



## Direct observations of basin-wide acidification of the North Pacific Ocean

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[1] Global ocean acidification is a prominent, inexorable change associated with rising levels of atmospheric CO<sub>2</sub>. Here we present the first basin-wide direct observations of recently declining pH, along with estimates of anthropogenic and non-anthropogenic contributions to that signal. Along 152°W in the North Pacific Ocean (22–56°N), pH changes between 1991 and 2006 were essentially zero below about 800 m depth. However, in the upper 500 m, significant pH changes, as large as –0.06, were observed. Anthropogenic and non-anthropogenic contributions over the upper 800 m are estimated to be of similar magnitude. In the surface mixed layer (depths to ~100 m), the extent of pH change is consistent with that expected under conditions of seawater/atmosphere equilibration, with an average rate of change of –0.0017/yr. Future mixed layer changes can be expected to closely mirror changes in atmospheric CO<sub>2</sub>, with surface seawater pH continuing to fall as atmospheric CO<sub>2</sub> rises. **Citation:** Byrne, R. H., S. Mecking, R. A. Feely, and X. Liu (2010), Direct observations of basin-wide acidification of the North Pacific Ocean, *Geophys. Res. Lett.*, 37, L02601, doi:10.1029/2009GL040999.

### 1. Introduction

[2] On time scales of several centuries, dominant controls on seawater pH include atmospheric CO<sub>2</sub> exchange and the oxidation of dissolved and particulate organic matter in the water column. Since preindustrial times, the partial pressure of CO<sub>2</sub> in the atmosphere has increased from approximately 280 to 387 ppm (P. Tans, Changes in atmospheric carbon dioxide—Mauna Loa, Earth System Research Laboratory, NOAA, 2009, available at [www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)). For seawater in equilibrium with the atmosphere, the resulting CO<sub>2</sub> influx translates into a decrease of surface ocean pH by approximately 0.11 pH units. (Surface pH of modern North Pacific seawater, measured at 25°C, is typically 7.6–8.0; Figure 1.) For a CO<sub>2</sub> level of 800 ppm, the pH of equilibrated surface seawater would decrease by at least an additional 0.29 units.

[3] Oxidation of organic matter, which is mediated by microorganisms, also lowers seawater pH by adding CO<sub>2</sub> into solution [Millero, 2007], and low pH values are generally found near the subsurface oxygen minimum layer. In North

Pacific waters (Figure 1), pH values near the O<sub>2</sub> minimum may be as low as 7.25 in the subarctic (~200 m depth) and 7.3 in the subtropics (~1000 m depth).

[4] Recent changes in seawater pH induced by ocean–atmosphere gas exchange are thought to be substantial, with far-reaching chemical and ecological effects [Doney *et al.*, 2009], yet direct observations are sparse. Here we present the first direct measurements of basin-wide pH change at depth and at the ocean’s surface, using data from two North Pacific hydrographic lines along 152°W, occupied in March 1991 and 2006. The 15-year pH differences are mapped and deconvolved into spatially explicit anthropogenic and non-anthropogenic components, and are discussed in the context of North Pacific circulation, thermodynamic predictions, and likely future evolution.

### 2. Data and Methods

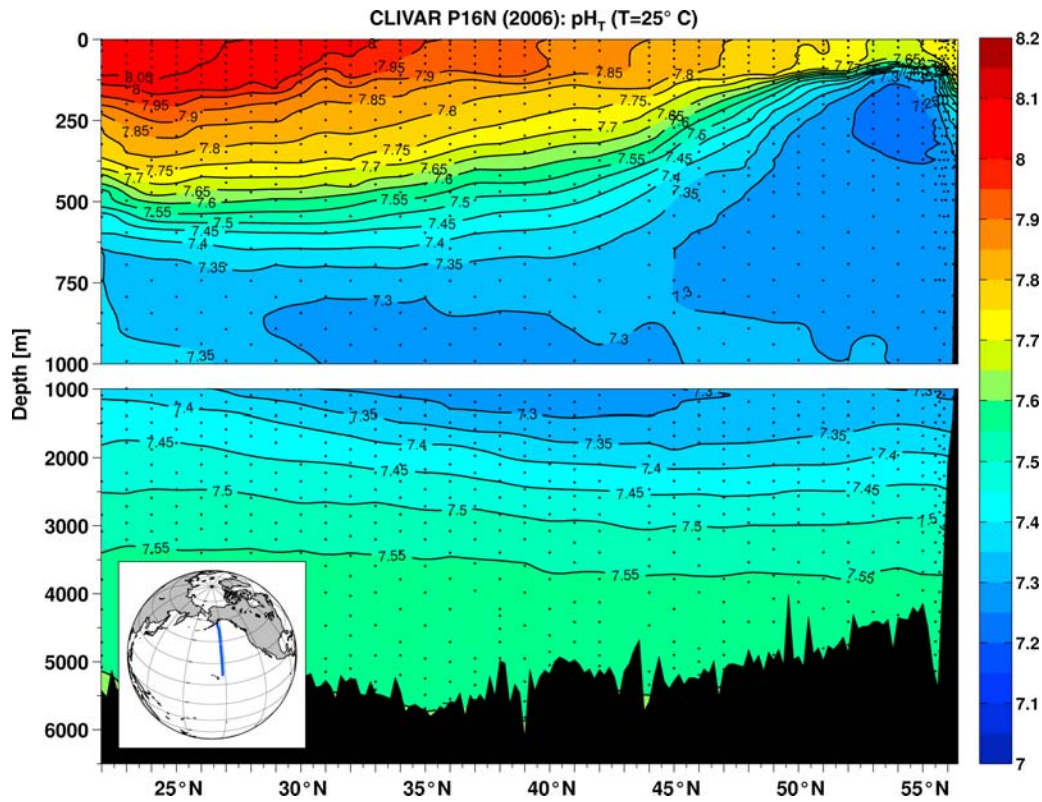
[5] Precise spectrophotometric procedures for seawater pH measurement were developed between 1985 and 1993 [Robert-Baldo *et al.*, 1985; Clayton and Byrne, 1993], and the first successful application on an ocean expedition occurred in March 1991 (WOCE P16N; 750 pH samples) along a cruise transect between Oahu, Hawaii, and Kodiak, Alaska (Figure 1). This transect was reoccupied in March 2006 (CLIVAR/CO<sub>2</sub> Repeat Hydrography Program P16N; 1356 pH samples). Both datasets, obtained at 25°C and reported on the total hydrogen ion concentration scale (pH<sub>T</sub> = –log[H<sup>+</sup>]<sub>T</sub>), are available from the CLIVAR & Carbon Hydrographic Data Office (CCHDO, <http://cchdo.ucsd.edu/pacific.html>). The spectrophotometric method [Clayton and Byrne, 1993] relies on molecular properties of the pH indicator meta-cresol purple. A small amount of dye ([mCP] ~ 3 μM) was added to each sample, and absorbance was measured at 434 and 578 nm and at a non-absorbing wavelength, against a reference solution of pure seawater. Directly measured pH, pH<sub>m</sub>, was then calculated from absorbance ratios. These data were collected before the practice of purifying indicators was adopted, so a correction for mCP impurities was applied to the 2006 pH data: 0.001 units at pH 7.4, increasing to 0.005 at pH 8.1 [Yao *et al.*, 2007]. Measurement precision on both transects was on the order of ±0.001 (somewhat smaller than the annual pH change expected for seawater in equilibrium with the atmosphere).

[6] Dissolved inorganic carbon (DIC) and other shipboard data were also obtained from CCHDO. Total alkalinity (TA) data were available for the 2006 cruise only, so for consistency TA<sub>2006</sub> and TA<sub>1991</sub> were calculated using DIC<sub>m</sub>, pH<sub>m</sub>, and the Mehrbach *et al.* [1973] dissociation constants as refit by Dickson and Millero [1987]. A correction of +4 μmol kg<sup>–1</sup> was applied to the 1991 DIC data [Lamb *et al.*, 2001].

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**Figure 1.** North Pacific Ocean pH along 152°W in 2006 ( $\text{pH}_T$ , 25°C).

[7] Changes in pH between 1991 and 2006,  $\Delta\text{pH}_m$ , were calculated using objective mapping techniques [Roemmich, 1983] on latitude-versus-potential-density sections. Average isopycnal depths were then used to project the results onto depth space (Figure 2) [Mecking *et al.*, 2008]. A negative  $\Delta\text{pH}_m$  indicates that lower pH was encountered in 2006 than in 1991.

[8] To deconvolve  $\Delta\text{pH}_m$  into components associated with anthropogenic change (*ant*) and natural background variability (*var*), we first estimated  $\Delta\text{DIC}_{\text{ant}}$  and  $\Delta\text{DIC}_{\text{var}}$  using the  $\Delta\text{C}^*$  method of isolating anthropogenic DIC from measured DIC [Gruber *et al.*, 1996; Sabine and Feely, 2001]. For temporal differences ( $\Delta X = X_{2006} - X_{1991}$ ) at a given point:

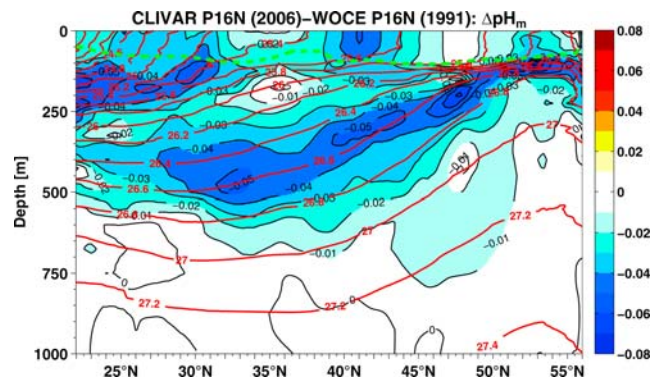
$$\begin{aligned}\Delta\text{DIC}_{\text{ant}} &= \Delta\text{DIC}_m - \Delta\text{DIC}_{\text{var}} \\ &= \Delta\text{DIC}_m - \Delta\text{DIC}_{\text{bio}} - \Delta\text{DIC}_{\text{eq},280} - \Delta\text{DIC}_{\text{diseq}}.\end{aligned}$$

Here we assumed that the air-sea disequilibrium,  $\text{DIC}_{\text{diseq}}$ , did not change significantly; i.e.,  $\Delta\text{DIC}_{\text{diseq}} = 0$ . The seawater DIC equilibrium concentration for preindustrial atmospheric  $\text{pCO}_2$ ,  $\Delta\text{DIC}_{\text{eq},280}$ , was calculated using a temperature- and salinity-dependent  $\text{CO}_2$  solubility function [Weiss, 1974]. The term  $\Delta\text{DIC}_{\text{bio}}$ , which represents the effects of organic matter remineralization and  $\text{CaCO}_3$  dissolution and is the largest component of  $\Delta\text{DIC}_{\text{var}}$ , was estimated from apparent oxygen utilization (AOU) and the difference between measured ( $\text{TA}_m$ ) and preformed ( $\text{TA}_0$ ) alkalinity [Sabine and Feely, 2001]:

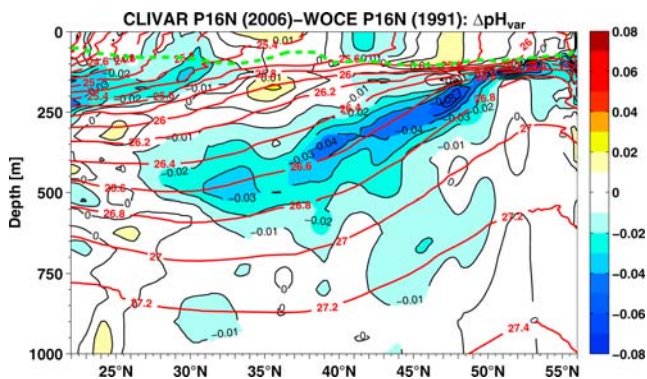
$$\begin{aligned}\Delta\text{DIC}_{\text{bio}} &= r_{\text{C:O}_2} \times \Delta\text{AOU} + 0.5 \\ &\quad \cdot (\Delta\text{TA}_m - \Delta\text{TA}_0 + r_{\text{N:O}_2} \times \Delta\text{AOU}).\end{aligned}$$

We used modified Redfield values of  $r_{\text{C:O}_2} = 117/170$  and  $r_{\text{N:O}_2} = 16/170$  [Anderson and Sarmiento, 1994] and an empirical multi-linear regression (MLR) fit to determine  $\text{TA}_0$  [Sabine *et al.*, 2002]. The difference between  $\Delta\text{TA}_m$  and  $\Delta\text{TA}_0$  is negligibly small, whereas the  $r_{\text{C:O}_2} \times \Delta\text{AOU}$  term provides the largest contribution to  $\Delta\text{DIC}_{\text{bio}}$  and hence  $\Delta\text{DIC}_{\text{var}}$ .

[9] Finally, *ant* and *var* pH components were calculated using the carbonate system equations [Zeebe and Wolf-Gladrow, 2001], shipboard salinities,  $S$ , and DIC (*ant* and *var*) and  $\text{TA}$ . To estimate the background-variability com-



**Figure 2.**  $\Delta\text{pH}_m$ , the change in seawater pH between 1991 and 2006:  $\text{pH}_{2006} - \text{pH}_{1991}$ . Red contours show isopycnal surfaces. The dashed green line marks the estimated 152°W late-winter mixed layer depth (Levitus 1998 climatology [Antonov *et al.*, 1998; Boyer *et al.*, 1998]) and is roughly equivalent to the average mixed layer depth between the two March cruises.



**Figure 3.**  $\Delta\text{pH}_{\text{var}}$ : pH change attributed to natural interdecadal/interannual DIC variability between 1991 and 2006. Details follow Figure 2.

ponent of pH change,  $\Delta\text{pH}_{\text{var}}$ , we first calculated what DIC would have been in 2006 had there been no anthropogenic change over the preceding 15 years:  $\text{DIC}_{\text{var},2006} = \text{DIC}_{1991} + \Delta\text{DIC}_{\text{var}}$ . The carbonate system equations with  $\text{DIC}_{\text{var},2006}$ ,  $\text{TA}_{2006}$ , and  $\text{S}_{2006}$  then yielded  $\text{pH}_{\text{var},2006}$ , from which  $\Delta\text{pH}_{\text{var}}$  and  $\Delta\text{pH}_{\text{ant}}$  could be estimated:  $\Delta\text{pH}_{\text{var}} = \text{pH}_{\text{var},2006} - \text{pH}_{1991}$  (Figure 3) and  $\Delta\text{pH}_{\text{ant}} = \Delta\text{pH}_{\text{m}} - \Delta\text{pH}_{\text{var}}$  (Figure 4).

[10] Because of nonlinearities in the pH equations, order of calculation influences the resulting  $\Delta\text{pH}_{\text{var}}$  and  $\Delta\text{pH}_{\text{ant}}$  fields. For comparison, we estimated the  $\Delta\text{pH}$  components by first examining the effects of  $\Delta\text{DIC}_{\text{var}}$  alone (as above) and then of  $\Delta\text{DIC}_{\text{ant}}$  alone (using  $\text{S}_{1991}$  and  $\text{TA}_{1991}$ ) as well as by starting off with DIC from the later cruise ( $\text{DIC}_{2006}$ ) and going backward in time. The difference in section averages of  $\Delta\text{pH}_{\text{var}}$  and  $\Delta\text{pH}_{\text{ant}}$  calculated these four different ways amounts to <3%. A larger source of error for the estimation of section averages is uncertainty in the stoichiometric ratios used to estimate  $\Delta\text{DIC}_{\text{bio}}$  – especially the  $\text{O}_2:\text{C}$  ratio, which has an estimated uncertainty of  $\pm 0.15$  [Anderson and Sarmiento, 1994] and is used to report our uncertainty estimates (section 3).

[11] All data and results are reported at  $25^\circ\text{C}$ , to isolate the effects of altered solution chemistry from the effects of temperature change. (A decrease of in situ pH, in contrast to constant-temperature pH, could be caused by a temperature increase with no change in DIC.)

### 3. Results and Discussion

[12] In 2006 (Figure 1), large-scale patterns in seawater pH along P16N were similar to those seen in 1991. High surface values somewhat greater than 8.05 were encountered in the south, with values decreasing northward, falling to near 7.7 poleward of  $50^\circ\text{N}$ . Lower temperature allows greater  $\text{CO}_2$  uptake, resulting in lower pH. At depth, a pH minimum zone with  $\text{pH} < 7.3$  was seen between approximately  $29^\circ$  and  $56^\circ\text{N}$ . This feature, generally coincident with the  $\text{O}_2$ -minimum zone, is largely attributable to  $\text{CO}_2$  production from organic matter oxidation.

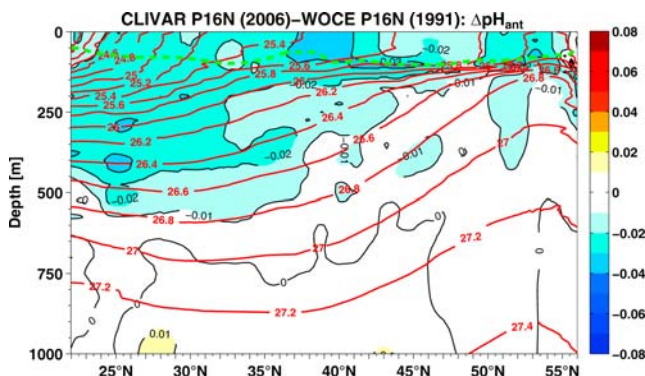
[13] The 15-year pH difference ( $\Delta\text{pH}_{\text{m}} = \text{pH}_{2006} - \text{pH}_{1991} = -\log([\text{H}^+]_{2006}/[\text{H}^+]_{1991})$ ) shows declining pH or no change over the entire transect (Figure 2). No significant positive differences are seen in any part of the water column. From the surface to  $\sim 800$  m,  $\Delta\text{pH}_{\text{m}}$  values generally range from 0 ( $[\text{H}^+]_{2006}/[\text{H}^+]_{1991} = 1.00$ ) to

$-0.06$  ( $[\text{H}^+]_{2006}/[\text{H}^+]_{1991} = 1.15$ ). The average difference over  $22^\circ$  to  $56^\circ\text{N}$  and 0 to 800 m depth is  $-0.023$ . Between the surface and 150 m, slightly below the depth of the winter mixed layer, it is  $-0.030$ . No significant pH differences are observed in deep waters, between 800 m and bottom depths as great as 6000 m. Very low rates of deepwater pH change have been similarly observed at Station ALOHA (1992–2007), near our transect’s southern terminus [Dore et al., 2009].

[14] The  $\Delta\text{DIC}_{\text{var}}$  and  $\Delta\text{DIC}_{\text{ant}}$  fields (not shown) agree well with an independent (MLR) estimate of  $152^\circ\text{W}$  anthropogenic and AOU-based DIC changes [Sabine et al., 2008]. The derived  $\Delta\text{pH}_{\text{var}}$  field (Figure 3) indicates that a significant fraction of  $\Delta\text{pH}_{\text{m}}$  is attributable to changes in the spatial distribution of AOU and therefore of DIC produced by respiration and remineralization of organic matter. In the upper 1000 m, both positive and negative  $\Delta\text{pH}_{\text{var}}$  are seen. Values as large as  $-0.04$  to  $-0.06$  correspond to a  $\Delta\text{AOU}$  maximum of  $+20$  to  $25 \mu\text{mol}/\text{kg}$  seen south of  $50^\circ\text{N}$  between 200 and 400 m depth [Mecking et al., 2008, Figure 2]. A second region of large negative  $\Delta\text{pH}_{\text{var}}$  is seen between  $22^\circ$  and  $32^\circ\text{N}$  for depths shallower than 250 m, again coincident with an area of positive  $\Delta\text{AOU}$ .

[15] Most of the recent North Pacific  $\Delta\text{AOU}$  signal has been attributed to changes in physical processes such as a slow-down in ventilation [Deutsch et al., 2006]. A slower rate of transfer of water from the surface ocean to the interior increases, for a given isopycnal, the age of the water since it left the surface – i.e., the amount of time that respiration processes have been in effect, increasing AOU and DIC and decreasing pH. The recent  $\Delta\text{AOU}$  signal has been most prominent on  $\sigma_\theta = 26.6 \text{ kg m}^{-3}$  [Mecking et al., 2006, 2008]; as a result, the largest  $\Delta\text{pH}_{\text{var}}$  signal also occurs on or near this isopycnal (Figure 3). Average  $\Delta\text{pH}_{\text{var}}$  between 800 m and the mixed layer is  $-0.012$  ( $\pm 0.001$ ), which amounts to 52% ( $\pm 10\%$ ) of the total pH change in this depth range (assuming 95% confidence limits).

[16] The component of pH change associated with penetration of anthropogenic  $\text{CO}_2$  into the upper ocean ( $\Delta\text{pH}_{\text{ant}}$ , Figure 4) is given by the difference between total pH change (Figure 2) and the pH change attributable to variations in respiration and ocean ventilation (Figure 3). Evidence of anthropogenic influence is seen to depths of 150 m along the entire section. In this zone,  $\Delta\text{pH}_{\text{ant}}$  varies



**Figure 4.**  $\Delta\text{pH}_{\text{ant}}$ : pH change attributed to the uptake of anthropogenic carbon between 1991 and 2006. Details follow Figure 2.



between  $-0.01$  and  $-0.03$  with a mean value of  $-0.023$  ( $\pm 0.001$ ). Between  $22^\circ$  and  $38^\circ\text{N}$ , anthropogenic acidification extends to more than 500 m and the  $-0.02$  contour extends to more than 400 m.

[17] The lack of substantial anthropogenic acidification between 150 and 500 m at latitudes north of  $38^\circ\text{N}$  (Figure 4) — where, in contrast, largest  $\Delta\text{AOU}$  and  $\Delta\text{pH}_{\text{var}}$  occur (Figure 3) — could be due to the postulated ventilation slow-down [Deutsch et al., 2006]. A complete cessation of ventilation of this area due to periodic changes in the maximum surface density in the northern North Pacific may have occurred throughout the 1990s [Mecking et al., 2006, 2008], perhaps resulting in only slight anthropogenic C uptake. Nevertheless, the section-wide ( $22^\circ$ – $56^\circ\text{N}$ ) average of  $\Delta\text{pH}_{\text{ant}}$  between 800 m and the mixed layer amounts to  $-0.011$  ( $\pm 0.001$ ). This change corresponds to 48% ( $\pm 10\%$ ) of the total pH change.

[18] On multidecadal time scales, pH changes attributable to anthropogenic  $\text{CO}_2$  can be expected to eventually dominate the signal.  $\text{CO}_2$  produced by respiration in the subsurface ocean (diagnosed from  $\text{O}_2$  measurements) can be expected to show positive and negative variations [Deutsch et al., 2006; Whitney et al., 2007; Mecking et al., 2008]. In contrast, anthropogenic  $\text{CO}_2$  in seawater should steadily increase as atmospheric levels continue to rise. By the end of this century, distinctions between total pH change (Figure 2) and pH change attributable to anthropogenic  $\text{CO}_2$  (Figure 4) will become increasingly subtle.

[19] One outcome of the observed widespread pH declines (Figures 2 and 4) is an increasingly inhospitable environment for calcifying marine plankton, such as pteropods, forams, and coccolithophorids. Decreasing pH translates directly to decreasing carbonate saturation states. The physiological status of these pelagic calcifying organisms currently abundant in the North Pacific is therefore likely to be adversely impacted [Feely et al., 2004, 2008; Fabry et al., 2008]. Many other chemical, physiological, and ecological processes are affected as well (e.g., trace metal speciation, photosynthesis, nitrogen fixation), to an extent that is not well characterized [Doney et al., 2009].

[20] The observed near-surface pH changes (Figure 2) are in good agreement with predictions based on  $\text{CO}_2$  system thermodynamics, consistent with attribution of most of this change to anthropogenic acidification (Figure 4) and with observations elsewhere. Average  $\Delta\text{pH}_m$  along  $152^\circ\text{W}$  in the zone shallower than the winter mixed layer is  $-0.026$ , equivalent to an average annual pH change rate of  $-0.0017$ . For seawater fully equilibrated with the atmosphere in 1991 and 2006, a  $\Delta\text{pH}$  of approximately  $-0.025$  would be expected. A directly measured surface-water decline of  $-0.0017 \text{ y}^{-1}$  ( $\text{pH}_T$ ,  $25^\circ\text{C}$ , 1995–2004) has also been reported at a time-series station in the subtropical North Atlantic [González-Dávila et al., 2007]. Rates of change consistent with long-term air/sea equilibration have been reported for other  $\text{CO}_2$  system parameters in the North Pacific [Takahashi et al., 2006; Dore et al., 2009] and North Atlantic [Bates, 2007; González-Dávila et al., 2007].

#### 4. Conclusions

[21] The P16N data, which quantitatively characterize changes in directly measured pH over  $34^\circ$  of latitude,

6000 m of depth, and 15 years of time, confirm on a large scale what has been observed at three time-series points in the north Atlantic and Pacific — significant upper ocean acidification, roughly keeping pace with rising atmospheric carbon dioxide. It appears that future acidification of the ocean's mixed layer can be expected to occur at rates that closely mirror changes in atmospheric  $\text{CO}_2$ , with some temporary local modulation by other processes that influence surface DIC budgets. If atmospheric  $\text{CO}_2$  continues to rise at an accelerating rate, ocean pH can be expected to fall at an accelerating rate.

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