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CO_2 in the North Pacific Ocean

PICES Working Group 13
Final Report

Edited by

Richard A. Feely

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Executive Summary

The North Pacific Ocean plays a significant role in controlling the long-term fate of CO_2 on Earth. Much of our understanding of the distribution of anthropogenic CO_2 in the North Pacific stems from intensive work conducted during the decade of the 1990s. Underway measurements were made for pCO_2 in the northern North Pacific from 1995 to 1999, as part of the Japan-Canada cooperative vessel-of-opportunity program. In addition, discrete high-quality dissolved inorganic carbon and total alkalinity data were acquired as part of the WOCE/JGOFS Global CO_2 survey in the Pacific Ocean between 1991 and 1999. This research was supported, in part, by the member nations of the North Pacific Marine Science Organization (PICES). This report describes the research and technical activities of the PICES Working Group 13 on *CO_2 in the North Pacific* from 1998 through 2001. The major scientific objectives of the Working Group were to: (i) synthesize CO_2 data from the North Pacific Ocean; (ii) determine the sources and sink for CO_2 and their regional fluxes; and (iii) provide a comprehensive picture of the distribution of anthropogenic carbon dioxide in the region. The major technical activities included: (i) supporting international cooperation in exchanges of samples from cruises; (ii) organizing measurement inter-comparison studies for carbonate parameters in seawater; and (iii) developing ongoing mechanisms for exchanging data at the international level; and (iv) sponsoring several meetings and symposia on CO_2 system dynamics in the North Pacific. We will discuss the implications of these research and technical activities with respect to climate change processes and provide recommendations for future directions by PICES for international cooperation on carbon cycle research in the North Pacific.

Richard A. Feely & Yukihiro Nojiri
WG 13 Co-Chairmen

1.0 Introduction

Over the past 200 years, human activities have led to a secular increase in atmospheric CO_2 from about 280 to greater than 365 ppmv (Keeling and Whorf, 2000; Carbon Dioxide Information Analysis Center, 2001). The impact of the CO_2 increase and that of other "greenhouse" gases on the global climate is at the center of a major international policy debate. Studies of the ocean's role in the uptake and storage of anthropogenic CO_2 and modulation of future atmospheric CO_2 levels are critical for understanding the global carbon cycle and for the prediction of future climate change. The North Pacific is an important sink region for atmospheric carbon dioxide in the oceans and, consequently, plays a significant role in controlling the long-term fate of CO_2 on Earth. Some biogeochemical processes relating to the oceanic CO_2 system are peculiar to the North Pacific. This occurs because (i) the North Pacific is the final destination of circulation of the deep water that contains a high level of preformed nutrients and dissolved inorganic carbon (DIC), and (ii) the North Pacific Intermediate Water stores dissolved CO_2 for more than a few tens of years.

Much of our understanding of the distribution and fate of anthropogenic CO_2 in the North Pacific stems from the high-quality carbon data that were acquired as part of the World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Study (JGOFS) Global CO_2 survey and subsequent cruises. In addition, underway measurements were made for pCO_2 in the northern North Pacific from 1995 to 1999, as part of the Japan-Canada cooperative vessel of opportunity program. This research was supported, in part, by the member nations of the North Pacific Marine Science Organization (PICES), through the activities of its Working Group 13. The group played a major role in fostering international cooperation in exchanges of samples from cruises, supporting CO_2 inter-comparison studies, and developing strategies for exchanging data at the international level. This report summarizes the research and technical activities that have been conducted by member nations of PICES to synthesize CO_2 data in the North Pacific, and provide a comprehensive picture of the distribution of anthropogenic CO_2 in this region. Then, the implications of the results with respect to climate change processes in the future are discussed. Finally, recommendations are made for future directions by PICES for international cooperation on carbon cycle research in the North Pacific.

2.0   Synthesis of the WOCE/JGOFS global CO_2 survey data in the North Pacific

The recently completed WOCE/JGOFS global CO_2 survey conducted during the 1990s produced over 15 times more high-quality carbon measurements than previous survey efforts. These data are an important asset to the scientific community investigating biogeochemical cycling of carbon species in the oceans. They are also a significant legacy to future generations of scientists by providing a baseline against which future changes in ocean geochemistry can be assessed. Most of the data have been reported to national archive facilities. Between 1991 and 1999, carbon system measurements were made on 14 WOCE/JGOFS cruises in the North Pacific Ocean by investigators from 9 different laboratories and 3 countries (Fig. 1, Table 1). At least two of the four inorganic carbon parameters were analyzed on each cruise, with the exception of CGC91 and P9. DIC was measured on all of the cruises, but additional measurements included one or more of the remaining parameters: TAlk, fugacity of CO_2 (fCO_2[1]), or pH. With support from PICES and several federal agencies at the

national level, an analysis of this data set was conducted in order to make specific recommendations for the adjustment of the Pacific carbon survey data to produce a uniformly calibrated data set.

2.1   Analytical methods

Analyses of all carbon parameters during the Pacific Ocean CO_2 survey cruises were generally performed following the techniques outlined in the *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater* (DOE, 1994).

2.1.1   Dissolved inorganic carbon (DIC) analysis

All DIC samples were analyzed by coulometric titration. The main differences between the various groups were the sample volume and the primary calibration method (Johnson, 1992; Johnson *et al.*, 1985, 1987, 1993, 1998, Ishii *et*
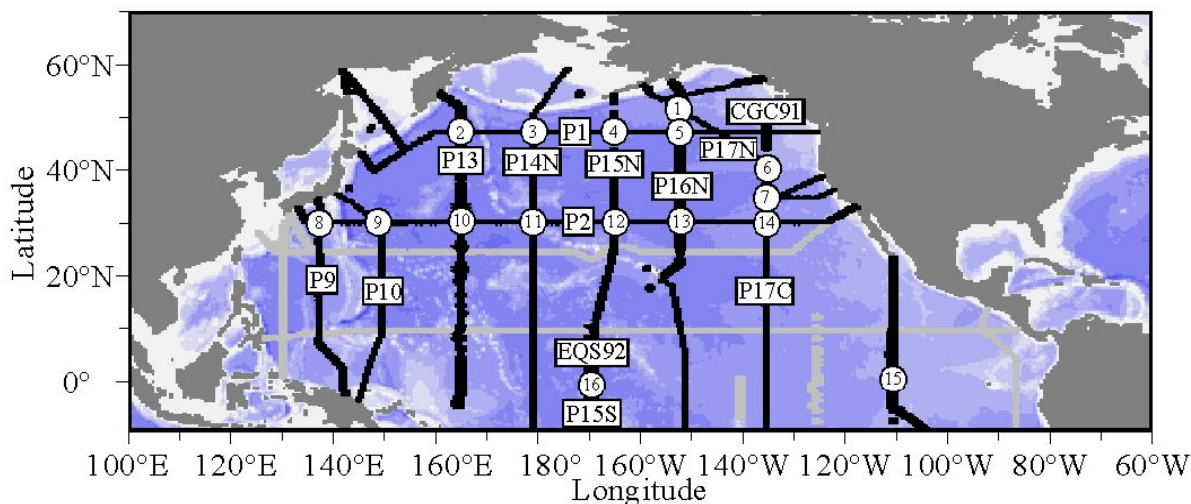
Fig. 1   Station locations for WOCE/JGOFS CO_2 survey cruises in the North Pacific Ocean. Cruise names are designated in the rectangles. Circles show crossover locations where carbon measurements were made; gray lines indicate cruises that had no carbon analyses.

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[1]   The fugacity of CO_2 takes into account the non-ideal nature of the gas. The values of fCO_2 are within 0.5-1.5 µatm of the partial pressure of CO_2 in surface waters.

Table 1 Summary of the carbon parameters analyzed during the North Pacific Ocean WOCE/JGOFS CO_2 survey (1991-1999).

Cruise Name	Cruise Date	Carbon Parameters Analyzed				Country/ [b]Institute	Archived Data Location
		DIC	TAlk	fCO_2	[a]pH		
P9	Jul-94	x				Japan/MRI	CDIAC
P10	Oct-93	x	x			USA/Princeton	CDIAC
P13	Aug-92	x	x			USA/SIO	CDIAC
P14N	Jul-93	x	x		x	USA/UH	CDIAC
P14S15S	Jan-96	x	x	x	x	USA/NOAA	CDIAC
P15N	Sep-94	x	x			Canada/IOS	WHPO/UCSD
EQS92	Mar-92	x	x	x	x	USA/NOAA	NOAA
P16N	Jan-91	x			x	USA/NOAA	CDIAC
P17C	May-91	x	x			USA/WHOI	CDIAC
P17N	May-93	x	x			USA/WHOI	CDIAC
CGC91	Feb-91	x				USA/NOAA	CDIAC
P18	Jan-94	x	x	x	x	USA/NOAA	CDIAC
P1	[c]99	x	x		x	Japan/JFA	N/A
P2	Jan-94	x	x			Japan/JFA	JODC

[a] Spectrophotometric technique
[b] Lead institute for carbon measurements
[c] Western section 3/99; Eastern section 9/99

Carbon Parameters Analyzed	DIC	TAlk	fCO_2	pH
No. of Cruises	14	11	3	6

Cruises with DIC-TAlk pair=11
Cruises with DIC-fCO_2 pair=3
Cruises with DIC-pH pair=6
Cruises with >2 parameters=5
Cruises with >3 parameters=3
Total number of carbon sample locations=~14,000

al., 1998). Certified Reference Materials (CRMs) (UNESCO, 1991; Dickson, 1992; Dickson *et al.*, 2003a, b) were used on most cruises as secondary standards for DIC. Certification of the CRM DIC is based on the vacuum extraction/manometric analysis of C. D. Keeling at the Scripps Institution of Oceanography (UNESCO, 1991; Guenther *et al.*, 1994). Routine shipboard CRM analyses helped verify sample measurement accuracy. Some laboratories reporting their DIC data to the archived data location did not normalize to CRMs.

2.1.2 Total alkalinity (TAlk) analysis

All shipboard TAlk measurements were made by potentiometric titration using a computer-controlled Dosimat™ titrator and a pH meter (Brewer *et al.*, 1986, Millero *et al.*, 1993, DOE 1994, Ono *et al.*, 1998). The primary analytical differences were the volume of sample analyzed, the use of either an open or closed titration cell, the method for fitting the titration results (*i.e.* Gran, nonlinear fit, or single point titration), and the calibration methods. Most groups routinely running CRMs for DIC also analyzed the CRMs

for TAlk despite the fact that the CRMs were not certified for TAlk until July 1996. Batches of CRMs bottled prior to July 1996 were certified by analyzing archived samples. This allowed post-cruise corrections to be made on many of the shipboard measurements (Lamb *et al*., 2002).

2.1.3   Discrete fCO₂ analysis

Each aliquot of seawater was equilibrated at a constant temperature of either 4°C or 20°C with a headspace of known initial CO_2 content. Subsequently, the headspace CO_2 concentration was determined by non-dispersive infrared analyzer (NDIR) or by gas chromatography. The initial fCO₂ in the water was determined after correcting for loss or gain of CO_2 during the equilibration process. This correction can be significant for large initial fCO₂ differences between headspace and water, and for systems with a large headspace to water volume ratio (Wanninkhof and Thoning, 1993; Chen *et al*., 1995).

2.1.4   pH analysis

With the exception of the potentiometric method of pH analysis used on P2, all the North Pacific samples were analyzed by a spectrophotometric method (Clayton and Byrne, 1993), with m-cresol purple as the indicator and either scanning or diode array spectrophotometers, and were measured at 25°C, with no conversion made to *in situ* temperatures. Since the precision of potentiometric pH is often no better than 0.02 pH units (SCOR, 1985), we have used only crossover data in this report that was analyzed spectrophotometrically.

All of the pH values were initially reported on the total hydrogen scale, and were then converted to the seawater scale (pH_{SWS}) to be consistent with published dissociation constants of carbonic acid. The seawater scale considers the interaction of hydrogen ions with bisulfate and fluoride ions in seawater, while the total scale only includes the bisulfate contribution (Dickson and Riley, 1979; Dickson and Millero,

1987). The two scales are linked by the following equation:

$$pH_{SWS} = pH_T - \log \{(1+[SO_4^{2-}]_T/K_{HSO4} + [F^-]_T/K_{HF})/(1 + [SO_4^{2-}]_T/K_{HSO4})\} \quad (1)$$

where pH_T is the hydrogen ion concentration on the total hydrogen scale, $[F^-]_T$ and $[SO_4^{2-}]_T$ are the total concentrations of fluoride and sulphate in seawater, and K_{HF} and K_{HSO4} are the dissociation constants of hydrogen fluoride and sulphate in seawater (Dickson and Riley, 1979).

2.2   Crossover comparisons of global CO₂ survey data

The goal of the crossover comparisons was to produce an accurate data set that was consistent between cruises. Despite greatly improved analytical techniques, the use of primary and secondary standards, and shore-based analysis of replicate samples for verification of accuracy for some carbon parameters, a few of the cruises still appear to have offsets when compared with other cruises in the same area. One approach for evaluating the consistency of the cruises was to compare data where cruises crossed or overlapped (Lamb *et al*., 2002). A location was considered a crossover if stations from two cruises were within ~100 km of each other. If more than one station from a particular cruise fell within the 100 km limit, the data were combined for the comparison. Table 2 provides a summary of the crossovers in the North Pacific. The crossover analysis is based on the assumption that the deep waters of the Pacific Ocean were constant within the 9 years of this study. The residence time of Pacific Deep Water is ~500 years (Stuiver *et al*., 1983), therefore, we can assume that these waters do not change significantly between cruises. For this analysis, only deep-water (>2,000 m) measurements were considered, because shallow water concentrations are highly variable and the penetration of anthropogenic CO_2 could potentially change relationships between the carbon parameters measured at different times.

Table 2 Summary of the results of the crossover comparisons for DIC, TAlk fCO$_2$ and pH during the North Pacific WOCE/JGOFS CO$_2$ Survey, modeled as a second-order polynomial function (Del Poly) to 3000 dbar (σ_3).

Crossover #	Latitude (°)	Longitude (°)	Cruise 1 Name	Cruise 1 Stations	Cruise 2 Name	Cruise 2 Stations	Delta DIC	Std Dev DIC	Delta TAlk	Std Dev TAlk	Delta fCO$_2$	Std Dev fCO$_2$	Delta pH	Std Dev pH
1	53N	152W	P16N	58,59,66	P17N	78	-9.0	5.1	[a]-23.6	5.8	[b]ND	[b]ND	[b]ND	[b]ND
2	47N	165E	P13	24	P1	42	-2.0	0.7	4.0	2.1	[b]ND	[b]ND	[b]ND	[b]ND
3	47N	179E	P14N	31	P1	60	0.2	2.6	5.2	1.5	[b]ND	[b]ND	[b]ND	[b]ND
4	47N	165W	P15N	18	P1	X15	-5.3	2.8	2.3	3.7	[b]ND	[b]ND	[b]ND	[b]ND
5	47N	152W	P16N	55	P1	X16	-8.3	0.6	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
6	40N	135W	CGC91	10	P17N	37,38,45	-7.9	1.5	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
7a	35N	135W	CGC91	12	P17N	28	-3.7	5.1	[b]ND	[b]ND	29.2	2.9	[b]ND	[b]ND
7b	35N	135W	CGC91	12	P17C	17	5.7	3.7	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
7c	35N	135W	P17N	28	P17C	17	9.4	3.4	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
8	30N	135E	P9	21	P2	19,21	1.6	2.4	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
9	30N	148E	P10	74,77	P2	37	-2.8	1.0	16.9	9.7	[b]ND	[b]ND	[b]ND	[b]ND
10	30N	165E	P13	54,55	P2	48,49	-5.5	2.1	12.9	1.2	[b]ND	[b]ND	[b]ND	[b]ND
11	30N	178E	P14N	63	P2	58	0.5	2.7	8.4	2.4	[b]ND	[b]ND	[b]ND	[b]ND
12	30N	165W	P15N	52,54	P2	65	-5.7	4.0	14.8	6.7	[b]ND	[b]ND	[b]ND	[b]ND
13	30N	152W	P16N	30,31,32	P2	70	-7.6	3.0	[a]3.2	0.2	[b]ND	[b]ND	[b]ND	[b]ND
14	30N	135W	P17C	26	P2	78	-3.1	4.6	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND	[b]ND
15	5N	110W	P18	155,159	EQS92	6	-7.5	4.9	-0.4	1.0	3.4	2.2	[b]ND	[b]ND
16a	0	170W	P14S15S	174	EQS92	56	2.8	2.3	-1.7	3.9	22.0	4.8	-0.0036	0.001
16b	0	170W	P14S15S	174	P15N	112	1.2	0.7	11.0	3.2	[b]ND	[b]ND	[b]ND	[b]ND
16c	0	170W	P15N	112	EQS92	56	1.5	2.0	-14.6	4.9	[b]ND	[b]ND	[b]ND	[b]ND
Average Absolute Value							**4.6**		**9.7**		**18.2**		**0.0036**	
Std Dev							**3.0**		**7.2**		**13.3**		**0.0000**	

[a] Crossovers on which TAlk values were calculated using a combination of DIC and either pH or fCO$_2$
[b] ND=No Data

Sixteen crossover locations were identified for analysis of DIC data. Only 9 locations had measured TAlk values for comparison. An additional 2 crossover locations were possible by comparing measured TAlk on one cruise to calculated TAlk values from another cruise. The calculated values were based on the combination of pH-DIC or fCO_2-DIC using the carbonate constants of Mehrbach *et al.* (1973) as refit by Dickson and Millero (1987), and ancillary constants (*e.g.*, boric acid and nutrients) based on DOE (1994) and Millero (1995). Just 3 crossover locations were available for fCO_2, and only 1 crossover could be used to examine the consistency of the pH data. Due to the problems associated with fCO_2 comparisons, and because of the paucity of pH crossover locations available, no additional statistical analyses were performed on either of these parameters.

Comparisons between two cruises at the crossover locations were made by fitting the data from each cruise with a 2nd order polynomial function, and examining the differences (deltas) between the two curve fits. Potential density referenced to 3,000 dbar (σ_3), rather than depth, was chosen as the independent variable for the analysis because water primarily moves along isopycnal surfaces. The average difference and standard deviation were determined from differences at 10 evenly spaced intervals along the curves. The number of points and their spread can affect the quality of the polynomial fits over the range. Differences in the number or distribution of points were notable in less than 10% of the DIC and TAlk comparisons examined.

Inspection of the polynomial residuals showed that the 2nd order function was inadequate for about 15% of the DIC and TAlk fits. In some cases, the residual patterns suggested that several different water masses were being examined. This occurred in areas of the North Pacific Ocean that have a complex vertical structure because of influences from the North Pacific Intermediate water and Pacific Deep Water. However, since we were more interested in the offsets than the nature of the curves, we maintained the 2nd order model to allow a uniform treatment of the crossover data while fitting a small number of parameters to the sometimes-limited deep-water (>2,000 m) data at each crossover.

To ensure that sparse sampling combined with either noisy data or variability resulting from water mass variations was not significantly biasing the estimates of the offsets, several approaches were examined. These include: same shape polynomial fits, multi-parameter linear regression (MLR) at crossover locations, basin-wide MLRs, isopycnal analyses, and internal consistency checks (Lamb *et al.* 2002). The overarching goal of this work was to assess the quality of the Pacific carbon survey data and to make recommendations for generating a unified data set that is both as accurate as possible, as well as consistent between cruises. To develop such a data set, some adjustments are necessary. Two important points must be considered when evaluating the various approaches used to examine the data quality of the cruises. First, most of the approaches assume that the deep ocean does not change over the time-period of the various cruises. As noted previously, the residence time for Pacific Deep Water is ~500 years (Stuiver *et al.*, 1983), almost two orders of magnitude longer than the difference in time between cruises. Thus, very little variability would be expected in the deep waters (pressure >2,000 dbar) at the crossover points. As a direct check on the constancy of the deep waters, DIC variability was examined as a function of latitude on deep isopycnal surfaces (Lamb *et al.*, 2002). The trend of increasing values from south to north results from re-mineralization of organic matter and dissolution of calcium carbonate in the waters as they spread northward from 20° to 40°N. Variability in these waters can be evaluated from the residuals of a linear fit of the large-scale trend. The residuals for points linearly interpolated onto the 41.5 σ_3 surface have a standard deviation of ±2.5 μmol kg^{-1}. If the vertical interpolation is determined by fitting the deep

data with a second order polynomial, such as that used in the crossover analysis, the standard deviation of the residuals drops to ±1.5 μmol kg^{-1}. This variability includes the effects of mesoscale features, temporal variations in preformed concentrations and analytical uncertainty. The combined effects of these are notably smaller than the estimated offsets on several of the cruises. Second, the various approaches have different strengths and weaknesses and may be more or less reliable in different oceanographic regions. Furthermore, the calculated offsets and associated errors may not be directly comparable. As a result, some level of subjectivity is necessarily a part of the adjustments proposed in this section. We have made every attempt to consider all of the various lines of evidence available. Adjustments were based on a preponderance of evidence and only implemented when we felt an adjustment was clearly necessary. Through consultation with the principle investigators involved in the Pacific survey, we feel that the adjustments proposed here are the best possible with our present understanding of the data quality.

The limited number of crossovers available for pH implies that the spectrophotometric measurements were very precise and consistent between cruises. DeValls and Dickson (1998) have suggested, however, that the pH values initially assigned to the "tris"-buffers used to characterize the indicator, m-cresol purple, should be increased by 0.0047. This revision would translate into a comparable increase in the pH$_T$ values reported for the Pacific (Lamb et al., 2002).

Table 3 summarizes our recommended adjustments for the DIC, TAlk and pH data from the North Pacific CO$_2$ survey cruises. Given the long timeframe over which the North Pacific survey was conducted, and the number of analytical groups and systems used to measure carbon in the Pacific, a thorough investigation into the quality and consistency of the data was a difficult task. Although we have done a careful analysis using several techniques, there is still a certain amount of subjectivity involved when recommending adjustments. Certainly, all available lines of evidence have contributed to a better understanding of the consistency of the North Pacific data set, and together have proven to be an invaluable tool for determining any necessary adjustments.

With the adjustments proposed in Table 3, the examined cruises can be combined to generate a North Pacific Ocean data set with over 14,000 unique sample locations analyzed for at least two carbon parameters, with the exception of P9 and CGC91. The overall accuracy of the DIC data was ~5 μmol kg^{-1}. TAlk, the second most common carbon parameter analyzed, had an overall accuracy of ~10 μmol kg^{-1}. The TAlk was calculated for all cruises where it was not measured using the carbonate dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987), and ancillary constants listed in the program of Lewis and Wallace (1998). Although TAlk, pH and fCO$_2$ were not sampled as frequently and their accuracy is not as well constrained, they also represent the state-of-the-art at the time the

Table 3 Summary of final recommended adjustments for DIC, TAlk and pH for the North Pacific WOCE/JGOFS CO$_2$ survey cruises.

Recommended adjustments	P14N	P14S15S	EQS92	P16N	P17C	P17N	P18	P1	P2
DIC (μmol kg^{-1})	[a]NA	[a]NA	[a]NA	+4	[a]NA	-7	[a]NA	[a]NA	-4
TAlk (μmol kg^{-1})	[a]NA	[a]NA	[a]NA	Calculated	-9	-12	[a]NA	[a]NA	+14
pH	+0.0047	+0.0047	+0.0047	+0.0047	[b]ND	[b]ND	+0.0047	+0.0047	[a]NA

[a] NA=No adjustment recommended
[b] ND=No data reported

measurements were made. To obtain additional details on this study including detailed crossover plots, and information and availability of the compiled, adjusted data set, visit the Global Data Analysis Project (GLODAP) web site at: http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm. Much of the data presented in this paper are currently available on the World Wide Web by contacting the WOCE Hydrographic Project Office (http://whpo.ucsd.edu/), the Carbon Dioxide Information and Analysis Center (http://cdiac.esd.ornl.gov/oceans/home.html) or the Japanese Oceanographic Data Center (http://www.jodc.jhd.go.jp/jodc.html).

3.0   Air-sea CO_2 fluxes

3.1   Data collection

Between March 1995 and March 1999, CO_2 measurements were continuously made using underway CO_2 partial pressure (pCO_2) systems during 68 crossings in the northern North Pacific Ocean aboard M/S *Skaugran* (Zeng *et al.*, 2002). Most transects from North America to Japan followed a great circle route through the Gulf of Alaska and Bering Sea, then southward along the Kuril Islands. Routes between Japan and North America ranged from 34°N and 50°N in the central North Pacific, except one passing though Hawaii (Fig. 2).   Measurements for

seawater were taken every minute, and hourly for air, in the units of the mole fraction of CO_2.

For every crossing, the means of the 1-min CO_2 data were averaged for each 1° of longitude. 5° means were computed from the 1° means for data between 145°E and 125°W. In order to avoid the strong effects of regional variability in near-shore waters, the 5° means at the route extremes (145°E and 125°W) were calculated using data between 145°E and 147.5°E, and between 125°W and 127.5°W due to their one-sidedness.
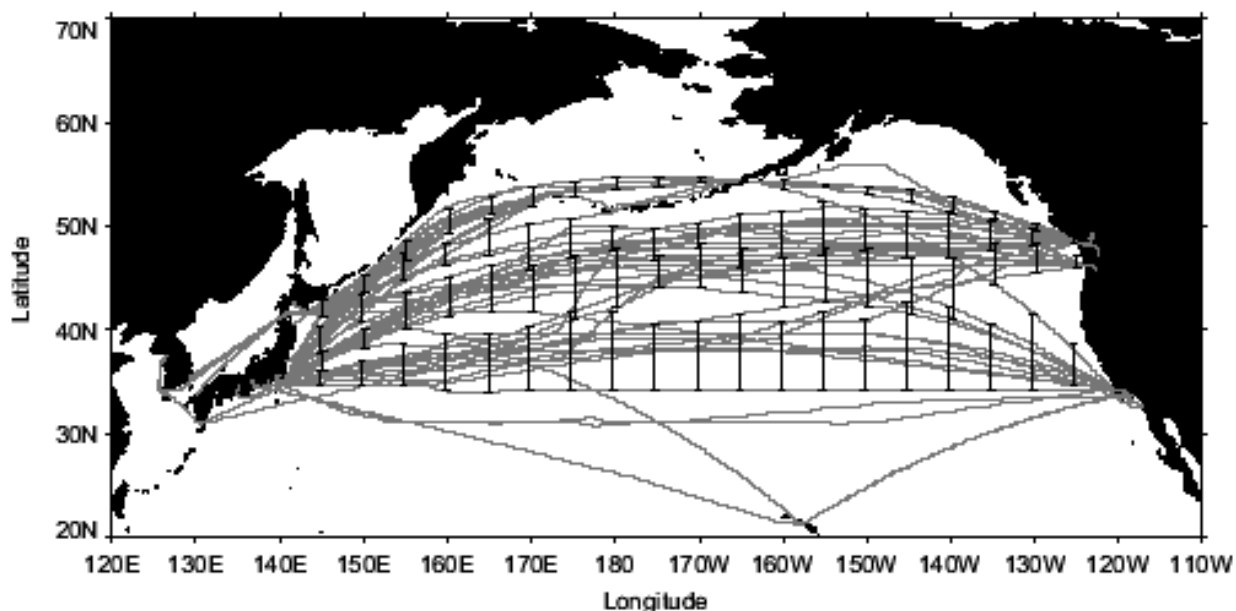

Fig. 2   Ship routes of M/S *Skaugran* from March 1995 to March 1999. Vertical lines intersecting ship routes mark the selected latitudinal bands for estimating coefficients of the seasonal function of pCO_2 using Eq. (2).

3.2   Data analysis

Nojiri *et al*. (1999) evaluated seasonal ΔpCO_2 at 5° x 5° resolution using a function consisting of four harmonic terms. This function contains a linear latitudinal gradient term independent of time, and utilized data that were collected

between 1995 – 1997. By using a longer 4-year time series, Zeng *et al.* (2002) found that the north–south gradient varied significantly with time and longitude. Therefore, they omitted the latitudinal gradient term in the model of Nojiri *et al*. (1999), and instead only used the harmonic function:

$$\Delta pCO_2 (t) = c_o + c_1 \sin(2\pi t) + c_2 \cos(2\pi t) + c_3 \sin(4\pi t) + c_4 \cos(4\pi t) \qquad (2)$$

to describe the seasonal ΔpCO_2 changes with time in a box of limited latitude and longitude. This is a spatially independent function requiring that the seasonal coverage of sampling be complete in the defined boxes, and therefore, the box size was chosen as a compromise between maximizing seasonal coverage and minimizing the spatial variations within each box.

In order to assure that there is at least one crossing per season, the box sizes were selected as follows: for each 5° longitudinal section, latitudinal bands were chosen within which intervals between any two crossings were less than three months. Two bands encompassing the northern and southern boundaries were selected first, after which two additional bands were inserted between the boundaries. The constraint for the maximum latitudinal range is

10°. Figure 2 shows the selected boxes with variable latitude range and fixed longitude range. When examining the monthly route maps, the latitudinal sampling distribution shown in Figure 2 is uneven, *i.e.*, there is only one crossing in the area of 170°E – 160°W and 35°N – 40°N during July – September.

The seasonal cycle of ΔpCO_2 (i.e., the coefficients c_o through c_4) were defined for each box using Eq. (2). Figure 3 shows the results for the 175°W section as an example of this selection and calculation process. Four latitudinal bands were selected for this longitude section, and the seasonal cycle of ΔpCO_2 is displayed for each box. The interpolation to 1° x 1° monthly resolution from the irregular grid of distributions of ΔpCO_2 (as shown in Fig. 2) allows computation of basin-wide fluxes and facilitates comparison with other regional estimates of ΔpCO_2 and fluxes.

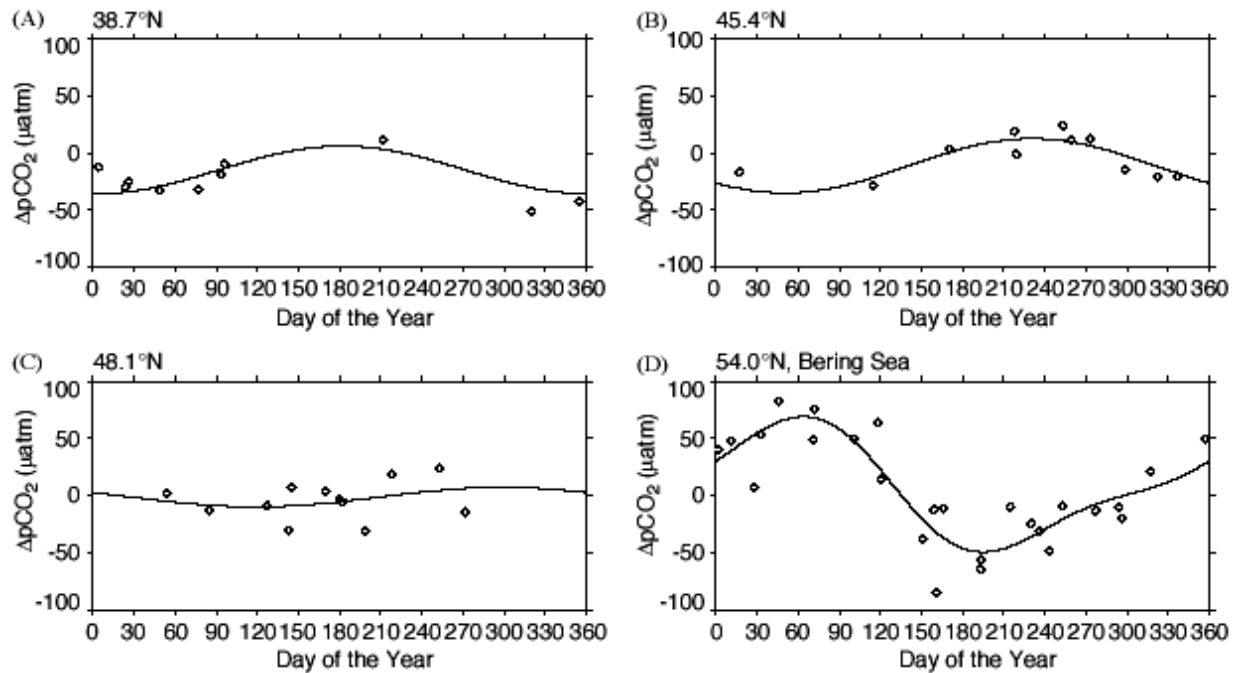**Fig. 3**   Seasonal functions of ΔpCO_2 for four latitudinal bands in the 175°W longitudinal section: (A) 38.7°N; (B) 45.4°N; (C) 48.1°N; and (D) 54.0°N. The solid line shows the seasonal function fit by Eq. (2); the diamond symbol shows the observed data.

3.3 CO₂ fluxes

Based on Eq. (2) of Wanninkhof (1992), the air-sea flux of CO_2 was calculated from wind speed. Monthly CO_2 fluxes were computed using monthly ΔpCO_2, monthly sea-surface temperature and salinity of World Ocean Atlas 1994 of National Oceanic and Atmospheric Administration (NOAA), and the monthly wind fields derived from the European Center for Medium-Range Weather Forecasts (ECMWF) 2.5° database. The ECMWF database contains winds (at 10 m height above sea surface) for every 12 hours. The monthly wind fields are means of 12-hour winds in January 1995 – December 1999.

Clear unsynchronized patterns of ΔpCO_2 changes were observed for different regions in the northern North Pacific. For the northern regions, ΔpCO_2 is highest in winter and lowest in summer. For the subtropics, this seasonal cycle is reversed, with lowest values in winter and highest values in summer. Due to vertical mixing in winter (January – March), seawater pCO_2 in the southern Bering Sea, off Kamchatka Island, and off the Kuril Islands is higher than in the atmosphere (by up to +80 μatm). In the remainder of the northern North Pacific, ΔpCO_2 is negative (by as much as –60 μatm), more than likely a result of seasonal cooling.

CO_2 fluxes from this analysis were compared with fluxes computed from the data of Takahashi *et al*. (1997). In order to compare results with 4° x 5° grid, their 1° x 1° data were averaged to this larger grid, and thus, fluxes for both studies were calculated using the same resolution of ΔpCO_2. Using that approach, both data sets show that the northern North Pacific is a net CO_2 sink throughout the year, weakest in summer (July – September) and strongest in autumn (October – December). The monthly mean CO_2 flux ranges between –0.06 and –4.7 moles m^{-2} yr^{-1}, with the negative sign indicating ocean uptake. Comparison of monthly mean fluxes for the northern North Pacific indicates that in spring (April – June) and autumn (October – December), monthly fluxes estimated from ΔpCO_2 of Takahashi *et al*. (1997) are systematically more negative than those estimated by Zeng *et al.* (2002); *i.e.*, on average 17% lower (–15 to –20%) in spring and 44% lower (–25% to –56%) in autumn.

Based on the ΔpCO_2 results, the region between 34°N and 50°N is estimated to be a small sink for carbon of –0.26 Pg C yr^{-1} (Zeng *et al.* 2002), while the integrated net annual flux using the data of Takahashi *et al*. is –0.33 Pg C yr^{-1}, suggesting 27% more uptake on an annual basis.

The vessel-of-opportunity measurement program aboard commercial vessels offers sampling frequency throughout all seasons, enabling the oceanographic community to better understand the long-term variability of the ocean carbon cycle.

4.0   DIC, TAlk and anthropogenic CO$_2$ distributions in the North Pacific

4.1   Distributions of DIC and TAlk

The lowest concentrations of DIC and TAlk in the North Pacific are observed in surface waters. Variations in surface carbon concentrations (DIC range: 1975 – 2200 μmol kg^{-1}; TAlk range: 2200 – 2400 μmol kg^{-1}) are roughly correlated with salinity. The general structure of the DIC and TAlk fields in the upper 1,000 m is similar to the density structure, suggesting that circulation plays a strong role in their distributions. The highest DIC concentrations are found in the intermediate waters and form a large maximum (2325 – 2375 μmol kg^{-1}) at approximately 1,800 – 2,200 m in the North Pacific (Fig. 4). In contrast, TAlk concentrations show a local minima in the Antarctic Intermediate Water (AAIW) to the south and in the North Pacific Intermediate Water (NPIW) to the north (Fig. 5). Below the NPIW, TAlk concentrations increase to a broad maximum at approximately 2,200 – 4,000 m (TAlk concentrations range from 2,400 – 2,460 μmol kg^{-1}). The differences between the DIC and TAlk, particularly in intermediate waters, are caused by *in-situ* re-mineralization processes. The DIC maximum is shallower than the TAlk maximum because the total inorganic carbon is more strongly influenced by the shallow re-mineralization of soft tissue organic matter, whereas the total alkalinity is more strongly influenced by the dissolution of calcium
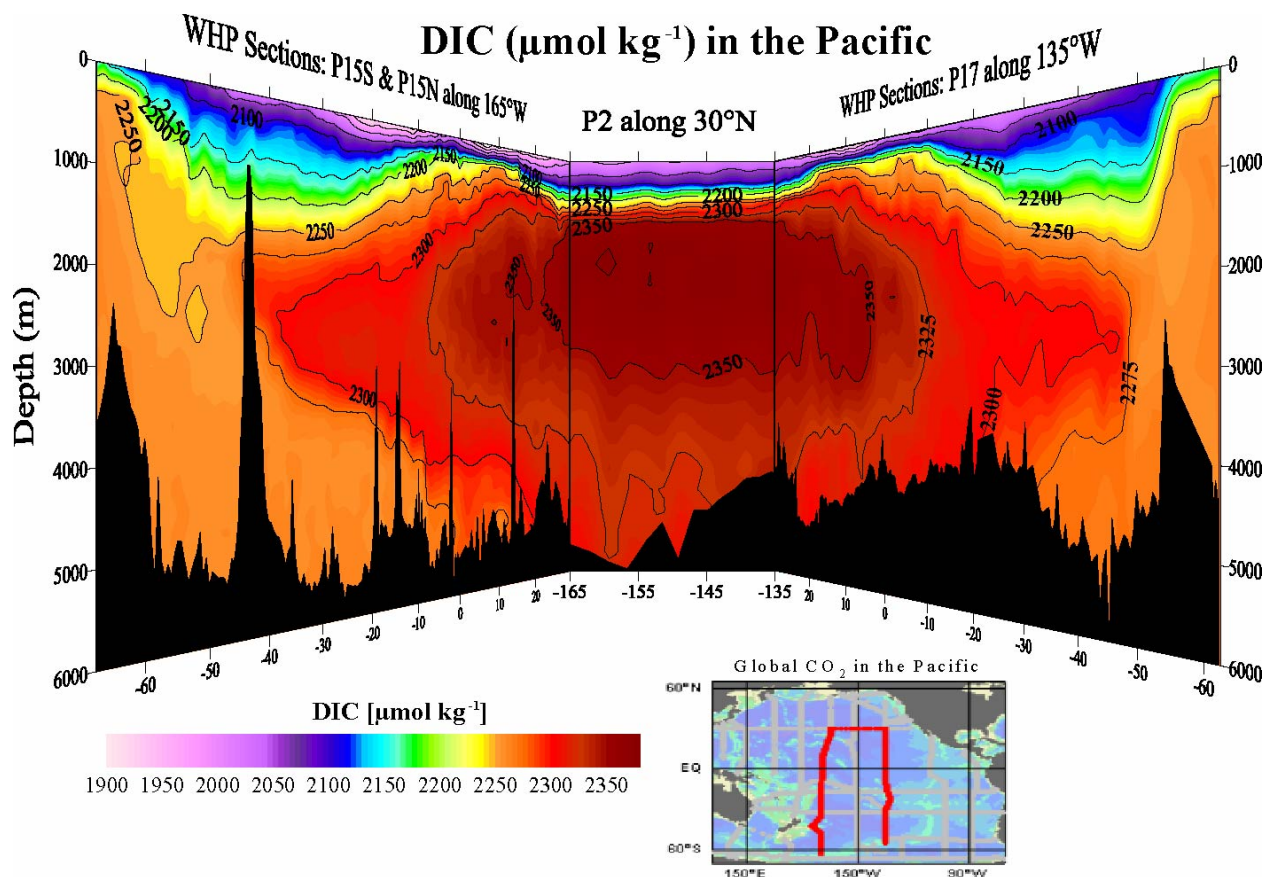

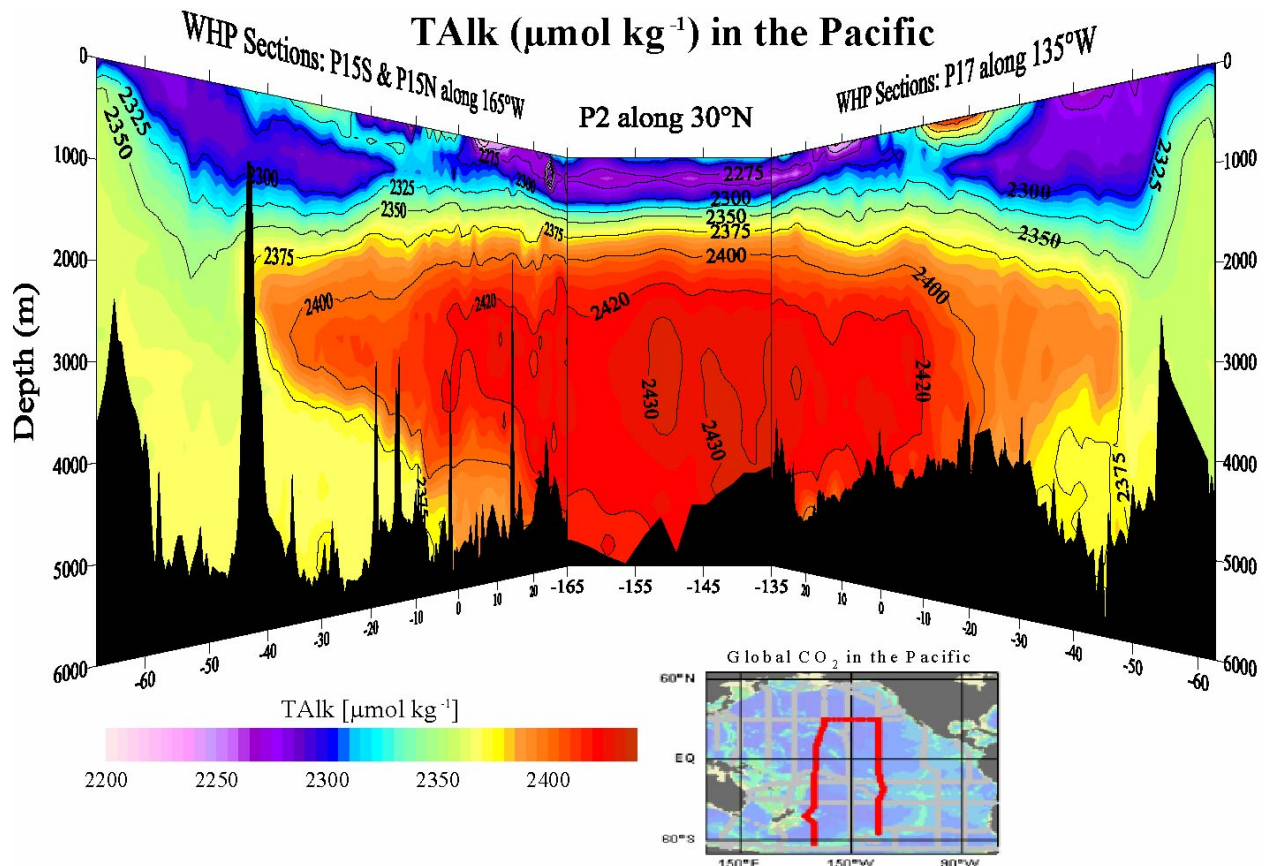**Fig. 4**   Wedge-like cutout section of DIC (μmol kg^{-1}) along 170°W, 30°N and 135°W in the Pacific Ocean.

Fig. 5 Wedge-like cutout section of TAlk (µmol kg^{-1}) along 170°W, 30°N and 135°W in the Pacific Ocean.

carbonate particles deeper in the water column (Chen, 1990). South of 30°N, bottom waters have lower DIC and TAlk concentrations than the waters at mid-depths because the northward moving bottom waters have not had time to accumulate as much carbon. The southward moving waters at 2,000 – 3,000 m in the North Pacific are among the oldest waters in the global ocean (Stuiver *et al*., 1983).

The zonal DIC and TAlk isolines shoal from west to east along the P2 section at 30°N in the North Pacific (Fig. 6). Deep ventilation near the Kuroshio Extension and the subsequent circulation in the subtropical gyre generates the zonal gradients of DIC and TAlk in the upper 1,500 m. Both DIC and TAlk concentrations show the deepest ventilation near the coast and

under the Kuroshio Extension, west of 160°E. These trends are also observed in the North Pacific chlorofluorocarbon (CFC) and anthropogenic CO_2 distributions providing further evidence of stronger ventilation in the western Pacific (Warner *et al*., 1996. Sabine *et al*., 2002).

4.2 Anthropogenic CO_2 distributions

The approach used here for estimating anthropogenic CO_2 in the Pacific Ocean is based on the ΔC* method first described by Gruber *et al*. (1996). Gruber *et al*. improved the earlier approaches of Brewer (1978) and Chen and Millero (1979) by developing the quasi-conservative tracer, ΔC*. The assumption is that the anthropogenic CO_2 concentration (C_{ant}) can
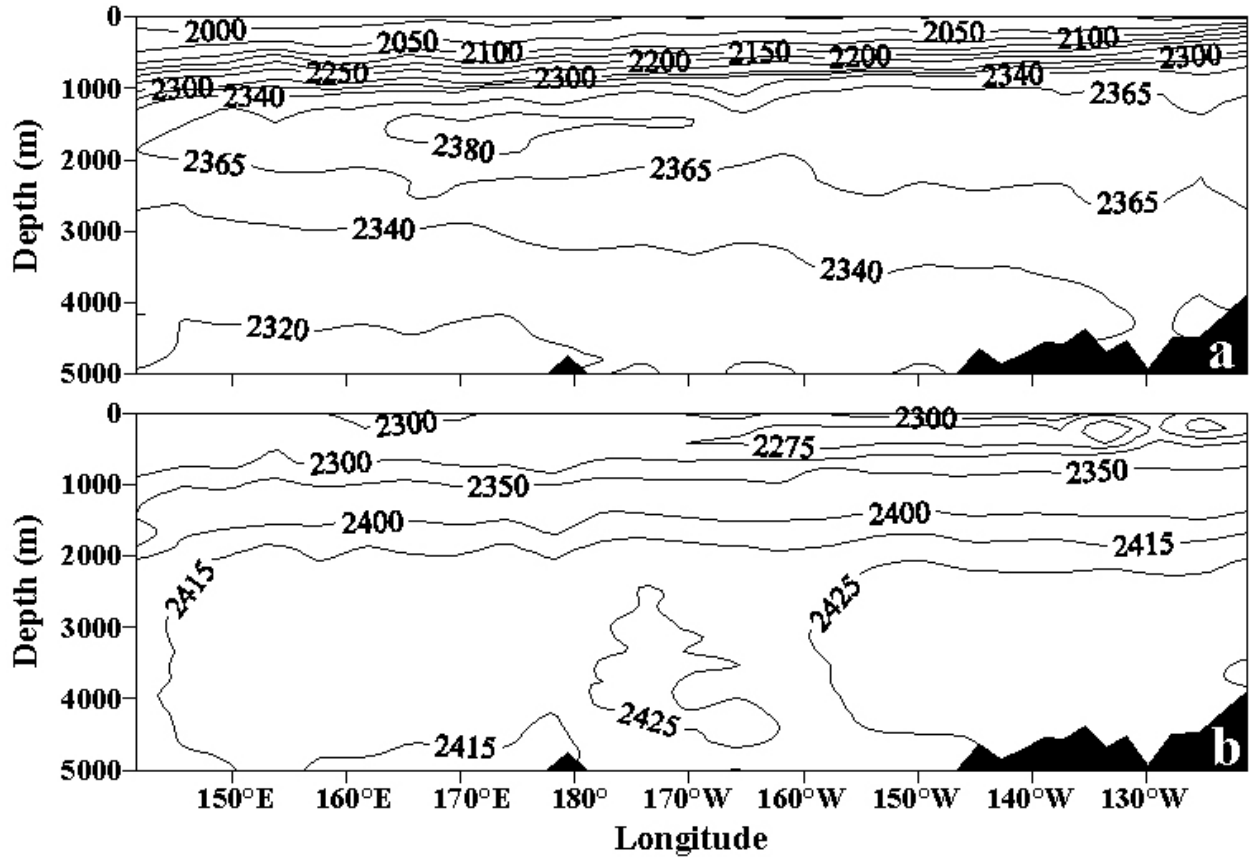
Fig. 6 Vertical distributions of: a) DIC in μmol kg^{-1} and b) TAlk in μmol kg^{-1} in the WOCE/JGOFS section P2 along 30°N in the North Pacific.

be isolated from measured DIC values (C_m) by subtracting the contribution of the organic and inorganic biological pumps (ΔC_{bio}), the DIC the waters would have in equilibrium with a pre-industrial atmospheric CO_2 concentration of 280 ppm (C_{eq280}), and a term (ΔC_{diseq}) that corrects for the fact that surface waters are not always in equilibrium with the atmosphere (air-sea difference in CO_2 concentration expressed in μmol kg^{-1} of DIC):

$$C_{ant} = C_m - \Delta C_{bio} - C_{eq280} - \Delta C_{diseq} = \Delta C^* - \Delta C_{diseq} \qquad (3)$$

The three terms to the right of the first equal sign make up ΔC^* (*i.e.*, $\Delta C^* = C_m - \Delta C_{bio} - C_{eq280}$), which can be explicitly calculated for each sample. The fact that ΔC^* is a quasi-conservative tracer helps remedy some of the mixing concerns arising from the earlier techniques (Sabine and Feely, 2001). The ΔC_{diseq} term is evaluated over small isopycnal intervals using a water-mass age tracer such as CFCs (Sabine *et al.*, 2002).

The biological correction in the ΔC^* calculation has two components. The organic component uses changes in apparent oxygen utilization (AOU), together with a stoichiometric C:O ratio, to estimate how much DIC has increased due to organic re-mineralization since leaving the surface. The second component uses the difference between the measured total alkalinity (TAlk) and a pre-formed total alkalinity (TAlk°) to estimate the changes in DIC resulting from the dissolution of calcium carbonate particles. There is also a small organic adjustment on the

carbonate correction term to account for the effect of the proton flux on TAlk. The stoichiometric ratios used for the biological corrections are based on the work of Anderson and Sarmiento (1994).

The C_{eq280} term uses a linearized form of the carbonate equilibrium equations, together with the preformed alkalinity and an fCO_2 value of 280 µatm, to calculate the equilibrium DIC concentration.

The ΔC^* calculation used for this study is essentially the same as that originally defined by Gruber et al. (1996) with two small differences: a modification of TAlk° based on the new global survey data, and the addition of a denitrification term in the biological correction:

$$\Delta C^* = C_m - C_{eq280} + 117/170(O_2 - O_2^{(sat)}) - 1/2(TAlk - TAlk° - 16/170(O_2 - O_2^{(sat)})) + 106/104N^*_{anom}, \quad (4)$$

where TAlk and O_2 are the measured concentrations for a given water sample in µmol kg^{-1}, $O_2^{(sat)}$ is the calculated oxygen saturation value that the waters would have at their potential temperature and one atmosphere total pressure (i.e. if they were adiabatically raised to the surface), and N^*_{anom} is the N* anomaly described later in this section.
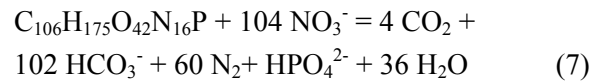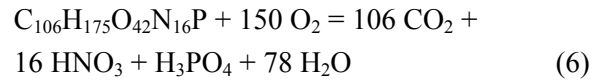
The TAlk° formulation of Gruber et al. (1996) was based on MLR fit of surface TAlk values from the GEOSECS, SAVE, and TTO cruises. Sabine et al. (1999) derived a revised TAlk° equation based on the WOCE/JGOFS Indian Ocean data. The Pacific TAlk° term proposed by Sabine et al. (2002) was estimated using all of the Pacific alkalinity data shallower than 60 m (~1,900 data points). The form of the equation is the same as that used by Sabine et al. (1999):

$$TAlk° = 148.7(\pm 9) + 61.36(\pm 0.3) * S + 0.0941(\pm 0.005) * PO - 0.582(\pm 0.07) * \theta \quad (5)$$

where PO is a quasi-conservative tracer similar to that introduced by Broecker (1974) (PO = dissolved oxygen – 170* phosphate (PO_4)). The standard error in the Pacific TAlk° equation is

± 9 µmol kg^{-1}. All four terms are highly significant as shown with a standard ANOVA analysis.

Sabine et al. (2002) also proposed a correction to the biological adjustment in (3) to account for denitrification in the water column. Denitrification re-mineralizes carbon with a very different stoichiometric ratio to nitrogen than standard aerobic respiration (Anderson, 1995; Gruber and Sarmiento, 1997):

$$C_{106}H_{175}O_{42}N_{16}P + 150 O_2 = 106 CO_2 + 16 HNO_3 + H_3PO_4 + 78 H_2O \quad (6)$$

$$C_{106}H_{175}O_{42}N_{16}P + 104 NO_3^- = 4 CO_2 + 102 HCO_3^- + 60 N_2 + HPO_4^{2-} + 36 H_2O \quad (7)$$

Sabine et al. (1999) estimated the denitrification signal using the N* tracer of Gruber and Sarmiento (1997). The slightly more generalized N* tracer of Deutch et al. (2001) was used by Sabine et al. (2002):

$$N^* = N - 16*P + 2.90 \quad (8)$$

The only change from Gruber and Sarmiento (1997) was that their original equation was scaled by a factor of 0.87. The revised equation is simpler and is more general because it removes built-in assumptions about the nitrogen loss from the organic reservoir (Deutsch et al., 2001). In practice, this modification actually has no impact on the final denitrification corrections since that signal is identified as an N* anomaly from the mean. The mean N* value for this data set was –1.5 µmol kg^{-1}, in agreement with the findings of Deutsch et al. (2001). The denitrification stoichiometric ratio of 106/104 from (7) (Gruber and Sarmiento, 1997) was used to correct the ΔC^* values in Eq. (4), where N* showed a negative anomaly.

For given isopycnal surfaces, the air-sea disequilibrium component can be discriminated from the anthropogenic signal using either information about the water age (e.g., from transient tracers such as CFCs or ^{3}H-^{3}He) or the distribution of ΔC^* in regions not affected by

the anthropogenic transient. In the case where C_{anth} can be assumed to be zero over some portion of an isopycnal surface (*i.e.*, $\Delta C^* = 0 + \Delta C_{diseq}$), the disequilibrium term is set equal to the average of the ΔC^* values for that portion of the surface. For shallow surfaces, that cannot be assumed to be free of anthropogenic CO_2, we use the ΔC^*_t term of Gruber *et al.* (1996). ΔC^*_t is derived in the same manner as ΔC^*, but rather than evaluating the carbon concentration the waters would have in equilibrium with a pre-industrial atmosphere, they are evaluated with respect to the CO_2 concentration the atmosphere had when the waters were last at the surface. In this study, calculations are based on the concentration ages determined from CFC-12 measurements (ΔC^*_{t12}):

$C^*_{t12} = C_m - C_{teq} + 117/170(O_2 - O_2^{(sat)}) - 1/2(\text{Talk} - \text{TAlk}° - 16/170(O_2 - O_2^{(sat)})) + 106/104 N^*_{anom},$ \hfill (9)

where C_{teq} is DIC calculated from TAlk° and the atmospheric fCO_2 value at the time the waters were last at the surface (date of sample collection minus CFC age). The ΔC_{diseq} terms for these surfaces are then set equal to the mean of the ΔC^*_{t12} values on each surface.

Several papers have been published recently evaluating the ΔC^* approach for calculating anthropogenic CO_2 (*e.g.* Wanninkhof *et al.*, 1999; Coatanoan *et al.*, 2001; Sabine and Feely, 2001; Orr *et al.*, 2001). It has been recognized that the evaluation of the ΔC_{diseq} term is one of the most problematic steps in the estimation of anthropogenic CO_2. One important assumption in the evaluation of ΔC_{diseq} is that the global mean air-sea CO_2 disequilibrium has remained constant over time. Although this assumption is consistent with most contemporary CO_2 time-series measurements in the Pacific (*e.g.* Inoue *et al.*, 1995; Winn *et al.*, 1998; Feely *et al.*, 1999; Takahashi *et al.*, 1999), it cannot be true over time-scales extending into the pre-industrial period or the oceans would not be acting as a sink for anthropogenic CO_2. Gruber *et al.* (1996) estimated that an average global uptake of about 2 Pg C yr^{-1} would correspond to an air-

sea disequilibrium of about 5 µmol kg^{-1} in ΔC_{diseq}. If this signal is spread out over the entire record since pre-industrial times, it would be very difficult to see in the ΔC^* value given the uncertainties in the calculation. This 5 µmol kg^{-1} uncertainty can be considered the theoretical minimum detection limit for this technique as it is currently used.

Anthropogenic CO_2 concentrations in the North Pacific reach a maximum value of about 40 - 50 µmol kg^{-1} in the subtropical surface waters (Fig. 7). These surface concentrations are slightly lower than observed in other oceans, but may reflect differences in the surface buffer factor of different oceans. The distribution patterns of anthropogenic CO_2 in the ocean interior generally follow density isolines. The relatively shallow penetration of anthropogenic CO_2 in the North Pacific is in strong contrast to the Atlantic distribution, where anthropogenic CO_2 has penetrated all the way to the bottom in the northern high latitudes (Gruber *et al.*, 1996; Wanninkhof *et al.*, 1999; Körtzinger *et al.*, 1999). These differences result from the lack of any significant deep-water formation in the North Pacific (Reid, 1997), and the long time-scales for replacement of North Pacific deep waters from the south (Stuiver *et al.*, 1983). In the North Pacific, deep ventilation within the Kuroshio Extension and the subsequent circulation in the subtropical gyre generates a strong zonal gradient in the anthropogenic CO_2 penetration depth (Fig. 8). At approximately 30ºN (WOCE line P2), the 5 µmol kg^{-1} contour is found at a depth of about 500 m near the North American coast, but deepens to approximately 1,000 m off Japan. The zonal gradient is also enhanced by the significant role that the Sea of Okhotsk plays in the formation of North Pacific Intermediate Water (Warner *et al.*, 1996). Although no data from the Sea of Okhotsk were included in this analysis, Figure 9 clearly shows unusually high anthropogenic CO_2 concentrations near the entrance to the Sea on a density surface that corresponds to the NPIW. The combined effect of the tilted density surfaces and the younger waters with higher

Anthropogenic CO$_2$ [μmol kg^{-1}] in the Pacific
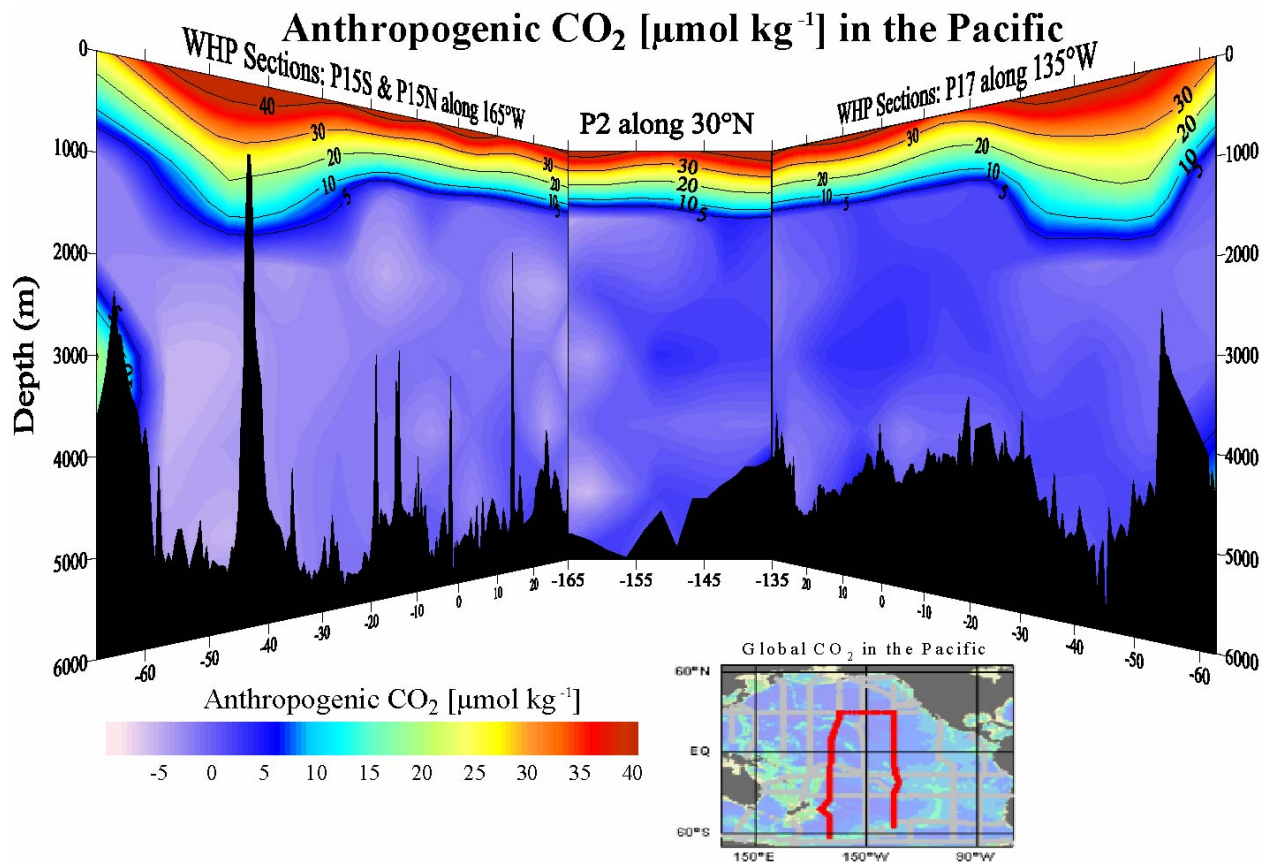
Fig. 7   Wedge-like cutout section of anthropogenic CO$_2$ (μmol kg^{-1}) along 170°W, 30°N and 135°W in the Pacific Ocean.

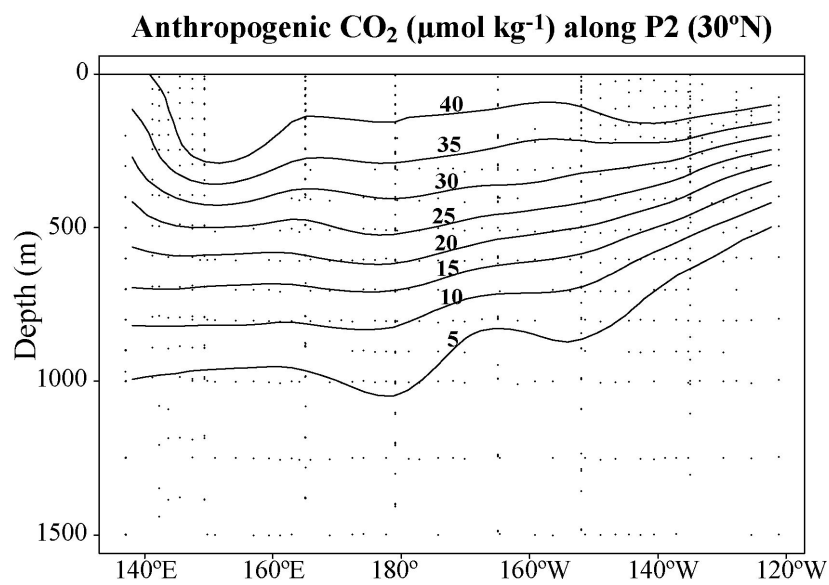## Anthropogenic CO$_2$ (μmol kg^{-1}) along P2 (30°N)

Fig. 8   Vertical distributions of anthropogenic CO$_2$ (μmol kg^{-1}) along the WOCE/JGOFS section P2 (30°) in the North Pacific.

anthropogenic CO_2 content leads to higher total column inventories in the western North Pacific (Fig. 10). The gyre circulation and mixing works to smear out the signal generating the broad feature observed in Figure 10. The integrated amount of anthropogenic CO_2 in the North Pacific is estimated to be 16.5 Pg C through 1994, north of the equator but not including the marginal seas (Sabine *et al*., 2002). This estimate is approximately 16% of the amount of anthropogenic CO_2 taken by the global oceans (Feely *et al*., 1999).

Data Interpolated to 27.0 Sigma Theta Surface

Anthropogenic CO_2 Concentration (μmol kg^{-1})
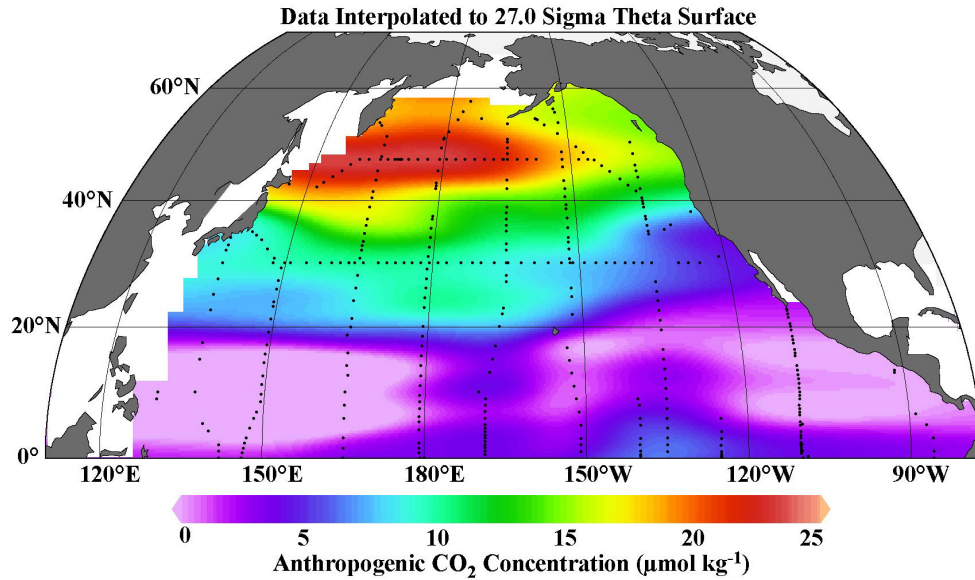
Fig. 9 Distribution of anthropogenic CO_2 (μmol kg^{-1}) on the 27.0 σ_θ surface in the North Pacific.

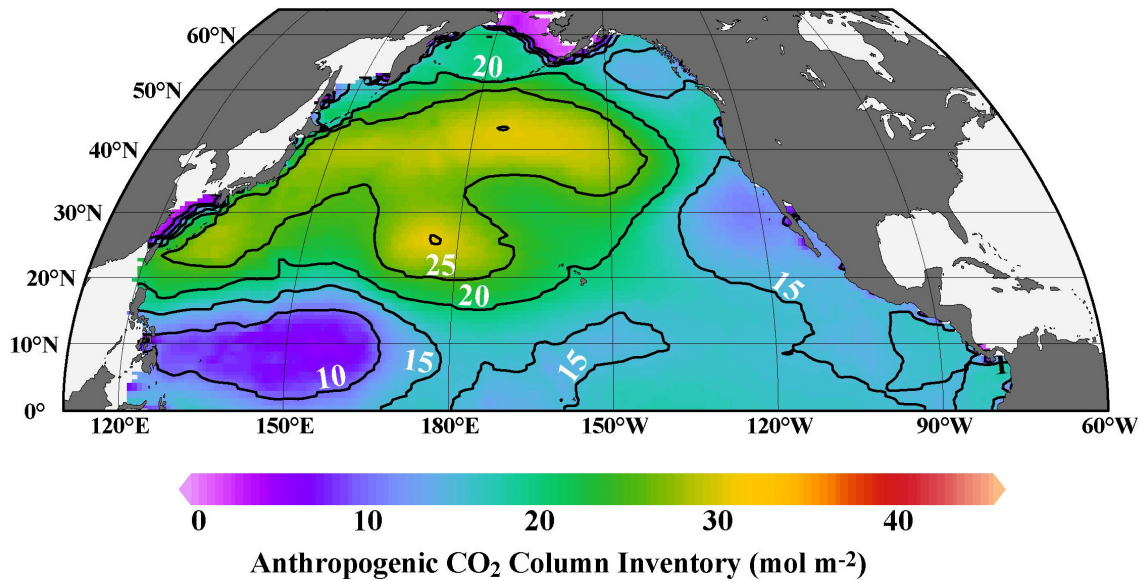Anthropogenic CO_2 Column Inventory (mol m^{-2})

Fig. 10 Map of anthropogenic CO_2 column inventory (mol m^{-2}) in the North Pacific.
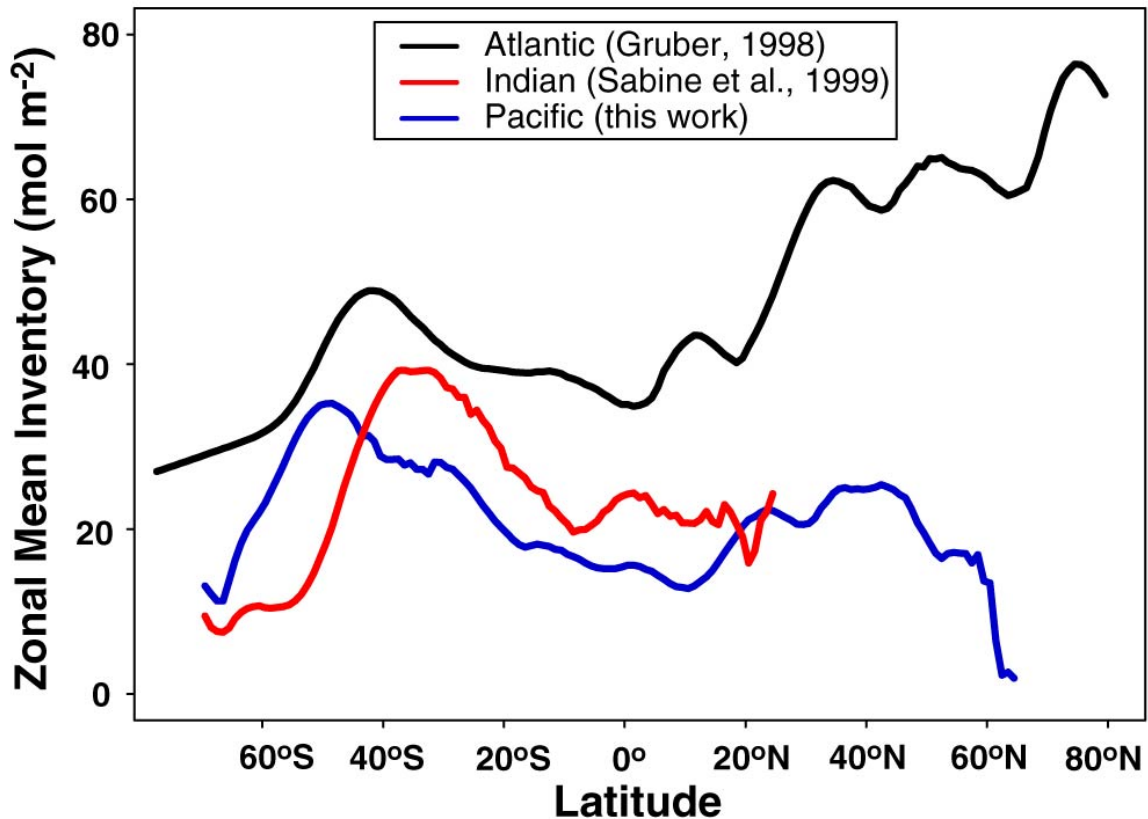
Fig. 11 Plot of the zonal total inventory in Pg C for the Pacific, Indian and Atlantic Oceans versus latitude. Indian values are from Sabine *et al.* (1999). Atlantic values are from Gruber (1998).

In the higher northern latitudes, the area-specific water column inventories of the North Atlantic can be higher than in the North Pacific, because of the formation of North Atlantic Deep waters that transport anthropogenic CO_2 into the ocean interior. These large values are sufficient to make total inventories highest in the North Atlantic despite the larger area of the North Pacific (Fig. 11). One should note that the North Atlantic values of Gruber (1998), given in Figure 11, represent inventories from the late 1980s. These values would be somewhat higher if they were scaled up to the WOCE timeframe.

Since the exact distribution of anthropogenic CO_2 cannot be directly measured, it is useful to compare estimates derived from different approaches. Recently, Xu *et al.* (2000) examined the uptake and storage of

anthropogenic CO_2 with a medium resolution (2° x 2° x 28 levels) basin-wide OGCM of the North Pacific. Their study tested the impact of changing the isopycnal diffusivity on the anthropogenic uptake of the model. Although all of the model runs presented by Xu *et al.* suggested higher North Pacific inventories (19.4 – 22.01 Pg C north of equator) than determined with this study, the model run with the lowest diffusivities gave results that were most consistent with the above estimates. Likewise, models can help evaluate various observational-based approaches. For example, Xu *et al.* also compared their results in the western North Pacific with the results of Chen (1993a). They noted that Chen had a deeper penetration and stronger meridional changes in penetration depth than could be generated with the model. Our results, however, are much more similar to the

model distributions with penetration depths close to 1,000 m and meridional changes in penetration depth about half (250 m) of that observed by Chen (1993a) in the western North Pacific.

The ΔC^* approach for estimating anthropogenic CO_2 has been applied now in the three major oceans: the Atlantic, Indian and Pacific. Small modifications to the technique continue to improve the quality of the results. Each time the technique is applied to a new region, new challenges are faced. The basic principles of the technique, however, have remained the same and appear to be sound. The total amount of anthropogenic CO_2 inventory in the North Pacific is approximately 37% of the total for the Pacific Ocean (Sabine *et al.*, 2002). This relatively low inventory in the North Pacific primarily results from large-scale circulation within the Pacific. The deep waters of the Pacific are among the oldest in the global oceans, and thus have not been exposed to anthropogenic contamination. The lack of deep-water formation in the North Pacific results in relatively little penetration of anthropogenic CO_2 into the ocean interior. The tremendous area, diversity of habitats, and corrosiveness of the Pacific waters with respect to carbonate minerals, however, provide the potential for significant changes in carbon cycling in this ocean as a result of future climate change. Some of these changes may lead to changes in the role of the Pacific as a sink for anthropogenic CO_2. The global CO_2 survey data and estimates provided here make an important baseline for assessing future changes in the Pacific carbon cycle.

4.3 Temporal variations in anthropogenic carbon accumulation

MLR analysis, as described by Brewer *et al.* (1995), and subsequently by others (Wallace, 1995, Slansky *et al.*, 1997, Goyet and Davis 1997, Sabine *et al.*, 1999), was used to estimate the anthropogenic CO_2 increase in the North Pacific from data collected between 1973 and 1999. In this procedure, the coefficients that describe the naturally occurring variations in oceanic CO_2 were calculated from a statistical model. The model used salinity (S), potential temperature (θ), apparent oxygen utilization (AOU), and concentration of silicate ($Si(OH)_4$) and phosphate (PO_4) to construct a forward linear stepwise regression to predict DIC.

The area chosen for this study was between 30 - 50°N, and 140 - 180°W (Fig. 12). All cruises within that region were included where high quality DIC data, along with other hydrographic parameters, was available throughout the water column (GEOSECS, NOAA ENP81, WHPs P16N, P15N, P2, P1, and NOPP).

In order to predict the DIC using the MLR technique, the equation derived for the best functional form for the regional data was:

$$DIC = a\theta + bS + cAOU + dSi(OH)_4 + ePO_4 \ (10)$$

where AOU, $Si(OH)_4$ and PO_4 are the measured concentrations for a given water sample in μmol kg^{-1}.

The DIC data were corrected to CRMs where available; otherwise, the only correction made was -29 μmol kg^{-1} to the GEOSECS DIC (Takahashi, pers. communication). A second-order polynomial equation for all parameters used in the MLR for each cruise was then fitted against mid- to deep (1,250 – 3,500 m) σ_θ ranging from 27.48 – 27.78. The deepest data (>3,500 m) was not used in the fit. The individual parameters for each cruise were then adjusted throughout the water column relative to P16N data as necessary.

Although the region of study crosses two major water mass systems (the subtropical gyre and subarctic gyre), a single set of P16N coefficients was used to predict DIC for each of the cruises. The mixed layer depth (MLD) for each cruise was determined using Levitus' wintertime conditions. MLD west of 160°W ranged from approximately 120 – 200 m, and 100 – 120 m east of 160°W. Each cruise was separated into

sections based on its MLD (surface to bottom of the MLD, and bottom of the MLD to 1,250 m). Anthropogenic CO_2 does not generally extend deeper than 800 – 1,000 m in the region of study based on CFC penetration (Bullister, personal communication), and therefore we chose 1250 m as the bottom depth of our study in order to encompass that depth and slightly beyond. Since mixing mostly occurs along isopycnal surfaces, the residual data from each cruise were then binned according to σ_θ ranges and the mean and standard deviation were determined.
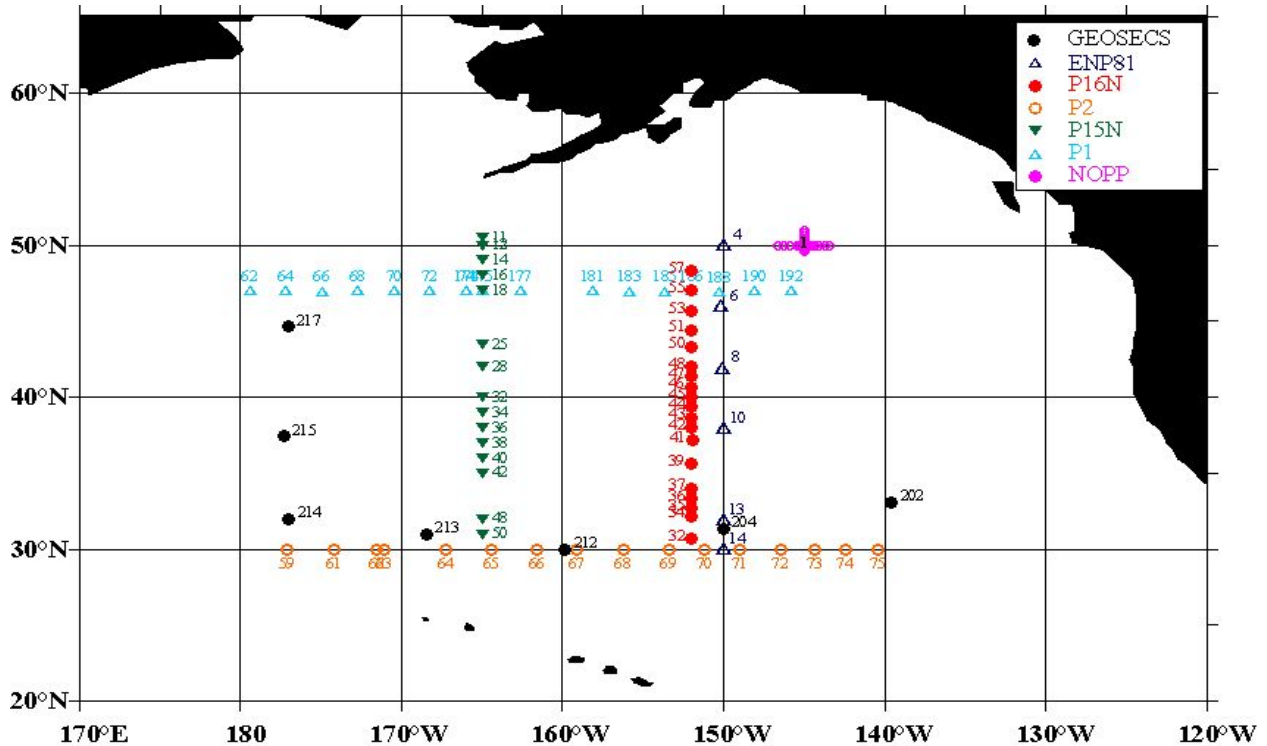

Fig. 12   Station locations used for MLR analysis to assess temporal variability in anthropogenic carbon accumulation.

Using P16N as a reference, the results of the MLR show an estimated CO_2 uptake rate through the mixed layer of 1.3 ± 0.2 µmol DIC kg^{-1} yr^{-1} in the North Pacific (Fig. 13). The uptake of CO_2 below the MLD (Fig. 14) was calculated by two different methods, each yielding similar results. The mean residual DIC for each cruise was plotted against time and an average slope was determined (0.62 ± 0.13 µmol kg^{-1} yr^{-1}). For comparison, a slightly more robust method was utilized for the deeper waters: the σ_θ binned residuals for each cruise were averaged and divided by the age of the cruise relative to P16N. The mean uptake rate of each cruise was then calculated, resulting in an estimate of 0.79 ± 0.4 µmol kg^{-1} yr^{-1}. The total integrated CO_2 uptake from the surface to 1,250 m is estimated to be approximately 1.1 ± 0.4 mol C m^{-2} yr^{-1}.
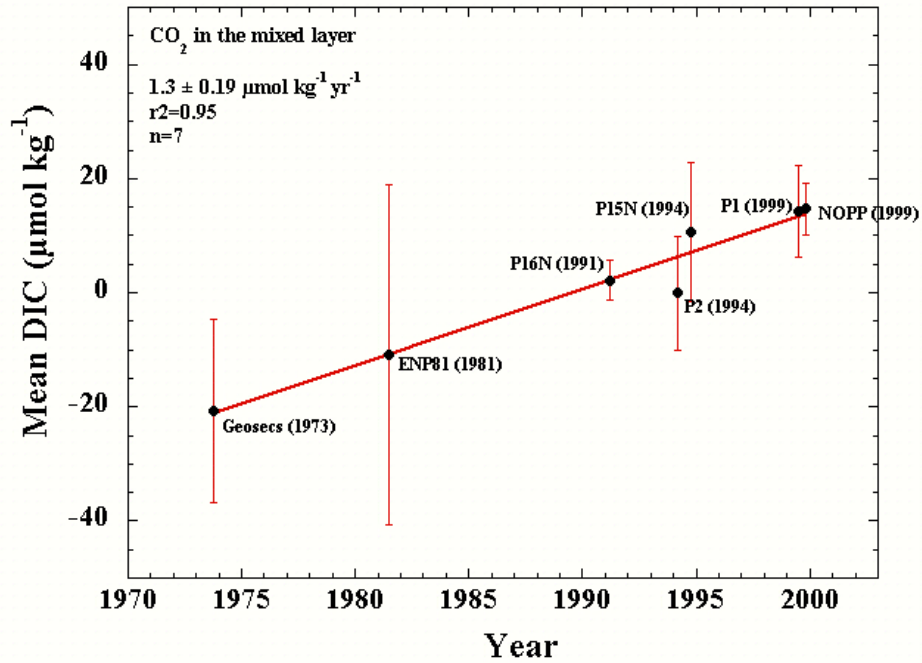
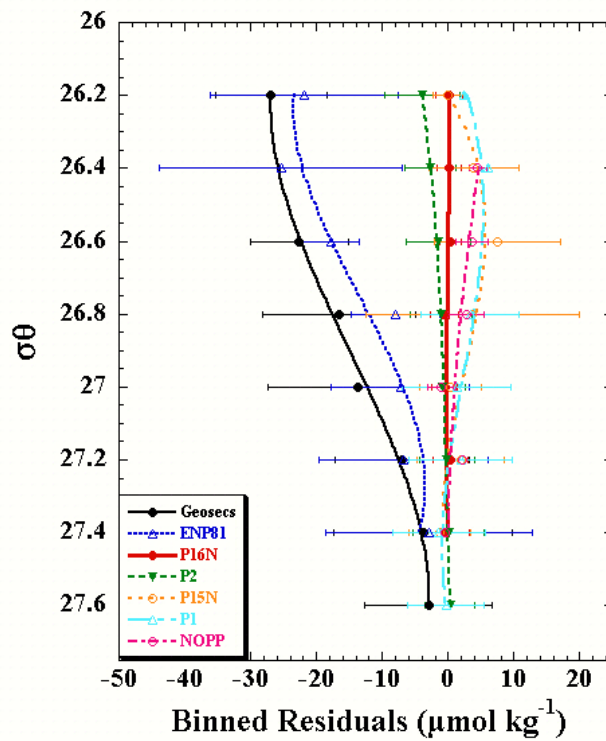**Fig. 13** Estimated change in DIC content in the North Pacific mixed layer between 30-50°N and 140-180°W.

Fig. 14 Comparison of North Pacific DIC binned residuals (μmol kg^{-1}) from the bottom of the MLD to 1250m.

Table 4 A comparison of anthropogenic CO_2 uptake rates in the oceans.

Total CO_2 uptake rate (mol C m^{-2} yr^{-1})	CO_2 uptake rate in the mixed layer (μmol DIC kg^{-1} yr^{-1})	Area of Study	Years of observations	Depth range (m)	Reference
0.83 ± 0.19	—	Northwestern Pacific	1973-1991	Sfc-2000	Tsunogai *et al.* (1993)
—	1	Northwestern Pacific	1984-1993	Sfc	Inoue *et al.* (1995)
—	0.75 to 0.90	S. Atlantic	1972-1993	Sfc-bottom	Wallace (1995)
0.63 ± 0.15	1.3 ± 0.7	Central North Pacific	1973-1991	125-1250	Slansky *et al.* (1997)
—	1.7	Subtropical Atlantic	1988-1998	Sfc-200	Bates *et al.* (1996a)
0.5	1.3	Subtropical Indian	1991-1994	Sfc-5000	Metzl *et al.* (1998)
0.36	—	Tropical/ Subtropical Indian	1978-1995	300-1000	Peng *et al.* (1998)
0.4	—	Tropical/ Subtropical Indian	1973-1995	Sfc-2600	Sabine *et al.* (1999)
0.9 ± 0.8	—	South Pacific	1973-1996	300-1250	Peng *et al.* (submitted for publication)
1.3 ± 2.1	—	North Pacific	1973-1991	300-1250	Peng *et al.* (submitted for publication)
1.1 ± 0.1	1.2 ± 0.2	Subtropical Pacific	1988-1999	Sfc-225	Dore *et al.* (submitted for publication)
0.39 ± 0.1	—	Pacific	1980-1999	Sfc-2000	McNeil *et al.* (2003)
0.54 ± 0.1	—	Atlantic	1980-1999	Sfc-5000	McNeil *et al.* (2003)
0.42 ± 0.2	—	Indian	1980-1999	Sfc-2000	McNeil *et al.* (2003)
1.1 ± 0.4	1.3 ± 0.2	Central North Pacific	1973-1999	Sfc-1250	This work

Table 4 shows a comparison of the estimated uptake rates by various investigators in recent years for the Atlantic, Pacific and Indian Oceans. The rates vary regionally by more than a factor of two, from 0.75 μmol kg^{-1} yr^{-1} in the South Atlantic, to 1.7 μmol kg^{-1} yr^{-1} in the Subtropical Atlantic. In the North Pacific, the uptake rates at the surface range from 1.0 – 1.3 μmol kg^{-1} yr^{-1}.

5.0 Biogeochemical impacts and global implications

Concern about long-term impacts of climate variability and anthropogenic CO_2 increases in the oceans has prompted North Pacific researchers to re-examine the fundamental processes controlling the organic carbon and $CaCO_3$ budgets in the region. The primary motivation for this research is that biological production and export of organic matter, and $CaCO_3$ production and export are important mechanisms by which carbon is exported from the surface ocean to the abyss. By looking at data in the main thermocline, longer-term secular trends and cycles have been observed. This approach takes advantage of the fact that the residence times of waters, and hence, biogeochemical properties increase with depth, and that flow in the ocean interior is primarily along constant potential density surfaces. Biogeochemical variations along isopycnal surfaces may therefore reflect past variations. Recent studies in the North Pacific have suggested that oxygen in the upper thermocline has decreased 10 – 15% over the past two decades (Emerson *et al*., 2001; Ono *et al*., 2001a; Keller *et al*., 2002). In the eastern Pacific, the observed 8 – 40 μmol kg^{-1} oxygen decrease between 100 and 500 m from 1991 to 1997 may reflect large-scale changes in thermocline ventilation and/or ecosystem dynamics. Similarly, Feely *et al*. (2002) found substantial upward migration of aragonite and calcite saturation horizons in the upper thermocline of the North Pacific, which they attributed to decreases in carbonate ion concentrations resulting from anthropogenic CO_2 penetration into the water column since pre-industrial time.

These biogeochemical effects follow other studies that have suggested large-scale variations in the Pacific. McPhaden and Zhang (2002) observed a 25% decrease in transport convergences and meridional overturning over the past 25 years, consistent with a decrease in thermocline ventilation. Karl and co-workers (Karl *et al*., 1997; Karl, 1999) found a two-fold primary production increase and corresponding increases in suspended particle N:P ratios at HOT between the 1980s and the 1990s. They attributed these changes to a major ecosystem domain shift from nitrate-based diatom-dominated ecosystem to a *Prochlorococcus*-dominated N_2 fixation ecosystem. Karl (1999) suggests that the shift may be related to the persistence of unusually warm waters in the Subtropical Pacific resulting from the long succession of ENSO events. These observations are also consistent with a regime shift from a negative to a positive phase of the Pacific Decadal Oscillation (PDO).

All of these independent observations indicate that the North Pacific Ocean is undergoing substantial physical, chemical and biological changes over time. The response of the ocean carbon cycle to climate variability and global warming will continue to undergo varying degrees of both positive and negative climate feedbacks. The magnitude of these feedbacks and their interactions are currently not well understood, but potentially could lead to significant changes in the ability of the ocean to sequester anthropogenic CO_2 in the future. If, as many models suggest, the net feedbacks are positive (*i.e.*, reduced uptake of anthropogenic CO_2 by the ocean in a warming world) the required socio-economical strategies to stabilize CO_2 in the future will be much more stringent than in the absence of such feedbacks. Future studies of the carbon system in the North Pacific should be designed to identify and quantitatively assess these feedback mechanisms in order to provide input to models that will determine their importance on the ocean's future capacity to absorb the anthropogenic CO_2 from the atmosphere.

6.0 Recommendations for the future of carbon studies within PICES

Over the past four years, PICES, through the activities of its Working Group 13, played a major role in fostering international cooperation among member nations towards the integration and synthesis of the WOCE/JGOFS global CO_2 survey data in the North Pacific. *Appendix A* summarizes the specific activities of the Working Group from 1998 through the end of 2001. The Working Group 13:

- supported CO_2 inter-comparison studies for carbon species;
- developed strategies for exchanging data at the international level;
- promoted collaborative interactions towards the analysis and synthesis of the global CO_2 survey data;
- sponsored several meetings and symposia on CO_2 system dynamics in the North Pacific.

These activities were essential for resolving data synthesis issues and developing strong collaborations for the integration of the large CO_2 data set in the North Pacific Ocean. As we strive to increase our understanding of how the carbon system in the North Pacific will respond to global warming and large-scale climate shifts in the future, there is an increasing need for PICES to continue its focus on carbon system dynamics. Below are several recommendations for future activities that PICES could support to greatly improve our knowledge of the carbon system in the North Pacific.

1. The next phase of carbon research in the North Pacific will involve repeat measurements of carbon system and biological parameters, tracers and hydrography at time-series stations and along repeat sections of the WOCE/JGOFS Global CO_2 survey. These studies are designed to determine the physical, chemical and biological changes controlling the carbon system in the North Pacific, and how these changes affect the ocean's response to climate variability and global warming. PICES should continue to provide a venue for data exchange and program coordination at the international level to ensure optimal use of resources to obtain appropriate temporal and spatial coverage as well as maximum comparability with historical data. This could be done as part of a joint effort with the Climate Variability and Predictability Program (CLIVAR) and Global Carbon Project (GCP).

2. Little is known about the exchange of anthropogenic CO_2 from the marginal seas to the open North Pacific. In some cases, particularly in the northwest Pacific including the Sea of Okhotsk and Bering Sea, water mass formation in the marginal seas plays a significant role in the formation of Intermediate Water. How anthropogenic CO_2 is ventilated and transported from the marginal seas to intermediate depths in the North Pacific Ocean is the subject of much research by member countries of PICES. PICES should support synthesis activities for carbon system parameters from these regional studies and foster integrated studies between the marginal seas and the open North Pacific.

3. In association with existing Data Centers, PICES should take the lead in developing a North Pacific database for ocean CO_2 and related parameters, and provide advice to Data Centers on which of the available historical data sets should be assigned a high priority for acquisition and conversion to an electronically readable form.

4. PICES should support the preparation of a written *Guide of best practices for oceanic CO_2 measurements and data reporting*, and carry out, as needed, inter-laboratory method comparisons to assure future measurement quality and encourage the availability of suitable reference materials.

5. PICES should continue to sponsor symposiums and/or annual meeting sessions on the impacts of climate change on the carbon cycle in the North Pacific Ocean.

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Summary of PICES Working Group 13 activities (1998 – 2001)

The PICES Working Group 13 on *CO₂ in the North Pacific* was established in 1998 under the direction of the Physical Oceanography and Climate Committee, and was co-chaired by Dr. Richard A. Feely of the Pacific Marine Environmental Laboratory (Seattle, U.S.A.) and Dr. Yukihiro Nojiri of the National Institute for Environmental Studies (Tsukuba, Japan). Table 5 provides a list of the Working Group members. The terms of reference for the Working Group were the following:

1. Review the present level of knowledge on the processes controlling CO_2 in the North Pacific, and identify the gaps and problems;
2. Review the existing methodology of CO_2 measurements, including the preparation of standards and reference materials, and advise on intercalibration and quality control procedures;
3. Identify and encourage ongoing and planned national and international CO_2-related scientific programs in the North Pacific region, including long-term time-series observations; and

4. In coordination with TCODE (PICES Technical Committee on Data Exchange), identify available and suitable data sets on the oceanic CO_2 system and recommend the mechanisms of data and information exchange.

Table 6 summarizes activities of the Working Group in chronological order; several of those were conducted jointly with the JGOFS North Pacific Task Team (NPTT). The Working Group met each year at the PICES Annual Meeting to coordinate research activities, exchange data and work to integrate the large-scale CO_2 data sets from the North Pacific. The meetings were well attended as each member presented a summary of country's research directions in carbon cycling, and invitees provided detailed information on ongoing and planned national and international CO_2-related scientific programs in the region. As a direct outcome, the Working Group recommended the re-occupation of, and exchange of samples during, the repeat WOCE/JGOFS sections P1, P2 and P16N in the North Pacific.

Table 5   Members of PICES Working Group 13.

Name	Affiliation	Country
Richard A. Feely	Pacific Marine Environmental Laboratory, NOAA	USA
Yukihiro Nojiri	National Institute for Environmental Studies	Japan
Andrew Dickson	University of California, San Diego	USA
Myung-Woo Han	Inha University	Republic of Korea
Akihiko Murata	Japan Marine Science and Technology Center	Japan
Galina Yu. Pavlova	Pacific Oceanological Institute	Russia
Paul Quay	University of Washington	USA
Igor Semiletov	Pacific Oceanological Institute	Russia
Pavel Tishchenko	Pacific Oceanological Institute	Russia
Zhang-Gui Wang	National Research Center for Marine Env. Forecast	People's Republic of China
C. S. Wong	Institute of Ocean Sciences	Canada

Table 6   Summary of PICES Working Group 13 activities (1998 – 2001).

Time	Location	Activity
October 1998	Fairbanks, U.S.A.	Working Group 13 Annual Meeting
January 1999	Tsukuba, Japan	*CO₂ in the Oceans* Symposium
April 1999	Tsukuba, Japan	*DIC Intercomparison* Workshop
October 1999	Vladivostok, Russia	Working Group 13 Annual Meeting
October 2000	Tsukuba, Japan	*TAlk Intercomparison* Workshop
October 2000	Tsukuba, Japan	*North Pacific CO₂ Data Synthesis* Symposium
October 2000	Hakodate, Japan	Working Group 13 Annual Meeting
October 2002	Hakodate, Japan	PICES/JGOFS Topic Session on *carbon cycling*
January 2001	Sidney, Canada	*CO₂ Data* Planning Workshop
August 2001	Tokyo, Japan	*CO₂ Data Integration* Workshop
October 2001	Victoria, Canada	Working Group 13 Annual Meeting

To improve the existing methodology of CO_2 measurements, the Working Group supported three international CO_2 measurement inter-comparison studies: for dissolved inorganic carbon (DIC), total alkalinity (TAlk) and the $^{13}C/^{12}C$ ratio of the inorganic carbon in seawater. The first two, each followed up with a Technical Workshop, were completed in April 1999 and October 2000 (see summary in *Appendix B*). The third inter-comparison was initiated in late 2001 and is still ongoing. Participants have been identified (8 laboratories from Canada, Japan, U.S.A., Australia, Germany, France and China-Taipei), and samples were distributed in the beginning of December 2001, and analyzed during 2002. This activity will be continued and summarized by a new Working Group on *Biogeochemical data integration and synthesis* (WG 17) established to retain a scientific focus on the carbon cycle within PICES. A workshop, if needed, will be organized to discuss the results from the $^{13}C/^{12}C$ inter-comparison.   The Working Group 17 has supported an on-land inter-comparison of underway and drifting/mooring pCO_2 measurement systems held in spring of 2003, in Japan, with participants from PICES countries as well as from Europe and Australia.

To review the present level of knowledge on the processes controlling CO_2 in the North Pacific, the Working Group co-sponsored an international symposium on *CO₂ in the Oceans* (January 1999, Tsukuba, Japan) and organized, jointly with the JGOFS NPTT, a Topic Session on *North Pacific carbon cycling and ecosystem dynamics* at PICES IX (October 2000, Hakodate, Japan) and an international *North Pacific CO₂ Data Synthesis* Symposium (October 2000, Tsukuba, Japan).

At the latter symposium, co-sponsored by the JST/CREST Program and hosted by the National Institute of Environmental Studies (Japan), a clear need was recognized to conduct an effort to bring scientists and data managers together to discuss the procedures for developing a North Pacific CO_2 database. This was implemented in 2001 as a series of two workshops that were organized jointly with TCODE. The first *CO₂ Data* Planning Workshop was held at the Institute of Ocean Sciences (Sidney, Canada) in January 2001, to discuss the likely technical issues involved in such a project, and to plan a second more detailed workshop that was held at the Japan Oceanographic Data Center (Tokyo, Japan) in August 2001. The objective for the

CO$_2$ Data Integration Workshop was to develop strategies for the exchange of CO$_2$ and related data at the international level, and to examine the technical issues in integrating presently available data into a uniform data structure or database. Both workshops met their goals (see summary in Appendix C), and PICES now has a unified plan for data submission and exchange. The PICES Working Group 17, in association with existing Data Centers, will continue this work to complete the North Pacific database for ocean CO$_2$ and related parameters and to ensure its continuous update.

Activities of the PICES Working Group 13 were recognized by the IOC-SCOR Ocean Carbon Advisory Panel as essential for improving the overall quality of oceanic CO$_2$ measurements, resolving data synthesis issues and developing strong collaborations for the integration of the large CO$_2$ data set in the North Pacific. The Panel emphasized the importance of international participation in the design of Ocean Carbon Observation System and supported PICES as an excellent forum for the Pacific region.

Appendix B.

Results of Working Group 13 method inter-comparison studies

One of the first questions asked of analytical measurements is: how reliable are they? This was a key concern of the PICES Working Group 13 on *CO₂ in the North Pacific*, which desired that measurements made at different times, by different investigators, from different laboratories in the various PICES nations, be comparable and correct.

In October 1998, at the first meeting of the Working Group (Fairbanks, U.S.A.), it was decided that, as one of the first steps towards this goal, the Working Group would plan and carry out a series of between-laboratory comparisons of measurement techniques for such carbonate parameters as dissolved inorganic carbon (DIC), total alkalinity (TAlk) and the $^{13}C/^{12}C$ ratio of the inorganic carbon in seawater.

For our initial studies, the Working Group decided to focus on the measurement of DIC and of TAlk in seawater. The plan was to conduct an inter-laboratory comparison of these measurements on some natural sea water samples, and then to hold a technical workshop to discuss the results of these studies, and to initiate detailed technical exchange regarding measurement techniques and data quality between the scientists involved in studying CO_2 in the North Pacific.

Inter-comparison conducted during 1999

Preparations for this exercise were started almost immediately after the Working Group meeting in Fairbanks. Four separate samples based on natural seawater were prepared:

- a Certified Reference Material (Batch 45) supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography (U.S.A.);
- an unknown surface seawater sample supplied by Dr. Dickson, and prepared in the

same way as the Scripps CRMs (it was, in fact, later distributed as CRM - Batch 46);
- an unknown surface seawater sample supplied by Dr. Nobuo Tsurushima of the National Institute of Environmental Studies (Japan), and prepared in the same way as the University of Hokkaido secondary standards for DIC; and
- an unknown deep-sea water sample supplied by Dr. Akihiko Murata of JAMSTEC, based on water collected in November 1998, on the R/V *Mirai* from a depth of 3,000 m, filtered and sterilized.

The samples were distributed to the participating laboratories in January 1999 (with one exception sent out in March 1999). In all, fourteen laboratories were involved: seven from Japan, four from the United States, and one from each of Canada, Korea, and China-Taipei (Table 7). Results were returned promptly from all of these laboratories!

A follow-up technical workshop took place April 20–22, 1999, at the National Institute for Research on the Environment (NIRE) in Tuskuba, Japan. The workshop was organized by Dr. Yukihiro Nojiri (NIES) and Dr. Koh Harada (NIRE), and was supported jointly by PICES, Kansai Environmental Engineering Center (KEEC) and JAMSTEC. A total of thirty-one participants from the various laboratories (including an observer from Russia) enjoyed a detailed discussion of the analytical techniques used by their laboratories for the measurement of DIC and TAlk (Fig. 15). This discussion was facilitated by having the analytical instruments from a number of the participating groups set up in a laboratory next to the meeting room.

The results of the actual inter-comparison were discussed in detail at the workshop, and were relatively encouraging. For DIC the results from a number of laboratories clearly reflected the

effects of calibration problems. However, once the various values for DIC had been adjusted to a common calibration scale (using the measurements made on the Certified Reference Material), the agreement between the various laboratories was excellent (±2 µmol kg^{-1}) (Fig. 16). For TAlk, the results were more disappointing, although reduction to a common calibration scale helped to reduce the extent of disagreement, there were still major inter-laboratory differences (±12 µmol kg^{-1}) (Fig. 17). A brief report describing this activity and the technical workshop was in July 1999, in PICES Press, Vol. 7 (2).

Table 7   Institutions participating in PICES inter-laboratory method comparisons for DIC and TAlk

Country	Institution	1999	2000
Canada	Institute of Ocean Sciences, Sidney	x	x
China-Taipei	National Sun-Yat Sen University, Kaohsiung	x	
Japan	Central Research Institute of Electric Power Industry, Abiko	x	x
	Hokkaido University, Sapporo	x	x
	Japan Marine Science and Technology Center, Yokosuka	x	x
	CREST: Japan Science and Technology Corporation		
	& Hokkaido University, Sapporo	x	x
	& National Institute for Environmental Studies, Tsukuba		
	Kansai Environment Engineering Center Ltd., Osaka	x	x
	& National Institute for Resources and Environment, Tsukuba		
	Meteorological Research Institute, Tsukuba	x	
	National Research Institute of Fisheries Science, Yokohama	x	
	University of the Ryukyus		x
Korea	Seoul National University, Seoul	x	x
Russia	Pacific Oceanological Institute, Vladivostock		x
USA	NOAA Atlantic Oceanographic and Meteorological Laboratory, Miami	x	x
	NOAA Pacific Marine Environmental Laboratory, Seattle	x	
	Scripps Institution of Oceanography, San Diego	x	x
	University of Hawaii, Honolulu	x	x

Inter-comparison conducted during 2000

As a result of the 1999 inter-comparison, it was decided that a further study should be conducted, which would focus on the measurement of TAlk to see just how effective the 1999 technical workshop had been. Again, four separate samples based on natural seawater were used:

- a CRM (Batch 50) supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography (U.S.A.);

- an unknown surface seawater sample supplied by Dr. Dickson, and prepared in the same way as the Scripps CRMs (it was, in fact, later distributed as CRM - Batch 51);
- an unknown surface seawater sample supplied by Dr. Nobuo Tsurushima, and prepared in the same way as the University of Hokkaido secondary standards for DIC;
- an unknown deep sea water sample supplied by Dr. Akihiko Murata of JAMSTEC, based on water collected in November 1999, on the R/V *Mirai* from a depth of 3,000 m, filtered and sterilized.

Fig. 15 Participants of the first PICES CO_2 Technical Workshop held April 20–22, 1999, at the National Institute for Resources and Environment, Tsukuba, Japan.
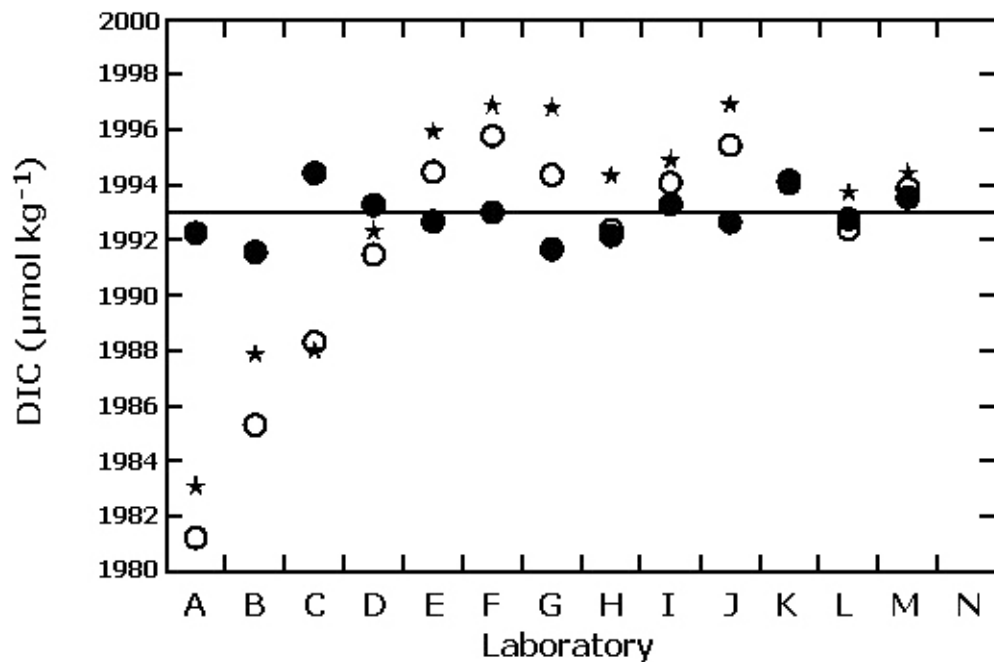

Fig. 16 Results from 1999 analyses of DIC. Asterisks are measurements on the CRM (CRM-45); open circles are the values measured on the PICES test sample (CRM-46); and closed circles are the values obtained for the PICES test sample after "calibration" with the reference material. The horizontal line is the "true" value for the PICES test sample.
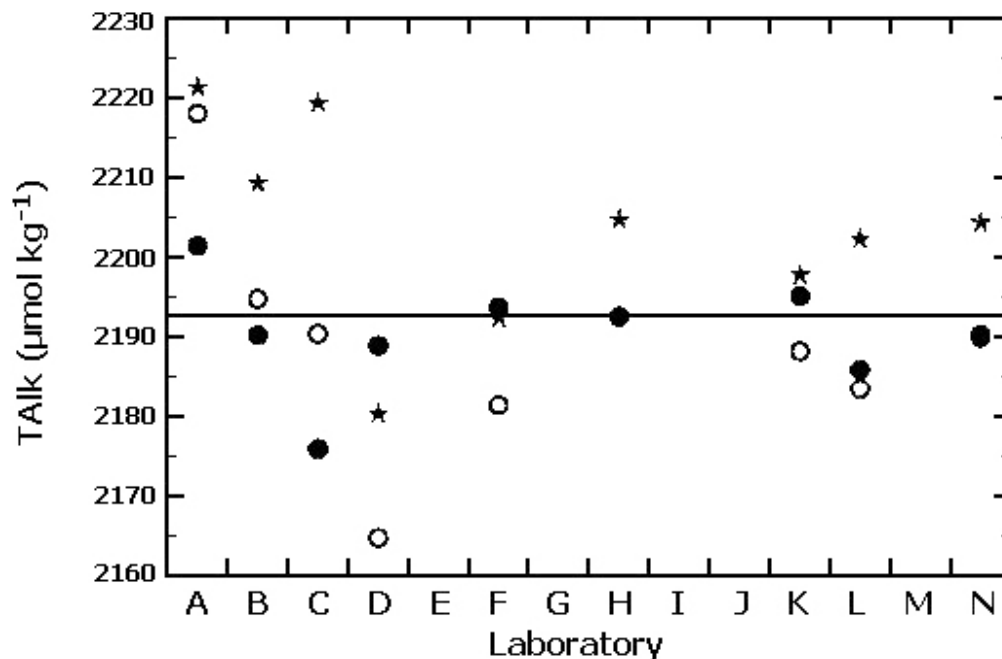
Fig. 17 Results from 1999 analyses of TAlk. Asterisks are measurements on the CRM (CRM-45); open circles the values measured on the PICES test sample (CRM-46); and closed circles are the values obtained for the PICES test sample after "calibration" with the reference material. The horizontal line is the "true" value for the PICES test sample.

Fig. 18 Discussion at the second PICES CO_2 Technical Workshop held October 20, 2000, at the EPOCHAL International Congress Center, Tsukuba, Japan.
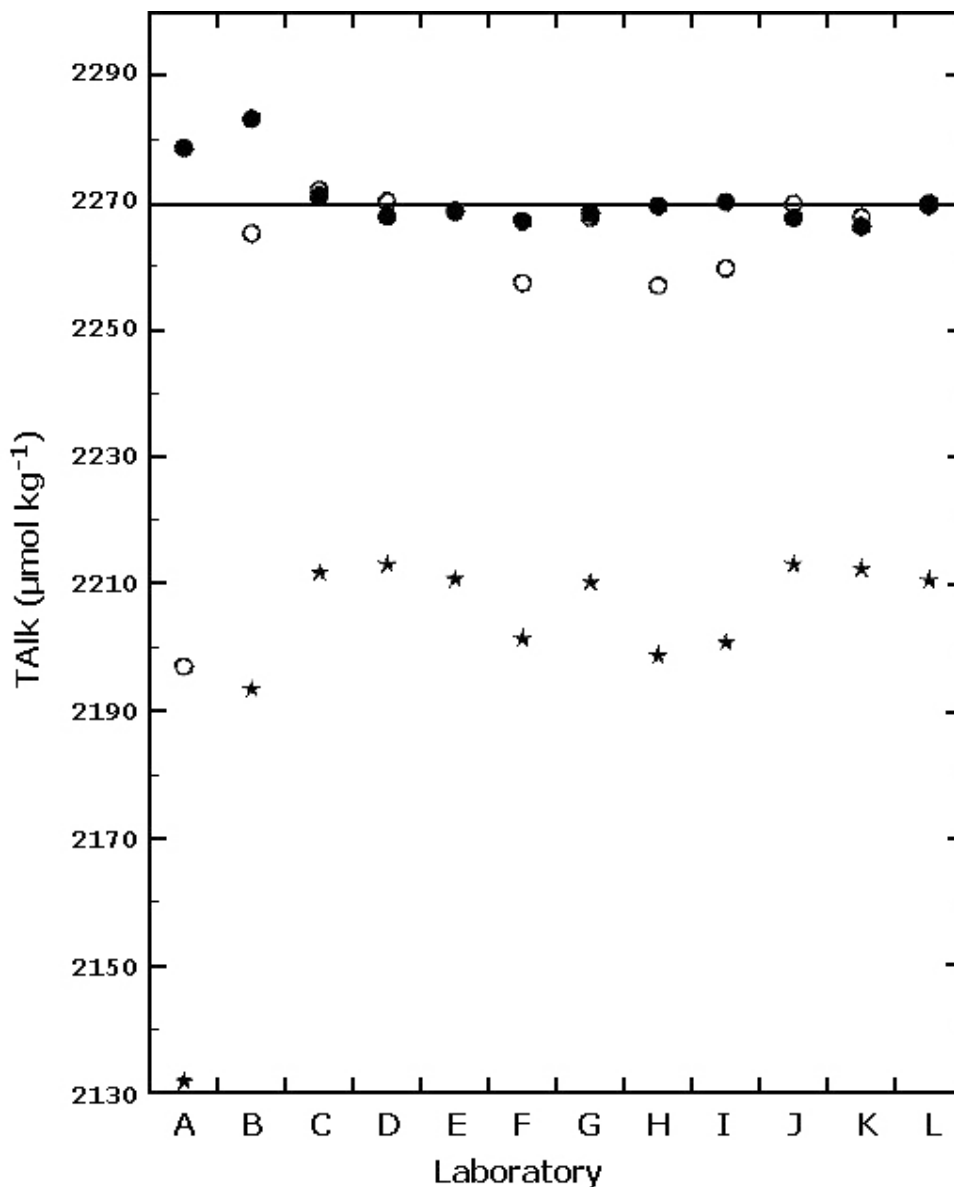
Fig. 19 Results from 2000 analyses of TAlk. Asterisks are measurements on the CRM (CRM 50); open circles the values measured on the PICES test sample (CRM 51); and closed circles are the values obtained for the PICES test sample after "calibration" with the CRM. The horizontal line is the "true" value for the PICES test sample.

The samples were distributed to the participating laboratories in March 2000. This time twelve laboratories were involved (Table 7): six from Japan, three from the United States, and one from each of Canada, Korea, and Russia. The follow-up workshop was held in October 2000, again in Tsukuba, Japan, and was attended by twenty-four scientists, including both members of the participating laboratories and some observers (Fig. 18).

Clear progress had been made in the year since the 1999 inter-comparison. After adjustment of the various data to a common calibration scale

set by CRM-50, the majority of the results (10 laboratories out of 12) were within a range of 5 μmol kg^{-1} (Fig. 19). This result is typical for laboratories with experience in this measurement, and indicates the increased skills of the participating laboratories have acquired over the past year. Nevertheless, it is essential to maintain an awareness of potential inter-laboratory calibration problems, and the sources of these were discussed at length during the workshop. One recommendation was that each laboratory develop an approach that independently calibrates the TAlk system, so that the CRMs can be used as an independent check on the calibration. The workshop again spent time reiterating the details of TAlk measurements so as to build upon this success. A brief report describing this activity and the technical workshop was in January 2001, in PICES Press, Vol. 9 (1).

Conclusion

The strategy used here, distribution of samples for analysis (including a calibration sample) followed by a technical workshop for detailed discussion of the results and of the various analytical techniques employed, is clearly very effective.

The present state-of-the-art methodology and technique for the analysis of DIC in seawater is mature. Most institutions use some variant of the extraction and coulometric analysis technique, and provided the instrument is well calibrated (*e.g.,* with appropriate reference materials), results of good quality can be obtained. This is in broad agreement with the experience of a variety of groups during the WOCE/JGOFS era.

Similarly, the problems with TAlk measurements also echo the experiences of a variety of groups in the WOCE/JGOFS era. The difficulties with this measurement cannot be attributed solely to calibration problems. Other factors play a clear role in the uncertainty of these measurements. A robust method for this parameter is still needed.

The likely quality of CO_2 measurements made in the future by the various PICES member countries thus seems assured. Nevertheless, it will be essential to

- ensure availability and distribution of suitable CRMs, and
- continue regular inter-comparison exercises to guarantee that all laboratories that are making oceanic CO_2 measurements are capable of such high-quality measurements.

Results of Working Group 13 data integration workshops

A necessity to identify available and suitable data sets on the oceanic CO_2 system and recommend the mechanisms of data and information exchange was explicitly included in the terms of reference at the establishment of the PICES Working Group 13 on *CO_2 in the North Pacific*. At the international *North Pacific CO_2 Data Synthesis* Symposium, co-sponsored by PICES and the JST/CREST Program and hosted by the National Institute of Environmental Studies in October 2000, in Tsukuba, Japan, a need to discuss the procedures for developing a North Pacific CO_2 database was re-instated. It was agreed that this project should be the primary activity of the Working Group during 2001, and in coordination with the PICES Technical Committee on Data Exchange, two workshops should be held in this direction to:

- review status of national/international CO_2 data inventories;
- discuss technical aspects involved in the development of a common database for CO_2 and CO_2-related data; and
- outline a possible mechanism for the international cooperation needed to realize this.

The first *CO_2 Data* Planning Workshop was held January 22-24, 2001, at the Institute of Ocean Sciences in Sidney, Canada (Fig. 20), to discuss the likely technical issues involved in developing of the North Pacific CO_2 database and to plan a second more detailed workshop. The participants included both CO_2 research scientists and specialists in oceanographic data from various Data Centers (JODC - Japan Oceanographic Data Center, MIRC - Marine Information Research Center of Japan Hydrographic Association, NODC - National Oceanographic Data Center of the United States, CDIAC - Carbon Dioxide Information and Analysis Center of the United States, and MEDS - Marine Environmental Data Service of Canada).

A series of presentations reviewed the present status of North Pacific CO_2 data in the participating PICES member countries, and essentially indicated that many of the recent and historic data holdings remain within individual laboratories, though steps are being undertaken to transfer the data to national and international Data Centers. It was also noted that even when such data resides at the Data Centers, integrating them into a coherent picture is a large task which requires a great deal of time and expertise. A common problem is that such data sets are often inadequately documented, making an objective assessment of their reliability very difficult. The workshop participants thus spent time developing draft guidelines for metadata (documentation of the methods, quality control procedures, etc.) that should accompany archived CO_2 data sets. Although it was recognized that in a number of cases, this information was perhaps unavailable, it was felt that such guidelines would help Data Centers to better assess the comprehensiveness of the metadata accompanying their data products. However, ultimately the most important part of the workshop was the opportunity it gave the participants to articulate a long-range vision for the future of CO_2 data sets for the North Pacific, and suggest approaches for the international coordination and cooperation needed to implement it.

To make the integration of both historic and future North Pacific CO_2-related data a reality, the workshop participants recommend that the Working Group 13 and TCODE:

- Work together with the Data Centers (JODC, MIRC, NODC, CDIAC, MEDS, etc.) and the JGOFS North Pacific Task Team to compile an international North Pacific data inventory for CO_2 and CO_2-related data, to be available as a web site by MIRC, and mirrored at the other Data Centers. Priority should be given to North Pacific open-ocean data; however, marginal seas will also be included.

Fig. 20 Participants of the PICES CO_2 Data Planning Workshop held October 22-24, 2001, at the Institute of Ocean Sciences, Sidney, British Columbia, Canada.

- Encourage PICES and non-PICES countries to contribute information on their North Pacific data holdings to this inventory.
- Persuade the Data Centers to adopt the proposed pH, pCO_2, DIC and TAlk metadata guidelines.
- Prepare and distribute a list of key stations for future replicate and shore-based analysis of deep-water samples, and to encourage the re-sampling of these stations in future national and international North Pacific CO_2 surveys. This would aid the assessment of the quality and utility of the historical databases.
- Use the quality-checked historical surface ocean pCO_2, data from Japan, Canada and the United States to test the Live Access Server concept for the display and distribution of combined data sets via the Internet.
- Promote the development of near real-time data exchange/data integration approaches for underway pCO_2, measurements in preparation for future observational programs, to ensure that timely repeated assessments of CO_2 exchange can be made.
- Support the continuation of underway pCO_2 inter-comparison studies to test the comparability of pCO_2 methods.

The second *CO₂ Data Integration* Workshop held at the Japan Oceanographic Data Center

(Tokyo, Japan) from July 31 to August 2, 2001, aimed at (i) developing strategies for the exchange of CO_2 and related data at the international level; and (ii) examining in more detail, the technical issues in integrating presently available data into a uniform data structure or database. Again this workshop was attended by a variety of PICES scientists and managers from existing Data Centers. The participants further explored the combined data set and debated a strategy for assessment and correction of systematic discrepancies. They also evaluated a proposed common data format and discussed the future home for a North Pacific database and plans for its accessibility.

A number of issues were agreed on at this meeting:

- a draft data format for future CO_2 data;
- the importance and success of the PICNIC (PICES CO_2 Related Data Integration for the North Pacific) data inventory developed by MIRC and now available on line at http://picnic.pices.jp; This web site incorporates the extensive information about Japanese cruises and information about Canadian (IOS) and U. S. cruises (linked to CDIAC holdings). At present, the inventory is linked to original data (at other locations on the Internet) wherever practical, and serves various historical data sets as they are digitized. However work is in progress to host some datasets at MIRC;

- the use of the Live Access Server (LAS) approach to serve distributed data sets so as to provide for improved data visualization over the Internet, and an agreement to share technical expertise to ensure this could be achieved; and
- the need to continue this project in future years.

Both workshops met their goals, and PICES now has a unified plan for submission and exchange of CO_2 and CO_2-related data at the international level. This work will be continued by the PICES Working Group 17 on *Biogeochemical data integration and synthesis*, established in 2002, to retain a scientific focus on the carbon cycle within PICES. The Working Group 17 declared collating historical, present day and future CO_2, carbon isotope and hydrographic data into an internationally accessible North Pacific database as one of its key activities. This effort will be conducted in collaboration with the existing national and international Data Centers and the Ocean Carbon Coordination Project of a joint IGBP/IHDP/WCRP Global Carbon Project.