

# Characterization of Water Constituents Spectra Absorption in Chagan Lake of Jilin Province, Northeast China

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**Abstract:** Research on the optical characteristics of water color constituents in Chagan Lake of Jilin Province, Northeast China was carried out in order to investigate the variability of the spectra absorption parameters as inputs to bio-optical models and remote sensing algorithms for converting observed spectral signals into water quality information. Samples of total particulates, non-algal particles and colored dissolved organic matter (CDOM) were first prepared by quantitative filter technique (QFT) and then absorption coefficients of these color producing agents were determined by spectrophotometry. Spectral characteristics of absorption coefficients by total particulate matter, spectral specific absorption dependency on chlorophyll concentration (Chl-*a*) of phytoplankton, spectral absorption slopes variation for CDOM and non-algal particles and their corresponding reasons were examined and clarified over five months of 2009 and 2010 in this study. Results suggest that total particulate spectral absorption in Chagan Lake is mainly dominated by non-algal particles in most cases, but phytoplankton could be the dominant contributor when chlorophyll concentration is high (up to 84.48 mg/m<sup>3</sup> in autumn 2010). The specific absorption coefficients of phytoplankton particulate ( $a^*_{ph}(\lambda)$ ) dependency on Chl-*a* is significantly variable due to relative contributions of package effect and accessory pigments, and the parameters of power function are clearly biased on a long time span. The sources of variability in spectral absorption slopes of CDOM and non-algal particles are mainly attributed to the changing proportions of high molecular weight humic acids and mineral suspended sediments in waters, respectively.

**Keywords:** colored dissolved organic matter; spectra absorption; water constituents; spectral slope; Chagan Lake

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## 1 Introduction

It is well known that the upwelling visible radiation or radiance (i.e. apparent optical properties (AOPs)) from a natural water body is determined by the inherent optical properties (IOPs) of the optically active constituents (OACs, i.e. particulate and dissolved material) (Gordon *et al.*, 1988). Thus, the accuracy of individual parameter retrieval or estimation from water color measurements can be improved by a deep understanding of the spectral absorption (both particulate and dissolved substance) and scattering properties of suspended (mainly particu-

late) constituents within water bodies. Generally, the absorption spectra by suspended substances can be divided into absorption by phytoplankton and detritus in the form of a decolorized suspension consisting of detritus of organic origin, inorganic suspension, and cell membranes of plankton. Moreover, the looseness of the co-variations between the detrital (dissolved and particulate) component and the algal stock is considered to be the main source of variability in inherent optical properties.

Over the past decades, the variability of characteristics for water constituents absorption has been thor-

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oughly documented in oceanic waters (Case-1 waters) where phytoplankton and their derivative products are optically dominant and other components are often assumed to co-vary with chlorophyll *a* (Chl-*a*) concentration (Morel, 1988; Bricaud *et al.*, 1998; Morel and Maritorena, 2001; Reynolds *et al.*, 2001). Allali *et al.* (1997) reported that significant variations in phytoplankton absorption and scattering cross-sections were in connection with phytoplankton cell size and species composition. Many researchers also observed that chlorophyll specific absorption coefficients at selected wavelengths, such as  $a_{ph}^*(440)$  and  $a_{ph}^*(670)$ , functioned non-linearly with Chl-*a* and they attributed the variations in the  $a_{ph}^*(\lambda)$  to differences in nutrient availability and correlatively in cell size (mainly from package effect). Sathyendranath *et al.* (1999) reported low  $a_{ph}^*(\lambda)$  and high package effect when small cell phytoplankton predominated during the inter-monsoon season when diatoms dominated in the Arabian Sea. Sathyendranath *et al.* (2001) observed that low absorption coefficients of diatom blooms might result in significant underestimation in Chl-*a* retrieval in the Labrador Sea, when using standard remote sensing algorithms. In coastal and inland waters (Case-2 waters), the optical properties are often dominated by the effects of terrigenous suspended inorganic particulate and dissolved organic matter that were considered to co-vary with neither phytoplankton nor each other, thus the parameterization of the spectra absorption can show significant spatial and temporal variability. A bulk of studies (Yu and Cai, 1998; Babin *et al.*, 2003; Cao *et al.*, 2003; Stramski *et al.*, 2004) have presented valuable evidence of the optical properties of the suspended substances, suggesting that the optical behavior of suspended sediments is mainly determined by its particle size and composition. However, there do exist large variations in the optical characteristics within dynamic coastal and shelf sea areas. Stuart *et al.* (2000) demonstrated that dominant diatoms in coastal areas caused lower spectral specific absorption than smaller non-diatom offshore phytoplankton because of the package effect. Recent studies have also reported the nature of colored dissolved organic matter (CDOM), the biochemical processes involved to transform it and the corresponding variations in its optical characteristics (Twardowski and Donaghay, 2002), and it can be changed by photo- and bio-degradation.

Due to the comparatively simple optical configuration

of Case-1 waters, single OAC models and algorithms based upon determinations of phytoplankton IOPs have performed satisfactorily in oceanic waters (Morel and Loisel, 1998). In Case-2 waters, because the non-algal particles or dissolved material are not proportional to phytoplankton absorption, the models and algorithms based solely upon chlorophyll-bearing biota are not applicable any more (Bukata *et al.*, 1981; 1995; Bowers *et al.*, 1996a; Babin *et al.*, 2003) due to the additional presence of land-derived inorganic and organic suspended materials within inland and coastal waters.

Therefore, in order to establish regional algorithms through satellite data aiming at evaluating the content of water color constituents within inland and coastal waters, it is necessary to have a better understanding of inherent optical absorption properties of main water constituents and obtain information associated with the natural variability of those absorption spectra parameters. At present there exists only a limited catalogue of spectral IOPs from seasonal ice-frozen inland waters in Northeast China and further observations are required in order to facilitate the improvements in the accuracy of the remote sensing water quality products for this region.

The main objective of this work is to separate the spectra absorption coefficients of the main OACs through laboratory analysis and study the variation in spectra characteristics (spectra absorption magnitude, shape, absorption cross-sections, and absorption slopes) of total particulate matter, phytoplankton, and CDOM in Chagan Lake, Jilin Province, Northeast China. The specific aims of the study are: 1) to quantitatively analyze the spectral absorption properties of these color producing particulate and dissolved components; 2) to explore the main source of the variability in their optical absorption parameters, which may subsequently facilitate improvements in the parameterization of optical models and remote sensing algorithms for the interpretation of remote sensing water color signals over inland waters.

## 2 Materials and Methods

### 2.1 Study area

Chagan Lake, located in the southwest of the Songnen Plain, Northeast China (Fig. 1), is the tenth largest lakes in China. It has a mean surface area of 372 km<sup>2</sup>, a mean depth of 1.52 m, and full storage capacity of  $5.98 \times 10^8$  m<sup>3</sup>. It is connected with the Songhua River through irri-

gation channels, and is a eutrophic lake with high Chl-*a* concentration and low Secchi Disk Depth. The Songhua, Huolin, Tao'er and Nenjiang rivers all provide inputs to Chagan Lake, and natural precipitation and ground water are ancillary water suppliers for the lake. The lake's primary economic value is linked to fishery, but it is also important for agriculture and recreational purpose, therefore a long-term of monitoring program for the lake's conservation is under consideration.

## 2.2 Sampling method

Field campaigns were carried out on July 15, August 29, October 12, 2009 and May 8, September 13, 2010 by motor boat. All together 100 water samples were collected (Fig. 1), providing a wide range of IOPs and water constituents' concentrations. At each sampling point, water samples for particulate and CDOM absorption measurements were collected from 20 cm below the water surface, which were stored in a cooler with ice bags and transported to laboratory for determination within 48 hours.

## 2.3 Laboratory analysis

In the laboratory, Chl-*a* was analyzed following the SM 10200 H-spectrophotometric method (Arnold Greenberg, 2005) with 90% buffered acetone. Total suspended sediments (TSS) were measured gravimetrically on pre-weighed Whatman GF/F filters after rinsing with distilled water. The dry filters were then burned at 500°C in a muffle furnace for four hours, to remove the organic fraction used for mineral suspended sediments (MSS) concentration measurements. The organic suspended sediments (OSS) lost on ignition could be then determined by subtracting the MSS concentration at each point from the TSS concentration.

The TSS spectra absorption was performed through quantitative filter technique (QFT). Samples filtrations were carried out (Whatman® 25 mm GF/F) for measurements of light absorption by particulate material. In the laboratory, optical density of the particulate matter was measured between 350 nm and 800 nm at 1 nm intervals with a dual-beam scanning spectrophotometer with a blank filter saturated with distilled water as a ref-

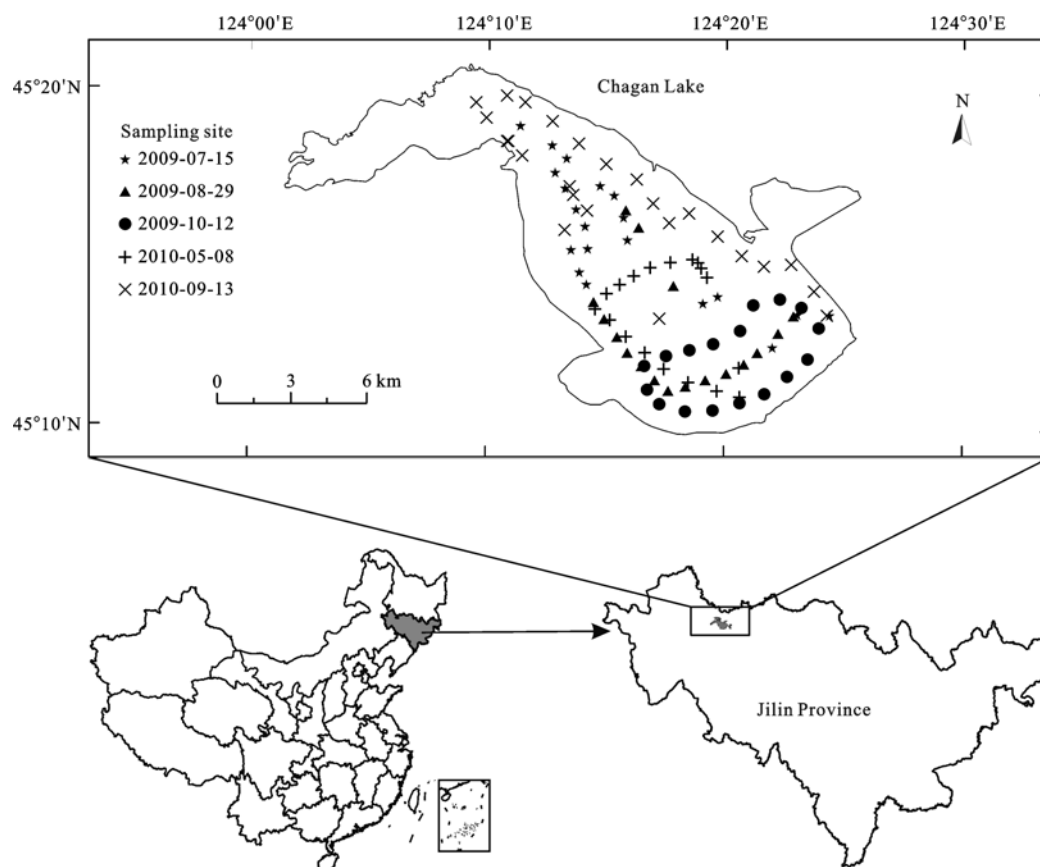


Fig. 1 Location of Chagan Lake and sampling sites

erence. Values corresponding to non-algal particles were determined after extraction of pigment with pure methanol. The spectral absorbance of CDOM was measured in a 10 mm quartz cuvette by using 0.22  $\mu\text{m}$  pore size Whatman GF/F filtered lake water with the UV-2550 spectro-photometer, with distilled water as reference between 200 nm and 800 nm with 1 nm interval.

## 2.4 Calculation method

### 2.4.1 Spectral absorption coefficients

Traditionally, the absorption spectra of total particulate matter retained on a filter are decomposed as phytoplankton and non-algal particles, the absorption signals separation of which can be performed through solvent extraction, bleaching or combustion of the pigmented organic material. Absorption coefficient of total particulate matter ( $a_p$ ) and non-algal particulate absorption coefficient ( $a_{\text{NAP}}$ ) were calculated by converting total and extracted optical densities respectively through Equation (1). The spectra absorption coefficients of phytoplankton ( $a_{\text{ph}}$ ) were computed as the difference between  $a_p$  and  $a_{\text{NAP}}$  estimated by Equation (2).

$$a_p(\lambda) = 2.303[OD_s(\lambda) - OD_{\text{null}}] / \beta(V_f / A_f) \quad (1)$$

$$a_{\text{ph}}(\lambda) = a_p(\lambda) - a_{\text{NAP}}(\lambda) \quad (2)$$

where  $\lambda$  is wavelength; 2.303 is the factor converting logarithms transformation from base 10 to base e;  $OD_s(\lambda)$  is sample absorbance;  $OD_{\text{null}}$  is null point correction performed by normalizing spectra to the average absorption measured between 740 nm and 750 nm assuming no wavelength dependence to correct for scattering by fine particles possibly remained in the filtered solution;  $\beta$  is path-length amplification factor, which is assumed to be a constant value of 2 after the theoretical calculation of Roesler (1998);  $V_f / A_f$  is the geometric absorption path length of suspended matter, where  $V_f$  is the column filtered and  $A_f$  is the clearance area of the filter.

The CDOM absorption coefficient ( $a_g$ ) was calculated from the measured optical density of the sample ( $OD_s$ ) by Equation (3).

$$a_g(\lambda) = 2.303[OD_s(\lambda) - OD_{\text{null}}] / \gamma \quad (3)$$

where  $OD_s(\lambda)$  is also sample absorbance;  $OD_{\text{null}}$  is the average optical density over 680–700 nm that the ab-

sorbance of CDOM can be assumed to be zero;  $\gamma$  is the cuvette path-length (1 cm).

### 2.4.2 Specific absorption coefficients

Vivo absorption capacities of living algal cells or absorption cross sections of algae per mass unit of Chl-*a* are the input parameters of the analytical algorithms for the phytoplankton growth and primary production mapping from remote sensing satellite data in order to estimate the carbon fixation rate at global or regional scales, and can be simply expressed as Equation (4).

$$a_{\text{ph}}^*(\lambda) = a_{\text{ph}}(\lambda) / \text{Chl-}a \quad (4)$$

where  $a_{\text{ph}}^*(\lambda)$  is the specific absorption coefficients of phytoplankton particulate at wavelength  $\lambda$ ;  $a_{\text{ph}}(\lambda)$  refers to the absorption coefficients; Chl-*a* stands for pigment concentration ( $\text{mg}/\text{m}^3$ ).

While the variation in the link between  $a_{\text{ph}}^*(\lambda)$  and Chl-*a* may be the consequence of the possible correlative change of the package effect and pigment composition with the trophic waters. In order to improve the parameterization of  $a_{\text{ph}}^*(\lambda)$  that will be introduced in the algorithms used to estimate primary production from waters, it is necessary to systematically investigate the relationship between  $a_{\text{ph}}^*(\lambda)$  and Chl-*a* for various kinds of trophic status at different times and validate whether such a relationship is ubiquitous or mutative. The relationships between  $a_{\text{ph}}^*(\lambda)$  at those wavelengths and Chl-*a* can be expressed as the power function (Yentsch and Phinney, 1989; Bricaud *et al.*, 1995; 1998):

$$a_{\text{ph}}^*(\lambda) = A(\lambda) \text{Chl-}a^{(-B(\lambda))} \quad (5)$$

where both  $A$  and  $B$  are wavelength-dependent positive parameters.

### 2.4.3 Spectral absorption slopes

The variation of spectral absorption slopes of dissolved and particulate matter offers important information about the CDOM and detritus composition and source. Moreover, it also helps to reveal the relative proportions of fulvic and humic acids in low or high molecular weight of CDOM and proportions of mineral and organic matter in non-algal particles in lake water samples at different periods. The last but not the least, the information mentioned above also plays important roles as inputs to optical models that seek to convert satellite observations into water quality information (Babin *et al.*, 2003; Twardowski *et al.*, 2004; Devred *et al.*, 2005). The spectra absorption of CDOM and non-algal parti-

cles are usually expressed in exponential forms as (Bricaud *et al.*, 1981; Carder *et al.*, 1989):

$$a_g(\lambda) = a_g(\lambda_0) \exp(-S_g(\lambda - \lambda_0)) \quad (6)$$

$$a_{\text{NAP}}(\lambda) = a_{\text{NAP}}(\lambda_0) \exp(-S_{\text{NAP}}(\lambda - \lambda_0)) \quad (7)$$

where  $\lambda_0$  refers to 440 nm in this study;  $S_g$  and  $S_{\text{NAP}}$  are the spectral slopes of CDOM and non-algal particles, which is variable among different sampling points, and  $a_g(\lambda)$  and  $a_{\text{NAP}}(\lambda)$  are the absorption coefficients at wavelength  $\lambda$  for CDOM and non-algal particles, respectively.

### 3 Results

#### 3.1 Water constituents characteristics

Water color constituents' concentrations of Chagan Lake over the study periods are summarized in Table 1. Chl-*a* concentrations values ranged from 1.24 mg/m<sup>3</sup> to 84.48 mg/m<sup>3</sup>, the Coefficient of Variance (COV) of which exceeded 1.0, representing extremely variable along five sampling periods, indicating that trophic status of waters

in Chagan Lake presented significant variations due to the changes of phytoplankton species composition from spring to summer (Dong and Zhang, 2007). The absorption coefficient of CDOM at 440 nm varied from 0.33/m to 45.89/m, the lower values were observed in the spring, and the higher values were associated with the summer and autumn. CDOM exhibited a significant positive correlation with total suspended sediments (TSS) ( $R^2 = 0.604$ ,  $p < 0.01$ ) and a low negative correlation with Chl-*a* concentration ( $R^2 = -0.524$ ,  $p < 0.01$ ), suggesting that there may exist both autochthonous and terrigenous CDOM in Chagan Lake. The vast shallow (depth < 2.5 m on average) region of Chagan Lake is usually dominated by suspended or re-suspended sediments (with a maximum value of 413.99 g/m<sup>3</sup> in this study) and low water clarity (< 0.5 m Secchi depth).

#### 3.2 Characteristics of spectra absorption

The average absorption spectra curves of total suspended particulate matter ( $a_p$ ) at five study periods are presented in Fig. 2a. It can be seen that the absorption

Table 1 Range and variation of concentrations of water color constituents

Variable	Mean	Min	Max	S.D.	COV
Chl- <i>a</i> (mg/m <sup>3</sup> )	16.68	1.24	84.48	18.33	1.09
TSS (g/m <sup>3</sup> )	112.68	9.99	413.99	91.02	0.81
MSS (g/m <sup>3</sup> )	24.01	0.50	79.00	20.11	0.81
$a_{\text{CDOM}}(440)$ (1/m)	7.99	0.33	45.89	7.93	0.99

Notes: Chl-*a* is pigment concentration (Chlorophyll *a* and phaeopigments); TSS is total suspended sediments concentration; MSS is mineral suspended sediments concentration;  $a_{\text{CDOM}}(440)$  is absorption by chromophoric dissolved organic matter at 440 nm; COV stands for coefficient of variance

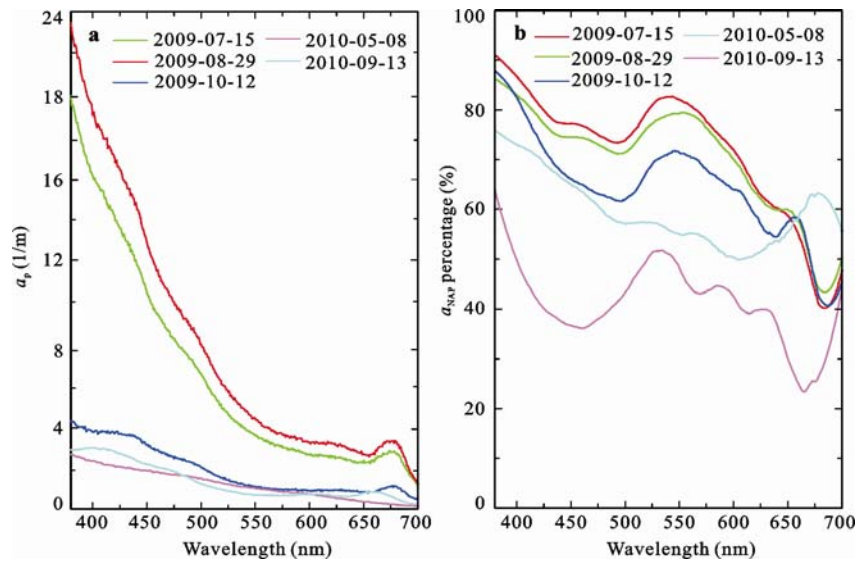


Fig. 2 Average absorption spectra of total suspended particles ( $a_p$ ) (a) and absorption contribution of non-algal particles ( $a_{\text{NAP}}$ ) (b)

spectra of total suspended particulate are dominated by strong absorption in the blue portion of the visible spectrum, with apparent chlorophyll *a* absorption peaks at 675 nm, which decreases from summer to autumn and spring (Fig. 2a). The absorption coefficients  $a_p$  at 440 nm were highly variable, ranging from 1.92/m to 14.77/m due to different proportions of phytoplankton and non-algal composition in total suspended sediments in lake water columns. It is also found that the relative contribution of non-algal or detrital matter to total absorption tends to increase with the decrease of Chl-*a* concentration.

For the purpose of quantifying the absorption contribution of the non-algal and phytoplankton particles at different wavelengths, calculations were carried out at 1 nm interval on the whole spectrum and produced average spectra curves of absorption percentage that, by which, the variance in  $a_p$  over five months could be explained. Figure. 2b shows that the contribution percentage of non-algal particles were generally higher than

50% in July 15, August 29, October 12, 2009 and May 8, 2010 while in September 13, 2010 it was below 50%, suggesting that although non-algal and phytoplankton contributions have significant variations on the whole spectrum (380–700 nm), in most cases non-algal particles actually dominate the absorption, especially at wavelengths around 380–600 nm, and phytoplankton contribution increases at red band 650–690 nm but still lower than non-algal particles. Meanwhile, it is worthwhile to point out that phytoplankton could be the dominant contributor to total particle absorption on the visible spectrum when the maximum Chl-*a* concentration was up to 84.48 mg/m<sup>3</sup> in the fall of 2010.

### 3.3 Characteristics of specific absorption

The variations of specific absorption coefficients of phytoplankton particulate ( $a_{ph}^*(\lambda)$ ) as a function of chlorophyll concentration (Chl-*a*) at six wavelengths 400 nm, 440 nm, 490 nm, 510 nm, 560 nm, and 675 nm are presented in Fig. 3. Though there are some obvious

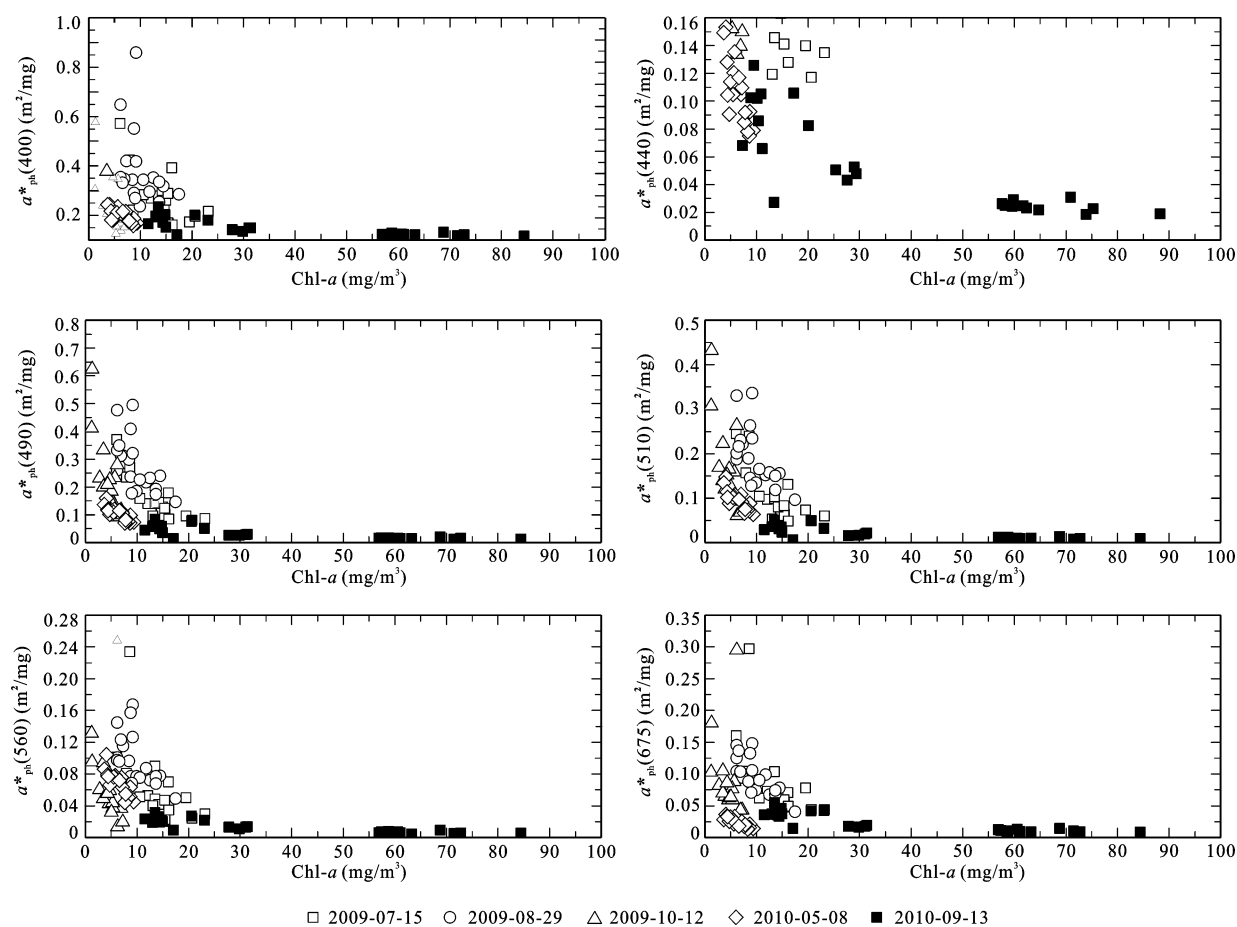


Fig. 3 Variations of phytoplankton specific absorption coefficient ( $a_{ph}^*(\lambda)$ ) with pigment concentration (Chl-*a*)

scatters at 440 nm,  $a_{ph}^*(\lambda)$  exhibits an prominent decreasing trend with increasing Chl-*a* concentration at other bands. For example, the magnitude of  $a_{ph}^*(490)$  decreases from 0.48 m<sup>2</sup>/mg to 0.01 m<sup>2</sup>/mg when Chl-*a* concentration increases from 1.24 mg/m<sup>3</sup> to 84.48 mg/m<sup>3</sup>. At the wavelengths where  $a_{ph}^*(\lambda)$  is clearly varying, the decrease of  $a_{ph}^*$  with increasing Chl-*a* concentration can be expressed as Equation (5). Least square fits to Equation (5) were carried out at 2 nm step from 380 nm to 700 nm, in order to validate the existence of this power functional relationship between  $a_{ph}^*(\lambda)$  and Chl-*a* concentration in Chagan Lake under various trophic conditions at different periods. The exponent ( $B$ ) and the determination coefficient ( $R^2$ ) representing the variations of  $a_{ph}^*(\lambda)$  are presented in Fig. 4.

It can be seen from Fig. 4 that  $B$  curves generally exhibit a similar pattern to  $R^2$  on the whole spectra. In July, August, and October, 2009 (Fig. 4a–c), the variability for  $B$  and  $R^2$  mainly takes place in the spectral range of 400–500 nm and 650–700 nm and presents obvious peaks around these wavelengths, representing that the

variation of  $a_{ph}^*$  spectrum with changing Chl-*a* concentration mainly concentrates on the absorption bands of accessory pigments and the red portion band of Chl-*a*. While in the green spectral domain (500–650 nm),  $B$  and  $R^2$  values remain on a relative low level, showing a weak correlation between  $a_{ph}^*(\lambda)$  and Chl-*a* concentration. But in 2010, except for the peak values of blue (440–480 nm) and red portion (around 675 nm),  $R^2$  curves seem to have apparent elevation in the green band, suggesting that the nonlinear relationship between  $a_{ph}^*$  and Chl-*a* concentration increases in this region (500–600 nm) (Fig. 4d–e).

To examine whether or not the parameters of power function would be biased across these five study periods,  $B$  and  $R^2$  were recalculated in 380–700 nm at 2 nm intervals with all data aggregated together. It is clearly shown in Fig. 4f and Fig. 4d that  $B$  value curve resembles closer to the shape of the absorption spectrum. There are obvious declines for both  $B$  and  $R^2$  curves on the whole spectrum. Therefore it is reasonable to conclude that the non-linear relationship between phyto-

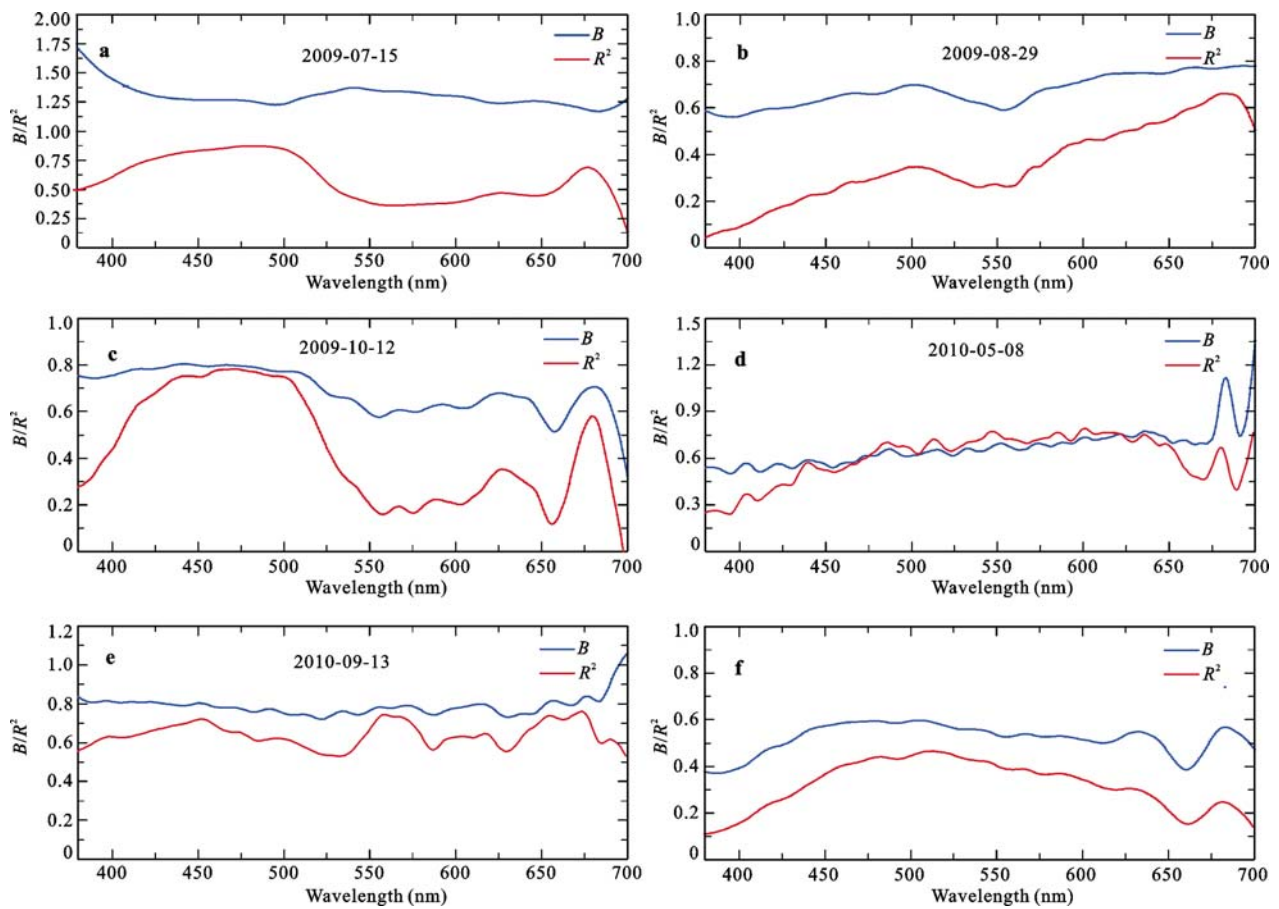


Fig. 4 Variations in exponent ( $B$ ) and determination coefficient ( $R^2$ ) calculated at 2 nm intervals



plankton specific absorption and Chl-*a* concentration is significantly affected by the water samples collected on a long time span (more than one year).

The power relationship between  $a_{ph}^*(\lambda)$  and Chl-*a* at wavelength 482 nm is plotted in Fig. 5a, and it can be seen that  $a_{ph}^*(482)$  functions well with Chl-*a* concentration at 95% confidence level. A high determination coefficient is yielded ( $R^2 = 0.89$ ) at spectral location of 482 nm in the blue spectral region with corresponding RMSE value of 0.028 m<sup>2</sup>/mg. The regular residual versus independent variable plot (Fig. 5b) suggests that the stability of power function would not be obviously affected when Chl-*a* concentration ranging from 6.11 mg/m<sup>3</sup> to 23.18 mg/m<sup>3</sup>.

### 3.4 Characterization of spectra absorption slopes

Based on the non-linear regression of exponential Equation (6) and Equation (7), the spectral slope coefficients  $S_g$  (300–500 nm),  $S_{NAP}$  (380–700 nm) for 100 sample points were calculated. The magnitudes and variation of exponential slopes,  $S_g$  of CDOM and  $S_{NAP}$  of non-algal

particles are illustrated in Table 2. It shows that CDOM spectral exponential slope  $S_g$  ranges from 0.006/nm to 0.022/nm, with a mean value of 0.0118/nm, and non-algal particles slope  $S_{NAP}$  ranges from 0.003/nm to 0.010/nm, over the course of the study.

Overall, values of  $S_g$  showed greater variation and higher magnitudes than  $S_{NAP}$  during the five periods.  $S_g$  was higher in autumn than in summer of 2009, while lower in autumn than in spring of 2010, meanwhile  $S_{NAP}$  varied within a narrow range among five periods and dropped to a minimum mean value of 0.004/nm in spring 2010 (2010-05-08).

Figure 6a presents a negative relationship between  $S_g$  and  $a_g(440)$  showing that the spectral slope of CDOM decreases exponentially with the increase of CDOM ( $R^2 = 0.817$ ), indicating an elevated proportion of high molecular weight humic acids. The  $S_{NAP}$ -MSS (mineral suspended sediments data of 2010) plot is presented in Fig. 6b. Despite significant scatter in the data, a decreasing trend in the  $S_{NAP}$  can be clearly seen with increasing mineral content of the suspended matter.

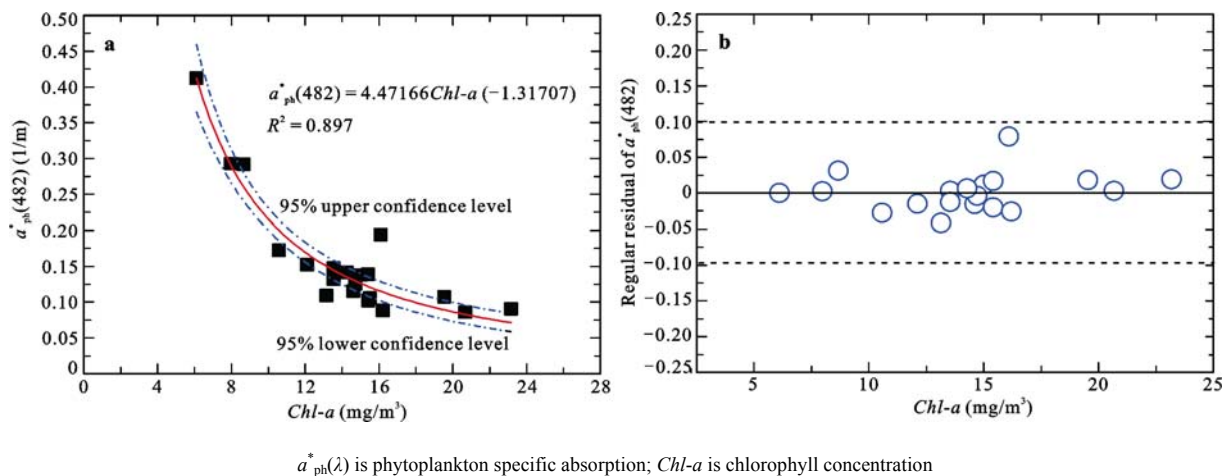
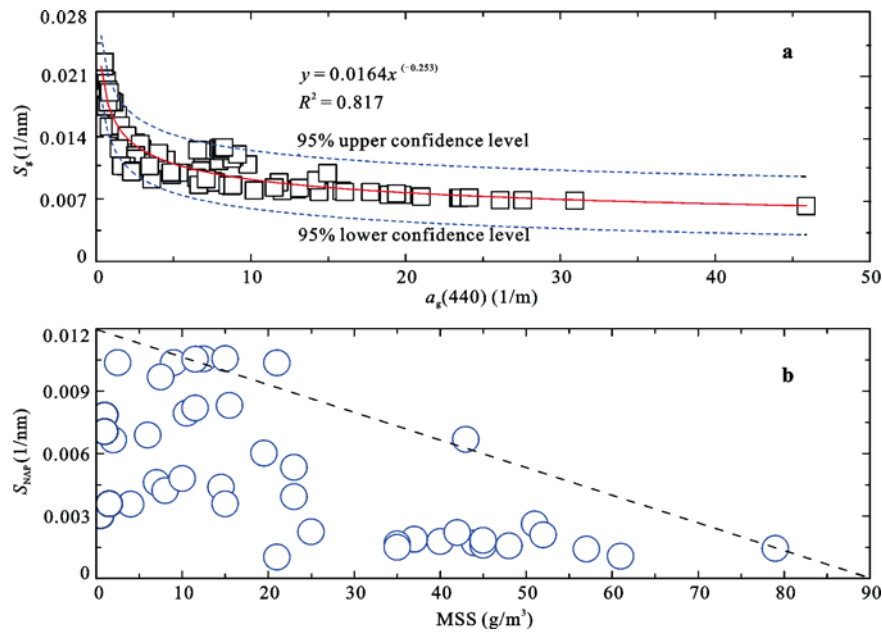


Fig. 5 Power function between  $a_{ph}^*(\lambda)$  and Chl-*a* at 482 nm (a) and its residual versus independent variable (b)

Table 2 Variations of spectral slopes of CDOM ( $S_g$ ) and non-algal particles ( $S_{NAP}$ ) in each period

	$S_g$ (1/nm)			$S_{NAP}$ (1/nm)		
	Range	Mean	S.D.	Range	Mean	S.D.
2009-07-15	0.006–0.018	0.008	0.003	0.005–0.001	0.006	0.001
2009-08-29	0.008–0.019	0.013	0.004	0.004–0.010	0.006	0.001
2009-10-12	0.008–0.022	0.016	0.005	0.004–0.009	0.006	0.001
2010-05-08	0.009–0.013	0.012	0.001	0.003–0.008	0.004	0.001
2010-09-13	0.009–0.013	0.010	0.001	0.003–0.010	0.007	0.003





$S_g$  is spectral slope of CDOM;  $a_g$  is CDOM;  $S_{NAP}$  is spectral slope of non-algal particles; MSS is mineral suspended sediments

Fig. 6 Relationships between  $S_g$  and  $a_g(440)$  (a) and between  $S_{NAP}$  and MSS

## 4 Discussion

It is well known that the spectral absorption coefficients of total particles are typically characterized of two kinds of particle compositional distribution. The first type of absorption spectrum is dominated by non-algal particles except the red band and the absorption coefficients distribution resembles that of non-algal particles. The second type is different from the first one, in which the absorption coefficient of total particles is mainly dominated by phytoplankton and the shape of the spectrum is similar with that of phytoplankton (Cao *et al.*, 2003).

Phytoplankton specific absorption ( $a_{ph}^*(\lambda)$ ) is dependent on regional and seasonal physiological due to the changes in species composition, light and nutrient conditions (Mitchell and Holm-Hansen, 1991). Many researchers have demonstrated that the relationship between  $a_{ph}^*(\lambda)$  and Chl-*a* concentration can be explicitly described as a power function (Sosik and Mitchell, 1995; Sathyendranath *et al.*, 1999; Stuart *et al.*, 2000), which is referred to as the 'pigment package effect' (Morel and Bricaud, 1981) caused by variations in cell size and pigment concentration in cell or overlapped pigments. With the increasing use of bio-optical models in the interpretation of remote sensing water quality and the limited records of spectral IOPs from inland seasonal ice-frozen waters of Northeast China, it is necessary to

systematically investigate and validate the existence of such a relationship between  $a_{ph}^*(\lambda)$  and Chl-*a* concentration for model parameterization.

Colored dissolved organic matter (CDOM) is composed by a mixture of humic and fulvic acids of terrestrial origin carried by river flow or locally produced as a byproduct of primary and secondary production. Information on seasonal variation in the absorption coefficients of dissolved and particulate matter is required as inputs to optical models that seek to convert satellite observations of water color into water quality information (Devred *et al.*, 2005). Moreover, the spectral characteristics can offer important information about CDOM and detritus composition and source (Babin *et al.*, 2003; Twardowski *et al.*, 2004).

### 4.1 $a_p$ variation interpretation

For Chagan Lake waters, the absorption spectra of total suspended particulates are dominated by strong absorption in the blue part of the visible spectrum, with apparent chlorophyll absorption peaks at 675 nm, suggesting that total suspended particulate matter, as one important composition of water color constituents, is presented in Chagan Lake waters, of which absorption coefficients are mainly associated with the non-algal particles, especially at short wavelengths. It is also proved that in most cases for Chagan Lake although the contributions of

non-algal and phytoplankton particles have significant variations on the absorption spectrum (380–700 nm), non-algal particles dominate the absorption especially at wavelengths around 380–600 nm and the absorption contribution of phytoplankton increases at 600–690 nm, but still lower than non-algal particles, with an exception that phytoplankton was the dominant contributor to total particle absorption on the visible spectrum in spring 2010.

#### 4.2 $a_{ph}^*$ versus Chl-*a* concentration

The increase of nonlinear relationship between  $a_{ph}^*$  and Chl-*a* from low concentration (with a mean value of 6.35 mg/m<sup>3</sup>) in May to higher concentration (with a mean value of 39.7 mg/m<sup>3</sup>) could be seen from  $R^2$  curves in the blue portion of 440–480 nm (Fig. 4). This phenomenon is mainly attributed to an increasing package effect from spring to autumn and a possible inverse covariation between the relative abundance of accessory pigments (chlorophyll *b*, chlorophyll *c*, and carotenoids) and the Chl-*a* concentration level. In the green domain around 500–600 nm, variations in pigment composition contribute to  $a_{ph}^*$ -Chl-*a* concentration function significantly, mainly due to the relative abundances of accessory pigments remained in waters, and the similar result was found by Bricaud *et al.* (1995). It is also supported by the occasional peak values in the shape of the  $B(\lambda)$  spectrum around this region, which are usually associated with the non-photosynthetic carotenoids, chlorophyll *b*, and divinyl chlorophyll *b* in oligotrophic waters, and can be more easily discerned from spring when the concentrations of these pigments are higher. Among all five periods, the determination coefficient  $R^2$  reached a maximum of 0.897 at 482 nm in July 2009 representing a strong nonlinear function when the package effect is maximal in summer eutrophic lake waters, linking with relatively high Chl-*a* concentration and big cell-size predominance in this period.

Through the above analysis, it is confirmed that the non-linear relationship between  $a_{ph}^*(\lambda)$  and Chl-*a* concentration is dependent on the relative contributions of the package effect and accessory pigments. It is also stated that the Chl-*a* concentration dependency of  $a_{ph}^*(\lambda)$  is rather variable across the study periods, and the parameters of power function would be significantly biased by the samples collected on a long time span. To minimize the sources of uncertainty and improve the

parameterization of  $a_{ph}^*(\lambda)$ , it is necessary to acquire sufficient samples within a moderate Chl-*a* concentration range (about 6–23 mg/m<sup>3</sup>) in a relatively short temporal scale. There is, however, some ambiguity in the partition of the relative contribution of the package effect and accessory pigments, which are intermingled in the domain of 400–500 nm, and further research is needed to resolve these problems.

#### 4.3 Slopes variation for $a_g$ and $a_{NAP}$

Slope values calculated in this work is slightly less than but very close to those previously measured in inland and coastal waters in literatures. Kirk (1994) reported  $S_g$  with a range of 0.012/nm to 0.018/nm in Australian inland waters, whereas in European waters  $S_g$  varied from 0.011/nm to 0.025/nm (Babin *et al.*, 2003). Bowers *et al.* (1996b) reported an exponential slope ( $S_{NAP}$ ) of 0.011/nm for mineral dominated waters for the Irish Sea. Babin *et al.* (2003) observed a range of  $S_{NAP}$  of 0.0089/nm–0.0178/nm, with an average of 0.0123/nm in European coastal waters. The variation of  $S_g$  and  $S_{NAP}$  observed here suggests that there may be large variations in the composition of the CDOM and non-algal components in Chagan Lake over the study period. The variability in  $S_g$  may be the consequence of relative proportion changes of fulvic and humic acids in CDOM (Zeep and Schlotzhauer, 1981; Carder *et al.*, 1989). And the variability in  $S_{NAP}$  may be attributed to the variation of mineral content of the suspended matter presented in Chagan Lake waters at different periods (Babin *et al.*, 2003).

A negative relationship between  $S_g$  and  $a_g(440)$  in Fig. 6a indicates a possible elevated proportion of high molecular weight humic acids, which is in agreement with the observations of Carder *et al.* (1989). Zeep and Schlotzhauer (1981) also suggested that the spectral slope of CDOM ( $S_g$ ) varied inversely with molecular weight, and further pointed out that high molecular weight humic acids exhibited slopes less than 50% of the lower molecular weight fulvic acids. The data distribution in Fig. 6a is in strong support of such a process occurring here, revealing that lower  $S_g$  (reached a minimum 0.006/nm in July 2009) has a good connection with higher CDOM concentration ( $a_g(440)$ ) reached a maximum of 19.45/m, using absorption coefficients at 440 nm to represent the concentration level) because of a possible growing high molecular weight humic acids

proportion in composition. The alteration of humic and fulvic acids proportion may be attributed to photo-oxidation (processes like photo degradation of terrestrially derived CDOM), selective absorption of dissolved organic matter (DOM) onto mineral sediments named as absorptive fractionation and seasonal and dynamic biological activity (the presence of phytoplankton-derived CDOM further processed by bacteria and/or by photo-oxidation in some literatures).

The  $S_{NAP}$  value decreases with increased mineral content of the suspended matter, which is in good agreement with the hypothesis of Babin *et al.* (2003) who suggested that lower  $S_{NAP}$  may correspond with mineral dominated waters and thus our results can be treated with reasonable confidence. It can be deduced that the inorganic (mineral) proportion of suspended sediments reaches a maximum which is responsible for the lowest spectral slopes of non-algal particles in May 2010. The variation of mineral and organic materials in total suspended sediments may be the consequence of dynamical land-derived inorganic or organic substances and re-suspension deposits from lake water bottom. In summary, the main source of variability in slopes value of  $a_g$  and  $a_{NAP}$  is proved to be mainly attributed to the changing proportions of high molecular weight humic acids and mineral suspended sediments in Chagan Lake in different periods.

## 5 Conclusions

This study presents new observations of IOPs in Chagan Lake, providing a good insight into the natural variations of IOPs for bio-optical model parameterization in this region. The  $a_p$  is mainly dominated by non-algal particles but phytoplankton becomes the dominant contributor when Chl-*a* concentration increases to certain extent. Evidence is also presented that the Chl-*a* dependency of  $a_{ph}^*(\lambda)$  is significantly variable due to relative contributions of the package effect and accessory pigments. To minimize the sources of uncertainty and improve the parameterization of  $a_{ph}^*(\lambda)$  to be introduced into remote sensing algorithms, it is required to obtain sufficient samples within a moderate Chl-*a* concentration range collected in a relatively short temporal scale.

A low slope value of  $a_g$  is found to be associated with a high molecular weight humic acids proportion which also serves as the reason of an increase of CDOM quan-

tity, and high mineral proportion of mineral suspended sediments is proved to be responsible for the low spectral slopes of non-algal particles. The alteration of CDOM and suspended sediments composition may be the consequence of photo-oxidation, sorptive fractionation and seasonal, dynamic biological activity, phytoplankton bloom and recession as well as the intensity of land drainage or river inputs loaded with inorganic or organic matter produced by natural and human activities.

However, to this day the interactions between suspended particulate sediments and CDOM and the subsequent effects on their optical properties have been not sufficiently observed yet. The interactions or co-variations among optical active substances may result in large variations in optical properties of water color constituents and produce significant uncertainties in the parameterization of bio-optical models. Therefore, further studies may be warranted to settle those problems.

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