Effects of anthropogenic surfactants on the conversion of marine dissolved organic carbon and microgels

Ruei-Feng Shiu ¹, Chon-Lin Lee ^{1,2,3,4*}

Abstract

The possible impact of three types of anthropogenic surfactants on the ability of marine dissolved organic carbon (DOC) to form self-assembled microgels was evaluated. The behavior of existing native microgels was also examined in the presence of surfactants. These results reveal that the release of surfactants even at low concentrations into the aquatic environment could effectively hinder the self-assembly of DOC polymers. The extent of the size reduction had the following order: anionic, cationic, and non-ionic. Furthermore, charged surfactants can disrupt existing native microgels, converting large assemblies into smaller particles. One possible mechanism is that surfactants are able to enhance the stability of DOC polymers and disrupt aggregates due to their surface charges and protein-denaturing activities. These findings suggest that the ecological system is altered by anthropogenic surfactants, and provide useful information for ecological assessments of different types of surfactants and raise warnings about surfactant applications.

Key words: Surfactants, Dissolved organic carbon, Microgel, Self-assembly

1. Introduction

Marine dissolved organic carbon (DOC) consists of compounds with complex chemical properties that play a crucial role in biogeochemical reactions (Falkowski et al., 2000). It makes up a huge carbon reservoir in the world's oceans, accounting for a conservative estimate of approximately 700 gigatons of total carbon (Hedges, 1992). Understanding DOC dynamics and phase transitions is therefore essential for establishing the fate of organic carbon and CO₂ sequestration.

Chin et al. (1998) were the first group to apply the principles of soft matter physics to DOC. They determined that around 10% of the marine DOC polymers exist as Ca ion-bound crosslinked and tangled three-dimensional microgels. This discovery opens up an intriguing new field in the DOC–particulate organic carbon (POC) shunts. In fact, this microgel formation is directly related to the gravitational sinking of organic carbon and elements in the ocean, which takes the organic particles from surface water into the deep ocean. This is a significant process in the marine carbon and nutrient cycle, as well as in the formation of cloud condensation nuclei (Verdugo and Santschi, 2010; Verdugo, 2012). These intermingled networks, with nutrients/pollutants carried from the surface, are also accessible to microbes, making the microgel important in biological pumps, bioavailability of pollutants, the food web, and microbe sustenance (Kepkay, 1994; Carlson et al., 2002; Verdugo et al., 2004; Koron et al., 2013; Yamada et al., 2016; Shiu and Lee, 2017). Many recent studies have focused on the mechanism of DOC polymer aggregation and the parameters controlling microgel formation. These observations have established that polyanionic DOC polymers can enmesh with each other through ionic bonds and hydrophobic forces (Chin et al., 1998; Ding et al., 2008). Other controlling factors include the lengths of the polymer chains, the polymer concentrations, and external changes (e.g., the pH value, temperature, and surrounding materials) (Orellana and

1 Verdugo, 2003; Chen et al., 2011; Chen et al., 2015). Our previously published data
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3 indicated that carbonaceous particles at ppb concentrations reduce microgel
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5 equilibrium sizes, possibly because the negative surface charges of carbonaceous
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7 particles decrease the Ca cross-linking bridges of DOC polymers (Shiu et al., 2014).
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9 Thus, contaminants, even at low concentrations, may have negative effects on the
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11 aggregation of marine DOC polymers and could potentially have far-reaching
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13 influences on marine biogeochemical processes.
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17 The present-day use of surfactants is an important component of anthropogenic
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19 activities. Surfactants have hydrophobic and hydrophilic sectors (polar head groups
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21 and nonpolar hydrocarbon tails) in one molecule; therefore, they readily interact with
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23 both polar and non-polar substances (Yamaguchi et al., 1999; Xiao et al., 2000). They
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25 also effectively lower the surface tension of liquids and reduce the interfacial tension
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27 between two liquids or between a liquid and a solid. For this reason, surfactants have
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29 found extensive use in a wide variety of products designed for household cleaning,
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31 emulsification, solubilization, sterilization, nanoparticle dispersion, oil dispersal,
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33 pollutant treatment, cell lysis, etc. (Schramm et al., 2003; Yang et al., 2015). After use,
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35 these surfactants are typically discharged into rivers or sewage treatment plants and
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37 eventually enter the coastal and open oceans (Ying, 2006). Recent studies have now
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39 recorded their presence at various concentrations in environmental media such as
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41 wastewater, seawater, suspended solids, and sediments (Clara et al., 2007; Cantarero
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43 et al., 2012; Huang et al., 2015). Therefore, the assessment of surfactant effects on the
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45 spontaneous assembly of DOC polymers and existing microgels requires a
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47 determination of which types of these materials might have adverse effects on organic
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49 carbon conversion.
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57 The complex nature of surfactants gives them distinct behaviors and fates in the
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59 environment and their effects on marine microgels are difficult to document in situ. In
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this study, we conducted laboratory simulations (adding surfactants in collected seawater) to evaluate the possible impacts of three surfactant types (cationic, anionic, and non-ionic) on the self-assembly of DOC polymers. Our choices were sodium dodecyl sulfate (SDS), benzyl-dimethyl-tetradecyl-ammonium chloride (BDTAC), and nonylphenol (NP), which are mostly produced from anthropogenic activities, as models of anionic, cationic, and non-ionic surfactants, respectively, to investigate their effects on the aggregation size of marine microgels. We also utilized atomic force microscopy (AFM) to observe surfactant-microgel interactions and to search for possible mechanisms underlying these interactions. The experiments described here provide new insights into the effects of different types of surfactants on marine DOC–POC exchanges and increase our understanding of the potentially far-reaching influences of anthropogenic pollutants on oceanic DOC–POC shunts.

2. Material and methods

2.1 Chemicals

Sodium dodecyl sulfate (SDS) and benzyldimethyltetradecylammonium chloride (BDTAC) were purchased from Sigma Aldrich (St. Louis, MO, USA). Nonylphenol (NP) was obtained from AccuStandard Inc., (New Haven, CT, USA). The chemical properties of the surfactants used in this study are shown in Table1.

Table 1. Chemical properties of the surfactants used in this study.

	Ionic type	Molecular structure	Molecular formula	Molecular weight (g/mol)
BDTAC	Cationic		C ₂₃ H ₄₂ ClN	368.04

SDS	Anionic	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{O}-\text{S}(=\text{O})_2\text{ONa}$	$\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$	288.38
NP	Non-ionic		$\text{C}_{15}\text{H}_{24}\text{O}$	220.35

2.2 Sample collection and DOC sample pre-treatment

Native seawater was collected from the Taiwan Strait in December 2013 (22°42'82.1, 120°13'87.1) from aboard the Taiwanese R/V Ocean Researcher III (cruise ORIII-1733). DOC samples were sequentially filtered through a 0.22 μm filter pre-washed (0.1 N HCl) and rinsed with Milli-Q water (Millipore 18.2 $\text{M}\Omega\cdot\text{cm}$). Microbial activity was inhibited by adding 3 mM sodium azide to the water samples, which were then stored in the dark at 4°C. The marine DOC ($0.44\pm0.01\text{ mgL}^{-1}$) concentration was measured by catalytic high temperature oxidation using a total organic carbon analyzer (OI Analytical, Aurora Model 1030 W).

2.3 Microgel size measurement.

The aggregate size of DOC was monitored using a MoFlo TM XDP flow cytometer (FC; Beckman Coulter, USA). The laser of this instrument was set at 488 nm and the power of the laser was set at 170 mW (Chin et al., 1998; Verdugo et al., 2008). The size calibration of the FC was evaluated using a standard suspension of polystyrene latex microspheres (Spherotech, Inc., USA). Each measurement was replicated (≥ 5) in a 1 mL water sample at room temperature.

2.4 Preparation of AFM samples

The assembled microgels were filtered through a 0.22 μm Millipore Isopore membrane (Fisher Scientific, Los Angeles, CA) to fix the microgel on the membrane, which was then soaked in test solutions (with/without surfactant). After 10 days, the membrane with the retained microgel was carefully glued onto a holder using a double-sided sticky carbon tape, with the microgel film upwards.

2.5 Measurement of particle thickness and dimensions

Microgel disruption or dispersion was estimated by AFM using a XE-100 microscope (Park System Corporation, South Korea) in the contact mode, performed using a gold-coated Si_3N_4 AFM cantilever (Microlever, Veeco/ThermoMicroscopes, Sunnyvale, CA). The nominal tip radius was 20 nm at a force constant of 0.12 N/m, the set point voltage was approximately 2.0 V, and the integral and proportional gains were adjusted at different scan rates at 0.50 Hz. The XEI 1.8.0.Build 20 software was used for analysis of the obtained data. Microgel diameters and thicknesses were measured on single particles at $5\mu\text{m} \times 5\mu\text{m}$ scan areas. The thickness data were digitally recorded to obtain surface topography, and these data were also used to evaluate the particle dimensions. All results were obtained from the analysis of at least 10 particles.

2.6 Statistical analysis

The data in this study were presented as means $\pm$ standard deviation (SD). Statistically, significant differences were based on results of Student's t-test analysis with p values of 0.05 (or indicated *). Statistical analysis was assessed using Microsoft Office Excel and GraphPad Prism 4.0 (GraphPad Software, Inc., San Diego, CA).

3. Results and discussion

3.1 Effects of surfactants on marine DOC assembly

As shown in Fig.1, we recorded the change in effects of anthropogenic interferences on the particle size of DOC-POC to understand the effect of different surfactants on marine DOC assembly. Our control experiment (0 mgL^{-1} surfactant) showed that marine DOC polymers can spontaneously assemble into gels with sizes around $4\mu\text{m}$ within 72 h, which is comparable to literature findings (Chin et al., 1998; Shiu et al., 2014; Chen et al., 2015). Notably, marine microgel formation was retarded and

reduced in the presence of anionic (SDS), cationic (BDTAC), and non-ionic types of surfactants when compared to the corresponding treatments without surfactants. The extent of the size reduction had the following order: anionic, cationic, and non-ionic. The addition of SDS at a concentration of 0.1 mgL^{-1} changed the final size of the microgels formed in equilibrium to roughly $2 \text{ }\mu\text{m}$. A further increase in the SDS concentration to 1 mgL^{-1} resulted in a complete inhibition of assembly (particles were all below $1 \text{ }\mu\text{m}$), as shown in Fig. 1a. Similarly, the average equilibrium size of marine microgels was around $2.6 \text{ }\mu\text{m}$ and $1.5 \text{ }\mu\text{m}$ in the presence of 0.1 mgL^{-1} and 1 mgL^{-1} of BDTAC, respectively (Fig. 1b). The equilibrium size of the microgel decreased to $3.0 \text{ }\mu\text{m}$ and $2.5 \text{ }\mu\text{m}$ in the presence of 0.1 mgL^{-1} and 1 mgL^{-1} NP, and these differences were significantly smaller than the control sizes at 240 h (Fig. 1c) (t-test, $p < 0.05$).

Figure 1. The influence of SDS (a), BDTAC (b), and NP (c) surfactants on the spontaneous assembly of marine DOC polymer. Different concentrations of surfactant were used, including 0 (solid squares), 0.1 (circles), and 1 (triangles) mgL^{-1} .

Interestingly, a sudden drop occurred in the size of the microgels with higher concentrations all three types of surfactants from 120 to 240 h (Fig. 1), indicating that surfactants may have the capability to unfold or disrupt DOC aggregates. We investigated the influence of surfactants on existing native microgels in greater detail by adding the surfactants to seawater in which the microgel had been allowed to

equilibrate (self-assembled DOC after 10 days; equilibrium size around 4 μm). Fig. 2 shows the results for 1 mgL^{-1} of SDS and BDTAC, where the pre-existing aggregated microgels (in equilibrium) were effectively unfolded or disrupted. By contrast, NP (also at 1 mgL^{-1}) caused no significant difference in the equilibrium microgel size. These results reveal that the release of surfactants at low concentrations into the aquatic environment could effectively hinder self-assembly of DOC polymers by affecting the equilibrium size and the assembly curves. In addition, the surfactants could even cause the existing microgels to unfold.

Figure 2. Control experiment (no added surfactants) and exposure of equilibrated microgels to 1 mgL^{-1} of surfactants for 10 days.

Based on published studies, DOC polymers comprise a broad spectrum of constituents, including polysaccharides, proteins, nucleic acids, and lipids, which are directly released into seawater by bacteria and phytoplankton (Xu et al., 2011). Their negative surface moieties can readily entangle with each other via electrostatic Ca crosslinks, ultimately forming the microgel phase (Chin et al., 1998; Verdugo, 2012). This biopolymer aggregation is also quite sensitive to environmental parameters such as pH, temperature, and polymer chain length (Orellana et al., 2011; Chen et al., 2015).

1 Previous studies have reported that negatively charged carbonaceous particles were
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3 able to block the self-assembly of polyanionic polymers. This is because the
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5 negatively charged particles decrease the numbers of Ca cross-linking bridges within
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7 the DOC polymers (Zhang et al., 2012; Shiu et al., 2014). In fact, surface-active
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9 materials that contain various charges also act as strong protein denaturants (Helenius
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11 and Simons, 1975; Lasch, 1995; Holmberg et al., 2003).
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15 Based on our findings, we hypothesize that the amphiphilic properties of
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17 surfactants could change the DOC–POC shunt by their charge effects and ability to
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19 disrupt the DOC interactions. The largest reduction in microgel size in all the treated
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21 samples was observed in response to the addition of SDS, suggesting that the
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23 negatively charged head was able to compete with calcium ions and induced a charge
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25 stabilization, while the disruption by surfactants caused the sudden drop in the size of
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27 the SDS-DOC at 240 h.
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32 Notably, a reduction in the hydrodynamic diameter was also observed following
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34 the addition of the positively charged surfactant (BDTAC). This reduction could be a
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36 result of protein lysis assisted by the electrostatic attraction between the positive
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38 charges of BDTAC and the negatively charged sites on the surface of DOC polymers
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40 (McDonnell and Russell, 1999; Liu et al., 2013). These observations are similar to
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42 those reported in other studies. For example, some wastewater treatment experiments
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44 documented that surfactants can cause protein and polysaccharides lysis and lead to
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46 the release of intracellular materials from activated sludge extracellular polymeric
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48 substances (Yuan et al., 2011; Wang et al., 2014a; Wang et al., 2014b). Other research
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50 also determined that specific surfactants are able to attach to cell surfaces, thereby
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52 disrupting the cell structure of microorganisms (Chen et al., 1999). Further
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54 investigation of the effects of protein lysis or disrupting could help in understanding
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56 the possible mechanism behind the phenomenon observed.
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3.2 Possible mechanisms for the hindrance of DOC assembly by surfactants

In the present experiment, we used AFM experiments to support this proposed disruption of polysaccharide assemblies. AFM images can provide high spatial resolution of the 3D structure of complex living cells or polymers while still fully hydrated (Santschi et al., 1998; Radić et al., 2011). As described in the Fig. 3, the scanned AFM area was $5\mu\text{m} \times 5\mu\text{m}$, giving micron resolution. Fig. 3a shows native marine microgel structure, while Fig. 3b, c and d corresponds to three specimens of marine microgels treated with SDS, BDTAC and NP, respectively. These micrographs confirm our conjectures and provide visual evidence of differences in the general appearance and thickness of the imaged gel networks treated with SDS and BDTAC, compared with the native microgel. The native microgel and microgel-NP samples had a significantly larger gel size and thickness than the microgel-SDS and microgel-BDTAC samples (Fig. 3 and 4). The mean thicknesses of the native microgels and following the addition of NP, SDS, and BDTAC were 1.5, 1.3, 0.6, and $0.7\mu\text{m}$, respectively. These micrographs confirm that SDS and BDTAC (at 1 mgL^{-1}) have the ability to unfold or disrupt microgel aggregates. The results are similar with those of other studies, which reported that surrounding materials effectively disrupt cell membranes and unfold protein structure, with a decreased thickness. For example, AFM was used to observe the effects of nanoparticles on the disruption and lysis of microbial cells, the AFM images of damaged cell showed a significantly changed profile, with a decreased height (thickness), compared to undamaged cells (Stoimenov et al., 2002; Wang et al., 2016). These observations, together with results from size measurements, confirm that the active characteristics of surfactants inhibited marine DOC aggregation and could unfold aggregated microgels as well.

Figure 3. AFM images of equilibrium marine microgel at different surfactants: (a) native microgels, (b) microgel-NP, (c) microgel-BDTAC and (d) microgel-SDS.

Figure 4. The mean thickness of native microgels (control) and following the addition of NP, SDS, and BDTAC.

3.3 Environmental implications

The increase in human activities has resulted in strong interactions between the rivers and the sea. Most of the marine pollution originates from land-based sources, as terrestrial chemicals ultimately are transported to the coastal and ocean systems. The increasingly widespread use of surfactants as traditional or emerging contaminants is therefore now an environmental problem. We also note that large volumes of chemical dispersants were cast into the Gulf of Mexico to treat the Deepwater Horizon crude oil spill (Lehr et al., 2010). Therefore, much research has been focused on the sources, transport, fates, toxicity, and impact of dispersants in different environmental media, including the atmosphere, on marine sediments (Roslan et al., 2010; Cantarero et al., 2012; Almeda et al., 2014; Passow, 2016). However, the impact of surfactants on the marine carbon cycle and the sinking particles is largely unexplored.

Exchanges between DOC and POC in the ocean environment are an attractive research issue, because the gravitational sinking and sedimentation speeds of marine organic carbon is directly dependent upon the particle size (De La Rocha and Passow, 2007). These colloid materials are involved in carbon sequestration and transporting elements from the ocean surface to the seafloor, as these particles have a high organic carbon content and high affinity for other elements. The results presented here clearly show that surfactants can reduce the self-assembly of DOC polymers and disrupt marine microgels to generate small organic particles rather than large microgel assemblies. This disruption of microgel formation would lead to a reduction in the flux of organic particles to the deep ocean. Therefore, the huge organic carbon flux and the transportation of needed microbial substrates and nutrients could be altered by anthropogenic pollutants like surfactants, which might have far-reaching influences on DOC–POC processes. These results also provide insight into the fate of surfactants

and methods for assessing their ecological impacts.

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