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Comprehensive review of several surfactants in marine environments: Fate and ecotoxicity

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Introduction

- Surfactants are a diverse group of economically important chemicals widely used on a global scale in a diverse range of products. Their global market is forecast to grow at a compound annual growth rate of 6.02% from 2015 to 2019 [1].
- Following their use, surfactants typically enter wastewater treatment plants, where removal is highly efficient. However, high consumption rates mean there is always a certain fraction that is not removed, hence surfactants enter aquatic ecosystems via wastewater discharge and have been detected in marine waters and sediments [2]. Although there are numerous freshwater environmental risk assessments, risk assessment based on experimental marine data has been scarcely investigated.
- Recognition of the economic and ecological importance of marine environments and their sensitivity towards anthropogenic impacts is growing. Consequently, increased emphasis is being placed on their protection.
- To investigate the extent and quality of available marine (water and sediment) experimental data, ERASM commissioned an extensive review of experimental marine fate (biodegradation, bioconcentration, monitoring) and ecotoxicity data for five key surfactants (chosen based on their production volume or historical significance). Surfactants chosen for review are presented in Figure 1.

Method

- Marine biodegradation studies reporting half-lives >60 days were considered unreliable based on ECETOC (**E**uropean **C**entre for **E**cotoxicology and **T**oxicology **o**f **C**hemicals) recommendations [3], hence were disregarded.
- Marine ecotoxicity data was considered as acute if they were described as such the study, if the endpoint was presented as an L(E)C50, or if exposure duration was equal or less than standardised test guideline recommendations (e.g. 96 h fish, 48 h invertebrates, etc). Data was considered as chronic if they were described as such the study, if the endpoint was presented as a LOEC, NOEC or L(E)C10, or if exposure duration was considerably longer than expected from a standardised acute study.
- Reviewed data from each surfactant were analysed to determine current data availabilities for each study type, data ranges, mean data values, and comparison with typical freshwater data from key reports [4-10].

Figure 2: Comparison of acute and chronic aquatic ecotoxicity data ranges of the surfactants from reviewed marine studies and typical freshwater data [4-10]. Blue bars: marine data; red bars: freshwater data. Mean values presented in individual bars. Number of marine data (*n*) used to calculate mean values for each type of study are given below bars. Data has been logarithmically scaled.

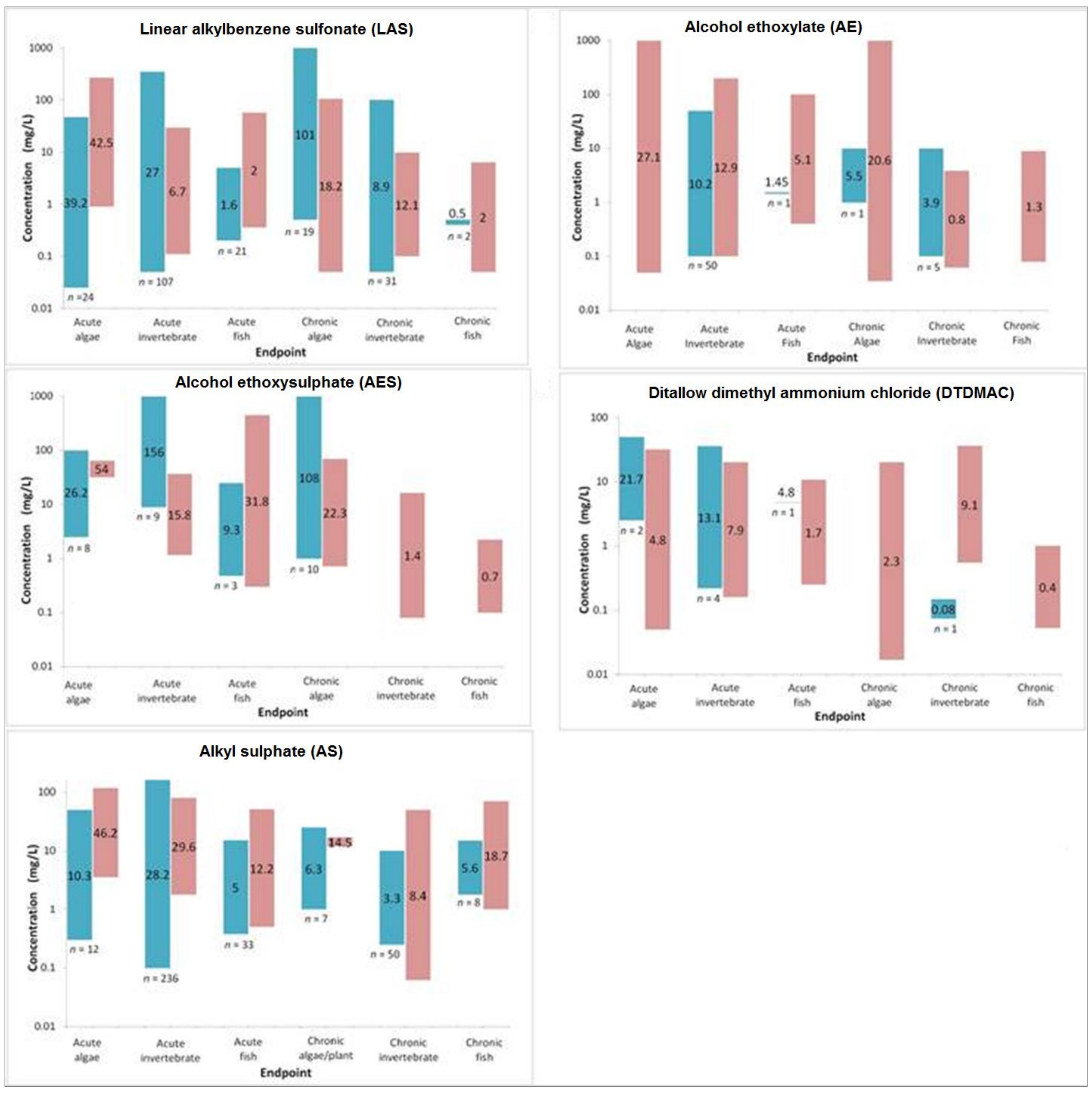

Table 2 – Summary of reviewed marine degradation data ranges for the surfactants and comparison with typical freshwater half-life values [4-7]. Marine studies were conducted at 20°C to 25°C (with the exception of three arctic studies). Data are based on first-order degradation models. Values in brackets are mean values, *n* = number of data).

	Marine degradation				Typical freshwater degradation
Compound	Primary degradation rate (d^{-1})	Lag (d)	Mineralization (%)	Half-life (d)	Half-life (d)
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)	0.025 – 0.5 (0.16)
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)	0.042 – 1.4 (0.72)
AS	–	7 – 14 (10.5; *n* = 2)	0 (*n* = 1)	0.26 – 20 (6.78; *n* = 7)	0.3 – 1.0 (0.75)
AE	0.02 – 0.34 (0.14; *n* = 13)	0 – 3 (0.86; *n* = 7)	8 – 87.2 (49.2; *n* = 11)	2.3 – 28 (11.76; *n* = 13)	0.17 – 1.0 (0.46)
DTDMAC	–	–	–	–	–

Figure 1– General chemical structures of the reviewed surfactants.

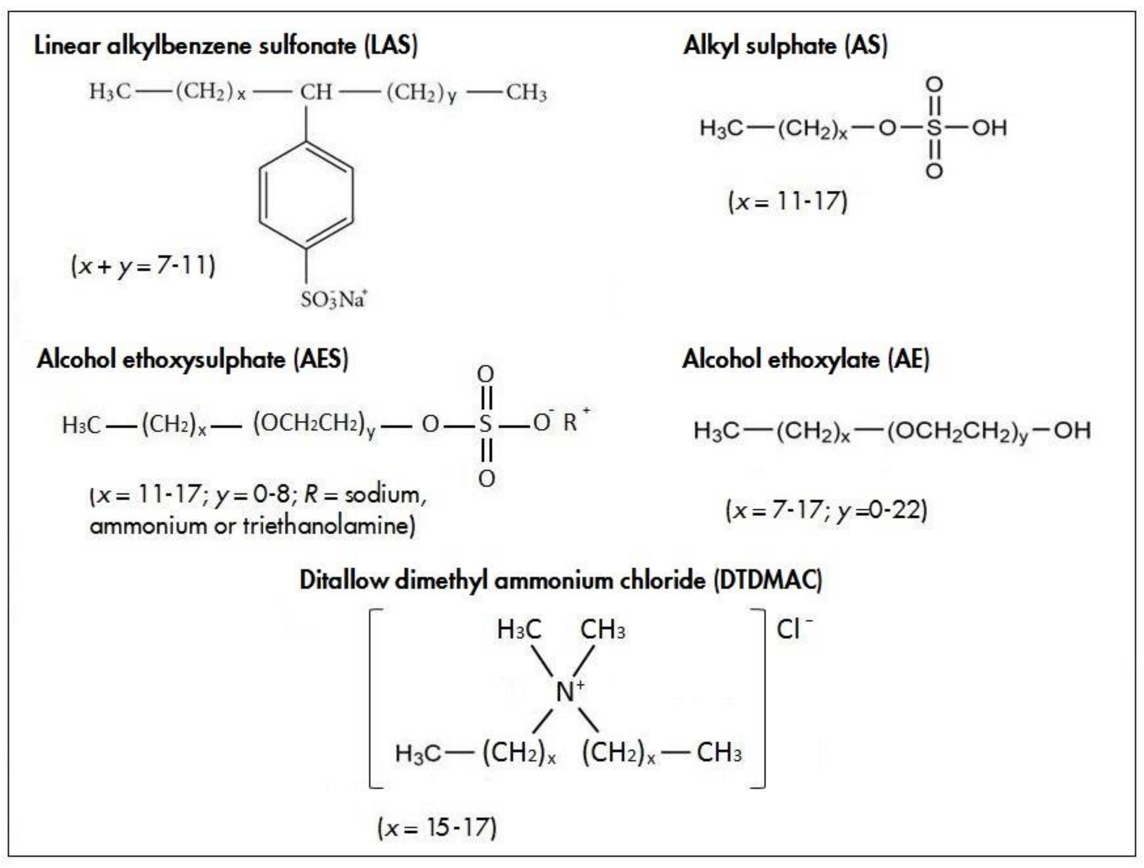

Table 1 – Summary of marine data values reported for the reviewed surfactants. Shaded boxes indicate no data found.

	LAS	AES	AS	AE	DTDMAC	Total
Degradation	37	8	7	13	0	65
Bioconcentration	3	0	1	0	0	4
Monitoring	19	4	1	20	10	54
Acute algae toxicity	26	8	12	0	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	0	37
Chronic invertebrate toxicity	41	0	50	4	1	96
Chronic fish toxicity	8	0	8	0	0	16
Marine bacteria toxicity	1	0	0	0	0	1
Total	304	42	360	90	18	

Results and Discussion

Marine data availability varied considerably between the five surfactants and type of study reviewed (Table 1):

- Marine biodegradation data availability from highest to lowest was: LAS > AE > AES > AS (no DTDMAC studies were found).
  - Biodegradability from highest to lowest was: AS > LAS > AE > AES (Table 2)
  - Marine biodegradation is generally comparatively slower than freshwater environments, possibly explained by lower activity towards xenobiotic chemicals of marine microbial communities relative to their freshwater counterparts. It was also suggested that complexation with calcium and magnesium ions in seawater reduces bioavailability, thus inhibiting biodegradation [11].
- Marine bioconcentration data is scarce in all surfactants examined. Freshwater data generally conclude that surfactants possess low accumulation potential due to metabolism and subsequent elimination.
- Marine sediment monitoring data availability from highest to lowest was: AE > LAS > DTDMAC > AES > AS, with detected concentrations ranging from 0.0074 – 9.19, <0.003 – 15.63, 0.0048 – >25, 0.061 – 14.32, and 0.13 mg/kg, respectively.
- Marine ecotoxicity data availability from highest to lowest was: AS > LAS > AE > AES > DTDMAC. Invertebrate studies are most common, compared to fish and algae/plant studies, particularly in chronic assessments.
  - Based on data ranges and mean values, marine toxicity from highest to lowest is: LAS > AS > AE > DTDMAC > AES, although data ranges do show wide variability (Figure 2).
  - Marine-freshwater ecotoxicity data comparisons have been inconsistent in the literature, with some studies reporting significantly higher marine species sensitivity, whereas others conclude no significant difference. Comparison of the reviewed marine data with typical freshwater data show that marine toxicity generally falls within freshwater toxicity ranges (Figure 2).

Conclusions

The following conclusions were derived from this review:

- Marine monitoring data are limited, particularly for AES and AS.
- Current marine biodegradation data are highly variable and predominantly focused on LAS. Based ion mean half-lives, marine biodegradation is generally rapid, but comparatively slower than freshwater.
- Marine bioconcentration data are severely limited. Based on freshwater data, bioconcentration and biomagnification is not expected.
- There are few chronic and sediment marine ecotoxicity studies for all surfactants, and a current lack of marine studies in AES in general (despite growing economic importance).
- Studies show wide variation in marine toxicity, however marine data generally falls within typical freshwater data ranges, suggesting similar sensitivity between marine and freshwater species. However, numerous key marine taxa cannot be tested (e.g. echinoderms, cephalopods, ctenophora [12]), hence marine species are underrepresented.
- Most marine ecotoxicity studies are based on nominal (rather than measured) concentrations, hence reliability of numerous marine studies may be limited.
- Additional marine studies, in particular; chronic AES studies, AES and AS monitoring studies, and bioconcentration studies (in all five surfactants), are encouraged to fill identified data gaps.

References
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