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Measurement of pH: comparing methods across the Kuroshio Extension

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NONTECHNICAL SUMMARY

The specter of ocean acidification caused by increasing CO_2 in the atmosphere can have severe impacts on biological ecosystems in the upper ocean. Precise and accurate pH measurements are the foundation for assessing the extent of ocean acidification, and provide the motivation for this study. We present pH values along a cruise track that crosses the Kuroshio Extension region, and show that pH levels decrease as we go from south to north. We compare two different methods of acquiring pH values: measured pH with a spectrophotometer, and calculated pH from other carbonate measurements. We found that measured pH gives results with better reproducibility than calculated pH, but the question of which method is more accurate remains unanswered. We also compared calculated pH levels between this year and two previous studies to see if ocean acidification is occurring in the region. We found that pH at surface levels decreased with time supporting this, however we also have evidence that ocean acidification caused by CO_2 input may not be the only factor causing pH change in the Kuroshio Extension.

ABSTRACT

In this study, we measure pH levels in a transect of the Kuroshio Extension, a turbulent ocean region that is known for high CO_2 drawdown in late winter, and therefore a potential site for intense spatial and temporal pH changes. We provide baseline pH levels down to 2000m across the transect using the spectrophotometric procedure and find that surface pH decreases 0.37 pH units as we progressed north along the cruise track (30-41°N). We compare this method of acquiring pH with the method of calculating pH from alkalinity and dissolved inorganic carbon. Calculated pH levels have larger differences from measured pH at depths below 1000m. However, a potential calibration of 0.0142 pH units causes pH differences at depth to be smaller between methods (going from 0.01 to -0.0008 pH difference in one case). Difference of pH between methods for near surface depths are also improved when the calibration is applied, but to a lesser extent. Lastly, we compare current calculated pH to data from previous cruises (WOCE 1993 and CLIVAR 2007) to assess pH changes with time. The overall trend at both stations is a decrease in pH by up to 0.053 pH units in near surface waters with time. The extent of pH change in the five-year span between CLIVAR and the current cruise (0.044 pH units) indicates that ocean acidification may not fully explain pH changes in this dynamic region.

The problem of ocean acidification is a fairly recent one, a direct result of human activities in the industrial age. The amount of carbon dioxide that is present in our atmosphere today (~400 ppm) far exceeds values in the earth's paleoclimate record (190-280 ppm; Petit et al., 1999). This increase in carbon dioxide has dire consequences for the world's oceans, which act as

the largest sink for atmospheric CO_2. Chemical reaction of CO_2 into water adds hydrogen ions, which is measured using the pH scale. Ocean acidification is a fairly new field of study and there is presently a limited amount of research available that directly measures pH values in surface waters of the ocean. The few studies that have been published, and ocean acidification model projections, all agree that pH levels are decreasing with time.

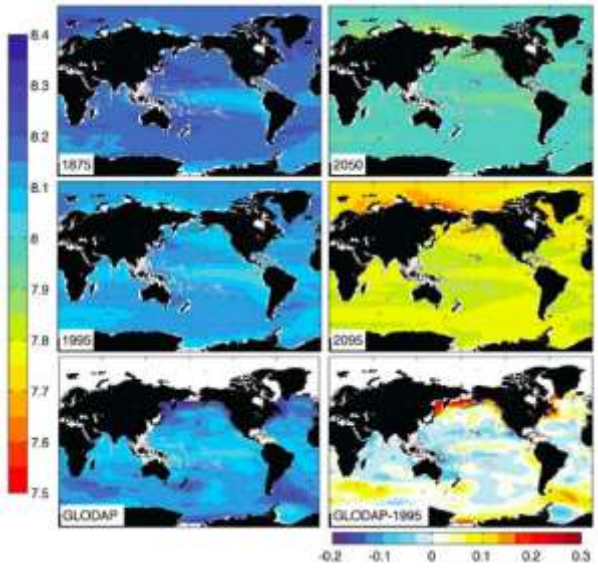

Figure 1. Top four panels are modeled decadal mean surface pH from the National Center for Atmospheric Research Community Climate System Model (CCSM) 3.1. Bottom left panel is a model from Global Ocean Data Analysis Project (GLODAP) for 1995. Bottom right panel is difference between CCSM and GLODAP models. *Feely et al., 2009*

Lower pH results in decreased concentrations of carbonate ions in the ocean. Calcium carbonate, formed from the reaction between calcium and carbonate ions, is a solid mineral utilized by certain marine organisms to build shells and exoskeletons. As atmospheric CO_2 levels rise, pH of the ocean decreases, favoring calcium carbonate dissolution instead of formation. Marine organisms dependent on calcium carbonate minerals will have an increasingly difficult time surviving in these conditions, which in turn will negatively impact the ecosystem in which they play a part (Feely et al., 2009).

Biogeochemical models provide most available data pertaining to global ocean acidification. Information is usually presented for the upper layers of the ocean where effects on marine ecosystems can be more easily observed. Fewer studies employ discrete measurements of pH throughout the water column, and primarily occur in smaller regions of interest such as coastal seas or specific transects across ocean basins. Researchers Byrne et al. measured pH down to a depth of 1000m across a vertical section of the North Pacific Ocean in 1991 and again in 2006. They discovered that pH had decreased in the upper 500 m and stayed relatively the same at lower depths during this time period.

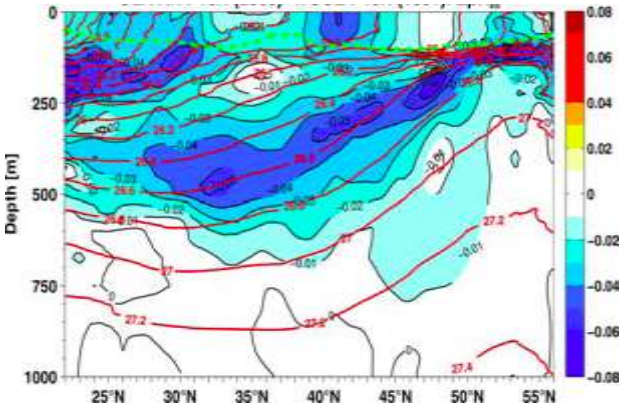

Figure 2. Change in seawater pH between 1991 and 2006 along 152°W in the North Pacific Ocean. Red lines show isopycnals. *Byrne et al., 2009.*

Accurate measurements of pH are necessary for scientists to make such time-lapse observations of change, especially in regions that are strongly affected by physical and biological conditions such as the Kuroshio Extension off the east coast of Japan. The main Kuroshio is a large, strong western boundary current in the North Pacific Ocean. Warm, less dense water is brought up from the tropics and cools rapidly off the east coast of Japan creating numerous eddies where biological activity is high (Sasai et al., 2010). The region has been shown to be one of the largest sinks for atmospheric CO_2 in the entire ocean, due to a combination of temperature effects, high biological activity facilitating carbon drawdown, and advection of low DIC waters (Ayers and Lozier, 2012). No pH values down the water column have been collected across the Kuroshio

Extension, however WOCE (World Ocean Circulation Experiment) cruises conducted by the National Oceanographic and Atmospheric Administration (NOAA) and repeat hydrography cruises by CLIVAR (Climate Variability and Predictability) have measured other carbonate parameters in the area. Seawater pH can be calculated from dissolved inorganic carbon (DIC) and total alkalinity (TA) using software such as CO2SYS (Lewis and Wallace, 1998).

The objectives of this project are: to provide baseline pH levels along the cruise track traversing the Kuroshio Extension for future studies to use as time series evaluation, compare spectrophotometric pH measurements with calculated pH from DIC and TA in order to assess accuracy of both methods and finally, compare calculated pH from current research cruise to calculated pH from previous WOCE/CLIVAR cruises at stations close to current cruise stations to determine changes in pH values over time.

METHODS

The Kuroshio Extension is defined as the area where the southward flowing Oyashia current joins with the main northward flowing Kuroshio and continues as one large current flowing eastward. We conducted our research cruise from 25 February – 17 March 2013 aboard the R/V *Melville*. Collection of pH samples began at the Kuroshio Extension Observatory (KEO), continued along the south to north transect across the extension, and along the return transect from north to south. We deployed Conductivity Temperature Depth (CTD) casts at 22 stations, eleven of which were used for pH measurements.

The CTD (SBE 911plus, Sea-Bird Electronics, Inc., Bellevue, WA) was equipped with a rosette of 24 Niskin bottles tripped at different water depths. Due to a limited number of sampling cells, water samples were taken from every second or third Niskin bottle per station. CTD casts were deployed down to 2000 m at most stations, five of the 22 stations were deep casts ~6000m (stations 4, 8, 13, 16, 22). In order to check reproducibility, during the first transect of the cruise (south to north), samples from the same water depth were drawn twice (two sampling cells per Niskin bottle). Each cell was sampled an average of three times; therefore most samples from the same water depth during the first transect of the cruise have approximately six replicates. Most samples from the second transect (return trip) have three replicates. Standard deviations and variances were calculated from all replicates of each sample.

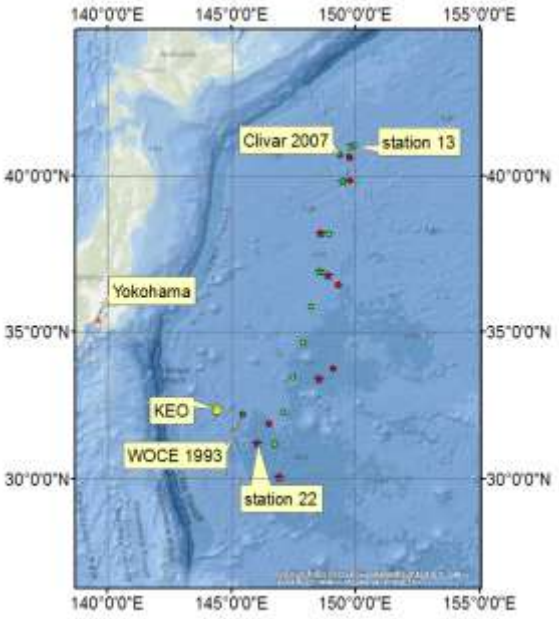

Figure 3. Map of Kuroshio Extension region with stations and KEO mooring which is considered station 2**.** Green color denotes northbound leg, red color is return leg heading southbound. Stars are stations where pH was measured with spectrophotometer and standard deviations of CRMs are below 0.002 pH units. Stations 13 and 22 are marked as well as CLIVAR repeat hydrography cruise P01 station 23, and WOCE cruise P10 station 80.

The development of spectrophotometric techniques offers a different approach from the usual methods of measuring pH such as Harned cells and combination glass electrodes (Marion et al., 2011). Marine chemists recommend the indicator dye *m*-cresol purple (*m*CP) for use in this technique for pH measurements from surface to deep in the open ocean (Clayton and Byrne, 1993). Price and availability of such instruments must be considered when going out to sea for research. Expensive equipment such as spectrophotometers and the accompanied indicator dyes may not be readily available or even an affordable option. One must consider the advantages of calculating pH

from other measured carbonate parameters in terms of monetary costs and labor. The spectrophotometric method while proven to be very precise (Byrne et al., 1999), requires analyzing samples on ship at a rate that ensures enough cells will be available for the next station/cast. Analysis time on ship can be lengthy if there is not enough assistance to run samples.

We borrowed a spectrophotometer (model 8543 Agilent Technologies, Santa Clara, CA) and constant temperature bath (Thermoscientific DC10) from the Pacific Marine Environmental Lab (PMEL) at NOAA for use on the Kuroshio cruise. A small amount (40 μL) of indicator dye *m*-cresol purple (*m*CP – purchased from Mark Patsavas) was added to each seawater sample for spectral analysis. The powder form of *m*CP-pure indicator dye dissolved with a combination of sonication and a warm thermal bath. The indicator dye was buffered with HCl and NaOH to a pH of 8.0 verified with a pH meter. The spectrophotometer recorded absorption at wavelengths 434 nm and 578nm (for the acidic and basic forms of *m*CP respectively) and a non-absorbing wavelength of 730nm against a pure seawater reference. The pH value of a sample is determined from the ratios of absorption spectra from the basic and acidic forms of *m*CP as a function of temperature and salinity of the sample (Liu et al., 2011). The water from the constant temperature bath ran through a custom-built aluminum compartment to keep samples at 25°C. Special cells (100 mm cylindrical cells with quartz ends, Starna Cells, Inc. Atascadero, CA) provided a clear path for spectral analysis of samples with the added indictor. A correction for the addition of indicator dye to the samples is calculated from the ratio of a pair of dye additions to samples with differing pH values (Dickson et al., 2007).

The software program CO2SYS was used to calculate pH from two other known carbonate parameters; dissolved inorganic carbon (DIC), total alkalinity (TA), and the equilibrium constants for the first and second dissociations of carbonic acid K_1 and K_2. The parameters of DIC and TA, which were measured by colleagues, have errors of ±1 μmol kg^{-1} and ±2 μmol kg^{-1} respectively (Dickson et al., 2007). Seawater pH from past WOCE/CLIVAR cruises is also calculated from recorded DIC and TA data using CO2SYS. There are several pH scales in use today that were developed to compensate for the strong ionic nature of seawater (Hansson 1973). We use the total pH scale with the preferred constants; K_1 and K_2 determined by Mehrbach and refit by Dickson and Millero, and KSO_4 determined by Dickson 1979 (Lueker et al., 2000).

RESULTS

Certified reference material (CRM batch 123) for oceanic measurements (http://cdiac.ornl.gov/newsletr/fall98/reference.htm) served as checks on reproducibility of pH measurements using the spectrophotometric method. We ran each CRM sample at a minimum of three replicates throughout the duration of the cruise. Standard deviations of the CRMs are 0.002 and below (average 0.0016) after 3 March corresponding to station 4, an indication that precision of data after that time is reliable.

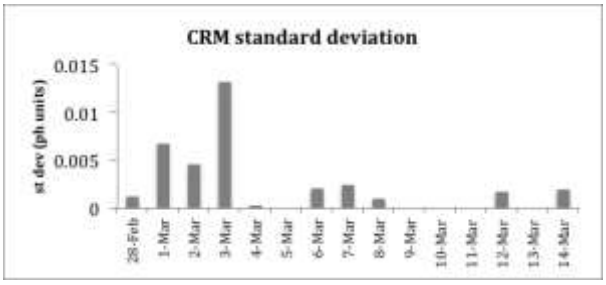

Figure 4. Standard deviation in repeated CRM measurements per day. Standard deviations reach consistent values of ≤ 0.002 pH units after 3 March equivalent of station 4.

We calculated the pH of the CRMs with CO2SYS from DIC and TA parameters supplied in the certificate, 2022.04 ±0.33 μmol kg^{-1} and 2225.21 ±0.34 μmol kg^{-1} respectively. Error for calculated CRM pH is less than 0.001 pH units when DIC and TA errors are applied in the CO2SYS program. The spectrophotometric measured pH values of each CRM are subtracted from the calculated pH value and the differences are on average 0.0142 pH units.

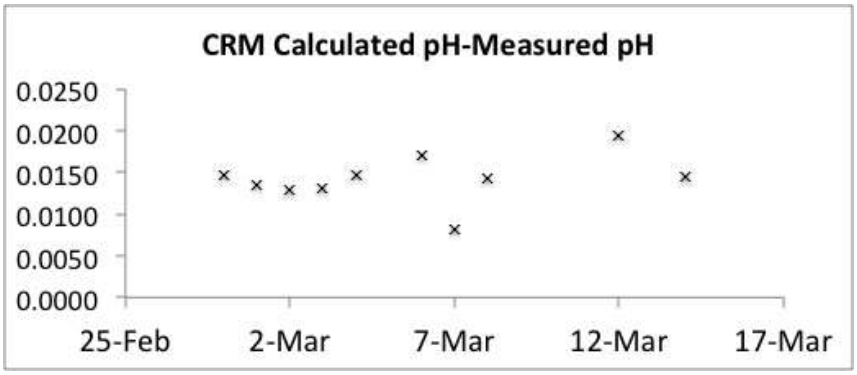

Figure 5. Graph of CRM calculated pH value minus CRM measured values for each batch sample throughout the duration of the cruise. Average difference is 0.014 pH units

Spectrophotometric pH measurements were taken at eleven out of the total 22 stations along the cruise track (Figure 3). During sampling of the stations before 4 March (stations 2-4), the incorrect amount of indicator dye (10 μL) was added to samples, and standard deviations of the CRMs during this time are inconsistent. Stations after this date are considered to have good data since the correct amount of added indicator dye (40 μL) gave more prominent spectra ratios for analysis. Precision after correction of dye amount is also supported by CRM calibration tests (Figure 4). Eight stations are used for spectrophotometric pH measurements down the water column.

Table 1. List of stations with pH measured by spectrophotometer. Samples were drawn throughout the water column and stations from which duplicate measurements were taken are marked with an x.

station	coordinates	max depth (m)	duplicates
9	37N, 148.6E	1998	x
11	39.8N, 149.5E	1998	x
13	40.9N, 149.9E	5079	x
16	38.2N, 148.6E	1997	
18	36.8N, 149E	1995	x
20	33.4N, 148.6E	6007	
22	31.3N, 146E	2005	
23	30N, 147E	2000	x

Stations 9 and 11 are along the northbound transect while stations 13-23 are along the return southbound leg (Figure 3). Profiles of each cruise transect are graphed in two-dimensional plots using the program Matlab. The program interpolates data at missing stations. Contours of pH are plotted as a function of latitude and 2000m depth, deep casts at stations 13 and 20 are plotted to 2000m for consistency.

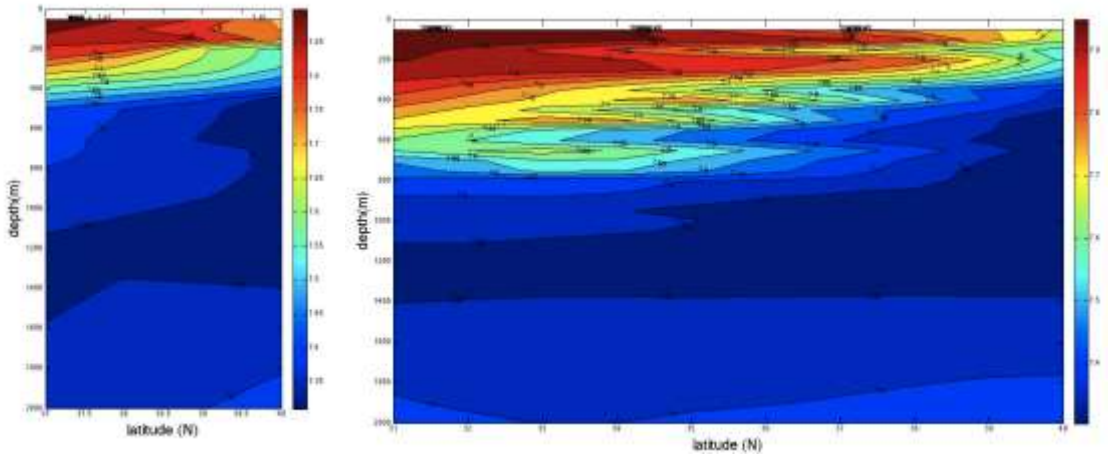

Figure 6. Two-dimensional sections of pH depth profiles A) station 9 (37N, 146.8E) to northernmost station 13 (41N, 149.9E). B) Return leg from station 13 (41N, 149.9E) south to station 23 (30N, 147E). Measurements of pH are taken at stations listed in Table 1. The program Matlab interpolates data for other stations

Levels of pH south of the Kuroshio Extension region (< 33°N) during March of 2013 are on average 8.0 towards the surface. Ocean pH decreased down to 7.63 (at 25°C) as we progressed to the northernmost station 13 (41°N). Resolution of the two-dimensional pH section is limited because pH was not measured at all stations. Intrusions of higher pH water which appear at 400m between 34° and 36°N are the result of interpolated data by the program Matlab as there are no pH stations in that latitude range (Table 1). Standard deviations are calculated between duplicate spectrophotometric measurements and displayed in Table 2. Standard deviations range between 0.0001 and 0.005 with an average of ± 0.003 pH units.

We compared spectrophotometric measured pH with calculated pH at two stations in order to assess accuracy of both methods; one station is located south of the Kuroshio Extension (station 22) and the other north of the current (station 13, Figure 3). Pooled standard deviation is used as the error analysis of the spectrophotometric measured samples. Pooled standard deviation is a method of estimating imprecision of a process where a series of measurements are performed under similar conditions, such as multiple spectrophotometric pH measurements down a water column in the ocean. It is the square root of the pooled variance and is defined by the following equation

$$s_p = \sqrt{\frac{(n_1 - 1)\,s_1^{\,2} + (n_2 - 1)\,s_2^{\,2} + \ldots + (n_k - 1)\,s_k^{\,2}}{n_1 + n_2 + \ldots + n_k - k}}$$

where n is sample size of the ith sample, s is variance of the ith sample, and k is number of samples being combined (http://goldbook.iupac.org/P04758.html). An example for n in this study is the number of replicates per Niskin bottle that are analyzed through the spectrophotometer; six for station 13 and three for station 22. The number k is the number of Niskin bottles per station cast. Pooled standard deviation is 0.0018 for spectrophotometric pH at station 13 and 0.0001 for station 22.

Error for calculated pH was determined with the monte carlo simulation in Matlab, which takes into account the errors of DIC and TA measurements, ±1 µmol/kg and ±2 µmol/kg respectively for station 22 (code by H.I. Palevsky, based on Monte Carlo framework from P.D. Quay). Error in station 22 ranges between 0.003 and 0.006 for an average of ±0.0055 pH units. During the time between stations 10 and 18, an overdose of mercuric chloride was dispensed to samples for DIC measurements, therefore an error of ±6 µmol kg^{-1} is applied for station 13 resulting in larger error ranging between 0.017 and 0.019 for an average of ±0.0182 pH units (Table 3).

Table 2. A list of samples in which duplicates were drawn from the CTD Niskin bottles. Each duplicate was analyzed with the spectrophotometer three times and the averages of those replicates are shown here. Standard deviations are calculated across all replicates of the sample.

duplicate 1 pH avgs	duplicate 2 pH avgs	st dev
7.3623	7.3702	0.00433
7.3360	7.3383	0.00467
7.7999	7.8014	0.00083
7.9125	7.9211	0.00469
7.4120	7.4191	0.00389
7.3771	7.3733	0.00206
7.3302	7.3335	0.00184
7.3523	7.3514	0.00052
7.4591	7.4697	0.00581
7.5808	7.5759	0.00272
7.8383	7.8406	0.00124
7.8537	7.8528	0.00047
7.4439	7.4448	0.00048
7.3133	7.3106	0.00151
7.2792	7.2772	0.00108
7.2928	7.2941	0.00074
7.3470	7.3373	0.00533
7.5052	7.5245	0.01056
7.4230	7.4183	0.00259
7.3540	7.3579	0.00211
7.4087	7.4021	0.00360
7.6953	7.6860	0.00506
7.9319	7.9459	0.00763
7.9481	7.9580	0.00543
7.9411	7.9301	0.00602
7.4247	7.4221	0.00142
7.3563	7.3565	0.00011
7.3379	7.3394	0.00083
7.4325	7.4339	0.00076
7.6716	7.6769	0.00291
7.8672	7.8634	0.00214
7.9651	7.9705	0.00292
7.9903	7.9904	0.00012

Table 3. Error for spectrophotometric measured pH and CO2SYS calculated pH at stations 13 and 22.

Station #	measured pH error	calculated pH error
13	0.0018	0.0182
22	0.0001	0.0055

The depth profiles of spectrophotometric measured pH plotted with calculated pH from DIC and TA display a similar pattern (Figure 7).

The differences between calculated and measured pH become larger with depth in both stations. Differences between calculated and measured pH at station 13 are 0.0056 pH units near surface (< 1000m), and 0.01 pH units at depth (>1000m). However, if we calibrate pH by a difference of 0.0142 pH units as determined by the CRM tests, then the differences are -0.0086 near surface and -0.003 at depth. Differences between calculated and measured pH at station 22 are 0.0088 pH units near surface and 0.013 pH units at depth. If the calibration is applied, the differences are -0.0054 near surface and -0.0008 at depth (Figure 8)

We compared calculated pH values between Kuroshio cruise station 13 and CLIVAR repeat hydrography line P01 station 23 (2007), and calculated pH between Kuroshio station 22 and WOCE cruise P10 station 80 (1993). Kuroshio station 13 is approximately 54 km northeast of P01 station 23 and station 22 is located 122 km southeast of P10 station 80 (Figure 3). Seawater pH is plotted against density (σ_T) in order to ensure comparison between similar water masses (Figure 9).

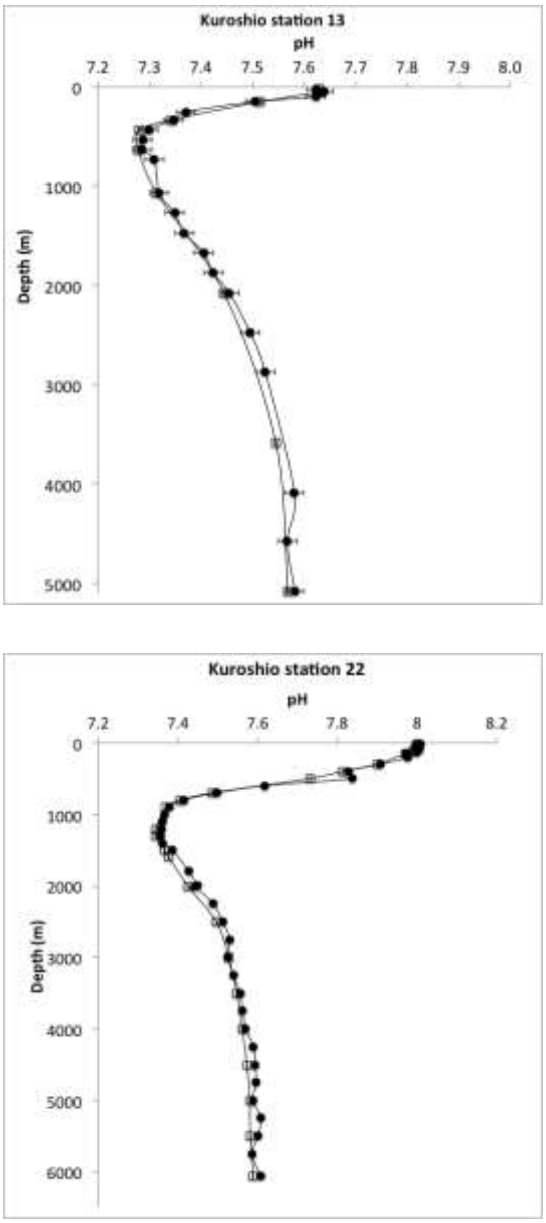

Figure 7. Depth profiles of pH at Kuroshio cruise stations 13 and 22. Spectrophotometric measured pH (squares) are graphed along with pH calculated with program CO2SYS from DIC and TA(circles). Error for measured pH is 0.00178 (pooled standard deviation), error for calculated pH is determined by monte carlo method and listed in table 3.

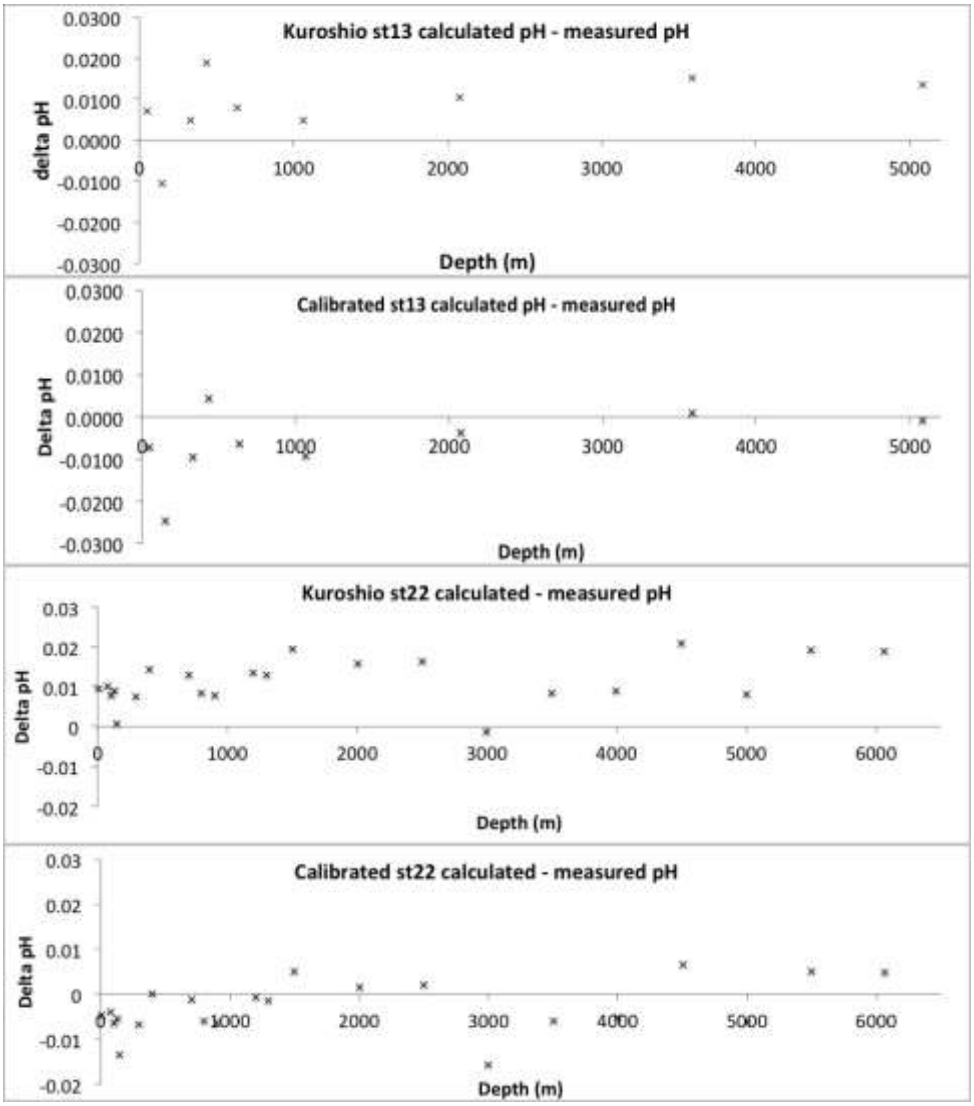

Figure 8. Differences between calculated pH minus measured pH at Kuroshio station 13 plotted against depth.

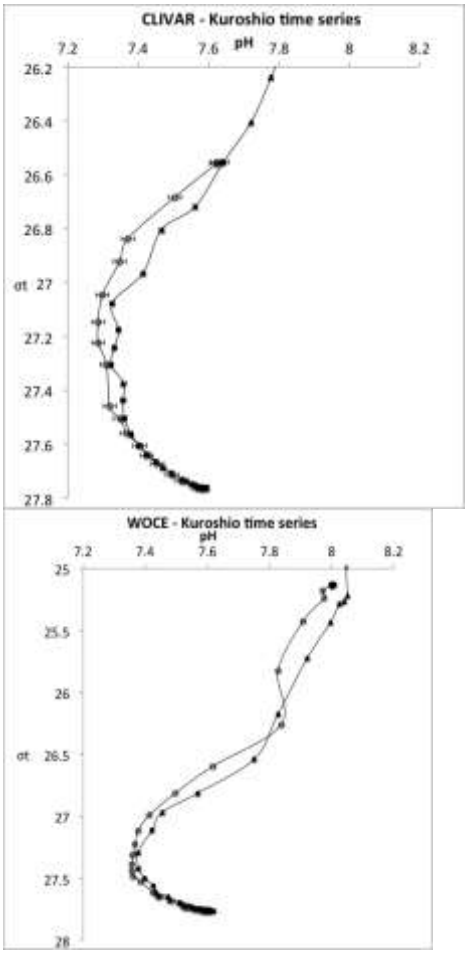

Figure 9. Time series – Calculated pH from CLIVAR 2007(triangles) and Kuroshio station 13 (circles) plotted against shared density values. Calculated pH form WOCE 1993 (triangles) and Kuroshio station 22 (circles).

DISCUSSION

The Kuroshio Extension region is a sight of turbulent mixing due to the physical nature of a large ocean front (Takeyoshi et al., 2012). Upwelling of colder, more acidic water from depth is a likely cause of lowering pH at surface water in the north (Figure 6). Higher surface pH levels south of the Kuroshio Extension is directly related to low pCO_2 content in the water, a catalyst for the drawdown of atmospheric CO_2 that the region is known for during this time of the year (Ayers and Lozier, 2012).

The spectrophotometric method developed over twenty years ago proves to be a high precision approach to directly measuring pH in open ocean waters as shown from the low standard deviations in CRM tests and between duplicate samples (Figure 4, Table 2). With great care taken by the sampler, this method yields highly reproducible results, a necessity for research that requires such precision. The average difference in accuracy of 0.0142 pH units between calculated pH and spectrophotometric measured pH for the CRMs is a calibration that shifts values from both methods closer together at both stations. The calibration for station 22 at depth is especially noteworthy as differences are reduced from an average of 0.01 pH units without the calibration to -0.0008 average pH units with it. The pH differences in near surface water are only slightly improved at station 22 (Figure 8). Deep-water pH differences are also markedly smaller at station 13 with calibration. However, the pH differences in shallower water are greater when the calibration is applied increasing to an average of -0.0086 from 0.0056 pH units indicating an overshoot (Figure 8). The larger error for calculated pH levels at station 13 must be taken into consideration when interpreting this apparent overshoot at near surface depths. The uncertainty in DIC measurements at that station coupled with possible advection of a different water mass may be affecting pH levels in the area north of the Kuroshio Extension (Talley 1996). The significantly reduced differences between calculated and measured pH levels gives evidence that the calibration should be applied for internal consistency of this study. The matter of whether one method is more accurate than the other is still under question because there is no definitive standard for comparison.

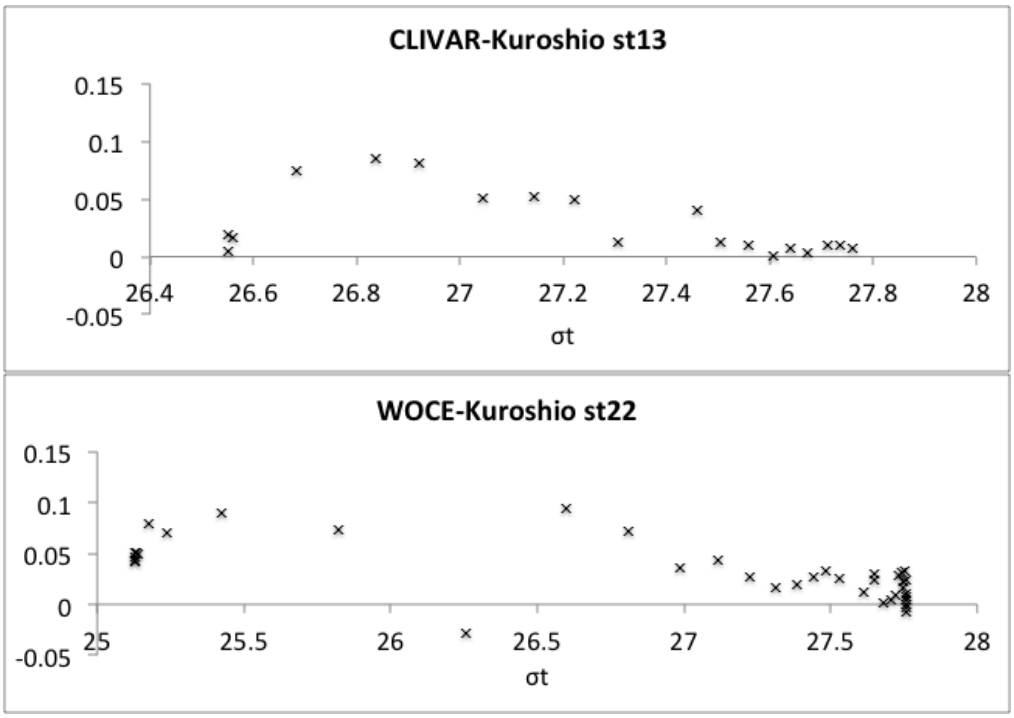

Figure 10**.** Values for calculated pH from CLIVAR 2007 minus Kuroshio station 13 pH, and calculated pH from WOCE 1993 minus Kuroshio station 22 pH.

The time series comparisons of calculated pH show greater differences in calculated pH near the surface for both stations 13 and 22. Plotting a profile of pH against potential density ensures that similar water masses are being evaluated considering the differences in time and distance between current cruise data and past data (Figure 10). Both WOCE (1993) and CLIVAR (2007) cruises have greater pH differences in the water masses shallower than 1100m. This pattern is consistent with previous findings by Byrne et al. in the North Pacific basin over a 15 year time span. Deep water pH differences are generally lower than 0.02 pH units. The two time comparisons are more similar than predicted given that CLIVAR occurred five years before the present study and WOCE almost twenty years before. Seawater pH in the North Pacific is expected to change within 0.05 pH units over 15 years as established by Byrne et al., 2010. The high differences between CLIVAR 2007 and station 13 pH levels above 1100m may be partially explained by advection of mode water formed initially near the Sea of Okhotsk (Talley 1996). A temperature effect on pH may also be partially responsible for the high pH differences in the five-year span. Shallow water temperatures in the region north of the Kuroshio Extension did not exceed 3.5°C. In contrast, water temperatures towards the surface at station 22 reached as high as17.9°C. The K_1 and K_2 dissociation constants used in CO2SYS are partly dependent on temperature and may be affected by the shift in surface water temperature as we crossed the Kuroshio Extension. An irregular pH value in station 22 at 26.56 σ_T occurs at a depth of 500m and indicates a possible localized advection, an occurrence that would not be unusual given the turbulent nature of the area. The pH differences between CLIVAR and the Kuroshio cruise cannot be explained by ocean acidification because the time difference of five years is too short to account for the numbers seen, therefore great care must be taken in comparing time series in this region.

The spectrophotometric method is recommended for use in extensive pH studies where precision of less than 0.005 pH units is sought. Further studies comparing pH methods are necessary to establish accuracy. Potential errors in the other carbonate measurements, the still evolving dissociation constants used in CO2SYS, temperature differences, and the advection of different water masses all contribute to uncertainty in calculating pH levels closer to surface levels (Liu et al., 2011, Talley 1996).

Studies on ocean acidification are increasing exponentially as CO_2 levels continue to rise. Accurate pH measurements are essential in analyzing the scope of ocean acidification in regions where CO_2 uptake intensifies pH changes. Despite uncertainties associated with accuracy and water density comparisons, the hope is that this study will provide a helpful framework for further comparisons of pH methods, and a baseline for future studies in the Kuroshio Extension region.

CONCLUSIONS

- The use of indicator dye and spectra analysis with a spectrophotometer produces high precision measurements as displayed by CRM calibration tests where standard deviations are on average 0.0016 pH units.
- There is an offset of 0.0142 pH units between calculated and measured pH of CRMs.
- The spectrophotometric method generates highly reproducible pH values. Standard deviations on sample duplicates are ±0.003 pH units.
- Surface pH decreased as we moved north across the Kuroshio Extension in March. Lowest pH values of 7.63 are at station 13 (41N, 149.9E) while highest pH values of 8.0 are at station 22 (30N, 147E). Low pH in the north may be due to ventilation.
- Precision of spectrophotometric method is higher than calculated pH method. Pooled standard deviations of measured pH at stations 13 and 22 are 0.0018 and 0.0001 pH units respectively. Error for calculated pH at stations 13 and 22 is 0.0182 and 0.0055 pH units respectively.
- Calculated pH from DIC and TA showed greater differences from measured pH at water depths below 1000 m. However, when calibrated by the offset of 0.0142 from CRM measurements, the differences are smaller overall, indicating that the calibration should be applied for internal consistency.
- Calculated pH from DIC and TA of past cruises (WOCE 1993 and CLIVAR 2007) have higher pH near surface levels than current calculated pH values; an average difference of 0.053 pH units between WOCE and station 22, and 0.044 pH units between CLIVAR and station 13. The magnitude of difference for CLIVAR and station 13 is outside the bounds of expected change given the relatively short time span between studies. This finding suggests that ocean acidification alone cannot explain differences in pH across time in the Kuroshio Extension region.
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