EVALUATION OF ANNUAL LOADINGS OF MAJOR IONIC SPECIES AND NUTRIENTS IN FORESTED WATERSHED, JAPAN

*Komai, Y.[1], Umemoto, S.[1], Inoue, T.[2], Imai, A.[3]

[1]Hyogo Prefectural Institute of Public Health and Environmental Sciences, 3-1-27 Yukihiracho Suma Kobe, 654 0037,Japan
[2]Department of Civil Engineering, Gifu Univ., 1-1 Yanagido Gifu, 501-1193, Japan
[3]National Institute for Environmental Studies, 16-2 Onogawa Tsukuba, 305-0053, Japan
[1]Yukio_komai@pref.hyogo.jp, [1]satoshi_umemoto@pref.hyogo.jp, [2]tinoue@cc-tut.gifu.ac.jp, [3]aimai@nies.go.jp

ABSTRACT
Water samples, including all rain events, gathered using an automatic water sampling system that we developed, in addition to a regular sampling once a week were taken in order to determine the reliable annual loadings in a forested watershed in Hyogo, Japan. The reliable specific loadings of nutrients, major ionic species, TOC, and SS were calculated. The specific material loadings by the regular sampling method were estimated less than their reliable loadings. The estimation of annual loadings varied widely according to sampling frequency, when the number of samplings was gradually decreased from once a week to once a month. The regression model, which is a combination of R-Q method and L-Q method, is capable of estimating the runoff loadings of major ionic species during rain events. On the other hand, the regression model sometimes results in overestimation, which ranges about two and three hundred percent, for runoff loadings of TOC, T-P, and T-N. These results suggest that we should consider an error with an approximate magnitude of error of at least two times when we evaluate specific annual loadings of TOC, T-P, and T-N in a forested watershed.
..

KEYWORDS: Nutrients, major ionic species, annual loadings, automatic sampling system, regular sampling, forested watershed

INTRODUCTION
The annual loadings of nutrients, major ionic species, and pollutants from streams in forested watersheds, which are non-point sources in Japan, have been estimated by using results based on a regular sampling taken once a week to once a month in many cases. However, it has been pointed out that a large number of water samplings, including those taken during rain events, are important in the evaluation of the annual loadings of materials from a watershed. Investigations which do not include samplings obtained during rain events would result in an underestimation of annual material loadings. Although the investigations that involve a large number of water samplings have increased recently, actually it is very difficult to take water samples during all rain events throughout a year. Some regression models such as the L-Q method (e.g., Ebise, 1984) or L-R method (Kunimatsu and Sudo,1997) have been used. It is important to reliably determine annual loadings and to evaluate whether or not these estimated values are in the allowable range. Although it is necessary to know the evaluation standard for predicting models or the relationship between sampling frequency and estimation values for annual loadings in a forested watershed, high frequency investigations intended for a forested watershed have been rarely carried out. Due to the availability of an automatic water sampling system to take water samples according to each hydrograph during many kinds of rain events, we performed an investigation in combination with a regular sampling once a week. The reliable annual loadings of nutrients, major ionic species, SS, and TOC were calculated the by using data obtained during a year by the both the automatic water sampling system and by means of a regular investigation.

METHODS
Study site
The investigation was carried out at the end point of a mountain stream in a forested watershed (5.8km^2) in Hyogo, Japan, between April 2001 and April 2002. The location map is shown in Figure1. The annual precipitation was 1869 mm and the average annual precipitation was 1820 mm for six years from April 1996 to April 2002. The details of climate, topography, geology, soil, and vegetation are described in former papers (Komai et al., 2001, Umemoto et al., 2001). Rain events occurred 43 times, with precipitation amounts ranging from several mm/day to about 100 mm/day during the investigation period.

Sampling and analytical methods
The water samples were collected by the automatic water sampling system, which consists of an automatic sampler (ISCO6700), a rain gauge, a water level meter, and a data logger, according to each hydrograph (Komai et al., 2002). In addition, a regular investigation was conducted once a week, usually on a Monday, Sunday or Tuesday if it was impossible. The discharges were calculated using the H-Q equation based on the relationship of water depth and discharge, which we had previously measured. Major ionic species, suspended solids (SS), total organic carbon (TOC), total nitrogen (T-N), and total phosphorus (T-P) were analyzed. These analytical methods are shown in Table 1. The annual loadings of these parameters were calculated using the data of both type of investigation.

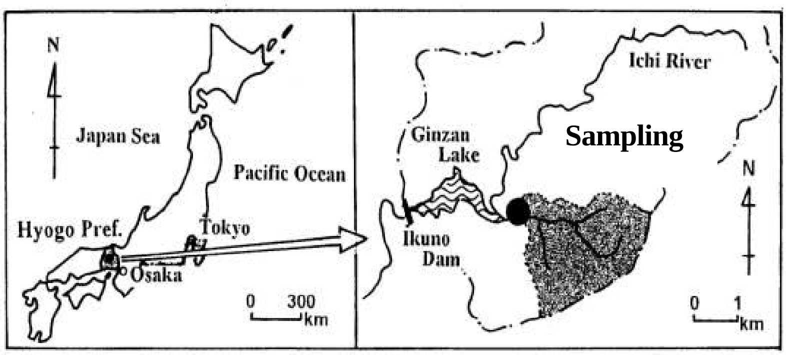

Figure 1 Study site and Sampling station

Table 1 Analytical method

Item	Analytical method
Major ionic species	Calculation from the value of NO_3^- measured by ion
SS	Glass fiber filter paper method (Whatman GF/C•j
TOC	TOC analyzer (Shimadzu TOC-5000A•j method
T-P	Ascorbic acid reduction-molybdenum blue absorptiometry after potassium peroxodisulfate decommposition
T-N	UV Absorptiometry after potassium peroxodisulfate-sodium hydroxide decomposition

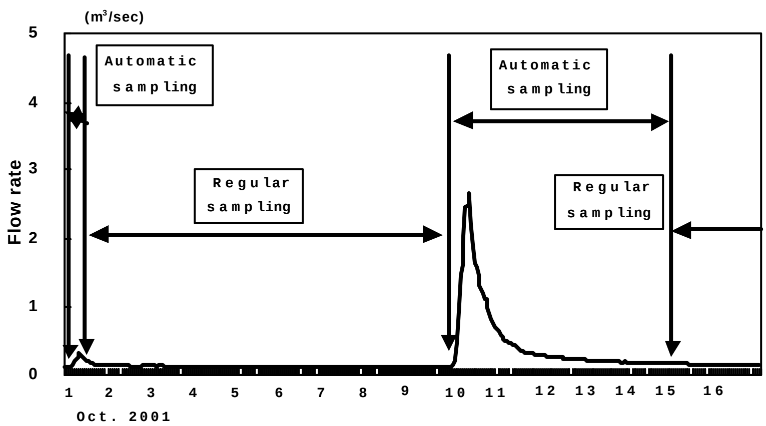

Figure 2 An example of automatic and regular sampling in hydrograph

All data was arranged in time series as shown in Figure 2. The specific loadings (L_{Ri}) of a material during a year was calculated using the following equation of Kunimatsu et al (1997). The annual loadings based on the results of a regular sampling once a week was also calculated by using the same equation.

$$L_{Ri} = \sum_{i=1}^{i=n} \left[C_i Q_i \left(t_i - t_{i-1} + t_{i+1} t_i \right) / 2 \right] \qquad (1)$$

where C_i and Q_i were the concentration and the discharge, respectively, measured at time t_i.

Precipitation - Discharge equations (R-Q equation) were derived by the linear regression of the relationship between the precipitation and the discharge, using the measurement data of the four rain events. The result is shown in Figure 3.

$$Q = aRi + b \qquad (2)$$

where Q_i and R_i were the discharge and the precipitation, respectively, and a and b the coefficients of the equation.

Loadings-Discharge equations (L-Q equation) were derived by the logarithmic linear regression of the relationship between the discharge and loadings, using the data measuring the four rain events.

$$L_i = aQ_i^{\,b} \qquad (3)$$

where L_i and Q were the loadings and the discharge, respectively, and a and b the coefficients of the equation. Precipitation less than 11 mm/day was neglected, because it did not result in an increase in discharge. The relationship between discharge and T-N loadings as an example is shown in Figure 4(Komai et al, 2000, Umemoto, 2002).

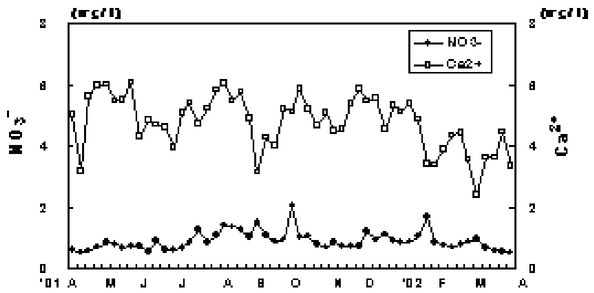

Figure 3 Relationship between precipitation and discharge in rain events

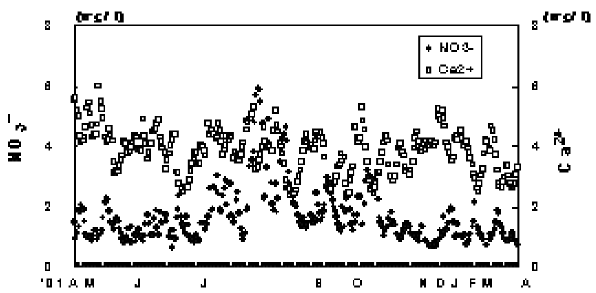

Figure 4 Relationship between dischargeand loading of T-N in rain events

Water depth was not measured in one rain event and water samples were not taken in two rain events because of a shutdown of the data logger and the automatic water sampler due to a brownout. We employed the data calculated using equation (2) and/or (3) for four rain events.

RESULTS AND DISCUSSION

Change of concentrations of material

The changes of NO_3^- and Ca^{2+} concentrations are shown in Figure 5 and 6, respectively. The concentrations of major ionic species, except for NO_3^- in the regular sampling and in the case of the samplings during rain events varied within a similar scale. However, NO_3^-, T-N, T-P, and TOC showed little change in concentration, except for some cases connected with rain events, in a regular sampling method. The concentrations of NO_3^-, T-N, T-P, and TOC, including all rain events throughout a year, indicated that the concentrations were larger than those taken using the regular sampling method. Especially, SS was less than 0.1 mg/l in the regular investigation and showed a large change in the concentration between 0.1mg/l to 132mg/l during rain events.

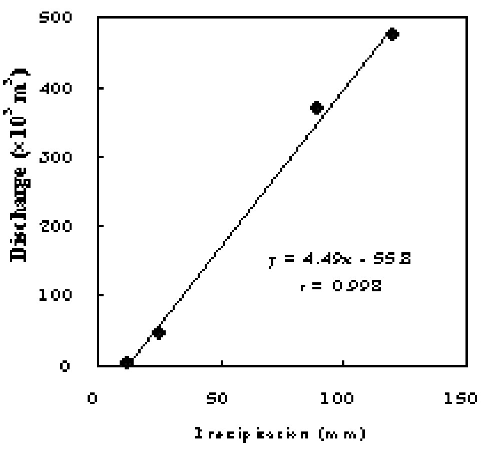

Figure 5 the changes of NO_3^- and Ca^{2+} concent rations in a regular investigation

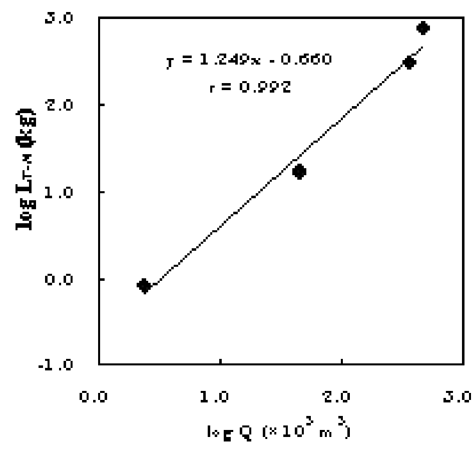

Figure 6 the changes of NO_3^- and Ca^{2+} concentrations during rain events

Evaluation of annual loadings

The reliable annual loadings, which are estimations including both the results of a regular investigation and rain events, and annual loadings determined using only the regular investigation method are shown in Table 2. Ratio of estimated annual loadings to the reliable annual loadings is shown in Table 3. The annual loadings of major ionic species of all material estimated by a regular investigation of once a month (B) were smaller than the reliable annual loadings (A), while the B/A ratios ranged between 1.1 and 1.2. On the other hand, the B/A ratios of NO_3^-, T-N, T-P, and TOC ranged between 1.7 and 3.0. The increase of NO_3^- concentrations in streams may be caused by the prompt subsurface runoff in the direct runoff from surface layer of soil. T-N and TOC may be related to both dissolved and particulate matter. T-P shows the close relationship with SS (Umemoto,2002).

Table 2 Comparison between the reliable and estimated annual loadings

	Specific discharge	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	SS	TOC	T-P	T-N
Regression Model (R-Q,L-Q equation) (A)	1.2	1.3	1.1	1.2	1.2	•\	1.2	1.1	1.1	5.7	1.7	2.3	1.6
Regular Investigation +Rain Event (B)	1.0	1.0	1.0	1.0	1.0	•\	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Regular Investigation(C)	0.8	0.9	0.6	0.8	0.9	•\	0.8	0.8	0.8	0.0	0.7	0.3	0.5

Table 3 Ratio of estimated annual loadings to the reliable annual loadings

		Specific discharge (10^3xm^3/da	Cl^- (kg/ha/year)	NO_3^- (kg/ha/year)	SO_4^{2-} (kg/ha/year)	Na^+ (kg/ha/year)	NH_4^+ (kg/ha/year)	K^+ (kg/ha/year)	Mg^{2+} (kg/ha/year)	Ca^{2+} (kg/ha/year)
Regression Model (R-Q,L-Q equation) (A)	Fine days	11.6	15.2	4.4	17.2	13.1	0.0	2.7	3.1	18.7
	Rainy days	19.5	25.7	7.0	29.1	22.9	0.0	4.7	5.2	32.0
	Total	31.1	40.9	11.4	46.3	36.0	0.1	7.3	8.3	50.7
Regular Investigation +Rain Event (B)	Fine days	11.6	15.2	4.4	17.2	13.1	0.0	2.7	3.1	18.7
	Rainy days	20.5	22.9	11.2	27.3	21.2	0.2	4.7	5.1	32.3
	Total	32.1	38.1	15.6	44.5	34.3	0.2	7.4	8.1	51.1
Regular Investigation(C)		26.2	33.5	9.7	37.8	29.5	•\	6.1	6.7	40.9

		SS (kg/ha/year)	TOC (kg/ha/year)	T-P (kg/ha/year)	T-N (kg/ha/year)
Regression Model (R-Q,L-Q equation) (A)	Fine days	0.0	5.0	0.02	1.2
	Rainy days	123	17.4	0.27	5.3
	Total	123	22.4	0.30	6.4
Regular Investigation +Rain Event (B)	Fine days	0.0	5.0	0.02	1.2
	Rainy days	23.0	12.1	0.12	3.7
	Total	23.0	17.1	0.15	4.9
Regular Investigation(C)		0.0	11.8	0.05	2.6

Precipitation input and stream water output are shown in Figure 4. The reliable annual specific discharge is 31.6x10^3 m^3/day, comprising 62 % of the precipitation in the watershed during the period of investigation. This runoff ratio is the standard value in the temperate area of Japan. The annual specific discharge as determined regular investigation is 26.0x10^3 m^3/day and the runoff ratio is 56 %.

Table 4 Precipitation input and stream water output

Precipitation:1,869mm (April 2001•`March 2002)			
Annual input	Regular Investigation +Rain	Regular Investigation	Regression Model (R-Q,L-Q equation)
	18690m^3/ha/year	18690m^3/ha/year	18690m^3/ha/year
Annual output	11350m^3/ha/year	9560m^3/ha/year	11900m^3/ha/year
Output/Input	61%	51%	64%

The underestimated specific discharge is related to specific material loadings. As it rains once every four days on average in Japan, the regular sampling performed by a weekly investigation would result in underestimation. The ratios of specific discharge and loadings in fine days and those of rainy days are shown in Table 2. Fine days include all days except for the days sampled by the automatic sampling system, while rainy days include extra days. All results indicate that the samplings performed on rainy days comprised 70 to 80 % of the reliable specific discharge and loadings. This result emphasizes the importance of the investigation method that includes rain events.

Relationship between the annual loadings and number of sampling in a regular investigation

The specific discharge and specific loadings of materials results in which sampling frequency in a regular investigation was changed from once a week to once a month are shown in Table 5. In addition, the specific material loadings of materials were calculated in two cases which used the monthly sampling, where weekly samplings was chosen random throughout a month or fixed in the first week. We gradually decreased the number of samplings from once a week to once a month, and thus the estimation of annual loadings varied widely according to the sampling frequency. For example, the specific loadings of Ca^{2+} in the sampling once every other week was 36.4 kg/ha/year and 45.0 kg/ha/year, respectively. In the case of sampling once a month, these ranged between 32.4 kg/ha/year and 47.2 kg/ha/year. The ratio of maximum to minimum values was up to 1.5. The ratio of each value to the reliable specific loadings ranged 0.6 and 1.1. The major ionic species except for NO_3^- showed the same tendency. The specific loadings of NO_3^- in the sampling once every other week was 7 kg/ha/year and 12.3 kg/ha/year, respectively. In the case of sampling once a month, these ranged between 5.4 kg/ha/year and 14.9 kg/ha/year. The ratio of maximum to minimum values was up to 2.6. The ratio of each value to the reliable specific loadings ranged between 0.4 and 1.0. Those of TOC, T-P, and T-N showed a tendency similar to that of NO_3^-.

Table 5 Changes of specific discharge and loadings due to number of samplings

Annual loadings		Specific Discharge ($10^3 \times m^3$/ha/day)	Cl^- (kg/ha/year)	NO_3^- (kg/ha/year)	SO_4^{2-} (kg/ha/year)	Na^+ (kg/ha/year)	NH_4^+ (kg/ha/year)	K^+ (kg/ha/year)	Mg^{2+} (kg/ha/year)	Ca^{2+} (kg/ha/year)
A		32.1	38.1	15.6	44.5	34.3	-	7.40	8.11	51.1
B		26.2	33.5	9.7	37.8	29.5	-	6.05	6.74	40.9
C	1	30.7	39.2	12.3	43.2	33.5	-	6.99	7.52	45.0
	2	21.5	27.6	7.0	32.0	25.4	-	5.08	5.91	36.4
D	1	38.0	48.4	15.6	52.7	40.2	-	8.33	9.01	54.2
	2	20.6	26.5	6.8	30.7	24.3	-	4.96	5.61	33.6
	3	20.6	26.5	7.2	30.6	24.5	-	5.02	5.71	35.6
E	1	31.7	39.3	10.3	42.9	34.5	-	7.09	7.29	43.8
	2	18.8	24.5	5.7	28.3	22.5	-	4.49	5.23	32.4
	3	30.6	40.1	14.9	44.7	33.2	-	7.05	7.90	47.2
	4	24.3	30.7	8.3	35.8	28.3	-	5.69	6.61	40.6
F	once a month at randam	23.9	30.5	8.6	34.8	27.7	-	5.61	6.46	39.8
	the first week in a month	29.5	36.6	11.3	41.2	32.0	-	6.56	6.96	41.2

Annual loadings		SS (kg/ha/year)	TOC (kg/ha/year)	T-P (kg/ha/year)	T-N (kg/ha/year)
A		23.0	17.1	0.147	4.87
B		0	11.1	0.050	2.58
C	1	0	13.3	0.062	3.37
	2	0	8.9	0.037	1.72
D	1	0	17.7	0.081	4.42
	2	0	8.1	0.034	1.69
	3	0	8.1	0.037	1.71
E	1	0	11.4	0.050	3.25
	2	0	7.3	0.031	1.45
	3	0	15.8	0.077	3.64
	4	0	10.5	0.044	2.01
F	once a month at randam	0	11.3	0.041	2.03
	the first week in a month	0	12.6	0.051	2.56

A: the actual measurement, B-F: estimate by regular investigation; B: once a week, C: once every other week, D: triweekly, E: once a month, F: once a month
Figures in C-E show the difference of start week

These items did not show any overestimation. These results suggest that specific discharge and specific material loadings fluctuate by a factor of more than two according to the number of samplings or sampling weeks in a month, and that the specific loadings of most items are underestimated in regular investigation by not including rain events despite of number of samplings, and thus the estimation of annual loadings varied widely according to the sampling frequency.

Comparison between the reliable specific loadings and the specific loadings by a regression models

In order to estimate the material loadings during rain events, we performed calculations using both the R-Q equation and the L-Q equation as a regression model. The first, discharge was calculated for daily precipitation by using equation (2), and then daily loadings were calculated for daily discharge by using equation (3). All results were shown as specific discharge and loadings in Table 2. The ratios of specific loadings by the regression model (R-Q and L-Q equations) to the reliable specific material loadings were about 1.1 to 1.3 for specific discharge and major ionic species, and 1.6 to 2.3 for T-N, TOC, and T-P, and notably 5.7 for SS. Although only four rain events a year were investigated for designing the regression model, the specific discharge and specific loadings of major ionic species by the regression model coincide very closely with the reliable values. On the other hand, the results of four items showed overestimation. We used daily precipitation to calculate the specific discharge; however, each actual rainfall pattern, that is, the intensity or continuity of rainfall during a rain event, is very different. This means that the runoff loadings of SS, T-N, TOC, and T-P may differ for each rain event, even if daily precipitation is the same. As amounts of SS may be associated with this rainfall pattern, and

T-N, TOC, and T-P relate to SS, estimation error may be larger than the major ionic species. These results show that the regression model is capable of estimating the specific loadings of major ionic species.

CONCLUSIONS

The reliable loadings of nutrients, major ionic species, TOC, and SS in a forested watershed provide a standard of evaluation for models designed to predict annual loadings in a forested watershed. The estimation of annual loadings varied widely according to the sampling frequency, so it is necessary to take water samples once a week according to the regular investigation method, even though the calculated values show underestimation. The regression model, which is the combination of the R-Q method and the L-Q method, is capable of estimating the runoff loadings of major ionic species during rain events. On the other hand, the regression model produces overestimation, ranging about two and three times larger, for runoff loadings of TOC, T-P and T-N. These results suggest that we should consider an error with an approximate magnitude of error of at least two times when we evaluate specific annual loadings of TOC, T-P, and T-N in a forested watershed.

ACKNOWLEDGEMENT

This research was supported in part by the River Environment Fund (REF) in charge of River and Watershed Environment Management (FOREM), Japan.

REFERENCES

Ebise,S.(1984).Regression models for estimating of storm runoff loading: *Proc. of Environ. & Sani.Eng.Res.*,**20**,27-38 (in Japanese).

Kunimatsu,T. and Sudo,M. (1997). Measurement and evaluation of nutrient runoff loads from mountainous forested lands:*J. Jpn. Soc. Water Environ.*, **20**(12), 810-815 (in Japanese).

Komai,Y., Umemoto S. and Inoue T.(2000b). Estimation for amount of annual runoff of major ionic species by regression model in forested watershed: *Proc. of 1st World Cong. of Int. Water Assoc.*,CD-ROM NP149.

Komai,Y., Umemoto S. and Inoue T.(2001) Runoff characteristics of major ionic species during rain events in forested watershed, *Water Science and Technology*, **44**, 420-426.

Umemoto,S., Komai,Y. and Inoue T.(2001) Runoff Characteristics of Nutrients in the Forest Streams in Hyogo Prefecture, Japan, *Water Science and Technology*, 44,359-450.

Umemoto,S.(2002) Study on the Runoff Characteristics of Pollutants from Non-point Source- In case of the Mountainous Forested Areas in Hyogo Prefecture-, doctoral thesis,

Komai,Y., Umemoto S. and Inoue T (2002) Application of Automatic Sampling and Measurement System to Mountainous Stream Investigation during Rain Events, *Water Science and Technology*, **45**, 213-218.