Exploring the relationship between colored dissolved organic matter and dissolved organic carbon at the Lower Amazon River

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Abstract Novel studies relate the colored dissolved organic matter (CDOM) to dissolved organic carbon (DOC) in coastal areas and emphasizes their high regional and seasonal dependency. The aim of this study is to explore the potential use of CDOM absorption coefficient (a_{cdom}) to estimate DOC concentration at the Lower Amazon

River region. The study area gathers contrasted water types as very turbid water of the Amazon River and clear waters of the Tapajos, Xingu and Paru rivers. Surface water samples were taken at 45 stations for CDOM absorption as well for DOC concentration measurements, during high, low and falling water seasons. The data were fitted by linear regression and the results demonstrate that a direct relationship between a_{cdom} and DOC is not possible in this study area (N= 45; R^2=0.24; RMSE = 55.95), but an alternative approach that relates the variation in the $a_{cdom}(412)$ to DOC ratio (a^*_{cdom} (412)) had a good assessment (N=45, R^2=0.65, RMSE=0.0024). We conclude that a_{cdom} represents a valuable proxy to retrieve DOC concentration in the study area. It is clear that seasonal discharges have a great influence on the results as well as the water color of the rivers. Considering that a_{cdom} can be estimated by orbital sensors, the possibility of exploring CDOM-DOC relationships empowers a synoptic monitoring of aquatic environments through remote sensing observations, expanding our comprehension of the global carbon cycle at the Lower Amazon River region.

Keywords: turbid water, carbon cycle, águas túrbidas, ciclo do carbono

1. Introduction

Terrestrial humic substances are the dominant dissolved organic matter (DOM) constituents added to freshwaters (Wetzel, 2002) and the dissolved organic carbon (DOC) is the most important fraction of DOM in the global carbon cycle. As discussed by Battin et al. (2009), the fluvial export of DOC provides the largest flux of reduced carbon (0.25 Pg C y^{-1}) from land to ocean. Nevertheless, studies that explore the role of rivers at the global carbon cycle are scarce especially in the tropical region (Richey et al., 2002; Lauerwald et al., 2015). A research effort should be developed to better understand a scenery that considers the transfer of the carbon from continent to ocean as an integrated system.

The fraction of DOM that absorbs ultraviolet (UV) and visible light is named as colored dissolved organic matter (CDOM) and it is largely responsible for the optical properties of most freshwaters. Recent works relates CDOM to DOC (Fichot and Benner, 2012; Spencer et al. 2012; Brezonik et al., 2015; Vantrepotte et al., 2015) and some studies at coastal and river dominated areas describe these relationships as highly variable among different regions and seasons (Vodacek et al., 1997; Chen et al., 2004). Considering that a_{cdom} can be estimated by orbital sensors, the possibility to explore these relationships empowers a synoptic monitoring of aquatic environments through remote sensing observations, expanding our comprehension of the global carbon cycle (Vantrepotte et al., 2015).

CDOM absorption is associated with DOM concentration, but its spectral slope (S) provides further insights about the inner characteristics as molecular weight, composition and origin (Helms et al., 2008; Fichot and Benner 2012). Additionally, when a narrow wavelength interval is selected, the spectral slope is independent of CDOM concentration (Brown 1977, Helms et al., 2008). Fichot and Benner (2011) demonstrated that $S_{275-295}$ can be used as an index of DOC-normalized absorption coefficient of CDOM in a river dominated coastal area, and consequently it is possible to retrieve DOC concentrations from CDOM.

The aim of our study is to propose a methodology to evaluate the potential use of CDOM absorption coefficient to estimate DOC concentration at the Lower Amazon River region where very turbid water from the Amazon River coexist with clear waters from Tapajos, Xingu and Paru rivers. Considering that CDOM has a direct impact on water colour while DOC hasn't the use of CDOM-DOC relationships can contribute with future carbon studies by water colour remote sensing.

2. Material and Methods

2.1 Study area

The Lower Amazon River region is here defined as a 900 km long transect between the upstream boundary at Óbidos (01°55.141′S; 55°31.543′W) and the Amazon River mouth. The downstream boundary are the North and South channels near Macapá, which are the last two

well-constrained channels near the Amazon River mouth (00°05.400′S; 51°03.200′W and 00°09.415′S; 50°37.353′W, respectively). The region near the Amazon River mouth is tidally influenced and experiences semi-diurnal flow reversals (Ward et al., 2015). In addition to the Amazon River, samples were also collected in the Tapajos, Xingu and Paru River as well as at the Great Lake Curuai (Figure 1A). These latter rivers are classified as clear water river (Sioli, 1984) and generally they show higher levels of in situ primary production than the turbid Amazon River (Ward et al., 2015). Surface water samples were taken during high water (T1, May 2014), low water (T2, November 2014) and falling water (T3, July 2015) seasons (Figure 1B).

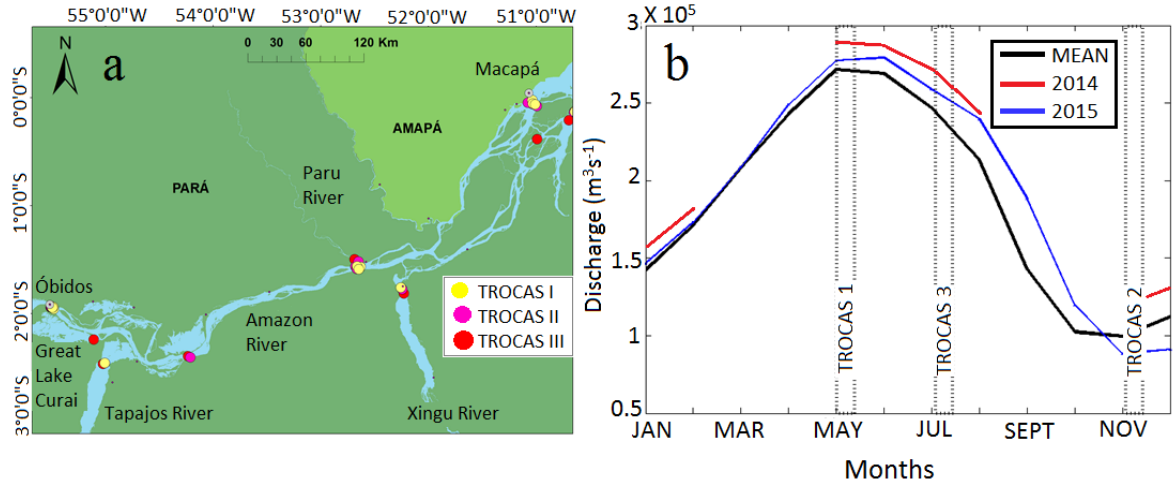

Figure 1. a) In situ sampling stations at the Lower Amazon River and tributaries (Tapajos, Xingu and Paru River); b) Seasonal discharge of the Amazon River in 2014-2015, and mean discharge in 2005-2016. The three TROCAS campaigns are highlighted: TROCAS 1 (high water), TROCAS 2 (low water) and TROCAS 3 (falling water). Discharge data acquired from Óbidos Station (National Agency of Waters of Brazil, ANA).

2.2 Methods

Surface water samples (N=45) were prior filtered through 25 mm GF/F Whatman glass fiber filters (0.7 µm nominal pore size) to remove the suspended matter. The resultant water was again filtered through 0.2 µm polycarbonate membranes (Whatman Nuclepore, 25 mm) under gentle vacuum (< 5 mm Hg) according to the NASA protocol (Mitchell et al., 2003). Samples were stored in pre-combusted glass bottles wrapped with aluminum foil and kept under refrigeration (4°C) until further laboratory analysis. CDOM samples were taken from the refrigerator before spectrophotometric analysis with the purpose of regulate with the room temperature and avoid any bias due the thermal difference between the samples and the reference water (Milli-Q water). CDOM absorbance spectra were measured from 250 to 850 nm, using a spectrophotometer Shimadzu UV 2450 with a 10 cm quartz cell. CDOM absorption coefficient ($a_{cdom}(\lambda)$) is calculated from absorbance measurements using the following Equation 1:

$$a_{cdom}(\lambda) = 2.303 * A(\lambda)/L \qquad \text{(Equation 1)}$$

where A(λ) is the absorbance of the filtered water sample at wavelength λ and L is the optical pathway of the quartz cell in meters.

As recommended by Babin et al. (2003) for waters with higher concentration of CDOM, a baseline correction was applied to each spectrum by subtracting the mean absorbance in the range of 680-690 nm from the whole spectrum. The absorption spectral shape of CDOM is

estimated using a linear fit of the log-linearized $a_{cdom}(\lambda)$ spectrum over their respective spectral range and usually are reported with units of nm^{-1} (Bricaud et al., 1981) (Equation 2):

$$a_{cdom}(\lambda) = a_{cdom}(\lambda_0)e^{-s(\lambda-\lambda_0)} \quad \text{(Equation 2)}$$

where $a_{cdom}(\lambda)$ is the absorption coefficient at wavelength λ, $a_{cdom}(\lambda_0)$ is the absorption coefficient at a reference wavelength λ_0 and S is the spectral slope in the spectral range from λ_0 to λ with $\lambda_0 < \lambda$.

Recent works have demonstrated the importance of the slope in the range of 275-295 nm ($S_{275-295}$) to define a relationship between DOC and CDOM (Helms et al., 2008; Fichot and Benner, 2011; Fichot and Benner, 2012; Vantrepotte et al., 2015). Therefore for this study this interval was adopted.

The concentration of DOC was measured on a Shimadzu total organic carbon-viral collagen prolyl hydroxylase analyzer using samples that were filtered in triplicates through precombusted (450º, 6 hours) 25 mm GF/F Whatman glass fiber filters (0.7 µm nominal pore size) on 20 mL glass vials and preserved with 50 µm of 50% HCl at 0-4°C. Only samples with an absolute difference below 10% among the triplicates were considered.

Measurements of DOC and $a_{cdom}(412)$ were used to calculate the DOC specific coefficient absorption ($a^*_{cdom}(\lambda) = a_{cdom}(412)$:DOC), expressed here in units of $m^2.mmol^{-1}$.

3. Results and Discussion

Figure 2 shows the boxplots of CDOM absorption and DOC in situ measurements. It is reasonably to consider that $a_{cdom}(412)$ at high water (TROCAS 1– T1) and falling water (TROCAS 3 – T3) has equivalent mean values, with more extreme (higher) values during T1 and lower mean value at low water (TROCAS 2 - T2) (Figure 2a). Mean $S_{275-295}$ values are homogeneous with higher values at T2 and lower values at T1 (Figure 2b). Mean DOC values are also reasonably homogeneous but with higher variability at T3 (Figure 2c).

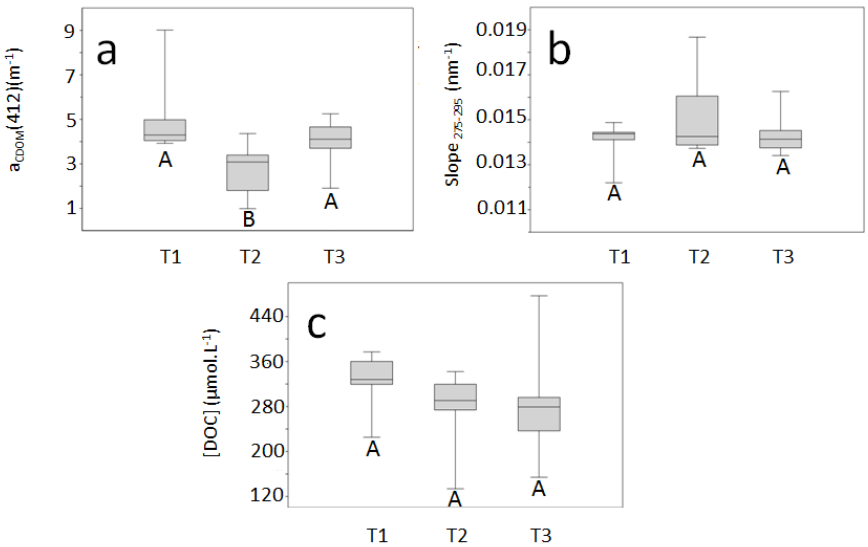

Figure 2. Boxplot of in situ-measured values of: a) CDOM absorption coefficient at 412 nm; b) Slope at the interval 275-295 nm; c) DOC concentration. A and B letter shows the result of multiple pair-wise comparisons of group means using Tukey's range test. Variables not sharing a letter have significant different means importance ($p < 0,05$).

Plotting DOC and $a_{cdom}(412)$ together (Figure 3a) shows a general similar variability pattern. However, no significant direct correlation could be evidenced considering our

complete data set (N= 45; R^2=0.24; RMSE = 55.95) (Figure 3b). The observed scattering is expected when the samples does not have a similar dispersion as usually noted for coastal waters influenced by terrestrial inputs of DOM. In the present case, no such dilution gradient can be observed. Rather, there are two different types of water, clear and white rivers, thus leading to the general dispersion here observed in the CDOM to DOC relationship (Figure 3b). When the rivers are discriminated (Figure 3b) it is noted that the dispersion is largely caused by the clear waters (Tapajós and Paru) while the Amazon River samples are gathered at ~4 m^{-1} $a_{cdom}(412)$ and ~ 300 µmol.L^{-1} [DOC].

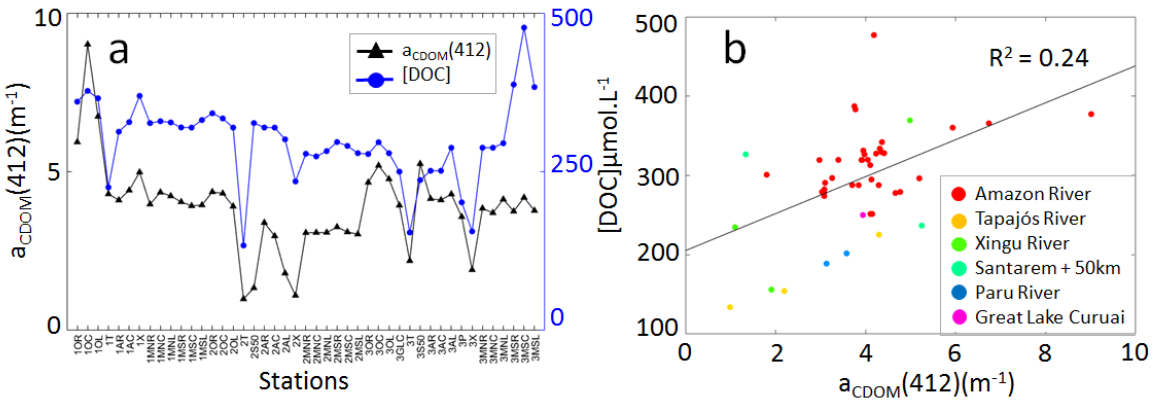

Figure 3. a) DOC and CDOM(412) in situ measurements at 3 cruises (T1, T2, T3); b) $a_{cdom}(412)$ *x* DOC linear relationship in the Amazon waters (Amazon River, Great Lake Curuai, Tapajos River, Paru River and Xingu River).

Another approach to relate CDOM with DOC is to consider the slope of the CDOM spectrum in a small interval of the UV domain. Previous works (Vantrepotte et al., 2015; Fichot and Benner, 2011; Fichot and Benner, 2012) have indeed demonstrated the possibility of relating the specific absorption of CDOM ($a^*_{cdom} = a_{cdom}/DOC$) with the CDOM spectral slope in the range of 275-295 nm ($S_{275-295}$). Despite some scattering, the relationship between CDOM and DOC is improved when $a^*_{cdom}(412)$ and $S_{275-295}$ are used (N = 45; R^2=0.52; RMSE=0.0028) and the values are in agreement with the results shown by Vantrepotte et al. (2015) from a variety of coastal sites, with a^*_{cdom} (412) and $S_{275-295}$ having opposite trend patterns (Figure 4a). As mentioned, $S_{275-295}$ has the potential of determine the natural variability of a^*_{cdom}. In the context of remote sensing application, the information in the UV is currently not directly available. However, Fichot et al., (2013, 2014) have demonstrated the possibility to estimate $S_{275-295}$ form a multilinear combination of the marine reflectance. Vantrepotte et al., (2015) have further emphasized that the latter relationships are in turn related to the link between CDOM quality and quantity. As a matter of fact, a nonlinear relationship between $S_{275-295}$ and $a_{cdom}(412)$ described by Vantrepotte et al., (2015) is also observed in the Amazonian waters (Figure 4b).

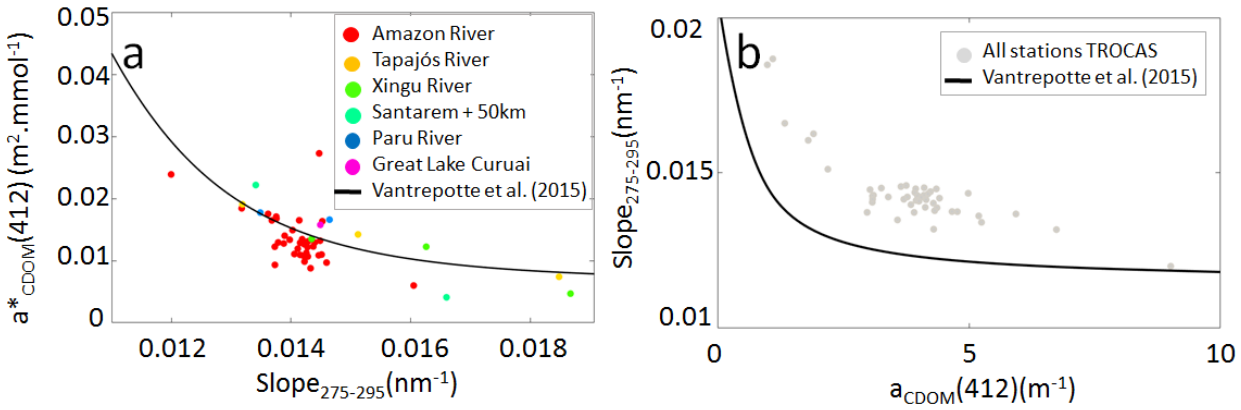

Figure 4. a) Relationship between a^*_{cdom} (412) and $S_{275\text{-}295}$ for Amazonian rivers (Amazon, Tapajos, Xingu, Paru, Great Lake Curuai) and the same relationship for coastal waters for comparison (from Vantrepotte et al., 2015); b) Comparison between the Amazonian waters $S_{275\text{-}295}$ and coastal waters (from Vantrepotte et al., 2015).

Considering the observed relationship between 1) $S_{275\text{-}295}$ and a^*_{cdom} (412), and 2) $S_{275\text{-}295}$ and $a_{cdom}(412)$, an alternative approach for estimating DOC from CDOM consists in relating directly a^*_{cdom} (412) to $a_{cdom}(412)$ itself (Vantrepotte et al., 2015). This approach improved the relationship (N=45, R^2=0.65, RMSE=0.0024), diminished the scattering and spotlighted the particularities about the origin of the dissolved organic matter (Figure 7), which can be expressed as follows (Equation 3):

$$a^*_{CDOM}(412) = 0.0023(a_{CDOM}412) + 0.0041 \qquad \text{(Equation 3)}$$

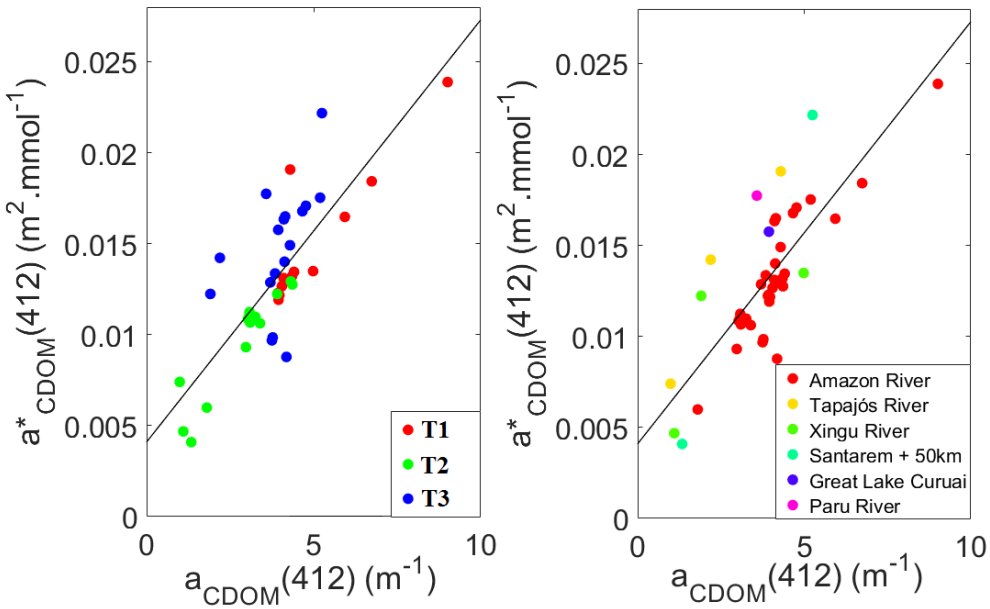

Figure 5. Relationship between $a_{cdom}(412)$ and a^*_{cdom} (412) for (a) different sampling seasons, and (b) different Amazonian rivers (Amazon, Tapajos, Xingu, Paru, Great Lake Curuai).

The scattering distribution of the samples according to the season is showed in Figure 5a, where is observed that during the T1 (higher water) the CDOM absorption reaches the higher values as well as during the T2 (low water), the CDOM absorption values were lower. At T3 (falling water), CDOM absorption values were intermediary between T1 and T2, showing a relatively higher scattering (Figure 5a). The clear waters rivers (Tapajos and Paru) have a

higher specific coefficient absorption contrasting with more turbid waters of the Amazon River. Even though the Xingu river is classified as clear water type, during T1 and T2 campaigns the DOC values were higher than the Tapajos and Paru measurements, with a^*_{cdom} (412) values closer to those of the Amazon River (Figure 5b).

4. Conclusion

The main goal of this study was to verify the potential use of $a_{cdom}(412)$ to estimate DOC concentration for the Lower Amazon region. This exploratory effort showed satisfactory results and interesting insights. The direct estimation of DOC from $a_{cdom}(412)$ was not viable at this stage, but an alternative approach as proposed by Vantrepotte et al. (2015) demonstrated a positive correlation between the variables explaining the variability observed in $a_{cdom}(412)$ to DOC ratio ($a^*_{cdom}(412)$). Furthermore, this alternative approach showed a minor scattering of the dataset.

It is clear that the seasonal discharge of the Amazon River, influence on the results as well the type of water color of the rivers. For DOC estimation, this study has showed that during the high and low water (T1 and T2, respectively) there is a better agreement with less scattering between $a_{cdom}(412)$ and DOC ratio than at falling water (T3). The clear water rivers showed a higher specific absorption coefficient contrasting to more turbid waters of the Amazon River.

We expect that our results would contribute with the comprehension of the carbon cycle at the lower Amazon River. In the future, a remote sensing algorithm to estimate DOC for this region could be developed.

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