Human & Environmental Risk Assessment
on ingredients of
European household cleaning products

Alkyl Sulphates

Environmental Risk Assessment

March 2002

1. Contents

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Further information on the HERA Project including the HERA Methodology document and other risk assessments can be found at www.heraproject.com.

2. Executive Summary

Alkyl Sulphates (AS) are a widely used class of anionic surfactants. They are used in household cleaning products, personal care products, institutional cleaners and industrial cleaning processes, and as industrial process aids in emulsion polymerisation and as additives during plastics and paint production. Uses in household cleaning products (the scope of HERA) include laundry detergents, hand dishwashing liquids, and various hard surface cleaners.

The HERA AS family encompasses commercial grades of linear-type primary alkyl sulphates in the C_{12} to C_{18} range. This assessment does not cover the AS present as a component of another major class of anionic surfactants, Alcohol Ethoxysulphates (AES). This will be covered separately, as part of the HERA AES risk assessment.

The total volume of AS surfactants used in Europe is estimated to be 102,000 tonnes/year on an active matter basis based on a survey of producers (1999). Based on a survey conducted among detergent formulator companies, and input from AS producers, the tonnage used in household detergents and cleaning products is estimated to be approximately 65,000 tonnes/year.

A large environmental data set is available for Alkyl Sulphates. On the environmental fate side, this includes standard biodegradation studies, advanced simulation studies of removal in treatment systems, and field monitoring data. On the environmental effects side, acute as well as chronic single-species data are available, as well as advanced studies in micro- and mesocosm systems.

Chemical removal in wastewater treatment plants was determined from advanced simulation test data, and to determine the ecotoxicological Predicted No Effect Concentrations, chronic ecotoxicity data were used.

Monitoring studies on sewage treatment plant effluents indicate that the exposure estimates in this assessment are likely to be conservative. In addition, mesocosm studies suggest that the effects assessment based on laboratory studies is also conservative.

By means of higher tier exposure and effects data, it could be shown that the use of Alkyl Sulphates in HERA applications (household detergents and cleaning products) poses no concern in any environmental compartment.

An additional exposure scenario was included in this risk assessment, by assuming the entire AS tonnage used in Europe is disposed of down the drain, rather than just the HERA tonnage.

Using the same exposure and effects assessment approach, the absence of environmental concerns can also be demonstrated for the total tonnage.

3. Substance Characterisation

Alkyl Sulphates (AS) are a widely used class of anionic surfactants. They are used in household cleaning products, personal care products including toothpaste and shampoos, hand and other personal cleaning products, institutional cleaners and industrial cleaning processes, and as industrial process aids in emulsion polymerisation and as additives during plastics and paint production. Uses in household cleaning products, the scope of HERA, include laundry detergents, hand dishwashing liquids, and various hard surface cleaners.

3.1. CAS No and Grouping information

There are numerous CAS Nos. describing AS. A comprehensive list is presented in Appendix 2 of this document. Although clearly important from a Regulatory perspective, this assessment is not based on CAS Nos., but on the product composition and specifically carbon chainlength distribution - which is key to the environmental profile of this family.

3.2. Chemical structure and composition

The Alkyl Sulphate family is defined for HERA purposes to encompass commercial grades of linear-type primary alkyl sulphates containing AS components of basic structure $C_nH_{2n+1}SO_4$ M, where n=12-18 and M = sodium, ammonium or triethanolamine (TEA). Sodium neutralised AS are by far the predominant grades. The environmental fate and effects of ammonium or TEA cations have not been further considered in this assessment. Further detail on the structures included in the AS family are given in Section 3.3.

3.3 Manufacturing Route and Production/Volume Statistics

Alkyl sulphates are produced by sulphation of detergent range primary alcohols using sulphur trioxide or chlorosulphonic acid followed by neutralisation with base to produce typically a sodium salt, less commonly an ammonium salt. Minor volumes are neutralised with alkanolamines, usually triethanolamine (TEA). Many grades of AS are produced commercially differing in the parent detergent alcohol, the concentration of AS active matter in water, or whether shipped as a solution, a paste or in solid form. Commercial sodium AS typically contains, based on the active matter content, approximately 2-4% of unsulphated alcohol, 1-2% sodium sulphate (or sodium chloride if produced via chlorosulphation), and optionally trace amounts of inorganic pH buffering agents.

The HERA AS family is derived from linear-type primary alcohols in the C_{12} to C_{18} range. As placed on the market, such alcohols usually contain a distribution of alkyl chain lengths. The linear-type alcohols include those which are mixtures of entirely linear alkyl chains, and those which are mixtures of linear and mono-branched alkyl chains, though still with a linear backbone. Such alcohols and their blends are substantially interchangeable as feedstocks for AS used in the major applications falling within the scope of HERA.

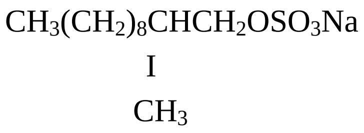
Excluded from the HERA AS family are alkyl sulphates derived from alcohols shorter than C_{12} or those with other alkyl chain structures such as multi-branched alcohols, for example commercial *iso*-tridecanols. These grades of AS are not typically used in household cleaning products. Their uses are small and specialised and they are not considered further in this assessment.

The linear-type alcohols used to produce HERA AS include those derived from vegetable or animal sources via oleochemical processes and those derived from ethylene via Ziegler chemistry. Such alcohols contain even carbon numbered alkyl chains only, and are produced in single carbon cuts or more usually wider cuts from C6 through C22+. C12 through C18 grades are feedstocks for HERA AS.

The essentially linear alcohols used to produce HERA AS, also known as linear oxo-alcohols, are derived from linear higher olefins via oxo-chemistry. The feedstock linear olefins are typically derived from ethylene or normal paraffins. Such alcohols contain mixtures of even/odd or odd carbon numbered alkyl chains depending on the feedstock olefin, and are produced in grades ranging from C7 through C15. Typically 90-40% of the carbon chains are linear, the remainder being mono-branched 2-alkyl isomers, predominantly 2-methyl. The mono-branched isomers thus have a linear backbone. C12 through C15 grades are feedstocks for HERA AS.

The principle structures present in HERA C_{12} AS for example are thus:

$CH_3(CH_2)_{11}OSO_3Na$



$$CH_3(CH_2)_8\underset{\substack{|\\CH_3}}{CH}CH_2OSO_3Na$$

with the linear isomer being by far the predominant overall.

Of the AS used in consumer cleaning applications in Europe, a preliminary estimate gives 85-90% derived from even carbon numbered linear alcohols (C12-14 and C16-18), with the remaining 10-15% derived from odd and even carbon numbered essentially linear-oxo alcohols.

The European (EU, CH and NO) production volume of AS surfactants on an active matter basis is estimated to be 114,000 tonnes/y (CESIO statistics for 1999; CESIO = European Committee for Surfactants and their Organic Intermediates, a sector group of the European Chemical Industry Council, CEFIC). About 102 000 tonnes/y are estimated to remain in Europe, the remainder is exported. The imported volume is thought to be negligible.

3.4. Use applications summary

Tonnage used in HERA applications (HERA Tonnage)

To determine the total AS tonnage used in products falling within the scope of HERA (i.e., household detergents and cleaning products), a survey was conducted among detergent formulator companies (data from members of AISE) and companies manufacturing AS (via the CESIO Statistics Group). From the data received from the major AS formulators (which accounts for a volume of 32,271 tonnes) an estimated distribution between carbon chain lengths has also been determined. This is shown in Table 1.

Table 1. Tonnage of AS within the scope of HERA, determined via AISE survey

	Estimated Carbon Distribution of AS (% weight)	Tonnage of AS (tonnes/year)
C12	29.6 %	9,567
C13	14.3 %	4,613
C14	17.0 %	5,481
C15	5.9 %	1,894
C16	11.9 %	3,851
C18	21.0 %	6,790
Total		32,271

(Note: C17 AS is essentially absent from commercial AS.)

The CESIO Statistics Group has estimated that 65,000 tonnes/year of AS are used in household detergents and cleaning products.

Of that 65 000 tonnes/year, the distribution between carbon chain lengths has also been determined for 58 095 tonnes. This is shown in Table 2.

Table 2. Tonnage of AS within the scope of HERA, determined via CESIO survey

	Estimated Carbon Distribution of AS (% weight)	Tonnage of AS (tonnes/year)
C10	0.1%	50
C12	29.2%	16942
C13	14.2 %	8221
C14	26.2 %	15238
C15	8.1 %	4722
C16	10.1 %	5846
C18	12.2 %	7075
Total		58095

(Note: C17 AS is essentially absent from commercial AS.)

This risk assessment is based on the higher of the two estimates available at the time of publication (65,000 tonnes/year). The carbon chainlength distribution of the 58 095 tonnes has been used as a reasonable representation of the distribution applicable to the full 65 000 tonnes which CESIO estimates are used in household detergents and cleaning products.

Total Tonnage Scenario

The majority of the total European AS tonnage, which includes uses outside the scope of HERA, is ultimately released down-the-drain, where depending on treatment it may reach the environment. Thus this risk assessment also includes an overall assessment using the total European usage estimate of 102 000 tonnes/year. Of that 102 000 tonnes/year, carbon chainlength distribution has been determined for 78 888 tonnes:

Table 3. European production tonnage of AS determined via CESIO survey

	Estimated Carbon Distribution of AS (% weight)	Tonnage of AS (tonnes/year)
C11 and below	1.4%	1179
C12	29.3%	23109
C13	10.6 %	8364
C14	25.6 %	20445
C15	6.0 %	4722
C16	11.7 %	9204
C18	13.2%	10404
C20 and above	1.9 %	1462
Total		78,888

(Note: C17 AS is essentially absent from commercial AS.)

Again, the carbon chainlength distribution available for the 78 888 tonnes is taken as a reasonable representation for the distribution applicable for the overall 102 000 tonnes. This total tonnage scenario is presented in an addendum to the HERA focussed environmental risk assessment.

4. Environmental Assessment

Industry has sponsored several publications summarising environmental data on alkyl sulfates (SDA 1991; Painter 1992). In addition, reports from various national and international programmes are available (OECD 1995; BUA 1996; SDA US HPVC (High Production Volume Chemicals) challenge programme (ongoing activity, unpublished)).

4.1. Environmental Exposure Assessment

The following risk assessment is based on the estimated AS tonnage of 65,000 tonnes/year in HERA applications. The chain length distribution was obtained from the CESIO survey of producers (Table 2). This tonnage scenario is further referred to as ‘HERA tonnage’.

Table 4. HERA Tonnage of AS

	Tonnage of AS (tonnes/year)
C12	18,956
C13	9,198
C14	17,049
C15	5,283
C16	6,541
C18	7,916
Total	65,000

It is recognised that the majority of the total European AS tonnage is ultimately released in the same way as the HERA volume, down-the-drain to the environment. As such, although not within the scope of HERA, a more conservative assessment using the total European usage estimate (i.e. 102,000 tonnes/year) is also presented in an addendum.

Important remarks

AS present in AES: Alkyl sulphate is present as a normal component of another major class of anionic surfactants, AES (alkyl ether sulphates) typically at levels averaging around 20%.

This assessment does not include such AS, which will be covered separately, as part of the HERA AES risk assessment.

Minor components: It should be noted that minor components normally present in commercial AS are not addressed explicitly in this assessment. They are included implicitly to some degree, since the eco-toxicity and fate data are typically generated using the technical or commercial samples of AS, which include other minor components. Note that among fate studies only those that measure ultimate degradation take account of all organic components of a complex substance.

Exposure Pathway and Detergent Scenario

The "HERA detergent scenario" was used for the environmental exposure calculations. The entire tonnage was assumed to follow the domestic down-the-drain pathway to sewage treatment and to the environment. Releases from production and formulation activities fall outside of the scope of HERA and were not explicitly considered, at the local level, although both production and formulation losses are included in the regional risk assessment. For the calculation of the EUSES (European Union System for the Evaluation of Substances) regional tonnage, 7% of the EU tonnage was assigned to the region (replacing the default 10%), and the local emissions were not increased by the default factor 4, but by a factor 1.5. FURTHER EXPLANATION OF AND JUSTIFICATION FOR THESE VALUES CAN BE FOUND IN CHAPTER 2.6 OF THE HERA METHODOLOGY DOCUMENT. AVAILABLE ON THE WEBSITE - www.heraproject.com.

4.1.1. Environmental Fate

A review of degradation data was based on BUA Report 189 (BUA, 1996) (covering all CAS numbers related to AS) and on IUCLID (covering CAS number 151-21-3, C12-AS), and the OECD SIAR on Sodium Dodecyl Sulfate (OECD). In addition, literature sources were consulted.

Biodegradation Properties

The available data indicate all AS chainlengths considered in this assessment are readily biodegradable (BUA, 1996).

The biodegradability of the branched components of the HERA AS family is similar to that of linear components. Degradation of C14/C15 AS derived from branched and linear fractions of an essentially linear modified-OXO alcohol were shown in OECD 301F tests to be equally extensive and rapid (Battersby *et al*, 2000)

Physical Chemical Properties (Appendix 3)

The most important phys/chem properties for an environmental risk assessment are aqueous solubility, vapour pressure, and the octanol/water partition coefficient, or other relevant partition coefficients such as those between water and environmental matrices such as soil, sediment, or sewage sludge.

For Alkyl Sulphate, all groups of homologues have sufficiently low volatility that the sensitivity of the risk assessment to the values of this parameter, other than to the order of magnitude, is negligible.

In the higher tier used in this risk assessment, measured values are used for removal in sewage treatment, hence, the partition coefficients based on Kow will be used only for soil/water and sediment/water partition. It should be noted that it is well recognised that for surfactants a physically meaningful log Kow cannot be established. Therefore, all assessments based on partitioning coefficients that are not established experimentally but calculated from log Kow-values should be considered only as a first and conservative estimate.

Solubility of the different homologues varies, with C16 and C18 homologues having the potential to be incompletely soluble at concentrations used in ecotoxicity tests or being present in the environment.

4.1.2. Removal

The assessment of alkyl sulphate removal during sewage treatment is presented at three different tiers, with additional data being required for the higher tiers of the risk assessment process. The lowest tier follows the default EUSES calculation, which uses the SimpleTreat model. The second tier follows a measurements-based assessment using continuous activated sludge (CAS) and/or field monitoring data to determine a percentage of removal during sewage treatment. The third tier of the risk assessment uses kinetic information available for the C14 and C15 hydrocarbon chain lengths to determine the effluent concentration which results from the Monod kinetics which should apply to readily biodegradable, high volume substrates such as alkyl sulphates during sewage treatment (Rittman and McCarty, 2001: Grady et al, 1980). These results are then compared with laboratory CAS studies and with available environmental monitoring data.

Tier 1. SimpleTreat calculation

At the first tier, a SimpleTreat calculation was used to determine removal of alkyl sulphates in wastewater treatment, and their partitioning between air, water and sludge. These calculations were based on the default rates assigned for readily biodegradable chemicals, and the octanol-water partition coefficient of the different AS homologues. The results of these calculations are shown in table 5A.

Table 5A. WWTP Removal –SimpleTreat prediction

	Fraction of WWTP emission to:				Concentration on dry sewage sludge (mg/kg)
	Air	Surface water	Sludge	Degraded	
C12	0	0.126	0.002	0.871	8.1
C13	0	0.126	0.007	0.867	11.5
C14	0	0.125	0.0169	0.858	52.5
C15	0	0.122	0.0414	0.837	39.8
C16	0	0.116	0.0951	0.789	113
C18	0	0.0887	0.351	0.561	505

Tier 2. Continuous Activated Sludge (CAS) test and field monitoring data

CAS studies for several AS homologues

Standard CAS data (OECD 303A) (based on DOC removal measurements) are available for C12 and C16-18 AS. For C12-AS, the removal is 96% (IUCLID, 1995). For C16-18-AS, data are available (BUA, 1996) showing a removal of 96% (= same removal as found for C12-AS).

More accurate confirmatory CAS data, using MBAS (methylene blue active substance), mass spectrometry or ^{14}C measurements to determine removal of the parent compound, are also available. In the OECD Confirmatory test using the MBAS analytical parameter, for C12-AS a 99 % MBAS-removal was determined (Fischer & Gerike, 1975). For C14/15-AS removal of the parent surfactant, as detected by LCMS, was 99.96% (Cano *et al.*, 2001; Salanitro, unpublished results). For C16/18-AS the MBAS-removal was 98-99% (Steber et al, 1988). The test of a ^{14}C-radiolabelled C18-AS in a CAS test (Steber et al, 1988) yielded a removal rate of > 99% of the parent surfactant.

The ^{14}C-radiolabelled C18-AS CAS study also showed that < 2% of the continuously dosed AS was present on the sludge as intact surfactant. For the C14/15 chain lengths in the CAS study, measurements showed that less than or equal to 0.04% of the dosed AS was present on the sludge. No data are available about sorption to sludge for the other chain-lengths and so for these, the fraction not going to surface water was assigned to “sludge” and “degraded” as predicted by SimpleTreat. The concentration in dry sewage sludge was then re-scaled, based on the new estimate for the fraction assigned to sludge. The concentrations of AS in sewage sludge calculated using this methodology are shown in Table 5B.

Risk assessment of a parent compound should be extended to include metabolites only if these are persistent and/or more ecotoxic than the parent. Based on the sound knowledge about the degradation pathway of AS including enzymatic cleavage of the sulphate ester and subsequent oxidation of the formed alcohol to the corresponding fatty acid which is ultimately biodegraded via ß-oxidation (Swisher 1987, Steber & Berger, 1995), there is no indication for any recalcitrant metabolite. Hence, the primary AS removal data obtained in the MBAS, LCMS and ^{14}C-radiolabelled studies are suitable for use in this assessment.

Field monitoring approach for C14 and C15 AS

The CAS study for C14/15 AS, conducted by Cano *et al.* (2001), showed a very high removal, i.e. 99.96%. However, the operating conditions of this CAS study were not representative of the typical European conditions applied in the TGD and EUSES. The Hydraulic Retention Time (HRT) for the CAS study was longer (18 hours instead of 7 hours), and so was the Sludge Retention Time (SRT) (19 to 25 days instead of 9 days). Hence, an additional confirmation of the high removal of C14 and C15 AS is required.

This confirmation is provided by a monitoring study (Matthijs *et al.*, 1999) showing an average AS effluent level (C12-15 range) in 7 activated sludge plants in The Netherlands of 5.7 µg/L. It can be conservatively assumed that the C14 and C15 homologues are removed at least as well as the shorter C12 and C13 chain lengths**,** as the longer hydrocarbon chains are more highly adsorptive to sludge and are also expected to degrade more readily than shorter chains, as established for several surfactant groups (Swisher, 1987). Hence, C14 and C15 will represent at the most the same fraction of the total AS in the effluent as their fraction in the tonnage put on the market. If extrapolated to the total EU tonnage of AS (102 000 tonnes per annum) the total tonnage of C12 through C15 AS is 73,233 tonnes/year (Table 3). The C14 and C15 chain lengths represent respectively 36% and 8% of this C12-15 total. Hence, C14 and C15 are expected to represent ≤36% and ≤8% of the measured total AS effluent concentrations.

The average C12-15 AS concentration in effluents in The Netherlands was 5.7 µg/L. This corresponds to average C14 and C15 concentrations of 2 µg/L and 0.5 µg/L, respectively. Taking into account the uncertainty factor of 1.5 to describe the variability between plants in the same region (see HERA exposure scenario in the HERA Methodology Document), the realistic worst case effluent levels become 3 µg/L for C14 and 0.75 µg/L for C15 respectively. To extrapolate this to the realistic worst case region in the EU, an additional safety factor of 1.7 has to be included, because detergent use in The Netherlands (7.5

kg/cap.year) is 1.7 times lower than in the regions with the highest consumption (12.5 kg/cap.year). This finally results in realistic worst case effluent concentrations of 5.1 µg/L for C14 and 1.3 µg/L for C15.

To calculate the percentage removal associated with these effluent levels, first the sewage treatment plant influent levels for C14 and C15, under realistic worst case conditions, need to be known. These can be calculated by the EUSES model. As the effluent monitoring data arise from the total tonnage of AS in the environment, for these calculations the total AS tonnage scenario was used instead of the HERA tonnage scenario. This resulted in calculated influent concentrations of 1900 µg/L for C14 and 439 µg/L for C15**.** This leads to removal estimations of 99.7% for C14-AS and C15-AS.

For the sake of a Tier 2 evaluation (being somewhat conservative), the CAS study for C14/15 AS could be considered to overpredict removal under European conditions, the 99.7% removal derived from the European monitoring studies was used instead of the 99.96% removal obtained from the CAS study. The fraction of alkyl sulphate released to surface water and to sludge for each hydrocarbon chainlength are summarised in Table 5B.

Table 5B. WWTP Removal – CAS data

	Fraction of WWTP emission to:				Concentration on dry sewage sludge (mg/kg)
	Air	Surface water	Sludge	Degraded	
C12	0	0.010	0.0027 (*)	0.9873 (*)	9.32
C13	0	0.010 (1)	0.0078 (*)	0.9822 (*)	13.1
C14	0	0.003 (3)	0.0004 (2)	0.9966	1.24
C15	0	0.003 (3)	0.0004 (2)	0.9966	0.39
C16	0	0.020 (4)	0.1054 (*)	0.8746 (*)	126
C18	0	0.010	0.020	0.9700	28.9

(*) assuming same split between ‘to sludge’ and ‘degraded’ as calculated by SimpleTreat

(1) C12 data were used as worst-case interpolation between C12 and C14

(2) C14/15 data were used as no specific C14 or C15 data are available

(3) based on field monitoring data

(4) C16/18 data were used as no specific C16 data are available

Tier 3. Derivation of Removal using Monod Kinetics

Although the EU Technical Guidance Documents allow a percentage removal treatment for removal during sewage treatment, they also have an option for Monod kinetics to be used to describe the biodegradation process. Provision for this is made in the EUSES program, where the Monod parameters μ_{max} and K_s can be used as input parameters to describe the removal process. Monod kinetics is generally shown by materials present at inlet concentrations of approximately 100 ppb or higher (Berg, 1996; Nyholm et al 1996), as exemplified by its use in the IWA models (IWA 2000) used to model operational activated sludge plants. Berg (Berg and Nyholm, 1996) specifically excludes high volume household chemicals, such as Linear Alkybenzene Sulphonale (LAS) and other surfactants, from a first order kinetic treatment because of the higher concentrations occurring in wastewater treatment plant influents. Thus, for higher production volume chemicals, such as surfactants like AS, it is more appropriate to use Monod kinetics to describe the biodegradation process and to estimate the effluent concentration.

In activated sludge systems, Monod kinetics are generally observed with substances present in the influent at 0.1 mg/L or higher. For Alkyl Sulphates, the average influent (raw sewage) concentration in the EU can be calculated from the total AS tonnage (102,000 t/y), the number of people in the EU (370 million), and the per capita water use (200 L/cap/day). The average per capita use of Alkyl Sulphates is 0.76 g/day, hence the average level in sewage is 3.8 mg/L. In the EU regions with the lowest detergent use, the consumption is estimated to be about half of the average. Furthermore, variation between different local situations can lead to a factor 1.5 variability (cf. HERA methodology document, section on detergent scenario). Hence, the lowest AS influent concentrations in the EU are estimated to be a factor 2 x 1.5 below the average, leading to 1.3 mg/L. This is an order of magnitude higher than the lowest concentration needed to induce Monod kinetics. Hence, Alkyl Sulphates degradation in sewage treatment plants is expected to follow Monod kinetics in all EU regions.

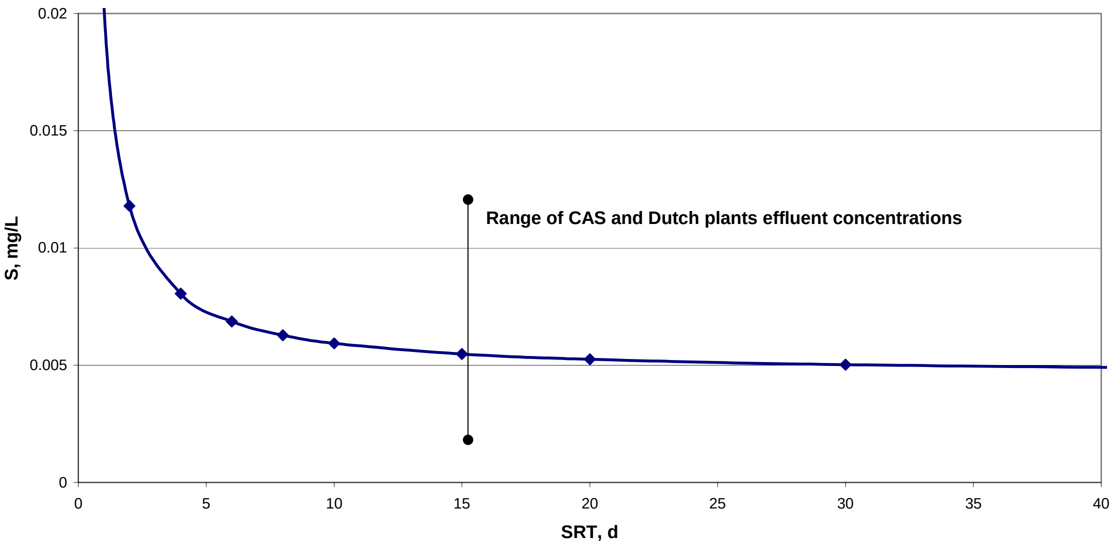
The application of Monod kinetics is important because this approach describes the ability of activated sludge biomass to grow on the substrate. As the loading of substrate on the activated sludge increases (due to i.e. higher use volumes), additional biomass grows on the additional substrate and the effluent concentration is thus kept the same (Rittman and McCarty, 2001; Grady et al, 1980.)

It can be shown (Birch, 1991) that substances following Monod biodegradation processes show a constant sewage treatment effluent concentration, which is independent of the influent concentration but varies slightly with sludge retention time. Thus it is the effluent concentration of the substance which will be constant, and not the percentage removal. The data for the flow proportional 24 hour composite AS effluent concentrations for the six well run activated sludge treatment plants in The Netherlands which have been reported by Matthijs et al. (Matthijs et al 1999), can be used to set a reasonable upper limit to the C14 and C15 AS levels, as has been done in Tier 2. In the tier 3 Monod based assessment, however, the effluent levels determined will not be expected to increase if the surfactant tonnage reaching the plant increases due to higher future use levels. This is because, using the more realistic Monod kinetics, the effluent concentrations are independent of the influent levels.

The effluent concentrations for the six well run activated sludge treatment plants in The Netherlands which have been reported by Matthijs et al. (1999) range from 1.2µg /l to 12 µg /l, with an average value of 5.7 µg /l. A reasonable worst case value for alkyl sulphate in sewage treatment effluent can be taken as the highest value observed, 12 µg /l. If it is assumed that 36% of the alkyl sulphate measured is C14 AS, as in the present study, then these results predict an effluent concentration of 4.3 µg /l of 14C alkyl sulphate. This assumption is conservative, as biodegradation will favour removal of the longer hydrocarbon chains (Swisher, 1987). These values for total AS and for C14 AS in activated sludge plant effluent are conservative, as can be seen by comparison with published US trickling filter effluent concentrations: C12-AS, 4.6 µg/L; C13-AS, 1.2 µg/L; C14-AS, 3.9 µg/L and C15-AS, 4.3 µg/L (McAvoy *et al*. (1998). As removal by activated sludge treatment is expected to be much better than removal in trickling filters, these results show that the worst case effluent concentration from the study in The Netherlands is indeed a reasonable worst case.

The variation in effluent concentration with sludge retention time is shown in Figure 1, for μ_{max} and K_s values which have been determined from laboratory CAS-generated biomass using Extant Kinetic Tests (Ellis et al 1996, Ellis and Eliosov, 2002 in press, Cano and van Compernolle, unpublished results). The predicted decrease in effluent concentration with increasing sludge retention time is shown in the figure. The variation across typical European sludge retention times (from approximately 6 days in the UK to over 20 days in the Netherlands and Germany) is well within the range of experimental effluent concentrations shown in the figure. Thus the reasonable worst case effluent concentrations determined from the highest effluent concentration observed in the study in The Netherlands effectively represent reasonable worst case effluent concentrations for alkyl sulphate under European conditions, with Monod kinetics effectively describing the expected removal mechanism.

Figure 1
Effluent AS concentration vs SRT using full Monod Kinetics
Ks=0.08 mg/L and umax = 0.3 1/hr



Although the more realistic tier 3 assessment has been carried out for the C14 and C15 alkyl sulphate chainlengths for which the laboratory CAS data are available, it is used in this risk assessment only to demonstrate the results of the more realistic Monod kinetics during removal in sewage treatment. This means that the reasonable worst case effluent concentrations found here will not be expected to increase, if alkyl sulphate inlet concentrations increase due to higher use in the future. The numerical results of the tier 2 risk assessment, which can be applied to all of the alkyl sulphate chainlengths, will be used in the remainder of this risk assessment.

Degradation in Anaerobic Sludge Digestion

Alkyl Sulphates are readily biodegradable under anaerobic conditions (ERASM, 1999). At least 80% ultimate degradation will occur during anaerobic sewage sludge digestion.

Within a 4-week digestion period at 35ºC a 90% ultimate degradation (i.e. CO_2 + CH_4 formation) was found for C12-AS and 94% for C18-AS (Steber et al., 1988). The test conditions were quite comparable with the practical situation except for the fact that a static system was used, whereas real digesters are mainly run semi-continuously. Nuck & Federle (1996) used a similar lab digester and found over a 15-day period C14-AS gave 80% gas formation. Anaerobic screening test results for C12/14- and C14/15-AS showed that the anaerobic primary biodegradation (parent compound removal) rate is far higher than the corresponding gas formation rate: while the gas formation was 77-84% and 65-78%, respectively, the MBAS removal was 98-99% and 97% (Salanitro and Diaz, 1995).

Taking these data into account there is a valid basis to assume that the removal of the parent surfactant compound under digester conditions is at least between 90% and 95%. However, it should be noted that the organic moiety of the sewage sludge (about 50% of the sludge dry matter) is also reduced during the digestion process, typically by about 50%. In other words, the total sludge dry matter is typically reduced by about 25%. This leads to an overall reduction of the actual chemical concentration on the sewage sludge by at least about 90%.

The EUSES program does not include anaerobic degradation during sludge digestion. Instead, this process has been included in the HERA risk assessment by manual modification (i.e. reduction by 90%) of the concentrations in agricultural soil calculated by EUSES.

Degradation in Surface Water

Two studies are reported in IUCLID (1995) for C12-AS. Kikuchi (1985) mentions 100% degradation after 1-3 days depending on the temperature. This corresponds with at least 3 half-lives (which lead to a reduction to 12% of the initial concentration). Hence, the half-life for C12-AS was less than 0.3-1 days. Knaggs et al. (1965) reported a similar half-life of 0.5–1 days. From these 2 studies, an average half life of 0.75 days was assumed for C12-AS.

Based on the ready biodegradability of AS of all chain lengths, it was assumed that the rate constant for degradation in bulk surface water for C12-AS is also valid for the other chain lengths. Hence, a half-life of 0.75 days (= a degradation rate of 0.92 d^{-1}) was also used for C13, C14, C15, C16 and C18.

Although this figure differs considerably from the half-life default value proposed in the TGD for readily biodegradable substances (14 days) its use as being representative and realistic can be justified. AS exceed all other surfactants in speed of primary and ultimate biodegradation (Swisher 1987). Taking the half-lifes in river water for other readily biodegradable surfactants like LAS and AES (Schröder 1995) into account (1-3 hours) it seems obvious that the assumed rate constant for AS in surface waters is rather conservative.

4.1.3. Monitoring

Monitoring data relate, of course, to concentrations of AS derived from all possible sources (HERA applications, other applications and AS from other sources, e.g. AES). Within the scope of HERA, they are therefore worst-case estimates, but may be used to investigate the conservatism of the HERA PEC estimates.

In Fendinger *et al.* (1992), AS could not be detected in surface water (in the USA) above the individual homologue limit of detection (5 µg/L). In receiving water sampled upstream of a sewage treatment plant outfall, Popenoe *et al* (1994) detected approximately 1.5 µg/L C12-AS (number read off figure in publication), but <0.3 µg/L for C13, C14 and C15-AS.

In effluent from a US trickling filter plant, McAvoy *et al*. (1998) detected C12-AS, 4.6 µg/L; C13-AS, 1.2 µg/L; C14-AS, 3.9 µg/L and C15-AS, 4.3 µg/L. In the effluent from a rotating biological contractor (RBC), Popenoe *et al*. (1994), detected C13 and C15-AS of <0.3 µg/L, (an experimental artefact prevented an assessment of C12 and C14-AS). Matthijs *et al.* (1999) showed AS removal in activated sludge plants was always > 99% (5 plants in The Netherlands) and the average AS effluent concentration in the C12 – C15 range was 5.7 µg/L (range 1.2-12µg/L). Assuming a dilution factor of 10, these data lead to estimated river water concentrations of about 1 µg/L.

In Matthijs *et al.* (1999), measured influent data in The Netherlands suggest 55% in-sewer removal of AS. Fendinger *et al.* (1992) estimated a similar figure of 58-78% in-sewer removal. However, in-sewer removal is not taken into account in this HERA assessment.

4.1.4. PEC Calculations

EUSES was applied to calculate the regional and local exposure to Alkyl Sulphates. Note that the resulting PECs (Predicted Environmental Concentrations) are based on the HERA tonnage (Table 4) and chain length distribution.

Local Predicted Environmental Concentrations (PECs)

The local predicted environmental concentrations (PECs), which include a regional PEC contribution, are reported below. The predicted environmental concentrations of total Alkyl Sulphates (sum of all chain lengths) are given for information only. Note that these PECs were not used in the risk characterisation, because a toxic units approach was used (See below).

Table 6. Local PECs

local PEC	Water (mg/L)	Soil 30d (mg/kg)	Soil 30d * (mg/kg) (digested sludge)	Sediment (mg/kg)	STP (mg/L)
Tier 1 - SimpleTreat					
C12-AS	0.0176	0.0083	0.0009	0.0233	0.1722
C13-AS	0.0085	0.0121	0.0012	0.0202	0.0832
C14-AS	0.0155	0.0554	0.0055	0.0743	0.1526
C15-AS	0.0047	0.0421	0.0042	0.0515	0.0463
C16-AS	0.0055	0.1199	0.0120	0.1447	0.0545
C18-AS	0.0051	1.254	0.1254	0.8076	0.0507
Total AS	0.0569	1.492	0.1491	1.121	0.5595

local PEC	Water (mg/L)	Soil 30d (mg/kg)	Soil 30d * (mg/kg) (digested sludge)	Sediment (mg/kg)	STP (mg/L)
Tier 2 - CAS data					
C12-AS	0.00162	0.0094	0.0009	0.0021	0.0136
C13-AS	0.0008	0.0136	0.0014	0.0018	0.0066
C14-AS	0.000563	0.00132	0.0001	0.0027	0.0037
C15-AS	0.000174	0.0004	0.00004	0.0019	0.0011
C16-AS	0.0010	0.1330	0.0133	0.0265	0.0094
C18-AS	0.0007	0.0717	0.0072	0.1033	0.0057
Total AS	0.0045	0.2294	0.0229	0.1358	0.0360

* taking into account chemical removal during anaerobic sludge digestion

Regional Environmental Concentrations

As explained in the HERA methodology document, use of production tonnage for HERA means that the losses to the region during formulation are automatically included when 100% of the production tonnage is released to the environment. The regional PECs in surface water are as follows:

Table 7. Regional PECs

regional PEC water (mg/L)	SimpleTreat	Tier 2 - CAS
C12-AS	0.0003	0.0002
C13-AS	0.0002	0.0001
C14-AS	0.0003	0.0002
C15-AS	0.0001	0.0001
C16-AS	0.0001	0.0001
C18-AS	0.0001	0.0001
Total AS	0.0011	0.0008

Indirect Exposure to Humans

As a starting point for the calculation of indirect human exposure via drinking water, the EUSES calculations for indirect uptake via regional exposure can be used (taking into account that drinking water will not be sourced immediately downstream of wastewater emissions). These are shown in Table 8 below, with the calculated uptake from a local source given for comparison. The total human uptake calculated by EUSES is also shown in the table, though known inadequacies with the current model for plant uptake mean that these calculated values will considerably overestimate the uptake from food. Thus these total regional uptake values may not be considered to be acceptably realistic for the HERA Human Health Assessment.

Table 8. Alkyl Sulphate uptake by Humans – as calculated with EUSES*

AS Fraction	Regional (mg/kg/day)		Local (mg/kg/day)	
	Drinking Water	Total Food + Water Uptake	Drinking Water	Total Food + Water Uptake
C12	6.37×10^{-6}	8.37×10^{-6}	4.52×10^{-5}	2.04×10^{-4}
C13	3.1×10^{-6}	5.85×10^{-6}	2.2×10^{-5}	1.24×10^{-4}
C14	5.57×10^{-6}	1.83×10^{-5}	1.61×10^{-5}	5.33×10^{-5}
C15	1.73×10^{-6}	1.15×10^{-5}	4.98×10^{-6}	3.43×10^{-5}
C16	2.28×10^{-6}	3.79×10^{-5}	2.91×10^{-5}	5.25×10^{-4}
C18	1.31×10^{-6}	2.7×10^{-4}	9.36×10^{-6}	1.99×10^{-3}

*EUSES defaults modified according to the HERA Detergent Scenario

The calculations in Table 8 are based upon the advanced data for alkyl sulphate removal during sewage treatment (CAS studies or field monitoring data). Note that the estimates for uptake via drinking water are expected to be conservative, as would be expected for a screening model. However, some provision is made in EUSES for surface water purification.

4.2. Environmental Effects Assessment

4.2.1. Toxicity

A review of ecotoxicity data was based on BUA Report 189 (BUA, 1996) (covering all CAS numbers related to AS) and on IUCLID (covering CAS number 151-21-3, C12-AS), and the OECD SIAR on Na Dodecyl Sulfate. In addition, a review of external literature was undertaken (Appendix 2).

For C12-AS, a large ecotoxicological dataset is available, containing single-species acute and chronic data, as well as mesocosm studies. For other chain lengths, a rich dataset is available for the commercial materials (e.g.. mixtures in the range of C12-14, C12-15, C12-18, C16-18). For individual homologues, the available information is typically limited to acute studies. However, chronic single-species data on the most sensitive taxonomic group (aquatic invertebrates) are available for all chain lengths except C13.

C12 Alkyl Sulphate

A **full ecotoxicological dataset** is available (e.g. summarized in IUCLID, 1995 and BUA (1996), as well as SDA HPVC challenge programme (ongoing activity, unpublished). This includes single species acute and chronic data, as well as a mesocosm study. An overview of the lowest chronic data is given in the table below:

Several terrestrial toxicity tests for C12 AS are reported in BUA (1996). The lowest effective concentration is the 48h EC50 (root growth inhibition) value of 361 mg/L for Chick Pea (*Cicer arietinum*). Several microbial toxicity tests are reported in IUCLID (1995) and BUA (1996). The lowest effective concentration is the 4h EC50 value of 24 mg/L for nitrifying bacteria in activated sludge.

Table 9. Lowest chronic ecotoxicological data for C12-AS

	Species	Test method	NOEC (mg/L)	Reliability
Fish [1]	*Saccobranchus fossilis*	60 days semistatic (water renewal every 48h)	>= 2.24	Unknown
Aquatic Invertebrates [2]	*Brachionus calyciflorus*	2 days life cycle test, static	EC20 = 0.77	1
Algae [3]	*Selenastrum*	4 days, growth inhibition	12	Unknown
Mesocosm [4]	Several	P&G ESF	0.224	1
Plants [5]	*Cicer arietinum*	48h root growth inhibition	361 mg/kg	Unknown
Microorganisms [6]	activated sludge	4h nitrification inhibition	24 mg/L	Unknown

1: Dalela et al (1981) 2: Versteeg *et al* (1997) 3: Nyholm & Damgaard (1990) 4: Belanger et al (1995) 5: Schmidt (1988) 6: King et al. (1984)

C13, C14 and C15 Alkyl Sulphate

Although ecotox data covering commercial grades in the ranges C12-14, C12-15 and C12-18 do exist, only limited information is available on the individual homologues C13, C14 and C15. **No ecotoxicity data for C13-AS** are available. The **ecotoxicity dataset for C14-AS and C15-AS is very limited**. An overview of existing acute data is given in BUA (1996). The only chronic datapoint for both homologues is for *Ceriodaphnia dubia.* Given that *Ceriodaphnia* is the most sensitive species for C12 and for C16-18 (see below), it is reasonable to assume it will also be the most sensitive species for C13, C14 and C15.

Table 10. Lowest chronic ecotoxicological data for C13,14,15-AS

	Species	Test method	NOEC (mg/L)	Reliability
C14				
Aquatic Invertebrates [1]	*Ceriodaphnia dubia*	7 days, flow through	LOEC = 0.062	1
C15				
Aquatic Invertebrates [1]	*Ceriodaphnia dubia*	7 days, flow through	0.230	1
C14-15				
Aquatic Invertebrates [1]	*Ceriodaphnia dubia*	7 days, flow through	0.081	1
Aquatic Invertebrates [2]	*Daphnia magna*	21 days, flow through	0.050	Unreliable *

1: Dyer *et al* (1997) 2: Procter & Gamble (1988, unpublished data)

* The highest toxicity of C14/15 AS was found in the (Procter & Gamble, unpublished) *Daphnia magna* study. This study is considered of limited reliability for several reasons:

(1) for the (non-GLP) analytical determination of the test substance concentration, the recovery was low (typically the measured concentrations were only 30% of the nominal values) and variable;
(2) in 2 of the 4 replicates of the NOEC concentration, 100% mortality was observed, presumably due to a contamination; and finally
(3) in a repetition of the C14-15 study at the same contract lab (in 1992), a NOEC above 1 mg/L was found.

Considering these uncertainties, it was decided not to use this specific study for the effects assessment. It should however be noted that the PNECs obtained for C14-AS and C15-AS (see below) are in line with the results of the *Daphnia magna* study.

C16 and C18 Alkyl Sulphate

For the **C16-18 commercial mixture** (1:2), a rich ecotox and fate dataset is available, and is reported in BUA (1996). The **ecotoxicity datasets for C16 and C18 AS individually are very limited**, but chronic data for *Ceriodaphnia* (which is the most sensitive species for C12) are available.

Next to the individual C16 and C18 data, for C16-18 AS the lowest chronic NOEC values, as well as the microcosm NOEC, are given in the table below.

The lowest chronic NOEC for C16-18 (for *Brachydanio rerio*) is higher than would be predicted for *Ceriodaphnia* (using the mixture toxicity approach). Hence, it can be concluded that *Ceriodaphnia* is the most sensitive species for C16 and C18 AS.

Several terrestrial toxicity tests for C16-18 AS are reported in BUA (1996). The EC50 values were always > 1000 mg/kg. However, for the risk assessment, the more conservative data obtained for C12-AS were used. Two microbial toxicity tests are reported in BUA (1996). The lowest effective concentration is the 30 minutes EC10 value of 50 mg/L for *Pseudomonas putida*, which was conservatively used to substitute the bacterial EC50 in the assessment.

Table 11. Lowest chronic ecotoxicological data for C16 and C18-AS

	Species	Test method	NOEC (mg/L)	Reliability
C16-18 (1:2)				
Fish [1]	*Brachydanio rerio*	OECD 204	1.7	2
Aquatic Invertebrates [1]	*Daphnia magna*	OECD 202	16.5	2
Algae [2]	*Scenedesmus subspicatus*	OECD 201	17	2
microcosm [1]	Several	-	0.550	2
C16				
Aquatic Invertebrates [3]	*Ceriodaphnia dubia*	7 days, flow through	0.204	1
C18				
Aquatic Invertebrates [3]	*Ceriodaphnia dubia*	7 days, flow through	0.602	1
C16-18 (1:2)				
Plants [4]	several	79/831/EEC (1986)	> 1000mg/kg	2
Microorganisms [1]	P. putida	OECD 209	EC10 = 50mg/l	2

1: Steber et al (1988) 2: Henkel (1996) 3: Dyer *et al* (1997) 4: BUA (1996)

Trends in toxicity

The trends in toxicity are explicable in terms of physical/chemical properties. As alkyl chain length increases toxicity increases, explaining the greater toxicity of C14 compared to C12. However,solubility decreases with increasing chain length. For C15, the solubility decreases to below the concentration causing toxic effects, hence the lower toxicity of C15, C16 and C18 compared to C14. Note that for C15, the threshold for chronic toxicity (NOEC) is similar to the solubility limit.

4.2.2. PNEC Calculations

Aquatic PNECs

For all AS homologues, invertebrates were found to be the most sensitive taxonomic group. For C12, *Brachionus calyciflorus* was the most sensitive species. For C14 to C18, *Ceriodaphnia dubia* was identified as the most sensitive species in chronic ecotoxicity tests.

For the C12 study with *Brachionus*, no NOEC (No Observed Effects Concentration) is reported – only a calculated EC20 value. Because of the high similarity between the *Ceriodaphnia* and *Brachionus* toxicity values for C12 (respectively a NOEC of 0.88 mg/L and an EC20 of 0.77 mg/L), and because *Ceriodaphnia* chronic studies are more generally accepted, it was decided to base the PNEC determination for C12 on the *Ceriodaphnia* study – for which a NOEC is available.

The following NOEC values were observed in a 7-day flow-through study with *Ceriodaphnia* (Dyer et al., 1997):

Table 12. *Ceriodaphnia* NOECs for Alkyl Sulphates

	NOEC (mg/L)	Remarks
C12	0.880	
C13	-	no chronic data available
C14	< 0.062	LOEC = 0.062 mg/L,
C14/15(45:55)	*0.081*	
C15	0.230	
C16	0.204	
C18	0.602	

Data gaps exist for C13 and C14. For C13, no chronic data are available. For C14, the only available chronic data point is the *Ceriodaphnia* study mentioned above, in which no NOEC was reported.

Given the large size of the ecotoxicological dataset for Alkyl Sulphates in general, it is not appropriate to revert to acute data or QSAR estimates to derive a PNEC for the C13 and C14 homologues. Instead, an expected NOEC value was determined by interpolation within the large *Ceriodaphnia* dataset, aided by QSAR calculations.

NOEC estimation for C14-AS

The NOEC for C14-AS was determined indirectly, using measured data for C15-AS and the

C14-15 mixture, using the mixture toxicity approach.

As the NOEC for both the C14-15 (45:55) commercial product and for the C15 individual homologue are known, it is possible to derive the C14 NOEC value as follows:

$$[\text{NOEC C14-15}] = 1 / \{ 45\% / [\text{NOEC C14}] + 55\% / [\text{NOEC C15}] \}$$

$$\Rightarrow 0.081 = 1 / (0.45/x + 2.391) \quad \Rightarrow \quad 0.45/x = 9.955 \quad \Rightarrow x = 0.045$$

Estimated C14 NOEC = 0.045 mg/L

This NOEC value of 0.045 mg/L is appropriate to be used in risk assessment. It is in line with the LOEC of 0.061 mg/L, which is about 50% higher than this NOEC. Furthermore, it is very similar to the calculated EC10 (Dyer et al, 2000) of 0.040 mg/L.

NOEC estimation for C13-AS

Based on measured NOEC data for C12 and the estimated NOEC for C14, a NOEC for C13 was interpolated, assuming an exponential increase of toxicity with chain length:

C12: NOEC = 0.880 mg/L	log=-0.0555
C14: NOEC = 0.045 mg/L	log=-1.3468
C13: NOEC = ???	log must be average of C12 and C14 = –0.701

⇒ C13 NOEC = 0.2 mg/L

It should be noted that an interpolation entirely based on measured data (i.e. between C12 and C15) would not be feasible, because for chain lengths of C15 and higher, a decrease in toxicity is observed due to solubility effects.

Effects of decreasing solubility on ecotoxicity are not expected in the C12-14 range because of the high (predicted) water solubility (> 5 mg/L). Hence, the proposed interpolation between C12 and C14 is appropriate.

PNEC determination and validation

The aquatic PNEC for each chain length was determined by using an application factor (AF) of 10 with the lowest chronic NOECs, which were obtained for *Ceriodaphnia dubia*. An AF=10 is justifiable for all chain lengths because a large chronic data set is available for Alkyl Sulphates, covering nearly the entire range of chain lengths in the assessment.

Table 13. Aquatic PNECs

Chain length	Aquatic PNEC (mg/L)
C12	0.088
C13	0.020
C14	0.0045
C15	0.023
C16	0.020
C18	0.060

For validation, these PNECs can be compared with mesocosm NOECs for AS:

- For C12-AS mesocosm data are available (Belanger, 1995). An AF between 1 and 3 is appropriate for mesocosm NOEC data giving a PNEC between 0.075 and 0.224 mg/L.
- For C16-18 AS (1:2 mixture) microcosm data are available (river community limited to algae, protozoans and rotifers, Steber et al, 1988). An AF of 5 is appropriate for microcosm NOEC data giving a PNEC of 0.110 mg/L.

Overall, the PNECs derived from the chronic single-species studies (for C12 and C16-18) are more conservative than the corresponding meso- or microcosm derived PNECs.

PNECs for other compartments

Sediment

Due to a general lack of data on sediment toxicity, the EUSES equilibrium partitioning method was used to derive the sediment PNECs from the corresponding aquatic PNECs. As none of the AS homologues has a log Kow > 5, an additional safety factor of 10 as specified in the EU TGD was not required in these calculations. The results of the EUSES calculation are shown below:

Table 14. Sediment PNECs

Chain length	Sediment PNEC (mg/kg)
C12	0.0963
C13	0.0406
C14	0.0186
C15	0.22
C16	0.468
C18	8.4

Terrestrial

The toxicity of AS to plants is low. The lowest reported EC50 is 361 mg/L, for C12 (Chick Pea) (BUA, 1996). For C16 and C18 no toxicity to plants nor earthworms was observed (EC0 = 1000 mg/kg for C16-18).

As within the AS family, data are available for 2 taxa (plants and earthworms), the application factor approach can be used (instead of the equilibrium partitioning method). The lowest EC50 (C12, Chick Pea) was conservatively used (with AF=1000) to derive a PNEC for all chain lengths except for C16 and C18, for which the EC0=1000 mg/kg was used.

Table 15. Terrestrial PNECs

Chain length	Terrestrial PNEC (mg/kg)
C12,13,14,15	0.361
C16,18	1

WWTP Micro-organisms

Across all chainlengths (IUCLID, 1995 and BUA, 1996), the lowest reported effective concentration is the 4h EC50 value of 24 mg/L for nitrifying bacteria in activated sludge (C12-AS). This value was conservatively applied to all chain lengths, giving a PNEC of 2.4 mg/L.

Table 16. WWTP PNECs

Chain length	WWTP PNEC (mg/L)
All	2.4

Endpoints/Mechanism of Action not included in EUSES

The possibility that various surfactants might be endocrine disruptors was investigated by Routledge and Sumpter (1996), using an estrogen-inducible yeast screen. Sodium n-octyl sulphate and sodium n-nonyl sulphate were tested and showed no activity. These researchers also tested a sodium C12-C15 linear-oxo type alcohol 3EO ethoxysulphate which would have contained around 20% of the corresponding alcohol sulphate, again without showing any activity.

4.3. Environmental Risk Characterization

In the tables below, the PEC/PNEC ratios (calculated with EUSES) are given, based on the different exposure scenarios (ie. different assumptions for removal), and PNEC derivations from chronic data. The PEC/PNECs for the different chain lengths were added up to obtain a total AS PEC/PNEC (= toxic units approach).

4.3.1. Standard EUSES removal scenario

Table 17. Risk Characterization Ratios (standard EUSES removal scenario)

PEC/PNEC	Water	Soil	Sediment	STP
C12	0.1995	0.0230	0.2404	0.0716
C13	0.4238	0.0335	0.4968	0.0343
C14	3.4505	0.1539	3.9939	0.0642
C15	0.2052	0.1164	0.2340	0.0192
C16	0.2777	0.1199	0.3092	0.0227
C18	0.0853	1.2541	0.0963	0.0211
Total AS	4.6421	1.7008	5.3706	0.2331

Using SimpleTreat removal estimates and chronic effects data, and not taking into account removal in anaerobic sludge digestion, leads to PEC/PNEC ratios >1 in the water, soil and sediment compartment. The assessment can be improved by using CAS test data to refine the removal estimates, and by including chemical removal from sludge during anaerobic digestion.

4.3.2. Realistic removal scenario

Table 18.Risk Characterization Ratios (realistic removal scenario)

PEC/PNEC	Water	Soil	Sediment	STP
C12	0.0179	0.0026	0.0222	0.0060
C13	0.0386	0.0034	0.0455	0.0026
C14	0.125	0.0037	0.144	0.0015
C15	0.0076	0.0011	0.0086	0.0005
C16	0.05116	0.0132	0.0570	0.0037
C18	0.0110	0.0070	0.0125	0.0025
Total AS	0.2513	0.0309	0.2898	0.0167

Using removal estimates based on more accurate advanced CAS test data and measurements of anaerobic degradation in sludge digestion, in combination with chronic effects data, it can be adequately demonstrated that the Alkyl Sulphate use in HERA products poses no environmental concerns.

4.3.3. Discussion and Conclusions

The absence of environmental concerns can be shown for current use levels of Alkyl Sulphates in HERA products. The Risk Characterization ratios (PEC/PNEC) are below 1 for all environmental compartments.

To demonstrate this, higher tier exposure and effects data were needed. Chemical removal in WWTPs was determined from advanced CAS test data or monitoring data, and to determine the Predicted No Effect Concentrations chronic ecotoxicity data were used.

In the assessment, it was shown that both the exposure and the effects assessment are conservative. Monitoring data indicate that exposure to surface water is overestimated, and mesocosm studies show that the PNEC is conservative. In the US, the actual AS levels in surface waters (coming from all sources – not only HERA applications) were below 5 μg/L per homologue (Fendinger *et al*, 1992) and 1-2 μg/L for selected homologues (Popenoe *et al*, 1994). In the Netherlands, effluent data from an activated sludge plant, suggest river water levels of < 1 μg/L (C12-15), whereas in the US, data from a trickling filter plant suggest a receiving water concentration of 1.4 μg/L (assuming a 10-fold dilution). These figures are several times lower than the predicted concentrations used in this assessment.

4.4. Addendum - “Total Tonnage” Scenario

4.4.1. Environmental risk characterization

The total AS tonnage used in Europe is 102,000 tonnes/year (1999 CESIO statistics). An alternative more conservative exposure scenario was included in this risk assessment by assuming that this entire tonnage is disposed of down-the-drain.

The chain length distribution for the total AS tonnage has been extrapolated from data available on 78 888 tonnes of the 102 000 tonnes total. Hence, the PEC/PNEC ratios for the HERA tonnage could be extrapolated to the overall tonnage by multiplying the PEC for each AS chain length by an appropriate factor, equal to the total production tonnage for this chain length divided by the HERA tonnage. This approach is valid from a mathematical point of view because of the linearity of the EUSES model.

Table 19. Risk Characterization Ratios (advanced removal scenario)
for the total CESIO tonnage (assuming HERA chain length distribution)

PEC/PNEC	Water	Soil	Sediment	STP
C12	0.02406	0.0034	0.0298	0.0080
C13	0.0389	0.0035	0.0459	0.0026
C14	0.2594	0.0076	0.2988	0.0032
C15	0.0105	0.0015	0.0120	0.0007
C16	0.0680	0.0175	0.0758	0.0049
C18	0.0094	0.0060	0.0107	0.0021
Total AS	0.4104	0.0395	0.4730	0.0214

As shown above, the absence of environmental concerns for the total AS tonnage can also be adequately demonstrated using the same exposure and effects assessment approach as for the HERA tonnage.

4.4.2. Indirect Exposure to Humans

The assessment of indirect exposure to humans can be re-scaled in a similar way.

Table 20. Alkyl Sulphate uptake by Humans – from Total CESIO tonnage, as calculated with EUSES*

AS Fraction	Regional (mg/kg/day)		Local (mg/kg/day)	
	Drinking Water	Total Food + Water Uptake	Drinking Water	Total Food + Water Uptake
C12	1.00×10^{-5}	1.32×10^{-5}	7.12×10^{-5}	3.22×10^{-4}
C13	3.64×10^{-6}	6.88×10^{-6}	2.59×10^{-5}	1.46×10^{-4}
C14	2.41×10^{-5}	2.84×10^{-5}	2.50×10^{-5}	8.26×10^{-5}
C15	2.00×10^{-6}	1.33×10^{-5}	5.76×10^{-6}	3.96×10^{-5}
C16	4.15×10^{-6}	6.90×10^{-5}	5.29×10^{-5}	9.55×10^{-4}
C18	2.23×10^{-6}	4.59×10^{-4}	1.59×10^{-5}	3.38×10^{-3}

*EUSES defaults modified according to the HERA Detergent Scenario

5. Human Health Assessment

[IN PROGRESS. CURRENTLY NOT INCLUDED]

6. References

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Appendix 1. Data for EUSES assessment

http://www.heraproject.com/files/AS_EUSES.zip

Appendix 2. Literature Search

A search of:

- BIOSIS Previews (1969-Present)
- CA SEARCH. Chemical Abstracts (1967-Present)
- TOXLINE
- Registry of Toxic Effects of Chemical Substances

was performed to supplement BUA (1996) and IUCLID. The search combined each of the following CAS numbers/chemical name descriptors with the toxicity/degradation terms:

CAS Number	CAS Description
139-96-8	Sulfuric acid, monododecyl ester, compd. w/ 2,2',2"-nitrilotriethanol (1:1)
142-31-4	sodium octyl sulphate
142-87-0	sodium decyl sulphate
151-21-3	Sulfuric acid, monododecyl ester sodium salt
1120-01-0	1-Hexadecanol, hydrogen sulfate, sodium salt
1120-04-3	Sulfuric acid, monooctadecyl ester, sodium salt
1191-50-0	1-Tetradecanol, hydrogen sulfate, sodium salt
2235-54-3	Sulfuric acid, monododecyl ester, ammonium salts
68081-96-9	Sulfuric acid, mono-C10-16-alkyl esters, ammonium salts
68081-98-1	Sulfuric acid, mono-C14-18-alkyl esters, sodium salts
68130-43-8	C8-18 alkyl sulfate, sodium salt
68140-10-3	Sulfuric acid, monotallow alkyl esters, sodium salts
68412-83-9	Sulfuric acid, mono-C8-30-alkyl esters, compds. with triethanolamine
68585-47-7	Sulfuric acid, mono-C10-16-alkyl esters, sodium salts
68611-55-2	Sulfuric acid, mono-C10-16-alkyl esters
68890-70-0	C12-15 alkyl sulfate, sodium salt
68955-19-1	Sulfuric acid, mono-C12-18-alkyl esters, sodium salts
68955-20-4	C16-18 alkyl sulfate, sodium salt
73296-89-6	C12-16 alkyl sulfate, sodium salt
85338-42-7	Sulfuric acid, mono-C8-10-alkyl esters, sodium salts
85586-07-8	C12-14 alkyl sulfate, sodium salt
85586-38-5	Sulfuric acid, mono-C8-18-alkyl esters, magnesium salts, compds. with triethanolamine
85665-45-8	Sulfuric acid, mono-C8-14-alkyl esters, compds. with triethanolamine
85681-68-1	Sulfuric acid, mono(C14-18 and C16-18-unsatd. alkyl) esters, sodium salts
86014-79-1	Sulfuric acid, mono-C13-15-alkyl esters, sodium salts
90583-10-1	Sulfuric acid, mono-C8-14-alkyl esters, ammonium salts
90583-12-3	Sulfuric acid, mono-C12-16-alkyl esters, ammonium salts

90583-13-4	Sulfuric acid, mono-C12-18-alkyl esters, ammonium salts
90583-16-7	Sulfuric acid, mono-C12-14-alkyl esters, compds. with ethanolamine
90583-18-9	Sulfuric acid, mono-C12-14-alkyl esters, compds. with triethanolamine
90583-19-0	Sulfuric acid, mono-C8-14-alkyl esters, lithium salts
90583-23-6	Sulfuric acid, mono-C12-14-alkyl esters, magnesium salts
90583-27-0	Sulfuric acid, mono-C8-16-alkyl esters, sodium salts
90583-31-6	Sulfuric acid, mono(C14-18 and C18-unsatd. alkyl) esters, sodium salts
91648-54-3	Sulfuric acid, mono-C14-C16-alkyl esters, sodium salts
91783-23-2	Sulfuric acid, mono-C12-C13-alkyl esters, sodium salts
92797-61-0	Sulfuric acid, mono(C13-15-branched and linear alkyl) esters, sodium salts
96690-75-4	Sulfuric acid, mono-C12-14-alkyl esters, ammonium salts, compds. with triethanolamine
117875-77-1	Sulfuric acid, mono-C10-16-alkyl esters, compds. with triethanolamine

alkyl sulfate alkyl sulphate alcohol sulfate alcohol sulphate

AND

terrestrial invertebrate Biodegrad*
ecotox* fish algae Bioaccum*
aquatic Daphnia Degradation

The search gave the following results (CAS #, number of records):

139968	7	85338427	0
142314	5	85586078	1
142870	11	85586385	0
151213	569	85665458	0
1120010	15	85681681	0
1120043	4	86014791	0
1191500	14	90583101	0
2235543	6	90583123	0
117875771	0	90583134	0
68081969	0	90583167	0
68081981	0	90583189	1
68130438	1	90583190	0
68140103	0	90583236	0
68412839	0	90583270	0
68585477	1	90583316	0
68611552	0	91648543	0
68890700	0	91783232	0
68955191	1	92797610	0
68955204	1	96690754	0
73296896	2		

The titles of the records were examined and the publication was acquired of any that were not included in BUA (1996) and appeared relevant.

APPENDIX 3. Physical Chemical Data

Chainlength : C12

Molecular weight	288.4	[g.mol-1]	
Melting point	205.5	[oC]	1
Boiling point	588.52	[oC]	SRC
Vapour pressure at 25 [oC]	6.27E-11	[Pa]	SRC
Octanol-water partition coefficient	1.6	[log10]	1,2
Water solubility	618.6 / 460	[mg.l-1]	SRC / 3

Chainlength : C13

Molecular weight	302.41	[g.mol-1]	
Melting point	259.37	[oC]	SRC
Boiling point	600.13	[oC]	SRC
Vapour pressure at 25 [oC]	2.68E-11	[Pa]	SRC
Octanol-water partition coefficient	2.18	[log10]	SRC
Water solubility	162.5	[mg.l-1]	SRC

Chainlength : C14

Molecular weight	316.4	[g.mol-1]	
Melting point	264.8	[oC]	SRC
Boiling point	611.7	[oC]	SRC
Vapour pressure at 25 [oC]	1.14E-11	[Pa]	SRC
Octanol-water partition coefficient	2.67	[log10]	SRC
Water solubility	5.13	[mg.l-1]	4

Chainlength : C15

Molecular weight	330.46	[g.mol-1]	
Melting point	270.21	[oC]	SRC
Boiling point	623.33	[oC]	SRC
Vapour pressure at 25 [oC]	4.80E-12	[Pa]	SRC
Octanol-water partition coefficient	3.17	[log10]	SRC
Water solubility	0.4	[mg.l-1]	4

Chainlength : C16

Molecular weight	344.49	[g.mol-1]	
Melting point	275.63	[oC]	SRC
Boiling point	634.94	[oC]	SRC
Vapour pressure at 25 [oC]	2.05E-12	[Pa]	SRC
Octanol-water partition coefficient	3.66	[log10]	SRC

Water solubility	0.08	[mg.l-1]	4

Chainlength : C18

Molecular weight	372.54	[g.mol-1]	
Melting point	212	[oC]	5
Boiling point	658.15	[oC]	SRC
Vapour pressure at 25 [oC]	3.67E-13	[Pa]	SRC
Octanol-water partition coefficient	4.64	[log10]	SRC
Water solubility	0.49 / insoluble	[mg.l-1]	SRC / 4

Data Sources:

SRC) SRC data are calculated by the EPIWIN programme, supplied by the Syracuse Research Corporation.

1) Verschueren, K., "Handbook of Environmental Data on Organic Chemicals", 2nd edition (1983), Van Nostrand Reinhold Company, 793.794

2) A. Leo et al., Chemical Reviews 71 (1971), 525.616

3) P&G, internal data

4) Dyer et al, 1997

5) Beilstein handbook