CO₂ system in the oligotrophic northwest Pacific Ocean during the Asian dust storm season

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1. Introduction

The subtropical oligotrophic areas of the open ocean generally act as a relatively weak overall sink for atmospheric CO₂, whose surface water fugacity of CO₂ (fCO₂) is controlled mainly by temperature (Takahashi et al., 2002 and 2009). However, some natural episodes, such as dust events, can induce significant atmospheric deposition of nutrients (e.g. iron, nitrate, and phosphorus) to the surface ocean (Jickells, 1995). This fertilization may stimulate biological production in the oligotrophic region, cannot take place during the ADS period. A model simulation further confirms that the increase of fCO₂ caused by CO₂ inputs from the subsurface water can nearly be compensated for by the fCO₂ decrease resulting from the accompanying cooling effect and the enhancement of biological production. Consequently, even if the Fe and/or P deposition may have increased, nitrogen fixation, a mechanism favoring CO₂ sequestration in the oligotrophic region, can- not take place during the ADS period. Analyses of ADS tracks show that these storms can be entrained into the troposphere and subsequently transported by the prevailing westerly winds to the northwest Pacific and beyond (Zhang et al., 1997). Analyses of ADS tracks show that these storms often pass through the highly populated and industrialized regions of China, such as the surroundings of Beijing and Shanghai, before leaving the coast (Hoell et al., 1997). Therefore, large quantities of air pollutants spewing out of mainland China can accompany the Asian dust advection. These anthropogenic pollutants are frequently rich in nutrients (e.g. NO₃, P) and/or they can leach the nutrients (e.g. Fe) from the dust particles into the surface ocean; thus they may also appreciably affect ecosystem productivity in the North Pacific Ocean (Meskhidze et al., 2005; Hsu et al., 2010a).

Compared to the well-documented enhancement of primary and export production and fCO₂ drawdown following dissolved iron addition in the "high-nutrient-low-chlorophyll" region during the mesoscale iron enrichment experiments, the present results show that no significant drawdown of fCO₂ was found following an ADS event, despite the fact that an approximately 3-fold increase of Chl a was observed. This may be attributed to the fact that nutrients from the wind-induced entrainment of subsurface water, rather than atmospheric deposition, were the major source stimulating biological production. The entrained nitrate not only comes with it high CO₂ but also may have rendered an unfavorable environmental condition for nitrogen fixers to compete with other picophytoplanktons. Consequently, even if the Fe and/or P deposition may have increased, nitrogen fixation, a mechanism favoring CO₂ sequestration in the oligotrophic region, cannot take place during the ADS period.

To explore the effect of atmospheric forcing on the CO₂ system in the subtropical northwest Pacific Ocean, which is oligotrophic and nitrogen limited, total alkalinity (TA), dissolved inorganic carbon (DIC), fugacity of CO₂ (fCO₂), and other pertinent data (i.e. temperature, salinity, and concentrations of nitrate and chlorophyll a (Chl a)) were collected from 7 cruises during the spring Asian dust storm (ADS) periods of 2007 and 2008. In contrast to the reported substantial fCO₂ decrease following dissolved iron addition in the “high-nutrient-low-chlorophyll” region during the mesoscale iron enrichment experiments, the present results show that no significant drawdown of fCO₂ was found following an ADS event, despite the fact that an approximately 3-fold increase of Chl a was observed. This may be attributed to the fact that nutrients from the wind-induced entrainment of subsurface water, rather than atmospheric deposition, were the major source stimulating biological production. The entrained nitrate not only comes with it high CO₂ but also may have rendered an unfavorable environmental condition for nitrogen fixers to compete with other picophytoplanktons. Consequently, even if the Fe and/or P deposition may have increased, nitrogen fixation, a mechanism favoring CO₂ sequestration in the oligotrophic region, cannot take place during the ADS period.

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North Pacific, Southern Ocean, and Equatorial Pacific) during the meso-scale iron enrichment experiments, which was designed to mimic the biogeochemical response to dust deposition (Boyd et al., 2007 and 2010 and references therein), reports on the effects of atmospheric dust on the biogeochemistry of oligotrophic regions are relatively scarce (Neuer et al., 2004). A few previous studies have shown significant correlations between the stimulation of primary and export production and episodic ADS events (Ditullio and Laws, 1991; Young et al., 1991; Hung et al., 2009), and as a result, one may speculate that sea surface CO₂ uptake may be enhanced as well. To our knowledge, the potential impact of ADS events on the surface CO₂ system has never been investigated in the oligotrophic subtropical North Pacific.

Within the framework of the Long-term Observation and Research of the East China Sea program (LORECS), a Taiwanese contribution to the international Surface Ocean–Lower Atmosphere Study (SOLAS), intensive sea-based observations were conducted during the prevailing ADS season (spring) in 2007 and 2008 to investigate the biogeochemical responses to ADS events in the subtropical northwest Pacific Ocean, which is oligotrophic and nitrogen-limited water (Gong et al., 1999). During this unique opportunity, we collected seawater samples in the top 250 m of the water column for determination of dissolved inorganic carbon (DIC) and total alkalinity (TA). Along with carbonate chemistry parameters, temperature, salinity, and concentrations of nitrate and chlorophyll a (Chl a) were also examined. The purpose of this study is to investigate the variability of the CO₂ system during the prevailing ADS season and to examine the potential impact of ADS events on the capacity for CO₂ sequestration in the oligotrophic northwest Pacific Ocean.

2. Materials and methods

2.1. Sampling

The sampling site is located in the subtropical northwest Pacific Ocean, approximately 160 km northeast of Taiwan (123.15°E, 25.10°N, water depth = 1690 m, asterisk in Fig. 1). Gong et al. (1999) reported in the upper 50 m of the water column, nitrate concentrations around the study area were under detection limit and Chl a concentrations were below 0.2 mg m⁻³ all year round, suggesting that the sampling site is oligotrophic. The wind speed data (daily average) used in this study was measured at the meteorological station on Pengjia Island (diamond in Fig. 1), provided by the Central Weather Bureau of Taiwan. Hourly aerosol concentrations data (suspended particulates < 10 μm, abbreviated as PM₁₀) were collected at Keelung City (square in Fig. 1), which is the nearest air quality monitoring station to the study site, maintained by the Environmental Protection Administration of Taiwan (http://taqm.epa.gov.tw/taqm/en/YearlyDataDownload.aspx). The details of the aerosol sampling can be found on the website of Taiwan air quality monitoring network (http://taqm.epa.gov.tw/taqm/en/default.aspx).

During the course of this study, the study site was visited 18 times during 7 discrete cruises aboard the R/V Ocean Researcher II. The cruises were conducted on March 16 (CR1), 21–22 (CR2), 29–31 (CR3) and April 10–12 (CR4) in 2007, and on March 27–29 (CR5), April 6–8 (CR6) and 11–13 (CR7) in 2008. Discrete water samples at twelve depths of 5, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 m were collected between 8:00 and 10:00 am during each investigation, using Go-Flo bottles mounted onto a rosette sampling assembly. Subsamples for DIC and TA analyses were transferred into 350 mL pre-cleaned borosilicate bottles, and 200 μL of HgCl₂-saturated solution was immediately added.

2.2. Analytical methods

Depth profiles of temperature and salinity were recorded using a Seabird SBE9/11-plus conductivity-temperature-depth (CTD) system. For the water samples collected in 2007, DIC was measured using the coulometric method (Johnson et al., 1993). The single operator multiparameter metabolic analyzer (SOMMA) system was used to extract
Fig. 2. Temporal variations of (a) and (b) daily wind speed, (c) and (d) daily concentration of aerosols (PM$_{10}$, averaged from hourly data); and (e) and (f) TA, (g) and (h) DIC, (i) and (j) fCO$_2$, (k) and (l) nitrate, and (m) and (n) Chl a for the surface waters (0 to 25 m) during the ADS season (between 15 March and 15 April) of 2007 (a, c, e, g, i, k and m) and 2008 (b, d, f, h, j, l and n). Asian dust storm (ADS) event is defined as when the concentrations of aerosols (PM$_{10}$) $> 100\ \mu g\ m^{-3}$.  

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CO₂ from acidified seawater samples, and the extracted CO₂ was quantified by a coulometric detector (UIC Coulometric Inc., model 5011). For the water samples collected in 2008, DIC was determined with an automated DIC analyzer (Apollo SciTech Inc., model AS-C3), in which a nondispersive infrared CO₂ analyzer (Li-COR, LI-7000) was used to detect the total CO₂ gas concentration (Cai and Wang, 1998). CO₂ certified reference materials (CRMs) provided by A. G. Dickson (SIO, UCSD) were used for calibration and accuracy.

Fig. 3. Depth distributions of (a) temperature, (b) salinity, (c) TA, and (d) DIC during the cruises in the spring 2007 (CR1 to CR4). Superimposed horizontal lines in (a) indicate the surface mixed-layer depth. Depth distributions of (e) fCO₂, (f) Nitrate and, (g) Chl a during the cruises in the spring 2007 (CR1 to CR4).
assessment for both methods. A comparison experiment showed that the difference between these two methods was 2.4 μmol kg\(^{-1}\) (n = 8; Chou et al., 2011), which is within the uncertainty of DIC measurements (both methods’ uncertainties are less than 0.1%). TA was measured by Gran titration of a 20 ml seawater sample in an open-cell setting (Cai et al., 2010). The titrant (0.1 N HCl) was standardized using the CRM. Each sample was titrated at least twice with a precision of 0.1%. Fugacity of CO\(_2\) (fCO\(_2\)) was calculated from DIC and TA using the CO2SYS program (Lewis and Wallace, 1998), in which the dissociation constants for carbonic acid of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and for KHSO\(_4\) of Dickson (1990) were used. Errors in the computed fCO\(_2\) were estimated to be ±5 μatm deriving from the uncertainties in the measurements of DIC and TA.

Water samples for Chl \(a\) analysis were immediately filtered through a GF/F filter paper (Whatman, 47 mm), and the filter paper was stored at −20 °C. The Chl \(a\) retained on the GF/F filters was determined fluorometrically on a Turner Design 10-AU-005 field fluorometer. Water samples for the determination of nitrate concentrations were placed in 100 ml polypropylene bottles and frozen immediately with liquid nitrogen. Nitrate was analyzed with a custom-made flow injection analyzer. The precision for the nitrate analysis was 0.3 μmol kg\(^{-1}\), based on 6 duplicated measurements of a reference solution with a concentration of 10 μmol kg\(^{-1}\). Detailed descriptions of Chl \(a\) and nitrate analyses were described elsewhere (Gong et al., 1999, 2003).

3. Results

3.1. Temporal variations of wind speed, PM\(_{10}\), TA, DIC, fCO\(_2\), nitrate, and Chl \(a\) in surface water

Temporal variations of daily wind speed and PM\(_{10}\) concentration between March 15 and April 15 in 2007 and 2008 are shown in Fig. 2a–d. According to the definition of the Environmental Protection Administration of Taiwan, only one ADS event was observed during the entire sampling period on April 2nd and 3rd (i.e. PM\(_{10}\) concentration > 100 μg m\(^{-3}\)), accompanied by a relatively high wind speed of about 10.2 m s\(^{-1}\). Two cruises, CR3 (29–31 March 2007) and CR4 (10–12 April 2007) were conducted, respectively, 6 days before and 7 days after the ADS event. Hereafter, results from CR3 and CR4 were used to represent the pre-ADS and post-ADS conditions.
Surface TA varied within a relatively narrow range from 2275 to 2287 μmol kg$^{-1}$ in 2007 and from 2252 to 2274 in 2008 (Fig. 2e and f). The apparently elevated TA in 2007 may reflect the fact that sea surface salinity (SSS) was higher in 2007 than that in 2008 (34.5 to 34.7 vs. 34.2 to 34.4; Figs. 3b and 4b), consistent with the consensus that TA is primarily controlled by the same factors affecting salinity (e.g. precipitation, evaporation, and water mass mixing) in the open ocean (Millero et al., 1998). DIC varied from 1943 to 1959 μmol kg$^{-1}$.

![Fig. 4. Depth distributions of (a) temperature, (b) salinity, (c) TA and, (d) DIC during the cruises in the spring 2008 (CR5 to CR7). Superimposed horizontal lines in (a) indicate the surface mixed-layer depth. Depth distributions of (e) CO$_2$, (f) Nitrate, and (g) Chl a during the cruises in the spring 2008 (CR5 to CR7).]
in 2007, and from 1925 to 1945 μmol kg⁻¹ in 2008 (Fig. 2g and h). Similar to the case of TA, DIC values in 2007 were appreciably higher than that in 2008, implying that the same factors affecting salinity may also play an important role in regulating DIC variation. The surface water’s fCO₂ remained fairly constant between 325 and 346 μatm in both 2007 and 2008 (Fig. 2i and j), which was lower than the atmospheric fCO₂ (376–378 μatm) measured at Yonagunijima Island (triangle in Fig. 1; http://www.esrl.noaa.gov/gmd/ccgg/globalview/co2/co2_intro.html). This indicated that the study area acted as a sink of atmospheric CO₂ during the sampling period. This result is in agreement with the previous finding that the subtropical and temperate North Pacific Ocean is a CO₂ sink in spring (Takahashi et al., 2009). Unlike TA and DIC, no appreciable fCO₂ difference was found between 2007 and 2008.

Nitrate concentration generally remained at a low level (<0.2 μmol kg⁻¹) throughout the period of this study except for a few relatively high values (>0.3 μmol kg⁻¹) that were observed during CR1 and CR4 (Fig. 2i and j). Chl a concentration varied from 0.10 to 0.55 mg m⁻³ (Fig. 2m and n) and, as expected, Chl a during CR4 was noticeably higher than that during CR3, suggesting that the ADS event may have led to an increase of phytoplankton biomass. The potential impact of the ADS event on carbon biogeochemical cycling in the study area will be examined in Section 4.1.

3.2. Depth distributions of temperature, salinity, TA, DIC, fCO₂, nitrate, and Chl a in spring 2007 and 2008

Depth distributions of temperature, salinity, TA, DIC, fCO₂, nitrate, and Chl a in 2007 and 2008 are shown in Figs. 3a–g and 4a–g, respectively.

Surface mixed layer depth (MLD), defined as the surface layer with a potential density (σθ) variation of less than 0.1 kg m⁻³ (Gong et al., 1999), was deepest during CR4 (86 to 90 m), followed by CR1 and CR2 (68 to 81 m), and shallowest during CR3 (28 to 50 m) in 2007 (horizontal lines in Fig. 3a). The remarkable deepening of MLD between CR3 and CR4 suggests that the high winds accompanying the ADS event may have greatly enhanced vertical mixing of the water column. In 2008, a dramatic MLD shoaling from 132 m (April 6) to 30 m (April 8) was found during CR6 (horizontal lines in Fig. 4a), implying that there might be a significant alteration in the horizontal advection pattern at the sampling site during this period.
As shown in Figs. 3b and 4b, salinity remains essentially constant within the MLD, and then it increases gradually with depth to a core with maximum of 34.85 to 34.90, centered at the depth range between 150 and 200 m, which represents the well-defined high-salinity North Pacific Tropical Water (Suga et al., 2000). Although the general vertical distribution pattern of salinity in 2007 and 2008 is very similar, the core salinity maximum is more pronounced and deeper in 2008 than that in 2007. In general, the vertical distribution of TA mimics the pattern of salinity, that is, it stays steady within the MLD and then increases to a maximum core of 2290 to 2300 μmol kg⁻¹ located between 150 and 200 m (Figs. 3c and 4c). The strong positive correlation between TA and salinity (r = 0.89, n = 200; data not shown) suggest that the same factors affecting salinity are the predominant process controlling vertical variations of TA.

As shown in Figs. 3b and 4b, DIC shows little variation within the MLD, and then it increases continuously with depth in both 2007 and 2008 (Figs. 3d and 4d). Unlike TA, DIC does not show a core with a maximum at depths between 150 and 200 m, implying that biological effects (e.g. respiration in subsurface water) dominate over the salinity-related effect in regulating the vertical variation of DIC. Consistent with the above pattern of TA and DIC vertical distributions, fCO₂ generally varies within a narrow range in the MLD, and then increases progressively with depth (Figs. 3e and 4e).

4. Discussion

4.1. Comparison between the pre-ADS (CR3) and post-ADS (CR4) cruises

With the intention of examining the potential impact of ADS events on the biogeochemical cycles in the surface ocean, average MLD, Chl a, nitrate, TA, DIC, and fCO₂ in surface waters (within the top 25 m) during cruises CR3 and CR4 were compared in Fig. 5. Differences in all parameters between the two cruises were assessed using an analysis of variance (F-test) followed by a comparison of means (t-test), and a significance level of 0.05 was used to determine significant statistical differences.

As shown in Fig. 5a and b, MLD was significantly deeper and Chl a was significantly higher during CR4 than CR3, suggesting that the enhanced vertical mixing after the ADS event may have delivered nutrients from the subsurface water into the photic zone and stimulated biological production. The enhanced biological production may consume nitrate and CO₂, and thus could partially cancel out the increments of nitrate and DIC derived from the MLD deepening (note that nitrate and DIC increased rapidly with depth below the MLD).
As depicted in Fig. 5f, fCO2 did not show significant difference either between CR3 and CR4. The potential effect of the ADS event on the variation of surface water fCO2 may largely depend on the major nutrient source stimulating biological production. The enhanced biological production associated with nutrient input from atmospheric deposition can result in a net CO2 uptake and reduce surface water fCO2. By contrast, the flux of nutrient from subsurface not only can stimulate production, but because the entrainment of subsurface water is accompanied by a corresponding upward flux of CO2, its net contribution to decrease surface water fCO2 is much reduced. The insignificant statistical difference in fCO2 between CR3 and CR4 implies that the entrainment of subsurface water may be the dominant nutrient source, rather than the atmospheric deposition, being responsible for the elevated biological production after the ADS event.

Recently, based on the data collected from drifting sediment traps during the same period of 2007 at our study site, Hung et al. (2009) reported that the POC export flux was 2–3-fold higher during the ADS period than non-ADS period. The authors estimated that nitrogen input from both dry and wet atmospheric deposition can accounts for only 10% of the nitrogen export through the base of the euphotic zone (Chen and Chen, 2008; Chen et al., 2010), and thereby they inferred that the wind-induced vertical mixing must be the primary mechanism delivering nutrients into the photic zone to stimulate the biological production and the subsequent enhancement of POC export flux during the ADS period. Our result thus is in good agreement with Hung et al’s (2009) finding. Furthermore, Hsu et al. (2010b) reported that the dust deposition flux of dissolved inorganic nitrogen (DIN, i.e. the sum of nitrate and ammonium) was about 56 ± 68 μmol m−2 day−1 during the cruises in 2007 noted in this study. Assuming an ADS event lasting approximately 3 days and MLD deepening to 88 m (the average MLD during CR4), the DIN contributed from dust deposition within the MLD is estimated to be 0.0019 ± 0.0023 μmol kg−1. This DIN input can cause a maximum DIC drawdown of 0.012 ± 0.015 μmol kg−1 through biological consumption with the conventional Redfield ratio (C/N = 106/16), which can lead to an fCO2 decrease of only 0.019 ± 0.024 μatm, providing that the initial DIC and TA is 1954 and 2282 μmol kg−1 (the average values of surface waters during CR4), respectively. This calculation, therefore, further supports the notion that the DIN input from dust deposition may not play a major role on fCO2 variation.

The net fCO2 change in response to the MLD deepening is mainly controlled by the preformed DIC/Nitrate ratio in the entrained subsurface water, the subsequent biological removal of C/N ratio, and temperature change. As shown in Fig. 6, the preformed DIC/Nitrate ratio in the subsurface water (75 to 150 m) in the study area was approximately 17.5, which is much higher than the Redfield ratio (6.6). Therefore, if the enhanced biological production followed the conventional Redfield ratio, there would be excess DIC left behind, which would lead to an increase of fCO2. However, this potential increase of fCO2 could be compensated for by the cooling effect accompanied with the MLD deepening (Fig. 3a). As a combined result, no significant statistical difference in fCO2 was found between CR3 and CR4 (Fig. 5f), suggesting that the combined effects of MLD deepening (i.e. the entrainment of nitrate and CO2-replete subsurface water, the cooling effect, and the stimulated biological production), indeed may largely account for the observed insignificant fCO2 variation between the pre-ADS and post-ADS cruises.

Moreover, we noticed that a dramatic MLD shoaling event from 132 m on April 6 to 30 m on April 8 occurred during CR6 in 2008 (Fig. 4a). This most likely reflected a change in lateral advection pattern. Similar to the above 2007 result, Chl a concentration was higher when MLD was deeper (0.29 vs. 0.11 mg m−2; Fig. 2n), while fCO2 was slightly higher when Chl a was greater (344 vs. 334 μatm; Fig. 2j). This result also supports our argument that the increase of biological biomass after MLD deepening does not necessarily lead to the decrease of fCO2, which is controlled by a complex interplay of physical, chemical and biological processes associated with the vertical advection of water column.

In contrast to the result of the present study (i.e. no significant fCO2 change before and after the ADS event), significant surface fCO2 drawdown induced by the Australian dust storms was observed in “High-Nutrient-Low-Chlorophyll” (HNLC) region of the Southern Ocean (Breivik et al., 2006; Grabin et al., 2010). The discrepancy between these studies may be attributed to the difference of limiting nutrients and the associated biological responses in the two diverse oceanic regimes. In the HNLC region such as the Southern Ocean, photosynthesis by marine phytoplankton is thought to be limited by the availability of iron (Martin, 1990). Dust emission can relax Fe limitation and produce significant increase of phytoplankton biomass, thus decreasing the surface fCO2 (Ptrat et al., 2007). The iron fertilization experiment in the Southern Ocean showed that the decrease in fCO2 estimated to be about 0.4 μmol kg−1 (ΔNO3 = 0.4 μmol kg−1), assuming a homogeneous vertical mixing of the top 100 m of water column during CR3.

The simulated results showed that fCO2 would concurrently increase by about 12 μatm (ΔfCO2 = 12 μatm) as a result of the deepening of MLD (solid arrow in Fig. 7). The cooling effect of 0.6 °C (i.e. the observed temperature difference between CR3 and CR4) would cause a decrease of fCO2 of 9 μatm (dotted arrow in Fig. 7). The stimulation of biological production could result in a maximum fCO2 reduction of only 4 μatm when the supplied nitrate was exhausted (dashed arrow in Fig. 7). In summary, the net fCO2 variation (ΔfCO2) in response to the MLD deepening would range from 3 to −1 μatm, depending on the subsequent consumption level of the supplied nitrate. This simulated result is reasonably consistent with the observed fCO2 variation between CR3 and CR4 (Fig. 5f), suggesting that the combined effects of MLD deepening (i.e. the entrainment of nitrate and CO2-replete subsurface water, the cooling effect, and the stimulated biological production), indeed may largely account for the observed insignificant fCO2 variation between the pre-ADS and post-ADS cruises.
may be mostly caused by the iron-mediated diatom bloom (Boyd et al., 2000; Watson et al., 2000). In contrary, the oligotrophic subtropical waters are generally nitrogen-limited and populated by nitrogen-fixers (Karl et al., 1997). It has been reported that nitrogen-fixers in these waters do respond to iron and/or phosphorus additions and hence may respond to aerosol Fe and/or P deposition during the dusty period (Mills et al., 2004). Similar to the diatom bloom in the HNLC region, if ADS event has induced the bloom of diazotrophs in the oligotrophic subtropical waters, it might also have the potential to cause fCO2 drawdown in surface water. However, as discussed earlier, nitrogen from the entrainment of subsurface water could be the dominant source responsible for the observed increase of phytoplankton biomass during the ADS period, and it would also concomitantly render an adverse ecological condition for the competition of nitrogen-fixers, as the absence of nitrate is one of conducive conditions to the occurrence of nitrogen fixation (Karl et al., 1997). In fact, Chung et al. (2010) recently reported that the observed elevated phytoplankton biomass during the ADS period of 2006 at our study site reflected mainly the stimulation of Synechococcus, and no Trichodesmium (the major nitrogen fixer in the study area; Chen et al., 2008) was found. Accordingly, it appears that even if the ADS event may have increased Fe and/or P deposition, nitrogen-fixers seemed to be hard to compete with other picophytoplanktons (e.g., Synechococcus), which could utilize nutrients from subsurface water entrainment and/or atmospheric deposition, and thus could not play a significant role on the variation of fCO2 in our study area.

Based on the above discussion, we suggest despite the fact that the elevated phytoplankton biomass might have resulted in the enhancement of POC export during the ADS period (Hung et al., 2009), it might not contribute much to sequestrate CO2 from the atmosphere in the oligotrophic subtropical northwest Pacific waters.

Fig. 8. Linear regressions of fCO2 vs. (a) temperature, (b) Chl a, and (c) salinity; DIC vs. (d) temperature, (e) Chl a, and (f) salinity; and TA vs. (g) temperature, (h) Chl a, and (i) salinity for the surface waters (0 to 25 m) in the spring 2007 and 2008 at the study site. The solid lines in each panel are the best fits of least squares to the annual data in 2007 and 2008, and the dashed lines in (f) and (i) are the best fits of least squares to the pool data of 2007 and 2008. r = correlation coefficient.
4.2. Relationships between carbon chemistry parameters and temperature, salinity and Chl a in surface waters in 2007 and 2008

The relationships between carbonate chemistry parameters (i.e., DIC, TA, and fCO₂) and temperature, salinity, and Chl a concentration in surface waters for data collected in 2007 and 2008 are shown in Fig. 8a-i. Unlike good positive correlations found in other oligotrophic areas (Bates et al., 1996; Winn et al., 1998; Chou et al., 2006), fCO₂ is moderately positively correlated with temperature in 2007 (r = 0.45), but negatively correlated in 2008 (r = −0.53) in the study area (Fig. 8a), suggesting that temperature is not the predominant factor regulating the intra seasonal variation of fCO₂ in spring. Weak negative correlations between fCO₂ and Chl a (Fig. 8b) were found both in 2007 (r = −0.27) and 2008 (r = −0.15), implying that the effect of biological production may have been masked by other processes as discussed earlier. A moderate correlation, either negative or positive, was found between fCO₂ and salinity in 2007 (r = −0.45) and 2008 (r = 0.40), respectively (Fig. 8c). In fact, no good correlations between fCO₂ and these parameters may not be unanticipated. As discussed in Section 4.1, temperature and Chl a changes were generally in tandem with the enhancement of vertical mixing, their effects on fCO₂ variation may largely be canceled out by the entrainment of CO₂-replete subsurface waters. Consequently, good correlation between fCO₂ and any single hydrographic parameter can not be expected.

Contrasting to the generally weak correlations between fCO₂ and environmental parameters, both DIC and TA have stronger correlations with salinity (Fig. 8f and i). Furthermore, the correlations between DIC and TA and salinity did not show strong inter annual variability between 2007 and 2008, suggesting that variation of salinity could be a good proxy for DIC and TA variations. The best fits of least squares of DIC and TA with salinity for the pool data of 2007 and 2008 were calculated as follows (the dashed lines in Fig. 8f and i):

$$\text{DIC} = 55.07 \text{ salinity} + 44 \quad (r = 0.93; \text{rms} = 3.8)$$
$$\text{TA} = 53.07 \text{ salinity} + 442 \quad (r = 0.93; \text{rms} = 3.9)$$

where rms denoting root mean square deviation between the measured values and those predicted from the equation. The good correlations of DIC and TA with salinity suggest that a high temporal resolution characterization of the entire carbonate system may be obtained using the above empirical algorithms, if high resolution salinity data in conjunction with temperature data were available, e.g., from moorings. Nonetheless, the overall uncertainty for the prediction of fCO₂ from the empirical relationships of DIC and TA can be as large as approximate ± 13 μatm, which represents the propagation error deriving from the uncertainties of DIC and TA both in their empirical functions and in their measurements. Therefore, the empirical algorithms would be more useful in studying the variation of carbonate system during the severe weather conditions, which can induce potentially large perturbation but hamper any vessel-based investigation (e.g. the passage of ADS).

Based on extensive historical data collected during the 1990s, Lee et al. (2000 and 2006) proposed that TA and DIC in the northern subtropical Pacific could be expressed as a function of sea surface salinity (SSS) and temperature (SST):

$$\begin{align*}
\text{TA} &= 2305 + 58.66(\text{SSS} - 35) + 2.32(\text{SSS} - 35)² - 1.41(\text{SST} - 20) + 0.04(\text{SST} - 20)² \\
\text{DIC} &= 1950 + 2.570(\text{SSS} - 29) + 0.640(\text{SSS} - 29)² \times \text{SSS} / 35
\end{align*}$$

Fig. 9 shows the comparison of the measured TA and DIC and those predicted from the empirical relationships established by Lee et al. (2000 and 2006) and this study. Both algorithms provided satisfactory predictions for TA with rms of 4.7 and 3.9 μmol kg⁻¹, respectively (Fig. 9a). However, the predicted DIC level from Lee et al. (2000) was consistently lower than the measured DIC by about 23 μmol kg⁻¹ (rms) (Fig. 9b). The discrepancy could be attributed to the different sampling time between that of Lee et al. (2000) and ours (1991–1996 vs. 2007–2008) because more anthropogenic CO₂ must have accumulated in surface waters. Assuming that the DIC increase rate at the Hawaii Ocean Time series (HOT) site, ranging from 1.2 to 2.8 μmol kg⁻¹ yr⁻¹ between 1988 and 2002 (Dore et al., 2003; Keeling et al., 2004), is applicable in our study area, the underestimate of ~23 μmol kg⁻¹ from Lee et al.’s (2000) algorithm was thus in reasonable agreement with the potential increase of DIC between 1991–1996 and 2007–2008 in the North Pacific. Based on this comparison, we suggest that the relationship of TA with other hydrographic parameters (e.g. SSS and SST) may be more suitable to serve as an time-independent empirical algorithm for the study of the carbonate system than DIC does, as the uptake invasion of anthropogenic CO₂ can cause DIC increase and thus alter its existing empirical algorithm, but does not change TA. Moreover, DIC increase...
induced by the invasion of anthropogenic CO₂ between different sampling periods need to be taken into consideration before using any documented DIC empirical equation.

5. Summary and concluding remarks

In contrast to the considerable surface fCO₂ drawdown in response to the dust storms in the HNLC region, this study shows no significant fCO₂ difference before and after an ADS event in the subtropical northwest Pacific Ocean, which is oligotrophic and nitrogen-limited. The insignificant variation of fCO₂ may be attributed to the fact that nutrients input through wind-enhanced vertical mixing, rather than atmospheric deposition, was the major source fueling the elevated biological production during the ADS period. A simple simulation further reveals that the controlling processes of fCO₂ associated with the MLD deepening, including the nutrient and CO₂ inputs from the subsurface water, the cooling effect, and the stimulated biological production, may cancel out one another and thus resulting in the observed insignificant variation of fCO₂ before and after an ADS event. Additionally, the nitrate from subsurface water entrainment might cause an adverse condition for diazotrophs to transition, was the major source fueling the elevated biological production before and after an ADS event. Additionally, the nitrate from subsurface waters accompanying the dust storm events also need to be taken into account for both modeling and observational studies ascribing distinct biogeochemical signals to dust supply, in particular to the oligotrophic waters.

Furthermore, the comparison of TA and DIC predictions from the present and previous empirical relationships shows that both algorithms provided satisfactory predictions for TA, but the predicted DIC from the earlier algorithm (Lee et al., 2000) was constantly underestimated by approximate 23 μmol kg⁻¹, which may reflect the accumulation of anthropogenic CO₂ since the sampling time of the data used in Lee et al. (2000). Accordingly, the relationship of TA with other hydrographic parameters would be better than that of DIC to be taken into account for both modeling and observational studies ascribing distinct biogeochemical signals to dust supply, in particular to the oligotrophic waters.

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