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**ENVIRONMENTAL RISK
CHARACTERIZATION OF 4 MAJOR
SURFACTANTS USED IN THE
NETHERLANDS**

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PREFACE

This report contains the results of environmental risk assessment carried out for 4 major surfactants. Framework of the report is the "Plan of Action Laundry and Cleaning Products for Households" agreed on between the Dutch Ministry of Housing, Physical Planning and Environment (VROM) and the Dutch Soap Association (NVZ) in 1990.

Results of the assessment have been extensively discussed first in a project-group consisting of J. de Bruijn (Ministry of Housing, Physical Planning and Environment), T. Feytel (Procter & Gamble), S. Marshall (Unilever), E. Matthijs (Procter & Gamble), E. v.d Plassche (National Institute of Public Health and Environmental Protection), R. Schröder (Henkel), R. Stephenson (Shell B.V.), and J. Struijs (National Institute of Public Health and Environmental Protection).

Thereafter results have been discussed in the Dutch Expert Group on Environmental Risks of Cleaning Products consisting of members of industry, government and scientific organizations.

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SUMMARY

An environmental risk assessment is carried out for 4 surfactants: LAS, AE, AES and soap. Framework of the report is the "Plan of Action Laundry and Cleaning Products for Households" agreed on between the Dutch Ministry of Housing, Physical Planning and Environment (VROM) and the Dutch Soap Association (NVZ) in 1990.

The assessment is based on data gathered from literature and evaluated by industry and on a monitoring programme on 7 representative locations in the Netherlands.

From the ratio between the MPC (Maximum Permissible Concentration) and the PEC (Predicted Environmental Concentration) it can be concluded that the risk for LAS, AE and AES is low: PEC/MPC ratios are less than 0.05. For soap the ratio is almost equal to 1. This means that there may be a risk due to soap for the aquatic environment. However, the MPC is based on acute toxicity data. Preliminary results of a chronic study with soap indicate that the toxicity of soap is similar to LAS, AE and AES. This means that the risk posed by soap is probably lower.

SAMENVATTING

In het kader van het in 1990 tussen VROM en NVZ overeengekomen "Plan van Aanpak Was- en Reinigingsmiddelen Huishoudelijk Gebruik" is een risico-evaluatie ten aanzien van het milieu uitgevoerd voor 4 detergenten: LAS, AE, AES en zeep.

De evaluatie is enerzijds gebaseerd op door de industrie verzamelde en geëvalueerde literatuurgegevens en anderzijds op een monitoring programma op 7 representatieve locaties in Nederland.

Uit de verhouding tussen het MTR (Maximaal Toelaatbaar Risiconivo) en de PEC (Predicted Environmental Concentration) kan geconcludeerd worden dat voor LAS, AE en AES het risico laag is: de PEC/MTR is kleiner dan $<0,05$ voor deze detergenten. Voor zeep is de PEC/MTR ratio ongeveer gelijk aan 1. Dit betekent dat er een mogelijk risico is voor het aquatisch milieu. De MTR is echter gebaseerd op acute gegevens. Voorlopige resultaten van een chronische studie met zeep geven aan dat de toxiciteit van zeep vergelijkbaar is met LAS, AE en AES. Dit betekent dat het risico van zeep waarschijnlijk lager is.

1. CHAPTER 1: Introduction.

The Dutch Soap Association (NVZ) and the Dutch Environmental Ministry (VROM) agreed in 1990 on a Voluntary Plan of Action for the next 10 years concerning detergents and the environment. The goal of the Ministry was to formulate a plan to evaluate and potentially reduce the environmental burden of detergent and cleaning products taking into account minimum hygiene needs.

The total consumption of detergent and cleaning products in the Netherlands which accounts for 330,000 tonnes yr⁻¹ (or 23 kg capita⁻¹ year⁻¹) was inventorized per individual ingredient. A priority list of all detergent ingredients (i.e. > 100 tonnes yr⁻¹) was developed in 1991 by the NVZ/RIVM based on aquatic hazard. Removal and ecotoxicity data have been taken from a report written by the "Hauptausschuss Detergentien" or Standing Committee on Detergents, which has been published by Schoerberl et al. in *Tenside Detergents* (1988), and from the AIS/CESIO task force "Ecotoxicity Data for Surfactants." Assuming a dilution factor of 10, the NVZ experts prioritized detergent ingredients on the basis of a PEC/LC50_{fish}. VROM and RIVM (National Institute of Public Health and Environmental Protection) agreed with the priority list as presented in Table 1 and suggested that a risk assessment methodology should be agreed before initiating the assessment of all four ingredients.

Table 1: Ranking on the basis of PEC/LC50 or acute assessment factors.

Ingredient	Tonnage-1991 tonnes/yr	Removal %	LC50 mg/L	PEC/LC50 * 10 ⁻³
LAS	16,154	95 (93 - 97)	4 (3.2 - 9.2)	15.5 (4.0 - 27)
AE	8,934	95 (93 - 98)	4 (0.6 - 460)	8.6 (0.03 - 77)
AES	3,798	96 (95 - 97)	4 (1.4 - 20)	2.9 (0.44 - 10)
SOAP	13,187	95 (94 - 96)	20 (6.7 - 150)	2.5 (0.27- 9)

A Risk Assessment workshop was organized on April 9th 1992 by NVZ, VROM and RIVM resulting in an agreed step-wise framework for the risk assessment of the priority surfactants. The stepwise or tiered PEC/PNEC approach - as described in the workshop proceedings - was adopted as the recommended approach. This implies that depending on the PEC/PNEC ratio, the sequential test program or assessment would proceed further, to ensure adequate protection of the ecosystem. The hierarchy in this tiered approach is data-driven, and ensures that higher quality data are used beyond the so-called base-set data and computer predictions.

An industry task force was created to initiate a joint project with an independent Consulting Bureau (BKH) to compile and review all existing environmental data on all priority surfactants. The member companies are AKZO-Nobel, BASF, Colgate, Condea, Enichem Augusta, Henkel, Hoechst, Huls, ICI, Unilever, Monsanto, Petresa,

Procter & Gamble, Shell, Vista, and Zeneca. BKH collected all available acute, subchronic, and chronic ecotoxicological Company data for LAS, AE, AES, and SOAP. All data were critically reviewed by company experts and BKH to present a rationale for a sound database for the derivation of a Maximum Permissible Concentration. In addition, BKH compiled all existing studies on sorption characteristics (sludge, sediment, soil); removal during sewage treatment (OECD confirmatory/monitoring BiAS and/or specific analyses), and environmental surface water monitoring studies (BiAS; specific analyses). These reports were the basis for this exercise and are published as separate background documents.

A joint monitoring programme was initiated with the co-operation of the Institute for Inland Water Management and Waste Water (RIZA), the University of Amsterdam (UvA), National Institute of Public Health and Environmental Protection (RIVM), and the Dutch Soap Association (NVZ). The pilot phase of the monitoring programme was initiated (1) to optimize sampling parameters and sampling statistics and (2) to examine if the monitoring protocol would be suited for future studies. The first phase focused on linear alkylbenzene sulfonate (LAS) and was executed at one pilot location i.e. "de Meern", a municipal sewage treatment plant discharging in the river "Leidsche Rijn". The second phase of the monitoring programme included besides LAS, also alcohol ethoxylates (AE), alcohol ethoxylated sulfates (AES), and soap. This programme was executed at seven representative municipal sewage treatment plants across The Netherlands, as chosen by the Institute for Inland Water Management and Waste Water (RIZA). The plants were selected on the basis of treatment type, ratio of domestic input versus industrial input, organic loading, capacity as well as logistic considerations. Results of this exercise are published as a separate background document.

Scientific and expert evaluation was judged essential at the comprehensive risk assessment stage, by both industry and RIVM/VRM. Regular communication between both parties has really contributed to the scientific quality and consensus of the risk assessment of all four priority chemicals.

2. CHAPTER 2: Derivation of 90th Percentile Concentration of Surfactants at 1000 meter below the sewage outfall.

2.1. Release Estimation.

The release(s) of substances will depend upon the industrial category and use patterns of the different products/articles containing the substance under consideration (EEC 1993, 1994a, 1994b; ECETOC 1993). The HEDSET (Harmonized Electronic Data Set) distinguishes 3 types of categories, i.e. main category, industrial category and use category (EEC, 1994b). The release of surfactants used in household detergents and cleaners has been described by the AIS and was included by the European Commission as "Use Category Document" in the Environmental Risk Assessment Technical Guidance Document for New Substances (EEC 1994b). For surfactants the categorization of the release is as follows:

Main category = IV or Wide Dispersive Use
Industrial category = 6 or public domain
Use category = 9 or cleaning and washing agents

The release or emission algorithm assumes that 100% of the release occurs at the use phase, with no significant loss at the production, compounding or processing stage.

The wastewater treatment system in The Netherlands covers about 14.8 million inhabitants and 9 million industrial equivalents or a total of 23 million equivalents. About 2% of this total capacity is treated mechanically, 7% is treated by trickling filters, and 91% is treated by activated sludge systems (RIZA, 1989a, 1989b). In the present document, it is assumed that all chemical substances which enter the waste water stream will pass through a waste water treatment plant before being discharged into the environment. Given the present situation in The Netherlands and the rapidly evolving situation in the European Union this assessment is seen as representative and conforms to the EC Technical Guidance Documents (EEC, 1994b). Article 4 of Council Directive 91/271/EEC concerning urban waste water treatment requires Member States, before 31 December 2000, to ensure that urban waste water discharged from agglomerations of more than 15000 population equivalents shall be subject to secondary treatment before being discharged to the environment (EEC, 1991). The assessment proposed below for the exposure assessment of detergent chemicals only considers discharge to the environment via biological sewage treatment processes as agreed among stakeholders (RIVM/VROM/NVZ workshop, 1991) and as specified in the EC Technical Guidance Document (Figure 1).

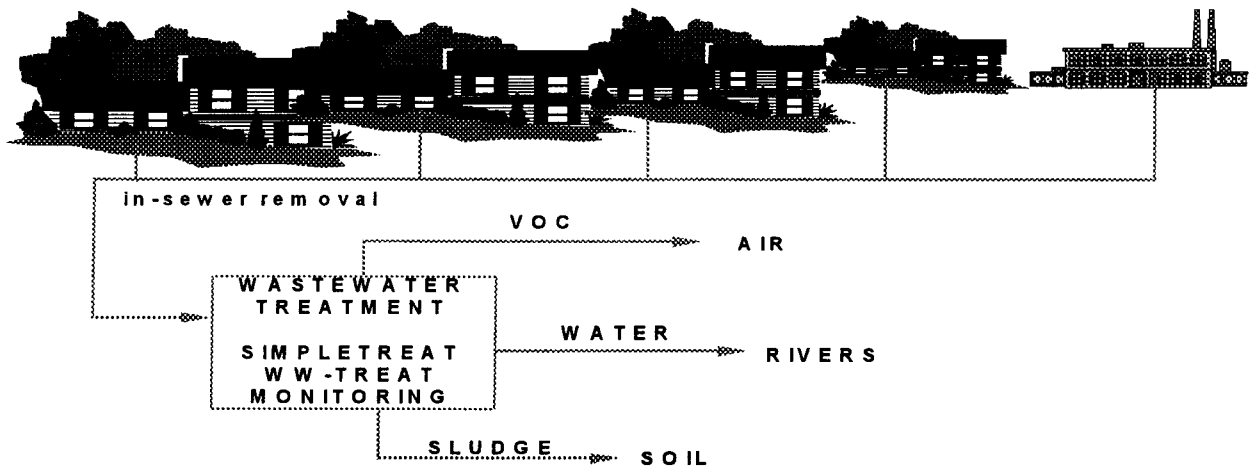


Figure 1: Representation of discharge scenario for detergent chemicals

2.2. Prediction of Concentrations in Raw Sewage.

The concentration in raw sewage, C_i , of a detergent ingredient can be estimated by:

$$C_i = X / (Y \cdot Q)$$

- C_i = concentration in influent wastewater (mg/L)
- X = detergent ingredient consumption on the market (mg/day)
- Y = population of market area (number of people)
- Q = per capita wastewater flow rate (L/capita * day)

In The Netherlands, having a population of 15.4 million people, the use of detergents and detergent ingredients is well documented (NVZ, 1994a). The emission of detergent and cleaning products/chemicals over the last decades has been compiled by the European Detergent Industry. This shows that within the last 2 decades the surfactant consumption has dropped from 65 grams/wash to less than 20 grams/wash. In addition, the total chemical use for laundry washing has significantly decreased from about 200 grams/wash to less than 100 grams/wash in compact powders (NVZ, 1994b).

Similar trends have been observed over the last 4 years where the consumption of major anionic surfactants decreased up to 15%. Figure 2 illustrates this for the combined consumption of surfactants (tonnes/yr) in household, industrial and institutional products (cleaners and detergents combined).

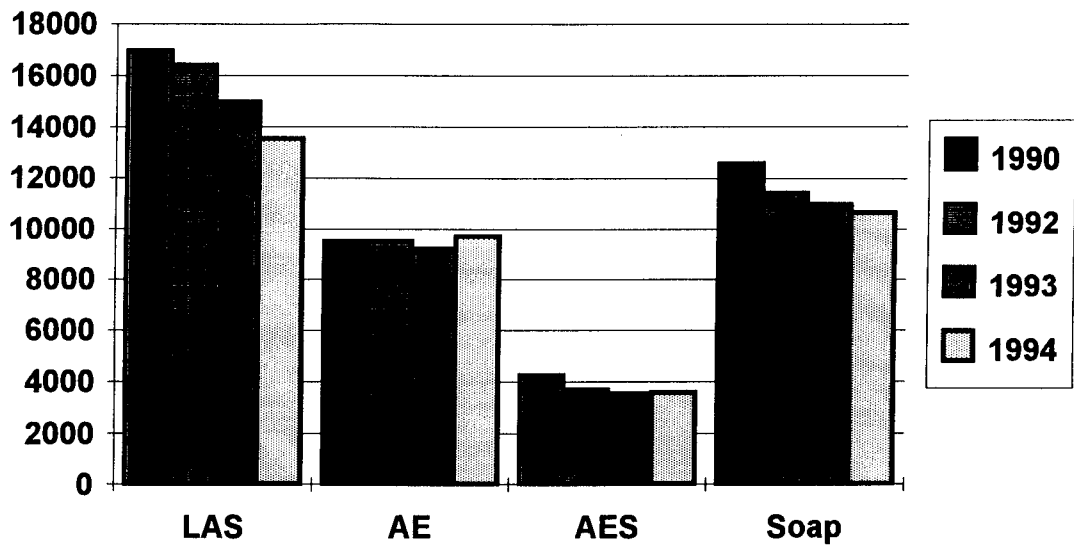


Figure 2: Consumption of priority surfactants (tonnes/yr) on Dutch Market

This allows a direct calculation of the quantity of detergent ingredient consumed in 1994 per person per day:

LAS

Main use LAS: Laundry Detergent Surfactant

The Netherlands = 13 550 tonnes

Per capita consumption: 0.915 kg/cap.year or 2.51 g/cap.day

AE

Main use: Laundry Detergent Surfactant

The Netherlands = 9 703 tonnes

Per capita consumption: 0.656 kg/cap.year or 1.80 g/cap.day

AES

Main use: Laundry Detergent Surfactant

The Netherlands = 3 587 tonnes

Per capita consumption: 0.242 kg/cap.year or 0.664 g/cap.day

SOAP

Main use: Laundry Detergent Surfactant

The Netherlands = 10 675 tonnes

Per capita consumption: 0.721 kg/year or 1.98 g/cap.day

The Central Bureau of Statistics (CBS, 1990) has listed per capita wastewater flow rates (Q), calculated from measured flow rates for each treatment plants and the population it served (RIVM/VROM/NVZ Proceedings, 1991). The median Q ranges from 252 to 347 L/capita*day, depending on the size of treatment plant (CBS, 1990). Larger treatment plants have lower per capita wastewater flow rates than smaller

plants. However, as agreed at the AIS workshop, and specified in EC Technical Guidance Documents, the raw sewage concentrations were calculated using a flow of 200 L/capita*day (Table 1).

Table 1: Raw wastewater concentrations for LAS, AE, AES, and SOAP.

	Tonnage total ton/yr	Raw Wastewater mg/l
LAS	13 550	12.5
AE TOTAL	9 703	9.0
AES	3 587	3.3
SOAP	10 675	9.9

The pilot study in The Netherlands (Feijtel et al. 1994) indicated that using dry weather sewage flows of 200 L/capita.day - predicted boron concentrations were in good agreement with measured dry weather boron concentrations (Table 2). However, measured LAS concentrations in raw sewage (3.0 - 7.5 mg/L) were found to be significantly lower than what was predicted on the basis of the annual LAS consumption data. The hydraulic residence time in most Dutch sewers exceeds 24 hours (RIZA, 1993), due to the low gradient (i.e. flow) and presence of several in-line storm tanks before arrival at the sewage treatment plant. Although it may be expected that certain parts of the sewer will be anaerobic, between 40 to 60% of the LAS load has been removed/biodegraded in the sewers and/or in the in-line storm tanks. In view of (1) the lack of LAS biodegradation under strictly anaerobic conditions and (2) rapid aerobic biodegradation in activated sludge and rivers, it can be postulated that aerobic biodegradation - possibly in micro-sites - is the main removal process. Similar observations on the rapid biodegradation of LAS in raw sewage were made by Matthijs et al. (1994) and Moreno et al. (1990).

Table 2: Predicted and measured raw sewage concentrations for LAS and perborates.

	1992 -Tonnage ton/yr	Predicted dry weather mg/l	Measured dry weather mg/L	Measured rainy day mg/L
LAS	16 500	15.9	7.5	3.0
Perborate (NaBO ₃)	7 456	0.9	0.9	0.25

2.3. Definition of Commercial Product.

The commercial surfactant is generally a mixture of various alkyl homologs and/or isomers. In view of differences in fate and effects of alkyl homologs, isomers and/or congeners, it is deemed necessary to define the commercial product. For linear alkyl benzene sulfonate, the alkyl chain distribution ranges from C-10 to C-13 (Table 3)

with different phenyl distributions according to production process (Table 4). Knowledge of the relative importance of each process, allows the calculation of so-called commercial LAS - with its typical mean alkyl chain length of 11.6 and typical isomer distribution.

Table 3: Range and typical homolog distribution of LAB/LAS.

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

Table 4: Typical phenyl position distribution of LAB/LAS

Process	2-phenyl	3-phenyl	4-phenyl	5-phenyl	6-phenyl
HF (%)	18	16	17	24	25
AlCl3 (%)	28	19	17	18	18

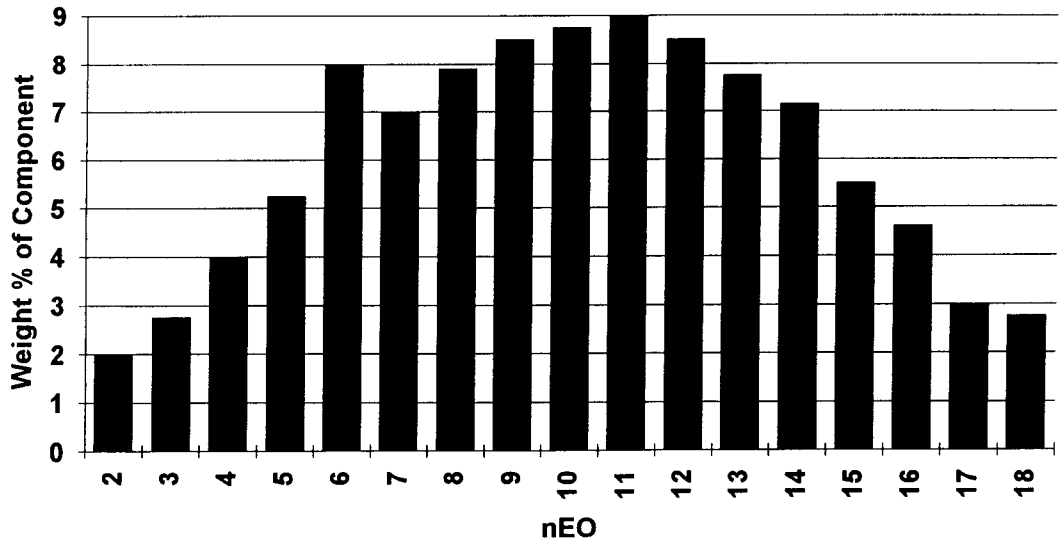
For alcohol ethoxylates (AE), the majority of products have an alcohol chain length between C9 and C18, and an ethoxylate chain length of 3 to 15 units (Table 5). The most common range of alkyl chain length is 12-15, whereas the ethylene oxide chain varies typically from 3 to 10. The proposed C12-C15/EO3-EO10 split represents the bulk part of NVZ inventory list (Table 5). Figure 2 represents the EO distribution of one commercial blend.

Table 5: Range of homolog and EO distribution of AEs

	Class- 1 < C12 EOx	Class-2 C12 - C15 EO3- EO10*	Class-3 > C15 EOy
Range (%)	10 - 30	60 - 80	5 - 15
Typical (%)	20	70	10

* Mean distribution - monitoring results may allow further refinement

Figure 2: Typical EO distribution in commercial AE blend



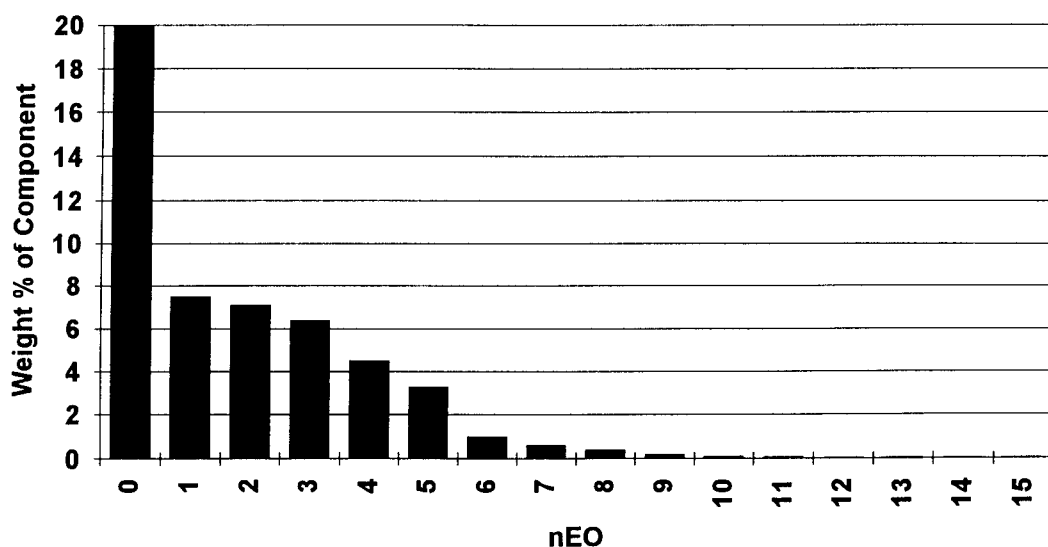
Alkyl ether sulphates are primary sulphate esters derived from alkyl ethoxylates. For alkyl ether sulfates (AES) - the majority of products have an alkyl chain length between 12 and 15C atoms, whereas the mean ethoxylate chain length varies between 0.5 and 4 (Figure 3). The proposed C12-C15/EO.5-EO4/S represents the bulk part of NVZ inventory list. Since it is expected that considerable amounts remain unethoxylated, it will be important to evaluate the mean EO chain length of AES in the environment.

Table 6: Range of homolog and EO distribution of AES

	C12 - C15 EO 0.5- EO 4*
Range (%)	90-100

* Mean distribution - monitoring results may allow further refinement

Figure 3: Typical EO distribution in commercial AES blend



Soap can be regarded as an anionic surfactant - normally produced from natural oils and fats, which are predominantly glyceride esters of fatty acids and which are typically hydrolyzed under alkaline conditions to fatty acids and glycerol. The most common fatty acids contain 12 to 18 carbon atoms (Table 7). A variable fraction of fatty acids is unsaturated with one or more double bonds.

Table 7: Range of homolog distribution of soap

	Class- 1 < C12	Class-2 C12 - C18	Class-3 > C18
Range (%)	<5	70 - 100	<5
Typical (%)	?	> 90 %	?

2.4. Removal during Sewage Treatment.

The scheme proposed below only considers discharge to the environment via primary and/or biological sewage treatment processes (Figure 3).

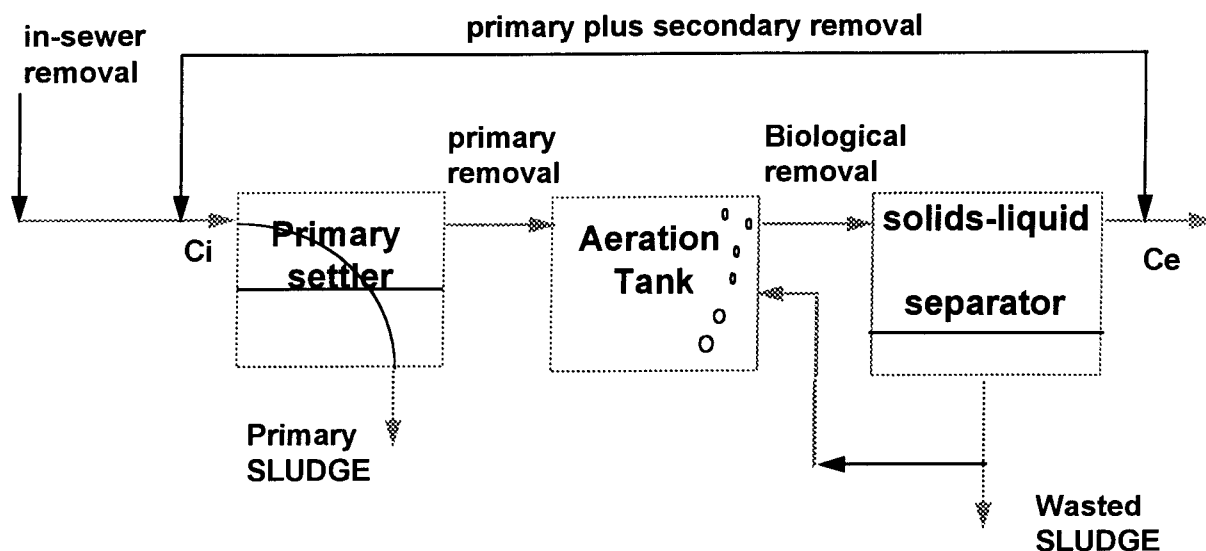


Figure 3: Schematic representation of wastewater treatment plants with primary and secondary removal.

According to the Technical Guidance Documents (EEC 1993), wastewater treatment plant (WWTP) models can be used to estimate removal on the basis of "EC base set" data. This implies that for new chemicals and for numerous existing chemicals, for which neither laboratory simulation tests of removability nor monitoring data are available, a calculation method can be used for estimating elimination during treatment.

SIMPLETREAT and WWTREAT are two environmental fate models developed to predict the emission of chemicals in conventional activated sludge wastewater treatment plants. Both WWTP models were used in a step-wise refinement using experimental data where available, and actual operating conditions in WWTREAT. In addition, WWTREAT has been verified to a limited extent for detergent chemicals (Cowan et al. 1993).

The standard output of both models shows the chemical's concentration in effluent and sludge, and indicates the relative amounts degraded and emitted via effluent, sludge and air. Both models use similar description of sorption and volatilization.

2.4.1. SIMPLETREAT.

SIMPLETREAT (Struijs et al. 1991) was developed as a box model to assess the probable fate of the chemical on the basis of the so-called base-set data as requested by the EEC upon the notification of new chemicals. SIMPLETREAT can be used as a diagnostic tool, providing regulatory authorities with a quick impression of the emission patterns of a chemical in a municipal wastewater treatment plant. It requires a minimum data input to calculate air-water and sludge solids-water partition coefficients. Distribution coefficients are calculated from solubility, vapor pressure, and octanol-water partition coefficients, or actual measured partition coefficients can

be entered. Biodegradability data and the degree of dissociation or protonation are the required input data to account for degradation and speciation changes of the chemical in the water phase. The biodegradation rate constant used in SIMPLETREAT is either 'zero' for non-biodegradable chemicals or 3 h^{-1} in the aqueous phase of activated sludge, if the chemical passes one of the stringent OECD tests for 'ready biodegradability' (OECD, 1981). The plant operating conditions are preset on high, medium and low sludge loading conditions, representing the more conservative or worst case treatment conditions for The Netherlands (Table 8).

Table 8: Operating Conditions of Dutch Wastewater Treatment Plants (CBS, 1988) versus SIMPLETREAT (Struijs et al. 1991)

DUTCH WASTEWATER TREATMENT PLANTS					
	MLSS (mg/l)	SRT (day)	HRT (hour)	Sludge Loading (kg BOD/kg SS.day)	Capacity* % total
Aeration Tank	3.8	12	>10	0.16	39.5
Carrousel	3.6	24	>24	0.05	19.0
Two Step 1st	(3.3)	(6)	(10)	(0.98)	
2nd	3.9	18	>10	0.11	15.7
Oxidation Tank	3.7	22	>24	0.06	4.7
Oxidation Ditch	3.6	22	>24	0.07	4.1

* Total Capacity = 23,786,000 equivalents

SIMPLETREAT

	MLSS (mg/l)	SRT (day)	HRT (hour)	Sludge Loading (kg BOD/kg SS.day)
High Loading	-	0.5	1.0	2.0
Medium Loading	-	1.7	3.1	0.6
Low Loading	-	5.5	10.2	0.18

SIMPLETREAT was run at screening level with the average physico-chemical properties and biodegradation data for commercial LAS, AE, AES, and soap (BKH report, 1994) (Table 9). The default rate constant was set on 3 h^{-1} or 72 d^{-1} because all surfactants are readily biodegradable, according to the OECD test system (OECD, 1981). In addition, it should be pointed out that the low loaded scenario was chosen to evaluate the removal of all 4 priority surfactants, since these operating conditions reflect most closely the actual operating conditions for The Netherlands (Table 8).

Table 9: Input data

Surfactant	Distribution Coefficient (L/Kg)	Henry's Law Constant (Pa m ³ /mol)	Readily Biodegradable
LAS	3500	< 10 ⁻¹⁰	yes
AE	1500	< 10 ⁻¹⁰	yes
AES	1000	< 10 ⁻¹⁰	yes
SOAP	10,000	< 10 ⁻¹⁰	yes

Table 10: Output data - Distribution and Fate under low loading conditions (SRT = 5.5 days and HRT = 10.2 hours)

Surfactant	% Sludge	% Degraded	% Effluent	% Removal
LAS	43.8	54.1	2.1	97.9
AE	29	68.6	2.4	97.6
AES	22.5	75.0	2.5	97.5
SOAP	59.4	38.5	2.1	97.9

Prediction of Effluent Concentrations:

Effluent concentration, C_e , can be calculated from the influent concentration, C_i , and the fraction removed, R , for each treatment type and/or specific site, using the following equation:

$$C_e = C_i * (1-R)$$

Table 11: Raw sewage, and Predicted Effluent concentrations for LAS, AE, AES, and SOAP.

	Raw Sewage mg/l	Removal %	Effluent mg/l	Sludge (g/kg)
LAS	12.5	97.9	0.262	481
AE TOTAL	9.0	97.6	0.216	182
AES	3.3	97.5	0.082	45
SOAP	9.9	97.9	0.208	560

2.4.2. WWTREAT.

WWTREAT model (Cowan et al., 1993) was developed to predict the degree of removal and distribution of consumer product chemicals among air, treated liquid effluent, and sludge for primary and activated sludge waste water treatment plants using independently determined distribution coefficients and biodegradation rate constants. The major difference between this model and previous models (Namkung and Rittman, 1987; Struijs et al. 1991) based on removal of BOD is that it assumes that the total chemical and not just the dissolved fraction is available for biodegradation (e.g. Shimp et al. 1988).

The rate constants used are experimentally determined in a batch activated sludge (BAS) system with a solids concentration of 2500 mg/L, and initial realistic chemical concentration of 0.01 to 0.1 mg/L, following a method similar to that described by Games et al. (1982). The rate constant, k , for the dissolved and sorbed chemical is assumed to be the same and equal to the overall rate constant measured in the BAS system. The chemical specific rate constant -preferably determined using specific analytical methodology - as determined in the BAS system will be used as input parameter in the model. At Base-set level, however, these biodegradation rate data will be lacking and limited to screening biodegradability test data. Refined laboratory simulation tests will frequently be required to assess the primary biodegradability of the ingredient during the sewage treatment and to determine its fate (e.g. sorption, biodegradation and volatilization). At this stage mathematical model predictions can be verified and refined to estimate the predicted removal efficiency.

Currently, suitable methods exist for simulating the principal processes in activated sludge sewage treatment plants in the laboratory. Provided specific analytical methods for the chemical or carbon-14 labelled samples are available, much of the above predicted data can be experimentally obtained and verified. The data can then be used directly to predict levels of the test material in the receiving environments with reasonable precision although some loss of realism may occur if synthetic wastewater is used in place of domestic sewage.

At present time, validation work is being performed and until this has been completed the reliability and limitations of the models cannot be considered to have been established. However, with some provisions WWTREAT can be used to get a better insight in the possible differences between the fate and distribution of homologues and/or isomers.

Since WWTREAT can accommodate experimentally determined biodegradation rate constants, and since all plant operating conditions can be independently changed to simulate any specific plant, the model will be used to compare with actual monitoring data in this exercise. In addition, issues surrounding the variability of input parameters (deterministic error), structure of the model (inherent error), and variability of environmental characteristics (stochastic error) and its influence on model output endpoints can be answered at this stage. Specifically, information on

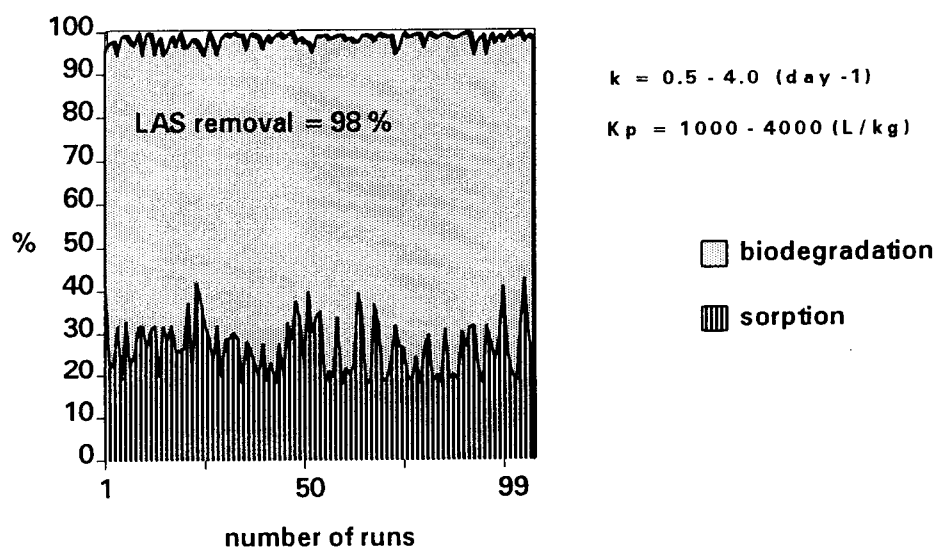
model output sensitivity is gathered for the specific chemical of interest by varying input model parameters and/or operating conditions (Table 12). The output of this Monte Carlo simulation is given in Figure 4.

Table 12: Input data range for LAS in WWTREAT sensitivity analysis

Distribution Coefficient (L/Kg)	Henry's Law Constant (Pa m ³ /mol)	Measured Biodegradation Rate Constant (d ⁻¹)
1000 - 4000	< 10 ⁻¹⁰	0.5 - 4.0

The relative importance of sorption and biodegradation processes is affected by the combination of chemical properties of the material i.e. input data. The experimentally derived input data are the most reliable source of the sorption and rate data for LAS. Examples of the use of laboratory data to parameterize fate models are numerous. For example, Holysh et al. (1986) used laboratory and field data to parameterize Mackay fugacity models for the surfactant LAS. This evaluative sensitivity analysis indicates that WWTREAT predicts an average LAS removal of 98.0 ± 1.7 % for the specified range in Table 12.

Figure 4: Two-parameter sensitivity analysis of WWTREAT for LAS



Similarly, WWTREAT model can be used to predict average AE, AES, and soap removal at screening level. The proposed range of biodegradation and sorption data (Table 13) reflect 1/ actual experimental data, and 2/ expert judgement.

Table 13: Input parameters for AE, AES, and soap used for WWTREAT

Surfactant	AE Mix	AES Mix	Soap Mix
SOL (MG/L)	1	1	1
k (d-1)	0.5 - 4	0.5 - 4	0.5 - 4
Kp (L/kg)	1000 - 3000	1000 - 3000	10 000 - 30 000

Predicted average removal for AE and AES is 98.0 ± 1.2 %. Predicted removal of soap is estimated at 99.0 ± 0.8 % (Table 14). These mean values and standard deviations were obtained in a similar manner than for LAS. An evaluative sensitivity analysis using the sorption and biodegradation constants from Table 13 was performed using a Monte Carlo procedure. The removal figures from Table 14 indicate that the removal of all 4 surfactants are not significantly different, using the specified input and within the limitations of the model.

Table 14: Predicted raw sewage and effluent concentrations for LAS, AE, AES, and SOAP.

	Raw Sewage mg/l	Mean WWTP Removal \pm SD %	WWTP Effluent mg/l (range)
LAS	12.5	98.0 ± 1.7	0.009 - 0.259
AE	9.0	98.0 ± 1.2	0.008 - 0.096
AES	3.3	98.0 ± 1.2	0.004 - 0.064
SOAP	9.9	99.0 ± 0.8	0.020 - 0.178

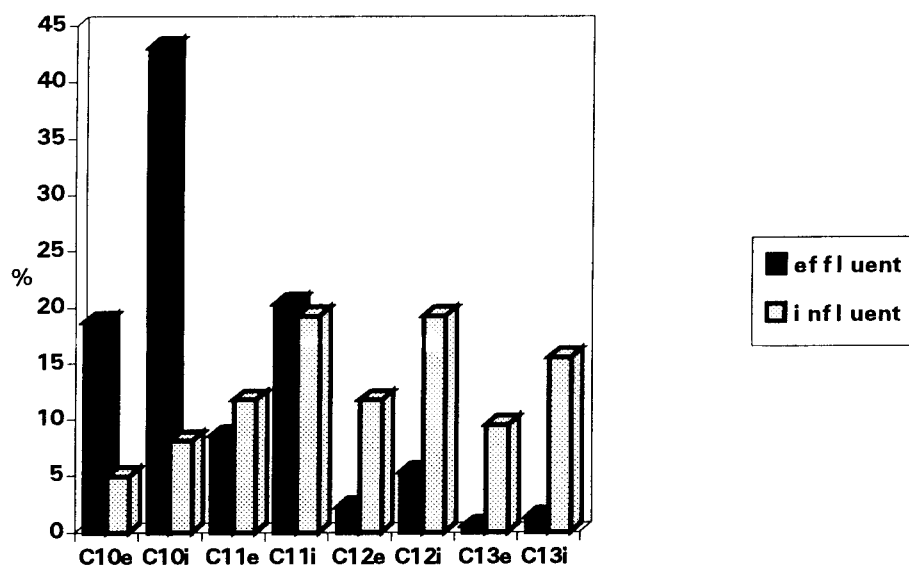
Due to preferential degradation and/or sorption, the relative distribution in effluent - as compared to influent - shifts to a lower predicted average alkyl chain length, with higher relative content of internal isomers (Figure 5). Input parameters of LAS isomers/homologs are given in Table 15.

Table 15: Input parameters of LAS used for WWTREAT*

LAS-homolog isomers	C10 ext	C10 int	C11 ext	C11 int	C12 ext	C12 int	C13 ext	C13 int
Typical %	4.9	8.1	11.7	19.3	11.7	19.3	9.5	15.5
i.e 70% HF	4.4	8.6	10.5	20.5	10.5	20.5	8.5	16.5
30% AlCl3	6.1	6.9	14.6	16.4	14.6	16.4	11.8	13.3
MW	320	320	334	334	348	348	362	362
SOL (MG/L)	20	20	15	15	10	10	5	5
k (d-1)*	2.0	1.33	2.60	1.73	3.38	2.25	4.39	2.93
Kp (L/kg)**	220	220	1000	1000	3070	3070	9330	9330
LOG Kp	2.3	2.3	3.0	3.0	3.5	3.5	4.0	4.0

- * Expert Judgement - Distance principle (LAS BKH report, 1994; Larson et al. 1993)
 - 30% increase in primary biodegradation rate per alkyl chain unit
 - 50% increase in primary biodegradation rate for external phenyl isomers
- ** Experimentally derived (Games et al. 1982)

Figure 5: Relative predicted alkyl homolog and isomer distribution in influent and effluent



* : i = internal isomers; e = external isomers

Results are presented in Table 17. Table 17 illustrates that a relative enrichment of higher alkyl homologs occurs for the sludge compartment. This is in contrast to the shift in alkyl chain length that occurs in for the effluent.

Table 17: Sewage Treatment Removal Efficiency of LAS (Predicted with WWTREAT)

		Removal Sorption		Biodegradation
		%	%	%
LAS	C10 - ext	91.2	9	83
	C10 - int	85.8	10	77
	C11 - ext	98.3	19	80
	C11 - int	97.5	20	77
	C12 - ext	99.6	34	66
	C12 - int	99.4	35	64
	C13 - ext	99.9	50	50
	C13 - int	99.8	51	49

Table 18: Predicted LAS effluent concentration (ug/L).

LAS	C10- ex	C10- in	C11- ex	C11- in	C12- ex	C12- in	C13- ex	C13- in	Total
dissolved	53	123	23	54	5	12	1	2	272
sorbed	1	3	2	6	2	4	1	2	20

The total LAS concentration leaving the plant is 292 ug/L, which corresponds with an overall predicted removal of 98%. Assuming a suspended solids concentrations of 10 mg/L in effluent and a solids/water partition coefficient of 1000 L/kg, only 6.8% of the total LAS concentration is predicted to be associated with the suspended solids. Association with DOC, rather than adsorption to suspended solids is the driving force in determining bioavailability (Traina et al. 1994). The log K_{OC} for the association of C12 LAS with DOC was reported as 4.83. Therefore at a DOC concentration of 15 mg/L approximately 50% of the total LAS will be associated with organic carbon, mainly humic acids (Traina et al. 1994).

2.5. Predicted Concentration in Surface Waters.

Dilution factors are often unknown for each situation (variability in space and time) and an arbitrary but realistic dilution factor (e.g. 5, 10, 30) is often assumed to estimate the concentration of a substance in a river receiving wastewater treatment plant effluent:

$$C_{sw} = \frac{C_e}{SDF}$$

where C_{sw} = total concentration of substance in surface water immediately below the outfall of a wastewater treatment plant (mg/L)

C_e = concentration of the substance in sewage effluent (mg/L)

SDF = stream dilution factor, which equals the stream flow + effluent flow rate at the plant site divided by the effluent discharge rate

Dilution factors for the discharge of all municipal wastewater treatment plants in The Netherlands have been reported (de Greef and de Nijs, 1990). The 10th, 50th, or 90th percentile dilution factor can be calculated as respectively SDF=3, SDF=32, and SDF=1740 at 1000m below the sewage outfall. To determine the dilution factor by treatment type, this dilution database can be linked to another sewage database (National Institute of Inland Water and Waste Water Management, RIZA, 1989) which lists the type of wastewater treatment applied, the number of inhabitants and the industrial equivalents served by each wastewater treatment plant. This linked database is referred to as the Generic Dutch Model (GDM).

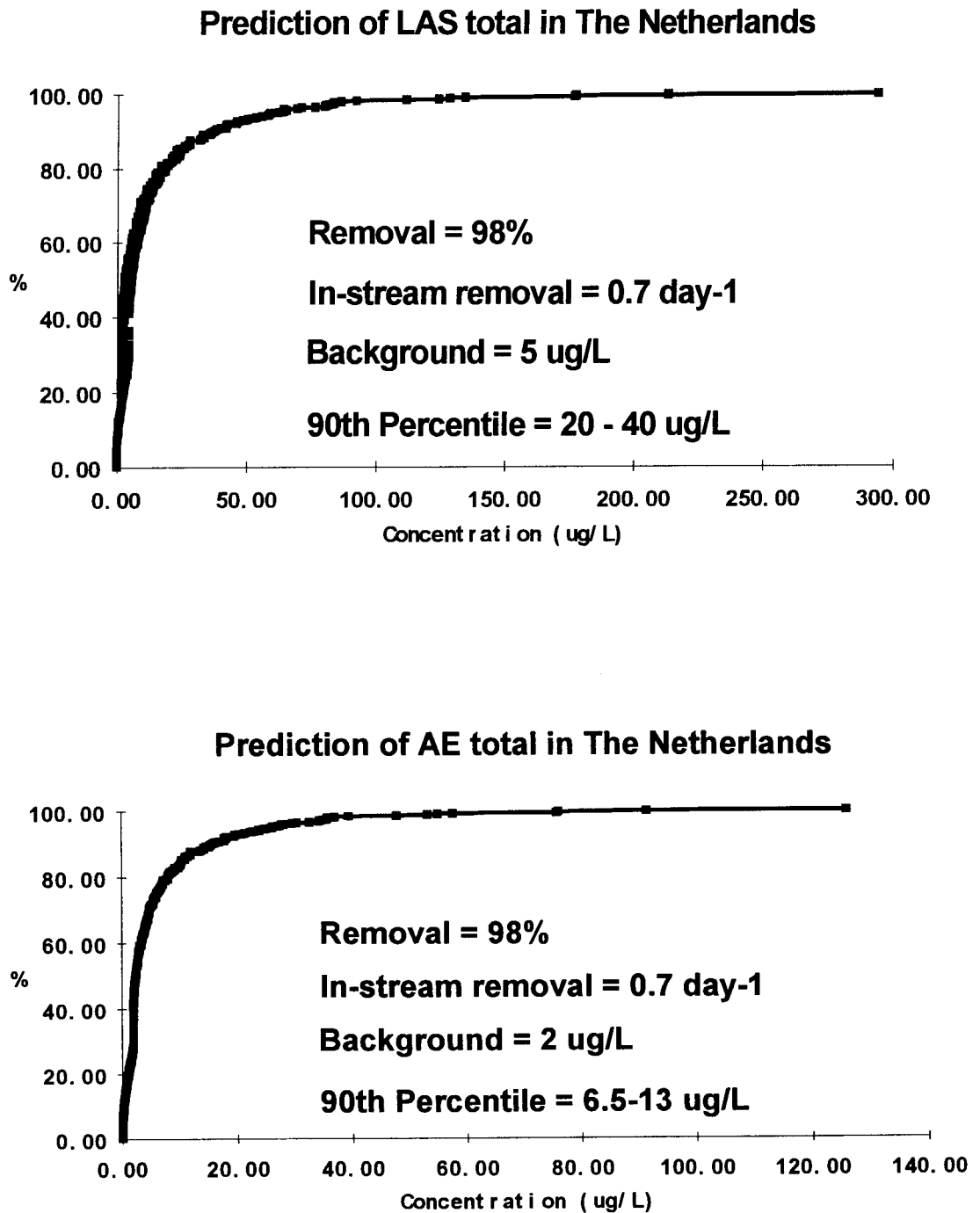
The predicted surface water concentrations are based on mass inputs and do not account for in-stream sorption, complexation, or degradation, nor for the presence of upstream background concentrations. Therefore, further refinement was introduced to account for in-stream removal and background concentrations. In-stream processes can be expected to result in significant changes in concentration and/or in substance form, distribution, and bioavailability. In-stream removal data for detergent ingredients have indicated that removal rates range from 0.5 - 1 day⁻¹ (Versteeg et al. 1992, Hennes and Rapaport, 1989). An in-stream loss rate of 0.7 day⁻¹ for surfactants, similar to instream BOD removal rates, might be used for a first evaluation. Similarly, background concentrations can be entered in the Generic Dutch Model to account for up-stream inputs (Figure 6). These background levels are based on expert judgement.

By using the dilution database, and linking each site to WWTREAT output, a first estimate can be obtained about the predicted 90th percentile of total surfacant concentration (ug/L) at 1000m below the sewage outfall (Table 18). The 90th percentile PEC of a ready biodegradable surfacant at 1000m below the sewage outfall can be calculated with different in-stream removal rates and compared to a worst-case situation where no in-stream removal took place. The proposed rates are respectively 0.70 d-1 ex. BKH report and 0.14 d-1 ex. USES (WVC, 1994). In addition, it is likely that in-sewer removal will be observed for all surfactants, since the rate of primary biodegradation of AE, AES, and soap is comparable to that of LAS (Matthijs et al. 1994). Matthijs et al. (1994) reported half-lives of respectively 3 and 4 hours for the primary biodegradation of AE and AES in raw sewage. Although actual raw sewage influent concentrations for LAS, AE, AES and soap will depend on the residence time in the sewer, it is very likely that the average raw sewage concentrations in most WWTP influents will be a factor 2 to 4 lower than the calculated values presented in Table 1. Therefore, two scenarios are proposed to account for in-sewer removal - i.e. 0 and 50% in-sewer removal. Results are presented in Table 18.

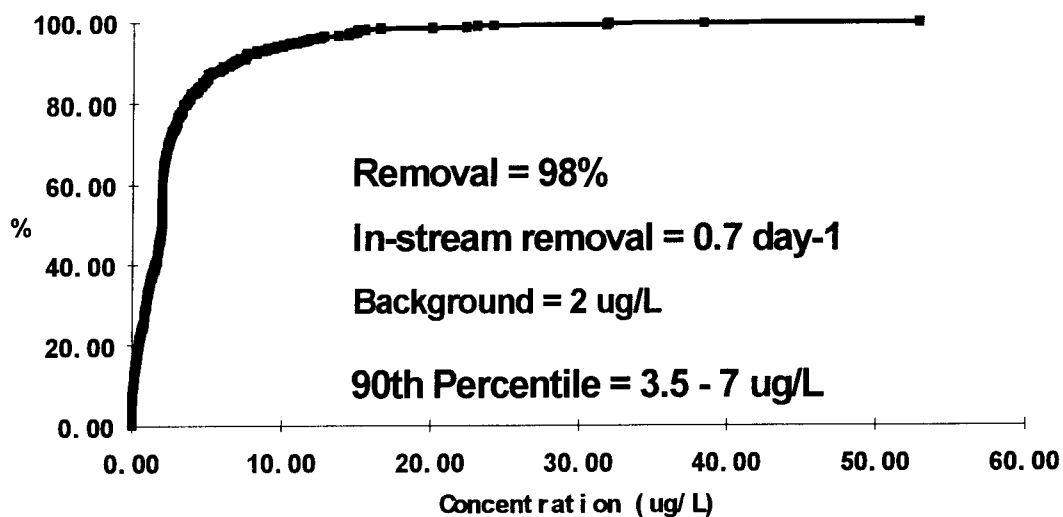
Table 18: Predicted 90th percentile of total surfacant concentration (ug/L) at 1000m below the sewage outfall for different in-sewer removal rate and instream removal rates

in-sewer removal	LAS-total 0 - 50%	AE-total 0 - 50%	AES-total 0 - 50%	SOAP-total 0 - 50%
in-stream rates				
k= 0.00	52 - 104 ug/L	20 - 40 ug/L	8.5 -17 ug/L	15 - 30 ug/L
k= 0.14	36 - 72 ug/L	14 - 28 ug/L	6- 12 ug/L	10.5 - 21 ug/L
k= 0.70	20 - 40 ug/L	6.5 -13 ug/L	3.5 - 7 ug/L	6 - 12 ug/L

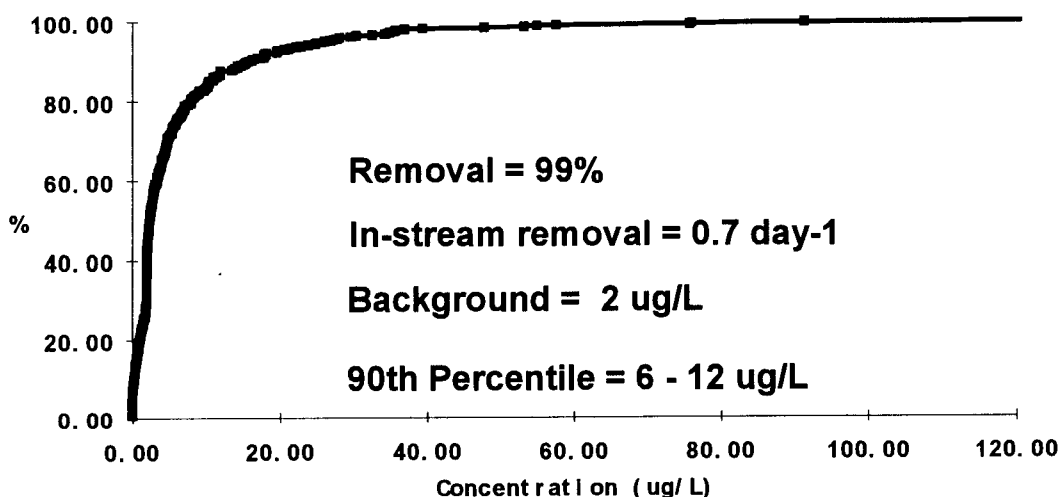
Figure 6: Frequency distribution of total surfactant concentration (ug/L) at 1000m below the sewage outfall in The Netherlands



Prediction of AES total in The Netherlands



Prediction of SOAP total in The Netherlands



Similarly, for LAS the 90th percentiles can be further refined according to alkyl homolog and isomer distribution. In this calculation, it is assumed that no further shifts occur in the receiving environment. This implies that, the model predictions reflect the isomer and alkyl chain shift from the sewage treatment only.

Table 19: Predicted 90th percentile of total surfactant concentration (ug/L) at 1000m below the sewage outfall - for both instream removal rates assuming no in-sewer removal

LAS	C10-ex	C10-in	C11-ex	C11-in	C12-ex	C12-in	C13-ex	C13-in	TOTAL
k= 0.14	14	31	6	15	2	4	0	1	72
k= 0.70	7	17	3	8	1	2	0	1	40

The 90th percentile PEC of mean LAS levels in surface waters range from 40 to 72 ug/L, depending on the assigned instream rate constants.

2.6. Monitoring Results.

A joint monitoring programme was initiated with the co-operation of the Institute for Inland Water Management and Waste Water (RIZA), the University of Amsterdam (UvA), National Institute of Public Health and Environmental Protection (RIVM), and the Dutch Soap Association (NVZ). The pilot phase of the monitoring programme was initiated (1) to optimize sampling parameters and sampling statistics and (2) to examine if the monitoring protocol would be suited for future studies. The first phase focused on linear alkylbenzene sulfonate (LAS) and was executed at one pilot location i.e. "de Meern", a municipal sewage treatment plant discharging in the river "Leidsche Rijn" (Feijtel et al. 1995).

The second phase of the monitoring programme included besides LAS, also alcohol ethoxylates (AE), alcohol ethoxylated sulfates (AES), and soap. This programme was executed at seven representative municipal sewage treatment plants across The Netherlands, as chosen by the Institute for Inland Water Management and Waste Water (RIZA) (Table 20).

Table 20: Characteristics of the selected municipal sewage treatment plants.

Site	Type	Loading (%)	Capacity (Inhabitants)	Domestic sewage (%)	Organic load (kg BOD/kg SS.d)
De Meern	carrousel	80	32,000	90	0.07
Kralingseveer	carrousel	97	293,000	79	0.07
Lelystad	carrousel	110	92,000	84	(0.07)
Hostermeer	aeration tank	82	132,000	81	0.09
Eindhoven	aeration tank	74	557,000	69	0.06
De Stolpen	oxydation ditch	100	45,000	70	0.06
Steenwijk	aeration tank	55	37,000	90	0.07

The plants were selected on the basis of treatment type, ratio of domestic input versus industrial input, organic loading, capacity as well as logistic considerations. The characteristics of the selected plants are described in Table 20.

The monitoring was executed at the 7 municipal sewage treatment plants during three consecutive days. 24-Hours flow proportional samples of raw, settled and treated sewage were collected using automatic samplers. All samples were preserved with 3% formaldehyde (or sodium azide for AE determination by HPLC/derivatisation) and stored at 4°C until analysis. Samples for determining the performance of the various plants were taken as well (BOD₅, COD, DOC, SS, pH, ammonium, nitrate..). At each plant, information on domestic inhabitants connected, industrial contribution and daily sewage flows were recorded in order to predict the surfactant concentrations of the raw sewage entering the treatment plants. Boron measurements were performed on all samples to check the validity of the calculations. At each side, quality assurance samples were prepared by standard additions of known amounts of the various types of surfactants to selected environmental samples in order to determine the efficiency of the storage procedures. In addition, standard amounts of surfactants were added to a limited number of environmental samples in the laboratory prior to the analysis in order to check the efficiency of the analytical procedures.

The environmental samples were analyzed for the selected surfactants using state-of-the-art analytical methods. Linear alkylbenzene sulphonate was analyzed by HPLC with fluorescence detection (Matthijs and De Henau 1987). Samples of raw and settled sewage were evaporated, redissolved in methanol and subsequently purified using a combination of anion exchange and octadecyl reversed phase chromatography. Samples of treated sewage (effluent) were passed directly over an octadecyl reversed phase column followed by further purification by anion exchange prior to HPLC analysis. Quantification is made using external calibration. The method allows the determine the chainlength range of interest from C10 to C13. The analytical recovery of field spikes was generally in excess of 90%.

The concentration of alcohol ethoxylates (AE) in raw and settled sewage samples was determined using a high performance liquid chromatographic method with UV detection after derivatisation of the analyte with phenyl isocyanate (Kiewiet 1995). The samples were pretreated using a combination of solvent sublation in ethyl acetate for the liquid phase and alkaline methanol extraction for the solid phase. The combined extracts were then further purified using alumina chromatography prior to HPLC analysis. Internal standards are used for peak identification. The method allows to determine the alkyl chainlength range from C12 till C18. Quantitation is made using an external calibration curve and assuming an average ethylene oxide value of 9. Laboratory spikes of AE are recovered for 100%. The analytical recovery for field spikes averaged 68%. The concentration of alcohol ethoxylates (AE) in samples of treated sewage (effluent) was determined using a liquid chromatography coupled to thermospray mass spectroscopy (Evans et al. 1994). Prior to mass spectroscopic analysis the analyte was concentrated on an octyl reversed phase column. Quantification was made using a deuterated internal standard. The method has been

validated for the C12 to C15 alkyl homologue range and an ethylene oxide distribution from EO 2 to EO 18. This alkyl chainlength range represents about 70% of the total commercial material. The analytical recovery averaged 79 and 76% for lab and field spikes respectively.

The concentration of alcohol ethoxy sulphates (AES) in both influent and effluent samples was determined using liquid chromatography coupled to ion spray mass spectroscopy. Prior to mass spectroscopic determination the liquid samples were concentrated over an ethyl reversed phase column. The recovery of field spikes of commercial material was 100%. The method was validated for the C12 to C15 alkyl homologue range and an ethylene oxide distribution from EO 0 to EO 8. This alkyl chainlength range represents about 70% of the total raw material. The species with EO 0 represent the concentration of alkyl sulphate (AS).

The concentration of soap in influent and effluent samples was determined by gas chromatography with flame ionisation detection. The aqueous samples were lyophilized and the free fatty acids and glycerides were eliminated by extraction with petroleum ether. In a next step, all fatty acid salts were converted into the free acid and subsequently methylated using boron trifluoride and methanol. The fatty acid methyl esters were then extracted with hexane and analysed by gas chromatography. The method allows to estimate the soap concentration within the C10 to C18 alkyl chainlength range. The analytical recovery of standard additions averaged 90% and 60% for influent and effluent samples respectively.

The results of the monitoring study are summarized in Table 21.

Table 21: Range and average WWTP removal and concentrations of LAS, AE, AES, and soap in influent and effluent.

Surfactant	Influent Range (mg/L)	Influent Average (mg/L)	Effluent Range (ug/L)	Effluent Average (ug/L)	Removal Range (%)	Removal Average (%)
LAS	3.4 - 8.9	5.2	19 - 71	39	98.0 - 99.6	99.2
AE (C12-C15)	1.6 - 4.7	3.0	2.2 - 13	6.2	99.6 - 99.9	99.8
AES (C12-C15)	1.2 - 6.0	3.2	3.0 - 11.5	6.5	99.3 - 99.9	99.6
AS (C12-C15)	0.1 - 1.3	0.6	1.2 - 12.1	5.7	99.0 - 99.6	99.2
Soap*	14 - 45	28	91 - 365	174	97.7 - 99.6	99.1

* 6 out of 7 plants

The data show that the removal of LAS, AE, AES and AS was relatively constant in all sewage treatment plants studied illustrating that the plant operating parameters do not essentially affect the surfactant removal. The analytical data obtained during the various European pilot studies (Waters and Feijtel, 1995) conducted in the course of 1993 had already demonstrated that the LAS removal was fairly constant across European plants as well. It must be noted that the information on the shift of alkylchain

lengths for LAS could not be obtained, mainly due to very low levels in effluent - close to detection limit. The removal of these surfactants was always higher than the measured average BOD removal of 98.0% (96.0 - 99.2%). The mass spectroscopic analysis for AE provided information on the homologue distribution and on the ethylene oxide chainlength. The measured alkyl chainlength averaged 13.3 with an average ethylene oxide number of 8.2. The concentration reported for AES represents only the ethoxylated material. The commercial material contains up to 20% of non-ethoxylated material (AS). However, since AS is also applied as a main surfactant e.g. in laundry and cleaning applications, the concentrations of AS have been reported separately. The alkyl chainlength of AES in the effluent averaged 12.5 with an EO value of 3.4. The EO value relates to the ethoxylated material only, excluding any contribution from AS. The average alkyl chainlength for AS was 12.3.

The monitoring data confirm the effective removal/degradation of all major priority surfactants during sewage treatment. The measured data derived from this monitoring programme can be used to further calibrate the Generic Dutch Model. This calibrated mathematical model can then further be used to account for spatial and temporal variations in the receiving environments and supplement the monitoring data.

Comparison of the measured raw sewage concentrations with predicted concentration provides an estimate of the in-sewer removal for the major surfactants. The predicted raw sewage concentration is based on the known surfactant consumption, the measured sewage flows and the domestic inhabitants connected to the individual sewage treatment plants. Boron is not removed during sewage treatment and has been used as a tracer. Comparison of the measured and predicted boron raw sewage concentrations has confirmed the validity of the above predictive procedure. Details on the calculated in-sewer removal data are provided in Table 22.

Table 22: Comparison of mean predicted and measured raw wastewater concentrations - based on actual measurements of total surfactant concentrations (7 plants)

	Tonnage total ton/yr	Predicted Wastewater (mg/l)	Measured Wastewater (mg/l)	In-sewer Removal (%) mean (range)
LAS	13 550	13.7 (8.1 - 18.2)	5.2 (3.4 - 8.9)	50 (10-68)
AE	9 703	5.1 (2.7 - 7.4)	3.0 (1.6 - 4.7)	42 (28-58)
AES	3 587	2.4 (1.3 - 3.5)	3.2 (1.2 - 6.0)	11 (0-40)
AS	2 700	1.8 (0.9 - 2.6)	0.6 (0.1 - 1.3)	55 (18-85)
Soap	10 675	7.9 (4.8 -11.6)	28 (14 - 45)	-

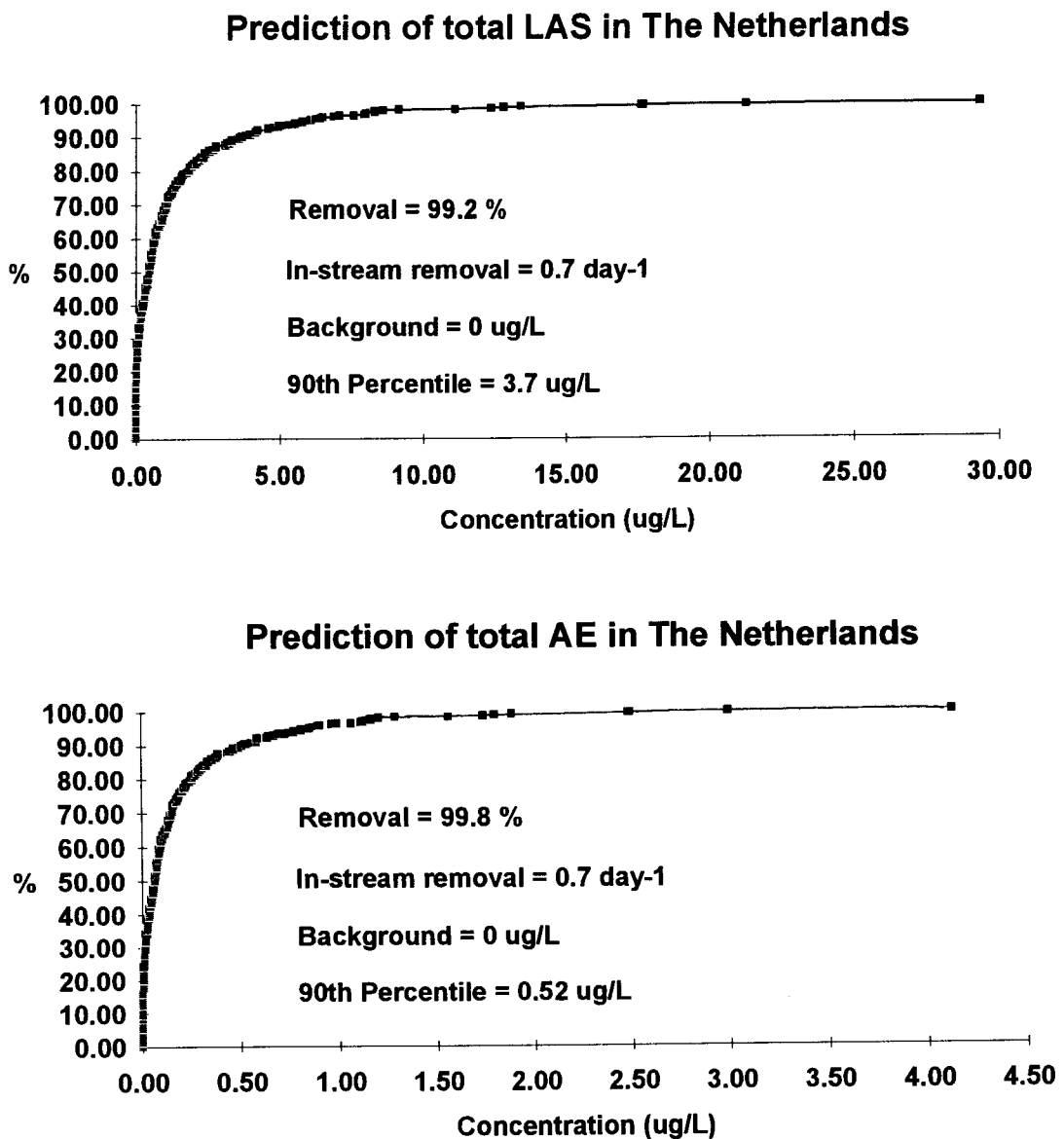
The comparison of mean predicted vs mean measured raw wastewater concentrations suggest that LAS is removed for about 60%. This removal is expected to be due to a combined action of various mechanisms including adsorption onto suspended solids, precipitation as calcium salts and biodegradation. As shown in the table, the in-sewer removal varies strongly from one plant to the other. This variation is related to differences in the length of the sewer and travel time and to microbiological activity in the sewer. The monitoring data show an in-sewer removal for AE of about 38%. This removal is expected to be due to a combined action of adsorption and biodegradation. The importance of biodegradation has been demonstrated in laboratory studies conducted with radiolabelled test material (Matthijs et al. 1994). These studies showed a half-life for parent AE in raw sewage of approximately 3 hours. The comparison of the measured concentration with the predicted concentration indicated an in-sewer removal for AES of 11%. This value is low considering the rapid biodegradation of AES as obtained in laboratory studies conducted with radiolabelled material. Calculated half-life for the parent molecule in these studies corresponded to about 4 hours (Matthijs et al. 1994). Most likely the consumption volumes used for AES, based on the known use in laundry and cleaning applications only, underestimates the real consumption. Contributions from other areas such as e.g. its use in shampoos are not well quantified and have not been incorporated. The calculated in-sewer removal for AS averaged 55%. The predicted concentration of AS was based on the sum of the consumption volume of AS used as main surfactant (about 2000 ton/year) and the contribution of AS delivered via the AES raw material (about 700 ton/year). For soap the measured raw sewage concentration is considerably higher than the predicted concentration based on consumption figures as supplied by NVZ. From figures presented in the use category document for detergents and household cleaners, it can be concluded that other sources - like personal care products - may contribute significant amounts (see appendix-1). Most likely the predicted raw sewage concentrations are underestimates which do not account for potential other sources/uses of soap. This was observed and consistent in all individual plants. It may also be expected that fatty acids are formed in the sewer by hydrolysis of fats and oils.

Calibration of influent data with the use of actual mean measured removal data allow the further refinement and prediction of 90th percentile concentrations (Table 23) (Figure 7). It must be noted that measured concentrations from treated effluents, diluted in the receiving waters are lower than the assumed background concentrations used in Figure 6. In addition, the dilution database of de Greef and de Nijs (1991) indicates that low dilution discharge situations are hardly affected by background concentrations. The opposite is true for the high dilution systems (e.g. Lek, Rhine) where background or up-stream input drives the actual exposure concentration. Since the 90th percentile situation corresponds to a low-dilution discharge and absence of upstream inputs, the background concentration was set to zero.

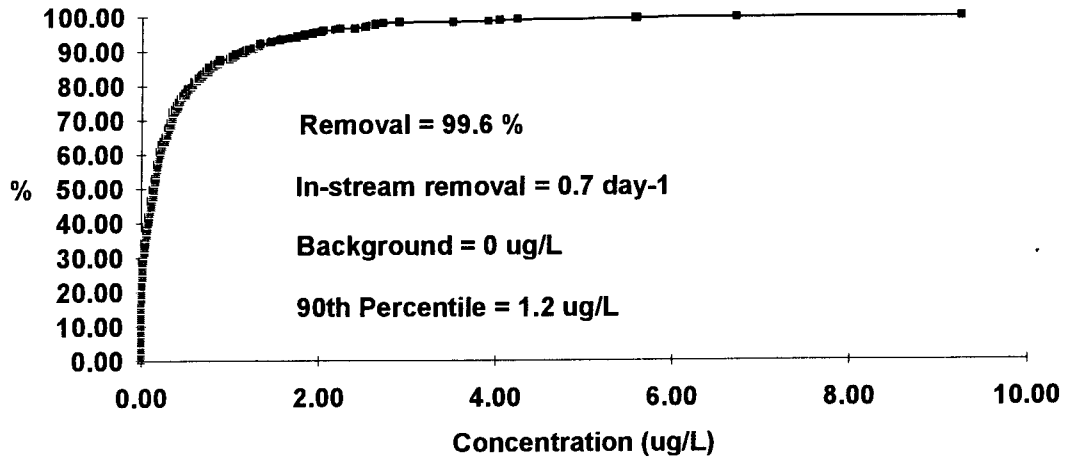
Table 23: Predicted 90th percentile concentration (ug/L) based on actual measured raw sewage concentrations and actual measured effluent concentrations. The 90th percentiles have been calculated for different instream removal rates

In-stream removal (day-1)	LAS-total (ug/L)	AE-total (ug/L)	AES-total (ug/L)	SOAP-total (ug/L)
k= 0.00	9.2	1.3	2.9	50
k= 0.14	6.4	0.9	2.1	35
k= 0.70	3.7	0.5	1.2	20

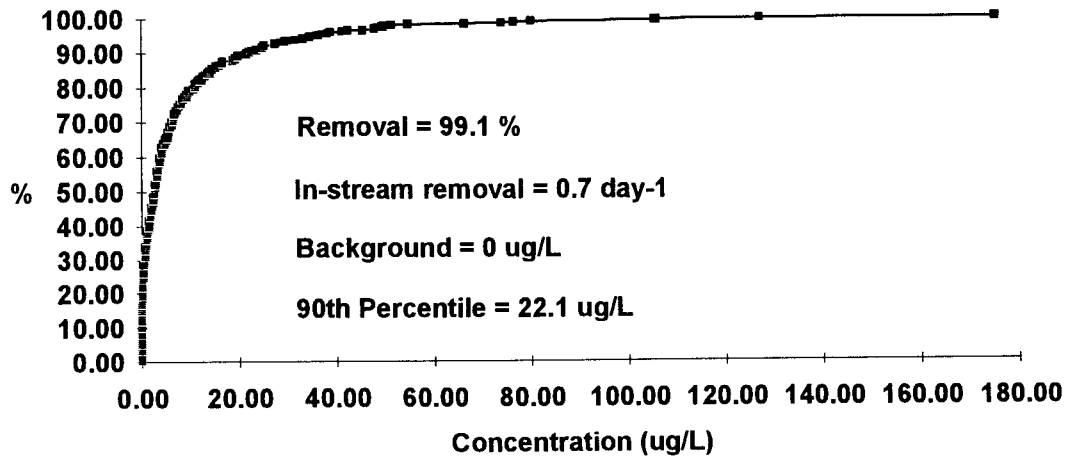
Figure 7: Frequency distribution of total surfactant concentration (ug/L) at 1000m below the sewage outfall in The Netherlands.



Prediction of total AES in The Netherlands



Prediction of total SOAP in The Netherlands



3. CHAPTER 3: Derivation of maximum permissible concentrations for LAS, AE, AES and soap.

3.1. Derivation of Maximum Permissible Concentrations (MPCs).

MPCs for water, sediment or soil are based on ecotoxicological data. Laboratory as well as field data can be available. If only single species toxicity data are available extrapolation methods are used to derive a MPC. These are described in paragraph 1.1.

Multi species testing and how to incorporate the results of such tests in effect assesment, is a rapidly evolving field in ecotoxicology the last few years (comprehensive effect assesment). Until now no completely elaborated strategy is available on how to incorporate these tests in deriving MPCs. In the present document the following strategy is followed:

- a MPC is derived based on single species toxicity data using extrapolation methods,
- if available, NOECs from multi species tests are compared with the MPC: if both values differ significantly, these differences should be explicable.
- a final MPC is derived. It is realized that extrapolated single species results as well as multi species tests do not give the exact value of a No Effect Concentration for all ecosystems: uncertainty in both results is always present. Therefore an attempt is made to indicate the uncertainty in this MPC value.

Results from field studies for LAS, AE, and AES are summarized in Appendix 9.

Ecotoxicological data for freshwater as well as marine organisms can be available. No clear answer can be given yet to whether these organisms differ in sensitivity to xenobiotics. Jonkers and Everts (1992) state that a general trend is not distinguishable. In the present document a procedure according to Slooff (1992) is used: toxicity data for both organisms are combined for the derivation of a MPC. Only if there are significant differences in sensitivity between marine and freshwater organisms caused by e.g. differences in bioavailability both data-sets are treated separately.

3.1.1. Extrapolation methods.

In the Netherlands two extrapolation methods are used for deriving MPCs, depending on the kind (short versus long term) and number of data available:

1. preliminary effects assesment using assesment factors: EPA method,
2. refined effects assesment using statistical extrapolation methods: a modification of the method of van Straalen and Denneman (1989) as developed by Aldenberg and Slob (1993).

These methods are described in detail by Slooff (1992), Aldenberg (1993), and Aldenberg and Slob (1993). A short description of both methods is given in the following paragraphs.

3.1.1.1. Preliminary effects assessment.

In the modified EPA method assessment factors are applied on toxicity data. The size of this factor depends on the number and kind of toxicity data. In Tables 1 and 2 the method is summarized for aquatic and terrestrial organisms, respectively. The outcome of the method is called an indicative MPC.

In the modified EPA method chronic as well as acute toxicity data are weighted over the species as follows (Slooff, 1992):

- if for a single species several L(E)C50 or NOEC values are derived for different effect parameters the lowest is selected,
- if for a single species several L(E)C50 or NOEC values are derived for the same effect parameter a geometric mean value is calculated.

In addition also acute/chronic ratios are used to derive NOEC values. These ratios are applied only within a taxonomical group.

Table 1. EPA method for aquatic organisms

available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1,000
lowest acute L(E)C50 or QSAR estimate for acute toxicity for minimal algae/crustaceans/fish	100
lowest chronic NOEC or QSAR estimate for chronic toxicity	10*
lowest chronic NOEC or QSAR estimate for chronic toxicity for minimal algae/crustaceans/fish	10

* this value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity values. The lowest one is selected

Table 2. EPA method for terrestrial organisms

available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1,000
lowest acute L(E)C50 or QSAR estimate for minimal three representatives of microbe-mediated processes, earthworms or arthropods and plants	100
lowest chronic NOEC or QSAR estimate for chronic toxicity	10*
lowest chronic NOEC or QSAR estimate for chronic toxicity for minimal three representatives of microbe-mediated processes, earthworms or arthropods and plants	10

* this value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity values. The lowest one is selected

3.1.1.2. Refined effects assessment.

In general statistical extrapolation methods work as follows: chronic toxicity data are log transformed and fitted according to the distribution function and a prescribed percentile of that distribution is used as criterion. Until now most authors have set this

percentile at 95%. This means that the NOEC may be exceeded for 5% of the species of the community. The 95% protection level may be regarded as a 'politically' fixed value (Løkke, 1994). In the Netherlands the 95% protection level is chosen as a cut-off value for deriving a MPC.

Several distribution functions have been proposed. The EPA (1985) assumes a log-triangular function, Van Straalen and Denneman (1989) a log-logistic function, and Wagner and Løkke (1991) a log-normal function (OECD, 1992). Aldenberg and Slob (1993) refined the way to estimate the uncertainty of the 95th percentile by introducing confidence levels. In the Netherlands the method of Aldenberg and Slob (1993) is used to derive MPCs. In Appendix 8 also results using other methods are presented for LAS, AE and AES and soap.

In the method of Aldenberg and Slob (1993) the 95% protection level can be calculated with a 50% and 95% confidence level. In the Netherlands the MPC is calculated as the former value, i.e. 50% confidence (Slooff, 1992). To indicate the uncertainty in the estimation of the MPC the 95% protection level with both 50 and 95% confidence is calculated. The method uses the lowest NOEC per species as input data and is applied when at least 4 long term NOEC values for different taxonomic groups are available. In the method of Aldenberg and Slob (1993) long term NOEC values used as input data are weighted over the species in the same way as described above for the EPA method.

The method of Aldenberg and Slob (1992) assumes that the NOEC values used for calculation fit the log-logistic distribution. For checking this assumption the data available are tested statistically with an empirical distribution function (EDF): Kolmogorov-Smirnov $D \cdot \sqrt{n}$ test (D'Agostino, 1986). Only if the NOEC values are not log-logistically distributed at a significance level of 1% and there are no reasons for leaving out outliers the modified EPA method is applied (Slooff, 1992).

3.1.2. Normalization of toxicity data.

The ecotoxicological data set for LAS, AE and AES consists of data for test-compounds differing in number of ethoxylate groups and differing in alkyl chain length. As toxicity depends on these characteristics of the chemical structure, these toxicity data are not comparable. This means that toxicity data have to be normalized to a specified number of EO groups and/or a specified alkyl chain length. In the present document MPCs for LAS, AE and AES are derived for compounds representative for the ones present in the aquatic environment in the Netherlands based on results from a monitoring study: LAS: C_{11.6}; AE: C_{13.3} EO_{8.2}; AES: C_{12.5} EO_{3.4} (see chapter). Although the alkyl chain length of LAS is expected to be lower, it was assumed to be equal to commercial product.

Ideally long term NOECs should be normalized using QSARs for long term toxicity. However, no reliable long term QSARs are available for surfactants. Therefore,

QSARs for short term toxicity have to be used. Normalization is carried out using the following procedure:

1. Log K_{ow} is calculated for the normalized structure (i.e. specified compounds stated above) and the structure tested using the 'standard' Leo and Hansch method (1979) with the modification for branching by Roberts (1989 and 1991). Roberts developed a method to calculate log K_{ow} values for surfactants using a position-dependent branching factor (PDBF).
An increment of 0.54 is used for a carbon unit based on the 'standard' Leo and Hansch method (1979). Based on the work of Roberts an increment of -0.10 is used for each EO group.
2. EC50s are calculated using the following QSARs for short term toxicity:
for AE:
 $\log (1/EC50) = 0.87 \log K_{ow} + 1.13$ (Könemann, 1981)
for LAS and AES:
 $\log (1/EC50) = 0.63 \log K_{ow} + 2.52$ (Saarikoski and Veluksela, 1982)
3. Ratios of predicted EC50s for normalized and tested compound are derived.
4. Long term NOECs with the tested compound are divided by this ratio.

3.2. Maximum Permissible Concentrations for LAS, AE and AES and soap

3.2.1. MPC for LAS.

3.2.1.1. Introduction.

Linear alkylbenzene sulfonate (LAS) has the following empirical formula: $RC_6H_4SO_3Na^+$ where R is an alkyl chain. The homologue distribution corresponding to the average LAS used in Europe is: C_{10} : 9-15%, C_{11} : 31-36%, C_{12} : 28-32%, C_{13} : 20-24% and C_{14} : <1% with an average alkyl chain of 11.6 (BKH, 1993a). The phenyl isomer distribution depends on the production process (BKH, 1993c):

Table 4. Phenyl isomer distribution of LAS C_{12} (BKH, 1993c).

phenyl isomer	distribution in %	
	HF catalyst	$AlCl_3$ catalyst
2 phenyl C_{12}	18	28
3 phenyl C_{12}	16	19
4 phenyl C_{12}	17	17
5 phenyl C_{12}	24	18
6 phenyl C_{12}	25	18

Circa 30% and 70% of LAS in Europe is produced using $AlCl_3$ and HF as catalyst, respectively.

A number of reviews are available on the effects of LAS on aquatic organisms (e.g. Kimerle, 1989; Painter, 1992; SDA, 1991 and IPCS, 1993). From these reviews it can be concluded that LAS must be regarded as one of the most intensely investigated chemicals in the field of ecotoxicology. The derivation of a MPC for LAS is based on the BKH reports (1993a, b). In the following paragraphs the data-base for LAS is described and discussed. Subsequently, a MPC is derived.

3.2.1.2. Ecotoxicological effects of LAS on aquatic organisms.

3.2.1.2.1. Short term effects.

The acute data base for LAS is enormous: in the BKH reports (1993a, b) short term data are presented for algae, crustaceans, insects, molluscs, worms, fish, plants and amphibians (freshwater as well as saltwater organisms). For LAS C₁₀₋₁₃ a summary is given in Appendix 1 based on list 2 of the BKH report (1993b).

As stated by BKH the intraspecies variation is almost as high as the interspecies variation (BKH, 1993a). E.g. for *Microcystis aeruginosa*, *Daphnia magna* and *Pimephales promelas* L(E)C50 values are 0.09-32, 0.26-55 and 0.40-100 mg/l, respectively. These huge ranges are caused by differences in the LAS compounds tested with respect to alkyl chain length and/or phenyl isomer distribution and differences in test design. So, the variability of short term data does not exclusively reflect the diversity of species sensitivity (Blok and Balk, 1993). If the geometric mean value per species is calculated the interspecies variation decreases considerably, as can be seen in Table 5.

Table 5. Geometric mean short term L(E)C50 values (mg/l) for species for which more than 4 data are available (BKH, 1993a).

species	geometric mean L(E)C50 (mg/l)	n
<i>Microcystis aeruginosa</i>	5.7	5
<i>Selenastrum capricornutum</i>	24	12
<i>Daphnia magna</i>	4.7	139
<i>Gammarus pulex</i>	6.2	25
<i>Mysidopsis bahia</i>	1.7	6
<i>Penaeus duorarum</i>	49	5
<i>Carassius auratus</i>	9.5	46
<i>Lepomis macrochirus</i>	3.0	88
<i>Leuciscus idus melonatus</i>	2.9	11
<i>Oncorhynchus mykiss</i>	3.0	10
<i>Oryzias latipes</i>	13	5
<i>Pimephales promelas</i>	3.2	35
<i>Poecilia reticulata</i>	3.8	9

Based on the geometric mean short term L(E)C50 values presented in this table it seems that there is little variation between the species. However, it has to be stated that for the short term data base, in contrast to the long term data base, the original data have not been reviewed by BKH. This means that the quality of the data has not been assessed. A number of duplicates may still be present, especially for organisms for which a large number of L(E)C50 values is given by BKH: e.g. *Daphnia magna*, *Carassius auratus*, *Lepomis macrochirus* and *Pimephales promelas*. Also, results from tests with different LAS compounds are used: no correction for differences in alkyl chain length is carried out.

3.2.1.2.2. Long term effects.

As stated before, original data on long term effects of LAS on aquatic organisms have been reviewed by BKH (1993a, b). A revised list, which is not presented in the BKH-report (1993b), resulted in 44 NOEC values for 23 species. Long term data are available for bacteria, algae, crustaceans, insects, molluscs and fish. These data are presented in Appendix 2 (letter of J. Blok to E. v.d. Plassche, 1994).

Several EC50 and NOEC data for algae are inconsistent. For *Microcystis spec.* one test is available, resulting in an EC50 and NOEC of 0.05 and 0.09 mg/l for LAS C_{11.8}. Four EC50 values for *Microcystis aeruginosa* are given by BKH (1993b): 0.9 mg/l for LAS C_{11.8}, 4.1 mg/l for LAS C_{11.9}, 5.0 mg/l for LAS C_{13.3}, 10 mg/l for LAS C_{11.6} and 32 mg/l for LAS (unspecified). Test durations are 72 to 120 hours. The effect type reported by BKH (1993b) for the value of 4.1 mg/l is "algistatic". This is remarkable, as the algistatic concentration is the concentration that totally inhibits algal growth but allows the growth to continue when the algae are recultured in a medium without the test compound; so it is an EC100!

For *Selenastrum spec.* an EC50 and NOEC of 29 and 0.5 mg/l is available for LAS C_{11.8} (BKH, 1993b). The difference between these two values is considerable as both are 96 hours values for the same endpoint. For *Selenastrum capricornutum* a NOEC of 0.5 mg/l for LAS C_{12.3} is present (BKH, 1993b), while 11 EC50 values range from 4.29 to 116 mg/l. For two of these EC50 values, 6.9 and 24 mg/l, the effect type reported by BKH is algistatic. For *Scenedesmus subspicatus* one test is available for LAS C_{11.6} resulting in an EC50 and EC10 of 9.0 and 0.8 mg/l, respectively (BKH, 1993b). The difference between these two values is considerable as both are 96 hours values for the same endpoint. BKH derived a NOEC of 0.8 mg/l. Next to this test an EC0 of 90 mg/l for LAS C_{11.8} and an EC50 of 30 mg/l for LAS C_{11.13} is given by BKH (1993b). In a review of Lewis (1990) on toxicity data of surfactants for algae no data are reported for this species.

As stated in paragraph 1.2 geometric mean NOEC values are calculated for each species if tested on the same parameter. However for several species, e.g. *Daphnia magna*, *Pimephales promelas* and *Oncorhynchus mykiss*, this is not possible as the effect parameter is often not specified. Therefore, a geometric mean is calculated using all NOECs. As stated in paragraph 2.2 toxicity data are contradictory for algae. It is decided to divide the EC50 values by 3 according to Van Leeuwen et al. (1992) to

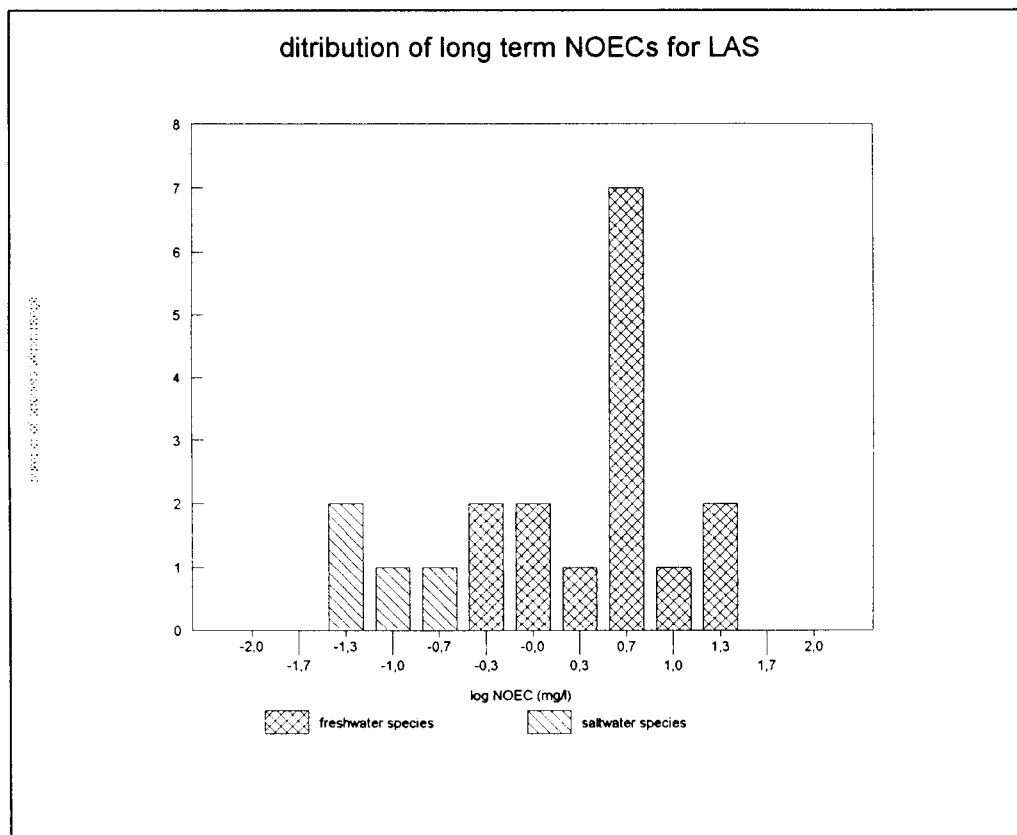
derive a NOEC, normalize these values, and calculate a geometric mean including the normalized NOEC values already present. The algistatic concentrations are excluded. Also toxicity data for *Pseudomonas putida* are excluded as these tests are based on oxygen consumption, being an insensitive parameter compared to e.g. growth. Next to this several values were not used as they were considered unreliable based on consultation of original sources. All long term NOECs derived per species are presented in Table 6.

Table 6. Normalized long term NOEC values (mg/l) per species. NOECs are normalized to an alkyl chain length of C_{11.6}.

species	NOEC (mg/l)	remark
<i>Chlamydomonas reinhardi</i>	12	
<i>Chlorella kessleri</i>	3.5	
<i>Microcystus spec.</i>	0.80	geometric mean of 0.058, 0.35, 3.3, and 6.1 mg/l
<i>Plectonema boryanum</i>	15	
<i>Scenedesmus subspicatus</i>	7.7	geometric mean of 0.80, 3.0, 14 and 105 mg/l
<i>Selenastrum spec.</i>	3.8	geometric mean of 0.58, 0.61, 1.0, 4.4, 4.9, 4.9, 8.2, 11, and 17 mg/l
<i>Ceriodaphnia spec.</i>	3.2	
<i>Daphnia magna</i>	1.4	geometric mean of 4.2, 0.3, 0.35, 1.4, 1.4, 1.5, 6.6, 1.9, 2.3, 2.1, 0.63, and 1.6 mg/l
<i>Mysidopsis bahia</i>	0.12	geometric mean of 0.34 and 0.13 mg/l
<i>Chironomus riparius</i>	2.8	
<i>Paratanytarsus parthenogenica</i>	3.4	
<i>Crassostrea virginica</i>	0.025	
<i>Mytilus edulis</i>	0.025	
<i>Brachydanio rerio</i>	2.3	
<i>Limanda yokohamae</i>	0.05	
<i>Pimephales promelas</i>	0.87	geometric mean of 4.8, 3.9, 0.30, 0.52, 1.1, 1.5, 0.34, 0.39, 0.5, 0.5, 0.63, 0.7, 1, 2 mg/l
<i>Poecilia reticulata</i>	3.2	
<i>Oncorhynchus mykiss</i>	0.34	geometric mean of 0.23, 0.3, 0.35, 0.43, 0.89, 0.35, 0.16 mg/l
<i>Tilapia mossambica</i>	0.25	

Marine species (*M. bahia*, *C. virginica*, *M. edulis*, and *L. yokohamae*) seem to be more sensitive than freshwater species for LAS: the average for marine and freshwater species is 0.055 ± 0.045 mg/l ($n = 4$) and 4.0 ± 4.3 mg/l ($n = 15$), respectively. Of freshwater species fish seem to be most sensitive. In the figure below a distribution graph of these NOECs is presented for freshwater and saltwater organisms.

The higher sensitivity of marine organisms can be explained by differences in bioavailability of LAS in saltwater compared to freshwater.



3.2.2. QSAR approach.

Roberts (1991) derived QSARs for short term toxicity for *Daphnia magna* and *Gammarus pulex*. For several anionics observed and calculated LC50 values agreed very well. It is interesting to compare calculated long term NOEC values with experimental ones for LAS. As no 'long term QSARs' are available for LAS QSARs derived by Van Leeuwen et al. (1992) for non-specific acting compounds are used. These QSARs are based on ecotoxicological results for 'non-detergents'.

QSARs for *Pseudomonas putida*, *Scenedesmus subspicatus*, *Selenastrum capricornutum*, *Daphnia magna* and *Pimephales promelas/Brachydanio rerio* are given in Appendix 3. A log K_{ow} and MW of 3.32 and 342 g/mol is used for LAS C_{11.6}, respectively. Results are presented in Table 7.

Table 7. Comparison of experimental long term NOECs and calculated NOECs (mg/l) using QSARs

species	experimental NOEC (mg/l)	calculated NOEC (mg/l)
<i>Pseudomonas putida</i>	35	65
<i>Scenedesmus subspicatus</i>	5.4	19
<i>Selenastrum capricornutum</i>	3.8	3.2
<i>Daphnia magna</i>	1.4	2.4
<i>Pimephales promelas</i>	0.87	2.0

Observed NOECs are for most species lower than the calculated ones. As LAS acts probably by "polar" narcosis and the QSARs are derived for non-specific acting compounds acting by narcosis instead of "polar" narcosis the results agree reasonably well.

3.2.2.1. Derivation of MPC.

As long term data are available for 4 taxonomic groups the statistical method of Aldenberg and Slob (1993) can be applied. Input data used are the NOECs as presented in Table 6.

Subsequently, a MPC of 36 µg/l is calculated with a 50/95 confidence ratio of 5.3. This value is slightly higher than the MPC of 21 µg/l based on species average NOEC values calculated by BKH in Appendix IV of their report (BKH, 1993a).

As marine species are clearly more sensitive for LAS than freshwater species only data for the latter organisms should be used to derive a MPC for freshwater systems in the Netherlands. If marine species are excluded the MPC is 320 µg/l with a 50/95

confidence ratio of 3.2. This value is somewhat higher than the lowest NOEC available being the one for *Tilapia mossambica*.

Using the Kolmogorov-Smirnov $D\sqrt{n}$ test (D'Agostino and Stephens (1986)) the distribution of NOEC values cannot be rejected as being log-logistic at a significance level of 10% for all MPCs calculated with and without toxicity data on marine organisms.

3.2.2.2. Field studies.

Results from field studies with LAS are reported in paragraph 3.9 of the BKH-report (BKH, 1993a). In appendix 9 results from these studies are summarized in two tables for microorganisms and ecosystem studies which are taken from the BKH report.

NOECs derived from multispecies studies with microorganisms varied from 0.24 to 9.8 mg/l with an outlier of 0.09 mg/l for photosynthetic response of phytoplankton (as the LOEC in this study was 0.87 mg/l the value of 0.09 mg/l was considered as an outlier). NOECs derived from ecosystem studies varied from ≤ 0.25 to 3.5 mg/l. From all studies it is concluded by BKH that the NOEC from field studies with higher and lower taxonomic groups is 0.25-0.5 mg/l for C_{12} LAS.

In field studies only freshwater organisms are tested. Therefore it is most appropriate to compare these results with the MPC of 320 $\mu\text{g/l}$. The MPC value of 320 $\mu\text{g/l}$ is in excellent agreement with the range of NOECs from field studies of 0.25-0.5 mg/l. Some field studies showed some effects at concentrations at the lower limit of this range: Lewis (1986): NOEC of 0.24 mg/l for relative abundance of phytoplankton, Lewis and Hamm: NOEC of 0.09 mg/l for photosynthetic response of phytoplankton, Chattopadhyay and Konar (1985): NOEC ≤ 0.25 mg/l for number and wet weight of chironomids and Fairchild et al. (199) NOEC ≤ 0.36 mg/l for fish growth and survival. Therefore a 'final' MPC of 250 $\mu\text{g/l}$, equal to the lower limit of the field NOECs, is derived for LAS, $C_{11.6}$.

The reliability of this final MPC value can be considered as rather high due to the availability of an extensive data set for LAS: short and long term studies performed in the laboratory for several taxonomic groups as well as many studies under more realistic conditions.

3.2.3. MPC for AE.

3.2.3.1. Introduction.

AE is a nonionic surfactant with a general structure of $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{O}(\text{CH}_2\text{-CH}_2\text{-O-})_m\text{H}$. The alkyl chain is either linear or mono-branched. Commercially the most important AEs at the moment in Europe are C₁₂₋₁₅ EO₃₋₁₀. For the derivation of a MPC an alkyl chain length of 13.3 and 8.2 ethoxylate groups is used based on results from a monitoring study in the Netherlands. The derivation of a MPC for AE is based on the BKH report (1994a). Some additional information is included (fax from G.C. Mitchell to E. v.d. Plassche, 1994; Dorn et al., 1993; Procter & Gamble, 1994).

3.2.3.2. Ecotoxicological effects of AE on aquatic organisms.

3.2.3.2.1. Short term effects.

A large data base is available on short term effects of AE. Short term data are present for bacteria, algae, diatoms, worms, insects, molluscs, crustaceans, fish and aquatic plants (freshwater as well as marine organisms). For C₁₂₋₁₅ EO₃₋₁₀ data are summarized in Table 8 based on an overview of short term data in Appendix 4.

As stated by BKH (1994a) intra- and interspecies variability is large, especially for algae. One reason is the chemical heterogeneity of AE, varying in alkyl chain and EO groups. Also, commercial products consist of mixtures of homologues, especially for the number of EO groups the range is rather broad. A further complication according to BKH (1994a) is the presence of 2-5% of non ethoxylated alcohol and 0.5-2.0% polyethyleneglycol. Subsequently, BKH was not able to derive a QSAR for AE based on the whole data-base.

3.2.3.2.2. Long term effects.

Long term data are available for several taxonomic groups: blue algae, diatoms, green algae, rotifers, crustaceans, molluscs, fish and worms. In Appendix 2 an overview is presented of NOECs based on the BKH report (1994) and some additional data as mentioned in paragraph 1 for C₁₀₋₁₇ EO₃₋₁₀, being the majority of long term data available. Also, some data for mono-branched AE are included.

Table 8. Short term data for AE C₁₂₋₁₅ EO₃₋₁₀ (see Appendix 1 based on BKH (1994)).

taxonomic group	species	chain length	EO	L(E)C50 (mg/l)	n
bacteria	<i>P. phosphoreum</i>	13.4	9	1.5	1
algae	<i>M. aeruginosa</i>	13-15	6-9	0.6-30	3
	<i>N. pelliculosa</i>	15	6	0.28	1
	<i>N. seminulum</i>	15	7	1.34	1
	<i>N. fonticola</i>	13	9	0.2	1
	<i>S. subspicatus</i>	15	10	1.53	1
	<i>S. capricornutum</i>	13-15	4-9	0.09-47	12
	crustaceans	<i>A. spec.</i>	15	7	6.2
<i>C. sapidus</i>		15	7	30.9	1
<i>C. crangon</i>		14	3-7	1.4-4.8	2
<i>C. dubia</i>		15	7	0.66	1
<i>D. magna</i>		13-15	3-10	0.41-4.17	17
<i>D. spec.</i>		13-14	6-9	0.76-13	5
<i>G. spec.</i>		15	7	1.4	1
<i>M. bahia</i>		13-15	7-10	0.2-2.24	2
<i>P. duorarum</i>		15	7	0.98	1
insects		<i>C. pipiens</i>	12-15	3-9	5-44
	<i>P. parthenogenica</i>	15	7	5	1
molluscs	<i>B. glabrata</i>	14	9	11	1
	<i>O. edulis</i>	14	9	0.11	1
	<i>C. virginica</i>	14	9	0.11	1
worms	<i>D. spec.</i>	15	7	2.6	1
	<i>D. gonocephala</i>	15	6	1	1
	<i>O. spec.</i>	15	7	2.6	1
	<i>P. spec.</i>	15	7	1	1
	<i>R. spec.</i>	15	7	6.8	1
fish	<i>B. rerio</i>	13-15	4-10	1.2-2.3	5
	<i>C. auratus</i>	13-14	6-9	1.4-5.1	4
	<i>I. punctatus</i>	14	9	1.2	1
	<i>L. macrochirus</i>	13-15	3-9	0.7-4.8	4
	<i>L. idus melonatus</i>	13-15	3-10	0.9-3.5	8
	<i>L. limanda</i>	14	3	1.8	1
	<i>O. latipes</i>	12	3-8	2.4-3.5	4
	<i>O. mykiss</i>	13-15	3-10	0.78-2.4	7
	<i>P. Promelas</i>	13-15	3-9	0.84-7.7	11
	<i>R. heteromorpha</i>	13	8	1.2	1
	<i>S. salar</i>	12	4	1.5	1
<i>S. trutta</i>	13	8	0.8	1	
plants	<i>L. minor</i>	15	7	1.9	1

Normalized NOEC values are presented in Table 9. Some NOEC values presented in Appendix 2 have been left out for deriving normalized NOEC values per species. The test on *Daphnia magna* with an alkyl chain length of 17 (record 338) has been excluded since the chain length is considered too long to extrapolate to an alkyl chain length of 13.3. The toxicity data on *Selenastrum capricornutum* are contradictory: EC50 values range from 0.09 to 47 mg/l and NOEC values from 0.60 to 25 mg/l. Clearly, there is no relationship between alkyl chain length, number of EO groups and toxicity. Probably, this large variation in results is caused by the different test compounds, the rapid biodegradation of alcohol ethoxylates and the static test design. Based on the non-specific mode of action of alcohol ethoxylates it cannot be expected that the toxicity results for *Selenastrum capricornutum* differs more than an order of magnitude with the results for other algae. Based on a comparison with the results for other algae the NOEC values of 20, 10 and 25 mg/l (records 331, 377 and 378) are considered as outliers and therefore excluded.

Table 9. Normalized long term NOEC values (mg/l) per species. NOECs are normalized to an alkyl chain length of C_{13.3} and EO_{8.2}.

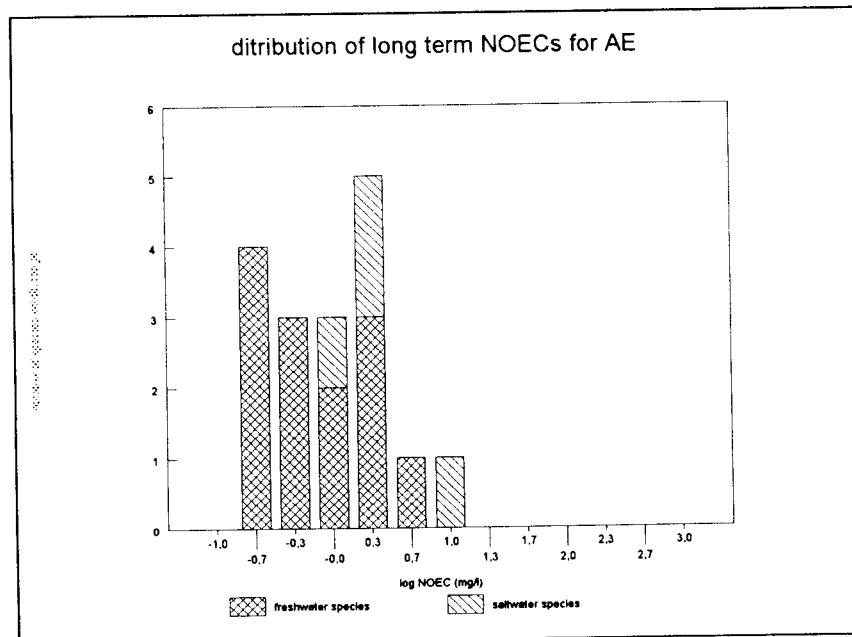
	species	'original' NOEC (mg/l)	NOEC (mg/l)
blue algae	<i>Microcystis aeruginosa</i>	0.30	1.9
diatoms	<i>Navicula pelliculosa</i>	0.14	0.93
	<i>Navicula seminulum</i>	1.6	8.7
green algae	<i>Selenastrum capricornutum</i>	1.2	0.74
	<i>Scenedesmus subspicatus</i>	0.55	1.3
	<i>Chlorella vulgaris</i>	2.5	0.20
rotifers	<i>Brachionus calyciflorus</i>	1.0	1.3
crustaceans	<i>Callinectes sapidus</i>	10	48
	<i>Ceriodaphnia dubia</i>	0.13	0.86
	<i>Daphnia magna</i>	0.38	0.59
	<i>Penaeus duorarum</i>	0.56	2.7
molluscs	<i>Mytilus edulis</i>	1.5	5.5
fish	<i>Brachydanio rerio</i>	0.82	1.5
	<i>Fundulus heteroclitus</i>	1.0	4.8
	<i>Pimephales promelas</i>	0.35	0.72
worms	<i>Dugesia gonocephala</i>	0.13	0.17
	<i>N. humilis</i>	0.13	0.17

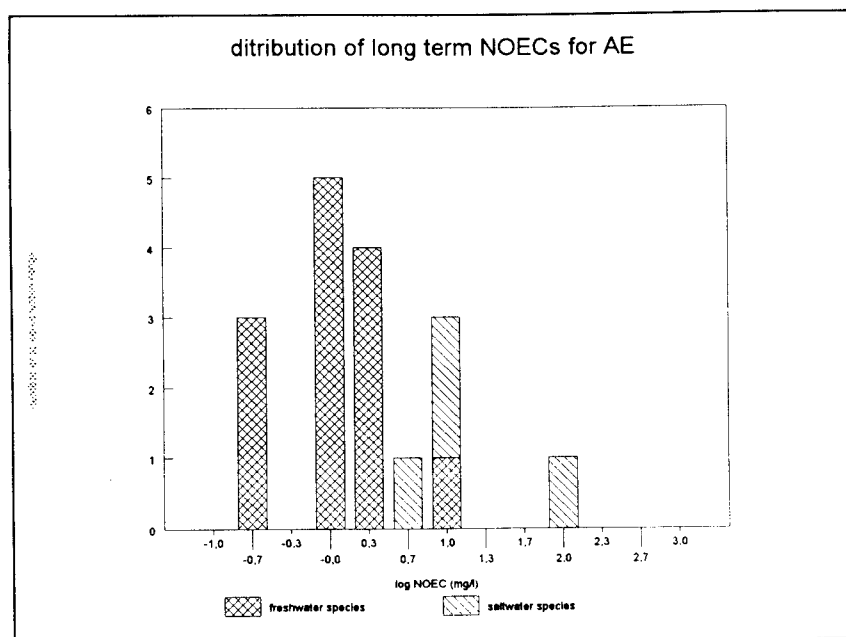
It can be concluded that marine species (*C. sapidus*, *P. duorarum*, *M. edulis* and *F. heteroclitus*) seem to be less sensitive than freshwater species: using normalized NOECs the average for marine and freshwater species is 15 ± 22 mg/l (n = 4) and 1.5 ± 2.2 mg/l (n = 13), respectively. Based on the 'original' NOECs these data are 3.3 ± 4.5 mg/l and 0.71 ± 0.71 mg/l, respectively.

Normalization can lead to a significant in- or decrease of the NOEC value per species; sometimes even more than a factor 10. As already stated such a large variation is not reflected in the experimental data. E.g., for *Daphnia magna* 13 NOEC values are available for C₁₂ - C_{14,5} and EO₃ - EO₁₀ varying from 0.14 to 1.0 mg/l with one outlier of 3.0 mg/l for C₁₄, EO₁₀ for the 'original' data while normalized NOECs vary from 0.10 to 3.9 mg/l.

In the figures below distribution graphs of long term NOECs are presented: the first one for the 'original' NOECs and the second one for the normalized NOECs. It can be expected that normalization of NOECs will lead to a 'more narrow' frequency distribution. However, this cannot be concluded from these figures. As already stated, this may be caused by the difficulty in testing such rapidly biodegrading substances as AEs.

For the derivation of a MPC the normalized NOEC values are used as stated in paragraph 1.1. Although the effect of normalization is not as expected this cannot be an argument to use the original NOECs as it is clear that the original experimental value does not represent the toxicity for the specified alkyl chain length and EO groups.





3.2.3.3. QSAR approach.

Roberts (1991) derived QSARs for short term toxicity for *Daphnia magna* and *Gammarus pulex* for anionics. Also, he compared short term toxicity data for AE with calculated values using the QSAR of K onemann (1981) for baseline toxicity. None of the AE, with C₁₀₋₁₈ EO₃₋₁₄, appeared to be significantly more toxic than predicted. Three AE were significantly less toxic, which is explained by Roberts by a solubility or micellisation cut-off.

It is interesting to compare calculated long term NOEC values with experimental ones for AE. As no 'long term QSARs' are available for AE QSARs derived by Van Leeuwen et al. (1992) for non-specific acting compounds are used. QSARs for *Scenedesmus subspicatus*, *Selenastrum capricornutum*, *Daphnia magna* and *Pimephales promelas/Brachydanio rerio* are given in Appendix 3.

Log K_{ow} for AE is calculated for C₁₃ EO₉ with 25% being methyl branched. The method as described in paragraph 2.3 is applied using the position-dependent branch factor (PDBF) as defined by Roberts (1991) as -1.44 log (CP+1), which leads to a log K_{ow} of 4.90. Results are presented in Table 10.

Table 10. Comparison of experimental long term NOECs and calculated NOECs (mg/l) using QSARs

species	experimental NOEC (mg/l)	calculated NOEC (mg/l)
<i>Scenedesmus subspicatus</i>	2.6	1.5
<i>Selenastrum capricornutum</i>	1.3	0.15
<i>Daphnia magna</i>	1.1	0.10
<i>Pimephales promelas</i>	1.2	0.15

Normalized values are for all species higher than the calculated ones. It seems that AE are circa a factor 10 less toxic than the predicted minimum toxicity. This can be explained by the use of experimental data for compounds differing in alkyl chain length and number of EO groups. It can also be the case that these QSARs are not suitable to predict the toxicity of AE.

3.2.3.4. Derivation of MPC.

As long term data are available for more than 4 taxonomic groups the statistical method of Aldenberg and Slob (1993) can be applied. Using normalized NOEC values MPCs are 110 and 130 $\mu\text{g/l}$ with and without marine species, respectively. As it is unlikely that marine organisms are different in sensitivity to AEs compared to freshwater organisms the MPC using the combined data-set is preferred. The 50/95 confidence ratio for the MPC of 110 $\mu\text{g/l}$ is 3.7. Using the Kolmogorov-Smirnov $D \cdot \sqrt{n}$ test (D'Agostino and Stephens (1986)) the distribution of NOEC values cannot be rejected for all calculations as being log-logistic at a significance level of 10%.

The MPC is close to some NOEC values (see Table 9) and also close to or sometimes even higher than some short term L(E)C50 values presented in Table 8. However, these short term data are not normalized.

3.2.3.5. Field studies.

Several field studies are available for AE:

- Tattersfield et al. (1994) tested DOBANOL 25-7 (C_{12-15} ; EO_7) in outdoor artificial streams for more than 51 days. Two concentrations were tested: 10 and 100 $\mu\text{g/l}$. These doses were increased in a stepwise incremental manner to 2000 $\mu\text{g/l}$. Measured concentrations were 10-20% of nominals.

Gammarus pulex were the dominant macroinvertebrates. Population density was reduced in both streams: a 30 day NOEC of 70-100 µg/l was estimated. No effects were observed on other species. Leaf processing rates were reduced at 200 µg/l: a 7 day NOEC of 70-100 µg/l was derived. No effects were observed on photosynthesis for 25 days leading to a NOEC of >70-100 µg/l.

It has to be stated that the principal objective of the study was method development, hence the data should be viewed as provisional.

- Dorn et al. (1994a) tested NEODOL 91-6 (C_{9/11}; EO₆) in stream mesocosms for 30 days. Concentrations tested ranged from 1 to 15 mg/l. Measured concentrations were 74 to 87% of nominals.
Secondary effects were observed on periphyton at 11.24 mg/l due to negative effects on invertebrates. No effects were observed on macrophytes. NOEC for copepoda and cladocera was 2.04 mg/l based on density and drift. 10 Days LC50 for caged *Hyalella azteca* was 9.1 mg/l based on effects on feeding and survival. *Pimephales promelas* were the most sensitive organisms with a NOEC for reproduction of 730 µg/l (egg production and larval survival). *Lepomis macrochirus* was less sensitive.
- Dorn et al. (1994b) tested NEODOL 45-7 (C_{14/15}; EO₇) in experimental streams for 30 days. Concentrations tested ranged from 100 to 600 µg/l. Mean measured concentrations were >80% of nominals.
No effects were observed on periphyton and macrophyte communities.
Invertebrates were largely not effected, except for *Simuliidae* in one experiment: a NOEC of 80 µg/l was found. Reproduction was the most sensitive endpoint for fish although the numbers of fish involved as well as reproductive activity was low.

These results lead to the following normalized values:

- C_{12/15}; EO₇: NOEC of 70-100 µg/l (*Gammarus pulex*, density and leaf processing rate) (Tattersfield et al., 1994), normalized value: 70-100 µg/l,
- C_{9/11}; EO₆: NOEC of 730 µg/l (fish, reproduction) (Dorn et al., 1994a) normalized value: 42 µg/l,
- C_{14/15}; EO₇: NOEC of 80 µg/l (*Simuliidae*, density) (Dorn et al., 1994b), normalized value: 380 µg/l.

The MPC based on single species data is in good agreement with the field NOECs. The field NOEC of 42 µg/l from Dorn et al. (1994a) is more than a factor 2 lower. However, in this test an AE with a short alkyl chain is tested. Normalizing is therefore carried out over 3 alkyl chain units: from C_{9/11} to C_{13.3}, which may be considered less reliable. A 'final' MPC of 110 µg/l is derived for AE, C_{13.3}; EO_{8.2}.

Considering the difficulties in carrying out long term tests with AE due to the rapid biodegradation the uncertainty in this MPC can be considered as rather high.

3.2.4. MPC for AES.

3.2.4.1. Introduction.

AES is an anionic surfactant derived from alkyl ethoxylates. The general structure of AES is $R(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{-Na}^+$. R is a mixture of straight or mono-branched alkyl chain containing 12 to 15 C atoms. The number of ethoxylate groups is 1 to 4. The commercial product contains considerable amounts of alkyl sulphates: according to the BKH report 20-50% (BKH, 1994b). For the derivation of a MPC an alkyl chain length of 12.5 and 3.4 ethoxylate groups is used based on the results of a monitoring study in the Netherlands.

Compared to data-bases for surfactants like LAS and alcoholethoxylates the data-base for ecotoxicological effects of AES on aquatic organisms is relatively small: the majority of the data are on short term effects (BKH, 1994).

The derivation of a MPC based on single-species studies for AES is based on the BKH report (1994b). Some additional information is included (fax from T. Feijtel of Procter & Gamble to E. v.d. Plassche, 16-05-1994; fax from M. Stalmans of Procter & Gamble to E. v.d. Plassche, 18-07-1994).

3.2.4.2. Ecotoxicological effects of AES on aquatic organisms.

In the BKH-report it is stated that the interpretation of tests with commercial products must be done with care (BKH, 1994b). First of all, these products may contain other constituents in significant amounts like unsulphated alkyl ethoxylates and alkyl sulphate. Secondly, biodegradation of the parent compound may occur. As most short term tests are static tests without analysis of the test compound biodegradation may have influenced the results, especially in tests with fish.

Results from short and long term tests are summarized in Appendix 1. In the following paragraphs these data are discussed.

3.2.4.2.1. Short term data.

Short term tests are available for green algae, crustaceans and fish. Almost all tests concern *Daphnia magna* and fish (freshwater as well as marine fish). L(E)C50 values are 3.5-10, 4.2-350 and 0.39-94.4 mg/l for algae, crustaceans and fish, respectively. LC50 values below 1 mg/l are reported for *Cyprinodon variegatus* (C₁₄-C₁₆; 2.25 EO) and *Pimephales promelas* (C₁₆; 2, 4 and 6 EO; C₁₄-C₁₆; 2.25 EO). It can be concluded that, based on short term data, fish may be more sensitive for AES compared to other taxonomic groups.

From these data no clear relation can be derived between alkyl chain length, number of EO groups and acute toxicity. Painter (1992) states that in general changes in EO numbers affect toxicity more than changes in alkyl chain length. In AES with an alkyl chain of less than C₁₆ the toxicity tends to decrease with increasing EO groups, whereas above C₁₆ this relationship is reversed.

3.2.4.2.2. Long term data.

Long term tests are available for green algae, rotifers, crustaceans and fish. Tests with the rotifer *Brachionus calyciflorus* are not presented in the BKH-report. These values are taken from a summary provided by Procter & Gamble (1994). In the BKH-report (1994) a NOEC value of 0.27 mg/l is reported for *Daphnia spec.* as test species. From the original publication of Maki (1979) it can be concluded that this must be *Daphnia magna*.

Acute chronic ratios (ACR) can be derived for *Daphnia magna* and *Pimephales promelas*. These are presented in Table 11.

Table 11. Acute chronic ratios for AES

species	test compound	L(E)C50 (mg/l)	NOEC (mg/l)	ACR
<i>Daphnia magna</i>	fatty alcohol ether (FES) C12-C14 + 2EO	72	0.7	103
<i>Daphnia magna</i>	C14/C16E2.25S	1.17 ^a	0.27	4.3
<i>Pimephales promelas</i>	C14/C16E2.25S	0.95-1.2	0.1	9.5-12
<i>Pimephales promelas</i>	C12/13E1S	13	0.88	15

^a 96 hr EC50; this value is not presented in the BKH-report but taken from Maki (1979)

ACRs for *Daphnia magna* are not consistent for both compounds due to the high EC50 for FES C₁₂-C₁₄; 2EO. An explanation may be the static test design of the 48 hr EC50 value for this compound. Assuming an ACR of c. 10 for AES seems reasonable.

3.2.4.3. Derivation of a MPC.

In Table 12 original and normalized long term NOEC values are presented.

Table 12. Original and normalized long term NOEC values (mg/l)

species	original NOEC (mg/l)	normalized NOEC (mg/l)
<i>Scenedesmus subspicatus</i>	0.35	0.73
<i>Scenedesmus subspicatus</i>	2.24	5.2
<i>Scenedesmus subspicatus</i>	1.6	3.7
<i>Selenastrum capricornutum</i>	0.82 ^a	1.2
<i>Selenastrum capricornutum</i>	2.3 ^a	5.0
<i>Brachionus calyciflorus</i>	0.97	0.36
<i>Brachionus calyciflorus</i>	2.26	1.4
<i>Brachionus calyciflorus</i>	0.49	1.0
<i>Daphnia magna</i>	0.18	1.1
<i>Daphnia magna</i>	0.70	1.5
<i>Daphnia magna</i>	0.27	2.3
<i>Pimephales promelas</i>	0.10	0.87
<i>Pimephales promelas</i>	0.88	1.6

^a calculated as EC50/3

As can be seen from this table, normalization of long term data doesn't lead to a substantial increase or decrease of the NOEC value for most tests. Obviously, this can be explained by the fact that most compounds tested have an alkyl chain length and number of EO groups close to 12.5 and 3.4, respectively. The NOEC value for *Pimephales promelas* of 0.13 mg/l has been excluded, as the test compound has an alkyl chain length of C₁₇. This chain length is considered too long for normalization.

As long term data are available for 4 taxonomic groups the statistical method of Aldenberg and Slob (1993) can be applied.

This leads to the following input data:

- *Scenedesmus subspicatus*: 2.4 mg/l,
- *Selenastrum capricornutum*: 2.4 mg/l,
- *Brachionus calyciflorus*: 0.80 mg/l,
- *Daphnia magna*: 1.6 mg/l,
- *Pimephales promelas*: 1.2 mg/l.

Subsequently, a MPC of 650 µg/l is calculated with a 50/95 confidence ratio of 3.4 using the method of Aldenberg and Slob as described in Aldenberg (1993) (version ETX 1.3a). Using the Kolmogorov-Smirnov D*sqrt(n) test (D'Agostino and Stephens (1986)) the distribution of NOEC values cannot be rejected as being log-logistic at a significance level of 10%. However, it must be stated that the data-set is limited.

The MPC is somewhat higher than the low short term LC50 values for *Cyprinodon variegatus* and *Pimephales promelas* mentioned in paragraph 2.3.2.1. Applying the

ACR of 10 on these values leads to NOEC values of 39-70 µg/l, considerably lower than the MPC of 650 µg/l. However, these LC50 values are determined for compounds with an alkyl chain length of C₁₄-C₁₆ and C₁₆.

3.2.4.4. Field studies.

Several field studies are available for AES:

- Belanger and Rupe tested C₁₄₋₁₅; EO_{2,17} to *Goniobasis spec.* and *Corbicula fluminea* in an experimental stream mesocosm for 8 weeks. Five concentrations were tested ranging from 12 to 1000 µg/l (measured concentrations 14 to 730 µg/l). No effects were observed on survival, shell length and growth of clams up to a measured concentration of 730 µg/l. For snails a NOEC of 75 µg/l based on weight gain was derived.
- Belanger and Rupe tested C₁₄₋₁₅; EO_{2,17} to 'acclimated' and 'unacclimated' periphyton communities in laboratory microcosms for 28 days. Main objective of the study was validation of a realistic periphyton community bioassay. Two concentrations were tested: 100 and 1000 µg/l (measured concentrations: 54 and 608 µg/l, respectively). Significant acclimation effects were observed. Based on 5 community level responses and 13 populations evaluated a NOEC of 608 µg/l was established. This is equal to a normalized value of 3.7 mg/l.
- Belanger et al. tested C₁₄₋₁₅; EO_{2,17} in a model stream ecosystem for 8 weeks. Five concentrations were tested ranging from 12 to 1000 µg/l (measured values ranged from 13 to 730 µg/l). Increased metabolism of the test compound as a carbon source by the heterotrophic periphyton community lead to an increase in bacterial density. No effects were observed on protozoans. At 774 µg/l bivalve molluscs, mayflies, stoneflies and caddisflies were reduced. One mayfly taxon, i.e. *Tricorythodes*, had a NOEC of 31 µg/l for density, however the NOEC for biomass was 251 µg/l. The authors derived an 'ecosystem level' NOEC of 251 µg/l. The NOEC values of 31 and 251 µg/l are equal to normalized NOECs of 190 µg/l and 1.5 mg/l, respectively.

In the second and third study no adverse effects were observed on algae up to the highest concentration tested of 1 mg/l. Only in the second study effects were detected on *Melosira varians*, *Schizothrix* and *Scenedesmus* based on algal cell and biovolume density. However, these effects were not exposure concentration related.

The tests with *Goniobasis spec.* and *Corbicula fluminea* can in fact be regarded as single species tests. The NOECs from these studies are measured total concentrations in natural waters, while the NOECs from laboratory single species studies are dissolved concentrations. However, the difference between total and dissolved concentrations are small. Including the NOECs of 730 and 75 µg/l in the data set used for the calculation of the MPC in paragraph 3.2 leads to a MPC of 400 µg/l with a 50/95 confidence ratio of 3.9 (normalized values are 4.4 and 0.48 mg/l for *Goniobasis spec.* and *Corbicula fluminea*, respectively). Subsequently, this MPC is compared with results from the microcosm and model stream ecosystem studies from Belanger et al.

The results from the field studies are in reasonable agreement with the MPC of 400 μ g/l if the results from field studies are also normalized to C_{12,5}; EO_{3,4}. However, it must be stated that all field studies are carried out with AES; C₁₄₋₁₅; EO_{2,17}, while different compounds were used in the single species tests. These compounds differed not only in their alkyl chain length and number of EO groups, but also in alkyl sulphate content (see paragraph 2.3.1). Also, normalized values for all field study results lead to a considerable increase of the field NOECs: circa a factor 6.

The MPC value of 400 μ g/l is a factor 3.8 below the normalized 'ecosystem level' NOEC of 1.5 mg/l of the study of Belanger et al. Other field study results are either higher or lower than the MPC of 400 μ g/l: the NOEC values of 190 μ g/l for *Tricorythodes* is somewhat lower while the NOEC of 3.7 mg/l for periphyton is considerably higher. Clearly, endpoints studied in the periphyton community bioassay are less sensitive compared to effects on other taxonomic groups. As the study of Belanger et al. can be regarded as the most extensive one with respect to taxonomic groups and endpoints studied comparison with this study is most appropriate. Considering this, there seems to be no reason to either lower or raise the MPC based on single species toxicity data: a 'final' MPC is derived of 400 μ g/l for AES, C_{12,5}; EO_{3,4}. Considering the narrow range in long term NOECs and the agreement between field NOECs and the MPC the uncertainty in the MPC seems rather low. Most important factor may well be the amount of alkylsulphates present. This will be further discussed in the risk characterisation chapter.

3.2.5. MPC for soap.

3.2.5.1. Introduction.

The anionic surfactant soap consists of a hydrophilic part, the carboxyl group, and a hydrophobic part, the alkyl chain. The general structural formula is $R\text{-COO}^-\text{Na}^+$ for sodium soaps and $R\text{-COO}^-\text{K}^+$ for potassium soaps. The alkyl chain R varies from C_{12} to C_{18} and is variably saturated due to the use of natural oils and fats for production. The data-base for ecotoxicological effects of soap on aquatic organisms is small: the majority of the data are on short term effects (BKH, 1994c). In the following paragraphs these data are described.

3.2.5.2. Ecotoxicological effects of soap on aquatic organisms.

According to the BKH-report the data are divided into three groups (see Appendix 1):

1. data for soaps with unspecified alkyl chain length,
2. data for soaps with an alkyl chain length of C_{12} - C_{14} ,
3. data for soaps with an alkyl chain length of C_{16} - C_{18} .

ad 1) Unspecified alkyl chain length

Short term L(E)C50 values range from 6.7 to 4233 mg/l for several taxonomic groups. Some values are clearly above the water solubility, whereas water hardness for the lowest value of 6.7 mg/l is reported as 0 mg CaCO_3 /l (BKH, 1994c). In the BKH the test species is reported as 'fish species', but from Schoeberl et al. (1988) it can be concluded that the fish tested is *Carassius auratus*. They also report that the LC50 value increases to 20-150 mg/l in water with a hardness of 85-425 mg CaCO_3 /l.

No long term data are presented in the BKH-report. However, a 96 h NOEC for algae and a 21 day NOEC for *Daphnia magna* are determined by Canton and Slooff (1982). Both NOECs are 10 mg/l.

ad 2) Alkyl chain length C_{12} - C_{14}

Only short term data are available. L(E)C50 values range from 3.3 to 118 mg/l for bacteria, green algae, crustaceans and fish. The lowest EC50 is for lauric acid with *Daphnia magna* as test species.

ad 3) Alkyl chain length C_{16} - C_{18}

Only short term data are available. L(E)C50 values range from 0.6 to 250 mg/l for bacteria, green algae, crustaceans and fish. The lowest value of 0.6 mg/l for *Oncorhynchus mykiss* is extremely low compared to the LC50 values for the other fish species. In contrast to the other values given in Appendix 1 a solvent was used. However, no details on the amount used are available on this experiment.

In the only marine test available using the sea urchin sperm toxicity test with *Strongylocentrotus purpuratus*, a solvent is used also (Cherr et al., 1987). Low EC50 values of 0.28 and 1.07 mg/l for linoleic and linolenic acid, respectively for effects on fertilization are determined. NOECs are 0.1 and <1.0 mg/l, respectively. Ethanol is used as a solvent. The ethanol concentration in each treatment is 0.1%, being indeed higher than the maximum amount recommended by the OECD but no adverse effects are reported for the solvent control. Probably the low values are caused by a specific sensitivity of the test, rather than by the use of ethanol as a solvent. Several L(E)C50 values may in reality be lower because in most tests some precipitation was observed (BKH, 1994c).

3.2.5.3. Derivation of MPC.

No clear conclusions can be drawn with respect to interspecies variation for soap and the influence of the alkyl chain length. The outcome of the tests seem to be highly influenced by test conditions like use of solvents and water hardness (possible formation of insoluble calcium and magnesium salts) and type of soap (BKH, 1994c). Actual concentrations are never measured.

As not enough long term data are available to apply the statistical extrapolation method, the EPA method is used to derive a MPC (Slooff, 1991; OECD, 1992). This leads to the following MPC values:

- unspecified chain length: the lowest L(E)C50 value of 6.7 mg/l is considered not useful due to the low water hardness. The second lowest value is an EC50 of 10 mg/l for *Daphnia magna*. Also another EC50 of 42 mg/l and a NOEC of 10 mg/l is available for this species. According to Slooff (1992) geometric mean L(E)C50 values are calculated for each species if tested on the same parameter. However, because the test compound is not specified no geometric mean EC50 is calculated. The EC50 value of 10 mg/l is used and divided by 100, which leads to a MPC of 100 µg/l,
- alkyl chain length C₁₂-C₁₄: the lowest L(E)C50 value of 3.3 mg/l for crustaceans divided by 100 gives a MPC of 33 µg/l,
- alkyl chain length C₁₆-C₁₈: the lowest L(E)C50 value is 0.6 mg/l for fish which leads to a MPC of 6 µg/l. It has to be stated that all other short term data are at least a factor 17 higher.

The difference between the MPC for an alkyl chain length of C₁₆-C₁₈ and the other 2 MPC values is a factor 5.5-15. It is uncertain whether the low value for C₁₆-C₁₈ is caused by an outlier or not. The use of a solvent doesn't increase the toxicity but leads to a maximum bioavailability of the test compound. On the other hand all other short term values show a much lower toxicity of soap. However, as in several other tests some precipitation was observed it may well be that the LC50 value of 0.6 mg/l is the 'true' toxicity of oleic acid to *Oncorhynchus mykiss*.

Based on these considerations a MPC of 27 µg/l, being the geometric mean of the three individual MPC values, is derived as an 'overall' MPC for soap. As this MPC is calculated using the EPA method the value of 27 µg/l must be considered as an indicative value.

4. CHAPTER 4: Risk characterization of LAS, AE, AES and soap.

4.1. Exposure Assessment.

The calculation scheme for the aquatic compartment is based on the comparison of the 90th percentile of Predicted Environmental Concentrations (PEC) in the Netherlands - at 1000 meter below the sewage outfall - to the Predicted No Effect Concentration (PNEC) for ecosystems or Maximum Permissible Concentration (MPC). The 90th percentile surfactant concentrations at 1000 meter below the sewage outfall can be calculated using information or data on 1/ release, 2/ in-sewer removal, 3/ treatment efficiency, 4/ dilution and 5/ instream-removal.

The release or emission algorithm assumes that 100% of the release occurs at the use phase, with no significant loss at the production, compounding or processing stage. In the present assessment, it is assumed that all chemical substances which enter the waste water stream will pass through a waste water treatment plant before being discharged into the environment. Given the present situation in The Netherlands and the rapidly evolving situation in the European Union this assessment is seen as representative and conform to the EU Technical Guidance Documents.

Since the rate of primary biodegradation of AE, AES, and soap is comparable to that of LAS (Matthijs et al. 1994), significant in-sewer removal was expected for all surfactants. The comparison of mean predicted vs mean measured raw wastewater concentrations for all 7 wastewater treatment plants suggest that LAS is removed for about 60%. This removal is expected to be due to a combined action of various mechanisms including adsorption onto suspended solids, precipitation as calcium salts and biodegradation. The monitoring data show an in-sewer removal for AE of about 38%. This removal is expected to be due to a combined action of adsorption and biodegradation. The comparison of the measured concentration with the predicted concentration indicated an in-sewer removal for AES of 11%. This value is low considering the rapid biodegradation of AES and is likely due to an underestimation of the consumption volumes of AES. Similarly to AES, the predicted raw sewage concentrations of soap are underestimates and do not account for potential other sources/uses of soap. This was consistent between the different plants and within all individual plants. It may also be expected that fatty acids are formed in the sewer by hydrolysis of fats and oils.

Predicted average removal for LAS, AE, AES and soap were high (98 - 99%) and not significantly different, using the specified input model input. This implies that - within the limitations of the model - only 1 to 2% of total mass will be discharged to the receiving surface waters. The monitoring data confirm the effective removal/degradation of all major priority surfactants during sewage treatment (Table 2), and indicate that the model predictions on removal are conservative. Average measured removal ranged from 99.1% for soap to 99.8% for AE.

Table 2. Range and average WWTP removal and concentrations of LAS, AE, AES, and soap in influent and effluent.

Surfactant	Influent Range (mg/L)	Influent Average (mg/L)	Effluent Range (ug/L)	Effluent Average (ug/L)	Removal Range (%)	Removal Average (%)
LAS	3.4 - 8.9	5.2	19 - 71	39	98.0 - 99.6	99.2
AE (C12-C15)	1.6 - 4.7	3.0	2.2 - 13	6.2	99.6 - 99.9	99.8
AES (C12-C15)	1.2 - 6.0	3.2	3.0 - 11.5	6.5	99.3 - 99.9	99.6
AS (C12-C15)	0.1 - 1.3	0.6	1.2 - 12.1	5.7	99.0 - 99.6	99.2
Soap*	14 - 45	28	91 - 365	174	97.7 - 99.6	99.1

* 6 out of 7 plants

Dilution factors for the discharge of all municipal wastewater treatment plants in The Netherlands have been reported (de Greef and de Nijs, 1990). The 10th, 50th, or 90th percentile dilution factor can be calculated as respectively SDF=3, SDF=32, and SDF=1740 at 1000m below the sewage outfall. By using the dilution database, and linking each site to WWTREAT output or actual measured data, an estimate can be obtained about the predicted 90th percentile of total surfactant concentration (ug/L) at 1000m below the sewage outfall. The measured data derived from this monitoring programme was used to calibrate this Generic Dutch Dilution Model. Calibration of influent data with the use of actual mean measured removal data allow the further refinement and prediction of 90th percentile concentrations. In addition, refinement was introduced to account for in-stream removal, since biodegradation and sorption can be expected to result in significant changes in concentration and/or in substance form, distribution, and bioavailability. In-stream removal data for detergent ingredients have indicated that removal rates range from 0.5 - 1 day⁻¹. An in-stream loss rate of 0.7 day⁻¹ for surfactants, similar to instream BOD removal rates, is chosen based on expert judgment. In order to evaluate the potential effect of in-stream removal on the 90th percentile PEC concentration, the calculation was extended with 0 and 0.14 day⁻¹ (Table 3).

Table 3. Predicted 90th percentile concentration (ug/L) based on actual measured raw sewage concentrations and mean wastewater removal figures. The 90th percentiles have been calculated for different instream removal rates

In-stream removal (day ⁻¹)	LAS-total (ug/L)	AE-total (ug/L)	AES-total (ug/L)	SOAP-total (ug/L)
k= 0.00	9.2	1.3	2.9	50
k= 0.14	6.4	0.9	2.1	35
k= 0.70	3.7	0.5	1.2	20

4.2. Effects.

Maximum Permissible Concentrations (MPCs) are derived using data presented in the BKH reports together with some additional data supplied by the NVZ. The latter consisted of additional long term studies for AES and field studies for AE and AES.

In the present document the following strategy is followed to derive a MPC:

- a MPC is derived based on single species toxicity data using extrapolation methods. Methods used are the statistical extrapolation method according to Aldenberg and Slob and the EPA method which uses assessment factors.
- if available, NOECs from multi-species mesocosm tests are compared with the MPC: if both values differ significantly, these differences should be explicable.
- a final MPC is derived.

The ecotoxicological data sets for LAS, AE and AES consist of data for test-compounds differing in number of ethoxylate groups and differing in alkyl chain length. As toxicity depends on these characteristics of the chemical structure, these data are not comparable. This means that toxicity data have to be normalized to a specified number of EO groups and/or a specified alkyl chain length. In the present document MPCs for LAS, AE and AES are derived for compounds representative for the ones present in the Dutch aquatic environment based on results from the monitoring study in the Netherlands: AE: C_{13.3} EO_{8.2}; AES: C_{12.5} EO_{3.4}. For LAS no mean alkyl length could be determined due to the low concentrations measured in the environment. Therefore a conservative chain length of C_{11.6} is used, being the one of the commercial product. It is realized that this may lead to an overestimation of the risk due to the preferential degradation of the longer chain length in WWTPs.

Normalization for LAS, AE and AES is carried out using correction factors based on QSARs calculations for short term toxicity for the specified compound and the test-compound. It is realized that using QSARs for short term toxicity in the normalization procedure can give only a coarse estimation of the influence of chain length and number of EO groups. Therefore no correction is carried out over more than 3 alkyl units.

Final MPCs are presented in Table 4. The value for soap must be considered an indicative value as short term toxicity data represent the majority of the data.

Table 4. Final MPC (ug/L) for LAS, AE, AES and soap.

surfactant	MPC based on single species data (ug/L)	range of field NOECs (ug/L)	final MPC (ug/L)
C _{11.6} LAS	320	250-500	250
C _{13.3} EO _{8.2} AE	110	42-380	110
C _{12.5} EO _{3.4} AES	400	190-3700	400
soap	27	-	27

It can be concluded that for LAS, AE and AES MPCs based on single species toxicity data calculated with the statistical extrapolation method of Aldenberg and Slob are in good agreement with results from multispecies studies under more realistic conditions. MPCs for LAS, AE and AES show that these surfactants have a comparable toxicity. AE is more toxic than LAS and AES, due to its non-ionic nature and higher alkyl chain length. The MPC for soap is a factor 4-15 lower than the other ones. Clearly, this is due to the use of a high assessment factor: comparing the short term toxicity data available for soap with the short term data for LAS, AE and AES it cannot be concluded that soap is the most toxic.

The final MPCs for AE, AES and soap are expressed as dissolved concentrations assuming 100% bioavailability in the laboratory. However, measured concentrations from the monitoring study are expressed as total concentrations. Theoretically, total concentrations consist of a dissolved fraction and fractions adsorbed to suspended solid and/or associated with DOC. Using the K_p values presented in Table 9 of Chapter 3 and assuming 15 mg/l suspended solids (SS) the MPCs expressed as total concentrations are 110, 410 and 31 ug/l for AE, AES and soap¹. The value for SS is taken from the Uniform System for the Evaluation of Substances and can be regarded as representative for Dutch surface waters (RIVM, VROM, WVC, 1994). It can be concluded that the difference between total and dissolved (i.e. non-sorbed to SS) concentrations are minimal for these surfactants.

According to Traina et al. (1994) association with DOC rather than adsorption to SS influences bioavailability. This has been investigated for LAS resulting in a log K_{OC} of 4.83 for association of C₁₂ with DOC (see section 2.4.2)¹ Assuming a DOC concentration of 10 mg/l, about 40% would be associated with DOC. The influence of association with DOC on bioavailability and toxicity has been investigated only in short term tests with fish for LAS (Traina et al., in press). In this test it was shown that toxicity was reduced with increasing DOC. However, as effects in long term tests may be different and results for the other surfactants are not available the extent of the effect of association with DOC cannot be quantified at the moment. Also, it must be noted that the nature and concentrations of DOC differs in the environment. Summarizing, it can be concluded that the MPCs can be compared directly to measured total concentrations in the aquatic environment.

¹ $MPC_{total} = MPC_{dissolved} * [1 + (K_p * SS)]$.

According to the BKH reports commercial AES contains 20-50% alkyl sulphates (AS). The MPC is based on single species toxicity tests performed with commercial AES. This means that exposure concentrations for 'pure' AES cannot be compared directly with the MPC presented in Table 4. Since AS has a different toxicity to AES the MPC has to be corrected. Since AES is less lipophilic than AS due to the presence of several EO groups, AES is probably less toxic than AS - with corresponding chainlengths. Subsequently the corrected MPC will be higher than the one presented in Table 4. Since toxicity data for AS have not been gathered the influence of AS present in commercial AES cannot be quantified at the moment. This means that the comparison of the PEC for AES with the MPC of 400 ug/L for AES may lead to an overestimation of the risk.

It is realized that extrapolated single species results as well as multi-species mesocosm tests do not give the exact value of a No Effect Concentration for all ecosystems: uncertainty in both results is always present. For LAS the uncertainty is considered to be low due to the presence of an extensive data set from laboratory short term studies to multispecies studies under more realistic conditions. For the other compounds the uncertainty will be higher, especially for soap as only short term data are available. Based on the number and variation in results from short term, long term and field studies and using expert judgement the uncertainty in the MPC values presented in Table 4 can be estimated as ranging from a factor 2 for LAS to 10 for soap. This means that MPCs can be a factor 2-10 lower as well as higher.

4.3. Risk characterization.

PEC/MPC ratios are presented in Table 5. PECs from Table 3 are used based on in-stream removal rates of 0, 0.14 and 0.70 day⁻¹. MPCs from Table 4 are used.

Table 5. PEC/MPC ratios for LAS, AE, AES and soap based on 3 in-stream removal rates.

in-stream removal rate (day ⁻¹)	LAS	AE	AES	soap
k = 0	0.04	0.01	<0.01	1.9
k = 0.14	0.03	0.01	<0.01	1.3
k = 0.70	0.02	<0.01	<0.01	0.74

From this table it can be concluded that for soap the MPC is exceeded for an in-stream removal rate of 0 and 0.14 day⁻¹. Assuming no in-stream removal is unrealistic as soap is a ready biodegradable compound. So, depending on the in-stream removal rate chosen the PEC is either higher or lower than the MPC. The risk of LAS, AE and AES for the aquatic environment is low. Also taking the estimated uncertainty into account MPCs are always considerably higher than the PEC.

The risk assessment of all surfactants can be further refined by:

- for soap: further refinement of the MPC on the basis of chronic test data. As only short term toxicity data are present for soap long term studies should be carried out. In the mean time a 28-day growth test with zebra fish for sodium laurate (C12 soap) has been conducted and a NOEC of 3.7 mg/L was reported based on measured concentrations (van Egmond et al. 1996). These test results indicate that the toxicity of soap is similar to the other surfactants.
- for AES and soap: although measured effluent concentrations are realistic, more information on product use and release to the environment is required, as well as a better understanding and quantification of saponification of fats in the sewer lines.
- for AES: studying the influence on toxicity of AS present in commercial AES,
- for all surfactants: determination of in-stream removal rate,
- for all surfactants: obtaining more information on the influence of possible reduction in bioavailability by association with DOC.

5. References.

- Aldenberg, T. (1993). ETX 1.3a. A program to calculate confidence limits for hazardous concentrations based on small samples of toxicity data. RIVM report No. 719102 015.
- Aldenberg, T., W. and Slob (1993). Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotox. Environ. Safety* 25, 48-63.
- Belanger, S.E., Guckert, J.B. and Bowling, J.W. (1995). Effects of alkyl ethoxylate sulfate (AES) on aquatic populations and communities in a model stream ecosystem. *Environ. Toxicol. Chem* (in press).
- Belanger, S.E. and Rupe, K.L. (1996 a). Responses of asiatic clams and pleurocerid snails during exposure to C_{14/15}E_{2.25}S (alkyl ethoxylate sulfate) in experimental stream mesocosms. *Environ. Toxicol. Chem.* (submitted).
- Belanger, S.E. and Rupe, K.L. (1996 b). Response of field colonized periphytic algal communities to alkyl ethoxylate sulfate (AES) in laboratory microcosms. *Environ. Toxicol. Chem* (submitted).
- BKH Consulting Engineers (1993a). The use of existing toxicity data for estimation of the Maximum Tolerable Environmental Concentration of Linear Alkyl Benzene Sulfonate. Part I: Main report. NVZ in cooperation with European surfactant industry. Delft, The Netherlands, May 1993.
- BKH Consulting Engineers (1993b). The use of existing toxicity data for estimation of the Maximum Tolerable Environmental Concentration of Linear Alkyl Benzene Sulfonate. Part II: Data lists. NVZ in cooperation with European surfactant industry. Delft, The Netherlands, May 1993.
- BKH Consulting Engineers (1993c). Environmental fate and behaviour of LAS. Literature review. NVZ in cooperation with European surfactant industry. Delft, The Netherlands, May 1993.
- BKH Consulting Engineers (1994a). Environmental data review of Alcohol Ethoxylates (AE). Final Report, October 1994. NVZ in cooperation with European surfactant industry. Delft, The Netherlands (including datalist).
- BKH Consulting Engineers (1994b). Environmental data review of Alkyl Ether Sulphates (AES). Final Report, October 1994. NVZ in cooperation with European surfactant industry. Delft, The Netherlands (including datalist).
- BKH Consulting Engineers (1994c). Environmental data review of Soap. NVZ in cooperation with European surfactant industry. Delft, The Netherlands.

- Blok, J., and Balk, F. (1993). Attempts to bridge the gap between laboratory toxicity tests and ecosystems: a case study with LAS. *Sci. Total Environ., Supplement* 1993, part 2, 1527-1538.
- Canton, J.H. and Slooff, W. (1982). Substitutes for phosphate containing washing products: their toxicity and biodegradability in the aquatic environment. *Chemosphere* 11, (9), 891-907.
- CBS, (1990). Centraal Bureau voor de Statistiek. Waterkwaliteitsbeheer. Deel B. Zuivering van afvalwater 1988. Voorburg/Heerlen, CBS.
- Chattopadhyay, D.N., and S.K. Konar (1985). Chronic effects of linear alkyl benzene sulfonate on aquatic ecosystem. *Environ. Ecol.* 3, (3), 428-433.
- Cherr, G.N., Shenker, J.M., Lundmark, C., and Turner, K.O. (1987). Toxic effects of selected bleached kraft mill effluent constituents on the sea urchin sperm cell. *Environ. Toxicol. Chem.* 6, 561-569.
- Cowan C.E., Larson R.J., Feijtel T.C.J. and R.A. Rapaport. (1993). An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants. *Water Research*, 27 (4), 561-573.
- D'Agostino, R.B. and Stephens, M.A. (1986). Goodness-of-fit techniques. M. Dekker Inc. New York.
- de Greef, J. and T. de Nijs (1990). Risk assessment of new chemical substances: dilution of effluents in The Netherlands, RIVM Report No. 670208001, Bilthoven.
- Dorn, P.B. et al. (1994a). An assessment of the ecological effects of a C9-11 linear alcohol ethoxylate surfactant in stream mesocosm experiments. Revision: June 10, 1994.
- Dorn, P.B. et al. (1994b). Assessing the effects of a linear alcohol ethoxylate surfactant in stream mesocosms. Revised: May 25, 1994.
- Dorn, P.B., Salanitro, J.P, Evans, S.H. and Kravetz, L. (1993). Assessing the aquatic hazard of some branched and linear nonionic surfactants by biodegradation and toxicity. *Environ. Toxicol. Chem.* 12, 1751-1762.
- ECETOC (1993). Environmental Hazard Assessment of Substances. Technical Report No. 51.
- ECETOC (1994a). Assessment of non-occupational exposure to chemicals. Technical Report No. 58.

- ECETOC (1994b). Environmental Exposure Assessment. Technical Report No. 61.
- ECETOC (1994c). HAZCHEM, a mathematical model for use in risk assessment of substances. Special Report.
- EEC (1991) EC Directive 91/271/EEC. Published in Official Journal of EEC. 30.5.91 Nr. L 135/40.
- EEC (1993). Commission Directive 93/67/EEC of 20 July 1993 laying down the principles for assessment of risks to man and the environment of substances notified in accordance with Council Directive 67/458/EEC. Off. J. of the European Communities L 227/9.
- EEC (1994a). Commission Regulation of laying down the principles for the assessment of risks to man and the environment of existing substances in accordance with Council Regulation (EEC) No 793/93/EEC.
- EEC (1994b). Technical guidance documents in support of the risk assessment directive (93/67/EEC) for substances notified in accordance with the requirements of Council Directive 67/548/EEC, Brussels.
- Evans, K.A., Dubey, S.T., Kravetz, L., Dzidic, I., Gumulka, J., Mueller, R., and Stork, J.R. (1994), Quantitative determination of linear primary alcohol ethoxylate surfactants in environmental samples by thermospray LC/MS. *Anal. Chem.* 66, 699-705.
- J.F. Fairchild et al. (1992). Evaluation of laboratory-generated NOECs for linear alkylbenzene sulphonate in outdoor experimental streams. *Environ. Toxicol. Chem.* 12, 1763-1775.
- Fax message from G.C. Mitchell, Shell Research Ltd. to E. v.d. Plassche, 20-05-1994 concerning a summary of Daphnia reproduction study with DOBANOL 25-9.
- Fax from M. Stalmans of Procter & Gamble to E. v.d. Plassche, 18-07-1994. Summary data sheet: test AES C_{12/15}-EO₃-S (Commercial mixture), *Scenedesmus subspicatus* in filtered Meuse and Bosbeek water.
- Fax from T. Feijtel of Procter & Gamble to E. v.d. Plassche, 16-05-1994. Measuring the chronic toxicity of AES compound to the freshwater rotifer *Brachionus calyciflorus*. Unpublished data Procter & Gamble, May 4, 1994.
- Feijtel, T.C.J., Matthijs E. , Rottiers A., Rijs G.B.J., Kiewit A., and A. De Nijs (1995). LAS Monitoring study in "de Meern" wastewater treatment plant and receiving river "Leidsche Rijn". *Chemosphere*, 30, 1053-1066.

- Games, L.M., King, J.E. and R.J. Larson (1982). Fate and distribution of a quaternary ammonium surfactant, octadecyltrimethyl ammonium chloride (OTAC), in wastewater treatment. *Environ. Sci. Technol.* 16: 483 - 488.
- Hennes, E.C. and R.A. Rapaport. (1989). Calculation and analytical verification of LAS concentrations in surface waters, sediment and soil. *Tenside Surfactants Detergents* 26: 141 - 147.
- Holysh, M., Paterson, S., Mackay, D., and M.M. Bandurraga (1986) Assessment of the environmental fate of linear alkylbenzenesulphonates. *Chemosphere* 15, 3-20.
- IPCS (1993). Environmental Health Criteria for linear alkylbenzene sulfonates (LAS) and related compounds - alkyl olefin sulfonates (AOS) and alkyl sulfates (AS). Draft August 1993. WHO, Geneva, Switzerland.
- Jonkers, D.A., and Everts, J.W. (1992). Seaworthy. Derivation of micropollutant risk levels for the North Sea and Wadden Sea. Publikatierreeks gebiedsgericht beleid. Zoetermeer.
- Kiewiet, A.(1995). Determination of nonionic surfactants in raw and treated sewage. In preparation.
- Kimerle, R.A. (1989). Aquatic and terrestrial ecotoxicology of linear alkylbenzene sulfonate. *Tenside Surf. Det.* 26, (2), 169-176.
- Könemann, W.H. (1981). Quantitative structure-activity relationships in fish toxicity studies. Part 1: relationship for 50 industrial pollutants. *Toxicology*, 19, 209-221.
- Larson, R.J. (1983). Comparison of biodegradation rates in laboratory screening studies with rates in natural waters. *Residue Rev.* 85: 159 - 171.
- Larson, R.J., Rothgeb, T.M., Shimp, R.J., Ward, T.E., and R.M. Ventullo (1993). Kinetics of biodegradation of linear alkylbenzene sulfonate (LAS) in the environment - A review. *J. Am. Oil Chemists Society* (in Press).
- Leeuwen, C.J. van, Zandt, P.T.J. van der, Aldenberg, T., Verhaar, H.J.M., and Hermens, J.L.M. (1992). Application of QSARs, extrapolation and equilibrium partitioning in aquatic effects assessment. I. Narcotic industrial pollutants. *Environ. Toxicol. Chem.* 11, 267-282.
- Leo, A.J., and Hansch, C. (1979). Substituent constants for correlation analysis in chemistry and biology. Wiley, New York.
- Letter of J. Blok (BKH Consulting Engineers) to E. v.d. Plassche, 02-02-1994 (reference 4505/Okk/tb).

- M.A. Lewis (1986). Comparison of the effects of surfactants on freshwater phytoplankton communities in experimental enclosures and on algal population growth in the laboratory. *Environ. Toxicol. Chem.* 5, 319-332.
- Lewis, M.A. (1990). Chronic toxicities of surfactants and detergent builders to algae: a review and risk assessment. *Ecotox. Environ. Saf.* 20, 123-140.
- Lewis, M.A. and B.G. Hamm (1986). Environmental modification of the photosynthetic response of lake plankton to surfactants and significance to a laboratory-field comparison. *Water Research.* 20, 1575-1582.
- Løkke, H. (1994). Ecotoxicological extrapolation: tool or toy? In: Donkers, M.H., H. Eijsackers and F. Heimbach (eds.). *Ecotoxicology of soil organisms*. pp. 411-425. SETAC Special Publication Series, Lewis Publishers.
- Maki, A.W. (1979). Correlations between *Daphnia magna* and fathead minnow (*Pimephales promelas*) chronic toxicity values for several classes of test substances. *J. Fish Res. Board Can.* 36, 411-421.
- Matthijs, E. and H. De Henau (1987). Determination of linear alkylbenzene sulphonate in aqueous samples, sediments, sludges and soils using HPLC. *Tenside Surfactants Detergents* 24, 4, 193-199.
- Matthijs, E., G. Debaere, N. Itrich, P. Masscheleyn, A. Rottiers, M. Stalmans, and T. Federle (1995). The behaviour of detergent surfactants in a raw sewage matrix. In press.
- Matthijs E., M. Holt, A. Kiewiet and G. Rijs (1996) Environmental Monitoring for Linear Alkylbenzene Sulphonate (LAS), Alcohol Ethoxylates (AE), Alcohol Ethoxy Sulphates (AES), Alcohol Sulphates (AS) and Soap. *Environmental Science Technology* (submitted)
- Measuring the chronic toxicity of AES compound to the freshwater rotifer *Brachionus calyciflorus*. Unpublished data Procter & Gamble, May 4, 1994.
- Moreno, A., Ferrer, J. and J.L. Berna (1990). Biodegradation of LAS in a sewer system. *Tenside Detergent Surfactants*, 27, 5, 312-315.
- Namkung, E. and B.E. Rittmann (1987). Estimating volatile organic compound emissions from publicly owned treatment works. *J. Wat. Pollut. Control Fed.* 59, 670-678.
- NVZ 1994a. Grondstoffen Enquete 1994. Consumentenprodukten.
- NVZ 1994b. Op weg naar minder milieubelastende wasmiddelen.

- OECD (1981). Guidelines for Testing Chemicals. Section 3. Degradation and Accumulation. Test Guidelines No 301 A, B, C, D, E. Paris.
- OECD Monograph No. 59 (1992). Report of the OECD workshop on the extrapolation of laboratory aquatic toxicity data to the real environment.
- Painter (1992). Anionic surfactants. In: Handbook of environmental chemistry (ed. O. Hutzinger). Vol. 3 Part F, anthropogenic compounds: Detergents. Volume editor: N.T. de Oude. p. 1-88. Springer-Verlag, Berlin.
- Popenoe, D.D., S.J. Morris, P.S. Horn and K.T. Norwood (1994) Determination of alkyl sulfates and alkyl ethoxysulfates in wastewater treatment plant influents and effluents and in river water using liquid chromatography/ion spray mass spectroscopy. *Anal. Chem.* 66, 1620-1629.
- RIVM, VROM, WVC (1994). Uniform System for the Evaluation of Substances (USES), version 1.0. National Institute of Public Health and Environmental Protection (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Welfare, Health and Cultural Affairs (WVC). The Hague, Ministry of Housing, Spatial Planning and the Environment, Distribution No. 11144/150.
- RIZA. (1989a). Jaarboek van Afvoeren, Waterstanden, Golven en Waterkwaliteit 1987. Dienst Binnenwateren/RIZA, Lelystad - Den Haag 1989.
- RIZA. (1989b). Kommunale Afvalwaterzuiveringsinrichtingen per waterkwaliteits-beheerder. Dienst Binnenwateren/RIZA. Ministerie van verkeer en waterstaat.
- Roberts, D.W. (1989). Aquatic toxicity of linear alkyl benzene sulphonates (LAS) - a QSAR analysis. In: J.E. Turner, M.W. England, T.W. Schultz and N.J. Kwaak (eds.). QSAR 88 Proc. Third Int. Workshop Quantitative Structure-Activity Relationships in Environmental Toxicology 22-26 May 1988, Knoxville, Tennessee, pp. 91-98.
- Roberts, D.W. (1991). QSAR issues in aquatic toxicity of surfactants. *Sci. Tot. Environ.* 109/110, 557-568.
- Saarikoski, J. and Veluksela, M. (1982). Relationship between physicochemical properties of phenols and their toxicity and accumulation in fish. *Ecotoxicol. Environ. Saf.* 6, 501-512.
- Schoeberl, P., Bock, K.J., and Huber, L. (1988). Ecologically relevant data on surfactants and cleansing agents. *Tenside Surf. Det.* 25, (2), 86-107.
- Shimp, R.J. and R.L. Young (1988) Availability of organic chemicals for biodegradation in settled bottom sediments. *Ecotoxicol. Environ. Saf.* 4, 31-45.

- Slooff, W., et al. (1992). RIVM guidance document. Ecotoxicological effect assessment: deriving Maximum Tolerable Concentrations (MTC) from single-species toxicity data. RIVM report No. 719102 018.
- Struijs, J., Stoltenkamp J. , and D. van de Meent (1991). A spreadsheet-based box model to predict the fate of xenobiotics in a municipal wastewater treatment plant. *Water Research* 25, 891-900.
- Tattersfield, L.J., M. Holt, G.M. Mitchell and N. Pearson (1994). Effects of DOBANOL 25-7 in outdoor artificial streams (Provisional study). May 1994.
- The Soap and Detergent Association (1991). Environmental and human safety of major surfactants - volume 1. Anionic surfactants - part 1. Linear alkylbenzene sulfonates. Final report by A.D. Little, Inc. Acorn Park, Cambridge, Massachusetts.
- Traina, S.J., McAvoy D., and D.J. Versteeg (1994). Association of LAS with dissolved Organic Matter. *Environ. Sci. Technol.* (in Press).
- Van Egmond R., S. Hambling and S. Marshall 1996. Chronic toxicity of sodium laurate to zebra fish (*Brachydanio rerio*). *Environ. Toxicol. Chem.* (submitted).
- Van Straalen, N.M. and C.A.J. Denneman (1989). Ecotoxicological evaluation of soil quality criteria. *Ecotox. Environ. Saf.* 25, 48-63.
- Versteeg D.J., Feijtel T.C.J., Cowan C.E., Ward T.E. and R. A. Rapaport (1993). An environmental risk assessment for DTDMAC in The Netherlands. *Chemosphere* 24:641-662.
- Wagner, C. and H. Løkke (1991). Estimation of ecotoxicological protection levels from NOEC toxicity data. *Wat. Res.* 25, 1237-1242.

Appendix 1. W-European consumption data

Table: Mean W-European consumption data of toilet products, fabric washing, dish cleaning and surface cleaning (AIS, 1994).

Products	Consumption (g/cap.day)
1. Toilet Products	
1.1. Toilet Soaps	1.6
1.2. Hard Soap	1.5
2. Fabric washing	
2.1. Washing powders	20
2.2. Washing liquids	4.0
2.3. Auxiliary products	0.6
2.4. Fabric rinsing products	7.0
3. Dish Cleaning	
3.1. Hand wash	7.0
3.2. Machine wash	1.6
4. Surface Cleaning	
4.1. General purpose	5.0
4.2. Lavatory cleaners	2.0
4.3. Special purpose	0.8
4.4. Scourers	1.5

Note:

1. European statistics indicate ± 50 g/cap.day of detergent and cleaning products. This corresponds well with the Dutch statistics.
2. European statistics indicate ± 7 g/cap.day of toilet and household soaps

The relative contribution of soap from shampoos, toilet, and household soaps is expected to match the contribution of household detergents, which partly explains the higher measured influent concentration. However, saponification of fats in sewers is expected to be the most significant source of the soap signal.

Appendix 2: Short term data for LAS C₁₀₋₁₃*

Short term data LAS C ₁₀₋₁₃				
	species	L(E)C50 (mg/l)	n	
algae	<i>Chlorella vulgaris</i>	5.8-20	2	
	<i>Microcystis aeruginosa</i>	0.9-32	5	
	<i>Microcystis spec.</i>	0.09	1	
	<i>Navicula pelliculosa</i>	1.4	1	
	<i>Nitzschia fonticola</i>	20	1	
	<i>Oocystis lacustris</i>	20	1	
	<i>Scenedesmus communis</i>	1	2	
	<i>Scenedesmus quadricauda</i>	60	1	
	<i>Scenedesmus subspicatus</i>	9-30	2	
	<i>Selenastrum capricornutum</i>	4.29-117	11	
	<i>Selenastrum spec.</i>	29	1	
	crustaceans	<i>Asellus spec.</i>	270	1
		<i>Balanus balanoides</i>	3-50	2
<i>Callinectes sapides</i>		29.9	2	
<i>Carcinus maenus</i>		100	1	
<i>Ceriodaphnia spec.</i>		5.3	1	
<i>Daphnia magna</i>		0.26-55	133	
<i>Daphnia pulex</i>		8.6	1	
<i>Daphnia spec.</i>		1.23-13.92	5	
<i>Eupagurus bernhardus</i>		100	1	
<i>Gammarus pulex</i>		1.5-36.6	24	
<i>Gammarus spec.</i>		3.3	1	
<i>Hyaella azteca</i>		3.5	1	
<i>Hyas areneus</i>		9-100	2	
<i>Leander adpersum</i>		50	1	
<i>Leander squilla</i>		100	1	
<i>Mysidopsis bahia</i>		1.3-3.6	5	
<i>Mysidopsis spec.</i>		1.4	1	
<i>Palaemonetas vulgaris</i>		13.85	1	
<i>Penaeus duorarum</i>		11-154	5	
<i>Simocephalus vetulus</i>		30	1	
insects	<i>Chironimus riparius</i>	6.5	1	
	<i>Paratanytarsus parthenogenica</i>	23	1	

molluscs	<i>Cardium edule</i>	15	1
	<i>Crassostrea virginica</i>	0.16-7.4	3
	<i>Mya arenaria</i>	70	1
	<i>Mytilus edulis</i>	100	1
	<i>Pecten maximus</i>	5	1
worms	<i>Dero spec.</i>	1.7	1
	<i>Dugesia spec.</i>	1.8	1
	<i>Limnodrilus hoffmeisteri</i>	0.96-1.8	3
	<i>Planaria</i>	1.8	1
	<i>Rhaditis spec.</i>	16	1
fish	<i>Brachydanio rerio</i>	0.6-5.1	2
	<i>Carassius auratus</i>	1.1-76	45
	<i>Carassius spec.</i>	8.5	1
	<i>Catostomus commersoni</i>	4	1
	<i>Chrystipera hollisi</i>	1.3	1
	<i>Cichlasoma nigrofasciatum</i>	5.1	1
	<i>Cyprinodon variegatus</i>	1.4-3.5	2
	<i>Cyprinus carpio</i>	5.0-5.4	2
	<i>Esox lucius</i>	3.7	1
	<i>Fundulus heteroclitus</i>	2.4	2
	<i>Gadus morrhua</i>	1.0-1.6	2
	<i>Heteropneustes fossilis</i>	9.8	1
	<i>Jordanella floridae</i>	8.6	1
	<i>Lepomis macrochirus</i>	0.25-30.3	84
	<i>Leuciscus idus melonatus</i>	0.26-16.6	11
	<i>Micropterus dolomieu</i>	3.7	1
	<i>Oryzias latipes</i>	5.9-70	4
	<i>Phoxinus spec.</i>	6.2	1
	<i>Pimephales promelas</i>	0.40-100	34
	<i>Pleuronectes flesus</i>	1.5	1
	<i>Pleuronectes platessa</i>	1	1
	<i>Poecilia reticulata</i>	1.0-50	9
	<i>Oncorhynchus mykiss</i>	0.85-7.8	10
	<i>Oncorhynchus spec.</i>	1.7	1
	<i>Salvelinus alpinus</i>	5	1
	<i>Tilapia melanopleura</i>	4.8-23	3
	<i>Tilapia mossambica</i>	1.5	1
plants	<i>Chara hispida</i>	1	1
	<i>Elodea canadensis</i>	1	1
	<i>Lemna minor</i>	2.5	1
amphibia	<i>Xenopus laevis</i>	5.6	1

Appendix 3: Long term data for LAS.

	species	chain length	NOEC (mg/l)	normalized NOEC LAS C _{11.6} (mg/l)
bacteria	<i>Pseudomonas putida</i>	11.8	30	35
algae	<i>Chlamydomonas reinhardi</i>	11.2	15	12
	<i>Chlorella kessleri</i>	11.8	3	3.5
	<i>Microcystus spec.</i>	11.8	0.05	0.058
	<i>Plectonema boryanum</i>	11.2	20	15
	<i>Scenedesmus subspicatus</i>	11.6	0.8	0.8
	<i>Scenedesmus subspicatus</i>	11.8	90	105
	<i>Selenastrum spec.</i>	11.8	0.5	0.58
	<i>Selenastrum capricornutum</i>	12.3	0.5	1.0
crustaceans	<i>Ceriodaphnia spec.</i>	11.7	3	3.2
	<i>Daphnia magna</i>	11-13	4.2	
	<i>Daphnia magna</i>	11.6	0.3	0.3
	<i>Daphnia magna</i>	11.8	0.3	0.35
	<i>Daphnia magna</i>	11.8	1.18	1.4
	<i>Daphnia magna</i>	11.8	1.2	1.4
	<i>Daphnia magna</i>	11.8	1.25	1.5
	<i>Daphnia magna</i>	12	4.9	6.6
	<i>Daphnia magna</i>	12.6	0.9	1.9
	<i>Daphnia magna</i>	13	0.8	2.3
	<i>Daphnia magna</i>	13.3	0.6	2.1
	<i>Daphnia magna</i>	LAS	10	
	<i>Daphnia spec.</i>	LAS	0.63	
	<i>Daphnia spec.</i>	LAS	1.63	
	<i>Mysidopsis bahia</i>	11.4	0.4	0.34
	<i>Mysidopsis bahia</i>	13.1	0.04	0.13
insecta	<i>Chironomus riparius</i>	11.8	2.4	2.8
	<i>Paratanytarsus parthenogenica</i>	LAS	3.4	
mollusca	<i>Crassostrea virginica</i>	LAS	0.025	
	<i>Mytilus edulis</i>	LAS	0.025	

fish	<i>Brachydanio rerio</i>	11.8	2	2.3
	<i>Limanda yokohamae</i>	LAS	0.05	
	<i>Pimephales promelas</i>	11	7.2	4.8
	<i>Pimephales promelas</i>	11.2	5.1	3.9
	<i>Pimephales promelas</i>	11.7	0.28	0.30
	<i>Pimephales promelas</i>	11.7	0.48	0.52
	<i>Pimephales promelas</i>	11.7	1.02	1.1
	<i>Pimephales promelas</i>	12	1.08	1.5
	<i>Pimephales promelas</i>	13	0.12	0.34
	<i>Pimephales promelas</i>	13.3	0.11	0.39
	<i>Pimephales promelas</i>	LAS	0.5	
	<i>Pimephales promelas</i>	LAS	0.5	
	<i>Pimephales promelas</i>	LAS	0.63	
	<i>Pimephales promelas</i>	LAS	0.7	
	<i>Pimephales promelas</i>	LAS	1	
	<i>Pimephales promelas</i>	LAS	2	
	<i>Poecilia reticulata</i>	LAS	3.2	
	<i>Oncorhynchus mykiss</i>	11-13	0.23	
	<i>Oncorhynchus mykiss</i>	11-13	0.3	
	<i>Oncorhynchus mykiss</i>	11-13	0.35	
	<i>Oncorhynchus mykiss</i>	11-13	0.43	
	<i>Oncorhynchus mykiss</i>	11-13	0.89	
	<i>Oncorhynchus mykiss</i>	11.8	0.3	0.35
	<i>Oncorhynchus mykiss</i>	12	0.12	0.19
	<i>Tilapia mossambica</i>	LAS	0.25	

Appendix 4: QSARs for long term toxicity according to Van Leeuwen et al. (1992).

species	QSAR (NOEC expressed as mol/l)
<u>bacteria</u>	
<i>Pseudomonas putida</i>	$\log \text{NOEC} = -0.64 \log K_{ow} - 1.60$
<u>algae</u>	
<i>Scenedesmus subspicatus</i>	$\log \text{NOEC} = -0.86 \log K_{ow} - 1.41$
<i>Selenastrum capricornutum</i>	$\log \text{NOEC} = -1.00 \log K_{ow} - 1.71$
<u>arthropods</u>	
<i>Daphnia magna</i>	$\log \text{NOEC} = -1.04 \log K_{ow} - 1.70$
<u>fish</u>	
<i>Pimephales promelas</i>	$\log \text{NOEC} = -0.87 \log K_{ow} - 2.35$
<i>Brachydanio rerio</i>	

Appendix 5: Long term data for AE.

record	chain length	EO	species	NOEC (mg/l)	normalized NOEC (mg/l) C _{13.3} EO _{8.2}
318	14.5	6	M. aeruginosa	0.30	1.9
319	14.5	6	N. pelliculosa	0.14	0.93
321	14.5	6	N. seminulum	2.5	16
320	14.5	7	N. seminulum	0.50	2.4
322	14.5	7	N. seminulum	3.5	17
328	11	5	S. capricornutum	1.65	0.37
330	13	7	S. capricornutum	1.9	1.9
327	13.5	9	S. capricornutum	0.60	0.58
325	13	3	S. subspicatus	0.56	1.9
326	13	3	S. subspicatus	1	3.4
323	13	7	S. subspicatus	0.52	0.53
324	13	8	S. subspicatus	0.56	0.43
375	13.5 (*)	3	S. subspicatus	0.32	1.9
376	14 (*)	7	S. subspicatus	0.56	0.43
P&G	12	3	B. calyciflorus	1.04	1.3
373	10	5	C. vulgaris	1.9	0.15
374	10	5	C. vulgaris	3.2	0.26
332	14.5	7	C. sapidus	10	48
333	14.5	7	C. dubia	0.085	0.41
334	14.5	7	C. dubia	0.35	1.7
335	14.5	7	C. dubia	0.20	0.99
336	14.5	7	C. dubia	0.17	0.81
345	12	9	D. magna	0.50	0.10
339	12.5	7	D. magna	0.24	0.15
343	12.5	7	D. magna	0.24	0.15
341	13	3	D. magna	0.18	0.64
344	13	7	D. magna	0.30	0.31
380	13.5	3	D. magna	0.32	1.9
Dorn et al.	13.5	9	D. magna	1	0.99
348	13.5	9	D. magna	1	0.99
379	14	7	D. magna	0.32	0.93
SHELL	14	9	D. magna	0.14	0.23
349	14	10	D. magna	3	3.9
342	14.5	7	D. magna	0.24	1.2
340	14.5	7	D. magna	0.24	1.2
352	14.5	7	P. duorarum	0.56	2.7
364	15	10	M. edulis	1.5	5.5
353	13	3	B. rerio	1	3.4
354	13	7	B. rerio	0.67	0.7
355	14.5	7	F. heteroclitus	1	4.8
382	13 (*)	7	P. promelas	1	1.0

362	13	7	P. promelas	0.32	0.32
363	14	9	P. promelas	0.40	0.64
360	14.5	7	P. promelas	0.18	0.87
361	14.5	7	P. promelas	0.23	1.1
365	14	10	D. gonocephala	0.13	0.17
366	14	10	N. humilis	0.13	0.17
(*) = branched					

Appendix 6: Data for AES.

In this Appendix short and long term data for AES are summarized. The majority of the data are taken from the BKH-report (1994). Results from standard test durations are preferred: 96 hr EC50 values for algae, 48 hr EC50 values for *Daphnia magna* and 96 hr LC50 values for fish.

Table 1. Short term data (in mg/l)

test species	L(E)C50 (mg/l)	number of values
<i>Selenastrum capricornutum</i>	3.5-10	2
<i>Daphnia magna</i>	4.2-72	9
<i>Daphnia pulex</i>	20.2	1
<i>Penaeus duorarum</i>	350	1
<i>Crassostrea virginica</i>	9	1
<i>Brachydanio rerio</i>	1.9-3.1	3
<i>Carassius auratus</i>	2.1-3.8	3
<i>Cichlasoma nigrofasciatum</i>	2.5-3.1	3
<i>Cyprinodon variegatus</i>	0.39-25	5
<i>Lepomis macrochirus</i>	1.11-74.5	4
<i>Leuciscus idus melonatus</i>	4.5-10	2
<i>Oncorhynchus mykiss</i>	1.9-94.4	9
<i>Oryzias latipes</i>	10-68	3
<i>Pimephales promelas</i>	0.7-13	8
<i>Poecilia reticulata</i>	2.1-2.4	3
<i>Rasbora heteromorpha</i>	3.9	1
<i>Salmo trutta</i>	1.5-1.6	2

EC50 values for *Selenastrum capricornutum* are 3.5 and 10 mg/l. As stated in the BKH-report these values are not corrected for active matter content. Based on information from SHELL these values are corrected for 70% a.i. (pers. comm. R. Stephenson) and converted to a NOEC by dividing the EC50 by 3. Normalized NOEC values are 1.0 and 2.1 mg/l, respectively.

The other values in the BKH-report (1994) are considered unreliable as the exposure time is unknown or considered too long for a static test with AES, i.e. 14 days.

Table 2. Long term data (in mg/l)

test compound	CL	EO	test species (mg/l) (mg/l)	NOEC	parameter
fatty alcohol ether sulfate C12-14 + 2EO	12-14	2	<i>Scenedesmus subspicatus</i>	0.35	growth
C12/15, E3	12-15	3	<i>Scenedesmus subspicatus</i>	2.24	growth
C12/15, E3	12-15	3	<i>Scenedesmus subspicatus</i>	1.6	growth
C14-15 ethoxylate sulfate	14-15	2.25 ^a	<i>Selenastrum capricornutum</i>	21	growth
A12-13 ethoxylate sulfate	12-13	2.25 ^a	<i>Selenastrum capricornutum</i>	50.5	growth
C12, E2S	12	2	<i>Brachionus calyciflorus</i>	0.97	biomass
C12, E4S	12	4	<i>Brachionus calyciflorus</i>	2.26	biomass
C13, E2S	13	2	<i>Brachionus calyciflorus</i>	0.49	biomass
NaC14/15, E2.25S	14-15	2.25	<i>Daphnia magna</i>	0.18	reproduction
fatty alcohol ether sulfate C12-14 + 2EO	12-14	2	<i>Daphnia magna</i>	0.70	reproduction
C14/16, E2.25S	14.67	2.25	<i>Daphnia magna</i>	0.27	reproduction
C14/16, E2.25S	14.67	2.25	<i>Pimephales promelas</i>	0.10	growth
C17, E3S	17	3	<i>Pimephales promelas</i>	0.13	growth
C12/13, E1S	12-13	1	<i>Pimephales promelas</i>	0.88	growth

^a estimate

Appendix 7: Data for soap.

In this Appendix short and long term data for soap are summarized. The majority of the data are taken from the BKH-report (1994). Only, if data are present for the same organism and the same test compound a geometric mean is calculated. All values are based on nominal concentrations.

Soaps with unspecified chain length.

Table 1. Short term data: L(E)C50 values in mg/l

bacteria	134	
green algae	240	
blue algae		24
crustaceans	10, 42	
insects	4233 ^a	
fish	6.7, 20 ^b , 423, 1342 ^a	
amphibians	423	

^a above water solubility

^b unknown fish species

Long term data: NOEC values in mg/l

algae	10 ^a
crustaceans	10 ^b

^a growth measured as biomass; species not given by the authors, probably *Microcystis aeruginosa*

^b mortality; no effects on reproduction at concentrations >10 mg/l

Soaps with a chain length of C₁₂-C₁₄.

Table 3. Short term data: L(E)C50 values in mg/l

bacteria	8.8
green algae	53
crustaceans	3.3 ^a , 5.4, 32, 48
fish	11, 42, 63, 118

^a geometric mean of two EC50 values for *Daphnia magna* of 2 and 5.4 mg/l determined for lauric acid

Soaps with a chain length of C₁₆-C₁₈.

Table 4. Short term data: L(E)C50 values in mg/l

bacteria	250
green algae	58, 140, 190
crustaceans	4.2, 25, 40, 88, 160
fish	0.6 ^a , 12, 12, 67, 125, 150, 205, 217

^a geometric mean of five 96 h acute LC50 values (0.1, 0.5, 0.6, 1.4 and 2.1 mg/l) for *Oncorhynchus mykiss* tested at pH values of 6.6-7.8, hardness of 9-32 mg CaCO₃/l and temperatures of 7-17 °C. Test compound is oleic acid and a solvent is used (amount unknown).

Appendix 8: MPCs based on different extrapolation methods.

MPC (µg/l)	Aldenberg and Slob	Wagner and Lokke	EPA triangular	EPA assessment factors	EU assessment factors
LAS	320	330	200	25	25
AE	110	120	100	17	17
AES	400	410	-	48	48
soap	-	-	-	27	2.7

Appendix 9: Summary of results from field studies with LAS from BKH (1993a).

Table 2 Best estimated NOECs derived from multispecies studies with microorganisms. A(nalyzed) or N(ot analyzed), test period, number of test concentrations*number of replicates + or - criterion fulfilled or not, n.r. not relevant, 0 no data, ? relation not clear

System used	Taxonomic groups	Effect parameter S(truct.)/F(unctional)	Best estimated		spec. LAS	Susp.solids measured	Conc./effect relation	Continuous dosing	Ref.
			NOEC	LOEC (mg/l)					
Aquaria (19 l) well water N, 28d, 4*2	bacteria	LAS degradation rate inhibition F	0.5	5.0	CL _{11,6}	n.r.	+	+	Maki, 1981 & Larson and Maki, 1982
Aquaria (19 l) LAS in effluent N, 26d, 4*2	bacteria	LAS degradation rate inhibition F	> 5.0 ¹⁾	-		n.r.	+	+	
Respirometer N, -, 6*2	bacteria	O ₂ consumption rate F	20	40	CL _{11,6}	n.r.	+	n.r.	Maki, 1982 & Larson and Maki, 1982
Bottles (300 ml) held in lake 3 h. A, 3h(6months), 9*3	phytoplankton	photosynthetic response F	0.09	0.87	CL _{11,8}	-	+	-	Lewis and Hamm, 1986
Bottles (26 l) held in lake A, 10d, 6*3	phytoplankton	relative abundance S similarity index S	0.24 27	0.8 108	CL _{11,8}	-	?	-	Lewis, 1986
River above a WWTP A, 21d, 4*3	periphyton	photosynthesis and F number of taxa S	1.1 1.1	9.8 9.8	CL _{11,9}	+	+	+	Lewis et al., 1991
River below a WWTP A, 21d, 4*3	periphyton	photosynthesis and F number of taxa S	9.8 ²⁾ >28.1	28.1	CL _{11,9}	+	+	+	
Beakers (100 ml) -, 21d, -	bacteria algae protozoans small multi- cellular org.	composition and individual numbers S	0.3	0	0	0	0	+	Guhl and Gode, 1989

¹ Effluent from laboratory Continuous Activated Sludge Unit (no details reported), 4-30% sewage concentrations.

² River water contained 20 to 30% effluent (with 6.4 mg s.s./l).

Table 3 Best estimated NOECs derived from ecosystem studies. A(nalyzed) or N(ot analyzed), dose interval, test period, number of test concentrations*number of replicates

System used	Taxonomic groups	Effect parameter	S(truct.)/F(unctional)	Best estimated		spec. LAS	Ref.
				NOEC	LOEC (mg/l)		
Aquaria (19 l) with sediment well water A, cont. dosing 28d, 4*2	bacteria periphyton plants daphnids midge bluegill	biomass production growth, reproduction reproduction ³⁾ development, growth growth	F	>4.0 >4.0 >4.0 no NOEC ³⁾ 2.0 1.0	4.0 2.0	CL _{11,9}	Maki, 1981 & Larson and Maki, 1982
Aquaria (19 l) with sediment effluent ¹⁾ water A, cont. dosing, 28d, 4*2	bacteria periphyton plants daphnids midge bluegill	biomass production ⁴⁾ growth, reproduction ⁴⁾ reproduction ³⁾ development, growth ⁵⁾	F	>4.0 no NOEC ⁴⁾ no NOEC ⁴⁾ 15% = 1-2 mg/l no NOEC ⁵⁾ <3.75% = 0.2-0.5 mg/l	30%		
Outdoor vats 60 l 1985 well water N, dosing 6* at 15 d intervals 90d, 4*5	phytoplankton rotifers chironomid zooplankton	primary productivity population density numbers, wet weight population density	S, F	0.25-0.38 n) ≤0.25 0.38	0.51 0.51 0.38 0.51	Parnol J.liquid 20% a.i.	Chattopadhyay and Konar,
Outdoor headwater streamsystems (3 * 50 m) A, dosing 8* at 7 d intervals 45d, 1*3	periphyton detritus invertebrates snails amphipods fish	growth degradation rate population, community effects density survival growth, survival	F >0.36	>0.36 >0.36 >0.36 no NOEC ≤0.36	0.36	CL _{11,9}	Fairchild et al., 1992
Outdoor pond with compartments with sediment (3 * 700 l) A, 7) 56d + 1yr, 2*1	phytoplankton plants cyclopodia cladocera	photosynthesis, chlorophyll species number, composition egg production development	S, F S	slightly below 5 10 3,5 5	10 5 10	CL ₁₂ ?	Huber et al., 1987

¹ Effluent from laboratory Continuous Activated Sludge Unit (no details reported), 4-30% sewage concentrations.

³ In the controls survival of daphnids was poor and no offspring was produced.

⁴ Overgrown by bacteria and fungi.

⁵ Strongly reduced survival due to low oxygen concentrations and high level of suspended solids.

⁶ A clear reduction of numbers was observed at 0.51 mg/l. Numbers were also reduced at 0.25 and 0.38 mg/l, but the author did not state whether these reductions were significant.

⁷ Dosed according to need.