Nutrient Regeneration at Bottom after a Massive Spring Bloom in a Subarctic Coastal Environment, Funka Bay, Japan

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Nutrient regeneration and oxygen consumption after a spring bloom in Funka Bay were studied on monthly survey cruises from February to November 1998 and from March to December 1999. A high concentration of ammonium (more than 4 μmol l^{-1}) was observed near the bottom (80–90 m) after April. Phosphate and silicate gradually accumulated and dissolved oxygen decreased in the same layer. Salinity near the bottom did not change until summer, leading to the presumption that the system in this layer is semi-closed, so regenerated nutrients were preserved until September. Nitrification due to the oxidation of ammonium to nitrate was observed after June. Nitrite, an intermediate product, was detected at 4–7 μmol L^{-1} in June and July 1999. Assuming that decomposition is a first order reaction, the rate constant for decomposition of organic nitrogen was determined to be 0.014 and 0.008 d^{-1} in 1998 and 1999, respectively. The ammonium oxidation rate increased rapidly when the ambient ammonium concentration exceeded 5 μmol L^{-1}. We also performed a budget calculation for the regeneration process. The total amount of N regenerated in the whole water column was 287.4 mmol N m^{-2} in 4 months, which is equal to 22.8 gC m^{-2}, assuming the Redfield C to N ratio. This is 34% of the primary production during the spring bloom and is comparable to the export production of 25 gC m^{-2} measured by a sediment trap at 60 m (Miyake *et al.*, 1998).

1. Introduction

In subarctic and temperate coastal regions, an intense phytoplankton bloom occurs in spring. Most of the production is classified as a new production because the nutrients utilized are supplied from the deeper layer as a result of vertical convection in winter. A massive spring bloom occurs in Funka Bay, consisting of diatom species (Odate, 1987; Maita and Odate, 1988; Kudo and Matsunaga, 1999). Nitrate depletion terminates the spring bloom in Funka Bay and silicate is further consumed after the depletion of nitrate (Kudo *et al.*, 2000). One third of annual primary production occurs during the spring bloom in the bay (Kudo and Matsunaga, 1999). Some of the carbon produced is exported to the deeper layer as settling particles. A large settling flux is observed a few weeks after the peak of the spring bloom in Funka Bay (Miyake *et al.*, 1998).

Settling and sedimentation of particulate organic matter onto the sediment surface are the fundamental processes connecting pelagic with benthic ecosystems. Decomposition of organic matter on the sediment surface layer is highly dependent on these processes. More than 80% of organic nitrogen compounds that deposit on the sediment are remineralized and return to the euphotic layer (Wollast, 1991). This benthic flux may support further primary production in the euphotic layer.

Decomposition of organic substances progresses through exudation by grazers or heterotrophic bacterial activity (Dickson and Wheeler, 1995; Ward, 2000). Nitrogen has several inorganic forms and ammonium is the first breakdown product of organic nitrogen. This ammonium is oxidized to nitrite and then to nitrate (nitrifica-

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tion). Nitrate is therefore the most oxidized form of dissolved inorganic nitrogen (DIN) and is stable and abundant in an aerobic environment. The nitrification rate is measured by accumulation of nitrite or nitrate in incubation bottles loaded with specific inhibitors (allylthiourea or methyl fluoride for ammonium oxidation and chlorate for nitrite oxidation; Bianchi *et al.*, 1997). Another approach is to use the stable isotope ^{15}N as a tracer (Olson, 1981; Ward *et al.*, 1984). These measurements are carried out in incubation bottles. If the decomposition of organic matter and the regeneration process take place in a closed system, one may observe the accumulation of regenerated nutrients and quantitative analysis may be possible, based on the changes in oxygen and nutrients *in situ*.

Funka Bay has an area of 2.3×10^3 km^2 with mean and maximum depths of 59 and 96 m, respectively. The bay is conical in shape, separated by a sill at 60 m depth at the mouth. Major water renewal occurs twice a year, via Oyashio water in spring and Tsugaru Warm Water in autumn (Ohtani, 1971). The bottom water tends to be isolated from the surface (Takahashi *et al.*, 2005) and the water turn over time is longest (200 days) after the bloom (Isoda *et al.*, 1998). A semi-closed system is thus maintained in the benthic layer in Funka Bay after the spring bloom.

In this study we quantified the processes by which nutrients are regenerated near the sediment water interface after the spring bloom in Funka Bay. The change over time of dissolved oxygen and nutrients permits a stoichiometric analysis of the nutrient regeneration processes. In particular, tracking the sequence of oxidation of nitrogenous nutrients enables us to estimate a first order reaction rate constant for each nitrification process.

2. Materials and Methods

Sampling cruises were conducted monthly aboard the R/V '*Ushio Maru*' during February and November, 1998, and March and December, 1999. More frequent sampling (weekly to bi-weekly) was conducted during the spring bloom in March. The sampling station was Stn 30 (42°16.2′ N, 140°36.0′ E, depth 92 m) in Funka Bay (Fig. 1). Water samples were taken vertically with 5 L Niskin samplers. Samples for DO analysis were siphoned from the sampler outlet into DO bottles, then fixed immediately. The sample bottles were kept in a dark place for no more than 12 h until analysis with a HIRAMA ART-3 automatic titrator with photometric end-point detection. The theoretical 100% saturation value was calculated according to Weiss (1970). The apparent oxygen utilization (AOU) was calculated according to the difference between the saturated DO and the DO concentration *in situ*.
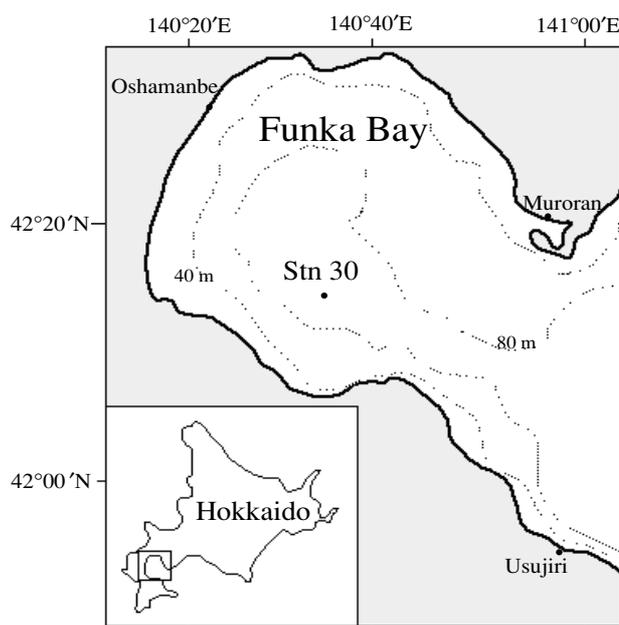
An aliquot of sample was filtered through a Whatman

Fig. 1. Sampling station.

GF/F filter. The filter was stored frozen in *N,N*-dimethylformamide to extract plant pigments (Suzuki and Ishimaru, 1990). The extracted chlorophyll *a* (Chl-*a*) was measured with a HITACHI F-2000 fluorescence spectrophotometer. The samples for nitrate (NO_3), nitrite (NO_2), ammonium (NH_4), phosphate (PO_4) and silicate (SiO_2) analysis were stored frozen for subsequent analysis with a Technicon Autoanalyzer II (Grasshoff *et al.*, 1999). Salinity and temperature were monitored with a Sea-Bird 911 CTD sensor.

Linear regression analysis was performed using Kaleida Graph (Synergy Software), and standard deviation (s.d.) for the slope and intercept of the regression line were obtained from a general curve fit program.

3. Results

3.1 Hydrography

Following the definition given by Ohtani (1971), the salinity of typical Funka Bay Winter water (FW) is more than 33.6 and that of Oyashio water (OW) is less than 33.3. Salinity in February, 1998 was 33.3 and was vertically homogeneous (Fig. 2). Surface salinity decreased gradually due to the inflow of Oyashio water and a spring thaw after April (Hasegawa and Isoda, 1997; Kudo and Matsunaga, 1998). This decrease in salinity was obvious in the upper 40 m depth. Salinity below 80 m was not influenced by the water mass exchange in the upper layer. Salinity in the deeper layer (80–90 m) ranged from 33.0 to 33.4 until August, when it increased to 33.7 due to
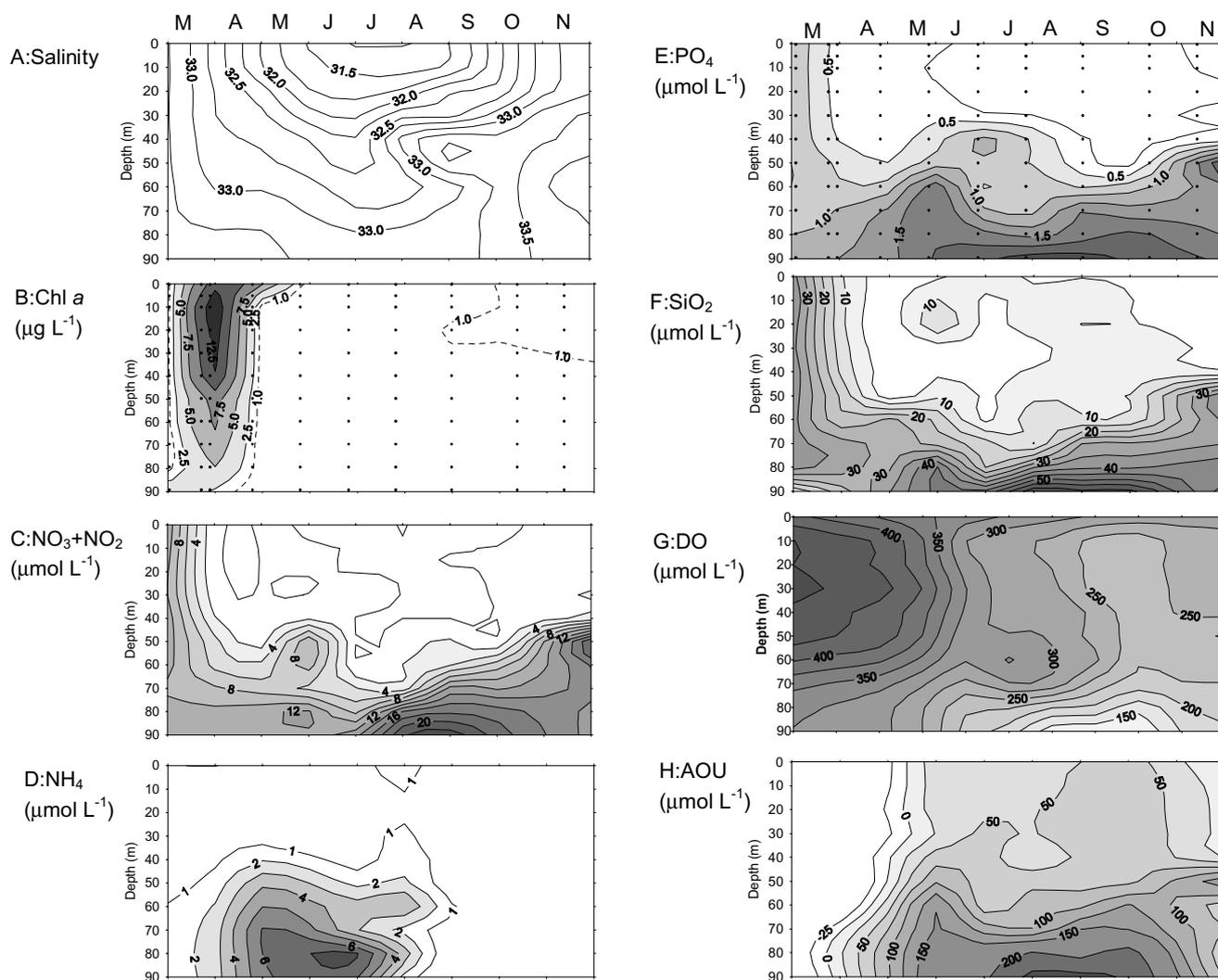
Fig. 2. Seasonal change in salinity (A), Chl-*a* (B), nitrate + nitrite (C), ammonium (D), phosphate (E), silicate (F), DO (G) and AOU (H) in 1998.

mixing with Tsugaru Warm water (Tw), which intruded into a middle layer (40–60 m) after August.

3.2 Nutrients and chlorophyll a

A massive spring phytoplankton bloom occurred in mid-March, 1998. The highest Chl-*a* value (more than 20 μg L^{-1}) was observed around 20 m on March 18 (Fig. 2). Chl-*a* decreased to less than 1 μg L^{-1} in April, indicating the decline of the spring bloom. Chl-*a* was as low as 1 μg L^{-1} in summer and autumn.

Nutrients were abundant and vertically homogenous in February at about 10, 40 and 1.2 μmol L^{-1} for nitrate, silicate and phosphate, respectively (Fig. 2). Nutrients were consumed in the upper layer (0–60 m) during the development of the spring bloom. Nitrate was depleted first in late March and silicate subsequently decreased to

below the detection limit. Phosphate remained at 0.3 μmol L^{-1} at the end of the bloom and decreased gradually until depletion in August. Ammonium in the upper layer was less than 1 μmol L^{-1} and the seasonal variation was small (Fig. 2). After the spring bloom, high concentrations of ammonium were observed in the deeper layer. The highest ammonium concentration (8.05 μmol L^{-1}) was found at 80 m in June. Silicate and phosphate also increased in this layer (Fig. 2).

3.3 Dissolved oxygen (DO) and apparent oxygen utilization (AOU)

Dissolved oxygen in March and April, 1998 was 400–430 μmol L^{-1} in the upper 60 m and 300–350 μmol L^{-1} in the deeper layer (60–90 m, Fig. 2). DO decreased vertically toward summer, reaching 240 μmol L^{-1} in the up-
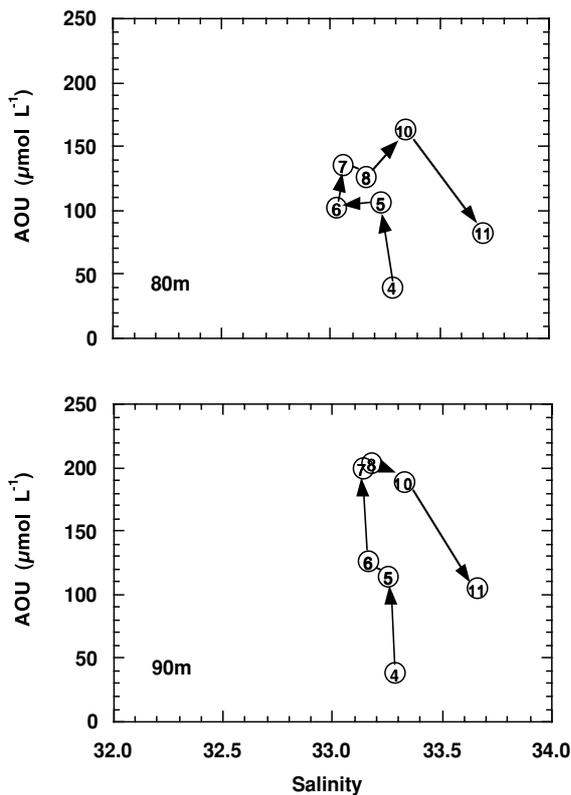
Fig. 3. Salinity vs. AOU plot at 80 m and 90 m from April to November in 1998. Number in symbol indicates month (e.g., 4: April).

Fig. 4. Time course change of AOU, DIN, NH_4, NO_2, NO_3, PO_4 and SiO_2 at 90 m in 1998.

per 30 m and 130 μmol L^{-1} at 90 m in August. AOU in spring was nearly zero or slightly negative in the upper 60 m and 50 μmol L^{-1} in the deeper layer (60–90 m, Fig. 2). AOU in the upper layer increased to 50 μmol L^{-1} in May and then showed little change until August. AOU near the bottom (80–90 m) increased with time and the highest AOU (260 μmol L^{-1}) was observed at 90 m in July and August.

Hydrography, nutrients, DO and Chl-*a* showed a similar pattern of seasonal change in 1999 (not shown) to that in 1998, except for a peak in nitrite at the bottom in July, 1999 (see below).

3.4 Nutrient regeneration in the deeper layer

After the spring bloom in March, active nutrient regeneration occurred in the deeper layer as the increase in ammonium and the consumption of oxygen were obvious in this layer (Fig. 2). A plot of salinity vs. AOU at 90 m indicated that AOU increased gradually while salinity changed little until August (Fig. 3). AOU at 90 m decreased in October and November with the increase in salinity, indicating mixing with another water mass (i.e., Tsugaru Warm water). At 80 m, AOU increased from April
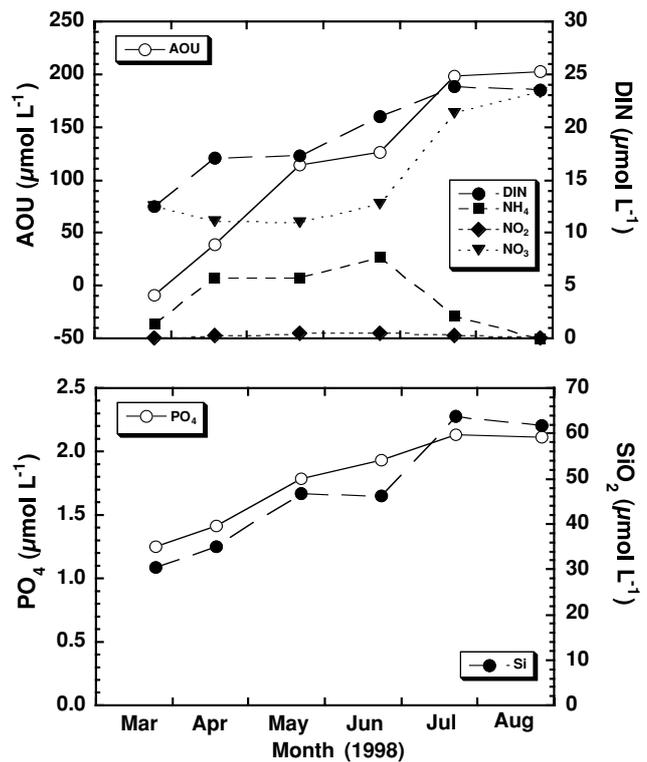
to August, but salinity dropped by 0.3 in June. Judging from the vertical profiles of AOU and salinity, these values at 80 m were likely to be influenced by the upper water mass through advection or diffusion processes. Since the change in salinity at 90 m was nominal until August, mixing of upper water mass seemed negligible. AOU, DIP and DIN at 90 m increased linearly with time between March and July in 1998 (Fig. 4) and 1999 (Fig. 5). There was no increase in concentrations from July to August. Ammonium increased from March to June and decreased to August while AOU increased linearly with time. The nitrate level was 13 μmol L^{-1} during March and June, increasing to 23 μmol L^{-1} after June when ammonium started to decrease. While nitrite at 90 m in 1998 was <0.5 μmol L^{-1}, elevated concentrations of nitrite (4–7 μmol L^{-1}) were observed in June and July, 1999, when nitrification from ammonium to nitrate was observed. The slope (error) of the regression analysis from March to July shows that the rate of increase of AOU, DIP and DIN was 1.66 (0.18), 0.0076 (0.0003) and 0.093 (0.005) μmol L^{-1} d^{-1}, respectively. The corresponding rates in 1999 were 1.93 (0.10), 0.0069 (0.0013) and 0.182 (0.052) μmol L^{-1} d^{-1}, respectively. The regression analysis for DIN in 1999 was conducted from April to July as no increase was observed until April. Silicate also increased
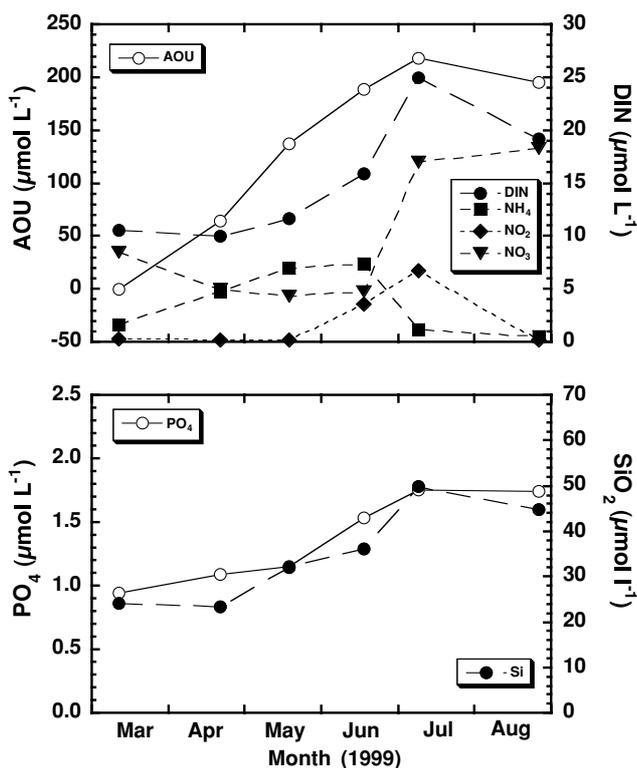
Fig. 5. Time course change of AOU, DIN, NH_4, NO_2, NO_3, PO_4 and SiO_2 at 90 m in 1999.
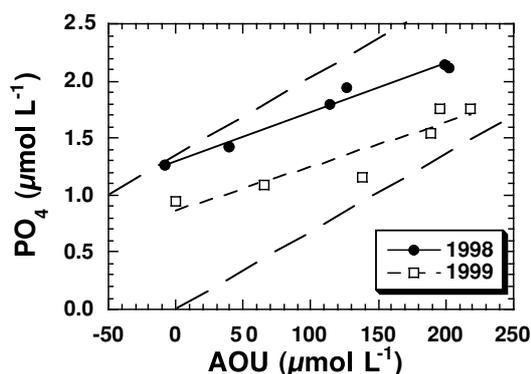

Fig. 6. Relationship between AOU and phosphate at 90 m from March to August in 1998 and 1999. Solid and dashed line indicate a regression line for each year and the broken lines indicate the Redfield stoichiometric ratio (AOU:PO_4 = 138:1) as a reference with a different offset.
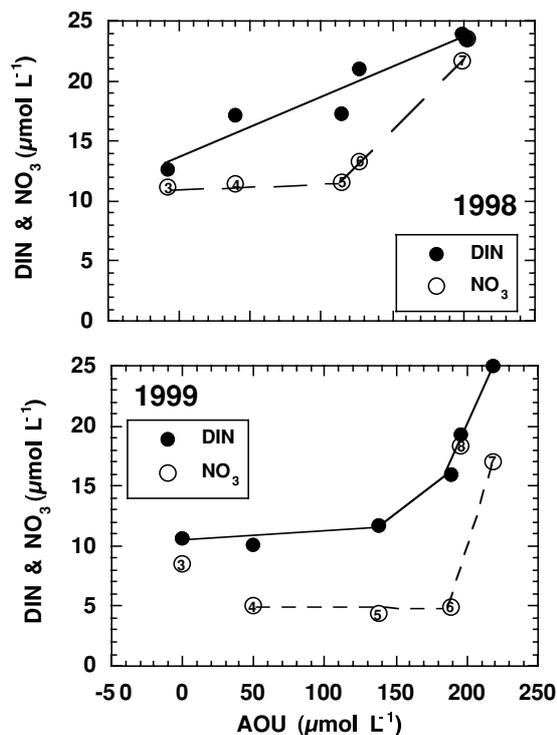

Fig. 7. Relationship between AOU and DIN at 90 m. The difference between DIN and nitrate plus nitrite indicates the amount of ammonium. Number in symbol indicates month.

linearly at this depth from 30 μmol L^{-1} in March to 64 μmol L^{-1} in July, 1998 and from 24 μmol L^{-1} in March to 45 μmol L^{-1} in August, 1999. The increase rate of silicate was 0.259 (0.047) and 0.210 (0.059) μmol L^{-1} d^{-1} for 1998 and 1999, respectively.

Phosphate at 90 m showed a good linear correlation with AOU, having a slope (s.d.) of 4.28×10^{-3} (0.32×10^{-3}) (r = 0.99) for 1998 and 3.83×10^{-3} (0.76×10^{-3}) (r = 0.93) for 1999 (Fig. 6). The y-intercept (error) was 1.29 (0.04) and 0.86 (0.12) μmol L^{-1} for 1998 and 1999, respectively. Dissolved inorganic nitrogen (DIN; NO_3 + NO_2 + NH_4) also showed good linearity with AOU (r = 0.95), but nitrate did not increase when AOU increased from 0 to 120 μmol L^{-1} in 1998 (Fig. 7). Nitrate increased linearly at >120 μmol L^{-1} of AOU. As nitrite was less than 0.5 μmol L^{-1} in 1998, the difference between DIN and nitrate was ascribed to ammonium. Thus, the earlier increase in DIN resulted from the remineralization of ammonium and the later increase in nitrate was attributable to the oxidation of ammonium to nitrate. A similar pattern of change in AOU vs. DIN and nitrate was found in 1999 (Fig. 7). However, the DIN concentration did not increase until AOU reached 130 μmol L^{-1}. In this region, nitrate decreased at 6 μmol L^{-1}, so the increase in ammonium was compensated by this decrease. The difference between DIN and nitrate at <140 μmol L^{-1} of AOU was ascribed to ammonium, but a difference of AOU > 140 μmol L^{-1} was due to nitrite and ammonium since a high concentration of nitrite was observed in 1999.

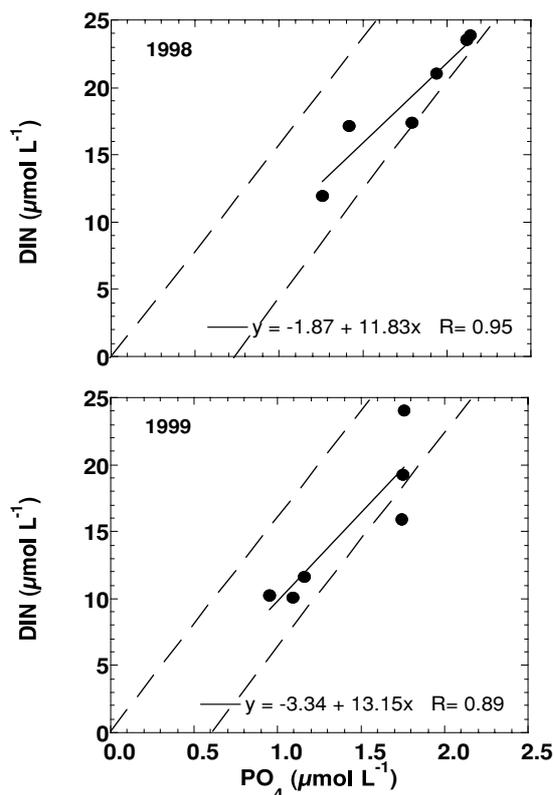There was a significant linear correlation (p < 0.01)

Fig. 8. Relationship between phosphate and DIN at 90 m from March to August, 1998 and 1999. Broken lines indicate the Redfield stoichiometric ratio (PO_4:NO_3 = 1:16) as a reference with a different offset.

Fig. 9. Relationship between phosphate and silicate at 90 m from March to August, 1998 and 1999.

between phosphate and DIN at 90 m with a slope (s.d.) of 11.8 (2.0) (r = 0.95) for 1998 and 13.2 (3.4) (r = 0.89) for 1999 (Fig. 8). DIN also showed a significant correlation (p < 0.01) with silicate at the same depth with a slope (s.d.) of 2.76 (0.56) (r = 0.92) for 1998 and 1.88 (0.21) (r = 0.98) for 1999 (Fig. 9).

4. Discussion

4.1 Decomposition and nitrification process

The accumulation of ammonium was obvious from April to June in the deeper layer in Funka Bay. The increase in nitrate was observed in July when ammonium concentration decreased. These changes were accompanied by a increase in AOU, so this process seems to be an aerobic nitrification. An elevated concentration of nitrite, an intermediate product of nitrification, was detected at 90 m in June and July, 1999, while it was not detected in 1998. Nitrite appeared when ammonium decreased and nitrate started increasing in 1999. The same trend was also observed from June to July, 1998, so nitrite seemed to be produced. A sampling interval of one month might
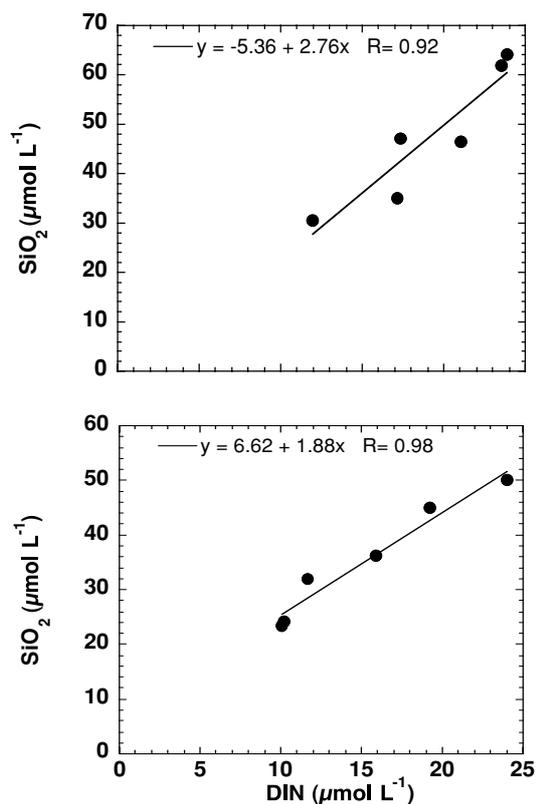
be the reason why no obvious nitrite peak was found in 1998. To quantify this process, we calculated the production and oxidation rate of ammonium. The gross production rate of ammonium was calculated from the increase in DIN for each period divided by the days of the period. The change in concentration of ammonium between sampling dates resulted from the difference between production and oxidation of ammonium, assuming a negligible loss due to diffusion or advection. Thus, the amount of ammonium oxidation in each period was calculated by subtracting the change in concentration of ammonium from the increase in DIN. The gross ammonium production rate ranged from 0.057 to 0.114 μmol L^{-1} d^{-1} while ammonium concentration at 90 m increased until June, 1998 (Fig. 4 and Table 1). The standing stock of ammonium decreased after July while the production was positive. This decrease was due to nitrification. The ammonium oxidation rate ranged from 0.006 to 0.292 μmol L^{-1} d^{-1}. The total concentration of oxidized ammonium was 12.0 μmol L^{-1}. This agrees well with the increase in nitrate concentration between July and August. The same calculation was conducted for 1999 (Table 2), resulting in a gross production rate of ammonium in the range from 0.056 to 0.438 μmol L^{-1} d^{-1} while the oxida-

Table 1. Change in concentration during the sampling interval for AOU and nutrients at 90 m in 1998. ΔDIN is the sum of ΔNH_4, ΔNO_2 and ΔNO_3 in μmol l^{-1}. NH_{4prod} and NH_{4ox} denote the rates for production and oxidation of NH_4 in μmol l^{-1} d^{-1}. Positive value means an increase and negative value means a decrease during the period.

Period	Days	ΔAOU	ΔDIP	ΔDIN	ΔNH_4	ΔNO_2	ΔNO_3	NH_{4prod}	NH_{4ox}
I (Mar.–Apr.)	24	48.5	0.16	2.61	2.38	0.18	0.05	0.108	0.010
II (Apr.–May)	34	74.9	0.37	1.95	1.76	0.23	−0.04	0.057	0.006
III (May–June)	32	11.8	0.15	3.66	1.97	0.01	1.72	0.114	0.053
IV (June–July)	29	72.5	0.20	2.89	−5.58	−0.14	8.57	0.100	0.292
V (July–Aug.)	34	4.0	−0.02	−0.36	−2.15	−0.25	2.04	—	—

—: Negative value.

Table 2. Change in concentration during the sampling interval for AOU and nutrients at 90 m in 1999. ΔDIN is the sum of ΔNH_4, ΔNO_2 and ΔNO_3 in μmol l^{-1}. NH_{4prod} and NH_{4ox} denote the rates for production and oxidation of NH_4 in μmol l^{-1} d^{-1}. Positive value means an increase and negative value means a decrease during the period.

Period	Days	ΔAOU	ΔDIP	ΔDIN	ΔNH_4	ΔNO_2	ΔNO_3	NH_{4prod}	NH_{4ox}
I (Mar.–Apr.)	40	65.2	0.14	−0.14	3.13	−0.09	−3.18	—	—
II (Apr.–May)	28	72.6	0.07	1.58	2.18	0.04	−0.04	0.056	—
III (May–June)	30	49.6	0.38	4.28	0.47	3.44	1.72	0.142	0.127
IV (June–July)	21	25.0	0.20	9.21	−6.27	3.20	12.28	0.438	0.737
V (July–Aug.)	49	−47.3	0.01	−5.62	−0.59	−6.57	1.54	—	—

—: Negative value.

tion rate of ammonium ranged from 0.127 to 0.737 μmol L^{-1} d^{-1}. The ammonium oxidation rate observed in the present study was in the same range as rates reported in the Cariaco Trench, Saanich Inlet and off the Peru (Ward *et al.*, 1989), measured with a ^{15}N method.

Nitrification from ammonium to nitrate requires two moles of oxygen for each mole of nitrogen: $NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$. Most of the nitrification from ammonium took place between June and July. During this period 16 μmol L^{-1} of oxygen was required to oxidize 8 μmol L^{-1} of the ammonium increment while 72.5 μmol L^{-1} of oxygen was consumed *in situ* in 1998. The decomposition of organic matter also took place during the same period because DIN and phosphate increased by 2.89 and 0.2 μmol L^{-1}, respectively. The oxygen requirement for decomposition was calculated as 45–55 μmol L^{-1} using the AOU to DIN or phosphate ratio observed in 1998. This suggests that the oxygen consumption for oxidizing ammonium was nominal (20%) compared to the overall consumption.

Assuming decomposition follows a first order reaction, the decomposition rates are expressed by the following equation: $dC/dt = kC$, where C, t and k are the concentration of substrate, time and a rate constant, respectively. Here the substrate concentration for decom-

position was not known. However, the spring bloom in the bay lasts for 2–3 weeks (Kudo and Matsunaga, 1999) and low Chl-*a* (<1.0 μg L^{-1}) values were maintained after the bloom (Fig. 2). A large increase in settling flux of organic matter is observed a few weeks after the bloom and this high flux continues for only two weeks and the flux then decreased to one fifth (Miyake *et al.*, 1998), indicating a major supply of organic matter to the bottom during this period. After this the increase in DIN was obvious and the increase in DIN at 90 m ceased in August, so we assumed that the total amount of DIN increase at this depth represents the total substrate concentration of biodegradable nitrogen in five months. This total substrate concentration was estimated as 11.3 and 15.1 μmol L^{-1} in 1998 and 1999, respectively. Thus, the change with time of biodegradable nitrogen concentration was calculated by subtracting the DIN increase from the total substrate concentration. A good exponential fit was obtained from March to June (1998) and April to June (1999) with a slope of −0.014 and −0.008 d^{-1}, representing the rate constant of decomposition for 1998 and 1999, respectively (Fig. 10). A half-value period for biodegradable N was calculated as −0.693/k, 49.5 and 86.6 days for 1998 and 1999, respectively. The decomposition rate is a function of temperature, but temperature near the bottom
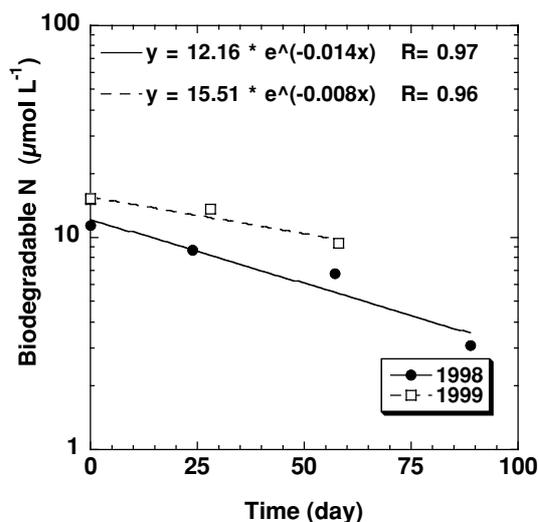
Fig. 10. Change in biodegradable N concentration (calculated) from March to June (1998) and April to June (1999). Time zero was set at March 18 (1998) and April 20 (1999) when minimum DIN was observed. Initial concentration was assumed to be the sum of regenerated DIN in August. Biodegradable N concentration was calculated by subtracting DIN concentration from initial concentration. Lines indicate exponential regression line.
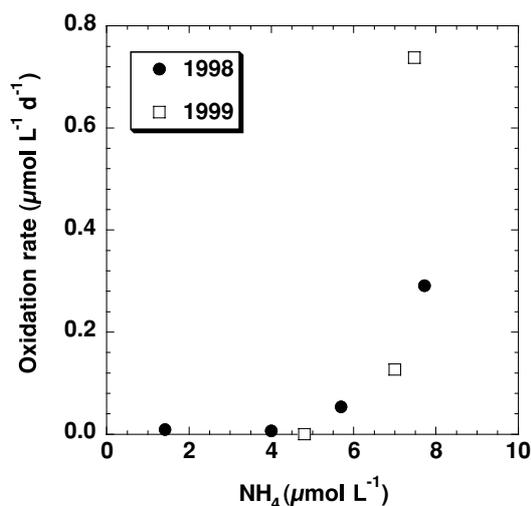

Fig. 11. Relationship between ambient ammonium and oxidation rate of ammonium at 90 m from March to August, 1998 and 1999. Ambient ammonium concentration was initial concentration in each period (Tables 1 and 2).

of Funka Bay was fairly constant (3–4°C), so we do not have to consider a temperature effect on the rate processes.

The oxidation rate of ammonium increased with ammonium concentration (Fig. 11), indicating a substrate dependency, but the rate increased suddenly when the ambient ammonium concentration increased to more than 5 μM. Ward (1985) reported a linear increase in the oxidation rate of ammonium with ambient ammonium concentration. Culture experiments show a Michaelis-Menten type kinetics in the relationship between oxidation rate and ammonium concentration (Suzuki *et al.*, 1976; Hyman and Wood, 1983). These facts suggest that the oxidation rate of ammonium reported here seems not to be solely a function of substrate. Ammonium oxidizing bacteria are inhibited by light and high levels of organic matter (Martin, 1978; Bedard and Knowles, 1989). Light inhibition is unlikely because the euphotic zone in the bay is about 30 m. Information on organic matter, which inhibits this reaction, was uncertain in the bay, but accumulation of organic matter near the bottom after the bloom was evident. While ammonium oxidizing bacteria require molecular oxygen to oxidize nitrogen compounds and for respiration, they are considered to grow best under relatively low oxygen conditions (Goreau *et al.*, 1980). The oxygen gradually decreased near the bottom after the bloom (Figs. 2 and 3), so a low oxygen condition, attained

in June and July, seemed suitable for them to flourish. Organic matter inhibition and oxygen concentration may be possible reasons for a non-linear response of the oxidation rate of ammonium to substrate in the bay.

4.2 Budget calculation

The total amount of regenerated nitrogen was estimated from the increase in DIN in the deeper part of the water column. The increase in DIN was observed at depths deeper than 60 m (Fig. 2). The integrated DIN standing stock between 60 m and 90 m was 246.4 mmol m^{-2} on March 24, increasing to 533.8 mmol m^{-2} on July 22, i.e., a difference of 287.4 mmol m^{-2}. The equivalent carbon production was 22.8 gC m^{-2} assuming the Redfield C to N ratio of 6.6. The primary production during the spring bloom was 66.5 gC m^{-2} in 1998 (Kudo unpublished, ^{13}C and *in situ* 24 hr incubation), 34% of the organic material produced was decomposed in the deeper layer after the spring bloom. This estimate is comparable to the export organic carbon flux of 25 gC m^{-2} after the spring bloom, measured by a sediment trap at 60 m (Miyake *et al.*, 1998).

All nutrients showed a concentration gradient toward the bottom (Fig. 2), so a diffusive upward flux may present. This diffusive flux was estimated to be 16.5 mmol m^{-2} month^{-1} for nitrate using the concentration gradient between 60 and 90 m on July 22 and the diffusion coefficient of 0.1 cm^{2}sec^{-1} at this depth range in Funka Bay (Uematsu and Tsunogai, 1983). This flux represents 3% of the total amount of DIN on July 22. This estimate would seem to be a maximum because the concentration gradient was attained the largest value in July. Thus, the

effect of the upward diffusive flux was negligible for the estimation of the total amount of regenerated DIN.

4.3 Oxygen consumption and nutrient regeneration processes

In Funka Bay, nutrient regeneration was accompanied by oxygen consumption at the bottom, but stoichiometric analysis suggests a higher oxygen consumption relative to the "classical" Redfield ratios. The ratio of AOU to PO_4 was 233 and 261 for 1998 and 1999, respectively (Fig. 6), which is 1.7 to 1.9 times higher ratio than the Redfield ratio (138). Takahashi *et al.* (1985) examined the actual $-O_2/P$ ratio on isopycnals in the major thermocline (250–1000 m) of the open ocean and reported a higher value (172) than the Redfield ratio. Similar examinations of the nutrient regeneration process were conducted in the open oceans (Anderson and Sarmiento, 1994). The reason for the relatively high AOU/PO_4 ratios found in Funka Bay is not clear, but the respiration quotient or composition of organic materials may change in time and space.

The y-intercept of AOU vs. PO_4 plots was 1.29 and 0.86 μmol l^{-1} for 1998 and 1999. This value was a preformed PO_4, with conservative properties. The different preformed PO_4 values suggest that PO_4 concentration after the winter vertical mixing was different in each year because this mixing replenished oxygen to the whole water column.

Jørgensen and Richardson (1996) pointed out that nutrient flux from sediment is an important source for pelagic algal production in shallow coastal areas. The water-sediment interface, a diffusive boundary layer, accumulates a high concentration of organic matter (detritus) from the euphotic zone. Most of the decomposition and remineralization takes place in this layer (Wollast, 1991).

In the regeneration of DIN and PO_4, the slope of correlation was 12–13, which is lower than the Redfield ratio (Fig. 8). The ratio of DIN to PO_4 in the surface water before the bloom was around 10 and as a result of consumption of DIN and PO_4 at the ratio of 16 during the bloom, phosphate remained in the surface water after the bloom (Kudo *et al.*, 2000). This ratio in the sinking particles was close to 16 after the bloom (Miyake *et al.*, 1998). There are thus two possibilities for explaining the lower DIN to PO_4 ratio during the regeneration process: loss of N or supply of P.

Watanabe and Tsunogai (1984) reported the phosphate concentration in interstitial water of sediment in Funka Bay. The upward flux of phosphate from sediment is 20 μmol m^{-2}d^{-1} from spring to summer. This may contribute some extent to the increase in phosphate in the bottom layer. However, DIN is also supplied from sediment, but nothing is known about the flux of DIN and the ratio of DIN to PO_4 from the sediment.

In considering denitrification near the sediment water interface, oxygen was never depleted near the bottom in Funka Bay while the concentration decreased after the bloom; the lowest value (130 μmol l^{-1}) was found in August, 1998. Although the redox potential in the sediment has not been reported, sulfate reduction occurs in the sediment around 10 cm and reaches a maximum in August (Watanabe and Tsunogai, 1984). We cannot rule out the possibility of denitrification in the sediment or microenvironment where anoxia persists.

Bacteria are responsible for much of the carbon and nutrient cycling in aquatic systems (Ducklow and Carlson, 1992; Simon *et al.*, 1992). High bacterial biomass and production at 90 m depth was found after the spring bloom in Funka Bay (Lee *et al.*, 2001). Particle attached bacteria (>1 μm fraction) contribute more than 50% of production in this layer. A high concentration of freshly deposited particulate organic matter was expected at the sediment-water interface. Thus, most of the decomposition of particulate organic matter should take place at this interface, producing ammonium as a first remineralized inorganic nitrogen. However, nitrification was likely to proceed in the water column because the ammonium produced diffused out of the interface and accumulated in the deeper layer.

Silicate regeneration was also observed as well as DIN and phosphate in the bottom layer of Funka Bay. The slope of the regression between DIN and silicate was 2.95, which is similar to the consumption ratio during the spring bloom (Kudo *et al.*, 2000). Silicon regeneration is a dissolution process and depends on temperature (Kamatani, 1982). However, microbial activity decomposes the organic surface coating on diatom frustules, resulting in the enhancement of silicate dissolution (Bidle and Azam 1999; Townsend and Thomas, 2002). Thus, a high microbial activity near the bottom in Funka Bay may enhance silicate regeneration with a similar ratio of Si to DIN in the consumption.

5. Conclusion

Regeneration of nutrients and consumption of oxygen were observed near the bottom of Funka Bay after the spring bloom. Nitrogenous nutrient regeneration exhibited the oxidation sequence from PON to nitrate through ammonium and nitrite. A similar nutrient regeneration process may occur in the natural environments, but water movement may disperse or weaken the signal of the process. The characteristic hydrography and topography of Funka Bay enabled us to observe this sequence and conduct a stoichiometric analysis of the nutrient regeneration process. Decomposition of organic matter produced during the spring bloom, which then settled down to the sediment, was mostly completed by August. De-

composition of organic matter followed a first order reaction and the rate constant for nitrogen ranged from 0.008 to 0.017 d^{-1}. The nitrification rate was substrate dependent, so we conclude that ammonium was first accumulated near the bottom and then ammonium oxidation occurred in July.

Acknowledgements

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