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Fluorescence measured using a field-portable laser fluorometer as a proxy for CDOM absorption

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ABSTRACT

The colored fraction of dissolved organic matter, CDOM, directly influences water optical properties and spectral quality, playing an important role in aquatic ecosystems, optical remote sensing and carbon circulation in the sea. Measuring in situ CDOM absorption coefficient, however, is difficult because it requires prefiltration of water samples. A field-portable laser fluorometer for fast acquisition of in situ CDOM fluorescence data without sample filtering was developed. Using the instrument in the Yangtze River estuary, the East China Sea coast, the West Lake, and the Qiandao Lake, good estimates of CDOM absorption were obtained from in situ fluorescence measurements. High correlation ($r = 0.94$) was observed between CDOM absorption coefficient and fluorescence normalized to Raman scattering in diverse water types. Comparison of different methods for measuring CDOM fluorescence was carried out. Fluorescence measured by in situ laser fluorometer compared very well to the values obtained using more sophisticated laboratory spectrophotofluorometer; a significant relationship ($r = 0.95$) was identified between the two methods. Spatial distributions of CDOM in the Yangtze River estuary and its adjacent sea compiled from discrete samples analyses were presented. A linear relationship was identified between CDOM fluorescence and salinity in surface water, reflecting the potential of CDOM fluorescence to be used as a passive tracer of freshwater input. The in situ measurement results demonstrated the utility of the laser fluorometer for rapid acquisition of high-resolution profiles, and that the work resulting from sample filtration or storage can be avoided.

1. Introduction

The colored fraction of dissolved organic matter (CDOM), also known as chromophoric dissolved organic matter, yellow substance or gelbstoff, is an important component in governing light propagation in coastal and open waters (Bricaud et al., 1981). It has a broad application prospect in aquatic ecosystem, optical remote sensing and carbon circulation. The optical properties of CDOM absorption, however, complicate the use of chlorophyll *a* retrieval algorithms that are based on remotely sensed ocean color (Carder and et al., 1991) and the development of phytoplankton production models (Lee and et al., 1994; Arrigo and Brown, 1996; Keith et al., 2002). Although CDOM strongly influences ocean optical properties, remotely sensed spectra, and biogeochemical processes, dynamics of CDOM in diverse aquatic environments remain largely undefined due partially to a sparse global database of CDOM absorption. Limited availability of such data is related to a lack of highly sensitive, portable optical systems that can provide in situ measurements at sea (Miller and et al., 2002).

CDOM is operationally defined as the colored fraction of material passing through a 0.2 um filter and quantified by the absorption coefficient, $a_g(\lambda)$, as measured on filtered samples using a spectrophotometer or an absorption meter. In situ determination of $a_g(\lambda)$ requires the use of in-line 0.2 um filters fitted to a spectral absorption meter (e.g., WET Labs ac-9). Fouling of these filters prevents their use over an extended period of time, and therefore complicates the acquisition of $a_g(\lambda)$ time-series from moorings (Belzile and et al., 2006). The absorption of CDOM may be measured directly using a spectrophotometer or may be inferred from fluorescence measurements (Ferrari and Dowell, 1998). Relative to absorption measurements, fluorescence measurements can be acquired more rapidly with greater sensitivity. The establishment of robust relationships between the level of CDOM fluorescence and absorption may provide a more rapid determination of $a_g(\lambda)$. Once

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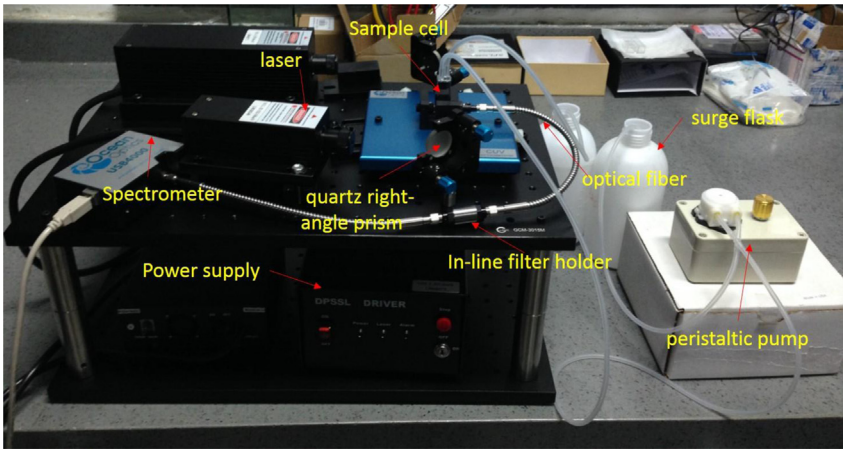

Fig. 1. Picture of the laser fluorometer.

the reference absorption coefficient $a_g(\lambda_0)$ is estimated from fluorescence, its spectral $a_g(\lambda)$ can be determined by assuming an exponential shape of the form (Bricaud et al., 1981; Twardowski and et al., 2004):

$$a_g(\lambda) = a_g(\lambda_0)\exp(-S_g(\lambda-\lambda_0)) \quad (1)$$

where $a_g(\lambda_0)$ is the magnitude of absorption at reference wavelength λ_0, and S_g is the slope parameter describing the wavelength dependence. It has been found that CDOM fluorescence of samples from a wide range of marine, riverine and estuarine waters is linearly related to $a_g(337)$ or $a_g(355)$, and that the use of a single equation derived from the ratio of fluorescence to absorption at all these sites would incur an error no worse than 100–150% in the retrieval of $a_g(\lambda)$ at 337 or 355 nm (Ferrari and Tassan, 1991; Hoge et al., 1993; Green and Blough, 1994; Belzile and et al., 2006). The total absorption coefficient, $a_{tot}(\lambda)$, includes the coefficients for total particulate matter of phytoplankton and non-algal particulates, $a_p(\lambda)$, $a_g(\lambda)$ and pure water $a_w(\lambda)$. Because $a_{tot}(\lambda)$ can be obtained by field spectral absorption meter(e.g., WET Labs ac-9), if $a_g(\lambda)$ also can be derived through in situ fluorescence measurements, $a_p(\lambda)$ can be obtained by the expression $a_p(\lambda) = a_{tot}(\lambda) - a_g(\lambda) - a_w(\lambda)$.

In the past two decades, fluorescence spectroscopy techniques, especially the excitation–emission matrices (EEMs), have been fruitfully used to investigate the composition and dynamics of dissolved organic matter (DOM) in aquatic environments (Coble, 1996; Stedmon et al., 2003; Chen and et al., 2004; Spencer and et al., 2007; Jiang and et al., 2008; Kowalczuk and et al., 2009; Yamashita and et al., 2010). However, current laboratory fluorescence spectrofluorometers (e.g., Shimadzu RF5301 spectrofluorometer, Shimadzu Inc.) (Zhang and et al., 2007; Foden and et al., 2008; Singh et al., 2010) are too bulky for routine use in the field and the measurement scans takes a long time. In recent years, portable or submersible field fluorometers have been employed to acquire rapid, real-time, high-frequency measurements of DOM in aquatic environments (Sivaprakasam and Killinger, 2003; Conmy et al., 2004; Baker and et al., 2004; Killinger and Sivaprakasam, 2006; Suping1a et al., 2010; Tedetti et al., 2010; Chekalyuk and Hafez, 2013, 2008; Tedetti et al., 2013). For instance, the WETStar and ECO Puck submersible fluorometers (WET Labs Inc., USA) use a near-UV light-emitting diode (LED) to measure a fulvic acid-like fluorophore at $\lambda_{Ex}/\lambda_{Em}$ of 370/460 nm (Niewiadomska and et al., 2008). The weakness of such an instrument is that most of these field instruments are designed to measure one specific parameter (e.g., Chl-a, CDOM, oil, or variable fluorescence) and do not provide full and detailed spectral information about other fluorescent constituents for more comprehensive characterization of aquatic environments (Chekalyuk and Hafez, 2008, 2013).

This paper presents an original field-portable laser fluorometer (FLF) for rapid, high-resolution fluorescence measurements on unfiltered samples, and for estimating absorptions through fluorescence-absorption relationship. The estimated absorptions inferred from fluorescence measured by the FLF in various aquatic ecosystems are compared to $a_g(\lambda)$ measured by ultraviolet–visible spectrophotometry on filtered samples. CDOM fluorescence obtained by the FLF is also compared to values measured using more sophisticated scanning spectrofluorometers. Application of the FLF in biogeochemical studies on organic matter is illustrated by in situ profiles obtained in the Yangtze River estuary and its adjacent sea.

2. Materials and methods

2.1. Mechanical and optical configurations of the FLF

The FLF is built on a porous aluminium alloy plate with orthogonal Czerny-Turner optical configuration (Fig. 1). A diagram of the FLF is presented in Fig. 2. The laser fluorescence system consists of an excitation source based on a micro blue-violet laser, a measurement cell (MC), collimating lens, two reflecting mirrors, a

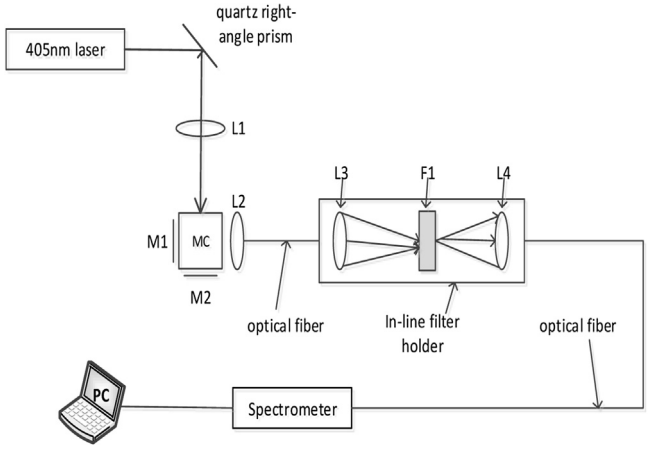

Fig. 2. Block diagram of the FLF instrument. MC – measurement cell; M1 and M2 – reflecting mirrors; F1 – long pass filter; L1 and L3– focusing lenses; L2 and L4– collecting lenses.