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Re: Comments on draft 2010 assessment of Washington's marine waters

Thank you for the opportunity to comment on Washington's draft assessment of marine waters. This letter is provided for further explanation and information about the methods and findings in our study: Wootton, J. T., Pfister, C. A., & Forester, J. D. 2008. Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. *Proceedings of the National Academy of Sciences*, 105(48): 18848.

Our methods

To the extent that the Department of Ecology is interested in the quality of the data in our paper, we used standard practices employing the same basic method that the Department uses in its own water quality monitoring program available at http://www.ecy.wa.gov/science/data.html. We used standard electrochemical methods, and while individual samples may not be as precise as spectrophotometric methods, our large sample size of 24,519 measurements provided high statistical precision in our analysis. Moreover, we statistically evaluated the drift-constant by generating a relationship between time since last service, assumed that such a relationship is due to sensor drift, and statistically removed it prior to the analysis. Therefore it should have minimal effects on the results. Additionally, drift cannot cause the long-term trend in the data, which we have now documented over the past 11 years, as the probes are serviced over a much shorter time scale (approximately 2 weeks in most cases) than the span of the temporal trend. Regarding the location of the probe, we analyzed only measurements that were taken when the site was not separated from the rest of the Pacific (i.e. was not functioning as a tide pool), and we explicitly presented data and analyses demonstrating that measurements taken within the sampling site and in the adjacent ocean are indistinguishable.

Moreover, it was unnecessary to measure anything other than pH to inform our findings on pH change. The carbon system of seawater (at least abiotic water with a defined content of salts typical of the ocean) is constrained such that having two measures of the inorganic carbon system necessarily determines the other two parameters typically used to characterize the carbon system. While it may have been helpful to have those measurements to interpret the contributions of inorganic carbon to pH changes,

they are unnecessary to measure pH per se. Furthermore, we have subsequently been measuring these data and they affirm our earlier findings. Our pH data taken using standard electrochemical methods generate essentially the same values as pH from water samples we have collected concurrently that are measured spectrophotometrically by us, which are tested against seawater pH standards provided by the Andrew Dickson lab at Scripps (i.e. the best practices for ocean acidification research), or calculated using measurements of DIC and total alkalinity made by the Dickson lab. Our data are more variable, as expected by known measurement errors of the methods, but they do not show appreciable bias. The massive number of samples we can take compared to those that can be feasibly made in a water collection/analysis program, however, offsets these wider measurement errors once statistical analyses are applied to the data. In any event, wide measurement errors make detecting patterns more difficult for a given number of samples, whereas there is no issue with discerning a temporal trend in our data set. The fact that our measurements based on DIC/TA fall comfortably within the measurements we make with our probe also indicates that one does not need to invoke other acid sources beyond CO_2 to recapture our recent pH measurements. In our paper, we reported TA estimates from our data based on published empirical relationships of TA with temperature and salinity, for which we have data. The TA data from water samples we have had analyzed do not follow the published relationship, but they do correlate very well with salinity (at least over the temperature ranges relevant to our site, temperature has little effect), and salinity does not change systematically through time. Therefore, our conclusion that TA does not systematically change remains valid, and we can make pretty good estimates of TA from our data using the revised relationship.

Our findings

With respect to our findings, we observed a rate of decline substantially faster than predicted by current models and our study concluded that, "[o]ur model includes all variables that are currently suggested to have a large impact on ocean pH. Of these, only atmospheric CO_2 exhibits a consistent change that can explain the persistent decline in pH." Applying the rate of pH change observed in our paper, simple math indicates a significant change in pH over just eight years -0.046 x 8 yr = 0.368 units, and this trend has continued, and perhaps increased, since the published study. While the mechanisms leading to rapid pH decline and how these link to changes in atmospheric CO_2 are not fully understood, our published study and subsequent research considers the known variables that could contribute to low pH and finds that the trend of rapidly declining pH is not supported by other explanations. For example, oxygen data do not appear to support the conventional notions that low pH is generated by CO_2 derived from respiration. While our data showed clearly that pH is affected by respiration in the water -- this both in the daily cycling of photosynthesis-respiration and the variability associated with upwelling -- there is no evidence that these processes led to observed sustained changes in pH over the span of the data, as these variables do not exhibit sustained trends through time. In contrast, we found that the best-fit parameter for explaining the change we observed in ocean pH was the contribution of atmospheric CO_2.

Since the published study, we have been analyzing water samples for spectrophotometric pH, DIC and Alkalinity (using the best methods for measuring the ocean carbon system), and analyzing extensive time series data. Notably, we have found that the pH levels continue to decline at a rapid rate (-0.058 units per year) for waters off of Tatoosh Island. We continue to suspect that atmospheric CO_2 is a key driver of the sustained pH decline, as we have eliminated alternative variables that could explain the change through time including changes in salinity, water temperature, the upwelling index, local surface winds, nitrate, phosphate, ammonia, precipitation, river discharge, two oceanographic condition indices (PDO, NPGO), precipitation chemistry, or dissolved organic carbon in river water.

Furthermore, the pH levels around Tatoosh are not unusual compared to pH measurements made by us and others elsewhere in the wider Strait of Juan de Fuca. This includes boat transects we have run up to 3.4 km offshore spanning 8 km^2 area and water depths to 210 m, and spot samples made at several stations in the western Strait. Furthermore, we have looked at pH data sporadically taken by the Washington State Department of Ecology (http://www.ecy.wa.gov/apps/eap/marinewq/mwdataset.asp) over the past decade or so, which also exhibit pH declines that are much more rapid than predicted (average of -0.018 units per year for open-water sites). Finally, NOAA did a survey of the Strait in 2007 and found high DIC values throughout the Strait, consistent with our measurements. (See Feely, R.A., S.R. Alin, J. Newton, C.L. Sabine, M. Warner, A. Devol, C. Krembs, and C. Maloy. 2010. The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. *Estuarine, Coastal and Shelf Science* 88, no. 4 (August 10): 442–449.)

If you should have any further questions about my research, please contact me.

Sincerely,

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