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

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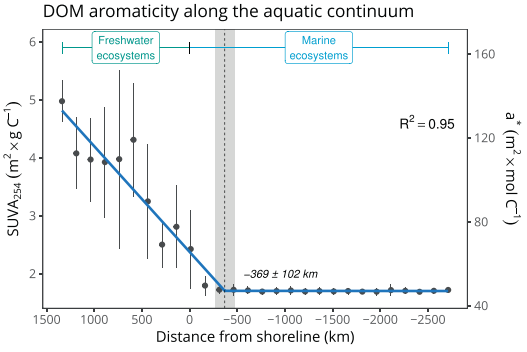
HIGHLIGHTS

- The distribution and transformation of DOM is ecosystem dependent.
- Gradual decoupling between DOC and CDOM along the lakes–oceans continuum.
- SUVA decreases more than 1300 times faster in freshwater than in marine ecosystems.
- Degradation processes act preferentially on CDOM rather than carbon content.

GRAPHICAL ABSTRACT



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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 a 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 $m^2 \times gC^{-1}$ 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.

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1. 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 (Häder 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 and Sinsabaugh, 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 and Moore, 2006; Massicotte et al., 2013; 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 CO_2 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 and Wetzel, 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.

2. Material and methods

2.1. 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 4712 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

2.2. 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 ($0.5 <$ salinity ≤ 5), coastal ($5 <$ salinity ≤ 30), ocean (salinity > 30). Based on available information, observations were classified as follows (Supplementary Fig. 1A): river ($n = 4896$), ocean ($n = 3439$), coastal ($n = 1405$), estuary ($n = 1367$), wetlands ($n = 954$), and lake ($n = 747$). Note that 81% of the oceanic samples were located at depth shallower than 1800 m.

2.3. Data processing and metrics calculation

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

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

where $a_{CDOM}(\lambda)$ 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 (Eq. (2)) has been used to extract quantitative information about optical properties of CDOM (Jerlov, 1968; Bricaud et al., 1981; Stedmon and Markager, 2001):

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