研 究 速 報

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Decomposition Rate of Dissolved Organic Nitrogen in River and Sewage Plant

汚濁水界における有機態窒素の分解

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Introduction

Since eutrophication became a conspicuous issue, number of works have been dedicated to clarification of role of nitrogen in eutrophication as well as of kinetics of nitrification and denitrification of ammonium nitrogen.

Considerable part of inorganic nitrogen originates from domestic sewage and thus from organic form of nitrogen. Despite the fact, it seems suprising to see how little work has been done on decomposition of dissolved organic nitrogen (DON) to result in inorganic forms.

One of the reasons why DON has been neglected so far may be that quantitative analysis of DON is sometimes troublesome, since Kjeldahl method most widely employed has insufficient accuracy and that it is sometimes difficult to detect low concentration of DON in certain accuracy.

The purpose of this present investigation is to make clear the role of DON in water environment including sewage treatment plant and to estimate a time constant of decomposition of DON.

This work consists of three experiments on the behavior of dissolved organic nitrogen.

(i) mesurement of DON concentration by means of TDN analyzer combined with gel filtration of a typical urban river, the Sen River, and sewage treatment plant.

(ii) laboratory decomposition experiment by using polypepton and meat extract as an organic nitrogen source to determine kinetics of decomposition, and

(iii) measurment of the change of gel chromatgram of organic nitrogen in the course of successive sewage treatment plant and in the course of meat extract decomposition experiment.

From the results of all the three experiments the decomposition rate of DON in water environment could be estimated.

Procedures

(1) Samples from the urbane river

Water samples from the Sen River which is a branch of the Nogawa River that flows into the Tama River and Mitaka Eastern sewage treatment plant, were collected in 633 m*l* dark glass bottles. The bottles were kept at 4°C, and brought to the laboratory. In all the cases $HgCl_2$(50mg/*l*) is added into the bottles immediately after sampling to prevent biological deterioration.

In the laboratory, the samples were first filtered through a 1 μm glass fiber filter (Millipore Type GFP) and then through a 0.45 μm filter (Millipore Co. HAWP 04700 Type HA). The samples were then kept below 8°C until the following analysis to minimize chemical change of water quality.

(2) Determination of DON concentration

DON concentration was calculated by subtracting the sum of the inorganic nitrogen concentrations from the total dissolved nitrogen (TDN), namely

$$DON = TDN - (NH_4^+ \cdot N + NO_2^- \cdot N + NO_3^- \cdot N)$$

In this method, each form of nitrogen is determined by following procedures.

The concentration of TDN and $NH_4^+ \cdot N$ was measured using the total nitrogen analyzer TNO-1 (Mitsubishi Chemical Co.) which is based on ter Meulen method: All the forms of nitrogen are changed into ammonium form on the Ni-Mg catalyst at temperature 320°C in flowing hydrogen. Then the ammonium nitrogen is absorbed by the solution water

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containing 1 wt % of Na_2SO_3. pH rise in the solution is detected and the following coulometric titration gives TDN concentration. For determination of NH_4^+·N, soda-lime bed (80°C) is used to gasify NH_3, and the same procedure (adsorption and titration) is used as the TDN determination.

The concentration of NO_2^-·N was measured by chlorimetric method using sulfunylamid and N-1 naphthylethylethylendiamine[1].

The concentration of NO_3^-·N was determined by cadimium column reduction method[1].

(3) Gel filtration

Since many types of DON, for example, Urea, Uric Acid, Amino Acid, Protein etc. are expected in polluted water, DON is characterized with molecular weight distribution by using gel chromatography in the present study. The procedure of gel filtration was as follows. The samples from the sewage treatment plant were filtered and concentrated using a vaccum evaporater at about 30°C- 30 mmHg when DON is low. By this means concentration factor of 10 to 20 was attained. The samples from the decomposition of meat extract were not concentrated, because it had high enough concentration for gel filtration. Then, the samples were filtered through a 0.45 μm membrane, and 5 ml of filtrate was introduced to a plastic column containing 150 ml of Sephadex G-25 gel and eluted by a buffer solution of pH 7.8 which consists of KH_2PO_4 34 mg/l and NaOH 9.0 mg/l in distilled water with a flow rate of about 1 ml/min. The solution was effective for protecting the adsorption of NH_4^+·N on Sephadex gel particles.

The column effluent was collected in 5 ml aliquots using an automatic fraction collector. The column dimension was about 2.6 cm in diameter and 28 cm in height.

The gel was kept in distilled water about one day at room temperature for swelling. And then, the gel was packed into column. For the calibration of this column, Poly ethylene glycoles of different molecular weights were used.

For the rapid determination of the concentration of NO_2^-·N and NO_3^-·N, Spectrophotometric Method[1] was used for gel filtration eluants.

(4) DON decomposition in a batch reactor

Polypepton (for bacteriological culture; manufactured by Daigoeiyo Chemical Co.) and meat extract (for bacteriological culture; manufacture by Mikuni Chemical Industory Co.) were used as the sources of DON.

The experiments were carried out as follows.

Then polypepton or meat extract were dissolved in 1.0 l buffer solution (pH : 7.0, KH_2PO_4 5.4 g/l, NaOH 0.96 g/l in distilled water). The reason for the use of buffer solution is to protect pH rise caused by NH_4^+·N which appeares in the progress of decomposition of polypepton or meat extract by bacteria.

The initial concentration of polypepton or meat extract were adjusted to 30~150 mg/l as organic nitrogen. No nutrients were added in the solution.

Temperature was controlled at 20°C, 25°C and 30°C using water bath type temperature controller. And all the experiments were carried out in aerobic condition by a commercial aeration device.

Batch decomposition run was started by adding 1 ml of activated sludge in the reactor. This activated sludge is continuously cultured in laboratory using polypepton and glucose.

50 ml of the solution was taken intermittently from the reactor by glass syringe for analysis of SS, TOC and nitrogens.

Results and Discussion

(1) Concentration level of DON in the Sen River

The concentration of each form of nitrogen in the Sen River were shown in Fig. 1. From this figure, it is apparent that there are little DON in the Sen River when compared with the inorganic nitrogens. Most of the water flowing here, however, came from the domestic sewage plant, and then most of the nitrogen is originated from organic types in domestic sewage. So it should be concluded that most of the organic nitrogen is decomposed in the drain channel and sewage treatment plant.

(2) DON disappearance in the course of sewage treatment

To estimate the organic nitrogen decomposition rate, the mass balance of organic nitrogen was taken in the Mitaka Eastern Sewage Treatment Plant. This plant accepts domestic sewage of the eastern area of Mitaka City (population about 91,000) and discharges the treated water (3.0×10^4 m^3/day) to the Sen River.

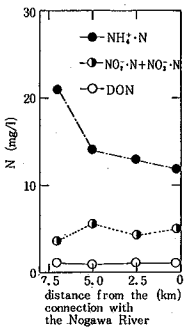

Fig. 1 Change of the N-concentrations in the Sen River

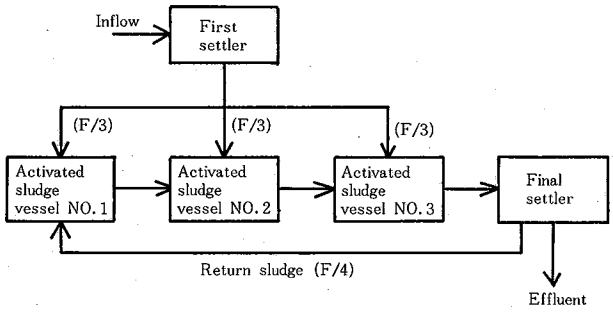

Fig. 2 Flowsheet of sewage treatment plant (Mitaka, Tokyo)(step aeration type)

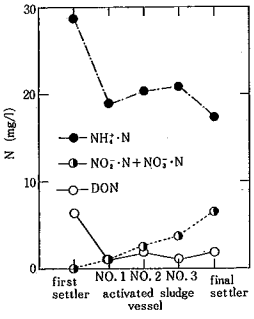

Fig. 3 Change of N-concentration in the sewage treatment plant (step aeration type)

Table 1

	First Set.	Act. S. V. 1	Act. S. V. 2	Act. S. V. 3	Final Set.
DON	6.40	1.01	1.79	1.23	1.94
DON M. W. >1000	0.51	0.32	0.49	0.29	0.24
DON M. W. <1000	5.90	0.59	1.30	0.94	1.70

Table 2

	Act. S. V. 1	Act. S. V. 2	Act. S. V. 3
DON	0.98	0.30	0.89
DON M. W. >1000	0.06	–	0.43
DON M. W. <1000	1.70	0.42	1.03

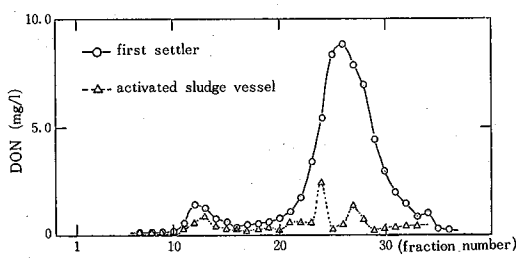

Fig. 4 Change of the chromatogram in the sewage treatment plant (Sephadex G-25, one fraction 5 ml, column dimension: d=1.3 cm, h=28 cm, 60 ml/hr)

Step aeration mode is adopted in sewage treatment plant, whose schematic flow sheet is shown in Fig. 2.

The concentrations of NH_4^+-N, NO_2^--N+NO_3^--N and DON in each vessel are shown in Fig. 3.

Gel chromatographic method was again used to charactarise organic nitrogen. Typical chromatograms are given in Fig. 4. From this figure, it is apparent that most of organic nitrogen in domestic sewage are present in low molecular range (around 100), and there is a little DON in high moleculer weight range (around 6000). From the chromatograms of the samples taken from the activated sludge vessels, it has become clear that the low molecular weight organic nitrogen disappears very rapidly to a certain extent. Concentration of organic nitrogen of molecular weight smaller or larger than 1000 are shown for each sample in Table 1.

From the concentrations given in Table 1, decomposition rate of DON in each aeration vessel can be estimated. For kinetics of decomposition, first order equation is assumed as a first approximation and each vessel is considered to be complete mixed. Each vessel has a volume, V, and because of step aeration mode, flow rate of effluent of primary sedimentation tank into each vessel is taken as $1/3F$. Then from a mass balance in each vessel, rate constant of decomposition is given as

$$k_1 = = \frac{1}{VC_1}\left(\frac{1}{3}FC_0 + \frac{1}{4}FC_4 - \frac{7}{12}FC_1\right) \qquad (1)$$

$$k_2 = \frac{1}{VC_2}\left(\frac{1}{3}FC_0 + \frac{7}{12}FC_1 - \frac{11}{12}FC_2\right) \qquad (2)$$

$$k_3 = \frac{1}{VC_3}\left(\frac{1}{3}FC_0 + \frac{11}{12}FC_2 - \frac{15}{12}FC_3\right) \qquad (3)$$

Using these equations decomposition rate constants were calculated for total DON, high molecular weight DON and low molecular weight DON separately. The results are given in Table 2. As is clear from this table, low molecular weight DON has larger decomposition rate than high molecular weight DON.

(3) Organic nitrogen decomposition in Laboratory

A typical behavior of DON decomposition in batch culture is shown in Fig. 5. Following the organic nitrogen decomposition, concentration of NH_4^+-N and SS (bacterial mass) increased. Fig. 6 shows decay of

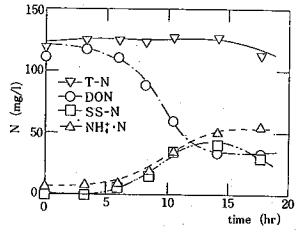

Fig. 5 Behavior of DON (meat extract) decomposition by bacteria in batch system

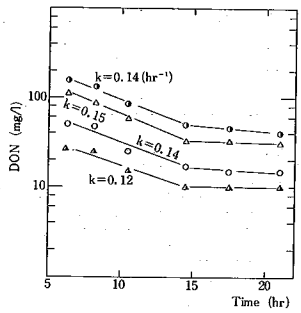

Fig. 6 Decomposition curve of DON (meat extract) at the tempera ture 25°C

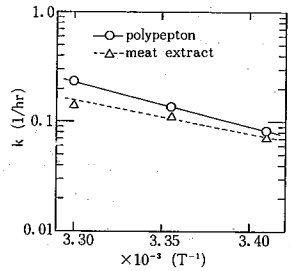

Fig. 7 Arrhenius plot of rate of DON decomposition

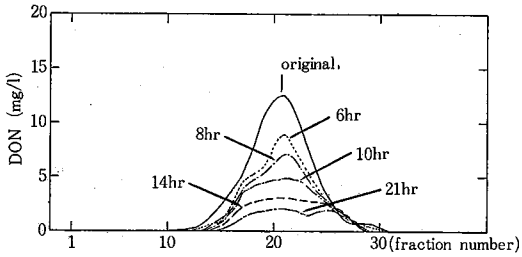

Fig. 8 Change of the chromatogram with decomposition of meat extract (25°C)

organic nitrogen concentration. Following a lag phase of about 5 hr at 25°C, maximum decomposition rate constant was given at the initial stage of decomposition in each case. This value (k=about 0.14 hr^{-1}) is in accordance with the decomposition rate of high molecular weight DON in the sewage treatment plant. Fig. 7 shown temperature dependence of the decomposition rates of polypepton and meat extract. The activation energies calculated from the plot are E=18.0 kcal/mole for polypepton and E=13.4 kcal/mole for meat extract.

Fig. 8 shows the change of DON chromatogram in the course of meat extract decomposition. From the figure only slight difference of DON decomposition rate is noticed for different molecular weight. This result seems contradictory with the observation from the sewage treatment plant. The reason of this may be that, all of the nitrogen in batch experiment are composed of protein and amino acids, while large amount of urea (came from human urine) is expected in the sewage treatment plant. So the rapid decay of urea in activated sludge vessel is the cause of the large decomposition rate obserbed for low molecular organic nitrogen. The decomposition rate of high molecular weight organic nitrogen in sewage treatment plant fell close to the rate obtained in laboratory experiment.

Conclusion

To assume first order decomposition kinetics, the decomposition rate constant of high molecular weight DON (M.W.>1000) is estimated to be about 0.16 hr^{-1}. The decomposition rate constant of low molecular weight DON in sewage plant was higher than this figure, likely because of rapid disappearance of urea in the sewage.

Since the both rates are greater than the rate constant of nirification, denitrification or algae decomposition. Decomposition of dissolved DON to ammonium nitrogen in polluted water may not become a rate controlling step in nitrogen in polluted water may not become a rate controlling step in nitrogen transport in natural ecological system.

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Nomenclature

F : inflow rate of the sewage treatment plant, 3.0×10⁴ [m^3/day]

V : volume of each activated sludge vessel, 1700 [m^3]

C : concentration of DON in each vessel [mg/l]

k : the first order decomposition rate observed in activated sludge vessel [hr^{-1}]

Subscript

0 : first settler, 1~3 : activated sludge vessel, 4 : final settler

Reference

1) Standard Method for the Examination of Water and Wastwater (14 th, 1975) APHA, AWWA