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QUANTITATIVE EVALUATION OF WATER POLLUTANT LOAD FROM KINOKAWA RIVER BASIN BY HIGH-FREQUENCY WATER QUALITY OBSERVATION

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ABSTRACT: In the Kinokawa river basin, as same as other watersheds around the world, excess runoff of nutrients to the ocean mainly due to human activities has become an environmental issue. This study conducted high-frequency total nitrogen (TN) and total phosphorus (TP) monitoring at several monitoring posts set downstream of the Kinokawa river in the Kii peninsula, Japan in order to evaluate water pollutant load from the basin quantitatively. The water sampling has been conducted about 90 times for over a year from May in 2018 at the monitoring posts. In the calm or the drought periods, TN and TP concentrations at Kinokawa river mouth were basically about 0.8 ~ 1.1 mg/L and under 0.05 mg/L, respectively. However, TN concentrations was exceeded 5.0 mg/L after one of the most intense storms, it was shown the TN concentration had a tendency extremely to rise rapidly in flooding condition. This tendency was similar in TP. The result of pollutant load analysis showed that 65% of the nitrogen load and 80 % of the phosphorus load from the basin was generated during a few and heavy flooding which were included in 5 % flow exceedance probability. These results imply it is essential that to understand and to predict how nutrients runoff in short-term during flooding events in order to accurately grasp long-term nutrient runoff amount.

Keywords: Pollutant loads, River water quality, Total nitrogen, Flooding, Kinokawa river basin

1. INTRODUCTION

Water quality conservation of rivers, lakes and ocean has still been a global issue. Therefore, a number of water quality observations and numerical analyses aiming at elucidating nutrients runoff mechanism has been conducted around the world. Donald and William (2001) showed that nitrogen flux from the basin to Gulf of Mexico was significantly increased in 1970s by using nitrogen concentration data of Mississippi river water during 100 years [1]. As studies targeting smaller spatial scale, [2] compared pollutant loads of pre-European settlement with ones of current into Great Barrier Reef by using numerical model. They utilized ten kind of pollutant substances as indicators, it was shown that almost all substances increased over 5 times from pre-European settlement. We also evaluated water quality and pollutant loads targeting in Kinokawa river basin, which is also the target basin in this study, by using numerical water-nutrient runoff model [3]. This study showed the indicator “2-MIB” tended to increase when total phosphorus (TP) concentration exceeded 0.02 mg/L. It was concluded that the measures to combine TP mass load reduction with an increase in river flow rate could reduce TP concentration to less than 0.015 mg/L and prevent increases in 2-MIB in tap water.

As well as long-term fluctuation characteristic, extreme events like storm and resulting floodings could have great impacts in river and ocean water quality. Several studies indicated almost all nutrients flux were generated by floodings. [4] conducted stormwater nutrients monitoring at some monitoring posts distributed whole Singapore. In [4], it was ascertained parklands could become main nutrient sources, including TN, TP and TSS in urbanized area. Although [5] also targeted in urbanized watershed in Korea to indicate mainly source of nutrients based on water quality monitoring, they concluded it was difficult to determine the non-point source by specific characteristics such as land cover.

These studies suggested nutrient runoff mechanism driven by storm has not explained well still now. In order to reveal the mechanism of nutrient runoff, there is a need for an accumulation of nutrient monitoring data in a various of basins. In addition, former studies to evaluate flooding influence mainly targeted on small/urban scale runoff phenomena, water quality monitoring data including flooding condition on the watersheds with middle or large spatial scale (>1000km^2) is insufficient.

In this study, firstly we conducted high-frequency water quality observation in downstream of Kinokawa river in order to accumulate vital data to understand the system of nutrient runoff. River water was sampled manually once every three or four days at four observation points on bridges. Then we estimated relationships between water volume and TN/TP concentrations. Finally, by multiplying the river flow rates by estimated concentrations of TN and TP, we calculated the annual nutrient loads from the Kinokawa river basin.

2. STUDY AREA

Figure 1 shows the land use in 2014 and observation points to sample river water. The length of Kinokawa river is about 136km, total watershed area is about 1750km^2. The basin extends from east to west, and after passing through the mountainous area in the central massif of Kii peninsula, the river flows to the east and flows into the Seto Inland Sea. Majority of land use is forest (about 75%), followed by agricultural fields (farmland and rice paddy fields were 10% and 6%, respectively). Urbanized areas are concentrated downstream area, and the ratio of cities to the total is 9%. We conducted 80~90 times of water sampling from Musota bridge, Iwade bridge, Isaka bridge (across Kinokawa main river) and Kitajima bridge (across Kishi river, a large branch of Kinokawa river). In addition, we sampled water at the mouth of small canal and tributaries located between Musota and Iwade (1) ~ 4)) on 2018/6/15 in order to evaluate the influence of small water flows.

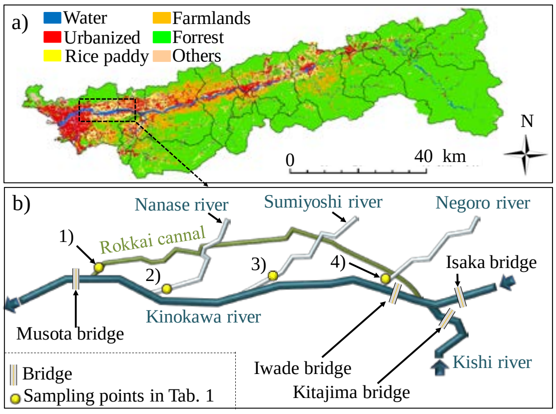

Fig. 1 a) Land use in Kinokawa river basin (Land Use Fragmented Mesh Data [6]). b) A thematic map indicated flow paths of Kinokawa main river and branches, canal, bridges and points we conducted water sampling. The numbers of sampling points were corresponding to ones of Tab.1.

3. METHODOLOGY

3.1 River Water Sampling

Samplings were performed by lowering tinplate bucket from center of Musota bridge, Iwade bridge, Isaka bridge and Kitajima bridge. Drowned water by the bucket was put in polyethylene bottle, immediately installed in a cooler and kept to cold. Here, temperature in the cooler was kept about 2 ~ 8 degrees Celsius. Sampled waters were chemically analyzed basically within 4 hours after sampling. In this article, we mainly analysed and discussed about nutrients concentrations observed at Musota and Iwade.

3.2 Measurement of TN and TP concentrations

Figure 2 shows equipment for chemical analysis to measure TN concentration and TP concentration. TN and TP concentrations were estimated by TNP-10 produced by TOA DKK [7]. TN concentration was measured based on peroxodisulfate 120°C decomposition method [8]. In this method, firstly all nitrogen compounds are replaced into nitrate ion. Secondly nitrate ion is reduced to nitrite ion. Then, sulfanilamide added into chemical sample is diazotized by nitrite ion. Finally, the absorbance of the red azo compound formed by adding N-1-naphthylethylenediamine to the sample is measured to estimate the concentration.

Fig. 2 Equipment for chemical analysis to measure Total Nitrogen (TN) concentration and Total Phosphorus (TP).

TP concentration was measured based on peroxodisulfate 120°C decomposition method [8]. Here, all phosphorus compounds are firstly oxidized to phosphate ion by added acidic reagent to the sample. Then a mixed solution of ammonium molybdate and ascorbic acid is added to the sample. Finally, the absorbance is measured to determine the concentration of TP. The detection limits for TN concentration and TP concentration in this device are 0.2 mg / L or more and 0.05 mg / L or more, respectively. Detected values below these limitations are untrustworthy.

3.3 Flow Rate Estimation

In this study, hourly river flow rate was estimated by using hourly time series data of water level and rating curves. hourly water level data observed at Funado (almost at the same place as Iwade) water level observation station has been provided by Japanese ministry of land, infrastructure, transport and tourism [8]. The rating curves at Funado station was also developed by the ministry, we used the curves directly. Note that the rating curves was optimized to estimate 2016's flow rate, the target period of this study was out of it. In addition, the scope to apply the curves was obviously stated, heavy flooding that water levels exceed 2.93m and strong drought with water levels below -1.25m were out of the applicable ranges. However, the rating curves were also applied in this study to calculate the flow rate under the un-applicable range because of no other way to estimate flow rate. Note that errors of flow rate under extreme storm/drought events could be large.

3.4 Estimation of Flow Rate - Concentration Relationship

We created regression lines of flow rate and TN/TP concentrations based on the assumption that there is a linear relationship between the flow rate at Funado and the TN and TP concentration at Iwade and Musota, respectively. Although this assumption might not appropriate for expression of nutrient runoff, we adopted it because of model simplification. This obvious weak point to express relationship between flow rate and nutrient concentrations should be discussed in future study. The reason why we used Musota's TP concentration data instead of Iwade's data here was because Musota had more data, and data on extreme phenomena such as floodings and droughts were also abundant.

3.5 Annual Pollutant Loads Estimation

Hourly TN and TP pollutant loads from Kinokawa river basin for the target period were calculated by multiplying the flow rate at Hunado by the nutrient concentrations estimated by the regression lines. Secondly, we created flow duration curves of flow rate, hourly loads of TN and TP. Then, in order to evaluate impacts of floodings in nutrient runoff phenomena quantitatively, we estimated TN load and TP load that runoff in the top 5% of the flow rate in the target period, and calculated the ratio of them in the all pollutant loads.

4. RESULTS AND DISCUSSION

4.1 Temporal Variation of TN, TP Concentrations

Figure 3 shows flow rate at Funado station and TN, TP concentrations of river water at Musota bridge and Iwade bridge from 2018/5/15 to 2019/6/10. Average TN concentrations for whole observation period at Musota and Iwade were 1.00 mg/L and 0.87 mg/L, respectively. Although TP was monitored simultaneously, TP concentrations were basically under detection limit. Therefore, we discussed about TN concentrations here.

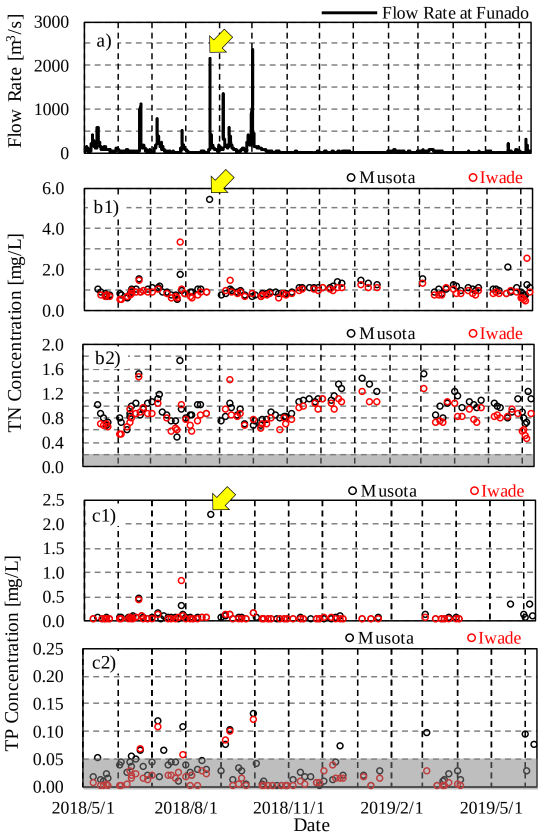

Fig. 3 a) Flow rate at Funado water level station, b1) & b2) TN concentrations observed at Musota bridge and Iwade bridge, c1) & c2) TP concentrations observed at Musota bridge and Iwade bridge. b2) & c2) are engaged figures of b1) and c1). Yellow arrow show observations on 2018/8/24. Grey masks in b2) and c2) show below of detectable range.

Fig.3 b2) indicates Musota's TN concentrations were chronically about 0.1~0.2 higher than Iwade's ones on the same date. This tendency implied the possibility that inflows with high TN from small tributaries or agricultural canal influenced total environment on Kinokawa river. Therefore, we conducted additional TN concentration observations at the mouths of these tributaries and canal. Fig. 1 also shows a map of tributaries/canal between Musota and Iwade. Table 1 shows TN concentrations observed at the mouth of each tributary or canal on 2018/6/15, which was sunny and in normal flow condition. The concentrations of TN at Musota and Iwade on June 15, 2018 were 0.98 mg/L and 0.79 mg/L, respectively. Although all TN concentrations of them were higher than ones of main Kinokawa river, Rokkai canal located at about 500 m upper Musota bridge was especially higher than the others. Therefore, inflow from Rokkai canal mainly could influence for Kinokawa river environment.

Table 1 TN concentrations observed at 1)Rokkai canal, 2)Nanase tributary, 3)Sumiyoshi tributary and 4)Negoro tributary. 1)~ 4) were sampled at the mouth of them on 2018/6/15.

	1)	2)	3)	4)
Sampling time	8:28	8:45	9:00	9:17
TN[mg/L]	2.00	1.27	1.48	1.76

Rokkai canal supplies water for rice paddies located in right bank of the Kinokawa Plain. The canal was opened only when irrigation period (2018/6/1~2018/9/30), no water flowed except this period. The upstream end of the irrigation canal is located about 500 m upstream of the Iwade Bridge, and it is designed that water of 4.96 m^3/s is always withdrawn from the Kinokawa river. Although actual and real time flow rate has not been confirmed, a portion of the water irrigated by the rice paddy fields will return to the canal and finally re-enter the Kino River at 1). Such hypothesis could be reasonable, however, it was difficult to prove them quantitatively due to the lack of TN observation data so far. In addition, since the discharge data of channel and tributaries are also insufficient either, additional observation of TN concentration and flow rate to assess of agricultural activities in the Kinokawa plains will be necessary.

Fig. 3 also shows that there were the data observed extremely high concentrations of TN and TP, such as 2018/8/24 (Yellow arraied points). High TN and TP concentrations were tended to be generated when flow rate at Funado were getting over 200m^3/s, which was equivalent to 3 times of average flow rate in target period (62.9m^3/s). Figure 4 shows relationships between flow rate at Funado and the concentrations. Because the number of TN concentration data was 90, we considered TN data could be analyzed statistically here. On the other hand, TP concentration data at Iwade whose values exceeded 0.05 mg/L (detection limit) were only two. Therefore, we utilized TP concentration data at Musota here, the number of Musota's TP was 13.

Although there was no obvious relationship between TN concentrations and the flow rate in calm condition (Flow rate < 100 m^3/s), we could confirm that the concentrations rises with increasing the flow rate when it got over 100 m^3/s. A coefficient of determination between TN and flow rate was calculated as 0.46, it was met the significance level of 5%. The increasing tendency of concentration with the increase of flow rate was much stronger in TP than TN. A coefficient of determination between TP and flow rate was as high as 0.97. However, this unnaturally high coefficient could be influenced by the extremely high concentration observed in August 24, 2018 (red circle in Fig. 4 b1)). In addition, the evaluation by calculating regression line, the value of segment became -0.081. A minus value in the segment can be inappropriate because negative concentration values could occur. Therefore, the coefficient excluding data observed on 2018/8/24 was also calculated, we obtained the value as 0.66, which was also significant met the significance level of 5%. This result indicated regression line of b2) was more reasonable than one of b1).

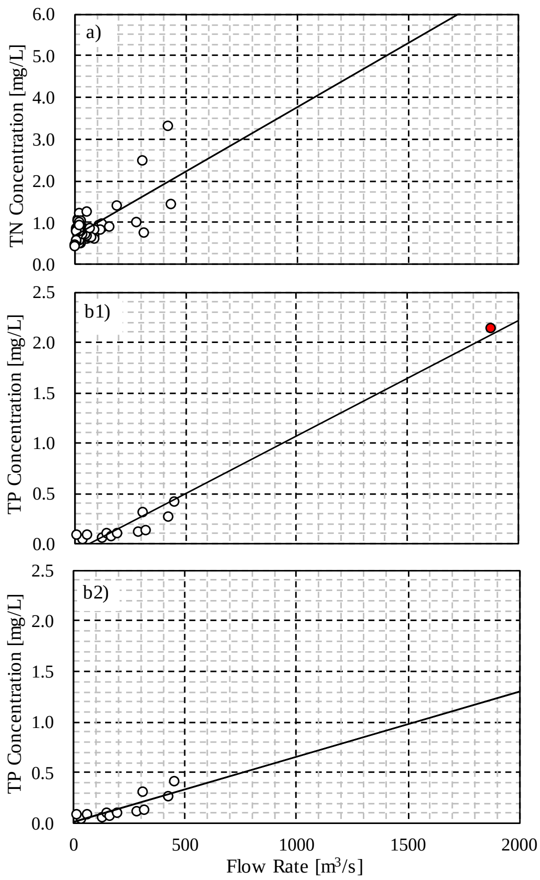

Fig. 4 a): Relationship between TN concentration at Iwade and flow rate at Funado. b1): Relationship between TP concentration at Musota and the flow rate. Although b2) also shows relationship between TP concentration and flow rate, extremely large value observed 2018/8/24 is excluded. Each figure has regression lines.

The tendency of this concentration rise could be considered caused by the increase in suspended solid in river water accompanying the increase in flow rate. Figure 5 shows pictures of sampled water at Musota bridges. The a) taken on 2018/8/24 under flooding condition, indicated that river water contained a large amount of suspended solid such as soil particles. The flow velocity at that time was large therefore these suspended solid was difficult to sink. Suspended solid have function as a nutrient carry, and it has been reported that this property in river water to be remarkable with phosphorus than nitrogen [10]. In order to evaluate an influence of suspended solid, suspended phosphorus and suspended nitrogen contained in river water during floods should be measured separately from TN and TP. This is a future issue.

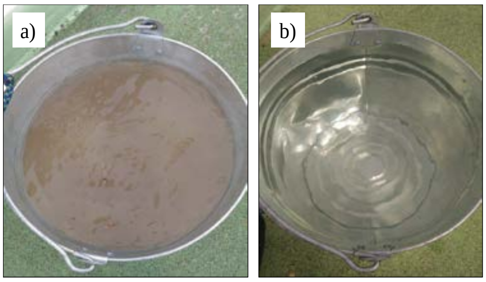

Fig. 5 a) River water under flooding condition sampled at Musota taken at 7:02 am, 2018/8/24. b) River water under calm condition sampled at Musota taken at 9:19 am, 2018/8/16.

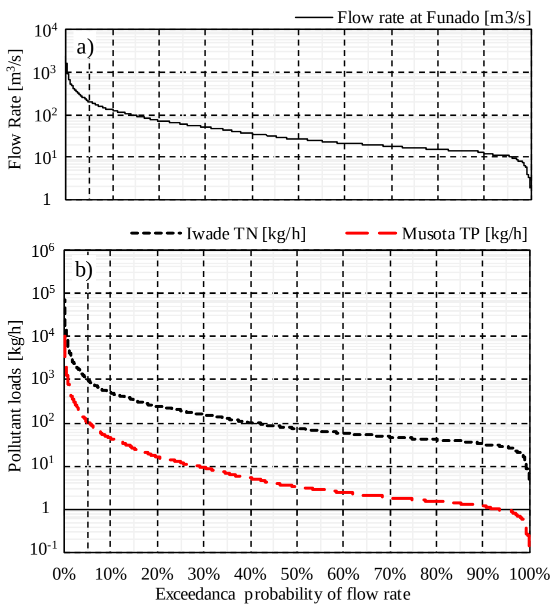

Fig. 6 Flow exceedance probabilities of a) flow rate, b) TN load and TP load.

Finally, we created regression lines between flow rate and concentrations. Note that regression line of TP was not one shown in b1) of fig.4 but one in b2) of fig.4 because of the reasonability.

Relationship between TN at Iwade and flow rate at Funado was expressed as follows;

$$C_{TN} = 0.0031Q + 0.687 \tag{1}$$

where C_{TN} and Q are TN concentration at Iwade and hourly flow rate at Funado, respectively. Then, the relationship between the TP at Musota and flow rate at Funado became as follows;

$$C_{TP} = 0.0006Q + 0.019 \tag{2}$$

where C_{TP} is TP concentration at Musota. Both segments in (1) and (2) were larger than 0, it is guaranteed that the concentration is 0 or more in these equations even if little flow rate.

4.2 Annual Pollutant Loads Estimation

Figure 6 shows flow duration curves of the flow rate and pollutant loads of TN and TP, whose vertical axis are logarithmic. Both TN load and TP load were calculated by multiplying flow rates with TN and TP concentrations which were obtained by equation (1) and (2), respectively. In other words, these load calculations used estimated concentrations obtained assuming a linear relationship with the flow rate, the load amounts in this study are, as a result, proportional to the square of the flow rate. By analysis of fig.6, TN load and TP load were about 150 kg/h and 15 kg/h when the flow rate was 100m^3/s whose excess probability was 10%. In addition, as excess probability of the flow rate decreased from 10%, the TN load and TP load increased rapidly. Although equations to estimate pollutant loads have obvious limitation caused by assumption of a linear relationship between concentration and flow rate, it was strongly implied floodings had great influences in total environments of the Kinokawa river and the ocean. By a comparison TN with TP, in addition, the rapid increase in loads associated with floodings were more pronounced in TP than in TN, which was consistent with the characteristic that phosphorus was more likely to flow out as suspended solid.

Table 2 Total amount of annual TN, TP loads, the summed loads generated top 5% excess probability of flow rate, and ratios of Sum of top 5% / annual total loads.

	TN load	TP load
Annual total [t]	3263.6	408.4
Sum of top 5% [t]	2019.9	326.7
Ratio [%]	64.6	80.0

Tab.2 shows the annual equivalent of TN and TP loads calculated by using fig.6. The annual equivalent of TN load was about 3300[t], and the sum of TN load on the flooding (included top 5% excess probability of flow rate) was 2100[t]. This result indicated that 65% of TN load runoff in the flooding condition. Sum of TP loads on the flooding was 326[t], which was equivalent to 80% of total annual TP runoff. These results suggest that accurate prediction of huge nutrient discharge during floods will be essential for quantitative assessment of nutrient discharge from the basin.

5. CONCLUSION

In this study, we conducted high-frequency water quality observation especially TN and TP aiming at quantitative evaluation of water pollutant loads from Kinokawa river basin. Results of the analysis based on TN and TP concentrations, flow rate of Kinokawa river and pollutant loads provided following considerations. (1) TN concentrations at Musota was chronically higher than ones of Iwade. It was shown that an agricultural canal flowing into Kinokawa main river influenced for environments of the main river although the scale of flow volume of the canal was much smaller than the main river. In order to understand this impacts, it will be necessary to accumulate quantitative data of flow rate and TN concentration of the canal. (2) In flooding condition, TN and TP concentrations in the river water rapidly increased. It might be caused by increase of nitrogen and phosphorus attached suspended solid under flooding condition. (3) Almost all TN and TP loads were runoff in flooding whose flow rate were over 5 % flow exceedance provability. It was strongly suggested an accurate understanding of the nutrient discharge mechanism during floodings were essential for understanding the nutrient discharge phenomenon to the sea area.

Finally, we stress the limitations of this research and discuss some remaining future issues. It should be emphasized that river water quantity in heavy flooding and strong drought condition might include large errors because of out of scope of H-Q equations. Especially there was a possibility the results of this study might be affected, if the estimated flood flow rate contained large errors. In addition, in calculation of the annual runoff loads of TN and TP, we made the strong assumption that these concentrations are linearly related to the flow rate for simplifying the models. Further work is necessary to investigate how the approach can be improved in this respect.

6. ACKNOWLEDGMENTS

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