Absorption and fluorescence characteristics of rainwater CDOM and contribution to Lake Taihu, China

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HIGHLIGHTS

- Rainwater CDOM was significantly higher in the dry season than in the wet season.
- Four fluorescence components were identified for rainwater CDOM using PARAFAC.
- N and P nutrients were easily coupled with CDOM in rainwater.
- Rainwater CDOM played an important role in the lake CDOM biogeochemistry cycle.

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ABSTRACT

We characterized the composition and sources of chromophoric dissolved organic matter (CDOM) in rainwater, and assessed the relative contribution of rainwater CDOM to lake water in Lake Taihu based on rainwater collected during 35 rainfall events in 2012. Chemical analysis, ultraviolet–visible absorbance, and three-dimensional fluorescence spectroscopy were used to characterize CDOM. The CDOM absorbance coefficient at 254 nm (a254) had a significant seasonal variation, with a mean of 3.67 ± 1.69 m−1 in the wet season (from April to early August), which was significantly lower than the means in the two dry seasons (8.26 ± 2.94 m−1 from January to March, and 7.60 ± 3.80 m−1 from late August to December). The mean humification index and the mean index of recent autochthonous contribution were 0.74 ± 0.48 and 1.31 ± 0.35, respectively, indicating that rainwater CDOM was dominated by an atmospheric microbial origin component. We identified four fluorescence components using parallel factor analysis modeling in the rainwater CDOM, i.e., two protein-like components (C1 and C2) and two fulvic-like components (C3 and C4), which had characteristics similar to those of protein and humic-like substances, respectively. The a254 was significantly and positively (p < 0.001) correlated with each of the five nutrient parameters: total dissolved nitrogen (r² = 0.76), ammonium (r² = 0.65), nitrate (r² = 0.36), total dissolved phosphorus (r² = 0.55), and phosphate (r² = 0.50) showing the tightly coupling between CDOM and nutrients. Based on the deposition of the rainwater CDOM and the storage of the CDOM in Lake Taihu, the annual relative contribution of rainwater CDOM to the lake water was 11.7% in 2012. The results showed the important effect of wet deposition on CDOM sources in Lake Taihu, which is located in a region with severe air pollution in the Yangtze River Delta.

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1. Introduction

Processes associated with environmental change, such as land use change, urbanization and air pollution, promote increased concentrations of dust and aerosols in the atmosphere. These trends have been accelerating in recent decades (Neff et al., 2008; VanCuren et al., 2012). The resulting increase in dry and wet deposition has important chemical and biological effects on aquatic ecosystems (Ballantyne et al., 2011). For instance, dust deposition is an important source of nitrogen and phosphorus in many alpine and eutrophic lakes (Ballantyne et al., 2011; Luo et al., 2007; Zhai et al., 2009), and can shift the N:P stoichiometry of the water; as...
a result, phytoplankton growth is promoted (Elser et al., 2009; Zhai et al., 2009).

Although the influence of nutrient input on aquatic ecosystems has been widely addressed, the specific role of dissolved organic matter (DOM) inputs to lake ecosystems via dry and wet deposition, a potentially important process, has been rarely studied (de Vicente et al., 2012; Mladenov et al., 2009). The few studies that have evaluated the influence of dust deposition on alpine lakes have shown that the input of chromophoric dissolved organic matter (CDOM) from dust deposition can significantly change the optical properties and reduce the penetration depth of ultraviolet radiation (UV) (de Vicente et al., 2012; Mladenov et al., 2009). For instance, the atmospheric CDOM input to Mediterranean reservoirs decreased the 10% penetration depth of UVR (320 nm) by 15–43 cm (approximately 24–39%) (de Vicente et al., 2012).

The presence of CDOM in rainwater may play a role in atmospheric radiative transfer, by affecting the attenuation and spectral distribution of sunlight reaching the Earth’s surface. In addition, CDOM is often coupled with nutrients, and biologically available nitrogen is released for phytoplankton growth (Bushaw et al., 1996; Stedmon et al., 2007; Zhang et al., 2011a). Thus, the coupling of CDOM and nutrients may be elucidated by examining the relationship between the CDOM absorption coefficient and the nutrient concentrations.

Recent studies have addressed the optical properties, composition, and potential sources of rainwater CDOM using three main techniques: (i) ultraviolet–visible (UV–Vis) spectral absorption, (ii) fluorescence excitation–emission matrices (EEMs), and (iii) nuclear magnetic-resonance spectroscopy (Kieber et al., 2006; Miller et al., 2009; Muller et al., 2008; Salve et al., 2012; Santos et al., 2009, 2013). UV–Vis spectroscopy is an important tool to evaluate CDOM composition and structure semi-quantitatively, using spectral slope, spectral slope ratio, and molecular size (MS) (Peuravuori and Pihlaja, 1997; Zhang et al., 2011b). EEMs combined with a parallel factor analysis (PARAFAC) model has been used to characterize DOM and CDOM in a wide range of aquatic environments (Fellman et al., 2010; Murphy et al., 2013; Stedmon et al., 2003; Zhang et al., 2009). EEMs represent a highly informative method of presenting fluorescence data by providing a nearly complete depiction of the steady-state fluorescence characteristics of the fluorophores in a particular sample. Identification of peak positions and intensities using PARAFAC modeling provides an assessment of the sources and the relative contribution of biologically derived and humic-like substances (Fellman et al., 2010). Proton nuclear magnetic-resonance spectroscopy was used to provide structural analysis of the fraction of the hydrophobic solid-phase extraction of rainwater CDOM. Integration of regions of the spectra, which were normalized to an internal standard, provides information on hydrodynamic distributions and major functional groups present in CDOM, as well as their relative abundances. This includes the relative aliphatic and aromatic character of CDOM, which presents fundamentally new insights into the chemical characteristics of CDOM (Miller et al., 2009).

Further insights of rainwater CDOM are provided by studies on aerosol-phase humic-like substances (HULIS) and water soluble organic carbon (WSOC) in the atmosphere (Feng et al., 2006; Graber and Rudich, 2006; Zheng et al., 2013); these subjects have received increasing attention in the last ten years. However, distinct differences were found for HULIS in the atmosphere and in rainwater CDOM due to their different extraction and isolation methods. HULIS in the atmosphere have been obtained through solid-phase extraction of DOM using C-18, HLB, XAD-8 and DEAE (Graber and Rudich, 2006; Zheng et al., 2013).

Although the composition and sources of rainwater CDOM have been studied (Kieber et al., 2006; Miller et al., 2009; Muller et al., 2008; Salve et al., 2012), there is limited knowledge of the dynamics, seasonal variations, material composition and controlling factors of rainwater CDOM in different regions of the world. Surprisingly, previous studies on rainwater CDOM have not focused on the most polluted regions of the world, and we are aware of few studies on rainwater CDOM in China (Cheng, 2010), even though China has high levels of atmospheric pollution and a high population density. However, chemical characterizations of rainwater CDOM in regions with distinct climate patterns and different levels of pollution are highly relevant because rain is an important source of fresh deposits of CDOM in terrestrial and aquatic ecosystems. Thus, additional studies on rainwater CDOM deposition are needed.

A significant limitation of our knowledge of the CDOM in rainfall is the scarcity of long-term observations of rainfall events and synchronous measurements of CDOM absorption and nutrients. Therefore, we conducted a one-year study, from January to December 2012, on the rainwater CDOM characteristics in Lake Taihu, China. The aims of this study were to 1) assess the optical properties and the potential sources of CDOM based on UV–Vis spectral absorption and EEMs, 2) determine the relationships between CDOM absorption coefficients and nutrient concentrations in rainwater and 3) estimate the amount of CDOM input and the relative contribution of rainwater CDOM to Lake Taihu.

2. Material and methods

2.1. Study site and sample collection

We conducted our CDOM rainfall study at the Taihu Lake Laboratory Ecosystem Research Station (TLLER) on the shore of Meiliang Bay, north of Lake Taihu (Fig. S1). Lake Taihu is approximately 150 km west of Shanghai, and it has a water area of 2338 km², which is highly eutrophic (Qin et al., 2007).

There were three parallel collection sites for rainwater in TLLER (Fig. S1). Samples were collected for different rainfall events to reflect varying synoptic situations and meteorological conditions. A total of 89 valid samples were collected from 35 rainfall events from January 1 to December 31 2012 (35 events × 3 parallel sites = 105 possible samples; of these, 2 could not be collected because of broken equipment and 14 were discarded because of possible contamination by bird droppings). The total rainfall amount of these 35 rainfall events was 818 mm, which accounted for 72.6% of the annual total rainfall amount (1127 mm) in 2012.

To ensure that the rain collectors and all other equipment were sterile and not pre-contaminated, we used a cleaning protocol with bleach, 10% hydrochloric acid and deionized water. Furthermore, all high-density polyethylene bottles, pipettes, test tubes, tubing, funnels and quartz micro-cuvettes that were used to collect, store and analyze the samples were soaked in 10% HCl for 24 h prior to use; then, these tools were transferred to deionized water and rinsed to ensure they were sterile. The polyethylene bottles were used to collect the samples. Other glass and quartz utensils were used to transfer, store and analyze the samples.

Samples were collected at varying intervals, depending on the rainfall intensity. The sampling apparatus, a 4 L PVC bottle connected to a glass funnel with a diameter of 120 mm, was exposed to the atmosphere just prior to the onset of rainfall and was retrieved within 2 h after the rain stopped. Because of the very short exposure time, the contamination and effect of dust were negligible.

The rain volume in the sampling apparatus was recorded, and a 200 ml aliquot was analyzed. If the rain volume was <200 ml, then the volume was increased to 200 ml using Milli-Q water and the dilution factor was noted; the rain volume was used to calculate CDOM absorption coefficient, fluorescence and deposition amount. After collection, the 200 ml aliquot of rainwater was immediately...