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Global distribution of dissolved organic matter along the aquatic continuum: across rivers, lakes and oceans

Philippe Massicotte ^{*1}, Eero Asmala¹, Colin Stedmon², and Stiig Markager¹

¹Aarhus University, Department of Bioscience, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

²Technical University of Denmark, National Institute for Aquatic Resources, Section for Marine Ecology and Oceanography, Kavalergården 6, 2920 Charlottenlund, Denmark

***Present address**

Takuvik Joint International Laboratory (UMI 3376)
Université Laval (Canada) & Centre National de la Recherche Scientifique (France)
Québec-Océan / Pavillon Alexandre-Vachon
1045, Ave de la Médecine, local 2064
Université Laval
Québec (Québec)
G1V 0A6 Canada
Tel.: 418 656-5193
Fax.: 418 656-2339
philippe.massicotte@takuvik.ulaval.ca

*Corresponding author

Abstract

Based on an extensive literature survey containing more than 12 000 paired measurements of dissolved organic carbon (DOC) concentrations and absorption of chromophoric dissolved organic matter (CDOM) distributed over four continents and seven oceans, we described the global distribution and transformation of dissolved organic matter (DOM) along the aquatic continuum across rivers and lakes to oceans. A strong log-linear relationship ($R^2 = 0.92$) between DOC concentration and CDOM absorption at 350 nm was observed at global scale, but was found to be ecosystem-dependent at local and regional scales. Our results reveal that as DOM is transported towards the oceans, the robustness of the observed relation decreases rapidly (R^2 from 0.94 to 0.44) indicating a gradual decoupling between DOC and CDOM. This likely reflects the decreased connectivity between the landscape and DOM along the aquatic continuum. To support this hypothesis, we used the DOC-specific UV absorbance (SUVA) to characterize the reactivity of the DOM pool which decreased from 4.9 to 1.7 $\text{m}^2 \times \text{g C}^{-1}$ along the aquatic continuum. Across the continuum, a piecewise linear regression showed that the observed decrease of SUVA occurred more rapidly in freshwater ecosystems compared to marine water ecosystems, suggesting that the different degradation processes act preferentially on CDOM rather than carbon content. The observed change in the DOM characteristics along the aquatic continuum also suggests that the terrestrial DOM pool is gradually becoming less reactive, which has profound consequences on cycling of organic carbon in aquatic ecosystems.

Keywords: Absorption, Chromophoric dissolved organic matter (CDOM), Dissolved organic carbon (DOC), Specific UV absorbance (SUVA), carbon cycling, biogeochemistry

Running head: DOM along the aquatic continuum

Introduction

Physico-chemical characteristics of dissolved organic matter (DOM) drive the functioning of aquatic ecosystems at different levels. The chromophoric fraction of the DOM pool (CDOM) is a major driver of underwater light penetration (Kirk, 1994) which modulates primary production (Markager et al., 2004; Thrane et al., 2014; Seekell et al., 2015), photochemistry and protects aquatic organisms against harmful ultraviolet (UV) radiation (Hader et al., 2011). Additionally, the carbon in the DOM pool, dissolved organic carbon (DOC), is the main source of metabolic substrates for heterotrophic bacteria and influences the composition of aquatic microbial communities (Findlay et al., 2003).

In recent decades, climate change, eutrophication and intensification of human perturbations on terrestrial systems have contributed to increased inputs of colored terrestrial DOM in aquatic ecosystems (Roulet et al., 2006; Massicotte et al., 2013b; Weyhenmeyer et al., 2014; Haaland et al., 2010). This has important consequences since the transformation of even a small fraction of the DOM pool can potentially have large impacts on ecosystem functioning (Prairie, 2008). Increases in CO₂ emissions (Lapierre et al., 2013) and reduction in primary production due to light shading (Seekell et al., 2015; Thrane et al., 2014) have already been documented as consequences of increases in terrestrial DOM at local and regional scales. However, generalizing these effects to global scales is a difficult task because our current understanding on the origin, fate and dynamics of DOM along the aquatic continuum from headwater streams to oceans is limited. Since most studies on the fate of DOM are either ecosystem or site specific, there is a need for integrative studies that will unify existing knowledge to better understand the fate and the dynamics of DOM from a broader perspective during its transport from headwaters to oceans.

DOC concentration and CDOM absorbance are routinely measured in many ecological and biogeochemical studies. This creates an opportunity to explore

the factors regulating the dynamics of DOM at global scales. In this study we have performed an extensive literature survey to extract datasets containing coupled DOC concentration and CDOM absorption measurements ($n = 12\,808$) to gain insights about the spatial distribution and the compositional characteristics of the DOM pool during its transport along the aquatic continuum. We hypothesize that a strong relationship between DOC concentration and absorption properties of CDOM would be a common characteristic in freshwater ecosystems receiving large amount of colored DOM from their surrounding terrestrial catchments. We further expected that the robustness of the observed relationship would weaken as DOM is transported from freshwater to ocean ecosystems as the dominant DOM sources will change and photochemical processes will preferentially remove CDOM over the bulk DOC (Vähätalo et al., 2004). Another key objective of this work was to gather and harmonize available published information to help the community to formulate and test new hypotheses about DOM biogeochemical cycling at global scales along the aquatic continuum.

Material and methods

Literature survey and spatial coverage

Web of Science, Google Scholar as well as public data repositories were searched using terms “dom”, “cdom”, “doc”, “dissolved organic carbon”, “dissolved organic matter”, “absorption” and “absorbance” for datasets presenting original (i.e. not summarized) values of DOC and optical properties of CDOM. The minimum variables required to be included in the dataset were DOC concentration, absorbance or absorption of CDOM (or an integrative value which could be used to infer the required values, such as SUVA), geographical coordinates and time of the sampling. When not explicitly provided, geographical coordinates were estimated using available sampling map in each study. For CDOM data, wavelengths

and information about the cuvette size or explicitly pathlength-normalized data were also required. Using these criteria, we compiled 65 datasets containing 12 808 unique observations of simultaneous DOC concentration and absorption properties of CDOM measured between 1991 and 2015 (Fig. 1, Table 1). A total of 4 712 observations with complete CDOM spectra (i.e. continuous measurements along a range of wavelengths) and 8096 observations with CDOM absorption measurement at discrete wavelengths were extracted.

Observations were distributed on four different continents and in seven oceans (Fig. 1, Supplementary Fig. 1A). A large proportion of the data was located in river and ocean ecosystems and to a lesser extent in estuaries, wetlands and lakes regions (Supplementary Fig. 1B). Oceanic observations were spread over all major basins. In North America, dense clusters of observations were mostly located in large rivers and estuaries of the East Coast of United States. and along the Gulf of Mexico from the Rio Grande, Texas to Anclote Island, Florida (Fig. 1). To the north, observations were mainly located in Alaska along the Mackenzie and the Tanana rivers. Additional observations were found for the St. Lawrence River, the Great Lakes and the Hudson Bay. In Europe, a large portion of the samples came from the Baltic Sea and the North Sea as well as from lakes in Sweden. Few observations were also located around Greenland. In Russia, the data originated from the river observatory stations on the Ob, Yenesy, Lena and Kolyma rivers as well as around the Laptev and Siberian shelf. In Asia, observations were located in South Korea rivers, in lake Taihu in China and on west coast of Taiwan. In Africa, most of the observations were located in Congo, Niger, Zambezi and the Ogooué rivers. In Australia, data stemmed from the St. Vincent gulf and the border of Timor Sea

Ecosystem classification

Each observation was assigned to a defined ecosystem using either the sampling location or the salinity when available (Supplementary Fig. 1B). Observations

with salinity values were classified as follows: river (salinity ≤ 0.5), estuary ($0.5 < \text{salinity} \leq 5$), coastal ($5 < \text{salinity} \leq 30$), ocean (salinity > 30). Based on available information, observations were classified as follows (Supplementary Fig. 1A): river ($n = 4\,896$), ocean ($n = 3\,439$), coastal ($n = 1\,405$), estuary ($n = 1\,367$), wetlands ($n = 954$), lake ($n = 747$). Note that 81% of the oceanic samples were located at depth shallower than 1 800 m.

Data processing and metrics calculation

Absorbance by CDOM were converted to absorption coefficients and expressed per meter using equation 1 (Kirk, 1994):

$$a_{\text{CDOM}}(\lambda) = \frac{2.303 \times A(\lambda)}{L} \quad (1)$$

where $a_{\text{CDOM}}(\lambda)$ is the absorption coefficient (m^{-1}) at wavelength λ , $A(\lambda)$ the absorbance at wavelength λ and L the pathlength of the optical cell in meters. Given that UV-visible absorption spectra of CDOM decrease approximately exponentially with increasing wavelength, a simple exponential model (equation 2) has been used to extract quantitative information about optical properties of CDOM (Jerlov, 1968; Bricaud et al., 1981; Stedmon et al., 2001):

$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S(\lambda-\lambda_0)} + K \quad (2)$$

where a_{CDOM} is the absorption coefficient (m^{-1}), λ is the wavelength (nm), λ_0 is a reference wavelength (nm) and K is a background constant (m^{-1}) accounting for scatter in the cuvette and drift of the instrument. S is the spectral slope (nm^{-1}) that describes the approximate exponential rate of decrease in absorption with increasing wavelengths. Specific UV absorbance (SUVA_{254} , $\text{m}^2 \times \text{g C}^{-1}$) was calculated by dividing absorbance at 254 nm by DOC concentration (Weishaar

et al., 2003). The $SUVA_{254}$ metric is commonly used as a proxy for assessing both chemical (Weishaar et al., 2003; Westerhoff et al., 2004) and biological reactivity (Berggren et al., 2009; Asmala et al., 2013) of the DOM pool in natural aquatic ecosystems. Note that whereas we used $SUVA_{254}$ to characterize the transformations of the DOM pool, $SUVA_{350}$ was used to maximise the number of observations to reveal the relationships between DOC and CDOM at the global scale across all aquatic ecosystems. In figures, along with the $SUVA_{254}$ parameter, we also present the value of specific absorption coefficient of DOC (a^* , $m^2 \times mol\ C^{-1}$) which is calculated by dividing the absorption coefficient measured at 254 nm by the DOC concentration expressed in mol of C per cubic meter. The motivation to use these two overlapping indices is the fact that the latter parameter is commonly used to parametrize bio-optical models which can be of interest for the community. For simplicity, only SUVA values are discussed in the text. However, note that the conversion between SUVA and a^* at a given wavelength can be done using a conversion factor of 27.64 ($a^* = 27.64 \times SUVA$). Spectral slope curves based on CDOM absorption spectra were calculated as described in Loiselle et al., (2009). Briefly, spectral slopes were calculated over a sliding window of 21 nm along the complete spectral range using equation 2. Each calculated slope value was associated to the middle wavelength of the current sliding window.

Given the wide range of wavelengths used in each study, absorption spectra were filtered to keep measurements between 250 and 600 nm at 1 nm increment. For the Nelson et al., 2010 dataset (Table 1), absorption spectra were only available between 275 and 600 nm and therefore not included in the spectral analysis. Five criteria were used to control the quality of absorption spectra: (1) $SUVA_{254}$ had to be smaller or equal to $6\ m^2 \times g\ C^{-1}$ (Weishaar et al. 2003), (2) the spectral slope (S , equation 2) had to be smaller than $0.08\ nm^{-1}$ (Stedmon et al., 2015), (3) the determination coefficient of the fit of the spectral slope (R^2 , equation 2) needed to be at least 0.95, (4) the value of $a_{CDOM}(440)$ needed to be positive and (5) the

value of $a_{\text{CDOM}(350)}$ needed to be $> 0.01 \text{ m}^{-1}$. The rationale behind these criteria was to exclude observations that had potentially issues with detection limits (very low and/or very noisy values), calculation or analytical errors (very high or very low values). Based on these criteria, 128 observations over a total of 12936 (0.98%) were discarded from further analyses.

Estimation of $a_{\text{CDOM}(350)}$

We found that a wide range of different wavelengths (between 250 and 490 nm) were used as reference wavelength to report absorption coefficients of CDOM (Supplementary Table 1). To make absorption coefficients comparable among studies, an interpolation procedure was used to estimate $a_{\text{CDOM}(350)}$ independently of the wavelength reported in each study (Supplementary section 2). This choice was motivated by the fact that absorption at 350 nm was among the most frequently reported wavelength in the available data. An additional motivation was its central position in the wide range of wavelengths reported. To achieve the interpolation, we used an empirical approach where complete absorption spectra ($n = 2\,379$) were used to predict the value of $a_{\text{CDOM}(350)}$ from observations measured at other wavelengths (Supplementary Fig. 2i). This was done by regressing all the absorption values at a specific wavelength against that measured at 350 nm (ex.: $a_{\text{CDOM}(254)}$ vs. $a_{\text{CDOM}(350)}$). Then, the slope (Supplementary Fig. 2iB) and the intercept (Supplementary Fig. 2iC) of the linear regression were used to predict $a_{\text{CDOM}(350)}$ from $a_{\text{CDOM}(\lambda)}$. Based on reported wavelengths, a total of 24 linear models were made (Supplementary Table 1). A minimum value of 0.98 for the determination coefficient (R^2) was used as a threshold for including observations from a given wavelength. In our data, observations above 417 nm were not converted to $a_{\text{CDOM}(350)}$ due to the suboptimal fit of the model. Regression coefficients used to estimate $a_{\text{CDOM}(350)}$ in this study are presented in Supplementary Table 1, but the complete list of

coefficients are also provided as a supplementary comma-separated values (CSV) file that enable the calculation of a given wavelength from another in the range of 250–500 nm. Detailed results of the procedure can be found in Supplementary section 2.

Estimation of the distance from shoreline as a proxy for the extent of DOM processing

We used the distance from the nearest coastline and $SUVA_{254}$ to estimate the extent of biogeochemical processing and the reactivity of DOM for freshwater and marine samples along the aquatic continuum. Here, distance can be seen as a crude proxy for stream order or stream size, which both typically increase from inland towards the river mouth at the coastline. More detailed standardised metadata was not consistently available from the published studies. The distance to the closest coastline was calculated using ocean shapefiles (resolution = 1:110000000) available on the Natural Earth website (<http://www.naturearthdata.com/>) and the `rworldmap` R package (South, 2011). For inland samples (rivers) the measured distances have been assigned as a positive value whereas for marine samples, the measured distances were assigned as a negative value. Lakes were not included in this analysis, since their connectivity to larger-scale aquatic continuum is less obvious than that of rivers. Because precise geographical coordinates were not always available and thus often estimated from available maps, calculated distances have been pooled to 150 km bins which was found to distribute the observations roughly equally in each bin.

Statistical analysis

Segmentation analysis were performed using the `segmented` R package (Muggeo, 2003; Muggeo, 2008) to determine breakpoints in relationships that were present-

ing bi-linear patterns. CDOM metrics were calculated using the cdom R package (Massicotte et al., 2016). Spatial analyses were done with the rgeos R package (Bivand et al., 2016). The expected conservative behaviour of $SUVA_{254}$ as a function of salinity has been modeled using a simple conservative approach. To do so, we calculated mean values of DOC and $a_{CDOM}(254)$ in both freshwater (salinity = 0) and marine ecosystem end members (salinity ≥ 35). For the freshwater endmember, mean DOC was $14.25 \text{ mg C} \times \text{L}^{-1}$ and mean $a_{CDOM}(254)$ was 60.82 m^{-1} . For the marine end member, mean DOC was $0.85 \text{ mg C} \times \text{L}^{-1}$ and mean $a_{CDOM}(254)$ was 0.80 m^{-1} . Between freshwater and marine ecosystems, DOC and $a_{CDOM}(254)$ values were calculated from linear regressions to analyze deviations from the conservative mixing (Officer, 1976). All statistical analysis were performed in R 3.4.1 (R Core Team, 2017).

Results

Estimation of DOC from CDOM absorption coefficients

Estimation of DOC concentration from CDOM absorption measurements is a commonly used technique in many ecological, biogeochemical and remote sensing studies. However, the relationship between these two key parameters is rarely evaluated at global scale. The robustness of the DOC predictions from absorption measured at different wavelengths is presented in Fig. 2. For this exercise, ecosystems were categorized into three groups as follows: freshwater (lakes, rivers, wetlands), coastal (coasts, estuaries) and ocean. This choice was motivated by the similarities in the CDOM-DOC relationships across the systems (Supplementary Fig. 3). For these three ecosystem classes, prediction of DOC as a function of $a_{CDOM}(\lambda)$ was found to decrease monotonically with increasing wavelengths but with varying magnitude (Fig. 2). In freshwater and coastal ecosystems, the goodness of the predictions remained relatively high across

the complete spectral range. In freshwater, the robustness of the relationship between $a_{\text{CDOM}}(\lambda)$ and DOC remained relatively high and stable between 250 and 400 nm with and the coefficient of determination averaged 0.91 before decreasing to 0.69 at 500 nm. Prediction of DOC was also relatively high for coastal samples where R^2 varied between 0.82 and 0.64. For ocean samples, the prediction of DOC from absorption measurements was much lower and R^2 decreased rapidly from 0.63 at 250 nm to 0.02 at 500 nm.

Distribution of $a_{\text{CDOM}}(350)$, DOC and SUVA_{350} along the aquatic continuum

The distributions of the main variables used to characterize the DOM pool along the freshwater-marine continuum are presented in Fig. 3. DOC concentrations ranged from 19 to 44 600 $\mu\text{mol C}\times\text{L}^{-1}$, with a median value of $769 \pm 1\ 855 \mu\text{mol C}\times\text{L}^{-1}$ (0.05 and 0.95 quantile values: 41-2867). Absorption coefficients at 350 nm varied by three orders of magnitude between wetland and ocean ecosystems (Fig. 3A, anova = $F(5, 12802) = 851.6$, $p < 1e-16$, see also Supplementary section 6). In wetlands, median $a_{\text{CDOM}}(350)$ was 87.2 m^{-1} and the CDOM absorption decreased linearly along the freshwater-marine continuum to reach 0.08 m^{-1} in ocean ecosystems. DOC concentration showed a similar negative trend along the aquatic continuum with median value decreasing from $3\ 250 \mu\text{mol C}\times\text{L}^{-1}$ in the wetlands to reach $50 \mu\text{mol C}\times\text{L}^{-1}$ in oceans (Fig. 3B, anova = $F(5, 12802) = 1388.9$, $p < 1e-16$, see also Supplementary section 6). Median value of SUVA_{350} varied between $1.34 \text{ m}^2 \times \text{g C}^{-1}$ in the wetlands and $0.09 \text{ m}^2 \times \text{g C}^{-1}$ in oceans (Fig. 3C, anova = $F(5, 12802) = 1981.1$, $p < 1e-16$, see also Supplementary section 6). Whereas $a_{\text{CDOM}}(350)$ and DOC values both negatively decreased along the freshwater-marine gradient, SUVA_{350} showed similar values among inland water ecosystems (wetland, lake and river) with a median value of $0.86 \text{ m}^2 \times \text{g C}^{-1}$. For marine-like ecosystems (coastal, estuary and ocean) median SUVA_{350} was 0.15

$\text{m}^2 \times \text{g C}^{-1}$ (Fig. 3C).

Global relationship between DOC and $a_{\text{CDOM}}(350)$

A strong positive log-linear relationship was found between $a_{\text{CDOM}}(350)$ and DOC (Fig. 4A, $n = 12\,808$, $R^2 = 0.92$, $p < 0.0001$). At low values of DOC concentration ($35 \mu\text{mol C} \times \text{L}^{-1}$), predicted value of $a_{\text{CDOM}}(350)$ was 0.03 m^{-1} . As DOC increased to a maximum of $44\,600 \mu\text{mol C} \times \text{L}^{-1}$ in wetlands, predicted $a_{\text{CDOM}}(350)$ reached $1\,097 \text{ m}^{-1}$ (Fig. 4A). The derived equation from the general log-linear model indicated that $a_{\text{CDOM}}(350)$ increases by 9.31 m^{-1} for each unit of increase in DOC concentration.

$$\log(a_{\text{CDOM}}(350)) = -15.09 + 9.31 \times \log([\text{DOC}]) \quad (3)$$

The robustness of the global relationship was found to vary greatly among the different ecosystems and R^2 averaged 0.68 (Fig. 4B, Supplementary Fig. 3). The individual relationships between DOC and $a_{\text{CDOM}}(350)$ for observations in ocean, coastal and lake was found to be weaker than the calculated average which caused larger scattering around the regression line at low DOC values (Fig. 4A, Supplementary Fig. 3). The weakest relationship between DOC and $a_{\text{CDOM}}(350)$ was found in the ocean ecosystem ($R^2 = 0.44$) whereas the strongest one was found in the wetland ecosystem ($R^2 = 0.94$) which presented similarities with river and estuary ecosystems (Fig. 4B). An analysis of covariance (ANCOVA, using type III sum of squares) revealed that ecosystem has a significant effect on the predicted DOC, $F(5, 12\,799) = 401$, $p < 2e-16$, which in this case can be interpreted as a significant difference in intercepts between the regression lines (Supplementary Fig. 3).

DOM characteristics along the aquatic continuum

SUVA₂₅₄ was used as an indicator of DOM chemical composition and as a proxy for both chemical and biological reactivity over 4 000 km along the aquatic continuum (Fig. 5). A piecewise regression adequately modelled the pattern observed in the data ($R^2 = 0.95$, $p < 0.0001$). A significant breakpoint ($p < 0.0001$) was identified between 300-400 km offshore. In freshwaters and up to this coastal break point mean SUVA₂₅₄ decreased rapidly from 4.79 to 1.68 $\text{m}^2 \times \text{g C}^{-1}$ with a slope of $1.825\text{e-}03 \text{ m}^2 \times \text{g C}^{-1} \times \text{km}^{-1}$ suggesting an important loss in DOM color and aromaticity. Beyond the identified breakpoint onward to the open ocean SUVA decreased more slowly with a slope of $1.311\text{e-}06 \text{ m}^2 \times \text{g C}^{-1} \times \text{km}^{-1}$. However this slope was not significant and SUVA₂₅₄ had an average value of $1.7 \text{ m}^2 \times \text{g C}^{-1}$.

Trends in SUVA across freshwater to ocean salinity gradient

The linear trend of SUVA₂₅₄ along the salinity gradient was modeled using a piecewise regression where two different breakpoints at salinity 8.7 ± 0.3 and 26.8 ± 0.8 were identified (Fig. 6, $R^2 = 0.74$, $p < 0.0001$). Between salinity 0 and 8.7, the slope of the linear regression was -0.3 indicating that SUVA₂₅₄ decreased by this amount for each unit increase in salinity. Between salinity 8.7 and 26.8, SUVA₂₅₄ remained stable and the slope of the regression was not significantly different from 0 ($p > 0.1$). Another significant slope with a value of -0.09 was found when the salinity was above 26.8. Values of SUVA₂₅₄ were found to be consistently lower than the expected conservative mixing behaviour (as indicated by the red curve in Fig. 6).

Spectral differences between freshwater and marine ecosystems

Spectral slope (S_λ) curves calculated on normalized and averaged CDOM spectra in contrasting ecosystems, which can be viewed as end-members of the global aquatic continuum; freshwater and marine systems, showed contrasting patterns (Fig. 7). S_λ calculated from the freshwater samples had the appearance of an inverted parabola. Spectral slopes showed a linear increase in the UV-C region (segment I, < 295 nm) before reaching a plateau in the UV-B and UV-A regions (segment II, 295–365 nm). Above 365 nm, S_λ decreased rapidly to 0.0095 nm^{-1} (segment III). For the marine end-member, a dominant peak in the spectral slope curve was found at approximately 280 nm (segment IV, 260–292 nm). A rapid decrease in S_λ was observed between 292–350 nm (segment V). Beyond 350 nm, the value of S_λ remained relatively stable (segment VI). Contrary to the freshwater curve, the quality of the computed slope, estimated using R^2 , decreased from 400 nm. This indicates that the non-linear model used (Equation 2) is not fully capturing the variation in absorption at higher wavelengths where oceanic absorption spectra are often characterized by long linear tails rather than curved tails.

Discussion

Relationships between DOC and a_{cdom} along the aquatic continuum

DOC concentration and a_{cdom} measurements are often used as proxies to characterize the quantity and the quality of the DOM pool in aquatic ecosystems. The coefficient of correlation between a_{cdom} and DOC concentration was highly

dependent on the wavelength used (Fig. 2). Similar, inverse relationship between correlation coefficient and absorption wavelength has been shown previously in freshwaters and estuaries (Asmala et al., 2012; Peacock et al., 2014). This decoupling of CDOM and DOC at higher wavelengths is likely due to the higher photobleaching of DOM at wavelengths above 400 nm (Osburn et al., 2009). The observed relationship decreases more gradually in freshwater and coastal waters, whereas in ocean the DOC-CDOM coupling weakens considerably already above around 350 nm. This supports the hypothesis of the role of photobleaching because the residence time is longer and light attenuation lower in the ocean compared to other systems, increasing the photobleaching potential (Del Vecchio et al., 2002; Swan et al., 2012; Nelson et al., 2013). The weak relationship between DOC concentration and CDOM absorption at wavelengths above 350 nm is relevant for remote sensing applications, which typically operate at wavelengths above 400 nm. Typical solution to overcome the inherently poor DOC-CDOM relationship is to use multiple wavelengths (satellite bands) and additional variables in the algorithms (Del Castillo et al., 2008; Mannino et al., 2008).

In freshwater ecosystems, absorption properties of the DOM pool were found to be highly correlated with DOC concentration. A likely explanation for this is that inland water ecosystems are known to be highly connected with their surrounding terrestrial catchment (Wiens, 2002; Frenette et al., 2012) which contribute to the delivery of large quantities of highly colored DOM (Massicotte et al., 2011; Lambert et al., 2016; Cole et al., 2007). In contrast, weaker relationships between absorption properties and DOC were observed in coastal and oceanic ecosystems (Fig. 5). Stedmon et al., (2015) suggested that kinetic processes (mixing, photochemical oxidation and microbial degradation) can operate at different rates on DOC and CDOM fractions of the DOM pool which in result can cause a decoupling and nonlinear relationships between these two pools. At a global scale, $a_{\text{CDOM}}(350)$ correlated strongly to the carbon content of the DOM pool (Fig. 4, supplementary Fig. 3). However, the relationships between DOC

and $a_{\text{CDOM}(350)}$ became gradually decoupled as the DOM pool was transported toward the oceans. One possible explanation is that as residence times of the water systems increase from headwater streams to oceans, also increases the importance of photochemical processes resulting in preferential removal of the colored fractions of the DOM pool (Vähätalo et al., 2004; Moran et al., 2000; Bittar et al., 2015; Hansen et al., 2016; Weyhenmeyer et al., 2012). This hypothesis can be further supported by exploring the negative relationship between DOC and a_{cdom} documented by Nelson et al., (2013) (Supplementary section 7). One characteristic of these sample points is that they are mainly located in open oceans where DOC concentrations are low ($< 100 \mu\text{mol C}\times\text{L}^{-1}$). Hence, one possible explanation behind this negative relationship is that carbon content and color are decoupled due to long exposure to solar irradiation and thus high potential of photobleaching. Below the surface the bleaching decreases rapidly, but production of DOC remains relatively high and the overall positive relationship is reestablished.

In wetlands, rivers and estuaries, a large fraction of the DOM pool originates from soil erosion, surface runoff (Massicotte et al., 2011; Lambert et al., 2015) as well as subsurface inputs. A large proportion of terrestrially-derived DOM is known to be of high molecular weight (Heinz et al., 2015). The so-called size-reactivity continuum concept proposed by Amon et al., (1996) suggests that once exported from soils to aquatic environments these highly reactive macromolecules are prone to intense biological and physical transformations. For example, photodegradation and bacterial degradation have been shown as active processes altering the color of DOM in natural aquatic ecosystems (Moran et al., 2000; Helms et al., 2014). Moreover, it was found that these processes had a greater influence upstream within rivers where the DOM pool is mainly composed of soil-derived carbon (Weyhenmeyer et al., 2012; Seidel et al., 2015). Hence, the DOM pool in lakes and oceans is a mixture of both old refractory and fresh reactive organic material. The changing balance between these two major fractions of the

DOM pool can be seen in the high variability in SUVA along the aquatic continuum with a general decrease in absorption, concentration and absorptivity. As shown by numerous earlier studies, both DOC concentration and CDOM absorption decrease when moving along the aquatic continuum (Fig. 3). Wetland ecosystems exhibited between two and three orders of magnitude higher values in both DOC and $a_{\text{CDOM}(350)}$ compared to oceans. Interestingly, the change in specific absorbance (SUVA_{350}) is more gradual (Fig. 3C), from average value of around 1 in wetlands to around $0.1 \text{ m}^2 \times \text{g C}^{-1}$ in oceans. The loss of specific absorbance when moving downstream along the aquatic continuum suggests continuous bleaching of terrestrial DOM, along with the distance from the terrestrial source. Such decoupling between DOC and CDOM were also observed in the open ocean (Nelson et al., 2002). When predicting $a_{\text{CDOM}(350)}$ from DOC concentration, it is apparent that modeled CDOM is underestimated at the higher end of the observed values and overestimated at the lower end (Supplementary. Fig. 4A). This discrepancy in CDOM-DOC relationship between higher and lower end of the DOC concentration gradient is apparent also in the residuals of the log-linear fit (Supplementary Fig. 4B). Ecosystems with lower DOC concentrations (such as oceans and coastal systems) have more negative residuals, whereas ecosystems with high DOC concentrations (wetlands, rivers) have more positive residuals. This trend also supports previous findings that along the aquatic continuum, photodegradation processes decrease CDOM absorption relatively more than DOC concentration (Vähätalo et al., 2004) because light absorbing compounds, or absorbing parts of larger molecules, are selectively degraded, while there is continuous production of new DOC from aquatic production that dilutes and eventually replaces the original terrestrial DOM dominance (Markager et al., 2011).

DOM characteristics in the transition from headwaters to oceans

During its transport from headwaters to oceans, DOM pool is in constant change due to microbial respiration and production (Giorgio et al., 1997; Kritzberg et al., 2006; Berggren et al., 2010), sedimentation and flocculation (Sholkovitz, 1976; Wachenfeldt et al., 2008), production by photosynthetic organisms (Descy et al., 2002; Kritzberg et al., 2005; Lapierre et al., 2009) and UV photodegradation (Benner et al., 1999; Amado et al., 2006; Zhang et al., 2009). As these processes operate simultaneously, they drive the fate of DOM transiting in the various habitats of aquatic ecosystems (Søndergaard et al., 2004; Massicotte et al., 2013a). Based on the size-reactivity continuum model proposed by Amon et al., (1996), it was expected that these degradation processes would actively act to decrease the molecular weight of organic matter and subsequently its reactivity along the aquatic continuum. In agreement with this conceptual model, we find in inland waters high $SUVA_{254}$ values (Fig. 5), suggesting relatively high proportion of aromatic compounds in the DOM pool (Weishaar et al., 2003). This is likely due to elevated lateral connectivity with surrounding terrestrial landscape and organic matter inputs from the tributaries (Massicotte et al., 2011; Lambert et al., 2016). Our results further agree with findings from Lapierre et al., (2013) who found a positive relationship between $a_{CDOM}(440)$ and the concentrations of biologically and photochemically degradable DOC in boreal aquatic ecosystems. This is suggesting that the highest rates of photochemical and biological processing are occurring when the DOM pool is dominated by macro molecules originating from the landscape which have a high absorbance at visible wavelengths. The decrease in $SUVA$, as terrestrially-derived DOM is transiting in the mosaic of aquatic ecosystems, infers that high molecular weight molecules are degraded into smaller and more refractory molecules. Interestingly, we found that the observed decrease in reactivity is also occurring in coastal shelf seas (Fig. 5). After this breakpoint, it is likely that freshly produced material from

phytoplankton become the dominant fraction of the DOM pool which is known to be characterized by low molecular weight and colorless molecules. Even though the optical signal of the autochthonous DOM might be similar to terrestrial DOM (Yamashita, 2004), the magnitude of the production of autochthonous DOM is similar to degradation processes, resulting in only minor apparent changes in the optical characteristics of the oceanic DOM pool (Fig. 5).

Processing of CDOM across the salinity gradient

A rich literature uses salinity as a tracer to estimate the conservative behavior of optical properties of DOM (e.g. Kowalczyk et al., 2010; Asmala et al., 2016). However, current findings are based on the assumption that dilution is the main process responsible for the decrease in DOM properties. Contrary to most studies, our results show that DOM dynamics deviates from the expected conservative behavior (Fig. 6) suggesting that concurrent degradation and production processes continually operate in conjunction with conservative mixing (Markager et al., 2011; Gonçalves-Araujo et al., 2015). To emphasize the deviations of $SUVA_{254}$ from conservative mixing along the salinity gradient, we fitted a piecewise regression which revealed breakpoints at salinities around 9 and 27. In agreement with finding from Gonçalves-Araujo et al., (2015), our results evidence that there are at least two distinct phases of processing at low and high salinity.

Between salinity 0 and 8.7 we observed a rapid decrease in $SUVA_{254}$ that may be partially explained by salt-induced DOM flocculation in the confluence of freshwater and seawater (Sholkovitz, 1976; Søndergaard et al., 2003). Flocculation occurs at low salinities in estuaries and its efficiency reflects the characteristics of the riverine organic matter (e.g. iron content or DOM molecular weight; Mayer, 1982; Forsgren et al., 1996; Asmala et al., 2014). However, it is unlikely that flocculation is the sole process causing deviations from conservative mixing. Increasing residence times of water bodies across the continuum from river to the

sea will also increase the importance of processes such as photo- and bacterial degradation which are known to act selectively on loss of CDOM prior to discharge into the sea (Weyhenmeyer et al., 2012). Hence, a more plausible scenario is that the observed kinetic of CDOM upon intrusion in marine ecosystems is a result of the combined effect of flocculation, photodegradation and biodegradation processes (see conceptual plots in Fig. 6). This salinity range covers productive estuarine and coastal waters where the selective degradation of non-colored DOM, or higher production of CDOM compared to DOC likely drives this trend. For example organisms from all trophic levels are known to contribute with CDOM (Steinberg et al., 2004; Stedmon et al., 2014) although microbially mediated transformation of the freshly produced DOM is likely dominating the net increase of CDOM (Rochelle-Newall et al., 2002; Yamashita, 2004).

Major differences between CDOM absorption spectra from freshwater and seawater

Loiselle et al., (2009) developed a method to identify the wavelength regions of CDOM spectra with the largest changes in the spectral slope (parameter S in equation 2). We found that averaged freshwater and marine spectral slope curves were different from each other (Fig. 7). Both curves show strongly increasing slope values at low wavelengths (260-295 nm, segments I and IV). Only ocean slope values decreased rapidly right after increasing between 292-350 nm (segment V). The large drop in slope values in freshwater occurs after 365 nm (segment III). These spectral regions are the most dynamic ones, indicating that the largest deviations from the general spectral slope occur at these wavelengths. This information could be used to update our current knowledge of optical indices inferred from the spectral data. We suggest using spectral slopes between 260-295 and 365-475 nm for freshwater systems, and 260-295 and 295-350 nm for marine systems. Because these wavelengths ranges present consistent changes

in slope values across a wide variety of different locations, it is likely that they could be used as proxies for e.g. distinction between similar DOM samples, or quantifying biogeochemical processing of DOM.

Limitations and future research

Our study uses data from an extensive literature survey to better understand the distribution of DOM along the aquatic continuum at global scale. All ecological studies tackling problems at global scales need to assume a certain level of abstraction that is necessary to discover general trends which comes at the cost of losing site specific details. For example, it is likely that water temperature, watershed characteristics, stream order and many other environmental variables play key roles in the dynamics of DOM. However, for the present global analysis it is impossible to gather all this specific information from the published datasets, as there are too much variability in the auxiliary data coverage and in the extent of metadata provided in the publications. Despite this, conclusions can be drawn based on the analysis of the spatial and temporal distribution of the data extracted from this study (Supplementary Fig. 5). Albeit our effort to extract all available information from the literature and open repositories, a striking finding is that aquatic ecosystems in the southern hemisphere ($n = 855$, 7%) are highly under represented compared to those in northern hemisphere ($n = 11\ 953$, 93%). Also, no data prior to 2010 was available from southern hemisphere. Furthermore, continental Africa ($n = 603$, 5%), Asia ($n = 423$, 3%) and South America ($n = 0$, 0%) are poorly represented in the dataset, all of which contain significant inland waters and are of major significance in global carbon cycle. It is evident that the relevant data is unevenly distributed across the globe and as a result, our understanding about the biogeochemical cycling of DOM on the global scale is inevitably limited. Another important fact is that the majority of samples are taken during summer (Supplementary Fig. 5). Because this corresponds to the productive season with

maximum primary production, this might lead to bias towards autochthonous signal. Collecting the dataset for this study demonstrated that a great deal of scientific data is still not made openly available. We therefore encourage the scientific community to continue with the efforts of making the research data available in open access databases so that the data collected can continue to contribute to progress in the field in the best possible way. Furthermore, from the analysis of spectral CDOM absorption and its relationship with DOC concentration, it is evident that the level of detail acquired from single wavelength measurements is considerably inferior compared to the use of spectral information. As the modern computational capabilities do not present obstacles for utilizing spectral analyses, we strongly recommend researchers to use and develop methods that use the full potential contained in the CDOM spectra, such as the spectral slope curve (Loiselle et al., 2009) and the Gaussian decomposition (Massicotte et al., 2016). Our data shows breakpoints in the DOM optical properties on the salinity gradient, but fully mechanistic understanding about the underlying factors is unclear. There is need for dedicated studies unraveling the role of the few key processes affecting the DOM transformation along the aquatic continuum, most importantly about the role of salt-induced flocculation and phytoplankton-derived DOM.

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