aliphatic alcohols in an aqueous environment. Chemosphere 2002;48:83–7.

Roghair CJ, Buijze A, Schoon HNP. Ecotoxicological risk evaluation of cationic fabric softener DTDMAC: I. Toxicological effects. Chemosphere 1992;24:599–609.

Salanitro JP, Diaz LA. Anaerobic biodegradability testing of surfactants. Chemosphere 1995;30:813–30.

Salanitro JP, Diaz LA, Kravetz L. Aerobic biodegradability of surfactants at low concentrations using an automated pressure transducer system. Chemosphere 1995;31:2827–37.

Scott MJ, Jones MN. The biodegradation of surfactants in the environment. Biochim Biophys Acta 2000;1508:235–51.

Singh RP, Gupta N, Singh S, Singh A, Suman R, Annie K. Toxicity of ionic and non-ionic surfactants to six microbes found in Agra, India. Bull Environ Contam Toxicol 2002;69:265–70.

Snyder SA, Keith TL, Verbrugge DA, Snyder EM, Gross TS, Kannan K, et al. Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. Environ Sci Technol 1999;33:2814–20.

Soto AM, Justicia H, Wray JW, Sonnenschein C. *p*-Nonylphenol: an estrogenic xenobiotic released from “modified” polystyrene. Environ Health Perspect 1991;92:167–73.

Steber J, Wierich P. The environmental fate of fatty acid α-sulphomethyl esters: biodegradation studies with a ^{14}C-labelled model surfactant. Tenside Surfact Deterg 1989;2:406–11.

Sweetman A, Rogers HR, Watts CD, Alcock R, Jones KC. Organic contaminants in sewage sludge – Phase III (Env 9031). Final Report to the UK Department of the Environment, Rep. No. DOE 3625/1, 1994.

Swisher RD. Surfactant biodegradation. Surfactant Science Series, vol. 18. New York: Marcel Dekker; 1987.

Szymanski A, Wyrwas B, Swit Z, Jaroszynski T, Lukaszewski Z. Biodegradation of fatty alcohol ethoxylates in the continuous flow activated sludge test. Water Res 2000;34:4101–9.

Takada H, Mutoh K, Tomita N, Miyadzu T, Ogur N. Rapid removal of linear alkylbenzenesulfonates (LAS) by attached biofilm in an urban shallow stream. Water Res 1994;28:1953–60.

Talmage SS. Environmental and human safety of major surfactants: alcohol ethoxylates and alkylphenol ethoxylates. A Report to the Soap and Detergent Association. Boca Raton, FL: Lewis Publishers; 1994.

Temart A, Carr G, Webb S, Versteeg D, Feijtel T. Marine risk assessment: linear alkylbenzenesulphonates (LAS) in the North Sea. Mar Pollut Bull 2001;42:635–42.

Thibaut R, Debrauwer L, Rao D, Cravedi JP. Urinary metabolites of 4-n-nonylphenol in rainbow trout (*Oncorhynchus mykiss*). Sci Total Environ 1999;233:193–200.

Thomas ORT, White GF. Metabolic pathway for the biodegradation of sodium dodecyl sulfate by Pseudomonas sp C12B. Biotechnol Appl Biochem 1989;11:318–27.

Tiehm A. Degradation of polycyclic aromatic hydrocarbons in the presence of synthetic surfactants. Appl Environ Microbiol 1994;60:258–63.

Tolls J, Sijm THM. A preliminary evaluation of the relationship between bioconcentration and hydrophobicity for surfactants. Environ Toxicol Chem 1995;14:1675–85.

Tolls J, Haller M, Seinen W, Sijm DTHM. LAS bioconcentration: tissue distribution and effect of hardness—implications for processes. Environ Sci Technol 2000;34:304–10.

Topping BW, Waters J. The monitoring of cationic surfactants in sewage treatment plants. Tenside Surfactants Deterg 1982;19:164–9.

Tsuda T, Takino A, Muraki K, Harada H, Kojima M. Evaluation of 4-nonylphenols and 4-tert-octylphenol contamination of fish in rivers by laboratory accumulation and excretion experiments. Water Res 2001; 35:1786–92.

Unilever. Effects on the growth of *Sorghum bicolour*, *Helianthus annuus* and *Phaselous aureus*. Contract study conducted for Unilever Research Port Sunlight laboratory, UK, by ICI, Brixham laboratory, UK. Study report no. BL/B/3078, 1987.

Utsunomiya A, Watanuki T, Matsushita K, Nishina M, Tomita I. Assessment of the toxicity of linear alkylbenzene sulfonate and quaternary alkylammonium chloride by measuring ^{13}C-glycerol in *Dunaliella* sp. Chemosphere 1997;35:2479–90.

VanGinkel CG. Complete degradation of xenobiotics surfactants by consortia of aerobic microorganisms. Biodegradation 1996;7(2): 151–64.

Verge C, Moreno A, Bravo J, Berna JL. Influence of water hardness on the bioavailability and toxicity of linear alkylbenzene sulphonate (LAS). Chemosphere 2000;44:1749–57.

Versteeg DJ, Feijtel TCJ, Cowan CE, Ward TE, Rapaport RA. An environmental risk assessment for DTDMAC in the Netherlands. Chemosphere 1992;24:641–62.

Waters J, Holt MS, Matthijs E. Fate of LAS in sludge amended soils. Tenside Surfactants Deterg 1989;26:129–35.

White GF. Multiple interactions in riverine biofilms-surfactant adsorption, bacterial attachment and biodegradation. Water Sci Technol 1995; 31(1):61–70.

Yadav JS, Lawrence DL, Nuck BA, Federle TW, Reddy CA. Biotransformation of linear alkylbenzene sulfonate (LAS) by *Phanerochaete chrysosporium*: oxidation of alkyl side-chain. Biodegradation 2001; 12:443–53.

Ying GG, Kookana RS. Endocrine disruption: an Australian perspective. AWA J Water 2002;29(6):53–7.

Ying GG, William B, Kookana R. Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. Environ Int 2002;28:215–26.

Ying GG, Kookana RS, Mallavarpu M. Release behaviour of triazine residues in stabilised contaminated soils. Environ Pollut 2005;134: 71–7.

Yoshimura K. Biodegradation and fish toxicity of non-ionic surfactants. J Am Oil Chem Soc 1986;63:1590–6.