



Role of microgel formation in scavenging of chromophoric dissolved organic matter and heavy metals in a river-sea system



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HIGHLIGHTS

- Different types of DOC polymers forming microgel were compared.
- The assembly effectiveness of marine DOC was much higher than riverine DOC.
- Types and sources of DOC polymers may control the aquatic microgel abundance.
- An alternative route for CDOM and heavy metals removal is presented.
- Ecological risk and fate assessments of pollutants may consider the microgel phase.

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ABSTRACT

We use riverine and marine dissolved organic carbon (DOC) polymers to examine their aggregation behavior, and to evaluate the roles of microgel formation in scavenging of chromophoric dissolved organic matter (CDOM) and heavy metals in a river-sea system. Our results indicate that riverine and marine microgels did not exhibit very much difference in size and self-assembly curve; however, the assembly effectiveness ([microgel]/DOC) of marine samples was much higher than riverine. Instead of concentration of DOC, other factors such as types and sources of DOC polymers may control the microgel abundance in aquatic environments. After filtering water samples (microgels removed), the CDOM and selected metals (Cu, Ni, Mn) in the filtrate were quantified. CDOM and metals were concurrently removed to an extent via DOC polymer re-aggregation, which also suggested that the microgels had sequestering capability in CDOM and metals. This finding provides an alternative route for CDOM and heavy metals removal from the water column. As such the process of re-aggregation into microgels should then be considered besides traditional phase partitioning in the assessment of the ecological risk and fate of hazardous materials.

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1. Introduction

Aquatic dissolved organic carbon (DOC) is one of the largest pools of reduced carbon on Earth and also one of the most complex organic mixtures in the environment system. Organic materials can be derived from various natural and anthropogenic sources including photosynthetic production, bacterial activity, terrestrial input, and industrial effluents. The impacts of these materials, including colloid or DOC biopolymers, on the ecosystem, could be vast, for

example, in their participation in various biogeochemical reactions such as microbial loop, element exchange, light absorption and food webs [1,2]. Some studies also indicated that DOC alters the mobility of pollutants which in turn affects their bioavailability, and acts as a critical regulator for pollutant toxicity [3–5]. The capability of these materials comes from some functional groups present within the natural organic matter structure, such as polysaccharides, proteins, lipids, nucleic acids and various functional group types (carboxylate, sulfate, and phosphate) [6–8]. These functional groups have the potential to provide highly stable binding and adsorbing sites with metal ions and organic compounds [9–11]. It is therefore generally acknowledged that DOC can serve as natural organic ligands

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to sequester organic and inorganic materials and thus influence their availability to organisms [4,12].

Marine DOC polymers were first shown to form self-assembly aggregates as an ionic-bond-stabilized tangle network, with size ranging from molecules to an approximate size of 3–5 μm microgels [13]. This DOC-particulate organic carbon (POC) conversion is also believed to play a crucial role in marine snow, micro-aggregates and biofilms formation [14] and in the vertical transport of carbon, nutrients and elements [15–17]. Recent observations confirmed unambiguously that, besides in the ocean, these self-assembly aggregates of DOC polymers are also present in natural environments such as coastal, lake and river water [13,18,19]. The process of self-assembly aggregation into larger sinking particles is not well studied in the river-sea system, although it should be an important process in the fate and transport of organic matter. This process should also have significant implications on contaminant or surrounding material transport, which has not been well studied either [20–23]. In addition, the scavenging of particulate pollutants is well known in the estuarine region and is a significant process in quantifying land-derived natural and anthropogenic chemicals into shelf seas [24,25]. It is believed that the microgel formation should have a contribution to the process through self-assembly and sinking particle processes [26,27]. Besides, anthropogenic activities such as wastewater discharge are believed to alter DOC composition, chemical characteristic, concentration, and reactivity, especially in densely populated or industrial areas. Therefore, further study of re-aggregation of aquatic DOC in river-sea systems is needed to understand the role of microgel formation in scavenging surrounding materials via vertical transport.

In this study, we collected water samples from the Houjin River basin to the Taiwan Strait. This river flows through a metropolitan area and receives domestic and industrial discharges, with heavy metals and organic pollutants [28]. As the adsorptive and adhesive behaviors of aquatic organic materials by micro- and macrogels in an aquatic system are currently unclear [29], our principal aim was to examine the mechanism of aquatic microgel formation and to investigate the interaction of microgels with CDOM and metals in samples with different environmental parameters (river to sea). We tested the capacity of different types of DOC polymers forming microgels and their sequestering inorganic/organic materials in a river-sea system. The results will facilitate progress in the understanding of the behavior of different types of DOC polymers forming microgels and provide new insights into the interaction between aquatic surrounding materials and microgels.

2. Material and methods

2.1. Sampling and pre-treatment

Three water samples were collected from the Houjin River to the Taiwan Strait in December 2013. The Houjin River originates from two upstream branches, passing through four major Kaohsiung industrial parks and Yuanjzhonggang Creek water intake stations and extending all the way down to the Taiwan Strait. Water samples were collected in precleaned glass bottles at each sampling site. Polyethylene bottles holding water samples for metal analysis were pre-cleaned by 10% HNO_3 and rinsed with Milli-Q water. After collection, these samples were returned to the laboratory and kept in the dark until further processing.

The analysis of chemical parameters (pH, salinity, temperature, suspended solid, Ca^{2+} and Mg^{2+}) was based on the standard methods of the National Institute of Environment Analysis (NIEA, Taiwan EPA). The DOC concentration (passed through a 0.22 μm PVDF filter, Merck Millipore Ltd.) was measured as total carbon by catalytic high-temperature oxidation using a total organic carbon analyzer

Table 1

Parameters of water samples collected from Houjin River and Taiwan Strait.

Location	Upstream	Downstream	Taiwan Strait
Longitude	120°19'34.1"	120°18'54.1"	120°13'87.1"
Latitude	22°43'31.7"	22°42'43.5"	22°42'82.1"
pH	7.21	7.62	8.12
Salinity (psu)	0.2	22.6	33.7
Temperature ($^{\circ}\text{C}$)	25.0	25.1	25.1
SS (mg L^{-1})	55.0 \pm 11.3	37.0 \pm 4.48	5.22 \pm 1.15
DOC (mg L^{-1})	10.7 \pm 0.7	5.9 \pm 0.9	0.44 \pm 0.01
Ca^{2+} (mg L^{-1})	94.5	294	444
Mg^{2+} (mg L^{-1})	129	865	1450

(OI Analytical, Aurora Model 1030 W). An overview of all chemical characteristics of the water samples is provided in Table 1. Salinity as an indicator of water types was ranged between 0.2 psu for fresh water (upstream), followed by brackish water (downstream, 22.6 psu), and sea water (Taiwan Strait, 33.7 psu). A similar trend was observed for the concentration of Ca^{2+} and Mg^{2+} . The upstream sample had the highest concentration of DOC and suspended solid (SS).

2.2. Self-assembly of DOC polymer and microgel concentration measurement

All DOC samples were passed through a 0.22 μm filter which was pre-washed (0.1 N HCl) and rinsed with Milli-Q water (Millipore 18.2 M Ω cm). To inhibit microbial activity, 3 mM sodium azide was added to water samples, which were then stored in the dark at 4 $^{\circ}\text{C}$. The aggregate size of DOC was monitored by MoFloTM XDP Flow Cytometry (FC, Beckman Coulter, Indianapolis, IN). This instrument was set at the 488 nm laser and the power of the laser was set at 170 mW [13,30]. The size calibration of the FC was evaluated using a standard suspension of polystyrene latex microspheres (Spherotech, Inc., Libertyville, IL). Each measurement was replicated (≥ 5) in a 1 mL water sample at room temperature. The microgel concentration was determined by weight method. In brief, samples of the microgel were collected at 240 h and filtered through a 0.22 μm membrane. Then the membrane was washed with three portions of Milli-Q water (150 mL) to avoid salt interference, and was weighed after drying the membrane (Mettler-Toledo XS105DU analytical balance).

2.3. Scanning electron microscopy (SEM)

SEM images were used to confirm aquatic DOC polymer networks. Samples of microgel collected at 240 h were taken and the assembled microgels retained on filters were observed using FEI Quanta 200 SEM (North America NanoPort, Portland, OR). The sample preparation was adopted from our previous study [31]. Microgel aggregation was filtered through a 0.22 μm Millipore IsoporeTM membrane (Fisher Scientific, Los Angeles, CA). The fixed microgels were dehydrated by soaking them in serially diluted ethanol (35%, 50%, 70%, 95%, and 100% ethanol) for 5 min and then coated in gold in preparation for viewing with SEM.

2.4. Fluorescence enhancement measurement

Chlortetracycline hydrochloride (CTC) was used as a bound Ca^{2+} indicator as in previous studies that reveal bound Ca^{2+} on polymers [32,33]. All of the water samples were labeled with CTC (100 μM). The fluorescence measurements were carried out with a Shimadzu RF-5000U spectrofluorophotometer ($\lambda_{\text{ex}} = 390 \text{ nm}$, $\lambda_{\text{em}} = 530 \text{ nm}$).

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