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Consistency and synthesis of Pacific Ocean CO_2 survey data

M.F. Lamb[a,*], C.L. Sabine[a], R.A. Feely[a], R. Wanninkhof[b], R.M. Key[c], G.C. Johnson[a], F.J. Millero[d], K. Lee[b,1], T.-H. Peng[b], A. Kozyr[e], J.L. Bullister[a], D. Greeley[a], R.H. Byrne[f], D.W. Chipman[g,2], A.G. Dickson[h], C. Goyet[i,3], P.R. Guenther[h], M. Ishii[j], K.M. Johnson[k,4], C.D. Keeling[h], T. Ono[l,5], K. Shitashima[m], B. Tilbrook[n], T. Takahashi[g], D.W.R. Wallace[k,6], Y.W. Watanabe[o], C. Winn[p,7], C.S. Wong[q]

[a] *NOAA/Pacific Marine Environmental Laboratory, 7600 Sandpoint Way NE, Seattle, WA 98115, USA*
[b] *NOAA/Atlantic Oceanographic and Meteorological Laboratory, 4301 Rickenbacker Causeway, Miami, FL 33149, USA*
[c] *Princeton University, Department of Geosciences, AOS Program/Sayre Hall, Princeton, NJ 08544, USA*
[d] *University of Miami/RSMAS, 4600 Rickenbacker Causeway, Miami, FL 33149, USA*
[e] *Carbon Dioxide Information Analysis Center, ORNL, Oak Ridge, TN 37831, USA*
[f] *Department of Marine Science/USF, 140 7th Avenue South, St. Petersburg, FL 33701, USA*
[g] *Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964, USA*
[h] *University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA*
[i] *Marine Chemistry & Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*
[j] *Meteorological Research Institute, 1-1 Nagamine, Tsukuba, Ibaraki 305-0052, Japan*
[k] *DOE/BNL, Building 318, Upton, NY 11971, USA*
[l] *National Research Institute of Fisheries Science, 12-4 Hukuura, Kanazawa-Ku, Yokahama 236-8648, Japan*
[m] *Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko, Chiba 270-1194, Japan*
[n] *Antarctic CRC and CSIRO Marine Research, GPO Box 1538, Hobart, Tasmania 7001, Australia*
[o] *National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba-shi, Ibaraki 305-8569, Japan*
[p] *University of Hawaii/Department of Oceanography, 1000 Pope Road, Honolulu, HI 96822, USA*
[q] *Institute of Ocean Sciences, 9860 W. Saanich Road, Sidney, British Columbia V8L 4B2, Canada*

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*Corresponding author.

[1] Now at: School of Environmental Science and Engineering, Pohang University of Science and Technology, San 31, Nam-gu, Hyoja-dong, Pohang, 790-784, Republic of Korea.

[2] Now at: RR1 Box 497, Orrs Island, ME 04066, USA.

[3] Now at: Universite de Perpignan, CEntre de Formation et de Recherche sur l'Environnement Marin, 52 Avenue de Villneuve, 66860, Perpignan, France.

[4] Now at: P.O. Box 483, Wyoming, RI 02898, USA.

[5] Now at: Ecosystem Change Research Program, FRSGC/IGCR, Sumitomo Hamamatsu-cho Bldg. 4F, 1-1, 16 Hamamatsu-cho, Minato-ku, 105-0013 Japan.

[6] Now at: Abteilung Meereschemie Institut fur Meereskunde an der Universitat Kiel, Dusternbrooker Weg 20, 24105 Kiel, Germany.

[7] Now at: Marine Science Program, Hawaii Pacific University, 45-045 Kamehameha Hwy., Kaneohe, HI 96744, USA.

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Abstract

Between 1991 and 1999, carbon measurements were made on twenty-five WOCE/JGOFS/OACES cruises in the Pacific Ocean. Investigators from 15 different laboratories and four countries analyzed at least two of the four measurable ocean carbon parameters (DIC, TAlk, fCO$_2$, and pH) on almost all cruises. The goal of this work is to assess the quality of the Pacific carbon survey data and to make recommendations for generating a unified data set that is consistent between cruises. Several different lines of evidence were used to examine the consistency, including comparison of calibration techniques, results from certified reference material analyses, precision of at-sea replicate analyses, agreement between shipboard analyses and replicate shore based analyses, comparison of deep water values at locations where two or more cruises overlapped or crossed, consistency with other hydrographic parameters, and internal consistency with multiple carbon parameter measurements. With the adjustments proposed here, the data can be combined to generate a Pacific Ocean data set, with over 36,000 unique sample locations analyzed for at least two carbon parameters in most cases. The best data coverage was for DIC, which has an estimated overall accuracy of $\sim 3\,\mu\mathrm{mol\,kg^{-1}}$. TAlk, the second most common carbon parameter analyzed, had an estimated overall accuracy of $\sim 5\,\mu\mathrm{mol\,kg^{-1}}$. To obtain additional details on this study, including detailed crossover plots and information on the availability of the compiled, adjusted data set, visit the Global Data Analysis Project web site at: http://cdiac.esd.ornl.gov/oceans/glodap.

1. Introduction

The recently completed World Ocean Circulation Experiment/Joint Global Ocean Flux Study/ National Oceanographic and Atmospheric Administration's (NOAA) Ocean Atmosphere Carbon Exchange Study (WOCE/JGOFS/OACES) global 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 in the oceans. They also provide 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, but have not as yet been synthesized into a unified, consistent global dataset. As a part of the US JGOFS synthesis and modeling project, several groups of investigators have been working to synthesize the global survey data to better understand biogeochemical cycling in the ocean. To ensure the highest quality results, the carbon synthesis group (Sabine, Bullister, Feely, Key, Kozyr, Millero, Peng and Wanninkhof) has been working closely with groups compiling the inorganic nutrients, chlorofluorocarbons (CFC), carbon-14, and carbon-13 data sets. The carbon synthesis group is also working through the Ocean Carbon Model Intercomparison Project (OCMIP) to compare these data directly with 13 global ocean carbon models. Our goal is to make specific recommendations for the adjustment of the Pacific carbon survey data to produce a uniformly calibrated data set. Model-data comparisons, including comparisons of data-based distributions of anthropogenic CO$_2$, provide a powerful constraint for evaluating the models. The global measurement databases are also potentially useful for model initialization.

Between 1991 and 1999, carbon measurements were made on twenty-five WOCE/JGOFS/ OACES cruises in the Pacific Ocean by investigators from 15 different laboratories and four

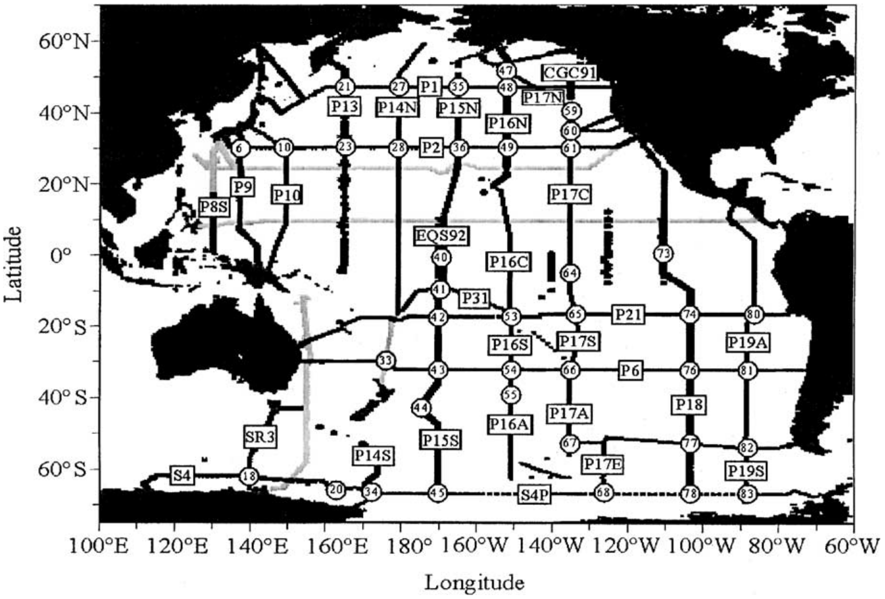

Fig. 1. Station locations for cruises during the Pacific Ocean survey. Cruise names are designated in the rectangles. Circles indicate crossover locations where carbon measurements were made; gray lines indicate cruises that had no carbon analyses.

countries (Fig. 1, Table 1). At least two of the four measurable inorganic carbon parameters were analyzed on each cruise, with the exception of CGC91 and P9. Dissolved inorganic carbon (DIC) was measured on all of the cruises, but additional measurements included one or more of the remaining parameters: Total alkalinity (TAlk), fugacity of CO_2 (fCO_2), or pH.

This work details our efforts to assess the quality of these measurements and suggest an approach for compiling these data into a basin-wide data set with values from the various cruises that are consistent with each other. Based on the preponderance of evidence, adjustments are proposed for particular data sets to improve consistency. Similar evaluations have been made for WOCE/JGOFS carbon data in other regions as well (e.g. Goyet et al., 1997, 2000; Johnson et al., 1998; Millero et al., 1998; Sabine et al., 1999). This work builds on the approaches described in these previous studies as well as comparable studies of Pacific Ocean carbon, salinity, oxygen and nutrient data (Feely et al., 1999; Gordon et al., 1998; Johnson et al., 2001). Compared to previous efforts, this study examines a more comprehensive carbon data set and considers a wider variety of evaluation techniques.

2. 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 Sea Water (DOE, 1994).

Table 1
Summary of the cruises on which carbon parameters were analyzed during the Pacific Ocean survey (1991–1999)

Cruise name	Cruise date	Carbon parameters analyzed				Country/ Institute[a]	Archived data location
		DIC	TAlk	$f\text{CO}_2$	pH		
P8S	June-96	x	x		x	Japan/CRIEPI	WHPO/UCSD
P9	July-94	x				Japan/MRI	WHPO/UCSD
P10	October-93	x	x			USA/Princeton	CDIAC
P13	August-92	x	x			USA/SIO	CDIAC
P14N	July-93	x	x		x	USA/UH	CDIAC
P14S15S	January-96	x	x	x	x	USA/NOAA	CDIAC
P15N	September-94	x	x			Canada/IOS	WHPO/UCSD
EQS92	March-92	x	x	x	x	USA/NOAA	NOAA
P16C	August-91	x	x			USA/WHOI	CDIAC
P16N	January-91	x			x	USA/NOAA	CDIAC
P16S17S	July-91	x	x	x		USA/LDEO	CDIAC
P16A17A	October-92	x		x		USA/LDEO	CDIAC
P17C	May-91	x	x			USA/WHOI	CDIAC
P17N	May-93	x	x			USA/WHOI	CDIAC
CGC91	February-91	x				USA/NOAA	CDIAC
P17E19S	December-92	x		x		USA/LDEO	CDIAC
P18	January-94	x	x	x	x	USA/NOAA	CDIAC
P19C	February-93	x		x		USA/LDEO	CDIAC
P1	99[b]	x	x		x	Japan/JFA	N/A
P2	January-94	x	x		x	Japan/JFA	JODC
P21	March-94	x	x		x	USA/UM	CDIAC
P31	January-94	x	x		x	USA/UH	CDIAC
P6	May-92	x		x		USA/BNL	CDIAC
S4P	February-92	x		x		USA/LDEO	CDIAC
SR3S4	December-94	x	x			Australia/ CSIRO	N/A
Carbon parameters analyzed		DIC	TAlk	$f\text{CO}_2$	pH		
No. of cruises		25	17	9	9		

Cruises with DIC–TAlk pair = 17
Cruises with DIC–$f\text{CO}_2$ pair = 9
Cruises with DIC–pH pair = 10
Cruises with > 2 parameters = 10
Cruises with > 3 parameters = 3
Total number of carbon sample locations ~ 36,000

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

2.1. Dissolved inorganic carbon (DIC) analysis

All DIC samples were analyzed by coulometric titration. The primary differences between the various groups were the sample volume and the primary calibration method. On many cruises the coulometer (UIC, Inc.) was coupled with a semi-automated sample analyzer (Johnson, 1992; Johnson et al., 1985, 1987, 1993, 1998; Ishii et al., 1998). The most common system, the Single Operator Multiparameter Metabolic Analyzer (SOMMA), was typically outfitted with a 20–30 ml pipette and was calibrated by filling a gas loop with a known volume with pure CO_2 gas, then introducing the gas into the carrier gas stream to be titrated (Johnson, 1992; Johnson et al., 1987, 1993, 1998). Other systems were calibrated by analyzing sodium carbonate standards. DIC systems that were not coupled with a semi-automated sample analyzer, typically, introduced the sample with either a manual pipette or syringe. Technical details of the DIC analysis techniques are outlined in Table 2 for the individual cruises.

2.1.1. DIC quality checks

Unless otherwise noted, Certified Reference Materials (CRMs; UNESCO, 1991; Dickson, 1992; Dickson et al., 2001a, b) were used on all cruises as secondary standards for DIC (Table 2). Certification of the CRM DIC is based on the vacuum extraction/manometric analysis of C. D. Keeling at SIO (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 (Table 2). For this study, DIC data not reported, as CRM normalized were corrected to the CRMs, if available, by adding the difference between the certified value and the mean shipboard CRM values ($DIC_{cert} - DIC_{ship}$) to every sample.

Replicate field measurements (Table 2) were used to determine the overall DIC precision on many of the cruises. On several cruises replicate samples were collected for analyses at C. D. Keeling's laboratory at Scripps Institute of Oceanography (SIO) following the procedures given in the DOE Handbook (DOE, 1994). The shore based manometric technique of C.D. Keeling (Guenther et al., 1994) is an accurate methodology that can provide information on the quality of shipboard analyses. In addition, samples were collected on the 1999 P1 cruise and shipped to R. Feely at NOAA/PMEL for shore side analysis (see Section 5.1 for further discussion). The at-sea/shore based comparisons, however, were not available for all cruises (Table 2).

2.2. Total alkalinity (TAlk) analysis

All shipboard TAlk measurements were made by potentiometric titration using a computer-controlled Dosimat™ titrator and a potentiometer (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. Details of the TAlk analysis techniques used on the various cruises are outlined in Table 3.

2.2.1. TAlk quality checks

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. Reported values that were not already corrected to the certified CRM TAlk were normalized by multiplying the reported values by the ratio of the

Table 2
Summary of analytical and standardization techniques, PIs, sample volumes, CRM analyses, replicate analyses, and shore based analyses for DIC during the global CO_2 Survey cruises in the Pacific

Cruise name	DIC analysis technique	PI /DIC	Standardization technique	Sample vol. (~ml)	CRM correction (SIO-cruise)	Data reported as CRM corrected[a]	Field replicate analyses average difference (μmol kg^{-1})	Shorebased analyses		
								Average difference (shore-ship) (μmol kg^{-1})	Std dev of difference (μmol kg^{-1})	*n*
P8S	Coulometer	Shitashima	Liquid Stds.	30	2.0 ± 2.8	No	1.8	ND[b]	ND[b]	ND[b]
P9	Coulometer	Ishii	Liquid Stds.	23	1.1 ± 1.3	No	2.0	ND[b]	ND[b]	ND[b]
P10	Coulometer/SOMMA[c]	Sabine	Gas loops	22	± 1.9	Yes	1.7	0.6[d]	1.8	9
P13	Coulometer/SOMMA[c]	Dickson	Gas loops[e]	30	± 2.4	Yes	0.9	−1.3d	3.1	138
P14N	Coulometer/SOMMA[c]	Winn/Millero	Gas loops	20	ND[b]	Yes	ND[b]	0.7[d]	2.3	27
P14S15S	Coulometer/SOMMA[c]	Feely	Gas loops	26	−1.1 ± 0.9	Yes	1.9	ND[b]	ND[b]	ND[b]
P15N	Coulometer/SOMMA[c]	Wong	Liquid Stds.	29	−0.1 ± 2.7	No	ND[b]	ND[b]	ND[b]	ND[b]
EQS92	Coulometer/SOMMA[c]	Feely	Gas loops	26	−0.8 ± 1.2	Yes	ND[b]	ND[b]	ND[b]	ND[b]
P16C	Coulometer/SOMMA[c]	Goyet	Liquid Stds.[e]	30	[b]	No	ND[b]	−2.1d	2.4	66
P16N	Coulometer	Feely	Liquid Stds.	50	3.0 ± 2.5	Yes	2.8	ND[b]	ND[b]	ND[b]
P16S17S	Coulometer	Takahashi	Gas loops	20	1.4 ± 1.5	No	0.6	−3.5[d]	2.0	11
P16A17A	Coulometer	Takahashi	Gas loops	20	1.3 ± 1.5	No	0.6	−3.4[d]	1.8	14
P17C	Coulometer/SOMMA[c]	Goyet	Liquid Stds.[e]	30	[e]	No	ND[b]	−3.4[d]	4.0	40
P17N	Coulometer/SOMMA[c]	Goyet	Liquid Stds.	30	[f]	[f]	ND[b]	−1.0[d]	4.1	9
CGC91	Coulometer	Feely	Liquid Stds.	50	3.0 ± 2.5	Yes	2.8	ND[b]	ND[b]	ND[b]
P17E19S	Coulometer	Takahashi	Gas Loops	20	1.4 ± 2.1	No	0.6	ND[b]	ND[b]	ND[b]
P18	Coulometer/SOMMA[c]	Feely	Gas loops	26	−1.3 ± 1.4	Yes	2.0	−0.4[d]	2.0	28
P19C	Coulometer	Takahashi	Gas loops	20	−0.2 ± 2.1	No	0.6	−1.0[d]	1.9	15
P1	Coulometer	Ono	Liquid Stds.	32/20[g]	1.7 ± 1.3	Yes	1.7	0.3[h]	2.1	48
P2	Coulometer	Ono	Gas loops	32	6.8 ± 3.1	Yes	ND[b]	ND[b]	ND[b]	ND[b]
P21	Coulometer/SOMMA[c]	Millero	Gas loops	20	0.9 ± 1.1	Yes	ND[b]	−2.3[d]	1.5	15
P31	Coulometer/SOMMA[c]	Winn	Gas loops	21	−0.9 ± 2.7	Yes	2.0	0.2[d]	3.4	8
P6	Coulometer/SOMMA[c]	Wallace	Gas loops	28	−0.6 ± 1.9	No	ND[b]	−2.6[d]	1.9	21
S4P	Coulometer	Takahashi	Gas loops	20	−0.9 ± 1.8	No	0.6	ND[b]	ND[b]	ND[b]
SR3S4	Coulometer/SOMMA[c]	Tilbrook	Gas loops	22	10.0 ± 0.95	Yes	2.0	ND[b]	ND[b]	ND[b]

[a] Original data submitted to data archival as CRM corrected (See Table 1 for location of archived data).

[b] ND = no data.

[c] SOMMA = Single operator multi-parameter metabolic analyzer.

[d] Shore based replicate analysis done at SIO.

[e] CRM used as a primary standard.

[f] CRM's not available.

[g] Two systems used on cruise, each with different sample volume.

[h] Shore based analysis done at PMEL.

Table 3
Summary of analytical techniques, PIs, sample volumes and shore based analysis for TAlk during the global CO_2 survey cruises in the Pacific

Cruise name	TAlk analysis technique	PI/TAlk	Sample vol. (~ml)	Data reported as CRM corrected	Cell type (open/ closed)	Curve fitting routine	Field replicate analyses average difference (μmol kg^{-1})	Shorebased analyses		
								Average difference (shore-ship) (μmol kg^{-1})	Std dev of difference (μmol kg^{-1})	*n*
P8S	Potentiometric	Shitashima	50	Yes	O	IPT[a]	4.3	ND[b]	ND[b]	ND[b]
P10	Potentiometric	Sabine	100	Yes	C	NLLSQ[c]	3.8	ND[b]	ND[b]	ND[b]
P13	Potentiometric	Guenther/Keeling	91	Yes	C	NLLSQ[c]	1.8	−3.4[d]	4.1	147
P14N	Potentiometric	Millero	200	No	C	NLLSQ[c]	2.0	ND[b]	ND[b]	ND[b]
P14S15S	Potentiometric	Millero	200	Yes	C	NLLSQ[c]	2.0	ND[b]	ND[b]	ND[b]
P15N	Potentiometric	Wong	203	[e]	C	NLLSQ[c]	ND[b]	ND[b]	ND[b]	ND[b]
EQS92	Potentiometric	Millero	200	Yes	C	NLLSQ[c]	2.3	ND[b]	ND[b]	ND[b]
P16C	Potentiometric	Guenther/Keeling	91	Yes	C	NLLSQ[c]	1.4	−0.4[d]	4.3	87
P16S17S	Potentiometric	Goyet	100	No	C	NLLSQ[c]	2.3	ND[b]	ND[b]	12
P17C	Potentiometric	Goyet	100	Yes	C	NLLSQ[c]	2.3	−10.6[d]	5.4	20
P17N	Potentiometric	Goyet	100	[f]	C	NLLSQ[c]	2.3	ND[b]	ND[b]	ND[b]
P18	Potentiometric	Millero	200	Yes	C	NLLSQ[c]	2.0	ND[b]	ND[b]	ND[b]
P1	Potentiometric	Ono	150	Yes	O	SPT[g]	3.2	5.9[h]	4.0	48
P2	Potentiometric	Ono	150	ND[b]	O	SPT[g]	3.1	ND[b]	ND[b]	ND[b]
P21	Potentiometric	Millero	200	Yes	C	NLLSQ[c]	2.0	ND[b]	ND[b]	ND[b]
P31	Potentiometric	Winn	200	Yes	C	NLLSQ[c]	NDb	ND[b]	ND[b]	ND[b]
SR3S4	Potentiometric	Tilbrook	210	Yes	C	NLLSQ[c]	2.4	ND[b]	ND[b]	ND[b]

[a] Inflection point titration method in the TitroLab (Radiometer Analytical A/S).

[b] ND = no data.

[c] Non-linear least-squares method.

[d] Shore based replicate analysis done at SIO.

[e] −23.6 adjustment to original data to agree with certified CRM values.

[f] CRM's not available.

[g] Single point titration method.

[h] Shore based analysis done at University of Miami.

certified TAlk to the mean of the shipboard CRM TAlk values ($TAlk_{cert}/TAlk_{ship}$) except, as noted in Table 3, where CRM results were not available. P15N TAlk data was reported as uncorrected; however, CRMs were analyzed for TAlk on that cruise. We have applied that correction ($-23.6\,\mu mol\,kg^{-1}$) to the P15N crossovers (noted in Table 3). As with DIC, shore based replicate samples were collected on some cruises (Table 3) for analysis in C. D. Keeling's laboratory at SIO. Samples collected on the 1999 P1 cruise were shipped to F. Millero at the University of Miami for shore side TAlk analysis (see Section 5.2 for further discussion).

2.3. fCO_2 analyses

Two different types of instruments were used to measure discrete fCO_2 samples (Table 4). With each an 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 nondispersive infrared analyzer (NDIR) or by quantitatively converting the CO_2 to CH_4 then analyzing using a gas chromatograph (GC) with flame ionization detector. The initial fCO_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 fCO_2 differences between headspace and water, and for systems with a large headspace to water volume ratio (Chen et al., 1995).

The system used by Takahashi (Chipman et al., 1993; DOE, 1994) involved equilibration of a ~50 ml headspace with a ~500 ml sample at either 4°C (T4 = Takahashi @ 4°C) or 20°C (T20 = Takahashi @ 20°C) depending on ambient surface water temperatures. Johnson and co-workers used a GC-based system with ~60 ml sample volume at an analytical temperature of 20°C (J20) on the P6 cruises. (Note that the Takahashi and Johnson values, reported as partial pressure of CO_2 (pCO_2), were converted to fCO_2 using the correction factor (~0.997) given by Weiss, 1974.) Wanninkhof and co-workers utilized two systems during the Pacific survey cruises. An NDIR based system (WI20 = Wanninkhof IR @ 20°C) with ~500 ml samples was used for analyses during EQS92 and P18 (Wanninkhof and Thoning, 1993). A GC-based system (WG20 = Wanninkhof GC @ 20°C) with samples collected in a closed, septum sealed bottle having a volume of ~120 ml of seawater and a headspace of ~10 ml was used for P14S15S (Neill et al., 1997).

For the crossover comparison, all samples run at 4°C were normalized to 20°C by calculating the alkalinity (TAlk) from fCO_2 (4°C) and DIC, and subsequently calculating fCO_2 (20°C) from the DIC and calculated TAlk. The carbonate dissociation constants of Merhbach et al. (1973) as refit by Dickson and Millero (1987) and ancillary constants listed in the program of Lewis and Wallace (1998) were used in the conversion. For Pacific deep waters, the temperature conversion from 4°C to 20°C using the Mehrbach constants yield fCO_2 values that are about 50 μatm higher than if the temperature conversion is performed with the Roy constants. Since the discrepancy in dissociation constants has not been fully resolved, the crossover comparison for fCO_2 data analyzed at different temperatures is problematic.

2.3.1. fCO_2 quality checks

Detectors were calibrated after every 4–12 samples with gas standards traceable to manometrically determined values of C. D. Keeling at SIO. Assessment of fCO_2 accuracy is difficult to determine because of the lack of aqueous standards. Estimates of precision based on

Table 4
Summary of analytical techniques, PIs and analysis temperatures for $f\mathrm{CO_2}$; PIs and sample volumes for pH analysis during the global $\mathrm{CO_2}$ survey cruises in the Pacific

Cruise name	$f\mathrm{CO_2}$ analysis technique	PI/$\mathrm{fCO_2}$	Analysis temperature (°C)	pH analysis technique	PI/pH	Analysis temperature (°C)	Sample vol. (~ml)
P8S	ND[a]	ND[a]	ND[a]	Potentiometric	Shitashima	25	30
P14N	ND[a]	ND[a]	ND[a]	Spectrophotometric	Winn	25	30
P14S15S	WG20[b]	Wanninkhof	20	Spectrophotometric	Byrne	25	10
EQS92	WI20[c]	Wanninkhof	20	Spectrophotometric	Byrne	25	10
P16N	ND[a]	ND[a]	ND[a]	Spectrophotometric	Byrne	25	10
P16S17S	T20[d]	Takahashi	20	ND[a]	ND[a]	25	ND[a]
P16A17A	T4[e]/T20[d]	Takahashi	$>45.5°$S; T = 4°C $<45.5°$S; T = 20°C[f]	ND[a]	ND[a]	25	ND[a]
P17E19S	T4[g]	Takahashi	4	ND[a]	ND[a]	25	ND[a]
P18	IR	Wanninkhof	20	Spectrophotometric	Byrne	25	10
P19C	T4[e]/T20[d]	Takahashi	$>45.5°$S; T = 4°C $<45.5°$S; T = 20°C[f]	ND[a]	ND[a]	25	ND[a]
P1	ND[a]	ND[a]	ND[a]	Spectrophotometric	Ono	25	2
P2	ND[a]	ND[a]	ND[a]	Potentiometric	Ono	25	150
P21	ND[a]	ND[a]	ND[a]	Spectrophotometric / Potentiometric[h]	Millero	25	30
P31	ND[a]	ND[a]	ND[a]	Spectrophotometric	Winn	25	30
P6	J20[g]	Johnson	20	ND[a]	ND[a]	25	ND[a]
S4P	T20[d]	Takahashi	4	ND[a]	ND[a]	25	ND[a]
SR3S4	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	25	ND[a]

[a] ND = No data.
[b] WG20 = GC system with 120 ml samples, run @ 20°C (Neill et al., 1997).
[c] WI20 = infrared analyzer run @20°C (Wanninkhof and Thoning, 1993).
[d] T20 = GC system with 500 ml samples, run @20°C (Chipman et al., 1993).
[e] T4 = GC system with 500 ml samples, run @4°C (Chipman et al., 1993).
[f] Latitude where measurement temperature was changed.
[g] J20 = GC system with 60 ml samples, run @20°C (Johnson et al., 1990).
[h] Eastern section of P21 analyzed using potentiometric technique.

duplicate samples range from 0.1% to 1% depending on $f\mathrm{CO}_2$ and measurement procedure, with higher $f\mathrm{CO}_2$ levels on the WI20 system ($>700\,\mu$atm) giving worse reproducibility (Chen et al., 1995). J20 standards were intercalibrated subsequently with standards maintained by T. Takahashi and D. Chipman at the LDEO; erroneously, in the original work (Johnson et al., 1990), no provision was made to measure the total gas phase pressure in the serum bottle after equilibration (P_{eq}). Since P_{eq} was not measured during P6 it had to be estimated. Subsequent laboratory tests (C. Neill and D. Wallace, unpubl. data) confirmed that the serum bottles were not subject to leakage and that the predicted pressure closely matched the actual headspace pressure.

2.4. pH analysis

Most of the Pacific Ocean pH measurements used a spectrophotometric method (Clayton and Byrne, 1993), with *m*-cresol purple as the indicator and either scanning or diode array spectrophotometers (Table 4). pH values on three cruises, P2 (Ono et al., 1998), P8S, and the eastern section of P21, involved potentiometric measurements with a glass electrode.

Some of the pH values were reported on the total hydrogen scale while others were reported on the seawater scale. 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:

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

where pH_{T} is a hydrogen ion concentration on the total hydrogen scale, $[\mathrm{F}^-]_{\mathrm{T}}$ and $[\mathrm{SO}_4^{2-}]_{\mathrm{T}}$ are the total concentrations of fluoride and sulfate in seawater, and K_{HF} and K_{HSO_4} are the dissociation constants of hydrogen fluoride and sulfate in seawater (Dickson and Riley, 1979). All total hydrogen scale pH values were converted to the seawater scale ($\mathrm{pH}_{\mathrm{SWS}}$) to be consistent with published dissociation constants of carbonic acid.

2.4.1. pH quality checks

Precision of the various pH measurements made during the Pacific Ocean CO_2 survey ranged from ± 0.0005 to ± 0.001 pH units. Generally, the precision of spectrophotometric pH is <0.001 in pH (Clayton and Byrne, 1993) while that of potentiometric pH is no better than 0.02 pH units (SCOR, 1985). All pH analyses were done at 25°C, and no conversion was made to in situ temperatures. pH accuracy is difficult to determine because no aqueous standards exist; however, there is some evidence to suggest that spectroscopic pH values may need to be revised upward (McElligott et al., 1998; DelValls and Dickson, 1998; Lee et al., 2000). This issue is discussed further in Section 5.4.

3. Statistical methods

The goal of this work 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. Several different techniques were used to quantify offsets as described below. All of the data were thoroughly checked for consistency along the section as the first order quality control (QC). In most cases, this level of QC was initially performed by the PI and/or CDIAC when the data were reported. We also performed these checks to ensure that the criteria for picking flyers or sudden shifts were consistent between cruises. Data points flagged as questionable were not used in these evaluations.

3.1. Crossover analysis technique

One approach for evaluating the consistency of the cruises was to compare data where cruises crossed or overlapped. 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. A summary table of the crossovers is given in the Appendix (Table 8). For this analysis, only deep-water (>2000 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. 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.

Sixty-eight crossover locations were identified for DIC. Only 36 locations had measured TAlk values for comparison. An additional 12 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 $f\mathrm{CO}_2$/DIC using the carbonate constants of Merhbach et al. (1973) as refit by Dickson and Millero (1987, 1989) and ancillary constants (e.g., boric acid and nutrients) listed in DOE (1994) and Millero (1995). Twenty-one crossover locations were available for $f\mathrm{CO}_2$. Because $f\mathrm{CO}_2$ concentration is a function of temperature, a direct comparison of samples analyzed at 4°C and 20°C only could be performed if the values were normalized to the same temperature. For this work, the 4°C samples were normalized to 20°C by calculating TAlk from $f\mathrm{CO}_2$ (4°C) and DIC, and subsequently calculating $f\mathrm{CO}_2$ (20°C) from the DIC and calculated TAlk. It should be noted that the refit Merbach et al. constants used for this temperature conversion yield $f\mathrm{CO}_2$ values that are about 50 μatm higher for Pacific Deep Water with $f\mathrm{CO}_2$ values of ~1100 μatm than the $f\mathrm{CO}_2$ values determined by using the Roy constants (Roy et al., 1993, 1994, 1996). Since the discrepancy in dissociation constants has not been fully resolved, the crossover comparison for $f\mathrm{CO}_2$ data analyzed at different temperatures is problematic. Only four crossovers could be used to examine the consistency of the pH data. Due to the problems associated with $f\mathrm{CO}_2$ comparisons, and because of the paucity of pH crossover locations available, no additional statistical analyses were performed on either of these parameters.

3.1.1. Crossover differences by polynomial fits

Comparisons between two cruises at the crossover locations were made by fitting the data from each cruise with a second-order polynomial function, and examining the differences (deltas) between the two curve fits. We chose a second-order polynomial for all the crossover differences, since in most cases, that was the best fit, and we were interested in consistency when comparing the crossovers. Potential density referenced to 3000 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 ten evenly spaced intervals along the curves. The quality of the polynomial fits can be affected by the number of points and their spread 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 second-order function was inadequate for about 15% of the DIC and TAlk fits (see examples in Figs. 2a and 3). In several cases, the

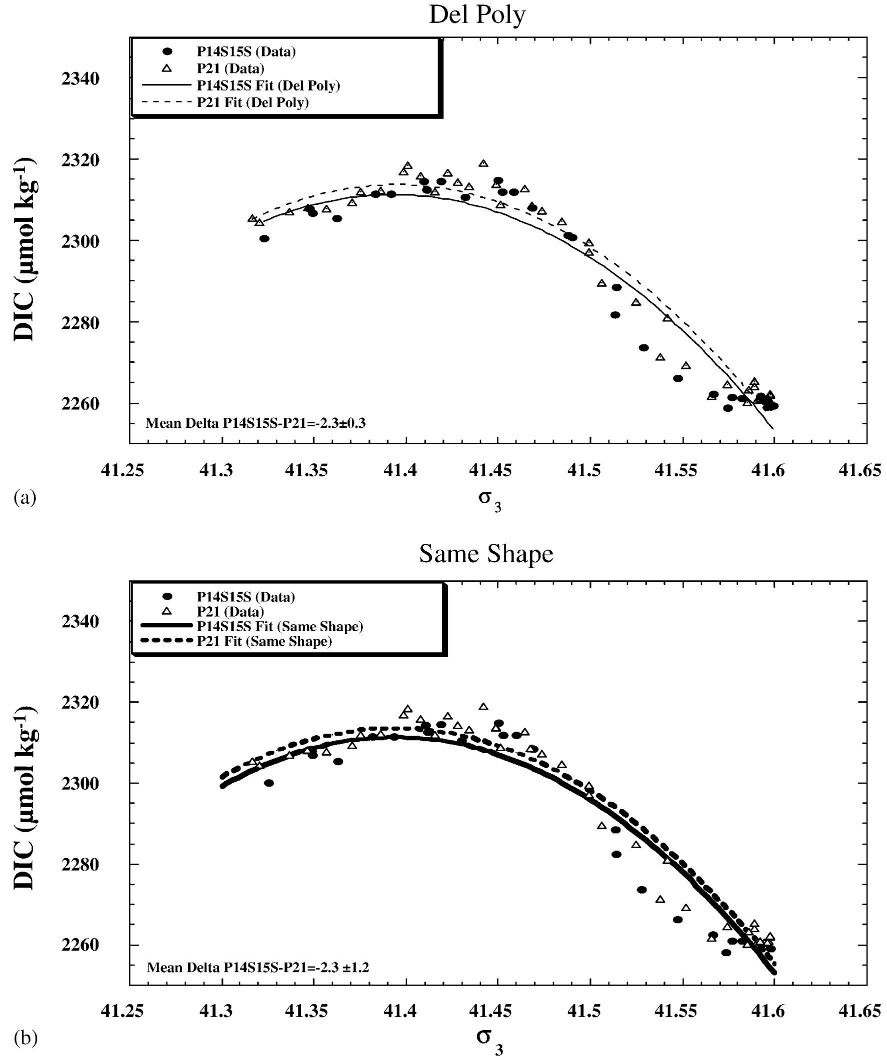

Fig. 2. DIC polynomial fits plotted against σ_3. Second-order polynomial fit (Del Poly) for data from Crossover 42 (a), second-order polynomial fit for data (Same Shape) for data from Crossover 42 (b). Del Poly (a) shows the influence of a complicated vertical structure. In this case, the fit of the Same Shape curve (b) is virtually the same.

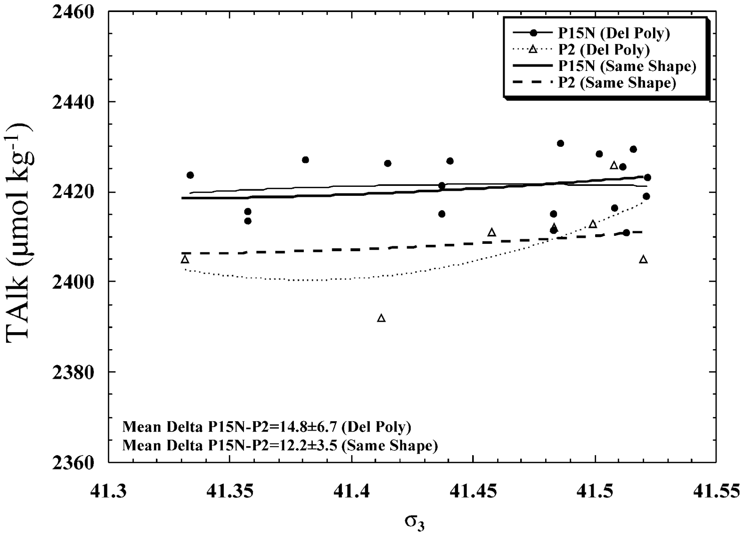

Fig. 3. TAlk polynomial fits plotted against σ_3 at crossover comparison #36 using Del Poly and Same Shape.

residual patterns suggested that several different water masses were being examined. This occurred in areas of the South Pacific that have a complex vertical structure because of influences from Pacific Deep Water, North Atlantic Deep Water, and Antarctic Bottom Water. However, since we were more interested in the offsets than the nature of the curves, we maintained the second-order model to allow a uniform treatment of the crossover data while fitting a small number of parameters to the sometimes-limited deep-water (> 2000 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, a second approach to the polynomial fit was examined. In the approach previously described, the data from each cruise were fit with an independent curve. We call this approach the Del Poly model. For the second approach (termed the Same Shape model), we fitted a second-order polynomial function to data from both Cruise 1 and Cruise 2 that allowed a constant offset for the two cruises but identical slope and curvature terms (Figs. 2b and 3):

$$\text{DIC or TAlk} = a * \text{cruise} + b * \sigma_3 + c * \sigma_3^2 + d, \tag{2}$$

where cruise denotes a Boolean term that is 1 for Cruise 1 data and 0 for Cruise 2 data. The assumption was made that for any given crossover, the differences between the data from the two cruises could be expressed in the Same Shape model as a constant offset for DIC and TAlk. The assumption of a constant offset was made partly because an offset was the simplest adjustment; however, with the relatively uniform oceanic values for DIC and TAlk, additive or multiplicative adjustments would give similar end results. The uncertainty for this model was estimated from the square root of the product of chi-square and the diagonal element of the model covariance matrix corresponding to the Boolean term.

Both approaches give very similar differences, but the uncertainties are generally smaller for the Same Shape model. It is difficult to say which approach is more appropriate for these data since the answer depends somewhat on the nature of the errors. If we assume a priori that the primary difference between the data sets results from a constant offset, then the Same Shape model is most appropriate. The Same Shape model also increases the degrees of freedom, useful when one or both cruises have data that are noisy and/or sparse (see example in Fig. 3).

3.1.2. Multi-parameter linear regression crossover analysis (MLR)

Another approach used to evaluate the data at the crossover locations was a multi-parameter linear regression analyses (MLR). Brewer et al. (1995) and subsequently others (Wallace, 1995; Slansky et al., 1997; Goyet and Davis, 1997; Sabine et al., 1999) have clearly demonstrated that both DIC and TAlk concentrations in deep and bottom waters can be fit with MLR functions using commonly measured hydrographic quantities for the independent parameters. The geographic extent over which any such function is applicable depends on the number of water masses present, and the uniformity of chemical and biological processes which have affected the carbon species concentration in each water mass.

We identified those crossovers where the difference and/or standard deviation between Cruise 1 and Cruise 2 was $> \pm 3\,\mu\text{mol kg}^{-1}$ for DIC, and $> \pm 5\,\mu\text{mol kg}^{-1}$ for TAlk (Table 8). Based on the relationship of DIC and TAlk to hydrographic properties, these fits should remain constant in deep water at the crossover locations despite the relatively short difference in time between two cruises that overlapped during the period of the survey. For the analysis of the differences, data in Cruise 1 stations were used as a reference to derive an equation that is the best fit between DIC or TAlk and three hydrographic parameters:

$$\text{DIC or TAlk} = a * S + b * T + c * O + d, \tag{3}$$

where a, b, c, and d are coefficients determined from data from the Cruise 1 crossover stations, S is salinity, T is in situ temperature, and O is oxygen concentration. Inorganic silicate was initially tested as an extra parameter; however, the improvement in the fit was insignificant. Once the constants were determined, DIC or TAlk was calculated using S, T, and O data from the Cruise 2 stations. This predicted value represents what the DIC or TAlk would be if the hydrographic properties from Cruise 1 were identical to those of Cruise 2. The difference between the predicted and the observed Cruise 2 DIC or TAlk was then calculated. Because the quality of hydrographic parameters can affect the fit of the function by creating an artificial offset, a thorough check was done prior to MLR analysis to ensure the quality of those data. Although no attempt was made to adjust the hydrographic parameters used in the MLR, the results of this work as well as previous crossover studies suggest that possible errors in the published salinity, oxygen and nutrient data are not of sufficient magnitude to influence the carbon fits (e.g. Johnson et al., 2001).

3.2. Internal consistency analysis

An additional independent approach for evaluating the accuracy of data is the examination of the internal consistency of the CO_2 system parameters. The CO_2 system in seawater is defined by knowing T, S, and nutrient concentrations (phosphate and silicate), and two of the four measurable carbon parameters: DIC, TAlk, $f\text{CO}_2$, and pH. Thus, the carbon system was over determined on cruises where three or more carbon parameters were measured. By comparing estimates using different pairs of carbon measurements, one can evaluate potential offsets.

Additionally, examination of internal consistency over several cruises lends confidence to the reliability of the equilibrium constants.

The constants of Merhbach et al. (1973) as refit by Dickson and Millero (1987, 1989) were used for this analysis, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of CO_2, water hydrolysis, and phosphoric and silicic acid dissociation) necessary to characterize the carbonate system in seawater as recommended in Millero (1995). This choice was made based on the analysis of a large data set (15,300 samples) obtained from all the ocean basins (Lee et al., 2000). For this analysis, TAlk was calculated using a combination of either DIC and fCO_2, or DIC and pH (adjusted upward by 0.0047 pH units DelValls and Dickson, 1998).

This approach relied heavily on two basic premises. The first was that all of the pH measurements needed to be adjusted upward by 0.0047 pH units (see Section 5.4). The second premise was that offsets in the internal consistency checks were attributed to errors in the TAlk measurements. This premise is supported by the crossover analysis and other approaches that suggested that the other carbon parameters were within acceptable ranges for the cruises in question (see Section 4.2).

3.3. Basin-wide MLR analysis (North Pacific)

The crossover analysis of the North Pacific was more problematic than for the South Pacific because there were only two zonal lines with carbon measurements (P1, P2) and, thus, relatively few crossover locations. As an additional check on the quality of the North Pacific data, the deep (>2500 m) DIC and TAlk data from all of the North Pacific lines were fit with a multiple linear regression (MLR) as a function of common hydrographic parameters. Relative to the rest of the ocean, the deep North Pacific is extremely uniform in almost all properties, and is therefore an ideal region in which to apply a basin-wide analysis of MLR. Only cruises whose stations were above 20°N were used in this analysis for DIC; all TAlk data from the Equator northward was used. The DIC criterion was chosen due to the fact that the residuals from the fit which included the 0–20°N data implied systematic differences between the two zones. When the DIC was limited to data north of 20°N, the fit improved significantly. The situation was reversed for TAlk; no significant difference in trend was seen across 20°N, and the fit degraded when the data range was limited to north of 20°N.

Once the linear regression had been calculated, it was possible to investigate the residuals for evidence of systematic differences between the various cruises. Details of the procedure can be found in Key (1999, 2000). For DIC, Eq. (4) gives the best functional form found for all of the North Pacific data:

$$\mathrm{DIC} = a\mathrm{NO_3} + b\mathrm{AOU} + c\mathrm{Si} + dS + eS^2 + f \tag{4}$$

where a, b, c, d, e and f are the coefficients, and DIC, NO_3, AOU, and Si are the measured total inorganic carbon, the inorganic nitrate, the apparent oxygen utilization (Garcia and Gordon, 1992) and the inorganic silicate concentrations in $\mu\mathrm{mol\,kg^{-1}}$, respectively, and S is the salinity. The S^2 term was included because without it the residuals were correlated with salinity. Similarly, salinity dependence exists in the residuals if carbon normalized to a constant salinity is substituted for carbon concentration.

For North Pacific TAlk data, the best fitting function found was in the form:

$$\mathrm{TAlk} = gS + h\mathrm{Si} + i\mathrm{PO} + j\theta + k, \tag{5}$$

where g, h, i, j, and k are the coefficients, and S is the salinity, Si is the inorganic silicate concentrations in μmol kg^{-1}, PO is $O_2 + 170PO_4$, and θ is potential temperature. As with the MLR crossover analysis, data quality of the independent variables was checked for the basin-wide MLR technique to minimize potential biases resulting from an artificial offset in one of the independent variables.

The independent variables used for the fits (T, S, and O) are closely related to response variables (DIC and TAlk). T and S, for example, represent physical factors that influence DIC and TAlk, while O accounts for the biological effects. However, several different parameters can represent the same process. The exact choice of parameters used to represent the known processes that affect DIC and TAlk were optimized based on statistical significance. It is not surprising that the most significant parameters were slightly different for the crossover MLR fits (which only examined a single location) than for the basin-scale fits that must account for regional variations not present in the crossover MLR fit.

3.4. Isopycnal analyses

At a few locations in the North Pacific the estimated offsets at the crossovers were not consistent with the offsets from the basin-wide MLR analysis. In an attempt to determine whether the limited number of stations analyzed biased the crossovers, we expanded the crossover analysis to include additional stations along each cruise and/or stations from neighboring cruises. The deep (>2200 m) station data were averaged at specific potential density (σ_3) values and fitted with a second-order polynomial function. The average differences and standards deviations were determined from evenly spaced differences along the curves. The range of values observed for a particular cruise at each isopycnal level indicated whether the stations initially used in the crossover analysis were offset from the surrounding stations. Although more assumptions about oceanographic consistency are necessary, the additional stations used in the isopycnal analysis can provide a better estimate of the difference between cruises since more data points are included in the analysis.

4. Results of statistical analysis

4.1. DIC

The DIC results from the various statistical analyses are summarized in Table 5 and Fig. 4a. The average of the absolute value of the differences for the 68 DIC crossovers was 3.0 ± 2.6 μmol kg^{-1} (Table 8). We further used the polynomial statistics described in Section 3.1.1 to estimate least-squares crossover adjustments to the DIC. We approached these adjustments and associated uncertainties with a hierarchy of three calculations of increasing sophistication, following recent work on a similar hydrographic adjustment problem for the WOCE Pacific salinity, oxygen, and nutrient data (Johnson et al., 2001). We assumed, based on

Table 5
Results of statistical analysis for recommended adjustments of DIC during the global CO_2 survey cruises in the Pacific

					MLR analyses				
Cruise name	Delta WDLSQ (Del Poly)	Std dev	Delta WDLSQ (same shape)	Std dev	Crossover (residual average)	Std dev	NP basin-wide (residual average)	Std dev	Delta isopycnal analysis
P8S	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P9	−3.2	2.0	−5.3	1.3	ND[a]	ND[a]	−1.9	2.7	ND[a]
P10	0.2	1.5	−0.3	1.2	ND[a]	ND[a]	0.9	2.6	ND[a]
P13	0.1	1.3	−0.1	1.0	−6.2	8.8	1.8	2.0	ND[a]
P14N	−1.9	1.7	−2.0	1.0	ND[a]	ND[a]	0.1	3.4	ND[a]
P14S15S	−0.1	1.6	−0.3	1.4	0.2	3.3	ND[a]	ND[a]	ND[a]
P15N	1.6	0.8	2.1	0.7	−0.4	2.4	1.5	3.4	ND[a]
EQS92	−1.5	1.0	−2.3	0.8	−1.6	1.7	ND[a]	ND[a]	ND[a]
P16C	−0.4	1.0	−0.1	0.8	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P16N	5.8	1.3	5.6	1.2	2.1	7.9	2.5	3.5	4.0
P16S17S	−0.7	0.8	−0.3	0.7	−3.7	1.6	ND[a]	ND[a]	ND[a]
P16A17A	2.8	0.9	3.2	0.8	−4.7	13.6	ND[a]	ND[a]	ND[a]
P17C	2.0	1.6	0.9	0.9	1.9	8.2	0.4	2.8	2.0
P17N	−5.3	1.8	−5.5	1.3	−9.7	1.8	−3.2	5.7	−10.0
CGC91	1.2	1.8	0.7	1.3	5.6	3.0	3.1	3.0	−5.7
P17E19S	3.1	0.9	2.5	0.8	3.8	1.3	ND[a]	ND[a]	ND[a]
P18	1.4	0.8	2.0	0.7	−1.2	2.5	ND[a]	ND[a]	ND[a]
P19C	1.2	0.8	1.4	0.8	2.2	2.3	ND[a]	ND[a]	ND[a]
P1	−2.2	1.2	−2.5	0.9	4.9	1.1	−2.0	4.6	ND[a]
P2	−2.5	1.3	−2.7	0.9	0.9	4.2	−3.3	4.7	−4.2
P21	−2.3	0.8	−1.5	0.7	−2.8	0.8	ND[a]	ND[a]	ND[a]
P31	0.1	0.9	−0.1	0.7	1.1	3.3	ND[a]	ND[a]	ND[a]
P6	1.2	0.8	2.0	0.8	3.7	1.6	ND[a]	ND[a]	ND[a]
S4P	1.0	0.8	1.9	0.7	6.6	3.4	ND[a]	ND[a]	ND[a]
SR3S4	−1.3	0.8	−0.5	0.9	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]

[a] ND = no data.

an initial examination of the data, that offsets at crossovers arose owing to systematic biases in the measurements that were constant throughout each cruise. We sought adjustments that, when applied to each cruise, minimized offsets at crossovers in a least-squares sense. In general, the more crossovers that influenced the adjustment for a given cruise, the smaller its estimated uncertainty.

4.1.1. Results of crossover differences by polynomial fits

The first set of adjustments were calculated using simple least-squares (SLSQ) approach, which, when applied to DIC, reduced the standard deviation of crossover offsets from 3.7 to 2.0 $\mu mol\,kg^{-1}$, a reduction of the variance at the crossovers to 29% of the original value. The second set of adjustments was calculated using weighted least-squares (WLSQ) technique; the weighting used the error estimates from the polynomial fits, and so focused on making adjustments to minimize offsets at crossovers where they were better determined. The more

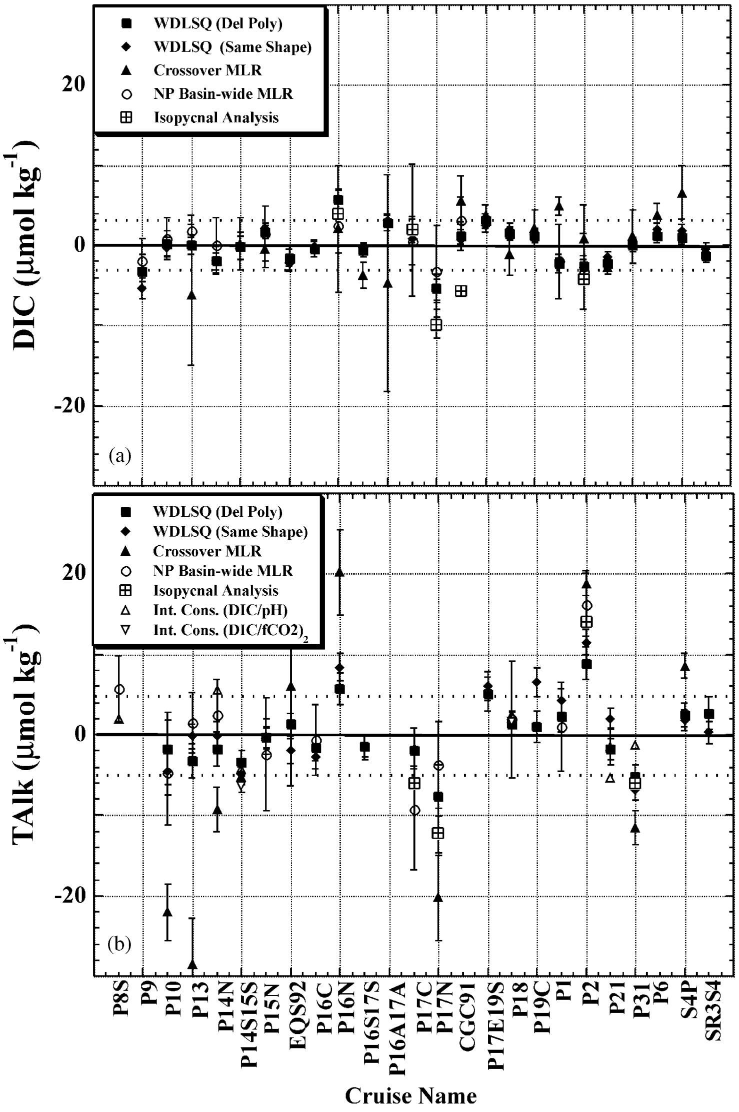

Fig. 4. Adjustments inferred from the statistical analyses of DIC (a) and TAlk (b) data for the cruises on the Pacific Ocean CO_2 survey.

crossovers used to determine the adjustments, and the smaller the offset uncertainties at those crossovers, the smaller the adjustment uncertainties. The WLSQ reduced the standard deviation of DIC crossover offsets to 2.1 µmol kg^{-1}, only slightly higher than the SLSQ method. The WLSQ adjustment uncertainties were overall somewhat smaller than for the SLSQ, reflecting the fact that the offset uncertainties were slightly less than the residual standard deviation used to estimate uncertainties for the first calculation. If one believes that the error estimates from the crossover differences truly represent the relative reliability of each crossover, then the WLSQ should be a better estimate of the offsets than the SLSQ. The third set of adjustments was calculated using weighted, damped least-squares (WDLSQ), formally equivalent to a Gauss–Markov model (Wunsch, 1996). The damping used was a prior guess of the variance at crossovers, estimated to be a constant $3^2\,\mu\text{mol}^2\,\text{kg}^{-2}$ for DIC, hopefully what one might have guessed prior to the survey. One also could choose to vary the damping on a cruise-by-cruise basis to reflect prior information on the accuracy of individual cruises (e.g., whether or not CRMs were used when determining DIC concentrations, or when the measurements were made, or even who made the measurements), but for this study a constant damping was used since nearly all groups reported a similar estimated accuracy within $3\,\mu\text{mol}\,\text{kg}^{-1}$. WDLSQ adjustments reflected the prior expectation of a certain variance; thus they were somewhat smaller than SLSQ or WLSQ adjustments. However, since the weighting variance was, in general, much smaller than the damping variance, the damping did not have much effect in these particular inversions (Table 5). The WDLSQ adjustments and errors make use of the most information (error estimates and prior guesses on crossover differences) to determine adjustments and their uncertainties.

The results from the WDLSQ show that almost all cruises during the Pacific Ocean CO_2 survey are within our $3\,\mu\text{mol}\,\text{kg}^{-1}$ cutoff for DIC. Based on this statistical analysis, a few cruises lie outside this cutoff; these results indicate that P9 should be decreased by 3–5 $\mu\text{mol}\,\text{kg}^{-1}$, P17N should be decreased by 5–6 $\mu\text{mol}\,\text{kg}^{-1}$, and P16N should be increased by 5–6 $\mu\text{mol}\,\text{kg}^{-1}$ (Table 5, Fig. 4a).

4.1.2. *Results of multi-parameter linear regression crossover analysis (MLR)*

Twenty-six DIC crossovers with differences from the polynomial fits $>3\,\mu\text{mol}\,\text{kg}^{-1}$ were examined further using the MLR crossover approach. Unlike the polynomial-fit crossover approach, the MLR method does not assume that the waters are identical, only that the relationships between DIC and the other properties do not change, and that the effects of measurement errors in the independent variables can be neglected. In the South Pacific, most of the crossovers with large differences were from the P14S15S-P15N crossover comparisons near the equatorial region (a series of meridianal crossover comparisons between the equator and 12°S along 170°W (Crossovers 40a–o)). In general, the use of the crossover MLR analysis resulted in smaller differences, suggesting that the assumption of identical waters may not be valid for this area. Based on the MLR crossover analysis, the results did show, however, that P13 and P17N should be decreased by 6 and $10\,\mu\text{mol}\,\text{kg}^{-1}$, respectively, and CGC91, and S4P should be increased by $6\,\mu\text{mol}\,\text{kg}^{-1}$ (Table 5, Fig. 4a.)

4.1.3. *Results of basin-wide MLR analysis (North Pacific)*

Applied to the North Pacific data north of 20°N, the basin-wide MLR for DIC had a residual standard error of $4.3\,\mu\text{mol}\,\text{kg}^{-1}$ on 1409 degrees of freedom and a multiple R^2 of 0.93. Based on the MLR basin-wide approach, these results indicate that only a few cruises are marginally in need of adjustment for DIC data in the North Pacific above 20°N.

4.1.4. *Results of isopycnal analysis*

Results of our isopycnal analysis of P2 and P16N DIC near 30°N, 152°W are shown in Fig. 5a. The data were fitted with a second-order polynomial fit of DIC versus σ_3. The plot indicates consistently higher DIC values ($4\pm3\,\mu\text{mol}\,\text{kg}^{-1}$) in deep water on the P2 line as compared with P16N. The P14N data along 179°W also show slightly higher deep-water values

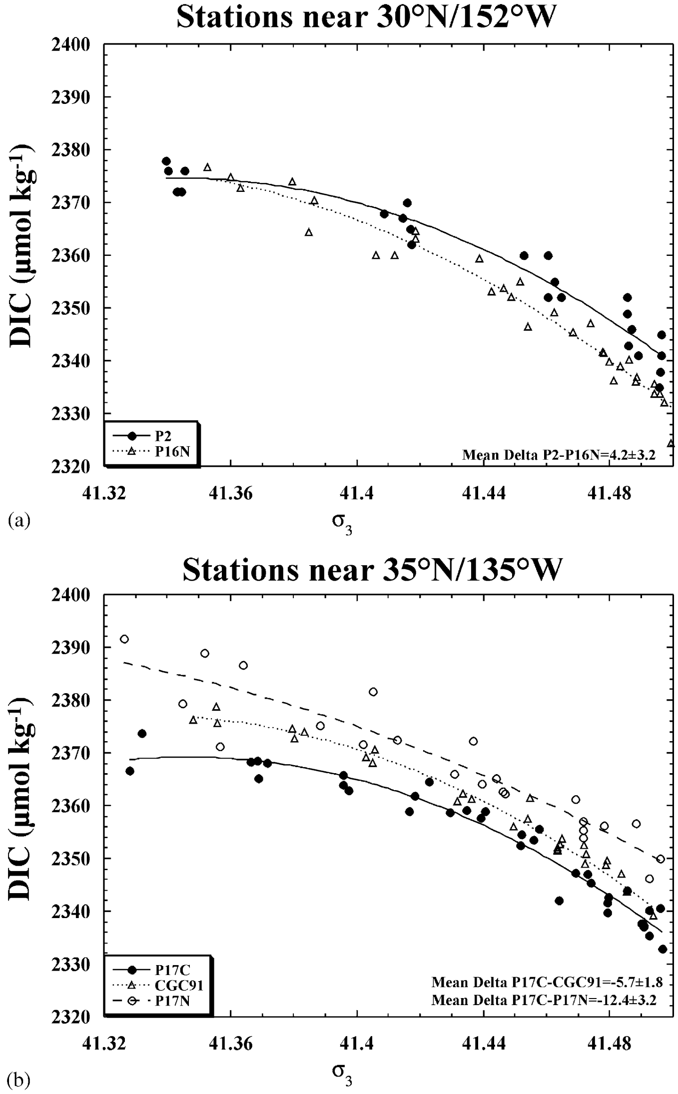

Fig. 5. DIC isopycnal analysis using second-order polynomial fits plotted against σ_3. Results are given for P2 and P16N (a) near crossover at ~30°N/152°W, and for P17C, CGC91 and P17N (b) near crossover at ~35°N/135°W.

(average = 4 μmol kg^{-1}) than the P16N results. In the previous crossover, and MLR analyses P14N showed no obvious offsets, whereas the P2 were generally found to be high and the P16N data were consistently low. The results of the isopycnal analysis can be reconciled with the findings of the other methods if the P16N data are increased by ~4 μmol kg^{-1} and the P2 data are decreased by 4 μmol kg^{-1}.

In the region near 35°N, 135°W, the isopycnal analysis indicated that the P17N data are consistently higher (12 ± 3 μmol kg^{-1}) than the P17C data (Fig. 5b). The CGC91 data are higher than the P17C results by 5 ± 1 μmol kg^{-1}. The crossover and MLR analyses of P17N indicate that the P17N data need to be decreased by 3–10 μmol kg^{-1}. An average decrease of 10 μmol kg^{-1} in

P17N will account for most of the observed differences with P17C. The MLR techniques suggest that P17C should be increased by 2 μmol kg^{-1}, but the crossover results are much smaller. All of these results cannot be reconciled, but a small increase of ~2 μmol kg^{-1} in P17C would minimize all of the observed offsets from the various approaches.

4.2. TAlk

The TAlk results from the various statistical analyses presented in Section 3 are summarized in Table 6 and Fig. 4b. The average difference of the absolute values TAlk was 4.7 ± 4.9 μmol kg^{-1}. If the calculated TAlk values are excluded ($n = 8$) the average of the absolute value of the differences was 4.2 ± 4.0 μmol kg^{-1}.

4.2.1. Results of crossover differences by polynomial fits

We approached the least-squares crossover adjustments to the TAlk in the same manner as was done with DIC. The results for the first set of adjustments (SLSQ) for TAlk reduced the standard deviation of crossover offsets from 7.4 to 4.4 μmol kg^{-1}, a reduction of the variance at crossovers to 32% of the original value. SLSQ produced the smallest offset residuals at the crossovers. The WLSQ reduced the standard deviation of TAlk offsets to 4.8 μmol kg^{-1}, only slightly more than with SLSQ. The WDLSQ adjustments used a damping of 5^2 μmol^2 kg^{-2} for TAlk and, as with DIC, resulted in a somewhat smaller reduction in the variance than the SLSQ or WLSQ (5.1 μmol kg^{-1}).

Based on all of the adjustment estimates from the various approaches, the Pacific TAlk data appear to be good to approximately ±5 μmol kg^{-1}. For the adjustments determined from the polynomial fits, three cruises fall outside this range. The crossovers suggest that P17N and P31 should be lowered by 7–12 and 6 μmol kg^{-1}, respectively. P2 should be increased by 8–10 μmol kg^{-1} (Table 6).

4.2.2. Results of multi-parameter linear regression crossover analysis (MLR)

Eighteen TAlk crossovers, where the difference in the polynomial fit was ⩾5 μmol kg^{-1}, were analyzed with the MLR approach. In every case, the offsets implied from the original crossover analysis was the same or larger with the MLR analysis indicating that the differences could not be explained by changes in the distribution of water masses.

4.2.3. Results of basin-wide MLR analysis (North Pacific)

The basin-wide MLR analysis in the North Pacific had a residual standard error of 7.4 μmol kg^{-1}. The residuals from this fit were binned by cruise and examined. Based on the initial fit, we eliminated two cruises, P2 and P17C, and the remaining cruises were then fit to the same model. The recalculated regression had a standard error of 6.0 μmol kg^{-1} with 1273 degrees of freedom and a multiple R^2 of 0.68. Based on these results, an increase of 16 μmol kg^{-1} is necessary for P2, and a decrease of 9 μmol kg^{-1} is needed for P17C (Table 6).

4.2.4. Results of isopycnal analysis

An isopycnal analysis was used to evaluate the P2 data relative to the meridianal cruises that it crossed. The P2 data were plotted as a function of longitude for three isopycnal intervals

Table 6
Results of statistical analysis for recommended adjustments of TAlk during the global CO_2 survey cruises in the Pacific

					MLR analyses						
Cruise name	Delta WDLSQ (Del Poly)	Std dev	Delta WDLSQ (Same Shape)	Std dev	Crossover (residual average)	Std dev	NP basin-wide (residual average)	Std dev	Delta isopycnal analysis	Int. cons. (DIC/pH)	Int. cons. (DIC/fCO_2)
P8S	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	5.7	4.1	ND[a]	1.9	ND[a]
P9	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P10	−1.7	4.5	−4.5	2.9	−22.0	3.5	−4.7	6.5	ND[a]	ND[a]	ND[a]
P13	−3.3	2.1	−0.2	1.6	−28.5	5.7	1.5	3.7	ND[a]	ND[a]	ND[a]
P14N	−1.8	2.1	−0.1	1.7	−9.3	2.8	2.5	4.4	ND[a]	5.5	ND[a]
P14S15S	−3.4	1.5	−4.9	1.3	−5.3	1.9	ND[a]	ND[a]	ND[a]	−4.2	−6.4
P15N	−0.3	1.3	−0.4	1.3	−0.2	2.2	−2.4	7.0	ND[a]	ND[a]	ND[a]
EQS92	1.3	1.4	2.0	1.5	6.0	12.3	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P16C	−1.6	1.6	−2.8	1.4	ND[a]	ND[a]	−0.6	4.4	ND[a]	ND[a]	ND[a]
P16N[b]	5.7	2.0	8.4	1.7	20.2	5.3	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P16S17S[c]	−1.4	1.4	−1.6	1.4	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P16A17A	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P17C	−2	1.9	−1.7	2.5	ND[a]	ND[a]	−9.2	7.6	−6.0	ND[a]	ND[a]
P17N	−7.6	3.9	−12.4	2.3	−20.2	5.3	−3.7	5.4	−12.2	ND[a]	ND[a]
CGC91	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P17E19S[c]	5.1	2.1	6.1	1.8	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P18	1.3	1.5	1.5	1.4	ND[a]	ND[a]	1.9	7.3	ND[a]	2.5	1.7
P19C[c]	1.0	1.9	6.5	1.8	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
P1	2.3	2.0	4.2	1.6	ND[a]	ND[a]	1.0	5.5	ND[a]	ND[a]	ND[a]
P2	8.9	2.0	11.5	1.6	18.8	1.6	16.1	3.9	14.0	ND[a]	ND[a]
P21	−1.8	1.3	1.9	1.3	−1.5	2.3	ND[a]	ND[a]	ND[a]	−5.4	ND[a]
P31	−5.2	1.4	−6.9	1.3	−11.6	2.2	ND[a]	ND[a]	−6.0	−1.3	ND[a]
P6	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
S4P[c]	2.5	1.5	1.8	1.3	8.6	1.6	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
SR3S4	2.7	2.1	0.3	1.4	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]

[a] ND = no data.

[b] No TAlk analyzed; data calculated from DIC/pH.

[c] No TAlk analyzed; data calculated from DIC/fCO_2.

representing data between 3000 and 4000 m (Fig. 6). Values from P10, P13N, P14N and P15N, with latitudes between 25 and 35°N, were consistently higher than the P2 data, indicating that a significant positive correction is necessary for P2. A similar analysis was conducted for P31. This cruise was compared with a nearly parallel cruise (P21) that was run along 20°S and the intersecting meridianal cruises P15N, P15S, and P16C (Fig. 7). The P31 data at either end of the section, where the meridianal lines intersect, are only slightly higher than the other lines. In the middle of the section, however, the P31 data are much higher than the P21 values, suggesting that a correction is in order. Fig. 8 is a plot of alkalinity as a function of latitude for σ_3 values between 41.44 and 41.51 on P17C and neighboring cruises. The larger density range was necessary to encompass enough data for comparison. The P17C data appear to be slightly higher than P16C or P15N. The low P2 data relative to P15N also are seen in Fig. 6. Finally, we reexamined the intersection of P17N with P16N. Fig. 9 includes data from a larger region and a wider depth range than initially considered with the crossover analysis. The calculated TAlk values for P16N also include a $+4\,\mu\mathrm{mol\,kg^{-1}}$ adjustment in the DIC values that is proposed from this study. The resulting extended crossover has an average offset of $12\,\mu\mathrm{mol\,kg^{-1}}$ at depths greater than 900 m.

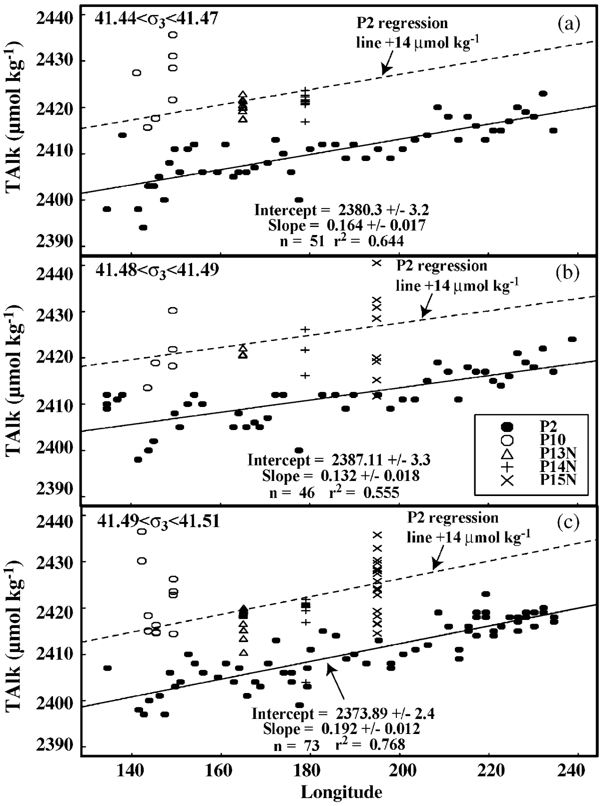

Fig. 6. Plots of measured TAlk versus longitude for three isopycnal intervals: (a) $41.44 < \sigma_3 < 41.47$, (b) $41.48 < \sigma_3 < 41.49$ and (c) $41.49 < \sigma_3 < 41.51$. Solid line is a linear regression through the P6 data. The dashed line is the P2 fit plus $11\,\mu\mathrm{mol\,kg^{-1}}$. P10, P13, P14N and P15N data are limited to latitude range 25–35°N.

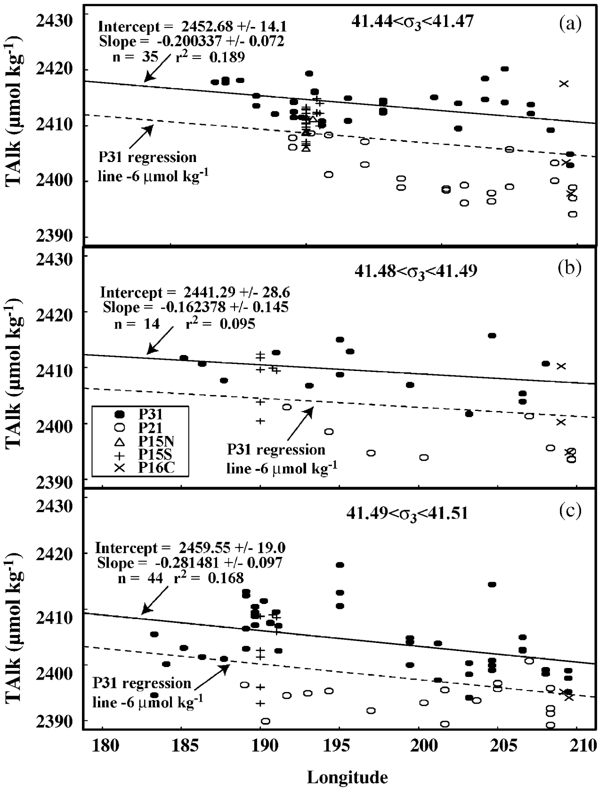

Fig. 7. Plots of measured TAlk versus longitude for three isopycnal intervals: (a) $41.44 < \sigma_3 < 41.47$, (b) $41.48 < \sigma_3 < 41.49$ and (c) $41.49 < \sigma_3 < 41.51$. Solid line is a linear regression through the P31 data. The dashed line is the P31 fit minus 6 μmol kg^{-1}. P15N, P15S, and P16C data are limited to latitude range 15–25°S.

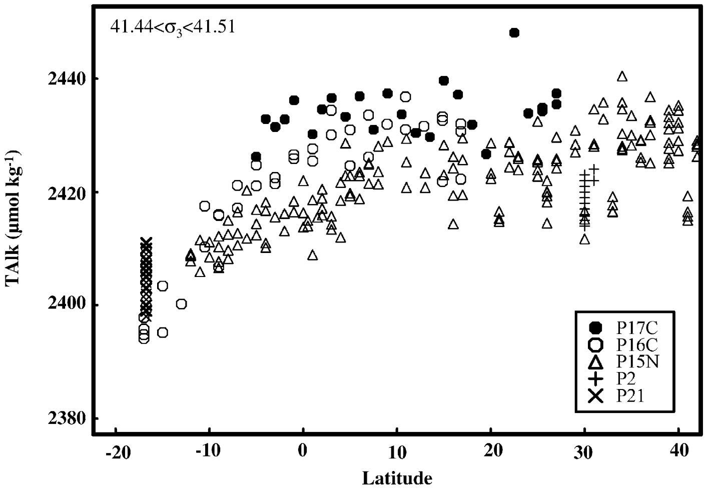

Fig. 8. Plot of measured TAlk versus latitude for σ_3 values between 41.44 and 41.51. P2 and P21 data are restricted to longitude range 120–140°W.

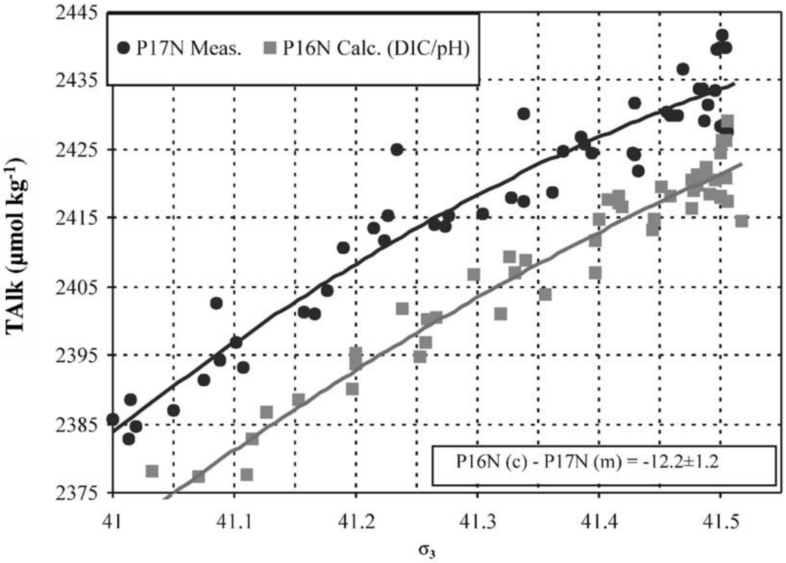

Fig. 9. Results of TAlk isopycnal analysis of P16N (calculated using adjusted DIC values and pH) and P17N (measured) plotted against σ_3 near crossover at 53°N/152°W.

4.2.5. *Results of internal consistency analysis*

Internal consistency calculations were used to evaluate TAlk on cruises where three or more carbon parameters were measured. This analysis showed that the measured values of TAlk for P14N are approximately 5 μmol kg^{-1} lower than the TAlk calculated from DIC and pH. P21 and P14S15S had measured values that were higher than the calculated values by 5 μmol kg^{-1} (based on DIC/pH) and 4–6 μmol kg^{-1} (based on DIC/pH and DIC/fCO$_2$), respectively, (Table 6). Note that proposed TAlk adjustments implicitly assume that pH, fCO$_2$ and DIC data are internally consistent from cruise to cruise.

4.3. *f*CO$_2$

The standard deviation for the 21 fCO$_2$ crossover comparisons was 16.0 μatm. The average of the absolute value of the differences was 13.4 ± 11.1 μatm. Notable offsets were observed for crossovers 82 and 83, with P19 showing a positive offset and S4P showing a negative offset relative to P17E19S. These two crossovers are both in the southern Pacific Ocean within 15° of each other. If this is systematic throughout the cruises, it would imply that the fCO$_2$ for S4P and P19 differ by about 30 μatm, which is roughly comparable to an offset of ~4–5 μmol kg^{-1} in DIC or TAlk. The largest offsets (35 μatm) were observed for EQS92. We suspect that the large offset observed on EQS92 is caused by a bias in the analytical system used during this cruise, although biases in the other crossovers involving the NDIR system at 20°C (WI20) were less pronounced. Crossover 73 shows excellent agreement where both cruises used the WI20 technique. The large headspace to water volume of the IR system may be the cause of the error. When comparing fCO$_2$ data obtained using the different types of instruments with the calculated fCO$_2$ values using TAlk and DIC, a bias between the NDIR and small volume GC systems becomes apparent. The GC-based

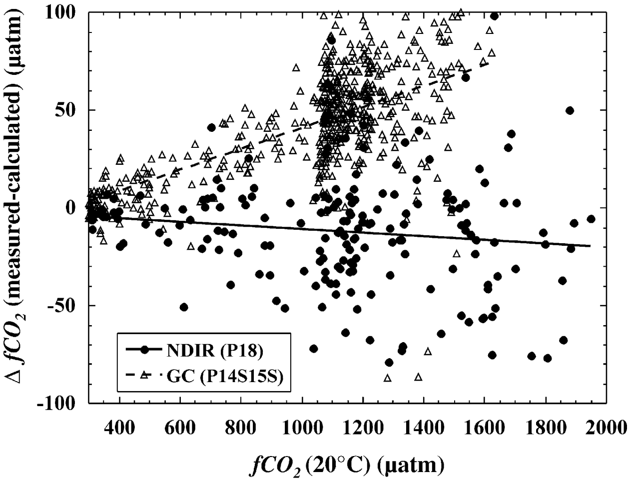

Fig. 10. Difference in measured $f\mathrm{CO}_2$ and calculated $f\mathrm{CO}_2$ (DIC and TAlk) for the NDIR based system used on P18 (WI20) and the GC-based system on P14S15S (WG20).

system (WG20) yielded significantly higher $f\mathrm{CO}_2$ values than calculated values using the recommended constants, while the IR based system did not show a clear trend, but rather increased scatter with increased $f\mathrm{CO}_2$ (Fig. 10). Based on careful laboratory studies, it appears that the NDIR based measurements may give low results at $f\mathrm{CO}_2$ values >700 μatm. The deep water data with WI20 are low by about 20–30 μatm in the range of 1000–1100 μatm. This result is in accordance with the recent findings of Lee et al. (2000). As suggested by Lee et al. (2000), the trend in the calculated values of $f\mathrm{CO}_2$ from TAlk and DIC most likely results from a thermodynamic inconsistency with the Merbach et al. constants. Until this is resolved, $f\mathrm{CO}_2$ values greater than 700 μatm should be used with caution in internal consistency determinations where imprecision of less than 3 and 5 μmol kg^{-1} in DIC and Talk, respectively, are desired.

4.4. pH

There were only four crossovers where both cruises measured spectrophotometric pH. The average of the absolute value of the differences of pH for those crossover locations was 0.0041 ± 0.0018. The crossover comparisons suggest very good precision, but because of the small number of comparisons available, no further statistical analysis was done with this carbon parameter. No crossover examinations were possible with the potentiometric pH measurements.

5. Recommended adjustments

The 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 >2000 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. Fig. 11a shows the variations in DIC on the surface $\sigma_3 = 41.5\,\mathrm{kg\,m^{-3}}$ from P16N. 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 (Fig. 11b). The residuals for points linearly interpolated onto the $41.5\sigma_3$ surface have a standard deviation of $\pm 2.5\,\mu\mathrm{mol\,kg^{-1}}$. 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

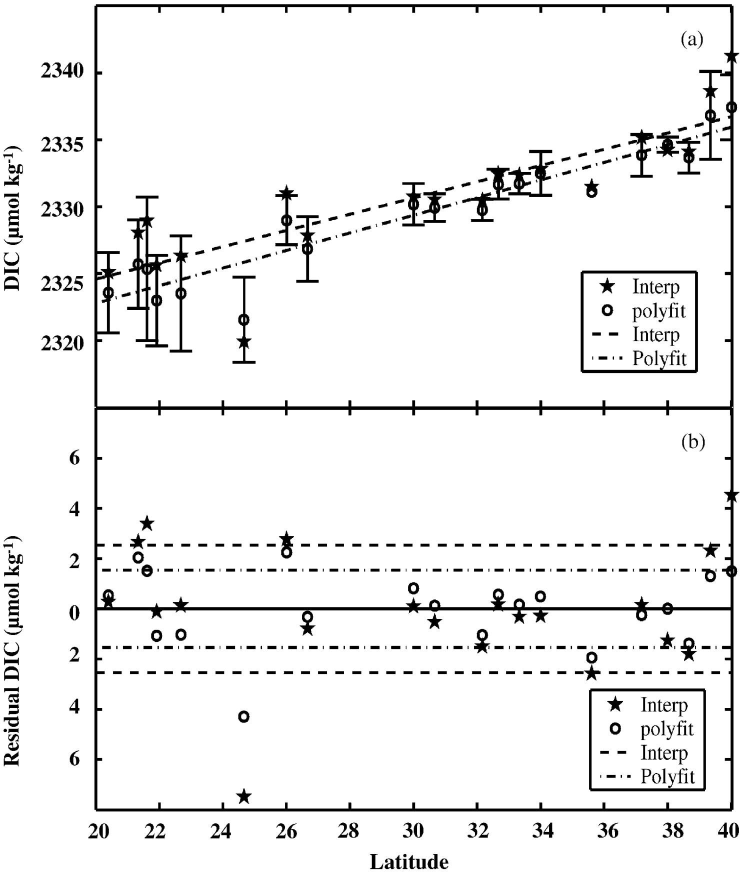

Fig. 11. DIC versus latitude on isopycnal surface $\sigma_3 = 41.5\,\mathrm{kg\,m^{-3}}$ at P16N (a), and variability evaluated from the residuals of a linear fit of the large-scale trend (b).

residuals drops to $\pm 1.5\,\mu\text{mol kg}^{-1}$ (Fig. 11b). 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.

5.1. DIC

The goal for DIC accuracy during the JGOFS field program was $\pm 3\,\mu\text{mol kg}^{-1}$. The results from 68 crossover comparisons and the MLR analyses suggest that the Pacific CO_2 survey data are generally within this range. The only adjustments considered here are those with sufficient evidence to support an adjustment that is larger than $3\,\mu\text{mol kg}^{-1}$. The results are summarized in Table 5, together with the cruise information from Table 2 show that only a few cruises fall outside this range. For the most part, the least-squares crossover adjustments for the South Pacific cruises were all well below $3\,\mu\text{mol kg}^{-1}$.

The crossover MLR technique examined the crossovers with the largest differences in the South Pacific and indicated that P16A17A, P16S17S, P17E19E, P6 and S4P were outside the $3\,\mu\text{mol kg}^{-1}$ criteria; however, these findings were generally based on a small number of crossovers (in some cases only 1). On all of these cruises the other approaches either suggested much smaller corrections or showed no consistent trends to justify a correction. The North Pacific was slightly more problematic. This may be due, in part, to the lack of zonal lines, which resulted in fewer crossovers to examine. The WDLSQ analyses both suggested P9 was in need of adjustment, but this is not supported by any other analyses, and therefore a correction is not recommended. Likewise, no adjustment is recommended for P13, which was only identified as offset by the crossover MLR analysis.

Both the polynomial fits indicated that P16N needed a substantial upward adjustment; however, neither MLR techniques indicated a need for an adjustment. We determined through the isopycnal analysis that an adjustment of $4\,\mu\text{mol kg}^{-1}$ best reconciled the potential conflict. As further evidence, during the 1999 occupation of P1, deep samples $>2000\,\text{m}$, were collected for shore side analysis where P1 crossed P13, P14N, P15N and P16N. When the shore based analysis was compared against these crossovers, the results show excellent agreement, with the exception of P16N. However, when the recommended adjustment discussed above ($+4\,\mu\text{mol kg}^{-1}$) was applied to P16N (Fig. 12), the results were excellent ($\text{delta} = 0.3 \pm 1.3\,\mu\text{mol kg}^{-1}$). These results, although based only on one comparison, confirm the integrity of shore based samples can be regarded as very high (Guenther et al., 1994); also the P1 shore based samples were analyzed almost one year after collection, indicating that shore based samples can, indeed, have a long 'shelf life'. Since the comparison of the samples was done almost a decade apart (P16N = 1991, P1 = 1999), these results demonstrate the uniformity of the deep North Pacific, as noted in Section

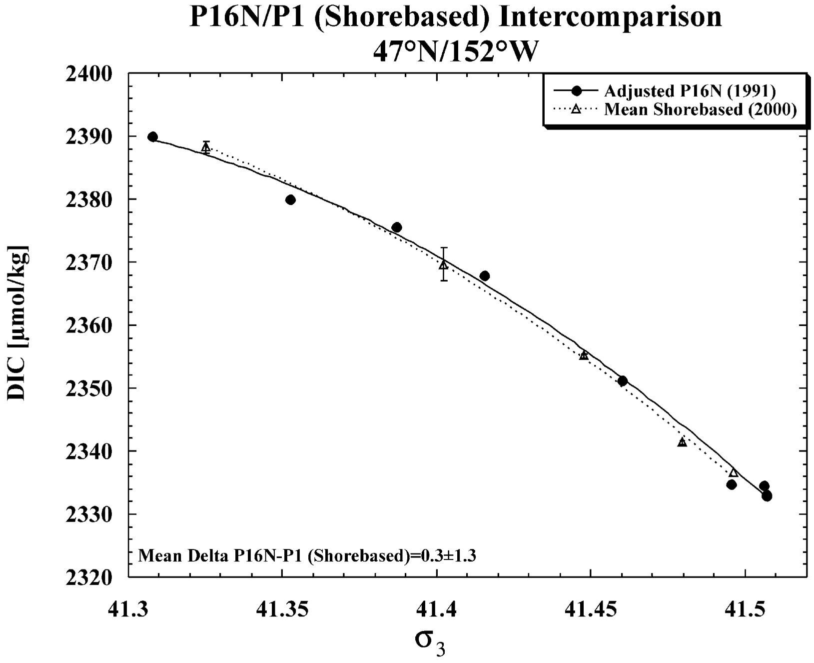

Fig. 12. Comparison of DIC for P16N (adjusted to recommendation of +4 μmol kg^{-1}) and samples collected during P1 for shore based analysis at NOAA/PMEL.

3.3. Based on all models and statistical techniques, P17N shows signs of needing adjustment. Our best recommendation is that 7 μmol kg^{-1} be subtracted from the P17N data. CGC91 is targeted as low by the crossover MLR technique. The crossover studies, however, had very small differences and the isopycnal analysis indicated that CGC91 was consistent with P17C, which was not recommended for adjustment by any of the techniques. The CGC91 cruise was relatively close to the coast in an area where changes in water mass properties are possible. Given the contradictory findings, no adjustment is recommended for CGC91. Although the least-squares crossover adjustments do not indicate a correction is needed for P2, both the basin-wide MLR and isopycnal analyses indicate that these data should be decreased by 4 μmol kg^{-1}. The recommended set of adjustments for DIC is summarized in Table 7.

Table 7
Summary of final recommended adjustments of DIC and TAlk during the global CO_2 survey cruises in the Pacific

Recommended adjustments (μmol kg^{-1})	Cruise name												
	P8S	P16N	P17C	P17N	P1	P2	P31	P16S17S	P14N	P14S15S	EQS92	P18	P21
DIC	NA[a]	+4	NA[a]	−7	NA[a]	−4	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
TAlk	+6	ND[b]	−9	−12	NA[a]	+14	−6	Calculated[d]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
pH	NA[a]	+0.0047	ND[b]	ND[b]	+0.0047	NA[a]	+0.0047	ND[b]	+0.0047	+0.0047	+0.0047	+0.0047	+0.0047[c]

[a] NA = no adjustment recommended.

[b] ND = no data reported.

[c] +0.0047 = Western section only.

[d] See discussion in Section 2.

5.2. TAlk

The absolute value of the differences for 48 TAlk crossover comparisons had an average of approximately 5 μmol kg^{-1}. The statistical results summarized in Table 6, together with the cruise information from Table 3, show that only a few cruises fall outside this range. Based on all of the lines of evidence we recommend that five cruises be adjusted.

P8S was a meridianal cruise that did not cross any other carbon cruise. The basin-wide MLR, the only tool available for determining the consistency between all the North Pacific cruises, indicated that an increase of 6 μmol kg^{-1} was in order for P8S. However, this cruise was the western most section in the North Pacific, relatively close to the Asian continent and the Kiroshio Current where water mass properties are the most likely to vary. A check of the internal consistency of the measured TAlk values with the DIC and pH measurements also suggested that a small increase was in order. Although CRMs were analyzed with a precision of ± 4 μmol kg^{-1}, we believe that the basin-wide MLR is the most reliable technique for evaluating this cruise and recommend an upward adjustment of 6 μmol kg^{-1}.

The basin-wide MLR technique suggests that a decrease should be applied to P17C. The isopycnal analysis, which examined measured TAlk values from neighboring cruises (but not necessarily crossovers), also indicates that the P17C data were high (Fig. 8). Given the scatter in the data and the complicated structure in the latitudinal variations, no attempt was made to quantify the apparent offset. Replicate TAlk samples were collected on P17C for shore based analysis which, when compared with the shipboard values, suggest a 10.6 μmol kg^{-1} offset. We believe the most reliable estimate for the TAlk adjustment is the basin-wide MLR analysis (-9 μmol kg^{-1}). Therefore, we recommend a decrease in the P17C TAlk data of 9 μmol kg^{-1}.

All of the approaches used to evaluate P17N indicate that the reported data are high relative to other cruises; however, the magnitude of the correction varies depending on the method. The crossover analyses for this cruise are based on a single station comparison of measured TAlk values relative to values calculated from DIC and pH. The three different crossover techniques suggest adjustments ranging from -8 to -20 μmol kg^{-1}. The basin-wide MLR analysis also suggests a decrease for P17N, but not as large as the crossover (-3 μmol kg^{-1}). The basin-wide MLR also indicated a smaller correction for the P17N DIC data than the other techniques. The DIC crossover adjustments were supported by more stations and crossovers with other cruises, and thus, were given more weight than the MLR analysis. The TAlk isopycnal analysis compared several additional stations over a wider depth range than the original crossover analysis (Fig. 9). In addition, the P16N TAlk values calculated for the comparison were adjusted to account for the DIC correction proposed in the previous section. This analysis clearly showed that the P17N data are high relative to P16N. Fitting each cruise with a second-order polynomial and evaluating the difference quantified the offset. We recommend that the P17N data be decreased by the mean deep-water offset from this analysis (-12 μmol kg^{-1}).

All of the statistical analyses suggest a sizeable correction for the P2 TAlk data. No CRMs were analyzed to provide information on the accuracy of the measurements. There were several cruises that were used for the crossover comparison, so the observed offset should be reliable. The basin-wide MLR approach also falls within the range of offsets indicated by the crossovers. The mean correction based on the various approaches is an increase of 14 μmol kg^{-1}. This correction is consistent with the offsets observed with the isopycnal analysis as indicated by the regression lines in Fig. 6.

The polynomial fits and MLR crossover analyses indicate that the P31 data are high. The internal consistency also suggests a small decrease is in order. Because the basin-wide MLR approach was not attempted for the South Pacific due to complicated carbon distributions and circulation, this MLR technique is not available for P31. The isopycnal analysis also indicates that the P31 data are high, but the offset cannot be quantified because of the complicated carbon distributions in this region (Fig. 7). On the right-hand side of Fig. 7, P21 and P31 are at the same latitude. Farther to the west, however, P31 is approximately 10° closer to the equator than P21 (see Fig. 1). There is a strong north–south TAlk gradient in the intermediate and deep waters in the region, which results in the different longitudinal trends between P21 and P31. The best technique for determining the P31 adjustment, therefore, is the least squares crossover analyses. Both models indicate that P31 should be lowered by $6\,\mu\text{mol}\,\text{kg}^{-1}$.

The recommended set of TAlk adjustments is summarized in Table 7. We also note that there are very few measured TAlk values for P16S17S relative to the number of stations sampled for DIC and $f\text{CO}_2$. The TAlk samples from P16S17S were analyzed in the laboratory at Woods Hole Oceanographic Institution (WHOI) after the cruise. Samples were also collected on P16S17S for analyses at SIO, but none of the samples were from the same bottles collected for analysis at WHOI. Measured TAlk values were not available at the crossover locations either to confirm the accuracy of these numbers. Furthermore, the data were observed to be noisy based on nested profiles. The TAlk values calculated from DIC and $f\text{CO}_2$ are much less noisy and agree with measured values from intersecting cruises at the crossovers. Given the relatively low number of measurements, our inability to confirm the accuracy, and the scatter in the data, we recommend calculating TAlk from the DIC and $f\text{CO}_2$ values for this leg. The shore based TAlk samples collected during the 1999 P1 cruise at crossovers P13, P14N and P15N and analyzed at the University of Miami generally show excellent agreement. We recommend no adjustment for TAlk for any of these cruises.

5.3. $f\text{CO}_2$

The $f\text{CO}_2$ crossover analysis results have indicated that the NDIR based measurements of Wanninkhof and Thoning (1993) underestimate the actual $f\text{CO}_2$ at values $>700\,\mu\text{atm}$. The exact nature of this error, however, is not sufficiently characterized to recommend a correction at this time. A further complicating factor is the apparent discrepancy between the measured $f\text{CO}_2$ values and the values calculated from DIC and TAlk (Lee et al., 2000). Until these issues can be resolved, DIC or TAlk values calculated from $f\text{CO}_2$ measurements in intermediate to deep waters may be up to $5\,\mu\text{mol}\,\text{kg}^{-1}$ low. Given the limited number of crossovers available for comparison, the problems associated with comparing samples measured at 20°C with samples measured at 4°C, and the apparent problems with the dissociation constants, no adjustments to the $f\text{CO}_2$ data are proposed at this time.

5.4. pH

The limited number of crossovers available for this study suggests that the spectrophotometric pH measurements were very precise and consistent between cruises. DelValls and Dickson (1998)

Table 8
Summary of the results of the crossover comparisons for DIC, TAlk, fCO_2 and pH during the Pacific Ocean Survey modeled as a second-order polynomial function (Del Poly) to 3000 dbar ($\sigma 3$)

Cross-over #	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
6	30N	135E	P9	21	P2	19,21	1.6	2.4	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
10	30N	148E	P10	74,77	P2	37	−2.8	1.0	16.9	9.7	ND[a]	ND[a]	ND[a]	ND[a]
18	63S	140E	SR3S4/1	33	SR3S4/2	65	−0.9	0.5	4.1	2.2	ND[a]	ND[a]	ND[a]	ND[a]
20	66S	164E	SR3S4	51	S4P	791	1.4	2.9	1.2b	1.1	ND[a]	ND[a]	ND[a]	ND[a]
21	47N	165E	P13	24	P1	42	−2.0	0.7	4.0	2.1	ND[a]	ND[a]	ND[a]	ND[a]
23	30N	165E	P13	54,55	P2	48,49	−5.5	2.1	12.9	1.2	ND[a]	ND[a]	ND[a]	ND[a]
27	47N	179E	P14N	31	P1	60	0.2	2.6	5.2	1.5	ND[a]	ND[a]	ND[a]	ND[a]
28	30N	178E	P14N	63	P2	58	0.5	2.7	8.4	2.4	ND[a]	ND[a]	ND[a]	ND[a]
33	31S	177E	P6	188	P6	191	−1.2	0.6	ND[a]	ND[a]	ND[a]	ND[a]	NDa	ND[a]
34	66S	171E	P14S15S	32	S4P	783,787,789	−0.4	0.2	5.6[b]	1.6	3.4	2.2	NDa	ND[a]
35	47N	165W	P15N	18	P1	X15	−5.3	2.8	2.3	3.7	ND[a]	ND[a]	NDa	ND[a]
36	30N	165W	P15N	52,54	P2	65	−5.7	4.0	14.8	6.7	ND[a]	ND[a]	NDa	ND[a]
40a	0	170W	P14S15S	174	EQS92	56	2.8	2.3	−1.7	3.9	22.0	4.8	−0.0036	0.001
40b	0	170W	P14S15S	174	P15N	112	1.2	0.7	11.0	3.2	ND[a]	ND[a]	ND[a]	ND[a]
40c	0	170W	P15N	112	EQS92	56	1.5	2.0	−14.6	4.9	ND[a]	ND[a]	ND[a]	ND[a]
40d	1S	170W	P14S15S	173	P15N	114	3.5	2.9	6.3	2.4	ND[a]	ND[a]	ND[a]	ND[a]
40e	2S	170W	P14S15S	172	P15N	116	10.6	2.0	4.8	3.5	ND[a]	ND[a]	ND[a]	ND[a]
40f	3S	170W	P14S15S	171	P15N	118	4.8	4.0	4.5	5.6	ND[a]	ND[a]	ND[a]	ND[a]
40h	4S	170W	P14S15S	170	P15N	120	3.5	0.9	1.0	3.2	ND[a]	ND[a]	ND[a]	ND[a]
40i	5S	170W	P14S15S	169	EQS92	63	−2.6	1.2	5.9	2.0	35.0	3.3	−0.006	0.001
40j	5S	170W	P14S15S	169	P15N	122	6.3	1.3	4.1	2.7	ND[a]	ND[a]	ND[a]	ND[a]
40k	5S	170W	P15N	122	EQS92	63	−8.6	2.3	6.6	1.9	ND[a]	ND[a]	ND[a]	ND[a]
40l	6S	170W	P14S15S	167	P15N	124	0.0	0.8	2.6	4.6	ND[a]	ND[a]	ND[a]	ND[a]
40m	7S	170W	P14S15S	165	P15N	126	2.8	0.7	1.9	1.4	ND[a]	ND[a]	ND[a]	ND[a]
40n	8S	170W	P14S15S	163	P15N	128	2.5	2.3	2.2	0.6	ND[a]	ND[a]	ND[a]	ND[a]
40o	12S	170W	P14S15S	155	P15N	134,136	1.4	1.1	2.8	1.0	ND[a]	ND[a]	ND[a]	ND[a]
41a	10S	170W	P14S15S	157,159,161	P15N	130,132	0.9	0.7	2.4	1.8	ND[a]	ND[a]	ND[a]	ND[a]
41b	10S	170W	P14S15S	157,159,161	EQS92	66	−1.5	3.0	0.2	3.8	29.2	2.9	−0.0018	0.001
41c	10S	170W	P14S15S	157,159,161	P31	54,57,61	−2.6	2.2	−0.5	3.5	ND[a]	ND[a]	−0.0049	0.001
41d	10S	170W	P15N	130,132	EQS92	66	−2.4	2.2	−0.7	2.7	ND[a]	ND[a]	ND[a]	ND[a]
41e	10S	170W	EQS92	66	P31	54,57,61	−0.8	5.8	−7.3	2.3	ND[a]	ND[a]	ND[a]	ND[a]
41f	10S	170W	P15N	130,132	P31	54,57,61	−3.2	3.6	−3.2	0.9	ND[a]	ND[a]	ND[a]	ND[a]
42	17S	170W	P14S15S	141,142,144	P21	193,195,197	−2.3	0.4	0.3	0.4	3.4	2.2	ND[a]	ND[a]
43	32S	170W	P14S15S	110,112,114	P6	153,165	−1.4	2.1	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
44	40S	173W	P14S15S/1	93	P14S15S/2	94	1.5	4.7	−0.4	5.0	−1.0	5.4	NDa	NDa
45	67S	169W	P14S15S	33	S4P	755	5.2	0.9	7.0b	1.0	−12.0	3.5	ND[a]	ND[a]
47	53N	152W	P16N	58,59,66	P17N	78	−9.0	5.1	−23.6[b]	5.8	ND[a]	ND[a]	ND[a]	ND[a]
48	47N	152W	P16N	55	P1	X16	−8.3	0.6	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
49	30N	152W	P16N	30,31,32	P2	70	−7.6	3.0	3.2[b]	0.2	ND[a]	ND[a]	ND[a]	ND[a]
53a	17S	150W	P16C	222	P16S17S	220	−1.1	1.5	−0.6[b]	3.3	ND[a]	ND[a]	ND[a]	ND[a]
53b	17S	150W	P16C	222	P31	2,5	0.6	0.8	−3.5	0.9	ND[a]	ND[a]	ND[a]	ND[a]
53c	17S	150W	P16C	222	P21	157,160	−1.4	1.4	−0.4	2.2	ND[a]	ND[a]	ND[a]	ND[a]

53d	17S	150W	P16S17S	220	P31	2,5	0.9	0.5	−6.5[b]	1.1	ND[a]	ND[a]	ND[a]	ND[a]
53e	17S	150W	P16S17S	220	P21	157,160	−0.8	1.0	7.1[b]	0.9	ND[a]	ND[a]	ND[a]	ND[a]
53f	17S	150W	P21	157,160	P31	2,5	2.7	3.3	−5.8	3.5	ND[a]	ND[a]	ND[a]	ND[a]
54	32S	150W	P16S17S	190	P6	127,129	5.9	4.7	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
55	37S	150W	P16S17S	180	P16A17A	3	0.1	2.4	ND[a]	ND[a]	−5.3	0.9	ND[a]	ND[a]
59	40N	135W	CGC91	10	P17N	37,38,45	−7.9	1.5	ND[a]	ND[a]	ND[a]	NDa	ND[a]	ND[a]
60a	35N	135W	CGC91	12	P17N	28	−3.7	5.1	ND[a]	ND[a]	29.2	2.9	ND[a]	ND[a]
60b	35N	135W	CGC91	12	P17C	17	5.7	3.7	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
60c	35N	135W	P17N	28	P17C	17	9.4	3.4	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
61	30N	135W	P17C	26	P2	78	−3.1	4.6	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
64	6S	135W	P17C	121	P16S17S	124	−1.0	2.5	0.8[b]	1.5	ND[a]	ND[a]	ND[a]	ND[a]
65	16S	133W	P16S17S	148	P21	131	−0.5	1.7	−20.5[b]	1.7	ND[a]	ND[a]	ND[a]	ND[a]
66a	33S	135W	P16S17S	179	P6	108	c	1.0	ND[a]	ND[a]	23.1	25.3	ND[a]	ND[a]
66b	33S	135W	P16S17S	179	P16A17A	119	2.8	2.2	ND[a]	ND[a]	1.0	3.8	ND[a]	ND[a]
66c	33S	135W	P16A17A	119	P6	108	−2.3	0.7	ND[a]	ND[a]	23.3	26.4	ND[a]	ND[a]
67	53S	135W	P16A17A	77	P17E19S	128	−4.4	2.9	ND[a]	ND[a]	−2.4	4.3	ND[a]	ND[a]
68	66S	126W	P17E19S	163	S4P	723,727	−1.1	1.5	ND[a]	ND[a]	−2.5	0.3	ND[a]	ND[a]
73	5N	110W	P18	155,159	EQS92	6	−7.5	4.9	−0.4	1.0	3.4	2.2	ND[a]	ND[a]
74	17S	103W	P18	105,106	P21	77	−2.7	1.5	−0.5	2.8	ND[a]	ND[a]	ND[a]	ND[a]
76	32S	103W	P18	73	P6	56,58	−0.5	0.4	ND[a]	ND[a]	−23.6	13.8	ND[a]	ND[a]
77	52S	103W	P18	37	P17E19S	194	3.4	0.8	4.5[b]	1.8	21.2	0.4	ND[a]	ND[a]
78	67S	103W	P18	10,11	S4P	711,712,713	−1.2	0.4	1.0	1.3	7.6	0.5	ND[a]	ND[a]
80	16S	86W	P19	333	P21	49	−3.1	0.9	−2.9[b]	1.6	ND[a]	ND[a]	ND[a]	ND[a]
81	32S	88W	P19	299	P6	32,34,36	−0.5	0.1	ND[a]	ND[a]	3.6	3.9	ND[a]	ND[a]
82	53S	88W	P19	256	P17E19S	206	1.8	0.9	ND[a]	ND[a]	13.6	3.8	ND[a]	ND[a]
83	67S	88W	S4P	703	P17E19S	229	−0.9	1.5	ND[a]	ND[a]	−15	3.8	ND[a]	ND[a]
						Average absolute value	**3.0**		**4.7**		**13.4**		**0.0041**	
						Std dev	**2.6**		**4.9**		**11.1**		**0.0018**	

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[a] ND = no data.

[b] Crossovers on which TAlk were calculated using a combination of DIC and either pH or $f\mathrm{CO}_2$.

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. An upward adjustment in the reported pH_T values is further supported by internal consistency evaluations by McElligott et al. (1998), Lee et al. (2000), and as a part of this study. Laboratory experiments are still necessary to better constrain the exact magnitude of this adjustment, however, we recommend adjusting all spectrophotometric pH values upward by 0.0047 pH units.

6. Conclusions

Table 7 summarizes our final recommended adjustments for the DIC, TAlk and pH data from the Pacific CO_2 survey cruises. As noted earlier, all DIC and TAlk data that were reported without normalization to the CRM values were normalized, if possible, for this study. Given the long timeframe over which the 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 Pacific data set, and together have proven to be an invaluable tool for determining any necessary adjustments.

With the adjustments proposed here, the examined cruises can be combined to generate a Pacific Ocean data set with over 36,000 unique sample locations analyzed for at least two carbon parameters with the exception of P9 and CGC91. The best data coverage is for DIC, which has an accuracy that is approximately an order of magnitude better than Pacific GEOSECS (Takahashi et al., 1982). 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 measurements were made. Our hope is that the unified data set, which is consistent between cruises, will be a resource to the community for future carbon studies. As noted in Section 2.1.1 and Table 2, some laboratories did not normalize their DIC data to the CRMs. We are assembling the data sets, and they will include the CRM corrections. We will make all of our results public through the Carbon Dioxide Information Analysis Center (CDIAC) as soon as possible.

7. Remote access to data listed in report

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 web site at: http://cdiac.esd.ornl.gov/oceans/glodap. Many of the data presented in this paper are currently available on the World Wide Web (WWW) by contacting:

CDIAC/ORNL at: http://cdiac.esd.ornl.gov/oceans/home.html

WOCE Hydrographic Programme Office at: http://whpo.ucsd.edu/data/ or the Japanese Oceanographic Data Center at: http://www.jodc.jhd.go.jp/jodc.html.

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Appendix A

A summary of Crossover analysis during the Global CO_2 Survey in the Pacific is provided in Table 8.

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