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Effects of Landcover, Soil Property, and Temperature on Covariations of DOC and CDOM in Inland Waters

Jiwei Li[1], Qian Yu[1], Yong Q. Tian[2], and David F. Boutt[1]

[1]Department of Geosciences, University of Massachusetts, Amherst, MA, USA, [2]Department of Geography/Institute for Great Lakes Research, Central Michigan University, Mount Pleasant, MI, USA

Key Points:

- DOC and CDOM are linearly related, and the slope of the linear relationship is modulated by source vegetation type and temperature
- Vegetation type is the key factor driving covariations of freshwater DOC/CDOM
- Controlled experiments provided useful information to establish analytical models at subbasin scale

Correspondence to:
Q. Yu,
qyu@geo.umass.edu

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Abstract Significant uncertainty exists in the estimation of dissolved organic carbon (DOC) concentration via remote sensing from colored dissolved organic matter (CDOM) absorption in inland waters pointing to a need for more process-based understanding of the relationship between CDOM and DOC. In this study, we examine the factors affecting the covariations of DOC and CDOM using controlled experiments combined with field measurements at subbasin scale that have varying environmental and biological conditions. Our analysis reveals that the DOC:CDOM ratio is mainly related to landcover types. Higher DOC:CDOM linear regression slopes observed in evergreen leaf litter leachate suggest that CDOM comprises a smaller fraction of the DOC pool in evergreen sites in comparison to agricultural and deciduous leaf litter leachates. Given the same DOC concentrations, the range of CDOM levels from deciduous forest plant varied 3 times greater than that from other plant types. Results indicate that soil narrows the slope differences in the linear regressions of DOC from CDOM for all plant types (by 19% of evergreen, 18% of agriculture, and 77% of deciduous). Raising soil temperature by 5°C could double the range of DOC concentration and CDOM absorption for all scenarios. We present a mathematical model to estimate DOC concentration in freshwater environment via CDOM variations with reference to land cover and soil effects. The model was able to explain 95% of field measurements of multiple years in four subbasins. This improved understanding is critical for the remote sensing of DOC directly via observations of CDOM.

1. Introduction

Terrestrially derived dissolved organic carbon (DOC) is a significant source of carbon to aquatic ecosystems (Battin et al., 2009). Inland surface waters actively transform the DOC to the CO_2 in the atmosphere (Del Giorgio et al., 1999; Holgerson & Raymond, 2016). Inland waters release about 1 Gt of carbon per year as CO_2 to the atmosphere (Tranvik, 2014). Therefore, terrestrial DOC dynamic is a crucial component in the global greenhouse gas budget (Pachauri et al., 2015). The significant losses of terrestrial DOC to inland and ocean waters have large implications for regional/global carbon cycling at the land-water interface (Borken et al., 2011; Kindler et al., 2011). Riverine DOC flux to the aquatic ecosystem also plays an important role in water quality such as controlling metal binding and modulating nutrients dynamics due to its labile properties in aquatic environments (Bianchi et al., 2015; Butman & Raymond, 2011; Spencer et al., 2013; Stedmon et al., 2006).

There have been significant efforts studying colored dissolved organic matter (CDOM) as a proxy to assess aquatic DOC information using satellite remote sensing over inland, coastal, and open ocean waters (Del Castillo & Miller, 2008; Ferrari et al., 1996). DOC is operationally defined as the organic matter that can pass through a filter with pore size between 0.7 and 0.22 μm. CDOM is the colored component of aquatic dissolved organic matter (DOM; Del Vecchio & Blough, 2004; Wetzel & Likens, 2013). CDOM changes the light field by preferentially absorbing shorter wavelength light (Rochelle-Newall & Fisher, 2002). This strong absorption signal can, in some cases, be retrieved from satellite remote sensing and has been used to map CDOM and DOC by proxy at high spatiotemporal resolutions (J. Li et al., 2017). Previous studies have demonstrated that remote sensing technology has the potential of offering a compelling alternative to DOC field monitoring through the estimation of CDOM (Brando & Dekker, 2003; Fichot & Benner, 2011; Vodacek et al., 1997).

For example, a strong correlation (R^2 = 0.7–0.95) between CDOM and DOC in previous observations is mostly based on the samples along single river plume-estuary regions (Del Castillo & Miller, 2008; Spencer et al., 2009; Vodacek et al., 1997). In these inland water observations, waters receive conservative terrestrially

Figure 1. Mesocosm experimental equipment at the Central Michigan University Biological Station on Beaver Island, Lake Michigan.

derived DOC/CDOM (Raymond et al., 2008). Spencer et al. (2009) observed that DOC and CDOM are linearly correlated (R^2 = 0.90) at Yukon River, whose watersheds were dominated by the needle leaf forest. Meanwhile, the linear relationships of DOC/CDOM usually exist in measurements from a short period or a single season without significant temperature variations (Qiao et al., 2017). For example, Brezonik et al. (2015) monitored a strong relationship of DOC/CDOM (R^2 = 0.93) in the Minnesota lakes during the summer of 2013.

Despite great potential, studies also identify high uncertainties in relating CDOM to DOC in many scenarios. Studies reporting decoupled relationships between CDOM and DOC are mostly based on observations across the watersheds/rivers and with seasonal variations (Tian et al., 2013). Fichot and Benner (2011) identified that CDOM and DOC correlations have strong seasonality, with weaker correlations observed at annual scales. CDOM/DOC ratios have been shown to vary across between wet and dry seasons in eastern Australian reservoirs (Hestir et al., 2015) and summer and fall in the Songhua river in China (S. Li et al., 2016). The high uncertainty occurred when observations were from multiple watersheds of different ecosystems (landcover, soil, or climate). Mann et al. (2017) found diverse DOC/CDOM relationships in six large Arctic rivers, which had different percentages of permafrost soil of the watersheds. Asmala et al. (2012) found relationships of DOC/CDOM were different across the watersheds with different landcover types in Finnish estuaries samples. Furthermore, different CDOM/DOC relationships were also found by comparing riverine and estuarine data in different climatic regions (pan-Arctic Rivers, Mississippi River, Florida Rivers, Middle Atlantic Bight, Chesapeake Bay, etc.) (Del Vecchio & Blough, 2004; Mann et al., 2017; Rochelle-Newall & Fisher, 2002; Spencer et al., 2009; Stabenau & Zika, 2004; Vantrepotte et al., 2015).

CDOM/DOC relationships vary widely, and the dominant controls on these processes have yet to be fully constrained (Huang & Chen, 2009). Therefore, it is essential to understand driving mechanisms to reduce uncertainty in remote sensing of DOC flux through CDOM in pathways from land to water. We advance a hypothesis in this manuscript that the vegetation type, soil presence or absence, and soil temperature are the three most important variables controlling the covariations of DOC/CDOM. We test this hypothesis by using series of controlled experiments combined with DOC and CDOM measurements from field samples at subbasin outlets over 6 years. The experiments were designed to vary temperature and vegetation types with or without soil support for carbon decomposition processes to analyze the variation of DOC/CDOM relationships. This study answers questions: (1) what forcing factors control the covariation of DOC/CDOM and (2) can the results from controlled experiments assist to elucidate the covariations of DOC/CDOM measured from field samples? These questions are fundamental to a robust remote sensing assessment of freshwater CDOM and DOC.

2. Materials and Methods

2.1. Controlled Experiments in Aquatic Environments

A mesocosm experiment was conducted at the Central Michigan University Biological Station on Beaver Island, Lake Michigan. The experiment was designed to understand how individual terrestrial vegetation type is associated with covariations of DOC/CDOM in freshwater. Six aquatic mesocosm tanks of 1,893 L (500 gallon cylinder tanks with a diameter of 1.5 m and a depth of 3.0 m) were used in the experiment (Figure 1). These mesocosms were filled with low DOC/CDOM lake water (DOC $<$ 2 mg/L and CDOM $<$ 0.13 m^{-1}). The water in the tank was set to two constant temperatures: 20 and 25°C for each of three scenarios: corn plants (*Zea mays L.*), red pine (*Pinus resinosa*), and red maple (*Acer rubrum*). The experiment worked with three types of leaf litters, red maple, red pine, and corn, representing deciduous broadleaf forest, evergreen conifers, and crop, respectively. Deciduous and evergreen forests can be composed of a wide variety of different tree species. The species in the experiment were selected to be broadly representative of those ecosystems. Before the experiment, the vegetation litter was cleaned with deionized water (DI water) and then oven dried at 60°C for 72 hr. Then the vegetation litter was put into the mesh bags and immersed in water of each mesocosm (Gulis &

Table 1
Details of Mesocosm Experiment and Soil Carbon Leaching Experiment

	Vegetation	Temperature (°C)	Tank count	DOC (mg/L)	CDOM (1/m)	Slope
Mesocosm experiment	Deciduous	20	1	22.40	9.6	2.48
	Deciduous	25	1	30.19	17.2	1.49
	Evergreen	20	1	25.14	2.8	5.84
	Evergreen	25	1	21.75	2.7	5.14
	Agriculture	20	1	11.54	2.5	2.83
	Agriculture	25	1	12.40	3.6	2.16
	Vegetation	Temperature (°C)	Tank count	DOC (g/m^2)	CDOM (1/m)	Slope
Soil carbon leaching	Deciduous + forest soil	Outdoor	3	6.18	5.3	1.39
	Deciduous + forest soil	Outdoor +4.5	3	13.80	13.1	1.58
	Evergreen + forest soil	Outdoor	3	6.17	4.9	0.77
	Evergreen + forest soil	Outdoor +4.5	3	11.89	9.3	1.04
	Forest soil	Outdoor	2	4.92	3.2	0.92
	Forest soil	Outdoor +4.5	2	9.90	7.1	1.01
	Agriculture + agriculture soil	Outdoor	3	2.54	2.0	0.36
	Agriculture + agriculture soil	Outdoor +4.5	3	5.61	4.2	0.93
	Agriculture soil	Outdoor	2	2.52	1.8	−0.43
	Agriculture soil	Outdoor +4.5	2	4.51	2.9	1.46

Note. Dissolved organic carbon (DOC) concentration and colored dissolved organic matter (CDOM) absorption at 440 nm at the last day of the mesocosm experiment were listed. DOC/CDOM values in the soil carbon leaching experiment were mean values of 10-g leaf litters per square meters surface.

Suberkropp, 2003; Rochelle-Newall, 1999). Each vegetation species (260-g dry weight terrestrial vegetation) was incubated individually (Table 1). DOC concentration and CDOM level were sampled daily for 11 days.

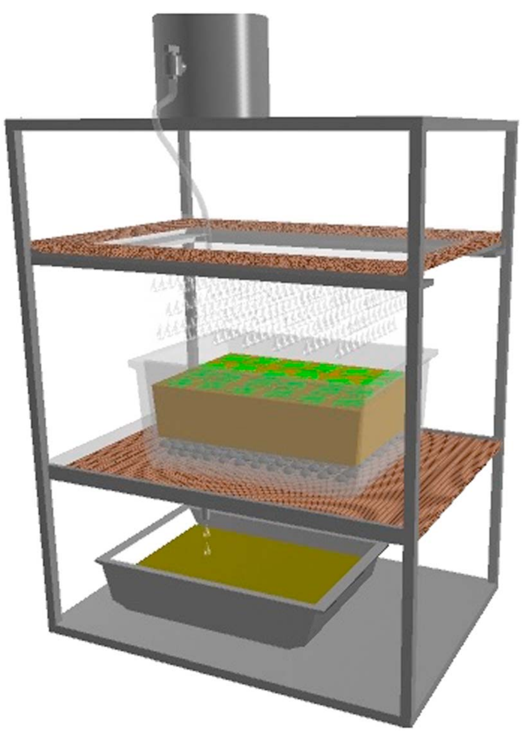

Figure 2. Three-dimensional visualization of the soil carbon leaching experiment. The artificial rainfall simulator (top two layers) was introduced for leaching the soil carbon. The leachate (bottom layer) was collected for measuring dissolved organic carbon/colored dissolved organic matter values.

2.2. Experiment with Interactive Processes Among Soil, Temperature, and Vegetation

Soil leaching experiments with a rainfall simulator were conducted to measure the changes of DOC/CDOM ratio in a minienvironmental ecosystem (Figure 2; Bowyer-Bower & Burt, 1989; Tian et al., 2007). The controlled variables were vegetation type, temperature, soil (presence or absence), and rainfall intensity. Three types of leaf litter (red maple, red pine, and corn) of the same dry weight (65 g) were prepared (Figures 3a–3c), and the dry weight was determined by the average annual litterfall of red maple (Smemo et al., 2006). The leaf litters were laid over 10-cm depth of soils in horizons O and A obtained from where vegetation was collected. The miniecosystem is 0.45-m long and 0.3-m wide. A bare soil scenario was arranged to examine DOC/CDOM contributions from soil without leaf litters (Figures 3d and 3e and Table 1). During the experiment, soil field capacity was maintained by spraying a consistent amount of DI water daily. Each week, the 60-mm/hr artificial rainfall (DI water) with 25 min of duration was used to leach the DOC/CDOM. A rainfall simulator was designed to allow the intensity and duration of the raindrop to be easily varied (Bowyer-Bower & Burt, 1989). The leachate was collected for the DOC/CDOM analysis (including volume and concentration). Half of the total 26 miniecosystems were placed outdoor, and the other equivalent half were in the greenhouse (Table 1). A greenhouse was used to establish daily temperatures differences. The hourly air temperatures were recorded at the outdoor groups and greenhouse groups. The greenhouse group was 4.5° higher on average than the outdoor group. Both the outdoor and greenhouse groups received the rainfall from an artificial simulator. The outdoor group was experimented in greenhouses with windows and doors widely open so

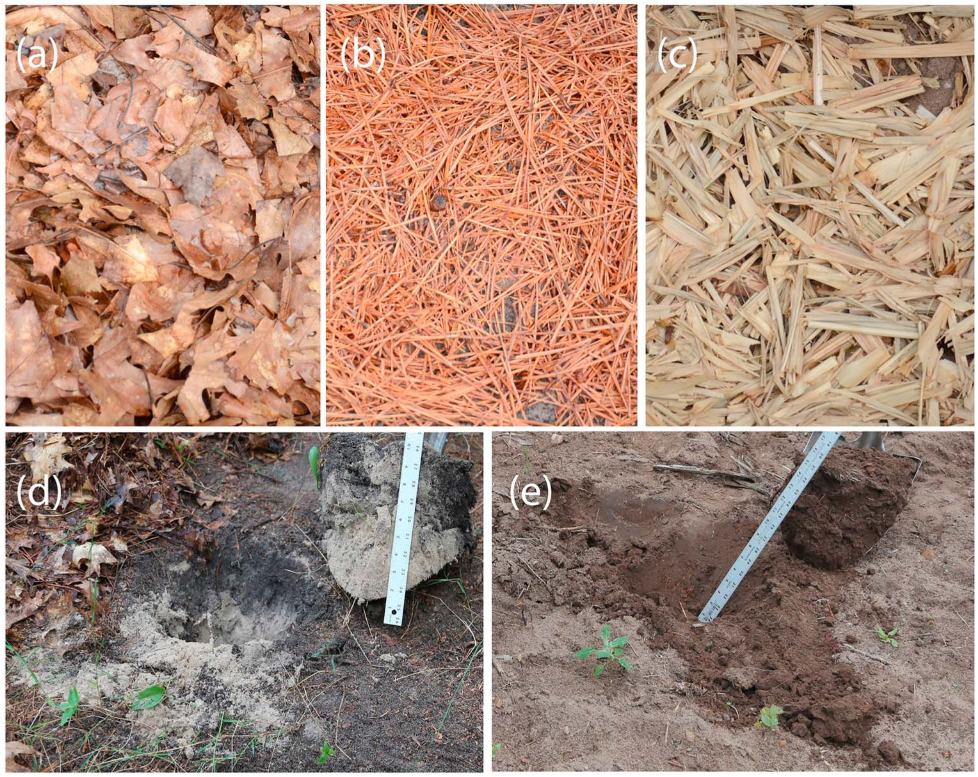

Figure 3. Photograph of different vegetation sources: deciduous leaf litters (a), evergreen leaf litters (b), and agricultural corn residue (c). The forest soil (d) and agriculture soil (e) were also collected for the soil carbon leaching experiment.

that temperature inside was the same as outdoor. Three replicas for each scenario were arranged for reliable measurements and for uncertainty analysis.

2.3. DOC/CDOM Field Sampling at Subbasin Scale

Six subbasins in Connecticut River watershed (Massachusetts, United States) and eight in Chippewa River watershed (Michigan, United States) were selected as study sites for sampling the seasonal dynamics of DOC/CDOM. Total drainage area of the selected subbasins in the Connecticut River watershed encompassed an area of 1,760 km^2, with land covers totaling 79% forest, 11% agricultural farm, and 10% other according to the National Land Cover Database 2011. Water samples were collected bimonthly across a period from the March 2011 to December 2016 at the outlets of six subbasins with different landcover (Figure 4). The total number of water samples is 150. We define subbasins as an agricultural category if they are dominated by at least 45% agricultural landcover. Similarly, a subbasin is defined as deciduous dominated if it has over 50% deciduous forest landcover and as evergreen dominated if over 40% evergreen landcover (Figure 4).

The Chippewa River watershed has a representative agricultural landscape (Figure 4). The total of 56 samples was collected in seven different months from November 2012 to May 2013 at the outlets of eight subbasins. The total drainage area associated with the samples is 1,410 km^2. These subbasins are dominated by agricultural landcover (agriculture 72%, deciduous 8%, wetland 11%, and others 9%).

2.4. Laboratory Measurements

All water samples were processed for DOC and CDOM in the laboratory within 6 hr of each experiment. The samples (50 ml, three replicates) were first filtered by GF/F glass microfiber filters (pore size 0.70 μm). Then the absorbance (A) from wavelength 200 to 800 nm was measured. The measurements were conducted using the Agilent Cary 60 UV-Vis spectrophotometer with the Milli-Q water as a blank reference. The absorption coefficient $a_g(440)$ then calculated through the measured absorbance $A(440)$ as follows:

$$a_g(440) = \frac{\ln(10)}{L} \times A(440) = 230.3 \times A(440) \tag{1}$$

where L is the path length, or diameter of the cuvette (0.01 m; Stedmon et al., 2000).

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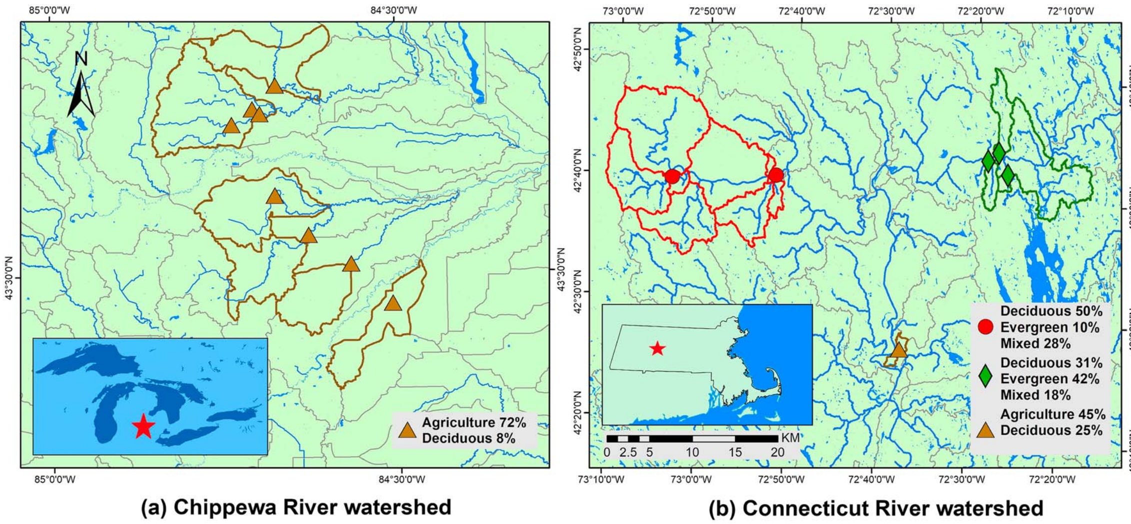

Figure 4. Field sampling sites in the Chippewa River watershed (a) and in the Connecticut River watershed (b). The eight sampling sites in the Chippewa River watershed were all dominated by the agricultural crops (agriculture 72%). Two sampling sites located in the West Connecticut River watershed were dominated by deciduous forest (deciduous 50%, evergreen 10%, and mixed forest 28%). The east three samplings sites in the Connecticut River watershed were dominated by the evergreen forest (evergreen 42%, deciduous 31%, and mixed forest 18%). The single south sampling sites in the Connecticut River watershed were the agricultural crops sites (agriculture 45% and deciduous 25%).

After filtering, 60 ml of each water samples was acidified with concentrated hydrogen chloride and stored in the refrigerator to maintain its pH of 1. The DOC concentration of water samples was measured through a Shimadzu TOC-V/TN analyzer within 2 weeks. To maintain instrument accuracy, internal standards and blanks (Milli-Q water) were included with each instrument run. The experiment and field water samples were processed with the same procedure of DOC and CDOM measurement.

2.5. Modeling DOC/CDOM Ratios at Subbasin Scales

We constructed a model describing the covariations of DOC/CDOM with varying landcover types and the soil characteristics as equation (2) in the general format below:

$$\mathrm{DOC} = \alpha(L, S) * \mathrm{CDOM} + \beta(L) \tag{2}$$

where DOC and CDOM stand for the DOC concentration (mg/L) and CDOM absorption (m^{-1}), respectively at subbasin scale. $\beta(L)$ is the intercept as a function of landcover types (L), and $\alpha(L, S)$ is the slope as a function of landcover types (L) and soil characteristics (S) in a subbasin. The $\alpha(L, S)$ is calculated as follows:

$$\alpha(L, S) = \sum_{i=1}^{n} S_i * Lt_i * N\mathrm{pct}_i \tag{3}$$

The i represents different landcover types (evergreen, agriculture, and deciduous). The $N\mathrm{pct}_i$ is the percentage of the landcover type (i). The Lt_i is the slope of the linear covariation of DOC/CDOM for landcover type (i), which was derived from the mesocosm experiments. The S_i is the soil effect based on the results from soil carbon leaching experiment for each landcover type (i) as follows:

$$S_i = a_{\mathrm{leach} \cdot i} - a_{\mathrm{soil} \cdot i} \tag{4}$$

where the $a_{\mathrm{leach} \cdot i}$ is the slope in the soil carbon leaching experiments. The $a_{\mathrm{soil} \cdot i}$ is the mean slope used in the scenarios of either the forest soil or agriculture soil.

$$\beta(L) = \sum_{i=1}^{n} b_i * N\mathrm{pct}_i \tag{5}$$

The values of b_i were determined by the biomass of the watersheds. It represents the noncolor-related DOC levels when the CDOM values are near 0.

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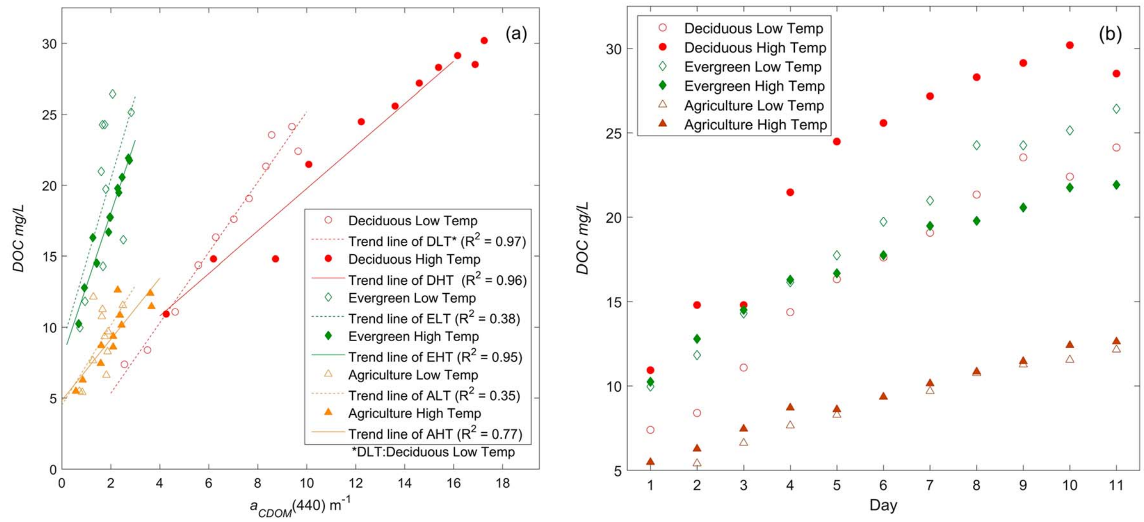

Figure 5. (a) Dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) variations in the mesocosm experiment. The slopes of the DOC/CDOM linear relationships varied according to the different vegetation species. Distinct DOC/CDOM patterns were found between the deciduous and evergreen litters. The relationship of DOC/CDOM was illustrated in the deciduous litters and agricultural plants. (b) DOC concentrations in different vegetation species from day 1 to day 11. Each point represents the DOC values in 1 day. Solid symbols indicate the scenarios with 5°C higher than the scenarios in hollow symbols.

3. Results and Discussion

3.1. DOC/CDOM Ratios Versus Vegetation Types From Mesoscosm Experiments

Figure 5a shows how DOC concentration and CDOM absorption change given the same biomass (260-g dry biomass), the same number of incubation days, and constant temperatures (20 or 25°C) for each mesocosm experiment of different vegetation types (no soil involvement). Results reveal that when vegetation types change, covariations of DOC and CDOM have one common characteristic and two significant differences (Figure 5a). The common characteristic is that the covariation of DOC and CDOM is always linear in the case of conservative vegetation sources when the number of incubation days increase (Figure 5b). However, across the vegetation source types, DOC concentration and CDOM level had different regression slopes and variation ranges. Table 1 shows the DOC concentrations and CDOM absorptions measured in the final day of mesocosm experiment from each tank. It was the mean DOC and CDOM among replicas on day 11 from soil experiments. The scenario of deciduous forest leaf litter had the broadest ranges for both DOC concentrations and CDOM levels across incubation days. In the case of low temperature, 20°C, DOC was arranged from 7 to 22.4 mg/L (mean = 16.9 and SD = 6) and CDOM absorption was arranged from 2.5 to 9.6 m^{-1} (mean = 6.7 and SD = 2.4; Figure 5). Comparatively, agricultural residue has the lowest DOC and CDOM range (DOC: 5.5 to 11.54 mg/L, mean = 8.9, and SD = 2.4, and CDOM: 0.7 to 2.5 m^{-1}, mean = 1.56, and SD = 0.51). At the end of the incubation, the DOC concentration from agricultural residue is only 50% of that from deciduous forest leaf litters. The range of DOC concentration for evergreen forest leaf litter was close to that of the deciduous forest leaf litter (10 to 26.3 mg/L). However, CDOM absorption in this scenario is closer to the agricultural scenario. The range of CDOM from the evergreen forest was between 0.8 and 2.2 m^{-1}. This range is much smaller than that from the deciduous forest where the CDOM were ranged from 2.2 to 9.6 m^{-1}.

Despite the different ranges, covariations of DOC and CDOM are linear for all scenarios of individual vegetation source. The actual value range differences did not affect the DOC estimations from CDOM, once the empirical linear equation was determined. There have been many field observations showing that DOC/CDOM ratios are quite reliable when the drainage basin is largely dominated by a landcover type, for example, the Yukon River watershed (evergreen dominated), the Mississippi watershed (agriculture dominated), and Lena River watershed (tundra dominated; Del Castillo & Miller, 2008; Gonçalves-Araujo et al., 2015; Spencer et al., 2009). Note that the ranges of DOC and CDOM are more than doubled from deciduous forest leaf litters to that from agricultural residuals, but the regression slopes between two vegetation scenarios are close (Figure 5a). This result indicates that if a linear model works well for remote sensing estimation of DOC from CDOM as the surrogate for deciduous forest landscape, it should be satisfactory to agricultural landscapes.

Since a consistent linear relationship exists between DOC concentrations and CDOM levels for all scenarios of mesocosm experiment, we can model the different linear relationships in Figure 5a with the following general form of the linear equation:

$$\mathrm{DOC} = a * \mathrm{CDOM} + b \quad (6)$$

where slope a and y intercept b can be significantly different values determined by the dominant vegetation types. The slope of the deciduous forest (a = 1.9) is almost 3 times lower than that for the evergreen forest (a = 5.49). The significant difference in slopes between deciduous forest and evergreen forest was consistent to the paired t test result ($P < 0.05$). This significant difference demonstrated that the covariations between DOC and CDOM will be weak and the variance will enlarge if the measurements from subbasins dominated by deciduous landcover are mixed with the measurements from subbasins dominated with evergreen forest (Figure 5a). This phenomenon suggests that high uncertainties in estimating DOC from CDOM from remote sensing data could be caused by applying a single model to samples collected from multiple river basins with different landcover types, for example, deciduous or evergreen forest (Hestir et al., 2015).

Aforementioned that the regression slopes between corn plant residue and deciduous leaf litter scenarios are very similar ($P > 0.05$ from paired t test) but have very different y intercept b (corn: 4.49 and deciduous: 0.38). Despite the significant difference in y intercepts, DOC concentration is still correlated to CDOM for those measurements from deciduous forest mixed with those from corn plant residue. This phenomenon indicates that the slope, a is a more influential factor than the y intercept, b when estimating DOC from CDOM. We further applied the regression analysis based on deciduous and agriculture data together by using the following equation:

$$\mathrm{DOC} = a * \mathrm{CDOM} + b * \mathrm{Type} \quad (7)$$

Without losing generality, we set the values of Type to 1 for the deciduous and 0 for the corn plant residue. It resulted in $P < 0.01$ for the CDOM variable and $P > 0.05$ for the Type variable. The model performed poorly when slope a was significantly different. For example, DOC concentration will not usually correlate well to CDOM measurement if data were collected from multiple rivers drained from different terrestrial ecosystems that cause the regression slope significantly different, for example, between deciduous and evergreen forest scenarios.

The ecosystems between agricultural landscapes and deciduous forest are different, but their slopes a are similar. In this case, the covariations between DOC and CDOM can be calibrated by fitting the different y intercept b to achieve a satisfactory performance. This analysis is consistent with the results from Finnish estuary watersheds, which have subbasins dominated by the mixture of agriculture and deciduous forest (Asmala et al., 2012). Similarity, the CDOM also proved to be the good indicator for the DOC in the Lake Taihu whose major landcover type was agriculture and deciduous (Yao et al., 2011).

The coincrease of DOC and CDOM was observed through the incubation period. Figures 5a and 5b show that production of DOC and CDOM increases steadily with incubation time for all three vegetation types (Hladyz et al., 2011; Rochelle-Newall, 1999). Increases in DOC concentration and CDOM absorption follow trend lines without diverging over the entire course of the incubation. It is very important to understand that the time length of decomposition since leaf litters and agricultural residue become part of the ground does not change the strong correlation of DOC to CDOM. This improved understanding explains the phenomena that DOC is always related to CDOM in lakes, rivers, and coastal waters no matter when the samples were collected, as long as they are associated to the same watershed (Brezonik et al., 2015). Therefore, this result supports that remote sensing technology is effective and reliable in estimating DOC concentrations from associated water colors (CDOM absorption) (Kutser et al., 2016; Olmanson et al., 2013; Palmer et al., 2015).

3.2. The Temperature Impacts on DOC/CDOM Ratios

Solid symbols in Figure 5a show that the trends of DOC/CDOM covariations when the temperature was 5°C higher than the dashed symbols. The increasing temperature resulted in a decreasing trend in slope (a)

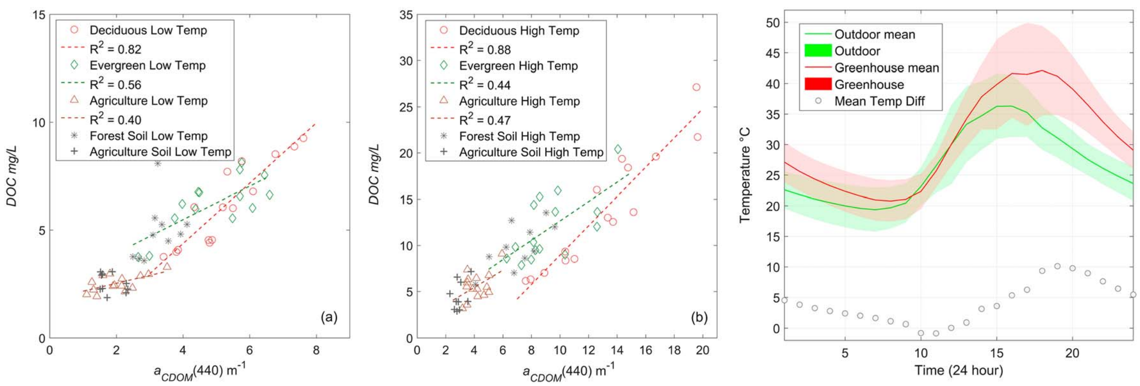

Figure 6. Dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) covariations in the soil leaching experiments under low temperature (a) and high temperature (b). The relationship of DOC/CDOM exhibited the similar ranks as the mecosoms experiments. DOC/CDOM were more correlated in the leaf litters + soils than the soils only. The range for *x* axis and *y* axis are different in (a) and (b). (c) The hourly temperature records in the outdoor and greenhouse for 14 days.

consistently for all vegetation types. The slopes were found significant differences between high and low temperatures ($P < 0.05$). The decreasing slope of the covariations means that higher temperature led to a faster CDOM production than DOC. In this experiment, raising 5°C temperature reduced the slopes by 40% for the deciduous forest, while the slope decrease is less dramatical but still substantial for evergreen (12%) and agriculture (23%; Figure 5a).

At each of the incubation days, the DOC concentrations in the high-temperature scenario are 35% higher for deciduous and 9% for agriculture than low-temperature scenario (Figure 5b). The increase rates of daily DOC concentration are 0.09 mg · L · °C for the deciduous and 0.01 mg/L for the agricultural crop. Comparatively, increase rates of CDOM were noticeably higher for deciduous (79%) and agricultural (44%) than that for DOC. Average daily CDOM levels are 0.13 m^{-1} higher for the deciduous and 0.028 m^{-1} for agriculture per temperature degree incensement. Temperature has more positive impacts on CDOM production rate than that for DOC for deciduous forest and agricultural residue scenarios.

Previous evidence showed that the level of temperature impacts on DOC/CDOM covariations varies according to the decomposition rate of the different vegetation types (Bothwell et al., 2014; Martínez et al., 2014). We found that CDOM from the evergreen forest is not sensitive to warming, while DOC production slightly decreased at high-temperature scenario. This observed stable status in DOC/CDOM releasing from evergreen forest leaf litter is likely due to the high lignin content in plants. In contrast, temperature catalyzes the decomposition rate of low lignin leaf litters (deciduous) through higher microbial activity (Davidson & Janssens, 2006; Gulis & Suberkropp, 2003; Martínez et al., 2014).

3.3. Soil Influence on DOC/CDOM Ratios Experiments

The covariations of DOC/CDOM resulting from the soil leaching experiment were compared to the results from mesocosm experiments. The results reveal the role of soil in controlling the covariations of DOC/CDOM. Despite soil decomposition and metabolic process, it maintained the linear trends of the covariations of DOC/CDOM for all scenarios (Figure 6a). The ranges of DOC and CDOM keep the same ranking: deciduous, evergreen, and agriculture as that for mesocosm experiment. Specifically, the DOC and CDOM ranges for the deciduous forest were 2 times greater than that from the corn plant residue.

The linear covariations of DOC/CDOM resulted from soil leaching had lower slopes than that from mesocosm experiments. The evidence shows that soil decomposition or metabolic processes do change the covariation of DOC/CDOM. By comparing Figure 5a and Figure 6a, the slopes from the evergreen forest and agricultural scenarios were much lower than that without soil involvements. Similar to the range, soil leaching experiment also resulted in the slopes ranking the same as deciduous broadleaf (the highest), evergreen needle leaf, and corn plant residue (the lowest). However, the slopes of evergreen forest reduced most compared to other two scenarios. This phenomenon suggests that soil metabolic processes for DOC decomposition are a slower progression than that for CDOM for plants with high lignin properties. This is consistent with results identified in previous studies that the concentrations of the lignin remarkably affect the

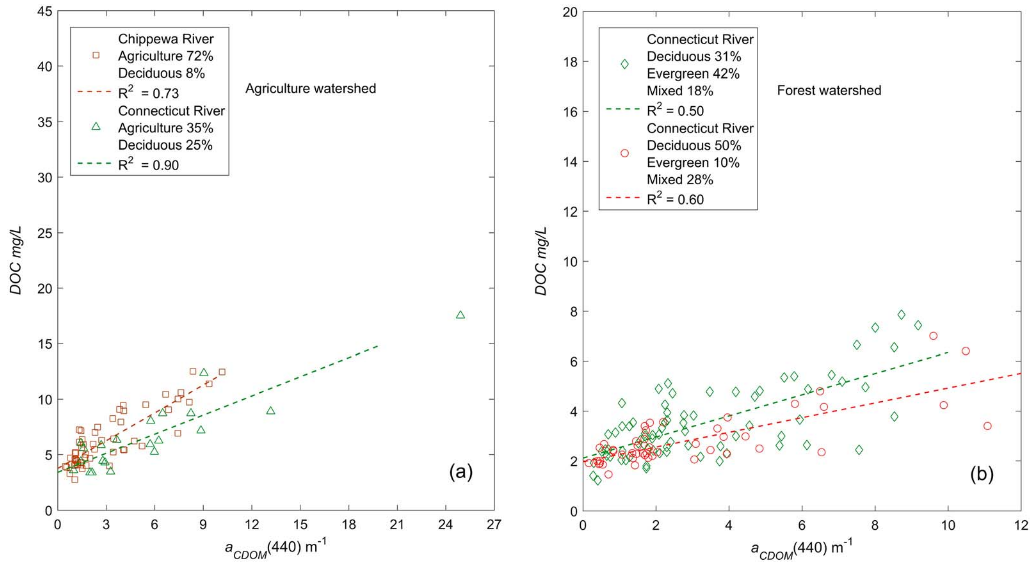

Figure 7. Covariations of dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) in the agricultural watershed (a) and in the forested watershed (b). The covariations of DOC/CDOM had different trends in the different landcover types. The same CDOM absorption represented different levels of DOC concentrations in the different watershed (slope rank as high percentage of farmland and low percentage of farmland in (a) evergreen and deciduous in (b)). The agricultural-dominated watershed had the more relevant trends than the mixed forest watershed.

decomposition rate of the leaf litters (Austin & Ballaré, 2010; Gartner & Cardon, 2004). The higher lignin concentration often leads to a lower decomposition rate (Austin & Ballaré, 2010; Fioretto et al., 2005). This scenario agrees with the comparing of lignin phenol across the pan-Arctic rivers, which show that the Mackenzie River had the lowest lignin phenol and the relative low DOC/CDOM slope (Mann et al., 2017). The soil used in this DOC leaching experiments are collected from original leaf litters/soil sampling locations. Investigating soil diversity would add another level of complexity on DOC/CDOM covariations, which is beyond the scope of this study.

Experiments of bare soil without leaf litters (hollow symbols in Figure 6a) were included to benchmark the processes of leaf litter interacting with soil (asterisk and plus symbols in Figure 6a). Results showed a random relationship between DOC and CDOM for scenarios of bare soils collected on sites of forest and agricultural landscapes. This random relationship implies that the vegetation is the active source for DOC and CDOM production and the soil is an important factor of the biological processes instead of the major DOC source.

Figures 6a and 6b showed that the ranges of the DOC/CDOM covariations are very different in the experiments conducted outdoor and inside the greenhouse with 4.5°C mean temperature difference over a day (Figure 6c). The deciduous forest from greenhouse experiments (high temperature) had the highest range of DOC concentration and CDOM level (DOC: 4.8 to 27 mg/L, and CDOM: 7.5 to 19.5 m^{-1}, Figure 6b). Under a 4.5°C temperature increase, weekly maximum DOC concentration is 5 times higher, and CDOM is 3 times higher than low-temperature scenario. Similarly, temperature impacts on the ranges of DOC and CDOM production are also significant for evergreen forest and corn plant residue scenarios, which are consistent with mesocosm experiments. However, the temperature did not have significant impacts on the slopes of DOC/CDOM ratios in the experiments with soil involvement. This suggests that temperature variation has less influence on DOC/CDOM covariations of terrestrial ecosystems than that of aquatic environments. Figure 5a showed, consistent with the study of Del Vecchio and Blough (2004), that DOC:CDOM ratios in aquatic ecosystems exhibit a temperature dependence.

3.4. Linking Experimental Results to Watersheds

Linkages between the experimental results and our field measurements with varying vegetation types, soil property, and temperatures are consistent. First, the covariation of DOC/CDOM from agricultural dominant watersheds followed a linear trend with variations influenced by the percentages of agricultural plant coverage (Figure 7a). The regression slopes for agricultural landscapes are much higher than other

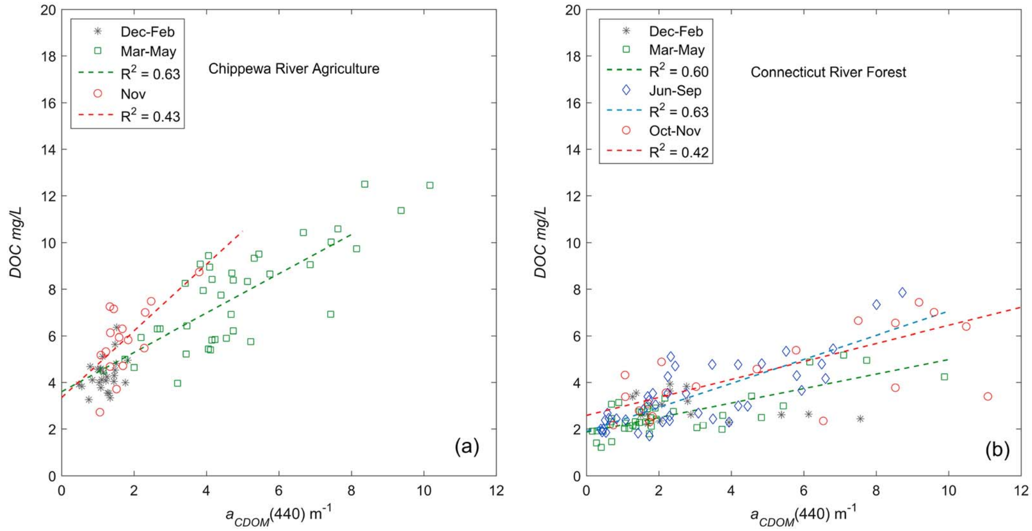

Figure 8. Seasonal covariations of the dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) in the Chippewa River agricultural watershed (a) and the Connecticut River forest watershed (b). The same CDOM absorption represents different levels of DOC in different seasons. The relationship of the DOC/CDOM was not correlated in the winter (R^2 = 0.02) due to the lack of the active carbon sources.

landcover types (e.g., forest in Figure 7b). The different coverage percentages of agricultural plants caused the discrepancy displayed in Figure 7a between Chippewa River watershed and Connecticut River watershed. The higher percentage of agriculture land use in Chippewa River watershed (agriculture 72% and deciduous 8%) led to the higher slopes of the linear DOC/CDOM relationship than that for the Connecticut River watershed (agriculture 45% and deciduous 25%). The covariations of DOC/CDOM from field samples matched with results of the experiments (Figure 7a) for the agricultural scenario.

The second agreement is that the evergreen forest-dominated watershed had a higher slope of DOC/CDOM ratios (green symbols) than that dominated by deciduous watershed (red symbols, Figure 7b). The slopes of DOC/CDOM ratios are ranked in order of high agriculture percentage, low agriculture percentage, evergreen forest, and deciduous forest. This order is the same as that from the aquatic mesocosm experiment. The slopes of DOC/CDOM from field samples were between the mesocosm experiments and soil carbon leaching experiments. It indicates that the DOC/CDOM slopes were decreased by soil processes.

Figure 7a shows a broader DOC/CDOM range than that from soil leaching experiment. This is due to the significantly different biomass and nutrient available on the land surface (Bernot et al., 2006; Wilson & Xenopoulos, 2008). While the ranges of the sampled DOC concentrations were lower than that of the experiments, the CDOM ranges between the field and experimental measurements were close.

Figure 8a shows seasonal variations on the DOC/CDOM ratio at the subbasin scale. In the Chippewa River watershed, the slope of the DOC/CDOM covariation in the spring (March–May) was lower than in the late fall (November) for agricultural landscape. The DOC/CDOM in spring is mainly contributed from the microbial degradation of humic substances over the winter months (Findlay & Sinsabaugh, 2003; Zhu et al., 2013). It appears more colored than DOC from fresh litters in the fall. This difference in color is reflected by CDOM absorption. The same amount of DOC is related to higher CDOM in spring than that in fall, consequently lower DOC/CDOM ratio. Furthermore, crop residues left in soil over the snow season would generate more humus materials that lift CDOM levels more in spring than that in fall. Meanwhile, in Chippewa River agriculture watershed, both high nutrient and snowmelt in spring might lead to the high CDOM levels, which maybe be a source of uncertainty (Wilson & Xenopoulos, 2008). Lastly, the DOC/CDOM ranges from both the spring and the late fall were at least 2 times higher than the samples from the winter (December–February). The less soil organic matter and low temperature would cause the low production rate of the DOC/CDOM in the watershed.

The high microbial activities in response to elevated temperature in summer (June–September) accelerated the release of the DOC/CDOM from the evergreen leaf drops in fall (October–November). Therefore, the slope

Table 2
Parameters in the DOC Model Based On the Experimental Results

Landcover (i)	$\alpha(L, S)$	Lt_i	S_i	$a_{leach \cdot i}$	$a_{soil \cdot i}$	b_i
Evergreen	0.41	5.14	0.08	1.04	0.96	2.40
Deciduous	0.64	1.49	0.43	1.39	0.96	3.83
Agriculture	0.93	2.16	0.43	0.93	0.5	4.82

Note. $\alpha(L, S)$ is slope as a function of landcover types (L) and soil (S) in dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) model. Lt_i is linear covariation of DOC/CDOM for landcover type (i) in mesocosm experiment. S_i is soil effect on DOC/CDOM relationship. $a_{leach \cdot i}$ is slope value in soil leaching experiment. $a_{soil \cdot i}$ is the mean slope of the forest soil and agriculture soil. b_i is biomass of the watershed.

of DOC/CDOM covariation in summer (June–September) and fall (October–November) was higher than in spring (March–May) due to the contributions of the evergreen-dominated DOC/CDOM.

The distinct linear trends of DOC/CDOM ratios between the evergreen and deciduous also matched the results from the experiments. However, the CDOM was less correlated to the DOC in the mixed forest scenarios (Connecticut River watershed) than that in the agricultural watershed, Chippewa River (Figure 8). The slopes and y intercepts of DOC/CDOM for the evergreen vegetation litter scenario were found significantly higher than that of the deciduous vegetation litters in the experiments. This implies that the DOC/CDOM ratios from the mixed forest are between evergreen and deciduous forest scenarios. The comparison between results from controlled experiments and field measurements improves the understanding of how DOC/CDOM covary as a function of environmental variables.

3.5. DOC/CDOM Model Parameters and Performance

The parameters of the DOC model (equations (2)–(5)) were derived from mesocosm and soil leaching experimental results (Table 2). The modeled slope $\alpha(L, S)$ for each landcover type are calibrated according to the controlled experiments: evergreen = 0.41, deciduous = 0.64, and agriculture = 0.93. The b_i was referenced to the watershed field measurements. The generalized reduced gradient nonlinear algorithm in Excel is used to calculate the b_i for minimizing the differences between modeled DOC and measured DOC (Lasdon & Waren, 1977). The intercept value b_i derived from the mesocosm experiments (evergreen = 7.72, deciduous = 4.83, and agriculture = 4.82 under same vegetation quantity) was used as the initial values required by the generalized reduced gradient nonlinear algorithm to calculate the model parameters. Then the b_i value in the model was calculated to represent different vegetation biomass of the watersheds (evergreen = 2.4, deciduous = 3.83, and agriculture = 4.82). The slope for wetland was set to 2.61 resulted from an additional mesocosm experiment for an aquatic plant, Cladophora.

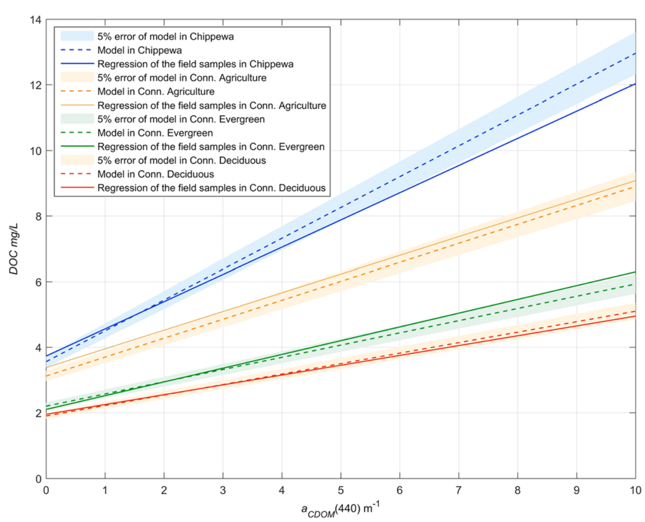

Figure 9. Dissolved organic carbon/colored dissolved organic matter (DOC/CDOM) regressions of modeled values versus field samplings' values. The shaded regions represent 5% errors. The DOC model could estimate DOC/CDOM regression with high accuracy. The DOC/CDOM regressions of the field samplings are the same as in Figure 7.

With the above parameterization, the model performance was evaluated by comparing to the field measurements sampled over past 6 years in our two study sites (the Chippewa River and Connecticut River watersheds). Figure 9 illustrates the covariations of DOC/CDOM by comparing the modeled versus and the field measurements. The modeled covariations are within 5% of errors for all ground truth scenarios (evergreen, deciduous, and agricultural landcovers). The best performance was for subbasins dominated by agriculture and evergreen landscapes because of their relative uniformity. The model performance for the deciduous forest in the subbasins in the Connecticut River watershed was affected by the high percentage of the mixed forest. The model performance demonstrates the potential to apply this formulation widely to locations outside the study areas if the impacts of different soil characteristics are calibrated. The model directly improves the assessment of terrestrial DOC dynamics from remote sensing imagery by referencing to terrestrial ecological characteristics.

4. Conclusions

This study examined several environmental variables hypothesized to drive the covariation of freshwater DOC and CDOM. The results improve our understanding of how the DOC/CDOM ratios vary in response to vegetation types, temperature, and soil metabolic processes. Methodological innovation is the combination of field measurements with controlled experiments (mesocosms and soil leaching with artificial rainfall simulator). The study resulted in following conclusions: (1) DOC/CDOM ratios in freshwater are linear functions in which slopes are depending on vegetation types, (2) landcover adaptive model of DOC from CDOM resulted in a satisfactory performance to the scenarios of both homogenous and heterogeneous vegetation (mixed forests) at subbasin scale, (3) soil has a function of modulating the temperature influences. Therefore, DOC/CDOM ratios became less sensitive to temperature in soil leaching experiments than the cases from mesocosms in relation to other two variables: vegetation types and soil physical properties. Finally, controlled experiments with mesocosm and artificial rainfall simulator are effective in studying the biological or chemistry cycling processes in complex environments.

Source vegetation type is the key factor determining the large dissimilarity in slopes of linear functions for estimating DOC from CDOM. The model would produce high uncertainty in relating freshwater CDOM to DOC when the sources are between evergreen and deciduous forest. The model uncertainty is potentially reducible if source vegetation type slopes are known. The *y* intercept can be calibrated with site-specific information such as the density and biomass of source vegetations.

Results from soil leaching experiments show that raising 5°C of daily mean temperature does not significantly change the slopes of terrestrial DOC/CDOM ratios (slopes of linear functions) for all scenarios. Although results from mesocosm experiments without soil suggested that temperature is negatively related to the slopes change, the effectiveness of temperatures on slopes is alleviated by soil adaptability as revealed from the soil leaching experiment.

The controlled experimental results improved our understanding of the relationship between the major driving factors and the covariations of DOC and CDOM. These results led to the establishment of a model that is able to estimate the covariations of DOC/CDOM in broad ranges of freshwater ecosystems and a way for estimating the DOC based on the CDOM and land cover percentage. This improved understanding of DOC in relation to CDOM is fundamental to remote sensing of carbon flux in inland waters.

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