Environmental Risk Assessment

LAS

Linear Alkylbenzene Sulphonate

(CAS No. 68411-30-3)

Revised ENVIRONMENTAL

Aspect of the HERA Report

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1. Contents

2. *Executive Summary*

Linear alkylbenzene sulphonate (LAS) is an anionic surfactant. It was introduced in 1964 as the readily biodegradable replacement for highly branched alkylbenzene sulphonates (ABS). LAS is a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the *para* position and attached to a linear alkyl chain.

The European consumption of LAS in detergents applications covered by HERA was about 350 kt in 2005. This represents more than 80% of the total European consumption of LAS, which was estimated to be about 430 kt in the year 2005. LAS is one of the major anionic surfactants used on the market. Important application products are household detergents, such as laundry powders, laundry liquids, dishwashing products and all-purpose cleaners. The minor other final uses of LAS, namely in the field of textile and fibres, chemicals, and agriculture, are outside HERA's scope.

Environmental assessment

- The present environmental risk assessment of LAS is based on the HERA methodology document, which in its turn is based on the EU Technical Guidance Document (TGD, 2003). It makes use of the EUSES programme following the HERA detergent scenario (EUSES, 2004). LAS concentrations (PEC values) measured or modelled in the various environmental compartments were compared with extrapolations of the many available eco-toxicity data leading to PNEC values protective of each compartment.

- In raw sewage, the LAS concentration was in the range of 1-15 mg/l. When the sewage was properly treated in activated sludge STPs (Sewage Treatment Plant). LAS was highly removed leading to an effluent concentration in the 0.008-0.27 mg/l range.

- LAS concentration was further decreased by dilution in the receiving waters where it could be found in the <0.002-0.047 mg/l concentration range. LAS degrades rapidly aerobically (half-life in rivers about 3 hours), whereas it does not degrade under anaerobic conditions, except under particular conditions.

- Typical LAS concentrations in aerobic sludge are <0.5 $g/kg_{dw\ sludge}$ (dry weight). In STP anaerobic sludge, the calculated median LAS concentration was 5.6 $g/kg_{dw\ sludge}$ (dry weight) (15.1 $g/kg_{dw\ sludge}$ at 95th percentile). During sludge transportation to the farmland, sludge storage, and application on agricultural soil, aerobic conditions are restored and rapid degradation of LAS resumes.

- In sludge-amended soils, LAS had a maximum half-life of one week (primary biodegradation) and monitored concentrations were around 1 $mg/kg_{dw\ soil}$ (maximum 1.4 $mg/kg_{dw\ soil}$) at harvesting time. No accumulation in soil and no bioaccumulation in plants could be detected experimentally.

- In freshwater sediments, measured LAS concentrations typically ranged from <1 $mg/kg_{dw\ sed.}$ to a maximum value of 5.3 $mg/kg_{dw\ sed.}$.

- Ecotoxicity data are abundant and well documented. The aquatic PNEC value (0.27 mg/l) was calculated from: i) a statistical extrapolation including a set of high quality single species chronic data and ii) the no-observed effect concentration of a stream community experimentally exposed to LAS.

- The terrestrial PNEC value (35 $mg/kg_{dw\ soil}$) was calculated from: i) a statistical extrapolation of a set of high quality chronic data on plants and soil fauna, ii) an expert judgement on the toxicity of several microbial processes and functions, iii) field toxicity studies, and 4) the equilibrium partitioning method.

- The sludge PNEC value (49 $g/kg_{dw\ sludge}$) was back-calculated from the soil PNEC on the basis of the EU TGD scenario (TGD, 2003).

- The sediment PNEC value (23.8 $mg/kg_{dw\ sed.}$) was calculated from i) the lowest available chronic effect value and an application factor, and ii) the equilibrium partitioning method, the PNEC was normalized for organic carbo content.

- The STP PNEC (5.5 mg/l) was calculated from acute and chronic microbial inhibition data and the use of the relevant application factor (TGD, 2003).

- The risk characterisation as expressed by the PEC/PNEC ratio was below 1 for all environmental compartments. It was concluded that the ecotoxicological parameters of LAS have been adequately and sufficiently characterized and that the ecological risk of LAS is judged to be low.

Human health assessment

- The presence of LAS in many commonly used household detergents gives rise to a variety of possible consumer contact scenarios including direct and indirect skin contact, inhalation, and oral ingestion derived either from residues deposited on dishes, from accidental product ingestion, or indirectly from drinking water.

- The consumer aggregate exposure from direct and indirect skin contact as well as from inhalation and from oral route in drinking water and dishware results in an estimated total body burden of 34.6 mg/kg bw/day. This body burden is significantly higher compared to the body burden of 0.4 µg/kg bw/day reported in the previous version of this HERA document. The higher estimated body burden is a result of using the information from the RIVM report Cleaning Products Fact Sheet - To assess the risks for the consumer (RIVM,2006), additional to the consolidated overview concerning habits and practices of use of detergents and surface cleaners in Western Europe which was tabulated and issued by AISE (THPCPWE,2002). Furthermore, some additional use scenarios have been identified.

- The toxicological data show that LAS was not genotoxic *in vitro* or *in vivo*, did not induce tumours in rodents after two years daily dosing, and failed to induce either reproductive toxicity or developmental or teratogenic effects. The critical adverse effect identified after repeated long term high dosing of LAS to animals was a change in renal biochemical parameters. A systemic NOAEL of 68 mg/kg bw/day was established.

- Comparison of the aggregate consumer exposure to LAS with the systemic NOAEL results in an estimated Margin of Exposure (MOE) of 1.97. The estimated Margin of Exposure is based on conservative estimations of both exposure and NOAEL (which is a systemic NOAEL given the existence of oral toxicokinetic data). This MOE is significantly lower compared to the MOE

of 17000 reported in the previous version of of this HERA document. The lower MOE is a direct result of the higher estimated body burden (see above).

- Neat LAS is an irritant to skin and eyes. The irritation potential of aqueous solutions of LAS depends on concentration. Local effects of hand wash solutions containing LAS do not cause concern given that LAS is not a contact sensitizer and that the concentrations of LAS in such solutions are well below 1% and therefore not expected to be irritating to eye or skin. Laundry pre-treatment tasks, which may translate into brief hand skin contact with higher concentrations of LAS, may occasionally result in mild irritation easily avoided by prompt rinsing of the hands in water. Potential irritation of the respiratory tract is not a concern given the very low levels of airborne LAS generated as a consequence of cleaning sprays aerosols or laundry powder detergent dust.

- In view of the extensive database on toxic effects, the low exposure values calculated and the resulting Margin of Exposure described above, it can be concluded that use of LAS in household laundry and cleaning products raises no safety concerns for the consumers.

3. Substance Characterisation

Linear alkylbenzene sulphonate (LAS) is an anionic surfactant. It was introduced in 1964 as the readily biodegradable replacement for highly branched alkylbenzene sulphonates (ABS). LAS is a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the *para* position and attached to a linear alkyl chain.

3.1 CAS No. and grouping information

LAS, used on the European market and covered in this focused risk assessment, is represented by the list in Table 1.

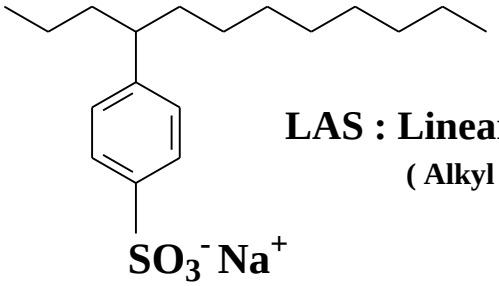
Table 1: CAS and EINECS numbers of LAS in the European market

CAS No.	EINECS No.	NAME
68411-30-3	270-115-0	Benzenesulphonic acid, C_{10-13} alkyl derivs., sodium salts
1322-98-1	215-347-5	Sodium decylbenzenesulphonate
25155-30-0	246-680-4	Benzenedodecylsulfonic acid, sodium salt
90194-45-9	290-656-6	Benzenesulphonic acid, mono-C_{10-13} alkyl derivs., sodium salt
85117-50-6	285-600-2	Benzenesulphonic acid, mono-C_{10-14} alkyl derivs., sodium salt

The present assessment focuses on LAS levels in consumer products used on the European market and found in the various environmental compartments. LAS represented by the CAS No. 68411-30-3 and EINECS No. 270-115-0 is by far the most used on the European market (>98%).

3.2 Chemical Structure and Composition

LAS on the European market is a specific and rather constant mixture of closely related isomers and homologues generated in the manufacture of the raw material Linear Alkyl Benzene (LAB), the LAS precursor, each containing an aromatic ring sulphonated at the “para” position and attached to a linear alkyl chain at any position except the terminal carbons (Schönkaes, 1998; Cavalli et al., 1999b; Valtorta et al., 2000), as shown in the figure below:



LAS : Linear Alkyl Benzene Sulfonate

(Alkyl Chain : C_{10} - C_{13})

The linear alkyl chain has typically 10 to 13 carbon units, approximately in the following mole ratio C_{10}:C_{11}:C_{12}:C_{13}=13:30:33:24, an average carbon number near 11.6 and a content of the most hydrophobic 2-phenyl isomers in the 18-29% range (Feijtel et al., 1995b; Feijtel et al., 1999; Cavalli et al., 1999b; Valtorta et al., 2000). This commercial LAS consists of more than 20 individual components. The ratio of the various homologues and isomers, representing different alkyl chain lengths and aromatic ring positions along the linear alkyl chains, is relatively constant across the various household applications. This LAS constant ratio is unique and does not apply to the other major surfactants. Therefore, the present assessment adopted a category approach, i.e., considered the fate and effects of the LAS mixture as described above rather than of each isomer and homologue separately. However, fingerprints in the different environmental compartments are reported.

The linearity of the alkyl chain is between 93% and 98% depending on the different manufacturing processes of LAB, the LAS precursor (Cavalli et al., 1999b). The mono-methyl substituted alkylbenzene sulphonate (iso-LAS) (Nielsen et al., 1997) represent on average 2 to 7% of the raw material. The kind of substitutions of iso-LAS was shown not to limit their biodegradation, which under realistic environmental conditions was comparable to the one of LAS (Nielsen et al., 1997; Dunphy et al., 2000). Non-linear components such as DiAlkylTetralin Sulphonates (DATS) can be present at levels of 3-10% in the LAS derived from $AlCl_3$ catalysed LAB process (see par. 3.3). This process, however, was less than 5% in 2005 (ECOSOL, 2005).

The data presented in Table 2 are fully described in IUCLID, 1994 and SIDS, 2005 and refer to the commercial $C_{11.6}$ LAS or the pure C_{12} homologue.

Table 2: Physical chemical data of the commercial $C_{11.6}$ LAS (IUCLID, 1994; SIDS, 2005)

LAS	Protocol	Results
Molecular description	Solid organic acid sodium salt	-
Molecular weight (g/M)	$(C_{11.6}H_{24.2})C_6H_4SO_3Na$	342.4
Vapour pressure at 25°C (Pa)	Calculated as C_{12}	$(3\text{-}17) \cdot 10^{-13}$
Boiling point (°C)	Calculated as C_{12}	637
Melting point (°C)	Calculated as C_{12}	277
Octanol-water partition coefficient ($\log K_{ow}$)	Calculated as $C_{11.6}$	3.32
Organic carbon-water partition coefficient K_{oc} (l/kg)	Calculated as $C_{11.6}$	2500
Critical micelle concentration (g/l)	Experimental	0.65
Water solubility (g/l)	Experimental	250
Sorption coefficient between soil/sediment and water,	Experimental	2-300

K_d (l/kg)		
Density (kg/l)	Experimental	1.06 (relative) 0.55 (bulk)
pH (5% LAS water solutions)	Experimental	7-9
Henry's constant (Pa · m^3/mole)	Calculated as C_{12}	$6.35 \cdot 10^{-3}$

Molecular weight was calculated according to the structure of the sodium salt of the benzenesulphonic acid with an average $C_{11.6}$ linear alkyl chain.
Vapour pressure ($3 \cdot 10^{-13}$ Pa) was estimated for C_{12}LAS (Lyman, 1985) and calculated ($17 \cdot 10^{-13}$ Pa) using EPI database by a Syracuse Research Corporation (SRC) software (SIDS, 2005).
Melting and boiling points were calculated using Estimation Program Interface (EPI) database by a SRC software (SIDS, 1999).
The octanol-water partition coefficient, log K_{ow}, cannot be experimentally measured for surfactants because of their surface–active properties, but only approximately calculated (Roberts, 2000). A log K_{ow} of 3.32, for the $C_{11.6}$LAS structure was calculated with a method (Leo et al., 1979) modified to take into account the various aromatic ring positions along the linear alkyl chain (Roberts, 1991). This value was used in the aquatic risk assessment carried out in the Netherlands (Feijtel, 1995b).
Organic carbon-water partition coefficient (K_{oc}) values of 110 and 278 were calculated for C_{12}benzenesulphonate using regression equations from water solubility and log K_{ow} data (Lyman, 1990).
A better indication of this association can, however, be represented by the sludge partition coefficient, K_p (l/kg), assessed by QSAR analyses (Feijtel et al., 1999; Garcìa et al., 2002)). For pure compounds, log K_p of 3.0 and 3.5 for C_{11}LAS and C_{12}LAS respectively were derived and used in full-scale studies of activated sludge plants (Feijtel, 1995a; Feijtel, 1995b). Laboratory experiments (Temmink et al., 2004) with LAS showed that sorption of the C_{12}LAS homologue over sludge is a fast and reversible process that can be described by a K_p value (K_p = 3210 l/kg) in agreement with the above QSAR calculations. Applying the same QSAR for the commercial $C_{11.6}$LAS mixture, a log K_p value of 3.4 (K_p = 2500 l/kg) can thus be derived and confidently assumed as a measure of the partition of the surfactant between organic matter and water and assimilated to K_{oc}. An average log K_{oc} value of 4.83 was also reported for C_{12}LAS as a measure of its association with dissolved organic compounds, basically represented by humic acids (Traina et al., 1996).
A critical micelle concentration (CMC) of 0.65 g/l for the commercial $C_{10\text{-}13}$LAS was reported (Smulders, 2002); the value is in line with that of other anionic surfactants. CMCs were also measured for the different LAS homologues in deionized and hard waters (Garcìa et al., 2002).
The reported water solubility and density values were experimentally derived (IUCLID, 1994). pH values in water solutions depend on the free caustic soda content in LAS after neutralisation of the sulphonic acid; in general, 5% water solutions of commercial LAS have pH values in the 7-9 range.
Soil/sediment and water sorption coefficients, K_d (l/kg), were experimentally measured; they ranged from 2 to 300 l/kg, depending on the organic content, and fit the Freundlich equation (Painter, 1992). K_d sediment values were higher than K_d soil ones, as a consequence of the higher organic content in sediment than in soil (Marchesi et al., 1991; TGD, 2003).
Using a structure estimation method (Meylan et al., 1991) the Henry's constant for C_{12} benzenesulphonate was calculated to be $6.35 \cdot 10^{-3}$ (Pa · m^3/mole).

3.3 Manufacturing route and production/volume statistics

LAS is produced by sulphonation of LAB with a variety of sulphonating agents. In the past, oleum (fuming sulphuric acid), as well as sulphuric acid were the predominant agents used either in batch

reactors or in the so-called “cascade” systems. The sulphonation technology, however, has been considerably improved since the mid 60s and nowadays, although oleum is still used, modern falling film reactors (FFR) (mono-tube or multi-tube) and SO_3 gas are the state of art of the technology in most of the sulphonation facilities in Europe. In these modern plants both the sulphonation of LAB and the sulphation of fatty alcohols are normally practised.

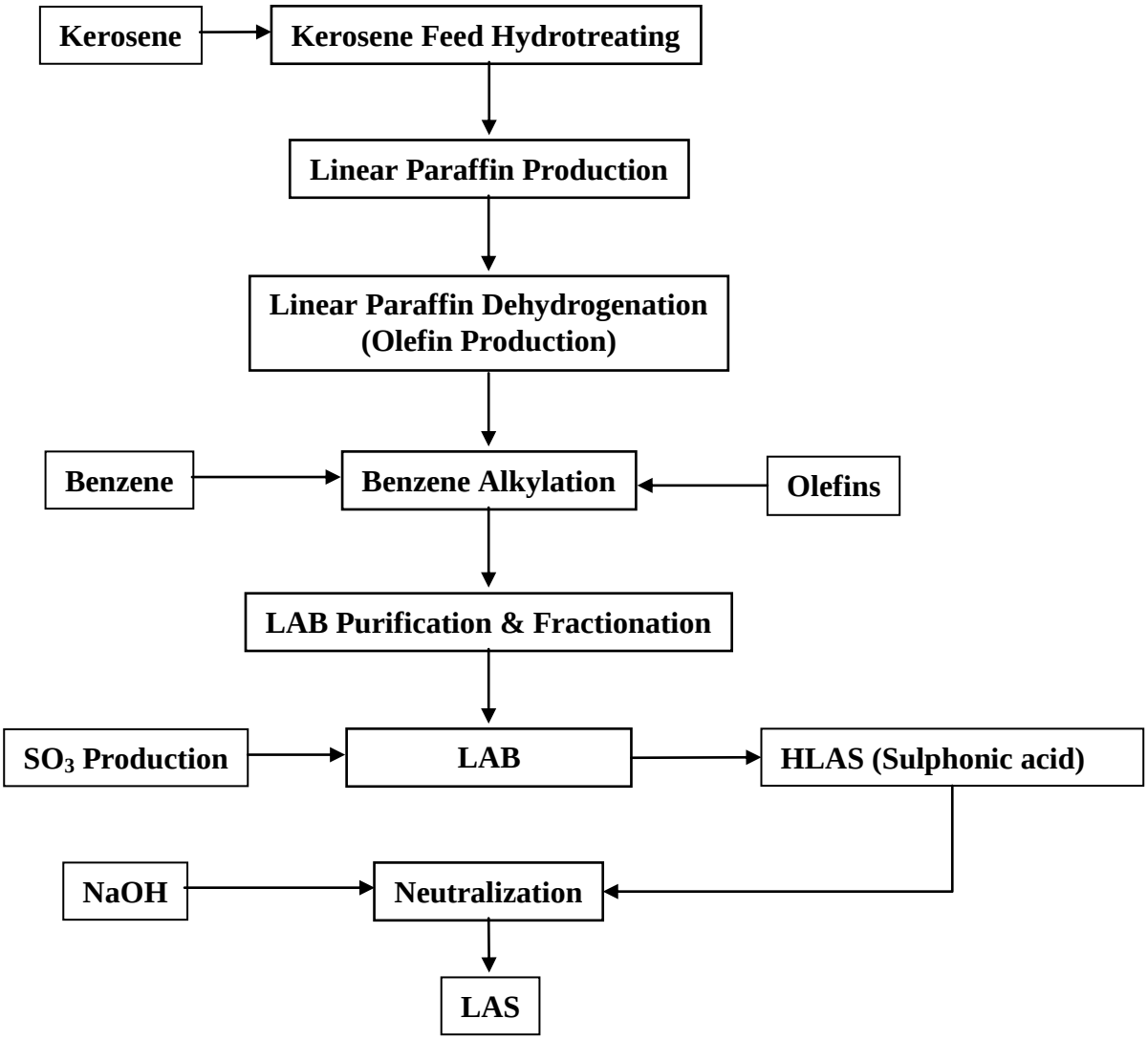
LAB, the precursor of LAS, is manufactured in large scale industrial processes by alkylating benzene with linear mono-olefins or alkyl halides such as chloro-paraffins by using HF or $AlCl_3$ as the alkylation catalyst (Cavalli et al., 1999b), and recently also over heterogeneous solid super-acids in a fixed-bed reactor (Erickson et al., 1996). LAB production quality, as measured by its bromine and colour indexes as well as by impurities and alkyl chain linearity, has been enhanced over time following significant technological improvements (Marr et al., 2000). Alkylation with $AlCl_3$ was the first commercial process used in the mid 60s when branched dodecylbenzene (DDB) was replaced by LAB. At the end of the 60s the HF technology was applied for the first time and immediately it became the preferred technology to be installed in the world to produce LAB.

In the mid 90s a new alkylation technology based on heterogeneous catalyst in a fixed-bed reactor, Detal®, appeared on the market (Berna et al., 1994) and was rapidly adopted, as testified by several new units recently installed with this technology. The new technology offers considerable advantages over the old ones, namely: process simplification, elimination of acids handling and disposal (HF, HCl) as well as an overall production yield improvement and improved LAB quality.
Production of commercial LAS involves a series of processes as shown schematically in the below scheme.

Total LAB world production capacity in the year 2005 is estimated to be more than 3 million tons, with a split by technology as follows: 75 % HF, 5% $AlCl_3$, and 20 % fixed-bed. In Europe, in the year 2005, the estimated installed LAB capacity was around 600 kt/y with a corresponding demand of 325 kt/y (ECOSOL, 2005; CESIO, 2005).

The result of sulphonating LAB is the formation of alkylbenzene sulphonic acid, which has the consistency of a liquid with a high active content, >97% by titration with hyamine (ISO 2271; EN 14480), containing about 1% of unsulphonated matter and 1-2% of H_2SO_4 (IUCLID, 1994; Schönkaes, 1998). It represents commercially the most important supply form. The acid is then neutralised with a base to give the final LAS surfactant salt. Sodium neutralised LAS is by far the predominant grade. As salt, it can also be supplied in various forms and active contents, for example as paste (50-75%) and powder (80-90%) (Schönkaes, 1998).

Processing Steps in LAB-LAS Production



3.4. Consumption scenario in Europe

The most recent and realistic market survey was completed by the Ecosol companies (ECOSOL, 2005), which estimated a total consumption tonnage of about 430 kt for the year 2005, with a breakdown by household applications of about 350 k, corresponding to more than 80% of the total according to an independent survey of AISE companies.

Table 3: Tonnage consumption estimates of LAS in Europe in 2005

Survey	Total kt	Household Kt
ECOSOL	430	350 (>80% vs. total)

The present focused risk assessment models the use of the highest realistic LAS figure available for the household products, namely 350 kt/y. In addition, the reported monitoring data, related to total

tonnage consumption and degradation in the environment, have been used in the final higher tier risk assessment.

3.5 Use application summary

Most of LAS European consumption is in household detergency (>80%). Important application products are laundry powders, laundry liquids, dishwashing products and all purpose cleaners. The remainder of the LAS (<20%) is used in Industrial and Institutional (I&I) cleaners, textile processing as wetting, dispersing and cleaning agents, industrial processes as emulsifiers, polymerisation and in the formulation of crop protection agents.

4. Environmental risk assessment

The extensive body of research studies on the environmental properties of LAS present in the literature is reported here below. This abundance of information is sometimes forgotten or wrongly quoted (Ying, 2006) and has to be again reminded (CLER, 2007).

4.1 Environmental exposure assessment

4.1.1 Biotic and abiotic degradability

Aerobic biodegradation in aqueous medium

LAS primary biodegradation is the transformation induced by microorganisms with formation of sulpho phenyl carboxylates (SPCs) as biodegradation intermediates (Swisher, 1987). This biodegradation stage corresponds to the disappearance of the parent molecule and to the loss of interfacial activity and toxicity towards organisms present in the environment (Kimerle et al., 1977; Kimerle, 1989). The change of the interfacial activity of the surfactant during biodegradation has much more importance on the aquatic toxicity than the biodegradation as measured, for example, by the biological oxygen demand (BOD); that was shown by a recent detailed study on the relation between interfacial activity and aquatic toxicity during primary LAS biodegradation (Oya et al., 2010).

Biodegradation proceeds further with i) the cleavage of the aromatic ring and the complete conversion of LAS and SPCs into inorganic substances (H_2O, CO_2, Na_2SO_4) and ii) the incorporation of its constituents into the biomass of micro-organisms (ultimate biodegradation) (Karsa et al., 1995).

One of the first evidences that the alkyl and ring portions of LAS can extensively biodegrade and convert to CO_2 in the environment was shown in a STP simulating laboratory equipment using a ^{14}C ring-labelled commercial product and some pure unlabelled homologues (Nielsen and Huddleston, 1981). The primary biodegradation of LAS, measured by MBAS (Methylene Blue Active Substance) or by specific analytical methods such as HPLC (High Performance Liquid Chromatography), in any OECD tests (OECD, 1993), is >99% (EU Commission, 1997). The ultimate biodegradation measured by DOC (Dissolved Organic Carbon) is in a range going from 80% to >95% for CAS (Continuous Activated Sludge) simulation tests (OECD 303 A), and in the 95-98% range for inherent tests (OECD 302) (EU Commission, 1997).

CAS simulation tests (OECD 303 A) were run for the commercial LAS product in the 9-25°C temperature range (Prats et al., 2003). The acclimation lag phase was significantly different at the various temperatures, being longer at lower temperatures. The percent LAS removal measured by MBAS and HPLC, however, was always similar and high (>95%) in all cases, indicating that the microorganism community can also reach a proper acclimation and that kinetics are also adequate

at low temperatures (Prats et al., 2006; Leòn et al., 2006). These results are in agreement with some stream mesocosm studies which concluded that the mineralization of surfactants under realistic environmental conditions, where various algal species are acclimated following natural temperature fluctuations, was at least maintained and often increased during significant seasonal decreases in temperature (Lee et al., 1997).

The commercial LAS product is readily biodegradable (EU Commission, 1997). The 10-day window is not deemed necessary for assessing ready ultimate biodegradability of surfactants in detergents (CSTEE, 1999). However, in the literature LAS is reported to pass the 10-day window rule as shown by: i) a comparative CO_2 evolution study (Ruffo et al., 1999; Anon, 2002), ii) OECD 301 F tests following the biodegradation by O_2-consumption and specific C_{12}LAS analysis (Temmink et al., 2004) and iii) recent tests run according to the GLP principles, namely, CO_2 evolution test following OECD 301B (LAUSa, 2005), DOC die-away test following OECD 301A (LAUSb, 2005) and mineralization under ISO 14593/1999 test in compliance with the Detergent Regulation 648/2004 (Lòpez et al., 2005). The formation of persistent biodegradation intermediates can be excluded as demonstrated by high tier tests (Gerike et al., 1986; Moreno et al., 1991; Cavalli et al., 1996b). Biodegradation intermediates, i.e. the sulpho phenyl carboxylates (SPCs), are not persistent and their toxicities are several orders of magnitude lower than that of the parent molecule (Kimerle et al., 1977).

Considering the absence of persistent metabolites and the relatively low toxicity of the transient degradation products, the rate of primary biodegradation, rather than that of the ultimate biodegradation is the relevant parameter for risk assessment purposes. Specific analytical methodologies based on High Performance Liquid Chromatography (HPLC), Gas Chromatography/Mass Spectrometry (GC/MS) and Liquid Chromatography/Mass Spectrometry (LC/MS) have been developed for LAS, which provided kinetic data relevant for exposure assessments (Matthijs et al., 1987; Trey et al., 1996; Di Corcia et al., 1999). Relevant kinetics of LAS biodegradation were obtained in a die-away laboratory test applying innovative testing procedures to radio-labelled materials, measuring $^{14}CO_2$ evolution by Liquid Scintillation Counting (LSC) and following the biodegradation by Radio Thin-layer Chromatography (RAD-TLC) (Federle et al., 1997). In these studies, using river water as test medium, the primary biodegradation rate was approximately $k = 0.06\ h^{-1}$ ($t_{0.5}$ = ca.12 h) (Itrich et al., 1995) and about 10-15 times lower than that found using activated sludge as test medium (Federle et al., 1997).
Field studies (further described in Section 4.1.3), carried out in some rivers under realistic environmental conditions specifically to measure in-stream removal kinetics of LAS, showed $t_{0.5}$ in the 1-3 h range indicating that kinetics are faster than those displayed in laboratory studies (Takada et al., 1992; Schröder, 1995; Fox et al., 2000),. This is due to the more favourable biodegradation conditions in the real environment vs. those reproduced in laboratory.
Considering the above available field data, **a protective primary biodegradation half-life of 3 hours in aqueous medium was considered in the present risk assessment.**

Biodegradation under anaerobic conditions
In the existing laboratory screening and simulation tests (ECETOC, 1994; OECD TG 307, 2002; OECD TG 308, 2002; OECD TG 311, 2006; ISO 11734: 1995; ISO 13641-1,-2: 2003), which are extensively reviewed in literature (ERASM, 2007; Berna et al., 2007; Berna et al., 2008), the ultimate biodegradation was measured by determining the final gas production (CO_2 and CH_4) after about two months of incubation. In these studies LAS did not show any significant biodegradation (Steber et al., 1989; Steber, 1991; Federle et al., 1992;; Gejlsbjerg et al., 2004; Garcìa et al., 2005). Loss of parent LAS was only claimed after several months of incubation (Prats et al., 2000a) and more recently by both laboratory and field specific experiments (Lara-Martin et al., 2007; Lara-Martin et al., 2008; see also par. 4.2.1.3).

Other approaches have been recently proposed to assess the anaerobic biodegradation of substances:

- OECD guideline (OECD TG 314, 2008). It is the description of an analytical procedure made by a set of five separate but complementary simulation tests, which assess the primary and ultimate biodegradation of chemicals in the sewer wastewater, in the secondary treatment of the activated sludge system, in the anaerobic sludge digester, in the treated effluent and surface water mixing zone, and in the untreated wastewater directly discharged to surface water. The third test (test C) evaluates biodegradation during anaerobic sludge digestion, in particular aims to demonstrate whether chemicals have the potential for anaerobic biodegradation or not. LAS has been tested with this method: results confirm the absence of anaerobic biodegradation (Procter & Gamble, 2008).
- DIN method (DIN 38414-8 modified, 2008). The method, as recently described (Willing, 2008), is an anaerobic sewage plant simulation test. It is presently under development with the aim to improve it in terms of repetibility, reproducibility and reduction of false negative results.

Screening and simulation tests, at any rate, are not essential for a good understanding of LAS risk assessment. Field testing takes precedence over simulation test data. There is a very significant amount of field monitoring data available for LAS in agricultural soils (Jensen et al., 2007; Schowanek et al., 2007) and anaerobic digesters (where no significant degradation of LAS is seen).

However, in oxygen-limited conditions, which occur in the real world, LAS biodegradation can initiate and then continue in anaerobic conditions (Larson et al., 1993; Leon et al., 2001).
Some inocula are indeed capable of converting LAS under some particular anaerobic conditions, e.g., in sulphate-limited environments where LAS is the only source of sulfur (Denger et al., 1999). In addition, according to some studies LAS can biodegrade under methanogenic conditions, but low bioavailability in waste water treatment plant reactors is the main factor which in reality prevents any substantial biodegradation (Angelidaki et al., 2000a; Mogensen et al., 2003). However, some biodegradation was shown as follows: 14-25% range in continuous stirred tank (CST) reactors (Angelidaki et al., 2000b; Haggensen et al., 2002) and 5-44% range in upflow anaerobic sludge blanket (UASB) reactors (Sanz et al., 1999; Mogensen et al., 2003). In any case, biodegradation under strict anaerobic conditions was shown to have little direct ecological relevance (Heinze et al., 1994; ERASM 2007) and not formally considered in the EUSES modelling program (see 4.1.4).
In addition, the opinion of the Scientific Committee on Health and Environment Risks (SCHER), a committee of experts who serve an advisory role within the European Commission (EC), on the environmental risk posed by detergent surfactants that are poorly biodegradable under anaerobic conditions, such as LAS, is as follows:…"A poor biodegradability under anaerobic conditions is not expected to produce substantial modifications in the risk for freshwater ecosystems as the surfactant removal in the STPs seems to be regulated by its aerobic biodegradability" (SCHER, 2005). This statement was again confirmed by SCHER in its opinion of 2008: "The LAS-HERA report of 2004 contained no recent publications which affected the conclusion of SCHER in its opinion of 2005. Similarly recent publication, later than 2004 (Garcia et al., 2005; Garcia et al. 2006a and b; references cited in LAS-HERA report of 2007), did not give grounds for any change of that opinion" (SCHER, 2008).
As a consequence, the requirement of ultimate biodegradability under anaerobic conditions cannot be considered an effective measure for environmental protection.
However, the following rationales position the relevance of anaerobic biodegradation in ecological risk assessment. In anaerobic environments, the redox potential is so low that O_2 is replaced by NO_3^-, SO_4^{2-} or CO_2 as ultimate electron acceptors. In such reduced environments, the effects assessment should include specific organisms, e.g., anaerobic bacteria, protozoa. The aquatic organisms (algae, crustaceans, fish) typically considered for the effects assessment are, therefore, not representative of these communities. Macro-invertebrates do live in deep anoxic sediment, but usually within oxic micro-environments (e.g., a burrow). Assessing the risk of surfactants to these

burrowed organisms would require a modelling of the diffusion of surfactants in deep sediment and their biodegradation rate once oxic conditions are restored. However, the oxic micro-environment used by sediment dwelling organisms is physically, chemically, and biologically closely connected with the thin surface sediment layer and the calculated PEC in that layer would be a better indicator of the exposure in such micro-environments.

A specific risk assessment in anaerobic environments would include effects on anaerobic bacteria in anaerobic digesters. It has been shown that LAS at concentrations up to 30 g/kg_{dw} sludge does not affect the microbial processes in these digesters (Berna et al., 1989). The LAS effect on the anaerobic sludge digestion process was investigated showing that toxicity on the anaerobic microorganisms depended on the concentration of the bioavailable LAS homologues in the liquid phase of the STP anaerobic digesters; an EC_{50} of 14 mg/l was calculated (Garcìa et al., 2006b). Poor primary LAS degradation in anaerobic discontinuous systems was confirmed showing also that the inhibition extent of the biogas production was significantly related to the sludge used as inoculum (Garcìa et al., 2006a).

Biodegradation in soil

Several measurements of LAS in sludge-amended soil from both laboratory and field studies have been carried out and are reviewed in the literature (De Wolf et al., 1998; Jensen, 1999; Cavalli et al., 1999a). These investigations were performed, after application of sludge containing LAS to soil usually at rates higher than that recommended in agriculture, maximum 5 t DS (Dry Solids)/ha/y (TGD, 2003). For example, the annual sludge spreading averaged 6 t/ha in the UK (Holt et al., 1989; Waters et al., 1989), 32 t/ha in Spain (Berna et al., 1989; Prats et al., 1993), 13.5 t/ha in Switzerland (Marcomini et al., 1988) and 6 t/ha in Germany (Matthijs et al., 1987). In all these studies the calculated LAS removal corresponded to half lives in the range of $t_{0.5}$= 3-33 days.

The most reliable results in the laboratory were obtained by investigating mixtures of sludge and LAS-spiked soils using ^{14}C materials, measuring ultimate biodegradation. LAS mineralization rates corresponding to $t_{0.5}$ = 13-26 days (Figge and Schöberl, 1989) and $t_{0.5}$ = 7.0-8.5 days (Gejlsbjerg et al., 2001) were estimated. Mineralization with $t_{0.5}$ = 2.1-2.6 days was obtained after a lag time of 1.9-2.5 days at 10 mg/kg_{dw} LAS concentration in soil, which is the highest expected environmental concentration of the surfactant in an agricultural land (Gejlsbjerg et al., 2003).

Laboratory sludge-soil mixtures with ^{14}C-labelled LAS at concentrations in the $\mu g/kg_{dw\ soil}$ range, corresponding to predicted steady concentrations (at least after a waiting period of 30 days from sludge application) of the surfactant in sludge-amended soil, were also investigated (Gejlsbjerg et al., 2004). After relative long lag times (ca. 2 weeks), LAS was mineralized rapidly and extensively showing two phase kinetics: a first rapid mineralization ($t_{0.5}$ = ca. 2 days) followed by a slow mineralization phase ($t_{0.5}$ = 7.9 days), the latter likely governed by sorption and desorption processes in the soil. Even subsurface soils, sampled below a septic system drain field and investigated in laboratory sorption and biodegradation studies using groundwater and radiolabeled materials, showed to have the potential to mineralize LAS (ultimate $t_{0.5}$ from 0.32 to 8.7 d) (Doi et al., 2002). Other LAS leaching properties in soils and groundwater were investigated to develop a mathematical model for septic systems to predict the fate and transport of consumer product ingredients (McAvoy et al., 2002).

However, most laboratory studies and all field monitoring studies in sludge-amended soil measure the disappearance of LAS, estimating, thus, the primary biodegradation.

In the laboratory tests it was shown that for soil spiked with aqueous LAS and LAS-spiked sewage sludge, the disappearance (primary biodegradation) of the surfactant was more than 73% after 2 weeks (Elsgaard et al., 2001b). A soil mesocosm study showed that the primary degradation of LAS was rapid with $t_{0.5}$ of 1-4 days (Elsgaard et al., 2003). A field study, at sludge application rates close

to those recommended in agriculture (equal or below 5 t_{dw}/ha/y), estimated $t_{0.5}$ values in the range of 3-7 days (Küchler et al., 1997).
Accurate data for degradation of LAS in sludge-amended soil under realistic field conditions were reported by Mortensen et al., 2001. Its degradation in soil increased by the presence of crop plants with soil concentrations decreasing from 27 mg/kg_{dw} to 0.7-1.4 mg/$kg_{dw\ soil}$ at harvesting time after 30 days ($t_{0.5}$ <4d).
Considering the above available field data**, a conservative protective primary biodegradation half-life of 7 days in agricultural soils was considered in the present risk assessment.**

Hydrolysis and photolysis degradation
Reactions of hydrolysis (Cross, 1977) and photolysis (Matsuura et al., 1970; Venhuls et al., 2005) of LAS are described in literature (Table 4) in conditions not relevant to the environment. The corresponding results are, thus, not considered in the present assessment.

The set of data on LAS biodegradation properties relevant to this risk assessment are summarized in Table 4.

Table 4: Biodegradation properties

LAS	Protocol	Results	References
Screening, confirmatory	OECD 301 D OECD 303 A	>99 (% primary biod.)*	EU Commission, 1997
Ready test	OECD 301 A, B, D, E, F ISO 1493/1999	Readily biodegradable >70 (% DOC removal) >60 (% CO_2 evolution) >60 (% O_2 uptake)	EU Commission, 1997 Ruffo et al., 1999 Temmink et al., 2004 LAUS, 2005a-b Lòpez et al.,2005
Inherent test	OECD 302 A, B	95-98 (% DOC removal)	EU Commission, 1997
Simulation test	OECD 303 A	80->95 (% DOC removal)	EU Commission, 1997
Biodegradation rate in activated sludge	Die-away	$t_{0.5}$ = 0.6-0.7 h (prim. biod.) $t_{0.5}$ = 1.3-1.4 h (ultim. biod.)	Federle et al., 1997
Biodegradation rate in river water	Die-away Die-away River monitoring	$t_{0.5}$ = 12 h (prim. biod.) $t_{0.5}$ = 18 h (ultim. biod.) $t_{0.5}$ = 1-3 h (prim. biod.)	Itrich et al., 1995 Itrich et al., 1995 Fox et al., 2000
Anaerobic biodegradation	ECETOC Research study	ca.0 (% ultim. biod.) 5-44 (% prim. biod. in UASB reactors)	AISE/CESIO, 1994 Mogensen et al., 2003
Biodegradation rate in soil	Field study	$t_{0.5}$ = 1-7 d (prim. biod.)	Küchler et al., 1997 Elsgaard et al., 2003

	Laboratory study	$t_{0.5}$ = 2-26 d (ultim. biod.)	Figge et al., 1989 Gejlsbjerg et al., 2001, 2003, 2004
Hydrolysis	Research study	Decomposition: 60-70% in presence of inorganic acids at 150-200°C	Cross, 1977
Photolysis	Research study	Degradation: 80-95% under mercury lamp (200-450 nm)	Matsuura et al., 1970 Venhuls et al., 2005

(*) measured by MBAS and by additional HPLC analysis

4.1.2 Removal

Sewers
LAS removal rates in sewers, due to a combination of biodegradation, adsorption and precipitation, were measured during field studies in different countries up to a degree of 68% (Moreno et al., 1990; Matthijs et al., 1999). Laboratory studies have demonstrated that the concentration of all surfactants can be significantly reduced in sewers, depending on the length of the sewer, travel time and the degree of microbial activity present in the sewer (Matthijs et al., 1995).

Laboratory CAS systems
Accurate confirmatory CAS data, using MBAS and specific analytical methods (such as HPLC) or ^{14}C measurements to determine the LAS removal rate, are available (Schöberl et al., 1988; Cavalli et al., 1996a; Leon et al., 2006). In these tests the removal rate of the parent surfactant was always >99%.

Sewage Treatment Plants
LAS removal in Activated Sludge Sewage Treatment Plants, (as-STPs), has been documented in several studies and found to be mostly in the 98-99.9% range (Berna et al., 1989; Painter et al., 1989; Waters et al., 1995; Cavalli et al., 1993; Matthijs et al., 1999). This elimination efficiency can be further increased when membrane biological reactors (MBR) will become economically available (Terzic et al., 2005). The LAS removal in as-STPs, measured in five European countries, averaged 99.2% (6 records in the range 98.5-99.9%) (Waters et al., 1995) and 99.4% (4 records in the range 98.9-99.9%) (Holt et al., 2003).
Total LAS removal in Trickling Filter Sewage Treatment Plants (tf-STPs), are lower and more variable and were found in the 89.1-99.1% range (24 records) in Europe with an average value of 95.9% (Holt et al., 2003). These values are higher than those reported for tf-STPs in USA where average removals of 83% (Trehy et al., 1996) and 77% (McAvoy et al., 1993) were recorded.
The following proportions are based on as-STP mass balance studies: 80-90% degraded, 10-20% adsorbed onto sludge and about 1% released to surface waters (Berna et al., 1989; Painter et al., 1989; Cavalli et al., 1993; Di Corcia et al., 1994).
For EUSES modelling assessment, Predicted Exposure Concentrations (PECs) were calculated assuming 79% degradation, 20% to sludge and 1% release to water (see 4.1.6).

The dataset of removal rates relevant to this risk assessment are summarised in Table 5.

Table 5: Removal data

LAS	Results	References
Removal in CAS test (%)	>99	Schöberl et al., 1988 Cavalli et al., 1996
Total STP removal (%)	as-STP: 98-99.9 (range) as-STP: 99.2 (arithmetic mean)	Matthijs et al., 1999 Waters et al., 1995
as-STP: degraded (%)	80-90	Berna et al., 1989 Painter et al., 1989 Cavalli et al., 1993 Di Corcia et al., 1994
as-STP: released to water (%)	ca. 1	
as-STP: adsorption into sludge in (%)	10-20	

4.1.3 Monitoring studies

Several monitoring studies on LAS in the different environmental compartments are available in Europe. Here below monitoring data for surface waters, ground waters, sludge, soils and sediments are summarized.

Surface waters

The present aquatic risk assessment refers specifically to the European monitoring project carried out in five different countries (UK, Germany, Netherlands, Spain, Italy), using a common and agreed protocol in the context of the Dutch risk assessment of surfactants (Feijtel et al., 1995b). The results of this multi-years EU monitoring project were consistent with previous monitoring studies (Berna et al., 1989; Painter et al., 1989; Cavalli et al., 1993) and with other recent monitoring programmes in Europe (Holt et al., 2003). The results illustrate well the actual European LAS content in the as-STP effluents and sludge as well as in the corresponding receiving rivers (Schöberl et al., 1994; Di Corcia et al., 1994; Sànchez Leal et al., 1994; Feijtel et al., 1995a; Holt et al., 1995; Waters et al., 1995; Matthijs et al., 1999).

In the EU monitoring study project LAS levels in raw sewage ranged from 1 to 15 mg/l (Feijtel et al., 1995b; Matthijs et al., 1999). In the same EU project LAS effluent concentrations under normal as-STP operating conditions were altogether in the 8-220 µg/l range with an arithmetic mean of 42.8 µg/l (46 records), considering all the available results.
In the receiving waters downstream the above as-STP effluents, just after the mixing zone, the LAS concentration was in the <2-47 µg/l range with an arithmetic mean of 14.2 µg/l (23 records) (Feijtel et al., 1995b; Matthijs et al., 1999). The highest LAS concentration (47 µg/l) would decrease to <2 µg/l in one day, considering a conservative in-stream biodegradation half-life of 3 hours (see par. 4.1.1).

LAS environmental fingerprints in effluent and surface waters differ from the composition of the commercial material. The relative ratio of the various homologues detected in the aquatic environmental samples is as follows: C_{10}:C_{11}:C_{12}:C_{13} = 45:30:23:2 with an average carbon number of 10.8 (Prats et al., 1993; Cavalli et al., 1993; Di Corcia et al., 1994; Tabor et al., 1996). That is a consequence of two processes: i) biodegradation in the water phase which is faster for the higher homologues and ii) adsorption into sediments and suspended solids which is more pronounced for higher homologues.

In another comprehensive European monitoring programme, carried out in the context of the GREAT-ER project (Geography-Referenced Exposure Assessment Tool for European Rivers), thousands of effluent samples from different STPs and samples of river waters were measured in

UK for their LAS content over a 2-year period (Holt et al., 2003). All effluents from as-STPs were in the 7-273 µg/l range; those with an additional tertiary treatment were found below 50 µg/l.

In US monitoring studies LAS concentrations in river waters below STP mixing zones were also generally found below 50 µg/l (McAvoy et al., 1993; Trehy et al., 1996; Tabor et al., 1996).
A US study conducted to assess a weight of evidence (WoE) risk of alkyl sulfates (AS), alkyl ethoxy sulfates (AES) and LAS was based on accurate monitoring of STP streams located in 3 different sites (Sanderson et al., 2006). The total LAS concentrations were in the range 2.75-3.96 mg/l in influents, 1.3-2.9 µg/l in effluents and 0.26-3.8 µg/l in the receiving river waters.
A study to evaluate the validity of as-STP fate models was carried out, monitoring the C_{12}LAS concentrations under controlled and well-established conditions in a pilot-scale municipal as-STP. C_{12}LAS concentrations were 2-12 mg/l in influents, 5-10 µg/l in effluents and 37-69 mg/kg_{dw} in the waste aerobic sludge. The removal of the LAS homologue (>99%) was totally ascribed to biodegradation (Temmink et al., 2004).

The tf-STP effluents, on the contrary, have usually higher and more variable LAS concentrations because these plants are not so efficient as the (as)-STPs. BOD_5 removals are in the 85-95% range for tf-STPs (Holt et al., 2000), whereas they are always >95% for as-STPs. tf-STP effluent LAS concentrations, in flow proportional composite samples, were in the 40-430 µg/l range with an average value of 240 µg/l in Europe (Holt et al., 2000; Holt et al., 2003) and up to 1.5 mg/l in the US (Rapaport et al., 1990; McAvoy et al., 1998).

In river waters receiving effluents either from tf-STPs (Fox et al., 2000) or from undersized as-STPs (Gandolfi et al., 2000), LAS was shown to be removed rapidly. Downstream the mixing zones of tf-STP, the LAS concentrations were 0.42-0.77 mg/l and decreased to 72 and 33 µg/l at 4.8 and 3.3 km respectively from the tf-STP outfall (Fox et al., 2000). From an undersized as-STP, LAS concentrations in 24-h composite samples were on average 120 µg/l at the mixing zones and 27 µg/l at 26 km (Gandolfi et al., 2000). These results indicate that in-stream removal is an efficient process and were used to validate a dynamic quality model to assess the fate of xenobiotics in the river water compartment and benthic sediment (Deksissa et al., 2004).
Other types of discharges, including direct discharges, exist in Europe. Downstream these discharges, higher concentrations of BOD, NH_3, LAS and other contaminants can be monitored. According to some studies (McAvoy et al., 2003; Dyer et al., 2003), the relative in-stream removal of LAS is higher than the removal of BOD and therefore the impact of untreated discharges on the receiving ecosystem is not caused by LAS but rather by low dissolved O_2 and high unionised ammonia.

As recommended by the TGD (TGD, 2003), only monitoring data of river waters receiving effluents from as-STPs, as well as the highest concentrations found in the European monitoring studies, were considered relevant to the present risk assessment.
Conclusion: PEC effluent (PEC_{STP}) = 0.27 mg/l; PEC river waters = 0.047 mg/l.

Ground waters
No LAS monitoring data in ground waters are available for Europe. In samples collected in the USA, LAS concentrations were below the detection limit in several monitored wells drilled in an area near a pond system exposed to high concentrations of detergent chemicals for more than 25 years (Larson, 1989). LAS concentrations in ground waters, 500 m downstream a sewage infiltration, were below the analytical detection limit (<10 µg/l). In one well, using an improved analytical methodology, a maximum LAS concentration of 3 µg/l was recorded (Field, 1992).

Sludge

Measured LAS concentrations in sewage sludge have been reviewed (De Wolf et al., 1998; Jensen et al. 1999; Cavalli et al. 1999; Fraunhofer, 2003; Leschber, 2004 Jensen and Jepsen, 2005; Schowanek et al., 2007). Typical LAS concentrations in aerobic sludge are <0.5 $g/kg_{dw\ sludge,}$ higher LAS concentrations are noted in anaerobic sludge (<1 $g/kg_{dw\ sludge}$ up to 30 $g/kg_{dw\ sludge}$). The highest LAS concentrations in anaerobic sludge (ca. 30 $g/kg_{dw\ sludge}$) were found in one specific Spanish region in the presence of a very high water hardness (>500 mg/l as $CaCO_3$) (Berna et al., 1989). Water hardness data collected by AISE companies are available for Europe and indicate that on average 13% of the European population use water with hardness <70 mg/l, 33% with medium hardness (70-212 mg/l) and 53% with hardness >212 mg/l (Jensen et al., 2006). This high LAS value in Spanish sludge is clearly an outlier.

Although these reports cover LAS concentrations in sludge for a number of wastewater treatment plants in different European countries, they do not represent the situation in one specific country. A comprehensive survey of LAS measurements in aerobic and anaerobic sludge was reported (Jensen and Jepsen, 2005) from the ongoing monitoring program of pollutants in sludge in Denmark. LAS concentrations are annually measured and reported to the Danish EPA for approximately 1,400 waste water treatment plants in Denmark. This survey allowed to derive the Danish LAS distribution in sludge: a mean concentration of 0.24 $g/kg_{dw\ sludge}$ (0.5 to 1.5 $g/kg_{dw\ sludge}$; 5^{th} to 95^{th} percentile) (Jensen et al., 2006).

At the European level, approximate sludge distributions were also calculated based on literature data over the time period 1988-2006 (Schowanek et al., 2007). The result of the distribution of the anaerobic sludges (ca. 155 records) was a mean of 5.56 $g/kg_{dw\ sludge}$ (0.49 to 15.07 $g/kg_{dw\ sludge}$; 5^{th} to 95^{th} percentile), where the highest point in the data set was the already mentioned Spanish value of ca. 30 $g/kg_{dw\ sludge}$, a clear outlier.

The LAS homologue distribution in sludge is approximately in the mole ratio C_{10}:C_{11}:C_{12}:C_{13} = 7:24:39:30 with an average carbon number of 11.9, as a consequence of a preferential adsorption of higher homologues (Berna et al., 1989; Cavalli et al., 1993; Di Corcia et al., 1994).

It is worth taking into account possible differences of LAS concentration in wet sludge, freshly produced at STP, from that in dry sludge, aged and dried before its use in agriculture (several months after). It was found that the LAS concentration in the bulk of dry sludge could drop by 74% compared to that of wet sludge (Carlsen et al., 2002). Removal of LAS from sludge can also effectively be performed by composting systems. This methodology for handling sludge in general was extensively discussed in a workshop in Denmark (SPT/EPA, 1999) and was recognised as a useful method to reduce the level of some xenobiotics. Several composting studies have demonstrated that LAS can be removed (>98%) with half-life of 7-9 days (Petersen, 1999; Prats et al., 2000b; Sanz et al., 2006).

Conclusion: PEC in anaerobic sludge = 5.56 $g/kg_{dw\ sludge}$ (mean 50^{th} percentile) and 15.07 $g/kg_{dw\ sludge}$ (95^{th} percentile).

Soil

Results from several monitoring studies of LAS concentrations in soil are available for various soil types, sludge application rates, and averaging times. For example, concentrations of up to 3.0 mg LAS/kg_{dw} were measured in sludge-amended soil at a sludge application rate of 6 t DS/ha/y for extended periods in the UK and Germany (Matthijs et al., 1987; Holt et al., 1989). LAS concentrations in sludge-amended soils were reviewed concluding that they were generally below 20 mg/kg soil, depending on the application rate or sampling time after sludge application (Solbè, 1999). At sludge application rates less than 5 t/ha/y, 30 days after its application, LAS concentrations in soil are expected to be in the low mg/kg range. With sludge application rates higher than those used in the normal agricultural practice (6-10 t/ha/y), LAS concentration in an

experimental field of soil-pots with rapes dropped from an initial measured value of 27 mg/$kg_{dw\ soil}$ to 0.7-1.4 mg/$kg_{dw\ soil}$ in soil at harvest time after 30 days (Mortensen et al., 2001).

A series of soils having a known history of sludge amendment and selected to be typical for Denmark were monitored (Carlsen et al., 2002). In regions where the sludge application was carried out according to the prevailing agricultural rules, the concentration of LAS in all soils was found to be <1 mg/$kg_{dw\ soil}$, well below the soil quality criterion for LAS of 5 mg/$kg_{dw\ soil}$ proposed in Denmark (Jensen et al., 1995). The LAS concentration that can be found in soil at any time after sludge applications, in any case, is always too low to contribute significantly to the mobilization of hydrophobic organic compounds in sludge-amended soil (Haigh, 1996).
Conclusion: PEC in soil = 1.4 mg/$kg_{dw\ soil}$.

Sediments
Available measured LAS data in fresh water sediments were reviewed (Cavalli et al., 2000). Typical LAS values in sediments below sewage outfalls were found in the 0.5-5.3 mg/$kg_{dw\ sed.}$ range with an arithmetic mean of 2.9 mg/$kg_{dw\ sed.}$ (12 records).
Homologue distributions were also measured for some river sediment samples and the corresponding fingerprint was found similar to that of sludge and soils (Cavalli et al., 2000).
Conclusion: PEC in sediment = 5.3 mg/$kg_{dw\ sed.}$.

The set of monitoring data relevant to this risk assessment are summarised in Table 6. The effluent and river data refer to representative EU monitoring studies and to samples collected downstream of (as)-STPs. Most of the data were used in the aquatic risk assessment carried out in the Netherlands (Feijtel et al., 1995b). Sludge and soil data refer to studies developed in the context of the terrestrial risk assessment in Europe (Jensen et al., submitted; Schowanek et al., 2007) .

Table 6: Monitoring data

LAS	Results	References
Effluent (µg/l)	as-STP: 8-220 (range) as-STP: 2-273 (range) as-STP: 42.8 (arithmetic mean) as-STP: 1.3-2.9	Feijtel et al., 1995b Holt et al., 2003 Matthijs et al., 1999 Sanderson et al., 2006
River water (µg/l)	down as-STP: <2-47 (range) down as-STP: 14.2 (arithmetic mean) down as-STP: 0.3-3.8	Feijtel et al., 1995b Matthijs et al., 1999 Sanderson et al., 2006
Ground water (µg/l)	0-3	Field et al., 1992
Anaerobic sludge (g/$kg_{dw\ sludge}$)	5.56 (median 50th percentile) 0.49-15.07 (5th to 95th percentile)	Schowanek et al., 2007
River sediment (mg/$kg_{dw\ sed.}$)	<1-5.3 (typical range) 2.9 (arithmetic mean)	Cavalli et al., 2000

Soil ($mg/kg_{dw\ soil}$)	0.7-1.4, measured at harvest time (30 d) <1, typical agricultural value	Mortensen et al., 2001 Carlsen et al., 2002

4.1.4 Exposure modelling: scenario description

The HERA environmental risk assessment of LAS is based on the Technical Guidance Document for new and existing substances (TGD, 2003). At screening level it makes use of the EUSES programme (EUSES, 2004) to calculate the local and regional exposure to LAS. The total estimated LAS tonnage of 330 kt/y was assumed to follow the down-the-drain pathway to the environment.

The production and formulation releases at local level were not considered because they fall outside the scope of HERA. For the calculation, the HERA exposure scenario was adopted; this scenario assigns 7% of the EU tonnage to the standard EU region, instead of the TGD default 10%, and a factor of 1.5, instead of the TGD default factor of 4, to increase the emissions at local level. These changes introduced by HERA more realistically represent the regional emissions and the local input of substances used in household detergents, as experimentally demonstrated (Fox, 2001). More details and justification of this modification can be found in chapter 2.6 of the HERA methodology document (www.heraproject.com).

Table 7: HERA exposure scenario

LAS	HERA scenario
Total yearly LAS use in household (HERA scope), kt	350
LAS continental usage going to standard EU region, %	7
Increase factor for local usage	1.5

4.1.5 Substance data used for the exposure calculations

The essential input data used for exposure calculations following the TGD and EUSES are derived from Table 2, 3, 4, and 5, and are summarized in Table 8.
The biodegradation rate in STP is the default value as assumed by TGD for readily biodegradable substances. It should be noted that this rate is not used in the assessment, as the Simple Treat output is overridden by experimental removal data. K_{ow} is also not considered in the calculations, which are rather based on K_{oc}.
The biodegradation rates in water and soil are experimentally measured values as reported in Table 4, whereas the biodegradation rates in aerated sediments and in bulk sediments are the default values as suggested in TGD (TGD, 2003).
The (as)-STP data, as measured by mass balance results and reported in Table 5, are the most protective ones for all environmental compartments. For the fraction to sludge, the extreme high value of the range, namely 0.20, was employed (see 4.1.2).

Table 8: Data for exposure calculations

General name	Linear Alkylbenzene Sulphonate (LAS)	References
Description	$(C_{11.6}H_{24.2})C_6H_4SO_3Na$	-
CAS No.	68411-30-3	-
EINECS No.	270-115-0	-
Average molecular weight (g/mole)	342.4	-
Melting point (°C)	277	SIDS, 2005
Boiling point (°C)	637	SIDS, 2005

Vapour pressure at 25 C° (Pa)	$3 \cdot 10^{-13}$	Lyman, 1985
Water solubility (g/l)	250	IUCLID, 1994
Henry's constant (Pa·m^3/mole)	$6.35 \cdot 10^{-3}$	Meylan et al., 1991
Octanol-water partition coefficient, log K_{ow}	3.32	Feijtel et al., 1995b
Organic carbon-water partition coefficient, K_{oc} (l/kg)	2500	Feijtel et al., 1999
Biodegradation rate in STP	k = 1 h^{-1} ($t_{0.5}$ = 0.693 h)	EU Commission, 1997
Biodegradation rate in river water (primary)	k = 0.23 h^{-1} ($t_{0.5}$ = 3 h)	Fox et al., 2000
Biodegradation rate in soil (primary)	k = 0.1 d^{-1} ($t_{0.5}$ = 7 d)	Küchler et al., 1997
Biodegradation rate in oxic sediments	k = 0.1 d^{-1} ($t_{0.5}$ = 7 d)	TGD, 2003
Biodegradation rate in bulk sediments	k = 0.01 d^{-1} ($t_{0.5}$ = 70 d)	TGD, 2003
STP removal (%)	99	Waters et al., 1995 Berna et al., 1989 Painter et al., 1989 Cavalli et al., 1993 Di Corcia et al., 1994
Fraction to air by STP	0	
Fraction to water by STP	0.01	
Fraction to sludge by STP	0.20	
Fraction degraded in STP	0.79	

4.1.6 PEC calculations

Column A of Table 9 reports values calculated by EUSES v2.1 (EUSES, 2008) on the basis of data in Table 7 and 8, according to the HERA scenario, considering the tonnage used in household applications (350 kt/y). In-sewer removal (50%) was not taken into account in this calculation.

Column B of Table 9 was not obtained by modelling but by using monitoring data. The values given are the high concentrations of the (as)-STP related monitoring findings in each environmental compartment, as presented in Table 6. The concentrations listed in column B can, thus, be considered the worst-case PEC of a realistic exposure scenario, excluding, as already said in 4.1.3, data related to (tf)-STPs and other discharges where LAS concentrations are only a marker of poor organic matter removal (McAvoy et al., 2003; Dyer et al., 2003). Data in the aquatic compartment are based on the monitoring results of the European project (Matthijs et al.,1999) and supported by the high tier modelling exercise of the GREAT-ER project (Fox et al., 2000; Holt et al., 2003).

The results of scenario A (modelling) and B (monitoring) are within a factor of 2 for all the environmental compartments except for soil. LAS, however, biodegrades during sludge storage, transport and the waiting period (several months) before its application to soil (Carlsen et al., 2002). A conservative degradation rate of 50% for the pre-application period would lead to a calculated soil concentration of 2.8 mg/kg$_{dw\ soil}$, closer to the highest measured ones (1.4 mg/kg$_{dw\ soil}$).

Table 9: Calculated environmental LAS concentrations

	A Modelling of household LAS usages	B LAS monitoring data
Local conc., influent, mg/l	23.7	**15**
Local conc., effluent, (PEC in STP), mg/l	0.237	**0.27**
Local conc., sludge, g/kg$_{dw\ sludge}$	12.1	**5.56** (50th percentile) **15.07** (95th percentile)
Local PEC in water, mg/l	0.027	**0.047**
Local PEC in soil (30 d), mg/kg$_{dw\ soil}$	10.9	**1.4**
Local PEC in sediment, mg/kg$_{dw\ sed.}$	1.51	**5.3**
Regional PEC in water, mg/l	0.004	-

The monitoring data presented in column B were used in the risk assessment.

4.1.7 Bioaccumulation potential

The purpose of the estimation of bioconcentration is to assess whether there is any potential for the chemical to accumulate in organisms to a high degree and hence, for further transfer up the food chain.

In the absence of measured data, the bioconcentration potential for fish, based on the lipid solubility characteristics of chemicals can be estimated based on QSARs (Quantitative Structure Activity Relationships). Due to the relationship between the bioconcentration of a chemical and its lipophilicity it is possible to predict the BCF for a particular organic compound from its octanol/water partition coefficient (K_{ow}). However, bioconcentration predictions based on K_{ow} are restricted to chemicals with a log K_{ow} <3 and >7. Such predictions are not applicable to surfactants because of their surface active properties. It must be also born in mind that bioconcentration is not a solely hydrophobicity/diffusion-driven process, and as such organismal (ADME) processes, i.e. Absorption, Distribution, Metabolism, Excretion, should as well be considered. Chemicals with a high molecular weight (MW >700) and certain molecular sizes (length, cross sectional diameters) are not likely to cross the biological membranes and therefore their bioconcentration in fish will be limited. Similarly, chemicals which can be metabolized (biotransformed) by an organism will not bioconcentrate to the extent that would be expected if diffusion was the only process involved. Reliable alternative methods already exist and are being further developed to estimate in vitro the absorption and biotransforrmation potential of chemicals in fish. These methods will finally limit the cost of in vivo bioconcentration tests on thousands of chemicals.

.

Early experimental studies on bioconcentration of LAS were not appropriate because of the analytical methods based on radio-analysis, which consistently overestimated the parent concentration present in the aquatic organism and consequently the true bioconcentration (reviewed by Tolls et al., 1994).

An in depth research project on bioconcentration of surfactants was completed and concluded that LAS is not bioaccumulative, likely due to biotransformation (metabolic) processes taking place in the fish, and therefore doesn't transfer through the aquatic food chain (Tolls, 1998).

LAS was studied employing a flow-through test system, in line with the OECD guidelines, using *Pimephales promelas* as test fish. Single homologue and isomer representatives of the commercial LAS were synthesised and then tested, determining their uptake and elimination rates in fish. Specific HPLC analysis in the water phase and in the fish body showed that LAS reaches a steady state concentration in the fish body in about 3 days. Biotransformation contributes to more than 40% of the elimination as shown for the C_{12}-2-LAS homologue (Tolls et al., 2000). BCF data for the tested LAS standards ranged between 2 l/kg (6-phenyl C_{10}LAS) to 990 l/kg (2-phenyl C_{13}LAS), allowing calculating the potential BCF of any LAS mixture (Tolls et al., 1997). BCFs were also calculated for the commercial LAS ($C_{11.6}$ alkyl chain length) and a representative sample found in river water ($C_{10.8}$ alkyl chain length, see 4.1.3). The respective BCFs were 87 l/kg and 22 l/kg, indicating that the bioconcentration potential of LAS is low and is decreased by environmental processes such as biodegradation and absorption (Tolls, 1998).

This has been confirmed recently by Dyer et al. (paper in prep.) and ERASM reports (www.erasm.org/study.html) evaluating the feasibility of *in vitro* assays with surfactants, including C_{12}LAS as prediction tools for their biotransformation and, hence, bioconcentration potential. All fish liver *in vitro* systems investigated are capable of transforming rapidly C_{12}LAS. The immortalised hepatocytes are less effective as immortalised cells and tend to loose much of their specific activity. It can be concluded that biotransformation (metabolic) processes in the fish are contributing to the lower than predicted bioconcentration potential of LAS in fish.

Pimephales promelas and three invertebrates species were caged in streams during a C_{12}LAS model ecosystem experimental study (Versteeg et al., 2003). Total C_{12}LAS BCFs for the investigated species ranged from 9 to 116 l/kg. In general, bioconcentration was affected by isomer position, exposure concentration, and species. BCF values tended to decrease as isomer position moved from external (e.g., 2-phenyl) to internal (e.g., 5,6-phenyl). BCFs also decreased as exposure concentration increased. BCFs for *Lumbriculus variegatus* exposed to freshwater sediments spiked with the C_{12}-2-LAS homologue were measured and found in the range 0.5-4.7 l/kg depending on the sediment organic content (Mäenpää and Kukkonen, 2006).

Bioconcentration potential estimation: i) ca. 87 l/kg for commercial LAS mixture ($C_{11.6}$ alkyl chain length); ii) ca. 22 l/kg for LAS in river water ($C_{10.8}$ alkyl chain length).

4.2 Environmental effects assessment

4.2.1 Ecotoxicity

The toxicity database of the present LAS risk assessment basically refers to that used in the risk assessments carried out for the aquatic compartment in the Netherlands (AISE/CESIO, 1995; Van de Plassche et al., 1999a) and to that used in a revisited risk assessment for the terrestrial environment (Jensen et al., 2007).
Robust summaries and validity ratings based on Klimisch scores have been validated for all studies during the compilation of this risk assessment and are available (www.lasinfo.org).

4.2.1.1 Aquatic ecotoxicity

The toxicity database for LAS (Kimerle, 1989; SDA, 1991; Painter, 1992; IPCS, 1996) is very rich and well documented. A comprehensive review of environmental information for the aquatic compartment that includes all data of the above mentioned literature is the BKH report (BKH, 1993). This report collects 749 records of toxicity data for LAS, specifically collated for an aquatic environmental risk assessment in the Netherlands (AISE/CESIO, 1995; Feijtel et al., 1995b; Van de Plassche et al., 1999a). The database covers several taxonomic groups; intra- and inter-species variability is large, particularly in case of algae. The reason is due to the fact that data refer to different individual compounds and mixtures of LAS and also to differences in test design as well as to the large range of species sensitivity.
In the aquatic environment, different homologues and isomers are present. Each of these components has a different degree of ecotoxicity, with the shorter chain lengths being less toxic than the longer ones. This trend is illustrated in Table 10, where geometric means of experimental aquatic toxicities of LAS homologues as extracted from the BKH review (BKH, 1993: list 12) are compared for two organisms, an invertebrate (*Daphnia magna*) and a fish (*Pimephales promelas*).

Table 10: Average measured aquatic toxicity (mg/l) of LAS homologues (BKH, 1993)

Alkyl chain	Invertebrate (*Daphnia magna*)		Fish (*Pimephales promelas*)	
	EC_{50}	NOEC	LC_{50}	NOEC
C_{10}	16.7 (7)	9.8 (2)	39.6 (4)	14 (1)
C_{11}	9.2 (17)	-	19.8 (4)	6.4 (3)
C_{12}	4.8 (37)	0.58 (7)	3.2 (9)	0.67 (3)
C_{13}	2.35 (20)	0.57 (1)	1.04 (10)	0.1 (1)
C_{14}	1.5 (13)	0.1 (2)	0.5 (3)	0.05 (1)

No. of records in parenthesis

The average chain length of the environmental fingerprint in water of LAS is $C_{10.8}$ (see 4.1.3). However, the actual ecotoxicity of the environmental fingerprint is probably not the same as the ecotoxicity associated with this average structure, because toxicity is not linearly related with chain length. Instead, ecotoxicity increases exponentially with the carbon chain length (see Table 10). Because of that, the contribution to the overall ecotoxicity of the longer (more toxic) homologues is probably more than proportional to their percentage in the fingerprint. Hence, the average structure is expected to be more ecotoxic than the real fingerprint. To take this into account, a toxicity-weighted average structure was calculated as shown in Table 11. To avoid influences of experimental variability, calculated toxicity values, instead of those reported in Table 10, were used for this exercise, obtained by means of QSAR calculations (Könemann, 1981). This resulted in a toxicity weighted average corresponding to a structure of LAS $C_{11.6}$, instead of the original LAS fingerprint average $C_{10.8}$.

Table 11: Toxicity-weighted average structure, LAS $C_{11.6}$

Chain length CL	Homologue % in fingerprint	Calculated LC_{50} (mg/l)	Weight % · $1/LC_{50}$	Weight · CL
10	45	12.48	3.6	36
11	30	4.89	6.1	67.1
12	23	1.91	12.0	144.0
13	2	0.75	2.7	35.1
SUM ⇒			24.4	282.2
Toxicity weighted average structure = SUM (weight · CL) / SUM (weight) ⇒				11.6

The ecotoxicity associated with the $C_{11.6}$ alkyl chain is, thus, expected to be representative of the overall LAS aquatic fingerprint. Below, all reported aquatic ecotoxicity data are related to, or normalised (Könemann, 1981), to this weighted average structure.

Aquatic acute ecotoxicity

Acute toxicity data, selected from the BKH report (BKH, 1993) for the commercial LAS (average carbon numbers near $C_{11.6}$) are summarized in Table 12. *Daphnia magna* and *Pimephales promelas* and *Lepomis macrochirus* were chosen as representative organisms of the toxicity of invertebrates and fish. Data for algae refer to various species. The toxicity values are the geometric means of several records as indicated in parenthesis. However, they were not used directly in the risk assessment, as higher tier data are available.

Table 12: Aquatic acute test results for commercial LAS

Taxon	$IC_{50,}$; EC_{50}; LC_{50} (mg/l) Geometric mean
Algae, IC_{50}	9.1 (n = 12, SD = ±3.9)
Invertebrate (*D. magna*), EC_{50}	4.1 (n = 17, SD = ±2.0)
Fish *(L. macrochirus*), LC_{50}	4.1 (n = 12, SD = ±1.7)
Fish (*P. promelas*), LC_{50}	3.2 (n = 4, SD = ±1.6)

No. of records in parenthesis with Standard Deviations (SD)

Aquatic chronic ecotoxicity

Chronic toxicity data from the BKH report are summarised in Table 13 (BKH, 1993). These long term toxicity data are geometric mean NOEC values obtained over fifteen freshwater species and normalised to the average structure of $LASC_{11.6}$ (Van de Plassche et al., 1999a).

Test durations for algae were 72 to 120 hours, whereas exposure periods of NOECs for crustacean and fish were at least 21 days. The lowest NOEC is that for the fish *Tilapia mossambica* (0.25 mg/l). All known literature data were incorporated and the use of a geometric mean allows deriving sound NOECs, as used in the Dutch risk assessment (Feijtel et al., 1995b). A validity rating of 1 to 2 (Klimisch et al., 1997) can be assigned to all these toxicity data points.

Table 13: Aquatic chronic NOEC data for commercial LAS (BKH, 1993; Van de Plassche et al., 1999a)

Species	End point	NOEC (mg/l) Geometric mean	Range (mg/l)
Chlamydomonas reinhardtii, alga	growth	12 (1)	-
Chlorella kessleri, alga	growth	3.5 (1)	-
Microcystis sp., alga	population density	0.80 (4)	0.05-6.1
Plectonema boryanum, alga	growth	15 (1)	-
Desmodesmus subspicatus, alga	growth	7.7 (4)	0.8-105
Selenastrum sp., alga	population density	3.8 (9)	0.58-17
Ceriodaphnia sp., crustacean	reproduction	3.2 (1)	-
Daphnia magna, crustacean	mobility	1.4 (12)	0.3-6.6
Chironomus riparius, insectum	emergence	2.8 (1)	-
Paratanytarsus parthenogenica, insectum	growth	3.4 (1)	-
Danio rerio, fish	mortality	2.3 (1)	-
Pimephales promelas, fish	mortality and others	0.87 (14)	0.5-4.8
Poecilia reticulata, fish	reproduction	3.2 (1)	-
Oncorhynchus mykiss, fish	-	0.34 (7)	0.23-0.89
Tilapia mossambica, fish	reproduction	0.25 (1)	-

No. of records in parenthesis

Since the outcome of the BKH report in 1993, several new chronic studies have become available with. These studies do not give new insight in the chronic toxicity of LAS. The outcome of these additional studies are summarised below. All studies described below (Klimish validity rating of 1 and 2) are within the range of values as reported in Table 13.

Chronic (32 days) toxicity tests of C_{12}LAS to single species (one fish and three new invertebrates), caged in model ecosystem streams, were also obtained (Versteeg et al., 2003). The chronic values, associated to body burden concentrations were: 1 mg/l for the fish *Pimephales promelas*, 0.27, 0.95, and >2.9 mg/l for the invertebrates *Corbicula fluminea*, *Hyalella azteca* and *Elimia* sp. respectively.

Two aquatic plant (other than algae) studies were conducted. In the first study (Maki, 1981), the chornic toxicity of $C_{11.6}$ LAS to the aquatic macrophyte (*Elodea canadensis*) was determined in a 28 day model ecosystem test. The nominal test concentrations were 0.5, 1.0, 2.0, and 4.0 mg/l and were confirmed by analytical measurements. Growth inhibition was not observed even at highest tested concentration (4 mg/l). Growth throughout the exposure period approximately doubled the initial biomass of the vegetative shoots used at the start of the exposure. Hence, the NOEC was found to be $\geq$4 mg/l. The data are for $C_{11.6}$LAS and no normalization is required.

In the second study (Bishop and Perry, 1981; Bishop, 1980; Van de Plassche et al, 1999a), the duckweed, *Lemna minor*, was exposed to $C_{11.8}$LAS. Endpoints included frond count, dry weight, growth rate and root length after a 7 day exposure period in a flow through study. The measured test concentrations were 0, 2.1, 3.8, 8, 17 and 34 mg/l. The resultant EC_{10} value, based on frond number,

was 0.21 mg/l. The EC_{50} value, also based on frond number, was 2.30 mg/l $C_{11.8}$ LAS. Normalizing the EC_{10} of 0.21 mg/l to $C_{11.6}$ LAS results in a final value of 0.30 mg/l.

In a more recent study (Unilever, 2010), fertilized eggs of rainbow trout (*Oncorhynchus mykiss*, formerly *Salmo gairdneri*) were exposed to mean measured concentrations of 0.03, 0.23, 0.35, 0.63, 0.95 and 1.9 mg/l, for 72 days. The responses recorded included the survival of eggs, time to eyed egg stage, time to hatch, survival and final weight of sac-fry (eleutheroembryos), and time and extent of swim-up (external feeding). The lowest NOEC value found was 0.23 mg/l based on survival of eggs exposed from eyed stage, survival of eggs exposed from fertilization, survival of sac fry, and overall survival from fertilization to swim-up. The data are for $C_{11.6}$ LAS and no normalization is required.

Furthermore, a chronic toxicity test (Maki, 1981) with juvenile bluegills (*Lepomis macrochirus*) was conducted on C_{12} LAS. Fish growth was determined after 28 days exposure in a flow-through model ecosystem to measured concentrations of 0, 0.5, 1.0, 2.0, and 4.0 mg/l. Results showed that the growth of juvenile bluegills was not affected at 0.5 and 1.0 mg LAS/l, but was reduced at 2.0 and 4.0 mg/l. At the end of the exposure period, fish at 1.0 mg/l LAS had a biomass of 44 g/m^2 compared to 10.5 g/m^2 for the 2.0 mg/l concentration. Based on these effects on growth rate, the NOEC was 1.0 mg/l.

Model ecosystem studies

A variety of model ecosystem and mesocosm studies have been conducted on LAS. Many of these studies have been evaluated and summarized in two papers (Van de Plassche et al., 1999a; Belanger et al, 2002). NOEC values for standing (lentic) and flowing (lotic) water model ecosystems varied from 0.12 to 3.5 mg/l. The lowest NOEC value (≥0.12 mg/l) was observed in an artificial stream study (Tattersfield et al., 1995, 1996).

In a specific stretch of the studied mesocosm (rifle zone) and after a prolonged exposure (56 days), some data appeared to show an exceptional sensitivity of the *Gammarus pulex* (NOEC = 0.03 mg/l), clearly an outlier in the sensitivity distribution. An ERASM study (ERASM, 2000) has tentatively tried to confirm this sensitivity in a 107 days single species laboratory exposure; the NOEC was significantly higher (0.1 mg/l), but the control mortality was particularly high (22-40%), which indicates that the study was not valid for risk assessment purposes (Klimish reliability score: 3).

The fate and effects of a C_{12}LAS homologue has been studied in an experimental stream facility (ESF) (Belanger et al., 2002). The C_{12}LAS test substance had a high content (35.7%) of its most hydrophobic and toxic 2-phenyl isomer. The 56-day ESF study included a representative community encompassing over 250 taxa. A NOEC of 0.27 mg/l, equivalent to 0.37 mg/l, if normalised to the commercial $C_{11.6}$LAS structure by QSAR calculations (Könemann, 1981), was found. A critical literature review of all mesocosm studies available for LAS (13 studies), including the Tattersfield et. al. studies, was conducted and concluded that a NOEC value of 0.27 mg/l was a reliable and robust value protecting aquatic ecosystems (Belanger et al., 2002). A validity rating of 1 can be applied to this toxicity value (Klimish et al., 1997). This value approximates the LTE (Long-Term Effect) of 0.30 mg/l for LAS present in the DID list (Detergent Ingredient Database) of the European eco-labelling of laundry detergents (EU Commission, 1999).

Table 14: Results of model ecosytem studies for commerical LAS (Van de Plassche et al., 1999a; Belanger et al., 2002)

	Lowest NOEC range (mg/l)
Mesocosm studies	0.12-0.50 (13)

No. of studies in parenthesis.

4.2.1.2 Terrestrial ecotoxicity

A large number of LAS toxicity data, both in laboratory and field, are available for the terrestrial environmental risk assessment. Data refer to the effects of LAS on soil organisms, namely toxicity to soil plants, soil fauna, soil micro-organisms and microbial soil processes (Kloepper-Sams et al., 1996; Jensen, 1999; Jensen et al., 2001; Holmstrup et al., 2001a; Elsgaard et al., 2001a).

Using new standard protocols, updated results were obtained to extend the existing toxicity data and to contribute to an improved terrestrial risk assessment (Krogh et al., 2007; Jensen et al., 2007). All available data were obtained with the commercial LAS (average alkyl chain length of $C_{11.6}$). The soil samples were collected in agricultural field. The soil was coarse with a total C content of about 1.5%, representative of cultivated area in Europe. Considering that the toxicities are mainly driven by the LAS pore water concentration, the same toxicity weighted average as that in water was used for the terrestrial and the sediment effects assessments (see par. 4.2.1.1).
The ecotoxicity of surfactants in the terrestrial environment were recently reviewed: eight groups of the most often used surfactants, representing the three largest classes (anionic, non-ionic and cationic), were selected and studied. Soil toxicity data in general are limited. Only for one group, represented by LAS, a full dataset of toxicity is available. The conclusion reported was: "The risk characterizations estimated for LAS are usually significantly lower than 1, what allows for the conclusion that the ecological risk of this surfactant in the terrestrial environment is relatively low" (Liwarska-Bizukojc, 2009).
The range of the acute and chronic test results on LAS are summarised in Table 15 and Table 16 respectively. A first terrestrial risk assessment, using data available at the time, was presented and discussed at an international workshop (SPT/EPA, 1999) and at a world surfactant Congress (Lokke et al., 2000; Solbè et al., 2000). The figures presented in Table 15 are indicative of acute effects. They were not directly used in the present risk assessment, as higher tier data are available. The figures in Table 16 are a summary of chronic effects, refer to updated results and are used for a revisited terrestrial risk assessment, as described below (Jensen et al., 2007).

Table 15: Terrestrial acute test results for commercial LAS.

Taxon	Range ($mg/kg_{dry\ soil}$)
Plants, EC_{50}	167 – 316
Soil fauna, EC_{50}	41 - >1000
Micro-organisms, EC_{50}	17 - >1000

Table 16: Terrestrial chronic test results for commercial LAS (Jensen et al., submitted)

Taxon	Range ($mg/kg_{dry\ soil}$)
Plants, NOEC or EC_{10}	52 - 200 (12)
Soil fauna, NOEC or EC_{10}	27 - 320 (9)
Micro-organisms, EC_{10}	<8 - >793 (10)

No. of records in parenthesis.

Terrestrial chronic ecotoxicity

Twenty one laboratory chronic data points for plants and soil fauna are available (Jensen et al., 2007). The values and the most sensitive endpoints for each species are indicated in Table 17. Following multi-peer reviews, a validity rating of 1 (Klimisch, 1997) can be assigned to all these chronic toxicity data.

The twelve data for plants were separated for crop and non-crop species, considering that only the former ones would be exposed to LAS via sludge application. The toxicity data were critically analysed reconsidering and consulting the original works. Toxicity results were calculated using graphical estimations and extrapolations with improved software and methodologies (Jensen et al., 2007).
The nine data for soil fauna were separated according to three classes: Oligochaetes, Insects and Arachnids. These toxicity data are basically the ones reported in the previous terrestrial risk assessment (Jensen et al., 2001) with the exception of the updated results for *Aporrectodea caliginosa*, *Enchytraeus sp.* and *Folsomia candida* (Krogh et al., 2007). The dataset was combined to develop a final $HC_{5,50}$ of LAS in soil (see par. 4.2.2.2).
As a measure of chronic toxicity, when possible, EC_{10} (equivalent to a no-observed effect concentration) were preferred to NOEC (no-observed effect concentration). A full discussion on the relevance of EC_x in risk assessments has been reported (Bruce and Versteeg, 1992).

The mixture toxicity of LAS with a PAH, pyrene, towards the micro-arthropod *Folsomia sp.* was tested (Holmstrup et al., 1996). No synergistic effects were observed and pyrene bioavailability was not enhanced by LAS in the experiment conditions. According to the authors, LAS is not likely to affect the solubility of PAH in soil at levels below its critical micelle concentration and LAS concentration in soil pore waters are orders of magnitude lower.

Table 17: Plants and soil fauna. Terrestrial chronic toxicity data for commercial LAS (Krogh et al., submitted; Jensen et al., submitted)

Species	Most sensitive end point	Value ($mg/kg_{dw\ soil}$)	
		EC_{10}	Extrapolated NOEC
Plants, non crop species:			
Malvia pusilla	growth	110	-
Solanum nigrum	growth	120	-
Chenopodium album	growth	120	-
Amaranthus retroflexus	growth	110	-
Nigella arvensis	growth	-	52
Galinsoga parviflora	growth	55	-
Plants, crop species			
Brassica rapa	growth	86	-
Avena sativa	growth	80	-
Sinapis alba	growth	200	-
Sorghum bicolor	growth	68	-
Helianthus annuus	growth	116	-
Phaseolus aureus	growth	126	-
Invertebrates: class oligocheates			
Eisenia foetica	growth	277	-
Aporrectodea caliginosa	reproduction	46	-
Enchytraeus sp.	reproduction	27	-
Invertebrates: class insects			
Folsomia fimetaria	reproduction	108	-
Folsomia candida	reproduction	205	-
Isotoma viridis	growth	41	-
Hypogastrura assimilis	reproduction	100	-
Invertebrates: class arachnids			

Hypoaspis aculeifer	reproduction	82	-
Platynothrus peltifer	reproduction	-	320

Ten chronic soil microbial data points (Table 18) are also available (Jensen et al., 2001; Elsgaard et al., 2001a).

Table 18: Microbial parameters. Effect of commercial LAS on micro-organisms and microbial processes in soil (Jensen et al., 2001; Elsgaard et al., 2001a)

Endpoint	Incubation (d)	EC_{10} ($mg/kg_{dw\ soil}$)
Ethylene degradation	0.5	9
Ammonium oxidation	7	<8
Dehydrogenase activity	7	22
ß-Glucosidase activity	7	47
Iron reduction	7	<8
Cellulolytic bacteria	7	11
Cellulolytic fungi	7	<8
Cellulolytic actinomycetes	7	8
Basal soil respiration	1-9	>793
PLFA content	11	>488

Effects of both chemical- and bio-surfactants on soil biochemical processes are extensively reported by review papers in literature. Many beneficial applications in microbial, environmental and agricultural biotechnology, oil processing, enzyme technology and other bioprocessing operations are described (Cameotra et al., 2004; Van Hamme et al., 2006; Muller et al., 2007; Singh et al., 2007).

Some key soil physico-chemical and bio-chemical parameters show to be temporarily affected by sludge amendment of soil (Dunbabin et al., 2006). As to LAS, for example:

- the presence of LAS in agricultural soil stimulated the uptake of N, P and K with a surfactant dose of 15-30 g/m^2; Ca and Mg were reduced (Moreno-Caselles et al., 2006); the average LAS doses in agriculture, however, with anaerobic sludge are much lower (2.8 g/m^2) (Schowanek et al., 2007);
- laboratory studies on the growth of isolated soil bacteria cultures in presence of 50 µg/ml LAS concentration indicate that application of sewage sludge (also wastewater or pesticides formulations) containing LAS to an agricultural soil could be considered a potential risk for selected aerobic heterotrophic soil microbiota and their microbial activities (Sanchez-Peinado et al., 2008).

As LAS degrades rapidly and the sludge integrates in the soil, such effects disappear rapidly. In addition, it is difficult to distinguish whether any observed effect is due to the sludge organic matter itself, LAS (ca. 10%, the lowest sludge organic fraction) or other components (e.g. metals) and to understand whether the disturbance is adverse and permanent. In any case, field studies have never provided evidence of adverse and permanent impact of LAS in sludge on these parameters.
Specific effects of surfactants, present in municipal wastewaters, considering in particular the main soil regulatory factors, haven't been much considered (Muller et al., 2006). Regulatory requirements relevant to "pristine/natural" soil should not be used for agricultural soil that receives sewage sludge. Again, as already said before, it is also impossible to separate effects related to the organic carbon of sewage sludge solids itself, and perhaps to other persistent contaminants, from effects of biodegradable surfactants.

On the contrary, no significant effects to the microbial community were observed after prolonged exposure to heterogeneous LAS distributions in agricultural soil following sludge amendment. For example:

- no effects were observed in the soil even at LAS concentrations >31 g/$kg_{dw\ sludge}$ (Brandt et al., 2003);
- LAS at the concentration levels of 22 and 174 mg/$kg_{dw\ soil}$ in sandy agricultural soil (worst-case scenario in terms of high bioavailability and toxicity in the soil environment) was rapidly degraded (>93% in 4 weeks) and had little or no significant influence of the functional diversity of aerobic heterotrophic bacterial community (Winther et al., 2003);
- effects of LAS (at concentrations of 10 or 50 mg/l for periods of time up to 21 days) on the bacterial community of a microcosm system consisted of agricultural soil columns were evaluated, applying a molecular-based community-level analysis. The structures of three bacteria communities (*Alphaproteo-*, *Actino- and Acido-bacteria*) were analysed. The conclusions were that the alphaproteobacterial population identified in the work was enriched in the LAS polluted soil, suggesting its relevant role and ability to biotransform and degrade LAS. LAS had no remarkable effects on the other two community bacteria, even when present at concentrations widely exceeding those reached in soil immediately after sludge application (Sànchez-Peinado et al., 2010).

Micro-organisms and overall soil processes were thus considered protected by the PNEC derived from the relative higher sensitivity of plants and invertebrates (Brandt et al., 2003; Petersen et al., 2003) and therefore not considered in the risk assessment.

Field observations are also available (Jensen, 1999; Jensen et al., 2001; Brandt et al., 2003) and are summarized in Table 19. The application of LAS-containing sludge generally stimulated the microbial activity and, hence, the abundance of soil fauna and growth of plants. Paddy growth was stimulated when LAS was <80 mg/$kg_{dw\ soil}$ (Liang-Qing et al., 2005). It was found that application of LAS-containing sludge on soil did not produce any short- and long-term adverse effects on microbial functions and processes or the abundance and diversity of soil invertebrates.

Table 19: Field studies for commercial LAS (Jensen et al. 2001; Figge and Schöberl, 1989)

Taxon	Range (mg/$kg_{dry\ soil}$)
Soil ecosystem, NOEC	>15
Biomass, NOEC	>16, >27

Selected microbial populations in sandy soils (low organic matter content) surrounding sludge bands spiked with high levels of LAS were also studied (Brandt et al., 2003). In this study the observed disturbance of the soil microbial community lasted only two months and was confined to soil close to sludge, confirming that LAS doesn't pose any significant threat to the function of the microbial community in sludge-amended soils. It was concluded that soil LAS concentrations of 5 to 15 mg/$kg_{dw\ soil}$ are not causing any harm to the soil ecosystem (Jensen et al., 2001). This conclusion is also consistent with the results of a laboratory agricultural ecosystems study using a "plant metabolism box" to measure the growth of grass, beans, radishes and potatoes for a period up to 106 days after application of sludge spiked with radiolabelled LAS material (Figge and Schöberl, 1989; Figge and Bieber, 1999). At LAS soil concentrations of 16 and 27 mg/$kg_{dw\ soil}$, no significant uptake and accumulation by plants and no adverse effects on the biomass were observed.

4.2.1.3 Sediment ecotoxicity

The organic carbon content of the sediment may influence the bioavailability and therefore the toxicity of the test substance. Therefore, for comparison of sediment tests, the organic carbon content of the test sediment should be within a certain range. The organic carbon content of a

standard sediment is set to 5 % (TGD, 2003). It is recommended that the organic carbon content of the test sediments is between these two values. As some of the available data are tested with sediments that have an organic carbon content that fall outside the ranges, all results are converted to a standard sediment, which is defined as a sediment with an organic matter content of 5%.
Toxicity information is available for sediments and is summarized in Table 20. A NOEC of 319 $mg/kg_{dw\ sed.}$. (Klimish score of 1) was observed for the larvae of a benthic organism, *Chironomus riparius* (Pittinger, 1989; Kimerle, 1989). The organic carbon content of the tested sediment was 4.2%. The organic carbon normalized NOEC is 380 $mg/kg_{dw\ sed.}$. New toxicity experiments for the same organism, looking at larval growth and mortality, were performed using two different sediments spiked with both radiolabelled and unlabelled C_{12}-2-LAS homologue (Mäenpää and Kukkonen, 2006). After 10-days exposure, NOECs were 362 $mg/kg_{dw\ sed.}$ and 537 $mg/kg_{dw\ sed.}$ (Klimish score of 1). The organic carbon content of the sediments were 1.06% and 1.57%, respectively. The organic carbon normalized NOECs are 1,710 $mg/kg_{dw\ sed.}$ for both sediments. For one sediment the NOEC as body residue (measure of internal exposure) was 30 mg/kg larval wet weight.
A tubificid species, *Branchiura sowerbyi*, a benthic filter organism, was exposed for a long period (220 days) to a sediment with LAS concentrations varying from 26 to 7 $mg/kg_{dw\ sed.}$ (Klimish score of 1, absence of any observed effect) over the exposure period and no effects were observed in any of the test concentrations (Casellato et al., 1992). While the absence of reported toxicity is reassuring, it appears that the range of exposure concentrations was too low to derive a toxicity data directly useful in risk assessment. However, the results of this test do not invalidate the PNEC calculation. Two freshwater mollusc species, *Unio elongatulus* and *Anodonta cygnea*, were exposed to sediments with LAS concentration >200 $mg/kg_{dw\ sed.}$ (Klimish score of 2, due to lack on description of the experimental details) without noticing any adverse effects (Bressan et al., 1989).

Chronic studies were conducted with *Lumbriculus variegatus* and *Caenorhabditis elegans* (Comber et al., 2006). As to the first species, a 28 days NOEC of 81 $mg/kg_{dw\ sed.}$ was derived for survival, reproduction and growth, using sediment spiked with radio-labelled material, the organic carbon content of the sediment was 1.7%. The organic carbon normalized NOEC is 238 $mg/kg_{dw\ sed.}$.For the second species, a 3 day NOEC of 100 $mg/kg_{dw\ sed.}$ was obtained for egg production, the organic carbon normalized NOEC is 294 $mg/kg_{dw\ sed}$. Both experiments are well described (Klimish score of 1).
LAS sorbed to sediments was assessed for its level and potential perturbations on benthos; comparative sediment contamination analyses came to the conclusion that LAS risk for both aquatic and sediment compartment is low (Sanderson et al., 2006).

Table 20: Sediment chronic test results for commercial LAS

Species	Most sensitive end point	NOEC ($mg/kg_{dw\ sed.}$)	Organic carbon normalized NOEC ($mg/kg_{dw\ sed.}$)	Organic carbon content (%)	References
Chironomus riparius	reproduction, survival	319	380	4.2	Pittinger, 1989 Kimerle, 1989
		362, 537	1,710	1.06, 1.57	Mäenpää and Kukkonen, 2006
Unio elongatulus	survival	>200	-	-	Bressan et al., 1989
Anodonta cygnea	survival	>200	-	-	
Lumbriculus	survival,	81	238	1.7	Comber et al.,

variegatus	reproduction, growth				2006
Caenorhabditis elegans	egg production	100	294	1.7	Comber et al., 2006

It is also worth mentioning the LAS safety in the coastal marine environment.
LAS is highly biodegradable, not only under aerobic conditions in sea water (Leon et al, 2004), but also under anaerobic conditions in marine sediments (Lara-Martin et al., 2007; Lara-Martin et al., 2008). Monitoring studies have shown that LAS is only present in coastal sediments close to points of municipal and industrial discharges (Petrovic et al., 2002).
Laboratory experiments, performed on anoxy marine sediments spiked with 10-50 ppm of LAS, showed that degradation is feasible reaching a value of 79% in 165 days, with a half-life time of ca. 90 days. The anaerobic process was also observed in the field with several marine sediment samplings: at anoxy depths in the sedimentary column, LAS concentrations in pore waters decreased sharply and the biodegradation intermediates (SPC) reached the maxima. These observations were claimed as the first real evidence of a partial degradation of LAS under anaerobic conditions (Lara-Martin et al., 2007; Lara-Martin et al., 2008).
Sortion and desorption experiments with two marine sediments were carried out using C_{12}-2-LAS molecule to study its toxicity on a marine mud shrimp, *Corophium volutator*, in water-only exposure as well as in spiked sediments (Rico-Rico A et al., 2009). Pore water LC_{50} values were calculated in the range 100-700 μg/l. These values are considerably higher than pore water concentrations for LAS (maximum 15 μg/l) found in marine sediments of coastal areas close to wastewater discharges (Lara-Martin et al., 2006).
The mud snail *Hydrobia ulvae* was exposed to marine LAS-spiked sediments: LC_{50} toxicity values were comprised between 203 mg/kg (48 h) and 94 mg/kg (9 d) (Hampel et al., 2009). The results confirm that *H. ulvae* is an appropriate candidate organism for routine marine sediment toxicity testing with surfactants.

4.2.1.4 Ecotoxicity to sewage microorganisms

The 3-h EC_{50} of LAS for microorganisms present in the aerobic activated sludge was experimentally measured at 550 mg/l (Verge et al., 1993; Verge et al., 1996). Assuming an average content of suspended matter in the activated sludge of 3 g/l, the EC_{50} value corresponds to about 18% LAS in sludge on dry basis (i.e., 183 g LAS/$kg_{dw\ sludge}$).
A consortium of two bacteria (*Pantoea agglomerans and Serratia odorifera*) was isolated from a STP sludge. They complement each other in the ability to degrade LAS. Optimizing their culture growth conditions, complete laboratory mineralization of 200 mg/l LAS was obtained within 48-72 h (Khleifat et al., 2006).
Laboratory toxicities of commercial surfactants were carried out using a specific type of micro organism isolated from a STP activated sludge (the phosphate-accumulating bacterium: *Acinetobacter junii*). The anionic surfactants were the most toxic, with LAS having a 50% growth inhibition of 0.15-1.8 mg/l (Ivankovic et al., 2009).
A NOEC value of 35 mg/l, normalised to the $C_{11.6}$LAS structure, was found for *Pseudomonas putida* after a growth inhibition test (Feijtel et al., 1995b).
The microbial population present in the STP activated sludge digesters was not found to be inhibited even by a high and atypical concentration (30 g/$kg_{dw\ sludge}$) of LAS in sludge (Berna et al., 1989).

4.2.1.5 Reassurance on absence of estrogenic effects

LAS was also investigated to check whether it could be an endocrine disruptor, using an estrogens-inducible yeast screen (Routledge et al., 1996; Navas et al., 1999) and the vitellogenin assay with

cultured trout hepatocytes (Navas et al., 1999). LAS as well as its biodegradation intermediates, Sulpho Phenyl Carboxylates (SPC), did not display any estrogenic effects.

4.2.2 PNEC calculations

4.2.2.1 Aquatic PNEC

In a previous environmental risk assessment of LAS for the aquatic compartment (Van de Plassche et al., 1999a), NOECs for fifteen freshwater species were considered (Table 13), a dataset that justified the application of a statistical extrapolation method (Aldenberg & Slob, 1993). They were normalised to the average structure $C_{11.6}$ LAS by the use of QSARs. A geometric mean NOEC for each species was calculated. $HC_{5,50}$, the median value of the 5^{th} percentile of the log-normal distribution including all available NOEC values, was derived and was 0.32 mg/l. This value is in good agreement with the lowest available freshwater NOEC, found for the fish *Tilapia mossambica* (0.25 mg/l).

Various mesocosm studies (Tattersfield et al., 1995; Tattersfield et al., 1996; Belanger et al., 2002) indicate that the lower limits of mesocosm studies can be considered between 0.12 to 0.5 mg/l. Following a critical review of all the mesocosm studies, however, it was also concluded that a NOEC = 0.27 mg/l for a C_{12}LAS homologue, corresponding to 0.37 mg/l when normalised to the $C_{11.6}$ LAS structure, is the most reliable, robust and defendable mesocosms value, to which an application factor of 1 has to be applied Belanger et al., 2002). The reasons for this are many, but include:

- presence of a large number of sensitive flora and fauna, accompanied by a high degree of overall biodiversity (a total of 149 alga species and 6 phylogenetic divisions; 117 benthic invertebrates including insects, molluscs, crustaceans, and aquatic worms; 77 macroinvertebrate taxa collected in drift; 110 adult insect species);
- 16 weeks of colonization and exposure, longer than single species chronic toxicity tests represented in the database;
- use of a large array of endpoints, including many that reveal subtle and indirect effects; endpoints combine relevant environmental aspects of fate (biodegradation, chemical metabolism, sorption, and exposure verification) with effects (invertebrate, autotrophic and heterotrophic periphyton);
- the experimental stream facility (ESF) has a long history of biological and chemical data that has been used to interpret and re-interpret past studies (Belanger et al., 1994, 1995, 2000); two pairs of studies have been conducted to assess repeatability and findings have been consistent in different years (Belanger, 1992; Belanger et al., 2000 and unpublished data);
- ESF streams have relatively low levels of variability and are sampled intensively (i.e., at relatively high levels of replication) (Lowe et al., 1996; Belanger et al., 2000);
- ESF stream population and community structure has been compared to local and regional flora and fauna to ensure that the ESF communities are representative of sensitive ecosystems (Belanger et al., 1995; Dyer and Belanger, 1999); ecological investigations of nutrient dynamics of ESF streams support their being representative of headwater streams at the relevant discharge levels (Peterson et al., 2001).

It seems reasonable and in agreement with the results on single species to assign a PNEC value of 0.27 mg/l to the PNEC of LAS in the water compartment.

Conclusion: PNEC in water = 0.27 mg/l.

4.2.2.2 Terrestrial PNEC

In a typical disposal scenario, LAS enters soil predominantly via addition of (anaerobic) sewage sludge to agricultural land.

Modelling approach: The terrestrial PNEC of LAS can be calculated by using the TGD equilibrium partitioning method (EqP - TGD, 2003, Part II: eq. 72, page 117). On the basis of a local PNEC in water of 0.27 mg/l and assuming a value of 2500 l/kg as partition coefficient between organic matter and water (see 3.2), a value of 11.9 mg/kg$_{dw\ soil}$ can be obtained. No additional safety factor is required for LAS because the substance has a log K_{ow} <5. This value is in the same order of magnitude as the values derived below based on the all available experimental toxicity results for soil organisms.

Analysis of soil experimental data: In a previous environmental risk assessment carried out for LAS in the soil compartment (Jensen et al., 2001), the estimation of PNEC, performed for soil fauna and plants using a data set of twenty three records and applying a statistical extrapolation method (Wagner et al., 1991), was 4.6 mg/kg$_{dw\ soil.}$ This PNEC was calculated as the $HC_{5,50}$, the median value of the 5th percentile of the log-normal distribution, and includes the microbial processes and functions that have been examined (Jensen et al., 2001).
Comparison with the EqP approach and with available more recent information suggest that this value can be considered as rather low/conservative. Following an extensive review and update of the plant and invertebrate ecotoxicological data, and a further interpretation of the relevance of the microbial endpoints for the functioning of the soil ecosystem, the terrestrial risk assessment of LAS has been revisited (Jensen et al., 2007). The new PNEC, using a data set of twenty one toxicity values (as reported in Table 17), was derived at 35 mg/kg$_{dw\ soil}$.

The opinion of SCHER (2008) however disagrees with the argument that soil microbial functions (and with particular reference to iron reduction) are adequately covered by the proposed PNEC of 35 mg/kg$_{dw\ soil}$, and considers that an evaluation of the relevance of LAS effects on microbial activity is essential for a proper $PNEC_{soil}$ derivation. Thus, SCHER considers that the information provided is not sufficient for justifying the newly proposed PNEC value of 35 mg/kg. In this respect, HERA experts remark that at present there is no consistent and universally accepted framework of how microbial species, and in particular single biochemical endpoints, should be included in a soil or sediment risk assessment for a given chemical. The EU TGD (2003) provides only very basic guidance in this respect, emphasizing the function of "primary producers" (plants), "consumers" (soil fauna) and "decomposers" (mainly microbes). Given the enormous diversity and metabolic/genetic flexibility of microbial communities, and the variability and diversity of potentially measurable microbial endpoints in soil, a careful interpretation is required. Each result should be evaluated for its true environmental relevance with respect to the size of the effect, duration, essential soil function impairment, etc.., and not necessarily the lowest observed number should therefore be retained as a NOEC.
The salt speciation of LAS and the soil type were included in the evaluation and did not significantly modify the toxicity of LAS to soil organisms (Holmstrup et al., 2001b; Jensen et al., 2001). Dosage of LAS via sewage sludge, instead, generally reduced the effects for microbial parameters, showing also recovery potentials for most parameters as a result of prolonged incubation (Elsgaard et al., 2001b). Disturbance of soil microbial community were confined to soil close to sludge and disappeared after two months (Brandt et al., 2003). In addition, field observations (Table 19) after experimental sludge amendment at high application rates concluded that LAS, at an average soil concentration of > 15 mg/kg$_{dw\ soil}$, does not seem to be detrimental to the soil ecosystem in the long term (Jensen et al., 2001). The HERA experts therefore judge that the impact of LAS on the soil community has been adequately assessed, in particular if one combines the laboratory data with the holistic weight of evidence provided by available controlled field studies at high LAS levels. These show no impact on 'ecosystem service' parameters such as soil fertility and crop yield (see studies reported in Schowanek et al. 2007, where a probabilistic pan-European risk assessment for LAS in soil is also presented). With respect to the protection of the agro-ecosystem, reference is also made to discussion on setting protection levels on the basis of 'ecosystem services" in the EU Commission document (2012) "Addressing the new challenges for Risk Assessment" (http://ec.europa.eu/health/scientific_committees/consultations/public_consultations/scenihr_consultation_16_en.htm)
In conclusion: the PNEC in soil = 35 mg LAS/kg$_{dw\ soil}$.

4.2.2.3 Sludge PNEC

A sludge PNEC, also called sludge quality standard (SQS), of LAS can be back-calculated from the soil PNEC taking into account the TGD (TGD, 2003) scenario for exposure of sewage sludge on agricultural soil and the soil PNEC of 35 mg/$kg_{dw\ soil}$ (see par. 4.2.2.2). A PNEC of 49 g/$kg_{dw\ sludge}$ was calculated (for details of its calculation and interpretation we refer to Schowanek et al., 2007)(*).

Conclusion: PNEC in sludge = 49 g/$kg_{dw\ sludge}$.

4.2.2.4 Sediment PNEC

As for soil, sediment PNEC of LAS can be calculated using the TGD equilibrium partitioning method (TGD, 2003: Part II, eq. 70, page 113). The resulting PNEC is 14.9 mg/$kg_{dw\ sed.}$.

Good quality chronic data on sediment toxicity for LAS are available for five species representing different living and feeding conditions. An application factor of 10 can be applied to the lowest available NOEC figure normalized for organic carbon, deriving a conservative PNEC for sediment of 23.8 mg/$kg_{dw\ sed.}$.

The available sediment toxicity data, as reported in Table 20, in particular those relative to oligochaetes, well represent the different benthic taxa (Comber et al., 2006) and are recommended by the European TGD (TGD, 2003) in the sediment testing for the risk assessment of chemicals.

Conclusion: PNEC in sediment = 23.8 mg/$kg_{dw\ sed.}$.

4.2.2.5 STP PNEC

Although the lowest effect concentration is a NOEC value of 35 mg/l, normalised to the $C_{11.6}$LAS structure, for *Pseudomonas putida* after a growth inhibition test, this value will not be taken into account. Results of the cell multiplication inhibition test with *P. putida* should only be used for calculation of the STP PNEC in cases where no other test results employing mixed inocula are available. As a respiration inhibition test with activated sludge is available, results from this study will be used to derive the STP PNEC (TGD, 2003). Thus te most relevant reported effective concentration for STP organisms is the 3-h EC_{50} value of 550 mg/l for activated sludge. This value with an application factor of 100 gives a PNEC of 5.5 mg/l, as recommended by the TGD.

Conclusion: PNEC in STPs = 5.5 mg/l.

4.3 Environmental risk assessment

PEC and PNEC values with the corresponding PEC/PNEC ratios are summarized in Table 21.

Table 21: Risk characterization

LAS	PEC	PNEC	PEC/PNEC
Water, mg/l	0.047	0.27	**0.17**
Soil (30 d), mg/$kg_{dw\ soil}$	1.4	35	**0.04**
Sludge, g/$kg_{dw\ sludge}$	5.56 (50th percentile) 15.07 (95th percentile)	49	**0.11** **0.31**
Sediment, mg/$kg_{dw\ sed.}$	5.3	23.8	**0.22**
STP, mg/l	0.27	5.5	**0.05**

(*) A LAS limit value in sludge of 1.3 g/$kg_{dw\ sludge}$ is actually in force in Denmark (Executive Order 823 DK).

This assessment shows that the use of LAS in HERA applications results in risk characterisation ratios (PEC/PNEC) less than one. To demonstrate this, higher tier exposure and effects data were needed. PEC values were estimated based on monitoring data for each environmental compartment and PNEC values were based on chronic effects data. This conclusion can be generalized to all LAS usages in Europe including the non-HERA minor applications, since exposure has been based on the actual LAS concentrations measured in the various environmental compartments.

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6. Contributors to this report

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    - CEPSA QUIMICA
    - SASOL Italy
    - HANSA GROUP

- **Formulators**
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6.2 HERA environmental task force

- AISE
- BASF
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- Clariant
- Dow Corning
- Henkel
- CEPSA QUIMICA
- Procter & Gamble, Eurocor.
- Rhodia
- Sasol Germany
- Sasol Italy.
- Shell Chemicals
- Solutia Services International
- Solvay
- Unilever

6.3 Industry coalition for the OECD/ICCA SIDS assessment of LAS

- Colgate
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