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The Importance of Nitrogen Release and Denitrification in Sediment to the Nitrogen Budget in Hiroshima Bay

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The main purpose of this study was to estimate the role of dissolved inorganic nitrogen (DIN) released from sediment and denitrification process in sediment on the nitrogen budget of Hiroshima Bay by means of collecting data on distributions and budgets of nitrogen and phosphorus in the bay, DIN fluxes across sediment-water interface and denitrification rates in the sediments of the same area. The TN : TP and DIN:DIP atomic ratios of the discharged freshwater were about 26 and 21, respectively. The standing stocks in the seawater of the TN : TP atomic ratio varied from 8 to 14 with an annual mean value of 11, while the DIN : DIP atomic ratio varied from 10 to 15 with an annual mean value of 12 in the bay. The residence time of nitrogen and phosphorus were estimated to be about 109 days and 200 days in the bay, respectively. The proportion of DIN released from sediment and denitrification rate to the loading of total nitrogen into Hiroshima Bay were 45% (37~82%) and 13% (0.0~37%), respectively, and the amount of nitrogen through denitrification process was 6.5 times larger than the outflow of nitrogen from the bay. The results show that DIN released from sediment and denitrification process in sediment play important roles on the nitrogen budget in Hiroshima Bay.

Key words : denitrification, nitrogen budget, nitrogen release, Hiroshima Bay

Introduction

In general, the water quality of the enclosed bay can be determined by the material balance including inflow and outflow of organic substance. Various kinds of substances flow into coastal area. For example, nitrogen compounds which flow into the bay are transformed to inorganic-organic nitrogen and dissolved-particulate nitrogen compounds by the biochemical processes, and a part of nitrogen spread out, while a portion of nitrogen precipitates and deposits on sediment. In the presence of dissolved oxygen, a portion of ammonium regenerated from benthic decomposition of organic material is oxidized to nitrite (NO_2^-) and nitrate (NO_3^-). A portion of nitrate is reduced to nitrous oxide (N_2O) and nitrogen gas (N_2) through denitrification process in anoxic condition and they are released to the water column and subsequently to the atmosphere.

The resulting gradients of the solutes cause a part of the mineralized compounds to be released to the water column. Denitrification mitigates coastal nitrogen loading from terrestrial sources and may in some cases limit coastal primary production (Seitzinger and Nixon, 1985). Thus, the two processes are considered important quantitatively in the nitrogen budgets of coastal area (Kemp et al., 1990). We have to control not only the nitrogen and phosphorus loading from terrestrial but also nitrogen and phosphorus released from sediment to prevent eutrophication in coastal area.

Recently, there have been several reports on the ammonium flux in sediment-water interface (Blackburn et al., 1983; Lohse et al., 1993; Kemp et al., 19

90) and the rate of denitrification in aquatic sediments (Sϕrensen, 1978; Nishio et al., 1983). However, there has been few studies on the estimation of the role of dissolved inorganic nitrogen (DIN; $NH_4^+ + NO_2^- + NO_3^-$) released from sediment and denitrification in sediment to nitrogen budgets of coastal area.

The main purpose of this study is to estimate the role of DIN released from sediment and the denitrification rate in sediment to the nitrogen budget in Hiroshima Bay. Among data used in this study were distributions and budgets of nitrogen and phosphorus (Kim et al., 1997a), DIN fluxes across the sediment-water interface (Kim, 1996), and denitrification rates in the sediments (Kim et al., 1997b) of the Hiroshima Bay.

Materials and Methods

The loading of total nitrogen (TN=PON+DON+DIN) and total phosphorus (TP=POP+DOP+DIP) into inner area and central areas of Hiroshima Bay were calculated by multiplying the loading of freshwater by the concentrations of total nitrogen and total phosphorus in every month from January 1991 to December 1993 in the bay. The freshwater discharged into Hiroshima Bay was reported by The Japan River Association from 1991 to 1993. The bay is located in the Seto Inland Sea and receives considerable input of nutrients and organic substances from several rivers (Fig. 1).

The standing stocks of total nitrogen and total phosphorus in seawater were calculated by multiplying the volume of sea water and the mean concentrations of total nitrogen and total phosphorus in the depth of each area. Monthly exchanges of seawater between inner and central areas of Hiroshima Bay and Aki-Nada were estimated by the difference of salinity between the two areas during the survey periods. The fluxes of total nitrogen and total phosphorus were calculated by multiplying the exchange of sea water by the concentrations of total nitrogen and total phosphorus in each sea area. The nitrogen budget was estimated, which includes inflowing and outflowing total nitrogen, with DIN released from sediment and nitrogen lost through denitrification in sediment of Hiroshima Bay. Finally, the proportion of DIN released from sediment and that of denitrification rate in sediment were estimated on the basis of the loading of total nitrogen into Hiroshima Bay seasonally.

The field investigation of DIN flux across the sediment-water interface and denitrification rate in sediment were carried out 4 times, August and October in 1994 and January and May in 1995 at inner area (stn.1) and central area stn.4 of the bay. Silt sediment prevails at almost all locations excepting the mouth of the bay where the sediment is sandy (Kim, 1996). One of the evaluation method for DIN fluxes was made from concentration gradients between sediment porewater and the overlying water, and the other method was also done as measuring DIN flux from the sediment-core experiment. The DIN fluxes were calculated from the change of concentration in the overlying water during the incubation and multiplying the obtained rate with the specific volume/area ratio of the core.

A acetylene (C_2H_2) inhibition method was used to estimate *in situ* denitrification rate in sediment of the same two areas. Denitrification rate was calculated as comparing N_2O the accumulation rates in sediments core with those in control core. The N_2O gas sample was analyzed by a chromatography (Shimazu, model GC-RIA) equipped with a thermal conductivity detector and the detection limit of N_2O was 0.01 μM.

Results and Discussions

Freshwater discharge into Hiroshima Bay was high in summer (0.84×10^9 m^3/month) due to high rainfall, but it was low in winter (0.24×10^9 m^3/month) from 1991 to 1993. An annual mean inflow of freshwater

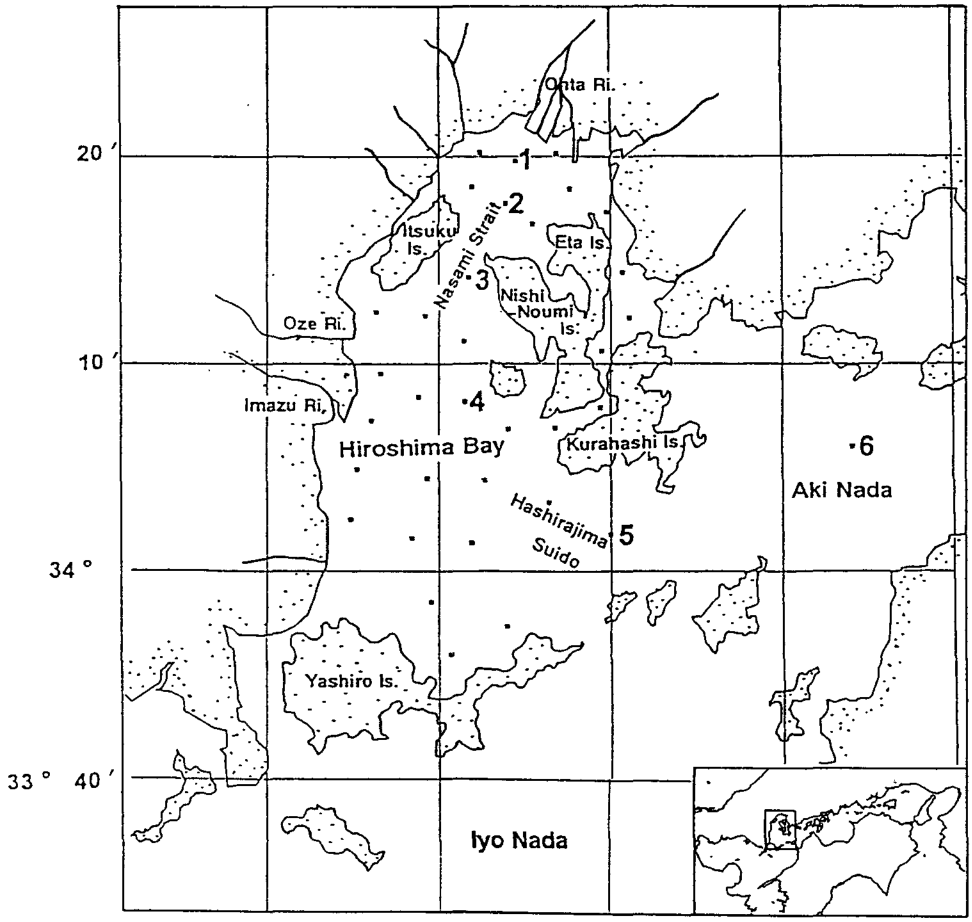

Fig. 1. Location of sampling stations in Hiroshima Bay, Japan. The dots and those with numbers indicate the stations where salinity and nutrient measurements were carried out from January 1991 to December 1993, respectively.

was to be 0.45×10^9 m^3/month. It was much higher in 1993 (0.67×10^9 m^3/month) when the rainfall was higher than the other years.

The precipitation of ammonium and nitrate from atmosphere was calculated by multiplying the rainfall in the bay and the concentration of ammonium and nitrate in rain, the result was about 7.72 ton/month annually. The rainfall was measured by the observatory of Kurahashi Island in Hiroshima Bay from 1991 to 1993 and the concentration of ammonium and nitrate in rain was measured by the Japan Chemistry Association in 1992. The mean loading of total nitrogen and total phosphorus into Hiroshima Bay was 870 tonN/month and 72.3 tonP/month, respectively.

About 79% of the total nitrogen and 93% of the total phosphorus of the discharged freshwater were loaded into inner area, and the remains were flowed into central area. The loads of total nitrogen and total phosphorus's seasonal patterns accompanied by the load of freshwater were higher in summer than in the other seasons due to heavy rainfall. The TN : TP and DIN : DIP atomic ratios of the discharged freshwater were about 26 and 21, respectively.

The standing stocks of total nitrogen and total phosphorus in sea water were estimated to be about 3163 tonN and 482 tonP, respectively. The 12% of the total nitrogen and total phosphorus were in inner area and the others were in central area of the bay. The TN

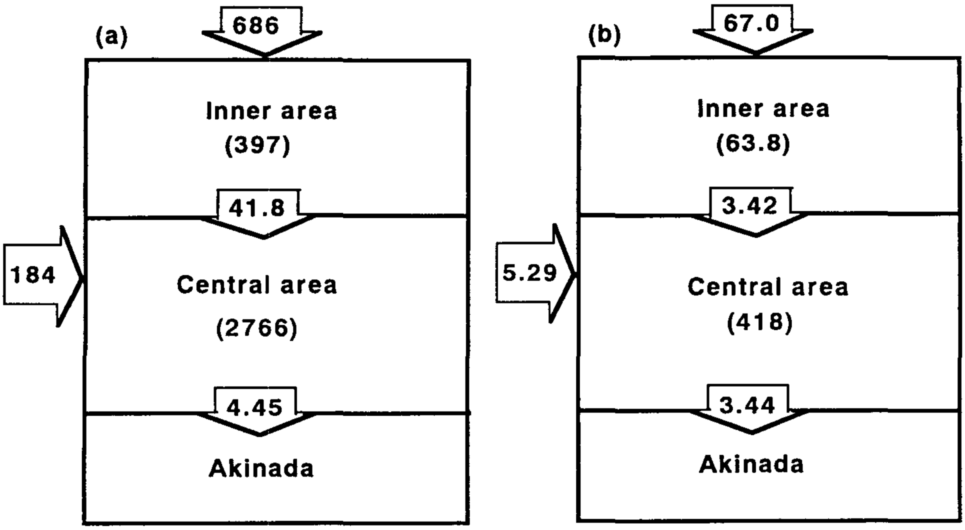

Fig. 2. The budget of (a) nitrogen and (b) phosphorus in Hiroshima Bay (an annual mean value from January 1991 to December 1993). Value in parenthesis is tonN and in arrow mark is tonN/month (Kim et al., 1997a).

: TP atomic ratio in the bay varied from 8 to 14, with a mean value of 11. The DIN : DIP atomic ratio varied from 10 to 15, with a mean value of 12 in the bay. Concerning the Redfield's ratio 16, nitrogen lack can be inferred in growth of phytoplankton in Hiroshima Bay.

The net exchange of seawater between inner area and central area was 9.47×10^9 m^3/month, and the exchange between central area and Aki-Nada was 13.2×10^9 m^3/month. The total nitrogen and total phosphorus flew into the inner area in summer because the water column became stratified and the nutrients of the lower layer flew into the bay more easily. However, during other seasons, total nitrogen and total phosphorus flew to outside of the bay. The fluxes of total nitrogen and total phosphorus out of the central area from the inner area were estimated to be 41.8 tonN /month and 3.42 tonP/month, and the fluxes out of Aki-Nada from the central area were about 4.45 tonN/month and 3.44 tonP/month, respectively.

The total nitrogen and total phosphrus budgets were estimated in every season and annually in the bay (Fig. 2; Kim et al., In Press). Based on this budgets, the precipitation of nitrogen and phosphorus were calculated by subtracting outflow of TN, TP from inflow of TN, TP and then dividing the remain by the area of the bay. The precipitation of nitrogen and phosphorus in the bay were calculated 9.87 gN/m^2 · yr and 0.84 gP/m^2 · yr, respectively. The residence times of nitrogen and phosphorus in the bay calculated by the standing stocks of TN, TP and the amount of the inflow of TN, TP were estimated to be about 109 days and 200 days, respectively. It showed that the residence times of nitrogen and phosphorus in Hiroshima Bay were shorter than the Harima-Nada and longer than the Osaka Bay (Yanagi et al., 1985).

The calculated and measured DIN fluxes from the sediment were 42.6 (18.4~79.0) μg-at/m^2 · hr and 113 (−263~194) μg-at/m^2 · hr, respectively (Fig. 3; Kim, 1996). They were maximum in summer, and the measured DIN flux was 2~5 times higher than the calculated one. The calculated DIN flux was considered to be more stable than the measured DIN flux, because the standard deviation of the former was $\pm$ 0.1~ $\pm$ 15, while the standard deviation of latter was $\pm$ 0.2~ $\pm$ 43.

The denitrification rate in the sediment was the highest in summer, while the denitrification rate was

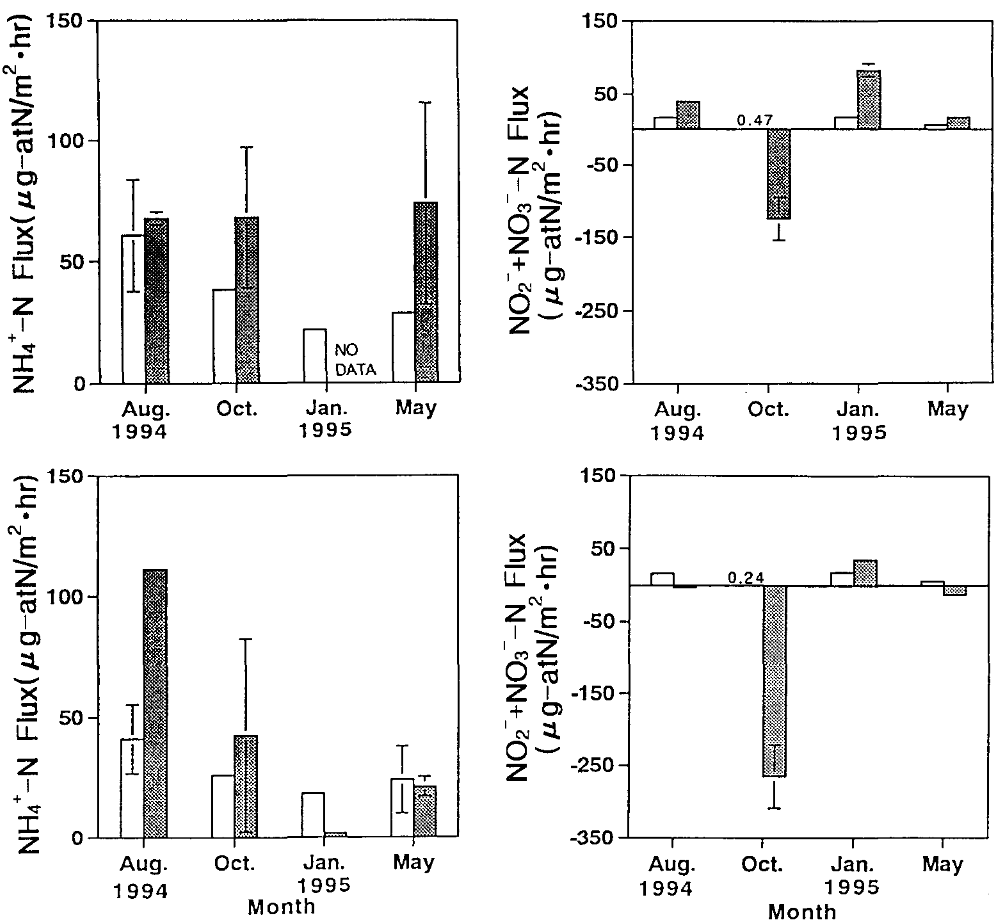

Fig. 3. Variation of ammonium and nitrite%nitrate fluxes across sediment-water interface in (upper) inner area and (lower) central area of Hiroshima Bay (annual mean value from August 1994 to May 1995). Open bars and shaded bars indicate the calculated and measured values, respectively (Kim, 1996).

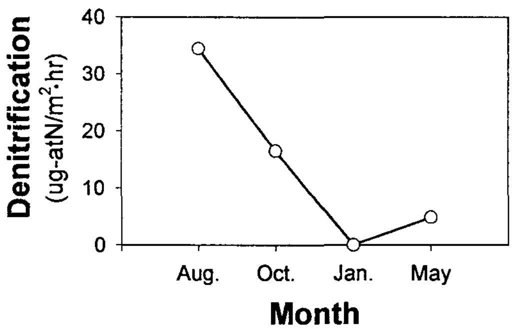

Fig. 4. Seasonal variation of denitrification in the sediment of Hiroshima Bay (annual mean values in two stations from January 1991 to December 1993).

zero at both stations in winter. In winter, dissolved oxygen in the overlying water was high (5.8 ml/l) and vertical mixing of water column resulted in the highly oxidized condition of the sediment (Eh: 153 mV and 302 mV) which suppressed the denitrification processes (Fig. 4). An annual average denitrification rate was 14.0 μg-at/m^2 · hr ranging from 0.00 to 34.5 μg-at/m^2 · hr. This result is contrast with the other areas, because the condition of Hiroshima Bay sediment is usually oxidized in all seasons except for summer.

Hosomi (1993) reported that the amount of interior loading of nutrients was the same as that of external loading of nutrient from terrestrial in lake Kasumigaura, Japan. Shiozawa et al (1984) also reported

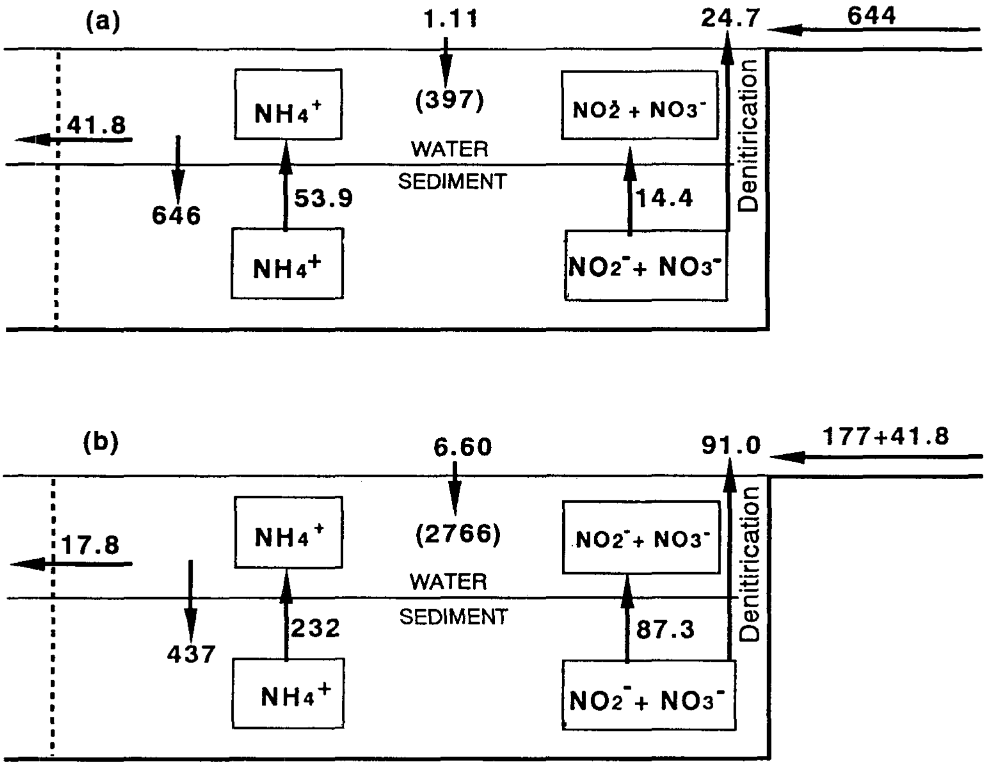

Fig. 5. Estimated nitrogen budget for N pools and DIN fluxes across the sediment-water interface of (a) the inner area and (b) the central area of Hiroshima Bay (an annual mean value from January 1991 to December 1993). Value in parenthesis is tonN and in arrow mark is tonN/month.

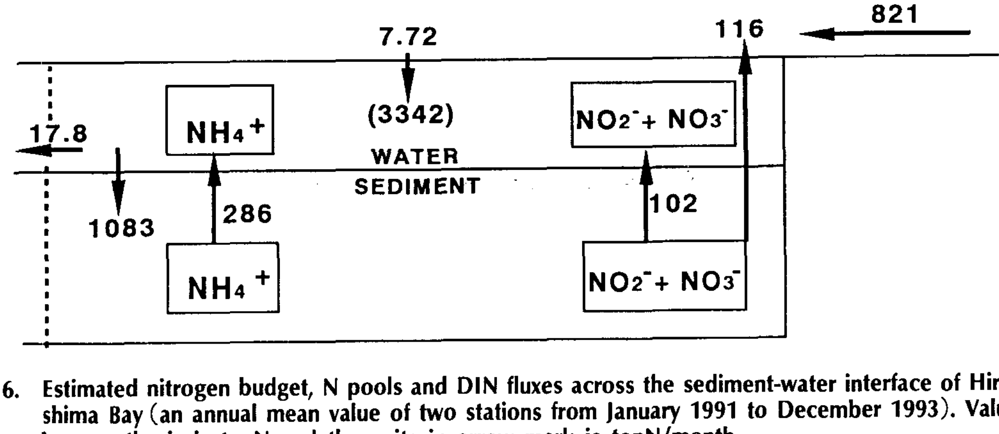

Fig. 6. Estimated nitrogen budget, N pools and DIN fluxes across the sediment-water interface of Hiroshima Bay (an annual mean value of two stations from January 1991 to December 1993). Value in parenthesis is tonN and the units in arrow mark is tonN/month.

that the amount of nitrogen released from sediment of Seto Inland Sea accounted for 1/5~1/2 nitrogen loading from terrestrial and in addition, it was almost equal to the amount of external nitrogen loading from terrestrial when the sea water was eutrophicated.

In this study, The nitrogen budget was estimated on the same unit (tonN/month) including of DIN released from sediment and nitrogen loss through denitrification process in sediment of each areas (Fig. 5) and in the total area of the bay (Fig. 6). The proportions of DIN released from sediment and denitrification in sediment to the loading of total nitrogen into the central area were higher than the inner area, where sea surface area is relatively small. The proportions of DIN released from sediment and that of denitrification rate to the loading of total nitrogen into the total area of the bay in summer were 37% and 6.0%, respectively. In autumn, the both proportions were 37%. In winter, the proportion of DIN released from sediment was 82%, higher than in the other seasons, because the input of nitrogen was small while the DIN released from sediment was high in this season. The proportion of denitrification rate was negligible, because the denitrification did not occurre in winter. In spring, the both proportions were 70% and 19%, respectively. An annual mean values of the both proportions were 45% (37~62%) and 13% (0.0~37%), respectively. The amount of nitrogen loss by denitrification process was 6.5 times higher than the outflow of total nitrogen from the bay. The results show that the DIN released from sediment and the denitrification process in sediment play important roles on the nitrogen budget in Hiroshima Bay.

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