



1 A systematic examination of the relationship between CDOM and
2 DOC for various inland waters across China

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8
9 **Abstract:** Chromophoric dissolved organic matter (CDOM) plays a vital role in
10 aquatic ecosystems. Strong relationship has been proven between CDOM and
11 dissolved organic carbon (DOC), which set the basis for remote estimation of DOC
12 with remote sensing data. An algorithm has been developed to retrieve DOC via
13 CDOM absorption at 275 and 295 nm with coastal waters. However, the relationship
14 between DOC and $a_{\text{CDOM}}(275)$ and $a_{\text{CDOM}}(295)$ for different types of inland waters are
15 still not clear. Further, is the relationship stable with different types of inland waters?
16 In the current investigation, samples from fresh lakes, saline lakes, rivers or streams,
17 urban water bodies, ice-covered lakes were examined. The regression model slopes
18 range from 1.03 for urban waters to 3.13 for river water, with extreme low slope value
19 for highly saline waters (slope is about 0.3); while coefficient of determinations (R^2)
20 range from 0.71 (urban waters) to 0.93 (winter waters). The specific CDOM
21 absorption (SUVA₂₅₄) showed the similar trend, i.e., low values were observed for
22 saline water and waters from semi-arid or arid regions, where strong photo-bleaching



23 is expect due to thin ozone layers, less cloud cover, longer water residence time and
24 sunshine hours. In the contrast, high values were measured with waters developed in
25 wetlands or forest in Northeast China, where inverse environmental settings were
26 witnessed. The investigation also demonstrated that stronger relationships between
27 CDOM and DOC were revealed when CDOM₂₇₅ were sorted by SUVA₂₅₄
28 ($0.78 < R^2 < 0.98$) or the ratio of CDOM₂₅₀:CDOM₃₆₅ ($0.78 < R^2 < 0.99$). Our results
29 highlight that non-unified relationship exhibits for different types of inland waters,
30 and remote sensing models for DOC need to be tuned with different inherent optical
31 parameters obtained from various types of waters for quantification of DOC in inland
32 waters.

33 **Keywords:** Absorption, CDOM, DOC, spectral slope, saline water, fresh water

34

35 1. Introduction

36 Inland waters play a substantial role for regulating climate at regional scale, and also
37 for global carbon cycling (Cole et al., 2007; Tranvik et al., 2009). Compared with
38 other terrestrial ecosystems, e.g., forest, grassland and agricultural ecosystem, inland
39 waters only occupy a small fraction (3.5%) of the earth surface (Verpoorter et al.,
40 2014). However, they play a disproportional role for global carbon cycling with
41 respect to carbon transportation, transformation and carbon storage (Tranvik et al.,
42 2009; Verpoorter et al., 2014). According to Tranvik et al. (2009), 2.9 Pg C/yr was
43 imported from terrestrial ecosystems to inland waters, of which about 0.6 Pg C was
44 buried in the lake sediment each year, 1.4 Pg C/yr was released into the air as CO₂ or



45 methane, and the rest of 0.9 Pg C/yr was exported to the ocean via river channels.
46 However, the amount of C retained in the inland waters is still not clear or the
47 uncertainty is still remained for the current knowledge (Raymond et al., 2013). It has
48 been proposed by several researchers that remote sensing might provide a promising
49 tool for quantification of various carbon fractions and carbon storage for inland waters
50 (Cole et al., 2007; Tranvik et al., 2009; Song et al., 2013; Kutser et al., 2015).

51 Colored dissolved organic matter (CDOM) is one of the largest bioactive
52 reservoirs at earth's surface (Para et al., 2010), and influences light transmittance in
53 aquatic ecosystems (Vodacek et al., 1997; Williamson and Rose, 2010). Dissolved
54 organic carbon (DOC), the major component of CDOM, is a source of nutrients and
55 energy for heterotrophic bacteria, and the mineralization of allochthonous DOC in the
56 aquatic systems into net source of CO₂ in the atmosphere (Jaffe et al., 2008; Raymond
57 et al., 2013). DOC also serves to mediate the chemical environment through
58 production of organic acids (Landon and Bishop, 2002; Brooks and Lemon, 2007),
59 enhance or alleviate toxicity of heavy metals (Cory et al., 2006). A bunch of
60 researches have been conducted to characterize the spatial and seasonal variations of
61 CDOM and DOC for both inland and oceanic waters (Vodacek et al., 1997; Neff et al.,
62 2006; Stedmon et al., 2011) in ice free season, but less is known about saline lakes
63 (Song et al., 2013; Wen et al., 2016), urban waters influenced by sewage effluent and
64 ice covered waters in winter (Belzile et al., 2000, 2002).

65 The relationship between DOC and CDOM sets a bridge for remote estimation of
66 DOC in both oceanic water (Hoge et al., 1996; Bricaud et al., 2012; Nelson et al.,



67 2012) and inland waters (Yu et al., 2010; Griffin et al., 2011; Song et al., 2013; Zhu et
68 al., 2013). Thus, various attempts have been made to examine the relationship
69 between DOC and CDOM. According to Fichot and Benner (2011), close
70 relationship between CDOM and DOC was observed for water from Mexican Gulf,
71 and stable regression model was established between DOC and $a_{\text{CDOM}(275)}$ and
72 $a_{\text{CDOM}(295)}$. Similar findings also observed in other estuary waters along a salinity
73 gradient, e.g., the Baltic Sea along the Finish Gulf (Kowalczyk et al., 2006), the
74 Chesapeake Bay (Le et al., 2013). However, investigation by Chen et al. (2004) also
75 indicated that the relationship between CDOM and DOC was not conservative due to
76 some process could either be estuarine mixing or photo-degradation. Similar
77 arguments were raised by Spencer et al. (2009) for waters from Congo River and for
78 waters across the mainland of USA (Spencer et al., 2012). Jiang et al. (2012) also
79 examined the relationship between DOC and CDOM for Lake Taihu, and found that a
80 relative stable relationship was observed for water samples collected in different
81 seasons except those measured in winter. Further, obvious seasonal variations were
82 observed, which could be explained by the mixing of various endmembers of CDOM
83 originated from different types of terrestrial ecosystems and internal source as well
84 (Zhang et al., 2010; Spencer et al., 2012).

85 As argued by Tranvik et al. (2009) and Raymond et al. (2013), remote sensing
86 technology was supposed to play a vital role in quantification of inland waters for
87 carbon cycling. To date, various attempts have been made to characterize DOC and
88 CDOM for both oceanic and inland waters and assess the relationship between these



89 two forms of carbons (Vodacek et al., 1999; Fichot and Benner, 2011; Griffin et al.,
90 2011; Spencer et al., 2012; Zhu et al., 2013). However, the variation for this
91 relationship with various types of inland waters, especially saline water and urban
92 water bodies were not examined in depth. In this study, the characteristics of DOC
93 and CDOM within different types of inland waters across China were examined to
94 determine its spatial feature associated with landscape variations, hydrologic
95 conditions and saline gradients. To specific, the objectives of this study are to: 1)
96 examine the relationship between CDOM and DOC concentrations across a wide
97 range of waters with various physical, chemical and biological conditions, 2) compare
98 the behavior of the relationships between DOC and CDOM for various water types,
99 and 3) establish model for the relationship between DOC and CDOM based on the
100 sorted CDOM absorption features, e.g., SUVA₂₅₄ and the ratio of $a_{250} : a_{365}$ (DeHaan,
101 1993; Weishaar et al., 2003). To address these objectives, 1504 water samples were
102 collected in fresh and saline water lakes, reservoirs, rivers and streams, ponds across
103 China that encompass a broad ranges of DOC, CDOM concentrations with various
104 natural conditions, e.g., temperature, precipitation, hydrology, morphology, soil type
105 and landscape gradients. The findings from this research is essential for understanding
106 the relationship between DOC and CDOM with various types of inland waters, which
107 set a bridge for remote estimation of DOC contained in lakes or reservoirs.

108 **2. Materials and Methods**

109 The dataset is composed of five subsets of samples collected from various types of
110 waters across China (Table 1), which encompassed a wide range of DOC and CDOM



111 originating from different sources. The first dataset (n = 288; from early spring 2009
112 to late October 2014) was measured from samples collected in fresh lakes and
113 reservoirs for describing variations in absorption properties of different CDOM and
114 DOC sources during the growing season with various landscape types. The second
115 dataset (n = 345; from early spring 2010 to late mid-September 2014) was measured
116 from samples collected in brackish to saline water bodies for investigating variations
117 in CDOM absorption properties and hydrological impact on DOC concentration. The
118 third dataset (n = 322; from early May 2012 to late October 2014) was measured from
119 samples collected in rivers and streams across a wide region in China. The fourth data
120 (n = 328; from 2011 to 2014 in the ice frozen season) was measured from samples
121 collected in northeast China in winter from both lake ice and underlying waters. The
122 fifth dataset (n = 221; from early May 2013 to mid-October 2014) was measured of
123 samples from urban water bodies, including lakes, ponds, rivers and streams, which
124 was severely influenced by sewage effluents. It is expected that CDOM and DOC
125 from various water types may illustrate a general trend between these two parameters.

126 **[Insert Fig.1 about here]**

127

128 **2.1 Water quality determination**

129 In the laboratory, water salinity was measured through DDS-307 electrical
130 conductivity (EC) meter ($\mu\text{S}/\text{cm}$) at room temperature ($20\pm 2^\circ\text{C}$) and transformed to
131 practical salinity units (PSU). Water samples were filtered and extracted with acetone
132 for chlorophyll-a (Chl-a) concentration determination using a Shimadzu UV-2050PC



133 spectrophotometer (Song et al., 2013). Total suspended matter (TSM) was determined
134 gravimetrically, details can be found in Song et al. (2013). DOC concentrations were
135 determined by high temperature combustion (HTC) with water samples filtered
136 through pre-combusted 0.45 μm GF/F filters (Song et al., 2013). The standards for
137 dissolved total carbon (DTC) were prepared from reagent grade potassium hydrogen
138 phthalate in ultra-pure water, while dissolved inorganic carbon (DIC) were
139 determined using a mixture of anhydrous sodium carbonate and sodium hydrogen
140 carbonate. DOC was calculated by subtracting DIC from DTC, both of which were
141 measured by a Total Organic Carbon Analyzer (Shimadzu, TOC-VCPN). Total
142 nitrogen (TN) was measured based on the absorption levels at 146 nm of water
143 samples decomposed with alkaline potassium peroxydisulfate. Total phosphorus (TP)
144 was determined using the molybdenum blue method after the samples were digested
145 with potassium peroxydisulfate (APHA, 1998). A PHS-3C pH meter was used to
146 determine pH at room temperature (20 ± 2 °C) in laboratory.

147

148 **2.2 CDOM absorption and spectral slope (S) derivation**

149 First, all the samples were filtered at low pressure, first through a pre-combusted
150 Whatman GF/F filter (0.7 μm) in the laboratory, and then the filtrate were further
151 filtered through pre-rinsed 25 mm Millipore membrane cellulose filter (0.22 μm) at a
152 low pressure. Absorption spectra were obtained between 200 and 800 nm at 1 nm
153 increment using a Shimadzu UV-2600PC UV-Vis (Shimadzu Inc., Japan) dual beam
154 spectrophotometer through a 1 cm quartz cuvette (or 5 cm cuvette for ice melted



155 water samples), and Milli-Q water was used as reference for CDOM absorption
 156 measurements. The absorption coefficient (a_{CDOM}) was calculated from the measured
 157 optical density (OD) of samples using Eq. (1):

$$158 \quad a_{CDOM}(\lambda) = 2.303[OD_{S(\lambda)} - OD_{(null)}] / \beta \quad (1)$$

159 where β is the cuvette path length (0.01 or 0.05m) and 2.303 is the conversion factor
 160 of base 10 to base e logarithms. To remove the scattering effect from fine particles
 161 remained in the filtered solutions, a necessitated correction was implemented. The
 162 $OD_{(null)}$ is the average optical density over 740–750 nm, which is assumed to be zero
 163 for the absorbance of CDOM (Zhang et al., 2007). All absorption measurements were
 164 conducted within 48 h after the samples were shipped back to the laboratory. The
 165 specific CDOM absorption coefficients were calculated as the ratio of $a_{CDOM}(\lambda)$
 166 against DOC concentration, and denoted as $a^*_{CDOM}(\lambda)$ with units of ($m^{-1}.L.mg^{-1}$). In
 167 the current study, the value of $a^*_{CDOM}(\lambda)$ at reference wavelength of 350 nm was
 168 calculated as suggested by previous investigations (Vodacek et al., 1999; Fichot and
 169 Benner, 2011), which will be further used as spectral index for establishing
 170 relationship between CDOM and DOC.

171 A CDOM absorption spectrum, $a_{CDOM}(\lambda)$, is generally expressed as an
 172 exponential function (Babin et al., 2003):

$$173 \quad a_{CDOM}(\lambda_i) = a_{CDOM}(\lambda_r) e^{-S(\lambda_i - \lambda_r)} \quad (2)$$

174 where $a_{CDOM}(\lambda_i)$ is the CDOM absorption at a given wavelength λ_i , $a_{CDOM}(\lambda_r)$ is the
 175 absorption estimate at the reference wavelength (i.e., $\lambda_r = 440$ nm) and S is the
 176 spectral slope. The S is calculated by fitting the data to a nonlinear model over a



177 wavelength range of 300 to 500 nm as suggested by Zhang et al. (2007).

178 **3. Results and discussion**

179 In all datasets collected over different types of water bodies across China, a large
180 diversity of inland waters with varying water qualities was encountered. High average
181 Chl-a concentrations ($46.44 \pm 59.71 \mu\text{gL}^{-1}$) are observed in these waters, which ranged
182 between 0.28-521.12 $\mu\text{g/L}$. As shown in Table 1, fresh water, saline water and
183 particularly urban water bodies all exhibited high TN and TP values, indicating that
184 most of the waters are highly eutrophic. It should be noted that even winter water
185 samples also revealed high Chl-a concentration ($7.3 \pm 19.7 \mu\text{gL}^{-1}$), which is resulted
186 from high TN ($4.3 \pm 5.4 \text{mgL}^{-1}$) and TP ($0.7 \pm 0.6 \text{mgL}^{-1}$) concentrations even under ice
187 covered conditions. Due to regional hydro-geologic and climatic conditions, most
188 waters in the semi-arid and arid regions have high electric conductivity (EC:
189 1067-41000 $\mu\text{s/cm}$) and pH values (7.1-11.4). Overall, waters are highly turbid by
190 showing high concentration of TSM ($119.55 \pm 131.37 \text{mgL}^{-1}$), but different water
191 types demonstrated obvious variations in the water column (Table 1). Hydrographic
192 conditions exert strong impact on water turbidity and TSM concentration, thus these
193 two parameters for river and stream samples were not measured in this study (Table 1).
194 Large variations of water quality parameters extensive geographic conditions set a
195 more representative basis for examination of the relationship between DOC and
196 CDOM, which is potentially helpful for remote estimate of DOC through CDOM
197 absorption properties (Kutser et al., 2015).

198 **[Insert Table 1 about here]**



199 **3.1. DOC concentrations in various types of waters**

200 The range of DOC concentrations spanned an order of magnitude over these waters
201 being investigated. As shown in Table 1, low averaged concentration of DOC was
202 observed for river waters, but even lower DOC concentrations were measured with
203 ice melting waters sampled in winter. It should be noted that large variations were
204 measured with waters from rivers and streams (Table 2). Generally, low DOC
205 concentrations were found in rivers or streams in the drainage systems developed in
206 Tibetan Plateau or arid regions where soil contains relative low concentration of soil
207 organic carbon, while inverse trend were found in rivers or streams surrounded by
208 forest or wetlands. Among the five types of waters investigated, high DOC
209 concentrations were recorded for saline waters, ranging from 2.3 to 300.6 mg/L. This
210 investigation indicated that saline waters originated from the Songnen Plain, the
211 HulunBuir Plateau and part of waters from Tibetan Plateau generally exhibits high
212 concentration of DOC, while some of waters supplied with snow melt water or ground
213 waters generally exhibit low DOC concentrations even with high salinity. Compared
214 with samples collected in growing seasons, higher DOC concentrations were observed
215 in ice covered water bodies (7.3-720 mg/L), which is due to the condensed effect
216 caused by the DOC expelled from ice formation (Bezilie et al., 2002). This condensed
217 effect is particularly marked for these shallow water bodies, where ice forming
218 remarkably condensed the DOC in the underlying waters (Zhao et al., 2016). As
219 shown in Table 2, even in river or saline water bodies, the concentrations of DOC
220 demonstrated obvious variations. Comparatively, river waters from Qinghai exhibited



221 lower DOC concentration, while these from Liaohe and Inner Mongolia showed much
222 higher concentration. Likewise, large variations were exhibited for saline waters of
223 different regions (Table 2). Saline waters from the Qinghai and Hulunbir showed
224 much higher DOC concentration, while these from the Xilinguole Plateau and the
225 Songnen Plain exhibited relative lower DOC concentrations.

226 **[Insert Table 2 about here]**

227 **3.2. DOC versus CDOM with various types of waters**

228 **3.2.1 Fresh waters**

229 The relationships between DOC and CDOM have been examined based on CDOM
230 absorption spectra at different wavelength (Fichot and Benner, 2011; Spencer et al.,
231 2012). As suggested by Fichot and Benner (2011), CDOM absorptions at 275 nm
232 (CDOM₂₇₅) and 295 nm have stable performances for DOC estimates. As shown in
233 Fig.2a, a strong relationship ($R^2 = 0.85$) between DOC and CDOM₂₇₅ was exhibited
234 with samples collected in fresh lakes and reservoirs. Regression analyses of the
235 dataset collected from different regions indicated that the slope values varied from
236 1.87 to 3.22. The results indicated that water samples from North China and East
237 China turned to have lower regression slope values, where lakes and reservoirs
238 generally ranged from mesotrophic to eutrophic status. Phytoplankton degradation
239 may contribute relative large portion of DOC in these water bodies (Zhang et al.,
240 2010). Comparatively, fresh water bodies from Northeast China revealed larger
241 regression slope values, and CDOM from these water bodies are surrounded by forest,
242 wetlands and grassland generally exhibit high proportion of colored fractions (Helms



243 et al., 2008). Further, soils in Northeast China are endorsed with high organic carbon,
244 which may also contribute high concentration of DOC and CDOM in waters from this
245 region (Jin et al., 2016). Compared with waters from East and South China, water
246 bodies in Northeast China show less algal bloom due to the low temperature, thus
247 autochthonous CDOM is less presented in waters from Northeast China (Song et al.,
248 2013; Zhao et al., 2016).

249 **3.2.2 Saline lakes**

250 As shown in Fig.2b, a strong relationship ($R^2 = 0.85$) between DOC and CDOM₂₇₅
251 was demonstrated for saline waters. However, compared to fresh waters, much lower
252 regression slope value (slope = 1.28) was exhibited for saline waters. Similar to fresh
253 water bodies, the slope values for most saline waters exhibited large variations from
254 different regions, ranging from 0.67 to 2.47. As the extreme case, the slope value is
255 only 0.33 as demonstrated in the embedded diagram in Fig.2b. Our analyses indicated
256 that the saline waters from semi-arid or arid regions, e.g., west Songnen Plain (2.47),
257 Hulunbir Plateau and East Inner Mongolia Plateau (1.79) generally exhibit higher
258 regression slope values. Whereas, water bodies from the western part of Inner
259 Mongolia Plateau (1.13), the Tibetan Plateau (0.86) exhibited low slope values, and
260 the extreme low value was measured with the Lake Qinhai from Tibetan Plateau, and
261 lakes from Tarim Basin, where lakes experience long resident time and strong solar
262 radiation enhances the photo-bleaching effects (Spencer et al., 2012; Song et al., 2013;
263 Wen et al., 2016). Thereby, less colored portion of DOC was presented in water
264 bodies in semi-arid to arid regions, especially for these closed lakes with enhanced



265 photochemical processes resulting in lower regression slope value (Spencer et al.,
266 2012). The findings highlighted that remote sensing of DOC through CDOM
267 absorption algorithm for saline waters was remarkably different from fresh waters.

268 **3.2.3 Stream and rivers**

269 Though some of the samples scattered from the regression line (Fig.2c), close
270 relationship between DOC and CDOM₂₇₅ was revealed for samples collected in
271 rivers and streams. Compared with the other water types (Fig.2), the highest
272 regression slope value (slope = 3.13) was exhibited with river and stream water
273 samples. Further regression analysis with sub-datasets measured with water samples
274 collected in different regions indicated that slope values presented large variability,
275 ranging from 1.84 to 8.41. The lower regression slope was recorded with water
276 samples collected in rivers and stream in semi-arid and arid regions, e.g., the Tibetan
277 Plateau, Mongolia Plateau and Tarim Basin, while the higher values were found with
278 samples collected in streams originated from wetland and forest in Northeast China.
279 Rivers and streams in North, East and South China generally exhibit intermediate
280 value, ranging from 2.5 to 4.2. In addition, large river water generally presented
281 relatively low slope value, streams, especially head water originating from forest and
282 wetland dominated regions show higher regression slope value, which is consistent
283 with the finding from Helm et al. (2008) and Spencer et al. (2012). In fact, landscape
284 pattern in a specific watershed, including soil organic carbon, may be important
285 factors governing the terrestrial DOC and CDOM characteristics in rivers and streams
286 encompassed in the watershed (Wilson and Xenopoulos, 2008; Jaffe et al., 2008).



287 **3.2.4 Urban waters**

288 Although close relationship between DOC and CDOM₂₇₅ was revealed with urban
289 waters (Fig.2d, $R^2 = 0.71$), it is much scattered compared with other water types
290 (Fig.2), particularly with samples presenting DOC concentration less than 60 mg/L.
291 Similarly, very large variability of regression slope values was demonstrated, ranging
292 from 0.78 to 4.16. It is apparent that urban water bodies are severely affected by
293 human activities, particularly sewage, effluents and runoff from urban impervious
294 surface containing large amount of DOM and nutrient discharge into urban waters.
295 Elevated nutrients generally result in algal bloom for some of the urban water bodies
296 (Chl-a range: 1.0-521.1 $\mu\text{g/L}$; average: 38.9 $\mu\text{g/L}$). Thereby, DOC and CDOM derived
297 from phytoplankton may also contribute a portion that should not be neglected (Zhao
298 et al., 2016; Zhang et al., 2010). More or less affected by sewage effluent, the DOM
299 in urban waters is much complex than those from natural water bodies. Thus, a large
300 variation of the relationship between DOC and CDOM₂₇₅ is expected with urban
301 waters.

302 **3.2.5 Ice covered lakes and reservoirs**

303 As demonstrated in Fig.2e, a closest relationship ($R^2 = 0.93$) between DOC and
304 CDOM₂₇₅ was recorded with waters beneath ice covered lakes and reservoirs in
305 Northeast China. It was argued that the close relationship indicated the concurrent
306 processes taken place for DOC accumulation and CDOM biogeochemical activities
307 (Finlay et al., 2003; Stedmon et al., 2011). The strong positive correlations between
308 DOC and CDOM₂₇₅ is probably due to ice formation condensed these two



309 parameters. The other possible explanation is that ice and snow cover shield out most
310 of the solar radiation that may cause a series of biochemical process for CDOM
311 contained in water, the inflows and direct rainfall over lakes or reservoirs also
312 diminished, thus causing limited effect on DOC concentration and CDOM
313 composition (Uusikiv et al., 2010; Belzile et al., 2002). Further, the autochthonous
314 DOC and CDOM for ice covered waters are also very limited due to the weak primary
315 production in winter (7.3 µg/L). Thus, much close relationship between DOC and
316 CDOM is expected for winter waters.

317 Comparatively, a loose correlation between DOC and CDOM₂₇₅ was
318 demonstrated for ice melting waters (Fig.2f) are probably due to the ice/water depth
319 ratio, which cause variation of dissolved components expelled during ice formation.
320 The other reason is probably due to the biologically derived DOC in the ice matrix,
321 which could be varied due to the light and nutrient conditions (Arrigo et al., 2010;
322 Muller et al., 2011). Apparently, CDOM from ice melting waters were mainly
323 originated from maternal water during the ice formation, also from algal biological
324 processes (Stedmon et al., 2009; Arrigo et al., 2010). The DOC and CDOM
325 concentrations in maternal waters, and ice formation processes may cause the
326 variations for their relationship, thus the regression slopes varies. Similarly, snow
327 cover, and nutrients in the ice also cause the variation for biochemical processes, that
328 ultimately result in the relationship between DOC and CDOM may differ from
329 corresponding waters (Bezilie et al., 2002; Spencer et al., 2009). Interestingly, the
330 regression slopes for ice samples (slope = 1.35) and under lying water sample (slope =



331 1.27) are very close, which may also explain that the dominant components of CDOM
332 and DOC in the ice are from maternal underlying waters.

333 **[Insert Fig.2 about here]**

334 **3.3 DOC versus CDOM based on SUVA₂₅₄ and M ($a_{250}:a_{365}$) values**

335 Through comparison of the relationships between DOC and CDOM₂₇₅, it can be seen
336 that the regression slope values exhibit large variability for various types of waters. The
337 underlying reasons may lie in the aromaticity and colored fractions in DOC
338 component (Spencer et al., 2009, 2012). Since SUVA₂₅₄ is an effective indicator to
339 characterize CDOM molecular weight, and is calculated by the ratio of CDOM
340 absorption at 254 nm to DOC (Weishaar et al., 2003), it may reflect the regression
341 slope value between DOC and CDOM absorption at 275 nm. As shown in Fig.3a, it is
342 obvious that SUVA₂₅₄ presented high values for both fresh water bodies, and waters
343 from rivers or streams as well. Saline water and winter water samples show
344 intermediate SUVA₂₅₄ values, while urban water and ice melting water show lower
345 values. The M value ($a_{250}:a_{365}$) is another indicator to demonstrate the variation of
346 molecular weight and aromaticity of CDOM components (Dehaan, 1993). As shown in
347 Fig.3b, fresh water, river and stream water, and urban water exhibit low values, which
348 indicated that larger aromaticity dominant for these three types of waters, whereas
349 saline water, winter water and ice melting water show higher M values. Since,
350 SUVA₂₅₄ and M values reveal molecular weight and aromaticity, it might help to
351 estimate DOC through CDOM absorption based on SUVA₂₅₄ and M threshold values



352 for various types of waters being investigated.

353 **[Insert Fig.3 about here]**

354 ***3.3.1 Regression based on SUVA254 grouping***

355 Based on the threshold value for SUVA254, eight subsets of paired DOC and
356 CDOM275 were grouped. Figs.4a to 4f demonstrated the regressions between DOC
357 and CDOM275 with a SUVA254 increment of unity. Fig.4g and 4h exhibited the
358 cases with SUVA254 threshold larger than unity. Except the regression model with
359 SUVA254 less than one (Fig. 4a), better performances were achieved for regression
360 models based on SUVA254 thresholds between 2 to 6 (Figs.4b-4f). As shown in
361 Fig.4a-4h, as a whole, the regression slope values have strong links with SUVA254
362 values, i.e., slope values increased with SUVA254 increment except for SUVA254
363 ranging from 6 to 8. It is still not clear whether it is because some outliers or the
364 complex relationship between SUVA254 and DOC, further investigation is required to
365 figure out the underlying reasons. It can be seen that in most of cases, the regression
366 models performed much better based on SUVA254 thresholds. The less promising
367 cases were related with subset of data with lower and high SUVA254 values,
368 relatively larger variations at inner groups are expected thus outperformed by
369 regression models with intermediate SUVA254 values.

370 **[Insert Fig.4 about here]**

371 ***3.3.1 Regression based on M value grouping***

372 Likewise, regression models between DOC and CDOM275 were established based on



373 M threshold values (Fig.5). A relative loose correlation between DOC and CDOM275
374 was revealed with dataset where M value was less than 5 (Fig.5a). It should be noted
375 that the highest regression slope value was achieved among different groups of subset
376 of data (Figs.5a-5h). The large range of M value ($0 < M < 5.0$) may explain the scattered
377 data pairs in Fig.5a; similar reason can be ascribed to the group with M value ranging
378 from 4 to 6 (Fig.5b). Better regression models were achieved with intermediate M
379 value groups (Figs.5c-5f), where regression slope values were close to each other
380 (ranging from 1.15 to 1.38) with high determination of coefficients ($R^2 > 0.88$). With
381 increased M values, small regression slope values were obtained (Figs.5g-h). Loose
382 relationship between DOC and CDOM275 was obtained with relative low or high M
383 values (Fig.5g). However, very close relationship ($R^2 = 0.99$) was yielded with
384 extremely high M values (Fig.5h). It can be seen that most of samples are from these
385 presented in embedded diagram in Fig.2b, the limited water bodies in the group may
386 be explain this coincidentally high R-square value. With more samples collected from
387 different water bodies in this extreme group, a loose relationship between DOC and
388 CDOM275 may be expected, which also needs future explorations.

389 As noted in Figs.5c-5f, close regression slope values were obtained, implicating
390 that a comprehensive regression model with intermediate M value groups may be
391 achieved. As expected, a promising regression model (the diagram was not shown)
392 between DOC and CDOM 275 was achieved ($y = 1.269x + 6.55$, $R^2 = 0.925$, $N = 998$,
393 $p < 0.001$) with pooled dataset presenting in Figs.5c to 5f. As shown in Fig.6a, a close
394 relationship between DOC and CDOM 275 was obtained with the pooled dataset ($N =$



395 1504) collected from different types of inland waters. However, it should be admitted
396 that the extremely high DOC samples may advantageously contribute the better
397 performance of the regression model. Thus, regression model was established without
398 these eight samples ($\text{DOC} > 300 \text{ mg/L}$), still acceptable accuracy can be achieved
399 (Fig.6b, $R^2 = 0.66$, $p < 0.01$). In addition, regression model based on logarithm
400 transformed pool dataset was also established (Fig.6c, $R^2 = 0.82$, $p < 0.01$). It can be
401 seen that most of the paired data sitting close to the regression line except some
402 scattered ones. Based on the regression analysis on pooled dataset, it can be
403 concluded that it is possible to derive DOC concentration based on CDOM absorption
404 spectra, and the latter parameter can be estimated from remotely sensed data (Zhu et
405 al., 2011; Kuster et al., 2015).

406 **[Insert Fig.5 and Fig.6 about here]**

407

408 **4. Conclusion**

409 As a powerful means, remote sensing plays a crucial role in assessing CDOM and
410 DOC in lake and reservoir waters. However, in order to get accurate estimates of
411 CDOM and DOC in waters, it is necessary to get insight into the regional water
412 optical properties for developing semi-analytical or analytical models with remotely
413 sensed data. Based on CDOM absorption spectral measurements and DOC laboratory
414 analysis, we have investigated the relationships between CDOM and DOC for various
415 water types systematically. The investigation showed that CDOM absorption varied
416 significantly, and generally river waters and fresh lake waters exhibit high CDOM



417 absorption values and specific CDOM absorption (SUVA₂₅₄) as well. On the contrast,
418 saline waters illustrate low SUVA₂₅₄ values due to the long residence time and strong
419 photo-bleaching effects on waters in the semi-arid regions. Influenced by effluents
420 and sewage waters, CDOM from urban water bodies showed much complex
421 absorption feature. With respect to ice melting water samples, SUVA₂₅₄ for CDOM
422 was lowest for all groups of waters concerned.

423 The current investigation indicated that the relationships between CDOM
424 absorption and DOC varied significantly by showing different slope values with
425 various water types of regression models. The slope values for saline and urban
426 waters are close to unity, while river water exhibited highest slope value (~ 3.1) of all
427 water types concerned, and other water types are in between. When all the data set
428 pooled together, the slope for regression model is about 1.3, but with much higher
429 uncertainty ($R^2 = 0.66$). Regression model accuracy for CDOM₂₇₅ against DOC was
430 improved when CDOM absorptions were divided into different sub-groups according
431 to SUVA₂₅₄ or M values ($a_{250}:a_{365}$). This finding highlights that remote sensing
432 models for DOC estimates based on the relationship between CDOM and DOC need
433 to consider water types or cluster waters into several groups according to their
434 absorption features, ultimately improved model accuracy is expected.

435

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441 analysis.

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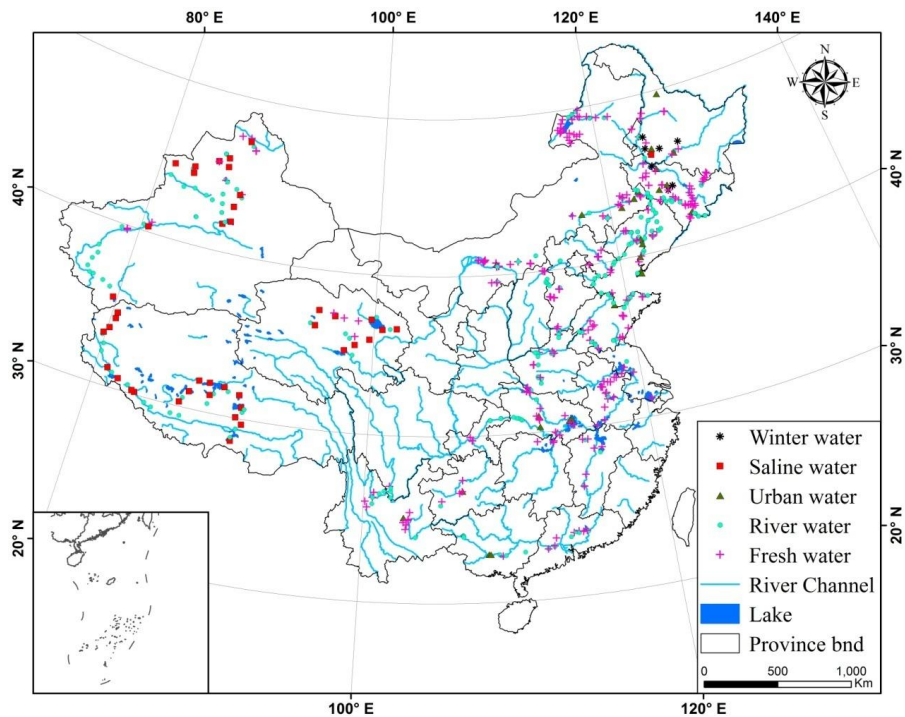
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593 **Figures**

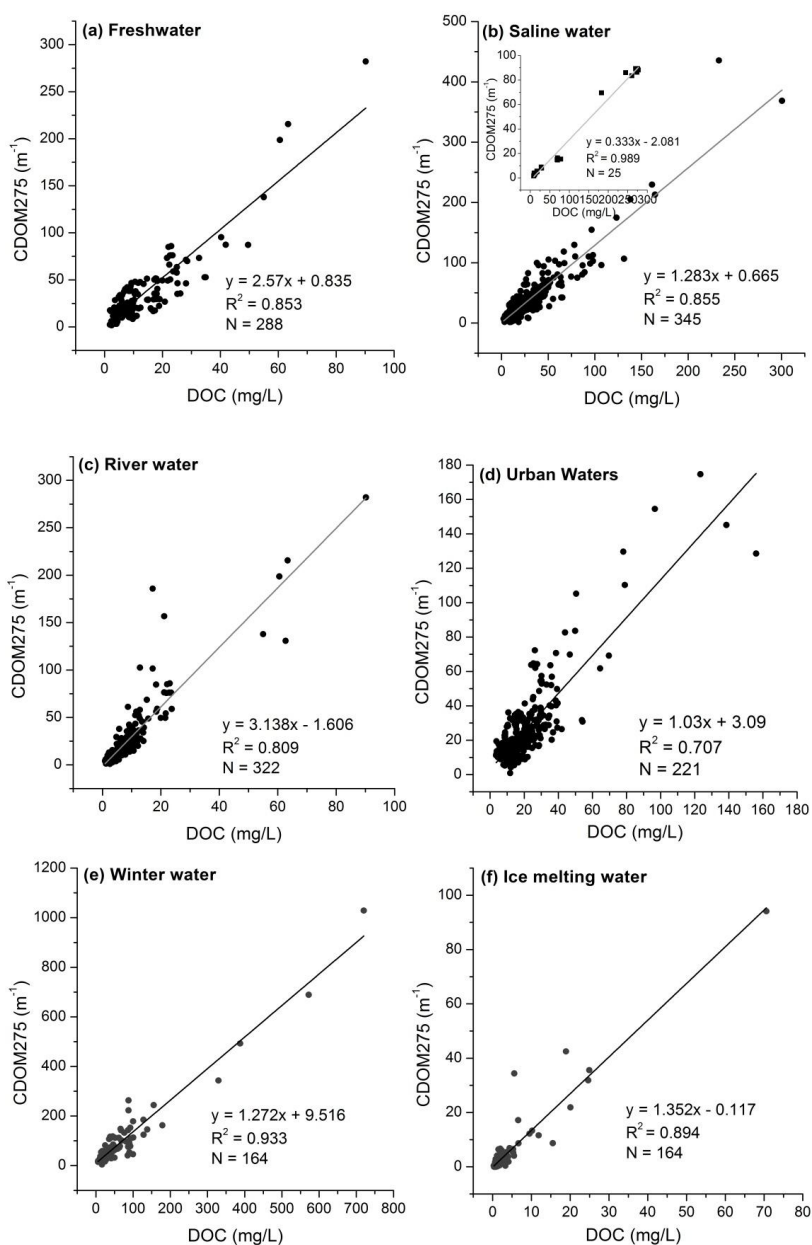
594 Fig.1. Water types and sample distributions across the mainland of China.



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615 Fig.2. Fitting equations of DOC against CDOM275 for different types of inland
 616 waters, (a) samples from fresh water lakes, (b) samples from saline water lakes, (c)
 617 samples from river waters, (d) samples from urban waters, (e) samples from ice
 618 covered waters, and (f) samples from ice melting waters.
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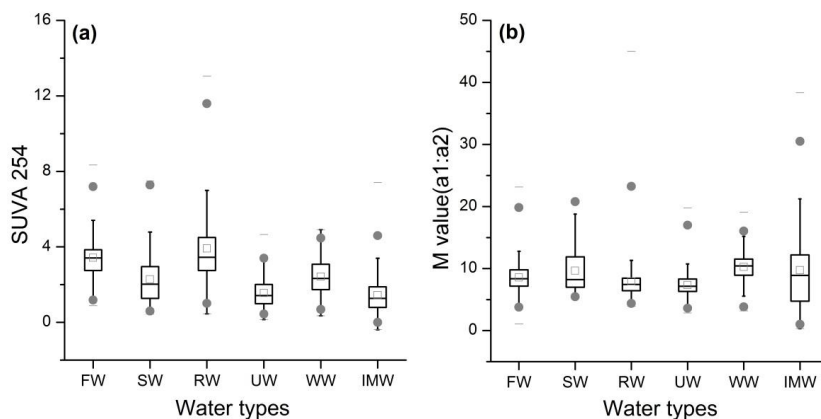
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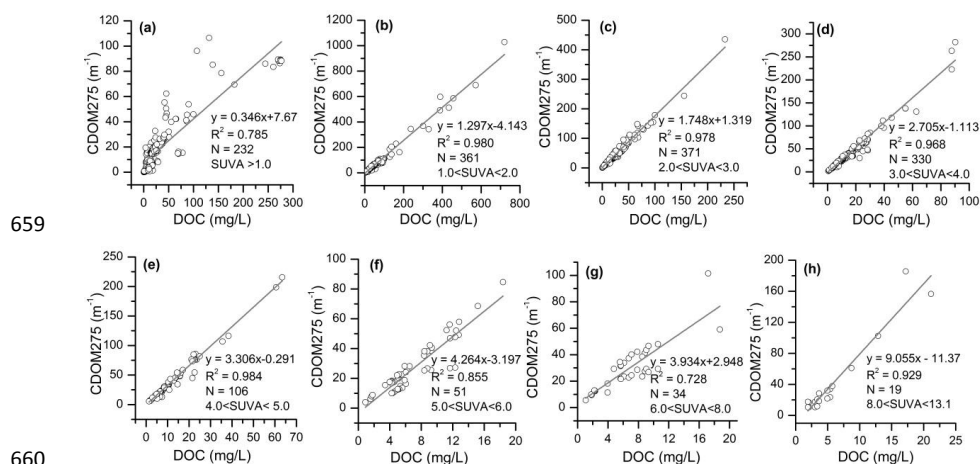
624 Fig.3. Comparison of (a) SUVA₂₅₄, and (b) M ($a_{250}:a_{365}$) values for various types of
625 inland waters. FW, fresh lake water; SW, saline lake water, RW, river or stream water;
626 UW, urban water; WW, winter water from Northeast China; IMW, ice melt water from
627 Northeast China.



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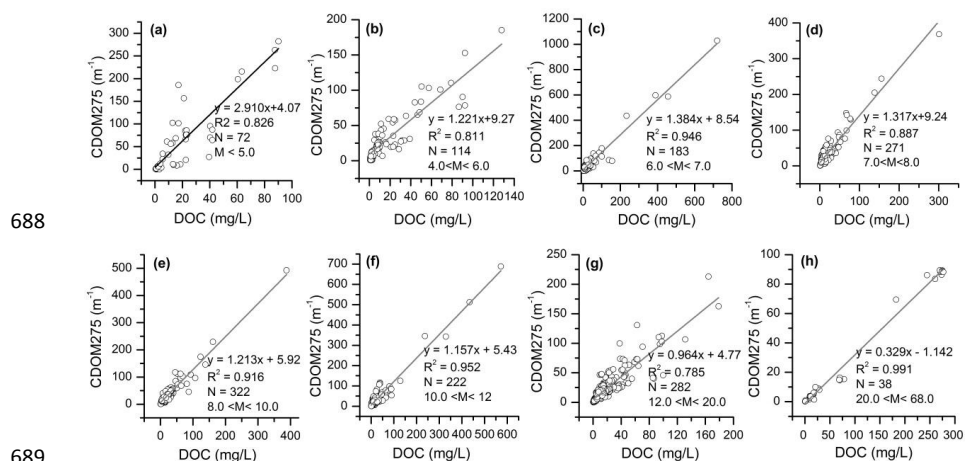


654 Fig.4. Regression models for DOC estimation via CDOM 275 sorted by SUVA254
 655 ranges, (a) SUVA254 > 1.0, (b) 1.0 < SUVA254 < 2.0, (c) 2.0 < SUVA254 < 3.0, (d)
 656 3.0 < SUVA254 < 4.0, (e) 4.0 < SUVA254 < 5.0, (f) 5.0 < SUVA254 < 6.0, (g) 6.0 <
 657 SUVA254 < 8.0, and (h) 8.0 < SUVA254 < 13.1
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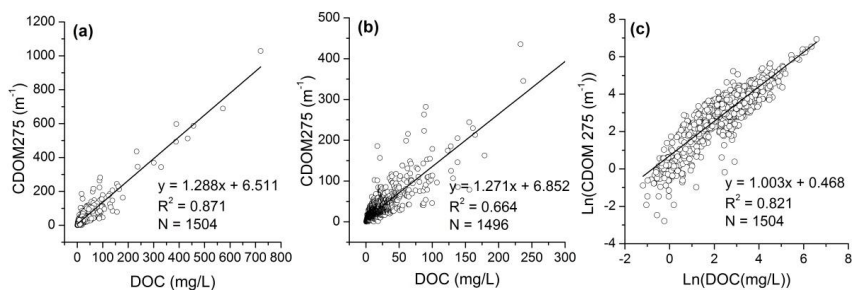


684 Fig.5. Regression models for DOC estimation via CDOM 275 sorted by M (a1:a2:
 685 CDOM250:CDOM365) values ranges, (a) $M < 5.0$, (b) $4.0 < M < 6.0$, (c) $6.0 < M <$
 686 6.0 , (d) $7.0 < M < 8.0$, (e) $8.0 < M < 10.0$, (f) $10.0 < M < 12.0$, (g) $12.0 < M < 20.0$, and
 687 (h) $20.0 < M < 68.0$.





714 Fig.6. Relationship between CDOM 275 and DOC concentration. (a) regression
715 model with pooled dataset; (b) regression model with DOC concentration less than
716 300 mg/L; (c) regression model with natural logarithmic transformed data.



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734 **Tables**

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736 Table 1 descriptive water quality characteristics of different types of waters

		DOC (mg/L)	EC µs/cm	pH	TP (mg/L)	TN (mg/L)	TSM (mg/L)	Chl-a (µg/L)
FW	Mean	10.2	434.0	8.2	0.5	1.6	67.8	78.5
	Range	1.9-90.2	72.7-1181.5	6.9-9.3	0.01-10.4	0.001-9.5	0-1615	1.4-338.5
SW	Mean	27.3	4109.4	8.6	0.4	1.4	115.7	9.0
	Range	2.3-300.6	1067-41000	7.1-11.4	0.01-6.3	0.6-11.0	1.4-2188	0-113.7
RW	Mean	8.3	10489.1	7.8-9.5	--	--	--	--
	Range	0.9-90.2	3.7-1000	8.6	--	--	--	--
UW	Mean	19.44	525.4	8.0	3.4	3.5	50.5	38.9
	Range	3.5-123.3	28.6-1525	6.4-9.2	0.03-32.4	0.04-41.9	1-688	1.0-521.1
WW	Mean	67.0	1387.6	8.1	0.7	4.3	181.5	7.3
	Range	7.3-720	139-15080	7.0-9.7	0.1-4.8	0.5-48	9.0-2174	1.0-159.4
IMW	Mean	6.7	242.8	8.3	0.19	1.1	17.4	1.1
	Range	0.3-76.5	1.5-4350	6.7-10	0.02-2.9	0.3-8.6	0.3-254.6	0.28-5.8

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738 Note: FW, fresh lake water; SW, saline lake water, RW, river or stream water; UW, urban water;

739 WW, winter water from Northeast China; IMW, ice melt water from Northeast China.

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762 Table 2 descriptive statistics of dissolved organic carbon (DOC) and $a_{\text{CDOM}(440)}$ in
763 various types of waters.

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Type	Region	DOC				$a_{\text{CDOM}(440)}$			
		Min	Max	Mean	S.D	Min	Max	Mean	S.D
River	Liaohe	3.6	48.2	14.3	9.49	0.46	3.68	0.92	0.58
	Qinghai	1.2	8.5	4.4	1.96	0.13	2.11	0.54	0.63
	Inner M	16.9	90.2	40.4	24.84	0.32	7.46	1.03	2.11
	Songhua	0.9	21.1	8.1	4.96	0.32	18.93	3.2	4.19
Saline	Qinghai	1.7	130.9	67.9	56.7	0.13	0.86	0.36	0.23
	Hulunbir	8.4	300.6	68.5	69.2	0.82	26.21	4.41	4.45
	Xilinguo	3.74	45.4	14.2	8.8	0.36	4.7	1.34	0.88
	Songnen	3.6	32.6	16.4	7.4	0.46	33.80	2.4	3.78

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