

Surfactants in sludge-amended agricultural soils: a review

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Abstract Surfactants are included in different detergent formulations and are one of the most ubiquitous and important families of organic compounds. Although the generic term applies to a great number of products, 80% of their demand is covered by only ten types of compounds. The global surfactant market volume size is more than 18 million tons per year. Large quantities of surfactants are continuously released into the environment, where they can or cannot be degraded depending on their structure. The alkylbenzenesulphonate (LAS) is the most widely used surfactant. LAS can be degraded under aerobic conditions but is persistent in the environment under anaerobic conditions. Surfactants may enter the terrestrial environment through several routes, with the use of sewage sludge as fertiliser on agricultural land being by far the most important. High concentrations of surfactants and their degradation products may affect the biota. On the other hand, due to their amphiphilic nature, surfactants may interact both with inorganic as well as organic contaminants affecting their bioavailability.

Keywords Surfactants · Environment · Degradation · Agricultural · Bioavailability

Introduction

Surfactants (surface-active agents) together with subsidiary components such as builders (e.g., tripolyphosphate), boosters, and auxiliary compounds are included in the formulation of detergents (Smulders 2001; Kreinfeld and Stoll 1997). In terms of environmental issues, the focus of concern is largely on the effects of surfactants from detergent formulations in the ecosystems, although there was a period several years ago when the increasing use of builders also presented environmental problems, until the introduction of restrictive legislation.

The presence of both hydrophobic and hydrophilic groups in each molecule is a fundamental physical property of surfactants, which allows these compounds to form micelles in solution. It is the formation of micelles in solution that gives surfactants their detergency and solubilization properties. The concentration of surfactants in water at which surfactant molecules aggregate into clusters (micelles) is known as the critical micelle concentration (CMC) (Rosen 2004).

Historically, potential pollution of the environment due to surfactants followed the shift from the use of soap-based detergents to synthetic surfactants (Hill et al. 1997). The transition period was approximately from 1940 to 1970 when the use of synthetics rose ca. three orders of magnitude, while the use of soap fell to less than a half. During this time, there was also a partial 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 appeared in wastewater treatment plants and rivers. PT benzene was being discharged into water systems and was found to be resistant to

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biodegradation by bacteria due to the branched alkyl chain. The prohibition of use of this non-biodegradable surfactant forced the switch to more biodegradable straight chain alkyl surfactants and now the major anionic surfactant being employed is linear alkylbenzene sulphonate (LAS) (Fischer 1982; Balson and Felix 1995; Swisher 1987).

After use, large quantities of detergents and their components are released into aquatic and terrestrial environments. LAS may enter the terrestrial environment by several routes, mainly through sludge amendments and pesticide applications. It is to be noted that formulation of pesticides for crop protection include surfactants, as happens with detergent formulations. However, in the last decades, the use of sewage sludge as fertiliser on agricultural land is by far the dominating input for soils. The load of LAS in sewage sludge may be considerable with concentrations of more than 10 g/kg dry weight (Jensen 1999). Therefore, LAS and its metabolites may appear in appreciable concentrations in sludge-amended soils. On the other hand, it has been estimated that 5% of LAS produced in the United States reach the aquatic environment (Liwarska-Bizukojc et al. 2005), where concentrations at $\mu\text{g/L}$ levels have been found, mainly due to the discharge of wastewater treatment effluents into surface waters.

The increasing use of sludge as soil organic amendment and pesticide application points out the relevance of the study of the behaviour of surface-active substances in agricultural soils. A review of the literature concerning the characteristics of surfactants, their transport and transformations in wastewater treatment plants, and their fate, once in the terrestrial environment, is provided.

Uses and consumption of surfactants

Surfactants are one of the most widely used families of organic compounds, being used in different formulations in a lot of industries like cosmetic, personal care, household, painting, coating, textile, dyes, polymer, food, agrochemical, and oils. 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. At concentrations above the critical micelle concentration (CMC) level, surfactants have the ability to solubilize more hydrophobic organic compounds than would be dissolved in water alone.

Types of surfactants

Surface-active agents have a characteristic molecular structure consisting of a structural group that has a very little attraction for water, known as a hydrophobic group, together with a group that has strong attraction for water,

called hydrophilic group. This is known as an amphiphilic structure. The hydrophobic group is usually a long-chain hydrocarbon, and the hydrophilic group is an ionic or highly polar group. According to the nature of the hydrophilic group, surfactants are classified as: anionic, cationic, nonionic, and amphoteric. The most used surfactants and their acronyms are shown in Table 1.

The hydrophilic and hydrophobic groups of the different types of surfactants as well as the structures of the most important compounds are shown in Table 2.

Uses of surfactants

Surfactants are one of the most ubiquitous and important families of organic compounds. In fact, life in earth is possible because special kinds of surfactants are present in all living cell membranes. Surfactants in different formulations are being used in almost all industries like cosmetic, personal care, household, painting, coating, textile, dyes, polymer, foodstuff, agrochemical, oils, and in relation with the environmental care, in applications like wastewater treatment (Castro et al. 2005).

A brief summary of surfactants development starting with soap, whose manufacture was described by the Sumerians as long ago as 2500 BC (Smulders 2001), is shown in Table 3.

Surfactants are widely used because of their two essential properties: their ability to reduce the surface or interfacial tension, and their capacity to solubilize water-insoluble compounds.

At present, the generic term *surfactant* applies to a great number of surface-active products. However, 80% of their demand is covered by a group of less than ten types of products, LAS, lauryl ether sulphate (LES), and alcohol ethoxylates (AEO) being the main ones (see Table 1), and

Table 1 Acronyms of surfactants

Acronym	Name
LAS	Linear alkylbenzene sulphonate
LES	Lauryl ether sulphate
FAS	Fatty alcohol sulphates
FAES	Fatty alcohol ethoxylate sulphates
CTAC	Cetyl trimethyl ammonium chloride
DODAC	Diocetadecyl dimethyl ammonium chloride
AEO	Alcohol ethoxylates
APEO	Alkylphenol ethoxylates
FAEO	Fatty acid ethoxylates
APG	Alkylpolyglycosides
CAPB	Cocamidopropyl betaine
CAHS	Cocamidopropyl hydroxysultaine

Table 2 Type of surfactants

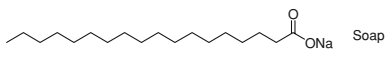
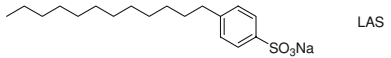
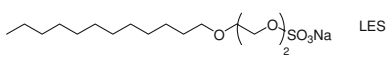
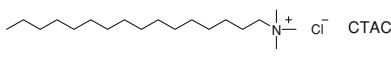
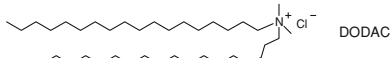
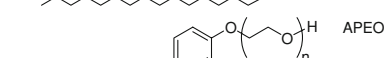
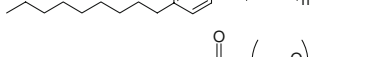
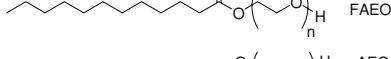
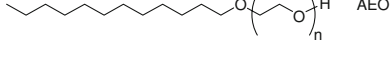
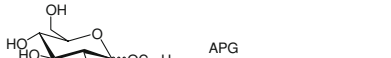
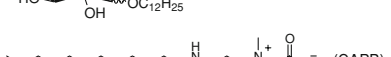
Surfactants	Alkyl tail	Polar head	Example
Anionic	C ₈ –C ₂₀ straight or branched-chain	–COOH	 Soap
	C ₈ –C ₁₅ alkylbenzene residues	–SO ₃ Na	 LAS
	C ₈ –C ₂₀ straight-chain ethoxylated	–OSO ₃ Na	 LES
Cationic	C ₈ –C ₁₈ straight-chain	–N(CH ₃) ₃ Cl	 CTAC
	C ₈ –C ₁₈ straight-chain	–N(CH ₃) ₂ Cl	 DODAC
Non-ionic	C ₈ –C ₉ alkylphenol residues	–(CH ₂ CH ₂ O) _n –OH n: 4–22	 APEO
	C ₈ –C ₂₀ straight of branched-chain	–COO(CH ₂ CH ₂ O) _n –OH n: 4–22	 FAEO
	C ₈ –C ₂₀ straight of branched-chain	–(CH ₂ CH ₂ O) _n –OH n: 2–22	 AEO
	C ₈ –C ₂₀ straight of branched-chain	Glucose	 APG
Amphoteric	C ₁₀ –C ₁₆ amidopropylamine residue	–N ⁺ (CH ₂) ₂ CH ₂ COO [–]	 (CAPB)
	C ₈ –C ₁₈ straight-chain	–N ⁺ (CH ₂) ₂ CH ₂ CH(OH)CH ₂ SO ₃ [–]	 (CAHS)

Table 3 Surfactants landmarks

Year	Surfactants development
2500 BC	Sumerians manufactured soap
1907	Soap commercial manufacture
1928	First anionic synthetic detergent
1946	Branched alkylbenzene sulphonate
1948	Non-ionic surfactants
1950	Cationic surfactants
1954	Anionic–nonionic combinations
1960	Linear alkylbenzene sulphonate (LAS)
1991	Gemini surfactants (Zana et al. 2004)

the surfactant that still has the highest consumption worldwide, namely soap.

The global surfactant market volume size is about 18 million tons (2003), with an overall rough value of 13 billion Euros (approx. 19 billion US\$). North America is the biggest surfactant market in the world with 35% of the total; Asia–Pacific follows next with 29%; Western Europe consumes 23%; while the rest of the world accounts in value for 13%. The global surfactant market considered by end-user applications shows that 40% of the

market is household detergents, followed by textile auxiliaries and personal care products (Hauthal 2004).

The surfactants volume forecast for the household detergent sector estimated for the period 2001–2012 shows an increase of 20% consumption for the industrialized countries in comparison with 70% for the future demands in Asia–Pacific countries (Liwarska-Bizukojs 2005). The world surfactants consumption in 2003 is shown in Fig. 1.

Anionics are the earliest and the most common surfactants that are not only used as detergents, but also widely

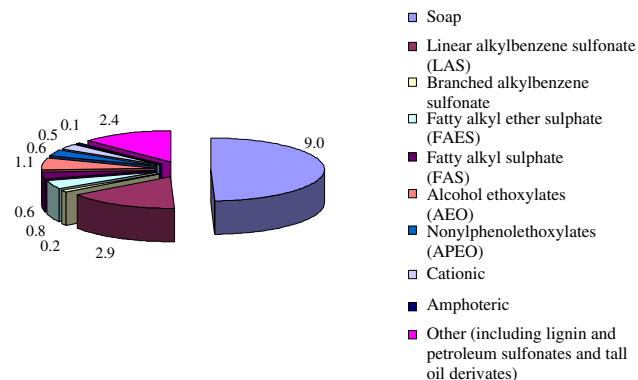


Fig. 1 World surfactants consumption in million tons (2003). Adapted from Liwarska-Bizukojs (2005)

applied in many fields of technology and research. They are usually considered to be the “workhorse” in the detergency world. They have been successfully employed to enhance the efficacy of the active ingredients in pharmaceutical and agriculture formulations, cosmetics, biotechnological compounds, and in several industrial processes. In some countries, particularly in the Asia-Pacific region and Latin America, the ecologically questionable branched alkylbenzene sulphonates are still in use. However, due to their limited biodegradability, it is only a matter of time before they are substituted by the already dominant linear type (LAS).

The increased use of dishwashing liquids and shampoos, and surfactant-based bath preparations—mainly in Asia—are the major contributory factors to the annual growth rate of 4.5% for LES. Fatty alcohol sulphates (FAS) will undoubtedly also increase in importance due to the substitution of traditional soap by synthetic surfactants offering higher performances.

Non-ionic surfactants have low sensitivity to water hardness and pH and are frequently used in mixtures with ionic surfactants resulting in beneficial associations. One of the major reasons for an annual growth rate of 4% for AEO is the substitution of ecologically questionable alkylphenol ethoxylates (APEO), which are still being used in some parts of the world.

Carbohydrate-based surfactants production is expected to grow visibly in the coming years. Alkylglycosides (APG, Table 2) are non-ionic surfactants with remarkable properties (Menger and Keiper 2000). In industrial scale, they are prepared from fatty alcohols and carbohydrates and are gradually replacing the other known non-ionic surfactants derived from the petrochemical industry. Combinations of FAS with APG in dishwashing liquid formulations are expected to prevail in the market. There is an increasing demand for APG both in the detergent market and in the cosmetics field. Due to their excellent biodegradability and the absence of toxic effects, food elaboration, polymer manufacture, and solubilization of biological membranes are some of the wide spectrum of their possible applications (Kreinfeld and Stoll 1997).

According to the different types of industries, Fig. 2 outlines the major uses of surfactants in the USA, Japan, and Western Europe (Scott and Jones 2000).

Analysis of surfactants in environmental matrices

The analytical methods for the determination of surfactants in environmental matrices have been continuously improved with regard to reproducibility, selectivity, and sensitivity over the last few years.

The main problem in the analysis of surfactants is that they tend to concentrate at interfaces due to their

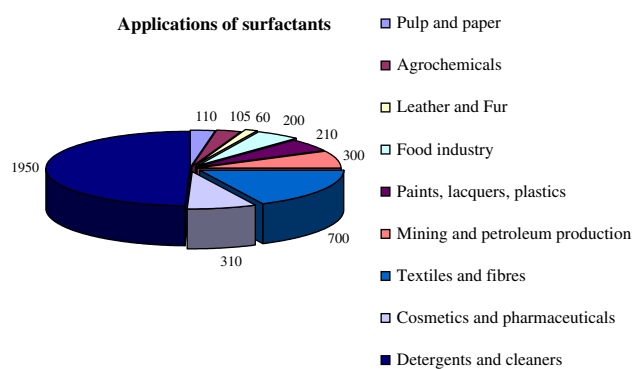


Fig. 2 Surfactant consumption (million tons) in the USA, Japan, and Western Europe. Adapted from Scott and Jones (2000)

amphiphilic nature. Consequently, losses of surfactants from aqueous solutions occur because of adsorption onto laboratory apparatus or suspended particles. Especially for matrices like sewage sludge, sediments, and biological samples, the quantitative recovery of the analytes becomes a major problem.

Fertilization of agricultural land with sewage sludge (see section “Surfactants in sludge-amended soils”) has resulted in the need to monitor surfactant concentrations in sludge-amended soils. Samples are usually collected from the soil’s upper 5 cm with a stainless steel corer, dried at 60°C, pulverized, and stored at 4–8°C in the dark (Marcomini et al. 1989a).

The method of choice for the extraction of surfactants from sewage sludge, sediments and soils is solid-liquid extraction (SLE). In most cases, however, further purification of the extracts is necessary prior to quantitative determination. LAS are desorbed from sewage sludge, either in a non-continuous procedure by extraction into chloroform as ion pairs with methylene blue (McEvoy and Giger 1986) or in a continuous procedure by the application of a Soxhlet apparatus and addition of solid NaOH to the dried sludge in order to increase extraction efficiency (Marcomini and Giger 1987). Heating of sludge or sediment samples in methanol under reflux for 2 h is also sufficient to extract LAS with recoveries of 85% (Matthijs and De Henau 1987).

The concentrations of surfactants in environmental samples are usually below the limit of the analytical method. Therefore, preconcentration is necessary before analysis. Interfering substances from the matrix have to be removed in an additional prepurification step prior to quantitative determination of the surfactants.

Anionic surfactants are efficiently concentrated at reversed-phase (RP) materials consisting of silica gel modified with alkyl groups of different chain lengths or graphitized carbon black (GCB). LAS have been extracted by C2 (Field et al. 1992), C8, (Marcomini and Giger 1987;

Trehy et al. 1990) or C18-silica gels (Kikuchi et al. 1986; Leon et al. 2000; Heinig et al. 1998; Sarrazin et al. 1997).

Marcomini et al. (1993a) developed a method for the simultaneous determination in water of LAS and nonylphenol ethoxylates (APEO) as well as their metabolites, sulphophenyl carboxylates (SPC) and nonylphenoxy carboxylates (NPEC), respectively. Wastewater or river water samples are adjusted to pH 2 with HCl and passed through C18 cartridges. The adsorbed analytes are eluted with methanol.

The earliest attempts to analyze surfactants in the environment relied on nonspecific analytical methods, such as colorimetry and titrimetry; the main disadvantage of these methods is that, apart from surfactants, other interfering organic compounds from the environmental matrices are recorded too, resulting in systematic errors. Nevertheless, colorimetric and titrimetric methods are still widely used for determination of anionic, nonionic, and cationic surfactants because of their easy handling and the need of relatively simple equipment.

Anionic surfactants are determined with methylene blue. The procedure is based on the formation of ion pairs between the cationic dye methylene blue and anionic surfactants, which are extractable into chloroform. The concentrations of anionic surfactants are determined colorimetrically at 650 nm after separation of the organic phase (DIN 1980). Other anionic organic compounds also form extractable complexes with methylene blue resulting in high values for methylene blue active substances (MBAS). On the other hand, a problem with the previous method is the presence of cationic substances, which lead to low values because of formation of ion pairs with anionic surfactants.

The ultimate goal in a detergent's environmental analysis is the quantification of individual compounds separated from all their isomers and/or homologues. Chromatographic methods like HPLC, GC, or SFC are amongst the most powerful analytical instruments with regard to separation efficiency and sensitivity. Because of the low volatility of surfactants, HPLC is used far more often than GC. Since the launch of atmospheric pressure ionization (API) interfaces, LC-MS coupling is increasingly used for determination of surfactants.

The majority of HPLC applications in the determination of anionic surfactants are only concerned with the analysis of LAS, the most used surfactants in present detergent formulations. Individual homologues of LAS are typically separated on reversed-phase columns with a NaClO₄-modified mobile phase using UV or fluorescence detection. Application of C-18 columns with gradient elution results in the separation not only of the LAS homologues but also of their isomers (Matthijs and De Henau 1987; Marcomini and Giger 1987; Marcomini et al. 1989b; Vogt et al. 1995).

However, short-chain alkyl-bonded reversed phases like C-8 (Marcomini and Giger 1987; Ahel and Giger 1985a; Leon et al. 2000; Ceglarek et al. 1999; Di Corcia et al. 1991) and C-1 columns (Castles et al. 1989), or long-chain C-18 phases with isocratic elution (Nakae et al. 1980; Holt et al. 1989), eluted the isomers of every single LAS homologue as one peak. Thus, the interpretation of the chromatograms becomes easier because of a greatly reduced number of peaks. Fluorescence detection is more selective and more sensitive than UV detection resulting in lower detection limits. Detection limits of 2 µg/L for water using fluorescence detection (Castles et al. 1989) compared to 10 µg/L for water using UV detection have been reported for determination of LAS by HPLC.

Simultaneous determination of LAS and their main metabolite, SPC, was enabled by LC-MS with electrospray ionization (ESI) interface. Problems with high salt loads of the mobile phase due to the ion pair reagent have been overcome by incorporation of a suppressor between the LC column and the mass spectrometer (Knepper and Kruse 2000).

A LC-MS method for the determination of LES and FAS was introduced by Popenoe et al. (1994). After separation on a C8 column, the analytes are determined by ion spray LC-MS. The mass chromatograms obtained give information about both the distribution of the alkyl homologues and distribution of the oligomeric ethoxylates as well.

The main nonionic surfactants as indicated before are AEO, APEO, and recently, APG. The hydrophobic part of AEO consists of *n*-alkanols with chain lengths between 8 and 20; typical AP are branched-chain octyl- or nonylphenol, and APG typically have alkyl groups with chain lengths in the range of 8–18. The degrees of polymerization of the polyethoxylate chains of AEO and APEO vary from 3 to 40 ethoxy units, while the average polymerization degree of APG is in the range of 1.3–1.7 moles glucose per mole of fatty alcohol. Giger et al. (1984) described a reversed-phase HPLC method for the determination of APEO on a C-8 column with isocratic water/methanol elution and UV detection at 277 nm. Under these conditions, the homologous compounds of alkylphenol ethoxylates series are separated into two peaks. Normal phase HPLC is mostly applied to obtain information about the ethoxylate chain distribution of APEO. Aminosilica columns with gradient elution and UV detection are well suited to determine the individual oligomers of APEO (Ahel and Giger 1985a, b; Marcomini and Giger 1987).

Fluorescence detection is also used for the simultaneous determination of LAS and APEO as well as their corresponding metabolites, SPC and NPEC, respectively, by reversed-phase HPLC and gradient elution (Marcomini et al. 1993a, b).

HPLC analysis of APG has also been carried out with C-8 (Steber et al. 1995) or C-18 columns by use of a refractive index detector (Spilker et al. 1996) or a conductivity detector after the addition of 0.3 mol/L NaOH to the eluate in a postcolumn reactor (Steber et al. 1995).

Several LC–MS methods using an ESI interface have been published for the analysis of APEO and AEO. The formation of crown ether-type complexes between the ethoxylate chain and cations like NH_4^+ or Na^+ leads to efficient ion formation of the APEO and AEO surfactants during the electrospray process (Loyo-Rosales et al. 2003; Ferguson et al. 2001; Cohen et al. 2001). By use of a C-18 HPLC column, APEO and AEO are separated according to their aliphatic chain lengths. In the subsequent MS analysis, coeluting ethoxylate homologues are individually detected because of their differences of 44 mass units ($\text{CH}_2\text{CH}_2\text{O}$, m/z 44) (Cohen et al. 2001).

Surfactants in sludge-amended soils

As stated, surfactants are widely used in formulations in many different industries such as personal care, household, agrochemicals, paints, mining, petroleum, paper. Laundry detergents, cleaning agents, and personal care products are by far the largest class of surfactant-containing products for domestic use. After use, they are mainly discharged into municipal wastewater, which enters sewage treatment plants. On the other hand, agricultural pesticides have to be formulated using surfactants in order to dissolve the active compounds into a hydrophilic system and in part they are discharged directly into the soil or reach it after some time because of rain or irrigation water. The different ingredients of a detergent formulation are stopped, modified, or eliminated there by biodegradation or adsorption. Consequently, in the case of insufficient biological degradability they are potential sources of environmental pollution.

Biodegradation of surfactants

Surfactants can be degraded mainly under aerobic conditions. Some of them are persistent under anaerobic conditions, such as LAS. APEOs are partially degraded in anaerobic conditions to form nonyl and octyl phenols, which are persistent and have shown estrogenic activity to organisms such as fish.

High concentrations of surfactants and their degradation by-products may affect the biota. The environmental risk posed by surfactants and their degradation by-products can be assessed in terms of toxicity based on the comparison of the predicted environmental concentration and the predicted no-effect concentration. Nevertheless, more toxicity

data are needed for terrestrial risk assessment of surfactants and their degradation products (Guang-Guo 2006).

LAS are generally regarded as biodegradable surfactants. It is to be noted that very high levels of biodegradation (97–99%) have been found in some wastewater treatment plants (WWTP) that use aerobic processes. In contrast, APEO are less biodegradable (0–20%) (Swisher 1987).

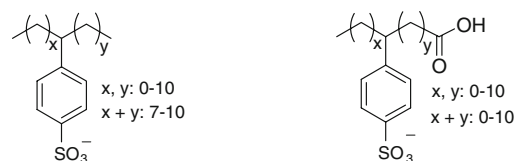
The mechanism of breakdown of LAS involves the degradation of the linear alkyl chain, the sulphonate group, and finally the benzene ring. The biodegradation pathways for LAS have been reviewed (Swisher 1987; Schöberl et al. 1988) and it is shown, as stated previously, that in general terms, their degradation pathway may be split into four different processes:

1. Oxidative conversion of one or two methyl groups of the alkyl chain into a carboxyl group (ω -oxidation);
2. Oxidative shortening of the alkyl chain by two carbon units' β -oxidation;
3. Oxidative ring splitting;
4. Cleavage of the carbon-sulphur bond, that is, sulphate liberation.

Many bacteria and a few fungi are reported to be able to partly degrade LAS. The complete biodegradation of surfactants requires a mixture of bacteria due to the limited metabolic capacities of individual microorganisms. The biodegradation of LAS requires a four member consortium, three members of which oxidize the alkyl chain, but synergism amongst the four members is essential for mineralization of the aromatic ring. The breakdown of the alkyl chain starts with the oxidation of the terminal methyl group to form sulphophenyl carboxylate (SPC). Degradation rates are faster for the longest alkyl chain LAS, and slower for LAS isomers having the sulphophenyl group situated in the middle of the alkyl chain (Fig. 3).

Perales et al. (2003) corroborate the metabolic route of LAS biodegradation proposed by several authors, in which the LAS first undergoes oxidation of the extreme terminal of the alkyl chain with the consequent formation of SPCs of long chain and subsequently a successive shortening of the alkyl chain takes place.

The biodegradation of LAS is affected by a number of factors amongst which are the concentration of dissolved



Linear alkylbenzene sulfonates (LAS)

Sulphophenyl carboxylates (SPC)

Fig. 3 General structure of LAS and SPC

oxygen, aggregation with cationic surfactants, formation of insoluble calcium and magnesium salts, presence of other organic contaminants and effect of LAS on the pH during aerobic degradation (Abd-Allah and Srorr 1998; de Wolf and Feijtel 1998; Fox et al. 1997; García et al. 1996; Krueger et al. 1998; Utsunomiya et al. 1997, 1998). The rates of LAS biodegradation increase with dissolved oxygen concentration and the longer alkyl chain homologues (C12 and C13) are preferentially biodegraded.

When discussing the further fate of LAS and its degradation product SPC in the coastal environment, it has to be taken into account that the overall metabolic activity of estuarine and marine microbial communities is generally lower compared with that of continental waters. The precipitation of LAS as magnesium and calcium salts might become the principal elimination route because of high concentrations of both ions in these environmental settings. Removal of dissolved LAS from the water phase may likewise occur by sorption onto particulate matter and sediments (Rubio et al. 1996). In the latter compartment, LAS is likely to be accumulated due to the low or null dissolved oxygen content near the bottom.

The highly polar character of SPC and the lack of a hydrophobic moiety, as present in the LAS molecule, which is essential for interaction with the organic matter, largely impede an accumulation of SPC in sediments. Whereas anionic surfactants have been found at mg/kg levels in riverine and lake sediments, the corresponding degradation products were not detected in any instance (Trehy et al. 1996).

García et al. (2005) studied the sorption of LAS homologues on anaerobic sludge and determined the distribution of each one between aqueous and solid phases and, consequently, its availability. The surfactant concentration in the liquid phase decreased significantly as the LAS chain length increased, and a linear relationship was found between the partition coefficient and the alkyl chain length. Negligible primary biodegradation of the LAS homologues and isomers was detected in anaerobic conditions. SPC analysis by LC–MS confirmed the poor transformation of the LAS molecules. However, significant differences on the extent of the biogas production were observed depending on the LAS homologue. Thus, the shortest LAS homologues (C10-LAS and C12-LAS) produced a certain extent of biogas production inhibition, whereas C14-LAS enhanced the production. The inhibition observed for most of the hydrophilic compounds could be related to its higher concentration in the aqueous phase. C14-LAS seems to promote the availability of organic compounds associated with the anaerobic sludge and consequently their mineralization.

SPCs present net rates of mineralization in seawater that are comparable to those of the compounds utilized as

reference in biodegradation assays in seawater (aniline, sodium benzoate). Thus, they can be considered highly susceptible to mineralization by the microbiota present in seawater (Perales et al. 2003).

APEOs undergo almost complete primary degradation in the presence of oxygen. Though rapid primary degradation takes place, degradation byproducts are not as available to microorganisms as the original product. The polyoxyethylene chain appears to be readily biodegradable but the nonylphenol (NP) derivative seems to be more resistant (Balson and Felix 1995).

FAS are rapidly degraded under aerobic conditions. Their degradation 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 beta-oxidation pathway. FAS and their degradation products are ultimately biodegradable (Bruce et al. 1966; Thomas and White 1989).

Transport and fate of surfactants in wastewater treatment plants

LAS (Table 2) are the most important anionic surfactants that reach the municipal wastewater treatment plants (WWTP) nearly unchanged. An extensive body of studies conducted on the fate of LAS during wastewater treatment has indicated that they are efficiently removed by physical, chemical, and biological processes. Apart from precipitation and adsorption onto suspended solids, which can range from 30 to 70% (Berna et al. 1989) of the initial contents, microbial degradation generally accounts for the major elimination route, typically around 80%, resulting in an overall reduction of 95–99.5% of the LAS load in activated sludge systems (Painter and Zabel 1989). Nonetheless, some residues of the intact surfactant together with its aerobic breakdown intermediates, SPC (Fig. 3), enter the receiving waters via WWTP outlets. In spite of the enormous amounts of LAS used, concentrations in surface waters are found in the lower $\mu\text{g/L}$ range (Schöberl 1995; Tabor and Barber 1996).

In contrast to this, if domestic wastewater is discharged directly into natural water streams because of deficient treatment facilities, the surfactant levels in water can be considerably higher. While in Western Europe and the USA, the majority of the households are connected to WWTP, the emission of untreated sewage into rivers is still widely practiced in many countries (Eichhorn et al. 2002; Ojeda and Fernandez-Cirelli 2008).

This causes particular concern since under these circumstances aquatic organisms are exposed to considerable levels of surfactants, which exhibit relatively high toxicities (Schöberl 1997).

In wastewater, the extent of LAS adsorption to particulate matter has been shown to be dependent upon a number of factors, with the type of LAS homologue present being significant. The longer alkyl chains confer greater hydrophobicity, thus increasing adsorptive tendency. 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 chemical composition of the effluent may have a significant effect upon the adsorption of LAS. Water hardness could significantly alter partition coefficients of LAS in raw wastewater. Waters high in Ca 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% (Berna et al. 1991). A significant proportion of LAS in raw wastewater (10–35%) adsorbs to particulate matter. Sediment removed from primary settling tanks is relatively rich in LAS, with concentrations ranging from 5–15 g/L (Brunner et al. 1988; de Henau et al. 1986; McEvoy and Giger 1985).

The presence of high concentrations of LAS in sewage sludge leaving the WWTP is dependent upon the type of treatment the sludge undergoes. As stated before, LAS are readily degradable under aerobic conditions, since the alkyl chain oxidation at the terminal methyl group requires the presence of molecular oxygen (Fig. 3).

The outcome of pilot surfactant monitoring studies at activated sludge WWTP in five European countries, using LAS as the reference compound has been reported. A very high average LAS removal from water of 99.2% has been found during aerobic wastewater treatment. Hence, only low concentrations of LAS were discharged to the receiving waters, the range being 0.009–0.140 mg/L, well below the predicted no effect concentrations (100–350 $\mu\text{g/L}$ for aquatic ecosystems). The concentrations of LAS found on sediments at river sampling sites below the effluent discharges were also low, ranging from 0.49–5.3 $\mu\text{g/g}$ (Waters and Feijtei 1995).

Transport of surfactants in WWTP is shown as an example in Fig. 4 (Scott and Jones 2000). Figures may vary from one plant to another.

Sewage sludge that is aerobically digested presents LAS concentrations of 100–500 mg/kg dry weight, considerably lower than those found in anaerobically treated sludge (5,000–15,000 mg/kg dry weight). Therefore, the extent of LAS contamination of sewage sludge is greatly dependent upon the individual WWTP and the method of sludge digestion employed.

Batch anaerobic biodegradation tests at laboratory scale with different LAS at increasing concentrations were performed in order to investigate the effect of LAS homologues on the anaerobic digestion process of sewage sludge. Addition of LAS homologues to the anaerobic digesters increased the biogas production at surfactant

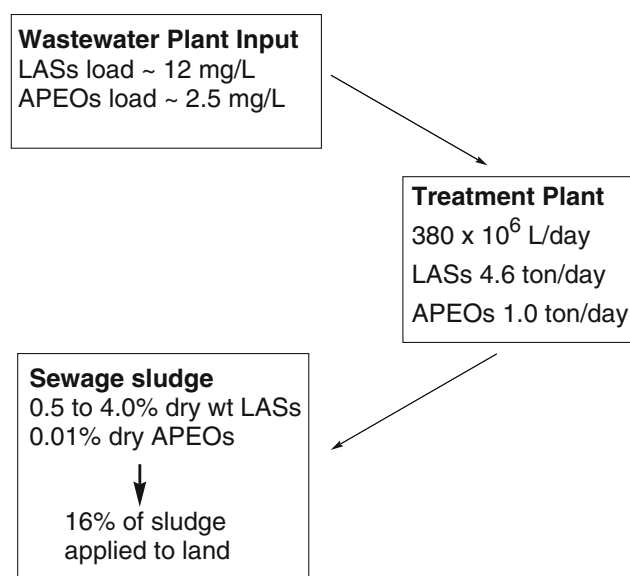


Fig. 4 Transport of surfactants through a WWTP

concentrations of 5–10 g/kg dry sludge and gave rise to a partial or total inhibition of the methanogenic activity at higher surfactant loads. Therefore, at the usual LAS concentration ranges in sewage sludge, no adverse effects on the anaerobic digesters in a wastewater treatment plant (WWTP) can be expected. The increase of biogas production at low surfactant concentrations was attributed to an increase of the bioavailability and subsequent biodegradation of organic pollutants associated with the sludge, promoted by the surfactant adsorption at the solid/liquid interface (García et al. 2006).

According to the results described above, it is evident that LAS, cationic surfactants, APEO, and AEO, are all relatively resistant to degradation in anaerobic environments. As anaerobic digestion is the predominant treatment of sludge from primary and secondary settling tanks, and because the amphiphilic nature of surfactants promotes their adsorption to particle surfaces in sewage, it appears that surfactants pass through a WWTP relatively untreated. Application of sludge to agricultural land may be a large source of surfactants in the soil environment. However, it appears that once re-introduced into an aerobic environment, such as the soil, the surfactants are rapidly degraded. Anionic and cationic surfactants are readily biodegradable in aerobic environments, but the latter group is toxic even at low concentrations. Therefore, application to agricultural soil may have detrimental effect to the soil biota. APEO molecules are readily degradable aerobically; however, nonylphenol (NP), one of its primary degradation products, has been described as an estrogenic compound active in the environment. NP has a strong affinity for soil particles and is less biodegradable than APEO. At present, the authors

could find scarce published literature concerning the estrogen mimicking properties of NP in sludge-amended soils, and this is a field that needs further research.

Fate of surfactants in waters and soils

Once surfactants enter the environment through treated wastewater discharge into surface waters, pesticide application, sludge disposal on land, or other activities, they undergo processes such as sorption onto soil or water particles and degradation. Knowledge of the processes involved in the distribution of these surfactants among ecosystem compartments (environmental dynamics) is essential to understand their behavior in the environment. Sorption of a surfactant on a sediment or soil depends on many factors including their physicochemical properties, sediment/soil nature, and environmental parameters. Sorption of surfactants on sludge, sediment, and soils is relatively high, and their order of sorption is: cationic > non-ionic > anionic. Cationic surfactants having a positive charge have a strong affinity for the surface of particulates in sewage sludge, which are predominantly negatively charged (Topping and Waters 1982).

The presence of LAS and SPC was investigated (Eichhorn et al. 2002) in a river located north-east from the city of Niteroi (State of Rio de Janeiro, Brazil) by monitoring the concentrations of both compounds at several stations along the river course, including their determination in the Bahía de Guanabara (representing the interface between the freshwater and the marine environment). This river, receiving discharges of untreated domestic wastewater from several villages with populations amounting to ca. 20,000 inhabitants, contained considerable amounts of LAS (from 12 to 155 $\mu\text{g/L}$), as well as its metabolite SPC (from 1.7 to 12 $\mu\text{g/L}$). The findings show that microbial communities present in the river are sufficient to oxidize LAS, yielding long-chain SPC.

The impact of discharges of raw wastewater of municipal and industrial origin on surface waters was studied in a Taiwanese river, determining, apart from LAS and SPC, non-ionic surfactants and their metabolites (Ding et al. 1998). Concentrations of the surfactants ranged between 11.7 and 135 $\mu\text{g/L}$, while the degradation products were found from 0.3 to 3.1 $\mu\text{g/L}$.

Trehy et al. (1996) reported on levels of LAS and SPC in the USA, receiving waters upstream and downstream of domestic WWTP. The values averaged 16 and 35 $\mu\text{g/L}$ for LAS, while the mean concentration of SPC amounted to 9.3 and 31 $\mu\text{g/L}$, respectively. A monitoring study performed in Italy comprised two strongly polluted riverine sites sampled upstream and downstream of a WWTP (Marcomini et al. 2000). The average concentration of LAS was slightly increasing from 177 to 187 $\mu\text{g/L}$, whereas the

SPC level ranged from 368 to 420 $\mu\text{g/L}$. From these data describing distinct wastewater disposal situations, the ratio of LAS to SPC may be indicative of the emitted treated wastewater. A low value of the ratio as found in the US (0.9) (Trehy et al. 1996) and the Italian work (0.2) (Marcomini et al. 2000) may be indicative of wastewater having been treated, whereas elevated values as observed in the Taiwanese study (ranging from 270 to 6.7) (Ding et al. 1998) and also in the Brazilian river (between 13 and 1.6) (Eichhorn et al. 2002) may be indicative of a high percentage of untreated wastewater.

In the Brazilian river, a rapid decrease has been observed in concentrations of LAS in the water, 1.5 km downstream from the discharge point, particularly when the flow in the river is high. The decrease in concentration relate to both biodegradation and the loss of surfactants due to adsorption on river sediments and suspended solids in the raw sewage (Eichhorn et al. 2002).

As for the fate of surfactants after environmental discharge of untreated wastewater, the concentration in the water might be reduced by sorption onto riverine sediments, as well as by biodegradation through endogenous bacterial communities present in the stream, with slower kinetics compared to WWTP (Eichhorn et al. 2002). The high water solubility of LAS and of their even more polar metabolites enables their convective transport over relatively long distances. Ultimately, mouthing of polluted rivers into estuaries and subsequently into the sea contributes to the contamination of coastal waters.

The fate and effects of LAS in the aquatic environment have been studied extensively, whereas the terrestrial environment has received considerably less attention. Soil is exposed to a considerable quantity of surfactants, and even at low concentrations, surfactants seem to alter soil physics, soil chemistry and soil biology significantly, with sorption processes playing a dominant role. The literature concerning the fate of surfactants in wastewater sludge-amended soil is heavily biased towards the study of LAS, with other surfactants receiving little or no attention.

LAS was monitored in sludge-amended soils in a Spanish grapevine farm and a vegetable farm. From relatively high sludge application concentrations of 7,000–30,200 mg/kg dry weight, initial soil concentrations of 16 and 53 mg/kg soil, respectively, were observed. After periods of 90 and 170 days, the soil concentrations of LAS were 0.3 mg/kg. After an initial period of LAS removal, soil concentrations appeared to level out and did not decrease further, suggesting that LAS may be incorporated into the soil particles and/or may be associated to the soil organic matter. This fact renders the surfactant unavailable to the microorganisms responsible for their biodegradation (Berna et al. 1989).

The concentration of surfactants in soils that having not received sludge recently is generally less than 1 mg LAS/kg and not more than 5 mg LAS/kg. This is below the lowest concentration of LAS for which effects have been observed in the laboratory. The laboratory data are in accordance with field studies using aqueous solutions of the LAS (sodium salt). However, observations on the ecological impact of sewage sludge applications, or application of LAS spiked into sludge, indicates a lower toxicity of LAS when applied via sludge. Jensen (1999) concluded that LAS could be found in high concentrations in sewage sludge, but that the relatively rapid aerobic degradation and the reduced bioavailability when applied via sludge will most likely prevent LAS from posing a threat to terrestrial ecosystems on a long term basis.

Once LAS is removed from the anaerobic environment of sludge digestion and/or storage, aerobic bacteria begin to metabolize these surfactants. 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 is little chance of accumulation of LAS in soil.

Experimental measurements of the adsorption of LAS on soils were made at 25°C using a continuous adsorption apparatus. The adsorption of LAS on natural soils could be divided into two stages: linear and exponentially increasing isotherms. At low LAS concentrations (<90 µg/mL), the adsorption isotherms were linear and K_d was from 1.2 to 2.0. At high LAS levels (>90 µg/mL), cooperative adsorption was observed and the amount of LAS adsorbed increased exponentially with the increase of LAS concentration in solution. LAS adsorption mechanisms on soil are mainly specific site surface interactions and hydrogen bonding. The LAS adsorption capacity of a soil significantly depended on its clay content. Under real soil environments where LAS levels are rather low, the LAS adsorption ability of a soil is very weak (Ou et al. 1996).

In order to investigate the behavior of surfactants in soil ecosystems, the sorption of LAS on soils from three different areas of Northern Greece and with different organic matter content was studied. LAS sorption on these soils decreased with increasing pH and correlated positively with the organic matter content of the soils (Fvtianos et al. 1998). The pH value controls the degree of sorption and desorption processes, the solubility, and the activity of potentially degrading microorganisms. As far as anionic surfactants are concerned, increasing adsorption has been reported with decreasing pH values, due to a higher positive charge of colloidal surfaces.

It has been shown that the saturated adsorption amount of LAS on soils was lower compared with the AEO. Adsorption of anionic surfactants decreased in the presence

of non-ionic surfactants. These could result from: (1) the difference of CMC of mixed surfactants at different molar ratios; (2) hydrocarbon chain–chain interactions between LAS and AEO; (3) saturation of a majority of adsorption sites by AEO. The adsorption of both surfactants on soils decreased with the increase of pH in mixed surfactant solutions, as well as with a decrease in ion strength (Rao and Re 2006).

On the other hand, FAS appear to be readily bioavailable by microorganisms under both aerobic and anaerobic conditions and easily degradable, both primarily and ultimately. Therefore, treatment in an aerobic WWTP is entirely sufficient to eliminate FAS and little possibility exists for these surfactants to reach the soil environment via sludge amendment. LAS are readily bioavailable in both aerobic and anaerobic environments, with primary and ultimate degradation rates comparable to FAS under aerobic conditions (Fischer 1982; Schöberl et al. 1988).

The effect of surfactant on plant growth from the use of sewage sludge in soils is difficult to assess because, in general, sludge promotes plant growth. Adverse effects on plant growth were observed at 392 µg/L, but long term monitoring of 46 environmental sites gave LAS concentrations of 63 µg/L, far from the concentration reported to have adverse effects (Scott and Jones 2000).

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-agricultural 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 ultimately result in surfactant contamination of the environment.

Interaction of surfactants with soil contaminants

As stated, surfactants may form micelles in solution due to the presence of both hydrophobic and hydrophilic groups in each surfactant molecule. The organic interior of micelles acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon can greatly enhance the total concentration of the contaminant in solution above its aqueous solubility limit if surfactants are present. In fact, the solubility of a hydrophobic solute in surfactant micelles has been found to be several orders of magnitude larger than its aqueous solubility in the absence of surfactants. The extent to which a solute will concentrate in a micelle can be related to the octanol–water partition coefficient (K_{ow}) of the solute. In general, the larger the K_{ow} of a solute, the greater its tendency to concentrate inside the micelle. There are two mechanisms by which surfactants can interact with organic compounds in soils. The first and most important mechanism involves solubilization of

contaminants in surfactant micelles. The second mechanism involves the mobilization of the contaminants from the soil; this depends on the tendency of surfactants to reduce the interfacial tensions and capillary forces trapping the contaminant in the soil. These interactions affect the bioavailability of soil pollutants, and therefore, can be used for soil bioremediation (Haigh 1996).

The use of surfactants to decontaminate ground water aquifers and in soil clean-up operations is perfectly established, and both anionic and nonionic surfactants have been used to remediate land polluted with oils and hydrocarbons as well, and both anionic and nonionic surfactants have been used to remediate land polluted with oils and hydrocarbons as well as with many other organic contaminants.

Surfactant addition has been investigated as an innovative technique for decreasing interfacial tension between the soil non-aqueous phase (NAP) and water, and for enhancing aqueous-phase solubility; the NAP contaminants can be solubilized through incorporation of contaminant molecules into micelles of surfactants. Water cannot be recommended for an efficient removal of pollutants from a contaminated soil, and thus, organic surfactants should be relied upon in soil washing procedures (Santharam et al. 1997).

Two synthetic surfactants, sodium dodecylsulphate (SDS) and Triton X-100 (TX100), and a solution of a natural surfactant, a humic acid (HA), at its critical micelle concentration (CMC), were used for soil depollution. Soil A was richer in polycyclic aromatic hydrocarbons, whereas soil B had a larger content of thiophenes. The synthetic surfactants mixture used was able to reduce the content of contaminants from 80% to more than 90% in both soils. Natural non-toxic surfactants such as HA removed similar amounts of contaminants from a polluted soil as the synthetic surfactants did. However, synthetic surfactants, which are efficient in soil washing, may become a further environmental problem because of their toxicity; as a conclusion, a natural surfactant such as a humic acid solution can be used for washing of a contaminated soil with the same efficiency and less toxicity as that of synthetic surfactants in order to avoid further environmental problems (Conte et al. 2005).

The potential effects of selected surfactants on the biodegradation of chlorinated hydrocarbons in wastewater have been also investigated. Biodegradation of a real waste containing a broad array of hazardous contaminants was significantly enhanced by the amendment of mineral nutrients and surfactants. Contaminants included hexachlorobutadiene (HCBT), hexachlorobenzene (HCB), trichloroethylene (TCE), halogenated organic solvents [1,2-dichloroethane (DCE), tetrachloroethane], volatile aromatic hydrocarbons including benzene and toluene, and polynuclear aromatic hydrocarbons (PAH). The reduction of contaminants was 49% higher for the mixture of

wastewater with surfactants. Both a non-ionic surfactant and SDS have been assayed (Zhang et al. 1998).

Soils contaminated with both heavy metals and hydrophobic organic contaminants are commonly found. EDTA and SDS-enhanced washing was studied for remediation of Pb- and/or marine diesel fuel-contaminated soils. The feasibility of recovery and reuse of EDTA and SDS, as well as the physicochemical interactions among the chemical agents, contaminants, and soils, were extensively investigated using batch experiments. The optimal washing sequence was then determined. The experimental results showed that EDTA could be recovered and reused for four cycles without significant loss of its chelating capacity, while the extraction capability of SDS was noticeably reduced after each reuse cycle. The free phase of marine diesel fuel (MDF) in soils physically isolated the sorbed Pb on soils, thus reducing its extraction by EDTA. The presence of SDS alone or together with low EDTA concentration was found to enhance Pb removal probably via electrostatic interaction and dissolution of soil organic matter (Zhang et al. 2007).

In addition to soil cleaning properties, some surfactants, even at very low concentrations, have been shown to enhance the biodegradation of certain xenobiotics in soil. However, at higher surfactant concentrations, it has been reported that degradation can be delayed due to the partitioning of xenobiotics into surfactant micelles. Surfactant-pollutant interactions in soil are very complex and depend heavily on a range of parameters including surfactant concentration in soil-water compared with critical micelle concentration (CMC), adsorption characteristics of the surfactant and pollutant, solubility of the pollutant, and soil type. The most important parameter in terms of the ability of a surfactant to mobilize hydrophobic xenobiotics in contaminated soil is the surfactant CMC. In general, concentrations of surfactant in soil-water below the CMC have little or no effect on solubilization of hydrophobic materials. Only when micelles are present does significant desorption of such pollutants from soil surfaces occur. Conversely, under some conditions, usually at concentrations well below the CMC, the presence of surfactant can enhance the adsorption of hydrophobic xenobiotics to soil particles (Haigh 1996). This fact has been attributed to partitioning of the xenobiotic into surfactant hemimicelles formed on the soil surface. In environments such as soils and sediments, adsorption of surfactants to surfaces results in much higher total surfactant concentrations being necessary to achieve micellization in pore water than would be necessary in clean water systems. Therefore, much higher concentrations of surfactant are required than might be expected to cause significant changes in xenobiotic behavior. Such high concentrations are not typical of those found in sludge-amended soil.

Conclusions

Detergents are widely used not only domestically but in many different industries such as cosmetic, personal care, household, painting, coating, textile, dyes, polymer, food, agrochemical, and oil. The formulations include all types of surfactants: anionic, cationic, non-ionic, and amphoteric, but the most common surfactant by far is LAS, an anionic surfactant.

Surfactants can reach agricultural soils by different ways, the soil amendment by sewage sludge and pesticides applications on the crops being the most relevant ones.

According to the type of surfactants, they can be degraded in aerobic or anaerobic conditions producing different types of metabolites. From the literature data, it is evident that LAS, cationic surfactants, and APEO are all relatively resistant to degradation in anaerobic conditions; then, the application of sludge to agricultural soils could be a large source of surfactants if sludge digestion has been performed anaerobically. However, when the compounds are re-introduced into an aerobic environment, such as soil, they are rapidly degraded. More studies regarding cationic surfactants degradation are needed in order to evaluate their potential toxicity in the environment due to its microorganism-inhibitory activity.

The interaction between surfactants and pollutants is an important subject of study nowadays because surfactants can be used in bioremediation of soils, due to their capacity to affect the bioavailability of contaminants such as heavy metals and organic compounds.

Finally, it is important to point out that surfactant input in agricultural soils is not negligible and is increasing worldwide. Therefore, knowledge on their introduction pathway, their interaction with polar and non polar contaminants, as well as their fate and persistence in the environment is required in order to evaluate their behavior in agricultural areas under increasing use of organic amendments and agrochemicals.

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