Ship-based observations of atmospheric potential oxygen and regional air–sea O₂ flux in the northern North Pacific and the Arctic Ocean

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ABSTRACT
Simultaneous observations of atmospheric potential oxygen (APO = O₂ + 1.1 × CO₂) and air–sea O₂ flux, derived from dissolved oxygen in surface seawater, were carried out onboard the research vessel MIRAI in the northern North Pacific and the Arctic Ocean in the autumns of 2012–2014. A simulation of the APO was also carried out using a three-dimensional atmospheric transport model that incorporated a monthly air–sea O₂ flux climatology. By comparing the observed and simulated APO, as well as the observed and climatological air–sea O₂ fluxes, it was found that the large day-to-day variation in the observed APO can be attributed to the day-to-day variation in the local air–sea O₂ fluxes around the observation sites. It was also found that the average value of the observed air–sea O₂ fluxes was systematically higher than that of the climatological O₂ flux. This could explain the discrepancy between the observed and simulated seasonal APO cycles widely seen at various northern hemispheric observational sites in the fall season.

Keywords: atmospheric potential oxygen, air-sea O₂ flux, ship observation

1. Introduction

High precision measurements of the atmospheric O₂/N₂ ratio have been carried out since the early 1990s to estimate the global terrestrial biospheric and oceanic CO₂ uptake (e.g. Keeling et al., 1996; Bender et al., 2005; Manning and Keeling, 2006; Tohjima et al., 2008; Ishidoya et al., 2012a, 2012b). The approach is based on the global mean O₂:CO₂ exchange ratios for the terrestrial biospheric O₂ and CO₂ fluxes (−1.1) and fossil fuel combustion (−1.17, −1.44 and −1.95 for coal, liquid and gaseous fuels, respectively) (Keeling, 1988; Severinghaus, 1995). By using the O₂:CO₂ exchange ratio of −1.1 for terrestrial biospheric activities, a quantity known as atmospheric potential oxygen (APO) is defined by APO = O₂ + 1.1 × CO₂ (Stephens et al., 1998). Since APO is essentially preserved for terrestrial biospheric activities, it has been used to evaluate air–sea O₂ fluxes associated with marine biological and physical processes (e.g. Keeling et al., 1998; Garcia and Keeling, 2001; Nevison et al., 2012).

In order to increase our understanding of the relationship between the local air–sea O₂ flux variation and APO, we need to observe APO just above the sea surface. However, shipboard observations of APO are still limited (Stephens et al., 2003; Tohjima et al., 2005, 2012, 2015; Battle et al., 2006; Thompson et al., 2007, 2008). Stephens et al. (2003) carried out continuous measurements of the atmospheric O₂/N₂ ratio and CO₂ concentration in the equatorial Pacific during April and May 1998 and in the Southern Ocean during October 1998. Thompson et al. (2008) also measured the
atmospheric $O_2/N_2$ ratio and CO$_2$ concentration continuously in the southern Pacific Ocean during February 2003 and April 2004. Both of these studies revealed larger spatiotemporal variations in the $O_2/N_2$ ratio than those in CO$_2$. As explained in these papers, the difference arises from the fact that the equilibration time for $O_2$ between the atmosphere and the surface ocean is much shorter than that for CO$_2$ since the air–sea exchange of CO$_2$ between the atmosphere and the ocean is influenced by an additional process involving the carbonate dissociation effect (Keeling et al., 1993). Therefore, short-term variations in APO can be exploited to evaluate local air–sea $O_2$ fluxes due to marine biological activities and thermally induced solubility changes.

Thompson et al. (2008) also compared the observed APO with those simulated using an atmospheric transport model (Heimann and Körner, 2003) driven by air–sea $O_2$ and CO$_2$ fluxes estimated from an ocean biogeochemistry model (Buitenhuis et al., 2005) or from climatologies (Najjar and Keeling, 2000; Takahashi et al., 2002). They found that the simulated APO agreed qualitatively with the observed characteristics of the APO latitudinal variation but underestimated the magnitude of the observed APO maximum in the mid-southern latitudes. On the other hand, Tohjima et al. (2005, 2012, 2015) have carried out long-term observations of APO in the Pacific region since the early 2000, elucidating in much more detail the salient features of the seasonal cycle, latitudinal gradient and secular trend in APO. In one of their studies (Tohjima et al., 2012), the observed seasonal APO cycles were reproduced relatively well by an atmospheric transport model (Maksyutov and Inoue, 2000) driven by an air–sea climatology of $O_2$ and N$_2$ fluxes (Garcia and Keeling, 2001).

In order to advance our understanding of the contribution the local air–sea $O_2$ fluxes make to the observed variations in APO, as well as to validate the air–sea $O_2$ flux climatologies reported in past studies (e.g. Garcia and Keeling, 2001), simultaneous observations of APO and the air–sea $O_2$ flux are needed. To achieve this objective, we collected flask air samples onboard the research vessel MIRAI during its cruises in the northern North Pacific and the Arctic Ocean during the fall seasons of 2012–2014, to analyse for the atmospheric $O_2/N_2$ ratio, CO$_2$ concentration and $\delta^{13}C$ of CO$_2$ left behind in the atmosphere. Here $\delta^{13}C$ of CO$_2$ measurements allow us to separate the atmosphere–terrestrial biosphere CO$_2$ exchange from the one between the atmosphere and the ocean (e.g. Keeling et al., 1989; Nakazawa et al., 1993; Battle et al., 2000). The terrestrial biosphere preferentially uptakes CO$_2$ with a lower $\delta^{13}C$ value, enriching $\delta^{13}C$ of CO$_2$ left behind in the atmosphere. On the other hand, a change in the atmospheric $\delta^{13}C$ of CO$_2$ due to an exchange of 1 mol of CO$_2$ between the atmosphere and the ocean is about 10 % of that observed between the atmosphere and the terrestrial biosphere. Therefore, simultaneous observations of APO and $\delta^{13}C$ of CO$_2$ can enhance our understanding of the causes of variations in the observed APO, since APO variations mainly reflect air–sea gas exchanges.

In this paper, we present observational results of these measurements and discuss the possible relationship between the observed APO and the air–sea $O_2$ fluxes derived from the observed dissolved oxygen concentration. We also compare the observed APO with simulated APO using an atmospheric transport model (Taguchi et al., 2002) driven by climatological air–sea $O_2$ and N$_2$ fluxes (Garcia and Keeling, 2001), to evaluate differences between the observed and climatological $O_2$ fluxes during the fall season in the northern North Pacific and the Arctic Ocean.

2. Method

Air samples to measure the $O_2/N_2$ ratio, CO$_2$ concentration and $\delta^{13}C$ of CO$_2$ were collected on average once per day onboard the research vessel MIRAI for the period 5 September–15 October 2012, 29 August–6 October 2013, and 1 September–9 October 2014. The MIRAI cruise reports are available from the Japan Agency for Marine–Earth Science and Technology database (www.godac.jamstec.go.jp/catalog/doc_catalog/e/index.html). Locations where the air samples were collected are shown in Fig. 1.
Each air sample was taken from an air intake at a flow rate of 7 L min$^{-1}$ using a piston pump (GAST co., LOA) and filled into a 1 L stainless-steel flask after removing water vapour using a cold trap at $-80$ °C. During the air sampling, an inner pressure of the flask was kept at an absolute pressure of 0.55 MPa using a backpressure valve (Tohjima et al., 2003). The air intake was mounted at a height of 25 m a.s.l. on the foredeck. The 1-L stainless-steel flasks used in 2012 were each equipped with a metal-seal valve (Nupro co., SS-4H) on each side. However, we found that a mass-dependent fractionation of O$_2$ and N$_2$ due to a small leak through the valve (e.g. Langenfelds et al., 1999) was significant for some flasks. The significance of the fractionation was confirmed by the simultaneously measured values of the Ar/N$_2$ ratio, stable isotopic ratios of N$_2$ and O$_2$ and CO$_2$ (Tanaka et al., 1983; Nakazawa et al., 1997). In this study, measured values of the Ar/N$_2$ ratio, stable isotopic ratios of N$_2$, O$_2$ and CO$_2$ were measured using a non-dispersive infrared analyzer (Li-7000) and a mass spectrometer (Thermo Electron Delta-S), respectively, at Tohoku University (Tanaka et al., 1983; Nakazawa et al., 1997).

The O$_2$/N$_2$ and Ar/N$_2$ ratios, as well as stable isotopic ratios of N$_2$, O$_2$, and Ar, were measured using a mass spectrometer (Thermo Scientific Delta-V) at the National Institute of Advanced Industrial Science and Technology (AIST) (Ishidoya and Murayama, 2014). The CO$_2$ concentration and $\delta^{13}$C of CO$_2$ were measured using a non-dispersive infrared analyzer (Li-7000) and a mass spectrometer (Thermo Electron Delta-S), respectively, at Tohoku University (Tanaka et al., 1983; Nakazawa et al., 1997). The O$_2$/N$_2$ ratio and $\delta^{13}$C of CO$_2$ are reported in:

\[
\delta^{(16)O^{16}O^{14}N^{14}N} = \left(\frac{\text{O}_{16}O^{16}O^{14}N^{14}N_{\text{sa}}}{\text{O}_{16}O^{16}O^{14}N^{14}N_{\text{st}}} - 1\right) \times 10^4 \text{(per meg)},
\]

\[
\delta^{(13)}C^{(12)}C = \left(\frac{\text{C}^{(13)}C^{(12)}C_{\text{sa}}}{\text{C}^{(13)}C^{(12)}C_{\text{st}}} - 1\right) \times 10^3 \text{(‰)},
\]
where subscripts ‘sa’ and ‘st’ indicate the sample air and the standard air, respectively. An increase of one mole of O$_2$ in $10^6$ moles of air corresponds to a 4.8 per meg change in $\delta$(O$_2$/N$_2$) since O$_2$ is 20.95 % of dry air (Machta and Hughes, 1970). In this study, measured values of $\delta$(O$_2$/N$_2$) in each air sample were determined against our primary standard air (cylinder No. CRC00045) with a reproducibility of $\pm$3 per meg. The CO$_2$ concentration was determined against our air-based CO$_2$ standard gas system with a precision of better than $\pm$0.05 ppm (Tanaka et al., 1983), and $\delta^{13}$C of CO$_2$ was determined against a primary standard CO$_2$ produced by reacting NBS-18 with 100 % phosphoric acid at 25 °C with a precision of 0.02‰ (Nakazawa et al., 1997). In this study, measured $\delta$(O$_2$/N$_2$) values were corrected for the mass-dependent fractionation of O$_2$ and N$_2$ by subtracting simultaneously measured $\Delta\delta$(Ar/N$_2$)/3 from the measured $\delta$(O$_2$/N$_2$) assuming that the variations in the atmospheric $\delta$(Ar/N$_2$) during the period of respective cruises were very small (e.g. Cassar et al., 2008) $\delta$(Ar/N$_2$) is defined in the same way as $\delta$(O$_2$/N$_2$) but for $^{4}$Ar/$^{14}$N ratio. Here $\Delta$ denotes the difference between the measured $\delta$(Ar/N$_2$) values and the average of the measured values of $\delta$(Ar/N$_2$) for the corresponding cruises. A typical correction was 3.0 per meg for a flask equipped with two metal-seal valves on each side, which was less than 50 % of the correction needed for a flask equipped with one metal-seal valve on each side (6.6 per meg). By using the measured CO$_2$ concentration and the corrected $\delta$(O$_2$/N$_2$), APO is calculated as:

\[\text{APO} = \delta$(O$_2$/N$_2$) + \frac{1.1}{X_{O_2}}([\text{CO}_2] - 381),\]

where [CO$_2$] is the CO$_2$ concentration in ppm, $-1.1$ is the O$_2$:CO$_2$ exchange ratio for the terrestrial biospheric activity, $X_{O_2} = 0.2095$ is the mole fraction of atmospheric O$_2$ (Machta and Hughes, 1970) and 381 is an arbitrary reference. It is noted that many previous APO studies expressed the measured values on the Scripps Institution of Oceanography (SIO) scale (e.g. Manning and Keeling, 2006; Kozlova et al., 2008; van der Laan et al., 2014) although the scale is not traceable to the International System of Units. A detailed comparison between our O$_2$/N$_2$ scale and the SIO scale is needed some time in the near future. If we simply compare our APO values obtained north of 55 °N (70 °N on average) with the average APO observed (based on the SIO scale) at Alert (82 °N, 63 °W), Canada and at Cold Bay (55 °N, 163 °W, Alaska during the same time period (Keeling et al., 1998; Keeling and Manning, 2014) (the APO data observed by SIO are taken from the Scripps O$_2$ Program database; www.scrippso2.ucsd.edu), then the APO values reported in this study are higher by about 370 per meg on average.

To compare the observed APO with those simulated using climatological air–sea O$_2$ and N$_2$ fluxes, we used a three-dimensional atmospheric transport model developed at the National Institute of Advanced Industrial Sciences and Technology, Tsukuba, Japan (Taguchi, 1996; Taguchi et al., 2002) (hereafter referred to as STAG). The STAG model is based on the NIRE-CTM 96 model and has a horizontal resolution of 1.125 ° and 60 vertical levels; advection is calculated using a semi-Lagrangian scheme. In this study, model simulations were performed using the European Centre for Medium-Range Weather Forecasts reanalysed meteorological data (ERA-Interim). Monthly seasonal climatological values of the air–sea O$_2$ and N$_2$ fluxes (hereafter referred to as $F_{O_2,sa}$ and $F_{N_2,sa}$ respectively) were taken from the TransCom experimental protocol.
(Garcia and Keeling, 2001; Blaine, 2005). The climatology of O$_2$ flux is based on weighted linear least squares regressions using monthly heat flux anomalies for spatial and temporal interpolation of historical O$_2$ data; the climatology of N$_2$ flux is computed as the product of the heat flux anomaly times the temperature derivative of the N$_2$ solubility (Garcia and Keeling, 2001). Model-based APO was calculated according to:

$$\text{APO} = \frac{[O_2]}{X_{O_2}} - \frac{[N_2]}{X_{N_2}} \times \frac{C_{0}}{C_{1}}.$$  \hspace{1cm} (4)

Here, [O$_2$] and [N$_2$] are the simulated respective concentrations of O$_2$ and N$_2$ in ppm of dry air, and $X_{N_2} = 0.7808$ is the fraction of N$_2$ in the atmosphere driven by air–sea O$_2$ and N$_2$ fluxes but also by air–sea CO$_2$ flux, although it is clear that the air–sea O$_2$ and N$_2$ fluxes account for much of the variations in APO on synoptic-to-seasonal time scales, due to the dampening of CO$_2$ flux by the ocean carbonate chemistry. Nevertheless, to examine the contribution of air–sea CO$_2$ flux on APO (APO$_{CO_2}$) more quantitatively, we also calculated the CO$_2$ concentration using the STAG model that incorporated the monthly climatological air–sea CO$_2$ flux (Takahashi et al., 2009), and converted it to APO in ppm as:

$$\text{APO}_{CO_2} = 1.1 \times \frac{[CO_{2,\infty}]}{X_{O_2}}.$$ \hspace{1cm} (5)

Here, [CO$_{2,\infty}$] is the simulated CO$_2$ concentration, driven by the air–sea CO$_2$ flux, in ppm of dry air. We used detrended values of APO$_{CO_2,\infty}$ in this study, and discuss its contributions to the day-to-day and seasonal variations in APO below. Detailed evaluations of the effect of air–sea CO$_2$ flux on APO are also found in Ro¨denbeck et al. (2008) and Tohjima et al. (2012).

In this study, we also made continuous measurements of dissolved oxygen at a water depth of 5 m at 1-minute intervals. For the measurements, an optical oxygen sensor (RINKO-II, JFE Advantech Co., Ltd., Kobe, Japan) was used, along with a thermosalinograph (SBE 45, Sea-Bird Electronics, Inc., Bellevue, Washington, USA). The optical oxygen sensor was characterised with standard gases by means of a nonlinear calibration equation (Uchida et al., 2010) with slight modification before each cruise. Raw data from the optical oxygen sensor and temperature and salinity data from the thermosalinograph were used to calculate dissolved oxygen. The dissolved oxygen data were determined as an output from the linear regression as a function of uncorrected dissolved oxygen (obtained from the Winkler method) (Dickson, 1996), sea water temperature and time. A bias in the Winkler method due to iodate interference was corrected by subtracting 0.52 µmol·kg$^{-1}$ from the dissolved oxygen data (Wong and Li, 2009). Precisions of the dissolved oxygen measurements were estimated to be 2 µmol·kg$^{-1}$ for the samples in 2012 and 1 µmol·kg$^{-1}$ for the samples in 2013 and 2014. Details of the dissolved oxygen measurement system on MIRAI are given in Uchida et al. (2015). The observed dissolved oxygen was used to calculate air–sea O$_2$ flux as:

$$F_{O_2,sw} = K_{O_2} \rho ([O_2] - [O_2]_{sat}).$$ \hspace{1cm} (6)

Here, $F_{O_2,sw}$ (µmol·m$^{-2}$·s$^{-1}$) is the air–sea O$_2$ flux (positive value denotes flux emitted from the ocean to the atmosphere). $K_{O_2}$ (m·s$^{-1}$) is the gas exchange velocity for O$_2$ (Wanninkhof, 1992) and $\rho$ (kg·m$^{-3}$) is the density of seawater. $[O_2]$ and $[O_2]_{sat}$ denote the observed and saturated concentrations of dissolved oxygen (µmol·kg$^{-1}$), respectively. $K_{O_2}$ is empirically expressed as:

$$K_{O_2} = 0.31u^2(S_{O_2}/660)^{-1/2} \times 10^{-2} \times 60^{-1} \times 60^{-1},$$ \hspace{1cm} (7)

where

$$S_{O_2} = 1638 - 81.83t + 1.483t^2 - 0.008004t^3.$$ \hspace{1cm} (8)

Here $u$ is the wind speed at height 10 m a.s.l., $S_{O_2}$ is the Schmidt number for oxygen, $t$ is the sea surface temperature (SST) in degree Celsius. $[O_2]_{sat}$ is defined by:

$$[O_2]_{sat} = f_{O_2} \frac{P - p_{sw}}{1 - p_{sw}},$$ \hspace{1cm} (9)

$$\ln f_{O_2} = A_0 + A_1T_s + A_2T_s^2 + A_3T_s^3 + A_4T_s^4 + A_5T_s^5,$$

$$+ A_6T_s^6 + S(B_0 + B_1T_s + B_2T_s^2 + B_3T_s^3) + C_0S^2,$$ \hspace{1cm} (10)

$$T_s = \ln \left[ \frac{(298.15 - t)(273.15 + t)}{100} \right]^{-1},$$ \hspace{1cm} (11)

$$\ln p_{sw} = \frac{24.5453 - 67.4509(100/T)}{-4.8489 \ln(T/100) - 0.000544S}.$$ \hspace{1cm} (12)

Here $f_{O_2}$ (µmol·kg$^{-1}$) is the solubility of O$_2$ calculated from eq. (8) in Garcia and Gordon (1992), $P$ is the sea level atmospheric pressure (atm) and the coefficients $A_0, A_1, A_2, A_3, A_4, B_0, B_1, B_2, B_3$ and $C_0$ are taken from Benson and Krause (1984) (also listed in Table 1 in Garcia and Gordon, 1992). $T_s$ is the sea surface temperature defined in Garcia and Gordon (1992). $p_{sw}$ (atm) is the vapour pressure of water from eq. (10) in Weiss and Price (1980), $T$ (K) and $S$ are the absolute temperature of SST and the Practical Salinity, respectively. $[O_2]_{sat}$, $f_{O_2}$ and $p_{sw}$ values are also related to oxygen partial pressure in surface seawater, $pO_2^{sw}$ (atm), as:

$$[O_2] = \frac{f_{O_2}P_{O_2}^{sw}}{0.21(1 - p_{sw})}.$$ \hspace{1cm} (13)

We will use the obtained $F_{O_2,sw}$ and $pO_2^{sw}$ values to interpret variations in the APO observed during the
MIRAI cruises. It should be noted that we neglected the bubble effects on $F_{O_2,obs}$, which is caused by steady state $O_2$ anomaly required to balance $O_2$ injected below the surface by bubbles (Keeling et al., 1993, 1998). Keeling et al. (1998) noted that the bubble effects would account for at most 20% of the $[^{[O_2]}] - [O_2]_{sat}$ values in eq. (6). Therefore, the $F_{O_2,obs}$ values in this study could be overestimated by at most 20% relative to the actual air–sea $O_2$ flux.

3. Results and discussion

3.1. $\delta(O_2/N_2)$, $CO_2$ concentration and $\delta^{13}C$ of CO$_2$ observed onboard a research vessel MIRAI

Figures 2–4 show the temporal variations in $\delta(O_2/N_2)$, CO$_2$ concentration and $\delta^{13}C$ of CO$_2$ observed onboard MIRAI for the period 5 September–15 October 2012, 29 August–6 October 2013, and 1 September–9 October 2014, respectively. Sampling locations (in latitude and longitude) are also shown at the bottom of each graph. As seen in Figs. 2–4, $\delta(O_2/N_2)$ and $\delta^{13}C$ show a gradual decrease with time, while CO$_2$ shows a gradual increase. Negative correlations of $\delta(O_2/N_2)$ and $\delta^{13}C$ with CO$_2$ were also observed in the day-to-day variations. It is known that $\delta(O_2/N_2)$ and $\delta^{13}C$ are negatively correlated with CO$_2$ due to fossil fuel combustion and terrestrial biospheric processes (e.g. Keeling et al., 1993; Nakazawa et al., 1997). Furthermore, while seasonal and subseasonal variations in $\delta(O_2/N_2)$ are also affected significantly by the air–sea exchanges of $O_2$ and $N_2$, similar variations in CO$_2$ are less affected by the air–sea exchange of CO$_2$ because of the bicarbonate equilibrium (e.g. Keeling et al., 1993).

To explore possible driver(s) of the variations in $\delta(O_2/N_2)$, $\delta^{13}C$ of CO$_2$ and CO$_2$ concentration, we show the relationships of $\delta(O_2/N_2)$ and $\delta^{13}C$ of CO$_2$ with CO$_2$ concentration in Fig. 5, respectively. By applying linear regression analyses to the $\delta(O_2/N_2)$ and CO$_2$ concentration values observed in 2012, 2013 and 2014, the rates of change in $\delta(O_2/N_2)$ with respect to CO$_2$ were calculated to be $-7.3 \pm 0.5$, $-5.7 \pm 0.3$ and $-6.2 \pm 0.3$ per meg-ppm$^{-1}$, respectively. On the other hand, rates of $-0.041 \pm 0.002$, $-0.046 \pm 0.003$ and $-0.043 \pm 0.001$%o, ppm$^{-1}$ were obtained when $\delta^{13}C$ was regressed against the CO$_2$ concentration values obtained in 2012, 2013 and 2014, respectively.
Past studies have indicated that the rate of change in $\delta^{13}C$ with respect to CO$_2$ is about $-0.05$‰ ppm$^{-1}$ for CO$_2$ exchange between the atmosphere and the terrestrial biosphere, and $-0.005$‰ ppm$^{-1}$ for exchange between the atmosphere and the ocean (e.g. Keeling et al., 1989; Nakazawa et al., 1997). Therefore, the observed rates of $-0.041$ to $-0.046$‰ ppm$^{-1}$ obtained in this study are much closer to the rate expected from the CO$_2$ exchange between the atmosphere and the terrestrial biosphere. The above results do not exclude the possibility of influence from fossil fuel combustion however, since the average $\delta^{13}C$ values in fossil fuels and the terrestrial biosphere are similar and estimated to be about $-28$‰ (e.g. Andres et al., 2000; Ito, 2003). However, we can use CO measurements as an indicator of fossil fuel influence. In Figs. 2–4, CO$_2$ and CO concentrations are also plotted, measured simultaneously by using a gas chromatograph equipped with an Hg reduction detector (Yashiro et al., 2009). We note that the correlations ranging between 0.20 and 0.36 between CO$_2$ and CO are not statistically significant (at $\alpha = 0.02$), and the rates of change of CO with respect to CO$_2$ are lower than 1.0 ppb-pm$^{-1}$ on every cruise. However, as reported in previous studies (e.g. Lai et al., 2010; Niwa et al., 2014), much higher change rates of CO/CO$_2$ (over 10 ppb ppm$^{-1}$) would be expected if fossil fuel combustion is the main contributor to the variations in the observed CO$_2$ concentration. Therefore, it would be reasonable to regard terrestrial biospheric activities as the main contributor to the variations in the CO$_2$ concentration values observed in this study.

If $\delta(O_2/N_2)$ also varies mainly due to terrestrial biospheric activities, then the rate of change in $\delta(O_2/N_2)$ with respect to CO$_2$ is expected to be $-1.1 \times (0.2095)^{-1} = -5.3$ per meg ppm$^{-1}$. Here the value of $-1.1$ is the O$_2$:CO$_2$ exchange ratio for terrestrial biospheric activities reported by Severinghaus (1995). Although there are some discussions about the universal validity of the value of $-1.1$
(e.g. Seibt et al., 2004; Masiello et al., 2008; Worrall et al., 2013; Ishidoya et al., 2015), we assume the value of $-1.1$ throughout this study. The observed rates of change in $\delta$(O$_2$/N$_2$) with respect to CO$_2$ concentration ($-7.3 \pm 0.5$ to $-5.7 \pm 0.3$ per ppm$^{-1}$) obtained in this study are lower than $-5.3$ per ppm$^{-1}$ that would be expected from terrestrial biospheric activities alone. This could result due to contributions from the air–sea O$_2$ and N$_2$ fluxes, as well as from fossil fuel combustion, since the O$_2$:CO$_2$ exchange ratio from the combustion of liquid fuel ($1.44$) and gases ($1.95$) are lower than $1.1$ (e.g. Keeling, 1988; Steinbach et al., 2011). However, based on the evidence given in the previous paragraph, we conclude that the observed change rate of $\delta$(O$_2$/N$_2$)/CO$_2$ can be attributed to the air–sea exchange of O$_2$ and N$_2$ rather than to fossil fuel combustion.

3.2. APO and air–sea O$_2$ fluxes observed onboard a research vessel MIRAI

Following the discussion in Section 3.1, we can extract the oceanic component from the measured values of $\delta$(O$_2$/N$_2$) by using APO defined by eq. (3). The APO values for the periods 5 September–15 October 2012, 29 August–6 October 2013, and 1 September–9 October 2014 are shown in Figs. 6–8, respectively (black filled circles). We have also plotted the APO values calculated from the STAG model driven by F$_{O_2,sw}$ and F$_{N_2,sw}$ (blue crosses). The average value of the simulated APO for each cruise was adjusted as a function of the differences between F$_{O_2,sw}$ and F$_{O_2,at}$ (see discussion below). It can be seen in Figs. 6–8 that the average value of the observed APO decreases from 2012 to 2014. This can be attributed not only to a secular increase in atmospheric CO$_2$ due to fossil fuel combustion for which the average O$_2$:CO$_2$ exchange ratio (about $1.4$) is lower than that of the terrestrial biospheric activity ($1.1$), but also to a secular oceanic CO$_2$ uptake. It can also be seen from Figs. 6–8 that the observed APO values decrease gradually with time for each cruise. This decrease from September to October has been widely observed in the Northern Hemisphere in other studies (e.g. Keeling et al., 1998; Tohjima et al., 2012), and reflects seasonal changes in the air–sea O$_2$ flux. While the simulated APO values show similar seasonal decreasing trend in APO for each cruise, the observed day-to-day variation is significantly underestimated by the model. This underestimation could be due to the difference between F$_{O_2,at}$ used to drive the model and the actual air–sea O$_2$ flux used to calculate the observed APO. In order to show this to be the case, we have also plotted in Figs. 6–8 F$_{O_2,at}$ and F$_{O_2,sw}$ for each cruise.

In Figs. 6–8, F$_{O_2,at}$ shows clear short-term (intra- to inter-diurnal) variations, while F$_{O_2,sw}$ does not. It can be seen that many positive peaks (i.e. emitted from the ocean to the atmosphere) larger than 1 $\mu$mol m$^{-2}$ s$^{-1}$ are associated with F$_{O_2,at}$, while F$_{O_2,sw}$ values are always lower than 0.4 $\mu$mol m$^{-2}$ s$^{-1}$. F$_{O_2,obs}$ is higher by about 0.3 $\mu$mol m$^{-2}$ s$^{-1}$ than F$_{O_2,at}$ on average, throughout the study period 2012–2014. These results strongly suggest
that the short-term variations detected in the observed APO are likely due to the short-term variations in \(F_{O_2,obs}\) as well as the fact that the simulated APO calculated by using \(F_{O_2,cli}\) underestimates the actual APO systematically. Furthermore, as shown in Figs. 6–8, when \(F_{O_2,obs}\) are positive, \(pO_2^{sw}\) values are larger than the partial pressure of \(O_2\) in air (\(pO_2^{air} \approx 0.2095\) atm), with variations in \(F_{O_2,obs}\) to be dependent on variations in \(pO_2^{sw}\) and wind speeds (also plotted in Figs. 6–8). In addition, temporal variations in the observed APO and \(pO_2^{sw}\) resemble each other in shape, especially in 2012 and 2014. These results provide additional evidence that the variation in \(pO_2^{sw}\) is one of the contributing factors in generating temporal variations in the observed APO. In Figs. 6–8, we also plotted the simulated APO values (blue dotted lines) that included the contribution of \(APO_{CO_2,sw}\). The differences between the simulated APO values with or without including the \(APO_{CO_2,sw}\) are very small (0.5 per meg on average). This means that the contribution from the air–sea \(CO_2\) flux to the short-term variations in APO is negligibly smaller than those from the air–sea \(O_2\) and \(N_2\) fluxes, as expected from the relationship between \(CO_2\) and \(\delta^{13}C\) of \(CO_2\) discussed above.

In order to provide a quantitative support for our suggested relationship between the observed APO and \(F_{O_2,obs}\), we used a simple model that assumed a well-mixed planetary boundary layer (PBL). Then, that portion of \(F_{O_2,obs}\) that remained after deducting \(F_{O_2,cli}\) was uniformly mixed into a column of air extended from the surface to PBL height (PBLH) over a 24-hour period (before and after 12 hours relative to the observation time). The PBLH values were taken from the ECMWF ERA-interim reanalysis datasets (Dee et al., 2011) and plotted in Figs. 6–8. Thus calculated values are added to the simulated APO by the STAG model driven by \(F_{O_2,cli}\) and \(F_{N_2,cli}\) and shown by green crosses in Figs. 6–8 (hereafter referred to as the ‘APO

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**Fig. 7.** Same as in Fig. 6 but for the 29 August–6 October 2013.

**Fig. 8.** Same as in Fig. 6 but for the period 1 September–9 October 2014.
calculated by using $F_{O_{2,cli}}$). As mentioned above for the purpose of display, the average values of the simulated APO by STAG have been adjusted to equalise the average values of the observed APO to those of the APO calculated by using $F_{O_{2,obs}}$ for the respective cruises.

Standard deviations (SD) of the observed APO, the APO calculated by using $F_{O_{2,obs}}$ and the APO simulated by using $F_{O_{2,cli}}$ from their respective 4-d running mean values were calculated to be 4, 5 and 1 per meg, respectively, throughout the observation period. Therefore, the short-term variations in APO calculated by using $F_{O_{2,obs}}$ are comparable in magnitude to those in the observed APO but larger than those simulated by using $F_{O_{2,cli}}$. This result is not changed even if we consider the possible overestimation of $F_{O_{2,obs}}$ in this study due to the bubble effects, since the above-mentioned SD of the APO calculated by using $F_{O_{2,obs}}$ is reduced by only 20% (changed from 5 to 4 per meg) by considering the largest bubble effects (see Methods). Furthermore, the gradual decrease in September and the slight increase in October in the observed APO are relatively well reproduced in the calculated APO using $F_{O_{2,obs}}$.

We have also confirmed, based on a backward trajectory analyses using HYSPLIT (Draxler and Rolph, 2003; Rolph, 2003; available from NOAA Air Resources Laboratory at www.ready.arl.noaa.gov/HYSPLIT_traj.php), that the average transport distance of an air parcel for 1-d backward trajectories is roughly about 500 km from the ship. Therefore, it is likely that the short-term variations seen in the observed APO are influenced by the variations in the air–sea $O_2$ flux within a few hundred kilometers from the ship; therefore, $F_{O_{2,obs}}$ has a certain level of regional representativeness. These results imply that a shipboard observation of APO will be a useful constraint for estimating the regional air–sea $O_2$ flux by an inversion analysis, and that a shipboard observation of $F_{O_{2,obs}}$ will be useful to validate the estimated air–sea $O_2$ flux. Estimating regional air–sea $O_2$ fluxes would also be important for evaluating regional marine biological activities. We plotted the partial pressure of $CO_2$ in surface water ($pCO_2^{sw}$) observed onboard MIRAI (Kosugi et al., submitted to Geophys. Res. Lett.) in Figs. 6–8. The $pCO_2^{sw}$ values are generally smaller than the partial pressure of $CO_2$ in air ($pCO_2^{air}$, ~390 μatm in this study), and vary roughly in opposite phase with $pO_2^{sw}$. This suggests that $pO_2^{aw} > pO_2^{air}$ observed in this study, which yields positive $F_{O_{2,obs}}$, is at least partly attributable to super- and under-saturation of $O_2$ and $CO_2$, respectively, caused by marine biological activities. In addition, some local maxima in chlorophyll-a concentration (measured by a fluorometer and calibrated by water-sampled chlorophyll-a data using the fluorometric non-acidification method (Welschmeyer, 1994; see the MIRAI cruise reports in detail)) in the surface water observed onboard MIRAI (also plotted in Figs. 6–8) show a correlation with some local $pO_2^{aw}$ maxima, as well as with positive peaks of $F_{O_{2,obs}}$. This indicates that marine biological activities are one of the significant drivers of $F_{O_{2,obs}}$. Therefore, an inversion
analysis by using ship-based APO is expected to be a useful tool to constrain regional ocean productivity, as Thompson et al. (2008) obtained rough estimates of regional marine net community production based on their ship-based observation by assuming that biology is the principle driver of air–sea O₂ fluxes.

Our results indicate that the simulated APO driven by FO₂cli underestimates the actual APO systematically. Although the region we observed in this study appears to have minimal contribution to the overall global air–sea O₂ flux, if we assume boldly that such an underestimation of the O₂ outflux (or overestimation of the O₂ influx) in FO₂cli is relatively common in other locations in the Northern Hemisphere in the autumn, then it is expected that a decreasing rate in APO from summer to winter will be more rapid in the seasonal cycle of the simulated APO using FO₂cli than that in the observed seasonal APO cycle. Figure 9 shows a comparison between average seasonal components of the observed and simulated APO at Ny-Ålesund (79°N, 12°E), Svalbard for the period 2001–2010 (Ishidoya et al., 2012a) and Sendai (38°N, 140°E), Japan for the period 1999–2009 (Ishidoya et al., 2012b). Best-fitted curves to the observed and simulated data consisting of two-harmonics are also shown. The error bands of the fitted curves to the observed data are evaluated by a similar bootstrap method used in Ishidoya et al. (2012a) (Press et al., 2007). The locations of Ny-Ålesund and Sendai are shown in Fig. 1. In Fig. 9, clear discrepancies in the fall-time temporal decreasing rates of APO can be seen between the observed and simulated APO at both sites. Similar discrepancies are widely seen in the seasonal APO cycles observed at other locations in the Northern Hemisphere (e.g. Battle et al., 2006; Tohjima et al., 2012). In Fig. 9, the best-fitted curves to the simulated APO that included the contribution of APOCO₂, are also shown (blue dashed lines). The seasonal cycles of the simulated APO without the contribution of APOCO₂, are found to be slightly different from those including the contribution, however the differences are much smaller than the fall-time discrepancies between the observed and simulated APO. Therefore, it is suggested that the discrepancy between the observed and simulated seasonal APO cycles is mainly attributable to an uncertainty of FO₂cli rather than that of the air–sea CO₂ flux.

To examine the potential impact of the underestimation of FO₂cli during the fall season, we simply calculated changes in APO expected when a uniformly distributed O₂ flux of 0.3 μmol m⁻² s⁻¹ is emitted into a well-mixed northern hemispheric air from mid-September to the end of November. For the calculation, the total global dry air mass of 5.124 × 10²¹ g was taken from Trenberth (1981) and a mean molecular weight of dry air was assumed to be 29 g mol⁻¹. Then, the calculated fall-time changes in APO were simply added to the best-fitted curves of the simulated APO at Ny-Ålesund and Sendai shown in Fig. 9. The resultant curves, indicated by the green dashed lines in Fig. 9, show similar decreasing rates in the fall as seen in the observed seasonal APO cycles, giving support to our suggestion that FO₂cli underestimates the fall-time fluxes by about 0.3 μmol m⁻² s⁻¹ on average in the Northern Hemisphere. A corollary analysis was conducted by running STAG driven by the adjusted FO₂cli values. In this experiment, the northern hemispheric FO₂cli values were enhanced by 0.3 μmol m⁻² s⁻¹ uniformly from early September to mid-November, and then an arbitrary constant value was subtracted from the global FO₂cli values to adjust the globally integrated annual mean FO₂cli to zero. The best-fitted curves to the simulated APO produced by the adjusted FO₂cli, indicated by the green dashed–two dotted lines in Fig. 9, match the observed fall-time enhancement of APO relative to those simulated by using FO₂cli. However, the seasonal maxima and summer-to-fall decreasing rates found in the simulated APO driven by the adjusted FO₂cli appear later and steeper, respectively, than those in the observed seasonal APO cycles. These results suggest that the discrepancies between the seasonal cycles of the observed APO and the simulated APO driven by FO₂cli cannot be entirely attributed to the underestimation of FO₂cli during the fall season, because the wintertime (December to February) decreasing rates seen in the observed seasonal APO cycles are clearly larger than those seen in the simulated APO.

Causes of the suggested underestimation of FO₂cli may be related to its calculation method, which is based on a linear regression analysis between the air–sea O₂ flux and the air–sea heat flux in 10° latitudinal bands covering the entire ice-free world ocean. Therefore, it is expected that the method would fail to capture that part of the air–sea O₂ flux (such as the one discussed in the paper) unrelated to the air–sea heat flux process. The total flux should include the influence due to a fall-time intrusion of biologically produced shallow oxygen maximum (SOM) to the surface due to the deepening of the mixed layer in the autumn (e.g. Shulenberger and Reid, 1981; Riser and Johnson, 2008). This process is not linearly related to the air–sea heat flux. In this regard, Nishino et al. (2015) reported that a clear SOM was observed in the Arctic Ocean in 2013 during the same MIRAI cruise discussed in this study, especially in the shelf break of Chukchi Sea. They concluded that the observed SOM was not produced by a local phytoplankton growth during the observation period, but might be a remnant of a previous phytoplankton bloom and/or resulted from the spread of O₂ rich water from the Canada Basin. Therefore, the parameterisation of air–sea O₂ flux may be improved by using some biological components, such as chlorophyll-a concentration from satellite observations, in combination with the air–sea heat flux.
4. Conclusions

Atmospheric $\delta(^{18}\text{O}/^{16}\text{O})$, CO$_2$ concentration and $\delta^{13}$C of CO$_2$ were observed onboard R/V MIRAI in the northern North Pacific and the Arctic Ocean during the autumn seasons of 2012–2014. Dissolved oxygen concentration in the near-surface water was also measured continuously during these cruises, and converted to air–sea O$_2$ flux ($F_{\text{O}_2}^{\text{obs}}$). The relationships of $\delta(^{18}\text{O}/^{16}\text{O})$ and $\delta^{13}$C with CO$_2$ concentration indicated that terrestrial biospheric processes and the air–sea O$_2$ flux are the main contributors to the observed variations in CO$_2$ concentration and APO, respectively.

To compare the observed APO values with those simulated using the monthly air–sea O$_2$ flux climatology taken from the TransCom experimental protocol ($F_{\text{O}_2}^{\text{cli}}$), a simulation of APO using the STAG three-dimensional atmospheric transport model forced by $F_{\text{O}_2}^{\text{obs}}$ was also carried out. The observed APO showed larger short-term variations than the simulated APO forced by $F_{\text{O}_2}^{\text{obs}}$, and $F_{\text{O}_2}^{\text{cli}}$ also showed larger variation than $F_{\text{O}_2}^{\text{obs}}$. A simple calculation indicated that the short-term variations in APO produced by using $F_{\text{O}_2}^{\text{obs}}$ were comparable in magnitude to the observed, and the characteristics of the temporal variations in the observed APO were relatively well reproduced by the calculated APO. We conclude that the short-term variations seen in the observed APO are attributable to the short-term variations in the air–sea O$_2$ flux around the observation area. The $F_{\text{O}_2}^{\text{obs}}$ values were systematically higher than the $F_{\text{O}_2}^{\text{cli}}$ values in all cruises, with an average difference of about 0.3 mmol m$^{-2}$ s$^{-1}$. By uniformly mixing the sea-to-air O$_2$ flux of 0.3 mmol m$^{-2}$ s$^{-1}$ from the Northern Hemisphere ocean into the overlying atmosphere during the fall season, it was possible to account for the discrepancies in the APO decreasing rates between the observed and simulated seasonal APO cycles at Ny–Ålesund and Sendai.

The results of the present study show that simultaneous ship observations of APO and $F_{\text{O}_2}^{\text{obs}}$ can be a powerful tool for detailed validation of regional air–sea O$_2$ fluxes, since we can examine the validity of the air–sea O$_2$ flux inferred by an inversion of APO in comparison with $F_{\text{O}_2}^{\text{obs}}$. If it is confirmed that the inversion of APO is valid to estimate the regional air–sea O$_2$ flux, then ship observations of APO is expected to be useful for estimating the regional ocean productivity and mixing, since their changes drive the regional air–sea O$_2$ fluxes.

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