Variability of particulate organic carbon in inland waters observed from MODIS Aqua imagery

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Abstract
Surface concentrations of particulate organic carbon (POC) in shallow inland lakes were estimated using MODIS Aqua data. A power regression model of the direct empirical relationship between POC and the atmospherically Rayleigh-corrected MODIS product \( \frac{R_{\text{rc,645}} - R_{\text{rc,1240}}}{R_{\text{rc,859}} - R_{\text{rc,1240}}} \) was developed \( (R^2 = 0.72, \text{RMSE} = 35.86 \mu \text{g L}^{-1}, p < 0.0001, N = 47) \) and validated \( (\text{RMSE} = 44.46 \mu \text{g L}^{-1}, N = 16) \) with field data from 56 lakes in the Middle and Lower reaches of the Yangtze River, China. This algorithm was applied to an 11 year series of MODIS data to determine the spatial and temporal distribution of POC in a wide range of lakes with different trophic and optical properties. The results indicate that there is a general increase in minimum POC concentrations in lakes from middle to lower reaches of the Yangtze River. The temporal dynamics of springtime POC in smaller lakes were found to be influenced by local meteorological conditions, in particular precipitation and wind speed, while larger lakes were found to be more sensitive to air temperature.

Keywords: POC, algorithm, inland lakes, remote sensing, carbon cycling

1. Introduction

Lakes and inland water bodies are active, changing, and important regulators of the carbon cycle and global climate (Tranvik et al. 2009). Collectively, nearly half as much organic carbon is buried in lakes globally as in the world’s oceans, and small lakes (<500 km²) account for 60–70% of this total organic carbon (TOC) burial (Alin and Johnson 2007). Particulate organic carbon (POC) is generally the form of carbon that most readily undergoes sedimentation and in-ecosystem loss. Even though POC is a small fraction of TOC present in most lakes (with respect to dissolved organic carbon, DOC), it plays an important role in sequestering carbon and associated compounds downward as part of the biological pump (Dhillon and Inamdar 2013, Son et al. 2009). To better explore carbon cycling in the freshwater ecosystems and understand the fate of the main organic components, it is important to quantify POC as well as DOC effectively (Jiang et al. 2012).

Satellite remote sensing observations provide a suitable means to explore temporal and spatial properties of inland lakes, allowing the possibility of measuring the limnological properties of many lakes simultaneously. Over the last three decades, significant contributions have been made to estimate the concentrations of phytoplankton pigments (e.g. chlorophyll a, Chla) using remote sensing (Clark 1981, Duan et al. 2010, Mittenzwey et al. 1992). However, the estimate of
total dissolved and particulate carbon presents a larger challenge, as optical properties of these two carbon pools can vary significantly in relation to their sources and sinks. The POC pool, in particular, may contain a wide variety of optically distinct components, from bacteria to macrophyte detritus (Morel and Ahn 1990) while the optical properties of DOC are highly sensitive to degradation processes (Loiselle et al. 2009).

To better understand the C cycling in surface waters, algorithms have been developed to estimate POC concentrations in the open ocean (Gardner et al. 2006, Mishonov et al. 2003, Stramski et al. 1999). In the first published algorithm for estimating POC from remote sensing, a two-step process was based on (Stramski et al. 1999): (1) the dependence of the backscattering coefficient ($b_{wp}$) by particles suspended in seawater on the POC concentration; (2) the dependence of the spectral remote-sensing reflectance ($R_{rs}(\lambda)$) on $b_{wp}$. The resulting correlation was associated to the dominance of the biologically produced POC in controlling changes in $b_{wp}$ in open oceans (Gardner et al. 2006, Legendre and Michaud 1999). There are clear difficulties in applying this to turbid inland waters, where inorganic particles play a more important role in the optical backscattering properties of the water body (Ma et al. 2009, Tzortziou et al. 2007). Algorithms to estimate POC concentrations in inland waters remain a challenge.

The objective of the present study is to develop an optical algorithm for the retrieval of surface water POC concentrations in inland water bodies from satellite imagery. To our knowledge, this is the first estimate of POC concentrations in inland lakes using MODIS Aqua data.

2. Study region

The Yangtze River (known locally as Chang Jiang, or ‘Long River’), is the longest river in Asia and third in the world (6300 km). The middle and lower reaches of the Yangtze River (28°50′–33°50′ N and 113°30′–121°00′ E, figure 1) have a total drainage area of about 8.0 × 10^4 km^2 (Chen et al. 2001) which include some of the most important agricultural areas in China. The Middle and Lower Reaches of the Yangtze River basin (MLY) contain 529 lakes (areas ≥1 km^2), accounting for 18.57% of all lakes in China, with most water bodies (94.52%) less than 50 km^2 (Ma et al. 2010, 2011).

In this study, field measurements were made in 56 lakes and used to develop a POC algorithm for inland water bodies (table 1 and figure 1). These lakes, distributed along the Yangtze River, are subject to various degrees of human impact from agricultural activities as well as effluent disposal from small villages and mega-urban areas, such as Wuhan and Nanjing.

3. Methods

3.1. Field data

Water samples and optical data were collected at 177 stations (3 or 4 stations per lake) by two survey groups using identical methodologies between 7 April and 20 April 2012. The selection of 56 sample lakes was made to be representative of water bodies along the MLY. Access to lakes for multiple sampling along a lake transect was also considered. POC...
concentrations were determined by combustion of sample filters through pretreated 47 mm Whatman GF/F filters (6 h at 450 °C) by an EA3000 elemental analyzer. The filters were dried at 50 °C for 8 h and then wrapped in aluminum foil. Acidification treatment was performed to remove the carbonates from the filter, after which the filters were dried again and weighed. POC concentrations were measured by combustion of sample filters in an EA3000 elemental analyzer (Biddanda and Benner 1997). Chla concentrations were extracted using 90% ethanol and measured with a UV2401 spectrophotometer (Duan et al. 2012, 2014a).

### 3.2. Satellite data processing

Seven scenes of MODIS Aqua Level-0 (raw digital count) data were obtained from the US NASA Goddard Space Flight Center (GSFC) from 7 April 2012 to 20 April 2012 and therefore consistent with the field sampling. Level-0 data were processed using SeaDAS version 6.0 to generate calibrated at-sensor radiance. An initial attempt to use SeaDAS to generate above-water remote-sensing reflectance (R\text{\nu}) was unsuccessful. This was due to elevated aerosol concentrations and sun glint, even after adjusting processing options (e.g., the default limit of aerosol optical thickness at 869 nm was raised from 0.3 to 0.5, the default cloud albedo was raised from 2.7% to 4.0%, etc) (Feng et al. 2012). Rayleigh-corrected reflectance R\text{\nu,\lambda} was derived after correction for Rayleigh scattering and gaseous absorption effects as (Hu et al. 2004):

\[ R_{\nu, \lambda} = \pi L_{\nu, \lambda} \lambda^4 (F_0 \nu \times \cos \theta_0) - R_{\nu, \lambda}, \]

where \( \lambda \) is the wavelength of the MODIS spectral band, \( L_{\nu, \lambda} \) is the calibrated at-sensor radiance after correction for gaseous absorption, \( F_0 \nu \) is the extraterrestrial solar irradiance, \( \theta_0 \) is the solar zenith angle, and \( R_{\nu} \) is the reflectance due to Rayleigh (molecular) scattering estimated using the 6S radiative transfer code. The \( R_{\nu} \) data were geo-referenced into a cylindrical equidistance (rectangular) projection.

Concurrent datasets of MODIS reflectance data and \textit{in situ} POC measurements were made using a time window of ±24 h between MODIS and \textit{in situ} measurements. To avoid potential influence of patchiness in the optical properties of the measurement, a homogeneity test of the 3×3-pixel box centered at the \textit{in situ} station was performed (note that each MODIS pixel represents 250 m×250 m). If the variance of

| Lake     | Long. (E) | Lat. (N) | Area | Num. | Lake     | Long. (E) | Lat. (N) | Area | Num. |
|----------|-----------|----------|------|------|----------|-----------|----------|------|------|
| Taibai_HB| 115.8100  | 29.9600  | 27.42| 3    | Zhupu    | 115.3842  | 29.8327  | 17.40| 3    |
| Wushan   | 115.5900  | 29.9000  | 15.81| 3    | Chi      | 115.7112  | 29.7875  | 59.43| 3    |
| Chidong  | 115.4010  | 30.1180  | 40.57| 3    | Changang | 115.8817  | 29.6833  | 35.16| 4    |
| Makou    | 115.4292  | 30.2541  | 9.06 | 3    | Xinxiao  | 116.1621  | 29.3560  | 30.85| 4    |
| Che      | 115.1492  | 30.4373  | 5.93 | 3    | Qili     | 115.9297  | 29.6649  | 8.02 | 2    |
| Wangtian | 115.0587  | 30.4373  | 5.93 | 3    | Bili     | 115.9333  | 29.6864  | 9.33 | 3    |
| Baitan   | 114.9411  | 30.4691  | 5.13 | 3    | Shenjin  | 117.0441  | 30.3920  | 96.03| 3    |
| HGdong   | 114.9135  | 30.4358  | 1.49 | 3    | Taibo    | 116.7121  | 30.0110  | 24.76| 3    |
| Sanshan  | 114.7650  | 30.3160  | 23.97| 3    | Huangni  | 116.9269  | 30.1380  | 6.90 | 3    |
| Baoan    | 114.7253  | 30.2229  | 45.46| 3    | Shangdu  | 117.2071  | 30.7398  | 8.70 | 4    |
| Zhuangzi | 114.7084  | 30.643   | 36.24| 3    | Wu       | 117.4935  | 30.7963  | 46.64| 3    |
| Guanlin  | 114.007   | 30.8662  | 7.93 | 3    | Wangmu   | 116.9160  | 30.7483  | 7.92 | 3    |
| Yezhu    | 114.0718  | 30.8475  | 25.88| 3    | Yezhu    | 117.6243  | 30.9246  | 16.98| 2    |
| Baishui  | 114.1659  | 30.8036  | 13.39| 3    | Baishui  | 117.6538  | 30.0026  | 11.52| 3    |
| WCdong   | 114.3827  | 30.561   | 34.35| 3    | WCdong   | 117.6845  | 30.9199  | 20.01| 3    |
| Shangshe | 114.218   | 30.132   | 10.24| 3    | Shangshe | 118.2874  | 31.2524  | 7.78 | 4    |
| Lu       | 114.1971  | 30.2591  | 47.53| 3    | Lu       | 120.7380  | 31.5794  | 17.51| 3    |
| Shanjiao | 114.1679  | 30.5244  | 2.27 | 3    | Shanjiao | 120.8820  | 30.1079  | 16.05| 4    |
| She      | 113.9871  | 30.4139  | 10.77| 3    | She      | 120.9172  | 30.8145  | 59.18| 2    |
| Guangli  | 114.0416  | 30.3869  | 4.67 | 3    | Guangli  | 120.9293  | 30.2083  | 5.08 | 3    |
| Qingling | 114.2447  | 30.447   | 7.21 | 3    | Qingling | 120.8868  | 31.1471  | 5.07 | 4    |
| Huangjia | 114.2736  | 30.4402  | 6.84 | 3    | Huangjia | 120.81496 | 31.9764  | 43.59| 3    |
| Baoxie   | 114.5859  | 30.3534  | 25.32| 3    | Baoxie   | 120.74668 | 31.13363 | 4.96 | 4    |
| Tangxun  | 114.3612  | 30.4341  | 44.83| 3    | Tangxun  | 120.7283  | 31.18104 | 2.91 | 4    |
| Nantan   | 115.0972  | 29.8473  | 8.60 | 3    | Nantan   | 118.92217 | 31.27603 | 31.22| 3    |
| Zhulin   | 115.2192  | 29.8466  | 3.30 | 3    | Zhulin   | 119.46619 | 32.57   | 103.73| 3    |
| Wang     | 115.3261  | 29.8637  | 42.87| 3    | Wang     | 118.7939  | 32.06284 | 4.00 | 4    |

**Table 1.** Location, area, number of samples taken for each of the 56 lakes along the Yangtze River.
the 3 x 3 box was >0.4, the corresponding matching pair was discarded from the regression. With this strict quality control criteria, a total of 63 matching pairs were selected. 47 samples (2/3) of this dataset were selected for training, while the other 16 samples were used for the algorithm validation.

The Normalized Difference Vegetation Index (NDVI), defined as \((R_{\text{NIR}} - R_{\text{RED}})/(R_{\text{NIR}} + R_{\text{RED}})\) was used to distinguish water bodies from surrounding dry soil or vegetation with threshold value set to zero (Haas et al. 2009, Kaptué Tchuenté et al. 2011). However, nonwater features in the NDVI image may not be completely eliminated in shallow turbid lakes. A modified NDVI threshold (\(<-0.05\)) was used to provide more accurate estimates of lake borders (Ma et al. 2011).

3.3. Statistical analysis

Daily data of precipitation rate (mm), wind speed (m s\(^{-1}\)) and air temperature (°C) were obtained from the China Meteorological Data Sharing Service System (http://cdc.cma.gov.cn/). Distance between lakes was determined using the ‘haversine’ formula (Rick 1999). Correlations between POC estimates, distance and meteorological data were identified using a linear model where direct correlations (increasing) had positive Pearson correlation coefficients (\(r\)) and indirect correlations (decreasing) had negative coefficients. A multiple regression of POC estimates with meteorological data was performed using a linear least squares fitting procedure.

4. Results and discussion

4.1. POC sources in inland waters

Field data indicated a large variability in the properties of 56 lakes studied, with a 50-fold range in POC (17–942 \(\mu\)g L\(^{-1}\)), a 60-fold range in SPM (1.39–68.95 mg L\(^{-1}\)), a 400 fold range in Chla (0.55–240 \(\mu\)g L\(^{-1}\)) (table 2, figure 2). The average Chla concentration was high, 42 \(\mu\)g L\(^{-1}\), as would be expected from an area which includes hyper-eutrophic waterbodies such as Lakes Taihu and Chaohu (Duan et al. 2009, Jin et al. 2012). SPM concentrations were dominated by SPOM, indicating that plankton and resuspended organic matter played an important role (Upsdell, 2005). POC correlated well with SPM (\(r=0.88\)) and SPOM (\(r=0.80\)) (figure 3(a)). Generally, the organic content of suspended matter from terrigenous sources can be expected to have a similar organic carbon content (Cauwet and Mackenzie, 1993). The correlation between POC and Chla (\(r=0.27\), figure 3(b)) was low, indicating that phytoplankton was not the dominant source particulate carbon in these waters. The mean ratio of DOC to POC concentrations indicated that DOC accounted for 96% of TOC in the study lakes.

The ratio of POC to SPM (POC%) was used to describe the relative fraction of organic matter composing the suspended particulate matter assemblage. The POC:Chla ratio was used to describe the relative proportion of organic material (both living and nonliving) relative to autotrophic organisms. The latter index is also influenced by variations in the intracellular photosynthetic pigment concentrations when diverse water bodies are compared (Loisel and Morel 1998, Vantrepotte et al. 2012). POC% ranged between 0.80% and 2.66% (average at 1.44%) (figure 2(d)), which is similar to that reported for the Yellow River (0.50%–5.00%) (Zhang et al. 2012). The POC:Chla ratio of the 56 lakes averaged 13 (0.75–157) (figure 2(e)), much smaller than that measured in Yangtze River (48–136) or similar rivers globally (Yellow River: 3988; lower Mississippi River: 256) (Duan and Bianchi, 2006, Zhang et al. 2012), typical coastal waters (Charente estuary: 232–13152; English Channel, Southern North Sea and French Guiana: 24–686) (Modéran et al. 2012, Vantrepotte et al. 2012), or marine waters (20–200) (Cifuentes et al. 1988).

Freshwater ecosystems receive organic matter from two distinct sources: primary production occurring within the waterbody (autochthonous production) and external loading of terrestrial organic matter from the watershed (allochthonous loading) (Prokushkin et al. 2011). As the POC concentrations were well correlated to the concentrations of SPM and SPOM but poorly correlated to Chla, the source of POC in many of these lakes was more closely tied to catchment sources or resuspended organic detritus. These lakes were small- to moderate-sized and surrounded by highly productive wetlands and agricultural lands that represent major sources of organic matter loading (Wetzel 1984). It should be noted that allochthonous and autochthonous POC sources will vary seasonally, typically with maximum phytoplankton production in summer and peak allochthonous inputs in the fall (Bianchi and Argyrou 1997, Cauwet and Mackenzie 1993).

4.2. POC algorithm development

Several POC algorithms have been proposed in the past, including the semi-analytical algorithms based on radiative transfer theory and empirical regression algorithms (Gardner et al. 2006, Son et al. 2009, Stramski et al. 1999). However, these algorithms were developed for ocean waters and rely on the dominance of phytoplankton biomass in the total POC concentration (Morel 1988, Pabi and Arrigo 2006). The optical properties of these study lakes were influenced not
only by phytoplankton and related (co-varying) particles, but also by inorganic particles and organic detritus (Duan et al. 2014a, IOCCG 2000). Hence, new algorithms were required for these more complex optical conditions and multiple POC sources.

As typical ocean bands often saturate over turbid lake waters, an approach using MODIS land bands to determine $R_{rc,\lambda}$ was developed. Regressions between in situ POC and single-band $R_{rc,\lambda}$ showed a very poor correlation ($r<0.4$), suggesting that aerosol contributions could not be ignored. In addition to the single-band algorithms, simple band-ratios were also explored but did not provide strong correlations.

Aerosol contributions to the satellite signal vary spatially along the Yangtze River (He et al. 2010). Water reflectance at 1240 nm is virtually null in coastal and inland waters (Hu et al. 2000). Assuming spectrally consistent but spatially variable impacts of aerosols, reflectance bands were corrected for aerosols using $R_{rc,1240}$ (Feng et al. 2012). For the atmospherically corrected data, $(R_{rc,645}-R_{rc,1240})/(R_{rc,859}-R_{rc,1240})$ showed the best relationship with POC concentrations.

Figure 2. Characteristics of suspended particulate matter measured on surface samples in 56 lakes along the Yangtze River, China. From top to the bottom, the graphs show the concentration of particulate organic carbon (POC), the concentration of suspended particulate matter (SPM), the concentration of chlorophyll-a (Chla), the ratio of POC to SPM, and the ratio of POC to Chla. Average values for each lake are shown.

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\[ R^2 = 0.72, \quad p < 0.0001 \] (figure 4(a), equation (2)). The fitted POC algorithm was:

\[
\text{POC (mg L}^{-1}\text{)} = 228.06 \times \exp\left(0.0966 \times \left(\frac{R_{\text{rc},645} - R_{\text{rc},1240}}{R_{\text{rc},859} - R_{\text{rc},1240}}\right)\right)
\]

\[ (2) \]

The validation of this relationship showed a strong correlation between in situ measured POC and MODIS estimated POC (figure 4(b)).

This is the first algorithm focused on POC dominated by detrital matter. It should be noted that this algorithm was developed and tested for the POC present in predominantly shallow lakes in the period of the year when algal blooms are low (Duan et al. 2014b, 2009). To best capture the seasonal variability of POC in these lakes, additional efforts would be required to develop and test POC algorithms for periods of algal blooms (May–August) and periods of low winds (October–November). Correction using \( R_{\text{rc},1240} \) would be important in both cases to reduce the effect of seasonal variation in atmospheric conditions. The resulting seasonal set of POC algorithms could be adapted for routine processing of MODIS data to produce maps of surface POC in these lakes using the same empirical approach.

Optical wavebands in the red and NIR have been widely used to examine different types of particulates, including floating algal biomass (Hu et al. 2010), general turbidity (Chen et al. 2007), dredging water plumes (Kutser et al. 2007), SPM (Feng et al. 2012) and Chla concentrations (Dall’Olmo et al. 2005). To date, these approaches have been most success when there is one dominating particulate, as they do not allow for differentiation between high concentrations of POC, Chla or SPM.
MODIS images have been used widely in routine monitoring of oceanic, coastal and inland lakes (Feng et al 2014, Hu et al 2012, Zhang et al 2010). To monitor lakes across a range of sizes requires the spatial resolution of the 250 and 500 m bands. However, the spectral resolution of the 250 and 500 m bands limits their use of lake color assessment, compared to the more appropriate spectral characteristics of the 1000 m bands (Kaptué et al 2013, Olmanson et al 2011).

Nonetheless, our analysis shows that it is possible to develop appropriate algorithms to monitor key carbon components of complex inland waters using the spectral characteristics of the MODIS 250 and 500 m bands, taking advantage of its high temporal resolution and wide swath.

4.3. Inter-annual variability of POC

The POC algorithm (equation (2)) and water area-delineation methods developed for the April 2012 dataset were then used with Rayleigh-corrected reflectance to explore a series of MODIS Aqua images from 2003 to 2013 (figure 5). All images were obtained in the same month (April) of each year to minimize seasonal variations in aquatic optical conditions (e.g. algal blooms) (Duan et al 2014b, 2009). The number of lakes explored in each image depended on the presence of clouds. The average POC concentrations for each lake were used to examine the inter-annual variability of all lakes in the MLY. Only lakes with at least 5 measurements in the 11-year dataset were considered. These lakes (55) were located throughout the MLY and represented a wide range of lake conditions, with lake area ranging from 0.32 to 2508 km².

The yearly lake POC averages demonstrated a high interannual variability, with POC concentrations generally highest in 2013 and lowest in 2004 (figure 6(a)). Interannual variability of individual lakes was compared to local meteorological data (rain, wind, and air temperature) to identify commonalities.

Lakes were grouped according to lake size in four categories: less than 5 km², between 5 km² and 25 km², between 25 km² and 100 km², and above 100 km² (figure 6(a)). The inter-annual POC dynamics of each lake category were compared to average meteorological conditions. Direct correlations were identified for one lake size category (n = 11, p < 0.01). The inter-annual POC concentrations in the third lake category (25 km² < lake area < 100 km²) were found to be well described by a linear equation that included the maximum air temperature on the preceding day of measurement (day2-maxtemp, 0.1 °C) (POC = 322 − 0.40 day2-maxtemp, $R^2 = 58\%$, $F$-ratio = 4.49, $p = 0.006$), indicating the higher sensitivity of these water bodies to temperature and mixing. Comparisons using multiple linear regression indicated that the inter-annual POC concentrations in the smaller lake category (lake area < 5 km²) were found to be well described by linear combination of precipitation on the day of estimation (day-rain, 0.1 mm), on the preceding day (day2-rain) and wind speed on the same day (wind, 0.1 ms⁻¹) (POC = 274 − 0.99 wind + 0.40 day2-rain − 20.0 day-rain, $R^2 = 86\%$, $F$-ratio = 4.49, p = 0.006).

Figure 5. Mean MODIS-derived POC distributions in April between 2003 and 2013. Zoom 1: Lake Liangzi; Zoom 2: Lake Longgan, Lake Huangda and Lake Bo; Zoom 3: Lake Baidang; Zoom 4: Lake Chen and Lake Dianshan.
ratio = 14.65, \( p = 0.002 \) indicating the sensitivity of these water bodies to mixing, run-off and dilution.

Spatially, there was a low correlation between lake geographic position in the MLY and its POC concentration (figure 6(b)). While the specific catchment land cover for each lake was not determined, the general trend from the Middle to Lower Yangtze is one of increasing crops cover and decreasing pasture cover (Ellis et al 2010). The minimum POC concentrations in the 11-year dataset of each of the 56 lakes were positively correlated (\( n = 56, r = 0.28, p = 0.03 \)) to increasing distance from Lake Taibai_HN, the westernmost study lake in the Middle Yangtze (29.0 °N, 112.1 °E) (figure 1). In addition, the standard deviations of 11-year POC dataset for each lake were negatively correlated (\( n = 56, r = -0.26, p = 0.05 \)) with distance from Lake Taibai_HN. These correlations indicated a general tendency for diminished inter-annual variability of POC and higher minimum POC in lakes of the Lower Yangtze. Higher agricultural activity favors increased nutrient inputs (promoting autochthonous POC production) as well as increased sediment inputs (including allochthonous POC) (Martinuzzi et al 2014). A more detailed study of individual catchments of each lake would provide a more complete analysis of the causes of inter-lake differences.

5. Conclusions

An empirical approach used to examine the surface concentrations of POC in inland lakes using optical remote sensing data was demonstrated to be robust. Among the algorithms examined, a power relation of the atmospherically Rayleigh-corrected reflectances at 645 nm, 859 nm and 1240 nm was found to provide the most accurate estimates. The algorithm provided good estimates of POC concentrations across a range of inland lakes over a large geographical area. This algorithm was used to study the inter-annual and spatial variation of POC concentrations of a large number of lakes, with varying characteristics, and provided new information on the dynamics of this important component of the aquatic carbon cycle. The data series was limited to a single
month (April) that is characterized by higher winds, lower rain and low algal blooms in the MLY lakes.

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