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FERNANDA SAYURI YOSHINO WATANABE

**PARAMETERIZATION OF BIO-OPTICAL MODELS FOR
ESTIMATING CHLOROPHYLL-A CONCENTRATION IN A
TROPICAL EUTROPHIC RESERVOIR**



Presidente Prudente – SP

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TROPICAL EUTROPHIC RESERVOIR**

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Advisor: Prof. Dr. Nilton Nobuhiro Imai

Co-advisor: Prof. Dr. Cláudio Clemente de Faria
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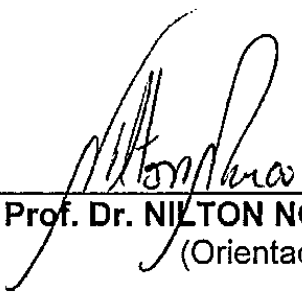
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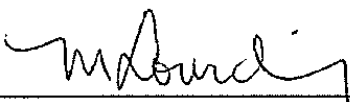
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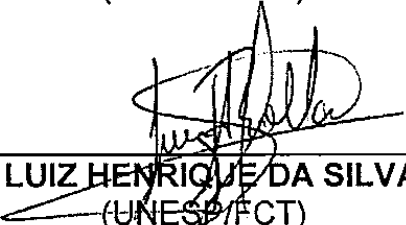
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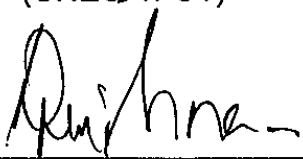
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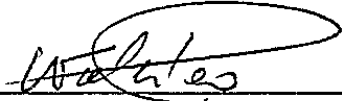
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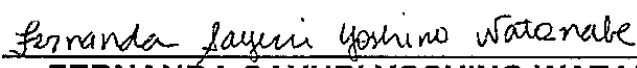
Prof. Dr. LUIZ HENRIQUE DA SILVA ROTTA
(UNESP/FCT)



Prof. Dr. DEEPAK RANJAN MISHRA
(University of Georgia)



Prof. Dr. WATERLOO PEREIRA FILHO
(INPE)



FERNANDA SAYURI YOSHINO WATANABE

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*To my parents,
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(Nikola Tesla)

RESUMO

O objetivo do presente trabalho foi parametrizar e calibrar modelos baseado em dados de sensoriamento remoto para estimar acuradamente a concentração da clorofila-*a*, [Chl-*a*], em um reservatório tropical e eutrofizado. Primeiramente, uma caracterização bio-óptica da área estudo foi realizada para identificar particularidades do ambiente. Então, modelos empíricos e algoritmos quase-analíticos (QAA) existentes foram testados e, posteriormente parametrizados e calibrados para o ambiente investigado. Tais modelos derivam a [Chl-*a*] e propriedades ópticas inerentes (POIs), respectivamente, a partir da reflectância de sensoriamento remoto (R_{rs}). Esta pesquisa foi desenvolvida no reservatório da hidroelétrica de Barra Bonita (RHBB), localizado no Rio Tietê (Brasil). Reservatórios são ambientes artificiais que modificam severamente a hidrodinâmica de rios e o equilíbrio biogeoquímico do ecossistema aquático. Tais alterações podem proporcionar características bio-ópticas únicas ao ambiente e modelos para rios e lagos podem não ser adequados para explicar os processos que ocorrem em reservatórios. O grau de eutrofização é um importante parâmetro de qualidade da água e pode ser determinado com base na [Chl-*a*], pigmento fotossinteticamente ativo presente em todas as espécies de fitoplâncton, detectado por sensores remotos. Portanto, o uso de imagens orbitais e aerotransportadas é uma alternativa viável para o monitoramento do estado trófico desses ambientes. Resultados mostram que as características bio-ópticas em RHBB são consideravelmente diferentes de outros ambientes pesquisados na literatura, corroborado com desempenho não acurado de modelos propostos para outros ambientes. A parametrização e calibração propostas nesta pesquisa estimaram acuradamente a [Chl-*a*], principalmente, adotando os coeficientes de absorção derivados do QAA. Os modelos ajustados podem ser utilizados no mapeamento do estado trófico e monitoramento periódico da qualidade da água em RHBB por agências ambientais e gestores de usinas hidroelétricas. Além disso, é provável que os parâmetros propostos nesta pesquisa sejam adequados para outras águas continentais.

Palavras-chave: Algoritmos quase-analíticos; caracterização bio-óptica; sensoriamento remoto; águas continentais; fitoplâncton

ABSTRACT

The aim of this research was to parameterize and calibrate models based on remote sensing data in order to estimate accurately the chlorophyll-*a* concentration, [Chl-*a*], in a tropical eutrophic reservoir. Firstly, a bio-optical characterization was conducted to identify particularities in the study area. Thus, existing empirical models and quasi-analytical algorithms (QAA) were tested and, after, parameterized and calibrated for the investigated environment. Such models derive [Chl-*a*] and inherent optical properties (IOPs), respectively, from remote sensing reflectance (R_{rs}). This research was developed in the Barra Bonita hydroelectric reservoir (BBHR), lies in Tietê River (Brazil). Reservoirs are artificial environments which change severely the hydrodynamic of rivers and the biogeochemical balance of aquatic systems. Such alterations can lead to unique bio-optical status and, consequently, models developed for rivers and lakes are not suitable to explain the processes which happen in reservoirs. The trophic state is an important water quality parameter and can be determined based on Chl-*a* concentration, photosynthetically active pigment present in all the phytoplankton species and detected by remote sensors. Therefore, the use of orbital and aerial images is a viable alternative to monitoring of trophic state in these environments. Results showed that bio-optical status in BBHR is remarkable different compared to other aquatic systems found in literature, corroborated by inaccurate performance of models proposed to other areas. The parameterization and calibration proposed in this research estimated accurately Chl-*a* concentration, mainly, adopting absorption coefficients derived by QAA. The fitted models can be used in mapping trophic state and frequent monitoring of water quality in BBHR by environmental agency and hydroelectric plant managers. In addition, it is likely that the parameters proposed in this research are suitable for other inland waters.

Keywords: Quasi-analytical algorithms, bio-optical status; remote sensing; inland waters; phytoplankton

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LIST OF ABBREVIATIONS AND ACRONYMS

a or a_t	Absorption coefficient of the total, $a_w + a_\phi + a_{CDM}$
a_{CDOM}	Absorption coefficient of colored dissolved organic matter
a_{CDM}	Absorption coefficient of colored dissolved organic matter and detritus
a_ϕ	Absorption coefficient of phytoplankton pigments
a_{TR}	Absorption coefficient of tripton or detritus
a_w	Absorption of pure water
AOP	Apparent optical properties
b	Scattering coefficient of the total, $b_w + b_p$
b_p	Scattering coefficient of suspended particles
b_w	Scattering coefficient of pure water
b_b	Backscattering coefficient of the total, $b_{bw} + b_{bp}$
b_{bp}	Backscattering coefficient of suspended particles
b_{bw}	Backscattering coefficients of pure water
CDOM	Colored dissolved organic matter
Chl- <i>a</i>	Chlorophyll- <i>a</i>
E_s	Irradiance incident onto the surface
L_r	Reflected radiance by the surface into the direction of the sensor
L_{sky}	Incident sky radiance
L_t	Total radiance
Lw	Water-leaving radiance
OAC	Optically active components
IOP	Inherent optical properties
ISS	Inorganic suspended solids
MAPE	Mean absolute percentage error
MERIS	Medium resolution imaging spectrometer
MODIS	Moderate resolution imaging spectroradiometer
NDCI	Normalized difference chlorophyll- <i>a</i> index
NRMSE	Normalized root mean square error
NTU	Nephelometric turbidity unit
OLI	Operational land imager
OSS	Organic suspended solids

QAA	Quasi-analytical algorithm
R	Irradiance reflectance
R_{rs}	Above-surface remote sensing reflectance
r_{rs}	Below-surface remote sensing reflectance
RMSE	Root mean square error
SAM	Spectral angle mapper
SRTM	Shuttle radar topography mission
TSS	Total suspended solids
u	Ratio of backscattering coefficient to the sum of the absorption and backscattering coefficient
β	Volume scattering function
λ	Wavelength
η	Spectral power for particle backscattering coefficient
ζ	$a_{\varphi}(411)/a_{\varphi}(443)$
ξ	$a_{\varphi}(411)/a_{\varphi}(443)$
S	Spectral slope for colored dissolved organic matter
f	Light field factor
Q	Angular distribution factor

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CHAPTER 1

INTRODUCTION

1.1. Overview

Researches on remote sensing of color waters have been developed for decades and certain concepts are already consolidated, mainly in marine waters. More recently, studies in inland waters have been developed; however, there is much to be investigated, due to optical complexity and particularities of each aquatic environment. Although Brazil has an extensive hydrographic network for all country; few works are found in the literature on optic hydrologic or more robust modeling based on physical fundamentals. Thereby, in this research it was explored a bio-optical, limnologic and radiometric dataset in order to develop models for estimating chlorophyll-*a* (Chl-*a*) concentration in a tropical eutrophic reservoir. The data were collected in the Barra Bonita hydroelectric reservoir (BBHR), a highly productive environment, lies on Tietê River, São Paulo State, Brazil. BBHR is the first one of the reservoirs cascading in the Tietê River and, hence, receives a high charge of effluents, coming from the São Paulo metropolitan region, main responsible for its eutrophication. The bio-optical complexity and water input from two great tributaries were the main challenge to understand and model the Chl-*a* distribution in this research.

1.2. Contextualization

Reservoirs are artificial aquatic environments, built for economic proposes such as power generation, changing the river hydrodynamic and the biogeochemical balance. Eutrophication is a problem commonly detected in reservoirs due to increasing nutrients availability, caused by elevation of the water retention time, becoming reservoirs in propitious environments to algal bloom (CALIJURI *et al.*, 2002). Phytoplankton plays an important role in aquatic ecosystems such as food chain, being associated with carbon cycle and atmosphere carbon sequestration (SAYRE, 2010), due to assimilation of carbon dioxide (CO₂) and storage carbon at the bottom of the oceans (BLAIN *et al.*, 2007; BOYD *et al.*, 2007) and primary productivity (ROESLER *et al.*, 1989). However, reservoirs were appointed as potential emissary of carbon dioxide (CO₂) (COLE *et al.*, 2007; KOSTEN *et al.*, 2010; MABERLY *et al.*, 2013). In reservoirs, the large community of phytoplankton increases the respiration rate (KOSTEN *et al.*, 2010), leading to saturation and emission of CO₂ to atmosphere (COLE *et*

al., 2007), besides other gases such as methane (CH_4) and nitrous oxide (N_2O) (ABE *et al.*, 2003). In addition, some species of phytoplankton yield toxins that can be harmful to aquatic communities and human beings (PEARSON *et al.*, 2010; JU *et al.*, 2014).

Thereby, trophic state monitoring and quantification of phytoplankton are important and it should be conducted frequently by environmental agency, hydroelectric plant managers and water supply companies. Chl-*a* is a pigment present in all phytoplankton species and widely adopted to determine the trophic state. Due to its photosynthetically active status, this pigment can be detected by remote sensors (BUKATA *et al.*, 1995; KIRK, 2011), becoming remotely sensed imagery an important data source for large-scale monitoring (KOPONEN *et al.*, 2002). Hence, traditional techniques of water quality monitoring based on punctual sampling can be replaced by mapping Chl-*a* from remote sensing images (JENSEN, 2007; PALMER *et al.*, 2015). However, to enable the use of images is necessary inverse models suitably fitted.

These models are based on principle that light interacts with certain water components such as phytoplankton pigments, suspended particles (sand, clay among others) and colored dissolved organic matter or CDOM (fulvic and humic acids), responsible by water color. Hence, these constituents are called optically active components (OACs) (MOREL & PRIEUR, 1977). These interactions are represented by absorption and scattering coefficients ($a(\lambda)$ and $b_b(\lambda)$, respectively), called inherent optical properties (IOPs) and depend only on the kind and concentration of OACs (MOBLEY, 1994; KIRK, 2011). On the other hand, radiometric quantities that depend both on the aquatic medium (IOPs) and the directional structure of light field, with regular and stable features, are called apparent optical properties (AOPs). The main AOPs are remote sensing reflectance (R_{rs}) and irradiance reflectance (R) measures (MOBLEY, 1994), commonly used in OACs retrieval models.

Different approaches have been adopted to estimate the water constituents and properties, being them: empirical, quasi-analytical and semi-analytical. Empirical models are based on statistic relationship between the radiometric quantity (R_{rs} or R) and the variable of interest (CARDER *et al.*, 1999; VINCENT *et al.*, 2004; GITELSON *et al.*, 2008). This approach can be quite accurate, but its application is limited to geographic location and date in which the dataset used in calibration were collected (MOSES *et al.*, 2012; LEE *et al.*, 2002). On the other hand, models based on physical principles of light absorption and scattering have been studied to OAC retrieval. However, there is no analytical solution for the radiative transfer equation, being necessary some empirical fits. For this reason, such models are named semi-analytical (HOOGE *et al.*, 1996; BRANDO & DEKKER, 2003;

ORDEMATT et al., 2012). They use data of specific inherent optical properties (SIOPs) of each OACs in order to estimate their concentrations. On the other hand, quasi-analytical algorithms (QAA) have been developed to derive IOPs by each OACs (LEE et al., 2002; LE et al., 2009; MISHRA et al., 2013; 2014; LI et al., 2013, 2015). These derived IOPs are useful to understand the light behavior in water column and associate with biogeochemical, photosynthetic processes, among others (RIDDICK et al., 2015). In addition, $a(\lambda)$ and $b_b(\lambda)$ derived by QAA can be used to retrieve concentrations of OACs.

Several models are found in literature developed for different aquatic environments in the world (CARDER et al., 1999; GITELSON et al., 2008; LEE et al., 2009; MISHRA et al., 2014). Nevertheless, bio-optical status of these locations must be quite different compared to tropical eutrophic reservoirs and, hence, such models should not be suitable for Brazilian reservoirs. So, the hypothesis of this work was that the models proposed in the literature must be fitted to become suitable for applications in tropical eutrophic reservoirs. In this research efforts were concentrated to develop a robust model for this kind of locations and it hopes that results obtained give support to understand the bio-optical status in BBHR and contribute to develop other bio-optical models in inland waters.

1.3. Objectives

The main aim of this research was parameterize and calibrate models to estimate Chl-*a* concentration adopting different approaches for BBHR, lies on Tietê River, São Paulo State.

1.3.1. Specific objectives

The specific objectives of this research were:

- a. To characterize bio-optically the BBHR;
- b. To verify the performance of models fitted for other aquatic ecosystems for retrieving Chl-*a* concentration in the BBHR;
- c. To assess the performance of the empirical and quasi-analytical models fitted using BBHR data for estimating Chl-*a* concentration.

1.4. Thesis Structure

This Thesis was divided in five chapters. Chapter 1 is introductory and contextualizes the themes covered in Chapter 2, 3 and 4. These chapters are structured as scientific papers and each one presents an overview and introduction about the studied target, data and methods used in the investigation, results and discussion, and conclusions. Finally, the Chapter 5 shows a general conclusion about all results obtained in this research and recommendations for future works. Following it is presented a review of which themes discussed at each chapter.

Chapter 2 – Study area

In Chapter it is presented the reservoir where this research was developed. The main physics characteristics of the study area such as area, volume, flow, retention time, weather among others. Furthermore, a brief art study is showed, indicating the main results obtained in several researches developed in this reservoir, associated especially with eutrophication, gases emission and identification of phytoplankton assemblages. In addition, fieldwork details are presented such as sampling point selection and data collected.

Chapter 3 – Variation of the absorption coefficient and its influence to bio-optical modeling in the Barra Bonita reservoir

In Chapter 2 it is briefly discussed the bio-optical status from BBHR, in terms of absorption coefficients, $a(\lambda)$, measured *in situ* and estimated in laboratory. This step is essential to understand the light behavior in the BBHR and identify possible bio-optical particularities, and just then try to quantify OACs and absorption measurements. Without such information it is difficult to justify modeling errors or find alternatives for solving anomalies. $a(\lambda)$ dataset were acquired during two field campaign conducted in May and October, 2014. Data were obtained using a *WET Labs* absorption and attenuation meter (*ac-s*) (*WET Labs*, Inc, Philomath, OR, USA), with 10 cm path length. The instrument works in a spectral range of 400 – 730 nm, with 4 nm resolution precision, accuracy of $\pm 0.01 \text{ m}^{-1}$ and dynamic range of $0.001 - 10 \text{ m}^{-1}$. The *ac-s* measurements were corrected of temperature and salinity effects, both collected by using a CTD sensor, as well as the scattering in the absorption tube of the instrument. Water samples were also collected to quantify the

absorption coefficient spectra by CDOM, phytoplankton pigments and tripton (a_{CDOM} , a_ϕ and a_{TR} , respectively) based on laboratory spectrophotometry. Data analysis was carried out based on statistic descriptive, spectral curves analysis and ternary plots. The last one was particularly important because it allows evaluating the contribution of each OACs in the total $a(\lambda)$ in a specific point from reservoir. a_{CDOM} , a_ϕ and a_{TR} measured in BBHR were compared to data obtained in other environments such as marine waters, rivers, lakes, ponds and reservoirs. Results showed that BBHR exhibited particular bio-optical status, even different from other reservoirs, and they give support for next chapters. More details can be verified hereafter.

Chapter 4 – Assessment of OLI, MERIS and MODIS data and empirical approach for chlorophyll-a concentration retrieval in a tropical eutrophic reservoir

In Chapter 3 it is presented the results obtained with the empirical model calibration for estimating Chl-*a* concentration. For this, three field surveys were carried out to collect calibration (two fieldworks) and validation (one fieldwork) dataset. Radiometric data were acquired to calculate the R_{rs} by using three RAMSES spectroradiometers (TriOS, Oldenburg, Germany). Water samples were collected to estimate the Chl-*a* and total, inorganic and organic suspended solids (TSS, ISS and OSS, respectively) concentrations in laboratory. The bands simulation of the OLI, MERIS and MODIS was carried out from R_{rs} spectra collected *in situ*, and different spectral indexes developed for other environments were tested, taking into account bands of these sensors. The calibration of models between the spectral indexes and Chl-*a* concentration was conducted by least square method. Results of validation showed that NIR-red algorithms are more suitable for BBHR, highlighting two band indexes. All results obtained with empirical models can be verified in Chapter 3.

Chapter 5 – Parameterization and calibration of a quasi-analytical algorithm for tropical eutrophic waters

More robust approach was tested to estimate the Chl-*a* concentration using absorption data derived of QAA. So, Chapter 4 shows the results of existing QAA versions applied to BBHR and details of parameterization and calibration of QAA for BBHR. QAA is very useful to because it derives absorption and backscattering coefficients by each OACs only from R_{rs} (LEE et al., 2002), important for radiative transfer studies and development of analytical

models (RIDDICK et al., 2015). Unfortunately, few researches have been conducted to develop more robust models based on physical principles such as QAA in Brazil, although there is an extensive hydrographic network and water bodies which are used to several human activities. Different QAA versions proposed by other aquatic system were applied to the BBHR; however without accurate performance. Therefore, the aim of the Chapter 4 was to parameterize and calibrate a QAA suited for BBHR and other inland waters with similar bio-optical status. Four remarkable changes were carried out: (a) parameterization of χ that represents the variability of $a(\lambda)$; (b) calibration of absorption coefficient at reference wavelength, $a_0(\lambda)$; (c) parameterization and calibration of ζ , factor associated with absorption by phytoplankton, $a_\phi(\lambda)$; and (d) calibration of the spectral slope by CDOM, S , related directly to ζ , factor associated with the absorption by CDOM. The changes proposed in (a) and (b) to estimated accurately $a(\lambda)$ are very important to derive the other IOPs; however, parameterization and calibration in (c) and (d) present the main contribution of this research, eliminating the estimative of negative values of absorption by phytoplankton and CDOM ($a_\phi(\lambda)$ and $a_{CDOM}(\lambda)$, respectively) yielded by other QAA versions. In addition, models based on $a_\phi(\lambda)$ to estimate Chl-*a* showed results better than models based on R_{rs} .

Chapter 6 – Conclusions and Recommendations

Finally, in the Chapter 5 the general conclusions accomplished based on the results obtained from investigations conducted in all research. Recommendations to future works also are presented, highlighting improvements in QAA and development of a semi-analytical model for eutrophic waters.

CHAPTER 2

STUDY AREA

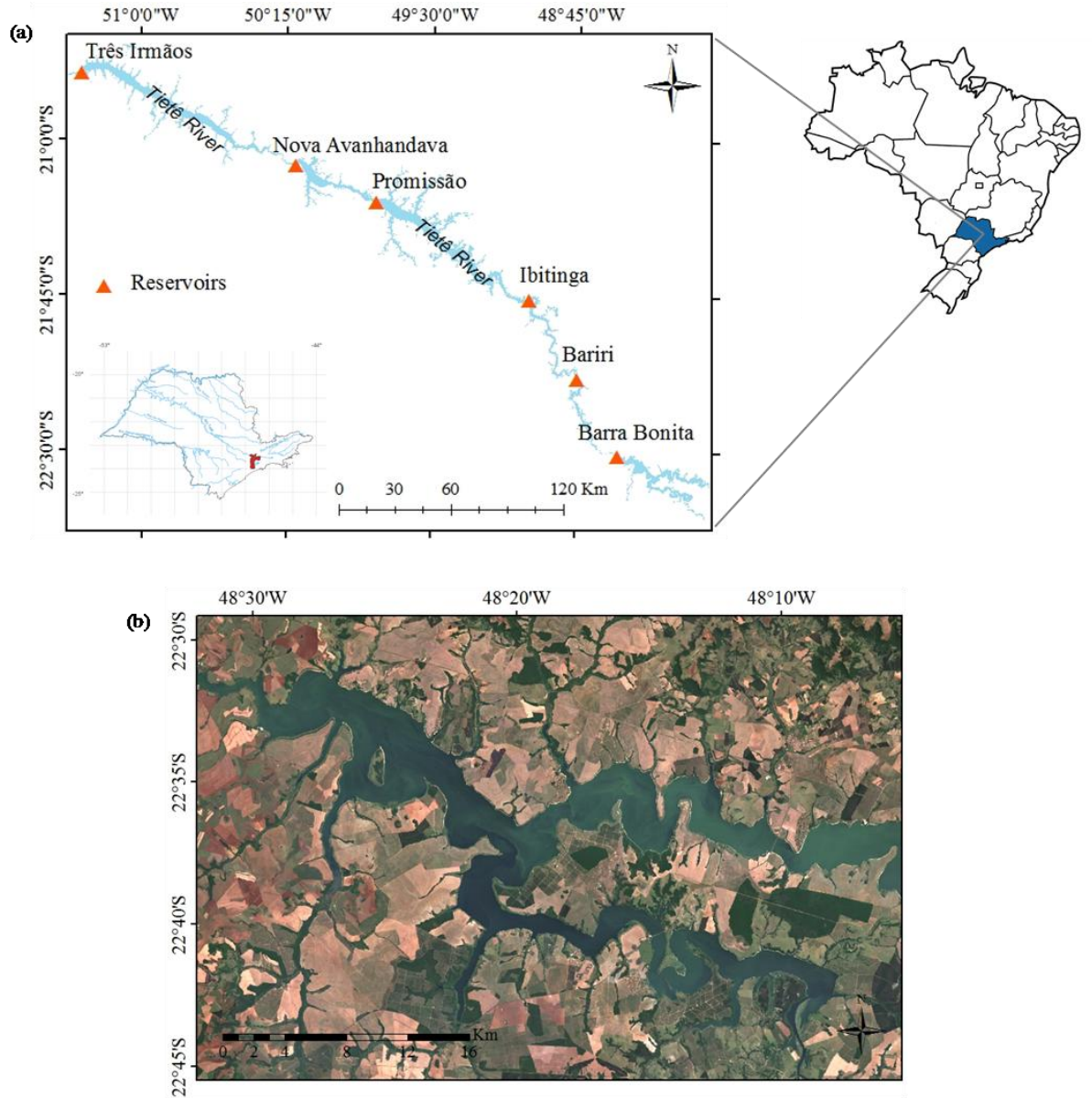
This research was developed in the Barra Bonita hydroelectric reservoir (BBHR) (22° 31' 10" S and 48° 32' 3" W), lies on the middle course of the Tietê River, São Paulo State, Brazil (Figure 1). The dam is located between the cities of Barra Bonita and Igarçu do Tietê and the power plant is administered by the company, operational since 1963 AES Tietê (2015). The dam is located to approximately 300 km downstream of São Paulo city, and 480 km of the river mouth, in Paraná River, between the States of São Paulo and Mato Grosso do Sul, Brazil. The impoundment is not only used for generating electric power, but also for recreation, fisheries, aquaculture, and navigation, among others (PETESSE et al., 2007; TUNDISI et al., 2008).

The BBHR has a flooded area of 310 km² and a volume of approximately 3.622 x 10⁶ m³ (AES Tietê, 2015). The average depth is of 10.2 m with maximum of 25 m (TUNDISI et al., 2008), whereas the quota range is of 439.5 m to 451.5 m (AES Tietê, 2015). The flow range is of 200 m³ s⁻¹ in the dry season (austral winter) to 1,500 m³ s⁻¹ in the wet season (austral summer), influencing the retention time from 30 days (austral summer) to 180 days (austral winter).

The dam was built just after the confluence between the Piracicaba and Tietê Rivers, forming one of the three storage reservoir of the Tietê cascade (ONS, 2013). The BBHR is the first of the six reservoirs cascading in the Tietê River. Therefore, the BBHR presents a high eutrophication level due to the discharge of wastewater coming from the São Paulo metropolitan region and Piracicaba region. BBHR is characterized as highly productive waters and presents a specie richness and high concentration of phytoplankton (CALIJURI et al., 1996; DELLAMANO-OLIVEIRA et al., 2008). The most frequently species of phytoplankton are *M. aeruginosa* and free cells of *Microcystis* sp. (Cyanophyceae), and *Aulacoseira granulata* filaments (Bacillariophyceae) and their variation in space and time are mainly associated with water column mixing events and residence time.

Furthermore, the eutrophication has been associated with the emission of greenhouse gases such as methane (CH₄), carbon dioxide (CO₂) and nitrous oxide (N₂O) in BBHR (ABE et al., 2003; TUNDISI et al., 2008). The production of these gases is related to the processes of decomposition of the organic matter (GILES, 2006), high rate of respiration for phytoplankton (KOSTEN et al., 2010), and denitrification (ABE et al., 2003).

Figure 1. Study area – Barra Bonita hydroelectric reservoir (BBHR). (a) Brazil, highlighting hydrographic network of São Paulo State and location of reservoirs in the Tietê River. (b) True color image (RGB-432) taken from OLI sensor onboard Landsat-8 satellite, acquired on October 13, 2014.



2.1. Weather

The BBHR is located in a transitional region between tropical to subtropical climate (CALIJURI *et al.* 2002), characterized by a dry period between May–October and a wet period between November–April (MATSUMURA-TUNDISI and TUNDISI, 2005). Figure 2 shows meteorological data of total precipitation and wind speed available by National Institute of Meteorology (INMET, 2016).

Figure 2. Meteorological data of (a) total precipitation, (b) wind speed collected in the Barra Bonita stations (INMET, 2016).

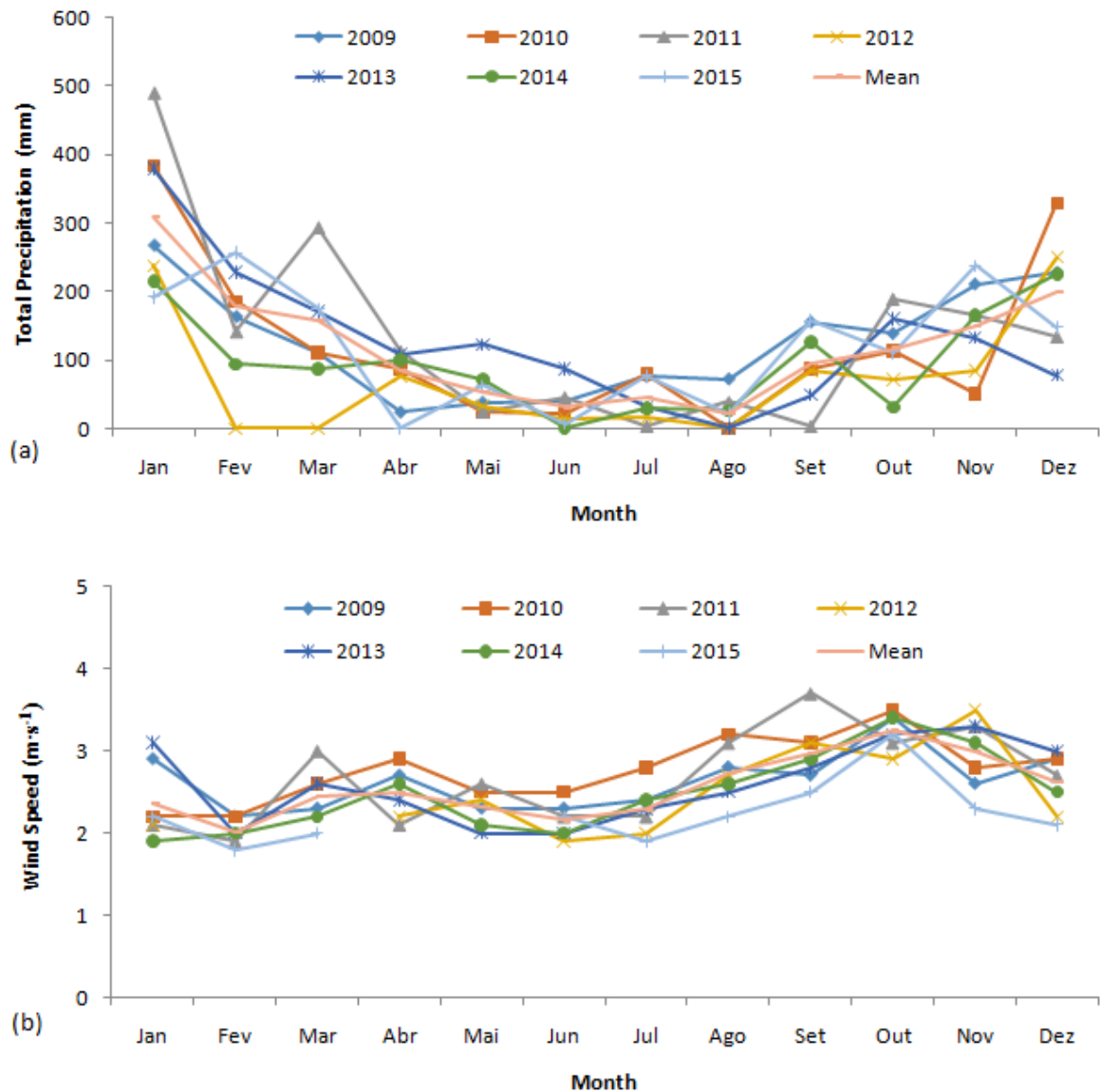
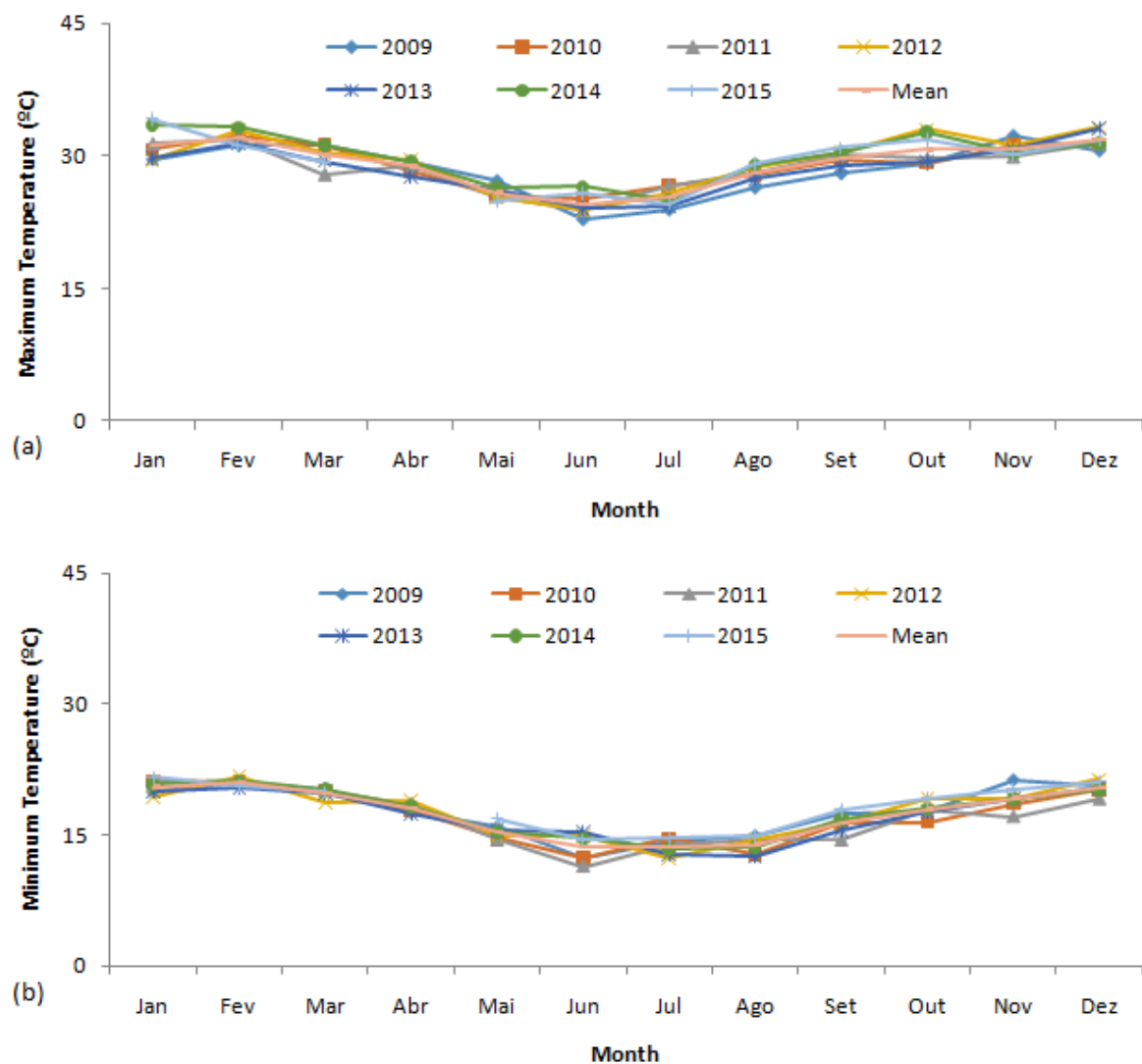


Figure 2a shows that monthly total precipitation between 2009 and 2015, with a mean annual precipitation of 1447.1 mm. The annual precipitation was quite lower than mean in 2012 (874.4 mm) and 2014 (1174 mm), the last one when fieldworks were carried out (INMET, 2016). Overall, seasons of lower precipitation (austral autumn and austral winter) match with lower sunlight incidence. High light intensity can cause inhibition of photosynthesis or, in other words, photoinhibition (Kirk, 2011). Some phytoplankton species such as dinoflagellates and blue-green algae have motion mechanisms which allow their migration to a depth where the light intensity is more suitable to photosynthetic activity (Kirk, 2011). Non-motile species also can change of depth due to currents. Wind is responsible for inducing circulatory currents in the water body in axes approximately parallel to the wind

direction (Kirk, 2011). Fitch and Moore (2007) showed that wind speed affects strongly the phytoplankton blooms dynamics in ice zones. Figure 2b shows that the wind speed observed during seven years, not exceeding $4 \text{ m}\cdot\text{s}^{-1}$. Periods with higher wind speed were austral spring and austral summer.

Figures 3c and 3d show plots of monthly maximum and minimum temperature reported from 2009 to 2015. As expected, the highest temperature occur in austral summer, especially in February (mean temperature of 32°C) and the lowest temperature were observed in austral winter (June and July), with mean temperature around 13°C . The temperature is a variable that strongly influence the phytoplankton community dynamics. Cold fronts promote vertical and horizontal mixture in water column, favoring the growth of determined species (TUNDISI et al., 2010).

Figure 3. Meteorological data of (a) maximum and (b) minimum temperature collected in the Barra Bonita stations (INMET, 2016).



In addition, wind and temperature are responsible for thermal stratification (WETZEL, 2001). There are studies that investigated the relationship between cyanobacteria blooms and thermal stratification (KUMAGAI et al., 2000; TUNDISI et al., 2010; DANTAS et al., 2011). According to Tundisi et al. (2010), cyanobacteria blooms in eutrophic reservoirs are frequently associated with occurrence of thermal stratification and stability of the water column. The BBHR is considered a polymictic ecosystem, affected by fluctuations in rainfall, wind, intrusion of water from tributaries, low retention time during austral summer and density currents due to contribution of two main tributaries (Tietê and Piracicaba Rivers), influencing the horizontal and vertical mixing processes in the reservoir (Barbosa et al., 1999).

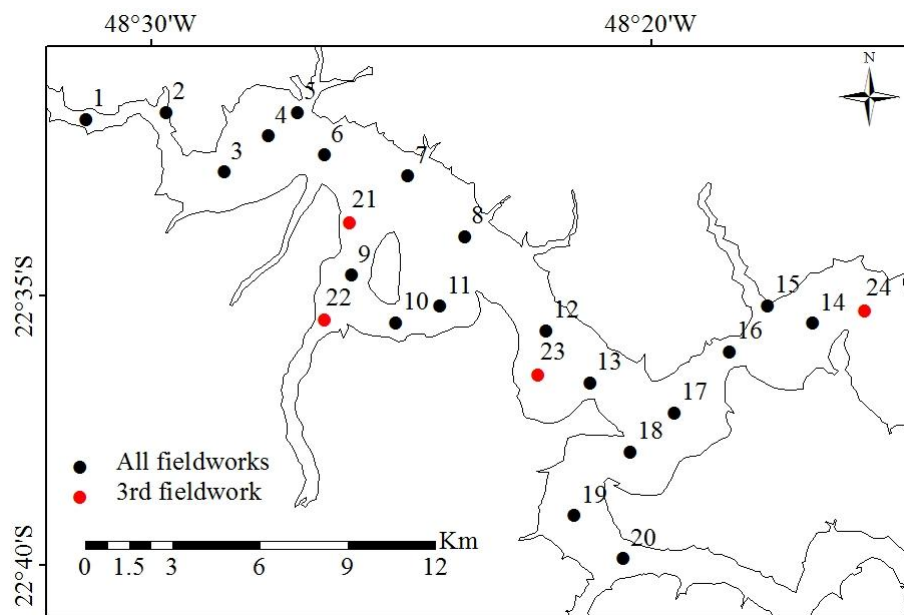
2.2. Fieldwork

Three field campaigns were conducted in BBHR, being two dataset for calibration carried out in 2014 and another independent dataset was collected for validation, in 2015. The fieldworks considered the weather historic of the region. Period of low precipitation and cloudiness were chosen. Cloudiness increase the diffuse sky irradiance, E_{sky} , impairing the quality of the radiometric measurements. In addition, the field surveys were scheduled to coincide with the overpass of the OLI (Operational Land Imager) sensor onboard the Landsat-8 satellite. The first calibration field campaign was conducted on May 5 – 9, 2014 (Austral Autumn). This period was selected for the first field survey because it matched to the beginning of the dry period, but the water still is influenced by the input from the drainage basin. The second calibration field campaign was carried out on October 13 – 16, 2014 (Austral Spring), period in which the water is influenced by all dried period. The validation field survey was carried out on September 13 – 15, 2015 (Austral Winter).

Sampling points were defined using the method proposed by Rodrigues et al. (accepted). The method consists in calculating the variance of an annual image series and stratified random sampling. A time series composed of nine ETM+/Landsat-7 images acquired during one year (August 2002 to June 2003) was used to calculate the variance of the R_{rs} . Before, at-surface reflectance of the images was retrieved using the Fast Line-of-sight Atmospheric Analysis of Spectral Hypercubes (FLAASH) tool. FLAASH uses the MODerate resolution atmospheric TRANsmision (MODTRAN4) code for solving the atmospheric radioactive transfer equation, implemented in software ENVI (ITT, 2009). The at-surface reflectance values were divided by π to convert them into R_{rs} (LI et al., 2013). The stratified

random sampling was applied to the standard deviation image using Hawth's Analysis Tools (GME, Brisbane, Australia), available for ArcGIS® (ESRI, 2016). Fifty one samples were randomly created, being someone removed in order to remain only representative 20 samples of spatial-temporal optical variability in the reservoir, avoiding the concentration of many points in an unique region. Figure 4 shows the 20 common sampling points for all fieldworks and 4 additional points randomly distributed in the BBHR.

Figure 4. Sampling points randomly distributed along the BBHR. Black circle represent common points for all fieldworks, while red circle are the additional sampling points for 3rd fieldwork.



Approximately 5 liters of water samples were collected at each sampling points. The samples were stored in a sterile plastic bottle, cool and in the dark until filtration. Physical-chemical water quality parameters were measured using portable meters. Physical parameters collected were turbidity (NTU – Nephelometric Turbidity Unit), temperature (°C), electrical conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) and Secchi disk depth (m), while chemical parameters were pH (-) and dissolved oxygen concentration ($\text{mg}\cdot\text{L}^{-1}$). Other data such as day and time of the sampling, water column depth, wind speed, photographs, weather conditions (cloudiness, rain, among others) and observations about the water color and land cover in the margins of the reservoir.

Radiometric measurements were acquired using three spectroradiometers RAMSES (TriOS, Oldenburg, Germany). The spectroradiometers were coupled to a metal structure to ensure the correct acquisition geometry. Also, bio-optical data were collected using absorption and attenuation meter, *ac-s* (WET Labs Inc, Philomath, OR, USA). *ac-s*

spectrophometer was remanded to a metal cage together with to a battery, CDT sensor and sensor interface module. CDT sensor (SEA-BIRD Electronic, Bellevue, WA, USA) collected conductivity, depth and temperature data. More details are presented in Chapters 3, 4 and 5.

CHAPTER 3

VARIATION OF THE ABSORPTION COEFFICIENT AND ITS INFLUENCE TO BIO-OPTICAL MODELING IN A TROPICAL EUTROPHIC RESERVOIR

3.1. Background

Natural waters present particles and substances responsible by the alteration of water color, called optically active components (OACs) (MOREL & PRIEUR, 1977). OACs show a great variability of types and concentration and, consequently, the optical properties (MOBLEY, 1994). The optical properties can be classified as inherent and apparent (MOBLEY, 1994; KIRK, 2011; BUKATA et al., 1995). The inherent optical properties (IOPs) depend only on the components present in the aquatic medium and the water itself; therefore, they are not influenced for changes in the angular distribution of the radiant flux (MOBLEY, 1994; KIRK, 2011). IOPs is directly associated with the variability of OACs and their concentrations (MOREL & BRICAUD, 1986). On the other hand, the apparent optical properties (AOPs) depend on the IOPs and the geometric structure of the field light (MOBLEY, 1994; KIRK, 2011).

The light photons are absorbed or scattered by aquatic medium and the magnitude of these processes depend on the composition of water body, and wavelength. The absorption and scattering properties are quantified in terms of the absorption coefficient, $a(\lambda)$, scattering coefficient, $b(\lambda)$, and volume scattering function, $\beta(\lambda)$ (KIRK, 2011). However, for remote sensing of water color only the $b(\lambda)$ fraction in backward directions is of interest, since, only light photons scattering in angle range between 90° to 180° may be detected by a sensor system (KIRK, 2011; MOBLEY, 1994).

The total absorption coefficient in the water column, $a_t(\lambda)$, is the sum of the absorption coefficients of phytoplankton pigments (a_ϕ), colored dissolved organic matter (a_{CDOM}), tripton or non-algal particles (a_{TR} or a_{NAP}), and pure water (a_w) as shown in Equation 1.

$$a_t = a_\phi + a_{CDOM} + a_{TR} + a_w \quad (1)$$

Analogously, $b_b(\lambda)$ is the sum of backscattering coefficient of phytoplankton pigments ($b_{b\phi}$), tripton or non-algal particles (b_{bTR} or b_{bNAP}), and pure water (b_{bw}) as shown in Equation 2. The CDOM contribution in backscattering coefficient is very low, being negligible in the equation (BUKATA et al., 1995).

$$b_b = b_{b\phi} + b_{bTR} + b_{bw} \quad (2)$$

Due to absorption and scattering properties of the water body, the magnitude of radiometric measurements such as radiance and irradiance change with depth (KIRK, 2011). According to Mobley (1994), an AOP must be well behaved, changing slightly with external environmental changes. Rate of change of radiometric quantities with depth and ratios of radiometric quantities compose the class of the AOPs.

Remote sensing reflectance, R_{rs} (sr^{-1}), is an essential AOP for the remote sensing of the water color above surface, widely used in the bio-optical modeling (CARDER et al., 1999; LEE et al., 2002; DALL'OLMO & GITELSON, 2005; GITELSON et al., 2008; LE et al., 2009; LI et al., 2013; MISHRA et al., 2013; 2014). Shape and magnitude of the R_{rs} spectrum are modeled by the ratio of light absorption coefficient to sum of absorption and backscattering coefficients times the ratio of geometry of the light field to angular distribution in aquatic medium as shown in Equation 3 (Gordon et al., 1988).

$$R_{rs}(\lambda) \approx \frac{f}{Q} \cdot \frac{b_b(\lambda)}{b_b(\lambda) + a(\lambda)} \quad (3)$$

where f is associated with the light field and volume scattering function (β) and Q is a parameter accounting for geometrical attenuation of light (GORDON et al., 1975; MOREL & GENTILI, 1991; MOREL & MUELLER, 2003); $a(\lambda)$ is the total absorption coefficient; $b_b(\lambda)$ is the total backscattering coefficient; and λ is the wavelength. Since R_{rs} is directly related to the type and concentration of the OAC in the water body, this has been being used in several models for retrieving the water quality optical parameters.

The effects of the multiple components on the optical properties of natural waters are defined as bio-optical status (SMITH & BAKER, 1978). Optical complexity hampers the extraction of quantitative information about these components (MOREL & PRIEUR, 1977). Knowledge about bio-optical status and understanding about their behavior in an environment are important to an accurate modeling. Thereby, the aim of this work is to investigate the variability of the absorption properties in the Barra Bonita hydroelectric reservoir (BBHR).

3.2. Data and Methods

3.2.1. *In situ absorption measurements*

Absorption and attenuation properties were collected using a *WET Labs* absorption and attenuation meter (*ac-s*) (*WET Labs Inc*, Philomath, OR, USA). A CTD sensor, model 37SI (*SEA-BIRD Electronic*, Bellevue, WA, USA), was used to measure conductivity, temperature and depth. Both instruments were connected to a Data Handler with 4 ports (DH-4) (*WET Labs Inc.*, Philomath, OR, USA). DH-4 is a sensor interface module that allows simultaneous collection, time stamping, storage and merging of data streams from all of the ports. DH-4 was setup using the software *WL Logger Host* (*WET Labs Inc.*, Philomath, OR, USA).

The *ac-s* data were processed using the software *wap34* (*WAP – WET Labs Archive File Processing*) (*WET Labs*, Philomath, OR, USA). This program allows the processing of data files created by DH-4 and sensors developed by *WET Labs*. However, before to use them, the temperature and salinity effects on pure water absorption were removed from the measures (*PEGAU & ZANEVELD*, 1993). The correction was carried out using the method proposed by *Sullivan et al.*, 2006.

The measurements of absorption were corrected due to scattering in the absorption tube of *ac-s* meter, using the protocol proposed by *WET Labs* (*WET Labs*, Philomath, OR, USA). Three methods were tested: flat, proportional and Kirk method (*KIRK*, 1992).

The flat method consists in the subtraction of the measured absorption by absorption value at a reference wavelength (λ_0) where the absorption is assumed to be zero, as shown in Equation 4. On the other hand, the assumption is that the absorption by *OAC's* is negligible at λ_0 and, hence the measured absorption is caused by the scattering error (*WET Labs*, Philomath, OR, USA).

$$a_{Flat} = a_m - a_m(\lambda_0) \quad (4)$$

where a_{Flat} is the absorption corrected by flat method; a_m is the absorption measured by *ac-s* meter; and $a_m(\lambda_0)$ is the absorption value at reference wavelength, λ_0 .

In clear waters such as marine waters, the wavelength at 715 nm is commonly used as λ_0 (*ZANEVELD et al.*, 1994). However, in inland waters the absorption by the *OAC's* is still higher and, therefore, the longer wavelengths need to be used as λ_0 in *ac-s* measures

(LEYMARIE et al., 2010; FERREIRA, 2014; CARVALHO et al., 2015). Although the temperature has influence to absorption by pure water at around 745 nm (ZANEVELD et al., 1994; PEGAU & ZANEVELD, 1993; SULLIVAN et al., 2006), this wavelength was used as λ_0 , since previous studies did not exhibit negative effects to correct absorption in inland waters (Carvalho et al., 2015).

The proportional method proposed by Zaneveld et al. (1994) considers a reference wavelength (740 nm) to determine the proportion of the scattering coefficient to be subtracted from the absorption measures. Scattering coefficient is obtained by subtracting absorption from attenuation (WET Labs, Philomath, OR, USA) as shown in Equation 5.

$$a_{prop} = a_m - a_m(\lambda_0) \cdot \frac{b_m}{b_m(\lambda_0)} \quad (5)$$

where a_{prop} is the absorption corrected by proportional method; a_m is the absorption measured by *ac-s* meter; $a_m(\lambda_0)$ is the absorption value at reference wavelength, λ_0 ; b_m is the scattering coefficient estimated by the attenuation minus absorption measured by *ac-s*; and $b_m(\lambda_0)$ is the scattering calculated from *ac-s* meter at reference wavelength, λ_0 .

The method proposed by Kirk (1992) considers that true absorption coefficient, a_{Kirk} , is the measured absorption coefficient, a_m , minus the product of the measured backscattering coefficient, b_m , and a constant coefficient related to a particular phase function, w (Equation 6). Both a_m and b_m were measured by *ac-s* meter.

$$a_{Kirk} = a_m - w \cdot b_m \quad (6)$$

3.2.2. *Optically active components determination*

Filtration process was accomplished in the same day of the samples collection. Water samples were filtered through Whatman GF/F glass fiber filter, with 0.7 μm size pore and 47 mm diameter, to estimate Chl-*a* and particulate material concentration. A vacuum pressure pump and a filter holder were used in the filtration. Due to high concentration of solids in the BBHR, a considerably small volume (250 ml) was filtered at each filter. Filters with retained material were stored frozen and in the dark until analysis.

Extraction by acetone method was used to estimate Chl-*a* concentration (GOLTERMAN, 1975). Chl-*a* was extracted using a 90% acetone solution. The samples

absorbance was measured at wavelengths of 663 nm and 750 nm using a spectrophotometer and a cuvette with 1cm length path. After, the samples were acidified using a 0.1 N hydrochloric acid (HCl) solution to correct the interference of the phaeophytin. Phaeophytin is degradation product of the Chl-*a* and absorb light at same wavelength of the Chl-*a*. After acidification, the absorbance was measured again at 663 nm and 750 nm.

Total suspended solids (TSS), organic suspended solids (OSS), inorganic suspended solids (ISS) concentrations were estimated by using method proposed by APHA (1998). The glass fiber filters must be prepared before filtration. The filters were previously ignited in muffle furnace at 500°C for 30 minutes, desiccated and weighed to determine the initial filter mass. After filtration, retained material on the filters was dried in an oven at 105°C to 110°C for 12 hours. The filters were desiccated and weighed to obtain the TSS mass from the subtraction of the initial filter mass. The volatile solids were ignited in the muffle furnace at 500°C for 30 minutes. The filters were again desiccated and weighed to obtain the ISS mass from the subtraction of the initial filter mass. Consequently, the OSS mass was determined by subtracting of TSS mass by ISS mass. The TSS, ISS and OSS masses were divided by the filtered water sample volume.

Although dissolved total carbon (DTC), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are not OACs, their concentrations were determined in laboratory. However, a DOC fraction is photoactive, called colored dissolved organic matter (CDOM) (Zhu et al., 2014). Water samples filtered though Whatman GF/F glass fiber filter were refiltered to dissolved carbon analysis. Water samples filtered were sent to laboratory ‘Venturo Análises Ambientais’ (www.venturoanalises.com.br). In the first field survey, dissolved carbon concentrations were carried out for only eleven samples (P1, P4, P7, P8, P9, P10, P11, P12, P14, P15, P18, P20). On the other hand, samples collected in all sampling points were analyzed in the second fieldwork. Water samples were sent to laboratory ‘Instituto Internacional de Ecologia e Gerenciamento Ambiental’ (<http://www.iie.com.br/>).

3.2.3. *IOP laboratory measurements*

3.2.3.1. Absorption coefficients of CDOM

Filtered water through the Whatman GF/F glass microfiber filter, with pore size of 0.7 µm and diameter of 47 mm, was filtered in a Whatman nylon membrane filter, with pore size of 0.22 µm and diameter of 47 mm. Filtered water sample for the second time was used to

estimate the absorption coefficient of the CDOM. The samples set were stored in sterile jars of 100 ml, kept cool and in the dark until the analysis. CDOM optical density (OD) were measured with the samples at room temperature and using UV-Vis spectrophotometer, model UV-2600 (Shimadzu, Kyoto, Japan) and a quartz cuvette with optical path of 10 cm. Optical density was measured in a spectral range of 280 – 800 nm with spectral resolution of 1 nm. Milli-Q water was used as blank reference. Absorption coefficient of the CDOM was derived from OD using Equation 7 (BRICAUD et al., 1981):

$$a_{CDOM} = \frac{2.3OD(\lambda)}{l} \quad (7)$$

where OD is the optical depth of the filtered water at wavelength, λ (nm); and l is the cuvette path length in meters (m).

3.2.3.2. Absorption coefficients of particles, detritus and phytoplankton

Water samples were collected at each sampling points to estimate the absorption coefficients of particles material, detritus and phytoplankton pigments. Water samples were filtered through Whatman GF/F glass microfiber filter, with 0.7 μm pore size and 47 mm diameter. The filters with retained material were stored in sterile jars, kept frozen and in the dark until analysis. Transmittance-Reflectance (T-R) method (TASSAN and FERRARI, 1995; TASSAN and FERRARI, 1998) was used to estimate the absorption coefficients of particle material, detritus and pigments. The reflectance and transmittance measurements were acquired using a UV-Vis spectrophotometer, model UV-2600 (SHIMADZU, Kyoto, Japan), dual-beam mode and integration sphere. The reflectance and transmittance were measured in a range of 280 – 800 nm with a spectral resolution of 1 nm. A Whatman GF/F filter was used as blank reference to correct the multiple scattering effects caused by the glass fiber filter (CLEVELAND and WEIDEMANN, 1993).

The OD of the retained particle sample ($OD_s(\lambda)$) on the filter and measured by the T-R method were converted into the optical density of the suspended particles, $OD_{sus}(\lambda)$ from empirical relationships. To measure the optical density of detritus ($OD_d(\lambda)$), the chemical oxidation of the pigments was carried out using a 10% sodium hypochlorite (NaClO) solution (MITCHELL et al., 2000) and measured T-R again. The absorption by the particles, a_s , and detritus, a_d , were calculated using the relation presented in Equation 8.

$$a_{s,d}(\lambda) = \frac{2.3OD_{sus,d}(\lambda)}{X \cdot C} \quad (8)$$

where OD_{sus} is the optical density of particles on filter; X is the ratio of filtered volume to filter clearance area (m); and C is the particle concentration (mass m^{-3}). The absorption by pigments (a_φ) was obtained by subtracting the a_d from a_p (Equation 9).

$$a_\varphi(\lambda) = a_p(\lambda) - a_d(\lambda) \quad (9)$$

3.2.4. Evaluation of correction methods

Statistics metrics were used to evaluate the absorption measures acquired using *ac-s* meters and corrected: root mean square error (RMSE – Equation 10), normalized root mean square error (NRMSE – Equation 11), and mean absolute percentage error (MAPE – Equation 12). a_t quantified by laboratory spectrophotometry were used as reference measures.

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (t_i - r_i)^2}{N}} \quad (10)$$

$$NRMSE = \frac{RMSE}{r_{\max} - r_{\min}} \quad (11)$$

$$MAPE = \frac{\sum_{i=1}^n \left(\left| \frac{t_i - r_i}{r_i} \right| \right)}{N} \quad (12)$$

where t is the absorption spectrum measured using *ac-s* meter and corrected; r is the absorption spectrum measured in laboratory; n is number of wavelength; and i is the position in the spectrum.

In addition, Spectral Angle Mapper (SAM – Equation 13) was used to compare the absorption measured by *ac-s* meters and obtained in laboratory. SAM determines the similarity level between spectral curves, calculating the angle between them at every

wavelength. This method is not influenced by magnitude of spectrum, taking into account only the shape of the curve (KRUSE et al., 1993).

$$SAM = \cos^{-1} \left(\frac{\sum_{i=1}^n t_i r_i}{\left(\sum_{i=1}^n t_i^2 \right)^{1/2} \cdot \left(\sum_{i=1}^n r_i^2 \right)^{1/2}} \right) \quad (13)$$

3.3. Results and Discussion

3.3.1. Physical-chemical parameters

Table 1 shows the descriptive statistics of physical-chemical parameters of water quality (transparency, turbidity, dissolved oxygen, electrical conductivity, water temperature, and pH), and wind speed collected in the three fieldworks. October exhibited the worst water quality, considering all the parameters adopted in this research. The Secchi transparency indicates eutrophication of BBHR, reflecting the high values of turbidity. In addition, high electrical conductivity values were found at every point, in the three fieldworks, which may indicate pollution of the BBHR.

Few points presented dissolved oxygen concentration lower than $5 \text{ mg}\cdot\text{L}^{-1}$, minimum value suitable for aquatic life. The high values, such as $15.7 \text{ mg}\cdot\text{L}^{-1}$, in October, are associated with the phytoplankton production. On the other hand, during the phytoplankton respiration the dissolved oxygen concentration must be very low. The pH values were next to neutral in almost all of the points, with exception of points located in the Piracicaba River which presented alkaline pH, associated likely with discharge of wastewater or agricultural corrective.

Table 1. Descriptive statistics of physical-chemical parameters of water quality: Secchi disk depth, turbidity, dissolved oxygen, electrical conductivity, water temperature, pH and wind speed. Dataset collected *in situ*, on (a) May, 2014, and (b) October, 2014. Statistics metrics used: minimum value (Min), maximum value (Max), mean, median, standard deviation (SD) and coefficient of variation ($CV = (SD/\text{mean}) \cdot 100$) in %.

a. Calibration dataset collected on May 5–9, 2014, $n = 20$ samples.						
Parameter	Min	Max	Mean	Median	SD	CV
Secchi disk, m	0.8	2.3	1.5	1.4	0.4	26.7
Turbidity, NTU	1.7	12.5	5.2	5.0	2.4	46.2
Dissolved oxygen, $\text{mg} \cdot \text{L}^{-1}$	3.8	12.9	8.2	8.1	2.3	28.0
Electrical conductivity, $\mu\text{S} \cdot \text{cm}^{-1}$	-	-	-	-	-	-
Water temperature, $^{\circ}\text{C}$	24.5	26.9	25.6	25.5	0.7	2.7
PH	7.2	9.3	8.4	8.6	0.7	8.3
Wind, $\text{m} \cdot \text{s}^{-1}$	0.6	4.9	1.8	1.6	1.1	61.1

b. Calibration dataset collected on October, 13–16, 2014, $n = 20$ samples.						
Parameter	Min	Max	Mean	Median	SD	CV
Secchi disk, m	0.4	0.8	0.6	0.6	0.1	16.6
Turbidity, NTU	11.6	33.2	18.6	17.6	5.3	28.5
Dissolved oxygen, $\text{mg} \cdot \text{L}^{-1}$	5.6	15.7	11.5	12.2	3.0	26.1
Electrical conductivity, $\mu\text{S} \cdot \text{cm}^{-1}$	365.8	455.9	408.2	407.2	22.9	5.6
Water temperature, $^{\circ}\text{C}$	24.5	32.1	28.1	28.5	2.2	7.8
PH	7.1	10.1	9.3	9.6	0.9	9.7
Wind, $\text{m} \cdot \text{s}^{-1}$	0.0	5.0	1.5	1.1	1.5	100

3.3.2. Active optically components

Table 2 shows the descriptive statistics of the water quality optical parameters such as Chl-*a* and TSS concentrations as well as OSS/TSS and ISS/TSS ratios, estimated from dataset collected in the fieldwork accomplished in May and October, 2014. Concentration range is very important for calibration of models because it needs to comprise all the variability of the optical component. Hence, calibrated for certain aquatic systems usually do not show satisfactory performance when applied on others. In addition, even models fitted in a certain environment cannot be suitable for a different season.

Table 2. Descriptive statistics of the water quality optical parameters, collected *in situ*, on (a) May, 2014; and (b) October, 2014. Statistics metrics used: minimum value (Min), maximum value (Max), mean, median, standard deviation (SD) and coefficient of variation (CV = (SD/mean)*100.

a. Calibration dataset collected on May 5 – 9, 2014, n = 20 samples.						
Parameter	Min	Max	Mean	Median	SD	CV(%)
Chl- <i>a</i> , mg·m ⁻³	17.7	279.9	120.4	101.3	70.3	58.4
TSS, g·m ⁻³	3.6	16.3	7.2	6.5	3.3	45.8
OSS, g·m ⁻³	2.8	14.7	6.1	5.2	3.2	52.0
ISS, g·m ⁻³	0.2	4.4	1.1	0.9	0.9	78.8
DTC*, mg·L ⁻¹	29.8	46.6	32.3	31.0	4.6	14.1
DIC*, mg·L ⁻¹	8.4	20.9	10.1	9.2	3.4	33.9
DOC*, mg·L ⁻¹	21.3	25.7	22.2	21.9	1.2	5.4
b. Calibration dataset collected on October, 13 – 16, 2014, n = 20 samples.						
Parameter	Min	Max	Mean	Median	SD	CV(%)
Chl- <i>a</i> , mg·m ⁻³	263.2	797.8	428.7	368.9	154.5	36.0
TSS, g·m ⁻³	10.8	44.0	22.0	21.2	7.0	31.8
OSS, g·m ⁻³	10.2	30.4	18.2	18.4	4.8	26.2
ISS, g·m ⁻³	0.6	3.8	2.6	2.8	0.96	37.3
DTC, mg·L ⁻¹	12.9	41.4	24.7	22.3	7.6	34.2
DIC, mg·L ⁻¹	7.8	30.8	14.6	12.7	6.4	50.5
DOC, mg·L ⁻¹	1.04	19.1	10.1	10	3.6	36.2

* Samples collected in only 11 stations.

In May, Chl-*a* concentration ranged from 17.7 mg·m⁻³ to 279.9 mg·m⁻³ (P3 and P19, respectively), with average of 120.4 mg·m⁻³. October dataset yielded a CV of the Chl-*a* concentration lower than May (CV = 58.4% in May, and CV = 36% in October), showing a more homogenous distribution in the BBRH in the second field survey. On the other hand, the Chl-*a* concentration was very higher in October with range of 263.2 mg·m⁻³ to 797.8 mg·m⁻³ (P9 and P3, respectively) and average of 428.7 mg·m⁻³. The minimum value (263.2 mg·m⁻³) obtained in October was practically equal to maximum value (279.8 mg·m⁻³) in May.

Taking into account the Chl-*a* parameter of the method of trophic state classification proposed by Lamparelli (2004) based on Carlson (1977), the sampling points were characterized as eutrophic, supereutrophic and hypertrophic in May; and hypertrophic in October. Although BBRH is classified as an eutrophic aquatic environment, the high concentrations around 700 mg·m⁻³ were not commonly reported in the literature (CALIJURI et al., 2002;

MATSUMURA-TUNDISI & TUNDISI, 2005; DELLAMANO-OLIVEIRA et al., 2008). Low rainfall regime observed in 2014 can be responsible for so high Chl-*a* concentrations.

Even studies conducted in other eutrophic reservoirs, Chl-*a* concentration higher than 300 mg·m⁻³ are rarely achieved. Gitelson et al. (2008) conducted studies in different lakes, reservoirs and rivers (Nebraska, Iowa, Minnesota and Maryland States, USA) with maximum Chl-*a* concentration of 236.5 mg·m⁻³. Campbell et al. (2011) found a maximum Chl-*a* concentration of 42.7 mg·m⁻³ in three Australian reservoirs (Wivenhoe, Fairbairn and Burdekin Falls). The authors showed that turbid reservoirs due to high inorganic sediments load had less phytoplankton biomass. Chl-*a* concentration also did not exceed 285 mg·m⁻³ in American, Australian and Chinese lakes and reservoirs investigated by Li et al. (2013). Lake Balaton and Kis-Balaton (Hungary) presented maximum concentration of 166.51 mg·m⁻³.

In eutrophic Brazilian waters such as Funil reservoir where there is high recharge of sewage in Paraíba do Sul River, the Chl-*a* concentration already reached values a little greater than 50 mg·m⁻³ (OGASHAWARA et al., 2013). Barbosa et al. (2010) reported Chl-*a* concentration of 350 mg·m⁻³ in Lago Grande de Curuai, Amazon River, September 2003. Although there is a high sediment load in the lake, the floodplain dynamic allows algal bloom in this environment. Chl-*a* concentrations as high as those found in BBHR were reported by Mishra et al (2013; 2014). These studies were carried out in fish farming impoundments where the Chl-*a* concentration achieved extreme values of 1376.57 mg·m⁻³. Such values are observed in this kind of impoundments because the water flow is very low or null. Naturally, oceanic and coastal waters have Chl-*a* concentrations lower than 3 mg·m⁻³ (ROESLER & PERRY, 1995). Roesler & Perry (1995) conducted studies in estuarine, coastal and oceanic environments, obtaining a Chl-*a* range of 0.07 mg·m⁻³ to 25.35 mg·m⁻³. Chl-*a* concentration varied from 0.10 mg·m⁻³ to 18.87 mg·m⁻³, in Patagonia Shelf (Ferreira et al., 2013). Ferreira et al. (2014) found an average value of 16.43 mg·m⁻³ in a Brazilian estuarine system in warm waters period.

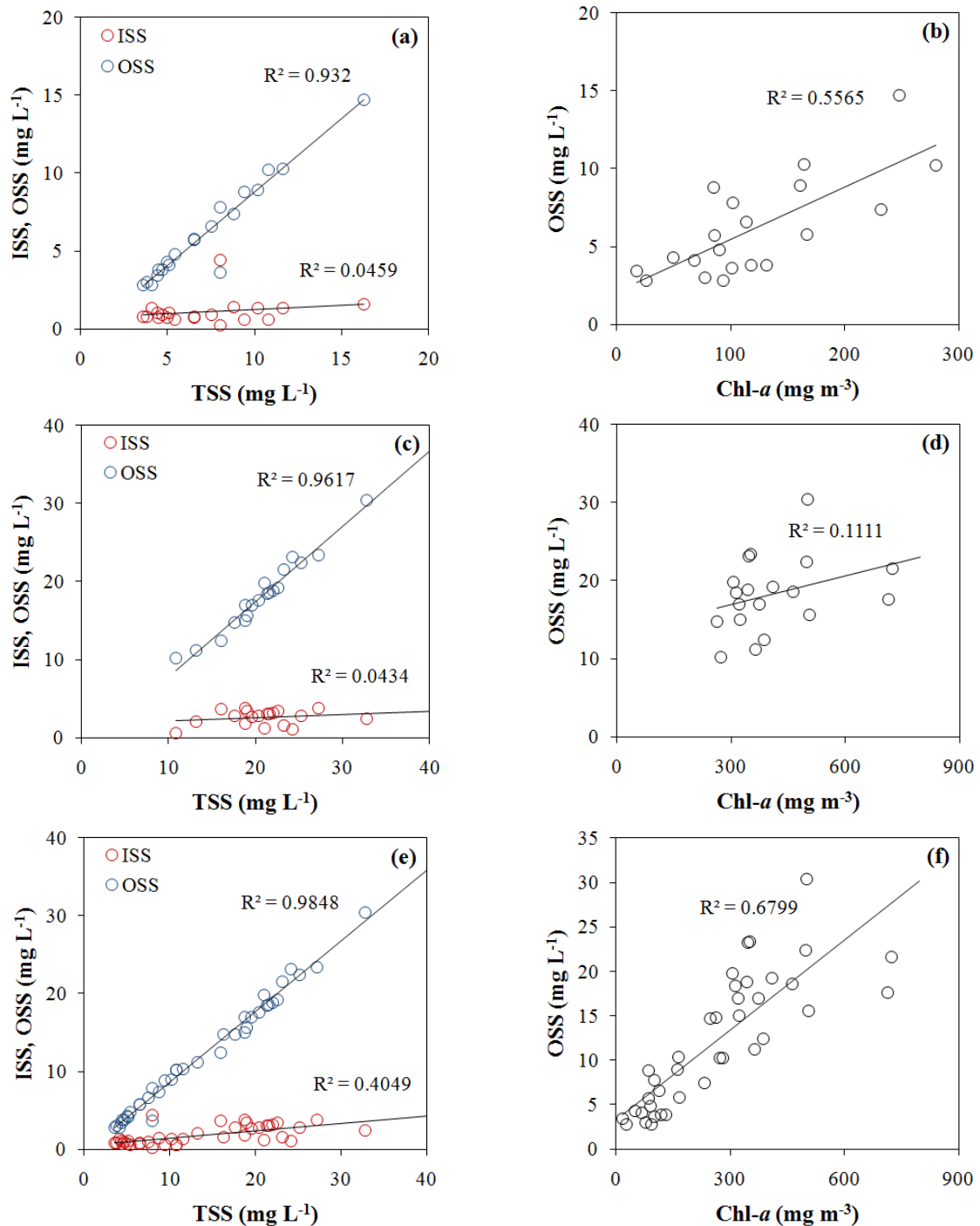
DTC, DIC and DOC concentration were also estimated in both fieldworks. DTC was slightly higher in May (mean of 32.3 mg·L⁻¹) compared to October (mean of 24.7 mg·L⁻¹). In May, DOC was higher than DIC (mean DOC/DTC of 54.5% and DIC/DTC of 31.3%), while in October, the DIC contribution was higher over DTC (mean DOC/DTC of 40.9% and DIC/DTC of 59.1%). The highest DOC contribution in May may be associated with algae decomposition (BUKATA et al., 1995) after algal bloom in the austral summer. On the other hand, the highest DIC contribution in October may be related to lower phytoplankton biomass in austral winter and increase of primary productivity in austral spring, elevating the rate of

respiration (WETZEL, 2001). DOC values obtained in the BBHR is close to observed in other freshwaters as Zhu et al. (2014) reported a DOC range of 3.3 to 17.9 $\text{mg}\cdot\text{L}^{-1}$ for samples collected in the Great Lakes region. In Grande Lago de Curuai, Amazon River, DOC varied from 2.45 to 7.02 $\text{mg}\cdot\text{L}^{-1}$ (Carvalho et al., 2015).

On the other hand, the TSS concentrations were not high compared with other water bodies (Fig. 2). October dataset presented the highest TSS concentrations with average value of 22 $\text{mg}\cdot\text{L}^{-1}$. The TSS range was of 3.6 $\text{mg}\cdot\text{L}^{-1}$ to 16.3 $\text{mg}\cdot\text{L}^{-1}$ in May 2014; and 10.8 $\text{mg}\cdot\text{L}^{-1}$ to 44 $\text{mg}\cdot\text{L}^{-1}$ in October 2014. In aquatic system where there is sediment contribution of floodplain such as Great Lake of Curuai, the TSS concentration can achieve extreme values of 1137.75 $\text{mg}\cdot\text{L}^{-1}$ (BARBOSA et al., 2010). Other reservoirs reached TSS concentration higher than 100 $\text{mg}\cdot\text{L}^{-1}$ (CAMPBELL et al., 2011; GITELSON et al., 2008; LI et al., 2013). Even oligotrophic waters such as the Nova Avanahandava reservoir (TSS = 10.18 $\text{mg}\cdot\text{L}^{-1}$) (CAVENAGHI et al., 2003) and Três Marias reservoir (TSS = 11.93 $\text{mg}\cdot\text{L}^{-1}$) (Ferreira, 2014) already showed values next to measured in BBHR.

TSS concentration is really a relative measure because if we consider the high relation between TSS and turbidity, the water quality can be considered suitable; on the other hand, considering that a mean of 80% of TSS is composed of OSS which can be directly associated with phytoplankton biomass (Fig. 5), BBHR waters does not reach the quality standards. TSS is predominantly composed of OSS in BBHR, where OSS/TSS ratio varied from 45% to 97.5%, with average of 83.7% in May, while a range of 78% to 96% and average of 87% in October (Tab. 2). In October, there was a decreasing the CV (13.5% to 5.7%), however, the OSS portion increased in relation to ISS. In May, TSS explained 93.2% of the OSS, while in October this percentade is greater (96.2%). For both filedworks data, the percentage increased to 98.48%.

Figure 5. Data of TSS, ISS, OSS and Chl-*a* concentration collected in calibration field surveys. Plots of (a) TSS versus ISS and OSS; and (b) Chl-*a* versus OSS for May; (c) TSS versus ISS and OSS; and (d) Chl-*a* versus OSS for October; (e) TSS versus ISS and OSS; and (f) Chl-*a* versus OSS for both dataset.



The relationship between OSS and Chl-*a* concentrations was considerable, with R^2 of 67.99% for May and October dataset together. The relation was very smaller in October ($R^2 = 11.11\%$) than May (55.65%). Overall, none of the aquatic systems (ROESLER & PERRY,

1995; CAVENAGHI et al., 2003; GITELSON et al., 2008; CAMPBELL et al., 2011; LI et al., 2013; BARBOSA et al., 2010; OGASHAWARA et al., 2013; FERREIRA et al, 2013, 2014; FERREIRA, 2014) presented Chl-*a* range similar to BBHR, not covering the minimum and maximum values. Even at locations where the Chl-*a* range were similar, the TSS range were totally different. TSS tend to increase the reflectance at red spectrum, masking pigment features. Then, models calibrated for these aquatic system must not be suitable when applied on BBHR.

3.3.3. Absorption coefficients – in situ measurements

The absorption and backscattering properties are important because define the shape and magnitude of the R_{rs} . Table 3 show the assessment of the correction method for the scattering error of reflecting tube absorption meter. Overall, the flat method showed the best performance to correct the scattering both in May (NRMSE = 7.07%, MAPE = 27.13% and SAM = 0.1 rad) and October (NRMSE = 22.19%, MAPE = 57.47% and SAM = 0.16 rad).

Table 3. Evaluation of the correction method for the scattering error of reflecting tube absorption meter applied on the dataset collected in May 2014

a. Evaluation of the correction methods, May 2014 dataset			
Method	NRMSE (%)	MAPE (%)	SAM (rad)
Flat	7.07	27.13	0.10
Proportional	7.48	29.20	0.10
Kirk	8.49	45.22	0.11
b. Evaluation of the correction methods, October 2014 dataset			
Method	NRMSE (%)	MAPE (%)	SAM (rad)
Flat	22.19	57.47	0.16
Proportional	22.51	58.45	0.14
Kirk	80.67	412.63	0.35

Due to similar results obtained for Flat and Proportional methods, a comparison using Test-t was applied, noting that the models produced different results and, therefore, Flat method is the most suitable for application in BBHR. Although the Kirk's method is the most recommended for turbid waters, the other methods kept the best shape and magnitude for the

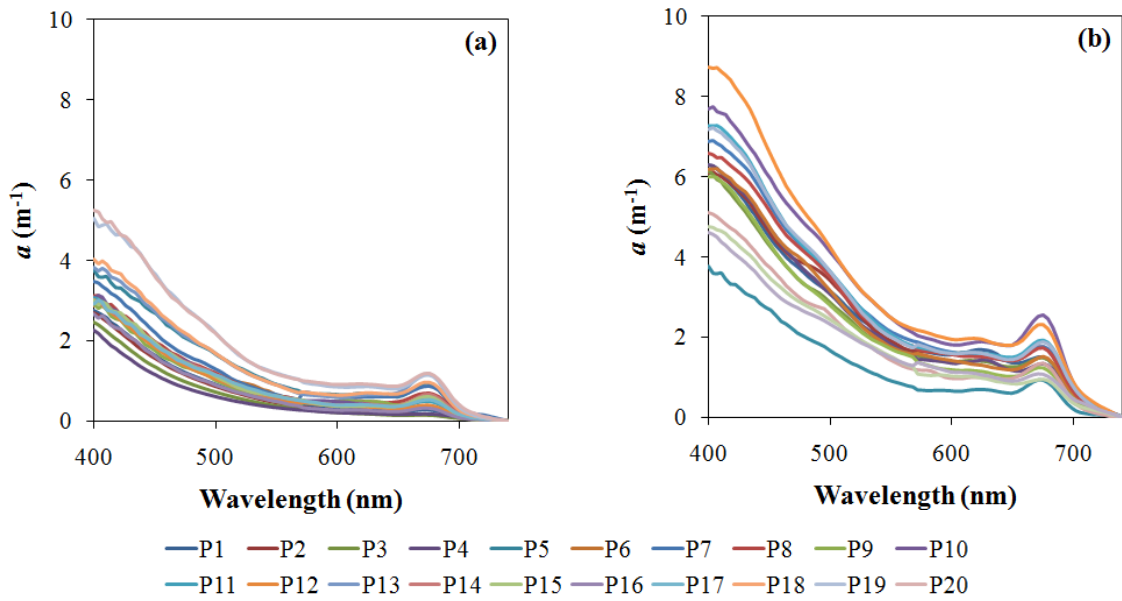
$a(\lambda)$ spectrum. All the tested methods presented a better performance for May dataset, when Chl-*a* and TSS concentrations are lower.

In Lago Grande de Curuai, Carvalho et al. (2015) obtained the best results using the method proposed by Kirk (1992), varying widely the w values. The researchers considered that the assumption of zero absorption at λ_0 by proportional and flat method is not reliable, due likely to the great absorption values caused by high TSS concentration. On the other hand, Ferreira (2014) opted by proportional method in his research in the Três Marias reservoir, due to clear water characteristics.

After absorption tube correction, the $a(\lambda)$ (m^{-1}) measurements can be used to analyze the reservoir. Figure 6a and 6b show the $a(\lambda)$ spectra acquired in May and October, respectively. In general, the magnitude of the $a(\lambda)$ spectra was higher in October than May, associated mainly with the increase of phytoplankton pigment concentration. P19 and P20 presented the highest absorption coefficients values in the May 2014 dataset (see location in Figure 4). These points are located in Tietê River before confluence with Piracicaba River, where color characteristics are very different of the reservoirs sectors. The highest values of Chl-*a* concentration are found in these points, with values higher than $200 \text{ mg}\cdot\text{m}^{-3}$. On the other hand, in May, P5 also exhibited high Chl-*a* concentration of $247.9 \text{ mg}\cdot\text{m}^{-3}$, but it is not highlighted in the ac -s measurement, indicating the influence of other OACs over $a(\lambda)$. A particular characteristic of P19 and P20 is the dark water color, but not muddy, indicating presence of CDOM that strongly absorb the light at shorter wavelength as shown in Figure 6.

Analyzing the spectra, $a(412)$ varied from 1.93 m^{-1} to 4.95 m^{-1} , in May, whereas, in October, the variation was from 3.52 m^{-1} to 8.58 m^{-1} . Overall, these values are representative of complex waters. Carvalho et al. 2015 obtained $a(412)$ values from 8 m^{-1} to 17 m^{-1} , in highly turbid waters (Lago Grande de Curuai, Amazon River, Brazil). The average TSM concentration was of $9 \text{ mg}\cdot\text{L}^{-1}$, with turbidity variation from 90 NTU to 1645 NTU. In highly productivity waters, the $a(\lambda)$ achieves values very high as $a(443)$ of 19.9 m^{-1} (MISHRA et al., 2014), while maximum $a(443)$ was of 7.08 m^{-1} in BBHR. On the other hand, oligotrophic environments have shown lower values. Ferreira (2014) obtained low values of $a(\lambda)$ for Três Marias Reservoir, upper São Francisco River, Brazil, with $a(412)$ maximum values of approximately 1.5 m^{-1} . In this reservoir the TSM concentration varied from $1.33 \text{ mg}\cdot\text{L}^{-1}$ to $11.93 \text{ mg}\cdot\text{L}^{-1}$, while the turbidity was of 0.1 NTU to 24.1 NTU. Roesler (1998) observed maximum $a(412)$ less than 2 m^{-1} for oceanic waters.

Figure 6. Total absorption coefficient spectra measured just below surface for every sampling point using an *ac-s* meter in (a) May and (b) October 2014.



3.3.4. Absorption coefficient – laboratory

Understanding the contribution of each component to total absorption coefficient is important to select the more suitable bands (parameterization) of bio-optical models. The laboratory spectrophotometry allows determining the absorption coefficient for each AOC. Figure 7a and 7b show the a_{CDOM} spectra for May and October 2014, respectively. We observed a significant increase of the $a_{CDOM}(\lambda)$ values from May (mean $a_{CDOM}(412) = 1.28 \text{ m}^{-1}$; mean $a_{CDOM}(440) = 0.79 \text{ m}^{-1}$) to October (mean $a_{CDOM}(412) = 1.74 \text{ m}^{-1}$; mean $a_{CDOM}(440) = 1.11 \text{ m}^{-1}$). In May, samples collected in P19 and P20 exhibited the highest values for a_{CDOM} and DTC ($39.8 \text{ mg} \cdot \text{L}^{-1}$ and $41.4 \text{ mg} \cdot \text{L}^{-1}$, respectively), probably, result of phytoplankton decomposition and high load coming from the São Paulo metropolitan area, respectively. The high a_{CDOM} values must masked Chl-*a* spectral features, mainly, at blue region and, consequently, impaired the Chl-*a* modeling. In general, $a_{CDOM}(\lambda)$ measured in BBHR was very higher compared with marine waters, since freshwaters receive CDOM contribution of allochthonous sources (input of terrestrial material) (BUKATA et al., 1995). Roesler et al. (1989) reported an $a_{CDOM}(440)$ range of 0.2 m^{-1} to 0.39 m^{-1} for marine and coastal waters.

Analyzing the Figure 7c and 7d, $a_{TR}(\lambda)$ spectra was higher in May than October. $a_{TR}(440)$ range was of 0.32 m^{-1} to 0.80 m^{-1} , with average value of 0.47 , in May, whereas $a_{TR}(440)$ presented a higher variability in October, with a range of 0.12 m^{-1} to 0.85 m^{-1} and average of 0.24 m^{-1}). The samples collected in the Tietê River before confluence with the

Piracicaba River (P17, P18, P19 and P20) exhibited the highest values for a_{TR} as well as the most different shapes for both May and October. These characteristics may be associated with the input of sediments coming from the basin of the lower course of Tietê River. Also it must be highlighted that in general a_{TR} decreased in most of sampling points from May to October, with exception of P17 to P20. In addition, it was noticed remarkable decreasing from upstream to downstream.

Figure 7e and 7f show the absorption coefficient spectra for phytoplankton pigments, $a_{\phi}(\lambda)$. It is notable that $a_{\phi}(\lambda)$ was lower in May, explained by the lower Chl-*a* concentrations observed in this period. It is clear a higher absorption in the blue region, highlighting two absorption peaks at 412 nm and 440 nm (CARDER et al., 1999), followed by absorption at red region and a slight absorption peak of Chl-*a* is also observed at 490 nm. October P3 (green line) presented the greatest values of a_{ϕ} , mainly, at blue and red regions. P3 is located before narrowing the channel close to the dam. On the other hand, P18 and P20 exhibited the smallest values of a_{ϕ} . P20 is located in the Tietê River before confluence with the Piracicaba River, while P18 found exactly in the confluence. P19 presented intermediate values of a_{ϕ} ; however, it exhibited a increase of a_{ϕ} between 443 nm and 490 nm that is not observed in the other a_{ϕ} spectrum. This reservoir section presented the most different bio-optical status, where the high DTC concentration interferes in the development of phytoplankton communities. In terms of shape, P5 (blue line) collected in October (Chl-*a* = 313.4 mg·m⁻³) showed one of the most different spectral curves with flattening, similar to that caused by package effect. Taking into account the Chl-*a* concentration, it was not expected a flattening very strong which must be associated with phytoplankton specie (structure and pigment composition).

There is a marked high absorption peak at 675 nm, associated with maximum Chl-*a* absorption in the red region of the spectrum. Absorption feature of phycocyanin pigment is visibly clear at 620 nm (WEAVER & WRIGLER, 1994). In October dataset, all of these features were more marked. Overall, $a(\lambda)$ values are more modest in ocean, coastal and estuarine waters. Roesler et al. (1989) obtained an $a_{\phi}(440)$ range of 0.03 to 0.58 m⁻¹. Ferreira et al. (2013) obtained an $a_{\phi}(440)$ average of 0.20 m⁻¹ in Patagonia Shelf.

Figure 7. Measurements in laboratory of the a_{CDOM} of (a) May and (b) October; a_{TR} of (c) May and (d) October; and a_ϕ of (e) May and (f) October.

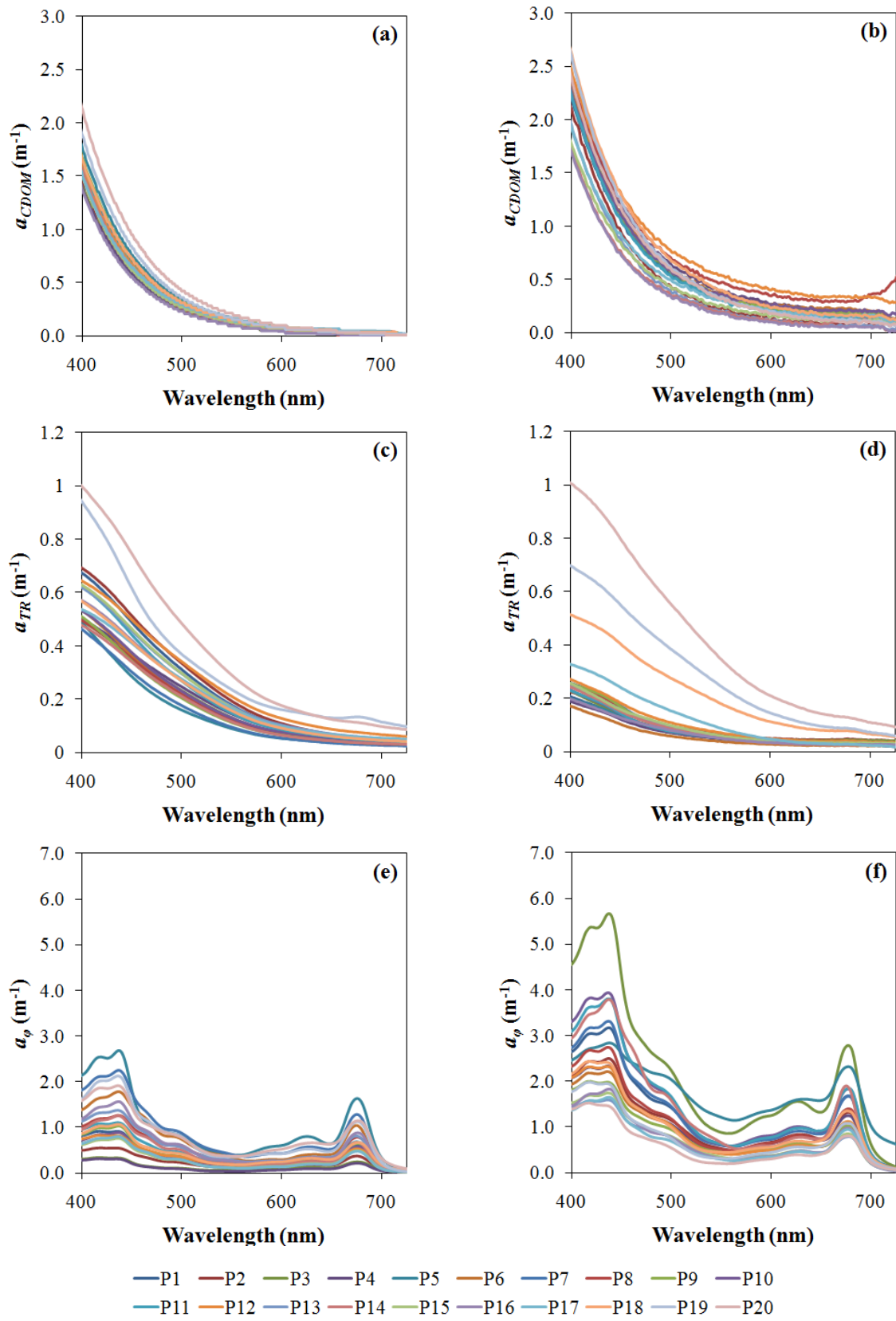
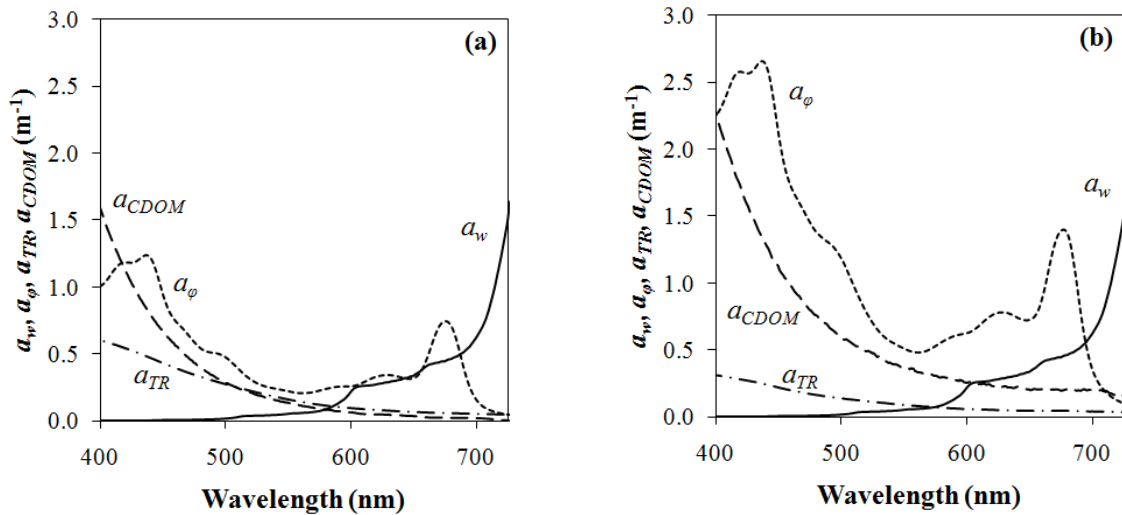


Figure 8a and 8b show the average of a_ϕ , a_{TR} and a_{CDOM} for May and October 2014, respectively. Overall, the total absorption coefficient is mainly influenced by a_ϕ in both field campaign. There were an $a_\phi(440)$ of 1.21 m^{-1} and an $a_\phi(675)$ of 0.74 m^{-1} . With exception of the a_{TR} , the other components increased in October in relation to May. In May it is observed a slightly higher influence of the CDOM over total absorption coefficient at the first shorter wavelengths. There are almost an overlap between a_{TR} and a_{CDOM} from 500 nm, approximately. In October, the elevation of the $a(\lambda)$ happened due mainly to increasing the phytoplankton contribution, higher at all the analyzed wavelength, with a average $a_\phi(440)$ of approximately 2.85 m^{-1} and average $a_\phi(675)$ of about 1.46 m^{-1} . On the other hand, it was checked out a decrease of the tripton contribution in relation to May.

Figure 8. Average absorption coefficient spectra for pigments, CDOM and tripton measured in (a) May and (b) October fieldworks from laboratory spectrophotometer.

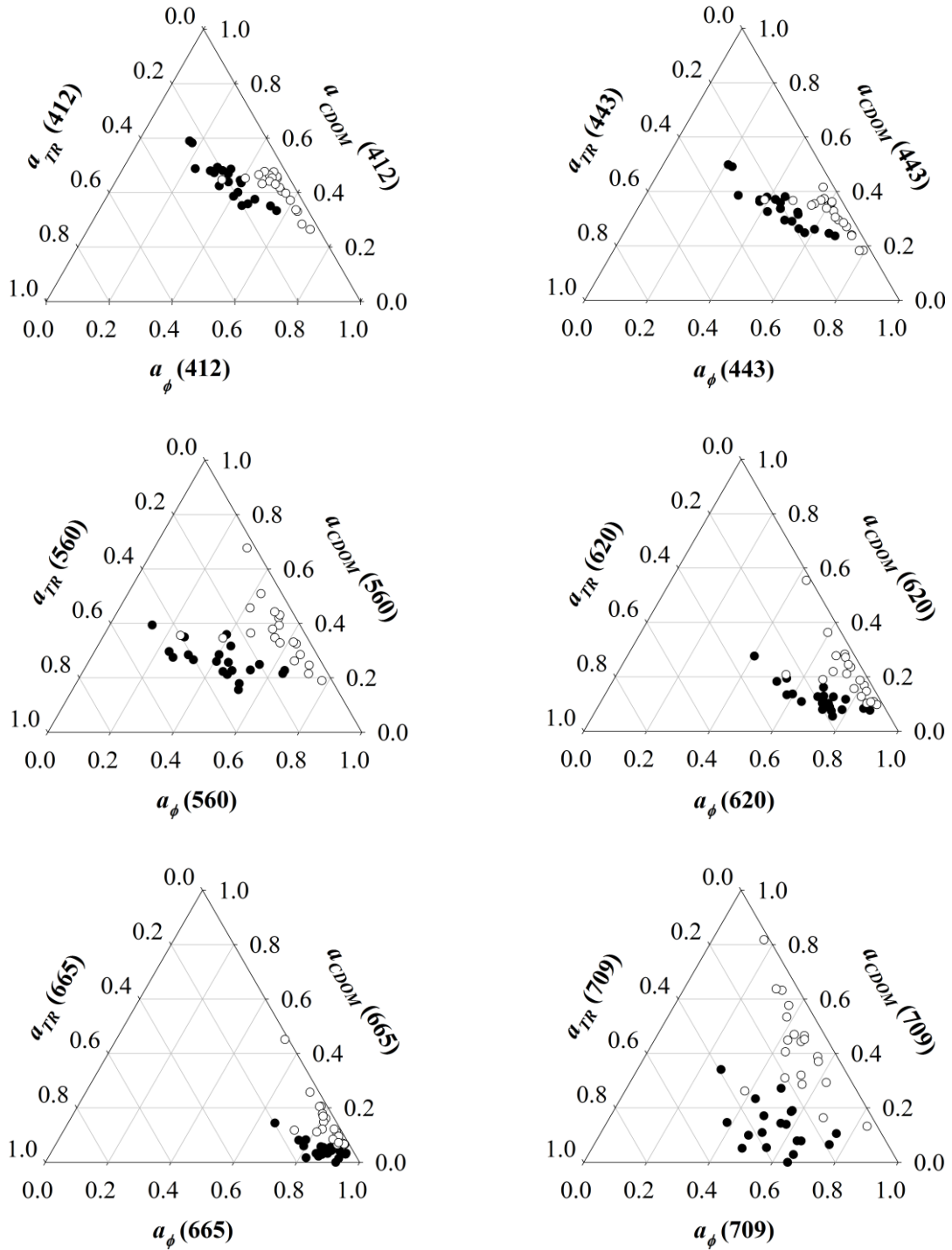


From 690 nm, $a_w(\lambda)$ presents the highest contribution for May field survey. On the other hand, in October, this edge is shifted to right at 710 nm. This information is important to point the wavelengths where there are low contribution for OACs. These wavelengths are widely used in order to minimize the influence of a OAC over other (LE et al., 2009; MISHRA et al., 2014; MATSUSHITA et al., 2015).

Figure 9 shows the ternary plots of absorption budget proposed by Prieur & Sathyendranath (1981) to analyze the contribution of each absorption component. Besides pointing the absorption bands, this kind of plots allows identifying the contribution of more than one component at the same wavelength (BABIN et al., 2003; RIDDICK et al., 2015). Triangular diagrams were plotted for six wavelengths (412, 443, 560, 620, 665 and 709 nm),

associated with absorption or reflectance for pigments or CDOM, and commonly used in models of retrieving Chl-*a* concentration.

Figure 9. Ternary plot showing the contribution of absorption coefficient (a) 412 nm, (b) 443 nm, (c) 560 nm, (d) 620 nm, (e) 665 nm and (f) 709 nm, being May data represented by filled circle and October data by unfilled circle.



May and October dataset were plotted in the same graphic to show the difference between the two periods. Overall, the October data presented larger dispersion than May, being that a_ϕ was the greatest contributor and a_{TR} the smallest. Analyzing the ternary plots, absorption behaved similarly at 412 nm and 440 nm and presented greater contribution of a_ϕ and a_{CDOM} . a_{CDOM} exhibited higher contribution at 412 nm (44.2% in May and 41.3% in October), while a_ϕ was higher at 440 nm (45.7% in May and 61.9% in October). In general, the contribution of a_{TR} is very small, however, higher in May with 19.5% at 412 nm and 20.6% at 443 nm). In October, contribution of a_{TR} did not exceed 10%, with exception of two samples collected in P19 and P20. P18 and P20 presented a smaller contribution of a_ϕ than the other points, corroborating with particular bio-optical status checked out in a_ϕ , a_{CDOM} and a_{TR} spectra for points in Tietê River before confluence.

The variation of the contribution was high at 560 nm, where it is observed the minimum absorption in all the visible spectrum (mean contribution of $a_\phi = 41.9\%$, $a_{CDOM} = 26.3\%$ and $a_{TR} = 31.7\%$ in May; and $a_\phi = 53.7\%$, $a_{CDOM} = 36.5\%$ and $a_{TR} = 9.8\%$ for October) (Fig. 9c). However, the greatest variability was observed at 709 nm, (Fig. 9f), wavelength strongly absorbed by pure water and, therefore, features in this region are associated with reflectance peak of Chl-*a* and TSS. Thereby, this wavelength has been widely adopted in Chl-*a* indexes in order to enhance the features of this pigment (GITELSON et al., 2008; LE et al., 2009; MOSES et al., 2012; LI et al., 2013; MISHRA et al., 2013; 2014).

The a_ϕ contribution was higher at 620 nm (mean of 68.8% in May and mean of 73.1% in October), absorption feature associated with phycocyanin pigment. Therefore, the contribution of phycocyanin must be taken into account in models for estimating a_t (Fig. 9d). Wavelength at 665 nm showed the lowest variation, with mean a_ϕ contribution of 85.7% in May and 82% in October, indicating suitability for developing bio-optical models in BBHR (Fig. 9e).

Some results obtained in BBHR were consistent with the portions found by Riddick et al. (2015) such as greater a_{CDOM} contribution at 440 nm, wider range of composition at green region, and remarkable a_{CDOM} contribution at wavelengths dominated by phytoplankton pigments (620 nm and 665 nm). According to Riddick et al. (2015), inland waters exhibit higher variations in the contributions of the COAs absorption to $a(\lambda)$ than ocean waters. Nevertheless, Babin et al. (2003) reported a wide range of each absorption component for samples collected in Mediterranean, Adriatic and North Seas.

3.4. Conclusions

From measures acquired in situ and in laboratory allow analyzing the bio-optical status of the BBHR waters. In summary, the BBHR exhibited a wide bio-optical variability, showing its optical complexity. The high pollutants load discharged in the reservoir grants a unique bio-optical status for BBHR. There were notable differences between bio-optical characteristics of the dataset collected in May and October 2014, showing the influence of the seasonality to bio-optical status. Not only there was great variability from first to second field survey, but also among the sample dataset of each campaign. The coefficient of variation was higher in May, on the other hand, the AOCs concentrations and IOPs were remarkable greater in October. After intense rainfall period (austral summer), bringing a high load of sediments and nutrients and promoting mixture of water mass, in May (the end of rainfall period), the reservoir undergoes a stabilization period (sedimentation, algal development, horizontal stratification, among others). On the hand, in October, the beginning of rainfall (bringing nutrients from watershed and resuspension) and the high temperature promote algal bloom in the entire reservoir.

Overall, the region of Tietê River before confluence with Piracicaba River exhibited the most different bio-optical status in relation to the rest of the reservoir. The main difference was observed in relation to a_{TR} which presented the highest values from P17 to P20, highlighting data collected in October when most o points exhibited low a_{TR} values. In addition, in May, the greatest values of a_{CDOM} were observed in P19 and P20, while a_{ϕ} presented intermediate values. In October, P18 and P20 exhibited the smallest values of a_{ϕ} , although both the points have presented high values of Chl-*a* of $713.7 \text{ mg}\cdot\text{m}^{-3}$ and $387.2 \text{ mg}\cdot\text{m}^{-3}$, respectively. Such particular characteristics must impair the Chl-*a* retrieval using a model fitted for the entire reservoir. In analogous situation, it is recommended the modeling in regional scale (Babin et al., 2003; Riddick et al., 2015).

In addition, BBHR exhibited bio-optical state considerably different compared with other aquatic environments. Likely, bio-optical models developed for this environments must not be suitable in BBHR. The analysis of the absorption by each OAC provide to choice the suitable bands for parameterization of algorithms. BBHR presents some specific characteristics. As expected for inland waters, a_{ϕ} undergoes high interference of absorption by other OACs at blue region. On the other hand, wavelength at 675 nm (red spectrum) separated the a_{ϕ} of other components. Likely, models for retrieval Chl-*a* using 675 nm must suitably work for BBHR. It was observed that from 690 nm, a_w has the highest contribution to a in

May field survey, while this edge is shifted to 710 nm in October. These wavelengths are widely used as reference in bio-optical modeling in order to minimize the multiple effects of different OAC (Le et al., 2009; Mishra et al., 2014; Matsushita et al., 2015).

Therefore NIR-red algorithms developed for inland waters application must be suitable for BBHR. However, BBHR showed Chl-*a* and TSS concentrations range very specific, mainly, in relation to Chl-*a* and calibrations proposed for other environments must not likely performance accuracy results. Thereby, even bands and indexes proposed for other environments are suitable for BBHR, the calibration parameters must be tuned.

CHAPTER 4

ASSESSMENT OF OLI, MERIS AND MODIS DATA USING AN EMPIRICAL APPROACH FOR CHLOROPHYLL-A CONCENTRATION RETRIEVAL IN A TROPICAL EUTROPHIC RESERVOIR

4.1. Background

Retrieving the concentration of optically active components (OACs) is a challenge for the remote sensing of water color. Different approaches have therefore been tested and adapted reflecting the diversity of aquatic environments (O'REILLY *et al.*, 1998; CARDER *et al.*, 1999; GITELSON *et al.*, 2008; DASH *et al.*, 2011; MOSES *et al.*, 2009). Empirical modeling is the simplest approach being implemented and calibrated using statistical regression between radiometric data (irradiance reflectance, R , or remote sensing reflectance, R_{rs}) and water quality parameters. They are better suited to environmental monitoring by satellite which needs quick results for decision making. Analytical models require more computational time and are harder to use in quasi-real time (MOSES *et al.*, 2009). Although empirical models are simple, they are quite accurate when suitably calibrated. Furthermore, the process of calibration and validation of the models does not need a dataset with many variables, only radiometric data and water optical property need be estimated. Several models of single band or different band combination (band algorithms) were developed to estimate the chlorophyll-*a* (Chl-*a*) concentration using data from different sensors. However, the empirical approach has the disadvantage of being limited to a geographic location and a seasonal regime (MOSES *et al.*, 2012).

Two band algorithms (2B) for estimating Chl-*a* were originally developed for marine waters using bands at the blue and green regions of the electromagnetic spectrum (AIKEN *et al.*, 1998; CLARK, 1997; CARDER *et al.*, 1999). In inland waters, the presence of CDOM, which absorbs strongly in the blue region, the region where Chl-*a* exhibits the highest absorption peak, masks the chlorophyll peak, making the spectral blue region inappropriate for correlation with reflectance (BUKATA *et al.*, 1995; CARDER *et al.*, 1999; MANNINO *et al.*, 2008). In addition, atmospheric influence is higher at shorter wavelength (ultraviolet and blue region) (GORDON *et al.*, 1988; SIEGEL *et al.*, 2000), hampering the performance of models using blue band (MANNINO *et al.*, 2008).

An empirical model using green and red bands was proposed by Tzortziou *et al.* (2007) for estuarine waters, with good the performance in turbid waters. Another structure

using the same band combination, named Slope, was proposed by Mishra & Mishra (2010) and Dash et al. (2011) and showed accurate performance. 2B models using near infrared (NIR) and red bands were also proposed for inland waters, where the bio-optical complexity is higher (DALL'OLMO *et al.*, 2005; GITELSON *et al.*, 2008), showing satisfactory performance. Another index using NIR-red bands and different structures is Normalized Difference Chlorophyll Index (NDCI), proposed by Mishra & Mishra (2012), which retrieved Chl-*a* accurately. The indexes of three band (3B) (GITELSON *et al.*, 2008) and four band (4B) (LE *et al.*, 2009; LE *et al.*, 2013) were also developed to minimize the influence of detritus.

Different parameter calibrations were proposed for several aquatic environments around the world (MOSES *et al.*, 2009; GURLIN *et al.*, 2011; GILSERSON, 2010), however, studies showed that such calibrations are not usually suitable in others locations (MISHRA & MISHRA, 2010; WATANABE *et al.*, 2015). Therefore, the aim of this work was to assess the band performance of the OLI (Operational Land Imager) (USGS, 2013), MERIS (Medium Resolution Imaging Spectrometer) (ESA, 2015), and MODIS (MOderate Resolution Imaging Spectroradiometer) (NASA, 2015) sensors and the empirical approach for estimating Chl-*a* concentration in tropical productive reservoir. Among the calibrate models, only that adjusted for OLI/Landsat-8 was applied to an image acquired during the second fieldwork. Models were not applied to MODIS images due to its low spatial resolution for a small reservoir such as the BBHR.

4.2. Data and Methods

4.2.1. Remote sensing reflectance

R_{rs} (Equation 3) can be quantified from radiometric data measurements collected above surface and calculated using Equation 14 proposed by Mobley (1999).

$$R_{rs}(\lambda) = \frac{L_t(\lambda) - \rho L_{sky}(\lambda)}{E_s(\lambda)} \quad (14)$$

where L_t ($\text{W} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$) is the total radiance, i.e., the sum of water-leaving spectral radiance (L_w , in $\text{W} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$) and reflected radiance from the sea surface in the direction of the sensor (L_r , in $\text{W} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$); the influence of L_r is corrected from the incident sky radiance (L_{sky} , in $\text{W} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$)

and surface reflectance factor ($\rho = 0.028$). ρ is related to direction, wavelength, wind speed, sky radiance distribution and detector FOV (field of view); and E_s ($\text{W}\cdot\text{m}^{-2}$) is the incident irradiance above the water surface.

Three RAMSES spectroradiometers (TriOS, Oldenburg, Germany) were used to measure the radiometric quantities required for the calculation of the R_{rs} . E_s was measured using a cosine collector, ACC-VIS RAMSES sensor, whereas L_t and L_{sky} were measured using two ARC-VIS RAMSES sensors, with a 7° FOV in air. The ACC-VIS and ARC-VIS works in a range of 320 to 950 nm with a spectral sampling and accuracy of 3.3 nm and 0.3 nm, respectively. The operational temperature range is between -10°C and $+50^\circ\text{C}$ with water resistance of 300 m. Radiometric data were collected using geometric acquisition proposed by Mobley (1999) and Mueller (2003). The cosine collector was pointed in an upward direction for collecting the incident spectral irradiance, $E_s(\lambda)$. The sensor was coupled to a structure of approximately 1.5 m to avoid shadows. One of the ARC-VIS sensors was pointed in an upward direction of 135° to measure the incident sky radiance, $L_{sky}(\lambda)$. Another radiance sensor was pointed in a downward direction of 45° to measure the surface radiance, $L_t(\lambda)$. All the sensors collected the measurements simultaneously.

4.2.2. OACs concentrations

The collected water samples were filtered through a Whatman GF/F glass fiber filter, with $0.7\ \mu\text{m}$ size pore and 47 mm diameter, to estimate Chl-*a* and particulate material concentration (BIDIGARE et al., 2003). A vacuum pressure pump and a filter holder were used in the filtration. Due to the high concentration of solids in the BBHR, a very small volume (250 mL) was filtered at each filtration. Filters with retained material were stored, frozen and in the dark, until analysis.

Extraction by the acetone method was used to estimate Chl-*a* concentration (GOLTERMAN, 1975). Chl-*a* was extracted using 10 ml of 90% acetone solution. Sample absorbance was measured at wavelengths of 663 nm and 750 nm using a spectrophotometer and a cuvette with 1 cm path length. The samples were afterwards acidified using a 0.1 N hydrochloric acid (HCl) solution to correct the interference of phaeophytin. Meanwhile, concentrations of TSS, OSS, and ISS were estimated using the method proposed by APHA (1998).

4.2.3. Calibration of empirical models

Existing models were tested using the bands of the OLI, MERIS, and MODIS sensors. OLI, MERIS and MODIS bands were simulated from *in situ* data and used to calibrate and validate models for Chl-*a* estimation. The simulation of bands was carried out from *in situ* R_{rs} measurements and the spectral response function of each sensor (BARSİ et al., 2014; NASA, 2016; NASA, 2012), using Equation 15 (VAN DER MEER, 1999).

$$R_{rs,k} = \frac{\int_{\lambda_{1k}}^{\lambda_{2k}} L_w(\lambda) S_k(\lambda) d\lambda}{\int_{\lambda_{1k}}^{\lambda_{2k}} E_d(\lambda) S_k(\lambda) d\lambda} \quad (15)$$

where, $S_k(\lambda)$ is the radiometric sensitivity of band k , whose band width is from wavelength λ_{1k} to λ_{2k} ($\lambda_{1k} < \lambda_{2k}$).

Simulated bands were used to test empirical models proposed by different authors to estimate the Chl-*a* concentration in BBHR. Empirical models were calibrated from spectral indexes proposed by different authors. Different band combinations were tested using two, three and four bands. Two-band (2B) and three-band (3B) models (Equation 16 and 17), originally developed to estimate Chl-*a* in terrestrial vegetation (Gitelson et al., 2003) and later adapted by authors for algal Chl-*a* in aquatic systems were tested. In both models, the first band position λ_1 must be maximally sensitive to absorption by Chl-*a* (a_ϕ). To minimize the absorption effects of other OACs, a second spectral band λ_2 is used, which must be minimally sensitive to a_ϕ , and present absorption by tripton and colored dissolved organic material (CDOM), a_{TR} and a_{CDOM} , similar to the finding at λ_1 . 2B is still affected by backscattering (b_b), which can produce different Chl-*a* estimates for locations with equal concentration. This influence can be eliminated by using a third spectral band λ_3 , where absorption must be associated only with pure water (Gitelson et al., 2008).

$$2B = [R_{rs}^{-1}(\lambda_1) \times R_{rs}(\lambda_2)] \quad (16)$$

$$3B = [R_{rs}^{-1}(\lambda_1) - R_{rs}^{-1}(\lambda_2)] \times R_{rs}(\lambda_3) \quad (17)$$

The slope model (Equation 18), developed by Mishra & Mishra (2010) for turbid waters, based on the red and green bands of the MODIS sensor was also tested. The Slope index represents the variation rate of reflectance from $R_{rs}(\lambda_2)$ to $R_{rs}(\lambda_1)$ in relation to the wavelengths λ_2 to λ_1 . The wavelength λ_1 is associated with minimum absorption by Chl-*a*, while λ_2 is related to maximum absorption.

$$Slope = \frac{R_{rs}(\lambda_2) - R_{rs}(\lambda_1)}{\lambda_2 - \lambda_1} \quad (18)$$

Finally, the Normalized Difference Chlorophyll-*a* Index (NDCI) model developed Mishra & Mishra (2012), based on MERIS bands for applications in estuarine and coastal turbid productive waters (Equation 19), was tested. Similar to the Normalized Difference Vegetation Index (NDVI), the first band position λ_1 is associated with maximally sensitive Chl-*a* in the red spectral region, while the second position λ_2 meets the band of minimally sensitive Chl-*a* in NIR region, in this case at 709 nm.

$$NDCI = \frac{R_{rs}(\lambda_2) - R_{rs}(\lambda_1)}{R_{rs}(\lambda_2) + R_{rs}(\lambda_1)} \quad (19)$$

Table 4 shows the band combinations used in the models and the site of the data calibration collections tested in this work. The selection of bands in a model is conducted with the aim of minimizing the effects of other OACs on the variable of interest (GITELSON et al., 2008; DASH et al., 2012). 2O-a, 2O-b and SLO indexes meet at 2B using two different band combinations and Slope for OLI bands, while 2ME and SLME indexes meet at 2B and Slope using MERIS bands. Lastly, 2MO-a and 2MO-b indexes indicate 2B using different MODIS band combinations.

Band combinations proposed for marine waters (AIKEN et al., 1998) were only tested for OLI bands due to the absence of specific bands for application to remote sensing of water color. All the models were calibrated using the least square method, testing linear and polynomial (2nd degree) adjustments. A prediction interval was taken into account, with a confidence level of 0.95, to calibrate the models. Samples positioned out of the prediction interval were considered as outliers and removed from the models.

Table 4. Abbreviations, band combinations using (a) OLI, (b) MIERIS and (c) MODIS data and references.

a. Bands combinations using OLI data			
Index	Input R_{rs}	Study area	References
2O-a	480, 560	Greenland, Iceland and Norwegian Seas; Georges Bank; Equatorial Pacific; Antarctica, Bermuda	Aiken <i>et al.</i> (1998)
2O-b	665, 560	Chesapeake Bay, Delaware Bay, Mississippi River Delta, Mobile Bay	Mishra & Mishra (2012)
SLO	665, 560	Lake Pontchartrain	Mishra & Mishra (2010)
b. Bands combinations using MERIS data			
Index	Input R_{rs}	Study area	References
2ME	709, 665	Nebraska & Iowa lakes	Gitelson <i>et al.</i> (2008)
NDCI	709, 665	Chesapeake Bay, Delaware Bay, Mississippi River Delta, Mobile Bay	Mishra & Mishra (2012)
SLME	709, 665	Barra Bonita	-
3B	665, 709, 754	Nebraska & Iowa lakes	Gitelson <i>et al.</i> (2008)
c. Bands combinations using MODIS data			
Index	Input R_{rs}	Study area	References
2MO-a	748, 667	Fremont State Lakes, Ginger Cove, Glen Cunningham, Branched Oak	Dall'Olmo <i>et al.</i> (2005)
2MO-b	748, 678	Fremont State Lakes, Ginger Cove, Glen Cunningham, Branched Oak	Dall'Olmo <i>et al.</i> (2005)

4.2.4. *Chl-a* mapping

The fieldworks were carried out to coincide with OLI/Landsat-8 images in order to map the *Chl-a* using a model calibrated for the bands of the OLI sensor. However, a unique OLI/Landsat-8 image was acquired on October 13th, 2014 in suitable conditions (without clouds) for processing. Before model application, the following preprocessing steps were taken: a) radiometric calibration to convert digital numbers (DN) into top-of-atmosphere radiance (L_{TOA}); b) atmospheric correction was applied and L_{TOA} was converted into at-surface reflectance (R_{sup}) using FLAASH (Fast Line-of-sight Atmospheric Analysis of Spectral Hypercubes) module; c) R_{sup} values were converted into R_{rs} , dividing the values by π (MOSES *et al.*, 2015); d) optical closure was conducted to evaluate the performance of the atmospheric correction, comparing R_{rs} simulated and retrieved from the image, relative to five

measures collected precisely on the day of satellite overpass. Finally, the best models calibrated for OLI bands were applied to the corrected image.

4.2.5. Validation

A 24-sample dataset collected on September 13 – 15, 2015 was used to validate the empirical models. The statistical metrics used were: Root Mean Square Error (RMSE – Equation 20); Normalized Root Mean Square Error (NRMSE – Equation 21); Mean Absolute Percentage Error (MAPE – Equation 22); bias (Equation 23); and determination coefficient (R^2).

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y'_i - y_i)^2} \quad (20)$$

$$NRMSE = \frac{RMSE}{y_{\max} - y_{\min}} \quad (21)$$

$$MAPE = \frac{\sum_{i=1}^n \left(\frac{|y'_i - y_i|}{y_i} \right)}{n} \quad (22)$$

$$bias = \frac{1}{n} \sum_{i=1}^n (y'_i - y_i) \quad (23)$$

where, $y_{\max}$ is the maximum measured value; $y_{\min}$ is the minimum measured value; y'_i are predicted values; y_i are measured values; and n is the number of samples.

4.3. Results and Discussion

Table 5 shows a summary of the water quality parameters collected along three field campaigns accomplished in BBHR. The difference between values exhibited for each parameter in different months can be noted.

Table 5. Descriptive statistics of the water quality parameters measured in the field campaigns carried out in (a) May, 2014, (b) October, 2014 and (c) September, 2015. Statistical metrics used were: minimum value (Min), maximum value (Max), mean, median, standard deviation (SD) and coefficient of variation (CV) in percentage (%).

a. Calibration dataset collected on May 5 – 9, 2014, n = 18 samples.						
Parameter	Min	Max	Mean	Median	SD	CV
Chl- <i>a</i> , mg·L ⁻¹	17.7	279.9	123.1	101.3	69.8	56.7
TSS, mg·L ⁻¹	3.8	16.3	7.4	7.0	3.3	44.6
OSS/TSS, %	45	97.5	83.4	86.6	11.8	14.1
ISS/TSS, %	2.5	55.0	16.6	13.4	11.8	71.2
Turbidity, NTU	2.1	12.5	5.3	5.0	2.4	45.3
Secchi disk depth, m	0.8	2.3	1.5	1.4	0.4	29.5
b. Calibration dataset collected on October, 13 – 16, 2014, n = 20 samples.						
Parameter	Min	Max	Mean	Median	SD	CV
Chl- <i>a</i> , mg·L ⁻¹	263.2	797.8	428.7	368.9	154.5	36
TSS, mg·L ⁻¹	10.8	44	22	21.2	7	31.8
OSS/TSS, %	78.0	96.0	87.0	86.0	5.0	5.7
ISS/TSS, %	4.0	22.0	13.0	14.0	5.0	38.5
Turbidity, NTU	11.6	33.2	18.6	17.6	5.3	28.5
Secchi disk depth, m	0.4	0.8	0.6	0.6	0.1	16.7
c. Validation dataset collected on September 13 – 15, 2015, n = 24 samples.						
Parameter	Min	Max	Mean	Median	SD	CV
Chl- <i>a</i> , mg·L ⁻¹	62.8	245.7	127.1	106.5	51.3	40.4
TSS, mg·L ⁻¹	16.6	22.0	17.6	17.3	1.1	6.4
Turbidity, NTU	3.1	6.8	4.2	4.1	0.8	20.3
Secchi disk depth, m	1.0	1.6	1.3	1.2	0.2	16.6

The month of October presented the highest values for all parameters. Along the three fieldworks, The BBHR exhibited high Chl-*a* concentrations in each of the fieldwork surveys, from which it is possible to classify it as a eutrophic environment (Chl-*a* > 60 mg·m⁻³) (CARLSON, 1977). October exhibited especially high concentrations of Chl-*a* (up to 797.8 mg·m⁻³), due to the below average rainfall in 2014, causing a remarkable decrease in the water levels in the São Paulo State reservoirs (INMET, 2015) and leading to a water supply crisis in some cities, and harming the commodity transportation via navigation. Hence, there was a greater water flow control in reservoirs, leading to an increase of time retention,

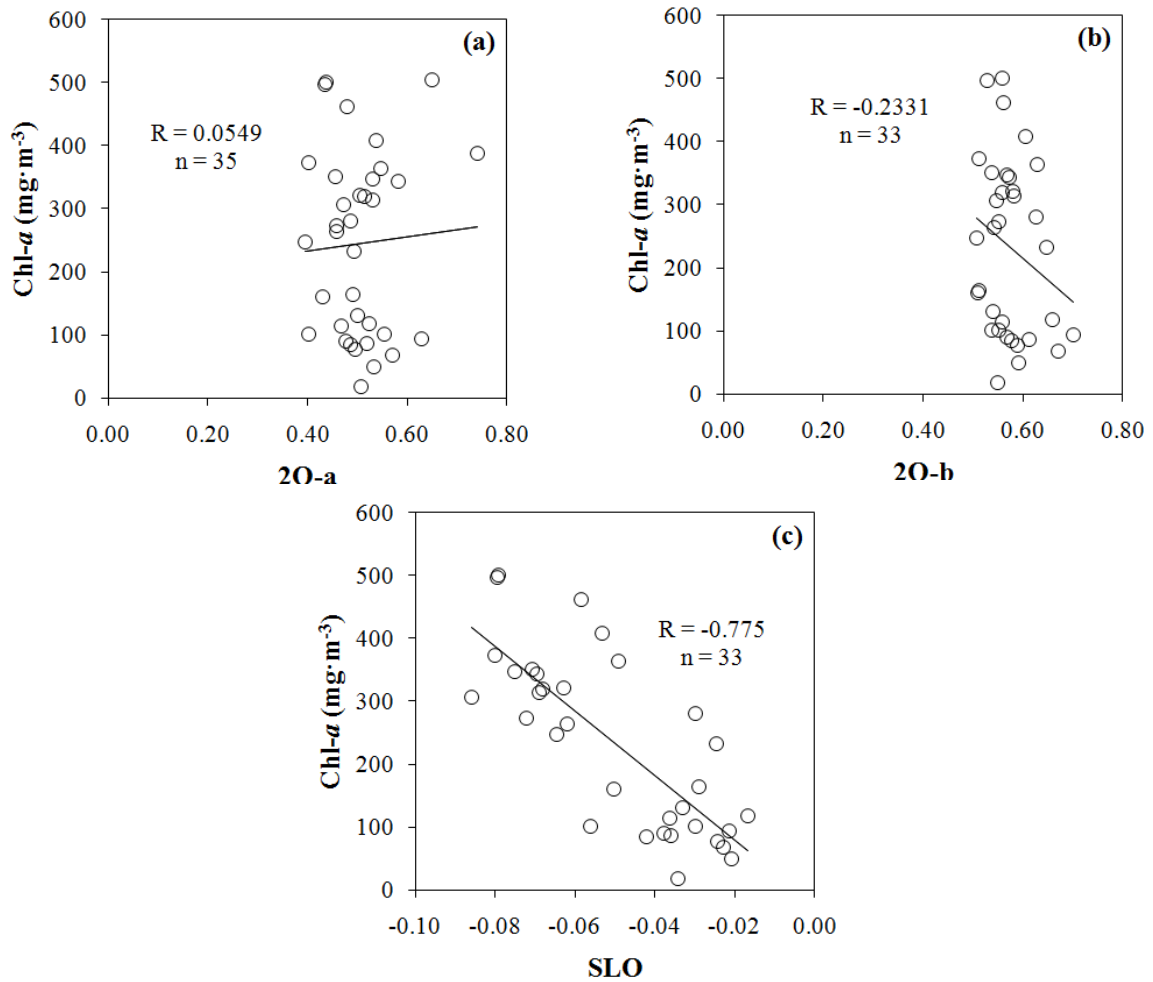
contributing to the development of algal communities (TUNDISI et al., 2008). According to Secchi disk depth, the BBHR can be considered as eutrophic, with values less than 1.1 m (CARLSON, 1977).

During data surveying, the presence of algal cells and filaments sparsely distributed in the water column was noted, making the measurements of turbidity difficult. In other words, there was a remarkable variation among the turbidity readings, because the beam was more attenuated in some samplings and less in others. Hence, three measurements were acquired at each sampling point and the average of the measures was used. In addition, it was noted that TSS was mainly composed of OSS, with a mean portion of 90%. Chl-*a* and OSS presented a positive correlation of approximately 0.82. Although October presented the highest Chl-*a* and OSS concentrations, correlation between both was low in this month, at about 0.33, while in May the correlation was 0.75. The low correlation in October can be strongly linked to pigment packaging due to high phytoplankton growth. Unfortunately, ISS and OSS could not be estimated due to problems in burning the filters.

Before calibration, two samples were removed due to interference of sunglint effect over R_{rs} spectra, both collected in May 2014. These samples were measured in P4 (Chl-*a* = 26.2 mg·m⁻³ and TSS = 3.6 mg·L⁻¹) and P13 (Chl-*a* = 166.6 mg·m⁻³ and TSS = 6.5 mg·L⁻¹). Fortunately, the samples did not present extreme lower and higher values, not affecting the covering range of the adjusted models. The linear relationship between the Chl-*a* and spectral indexes for calibration data and OLI bands are shown in Figure 10.

To calibration outliers were removed, therefore, that each model was adjusted with different number of samples. 2O-*a* index was calibrated without the samples P3 (Chl-*a* = 797.8 mg·m⁻³ and TSS = 44 mg·L⁻¹), P14 (Chl-*a* = 723.5 mg·m⁻³ and TSS = 23.2 mg·L⁻¹) and P18 (Chl-*a* = 713.7 mg·m⁻³ and TSS = 20.4 mg·L⁻¹) collected in October, 2014. These three samples matched to the highest values of Chl-*a* concentration obtained and, consequently, the removal of these samples decreased the model reach. The same samples were removed for SLO index (P3, P14 and P18). On the other hand, 2O-*b* index removed P3, P14 and P18 collected in October and more two samples identified as outlier, P19 (Chl-*a* = 505.1 mg·m⁻³ and TSS = 19 mg·L⁻¹) and P20 (Chl-*a* = 387.2 mg·m⁻³ and TSS = 16 mg·L⁻¹) acquired in October, 2014. Along with P18, these points are located in the Tietê River before confluence with the Piracicaba River, showing that there is a bio-optical difference in this region compared to the rest of the reservoir.

Figure 10. Scatter plot between spectral indexes and Chl-*a* concentration using OLI bands. The spectral indexes tested were: (a) 2O-a; (b) 2O-b and (c) Slope.

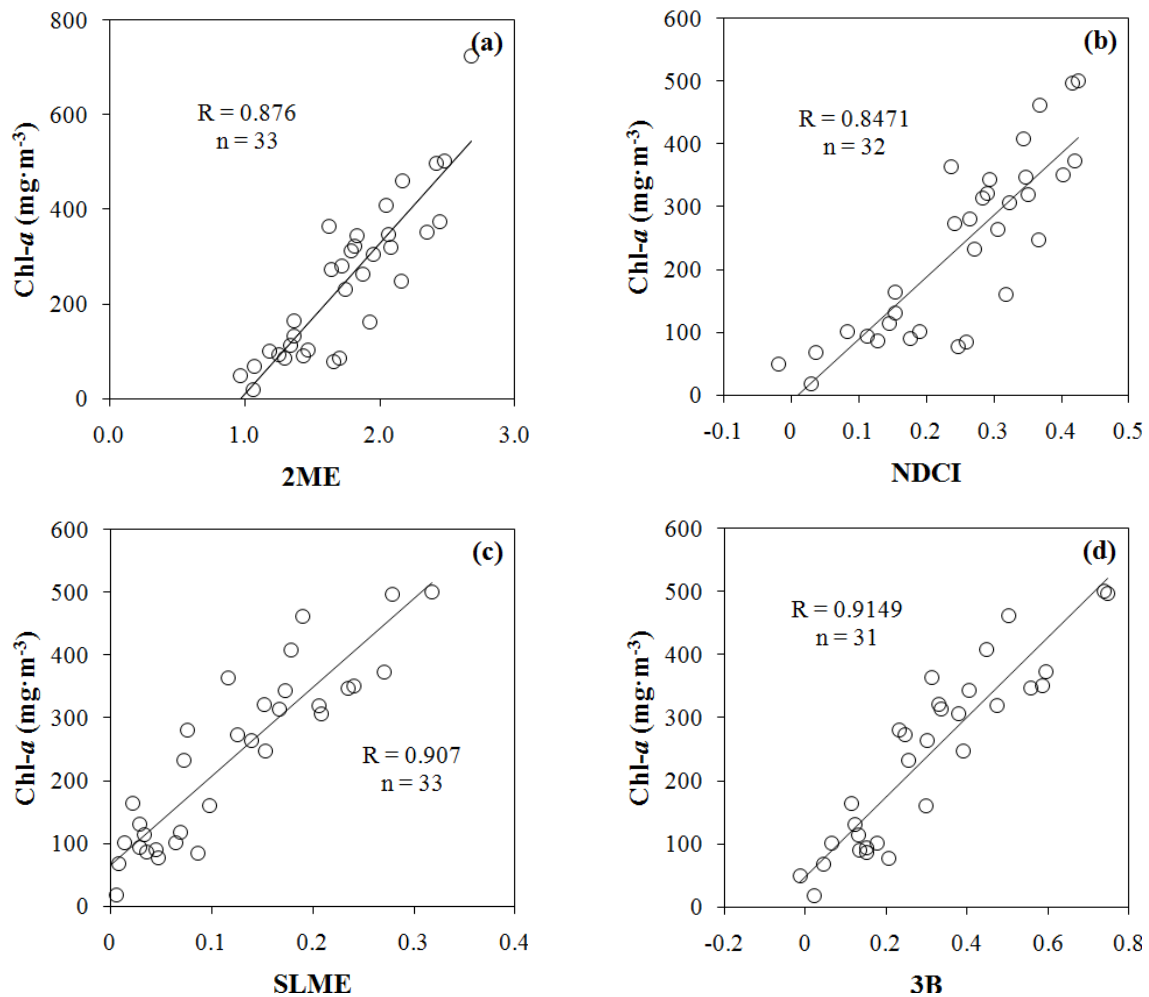


The results with R^2 lower than 1%, suggesting no correlation between 2O-a and 2O-b indexes and Chl-*a* concentration for BBHR, indicate that these indexes are not sufficient for Chl-*a* estimate models in BBHR. As expected, the optical complexity of inland waters, with solute and particle inputs coming from the drainage basin, impairs the use of shorter wavelengths, strongly influenced by different OACs. Despite this, even using the same bands of 2O-b index, the Slope structure considerably improved the relationship with Chl-*a*, increasing R to 0.78. In this case, the Slope can be seen as the derived value in that spectral range (560 – 665 nm), minimizing multiple effects of OAC such as TSS and highlighting the Chl-*a* feature (GOODIN et al., 1993).

Plots between the Chl-*a* and spectral indexes proposed for applications to MERIS bands are presented in Figure 11. Outliers were also removed of the models proposed for MERIS. The samples P3, P18, P19 and P20 collected in October and P16 (Chl-*a* = 117.7

$\text{mg}\cdot\text{m}^{-3}$ and $\text{TSS} = 4.5 \text{ mg}\cdot\text{L}^{-1}$) measured in May were identified as outliers for 2ME. For NDCI, the same five samples for 2ME (P3, P18, P19 and P20 in October and P16 in May) and P14 collected in October were removed. SLME index removed the same samples identified as outliers by SLO index (P3, P14, P18, P19 and P20 measured in October). Since, 3B index removed the highest number of samples (7 samples). Besides the 5 samples excluded in other index (P3, P14, P18, P19 and P20 measured in October), samples P1 ($\text{Chl-}a = 84.9 \text{ mg}\cdot\text{m}^{-3}$ and $\text{TSS} = 9.4 \text{ mg}\cdot\text{L}^{-1}$) and P16 ($\text{Chl-}a = 164.6 \text{ mg}\cdot\text{m}^{-3}$ and $\text{TSS} = 11.6 \text{ mg}\cdot\text{L}^{-1}$) acquired in May were also withdrawn.

Figure 11. Scatter plot between spectral indexes and Chlorophyll-*a* concentration using MERIS simulated bands. The spectral indexes tested were: (a) 2ME; (b) NDCI; (c) SLME; (d) 3B.

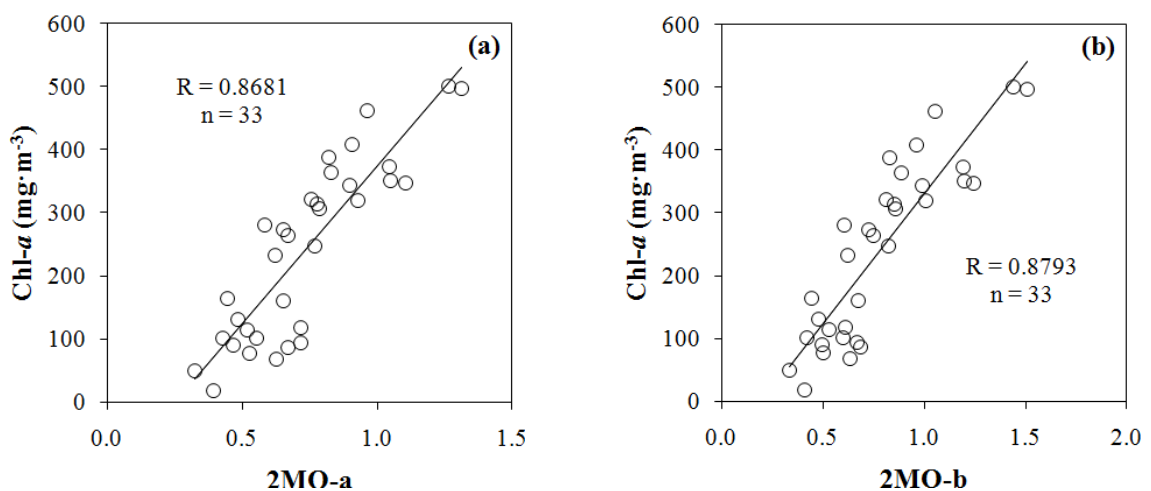


The indexes of two bands presented satisfactory correlation with Chl-*a* ($R = 0.876$ for 2ME, $R = 0.847$ for NDCI and $R = 0.907$ for SLME), showing that the replacement of the wavelength at 560 nm by 709 nm improve the estimation of Chl-*a*, in BBHR. A satisfactory

correlation was also found for 3B index ($R = 0.915$), corroborating the evidence that NIR-red combination produces high correlation with Chl-*a*. In this case, wavelength at 754 nm still improved slightly the relation with Chl-*a*, due probably to minimization of the backscattering effects.

Outliers were also removed before calibration using MODIS indexes. Both 2MO-a and 2MO-b indexes excluded the samples P1 collected in May and P3, P4, P18 and P19 acquired in October. The MODIS indexes (2MO-a and 2MO-b) also showed satisfactory correlation between the Chl-*a*, with R greater than 0.85; although the 2MO-b index presented a slightly better fit (Fig. 12). The difference is the wavelength in the red spectral region, 667 in the first and 678 nm in the second. There was no significant difference between R^2 produced by 2ME and 2MO-a. Although 709 nm is directly associated with the maximum reflectance peak, NIR region (720 – 760 nm) likely behaved according to Chl-*a* variation. Wavelength at 754 nm (MODIS) is used in terrestrial vegetation applications, due to reflection by the cellular structure of plants. During the process of outlier removal, it was noticed that most points indicated as outliers were located in the Tietê River before the confluence with the Piracicaba River. Bio-optical characteristics in this section are very different of the other regions of the reservoir, due to the high discharge of sewage, industrial waste and fertilizers coming from upper down the Tietê River.

Figure 12. Scatter plot between spectral indexes and Chlorophyll-*a* concentration using MODIS bands. The spectral indexes tested were: (a) 2MO-a; and (b) 2MO-b.



Another outlier was the sample P3 collected in October, which exhibited the greatest Chl-*a* value (797.8 mg·m⁻³) and the most different shape of absorption coefficient by phytoplankton, $a_{\phi}(\lambda)$. P3 presented other different bio-optical status such the lowest dissolved

organic carbon (DOC) concentration of $1.04 \text{ mg}\cdot\text{L}^{-1}$, with a mean DOC of $10.1 \text{ mg}\cdot\text{L}^{-1}$ (Tab. 2 – Chapter 3). Furthermore, this sample is affected by pigment packaging or self-shading (BRICAUD et al., 1995; CARDER et al., 1999; CIOTTI et al., 2002), which can lead to flattening the absorption coefficient spectra (BRICAUD et al., 1995). So, even though Chl-*a* concentrations increase, the Chl-*a* features are not still more highlighted in the absorption spectra, leading to underestimation of high concentrations. P3 is next to the dam, located before the channel narrows in the lacustrine zone, where conditions for algal blooms are favorable (Fig. 7). Also P14 measured in October was excluded in almost all the indexes tested, exhibiting the second highest Chl-*a* concentration ($723.5 \text{ mg}\cdot\text{m}^{-3}$). P14 presented one of the highest $a_{\phi}(\lambda)$ values, with 3.599 m^{-1} . P14 exhibited one of the most different spectral shape compared to the other $a_{\phi}(\lambda)$ curves, showing the highest difference between $a_{\phi}(412)$ and $a_{\phi}(443)$, where the first one was remarkably lower. In addition, the spectra presented an absorption increasing at about 460 nm which was not observed in the other curves. The calibration parameters of the models fitted for OLI, MERIS and MODIS sensors are showed in Table 6.

Table 6. Calibration parameters of the models proposed in this work: intercept (a), slope (b) and quadratic coefficient (c). Models were calibrated using data from the (a) OLI, (b) MERIS and (c) MODIS sensors.

a. Models calibrated using OLI/Landsat-8 bands					
Index	<i>n</i>	Fit	a ¹	b ¹	c ¹
2O_a	35	Linear	187.24	113.1	-
2O_a	35	Quadratic	1615.28	-5231.71	4891.71
2O_b	33	Linear	625.09	-684.28	-
2O_b	33	Quadratic	-1851.88	7710.52	-7059.77
SLO	33	Linear	-23.52	-5127.78	-
SLO	33	Quadratic	14.33	-3310.49	18049.58
b. Models calibrated using MERIS bands					
Index	<i>n</i>	Fit	a ¹	b ¹	c ¹
2ME	33	Linear	-307.61	317.77	-
2ME	33	Quadratic	-27.49	-15.98	93.31
NDCI	32	Linear	-10.942	991.42	-
NDCI	32	Quadratic	40.43	321.41	1517.6
SLME	33	Linear	66.133	1412.51	-
SLME	33	Quadratic	46.503	1906.39	-1770.64
3B	31	Linear	47.77	633.24	-
3B	31	Quadratic	17.82	886.22	-354.76
c. Models calibrated using MODIS bands					
Index	<i>n</i>	Fit	a ¹	b ¹	c ¹
2MO_a	33	Linear	-125.42	499.01	-
2MO_a	33	Quadratic	-202.18	710.97	-132.16
2MO_b	33	Linear	-83.85	415.41	-
2MO_b	33	Quadratic	-219.77	763.8	-195.89

¹ Structure of linear and quadratic fit, $y = a + bx$ and $y = a + bx + cx^2$, respectively.

The regression fits were evaluated using the statistical parameters shown in Table 7. As expected, the indexes proposed for marine and coastal waters (2O-a and 2O-b, respectively) did not exhibit satisfactory fit with R^2 , less than 10% and p -value greater than 0.01. The statistic F and p -values showed that such indexes are not significant to explain Chl-*a* concentration. Of the fits using OLI bands, the SLO using quadratic fit exhibited the best

adherence, while simple band ratios using the same bands presented expressionless R^2 values of 5.4% to 7.4% (linear and quadratic fits, respectively).

Table 7. Index and fit used to calibrate empirical models and assessment parameters of adjustment: standard error of estimate (S); determination coefficient (R^2); adjusted determination coefficient (Adj- R^2), F statistic; and p -value.

a. Models calibrated using Landsat bands							
Index	n	Fit	S	R^2	Adj- R^2	F	p -value
2O-a	35	Linear	147.93	0.3	-2.72	0.099	0.7541
2O-a	35	Quadratic	144.28	8.04	2.3	2.4	0.262
2O-b	33	Linear	138.75	5.43	2.38	1.78	0.1917
2O-b	33	Quadratic	139.61	7.35	1.2	1.19	0.318
SLO	33	Linear	90.17	60.1	58	46.62	0.000
SLO	33	Quadratic	91.44	60.3	57.6	22.74	0.000
b. Models calibrated using MERIS bands							
Index	n	Fit	S	R^2	Adj- R^2	F	p -value
2ME	33	Linear	79.78	76.7	76.0	102.26	0.000
2ME	33	Quadratic	78.36	78.3	76.8	54.07	0.000
NDCI	32	Linear	76.25	71.8	70.8	76.22	0.000
NDCI	32	Quadratic	73.78	74.4	72.7	42.23	0.000
SLME	33	Linear	60.10	82.3	81.7	143.71	0.000
SLME	33	Quadratic	59.48	83.2	82.1	74.2	0.000
3B	31	Linear	57.77	83.7	83.2	149.03	0.000
3B	31	Quadratic	56.41	85.0	83.9	79.35	0.000
c. Models calibrated using MODIS bands							
Index	n	Fit	S	R^2	Adj- R^2	F	p -value
2MO-a	33	Linear	70.8	75.4	74.6	94.82	0.000
2MO-a	33	Quadratic	71.30	75.8	74.2	47.02	0.000
2MO-b	33	Linear	67.94	77.3	76.6	105.64	0.000
2MO-b	33	Quadratic	65.95	79.3	77.9	57.49	0.000

In relation to adjustments using MERIS wavelengths, of all the tested indexes, the calibration of the 3B index presented the best adjustments with R^2 of 83.7% (linear) and 85% (quadratic). Other MERIS models also showed satisfactory adjustments, in which quadratic 2ME showed an R^2 of 78.3%, while quadratic NDCI showed R^2 of 74.4%, while SLME

models exhibited adjustments as satisfactory as 3B models ($R^2 = 83.18\%$ for quadratic fit). The significant improvement is associated with the insertion of 709 nm, wavelength related to the peak of Chl-*a* reflectance.

NIR-Red algorithms for MODIS also presented a satisfactory fit with R^2 greater than 75%, although they have a wavelength of 748 nm rather than 709 nm. Even though the wavelength at 748 nm is mainly associated with aerosol properties, wavelengths around 754 nm (such as MERIS) have been used in terrestrial vegetation applications (ESA, 2015). Statistical parameters of fit showed that the wavelength at 678 nm had a performance slightly better than 667 nm. There is a divergence in relation to wavelength of maximum absorption in the red region, being greater 667 nm in May and 678 nm in October.

According to the validation results, the linear 2O-b model exhibited the best performance (NRSME = 28.9% and MAPE = 31.4%), followed by the Slope model with a quadratic fit (NRSME = 46.4% and MAPE = 47.1%) (Table 8). An opposite result was expected, since the Slope showed the best fit among models for OLI and 2O-b models did not show statistically suitable fits (inadequate F statistic and p -values). Unexpectedly, the models fitted for MERIS (quadratic 2B, quadratic NDCI and linear 3B models) showed errors greater than linear 2O-b, although they presented a better fit and better relation between measured and estimated Chl-*a* ($R^2 > 80\%$) (Fig. 13). This occurs probably because 2O-b worked accurately only for lower concentrations, while MERIS models underestimated Chl-*a*, but its prediction line is almost parallel to 1:1 line.

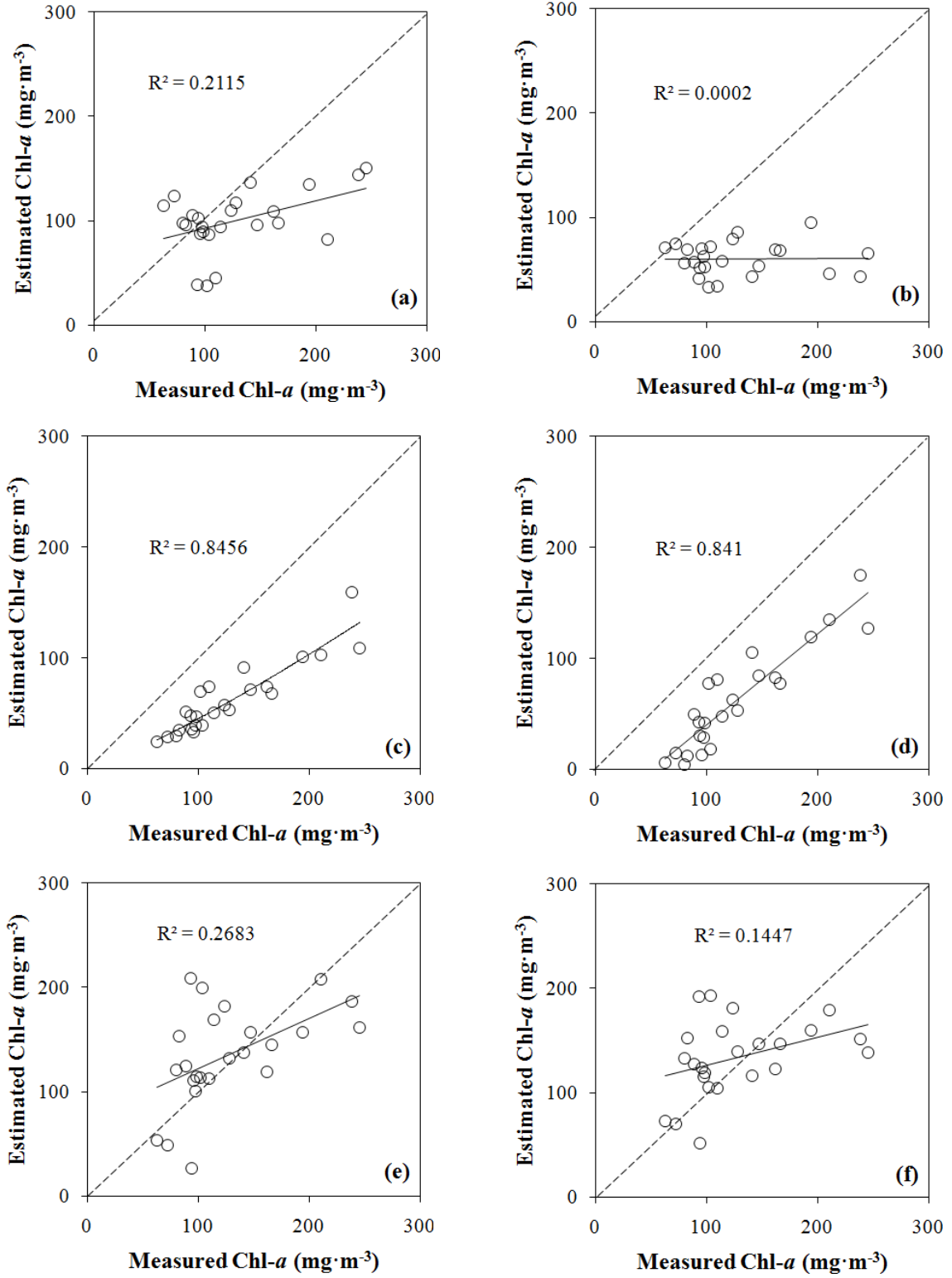
According to the validation results, all models for MERIS bands presented similar errors. Although SLME had, by a slight margin, the lowest NRMSE, MAPE and bias, it showed the lowest R^2 (Fig. 13). The linear 3B model exhibited a better sample distribution, almost parallel to 1:1 line, i.e., the underestimation level of 3B model is almost constant for some concentrations (Fig. 12), indicating that the wavelength at 754 nm improved the performance of the empirical model, minimizing the backscattering effects. Measured versus estimated Chl-*a* plot shows that the 3B model is suitable for BBHR, but the calibration parameters are not well fitted to the September dataset, indicating, once again, that empirical models are limited for application to the period of calibration data collection.

Table 8. Validation of the models considering RMSE ($\text{mg}\cdot\text{m}^{-3}$), NRMSE (%), MAPE (%), bias ($\text{mg}\cdot\text{m}^{-3}$) and R^2 (%). (a) OLI, (b) MERIS and (c) MODIS

a. Validation of the models calibrated using OLI bands						
Index	Fit	RMSE	NRMSE	MAPE	Bias	R^2
2O-a	Linear	151.53	82.83	141.44	141.09	12.12
2O-a	Quadratic	1177.66	643.77	1011.14	-1154.69	8.6
2O-b	Linear	52.79	28.85	31.44	-27.60	21.15
2O-b	Quadratic	266.78	145.83	207	-234.19	8.3
SLO	Linear	100.56	54.97	61.70	-84.62	0.01
SLO	Quadratic	84.95	46.44	47.14	-66.86	0.02
b. Validation of the models calibrated using MERIS bands						
Index	Fit	RMSE	NRMSE	MAPE	Bias	R^2
2ME	Linear	101.97	55.74	89.1	-99.79	83.71
2ME	Quadratic	70.01	38.27	52.65	-65.35	84.56
NDCI	Linear	122.45	66.94	111.13	-117.66	82.58
NDCI	Quadratic	75.38	41.21	58.23	-71.35	82.05
SLME	Linear	68.04	37.19	41.68	-57.22	77.55
SLME	Quadratic	82.02	44.83	59.48	-75.29	77.74
3B	Linear	68.29	37.33	56.44	-65.27	84.1
3B	Quadratic	94.95	51.9	84.28	-91.57	83.43
c. Validation of the models calibrated using MODIS bands						
Index	Fit	RMSE	NRMSE	MAPE	Bias	R^2
2MO-a	Linear	48.39	26.45	32.72	7.96	26.83
2MO-a	Quadratic	51.62	28.22	35.75	4.67	26.9
2MO-b	Linear	49.8	27.23	32.81	6.19	14.47
2MO-b	Quadratic	54.87	30	37.87	-2.61	15.14

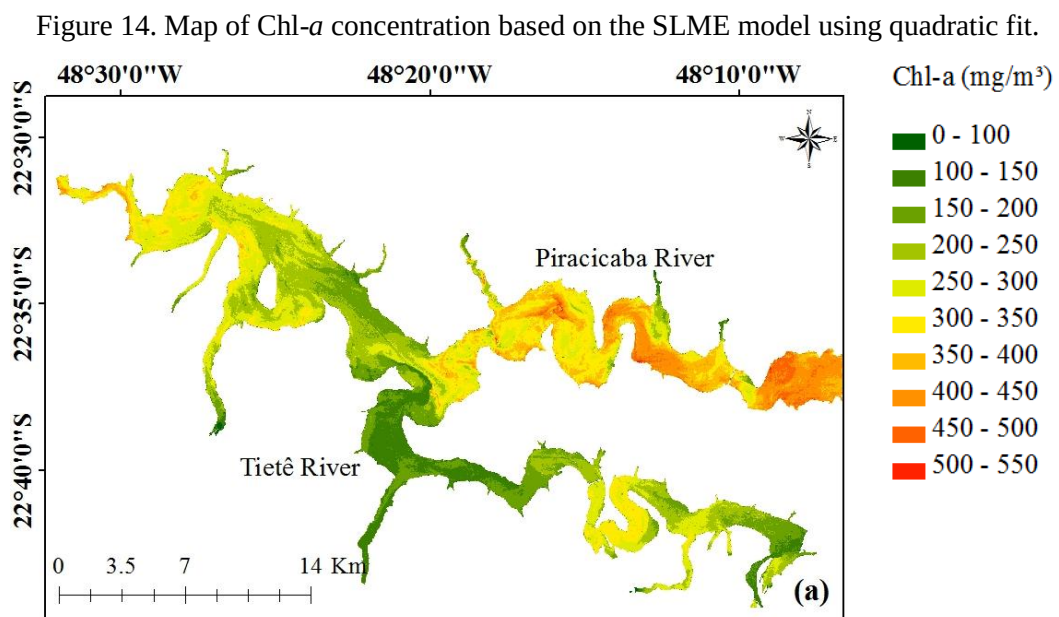
With the exception of one fit, all models for OLI and MERIS bands underestimated the Chl-*a*, while most models for MODIS overestimated. In absolute values, the overestimation of the MODIS models is much lower than the underestimation for OLI and MERIS (Tab. 8). MODIS models exhibited the lowest errors, as linear fits presented the best performance. Nevertheless, this is the result of the under and overestimation, eliminating the effect of others as shown in Figure 13.

Figure 13. Measured versus estimated Chl-*a* plotted for the two best fits obtained for each sensor (OLI, MODIS and MERIS): (a) linear 2O-b; (b) quadratic slope; (c) quadratic 2ME; (d) linear 3B; (e) linear 2MO-a; and (f) linear 2MO-b.



2MO-a and 2MO-b models presented similar validation results, being equal statistically; however, 2MO-a showed a better R^2 , indicating that the gradient between 667 nm and 748 nm is more representative of the Chl-*a* than 678 nm and 754 nm. Taking into account the fits for each sensor, the model with the best fit showed the best validation, which supports the accuracy of this model. Despite this, the use of MODIS images is not the most suitable option due to its spatial resolution of 1 km, while the maximum width of the reservoir is not higher than 5 km.

The SLO model using quadratic fit was applied on an OLI/Landsat-8 image acquired on October 13th, 2014, whose map of Chl-*a* concentration is illustrated in Figure 14. Comparing the Chl-*a* range in the map and collected in situ (17.8 to 797.8 mg·m⁻³), the underestimation in the model is apparent. These occurred due to removal of samples with the highest Chl-*a* concentrations which were identified as outliers during calibration process. The Chl-*a* range for calibration dataset was from 17.8 to 501.3 mg·m⁻³, compatible with the interval obtained from model application to image. Model strongly underestimated the Chl-*a* especially in Tietê River before confluence with the Piracicaba River. Samples collected in that region were identified as outliers and removed from the calibration of models; hence, the models are not representative of that reservoir region. In other words, these points are not bio-optically similar in relation to the rest of the reservoir. Certainly, the high wastewaters load coming from the lower course of the Tietê River is responsible for the singular bio-optical status found in this section.



Nonetheless, SLO represented satisfactory the Chl-*a* distribution in BBHR, with exception in Tietê River before confluence. Although SLO has not shown the best validation results, the fit was statistically significant (p -value = 0.0000) and its application on the image from October, 2014, matching with the fieldwork date, was performed satisfactorily. Furthermore, the underestimation of the model can also be related to pigment package effect, in which the Chl-*a* concentration increases, but the absorption by Chl-*a* does not. Therefore, the use of the wavelength at 665 nm, associated with the absorption by Chl-*a*, in models undergoes influence of pigment packaging.

Taking into account the spatial resolution of the OLI sensor (30 m), the Slope model can be considered to have shown satisfactory results. The model was sensitive in detecting the changes in water color associated with Chl-*a* concentration variation, although the calibration data were acquired in a GSD (Ground Sampling Distance) much smaller than the image.

4.4. Conclusion

The results obtained in this work showed that the band ratios based on NIR-red algorithms presented the best performance for estimating Chl-*a* in BBHR. Probably, the insertion of the reflectance peak at 709 nm was a differential, due to the contrast with maximum absorption in the red region (about 665 nm). Unfortunately, we do not have a MERIS image matching one of the fieldworks to map the Chl-*a*, because, it will likely produce good results. In relation to the red spectral region, the wavelength at 667 nm exhibited a performance slightly better than 678 nm.

Despite this, the results obtained in this work showed the potential of the OLI sensor to quantify Chl-*a* concentration. The quadratic Slope model (a better fit for OLI) highlighted the difference between the gradient produced by the reflectance peak in the green region and absorption in the red, which the simple ratio (2O-b) was not able to show. Even though the Slope model has not obtained the best results in validation, it exhibited a satisfactory performance in mapping. The divergent results of fit and mapping with the validation confirm that the empirical models are limited by time. It is also possible that the atypical climate conditions found in 2014 caused the models not to be representative of other years. Below average rainfall required greater flow control in BBHR, increasing time retention, Chl-*a* concentration (greater than $700 \text{ mg}\cdot\text{m}^{-3}$) and, consequently, changed the bio-optical status.

Samples collected in the Tietê River before confluence with the Piracicaba River were identified as outliers, due to the singular bio-optical status of this reservoir region. The

discharge of wastewater coming from the São Paulo metropolitan area is certainly mainly responsible for this bio-optical difference (Chapter 3). In addition, the pigment packaging was shown to interfere strongly in the performance of the Chl-*a* estimation model, since a_ϕ does not increase proportionally with the elevation of concentration, promoting underestimation of Chl-*a*. Therefore, these results indicate that a unique model cannot be enough to explain the Chl-*a* in the entire reservoir. Thus, the development of regional models must be better investigated where the bio-optical status are partitioned horizontally.

CHAPTER 5

PARAMETERIZATION AND CALIBRATION OF A QUASI-ANALYTICAL ALGORITHM FOR TROPICAL EUTROPHIC WATERS

5.1. Background

Proximal and satellite remote sensing over marine and freshwater systems aims to estimate the optically active components (OACs) such as phytoplankton, total suspended sediments (TSS), and colored dissolved organic matter (CDOM) concentrations within the water column from remote sensing reflectance (R_{rs}). R_{rs} is directly related to the inherent optical properties (IOPs) of the water, i.e., absorption (a) and backscattering coefficients (b_b) as described by Gordon et al. (1988a) (Equation 24).

$$R_{rs}(\lambda) \propto \frac{b_b(\lambda)}{b_b(\lambda) + a(\lambda)} \quad (24)$$

where $a(\lambda)$ is the sum of absorption coefficients of phytoplankton, detritus, CDOM, and pure water and $b_b(\lambda)$ is represented by the sum of backscattering of particulate material and pure water.

Marine and freshwater systems contain a differing variety of particles and dissolved substances and the variability in absorption and scattering properties associated with these constituents hampers the extraction of quantitative information about them (MOREL & PRIEUR, 1977). Several remote sensing methods have been developed to quantify OACs responsible by water color using statistical regressions (VINCENT et al., 2004; GURLIN et al., 2011; ODERMATT et al., 2012) and inversion algorithm techniques (HOGE & LYONS, 1996; BRANDO & DEKKER, 2003; DOERFFER & SCHILLER, 2007; ODERMATT et al., 2012). These models are based on remote sensing reflectance (R_{rs}) or irradiance reflectance (R) and use empirical, semi-analytical and quasi-analytical approaches.

Empirical models are based on statistical regression between water properties and R_{rs} or R measurements. These models do not utilize the IOPs which limits their applicability in terms of temporal and geographic spread (MISHRA & MISHRA, 2012; ORDEMATT et al., 2012; LEE et al., 2002). Semi-analytical models involve numerical optimization and are based on solutions for radiative transfer equations (HOGE & LYON, 1996; BRANDO & DEKKER, 2003; LEE et al., 2002). Nevertheless, they require some empirical solution (Ordematt et al., 2012). These models have the geographic and temporal flexibility and can be applied on other

aquatic environments (LEE et al., 2002). However, their performances depend on the parameterization to be representative of the IOPs of that environment, which are often acquired *in situ* or in the laboratory (LEE et al., 2002).

The quasi-analytical algorithm (QAA) was originally developed by Lee et al. (2002) to derive analytically $a(\lambda)$ and $b_b(\lambda)$ from remote sensing reflectance directly below the air-sea interface (r_{rs}). Derived $a(\lambda)$ are decomposed to absorption by phytoplankton (a_ϕ) and CDOM plus detritus (CDM) (a_{CDM}), whereas, $b_b(\lambda)$ is estimated from the backscattering coefficient for particulate material (b_{bp}) (LEE et al., 2002; LEE et al., 2009; MISHRA et al., 2013; MISHRA et al., 2014; LEE, 2014). Lee et al., (2002) showed that QAA presented similar accuracy when compared to approaches using optimization techniques. Several versions of QAA have been parameterized and tested for aquatic environments with different IOPs such as open ocean and coastal waters (LEE et al., 2002; IOCCG, 2006; LEE et al., 2009; LEE, 2014; WEI et al., 2015; CHEN & ZHANG, 2015), lakes (LE et al., 2009), rivers (LI et al., 2013; LI et al., 2015), and ponds (MISHRA et al., 2013; MISHRA et al., 2014).

Wavelength reference and the spectral power for particle backscattering coefficient (η) have been appointed as the main source of errors in estimating $a(\lambda_0)$ (LE et al., 2009; YANG et al., 2013). The selection of the reference wavelength is essential for an accurate performance of the QAA and must be dominated by pure water absorption (a_w). QAA was originally developed for open ocean waters by Lee et al. (2002) using 555 nm as the wavelength reference (λ_0). The algorithm was parameterized and calibrated using ocean R_{rs} data available by NASA bio-Optical Marine Algorithm Dataset (NOMAD) (SeaBASS, 2015). Lee & Carder (2004) applied QAA proposed by Lee et al. (2002) to coastal waters, with Chl-*a* concentration range of 0.16 to 11.3 mg·m⁻³. Other versions up to version 5, all developed for marine environments, adopted 555 nm as λ_0 (Lee et al., 2009). Lee (2014) proposed 667 nm as λ_0 for waters with $R_{rs}(670) > 0.0065$ sr⁻¹, i.e., waters with higher concentrations of phytoplankton.

In inland waters, there is a high influence of $a_\phi(\lambda)$ and $a_{CDM}(\lambda)$ over $a(\lambda)$ at shorter wavelength and hence, other authors (LE et al., 2009; MISHRA et al., 2013; LI et al., 2013; MISHRA et al., 2014; LI et al., 2015) shifted λ_0 toward the red-edge region, improving significantly the estimation of $a(\lambda_0)$. Le et al. (2009) conducted a study in Taihu Lake, a highly turbid, eutrophic water body. The authors used the wavelength at 710 nm as λ_0 . Mishra et al. (2013) and Mishra et al. (2014) developed a version for highly productive waters with Chl-*a* range of 59.40 to 1376.60 mg·m⁻³ and TSS range of 69.80 to 401.20 mg·L⁻¹. The authors did not immediately obtain an improvement of the model by shifting λ_0 to 708 nm,

because there still was influence of particles absorption at this wavelength. Several attempts were carried out until they found a satisfactory empirical relationship between a and r_{rs} .

Li et al. (2013) and Li et al. (2015) also developed QAA versions for inland waters. The first model developed by Li et al. (2013) was parameterized for an environment with Chl- a range of 1.85 to 285.8 $\text{mg}\cdot\text{m}^{-3}$ and TSS range of 1.51 to 211.91 $\text{mg}\cdot\text{L}^{-1}$. The second model by Li et al. (2015) was a QAA for an environment with Chl- a range of 2.93 to 285.8 $\text{mg}\cdot\text{m}^{-3}$ and TSS of 2.34 to 123.79 $\text{mg}\cdot\text{L}^{-1}$. Li et al. (2013) and Li et al. (2015) changed the structure of some QAA steps while using 709 nm as λ_0 . Yang et al., (2013) developed a study in three turbid Asian lakes with Chl- a range of 9.79 to 153.92 $\text{mg}\cdot\text{m}^{-3}$ and TSS range of 4.81 to 61.00 $\text{mg}\cdot\text{L}^{-1}$. They shifted the position of λ_0 to 753 nm to prevent the interference of the high turbidity over $a(\lambda_0)$.

Bio-optical status in these locations is very different from each other; and therefore, these versions must not be directly applied for all aquatic systems, which hold a different range of OACs. Summarily, our study area exhibited Chl- a range of 17.7 to 797.8 $\text{mg}\cdot\text{m}^{-3}$ and TSS range of 3.6 to 44 $\text{mg}\cdot\text{m}^{-3}$; therefore, QAA versions developed for marine, lakes and rivers waters do not cover the maximum Chl- a values, while versions for ponds do not range the minimum values. Thereby, the aim of this work was to parameterize and calibrate a QAA to retrieve a and b_b from R_{rs} and use them in a bio-optical model for estimating the Chl- a concentration in a tropical eutrophic reservoir. Radiometric data and water samples collected *in situ* were used to parameterize and calibrate the empirical steps (LEE et al., 2002) of QAA.

In this research, a QAA based on the QAA_v5 proposed by Lee et al. (2009) was parameterized and calibrated. Alterations to some empirical steps of the algorithm considerably improved the retrieval of $a_t(\lambda)$, $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$. The critical alteration as part of the parameterization were (a) the selection the wavelengths suitable for the OACs composition; (b) calibration of $a(\lambda_0)$; (c) parameterization and calibration of ζ that is a value associated with the Chl- a absorption; and (d) calibration of ξ that is a value associated with the CDM absorption. The accurate calibration and parameterization of absorption coefficient of the total less pure water at reference wavelength ($a_{t-w}(\lambda_0)$) was essential to derive $a(\lambda_0)$ and other IOPs, being that the wavelengths associated with absorption by Chl- a and phycocyanin (PC) (443, 620 and 665 nm) were the most appropriate. However, the most important novel is related to estimation of $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$, which were underestimated for all existing QAA, yielding negative values. The fit of CDOM spectral slope (S) improved the accuracy of algorithm, but the alterations carried out in ζ were the key point of this study.

5.2. Data and Methods

5.2.1. Remote sensing reflectance

Radiometric measurements collected *in situ* were used to calculate R_{rs} using the equation proposed by Mobley (1999) (Equation 25).

$$R_{rs} = \frac{L_w}{E_s} = \frac{(L_t - \rho L_s)}{E_s} \quad (25)$$

where L_s is the incident sky radiance; L_t is the total radiance measured above surface and composed of the leaving-water radiance (L_w) and the portion of the L_s that is reflected by water surface (L_r); and E_s is the incident sky irradiance; and ρ is a reflectance factor related to direction, wavelength, wind speed, sensor field of view (FOV) taken equal to 0.028, and sky radiance distribution (MOBLEY, 1999).

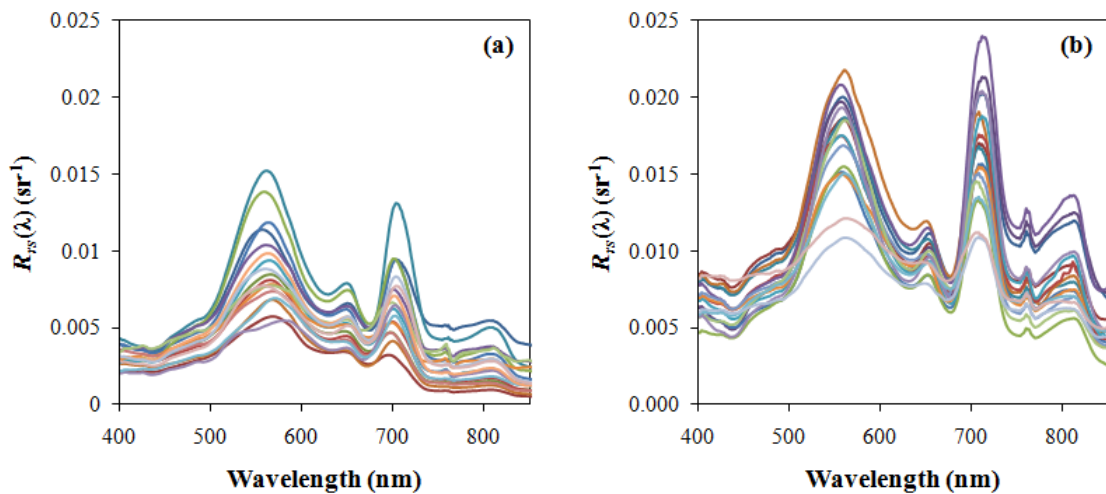
Acquisition geometry was adopted from Mobley (1999) and Mueller (2003). Three spectroradiometers, one ACC-VIS RAMSES with cosine collector and two ARC-VIS RAMSES with a 7° field-of-view (TriOS, Oldenburg, Germany) were used to acquire the radiometric measurements. The ACC-VIS sensor was pointed upward to collect $E_s(\lambda)$ ($\text{W}\cdot\text{m}^{-2}$). Meanwhile, one ARC-VIS sensor was pointed in downward direction (water surface) with an angle of 45° in relation to nadir position of the zenith angle to measure the $L_t(\lambda)$ ($\text{W}\cdot\text{m}^{-2}\cdot\text{sr}^{-1}$). Another ARC-VIS sensor was pointed upward direction (sky) with an angle of 135° in relation to nadir position of the zenith angle to measure $L_s(\lambda)$ ($\text{W}\cdot\text{m}^{-2}\cdot\text{sr}^{-1}$). The radiometers acquire data in a wavelength range of 320 nm to 950 nm and spectral sampling of approximately 3.3 nm; therefore, all of the $E_s(\lambda)$, $L_t(\lambda)$ and $L_s(\lambda)$ measurements were interpolated to 1 nm.

Eighteen samples were collected in May 2014 and 20 samples in October 2014. P4 and P13 samples acquired in May 2014 were affected by sunglint effect. Then, 38 measurements of R_{rs} were used as input to parameterize the QAA. Figure 15 shows the R_{rs} spectra measured in both field surveys carried out in BBHR. Analyzing the curves, it is noticed that R_{rs} was higher in October than May. High absorption was observed in blue light region with maximum at about 430 nm, associated with high Chl-*a* concentration (RUNDQUIST et al., 1996; KIRK, 2011). As expected, there was higher reflectance in green light region, due to low absorption by phytoplankton pigments (KIRK, 2011).

The absorption feature of the phycocyanin (PC) pigment at approximately 620 nm associated with presence of cyanobacteria (WEAVER and WRIGLEY, 1994; SIMIS et al., 2005; MISHRA and MISHRA, 2012; MISHRA et al., 2014) is clearly identified in both field campaigns. The low reflectance in red light region, especially around 680 nm, is related to high absorption of algal Chl-*a* (RUNDQUIST et al., 1996), while reflectance peak at approximately 710 nm, associated with high backscattering by concentrations of Chl-*a* indicating the eutrophic status of the study site (GITELSON, 1992; RUNDQUIST et al., 1996). NIR region is strongly affected by pure water absorption (POPE and FRY, 1997; LE et al., 2009; MISHRA et al., 2014) and temperature (PEGAU and ZANEVELD, 1993; SULLIVAN et al., 2006), therefore, reflectance tends to be lower (RUNDQUIST et al., 1996). The small peak at 760 is associated with Chl-*a* fluorescence (MOYA et al., 2004), whereas the reflectance peak at approximately 810 nm is associated with backscattering by algal cells (RUNDQUIST et al., 1996).

Central wavelengths of the bands available in the MEdium Resolution Imaging Spectrometer (MERIS) sensor, onboard ENVISAT-1 satellite (ESA, 2015), were adopted as reference to parameterize the QAA because its bands are appropriate to color water applications. Although MERIS is non-operational, the results obtained in this research can be compared with published literature those used MERIS data. In addition, MERIS bands are compatible with of other operational or upcoming sensor systems such as MSI/Sentinel-2A, launched in June 2015, and OLCI/Sentinel-3, launched in February 2016 (ESA, 2015).

Figure 15. Measured R_{rs} spectra collected in (a) May 2014 ($n=18$) and (b) October 2014 ($n=20$).



5.2.2. *Optically active components*

Water samples were collected *in situ* to measure Chl-*a*, total suspended solids (TSS), inorganic suspended solids (ISS) and organic suspended solids (OSS) concentrations. 250 ml water was filtered per each glass fiber GF/F Whatman, 47 mm diameter and 0.7 μm pore size filter. A vacuum pressure pump and a filter holder were used to help in the filtration process. The filter was frozen and kept in the dark until further analysis. The residue on the filter was used to estimate the Chl-*a* concentration in the laboratory. Extraction by acetone was the method adopted to estimate the Chl-*a* concentration (GOLTERMAN, 1975).

Water samples were filtered in glass fiber filter GF/F Whatman (47 mm diameter and 0.7 μm pore size) and stored frozen and in the dark to estimate TSS. The filters were dried in an oven at 105°C for 12 hours, desiccated and weighed to obtain the TSS. The filters were ignited at 550°C for 30 minutes in the muffle furnace, and then desiccated and weighed to acquire the inorganic suspended solids (ISS). Subtracting the ISS from the TSS yielded the organic suspended solids (OSS), and dividing each component of solids by filtered volume provided the concentrations of each constituent (APHA, 1998).

5.2.3. *Inherent optical properties*

$a_p(\lambda)$, $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$ were estimated in laboratory and were used to assess the QAA performance. Water samples were collected from 20 sampling locations during both field trips (May 2014 and October 2014). 250 ml of water from each location was filtered using GF/F Whatman glass fiber filters with 0.7 μm pore size and 47 mm diameter, kept frozen and in the dark until the analysis to estimate the absorption coefficient by phytoplankton, detritus and total particulate material. The measurements were acquired over the 280 – 800 nm spectral range in 1 nm by using a 2600 UV-Vis spectrophotometer (Shimadzu, Kyoto, Japan) with dual beam and an integrating sphere. The optical density of the particulate materials was obtained from the first reading. After, the pigment in the filter was extracted with sodium chloride, the filter was measured again to determine the optical density of detritus. These optical densities were corrected for multiple scattering effects caused by the glass-fiber filter (CLEVELAND & WEIDEMANN, 1993). The a_p and a_d were estimated from the corrected optical densities (TASSAN & FERRARI, 1998). Finally, the a_ϕ was obtained by subtracting the a_d from a_p .

Water samples were filtered through a nylon membrane Whatman filter with 0.22 μm pore size and 47 mm diameter to measure the CDOM (colored dissolved organic material) optical density (A_{CDOM}). The filtrates were stored, kept cool and in the dark until the analysis. The samples were measured at room temperature using a quartz cuvette with 10 cm optical path. The measurements was done in a spectral range of 280-800 nm using a 2600 UV-Vis spectrophotometer (Shimadzu, Kyoto, Japan) with a single beam. Milli-Q water was used as blank reference. From the A_{CDOM} , CDOM absorption coefficients were calculated by using Equation 26 (BRICAUD *et al.*, 1981).

$$a_{CDOM} = 2.3 \frac{A_{CDOM}(\lambda)}{l} \quad (26)$$

where $A_{CDOM}(\lambda)$ is the optical density at wavelength (λ) and l is the cuvette path length in meters (BRICAUD *et al.*, 1981).

5.2.4. Quasi-analytical algorithm

QAA is used to retrieve $a(\lambda)$ and $b_b(\lambda)$ coefficients from R_{rs} of the water (LEE *et al.*, 2002). QAA is based on the principle that R_{rs} behavior depends on the IOPs of the OACs present in the water. Table 9 shows the altered steps of the inversion model to derived $a(\lambda)$ and $b_b(\lambda)$ from R_{rs} . Five versions of the QAA proposed by different authors were tested in this study. Three out of the five were developed for application on open ocean and coastal waters: QAA_v4 (IOCCG, 2006), QAA_v5 (LEE *et al.*, 2009), and QAA_v6 (LEE, 2014). QAA_v4 and QAA_v5 are recommended for water with low absorption coefficients ($R_{rs}(670) < 0.0065 \text{ sr}^{-1}$) (LEE *et al.*, 2009; LEE *et al.*, 2014).

Table 9. Comparison between empirical steps of the QAA_BBHR and QAA_v5 to derive absorption and backscattering coefficients from R_{rs} .

	QAA_BBHR	QAA_v5
$a(\lambda_0)$	$\lambda_0 = 709 \text{ nm}$ $\chi = \log \left(\frac{r_{rs}(443) + r_{rs}(665)}{r_{rs}(\lambda_0) + 5 \frac{r_{rs}(620)}{r_{rs}(443)} r_{rs}(620)} \right)$ $a(\lambda_0) = a_w(\lambda_0) + 10^{-0.7702 + 0.0999\chi + 0.0566\chi^2}$	$\lambda_0 = 555 \text{ nm}$ $\chi = \log \left(\frac{r_{rs}(443) + r_{rs}(490)}{r_{rs}(\lambda_0) + 5 \frac{r_{rs}(667)}{r_{rs}(490)} r_{rs}(667)} \right)$ $a(\lambda_0) = a_w(\lambda_0) + 10^{-1.146 - 1.366\chi - 0.469\chi^2}$
η	$\eta = 2.0 \left(1 - 1.2 \exp \left(-0.9 \frac{r_{rs}(443)}{r_{rs}(555)} \right) \right)$	$\eta = 2.0 \left(1 - 1.2 \exp \left(-0.9 \frac{r_{rs}(443)}{r_{rs}(555)} \right) \right)$
ζ	$\zeta = a_\varphi(665)/a_\varphi(709)$ $\zeta = 0.3 + \frac{0.2}{0.8 + r_{rs}(665)/r_{rs}(709)}$	$\zeta = a_\varphi(411)/a_\varphi(443)$ $\zeta = 0.74 + \frac{0.2}{0.8 + r_{rs}(443)/r_{rs}(\lambda_0)}$
ξ	$\xi = a_{CDM}(411)/a_{CDM}(443)$ $\xi = e^{S(443-411)}$ $S = 0.014 + \frac{0.002}{0.6 + r_{rs}(443)/r_{rs}(\lambda_0)}$	$\xi = a_{CDM}(411)/a_{CDM}(443)$ $\xi = e^{S(443-411)}$ $S = 0.015 + \frac{0.002}{0.6 + r_{rs}(443)/r_{rs}(\lambda_0)}$

QAA approach developed for inland waters by MISHRA et al. (2013) and MISHRA et al. (2014) was also tested and labeled QAA_M13 and QAA_M14, respectively. Both QAA_M13 and QAA_M14 used 708 nm as the reference wavelength (λ_0) and were parameterized to quantify PC concentration (MISHRA et al., 2013; MISHRA et al., 2014). In turbid waters, the λ_0 should be shifted to longer wavelengths where water absorption is predominant in order to avoid strong interference from other OACs (LEE et al., 2002; LE et al., 2009; MISHRA et al., 2014).

Both QAA_M13 and QAA_M14 were parameterized and calibrated for waters with characteristics somewhat similar to BBHR. QAA_M13 and QAA_M14 were originally parameterized and calibrated using data collected at aquaculture ponds in Thad Cochran National Warmwater Aquaculture Center, Mississippi, USA. Ponds were used for catfish aquaculture and presented characteristics of high algal turbidity and primary productivity. A dataset with 24 samples was used to calibrate the QAA_M13, whereas, 20 samples were used

to calibrate QAA_M14. Chl-*a* concentration varied from 59.4 mg m⁻³ to 1376.6 mg m⁻³ and average of 293.3 mg m⁻³, while *a*(443) range was of 4.99 m⁻¹ to 47.21 m⁻¹.

5.2.5. Parameterization and calibration of QAA

These different versions of the QAA found in the literature frequently point to the fact that the IOPs for the water system must be taken into account in order to develop an accurate QAA. In inland waters, the bio-optical parameters depend on the geological and soil characteristics and runoff activities of the drainage basin. Therefore, it is expected that the versions found in the literature may not be suitable for reservoirs in tropical regions. Parameterization and calibration existing QAA maybe the only option to improve their performances (LEE *et al.*, 2009; MISHRA *et al.*, 2013; MISHRA *et al.*, 2014; LEE, 2014). In this paper empirical steps of the QAA were tuned based on the bio-optical characteristics in BBHR. Empirical steps were modified to improve the performance of the QAA and are indicated in Table 9. After applications of existing versions, it was retained the basic framework of QAA_v5 for new version proposed in this research, being referred as QAA_BBHR. *a*(λ) and *b_b*(λ) were retrieved from *r_{rs}* measurements. The *r_{rs}* can be analytically derived from *u* (ratio of *b_b* to the sum of *a* and *b_b*) or empirically from *R_{rs}* as shown in the Equations 27 and 28.

$$r_{rs} = g_0 u(\lambda) + g_1 [u(\lambda)]^2 \quad (27)$$

$$r_{rs} = R_{rs} / (0.52 + 1.7 R_{rs}) \quad (28)$$

where, *g₀* = 0.0895 and *g₁* = 0.125 are average of the values proposed by Gordon *et al.* (1988) and Lee *et al.* (1999) that vary with the phase function of particle and are not remotely measured (LEE *et al.*, 2002). *u* can be derived from *r_{rs}* (Equation 29) as shown in Equation 30.

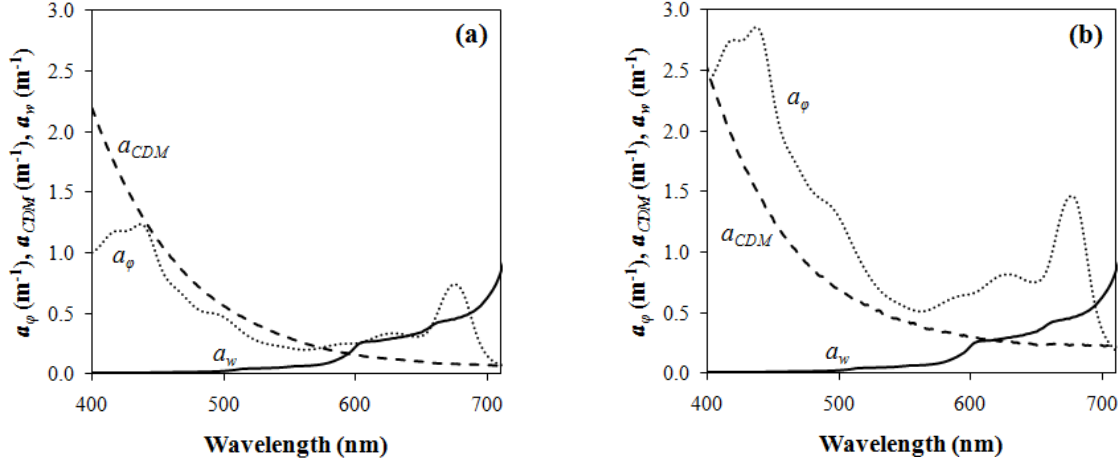
$$u = \frac{b_b}{a + b_b} \quad (29)$$

$$u = \frac{-g_0 + \sqrt{(g_0)^2 + 4g_1 \times r_{rs}(\lambda)}}{2g_1} \quad (30)$$

Parameterization and calibration of QAA began by determining the reference wavelength (λ_0). According to Lee et al. (2002), the λ_0 is the position where the elastic scattering can be accurately measured and $a(\lambda_0)$ can be estimated from $r_{rs}(\lambda_0)$. In this study, the parameterization of the algorithm considered 709 nm as λ_0 , assuming $a_t(709)$ equals to $a_w(709)$ (LEE et al., 2002; LE et al., 2009; MISHRA et al., 2014). At 709 nm, the a_w has a greater contribution toward the $a_t(\lambda)$. The average $a_w(709)$ contributed 75% toward the $a_t(709)$ in our dataset. That contribution was much higher in May (84.4%) compared to October (65.5%). Whereas, the average $a_w(560)$ and $a_w(670)$ contributed 9.2% and 28.6% toward the corresponding a_t . $a_w(\lambda)$ proposed by Pope and Fry (1997) and $b_{bw}(\lambda)$ proposed by Smith & Baker (1981) were adopted for the parameterization of QAA_BBHR.

Figure 16 shows the average absorption coefficient by phytoplankton (a_ϕ) and CDOM plus detritus (CDM) (a_{CDM}) acquired from BBHR, in (a) May 2014 and (b) October 2014. It is noticeably clear that $a_\phi(\lambda)$ and $a_{CDM}(\lambda)$ determine the shape and magnitude of $a_t(\lambda)$ at 555 nm and 665 nm as opposed to at 709 nm. Contribution of phytoplankton absorption was 48.3% at 560 nm and 63.2% at 670 nm, whereas, CDM absorption was 43.4% and 9.9% of a_t at 560 nm and 670 nm, respectively. It was also observed that $a_{CDM}(\lambda)$ has consistently higher influence than $a_\phi(\lambda)$ toward $a_t(\lambda)$. Finally, the pigment absorption features were mainly, related to Chl-*a* and PC.

Figure 16. Average absorption coefficient by phytoplankton (a_ϕ – dotted line), CDM (a_{CDM} – dashed line), and pure water (a_w – continuous line) (Pope & Fry, 1997) measured in (a) May 2014 and (b) October 2014



$a(\lambda_0)$ is composed of the sum of $a_w(\lambda_0)$, $a_\phi(\lambda_0)$ and $a_{CDM}(\lambda_0)$ (Equation 31) and can be empirically derived from Equation 32 (LEE et al., 2009).

$$a(\lambda_0) = a_w(\lambda_0) + a_\phi(\lambda_0) + a_{CDM}(\lambda_0) \quad (31)$$

$$a(\lambda_0) = a_w(\lambda_0) + 10^{h_0 + h_1\chi + h_2\chi^2} \quad (32)$$

where χ is a value obtained from the ratio of r_{rs} at different wavelengths associated with spectral features of pigments and CDOM (Equation 33) (LEE et al., 2009); h_0 , h_1 and h_2 are the calibration coefficients of the polynomial fit between $a_{t-w}(\lambda_0)$ and χ . Overall, r_{rs} at wavelengths associated with absorption of pigments performs most accurately for the estimation of $a(\lambda_0)$.

$$\chi = \log_{10} \left(\frac{r_{rs}(\lambda_1) + r_{rs}(\lambda_2)}{r_{rs}(\lambda_0) + r_{rs}(\lambda_3)^2 \times r_{rs}(\lambda_4)^{-1}} \right) \quad (33)$$

where $r_{rs}(\lambda_0)$ is below surface remote sensing reflectance at reference wavelength; λ_1 , λ_2 , λ_3 , and λ_4 are wavelengths associated with dominant spectral features of the phytoplankton pigments and/or CDOM. Parameterization and calibration of χ was performed based on the band center of MERIS and upcoming Sentinel-3 sensor. The wavelengths (λ_1 , λ_2 , λ_3 , and λ_4) associated with the absorption by the Chl-*a* and PC (443, 665, 620, and 443 nm) showed the best performance (Tab.12).

$b_{bp}(\lambda_0)$ was retrieved from $a(\lambda_0)$ analytically (Equation 34).

$$b_{bp}(\lambda_0) = \frac{u(\lambda_0)a(\lambda_0)}{1 - u(\lambda_0)} - b_{bw}(\lambda_0) \quad (34)$$

where $u(\lambda_0)$ value is obtained from Equation 30 and $b_{bw}(\lambda_0)$ is the b_{bw} proposed by Smith & Baker (1981).

$b_{bp}(\lambda)$ was derived from $b_{bp}(\lambda_0)$ based on Smith & Baker (1981) (Equation 35).

$$b_{bp}(\lambda) = b_{bp}(\lambda_0) \left(\frac{\lambda_0}{\lambda} \right)^\eta \quad (35)$$

Spectral power for $b_{bp}(\eta)$ (Tab. 9) was also parameterized, changing the wavelength of denominator in Equation 36. Based on calibration the coefficients of η were changed and evaluated to determine the most accurate coefficients. A value range of 1.0 to 1.9 was tested for a , 1.3 to 1.5 for b , and 0.1 to 0.8 for c . Although alterations were tested, the η proposed by Lee et al. (2009) showed the best performance.

$$\eta = a \left(b - c \times \exp \left(-d \frac{r_{rs}(443)}{r_{rs}(\lambda)} \right) \right) \quad (36)$$

Spectral curve of $a(\lambda)$ was analytically estimated (Equation 37) from $u(\lambda)$, $b_{bp}(\lambda)$ and $b_{bw}(\lambda)$.

$$a(\lambda) = \frac{(1 - u(\lambda))(b_{bw}(\lambda) + b_{bp}(\lambda))}{u(\lambda)} \quad (37)$$

$a_\phi(\lambda)$ and $a_{CDM}(\lambda)$ were estimated from $a(\lambda)$. ζ and ξ (Tab. 9) values depend on pigment composition, humic versus fulvic acids, and abundance of detritus. ζ is related to Chl- a concentration or pigment absorption, while ξ is related to the CDM absorption (LEE et al., 2002). ζ and ξ were derived empirically based on Equations 38 and 39. Miscalibration of ζ and ξ can lead to under- or overestimation of a_{CDM} and a_ϕ .

$$\zeta = \frac{a_\phi(411)}{a_\phi(443)} = a + \frac{b}{c + r_{rs}(443)/r_{rs}(560)} \quad (38)$$

$$\xi = \frac{a_{CDM}(411)}{a_{CDM}(443)} = e^{S(443-411)} \quad (39)$$

ξ was modified based on the a_{CDM} spectral slope (S) values obtained from laboratory analysis. Empirically, S was also derived from the band ratio of absorption by pigments and CDOM (560 nm and 443 nm, respectively) (Equation 40). A magnitude difference was detected between measured and estimated S , with average values of 0.127 nm^{-1} and 0.171 nm^{-1} , respectively, and NRMSE (Normalized Root Mean Square Error) of 46.6%. Thus, an alteration was applied to the intercept of the equation (Tab. 9) as presented in Equation 40. Even after changing S , a_{CDM} still produced negative values, consequently, a_ϕ presented negative values; therefore, ζ (Tab. 9) also was calibrated. ζ works as multiplicative factor, always associated with a subtractive term. Therefore, ζ was likely being overestimated. Different values of offset (equation of the Tab. 9) were tested, varying from 0.1 to 0.9.

$$S = a + \frac{b}{c + r_{rs}(443)/r_{rs}(560)} \quad (40)$$

$a_{CDM}(443)$ was analytically derived (Equation 41) removing the influence of a_ϕ and a_w from the a and by defining the proportion of CDM and phytoplankton absorption at wavelengths 411 nm and 443 nm. a_{CDM} is stronger at 411 nm than at 443 nm and phytoplankton absorbs more at 443 nm than at 411 nm (CARDER et al. 1999). Therefore, the proportion of CDM and phytoplankton absorption can be determined using ζ and ξ values. The spectral curve of $a_{CDM}(\lambda)$ can be analytically expressed by Equation 42. $a_\phi(\lambda)$ was derived from $a(\lambda)$ and $a_{CDM}(\lambda)$ using Equation 43.

$$a_{CDM}(443) = \frac{(a(411) - \zeta a(443)) - (a_w(411) - \zeta a_w(411))}{\xi - \zeta} \quad (41)$$

$$a_{CDM}(\lambda) = a_{CDM}(443) e^{-S(\lambda-443)} \quad (42)$$

$$a_\phi(\lambda) = a_t(\lambda) - a_w(\lambda) - a_{CDM}(\lambda) \quad (43)$$

5.2.6. Chl-*a* retrieval from IOPs derived by QAA

IOPs derived by QAA were used to parameterize bio-optical models for estimating the Chl-*a* which can be used as bio-indicator of phytoplankton biomass (GOODIN et al., 1993). Phytoplankton absorbs strongly at 443 nm and commonly used ocean color algorithms were designed using the blue-green ratio to estimate Chl-*a* (O'REILLY et al., 1998; CARDER et al., 1999). However, in eutrophic water bodies such as BBHR, absorption coefficients at blue region can be highly influenced by other components such as CDOM. Therefore, red-NIR wavelengths have been used in several bio-optical algorithms to estimate Chl-*a* because these wavelengths have low interference from the absorption or backscattering coefficients of CDOM and detritus (GITELSON et al., 2008; MISHRA & MISHRA, 2012; LE et al., 2013; MATSUSHITA et al., 2015). In highly turbid waters, 754 nm can also be used to minimize the effects from detritus and CDOM (GITELSON et al., 2008; MATSUSHITA et al., 2015).

We tested the a_ϕ derived by QAA in redesigning the red-NR based Chl-*a* algorithms to retrieve Chl-*a* concentration. Comparison between the models was used as a way of evaluating the performance of the estimated a_ϕ . The two-band (2B), three-band (3B) indexes (Gitelson et al. 2003) and Normalized Difference Chlorophyll Index (NDCI) (MISHRA & MISHRA, 2012) were tested. 2B and 3B indexes were decomposed in terms of a_ϕ and a_w (semianalytical approaches) as proposed by Le et al. (2013). Similarly, an index based on absorption coefficients was proposed for NDCI. Wavelengths at 665, 709 and 754 nm (GITELSON et al., 2008; MISHRA & MISHRA, 2012) were used based on MERIS band configuration. Equations 44 and 45 show the structure of 2B index (GITELSON et al., 2008) using a_ϕ and a_w (LE et al., 2013). Similarly, Equations 46 and 47 show the 3B index (GITELSON et al., 2008) and Equations 48 and 49 show the architecture of NDCI (MISHRA & MISHRA, 2012). The models were calibrated by the least square method using a prediction interval with a confidence level of 0.95.

$$2B = R_{rs}(709)/R_{rs}(665) \quad (44)$$

$$\psi_1 = [a_\phi(665) + a_w(665)]/a_w(709) \quad (45)$$

$$3B = [R_{rs}^{-1}(665) - R_{rs}^{-1}(709)] \times R_{rs}(754) \quad (46)$$

$$\psi_2 = [a_\varphi(665) + a_w(665) - a_\varphi(709) - a_w(709)] / a_w(754) \quad (47)$$

$$NDCI = \frac{R_{rs}(709) - R_{rs}(665)}{R_{rs}(709) + R_{rs}(665)} \quad (48)$$

$$\psi_3 = \frac{a_w(665) + a_\varphi(665) - a_w(709)}{a_w(665) + a_{CDM}(665) + a_\varphi(665) + a_w(709) + a_{CDM}(709)} \quad (49)$$

5.2.7. Validation

Validation of the models was performed using the statistic metrics: root mean square error (RMSE – Equation 50), normalized root mean square error (NRMSE – Equation 51), mean absolute percentage error (MAPE – Equation 52) and bias (Equation 53).

$$RMSE = \left\{ \frac{\sum_{i=1}^n [(x_i^{estimated}) - (x_i^{measured})]^2}{N} \right\}^{1/2} \quad (50)$$

$$NRMSE = \frac{RMSE}{x_{\max}^{measured} - x_{\min}^{measured}} \quad (51)$$

$$MAPE = \frac{\sum_{i=1}^n \left(\frac{|x_i^{estimated} - x_i^{measured}|}{x_i^{measured}} \right)}{N} \quad (52)$$

$$Bias = \frac{1}{n} \sum_{i=1}^n (x_i^{estimated} - x_i^{measured}) \quad (53)$$

5.3. Results and Discussion

5.3.1. Water quality parameters

BBHR presents characteristics of highly productive waters with an average Chl-*a* concentration of 123.1 mg m⁻³ (Table 10). An elevation of the trophic level occurred from May (austral autumn) to October (austral spring), 2014. Chl-*a* concentration showed a range of 17.7 mg m⁻³ to 279.9 mg m⁻³ in May, 2014 and a range of 263.2 mg m⁻³ to 797.8 mg m⁻³ in October, 2014.

The minimum Chl-*a* in October was close to the maximum Chl-*a* concentration in May. An average OSS/TSS ratio of 0.83 in May and 0.9 in October was found, which explains the dominance of organic matter in the total particulate material in BBHR. $a_{\phi}(\lambda)$ values were much higher than $a_{CDM}(\lambda)$ from May to October, corroborating that turbidity and TSS were mainly associated with phytoplankton concentration in BBHR. There was a considerable increase in the average $a_{\phi}(440)$ from May to October, with a range of 1.25 m⁻¹ to 2.81 m⁻¹, whereas, average $a_{CDM}(412)$ ranged from 1.86 m⁻¹ to 2.12 m⁻¹. In other words, average $a_{\phi}(440)$ increased 55.5% and $a_{CDM}(412)$ increased only 12.3%. Average $a_{\phi}(\lambda)$ and $a_{CDM}(\lambda)$ (Fig. 16) and $a_{\phi}(440)/a_{CDM}(440)$ (Table 10) show that on average the contribution of $a_{CDM}(\lambda)$ to the $a(\lambda)$ was equal to $a_{\phi}(\lambda)$, in May, in contrast to October when the contribution of $a_{\phi}(\lambda)$ was higher. The elevated levels of Chl-*a* led to rising algal turbidity with an average of 5.2 NTU in May and 18.6 NTU in October as a result the Secchi disk depth decreased significantly with maximum value of 2.3 m in May and a maximum of 0.8 m in October.

Table 10. Descriptive statistics of the optical and water quality parameters measured *in situ* or in the laboratory: Chl-*a* concentration ($\text{mg}\cdot\text{m}^{-3}$); Secchi disk depth (m); turbidity (NTU); TSS concentration ($\text{mg}\cdot\text{L}^{-1}$); OSS/TSS ratio (%); ISS/TSS ratio (%); a_ϕ at 440, 620 and 665 nm (m^{-1}); a_{CDM} at 412 and 440 nm (m^{-1}); and $a_\phi(440)/a_{\text{CDM}}(440)$ ratio. Statistical metrics used: minimum value (Min), maximum value (Max), mean, median, standard deviation (SD) and coefficient of variation (CV) in percentage (%), that is $\text{CV} = (\text{SD}/\text{mean})\cdot 100$.

a. May 5-9, 2014, n = 18 stations						
Parameter	Min	Max	Mean	Median	SD	CV
Chl- <i>a</i>	17.7	279.9	123.1	101.3	69.8	56.7
Secchi disk depth	0.8	2.3	1.5	1.4	0.4	26.7
Turbidity	1.7	12.5	5.2	5	2.4	46.2
TSS	3.8	16.3	7.4	7.0	3.3	44.6
OSS/TSS	45.0	97.5	83.4	86.6	11.8	14.1
ISS/TSS	2.5	55.0	16.6	13.4	11.8	71.2
a_ϕ (440)	0.31	2.62	1.25	1.05	0.63	50
a_ϕ (620)	0.12	0.78	0.34	0.31	0.18	51.9
a_ϕ (665)	0.2	1.26	0.61	0.52	0.28	45.1
a_{CDM} (412)	1.57	2.68	1.86	1.78	0.27	14.5
a_{CDM} (440)	1.06	1.91	1.26	1.21	0.21	16.5
$a_\phi(440)/a_{\text{CDM}}(440)$	0.3	2.15	0.99	0.84	0.49	49.8
b. October 13-16, 2014, n = 20 stations						
Parameter	Min	Max	Mean	Median	SD	CV
Chl- <i>a</i>	263.2	797.8	428.7	368.9	154.5	36
Secchi disk depth	0.4	0.8	0.6	0.6	0.1	16.7
Turbidity	11.6	33.2	18.6	17.6	5.3	28.5
TSS	10.8	44	22	21.2	7	31.8
OSS/TSS	80	96	90	90	10	11.1
ISS/TSS	4	20	10	10	5	40
a_ϕ (440)	1.56	5.59	2.81	2.57	1.03	36.8
a_ϕ (620)	0.44	1.56	0.79	0.76	0.31	39.4
a_ϕ (665)	0.63	2.1	1.16	1.08	0.43	36.8
a_{CDM} (412)	1.6	3.26	2.12	2.11	0.36	16.8
a_{CDM} (440)	1.02	2.6	1.45	1.42	0.33	22.6
$a_\phi(440)/a_{\text{CDM}}(440)$	0.64	2.61	1.36	1.2	0.56	48.9

5.3.2. $a(\lambda)$ retrieval

Table 9 shows the parameterizations and calibrations accomplished in QAA_BBHR. Among the four alterations carried out, two of them are very important for accurate estimation of $a_t(\lambda)$. First, the selection of the wavelength suitable to estimate the absorption coefficient of the pigments, detritus and CDOM made a difference as well as the calibration of χ . Figure 17 shows the $a(\lambda)$ spectra determined by: spectrophotometer in laboratory (Fig. 17a), QAA_v4 (Fig. 17b) (LEE *et al.*, 2009), QAA_v5 (Fig. 17c) (LEE *et al.*, 2009), QAA_v6 (Fig. 17d) (LEE, 2014), QAA_M13 (Fig. 17e) (MISHRA *et al.*, 2013), QAA_M14 (Fig. 17f) (MISHRA *et al.*, 2014) and QAA_BBHR (Fig. 17g). Among all the versions of QAA tested, the most recent version of the QAA proposed by Mishra *et al.* (2014) presented the best performance in estimating $a_t(\lambda)$, because this version was fitted for waters with bio-optical status more similar to BBHR. Meanwhile, QAA_v4, QAA_v5 and QAA_v6 underestimated $a_t(\lambda)$, since they were developed for waters with very low $a(\lambda)$. Although QAA_M13 is similar to QAA_M14, the first overestimated $a_t(\lambda)$, due likely to χ has been fitted for more productive waters than BBHR. As expected, the version fitted with BBHR dataset (QAA_BBHR) shows the best performance, because it is considered the bio-optical status of the reservoir itself.

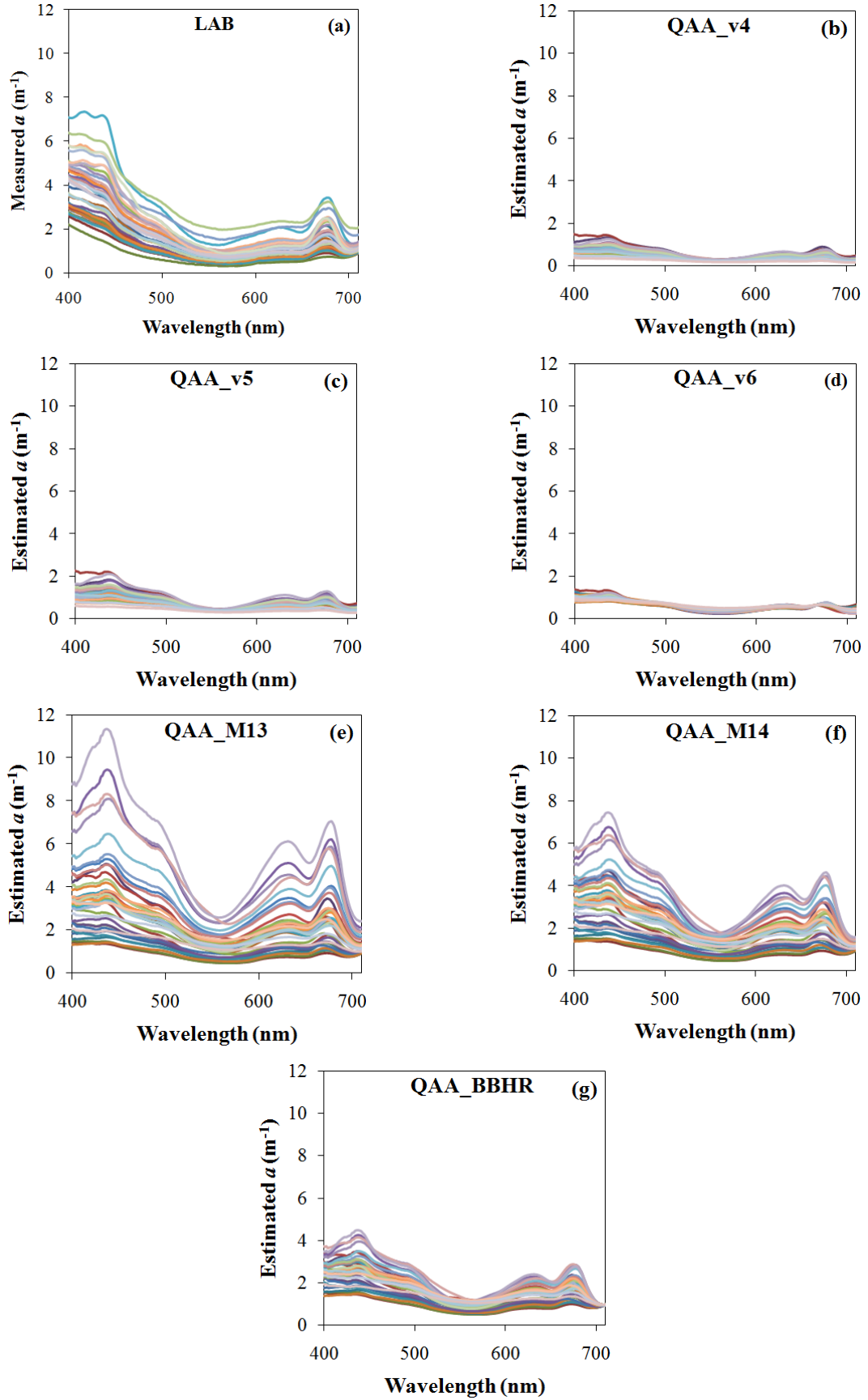
Parameterization and calibration of χ presented considerable change to $a_t(\lambda)$ estimation, even though χ is defined as importance of second order (LEE *et al.*, 2002). The QAA versions parameterized for ocean and coastal waters highly underestimated $a_t(\lambda)$ across all wavelengths, The QAA_v4, QAA_v5 and QAA_v6 showed an average bias ranging from -1.31 m^{-1} to -1.04 m^{-1} . The most underestimated wavelength was observed to be 412 nm (range of -3.18 m^{-1} for QAA_v4 to -2.79 m^{-1} for QAA_v5), and the least was observed at 560 nm (range of -0.5 m^{-1} for QAA_v4 to -0.36 m^{-1} for QAA_v5). The lowest accurate performance to retrieve $a_t(\lambda)$ was exhibited by the QAA_v4 version, due likely to parameters used to determine χ . The main difference between QAA_v4 and QAA_v5 is the wavelength at red spectral region adopted (640 nm in QAA_v4 and 667 nm in QAA_v5). Taking into account the maximum Chl-*a* absorption in red light is around 675 nm in BBHR (Figure 15), 667 nm is more representative that pigment than 640 nm. Both versions used 555 nm as λ_0 to estimate χ (Lee *et al.*, 2009), which has shown impropriated for inland waters (LE *et al.*, 2009; MISHRA *et al.*, 2013; 2014). Other wavelengths used to parameterize χ were absorption bands of Chl-*a* at 443 nm and 490 nm (LEE *et al.*, 2009). On the other hand, QAA_v6 do not use the χ factor to estimate the absorption coefficients of OACs [$a_\phi(\lambda)$ and $a_{CDM}(\lambda)$]. To estimate $a_t(\lambda_0)$ QAA_v6 considered a potential function ($y = x^n$) using R_{rs} at wavelengths 443,

490 and 670 nm to represent the sum of $a_\phi(\lambda_0)$ and $a_{CDM}(\lambda_0)$ (LEE, 2014). QAA_v6 was proposed for situations where $R_{rs}(670) > 0.0065 \text{ sr}^{-1}$ (LEE, 2014) and showed lower accuracy than QAA_v5 in BBHR, which the overall average $R_{rs}(670)$ was of 0.0059 sr^{-1} (average of 0.004 sr^{-1} in May and 0.0076 sr^{-1} in October), i.e., the application of QAA_v6 is recommended. The use of 670 nm as λ_0 must impaired its performance in inland waters, since this wavelength undergoes influence of absorption by OACs.

The models proposed for inland water such as QAA_M13 and QAA_M14 were parameterized and calibrated in highly turbid productive waters (MISHRA *et al.*, 2013; MISHRA *et al.*, 2014). In turbid productive waters, there is a high influence of $a_\phi(\lambda_0)$ and $a_{CDM}(\lambda_0)$ over $a(\lambda_0)$ at 555 nm and 667 nm. Thus, 555 nm and 667 nm are not suitable as λ_0 in those waters (LE *et al.*, 2009; MISHRA *et al.*, 2013; LI *et al.*, 2013; MISHRA *et al.*, 2014; LI *et al.*, 2015). For that reason, 708.75 nm (red edge region and central wavelength of band 9 of the MERIS sensor) has been used as λ_0 ; where $a_w(\lambda_0)$ is expected to dominate the total absorption (LEE *et al.*, 2002; MISHRA *et al.*, 2013; MISHRA *et al.*, 2014). Other researchers also tuned QAA using wavelength around 708.75 nm as λ_0 . For example, Le *et al.* (2009) conducted a study in Taihu Lake, China where they used 710 nm as λ_0 . The shifting of λ_0 to red-edge region resulted in a high improvement for estimating the $a(\lambda_0)$. In their research (LI *et al.*, 2013; LI *et al.*, 2015), a λ_0 was not adopted at every step. Nevertheless, the estimation of $a_{t-w}(\lambda)$ was done considering $R_{rs}(709)$ and $b_b(709)$. The wavelength of 753 nm also was used as λ_0 in three turbid Asian lakes, and λ_0 was shifted to prevent the interference of the high turbidity over $a(\lambda_0)$ (YANG *et al.*, 2013).

Upon application, QAA_M13 and QAA_M14 overestimated $a(\lambda)$ in the BBHR (Fig. 17). Although both models were originally developed to quantify PC ($\lambda_1 = 443 \text{ nm}$, $\lambda_2 = 620 \text{ nm}$, $\lambda_3 = 620 \text{ nm}$ and $\lambda_4 = 443 \text{ nm}$) (MISHRA *et al.*, 2013; MISHRA *et al.*, 2014) and share the same wavelengths to parameterize χ , QAA_M13 showed higher overestimation than QAA_M14. QAA_M13 yielded an average bias of 0.65 m^{-1} with minimum and maximum being 0.21 m^{-1} (709 nm) and 1.1 m^{-1} (620 nm), whereas, QAA_M14 yielded an average bias of 0.41 m^{-1} , with minimum and maximum bias of 0.12 m^{-1} (709 nm) and 0.88 m^{-1} (620 nm). The suitable calibration and parameterization of χ showed important, changing significantly the estimation of $a_t(\lambda)$. Even though samples used to calibrate QAA_M13 and QAA_M14 were collected in the same environment, they produced different results for each dataset, due to fits carried out in the empirical steps (MISHRA *et al.*, 2013; 2014).

Figure 17. Estimated a spectra using **(a)** measured spectra in the laboratory, **(b)** QAA_v4 (LEE et al. 2002), **(c)** QAA_v5 (LEE et al., 2009), **(d)** QAA_v6 (LEE et al., 2014), **(e)** QAA_M13 (MISHRA et al., 2013), **(f)** QAA_M14 (MISHRA et al., 2014) and **(g)** QAA_BBHR.



Different wavelength combinations were tested to parameterize χ with the final aim of estimating Chl-*a* concentration. The best combination of bands were 709 nm as λ_0 and the wavelengths representing absorption by Chl-*a* and PC such as $\lambda_1 = 443$ nm, $\lambda_2 = 665$ nm, $\lambda_3 = 620$ nm and $\lambda_4 = 443$ nm. Parameterization and calibration coefficients are presented in Table 9. Although 620 nm is associated with the absorption by PC (WEAVER & WRIGLEY, 1994), 620 nm was kept in χ calibration because although the band combination using only 443, 665 and 709 nm presented good results, inclusion of 620 nm improved the estimation as shown in Figure 18. This improvement can be associated with the predominance of cyanobacteria in BBHR. The absorption by PC pigment is clearly observed in R_{rs} spectra at 620 nm (Fig. 15). Both Chl-*a* and PC are present in cyanobacteria, consequently, these pigments can be highly correlated in environments where cyanobacteria is the predominant species (SIMIS et al., 2005; MISHRA et al., 2014). Parameterization and calibration of QAA_BBHR (Fig. 17g) considerably improved the estimation of $a_t(\lambda)$. Comparing the $a_t(\lambda)$ spectra between laboratory measurements and QAA_BBHR, underestimated values were observed at shorter wavelengths with a maximum bias of -1.42 m^{-1} at 412 nm. Additionally, there was a slight overestimation at 681 nm, with a bias of 0.06 m^{-1} . Overall, the model showed an average bias of -0.11 m^{-1} .

Figure 18. Comparison of the total absorption coefficients measured in laboratory and obtained using QAA_BBHR and QAA parameterized without 620 nm

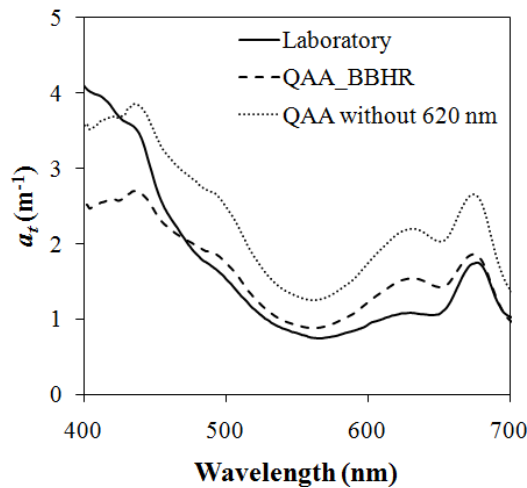


Figure 19 shows the relationship between the measured versus estimated a_t at nine MERIS central wavelengths using all models. QAA_v4 and QAA_v5, proposed for sites where $R_{rs}(670) < 0.0065 \text{ sr}^{-1}$ (LEE, 2014), produced maximum R^2 at 709 nm (0.21 and 0.19, respectively) and minimum R^2 at 443 nm (0.0001 and 0.0037, respectively). QAA_v6

presented the maximum R^2 of 0.33 at 681 nm associated with chlorophyll-*a* fluorescence (GORDON, 1979), and inexpressible R^2 (of 2×10^{-16}) at 665 nm. Both QAA_M13 and QAA_M14 presented the maximum R^2 at 681 nm (0.43 and 0.51, respectively) and minimum R^2 at 709 nm (0.17 and 0.24, respectively). QAA_BBHR presented slight improvement in terms of R^2 with maximum of 0.55 at 681 nm. Surprisingly, 709 nm showed the worst fit with an inexpressible R^2 .

QAA_BBHR primarily overestimated at shorter wavelengths. Three points 3, 7, and 19 (P3, P7 and P19, respectively) collected in October 2014 (Fig. 4) fell farthest from the 1:1 line at 412 and 443 nm (Fig. 19f). It was not observed a common characteristics in terms of Chl-*a* concentration (797.8, 461.4 and 505.1 $\text{mg} \cdot \text{m}^{-3}$, respectively) or TSS (44, 21.6 and 19 $\text{mg} \cdot \text{m}^{-3}$). The P3 located in an area with lacustrine characteristics before the channel narrows (see Fig. 4 for location), which produces algal bloom events, mainly, in austral summer. This point exhibited the highest $a_t(\lambda)$ spectrum in October, mainly associated with the maximum $a_\phi(\lambda)$ found in BBHR. According to laboratory measurements, the P7 presented the second highest $a_t(\lambda)$ spectrum, however, in this case related to the greatest absorption by CDOM. Since, P19 located in Tietê River before its confluence with Piracicaba River presented the second highest $a_{CDM}(\lambda)$ spectrum.

Figure 19. Measured vs. estimated $a(\lambda)$ plot (line 1:1) using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014) and (f) QAA_BBHR.

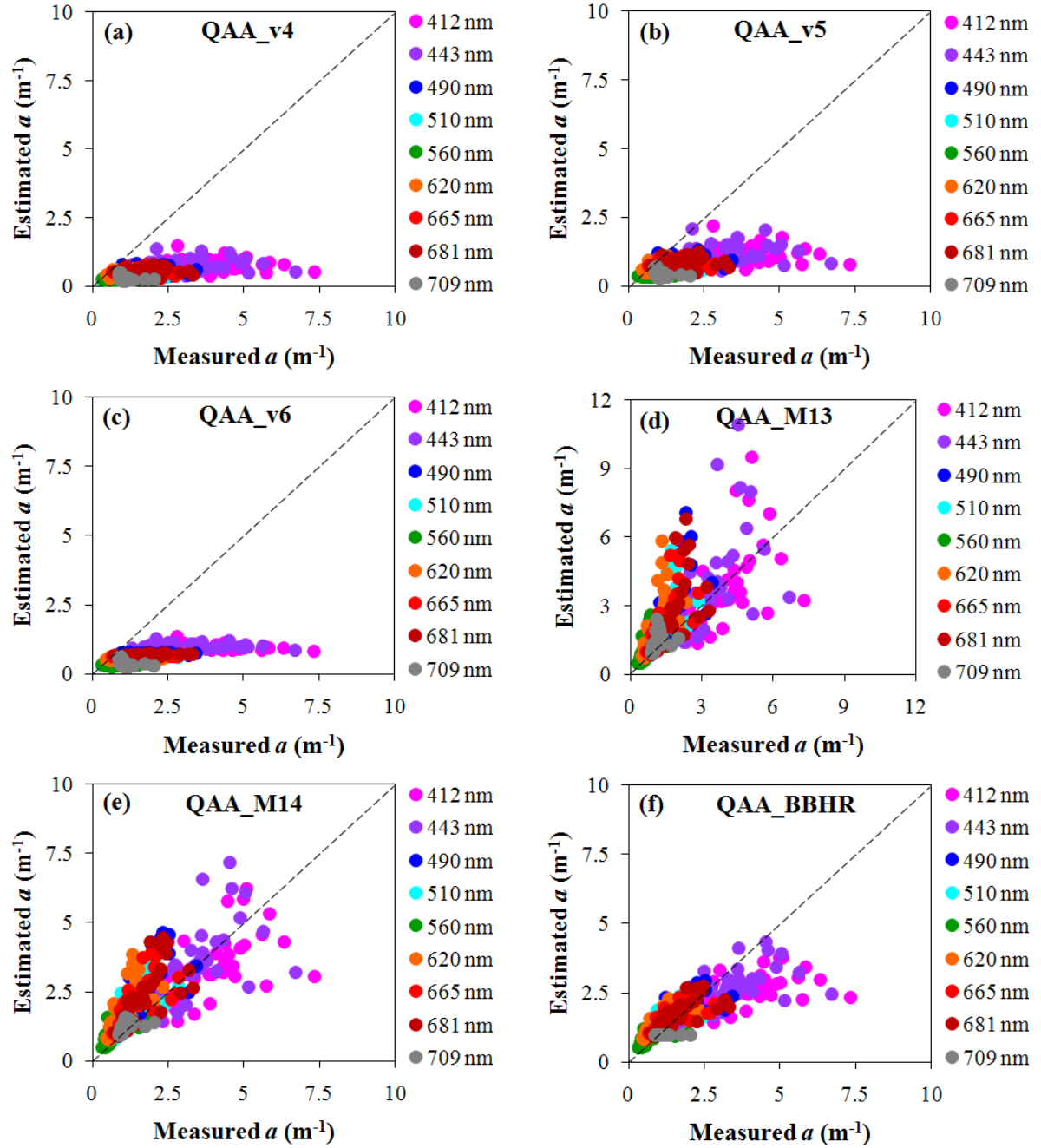
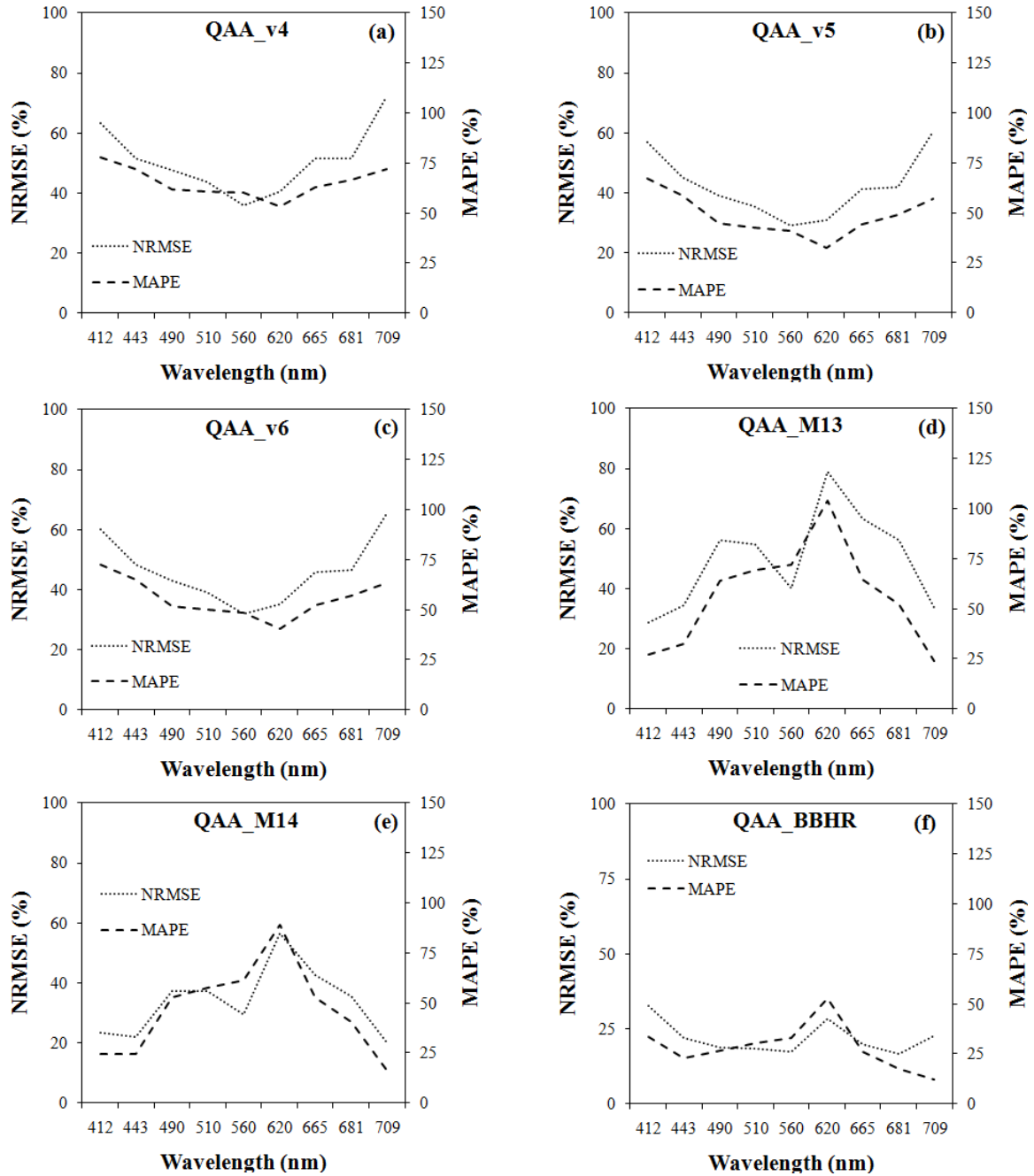


Figure 20 shows the NRMSE and MAPE plots produced by all models for estimating $a_t(\lambda)$ spectra. QAA_v4, QAA_v5 and QAA_v6 presented similar NRMSE and MAPE values, being that the highest average errors were yielded by QAA_v4. Wavelengths at 412 and 709 nm exhibited the highest errors, while intermediate wavelengths presented the lowest errors, with minimum at 560 nm. QAA_v5 presented the lowest NRMSE and MAPE at 620 nm (PC absorption feature) among all the models (NRMSE of 30.84% and MAPE of 32.63%).

QAA_v5 presented better performance than QAA_v6, associated likely with the λ_0 at 670 nm, because this wavelength undergoes with the OACs absorption, mainly, Chl-*a*, and one of the criterion for selection of λ_0 is that the influence of OACs absorption is minimum.

Figure 20. NRMSE and MAPE of estimated $a(\lambda)$ using **(a)** QAA_v4 (LEE et al. 2002), **(b)** QAA_v5 (LEE et al., 2009), **(c)** QAA_v6 (LEE et al., 2014), **(d)** QAA_M13 (MISHRA et al., 2013), **(e)** QAA_M14 (MISHRA et al., 2014) and **(f)** QAA_BBHR.



Between all five published QAA, QAA_M14 proposed by Mishra et al. (2014) presented the best performance to estimate $a(\lambda)$, with the lowest average NRMSE of 33.81%

and MAPE of 46.55%. Errors were the lowest at 709 nm, with NRMSE of 20.19% and MAPE of 16.47%. Prediction at the PC absorption band was highly erroneous with a NRMSE of 56.54% and MAPE of 88.9%. Although QAA_M13 was parameterized with the same data as QAA_M14 from turbid productive waters, this version did not produce the same satisfactory results obtained by QAA_M14. QAA_M13 presented similar errors as QAA_v5, with an average NRMSE of 49.58% and MAPE of 56.6%; however, QAA_v5 underestimated $a_t(\lambda)$, whereas, QAA_M13 overestimated the variable. The difference between QAA_M13 and QAA_M14 is basically the calibration parameters h_1 , h_2 and h_3 (Equation 32), showing the importance of a suitable calibration during this step. Overall, QAA_M13 performed better at shorter wavelengths (NRMSE: 28.7% and MAPE: 27.1% at 412 nm) and the worst results were obtained at 620 nm (NRMSE: 78.95% and MAPE: 103.93%). QAA_M13 (MISHRA et al., 2013) and QAA_M14 (MISHRA et al., 2014) were originally designed to quantify PC; however, surprisingly, these versions produced high errors at 620 nm in BBHR. A possible reason for the overestimation of wavelengths associated with the absorption by pigments is the package effect. The pigment packaging leads to flat of the absorption spectrum with the increase of phytoplankton concentration (ROESLER & PERRY, 1989; BRICAUD et al., 1995; CARDER et al., 1999; CIOTTI et al., 2002). So, the algorithm can be representing the increase of absorption spectrum with high Chl-*a* concentration, but this increase is not observed in laboratorial measures likely to package effect. The above analysis reiterates the fact that calibration of χ plays a crucial role to retrieve $a(\lambda)$.

The combinations of wavelengths to parameterize χ and the calibration parameters obtained to derive $a_{t-w}(\lambda_0)$, and consequently, $a(\lambda_0)$ was essential to accurate estimation of $a_t(\lambda)$. The new parametrization yielded a accurate estimation of $a_t(\lambda)$, with an average NRMSE of 21.88% and MAPE of 28.27%, with best performance at 681 nm, wavelength associated with Chl-*a* fluorescence (GORDON, 1979), with a NRMSE of 16.53% and a MAPE of 17.43%. On the other hand, the algorithm exhibited the worst performance at 620 nm (NRMSE: 37.29% and MAPE: 117.78%) as QAA_M13 and QAA_M14, likely associated with pigment packaging.

5.3.3. $a_{CDM}(\lambda)$ retrieval

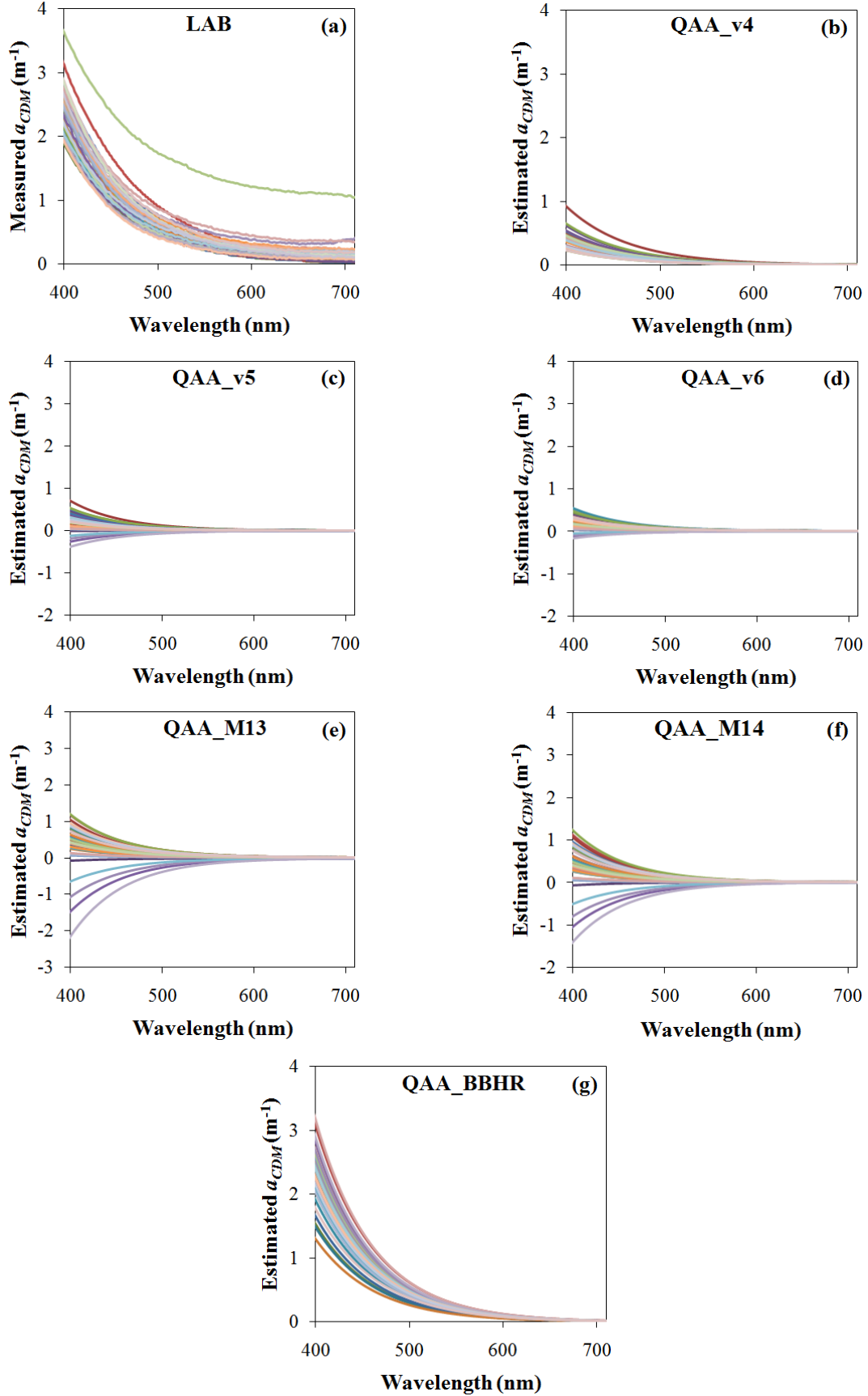
Figure 21 shows the $a_{CDM}(\lambda)$ spectra estimated by each tested version. None of the existing QAA versions tested in this study yielded satisfactory results for $a_{CDM}(\lambda)$ for BBHR data, underestimating strongly $a_{CDM}(\lambda)$. It indicates the necessity of accurately parameterizing

and calibrating the other steps of QAA. Accurate retrieval of $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$ depends basically on the suitable estimation of $a_t(\lambda)$ (LEE et al., 2010; MISHRA et al., 2014) and suitable parameterization and calibration in terms of ξ and ζ . QAA_v5, QAA_v6, QAA_M13 and QAA_M14 versions yielded negative values for samples P4, P5, P10, P11 and P16 at shorter wavelengths. With the exception of P5, the negative values were computed for samples collected during the second field campaign (October 2014), when the $a_{CDM}(\lambda)$ values measured in laboratory were higher. Lee et al. (2010) and Mishra et al. (2014) have discussed obtaining negative values for $a_{CDM}(\lambda)$. Mishra et al. (2014) verified that negative $a_{CDM}(\lambda)$ did not impair the retrieval of $a_\phi(\lambda)$; however, the use of $a_{CDM}(\lambda)$ derived by QAA is prevent.

QAA_v4 did not yield negative values, although it was developed for the open ocean with low CDM. With exception of QAA_v4, all tested models adopt practically the same formula to estimate ζ and ξ (Equation 38 and 39, respectively) unlike QAA_v4. Although the models adopted by QAA_v4 to estimate ζ and ξ have not yielded negative values, they still were not suitable to estimate $a_{CDM}(\lambda)$ in BBHR, showing a high underestimation, with a negative bias of -0.53 m^{-1} . Thus, the underestimation of $a_{CDM}(\lambda)$ cannot only be associated with the underestimation associated with $a_t(\lambda)$, since QAA_M13 and QAA_M14 have overestimated $a_t(\lambda)$ and also yielded negative values. According to Mishra et al. (2014), overestimation of ξ and underestimation of ζ can underestimate $a_{CDM}(443)$. Therefore, QAA_BBHR was calibrated to fit ζ and ξ and solve the problem of underestimation of $a_{CDM}(\lambda)$ and, consequently, overestimation of $a_\phi(\lambda)$.

The overestimation of S was the first problem detected. The existing versions tested in this study use models that estimate S around 0.015 nm^{-1} . QAA_v4 uses a fixed value of S equal 0.015 to estimate ζ . Although QAA_v5, QAA_v6, QAA_M13 and QAA_M14 do not use fixed S values, they use models that consider an intercept of the function that equate to a value of S around 0.015. This value is adopted because studies have shown that S varies between 0.01 and 0.02 nm^{-1} (HOOGENBOOM et al., 1998); hence, the average value of 0.015 nm^{-1} is used (LEE et al., 2002; LEE et al., 2004). However, this value is considerably high if compared to minimum values of S obtained from laboratory measurements of a_{CDM} in BBHR, yielding a NRMSE of 15.5%. BBHR dataset presented S varying from 0.012 to 0.023 nm^{-1} , with average of 0.016 nm^{-1} . In this work, the intercept value was replaced with 0.014, which yielded satisfactory results, deriving an average S of 0.016 nm^{-1} , with a low NRMSE of 14.4%.

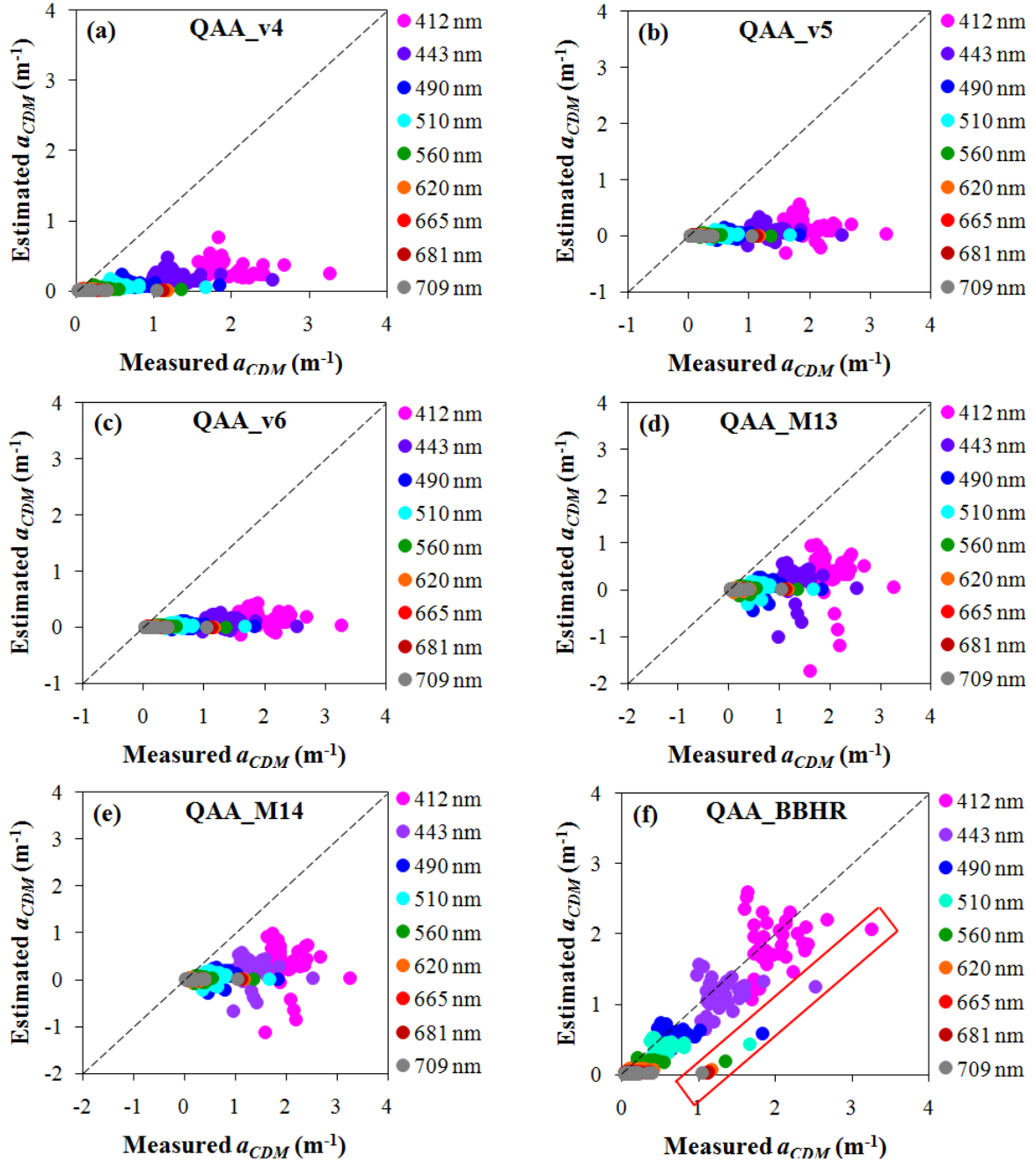
Figure 21. Estimated a_{CDM} spectra using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014) and (f) QAA_BBHR.



QAA_BBHR produced negative values of $a_{CDM}(\lambda)$ even after the calibration of ζ . Hence, Equation 38 was also tuned to improve the estimation of ζ . QAA versions tested in this research yielded an average of 0.91 for ζ which is much closer to the ζ produced by $a_{\phi}(411)/a_{\phi}(443)$ ratio using a_{ϕ} obtained in laboratory. According to Mishra et al. (2014), underestimated values of ζ can lead to underestimation of $a_{CDM}(\lambda)$; however, the opposite was observed. ζ derived from $a_{\phi}(411)/a_{\phi}(443)$ ratio yielded negative values of $a_{CDM}(\lambda)$. Therefore, we concluded that the previously used ratio of $a_{\phi}(411)/a_{\phi}(443)$ ratio cannot likely be suitable to represent the pigments in inland waters. Combinations of wavelengths were tested and $a_{\phi}(665)/a_{\phi}(709)$ emerged as the ratio to generate lowest NRMSE and MAPE. The new ratio produced an average ζ of about 0.50 and adjustments were done in QAA_BBHR to estimate ζ accurately. Thus, the modification of ζ improved the estimation of $a_{CDM}(\lambda)$ and, consequently, $a_{\phi}(\lambda)$.

Figure 22 shows the plots of the measured versus estimated $a_{CDM}(\lambda)$. All tested QAA version underestimated $a_{CDM}(\lambda)$, with negative average bias varying from -0.58 m^{-1} (QAA_v5 and QAA_v6) to -0.53 m^{-1} (QAA_v4). Wavelength at 412 nm produced the highest bias, due to uncorrected fit of ζ and ξ , while 709 nm showed the lowest bias. Although QAA_v4 did not produce negative $a_{CDM}(\lambda)$, this version showed a considerably high average bias of -0.53 m^{-1} , with maximum of -1.67 m^{-1} at 412 nm, and minimum of -0.14 m^{-1} at 709 nm. QAA_M13 and QAA_M14 versions presented intermediate average bias of -0.55 and -0.54 m^{-1} , respectively.

Figure 22. Estimated versus measured a_{CDM} using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014) and (f) QAA_BBHR.



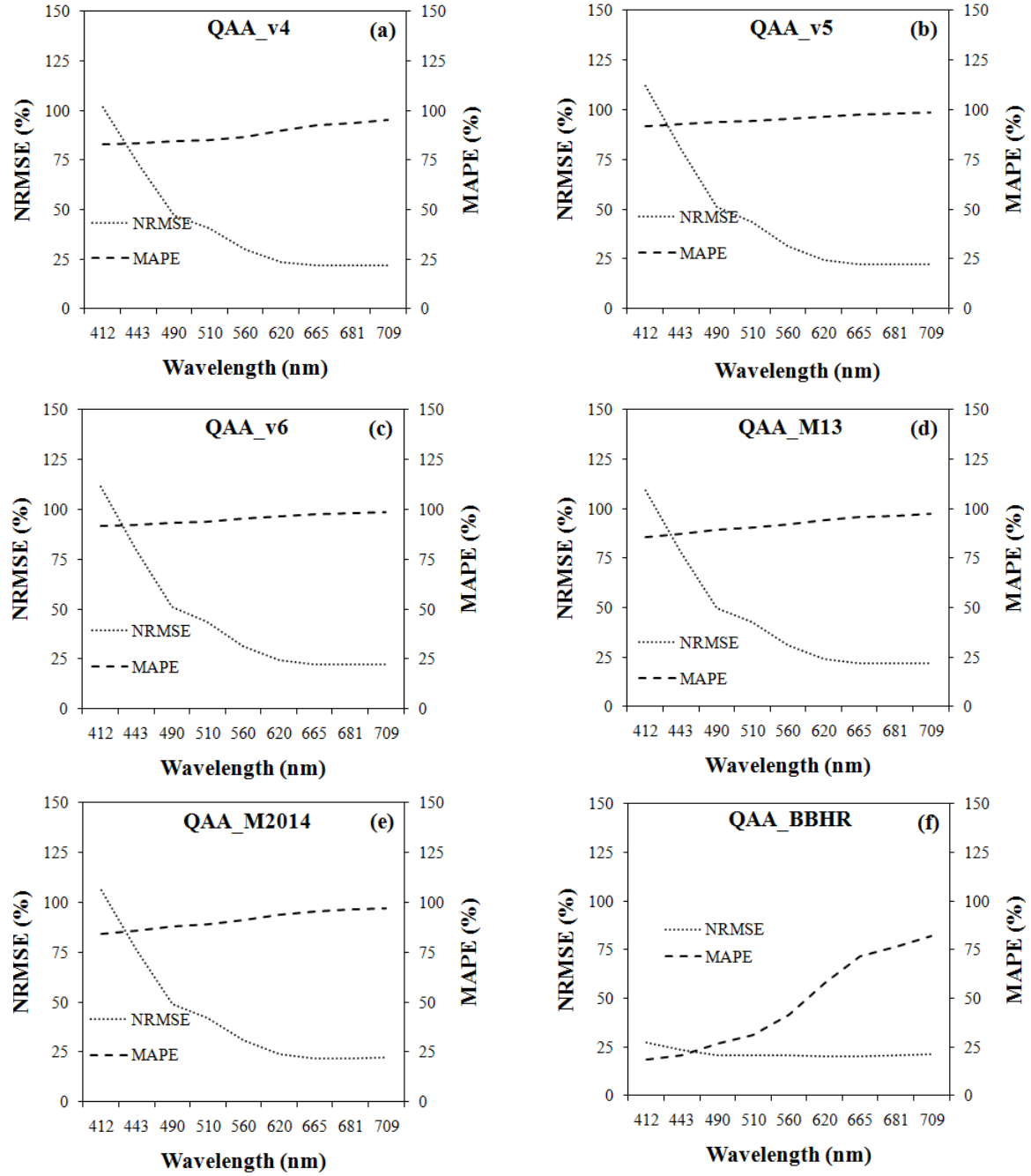
The modification proposed in QAA_BBHR to estimate ζ and ξ significantly improved the estimation of $a_{CDM}(\lambda)$. QAA_BBHR produced a considerably low average bias of -0.03 m^{-1} and did not show underestimation at 443, 510 and 560 nm unlike other versions. Figure 22f highlights a systematic error rated to sampling location P7, collected in October 2014, which exhibited higher underestimation at every wavelength and created a line almost parallel to 1:1

line. It was not possible to isolate sample P7 bias in other QAA versions because of the overall severe underestimation. Sample P7 did not show discrepant values for any laboratory measurement ($\text{Chl-}a = 461.4 \text{ mg}\cdot\text{m}^{-3}$, $\text{TSS} = 21.6 \text{ mg}\cdot\text{L}^{-1}$), with exception of very high $a_{\text{CDM}}(\lambda)$ values and a low S of 0.0124 nm^{-1} , while the mean was of 0.016 nm^{-1} . Eliminating the sample P7 and recalculating the bias substantially improved the errors; however, the removal of P7 at the calibration worsened the QAA_BBHR fit.

Figure 23 shows the NRMSE and MAPE obtained for a_{CDM} after applying each one of the QAA versions studied in this research. QAA_BBHR showed a consistently lower NRMSE and MAPE compared to other QAA versions, whereas, QAA_v4, QAA_v5, QAA_v6, QAA_M13 and QAA_M14 produce similar error pattern. Higher NRMSE was observed at shorter wavelengths (412 and 443 nm) and higher MAPE at longer wavelengths (709 nm), due to severe underestimation of these spectral regions. The negative values produced at shorter wavelength reflected considerably in errors obtained. Among the existing tested models, none yielded a MAPE lower than 88%, being that $a_{\text{CDM}}(\lambda)$ estimation accuracy by QAA_v4 was comparatively higher than other models because it did not generate negative values, with an mean NRMSE of 42.39% and MAPE of 88.16%. QAA_v5 was the least accurate in estimating $a_{\text{CDM}}(\lambda)$ among all algorithms, resulting an average NRMSE of 45.54% and MAPE of 95.46% across the visible spectrum; however, it produced good estimative at longer wavelengths, with NRMSE of 22.08% at 681 nm and 24.38% at 620 nm. The algorithms for inland waters, QAA_M13 and QAA_M14, also produced similar errors values, with an average NRMSE of up to 44.52% and MAPE of up to 92.12%. These versions also presented similar error patterns to QAA versions for marine waters, because they yielded negative values of $a_{\text{CDM}}(\lambda)$. As expected, the highest NRMSE was observed at 412 nm (106.03%) and lowest at 665 nm (22.03%). On the contrary, MAPE presented higher values at larger wavelength. Divergence between NRMSE and MAPE occurs when the difference of estimated and measured values is high and the variance of the observations also is high, that is, when the measured value is close to minimum value. In this case, such behavior is associated mainly with variance observed $a_{\text{CDM}}(\lambda)$ caused by high $a_{\text{CDM}}(\lambda)$ of P7.

QAA_BBHR was successful in producing accurate estimation of $a_{\text{CDM}}(\lambda)$ with an average NRMSE of 21.71% and MAPE of 47.41%. The best results were obtained in red region, with NRMSE of 20.3% at 620 nm and NRMSE of 20.2% at 665 nm. Short wavelengths produced higher errors, mainly at 412 nm where NRMSE was of 27.5% and MAPE of 18.23%.

Figure 23. NRMSE and MAPE of estimated $a_{CDM}(\lambda)$ using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014) and (f) QAA_BBHR.

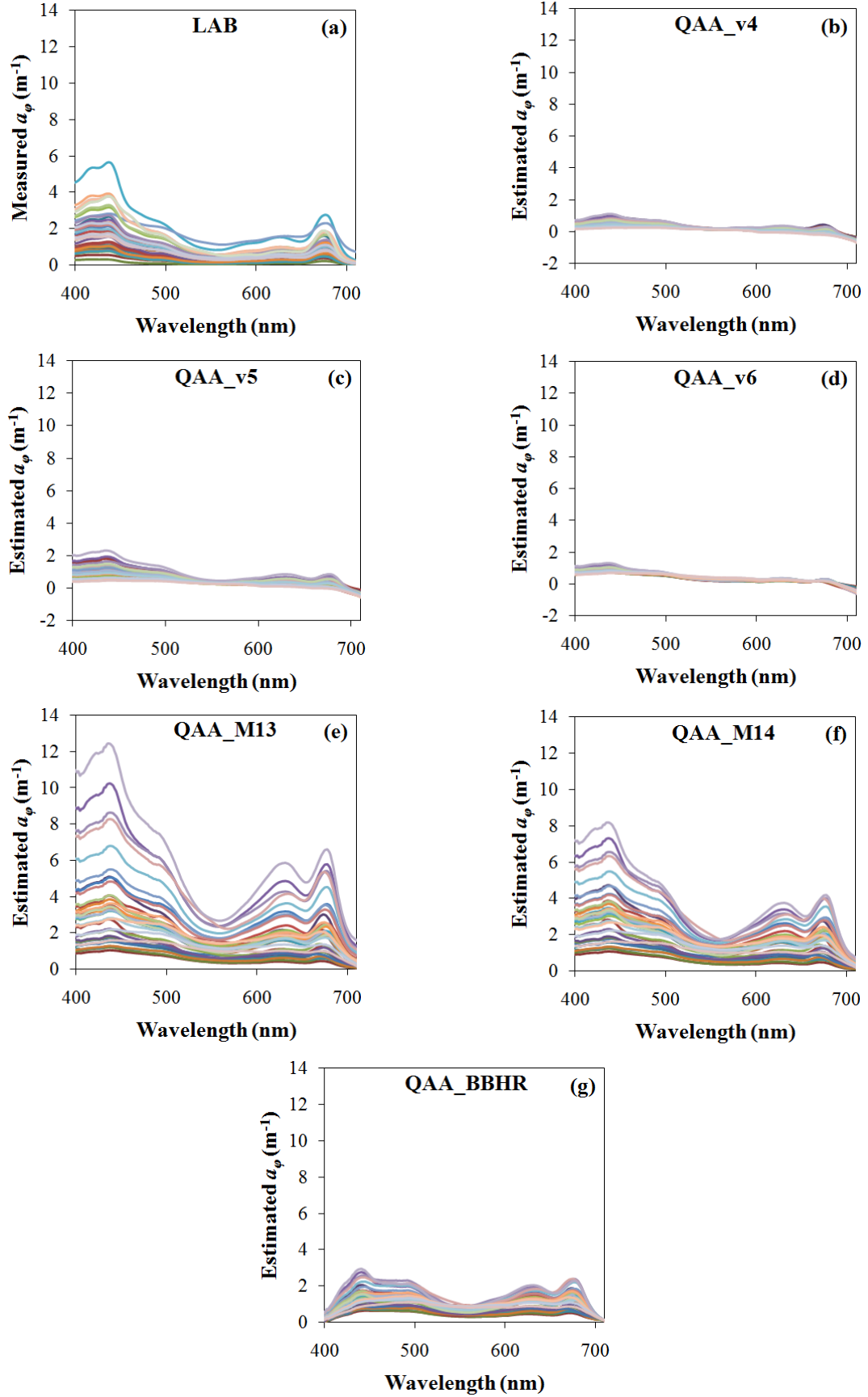


5.3.4. $a_\phi(\lambda)$ retrieval

Figure 24 shows the a_ϕ spectra estimated by QAA_v4 (Fig. 24a), QAA_v5 (Fig. 24b), QAA_v6 (Fig. 24c), QAA_M13 (Fig. 24d), QAA_M14 (Fig. 24e) and QAA_BBHR (Fig. 24f). An accurate estimation of $a_\phi(\lambda)$ is entirely dependent on previous accurate estimation of $a_t(\lambda)$ and $a_{CDM}(\lambda)$. In addition, errors in estimating ζ and ξ can result in large errors of estimation for $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$, generating negative or zero values (Lee et al., 2010).

The underestimation of $a_t(\lambda)$ by QAA_v4, QAA_v5 and QAA_v6 consequently underestimated $a_\phi(\lambda)$, producing negative values, while QAA_M13 and QAA_M14 overestimated $a_t(\lambda)$ and $a_\phi(\lambda)$. The main problem of existing tested versions was the estimation of ζ and ξ . Therefore, such values (ζ and ξ) were fitted for bio-optical status of the BBHR. ξ value was calibrated in relation to S (spectral slope of CDOM) observed in BBHR, while ζ was parameterized in order to represent better the pigments variation; in other hands, $a_\phi(411)/a_\phi(443)$ ratio was replaced for $a_\phi(665)/a_\phi(709)$ ratio to define ζ . The fits of ζ and ξ values improved remarkable the estimation of $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$. Even so, QAA_BBHR still is possible to observe a underestimation of $a_\phi(\lambda)$ at 412 and 443 nm, and 709 nm as displayed in Figure 24g.

Figure 24. Estimated a_ϕ spectra using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014), and (f) QAA_BBHR.



Measured versus estimated $a_\phi(\lambda)$ for all models is shown in Figure 25. As expected, all QAA versions developed for open ocean waters (QAA_v4, QAA_v5, and QAA_v6) underestimated $a_\phi(\lambda)$, since $a_t(\lambda)$ already was lower than $a_\phi(\lambda)$ obtained in laboratory. Among the three versions for ocean water, QAA_v5 showed the least underestimation, with an average bias of -0.46 m^{-1} and a bias range of -0.94 m^{-1} (412 nm) to -0.05 m^{-1} (560 nm). However, the apparent good performance is not true because the negative $a_{CDM}(\lambda)$ is adding to $a(\lambda)$ in order to obtain $a_\phi(\lambda)$, while it should be subtracting. On the other hand, among the versions tested for inland water, QAA_M13 showed the highest overestimation of $a_\phi(\lambda)$ at every wavelength with a large average bias of 1.2 m^{-1} , maximum of 1.69 m^{-1} at 443 nm and minimum of 0.36 m^{-1} at 709 nm. QAA_M14 also overestimated a_ϕ at every wavelength with a high average bias of 0.95 m^{-1} .

Overall, QAA_BBHR showed a slight underestimation with an average bias of -0.08 m^{-1} mainly due to the high bias of -1.13 m^{-1} observed at 412 nm. Sample P3 collected in October 2014 produced the highest underestimation at 412 and 443 nm as observed in Fig. 25f. This sample exhibited the highest Chl-*a* concentration of $797.8 \text{ mg}\cdot\text{m}^{-3}$ and, consequently, the highest $a_\phi(\lambda)$ measured in laboratory. Likely, the calibration of QAA_BBHR that considers a mean of the samples was not capable of estimating accurately extreme values of $a_\phi(\lambda)$. Other sample significantly underestimated was P14 collected also in October, with the second highest Chl-*a* concentration of $723.5 \text{ mg}\cdot\text{m}^{-3}$ and high $a_\phi(\lambda)$. The main peculiarities of $a_\phi(\lambda)$ of this sample is the greatest gradient between 412 and 443 nm, and the median absorption at 665 nm compared to samples with lower concentrations.

Figure 25. Estimated a_ϕ spectra using (a) QAA_v4 (LEE et al. 2002), (b) QAA_v5 (LEE et al., 2009), (c) QAA_v6 (LEE et al., 2014), (d) QAA_M13 (MISHRA et al., 2013), (e) QAA_M14 (MISHRA et al., 2014) and (f) QAA_BBHR.

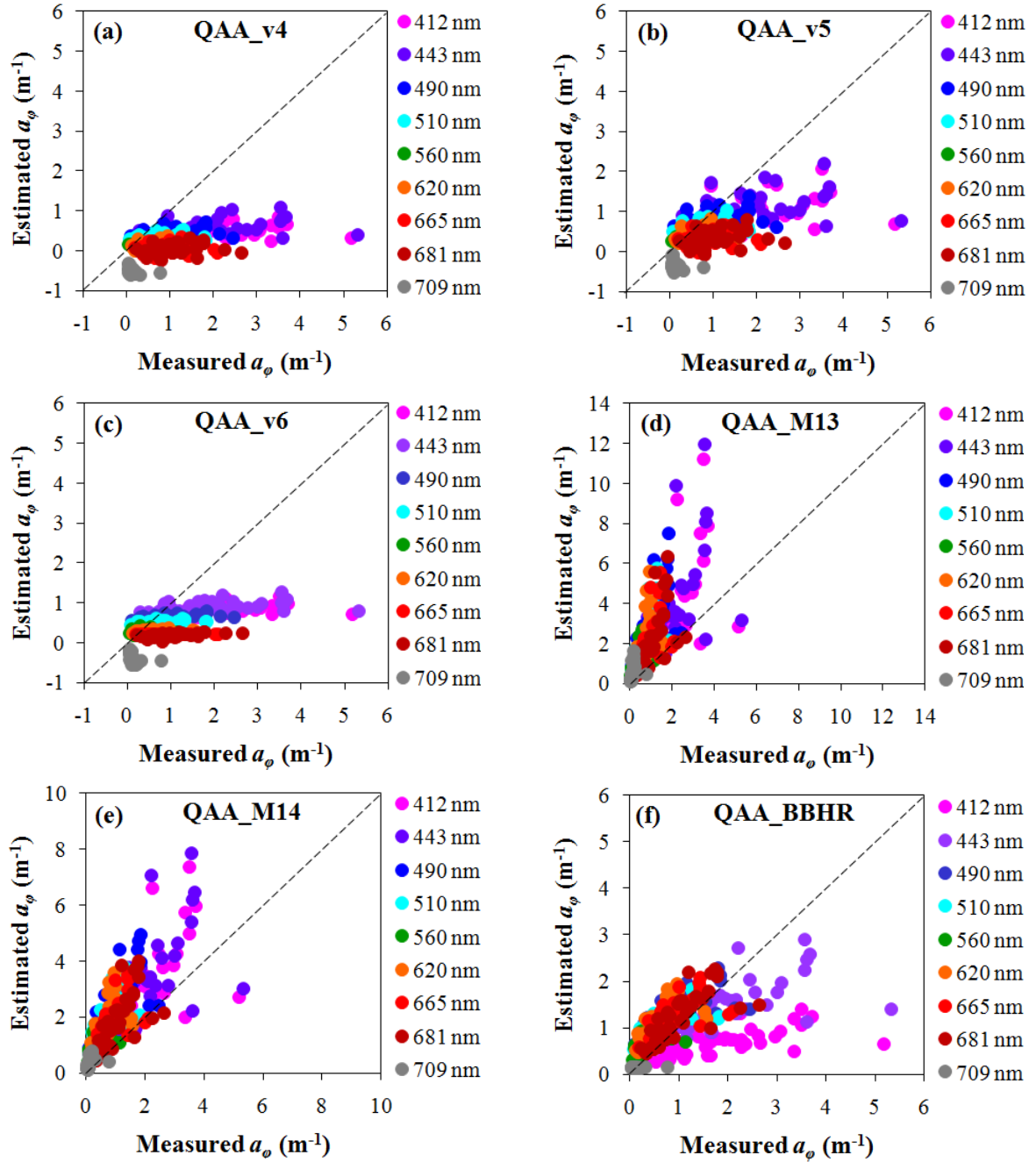
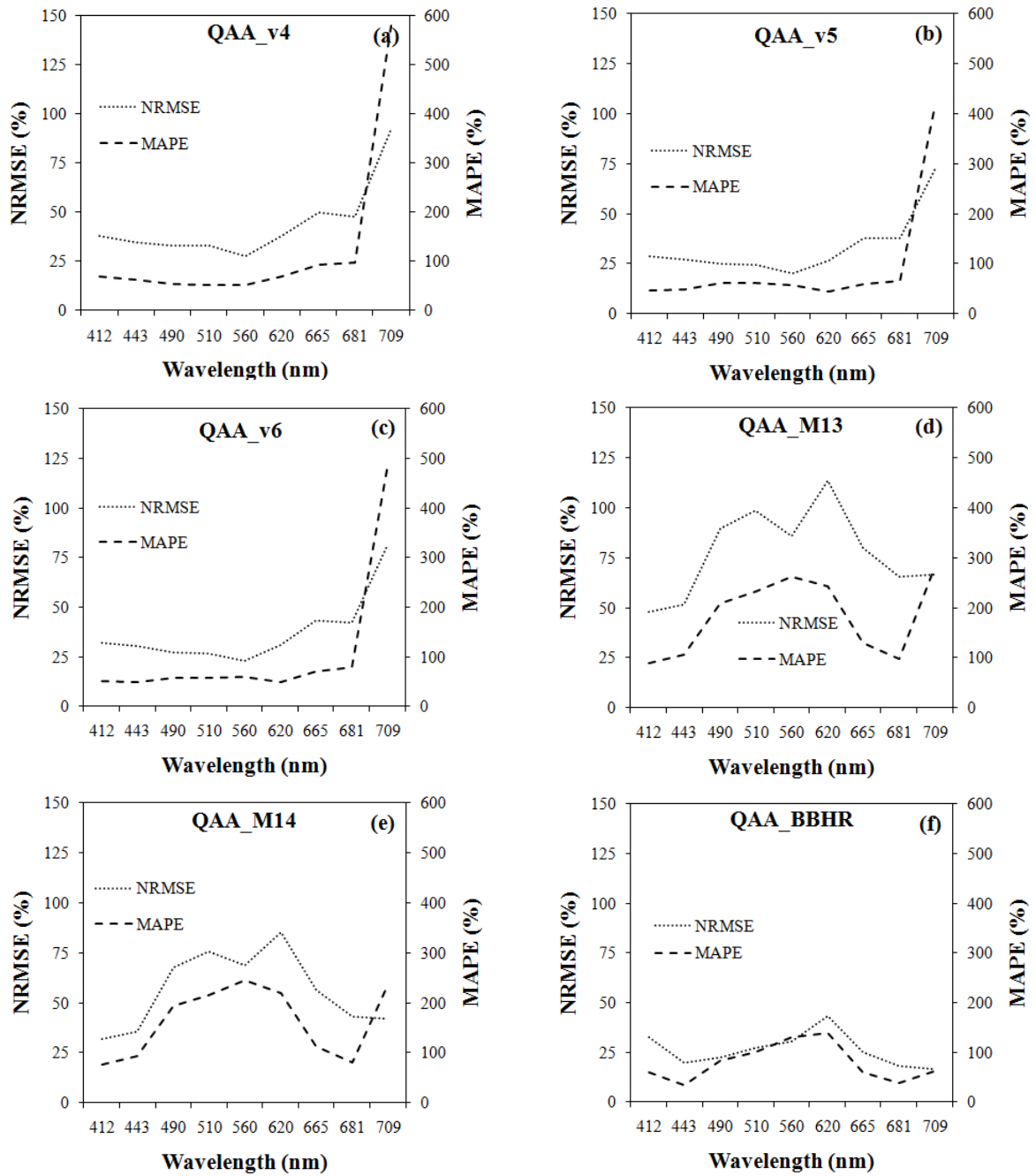


Figure 26 shows the plots of the NRMSE and MAPE obtained for $a_\phi(\lambda)$. QAA_v4, QAA_v5 and QAA_v6 showed considerably low NRMSE and MAPE, except at 709 nm. The high underestimation and negative $a_{CDM}(\lambda)$ values reflected to $a_\phi(\lambda)$ estimation. Apparently, versions for marine waters exhibited low NRMSE and MAPE at every wavelength, except at 709 nm; however, these good results are false, because $a_{CDM}(\lambda)$ is added to $a(\lambda)$ to estimate

$a_\phi(\lambda)$. Among the three versions for ocean waters, QAA_v5 showed the lowest errors and QAA_v6 yielded the highest average error. Surprisingly, QAA_M13 and QAA_M14 presented higher NRMSE and MAPE compared to open ocean versions, due to overestimation, mainly at intermediate wavelengths.

Figure 26. NRMSE and MAPE of estimated a_ϕ using (a) QAA_v4 (Lee et al. 2002), (b) QAA_v5 (Lee et al., 2009), (c) QAA_v6 (Lee et al., 2014), (d) QAA_M13 (Mishra et al., 2013), (e) QAA_M14 (Mishra et al., 2014) and (f) QAA_BBHR.



Among all five previous QAA versions, QAA_M13 presented the highest average NRMSE (77.63%) and MAPE (182.91%). With the exception of 412 and 443 nm every wavelength presented NRMSE higher than 65% with maximum value of 113% at 620 nm as well as MAPE range of 88.83% (412 nm) to 278.47% (709 nm). Similarly, QAA_M14 yielded a high average NRMSE of 56.25% and MAPE of 163.32%. Overall, QAA_BBHR considerably improved the accuracy estimation of $a_\phi(\lambda)$ with an average NRMSE of 26.08% and MAPE of 78.08%. The best accurate results were obtained at longer wavelengths such as 681 nm (NRMSE: 18.02% and MAPE: 37.5%), with a slight improvement at shorter wavelengths (NRMSE: 19.6% and MAPE: 32.8% for 443 nm). High errors were observed at intermediate wavelengths, with maximum at 620 nm (NRMSE: 43.1% and MAPE: 138.1%).

5.3.5. Chl-*a* retrieval from derived $a_\phi(\lambda)$

To further assess the $a_\phi(\lambda)$, some Chl-*a* models were reparameterized using $a_\phi(\lambda)$ and $a_w(\lambda)$, validated and compared with their R_{rs} counterparts. The 2B (GITELSON et al., 2008), 3B (GITELSON et al., 2008), and NDCI (MISHRA & MISHRA, 2012) Chl-*a* models were tested. The $a_\phi(\lambda)$ and $a_w(\lambda)$ based models representing the 2B, 3B, and NDCI were labeled as Ψ_1 , Ψ_2 and Ψ_3 as shown in Equations 45, 47, and 49. Figure 27 shows the fit of the models for 2B (Fig. 27a), 3B (Fig. 27b), NDCI (Fig. 27c), Ψ_1 (Fig. 27d), Ψ_2 (Fig. 27e), and Ψ_3 (Fig. 27f). The indexes using R_{rs} exhibited high correlation with the Chl-*a*, being 0.88 for 2B, 0.91 for 3B, and 0.81 for NDCI, while the indexes based on $a_\phi(\lambda)$ and $a_w(\lambda)$ presented correlation of 0.88 for Ψ_1 , 0.88 for Ψ_2 , and 0.81 for Ψ_3 . With exception of Ψ_2 , models based on QAA $a_\phi(\lambda)$ and $a_w(\lambda)$ provided the same correlation with Chl-*a* compared to their R_{rs} counterparts. This serves as an indirect validation of the QAA_BBHR and the derived IOPs.

Figure 27. Scatter plot showing empirical fit between Chl-*a* and (a) 2B; (b) 3B; (c) NDCI; (d) Ψ_1 ; (e) Ψ_2 ; and (f) Ψ_3 .

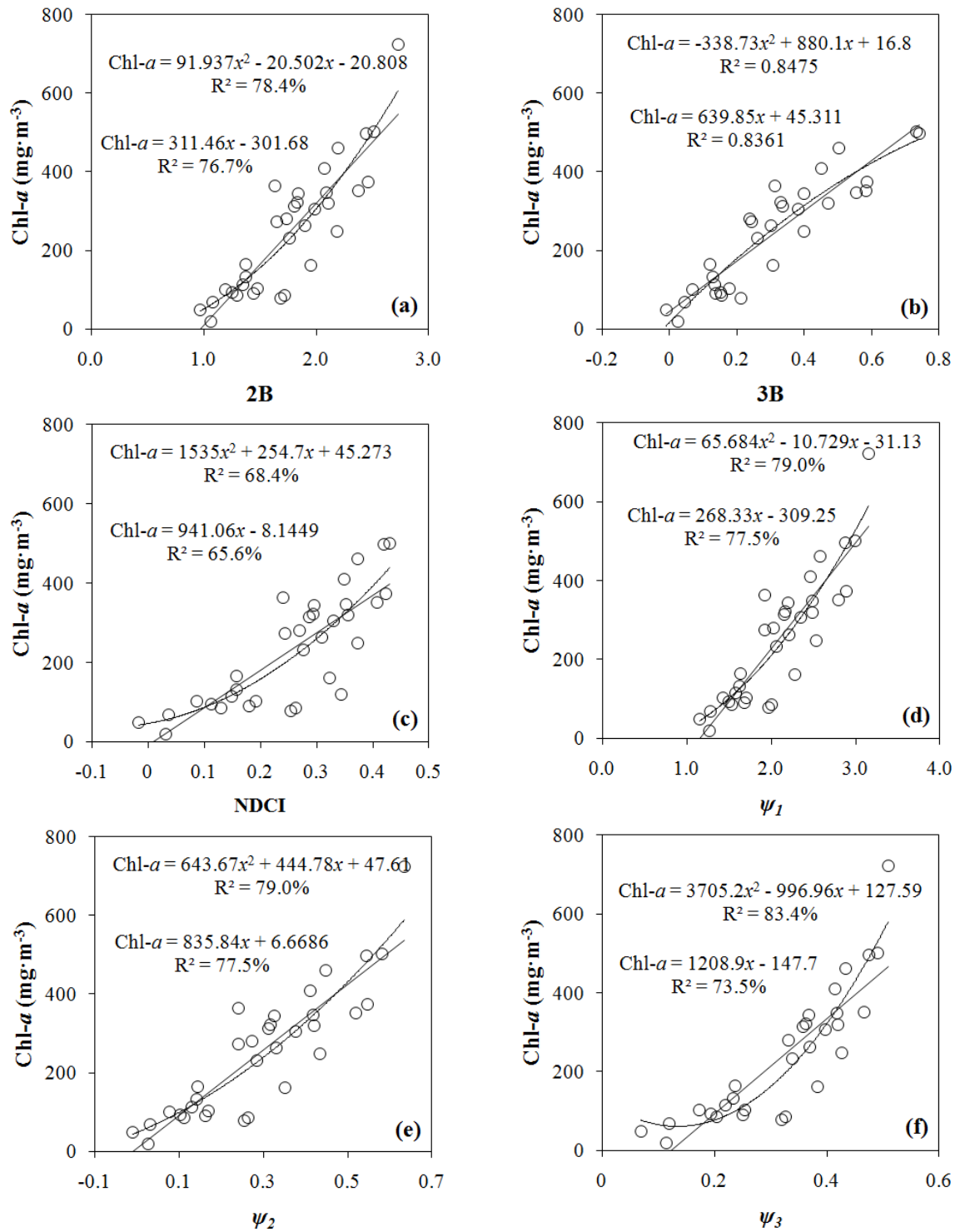


Table 11 shows calibration results, using n samples number, in terms of standard error of estimative (S), determination coefficient (R^2 , in %), adjusted R^2 (Adj- R^2 , in %), F statistic (F), and p -value. Most of the calibration variants produced significant results with R^2 of

approximately 0.7 and p -value equal or close to zero. The linear fits are statistically more significant than quadratic fits, with the highest F values.

Table 11. Fits used to calibrate model and assessment parameters: standard error of estimative (S), determination coefficient (R^2), F statistic and p -value using the indexes 2B, 3B, NDCI, Ψ_1 , Ψ_2 and Ψ_3 for retrieving the Chl- a concentration.

a. Models calibrated using R_{rs}							
Index	n	Fit	S	R^2	Adj- R^2	F	p -value
2B	33	Linear	79.82	76.7	76.0	102.15	0.000
2B	33	Quadratic	78.24	78.3	76.9	54.28	0.000
3B	31	Linear	57.94	83.6	83.0	147.96	0.000
3B	31	Quadratic	56.89	84.7	83.7	77.78	0.000
NDCI	33	Linear	83.68	65.6	64.5	59.13	0.000
NDCI	33	Quadratic	81.58	68.4	66.3	32.42	0.000
b. Models using a_ϕ and a_w derived from QAA_BBHR							
Index	n	Fit	S	R^2	Adj- R^2	F	p -value
Ψ_1	33	Linear	78.40	77.5	76.8	107.00	0.000
Ψ_1	33	Quadratic	77.06	79.0	77.6	56.43	0.000
Ψ_2	33	Linear	78.42	77.5	76.8	106.9	0.000
Ψ_2	33	Quadratic	77.02	79.0	77.6	56.51	0.000
Ψ_3	34	Linear	87.99	73.5	70.8	78.56	0.000
Ψ_3	34	Quadratic	79.32	83.4	76.3	52.40	0.000

To assess the performance of the fitted models was carried out a validation using a dataset collected in September, 2015. Table 12 shows the validation results of the Chl- a estimation models in terms of RMSE, NRMSE, MAPE, bias and R^2 between measured and estimated Chl- a . The quadratic adjustment was more suitable for 2B and NDCI, producing least errors, whereas, the linear fit was better for 3B index. Among all the models, Ψ_1 exhibited the best performance, with NRMSE = 13.84% and MAPE = 16.22%, while the second best performance (2B) presented NRMSE = 35.32% and MAPE = 44.33%. The improvement shown by Ψ_1 compared to 2B is likely associated with the efficiency of the QAA_BBHR in minimizing the influence of absorption by other OACs, not totally removed by $R_{rs}(709)/R_{rs}(665)$ ratio. The insertion of a third wavelength (754 nm) did not improve the 3B performance or Ψ_2 , indicating that backscattering influence to Chl- a estimating was not

very strong in the spectral bands used. Overall, quadratic NDCI, quadratic 2B and linear 3B exhibited similar errors; despite this, a t-student test for paired samples showed that models did not present similar results each other.

Table 12. Validation of the Chl-*a* estimation models using RMSE ($\text{mg}\cdot\text{m}^{-3}$), NRMSE (%), MAPE (%), bias ($\text{mg}\cdot\text{m}^{-3}$) and R^2 .

a. Models calibrated using R_{rs}						
Index	Fit	RMSE	NRMSE	MAPE	Bias	R^2
2B	Linear	101.46	55.46	88.58	-99.27	83.67
2B	Quadratic	69.06	37.75	51.48	-64.21	82.93
3B	Linear	69.35	37.91	57.74	-66.41	84.14
3B	Quadratic	94.53	51.68	83.94	-91.09	83.57
NDCI	Linear	118.60	64.83	107.32	-114.28	82.65
NDCI	Quadratic	72.15	39.44	53.27	-67.01	80.41
b. Models using a_ϕ and a_w derived from QAA_BBHR						
Index	Fit	RMSE ($\text{mg}\cdot\text{m}^{-3}$)	NRMSE (%)	MAPE (%)	Bias ($\text{mg}\cdot\text{m}^{-3}$)	R^2 (%)
ψ_1	Linear	94.59	51.71	81.91	-91.79	81.03
ψ_1	Quadratic	25.31	13.84	16.22	1.01	80.91
ψ_2	Linear	95.01	51.94	82.47	-92.30	81.67
ψ_2	Quadratic	66.24	36.21	49.25	-61.3	81.47
ψ_3	Linear	141.91	77.58	129.11	-134.44	79.0
ψ_3	Quadratic	71.37	39.15	41.95	-47.50	0.59

5.4. Conclusions

The new parameterization and calibration of the proposed QAA_BBHR exhibited satisfactory results in estimating $a_t(\lambda)$, $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$ in the tropical productive reservoir. QAA versions proposed for open ocean and coastal waters (QAA_v4, QAA_v5 and QAA_v6), and turbid highly productive pond waters (QAA_M13, QAA_M14) were not able of deriving IOPs accurately in BBHR. The results derived from testing the aforementioned models clearly indicated the need for re-parametrization. Thereby, we developed the QAA_BBHR in order to supply the necessities of tropical aquatic systems. Furthermore, the parameterizations and calibrations of ζ and ξ proposed by all tested models were not suitable to estimate $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$.

The fine tuning and recalibration of the empirical steps of these established QAAs considerably improved the performance of QAA_BBHR version. The use of the wavelength at 709 nm and a calibration of χ produced more accurate estimations of $a(\lambda_0)$ and, consequently, $a_t(\lambda)$. Comparison with laboratory data showed that QAA_BBHR generated accurate results, with an average NRMSE of 21.88% and MAPE of 28.27% in estimating $a_t(\lambda)$, while the best performance for existing version was a NRMSE of 31.8% and MAPE of 46.5%. The novel parameterization of χ using the combination of wavelengths: 443, 665, 709, 620 and 443 nm and the adjustment of the calibration coefficients (h_1 , h_2 and h_3) can be considered as the most important steps for estimation of $a_t(\lambda)$ (Tab. 9). The use of wavelengths at 620 and 665 nm exhibited a performance better than the use of only 665 nm. Other important modifications were the calibrations and parameterizations of ζ and ξ . The changes carried out in these two factors were essential to reduce the severe underestimation (negative values) in $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$ observed before calibration.

After adjustments, some tests showed that $a_\phi(\lambda)$ estimated by QAA_BBHR can be used to retrieve Chl-*a* concentration. The performance of models based on $a_\phi(\lambda)$ and $a_w(\lambda)$ and their R_{rs} counterparts were compared in order to validate the QAA_BBHR. According to validation results, in general, the use of indexes based on a_ϕ and a_w exhibited better performance than their R_{rs} counterparts. The index Ψ_1 exhibited the best performance, much higher than its analogy 2B (NRMSE = 13.8% and MAPE = 16.2% for Ψ_1 and NRMSE = 37.8% and MAPE = 51.5 for 2B), which indicate more accuracy of models based on absorption data.

Brazil has an extensive hydrographic network which impairs a suitable periodic monitoring for environmental agency and managers. So, the application of QAA could be adopted as an option for mapping of OACs, since it is necessary a dense punctual sampling to represent large water bodies. The accurate results obtained by QAA_BBHR shows that once calibrated the algorithm can be applied to the monitoring of the reservoir in time. Furthermore, the QAA_BBHR can be recalibrated to applications in other tropical reservoir, remaining the $\lambda_0 = 709$ nm and $\zeta = a_\phi(665)/a_\phi(709)$. According to QAA_BBHR parameterization, bands of Sentinel-3 satellite (the first satellite must be launched in 2016) are the most appropriate. Although not ideal due to absence of a band at 620 nm, the MSI sensor onboard the Sentinel-2 can be used, replacing the wavelength at 620 nm for 665 nm and obtaining a accuracy very better than applying the existing QAA versions.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This research proposed to parameterize and calibrate models testing different approaches for estimating accurately Chl-*a* concentration in a tropical eutrophic reservoir, in Brazil. According to results obtained at each investigation conducted in this study, it is possible to conclude that all objectives, general or specific, were successfully obtained.

According to the results of $a(\lambda)$ investigation presented in Chapter 3, bio-optical status exhibits a large variability as temporal as spatial. With the exception of $a_{TR}(\lambda)$, the highest variability was observed in October. In addition, the magnitude of $a_{CDOM}(\lambda)$ and $a_{\varphi}(\lambda)$ also were higher in that month, reflecting the highest Chl-*a* concentration of until $797.8 \text{ mg}\cdot\text{m}^{-3}$. Ternary plot presented one of the most interesting results in that chapter, showing the contribution by each OAC to $a(\lambda)$. Phytoplankton contribution was higher in both fieldworks, highlighted in the red spectral region (665 nm), with a_{φ} contribution of 85.7% in May and 83.1% in October. Graphics also showed that a_{TR} contribution was higher than a_{CDOM} in May, while the opposite was observed in October, reflex of ISS concentration slightly higher in May. In addition, organic portion of TSS was quite high for both months (OSS/TSS of 45 – 98% in May; and OSS/TSS of 78 – 96% in October).

Spatially, the section of the Tietê River before confluence with the Piracicaba River showed the most different $a(\lambda)$ in comparison with the rest of reservoir. In May, samples collected in this section exhibited the highest values of $a_{TR}(\lambda)$ and $a_{CDOM}(\lambda)$. Meanwhile, in October, samples presented the smallest values of $a_{\varphi}(\lambda)$, although this points have been exhibited high Chl-*a* concentration of $387.2 – 713.7 \text{ mg}\cdot\text{m}^{-3}$. Probably, this status is linked to specific $a_{\varphi}(\lambda)$ ($a_{\varphi}^*(\lambda)$), which also varies in relation to phytoplankton specie. Dynamic of this section of reservoir and the significant contribution of CDOM and ISS can change phytoplankton communities. Rainfall season regime is essential for understanding the bio-optical variation in BBHR, because it is responsible by control of higher or lower input of wastewater coming from upstream and fertilizers from watershed. Overall, the results obtained in this chapter were quite useful to other steps of this Thesis, which requires bio-optical knowledge to parameterize and calibrate models.

As expected for all inland waters, the ternary plot showed that wavelength in blue region is not the most suitable to isolate $a_{\varphi}(\lambda)$, so models based on blue spectral response

probably must not be accurate for the BBHR. This assumption was stated by the results obtained with the calibration of empirical models. In general, the spectral indexes based on combinations of the blue, green and red bands did not present accurate estimative for Chl-*a* concentration, not presenting statistic significance. An exception was Slope index, which enables the use of OLI images for quantifying Chl-*a*. On the other hand, NIR-red algorithms presented satisfactory fits with R^2 always higher than 70%. During the calibration of models for MERIS bands, 3B index with quadratic fit presented the best adherence; however, the validation results showed that 2ME index performance was better. The lowest errors (NMRSE and MAPE) were obtained by models calibrated using MODIS bands, with NRMSE lower than 30%. Despite this, MODIS images are not the best option for mapping in the BBHR, due to its 1 km spatial resolution and 5 km maximum width of the reservoir. Thus, MERIS bands would be the most adequate, but it is not operational. Sentinel-2 and Sentinel-3 satellites will provide images at bands meet from MERIS and could replace it, with suited spectral and spatial resolution.

During the calibration, samples collected in the Tietê River before confluence with the Piracicaba River were pointed as outliers, which are exactly the samples with particular bio-optical status identified in Chapter 3. The removal of these points affected the Chl-*a* estimation in this section, where there was strong underestimation as shown in the Chl-*a* map using OLI image (Fig. 12 – Chapter 3). Another factor that impaired the performance of the empirical models was the packaging effect, which causes flattening of $a(\lambda)$. Therefore, $a(\lambda)$ and $R_{rs}(\lambda)$ would not present absorption features proportional to increasing pigments concentration, and, consequently, the models would not be capable of covering whole Chl-*a* concentration range.

Pigment packaging also prevented that QAA performance was more accurate, impairing mainly at shorter wavelength and red region. Despite this, the most relevant results obtained about modeling were obtained from QAA parameterization and calibration as shown in Chapter 4. Results of the applications of existing QAA versions showed the necessity of adjustments for using it in the BBHR. The strong underestimation for these versions, yielding negative values of $a_{CDOM}(\lambda)$ and $a_\phi(\lambda)$, was the critical point observed. Fits carried out for estimating $a(\lambda_0)$ and $a(\lambda)$ exhibited a considerably improvement in their estimative, obtaining an average NRMSE of 21.88% and MAPE of 28.27% for $a(\lambda)$. However, $a_{CDOM}(\lambda)$ and $a_\phi(\lambda)$ estimative only improved after parameterization and calibration of ζ and ξ , which eliminated negative values. Parameterization of ζ , replacing $a_\phi(665)/a_\phi(709)$ ratio for $a_\phi(665)/a_\phi(709)$ ratio, was the most important change proposed in this research for tropical eutrophic waters.

The improvement was so significant that the use of $a_\phi(\lambda)$ derived yielded an accurate estimation of Chl-*a* concentration, with NRMSE of 11.3% and MAPE of 38.5%.

Finally, we hope this work incentive the development of more researches in modeling of OACs, based mainly on physical fundamentals. The results obtained in this research must be useful to future works on remote sensing of color inland water, mainly, in tropical and eutrophic environments.

6.2. Recommendations

In this research was obtained important results for studies about eutrophic inland water. However, more investigations must be carried out about bio-optical status and modeling in BBHR. Bio-optical differences were identified among the reservoir sections, especially in the Tietê River before confluence with the Piracicaba River, hampering the calibration of a unique model which is accurate for the entire reservoir; nevertheless, these differences are not totally understood. A great amount of data was collected in the three fieldworks carried out in the BBHR which still was not totally explored and could help to explain the phenomena that occur in BBHR. The less explored data are of backscattering coefficient by particles, $b_{bp}(\lambda)$, collected *in situ* by *Hydroscat-6P* (HOBI Labs Inc., Tucson, AZ, USA) and *ECO BB-9* (WET Labs Inc, Philomath, OR, USA) meters. From dataset available it is possible to calculate every SIOP, which allows understanding the reservoir in terms of distribution of the kind of organism and particles in the reservoir.

Other important point to be investigate it is the influence of the package effect to $a_\phi(\lambda)$ and, consequently $a_t(\lambda)$ and $R_{rs}(\lambda)$. This factor is important because these data are widely used in bio-optical modeling and the curve flattening effect spreads remarkable errors for Chl-*a* estimative. According to results obtained in Chapter 3, it is probable that methods for reducing the pigment packaging proposed for marine water (BRICAUD et al., 1981; ROESLER & PERRY, 1989), due to much different bio-optical status between marine and reservoir waters. Therefore, it is necessary to concentrate efforts for developing techniques specific for inland water.

In relation to modeling, in future researches more attention must be given to improve the estimation of $a_t(\lambda)$. Nowadays, it is probable that the estimation of $a_\phi(\lambda)$ will be only improved with the increase of the accuracy of $a_t(\lambda)$. Satisfactory estimations of $a_t(\lambda)$ are essential to retrieve accurate $a_{CDM}(\lambda)$ and $a_\phi(\lambda)$. Additionally, increasing the samples size can be an alternative that improves the fine-tuning $a(\lambda_0)$. Other important step that can improve

the $a_t(\lambda)$ estimative, not explored in this research, is the calibration and parameterization of η for accurate estimation of $b_{bp}(\lambda)$, using *Hydroscat-6P* and *ECO BB-9* data. Parallel to improvement of the algorithm, applications of QAA_BBHR proposed in this research could be tested for other tropical reservoirs in order to assess its accuracy. Moreover, we would like to apply QAA_BBHR to images from sensors onboard Sentinel-2 and Sentinel-3 satellites.

Another challenge to be faced in tropical eutrophic waters it is the development of a semi-analytical model in order to estimate the OACs concentrations, simultaneously. From the dataset available it is possible to parameterize and calibrate this kind of model. The next efforts in modeling will be concentrated in developing a semi-analytical model for BBHR and comparing its performance in relation to empirical and quasi-analytical models presented in this Thesis.

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