



# An assessment of remote sensing algorithms for colored dissolved organic matter in complex freshwater environments



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## ARTICLE INFO

### Article history:

Received 2 May 2013

Received in revised form 12 October 2013

Accepted 12 October 2013

Available online 8 November 2013

### Keywords:

CDOM

Algorithm

Freshwater environments

Saginaw River

Lake Huron

## ABSTRACT

This study evaluated fifteen algorithms representing four major categories of retrieval algorithms for aquatic colored dissolved organic matter (CDOM): empirical, semi-analytical, optimization, and matrix inversion methods. The specific goal here was to evaluate (and understand) the strengths and limits of these algorithms in predicting CDOM dynamics along a gradient of varying water quality in a large, freshwater ecosystem. The data were collected in May and October of 2012 from the estuarine areas of the Kawkawlin and Saginaw Rivers, and Lake Huron. Algorithms were evaluated through comparisons to in-situ CDOM measurements, such that the analysis of these field measurements showed that CDOM levels in these areas displayed a range of CDOM absorption coefficients  $a_{CDOM}(440)$  ( $0.1\text{--}8.5\text{ m}^{-1}$ ). In general, the majority of the algorithms underestimated high CDOM waters ( $a_{CDOM}(440) > 2\text{ m}^{-1}$ ) and overestimated low CDOM scenarios ( $< 0.5\text{ m}^{-1}$ ). Six algorithms that performed consistently better compared with the other models (overall RMSE of  $< 0.45$ ) in estimating in-situ CDOM levels were three empirical, two semi-analytical, and one MIM algorithms. Our analysis identified a set of parameters for the matrix inversion methods (MIM) that allow them to work effectively across a broad range of CDOM levels. Analysis of our results indicated that the most effective wavelengths/band locations for estimating CDOM could vary depending on the levels of spectral interference from high concentrations of particulate matter in the water column. In addition, our results suggest that including wavelengths  $> 600\text{ nm}$  in the algorithms improves CDOM estimation accuracy significantly, particularly for complex freshwater environments.

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## 1. Introduction

Colored dissolved organic matter (CDOM), the photo-active component of dissolved organic carbon (DOC), is often viewed as a reliable tracer of DOC. Many study results reported good correlations between CDOM and DOC (Blough, Zafriou, & Bonilla, 1993; Del Castillo, Coble, Morell, Lopez, & Corredor, 1999), but their real relationships are complicated by environmental factors and human related contaminations (Chen et al., 2004). Due to its chromophoric and optical properties, CDOM is capable of being estimated by remote sensing inversion algorithms. Early attempts of CDOM-related remote sensing were mainly focused on estimations from open sea environments where CDOM absorptivity is generally low and spatially homogeneous. Open sea CDOM is dominantly autochthonous through interactions with resident biological assemblages via formation and deposition (Nelson &

Siegel, 2002). More recently, the estimation of CDOM in fresh, marine, or mixed water in both estuarine and coastal regions has been studied using a variety of techniques and applications (Miller, Del Castillo, & Mckee, 2005), aimed at assessing changes in salinity (Bowers & Brett, 2008) or the occurrence and distribution of red tides (Hu et al., 2005). To date, many CDOM estimation studies (Ammenberg, Flink, Lindell, Pierson, & Strombeck, 2002; Bracchini et al., 2006; Stedmon et al., 2006) have been directed towards inland relatively CDOM-rich freshwaters, where CDOM is greatly influenced by sources from land surface processes (i.e. allochthonous). Since suspended solids affect the optical properties of water containing CDOM, the optical estimations of CDOM in freshwaters are also affected by a variety of aquatic components, such as microbiological assemblages and suspended substances. In addition, CDOM absorptivity can be affected by environmental factors, such as hydrodynamics and anthropogenic activities (Hoge & Lyon, 2002). Accordingly, CDOM absorptivity (i.e. visible and near-IR) in inland freshwater environments can be quite high, with absorption coefficients as high as  $20\text{ m}^{-1}$  (Brezonik, Menken, & Bauer, 2005).

As interest in estimating CDOM absorptivity in inland environments increases, accurate and robust algorithms will be needed. However, the

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validity of previous and current CDOM estimation algorithms has not been well investigated.

Many CDOM estimation algorithms have been developed in the last three decades (IOCCG 2006), such as empirical (band ratios) (Mannino, Russ, & Hooker, 2008), semi-analytical/quasi-analytical (Lee, Carder, & Arnone, 2002; Lee et al., 2007; Zhu & Yu, 2013), matrix inversion methods (MIM) (Brando & Dekker, 2003; Hoge, Wright, Lyon, Swift, & Yungel, 1999; Wang, Boss, & Roesler, 2005), spectral matching (Liu & Miller, 2008), and artificial neural network (ANN) (Sandidge & Holyer, 1998; Tanaka & Oishi, 1998). Empirical approaches require less knowledge of the fundamental relationships between water's apparent and inherent optical properties, but require adequate data to parameterize the model. The primary limitation to empirical algorithms is that the derived relationship may only be valid for parameter specific locations. These algorithms are thus particularly sensitive to changes in the specific composition of water constituents when boundary conditions are changed (IOCCG, 2000).

Semi- or quasi-analytical algorithms incorporate both empirical parameters and bio-optical models (i.e. radiative transfer models). They describe the relationship between in-water constituents and water-leaving radiance or reflectance analytically or semi-analytically (IOCCG, 2000; Sathyendranath & Platt, 1997). The MIM algorithms also use some semi-analytical methodologies, but require knowledge about specific inherent optical properties (SIOPs) to be preset, such as the specific absorption coefficient of chlorophyll and the absorption slopes of CDOM and non-algal particles (Brando & Dekker, 2003). Again, because these parameters can be site specific, MIM approaches are generally not applicable across different environments without field measured SIOPs. Other algorithms, such as ANN and LUT, require multiple regions of interest to be painstakingly identified and delineated as input for forward spectral matching, making them difficult to apply to a large set of satellite images. While the above algorithms have been thoroughly developed and successfully applied to specific regional environments (i.e. open sea and coastal regions), their utility to make predictions across a range of varying water quality conditions, or within a single, complex freshwater ecosystem have not been sufficiently tested. Thus, it is necessary to evaluate the performance of current algorithms in complex freshwater environments, (i.e. inland river mouths) where CDOM absorptivity is often spatially and temporally quite diverse.

This study evaluated 15 CDOM estimation algorithms with samples collected within and near plume areas of the Kawkawlin and Saginaw Rivers, where each enters into Lake Huron. CDOM absorptivity is generally high, due to the terrestrial input from each watershed (i.e. forested and agricultural regions). We analyzed the relative strengths and weaknesses of these algorithms, as well as examined the influence that specific algorithm parameters had on their estimation performance (e.g. wavelength selection, CDOM absorption slopes).

## 2. Methods

### 2.1. Study sites

Sampling was conducted along a spatial gradient where two major tributaries (Kawkawlin and Saginaw Rivers) discharge into Saginaw Bay, Lake Huron; sites were selected to encompass the conditions within each river, the sediment plumes at their confluence into the bay, and conditions that reflected offshore waters of the inner bay (Fig. 1). The Saginaw River is the largest river flowing into the Saginaw Bay, with an overall length of 36 km and a watershed of 22,260 km<sup>2</sup>. The headwaters of the Saginaw River are mainly forested, which represent approximately 30% of the overall watershed. The majority of the lower portions of the watershed are agricultural, which represent approximately 52% of the overall watershed. An additional 10% of the watershed is designated as wetland, which is largely found directly adjacent to the river channel.

The Kawkawlin River is a smaller river with an overall length of 28.2 km and a watershed of 647 km<sup>2</sup>, whose mouth is less than a kilometer from that of the Saginaw River (Fig. 1). This watershed is dominated by deciduous forests (40.2%), with a significant amount of wetland habitat (7.9%) found adjacent to the channel. The rivers also differ in water clarity, with the Saginaw River typically clouded with a much heavier sediment load, while the Kawkawlin River generally discharges clearer but stained waters.

### 2.2. Field measurements

Field measurements were made on May 10, 2012 and October 18, 2012 at which time 10 and 18 samples were retrieved, respectively (Fig. 1). Whenever possible, the locations of sampling sites were kept constant between the two dates (GPS identified locations); this allowed for more meaningful seasonal inferences to be made between specific locations. Surface water samples were collected using a bucket, dispensed into amber bottles (polypropylene 500 mL), and stored in a cooler kept at ambient water temperatures until further processed in the laboratory (within 6 h in Mount Pleasant, Michigan). Concurrent to the collection of water samples, above-surface spectra, including water leaving radiance  $L_t$  and sky radiance  $L_i$ , were measured via a HyperSAS (Hyperspectral Surface Acquisition System; Satlantic Inc.) spectroradiometer. A HyperOCR (Hyperspectral Ocean Color Radiometer) was also used to measure above-surface downwelling irradiance  $E_d$ . The HyperSAS and HyperOCR were deployed as outlined in their operation manuals, making sure to adjust the zenith and azimuth angles of the HyperSAS according to the solar position before the spectra were collected. The  $L_t$  sensor was pointed at the water surface at an angle of 40° from Nadir, and at an angle 90° from the sun's azimuth, the  $L_i$  sensor was at the identical azimuth angle with  $L_t$  and pointed to the sky at an angle of 40° from the Zenith, and the  $E_d$  sensor was mounted at the highest point of the boat. The HyperSAS is specially designed for use in an aquatic environment, in which  $L_t$ ,  $L_i$ , and  $E_d$  are measured by three sensors simultaneously. Therefore spectra derived from this system are generally of higher quality/accuracy than those from other less robust instruments.

Once in the laboratory, water samples were filtered through GF/F glass microfiber membrane (0.70 μm) under low pressure (<5 atm). The filters were retained to measure chlorophyll-a pigment in support of a second research initiative. The filtrate was collected and CDOM absorbance  $A(\lambda)$  within wavelength range 200–800 nm was measured by a Cray-60 spectroradiometer with a 1-cm cuvette and Milli-Q blank correction. CDOM absorption coefficients were determined by

$$a_{CDOM}(\lambda) = A(\lambda) \times \frac{\ln(10)}{\text{Pathlength}} = A(\lambda) \times 230.3. \quad (1)$$

The remote sensing reflectance ( $R_{rs}$ ) required for nearly all of the CDOM estimation algorithms was calculated by

$$R_{rs} = \frac{L_t - \rho L_i}{E_d} \quad (2)$$

where  $\rho = 0.028$  was set according to the operation manual of HyperSAS and Mobley (1999). A second filtrate sample was retained to determine DOC concentrations. DOC concentration was measured using a Shimadzu TOC-V analyzer with high temperature combustion (Vlahos, Chen, & Repeta, 2002). In this process, 50 μL injections of water samples were combusted at 800 °C and the sample DOC concentration was calculated from the resultant CO<sub>2</sub> measured with a non-dispersive infrared detector. Both response factors and blanks were compared with inter-comparison standards provided by J. Sharp (U. Delaware) and D. Hansell (U. Miami).

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