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Seasonal pH and aragonite saturation horizons in the Gulf of Alaska during the North Pacific Survey, 1956–1957

S. McKinnell[1] **and J. R. Christian**[2,*]

[1]North Pacific Marine Science Organization, c/o Institute of Ocean Sciences, P.O. Box 6000,
Sidney, BC, V8L 4B2, Canada
[2]Fisheries & Oceans Canada, Institute of Ocean Sciences, P.O. Box 6000, Sidney,
BC, V8L 4B2, Canada
[*]also at: Canadian Centre for Climate Modelling and Analysis, University of Victoria, Victoria,
BC, V8W 3V6, Canada

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Correspondence to: S. McKinnell (mckinnell@pices.int)

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Abstract

The extent of global change in carbon system parameters can only be evaluated by comparing present with past measurements. In the northern North Pacific, where aragonite saturation horizons are among the shallowest in the world, historical measurements of carbonate parameters vary from rare to nonexistent. However, during the summer of 1956 and winter of 1957, an extensive survey of the oceanography of the Northeast Pacific, under the auspices of the Canadian Committee on Oceanography, was conducted by the Fisheries Research Board of Canada. Approximately 2500 measurements of pH at depths from surface to 2000 m were taken throughout the Gulf of Alaska, in addition to measurements of nutrient and hydrographic properties. After conversion to the contemporary total pH scale, these data revealed significant seasonal and latitudinal differences in pH in the upper 200 m. Estimates of aragonite saturation indicate that undersaturated water was a common feature of the surface mixed layer north of 51° N latitude in the winter of 1957. The North Pacific Survey data were compared with the results of a summer 2007 survey of the west coast of North America where pH levels were ~0.1 pH units lower (at a reference density of $26.2\sigma_\theta$) than was found in the summer of 1956.

1 Introduction

In a time of global change it is important to have a clear understanding of the magnitudes and rates of change, the extent to which they have precedent, and if so, the likely consequences of such change. During the 20th century, the concentration of CO_2 in the atmosphere has risen rapidly from widespread combustion of deposits of carbon-based fuels by humans (Keeling et al., 1976). Simple chemical principles indicate that the pH of the ocean will decline as it absorbs increasing amounts of CO_2 from the atmosphere. Changing the chemical composition of seawater has the potential to affect the biology of organisms that are sensitive to pH, particularly those with skeletal structures made of calcium carbonate (aragonite or calcite).

Seawater that is undersaturated with respect to aragonite is making incursions onto the North American continental shelf during periods of upwelling. During the summer of 2007, Feely et al. (2008) found widespread evidence of low-pH seawater (defined as pH$<$7.75 and $\Omega_{\text{arag}}<1$) along the North American continental shelf. This water was associated with the 26.2 potential density (σ_θ) surface that shoaled from a depth of ~150 m offshore to 40–120 m on the continental shelf during the summer upwelling season of 2007. While shoaling isopycnals are typical of coastal upwelling regions, it is of interest to understand whether the chemistry associated with certain isopycnals has changed or not. Because pH and carbon system measurements in the northern North Pacific are limited, particularly prior to about 1990 (Key et al., 2004), potential records of seawater pH from the past take on a special significance.

The International North Pacific Fisheries Commission was established in the early 1950s with Canada, Japan, and the United States as members. Its responsibility was the high seas fisheries of the North Pacific, a region about which little was known. Thus a program of scientific exploration was begun under the auspices of the scientific committees of the new Commission. Canada's contributions included a North Pacific Survey to describe the oceanography of the Northeast Pacific. It was begun under the direction of the Canadian Committee on Oceanography and was implemented beginning in 1956 by the Pacific Oceanographic Group of the Fisheries Research Board of Canada. One of the chemical properties measured, if only briefly, during the survey was pH.

2 Sampling in 1956–1957

From 31 July to 2 September 1956, 85 oceanographic stations were occupied by the H.M.C.S. *New Glasgow* (Fig. 1). At each station, shallow (300 m) and deep (2000 m) casts were made to standard target depths. Observations included temperature, salinity, dissolved oxygen, inorganic nutrients (phosphate, nitrate + nitrite, silicate), and pH (POG, 1957a). From 23 January to 4 March 1957, 68 stations were occupied by H.M.C.S. *Oshawa* (POG, 1957b). The range of latitudes sampled spanned from northern subtropical (North Pacific Transition Zone) to subarctic. The pH measurements were made using a Beckman model H pH meter, under the direction of J. D. H. Strickland who was on both cruises (POG, 1957a, b; T. R. Parsons, personal communication, 2009). Hereafter, the 1956 samples are identified as Summer data (n=1232) and the 1957 samples as Winter data (n=1115). The data were retrieved from a Japanese submission to the US NODC World Ocean Database (http://www.nodc.noaa.gov/OC5/SELECT/dbsearch/dbsearch.html)[1].

3 pH measurement and carbon system calculations

An issue of uncertain importance for interpreting archival data is the quality of the pH measurements made in the 1950s and their conversion to the pH scales in current use. The equilibrium constants for carbonic and boric acids that are now widely used in oceanography are for the total or SWS scales, so our objective was to convert the data collected during the 1950s to the total scale so that the most up-to-date values of the equilibrium constants can be used to estimate $[CO_3^{2-}]$. The assumptions made about the original data are: (a) that they are internally consistent, (b) that they are of high quality given the methods of the day (Strickland, 1958), and (c) that the spatial and temporal patterns observed are not a result of biases arising from conversion. This latter point needs careful consideration because the offset between scales is a function of temperature and salinity.

Strickland (1958) describes a method of pH determination based on standardization to a phosphoric acid buffer of pH 6.87 at 25°C (0.025 mol/kg each Na_2HPO_4 and KH_2PO_4). This is a standard NBS buffer (Culberson, 1981; Covington et al., 1985), and these data can be assumed to fall on the NBS scale, which is approximately equivalent

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[1] The vessel *New Glasgow* mistakenly appears as *New Glascow*.

to the free hydrogen ion scale. Of the four scales used for seawater pH, the NBS scale and the free scale differ by about 0.01 unit, as do the total and SWS scales (Culberson, 1981; Zeebe and Wolf-Gladrow, 2001). The latter scales, however, differ from the NBS scale by more than 0.1 unit at 25°C, although the offset is less at the temperatures and salinities characteristic of the eastern subarctic Pacific. The offset between the free and NBS scales is small and not well known (Culberson, 1981; Zeebe and Wolf-Gladrow, 2001), and we have not attempted to correct for it here. The offset between the free and total scales arises from the inclusion of HSO_4^- in the definition of the "total" hydrogen ion concentration and can be estimated from total sulfate concentration (S_T) and the equilibrium constant for dissociation of HSO_4^- (K_S), which can in turn be estimated from temperature and salinity as described by Zeebe and Wolf-Gladrow (2001) and Dickson et al. (2007). The offset is $\log_{10}(1+S_T/K_S)$ where S_T is estimated from salinity as in Zeebe and Wolf-Gladrow (2001) and K_S is estimated as in Chapter 5 of Dickson et al. (2007). For these data, the offset ranged from 0.044–0.096 (<0.06 for 80% of data points). Strickland (1958) states that a precision <0.02 is achievable under seagoing conditions, so the offset between the NBS and free scales is insignificant by comparison. The adjustment between scales is not, but the variability of the adjustment is small compared to the range of variability of the full data set, and the small variations in the adjustment with temperature are not the source of the geophysical patterns observed in these data. The average difference between the estimated carbonate ion concentration and one calculated using a constant offset (0.0506=median observed) is less than 1%, whereas the difference from values calculated using the uncorrected NBS pH is about 12%.

Calculating the saturation state with respect to calcite or aragonite requires that two of the four CO_2 system properties (DIC, alkalinity, pH, and pCO_2) be measured (Dickson et al., 2007). In this case we have only one, pH, and must therefore estimate another indirectly. The critical assumption made is that total alkalinity has not changed as a result of accumulation of anthropogenic CO_2. Because accumulation of anthropogenic DIC has only a limited and indirect effect on alkalinity, our approach was to: (a) estimate alkalinity as an empirical function of temperature and salinity with regression coefficients estimated using contemporary data, (b) apply this function to the temperature and salinity data from the North Pacific Survey, and (c) solve the CO_2 system from alkalinity and pH. All CO_2 system calculations were made as described in Chapter 2 of the Guide to Best Practices (Dickson et al., 2007), using the total hydrogen ion concentration scale and the equilibrium coefficients of Lueker et al. (2000), after first adjusting the measured pH to the total scale.

4 Results

The North Pacific Survey data indicated a strong latitudinal effect on pH associated with a relatively abrupt shoaling of the $26.2\sigma_\theta$ potential density layer near 51° N (Fig. 2). This density feature is associated with the southern boundary of the Ridge Domain (Favorite et al., 1976) and it can be considered as an indication of a gradient between water masses. At depths <200 m, mean pH was significantly different between seasons (ANOVA, $P \ll 0.001$, Fig. 3), was significantly lower at northern latitudes than southern latitudes (ANOVA, $P \ll 0.001$, Fig. 3), and was significantly lower at potential density (ANOVA, $P \ll 0.001$), and there was significant interaction between region and season on mean pH (ANOVA, $P \ll 0.001$). There was no significant effect of longitude on mean pH at depths <200 m depth. Overall, mean pH varied most in the Gulf of Alaska at depths <200 m from variation in latitude, especially in winter. Lower mean pH in the surface layers in winter at northern latitudes was a result of isopycnal shoaling and deeper wind mixing in winter that brings lower pH waters at depth toward the surface and from biological activity (excess of photosynthesis over respiration in summer). The seasonal difference in mean pH in the upper 200 m was 0.17 units for samples taken north of 51° N and 0.06 units south of 51° N whereas the regional difference in mean pH at depths <200 m was approximately 0.21 units in winter, 0.1 in summer.

In 1956 and 1957, the depth of the $26.2\sigma_\theta$ isopycnal (range: 26.15–26.25) was shallowest in the northwestern Gulf of Alaska and deepest in the transition zone waters to the south (Fig. 2). A significant difference between summer and winter was the shoaling of this potential density layer to the surface in the northwestern Gulf of Alaska. In winter, this layer appeared frequently at depths <30 m, where it had lower pH (mean and median pH=7.59) compared with other winter samples (mean and median pH=7.77) in this potential density layer. There was also a widespread seasonal difference in pH at this potential density layer at depths >30 m with pH being significantly lower in winter than in summer (ANOVA; $p \ll$; Fig. 4). There was no significant variation in pH with longitude at this potential density layer, but higher latitudes had significantly lower pH than did lower latitudes (ANOVA; $p \ll 0.001$). The pH of ~7.75 observed by Feely et al. (2008) for aragonite-undersaturated waters on this potential density surface during the summer of 2007 was more typical of winter 1957 than summer 1956 (Fig. 4).

Water that was undersaturated with respect to aragonite ($\Omega_{\mathrm{arag}}<1$) was also found to have higher potential density ($\sigma_\theta \sim 27.0$) in both the northern and southern Gulf of Alaska (Fig. 5). These are generally deeper waters below the mixed layer so it was not unexpected. Undersaturated water was also found at $\sigma_\theta \sim 26.0$ but this was largely a wintertime phenomenon of the northern Gulf of Alaska, although it was occasionally present in summer (Fig. 5). Profiles of Ω_{arag} by depth stratum (Fig. 6) indicate widespread undersaturation in the Gulf of Alaska in wintertime, especially in the north where median values of Ω_{arag} were <1 at all depth strata. Likewise, the upper layer was supersaturated in summer in both the northern and southern Gulf of Alaska.

5 Discussion

Few surveys of carbonate parameters have been made in the Gulf of Alaska which limits our understanding of its state and rate of change. The North Pacific Survey data from the mid-1950s indicate that aragonite saturation horizons and their associated pH levels in the Gulf of Alaska vary according to the latitude and season of observations. Little variation in these parameters arises from changes in longitude, at least in the surface waters, until near the continental shelves of British Columbia, Washington and

Oregon where density surfaces shoal in summer (Feely et al., 2008).

The entire water column throughout the northern Gulf of Alaska north of 51° N was generally undersaturated with respect to aragonite in the winter of 1957. This state can arise from a combination of physical, chemical, and biological forces, each with a tendency to lower pH and reduce Ω_{arag}. During winter, atmospheric CO_2 is greater (Keeling et al., 1976); upwelling and turbulent wind-driven mixing brings less saturated, lower pH subsurface water toward the surface, and photosynthesis declines from lack of light. So it appears that even in the mid-1950s, pelagic organisms with aragonitic exoskeletons living in the northern Gulf of Alaska may have already faced the challenges of producing (or maintaining) shells in undersaturated seawater. Conversely, in the southern Gulf of Alaska, which has a greater influence of subtropical waters of the North Pacific Transition Zone, higher winter light levels, and greater stratification, median Ω_{arag} values in the upper water column were generally supersaturated even in winter.

Along the North American upwelling region, Feely et al. (2008) found $\Omega_{arag}<1$ at pH~7.75 in waters with potential densities of ~$26.2\sigma_\theta$ at relatively shallow depths (40–120 m). In the winter of 1957, this combination of pH and potential density was found near the surface (<30 m) in the northwestern Gulf of Alaska. At depths below 30 m, a pH of 7.75 on this potential density layer was characteristic of winter pH with average values of 7.65 (Fig. 4). In the summer of 1956, 42 of 44 pH values were >7.75 on this density layer. Considering only the samples collected south of 51° N in summer, the minimum pH observed on the 26.15–$26.25\sigma_\theta$ layer at all stations was 7.83 (n=23, mean pH=8.00; mean depth of layer=136 m). These results suggest that the pH measured on samples taken in July 2007 would have been observed very rarely, if at all, during the summer of 1956.

During the North Pacific Survey, the shallowest appearances of the $26.2\sigma_\theta$ layer occurred in the northwestern Gulf of Alaska during winter at 0–30 m. All of these samples were located in the region of the Alaska Current and Alaska Stream (adjacent to the Alaska Peninsula and Aleutian Archipelago) between 142–162° W (Fig. 1). While wind-forced upwelling is not unknown in this region, it is more widely known for its role as a source and conduit for mesoscale cyclonic eddies that propagate westward along the continental shelf (Ladd, 2007). These cyclonic eddies are characterized by upwelling cores where isopycnals are elevated above background. Eddy kinetic energy in this region is higher in winter than in summer (Ladd, 2007) and this may explain some of the differences between seasons in this region. In summer, the shallowest appearance of the $26.2\sigma_\theta$ layer in this region was at 48 m. Eddies may serve as another important mechanism for entraining low pH, aragonite undersaturated water toward the surface.

These historical data were collected by one of the pioneers of ocean chemistry, John Strickland, who likely collected as high quality data as was possible at the time. While there is indeed some uncertainty about the conversions presented here, there is useful information in these historical data that can not be acquired any other way. We think that the patterns observed in the data are real, and that the spatial and seasonal variability observed should be considered in future sampling programs. These data are a useful baseline for evaluating the consequences of anthropogenic perturbations that will be evident in data collected later with more modern methods.

Acknowledgements. We are indebted to John Strickland and others who originally collected the data, and the anonymous person(s) at JODC for contributing an electronic version of the Canadian data to the U.S. NODC. Tim Parsons provided useful information on the cruise logistics and pH analysis of the late 1950s. Andrew Dickson provided useful advice on conversions between pH scales. This paper was inspired by the SCOR-IOC-IAEA-IGBP Symposium on “*The Ocean in a High-CO2 World*” held 6–9 October 2008 in Monaco.

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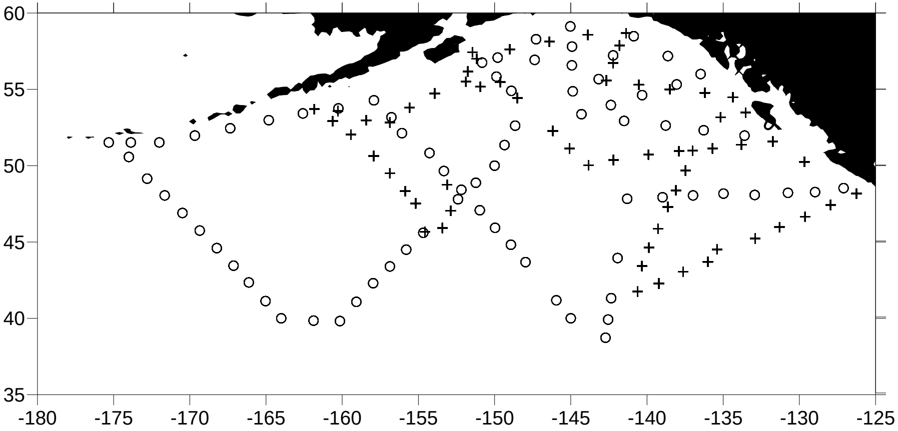

Fig. 1. Locations of stations in the Gulf of Alaska with pH profiles measured in summer 1956 and winter 1957 (○=Summer, +=Winter).

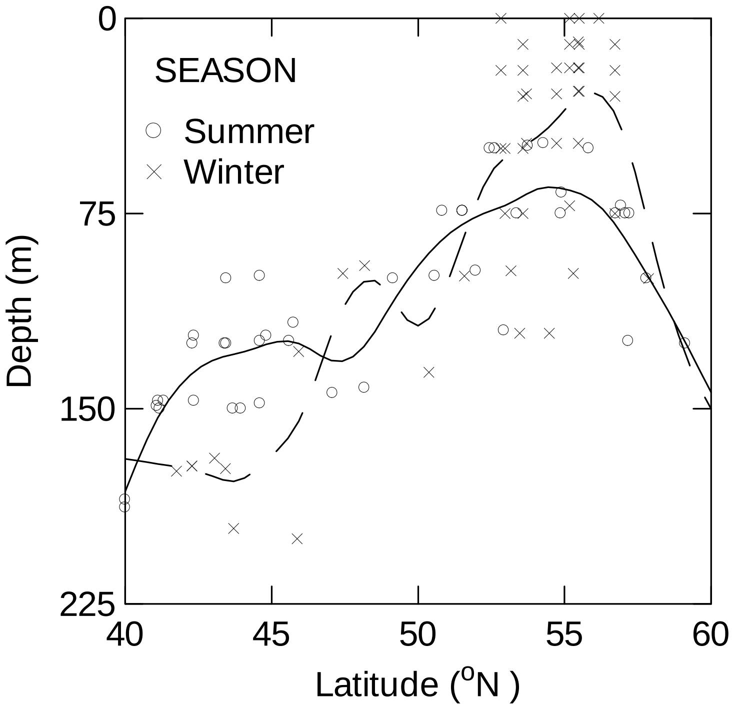

Fig. 2. Depths of samples with potential densities in the range 26.15–26.25 taken in the Gulf of Alaska in summer 1956 and winter 1957. DWLS (distance-weighted least squares) smoother of depth versus latitude was used to produce the trend lines (dashed line is winter).

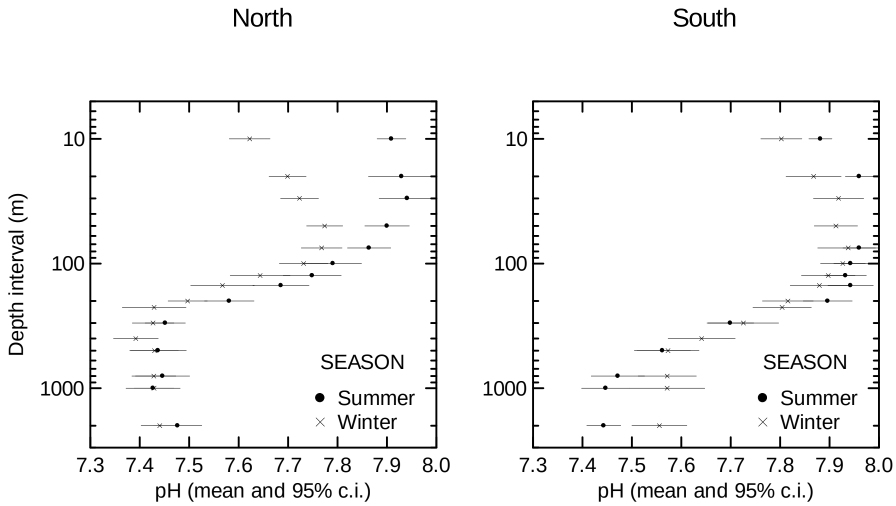

Fig. 3. Mean and 95% confidence interval of pH measurements by depth interval, season and region. Depth intervals are indicated by the deepest depth included in the interval (e.g. the statistics for the 10 m interval include pH measurements from 0–10 m). Where the horizontal lines (indicating the range of the confidence interval) are separated, there are statistically significant differences between seasons in mean pH values at that depth interval.

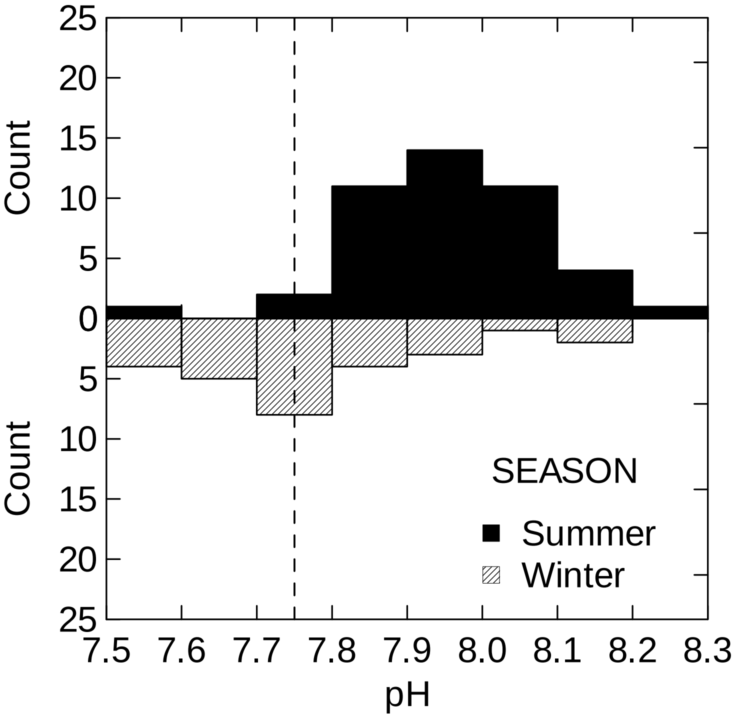

Fig. 4. Histograms of pH on the 26.15–26.25σ_θ potential density layer in summer and winter at depths greater than 30 m in the Gulf of Alaska. The vertical line at pH=7.75 was the summer observation from 2007 by Feely et al. (2008) associated with undersaturated water in summer.

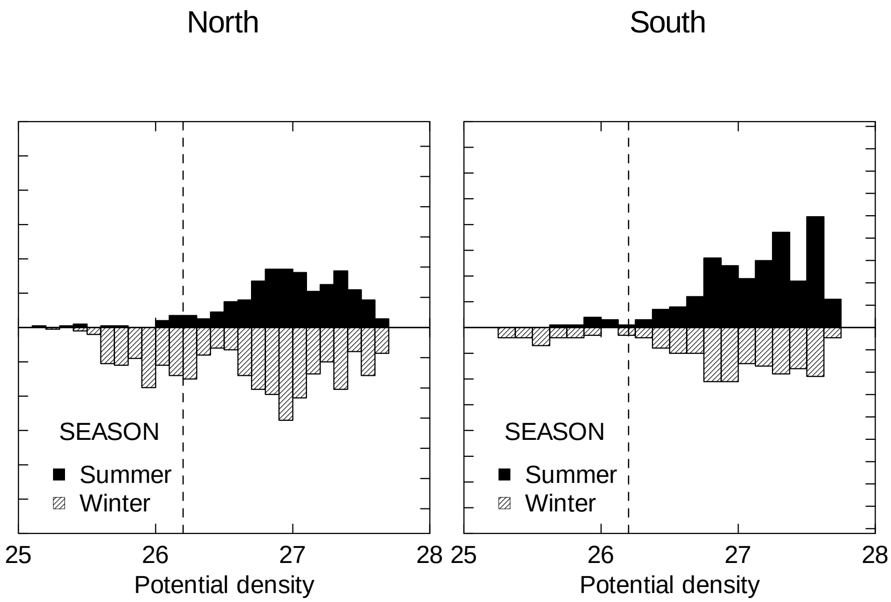

Fig. 5. Potential densities where Ω_{arag} undersaturated water (<1.0) was found in summer 1956 and winter 1957. The right modes are deeper waters in both seasons while the left mode is a mixed layer feature of winter in the northern Gulf of Alaska. The vertical line represents the approximate potential density of $\Omega_{arag}=1.0$ in summer 2007 along the North American continent (Feely et al., 2008).

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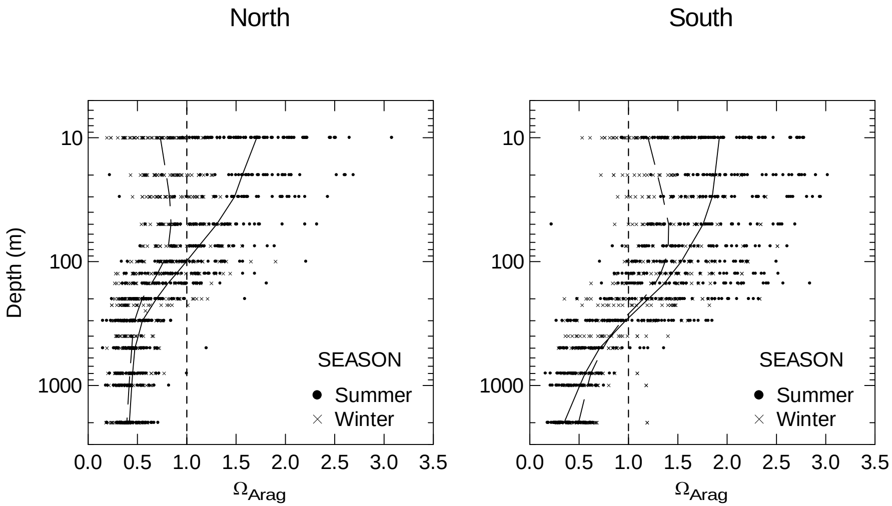

Fig. 6. Aragonite saturation estimates by season, region (north/south of 51° N), and based of depth stratum. Loess trend lines are indicated (winter=dashed line).