



Diel variability of vertical distributions of chlorophyll a at the SEATS and ALOHA stations: implications on remote sensing interpretations

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ABSTRACT

The effects of the diel (involving a 24 hour period) variations in the surface concentrations of chlorophyll a (C) on the use of once-daily remotely sensed C as the diel average were assessed from the diel records in the derived depth-weighted C (C_d) that should be detected by remote sensing and the *in situ* surface C at two time-series stations in the North Pacific: the SEATS (SouthEast Asian Time-series Study) station in the northern South China Sea and the ALOHA (A Long-Term Oligotrophic Habitat Assessment) station in the North Pacific subtropical gyre. *In situ* surface C varied by a factor of about 2.0 and 1.3 over a diel cycle, and by $\pm 20\%$ and $\pm 9\%$ over the diel average at the SEATS and ALOHA stations, respectively. As the overpass-times of the different satellites were not identical, C_d was satellite-dependent. While the C_d corresponding to MODerate resolution Imaging Spectroradiometer on Aqua (MODIS-Aqua) and Sea-viewing Wide Field-of-view Sensor (SeaWiFS) overpass-times agreed to $\pm 10\%$, the C_d corresponding to MEdium Resolution Imaging Spectrometer (MERIS) overpass-time could differ from the other two by -22% to $+28\%$ at the SEATS station and -1% to $+12\%$ at the ALOHA station. In addition, C_d corresponding to the overpass-times of the three satellites deviated from the observed diel average *in situ* surface C by -19% to $+32\%$ at the SEATS station and by -6% to $+13\%$ at the ALOHA station. These results indicate that, as a result of diel variations, neither a one-time remotely-sensed nor a one-time observed *in situ* surface C can represent the diel average *in situ* surface C accurately. Furthermore, diel variations are an inherent source of uncertainty when data from multiple satellites are pooled for use. The magnitudes of these discrepancies can be comparable to the commonly claimed uncertainties in remotely sensed C and thus should be taken into consideration in its interpretation and use.

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1. Introduction

Diel (involving a 24 hour period) variations in the surface concentrations of chlorophyll *a* (*C*) in the oceans have been widely reported (Chen et al. 2010; Claustre et al. 1999; IOCCG 2012; Lee et al. 2012; Neveux et al. 2003; Woods and Onken 1982). They may be driven by physical, biological or physiological processes, such as vertical mixing, phytoplankton growth and light-related variations in the cellular concentrations of the pigments. As a result, the surface *C* may vary by a factor of two or more within a diel cycle (Chen et al. 2010; Claustre et al. 1999; MacIntyre et al. 2002; Neveux et al. 2003; Stramski and Reynolds 1993; Woods and Onken 1982). Thus, in once-through-sampling schemes, the surface *C* found may be dependent on the sampling time, and the interpretation of the results may be biased if the effect of this short term phenomenon is overlooked.

Currently, the most widely used satellite remotely sensed surface *C*, C_{rs} , are obtained from the sun-synchronous ocean color sensors, primarily the Sea-viewing Wide Field-of-view Sensor (SeaWiFS; 1997–2010), the MODerate resolution Imaging Spectroradiometer on Aqua (MODIS-Aqua; since 2002), the MEdium Resolution Imaging Spectrometer (MERIS; 2002–2012) and the Visible and Infrared Imager/Radiometer Suite (VIIRS; since 2012), in polar-orbiting satellites (Brewin et al. 2014; IOCCG 1999; McClain 2009). These satellites pass over a given location in the ocean at different prescribed times in the daytime typically only once in a 24 hour period. Yet the C_{rs} derived from these daily observations have been treated as the diel average surface *C* and these concentrations have frequently been further extrapolated for the estimation of other biogeochemical parameters, such as the depth-integrated standing stock of *C* (Morel and Berthon 1989) and primary production (Behrenfeld and Falkowski 1997). There are two major sources of uncertainty in these extrapolations: first, the uncertainty in C_{rs} itself, and, secondly, the uncertainty in assuming that the once-daily observation represents the diel time-averaged value. The first source of uncertainty has been studied extensively and, at the present time, it is about $\pm 35\%$ (McClain 2009). The second source of uncertainty is generally not as well studied, and it is increasingly recognized. It can be caused by any natural temporal variation in *C* within the time period of interest, daily in this case, and such short term variations in C_{rs} have been reported particularly in coastal waters (Chen et al. 2010). Diel variations in the surface *C* can obviously contribute to the second source of uncertainty in the open oceans. It has not been extensively documented and quantitatively assessed, probably because repeated *in situ* observations on the distributions of *C* at individual locations in the oceans over diel cycles have seldom been made.

At two time-series stations in the North Pacific (Figure 1), the SEATS (SouthEast Asian Time-series Study) station at 18.00° N and 116.00° E in the tropical northern South China Sea and the ALOHA (A Long-Term Oligotrophic Habitat Assessment) station at 22.75° N and 158.00° W in the subtropical gyre, observations on the vertical distributions of the chlorophyll in discrete water samples were made in several occasions over diel cycles. These time-series stations are located in the tropical-subtropical waters which may be particularly prone to diel variations in the surface *C* as a result of their thinner mixed layer and higher solar irradiance (Claustre et al. 1999; Kirk 1994; Neveux et al. 2003). Although both stations are located in the North Pacific, the SEATS station is situated in a biogeochemically dynamic marginal sea (Wong et al. 2007) while the ALOHA station is at the middle of a relatively stable ocean gyre (Karl and Lukas 1996). In this study, by

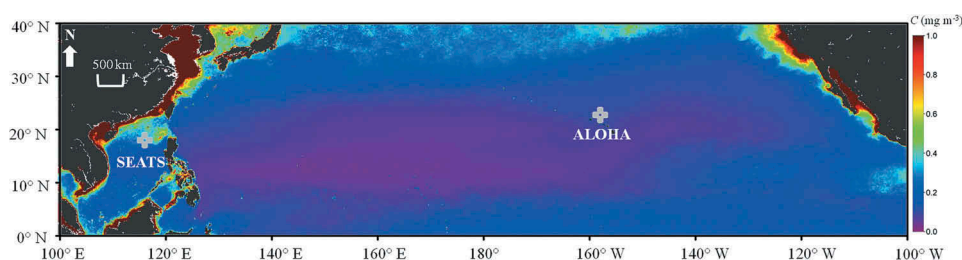


Figure 1. Locations of the SEATS station and the ALOHA station in the North Pacific. Color image – MODIS-Aqua derived climatological (2003–2017) monthly C in January.

making use of the data sets from these two time-series stations, the effects of the diel variations in the surface C on the interpretation and application of the corresponding C_{rs} were examined for the sensors on three satellites, the MERIS, SeaWiFS and MODIS-Aqua satellites by considering the diel variations in the derived depth-weighted C (C_d) that should have been detected by remote sensing and in the *in situ* surface C observed at these two time-series stations. The purposes of this study were then two-fold: (1) to characterize the diel variations in the C in the tropical-subtropical waters at the SEATS and ALOHA stations; and (2) to evaluate the effect of diel variations in the C on the interpretation of the corresponding C_d .

2. Data and methods

2.1. The environmental setting at the SEATS station and the ALOHA station

The SEATS station has been maintained by Taiwanese oceanographers since 1999 (Wong et al. 2007). Previous works indicate that the hydrographic characteristics in its upper waters are primarily influenced by the combined effects of the seasonal monsoons and surface heating and cooling (Liu et al. 2002, 2013; Pan et al. 2015; Tseng et al. 2005; Wong et al. 2007). The stronger northeast monsoon is found between October and April while the weaker southwest monsoon is found between June and August. Sea surface temperature (SST) invariably stays above 28.0 °C in the summer but it can drop below 24.0 °C in the winter. As a result of the combined effect of the stronger wind and surface cooling in the winter, vertical mixing is enhanced so that the mixed layer depth (MLD) is about 25 m in the summer and it deepens to about 80 m in the winter (Tai, Wong, and Pan 2017). Concomitantly, the enhanced vertical mixing increases the availability of the nutrients and the associated photosynthetic activities in the upper water, and this results in a distinct seasonal pattern in the surface C such that a prominent surface C maximum is regularly found in the winter (Liu et al. 2002, 2013; Pan et al. 2012, 2013, 2015; Tseng et al. 2005; Wong et al. 2007). The surface C around the SEATS station reaches $> 0.30 \text{ mg m}^{-3}$ in the winter (Figure 1) but drops to $< 0.10 \text{ mg m}^{-3}$, the typical level found in tropical waters (Yoder et al. 1993), in the summer. This is a distinguishing characteristic at the SEATS station as uniformly low surface C are typically found year round in other tropical waters (Messié and Radenac 2006). The influence of terrestrial sources of nutrients, namely, river runoff and submarine ground water, on the waters at the SEATS station is expected to be minimal as the station is located at least 500 km from land and is effectively isolated from the plumes of these terrestrial sources (Liu et al. 2012; Pan et al. 2015; Wong et al.

2007). On the diel time scale, variations in the wind speed, usually within $\pm 1 \text{ m s}^{-1}$ from the mean, are small (Chen et al., 2009), while variations in the MLD and the SST are about $\pm 4 \text{ m}$ and $\pm 0.1^\circ\text{C}$, respectively (Tai, Wong, and Pan 2017).

The ALOHA station has been maintained since 1988 (Karl and Lukas 1996). It is located in the middle of a warm and isolated subtropical gyre. The permanent anticyclonic circulation in the gyre leads to an Ekman downwelling, a deep pycnocline, and, as a result, a limited supply of nutrients by vertical mixing (Church, Lomas, and Muller-Karger 2013; Dave and Lozier 2010; Karl and Church 2014). The upper waters at the ALOHA station are thus extremely oligotrophic, with low surface nitrate, $< 0.01 \mu\text{M}$ year round (Karl and Church 2014), and low surface C , at about 0.08 mg m^{-3} in the summer and 0.13 mg m^{-3} in the winter (HOT (Hawaii Ocean Time-series) 2017). Intra-annual variations in the hydrographic characteristics in the upper layer are primarily linked to the seasonal changes in the incident solar radiation, which results in warmer SST and shallower MLD in the summer (around 27.0°C and 30 m respectively) than in the winter (around 23.0°C and 100 m) (Church, Lomas, and Muller-Karger 2013; Karl and Church 2014; Karl and Lukas 1996). The small seasonal variations in the surface C are not associated with the corresponding change in the phytoplankton biomass, but rather, they are linked to the seasonal change in the MLD and the resulting photo-adaptation of the phytoplankton to the lower average light intensity in the mixed layer in the winter (Church, Lomas, and Muller-Karger 2013; Karl and Church 2014; Letelier et al. 1993; Winn et al. 1995). Thus, the C and primary production actually follow opposite seasonal trends (Church, Lomas, and Muller-Karger 2013). In addition to the physical controls, nitrogen fixation, whose peak rate occurs in the summer, is a key process influencing phytoplankton activities at the ALOHA station as it accounts for $> 50\%$ of the supply of the new nitrogen to the upper waters (Karl and Church 2014; Karl et al. 1997). This general seasonal pattern in the C can be punctuated by episodic phytoplankton blooms (Karl and Church 2014; Sakamoto et al. 2004) which may be triggered by mesoscale eddies, Rossby Waves and submesoscale density fronts (Ascani et al. 2013; Letelier et al. 2000; White, Spitz, and Letelier 2007). On the diel time scale, variations in the MLD, SST and C , by about 30 m , 0.2°C and 0.03 mg m^{-3} respectively, are relatively small (Nicholson et al. 2015). Inter-annually, the annual mean SST, surface C and primary production at the ALOHA station vary by 1.5°C (24.0°C to 25.5°C), a factor of 2.2 (0.06 mg m^{-3} to 0.13 mg m^{-3}) and a factor of 1.5 ($400 \text{ mg m}^{-2} \text{ d}^{-1}$ to $600 \text{ mg m}^{-2} \text{ d}^{-1}$ in fixed carbon) between 1988 and 2015, respectively (HOT (Hawaii Ocean Time-series) 2017). Inter-annual mesoscale variability in vertical velocity, which may be associated with the North Pacific Gyre Oscillation, rather than the El Niño–Southern Oscillation and the Pacific Decadal Oscillation, is a major contributor for the inter-annual changes (Dave and Lozier 2010; Luo et al. 2012).

2.2. Field observations

At the SEATS station, time-series *in situ* observations stretching over 27 hours, 39 hours and 28 hours in three cruises, OR1-0944 (13 to 15 October 2010), OR1-0988 (23 to 25 December 2011) and OR1-1010 (31 August to 1 September 2012), were used in this study. During each occupation of the station, vertical distributions of temperature, salinity and photosynthetically available radiation (PAR) were recorded repeatedly in 1

hour to 3 hour time intervals. Water temperature and salinity were recorded by using a conductivity-temperature-depth (CTD) recorder (SeaBird SBE9/11), while PAR was measured by a Biospherical model QSP-200L or QSR-240 quantum scalar irradiance sensor. The vertical profiling data were binned to 1 m intervals. Discrete water samples were collected at 6 depths to 9 depths in the top 200 m of the water column in each cast, typically at nominal depths of 5 m, 10 m, 20 m, 30 m, 50 m, 80 m, 100 m, 150 m and 200 m, by using 20 L Go-Flo bottles mounted onto a Rosette sampling assembly (General Oceanic Inc.). Samples for the determination of the C were collected by filtering about 2 L of seawater each onboard ship through 47 mm Whatman GF/F glass fiber filters. The filters were stored in liquid nitrogen and were returned to a shore-based laboratory at the Academia Sinica (Taipei) for further analyses. In the laboratory, the C was determined by reverse-phase high-performance liquid chromatography (HPLC) by using a Shimadzu LC-10A HPLC system equipped with a C18 column (Ho et al. 2015).

Field observations at the ALOHA station were extracted from the Hawaii Ocean Time-series program (HOT (Hawaii Ocean Time-series) 2017). Time-series *in situ* observations, including vertical distributions of temperature and salinity from the CTD recorders and C from discrete water sampling, stretching over 46 hours, 62 hours and 50 hours, in about 3 hour time intervals, in three cruises, CR-66 (26 to 28 September 1995), CR-67 (26 to 28 October 1995) and CR-68 (16 to 18 November 1995), were used in this study. Details in the sampling method and the method for the analyses of discrete samples have been described in the webpage and reported in Letelier et al. (2000).

2.3. Deriving the depth-weighted C , C_d

The depth-weighted C , C_d , derived from *in situ* observations has been used to represent the C that should be detected by remotely sensing, C_{rs} (Cannizzaro et al. 2013). The calculation scheme for the derivation has been known for a while (Morel and Berthon 1989). In a given cast in a cruise, C_d is derived from the vertical profiles of the PAR and the C in the discrete samples by following the method of Morel and Berthon (1989) such that:

$$C_d = \frac{\int_0^{Z_{pd}} C(Z) [\exp(-2KZ)] dZ}{\int_0^{Z_{pd}} [\exp(-2KZ)] dZ} \quad (1)$$

Here, $C(Z)$ is the C at depth Z , Z_{pd} is the penetration depth at which the PAR has been reduced to about 37% of the surface value (Pan and Zimmerman 2010), and K is the attenuation coefficient of PAR. In the euphotic zone, the PAR decreases approximately exponentially with depth (Kirk 1994; Pan and Zimmerman 2010) so that:

$$PAR_Z = (PAR)_0 [\exp(-KZ)] \quad (2)$$

where PAR_Z and PAR_0 are the PAR at depth Z and at the sea surface. Thus, K may be calculated as the slope in a linear regression analysis between $\ln(PAR_Z)$ and Z from the sea surface to the euphotic zonal depth (EZD) at which the PAR drops to 1% of the surface value. Then, Z_{pd} is calculated as (Morel and Berthon 1989):

$$Z_{pd} = \frac{1}{K} \quad (3)$$

Since $C(Z)$, K and Z_{pd} are known, C_d may be estimated. In the absence of light in the nighttime, obviously, the PAR cannot be measured and the C_d cannot be derived. However, the theoretical C_d may still be estimated by assuming that the diel variations in K and Z_{pd} are small so that their average values found in the daytime may be used for estimating C_d in the nighttime. The depth-integrated standing stock of C , I_{chl} , was calculated by a trapezoidal integration of the C in the discrete samples from the surface down to 200 m.

At the ALOHA station, the vertical profiles of the PAR were not available during the three cruises CR-66, CR-67 and CR-68. Long-term (1995–2015) observations (HOT (Hawaii Ocean Time-series) 2017) indicate that the EZD between September and November, 99 ± 6 m (number of observations $n = 44$), does not vary greatly with time. Since the PAR drops to 1% of the surface value at the EZD, Equation (2) can be re-written as:

$$1\%PAR_0 = (PAR)_0 \exp[-K (EZD)] \quad (4)$$

Thus, assuming a constant EZD, 99 ± 6 m, K (unit of m^{-1}) can be estimated as:

$$K = \frac{\ln(100)}{(EZD)} = 0.046 \pm 0.003 \quad (5)$$

Furthermore, Z_{pd} (unit of m) may be estimated as:

$$Z_{pd} = \frac{1}{K} = 22 \pm 2 \quad (6)$$

These K and Z_{pd} values were applied to Equation (1) to estimate the C_d in the three cruises.

2.4. Remotely sensed C

Daily Level 2 remotely sensed surface C acquired by the MERIS (Reprocessing R2012.1), SeaWiFS (Reprocessing R2014.0) and MODIS-Aqua (Reprocessing R2014.0) at the SEATS station during the cruises were downloaded from the National Aeronautics and Space Administration (NASA) OceanColor Web (2017). No remotely sensed surface C , however, were available at the ALOHA station during the cruises. The uncertainties of the remotely sensed surface C at these stations have been shown (Liu et al. 2013; White, Spitz, and Letelier 2007) to agree with *in situ* observed values to within the generally accepted level of $\pm 35\%$ (McClain 2009).

3. Results and discussion

3.1. Diel variations in the hydrographic characteristics

The diel variations in the vertical distribution of temperature and in the MLD, which is defined as the depth at which the temperature was 0.5°C lower than the surface value (Levitus 1982), in the cruises at the SEATS station and the ALOHA station are shown in Figure 2. The statistics in these variations are summarized in Table 1.

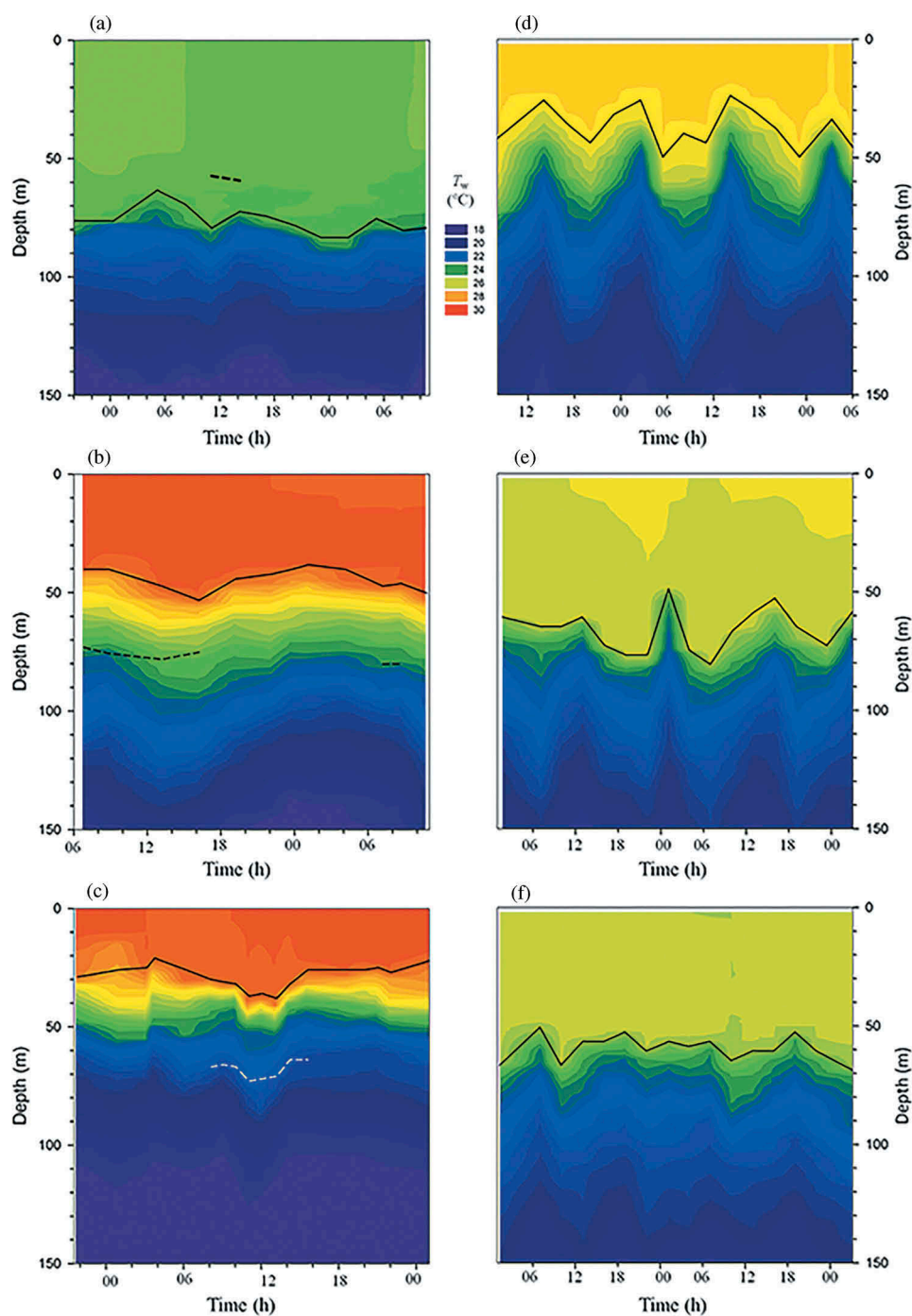


Figure 2. Variations in the water temperature (T_w) over a diel cycle at the SEATS station in the cruises of (a) OR1-0988 (23 to 25 December 2011), (b) OR1-1010 (31 August to 1 September 2012) and (c) OR1-0944 (13 to 15 October 2010), and at the ALOHA station in the cruises of (d) CR-66 (26 to 28 September 1995), (e) CR-67 (26 to 28 October 1995) and (f) CR-68 (16 to 18 November 1995). Local times, which are different from the Greenwich Mean Time by +8 hours at the SEATS station and –10 hours at the ALOHA station, were used. Solid line – MLD; dashed line – EZD.

Table 1. Statistics of the hydrographic properties in the cruises in a diel cycle. The number of observations is shown in bracket. The EZD and *K* values for the ALOHA cruises are estimated from the long-term averages.

Parameter	SEATS cruise				ALOHA cruise			
	OR1-0988	OR1-1010	OR1-0944	CR-66	CR-67	CR-68		
Sampling date	23 to 25 December 2011	31 August to 1 September 2012	13 to 15 October 2010	26 to 28 September 1995	26 to 28 October 1995	16 to 18 November 1995		
SST (°C)	24.7 ± 0.1 (9)	29.3 ± 0.1 (10)	29.2 ± 0.1 (16)	26.9 ± 0.1 (15)	26.1 ± 0.1 (17)	25.7 ± 0.1 (16)		
MLD (m)	77 ± 5 (9)	44 ± 5 (10)	29 ± 5 (16)	37 ± 9 (15)	66 ± 9 (17)	61 ± 5 (16)		
EZD (m)	58 ± 1 (2)	78 ± 3 (4)	68 ± 4 (8)	99 ± 6	99 ± 6	99 ± 6		
<i>K</i> (m ⁻¹)	0.068 ± 0.002 (2)	0.055 ± 0.001 (4)	0.064 ± 0.004 (8)	0.046 ± 0.003	0.046 ± 0.003	0.046 ± 0.003		
Diel <i>C_{surf}</i> (mg m ⁻³)	0.50 ± 0.10 (7)	0.13 ± 0.03 (7)	0.09 ± 0.02 (7)	0.07 ± 0.01 (8)	0.07 ± 0.01 (8)	0.10 ± 0.01 (6)		
Daytime <i>C_{surf}</i>	0.48 ± 0.16 (3)	0.14 ± 0.02 (3)	0.10 ± 0.03 (3)	0.07 ± 0.01 (4)	0.07 ± 0.01 (4)	0.11 ± 0.01 (4)		
Nighttime <i>C_{surf}</i>	0.51 ± 0.05 (4)	0.12 ± 0.02 (4)	0.08 ± 0.01 (4)	0.06 ± 0.01 (4)	0.07 ± 0.01 (4)	0.09 ± 0.01 (2)		
Diel <i>I_{chl}</i> (mg m ⁻²)	32.6 ± 10.0 (7)	24.1 ± 7.2 (7)	18.2 ± 5.7 (7)	18.6 ± 2.8 (8)	18.8 ± 2.9 (8)	20.0 ± 1.8 (6)		
Daytime <i>I_{chl}</i>	34.7 ± 12.1 (3)	29.2 ± 7.3 (3)	22.7 ± 4.2 (3)	18.9 ± 2.8 (4)	18.7 ± 4.2 (4)	20.7 ± 1.6 (4)		
Nighttime <i>I_{chl}</i>	31.1 ± 9.8 (4)	20.2 ± 4.6 (4)	14.9 ± 4.4 (4)	18.3 ± 3.2 (4)	19.0 ± 1.1 (4)	18.6 ± 1.1 (2)		

At the SEATS station, the diel average SST and MLD in the cruises (Figure 2(a) – (c)) were within the historical ranges found in the corresponding months (Tai, Wong, and Pan 2017). The diel average SST in OR1-0988, 24.8 °C, was lower than those, 29.2 °C and 29.1 °C, in OR1-1010 and OR1-0944, while the corresponding MLD, 76 m, was deeper than those, 45 m and 29 m, in OR1-1010 and OR1-0944 (Figure 2(a) – (c)). The diel variabilities in the SST, ± 0.1 °C to ± 0.2 °C, were small in all cases. On the other hand, while the diel variabilities in the MLD, ± 5 m to ± 6 m, fell within a relative narrow and well defined range, as a result of the seasonal variability in the MLD, they were equivalent to $\pm 7\%$ to $\pm 19\%$ of the diel average. The EZDs stayed around 58 m, 78 m and 68 m in OR1-0988, OR1-1010 and OR1-0944 respectively, and did not change significantly through a diel cycle. The EZD in OR1-0988 was shallower, when the depth-integrated standing stock of C , I_{Chl} , and thus possibly the particulate load, was higher (Table 1). The EZD was shallower than the corresponding MLD in OR1-0988 but was deeper in OR1-1010 and OR1-0944, suggesting that, except in the deepest portion of the mixed layer in OR1-0988, light was not a limiting factor in photosynthetic activities.

The diel average SST and MLD at the ALOHA station in the three cruises (Figure 2(d) – (f)) were also within the historical ranges found in the corresponding months (Church, Lomas, and Muller-Karger 2013). The diel average SST in CR-66, 26.9 °C, was slightly warmer than those, 26.1 °C and 25.7 °C, in CR-67 and CR-68, while the corresponding MLD, 37 m, was shallower than those, 66 m and 61 m, in CR-67 and CR-68 (Table 1). The diel variabilities in the SST, around ± 0.1 °C, were small. The diel variabilities in the MLD, ± 5 m to ± 9 m, accounted for about $\pm 9\%$ to $\pm 23\%$ of the diel average. Given that the EZD at the ALOHA station was deeper than about 90 m (HOT (Hawaii Ocean Time-series) 2017), the MLD, 37 m to 66 m (Table 1), was within the euphotic zone, consistent with previous reports (Church, Lomas, and Muller-Karger 2013; Karl and Church 2014). Thus, light was not a limiting factor in photosynthetic activities.

3.2. Diel variations in C observed *in situ*

The diel variations in the vertical distribution of C are shown in Figure 3. At the SEATS station, in OR1-0988, the highest C at any given time in the day was found mostly at or near the sea surface (Figure 3(a)). Taking the isopleth in the C of 0.40 mg m^{-3} as a guide, the layer of surface water with elevated C ($> 0.40 \text{ mg m}^{-3}$) was thinner, about 20 m thick, in the early morning and the thickest, at about 65 m thick, in the afternoon. A sub-surface maximum at around the bottom of the mixed layer, which is commonly found in many parts of the oceans (Mann and Lazier 1996), was absent. In fact, since the MLD was deeper than the EZD, the availability of light could have limited photosynthetic activity at the base of the mixed layer below the EZD and led to the abrupt decrease in the C with depth at these depths. In contrast, in OR1-1010 and OR1-0944 when the MLD was substantially shallower than the EZD, the sub-surface maximum in the C , with concentrations reaching about 0.50 mg m^{-3} , was clearly present at around 50 m to 60 m between the bottom of the mixed layer and the EZD (Figure 3(b) – (c)), consistent with reports in other oligotrophic environments (Mignot et al. 2014). In the surface waters, the C was generally low and fell within 0.05 mg m^{-3} to 0.20 mg m^{-3} .

At the ALOHA station, the vertical distributions of the C generally followed the pattern found in cruises OR1-0944 and OR1-1010 at the SEATS station (Figure 3). The diel variations in the vertical distribution of C were observed in all three cruises at the ALOHA station (Figure 3(d) – (f)). A sub-surface maximum in the C was present in all cases, and was found in both the daytime and the nighttime. Its concentration, around 0.20 mg m^{-3} , however, was only about

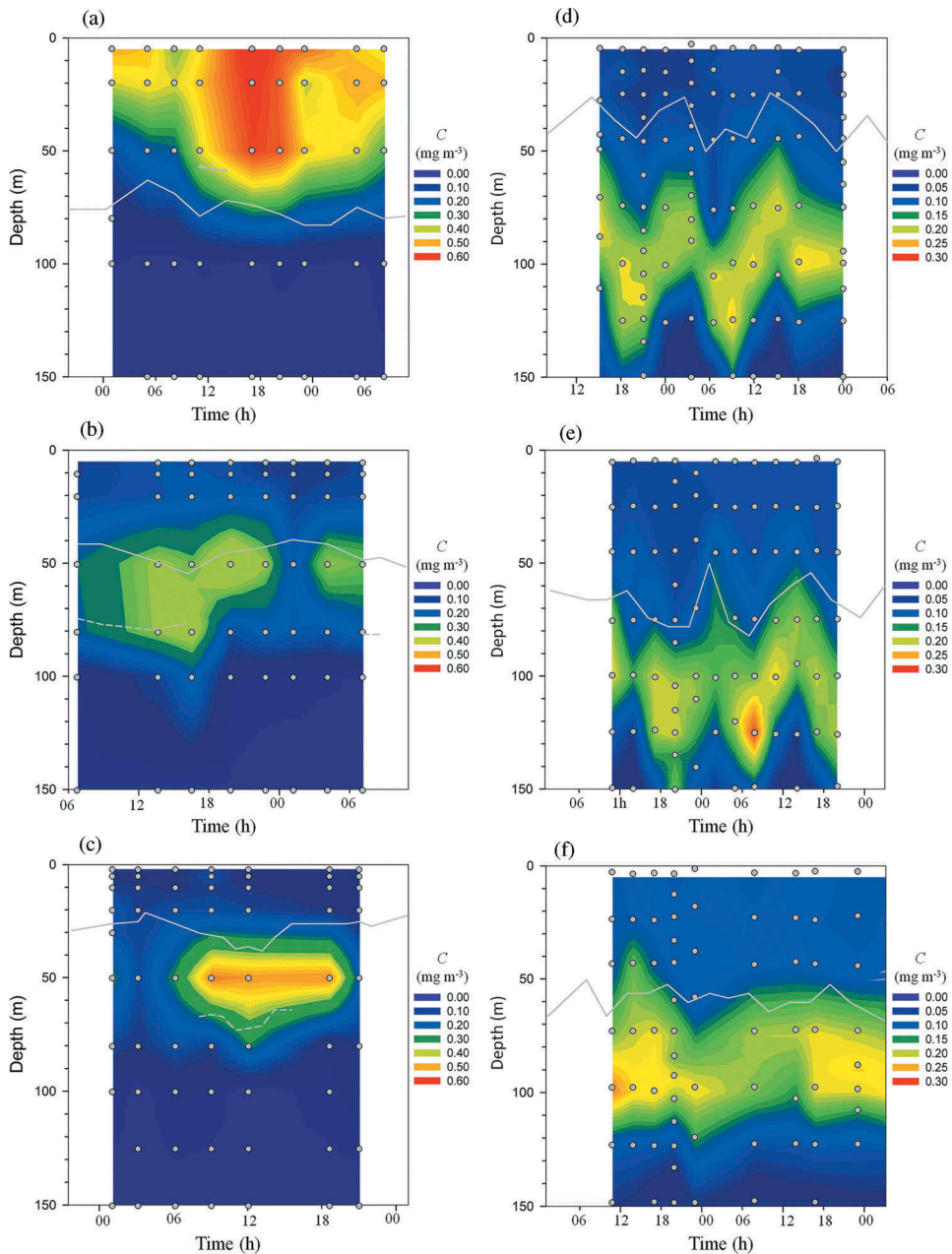


Figure 3. Same to Figure 2 but for C . ○ – Times and depths of the sample collections.

half of that, 0.40–0.50 mg m⁻³, at the SEATS station. Taking the isopleths in the C of 0.15 mg m⁻³ as a guide, the layer of the sub-surface water with elevated C (> 0.15 mg m⁻³), about 40 m thick in all cases, was located about 30 m below the MLD in

CR-66 but at the bottom of the mixed layer in CR-67 and CR-68. The surface C at the ALOHA station, 0.07 mg m⁻³ to 0.10 mg m⁻³, which was within the range found in the typical tropical waters (Yoder et al. 1993), was generally lower than that found at the

SEATS station. These diel patterns did not seem to be controlled by light availability alone. Light availability should cause the growth of phytoplankton (e.g. enlarged cell size), and thus the elevated C , by photosynthesis in the daytime (Kirk 1994; Prézelin 1992; Woods and Onken 1982). Such a light-dark cycle should be more pronounced in the lower layer of the euphotic zone where processes to counteract the effect of photosynthesis, such as photoinhibition and downward migration of phytoplankton in the daytime at the surface (Kirk 1994; Prézelin 1992; Woods and Onken 1982), would be minimal. However, it was not always followed. It is possible that other processes, such as tidal effect (Chen et al. 2010) and episodic horizontal advective events, might have contributed to the observed pattern. Thus, at the ALOHA station, the diel variations in the vertical distribution of C (Figure 3(d) – (f)) followed a semi-diurnal cycle in the lower layer of the euphotic zone and active semi-diurnal M2 internal tides have been found at this location (Zilberman et al. 2011). Nevertheless, given the limited data set presented here and the scope of this study, it would not be prudent to speculate further on how these processes might have interacted to produce the observed pattern.

The diel variations in the surface (top 10 m) C and the I_{chl} are shown in Figure 4. The statistics in these variations are summarized in Table 1. At the SEATS station, the diel average surface C , $0.50 \pm 0.11 \text{ mg m}^{-3}$, $0.13 \pm 0.02 \text{ mg m}^{-3}$ and $0.09 \pm 0.02 \text{ mg m}^{-3}$ in OR1-0988, OR1-1010 and OR1-0944 respectively (Figure 4(a) – (c)), were within the reported historical ranges in the corresponding months (Liu et al. 2002, 2013; Pan et al. 2015; Tseng et al. 2005). The concentration in OR1-0988 was about 4.0 to 5.0 times of those in the other two cruises. The variations in the I_{chl} among the cruises followed a similar trend: I_{chl} in OR1-0988 was about 1.5 to 2.0 times of those in the other two cruises. The elevation of the surface C and the I_{chl} in the winter, when OR1-0988 was conducted, in the open northern South China Sea have been reported previously and they were attributed to the increased input of nutrients to the mixed layer from the nutrient-rich sub-surface waters by enhanced vertical mixing by surface cooling and the stronger northeast monsoonal wind (Pan et al. 2015; Tseng et al. 2005; Wong et al. 2007, 2015). On the diel time scale, variations in the surface C and the I_{chl} followed qualitatively a general similar pattern in all three cruises with the highest values found in the daytime and generally lower values found in the nighttime. The difference between the average daytime and nighttime values was least distinct in OR1-0988. In the records that extended beyond 24 hours, the pattern started to repeat itself at least qualitatively, indicating that the diel patterns were unlikely to be fortuitous. Both the surface C and I_{chl} varied by about a factor of two over the diel cycle. The resulting variabilities over the diel average were about $\pm 20\%$ in the surface C and $\pm 30\%$ in I_{chl} . In a finer scale, the diel variations in the I_{chl} followed a more consistent pattern than the surface C among the three cruises. I_{chl} increased steadily in the daytime from the morning to a maximum in the afternoon before it dropped progressively into the night. This pattern may be explained by a net gain in phytoplankton biomass by photosynthetic activity during the daytime and a net loss by grazing, death and/or sinking during the nighttime (Kirk 1994; Platt, Gallegos, and Harrison 1980). In the case of surface C , while the pattern followed that of the I_{chl} closely in OR1-0988 and OR1-1010, the diel maximum in the surface C was found earlier in the day in OR1-0944. As a result, in OR1-0988 and OR1-1010, the surface C was well correlated (correlation coefficient $r = 0.805$ and 0.896 , both

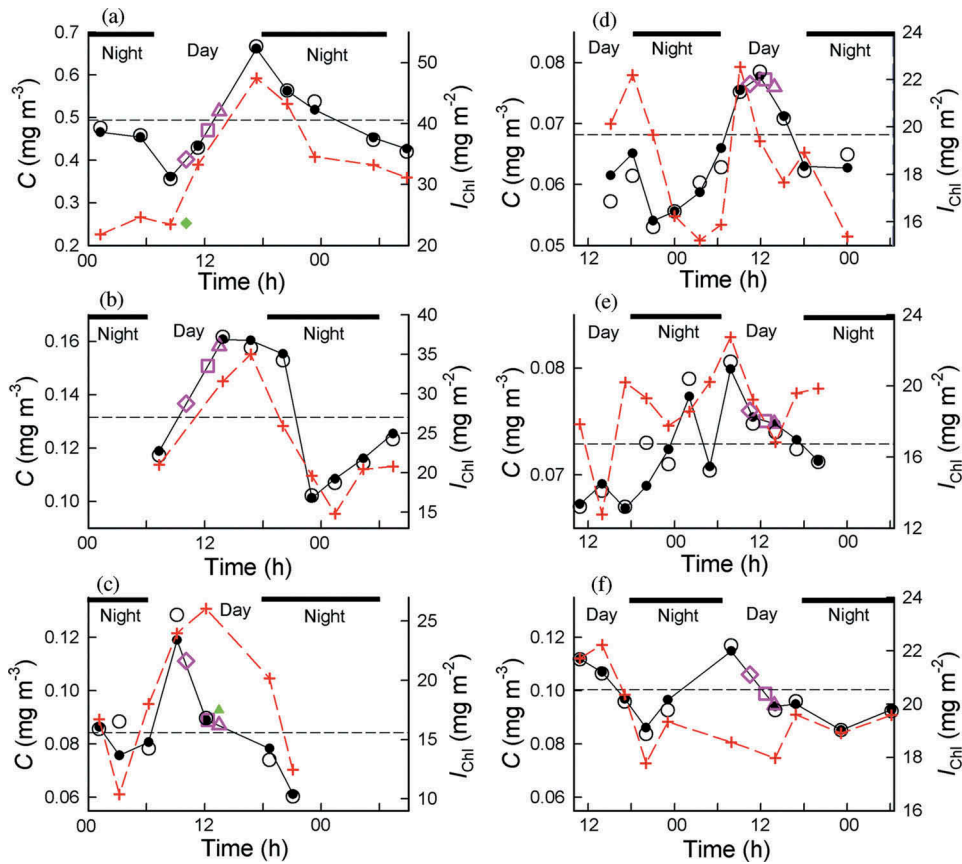


Figure 4. Diel variations in the concentrations of surface C (\circ), C_d (\bullet) and I_{Chl} (+) at the SEATS station during cruises of (a) OR1-0988, (b) OR1-1010 and (c) OR1-0944, and at the ALOHA station during cruises of (d) CR-66, (e) CR-67 and (f) CR-68. \diamond , \square , Δ – C_d at the overpass-times of MERIS, SeaWiFS and MODIS-Aqua; \blacklozenge , \blacktriangle – C sensed by MERIS and MODIS-Aqua satellites at the SEATS station on 24 December 2011 and 14 October 2010, respectively. Black bar – nighttime period; horizontal dashed line – diel average C_d .

$P < 0.001$; Figure 4(a) – (b)) with the I_{Chl} over the diel cycle so that it could be a reasonable proxy of the I_{Chl} . On the other hand, in OR1-0944, the correlation between the two was poor ($P = 0.217$). The presence of a sub-surface C maximum in some but not all the months in the year, the variability in the tidal effect and episodic horizontal advective events over the year could all have contributed to a more variable relationship between the surface C and the I_{Chl} . Regardless of the exact cause, the variable relationship between the two can be a source of inherent uncertainty when I_{Chl} is estimated by an extrapolation from surface C .

At the ALOHA station, the diel average surface C , $0.07 \pm 0.01 \text{ mg m}^{-3}$, $0.07 \pm 0.01 \text{ mg m}^{-3}$ and $0.10 \pm 0.01 \text{ mg m}^{-3}$ in CR-66, CR-67 and CR-68 respectively (Figure 4(d) – (f), Table 1), were also within the reported historical ranges in the corresponding months (Letelier et al. 1993). The increase in surface C from the summer (CR-66) to the late fall (CR-68) might result primarily from the photo-adaptation (Letelier et al. 1993; Winn et al. 1995) in response to the deepened

mixed layer and decreased incident solar light. Any increase in phytoplankton biomass was not happened as the surface concentration of particulate organic carbon, which might be an indicator of phytoplankton biomass, in CR-68, $1.9 \mu\text{mol kg}^{-1}$, was not substantially different from or even lower than those in CR-66 and CR-67, $1.8 \mu\text{mol kg}^{-1}$ and $2.4 \mu\text{mol kg}^{-1}$ respectively (HOT (Hawaii Ocean Time-series) 2017). The variations in the I_{chl} among the cruises, $18.6 \pm 2.8 \text{ mg m}^{-2}$, $18.8 \pm 2.9 \text{ mg m}^{-2}$ and $20.0 \pm 1.8 \text{ mg m}^{-2}$ in CR-66, CR-67 and CR-68 respectively (Table 1), followed a similar trend. On the diel time scale, variations in the surface C in all three cases at the ALOHA station (Figure 4(d) – (f)) followed the general pattern as in the cruise OR1-0944 at the SEATS station (Figure 4(c)). A diel maximum in the surface C was found in the early-to-late morning, and a diel minimum was found at around sunset. The surface C and I_{chl} varied by a factor of about 1.3 over the diel cycle. The resulting variabilities over the diel average were about $\pm 9\%$ in both cases. These variabilities were about half of those found at the SEATS station. The diel variations in the I_{chl} were poorly correlated ($P = 0.338, 0.176$ and 0.126 in CR-66, CR-67 and CR-68) to the diel variations in the surface C (Figure 4(d) – (f)) as in the cruise OR1-0944 at the SEATS station. Such poor correlations have been explained by the differential interactive effects and processes, such as the diel cycle of photosynthesis (Kirk 1994; Platt, Gallegos, and Harrison 1980), tidal effects (Zilberman et al. 2011), and photo-adaption (Winn et al. 1995), on surface C and I_{chl} .

3.3. Effects of diel variations in the surface c on the interpretation of remotely sensed surface C

The depth-weighted C as derived from Equation (1), C_d , is also shown in Figure 4. The derived C_d was strongly correlated to the corresponding *in situ* observed surface C , C_{surf} , in all cruises at both stations such that (coefficient of determination $R^2 = 0.998$, $n = 57$):

$$C_d = (-0.0003 \pm 0.0011) + (0.993 \pm 0.005)C_{\text{surf}} \quad (7)$$

The slope of the relationship was indistinguishable from unity and the intercept included zero within their statistical uncertainties. Thus, in these six cruises, the derived C_d , although it represented the C within one optical depth (Morel and Berthon 1989), was virtually the same as the surface C .

The satellites passed over the SEATS and ALOHA stations daily in the daytime at the local times of 10:05 (± 13 minutes) and 10:29 (± 15 minutes) for MERIS, 12:18 (± 20 minutes) and 12:36 (± 20 minutes) for SeaWiFS, and 13:28 (± 21 minutes) and 13:52 (± 27 minutes) for MODIS-Aqua. The derived C_d at these overpass-times, based on a linear interpolation from the individual derived values during the cruises, are also marked in Figure 4. In two occasions at the SEATS station, the remotely sensed surface C detected by one of these three satellite sensors were also available. On 24 December 2011, the MERIS satellite sensed a surface C of 0.25 mg m^{-3} while the corresponding derived C_d was 0.40 mg m^{-3} . On 14 October 2010, the MODIS-Aqua satellite gave a remotely sensed surface C of 0.09 mg m^{-3} and the corresponding C_d was also about 0.09 mg m^{-3} . The differences between the remotely sensed surface C and C_d were -37% and virtually none, respectively. The agreement between the two was not unreasonable, given that the commonly claimed uncertainty in the remotely sensed C alone was $\pm 35\%$ (McClain 2009). While this match up comparison, in itself, was too limited to be a definitive validation, they do indicate that the derived C_d at the overpass-times of the MERIS, SeaWiFS and MODIS-Aqua satellites may be a good representative of remotely sensed surface

C that should be detected by satellites. In fact, the derived C_d has been used for evaluating the accuracy of the satellite remotely sensed surface C (Cannizzaro et al. 2013). The C_d are listed in Table 2. If these interpolated C_d at the overpass-times were to be interpreted as the diel average surface C , the diel variations in C_d may affect this interpretation in three ways:

First, C_d , and thus by inference the remotely sensed surface C , was not the same as the diel average C that the latter was used to represent (Table 2). For the MERIS, SeaWiFS and MODIS-Aqua satellites, the ratios of the C_d at their overpass-times to the diel average C varied between 0.81–1.32 at the SEATS station and 0.94–1.13 at the ALOHA station. Thus, there could have been an underestimation of up to –19% and –6% to an overestimation of up to +32% and +13% at the SEATS station and the ALOHA station, respectively. The magnitude of this source of uncertainty, was comparable to the commonly claimed uncertainty in remotely sensed surface C , $\pm 35\%$ (McClain 2009). While it was not large enough as to be overwhelming, it was clearly not small enough to be dismissed off-hand. Considering that the overpass-time of the different satellites may occur at any times during the day, the maximum deviation of C_d , which is the potential satellite remotely sensed surface C , from the diel average may range between an underestimation of up to –27% and –19% to an overestimation of up to +41% and +14% at the SEATS station and the ALOHA station, respectively (Figure 4).

Secondly, C_d , and thus remotely sensed surface C found, may be satellite-dependent. At the SEATS station, for the MODIS-Aqua and SeaWiFS satellites, the C_d at their overpass-times were more consistent with each other and with the diel average C_d (Table 2). The ratios of the C_d at the overpass-times of these two satellites ranged between 0.91–1.02 (average 0.96 ± 0.05). The ranges in the ratio of these C_d to the diel average C_d were 1.03–1.20 (average 1.09 ± 0.09) and 0.95–1.15 (average 1.05 ± 0.10). Thus, the C_d corresponding to the overpass-times of these two satellites agreed to about $\pm 10\%$. On the other hand, the ratio of the C_d at the MERIS overpass-time to the diel average C_d yielded a significantly larger range, 0.81–1.32. The ratios of the C_d at the MERIS overpass-time to the C_d at the overpass-times of MODIS-Aqua and SeaWiFS ranged between 0.78–1.28 and 0.85–1.25, respectively. In other words, the C_d corresponding to the MERIS overpass-time agreed with the C_d corresponding to the overpass-times of the other two satellites only to about –22% to +28%. At the ALOHA station, similar results were found but the uncertainties, about half of those found at the SEATS station (Table 2), were less prominent. The magnitude of this source of uncertainty, especially at the SEATS, was again similar to that of the commonly claimed uncertainty in remotely sensed C . It should be taken into consideration when data obtained by multiple satellites were pooled together for use in a study (Maritorena and Siegel 2005; Morel et al. 2007).

Thirdly, even for a single satellite, the slight variability in the overpass-time from day to day may introduce uncertainties in the remotely sensed surface C detected. For the MERIS, SeaWiFS and MODIS-Aqua satellites, the overpass times varied between 13 minutes to 21 minutes at the SEATS station and between 15 minutes to 27 minutes at the ALOHA station. Although these time-windows were relatively narrow, since the overpass-times may fall in the time period when the C_d changes more abruptly with the time of day (Figure 4), the remotely sensed surface C could still vary by up to $\pm 7\%$ within these time windows.

While this study has demonstrated qualitatively that the diel variations in the surface C may lead to a significant additional source of uncertainty in the interpretation of the

Table 2. Statistics in the diel variations in C_d and the C_d sensed by the MERIS, SeaWiFS and MODIS-Aqua satellites. C sensed synchronously by the MERIS and MODIS-Aqua satellites are given in brackets.

Parameter	SEATS cruise			ALOHA cruise		
	OR1-0988	OR1-1010	OR1-0944	CR-66	CR-67	CR-68
Diel variation in C_d	Minimum	0.10	0.06	0.05	0.07	0.09
	Maximum	0.16	0.12	0.08	0.08	0.12
	Maximum/Minimum	1.59	1.94	1.41	1.19	1.33
C_d at overpass times	Diel average	0.49 ± 0.10	0.08 ± 0.02	0.07 ± 0.01	0.07 ± 0.01	0.10 ± 0.01
	MERIS	$0.40 (0.25)$	0.14	0.08	0.08	0.11
	SeaWiFS	0.47	0.15	0.08	0.08	0.10
	Aqua	0.51	0.16	0.08	0.08	0.10
C_d at overpass time/diel average	MERIS	0.81	1.04	1.12	1.04	1.06
	SeaWiFS	0.95	1.15	1.13	1.03	0.98
	Aqua	1.04	1.20	1.11	1.03	0.94
Ratio of C_d between satellites	MERIS/Aqua	0.78	0.86	1.01	1.02	1.12
	SeaWiFS/Aqua	0.91	0.95	1.02	1.00	1.05
	MERIS/SeaWiFS	0.85	0.91	0.99	1.01	1.07

remotely sensed surface C , it was based on a limited data set in areas where diel variations may be large (Claustre et al. 1999; Kirk 1994; Neveux et al. 2003). Extrapolating the conclusions quantitatively to other parts of the oceans may not yet be warranted. However, since diel variations in the surface C is a global phenomenon, it suggests that further studies for assessing the global implication of this phenomenon on interpreting remotely sensed surface C is needed. Nevertheless, it should be noted that this source of uncertainty in the estimation of the diel average C from once-daily remotely sensed C is independent of the uncertainties in the remotely sensed C itself. Thus, it cannot be reduced by improvements in the estimation in the remotely sensed C , such as additional regional tuning. The uncertainty can be reduced only through an increase in the frequency of the observations in each day. This would argue for more observations using geostationary satellites, such as the Geostationary Ocean Color Imager (GOCI) and the future Geostationary Coastal and Air Pollution Events (GEO-CAPE), rather than sun-synchronous satellites, as the former can provide hourly data while the latter can only produce once-daily data (Choi et al. 2012; Feng et al., 2017; Ruddick et al. 2014). Furthermore, although these hourly observations from the geostationary satellites cannot eliminate the problem of not being able to obtain valid C_{rs} as a result of cloud cover, they would certainly increase the chances of getting one (Feng and Hu 2016; Feng et al. 2017).

4. Conclusions

Diel variations in the surface C and the I_{chl} in the tropical northern South China Sea at the SEATS station and in the North Pacific subtropical gyre at the ALOHA station were found to follow well defined patterns. The values varied by a factor of around 2.0 at the SEATS station and around 1.3 at the ALOHA station over a diel period. These diel variations may affect the interpretation and use of the remotely sensed C in three ways. First, the once-daily remotely sensed C is not identical to the diel average. The C that were sensed by the MERIS, SeaWiFS and MODIS-Aqua satellite could differ from the diel average by -19 to $+32\%$ at the SEATS station and by -6% to $+13\%$ at the ALOHA station. This is a source of uncertainty when the remotely sensed C are treated as the diel average. Secondly, since the remotely sensed C depends on the exact overpass-time of the satellites and these overpass-times may vary from satellite to satellite, the remotely sensed C is satellite-dependent. The C sensed by the MERIS, SeaWiFS and MODIS-Aqua satellites differed from each other by -22% to $+28\%$ at the SEATS station and by -1% to $+12\%$ at the ALOHA station. This is an inherent source of uncertainty when data from different satellites are pooled together for use. Thirdly, even for a single satellite, the exact overpass time may vary from day to day, albeit within a narrow time-window. At both stations, this variability in the overpass time could lead to uncertainties in remotely sensed C of $\pm 7\%$.

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