



# 學位申請論文

神山孝吉

主論文

A MODEL FOR MOVEMENT AND TRANSFORMATION OF  
AMMONIUM NITROGEN IN SEDIMENT-WATER SYSTEM  
IN NATURAL WATER REGIONS

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## 1. INTRODUCTION

The eutrophication in natural water regions has recently become a serious problem from the view point of the conservation of water resources. Quantitative information on the circulation of substances in the hydrosphere, which depends on physical, chemical and biological processes, should be obtained for the control of the eutrophication processes.

Each form of the nutrients, however, shows different behaviour in physical and biochemical processes. The present paper deals with ammonium nitrogen, a nutrient which is closely related to eutrophication. Figure 1 is a schematic diagram of the transformation and circulation processes of nitrogenous compounds which are found in water regions. Various kinds of nitrogenous compounds, originated from the activities of human living, animals and plants and also from volcanic activities and so on, are brought into water regions via rivers and the atmosphere. These inputs into water regions consist of particulate and dissolved nitrogenous compounds. The dissolved nitrogenous compounds are transformed into particulate form through biological processes in water. A part of these particulate nitrogenous compounds in water arrives at the bottom through precipitation processes. Continuous decomposition of the compounds in the sediments contributes to the increase in the concentration of dissolved forms, the major portion of which is occupied by ammonium nitrogen, in the pore water of the sediments. Ammonium nitrogen in the pore water is brought into the overlying water by a diffusion process.

The release of nutrients from the bottom sediments into the overlying water plays an important role in this circulation of substances. Pomeroy et al. (1971) have demonstrated that the release from the sediments can maintain nutrient concentrations in the overlying water high enough to support significant algal growth.

A mathematical model for these physical and biochemical processes occurring in sediment-water system is needed in order to acquire quantitative information on the circulation of nitrogenous compounds in the sediments, thereby enabling some explanation of the vertical distribution of ammonium nitrogen in the interstitial water of the bottom sediments. The models which had been hitherto proposed for the movements and the reactions occurring in the sediments were summarized by Lerman (1977). Most of them, however, were of deep water regions where the microbiological activity was extremely low and dealt only with a steady state condition. Imboden (1975) proposed a mathematical model on the vertical profiles of porosity and chemically or biologically inert substances in the surface layer of the sediments. To investigate the movement and the transformation of ammonium nitrogen in marginal water regions, the mathematical models for the active microbiological processes in the surface layer of the bottom sediments should be proposed.

Ammonium nitrogen is generated microbiologically from particulate organic nitrogen (PON) in the sediments. Therefore, a mathematical model with the biochemical process is proposed in this paper to explain the vertical distribution of ammonium nitrogen in the sediments, then quantitative information on the

biochemical reaction as well as physical movements was obtained.

## 2. OBSERVATION - I

In the bottom sediments of aquatic environments, there exists a large amount of ammonium nitrogen both in adsorbed form and in dissolved form, and an equilibrium state between these forms of ammonium nitrogen as well as their mutual interactions in the sediments (adsorption and desorption) has been investigated in the laboratory experiments (Kamiyama et al., 1977b). In natural water regions, the dissolved form of ammonium nitrogen in the sediments might be important in considering its release rate from the bottom sediments into the overlying water. Therefore, the vertical distribution of ammonium nitrogen in the sediments should be observed and the *in situ* relationship between ammonium nitrogen on mud particles in adsorbed form and that in interstitial water in dissolved form should be investigated in the sediments of different water regions.

### 2.1 Methods and Materials

The sediment column was collected by the use of a K.K. core sampler (Kimata et al., 1960) equipped with a plastic tube of 7 cm diameter, and was sliced into 5 mm thickness. After the measurement of the temperature of each slice with a thermistor-sensor thermometer (Shibaura Electric Co., Model MGA - III), it was put into a plastic bottle, sealed tightly, kept cool in an ice box as soon as possible on a survey boat.

In the laboratory, each sediment sample in the plastic bottle was mixed homogeneously, 0.5 g of which was mixed with dis-

tilled water and filled up 100 ml in total volume, then shaken vigorously for 1 min. Whole amount of dissolved nitrogenous compounds including adsorbed forms was extracted in the supernatant solution obtained by the centrifugation (6,000 g, 15 min).

Interstitial water was collected from the sediment sample by the centrifugation (6,000 g, 30 min) at *in situ* temperature.

Ammonium nitrogen was determined by the method of Nimura (1973) and PON by the method of Strickland and Parsons (1965) with some modifications. Other inorganic nitrogenous compounds ( $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ ) were determined by the method described by Kawai et al. (1971). Moisture content of the bottom sediments was measured by the weight loss after drying the sample at  $100^\circ\text{C}$  for 2 hours.

The sampling stations are shown in Fig. 2. Station A (Ie-1) is located in the north basin of Lake Biwa and station B at the center of Akanoi Bay in the south basin of the Lake. Station C was set up off Gamagori in Mikawa Bay of a sea-water region.

## 2 2 Results and Discussion

The vertical distribution of ammonium nitrogen in the interstitial water of the sediments in these water regions is shown in Fig. 3, and the concentration of ammonium nitrogen in the overlying water in Table 1. It is demonstrated that the concentration of ammonium nitrogen in the interstitial water was always higher than that in the overlying water. Then, ammonium nitrogen is considered to be released from the sediments into the overlying water by a diffusion process. At station A, the concentration

of ammonium nitrogen in the interstitial water is kept at almost a constant level through winter and summer. On the other hand, it becomes high in summer and low in winter at station B, and a maximum value in summer was observed at about 2 cm depth below the sediments surface. At station C, a similar increase is observed in summer, but a maximum value in summer appeared at the top of the sampling depth in the sediments (ca. 0 - 0.5 cm). The sediment temperature is shown in Table 1. The water depths are comparatively shallow at stations B (ca. 1 m) and C (ca. 7 m) and there exists a considerable periodic change in the sediment temperature throughout a year. The increase in the concentration of ammonium nitrogen in the interstitial water in summer is considered to be caused by the increase in its generation rate, which probably depends on microbiological processes. In general, biological activities are affected by the environmental temperature and the generation rate of ammonium nitrogen in each depth will decide its vertical distribution.

The vertical distribution of ammonium nitrogen in whole sediments and that occurring in the interstitial water are shown in Fig. 4. It can be clearly seen that the ratio of ammonium nitrogen occurring in the interstitial water to the residual part in the sediments varied from station to station and that it was greater at station C than stations A and B. The amounts of ammonium nitrogen adsorbed on mud particles are plotted to the concentrations in the interstitial water in Fig. 5. Though a certain relationship is found at each water region irrelevant to the depth of mud samples, the ratio of ammonium nitrogen dissolved in the interstitial water to that adsorbed on mud parti-

cles is higher at station C than at stations A and B.

In order to clarify the difference between in the sediments of freshwater and seawater regions as to the ratio of dissolved ammonium nitrogen to the adsorbed one, the following experiments were carried out. The mud sample from station A was mixed with the equal weight of sodium chloride solution with various concentrations, then stirred for 30 min at room temperature. The supernatant of the mud suspension was separated by centrifugation and submitted to the analyses. The concentration of ammonium nitrogen in the supernatant increased with the concentration of sodium chloride in the suspension, which shows the fact that ammonium nitrogen adsorbed on mud particles has come to be liberated into the supernatant by the increase in sodium chloride concentration and that a new equilibrium between two forms of ammonium nitrogen in the suspension has been attained. The results agrees well with the fact that the equilibrium state between ammonium nitrogen in dissolved form and that in adsorbed form depends on the concentration of other ions in the suspension (Kamiyama et al., 1977b). The ratio of ammonium nitrogen dissolved in the supernatant to that adsorbed on mud particles is plotted to the electric conductivity of the supernatant, the value of which reflects the concentration of ions in it, as shown in Fig. 6. With the increase in the electric conductivity of the supernatant, ammonium nitrogen adsorbed on mud particles decreases and come to be liberated into the supernatant, which increased the ratio of dissolved ammonium nitrogen to adsorbed one. By the experiments, it could be explained that the difference between in freshwater regions (stations A and B) and in a

sea-water regions (station C) as to the equilibrium state of ammonium nitrogen occurring in the bottom sediments is due to the salinity in the interstitial water.

### 3. OBSERVATION - II

It was reported in the previous section that the concentration of ammonium nitrogen in the sediments is higher in summer than in winter in shallow-water regions, where the seasonal variation of the sediment temperature is observed.

Mortimer (1971) has reported that the vertical distribution of redox potential in the sediments shows a seasonal variation, which may affect the exchange rate of chemical species between the sediments and water. Jørgensen (1977) has reported that the rate of sulfate reduction in the bottom sediments varies seasonally in the upper 10-cm layer. These facts imply seasonal variations in the biological activities and chemical reactions occurring in the bottom sediments near the surface. Little information, however, has been obtained on the seasonal distribution of chemical species in the sediments of natural water regions.

In this section is discussed the vertical distribution of ammonium nitrogen in the sediments observed approximately monthly over one year in order to make clear the rates of microbiological activities and chemical reactions and of the physical movements occurring in the sediments.

#### 3.1 Methods and Materials

The sampling stations are shown in Fig.7. They are located

in the south basin of Lake Biwa, where water depths range from 1 m to 3 m. Samples were taken approximately monthly from July 1977 to July 1978. Redox potential and pH were measured on a survey boat with a portable water pollution monitor (Kyoto Denshi Kogyo, WP-02) as soon as possible after taking the sediment samples.

### 3.2 Results and Discussion

Typical seasonal changes in the temperature of the bottom sediments and of water at 1 m depth are shown in Fig. 8 for the Yabase station. The temperature change in the lower layer of the sediments lagged behind that in the water, possibly because of the time required for heat transfer through the sediments. In the bottom sediments, the seasonal variations in temperature were observed to almost same degree both at the sediment surface and at a depth of 12 cm.

The seasonal change in the redox potential of the bottom sediments at each station is shown in Fig. 9. At each station, redox potential tended to rise in winter and fall in summer, as was observed by Mortimer (1971). The redox potential is considered to affect microbiological processes in the sediments and play an important role in environmental problems.

The seasonal variations in temperature and redox potential at the surface of the bottom sediments and in dissolved oxygen and redox potential in the overlying water at each station are shown in Fig. 10. Dissolved oxygen saturation remained high through the year in the marginal water bodies in the south basin of Lake Biwa. Redox potential in the surface layer of the bottom

sediments was generally lower than that in the overlying water, and considerably lower in summer. It is interpreted that the lower potential in the bottom sediments is due to the higher microbiological activities in the bottom sediments, which become marked in summer.

The vertical distribution of ammonium nitrogen in the interstitial water of the bottom sediments at each station is shown in Fig.11. At each station, the concentration of ammonium nitrogen in the interstitial water was high in summer and low in winter. This annual variation was not distinct in the lower layer of the sediments although the temperature showed a clear seasonal variation both in the lower and upper layers of the sediments. It would be concluded that such microbiological activities as the generation of ammonium nitrogen are low in the lower layer of the sediments in the whole range of the temperature observed. The concentration of ammonium nitrogen in the interstitial water was the highest, at all stations, in autumn at a few centimeters below the sediment surface, though the depth of the highest concentration differed from station to station. It is considered to be dependent on the seasonal change in the ammonia generation rate at different depths in the sediments.

#### 4. MODELING

A mathematical model applicable to the movement and the transformation of materials in the sediments will be developed here. The general aim is to formulate the fundamental equation in terms of measurable quantities such as layer distance, the

concentration of materials and biological activities as a function of depth.

#### 4.1 Development of Theory

Special emphasis is placed on the exact definition of the variables used here and on the formulation of restricting assumptions where they are needed for mathematical reasons.

##### 4.1.1 Nomenclature

$C$  ( $\mu\text{g atoms/cm}^3$ ): concentration of ammonium nitrogen in interstitial water.

$C^A$  ( $\mu\text{g atoms/g dry mud}$ ): amount of ammonium nitrogen adsorbed on mud particles.

$C^*$  ( $\mu\text{g atoms/g dry mud}$ ): amount of PON in mud particles.

$C_d^*$  ( $\mu\text{g atoms/g dry mud}$ ): amount of PON easily decomposed in the surface layer of sediments.

$C_s^*$  ( $\mu\text{g atoms/g dry mud}$ ): amount of stable PON in the surface layer of sediments.

$D$  ( $\text{cm}^2/\text{day}$ ): diffusion coefficient of ammonium nitrogen in interstitial water.

$K$  ( $[\mu\text{g atoms/g dry mud}]/[\mu\text{g atoms/cm}^3]$ ): ratio of ammonium nitrogen in adsorbed form to that in dissolved form.

$\alpha$  (/day): coefficient of the first-order kinetics for the decomposition of PON in the surface layer of sediments.

$\phi$  ( $\text{cm}^3/\text{cm}^3$ ): porosity of sediments.

$\rho$  ( $\text{g/cm}^3$ ): density of mud particles.

$t$  (day): time.

$x$  (cm): depth from the sediment surface (not fixed in absolute space)

$v$  (cm/day): vertical velocity of advection of sediments induced by continuous sedimentation.

$-v^*$  (cm/day): vertical velocity of advection of pore water induced by compaction of sediments or vertical current of underground water.

$U_0$  (cm<sup>3</sup>/cm<sup>2</sup>/day): accumulation rate of particles on the sediment surface, i.e. volume sedimentation rate.

$F$  (μg atoms/cm<sup>2</sup>/day): vertical flux of ammonium nitrogen in sediments, i.e. mass velocity per unit area and per unit time.

$G$  (μg atoms/cm<sup>3</sup>/day): generation rate of ammonium nitrogen in sediments.

$S$  (μg atoms/cm<sup>3</sup>/day): decomposition rate of PON in the surface layer of sediments.

$R$  (μg atoms/cm<sup>2</sup>/day): release rate of ammonium nitrogen from sediments into overlying water

$I$  (μg atoms/cm<sup>2</sup>/day): amount of PON deposited on the sediment surface, i.e. input of nitrogenous compounds to sediments.

The index 0 is used for the quantities in the overlying water immediately above the sediment surface; The symbol  $v_0$ , for example, shows the velocity of deposition of particles in the water mentioned above. The index N denotes quantities in the sediments at the depth, below which compaction is almost completed and the porosity maintains a constant level:  $\phi = \phi_N$  where  $x \geq x_N$ .

#### 4.1.2 advection in Sediments

For the first time, the movements of mud particles and pore water, in which neither diffusion nor biochemical reaction does not take part, are formulated here.

*Assumption I* "The sediments consist of mud particles and pore, and the pore is filled with pore water. The concentration of ammonium nitrogen in the pore water is considered to be the same as that in the interstitial water obtained by centrifuging the sediments, which has been reported by Kamiyama et al (1977b) "

The vertical fluxes of the volume of mud particles and that of pore are expressed as  $v(1-\phi)$  and  $\phi v - v^*$ , respectively. They obey the following equations of mass conservation, respectively.

$$\frac{\partial(1-\phi)}{\partial t} = - \frac{\partial}{\partial x} v(1-\phi) \quad (1)$$

$$\frac{\partial \phi}{\partial t} = - \frac{\partial}{\partial x} (\phi v - v^*) \quad (2)$$

From Eqs. (1) and (2), it follows that

$$\frac{\partial (v^* - v)}{\partial x} = 0 \quad (3)$$

*Assumption II* "The vertical distribution of porosity in the surface layer of the sediments depends on the properties of the deposits, and the porosity at a definite depth  $x$  does not change with time. This assumption has been confirmed by Imboden (1975) "

$$\frac{\partial \phi}{\partial t} = 0 \quad (4)$$

Then from Eq. (1),

$$v(1-\phi) = v_0(1-\phi_0) \equiv U_0 \quad (5)$$

*Assumption III.* "In the surface layer of the sediments, the rate of porosity decrease with the depth induced by compaction is distinguished, but the porosity gradually reaches its ultimate value, and  $x_N$  shows the depth where  $\phi$  has already reached its ultimate value  $\phi_N$  as shown by Morse (1974) "

Then from Eqs. (2) and (3),

$$\frac{\partial v_N^*}{\partial x} = 0 \quad (6)$$

*Assumption IV.* "The vertical current induced by underground water movement under geohydrological causes does not exist in the sediments "

$$v_N^* = 0 \quad (7)$$

Then, from Eqs. (5) and (7)

$$v_N^* - v_N = - \frac{U_0}{1 - \phi_N} \quad (8)$$

Therefore, from Eqs. (3), (5), (7) and (8), it follows

$$v^* = \left( \frac{1}{1 - \phi} - \frac{1}{1 - \phi_N} \right) U_0 \quad (9)$$

#### 4.1.3 Vertical Distribution of Ammonium Nitrogen in Sediments

Ammonium nitrogen in the sediments exists in two forms; one dissolved in pore water, the other adsorbed on the mud particles. The overall amount of ammonium nitrogen in a unit volume of the sediments is expressed as  $(1 - \phi) \rho C^A + \phi C$ .

The vertical flux of ammonium nitrogen in the sediments per unit area of the sediments per unit time is expressed as

$$F = -\phi D \frac{\partial C}{\partial x} + (\phi v - v^*)C + (1 - \phi)v\rho C^A \quad (10)$$

The first term of the right side of Eq (10) is a diffusional flux of dissolved ammonium nitrogen, the second an advective flux of dissolved ammonium nitrogen, and the third an advective flux of adsorbed ammonium nitrogen.

Then, the following equation is obtained.

$$\frac{\partial}{\partial t} \{ (1 - \phi)\rho C^A + \phi C \} = - \frac{\partial F}{\partial x} + G \quad (11)$$

Here, G is a term for generation per unit volume of the sediments per unit time.

*Assumption V.* "The following simple relationship exists between ammonium nitrogen in dissolved form and in adsorbed form in the sediments

$$C^A = KC \quad (12)$$

This assumption has been confirmed by the field work in a previous section (2.2) and the laboratory experiments (Kamiyama et al , 1977b), and it is reported that the ratio K is constant independently of the depth in the sediments and that it depends on the water region and the season "

By substituting Eqs. (5), (9), (10) and (12) into Eq. (11), the following equation is obtained for the concentration of am-

monium nitrogen in the interstitial water of the sediments.

$$\frac{\partial}{\partial t} [(1-\phi)\rho K + \phi]C = \frac{\partial}{\partial x} (\phi D \frac{\partial C}{\partial x}) - (\frac{1}{1-\phi_N} - 1 + K\rho)U_0 \frac{\partial C}{\partial x} + G \quad (13)$$

#### 4.1.4 Vertical Distribution of Particulate Organic Nitrogen in Sediments

Particulate organic nitrogen in the sediments is decomposed into ammonium nitrogen through microbiological activities. Therefore, PON deposited on the sediment surface decreases its concentration in the sediments by the decomposition with the lapse of time, during which the sediments move downwards gradually by the continuous sedimentation process. Then, the vertical distribution of PON in the sediments depends both on the decomposition rate and on the sedimentation rate.

The whole amount of PON in a unit volume of the sediments is expressed as  $(1-\phi)\rho C^*$ . Mud particles, which move by advection, not by diffusion, are partially composed of PON. Therefore, the following equation is obtained for the amount of particulate organic nitrogen in the sediment.

$$\frac{\partial}{\partial t} \{(1-\phi)\rho C^*\} = - \frac{\partial}{\partial x} \{v(1-\phi)\rho C^*\} - S \quad (14)$$

Here,  $S$  is a term of consumption per unit volume of the sediments per unit time.

*Assumption VI* "Since the change in the density of mud particles in the surface layer of the sediments, where microbiological activities are active, is relatively small compared to the changes in porosity and in the concentration of materials (Yama-

At station A, set up in the north basin of Lake Biwa, where the water depth is about 70 m and the temperature of the sediments shows little seasonal variation, ammonium nitrogen in the sediments remains at a fixed concentration through a year. In this case, the left side of Eq. (13) is equal to zero. Therefore, the rate of ammonium nitrogen generation is obtained by the following equation.

$$G = \left( \frac{1}{1-\phi_N} - 1 + K\rho \right) U_0 \frac{\partial C}{\partial x} - \frac{\partial}{\partial x} \left( \phi D \frac{\partial C}{\partial x} \right) \quad (19)$$

The vertical distribution of ammonium nitrogen in the interstitial water and that of sediment porosity at station A are approximated by the following equations as shown in Fig. 12.

$$C = 0.44 - 0.36 \times 0.69^x \quad (20)$$

$$\phi = 0.77 + 0.11 \times 0.49^x \quad (21)$$

In the field data, the ratio  $K$  and the density of mud particles  $\rho$  were found to be  $13 \text{ cm}^3/\text{g}$  dry mud and  $2.6 \text{ g/cm}^3$ , respectively.

Then, the vertical distribution of the rate of ammonium nitrogen generation in the sediments is obtained as follows from Eqs. (19), (20) and (21).

$$G = D \{ 0.053 \times 0.34^x + (0.037 + 4.84 \frac{U_0}{D}) \times 0.69^x \} \quad (22)$$

Here, it was assumed that the diffusion coefficient of ammonium nitrogen in the interstitial water was constant independently of the sediment porosity. Yamamoto et al. (1973) estimated the

sedimentation rate  $U_0$  at the same station to be  $3.4 \times 10^{-10}$  cm<sup>2</sup>/sec and Manheim (1970) reported that the diffusion coefficient of irons  $D$  in the unconsolidated sediments was  $10^{-7}$ - $10^{-5}$  cm<sup>2</sup>/sec.

$$\text{Then, } \frac{U}{D} \ll \frac{0.037}{4.84} \quad (23)$$

and the term  $4.84 \frac{U_0}{D}$  is negligibly small in Eq. (22). Therefore, the generation rate calculated from Eq. (22) is hardly dependent on the change in the sedimentation rate but is almost in proportion to the diffusion coefficient. The vertical profile of the generation rate, in which  $D = 2.0$  cm<sup>2</sup>/day was assumed, is shown in Fig. 13.

The vertical distribution of particulate organic nitrogenous compounds easily decomposed in the surface layer of the sediments was obtained as the solution of Eq. (19). In the steady-state model where  $\frac{\partial}{\partial t} C_d^* = 0$  and the sedimentation rate  $U_0$  is constant with time, the following equation is obtained from Eq. (18).

$$\frac{\partial}{\partial x} C_d^* = - \frac{\alpha}{U_0} (1 - \phi) C_d^* \quad (24)$$

By giving the boundary condition:

$$C_d^* = C_{d_0}^* \quad \text{where } x = 0$$

the following solution is obtained from Eq. (24) as to  $C_d^*$  at a definite depth  $x_1$ .

$$C_d^* = C_{d_0}^* \times \text{Exp.} \left\{ - \frac{\alpha}{U_0} \int_0^{x_1} (1 - \phi) dx \right\} \quad (25)$$

By assuming that  $C_{d0}^* = 100$  and  $C_s^* = 100$  according to Kamiyama et al. (1977a),  $\frac{\alpha}{U_0}$  was obtained by the most fitting method as shown in Fig. 14. Then, the following relationship was obtained.

$$\frac{\alpha}{U_0} = 5 / \text{cm}$$

Particulate organic nitrogen is transformed into ammonium nitrogen through the microbiological decomposition, which results in the real generation of ammonium nitrogen in the sediments. Ammonium nitrogen, however, may be further transformed into nitrite and nitrate nitrogens through oxidation processes. The rate of ammonium nitrogen generation in this paper  $G$  means the net generation rate (i.e. accumulation rate in the sediments)

Then, in general

$$S \geq G \tag{26}$$

The transformation of ammonium nitrogen into nitrite or nitrate nitrogen hardly occurs in the anoxic sediments.

*Assumption VIII* "Particulate organic nitrogen is decomposed into ammonium nitrogen, which is the final product in the sediments"

$$S = G \tag{27}$$

The following equation is obtained from Eqs. (15) and (27).

$$\frac{\partial C^*}{\partial x} = - \frac{G}{U_0 \rho} \tag{28}$$

By using Eq. (22),

$$\frac{\partial C^*}{\partial x} = -0.86 \times 0.69^x - \frac{D}{U_0} (0.014 \times 0.69^x + 0.020 \times 0.34^x) \quad (29)$$

By integrating Eq. (29) with giving the boundary condition:  $C^* = 132$ , where  $x = 0.25$ , the vertical distribution of particulate organic nitrogen is estimated and the value of  $\frac{D}{U_0}$  was obtained by the most fitting method as shown in Fig. 15.

Then, the following value was obtained.

$$\frac{D}{U_0} = 2,000 \text{ cm}$$

The release rate of ammonium nitrogen from the bottom sediments into the overlying water is represented from Eq. (10) as

$$R = -F_{x=0} = \left( \phi D \frac{\partial C}{\partial x} - \frac{\phi N}{1-\phi} U_0 C - U_0 \rho C^A \right)_{x=0} \quad (30)$$

The input of nitrogenous compounds to the bottom sediments results from the deposition of particulate organic nitrogenous compounds, the rate of which is represented as follows;

$$I = U_0 \rho C^* \quad (31)$$

By using Eqs. (12), (20), (21), (30) and (31), the following relationship was obtained.

$$\frac{R}{I} = 0.44$$

This means that almost half of the particulate organic nitrogen deposited on the bottom sediments returned into the overlying water in the form of ammonium nitrogen through the microbiological transformation in the sediments. Therefore, the sediments play an important role on the nitrogen cycle in the water region as the sink of particulate organic nitrogen and as the source of ammonium nitrogen.

## 5.2 Unsteady State Model for Vertical Distribution of Ammonium Nitrogen in Sediments

In previous parts, a mathematical model for the nitrogen cycle in the sediments and the overlying water was proposed and used to explain the vertical distribution of nitrogenous compounds in the bottom sediments at station A in the north basin of Lake Biwa. Since the concentration of ammonium nitrogen did not vary through a year at the station, the model was applied only to the steady-state case.

It was found, however, that the concentration of ammonium nitrogen in the sediments varied seasonally in Mikawa Bay and in the south basin of Lake Biwa. The model, therefore, should be modified to account for these unsteady-state cases. This section deals with the unsteady-state conditions, taking the seasonal variation of the microbiological activities in the bottom sediments into consideration.

### 5.2.1 Movement and Transformation of Ammonium Nitrogen in Sediments

At station C in Mikawa Bay, the concentration of ammonium nitrogen in the interstitial water in the bottom sediments showed

a periodic change through a year in 1977, which is probably caused by the seasonal change in the generation rate of ammonium nitrogen in the sediments.

The net generation rate averaged over the observation period can be calculated numerically from Eq. (13) by the method shown in Appendix. The time-step used here was 0.1 day, the vertical distance between the grid points was 1.0 cm and the number of grid points 12 in the x-direction.

In this calculation, the assumption of the concentration of ammonium nitrogen at the sediment-water interface is necessary. However, "overlying water" defined in previous sections corresponds to the water collected several centimeters above the bottom surface in the core sample. According to Morse (1974), there possibly exists a stagnant benthic boundary layer of water, which is in contact with the sediment-water interface and in which dissolved materials can move by molecular diffusion as well as in the interstitial water, and that the concentration in the overlying water can be measured only in the more rapidly mixing layer above the stagnant benthic boundary layer. Therefore, an approximate equation, describing the vertical distribution of ammonium nitrogen in the interstitial water in winter, was obtained and, by the extrapolation to the concentration in the overlying water obtained at that time, the thickness of the stagnant benthic boundary layer was estimated to be 0.45 cm. This value agrees well with that estimated in the same way as to the distribution of dissolved silica by Morse.

The following boundary conditions are assumed:

$$C = C_0, \quad \text{at } x = -l$$

$$C = C_\infty, \quad \text{at } x = L$$

where  $l$  is the thickness of the benthic boundary layer above the bottom surface and  $L$  is the depth of the sediments below which the concentration shows no seasonal variation and the biological activities are negligibly small.

The vertical profile of the net generation rate of ammonium nitrogen in the sediments averaged over the observation periods is shown in Fig. 16. The value of the parameters necessary for the calculation is tabulated in Table 2. The generation rate of ammonium nitrogen was far greater in the interval from May to September than that from September to May.

A similar calculation was made for vertical profiles obtained in the south basin of Lake Biwa, and the results are shown in Fig. 17, where grid points are represented by circles. The generation rate was greater in the uppermost layer of the sediments than in the lower layers and was higher in summer than in winter. Sensitivity analyses were conducted to test the relative importance of each coefficient in this model to predict the generation rate. They revealed that the calculated generation rate is almost proportional to the diffusion coefficient used and almost independent of the sedimentation rate, which is similar to the result obtained for the steady-state case in the previous section. Lerman (1975) has proposed that the diffusion coefficient is proportional to the square of porosity in the sediments  $\phi^2$ , while, in the calculation, such a modification of the diffusion coefficient made

little difference to the generation rate.

Lerman (1975) has reported that the maximum generation rate of ammonium nitrogen in deep-sea sediments is  $3 \times 10^{-9} \mu\text{g atoms/cm}^3/\text{day}$ . I found in the previous section that the maximum in the north basin of Lake Biwa is  $1.5 \times 10^{-1} \mu\text{g atoms/cm}^3/\text{day}$ . At the stations in the south basin of Lake Biwa, the generation rate in the upper layer is somewhat greater than that in the north basin, but, even in the lower layer of the sediments, far greater values are obtained in the south basin. At station C in Mikawa Bay, far greater values are obtained. These values may reflect the eutrophication level in each water region mentioned above.

#### 5.2.2 Microbiological Processes in Sediments

Figure 18 shows metabolic processes, reflected to the nitrogen cycle in water regions, and the concentration of nitrogenous compounds in winter and summer at station C in Mikawa Bay. Among the nitrogenous compounds in the sediments, particulate organic nitrogen (PON) and ammonium nitrogen are predominant. In general, the concentration of each compound is dependent on the rate of generation and decomposition. These processes are considered to depend on the environmental redox potential (Billen, 1975; Vanderborght et al., 1975; and Grundmanis et al., 1977). There is, however, little information available on the *in situ* effect of the redox potential in the bottom sediments.

At station C in Mikawa Bay, the generation rate of ammonium nitrogen in the uppermost layer of the sediments was greater in summer than in winter, which possibly shows the temperature dependence of the ammonia generation rate as was reported in the laboratory experiment by Ukita et al. (1975). But in the lower layer of the

sediments, the generation rate in summer was very low. The seasonal fluctuation in the generation rate was calculated in greater detail in the south basin of Lake Biwa. Negative values were obtained at the Sakamoto and Shina stations in periods when the concentration of ammonium nitrogen was decreasing in the sediments. The generation rate estimated in this paper represents the net generation rate, and, in general, the generation rate of ammonium nitrogen from PON by bacterial decomposition (ammonification) is considered dominant in the bottom sediments over the metabolic rates at which ammonium nitrogen is oxidized into nitrite and nitrate and denitrified to form gaseous nitrogen. A negative value, however, may indicate that denitrification proceeded faster than ammonification in spite of the low concentration of nitrite and nitrate in the interstitial water. It was assumed in a previous part (5.1) that denitrification did not occur in the sediments at station A, in which the redox potential did not show a seasonal variation. Reddy et al. (1975) have reported that the decomposition rate of organic nitrogen is high during alternate aerobic and anaerobic conditions. Stumm et al. (1978) have reported that both of the processes of transformation (ammonification and denitrification) occur in the range of Eh 100 - 300 mV. These reports support the possibility that there occurs denitrification in sediments in which the redox potential shows a seasonal fluctuation because of the variation in the microenvironmental redox potential in the sediments. In this case, the decomposition rate of PON into ammonium nitrogen will be far greater than the net generation rate of ammonium nitrogen, because a part of the latter is consumed by denitrification.

The generation rate was the greatest at the uppermost sediment layer and higher in summer than in winter at each station, which coincided with the viable counts of ammonifying bacteria observed in the sediments (Kamiyama et al., in press).

### 5.2.3 Release Rate of Ammonium Nitrogen from Bottom Sediments into Overlying Water

To consider nutrient input into the water in marginal regions, it is important to estimate the release rate of ammonium nitrogen from the bottom sediments into the overlying water. A previous part (5.1) demonstrated that sediments play an important role in the water region as the source of ammonium nitrogen and reservoir of particulate organic nitrogen in the nitrogen cycle. Figure 19 is a schematic illustration of the sediment-water interface. The release rate of ammonium nitrogen through the sediment-water interface can be calculated from the following equation based on the Fick's law (in this equation, the advective term induced by the sedimentation is neglected and it is assumed that ammonium nitrogen is not accumulated at the sediment-water interface):

$$R = D_2 \frac{C_i - C_0}{l} = D_1 \phi_1 \frac{C_1 - C_i}{\Delta x} \quad (32)$$

where  $C_0$  is the concentration of ammonium nitrogen in the overlying water;  $C_i$ , that at the sediment-water interface;  $C_1$  that in the interstitial water of the uppermost layer of the sediments which can be obtained; and  $\Delta x$  is the distance from the bottom sediment surface to the central plane of the uppermost sediment layer, the thickness of which  $2\Delta x$  is determined by the technical reason.  $l$  is the thickness of the benthic boundary layer and  $\phi_1$

is the porosity at the uppermost sediment layer.  $D_1$  and  $D_2$  are the diffusion coefficients of ammonium nitrogen in the uppermost sediment layer and in the benthic boundary layer. Eq. (32) can be rearranged to give:

$$R \div \frac{C_1 - C_0}{\frac{z}{D_2} + \frac{\Delta x}{D_1 \phi_1}} = D_1 \frac{C_1 - C_0}{\frac{D_1 z}{D_2} + \frac{\Delta x}{\phi_1}} \div D \frac{C_1 - C_0}{z + \frac{\Delta x}{\phi_1}} \quad (33)$$

where the diffusion coefficients in the uppermost sediment layer and in the benthic boundary layer are assumed to be equal to  $D$  ( $\frac{D_1}{D_2} \div 1$ ).

The diffusion coefficient in the interstitial water has been estimated by several researchers. In deep-water sediments, it is reported to be in the range of  $1 - 3 \times 10^{-6} \text{ cm}^2/\text{sec}$  (Fanning et al., 1974; Berner, 1974; and Kamiyama et al., 1977a). In shallow-water sediments and in laboratory experiments in which the overlying water is disturbed, it is reported to be  $2 \times 10^{-5} \text{ cm}^2/\text{sec}$  (Manheim, 1970; Kamiyama et al., 1976; and Freedman et al., 1977). In the upper sediment layer, the diffusion coefficient is affected mainly by the turbulence of the overlying water and bioturbation in the sediments, which may increase the diffusion coefficient in shallow-water sediments. Lerman (1979) has reported that the diffusion coefficient in the uppermost sediment layer in near-shore environments may be 5-100 times that in the undisturbed sediment layer. In Fig.18, therefore, the gradient of ammonium nitrogen in the water at the sediment-water interface ( $\frac{C_1 - C_0}{z + \frac{\Delta x}{\phi_1}}$ ) in the south basin of Lake Biwa is represented, which will suggest a seasonal variation of the release rate, increasing in summer and decreasing in winter, and sometimes showing a negative value (absorption). Here, the value  $D$  may be assumed to be

in the range of  $10^{-6} - 10^{-5} \text{ cm}^2/\text{sec}$  ( $10^{-1} - 1 \text{ cm}^2/\text{day}$ ), depending on the disturbance of the upper sediment layer.

The change in the release rate of ammonium nitrogen will be affected not directly by the change in the redox potential but by that in microbiological activities in the sediments. This consideration agrees with the results obtained in the experiments (- Fillos et al., 1975).

## 6. CONCLUSION

In natural water regions, there exists a large amount of ammonium nitrogen in sediments both in adsorbed form and in dissolved form. In order to make clear the movement of ammonium nitrogen in the sediments and to estimate its release rate from the sediments into the overlying water, the vertical distribution of ammonium nitrogen in the sediments in these forms was investigated. The following results were obtained: A seasonal variation was observed in the concentration of ammonium nitrogen in the interstitial water of the sediments where the temperature changed with seasons, and the concentration in summer was higher than that in winter. However, it was not observed in the sediments where the temperature did not show a remarkable change. In the sediments of each water region, there existed an obvious relationship between the amount of ammonium nitrogen dissolved in the interstitial water and that adsorbed on the mud particles. However, a local difference was observed in the relationship, and the ratio of the former to the latter was higher in a sea-water region than in freshwater regions.

From the results, a model applicable to the movement and the transformation of nitrogenous compounds in the sediments was developed, and it was found useful in the estimation of biological activities in the sediments.

The model presented herein to describe the movement of ammonium nitrogen in the sediments rests on the assumption, borne out by the results, that biological processes as well as physical ones play an important role. And in the movement of such ions as phosphates and iron, chemical processes as well as physical ones are important, as suggested by Fillos et al. (1975) from experimental findings. The movement of these chemical species might also be describable by a modification of the model.

The information obtained in this study will be useful in considering the decomposition of particulate organic nitrogen in water bodies and the interaction between particulate and dissolved nitrogenous compounds and in combining the nutrient release from the bottom sediments to the physical and microbiological processes in the water regions.

#### ACKNOWLEDGEMENTS

I am sincerely grateful to Dr. S. Okuda of the Disaster Prevention Research Institute, Kyoto University for his valuable encouragement. I also thank Dr. A. Kawai of the Research Institute for Food Science, Kyoto University for his advice on microbiological processes in water regions. Thanks are extended to Dr. Y. Oonishi of the former Institute for his discussion on the numerical methods. The numerical calculation in this study was

carried out on FACOM M190 in the Data Processing Center of Kyoto University.

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## APPENDIX

### *The Method for Calculation of the Generation Rate of Ammonium Nitrogen in the Sediments*

The region is divided in the direction of the x axis into n segments, and the time is divided into small intervals  $\Delta t$ . The index i is used for the quantities in the sediments in the i-th segment and (k) denotes the quantities at time  $t = k\Delta t$ . The concentration of ammonium nitrogen is represented as C. The generation rate of ammonium nitrogen averaged over a cer-

tain time interval is shown as G.

First, the partial differential equation (13) is transformed into the difference equation. The solution of the difference equation for C obtained by numerical integration with respect to time is represented as F. For example, the solution in the i-th segment after a time interval  $k\Delta t$  with the initial values  $(C_1^{(0)}, C_2^{(0)}, \dots, C_n^{(0)})$  and with the generation rates averaged over the period from  $t=0$  to  $t=k\Delta t$  ( $G_1, G_2, \dots, G_n$ ) is represented as  $F_i^{(k)}(C_1^{(0)}, C_2^{(0)}, \dots, C_n^{(0)}, G_1, G_2, \dots, G_n)$ . The value of  $F_i^{(k)}$  with the initial values and no generation rates is defined as  $N_i$ :

$$N_i = F_i^{(k)}(C_1^{(0)}, C_2^{(0)}, \dots, C_n^{(0)}, 0_1, 0_2, \dots, 0_n)$$

The value of  $F_j^{(k)}$  with the zero initial values and no generation rates except a unit value in i-th segment ( $G_i = 1$ ) is defined as  $U_{ji}$ :

$$U_{ji} = F_j^{(k)}(0_1, 0_2, \dots, 0_n, 0_1, 0_2, \dots, 1_i, \dots, 0_n)$$

Since Eq. (13) is linear, the following equations are obtained:

$$C_j^{(k)} = N_j^{(k)} + \sum_{i=1}^n U_{ji}^{(k)} G_i \quad (j = 1, 2, \dots, n) \quad (A)$$

In the field observation, the concentration of ammonium nitrogen ( $C_i^{(0)}$  and  $C_i^{(k)}$  ( $i=1, 2, \dots, n$ )) was measured over a certain observation period. From the values,  $N_j^{(k)}$  and

$U_{ji}^{(k)}$  in Eqs. (A) can be calculated. The generation rate of ammonium nitrogen in each segment ( $G_i$ ) can then be obtained by solving Eqs. (A), because the number of the equations is equal to that of unknown quantities ( $G_i$ )

# TABLES

| Station | Date       | Temperature<br>of sediments<br>(°C) | NH <sub>4</sub> -N in<br>overlying water<br>(µg atoms/l) |
|---------|------------|-------------------------------------|----------------------------------------------------------|
| A       | 3/15, 1975 | 4.3                                 | 3.26                                                     |
|         | 7/12, 1975 | 6.2                                 | 1.51                                                     |
| B       | 1/10, 1976 | 5.2                                 | 31.9                                                     |
|         | 9/16, 1975 | 25.8                                | 12.3                                                     |
| C       | 3/4, 1977  | 3.8                                 | 1.80                                                     |
|         | 9/16, 1977 | 22.0                                | 0.49                                                     |

TABLE 1. Concentration of ammonium nitrogen in overlying water and temperature of sediments in three different water regions.

|                |       |                                                  |
|----------------|-------|--------------------------------------------------|
| $\rho^*$       | 2.6   | g/cm <sup>3</sup>                                |
| $K^*$          | 1.6   | (µg atoms/g dry mud)/(µg atoms/cm <sup>3</sup> ) |
| $Z^*$          | 0.45  | cm                                               |
| $L^*$          | 12.0  | cm                                               |
| $C_0^*$        | 0.001 | µg atoms/cm <sup>3</sup>                         |
| $C_{\infty}^*$ | 0.800 | µg atoms/cm <sup>3</sup>                         |
| $D$            | 2.0   | cm <sup>2</sup> /day                             |
| $U_0^{**}$     | 0.001 | cm/day                                           |

\* shows data obtained in the field (Kamiyama et al., 1978) and \*\* shows an estimated order of the value for lake and near-continent oceanic sediments (Lerman, 1979)

TABLE 2 Value of parameters employed in the model.

# FIGURES

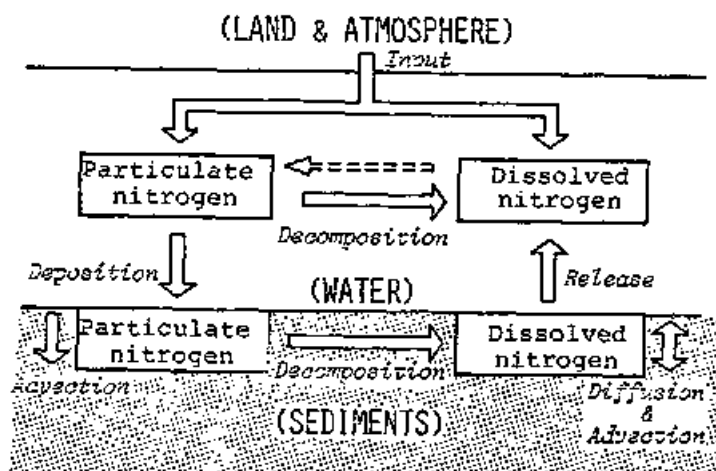


FIG. 1. Schematic diagram of movement and transformation processes of nitrogenous compounds in water regions.

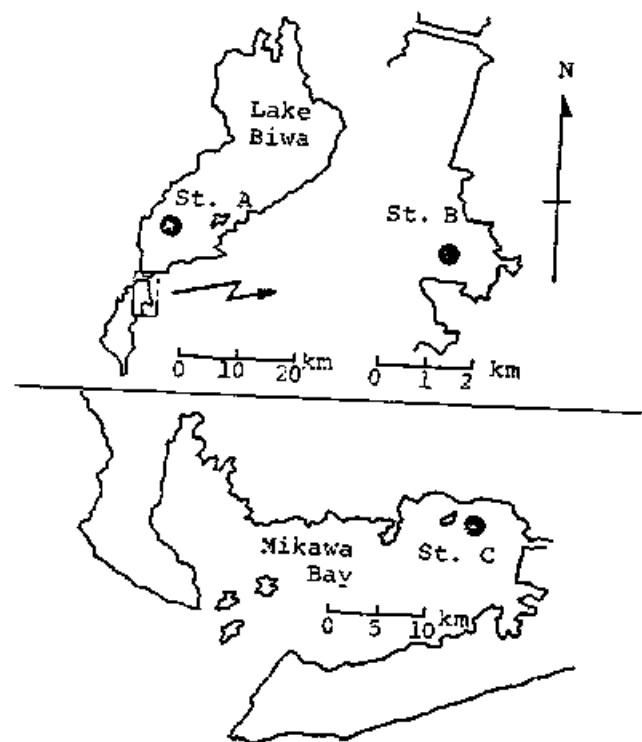


FIG. 2. Location of sampling stations.

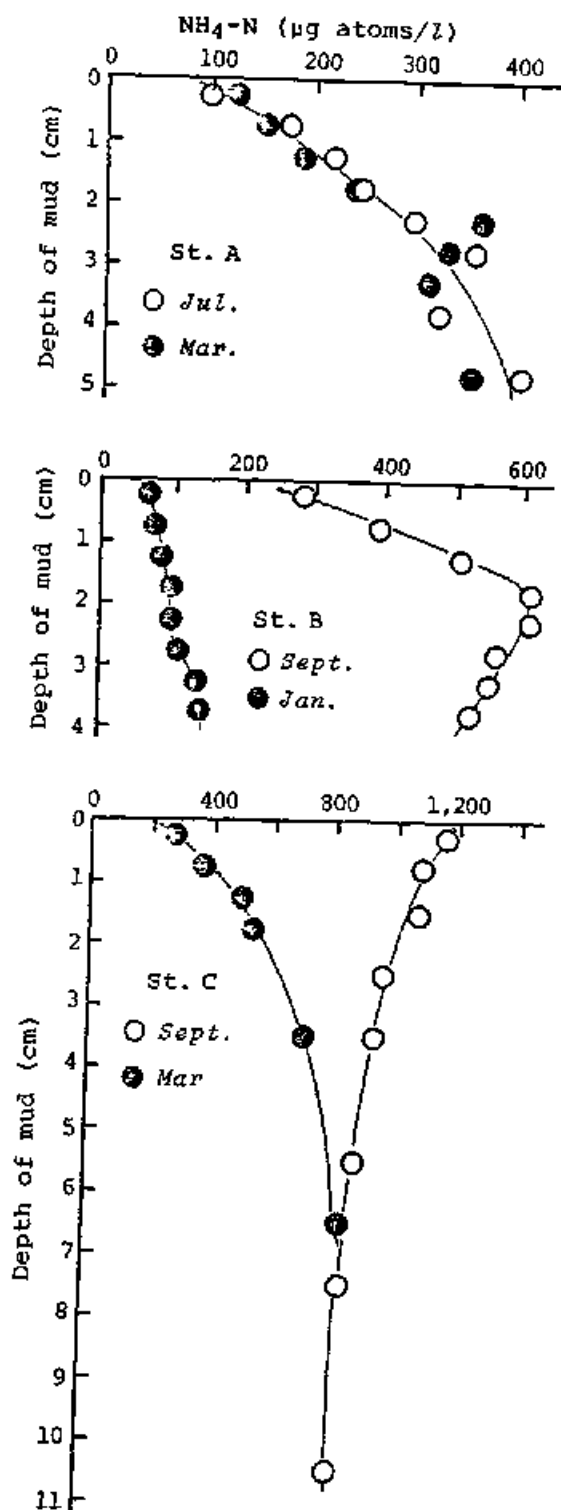


FIG. 3. Vertical distribution of ammonium nitrogen in interstitial water of sediments in three different water regions.

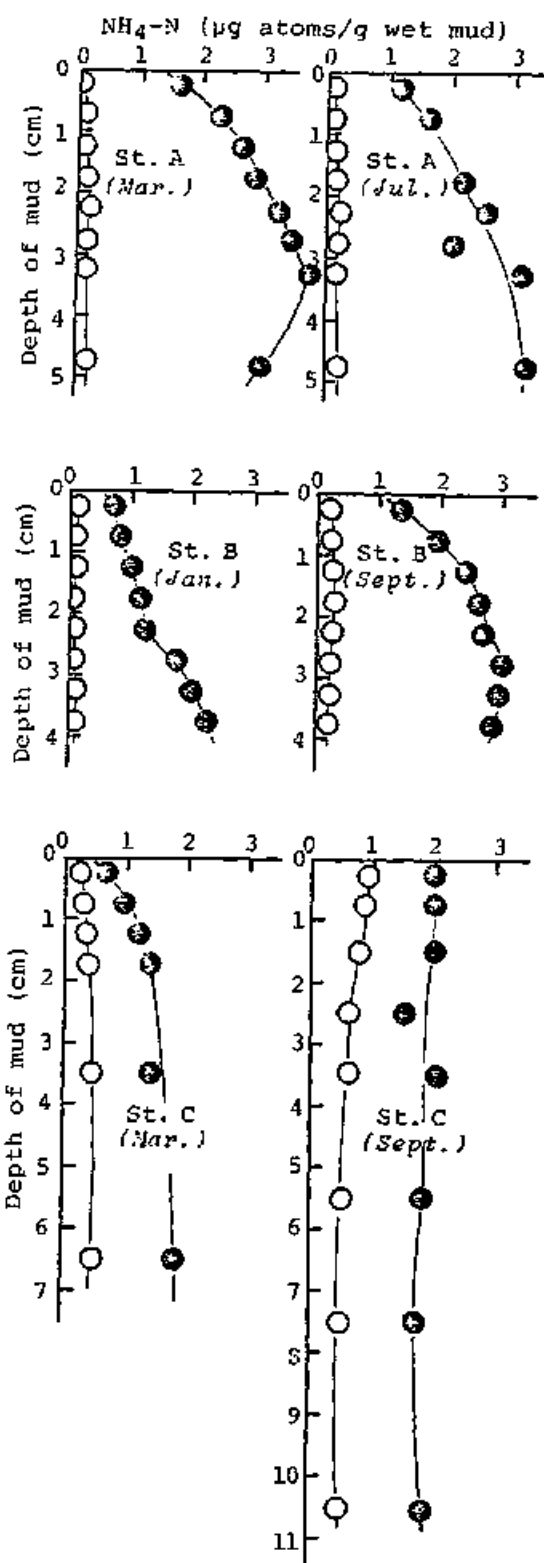
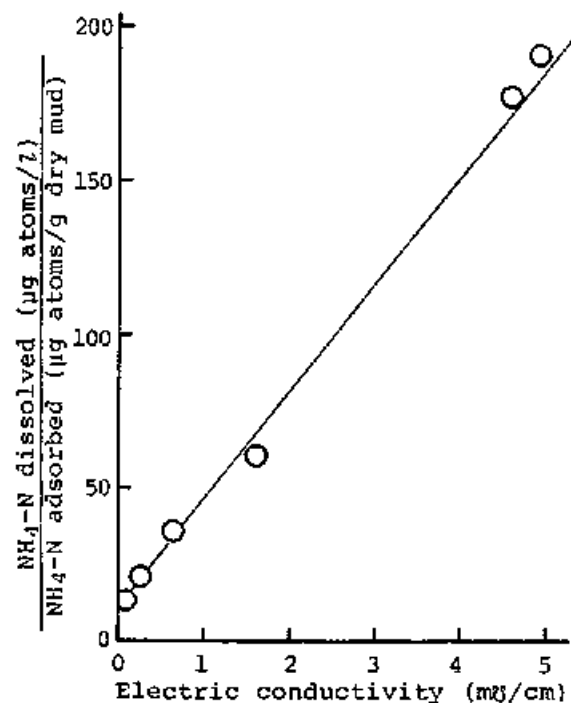
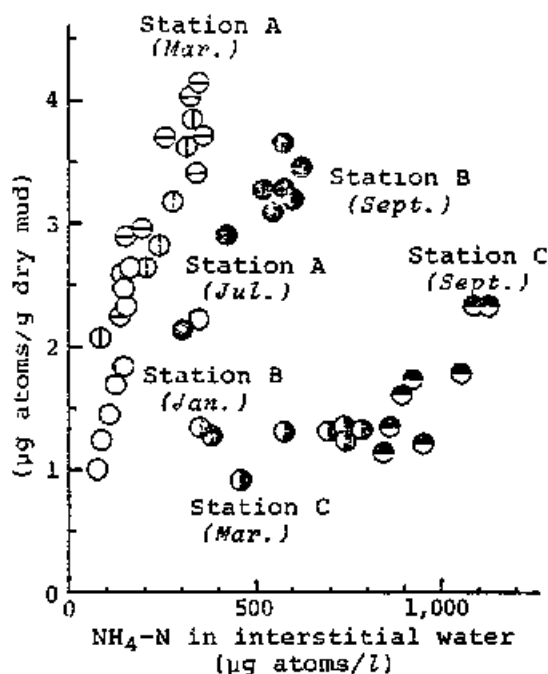
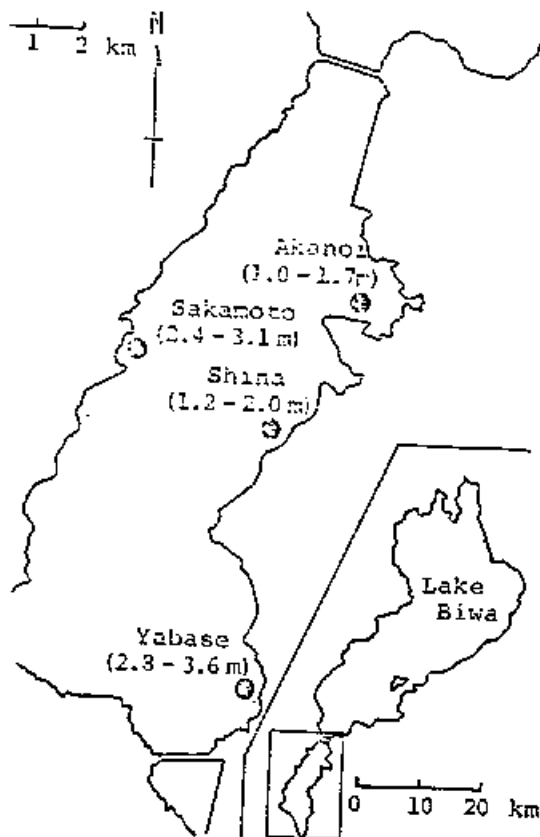


FIG. 4. Vertical distribution of ammonium nitrogen in sediments in three different water regions (○ in interstitial water, ● in whole sediments).



- 5 Relationship between amount of ammonium nitrogen dissolved in the interstitial water and that adsorbed on mud particles ( $\ominus$  station A, Mar.,  $\odot$  station A, Jul.,  $\circ$  station B, Jan.,  $\bullet$  station B, Sept.,  $\oplus$  station C, Mar.,  $\bullet$  station C, Sep.)

FIG. 5 Relationship between electric conductivity of the supernatant of mud suspension and the ratio of ammonium nitrogen dissolved in the supernatant and that adsorbed on mud particles.



7 Location of sampling stations.  
Depth of water at each station is  
given in parentheses.

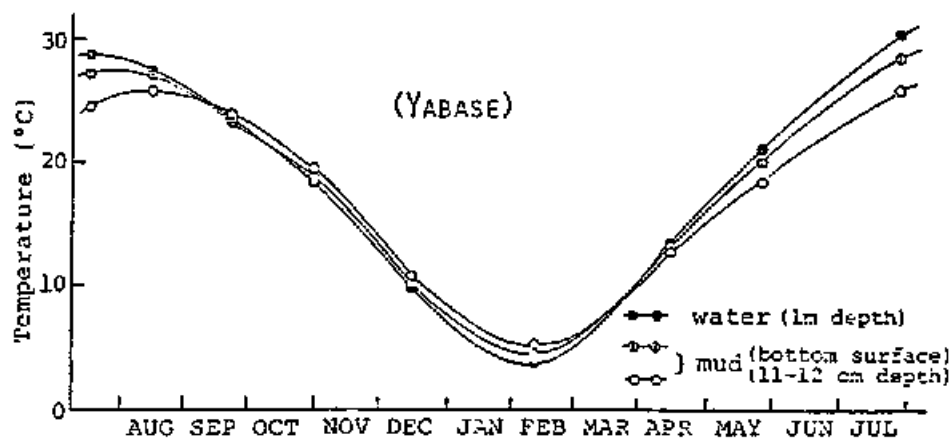


FIG. 8 Seasonal variation in temperature  
of bottom sediments and overlying  
water at the Yabase station.

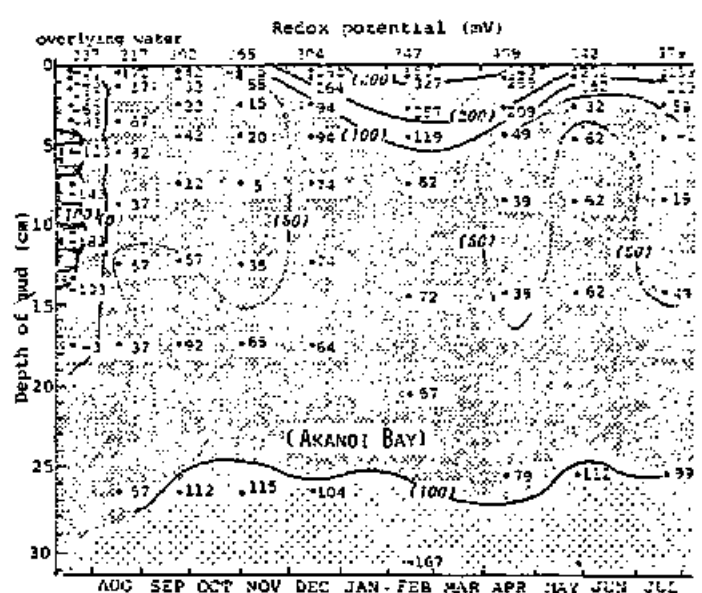
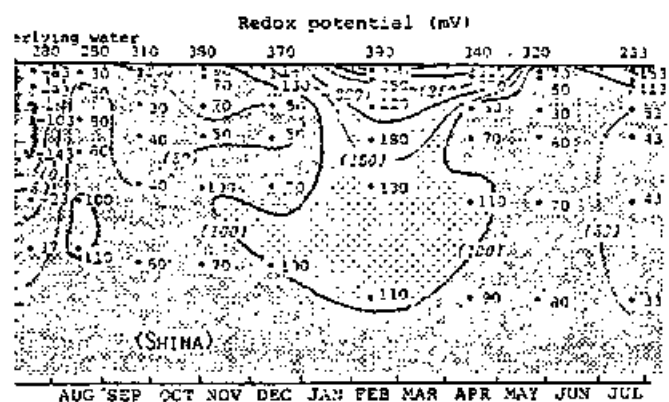
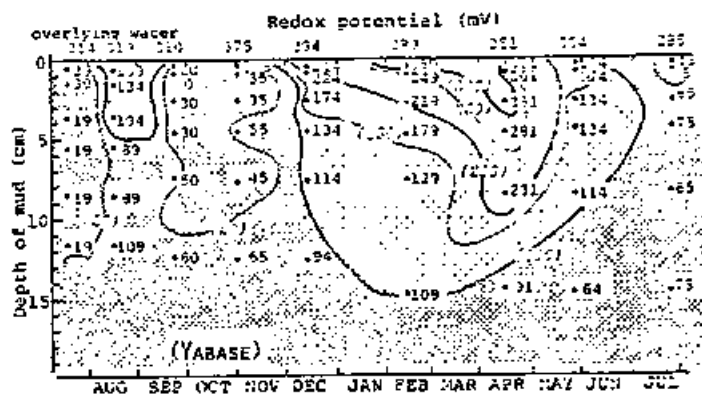
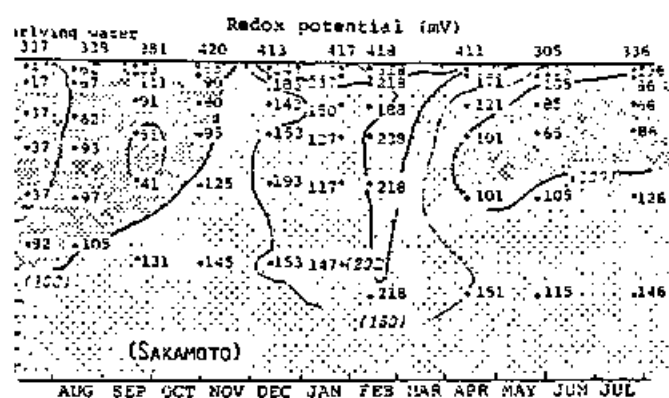
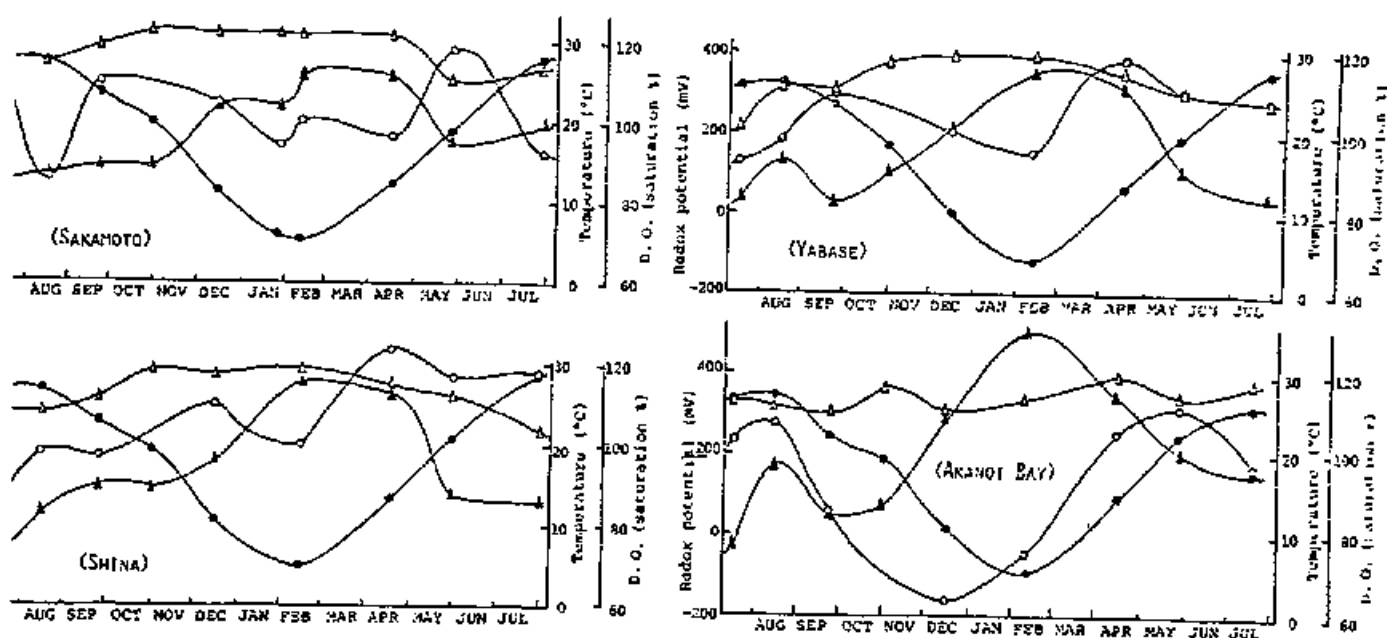


FIG. 9 Seasonal variation in redox potential (Eh) of bottom sediments and overlying water at each station.



- 10 Seasonal variations in temperature (●) and redox potential (Eh) (Δ) at the uppermost sediment layer and in dissolved oxygen (○) and redox potential (Eh) (Δ) in overlying water at each station.

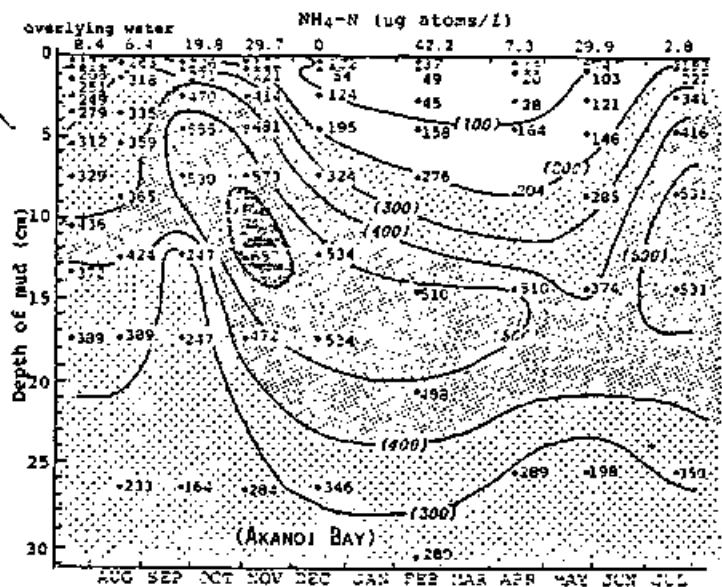
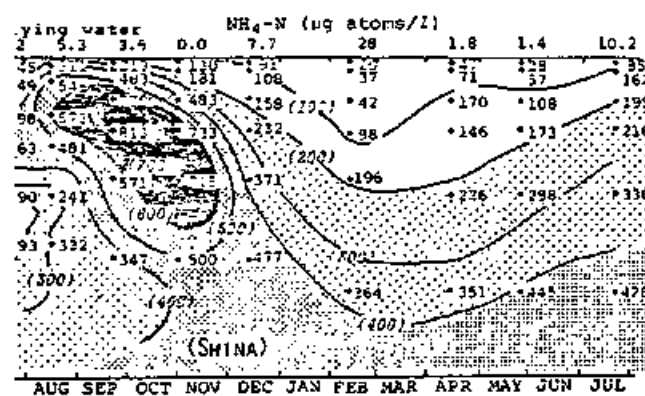
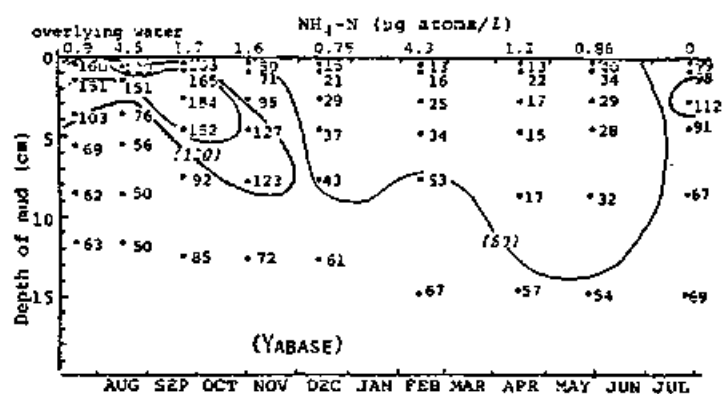
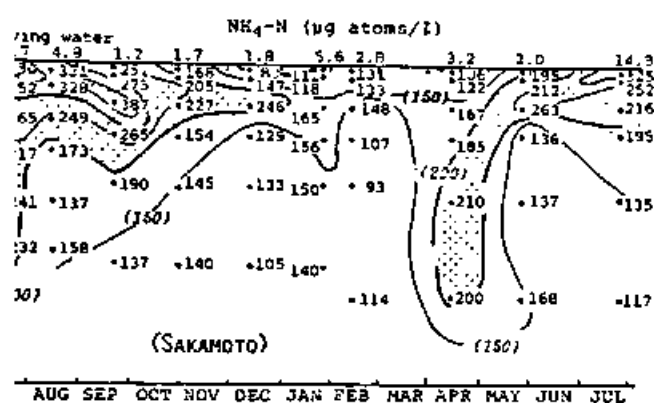
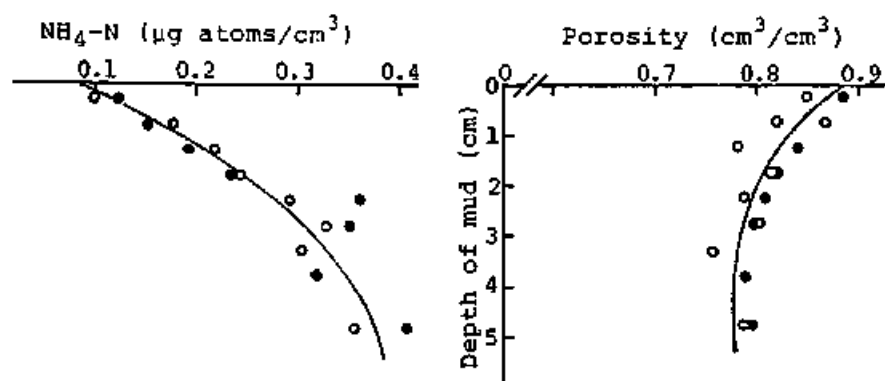


Fig. 11 Seasonal variation in ammonium nitrogen in interstitial water of bottom sediments and in overlying water at each station.



- 12 Vertical distributions of ammonium nitrogen in interstitial water and of porosity of sediments at station A in the north basin of Lake Biwa. Solid lines show Eqs. (20) and (21) and circles show the observed values (● in March and ○ in July)

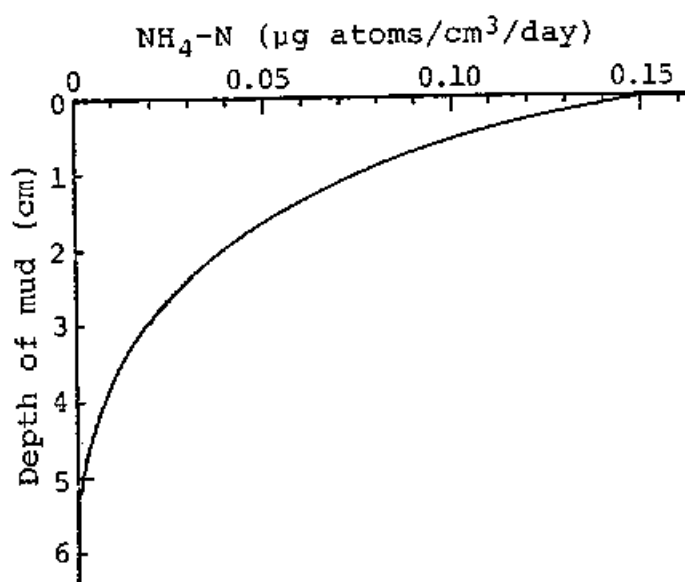
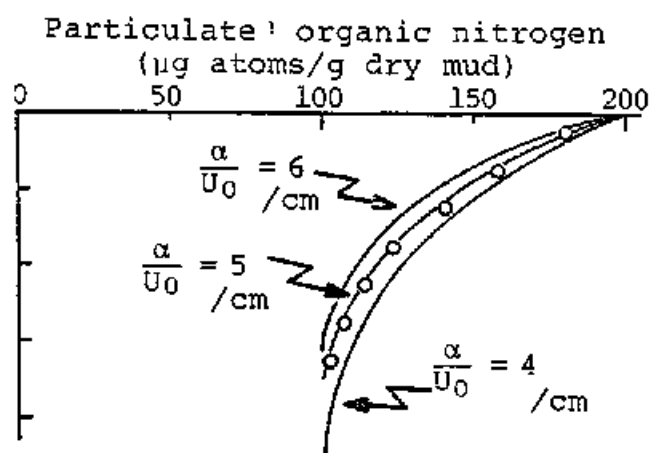


FIG. 13 Estimation of vertical profile of generation rate of ammonium nitrogen in the sediments in the north basin of Lake Biwa (in the case, diffusion coefficient,  $D = 2.0 \text{ cm}^2/\text{day}$ , was employed)



- 4 Vertical distribution of particulate organic nitrogen in the sediments (Circles show the observed values and solid lines show the values calculated from Eq (25))

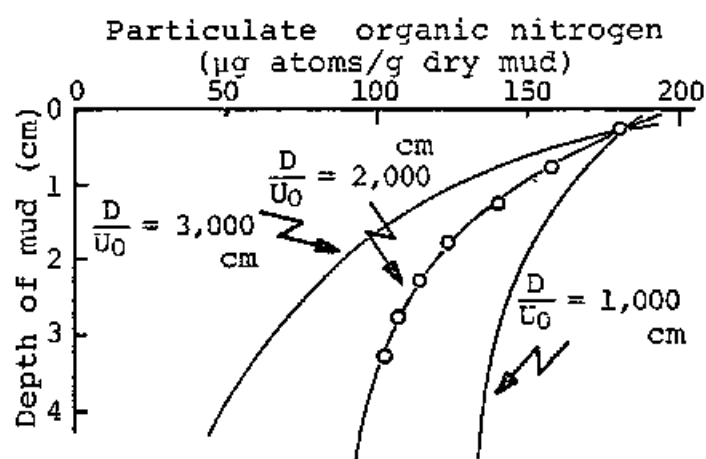


FIG. 15 Vertical distribution of particulate organic nitrogen in the sediments (Circles shows the observed values and solid lines show the values calculated from Eq (29))

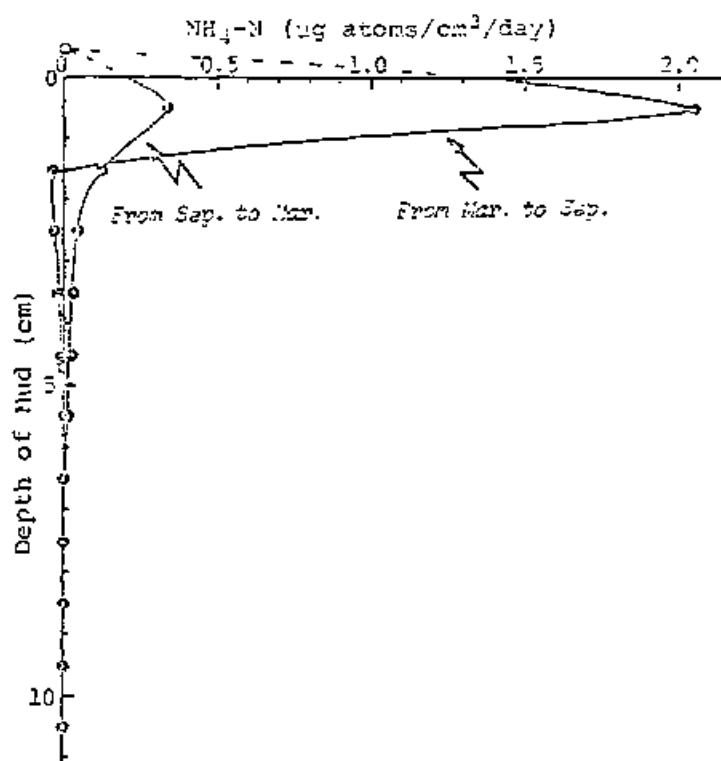
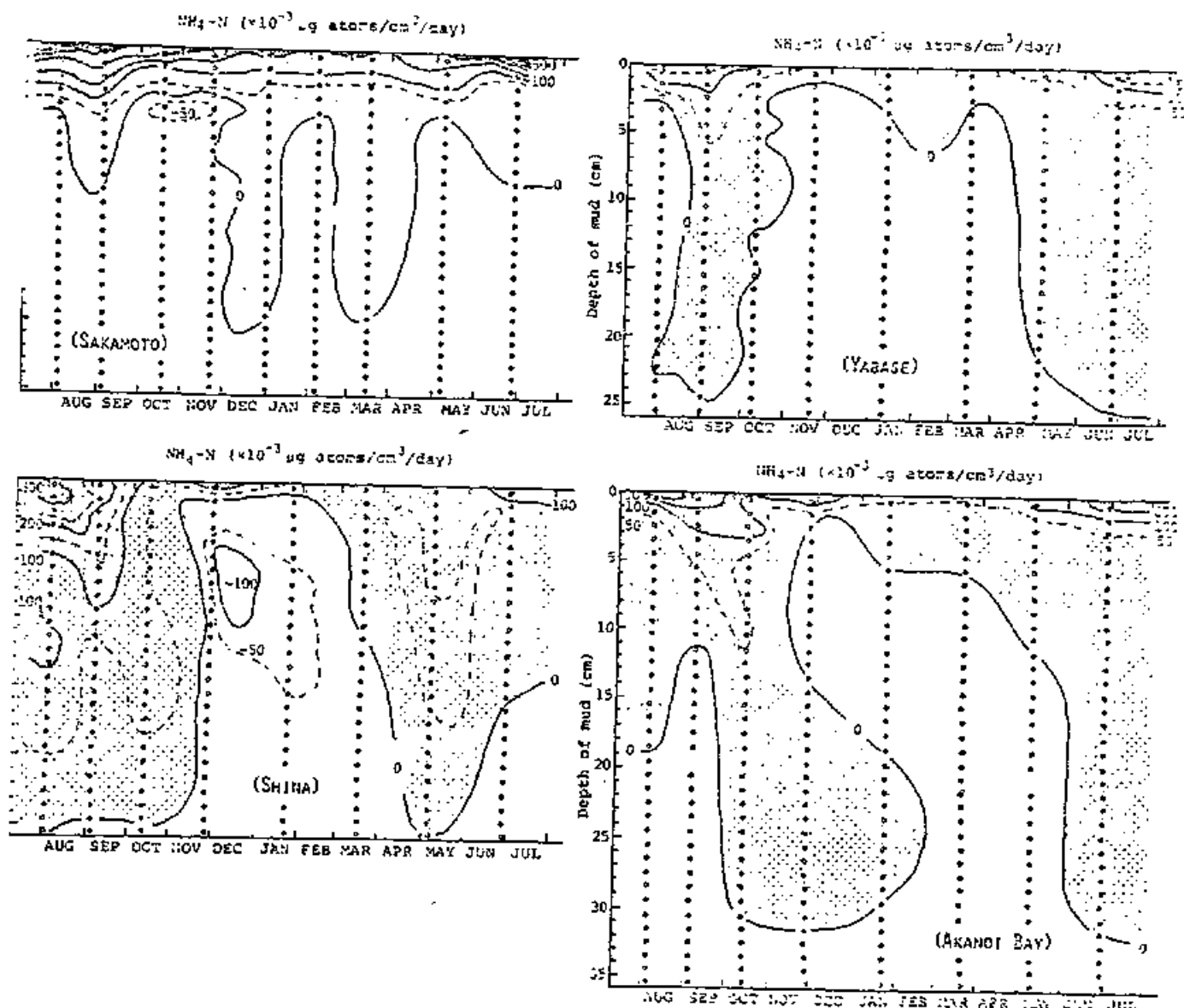
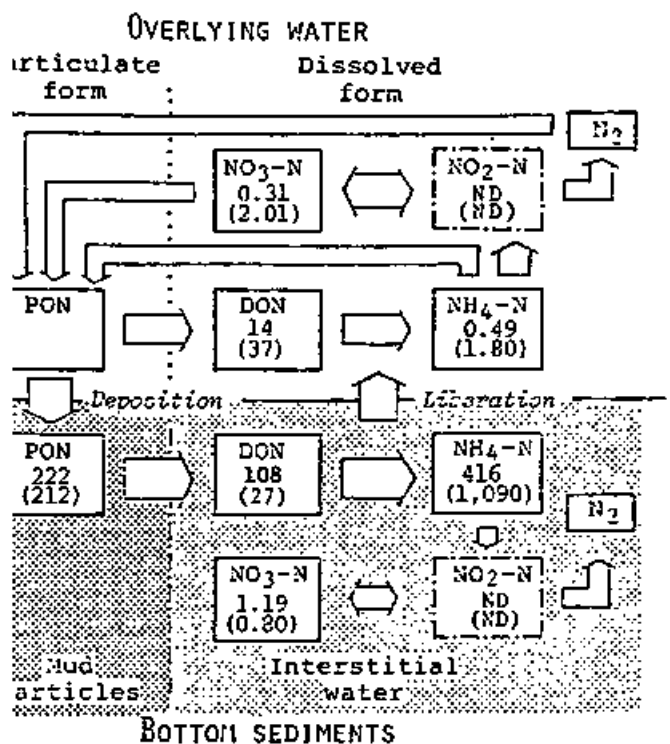


FIG. 16 Estimation of vertical profile of generation rate of ammonium nitrogen in the sediments in Mikawa Bay (in the case, diffusion coefficient,  $D = 2.0 \text{ cm}^2/\text{day}$ , was employed)



6. 17 Estimation of vertical profile of generation rate of ammonium nitrogen in the sediments at four stations in the south basin of Lake Biwa (in the case, diffusion coefficient,  $D = 2.0 \text{ cm}^2/\text{day}$ , was employed)



- 18 Metabolic processes of nitrogen cycle in water regions and concentration of nitrogenous compounds in winter and summer in Mikawa Bay ( $\mu\text{g atoms/l}$  except PON ( $\mu\text{g atoms/g dry mud}$ )). The value in summer is shown in parentheses.

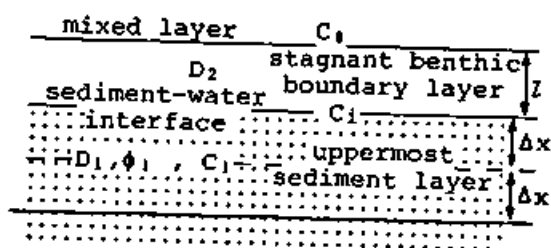
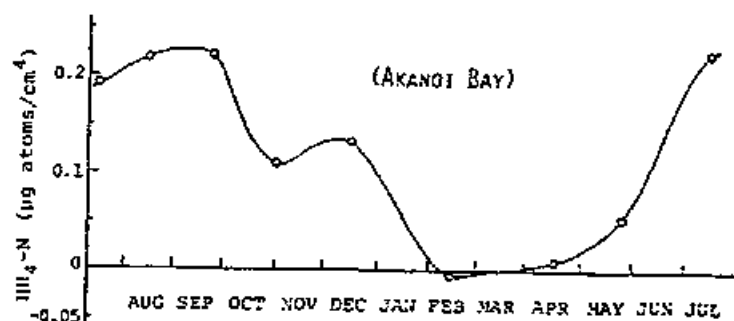
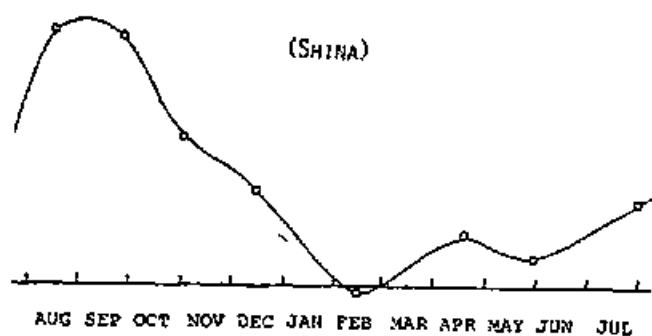
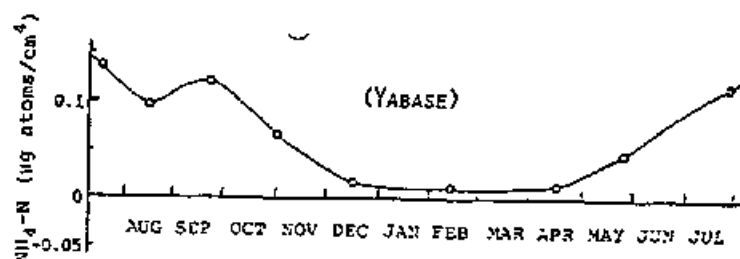
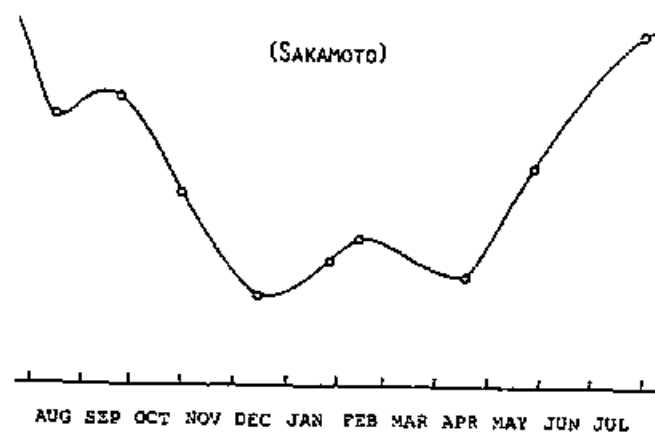


FIG. 19 Schematic illustration of sediment-water interface.



3. 20 Gradient of ammonium nitrogen in the water at sediment-water interface at four stations in the south basin of Lake Biwa.