Ocean Science Journal, *Vol. 43 No. 4, 195-208(2008)*

Article

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Prediction of Surface Ocean pCO_2 from Observations of Salinity, Temperature and Nitrate: the Empirical Model Perspective

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Received 12 August 2008; Revised 2 December 2008; Accepted 11 December 2008

Abstract – This paper evaluates whether a thermodynamic ocean-carbon model can be used to predict the monthly mean global fields of the surface-water partial pressure of CO_2 (pCO_{2SEA}) from sea surface salinity (SSS), temperature (SST), and/or nitrate (NO_3) concentration using previously published regional total inorganic carbon (C_T) and total alkalinity (A_T) algorithms. The obtained pCO_{2SEA} values and their amplitudes of seasonal variability are in good agreement with multi-year observations undertaken at the sites of the Bermuda Atlantic Time-series Study (BATS) (31°50′N, 60°10′W) and the Hawaiian Ocean Time-series (HOT) (22°45′N, 158°00′W). By contrast, the empirical models predicted C_T less accurately at the Kyodo western North Pacific Ocean Time-series (KNOT) site (44°N, 155°E) than at the BATS and HOT sites, resulting in greater uncertainties in pCO_{2SEA} predictions. Our analysis indicates that the previously published empirical C_T and A_T models provide reasonable predictions of seasonal variations in surface-water pCO_{2SEA} within the (sub) tropical oceans based on changes in SSS and SST; however, in high-latitude oceans where ocean biology affects C_T to a significant degree, improved C_T algorithms are required to capture the full biological effect on C_T with greater accuracy and in turn improve the accuracy of predictions of pCO_{2SEA}.

Key words – global carbon cycle, pCO_2, total inorganic carbon, total alkalinity, remote sensing

1. Introduction

Varying rates of CO_2 exchange between the atmosphere and ocean are one of the key factors in regulating the rate of increase in atmospheric CO_2 concentrations (*e.g.* Tans *et al.* 1990; Quay *et al.* 1992; Keeling *et al.* 1996; Takahashi *et al.* 1997, 2002; Sabine *et al.* 2004). Our understanding of CO_2 fluxes at the air–sea interface is derived mainly from conventional shipboard measurements of the partial pressure difference in CO_2 ($\Delta pCO_2 = pCO_{2AIR} - pCO_{2SEA}$) between surface-water pCO_2 (pCO_{2SEA}) and marine atmospheric pCO_2 (pCO_{2AIR}) (*e.g.* Poisson *et al.* 1993; Inoue *et al.* 1995; Takahashi *et al.* 1997, 2002, 2006; Feely *et al.* 1999, 2006; Zeng *et al.* 2002; Metzl *et al.* 2006); however, *in situ* shipboard pCO_{2SEA} measurements fall far short of the spatial and temporal resolution required to determine monthly, seasonal, or interannual variability in pCO_2 for the global ocean.

To overcome this lack of *in situ* pCO_{2SEA} data, many previous studies have deduced pCO_{2SEA} from changes in sea surface temperature (SST) via algorithms that relate regionally and seasonally variable values of pCO_{2SEA} to SST (*e.g.* Tans *et al.* 1990; Stephens *et al.* 1995; Landrum *et al.* 1996; Bates *et al.* 1998; Lee *et al.* 1998; Lefèvre and Taylor 2002; Cosca *et al.* 2003; Olsen *et al.* 2003; Park *et al.* 2006). This approach is founded on the assumption that variations in SST capture much of the variability of surface-water pCO_{2SEA} associated with the influence of thermodynamic, transport, and biological effects.

Surface-water pCO_{2SEA} values are also predicted from total dissolved inorganic carbon (C_T) and total alkalinity (A_T) using a thermodynamic ocean-carbon model (*e.g.* Loukos *et al.* 2000; Gruber *et al.* 2002; Dore *et al.* 2003; Bates, 2006; Sarma *et al.* 2006; McNeil *et al.* 2007).

Such studies have documented strong region-specific relationships between marine inorganic CO_2 parameters (*e.g.* C_T and A_T) and hydrographic (*e.g.* salinity and temperature) and/or biological (*e.g.* nutrients or chlorophyll *a*) parameters.

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Of the predictor variables that are directly or indirectly related to variations in C_T and A_T, variations in sea surface salinity (SSS) are known to be the key factor that affects variations in both C_T and A_T concentrations. In addition to the effects of variations in SSS, seasonal changes in the intensity of higher-latitude convective mixing of deep C_T- and A_T-rich water commonly make a significant contribution to variations in C_T and A_T concentrations. Accordingly, many previous studies have used variations in SST as a proxy for changes in surface-water A_T and C_T related to convective mixing.

An important factor that affects only surface-water C_T to a significant degree is biological activity. As part of the variation in C_T in high-latitude regions is attributed to biological activity, the values of C_T in many previous studies were generally parameterized using both physical (SSS and SST) and biological parameters (nutrients or chlorophyll *a*) (*e.g.* Baker *et al.* 1999; Lee *et al.* 2000a; Ishii *et al.* 2004; Bates 2006; Sarma *et al.* 2006; McNeil *et al.* 2007). The derived region-specific C_T and A_T relationships, along with SSS, SST, and/or chlorophyll *a* (or nitrate) concentrations, yield basin-scale C_T and A_T fields that in turn yield pCO_{2SEA} fields when combined with a reliable thermodynamic model (*e.g.* Loukos *et al.*2000; Ishii *et al.* 2004; Sarma *et al.* 2006).

In the present paper, we evaluate the abilities of the empirical C_T (Lee *et al.* 2000a) and A_T (Lee *et al.* 2006) models in predicting surface-water pCO_{2SEA} by comparing our modeled C_T, A_T, and pCO_{2SEA} values with multi-year observations from three time-series locations, with measurement-based pCO_{2SEA} climatology (Takahashi *et al.* 2002), and with pCO_{2SEA} values predicted from changes in SST via regionally and seasonally varying pCO_{2SEA}/SST algorithms (Lee *et al.* 1998; Park *et al.* 2006). Predicted pCO_2 values using our regional C_T and A_T algorithms are also compared against those derived from other empirical algorithms for the equatorial Pacific (Loukos *et al.* 2000; Ishii *et al.* 2004), Indian (Bates *et al.* 2006), and Southern Oceans (McNeil *et al.* 2007). Finally, we estimate the degree to which pCO_{2SEA} values calculated from C_T and A_T via a thermodynamic ocean-carbon model are sensitive to seasonal variations in C_T and A_T predicted for different parts of the global ocean.

2. Calculation Methods

Monthly mean global C_T and A_T fields on 4° latitude × 5° longitude grid cells for the reference year 1995 were estimated from 24 equations relating NC_T to SST and NO_3^- (Lee *et al.* 2000a) and 5 equations relating A_T to SSS and SST, along with monthly mean SSS (Antonov *et al.* 2006) and NO_3^- (Garcia *et al.* 2006) fields from the World Ocean Atlas 2005 (hereafter referred to as WOA05) and monthly mean SST fields for 1995 sourced from the National Centers for Environmental Prediction/Atmospheric Model Intercomparison Project II (NCEP/DOE AMIP-II Reanalysis, hereafter referred to as NCEP, available at http://www.cpc.ncep.noaa.gov/products/wesley/reanalysis.html). Simple two-parameter functions with SST and NO_3^- for NC_T and with SSS and SST fit surface NC_T and A_T data within an area-weighted uncertainty of approximately 8 μmol kg^{-1} (Lee *et al.* 2000a; 2006).

The resulting NC_T fields were then converted to C_T using monthly mean SSS fields from the World Ocean Atlas 2005. The annual cycles of global surface-water C_T and A_T for 1995 used in this paper were previously published in Lee *et al.* (2000a) and Lee *et al.* (2006), respectively. The companion fields of pCO_{2SEA} fields for 1995 were then constructed from the resulting C_T and A_T fields using the carbonic acid dissociation constants of Mehrbach *et al.* (1973) that were refitted in different functional forms by Dickson and Millero (1987).

3. Results and Discussion

Global distributions of modeled pCO_{2SEA} and seasonal pCO_{2SEA} variability

Surface-water pCO_{2SEA} values predicted for February and August in the global ocean are shown in Figures 1(a) and 1(b) as examples of the monthly mean distributions. In the eastern equatorial Pacific, high pCO_{2SEA} values (yellow to red areas) reflect the upwelling of subsurface water with high pCO_{2SEA} values and its subsequent advection from the site of upwelling. Low pCO_{2SEA} values (blue areas) are generally found in the Southern Ocean (> 60°S) during the austral summer and in the North Atlantic and North Pacific (>40°N) during the boreal summer; in contrast, relatively high pCO_{2SEA} values are found in these regions during winter. In these high-latitude regions, C_T at the surface increases during seasonal cooling due to the convective mixing of subsurface waters rich in C_T. In this case, the convective mixing and thermodynamic effects are out of phase, and reductions in pCO_{2SEA} associated with cooling are usually

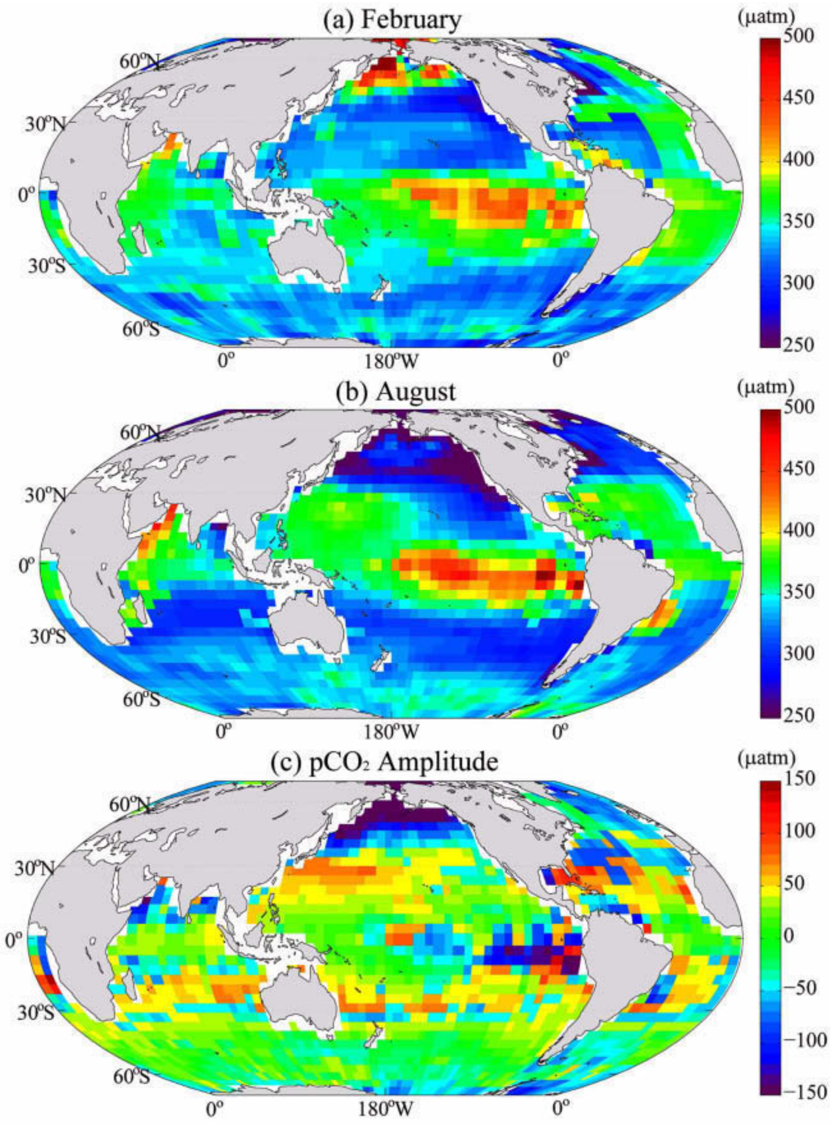

Fig. 1. Climatological surface-water pCO_{2SEA} fields for (a) February and (b) August estimated from the $NC_T/SST/NO_3^-$ (Lee *et al.* 2000a) and $A_T/SSS/SST$ algorithms (Lee *et al.* 2006), as well as monthly mean SST fields for 1995 sourced from the National Centers for Environmental Prediction/Atmospheric Model Intercomparison Project II and SSS (Antonov *et al.* 2006) and NO_3^- fields (Garcia *et al.* 2006) from the World Ocean Atlas 2005. (c) Distribution of the seasonal amplitude (maximum pCO_{2SEA}– minimum pCO_{2SEA}) of surface-water pCO_{2SEA}. Positive amplitudes (yellow to red areas) indicate that maximum pCO_{2SEA} values occur during summer; whereas negative amplitudes (light blue to blue areas) indicate that maximum pCO_{2SEA} values occur during winter.

overtaken by increases due to vertical mixing. In contrast, a combination of phytoplankton blooms and reduction in convective mixing during the warming period leads to a rapid decrease in pCO_{2SEA} at high latitudes. The pCO_{2SEA} values found in temperate and tropical oceans are nearly in equilibrium or slightly undersaturated with respect to atmospheric pCO_{2SEA} (green areas). In these warm waters, limited photosynthesis and longer periods of exposure of surface water to the atmosphere due to strong stratification collectively act to bring surface pCO_{2SEA} close to atmospheric values.

The magnitude of predicted seasonal pCO_{2SEA} variability largely falls within the range from –200 to +150 μmol kg^{-1} (Figure 1c). Positive amplitudes (yellow to red areas), which indicate that maximum pCO_{2SEA} values occur during summer, are generally found in the temperate and tropical oceans where temperature changes account for more than 50% of the seasonal pCO_2 changes (Takahashi *et al.* 2002). In these oceans, seasonal warming leads to an increase in pCO_{2SEA}, meaning that summer pCO_{2SEA} values are higher than those in winter. Negative amplitudes (blue areas), which indicate that maximum pCO_{2SEA} values occur during winter, are usually found in high-latitude areas and regions of equatorial upwelling. Negative seasonal amplitudes arise from the biological reduction of pCO_{2SEA} in summer and the increase of pCO_{2SEA} in winter associated with convective mixing of subsurface water that is rich in pCO_{2SEA} (Takahashi *et al.* 2002).

Comparison with multi-year time-series observations

The accuracy of the predicted pCO_{2SEA} fields and their seasonal variability presented in the preceding section depend on the accuracy of published C_T (Lee *et al.* 2000a) and A_T (Lee *et al.* 2006) algorithms in terms of describing seasonal trends. Therefore, in the present paper we assess the abilities of the published C_T (Lee *et al.* 2000a) and A_T (Lee *et al.* 2006) algorithms in predicting surface-water pCO_{2SEA} by comparing our modeled C_T, A_T, and pCO_{2SEA} values against time-series measurements obtained from the sites of the Bermuda Atlantic Time-series Study (BATS) (31°50′N, 60°10′W), the Hawaiian Ocean Time-series (HOT) (22°45′N, 158°00′W), and the Kyodo western North Pacific Ocean Time-series (KNOT) (44°N, 155°E).

The BATS and HOT sites, which represent subtropical conditions, have near-monthly records of SSS, SST, C_T, and A_T for the period 1988-2003 (Bates, 2001, 2002; Gruber *et al.* 2002; Dore *et al.* 2003; Keeling *et al*. 2004), whereas the KNOT site, which represents subarctic conditions, has only seasonal records of SSS, SST, C_T, and A_T for the shorter period of 1998-2000 (Tsurushima *et al.* 2002). Over the observational periods for the three time-series locations, we first compared measured C_T and A_T values with those predicting the published C_T and A_T algorithms that are applicable to these time-series locations in conjunction with SSS and SST data collected from the three time-series locations and then compared pCO_{2SEA} values predicted from measurements of C_T and A_T with predictions of the same parameters made using the C_T and A_T algorithms and the optimal thermodynamic model. In addition, we evaluated the reliability of climatological SSS (WOA05) and SST (NCEP) data in predicting C_T, A_T, and pCO_{2SEA} when combined with the published C_T (Lee *et al.* 2000a) and A_T (Lee *et al.* 2006) algorithms.

Prior to the comparisons with time-series observations, we applied one adjustment factor to the predicted C_T values to account for C_T increases due to the influx of CO_2 from the

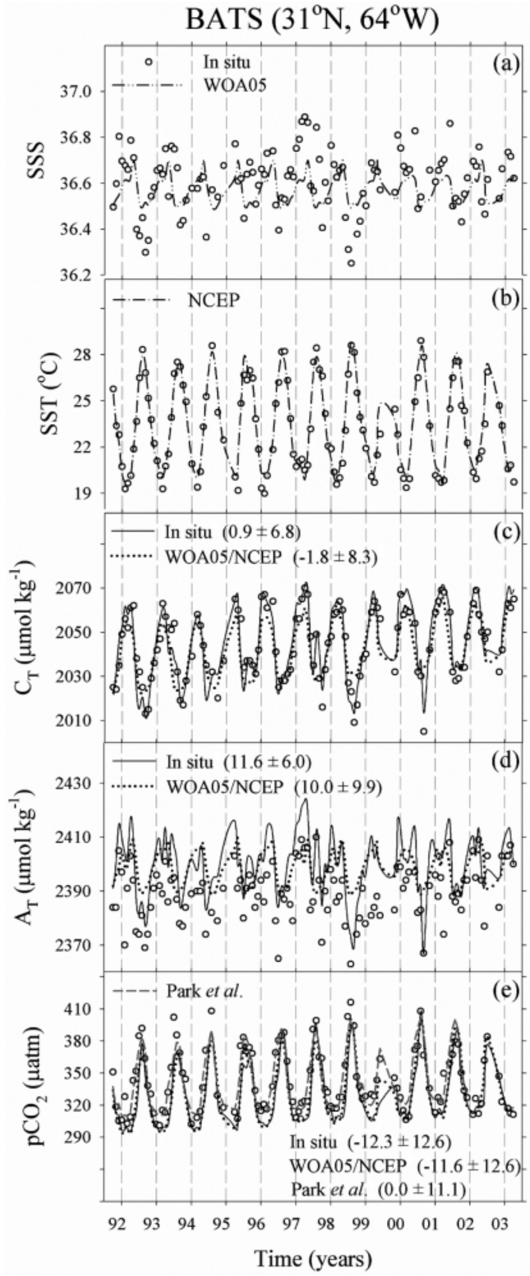

Fig. 2. Comparisons of (a) WOA05 sea surface salinity (SSS) and (b) NCEP sea surface temperature (SST), and modeled C_T, A_T and pCO_{2SEA} values with observations undertaken at the Bermuda Atlantic Time-series (BATS) site (31°50′N, 64°10′W). C_T and A_T values were predicted using in situ SSS and SST values (solid lines, This study) and using WOA05 SSS and NCEP SST values (dotted lines, This study). WOA05 SSS and NCEP SST values are averages of four values from the four grid boxes (4° latitude × 5° longitude) surrounding the BATS site. Means and standard deviations (1σ) of the differences between measured values and those calculated are shown. Calculated pCO_{2SEA} values using pCO_2-SST algorithms of Park *et al.* (2006) along with in situ SST data and their deviations from observations are presented in (e).

atmosphere. This adjustment was applied to the C_T values predicted for the BATS and HOT where surface C_T increases with a rate similar to the atmospheric CO_2 increase; however, it was not applied to the C_T values predicted for the KNOT site where outcropping of deep isopycnal surfaces dilutes the small signals of anthropogenic CO_2 component throughout the entire water column.

At the BATS and HOT sites, the empirical C_T models predict seasonal and interannual trends within ±7 to ±9 μmol kg^{-1} for C_T without any significant biases and within ±5 to ±7 μmol kg^{-1} for A_T with the overestimations of 4 to 12 μmol kg^{-1} (close to fit uncertainties) (Figure 2 and 3). Overall, the magnitudes of the differences between measurements and predictions are comparable to the uncertainties of the derived C_T (Lee *et al.* 2000a) and A_T relationships (Lee *et al.* 2006). This indicates that in situ SSS and SST are reliable proxies for variations in surface-water C_T and A_T in (sub)tropical oceans, with the exception of the equatorial upwelling Pacific. A further implication of this good agreement is that the effects of phytoplankton activity on C_T in these warm waters are relatively weak due to low concentrations of nutrients throughout the year; however, there is an exception to this generalization. At the BATS site, deep wintertime mixing of nutrients supports a springtime phytoplankton bloom, implying that phytoplankton activity becomes an important factor in determining springtime surface C_T and A_T in the tropical and subtropical North Atlantic (Bates, 2001); its effect on C_T is more pronounced than that on A_T. As one can predict from the good agreement between the measured and predicted C_T and A_T trends, the pCO_{2SEA} values predicted from the C_T and A_T algorithms using the thermodynamic ocean-carbon model are in good agreement with measured values; the mean pCO_{2SEA} differences are −12.3 ± 12.6 μatm at BATS and −0.6 ± 14.9 μatm at HOT. The overestimation at the BATS site is due to A_T overestimation.

In the western subarctic North Pacific (KNOT), the A_T model accurately predicts seasonal and interannual trends whereas the C_T model predicts less accurately; the mean differences between measurements and predictions are −24.0 ± 24.9 μmol kg^{-1} for C_T and −4.5 ± 8.9 μmol kg^{-1} for A_T. The resulting pCO_{2SEA} predicted from these C_T and A_T algorithms using the thermodynamic model reasonably predicts seasonal variations, but differs from measurements by −45.9 ± 33.1 μatm, with larger discrepancies recorded for the springtime and wintertime comparisons for 1999

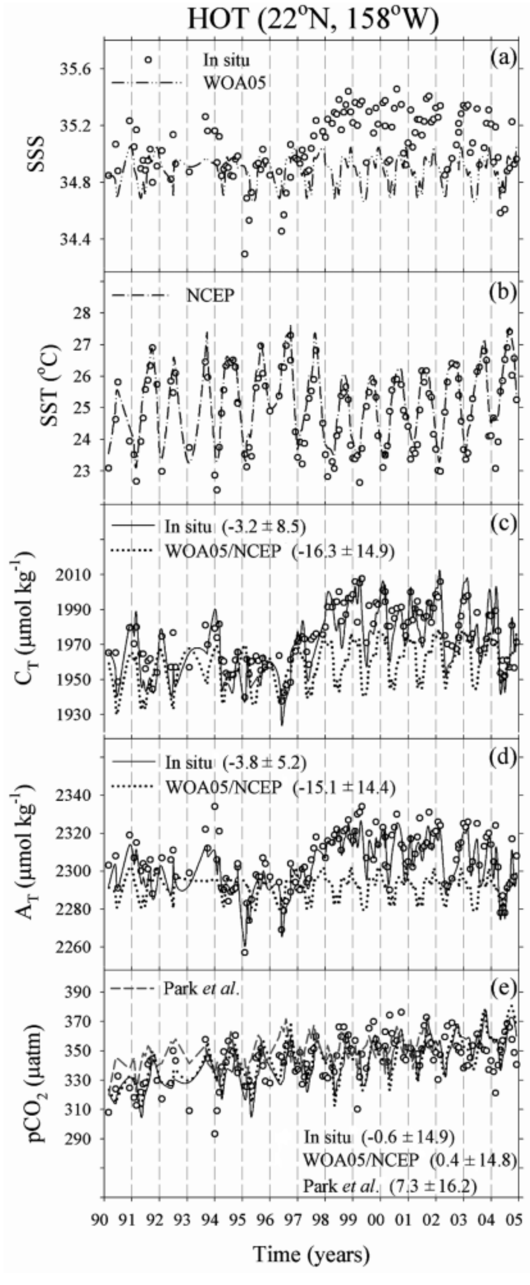

Fig. 3. Comparisons of (a) WOA05 sea surface salinity (SSS) and (b) NCEP sea surface temperature (SST), and modeled C_T, A_T and pCO_{2SEA} values with observations undertaken at the Hawaiian Ocean Time-series (HOT) site (22°45'N, 158°00'W). C_T and A_T values were predicted using in situ SSS and SST values (solid lines, This study) and using WOA05 SSS and NCEP SST values (dotted lines, This study). WOA05 SSS and NCEP SST values were averages of values from 4 grid boxes (4° latitude × 5° longitude) surrounding the HOT site. Means and standard deviations (1σ) of the differences between measured values and those calculated are shown. Calculated pCO_{2SEA} values using pCO_2-SST algorithms of Park *et al.* (2006) along with in situ SST data and their deviations from observations are presented in (e).

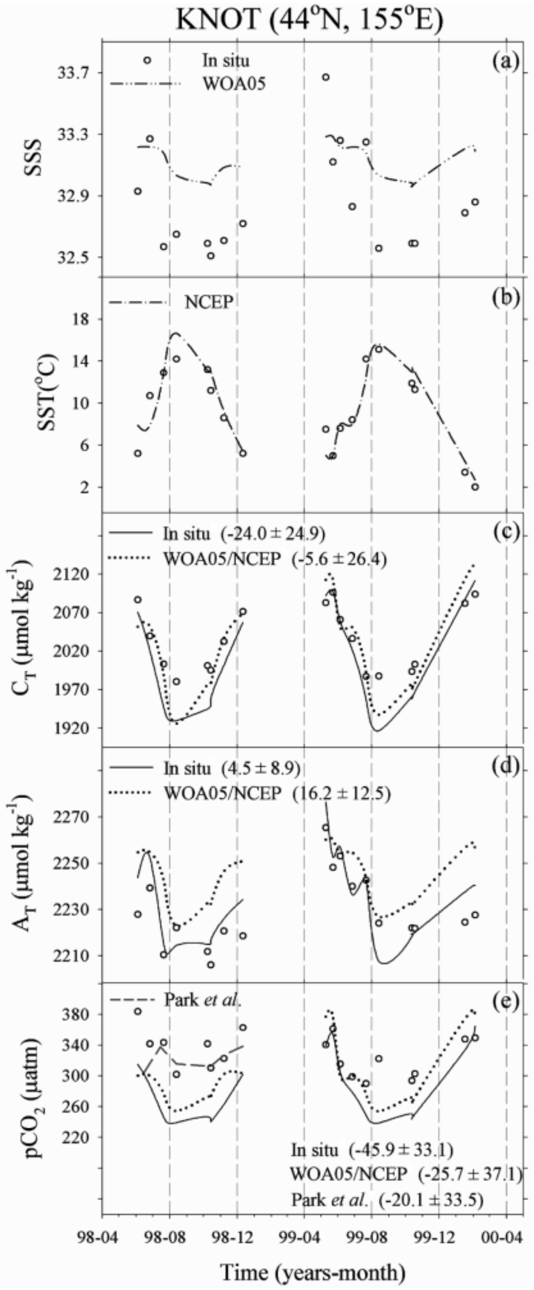

Fig. 4. Comparisons of (a) WOA05 sea surface salinity (SSS) and (b) NCEP sea surface temperature (SST), and modeled C_T, A_T and pCO_{2SEA} values with observations undertaken at the at the Kyodo western North Pacific Ocean Time-series (KNOT) site (44°N, 155°E). C_T and A_T values were predicted using in situ SSS and SST values (solid lines, This study) and using WOA05 SSS and NCEP SST values (dotted lines, This study). WOA05 SSS and NCEP SST values were averages of values from 4 grid boxes (4° latitude × 5° longitude) surrounding the KNOT site. Means and standard deviations (1σ) of the differences between measured values and those calculated are shown. Calculated pCO_{2SEA} values using pCO_2-SST algorithms of Park *et al.* (2006) along with in situ SST data and their deviations from observations are presented in (e).

(Figure 4).

In addition, when the empirical C_T and A_T algorithms were combined with climatological SSS, SST, and NO_3^-, we found good agreement between the predicted and measured values at BATS, but we found poor agreement at HOT. At all thee locations, the NCEP SST data accurately represent interannual variations in SST. Therefore, the poor agreement at the HOT site is largely due to the inaccurate representation of interannual and seasonal variations in SSS. Although climatological SSS data were found to underestimate C_T and A_T values at the HOT site, the calculated pCO_{2SEA} values are in good agreement with measured values to within ±15 μatm, with no systematic biases. Such good agreement at BAT is fortuitous. The overestimation of C_T would lead to pCO_{2SEA} overestimation whereas A_T overestimation leads to pCO_{2SEA} underestimation. As a result, they compensate each other. At the KNOT site, we only tested the accuracy of climatological data by comparing A_T predictions against measurements, because the C_T algorithms applicable to this site resulted in a mean bias of −24.0 μmol kg^{-1}. Our analysis indicates that climatological data less accurately predict A_T values than do in situ measurements; however, they capture seasonal A_T trends.

Overall, the empirical models predict C_T less accurately at the KNOT site than at the BATS and HOT sites, suggesting that our C_T prediction models, which are applicable to the western subarctic North Pacific, may not account for the full extent of biological effects on C_T variations, thereby limiting the accuracy of pCO_{2SEA} predictions. Sarma *et al.* (2006) also showed that the "chlorophyll *a*" rather than "NO_3^-" is probably more adequate to account for the biological effect on C_T, giving rise to smaller random errors.

Comparison with the modeled pCO_{2SEA} data using the method Park *et al.* (2006)

For the periods over which direct measurements are available from the BATS, HOT, and KNOT sites, we compared our modeled pCO_{2SEA} with those predicted independently from SST variations via seasonal pCO_{2SEA}/SST relationships derived for 4° latitude × 5° longitude pixels, including the time-series locations (Park *et al.* 2006) (Figures 2c-4c). In contrast, for the equatorial upwelling Pacific (10°N-10°S, 75°W-160°W), net annual CO_2 efflux estimates obtained using direct observations are subject to large uncertainties because they were derived from biannual observations from 1992 to 1998; therefore, we only compared those efflux

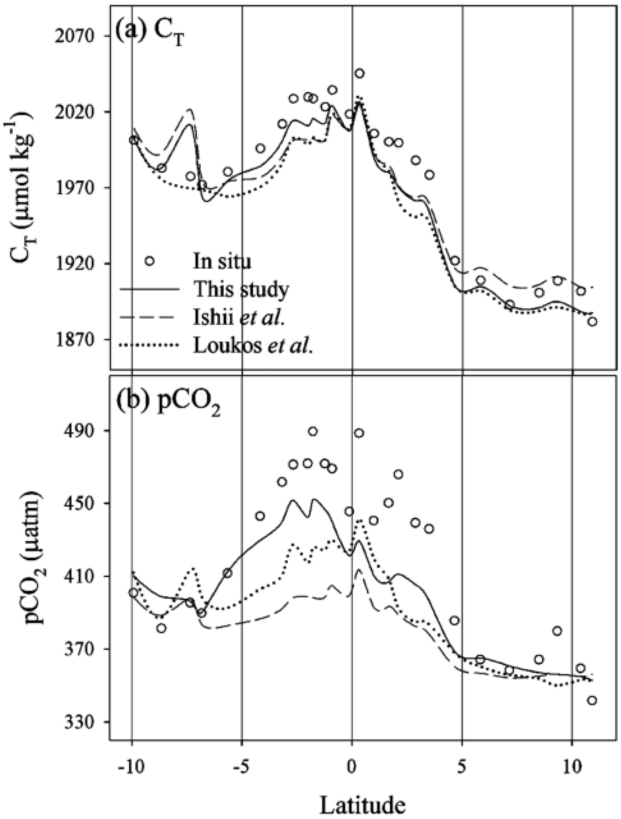

Fig. 5. Comparisons of (a) C_T and (b) pCO_{2SEA} observations with those modeled using published C_T (Lee *et al.* 2000a) and A_T algorithms (Lee *et al.* 2006), using C_T and A_T algorithm of Ishii *et al.* (2004), and using C_T algorithms of Loukos *et al.* (2000) and A_T algorithms of Lee *et al.* (2006) for the equatorial Pacific (10°N-10°S) along 110°W.

estimates modeled using the present approach with the pCO_{2SEA}/SST relationships (Cosca *et al.* 2003; Park *et al.* 2006) derived from the biannual observations (Figure 5).

Overall, the comparison of two independently modeled values with time-series measurements at the BATS, HOT, equatorial upwelling Pacific, and KNOT sites indicates that regardless of location, the empirical C_T/A_T-based approach appears to predict surface-water pCO_{2SEA} variations as accurately as the pCO_{2SEA}/SST-based approach (Figures 2c-4c, 5). More precisely, the pCO_{2SEA}/SST-based approach yields predictions of surface-water pCO_{2SEA} variations at the HOT site that are less accurate than those of the empirical C_T/A_T-based approach; the opposite is true at the KNOT site. Overall, both methods predicted surface pCO_{2SEA} values less accurately in high-latitude regions (*e.g.* the KNOT site) than in subtropical oceans (*e.g.* the BATS and HOT sites). These limited comparisons of observations with predicted pCO_2 values obtained using the two empirical methods make it difficult to determine the superior empirical method.

Comparison with pCO_{2SEA} predictions using other published algorithms

To further validate the accuracy of pCO_{2SEA} predictions using C_T (Lee *et al.* 2000a) and A_T (Lee *et al.* 2006) algorithms, we compared our predictions of pCO_{2SEA} with those modeled using other published algorithms for the Equatorial Pacific (Loukos *et al.* 2000; Ishii *et al.* 2004), the Indian Ocean (Bates *et al.* 2006), and the Southern Ocean (McNeill *et al.* 2007).

For the eastern equatorial Pacific along the line 110°W, all three C_T algorithms reasonably captured C_T variations measured in 1995 (Figure 5); however, they underestimated C_T values to some extent near the equator (5°N-5°S). As a result, predictions of seawater pCO_{2SEA} for this line using three algorithms were correspondingly underestimated. Although our algorithms predicted pCO_{2SEA} more accurately, the differences in pCO_{2SEA} predictions are not statistically significant.

For the Indian Ocean, our modeled pCO_{2SEA} fields were on a basin-wide average −23 to −40 μatm consistently less than those predicted using C_T and A_T algorithms of Bates *et al.* (2006) when the same SST (NCEP), and SSS and nitrate fields were used (Figure 6). The underestimation is largely due to inaccurate representation of the C_T fields produced by Lee *et al.* (2000a). According to the analysis of Bates *et al.* (2006), four separate C_T algorithms for two monsoon and two inter-monsoon periods yielded the smallest interpolation errors in predicting the C_T fields for the respective monsoon and inter-monsoon seasons; the use of a single algorithm in our study yielded prediction errors considerably greater than the use of the four seasonal algorithms. The fact that the use of four algorithms resulted in the smallest errors indicates that the relative importance of the controlling factors for seawater C_T (and pCO_{2SEA}) differs by seasons.

For waters south of 40°S in the Southern Ocean, regardless of seasons, our algorithms predicted pCO_{2SEA} fields on an average of 20 ± 10 μatm higher than those predicted from the C_T and A_T algorithms derived by McNeill *et al.* (2007) (Figure 7). Such systematic difference is likely to be due to inaccuracy in our C_T algorithm for the Southern Ocean. This inaccuracy is largely caused by two factors. One is the number of C_T data used to derive Lee *et al.*'s algorithm,

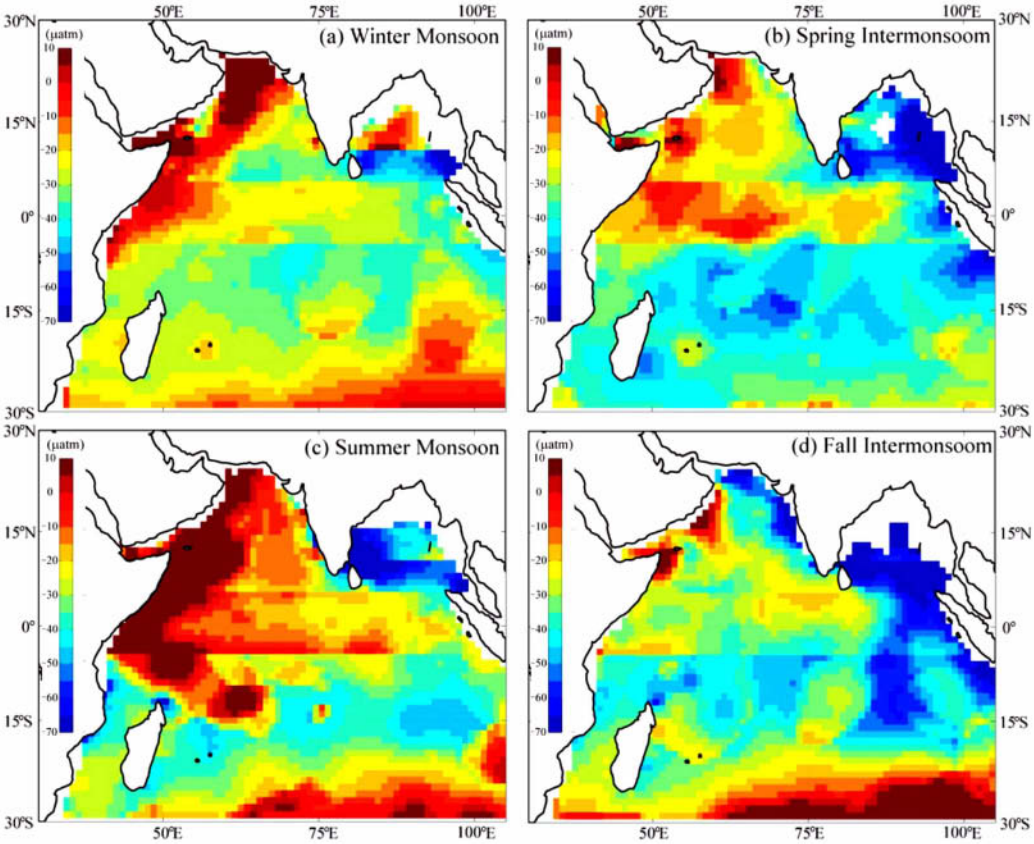

Fig. 6. Comparison of our modeled pCO_2 fields for (a) winter (December to February), (b) spring (March to May), (c) summer (June to August), and (d) fall (September to November) with those obtained using C_T and A_T algorithms of Bates *et al.* (2006). Positive values indicate our modeled values higher than Bates *et al.*'s estimations whereas negative values indicate the opposite case.

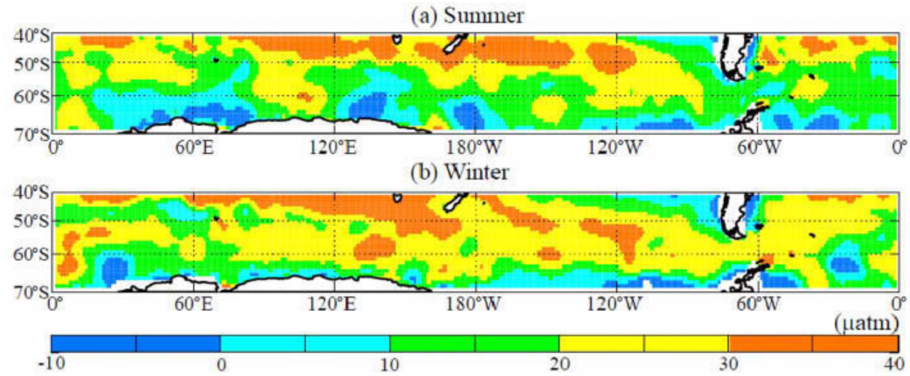

Fig. 7. Comparison of our modeled pCO_2 fields for (a) summer (June to August) and (b) winter (December to February) with those obtained suing C_T and A_T algorithms of McNeil *et al.* (2007). Positive values indicate our modeled values higher than McNeil *et al.*'s estimations whereas negative values indicate the opposite case.

which are about two-thirds of data points used in deriving McNeill *et al*.'s algorithm. Another is the difference in the choice of predictable parameters, which account for changes in C_T due to biological activity. McNeill *et al*.'s analysis indicated that the parameter "nitrate only" cannot fully capture C_T changes due to biology in the Southern Ocean. In their analysis, therefore, they used the parameters "oxygen" and "silicate".

Comparison with measurement-based pCO_{2SEA} fields (Takahashi *et al.* 2002)

The modeled surface-water pCO_{2SEA} maps for 1995 are

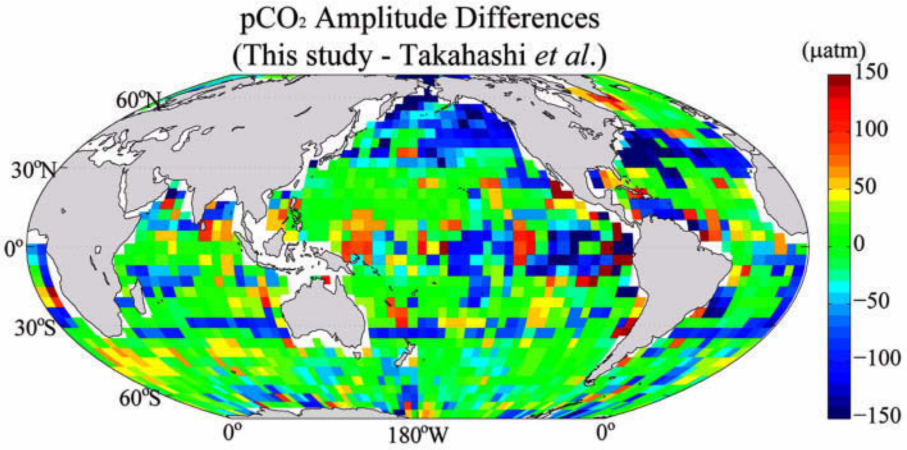

Fig. 8. Comparison of model predictions with measurement-derived pCO_{2SEA} fields (Takahashi *et al.* 2002) for seasonal amplitudes of pCO_{2SEA} variability. Positive values indicate modeled amplitudes are overestimated, whereas negative values indicate underestimates.

compared with corresponding maps compiled from 940,000 shipboard measurements of pCO_{2SEA} taken over the past 40 years (Takahashi *et al.* 2002). In compiling the pCO_{2SEA} maps for 1995 using the C_T algorithms derived from data normalized to the year 1990, our empirical C_T models did not account for increases in C_T due to oceanic uptake of anthropogenic CO_2 over a 5-year period between 1990 and 1995. Therefore, we compared the magnitudes of modeled seasonal pCO_{2SEA} variability with those of measurement-derived values (Takahashi *et al.* 2002) (Figure 8). Positive values indicate that our modeled seasonal pCO_{2SEA} variations are greater than observed variations. Seasonal amplitudes of pCO_{2SEA} calculated in this way are in broad agreement with those calculated from the monthly mean pCO_{2SEA} maps of Takahashi *et al.* (2002), with a mean difference in the seasonal amplitude of approximately ±40 µatm (yellow to light blue areas in Figure 6). Our estimates capture many of the key features that are present in Takahashi *et al.*'s map of seasonal pCO_{2SEA} variability, although the degree of concordance between the two global maps varies regionally. The largest differences are found in the North Pacific (>45°N), where two contrasting trends are observed in the differences in the seasonal pCO_{2SEA} amplitudes. In the northern North Pacific (>45°N), the modeled seasonal amplitudes of pCO_{2SEA} were underestimated by 100 to 150 µatm compared to observed values. In contrast, in the temperate central North Pacific (30°N-45°N) the predicted seasonal amplitudes are close to or slightly lower than the observed amplitudes. The observed seasonal trends for the northern North Pacific are probably robust, as the measurements have a dense coverage for all seasons (Takahashi *et al.* 2002). Hence, our modeled seasonal amplitudes are most likely to be underestimates in the northern North Pacific (>45°N).

Estimation of errors in predicted pCO_{2SEA}

The systematic errors in estimated pCO_{2SEA} values are largely due to possible biases in climatological data of SSS, SST and NO_3^- (obtained from WOA05 and NCEP) and in the selected thermodynamic model. Of these factors, uncertainties in SSS make the largest contribution to the overall systematic errors in C_T, A_T, and pCO_{2SEA} predictions. In particular, the analysis of data at the three time-series locations indicate that the lack of interannual variations in SSS led to errors in predicted C_T, A_T, and pCO_{2SEA} values that are comparable or greater than fit errors in C_T and A_T equations. Another less significant contributor is uncertainty in the carbonic acid dissociation constants. This set of thermodynamic constants has proved to be the most consistent with laboratory (Lee *et al.* 1996; Lueker *et al.* 2000; Mojica Prieto and Millero, 2002; Millero *et al.* 2006) and field (Lee *et al.* 1997; Wanninkhof *et al.* 1999; Lee *et al.* 2000b; Millero *et al.* 2002) measurements of carbon parameters over oceanic ranges of temperature and salinity. Therefore, the uncertainty in the thermodynamic model leads to biases in calculated carbon parameters that are smaller than mean fit errors in C_T and A_T equations.

The random errors associated with the estimated values of pCO_{2SEA} mostly come from uncertainties in the published C_T and A_T algorithms. The uncertainties (approximately ±8 µmol kg^{-1}) in the published C_T and A_T algorithms taken from

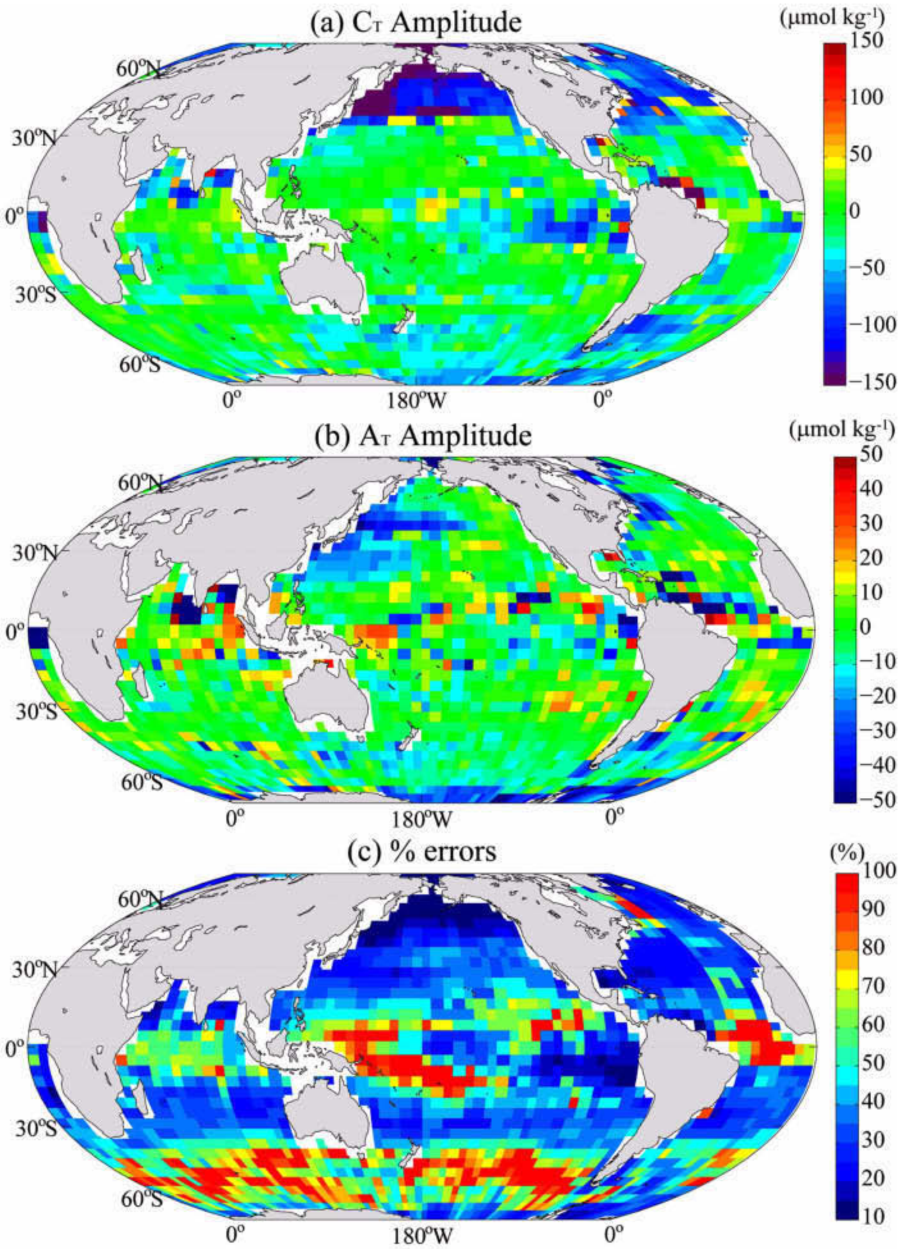

Fig. 9. (a) Distribution of the seasonal amplitudes (maximum –minimum) of surface-water C_T, A_T, and pCO_{2SEA}. Positive amplitudes (yellow to red areas) indicate that maximum pCO_{2SEA} values occur during summer; whereas negative amplitudes (light blue to blue areas) indicate that maximum pCO_{2SEA} values occur during winter.(c) Percentage errors (%) of ±5% in calculated pCO_{2SEA} (errors associated with the C_T and A_T algorithms) relative to the magnitudes of seasonal pCO_{2SEA} variability.

Lee *et al.* (2000a) and Lee *et al.* (2006) result in an overall uncertainty in pCO_{2SEA} of approximately ±5%.

Effects of predicted seasonal variations in A_T and C_T on calculations of pCO_{2SEA}

Predictions of seasonal changes in surface-water pCO_{2SEA} values made from C_T and A_T via a thermodynamic model are sensitive to seasonal changes in C_T (ΔC_T) and A_T (ΔA_T). In the (sub)tropical ocean, except for the equatorial upwelling Pacific, both C_T and A_T change to a similar degree and in the same direction (yellow area in Figures 9a and 9b). In this case, a seasonal increase in A_T acts to lower surface-water pCO_{2SEA}, whereas an increase in C_T acts to increase pCO_{2SEA}. The net effect is a suppression of the variability in predicted values of pCO_{2SEA} (yellow area in Figure 1c), as the effects of these two competing factors approximately cancel each other out. As a result, an estimated error of ±5% in predicted pCO_{2SEA} associated with errors in the C_T and A_T algorithms generally contributes to 50-100% of the seasonal amplitudes of pCO_{2SEA} found in these regions (yellow to red areas in Figure 9c). In particular, the error in pCO_{2SEA} can be substantial in the western equatorial Pacific and the central equatorial Atlantic where measured magnitudes of pCO_{2SEA} seasonality slightly exceed the estimated pCO_{2SEA} error. In these regions, direct pCO_{2SEA} measurements are strongly recommended.

Contrary to the prevailing trend in ΔC_T and ΔA_T for the (sub)tropics, in the equatorial upwelling area the magnitudes of ΔC_T are much greater than those of ΔA_T, and C_T and A_T occasionally vary in opposite directions. The net effect of variations in C_T and A_T on predictions of pCO_{2SEA} is an increase in the variability of predicted pCO_{2SEA} (blue or orange to red areas in Figure 1c), as the effect of ΔC_T on pCO_{2SEA} is pronounced and the counteracting effect of ΔA_T on pCO_{2SEA} is relatively small; consequently, the estimated pCO_{2SEA} error of ±5% accounts for less than 20% of the total variability of pCO_{2SEA} found in this region (blue area in Figure 9c).

In most high-latitude regions, the magnitudes of seasonal ΔC_T (blue to purple areas in Figure 9a) are significantly greater than those of seasonal ΔA_T; hence, the effect of ΔC_T on pCO_{2SEA} is dominant. There are two major trends in ΔC_T within high-latitude oceans. The first trend is more general and thus found across large areas of high-latitude oceans (blue to purple area in Figure 9a), particularly in the North Pacific and North Atlantic. In these areas, the magnitudes of seasonal ΔA_T are generally one-fifth of those of ΔC_T. Hence, the effect of ΔC_T on ΔpCO_{2SEA} is significantly greater than that of ΔA_T on pCO_{2SEA}. As with the case in the equatorial upwelling area, changes in C_T make a dominant contribution to seasonal changes in pCO_{2SEA} in these high-latitude regions. In this case, the estimated pCO_{2SEA} error of ±5% is considerably smaller in magnitude than the total seasonal pCO_{2SEA} variability (blue area in Figure 9c).

The second trend is found in the Southern Ocean. For waters at 30°S-60°S, the magnitudes of ΔC_T are only one-fifth of those found in the North Pacific and North Atlantic; in contrast, ΔA_T in these contrasting regions are similar in magnitude. The resulting smaller magnitudes of seasonal variability in C_T act to depress the degree of seasonal variability in pCO_{2SEA} in the Southern Ocean; this effect is enhanced by locally opposite trends in ΔC_T and ΔA_T. As a result, the magnitudes of seasonal variability in pCO_{2SEA} in the Southern Ocean are minor compared to those observed in the northwestern North Atlantic and North Pacific (see Figure 1c). In this case, the magnitudes of the errors in predicted pCO_{2SEA} are comparable to those of seasonal variability in pCO_{2SEA}; thus, substantial errors are found in the Southern Ocean (yellow to red areas in Figure 9c). Although the smaller magnitudes of seasonal pCO_{2SEA} variability for the Southern Ocean inferred from our empirical model are broadly consistent with those found in Takahashi *et al.*'s map, a firm conclusion can only be drawn once additional pCO_{2SEA} measurements become available in the future.

4. Conclusion

The principal benefit of using the empirical model described in the present study is the interpolation or extrapolation of surface-water C_T and A_T, which in turn leads to predictions of surface-water pCO_{2SEA}. The broad concordance between modeled values and those observed at the time-series locations suggests that the published C_T and A_T algorithms, when combined with SSS, SST, and nitrate concentration data, are able to predict the corresponding global fields and thereby pCO_{2SEA} fields using the thermodynamic model. Within the (sub)tropical oceans (*i.e.* 30°N-30°S), seasonal variations in C_T and A_T collectively act to suppress variations in surface-water pCO_{2SEA}. In contrast, the effect of seasonal variations in C_T on pCO_{2SEA} within the equatorial upwelling Pacific and high-latitude oceans (*i.e.* north of ~30°N and south of ~30°S) is generally strong, as the counteracting effect of seasonal variations in A_T on pCO_{2SEA} is relatively small.

The results presented in this paper provide guidelines for the prediction of surface-water pCO_{2SEA} using the C_T and A_T empirical models. Because the real-time observations of SSS, SST, and biological parameters using various tools including Argo float or satellite are increasing (*e.g.* Kilpatrick *et al*. 2001; Koblinsky *et al*. 2003; Gabarró *et al*. 2004; Gould *et al*. 2004), those observations will provide a potentially powerful tool in constraining monthly to interannual variability in the oceanic uptake of CO_2 when they are jointly used with empirical algorithms that relate C_T to SSS, SST, and nitrate (or other biological parameters) concentration and that relate A_T to SSS and SST.

Acknowledgements

We also thank Dr. Rik Wanninkhof of the Atlantic Oceanographic and Meteorological Laboratory for providing valuable comments on an earlier version of this paper. This work was financially supported by the National Research Laboratory Program of the Korea Science and Engineering Foundation. Partial support was also provided by AEBRC at POSTECH, the Korea Aerospace Research Institute, and the Korea Polar Research Institute (PE08030).

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