

Review

The biodegradation of surfactants in the environment

Matthew J. Scott, Malcolm N. Jones *

School of Biological Sciences, University of Manchester, Oxford Road, Manchester M13 9PT, UK

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Abstract

The possible contamination of the environment by surfactants arising from the widespread use of detergent formulations has been reviewed. Two of the major surfactants in current use are the linear alkylbenzene sulphonates (LAS) and the alkyl phenol ethoxylates (APE). These pass into the sewage treatment plants where they are partially aerobically degraded and partially adsorbed to sewage sludge that is applied to land. The biodegradation of these and a range of other surfactants both in wastewater treatment plants and after discharge into natural waters and application to land resulting in sewage sludge amended soils has been considered. Although the application of sewage sludge to soil can result in surfactant levels generally in a range 0 to 3 mg kg⁻¹, in the aerobic soil environment a surfactant can undergo further degradation so that the risk to the biota in soil is very small, with margins of safety that are often at least 100. In the case of APE, while the surfactants themselves show little toxicity their breakdown products, principally nonyl and octyl phenols adsorb readily to suspended solids and are known to exhibit oestrogen-like properties, possibly linked to a decreasing male sperm count and carcinogenic effects. While there is little serious risk to the environment from commonly used anionic surfactants, cationic surfactants are known to be much more toxic and at present there is a lack of data on the degradation of cationics and their fate in the environment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Surfactant; Linear alkylbenzene sulphonate (LAS); Alkyl phenol ethoxylate (APE); Wastewater treatment; Sludge amended soil; Environment

1. Introduction

Detergents are formulations designed to have cleaning/solubilisation properties. These formulations consist of surface-active agents (surfactants) together with subsidiary components including builders (e.g. tripolyphosphate), boosters, fillers and auxiliary compounds. In terms of environmental issues the focus of concern has largely been on the effects of the surfactant in a detergent formulation, although there was a period when the increasing use of builders presented problems. From 1947 to 1970 the use of tripolyphosphates in the USA rose from approximately 100 × 10³ tons pa to 100 × 10⁶ tons pa before

Abbreviations: AS, fatty alcohol sulphates; AE, fatty alcohol ethoxylates; AES, alcohol ether sulphates; APE, alkyl phenol ethoxylates; DDT, dichloro diphenyl trichloroethane; DM, dialkyldimethylammonium chloride; DTDMAC, ditallowdimethylammonium chloride; FES, fatty acid esters; OECD, Organisation for Economic Cooperation and Development; LAB, linear alkylbenzene; LAS, linear alkylbenzene sulphonates; NP, nonyl phenol; NPE, nonyl phenol ethoxylate; PEC, predicted environmental concentration; PNEC, predicted no effect concentration; PT, propylene tetramer; SDS, sodium dodecyl sulphate; SAS, secondary alkane sulphonates; TM, alkyltrimethylammonium chloride; WWTP, wastewater treatment plant

* Corresponding author. E-mail: m.jones@fs1.scg.man.ac.uk

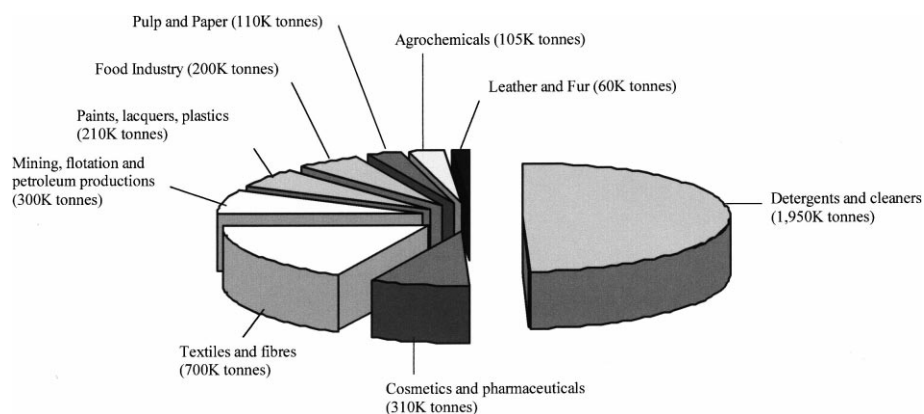


Fig. 1. Surfactant consumption in the USA, Japan and western Europe during 1982 [94].

the introduction of restrictive legislation [1]. In this review we will focus on the major surfactants which pass into the environment and the potential problems which can arise as a consequence. The bulk of the materials reaching the environment (soil and natural waters) do so from consumer products via the use of sewage sludge on land, effluents from wastewater treatment plants (WWTP) and industrial discharges into freshwater and marine sites. Fig. 1 outlines the major uses of surfactant in the USA, Japan and western Europe. Other sources of surfactant contamination are the use of surfactant dispersants for fuel oil spillages and surfactant-enhanced remediation of subsoil after spillage and contamination with non-aqueous liquids.

Historically, potential surfactant contamination of the environment followed the shift from the use of soap-based detergents to synthetic surfactants. The transition period was approximately the 30 years from 1940 to 1970 when the use of synthetics rose from 4.5×10^3 tons pa in the USA to approximately 4.5×10^6 tons pa, while the use of soap fell from 1.4×10^6 tons pa to 0.6×10^6 tons pa [1]. During this time there was also a transition from the use of solid domestic detergents (powders) to liquids. Until 1960 the major surfactant used in detergency was propylene tetramer benzene sulphonate (PT benzene). It was about this time when sewage treatment problems began to arise and foaming problems arose on rivers. PT benzene was being discharged into water systems and was found to be resistant to biodegradation by bacteria due to the branched alkyl chain. The prohibition of this non-biodegradable sur-

factant forced the switch to more biodegradable straight chain alkyl surfactants and now the major anionic surfactant in use is linear alkylbenzene sulphonate (LAS). The production of surfactants of various types in the USA, Japan and western Europe is shown in Fig. 2. The place of LAS in the detergent industry has been reviewed by Schoenkaes [2]. In 1994 the production of LAS in the USA, western Europe and Japan was 840×10^3 (metric) tons pa [3] although consumption is currently falling as new alternatives are introduced. LAS represent more than 40% of all surfactants used. It is not surprising that a large part of the literature is focussed on the environmental problems arising from LAS.

Another widely used class of surfactant is the alkyl phenol ethoxylates (APE), which are used in detergents, paints, pesticides, textile and petroleum recovery chemicals, metal working and personal products. Worldwide production of APE is 500×10^3 tons pa [4]. Commercial formulations usually contain mixtures of APE (different chains length and isomers) but with high proportions of nonyl and octyl alkyl groups. Restrictions on the use of APE have arisen since the discovery in 1984 that their breakdown products are more toxic to aquatic organisms than the APE themselves. Biodegradation of APE leads to the shortening of the ethoxylate chains to alkyl phenol carboxylates leading ultimately to nonyl and octyl phenols, which have low water solubility and adsorb to suspended solids and sediments. Nonyl phenol (NP) is approximately 10 times more toxic than its ethoxylate precursor [4]. It is known to mimic the effect of the hormone oestrogen. Nonyl

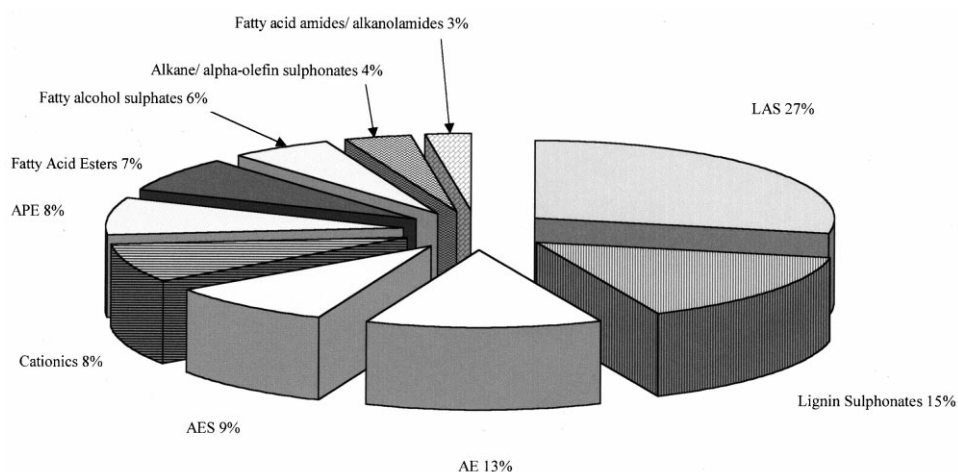


Fig. 2. Production of the different types of surfactants used in the USA, Japan and western Europe in 1982 [94].

phenolics in wastewater extracted from digested sewage sludge can pass into rivers. It has been hypothesised that endocrine disruptors may be responsible for a decreasing male sperm count, testicular and breast cancers [5]. Sublethal toxic effects of NP on zooplankton in natural waters interferes with their sex determination and development [6]. These problems are leading to bans and restrictions on the use of APE for household and industrial cleaning applications in Europe but not in the USA. In the US researchers are less convinced of the adverse effects of alkyl phenols, possibly because of differences in wastewater treatments in the USA which result in higher removal rates as compared to Europe [4].

As the above indicates, the major problems of surfactants in the environment arise from the two major classes of materials LAS and APE but in the case of the APE the environmental problems relate more to the biodegradation products rather than to the APE themselves. In this review we will concentrate largely on the LAS where effects relate directly to the surfactant.

2. Biodegradation and ecological impact of surfactants

Balson and Felix [80] described biodegradation as the destruction of a chemical by the metabolic activity of microorganisms. When reviewing the literature concerning the degradation of surfactants it is apparent that studies quote figures for primary and/or ul-

timate biodegradation. Primary degradation can be defined as to have occurred when the structure has changed sufficiently for a molecule to lose its surfactant properties. Ultimate degradation is said to have occurred when a surfactant molecule has been rendered to CO_2 , CH_4 , water, mineral salts and biomass.

LAS are generally regarded as biodegradable surfactants. Very high levels of biodegradation (97–99%) have been found in some WWTP using aerobic processes [7–9]. In contrast, APE are less biodegradable and values of 0–20% have been quoted [10] based on oxygen uptake and 0–9% based on spectroscopic techniques [10].

The mechanism of breakdown of LAS involves the degradation of the straight alkyl chain, the sulphate group and finally the benzene ring [11,12]. The breakdown of the alkyl chain starts with the oxidation of the terminal methyl group (ω -oxidation) through the alcohol, aldehyde to the carboxylic acid as follows (see Fig. 3). The reactions are enzyme catalysed by alkane monooxygenase and two dehydrogenases. The carboxylic acid can then undergo β -oxidation and the two carbon fragment enters the tricarboxylic acid cycle as acetylCo-A. It is at this stage that problems arise with branched alkyl chains, a side chain methyl group or a gem-dimethyl-branched chain cannot undergo β -oxidation by microorganisms and must be degraded by loss of one carbon atom at a time (α -oxidation).

The second stage in LAS breakdown is the loss of

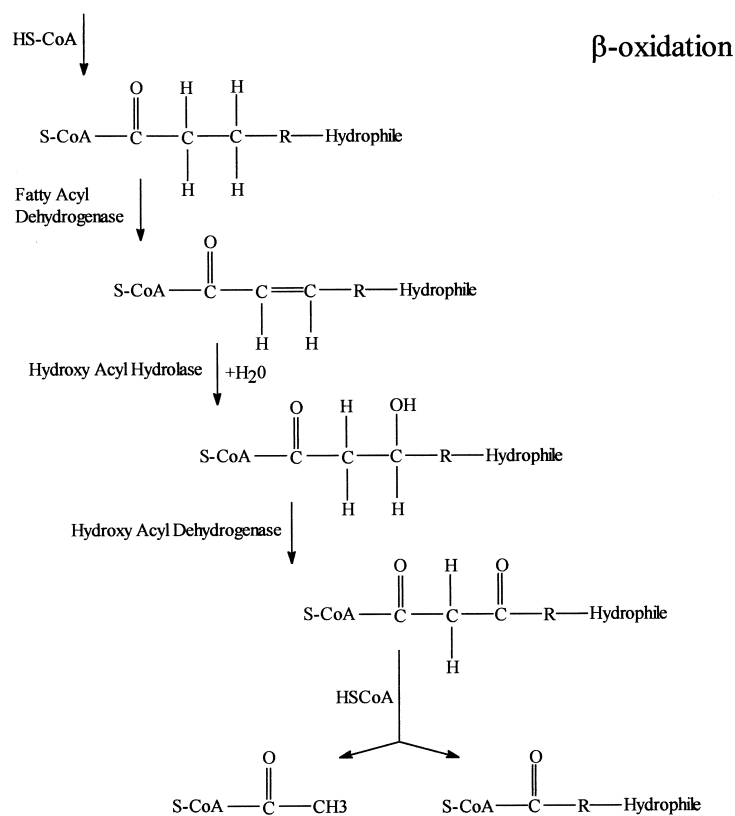
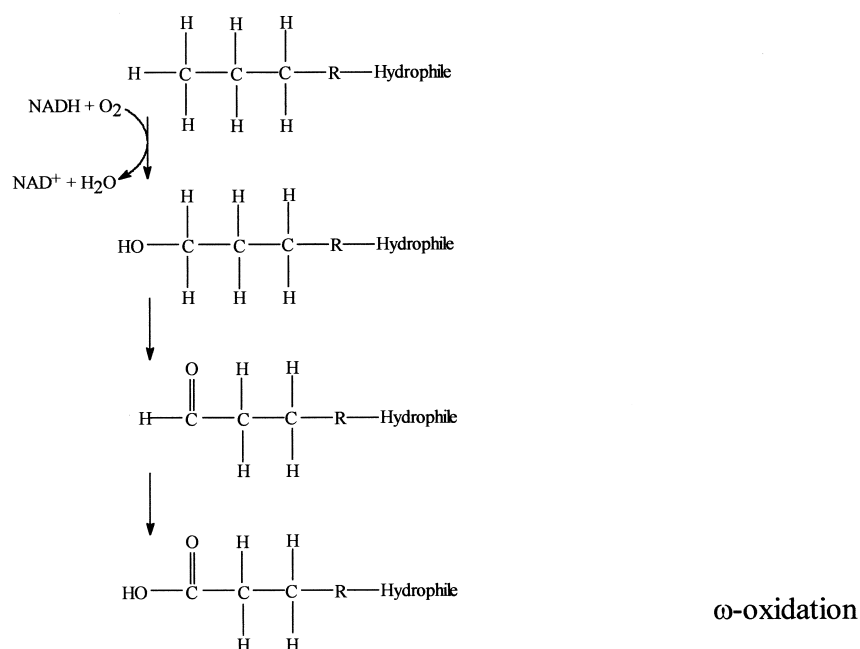


Fig. 3. The reaction pathways of ω - and β -oxidation of the alkyl chain during surfactant degradation [80].

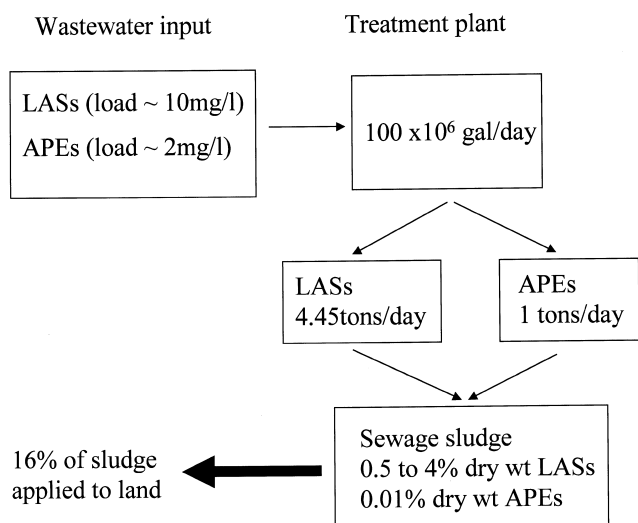
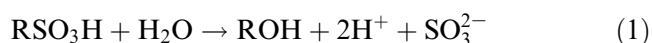


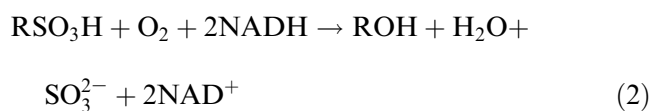
Fig. 4. Transport of surfactants through a WWTP. The figures will vary from one plant to another. The figures shown are approximate values taken from reported values (data from Dentel et al. [17]).

the sulphonate group, although there has been some discussion about the sequence of steps [11]. Three mechanisms have been proposed for desulphonation according to the following reactions.

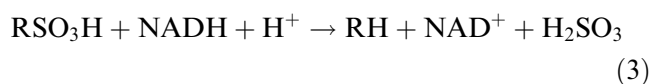
Hydroxyative desulphonation:



Monooxygenase catalysis under acid conditions:



Reductive desulphonation:



Whichever mechanism prevails the breakdown product of the LAS is sulphite which can be oxidised to sulphate in the environment.

The loss of the alkyl and the sulphonate group from LAS leaves either phenylacetic or benzoic acids. Microbial oxidation of phenylacetic acid can result in fumaric and acetoacetic acids and benzene can be converted to catechol [11].

Studies on the biodegradation of LAS and other surfactants by biofilms of bacterial populations isolated from riverine [13] and estuarine [14] sites have

been reported. A study of biodegradation of a range of anionic surfactants at a river site (river Ely, South Wales, UK) located near a sewage treatment plant outfall has been made [13]. Experiments were conducted in the laboratory using a population of bacteria isolated from river stone biofilms. Water collected at the outflow (BO), upstream (BU) and downstream (BD) of the site was incubated with the isolated bacteria. It was found that the reciprocal half-life (or 'die-away' time) for biodegradation of surfactants followed the sequence alkyl sulphates > alkyl ethoxy sulphates > secondary linear alkyl sulphates > primary alkane sulphonates > LAS, and that 'die-away' time of surfactants depended on the site in the sequence BO > BD > BU [13]. The ability of bacterial species in the population to biodegrade sulphonated surfactants was less widely distributed than the ability to biodegrade sulphate ester surfactants.

In a study of LAS biodegradation by bacterial cultures originating from an estuarine site (Krka river estuary, Croatian Mid Adriatic region; a highly stratified karstic estuary) it was found that the rate of biodegradation depended on the origin of the culture, temperature and the structure of the alkylbenzene group [14]. Cultures isolated from the freshwater layer of the river had a greater ability to degrade LAS than those from the underlying saline water layer. Degradation rates were faster for the longest alkyl chain LAS (in this study C₁₃), and slower for LAS isomers having the sulphophenyl group situated in the middle of the alkyl chain. The complete biodegradation of surfactants requires a consortium of bacteria due to the limited metabolic capacities of individual microorganisms [15]. The opportunity for commensalism (benefit to one microorganism) and synergism to develop exists in a consortium. Such interactive effects lead to more effective biodegradation than is possible by any individual microorganism. The biodegradation of LAS requires a four membered consortium, three members of which oxidise the alkyl chain but synergism amongst the four members was essential for mineralisation of the aromatic ring [16].

A large amount of surfactant is associated with sewage sludge solids. However, LAS are not biodegraded by either mesophilic or thermophilic anaerobic digestion. Various estimates of the load of LAS

and APE in a typical WWTP and their subsequent fate have been given by Dentel et al. [17]. Fig. 4 is based on data quoted by Dentel et al. [17]. Although there are wide ranges in some of the values, e.g. values quoted for the load of LAS in treatment plants range from 3 to 21 mg l⁻¹, it is clear that significant amounts of surfactant are transported into the environment from treatment plants. Dentel et al. [17] estimate a discharge of over 100 kg day⁻¹ of anionic surfactants and approximately 300 kg day⁻¹ of cationic surfactants from a 90 × 10⁶ gal day⁻¹ WWTP. It should also be noted that the presence of surfactants in water at concentrations below and above the critical micelle concentration can also lead to the solubilisation of other oil-soluble pollutants such as DDT and trichlorobenzene [18]. The problem of the analysis of surfactants in the aqueous environment has recently been reviewed by Lukaszewski [19]. With the introduction of new types of surfactants developed to replace ethoxylates such as alkyl polyglucosides it is necessary to have methods for their detection and for the detection of their breakdown products as well as improving existing methods for specific determination of different classes of anionic and non-ionic surfactants. The behaviour of LAS in sewage by using direct UV absorption spectra deconvolution has been described by Djellal et al. [20].

The assessment of risk to the environment from surfactant contamination and surfactant catabolites is an important and by no means a simple issue [21–23]. A study in the Netherlands [21] of the risk to the aquatic environment from a range of surfactants and soaps, placed the materials in the priority order LAS, alcohol ethoxylates, alcohol ethoxylated sulphates and soap. The study looked at the ratio of the parameters ‘predicted environmental concentration’ (PEC) at 1000 m below the sewage outfall to the ‘predicted no effect concentration’ (PNEC). The data were gathered from seven locations and supplied by Netherlands industries. For the surfactants the PEC/PNEC ratio was 0.05 but for soap it was almost 1. These results suggest that little risk to the aquatic environment is expected.

The risk assessment of LAS to terrestrial plants and animals reported by Mieure et al. [23] also concludes that there are adequate margins of safety in the use of wastewater for the irrigation of plant spe-

cies. The most vulnerable plant species are orchids and vegetables grown hydroponically (radish, Chinese cabbage and rice). Adverse effects on plant and animal species (earthworms *Eisenia foetids* and *Lumbricus terrestris*) were observed at LAS concentration of 10 mg l⁻¹, however LAS concentrations in wastewater effluents are in a range 0.09 mg l⁻¹ to 0.9 mg l⁻¹. These figures give a safety margin in a range 10 to 100. The effect of surfactant on plant growth from the use of sewage sludge is difficult to assess because in general the sludge promotes plant growth. Adverse effects on plant growth were observed at 392 µg g⁻¹ but long term monitoring at a range of 46 environmental sites gave LAS concentrations of < 3 µg g⁻¹. These figures give a safety margin of 131. For terrestrial animals the limit of no adverse effects was 235 µg g⁻¹ giving a safety margin of 78.

However, in looking at ecotoxicity from sewage effluents the less toxic surfactant residues and surfactant catabolites must be considered and this requires analytical tests for these entities [22]. The monitoring of LAS and their degradation products in the marine environment, especially from littoral zones, is more complex due to potential interference from other natural surfactants and other organic compounds [24]. Some of the problems of surfactant detection and estimation in the environment may be solved in the future by the use of specific biosensors. An optical biosensor for the determination of ionic surfactants based on the immobilisation of acrylodan labelled bovine serum albumin onto silanised silica optical fibre has been developed. It had a linear dynamic range from 5 to 60 µM and a response time of less than 30 s, although the long term stability of the biosensor needs improving [25].

The biodegradation of LAS is effected by a number of factors amongst which are the concentration of dissolved oxygen [26], complexing with cationic surfactants [27,28], the formation of insoluble calcium and magnesium salts [29], the presence of other organic contaminants [30,31] and the effect of LAS on the pH during aerobic degradation [32]. In sewage-contaminated groundwater the rates of LAS biodegradation increase with dissolved oxygen concentration and the longer alkyl chain homologues (C₁₂ and C₁₃) are preferentially biodegraded. However, the removal of LAS was found to be 2–3 times greater under laboratory conditions than in field tracer

studies [26]. The formation of LAS complexes with cationic surfactants (alkyltrimethylammonium chloride (TM) and dialkyldimethylammonium chloride (DM)) leads to complex adsorption onto river sediments [27]. The adsorption of complexes which form with molar ratios of LAS to cationic surfactant in the range 1:1 to 6:1 (with TM) and 1:1 to 2:1 (with DM) obey the Freundlich adsorption isotherm. The rates of biodegradation as measured over 14 days for 1:1 and 2:1 complexes relative to the rate of biodegradation of LAS (taken as 100%) were as follows: 2LAS:TM (56%), LAS:TM (36%), 2LAS:DM (31%) and LAS:DM (29%). The kinetics of biodegradation of LAS and other organic matter by mixed bacterial cultures as used in activated sludge treatment can be affected by LAS at high concentrations ($> 20 \text{ mg l}^{-1}$). This arises as a consequence of LAS decreasing the pH during aerobic degradation [32]. The highest rates of biodegradation are found for the longest alkyl chain homologues.

The biodegradation of APE by bacteria in seawater polluted with urban sewage is brought about by bacteria of the *Pseudomonas* genus of marine origin. Few other species of Gram-negative bacteria are able to degrade APE with nine-ten ethoxy groups. *Pseudomonas* strains degrade only down to four or five ethoxy groups, although other species of bacteria which are unable to degrade the long chain APE are able to degrade the APE with four or five ethoxy groups down to the two ethoxy group compounds [33].

3. Surfactants in sewage sludge

The literature concerning the fate of surfactants in sewage sludge amended soil is heavily biased towards the study of LAS with other surfactants receiving little or no attention.

Due to their amphiphilic nature surfactants in raw sewage can adsorb to the surface of resident particulate matter. Surfactants may also precipitate from solution in the presence of metal ions (particularly Ca^{2+}). Such behaviour may result in a significant proportion of the surfactant load of raw sewage being associated with the particulate fraction. A common initial step in a WWTP is the removal of particulate matter in primary settling tanks. Sludge

collected from these tanks is relatively rich in surfactant. Treatment of such sludge is commonly anaerobic digestion at elevated temperature. Many common surfactants used are easily biodegradable in aerobic conditions but due to restricted metabolic pathways the majority are not degradable under anaerobic conditions. Therefore, sludge treated anaerobically may still be relatively rich in surfactants post treatment. Matthews [34] reported that during 1977 of the 1.3 M tons of sewage sludge produced in the UK 45% was disposed of as a fertiliser to agricultural land. The remaining 55% was disposed of via landfill sites or incineration. Anaerobically digested sludge (dry weight) can contain 0.3–1.2% LAS [35–37]. The addition of anaerobically digested sewage sludge to agricultural land is a large potential source of LAS and other surfactants to the soil environment.

3.1. Linear alkylbenzene sulphonates

Berna et al. [38] reported that a significant proportion of LAS in raw sewage (10–35%) adsorbs to particulate matter. Sediment removed from primary settling tanks is relatively rich in LAS, with concentrations ranging from 5000–15 000 mg l^{-1} being reported [7,35,37,39,40].

The process of adsorption of LAS to particulate matter is primarily driven by the hydrophobic effect and specific or electrostatic interactions [41]. The extent of adsorption has been shown to be dependent upon a number of factors. Prats et al. [42] suggested that the type of LAS homologue present might be significant. Longer alkyl chains conferred greater hydrophobicity thus increasing adsorptive tendency. Painter [43] stated that for each carbon atom added to the alkyl chain a two- to three-fold increase in the K_a (association constant) for LAS was observed.

The characteristics of the water carrying the effluent can have a significant effect upon the adsorption of LAS. Berna et al. [38] showed that water hardness could significantly alter partition coefficients of LAS in raw sewage. Waters high in Ca^{2+} concentrations yielded sludge from primary settling tanks that contained 30–35% of the LAS concentration of the raw sewage, but relatively soft water yielded only 10–20%.

The presence of high concentrations of LAS in sewage sludge leaving the WWTP is dependent

Table 1
Fate and persistence of surfactants in sludge amended soils

Application form	Location	Surfactant/ derivative	Soil concentration post application (mg kg ⁻¹)	Monitoring period	Final soil concentration (mg kg ⁻¹)	Half-life (days)	Author
Sludge onto soil	Spain	LAS	22.4	6 months	3.1	not reported	Prats et al. [42]
Sludge onto soil	Switzerland	LAS	45	12 months	0.7	9	Marcomini et al. [53]
Surfactant onto soil	Germany	NP LAS	4.7 not reported	2 months	0.5 not reported	5–25 summer	Litz et al. [92]
Sludge onto soil	Germany	LAS	16	6 months 76 days	0.19	68–117 winter 13	Figge and Schöberl [93]
Surfactant onto soil	USA	LAS	27 0.05	106 days 40 days	0.44 not reported	26 1.1–3.6	Knaebel et al. [86]
Sludge onto soil	Spain	LAE LAS	0.05 16	90 days	0.3	26	Berna et al. [52]
Sludge onto soil	UK	LAS	53	170 days	not reported	33	
Sludge onto soil	UK	LAS	2.6–66.4 (estimated cumulative load)	5–6 months	< 1	7–22	Waters et al. [51], Holt et al. [44]
Sludge onto soil	UK	LAB	0.3–9.5 (estimated cumulative load)	55 days	0–0.38	15	Holt and Bernstein [45]
Composted wool scour sludge	Australia	NPE	14 000	14 weeks	1200	not reported	Jones and Westmoreland [81]

upon the type of treatment the sludge undergoes. It is well reported that LAS is readily degradable under aerobic conditions. The alkyl chain oxidation at the terminal methyl group (ω -oxidation) requires the presence of molecular oxygen. Subsequent degradation of the chain (β -oxidation) is followed by oxidative fission of the aromatic ring to give sulphonate-substituted dicarboxylic acids. Finally, desulphonation of ring degradation products occurs [23,44–46,89]. The ω -oxidation of the alkyl chain and the cleavage of the benzene ring require molecular oxygen, therefore under anaerobic conditions degradation via these pathways is unlikely. At present no evidence exists for comparable degradation of LAS under anaerobic conditions [47–49]. Holt et al. [44] stated that sewage sludge is generally digested under anaerobic conditions. Jensen [50] compiled results

from ten studies of LAS in treated sewage sludge from various locations around the world. He found that sewage sludge that had been aerobically treated had LAS concentrations of 100–500 mg kg⁻¹ dry weight. This was considerably lower than levels found in anaerobically treated sludge (5000–15 000 mg kg⁻¹ dry weight). Therefore, the extent of LAS contamination of sewage sludge is greatly dependent upon the individual WWTP and the method of sludge digestion it employs.

During the past 15 years the fate of LAS in sludge amended soils has received a great deal of attention. Table 1 shows a summary of the results reported from studies examining the fate and persistence of surfactants. The most comprehensive studies were carried out by Holt et al. [44], Holt and Bernstein [45] and Waters et al. [51]. These studies examined

LAS and LAB (un-reacted precursor of LAS constituting approximately 1–3% of LAS concentration) in agricultural sludge amended soils. Comparisons were made between estimated cumulative soil load of LAS/B (calculated from previous sludge application amounts and LAS/B contents of those sludges) and soil LAS/B concentration. These studies encompassed 51 fields on 24 farms situated in the Thames Water Authority region of southern England. The sample sites included different soil types (clay, silt clay, clay loam and sandy loam) and agricultural use (arable or pasture); sludge of different compositions and origins (homologue distributions; 2.7–34% dry solids; 15–341 mg LAS l⁻¹ sludge); frequency of application (0–6 annually), post application soil concentrations (0–293 mg LAS kg⁻¹ soil) and methods of sludge application (subsurface injection or surface dressing). Results showed that the 42 fields that had not been treated within 1987 (the year of the studies) exhibited soil concentrations of LAS of 0–2.5 mg kg⁻¹ (83% containing < 1 mg kg⁻¹). For the majority of sites this constituted a > 98% removal of LAS when compared to the cumulative estimated load. Nine fields that had been treated within 1987 showed soil concentrations of 0.2–19.8 mg kg⁻¹ compared to estimated cumulative loads of 15–206 mg kg⁻¹, losses of LAS constituted 70–90% of the estimated cumulative load. Five fields that were monitored in a time course to determine disappearance rates of LAS showed degradation half-lives to be approximately 7–22 days. Holt et al. [44] concluded that degradation 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 upon degradation rates. LAS homologue distribution showed no significant changes post application suggesting no differential degradation. LAB was found to have a soil residence half-life of approximately 15 days. Fields with applications during 1989 (year of sampling) exhibited concentrations of 5–390 µg kg⁻¹ soil and fields not receiving an application during 1989 generally had concentrations < 5 µg kg⁻¹ (constituting 99% loss).

Berna et al. [52] monitored LAS concentrations in a sludge amended Spanish grapevine farm and a vegetable farm. From relatively high sludge application concentrations of 7000–30 200 mg kg⁻¹ dry weight initial soil concentrations of 16 and 53 mg kg⁻¹

soil respectively were observed. After a period of 90 and 170 days the soil concentration of LAS was 0.3 mg kg⁻¹, calculated half-lives were 26 and 33 days.

Marcomini et al. [53] observed that after an initial period of LAS removal soil concentrations appeared to level out and not decrease further. Soil levels post sludge application rapidly fell from 45 mg kg⁻¹ soil to 5 mg kg⁻¹, from which point no further significant changes were observed. The authors suggested that this observation might be due to the LAS being incorporated into the soil particles and/or being associated with the soil organic matter. This effectively rendered them unavailable to the microorganisms responsible for their biodegradation.

From the studies carried out it is evident that once applied to the aerobic soil environment LAS is readily degradable with a half-life of 1–87 days. Once removed from the anaerobic environment of sludge digestion and/or storage, bacteria begin to metabolise LAS. Rapid metabolism leads to relatively short half-lives of LAS. Most authors who have carried out monitoring of LAS residence in sludge amended soils agree that due to their relatively high biodegradability in the aerobic environment there exists little chance of accumulation of LAS in soil.

3.2. Soap

Soap is still a commonly used surfactant. Steber and Berger [54] reported that C₁₂–C₁₈ soaps are readily available to microbes. However, the poor solubility of soaps precipitated with metal ions influences biodegradation rates. Soaps are susceptible to precipitation within hard water environments. Schöberl et al. [55] reported that Sturm-tested sodium soap salts exhibited mineralisation rates of 80–90% whereas calcium soap salts were significantly less biodegradable with only 67% mineralised. Association of soaps with metal ions leads to precipitation of a significant quantity of soap. Precipitation leads to sedimenting of soap in the primary settling tanks at WWTP. Therefore, depending upon the hardness of water at an individual WWTP sewage sludge may contain a significant amount of soap. Anaerobic degradation of soap is an important factor in determining the effectiveness of WWTP and the degradation of these compounds. The main degradation pathway involved

in soap breakdown is the β -oxidation of the alkyl chain [54]. This step does not require the presence of molecular oxygen and therefore anaerobic conditions should not hinder soap degradation. Steber and Weirich [56] placed a $^{14}\text{C}_{16}$ soap in an anaerobic bioreactor for 28 days and observed $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ production. Results suggested that the soap was 92–97% degraded during that time period. Birch et al. [48] observed a 79–94% degradation of sodium palmitate during a 3–4 week period of anaerobic digestion of sludge. The data suggest that soap is readily biodegradable in both aerobic and anaerobic environments and therefore is ultimately treatable within the conditions and residence time of wastewater within a WWTP.

3.3. Secondary alkane sulphonates

When compared to LAS, SAS have had few direct measurements made upon their biodegradability. Little is known about their degradation pathways and their resistance to biodegradation in the WWTP. In the aerobic environment SAS are considered to be readily biodegradable. Swisher [10], Schöberl et al. [55] and Painter [43] have all reported rapid primary degradation of SAS with >90% removal in less than 3 days. Löttsch et al. [58] incubated uniformly labelled C_{17} SAS and observed 61% ultimate degradation, producing CO_2 . Neufahrt et al. [59] incubated $^{14}\text{C}_{17}$ SAS for 3 days observing 47% degradation to CO_2 and 25% incorporation into the biomass. Both studies suggest that SAS are readily ultimately degradable under aerobic conditions. Steber and Berger [54] assuming that SAS had similar degradation characteristics to LAS stated that SAS might not be available during anaerobic digestion. Bruce et al. [57] observed that SAS concentrations did not appear to fall during anaerobic digestion of sludge. It is suggested that as LAS and SAS have similar molecular characteristics their degradation pathways may be similar. Therefore, a lack of molecular oxygen will inhibit primary ω -oxidation of the alkyl chains and oxidative desulphonation. Like LAS, SAS is readily degradable in aerobic conditions but a proportion may adsorb to particle surfaces in the raw sewage and be removed in primary settling tanks. If such sludge is not aerobically digested then SAS concentrations in sludge may well be rela-

tively high. Like LAS it is thought that once amended to a soil SAS in sludge will be rapidly biodegraded in the aerobic conditions, suggesting chance of accumulation in soil is remote. However, until monitoring studies of SAS in sludge amended soils are performed such statements have to be acknowledged as conjecture.

3.4. Fatty acid esters

Fatty acid esters (FES) are readily degradable under aerobic conditions. Gode et al. [60] observed a 99% primary degradation of FES in an OECD (Organisation for Economic Cooperation and Development) screening test, and a 76% ultimate degradation in a closed bottle test. Similar results were reported by Steber and Weirich [61] who outlined possible degradation mechanisms including ω -oxidation of the terminal alkyl group followed by β -oxidation of the alkyl chain and a subsequent desulphonation of the resultant short chained carboxy ester sulphonate. Steber and Berger [54] point out that this is a similar degradation mechanism as that for LAS and therefore FES may be poorly degradable under anaerobic conditions. Maurer et al. [62] observed FES concentrations in an anaerobic digester, commenting that no primary degradation was observed within the 30 days experimental period. Steber and Weirich [61] observed that of a ^{14}C labelled FES digested anaerobically for 4 weeks less than 5% of the label was observed as CO_2 or CH_4 production. This suggests that any FES associated with sludge particles may pass through a WWTP being relatively untreated. Steber and Weirich [61] did report that FES in anaerobically treated sewage sludge was quickly degraded when applied to aerobic soils.

3.5. Fatty alcohol sulphates

Fatty alcohol sulphates (AS) are rapidly aerobically degraded. Swisher [57] reported primary degradation figures of 100% after 1+ day(s). Steber et al. [63] reported primary degradation rates of 95–98% in a 5 days period. Schöberl et al. [55] reported primary degradation figures of 99% for an OECD test and ultimate degradation figures of 64–96% in a closed bottle test. Swisher [57] stated that as biodegradation of AS is so rapid it could be assumed that the pro-

cesses involved in the primary and ultimate degradation are effective in a broad range of microorganisms. The degradation of AS is thought to involve the enzymatic cleavage of the sulphate ester bonds to give inorganic sulphate and a fatty alcohol. The fatty alcohol is oxidised to an aldehyde and subsequently to a fatty acid with further oxidation via the β -oxidation pathway. AS and their degradation products are ultimately biodegradable, Thomas and White [64] observed that of ^{14}C SDS 70% was degraded to CO_2 and all the remaining 30% was incorporated into the microbial biomass, i.e. 100% of the SDS was utilised for either energy or biomass production. Under anaerobic conditions digestion is rapid, as none of the degradation pathways requires the presence of molecular oxygen. Swisher [10] reported >90% removal of AS in anaerobic test system. Steber et al. [63] reported >90% release of ^{14}C labelled AS as CO_2 and CH_4 . Birch et al. [48] reported values of 88% for a similar experiment involving degradation of stearyl sulphate. AS appear to be readily bioavailable under both aerobic and anaerobic conditions and easily degradable both primarily and ultimately. Therefore, treatment in a WWTP is entirely sufficient to eliminate AS and little possibility exists for these surfactants to reach the environment via sludge amendment.

3.6. Alcohol ether sulphates

Alcohol ether sulphates (AES) degrade well under aerobic conditions with comparable primary and ultimate degradation rates to AS. Fischer [65] reported primary degradation rates of 96% in 30 days in a closed bottle test; Schöberl et al. [55] reported ultimate degradation rates of 98–99% in the OECD screening test. Steber and Berger [54] suggested three possible degradation pathways for AES. (i) ω/β -oxidation of the alkyl chain; (ii) cleavage of the sulphate bond; and (iii) cleavage of an ether bond. Swisher [57] stated that all three mechanisms are realised. Hales et al. [66] suggested that ether cleavage is the predominant mechanism but all three have been shown to occur [66–68]. Very little data have been published concerning the fate of AES in the anaerobic environment. Examination of the degradation pathways suggests that cleavage of the sulphate bond and ether bonds is possible without the pres-

ence of molecular oxygen. Oba et al. [69] reported significant primary degradation of AES when anaerobically digested. Painter [43] reported high AES primary degradation in an anaerobic digester and a septic tank over a period of 6–8 months. Itoh et al. [70] revealed CO_2 and CH_4 production from AES digestion, suggesting ultimate biodegradation if at a somewhat reduced rate. Such data suggest that AES are readily bioavailable in both aerobic and anaerobic environments.

3.7. Cationic surfactants

Cationic surfactants having a positive charge have a strong affinity for the surface of particulates in sewage sludge, which are predominantly negatively charged. Kupfer [71] and Topping and Waters [72] observed that in activated sludge 95% of the cationic surfactants were adsorbed to the surface of particulate matter. Huber [73] observed that 20–40% cationic surfactants in primary settling tanks were associated with particulate matter. Cationic surfactants are considered very biologically available [74]. Games et al. [75] reported half-lives of 2.5 h for octadecyltrimethylammonium chloride in wastewater. Krzeminski et al. [76] reported alkylbenzyltrimethylammonium chloride to be ultimately biodegradable with >80% of the ^{14}C labelled compound being released as $^{14}\text{CO}_2$. Sullivan [77] stated that ditallowdimethylammonium chloride (DTDMAC) in activated sludge was predominantly associated with the particulate matter and after digestion 40% was released as $^{14}\text{CO}_2$. The adsorption of cationic surfactants to particulate matter increases the importance of understanding the anaerobic degradation processes. However, literature concerning cationic surfactant fate under anaerobic conditions is scarce. Janicke and Hilge [78] reported that quaternary ammonium salts exhibited little or no degradation under anaerobic conditions. Battersby and Wilson [79] observed that concentrations of 200 mg l^{-1} hexadecyltrimethylammonium bromide inhibited the production of methane, suggesting that such concentrations are inhibitory to the resident microbes. However, van Ginkel [74] states that at the concentrations that cationic surfactants are found in raw sewage there appears to be no effect upon wastewater treatment processes. Aerobic degradation pathways for quaternary am-

monium salts are suggested in van Ginkel [74]. However, no pathways for anaerobic degradation exist within the literature. The initial oxidation of the surfactant cannot take place without the presence of molecular oxygen. Therefore, it can be assumed that cationic surfactants are not anaerobically biodegradable either because of a lack of appropriate metabolic pathways and/or a possible toxic effect of the surfactant upon the relevant anaerobic microorganisms.

3.8. Alkyl phenol ethoxylates

APE undergo almost complete primary degradation in the presence of oxygen [80]. Jones and Westmoorland [81] observed nonyl phenol ethoxylate (NPE) degradation in composted sludge collected from wool scouring. They observed a 98% net primary degradation of NPE in 100 days. ω/β -oxidation was attributed to the degradation of the alkyl chain, but little evidence was observed of any degradation of the aromatic ether bond. This observation was supported by the build up of NP towards the end of the monitoring period. Kravetz et al. [82] observed a similar difference in the degradation rates of the breakdown products of APE. Radiolabelled APE (^3H labelled aromatic constituent; ^{14}C labelled alkyl chain) was placed in a bioreactor and terminal degradation products monitored. Twenty nine percent of the ^3H label was converted to water but 58% of the ^{14}C was converted to CO_2 . This suggests that though rapid primary degradation takes place, degradation products are not as available to microorganisms. The polyoxyethylene chain appears to be readily biodegradable but the NP derivative appears more resilient. Due to their amphiphilic nature APE and their breakdown products show an affinity for particulate surfaces, and a significant proportion is observed within the sludge fraction. Concentrations of APE reported in the literature appear to be much higher in anaerobically digested sludge (900–1100 mg kg^{-1} [53]) than in aerobically digested sludge (0.3 mg kg^{-1} [83]). The degradation of APE and their breakdown products appears restricted in the anaerobic environment. Without the presence of molecular oxygen the initial ω -oxidation of the alkyl chain cannot take place, restricting breakdown. Therefore, elevated concentrations of APE and its breakdown de-

rivatives are present in relatively high concentrations in sludge and can enter the environment via application to agricultural land. However, Marcomini et al. [53] observed that sewage sludge amended soil exhibited a rapid drop in NP concentration post application with approximately 80% degradation within 3 weeks, suggesting that within the aerobic soil environment NP will not accumulate.

3.9. Fatty alcohol ethoxylates

Fatty alcohol ethoxylates (AE) were developed as an eco-friendly alternative to APE. A great deal of literature exists upon the biodegradability of these compounds. Linear AE are considered readily biodegradable, Kravetz et al. [84] observed >80% primary degradation in 28 days for linear AE and 40% for branched AE. Balson and Felix [80] suggest that the breakdown mechanism of these compounds involves the initial hydrophobe–hydrophile scission of the AE yielding a hydrophobe and a polyalkoxylate, effectively achieving primary degradation. The hydrophobe then undergoes ω/β -oxidation. Klotz [85] reported AE concentrations in sludge of <700 mg kg^{-1} . Such concentrations suggest that AE is not entirely degradable under anaerobic conditions. However, present understanding is somewhat limited and too sparse to conclude such a fact. Knaebel et al. [86] showed linear alcohol ethoxylates (LAE) to be readily bioavailable in a variety of different soil types, suggesting that aerobic soil amended with sludge rich in AE will not accumulate the surfactant.

4. Surfactants in wastewater

Surfactants can reach the environment as a result of discharge from WWTP into rivers and estuaries or by direct discharge of raw sewage. Raw sewage discharge is increasingly rare in most industrial nations although small amounts are still disposed of in this way. The fate of all organic pollutants in WWTP is determined by several processes including gas exchange with the atmosphere, sorption to suspended solids and aerobic and anaerobic biodegradation [87]. Efficient treatment in WWTP will result in discharge of very low levels of surfactants into the environment. For LAS, SAS and the cationic surfac-

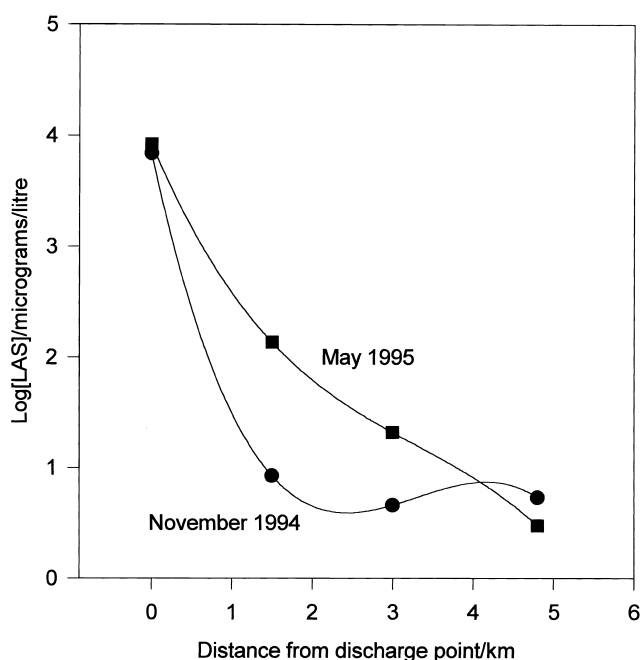


Fig. 5. The decrease in water concentration of LAS in the river Llobregat as a result of biodegradation/bioadsorption after the discharge of raw sewage from Caserres (Barcelona, Spain) as a function of distance from the discharge point.

tant DTDMAC sorption to sewage sludge accounts for 26, 16 and 23 to 53% respectively of the influent materials, while biodegradation removes 73, 43 and 36 to 43% respectively. The effluent from the WWTP leaves only 1% LAS, <1% SAS and 6–41% DTDMAC. The surfactants will undergo further biodegradation in the environment that together with dilution will reduce their toxicological effects further.

Studies of particular WWTP in Germany have been reported by Schröder et al. [88,89]. These cover discharge from WWTP on the rivers Rur [88] and Angerbach, a small tributary in the vicinity of Düsseldorf [89]. In the latter study the WWTP served a population of approximately 59 000 plus an industrial equivalent of 10 000 and the total plant capacity was 25 000 m³ of water. The LAS concentrations in the influent peaked during daytime at around 19.00 h at approximately 3500 µg l⁻¹, for AES the peak was 4500 µg l⁻¹ and for alcohol sulphates (AS) 600 µg l⁻¹. Monitoring of the surfactant influent and effluent concentrations enabled elimination rates to be calculated for anionic surfactants. These were found to be 99.7% (LAS), 99.9% (AS) and 99.99% (AES).

It is clear from these studies [88,89] and the data reported by Alder et al. [87] for various WWTP that anionic surfactant elimination is highly efficient in modern WWTP, but somewhat less so for cationic surfactants. This should not however, be cause for complacency, the removal of constituents in detergent formulations such as fluorescence whitening agents, naphthalene sulphates used in chemical, pharmaceutical and textile industries and also the organotin compounds in marine antifouling paints such as tributyltin, is much less efficient. In the case of naphthalene sulphates 95% of these pollutants is still present in WWTP effluents [87].

Direct discharge of raw sewage is becoming increasingly rare, but a study of the Llobregat river near Barcelona (Spain) where raw sewage from Caserres is discharged, showed that the rate of biodegradation of LAS was rapid provided the flow conditions in the river were adequate [90]. Fig. 5 shows the decrease in concentration of LAS (on a log scale) as a function of the distance from the discharge point of the sewage. There is a rapid decrease in concentrations of LAS in the river water by 1.5 km from the discharge point particularly in winter months when the water flow in the river is high (75 m³ min⁻¹). In summer months (flow rate 4.5 m³ min⁻¹) the decrease is less marked. At 4.8 km from the discharge point the concentrations are similar in both seasons and correspond to approximately 0.06% of the discharge concentration. It should be noted that the decreases in concentration relate to both biodegradation and the loss due to adsorption on river sediments and suspended solids in the raw sewage.

The concentrations of LAS in surface water of the North Sea, between 1 and 70 km from the coast, were measured by Proctor and Gamble in February 1989. The results together with those of further measurements, starting from the mouth of the river Scheldt up to 15 km offshore, made in October 1989 were reported in 1991 [91]. The LAS concentrations in these studies ranged from <0.05 µg l⁻¹ to 9.4 µg l⁻¹. The salinity of the water is a major factor controlling the LAS concentration in the marine environment. LAS adsorbs on river sediments in estuaries and the settling rates of sediments increase with salinity when the river water mixes with the seawater. The decreases in surfactant levels due to salinity are much greater than predicted due to dilution. Stal-

mans et al. [91] conclude that typical LAS concentrations in the North Sea will be lower than $1 \mu\text{g l}^{-1}$. Taken in the context of margins of safety to marine organisms, the LC_{50} values for various species are as follows: cod (*Gadus morrhua*) 1 mg l^{-1} , flounder (*Platichthys flesus*) 1.5 mg l^{-1} , plaice (*Pleuronectes platessa*) 5 mg l^{-1} , oyster 0.025 mg l^{-1} and pink shrimp $19\text{--}154 \text{ mg l}^{-1}$, even for the most sensitive organisms (e.g. oyster) the safety margin is 25.

5. Conclusions

Examination of the data available suggests that raw sewage passing through a modern WWTP has a significant proportion of its surfactant load removed. Aerobic treatment processes appear to provide ideal conditions for rapid primary and ultimate biodegradation via a consortium of bacteria. Wastewater effluent released into the environment appears to have had its surfactant load reduced to an extent that lethal effects on aquatic organisms are negligible. Safety margins exist in excess of 25 for a variety of organisms. Problems associated with degradation products of APE, particularly NP, have led in recent years to a reduction in APE usage with an agenda towards eventual replacement by more ultimately degradable substitutes. Meanwhile it is acknowledged that release of the more recalcitrant NP may be implicated in the problems experienced from environmental oestrogen mimics.

From the data available it is evident that LAS, SAS, FES, cationic surfactants, APE and AE are all relatively resistant to degradation in anaerobic environments. As anaerobic digestion is the predominant treatment of sludge from primary settling tanks, and the amphiphilic nature of surfactants promotes their adsorption to particle surfaces in sewage, there appears an opportunity for surfactants to pass through a WWTP relatively untreated. Application of sludge to agricultural land may provide a large source of surfactants to the soil environment. However, it appears that once re-introduced into an aerobic environment, such as soil, the surfactants are once again readily bioavailable. From studies on LAS, APE (and its derivatives) and FES, it can be concluded that some surfactants are not anaerobically degradable during sludge treatment, but are rap-

idly degraded when applied to aerobic soils. In the literature it is suggested that SAS and AE will be readily available in the aerobic soil environment, however there is a severe lack of relevant field studies available to support such a statement. Of greater worry is the lack of data concerning the degradation of cationic surfactants and the oestrogen mimicking properties of APE. Cationic surfactants, though readily biodegradable in aerobic environments, are toxic even at low concentrations. Therefore application to agricultural soil may have detrimental effect to the soil biota. APE is readily primarily degradable aerobically, however NP, one of the primary degradation products has been implicated as an environmental oestrogenic compound. NP has a strong affinity for soil particles and is less biodegradable than APE. At present the authors could find little published literature concerning the oestrogen mimicking properties of NP in sludge amended soils, this is a field that needs further research. Also failure of WWTP to remove more effectively other constituents present in wastewater arising from detergents (builders, whiteners, blueing and bleaching agents, etc.) is a cause of some concern.

Three major routes of sewage sludge disposal exist in the UK, application to soil, landfill and incineration. Pressure from environmentalists and rising costs are gradually making landfill and incineration less attractive. This combined with increasing amounts of sludge produced, is increasing the pressure on agricultural application. It appears that surfactant application to aerobic soils is quite safe due to rapid biodegradation rates. However, the temptation to dispose of sludge on non-agriculture soils should be carefully investigated. Soils that are anaerobic may not be appropriate sites for amendment. Such soils may exhibit accumulation of surfactants as biodegradation is retarded and may result in surfactant contamination of the environment.

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