Spatial and temporal variations of the inherent optical properties in a tropical cascading reservoir system

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Abstract In order to verify the effect of a cascade system in the water quality of two tropical reservoirs in Brazil, this work proposed to make use of the inherent optical properties (IOPs) as well as the specific inherent optical properties (SIOPs). From upstream to downstream, Barra Bonita (BB) is the first in a set of six reservoirs along Tietê River and Nova Avanhandava (Nav) is the fifth reservoir. BB is eutrophic whilst Nav is an oligotrophic environment. According to the IOP and SIOP analysis, it was possible to attest that BB was organic matter dominated and Nav was inorganic matter. These differences are noticeable in bio-optical modeling, must be considered different approaches to retrieve water quality parameters in both sites, once, the models take into account the specific information about the IOP and their relation with the optically active components (OACs) concentration. In addition, the results of this paper can provide comparable data to other water systems and improve the comprehension about the optical properties of complex water bodies.

Keywords Water quality · Remote sensing · Inherent optical properties · Reservoirs cascade system

Introduction

Optical properties of water are the basis of watercolor retrieval algorithms. Variations of these properties can change the model parameters, optimal spectral bands and the accuracy of retrieval algorithms. In order to improve the performance of bio-optical models (semianalytical approaches), a better understanding about the variability in the absorption (a , units in m^{-1}) and backscattering (b_b , units in m^{-1}) coefficients is crucial. These coefficients influence the magnitude and the spectral distribution of the water-leaving reflectance. Inland waters typically present high concentration of coloured dissolved organic matter (CDOM), phytoplankton and inorganic particles (Riddick et al. 2015). The mass-specific inherent optical properties (SIOPs) are considered the main source of uncertainty in the water-leaving reflectance interpretation. The IOPs and SIOPs in inland waters as suggested by Pérez et al. (2011) and Zhang et al. (2010) exhibit significant variability.

Environments such as reservoirs designed in a cascade system causes limnological modifications from the upstream to downstream reducing the turbidity and increasing the transparency of water, and the biotic and abiotic factors of water accumulate until the last dam, which receives input from all the previous water bodies (Barbosa et al. 1999). The SIOPs can be somehow modulated by biogeochemical filtration from upstream to downstream reservoirs. Studies highlighted the improvement of water quality from upstream to downstream reservoirs (Smith et al. 2014), although, up to now there are no studies discussing how the IOPs and SIOPs vary in tropical inland waters designed in a cascade system in Brazil. The investigation of the SIOP's variability in optically complex inland waters can aid information about many biogeochemical processes, such as carbon cycling,

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primary production (photosynthesis) and development of satellite-based algorithms.

Thus, the scientific question raised in this research is that although there is a need to develop algorithms to estimate the optically active components (COAs) in the water in cascading systems this task can be challenging due to a different biogeochemical concentration along the cascading. The satellite algorithms development is beyond the objective of this manuscript but the obtained results will help the researchers to find out the most appropriate approach for cascading reservoir systems. In order to address this issue, the aim of this work was to investigate the seasonal variability of the IOPs and SIOPs in a cascading reservoir system situated along the Tietê River, São Paulo State, Brazil.

Materials and methods

Study area

The reservoirs of Barra Bonita (BB) and Nova Avanhandava (Nav) (Fig. 1) are situated in the middle and lower portion of the Tietê River, São Paulo State, respectively. Barra Bonita (22°31'10"S, 48°32'3"W) is a storage reservoir and began its operation in 1963 flooding an area of 310 km², with a dam length of 480 m, 90.3 days of mean residence time, being formed from the damming of Tietê and Piracicaba Rivers (Soares and Mozeto 2006). Nova Avanhandava (21°7'1"S, 50°12'6"W) is a run-of-river reservoir and was created in 1982, flooding an area of 210 km² (at its maximum quota), with a dam length of 2038 m and mean residence time of the water around 46 days.

Barra Bonita reservoir is an ecosystem characterized as polymictic and eutrophic, with a high content of nutrients, whose contribution leads to the blooms of cyanobacteria during the summer, and Bacillariophyceae during the winter (Dellamano-Oliveira et al. 2007). The Piracicaba and Tietê Rivers, which along their courses are subject to the carrying of organic and inorganic origin waste, arising from agricultural, urban and industrial activities, affect water quality. Nav reservoir is characterized as an oligo-mesotrophic environment with the upper portion of the water column well oxygenated, pH ranging from slightly acid to alkaline, relatively high conductivity, and moderate concentrations of nutrients.

Fieldwork

Fieldwork at the sites occurred in two periods of the year, the first coinciding with the beginning of the dry season (Nav: April 28th to May 2nd and BB: May 5th to 9th, 2014)

and the other with the end of the dry season (Nav: September 23rd to 26th and BB: October 13th to 16th, 2014). For each field campaign, 20 samples were collected, totalizing a dataset with 80 samples (see Fig. 1 for samples location).

Biogeochemical characterization

Water samples were collected in the surface layer of the water column and then filtered under vacuum pressure through a Whatman fiberglass GF/F filter with a porosity of 0.7 µm, and then frozen (−25 °C) for laboratory analysis. The chlorophyll-*a* (chl-*a*) was extracted by maceration in 90 % acetone solution, stored in 20 ml tubes, and placed in a centrifuge to have the absorbance read later in a spectrophotometer. The method described by APHA (1998) was used to determine the total suspended material concentration. The water volume was filtered on the same day of collection through a Whatman fiberglass GF/F filter with 0.7 µm pores previously calcined at 470 °C, then refrigerated until analysis. The filters were placed for 12 h in an oven at 100 °C, after which they were weighed, then placed in a muffle furnace at 470 °C for 1 h and, finally, weighed again. As a result, total solid matter (TSM), inorganic solid material (ISM) and organic solid material (OSM) concentrations were determined. A replica was used for each sampling station and water quality parameter in order to ensure the consistency of the measurements.

Optical properties

Water samples were filtered through a 0.7 µm porosity GF/F fiberglass that was stored flat under freezing condition. The determination of the total particulate (algal and detritus) absorption (a_p) was performed by an integrating sphere module presented in the double-beam Shimadzu UV-2600 UV-Vis spectrophotometer, with spectral sampling from 280 to 800 nm. A white filter, wetted with ultrapure water was used as reference. The filter containing collected particulates was positioned in the integrating sphere to measure their optical density (OD). The transmittance–reflectance (T–R) method presented by Tassan and Ferrari (1995) was employed to obtain the total particulate absorption coefficient.

To acquire the phytoplankton and detritus absorption coefficients, a_ϕ and a_d , respectively, the filter undergoes depigmentation by oxidation in 10 % sodium hypochlorite (NaClO) solution, ensuring that the samples do not contain pigment interference. Using empirical relationships described by Tassan and Ferrari (1995), the respective coefficients were determined and a_ϕ is obtained by the difference between the optical density of the total particulate and detritus fractions.

Fig. 1 Graphic representation of the study area emphasizing **a** Brazil's territory, with São Paulo State highlighted; **b** Tietê River and the cascade system (from upstream to downstream: Barra Bonita,

Ibitinga, Bariri, Promissão, Nova Avanhandava, and Três Irmãos); number 1 showed **c** Barra Bonita and number 2 referred to **d** Nova Avanhandava Reservoir

To estimate the CDOM absorption coefficient (a_{CDOM}), water samples were filtered through a fiberglass Whatman GF/F with 0.7 μm pores, and then re-filtered under low vacuum pressure using a nylon membrane filter with 0.2 μm pores. The readings were performed using the absorbance mode, and the samples were placed in 10 cm quartz cuvettes. For each set of measurements, we performed a reference reading containing Milli-Q water, and for each read sample ($\text{OD}_{\text{sample}}$), the reference absorbance ($\text{OD}_{\text{reference}}$) value was subtracted. The measured optical densities ($\text{OD}_{\text{sample}}$) were converted to absorption coefficient by multiplying by 2.303 and dividing by the path length ($l = 0.1$ m for a 10 cm cuvette). Therefore, a_{CDOM} at wavelength λ was calculated as:

$$a_{\text{CDOM}}(\lambda) = 2.303 \frac{\text{OD}_{\text{sample}}}{l} \quad (1)$$

A baseline correction was performed by subtracting the average value between 700 and 750 nm from all the spectra

values. The specific absorption coefficients of phytoplankton (a_{ϕ}^* , m^2mg^{-1}) and detritus (a_{d}^* , m^2g^{-1}) were obtained by normalizing the absorption due to phytoplankton and detritus by the chl-*a* and detritus concentration, respectively. The specific absorption coefficient of CDOM (a_{CDOM}^*) was calculated considering the spectral range of 400–700 nm by applying an exponential fit (Bricaud et al. 1981):

$$a_{\text{CDOM}}^*(\lambda) = a_{\text{CDOM}}^*(\lambda_0) e^{(-S_{\text{CDOM}}(\lambda - \lambda_0))} \quad (2)$$

where $a_{\text{CDOM}}^*(\lambda_0)$ is the specific CDOM absorption at the reference wavelength, λ_0 ($=440$ nm) and the respective value is equal to 1, and S_{CDOM} (nm^{-1}) is the spectral slope of the $a_{\text{CDOM}}(\lambda)$ spectrum. Values of S_{CDOM} were estimated through a nonlinear regression fitting approach (Twardowski et al. 2004) over the 350–500 nm wavelength interval (Babin et al. 2003). The detritus specific absorption coefficient (a_{d}^*) was described in the same way as a_{CDOM}^*

after normalization by detritus concentration (Campbell et al. 2011):

$$a_d^*(\lambda) = a_d^*(\lambda_0)e^{(-S_d(\lambda-\lambda_0))} \quad (3)$$

where $a_d^*(\lambda_0)$ is the detritus absorption at the reference wavelength, λ_0 (=550 nm), and S_d (nm^{-1}) is the spectral slope of the $a_d(\lambda)$ spectrum. The slope was measured as described by Babin et al. (2003) in order to avoid any trace of pigment.

Data interpolation

The IOPs based on the wavelength at 440 and 443 nm were used for interpolation using the ordinary Kriging method from Isaaks and Srivastava (1989). The wavelength at 440 nm was chosen to represent the main absorption feature of dissolved and particulate matter, however, the $a_{\text{CDOM}}^*(443)$ was used instead of $a_{\text{CDOM}}^*(440)$, because the latter one after modeling was equal to 1. Several semi-variogram methods were performed and further evaluated by the standard error. The best result was achieved by using the Gaussian fit and according to Burrough and McDonnell (1998), this adjust suggests the presence of a smooth spatial variance pattern at the study area.

Results and discussion

Water quality characterization

The limnological variables distribution in both reservoirs was highly distinct (Table 1). The average chl-*a* concentration in BB were much higher in October (413.2 mg m^{-3}) than in May (120.4 mg m^{-3}) compared to Nav where the average chl-*a* did not exceed 7 mg m^{-3} in either season (Table 1). In addition, Nav exhibited very low TSM values with an average of approximately 1 mg l^{-1} compared to BB where it showed significant

seasonal variability with mean TSM of 7.40 mg l^{-1} in May and 21.91 mg l^{-1} in October.

Overall, BB exhibited the characteristics of a hypereutrophic-eutrophic environment and Nav of an oligo to mesotrophic environment. The spatial distribution of TSM and chl-*a* showed a decreasing trend from BB to Nav and the concentration magnitude was affected by the precipitation rate which remained low during the dry season and elevated near the end of the dry season.

The proximity of BB to pollution sources as urban, agriculture and industrial areas might be the cause of this limnological variability. The water from rain runs off roads and chemical treated soil toward the aquatic systems carrying waste and increasing nutrients load. In contrast, Nav is far from urban centers and is mostly affected by agriculture source. The chl-*a*:TSM ratio exhibited low values in Nav compared to BB indicating the dominance of suspended matter in Nav and dominance of phytoplankton in BB.

The Secchi disk depth corroborated with TSM values. In Nav, due to the low suspended sediment, the water was more transparent reaching maximum of 4.80 m and minimum of 2.29 m during the first field campaign. A maximum Secchi depth of 2.30 m was observed during first field campaign in BB and a minimum of 0.40 m during second field campaign. Although our dataset involves only 1-year period, the sample collections covered two specific seasons (rainy and dry) and according to Smith et al. (2014), the main factors responsible for chemical and physical dynamics are water fluctuation and seasonality, and the observations collected for this work suggested a seasonal pattern, also highlighted by Barbosa et al. (1999).

Absorption budget

The relative contribution of phytoplankton, CDOM and detritus relative to the total absorption without the water fraction (a_{t-w}) can be seen in Fig. 2. The wavelengths

Table 1 Descriptive statistics of limnological variables (concentration of chl-*a* and TSM, chl-*a*:TSM ratio, depth and Secchi disk measures) in Nav and BB reservoirs during first (April/May) and second (September/October) field campaigns

		Nav (Apr/May)	Nav (Sep)	BB (May)	BB (Oct)
chl- <i>a</i> (mg m^{-3})	Min-max	2.46–12.56	4.51–9.42	17.75–279.90	263.20–797.80
	Mean $\pm$ SD	6.48 ± 2.52	6.94 ± 1.59	120.4 ± 70.31	413.20 ± 138.01
TSM (mg l^{-1})	Min-max	0.10–2.60	0.50–1.20	3.80–16.30	10.80–44.00
	Mean	1.01 ± 0.62	0.81 ± 0.20	7.40 ± 3.15	21.91 ± 7.04
chl- <i>a</i> :TSM	Min-max	2.47–68.26	4.75–18.57	10.27–28.81	12.93–34.99
	Mean $\pm$ SD	11.49 ± 15.63	9.18 ± 3.66	18.84 ± 6.18	19.56 ± 5.65
Depth (m)	Min-max	5.30–29.60	–	10.00–30.00	8.00–18.5
	Mean $\pm$ SD	16.37 ± 7.96	–	15.33 ± 4.18	12.96 ± 2.80
Secchi disk (m)	Min-max	2.29–4.80	2.45–4.65	0.80–2.30	0.37–0.78
	Mean $\pm$ SD	3.13 ± 0.66	3.35 ± 0.56	1.47 ± 0.42	0.56 ± 0.09

SD standard deviation

Fig. 2 Ternary graphics showing the relative contribution (%) of a_d (m^{-1}), a_{CDOM} (m^{-1}) and a_{ϕ} (m^{-1}) to absorption in three different wavelengths (440, 550 and 675 nm) relative to the 1st field campaign of **a** Nav and **b** BB and 2nd field campaign of **c** Nav and **d** BB

chosen for analysis (440, 550 and 675 nm) characterize the light interaction with particulate matter and dissolved organic material (Babin et al. 2003; Le et al. 2013).

In Fig. 2a, the absorption components in Nav (1st field campaign) influence the absorption property almost equally (black dots) with a slight predominance of detritus with 43 % followed by CDOM with 34 % and phytoplankton with 23 %. The diagram at 440 nm relative to BB (Fig. 2b) (1st field campaign) showed a predominance of phytoplankton with 46 % followed by CDOM (34 %) and detritus (20 %).

At 550 nm, the detritus fraction was more evident in Nav with 51 % while for BB, the components were spread

almost equally in the center of the ternary graphic with a slight dominance of phytoplankton (40 %). A different scenario was observed at 675 nm in both reservoirs, with phytoplankton dominating the absorption in Nav (59 %) and BB (89 %) and noticed by Babin et al. (2003) and Riddick et al. (2015).

The second field campaign displayed a different scenario in both reservoirs. In Fig. 2c representative to Nav, at 440 nm, the samples were also spread within the center zone of the ternary plot indicating that all three absorption coefficients covary somehow. This time, CDOM had 40 % of absorption, followed by detritus 31 % and phytoplankton (29 %). For BB (Fig. 2d), at 440 nm the phytoplankton

component dominated the absorption with 65 %, followed by CDOM (30 %) and detritus (5 %). At 550 nm, Nav was represented by detritus (48 %) while BB had also the dominance of phytoplankton (63 %) and at 675 nm, the phytoplankton had a smooth dominance in Nav with 42 % and in BB, the dominance was also by phytoplankton with 95 %.

In general, the ternary graphic showed clearly the spectral difference in Nav and BB revealing the dominance of phytoplankton at 440, 550 and 675 nm in BB and detritus in Nav at 440 and 550 nm. The graphic also highlighted that BB is very productive water leading us to believe that BB catchment receives a significant amount of nutrient loads from urban, agriculture and industrial activities. On the other hand, Nav showed to be influenced mainly by detritus, however, the magnitude of this predominance is not as prominent as a_ϕ in BB.

According to these findings, the bio-optical modeling in Tietê River must consider different approaches to retrieve water quality parameters in BB and Nav reservoirs, once, the models take into account the specific information about the inherent optical properties and their relation with OACs concentration.

SIOP characterization

The a_ϕ^* spectra in Nav and BB (Fig. 3a, b) during the first field campaign presented the same peaks of absorption at 440 and 675 nm, however, the magnitude variability was different, mainly in blue and red regions. Roesler et al. (1989) found that this variance in spectral shape matches with the blue and red absorption features of chl-*a* and the accessory pigment absorption peaks. The same pattern was also observed during the second field campaign.

According to Bricaud et al. (1995) the a_ϕ^* values tend to decrease with increasing chl-*a* concentrations probably due to package effect. The average of $a_\phi^*(675)$ values for Nav's first and second field campaigns were 0.018 and 0.014 $\text{m}^2 \text{mg}^{-1}$, respectively whilst for BB, the values were 0.007 and 0.004 $\text{m}^2 \text{mg}^{-1}$. Matthews and Bernard (2013) highlighted that the mean value of $a_\phi^*(440)$ is affected by the trophic state of the water decreasing from oligotrophic to hypertrophic classes. In this case, the mean $a_\phi^*(440)$ values related to the first and second field campaigns for Nav were 0.033 and 0.036 $\text{m}^2 \text{mg}^{-1}$ and for BB were 0.011 and 0.006 $\text{m}^2 \text{mg}^{-1}$, which agreed with the previous authors.

Values of a_{CDOM} are independent of trophic status (Matthews and Bernard 2013) and their shapes are very similar to a_ϕ . The variability in a_{CDOM}^* was very low and according to Roesler et al. (1989) this fact is similarly controlled by concentration and compositional changes of

CDOM. The spectral slope of CDOM (S_{CDOM}) depends on the relative proportions of organic matter types and is considered a good proxy to CDOM (Twardowski et al. 2004). In general, the S_{CDOM} varies between 0.01 and 0.02 nm^{-1} (Kirk 1994). In this study, the mean values for the first and second field campaigns for Nav were 0.020 and 0.018 nm^{-1} (Fig. 2c), respectively, whereas for BB, the values were 0.018 and 0.017 nm^{-1} (Fig. 2d), respectively. Those S_{CDOM} values are in accordance with Babin et al. (2003), who found average values ranging from 0.017 to 0.019 nm^{-1} in coastal waters around Europe considering a spectral slope between 350 and 500 nm. Studying reservoirs in Australia, Campbell et al. (2011) found values ranging from 0.016 to 0.019 nm^{-1} , however, using a spectral slope between 350 and 680 nm. Matthews and Bernard (2013) found mean values between 0.014 and 0.017 nm^{-1} in three reservoirs in South Africa using the same spectral interval of Babin et al. (2003).

The a_d^* variability increased from longer to shorter wavelengths, this variance is also determined by both concentration and compositional changes, which means that Nav is highly affected by inorganic particle in relation to BB that presented low variability mainly in the second field campaign (Roesler et al. 1989). The S_d described how fast the absorption decreases with increasing wavelength. Nav's first and second campaigns had mean values of 0.009 and 0.006 nm^{-1} (Fig. 2e), respectively, and for BB the values were 0.007 and 0.008 nm^{-1} (Fig. 2f), respectively. Zhang et al. (2013) also found similar values ranging between 0.006 and 0.012 nm^{-1} in Chesapeake bay, USA, while Campbell et al. (2011) found a narrow range between 0.0080 and 0.0088 nm^{-1} in Wivenhoe and Fairbairn dams in Australia.

The study of the SIOPs can provide information about the land use and land cover properties. As stated by Le et al. (2015), the SIOPs retrieved across the Gulf Coast estuaries were linearly correlated to the proportion of developed land like urban and agriculture. This information is very useful to improve the accuracy of semianalytical models in optically complex waters.

Spatial variability

In general, the $a_\phi^*(440)$ in Nav (Fig. 4a) presented low values compared to BB (Fig. 4d) and for Nav the highest values were observed closed to Bonito River and further upstream (Fig. 4g), and the same pattern was also seen in BB (Fig. 4j). According to Smith et al. (2014), the upstream regions of the reservoirs receive high loads of effluents from different sources of pollution corroborating to the primary production in that region. Overall, the $a_{\text{CDOM}}^*(443)$ presented low variability in both reservoirs

Fig. 3 Graphics illustrating the SIOPs spectrum in two different seasons in Nav and BB. The a^*_ϕ ($\text{m}^2 \text{mg}^{-1}$) related to the **a** 1st field campaign and **b** 2nd field campaign; the a^*_{CDOM} (dimensionless) related to the **c** 1st field campaign and **d** 2nd field campaign; and a^*_d

($\text{m}^2 \text{g}^{-1}$) related to the **e** 1st field campaign and **f** 2nd field campaign. Dotted red lines indicated the data from BB and the solid black line from Nav. For each spectrum, the standard deviation was added to show the sample's variability

and in both seasons. The values were closed to 0.96 (dimensionless) in Nav (Fig. 4b) and BB (Fig. 4e) during first fieldwork; however, the region near to the dam in Nav (Fig. 4h) presented values close to 0.49. The $a^*_d(440)$ varied with season and during the first fieldwork, high values were seen from the center toward the dam in Nav (Fig. 4c) and during the 2nd fieldwork, the highest values were displayed in the center of the reservoir coming from the tributaries (Fig. 4i). BB showed to be homogeneous in both seasons taking into account the range used to depict the $a^*_d(440)$. The 1st fieldwork (Fig. 4f) presented values higher than that from the 2nd fieldwork (Fig. 4m), corroborating to the fact that from the total particulate matter in BB the organic matter was dominant. The variability in catchment state and geomorphology can lead to different SIOP sets for different study areas, in addition the rainfall and runoff pattern were expected to be the reasons of optical change from upstream to downstream reservoirs (Campbell et al. 2011, Alcântara et al. 2016).

Conclusion

In summary, the environments studied here showed optical and limnological differences between each other. Nav was considered an inorganic matter dominated water while BB, a phytoplankton dominated water. The a^*_ϕ values from Nav and BB corroborate with the assumption that at 440 nm the trophic state of the water decrease from oligotrophic to hypereutrophic. Nav presented $a^*_\phi(440)$ values of $0.033 \text{ m}^2 \text{mg}^{-1}$ during first field campaign and $0.036 \text{ m}^2 \text{mg}^{-1}$ during the second field campaign whilst BB, presented 0.011 and $0.006 \text{ m}^2 \text{mg}^{-1}$, respectively. The S_{CDOM} values from both sites were in accordance with other studies developed in coastal waters as well as reservoirs. The same was noticed to S_d , that was included in the range of many studies carried out in coastal waters as well as reservoirs. The results showed that exist somehow a water filtration process along the system and the different optical properties from both sites highlighted that one single model

Fig. 4 Graphics illustrating the spatial variability of SIOP in two different seasons in both reservoirs. In Nav, the $a_{\phi}^*(440)$ depicted the **a** 1st field campaign and **g** 2nd field campaign; the $a_{CDOM}^*(443)$ represented the **b** 1st field campaign and **h** 2nd field campaign; and $a_d^*(440)$ showed the **c** 1st field campaign and **i** 2nd field campaign. In

BB, the $a_{\phi}^*(440)$ depicted the **d** 1st field campaign and **j** 2nd field campaign; the $a_{CDOM}^*(443)$ represented the **e** 1st field campaign and **l** 2nd field campaign; and $a_d^*(440)$ showed the **f** 1st field campaign and **m** 2nd field campaign. Once the a_{CDOM}^* at 440 nm is 1, the diagnostic wavelength was changed to 443 nm

would not be suitable to model the water quality. For future works, new sampling collection will be carried out in order to increase the temporal observation of bio-optical properties along the cascade system.

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