SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 35, No. 5, pp. 1077–1086, 2016

Printed in the USA

Critical Review

COMPREHENSIVE REVIEW OF SEVERAL SURFACTANTS IN MARINE ENVIRONMENTS: FATE AND ECOTOXICITY

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(Submitted 15 July 2015; Returned for Revision 22 August 2015; Accepted 31 October 2015)

Abstract: Surfactants are a commercially important group of chemicals widely used on a global scale. Despite high removal efficiencies during wastewater treatment, their high consumption volumes mean that a certain fraction will always enter aquatic ecosystems, with marine environments being the ultimate sites of deposition. Consequently, surfactants have been detected within marine waters and sediments. However, aquatic environmental studies have mostly focused on the freshwater environment, and marine studies are considerably underrepresented by comparison. The present review aims to provide a summary of current marine environmental fate (monitoring, biodegradation, and bioconcentration) and effects data of 5 key surfactant groups: linear alkylbenzene sulfonates, alcohol ethoxysulfates, alkyl sulfates, alcohol ethoxylates, and ditallow dimethyl ammonium chloride. Monitoring data are currently limited, especially for alcohol ethoxysulfates and alkyl sulfates. Biodegradation was shown to be considerably slower under marine conditions, whereas ecotoxicity studies suggest that marine species are approximately equally as sensitive to these surfactants as freshwater species. Marine bioconcentration studies are almost nonexistent. Current gaps within the literature are presented, thereby highlighting research areas where additional marine studies should focus. *Environ Toxicol Chem* 2016;35:1077–1086. © 2015 SETAC

Keywords: Marine toxicity test Biodegradation Bioconcentration Environmental fate Ecotoxicology

INTRODUCTION

Surfactants are a diverse group of economically important chemicals widely used in cleaning detergents, personal care products, and various industrial applications (e.g., oil, textiles, polymers, agriculture, paints) [1]. The global surfactant market is forecast to grow at a compound annual rate of 6.02% from 2015 to 2019 (key regions being Asia-Pacific, Europe, North and South America, and the rest of the world), with rising demand for personal care products being the market driver [2]. Surfactants are comprised of both hydrophobic and hydrophilic moieties and are classified by their ionic properties in water as either anionic (negative charge), nonionic (no charge), cationic (positive charge), or amphoteric (positive/negative charge depending on pH) [3]. Among the most important anionic surfactants (by production volume) are the linear alkylbenzene sulfonates (LAS), alcohol ethoxysulfates (AES), and alkyl sulfates (AS). The most important nonionic surfactants (by volume) are the alcohol ethoxylates (AE). Ditallow dimethyl ammonium chloride (DTDMAC), a quaternary ammonium compound is a historically commonly used cationic surfactant [4]. Given their importance, these 5 surfactant groups (Figure 1) are the focus of the present review.

Commercial LAS contain homologous mixtures from C_{10} to C_{14} (average chain length, $C_{11.7}$–$C_{11.8}$) [5] and are currently the most commonly used group of anionic surfactants in Europe, with consumption estimates of 497 818 tons in 2013 (European Committee of Organic Surfactants and their Intermediates [CESIO], Brussels, Belgium, personal communication). However, commercial AES are notably becoming increasingly important, with consumption rates increasing to overtake those of LAS in certain parts of the world (e.g., North America) [6]. Alcohol ethoxysulfates contain variable alkyl chain lengths (C_{12}–C_{18}) and ethoxylated chain lengths (0–8) [7]. European AES consumption estimates were 456 160 tons in 2013 (CESIO, Brussels, Belgium, personal communication). Commercial AS contain variable chain lengths from C_{12} to C_{18} [8]. European AS consumption estimates were 65 885 tons in 2013 (CESIO, Brussels, Belgium, personal communication). Commercial AE contain variable hydrocarbon chain lengths (C_8–C_{18}) and ethoxylated chain lengths (0–22). European AE consumption estimates were 371 609 tons in 2013 (CESIO, Brussels, Belgium, personal communication). The DTDMAC surfactant is no longer used commercially on a large geographic scale and has since been substituted with readily biodegradable alternatives [4].

Following their use, surfactants will typically enter wastewater-treatment plants, where removal has been shown to be highly efficient (95–99% average removal [7–11]). However, given their globally high consumption volumes, there is always a certain fraction that is not removed. Thus, surfactants enter aquatic ecosystems via wastewater discharge [12,13]. The marine environment therefore receives almost continuous surfactant input, either directly (from treated and untreated wastewaters discharges) or indirectly (via contaminated rivers) and is regarded as the final site of deposition for surfactants [14–17]. Consequently, surfactants have been

This article includes online-only Supplemental Data.

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Published online 3 November 2015 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.3297

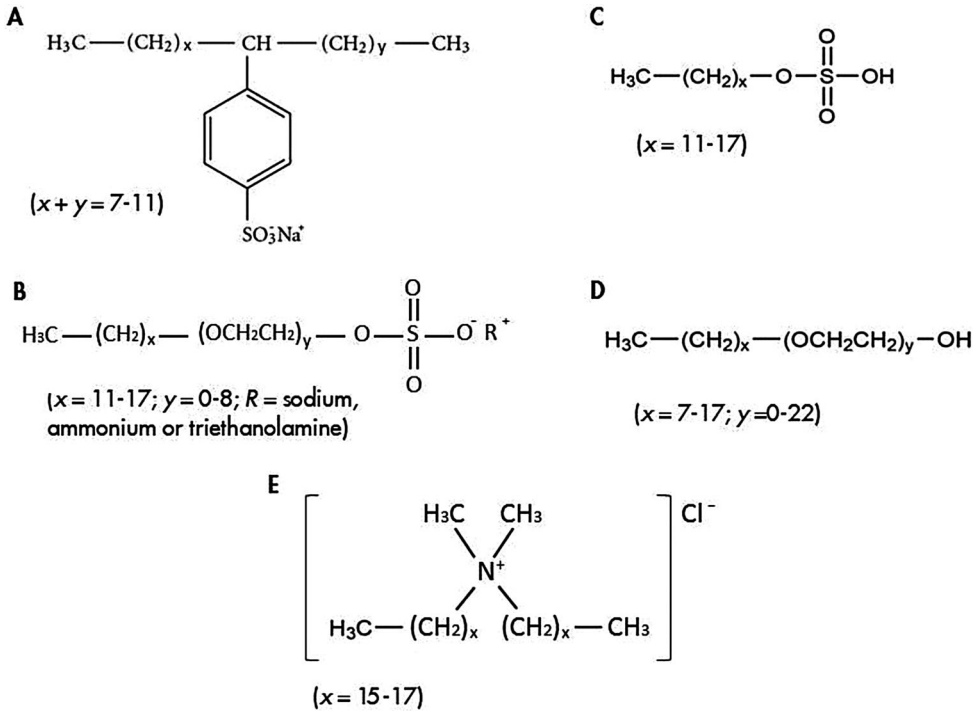

Figure 1. General chemical structures of the surfactants (**A**) linear alkylbenzene sulfonate, (**B**) alcohol ethoxysulfate, (**C**) alkyl sulfate, (**D**) alcohol ethoxylate, and (**E**) ditallow dimethyl ammonium chloride.

detected within marine waters and sediments [18–21]. Once within the marine environment, surfactants may be removed via volatilization (albeit only to a limited extent), adsorption to particles, abiotic or microbial degradation, or uptake by marine organisms [3]. Degradation and sorption are the main mechanisms involved [1].

As such, marine environments may act as sinks for surfactants as a result of sorption to particles that sink to the sediment bed, potentially leading to their accumulation [3]. Rubio et al. [22] observed <6% LAS recovery from marine sediments and concluded (by fitting experimental data to a Freundlich model) that sorption of surfactants to marine sediments was irreversible. Estuarine and coastal environments are considered the most productive yet sensitive ecosystems on earth; hence, exposures can have significant environmental implications [23,24]. Furthermore, some studies suggest that certain marine organisms are more sensitive than freshwater organisms [25,26] (although it is suggested that such variability in toxicity depends largely on species choice [27]). Marine studies should therefore be strongly considered when addressing the environmental effects of surfactants.

Emphasis on protecting the marine environment has increased over the years, with concerns that hazardous substances may accumulate to significant toxic concentrations to cause unpredictable, potentially irreversible long-term effects. It has also been emphasized that remote ocean areas should remain untouched by hazardous substances and that pristine marine environments should be protected [28]. Similar to other environmental compartments, the most important surfactant-related environmental issues considered in the marine environment are whether there is risk of direct toxicity or whether biodegradation, bioaccumulation, and biomagnification pose reason for concern [3]. However, most reported ecotoxicity studies concerning surfactants have focused on freshwater species, whereas marine studies are comparatively lacking. The same is true of marine biodegradation studies, whereas marine bioaccumulation studies are practically nonexistent [3,29].

An extensive review of currently available marine studies on the 5 previously mentioned surfactants (LAS, AES, AS, AE, and DTDMAC) was therefore conducted in association with the Environmental Risk Assessment of Surfactants Management (although, given the diverse and large-scale application of surfactants, this work would also be of interest to other organizations, such as the Oslo/Paris convention for the protection of the marine environment of the northeast Atlantic and the European Oilfield Specialty Chemicals Association), taking into account monitoring, biodegradation, bioaccumulation, and ecotoxicity studies. Comparison is also made with general freshwater data. The present review ultimately aims to provide a comprehensive summary of such studies and to highlight current gaps within the literature.

FATE

Monitoring

The amount of marine sediment monitoring data found, from highest to lowest, was AE > LAS > DTDMAC > AES > AS (Table 1). Detected concentrations ranged from 0.0074 mg/kg to 9.19 mg/kg in AE [30], <0.003 mg/kg to 15.63 mg/kg in LAS [13,21,30,31], 0.0048 mg/kg to >25 mg/kg in DTDMAC [30], 0.061 mg/kg to 14.32 mg/kg in AES [21,32–34], and 0.13 mg/kg in AS [21]. Measured concentrations in sediment were higher when sampling was undertaken in close proximity to direct discharge from sewage-treatment plant effluents, whereas samples taken from offshore locations were not impacted by direct discharge and consequently showed much lower surfactant concentration levels. Based on the upper range values, detected concentration levels are, from highest to lowest, DTDMAC > LAS > AES > AE > AS. High

Table 1. Summary of marine data values reported for the surfactants: Linear alkylbenzene sulfonate, alcohol ethoxysulfate, alkyl sulfate, alcohol ethoxylate, and ditallow dimethyl ammonium chloride[a]

	LAS	AES	AS	AE	DTDMAC	Total
Degradation	37	8	7	13	ND	65
Bioconcentration	3	ND	1	ND	ND	4
Monitoring	19	4	1	20	10	54
Acute algae toxicity	26	8	12	ND	2	48
Acute invertebrate toxicity	127	9	240	51	4	431
Acute fish toxicity	23	3	34	1	1	62
Chronic algae/marine plant toxicity	19	10	7	1	ND	37
Chronic invertebrate toxicity	41	ND	50	4	1	96
Chronic fish toxicity	8	ND	8	ND	ND	16
Marine bacteria toxicity	1	ND	ND	ND	ND	1
Total	304	42	360	90	18	

[a]Note that classification of chronic studies is somewhat subjective.
LAS = linear alkylbenzene sulfonate; AES = alcohol ethoxysulfate; AS = alkyl sulfate; AE = alcohol ethoxylate; DTDMAC = ditallow dimethyl ammonium chloride; ND = no data found.

DTDMAC concentrations can be attributed to their higher persistence levels (because of their poor biodegradability coupled with their positive cationic charge, causing them to strongly adsorb to negatively charged sediment surfaces). As mentioned, DTDMAC commercial consumption has been considerably reduced on a geographic scale because of their high persistence levels [4]. The concentration trend seen in the other surfactants corresponds to their reported consumption rates. Monitoring data for AS and AES are comparatively scarce in comparison with the other surfactants reviewed in the present study. Lara-Martin et al. [19] argued (in the case of AES) that the main reason for this is that these compounds are not volatile and do not fluoresce; therefore, conventional high-performance liquid chromatography with ultraviolet or fluorescence detectors and gas chromatography with mass spectrometry cannot be used. However, gas chromatography with mass spectrometry and liquid chromatography with mass spectrometry are now being applied more frequently for specific analysis of surfactants [35–41].

Biodegradation

Evidence on surfactant removal by abiotic or biotic degradation is important, since this largely determines their fate and persistence in the environment. The number of marine degradation studies found during the present review, from highest to lowest, is LAS > AE > AES > AS (no marine DTDMAC studies were found; Table 1). Marine studies are evidently scarce, despite the role of these environments as ultimate recipients of domestic and industrial wastewaters. The most common endpoints from the obtained studies were parent disappearance in LAS and AS and $^{14}CO_2$ evolution in AE and AES. Table 2 provides a summary of the marine degradation data found as well as a comparison with typical freshwater half-life values. Studies that reported half-lives >60 d were considered unreliable based on European Centre for Ecotoxicology and Toxicology of Chemicals recommendations [28] and therefore were excluded. Based on the mean half-lives presented, marine degradability of the 5 surfactants, from highest to lowest, is AS > LAS > AE > AES (although there is evidently large overlap between half-life data across all 4 surfactants, suggesting similarity). This trend is consistent with previous results in that AS exceeds all other anionic surfactants in biodegradation rates [4,42,43]. However, it should be noted that although AS presents the lowest mean half-life of the 4 surfactants examined, it is also the most data-deficient; hence, the calculated mean is not considered as reliable as that of LAS

Table 2. Summary of marine degradation data ranges for the surfactants and half-life comparison with typical freshwater values[a]

	Marine degradation					Typical freshwater degradation	
Compound	Primary degradation rate (d^{-1})	Lag (d)	Mineralization (%)	Half-life (d)	References	Half-life (d)	Reference
LAS	0.02 – 0.19 (0.11; $n = 9$)	0 – 6.67 (1.45; $n = 15$)	10 – 60.4 (24.52; $n = 13$)	0.3 – 45 (8.67; $n = 37$)	[11,15,23,24,29,42–44,46,48,50,51,55,83–86]	0.025–0.5 (0.16)	[10]
AES	0.1 – 0.39 (0.28; $n = 4$)	0.65 – 26.5 (10.15; $n = 3$)	0 – 96.7 (71.79; $n = 7$)	1 – 49.8 (14.07; $n = 8$)	[11,83–85]	0.042–1.4 (0.72)	[7]
AS	—	7 – 14 (10.5; $n = 2$)	0 ($n = 1$)	0.26 – 20 (6.78; $n = 7$)	[11,42,43,49,84]	0.3–1.0 (0.75)	[8]
AE	0.02 – 0.34 (0.14; $n = 13$)	0 – 3 (0.86; $n = 7$)	8 – 87.2 (49.2; $n = 11$)	2.3n– 28 (11.76; $n = 13$)	[83,87,88]	0.17–1.0 (0.46)	[9]
DTDMAC	—	—	—	—	—	—	—

[a]Marine studies were conducted at 20 °C to 25 °C (with the exception of George [49], Leon et al. [50], and Mauffret et al. [51], which included studies performed at –1.8–0.65 °C, 10 °C, and 10–18°C, respectively). Representative freshwater data were collected at lower temperatures than marine studies (7–27 ° C). Data are based on first-order degradation models. Mean values are given in parentheses, followed by the number of data values used.
LAS = linear alkylbenzene sulfonate; AES = alcohol ethoxysulfate; AS = alkyl sulfate; AE = alcohol ethoxylate; DTDMAC = ditallow dimethyl ammonium chloride.

(the second most rapidly degradable surfactant examined in the present review). Current studies suggest that mineralization in marine conditions is highest in AES (mean, 71.8%), followed by AE (mean, 49.2%) and LAS (mean, 24.5%; Table 2); AS mineralization data are currently severely limited. There is considerable variability among studies in all 4 surfactants (shown by large data ranges), with many studies revealing marine surfactant biodegradation to be a long process. It is argued that such data variability may be explained by natural variation (between different environments) and microbial variation by different pretreatment methods (e.g., acclimation history of associated microbial communities to surfactants [24,44,45]), humic substance association, cometabolic transformation, or nutrient-level variation [46]. Primary biodegradability of LAS homologs has been shown to increase with alkyl chain length [23,47], although Larson et al. [24] found that LAS mineralization was relatively unaffected by such structural differences. The biodegradability of AE and AES is relatively unaffected by alkyl and ethoxylated chain lengths, although branching does hinder it [4]. Studies that included marine sediments showed increased extent [24,44] and rates [15,48] of biodegradation as a result of additional microbial biomass, organic matter, or nutrients [3].

Although the majority of marine studies obtained in the present review were conducted at 20 °C to 25 °C, some were conducted at lower temperatures (–1.8–0.65 °C [49], 10 °C [50], 10–18°C [51]), demonstrating comparatively longer half-lives. Temperature is widely known to influence biodegradation, with higher temperatures causing enhanced microbial metabolic activity and reduced lag times and lower temperatures inhibiting degradation [3,49,50,52]. Terzić et al. [23] detected a lag time of 2 d for LAS at 14 °C but not at 23 °C (although this difference was detected within freshwater estuary layers as opposed to saline layers). Antarctic coastal half-lives generally have been shown to be far longer than those in temperate waters [49]. Some studies have therefore argued that marine surfactant contamination may worsen in winter months as a result of reduced biodegradation rates [23,48,50,52]. In contrast, however, other studies suggest that seasonal temperature variations have little to no effect on surfactant biodegradation under realistic environmental conditions [49,53].

Comparison with typical freshwater half-life values suggests that (like other chemicals) degradation of surfactants is much slower in marine than freshwater environments, thereby corresponding with previous reports [3,24,29,44]. It was suggested that this comparatively slower degradation might be explained by marine microbial communities being less active than their freshwater counterparts toward xenobiotic chemicals. It was also suggested that complexation with calcium and magnesium ions in seawater reduces bioavailability (particularly at low concentrations), thereby inhibiting biodegradation [44]. In contrast, Quiroga and Sales [54] found no difference in the extent of LAS biodegradation over 21 d under varying salinities (16–65‰); however, induction periods were notably shorter under higher salinities (50–65‰). It was argued that this may have been an artifact of bacterial culture dilution causing reduced culture numbers (and consequently reduced biodegradation). Many of the representative freshwater data in Table 2 reportedly used temperatures that were comparatively lower than (most) marine studies found in the present review (freshwater temperatures: AE, ∼12 °C; AES, 22 ± 3 °C; AS, 10–27°C; LAS, 7–27 °C). However, despite these lower temperatures, half-lives were still faster in freshwater than marine conditions. Perales et al. [29] concluded that under similar temperatures (and initial concentrations), LAS degraded more slowly in marine than freshwater conditions, demonstrating slower half-life and lag times in marine conditions.

Bioconcentration

Bioconcentration and bioaccumulation measure the net accumulation of a chemical within an organism as a result of uptake via exposure to the material (from either the surrounding environment only [bioconcentration] or the surrounding environment and food [bioaccumulation]). Such accumulations may eventually lead to concentration levels capable of causing toxic effects within the organism or net accumulation of the chemical to predator organisms through the food chain (biomagnification).

Current aquatic bioconcentration/bioaccumulation studies in surfactants have almost exclusively focused on freshwater species, generally concluding that surfactants (LAS, AES, AS, and AE) possess low accumulation potential because of metabolism and subsequent elimination from the organism [4]. Marine studies are practically nonexistent. Guarino et al. [55] reported sodium lauryl sulfate (AS) bioaccumulation in the spiny dogfish (*Squalus acanthias*) following a 1-mg/kg dose via injection over 2 h to 144 h. However, the study was nonstandard, given the method of exposure used (injection into body tissue). According to Sáez et al. [56], C_{11}LAS body concentrations between 1 mg/kg and 3 mg/kg wet weight were found in bivalves and fish collected from less contaminated sites (0.005 mg/L C_{11}LAS in water samples) and more contaminated sites (0.05 mg/L C_{11}LAS in water samples), respectively, of the Bay of Cadiz (Spain) [56,57], with bioconcentration factors (BCFs) said to range from 60 L/kg to 200 L/kg [58]. Furthermore, body concentrations of LAS metabolites (i.e., sulfophenylcarboxylic acids) were below detection limits, suggesting that they were eliminated from organisms [56]. Renaud et al. [59] reported a mean BCF of 120 L/kg in the marine shrimp *Palaemonetes varians* after 7-d C_{12}-6-LAS exposure under realistic environmental concentrations. The estimated BCF at steady state (BCF_{ss}) was 159 L/kg, which was reached after 11.5-d exposure. Major accumulation was found in the cephalothorax circulatory system (gills, heart, hepatopancreas) and ocular peduncle but not flesh (implying limited transfer potential to human consumers). Depuration was rapid, showing <1% of initial LAS after 8 d [59]. Álvarez-Muñoz et al. [60] found BCF_{ss} values of 17 L/kg for C_{10}-2-LAS and 387 L/kg for C_{12}-2-LAS in *Solea senegalensis* under realistic environmental concentrations. Biotransformation and elimination also were reported by identifying and quantifying LAS metabolites in organisms and depuration water. From these limited marine studies, it has been concluded that LAS presents no risk of bioaccumulation at environmental concentration levels [59,60].

Renaud et al. [59] noted that marine BCF values obtained in their study were similar to those previously observed for freshwater organisms and concluded that salinity has no significant impact on LAS bioconcentration. However, it has also been argued that extrapolating freshwater data to marine conditions should be done with caution, given the lower relevance of freshwater data compared with marine data, particularly for surfactants that are used offshore [3]. Freshwater results have shown that the accumulation potentials of surfactants in the aqueous phase are generally below the conventional levels for concern (i.e., log octanol–water

partition coefficient values of 3–4) [3]. Freshwater studies have also shown high rates of biotransformation in surfactants (in vitro studies in freshwater fish have also shown this to be the case [61]); hence, their accumulation potential is considered to be low [62–64]. Moreover, some freshwater bioconcentration data generated with radiolabeled test compounds should be regarded as overestimates if parent and metabolites have not been quantified separately and the BCF is based on the total combined fractions [3]. Slight increases in LAS and AE alkyl chain lengths (and decreasing ethoxylated chain length in AE)—that is, increasing hydrophobicity—were shown to significantly increase bioconcentration potential in *Pimephales promelas* [63,65], whereas increasing hydrophilicity reduces bioconcentration potential [3]. Furthermore, the closer the positioning of the *p*-sulfophenyl group to the terminal carbon of the alkyl chain in LAS, the higher the BCF [65]. Biomagnification is also considered unlikely since surfactants lack the properties necessary to remain stable in the environment (i.e., they are rapidly degraded and metabolized and are not highly hydrophobic) [3].

EFFECTS

The number of reported marine ecotoxicity data on the 5 surfactants, from highest to lowest, is AS > LAS > AE > AES > DTDMAC (Table 1). The taxa most commonly used, from highest to lowest, are invertebrates > algae > fish (1 marine bacteria study was found for LAS [66]); however, the exact marine species used vary considerably between studies. In the present review, data are considered acute if they were described as such in the study, if the endpoint was presented as a 50% effective or lethal concentration (EC50 or LC50), or if exposure duration was equal to or less than that recommended in standardized test guidelines (e.g., 96-h fish exposure, 48-h invertebrate exposure). Data are considered chronic if they were described as such in the study; if the end point was presented as a lowest-observed-effect concentration (LOEC), a no-observed-effect concentration (NOEC), a 10% lethal or effective concentration (LC10 or EC10), or an effect that would influence the long-term well-being of the test species (e.g., reduced byssal activity in *Mytilus edulis*); or if exposure duration was considerably longer than would be expected from a standardized acute study. Acute studies (particularly lethality) are most abundant (especially in invertebrates), whereas chronic studies are much less common (particularly in fish). Marine study data are currently lacking for acute algae and chronic fish for AE, chronic invertebrate and fish for AES, and chronic algae and fish for DTDMAC. It is also apparent (from Supplemental Data, Tables S1 and S2) that marine sediment studies are scarce, relative to seawater studies, and mostly use bulk sediment (mg/kg) as an exposure metric. These marine sediment studies all used LAS as a test compound, with acute toxicity ranging from 4.18 mg/kg to 4.77 mg/kg (mean, 4.48 mg/kg) [67,68], 2 mg/kg to 295 mg/kg (mean, 102.06 mg/kg) [14,25,69–73], and 876 mg/kg to 2180 mg/kg (mean, 1528 mg/kg) [73,74] in algae, invertebrates, and fish, respectively. Chronic toxicity ranged from 0.35 mg/kg to 561 mg/kg (mean, 105.4 mg/kg) [25,70,73,75] and 223 mg/kg to 755 mg/kg (mean, 601 mg/kg) [73,74] in invertebrates and fish, respectively (chronic algal sediment data were lacking). Adsorption of surfactants to marine sediments is believed to be one of their main removal mechanisms [1]; thus, marine sediment toxicity data should be considered important. However, given that exposure of benthic organisms occurs via interstitial water, it is suggested that an alternative exposure metric (rather than bulk sediment) should be adopted in such studies (i.e., porewater). Rico-Rico et al. [69] showed that C_{12}-2-LAS effect concentrations in porewater were similar to those obtained via water-only exposures in the marine benthic amphipod *Corophium volutator*, suggesting that this would be a suitable alternative metric.

There is evidently considerable variability among the marine data ranges reviewed in the present study (Figures 2 and 3) and, consequently, reason for caution when drawing conclusions. It is suggested that variable test conditions (e.g., temperature, salinity [76,77]), species, and chemical structure among studies may partially explain this [4]. It is also apparent that the vast majority of current marine data are based on nominal rather than measured concentrations (see Supplemental Data, Tables S1 and S2), thereby potentially limiting their reliability. This is because of the difficulty in the separation and quantification of individual components of surfactant products at the required low concentration levels in such toxicity tests. Furthermore, real exposures (i.e., truly dissolved fractions) are often unknown. In general, surfactant toxicity varies among homologs depending on their respective alkyl chain lengths and ethoxylated chain lengths, with longer alkyl chains corresponding to higher toxicity (e.g., C_{14}LAS is more toxic than C_{10}LAS), whereas increasing ethoxylated chain lengths reduce toxicity [4,10]. For instance, the growth inhibition rate was considerably lower in 3 marine microalgae (*Tetraselmis suecica*, *Isochrysis galbana*, and *Rhodomonas salina*) when exposed to C_{11}LAS (72-h EC50 values for reduced algal biomass: 13.37 mg/L, 7.7 mg/L, and 4.43 mg/L, respectively) relative to C_{13}LAS (72-h values for reduced algal biomass values: 1.23 mg/L, 0.54 mg/L, and 0.36 mg/L, respectively) [78]. Likewise, 48-h LC50 values in *Crassostrea gigas* larvae were lower in $C_{10\text{-}12}$LAS (0.56 mg/L) compared with $C_{12\text{-}14}$LAS (0.1 mg/L) exposures [79]. Currently, typical LAS homologs within the marine environment have not been studied in detail. Rather, $C_{11.6}$ LAS has been emphasized as a representative homolog for aquatic environmental testing in general and has largely been adopted in marine testing [10]. However, it appears that representative homologs for environmental testing for the other surfactants examined in the present study have not been established (for AE and AES surfactants, this is normally because of the added complexity resulting from variable ethoxylated chain lengths). However, it has been noted that AES toxicity peaks at C_{16} alkyl chains [4] and that most AS studies have focused on C_{12} homologs. Toxicity also varies depending on whether a surfactant is linear or branched, with branching leading to increased toxicity (however, it has been shown that this is not always the case [9]).

Comparison of freshwater and marine surfactant toxicity has been largely inconsistent within the literature. Ezemonye et al. [71] reported significantly lower 10-d LC50 values in freshwater *Desmoscaris trispinosa* (139 mg/kg) compared with brackish water *Palaemonetes africanus* (259 mg/kg) under LAS exposures. Van de Plassche and de Bruijn [80] considered it unlikely that marine and freshwater organisms differed in sensitivity to AE, although they did conclude that marine species were more sensitive to LAS than freshwater species. In contrast, Swedmark et al. [81] concluded that marine and freshwater fish species show similar sensitivity to LAS. Similarly, Temara et al. [58] argued that there was no significant difference between mean acute LC50 values of

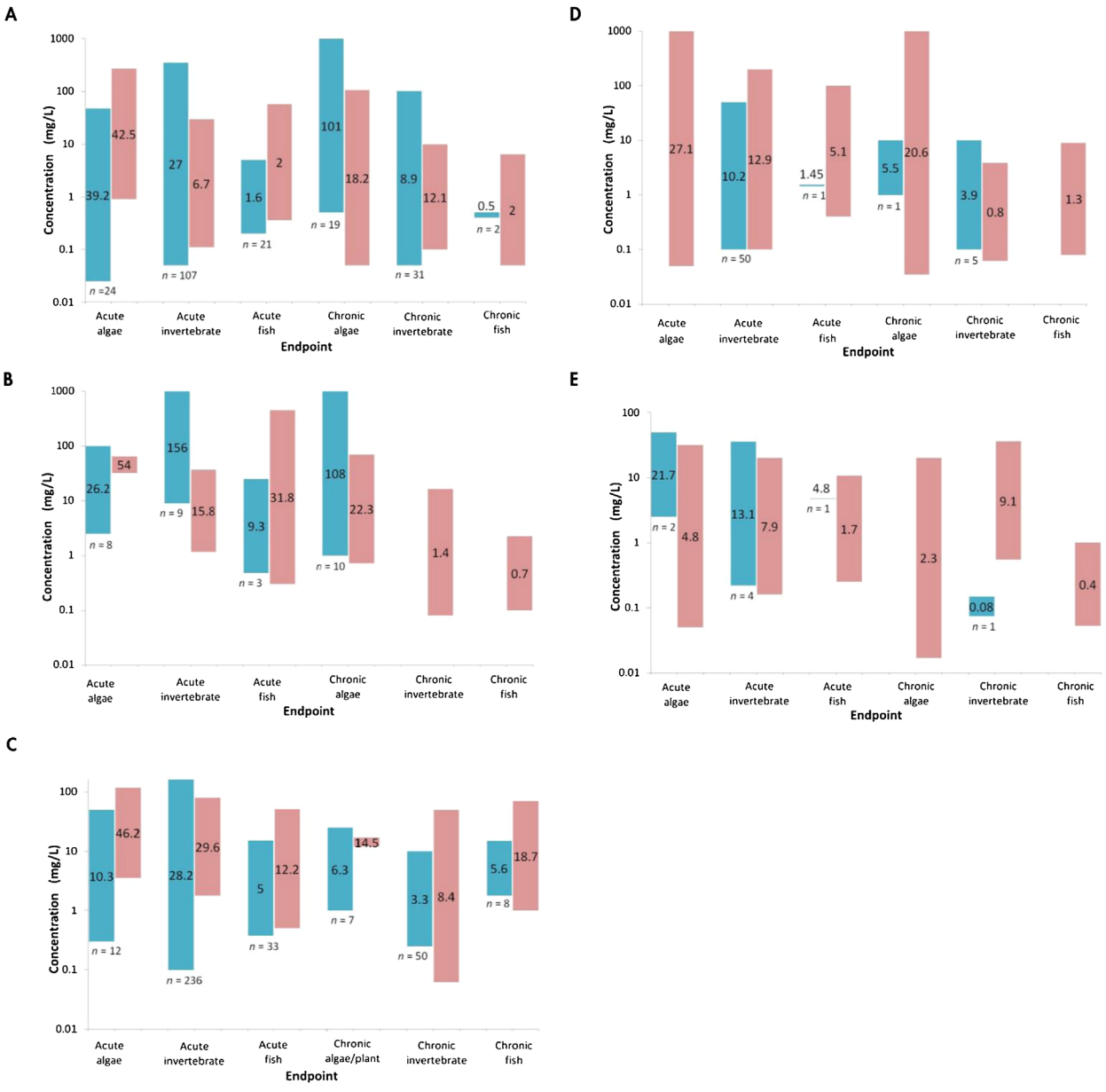

Figure 2. Comparison of acute and chronic aquatic ecotoxicity data ranges of the surfactants (**A**) linear alkylbenzene sulfonate, (**B**) alcohol ethoxysulfate, (**C**) alkyl sulfate, (**D**) alcohol ethoxylate, and (**E**) ditallow dimethyl ammonium chloride from marine studies reviewed in the present study (see Supplemental Data, Tables S1 and S2) and typical freshwater data [4,8–11,89–92]. Blue bars show marine data; red bars show freshwater data. Mean values are presented within individual bars. Acute endpoints include 50% lethal (effective) concentrations and others (Supplemental Data, Table S1). Chronic end points include lowest-observed-effect concentration, no-observed-effect concentration, 10% lethal concentration, and others (Supplemental Data, Table S2). Numbers of marine data (*n*) used to calculate mean values for each type of study are given below bars. Data have been logarithmically scaled.

freshwater and marine organisms to LAS (4.1 mg/L and 4.3 mg/L, respectively); however, comparison of mean chronic NOEC values revealed significantly higher sensitivity in marine organisms than freshwater organisms (0.3 mg/L and 2.3 mg/L, respectively). Figure 2 reveals that marine data generally seem to fall within freshwater data ranges, leading to the conclusion that marine species are approximately equally sensitive to surfactants as freshwater species, thereby agreeing with previous conclusions made by the European Centre for Ecotoxicology and Toxicology of Chemicals [82]. The comparison of marine and freshwater mean toxicity values provided within the present review also largely suggests this; however, there are occasional discrepancies because of limited and highly variable data (e.g., mean AES acute invertebrate toxicities were 156.4 mg/L and 15.75 mg/L for marine and freshwater species, respectively; however, this marine value is derived from just 9 data values, ranging from 9 mg/L to 1000 mg/L).

Based on the data ranges shown in Figure 3 and the mean toxicities shown in Figure 2, it is concluded that the toxicity of the 5 surfactants, from highest to lowest, is LAS > AS > AE > DTDMAC > AES. Consistently, LAS produced the lowest effect concentration range in all study types (as low as 0.025 mg/L in acute algae studies), whereas AES consistently showed the highest (as high as 1000 mg/L in acute invertebrate studies; Figure 3). The second lowest mean toxicity range was produced by AS, whereas AE produced a lower toxic concentration mean and range compared with DTDMAC

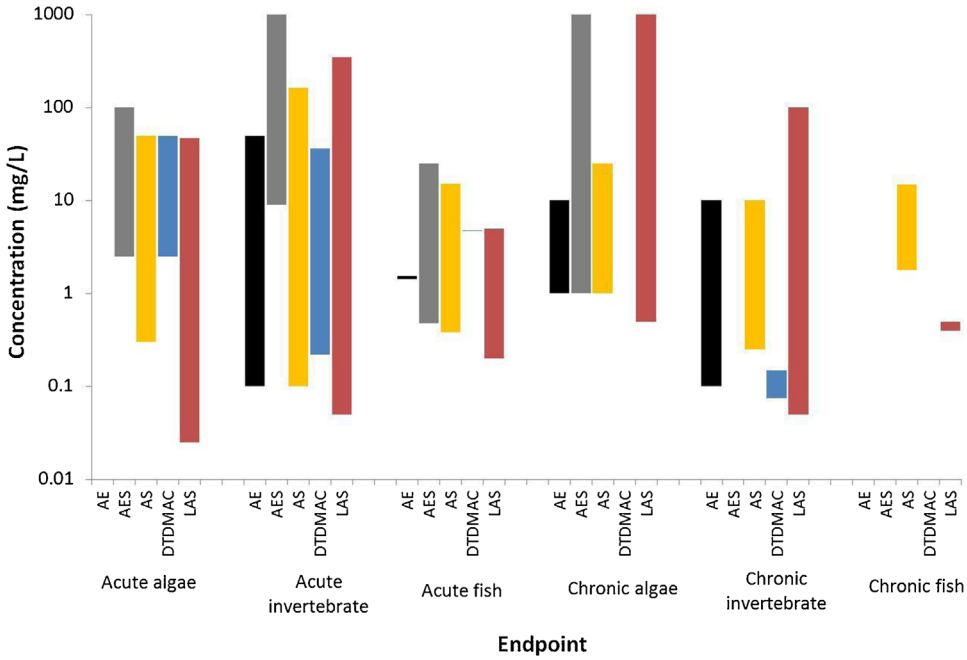

Figure 3. Comparison of acute and chronic marine ecotoxicity data ranges of the surfactants alcohol ethoxylate (AE), alcohol ethoxysulfate (AES), alkyl sulfate (AS), ditallow dimethyl ammonium chloride (DTDMAC), and linear alkylbenzene sulfonate (LAS) from marine studies reviewed in the present study (Supplemental Data, Tables S1 and S2). Black bars represent AE; grey bars represent AES; yellow bars represent AS; blue bars represent DTDMAC; red bars represent LAS. Acute end points include 50% lethal (effective) concentrations and others (see Supplemental Data, Table S1). Chronic end points include lowest-observed-effect concentration, no-observed-effect concentration, 10% lethal concentration, and others (see Supplemental Data, Table S2). Data have been logarithmically scaled.

(Figures 2 and 3). Acute toxicity for the 5 surfactants examined (for algae, invertebrates, and fish) was generally equisensitive across the board.

CONCLUSIONS

Having reviewed the available marine fate and effects data on the surfactants LAS, AES, AS, and DTDMAC, we can draw several conclusions.

Although these surfactants have been detected in marine environments, monitoring data are limited, especially for AES (4 studies) and AS (2 studies). Marine biodegradation data are scarce, highly variable, and predominantly based on LAS (33 of the 59 reported data were LAS data). Based on mean half-lives given in Table 2, marine degradation is generally a rapid process (although some studies suggest otherwise) but is comparatively slower than freshwater degradation (approximately 54, 20, 9, and 26 times slower for LAS, AES, AS, and AE, respectively).

Marine concentration data are limited to only a few reliable studies for LAS. Based on the available marine data for LAS and other freshwater data for other surfactants, bioconcentration and biomagnification of these surfactants are not expected. Areas where marine ecotoxicology studies are lacking have been identified for the 5 surfactants, particularly highlighting a shortage of chronic and sediment studies (see Table 1) and a current lack of attention toward AES (despite its growing commercial importance).

Available studies show wide variation in marine toxicity; in general, however, marine data fall within typical freshwater data ranges, suggesting approximately equal sensitivity to freshwater species. Although there is similarity in sensitivity for marine and freshwater species for the 3 common trophic levels (i.e., fish, invertebrates, and algae), there is still uncertainty because there are other key marine taxa that cannot be tested (e.g., echinoderms, mollusks, cephalopods, ctenophora [82]); hence, marine species are underrepresented.

The present review has revealed that the vast majority of available marine ecotoxicity studies are based on nominal rather than measured concentrations (likely the result of technical difficulties associated with analytical measurements of components of these surfactants). Consequently, it could be argued that the reliability of numerous current marine ecotoxicity studies is limited.

It is clear that there is a real limitation in the required fate and toxicity data for these surfactants, which results in uncertainties in their risk assessment in the marine environment. More information needs to be generated in laboratory and field studies on the occurrence, distribution, and degradation of these surfactants in the marine environment, including a better understanding of their mobility and interstitial partitioning as well as the development of estuarine and marine exposure models.

Recognition of the economic and ecological importance of the marine environment and its sensitivity toward anthropogenic impacts is growing. Consequently, increased emphasis is being placed on their protection. Commercial surfactants are consumed on a massive global scale, with growing demands showing no signs of slowing. Given that marine environments are considered the ultimate disposal sites of surfactants, additional marine studies—in particular bioconcentration studies, chronic AES studies, and AES and AS monitoring studies—within the present review are encouraged.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3297.

Acknowledgment—The authors acknowledge Environmental Risk Assessment of Surfactants Management for funding this review. Environmental

Risk Assessment of Surfactants Management was created in 1991 and is a joint platform of the European detergent and surfactants producers represented by the Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien and the Comité Européen des Agents Surface et de leurs Intermédiaires Organiques. Environmental Risk Assessment of Surfactants Management initiates and coordinates joint industry activities for improving and enlarging the basis for and the knowledge about the risk assessment and sustainability of detergent-based surfactants in environmental compartments.

Data availability—Data references are provided.

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