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## TERRESTRIAL RISK ASSESSMENT FOR LINEAR ALKYL BENZENE SULFONATE (LAS) IN SLUDGE-AMENDED SOILS

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### ABSTRACT

A comparison of the estimated environmental concentration and the effect concentrations (in the laboratory or field) in the receiving compartment form the basis of environmental risk assessments. This paper reviews processes that critically influence the fate of LAS in the terrestrial environment. Concentrations of LAS in sludge are quite high due to sorption to primary sludge, precipitation of Ca and Mg-salts of LAS, and lack of biodegradation under anaerobic digestion. This implies that when sludge is applied to soil e.g. as a fertilizer, considerable amounts of this important surfactant may enter the terrestrial environment. Influence of aerobic situations on LAS concentrations during sludge storage needs further research to allow incorporation into the risk assessment. Aerobic biodegradation in soil is considered the most important removal mechanism of LAS loading to the terrestrial environment through sludge-amendment. Sorption plays a role in determining the residence time of a chemical in the soil, hereby enabling more time for biodegradation to occur. In addition, sorption may affect the expression of effects of surfactants towards benthic and soil dwelling organisms and plants. Another factor that needs further attention is the form of LAS in the environment, which is not similar to the commercial material applied in detergents. The differential sorption and biodegradation of the LAS components lead to a shift in the alkyl chain length (homologue), and phenyl-isomer distribution towards increased hydrophobicity. Also, occurrence of Ca/Mg-salts in the environment versus the Na-salt for the commercial material critically impacts the extrapolation of effects data obtained in lab studies (mostly performed with the commercial material) to the field. The literature data were used in combination with strategies and methods provided by the European Union Technical Guidance Document in support of risk assessment of new and notified substances (1996) for the prediction of environmental concentrations of LAS entering the soil system through sludge applications. Soil biodegradation is an essential, necessary element for the PEC-calculations of LAS. The initial realistic worst case assessment presented indicates no human health risks exists with indirect exposure to LAS through either food or drinking water. Also, current LAS use does not pose a risk to terrestrial organisms such as plants and invertebrates. ©1998 Elsevier Science Ltd

### 1. INTRODUCTION

All substances entering the environment have the potential to influence microbial, plant and animal life. Thus, information on the possible impact on biota, is of a decisive importance to determining acceptable levels of use and release to the environment. The environmental impact of a compound depends on : i) its

inherent properties relevant to the fate in and the effects on the environment (e.g. biodegradability, ecotoxicity), and ii) current ambient conditions of receiving compartment (e.g. use pattern of the chemical, wastewater treatment situation, dilution factors, soil type).

A comparison of the estimated concentration and the effect concentrations (in the laboratory or field) in the receiving compartment form the basis of an environmental risk assessment. These two parameters, PEC (predicted environmental concentration) and L(E)C<sub>50</sub> or NOEC do not represent absolute figures. Their accuracy and reliability depends strongly on the quantity and the quality of the available information. To prevent wrong conclusions, it is therefore sensible and necessary to evaluate the validity and reliability of the data used for the risk assessment and to link the implications of resulting decisions with the uncertainty of such an assessment.

Detergents are manufactured in large quantities, used by many people, and disposed after household use into the environment. The vast majority of this waste stream is treated via domestic wastewater treatment plants (WWTPs). Waste water treatment plants reduce significantly the load of chemical substances to the receiving surface waters, and have become an intrinsic part of exposure and risk assessment of detergent chemicals. Fate and effects of surfactants in aquatic surface waters has been studied extensively and was subject of a risk assessment evaluation within the Dutch NVZ/VROM Voluntary Agreement (Plan van Aanpak). This evaluation lead to the conclusion that the surfactants studied do not pose a risk to the aquatic environment [1]. The terrestrial environment (soils, groundwater, and interstitial

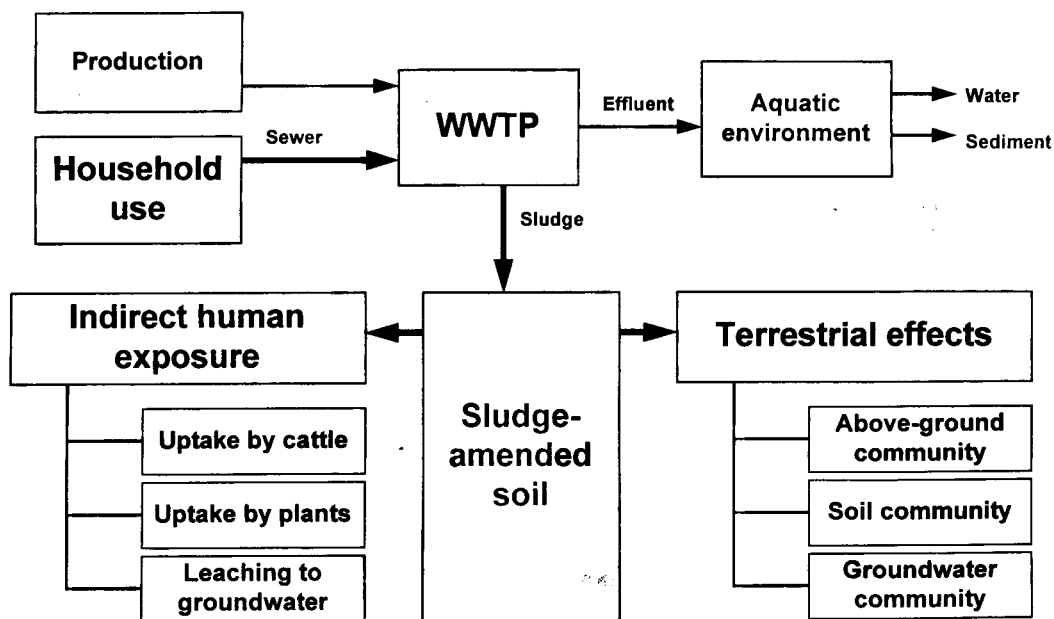


Figure 1: Fate of LAS in the environment

water) has received considerably less attention. Nevertheless, surfactants may be introduced in/onto the soil by various routes: leakage of sewer lines, presence of septic tanks, application of sewage sludge as a fertilizer on arable land, and use of sewage effluents as irrigation water. Consequently, attention has to be paid towards effects of surfactants on soil dwelling organisms, plant growth and uptake (especially for terrestrial crops), and potential infiltration to groundwater (an important source of drinking water). Leaching, adsorption and biodegradation in soil can serve as important removal mechanisms, and each removal process needs to be quantified to assess the fate of chemicals in the soil compartment (Figure 1).

LAS is the major surfactant used in detergents throughout the world because of its effectiveness, versatility, cost/performance ratio and environmental safety. The widespread and relatively large usage of LAS (1.5 to 2 million ton per year worldwide and 300 000 ton/yr within the EU) has led to extensive research by both industry and academia, and there is a wealth of literature covering environmental fate and effects in the terrestrial environment. Laboratory and environmental studies indicate LAS to be ultimately biodegraded at high rates under aerobic conditions. In sewage treatment, however, a proportion of the LAS is removed by adsorption onto sewage solids during primary settlement of sewage and will not undergo normal aerobic treatment since this sludge stream will not reach the aeration tank. The resulting sludge is generally digested under anaerobic conditions and a high proportion may then be applied (raw or digested), in some countries, as a valuable source of plant nutrients. Aerobic conditions may be restored during storage of sludge, and after application to land thus preventing LAS accumulation in the soil environment [2].

This document aims to review the fate of LAS in sludge and soils based on available literature data. These data are used in combination with strategies and methods provided by the European Union Technical Guidance Document (EU-TGD) in support of risk assessment of new and existing substances [3] for the prediction of environmental concentrations of LAS entering the soil system through sludge applications. An initial risk assessment for indirect human exposure and soil organisms is presented.

## 2. FATE PROCESSES

### 2.1. Sorption

Sorption is an important mechanism that influences fate and effects of organic chemicals e.g. surfactants when released into the aquatic and/or terrestrial environment. Through sorption to sludge, LAS can enter the terrestrial environment.

A negative correlation between the sorption coefficient, the biodegradation rate constant  $k$  and extent of total mineralization was reported by Knaebel et al. [4,5]. This indicates that a greater affinity for the environmental matrix lowers the bioavailability for degradation. In contrast, Larson et al. (1989) claim that biodegradation rates of LAS are not influenced by soil type, which may be explained by the use of different kinetic models to fit the experimental data [6]. Overall, the weight of evidence indicates soil type can influence biodegradation.



adsorption sites are gradually filled. In their study, the distribution coefficient  $K$  of LAS was  $237 \pm 77$  l/kg. This narrow range indicates that the source and nature of the sediment only have a small effect on adsorption. The adsorption of LAS to humic acid also followed the Langmuir isotherm, but the attractive forces were much stronger. In contrast, the adsorption to kaolinite was very low, due to the negative charge of the clay mineral which repels the anionic surfactant. The adsorption of LAS on iron and aluminium oxides, which have a positive charge per atom, follows a cooperative adsorption isotherm (no Langmuir isotherm as the Freundlich constant  $1/n > 1$ ). Adsorption is situated in multiple layers. The low  $K$  value indicates that adsorption is still localized in a monolayer at low equilibrium concentrations, but the high slope indicates the higher sorption activity at higher concentrations [9].

Overall, the adsorption coefficient seems to be higher for sediments than for soils. This could be due to a difference in composition e.g. more organic carbon in sediments. However, generalization remains difficult as not enough results were available, and as sorption is a complex process depending on soil composition and hydrophobicity of the molecule. Even for one sediment, sorption can differ with a factor of 100 for the different phenyl and alkyl chain isomers of LAS [13].

### 2.1.2. Influence of the physico-chemical characteristics of the chemical on sorption

LAS homologues and isomers differ in the alkyl chain length and the position of the benzenesulphonate on the alkyl chain. The mixture most frequently used in detergent formulations has an average chainlength of 11.6 carbon atoms with phenyl positions between 2 and 6. Hand and Williams (1987) studied the sorption of LAS homologues and isomers in 4 river sediments in a laboratory experiment at a LAS concentration of 10-1000 ppb [13]. For each sediment type, sorption increased significantly as the LAS chain length was increased:  $K$  values increased with a factor of 2.8 for each additional methylene group. For isomers, sorption increased significantly as phenyl position was changed from the 5 or 6 position to the 2 position.

The results suggest that LAS is sorbed by a hydrophobic mechanism. As the alkyl chain length increases, the hydrophobicity of the molecule increases and the negative charge of the sulphonate group has a smaller impact on hydrophobic interactions.

In the model of Di Toro et al. for anionic surfactant sorption, the sorption coefficient was related to the critical micelle concentration of the surfactant, as a measure of hydrophobicity [14]. The relation was non-linear.

Bintein and Devillers developed a model for sorption of chemicals to sediments and soils [15]. In the model,  $K_{ow}$  as a measure of hydrophobicity, and  $pK_a$  as a measure of the neutral (acids) or protonated (bases) molecules were included.

The amount of adsorbed surfactant will depend on its hydrophobicity (determined by the chainlength, critical micelle concentration or  $K_{ow}$ ) and speciation. A percentage of LAS entering the sewage treatment

plant with the raw sewage precipitates in the primary settler thus "bypassing" treatment. Berna et al. observed that LAS elimination by physical removal during primary treatment is positively correlated with water hardness, e.g. the higher the water hardness the higher the LAS elimination [16]. These precipitated Ca/Mg-salts may have a lower bioavailability than the Na-salt of LAS, thus potentially influencing toxicity and biodegradation. Insufficient information is available to properly address this influence in an environmental risk assessment (ERA), but this potential modifying effects merits further investigation.

### 2.1.3. Influence of sediment/soil characteristics on sorption

Adsorption coefficients, measured at a low redox potential (Eh), in order to simulate anaerobic conditions, showed a slight increase in comparison to more aerobic conditions [10].

Adsorption of C12LAS on 10 soils was studied in a laboratory experiment [17]. The soils differed in organic carbon content, content of sesquioxides and in the kind of clay minerals. Although clay minerals are surface active colloidal material, no correlation was found between the amount adsorbed and the clay content. This could be due to the fact that in the soils different clay minerals were present, resulting in a different adsorption characteristics for each soil and a lower significance level. Also the organic matter was not correlated to the adsorption. The most important component determining adsorption was the content of free sesquioxides.

In laboratory tests, the influence of various soil characteristics on the sorption of LAS in soils was investigated [10]. Iron oxide levels, humic content and also pH proved to be the decisive soil parameters which influence the sorption of LAS.

Adsorption of anionic surfactants by the soil depends mainly on their organic matter [18].

In sediments, positive correlations were found between K and the organic matter content, % CaCO<sub>3</sub> and % clay in the sediment [9]. Although a strong affinity of LAS towards pure metal oxides was measured, a negative correlation was found between the adsorption of LAS and the sediment content of Fe and Al oxides. This may be explained by the fact that the strong affinity of metaloxides for LAS only exists at a high concentration where multilayer adsorption occurs, and that in river sediments the critical concentration is not obtained [9]. However, it cannot be excluded that pH and/or redox conditions may have had an important influence on the speciation of the metals present thus influencing its sorption.

Hand and Williams (1987) investigated LAS sorption to 4 different sediments under environmentally realistic concentrations (10-1000ppb) [13]. The correlation between LAS sorption and sediment properties was not straightforward. Sorption was not correlated with % organic carbon, nor with % clay, positively correlated with % silt, and negatively correlated with % sand.

A model for anionic surfactant sorption was developed by Di Toro et al. (1990) [14]. It relates the partition coefficient to the critical micelle concentration (CMC) as a measure of hydrophobicity, to the organic carbon content or the CEC of the particles and to the particle concentration itself. The investigation

was restricted to concentrations in soils, sediments and sludges that are directly relevant to environmental fate and effect and to low concentrations, ranging in the linear part of the sorption isotherm. A reasonable fit to the available sorption data was obtained. However, the relationship between  $f_{oc}$  and  $K_c$  was non-linear. Hydrophobic interactions play a role in surfactant sorption. The non-linear relationship could be due to electrostatic repulsion between the negatively charged surfactant and the soil or sediment particles. CEC and  $f_{oc}$  covary, hence, as  $f_{oc}$  increases the CEC increases and the surface becomes more negatively charged. Thus, the increase in hydrophobic bonding is diminished by the increased repulsion. This results in a more gradual increase of  $K_c$  with respect to  $f_{oc}$ .

Next to the conventional adsorption/desorption, a third reaction (parameter  $v_x$ ) induced by particle interactions exists that causes an additional desorption as particle concentrations increase. If  $v_x$  is caused by an actual collision,  $v_x$  should be constant and independent of particle and chemical properties. This hypothesis was supported by the fact that  $v_x$  was the same for anionics, neutral hydrophobics and metals. In this model, when the particle concentration is very high,  $K$  is only a function of the particle concentration, and not of the chemical or particle properties.

The particle concentration effect, as measured by Di Toro et al. [14] was not confirmed by McAvoy et al. [12]. For LAS,  $K$  remained constant over the broad range of particle concentrations (3-67% w/v) tested for sites 4m below the surface in the vicinity of a septic tank. But, given the low  $K$  for LAS on the aquifer solids ( $\pm 1.0$  l/kg) it is possible that a concentration effect could not be detected. This is in contrast with the analysis by Di Toro et al., [14] which indicates that anionic surfactants display decreased sorption with increased particle concentrations.

Overlooking the models and correlations concerning the influence of soil and sediment properties on sorption, it is difficult to come to a clear conclusion. The sorption coefficient is probably positively correlated to the % organic matter [9, 10, 12, 14, 15], although no correlation was found by Hand and Williams [13]. The effect of clay remains unclear, a correlation was estimated by Matthijs and De Henau [9] and McAvoy et al. [12], but not by Hand and Williams [13] and Litz et al. [10]. As different clay minerals have different sorption characteristics [4], correlations should be based on clay mineral type and not for clay content in general. The CEC does not interfere in the sorption of LAS [9,13] but has been included in the model for anionic sorption of Di Toro et al. [14].

#### 2.1.4 Desorption

Litz et al. [10] found that desorption coefficients were always higher than adsorption coefficients, which indicates that LAS is quite strongly bound to soils. Desorption ranged between 35.3% and 65.9% of the adsorbed amount in desorption studies on natural river sediments [9]. The corresponding  $K$  for the irreversible adsorption of LAS ranged between 53 and 137 l/kg and was lower than the adsorption coefficient. Sorption and desorption were rapid and nearly reversible in the experiments of Hand and

Williams [13]. It can be concluded that a part of the sorbed LAS is irreversibly bound either as part of the humus fraction or closely associated to the mineral fraction of the soil.

## **2.2. Anaerobic Degradation**

Hršak showed that methanotrophic and heterotrophic interactions are important in transformation of pure C<sub>9</sub>-, C<sub>10</sub>-LAS and commercial LAS [19]. Methanotrophic activity possibly involves the methane monooxygenase enzyme system to initiate cometabolic transformation.

Wagener and Schink investigated the anaerobic degradation of 3 anionics (C<sub>12</sub> Linear alkyl benzene sulphonate (LAS), Sodium dodecyl sulphonate (AS), and Sodium dodecyl sulphate (SDS)) in incubation experiments and in a lab scale anaerobic fixed bed reactor [20]. These anionics showed an inhibitory effect on the methanogenesis at concentrations of >100 mg/l anoxic digester sludge and >50 mg/l anoxic creek sludge. At lower concentrations no inhibition nor stimulation of the methanogenesis occurred. The microbial degradation of the anionics under anaerobic conditions was significantly reduced.

The results of Wagener and Schink [20] were confirmed by Federle and Schwab [21]. They compared the mineralization of radiolabeled LAS in the anaerobic sediments of a laundromat waste water pond and a non-polluted pond as a control. LAS was not mineralized in anaerobic sediments, even though the microorganisms had been exposed to a very high level of LAS for over 25 years. Extended acclimation did not create a degradative mechanism for LAS, suggesting the need for molecular oxygen for initial degradation.

McEvoy and Giger measured LAS concentration in sludge before and after anaerobic digestion [22]. The concentration of LAS was not decreased, suggesting that no degradation of LAS occurs during anaerobic treatment. Matthijs and De Henau measured significantly higher levels of LAS in anaerobically digested sludge than aerobic sludge [23].

It can be concluded that anaerobic conditions favor the relative enrichment of LAS.

## **2.3. Aerobic Biodegradation**

Strictly anaerobic environments are not prevalent in nature and for chemicals such as surfactants, which enter the environment with domestic sewage, are primarily transitory repositories for a minor percentage of the total volume used [2]. The agricultural environment is predominantly aerobic, and as a result LAS loading of the soil is greatly reduced as this surfactant is aerobically biodegradable. An overview on the aerobic biodegradation kinetics, rate constant and extent of biodegradation, is given in Table 2.

### **2.3.1. Soil**

The environmental form of a chemical has a significant influence on its eventual microbial metabolism. This form is defined by the physico-chemical characteristics of the chemical, the composition

and mineralogy of the soil, and the mode of entry of the chemical into the soil environment [5,24]. Interactions with montmorillonite, illite and sand soil had little effect on microbial metabolism of LAS, while humic acids and especially fulvic acids significantly reduced the bioavailability of the chemicals to the microbial community [5,24]. The chemical-soil constituent complexes degraded similarly in woodlot soil [5] and sludge-amended agricultural soil [24]. The applied form of the chemical (surfactant in association with sewage sludge) adds another level of complexity to understanding the fate of chemicals in soils.

#### 2.3.1.1. Degradation in sludge amended soils

By the use of a plant metabolism box, representing the terrestrial plant ecosystem, degradation and fate of LAS introduced with digested sludge was studied [25]. Two different soil cores were introduced in the box: soil I was a heavy, clay like soil, cultivated with grass, bush beans and radishes after the digested sludge was incorporated, soil II was a loose, sandy soil, cultivated with potatoes. The sludge was mixed with the soil surface over a depth of 20cm, resulting in an applied amount of 27.2 $\mu$ g LAS/g dry soil and 16.2  $\mu$ g LAS/g dry soil for the two ecosystems respectively.

The mineralisation half-life of LAS introduced on topsoils with digested sewage sludge was calculated from the amount of  $^{14}\text{C}$  released in the atmosphere, taking the transfer of  $\text{CO}_2$  from soil into the air into consideration. The half life was 26 and 13 days for the two ecosystems respectively. Thus, the aerobic degradation in the loose sandy soil was twice as fast as in the clays soil. Still, LAS was rapidly converted in both the ecosystems. The only radioactivity in the atmosphere measured came from  $\text{CO}_2$ . No other gaseous secondary products of LAS were measured. The extent of biodegradation was 63.6% and 72.3% after 76 and 106 days for the 2 ecosystems respectively.

#### 2.3.1.2. Degradation in (sub)surface soils

Biodegradation of surfactants measured by the soil perfusion method showed that a lag phase occurs in the biodegradation of commercial LAS and C12LAS, but not for SDS [26] This lag phase becomes more distinct and longer with the higher concentrations tested, and can be attributed to an inhibition of enzymes, being more important at higher surfactant concentrations [27]. After a second addition of surfactant, no lag phase occurred due to adaptation of the soil microorganisms.

Prior exposure of porous sand samples collected at the unsaturated zone of an unconfined aquifer to trace levels of LAS (0.2 $\mu$ g/g) during 53 and 250 days lead to the development of a biodegradation response which is significantly improved compared to the unexposed microcosms[6]. This response was maintained for a long period of time (250 days). A lag phase of 25 days occurred in the unexposed microcosm. Half-lives were about 20 days for the pre-exposed microcosms, and could not be calculated for the unexposed microcosm. The extent of biodegradation was 57% and 40% after 100 days for the pre-exposed and non-exposed microcosms respectively.

The mineralization of LAS and the vertical distribution of microbial biomass and activity was determined in samples taken from subsurface soils at 2 sites in north-western Wisconsin [28]. One site was impacted by infiltrating wastewater from a rural laundromat since 1962. The other was not affected by waste water. The first site represents a worst case situation since the waste water was not diluted and therefore contained a high concentration of surfactants. Active microbial communities were present in the subsurface soil. Their distribution seriously declined at a depth of 2-3m (100 fold). LAS mineralization likewise exhibited a sharp decrease below this level.

The profile impacted by the infiltrating wastewater was characterized by a higher microbial biomass concentration (measured as phospholipid derived fatty acids) and higher microbial activity (measured as thymidine incorporation in DNA and FDA hydrolysis). This is probably due to the higher amount of organic carbon and nutrients in the laundromat profile, and the microbial utilization of surfactants as organic carbon and energy source [29].

Microbial biomass in the upper 2 m of the vadose zone and in the saturated zone mineralized LAS. Little or no LAS biodegradation occurred at the intermediate depths between 2 and 14 m [28]. Maximum biodegradation was 50%, with probably part of the LAS incorporated in the microbial biomass, organic matter or other material. Only in the upper layer was a difference in the biodegradation rate measured in the two fields with the leach field having a higher  $k$  value. This suggests adaptation of the microbial community in response to LAS exposure.

Mineralization was also studied in the vicinity of a septic tank. The tank is 10 years old and discharges its effluent at a depth of 0.5 m in a sandy soil. The tile field is underlain with a 2.5 m thick unsaturated zone and a 3-4 m thick sand aquifer. Ground water velocities in the aquifer are 20-40 m/year. The concentration of LAS decreased from 10 000  $\mu\text{g/l}$  in the effluent to 30  $\mu\text{g/l}$  at a horizontal distance of 10 m. The average biodegradation half-life in soil samples taken over a depth of 5 m and over a distance of 20 m was  $18.7 \pm 7.4$  days. LAS degradation half-lives in the soil were shortest in the vicinity of the effluent plume itself. No consistent biodegradation results could be obtained beyond a distance of 20 m. The results did suggest adaptation of the microbial community [6].

#### 2.3.1.3. Factors affecting soil degradation

Microbial communities associated with the rhizosphere are biochemically more diverse, and possibly more active towards detoxification of pollutants in soil. The effect of intact rhizosphere microbial communities and soil on mineralization of radiolabeled surfactants was investigated by Knaebel and Vestal by the use of a mineralization chamber [14]. The rhizosphere microbial communities (soybean or corn rhizosphere) enhanced the biodegradation of LAS in soils in terms of their effects on the initial rates without affecting the total amount of  $\text{CO}_2$  production.

Laboratory experiments involving wetting and drying of soils indicated that both rate and extent of mineralization may be affected by climatological events [30].

In soils with a large amount of sesquioxides and lower CEC, LAS was partially protected against biodegradation with an asymptotic yield of only 40-50% whereas biodegradation reached 90% in a soil with a low content of sesquioxides [17]. Thus adsorption retards biodegradation.

Abe and Seno noted that the type of soil also influences biodegradation [26]. They observed that a sandy loam soil showed less initial adsorption than a clay loam soil and a longer lag phase. In contrast, biodegradation half-lives were not affected by the soil type, and cumulative values for CO<sub>2</sub> production reached 50% to 70% after 10 days [6]. The short half-life and the absence of a lag phase in the mineralization of LAS in soil types including loam, sand and clay, indicate that soil microorganisms were already adapted to the biodegradation of LAS.

The effect of the association of organic chemicals and different soil constituents on their subsequent biodegradation in soil was studied in more detail by Knaebel et al. [5]. The study was carried out under realistic conditions, where the biological, chemical and physical characteristics of a natural soil were largely preserved. <sup>14</sup>C labeled C12LAS was aseptically adsorbed to montmorillonite, kaolinite, illite, sand and humic acid, then small amounts of these complexes were mixed with a woodlot soil (final concentration ± 50ng/g soil) and <sup>14</sup>CO<sub>2</sub> production was measured during 60 days. The dispersed surfactant in water, added to the soil served as a control.

Mineralization data were fitted following a 3/2 order model, which includes a zero order process ( $k_0$ ; represents the biodegradation of chemicals incorporated into microbial biomass or organic matter or slowly desorbed from solids), and a first-order process ( $k_1$ ; represents the mineralization of the readily bioavailable part).

Kinetic parameters differed largely as a function of the soil constituent to which the surfactant was associated. Thus mineralization in the soil is expected to be a function of the soil composition. Differences in mineralization kinetics for sand and the different clay minerals could be attributed to relative abundance of binding sites: sand has exclusively external binding sites; clay minerals kaolinite and illite are non-swelling 1:1 clays with external binding surfaces; illite has 3 to 5 times the ion exchange capacity and 5 to 10 times the surface area of kaolinite; montmorillonite has 2 to 7 times the ion exchange capacity and 3 to 8 times the surface area of kaolinite, but 80% of the bounds are interstitial or internal which explains the high CEC of montmorillonite. However, LAS exhibited a low  $K_d$  with montmorillonite, which is likely due the fact that LAS is excluded from the interstitial part due to the presence of the large sized benzene group.

The initial mineralization rate ( $k_1$ ) of the chemical/ humic substances was much lower than those of the other substances. This could be due to the hydrophobic interaction between the chemical and the humics instead of the more ionic interactions between the chemicals and the clay.

The  $K_d$  for humic acid bound surfactant was quite high, while for sand and montmorillonite the  $K_d$  values were low. Log  $K_d$  was negatively correlated with  $k_1$  ( $r = -0.86$ ),  $P_0$  ( $r = -0.66$ ) and the total recovery of  $CO_2$  ( $r = -0.62$ ). This suggests that the greater the affinity of a chemical for the environmental matrix, the lower the availability of a chemical to the degrading populations. No correlation was found between  $K_d$  and  $k_0$ . If  $k_0$  represents the loss of  $^{14}C$  from biomass into which it has become incorporated (i.e. via growth), then one would expect no correlations between  $K_d$  (related to initial sorption) and  $k_0$  (related to cell death, and subsequent use of cell matter in metabolism by other cells).

#### 2.3.1.4. Field tests: degradation in soil

An overview of the available data is given in Table 2 on LAS degradation in sludge-amended soils under field conditions is given in Table 2.

Marcomini carried out a field study at an experimental plot at Liebefeld, near Bern, Switzerland) [31]. The field received 142 t dry weight/ha since 1976 in total (13.5 t/ha year which is 6 times the average application rate in Switzerland). The rate of biodegradation could best be described by establishing three periods: an initial period (first 10 days), a time of transition (90 days) and a long term residence in the soil (>150 days). This can be explained by competition between biodegradation and sorption on and into soil

Table 2: Biodegradation half-lives of LAS in the terrestrial environment

Soil	Initial conc. (mg/kg)	Test period	Biodegradation half life (days)	Extent	Reference
Two fields in Spain	16.4	-	25.7	-	[16]
	52.5	-	33.0	-	[16]
Heavy clay soil	27.2	76d	25.7	63.6%	[25]
Loose sandy soil	16.2	106d	13.1	72.3%	[25]
Experimental plot in Switzerland	45	initial ( $\pm 10$ d)	5.0	-	[31]
		transition ( $\pm 90$ d)	77.9	-	[31]
		final (>150d)	<3465	-	[31]
Five fields in the UK	-	-	7.0 - 21.7	-	[32]
Spain	22.4	6 months	-	86	[33]
		1 year	-	97	[33]
Monitoring study in the UK including 51 fields					[34]
	-	-	15 sites	>99%	
	-	-	10 sites	>98-98.9	
	-	-	9 sites	>95-97.9%	
	-	-	3 sites	>80-94.9%	

particles. The quick disappearance in the initial period is caused by the biodegradation of the fraction readily bioavailable to soil microorganisms, e.g. the fraction in the aqueous phase or sorbed to the surface of the particles. The residues are more strongly bound to the soil organic fraction or incorporated in the soil organic particles, making them less available (transition period) or unavailable (final period) to biodegradation. An increase in residual level of LAS due to yearly application of sludge is thus theoretically possible for the non-readily available fractions.

Berna et al. studied the evolution of LAS after soil amending in two different fields in Spain [16]. The LAS input on amending was 16.4  $\mu\text{g/g}$  and 52.5  $\mu\text{g/g}$  for the two different fields respectively. The first field received 1.6 g dry sludge/ $\text{m}^2$  twice a year for 3 years, the other field showed no previous history of LAS exposure. The half-lives were respectively 26 and 33 days.

Holt et al. monitored the concentration of LAS in soils for a large number of locations in the UK (24 farms and 51 fields of which 35 were pasture and 16 arable land.) [34]. The sites did not receive any application of sludge before 1974 to avoid confusion with branched alkyl benzene sulphonates (ABS). Removal of LAS was calculated on the basis of the estimated total cumulative load and the measured concentration. The removal of LAS in sludge amended soils (application before 1987) was for 15 sites > 99%, for 10 sites between 98% and 98.9%, for 9 sites between 95% and 97.9%, for 3 sites between 80% and 94.9% indicating rapid and complete removal of LAS over time.

The disappearance of LAS with time, following application of sludge, was studied in 5 fields in the UK, at three different locations and with three different application methods: subsurface injection, surface spreading onto arable land followed by ploughing and surface spreading onto pasture land [32]. Half-lives ranged between 7 and 22 days, and was not depending on the method of application. The minimum and maximum rate that has been quoted for two fields are related to a rapid initial rate followed by a reduced rate. This may relate to the bioavailability of LAS. Also the homologue distribution was investigated. No marked preferential biodegradation of LAS with a specific chainlength was noticed. This suggests that the primary mechanism of disappearance of LAS is microbial degradation rather than physicochemical since leaching should result in an increased percentage of higher homologues.

#### 2.3.1.5. Groundwater

In sandy soils with a low organic content, LAS was not mobile at realistic concentrations: it did not leach from the bottoms of approximately 40 cm deep lysimeters though higher concentrations of LAS were more mobile, at least to 10 cm depth [35]. Lack of leaching at the bottoms negated the influence of the small lysimeters used, which may have had large wall-effects that could have given increased leaching. Biodegradation of LAS was very rapid with half-lives of 7-days in the field and 3-days in the lysimeters.

Figge and Schöberl performed an exhaustive study on the fate and distribution of radiolabelled LAS using a plant metabolism box with two crop ecosystems (bush beans, grass and radish grown on heavy clay-

like soil; potatoes grown on a loose, sandy soil) [25]. Less than 1.5% of the radioactivity originally applied transferred with the percolating water through the 50 cm soil cores. The radioactivity comprised mainly soluble  $^{14}\text{C}$ -containing carbonates and smaller amounts of mixed organic substances, with only traces of intact LAS, if any at all.

The mineralization of LAS and the vertical distribution of microbial biomass and activity was determined in groundwater through monitoring of two wells, upgradient and downgradient of the leach field from the wastewater from a rural laundromat [28]. Direct counts of microbial biomass were 10 to 100 times lower in the groundwater compared to the aquifer solids from the same site and depth. The mineralization of LAS did not occur in either well, although significant activity was associated with the solids at the same depth. Thus, biodegradation measured in the groundwater is not an accurate measure of the potential for biodegradation in the subsurface.

The removal of LAS from groundwater in a plume of groundwater contamination, caused by infiltration of secondary treated sewage disposed on sand beds (Cape Cod, Massachusetts), was studied by Field [36]. The LAS concentration in a well, 500 m south east of the sand bed, was measured. During ground water transport, removal is due to sorption and biodegradation. Low suspended solids concentration (0.3mg/l) and a low fraction of organic carbon of 0.0075 on sediments near the infiltration beds, suggest less removal though sorption than through biodegradation. The residence time was estimated to be  $>986$  days (assuming  $K=0$  and  $\max v=0.5\text{m/d}$ ). Based on first order kinetics the rate constant  $k$  was  $\geq 2.5 \times 10^{-3}/\text{day}$  and the corresponding half-life was  $\leq 201$  days ( $0.693/k$ ). This half life is ten times greater than the half life for laboratory mineralization essays using sediments acclimatized to LAS [7,29]. No complete mineralization occurred. This can be due to decreased activity of groundwater microbial populations, low temperature ( $10^\circ\text{C}$ ) and DO (0.1 mg/l), and possibly due to some differences in the degradation of certain homologues and isomers.

In conclusion, leaching of intact LAS to groundwater is highly unlikely under typical European conditions.

#### 2.3.1.6 Plant uptake

Knaebel and Vestal found some of the  $^{14}\text{C}$  from LAS applied to soil in the plant biomass (soybean and corn) [24]. The highest levels found were less than 1% of the total amount added. Uptake of the radiolabel by the plant tissues was possible through two sources: 1) parent compound (or metabolites) taken up by the roots and transported throughout the plant, and 2) uptake through the foliage of  $^{14}\text{CO}_2$  (generated by the mineralization of the surfactant by soil microbes).

Figge and Schöberl performed an exhaustive study on the fate and distribution of radiolabelled LAS using a plant metabolism box with two crop ecosystems (bush beans, grass and radish grown on heavy clay-like soil; potatoes grown on a loose, sandy soil) [25]. They found similar results as Knaebel and Vestal [24]

e.g. limited uptake of radiolabelled material and no distinction possible between exposure route (roots vs foliage) or radiolabel form (parent vs. metabolites).

### 3. ENVIRONMENTAL CONCENTRATIONS OF LAS

#### 3.1. Wastewater Treatment Sludge

Concentrations of LAS in sludge are quite high; in the order of g/kg dry sludge (Table 3). This implies that when sludge is applied to soil e.g. as a fertilizer, considerable amounts of surfactant may enter the terrestrial environment.

LAS concentration in anaerobically digested sludge was found to be much higher than in aerobically stabilized sludges. This further substantiates the conclusion that the degradation of LAS is not favored in anaerobic conditions [16,23,37].

#### 3.2. Soils

An overview of the concentrations of LAS found in sludge amended soils is given in Table 4. Table 4 indicates that soil concentrations are lower than would be expected considering the amount of sludge applied in the US and Europe, and the high sludge concentrations of LAS (Table 3). Hence, biodegradation acts as an important removal mechanism thereby minimizing exposure concentrations. It must be pointed

out that the specifications of sampling depth represents a difficulty in the interpretation of results. The deeper the soil sampled, the lower the measured concentration - either due to dilution and/or (bio)degradation.

Another way for surfactants to enter the terrestrial environment, next to sludge application, is soil infiltration of waste water or polluted river water. In the US, 25% of LAS used in laundry and cleaning products are disposed to home or on-

Table 3. Concentration of LAS and their degradation products in sludge

Country	Description	Concentration (mg/kg dry weight)	Reference
CH	anaerobically digested sludge	2900-11900	[22]
CH	sewage treatment plants	5500	[31]
D	aerobic sludge	281 (182-432)	[23]
	anaerobic digested sludge	4917 (1327-9927)	
E	non-treated sludge	400-700	[16]
	aerobically treated	100-500	
	anaerobically treated	7000-30 200	
E	non-treated sludge	8400-14000	[33]
	anaerobically digested	12100-17800	
NL	non-treated sludge	3400-5930	[39]
US	anaerobic	10 462±5 170	[37]
	aerobic	152 ± 119	
US	anaerobically digested sludge	4660±1540	[38]

Table 4. Concentration of LAS in sludge amended soils

Country	Study field/type	Application rate (t/ha/year)	Concentration (mg/kg)	Reference
D	Monitoring	6 (since 1983)	1.4 (n=4)	[23]
CH, Berne	Experimental plot	13.5 (since 1976)	5.1 (in upper 5 cm)	[31]
UK	Monitoring	6	0.0-3.0 (n=51)	[34]
E	Alicante	32	0.3 (upper 25cm)	[16]
E	Vineyard	32	22.4 (after amend.) 3.1 (6 months later) 0.7 (12 months later)	[33]

Table 5. Concentration of LAS in soil contaminated by infiltration of waste water

Study field	Sampling	Concentration in mg/kg	Reference
Pond created by the discharge of laundromat waste water (worst case situation)			[29]
	depth 0-0.6m	218.0	
	depth 0.6-1.2m	198.0	
	depth 1.8-2.1m	19.7	
	depth 2.4-2.7m	1.8	
	depth 3.3-3.7m	1.9	
Septic tank tile field			[12]
	15 cm gravel layer around the tiles	20	
	5 cm beneath the gravel bed	<1	

Table 6. Concentration of LAS in groundwater

Study field	Sampling	Concentration (ug/l)	References
Wells at x m downfield of a sewage infiltration pond, Cape Cod, US			[40]
	500m	0.3	
	3000m	not detected	
Well at x m downfield of a sewage infiltration pond, 50 feet below sea level, Cape Cod, US			[36]
	500m	3	
Septic tank tile field			[12]
	immediate vicinity	1640-13 850	
	0.5 m beneath	< 10	

site disposal systems, discharging their effluents directly to drainage fields [7]. Concentrations under these conditions are given in Table 5.

The LAS concentration in the leach field of the laundromat decreases significantly with depth, from 218 g/kg to 2 mg/kg within a distance of less than 4m. This steep decrease can be explained by a combination of biodegradation, dilution and/or sorption [29]. The same steep decrease in LAS concentration with depth was measured by McAvoy et al. [12].

### **3.3. Groundwater**

Due to discharge into drainage fields, soil infiltration of waste water and river water or sludge application on agricultural land, surfactants can potentially reach groundwater and thus even drinking water supplies.

A sharp decrease of LAS in the water phase as a function of depth as seen in the study of McAvoy et al. is important to prevent contamination of the groundwater [12].

No LAS was detected in the groundwater upgradient and downgradient of a leach field from the wastewater from a rural laundromat [28]. The high levels of biodegradation activity in the upper 3 m zone associated with the solids and the low activity below is sufficient to fully remove these compounds before they adversely affect groundwater quality. Probably, adsorption plays also a role in the removal of LAS [28].

## **4. HOMOLOGUE AND ISOMER SHIFT OF LAS RELEASED INTO THE ENVIRONMENT**

LAS is not a single chemical entity, but a mixture of several alkyl chain homologues and phenyl positional isomers. The differential fate of the constituents of LAS make the environmental distributions in effluent, and sludge different from the influent and commercial distributions of LAS.

### **4.1 Commercial material characterisation [1]**

The commercial surfactant is generally a mixture of various alkyl homologues and/or isomers. In view of differences in fate and effects of alkyl homologues, isomers and/or congeners, it is deemed necessary to define the commercial product. For linear alkyl benzene sulfonate, the alkyl chain distribution ranges from C-10 to C-13 (Table 7) with different phenyl distributions according to production process (Table 8). Knowledge of the relative importance of each process, allows the calculation of so-called commercial LAS - with its typical mean alkyl chain length of 11.6 and typical isomer distribution.

Characterization of a material provides the first indications how a material will behave in the environment (Table 9). This information will provide a basis for future environmental fate and effects testing strategies.

Table 7: Range and typical homologue distribution of LAB/LAS.

	C-10	C-11	C-12	C13
Range (%)	5-15	30-40	20-40	15-30
Typical (%)	13	31	31	25

Table 8: Typical phenyl position distribution of LAB/LAS

Production Process	Phenyl position				
	2-	3-	4-	5-	6-
HF (%)	18	16	17	24	25
AlCl <sub>3</sub> (%)	28	19	17	18	18

Table 9: Physico-chemical Characteristics of LAS

LAS-homolog isomers	C10	C10	C11	C11	C12	C12	C13	C13
	ext	int	ext	int	ext	int	ext	int
Typical %	4.9	8.1	11.7	19.3	11.7	19.3	9.5	15.5
i.e 70% HF	4.4	8.6	10.5	20.5	10.5	20.5	8.5	16.5
30% AlCl <sub>3</sub>	6.1	6.9	14.6	16.4	14.6	16.4	11.8	13.3
MW	320	320	334	334	348	348	362	362
SOL (MG/L)	20	20	15	15	10	10	5	5
k (d-1)*	2.0	1.33	2.60	1.73	3.38	2.25	4.39	2.93
Kp (L/kg)**	220	220	1000	1000	3070	3070	9330	9330
LOG Kp	2.3	2.3	3.0	3.0	3.5	3.5	4.0	4.0

\* Expert Judgement - Distance principle [7]

- 30% increase in primary biodegradation rate per alkyl chain unit

- 50% increase in primary biodegradation rate for external phenyl isomers

\*\* Experimentally derived

#### 4.2 LAS in the environment

In the influent most LAS (>95%) is in the aqueous phase, and removal is predominantly due to biodegradation, with preferential degradation of the longer chain homologues and outer isomers. This is due to their higher hydrophobicity and more rapid degradation of the higher homologue [31].

The importance of adsorption in changing the LAS composition, is seen by comparing the LAS distribution in the influent with the LAS distribution in the sludge. The longer alkyl chains and outer isomers were preferentially adsorbed [31]. The suspended solids removed almost all LAS from the aqueous phase.

Table 10. LAS homologue distribution shift during waste water treatment and composting (Prats et al., 1993)

Sampling	Remark	Avg. alkyl chain length
Domestic discharge	-	11.7
Wastewater	Dissolved	11.3
	Ads/precip <sup>a</sup>	12.0
Treated water	Dissolved	10.9
	Ads/precip <sup>a</sup>	11.8
Sludge	Ads/precip <sup>b</sup>	12.0
	Stabilized sludge (after anaerobic digestion)	12.0
Dried sludge	Ads/precip <sup>b</sup>	12.3
Sludge amended soil	After amend.	12.3
	6 months later	12.4
	12 months later	12.4
Marine sediments	outfall vicinity	11.7

a referred to filtered suspended solids

b referred to dry sludge

LAS during the treatment process most likely leaves the plant with the sludge and reaches the environment as Ca-LAS. There was no significant change in the alkyl chain length during sludge digestion. In the sludge amended soil, the alkyl chain length composition indicates an increase in %C13 and %C14 during mineralization.

Time course studies in sludge amended soil [34] indicate that during 130 days after sludge amendment, the homologue distribution of LAS in soils did not change significantly. Also, the homologue distribution gave evidence that removal was due to biodegradation rather than leaching. For the latter process, higher alkyl chain homologues should have increased in concentration.

Table 11. LAS homologue distribution shift during groundwater transport [36]

LAS homologue (%)	C10	C11	C12	C13	C14	Mean
Sewage effluent	21	38	22	6	2	11.2
Groundwater	43	39	21	0	0	10.8

The homologue distribution shift of LAS during its transport was monitored in samples of influent (raw water) and effluent of treatment stations, digested sludge, amended soil and marine sediment [33]. Results are presented in Table 10.

The homologue distribution of dissolved LAS in the waste water has a lower molecular weight than the adsorbed precipitated LAS. This may be attributed to the higher adsorptivity of the solids for the heavier LAS homologues as shown by Hand and Williams [13]. As a consequence, the solid phase will be enriched by the higher alkyl chain homologues of LAS. The highest proportion of the non-biodegraded

Field investigated the homologue composition of LAS in the effluent of a sewage treatment plant and a well, 50 feet beneath sea-level and located in the vicinity of the treatment plant [36]. A

Table 10. LAS homologue distribution shift during waste water treatment and composting (Prats et al., 1993)

Sampling	Remark	Avg. alkyl chain length
Domestic discharge	-	11.7
Wastewater	Dissolved	11.3
	Ads/precip <sup>a</sup>	12.0
Treated water	Dissolved	10.9
	Ads/precip <sup>a</sup>	11.8
Sludge	Ads/precip <sup>b</sup>	12.0
	Stabilized sludge (after anaerobic digestion)	12.0
Dried sludge	Ads/precip <sup>b</sup>	12.3
Sludge amended soil	After amend.	12.3
	6 months later	12.4
	12 months later	12.4
Marine sediments	outfall vicinity	11.7

a referred to filtered suspended solids

b referred to dry sludge

LAS during the treatment process most likely leaves the plant with the sludge and reaches the environment as Ca-LAS. There was no significant change in the alkyl chain length during sludge digestion. In the sludge amended soil, the alkyl chain length composition indicates an increase in %C13 and %C14 during mineralization.

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Field investigated the homologue composition of LAS in the effluent of a sewage treatment plant and a well, 50 feet beneath sea-level and located in the vicinity of the treatment plant [36]. A

shift towards the shorter chain homologues was observed (Table 11). This was due to preferential sorption and/or biodegradation of the longer chain homologues. Determination of the isomers indicated preferential removal of external isomers (2-phenyl and 3-phenyl) during groundwater transport. This can be explained by a higher adsorption for 2-phenyl isomers than for 5-phenyl isomers [13] and preferential biodegradation of external isomers [41]. Consequently only internal isomers were detected in groundwater 500m from infiltration.

Overall, it can be concluded that the longer alkyl chain homologues and outer isomers will be more rapidly biodegraded (in the aqueous phase) or sorbed (in the solid phase). This can be explained by a higher hydrophobicity of the longer alkyl chains and outer isomers.

## 5. PERSPECTIVES FOR A TERRESTRIAL RISK ASSESSMENT

### 5.1 PEC calculations

Risk assessments have two components: an assessment of the potential environmental concentrations, and an assessment of the environmental effects of the chemical. The European Union Technical Guidance Document in support of risk assessment of new notified and existing substances [3] provides a methodology and testing strategy for the risk assessment of substances entering the soil environment through sludge-amendment. Exposure assessment for the soil compartment is important with respect to exposure of terrestrial organisms, crops grown on agricultural soils for human exposure, and cattle producing meat and milk. These three different terrestrial endpoints employ different scenarios (Table 12) for the calculation of predicted environmental concentrations (PEC).

Table 12: Characteristics of soil and soil-use for the three different endpoints indicated in the EU-TGD [3]

	Depth of soil compartment (m)	Averaging time (days)	Rate of sludge application (kg * m <sup>-2</sup> * yr <sup>-1</sup> )	Endpoint
PEC <sub>local,soil</sub>	0.20	30	0.5	terrestrial ecosystem
PEC <sub>local,agric. Soil</sub>	0.2	180	0.5	crops for human consumption
PEC <sub>local grassland</sub>	0.10	180	0.1	grass for cattle

Sludge application is treated as a single event once a year. The concentration will be high just after application and lower at the end of the year due to biodegradation processes. Therefore, the concentrations need to be averaged over a certain time period. Sludge will be applied through spraying, harrowing, or ploughing (depending on the intended agricultural use). The application practice influences the depth of sludge distribution in the soil.

The PEC calculations are used for two purposes: characterisation of risk to terrestrial ecosystems and as the starting point for calculation of indirect exposure of humans via crops and cattle products (Figure 1). We use the maximum, 90th-percentile and average LAS concentration values observed in anaerobically treated sewage sludge in Europe as initial values for PEC calculations. Biodegradation half-lives in soil of approximately 15-30 days have been observed (Table 2) and will be used in addition to the scenario of complete lack of biodegradation. Results of the PEC calculations are presented in Table 13.

Table 13: PEC calculations for LAS in soil (mg/kg)

Csludge	Biodegradation half life (days)	PEC <sub>local, soil</sub>	PEC <sub>local, agricultural soil</sub>	PEC <sub>local, grassland</sub>
Max. EU-value: 30200 mg/kg	none	44.4	44.4	17.8
	30	32.0	10.5	4.2
	15	24.3	5.3	2.1
90% EU-value: 11900 mg/kg	none	17.5	17.5	7.0
	30	12.6	4.1	1.7
	15	9.5	2.1	0.84
Avg. EU-value: 6282 mg/kg	none	9.2	9.2	3.7
	30	6.7	2.2	0.87
	15	5.0	1.1	0.44

## 5.2 Indirect human exposure

Indirect human exposure to LAS is potentially possible via drinking water and plant products. This indirect exposure needs to be compared to the exposure through use of household products containing LAS, such as detergents and dishwashing liquids. ECETOC calculated a total daily exposure through the dermal and oral route as 81 ug/day for children and 178 ug/day for adults [42]. Over 25 years of use has shown no human health risks exists with such direct exposure to LAS.

The EU-TGD provides a worst-case scenario to calculate the PEC in groundwater, which is assumed equivalent to the soil pore-water concentration in agricultural soil. The latter concentration is calculated by using the PEC<sub>local, agricultural soil</sub> (2.2 mg/kg, Table 12), soil density (1700 kg\*m<sup>-3</sup>) and the K<sub>soil-water</sub> (100 L/kg, Table 1). The PEC<sub>local, groundwater</sub> is 37.4 ug/L. This worst-case approach overestimates concentrations observed in field situations (Table 6).

Assuming that the maximum concentration found in groundwater equals the concentration in drinking water (e.g. 3 ug/L), a human being has to drink approximately 25-50 L of water per day for intake of a similar amount of LAS through the other exposure routes.

We also used the observed groundwater concentrations as PEC<sub>local</sub>, pore-water values to estimate expected concentrations of LAS in plants. As an initial approach, it is assumed that the BCF of LAS in plants is similar to those of fish (e.g. 91 [43]). The expected concentration of LAS in plants is 0.34 mg/kg. The average European daily plant consumption (fruit, vegetables, cereals and potatoes) for children and adults is 1.02 and 1.26 kg/day, respectively [42]. Thus, LAS uptake by human beings through plants is at maximum 27.8 to 34.4 µg/day, clearly well below the consumer exposure through LAS containing products.

In conclusion, the initial realistic worst case assessment presented indicates no human health risks exists with indirect exposure to LAS through either food or drinking water.

### 5.3 Terrestrial organisms

A review of the literature by Kloepper-Sams et al. indicates that terrestrial toxicity data for invertebrates, and numerous higher plants are available for LAS [8]. Factors that significantly impact the toxicity results are different modes of exposure (hydroponic medium, addition to irrigation water, spiked soil, spiked sludge) and types of soil. These must be taken into account when performing a definitive risk assessment.

Another factor that needs to be taken into account is the form of LAS in the environment, which is not similar to the commercial material applied in detergents. The differential sorption and biodegradation of the LAS components lead to a shift in the alkyl chain length (homologue), and phenyl-isomer distribution towards increased hydrophobicity. Also, occurrence of Ca/Mg-salts in the environment versus the Na-salt for the commercial material critically impacts the extrapolation of effects data obtained in lab studies (mostly performed with the commercial material) to the field.

Limited acute toxicity data were available for invertebrates, however, recently Homstrup and Krogh published a chronic toxicity study with the springtail, *Folsomia fimetaria* [44]. Effective concentration, 10%, values were estimated, based on measured concentrations, as 163 mg LAS/kg for growth of juveniles, 185 mg/kg for molting frequency, and 147 mg/kg for reproductive output. An aqueous solution of LAS was spiked to a natural soil (LUFASpeyer 2.2). This addition of LAS to soil can be considered as worst-case compared to sludge-amended soil due to the high bioavailability of LAS. The average predicted environmental concentrations of LAS in the terrestrial soil after sludge-amendment is 6.7 mg/kg, well below the critical effect concentration for this collembolan.

Numerous terrestrial plant LAS studies are available. The study by Figge and Schöberl extended throughout the growing season, and was the most realistic in terms of sludge application to agricultural land and plant growth, but did not attempt to establish an NOEC [25]. Kloepper-Sams et al. recognized that no doses were utilized which yielded effects, hence the NOEC-values of 27 and 16 mg/kg soil are minimum values [8]. This study can be considered a model ecosystem study, and these worst-case values are already much higher than the PEC<sub>local</sub>, agricultural soil of 2.2 mg/kg.

In conclusion, current LAS use does not pose a risk to terrestrial organisms such as plants and invertebrates.

## 6. CONCLUSIONS

Concentrations of LAS in sludge are quite high due to sorption to primary sludge, precipitation of Ca and Mg-salts of LAS, and lack of biodegradation under anaerobic digestion. This implies that when sludge is applied to soil e.g. as a fertilizer, considerable amounts of this important surfactant may enter the terrestrial environment.

Anaerobic conditions are not prevalent in nature and constitute a transient situation. Aerobic situations prevail probably during sludge storage and surely after sludge-amendment to soil. Currently, insufficient information is available on the behaviour of LAS in stored sludge to fully incorporate these aspects into the environmental risk assessment. Research is underway to further elucidate this. Aerobic biodegradation in soil can thus be considered the most important removal mechanism of LAS loading to the terrestrial environment.

A negative correlation between the sorption coefficient, the biodegradation rate constant  $k$  and extent of total mineralization was reported by Knaebel et al. [4,5]. This indicates that a greater affinity for the environmental matrix lowers the bioavailability for degradation. Therefore, soil type can influence biodegradation. To the contrary, Larson et al. claim that biodegradation rates of LAS are not influenced by soil type [6]. This discrepancy may be explained by the use of different kinetic models to fit the experimental data.

Sorption also plays a role in determining the residence time of a chemical in the soil. As sorption increases, the residence time increases, hereby enabling more time for biodegradation to occur [7]. In addition, sorption may affect the expression of effects of surfactants towards benthic and soil dwelling organisms and plants. In most cases, a mitigation of the effects in the soil or sediment compared to similar concentrations in the water phase were measured [8].

A factor that needs further attention is the form of LAS in the environment, which is not similar to the commercial material applied in detergents. The differential sorption and biodegradation of the LAS components lead to a shift in the alkyl chain length (homologue), and phenyl-isomer distribution towards increased hydrophobicity. Also, occurrence of Ca/Mg-salts in the environment versus the Na-salt for the commercial material critically impacts the extrapolation of effects data obtained in lab studies (mostly performed with the commercial material) to the field.

For the initial terrestrial risk assessment PEC<sub>local,soil</sub> calculations were performed. These calculations indicate that dismissing the influence of soil biodegradation provides a scenario which is unrealistic as compared to the approach advocated by the EU-TGD. Hence, only PEC-values obtained with the EU-scenario were further considered.

The initial realistic worst case assessment presented indicates no human health risks exists with indirect exposure to LAS though either food or drinking water. Also, current LAS use does not pose a risk to terrestrial organisms such as plants and invertebrates.

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