Estuarine, Coastal and Shelf Science 175 (2016) 118–125

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

A new insight into black blooms: Synergies between optical and chemical factors

Hongtao Duan [a, *], Steven Arthur Loiselle [b], Zuochen Li [a], Qiushi Shen [a], Yingxun Du [a], Ronghua Ma [a]

[a] Key Laboratory of Watershed Geographic Sciences, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
[b] Dipartimento Farmaco Chimico Tecnologico, CSGI, University of Siena, 53100 Siena, Italy

ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form
15 March 2016
Accepted 29 March 2016
Available online 6 April 2016

Keywords:
CDOM
Iron
Bio-optical
Hypoxia
Brown water

ABSTRACT

Black blooms have been associated with fish-kills and the loss of benthic fauna as well as closure of potable water supplies. Their frequency and duration has increased in recent decades in rivers, inland lakes and reservoirs, and has often been associated with the decay and release of organic matter (planktonic algae, aquatic macrophytes, sediment release, etc.). However, the interactions between microbial, chemical, hydrodynamic and optical conditions necessary for black blooms are poorly understood. The present study combines field investigations and laboratory mesocosm studies to show that black blooms are caused by a combination of high CDOM (chromophoric dissolved organic matter) absorption, the formation of CDOM-Fe complexes and low backscattering. Mesocosm experiments showed that black bloom conditions occur after 4 days, with a significant increase in the concentrations of Fe^{2+} and $\sum S^{2-}$. Total absorption (excluding absorption due to water) at 440 nm increased by 30% over this time to 7.3 m^{-1}. In addition, the relative contribution of CDOM absorption to the non-water total absorption increased from 18% to 50%. Regression analyses between chemical and bio-optical data in both field and mesocosm experiments indicated that the concentrations of Fe^{2+} co-varied positively with CDOM absorption $a_g(440)$ ($R^2 > 0.70$), and the specific CDOM absorption ($a_g(440)$/DOC). Conditions that favored the development of black blooms were elevated algal or macrophyte biomass and limited water column mixing.

1. Introduction

“Black blooms”, also known as “black water agglomerates”, “black spots” or “dead zones”, are a reoccurring phenomenon in eutrophic freshwater and marine ecosystems (Diaz and Rosenberg, 2008; Frazier and Page, 2000). Black blooms are highly hypoxic (DO < 2 mg/L), geographically and temporally limited and often malodorous (Feng et al., 2014; Shen et al., 2013; Yang et al., 2008). Their origin has been linked to the decay of planktonic algae, aquatic macrophytes or multiple sources of organic matter which increase microbial respiration (Rabalais et al., 2002). They represent a serious management challenge in many rivers, inland lakes and continental seas, including Rio Negro River (Brazil) (Dierssen et al., 2006), Lake Garda (Italy) (Frazier and Page, 2000), Lake Taihu (China) (Duan et al., 2014b), Florida Keys (USA) (Hu et al., 2004), Baltic Sea (Europe) (Berthon and Zibordi, 2010), and northern Gulf of Mexico (Rabalais et al., 2002).

Black blooms follow a predictable pattern (Diaz and Rosenberg, 2008): (1) excessive organic matter production favors increased microbial activity and increased oxygen demand; (2) hypoxia occurs with a buildup of nutrients and organic matter in the sediments and in the water column; (3) anoxia is established and H_2S and Fe^{2+} begin to accumulate; (4) a bloom of dark colored water occurs. Blooms are considered black because of the reduced lightness (brightness) experienced by a particular section of a water surface with respect to its surroundings. This somewhat subjective definition is directly related to the concentrations and optical properties of the dissolved and suspended matter and their impact on the upward flux of scattered radiance perceived by the observer (IOCCG, 2000, 2008). These optically active components are usually limited to phytoplankton, non-algal particulate matter, chromophoric dissolved organic matter (CDOM) and the water itself (Morel, 1988). Reduced water leaving radiance (L_w) results from an

* Corresponding author.
E-mail address: htduan@niglas.ac.cn (H. Duan).

http://dx.doi.org/10.1016/j.ecss.2016.03.029
0272-7714/

increase of absorbing particulate or dissolved substances, or a reduction of backscattering constituents within the effective upwelling depth of the water column (Ma et al., 2011). However, the links between the dissolved and particulate fractions, and their optical properties in black blooms is poorly understood.

Recent research has pointed to several possible causes for black blooms: (1) increased absorption due to CDOM production (Dierssen et al., 2006; Duan et al., 2014b); (2) increased absorption associated to the presence of high amounts of ferric and ferrous ions (Kritzberg and Ekström, 2012; Weyhenmeyer et al., 2014), and (3) reduced suspended particulate inorganic matter (SPIM) backscattering from a reduction of particulate matter (Duan et al., 2014b). In this study, we aim: 1) to characterize the bio-optical and chemical properties of natural black bloom events compared to background lake water; 2) to demonstrate the variations of optical, biological and chemical conditions during the process of black bloom formation in laboratory mesocosm studies; 3) to compare field investigations and laboratory mesocosms studies to identify typical conditions that favor black bloom formations. To the best of our knowledge, this is first study to explore the links between optical and chemical causes of black blooms in both natural and controlled conditions.

2. Materials and methods

2.1. Field study of black blooms

Black blooms were found in two separate nearshore zones in the Gonghu Bay of Lake Taihu in May 2012 (Fig. 1a–b). Water samples were collected from two black water areas (Zones 1 and 2) and an area of unaffected lake water (Zone 3) by two independent groups on 16–17th May 2012. Bio-optical data included remote sensing reflectance (R_{rs}), spectral absorption coefficients of CDOM ($a_g(\lambda)$), total particulate matter ($a_p(\lambda)$), phytoplankton pigments ($a_{ph}(\lambda)$), and non-phytoplankton particulate matter ($a_d(\lambda)$) and total backscattering coefficient (b_b) (Duan et al., 2014b). Geochemical data included the concentrations of chlorophyll-a (Chla), suspended particulate matter (SPM), SPIM, suspended particulate organic matter (SPOM), dissolved organic carbon (DOC), Fe(II), $\sum S^{2-}$, dissolved oxygen (DO), and pH (Shen et al., 2014a).

2.2. Mesocosm simulations of black blooms

Sediment cores were positioned at the bottom of six tube shaped 2.5 m mesocosms made with clear Plexiglas (Fig. 1c) (Feng et al., 2014; Liu et al., 2010). Water samples were collected from Lake Taihu and injected slowly over the sediment surface without disturbance. The sediment core and overlaying water column extended 20 cm and 160 cm in the mesocosm, respectively. To simulate algal conditions of the lake waters, 47.5 g of drained algae from the lake were added to each overlying water column to achieve Chla concentrations of 40 $\mu g L^{-1}$. To simulate typical mixing conditions due to background wind (3.2 m/s) of Lake Taihu Side, the side and upper mixing motors were set to 6.4 and 7 Hz respectively from 13:00 to 17:00 each day. The surrounding temperature was maintained at (29 ± 1) °C to simulate summer temperatures, and daylight illumination was provided by neon lighting. Water samples (48) were taken from each water column at the same time each day during all 6 running days and stored at 4 °C until analysis. Bio-optical and geochemical data were measured together. R_{rs} and b_b data were not obtained due to the limited available space for measurements at the mesocosm surface.

2.3. Measurements

2.3.1. Optical characteristics

R_{rs} was measured in the field with an ASD hand-held spectrometer, following the NASA Ocean Optics protocols (Mueller and Fargion, 2003). Spectral absorption coefficients of total particulate matter ($a_p(\lambda)$), phytoplankton pigments ($a_{ph}(\lambda)$), and non-phytoplankton particulate matter ($a_d(\lambda)$) were determined using the quantitative filter technique with 47-mm GF/F filters and a Shimadzu UV2401 spectrophotometer (Mitchell, 1990; Mueller and Fargion, 2003; Yentsch, 1962). CDOM absorption ($a_g(\lambda)$) was determined following filtration (Millipore filter with 0.22-μm pore size) using a spectrophotometer and distilled water as the reference and spectral slope curves were calculated (Loiselle et al., 2009). A HydroScat-6 backscattering sensor was used to measure total backscattering coefficient (b_b) at six wavelengths of 420, 442, 470, 510, 590 and 700 nm following the standard protocol (Maffione and Dana, 1997).

2.3.2. Chemical characteristics

Chla concentrations were extracted using 90% ethanol and measured with a UV2401 spectrophotometer (Duan et al., 2012; Taranu and Gregory-Eaves, 2008). SPM concentrations were determined gravimetrically from samples collected on precombusted and pre-weighed 47 mm GF/F filters, and dried at 95 °C overnight. SPM was differentiated by gravimetric analysis into SPIM and SPOM after heating the filters at 550 °C for 3 h (Duan et al., 2014a; Duan et al., 2012). Dissolved organic matter (DOC) concentrations were determined after filtration through precombusted 47 mm GF/F filters, with a Shimadzu TOC-5000A analyzer (Jiang et al., 2012). DO and pH were determined using a portable analyzer (Mettler Toledo Seven-Go). $\sum S^{2-}$ (aqueous sulphides: H_2S, HS^- and S^{2-}) was determined by the methylene blue method, and Fe(II) was determined using the Ferrozine spectrophotometry method (Shen et al., 2014a).

2.4. Statistical analysis

Correlations between chemical and bio-optical data in both field and mesocosm were conducted using SigmaPlot 12.5. Liner or power regressions were performed based on the data distribution and their precision.

3. Results

3.1. Field studies of black blooms

The analysis of the optical and geochemical properties of the three field sites showed clear differences in the black bloom zones (1 and 2) with respect to background lake water (Table 1). The black bloom zones were characterized by high CDOM absorption and low SPIM backscattering with respect to the surrounding lake conditions. These conditions led to an elevated difference in reflectance (R_{rs}) with the surrounding lake waters. The black blooms were characterized by a markedly higher Fe^{2+} and $\sum S^{2-}$ concentrations as well as lower DO concentration and pH. Interestingly, the concentration of FeS increased in the black bloom zones while the concentration of total inorganic particulates (SPIM) decreased.

3.2. Mesocosm simulations of black blooms

All mesocosms turned black after 4 days. Concentrations of Fe^{2+} increased to a maximum concentration (0.59 $mg L^{-1}$) on the 4th day after incubation, while $\sum S^{2-}$ concentrations increased throughout the experiment (Fig. 2a). DO showed an irregular trend but remained low (<0.68 $mg L^{-1}$).