

2.0 Synthesis of the WOCE/JGOFS global CO₂ survey data in the North Pacific

The recently completed WOCE/JGOFS global CO₂ 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 CO₂ ($f\text{CO}_2^1$), 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 CO₂ 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*

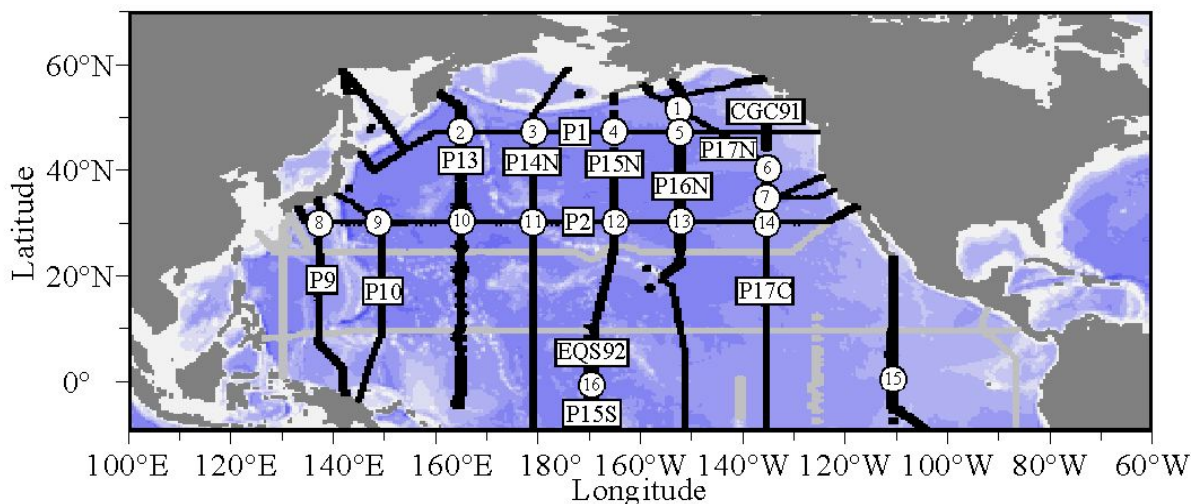


Fig. 1 Station locations for WOCE/JGOFS CO₂ survey cruises in the North Pacific Ocean. Cruise names are designated in the rectangles. Circles show crossover locations where carbon measurements were made; gray lines indicate cruises that had no carbon analyses.

¹ The fugacity of CO₂ takes into account the non-ideal nature of the gas. The values of $f\text{CO}_2$ are within 0.5-1.5 μatm of the partial pressure of CO₂ in surface waters.

Table 1 Summary of the carbon parameters analyzed during the North Pacific Ocean WOCE/JGOFS CO₂ 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-fCO₂ 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 $f\text{CO}_2$ 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 $f\text{CO}_2$ 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 $f\text{CO}_2$ 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:

$$\text{pH}_{\text{SWS}} = \text{pH}_{\text{T}} - \log \left\{ \frac{(1 + [\text{SO}_4^{2-}]_{\text{T}}/K_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/K_{\text{HF}})}{(1 + [\text{SO}_4^{2-}]_{\text{T}}/K_{\text{HSO}_4})} \right\} \quad (1)$$

where pH_{T} is the hydrogen ion concentration on the total hydrogen scale, $[\text{F}^-]_{\text{T}}$ and $[\text{SO}_4^{2-}]_{\text{T}}$ are the total concentrations of fluoride and sulphate in seawater, and K_{HF} and K_{HSO_4} are the dissociation constants of hydrogen fluoride and sulphate in seawater (Dickson and Riley, 1979).

2.2 Crossover comparisons of global CO_2 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, $f\text{CO}_2$ 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 $f\text{CO}_2$	Std Dev $f\text{CO}_2$	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 $f\text{CO}_2$

^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 $f\text{CO}_2$ -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 $f\text{CO}_2$, and only 1 crossover could be used to examine the consistency of the pH data. Due to the problems associated with $f\text{CO}_2$ 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 remineralization 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 $\pm 2.5 \mu\text{mol kg}^{-1}$. 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 $\pm 1.5 \mu\text{mol kg}^{-1}$. 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 $\sim 5 \mu\text{mol kg}^{-1}$. TALK, the second most common carbon parameter analyzed, had an overall accuracy of $\sim 10 \mu\text{mol kg}^{-1}$. 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 $f\text{CO}_2$ 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 ($\mu\text{mol kg}^{-1}$)	^a NA	^a NA	^a NA	+4	^a NA	-7	^a NA	^a NA	-4
TALK ($\mu\text{mol kg}^{-1}$)	^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>).