Time-series observations of photosynthetic oxygen production in the subtropical western North Pacific by an underwater profiling buoy system

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Abstract

We conducted time-series observations in the northwestern part of the North Pacific subtropical gyre (30°N, 145°E) from July 2012 to March 2013 using a profiling buoy system equipped with a fast repetition rate fluorometer and dissolved oxygen (DO) sensor in order to understand vertical and temporal variations in gross oxygen production (GOP) by phytoplankton and its contribution to the oxygen cycle in the upper ocean. Under stratified conditions (July–November), daily GOP slightly exceeded 2 mmol O2 m⁻³ d⁻¹ and only in near-surface waters. However, during periods of vertical mixing (December–March) when phytoplankton blooms occurred, daily GOP increased in the upper 30 m and often exceeded 5 mmol O₂ m⁻³ d⁻¹. The depth-integrated daily GOP within the euphotic layer ( GOP_EL ) was relatively low (84.0 ± 23.6 mmol O₂ m⁻² d⁻¹) during stratification, but increased gradually with vertical mixing and reached 460 mmol O₂ m⁻² d⁻¹ on 17 March 2013. Additionally, during stratified conditions, a subsurface oxygen maximum (SOM) formed below the mixed-layer depth (MLD) because the steep density gradient constrained upward diffusion of oxygen produced below the MLD. During the period of vertical mixing, the SOM disappeared, and DO concentrations within the upper 100 m increased through both increasing GOP_EL and atmospheric oxygen uptake. Using our buoy observations and air–sea gas flux model, we estimated that 24% ± 7% of GOP_EL was emitted to the atmosphere during the stratification period, and GOP_EL during the mixing period was about 2.4 times the rate of oxygen uptake by the ocean from the atmosphere.

Phytoplankton photosynthesis is the first step in the biogeochemical cycle in the ocean and affects the global climate through air–sea gas exchange (Falkowski and Raven 2007). Understanding temporal and spatial patterns in the primary productivity (the ecological term for photosynthesis) of phytoplankton and its response to environmental variability is thus one of the prime goals in modern ocean biogeochemistry. From the perspective of the carbon cycle and the marine food web, primary productivity in the world’s oceans has been measured mostly by the radiocarbon (¹⁴C) tracer method (Steemann-Nielsen 1952; Longhurst et al. 1995), which uses ¹⁴C uptake into particulate matter in bottles incubated for periods ranging from several hours to 1 d. On the basis of primary productivity data measured with the ¹⁴C tracer method in various ocean regions, Field et al. (1998) estimated that marine phytoplankton account for almost half of the total worldwide carbon fixation each year.

From another perspective, the oxygen produced by phytoplankton photosynthesis plays an important role in biological metabolism and chemical oxidation reactions in the ocean (Sumich 1999; Sarmiento and Gruber 2006), and also contributes to the composition of the present-day atmosphere (Berner 2001). Oxygen production by phytoplankton has been measured traditionally by the light and dark bottle (Gaarder and Gran 1927) and H₂¹⁸O spike (Bender et al. 1987) incubation methods. These methods rely on the change in oxygen concentrations or the evolution of O₂ from H₂¹⁸O during water splitting in incubation bottles containing the phytoplankton. However, despite its recognized importance, information on
spatial and temporal variability in oxygen production by phytoplankton is extremely limited in the open oceans compared with widely measured carbon fixation. It is therefore difficult to quantitatively assess phytoplankton oxygen production in the oceans and its contribution to the biogeochemical cycles.

Early in the process of photosynthesis, oxygen is formed with the release of an electron and proton from the splitting of water using light energy absorbed by plant pigments (Whittmarsh and Govindjee 1995). The oxygen production is closely related to electron and proton transfer reactions in photosystem II (PSII) (Kramer et al. 2004). The electron transfer rate can be measured optically with active fluorescence techniques based on the theory of Kautsky curves (Kautsky and Hirsh 1931). One such active fluorescence technique—fast repetition rate (FRR) fluorometry—reduces the primary electron acceptor in PSII by using a series of subsaturating flashlets of blue light and measures a single turnover fluorescence induction curve in PSII (Kolber et al. 1998). The PSII parameters derived from the fluorescence induction curve provide the rate of electron transport in PSII and can be used to estimate the oxygen production rate. The utility of FRR fluorometry in estimating oxygen production has been documented by several studies (Suggett et al. 2001, 2003; Sarma et al. 2006). It is noteworthy that measurements made by FRR fluorometry can be carried out without the need for time-consuming bottle incubations, and this method enables estimates of oxygen production at high spatial and temporal resolution by incorporating an FRR fluorometer in autonomous observation platforms (e.g., moorings, drifters, and floats). In a previous study (Fujiki et al. 2008), we developed an underwater profiling buoy system equipped with an FRR fluorometer and succeeded in observing vertical and temporal variations in oxygen production by phytoplankton in Sagami Bay, Japan, over about a month. Such high-frequency observations can provide a clear understanding of the controlling factors for oxygen production (abiotic and biotic) and their linkage to biogeochemical cycles.

The North Pacific subtropical gyre (NPSG) is the largest circulation feature of the global ocean and has generally been considered to have invariably low biological productivity throughout the year because persistent stratification of the upper water layers restricts the supply of nutrients from deep waters (McGowan and Hayward 1978). However, despite such oligotrophic conditions, the Hawaii Ocean Time-series (HOT) program showed that the phytoplankton productivity in the eastern part of the NPSG is temporally and spatially variable because of aperiodic mixing events, atmospheric dust deposition, and nitrogen fixation (reviewed by Karl 1999; Dore et al. 2008). In addition, using satellite chlorophyll a (Chl a) images from SeaWiFS, Wilson (2003) found occasional phytoplankton blooms in the NPSG near 30°N and between 130°W and 160°W in the late summer of 1997, 1999, and 2000.

Although long-term time-series observations by research vessel and moored systems such as in the HOT program have not been carried out in the western part of the NPSG, a time series of satellite Chl a images from 1997 to 2013 revealed the occurrence of blooms during winter/early spring every year in the northwestern part of the NPSG (Siswanto et al. 2015). Throughout this region, which is affected by the East Asian winter monsoon, vertical mixing of the upper water column is enhanced in winter by the increase of heat exchange between the atmosphere and the ocean (Oka and Qiu 2012), probably resulting in seasonal blooms. These studies suggest that phytoplankton oxygen production in the NPSG would vary substantially, and these changes could affect the biogeochemical cycle. However, it remains a challenge to accurately quantify oxygen production with spatial and temporal resolutions that can be related to the biogeochemical cycle.

In this study, we have attempted to address these questions by conducting time-series observations with our profiling buoy system in the northwestern NPSG. Our aim in the present article is to elucidate vertical and temporal variations in phytoplankton oxygen production in this region and the key factors controlling its variations. Additionally, as the first step to quantitatively assess the role of phytoplankton in the oceanic oxygen cycle, we examine the relationship between oxygen production by phytoplankton and the dissolved oxygen (DO) in the upper water-column.

**Methods**

**Profiling buoy system**

The following is a brief description of the profiling buoy system (for details, see Fujiki et al. 2008). The profiling buoy system consisted mainly of an underwater winch and an observation buoy (POPPS vertical profiler, Nichiyu Giken Kogyo, Kawagoe, Japan). The observation buoy was equipped with a conductivity/temperature/depth (CTD) sensor (MCTD; Falmouth Scientific, Cataumet, MA, U.S.A.), a scalar irradiance sensor (QSP-2200; Biospherical Instruments, San Diego, CA, U.S.A.), a DO sensor (Optode 3830; Aanderaa Data Instrument AS, Bergen, Norway), and an FRR fluorometer (Diving Flash-03; Kimoto Electric, Osaka, Japan). Before mooring, the DO sensor was calibrated with Winkler titration measurements (Supporting Information Fig. S1). The observation buoy moved from the winch depth to the surface at a profiling rate of 0.2 m s⁻¹ and measured vertical profiles of temperature, salinity, irradiance, DO concentration, and phytoplankton fluorescence, in the upper 130 m. The profile data were averaged at intervals of approximately 1 m in an embedded central processing unit of the observation buoy because of data compression. After taking measurements, the observation buoy returned from the surface to the winch depth. To minimize biofouling of instruments, the underwater winch was placed below the euphotic zone so that the observation buoy was exposed to light only during measurement periods. The vertical movement of the observation buoy also reduced biofouling.

**Buoy observations**

For this study, the profiling buoy system was deployed at time-series Sta. S1 (30°N, 145°E; water depth approximately...
calculate the mixed-layer depth (MLD), which we equated to 1.0 m.

had little effect on data collected during the observation zone. After recovery of the profiling buoy system were successfully made at 03:00 h local time (nighttime) and 12:00 h local time (daytime) every 6 d from 08 July 2012 to 17 March 2013 except on 17 December 2012. On this day, strong currents pulled the observation buoy below 350 m, so there were no data collected within the euphotic zone. After recovery of the profiling buoy system on 14 July 2013, there was no visible biofouling of sensors on the observation buoy, and the FRR fluorometer blank values for 0.2-μm-filtered seawater were not significantly different from those before deployment (data not shown), indicating that biofouling had little effect on data collected during the observation period.

We used continuous vertical profiles of seawater density to calculate the mixed-layer depth (MLD), which we equated to the depth at which the density was 0.125 kg m⁻³ greater than the density at the surface (de Boyer et al. 2004). The euphotic layer depth (ELD) was defined as the depth where the irradiance was diminished to 1% of the surface value (Ryther 1956). In addition, we estimated the saturation concentration of DO for each depth from the observed temperature and salinity (Weiss 1981; Garcia and Gordon 1992). We calculated the DO percent saturation by dividing the observed DO concentration by the DO saturation concentration. During six cruises of R/V Mirai from 2010 to 2012 (MR10-01, 20 January 2010–24 February 2010; MR10-06, 18 October 2010–16 November 2010; MR11-02, 11 February 2011–09 March 2011; MR11-03, 14 April 2011–05 May 2011; MR11-05, 27 June 2011–04 August 2011; and MR12-02, 04 June 2012–12 July 2012), we performed onboard nutrient measurements on discrete seawater samples collected with Niskin-X bottles (General Oceanics, Miami, FL, U.S.A.) attached to a CTD sensor carousel system (SBE 911plus; Sea-Bird Electronics, Bellevue, WA, U.S.A.). For this study, we estimated the depth of the top of the nitracline from the relationship between nitrate and nitrite (NO₃ + NO₂⁻) concentrations and seawater density within the upper 150 m obtained from these ship-based studies (see “Results” section).

Use of an air–sea gas exchange model that included diffusive gas exchange and bubble-mediated exchange (Liang et al. 2013) allowed us to estimate air–sea O₂ fluxes from 6-hourly meteorological data (wind speed and atmospheric pressure) from the National Center for Environmental Prediction (NCEP) reanalysis data in combination with oxygen, temperature, and salinity measurements from the buoy observations. We also calculated the vertical diffusive O₂ flux (F_KZ) at a depth of 100 m using the following equation:

\[ F_{KZ} = -K_Z \cdot \frac{\partial O_2}{\partial z}, \]

where K_Z is the vertical diffusivity coefficient, which was assumed to be 10⁻⁵ m² s⁻¹ at 100 m (Bushinsky and Emerson 2015), and \( \partial O_2/\partial z \) is the vertical gradient of DO in the water column.

FRR fluorometry

Parameters for PSII were examined with an FRR fluorometer attached to the observation buoy (for details of the FRR fluorometer and its measurement protocol, see Fujiki et al. 2008). The FRR fluorometer consisted of closed “dark” and open “light” chambers that measured the fluorescence induction curves of phytoplankton in darkness and under ambient irradiance. In daytime observations, the dark chamber allowed phytoplankton samples to dark-adapt for about 1 s before measurements to relax photochemical quenching of fluorescence (Smyth et al. 2004). To generate single-turnover fluorescence induction curves, the instrument emitted a series of blue-light excitation flashes of 30 mmol photons m⁻² s⁻¹ at a repetition rate of about 250 kHz. The PSII parameters were derived from the fluorescence induction curve by using the numerical fitting procedure described by Kolber et al. (1998). These parameters included the initial fluorescence (\( F_i \)), maximum fluorescence (\( F_{m} \)), and effective absorption cross-section of PSII (\( \sigma_{PSII} \)) under ambient light, as well as minimum fluorescence (\( F_o \)) and maximum fluorescence (\( F_m \)) in darkness.

The Chl a-specific electron transport rate (ETR_Chl [-mol e⁻ mol Chl a⁻¹ s⁻¹]) was determined by substituting the PSII parameters measured in daytime into the following equation based on Suggett et al. (2011):
where $E$ is the ambient irradiance (μmol photons m$^{-2}$ s$^{-1}$), $F_{v}'/F_{m}'$ is the PSII efficiency factor under ambient light [$=(F_{m}' - F_{v}')/(F_{m}' - F_{0}')$], $\Phi_{RC}$ is the quantum yield of electron transfer within a reaction center (RC) (mol e$^{-}$ [mol photon]$^{-1}$), and $n_{PSII}$ is the ratio of PSII reaction centers to Chl $a$ (mol e$^{-}$ [mol Chl $a$]$^{-1}$). The minimum fluorescence yield under ambient light ($F_{0}'$) was estimated from $F_{0}' = F_{0}/[[F_{0}' - F_{0}]/F_{0}' + (F_{0}'/F_{m}')]$ (Oxborough and Baker 1997). The value of $\Phi_{RC}$ is taken to be unity because one electron is transferred from the primary donor P680 to the primary electron acceptor QA within a reaction center (RC) (mol e$^{-}$/C$_{0}$/C$_{1}$). The minimum fluorescence yield relative to the surface value (between 0 and 1) determined by the daytime observations. The daily integrated ETR$_{PSII}$ at any depth [$\text{daily}_{-}\text{ETR}_{PSII}(z)$, mmol e$^{-}$ m$^{-3}$ d$^{-1}$] was calculated using the following equation:

$$\text{daily}_{-}\text{ETR}_{PSII}(z) = \int_{t_1}^{t_2} \text{ETR}_{PSII}^{Chl a}(z,t)dt \times \text{Chl } a(z),$$

where Chl $a$ (z) is the Chl $a$ concentration (mg m$^{-3}$) at depth $z$.

The $F_{m}$ measured with the FRR fluorometer can be used to estimate Chl $a$ concentration from in vivo fluorescence (Estévez-Blanco et al. 2006; Melrose et al. 2006). The relationship between in vivo fluorescence and Chl $a$ concentration is inherently variable because the relationship depends on species, growth phase, nature of nutrient limitation, and photoacclimation (Roesler et al. 2017). For example, during the daytime, it is known that a drastic decline of in vivo fluorescence due to nonphotochemical quenching, which is one of the photo-protective mechanisms against excess light energy, would cause an underestimation of Chl $a$ concentrations (Falkowski and Raven 2007). For this study, Chl $a$ (z) was estimated using the $F_{m}$ value from the nighttime observations to remove the effect of nonphotochemical quenching. The factor for converting $F_{m}$ to Chl $a$ concentration was determined by using discrete samples obtained from 0 to 100 m at Sta. S1 before and after deployment of the profiling buoy system (Supporting Information Fig. S4). The factor was assumed to be constant during the buoy observations.

### Relationship between ETR and gross oxygen production

To estimate gross oxygen production (GOP) from measurements of daily ETR$_{PSII}$ by the profiling buoy system, we used data from measurements of GOP using the H$_2$O$^{18}$O spike incubation method (Bender et al. 1987; Matsumoto et al. 2016) in conjunction with ETR measurements by FRR fluorometry at Sta. S1 from four cruises of R/V Mirai in the western North Pacific: MR11-02 (11 February 2011–09 March 2011), MR11-03 (14 April 2011–05 May 2011), MR11-05 (27 June 2011–04 August 2011), and MR12-02 (04 June 2012–12 July 2012). On each cruise, before dawn, water samples for H$_2$O$^{18}$O spike incubations were collected from seven depths corresponding to light levels of approximately 50%, 25%, 10%, 5%, 2.5%, 1%, and 0.5% of surface irradiance using 12-liter Niskin-X bottles (General Oceanics) attached to a CTD carousel system (SBE 911 plus; Sea-Bird Electronics). Light-depths were determined by using the scalar irradiance sensor during daylight on the day before seawater sampling. The seawater samples from each light-depth were immediately transferred into duplicate transparent glass bottles (100 mL), spiked with 125 μL of 95 atom %-enriched $^{18}$O-labeled water (Cambridge Isotope Laboratories, Tewksbury, MA, U.S.A.), and then incubated for 24 h from dawn to the next dawn using an on-deck incubation system that simulated light conditions at
the sampling depths. After incubation, approximately 50-mL subsamples were drawn into 300-mL pre-evacuated gas extraction flasks containing 250 μL of saturated HgCl₂ solution that terminated the biological activity. In an onshore laboratory, the flasks were gently shaken for 24 h at room temperature to equilibrate dissolved gases between the seawater and headspace in the flasks. After equilibration, oxygen was separated from the mixed gases in the flask by chromatography (Sarma et al. 2003), and then the isotopic composition of the oxygen was determined with a dual-inlet, isotope ratio mass spectrometer (Delta Plus, Thermo Fisher Scientific, Waltham, MA, U.S.A.). Daily GOP was computed from the initial and final isotopic compositions of the DO in the incubated water (Bender et al. 1999).

For FRR measurements, the FRR fluorometer with the scalar irradiance sensor was deployed before dawn and at noon using a ship’s winch. We measured vertical profiles of fluorescence induction curves and irradiance at intervals of approximately 1 m by lowering the instrument package gently through the water column to a depth of 120 m and then raising it again at a rate of 0.2 m s⁻¹. For this study, we used the data from the upward casts. Similarly, daily ETRₚₛᵣᵢᵤ(μ) was calculated using Eqs. 2–5. Theoretically, the ETRₚₛᵣᵢᵤ determined by FRR fluorometry is proportional to GOP. In the present study, the FRR-based daily GOP was estimated empirically from the daily ETRₚₛᵣᵢᵤ by using the relationship between daily ETRₚₛᵣᵢᵤ and GOP determined by the H₂¹⁸O spike incubation method.

Results

In the first half of July 2012 when the observations with the profiling buoy system started, sea surface temperature (SST) was around 24.1–26.4°C, and a relatively strong thermocline had formed in the upper layer (Fig. 2a). The SST increased to about 28.5°C by the end of August. After October, the SST decreased gradually through seasonal surface cooling, and we observed a weakening of the thermocline in the upper water column. Temperatures in the upper 120 m decreased to 17.5–20.0°C by mid-January 2013 and remained there. Similarly, less saline water (<34.4) at the surface produced a halocline at depths of 20–80 m between July and November 2012, and then the halocline in the upper layer disappeared as a result of increased vertical mixing (Fig. 2b). The ELD was almost constant (84–105 m) between July and November 2012 but was variable and ranged from 59 to 102 m between December 2012 and March 2013 (Fig. 2c).

The MLD was relatively shallow (10–40 m) between July and October 2012, and then it deepened gradually to about 100 m by December 2012 (Fig. 2d). After January 2013, the MLD frequently reached below 130 m. Using data from the ship-based studies between 2010 and 2012 (Fujiki et al. 2016), we found a significant linear relationship between NO₃⁻+NO₂⁻ concentrations >0.1 μmol kg⁻¹ and seawater density within the upper 150 m (Fig. 3). The depth of the top of the nitracline (hereafter referred to as nitracline depth) was defined as the depth at which the NO₃⁻+NO₂⁻ concentration exceeded 0.1 μmol kg⁻¹ (Campbell and Vaulot 1993) and was set as the depth coincident with a seawater density of 1024.81 kg m⁻³, which was determined by substituting a NO₃⁻+NO₂⁻ concentration of 0.1 μmol kg⁻¹ into the regression equation for the linear relationship. In July 2012 when the buoy observations started, the nitracline depth was below the MLD, between 47 and 67 m (Fig. 2d). The nitracline depth deepened gradually as the season progressed from summer to autumn and then reached to below 100 m by November 2012. The MLD was deeper than the nitracline depth after January 2013; the nitracline depth was the shallowest (close to 0 m) in the second half of February 2013.

DO concentrations were relatively low (<210 μmol O₂ kg⁻¹) in the surface layer from July to November 2012, and a subsurface oxygen maximum (SOM, >230 μmol O₂ kg⁻¹) was observed below the MLD (Fig. 2e). The DO percent saturation was >110% just below the MLD between July and November 2012 (Fig. 2f). After December 2012, the SOM disappeared, and the DO concentration was almost constant (210–220 μmol O₂ kg⁻¹) within the upper 100 m (Fig. 2e). In March 2013, the DO concentration increased again to >220 μmol O₂ kg⁻¹ through the observed water column to a depth of 130 m. The DO percent saturation in the upper 100 m decreased gradually from 100% to 92% after December 2012 and increased again to >95% around mid-March 2013 (Fig. 2f).

Chl a concentrations were very low (<0.1 mg m⁻³) in the surface layer in July, and the deep chlorophyll maximum (DCM) of >0.3 mg m⁻³ formed below the nitracline depth at the 1–5% light depth (relative to 0 m) (Fig. 2c,g). The magnitude of the DCM decreased gradually with a deepening of the nitracline and decline in seasonal insolation, and the DCM nearly disappeared in November 2012, when the nitracline deepened to below the ELD. The Chl a concentration increased gradually after December 2012, and reached >0.3 mg m⁻³ in the upper 50 m between February and March 2013, when the nitracline depth shoaled to the surface.

The potential photochemical efficiency of PSII, Fᵥ/Fₘ, has been generally used as an indicator of nutrient stress (e.g., Cleveland and Perry 1987; Geider et al. 1993). A higher value of Fᵥ/Fₘ implies less stress, and vice versa. From July to November 2012, Fᵥ/Fₘ was relatively low (<0.35) in the surface waters but increased to >0.45 beneath the nitracline depth (Fig. 2h). In late December, when the MLD deepened to about 100 m and approached the nitracline depth, Fᵥ/Fₘ became almost constant vertically and increased to around 0.45 in the upper 100 m. After January 2013, when NO₃⁻ and NO₂⁻ were supplied from deeper layers to the surface waters, Fᵥ/Fₘ above the ELD remained in the 0.40–0.45 range. These features of the Fᵥ/Fₘ profiles indicate that nutrients were more growth-limiting to the near-surface phytoplankton between July and November 2012 but became less limiting within the euphotic layer after December 2012.
Fig. 2. Vertical and temporal maps of (a) temperature, (b) salinity, (c) relative irradiance (compared to 0 m [just below the surface]), (d) density, (e) DO concentration, (f) DO percent saturation, (g) Chl a concentration, (h) $F_s/F_m$, and (i) FRR-based GOP measured every 6 d during the study period. We used nighttime and daytime data in (a, b, d, l), daytime data only in (c, e, f), and nighttime data only in (g, h). The red, white, and black lines in (d–i) denote the MLD, the nitracline depth, and the ELD, respectively.
To estimate the daily GOP from the daily ETRPSII, we examined the empirical relationship between the daily GOP determined by the H$_2^{18}$O spike incubation method and the FRR-based daily ETRPSII during the four cruises in 2011 and 2012 (Fig. 4). This relationship was significant ($r^2 = 0.62$, $p < 0.001$); we therefore estimated the FRR-based daily GOP empirically by extrapolating the daily ETRPSII to the 18O-based daily GOP. From July to November 2012, the FRR-based daily GOP in near-surface layers was around 2 mmol O$_2$ m$^{-3}$ d$^{-1}$ at most and was $> 0.5$ mmol O$_2$ m$^{-3}$ d$^{-1}$ close to the DCM (Fig. 2i). After December 2012, the FRR-based daily GOP was much higher in the upper 30 m and often exceeded 5 mmol O$_2$ m$^{-3}$ d$^{-1}$ in the upper 10 m.

To better explain the day-to-day variations in DO concentration, Chl $a$ concentration, FRR-based daily GOP, and surface irradiance, we calculated the depth-integrated values of DO concentration within the upper 100 m ($\int$DO$_{100m}$), Chl $a$ concentration within the euphotic layer ($\int$(Chl $a$)$_{EL}$), daily GOP within the euphotic layer ($\int$GOP$_{EL}$), and the total daily surface irradiance ($E_{0,day}$) (Fig. 5a,b). The $\int$DO$_{100m}$ was as high as 23,300–23,700 mmol O$_2$ m$^{-2}$ between July and mid-August 2012 (Fig. 5a). After late August 2012, however, the $\int$DO$_{100m}$ decreased to 21,300 mmol O$_2$ m$^{-2}$ around 05 December 2012. After that, the $\int$DO$_{100m}$ increased to 23,100 mmol O$_2$ m$^{-2}$ on 17 March 2013, when observations with the profiling buoy system were finished. The $\int$(Chl $a$)$_{EL}$ remained in the 6.5–15.9 mg m$^{-2}$ range between July and November 2012 (Fig. 5a). However, the $\int$(Chl $a$)$_{EL}$ increased gradually after December 2012 and reached as high as 34.9 mg m$^{-2}$ on 17 March 2013. Although the $E_{0,day}$ was high (mean $\pm$ SD; 48.8 $\pm$ 12.9 mol photons m$^{-2}$ d$^{-1}$) between July and November 2012, the $\int$GOP$_{EL}$ was relatively low and ranged from 33.3 to 132 (84.0 $\pm$ 23.6) mmol O$_2$ m$^{-2}$ d$^{-1}$ (Fig. 5b). The $\int$GOP$_{EL}$ observed between July and November 2012 in this study corresponded roughly to the $\int$GOP$_{EL}$ values of 44–117 (78 $\pm$ 17) mmol O$_2$ m$^{-2}$ d$^{-1}$ at time-series Sta. ALOHA (23°N, 158°W) in the eastern part of the NPSG, which were measured with the H$_2^{18}$O spike incubation method nearly every month between March 2006 and February 2008 (Quay et al. 2010). In the present study, the $E_{0,day}$ decreased gradually as the season progressed from autumn to winter, whereas the $\int$GOP$_{EL}$ gradually increased and the estimated $\int$GOP$_{EL}$ reached its maximum of 460 mmol m$^{-2}$ d$^{-1}$ on 17 March 2013, when both $E_{0,day}$ and $\int$(Chl $a$)$_{EL}$ were relatively high (Fig. 5a,b).

The wind speed at a height of 10 m was typically less than 10 m s$^{-1}$ during the buoy observations (Fig. 5c). The calculated air–sea O$_2$ flux ($F_{A,S}$), which incorporated diffusive gas exchange and bubble-mediated exchange, was lowest (−63.6 mmol O$_2$ m$^{-2}$ d$^{-1}$) at the end of August 2012 (Fig. 5c).
uptake of oxygen. The euphotic layer (EL) \( (\text{Eq. 1, was } 0.09 \text{ m}) \) upper 100 m \( (2016) \). In the present study, in order to estimate GOP from an incubation period (Falkowski and Raven 2007; Ferrón et al. 2016), we considered the most direct method for measuring GOP in the oceans because it is unaffected by respiratory processes and is considered the most direct method for measuring GOP in the atmosphere (oxygen uptake from the atmosphere to the ocean). Above all, the latter method is considered the most direct method for measuring GOP in the atmosphere (oxygen uptake from the atmosphere to the ocean).

The implication is that the oxygen emission from the ocean surface to the atmosphere was highest during the observation period. The \( F_{\text{AS}} \) increased gradually with time and changed from negative to positive in November 2012. The implication is that the gas flux in the study area shifted from emission to uptake of oxygen. The \( F_{102} \) at a depth of 100 m, estimated from Eq. 1, was \( 0.09 \pm 0.14 \text{ mmol } \text{O}_2 \text{ m}^{-2} \text{ d}^{-1} \) (data not shown).

Discussion

Estimates of daily GOP

The most common methods for measuring GOP include the light and dark bottle incubation method and the \( \text{H}_2^{18}\text{O} \) spike incubation method. Above all, the latter method is considered the most direct method for measuring GOP in the oceans because it is unaffected by respiratory processes and incubation period (Falkowski and Raven 2007; Ferrón et al. 2016). In the present study, in order to estimate GOP from ETR\(_{\text{PSII}} \) measurements from the profiling buoy system, we examined the relationship between FRR-based daily ETR\(_{\text{PSII}} \) and \( ^{18}\text{O} \)-based daily GOP during the four cruises in 2011 and 2012, and we derived an empirical linear relationship (Fig. 4).

In conjunction with \( \text{H}_2^{18}\text{O} \) spike incubations, the buoy system with an FRR fluorometer can measure GOP over vertical and temporal resolutions that are unprecedented in ocean biogeochemistry research. Note, however, that the conversion of daily ETR\(_{\text{PSII}} \) to daily GOP by using the empirical relationship described above is not always accurate. For example, if there is a substantial decrease in ambient irradiance due to cloud cover only around noon when the profiling buoy observations are made, a low value for daily ETR\(_{\text{PSII}} \) is obtained and the daily GOP would be underestimated, and vice versa. Thus, large changes in ambient irradiance in daytime due to cloud cover could have caused errors in estimates of daily GOP from the relational expression. This cloud-induced error is difficult to assess quantitatively because we did not continuously measure the ambient irradiance during the buoy observations. Although there is uncertainty in estimates of daily GOP for days with changeable weather conditions, we consider the daily ETR\(_{\text{PSII}} \) measured with the profiling buoy system as sufficient for rough estimates of the daily GOP in the study area.

Variations in phytoplankton biomass and GOP

For the observation period from July 2012 to March 2013, the study area was characterized by strong stratification in the summer and autumn, and deep mixing in the winter and early spring. Chl \( a \) concentration peaked between 60 and 120 m, which was below the nitracline depth, between July and November 2012 (Fig. 2g). High surface Chl \( a \) concentrations between December 2012 and March 2013 were associated with the deepening of the MLD. Based on these observations, we divided the data collected during this study into two periods: the stratification period (July–November) and the mixing period (December–March).

During the stratification period, the distribution patterns of Chl \( a \) concentration and daily GOP were uncoupled, and varied both vertically and temporally (Fig. 2g,i). This apparent contradiction occurred because the magnitude and depth of the DCM were related to the nitracline depth combined with the ELD, whereas the daily GOP was always high at the surface and was controlled predominantly by the ambient irradiance. The DCM was observed beneath the nitracline depth and at the 1–5\% light depth in July and September (Fig. 2c,g). Around the DCM, the increase in \( F_{\text{AS}} \) was also probably caused by an improved \( \text{NO}_3^- + \text{NO}_2^- \) availability (Fig. 2h). In contrast, the daily GOP was highest near the surface, where there was sufficient light but \( \text{NO}_3^- + \text{NO}_2^- \) concentrations were very low (<0.1 \( \mu\text{mol kg}^{-1} \)) (Fig. 2i). These results suggest that photochemical energy associated with oxygen production in the surface waters may not be ultimately available to increase phytoplankton biomass because of chronic nutrient limitation. On the other hand, the phytoplankton biomass in the surface...
waters was thought to be maintained by utilization of regenerated forms of nitrogen such as ammonia (Karl 1999). In addition, ship-based observations between 2010 and 2012 showed the phytoplankton community at Sta. S1 during the stratification period was consistently dominated by picoplankton (77–89% of Chl a standing stock), which have high surface-area-to-volume ratios that allow them to take up nutrients efficiently (Fujiki et al. 2016).

During the mixing period, the DCM and the peak \( F_s/F_m \) disappeared, followed by the enhancement of Chl a concentrations and \( F_o/F_m \) throughout the euphotic layer (Fig. 2g,h). At the same time, there was a distinct increase in daily GOP in near-surface layers (Fig. 2i). In contrast to the stratification period, the \( [\text{Chl } a]_{\text{EL}} \) increased synchronously with the \( [\text{GOP}]_{\text{EL}} \) (Fig. 5a,b). The \( E_{\text{day}} \) was relatively low (24.9 ± 12.8 mol photons m\(^{-2}\) d\(^{-1}\)) during the mixing period with the seasonal decrease of insolation, compared to the stratification period (48.8 ± 12.9 mol photons m\(^{-2}\) d\(^{-1}\)) (Fig. 5b). However, the nitrate supply was shallow (close to 0 m) because of winter mixing, and new nitrogen was supplied from deeper waters into the euphotic zone. Thus, a reduction of nutrient stress through winter mixing likely promoted the efficient use of photochemical energy linked to GOP for increases in phytoplankton biomass, resulting in the occurrence of phytoplankton blooms in this region.

Fujiki et al. (2016) showed that large diatoms (Chaetoceros spp. and Pseudo-nitzschia spp.) became the most abundant group in February 2011, when phytoplankton blooms were observed. Winter mixing can supply enough nutrients to cause the diatom blooms in this region. In the oligotrophic regions in the western North Pacific, episodic events such as mesoscale eddies (Honda et al. 2018), typhoons (Lin 2012) and eolian dust inputs (Taketani et al. 2018) are considered as potential mechanisms for nutrient injection into the euphotic zone. The meteorological satellite data showed the propagations of cyclonic eddies in August 2012 (stratification period) and of anticyclonic eddies in December 2012 (mixing period) in the vicinity of Sta. S1 (Inoue and Kouketsu 2016). However, changes of Chl a and \( F_o/F_m \) due to eddy propagation were unclear in our buoy observations (Fig. 2g,h). The satellite data also revealed that two typhoons—MARIA and PRAPIROON—were passing Sta. S1 in mid-October 2012 (Inoue and Kouketsu 2016). At that time, there was a transient increase in \( F_o/F_m \) in the water column from deeper waters to the near-surface layer, indicating a sporadic input of nutrients from deeper waters (Fig. 2h), but the increase in Chl a concentration was only observed at around 80 m depth (Fig. 2g). Therefore, the nutrient injection due to such episodic events may not be sufficient to cause phytoplankton blooms.

**Relationship between GOP and DO**

Vertical profiles of DO concentration differed from those of Chl a concentration and daily GOP throughout the observation period (Fig. 2e,g,i). During the stratification period, the SOM was located below the MLD and was mostly supersaturated (110–125%) (Fig. 2f). The DO concentrations were saturated (100–110%) in the upper mixed layer and unsaturated (< 95%) at the depth of the DCM. In theory, oxygen saturation/supersaturation is due to surplus oxygen associated with an exceedance of respiration by photosynthesis, an input of air bubbles into surface waters through air–sea gas exchange, and surface heating by solar radiation (Spitzer and Jenkins 1989; Schudlich and Emerson 1996; Sarmiento and Gruber 2006). Using two profiling floats with DO sensors, Riser and Johnson (2008) conducted time-series observations for 3 yr near the HOT station (23°N, 158°W) in the North Pacific and near an oligotrophic site (22°S, 120°W) in the South Pacific. They found that DO concentrations increased below the MLD in these regions during periods with a seasonal thermocline. During the Western North Pacific Integrated Physical-Biogeochemical Ocean Observation Experiment (INBOX) conducted in 2011 (the year before buoy observations in this study), Inoue et al. (2016) deployed 18 profiling floats with DO sensors in an area of about 150 × 150 km centered around Sta. S1 and observed that the SOM was widely distributed below the MLD during the stratification period. An interesting observation of the present study is the fact that the high DO concentrations during the stratification period were not in the surface layers where the daily GOP was higher but were just below the MLD (Fig. 2e). Additionally, in mid-October 2012, when the two typhoons referenced above were passing near Sta. S1, the oxygen accumulated below the MLD was transiently exported to the mixed layer. After the passing of the typhoons, the SOM again formed below the MLD. Thus, the accumulation of DO below the MLD was mainly oxygen produced by photosynthesis below the MLD and was probably caused by a constraint on upward diffusion due to the steep density gradient. This assessment agrees with that of Shulenberger and Reid (1981), who proposed that produced oxygen is prevented from escaping to the atmosphere by a density cap created by surface warming during the summer.

As was the case below the MLD, DO in the upper mixed layer was saturated but relatively low compared to below the MLD. The lower DO concentrations might primarily reflect the emission of oxygen to the atmosphere through air–sea gas exchange, combined with oxygen consumption through biological metabolism and chemical oxidation reactions in the upper mixed layer. During the mixing period, when daily GOP increased substantially in the surface layers, the entrainment of water caused the SOM to disappear and led to a reduction in oxygen saturation (< 100%) throughout the euphotic layer due to the inflow of deeper waters with low temperature and low DO concentrations (Fig. 2a,e,f,i). The formation of oxygen-unsaturated water in the surface layers has the potential to promote the uptake of oxygen from the atmosphere into the ocean. This possibility is supported by the shift of \( F_{\text{Ap}} \) from negative to positive (Fig. 5c). In addition, Tohjima et al. (2012) found, through atmospheric observations and model
simulations, that the seasonal cycle of atmospheric potential oxygen in the western North Pacific Ocean is closely related to the summertime oxygen emissions from the ocean due to photosynthesis and the wintertime oxygen uptake into the ocean due to rapid cooling and deeper mixing.

During the stratification period, the \( \int \text{DO}_{100m} \) gradually decreased with time, whereas \( \int \text{GOP}_{\text{EL}} \) was nearly constant (Fig. 5a,b). There was a significant negative linear relationship between MLD and \( \int \text{DO}_{100m} \) (Fig. 6), and the mean rate of decrease in \( \int \text{DO}_{100m} \) was 22.8 \( \pm 5.0 \) mmol O\(_2\) m\(^{-2}\) with every meter deepening of the MLD. The deepening of the MLD relative to the ELD led to lower DO below the mixed layer and hence lower \( \int \text{DO}_{100m} \). In contrast, during the mixing period, the \( \int \text{DO}_{100m} \) increased with the combined accumulation of increasing \( \int \text{GOP}_{\text{EL}} \) and oxygen uptake from the atmosphere (Fig. 5a–c).

The time-integrated value of \( \int \text{GOP}_{\text{EL}} \) (\( \int \text{GOP}_{\text{EL}} \)) over the 144 d of the observed stratification period was 12,053 \( \pm 864 \) mmol O\(_2\) m\(^{-2}\) (Table 1). The integrated value of GOP from the ELD to the MLD over the 144 d was 6623 \( \pm 475 \) mmol O\(_2\) m\(^{-2}\) and constituted about 55% of \( \int \text{GOP}_{\text{EL}} \). The GOP at depths below the MLD probably contributed to the formation of the SOM below the MLD. However, part of the DO within the mixed layer was emitted from the ocean surface to the atmosphere. The time-integrated value of \( F_{\text{AS}} \) (\( F_{\text{AS}} \)) over the stratification period was 2942 \( \pm 765 \) mmol O\(_2\) m\(^{-2}\) and corresponded to about 24% of \( \int \text{GOP}_{\text{EL}} \) during that time (Table 1). \( \int \text{DO}_{100m} \) decreased with time and was lower by 1877 \( \pm 239 \) mmol O\(_2\) m\(^{-2}\) by the end of the stratification period (\( \Delta \int \text{DO}_{100m} \); Table 1). These results suggest that the total amount of oxygen emitted to the atmospheric and consumed by respiration in the seawater exceeded the amount of oxygen produced. By using a one-dimensional model of the upper 100 m of the water column, we estimated the oxygen consumption (\( \int |R| \)) integrated over the upper 100 m and over the stratification period as follows:

\[
\int R = \int \text{GOP}_{\text{EL}} + \int F_{\text{AS}} + \int F_{KZ} - \Delta \int \text{DO}_{100m},
\]

where \( \int F_{KZ} \) is the vertical diffusive O\(_2\) flux at 100 m integrated over the stratification period. During the stratification period, \( \int R \) was 10,970 \( \pm 1179 \) mmol O\(_2\) m\(^{-2}\) and corresponded to about 91% of \( \int \text{GOP}_{\text{EL}} \) during that time period, indicating that net community production (\( \int |\text{NCP}| = \int \text{GOP}_{\text{EL}} - \int |R| \)) was 1083 \( \pm 801 \) mmol O\(_2\) m\(^{-2}\) (Table 1).

In contrast, the \( \int \text{GOP}_{\text{EL}} \) during the 102 d of the observed mixing period was estimated to be 11,243 \( \pm 806 \) mmol O\(_2\) m\(^{-2}\).

Table 1. Comparison of oxygen-related parameters (units: mmol O\(_2\) m\(^{-2}\)) between periods of stratification (08 July 2012–29 November 2012) and mixing (05 December 2012–17 March 2013). \( \int \text{GOP}_{\text{EL}} \), GOP integrated over the euphotic layer (\( \int \text{GOP}_{\text{EL}} \)) and over each period; \( \int \text{GOP}_{0m-MLD} \), integrated value of GOP from the surface to the MLD during the stratification period; \( \int \text{GOP}_{\text{ELD}} \), integrated value of GOP from the ELD to the MLD during the stratification period; \( F_{\text{AS}} \), air–sea O\(_2\) flux integrated over each period; \( F_{KZ} \), vertical diffusive O\(_2\) flux at 100 m integrated over each period; \( \Delta \int \text{DO}_{100m} \), change in DO concentrations integrated over the upper 100 m (\( \int \text{DO}_{100m} \)) within each period as calculated from a linear regression for \( \int \text{DO}_{100m} \); vs. time; \( \int |R| \), oxygen consumption integrated over the upper 100 m and over each period (see Eq. 6); \( \int |\text{NCP}| \), net community production integrated over the upper 100 m and over each period.

|                      | Stratification period                      | Mixing period                       |
|----------------------|-------------------------------------------|-------------------------------------|
|                      | 08 Jul 2012–29 Nov 2012 (144 d)           | 05 Dec 2012–17 Mar 2013 (102 d)     |
| \( \int \text{GOP}_{\text{EL}} \)  | 12,053 \( \pm 864 \)                     | 11,243 \( \pm 806 \)               |
| \( \int \text{GOP}_{0m-MLD} \)  | 5430 \( \pm 389 \)                      | —                                   |
| \( \int \text{GOP}_{\text{ELD}} \)  | 6623 \( \pm 475 \)                      | —                                   |
| \( F_{\text{AS}} \)  | -2942 \( \pm 765 \)                     | 4631 \( \pm 1204 \)               |
| \( F_{KZ} \)  | -18 \( \pm 9 \)                         | -4 \( \pm 2 \)                    |
| \( \Delta \int \text{DO}_{100m} \)  | -1877 \( \pm 239 \)                     | 1123 \( \pm 197 \)               |
| \( \int |R| \)  | 10,970 \( \pm 1179 \)                    | 14,747 \( \pm 1462 \)             |
| \( \int |\text{NCP}| \)  | 1083 \( \pm 801 \)                      | -3504 \( \pm 1220 \)              |

*Error in \( \int \text{GOP}_{\text{EL}} \) was calculated from standard error of the linear regression slope between the ETR determined by FRR fluorometry and the GOP determined by the H\(_2\)O\(^18\)O spike incubation method (Fig. 4).

†Errors in \( F_{\text{AS}} \) and \( F_{KZ} \) were assumed to be \( \pm 26\% \) and \( \pm 50\% \), respectively, based on Bushinsky and Emerson (2015).

‡Error in \( \Delta \int \text{DO}_{100m} \) was derived from the standard error of the rate of change of \( \int \text{DO}_{100m} \) with time during each period (Fig. 5a).

§\( \int |\text{NCP}| = \int \text{GOP}_{\text{EL}} - \int |R| \).
Note that the number of days integrated for the estimated $\int \text{GOP}_{\text{EL}}$ differed between the stratification and mixing periods. The mean value of $\text{GOP}_{\text{EL}}$ during the mixing period was 110 mmol O$_2$ m$^{-2}$ d$^{-1}$ and was higher by a factor of about 1.3 than the rate during the stratification period. Along with the increase in $\text{GOP}_{\text{EL}}$, the oxygen influx to the ocean from the atmosphere increased gradually during the mixing period (Fig. 5b,c). The $F_{\text{AS}}$ during the mixing period was $4631 \pm 1204$ mmol O$_2$ m$^{-2}$, which corresponded to about 41% of $\int \text{GOP}_{\text{EL}}$ (Table 1). As was the case during the stratification period, $\int R$ during the mixing period was estimated using Eq. 6. Although the entrainment of seawater from depths below 100 m occurred during the mixing period, we did not include the entrainment of seawater in this calculation because the MLD often deepened to below the greatest observation depth (130 m) during the mixing period, and data were therefore unavailable to estimate the entrainment of seawater (Fig. 2e). The $\int R$ during the mixing period was therefore biased by the entrainment of oxygen due to vertical mixing. During the mixing period, the $\int R$ was $14,747 \pm 1462$ mmol O$_2$ m$^{-2}$ and was about 1.3 times the $\int \text{GOP}_{\text{EL}}$, indicating that $\int \text{NCP}$ was $-3504 \pm 1220$ mmol O$_2$ m$^{-2}$ (Table 1). As a result, the $\text{DO}_{100\text{m}}$ apparently increased by 1123 mmol O$_2$ m$^{-2}$ during the mixing period because the total amount of oxygen production and oxygen uptake from the atmosphere exceeded the amount of oxygen consumed in the seawater and entrained by vertical mixing (Table 1). In addition, the surplus oxygen due to $\int \text{GOP}_{\text{EL}}$ and $F_{\text{AS}}$ during the mixing period might have partially compensated for the decline in $\text{DO}_{100\text{m}}$ during the stratification period and thereby sustained the overall oxygen balance in this region throughout the year.

**Conclusions**

Detailed vertical and temporal maps of biogeochemical parameters observed with the profiling buoy systems greatly increased our understanding of how phytoplankton biomass and productivity were affected by water-mass structure and nutrient distribution in the northwestern NPSG. In this study, by calibrating FRR-based ETR$_{\text{PSII}}$ against discrete measurements by the H$_2$18O spike incubation method, we conducted time-series observations of GOP by phytoplankton in this region. To determine the applicability of this procedure for global GOP observations, it will be necessary to examine the relationship between the two methods in various ocean regions.

We found that the vertical distribution and temporal changes in GOP did not necessarily correspond to those of DO concentrations in the upper water column depending on the degree of stratification, oxygen consumption, and air–sea gas exchange, implying that GOP cannot be reliably estimated from DO measurements alone. On the other hand, DO was supplied mainly from GOP during the stratification period, and from both GOP and atmospheric input during the mixing period. Estimates of the oxygen flux between the atmosphere and ocean, along with DO and GOP measurements, are needed for a better understanding of the role of phytoplankton in the oxygen cycle in the upper ocean. These approaches will also aid in clarifying how the oceanic oxygen cycle is affected by global environmental changes, such as global warming or ocean deoxygenation.

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Conflict of Interest

None declared.