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Interactions between algal (AOM) and natural organic matter (NOM): Impacts on their photodegradation in surface waters☆

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ABSTRACT

The occurrence of algae bloom would lead to the release of algae-derived organic matter (AOM) and then alter the abundance and behavior of dissolved organic matter (DOM) in aquatic ecosystems. In this study, the characteristics and photodegradation of AOM, naturally occurring organic matter (NOM) derived from soil and plants and their mixtures were explored to reveal the potential interactions between AOM and NOM in water. Results indicated that the protein-like components from AOM and the humic-like components from SRNOM took place inter-component interactions in the AOM-NOM mixtures. Meanwhile, application of two-dimensional Fourier transform infrared correlation spectroscopic (2D-FTIR-COS) analysis revealed that carboxylic C=O had a high priority to bind with other functional groups (e.g., phenolic-OH, polysaccharides C-O, amideIIC-N/N-H and celluloses C-H). More crucially, it was found that the AOM-NOM mixtures subjected to a very different photodegradation behavior to their end-members (i.e., AOM and NOM), likely because of the occurrence of AOM-NOM interactions as well as their roles in mediating the yield of reactive oxygen species. For instance, the presence of AOM led to increased photodegradation degrees of the chromophoric fraction in NOM. In contrast, the NOM did not exhibit any photosensitization role in the photodegradation of the proteins from AOM. This study has potential implications for our understanding of the carbon cycling in anthropogenically impacted aquatic systems such as inland rivers and lakes.

1. Introduction

The excessive growth of harmful algae, which is normally driven by the high inputs of phosphorous and nitrogen to the ecosystems (Lewis et al., 2011), leads to subsurface hypoxia (dissolved oxygen < 2 mg/L) in lakes or oceans (Wang et al., 2016a), impairment of drinking water treatment (Pivokonsky et al., 2015a) and perturbation of aquatic community (Sheik et al., 2014). Previous investigations have shown that the growth and metabolism of phytoplankton can greatly contribute to the yield of autochthonous dissolved organic matter (DOM) in water (Zhang et al., 2009), likely because of the release of extracellular and intracellular organic matter. For instance, it was found that algae contributed 18–62% to the DOM in Oura Bay, Japan (Wada et al., 2007). In addition to the large quantitative contribution to DOM, algae-derived organic matter (AOM) delivers also diverse organic molecules related to its unique chemical compositions. AOM is operationally rich in organic-N, including amino acids, proteins and aliphatic amines (Henderson et al., 2008; Qi et al., 2016). Villacorte et al. found that the AOM is mainly composed of biopolymers (acidic polysaccharides and proteins) but some humic-like compounds and other low molecular weight compounds (Villacorte et al., 2015). Thus, it can be anticipated that the occurrence of AOM in natural

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waters would greatly alter the composition and chemical reactivity of DOM.

Once being released into the aquatic environment, AOM would undergo various dynamic changes due to interaction with other aquatic species, biodegradation and photodegradation (Liu et al., 2012). AOM molecules can potentially bind with the naturally occurring organic matter (NOM) derived from soil and plants (Yang and Hur, 2014). Previous attempt has shown that the presence of humic-like components can lead to fluorescence quenching of protein-like compoents, attributable to the interactions between protein-like and humic-like components (Wang et al., 2015). Particularly, the presence of divalent ions can greatly promote interactions between biomolecules (Wang et al., 2012; Liu et al., 2018; Xu et al., 2018; Wu et al., 2012; Yuan et al., 2015). Pivokonsky et al. found that the inter-component interactions in the DOM resulted in significant decrease in coagulant dosage during coagulation treatment (Pivokonsky et al., 2015a). In addition, the NOM or AOM components were also found to bind with chemicals (Chen et al., 2017). For instance, it was found that the protein-like and humic-like components from *Microcystis aeruginosa* posess opposite binding potential to pyrene (Yang et al., 2016). In addition to protein and humic substances, the AOM also contains considerable polysaccharides such as alginate. In fact, polysaccharides, which are of much high molecular weight and strong gelling property, are expected to have different binding properties to proteins and humic substances. A recent study by Myat et al. showed that alginate can bind with humic substances with the bridging of calcium ion (Myat et al., 2014). So far, little investigation has been conducted to reveal the interaction behavior between AOM and NOM and the subsequent impacts on their transport and transformation in water.

Biodegradation and photodegradation are the two major mechanisms mediating AOM or NOM dynamics. Polysaccharides and some amino acids could be utilized by bacteria or their own producers (Zhu et al., 2013; Meng et al., 2012). In comparison, the bio-refractory compounds, such as some proteins and humic substances, are susceptible to phototransformation (Benner and Kaiser, 2011). Organic matter in surface waters is inevitably exposed to strong solar radiation, particularly ultraviolet irradiation during algae-blooming season (Lurling and Tolman, 2014; Xu and Jiang, 2013). Although degradation kinetics is often lower than the catalytic oxidation, the strong solar radiation leads to structural alteration and gradual decomposition of organic matter in aquatic environment (Xu and Jiang, 2013; Wang et al., 2016b; Li et al., 2014). Previous study has documented that photobleaching rate and mineralization rate of aquatic humic substances were up to 80% and 70%, respectively, when being exposed to four times the strong solar light in the Amazon region (Rodríguez-Zúñiga et al., 2008). Most of the previous studies focused on photodegradation of either DOM or AOM in rivers, lakes and oceans (Benner and Kaiser, 2011; Xu and Jiang, 2013; Borisover et al., 2009; Dittmar et al., 2007; Cory et al., 2007; Bittar et al., 2015). In comparison, the phototransformation of the mixture of AOM and NOM was rarely investigated.

The objectives of this study, thus, were to reveal the interaction between AOM and NOM and its roles in changing the sunlight-induced photodegradation of AOM or NOM. In this study, the AOM was extracted from *Microcystis aeruginosa* and *Scenedesmus obliquus*. In this study, the soluble organic matter released by algea was defined as AOM, which is mainly composed of biopolymers such as polysaccharides and proteins (Chu et al., 2015). Suwannee River NOM (SRNOM), which is dominated by humic-like substances, was used as the proxy of hydrophobic NOM. After a series of transformation such as biodegradation and photodegradation, the AOM can be a potential contributor to hydrophobic NOM in aquatic ecosystems. In this current study, we only focused on the interaction of fresh AOM released by algae and hydrophobic NOM that is already present in water. The AOM, NOM and AOM-NOM mixtures were characterized by three-dimensional excitation-emission matrix (EEM) spectroscopy, UV–vis absorption spectroscopy and liquid chromatography with organic carbon detection (LC-OCD). The interaction mechanisms between model biopolymers (i.e., proteins and polysaccharides) and NOM were explored using two-dimensional Fourier transform infrared correlation spectroscopic (2D-FTIR-COS) analysis. The yield of reactive oxygen species was also analyzed to reveal the photodegradation mechanisms.

2. Materials and methods

2.1. Sample preparation

Microcystis aeruginosa (FACHB-930, a blue algae) and *Scenedesmus obliquus* (FACHB-12, a green algae), previously isolated from Lake Dianchi, China, were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, China. Algae cells were cultured in 1L conical flask containing autoclaved BG11 medium at 25 °C. Cultures were provided with a 12/12 h (Light/Dark) cycle and gentle magnetic agitation. To avoid the interference of BG11 medium on photochemical reaction, the algal cells were centrifuged at 3500 g for 5 min and rinsed three times with ultrapure water when the OD_{680} of algal cultures was approximately 0.60. Then, concentrated cells were re-suspended in ultrapure water and subsequently re-cultured until OD_{680} reached 0.15. Thereafter, the cultures were centrifuged at 10,000 g for 5 min and subsequently filtered through 0.45 μm nitrocellulose membrane filters. The filtrate was generally termed soluble algal organic matter (AOM). SRNOM (International Humic Substance Society) stock solution (100 mg-C L^{-1}) was prepared with ultrapure water and filtered through 0.45 μm pore size nitrocellulose membrane filters. The AOM-SRNOM mixtures were prepared by using the AOM and SRNOM stock solution and slowly stirred (200 rpm) for 10 min to ensure complete mixing. Note that the preparation of AOM, SRNOM and AOM-SRNOM solutions was conducted in a superclean bench to avoid the involvement of microbes in these DOM solutions.

2.2. Photodegradation experiment

To examine the co-photodegradation of AOM and SRNOM under different concentrations of SRNOM, the solutions of AOM and SRNOM were mixed at a fixed AOM concentration (3 mg-C L^{-1}) and a series of SRNOM concentrations of 0, 2, 4 and 6 mg-C L^{-1}, respectively. The solution pH was adjusted to 7 ± 0.20 using HCl or NaOH solutions at concentrations of 0.01, 0.1 and 1 mol/L. The background ion strength of solutions was controlled to 40 mM by sodium chloride solution. Photochemical experiments were performed in sealed borosilicate vials and in duplicate under natural sunlight (August, 2016). The ambient temperature was in the range of 28–38°C and all solutions accumulatively received a total sunlight power of 5.5×10^5 J as measured by a solar irradiator over the irradiation period. The details of photochemical experiment have been described elsewhere (Yang et al., 2014). In order to obtain solid data on the photodegradation behavior of AOM and SRNOM, AOM from both *Microcystis aeruginosa* and *Scenedesmus obliquus* were explored.

Meanwhile, a set of test solutions were purged with N_2 for 10 min before exposure to sunlight irradiation in order to evaluate the effect of DO on co-photodegradation of AOM and SRNOM. In comparison, aqueous SRNOM solutions with concentrations of 2, 4 and 6 mg-C L^{-1} were exposed to natural sunlight irradiation under the same condition. Following irradiation, aliquots of light-exposed