

Biodegradation of a Range of Non-Polymeric and Polymeric Surfactants in Seawater



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Background

Surfactants are used in large quantities in a variety of domestic and industrial products. Despite efficient removal during wastewater treatment, fractions of surfactants may reach aquatic and eventually marine environments. Screening tests for ready biodegradability describe the ultimate biodegradation potential of chemicals, but there is a lack of systematic biodegradation data across various classes of surfactants in the marine environment. In addition, few studies have focused on biodegradation of polymeric surfactants in natural seawater.

Materials and Methods

- The biodegradability of Amphoteric, anionic, non-ionic and cationic surfactants was tested in seawater (SW) from a Norwegian fjord (Trondheimsfjord) according to OECD 306
- A total of 18 surfactants (**Table 1**) were included in the study, of which 11 were polymeric ethoxylates with ≥2.5 moles of ethylene oxide (EO) groups
- 2 mg/L active ingredients were tested in amended SW at 20±2°C for up to 65 or 75 days
- Ultimate biodegradation determined by biochemical oxygen demand (BOD) as % of theoretical oxygen demand (ThOD)
- Ready biodegradation were concluded if >60% biodegradation were obtained within 28 days
- Primary biodegradation of polymeric C12-EO9; (500 µg/L final concentration) and its (PEGylated) metabolites was assessed in a rotating (0.75 r.p.m.) carousel (**Fig. 1**) in natural and sterilized (100 mg/L HgCl₂) SW by targeted LC-MS/MS analyses.
- One experiment was performed in SW containing marine particles (marine phytoplankton (*Skeletonema pseudocostatum*, 1x10⁴ cells/mL and kaolin, 5 mg/L).



Fig. 1. A slowly rotating carousel system with two units containing eight 2-L flasks with test solutions and with 300 mL headspace in the flasks (A). In experiments with marine particles, samples (100 mL) were filtered through steel filters with mesh size 20 µm (B) to separate particles/aggregates and filtrates (C).

Surfactant	C-chain	EO	SF	MW	ThOD _{NH3}	ThOD _{NO3}
Cocoamidopropyl betaine (CAPB) – amphoteric	12-14	--	C19 H38 N2 O3 Na	365.5	2.25	2.60
Sodium dodecyl sulphate (SDS) – anionic	12	--	C12 H25 O4 S Na	288.4	2.00	--
C12-14 EO4 S – anionic	12-14	4	C20 H41 O8 Na	464.6	1.97	--
C8 EO5 C – anionic	8	5	C18 H38 O6 C	350.5	2.24	--
C12 EO5 C – anionic	12	5	C22 H46 O6 C	406.6	2.40	--
C12 EO11 C – anionic	12	11	C34 H70 O12 C	670.9	2.17	--
C12 EO5 – non-ionic	12	5	C22 H46 O6	406.6	2.40	--
C12 EO9 – non-ionic	12	9	C30 H62 O10	582.8	2.23	--
C12 EO23 – non-ionic	12	23	C58 H118 O24	1199.6	2.01	--
C12 EO40 – non-ionic	12	40	C92 H186 O41	1948.5	1.94	--
C10 EO8 – non-ionic	10	8	C26 H54 O9	510.7	2.19	--
C13 EO18 – non-ionic	13	18	C49 H100 O19	993.3	2.08	--
C16-18 EO50 – non-ionic	16-18	50	C116 H234 O51	2445.1	1.95	--
n-Dodecyl β-D-glucopyranoside (DDGP) – non-ionic	12	--	C18 H36 O6	348.5	2.20	--
n-Dodecyl β-D-maltoside (DDM) – non-ionic	12	--	C24 H46 O11	510.6	1.88	--
Dodecyltrimethylammonium chloride (DTAC) – cationic	12	--	C15 H34 Cl N	263.9	2.73	2.97
Hexadecyltrimethylammonium chloride (HTAC) – cationic	16	--	C19 H42 Cl N	320.0	2.85	3.05
N-Benzyl-N,N-dimethyltetradecan-1-aminium chloride (BAC) – cationic	14	--	C23 H42 Cl N	368.0	2.83	3.00

Table 1. Surfactant properties: C-chain, average EOs, structural formulas (SF) and molecular weights (MW). ThOD_{NH3} was calculated for all surfactants and ThOD_{NO3} for nitrogen-containing substances.

Ultimate Biodegradation Results

- 12 of the 18 surfactants reached 60% biodegradation after 28 days and are considered readily biodegradable in SW
- 6 of the tested surfactants were able to reach 60% biodegradation by extended incubation time
- Reduced biodegradation of some cationic surfactants are associated with their known biocidal activity and toxicity to microorganisms
- Polymeric alcohol ethoxylates with the highest numbers of EO groups (40-50) were less promptly biodegraded than those with lower numbers (4-23)
- All surfactants showed >20% biodegradation after 28 days, indicating primary biodegradation in SW

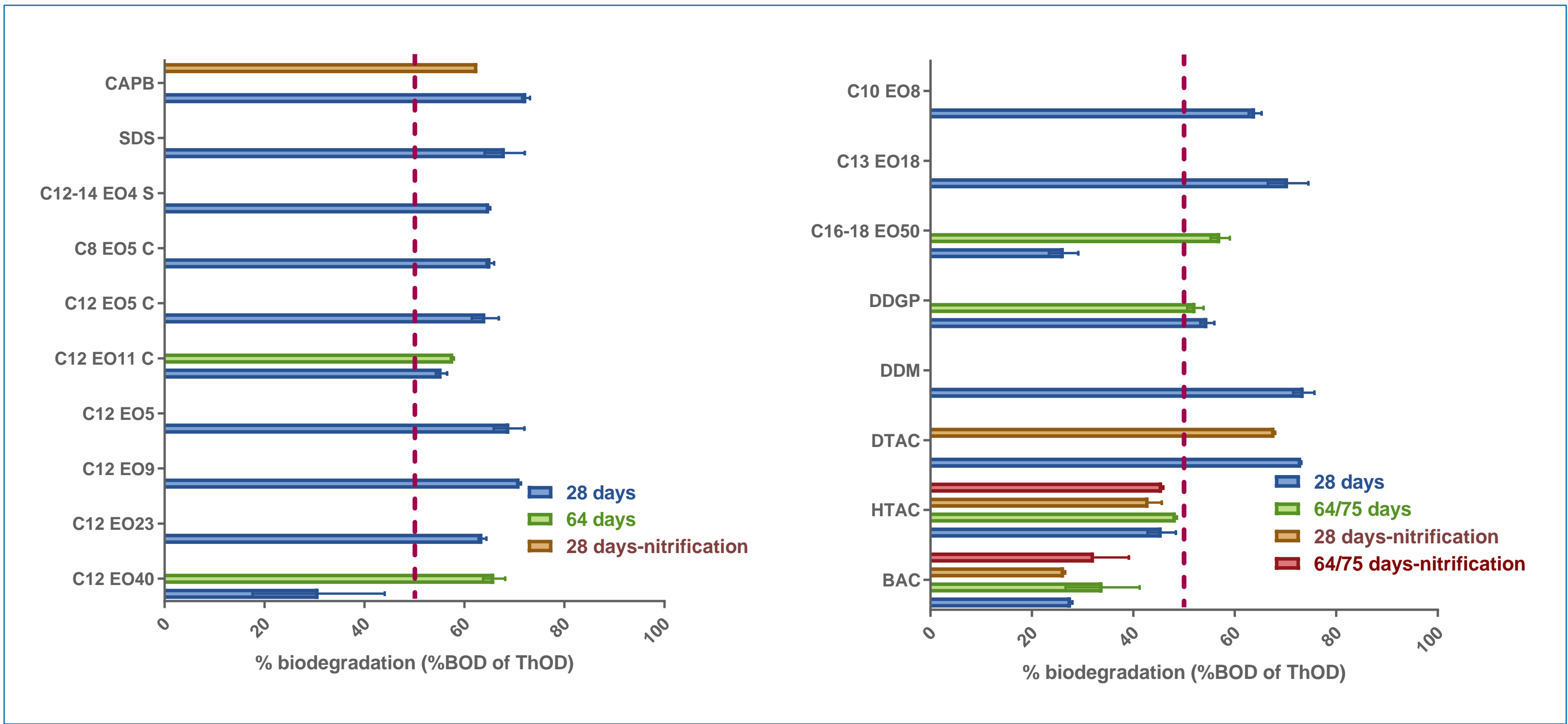


Fig. 2. Ultimate biodegradation of the 18 surfactants after 28 days of incubation in SW, and after 64/75 days for those not reaching 60% biodegradation after 28 days. The results shown as mean ± SD. Results for nitrogen-containing surfactants report both to ThOD_{NH3} and ThOD_{NO3} (nitrification). The broken lines describe the pass level of 60% for demonstrating ultimate biodegradation.

Primary Biodegradation Results

- Rapid primary biodegradation of C12-EO9 polymeric alcohol ethoxylate (99% depletion after 2 days in nSW) was determined, and parent surfactant depletion coincided with temporary formation of PEGs with 5 to 18 EO-groups (Fig. 3A)
- PEG concentrations became 12 times higher after 2 days than at the start of the experiment, and temporary PEG accumulations occurred across the EO5 to EO18 compounds after 2-4 days of incubation, followed by rapid decline (Fig. 3A and B).
- This indicated central fission as a mechanism for rapid biodegradation of polymeric alcohol ethoxylates in SW
- Near-complete depletion (≥95.5%) of C12-EO9 after 7 days of incubation at 20°C was also determined in non-amended natural SW with suspended particulate materials (SPMs) by targeted LC-MS analyses (Fig. 4A).
- When filtrates and particles >20µm were separated by filtration (steel filter), particle association was also indicated from the measurements, since fractions of the surfactants were measured in the filter-trapped materials (Figure 4B).

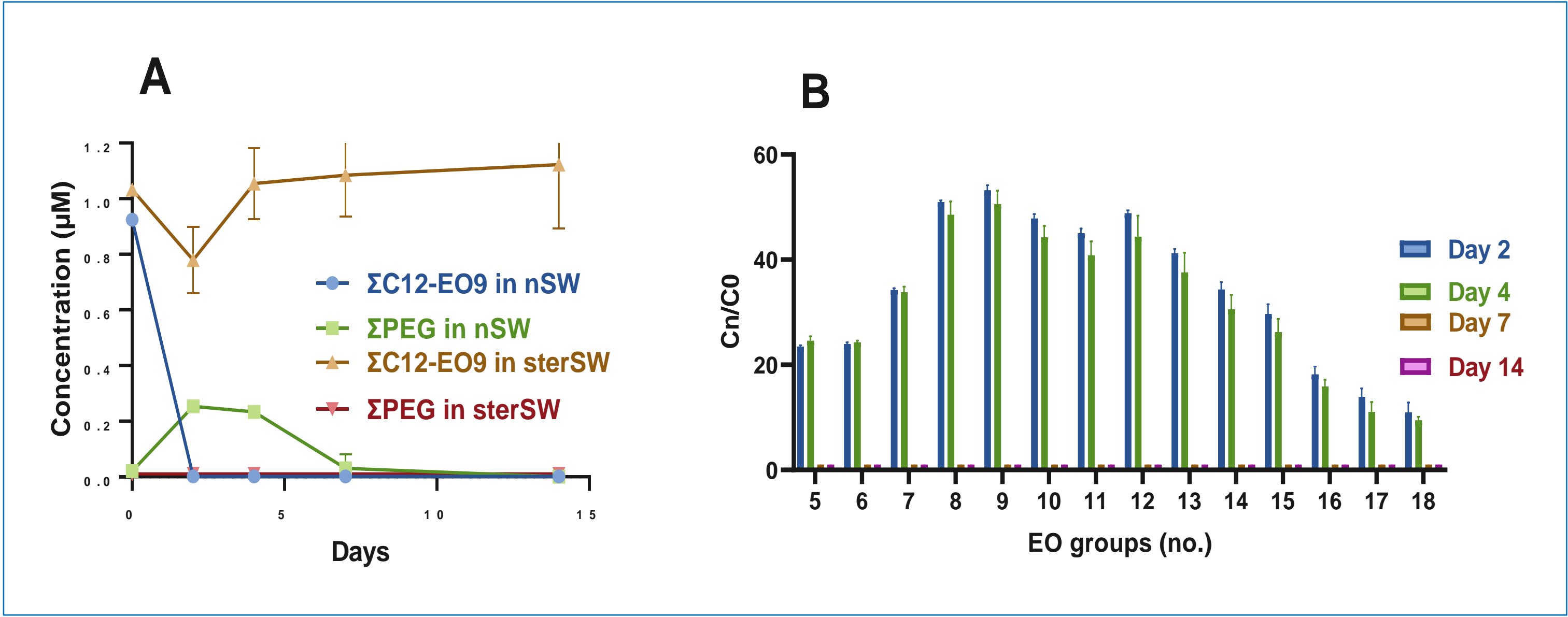


Fig. 3. (A) LC-MS targeted analyses of C12-EO9 depletion (ΣEO homologues) in normal SW (nSW) and sterilized SW (sterSW), (B) ratios between concentrations of PEGs after incubations for 2 to 14 days (Cn) compared to start C0. Results are shown as mean ± SD of three replicates.

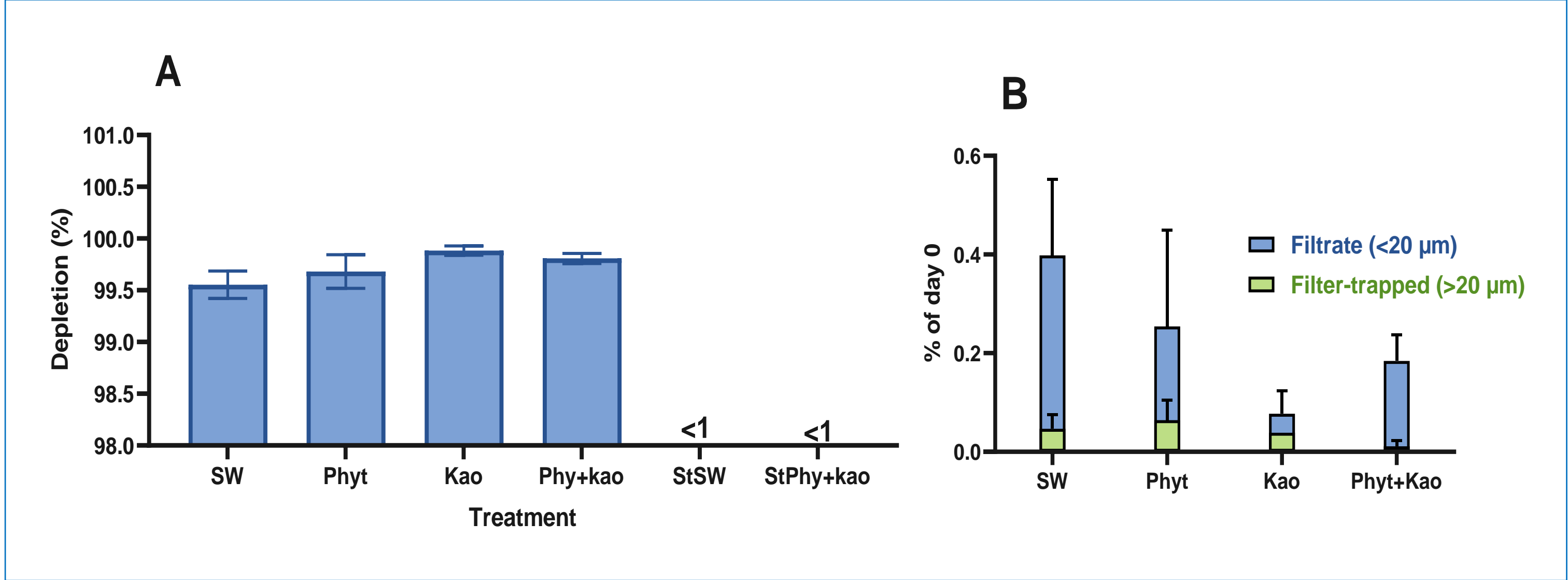


Fig. 4. (A) Depletion of C12-EO9 after 7 days of incubation in natural SW and natural SW with SPMs, which were applied as phytoplankton (Phyt), kaolin (kao), or as phytoplankton and kaolin (Phy+kao). Sterilized controls were also included. (B) Depletion determined as reductions in surfactant concentrations compared to measured initial concentrations. Results are shown as mean ± SD. % of three replicates

Conclusions

Biodegradation testing indicates that most surfactants tested exhibited high biodegradation potential in SW and will be quickly degraded in the marine environment if directly discharged (e.g. from ships or offshore oil and gas installations) or indirectly via sewage runoffs. When released to SW, surfactant associations to SPMs may be expected, although SW with SPM did not affect primary biodegradation of a selected polyethoxylated surfactant when compared to the SW without SPMs.

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