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Nitrate anomaly in the upper nutricline in the northern South China Sea - Evidence for nitrogen fixation

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[1] Up to 2 μM of nitrate anomaly, N^* , were found in the upper nutricline at the South East Asia Time-series Study (SEATS) site in the northern South China Sea (SCS). These concentrations were among the higher values reported in the Pacific and indicate the significant contribution of the remineralization of nitrogen-rich organic matter formed by nitrogen fixation to the nutrient dynamics of the area. The concentrations were systematically higher, by up to 2.5 μM , in the Fall through the early Spring, during the northeast monsoon, than in the Summer, suggesting that the impact of nitrogen fixation was higher during the former time period. This pattern is in phase with that of the atmospheric deposition of Asian dust to the northern SCS. The coherence is consistent with a coupling between nitrogen fixation and the availability of atmospherically derived iron.

INDEX TERMS: 1050 Geochemistry: Marine geochemistry (4835, 4850); 4835 Oceanography: Biological and Chemical: Inorganic marine chemistry; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 1615 Global Change: Biogeochemical processes (4805); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4227 Oceanography: General: Diurnal, seasonal, and annual cycles; 4243 Oceanography: General: Marginal and semienclosed seas. **Citation:** Wong, G. T. F., S.-W. Chung, F.-K. Shiah, C.-C. Chen, L.-S. Wen, and K.-K. Liu, Nitrate anomaly in the upper nutricline in the northern South China Sea - Evidence for nitrogen fixation, *Geophys. Res. Lett.*, 29(23), 2097, doi:10.1029/2002GL015796, 2002.

1. Introduction

[2] The marine nitrogen cycle plays a major role in controlling the biological pump for the sequestration of atmospheric carbon in the deep sea [Falkowski, 1997]. Nitrogen fixation has long been proposed as a dominant allochthonous source of combined nitrogen to the ocean [Codispoti and Christensen, 1985]. Yet it is still not well understood or quantified [Capone *et al.*, 1997] as its episodic nature poses severe constraints on direct observations. The environmental conditions that are conducive to the occurrence of nitrogen fixation are: a water temperature exceeding 20°C, the absence of inorganic combined nitro-

gen, a stratified water column and the availability of iron [Karl *et al.*, 1997]. All four conditions are met in the northern South China Sea (SCS) [Duce and Tinsdale, 1991; Gong *et al.*, 1992; Chao *et al.*, 1996] so that it should be a preferred site for nitrogen fixation. Indeed, among the small number of measurements of the rates of nitrogen fixation in the world oceans, the rates found in the SCS were among the higher values reported [Capone *et al.*, 1997]. Nonetheless, while the first three conditions are met year-round, the input of iron, through the atmospheric deposition of dust, to the SCS is not uniform through the year although the annual flux is among the highest to oligotrophic waters [Duce and Tinsdale, 1991]. The depositions occur primarily from the Fall through the early Spring during the northeast monsoon and are sparse during the southwest monsoon in the Summer [Merrill *et al.*, 1989; Husar *et al.*, 1997]. Thus, if the availability of iron is the controlling factor for nitrogen fixation in the northern SCS, the intensity of the process may vary temporally.

[3] Organic matter formed by nitrogen fixation is enriched in nitrogen relative to phosphorus [Karl *et al.*, 1992]. Its subsequent remineralization in the nutricline results in a nitrate anomaly which integrates the effect of nitrogen fixation over time, averages out the episodic signal and can then be used as an indicator of this process [Deutsch *et al.*, 2001]. The South East Asia Time-series Study (SEATS) in the northern SCS was initiated by the National Center for Ocean Research of Taiwan in September 1998 and the station has been maintained since September 1999. Here, we report evidence for nitrogen fixation at the SEATS site from the nitrate anomaly in its upper nutricline.

2. Methods

[4] The SEATS station, S1, is located at 18°N and 116°E (Figure 1). It was occupied six times between September, 1999 and July, 2000 aboard R/V Ocean Researcher III during cruises 561 (September 17–22) and 585 (November 22–26) in 1999, and, 600 (January 17–18), 607 (March 12–17), 629 (May 23–26) and 644 (July 25–27) in 2000. During each occupation of the station, the distributions of temperature and salinity were recorded with a SeaBird model SBE9/11 conductivity-temperature-depth (CTD) recorder. Discrete water samples were collected with GO-FLO bottles mounted onto a Rosette sampling assembly (General Oceanic). Sub-samples were quick-frozen with liquid nitrogen on board ship and returned to a shore-based laboratory for the determination of nitrite, (nitrate + nitrite),

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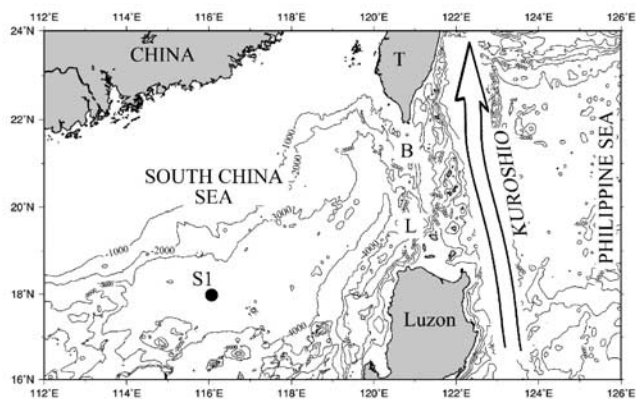


Figure 1. The location of the South East Asia Time-series Study (SEATS) station S1. B - Bashi Channel; L - Luzon Strait; T - Taiwan.

or (N + N), and phosphate. (No nutrient data was available from cruise 600.) Nitrite and (N + N) were determined by the standard pink azo dye method which has been adapted for use with a flow injection analyzer [Strickland and Parsons, 1972; Pai *et al.*, 1990]. Phosphate was determined manually with the standard molybdenum blue method [Strickland and Parsons, 1972]. The precisions for the determinations of nitrite, (N + N) and phosphate were ± 0.03 , ± 0.3 and ± 0.01 μM , respectively.

[5] Samples at a nearby location ($18^\circ 8'N$, $115^\circ 36'E$) were obtained in April, 1997 (R/V Ocean Researcher I Cruise 484) and analyzed for $\delta^{15}N$ in (N + N) by the method of Liu *et al.* [1996], with a precision of $\pm 0.3\text{‰}$ at concentrations of (N + N) exceeding 20 μM .

3. Results and Discussion

[6] The relationships between potential temperature and salinity (Figure 2a) were typical of those observed previously in the northern SCS [Shaw *et al.*, 1996]. The Tropical Water and the Intermediate Water were represented as a salinity maximum ($S > 34.6$; $\sigma_\theta \approx 25.2$) at around 150 m and a salinity minimum ($S \approx 34.4$; $\sigma_\theta \approx 26.8$) at around 500 m. Below 15°C , which corresponded to a depth of about 200 m, the relationships were indistinguishable from each other through the year, indicating that seasonal effects on the hydrography were confined to the top 200 m of the water column. The profiles of potential temperature in the top 300 m (Figure 3b) indicated the expected seasonal pattern of Summer heating and Winter cooling in the surface waters. The surface temperature was at a maximum of 28°C in July and it dropped systematically to a minimum of 24°C in January before it rebounded in March. The mixed layer was about 30 m thick in July. It thickened progressively to 100 m in January before it thinned again.

[7] The distributions of (nitrate + nitrite) or (N + N), nitrite and phosphate in September 1999 are shown in Figures 3 and 4. The upper nutricline, where the gradients in the concentrations of (N + N) and phosphate were the steepest and the remineralization of sinking organic matter was the most intensive, was located between the base of the mixed layer and 500 m. The primary nitrite maximum, which is indicative of nitrification, was located at the top of the upper nutricline (Figure 4). Below 500 m, the concen-

trations of (N + N) and phosphate changed more gradually with depth until they reached an almost constant level below 1000 m.

[8] In the normal biological pump, remineralization leads to the release of (N + N) and phosphate to the water column in a molar ratio of 16:1 [Redfield *et al.*, 1963]. The remineralization of nitrogen-rich organic matter formed by nitrogen fixation elevates while denitrification reduces this ratio. Nitrate anomaly, N^* , is defined as [Deutsch *et al.*, 2001]:

$$N^* (\mu\text{M}) = N - 16 P + 2.90$$

where N and P are the concentrations of (N + N) and phosphate. Aside from the effects of mixing, N^* represents the deviation from the normal biological pump as a result of the sum of the effects of denitrification and nitrogen fixation. The constant of 2.90 μM is the global average deficit of nitrate resulted from denitrification. Thus, the global average N^* is assumed to be 0 and N^* is a relative value, with a more positive value indicating a more dominant effect of nitrogen fixation over denitrification. Concentrations of N^* at St. S1

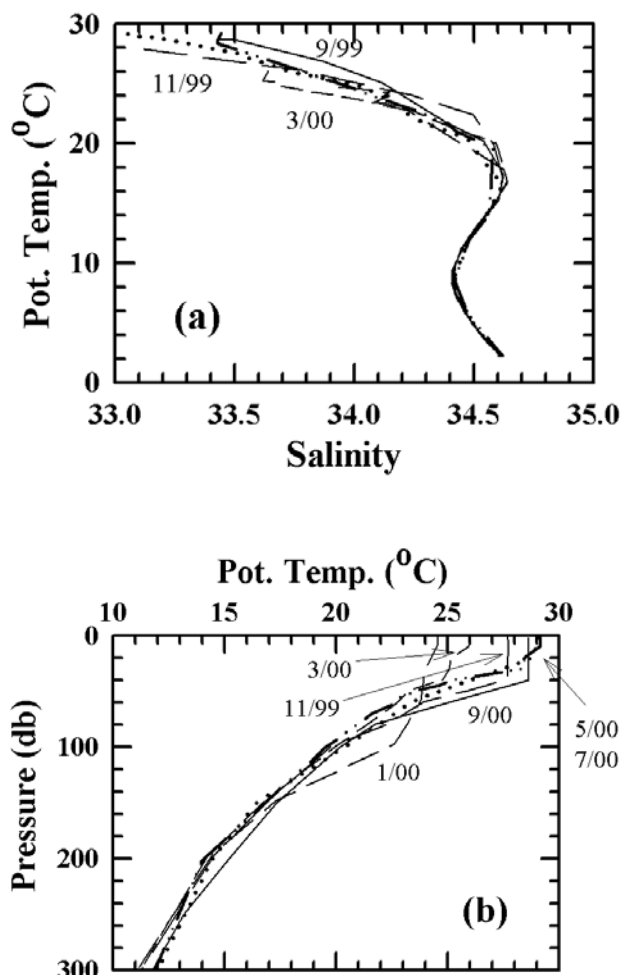


Figure 2. (a) The relationship between potential temperature (Pot. Temp.) and salinity at the SEATS site, and (b) the vertical distributions of potential temperature in the top 300 m. _____ - 9/1999; long dash - 11/1999; medium dash - 1/2000; short dash - 3/2000; ... - 5/2000; ____ - 7/2000.

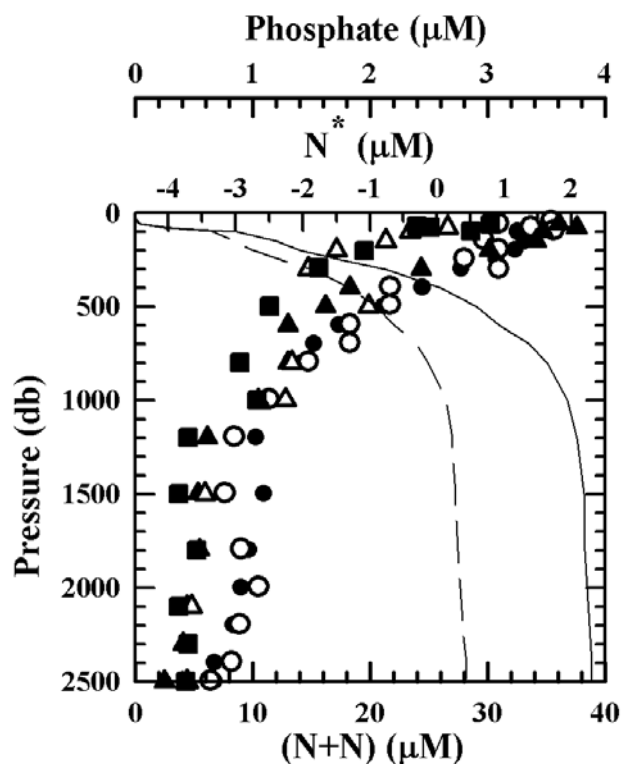


Figure 3. The vertical distributions of (N + N) (○) and phosphate (△) in September, 1999, and N* (● - 9/1999; ○ - 11/1999; ▲ - 3/2000; △ - 5/2000; ■ - 7/2000).

were computed in samples where the concentrations of (N + N) and phosphate exceeded 1 and 0.1 μM respectively. At lower concentrations, the estimated values of N^* were too uncertain to be meaningful. Based on the analytical uncertainties in the determinations of (N + N) and phosphate, the uncertainty of N^* was estimated to be $\pm 0.5 \mu\text{M}$. Another indication of the uncertainty is the variations in N^* in the deep waters where it should have remained constant. Below 2000 m, the average concentration of N^* during the sampling period was $-3.4 \pm 0.4 \mu\text{M}$. Thus, both approaches estimated similar uncertainty. Nonetheless, the data from September and November were consistently higher than those from March, May and July (Figure 3). The average difference between these two subsets of data was about $0.7 \mu\text{M}$. The variations in N^* at a given depth in the deep water was caused primarily by this systematic offset. Within each subset, the data were highly coherent and the average deviation from the mean was $\pm 0.2 \mu\text{M}$. Thus, concentration differences exceeding $0.2 \mu\text{M}$ within each subset and exceeding $0.7 \mu\text{M}$ between the two subsets would indicate real temporal changes.

[9] High concentrations of N^* were found at the top of the upper nutricline through the year (Figure 3). The higher values, about $2 \mu\text{M}$, were at the higher end of the values reported in the Pacific [Deutsch et al., 2001]. These elevated concentrations of N^* were found in close proximity to the primary nitrite maximum, which associates with nitrification, and the $\delta^{15}\text{N}$ minimum, which is indicative of the remineralization of ^{15}N -poor organic matter formed by nitrogen fixation [Liu et al., 1996], observed at about the same location in April, 1997 (Figure 4). Linear regression

analyses of the relationships between (N + N) and phosphate for all data points below 150 m yielded N:P molar ratios of 13.4–14.7 (average = 14.0 ± 0.6). However, when the data points in the upper nutricline (150 to 500 m) and below 500 m were treated separately, the ratios were invariably higher in the former (13.5–15.8; average = 14.5 ± 0.8) than in the latter (11.2–13.5; average = 12.2 ± 0.7) in each cruise. The elevated N:P ratio in the upper nutricline is also consistent with the suggestion that the remineralization of nitrogen-rich organic matter formed by nitrogen fixation is an important contributor to the nutrient dynamics of the northern SCS. Any preferential regeneration of nutrients during the early stage of remineralization would favor phosphate over nitrate [Karl et al., 2001] and lead to low rather than high N^* in the upper nutricline. Below the upper nutricline, N^* decreased rapidly with depth to $-3 \mu\text{M}$ at 1000 m at the bottom of the nutricline, and then more gradually to $-3.5 \mu\text{M}$ at 2500 m. Both the shape of the profiles and the concentrations found were similar to those reported in the northwestern Subtropical Pacific [Deutsch et al., 2001].

[10] In the relationships between N^* and potential density, σ_θ , the data from May and July coalesced around one trend while the data from September, November and March followed another trend (Figure 5). The concentrations of N^*

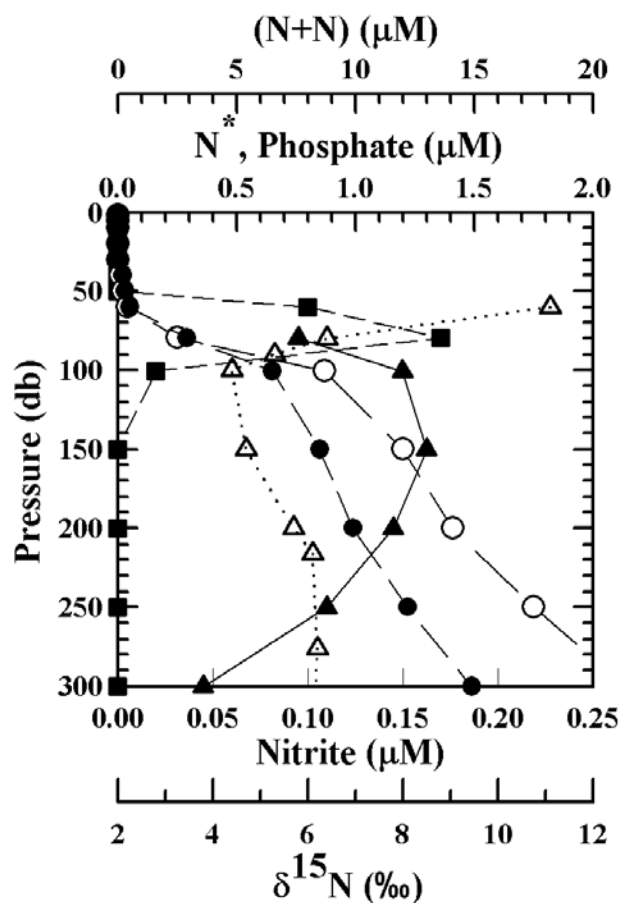


Figure 4. The vertical distributions of (N + N) (○), phosphate (●), N^* (▲) and nitrite (■) in the top 300 m in September, 1999. △ - $\delta^{15}\text{N}$ in April, 1997 at $18^\circ 8' \text{N}$, $115^\circ 36' \text{E}$.

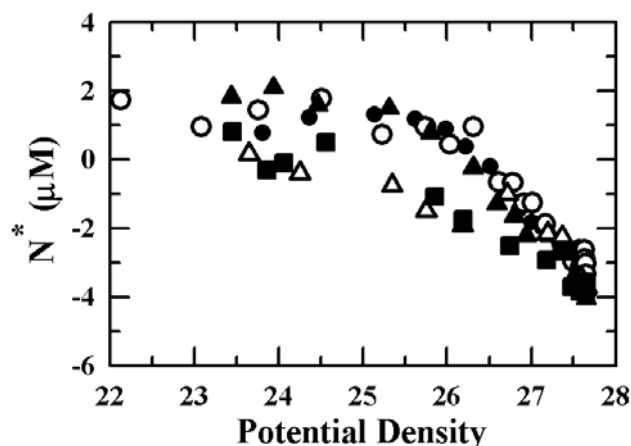


Figure 5. The relationship between N^* and potential density. Symbols - same as in Figure 3.

were higher in the latter below a σ_θ of 26.8 in the upper nutricline from the bottom of the mixed layer to the Intermediate Water at 500 m. At higher σ_θ in the deep water, the two trends merged together and the concentration differences were within the uncertainty of N^* . The concentration differences between these two trends ranged mostly between 1 and 2.5 μM in the upper nutricline. These differences were too large and the pattern in their variations with σ_θ was too consistent to be attributed to analytical uncertainties or coincidence alone. Another possible explanation is the advection of water with seasonally variable concentrations of N^* from the Philippine Sea into the northern SCS through the intrusion of the Kuroshio. The intrusion of the Kuroshio into the SCS from the Philippine Sea is stronger in the Winter than in the Summer [Shaw *et al.*, 1996]. While the database is limited, the distributions of N^* reported by Deutsch *et al.* [2001] on two isopycnal surfaces within the upper nutricline in the Pacific, at $\sigma_\theta = 25.6$ and 26.4, suggest that the concentration of N^* is lower in the adjacent Kuroshio than in the northern SCS. Thus, the intrusion of the Kuroshio should lead to lower, rather than the higher, concentrations of N^* in the Winter over the Summer. Then, if the concentration differences in N^* between the seasons at the SEATS site were the result of *in situ* processes, they suggest a seasonal variation in the impact of nitrogen fixation on the nutrient dynamics in the northern SCS such that the remineralization of these nitrogen-rich material was lower in the Summer and higher in the Fall through the early Spring. This pattern is in phase with that in the atmospheric deposition of Asian dust, and thus iron, to the study area. The frequency of dust storm occurrences in Asia is lower during the Summer months [Merrill *et al.*, 1989]. The concentration of mineral dusts over the SCS is also lower in the Summer and higher between the Fall and the early Spring [Husar *et al.*, 1997]. The coherence between these two patterns supports the hypothesis that nitrogen fixation in the northern SCS is triggered by the availability of iron that originates from the atmospheric deposition of Asian dust.

[11] Within the upper nutricline, the concentrations of N^* varied more irregularly in the shallower water ($\sigma_\theta < 25.2$) between the bottom of the mixed layer and the Tropical

Water at 150 m (Figure 5). The preferential release of phosphate over nitrate during the early stage of the remineralization of organic matter [Karl *et al.*, 2001] could result in lower N^* and contribute to this higher variability. In the deeper zone between the Tropical Water and the Intermediate Water ($25.2 < \sigma_\theta < 26.8$; 150 to 500 m), the release of phosphate and nitrate should be more tightly coupled and the concentrations were indeed less variable.

[12] **Acknowledgments.** SEATS and Wong's stay at NCOR as a visiting scientist were supported by the National Science Council, Taiwan. This is NCOR contribution no. 57.

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