TEMPORAL VARIATIONS OF POLLUTANT LOADS DURING STORM EVENTS IN A SMALL RIVER BASIN

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ABSTRACT

Not only to estimate the impact of storm water on receiving waters but also to deduce the origin of the pollutants, it is important to analyze the runoff characteristics of pollutants during storm events. We conducted seven surveys during storm events to clarify the runoff characteristics of various pollutants and relationships between pollutant loads and runoff patterns. In addition, origins of various ions were deduced by examining the temporal variations of ion composition. Typical first flush effects in VSS and T-BOD concentrations were observed, and it was estimated that river sediments deposited in fine days strongly affect the runoff of VSS during a storm event. NO_3^- -N concentration decreased by the early runoff, but kept up higher level at the recession stage, while ion concentrations decreased during the rising stage and increased again at the recession stage, indicating that ions were diluted by the major runoff. Relationships between pollutant loads and runoff were examined by the empirical equation " $L/A = a (Q/A)^n$ ". Judging from the n values, ash, SS, VSS, NH_4^+ -N and TP were easily flushed out during storm events, while TN, DN, NO_3^- -N, K^+ and DOC kept almost constant concentration during a storm event. Most ions seemed to be diluted by storm water. It was indicated that NO_3^- , SO_4^{2-} and K^+ were mainly originated from diffuse sources during storm events in the surveyed watershed, while Mg^{2+} and Na^+ was from the same source as Cl^- . Most of the nitrate and sulfate loads seemed to be drained out from the surface soil layer of river basins and carried by subsurface runoff.

KEYWORDS

First flush effect, Ion composition, Pollutant loads, Small river basin, Storm events, Temporal variation,

INTRODUCTION

Pollutant loading from the storm water runoff has been identified as one of the major causes of deterioration of the quality of receiving water bodies. Runoff characteristics of pollutants differ widely, depending on their origin and runoff behavior in transit. Therefore, analysis of the characteristics is important not only to estimate the impact of storm water on receiving waters but also to deduce the origin of the pollutants. Patrick *et al.* (Patrick *et al.*, 2002) characterized stormwater runoff loads and concentrations of 10 common constituents and analyzed effects of season and land use. They also propose the predictive models of stormwater runoff volumes, loads and pollutant concentrations from watershed. Ana (Ana, 1998) analyzed evidence for the existence and nature of the first flush load of pollution input into drainage systems, using data of storm surface runoff. Ralf (Ralf, 2001) clarified rainfall-induced sediment and pesticide input from orchards into a river. Gregory *et al.* (Gregory *et al.*, 2005) estimated the fraction of organisms associated with settleable particles in stormwater. Many other researchers (Rimer *et al.* 1978; Ebise *et al.*, 1982; Lee *et al.*, 2000) have investigated the pollutant loads for many constituents during storm events. We also clarified the runoff characteristics of pollutants during a rising stage of the river flow precisely with many water quality indices observed in a small river basin through principal component analysis (Fujiwara *et al.*, 2002). In many previous works, however, only a few water quality indices were observed during stormwater runoff and few researchers analyzed the change in ion composition during storm events to deduce the origins of those.

This study aims to clarify the runoff characteristics of various pollutants during storm events and relationships between pollutant loads and runoff patterns, and to analyze the first flush effect. In addition, origins of various ions are deduced by examining the temporal variations of ion composition. Seven storm events were surveyed in a small river basin during the period from October 2000 to November 2003. Flow rate and 29 water quality indices such as biochemical oxygen demand (BOD), suspended solids (SS), volatile suspended solids (VSS), total nitrogen (TN), nitrate nitrogen (NO_3^- -N), SO_4^{2-} , Na^+ , Cl^- , among others, were observed for the analysis of storm water runoff.

MATERIALS AND METHODS

Site description

Fig.1 shows the Uji River basin investigated in this study. The river is a tributary of Niyodo River and is located in Ino town, the central part of Kochi prefecture, Japan. The area of watershed is 14.7 km^2 and the mainstream length is 7.5 km. Forests, residential districts and agricultural fields account for 76%, 13% and 11% of the watershed, respectively. Residential districts shown as the shaded portion in **Fig.1** are located around the junction of Uji River and Tenjindani River, and around the downstream area of Saina River. Paddy fields, the dotted portion in the figure, are located around the midstream area of Uji River and around the junction of Uji River and Niyodo River. There are many pulp factories around the downstream area of Saina River, and the wastewater from the factories is discharged into Saina River. The wastewater has high concentration of particulate organic compounds but low concentrations of nitrogen, phosphorus, and ions. According to our periodical observations once a week or two weeks from June 7 to December 13 in 2000, the average T-BOD concentration at Ekiminami of Saina River was as high as 10mg/L. In addition, the average T-BOD loading at the same point was 24.5% of that at Sunagamori about 400m downstream from junction of Uji River and Saina River. Domestic sewage except night soil is directly discharged into the rivers in most areas of the watershed. A lot of particulate organic compounds are expected to be deposited in fine days due to not only the slow flow velocity of the river, but the high concentration of particulate organic compounds in effluent from factories or residential districts. These river sediments seem to be flushed out during storm events.

Fig.1 Surveying watershed

Sampling and analysis

Seven storm events were surveyed at Sunagmaori shown in **Fig.1** from October 2000 to December 2003. Duration and hydrological condition in each survey are listed in **Table 1**. Total precipitation during the survey ranged from 15mm to 186mm and the preceding precipitation in the 2nd survey was as much as 160 mm/10days. Both the rising stage and the recession stage of the river flow were observed except the 1st survey. In the 3rd and 4th survey, the authors surveyed the second and the third storm event out of the series of three storm events.

Sampling was conducted at approximately 15-60 minutes intervals for rising flow stage and 1- 24h intervals for recession flow stage. The samples were transported to the laboratory and filtered through 1 μ m glass fiber filters (Whatman GF/B). The water quality indices analyzed are summarized in **Table 2**. Water temperature (W.T.), pH, DO, ORP, EC were measured on site. The other analyses were performed in

Table 1 Characteristics of each survey

Number of the survey	Duration of the survey	Precipitation during the survey	Sum of the preceding precipitation	Remarks
1	Oct.9 th 10:00–24:00 (2000)	75 mm	65 mm/10days	During the rising stage
2	Oct.16 th 2:00 – Oct.17 th 20:00 (2001)	105 mm	160 mm/10days	
3	Sep.15 th 14:00 – Sep.16 th 5:00 (2002)	21 mm	16 mm/10days	2 nd storm out of the series of 3 storm events
4	Sep.16 th 6:00 – Sep.17 th 20:00 (2002)	33 mm	37 mm/10days	
5	Apr.29 th 18:00 – May.2 th 12:00 (2003)	15 mm	40 mm/10days	3 rd storm out of the series of 3 storm events
6	July 17 th 23:00 – July 21 st 9:00 (2003)	95 mm	64 mm/10days	
7	Nov. 27 th 16:00 – Dec. 5 th 11:00 (2003)	186 mm	24 mm/10days	

Table 2 Water quality indices and their analytical methods

Index	Unit	Method
W.T.	°C	EC Meter (TOA, CM-21P)
pH	-	pH Meter (TOA, HM-12P)
DO	mg/L	Membrane electrode method (*4500O-G) (TOA, DO-21P)
ORP	mV	Oxidation-Reduction Potential measurement in clean water (*2580 B) (TOA, HM-14P)
EC	mS/m	EC Meter (TOA, CM-21P)
SS	mg/L	Total suspended solids dried at 103-105°C (*2540 D) Filters of 1.0 μ m nominal pore size (Whatman GF/B) were used.
Ash	mg/L	3 -hr ignition at 400°C of a filter used for determination of SS.
VSS	mg/L	Difference between SS and Ash
T, D-BOD	mg/L	5-Day BOD Test (*5210-B)
TOC, DOC	mgC/L	High-temperature combustion method (*5310-B) (Shimazu TOC-5000A)
TN, DN	mgN/L	Persulfate method (4500-N C) and automated cadmium reduction method (*4500-NO ₃ -F) (Bran+Luebbe AACS II)
NO ₃ ⁻ -N	mgN/L	Automated cadmium reduction method (*4500-NO ₃ -F) (Bran+Luebbe AACS II)
NO ₂ ⁻ -N	mgN/L	Colorimetric method (*4500 NO ₂ -B) (Bran+Luebbe AACS II)
NH ₄ ⁺ -N	mgN/L	Automated phenate method (*4500-NH ₃ -G) (Bran+Luebbe AACS II)
TP, DP	mgP/L	Persulfate digestion and automated ascorbic acid reduction method (*4500-P F) (Bran+Luebbe AACS II)
PO ₄ ³⁻ -P	mgP/L	Automated ascorbic acid reduction method (*4500-P F) (Bran+Luebbe AACS II)
Na ⁺ , K ⁺	mg/L	Determination of cations by Ion Chromatography (Dionex DX-120)
Ca ²⁺ , Mg ²⁺	mg/L	Cation separator column: Dionex CS12A, Eluent solution: 20mM methanesulfonic acid
Cl ⁻ , SO ₄ ²⁻	mg/L	Determination of anions by Ion Chromatography (*4110) (DionexDX-120)
F ⁻ , Br ⁻	mg/L	Anion separator column: Dionex AS12A, Eluent solution: 2.7mM Na ₂ CO ₃ /0.3mM NaHCO ₃
HCO ₃ ⁻	mg/L	Equivalent by alkalinity, Alkalinity: Titration method (*2320 B)

Analytical methods are numbered in Standard Methods for the examination of water and wastewater.

the laboratory in accordance with the official methods (APHA, AWWA and WEF; 1998). T-BOD, TOC, T-N and T-P were analyzed with samples which were not filtered. The other indices were determined with samples after filtration.

RESULTS AND DISCUSSIONS

Temporal variations of water quality

The results for the 2nd and 7th survey are shown in **Fig.2** and **Fig.3** to give examples of the surveys. The concentration peaks for VSS and T-BOD, which occurs before the flow peak, was caused by the early runoff, flushing the pollutants accumulated in fine days from the riverbed. It was noted from the curbs of **Fig.3** that typical first flush effects in concentrations, which has been observed by other investigators (Rimer *et al.*, 1978; Lee *et al.*, 1996, Lee *et al.*, 2000), occurred for storm events. The peak concentrations of VSS and T-BOD at 1:30 on November 28th in 2003, were as high as 50.5mg/L and 24.2mg/L, respectively. River flow rate at the time was 0.55m³/s and precipitation just before the concentration peaks was 11mm/3hrs. On the other hand, sharp concentration peaks were not observed during the 2nd survey as shown in **Fig.2**. Although river flow rate of 0.93m³/s at the concentration peak and precipitation of 9mm/3hrs just before the peak were nearly the same with those in 7th survey, the peak concentrations of VSS and T-BOD were as low as 11.8mg/L and 6.0mg/L, respectively. Because the preceding precipitation was much more in the 2nd survey, most of the deposited pollutants in fine days seemed to have been flushed out during that precipitation. Similarly, low peak concentrations (VSS=13.5mg/L and T-BOD=4.3mg/L) were observed in the 4th survey in which the third storm out of the series of three storm events was surveyed. Most of the pollutants were judged to have flushed out in the first and second storm events. Except for the 2nd and 4th survey, sharp concentration peaks were observed in all surveys and measured peak of VSS and T-BOD concentration ranged from 14.9mg/L to 62.8mg/L and from 8.5mg/L to 28mg/L, respectively.

Fig.2 Time courses of precipitation, flow rate and water quality (2nd survey)

Fig.3 Time courses of precipitation, flow rate and water quality (7th survey)

Fig.4 relationships between specific loading and specific flow rate (7th survey)

Fig.5 regression coefficient of n for each constituent

Fig.6 relationship between n value for VSS and preceding precipitation

NO₃⁻-N concentration decreased by the early runoff, but gradually increased and kept up higher level at the recession stage. Other researcher also observed these phenomena (Ebise *et al.*, 1982). Ion concentrations decreased during the rising stage and increased again at the recession stage, indicating that ions were diluted by the major runoff.

Relationships between pollutant load and flow rate

Relationships between pollutant loads and runoff are examined by the following empirical equation.

$$L/A = a (Q/A)^n \quad (1)$$

In which L is pollutant load (g/s), A is watershed area (km²), Q is river flow rate (m³/s) and a and n are regression coefficients. Fig.4 shows the relationships between the load and runoff for selected constituents in the 7th survey. Because typical first flush effects were observed in T-BOD concentration, the regression line has poor agreement for T-BOD. The regression lines for most constituents such as NO₃⁻-N, Cl⁻ and SO₄²⁻ have good agreement as shown in the figure. Generally, runoff characteristics of pollutants are evaluated by the regression coefficient of n as shown below.

$n > 1$: flushing

$n = 1$: constant concentration

$n < 1$: dilution

Fig.5 demonstrates the runoff characteristics of each constituent. If coefficient of determination for the regression line is less than 0.7, the authors omit the regression coefficients from this analysis. Four and six out of seven coefficients are omitted for VSS and T-BOD, respectively, because of the first flush effect. As shown in **Fig.5**, the average values of n for ash, SS, VSS, $\text{NH}_4^+\text{-N}$ and TP are more than 1.5, indicating that these constituents are easily flushed out during storm events. **Fig.6** shows the relationship between n value for VSS and preceding precipitation. As shown in the figure, the more preceding precipitation becomes, the lower n value is calculated. This result implies that river sediments deposited in fine days strongly affect the runoff of VSS during a storm event. **Fig.5** also shows that the average values of n for TN, DN, $\text{NO}_3^-\text{-N}$, K^+ and DOC are around 1.0. This result indicates that these constituents keep almost constant concentration during a storm event. Most ions seem to be diluted by storm water. The averages of n value for Cl^- and Na^+ are as low as 0.71 and 0.68, respectively. This result indicates that these ions are strongly affected by point sources such as domestic sewage. The fact that domestic sewage except night soil is directly discharged into the rivers in most areas of the watershed supports this deduction.

Temporal variations of ion composition

Temporal variations of ion composition during storm events are examined. **Fig.7** and **Fig.8** show relationships between flow rate and ion composition in 2nd and 7th survey, respectively. As shown in the figures, both $\text{NO}_3^-/\text{Cl}^-$ and $\text{SO}_4^{2-}/\text{Cl}^-$ equivalent ratio rose with the increase of flow rate, while Na^+/Cl^- equivalent ratio kept nearly constant during storm events. As mentioned above, Cl^- seems to be strongly affected by point sources such as domestic sewage. Therefore, this result indicates that NO_3^- and SO_4^{2-} are mainly originated from diffuse sources during storm events in the surveyed watershed, while Na^+ is from point sources. These figures also demonstrate that $\text{NO}_3^-/\text{Cl}^-$ and $\text{SO}_4^{2-}/\text{Cl}^-$ equivalent ratio during recession stage are higher than those during rising stage. This fact implies that most of the nitrate and sulfate loads

Fig.7 Relationships between flow rate and ion composition (2nd survey)

Fig.8 Relationships between flow rate and ion composition (7th survey)

Fig.9 RPI for various ions

Fig.10 Relationships between RPI and total precipitation

are drained out from the surface soil layer of river basins and carried by subsurface runoff.

To analyze the change in ion composition accompanied with the increase of flow rate, the following index is defined.

$$RPI = ([A]/[Cl])_p / ([A]/[Cl])_i \quad (2)$$

Where, $[A]$ is the concentration of ion "A" (meq/L), $[Cl]$ is the Cl^- concentration (meq/L), $([A]/[Cl])_p$ and $([A]/[Cl])_i$ are $[A]/[Cl]$ ratio at the flow peak and at the initial condition, respectively. **Fig.9** gives the RPI for various ions. This result indicates that NO_3^- and K^+ are strongly affected by diffuse sources during storm events in the surveyed watershed, while Mg^{2+} and Na^+ are mainly discharged by the same source as Cl^- . **Fig.10** shows the relationships between RPI and total precipitation. RPI for NO_3^-/Cl^- and SO_4^{2-}/Cl^- increase with total precipitation, while RPI for Na^+/Cl^- keeps almost 1 for all storm events. This result supports the deduction for the origins of these ions mentioned above.

CONCLUSIONS

Seven storm events were surveyed in a small river basin to clarify the runoff characteristics of various pollutants during storm events and relationships between pollutant loads and runoff patterns. In addition, origins of various ions were deduced by examining the temporal variations of ion composition. The following results are obtained:

- (1) Except for the 2nd and 4th survey in which most of the pollutants had been flushed out from the riverbed during the preceding precipitation, sharp concentration peaks of VSS and T-BOD were observed in all surveys and the measured peak concentration ranged from 14.9mg/L to 62.8mg/L and from 8.5mg/L to 28mg/L, respectively.
- (2) NO_3^- -N concentration decreased by the early runoff, but gradually increased and kept up higher level at the recession stage. Ion concentrations decreased during the rising stage and increased again at the recession stage, indicating that ions were diluted by the major runoff.
- (3) Relationships between pollutant loads and runoff were examined by the empirical equation " $L/A = a(Q/A)^n$ ". Judging from the n values, ash, SS, VSS, NH_4^+ -N and TP were easily flushed out during storm events, while TN, DN, NO_3^- -N, K^+ and DOC kept almost constant concentration during a storm event. Most ions seemed to be diluted by storm water.
- (4) The more preceding precipitation became, the lower n value for VSS was calculated. Hence, it was estimated that river sediments deposited in fine days strongly affected the runoff of VSS during a storm event.
- (5) Origins of various ions were deduced by examining the temporal variations of ion composition. As a result, it was indicated that NO_3^- , SO_4^{2-} and K^+ were mainly originated from diffuse sources during storm events in the surveyed watershed, while Mg^{2+} and Na^+ was from the same source as Cl^- . In addition, most of the nitrate and sulfate loads seemed to be drained out from the surface soil layer of river basins and carried by subsurface runoff.

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REFERENCES

- Ana Deletic (1998). The first flush load of urban surface runoff, *Water Research*, **32** (8), 2462-2470
- Ebise S., Muraoka K. and Otubo K. (1982). Separation of run-off components by water quality, *Proceedings of the 26th Japanese conference on Hydraulics*, **21**, 279-284
- Fujiwara T., Ohtoshi K., Ishikawa R. and Ikebe M. (2002). Runoff characteristics of pollutants from a small river basin during a rising stage of river flow, *Advances in Asian Environmental Engineering*, **2** (2), 1-7
- Lee J. H., Bang K. W. and Lee J. K. (1996). A study of runoff characteristics of pollutants in combined sewer overflow. *J. Korean Soc. Environ. Eng.* 18(10), 1147-1160
- Lee J. H. and Bang K. W. (2000). Characterization of urban stormwater runoff, *Water Research*, **34** (6), 1773-1780.
- Patrick L. B. and Teresa H. S. (2002). Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA, *Water Research*, **36** (7), 1743-1757
- Ralf Schulz (2001). Rainfall-induced sediment and pesticide input from orchards into the lourens river, western cape, south africa: importance of a single event, *Water Research*, **35** (8), 1869-1876
- Rimer A. E., *et al.* (1978). Characterization and impact of storm water runoff from various land cover types. *J. Water Pollut. Control Fed.*, 252-264
- Standard Methods for Examination of Water and Wastewater* (1998). 20th edition, American Public Health Association / American Water Works Association / Water Environment Federation, Washington DC, USA.