Pergamon

Marine Pollution Bulletin Vol. 42, No. 8, pp. 635–642, 2001

Printed in Great Britain

PII: S0025-326X(01)00061-3

0025-326X/01 $ - see front matter

Marine Risk Assessment: Linear Alkylbenzenesulponates (LAS) in the North Sea

ALI TEMARA†*, GREG CARR‡, SIMON WEBB†, DONALD VERSTEEG§ and TOM FEIJTEL§

†*Environmental Safety, European Technical Center, The Procter & Gamble Company, Brussels, Belgium*

‡*Statistics Department, Miami Valley Laboratory, Cincinnati, USA*

§*Environmental Science Department, Miami Valley Laboratory, Cincinnati, USA*

The fate of linear alkylbenzenesulponates (LAS) in estuaries and coastal areas of the North Sea has been characterized with simple environmental models. The predicted concentration range in the estuaries around the North Sea (0.9–9 μg LAS l^{-1}) was validated by monitoring data (1–9 μg LAS l^{-1}). In offshore sites of the North Sea, it is estimated – and experimentally verified for a few sites – that the LAS concentration is below analytical detection limit (i.e., 0.5 μg LAS l^{-1}). The effects of LAS on marine organisms have been reviewed. For short-term acute tests, there was no significant difference ($p = 0.83$) between the mean LC_{50} values of freshwater and marine organisms (mainly pelagic species tested, 4.1 and 4.3 mg LAS l^{-1}, respectively). For longer-term chronic tests, it appeared that the sensitivity (mean no-observed effect concentration (NOEC) value) of marine and freshwater organisms (0.3 and 2.3 mg LAS l^{-1}, respectively) was significantly different ($p_{t\text{-test}} = 0.007$). The predicted no-effect-concentrations (PNEC) were 360 and 31 μg LAS l^{-1}, for freshwater and marine pelagic communities, respectively. Given that the maximum expected estuarine and marine concentrations are 3 to >30 times lower than the PNEC, the risk of LAS to pelagic organisms in these environments is judged to be low.

Introduction

Surfactants are the major active ingredients of laundry detergents. During the washing process, they lower the surface tension of water. They loosen and release stains and soils from fabrics. Historically, the first surfactant used in laundry cleaning was soap (mixture of animal fats and ashes) whose preparation is described in antique Roman manuscripts. Soap is not stable in hard or acid waters (Modler *et al*., 1993). It readily precipitates with divalent metal ions and is thus only soluble in alkaline soft waters (Lomax, 1997). Other surfactants, including anionic, cationic, non-ionic, and amphoteric surfactants, have been developed to improve cleaning performance. linear alkylbenzenesulponates (LAS) (Fig. 1) is the major anionic surfactant currently on the global market.

LAS is composed of a linear alkyl chain consisting of 10–14 carbon atoms, a benzene ring, and a sulponate group. C12 LAS has a molecular weight of 342. In commercial LAS, the alkyl chain includes on average 11.7 carbon atoms. The benzene ring is randomly distributed in all positional isomers except the 1-phenyl and the sulponate group is in *para* position. LAS is readily biodegradable in aerobic conditions. The global production of LAS is 2.2×10^6 t yr^{-1} (see Larson and Woltering, 1995).

Formal environmental risk assessments of LAS have been published in freshwater environments and the risk of adverse effects on aquatic organisms is characterized as low (Fendinger *et al*., 1994; Plassche van de *et al*., 1999; Versteeg *et al*., 1999).

LAS is used in the present study as an ingredient to demonstrate a possible approach to marine ecological risk assessment for readily biodegradable, high production volume chemicals. Technical procedures for marine risk assessments are currently under development in the European Union and by the Oslo and Paris Commissions (OSPARCOM). The North Sea is one of the semi-closed seas that OSPARCOM aims at protecting.

The predicted no-effect-concentrations (PNEC) proposed here has been derived by probabilistic analysis, aiming at protecting the community and is based on data obtained from single species. The test organisms provided a good representation of the biodiversity in marine communities with species of macro- and microalgae, polychaetes, crustaceans, molluscs, echinoderms, urochordates, and teleosts. Moreover, most species are well distributed in the North Sea and some (e.g., *Asterias rubens*) are considered keystone predators in marine

*Corresponding author.

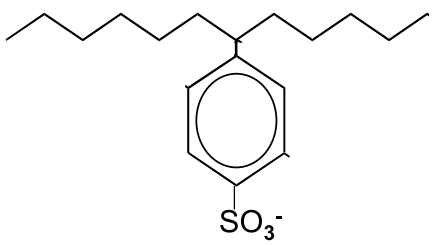

Fig. 1 Linear alkylbenzenesulponate (LAS), molecular structure.

benthic communities (Sloan, 1980). According to Temara *et al*. (1999), keystone species should be included as surrogate species used to derive the sensitivity of environmental communities. The present study focuses on the environmental risk of LAS (parent compound) in the water column.

Method

Predicted environmental concentration (PEC) of LAS in the North Sea

LAS environmental concentrations were predicted from per capita LAS use (2.5 g LAS cap^{-1} day^{-1} in Western Europe; Feijtel and van de Plassche, 1995), water treatment, and population estimates for western Europe (NSTF, 1993). Coverage of wastewater treatment in the North Sea drainage area is described in Table 1. In this region, 17% of the water is not treated, 16% of the water is treated by a primary treatment, 67% of the water is treated by at least a secondary treatment (Mance, 1993; OECD, 1995). Data on removal during primary (i.e., 27%, Rapaport and Eckhoff, 1990) and secondary treatment (i.e., 97%, Rapaport and Eckhoff, 1990; Feijtel *et al*., 1999) were included in the algorithm to assess release of LAS into surface waters. The total quantity of LAS released to surface waters in the North Sea drainage area was calculated by

$$R_{(\mathrm{LAS})} = (\mathrm{TQ} * \mathrm{F1T} * (1 - R_1)) + (\mathrm{TQ} * \mathrm{F2T} * (1 - R_2)) + (\mathrm{TQ} * \mathrm{FNT}), \quad (1)$$

where $R_{(\mathrm{LAS})}$ is the total quantity of LAS released into surface waters in the North Sea drainage area, TQ the total quantity of LAS used in the North Sea drainage area, F1T the fraction of wastewater treated by primary treatment in the North Sea drainage area (i.e., 0.16, see Table 1), F2T the fraction of wastewater treated by at least a secondary treatment in the North Sea drainage area (i.e., 0.67, see Table 1), R_1 the removal in primary wastewater treatment plant (i.e., 0.27, Rapaport and Eckhoff, 1990), R_2 the removal in secondary wastewater treatment plant (i.e., 0.97, Rapaport and Eckhoff, 1990; Plassche van de *et al*., 1999), FNT is the fraction of wastewater not treated in the North Sea drainage area (i.e., 0.17, see Table 1).

Predicted initial concentrations of LAS (i.e., C_0) in surface waters of the North Sea were estimated by a simple dilution model that included the consumer population in the North Sea drainage area, the distribution and the types of wastewater treatment plants, the quantity of LAS released (R_{LAS}), the usage of water (average: 239 l cap^{-1} day^{-1}) (Water UK, 1998), and the dilution factors according to EEC (1997). In-stream removal was estimated by a steady-state stream model (Eq. (2)) applicable to first-order decaying substances.

$$C = C_0 * \exp^{-kt}, \quad (2)$$

where k is the 0.06 h^{-1} (Fox *et al*., 1999; Boeije *et al*., 2000), t the average residence time of surface water in the North Sea drainage area (60 h, calculated from Eurostat, 1995), C_0 the concentration before decay, C is the concentration after residence in rivers.

Effect of LAS on marine organisms

Short-term acute toxicity endpoints (Lethal Concentration to 50% of the population – LC_{50} values) related to freshwater and marine organisms exposed to LAS

TABLE 1

Estimated population in the North Sea drainage area (10^6 people, data from NSTF, 1993), description of the water treatment (10^6 people, calculated from Mance, 1993; OECD, 1995), and estimated LAS consumption (t yr^{-1}, Plassche van de *et al*., 1999).[a]

Country	Popul. (10^6 people)	Untreated (10^6 people)	1ary treatment (10^6 people)	2ary treatment (10^6 people)	LAS consumption (t yr^{-1})
Belgium and Luxembourg	10	3.6	2.9	3.5	9125
Czech and Slovak Republics	5	1.7	0.0	3.3	4563
Denmark	2	0.0	0.4	1.6	1825
France	20	0.0	7.0	13	18 250
Germany	70	9.8	6.3	54	63 875
Netherlands	16	1.6	1.4	13	14 600
Norway	3	1.3	0.39	1.3	2738
Sweden	3	0.2	0.0	2.8	2738
Switzerland	5	2.2	0.65	2.2	4563
United Kingdom	30	7.8	6.9	15.3	27 375
Total	164	28	26	110	149 650

[a] Popul.: Population in the drainage area. Untreated: Equivalent number of people using water that is not treated. 1ary treatment: Equivalent number of people using water that is treated by a primary treatment. 2ary treatment: Equivalent number of people using water that is treated by at least a secondary treatment.

were obtained from BKH (1994). The marine taxa in the BKH database included: algae, molluscs, crustaceans, echinoderms, tunicates, and fishes. Genera and environmental habitats of the tested life-stages are described in Table 2. These data were used to compare the relative sensitivity of freshwater and marine organisms. Mean LC_{50} values were calculated for the three classical groups of organisms, namely fishes, crustaceans, and algae, used by risk assessors (EEC, 1997) and compared between freshwater and marine organisms. Chronic toxicity endpoints (no-observed effect concentration (NOEC) values) for freshwater and marine organisms exposed to LAS were obtained from various sources presented below. When NOEC values were not presented in the original publications, they were derived from illustrations in the original references. NOEC values of freshwater organisms were reported in Plassche van de *et al*. (1999) and were normalized to an LAS alkyl chain length of 11.6 (Plassche van de *et al*., 1999). NOEC values for marine organisms are referred to commercial (C10–C14 alkyl chain length distribution with carbon number averaging 11.7) or average alkyl chain lengths of 11.6–12. The various NOEC values were used to compare the sensitivity of the organisms in the two communities (freshwater and marine) and to derive a preliminary marine PNEC for LAS.

Statistical analyses

Sensitivity (LC_{50} values) of marine and freshwater species exposed to LAS in acute tests was compared using two-sample *t*-tests. To remove the statistical influence of unequal representation of test species, the mean LC_{50} values were calculated for each species and the mean LC_{50} values were subsequently analysed statistically. To remove the statistical influence of unequal representation of tested congeners, some statistical analyses were limited to LAS having average alkyl chain lengths of 11.7–12, i.e., the commercially relevant congeners. The significance of the effect of the LAS alkyl chain length on toxicity towards freshwater organisms was assessed by an analysis of covariance (ANCOVA). The relative paucity of short-term acute toxicity data for marine organisms did not allow a similar comparison for the marine organisms. *t*-test and ANCOVA analyses were carried out on the log 10 transformed data.

The probabilistic approach of Aldenberg and Slob (1993) was used to estimate a PNEC of LAS in marine communities. The 95th percentile of the log-logistic distribution of marine NOEC values was calculated according to Van Straalen and Denneman (1989) with the PNEC set at the 50% confidence level of the 95th percentile, as recommended by Plassche van de *et al*. (1999). The geometric mean of NOEC values of different species of a single genus was used for the probabilistic assessment of the PNEC (Plassche van de *et al*., 1999).

TABLE 2

Ecological distribution of marine tested life-stages.[a]

Genus	Ecological distribution of tested life-stages	Ref.
Laminaria	Pelagic	1
Botrylloides	Benthic	2
Molgula	Pelagic	3
Spisula	Pelagic	3
Botryllus	Benthic	2
Arbacia	Pelagic	3
Chaetopterus	Pelagic	3
Asterias	Pelagic	3
Arcatia	Benthic	4
Mysidopsis	Pelagic and Benthic	5, 6
Dunaliella	Pelagic	7
Limanda	Pelagic	5
Crassostrea	Pelagic	6, 8
Mytilus	Pelagic and Benthic	6, 9

[a] References: 1: Pybus (1973); 2: Marin *et al*. (1991); 3: Moffet and Grosch (1967); 4: Kusk and Petersen (1997); 5: Plassche van de *et al*. (1999); 6: BKH (1994); 7: Unpublished data; 8: Calabrese and Davis (1967); 9: Granmo (1972).

Results

PEC of LAS in the North Sea

The national consumptions within the North Sea drainage area are presented in Table 1. Approximately 1.5×10^5 t of LAS are consumed on a yearly basis in the North Sea drainage area with Germany and the U.K. accounting for approximately 60% of the usage (Table 1). Of this quantity, 4.6×10^4 t LAS yr^{-1} ($R_{(LAS)}$) are released to surface waters in the drainage area (Eq. (1)). This LAS undergoes further biodegradation flowing downstream to the estuaries. From Eq. (2) above, the predicted concentration in rivers entering estuaries around the North Sea was 8.8 μg LAS l^{-1} (C of Eq. (2)). Using a conservative dilution factor of 10, concentrations at the marine end of the estuaries would be 0.9 μg LAS l^{-1}. This concentration (0.9 μg LAS l^{-1}) may also be considered a preliminary conservative PEC of LAS in coastal areas of the North Sea until a more realistic dilution factor is assessed, or more monitoring data are available.

Effect of LAS on marine communities

LAS toxicity to freshwater and marine organisms was affected by alkyl chain length and exposed species. The effect of the alkyl chain length on the toxicity of LAS congeners toward freshwater fishes and crustaceans was significant ($p_{ANCOVA} =< 0.0001$). The chain length term of the ANCOVA model accounted for 67% of the variation explained collectively by environment, species, and chain length terms used in the ANCOVA model. In contrast, there was no significant effect of alkyl chain length on the toxicity of LAS congeners toward freshwater algae ($p > 0.5$). In a two-sample *t*-test using all data in the alkyl chain length interval 11.7–12, there was no significant difference in LC_{50} values between freshwater and marine species ($p = 0.83$, Table 3). Taxon-stratified data were compared (Table 3). In these analyses, the mean LC_{50} value of marine fishes

TABLE 3
Comparisons between freshwater (FW) and marine (Mar) LAS LC_{50} values.[a]

	All spp		Fishes		Crustaceans		Algae	
	FW	Mar	FW	Mar	FW	Mar	FW	Mar
Mean (Log)	0.61	0.64	0.56	0.20	0.97	1.23	0.93	−0.11
SD (Log)	0.75	0.79	0.53	0.16	0.50	0.68	0.75	0.58
Mean	4.07	4.36	3.63	1.58	9.33	17.0	8.51	0.77
n	72	36	31	6	13	14	19	2
p	0.83		0.004		0.26		0.07	
Statistical test	2 sample *t*-test		2 sample *t*-test for unequal variances		2 sample *t*-test		2 sample *t*-test	
Alkyl chain	11.7–12 C range		11.7–12 C range		All congeners range[b]		All congeners range[b]	

[a] SD: standard deviation of the statistical tests. *p*: probability of the test. Units of concentrations are log 10 or back-transformed (mg l^{-1}).
[b] Toxicity data of C10–C14 LAS.

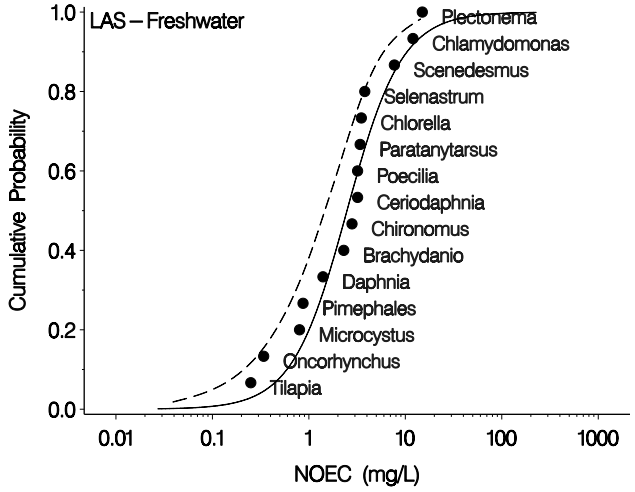

Fig. 2 Cumulative probability of NOEC values (solid dots) of freshwater organisms with fitted log-logistic distribution (solid line). The lower 95% confidence limit of the distribution percentiles is shown (dashed line). NOEC values are from Plassche van de *et al.* (1999) and are given for comparison purposes with Fig. 3 (i.e., marine organisms).

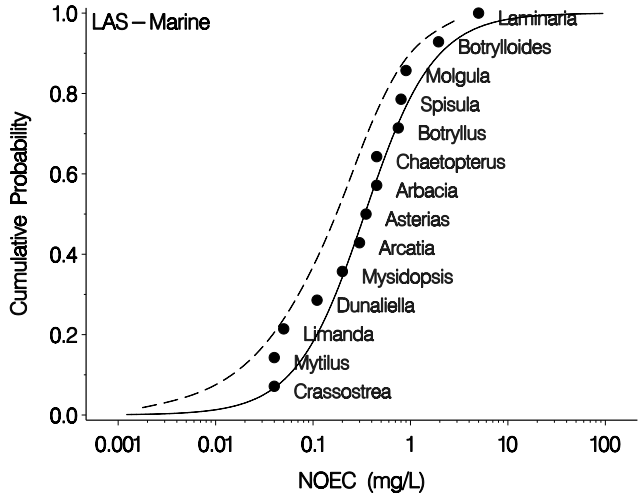

Fig. 3 Cumulative probability of NOEC values (solid dots) of marine organisms with fitted log-logistic distribution (solid line). The lower 95% confidence limit of the distribution percentiles is shown (dashed line). References are given in Table 4.

(Back-transformed mean = 1.6 mg l^{-1}) was significantly ($p_{t\text{-test}} = 0.004$) lower than the mean LC_{50} value of freshwater fishes (Back-transformed mean = 3.6 mg l^{-1}). Comparisons within the 2 other taxa (crustaceans and algae) showed no significant difference between freshwater and marine species.

Long-term chronic toxicity endpoints (NOEC values) used in statistical analyses are reported in Figs. 2 and 3, and in Table 4. Mean NOEC values of marine and freshwater organisms (0.3 and 2.3 mg LAS l^{-1}, respectively) were significantly different ($p_{t\text{-test}} = 0.007$). According to the results presented in Table 5, the 95th percentile of the log-logistic distribution of the marine NOEC values (50% confidence level) was 31 μg LAS l^{-1}. This may be considered a preliminary PNEC of LAS in marine communities.

Risk characterization

Based on the toxicity data and the modelling result presented here, the range of PEC/PNEC ratios in the North Sea estuaries was 0.03–0.3. The ratio of 0.3 was calculated at the point where the river water first enters the estuary. It did not include biodegradation or other removal processes in the estuary. The ratio of 0.03 was calculated at the point of a 10*x* dilution of the river water with estuarine water but again did not include removal processes in the estuary. The safety factor, calculated as the ratio between the PNEC and the PEC, for LAS in estuarine pelagic communities around the North Sea ranged from around 3.4–34.

Discussion

The present study has characterized the environmental risk of LAS in the water column of estuaries around the North Sea. The predicted estuarine concentrations were calculated using simple algorithms. This modelling exercise is in agreement with monitoring data in the western Scheldt estuary (Stalmans *et al.*, 1991, measured concentrations: 2–10 μg LAS l^{-1}, salinity: 16–22 ppt). Measured LAS concentration in the Scheldt decreased exponentially with the distance from the coast. Fifteen

TABLE 4

Long-term chronic toxicity endpoints (NOEC values, mg LAS l^{-1}, geometric mean of data of various species of the same genus) of freshwater and marine genera.[a]

Freshwater organisms		Marine organisms		Ref.
Genus	Geometric mean	Genus	Geometric mean	
Plectonema	15	*Laminaria*	5.00	1
Chlamydomonas	12	*Botrylloides*	1.94	2
Scenedesmus	7.7	*Molgula*	0.90	3
Selenastrum	3.8	*Spisula*	0.80	3
Chlorella	3.5	*Botryllus*	0.75	2
Paratanytarsus	3.4	*Arbacia*	0.45	3
Ceriodaphnia	3.2	*Chaetopterus*	0.45	3
Poecilia	3.2	*Asterias*	0.35	3
Chironomus	2.8	*Arcatia*	0.30	4
Brachydanio	2.3	*Mysidopsis*	0.20	5, 6
Daphnia	1.4	*Dunaliella*	0.11	7
Pimephales	0.87	*Limanda*	0.05	5
Microcystis	0.8	*Crassostrea*	0.04	6, 8
Oncorhynchus	0.34	*Mytilus*	0.04	6, 9
Tilapia	0.25			

[a] Data on freshwater organisms are from Plassche van de *et al.* (1999) and are given for comparison purposes. References: 1: Pybus (1973); 2: Marin *et al.* (1991); 3: Moffet and Grosch (1967); 4: Kusk and Petersen (1997); 5: Plassche van de *et al.* (1999); 6: BKH (1994); 7: Unpublished data; 8: Calabrese and Davis (1967); 9: Granmo (1972).

TABLE 5

Results of the probabilistic assessment of the effects of LAS in freshwater and marine communities.[a]

Percentile (%)	Freshwater	Marine
95	360	31
90	590	57
85	800	83
80	1000	110
75	1200	140
70	1400	170

km offshore, LAS concentrations were below the detection limit of the analytical methods used at the time of the study (i.e., 0.5 μg LAS l^{-1}). The western Scheldt estuary receives water from the Rupel river basin (including the untreated water of the Brussels region) and is, thus, an estuary relatively contaminated by untreated domestic sewage. This stresses the need to introduce better wastewater treatment facilities in Western Europe. According to Stalmans *et al.* (1991), the decrease in LAS concentration with the distance from the source of contamination was faster than that predicted based on dilution only. It is anticipated that removal mechanisms from the seawater column include biodegradation (Lopez-Amoro *et al.*, 1998), sorption to suspended solids (Westall *et al.*, 1999), and precipitation with divalent cations (Xie *et al.*, 1997). Since sorption of LAS on sediment is promoted when Ca^{2+} concentration increases (Westall *et al.*, 1999), adsorption is likely to be higher in estuaries where salinity gradients are steep.

As predicted by adsorption coefficients, the adsorbed fraction of LAS is enriched in longer chain homologues while the water column is enriched in shorter chain homologues (Matthijs and De Henau, 1985; Rubio *et al.*, 1996). Considering the significant positive correlation between chain length and acute toxicity presented here and by others (Maki and Bishop, 1979; Fendinger *et al.*, 1994), it can be postulated that the risk characterization of LAS in the North Seawater column is conservative. Moreover, LAS concentration in the water column is much lower in the sea than in rivers where the environmental risk of LAS has been characterized as minimal (Fendinger *et al.*, 1994; Plassche van de *et al.*, 1999; Versteeg *et al.*, 1999). Sediment exposure to LAS is probably ecologically more relevant than water exposure in the marine environment, but the present exercise was needed to objectively quantify the risk of LAS in the seawater column.

In contrast to the toxicity data on LAS in the seawater column, less information is available on effects of LAS in marine sediments. According to Bressan *et al.* (1989), the NOEC value for marine mussels exposed to spiked sediments was > 280 mg LAS kg^{-1} (initial exposure concentration). Reported LAS concentrations in coastal and estuarine sediments around the globe are generally below 20 mg LAS kg^{-1} (Ambe, 1973; Utsunomiya *et al.*, 1980; Kiruchi *et al.*, 1986; Takada *et al.*, 1992; León *et al.*, 2000). Some hot spots with higher concentrations (up to 70 mg LAS kg^{-1}, Severinsen *et al.*, 1996; Mazo *et al.*, 1997) have been reported but further analyses are required to assess if the measured residues were LAS or the highly branched alkylbenzenesulponate (ABS). ABS has not been used as a detergent surfactant for approximately 25 years due to the poor degradation profile of this compound. In contrast to ABS, LAS is readily biodegradable in seawater and aerobic sediments as shown by Shimp (1989).

The present study has examined the effects of LAS on marine organisms and has proposed a preliminary PNEC of 31 μg LAS l^{-1} for marine organisms exposed to LAS in the water column. This PNEC is an order of

magnitude lower than the freshwater PNEC (320 μg LAS l^{-1}) for average carbon chain length of 11.6, as reported in Plassche van de *et al.* (1999). To our knowledge, there has been no mechanistic studies on the apparent difference in sensitivity in the two aquatic communities. However, it should be noted that the predicted and measured concentrations of LAS in estuaries and in coastal areas of the North Sea are below the PNEC and that comfortable safety margins have been assessed (3.4 to > 34 in the estuaries and in coastal areas of the North Sea, respectively).

Bioaccumulation of LAS is low, even in contaminated sites. According to Sáez *et al.* (2000), LAS body concentrations in bivalves and fishes collected in various sites in the Bay of Cadiz (Spain) varied between 1 (in less contaminated areas) and 3 (in more contaminated areas) mg C11-LAS kg^{-1} wet weight. Concentrations of C11-LAS in water samples collected in estuaries of the Bay of Cadiz receiving domestic untreated wastewater ranged from 0.005 (in less contaminated areas) to 0.050 (in more contaminated areas) mg C11-LAS L^{-1} (León *et al.*, 2000). Therefore, bioconcentration factors ranged from 60 to 200 L kg^{-1}. This confirms the low bioaccumulation potential of LAS measured in fathead minnows (*Pimephales promelas*, Tolls *et al.*, 1997). Rather than being bioaccumulated, LAS taken up by organisms is biotransformed, forming various metabolites, including the non-toxic, polar, carboxylated dialkyltetralinesulponates and sulfophenylcarboxylates (SPC, Kolbener *et al.*, 1995). SPC have been detected in the contaminated Bay of Cadiz at concentrations up to 5 μg C6-SPC l^{-1} in the estuarine waters, and up to 90 μg C5-SPC kg^{-1} in the sediments (León *et al.*, 2000). Body concentrations of SPC were below the detection limit (30 ng g^{-1} wet weight) in organisms collected in the same area (Sáez *et al.*, 2000), indicating probable elimination from the organisms.

In the field, organisms are exposed to multiple contaminants and the toxicity of LAS in the presence of mixtures has seldom been studied in the marine environment. According to Venezia *et al.* (1996), LAS did not promote the bioaccumulation of Cd in mussels and there was no synergistic effects between the two contaminants on the gill structure of exposed mussels. Considering the risk characterization of LAS in the seawater column, the biodegradation of LAS in seawater (see e.g., Lopez-Amoro *et al.*, 2000), and the reported stimulating effect of LAS on growth of marine bacteria (Prior and Riemann, 1998), it appears that the environmental risk of LAS in the seawater column is negligible.

Technical procedures for marine risk assessment are currently under development in the European Union and in OSPARCOM. In the typical procedure of environmental risk assessment, a PNEC protective of a community can be derived from partial toxicity data on one or few surrogate species (EEC, 1997). Partial toxicity data typically include the concentration that is lethal to a fraction (x) of an exposed population in short-term acute tests (LC_x value), or the concentration that causes no significant effect in a standardized long-term chronic test (NOEC value). Extrapolation to the community PNEC includes application factors that diminish with additional data and a better understanding of the sensitivity of organisms to the studied contaminant. For example, EEC (1997) recommends a factor of 1000 be applied to the lowest of three LC_{50} values with surrogate species or a factor of 10 be applied to the lowest NOEC value of three tests. This empirical approach was supported in freshwater environments by comparing the endpoints of acute and chronic tests of single test species with mesocosm studies (see e.g., ECETOC, 1995, 1997). Less is known concerning the sensitivity of marine communities and the most appropriate application factors. The authors of the present study are currently involved in an effort to characterize these factors for most high production volume chemicals and for recognized environmental contaminants (ECETOC LRI Eco 1b project). The data presented for LAS suggest that the acute/chronic, i.e., LC_{50}/NOEC values, ratio is different in marine and freshwater communities (Table 6) but additional data are needed for a firm conclusion.

TABLE 6
Mean acute (LC_{50}) and chronic (NOEC) values, and PNEC of LAS (mg LAS l^{-1}) in freshwater and marine communities.

	Freshwater	Marine
LC_{50} values	4.1	4.3
NOEC values	2.3	0.33
Acute/chronic ratio	1.8	13.0
Probabilistic PNEC	0.36	0.031

A better understanding of the physiological mechanisms leading to this difference should be developed. However, for risk assessment purposes, this is not fundamental as a sufficient number and diversity of species has been tested in the marine environment to assess risk without knowledge of toxicity mechanisms.

It is concluded from the present study, that the environmental risk of LAS in the North Sea and North Sea estuaries is low. Predicted and measured exposure of estuarine and marine organisms (0.9–9 μg LAS l^{-1}) was below the probabilistic PNEC (30 μg LAS l^{-1}). It is suggested that removal from the seawater column by precipitation, adsorption, and biodegradation should be further studied. Removal from the seawater column is an important factor if any higher tier assessment of the marine environmental risk of LAS is to be undertaken. Refinement of the fate assessment should also include the circulation of LAS in estuarine and marine systems. The database on the effects of LAS on marine organisms exposed through spiked sediment is relatively limited and we are developing a research programme to refine fate and effects assessment of LAS in marine sediments.

Thanks are due to our anonymous reviewers whose comments have upgraded the original manuscript.

Aldenberg, T. and Slob, W. (1993) Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotoxicol Environmental Safety* **25**, 48.

Ambe, Y. (1973) Determination of alkylbenzenesulponate (ABS) in bottom sediment. *Environmental Science and Technology* **7**, 542–545.

BKH (1994) Environmental data review of Linear Alkyl benzene Sulfonate (LAS). BKH Consulting Engineers, Electronic database, P.O. Box 5094, 2600 GB Delft, The Netherlands.

Boeije, G. M. Schowanek, D. R. and Vanrolleghem, P. A. (2000) Incorporation of biofilm activity in river biodegradation modelling: a case study for linear alkylbenzene sulphonates (LAS). *Water Research* **34**, 1479–1486.

Bressan, M. Brunetti, R. Casellato, S. Fava, G. C. Giro, P. Marin, M. Negrisolo, P. Tallandini, L. Thomann, S. Tosoni, L. and Turchetto, M. (1989) Effects of linear alkylbenzene sulponate (LAS) on benthic organisms. *Tenside Surface Determination* **26**, 148–158.

Calabrese, A. and Davis, H. C. (1967) Effects of 'soft' detergents on embryos and larvae of the American oyster (*Crassostrea virginica*). *Proceedings of National Shellfish Association* **57**, 11–16.

ECETOC (1995) Aquatic Toxicity Data Evaluation. Report No. 56. Appendix C: The Database, Brussels.

ECETOC (1997) The Value of Aquatic Model Ecosystem Studies in Ecotoxicology. Report No. 73, Brussels.

EEC (1997) Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No. 1488/94 on Risk Assessment for Existing Substances. Luxembourg.

Eurostat (1995) *Europe's Environment: Statistical Compendium for the Dobris Assessment*. Office for Official publications of the European Communities, Luxembourg.

Feijtel, T. C. J. and van de Plassche, E. J. (1995) Environmental Risk Characterization of 4 Major Surfactants Used in the Netherlands. VROM/NVZ Report no. 679101 025. The Netherlands, 85 p.

Feijtel, T. C. J. Struijs, J. and Matthijs, E. (1999) Exposure modelling of detergent surfactants – prediction of 90th-percentile concentrations in the Netherlands. *Environmental Toxicology and Chemistry* **18**, 2645–2652.

Fendinger, N. J. Versteeg, D. J. Weeg, E. Dyer, S. D. and Rapaport, R. A. (1994) Environmental behavior and fate of anionic surfactants. In *Environmental Chemistry of Lakes and Reservoirs, Advances in Chemistry Series No. 237*, ed. L. A. Baker, pp. 527–557. American Chemical Society, Washington DC.

Fox, K. Holt, M. Daniel, M. Gandolfi, C. Buckland, H. and Guymer, I. (1999) *Removal of LAS from Four Rivers – Determination of Removal Rate for the GREAT-ER Project*. Society of Environmental Toxicology and Chemistry, Ninth Annual Meeting, Leipzig, p. 55.

Granmo, A. (1972) Development and growth of eggs and larvae of *Mytilus edulis* exposed to a linear dodecylbenzenesulphonate, LAS. *Marine Biology* **15**, 356–358.

Kiruchi, M. Tokai, A. and Yoshida, T. (1986) Determination of trace levels of linear alkylbenzenesulponates in the marine environment by high-performance liquid chromatography. *Water Research* **20**, 643–650.

Kolbener, P. Baumann, U. Leisinger, T. Cook, A. M. (1995) Nondegraded metabolites arising from the biodegradation of commercial linear alkylbenzenesulponate (LAS) surfactants in a laboratory trickling filter. *Environmental Toxicology and Chemistry* **14**, 561–569.

Kusk, K. O. and Petersen, S. (1997) Acute and chronic toxicity of tributyltin and linear alkylbenzene sulponate to the marine copepod *Acartia tonsa*. *Environmental Toxicology and Chemistry* **16**, 1629–1633.

Larson, R. J. and Woltering, D. M. (1995) In *Linear Alkyl Benzene Sulfonate (LAS). Aquatic Toxicology*, ed. G.M. Rand. Taylor & Francis, Washington DC.

León, V. M. González-Mazo, E. and Gómez-Parra, A. (2000) Handling of marine and estuarine samples for the determination of linear alkylbenzene sulponates and sulfophenylcarboxylic acids. *Journal Chromatotography A* **889**, 211–219.

Lomax, E. (1997) *Surfactant dictionary and encyclopedia*. Speciality Training Limited, Warwickshire.

Lopez-Amoro, R. Comas, J. Garcia, M. T. and Vives-Rego, J. (1998) Use of 5-cyano-2,3-ditolyl tetrazolium chloride reduction test to assess respiring marine bacteria and grazing effects by flow cytometry during linear alkylbenzene sulponate degradation. *FEMS Microbiol Ecology* **27**, 33–42.

Lopez-Amoro, R. Comas, J. Garcia, M. T. and Vives-Rego, J. (2000) Flow cytometric analysis of a marine LAS-degrading consortia. *Microbioscopy* **101**, 23–36.

Maki, A. W. and Bishop, W. E. (1979) Acute toxicity studies of surfactants to *Daphnia magna* and *Daphnia pulex*. *Archives of Environmental and Contamination Toxicology* **8**, 599–612.

Mance, G. (1993) Effluent and river quality: How UK compares with other EC countries. *Journal of IWEM* **7**, 592–598.

Marin, M. G. Bressan, M. and Brunetti, R. (1991) Effects of linear alkylbenzene sulphonate (LAS) on two marine benthic organisms. *Aquatic Toxicology* **19**, 241–248.

Matthijs, E. and De Henau, H. (1985) Adsorption and desorption of LAS. *Tenside Surface Determination* **22**, 299–304.

Mazo, E. G. Quiroga, J. M. Sales, D. and Parra, A. G. (1997) Levels of linear alkylbenzenesulponate (LAS) in waters and sediments of the coastal ecosystems of the Gulf of Cadiz. *Toxicology Environmental Chemistry* **59**, 77–87.

Modler, R. F. Willhalm, R. and Yoshida, Y. (1993) *Linear Alkylate Sulfonates. Chemical Economics Handbook*. SRI International, Menlo Park, CA.

Moffet, D. F. and Grosch, D. S. (1967) Detrimental effects of linear alkylate sulphonate on larvae of selected marine invertebrates. *Biological Bulletin* **133**, 476–477.

NSTF (1993) *North Sea Quality Status Report*, eds. OSPAR and ICES. London.

OECD (1995) Environmental Data, Compendium Organization for Economic Cooperation and Development, Paris.

Plassche van de, E. J. Bruijn de, J. H. M. Stephenson, R. R. Marshall, S. J. Feijtel, T. C. M. and Belanger, S. E. (1999) Predicted no-effect concentrations and risk characterization of four surfactants: linear alkyl benzene sulponate, alcohol ethoxylates, alcohol ethoxylated sulfates, and soap. *Environmental Toxicology and Chemistry* **18**, 2653–2663.

Prior, S. and Riemann, B. (1998) Effects of tributyltin, linear alkylbenzenesulponates, and nutrients (nitrogen and phosphorus) on nucleoid-containing bacteria. *Environmental Toxicology and Chemistry* **17**, 1473–1480.

Pybus, C. (1973) Effects of anionic detergent on the growth of *Laminaria*. *Marine Pollution Bulletin* **4**, 73–77.

Rapaport, R. A. and Eckhoff, W. S. (1990) Monitoring Linear Alkyl Benzene Sulfonate in the environment – 1973–1986. *Environmental Toxicology and Chemistry* **9**, 1245–1257.

Rubio, J. A. Gonzalez-Mazo, E. and Gomez-Parra, A. (1996) Sorption of linear alkylbenzenesulponates (LAS) on marine sediment. *Marine Chemistry* **54**, 171–177.

Sáez, M. León, V. M. Gómez-Parra, A. and González-Mazo, E. (2000) Extraction and isolation of linear alkylbenzene sulponates and their intermediate metabolites from various marine organisms. *Journal of Chromatography A* **889**, 99–104.

Severinsen, M. Andersen, M. B. Chen, F. and Nyholm, N. (1996) A regional chemical fate and exposure model suitable for Denmark and its coastal sea. *Chemosphere* **32**, 2159–2175.

Shimp, R. D. (1989) LAS biodegradation in estuaries. *Tenside Surface Determination* **26**, 390–393.

Sloan, N. A. (1980) Aspects of the feeding biology of asteroids. *Oceanography and Marine Biology – A Review* **18**, 57–124.

Stalmans, M. Matthijs, E. and Oude de, N. T. (1991) Fate and effect of detergent chemicals in the marine and estuarine environment. *Water Science Technology* **24** (10), 115–126.

Takada, H. Ishiwatari, R. and Ogura, N. (1992) Distribution of linear alkylbenzenes (LABs) and linear alkylbenzene-sulponates (LAS) in Tokyo Bay sediments. *Estuarine Coast Shelf Science* **35**, 141–156.

Temara, A. Gulec, I. and Holdway, D. A. (1999) Oil-induced disruption of the foraging behaviour of the asteroid keystone predator, *Coscinasterias muricata* (Echinodermata). *Marine Biology* **133**, 501–507.

Tolls, J. Haller, M. de Graaf, I. Thijssen, M. A. and Sijm, D. T. (1997) Bioconcentration of LAS: experimental determination and extrapolation to environmental mixtures. *Environmental Science and Technology* **31**, 3426–3431.

Utsunomiya, A. Itoh, S. I. Setsuda, S. Naito, S. and Shimozato, T. (1980) Studies on sodium linear alkylbenzenesulponate (LAS). I. Distribution of LAS in the sediments of Sagami river estuary. *Eisei Kagaku* **26**, 159–166.

Van Straalen, N. M. and Denneman, C. A. J. (1989) Ecotoxicological evaluation of soil quality criteria. *Ecotoxicol Environmental Safety* **18**, 241–251.

Venezia, L. D. Stradella, S. Campesan, G. and Menetto, A. (1996) Damage to fine structure of gills of *Mytilus* sp. Due to pollution by LAS (linear alkyl benzene sulphonate) and cadmium. In *Land-Based and Marine Hazards*, ed. M. I. Sabh. Kluwer Academic Publisher, The Netherlands.

Versteeg, D. J. Belanger, S. E. and Carr, G. J. (1999) Understanding single species and model ecosystem sensitivity: a data based comparison. *Environmental Toxicology and Chemistry* **18**, 1329–1346.

Water U K (1998) The water consumption data account for household and industry water consumption. Water facts '98, London.

Westall, J. C. Chen, H. Zhang, W. and Brownawell, B. J. (1999) Sorption of linear alkylbenzenesulponates on sediment materials. *Environmental Science and Technology* **33**, 3110–3118.

Xie, W. H. Shiu, W. Y. and Mackay, D. (1997) A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research* **44**, 429–444.