Jour. Korean For. Soc. Vol. 96, No. 5, pp. 561~566 (2007)

JOURNAL OF KOREAN FOREST SOCIETY

Hydrograph Separation using Geochemical tracers by Three-Component Mixing Model for the Coniferous Forested Catchment in Gwangneung Gyeonggido, Republic of Korea

Kyongha Kim* and Jae-Yun Yoo

Department of Forest Environment, Korea Forest Research Institute, Seoul 130-712, Korea

Abstract : This study was conducted to clarify runoff production processes in forested catchment through hydrograph separation using three-component mixing model based on the End Member Mixing Analysis (EMMA) model. The study area is located in the coniferous-forested experimental catchment, Gwangneung Gyeonggido near Seoul, Korea (N 37 45', E 127 09'). This catchment is covered by *Pinus Korainensis* and *Abies holophylla* planted at stocking rate of 3,000 trees ha^{-1} in 1976. Thinning and pruning were carried out two times in the spring of 1996 and 2004 respectively. We monitored 8 successive events during the periods from June 15 to September 15, 2005. Throughfall, soil water and groundwater were sampled by the bulk sampler. Stream water was sampled every 2-hour through ISCO automatic sampler for 48 hours. The geochemical tracers were determined in the result of principal components analysis. The concentrations of SO_4^{2-} and Na^+ for stream water almost were distributed within the bivariate plot of the end members; throughfall, soil water and groundwater. Average contributions of throughfall, soil water and groundwater on producing stream flow for 8 events were 17%, 25% and 58% respectively. The amount of antecedent precipitation (AAP) plays an important role in determining which end members prevail during the event. It was found that ground water contributed more to produce storm runoff in the event of a small AAP compared with the event of a large AAP. On the other hand, rain water showed opposite tendency to ground water. Rain water in storm runoff may be produced by saturation overland flow occurring in the areas where soil moisture content is near saturation. AAP controls the producing mechanism for storm runoff whether surface or subsurface flow prevails.

Key words *: hydrograph separation, EMMA model, geochemical tracer, coniferous forest catchment, antecedent precipitation index*

Introduction

Forest hydrology deals with flow paths and runoff components in a forested catchment. Understanding on flow paths and runoff components plays an important role in predicting water quantities and qualities of stream flow water in mountainous landscape (Christophersen *et al.*, 1990; Hooper, 2001; Kim *et al.*, 2006). Studies on the runoff component by hydrograph separation have dealt with several kinds of tracers such as a stable isotope (i.e. ^{18}O and ^{2}H) and a radioactive isotope (i.e. ^{3}H) and a geochemical element (i.e. Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, Cl^- and Br^-) (Hooper *et al.*, 1990; Bazemore *et al.*, 1994; Buttle, 1994).

The analysis of storm runoff chemical patterns has become a tool to infer flow path contributions of pre-event and event water components. As a result, the research on tracers to identify pathways of water in the catchment has been conducted. Pinder and Jones (1969) introduced the basic hydrograph separation technique based on a mass balance approach. This two-component model has been applied widely and it can be expanded to three-component model in cases where either the discharge of one of the components was known or two tracers were used simultaneously (Genereux *et al.* 1993).

Two-component mixing model is powerful tools for the study of hydrological processes at the catchment scale. Nevertheless the validation of the assumptions of the two-component model has been often questioned because conditions required for the application of these models are not satisfied essentially. More precisely, the pre-event water presents a large spatial variability. The limitations of two-component mixing models have resulted in attempts to extend geochemical hydrograph separation to three components using multiple environ-

*Corresponding author
E-mail: KKYHA@foa.go.kr

mental tracers (Joerin *et al.*, 2002).

Christophersen *et al.* (1990) and Hooper *et al.* (1990) introduced a prediction method to evaluate proportions of contributing sources, on the assumption that stream water quality can be predicted as a mixture of subsurface sources (e.g. ground water and soil water). These sources are called end-members, and the chemical compositions of each end-member form limiting values in the stream water (Elsenbeer *et al.*, 1995). Therefore End Member Mixing Analysis (EMMA) model has been used to estimate contributions of end-members (or components).

The identification of flow sources and pathways using tracers in forest lands of Korea has been started only a few years ago. In their pioneering work, Kim and Jeong (2002) investigated the contribution of new and old water in the stream depending on forest types including the natural-mature deciduous and two planted-young coniferous forests through the two-component mixing model using electrical conductivity (EC) as a natural chemical tracer. They concluded that the hydrograph separation technique using two-component mixing model is useful for searching a fingerprint of hydrological component, and EC served as a good tracer. Kim *et al.*, (2006) also tested the EMMA model in the coniferous forest catchment, and showed that three components including groundwater, soil water and throughfall contribute to the formation of stream flow. They also suggested that chloride-nitrate ion may serve the most suitable tracer for the three-component mixing analysis using the EMMA model in the coniferous forest catchment.

These studies have been continued now, and the results clearly suggest that natural geochemical tracers such as Na^+, SO_4^{2-}, Ca^{2+} and Acid Neutralizing Capacity (ANC) were useful to the three-component mixing analysis, and Na^+ concentration was especially meaningful in the all sampled events (Yoo *et al.*, 2006). Joerin *et al.*, (2002) analyzed uncertainty in hydrograph separations using a three-component mixing model based on SiO_2 and Ca^{2+} concentrations as geochemical tracers. Inamdar and Mitchell (2007) separated the sources of runoff such as throughfall, groundwater discharged at hillslope seeps and valley-bottom riparian water using end member mixing analysis (EMMA). They used Si and DOC concentrations.

Therefore, as a follow-up study of hydrograph separation using the EMMA model for the coniferous forest catchment in Korea, we have tested the effectiveness and consistency of using SO_4^{2-} and Na^+ concentration as geochemical tracers on the three-component mixing analysis to identify flow paths and separate hydrographs in this study, and evaluate factors effecting significantly in variations of the contributions of runoff components.

Material and Mathods

1. Site description

This study was performed in the coniferous experimental catchment (13.6 ha; Figure 1), located on Gwangneung experiment forest (N 37° 45, E 127° 09), Gyeonggi-do near Seoul metropolitan, Korea. This coniferous forest of *Pinus Korainensis* and *Abies holophylla* was planted at stocking rate of 3,000 stems ha^{-1} in 1976. Thinning and pruning were carried out two times in the spring of 1996 and 2004. The altitude of the experimental catchment ranges from 160 m to 290 m. The slope shows from 13° to 35°. The underlying bedrock consists of gneiss and the soil texture is classified as sandy loam.

2. Methods of sampling and chemical analysis

Stream flow level was measured every 10 minutes

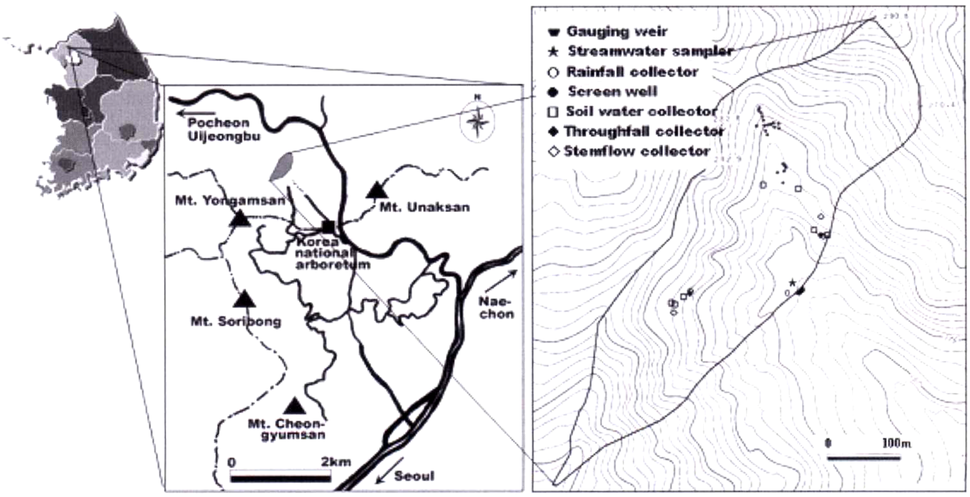

Figure 1. Location and topography of the experimental catchment in Gwangneung, Gyeonggi-do.

using the float-encoder water level gauge (OTT, Thalimedes) at the catchment outlet with a 120° V-notch sharp crest weir. Rainfall was recorded at 10 minutes interval in the weighing rain gauge (OTT, Pluvio) with a data logger. Stream water samples were collected automatically at 2 hours interval during event (ISCO, 6712FR). Groundwater was sampled directly from screen well (depth 0.5~1.0m) with 10 cm diameter, periodically. Groundwater level was measured at every 10 minutes by ground water level gauge (Van Essen, DI-241). Soil water was collected by zero tension lysimeters in the soil depth 10~15 cm on hillslope. The samples of throughfall water take from automatic wet-deposit sampler (Sin-il, SL12001). All water samples obtained from the stream, screen well, lysimeters and wet-deposit sampler were analyzed in the laboratory, immediately. Concentrations of cations and anions were determined with ion chromatography (Anion, Sykam, DE/S-135; Cation, Dionex, DX-320 IC System).

3. Three-component mixing model

Three-component mixing models are used to separate runoff components in stream flow water. In this study, SO_4^{2-} and Na^+ concentration data of throughfall, soil water, ground water and stream flow were applied to three-component mixing model through mass balance equation 1, 2 and 3.

$$f_a + f_b + f_c = 1 \quad (1)$$

$$C1_a f_a + C1_b f_b + C1_c f_c = C_{st} \quad (2)$$

$$C2_a f_a + C2_b f_b + C2_c f_c = C_{st} \quad (3)$$

where, the subscript *a, b* and *c* refer to the runoff components, *f* is the contribution of each runoff component, *C*1 *and C*2 are the tracer concentrations and the subscript *st* refers to the streamflow.

Several conditions must be met for this three-component mixing model: (1) Tracer concentrations of each component must be significantly different, (2) there are only three components contributing to streamflow, and (3) the tracer compositions of each component are constant for the duration of the event, or variation is known from measurements (Elsenbeer *et al.*, 1995; Liu *et al.*, 2004).

Results and Discussion

1. Hydrological responses

8 rainfall events were sampled to apply the mixing model from June 15 to September 15, 2005. Table 1 shows the hydrological characteristics of the sample events. The amount of rainfall for each event ranged from 7.2 mm for the event 3 to 147.2 mm for the event 2. Runoff rates were calculated from 10.1% as minimum value to 51.0% as maximum one. Intuitively, the amount of antecedent precipitation (AAP) affects the runoff rate. For instance, the event 2, which had the amount of rainfall of 147.2 mm and AAP for 10-day of 1.3 mm, was less one fifth times in the runoff rate than the event 4, which had the amount of rainfall of 105.6 mm and AAP for 10-day of 169.1 mm. Peak flow showed the same tendency to the runoff rate as the peak flows of the event 2 and 4 were 0.16 and 1.28 mm for 10 minutes. It seems to be caused that there is big difference of soil water storage between two events. High soil moisture content may be easy to produce saturated overland flow in the catchment.

2. Temporal variations of water quantity and quality

Figure 2 represents the temporal changes of rainfall, runoff, ground water level and tracer concentration for each event. The ground water level generally responded to runoff concurrently in all events. Especially groundwater level in the event 4 reached to land surface at the peak flow period. It affords an illustration of a great contribution of saturated overland flow on stream flow during the event 4.

The concentration of Na^+ decreased suddenly from a rising limb to peak flow and resumed slowly in a recession limb of the hydrographs. It indicates that Na^+ controlled geologically shows a very good dilution response with increasing runoff. Na^+ enriches to pre-event con-

Table 1. Hydrological characteristics of the sampled events.

	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7	Event 8
Observed period	15~17, Jun.	26~28, Jun.	29~30, Jun.	1~2, Jul.	3~5, Jul.	9~10, Jul.	24~26, Aug.	13~15, Sep.
Precipitation (mm)	11.7	147.2	7.2	105.6	33.6	40.6	83.5	85.5
Maximum rainfall intensity (mm/10 min)	5.6	11.1	2.1	17.7	2.4	2.5	4.5	7.5
AAP for 5-day (mm)	0.2	0.0	154.7	161.9	120.3	1.3	1.5	7.0
AAP for 10-day (mm)	12.4	1.3	154.7	161.9	267.5	154.3	19.5	7.0
Total runoff (mm)	1.4	14.9	3.0	51.0	17.1	9.1	16.8	14.1
Peak flow (mm/10 min)	0.01	0.16	0.02	1.28	0.09	0.05	0.10	0.11
Runoff rate (%)	11.9	10.1	41.1	48.3	51.0	22.3	20.1	16.5

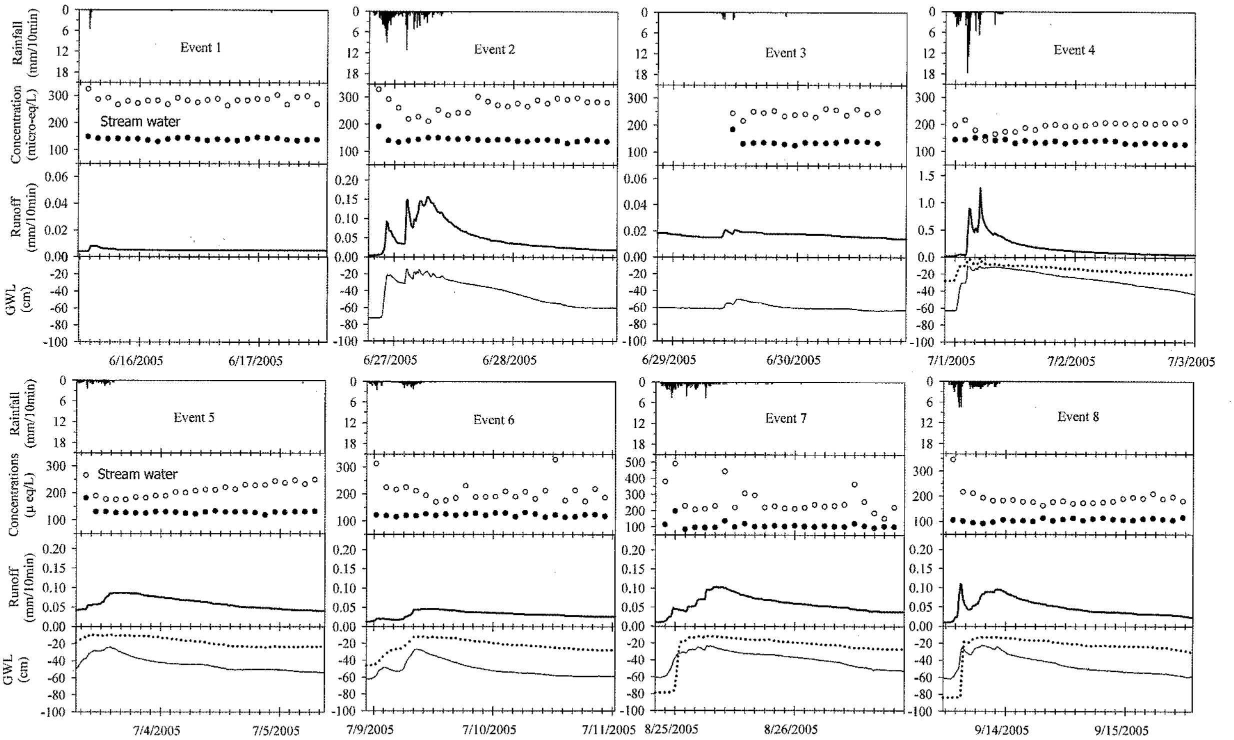

Figure 2. The temporal changes of ion concentrations, rainfall, stream discharge and ground water level (GWL) for a period of storm runoff. closed circles (●) : SO_4^{2-} conc. in the stream water, open circles (○) : Na^+ conc. in the stream water, solid line (–) : well No.7, doted line (···) : well No.22.

centration as groundwater flow was prevailing after peak flow (Caissie *et al.*, 1996). However, the concentration of SO_4^{2-} showed little changes in comparisons of Na^+ because it usually was released from a soil column.

3. Hydrograph separation using three-component mixing model

Figure 3 shows the bivariate plot for SO_4^{2-} and Na^+ for stream water and the end members during the events.

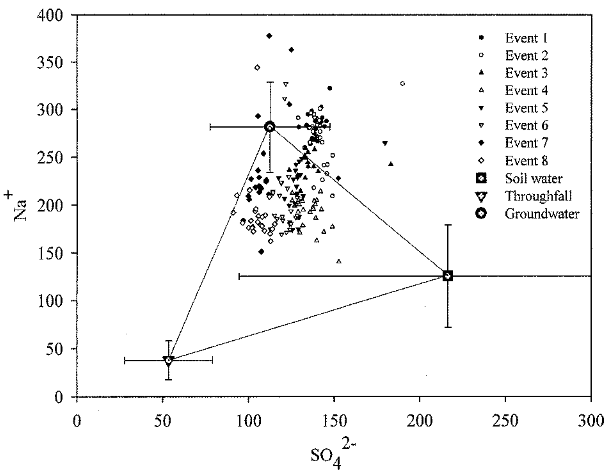

Figure 3. Bivariate plot for SO_4^{2-} and Na^+ for throughfall, soil water, ground water and stream water. The bars represent standard deviation.

The concentrations of those for stream water almost distributed within the plot of the end members including throughfall, soil water and groundwater during the events. SO_4^{2-} and Na^+ were suitable as the natural tracer as shown in the figure. Average contributions of throughfall, soil water and groundwater on producing stream flow were 17%, 25% and 58% respectively. The amount of antecedent precipitation (AAP) plays an important role in determining which end member prevails during events. There was a big difference of APP between the event 2 and 4 in table 1. It found that the event 2 of small AAP produced more ground water compared with the event 4 of large one. On the other hand, throughfall in the event 4 contributed on producing runoff much more than that in the event 2. That may be caused by saturation overland flow producing in areas where soil water content is near saturation. In the event 2, much rainfall infiltrated and stored in soil resulted in runoff rate less than 10%, while the event 4 showed higher runoff rate in 48%.

Figure 4 showed the results of hydrograph separation using three-component mixing model for 4 events; 2, 4, 7 and 8. The early stage in the event 2 only produced ground water but the event 4 did throughfall and soil water. Resultantly AAP controls producing mechanism of storm runoff whether surface or subsurface flow prevails in the catchment scale.

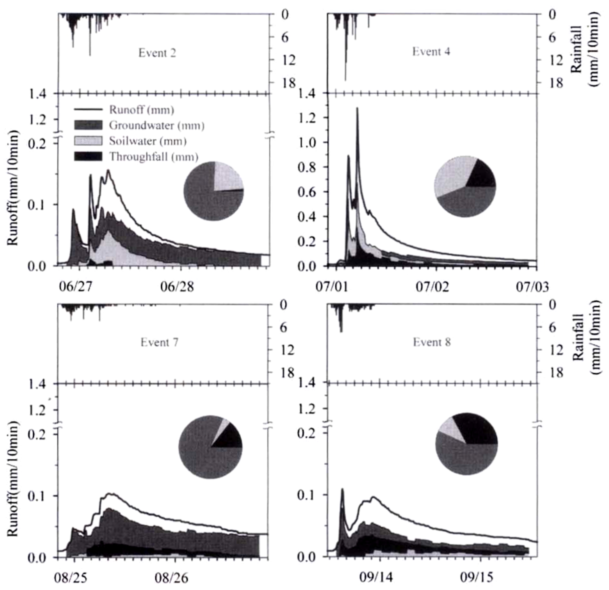

Figure 4. Three-component hydrograph separation of catchment runoff for event 2, 4, 7 and 8. Pie charts represent the relative proportions of throughfall, soil water and groundwater in the stream waters.

Conclusion

Hydrological processes on producing mechanism of storm runoff in a forested catchment have been studied since 1960s. Hydrograph separation techniques are useful tools for information on producing mechanism of storm runoff. We separated hydrographs using SO_4^{2-} and Na^+ as a geochemical tracer and end-member mixing model. Hydrograph separation can supply valuable information on the hydrological processes of storm runoff in a forested catchment. 8 sample events during the four months from June 15 to September 15, 2005 showed very different situations of partitioning end members; throughfall, soil water and ground water. It may be suggest that all events of this study experienced different hydrological situations. In particular, the amount of antecedent precipitation (AAP) plays an important role in partitioning of end members; throughfall, soil water and ground water. In general, high the amount of antecedent precipitation may cause high contribution of rain water. It may be due to saturated overland flow where soil moisture content or ground water level was high. High proportion of rain water may cause to land surface erosion and high turbidity of stream flow.

Literature Cited

1. Buttle, J.M. 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Progress in Physical Geography 18(1): 16-41.
2. Bazemore, D.E., K.N. Eshleman and K.J. Hollenbeck. 1994. The role of soil water in stormflow generation in a forested headwater catchment: synthesis of natural tracer and hydrometric evidence. Journal of Hydrology 162: 47-75.
3. Caissie, D., T.L. Pollock and R.A. Cunjak. 1996. Variation in stream water chemistry and hydrograph separation in a small drainage basin. Journal of Hydrology 178: 137-157.
4. Christophersen, N., C. Neal., R.P. Hooper., R.D. Vogt and S. Andersen. 1990. Modeling streamwater chemistry as a mixture of soil water end-members-A step towards second generation acidification models. Journal of Hydrology 116: 307-320.
5. Elsenbeer, H., D. Lorieri and M. Bonell. 1995. Mixing model approaches to estimate storm flow sources in an overland flow-dominated tropical rain forest catchment. Water Resources Research 31(9): 2267-2278.
6. Genereux, D.P., H.F. Hemond and P.J. Mulholland. 1993. Use of radon 222 and calcium as tracers in al three-end-member mixing model for streamflow generation on the West Fork of Walker Branch watershed. Journal of Hydrology 142: 167-211.
7. Hooper, R.P. 2001. Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. Hydrological Processes 15: 2039-2050.
8. Hooper, R.P., N. Christophersen and N.E. Peters. 1990. Modeling streamwater chemistry as a mixture of soil water end-members - An application to the Panola Mountain catchment, Georgia, USA. Journal of Hydrology 116: 321-343.
9. Inamdar S.P. and M.J. Mitchell. 2007. Contributions of riparian and hillslope waters to storm runoff across multiple catchments and storm events in a glaciated forested watershed. Journal of Hydrology doi: 10.1016/j.jhydrolo.2007.05.007.
10. Joerin, C., K.J. Beven, I. Iorgulescu and A. Musy. 2002. Uncertainty in hydrograph separations based on geochemical mixing models. Journal of Hydrology 255: 90-106.
11. Kim, K. and Y.H. Jeong. 2002. Hydrograph separations using the two-component mixing model with electrical conductivity as a chemical tracer in the three small forested catchments. Journal of Korean Forestry Society 91(5): 624-631.
12. Kim, K., J.Y. Yoo, J.H. Jun, H.T. Choi and Y.H. Jeong. 2006. Hydrograph Separation by using EMMA model for the Coniferous Forest Catchment in Gwangneung Gyeonggido, Republic of Korea (I)-Determination of the End Members and Tracers-Journal of Korean Forestry Society 95(5): 556-561.
13. Liu, F., M.W. Williams and N. Caine. 2004. Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. Water Resources Research 40(9): W09401, doi:10.1029/2004WR003076. 1-16.

14. Pinder, G.F. and J.F. Jones. 1969. Determination of the groundwater component of peak discharge from the chemistry of total runoff water. Water Resources Research 5(2): 438-445.
15. Sueker, J.K., J.N. Ryan, C. Kendall and R.D. Jarrett. 2000. Determination of hydrologic pathways during snowmelt for alpine/subalpine basins, Rocky Mountain National Park, Colorado. Water Resources Research 36(1): 63-75.
16. Yoo, J.Y, K. Kim, J.H. Jun, H.T. Choi and Y.H. Jeong. 2006. Searching the natural tracers for separation of runoff components in a small forested catchment. J. Korean Env. Res. & Reveg. Tech. 9(4): 52-59.

(Received July 10, 2007; Accepted July 27, 2007)