APPENDIX D

SPATIAL AND TEMPORAL VARIABILITY OF SURFACE WATER pCO₂ AND SAMPLING STRATEGIES

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Introduction

The difference between the partial pressure of CO₂ (pCO₂) in surface ocean water and that in the overlying air represents the thermodynamic driving force for the CO₂ transfer across the sea surface. The direction of the net transfer flux of CO₂ is governed by the pCO₂ differences, and the magnitude of the flux may be expressed as a product of the pCO₂ difference and the gas transfer coefficient. Presently the only practical means for estimating the net sea-air CO₂ flux over the global oceans is a combination of the sea-air pCO₂ difference and the CO₂ gas transfer coefficient. Although an eddy correlation method aboard a ship at sea (Wanninkhof and McGillis, 1999) was successfully deployed over the North Atlantic during the recent GASEX–99 program, its applications is still limited. The objective of this report is (1) to analyze the spatial and temporal variability of surface water pCO₂ based on the available field observations; and (2) to recommend sampling frequencies in space and time needed for estimating net sea-air CO₂ flux in regional scales with a specified uncertainty and a known sea-air gas transfer coefficient on wind speed. It should be noted that the sampling frequencies needed for investigation of governing processes such as photosynthesis and upwelling are not addressed in this report.

General Background

Over the global oceans, the pCO₂ in surface ocean water is known to vary geographically and seasonally over a wide range between about 150 µatm and 500 µatm, or about 50% below and above the 2001 atmospheric pCO₂ level of about 360 µatm (or 370 ppm in CO₂ mole fraction concentration in dry air).

Factors that determine variability of pCO₂

The pCO₂ in mixed layer waters, which exchange CO₂ directly with the atmosphere, is affected by temperature, the total CO₂ concentration and the alkalinity. While the water temperature is regulated by physical processes (i. e. solar energy input, sea-air heat exchanges and mixed layer thickness), the latter two are primarily controlled by
biological processes (i.e. photosynthesis and respiration) and by upwelling of subsurface waters enriched in CO$_2$ and nutrients. The pCO$_2$ in surface ocean waters doubles for every 16°C temperature increase. For a parcel of seawater with constant chemical composition, pCO$_2$ would increase by a factor of 4 when it is warmed from polar water temperatures of about –1.9°C to equatorial water temperatures of about 30°C. On the other hand, the total CO$_2$ concentration in surface waters ranges from about 2150 µmol/kg in polar waters to 1850 µmol/kg in equatorial waters. If a global mean Revelle factor of 10 is used, this reduction of TCO$_2$ should cause a reduction of pCO$_2$ by a factor of 4.5. Thus, on a global scale, the effect of biology and upwelling on surface water pCO$_2$ is similar in magnitude but often opposite in direction to the temperature effect. The increasing effect on seawater pCO$_2$ of summer warming of water is commonly opposed by the lowering effect of photosynthesis during summer months. The decreasing effect on pCO$_2$ of winter cooling of water is counteracted by the increase in the total CO$_2$ concentration caused by winter convective mixing of deep waters rich in CO$_2$. It is therefore the interactions of the three major effects (i.e. temperature, upwelling and biological utilization of CO$_2$) that determine the annual mean pCO$_2$ and variability about the mean in space and time.

**Variability of surface water pCO$_2$**

The spatial variability of the surface water pCO$_2$ is demonstrated in Fig. 1 using about 700,000 pCO$_2$ observations made in past 40 years by Takahashi et al. (1999). The standard deviation of observed pCO$_2$ values in each 4° x 5° pixel was computed for each month, and the mean of the monthly standard deviation values have been plotted in color. The white areas indicate the pixels with no observations. The map, therefore, shows the magnitude of mean pCO$_2$ variability over the period of a month within each pixel area. It should be noted that some pixels have observations in all 12 months, whereas some pixels have observations only in one or more months. Small spatial variability (magenta-blue) is found mainly in the subtropical oceans, whereas large variability (green-yellow-orange) is found in the equatorial Pacific and the high latitude oceans of both hemispheres, where the concentrations of nutrients are large and the productivity is high. The large pCO$_2$ variability in these areas may be attributed to meso-scale variability in biology as well as physical features such as eddies and internal waves.
Fig. 1 - Spatial variability of the surface water $pCO_2$ represented by the standard deviation of observed $pCO_2$ values in a month.

Large spatial variability also has been observed in the areas affected by major western boundary current systems (Gulf Stream, Labrador Current, Brazil-Malvinas Confluence areas, Kuroshio and Oyashio), along which eddies and filaments are formed. *Sampling strategies for surface water $pCO_2$ must be formulated by taking these areas of large spatial variability into consideration.*

The seasonal variability of surface water $pCO_2$ varies geographically and has a peak-to-peak amplitude which is as large as 280 $\mu$atm in some regions. Seasonal amplitudes exceeding 100 $\mu$atm have been observed in the northwestern Arabian Sea, the northwestern subarctic Pacific, the subarctic North Atlantic, the eastern Sargasso Sea (Bermuda area) and the Ross and Weddell Seas, Antarctica. In subtropical gyre areas (e.g. Bermuda area), the seasonal variation in surface water $pCO_2$ is primarily driven by seasonal temperature changes, and hence $pCO_2$ is highest during summer and lowest in winter. On the other hand, in subpolar and polar oceans, the $pCO_2$ is highest during winter due to upwelling and is lowest during summer due to photosynthesis. Therefore, seasonal changes in high latitude areas are about 6 months out of phase from those in subtropical areas. Transition areas in-between these two regimes (e.g. Weather Station “P”) exhibit small seasonal amplitudes as a result of interactions of these out of phase forcings. The seasonal and temporal variability of surface water $pCO_2$ in specific areas will be discussed in Section 4.

**Regional CO$_2$ Flux and Sea-air $pCO_2$ Difference**

The monthly distributions of the sea-air $pCO_2$ difference over the global oceans for a reference year 1995 have been estimated using about 700,000 $pCO_2$ measurements made over the past 40 years. The methods for data corrections and interpolation used have been described in Takahashi et al. (1997, 1999). The monthly distribution maps produced represent a climatological mean for non-El Nino conditions with 4° x 5° spatial
resolution. The net flux values for the global oceans and various oceanic regions have been estimated on the basis of the sea-air pCO₂ difference maps and the dependence of the CO₂ gas transfer coefficient across the sea surface on long term wind speed, that has been formulated by Wanninkhof (1992). If the monthly mean climatological wind speeds of Esbensen and Kushnir (1981) is used, the pCO₂ data yield a global oceanic uptake of 1.94 Pg-C/yr. If the 40-year mean NCEP/NCAR wind speed data are used, a global ocean uptake of 2.45 Pg-C/yr is obtained. Table D-1 shows the annual mean sea-air pCO₂ difference and the net CO₂ uptake flux in various oceanographic regions, that was estimated using the wind speed data of Esbensen and Kushnir (1981).

Table D-1 - Mean annual sea-air pCO₂ difference, annual flux and the sea-air pCO₂ required for 0.1 Pg C flux. All the values are for the reference year 1995. The wind speed data of Esbensen and Kushnir (1981) and the wind speed dependence of gas transfer coefficient of Wanninkhof (1992) have been used.

<table>
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<th>OCEAN REGIONS</th>
<th>Average Ocean Δ pCO₂ (µatm)</th>
<th>Ocean Area 10⁶ km²</th>
<th>Δ pCO₂ per 0.1 Pg C per yr uptake</th>
<th>Annual Flux Pg C yr⁻¹</th>
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Table D-1 shows that, in order to estimate a regional CO₂ flux within +/- 0.1 Pg C yr⁻¹ for the major oceanic regions, the sea-air pCO₂ difference should be determined within 3 to 15 µatm. Fig. 2 shows the geographical distribution of the sea-air pCO₂ differences required for constraining flux estimates within +/- 0.1 Pg-C/yr. Small oceanic regions such as Northern North Pacific and Temperate North Indian Oceans (area< 4 x10⁶ km²) are exceptions, since the net flux for these areas are much smaller than 0.1 Pg-C/yr.
Fig. 2 – Target $pCO_2$ to estimate a regional CO$_2$ flux within +/-0.1 Pg-C/yr for the major oceanic regions from Table D-1. Polar regions cover areas between 50° and 90° (North and South), temperate regions cover areas between 14° and 50° (North and South) and equatorial regions are between 14°N and 14°S.

In order to estimate the terrestrial ecosystem uptake flux of CO$_2$ reliably on the basis of an inversion of atmospheric CO$_2$ concentration data, it has been suggested that the net CO$_2$ flux over each oceanic region be known within +/- 0.1 Pg-C/yr. For this reason, the analysis presented below is focused on evaluating the error in air-sea $pCO_2$ difference, that corresponds to a flux error of +/- 0.1 Pg-C/yr.

**Temporal Variability of $pCO_2$ and Sampling Frequency**

There are only a few locations, where seasonal changes in surface water $pCO_2$ have been determined throughout a year. Below, the data obtained at three locations, i.e. in the vicinity of Bermuda, Equatorial Pacific and Weather Station “P”, will be presented and analyzed. Each of these three locals represents the temperate gyre regime (Bermuda), the high seasonal upwelling regime (equatorial Pacific and a subarctic area north of Iceland) and the transition zone between the temperate and subarctic regimes (Weather Station “P”), respectively.

**Temperate Gyre Regime**

The temporal (seasonal) variability of $pCO_2$ and SST observed in the vicinity of the BATS Site (31°N, 64°W) are shown in Fig. 3. Seasonal amplitude of about 100 µatm for $pCO_2$ and that of 8 °C for SST are observed. The seasonal changes for $pCO_2$ appear to be in phase with those for SST. However, the observed $pCO_2$ amplitude is much smaller than that anticipated from a temperature change of 8 °C, that should cause a $pCO_2$
change of about 150 µatm. This difference has been attributed to the effect of biological drawdown of pCO$_2$ (about 50 µatm), which is about 6 months out of phase from the effect of temperature changes (Takahashi et al., submitted).

Fig. 3 - Temporal variation of surface water pCO$_2$ observed in the vicinity of the BATS Site (31 °N, 64 °W) observed in mid-1994 through early 1998 by N. Bates (BBRS).

Fig. 4 - Error for the annual mean value as a function of sampling frequency per year in the temperate North Atlantic in the vicinity of the BATS site. The standard error of the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The horizontal dashed-dotted line refers to the error in ΔpCO$_2$ needed for the estimated flux of CO$_2$ to the nearest 0.1 Pg-C in the temperate North Atlantic.
Using these data, we have computed the following two quantities. A) Errors anticipated from measurements made at random sampling intervals, where errors are represented by the standard error of the mean ($\sigma/\sqrt{n}$). The dashed curve in Fig. 4 shows the anticipated error in annual mean as a function of the number of measurements made in a year. For a calendar year of 1997, 104 measurements were made in the area yielding a mean pCO$_2$ of 347.9 $\mu$atm with a one-sigma of 33 $\mu$atm. This curve represents simply this standard deviation ($\sigma$) value divided by the square root of the number of observations, $n$, per year. In order to obtain an error in the mean of 6 $\mu$atm or better (see Table D-1), measurements must be made as frequently as 30 times a year. B) The solid curve shows errors anticipated in the mean value calculated at equally spaced sampling distances. The mean at each sampling interval was calculated by sub-sampling the originally over sampled time series and using a piece-wise linear interpolation to interpolate the sub-sampled time series back to the original sampling interval of the time series. Thus, the mean of the sub-sampled time series is calculated using the same number of observations as the mean calculated from the original time series. The mean for each sampling interval was calculated a number of times by sub-sampling different parts of the original time series. The error in the predicted mean was computed by calculating the difference between the mean value of the linearly interpolated sub-sampled time series and the mean obtained for the entire data set. To achieve level a +/- 6 $\mu$atm of precision in the prediction of the mean using equal sampling intervals in time 9 observations are needed a year. C) The solid line open with circles shows errors in the calculated mean if samples are taken at randomly spaced intervals in time and interpolated with a piece-wise linear fit to the original sampling intervals. As above, the error in the prediction of the mean is calculated as the difference between the mean value of the linearly interpolated sub-sampled time series and the mean obtained for the entire data set. Fig. 3 indicates that if the time series is sampled at randomly spaced intervals in time it will require at least 15 samples a year to predict the mean annual pCO$_2$ to within +/- 6 $\mu$atm.

The error for annual mean pCO$_2$ value depends not only on the total number of measurements made in a year, but also on time-intervals for measurements. Considering that the temporal pattern of seasonal pCO$_2$ changes might be somewhat different from year to year, measurements should be made more often than 9 times a year. Therefore, we estimate that one set of measurements for every one to 1.3 months annually should yield an annual mean value within the desired +/- 6 $\mu$atm (needed for +/- 0.1 Pg-C/yr, see Table D-1) over the temperate North Atlantic region.
Equatorial Pacific Regime
The temporal variability of the sea-air pCO$_2$ difference ($\Delta$pCO$_2$) at the Equatorial Pacific is shown from mooring data taken at 2°S and 170°W from June 22, 1998 to May 3, 2000 (Gernot Friederich and Francisco Chavez, MBARI, Fig. 5). The variability of surface water pCO$_2$ in this region is very closely associated with sea surface temperature values indicating upwelling events due to a combination of local wind events, the remnants of tropical instability waves and Kelvin waves propagated by Madden and Julian Oscillation in the atmosphere (Chavez et al., 1999). The increase in $\Delta$pCO$_2$ over the measurement period is most likely due to the increase in upwelling as the Eastern Equatorial Pacific recovers from El-Nino conditions. Fig. 6 shows the error in the estimate of the mean from the standard error (dashed curve), randomly spaced sampling (open circles and solid line) and evenly spaced sampling (solid curve) over an annual cycle. This data set would need to be sampled ~30 times a year randomly or ~15 times a year at equal intervals to achieve an average annual $\Delta$pCO$_2$ of 4.4 µatm (the $\Delta$pCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the North Pacific, Table D-1).
Fig. 6  - Error for the annual mean value as a function of sampling frequency per year in the Equatorial Pacific at 2° S and 170° W. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the ΔpCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the Equatorial Pacific.

Subarctic Regime
The temporal (seasonal) variability of the surface water pCO$_2$ in an approximately 4° x 5° area located north of Iceland is shown in Fig. 7. The pCO$_2$ values were obtained by Jon Olafsson of MRI, Reykjavik, and the LDEO staff over the 14-year period, 1983-1997. Since no obvious interannual changes can be identified, the data in this period are plotted against a time span of one year, and thus the plot includes the interannual variability as well as the spatial variability within this area box. The data associated with salinity values less than 34.0 have been removed in order to eliminate the effects of low salinity arctic waters. An abrupt drawdown of surface water pCO$_2$ amounting to about 250 µatm is observed about Julian day 150, and this coincides with the formation of well stratified mixed layer and a rapid increase in the temperature of the mixed layer. The sudden decrease in pCO$_2$ is attributed primarily to the biological utilization of CO$_2$, but is partially compensated by the concurrent increase in temperature (Takahashi et al., 1993). The mean annual pCO$_2$ in surface waters is 311.3 µatm with a standard deviation of 41 µatm and a standard error in the mean of +/- 2.4 µatm (with a total number of measurements of 284).
Fig. 7 - The temporal (seasonal) variation of surface water pCO$_2$ in a 4° x 5° area located north of Iceland. The data were obtained by Jon Olafsson (MRI, Reykjavik) and the LDEO staff over the 14 year period, 1983-1997.

Fig. 8 - Error for the annual mean value of surface pCO$_2$ as a function of sampling frequency per year in a 4° x 5° area located north of Iceland. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the $\Delta$pCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the subarctic North Atlantic region.

The error for the annual mean pCO$_2$ calculated by randomly and evenly time-spaced sampling of the observation is shown in Fig. 8 as a function of the number of
sampling events per year. Based on this plot, we estimate that 5-8 evenly spaced observations or 8-15 randomly spaced observations annually should yield an annual mean value within the desired +/- 11 µatm (needed for +/- 0.1 Pg-C/yr, see Table D-1) over the subarctic North Atlantic region.

**Transition Zone between the Temperate and Subarctic Regimes**

The temporal (seasonal) variability of the surface water pCO$_2$ in an approximately 4° x 5° area that includes the Weather Station “P” in the northeastern North Pacific (50°N, 145°W) is shown in Fig. 9. The observations were made in the three-year period, 1972-1975, and are plotted against Julian day as though all measurements were made in one year. Therefore, the plot includes the inter-annual variability. Fig. 9 shows relatively small seasonal peak-to-peak amplitude of about 50 µatm (compared with 100 µatm near Bermuda (Fig. 3) and 250 µatm near Iceland (Fig. 7)), and shows no simple sinusoidal seasonal patterns (like that observed near Bermuda (Fig. 3)). This may be attributed to the fact that the seasonal temperature effect on pCO$_2$ is similar in amplitude but about 6 months out of phase from the biological effect (Takahashi et al., 1993). While the effect of summer warming of water increases surface water pCO$_2$, the biological CO$_2$ utilization which increases toward a summer maximum reduces pCO$_2$, thus partially or entirely canceling each other. Large oceanic areas located along the boundary between the temperate and subpolar regimes, especially in the southern hemisphere oceans between 40°S and 60°S, also exhibit a zone of small seasonal amplitude in surface water pCO$_2$ (Takahashi et al., submitted).

![Station P time series](image)

**Fig. 9 -** Seasonal variation of surface water pCO$_2$ and SST observed at the Weather Station “P” (50°N and 145°W) by Wong and Chan (1991) in 1972-1975. Note that the SST changes more or less sinusoidal with a seasonal amplitude of 8 °C, and that the surface water pCO$_2$ does not exhibit a simple sinusoidal pattern and changes only by 50 µatm (compared to 130 µatm expected from a 8 °C temperature change).
The error for the annual mean pCO₂ anticipated for measurements with evenly time-spaced sampling, is shown in Fig. 10 as a function of the number of sampling events per year. Based on this plot, we estimate that ~9 evenly spaced observations or ~15 randomly spaced observations a year should yield an annual mean value within the desired +/- 3 μatm (needed for +/- 0.1 Pg-C/yr, see TableD-1) over the temperate/subarctic North Pacific region.

Fig. 10 - Error for the annual mean value at Weather Station “P”. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the ΔpCO₂ needed to estimate the flux of CO₂ to the nearest 0.1 Pg of C in the Temperate North Pacific.

**Spatial Variability of CO₂ and Sampling Intervals**

We have also analyzed scales of variability in the surface water pCO₂ values measured along ship’s tracks using semi-continuous equilibrator-IR systems. To represent different oceanographic regimes, we have chosen a) an E-W traverse across the temperate North Atlantic, b) a N-S traverse across the central Pacific including the high pCO₂ equatorial zone, and c) a pair of N-S traverses during summer and winter across the sub-polar and polar regimes in the Pacific sector of the Southern Ocean. The analysis of these data sets, which cover major oceanographic regimes should yield the basis for designing sound strategies for mapping of the surface ocean pCO₂ over the global oceans.

**E-W Traverse across the Temperate North Atlantic Ocean**

The spatial variability in pCO₂ for the Temperate North Atlantic is illustrated using a transects from Punta Del Gado, Azores to Miami, FL (Fig. 11A) during the GASEX 98 cruise using measurements made on the NOAA research vessel R.V. Ron Brown. The measurements of pCO₂ were made over a 10-day period extending from June 28, 1998 to July 7, 1998 and show a steady increase in pCO₂ over the westward transect to Miami.
with a peak in the Gulf Stream (~5000 km from the Azores, Fig. 11B). This data were provided by the joint collaboration of AOML and PMEL (http://www.aoml.noaa.gov/ocd/oaces/mastermap.html).
Fig. 11 - A) Cruise track of the NOAA R.V. Ron Brown from Punta Del Gado, Azores to Miami, FL from June 28, 1998 to July 7, 1998 during GASEX 98. B) Surface water pCO$_2$ as a function of the distance from Azores. This data were provided by the joint collaboration of AOML and PMEL (http://www.aoml.noaa.gov/ocd/oaces/mastermap.html).

The large-scale change in surface water pCO$_2$ over the course of the transect clearly dominates the variance about the mean. When the error in the estimates of the transect mean is computed for equally spaced samples (Fig. 12), we observe that randomly spaced samples taken every ~750 km and evenly spaced samples taken every 1500 km should yield an annual mean value within the desired +/- 5.6 µatm (needed for +/- 0.1 Pg-C/yr, see Table D-1).
Fig. 12 - Error estimate of mean surface pCO$_2$ during transect of the NOAA R.V. Ron Brown from Punta Del Gado, Azores to Miami, FL. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the ΔpCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the Temperate North Atlantic.

N-S traverse across the Central North and Equatorial Pacific Ocean
As in the Temperate North Atlantic, the required sampling intervals to make flux estimates with errors less than 0.1 Pg-C/yr requires less sampling because of a reduced level of meso-scale variability in surface pCO$_2$ in these areas. This is demonstrated by a transect from Hololulu, HI to Dutch Harbor, AK along the ~170°W meridian during a 8-day period between September 26, and October 3, 1999 (NOPP99, Fig. 13). A similar transect is also shown from a transect that took place a year later from Dutch Harbor, AK to San Diego, CA during a 12 day period between September 27, and October 9, 2000 (NOPP2000, Fig. 13). This data were provided by the joint collaboration of AOML and PMEL (http://www.aoml.noaa.gov/ocd/oaces/mastermap.html). Both surface pCO$_2$ profiles indicate strong fronts at ~34°N, ~50°N and ~54°N where surface pCO$_2$ varies by as much as 60 µatm. However, between fronts the mesoscale (~100 km) variability is small. Sub-sampling the original datasets (Fig. 14) indicates that with evenly spaced sampling intervals of ~300-700 km should yield an annual mean value within the desired +/- 2.9 µatm (needed for +/- 0.1 Pg-C/yr, see Table D-1).
Fig. 13 - Surface pCO$_2$ at sea surface temperature measured on the NOAA R.V. Ron Brown from Honolulu, HI to Dutch Harbor, AK along the ~170°W meridian between September 26, and October 3, 1999 (NOPP99, ‘--’). Surface pCO$_2$ at sea surface temperature measured on the R.V. Ron Brown from Dutch Harbor, AK to San Diego, CA during a 12-day period between September 27, and October 9, 2000 (NOPP2000 ‘-’). This data were provided by the joint collaboration of AOML and PMEL (http://www.aoml.noaa.gov/ocd/oaces/mastermap.html).

Fig. 14 - Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals during the transect of the NOAA R.V. Ron Brown from Honolulu, HI to Dutch Harbor, AK along the ~170°W meridian between September 26, and October 3, 1999 (NOPP99, dashed line). Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals during the transect of the NOAA R.V. Ron Brown from Dutch Harbor, AK to San Diego, CA during a 12-day period between September
27, and October 9, 2000 (NOPP2000, solid line). The dotted dashed line refers to the ΔpCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the Temperate North Pacific.

The spatial variability in surface pCO$_2$ in the Temperate and Northern Pacific appears to be small compared to those found in the equatorial zone (Fig. 1). Two transects across the equator along the 95°W (Eastern Pacific, the data obtained by the LDEO staff) and 170°W (Central Pacific, the data provided by R. A. Feely, PMEL/NOAA) meridians show closely spaced fronts less than 200 km apart which exhibit changes in surface pCO$_2$ of greater than 100 µatm (Fig. 15). A sub-sampling in the Central and Eastern Equatorial Pacific (Fig. 16) and indicates that evenly spaced sampling of 200-500 km intervals should yield an annual mean value within the desired +/- 4.4 µatm (needed for +/- 0.1 Pg-C/yr, see Table D-1).

Fig. 15 - Surface pCO$_2$ at sea surface temperature measured on the R.V. I. B. Nathaniel B. Palmer from Punta Arenas, Chile to Seattle, WA along the ~95°W meridian between July 26, and August 12, 1998 (NBP9805, solid line). Surface pCO$_2$ at sea surface temperature measured on the NOAA R.V. M. Baldridge from Darwin, Australia to Rodman, Panama between November 21, 1995 and January 17, 1996 (MB95, dashed line).
Equatorial Pacific

Fig. 16- Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals during the transect on the R.V. I. B. Nathaniel B. Palmer from Punta Arenas, Chile to Seattle, WA along the ~95°W meridian between July 26, and August 12, 1998 (NBP9805, solid line). Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals during the transect on the NOAA R.V. M. Baldridge from Darwin, Australia to Rodman, Panama between November 21, 1995 and January 17, 1996 (MB95, dashed line). The dotted dashed line refers to the ΔpCO$_2$ uncertainty needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the Equatorial Pacific region.

N-S Traverses across the High Latitude Southern Ocean

The Southern Ocean exhibits the same degree of variability seen in the Pacific equatorial zone, through a combination of the ACC, strong Coriolis forcing and a large biological drawdown of CO$_2$ which act together to increase the meso-scale variability in this region. The effect of biology on meso-scale variability in the Southern Ocean is demonstrated by Fig. 17 which shows two transects, one prior to the phytoplankton bloom (winter-NBP9708) and one following the phytoplankton bloom (summer-KIW18), along ~170°W from 45°S to 63°S. It is important to note the variability north of 50°S in both transects. Variability in pCO$_2$ due to primary productivity during the summer months in the lower latitudes significantly effects our ability to estimate the mean by sub-sampling the original data set. Fig. 18 suggests that during the summer samples need to be taken every 400-800 km to get a robust estimate of the basin-scale mean value within the desired +/- 4.3 µatm (needed for +/- 0.1 Pg-C/yr, see Table D-1).
Fig. 17- Surface pCO$_2$ at sea surface temperature measured on the R.V. I. B. Nathaniel B. Palmer along ~170°W meridian between November 7 and November 11, 1997 (Winter- NBP9708, solid line). Surface pCO$_2$ at sea surface temperature measured on the R.V. Revelle along ~170°W meridian between February 2 and February 11, 1998 (Summer-KIWI 8, dashed line).

Fig. 18- Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals on the R.V. I. B. Nathaniel B. Palmer along ~170°W meridian between November 7 and November 11, 1997 (Winter- NBP9708, green solid line). Error estimate of mean surface pCO$_2$ using evenly spaced sampling intervals during transect on the R.V. Revelle along ~170°W meridian between February 2 and February 11, 1998 (Summer-KIWI 8, black open circles and solid line). The dotted dashed line refers to the uncertainty of ΔpCO$_2$ needed to estimate the flux of CO$_2$ to the nearest 0.1 Pg of C in the Polar South Pacific. The smooth dashed curve indicates the estimated standard error.
Conclusion

Temporal and spatial sampling requirements
In the above analysis we have shown how often the sea-air pCO$_2$ difference in the temperate regions of North Pacific and North Atlantic need to be sampled using evenly spaced sampling to estimate regional fluxes to better than 0.1 Pg-C yr$^{-1}$ (Table D-2). In addition, we have also included the Equatorial Pacific and Southern Pacific Polar Ocean because of the high meso-scale variability in these areas. The results presented assume that the uncertainty in the estimated fluxes are due entirely to the precision of the sea-air pCO$_2$ difference and do not include the errors from the sea-air gas transfer coefficient. Our analysis points out that a desired uncertainty of +/- 0.1 Pg-C/yr in the basin-scale mean annual estimates for net sea-air CO$_2$ flux may be achieved by evenly spaced measurements of pCO$_2$ in time 6–15 times a year throughout the regions of the world ocean with evenly spaced sampling 200-1500 km apart (or 2-20 degrees longitude depending on region and latitude). This analysis also points out the advantage of evenly spaced sampling over randomly spaced sampling in time and space.

Table D-2 - Mean annual sea-air pCO$_2$ difference, the sea-air pCO$_2$ required for 0.1 Pg-C flux, the required evenly spaced spatial and temporal sampling needed to achieve the sea-air pCO$_2$. All the values are for the reference year 1995. The wind speed data of Esbensen and Kushnir (1981) and the wind speed dependence of gas transfer coefficient of Wanninkhof (1992) have been used.

<table>
<thead>
<tr>
<th>Region</th>
<th>Average ΔpCO$_2$ (µatm)</th>
<th>ΔpCO$_2$ Flux=0.1 PgC yr$^{-1}$ (µatm)</th>
<th>Samples Spacing (km)</th>
<th>Samples per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern North Atlantic</td>
<td>-47.4</td>
<td>10.8</td>
<td>~1500</td>
<td>~5-9</td>
</tr>
<tr>
<td>Temperature North Atlantic</td>
<td>-9.3</td>
<td>5.6</td>
<td></td>
<td>~6</td>
</tr>
<tr>
<td>Temperate North Pacific</td>
<td>-10.0</td>
<td>2.9</td>
<td>200-600</td>
<td>~9</td>
</tr>
<tr>
<td>Equatorial Pacific</td>
<td>29.6</td>
<td>4.4</td>
<td>200</td>
<td>~15</td>
</tr>
<tr>
<td>Polar South Pacific</td>
<td>-9.0</td>
<td>4.3</td>
<td>300-800</td>
<td></td>
</tr>
</tbody>
</table>

In real ocean environments, wind speeds changes with short time scales, and hence the sea-air CO$_2$ flux as the gas transfer piston velocity is affected sensitively with win speed. Using the wind speed and pCO$_2$ data observed by the AOML and PMEL staff during NOAA Ron Brown cruise (98-3) over the subtropical North Atlantic, we have computed the sea-air CO$_2$ flux using the ship board wind speed data, and the flux data have been analyzed similarly as done for the pCO$_2$ data shown in Fig. 12. While we have found on the basis of the pCO$_2$ data analysis that a sampling spacing of 750 km should give a precision of 0.1 Pg C in the temperate North Atlantic, an analysis of the flux data gives that about 250 km sampling spacing is needed to obtain the same precision. This suggests that the sampling spacing values evaluated in Table D-2 above represent a maximum spacing applicable to wind speeds averaged over a month rather than those averaged over a shorter time (hourly) period. We therefore recommend that surface water pCO$_2$ measurements be made with greater frequencies (or shorter spatial intervals) comparable to wind speed variability, so that the magnitude of the cross correlation term for pCO$_2$ and wind speed variations can be evaluated.
Ways to lower sampling requirements
The above sampling recommendations assume that we have no prior knowledge about the spatial and temporal variability and no other proxies estimating the surface concentration of pCO$_2$.

Subjective sampling
Given some knowledge of the known spread of variance throughout time and space it may be possible to improve our estimate of the mean by sampling at high resolution in spatial or temporal gradients and lower resolution in areas where the known gradients are not as steep. This subjective approach may serve to reduce the required number of samples in a given area. In order to insure that no bias results from this “subjective approach” to sampling each region will need to be over sampled initially.

Use of proxies
The fact that we are able to predict the mean value of the sea-air pCO$_2$ difference with evenly spaced sampling so much better than randomly spaced sampling is directly related to the fact that the sea-air pCO$_2$ difference is autocorrelated. Simply stated, sequential measurements of surface pCO$_2$ in time and space are correlated with each other over some distance which is related to the sampling frequency that we have specified in Table D-2. Without prior knowledge of the field, it is more efficient to sample at evenly spaced intervals than randomly spaced intervals.

In addition to being autocorrelated, surface pCO$_2$ also is also correlated with other parameters such as temperature (Stephens et al., 1995) and chlorophyll concentrations which can be observed remotely using instruments like the Pathfinder AVHRR for sea surface temperature and SeaWiFS for ocean color and biological productivity estimates. By building regionally specific algorithms to take advantage of these correlations we should be able to further decrease samples needed to predict the mean surface water pCO$_2$ for both regional and annual estimates.

While it is clear from this analysis that the mean surface water pCO$_2$ is driven primarily by large scale variability in the ocean (>300 km), it important that meso-scale processes not be disregarded. Multi-parameter observations of meso-scale processes using moorings and high resolution underway sampling techniques will be essential to understanding the processes that are responsible for the statistical covariance observed. It is therefore important to design a sea-air CO$_2$ flux program that combines the regional scale surface ocean pCO$_2$ observations with an ample dose of relevant process studies.

References Cited


