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Variability of nutrient, dissolved inorganic carbon concentration at the base of Euphotic Zone in the NW Pacific observed by moored water samplers

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Abstract

We observed seasonal variability of nitrate and nitrite (NO_x), dissolved silicate [Si(OH)₄] and dissolved inorganic carbon (DIC) at the two Subarctic Gyre stations; K-1 (51°N, 165°E) and K-2 (47°N 165°E), at the approximate bottom of the Euphotic layer, 45 m and 47 m, by using the newly developed time-series water sampler (RAS). The RAS provided 48 samples with 8-day resolution from October 1, 2001 to September 26, 2002 using HgCl₂ as preservative. Timings of water collection at each station were synchronized. Concentrations of normalized nutrients ranged from 15.4 to 25.7 $\mu\text{mol kg}^{-1}$ for NO_x and from 19.7 to 43.6 $\mu\text{mol kg}^{-1}$ for Si(OH)₄ at station K-1, and from 9.5 to 24.6 $\mu\text{mol kg}^{-1}$ for NO_x and from 13.1 to 39.3 $\mu\text{mol kg}^{-1}$ for Si(OH)₄ at K-2. Although both stations were 616 km apart, timings of water collection at each station were synchronized. We distinguished 3 periods in 12 months in 2001 and 2002 that were distinctive by their characteristic time-series patterns of nutrients and DIC variability. They were: I. The Autumn Mixing Period that covered October to late November, which was characterized by vigorous mixing driven by the extensive upper layer instability by rapid cooling of the sea surface; II. The Winter Mixing Period (early December to late March) when the nutrients/DIC concentration at the bottom of the Euphotic Zone steadily recuperated until the concentration reached an annual maximum in late March; and III. A relatively stable transient period when upper water column gains indicated more robust stratification.

1. Introduction

A high concentration of dissolved nutrients in the upper Mesopelagic Zone in the NW Pacific and Western Bering Sea characterizes these areas from the rest of the world ocean. For example, dissolved silicate concentration at 200 m exceeds $50 \mu\text{mol kg}^{-1}$ in the Subarctic Gyre while the concentration is $10 \mu\text{mol kg}^{-1}$ or less in the rest of world's open ocean at this depth except in the southern area of the Antarctic Polar Front where the dissolved SiO_2 reaches $30 \mu\text{mol kg}^{-1}$. (e.g., Tsunogai, 1997; Broecker et al., 1982; Loarchi and Najjar, 2000.) In addition, researchers observed extensive seasonal fluctuation of settling particle fluxes to the oceanic interior in this region (Wong, 1994; Takahashi et al., 2000; Kawahata et al., 1998; Honda et al., 2002). As in any other productive ocean, vigorous activity of the biological pump in the NW Pacific removes dissolved nutrients and CO_2 as settling particles to the interior sink by annual blooms in the depletion of nutrients in the Euphotic and mixed layers (e. g. Honjo and Manganini, 1993). The question arises that by what processes is the winter stratification replenishing dissolved nutrients thereby preparing for the next annual cycle of biological pump activity?

The long term (at least one year), high resolution (preferably a duration of a week or less) in situ observation of oceanographic properties in the Euphotic/mixed layer is highly desirable for many disciplines of oceanography including the verification of satellite based remote sensing. (e. g. Wong and Mearns, 1999). Researchers found large amplitude and high frequency cycles of fundamental ocean properties in the productive layers of open oceans (e. g. Taylor and Howes, 1994; Dickey et al., 1998; Weller et al. 1998; Falkowski et al., 1998; Karl et al., 2001). However, traditional water castings and the overboard lowering of instruments do not allow for the continuous, long-term data collection that extends through all seasons for at least a full year.

As part of the effort toward understanding the processes of altering the concentration of nutrients in the Euphotic layers, a newly developed microprocessor-controlled, time-

series water sampler [Remote Access Sampler, (RAS)] <<http://jpac.whoi.edu/hilats>> was successfully deployed recently. In this beginning effort, we have constrained, in time-series, the variability of dissolved nutrients and dissolved inorganic carbon (DIC) at the base of the Euphotic layer, approximately 45 m and 47 m, of the Pacific Western Subarctic Gyre, [PSAG(W); Longhurst et al., 1995] (Fig. 1). We have found some complex processes of seasonal mixing that replenish nutrients to the surface and allow the ocean to recommence primary production. The objectives of this paper are twofold: First, to demonstrate our open ocean water sampling procedure and our rationale to reduce the biases and effects of long-term storage to a minimum. Secondly, we explain our interpretation of the data to illustrate a plausible scenario of how the mixed layer evolves along the procession of seasons. However, we also come up with far more questions than we had in the beginning.

2. Method

2. 1. Mooring Locations and the depths of RAS'

We deployed time-series instrumentation moorings from September 2001 to October 2002, each including a RAS, at stations K-1 (51°19N, 165° 12E, 5,132m deep) and K-2 (47°00N, 159°58E, 5,206m) (Fig. 1) <<http://jpac.whoi.edu/hilats>> . The former is located at the north edge and the latter was at the approximate center of PSAG(W). These moorings were bottom tethered and the apex flotation spheres were as shallow as 30 to 40 m below the surface. The RAS' were deployed at 44.8 m below the ocean's surface at station K-1 and 47.4 m at station K2. The mixed layer at these stations extensively changed by seasons (e.g., Suga et al, 2004). The depths of the RAS' were kept at the approximate bottom of the local mixed layer during the autumn when the vigorous mixing took place. The mixed layer lowered to 150 m as the result of winter convection. The depth of Euphotic layer in this area was approximately 50 m (e.g., Imai et al., 2002). The maximum flow velocity at this instrument depth is estimated as 30 cm sec⁻¹ based on the time-series observation by a moored profiler. There were perhaps several events when RAS' dipped for the maximum of 10 m but they stayed at the initial depth at the majority

of the term. The total length of pre-stretched wire shots of the RAS and the moored profiler (MMP) moorings did not change after one year of deployment.

2. 2. Instrumentation

We sampled 48 *in situ* seawater samples, approximately 450 ml each, at the depth of the RAS every 8 days starting at 00:00 from October 1, 2001 to September 26, 2002 over a span of 361 days. Two consequent samples were collected one hour apart on November 2, 2001 and on April 3 2002 in order to estimate close temporal repeatability (Table 1). Since a detail description of the instrumentation of a RAS is described elsewhere, only minimal explanation of the relevant functions for our present study is given here (Fig. 2). An acid-cleaned, flattened 500 ml–capacity bag that is made of the following 3 laminated layers; a thin exterior Mylar® film for protection, a vacuum coated aluminum foil layer for blocking solar radiation and minimizing gas diffusion and an interior, Teflon® film for reinforcement and insulation of sample water from the Al layer was pre-loaded with a preservative solution. A bag was connected to a distribution valve and housed in a sturdy 600 ml acrylic sheathe. The interior space of a flattened sampling bag was filled with distilled water before deployment. There are 49 identical bag assemblages on a RAS. Among them, 48 were used to sample seawater in a scheduled sequence. We used one bag filled with 6M HCl for flushing of the intake path before each water sampling procedure.

Sampling schedules for 48 events can be programmed independently or universally with intervals ranging from 10 minutes to months by exporting commands to an internal microprocessor before deployment from an external computer. Initially, the multi-port valve stays at the home position blocking all intake paths. Five minutes before sampling, the multi-port valve aligned with the intake path and a cleansing acid bag. Then a 5 ml jet of 6M HCl flushes intake manifolds (Acid flush path; Fig. 2, the left panel). After a one-minute pause, the same path was rinsed with 100ml of *in situ* seawater (Water rinse path: Fig. 2, the left panel). Finally, the multi port valve aligns the intake valve to a designated sampling bag assemblage. As the distilled water is removed from the acrylic sheathe by

turning the pump in reverse to the previous paths, a created low pressure induces the *in situ* water to move into the sampling bag (Sampling path; Fig. 2, the right panel). To minimize the cross contamination of water samples, the graphite gear pump is not exposed to the sample water but only to evacuated distilled water in the sheathes. Sampling volume and flushing and cleansing schedules were programmed into a stepping motor that runs the gear pump. At stations K-1 and K-2, approximately 450 to 480 ml samples were collected at events as programmed. Execution records of sample timing, estimated sample volume, flushing records, and electricity consumption etc. were retrieved from the memory.

The two RAS' collected a total of 95 out of an expected 96 samples. Self-diagnosis records left in the microprocessor indicated all processes were completed as designed. A sample bag assemblage did not function because of a simple mechanical failure. There was not detectable effect of contamination from biofouling on our chemical analysis.

2.3. *Sample preservative*

We used mercury chloride (HgCl_2) solution as the single preservative. Kattner (1999) reported that sea water nutrients including NO_x and $\text{Si}(\text{OH})_4$ can be preserved as long as 2 years in a HgCl_2 solution. We pre-installed 5 ml saturated HgCl_2 solution to a sampling bag a few days before the RAS deployment. Although solubility of HgCl_2 in distilled water depends on water temperature, 5 ml saturated HgCl_2 solution was expected to include 180 mg to 370mg HgCl_2 under water temperature between 0 and 20 °C. Under these conditions the HgCl_2 concentrations in 450 ml seawater was 397 to 830 ppm and was substantially higher than Kattner's 105 ppm solution.

2. 4. *Chemical analysis and errors*

Immediately after the recovery, water samples collected by the RAS were divided into four aliquots to analyze total dissolved inorganic carbon, nutrients, salinity and other

biogeochemical constituents (not included in this article). Salinity in RAS samples was measured with a salinometer on board (AutoSal® Model 8400B; Guildline Instruments). An aliquot for nutrient analysis was filtered through 0.45 μm Durapore® syringe filters. Nutrients ($\text{NO}_x = \text{NO}_2 + \text{NO}_3$ and $\text{Si}(\text{OH})_4$) for filtered water samples were measured with a continuous flow analytical system on board (BRAN+LUEBEB TRAACS® 800). For DIC analysis sample water was introduced directly from the sampling bag assemblage into a DIC extraction module with a CO_2 coulometer (Ishii et al., 1998) by applying a gentle N_2 -gas pressure to the sheath cavity. Measurement errors based on duplicate sample at both station ($n=4$) were 0.32, 0.72 and 2.88 $\mu\text{mol kg}^{-1}$ for NO_x , $\text{Si}(\text{OH})_4$ and DIC, respectively, while analytical error based on repeatability of reference material were less than 0.17, 0.37 and 0.55 $\mu\text{mol kg}^{-1}$ for NO_x ($n=13$), $\text{Si}(\text{OH})_4$ ($n=23$) and DIC ($n=6$), respectively.

2. 5. *Effect of HgCl_2 preservative on salinity and nutrient concentrations*

Salinity ranged from 30.24 to 33.06 psu for RAS samples at station K-1 and from 31.79 to 32.32 psu at station K-2 and averages at stations K-1 and K-2 were 32.13 and 32.09 psu, respectively. Previous shipboard reports (e.g. MIRAI Cruise Report, 1998, 1999, 2000, 2001) and the time-series CTD data obtained from moored ocean profiler (Toole et al., 1999) data at these stations indicate salinity at the base of Euphotic zone (approximately 50 m) in the WSG is expected to be 33.0 ± 0.3 psu. The salinity of RAS water samples was significantly lower than previous data. This was plausibly attributed to the dilution effect of RAS samples by the HgCl_2 solution. We further suspected that the elevated HgCl_2 concentration in the sampled water (approximately 400 ~ 800 ppm) on Auto Sal salinity measurements might have interfered with the electrode potential. We compared the salinity of RAS samples measured by an electrode –based instrument, (the AutoSal), and an inductively coupled salinometer (AutoLab®: YEO-KAL). Two sets of salinity measurements were in excellent agreement ($r^2=0.994$). An elevated HgCl_2 concentration might also interfere with NO_x measurements because of the decreased reduction rate of the Cd-Cu column used for analysis. In reality the reduction rate during

the NO_x measurement did not decrease significantly; from 97 % to 93 % for K-1 samples and 98 % to 92 % for K-2 samples. This suggested that the effect of high HgCl₂ concentration in a water sample had a negligible effect on NO_x analysis.

3. Results

3. 1. *Nutrients and DIC concentrations*

Fig. 3 shows the time-series procession of nutrients and DIC variability at K-1 and K-2. Concentrations of DIC, NO_x and Si(OH)₄ were normalized to the standard salinity of 33 psu. At station K-1, concentrations of normalized NO_x (N-NO_x) ranged from 15.4 to 25.7 $\mu\text{mol kg}^{-1}$ and N-Si(OH)₄, from 19.7 to 43.6 $\mu\text{mol kg}^{-1}$ during the deployment of RAS'. Concentration of N-DIC ranged from 2022.7 to 2126.8 $\mu\text{mol kg}^{-1}$. The highest concentrations for each component were observed in February or March 2002. Nutrient concentrations decreased from April 2002 to early July 2002. It was notable that concentrations for each component varied largely in October and November 2001. Annual minimum concentrations were observed in this period. High concentrations comparable to the annual maximum in March were also observed during this period (Table 1, Fig. 3). The concentrations of nutrients at station K-2 ranged from 9.5 to 24.6 $\mu\text{mol kg}^{-1}$ for N-NO_x; from 13.1 to 39.3 $\mu\text{mol kg}^{-1}$ for N-Si(OH)₄ and N-DIC, from 2048.5 to 2123.9 $\mu\text{mol kg}^{-1}$. Although high concentrations of N-NO_x, N-Si(OH)₄ and N-DIC were observed in March 2002, annual maximum appeared in October 2001 for N-NO_x and N-DIC and in April 2002 for N-Si(OH)₄. A decrease in nutrients and N-DIC from April to July was not clear unlike K-1 (Table 1, Fig. 3). A large variability of nutrients and N-DIC in October and November 2001 was also observed at station K-2.

3. 2. *Comparison of RAS data with previous observed data*

In order to evaluate the reliability of RAS data, we compared our RAS-based nutrients and N-DIC data with data observed previously by CTD-hydrocasts. Fig. 4 shows vertical

profiles of (c) (d) N-NO_x, (e) (f) N-Si(OH)₄ and (g) (h) N- DIC for upper 200 m at stations K1 and K2, respectively. These profiles were observed by using CTD/MWS in early and middle autumn, and winter during R/V Mirai cruise (MIRAI Cruise Report, 2001, 2002, 2003). Concentrations of both nutrients and DIC for surface seawater were minimum in September and maximum in February. These were attributed to the biological consumption of nutrients and DIC from spring to the early autumn for the former and winter mixing for the latter. Such seasonal variability in surface nutrients was also reported previously by a ship of opportunity (Wong et al., 2002). In the winter, (February 27, 2003 for K1 and February 25, 2003 for K2) all the components were constant in the upper 100 m at both stations indicating that the surface mixed layer is approximately 100 m. In Fig. 4 the range of NO_x, Si(OH)₄ and DIC observed by the RAS at 50 m was overlapped with quasi-time-series onboard CTD observation. Maximum values of N-NO_x, N-Si(OH)₄ and N-DIC observed by RAS were comparable to winter constant values observed by R/V. In addition, low values observed by RAS in autumn were also observed by R/V in the autumn season.

3. 3. Time-series variability through the seasons

It is noted that the pattern of seasonal variability of the concentrations are almost identical at both stations despite the distance between these stations. We identified 3 periods in the annual patterns of variability of N-NO_x, N-Si(OH)₄ and N-DIC concentrations. We discuss the oceanographic significances of these divisions in the following section:

- I. Late autumn Mixing Period from October to late November.
- II. Winter Mixing Period from early December to middle March.
- III, Stable Period from early April to late September.

4. Discussion

4. 1. Vigorous autumn mixing (Period I)

An MMP was deployed at approximately 8 km from K-1 in the same topographic area (K-1 Physical Oceanography Station; 51°18N, 165°18E) during the overlapping period with the K-1 RAS. The salinity and temperature at 50 m from mid September to mid October of Period I were modestly fluctuating from 33.03 to 33.10 psu and 3.1 to 3.9°C except for a few weeks (Fig. 5). During the 10 days between September 27 and October 6 the salinity first dropped to 32.88 from 33.08 psu and further dropped to 32.81 psu on October 6 and then abruptly returned to 33.03 psu on October 7.

We noted that on September 27 the temperature at RAS depth soared to 8.5°C from 3.5°C and it appeared that the temperature was maintained at 8.5°C until October 6. We do not know how rapidly the salinity and temperature shifted within this 10-day duration since we have no MMP data between September 27 and October 6 (Fig. 5). On October 7, the temperature and salinity returned to 33.03 psu and 5.1°C, respectively. The period of vigorous change of temperature and salinity ended on November 15 when the temperature and salinity reached the stable level that were observed during the early winter mixing period: 3.3°C and 33.06 psu.

The pattern of temporal variability of N-NO_x, N-Si(OH)₄ and N-DIN at station K-1 generally followed the variability of the salinity and in reverse to the temperature during this turbulent duration in the autumn. The annual minimum of N-NO_x and N-Si(OH)₄ at K-1 station observed on October 1 overlapped with the 10 day duration of high temperature and low salinity. The timing of another deep dip of the nutrients and DIC observed on November 2 was also close to the high temperature /low salinity event on October 26/27. On the other hand, high nutrients and DIC period between October 9 and 25 at K-1 corresponded to the low-temperature /high-salinity observed on October 16/17. The strong increasing trend of nutrients and DIC in the duration after the dip on November 2 to 26 also matched the period of decreasing temperature and increasing salinity (November 5/6 to November 25/26). The variability of the nutrients and N-DIC

did not always exactly overlap with the TS events. Such discrepancy could be attributed to the resolution of observational intervals of both the moored profiler and the RAS.

The minimum values of salinity at 50 m such as those observed on October 6 and October 27, 32.81 and 32.88 psu, were less than the surface water salinity observed in October, 2002 (R/V Mirai Cruise Report, 2002) and were significantly lower than the salinity at 50 m, which is usually over 33.00 psu (R/V Mirai Cruise Report, 2001, 2002 and 2003). The high water temperature associated with salinity minima were often only a few degrees lower than the SST and several degrees higher than the temperature normally observed at 50 m. These observations indicate that the above described vigorous vertical mixing in September and October pumped down nutrients and DIC depleted “late summer or early autumn surface water” to the bottom of the Euphotic Zone. MMP profiles suggested that such vertical mixing reached even deeper (Fig. 5, base panel). The maximum concentration of nutrients found at 50 m on October 25 at both stations was comparable to the maximum concentration when the winter mixing was completed. When the maximum concentration of RAS nutrients on October 25 was compared to those at 50 m in shipboard bottle casting at K-1 on October 16 or at K-2 station on October 21, 2001 the former were significantly larger. This can be interrelated, as the minimum concentration on November 2 was significantly smaller than the surface concentration (to 20m) measured by the above-mentioned castings.

At this time, we can only guesstimate the forcing factor of the vigorous vertical mixing during the autumn in this area. The SST and the air temperature at station K-1 and 2 were highest between late August and mid September (NCEP Reanalysis Data, NOAA-CIRES Climate Diagnostics Center <<http://www.cdc.noaa.gov/>> ; Fig. 6). Before October 2001, the air temperature and SST with summer freshwater layer are warmer than the upper layer, which only reinforces the stratification (Fig. 6). Since late September and October, the air temperature dropped rapidly by the coverage of several cold spills resulting in the SST being pushed down at a higher rate. For example, in NCEP data in the first 2 weeks of November, the rate of the lowering of SST was as large as $0.23^{\circ}\text{C day}^{-1}$ (November 1 to 14) while it was $0.14^{\circ}\text{C day}^{-1}$ in the preceding 10 days. The rate for one month after

November 15 was $0.03^{\circ}\text{C day}^{-1}$ at station K-1 and the temperature decline further slowed toward spring. NCEP data indicated a similar plunge of SST at K-2 during this season (Fig. 6). It is conceivable that this rapid cooling of SST triggered upper ocean instability and resulted in vigorous mixing in autumn. Plueddemann et al. (1995) found a “thermal cap” in the south of Iceland that is a warm and less-saline rain water pond maintained on the surface for only several days. Although speculative, such a thermal cap gave way to episodic mixing to supply fresher and warmer water to the bottom of the Euphotic Zone.

The close synchronization and agreement of the amplitude found in the variability of nutrients at K-1 and K-2 station was startling when we consider the distance between the two stations (616 km). We believe this similarity of nutrient behavior, particularly during October and November, was due to the fact that these two stations were under a common mesoscale meteorological province in regards to the essential climatology particularly the air temperature and the SST. We repeatedly found a rapid dropping of SST that might have triggered the successive coverage of the several cold spells in several years of NCEP data in similar autumn durations. Thereby, this characteristic mixing at the bottom of the Euphotic Zone could be an annual routine in the Western Subarctic Gyre.

A biogeochemical implication of the vigorous autumn mixing might offer an explanation why the second bloom, often as significant as the spring bloom, took place in autumn in boreal oceans (e. g., Honjo, 1990). Upper ocean instability that was caused by rapid cooling of the sea surface introduced vigorous and deep convection to bring nutrients from the deeper pool to the depleted surface that might induce a bloom often as late as November. Estimating from the particle export flux records of organic carbon and other biogenic matters (Honda et al., 2002), the autumn bloom was particularly conspicuous in the WSG.

4. 2. Establishment of the winter mixed layer (Period II)

The SST and the water temperature at 50 m deep became close and started to decrease in parallel in early November (Fig. 5, the upper panel). A climatology benchmark was mid

November when the SST and the water temperature were at 50 m (MMP data) and they decreased in parallel thereafter. Stability of the water column was established starting in mid November (Period II) while the cooling of the upper layer water intensified. Strong thermal convection took over the role of mixing from vigorous deep mixing caused by the upper ocean instability during autumn (Period I Autumn mixing period).

While the thermal convection proceeded, N-NO_x, N-Si(OH)₄ and N-DIC at 50 m increased quasi monotonically at both stations until the annual maximum was achieved in late March 2002. Between November 26 to March 26, N-NO_x and N-Si(OH)₄ at K-1 increased by 2.4 and 6.5 $\mu\text{mol kg}^{-1}$, respectively. These are smaller than those at K-2 between November 26 and April 3: 3.7 for N-NO_x and 9.0 for N-Si(OH)₄. At both stations, N-NO_x correlated with N-Si(OH)₄ ($r^2=0.99$) and the ratios of increase in N-Si(OH)₄, N-NO_x (i. e., Si/N ratio) were 2.6 at K-1 and 2.3 at K-2.

4. 3. Effect of blooms on the nutrients concentration at 50 m (Period III)

After the N-NO_x and N-Si(OH)₄ reached the annual maximum in late March at both stations they kept decreasing until early June. The annual benchmark when the ΔT (SST – air temperature) turned negative was achieved around March 27 (178th day) at both stations (NCEP Data; Fig.6c). This event provided more stability to the upper water column thereafter to stage the spring bloom conditions. The rates of depletion were small at K-2 but relatively large at K-1 (the early Period III). This duration of gentle depletion of nutrients corresponded to the reported timings of the spring bloom and vigorous export of organic carbon, CaCO₃, biogenic silica and other elements that participate in the biological pump (Wong, 1993; Takahashi, 2000; Honda et al 2002). The depletion of nutrients during the early Period III was, perhaps, caused by the uptake of phytoplankton and primary producers while their activity reached as deep as 50 m. Between mid June and mid July the concentration of nutrients was more constant than during any other period (the mid Period III). RAS depth was suspected to be below the surface mixed layer during this period. In addition, the increase of biological activity in the surface mixed

layer might have blocked the light transmission and biological activity at the RAS depth resulting in no change in nutrients and N-DIC concentration at 50 m.

After late July until September, the nutrient concentration was less consistent; N-Si(OH)₄ showed a slight increase at K-1 (the-late-Period III). According to NCEP data, the autumn meteorological setting had already sneaked into this area in mid August; the first positive $\square$ T after March 27 was found on August 10 at K-2. Although speculative, the mild fluctuation of nutrient concentrations during Stage III-3, particularly at K-2, was more related to the water column instability like that observed during October and November but on a minor scale (Fig. 6). We only observed slight depletion of nutrients early in this period at the bottom of the Euphotic Zone (Fig. 3). The annual transition patterns of nutrients/DIC at the bottom of the Euphotic Zone were significantly different from the pattern of nutrients and DIC cycles that were characterized by the deep depletion usually expected in the productive surface ocean that is controlled by primary production.

4. 4. Link with primary production

The annual transition patterns of nutrients/DIC concentration at the bottom of the Euphotic Zone at stations K-1 and 2 were more controlled by meteorological forcing and significantly different from the patterns usually expected in the productive surface ocean that is controlled mainly by primary production. The variability of nutrient concentrations in the surface was generally characterized by the deep depletion during the spring and autumn bloom. Contrarily, we observed only slight depletion of nutrients early in Period III at the bottom of the Euphotic Zone at station K-1 and this was the only sign of a link with the biology.

6. Summary and Conclusions

We first found intricate, sometimes vigorous, seasonal processions of the nutrients and DIC variability at the bottom of Euphotic Zone by sampling in situ water at high temporal resolution of 8-days for one year at two stations that parted for 616 km. These

changes were repeated at both stations in a synchronized manner all year. These changes, including the fast mixing in high amplitude that occurred in autumn, 2001, could have never been discovered by conventional shipboard observation. The annual pattern of variability was largely different from that in the upper Euphotic Zone while no effect of a primary production bloom was observed.

Several tough technical challenges had to be met in order to understand the time-series variability of dissolved chemical properties including nutrients and dissolved inorganic carbon at high resolution in the upper ocean layers covering the passage of the entire seasons in the open ocean. Such challenges included the fundamental task of finding a preservative that maintains the original property of the sample water in the Euphotic environment at least for a year and to develop a series of analytical methods by overcoming the effects of the preservative. We found laminated aluminum foil bags for sampling and safekeeping of water in time series worked well. A HgCl_2 solution that mixes with the sample water at the time of collection preserved the original concentration of Si(OH)_4 , NO_x and DIC for 1-year deployment to a level of our satisfaction. HCl flushing of the intake path prevented the effect of biofouling (Fig. 2). One of our conclusions from this research is that high resolution, long term water sampling (deployed for up to 1-year) to gather biogeochemical properties at any depth of an open ocean including the upper ocean is now available although further improvements must be implemented (Fig. 2).

A time-series water collection (RAS) was deployed at the approximate bottom of the Euphotic Zone in the NW Pacific Subarctic Gyre at two deep ocean stations K-1 (45 m, 51°N, 165°E) and K2 (47 m, 47°N, 160°E) for one year along bottom tethered high tension moorings (Fig. 1). Forty-eight water samples were collected every 8 days at each station (one sampling failed at K-2). Timings of water collection at each station were synchronized. The analytical results on the time-series variability of the concentration of NO_x and Si(OH)_4 showed intricate short (few weeks) and long term (seasonal) changes. Patterns of the time series variability of these 3 components closely resembled each other at both stations keeping less concentration at K-2 relative to K-1 except in the summer.

Quasi time-series shipboard observations at both stations at approximately 50 m were comparable to the RAS based observations although the former completely missed to visualize the pattern of variability at the base of the Euphotic layer observed by the latter method.

The patterns of transition of nutrients and DIC at the bottom of the Euphotic layer at both stations were significantly different from the patterns usually expected in the surface ocean that is more controlled by primary production and the removal of nutrients such as settling particle fluxes to the interior of ocean (Fig. 3). Despite the mesoscale distance between K-1 and K-2, (616 km), the patterns of variability were synchronized within an 8-day resolution. We distinguished 3 periods in 12 months in 2001 and 2002 that were distinctive by characteristic patterns of nutrients and DIC variability. They were: I. Autumn Mixing Period that covered early October to late November. Estimating from the 2002 data, this period might have started in late September 2001. II. Winter Mixing Period, early December to late March. And III. Stable Period, early April to mid/late September.

The Autumn Mixing Period was characterized by the vigorous mixing of upper ocean water that reached the base of the Euphotic Zone. We hypothesize that the autumn mixing caused a second bloom in autumn that was observed in boreal oceans by a rapid and deep convection. The timing of vigorous pumping coincided with the accelerated descending of the air temperature compared to the SST (NCEP data) (Fig. 6). Apparently a major event that occurred between October 25 and November 2, 2001 at K-1 and K-2 lowered N-NO_x, Si(OH)₄ and DIC to a large extent. In mid November the SST (NCEP data) and water temperature at K-1 at 50 m (MMP data) reached an equilibrium at station K-1, while winter conditions set in this area (NCEP data) resulting in a more consistent winter convection that took over the upper water column. During this Winter Mixing Period the nutrients and DIC at 50 m increased near linearly.

March 26 was another benchmark date in 2002 around when the air temperature turned higher than the SST synchronously at both stations thus the thermal convection ceased in

this area until the autumn (Fig. 6). Upper ocean layers were much more stable and this condition that helped to foster the spring bloom condition at the surface. The steady lowering of the N-NO_x and Si(OH)₄ until early June at 50 m (Fig. 3) could have resulted from the bloom. However, the depletion of nutrients and DIC at the bottom of the Euphotic layer was very small. Such depletion of nutrients did not take place during mid summer.

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Captions

Table 1. Sampling schedule and analytical results of NO_x, Si(OH)₄ and dissolved inorganic carbon (DIC) in $\mu\text{mol kg}^{-1}$ in each 48 time-series samples collected by RAS' at 45 m (K-1) and 47 m (K-2) at 8-day intervals from October 1, 2001 to September 26, 2002. They are normalized to the standard salinity of 33 psu.

Fig. 1. Mooring locations.

Fig. 2. A function diagram of a RAS. During the preparative stage (left panel) a RAS executes two functions in order to avoid contamination from biofouling the intake path **a** (left-upper corner). First, through the acid flush path, a pair of APF valves opens and a pump applies pressure to an HCl bag that flushes the intake manifold **a** and closes the APF valves to isolate the HCl tank. Second, through the water rinse path, WFP valves open and the pump sends filtered in situ water directly to rinse out remaining HCl from **a**. WFP valves close thereafter. A RAS is then ready for water sampling through the sampling path (right panel). Microprocessor commands to open twin valves of the next empty bag where a preservative is pre-loaded (P-3, for example). The pump runs in reverse to generate a lower pressure in the sheath resulting in the drawing of the in situ water of programmed volume. Then the bag is isolated for preservation by closing P-3 until the next programmed cycle that starts with HCl flushing. In an actual RAS, all valves are arranged along two circumferences and virtual manifold **t** and **t'** do not exist.

Fig. 3. Seasonal variability in (a) NO_x, (b) Si(OH)₄, and (c) DIC measured by RAS at stations K-1 (solid triangles) and K-2 (open circles) against the calendar dates in 2001 (September to December) and in 2002 (January to September). Plotted data are normalized to standard salinity of 33 psu.

Fig. 4. Vertical profiles in (a), (b) Si(OH)_4 , (c), (d) N-NO_x, (e), (f) Si(OH)_4 and (g), (h) N-DIC observed by hydrocasting at stations K1 and K2, respectively, in September 2001 (open circles), October 2002 (open squares) and February 2003 (open diamonds).

Fig. 5. Upper panel: A time-series variability of SST (open circles with dotted line) from NCEP data file <<http://www.cdc.noaa.gov/>>, water temperature (open circles with solid line) and salinity (solid squares with solid line) at 50 m, approximate RAS depths, observed by a moored ocean profiler (MMP; deployed 8km apart from K-1 RAS mooring) during the first 100 days of deployment of a RAS at station K-1. Mid panel: Pattern of variability of N-NO_x and N-Si(OH)₄ concentration during the same period at station K-1. Base panel: A vertical section of sigma-theta between 50 m and 200 m observed by an MMP at station K1 from September 5, 2001 (experimental day: -24) and 8 January 2002 (experimental day: 100). Overlapped to the Si(OH)_4 profile is the variability of N-NO_x at $\sigma_{\theta} = 1$ as an example of the time-series nutrient variability.

Fig. 6. Upper (station K-1) and mid panel (K-2): The air temperature (solid line) and SST from NCEP data that plotted for the duration of the term of RAS deployment. Base panel: A comparison of the delta-T (NCEP SST – NCEP Air Temperature) at station K-1 (solid line) and K-2 (broken line).

Table 1. Sampling schedule and analytical data

Sampling No.	Sampling Date & Time (UTC)	Deployment Date	Station K-1			Station K-2		
			N-DIC ($\mu\text{mol kg}^{-1}$)	N-NOx ($\mu\text{mol kg}^{-1}$)	N-Si(OH) ₄ ($\mu\text{mol kg}^{-1}$)	N-DIC ($\mu\text{mol kg}^{-1}$)	N-NOx ($\mu\text{mol kg}^{-1}$)	N-Si(OH) ₄ ($\mu\text{mol kg}^{-1}$)
1	1-Oct-01 0:00	1	2022.7	15.4	19.7	2113.2	23.6	37.7
2	9-Oct-01 0:00	9	2111.6	22.1	38.5	2113.0	21.1	33.7
3	17-Oct-01 0:00	17	2107.6	22.3	36.7	2097.8	19.1	28.9
4	25-Oct-01 0:00	25	2125.2	25.4	42.8	2123.9	24.6	38.6
5	2-Nov-01 0:00	33	2081.3	16.3	21.2	2049.1	9.6	13.3
6	2-Nov-01 1:00	33	2079.4	17.1	23.2	2048.5	9.5	13.1
7	10-Nov-01 0:00	41	2100.0	20.3	29.8	2068.6	13.7	20.0
8	18-Nov-01 0:00	49	2112.5	22.2	34.3	2073.9	14.5	21.4
9	26-Nov-01 0:00	57	2116.7	23.2	37.1	2099.8	19.1	29.8
10	4-Dec-01 0:00	65	2104.4	22.3	34.9	2096.4	16.8	25.8
11	12-Dec-01 0:00	73	2114.5	22.4	35.3	2093.7	17.4	26.3
12	20-Dec-01 0:00	81	2108.6	22.1	34.6	2094.2	17.7	26.9
13	28-Dec-01 0:00	89	2105.2	21.9	34.3	2098.8	18.0	27.9
14	5-Jan-02 0:00	97	2113.4	22.9	36.0	2100.3	18.9	29.7
15	13-Jan-02 0:00	105	2107.1	22.7	35.9	2102.1	18.4	28.7
16	21-Jan-02 0:00	113	2112.7	22.9	36.5	2098.2	18.6	29.0
17	29-Jan-02 0:00	121	2115.4	23.6	37.9	2104.0	19.3	30.7
18	6-Feb-02 0:00	129	2113.2	24.0	39.1	2115.3	20.2	32.5
19	14-Feb-02 0:00	137	2126.8	24.3	40.1	2108.5	19.6	31.5
20	22-Feb-02 0:00	145	2117.6	24.0	39.5	2106.1	19.1	30.4
21	2-Mar-02 0:00	153	2114.3	25.2	42.7	2111.8	20.2	33.2
22	10-Mar-02 0:00	161	2125.1	25.5	43.6	2121.5	21.6	36.1
23	18-Mar-02 0:00	169	2123.0	25.5	43.5	2118.6	22.7	38.5
24	26-Mar-02 0:00	177	2125.5	25.7	43.6	2114.5	21.8	36.5
25	3-Apr-02 0:00	185	2123.6	25.1	43.1	2115.4	22.8	38.8
26	3-Apr-02 1:00	185	2123.6	25.5	43.5	2123.3	22.7	38.9
27	11-Apr-02 0:00	193				2121.5	22.2	37.5
28	19-Apr-02 0:00	201	2119.4	23.6	40.0	2109.6	21.9	37.1
29	27-Apr-02 0:00	209	2117.2	22.9	38.9	2094.9	22.0	37.6
30	5-May-02 0:00	217	2108.7	22.5	38.8	2119.2	21.9	38.0
31	13-May-02 0:00	225	2117.2	22.3	38.7	2103.7	21.9	38.3
32	21-May-02 0:00	233	2116.6	21.7	38.7	2117.3	22.0	39.3
33	29-May-02 0:00	241	2114.7	21.7	38.1	2102.9	21.2	37.7
34	6-Jun-02 0:00	249	2113.5	21.5	37.6	2096.8	21.4	37.8
35	14-Jun-02 0:00	257	2114.3	21.6	37.7	2115.1	21.1	37.1
36	22-Jun-02 0:00	265	2116.1	21.8	38.1	2113.2	21.6	37.9
37	30-Jun-02 0:00	273	2116.5	22.3	38.6	2108.6	21.2	37.8
38	8-Jul-02 0:00	281	2115.2	21.7	38.2	2118.0	21.4	38.0
39	16-Jul-02 0:00	289	2107.2	21.1	36.5	2114.6	21.2	37.6
40	24-Jul-02 0:00	297	2111.4	21.3	37.5	2079.4	18.2	34.0
41	1-Aug-02 0:00	305	2106.0	22.2	38.3	2119.9	22.2	36.7
42	9-Aug-02 0:00	313	2103.9	21.7	39.9	2098.5	21.4	36.7
43	17-Aug-02 0:00	321	2115.1	22.6	39.0	2106.7	21.7	35.7
44	25-Aug-02 0:00	329	2101.4	21.9	39.8	2105.7	20.8	35.2
45	2-Sep-02 0:00	337	2088.1	21.6	38.0	2108.8	22.0	37.1
46	10-Sep-02 0:00	345	2112.0	21.4	34.4	2091.3	21.6	36.4
47	18-Sep-02 0:00	353	2100.3	21.5	36.7	2109.9	22.4	36.1
48	26-Sep-02 0:00	361	2096.7	22.1	37.8	2087.8	17.9	32.6

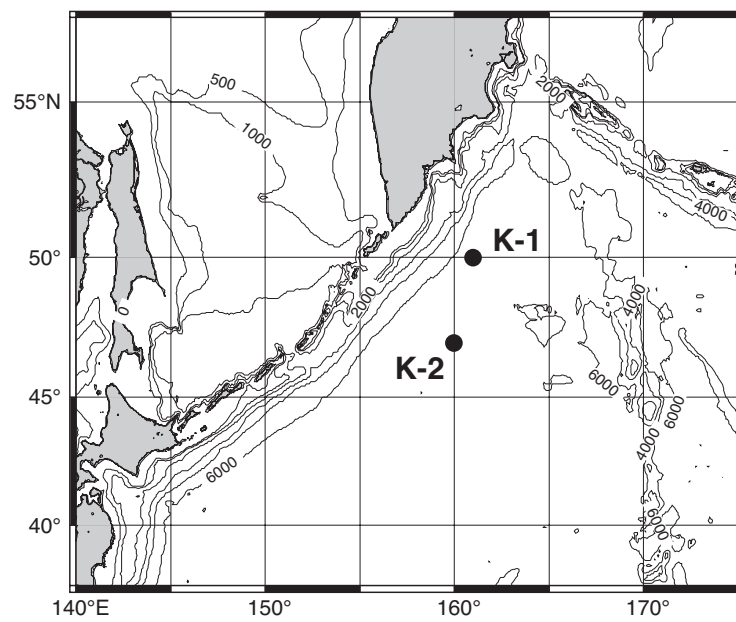


Figure 1

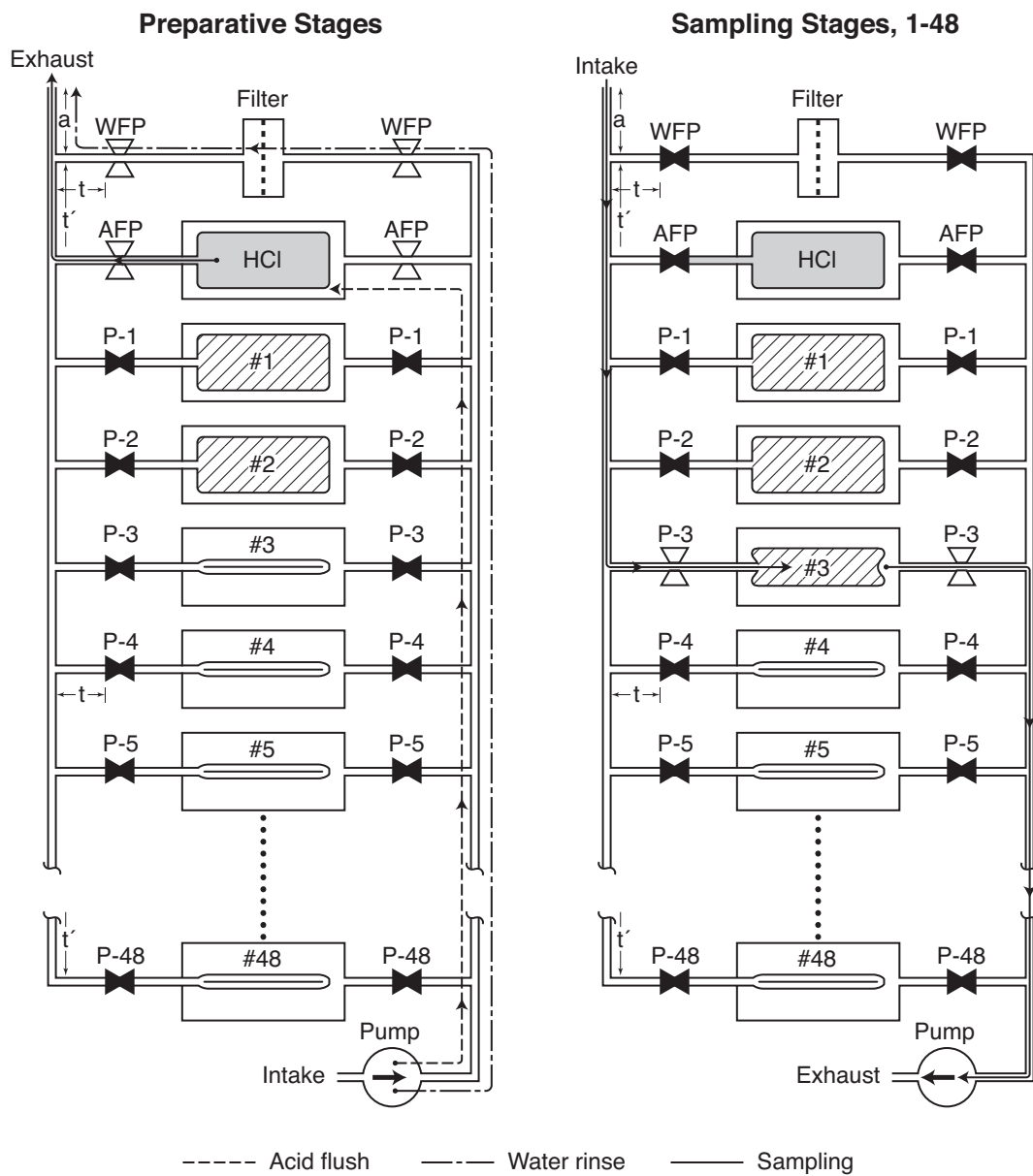


Figure 2

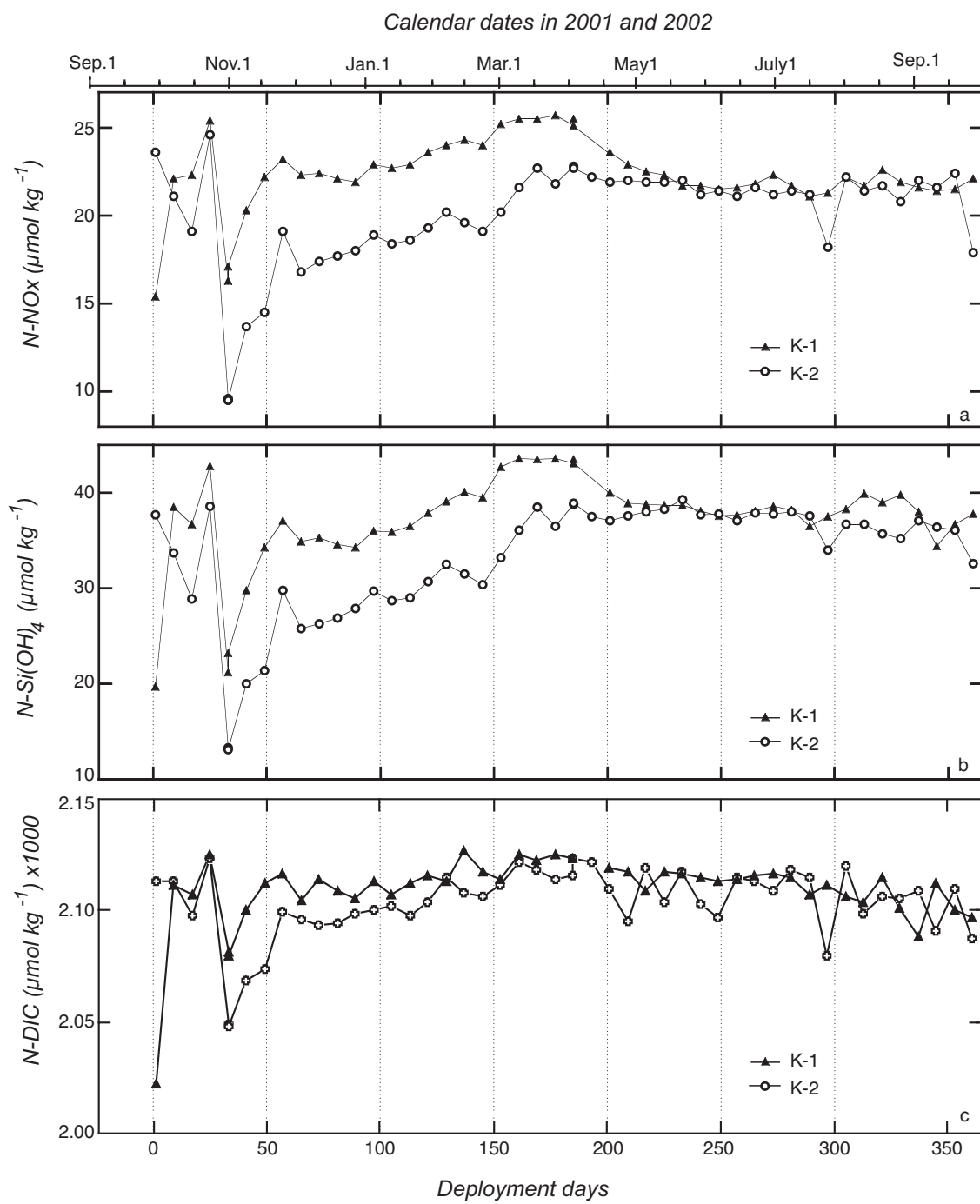


Figure 3

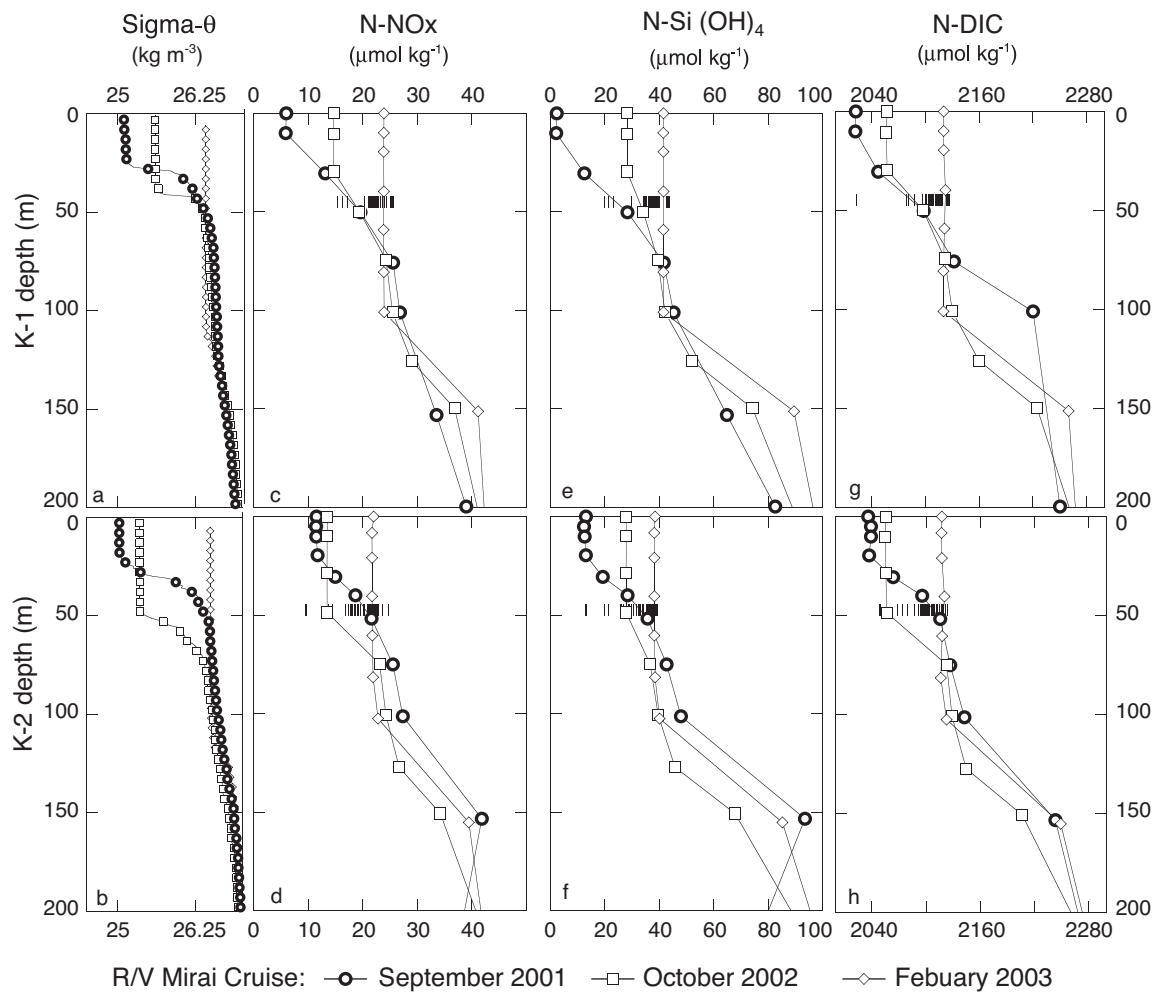


Figure 4

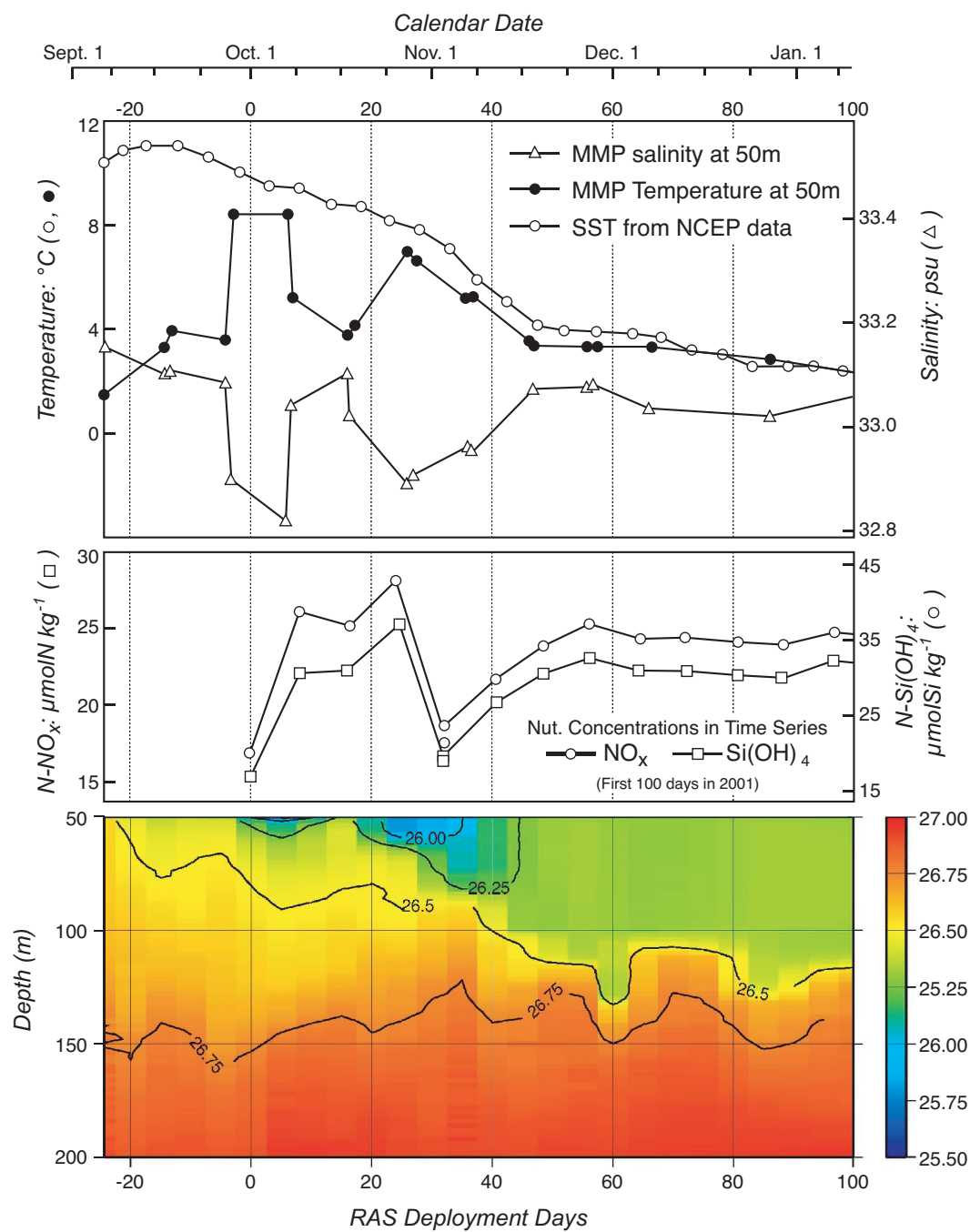


Figure 5

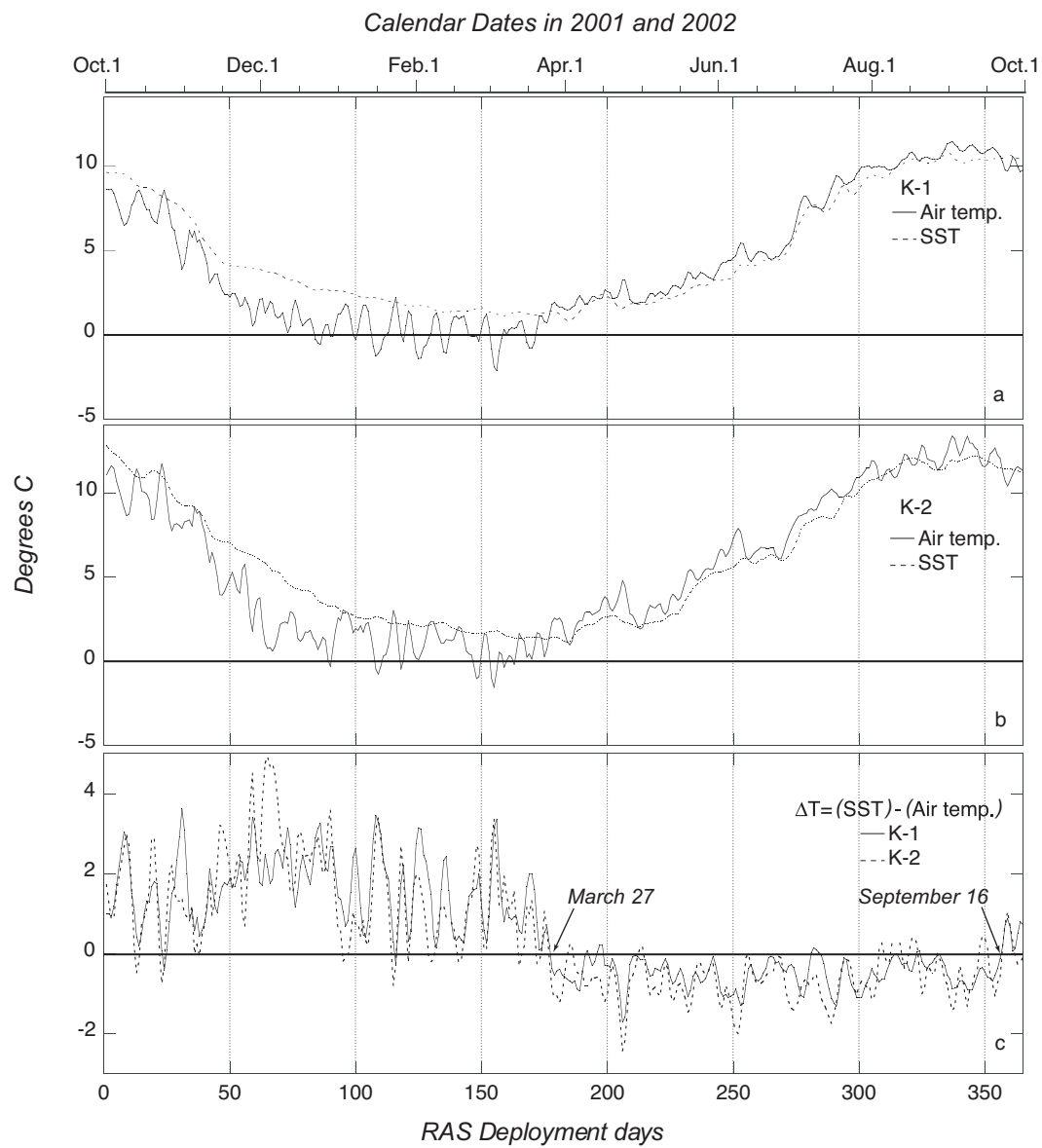


Figure 6