

Climatological Estimation of Sea Surface CO₂ Partial Pressure in the North Pacific Oceans by Satellite data

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<Keyword>
CO₂ flux, pCO₂,

Abstract

As one of the key parameters to determine CO₂ flux between air – sea interface, it is quite important to know pCO₂, which has involved much uncertainty, mainly due to the complex variations of sea surface pCO₂ and the paucity of samples, made in ocean. In order to improve the interrelationship between partial pressure (pCO₂) and different physical and biochemical parameters in global sea surface water, a new empirical relation is established to correlate and parameterize pCO₂ in the mixed layer using the data from recent WOCE cruises. Meanwhile, by new empirical relation, abundant historical hydrographic and nutrients ship data, Levitus data set and NOAA/AVHRR(SST), pCO₂ have been accumulated and applied. Then effort has to be made for promotion of this study to correlate and parameterize pCO₂ in the mixed Layer with different physical and biochemical parameters, and further attribute this huge historical data sets and NOAA/AVHRR(SST) data to estimate pCO₂. In this paper we analyzed more interrelationship between the model and ship/satellite data set. Finally, the inter-annual variations of pCO₂ in sea are presented and discussed.

1. Introduction

It is beyond question that atmospheric CO₂ keeps increasing ever since the industrial revolution due to the fossil fuel combustion and other human activities, which is believed to potentially lead to a global warming. As a result whether or not and how the ocean could become the reservoir of the emitted CO₂ and henceforth regulate our climate is of great concern for human society. Although CO₂ exchanges between the air- sea interface can be directly measured on the sea (Smith and Jones 1985, Katayama 1997), it is extremely difficult to perform so far on large spatial scale and for long term observations. Therefore we are currently expecting a calculated instead of directly measured CO₂ flux based on an improved understanding of CO₂ properties in the seawater and its estimation by comprehensive models and empirically derived relationship with other physical and biochemical parameters. The estimate of CO₂ flux between air – sea interface is universally accepted in a form of (Liss 1973, Monahan 1984, Tans 1990, Sugimori and Zhao 1995).

$$F=K \Delta PCO_2 \quad (1)$$

Where F is CO₂ flux between the air – sea interface; K is the CO₂ exchange coefficient determined by piston velocity (CO₂ exchange velocity) and CO₂ solubility in seawater, ΔPCO₂ is the difference between CO₂ Partial

Pressure in sea and that in atmosphere. K is regarded as closely related with mechanisms of turbulence (Tan, 1990) and wave breaking (Monahan and spillance 1984, Wu 1988,1995, Sugimori and Zhao 1996). The variation of $\Delta p\text{CO}_2$ in time and space are mainly characterized by that of $p\text{CO}_2$ in the seawater under the complex influence of various physical and biogeochemical process, whereas the $p\text{CO}_2$ in the air may shows very small variations due to the inert property of CO_2 as well as the relatively well mixed troposphere(Goyet 1993). At present the estimation of both CO_2 exchange coefficient and $\Delta p\text{CO}_2$ involve large uncertainties. As one of the two key factors for CO_2 flux estimation, $\Delta p\text{CO}_2$ is currently obtained on a global scale based on the extrapolation of historical field measurements of $\Delta p\text{CO}_2$ made at sea in different seasons(Broecker 1986, Takahashi 1989, Tans 1990, Takahashi 1997). However, currently available ship data far from enough to provide a high resolution mapping on seasonal scale and especially, the extrapolation scheme assumes an equal weight in time to different $\Delta p\text{CO}_2$ measurements which is not true because the time scale of different processes that affects $\Delta p\text{CO}_2$ in surface water may differ significantly from one another. Such an influence can not be easily eliminated to the paucity samples, with the exception of limited intensively investigated area.

In this work effort is made to correlate surface TCO_2 and $p\text{CO}_2$ with different physical and chemical parameters using field measurements taken on recent WOCE cruises, which cover wide range of different water masses. Then the derived empirical relationship is used to calculate seasonal distribution of TCO_2 and $p\text{CO}_2$ in surface waters of Pacific Ocean which is the largest ocean basin and well known for its importance in regulating the carbon cycle with in the ocean and atmosphere system.

2. Method

2.1 Ship date

The ship data used in this study are Numeric Data Packages (NDP) made available at Carbon Dioxide Information Analysis Center (CDIAC). Detailed information of the data set can be found in Table1. In this study, CO_2 gas concentration made in different manners at sea, dry gas mole fractions of CO_2 , fugacities of CO_2 and $p\text{CO}_2$ are treated identically assuming a very good approximation of them (Weiss 1992) Only WOCE data are used for regression procedures.

Table.1

Cruise	Area	Cruise period	Souses
WOCE P16C	Tro and subtro. Pacific Ocean	Aug.31-Oct.1 1991	NDP 060
WOCE P16&17S	Central South Pacific Ocean	Jul.16-Aug.25 1991	NDP 054
WOCE A21&A-12	S.atl.Ocean and N.Weddel Sea	Jan.23-Mar.8 1990	NDP 045
WOCE A9	South Atlantic Ocean	Feb-Mar., 1991	NDP 051
WOCE A1E	Subarctic Atlantic Ocean	Sep.2-sep.25., 1991	NDP 056
TTO/NAS	North Atlantic Ocean	Apr.1-Oct.19,1981	NDP 044
TTO/TPS21 2	North Pacific Ocean	May 2-Jun.4, 1985	NDP 044
TTO/TPS47 1	North Pacific Ocean	Aug 4-Sep.7 1985	NDP 044

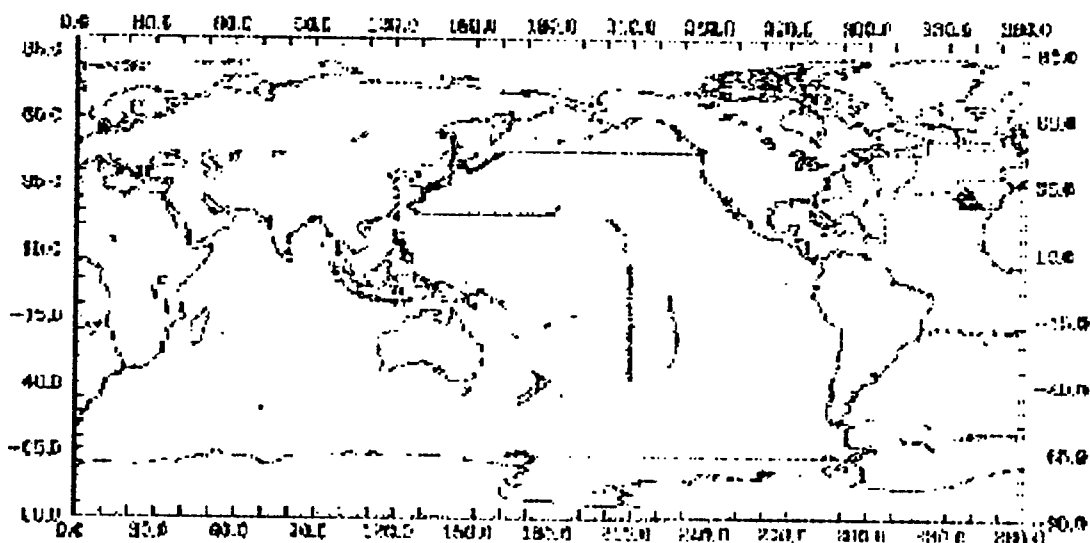


Fig.1 Geographical locations of the ship data used in this study

2.2 Parameterization of TCO_2 and PCO_2 in surface seawater

In sea surface temperature and TCO_2 have great influences on pCO_2 and the two factors often weaken or even counteract each other. The Revelle factor varies from 8 for tropical water to 12 for polar waters, with a global average of 10. The pure temperature effect on pCO_2 has been recently determined as $0.0423 \pm 0.0002^\circ\text{C}$ by Takahashi(1993). Moreover, temperature and salinity combines to determine the solubility of CO_2 as well as the dissociation constant of carbonate acid (Goyet 1989). As the conventional linear relationship between TCO_2 and nutrients like Redfield ratios which reflects the stoichiometry of plants and particulate matters loses much of its validity in the upper ocean especially in area where nutrients are almost exhausted, nitrate or phosphate on its own won't be promising to extrapolate the addition or remove of TCO_2 from surface seawater. A new parameterization method is developed in this study to directly link seawater pCO_2 with TCO_2 , temperature and salinity in the mixed layer. Another challenging problem for which we have to find a solution is the determination of TCO_2 in mixed layer where large seasonal variations take place. Brewer et al (1995) derived an empirical relation in north Atlantic ocean between TCO_2 above 250m and corresponding physical and biochemical parameters. We used here a similar method but in a modified manner with more ship data to derive a new empirical relation estimating TCO_2 in surface water. The data used for this purpose covers from tropical ocean to both polar regions and may be regarded as characteristic of most properties of different water masses. A multi-variable linear combination strategy is taken in following form to correlate pCO_2 with different physical and biochemical parameters,

$$\text{PCO}_2 = a\text{SST} + b\text{Salinity} + c\text{TCO}_2 \quad (2a)$$

$$\text{TCO}_2 = a_{tc}\text{SST} + b_{tc}\text{Alinity} + c_{tc}\text{Oxygen} + d_{tc}\text{NO}_3 + e_{tc}\text{PO}_4 \quad (2b)$$

Where Oxygen, NO_3 , PO_4 , TCO_2 are concentrations of Oxygen, nitrate, phosphate and TCO_2 in $\mu\text{mol/kg}$. While PCO_2 in

μatm , salinity in psu and SST in $^{\circ}\text{C}$. The regression coefficients are to be determined by ship data collected in mixed layer. Alkalinity has not been involved because the change of alkalinity in surface waters are mainly attributed to CaCO_3 formation and its effect on pCO_2 may be regarded as reversely proportional to that TCO_2 (Takahashi 1993). Moreover, anthropogenic CO_2 does not affect alkalinity in surface waters. For both pCO_2 and TCO_2 estimation, the large background signal free of biological activities is simulated by conservative parameters as temperature and salinity. The mathematical approach is quite straightforward and based on a least-square sense which may be described as following,

$$\text{OBSC}=\text{OBSV}\times\text{COEFF} \quad (3a)$$

Where OBSV is a $m\times 1$ matrix, m is the number of observed pCO_2 . OBSV is a $m\times n$ matrix representing the n observed variables involved in the regression which is 5, i.e., temperature, salinity, phosphate, nitrate and oxygen for TCO_2 estimation while 3, i.e., temperature, salinity and TCO_2 for pCO_2 estimation. COEFF is $n\times 1$ matrix representing the coefficients of the n variables. The least- square solution of Eq .(3a) is,

$$\text{COEFF}=(\text{OBSV}^{-1}\times\text{OBSV})^{-1}\times\text{OBSV}'\times\text{OBSC} \quad (3b)$$

The ship data used for the multi-variable regression of pCO_2 was collected during WOCE section, i.e., WOCE A-12. A-21 17s and 16S the data gathered for regression vary from low to high latitudes and covers most of the dynamic ranges of all related parameters. As pCO_2 was measured at 20°C during WOCE cruises, it is converted to the value at in situ SST according to following relation(Takahashi 1993)

$$\text{PCO}_2/\text{in-situSST}=\text{pCO}_{220^{\circ}\text{C}}/e^{(0.0423*(20.0-\text{in-situSST}))} \quad (4)$$

The liner combination of these parameters based on a least square constraints is shown in Equ (5a) , yielding a standard deviation of $10.6 \mu\text{atm}$. It should be noted that the coefficient of SST shows the data set for regression is nearly a closed system according to Takahashi(1993)

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$$\text{PCO}_2=13.46\text{SST}+1.20\text{TCO}_2-67.09\text{Salinity} \quad (5a)$$

Three more WOCE sections plus the former four ones have been used to determine TCO_2 in surface water. They are WOCE A9, A1E and P16C. Only date above 30m are used to determinate the relation between TCO_2 , SST, salinity, nitrate, phosphate and oxygen. The data set for regression covers different seasons and wide range of the world oceans. The derived relationship is shown in Equ (5b) with a standard deviation of $11.7 \mu\text{mol/kg}$.

$$\text{TCO}_2=-5.98\text{SST}+58.60\text{Salinity}+0.22\text{Oxygen}-1.55\text{NO}_3+77.73\text{PO}_4 \quad (5b)$$

3. Result

In surface waters the highest TCO₂ concentrations are mainly found south of 50°S in the southern oceans, which may reach as high as 2150 μmol/kg. The lowest TCO₂ concentration in surface waters is found in equatorial Pacific Ocean for all seasons, which is closely related with the salinity and SST distribution pattern in these regions. Upwellings occurring in winter seasons for both hemispheres bring up deep waters rich in nutrients and carbon and increase significantly the surface TCO₂ concentration at high latitudes. However, the surface TCO₂ for such waters is apparently lowered in summer due to the active photosynthetic utilization. As a result, pCO₂ for the high-latitude waters follows such a trend of TCO₂. Another dominant feature is that TCO₂ remains in low level for equatorial waters, which implies that high surface pCO₂ frequently observed in such waters as EEP area is not governed by the high concentration of TCO₂, but the heating of upwelled subsurface waters rather than deep waters.

Seasonal pCO₂ distribution shows that the dominant oceanic CO₂ sources are tropical waters, with the most intensive regions located in central and eastern Pacific Ocean for winter and summer season, respectively, which may reach as high as 450 μatm. Wintertime upwelling plays an important role in regulating surface pCO₂ at polar and subpolar surface waters, like that in Bering Sea, with seasonal differences reaching more than 100 μatm. For the subantarctic belt many sites demonstrate a near neutral feature of weak atmospheric CO₂ sources or sinks except waters south of Australia. As a result, the subantarctic belt can not be regarded as a major oceanic CO₂ sinks as a whole. The seasonal pCO₂ in the subtropical surface waters of different oceans are mainly controlled by the seasonal change of SST and act as the another main atmospheric CO₂ sinks for winter season.

Acknowledgments

The authors would like to express thanks to CDIAC for providing NDP data set, JMA for provide WMO CO₂ observations, NODC/OCL for providing Levitus data set.

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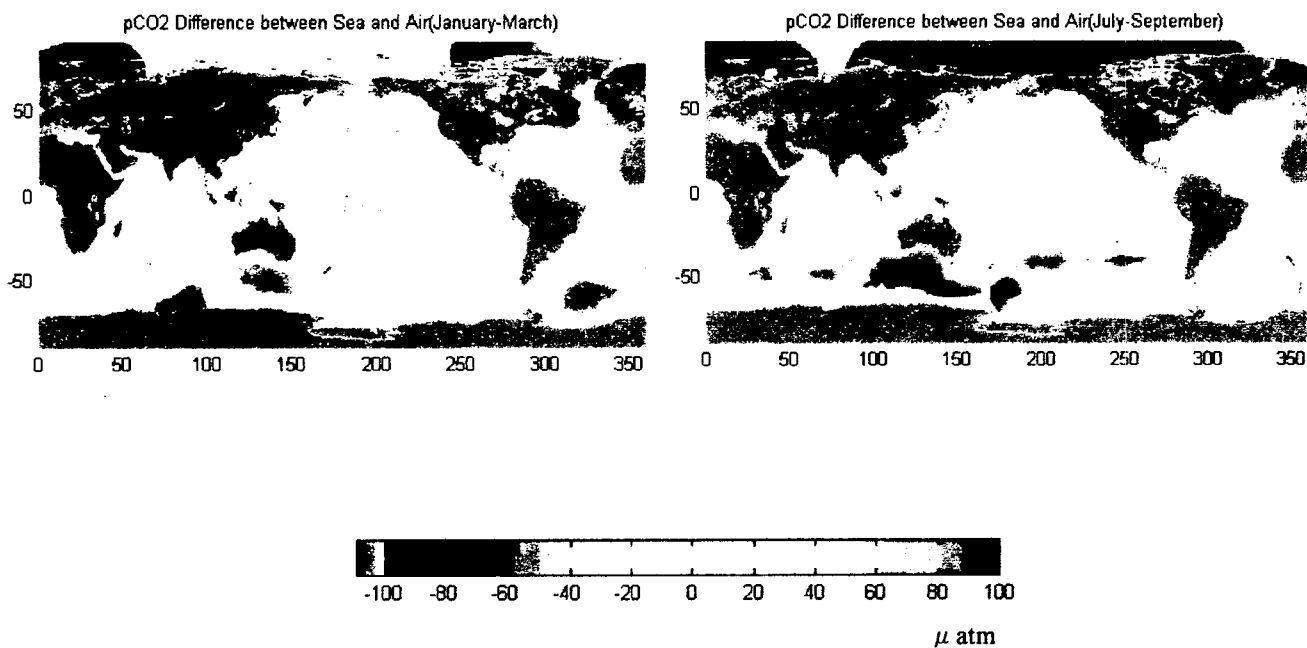


Fig.2 Computed seasonal partial pressure carbon dioxide in surface waters

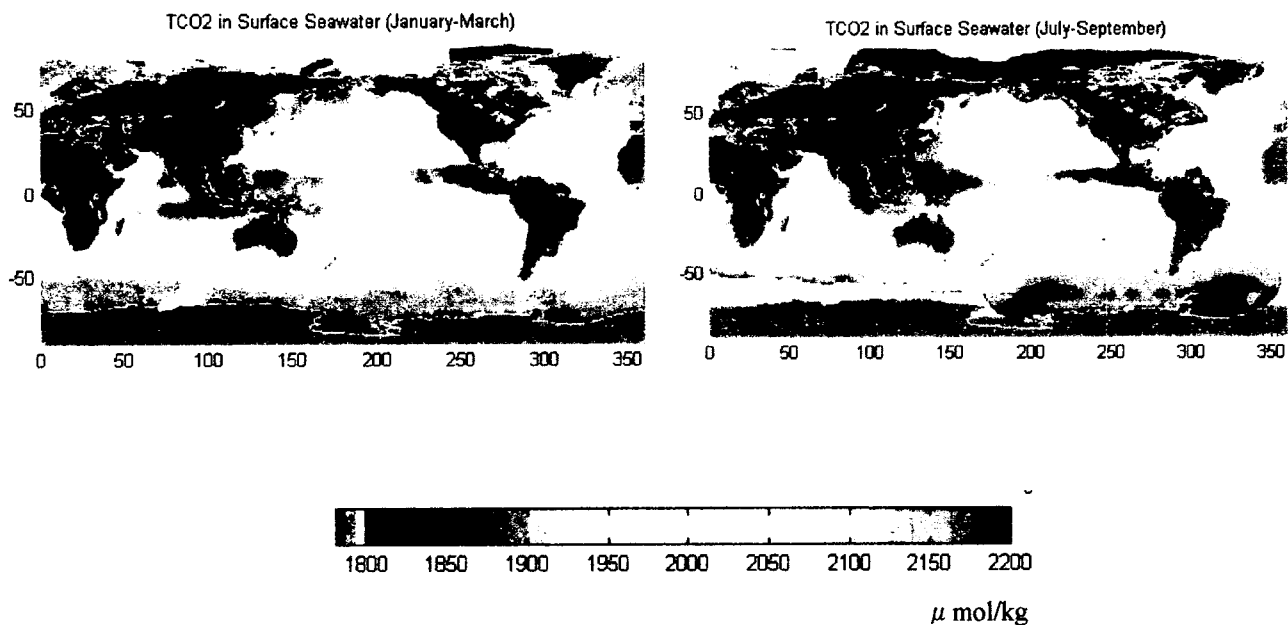


Fig.3 Computed seasonal total inorganic carbon dioxide in surface waters