

# Runoff Characteristics of COD, BOD, C, N and P Loadings from Rivers to Enclosed Coastal Seas

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It is well known that the three nutrient elements of carbon (C), nitrogen (N) and phosphorus (P), are very important in the eutrophication in enclosed coastal seas. The major source of the C, N and P is the inflow from rivers rather than the release from sediment in the closed sea. In Japan, the environmental quality standards which indicate organic pollution in both river and sea are different from one another; in a river, it is based on BOD and in the sea, on alkaline COD<sub>Mn</sub>. Therefore, these different standards lead to difficulties in obtaining consistent water quality management of the water system from rivers to enclosed coastal seas. Hinuma River observed runoff loading of alkaline COD<sub>Mn</sub>, BOD, C, N and P by weekly observation in 1988 and 1989. When the flow increases, the order of increasing ratio is phosphorus, followed by carbon, and nitrogen. It was found that 88% of phosphorus runs off in the form of particulate phosphorus and 84% of nitrogen runs off in the form of dissolved nitrogen; and though nitrogen runs off in an almost constant concentration, most phosphorus runs off during the high flow stage. The behavior of the particulate phosphorus after flowing in to the enclosed coastal sea is an important factor in eutrophication.

## Introduction

It is well known that nutrient elements, the three elements of carbon (C), nitrogen (N) and phosphorus (P), are very important in the eutrophication in enclosed coastal seas. Although few case studies have been done for inflow nutrients loads from river to closed water areas (Ebise and Goda, 1985), it has become clear that the major source of the C, N and P is inflow from rivers rather than the release from sediment in enclosed seas.

In Japan, the environmental quality standards which indicate organic pollution for rivers and seas it differ from one another; in the river, the water quality indicator is BOD, whereas in the sea is alkaline COD<sub>Mn</sub>. Therefore, these different water quality indicators cause difficulty in the consistent water quality management of the water system from rivers to enclosed coastal seas. It is necessary for the purpose of water pollution control in enclosed coastal seas to clarify each inflow loading per unit area of alkaline COD<sub>Mn</sub>, BOD, C, N, P and the ratio of the three elements of C, N and P, based on frequent observation of runoff loading characteristics from the river throughout the year.

## Materials and Methods

Hinuma River (Figure 1), which flows from west to east through the middle of Ibaraki Prefecture and into the Pacific, was observed for runoff loading weekly, including detailed observations during storm runoff events. The catchment area of R. Hinuma, which is 141.9 km<sup>2</sup>, includes the urban area of Kasama and Tomobe and paddy fields and forested lands. The domestic wastewater and drainage from the fields flow into R. Hinuma similar to the case of many rivers in Japan.

The major analytical methods are listed in Table 1, PO<sub>4</sub>-P, NO<sub>3</sub>-N,

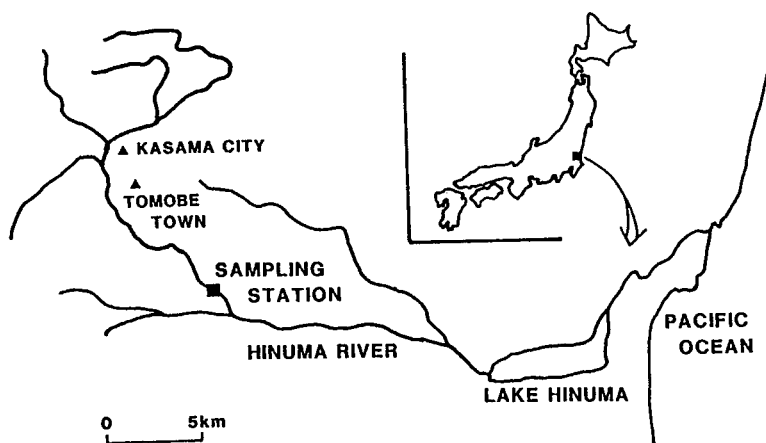


Figure 1 Location map of Hinuma River

$\text{NO}_2^-$ -N,  $\text{NH}_4^+$ -N,  $\text{SiO}_2^-$ , and the main cations and anions were also determined. For data on precipitation, the point of Kasama, the center of the river basin, was used (Mito Local Meteorological Observatory, 1989). In order to compare the water quality of the rivers and the enclosed coastal seas, we used the data from April 1987 to March 1989 of Osaka Bay (Osaka Prefecture, 1987-1989), which is representative of enclosed coastal seas in Japan.

Table 1 Water quality indicators and their analytical method

Item	Method
Flow	propeller-typed current meter
DOC	TOC analyzer (Shimadzu TOC-500)
POC, PON	CHN corder (Yanako MT-5)
T-N, D-N	nitrification by oxidation with potassium peroxodisulfate and Cu-Cd column reduction method
T-P, D-P	decomposition to $\text{PO}_4$ with potassium peroxodisulfate and molybdate-blue method
T-COD, D-COD	alkaline potassium permanganate method
BOD	titration method with DO bottle
TOC	DOC + POC
P-COD	T-COD - D-COD
P-P	T-P - D-P
dissolved component	filtrated sample with glassfiber (1 $\mu\text{m}$ pore size)

## Results and Discussion

### Relationship between flow and runoff loading

The change of runoff loading ( $L$ : g/s) is usually shown by the regression equation,  $L=a \cdot Q^n$ , which meaning the function of the flow ( $Q$ :  $\text{m}^3/\text{s}$ ). Table 2 shows the coefficient ( $a$ ) and exponent ( $n$ ) of each water quality component, for R. Hinuma, and the correlation coefficient calculated with the method of least squares. This equation indicates that if " $n$ " is larger than 1.0, the increase of flow causes a high concentration of pollutants and nutrients, and if " $n$ " is smaller than 1.0, the concentration are reduced. The values " $n$ " of D-COD, DOC, D-N and D-P were nearly 1.0, and the concentration of dissolved components was usually constant, during the high flow stage. Since the values " $n$ " of P-COD, POC, P-N and P-P were larger than 1.0, the increased of flow raised their concentrations. These results will be made clear by the fact that the discharge-weighted mean concentration is higher than the arithmetic mean concentration as described in the latter. They were caused by the exfoliation of the biofilm on the riverbed, the runoff of the sediment on the riverbed and the muddy particles from the forested land and fields. The increased flow raises the concentration of TOC, T-COD, T-P and T-N, especially because of the particulate components. For the increasing ratio of loading due to the increase of flow, T-P was highest, followed by TOC, T-COD and T-N. The concentration of BOD changed according with the season, becoming higher in winter and lower in summer, rather than according to the flow changes. In regard to organic pollution, BOD has some different runoff characteristics from other water quality standards, TOC or COD. The " $n$ " for dissolved silicate was nearly 1.0, and its concentration was almost constant even if the flow increased.

Table 2 Coefficients of  $L=a \cdot Q^n$  and correlation coefficients ( $L$ =g/s,  $Q$ = $\text{m}^3/\text{s}$ )

	a	n	r
T-COD	2.19	1.25	0.879
TOC	1.62	1.26	0.872
BOD	2.16	0.894	0.727
T-N	1.10	1.16	0.970
T-P	0.0374	1.35	0.836
P-COD	0.471	1.61	0.828
POC	0.532	1.45	0.817
P-N	0.0914	1.22	0.771
P-P	0.0216	1.48	0.805
D-COD	1.76	0.985	0.870
DOC	1.08	1.02	0.895
D-N	1.01	1.12	0.975
D-P	0.0154	0.925	0.818
Cl <sup>-</sup>	9.27	0.836	0.959
SS	6.79	1.72	0.803

Table 3 Specific discharge and load at 1988, 1989 and its ratios

	1988	1989	1989/1988
Rainfall (mm)	1404	1753	1.25
Discharge (mm)	771	939	1.22
T-COD ( $\text{O}_2$ kg/ $\text{km}^2$ )	3665	4725	1.29
TOC (kg/ $\text{km}^2$ )	2781	4112	1.48
BOD ( $\text{O}_2$ kg/ $\text{km}^2$ )	1216	1759	1.45
T-N (kg/ $\text{km}^2$ )	1180	1346	1.14
T-P (kg/ $\text{km}^2$ )	88.0	132	1.50
P-COD ( $\text{O}_2$ kg/ $\text{km}^2$ )	2012	3157	1.57
POC (kg/ $\text{km}^2$ )	1878	3060	1.63
P-N (kg/ $\text{km}^2$ )	169	243	1.44
P-P (kg/ $\text{km}^2$ )	76.4	118	1.54
D-COD ( $\text{O}_2$ kg/ $\text{km}^2$ )	1653	1568	0.95
DOC (kg/ $\text{km}^2$ )	903	1052	1.17
D-N (kg/ $\text{km}^2$ )	1011	1102	1.09
D-P (kg/ $\text{km}^2$ )	11.6	14.1	1.21
Cl <sup>-</sup> (kg/ $\text{km}^2$ )	6089	6512	1.10
SS (kg/ $\text{km}^2$ )	44823	78606	1.75
$\text{SiO}_2^-$ (kg/ $\text{km}^2$ )	12858	14502	1.13

*Relationship between annual precipitation and specific loads*

Table 3 shows the annual precipitation, specific discharge and specific loads in 1988 and 1989 and the ratio of 1989 relative to 1988. In 1989 precipitation was 1.3 times higher than that in 1988 and its specific discharge was 1.2 times that in 1988. In addition to the relationship between the flow and the runoff loading, the specific loads of D-COD, DOC, D-N and D-P for both years were almost the same and almost unrelated to annual precipitation. On the other hand, the particulate components in the specific loads increased when the annual precipitation was high. The POC, P-P and P-N in the specific loads in 1989 were about 1.5 times that in 1988. The TOC and T-P loadings in 1989 became 1.5 times that in 1988, which is higher than the increasing ratio of the annual precipitation and the specific discharge. The T-N loading, ratio increased only 1.1 times. Its concentration has been virtually constant every year and has little correlation with the annual precipitation. The increase in the dissolved silicate, ratio was also only 1.1 times, and its concentration remained almost constant.

Since the specific load is greatly affected by annual precipitation, weekly observation was never enough to understand the effects of the precipitation which occurs almost every 4 days. One must observe runoff loading, including detailed observations during storm runoff events, for several years.

*Ratios of C, N and P in specific loads*

Table 4 shows the ratios of C, N and P through arithmetic mean concentration and discharge-weighted mean concentration. In Comparing the discharge-weighted mean concentration with the arithmetic one, the ratios of P-P, P-COD and POC were higher than P-N, whereas the ratios of D-P, D-COD and DOC were lower than D-N. Arithmetic mean concentration overestimates the ratios of T-N/T-P and T-N/T-COD, because the discharge and concentration of phosphorus and carbon became high when the flow increased. Since the ratio of P-N/P-P at 2.13 was lower than that of the biofilm on the riverbed (Tachibana et al, 1988), in discharge-weighted mean concentration, the major part of P-P was adsorbed in the clay and organic particulate matter.

Table 4 Ratios of carbon : nitrogen : phosphorus

[arithmetic mean concentration]							
T-COD:TOC:T-N:T-P	44.9	: 34.7	: 18.0	: 1	T-COD:T-N	2.49	: 1
P-COD:POC:P-N:P-P	24.4	: 23.9	: 2.74	: 1	P-COD:P-N	8.91	: 1
D-COD:DOC:D-N:D-P	118	: 73.3	: 72.6	: 1	D-COD:D-N	1.6	: 1
[discharge-weighted mean concentration]							
T-COD:TOC:T-N:T-P	38.2	: 31.4	: 11.5	: 1	T-COD:T-N	3.32	: 1
P-COD:POC:P-N:P-P	26.7	: 25.5	: 2.13	: 1	P-COD:P-N	12.5	: 1
D-COD:DOC:D-N:D-P	125	: 76.0	: 82.1	: 1	D-COD:D-N	1.52	: 1

Table 5 The ratio of dissolved carbon, nitrogen and phosphorus

	arithmetic mean concentration	discharge-weighted mean concentration
D-COD / T-COD	0.58	0.38
DOC / TOC	0.46	0.28
D-N / T-N	0.88	0.84
D-P / T-P	0.22	0.12

Table 5 and Figure 2 show the ratios of each dissolved component relative to each total component. The ratios of dissolved components, especially phosphorus and carbon, were lower in discharge-weighted mean concentration, as compared to the arithmetic one. Although 84% of nitrogen ran off in the form of dissolved nitrogen, only 12% of phosphorus and 28% of carbon ran off in the form of dissolved phosphorus and carbon. It became clear that phosphorus and carbon mainly run off in the form of particulate components, and similar nutrient runoff characteristics were observed in R. Koise (Ebise and Inoue, 1990).

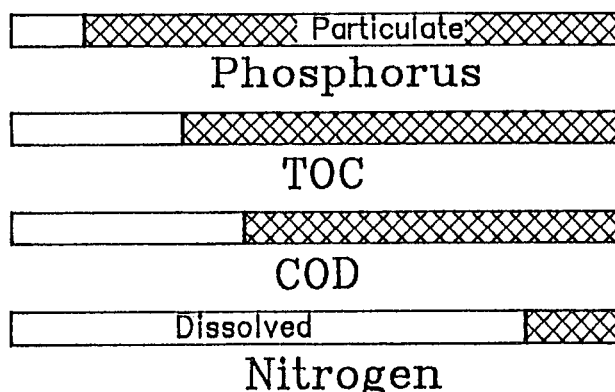


Figure 2 The ratios of each dissolved component relative to each total component

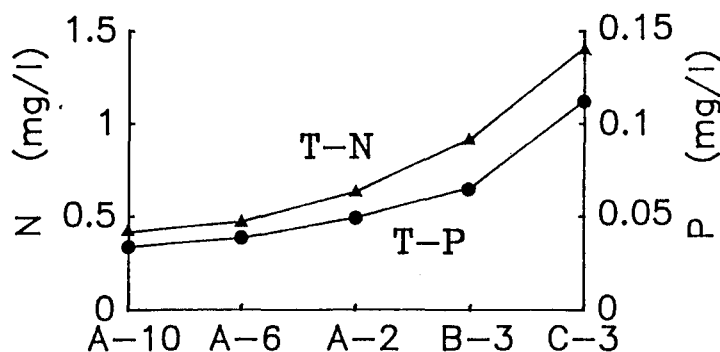


Figure 3 Changes of nutrients in Osaka Bay

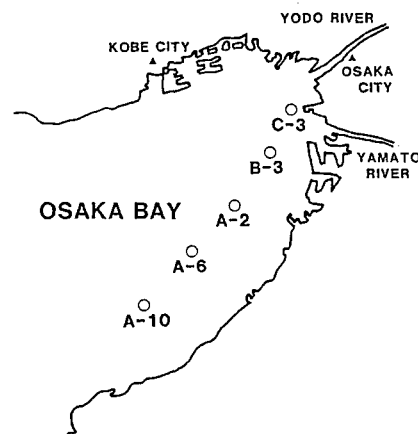


Figure 4 Location of observation points in Osaka Bay

#### *Eutrophication in sea and in-flow loading characteristics*

Figure 3 shows the concentration range of N and P from the shoreline to the entrance of Osaka Bay (Figure 4). Osaka Bay is representative of enclosed coastal seas in Japan that are being affected by progressive eutrophication. The strong effect of pollutants and nutrients inflow loading was noted due to the decrease in concentrations of N and P from the shoreline to the entrance of the bay.

As to the inflow loading characteristics from a river, it is known that a large amount of nitrogen inflow to the area in the form of dissolved nitrogen, and that most phosphorus flows in the form of particulate phosphorus. It is also known that nitrogen flows in an almost constant concentration and in proportion to the flow, while most phosphorus flows at the flooding time when the flow increases. The behavior of the particulate phosphorus, which increases when flow increases, after flowing into the enclosed coastal sea, is an important factor of eutrophication.

#### Conclusion

The data of specific load for a inflowing river, which are based on one year of weekly river observation, are not sufficient for full evaluation of the effects on runoff loading by storm events. However, there is useful information concerning pollution loading. Though the concentration of dissolved components is almost constant in the increasing flow, the concentration of particulate components rises in the increasing flow. When the flow increases, the order of increasing ratio is phosphorus, followed by carbon, and nitrogen. The specific load is affected by the annual precipitation and the specific discharge. For T-P and TOC, these runoff loads were 1.5 times greater when the annual precipitation and specific discharge were 1.2 times greater. It was found that 88% of phosphorus runs off in the form of particulate phosphorus and 84% of nitrogen runs off in the form of dissolved nitrogen. Nitrogen runs off in an almost constant concentration, whereas most phosphorus runs off during the high flow stage. The behavior of the particulate phosphorus which increases when flow increases, after inflowing to the enclosed coastal sea, is an important factor in eutrophication.

#### REFERENCES

- Ebise, S., Goda, T. (1985). Regression models for estimating storm runoff load and its application to Lake Kasumigaura. *Intern. J. Environmental Studies*, 25, 73-85.
- Ebise, S., Inoue, T. (1990). Change in C : N : P ratios during passage of water areas from rivers to a lake. *Water Research* (in press)
- Mito Local Meteorological Observatory (1988, 1989). Monthly meteorological report
- Osaka Prefecture (1988, 1989). Measurement report of public water areas
- Tachibana, H., Moriguchi, A., Inoue, T., Kimura, N., and Omuro, S. (1988). Composition and its water purification ability of biofilm on river bed. *Proc. Environ. Sani. Eng. Research*, 24, 1-12