Studies on the Release of Ammonium Nitrogen from the Bottom Sediments in Freshwater Regions

I. Generation of Ammonium Nitrogen in the Bottom Sediments in Lake Biwa

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Abstract

In the bottom sediments of aquatic regions, the decomposition of organic nitrogenous matter and the generation of ammonium nitrogen result in the vertical distributions of their concentrations. On the assumption that the sedimentation rate has been almost constant through the last several ten years, the elapsed time of the sediments in near surface layer from their deposition on the lake floor as well as the decomposition rate of the organic matter can be estimated. The rate constant in the decomposition process in the sediments was estimated to be 10^{-4} /day in the center of Lake Biwa, and the similar value was obtained in each 0.5 cm layer through a depth of several centimeters. Ammonium salts produced by the decomposition of organic nitrogenous matter enter into the interstitial water, then diffuse through the porous media of the sediments into the overlying water. The diffusion coefficient of ammonium nitrogen in the interstitial water was estimated to be 1×10^{-6} cm²/sec and the rate of its release into the overlying water was found to be $4.2 \mu\text{g atoms/cm}^2/\text{year}$ in the center of Lake Biwa.

1. Introduction

Quantitative studies on the nitrogen cycle in lake ecosystems are important in understanding the basic processes of production in the lake. In the research study, it is necessary to estimate the liberation rate of nitrogenous compounds from the bottom sediments into the overlying water. Particulated nitrogenous compounds in the bottom sediments are decomposed by the bacterial action to the dissolved forms, which are transported through interstitial water of the bottom sediments by diffusion process. In this way, the release of nitrogenous compounds occurs from the bottom sediments into the overlying water. The mathematical models which can be applied to the vertical distribution of chemical species in the sediments were proposed by BERNER

(1975). KAPLAN *et al.* (1963) and BERNER (1971, 1974) made such studies on the bacterial decomposition of organic nitrogenous compounds and diffusion of ammonium nitrogen in the bottom sediments in the ocean. The present paper deals with the estimation of decomposition rate of organic matter in the upper few centimeters depth of the sediments in Lake Biwa and some problems in applying a mathematical model to movement of nitrogen through the porous media of the sediments.

2. Methods and Materials

1. Sampling of the bottom sediments

The sediments 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 at the station Ie-1 near the center of Lake Biwa (water depth ca. 70

m). The sediment column was sliced into 5 mm thicknesses, and each slice was put into a plastic bottle, sealed tightly, kept cool in an ice box, and then brought to the laboratory.

2. *Extraction of dissolved nitrogenous compounds from the sediment*; Each sediment sample in the plastic bottle was mixed homogeneously, 0.5 g of it was mixed with distilled water and filled up 100 ml in total volume, then shaken vigorously for 1 min. Dissolved nitrogenous compounds were extracted in the supernatant solution obtained by the centrifugation (6,000 g, 15 min).

3. *Collection of the interstitial water in the sediments* Interstitial water was collected from the sediments by the centrifugation at 6,000 g for 30 min.

4. *Analyses of the bottom sediments* Kjeldahl nitrogen was determined by the method of STRICKLAND and PARSONS (1965) with some modifications. Inorganic nitrogenous compounds ($\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$), pH and redox potential were determined as in the study earlier of the authors (KAWAI *et al.*, 1971). Moisture content was measured by the method described in the previous paper (KAMIYAMA *et al.*, 1976).

3. Results and Discussion

1. Compaction in the bottom sediments

In the natural aquatic environments the deposition of organic and inorganic particles occurs continuously on the bottom sediments. As the result, the bottom sediment at a definite depth is compressed by the overlying layer of the sediments, which in turn brings about the decrease in moisture content of the sediments. The loss of water from the sediments is defined here as "compaction." The moisture content of the bottom sediments was shown in Fig. 1, in which the compaction above mentioned was observed clearly. Since the

Fig. 1. The vertical profile of moisture content in the bottom sediments.

Fig. 2. The vertical profile of porosity in the bottom sediments.

sediments consist of solid particles and water, porosity (ϕ) is defined as a volume of water in the unit volume of sediments and the following equation is given,

$$\phi = \frac{\alpha/\rho_w}{(1-\alpha)/\rho_s + \alpha/\rho_w}$$
 where ρ_s : average density of solid particles (g/cm^3), ρ_w : density of interstitial water (g/cm^3), α : moisture content. Porosity calculated from the moisture content and ρ_s (determined experimentally) was given in Fig. 2. Porosity

decreased with the compaction in terms of depth of the bottom sediments.

Time required for the deposits to sedimentate a unit thickness of the layer in a definite depth of the bottom sediments is given by the equation

$$\frac{\Delta t}{\Delta z} = \frac{(1-\alpha)\rho_s}{R} \dots (1)$$

where t : time (year); R : the rate of deposition ($\text{g}/\text{cm}^2/\text{year}$), z : distance from the bottom surface (cm). The time elapsing since sediments were deposited on the lake floor can be estimated by summing up the equation (1) from the surface to that depth.

2. *The decomposition of organic nitrogenous matter in the bottom sediments*
The vertical distribution of Kjeldahl nitrogen in the sediments was shown in Fig. 3.

Fig. 3. The vertical distribution of Kjeldahl nitrogen in the bottom sediments.

Table 1. The decomposition rate and rate constant of Kjeldahl nitrogen at various depth of the bottom sediments.

Depth of sediments (cm)	Kjeldahl nitrogen (μg atoms/g)	Time elapsing (year)	Rate of decomposition (μg atoms/g/year)	Rate constant ($\times 10^{-4}/\text{day}$)
0.0~0.5	182	1.2		
0.5~1.0	160	6.7	4.0	1.5
1.0~1.5	145	14	2.1	1.1
1.5~2.0	124	22	2.6	2.0
2.0~2.5	114	31	1.1	1.5
2.5~3.0	109	41	0.5	1.2

Its concentration in the sediments per dry basis was calculated from the equation,

$$\frac{C-C^*\alpha}{1-\alpha},$$

where C : concentration of Kjeldahl nitrogen in wet sediments (μg atoms/g), C^* : concentration of Kjeldahl nitrogen in interstitial water (μg atoms/ml). The concentration of Kjeldahl nitrogen in the bottom sediments decreased with depth. The phenomenon may be explained by the fact that the deeper the depth of the bottom sediments, the greater the decomposition by increasing the period elapsing from their deposition. YAMAMOTO *et al.* (1973) reported the deposition rate at this sampling station as $R=0.028 \text{ g}/\text{cm}^2/\text{year}$. On the assumption that the deposition rate has been constant through out the period of several centimeters' sedimentation, the time elapsing since each layer of sediment was deposited on the lake floor was estimated from the equation (1). Then, the decomposition rate of organic nitrogenous compounds (μg atoms/g/year) was calculated from the value of Kjeldahl nitrogen and the elapsed time of adjacent two layers as shown in Table 1. As a result, the values were found to decrease with the depth of the bottom sediments. It is generally agreed that the decomposition of organic nitrogenous compounds proceeds according to first-order kinetics (Ogura, 1972), and the decomposition rate can be expressed by an equation such as

$$dN^*/dt = -kN^* \dots (2)$$

where N^* : concentration of organic nitrogenous compounds which is able to be decomposed by the natural process in the sediments ($\mu\text{g atoms/g}$); and k : rate constant (/day). The value of N^* forms a part of Kjeldahl nitrogen obtained, however we have no information about the ratio of them in the sediments. In natural water regions such as Lake Biwa (TOYODA *et al.*, 1968), Lake Suwa (TOMINO, 1970) and Matsushima Bay (OKUDA, 1960), it is well known that the distinct decrease in organic nitrogen with the depth of the bottom sediments occurs from the surface to only few centimeters' depth.

In this study, therefore, the amount of organic nitrogen exceeding the constant level ($100\mu\text{g atoms/g}$) was regarded as N^* value, and the rate constant was then calculated from the equation (2) using an average value of N^* between the layers as shown in Table 1. The results show that the rate constant of the decomposition of organic nitrogenous compounds in each bottom sediment layer is almost constant for several centimeters depth from the bottom surface, while the rate of decomposition in the layer of 0.0~0.5 cm depth is four times greater than the one in 2.5~3.0 cm layer. BERNER (1974) reported that the rate constant of the decomposition of nitrogenous compounds in the sediments of the ocean was $10^{-4}/\text{day}$ in Somes Sound and $10^{-6}/\text{day}$ in the Santa Barbara Basin, respectively, by the estimation from the vertical distribution of ammonium nitrogen in the sediments. UKITA *et al.* (1975) calculated from an experimental data of the incubation of the sediments of Matsushima Bay that the rate constant of the increase in ammonium nitrogen in the sediments was $10^{-2}/\text{day}$. Because the depth of Matsushima Bay is very shallow, organic particles reach the bottom surface before complete decomposition in the overlying water.

The organic compounds in the sediments of Santa Barbara Basin have been decomposed prior to the deposition on the bottom surface, because it takes a long time for organic particles to reach the bottom in such deep water regions. The degree of the past decomposition of organic particles passing through water layers before deposition on the bottom is considered to decide the rate constant. With respect to the rate constant in the present study, Lake Biwa is in a class with the polluted deep depression in Somes Sound and falls between the very deep station in the Santa Barbara Basin and Matsushima Bay which is highly polluted with organic contaminants. This finding is very interesting in comparing the bottom sediments in various water regions. More precise follow-up investigations should be undertaken.

3. *Generation of ammonium nitrogen in the bottom sediments* In the bottom-sediments, organic nitrogenous compounds are decomposed to ammonium salts, which dissolve in interstitial water, then diffuse through it and further into the overlying water. The vertical distribution of ammonium nitrogen in interstitial water was shown in Fig. 4, in which little seasonal differences were observed at the sampling station. This might be due to the fact that the decomposition rate is almost constant through the year since the station is so deep that the temperature of the bottom sediments scarcely changes. On the other side, the authors have observed the seasonal change in the vertical distribution of ammonium nitrogen in a shallow station in the lake (KAMIYAMA *et al.*, 1975). The flux of ammonium nitrogen from the bottom sediments into the overlying water ($\mu\text{g atoms/cm}^2/\text{sec}$) is expressed as $D(\partial C_a/\partial z)_{z=0}$ where C_a : concentration of ammonium nitrogen in interstitial water ($\mu\text{g atoms/ml}$); and D : diffusion coefficient of ammonium nitrogen in interstitial water ($\text{cm}^2/$

Fig. 4. The vertical distribution of ammonium nitrogen in interstitial water of the bottom sediments in various seasons. ○—○: in winter, ●—●: in summer

sec). The flux is considered to be approximately equivalent to the total rate of decomposition obtained in Table 1. The value was $2.3 \mu\text{g atoms/cm}^2/\text{year}$, from which the diffusion coefficient was calculated to be $0.7 \times 10^{-6} \text{cm}^2/\text{sec}$. The diffusion coefficient obtained here seems to be somewhat small, however, the larger estimation can be taken under the consideration that the rapid decomposition (not detected in the present study) actually occurs at the water-bottom interface. By the use of the annual average value of organic nitrogen in the deposits on the bottom obtained by TOYODA *et al.* (1968) at the station, the decomposition rate in the water-bottom interface was estimated, and the flux mentioned above and the diffusion coefficient were obtained as $4.2 \mu\text{g atoms/cm}^2/\text{year}$ and $1.3 \times 10^{-6} \text{cm}^2/\text{sec}$, respectively. The diffusion coefficient obtained here fairly coincides with that reported by BERNER (1975).

4. *General discussion in the study* In this paper, organic nitrogenous compounds are considered to be decomposed to ammonium nitrogen, which is not transformed into other compounds such as nitrite, nitrate or gaseous nitrogen. The redox poten-

Fig. 5. The vertical profile of redox potential (Pt electrode) and pH values in the bottom sediments. ○—○: pH, ●—●: redox potential

tial and pH values shown in Fig. 5 may exclude the possibility of nitrite or nitrate generations in the sediments (VANDERBOUGHT *et al.*, 1975). In our chemical analyses, however, the concentrations of nitrite and nitrate in interstitial water were higher than those in the overlying water, being two or three orders lower than that of ammonium nitrogen. There have been no data available yet on the nitrite and nitrate generation in the sediments and further investigations are needed. The ammonium nitrogen occurring in interstitial water represented only a small part of that in whole bottom sediments as shown in Fig. 6. Thus, a large portion of ammonium nitrogen in the bottom sediments remains adsorbed on the sediment particles.

There occurs an exchange of ammonium nitrogen in the sediments between the interstitial water and the sediment particles, which may be in equilibrium under a definite condition. LERMAN *et al.* (1975) explained the distributions of ^{90}Sr and ^{127}Cs in the interstitial water of the bottom sediments by assuming the adsorption equation, $A = \bar{S}\bar{A}^n$, where A: concentration of the

Fig. 6. The vertical distribution of ammonium nitrogen in the bottom sediments. ○—○: in interstitial water
●—●: in whole sediments

ions in interstitial water, $\bar{A}$: amount of those which are adsorbed on the sediment particles, S and n : constant determined by the qualities of the bottom sediments and ions. The relationship between ammonium nitrogen in both phases, however, is not clear at present, and the authors intend to pursue this. The calculated value of Kjeldahl nitrogen in the sediments per dry basis discussed above includes ammonium nitrogen adsorbed on the sediments particles. Ammonium nitrogen adsorbed on the sediment particles shows the same behavior as particulate organic nitrogen in the sediments, because it moves with the sediment particles from the bottom surface to the depth with the elapsing time and is not diffusible in the bottom sediments. The decomposition, therefore, in the discussion represents the liberation of ammonium nitrogen from the sediment particles into interstitial water, which is not the real transformation of organic nitrogen to ammonium nitrogen but an apparent decrease in nitrogen present in the sediments. The authors have already found the diffusion coefficient of ammonium nitrogen in the sediments, in the previous study, to be $5 \sim 20 \times 10^{-6} \text{ cm}^2/\text{sec}$ (KAMIYAMA *et al.*, 1976).

The value is somewhat larger than that obtained in the present paper. The diffusion coefficient in the former was calculated from the distribution of ammonium nitrogen in whole sediments. Therefore, it does not show a real value of diffusion coefficient but apparent one, because the liberation of ammonium nitrogen from the sediment particles into interstitial water was involved. More precise models, therefore, are needed in estimating the physical migration and biological transformation of nitrogenous compounds in the sediments.

4. Conclusion

The vertical distribution of organic nitrogenous compounds and ammonium nitrogen in the bottom sediments of water regions depend on the decomposition of the former and concomitant generation of the latter in the sediments. On the assumption that a steady state has been kept in the sedimentation as well as the decomposition of organic compounds, the release rate from the sediments into the overlying water and diffusion coefficient in the interstitial water were estimated to be $4.2 \mu\text{g atoms/cm}^2/\text{year}$ and $1 \times 10^{-6} \text{ cm}^2/\text{sec}$, respectively. The rate constant of the decomposition was estimated to be $10^{-4}/\text{day}$ and the value scarcely changed over several centimeters depth of the bottom sediments. The rate constant is considered to vary depending on the environmental condition of the water regions. In the study, the values described above were calculated based on the fact that ammonium nitrogen adsorbed on the sediments particles behaves with the particulated organic nitrogen. In order to clarify the detailed mechanism of interaction between the bottom sediments and the overlying water, more precise models involving nitrogenous compounds present in interstitial water and adsorbed on the sediments particles are needed. On the other hand, an attempt to obtain the

rate of generation or decomposition under *in situ* condition may be effective to corroborate the models of the study.

5. 摘 要

湖沼におけるアンモニア態窒素の底土から水中への溶出機構を明らかにするうえで、底土中のアンモニア態窒素の生産速度を定量的に把握することは非常に重要である。本報では、水深の大きい琵琶湖中央部の湖底泥中の窒素化合物の鉛直分布から、表層近くの底土中における有機態窒素の分解速度およびアンモニア態窒素の年間生産量を推定した。底土表面に堆積した有機懸濁物は、年代とともに、さらにその上部に堆積したもののために圧密を受け、また生物作用を受けて分解していく。この分解過程が一次反応に従うとすると、反応係数は 1×10^{-4} /日となり、この値は表層附近では深さが変化してもほとんど変化しなかった。そしてこの反応係数は、各々の水域において固有の値を示すものと思われる。有機態窒素が分解されてアンモニア態窒素を生成し、それが底土中を拡散作用によって移動していくものとする、そのときの拡散係数、 $1 \times 10^{-6} \text{cm}^2/\text{秒}$ 、が求められた。またこの地点における底土から水中へのアンモニア態窒素の溶出速度は、 $4.2 \mu\text{g atoms/cm}^2/\text{年}$ と推定された。

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