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# Modification of NO, PO, and NO/PO during flow across the Bering and Chukchi shelves: Implications for use as Arctic water mass tracers

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**Abstract.** The NO and PO tracers ( $9[\text{NO}_3^-] + \text{O}_2$  and  $135[\text{PO}_4^-] + \text{O}_2$ , respectively,) and their derivative NO/PO have found increasing use in Arctic water mass analyses for identifying the specific basin or shelf areas from which surface waters originate, based upon assumed differences in Pacific- and Atlantic-derived content and basin-to-basin differences within the Arctic. Following shipboard sampling in June–September 1993 and May–June 1994, both north and south of Bering Strait, we have found evidence that Pacific-derived waters flowing north to Bering Strait do not necessarily have any unique NO, PO, or NO/PO identity that would permit unequivocal use as a water mass tracer. In particular, NO/PO ratios in the Bering Sea continental shelf (<150 m) waters varied from 0.7 to 1.1, which encompasses ratios previously reported for Arctic continental shelf and Atlantic origin waters in the Arctic Ocean. The highest NO/PO ratios (~1) in the Bering Sea were observed to the southwest of St. Lawrence Island, close to where high nutrient waters are first upwelled onto the shelf, and seasonally early in the biological production cycle. By contrast, later in the summer, north of Bering Strait, at the depth of the Arctic Ocean nutrient maximum, the highest concentrations of silica (~60  $\mu\text{M}$ ) were associated with low NO/PO ratios (~0.7). Apparent increases in the proportions of sea ice melt in these waters, inferred from  $^{18}\text{O}$  and salinity regressions, were associated with lower NO/PO ratios. This pattern, the potential for sea-air exchange, and a significant relationship between decreases in nitrate/phosphate ratios and both NO/PO ratios and silica concentrations indicate that biological and physical processes north and south of Bering Strait affect the fidelity of these nutrient-based tracers. These results indicate the need for consideration of shelf-based processes before NO/PO ratios and other nutrient-based tracers can be successfully applied as Arctic circulation tracers.

## 1. Introduction

Broecker [1974] defined the conservative water mass tracers NO and PO as  $9[\text{NO}_3^-] + \text{O}_2$  and  $135[\text{PO}_4^-] + \text{O}_2$ , respectively, corresponding to the approximate stoichiometric ratios linking the consumption and production of dissolved oxygen in seawater with nutrient use and regeneration in water parcels isolated from the sea surface. As originally defined, these tracers are most applicable to studies of intermediate and deep

water sources. Nevertheless, in the Arctic Ocean, NO and PO and the combined derivative NO/PO have been used to investigate the source regions of relatively shallow waters above the lower halocline [Jones and Anderson, 1986; Wilson and Wallace, 1990; Anderson and Jones, 1992; Salmon and McRoy, 1994; McLaughlin et al., 1996]. These tracers have proven potentially useful for defining the boundary between water of Pacific and Atlantic origins, particularly since there is evidence for basin-to-basin differences in these parameters [Salmon and McRoy, 1994].

One of the underlying assumptions in the use of the NO/PO ratio, in particular, is that values of this parameter in Atlantic and Pacific source waters are consistently different and distinguishable. This is based upon the significant difference in NO/PO ratios observed in the North Pacific (0.87 to 0.91) relative to North Atlantic waters (~1.0, both [cf. Wilson and Wallace, 1990]). Even lower NO/PO ratios (~0.7) are observed, for the most part in summer, in surface waters of the Chukchi, Beaufort, and East Siberian Sea waters. These lower NO/PO ratios are generally observed in Arctic surface waters with salinities less than 33.1 practical salinity units (psu). At salinities higher than 33.1, below the Arctic Ocean upper halocline, a transition to higher Atlantic-derived ratios occurs [Wilson and Wallace, 1990]. The 33.1 salinity isoline is consistent with the brine-influenced Pacific inflow through Bering Strait [Macdonald et al., 1989; Cooper et al., 1997], supporting the assumption that NO/PO ratios in Pacific-

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derived waters are consistently low [Wilson and Wallace, 1990; Salmon and McRoy, 1994; McLaughlin et al., 1996]. However, the NO/PO values ultimately attributed to North Pacific water are based upon Geochemical Ocean Sections Study (GEOSECS) data obtained from midlatitude waters (44°–53°N [cf. Wilson and Wallace, 1990]), far south of the entry point for Pacific Ocean waters flowing into the Arctic Ocean, Bering Strait. Although deep Bering Sea waters have lower NO values (which correspond to lower NO/PO ratios) than waters in the North Pacific with the same dissolved oxygen content [Tsunogai et al., 1979], it is not clear that this observation or the midlatitude GEOSECS data are important for defining the nutrient tracer content of Arctic surface waters in the vicinity of Bering Strait. The waters transported through Bering Strait are derived from much shallower Pacific/Bering waters that are upwelled onto the north Bering Sea shelf. Over the Bering and Chukchi shelves, three separate physical and biological processes could influence the NO, PO, and NO/PO ratios of those waters. In addition, we have found evidence that sea ice melt and runoff may also directly or indirectly impact these parameters. The three more readily recognizable processes are air-sea exchange, denitrification, and the biological recycling rates of inorganic nitrogen and phosphorus released from the sediments.

First, these Pacific-derived waters have flowed across hundreds of kilometers of shallow (50 m) continental shelf before they reach the Chukchi shelf break. The potential exists for oxygen exchange across the air-sea boundary on the shallow shelf, and this air-sea exchange may vary because of seasonal sea ice cover and wind forcing. In instances where surface waters are supersaturated with dissolved oxygen, NO/PO ratios should decline as oxygen is lost to the atmosphere because a decline in the oxygen concentration will have a proportionally larger effect on the NO parameter. Although this is the appropriate direction to explain the apparent decrease in NO/PO ratios observed from North Pacific values (0.87–0.91) to lower values observed in Amerasian Arctic surface waters (~0.7), the magnitude of the observed change is too large to be explained solely on the basis of a decrease in those waters that are supersaturated with oxygen to levels of near saturation. For example, Wilson and Wallace [1990] point out that for typical Arctic shelf nutrient concentrations, a 100  $\mu\text{M}$  decrease in dissolved oxygen, such as might happen as a result of gas exchange at the sea surface, results in a change of only 0.03 in the corresponding NO/PO ratio. This leads us to consider two biologically mediated factors that would affect the rates of use and the rates of recycling of nitrate and phosphate in the highly productive waters of the Bering and Chukchi shelf.

The availability of recycled nitrate is, in part, affected by rates of sediment-based denitrification. Where this process is significant, nitrate loss will decrease the NO parameter but

leave the PO parameter unchanged. In the Bering and Chukchi Seas, sediment-based denitrification is often cited as probably affecting water column nitrate/phosphate ratios and, by extension, the NO/PO ratio [e.g., Codispoti et al., 1991; Jones et al., 1998]. Nevertheless, it is uncertain whether denitrification rates in these high-latitude sediments are significantly higher than global averages [Koike and Hattori, 1979; Tsunogai et al., 1979; Haines et al., 1981; Gruber and Sarmiento, 1997; Devol et al., 1997; Tyrrell and Law, 1997, 1998]. However, predictive modeling indicates that denitrification rates on continental shelves will be positively correlated to sediment oxygen demand and will also be higher on continental shelves with high primary productivity [Seitzinger and Giblin, 1996]. Significantly, sediment oxygen demand, as well as primary production, are very high on portions of the Bering and Chukchi shelves [Grebmeier and Barry, 1991; Springer et al., 1996].

The third and final factor that we hypothesize may be important in determining nitrate/phosphate ratios in Bering and Chukchi continental shelf waters is high primary production itself (reviewed by Walsh et al. [1989] and Springer et al. [1996]), including the uptake of nutrients at rates that vary from classical Redfield expectations. Cooper et al. [1997] found that for Bering and Chukchi Sea water with the same  $\delta^{18}\text{O}$  (conservative tracer) content, nitrate concentrations in the summer are more variable than phosphate or silica concentrations. One possible reason for this pattern is that nitrate may be removed from the water column and not as quickly or effectively recycled as phosphate, resulting in lower water column nitrate/phosphate ratios during the northward transit across the shelf. Sediments underlying highly productive waters on the Bering and Chukchi shelves have characteristically low carbon/nitrogen ratios [Grebmeier et al., 1988], suggesting that proportionally high amounts of organic nitrogen are deposited to the sediments during the summer season. It is worth noting that a first-order or better estimate of new production on the Bering and Chukchi shelves can be made solely from nitrate concentration deviations from a late winter regression between salinity and nitrate [Hansell et al., 1993], without reference to phosphate concentrations, so biological productivity may be significant in determining nitrate/phosphate ratios in Bering and Chukchi Sea continental shelf waters. Our present study indicates that NO/PO ratios on the Bering and Chukchi continental shelf are strongly affected by biological activity.

## 2. Methods

Water samples for dissolved oxygen and nutrients were collected on three cruises during the summer of 1993 and one in 1994 (Table 1) that spanned a wide region both north and

**Table 1.** Ship Platforms Used in Summer Sampling.

Ship Platform	Dates of Cruise	Nutrient Analyses
<i>Alpha Helix 171</i>	June 9 to July 5, 1993	shore laboratory autoanalyzer, frozen samples
<i>Polar Star</i>	July 25 to Aug. 16, 1993	some data from Cota et al. [1996], shore laboratory autoanalyzer, frozen samples
<i>OKEAN</i>	Aug. 1 to Sept. 18, 1993	shore laboratory autoanalyzer, frozen samples
<i>Alpha Helix 177</i>	May 3 to June 11, 1994	shore laboratory autoanalyzer, frozen samples

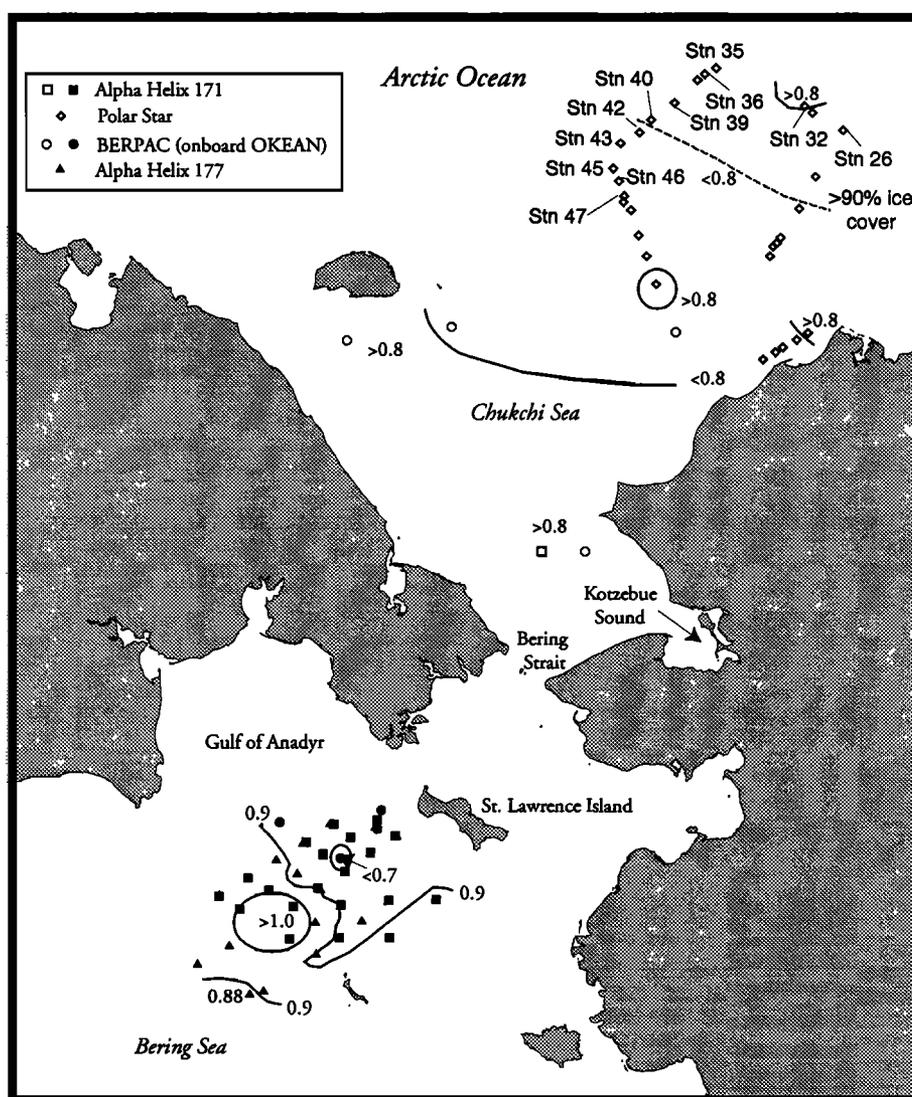
*OKEAN* is an English transliteration of the Russian name of the vessel (*Ocean*)

south of Bering Strait (Figure 1). Nutrient measurements were made using standard autoanalyzer methods, on frozen samples following each cruise, as outlined by *Cota et al.* [1996] and *Cooper et al.* [1997]. Dissolved oxygen measurements were made aboard ship using Winkler or automated micro-Winkler titrations. The conservative tracer  $\delta^{18}\text{O}$  in seawater samples was measured following carbon dioxide equilibrations [*Epstein and Mayeda*, 1953]; mass spectrometric determinations were made using a VG Sira Series II stable isotope mass spectrometer with an external reproducibility of  $\pm 0.1\%$ . Some of these dissolved oxygen, nutrient, and  $^{18}\text{O}$  data have been previously presented as part of other studies, and additional details can be obtained from those sources [*Cota et al.*, 1996; *Cooper et al.*, 1997].

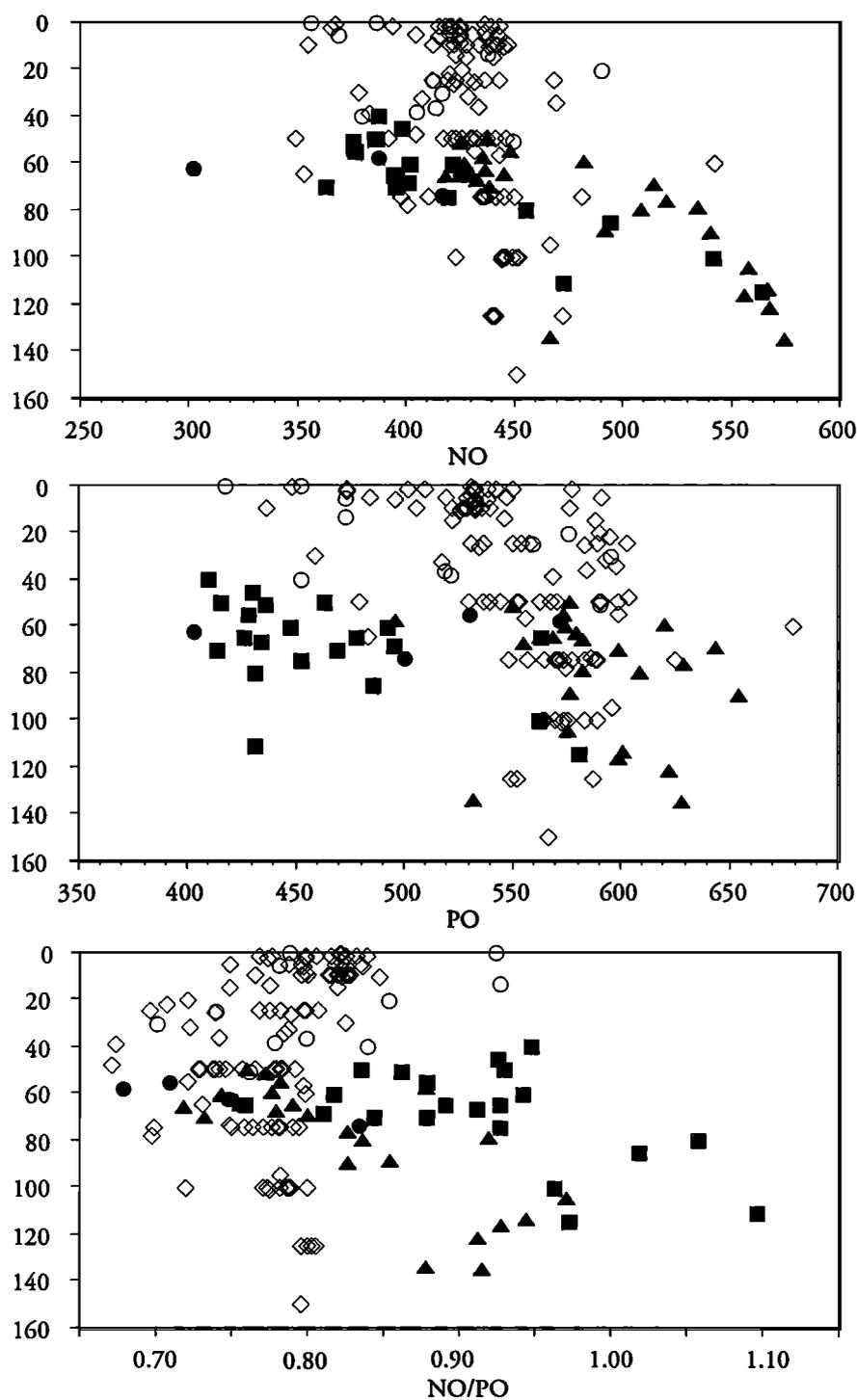
### 3. Results and Discussion

Our water sampling, accomplished during the open water period of June to September 1993 and May-June 1994, indicates that significant deviations from the expected Pacific Ocean NO/PO ratio (0.87 to 0.91) are common (Figures 1 and 2). NO/PO ratios in Bering Sea continental shelf (<150 m) waters varied from 0.7 to 1.1, which encompasses ratios previously reported for Arctic continental shelf (0.7 to 0.8) and Atlantic origin waters ( $\sim 1.0$ ) in the Arctic Ocean.

The highest NO/PO ratios ( $\sim 1$ ) in the Bering Sea were primarily observed in June 1993, shortly after ice breakup, on *Alpha Helix* cruise 171 and on *Alpha Helix* cruise 177 during May-June 1994, which occurred during ice breakup (Figures 1



**Figure 1.** Locations of sampling stations, 1993-1994. NO/PO ratio contours are based upon water column values for waters with salinities <33.2 psu (no Atlantic water). At individual stations, where multiple samples were collected at different depths in the water column, the contours correspond to the mean NO/PO ratios obtained over the water column for salinities less than 33.2 psu. The numbered stations show the location of stations on the 1993 USCGC *Polar Star*, where sufficient numbers of water samples were collected to construct  $\delta^{18}\text{O}$  - salinity regressions, permitting evaluation of the proportions of melted sea ice contributing to the freshwater end-member (see text and Table 3). A dashed line denotes the approximate boundary of 90% sea ice coverage at the time of the *Polar Star* cruise.

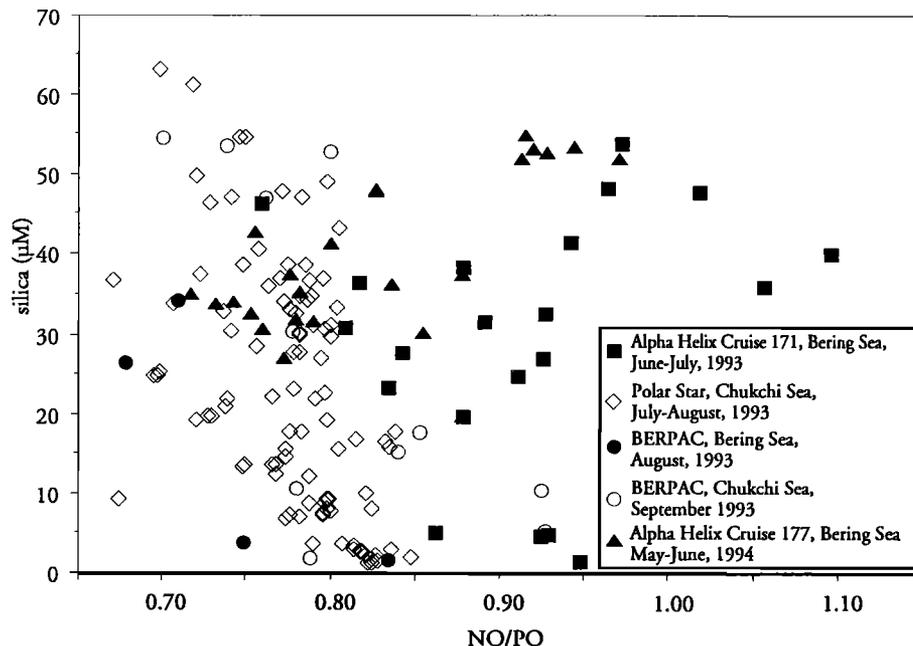


**Figure 2.** (top) NO, (middle) PO, and (bottom) NO/PO ratios in Bering and Chukchi Sea summer water, sampled in 1993 and 1994, relative to depth. Salinities are all <33.2 psu (no Atlantic Water). Open symbols were collected in the Chukchi Sea with diamonds denoting USCGC *Polar Star* and circles denoting the 1993 Fourth Joint United States-Russia Bering and Chukchi Sea Expedition (BERPAC) aboard the vessel *OKEAN*; one station (open square) was collected on *Alpha Helix* cruise 171 in the Chukchi Sea. Solid symbols were collected in the Bering Sea with squares representing *Alpha Helix* cruise 171, circles denoting the 1993 BERPAC cruise, and triangles representing *Alpha Helix* cruise 177.

and 2). An increase in NO/PO ratios within 20 m of the air-sea interface is apparent (Figure 2), particularly in samples collected in waters with significant ice cover on the *Polar Star* cruise. However, the increase ( $\sim 0.1$ ) is larger than might be expected solely from injection of oxygen at the sea-air exchange under near-saturated conditions [Wilson and Wallace, 1990]. Comparison of NO versus depth and PO versus depth plots (Figure 2) for the *Polar Star* cruise indicates that the increase in NO/PO ratios near the sea surface may have been more due to decreases in PO, rather than changes in NO. For water samples collected on the *Polar Star* cruise, the mean PO value for samples collected from deeper than 20 m was  $565.8 \pm 32.3$  standard deviation (number of samples  $n=68$ ), which declined marginally to a mean of  $526.2 \pm 32.3$  standard deviation for samples collected within 20 m of the surface ( $n=39$ ). NO, by contrast, showed little dependence on proximity to the sea surface, with mean values increasing from  $424.1 \pm 21.5$  standard deviation for water samples from greater than 20 m depth to  $433.3 \pm 27.5$  for *Polar Star* samples collected within the surface 20 m. This implies a possibly higher rate of phosphate utilization in near-surface waters, which is consistent with the apparent availability and use of recycled ammonium that was observed during the *Polar Star* cruise in these ice-associated waters [Cota et al., 1996].

The highest NO/PO ratios ( $\sim 1$ ) in the Bering Sea coincided with the highest silica concentrations ( $\sim 60 \mu\text{M}$ ) that were simultaneously measured (Figure 3). The highest NO/PO ratios were observed to the southwest of St. Lawrence Island (Figures 1 and 2), over sediments with relatively high benthic biomass and sediment oxygen demand [Grebmeier and Cooper, 1995]. If we assume that water advected onto the north Bering shelf at a depth of 65 to 75 m has an initial nitrate concentration of  $15 \mu\text{M}$  [Cooper et al., 1997] and a high dissolved oxygen content

( $\sim 350 \mu\text{M}$ ), NO values approaching  $500 \mu\text{M}$  should be expected in waters advected onto the Bering shelf. Analogously, for phosphate, in the Gulf of Anadyr, bottom water concentrations at this depth range from 2 to  $3 \mu\text{M}$  [Whitledge et al., 1992]. If we assume that  $2 \mu\text{M}$  phosphate is better matched as a nutrient endpoint on a stoichiometric basis with  $15 \mu\text{M}$  nitrate, expected PO values in water as it is brought onto the Bering shelf should be in excess of  $600 \mu\text{M}$ , leading to NO/PO ratios of  $\sim 0.83$ . Our observations southwest of St. Lawrence Island are only partly consistent with these expectations. While some PO values in excess of  $600 \mu\text{M}$  were observed (Figure 2), NO values exceeded expectations ( $\sim 500 \mu\text{M}$ ) in a number of instances, and exceeded PO values for the three stations collected on the early season cruise of the R/V *Alpha Helix* in 1993 (Figures 1 and 2). For 18 individual water samples collected during this study in the Bering Sea that had NO/PO ratios in excess of 0.90, mean concentrations of phosphate and dissolved oxygen (Table 2) were below levels expected for waters advected onto the Bering shelf, as discussed above. However, nitrate was, in places and on a mean basis, relatively higher than expectations ( $16.7$  versus  $15 \mu\text{M}$ ), and ammonium was present, particularly in bottom water samples, where it made up a significant fraction of total inorganic nitrogen (Table 2). Salinity and oxygen 18 data (Table 2) indicate that these waters with high NO/PO ratios have a conservative tracer content similar to water passing through Bering Strait [Cooper et al., 1997]. Consequently, it appears that these waters with high NO/PO ratios may have been enriched in nitrate by a mean  $\sim 10\%$  (the difference between 15 and  $16.7 \mu\text{M}$ ; see Table 2) upon reaching the Bering shelf, probably through nitrification of ammonium released from the sediments. During transport over the Bering and Chukchi shelves, NO/PO ratios must then



**Figure 3.** NO/PO ratios in Bering and Chukchi Sea summer water, sampled in 1993 and 1994, relative to silica. Depths are  $>20$  m to exclude any potential effects to NO/PO ratio resulting from oxygen injection or evasion at the sea surface. Salinities are all  $<33.2$  psu (no Atlantic Water); these data indicate higher NO/PO ratios were present in June 1993 and 1994 in the Bering Sea, shortly after ice retreat. Reoccupation of Bering and Chukchi stations during the BERPAC cruise in late summer 1993 shows that water column NO/PO ratios may have declined over the course of the summer.

**Table 2.** Mean and Standard Deviation Nutrient and Tracer Content of 18 Water Samples Collected in the Bering Sea with High NO/PO ratios (>0.90) on *Alpha Helix* Cruises 171 and 177.

	Mean	Standard Deviation
Nitrate, $\mu\text{M}$	16.7	9.9
Phosphate, $\mu\text{M}$	1.3	0.7
Ammonium, $\mu\text{M}$	1.7	1.4
Salinity, psu	32.449	0.430
$\delta^{18}\text{O}_{\text{V-SMOW}}$ , ‰	-0.62	0.24
Dissolved oxygen, $\mu\text{M}$	332.0	27.0

See Figure 2.

reverse and decrease to the ratios observed in most of the Chukchi Sea (Figure 1). Denitrification is one likely mechanism for such a decrease, although it is possible that our sampling, limited to summer, would also not detect a differential rate of recycling of phosphate and nitrate from sedimenting particulate matter.

*Seitzinger and Kroeze* [1998] recently estimated that nitrous oxide emission rates from continental shelves are in the range of 2 to 3.6 g N m<sup>-2</sup> yr<sup>-1</sup>, which over a ~50 m deep water column on the Bering and Chukchi shelves, would imply an annual flux introduced into each 5 x 10<sup>5</sup> L water column above each m<sup>2</sup> of continental shelf sediments of 1.4 to 2.6 x 10<sup>5</sup>  $\mu\text{mol}$  of

nitrogen. If we make the simplifying assumption that all water passing over the Bering and Chukchi shelves comes into contact with bottom sediments and divide the total flux introduced from each m<sup>2</sup> of continental shelf sediment by a 50 m water column, the annual contribution of nitrous oxide (and corresponding loss of nitrate) into (and from) each liter of water is 2.8 to 5.1  $\mu\text{mol}$ . However, the approximate time for transit of the Bering and Chukchi shelf is of the order of 6 months [see, e.g., *Weingartner et al.*, 1998], so loss of 1 to 3  $\mu\text{mol L}^{-1}$  of nitrate during a 6 month transit of shelf waters would seem to be a more reasonable estimate. If this first-order estimate is correct, 5 to 20% of the ~15  $\mu\text{M}$  nitrate

**Table 3.** The  $^{18}\text{O}$  - Salinity Regression Data for Selected Stations From *Polar Star* Cruise, July 25- August 16, 1993.

Station	y intercept	Correlation Coefficient $r^2$	Number of Samples Analyzed	Depth of Silica Maximum Sampled, m	Silica Maximum, $\mu\text{M}$	NO/PO at Depth of Silica Maximum
47	-3.2	0.64	7	75	54.6	0.75
45	-5.8	0.91	3	75	40.7	0.76
46	-6.4	0.93	11	75	63.6	0.70
43	-8.1	0.96	8	74	38.6	0.77
35	-9.5	0.53	9	100	34.3	0.79
40	-10.4	0.98	9	100	36.7	0.79
36	-10.9	0.96	9	100	34.0	0.77
39	-11.0	0.97	6	100	34.7	0.78
42	-11.2	0.97	8	101	38.7	0.77
32	-12.6	0.82	4	150	33.3	0.81
26	-15.5	0.96	7	125	43.2	0.81

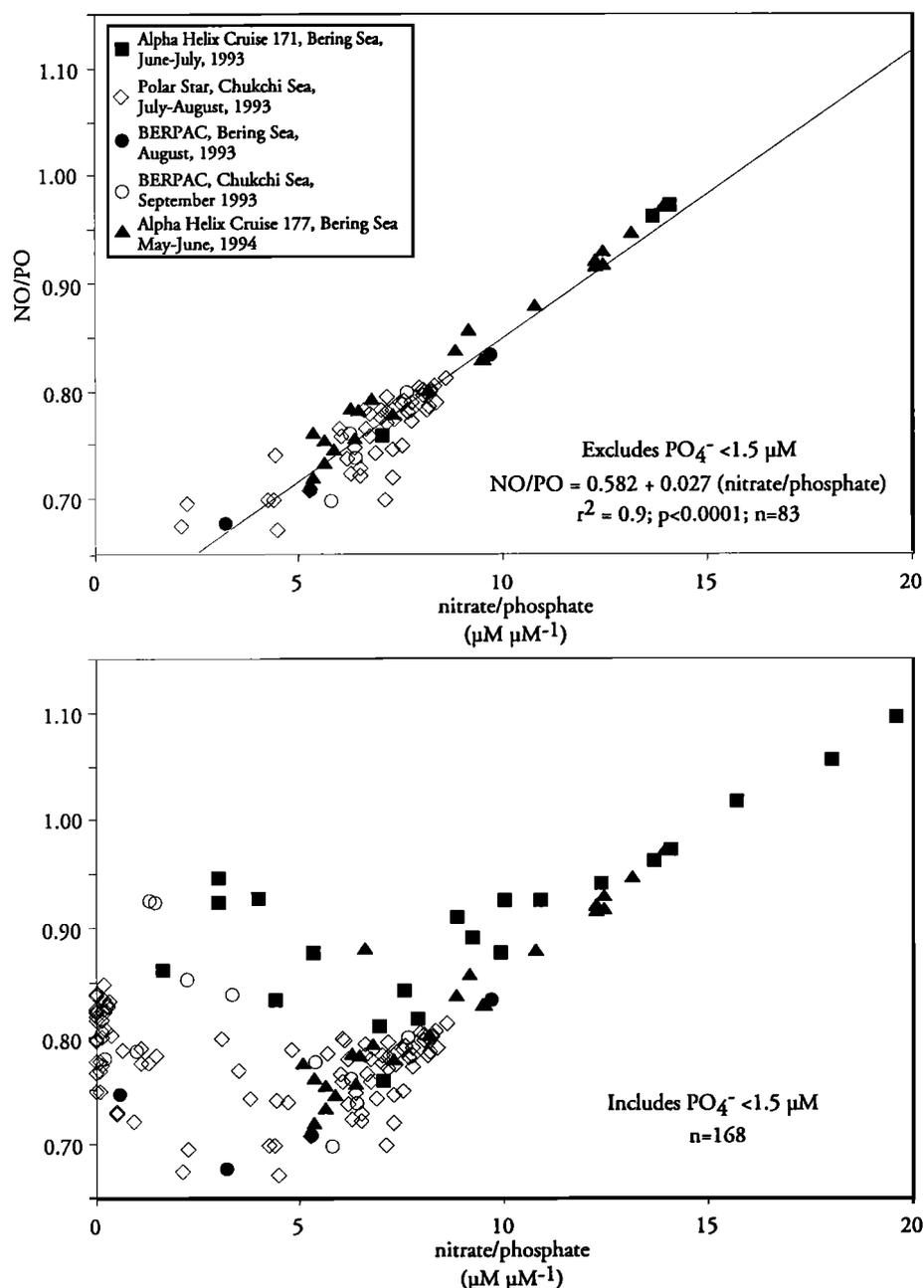
The 11 stations (locations shown in Figure 1) were selected based upon the criteria that sufficient samples of varying isotopic content and salinity had been collected in surface waters to derive a significant relationship between salinity and  $\delta^{18}\text{O}$ . The y intercept shown is the solution to the equation, salinity =  $\delta^{18}\text{O}$  + intercept, which estimates the  $\delta^{18}\text{O}$  value of the freshwater (end-member) component of the surface seawater. The y intercept for Arctic river inflows (no sea ice melt) is approximately -21.1; sea ice, including overlying snow, is ~-2 [cf. *Cooper et al.*, 1997]. The less negative the y intercept is, the higher is the proportion of sea ice melt contributed to the freshwater component of surface water. The stations are arranged in approximate descending order of sea ice melt contributions. The equation parameters shown are for Arctic Ocean surface waters with salinities less than 33.2 psu (no Atlantic Ocean contributions). Nutrient, dissolved oxygen and salinity data are derived from *Cota et al.* [1996] or unpublished bottle data from the same cruise.

brought onto the Bering shelf is lost through denitrification before transfer off the Chukchi shelf.

North of Bering Strait, at the depth of the Arctic Ocean nutrient maximum, we observed the highest concentrations of silica ( $\sim 60 \mu\text{M}$ ), of presumed Pacific origin, associated with low NO/PO ratios ( $\sim 0.7$ ). For all waters sampled on the U.S. Coast Guard *Polar Star* cruise in which the salinity was  $<33.2$  psu (no Atlantic water), mean  $\text{O}_2$  concentrations were  $366.7 \pm 56.7$  ( $n=121$ ), mean NO was  $429.9 \pm 25.7$  ( $n=108$ ), mean PO was  $551.8 \pm 37.4$  ( $n=108$ ), and the mean concentration of  $\text{NO}_3^-$  was  $7.0 \pm 6.6 \mu\text{M}$  ( $n=113$ ). If our estimates of the loss of nitrate due to denitrification during shelf transit are added to the mean nitrate concentrations observed on the *Polar Star*

cruise, NO/PO ratios in Chukchi Sea waters with salinities  $<33.2$  psu would approach or exceed 0.90. Therefore it seems entirely possible that denitrification is the significant factor governing the apparent decrease we observe in NO/PO ratios between the Bering shelf region, where Pacific waters are first advected onto the shelf, and the Chukchi shelf waters, where contact with bottom sediments are lost.

The upper halocline waters in the Chukchi Sea with the highest silica concentrations were also sampled where overlying surface waters contained relatively high proportions of freshwater originating from sea ice melt compared to river runoff. These inferences of varying freshwater origin are based upon calculated freshwater end-



**Figure 4.** NO/PO ratios in Bering and Chukchi Sea summer water, sampled in 1993, relative to nitrate/phosphate ratios, (top) excluding phosphate concentrations  $<1.5 \mu\text{M}$  [Tyrell and Laws, 1997] and (bottom) including such concentrations in the regression analysis. Salinities are all  $<33.2$  psu (no Atlantic Water).

members, using  $^{18}\text{O}$  and salinity regressions (Table 3). Stations sampled in >90% ice cover (Figure 1) tended to have lower proportions of melted sea ice relative to river runoff in surface waters (Table 3). These distributions of  $^{18}\text{O}$  and salinity indicate that summer sea ice melt in the surface waters of the Chukchi and Beaufort Seas may help restrict vertical mixing and dilution of the Bering Sea contribution to the Arctic Ocean upper halocline, facilitating its wide lateral dispersion. For example, we observed the highest silica concentrations at stations with apparently high proportions of sea ice melt (e.g., stations 43 and 44-47; see Table 3). Silica maxima were shallower at such stations, and NO/PO ratios also tended to be lower (Table 3). This observation indicates that the melting of sea ice may also play some role in modifying the NO/PO ratio, either by decreasing NO or increasing PO. Evaluation of NO and PO separately relative to silica in the four stations (43 and 44-47, Table 2) with high ice melt and a shallow silica distribution indicated that a combination of relatively low NO (410.7-442.0  $\mu\text{M}$ ) and relatively high PO (583.3-589.4  $\mu\text{M}$ ) were responsible for the low NO/PO ratios observed. In waters where sea ice melt was less important, the nutrient maximum showed wider dispersion in the water column with generally lower maximum values, and the depths of the silica maxima were also typically lower (Table 3).

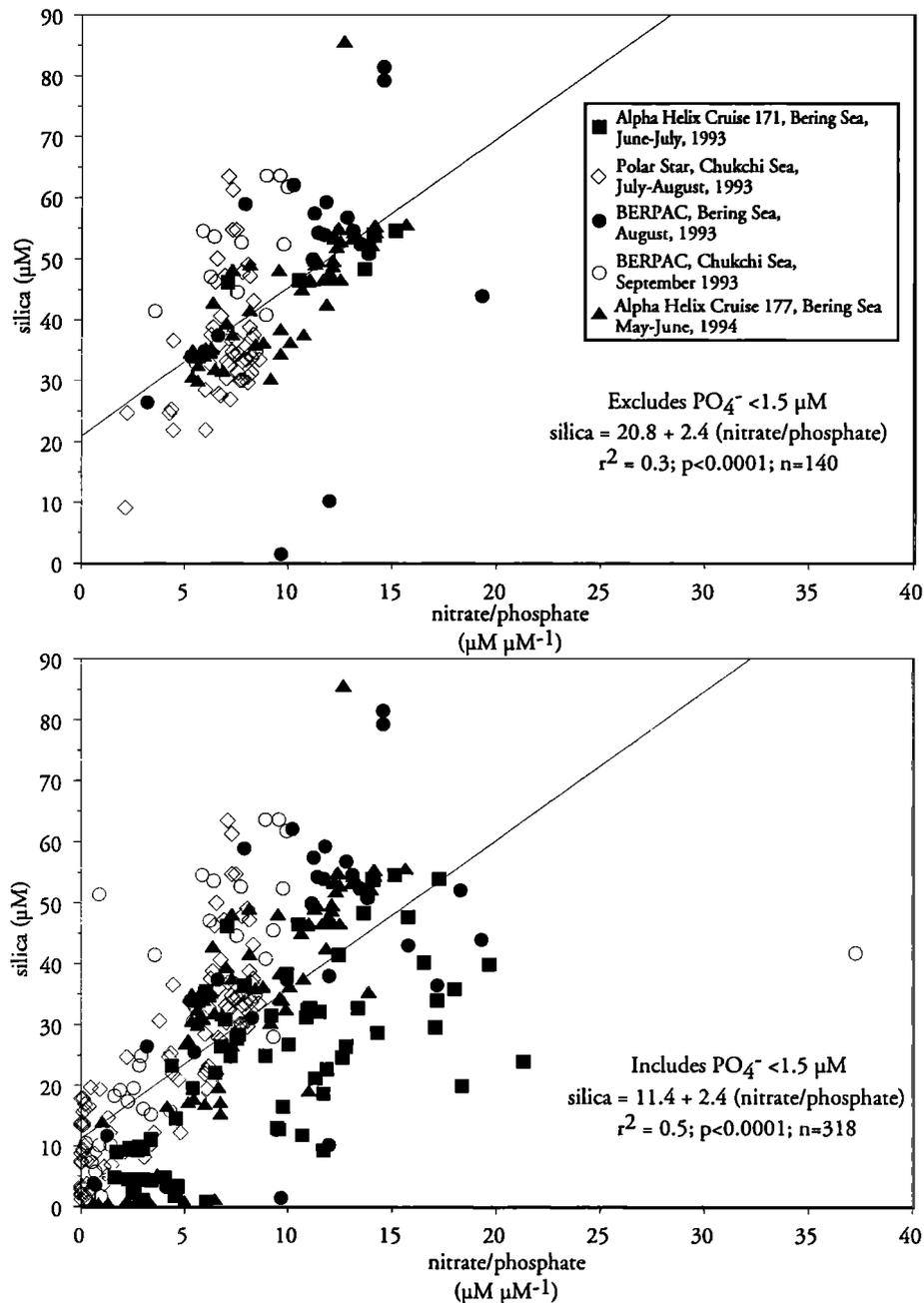
During this study, we found that near-classical Redfield nitrate/phosphate ratios of  $\sim 15$  were predominantly found either in the Bering Sea early in the season and/or to the southwest of St. Lawrence Island, where nutrient-rich waters are first brought up onto the northern Bering Shelf (Figure 4). This implies some degree of dependence of nitrate/phosphate ratios upon biological activity in the Bering Sea, indicating that as biological activity draws down silica concentrations in the water column during the northward transit toward Bering Strait, nitrate simultaneously is also being removed but at a proportionally faster rate than phosphate. In many instances, particularly north of Bering Strait, we observed nitrate/phosphate ratios lower than the classical Redfield expectations of  $\sim 15$  (Figures 4 and 5). In addition to denitrification and the possibility of different rates of recycling of inorganic nitrogen and phosphate, it is also possible that specific phytoplankton communities might be removing nitrate and phosphate at ratios independent of Redfield expectations, but we have no independent evidence that such a process is operative on the Bering and Chukchi shelves. The decline in nitrate/phosphate ratios is also significantly correlated with a decline in NO/PO and silica (Figures 4 and 5), particularly for those samples with phosphate concentrations in excess of 1.5  $\mu\text{M}$ . Using the reasoning of Tyrell and Law [1997], in evaluating nitrate/phosphate ratios, we excluded samples with phosphate concentrations below 1.5  $\mu\text{M}$ , based upon the presumption that a larger proportional error would bias the nitrate/phosphate ratio at low nutrient concentrations (Figures 4 and 5). While it is not surprising that two semi-independent variables (NO/PO and nitrate/phosphate) were significantly correlated, the high degree of correlation ( $r^2 = 0.90$ ) explained by the least squares regression suggests that other processes that affect the NO/PO parameter alone, such as air-sea exchange, are of relatively minor importance on the Bering and Chukchi shelves. Clearly, some additional work is needed to verify independently the decrease in NO/PO relative to biologically important nutrients. Despite this positive correlation south of Bering Strait, there is no clear

relationship or perhaps even a weak negative correlation between NO/PO ratios and silica within the Chukchi Sea (Figure 3). North of Bering Strait, greater contributions of ice melt to surface waters and silica from rivers draining into Kotzebue Sound [Cooper *et al.*, 1997] may tend to confound any hypothesized relationship between NO/PO ratios and a biologically important nutrient such as silica. Another uncertainty is variability in dissolved oxygen concentrations on the Chukchi shelf, which are controlled by much higher biological production in Anadyr versus Alaska coastal waters [Penta and Walsh, 1995]. While additional data are needed to fully assess the causes of change in NO/PO ratios across the Bering and Chukchi shelves, our observations in 1993 and 1994 suggest that biological utilization of nutrients has an important influence on summer NO, PO, and NO/PO ratios observed on these Arctic continental shelves.

#### 4. Conclusions

We hypothesize that the apparent difference in NO/PO ratios between the Bering and Chukchi Seas, and possibly also on a seasonal basis between May-June and August in the Bering Sea, is related to a greater proportional loss of inorganic nitrate relative to phosphate from northward flowing Bering Sea waters before incorporation into the Arctic Ocean nutrient maximum. At least during the summer period when we sampled, a larger proportion of metabolized nitrate (relative to phosphate) was not effectively recycled from the sediments or within the water column, leading to a decline in both nitrate/phosphate ratios and the NO/PO parameter. The apparent decreases we observe in NO/PO ratios are also consistent with denitrification during shelf transport. In addition, we found that the proportions of sea ice melt that are contributed to the Polar Mixed Layer of the Arctic Ocean appear to play a role in influencing NO/PO ratios during the summer (Table 3). These processes appear to be more important in influencing NO/PO ratios than air-sea exchange of oxygen.

Our data do not contradict previous observations that surface summer waters north of Bering Strait have low ( $\sim 0.7$ ) NO/PO ratios but, instead, suggest that these low ratios are not necessarily related to a Pacific origin and may be established north of the Bering Sea or during the transit of the Bering and Chukchi shelves. The paucity of NO and PO data available from the Chukchi Sea outside of the summer season limits our capabilities to evaluate all of the potential mechanisms that may determine the fidelity of these nutrient-based tracers in Arctic surface waters. Better sampling coverage at other times of the year could establish whether these low NO/PO ratios ( $\sim 0.7$ ) are possibly established in the Arctic Ocean, rather than preformed in the Bering Sea, and if the ratios are consistently present in the early season when we observed higher ratios in the Bering Sea. The wide range of NO/PO ratios observed also suggests that differentiation between upper and lower halocline waters in Arctic Ocean, based upon nutrient-based tracers, may require reassessment. For example, if higher NO/PO ratios ( $\sim 1.0$ ) are observed in the winter time period in Arctic Ocean waters with Pacific tracer compositions, the results could be important for reinterpreting existing Arctic Ocean data sets. In either case, these results could have a bearing on understanding the potential for alteration in NO, PO, and NO/PO ratios in waters transiting the shallow Bering and Chukchi continental shelves as a function of biological processes.



**Figure 5.** Relationship between silica concentrations and nitrate/phosphate ratios for samples collected in 1993-1994, (top) excluding phosphate concentrations  $< 1.5 \mu\text{M}$  [Tyrell and Laws, 1997] and (bottom) including such concentrations in the regression analysis. In the Bering Sea, (but not in Chukchi) at high NO/PO ratios and covarying high silica concentrations, nitrate/phosphate ratios are close to Redfield expectations ( $\sim 15$ ), but decrease during summer transport north of Bering Strait.

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