Study on relationship between spatial variability in streamwater characteristics and catchment scale in forested headwaters

(森林流域における渓流水の流量・水質の空間分布と集水面積との関係に関する研究)

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Chapter 1

Introduction

1.1 Scale issues in catchment hydrology

Fresh water is a key resource for human health, prosperity, and security. It is as essential to sustainable development as it is to life (UNESCO International Hydrological Programme VII). In arid and semi-arid areas, severe droughts often affect the livelihoods of many people, and the prediction of discharge in low-flow conditions is important in ensuring a stable supply of drinking water. In countries with large amounts of precipitation, such as Japan, heavy rainfall can lead to landslide disasters that sometimes claim lives and have large economic impacts (Japan Statistical Year Book, 2013). Thus, the prediction and prevention of such disasters based on an understanding of hydrological processes are important (Onda *et al*., 2001; Kosugi *et al*., 2006). With regard to water chemistry, nutrient concentrations must be monitored and controlled to protect drinking-water supplies and prevent the eutrophication of lakes and the sea (Ryther and Dunstan, 1971; Schindler, 1974; Diaz and Rosenberg, 2008; Conley *et al*., 2009). Heavy metal contamination, for example, has resulted in serious environmental pollution of watercourses (Kudo and Miyahara, 1991; Rai, 2008).

Many studies have investigated hydrological processes to determine the quantity and quality of fresh water required to meet social demands. In the 1930s, pioneer studies investigated rainfall infiltration into the soil layer (Horton, 1933; 1936). In the 1960s and 1970s, the variable source area concept was proposed and verified in actual catchments (e.g., Tsukamoto, 1963; Hewlett and Hibbert, 1967; Dunne and Black, 1970). Since the 1980s, piezometric methods and chemical tracer techniques have revealed more details of hydrological processes. Pipe flow, for example, has been identified from the rapid hydrograph responses following storm events (e.g., Tsukamoto and Ohta, 1988; McDonnell, 1990; Peters *et al*., 1995). Some studies have shown that the bedrock beneath soil layers is not perfectly impermeable and has a large influence on the discharge rate, water chemistry, and water residence time (Mulholland, 1993; Anderson *et al*., 1997; Burns *et al*., 1998; Asano *et al*., 2002; Uchida *et al*., 2003).

These process studies have greatly advanced our knowledge and have significantly contributed to the development of rainfall-runoff modeling (Beven and Kirkby, 1979; Abbott *et al*., 1986). However, hydrological processes have also been found to vary widely among catchments (Sharma *et al*., 1980; Huff *et al*., 1982). The heterogeneity among small catchments, including variations in soil, topography, geology, and climate, contributes to the variability in hydrological processes (Beven *et al*., 1988; Sivapalan, 2003; McDonnell *et al*., 2007). In addition, some studies have noted a change in the dominant hydrological processes with an increase in the size of the catchment area (Blöschl, 2001). For example, some studies have reported that bedrock groundwater discharge increases with the size of catchment area (Brown *et al*., 1999; Shaman *et al*., 2004). Therefore, we cannot simply extrapolate the hydrological processes, hydrological models, and model parameters obtained from small-scale catchments to larger catchments, when accurate predictions are needed for practical applications (Sivapalan, 2003). Methods are needed to treat heterogeneity and scale up hydrological processes in small catchments to larger scale catchments (Sivapalan *et al*., 2003; Bonell *et al*., 2006).

1.2 Previous studies of scale issues

Many researches have used inter-site comparisons to study the relationships between hydrological processes and environmental factors, such as soil (Kirkby *et al*., 2002; Soulsby *et al*., 2004), bedrock geology (Hattanji and Onda, 2004; Uchida *et al*., 2005), topography (Anderson and Burt 1978; Jensco *et al*., 2009), and climate (Devito *et al*., 2005; Hrachowitz *et al*., 2009). However, although such studies have provided valuable information, the spatial variability of discharge and chemistry for all small catchments cannot be predicted yet.

This study investigated the relationships between the spatial variability of stream discharge and chemistry and catchment area, focusing on changes in catchments of different sizes. The process that formed the relationships is referred to as a confluence process. It has long been known that, in small catchments, stream water discharge and chemistry are highly variable but the variability decreases gradually with an increase in the catchment area (Eriksson, 1929). Wood *et al*. (1988) showed that model calculations of infiltration and the runoff rate became constant above a certain threshold area. They defined the threshold area as the representative elementary area (REA) and stated that above the REA only minimum knowledge of the underlying parameters is needed to explain the stream water discharge and chemistry. Therefore, it is useful to determine the relationships between the heterogeneity of environmental factors and hydrological processes.

Subsequently, empirical studies conducted in several catchments have confirmed the existence of the REA and have also indicated that the size of the REA varies among catchments. For example, Woods *et al*. (1995) observed stream discharges in two catchments and confirmed that convergence was found above 0.5 km^2 and 2 km^2, respectively. Wolock *et al*. (1997) showed that convergence occurred above 3 km^2 based on six variables of water chemistry. Likewise, Temnerud and Bishop (2005) confirmed that convergence occurred above 15 km^2 at two catchments based on four water chemistry variables. Asano *et al*. (2009), on the basis of discharge and eight chemical variables, reported convergence at sizes ranging from 0.1–1.5 km^2.

These studies all verified the existence of an REA in real catchments and indicated that the REA values differed among catchments. The results also suggested that the confluence processes differed among catchments. However, it has not been clarified how the confluence processes behave and why processes differ among catchments. A better understanding of confluence processes is required to aid in predicting the REA and understanding the scale issue.

Several issues must be solved. The first regards the variability of stream water discharge and chemistry in small catchments and its confluence. It is not clear whether the variability of discharge and chemistry among small catchments can be regarded as randomness or if it is organized. Woods *et al*. (1995) reported that organization was apparent from their observations of specific discharge. However, Asano and Uchida (2010) stated that their results for SiO_2 could be regarded as randomness. The second issue is whether the groundwater contribution to stream discharge increases with catchment area. Shaman *et al*. (2004) showed that groundwater discharge increased with the increasing size of the catchment area. However, Uchida and Asano (2010) indicated that, on average, groundwater discharge did not increase with catchment size. The final issue is whether nutrient uptake in streams decreases the nutrient concentrations within a catchment as the area increases. Several previous studies have reported the large influence of in-stream processes on nutrient concentrations (e.g., Howarth *et al*., 1996; Alexander *et al*., 2000). However, nutrient uptake is highly variable among catchments (Hall and Tank, 2003; Mulholland *et al*., 2008). It is difficult to compare and discuss the differences in confluence processes among catchments without a good general knowledge of confluence processes. Comprehensive investigation of confluence processes and inter-site comparison is thus needed to consider all of the above mechanisms and attempt to determine the factors generating the differences among catchments.

1.3 Objectives of this study

This study sought to elucidate the confluence process and to determine the factors generating differences among catchments. For this purpose, I compared three catchments and considered the changes with catchment area and stream confluences from observations of the spatial variability of stream water discharge and chemistry. Nutrient addition experiments were undertaken to assess the effects of in-stream processes. Figure 1.1 shows the structure of this paper.

Chapter 2 discusses the spatial pattern of bedrock groundwater discharge in the three catchments, each with a different geology, based on observations of the spatial variability of stream discharge and chemistry. It was confirmed that bedrock groundwater discharge increased with increasing catchment area.

Chapter 3 presents the nitrate and phosphate uptake rates in two streams and discusses the influence of environmental factors on their uptake characteristics. This chapter is based on the nutrient addition experiments.

Chapter 4 discusses the differences in the confluence process among observations and among catchments with different geologies. This chapter is based on a statistical analysis of the spatial variability of observed stream discharge and chemistry described in Chapter 2.

Chapter 5 discusses whether the mixing of soil water and bedrock groundwater can explain the characteristics of variability in small catchments. The influence of micro-topography on stream confluences is also examined. This chapter is based on a comparison between observed data and model calculations.

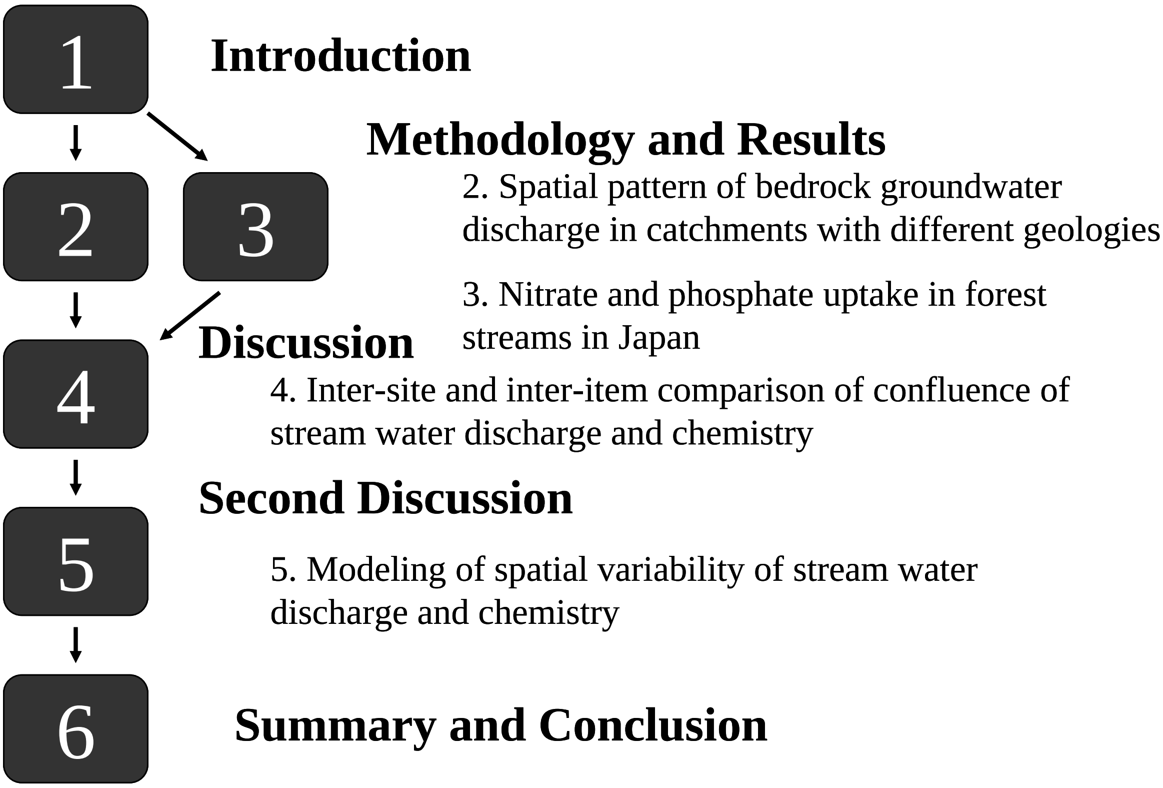

Figure 1.1 Structure of this study

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Chapter 2

Spatial pattern of bedrock groundwater discharge in catchments with different geologies

2.1 Introduction

Studies of small forested catchments have revealed the importance of the flow path through bedrock (Terajima and Moroto, 1990; Mulholland, 1993; Burns *et al*., 1998; Asano *et al*., 2002). Since the 1980s, much research has assessed the volume of bedrock groundwater infiltration, and a wide range of 18–71% has been reported for annual precipitation infiltration into bedrock (Terajima *et al*., 1993; Anderson *et al*., 1997; Montgomery *et al*., 1997; Kosugi *et al*., 2006). Generally, bedrock groundwater has a long residence time and high concentrations of mineral-derived solutes. Consequently, it becomes a factor in low-flow discharge (Mulholland, 1993; Burns *et al*., 1998) and influences the mean residence time of stream water (Katsuyama *et al*., 2010) and water chemistry (Anderson *et al*., 1997; Uchida *et al*., 2003; Asano *et al*., 2003).

Since several decades, it has been known that stream water discharge and chemistry have large spatial variability. About discharge and chemistry in low-flow conditions, some studies focused the relationship between such variability and catchment area (Woods *et al*., 1995; Wolock *et al*., 1997; Temnerud *et al*., 2005). There are many reasons why run-off processes in small catchments have large spatial variability; heterogeneity of landscape, soil, geology and climatic inputs. Asano *et al*.,

(2009) showed that variability also occurs in catchment with uniform soil and geology, and showed that the variability cannot be explained by catchment area, slope gradient, or topographic index defined by Beven and Kirkby (1979). And in the same catchment, Uchida and Asano (2010) showed that spatial variability of stream water discharge and chemistry were explained by mixing of soil water and bedrock groundwater.

There has been a problem that we need to clarify on relationship between bedrock groundwater dynamics and catchment area is whether bedrock groundwater discharge increases with catchment area . Generally, bedrock groundwater has been thought to increase as catchment area increases, because it percolates in upstream and recharges in downstream. However, two studies, which examined this hypothesis, showed different results. Shaman *et al*, (2004) examined four-year runoff data in a set of 11 catchments and used longitudinal alkalinity and SiO_2 data of three sub-streams from Wolock *et al*., (1997). And they insisted that bedrock groundwater increase to 8 km^2 with catchment area. However, Uchida and Asano (2010) used stream discharge and chemistry data from Asano *et al*., (2009), which examined almost all sub-streams in 4.27km^2 catchment. They showed bedrock groundwater contributions have large variability in small catchments, but the average contribution of each stream order was not increase and almost constant against catchment area. Therefore, whether bedrock groundwater increases with catchment area has still been unclear.

Difference in bedrock geology has been known to affect rainfall-runoff processes owing to differences in geophysical characteristics (Hattanji and Onda, 2004). These differences might also affect spatial pattern of bedrock groundwater discharge. I observed spatial variability of stream water discharge and chemistry in three selected catchments with different geologies. I discussed spatial variability of bedrock groundwater discharge using End Members Mixing Analysis (EMMA).

Objectives of this chapter were following.

To clarify spatial pattern of bedrock groundwater discharge in three catchments with different geologies.

To examine whether bedrock groundwater discharge increase with catchment area.

2.2 Methods

2.2.1 Site description

Inokawa catchment

The Inokawa catchment is located in the Kiyosumi Mountains on the Boso Peninsula, Japan. (35°11~13′ N, 140°06′~07′ E; Fig. 2.1.a) The stream flows from south to north and the catchment area is 5.03 km^2, with an altitude range of 90 to 346 m above sea level. The climate is classified as warm humid. The mean annual precipitation is 2304 mm (for 1994–2010) and the mean annual temperature is 14.2°C (for 1998–2000) in a meteorological station. (Fig. 2.1.b)

The bedrock geology is Neogene sedimentary rocks, classified in the Awa group, which comprises different formations. (Fig. 2.1.b) From north to south, the Inokawa catchment includes the Anno, Kiyosumi, and Amatsu formations. These formations are all folds, and the anticlinal axis runs east to west. In the southern part of the catchment, the formations dip toward the south, while in the northern part, they dip toward the north (Nakajima *et al*., 1981). The Anno Formation is mainly flysch-type alternation of sandstone and mudstone. The Kiyosumi Formation is characterized by the predominance of thicker turbidite sandstones (here after, we call sand stone area). The Amatsu Formation is composed mainly of massive bluish gray mudstone that was probably deposited in a hemipelagic mud belt on the continental shelf (here after, we call mud stone area). The soil is mainly brown forest soil. Gray lowland soil is found only along the stream. Forests consisting of coniferous plantations of Japanese cedar (*Cryptomeria japonica*) and cypress (*Chamaecyparis obtusa*) and natural broadleaf deciduous forest cover the entire catchment.

A water intake is located at the pont of the main stream (Fig 2.1b, the catchment area is 4.02 km^2) Water is taken for irrigation using a flume from the end of February until September,. So downstream of this point (three points of observations) are affected by this diversion. The amount of withdrawal is changed with water level and discharge of main stream at low-flow conditions. In seasons without withdrawal, we can estimate the relationship between before and after withdrawal. (4.48 km^2 discharge = 3.97 km^2 discharge × 1.2834 + 0.0014, R^2=0.86, n=7). So, we calculated the amount of withdrawal by using following equation. (The amount of withdrawal = the predicted value at 4.48 km^2 - the observed value at 4.48 km^2) I multiplied the amount of withdrawal and water chemistry at 3.97 km^2 point, and obtained loss flux of dissolved matters by withdrawal. Water discharge and chemistry were obtained by adding this flux at three points, which are influenced by withdrawal.

In the Fukuroyamasawa Experimental Watershed-B (FEW-B; 0.012 km^2; Fig. 2.1.e), which was located at northwest of Inokawa catchment, continuous observations of the stream discharge were conducted. FEW-B was clear-cut in spring 1999, and was planted in summer 2000. Annual average discharge was 1294mm (2003-2008; annual average precipitation in the same period is 2509mm). The altitude ranged from 126 to 230 m above sea level. The average gradient is 23.5°. The average soil depths are 2.22m (Shiraki *et al*., 1999). There exists an aquifer in bottom of FEW-B (Oda *et al*., 2009;

Hotta *et al*., 2010). At the observation points of soil water, the perennial groundwater level was approximately 100 cm below the surface (Oda *et al*., 2009).Oda *et al*. (2008) examined water infiltration into bedrock in this catchment and reported that 520 mm (22% of the annual precipitation) infiltrated bedrock and ran-off without passing through the weir gauge. Mean residence time estimated by Cl^- concentration was about three years (Oda *et al*., 2009).

Yozukugawa catchment

The Yozukugawa catchment (35°24~29′ N, 138°55′~139°2′ E) is located in the Tanzawa Mountains in Kanagawa prefecture. The 55.6 km^2 Yozukugawa catchment is underlain by ten different geologies (Fig. 2.1.c). The Tanzawa Mountains consist of a central plutonic body surrounded by marine-derived volcanic tuffs and clastic rocks including conglomerates. The plutonic body is thought to be a magmatic intrusion. The volcanic tuffs formed in an accretionary prism, and the clastic rocks are thought to be trough-fill sediments (Amano *et al*., 2007). The northern part of the catchment is underlain by plutonic rocks: granodiorite (42.1% of the catchment), gabbro (5.5%), and granitoid plutonic rocks (5.8%). In the southern part of the catchment, basaltic and andesitic volcanic rocks (20.0%, 7.7%, 3.9%, and 3.1% as distinguished by the age and characteristics of the rocks) occur. In addition, tephra layers occur in some mountain ridges.

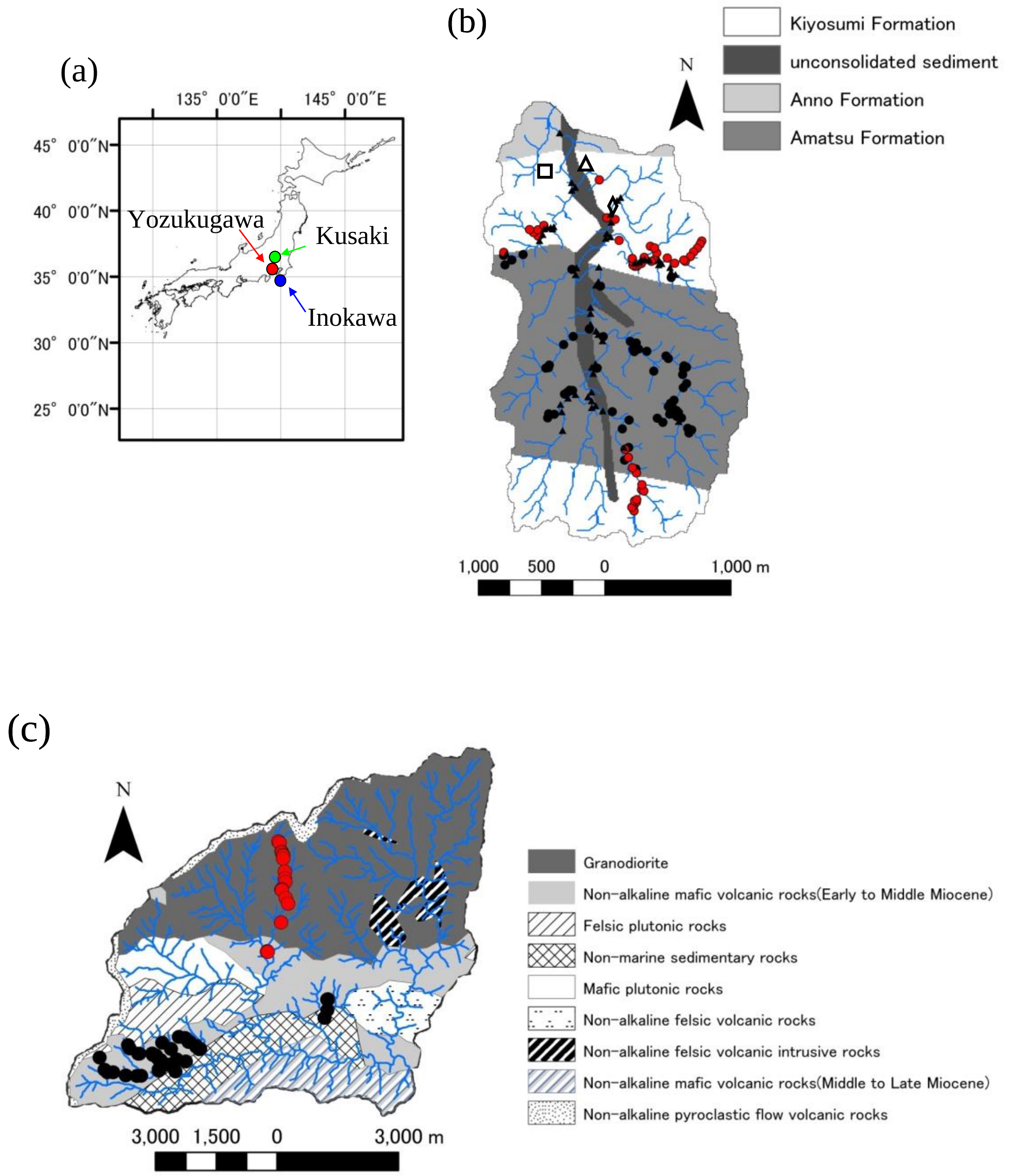
The altitude ranges from 340 to 1375 m above sea level, and the mean slope gradient is 31.4°. The mean annual precipitation for the period 1991–2010 was 2281 mm at Tanzawako, which is 3 km east of Yozukugawa, and the mean annual temperature was 9.0°C at Yamanaka, 8 km west of Yozukugawa. The precipitation and temperature were measured at the respective stations by the Automated Meteorological Data Acquisition System (AMeDAS) of the Japan Meteorological Agency.

Forests cover the entire catchment and consist mainly of coniferous plantations of Japanese cedar (*Cryptomeria japonica*) and cypress (*Chamaecyparis obtusa*). Japanese cypress accounts for 80% of conifers. A natural broadleaf desiduous forest of Fagaceae (*Fagus crenata*) also exists at high altitude. A typical brown forest soil occupies 90% of the catchment, with Andosol occupying the remaining 10%.

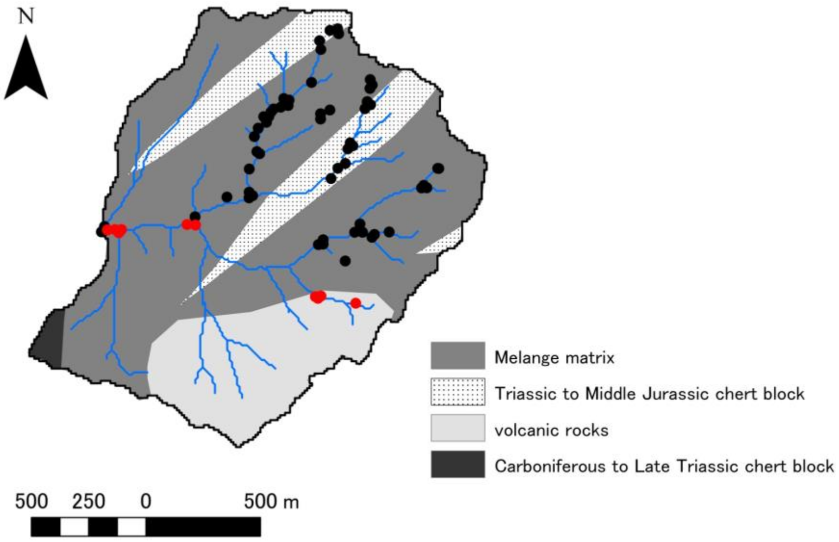
Kusaki catchment

The Kusaki catchment (36°34~36′ N, 139°22~26′ E) is located in Gunma prefecture. Kusaki catchment is one of the sub-streams of Watarase River. The whole catchment area is 2.27km^2. The bedrock geology is mainly Jurassic sedimentary rock (Fig. 2.1.d). This Jurassic sedimentary rock is Middle to Late Jurassic accretionary prism. There exists Triassic to Middle Jurassic chert block in the melange matrix of accretionary complex. This chert blocks is underlain from northeast to southwest with parallel structure. I defined these two as a single geology because it was the structure derived from sedimentary style of accretionary prism. And volcanic rocks occupy some part of Kusaki catchement. The volcanic rock is Middle to Late Miocene non-alkaline felsic volcanic rocks. In addition, there exists Carboniferous to Late Triassic chert block in only vanishingly small area in south east of the catchment.

Forests cover the entire catchment and consist of natural broadleaf deciduous forest and coniferous plantations of Japanese cedar (*Cryptomeria japonica*) and cypress (*Chamaecyparis obtusa*). A typical brown forest soil occupies 90% of the catchment, with Andosol occupying the remaining 10%. The altitude ranges from 748 to 1140m above sea level, and the mean slope gradient is 28.8°. The mean annual precipitation for the period 1991–2012 was 1477 mm at Kurohone, which is 3 km southwest of Kusaki and the mean annual temperature was 14.6°C (2008-2012) at Kiryu, 6 km south of Kusaki. The precipitation and temperature were measured by the Automated Meteorological Data Acquisition System (AMeDAS) of the Japan Meteorological Agency.



(d)



(e)

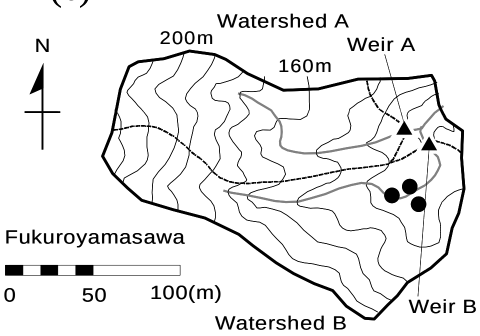


Figure 2.1 (a) Location of three catchments. (b) Snapshot sampling points in Inokawa. Black circles show observation points of Amatsu formation. Red circles show observation points of Kiyosumi formation. And solid triangles indicate the mixing observation points of the two geologies. The open square marks the Fukuroyamasawa Experimental Watershed, the open triangle indicates the meteorological station, and the open diamond shows the location of channel of withdrawal. (c) Snapshot sampling points in Yozukugawa. Black circles show observation points of Early to Middle Miosene non-alkaline mafic volcanic rocks. Red circles show ones of granodiorite. (d) Snapshot smapling points in Kusaki. Black circles show sedimentary rocks. And red circles indicate observation points, which have more than 20% of volcanic rocks. (e) Fukuroyamasawa Experimental Watershed. The north part is watershed-A and the south is watershed-B. Solid triangles show weir for discharge observation. Solid squares show lysimeters for the sampling of soil water.

2.2.2 Sampling and measurements

In Inokawa, snapshot samplings were conducted on seventeen times from August 2007 to December 2010. I show observation date and the numbers of each observation with discharge of FEW-B (Table. 2.1). All observations were conducted in low-flow condition. Stream discharge was measured at 113 points and water chemistry was measured at 159 points. Observation points which observed more than once were 36points about discharge and 48 points about water chemistry.

Table 2.1: Observation date of snapshot sampling, the numbers of observation , and the daily discharge of FEW-B

Observation date	The numbers of observation	FEW-B discharge (mm/day)
2007/8/22	8	0.08
2007/10/24	14	0.13
2007/10/25	15	0.12
2008/6/19	15	0.49
2008/7/24	19	0.07
2008/7/25	15	0.17
2008/8/5	23	0.17
2008/8/6	17	0.04
2008/9/17	19	0.13
2009/8/3	44	0.50
2009/8/4	55	0.41
2009/8/5	22	0.33
2010/1/20	12	0.22
2010/5/19	12	0.28
2010/7/28	26	0.14
2010/8/19	12	0.09
2010/10/20	12	0.64

In Yozukugawa, snapshot samplings were conducted on nine times in low-flow condition in 2008: August 10-12, September 25-26, and October 14-17. Discharge was measured at 65 points and water chemistry was measured at 157 points; 25 points were observed repeatedly. The differences among observations were small (second or third EC = first EC × 0.94 + 8.4, R^2 = 0.48, n = 32). In Kusaki snapshot sampling on August 27-29 in 2012, in low flow conditions. I measured discharge at 49 points and water chemistry at 65 points

In Inokawa catchment, soil water and stream water were sampled regularly at FEW-B and precipitation was sampled at meteological station located at near FEW. The sampling of soil water was conducted by tension-free lysimeters at three locations in the catchment. Observations were conducted about once in a month from August 2006 to November 2009. The numbers of samples were 30, 35, and 38 at each sampling point. Stream water was sampled at 56 times from January 2007 to September 2009. Precipitation was sampled at 64 times January 2007 to November 2009.

Electrical conductivity (EC) was measured in situ. The concentrations of major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) were measured in the laboratory of the University of Tokyo using ion chromatography (Shimadzu LC10-A), and the concentration of SiO_2 was measured using the molybdenum yellow method. HCO_3^- was calculated from ion balance. In addition, the accuracy of the analysis was confirmed by comparing observed EC and calculated EC from major ion concentrations.I multiplied specific electrical conductivity to concentration of each ions and added all of them. I measured water velocity with an electromagnetic velocity meter (KENEK, VE-20) and calculated the discharge by multiplying the cross-sectional area and water velocity. In addition, specific discharge was calculated by dividing the discharge by the catchment area.

The catchment size, soil, and geology of the catchment area were described using a 10-m digital elevation model (DEM; Geographical Survey Institute), a soil map at a scale of 1:200,000 (Geographical Survey Institute), a geological map at a scale of 1:200,000 (Geological Survey of Japan, AIST), and ArcGIS (ESRI). The boundaries of the geology differ from the watershed boundary. In many observed points, there existed multiple geologies. I differenciated observed points with geology. I defined uniform geologies as the points, more than 80% of which are occupied single geology. I defined multiple geologies as the points, no single geology occupied more than 80%.

2.2.3 Data Analysis

Conceptual diagram in a small catchment was shown in Figure 2.2. Precipitation infiltrates soil layer and some portion of them infiltrate even in bedrock layer. Bedrock groundwater recharges to soil layer or infiltrates deeper. Soil water and bedrock groundwater are mixed in aquifer and formed first-order stream. Bedrock groundwater has possibility to recharge in downstream. As a result, it is considered that stream water discharge and chemistry are composed of soil water and bedrock groundwater. This conceptual diagram was confirmed in observation of FEW-B.

I used End-Members Mixing Analysis (EMMA; Christopherson *et al*., 1990; Hooper *et al*., 1990) and separated stream water into two component: soil water and bedrock groundwater. In Inokawa, there existed four components and EM1 was defined (soil water component) as the average value of soil water, and EM2~4 (bedrock groundwater components) were defined as the values of springs, which were obtained from snapshot samplings. End Members were selected by using Principle Component Analysis (PCA; Christopherson and Hooper, 1992). Five solutes (Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}) were used for PCA. I used first-three PCA scores for EMMA. In Yozukugawa and in Kusaki two components (soil water and bedrock groundwater) were defined. Mineral derived dissolved matters (SiO_2 and HCO_3^- in Yozukugawa; SiO_2 and Na^+ in Kusaki) were used for definition of End Members. I used average values of three stream water, which had highest and lowest values of these dissolved matters.

The contribution of each component was calculated from the concentration of stream water. When the contribution of component dipped from zero, it was calculated as zero. About the points observed specific discharge, I multiplied specific discharge and the contribution of each component to calculate the specific discharge of each component.

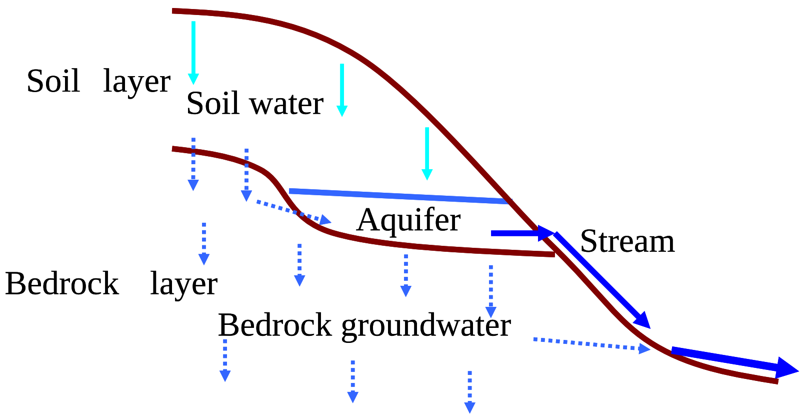


Figure 2.2 Conceptual model of hydrologic flow paths in small catchments. Stream water is mixed by soil water and bedrock groundwater.

2.3 Results

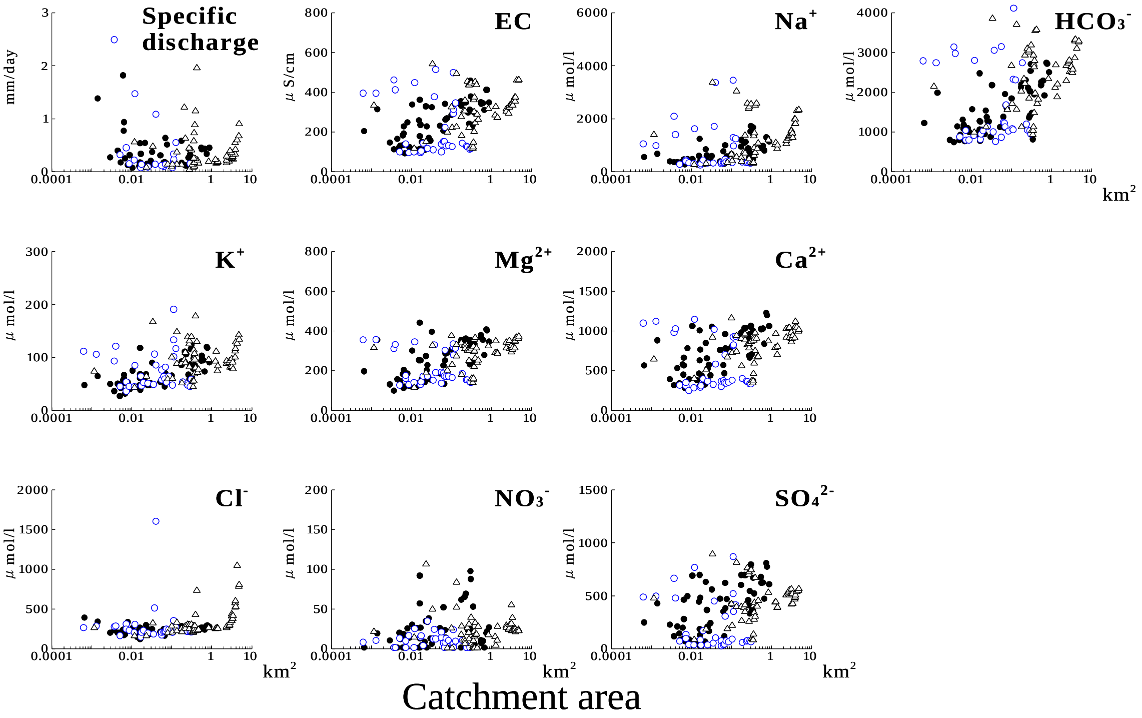
2.3.1 Relationships between specific discharge and chemical parameters and catchment area

Specific discharge and chemical parameters of three catchments are plotted against catchment area (Fig. 2.3). Observed values of specific discharge and chemical parameters differed largely among three catchments. Specific discharge was largest in Yozukugawa and lowest in Inokawa. EC, Na^{+}, Mg^{2+} and Ca^{2+}, which are mainly mineral-derived dissolved matters, were largest in Inokawa and lowest in Kusaki. Cl^{-} and SO_4^{2-}, which are mainly precipitation derived dissolved matter were also highest in Inokawa. K+, which are mainly leached from decomposition of litter, was also highest in Inokawa. Those concentrations of Yozukugawa and those of Kusaki were similar. About NO_3^{-} concentration, Yozukugawa was highest and Inokawa and Kusaki were in the same range.

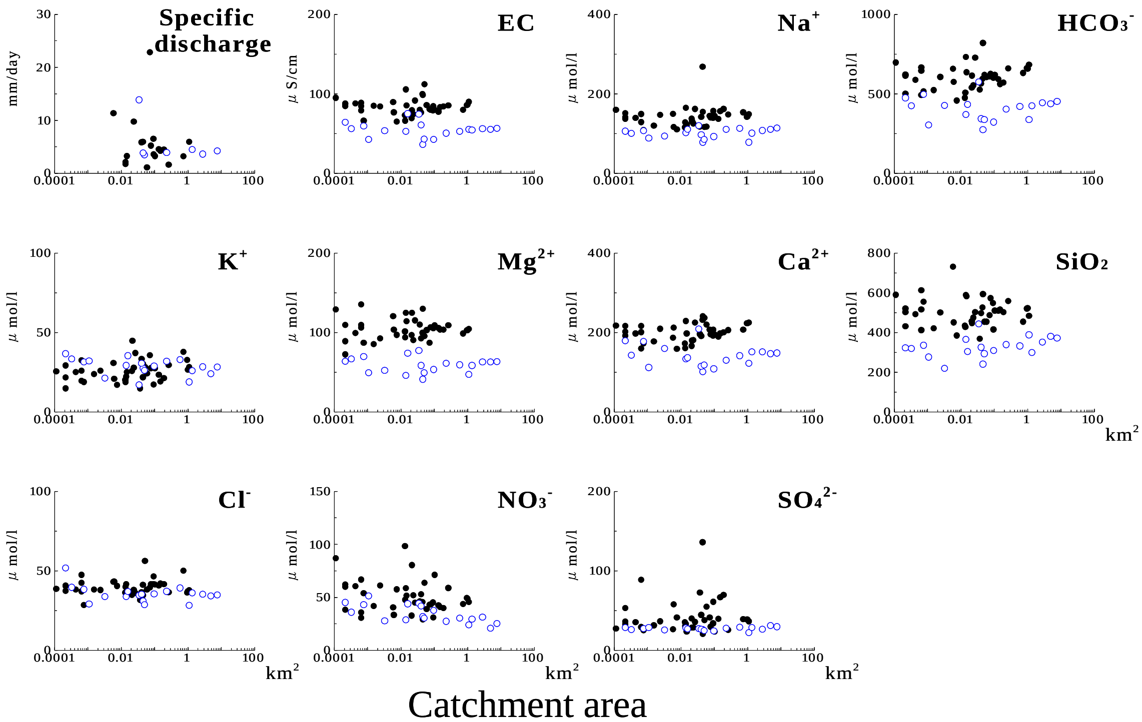
I mentioned the change of variability of specific discharge and chemical parameters as cathcment area increases. In all catchments, the discharge and chemical parameters had large spatial variability among small catchments with less than 0.1km^2. In Inokawa, the ranges of concentration were not much different between two geologies. The variability of Mg^{2+}, Ca^{2+}, NO_3^- and SO_4^{2-} decreased with increasing area and the values converged at 1-2 km^2 . However, other variables did not converge to a constant values. Those continued to increase at over 2 km^2. Especially, Na^+ and Cl^- showed obvious increase with catchment area above few square kilometers.

In Yozukugawa, the differences of concentrations between volcanic rocks and granodiorite were significant. Both in volcanic rocks and in granodiorite, the variability start to decrease from 0.1km^2. It became constant at above 0.5-1 km^2, although there was slight difference among chemical parameters. In Kusaki, almost all observed variables became constant above 0.7 km^2. However, a part of observed items (K^+, $Mg^{2+}$and Ca^{2+}) increased from 0.7 km^2 to 2.24 km^2 significantly. Those ions were higher in volcanic rocks than in sedimentary rocks in Kusaki. So, in this point (2.24 km^2), volcanic rocks might strongly influence on water chemistry, though more than 80% were occupied by sedimentary rocks.

(a) Inokawa



(b) Yozukugawa



(c) Kusaki

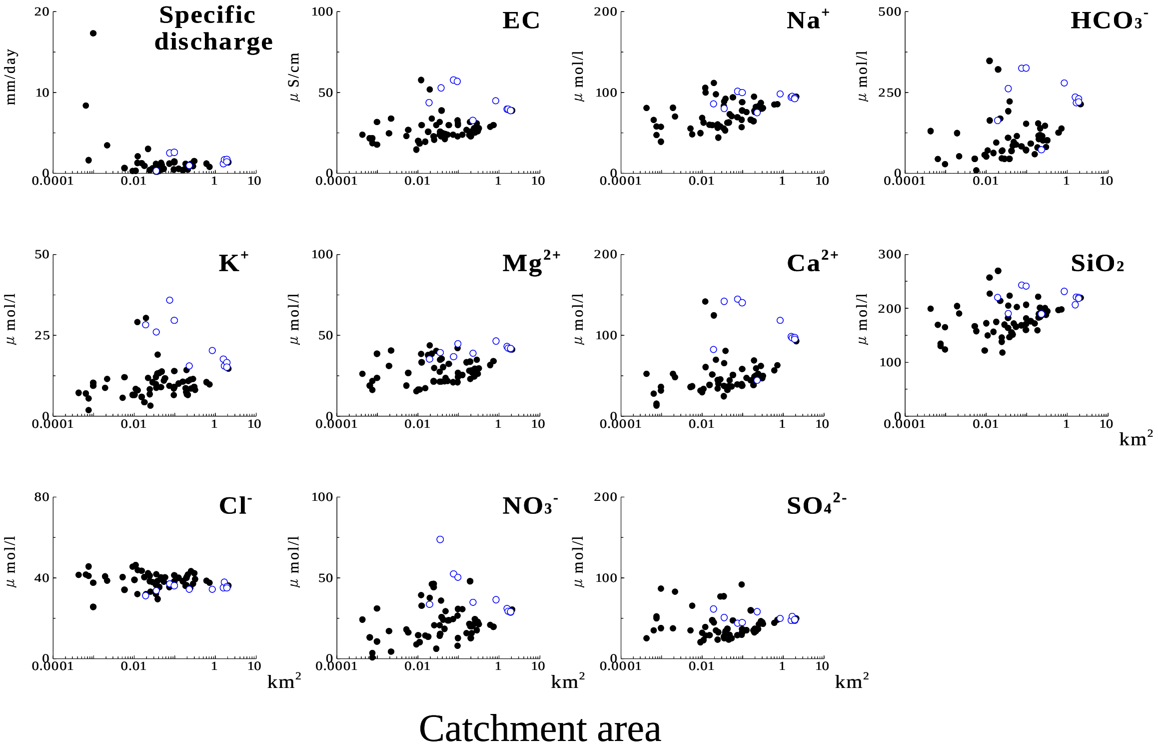


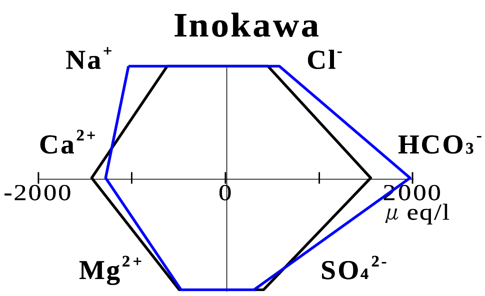
Figure 2.3 Specific discharge and solute concentrations as a function of catchment area. We use logarithmic values for catchment area. Each point shows each geology. (a) Black circles show mud stone and blue circles show sand stone area in Inokawa. Triangles show the mixture of the two geologies. (b) Black circles show volcanic rocks and blue circles show granodiorite in Yozukugawa. (c) Black circles show sedimentary rocks and blue circles show volcanic rocks in Kusaki.

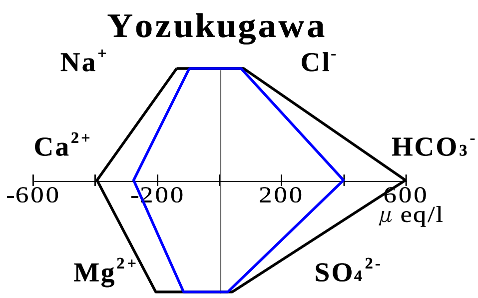
2.3.2 Ion balance of stream water

I showed hexa-diagram and examined the difference of ion balance among catchments and geologies (Fig. 2.4). Average values were used in each geology in hexa-diagrams. On the whole, two geologies in Inokawa had highest concentration, and two catchments in Kusaki had lowest. The tendencies of ion balance were almost the same among catchments and geologies. That is, in almost all geologies, main cation was Ca^{2+}

and main anion was HCO_3^-. Generally, in low flow conditions, stream water is consisted of soil water and shallow bedrock groundwater, and has Ca-HCO_3 type. Only sedimentary rock in Kusaki had low concentration of Ca^{2+} and HCO_3^-.

In Inokawa, the ranges between two geologies were not much different, but sand stone area had slightly higher $Na^+$and Cl^- values than mud stone area. In Yozukugawa, about mineral-derived dissolved matters, volcanic rocks had higher concentrations than granodiorite. In Kusaki, about mineral-derived dissolved matters, volcanic rocks had higher values than sedimentary rocks. About Inokawa, the results showed the tendency in excess of chemical characteristics of geology, so I used all observation values for EMMA. On the other hand, in Yozukugawa and in Kusaki, the differences between geologies were significant, so I used only volcanic rocks in Yozukugawa, and only sedimentary rocks in Kusaki.





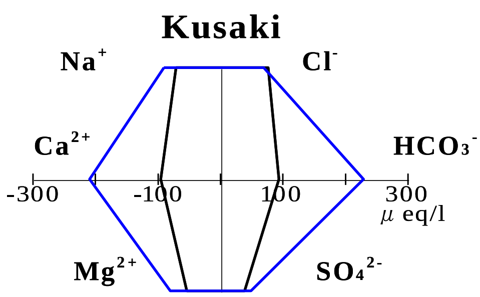


Figure 2.4 Hexa-diagrams of three catchments. Black lines show mud stone in Inokawa, volcanic rocks in Yozukugawa, and sedimentary rocks in Kusaki. Blue lines show sand stone area in Inokawa, granodiorite in Yozukugawa, and volcanic rocks in Kusaki.

2.3.3 Determination of end-members

In Inokawa, I subjected stream water chemistry of five solutes (Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}) to principle component analysis (PCA; n=159). K^+ and NO_3^- was not used for the possibility of absorption by microbe and algae. I used average values for points, which I observed more than once. The cumulative contribution to the first two principle components (PC) was 90.1%, and first three was 97.2%, indicating that they represent the stream solute concentrations well. First three PCA scores of stream water with soil water observed in FEW-B and bedrock groundwater observed in snapshot samplings were shown in Figure 2.5. Stream water almost fell in the range, which is formed by soil water and bedrock groundwater. This result confirmed that the mixture of soil water and bedrock groundwater explains stream water in Inokawa. It also showed there exists several different bedrock groundwater. Bedrock groundwater was classified into three types (type-A, B, and C; Fig. 2.5)

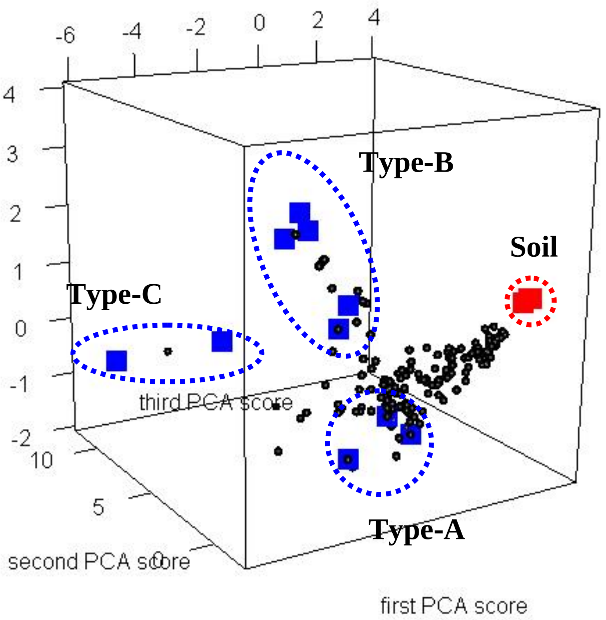


Figure 2.5 Results of principle component analysis in Inokawa. Black circles show stream water, red squares show average values of soil water, and blue squares show three types of bedrock groundwater.

I showed the relationships between SiO_2 and HCO_3^- in Yozukugawa and between SiO_2 and Na^+ in Kusaki, which I used for determining end-members (Fig. 2.6). There was significant correlation between SiO_2 and HCO_3^- in Yozukugawa and between SiO_2 and Na^+ in Kusaki. I extracted highest three and lowest three of these concentrations. Soil water concentration was determined by the average of lowest three and bedrock groundwater concentration was determined by the average of highest three.

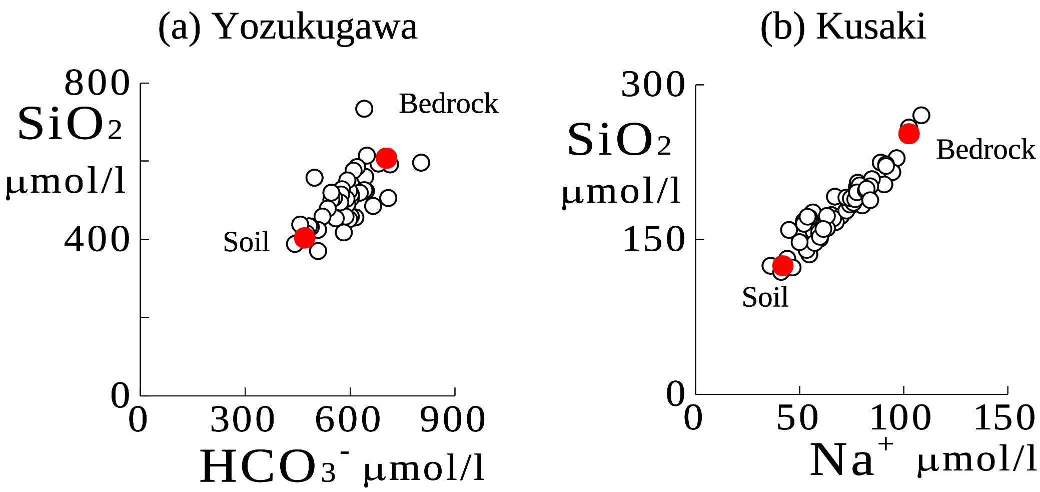


Figure 2.6 The determination of end-members in Yozukugawa and in Kusaki. Open circles show observed values. And red solid circles show end-members (Soil water and bedrock groundwater component).

2.3.4 Spatial pattern of bedrock groundwater discharge

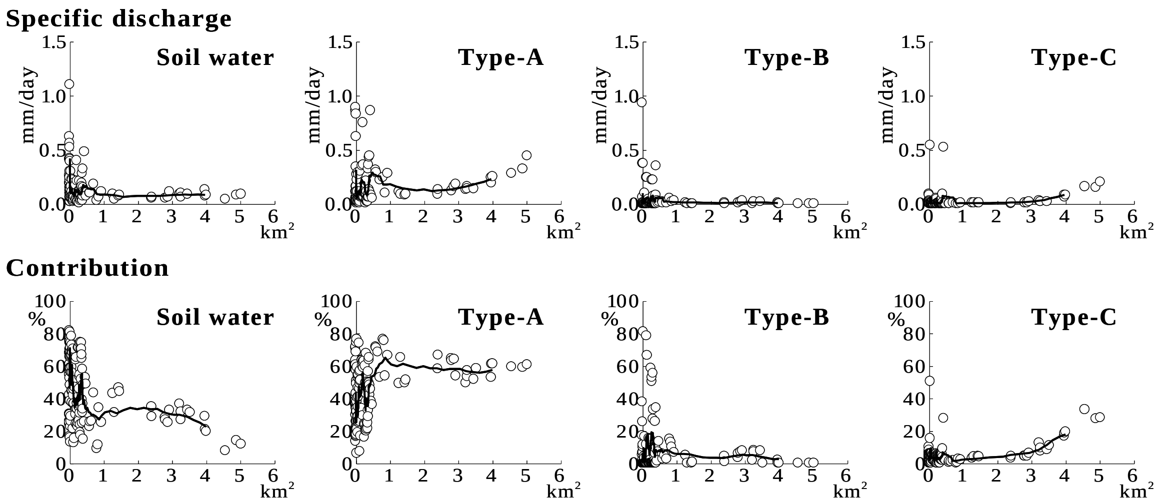
I showed that the contribution and amount of each component occupied stream water against catchment area in three catchments (Fig. 2.7). All components showed large variability in small catchments (<0.1 km^2). In Inokawa, bedrock groundwater discharge (The sum of type-A, B, and C) and contribution increased averagely as catchment area increased. And, different types of bedrock groundwater showed different tendencies. Type- A component was occupied highest contribution of the three types.

Type-B component did not discharge in headwater, which have high altitude and small catchment area. It began to discharge from 0.1-0.4 km^2. And it hardly discharged above 3 km^2. Type-C discharged in sub-streams quite little, and increased with catchment area above 1 km^2.

In Yozukugawa, the variability of contribution and amount of bedrock groundwater discharge were large below 0.05km^2. However, they became constant averagely above 0.05km^2. And it did not increase with catchment area increase.

In Kusaki, the result from the data at the point with 2.24 km^2 was eliminated because it might be much influenced by the volcanic rocks. The variability in small catchments was also large. The contribution of bedrock groundwater increased from 0.1 to 0.3 km^2. And then, it became constant above 0.3 km^2. The discharge rate of bedrock groundwater significantly decreased in small catchments and increased slightly from 0.1 to 0.3 km^2. Simultaneously, specific discharge of soil water decreased slightly.

(a) Inokawa



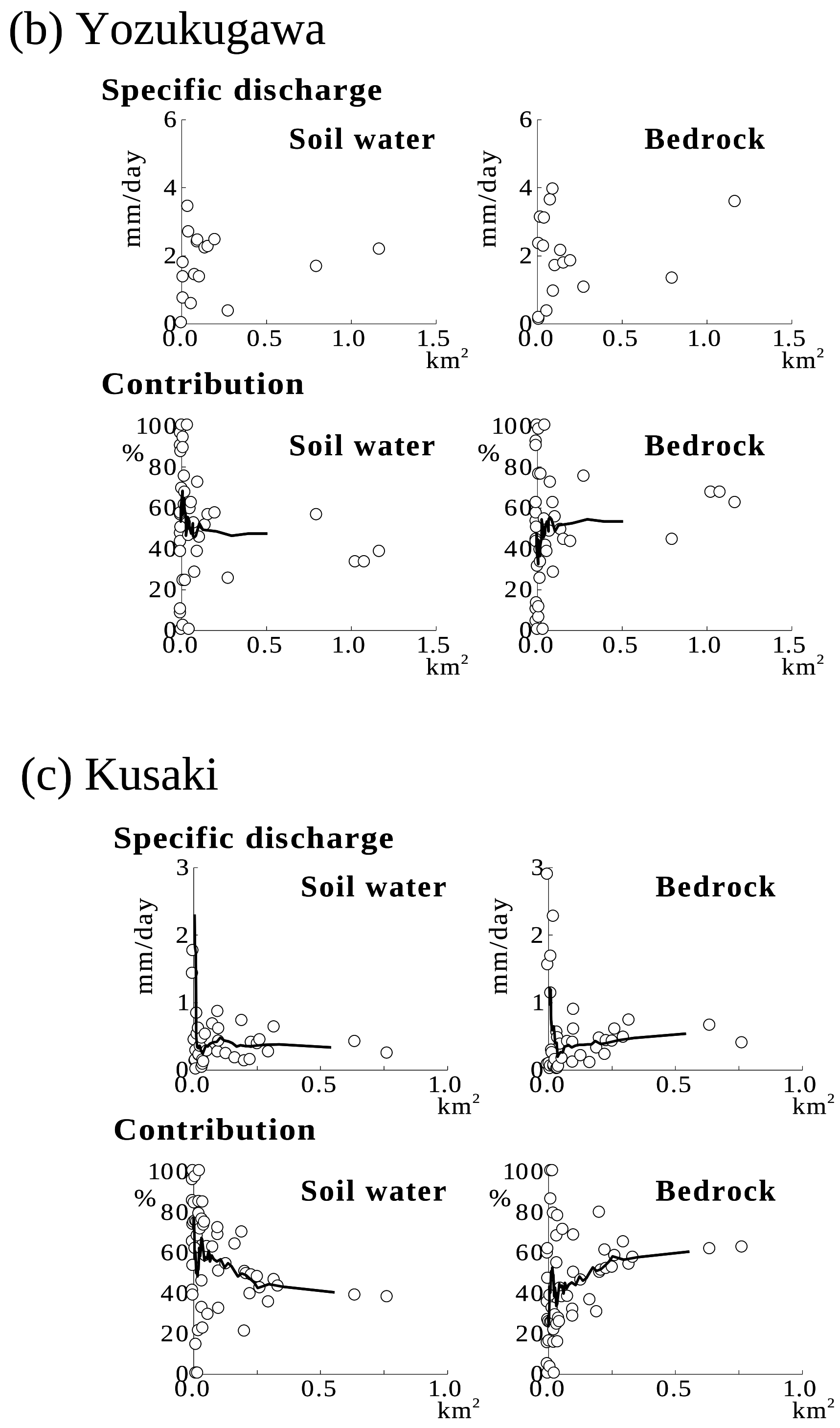


Figure 2.7 Specific discharge and Contribution of soil water and bedrock groundwater occupied in stream water as a function of catchment area. The line shows moving average of each 10-value.

2.4 Discussion

2.4.1 Bedrock groundwater dynamics in Inokawa

In Inokawa, three types of bedrock groundwater existed and it showed clearly different tendencies from other catchments. Type-B and type-Cwere rarely observed at observation points with high altitudes regardless of surface geology(Fig. 2.8). This means that difference among three types of groundwater was not derived from the difference of chemical characteristics of bedrock geology (sand stone or mudstone). Type-A might be formed in shallow bedrock layer near soil layer, because Na/Ca ratio of type-A was the same of soil water of FEW-B (Fig. 2.9.a).

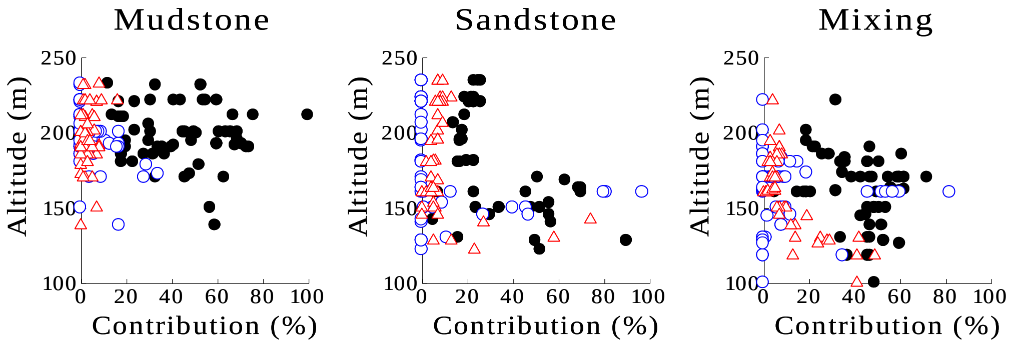


Figure 2.8 The relationship between contribution of each bedrock groundwater and altitude in Inokawa. Black circles, blue circles and red triangles indicate type-A, B and C respectively. And we divided figures depending on surface geologies.

Type-B had higher Na^{+} concentration and higher Na/Ca ratio than type-A (Fig. 2.9.a). Ca^{2+} of type-B was the same range as type-A. Generally, Mg^{2+} and Ca^{2+} have higher cation selectivity of exchange sites than Na^{+}.They are easier to absorb than Na^{+}, in the concentration range of the springs of my observations (Stumm, 1992). Although both Ca^{2+} and Na^{+} are added to groundwater from chemical weathering in bedrock, groundwater Na^{+} increased and Ca^{2+} decreased simultaneously due to the cation exchange reaction resulting the change of Na/Ca ratio. Therefore, type-B might be formed at deeper bedrock than type-A and might have longer residence time.

Type-C was characterized by higher concentration of Cl^- than type-A and type-B (Fig. 2.9.b). Cl^- concentrations of soil water, type-A and type-B were within the same range. This range was derived from condensation of Cl- in rainwater by evapotranspiration. The high level in Cl^- concentration of type-C could not be explained by condensation. As the Inokawa catchment is underlain by marine-derived sedimentary rocks(Nakajima *et al*., 1981), it is possible that high Cl^- concentration of type-C was supplied by fossil salt water. In addition, type-C had lower Cl^- concentration than marine water and had higher Na^+/Cl^- ratio than marine water. Fossil salt water might mix with type-A and B in aquifer. It is considered that type-C is mixture of fossil salt water and type-A and type-B. Geological folds are occuured in Inokawa catchments, and there are many faults (Nakajima *et al*., 1981). It is also considered that these types of bedrock groundwater discharge with upwelling through fissure or faulting in bedrock.

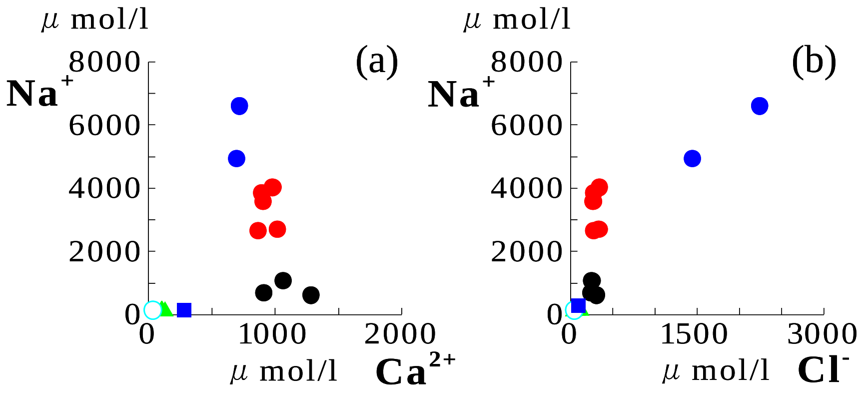


Figure 2.9 The relationship between (a) Na^+ and Ca^{2+} (b) Na+ and Cl^- in Inokawa. Open circle shows precipitation. Triangles indicate soil water, and square shows stream water of FEW-B. Type-A, B, and C of bedrock groundwater were expressed by black, red, and blue solid circles respectively.

Sakai *et al*., (2007, 2009) observed stream water, springs, and wells in Yourou River which is located at a few km north from Inokawa, and its geology is alternative layer of sand stone and mud stone). They confirmed that two types of groundwater (Ca-HCO_3 and Na-HCO_3 type) exist separately. Ca-HCO_3 type existed in shallow layer above 200m. Na-HCO_3 type groundwater existed below 200-300m from surface. Residence time of those groundwater ranged from a few to twenty thousands years. They also showed Na-HCO_3 type groundwater up welled and sprung diluted by shallower groundwater. In the same way, in Inokawa, typeB and type C might be influenced by upwelling deep groundwater (Na-HCO_3 and NaCl type groundwater).

The conceptual diagram of bedrock groundwater discharge in Inokawa, obtained from the results was shown in Figure 2.10. Bedrock groundwater percolated into deeper bedrocks with changing water chemistry. It discharged as altitude decreased. Type-B began to discharge below 170m, and type-C began to discharge below 150m. The recharge points of these deep bedrock groundwater were not only in zero-order hollows or side slopes but also in main streams(> 2-3km^2) at low altitudes. As a result, bedrock groundwater discharge increased as catchment area increased averagely. And deeper bedrock groundwater, which infiltrated and went through deeper bedrock, began to discharge with catchment area increase.

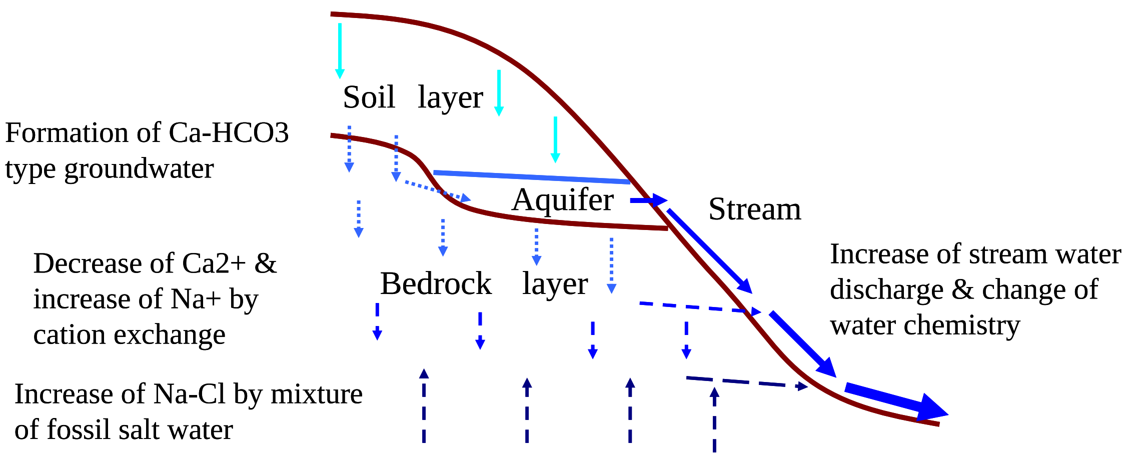


Figure 2.10 Conceptual diagram of discharge process of bedrock groundwater in Inokawa

2.4.2 Relationship between variation of bedrock groundwater discharge and catchment scale

Two types of results have previously been reported about relationships between bedrock groundwater discharge and catchment area. One is bedrock groundwater increased with catchment area (Shaman *et al*., 2004), and another is the decreased case (Uchida and Asano, 2010). It has not been confirmed whether bedrock groundwater increase. The results showed the relationships between bedrock groundwater discharge and catchment area differed much among catchments. Bedrock groundwater had large variability in small catchments, but it averagely increased with catchment area in Inokawa. And the contributions of three types of bedrock groundwater changed with catchment area (Fig. 2.7.a). In Yozukugawa, obvious increase of bedrock groundwater was not confirmed (Fig. 2.7.b). And, in Kusaki, it slightly increased to about 0.3km^2 (Fig. 2.7.c).

In weathered granite catchments, which Uchida and Asano (2010) targeted, bedrock groundwater discharge increased only at hillslope (Uchida *et al*., 2005). Large deep percolation rates were observed in headwater catchments (<0.01km^2). And this deep percolation gradually recharged in small catchments (<0.05 km^2; Terajima *et al*., 1993; Kosugi *et al*., 2006). These researches all meant that bedrock groundwater increased with catchment area at hillslopes or in small catchments. However, such increase stopped soon. And so, the increase of bedrock groundwater with catchment area might not become detectable behind the variability of small catchments. So, obvious increase of bedrock groundwater might not be confirmed in weathered granite targeted by Uchida and Asano (2010).

These results suggested that the difference of bedrock groundwater discharge with catchment area among catchments reflected the difference of infiltration and recharge process of each geology. And it might be explained by the difference of hydraulic conductivity and homogeneity of bedrock. Hydraulic conductivity might determine the degree of infiltration rate into bedrock in each catchment. And It is largely different among bedrocks(Domenico and Schwartz, 1997). For example, sand stone had several order larger infiltration rate than granite (Tsukamoto, 1992). In addition, there might be the specific reasons for each catchment. For example, in Inokawa (Neogene age sedimentary rocks), several structures like fracture and fault have been well developed (Nakajima *et al*., 1981) and it might make the hydraulic conductivity higher.

Homogeneity of bedrock might form the difference of bedrock groundwater recharge process. Even in low permeable bedrock, previous studies reported the existence of deep bedrock groundwater (e.g., Fritz and Frape, 1987). Though the hydraulic conductivity is low, groundwater infiltrate and is stored into bedrock for a long time. There should be the difference among catchments about whether the groundwater recharges or not. Bedrock groundwater moves with Darcy's law and with hydraulic head(Domenico and Schwartz, 1997). Some research showed bedrock groundwater movement from model calculation (Tóth, 1963; Freeze and Witherspoon, 1967). Heterogeneity of bedrock influences spatial variability of hydraulic conductivityin the bedrock and also influences the formation of hydraulic head. If the bedrock is uniform, hydraulic conductivity in the bedrock has spatial variability (Domenico and Schwartz, 1997). If there exists several types of bedrock, the spatial variability of hydraulic conductivity becomes larger. If geology is homogeneous like plutonic rocks and volcanic rocks, hydraulic conductivity is comparatively homogeneous, and the moving direction of groundwater in bedrock is thought to be downward or lateral direction. However, if geology is heterogeneous like sedimentary rocks, hydraulic conductivity is heterogeneous, and water might infiltrate and go through higher permeable layer preferentially. It might form artesian groundwater sandwiched by impermeable layers and might move upward. Therefore, heterogeneous bedrock would have higher possibility for bedrock groundwater to recharge than homogeneous bedrock.

Shaman *et al.,* (2004) discussed whether big basins are just the sum of small catchments. In Inokawa and in Kusaki moving average of groundwater contribution and discharge increased as streams flew down and catchment area increased. However, in Yozukugawa, the bedrock groundwater discharge did not increase. My answer to their question was that it depends on bedrock geology. And, in all catchments, maximum and minimum values of bedrock groundwater discharge were observed in small catchments smaller than 0.1km^2. Therefore, even in catchments, where bedrock groundwater increased with catchment area, thinking spatial variability of small catchments has important meanings as Uchida and Asano (2010) pointed. Even in such catchments, stream discharge and chemistry of large scale catchments may be predicted from minimum observations of small scale catchments.

2.5 Conclusion

The results showed that the relationship between bedrock groundwater discharge and catchment area was different among catchments with different geologies. Bedrock groundwater increased averagely with catchment area in Inokawa and in Kusaki. Especially in Inokawa, deeper bedrock groundwater sometimes began to discharge and increase as catchment area increased. However, bedrock groundwater did not increase with catchment area in Yozukugawa. It is because the variability in small catchments cover over the weak signal of bedrock groundwater increase in such catchments. The infiltration rate and homogeneity of the bedrock is thought to influence the bedrock groundwater discharge rate. Especially, sedimentary rocks, which include sand stone and tuff, have high infiltration rate and much heterogeneity, and have large bedrock groundwater discharge. Therefore, when we think about the relationships between catchment area and spatial variability of stream water discharge and chemistry, we should consider the difference of bedrock geology.

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Chapter 3

Nitrate and phosphate uptake in forest streams in Japan

3.1 Introduction

Streams transport nutrients, such as nitrate (NO_3^-) and phosphate (PO_4^{3-}), which are introduced by precipitation and production in soils, and then supply them to lakes and seas. These nutrients are also produced in streams by mineralization of organic matter. At the same time, algae and microbes in streams absorb nutrients. Therefore, they are thought to undergo repeated absorption and release as they flow downstream. This has been recognized as the “Nutrient Spiral Concept” (Newbold *et al*., 1982). Nutrient uptake and release in streams are among the factors determining nutrient supply to lakes and seas. For example, in one stream in North America, only 20% of the NO_3^- that was loaded by precipitation and production in the soil layer was transported to the sea (Howarth *et al*., 1996). Nutrient uptake and release also influence the temporal and spatial variability of stream nutrient concentrations (Alexander *et al*., 2000; Mulholland, 2004).

Since the 1980s, nutrient addition experiments, which measure the nutrient uptake rate directly in actual streams, have been performed in many streams and rivers (e.g., Davis and Minshall 1999; Hall *et al*., 2002 and Simon *et al*., 2005). Mulholland *et al*. (2008) investigated the NO_3^- uptake velocity, which shows the vertical downward uptake speed (Vf; mm/min), in 72 streams in North America, and showed that it varied across four orders of magnitude (about 0.06 – 60 mm/min) in forest, agricultural, and urban streams. Several studies also indicated that the PO_4^{3-} uptake velocity variability was large (about 0.006 – 11.6 mm/min; Hall *et al*., 2002; Doyle *et al*., 2003; Ryan *et al*., 2007).

Many studies have discussed the factors that determine nutrient uptake and its variability, including the nutrient concentration (Doods *et al*., 2002; Mulholland *et al*., 2008), light levels (Mulholland *et al*., 2006), gross primary production (Hall and Tank, 2003; Fellows *et al*., 2006; Roberts and Mulholland, 2007), physical conditions (Hall *et al*., 2002; Doyle *et al*., 2003; Ryan *et al*., 2007), and time after flooding (Marti *et al*., 1997). These results showed that the determining factors may differ among streams, or there may be multiple factors in each stream.

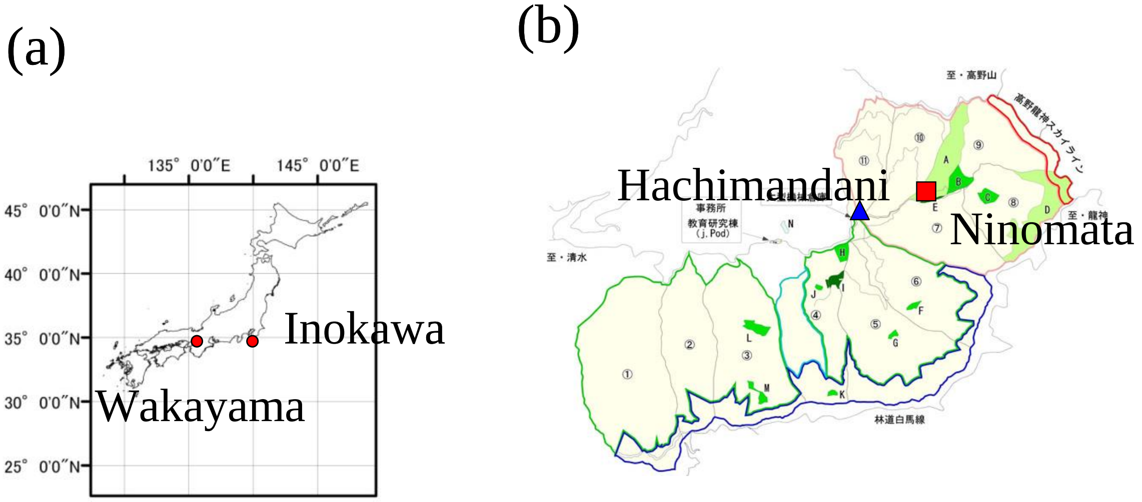
Few studies have directly measured the nutrient uptake in streams in Japan. Tanio *et al*. (2009) confirmed comparable uptake velocities for PO_4^{3-} in foreign streams (0.58 – 2.95 mm/min), while NO_3^- uptake only occurred once. They suggested that the NO_3^- uptake rate was determined by the discharge rate, because the only time that NO_3^- uptake occurred was under extremely low flow conditions. If their hypothesis is true, in drought periods the NO_3^- and PO_4^{3-} uptake should have a marked influence on the spatial variability of NO_3^- and PO_4^{3-}. However, this hypothesis has yet to be verified. In addition, generally, streams in Japan are steeper than the streams of Europe and America. Climatic conditions are quite different between Japan and the other sites, where previous studies were conducted. Therefore, we should not simply extrapolate previous results to streams in Japan, and it is necessary to obtain sufficient knowledge regarding nutrient uptake rate and characteristics in Japanese streams.

Nutrient uptake was examined in two streams in Japan. Nutrient addition experiments were conducted in two experimental sections in each stream. Indoor nutrient addition experiments were also conducted. This chapter presents quantitative results regarding the nutrient uptake in two streams in Japan, and discussed the influence of environmental factors (including discharge rate) on nutrient uptake characteristics.

3.2 Methods

3.2.1 Site description

Nutrient addition experiments were conducted at two sites, i.e., the Aridagawa catchment in Wakayama prefecture and the Inokawa catchment in Chiba prefecture (Fig. 3.1). Two experimental sections were established in each catchment (Ninomata and Hachimandani in Aridagawa catchment, and Huchi and Se in Inokawa). The Aridagawa catchment lies in the Wakayama experimental forest of Kyoto University (34°04′ N, 135°31′ E). It is the uppermost stream of Yugawa River, which is a sub-stream of Arida River. The altitude range is 455 to 1261 m. The location of the experimental sections is shown in Figure 3.1.b. The geology is Mesozoic-age sedimentary rocks. The soil layer is relatively deep, rudaceous, rich in organic matter, and comparatively fertile. The streambeds are almost completely covered by coarse fragments. Little sand or clay sediment was present on the streambed. The annual temperature was 12.3°C (1971 – 2000), and the annual precipitation was 2647 mm (1971 – 2000). Much rainfall occurred in summer. From April to September, the mean monthly precipitation surpassed 200 mm. The site characteristics of Inokawa were described in Chapter 2. The location of the experimental sections is shown in Figure 3.1.c.



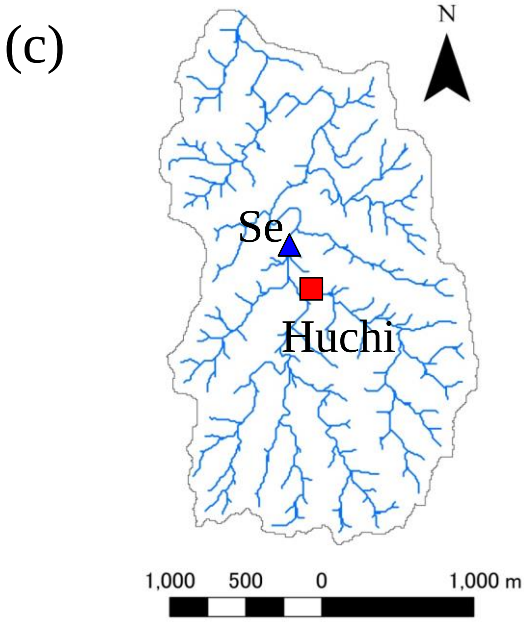


Figure 3.1 (a) Locations of the Wakayama and Inokawa catchments. (b) Experimental sections in Wakayama. The square shows Ninomata, and the triangle indicates Hachimandani. (c) Experimental sections in Inokawa.

3.2.2 Nutrient addition experiment

Nutrient addition experiments were conducted six times in Ninomata (2010/6/11, 8/11, 9/29, 2011/8/31), four times in Hachimandani (2010/8/11, 10/2), eight times in Huchi (2010/9/14, 9/15, 2011/1/19, 6/1, 8/24), and twice in Se (2011/1/20).

First, 10 L of stream water was stored in a reservoir. NO_3^- ($NaNO_3$), PO_4^{3-} ($KH_2PO_4^3$), and NaCl were added in solution using a pump (Fig. 3.2). During the addition, the electrical conductivity (EC) was measured continuously and whether the stream water chemistry reached a steady state was assessed. Near the point of addition, the EC was observed and stream water was sampled every few meters (Fig. 3.2). These samples were filtered in the laboratory, and frozen until analysis. NO_3^- and PO_4^{3-} were analyzed using an Auto Analyzer (BL-Teck, AA-III) in the Field Science Education and Research Center of Kyoto University. Cl was analyzed by ion chromatography.

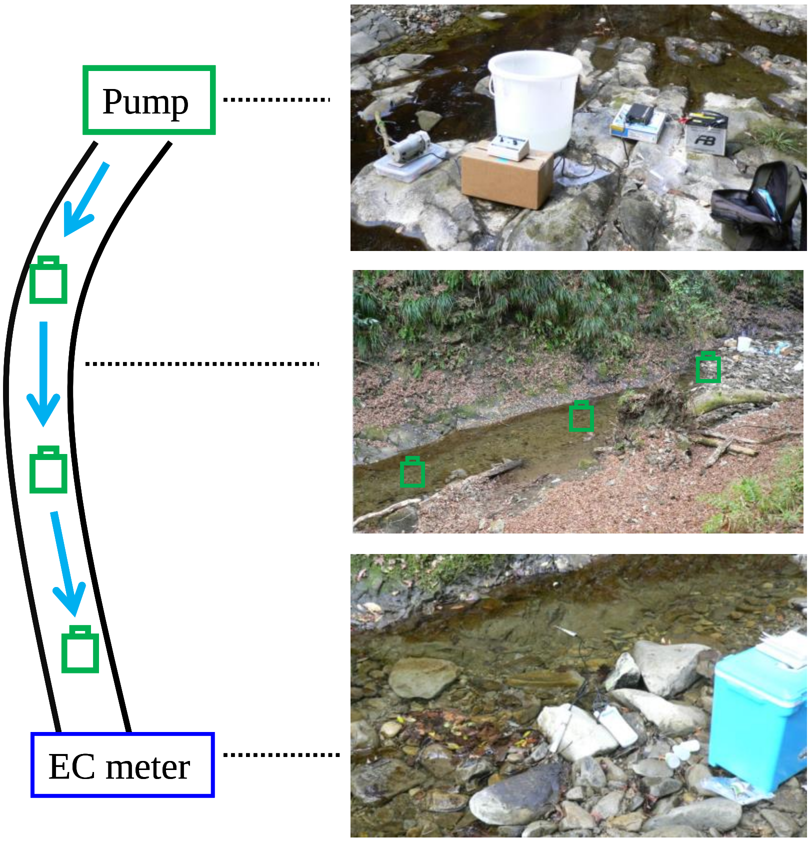


Figure 3.2. Schematic and photographs of the nutrient addition experiment.

3.2.3 Indoor nutrient addition experiment

Indoor nutrient addition experiments were conducted in 2012/1/25 – 26 at Kiyosumi in the Chiba experimental forest. Schematic and photographs of the indoor nutrient addition experiment was shown in Figure 3.3.About 100 L of stream water was stored in the reservoir, into which was placed a cylindrical plastic tube (diameter 38 mm, length 60 cm) containing nine pieces of tile (3 cm × 4 cm), which were left in the stream for three weeks. The plastic tube was then filled with stream water and sealed with a plug. NO_3^- (PO_4^{3-} in some experiments) was injected with a syringe. For five minutes, water was circulated by a pump without light, after which the water was sampled with a syringe. Water was then circulated by a pump with light. After 1 h, the pump was stopped, the light was turned off, and the water in the plastic tube was sampled. At the same time, the dissolved oxygen (DO) was measured in the reservoir and in the plastic tube. The decrease of DO, when the light was zero, can be regarded as ecosystem respiration (ER). I calculated the gross primary production (GPP), when the light was not zero, as the sum of the change of DO and the value of ER. Different tiles were used for each experiment. NO_3^- and PO_4^{3-} concentrations were quantified using an Auto Analyzer (BL-Teck, AA-III) in the Field Science Education and Research Center of Kyoto University.

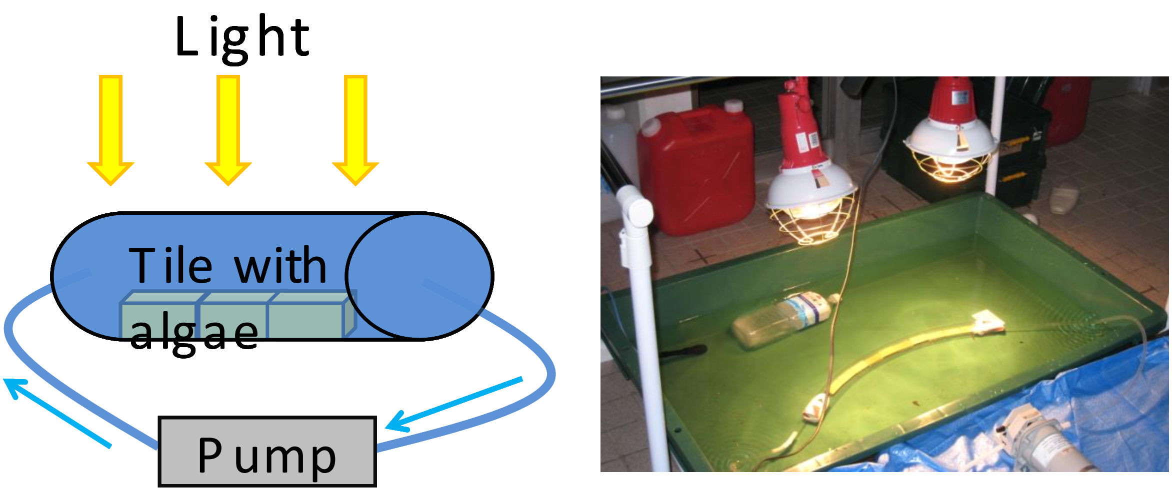


Figure 3.3. Schematic and photographs of the indoor nutrient addition experiment.

3.2.4 Mathematical analysis for field experiment

Two indices were used to evaluate the nutrient uptake rate outside the nutrient addition experiments, i.e., the uptake length (S_w: m) and the uptake velocity (Vf: mm/min). The uptake length (S_w: m) was calculated from the relationship between the logarithmic values of standardized change of concentration and the distance from the nutrient addition points.

$$S_w = -\Delta\left[\ Log\left(\frac{N_{add} - N_{ambient}}{C_{add} - C_{ambient}}\right)\ \right] / \Delta x \qquad (1)$$

In Equation (1), N_{add} is the concentration of nutrients after addition and $N_{ambient}$ is that before addition. C_{add} is the concentration of conservative tracer (EC or Cl^-) after addition and $C_{ambient}$ is that before addition. Then, x means the distance from injection point. If this value decreases downstream, it shows that nutrients are absorbed. If it increases downstream, this means that nutrients are released (Fig. 3.4).

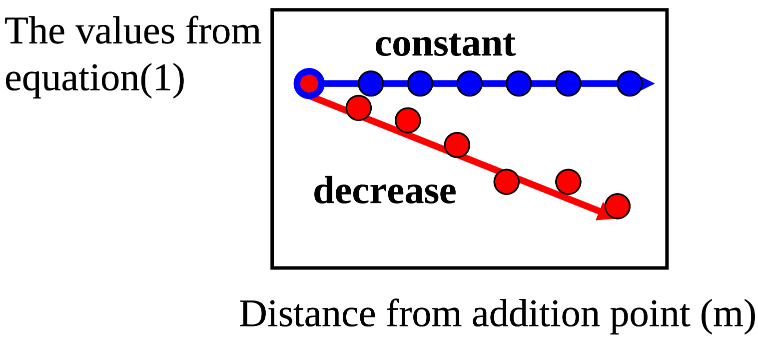


Figure 3.4 Schematic of the uptake length calculation. If the slope of this linear relationship is negative, uptake occurs. The inverse of the slope is the uptake length.

Linear regression relationships between the standardized change in the above equation of nutrients and flow-down distance were calculated. The inverse of the slope of this relationship is defined as the uptake length (S_w: m). Each experiment was defined as having an increasing or decreasing tendency if the correlation coefficient (R^2) of each was higher than 0.2. If R^2 was lower than 0.2, the experiment was regarded as having no significant tendency.

The uptake velocity (Vf: mm/min) was expressed using S_w as

$$V_f = \frac{Q}{S_w w}, \tag{2}$$

where Q is the discharge rate (m^3/s), w is stream width (m). S_w means the distance that nutrients in the stream flow until they are absorbed. Vf is the velocity at which nutrients are absorbed (sink down). Lower S_w values and higher Vf values imply a greater nutrient uptake rate.

The physical parameters of the stream were calculated by fitting the change of EC with one-dimensional transport with the inflow and storage model (OTIS model: Bencala and Walters, 1983). The OTIS model is based on the one-dimensional advection-diffusion equation. This model hypothesizes the existence of a transient storage zone along the river. It considers the stream flow and water exchange between the stream and storage zone. Four parameters were calculated: the diffusion coefficient (D; m^2/s), the main channel cross-sectional area (A; m^2), the cross-sectional area of the transient storage zone (As; m^2), and the storage zone exchange coefficient (α; /s). In this chapter, D and the ratio of As divided by A (As/A) were used. D is an index that describes the degree of mixing of stream water.

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \alpha(C_S - C) \tag{3}$$

$$\frac{dC_S}{dt} = \alpha\frac{A}{A_S}\left(C - C_S\right) \tag{4}$$

Here, C is the concentration of EC in stream (μS/cm) and Cs is the concentration of EC in the storage zone (µS/cm). Q is the discharge rate (m^3/s), t is time (s), and x is distance in the downstream direction.

3.3 Results

3.3.1 Physical properties of experimental sections

Physical parameters were calculated using the OTIS model. Physical parameters could not be detected in only two experiments (2010/9 and 2011/1 in Huchi). As an example, one result (from Ninomata in 2010/6) is shown in Figure 3.5.

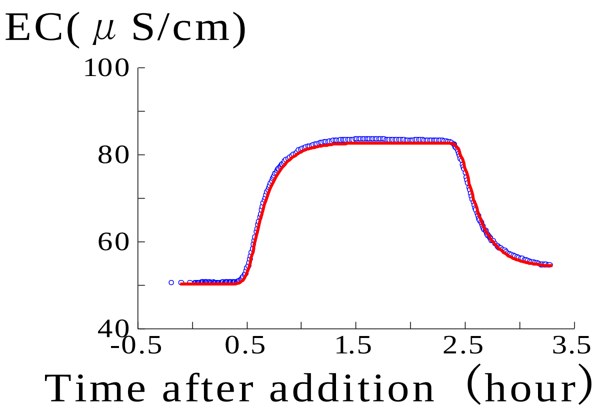


Figure 3.5 Results of the calculation with the OTIS model. Blue points are the observed change of EC. The red line shows the EC calculation.

Even in the same section, D varied among the observed times. Each section was classified, although there was considerable variability. Ninomata had high D and high As/A. The As/A in 2010/6 at Ninomata was lower than the following three observations. In Ninomata, sand and gravel were supplied by precipitation in 2010/6 – 8. Hence, the obstacles in the stream may have increased, thus increasing the value of As/A. Hachimandani had a large discharge and D and small As/A. However, in Huchi, parameters could not be obtained at several time points, because of the low D values. The whole trend of Huchi was toward low D and large As/A. In 2011/6, it had rained just before the experiment, and so D in Huchi was also large. Se had low values of D and As/A.

Table 3.1 (a) Results of physical parameters calculated from the OTIS model. D is the diffusion coefficient (m^2/s), and As/A is cross-sectional area of the transient storage zone divided by the main channel cross-sectional area (m^2/m^2). (b) Classification of the experimental sections from physical parameters.

(a)

Study site	Observation date	D (m^2/s)	As/A (m^2/m^2)
Ninomata	2010/6/11	0.16	0.18
Ninomata	2010/8/11	0.89	0.49
Ninomata	2010/9/29	0.25	0.36
Ninomata	2011/8/31	0.40	0.25
Hachimanadni	2010/8/11	0.39	0.11
Hachimanadni	2010/10/2	0.42	0.12
Huchi	2010/9/14	0.05	0.28
Huchi	2010/9/15	NA	NA
Huchi	2010/1/19	NA	NA
Huchi	2011/6/1	0.29	0.35
Huchi	2011/8/24	0.02	0.44
Se	2011/1/20	0.04	0.17

(b)

		As/A	
		small	large
D	small	Se	Huchi
	large	Hachimandani	Ninomata

3.3.2 Nutrient addition experiment

The results of the field nutrient addition experiments are shown in Figure 3.6. The results on the *y*-axis of this graph were calculated from equation (1). A decrease in this value downstream indicates nutrient absorption, while an increase downstream indicates nutrient release.

In six experiments in Ninomata, NO_3^- uptake was detected only once (2010/6). Four experiments did not show any tendency (twice in 2010/8, and in 2010/9 and 2011/8). NO_3^- emission was observed once (first time in 2010/8). In other cases, NO_3^- uptake was also rare (Fig. 3.6).

The differences in PO_4^{3-} between the two catchments were significant. In Ninomata and Hachimandani, PO_4^{3-} was always absorbed. In Huchi and Se, PO_4^{3-} was absorbed three times in all ten experiments. Uptake of NO_3^- and PO_4^{3-} did not occur in most experiments. Both nutrients were absorbed simultaneously only twice (2010/6 in Ninomata and 2010/8 in Hachimandani).

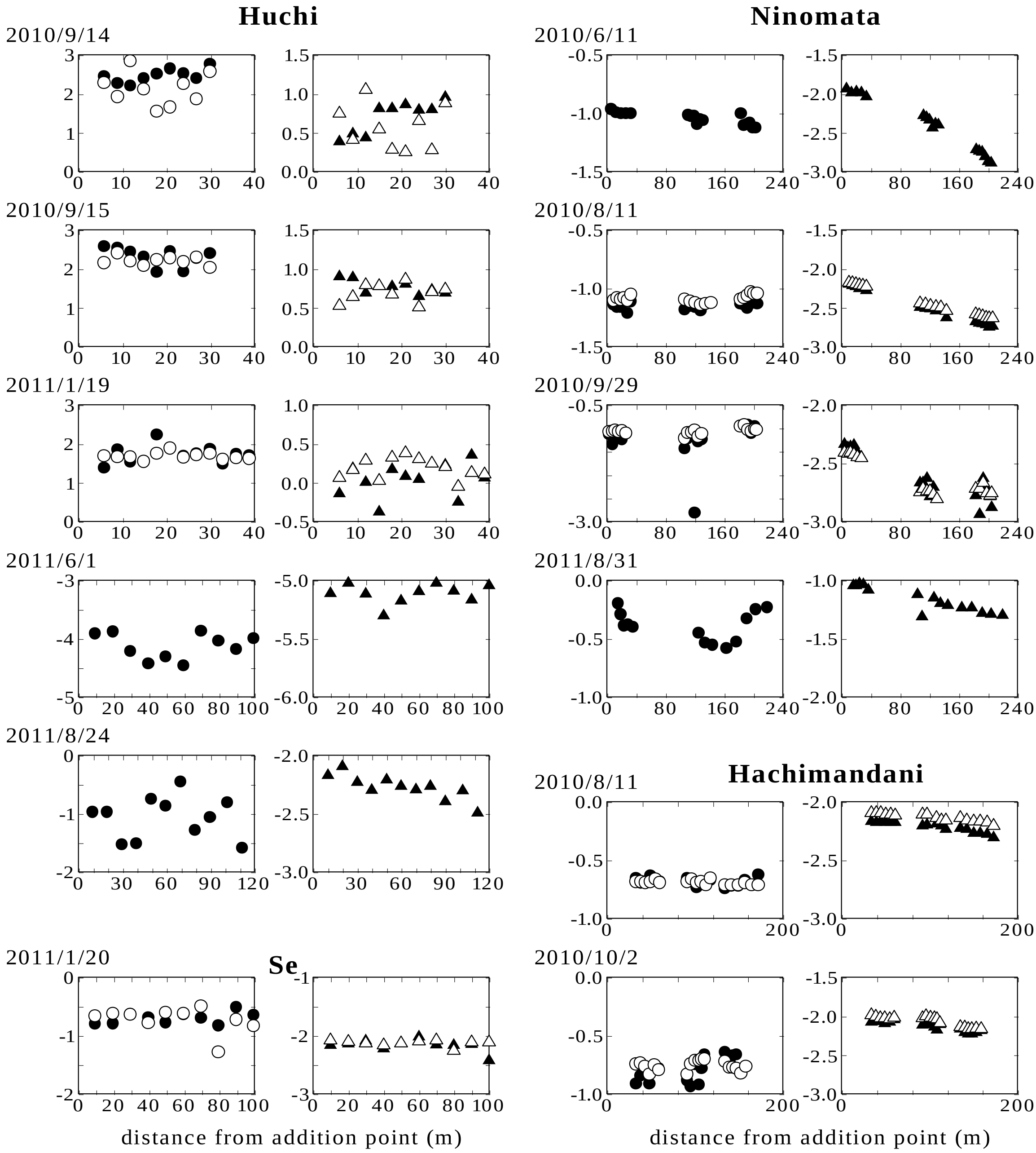


Figure 3.6 Results of the nutrient addition experiments. Circles show nitrate and triangles show phosphate. The solid and open marks indicate the first and second experiments in that day, respectively.

When uptake occurred, the uptake velocities of NO_3^- were 1.33 mm/min in Huchi, 0.81 mm/min in Ninomata, and 0.39 mm/min in Hachimandani. These values were within the ranges of previous studies conducted in North America (0.06 – 60 mm/min; Mulholland *et al*., 2008). Ninomata showed a higher uptake velocity of PO_4^{3-} (2.03 – 6.46 mm/min) than Hachimandani (1.15 – 2.02 mm/min). These values were also within the ranges reported previously (0.006 – 11.6 mm/min; Hall *et al*., 2002; Doyle *et al*., 2003; Ryan *et al*., 2007). PO_4^{3-} uptake was not always observed in two sections in Inokawa. However, when PO_4^{3-} uptake occurred in these two sections, the uptake velocities had similar values (0.77 mm/min and 0.94 mm/min in Huchi, and 1.69 mm/min in Se).

The NO_3^- and PO_4^{3-} uptake velocities were compared according to environmental factors, discharge rate, D, As/A, water temperature, and ambient concentration (Fig. 3.7). In addition, in Huchi and in Se, comparisons were made with solar radiation measured at a meteorological station (the station location is shown in Chapter 2, Figure 2.1). Positive values on the *y*-axis indicate nutrient uptake, a zero value shows that the experiment had no significant tendency, and negative values indicate nutrient emission.

Environmental factors showed no significant relationships with NO_3^- uptake or emission. With regard to PO_4^{3-}, the relationships to water temperature and As/A were ambiguous. However, positive relationships with discharge and D were observed. In addition, there was a negative relationship with ambient concentration.

The NO_3^- uptake was caused by biological factors, i.e., assimilation by algae and microbes as well as denitrification. However, phosphorus uptake also occurred by physical absorption in addition to the biological factors. NO_3^- and PO_4^{3-} were not always absorbed together (Fig. 3.6). PO_4^{3-} uptake was much more frequent than NO_3^- uptake. Therefore, it was speculated that PO_4^{3-} uptake was mainly derived from physical absorption.

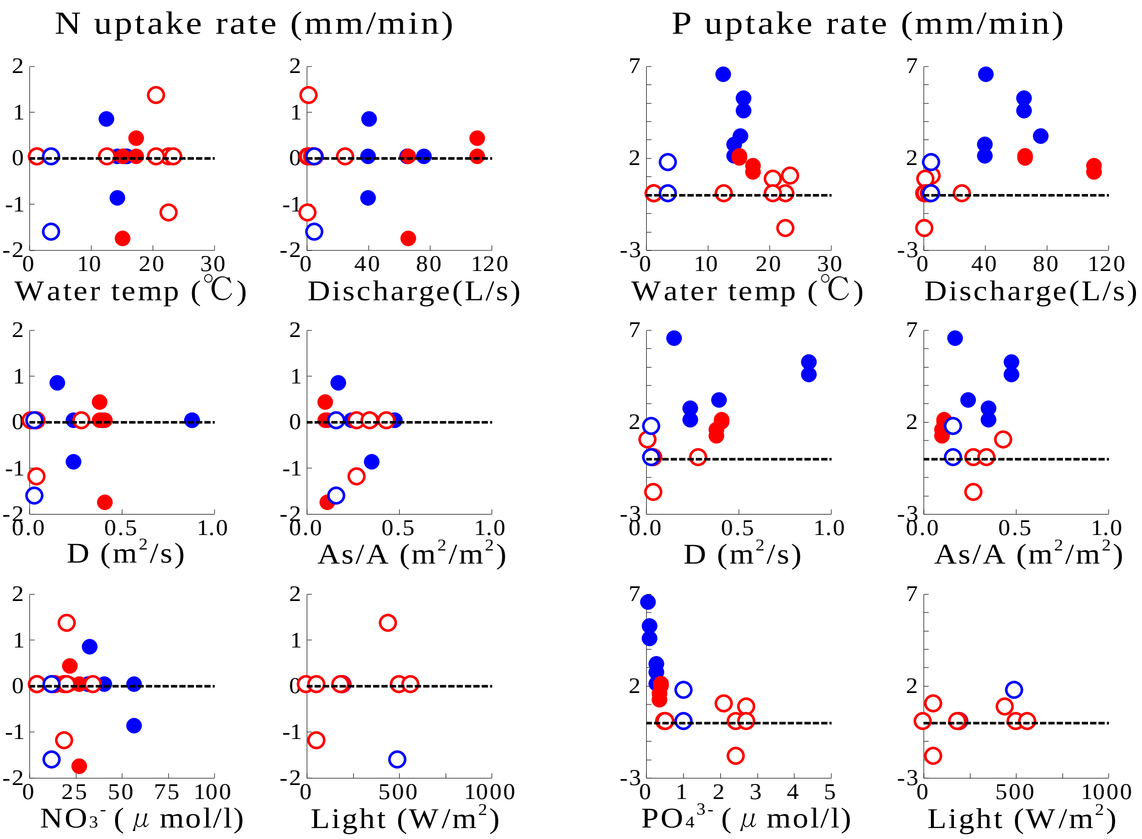


Figure 3.7 Relationships between uptake rate and environment settings. Blue solid and red solid circles show Ninomata and Hachimandani, respectively. Red open and blue open circles show Huchi and Se, respectively. Dashed lines indicate zero value of uptake rate.

In addition, the values of photosynthetically active radiation (PAR) in Ninomata in 2011/8 are shown in Figure 3.8. On the road, which was slightly removed from the section, the PAR value was about 300 μmol/m²/s. However, the PAR values in the stream were much lower. Most sampling points were around 10 μmol/m²/s. A few points over which there was no tree canopy showed values of 50 – 80 μmol/m²/s. Thus, the light intensity around the experiment was not as high as outside.

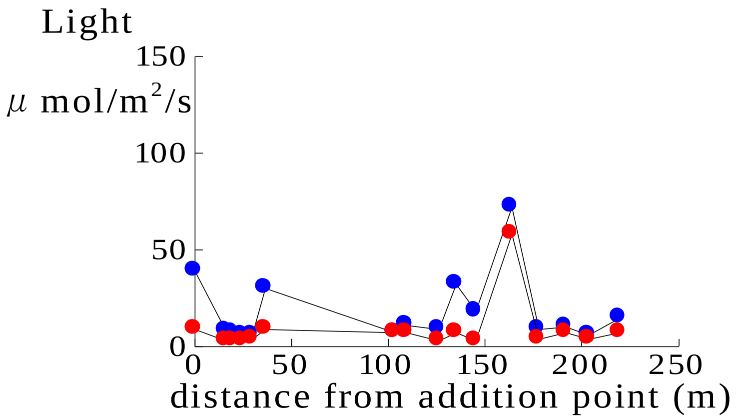


Figure 3.8 Light conditions in Ninomata on August 31, 2011. The blue and red circles correspond to values before and after addition, respectively.

3.3.3 Indoor nutrient addition experiment

The results of the indoor nutrient addition experiment are shown in Figure 3.9. There were differences in NO_3^- between before and after the experiments. The NO_3^- concentration was increased by addition of NO_3^-. Therefore, in this graph a lower increase in NO_3^- concentration indicates higher NO_3^- uptake. As the light increased, the gross primary production (GPP) became markedly stronger. The NO_3^- uptake rate also became slightly larger using the average value of each light intensity.

The highest light intensity applied was as strong as that outside on a cloudy day. This was in the light intensity range of the experiment. The PO_4^{3-} concentrations were too low to quantify. However, the GPP and NO_3^- uptake did not increase as PO_4^{3-} was added. In addition, a slight increase in flow velocity caused a large increase in GPP, although there was no obvious influence of flow velocity on NO_3^- uptake (Fig. 3.10).

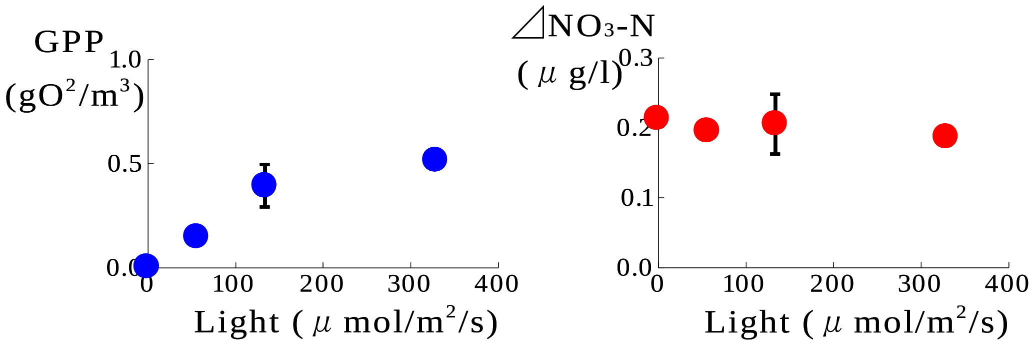


Figure 3.9 Results of the indoor nutrient addition experiment. The blue points show the relationships between GPP and light intensity. The red points show the change in relationship of NO3-N and light intensity.

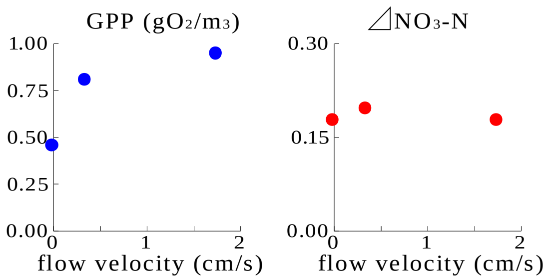


Figure 3.10 Influences of flow velocity on GPP and nitrate uptake.

3.4 Discussion

3.4.1 Determining the mechanism of nitrate uptake

Many nutrient addition experiments did not show obvious NO_3^- uptake (Fig. 3.6). This indicated that the NO_3^- uptake rate did not increase with the NO_3^- concentration. Some groups reported a positive relationship between GPP and NO_3^- uptake (Hall *et al*., 2003; Fellows *et al*., 2007; Roberts and Mulholland *et al*., 2007). Therefore, factors other than NO_3^- concentration should limit the increase in GPP and NO_3^- uptake. These factors are discussed below.

Discharge rate and physical environment

Tanio *et al*. (2009) speculated that the flow condition is the main factor determining the NO_3^- uptake rate. Several groups reported the influence of discharge rate on NO_3^- uptake length (S_w; Doods *et al*., 2002; Tank *et al*., 2010). However, the results of the present study showed that NO_3^- uptake did not occur so often under low-flow conditions or in sections with low discharge rates (Fig. 3.7). In addition, in indoor experiments, a small increase in flow velocity discharge markedly increased GPP (Fig. 3.10).

The low discharge rate may prolong the transient time in streams and increase the possibility of uptake. In indoor experiments, the differences in experimental time (30 min – 1 h) were compared under the same light conditions. The GPP in 1-h experiments was about double than in the 30-min experiments (not shown). These results suggested that the high discharge rate caused the NO_3^- uptake to be less detectable. However, only a low discharge may not markedly improve GPP and NO_3^- uptake.

The NO_3^- uptake had no significant relationship to D or As/A (Fig. 3.7). A greater As/A value indicates a longer residence time in the stream. However, if the uptake rate was too small, a twofold increase in residence time may not cause obvious increases in GPP and NO_3^- uptake. Hence, other factors may play more important roles in determining the NO_3^- uptake rate.

Phosphate concentration

NO_3^- uptake is caused by biological factors: assimilation by algae and microbes as well as denitrification. However, phosphorus uptake also occurs due to physical absorption in addition to the biological factors. NO_3^- and PO_4^{3-} were not always absorbed together (Fig. 3.6). PO_4^{3-} uptake was much more frequent than NO_3^- uptake. Therefore, we speculated that PO_4^{3-} uptake was mainly derived from physical absorption.

In benthic algae, if the N:P ratio is < 10 with the mole ratio, N limits the growth. Conversely, if the N:P ratio is > 20, P limits the growth. In the range from 10 to 20, the limit is ambiguous (Shanz and Juon, 1983). The N:P ratios (NO_3^-:PO_4^{3-} ratios) were 7 – 26 in Inokawa and 56 – 360 in Aridagawa. From the above-mentioned threshold, the P limit may sometimes occur in Inokawa, and should always occur in Aridagawa. However, sufficient amounts of NO_3^- and PO_4^{3-} were always added simultaneously in this study. If PO_4^{3-} limits the GPP in streams, addition of PO_4^{3-} should increase GPP and NO_3^- uptake. In the indoor experiments, the PO_4^{3-} concentration was below the limit of detection, but GPP and NO_3^- uptake did not show obvious responses to addition of PO_4^{3-}. This suggested that the necessary PO_4^{3-} may have already been supplied.

Light

The light conditions were measured in only one experiment, and the light intensity was shown to be not as high as that outside (Fig. 3.8). Some groups have reported that light limits GPP and NO_3^- uptake (Mulholland *et al*., 2006; Fellows *et al*., 2006) in well-shaded streams. Generally, mountainous streams in Japan have steep side slopes. The light conditions of mountainous streams are thought to be poorer than those of flat streams, because their topography (especially the side slopes) hinder light propagation. In indoor experiments, under the same range of light conditions, algae showed an obvious response to light irradiation, and the NO_3^- concentration decreased markedly (Fig. 3.9). Therefore, light is speculated to be an important limiting factor for

GPP and NO_3^- uptake.

Disturbance

The disturbance was not quantified in this study. However, at the study site, the annual precipitation was over 2000 mm and was influenced by the rainy season or typhoons. In Ninomata, large nutrient uptake was observed in July 2010, but the precipitation derived by the typhoon supplied a large amount of sand and gravel after this observation. In Inokawa, a large amount of sand and sometimes logs were also supplied frequently to streams. These disturbances may flush algae and microbes with sand and gravel and make it difficult for them to become established for prolonged periods. In Ninomata, Sato *et al*. (2012) reported 3.8 mg/m^2 of chlorophyll *a* algae (maximum value from August to October 2010). This was a comparatively low value compared to other areas where nutrient addition experiments were conducted (Hill *et al*., 2001; Simon *et al*., 2005).

The disturbance may be related to NO_3^- uptake under extremely low-flow conditions reported by Tanio *et al*. (2009). That is, extremely low-flow conditions mean long periods of drought. Marti *et al*. (1997) reported that the NO_3^- uptake rate was reduced after floods and then recovered gradually. In that time, algae and microbes may recover from the influence of the disturbance. NO_3^- uptake could occur if light conditions improve under such conditions.

3.4.2 Influence of physical characteristics on adsorption of phosphate

The results indicated that most PO_4^{3-} uptake was due to physical adsorption. PO_4^{3-} uptake showed a positive relationship with discharge rate and D. However, the relationship to As/A was ambiguous (Fig. 3.7). The relationships between PO_4^{3-} uptake velocity and As/A were also examined in previous studies, and no significant relationships were observed between the two (Hall *et al*., 2002; Ryan *et al*., 2007). As mentioned above, larger As/A values indicate a longer residence time in streams. Longer residence times increase the opportunity for NO_3^- and PO_4^{3-} concentrations to change by uptake and adsorption. However, factors other than biological uptake may play important roles. Therefore, one reason for the weak relationship between PO_4^{3-} uptake and As/A may be the influence of biological uptake.

The results from 2010/6 in Ninomata showed the most obvious NO_3^- uptake and highest uptake velocity of PO_4^{3-} (Vf = 6.46 mm/min). This experiment departed from the positive line in the relationships between PO_4^{3-} uptake and D or discharge rate (Fig. 3.7). These results suggested that biological uptake may have been active and of a similar degree to physical absorption in this experiment. Conversely, in other experiments, physical absorption was much greater than biological uptake. Both NO_3^- and PO_4^{3-} uptake occurred in 2010/6 in Ninomata and 2010/8 in Hachimandani. Excluding these results, the relationship between PO_4^{3-} uptake and As/A showed a weak positive relationship. Considering zero or minus values of Vf, R^2 was 0.15 (n = 18), while excluding these values led to an R^2 value of 0.33 (n = 11). Hence, when physical adsorption completely controls PO_4^{3-} uptake, PO_4^{3-} uptake will show a positive relationship to As/A.

Although As/A in Huchi was higher than that in Hachimandani, the PO_4^{3-} uptake was greater in Hachmandani than in Huchi (Fig. 3.7). Another physical parameter, D, may explain these results. The stream transported dissolved matter with the water flow. The value of D shows the degree of vertical mixing of dissolved matter. Adsorption is thought to occur mainly in the stream bed. Therefore, large D may result in many opportunities for contact with the stream bed and adsorption (Fig. 3.11).

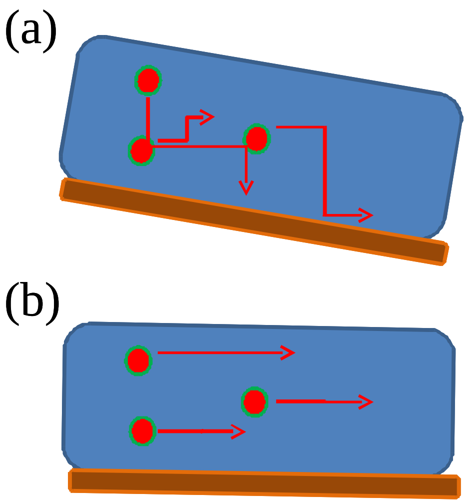


Figure 3.11 Schematic of relationships between diffusion coefficient and physical adsorption. (a) High diffusion coefficient and high adsorption. (b) Low diffusion coefficient and low adsorption.

3.5 Conclusion

NO_3^- uptake was rarely observed in the catchments examined in this study. PO_4^{3-} uptake was always observed in Aridagawa and rarely observed in Inokawa. When uptake occurred, uptake rates were within ranges reported previously. In the catchments examined here, the NO_3^- and PO_4^{3-} concentrations of stream water were high compared to biological demand in streams. Hence, the biological response to an increase of nutrient concentration would be very weak. It may be because of weak light intensity and large number of disturbance. Therefore, elucidation of biological uptake in streams may not be a valuable means of determining the spatial variability of NO_3^- and PO_4^{3-} in these catchments except for the seasons, which are suitable to algae growth like spring before leafing.

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Chapter 4

Inter-site and inter-variable comparison of confluence processes

4.1 Introduction

The confluence of two streams has a significant role in the convergence of the spatial variability and chemistry of stream discharges. At the confluence of two streams, the stream discharge rate and chemical variables can be averaged. Wood *et al*. (1988) proposed the concept of the representative elementary area (REA), which suggests that spatial variability in small catchments declines across the area of the catchment and can be ignored as a result of confluences. This concept has been used in the modeling of rainfall-runoff processes. Gradually, it has been adapted for studies of low-flow discharge (Woods *et al*., 1995) and low-flow chemistry (Wolock *et al*., 1997).

Some studies have examined REA in real catchments. For example, Woods *et al*. (1995) observed stream discharges at two catchments under low-flow conditions and examined convergences above 0.5 km^2 and 2 km^2, respectively. Wolock *et al*. (1997) showed that convergence occurred above 3 km^2 based on six variables of water chemistry. Temnerud and Bishop (2005) also found convergence in four water chemistry variables for areas larger than 15 km^2 at two catchments. Asano *et al*. (2009) reported convergence at sizes ranging from 0.1 to 1.5 km^2 based on discharge and eight water chemistry variables.

Although these studies revealed that REA values (the lower limits of REA) differ among catchments and among observed variables, detailed knowledge of confluence processes and the determining factors of REA have not been realized. In confluence processes, whether the spatial variability of stream water discharge and chemistry can be regarded as randomly distributed remains uncertain.

Two previous studies have considered this problem. Woods *et al*. (1995) compared their data on specific discharge in two catchments with a theoretical relationship that indicated a decrease in randomly distributed variables as the catchment area increased. Their results showed more rapid decrease than indicated by the theoretical relationship in both catchments. They suggested that “organization” might occur, referring to an interconnected assembly of parts and sub-parts (Denbigh, 1975). Woods *et al*. (1995) used the term to describe catchments that were organized into collections of hillslopes, channels, and other features. In a later study, Asano and Uchida (2010) compared their SiO_2 data against the same theoretical relationship. Their results differed from those of Woods *et al*. (1995). They showed that variability decreased more slowly than the theoretical relationship suggested in small catchments (under 0.01 km^2) and decreased at about the same rate as the theoretical relationship suggested in catchments above 0.01 km^2. They considered the slower decrease in small catchments to be derived from a bias in their observations. They also assumed that a mixture of randomly distributed variables approximately explained the spatial variability in their catchment.

The difference between these results highlighted the different spatial variability tendencies in the two catchments and suggested that different processes were operating in each catchment. However, it could not be concluded that the difference in their results was related to actual differences between the two catchments because the two studies observed different variables. To derive useful information from field observations, we need to recognize the differences among the variables observed and among catchments.

In Chapter 2, I showed that bedrock groundwater discharge has a large influence on the spatial variability of stream discharge and chemistry. It was also suggested that spatial patterns of bedrock groundwater and stream water vary between catchments with different bedrock geologies. Therefore, confluence processes must be compared among catchments that have different bedrock geologies.

I observed the spatial variability of stream water discharge and chemistry in three catchments with different geologies (Neogene-age sedimentary rocks, volcanic rocks, and Jurassic sedimentary rocks). I also compared confluence processes by observing different variables and different catchments using statistical methods including the theoretical relationship employed by Woods *et al*. (1995).

The objective was to clarify the impact that differences in the observed variables and in the catchments themselves have on the convergence process in catchments with different geologies.

4.2 Methods

Site description, observations, and analyses were as described in Chapter 2. The only addition was the definition of stream order. I defined the area of a first-order catchment as the average catchment area of all springs or first-order streams (Inokawa, 0.0080 km^2, n = 29; Yozukugawa, 0.0130 km^2, n = 15; Kusaki, 0.0186 km^2, n = 9). Stream order was defined by the method of Strahler (1952).

Statistical analyses

I used a moving average and moving coefficient of variance (hereafter, moving CV). In each method, the moving average and moving CV were calculated in a 10-value window moving along the sample points sorted by area (Asano *et al.*, 2009). From the moving CV, I calculated two indices, CV_{max} and $CV_{(0.3)}$, to evaluate convergence, where CV_{max} was the maximum value of the moving CV, and $CV_{(0.3)}$ was the value of the moving CV at which the average catchment area was nearest to 0.3 km^2 (Fig. 4.1).

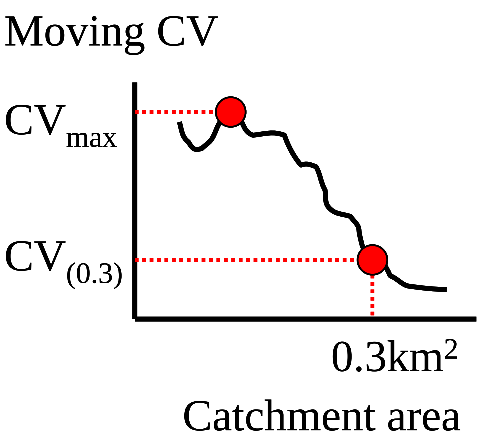


Figure 4.1 Schematic diagram of the moving CV and two indices (CV_{max} and $CV_{(0.3)}$).

Additionally, I also used random mixing theory (Woods *et al.*, 1995).

$$Var(\overline{X}_A) = \sigma^2 / A,$$

where $\overline{X}_A$ is the sample mean whose averaging area is A, and σ^2 is the variance. This equation indicates that if a random distribution is observed, the magnitude of the variability decreases at a constant rate (1/A) as the catchment area increases. I calculated standard deviations for each stream order. The theoretical relationship was plotted through the standard deviations of the highest order streams.

4.3 Results

4.3.1 Moving averages and moving CVs

Figures. 4.2 and 4.3 show the moving averages and moving CVs of specific discharge and chemical variables against catchment area. For the moving average, in Inokawa the specific discharge and the observed variables, except for NO_3^-, increased significantly. In Yozukugawa, all the observed variables were constant, with no relationship to catchment area. In Kusaki, some observed variables (Na^+ and SiO_2) increased slightly, but the others were constant. No observed variables decreased in any catchment. In the small catchments, the moving average of specific discharge in Inokawa and in Kusaki was much higher than the overall average value (<0.1–0.2 km^2, Fig 4.2).

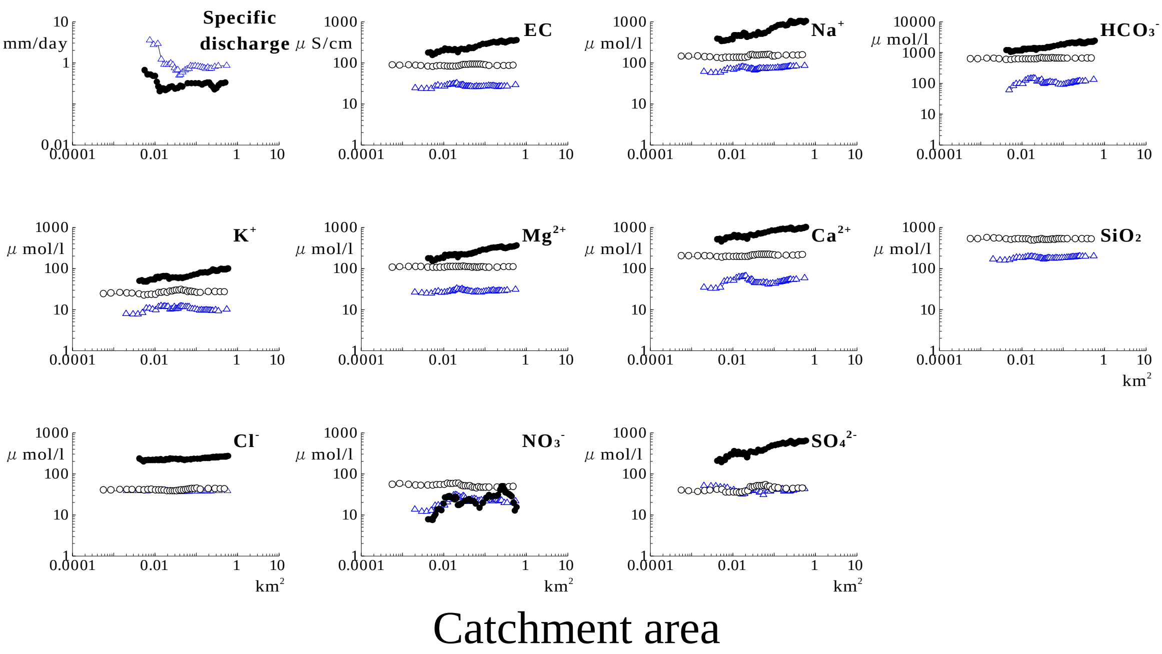


Figure 4.2 Ten-value moving average of three catchments. We used logarithmic values for both axes. Solid circles show mudstone in Inokawa. Open circles show volcanic rock in Yozukugawa. Triangles show sedimentary rock in Kusaki.

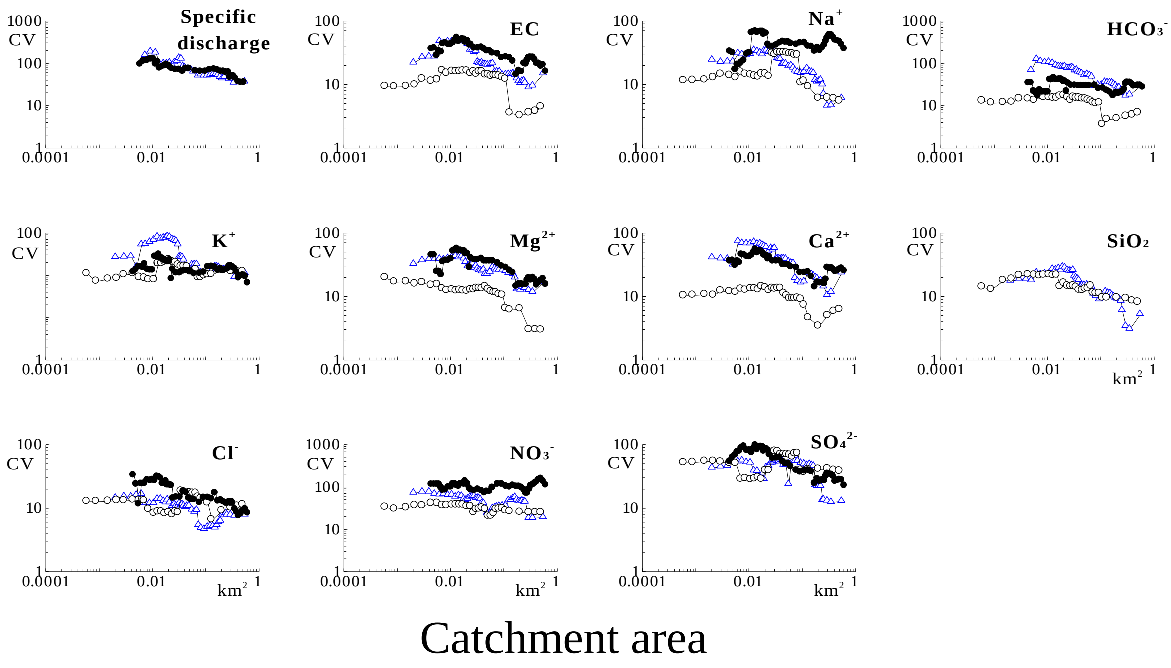
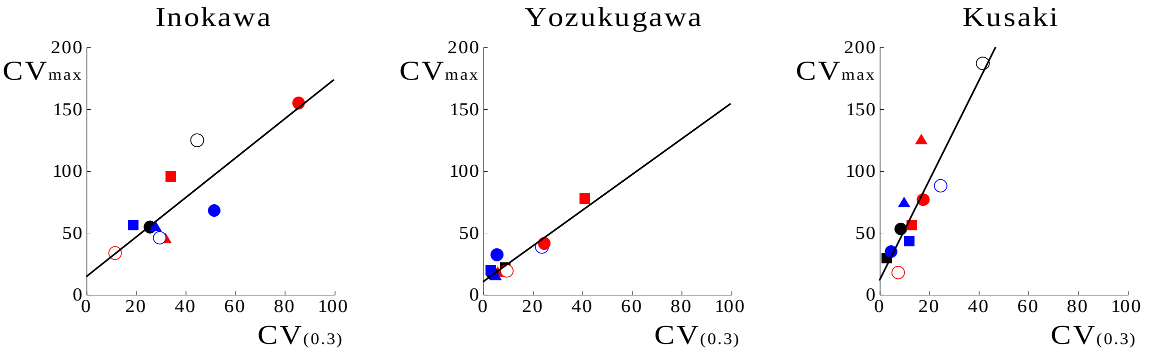


Figure 4.3 Ten-value moving CV of three catchments. We used logarithmic values for both axes. Solid circles show mudstone in Inokawa. Open circles show volcanic rock in Yozukugawa. Triangles show sedimentary rock in Kusaki.

For each geology, almost all moving CVs fluctuated and decreased gradually in relation to the catchment area. Only in Inokawa did some observed variables (Na^+ and NO_3^-) repeatedly increase and decrease, failing to decrease overall. These figures revealed no obvious tendencies among catchments. For example, for SO_4^{2-}, Yozukugawa had a higher variability than did Kusaki for almost all catchment sizes. However, for Mg^{2+}, the opposite tendency was observed.

Figure 4.4 shows the relationship between CV_{max} and $CV_{(0.3)}$ for each catchment. Each point indicates the variables observed. The ranges of CV_{max} were lowest and narrowest in Yozukugawa (CV_{max} = 29±19, n = 10). Inokawa and Kusaki had comparable ranges of CV_{max} (Inokawa = 73±39, n = 10; Kusaki = 71±49, n = 11). However, $CV_{(0.3)}$ was highest in Inokawa (36±21, n = 10), and Yozukugawa and Kusaki had similar ranges (Yozukugawa: 13±13, n = 10; Kusaki: 15±11, n = 11). The observed variables that had high CV_{max} values also had high $CV_{(0.3)}$. In every catchment, a positive linear relationship between CV_{max} and $CV_{(0.3)}$ was observed. This result indicates that variability decreases at a specific rate in each catchment. The slopes of the regression line at Inokawa and Yozukugawa were similar, but the slope at Kusaki was very different. These results indicate that the convergence at Kusaki is steeper and faster than that for the other two catchments.



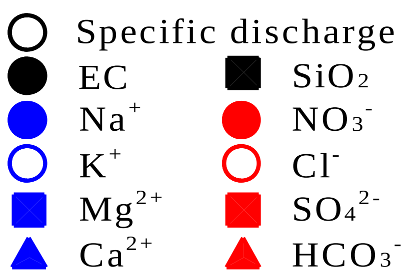
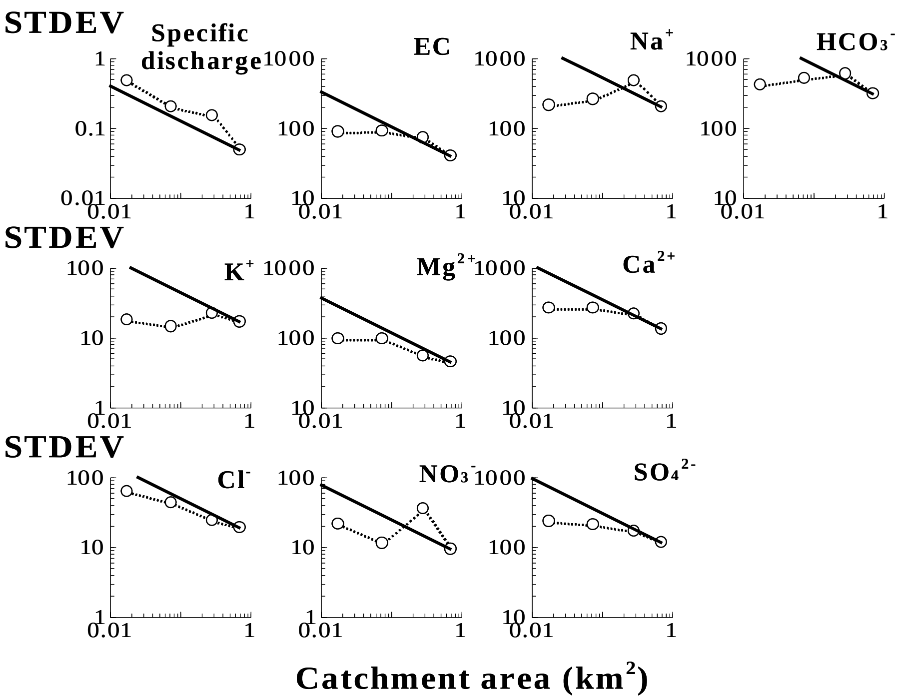


Figure 4.4 Relationship between CV_{max} and $CV_{(0.3)}$. Each point shows the observed variables. The lines show the linear regression for each catchment.

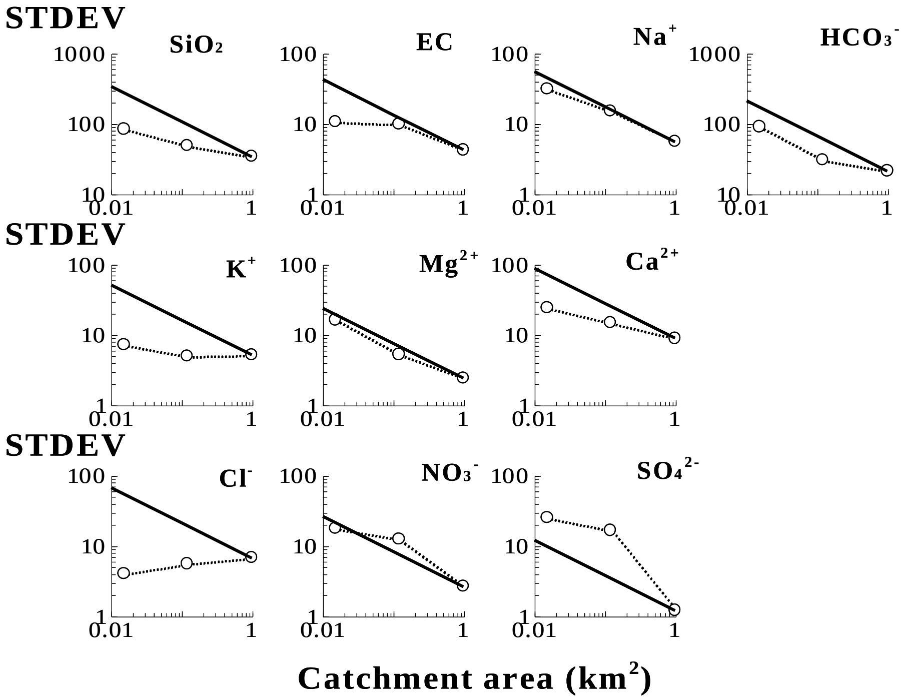
4.3.2 Comparison of the convergence of observed variables with the theoretical relationship

I compared each observed variable to the theoretical relationship (Woods *et al.*, 1995; Fig. 4.5). The standard deviation of each point was calculated for every stream order. In Inokawa, almost all of the observed variables displayed more gentle slopes than the theoretical relationship suggested. Only the slope of the specific discharge was steeper than the line representing the theoretical relationship. In Yozukugawa and Kusaki, the tendencies were slight different for dissolved matter. In Yozukugawa, EC, SiO_2, Na^+, HCO_3^-, K^+, Mg^{2+}, Ca^{2+}, and Cl^- were below the line representing the theoretical relationship, whereas SO_4^{2-} was above the line, and NO_3^- was difficult to categorize. In Kusaki, EC, SiO_2, Na^+, HCO_3^-, and Ca^{2+} were almost on the line or slightly above it. The specific discharge decreased at a faster rate than the theoretical relationship suggested, whereas Cl^- and K^+ decreased at a slower rate than the theoretical relationship suggested. NO_3^-, SO_4^{2-}, and Mg^{2+} were difficult to categorize. The results indicated differences among the observed variables, but the results suggested different tendencies among the catchments. The decrease in variability in Kusaki agreed with the theoretical relationship. However, the decreases in Yozukugawa and Inokawa were less than that suggested by the theoretical relationship.

(a) Inokawa



(b) Yozukugawa



(c) Kusaki

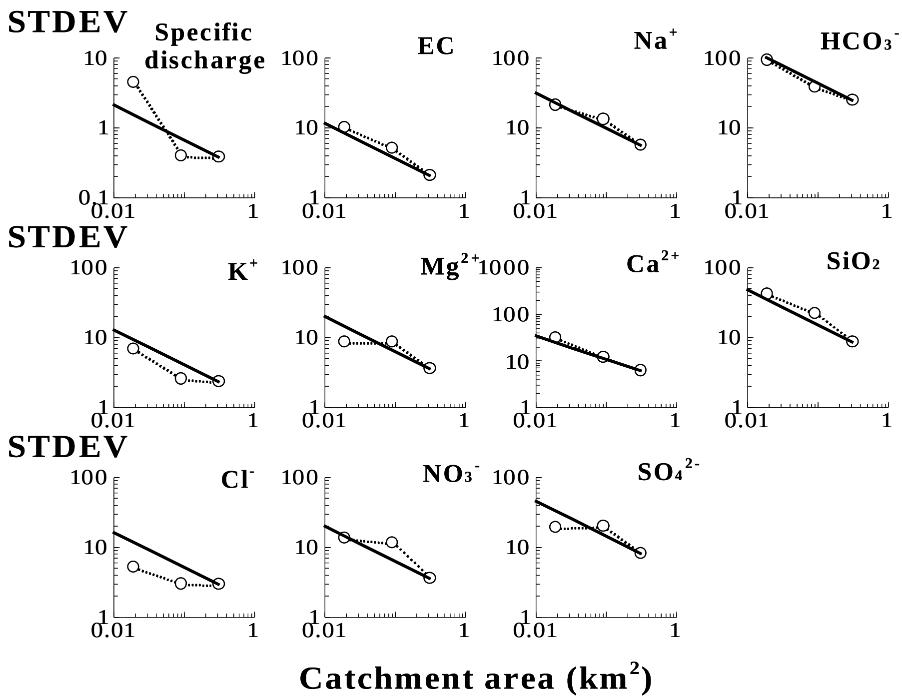


Figure 4.5 Relationships between the standard deviation of observed variables and the catchment area. The solid lines represent the theoretical relationship proposed by Woods et al. (1995). Each point is the standard deviation of a given stream order.

4.4 Discussion

4.4.1 Effect of confluence process on discharge and chemical variables

Woods *et al*. (1995) recorded more rapid decrease in specific discharge than was suggested by the theoretical relationship. Asano and Uchida (2010) observed that variability decreased more slowly than suggested by the theoretical relationship in small catchments (under 0.01 km^2) and decreased at about the same rate as the theoretical relationship for catchments above 0.01 km^2.

In our results, the standard deviations of specific discharge decreased more rapidly than the standard deviations of dissolved matter. In small catchments, the moving averages of specific discharge were higher than the overall average value (Fig. 4.2). Woods *et al*. (1995) reported that the specific discharge was highly variable and was large in small catchments. Woods *et al*. (1995) did not use a moving average, but it was obvious that the average specific discharge in a small catchment was higher than the average of the entire catchment. I divided the standard deviation of specific discharge by the average of each stream order (Fig. 4.6). In Inokawa, the result was close to the theoretical relationship, but still produced a slightly steeper slope, especially for third- to fourth-order streams. In Kusaki, the slope was about the same as for the theoretical relationship and was similar for other variables.

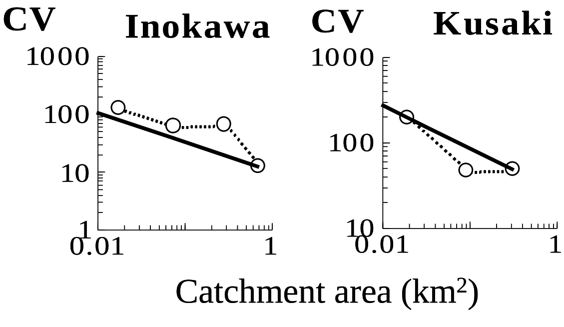


Figure 4.6 Relationships between the CV of specific discharge and catchment area. The solid lines represent the theoretical relationship proposed by Woods et al. (1995). Each point is the standard deviation of a stream order.

These results suggest that the standard deviation of specific discharge was higher in small catchments because of the higher average values. This caused a more rapid decrease than suggested by the theoretical relationship and resulted in the difference between specific discharge and dissolved matter. Specific discharge was calculated by dividing the discharge by the catchment area. In small catchments, specific discharge might have large variance and a different average from the overall average. The results of specific discharge and dissolved matter should be differentiated.

4.4.2 Difference in the effect of the confluence process on dissolved matter

Asano *et al*. (2009) concluded that the decrease in spatial variability in the concentration of solutes primarily results from hydrological mixing rather than biogeochemical reactions because the moving CV of all dissolved matter (both conservative solutes such as Na^+ and biologically reactive solutes such as NO_3^-) decreases with the decrease in catchment area. Our results support this. In each catchment, CV_{max} and $CV_{(0.3)}$ displayed strong linear relationships (Fig. 4.4). Because hydrological mixing mainly controlled the decrease in variability, the decrease in variability occurred at a constant rate regardless of the dissolved matter content. Departures from the linear regression indicated differences among dissolved matter content. However, a comparison to the theoretical relationship indicated little difference among dissolved matter content (Fig. 4.5).

In Inokawa, bedrock groundwater increased with the increase in catchment area. I also observed that the characteristics of bedrock groundwater changed as water flowed downstream (Chapter 2). In Inokawa, Na^+ and K^+ displayed a slightly more gentle decrease than did Ca^{2+} and Mg^{2+} (Fig. 4.5). Na^+ and K^+ were rich in type B bedrock groundwater and began to discharge downstream (Chapter 2). Therefore, the results might suggest that a change in bedrock groundwater chemistry had an influence on the confluence of the variability. I targeted a mud stone area, where bedrock groundwater discharge was smaller than in a sandstone area. If the sandstone area had been targeted, the difference in dissolved matter content may have been larger.

In Yozukugawa, almost all dissolved matter was located on the line suggested by the theoretical relationship (Fig. 4.4). Only SO_4^{2-} decreased more rapidly than suggested by the theoretical relationship (Fig. 4.5). SO_4^{2-} concentrations in Yozukugawa were low (Chapter 2, Figs 2.2 and 2.3) and were assumed to be mainly derived from precipitation. However, some values were higher than expected in catchments smaller than 0.3 km^2. I defined "single geology" to include situations in which any single geology occupied more than 80% of the catchment area at each observation point. Therefore, one possibility was that the different geology included in the catchment supplied mineral-derived SO_4^{2-}, which led to relatively high values in some locations. As a result, the variability in small catchments may have been overestimated.

In Kusaki, the results displayed two different tendencies (Figs. 4.4 and 4.5). Cl^- K^+, NO_3^- , SO_4^{2-}, and Mg^{2+} either produced ambiguous results or had a tendency to be below the line suggested by the theoretical relationship (Fig 4.5). They were also plotted below the CV_{max} and $CV_{(0.3)}$ regression line (Fig. 4.4). Almost all of the dissolved matter was precipitation derived (especially in Kusaki). There was a difference between mineral-derived and precipitation-derived dissolved matter. The reason for this is given more consideration in the next section.

The difference among dissolved matter content was small compared with the difference between specific discharge and solutes. In Chapter 3, I showed that biological uptake rarely occurs in streams. Snapshot samplings were conducted mainly from August to October, when the light intensity in the streams was not strong. Therefore, almost all the decrease in variability for every solute resulted only from hydrological mixing. Thus, comparisons could be made among catchments without considering the differences in dissolved matter content.

4.4.3 Inter-site comparison of the confluence process

Our results suggested similar tendencies following two different statistical analyses (Figs. 4.4 and 4.5). Kusaki displayed an earlier confluence than Inokawa and Yozukugawa. Kusaki was almost on the line of the theoretical relationship. In the other catchments, the convergence of variability occurred less rapidly than the theoretical relationship suggested, especially from first- to second-order streams. Asano and Uchida (2010) also showed a more moderate decrease in their study catchment. According to the organization concept (Woods *et al*. 1995), the variation should have decreased faster than the theoretical relationship suggested in all catchments. However, our results suggested the existence of different processes.

In Inokawa, as discussed in Chapter 2, bedrock groundwater discharge increased with increasing catchment area. So in Inokawa, the assumption of randomly distributed variation may not be correct. Therefore, an increase in concentration may increase the standard deviation and may hinder the decrease in variability. I compared the decrease in the CV of EC and Ca^{2+} to the theoretical relationship in Inokawa (Fig. 4.7). The results were close to the theoretical relationship but still decreased less rapidly than the line of the theoretical relationship, especially from first- to second-order streams.

Therefore, bedrock groundwater discharge hindered the decrease in the standard deviation but could not explain the full extent of the moderate decrease.

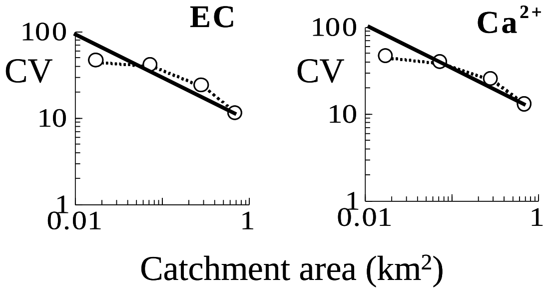


Figure 4.7 Relationships between the CV of EC and Ca^{2+} and catchment area in Inokawa. The solid lines represent the theoretical relationship proposed by Woods et al. (1995). Each point is the standard deviation of a stream order.

These tendencies allowed us to generate a new hypothesis. The theoretical relationship may not necessarily express the full extent of hydrological mixing in real catchments. The equation describing the theoretical relationship was applied to catchment hydrology as an analogy to sampling theory (Mood *et al.*, 1974). The implication was that if randomly distributed variation and simple mixing can be applied, the size of variability decreases at a constant rate (1/A) as the catchment area increases. However, catchments are composed of zero-order hollows, side slopes, and streams. Some studies have revealed that zero-order hollows and side slopes experience different hydrological processes (Troch *et al.*, 2003; Fujimoto *et al.*, 2008; and others). The confluence may not be the same as the increase in catchment area in real catchments. For example, if the catchment area increases tenfold, the confluences might not increase proportionally. As a result, our observations might indicate a more moderate decrease than the theoretical relationship would suggest in the three catchments. This may reflect a form of "organization," although it is differs from that expected by Woods *et al.* (1995). The stream may be organized, and variations may not be fully randomly distributed. Additionally, this hypothesis could possibly explain the characteristics of specific discharge (large average values in small catchments and a steep decrease in variability). If the specific discharges of zero-order hollows are larger than those for side slopes, an increase of side slopes in a catchment may decrease the specific discharge and lead to a decrease in variability.

However, even if the hypothesis is correct, a problem remains. The theory should be applied to all catchments. However, our results in Kusaki showed a decrease that was about the same as that suggested by the theoretical relationship (Fig. 4.5). Therefore, in Kusaki, a process may be operating to make the decrease steeper. One possible reason could be the interchange of groundwater in small catchments. Oda *et al*. (2012) observed that bedrock flow pathways and inter-catchment groundwater transfers may result in differences in the water balance and runoff characteristics during low flow in headwater catchments. In Kusaki, two samples had extremely high concentrations of mineral-derived dissolved matter (Chapter 2 Fig. 2.2). They were located adjacent to volcanic rocks (Fig. 4.8). In volcanic rock, the concentration of mineral dissolved matter is much higher than that in sedimentary rocks (Fig. 4.4). Therefore, an increase in the concentration of mineral dissolved matter might result from the exchange of groundwater between small catchments with different geologies. This increase in the concentration of mineral-derived dissolved matter occurred only in limited numbers of small catchments. Stream water at these two locations discharged directly into a high-order stream (Fig. 4.4). Therefore, the variability might be large only in small catchments, and it might decrease with an increase in catchment area.

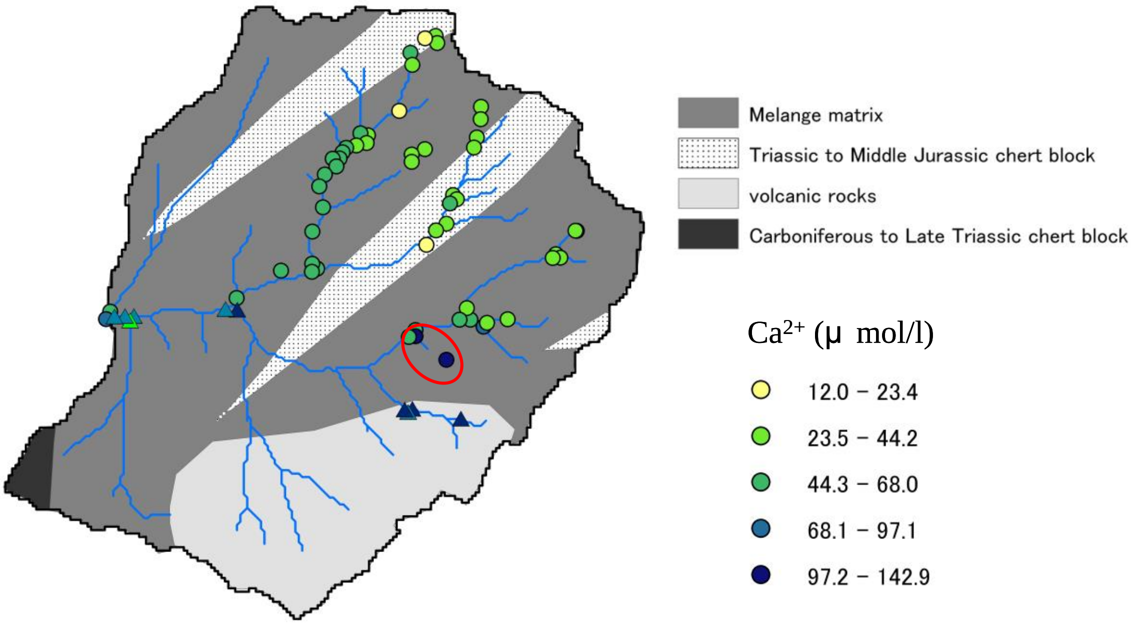


Figure 4.8 Spatial variability of Ca^{2+} in Kusaki. Circles indicate observation points of sedimentary rock, and triangles indicate observation points containing more than 20% volcanic rock. The color of each point indicates the Ca^{2+} concentration. Red circles are observation points with extremely high values in the sedimentary rock area.

4.5 Conclusion

Results showed that specific discharge and dissolved matter content clearly differed, as the average specific discharge was larger in small sub-catchments than the whole catchment. These results suggested that the differences reported in previous studies might be derived from the differences in observed variables.

From inter-site comparisons, I showed that the decrease in variability was moderate in small catchments and exceeded the influence of bedrock groundwater discharge as the catchment area increased. I proposed the hypothesis that the differences in hydrological processes derived from microtopography moderate the decrease in variability.

Comparison of this chapter made it clear that there were differences in the observed variables among the catchments. This observation will improve our general knowledge of confluence processes.

4.6 References

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Chapter 5

Modeling of spatial variability in stream water discharge and chemistry

5.1 Introduction

Previous studies have reported that the catchment area for which variability is ignorable differs among catchments and among observed variables. We have yet to fully elucidate why variability in small catchments occurs and how stream confluences influence the relationships between spatial variability and catchment area.

With respect to the first problem, many researchers have revealed that heterogeneity of geological environments (soil type and bedrock geology) influences hydrological processes (Carey and Woo, 2000; Uchida *et al*., 2005; and others). However, even if these characteristics were all the same, water discharge and chemistry of small catchments would be highly variable (Wolock *et al*., 1997; Asano *et al*., 2009; and more). Some studies have examined the relationships between spatial variability in small catchments and topography. Although some of these have reported that the concentrations of mineral-derived dissolved matter increased as altitude decreased, the percentage differences with varying altitude were small (Ohrui *et al*., 1994; Fukushima and Tokuchi, 2009). With respect to slope or topographic index (suggested by Beven and Kirkby, 1979), Fukushima and Tokuchi (2009) and Asano *et al*. (2009) showed no significant relationship.

From the 1980s, flow path through bedrock has been recognized as having large importance for determining discharge and chemistry in small catchments (Mulholland, 1993; Anderson *et al*., 1997; Burns *et al*., 1998; Uchida *et al*., 2003; and others). Also, Uchida and Asano (2010) showed that mixing of soil water and bedrock groundwater could explain the ranges of SiO_2 and Na^+ concentrations of stream water. Their research suggested the possibility that variability in small catchments can be determined by the mixing of soil water and bedrock groundwater. However, whether this mixing can explain spatial variability characteristics (e.g., shape of the distribution curve, degree of variability, and differences among dissolved components) is yet to be confirmed

Many understandings about the effects of stream confluences also require clarification. In Chapter 4, my result showed that the spatial variability in dissolved components does not completely decrease along the theoretical line suggested by Woods *et al*. (1995) in many cases. Furthermore, the results for dissolved matter were different from the results for specific discharge. Specific discharge showed higher average values in small catchments than in the entire catchment, and convergence of specific discharge occurred more quickly than did convergence of dissolved components. These results mean that the variability and convergence of stream water discharge and chemistry cannot be regarded as simple mixing of randomly distributed variability.

These results suggest the existence of organization. Several studies have revealed differences in hydrological processes between zero-order hollows and side slopes from both observations and model calculations, with a focus on mainly rainfall events (Takasao and Shiiba 1981; Troch *et al*., 2003; Fujimoto *et al*., 2008; and so forth). For example, Troch *et al*. (2003) showed from model calculations that zero-order hollows drain more slowly than side slopes. Fujimoto *et al*. (2008) observed several rainfall events and reported that the contributions of these two features changed with rainfall amount. They showed that when large amounts of precipitation occurred, zero-order hollows drained faster than side slopes because of the existence of soil pipes. However, in moderate precipitation, side slopes showed peak discharge and drained faster. I considered that the faster drainage of side slopes, which previous studies have reported, might be linked to differences in discharge rate between zero-order hollows and side slopes under the low-flow condition, so I hypothesized that the possible difference between zero-order hollows and side slopes might influence the confluence of stream discharge and chemistry.

I examined these mechanisms (formation of variability in small catchments and decrease of variability by stream confluence) from observed data and a conceptual model. The conceptual model hypothesized that the mixing of two components (soil water and bedrock groundwater) resulted in variability in stream discharge and chemistry in headwater streams. To better understand confluence, I considered the difference between zero-order hollows and side slopes and also considered deep bedrock groundwater discharge according to geology.

The objectives of this chapter are as follows: 1) to determine whether the mixing of soil water and bedrock groundwater can explain the variability characteristics of small catchments and 2) to examine the influence of microtopography on stream confluences.

5.2 Materials and methods

The observational data from Chapter 2 were used for the modeling of this chapter. I used Ca^{2+} in Inokawa, SiO_2 in Yozukugawa and SiO_2 in Kusaki as conservative tracers.

5.2.1 Topographic analysis

Topographic maps of the catchments used for the modeling approach are shown in Fig. 5.1 (b, c, and d). I used a 10-m digital elevation model (DEM; Geographical Survey Institute) and ArcGIS (ESRI).

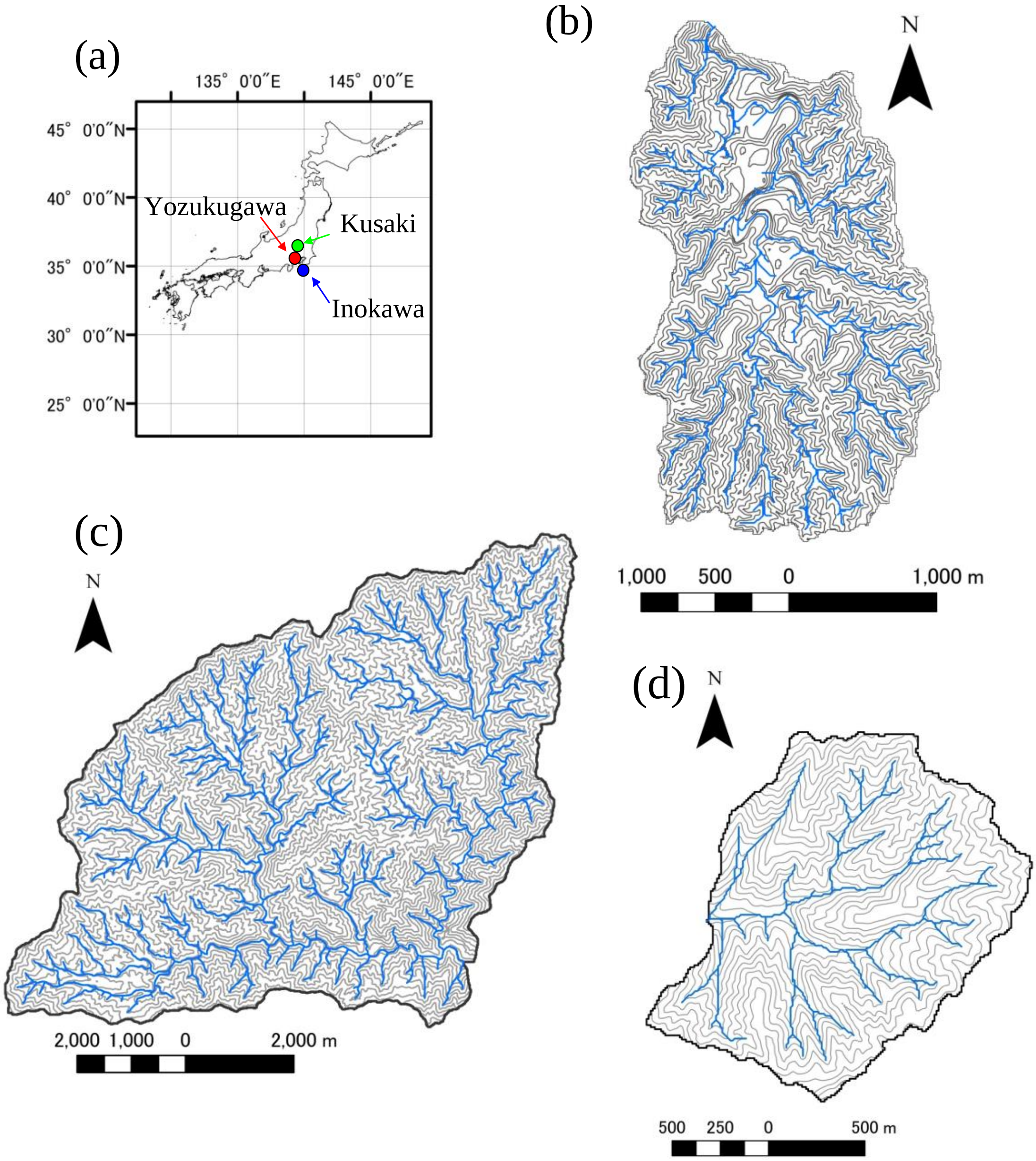


Figure 5.1 (a) Locations of the catchments. (b) Contour map of the Inokawa catchment. (c) Yozukugawa catchment. (d) Kusaki catchment. The contour interval is 20 m for the Inokawa and Kusaki catchments and 50 m for the Yozukugawa.

First, streams were defined by the observed catchment area of zero-order hollows and headwater streams. These were 0.0080 km^2 for Inokawa, 0.0130 km^2 for Yozukugawa, and 0.0186 km^2 for Kusaki. Then, I extracted catchments having a specific catchment area. The catchment areas of streams had discrete values, so I extracted catchments that had 0.9–1.1 times the number of larger catchments than the targeted catchment area (Fig. 5.2). For example, if I wanted to extract 0.05-km^2 catchments, I extracted those ranging from 0.045 to 0.055 km^2. Then, I excluded redundant catchments by choosing the smallest one.

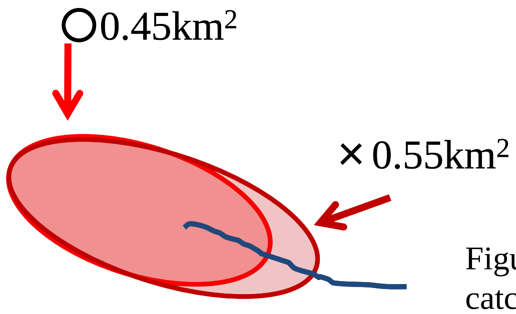


Figure 5.2 Schematic design of extracting catchments of specific catchment area. In this figure, we targeted 0.05 km^2.

Next, I calculated the number and increasing ratio of first-order streams and the contributions of zero-order hollows and side slopes in these extracted catchments. We defined a zero-order hollow as the catchment area above a pour point, and we defined side slopes as the catchment area excluding zero-order hollows and channels (Fig. 5.3). We defined the increasing ratio of first-order streams by the equation below:

$$\text{Increasing ratio} = \frac{N_{i+1} / N_i}{A_{i+1} / A_i} ,$$

where N is the number of first-order streams, and A is the catchment area. For example, in Kusaki, there were 1.2 first-order streams, on average, in a 0.048-km^2 catchment and 2.0 first-order streams in a 0.097-km^2 catchment area. Although catchment area increased by a factor of two, the number of first-order streams increased by a factor of about 1.7. Therefore, in this case, the increasing ratio was 0.85. I then plotted this value using A_{i+1} as the *x*-axis value (in this case, 0.097 km^2).

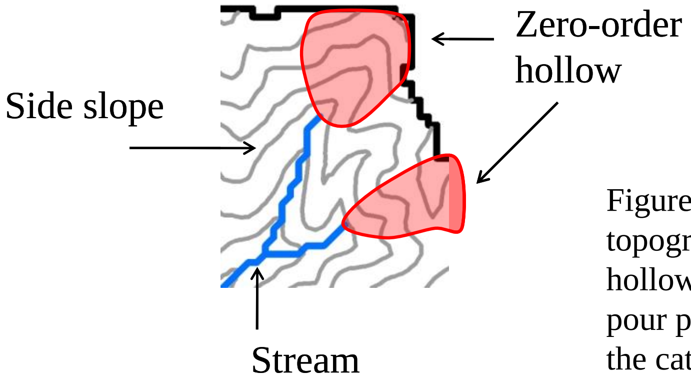


Figure 5.3 Schematic design of micro topography. We defined a zero-order hollow as the catchment area above the pour point. Side slope was defined as the catchment area not occupied by zero-order hollow or stream.

5.2.2 Model concept

Model concepts were the following: 1) the spatial variability in small catchments is determined by the mixing of two components (soil water and bedrock groundwater); 2) the convergence of discharge and chemistry are determined mainly by stream confluences and the contributions of side slopes; and 3) deep bedrock groundwater discharge may be considered, depending on geology.

Concept 1

The conceptual model of hydrological flow paths is shown in Figure 5.4. I hypothesized the existence of three components: soil water, bedrock groundwater, and deep bedrock groundwater. In headwater catchments, stream water is composed of two components: soil water and bedrock groundwater. I assumed that deep bedrock groundwater does not discharge in headwater catchments.

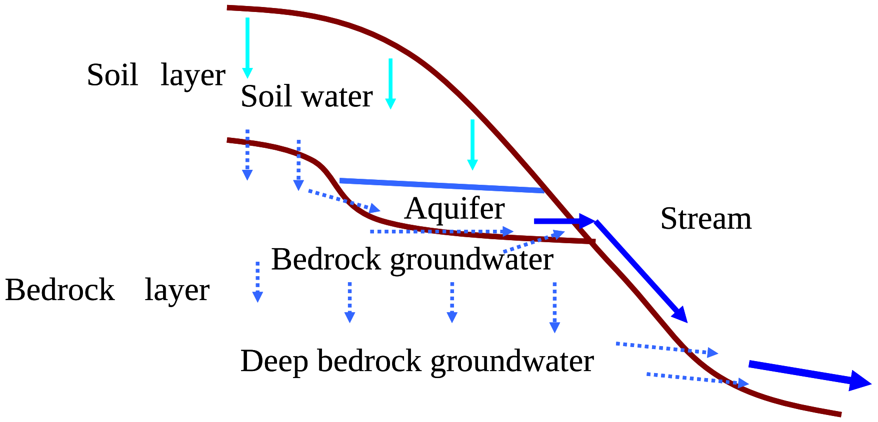


Figure 5.4 Conceptual model of hydrological flow paths. In small catchments, stream water is composed of soil water and bedrock groundwater. In the Inokawa and Kusaki catchments, deep bedrock groundwater discharges and increases with catchment area.

The specific discharge of each component changes independently. The discharge and chemistry of headwater catchments were expressed by following equations:

$$SD_{str} = SD_{soil} + SD_{bed}$$

$$C_{str} \times SD_{str} = C_{soil} \times SD_{soil} + C_{bed} \times SD_{bed} \quad ,$$

where SD_{str}, SD_{soil}, and SD_{bed} are the specific discharges of stream water, soil water, and bedrock groundwater, respectively, and C_{str}, C_{soil}, and C_{bed} are the concentrations of each component. In Inokawa, I used observed values of soil water and bedrock groundwater as the values of C_{soil} and C_{bed} (the same as in Chapter 2: soil water and type-A bedrock groundwater). In the other catchments, I used the maximum values (minimum value for NO_3^-) of stream water as values of C_{bed} and the minimum values (maximum value for NO_3^-) as values of C_{soil}.

These two equations mean that specific discharge and the concentrations of stream water change simultaneously with changes in soil water and bedrock groundwater (Fig. 5.5). I used a log-normal distribution to express the distribution of the two contributing components. I generated random numbers with average values of 1, and multiplied them by the average specific discharge of soil water and bedrock groundwater. The average specific discharges of these two components were calculated by substituting the average stream water discharge and concentrations into the above equations. In Inokawa and Kusaki, as I showed in Chapter 2, bedrock groundwater increased with catchment area. Thus, I used the average values of catchments of less than 0.1 km^2.

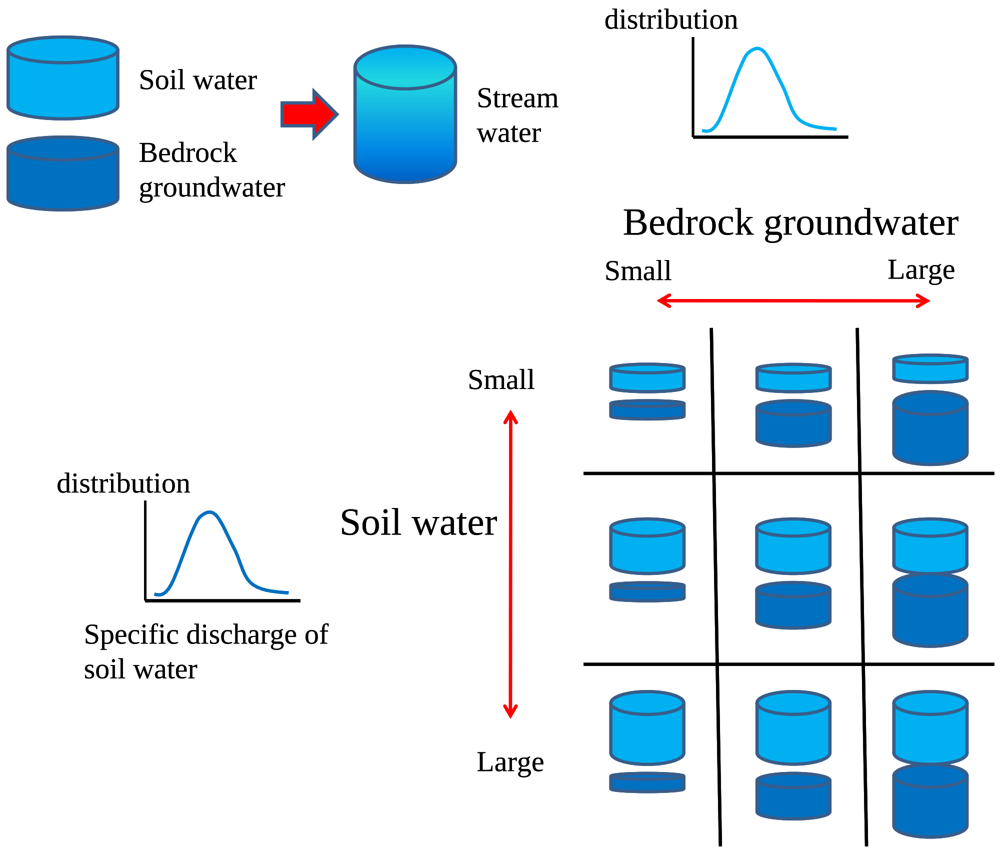


Figure 5.5 Schematic diagram of the generation of spatial variability in small catchments. Soil water and bedrock groundwater vary independently, generating variability in stream water discharge and chemistry. The size of the cylinders indicates the specific discharge of each contributing component.

Average specific discharges were calculated for each dissolved chemical component. I used these average values to examine differences among the dissolved matter species and used specific values to examine the differences among catchments.

Concept 2

I expressed stream water confluence as simple mixing of stream water in small catchments (Fig. 5.6). Mixing occurred depending on catchment area.

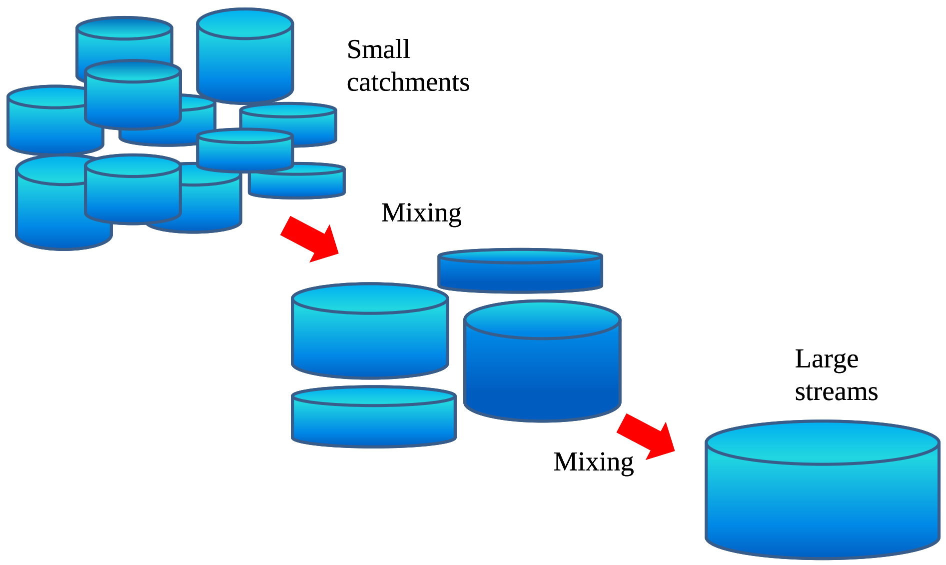


Figure 5.6 Schematic diagram of stream water mixing with increasing catchment area. The vertical dimension of the cylinders indicates the specific discharge of each component, and the horizontal dimension of the cylinders indicates the size of the catchment area.

I also developed several mixing patterns by considering the contribution of side slopes. These were (1) zero contribution of side slopes (Fig. 5.7.a); (2) a side slope contribution less than the contribution of zero-order hollows (Fig. 5.7.b and c); and (3) equal contributions of each (Fig. 5.7d).

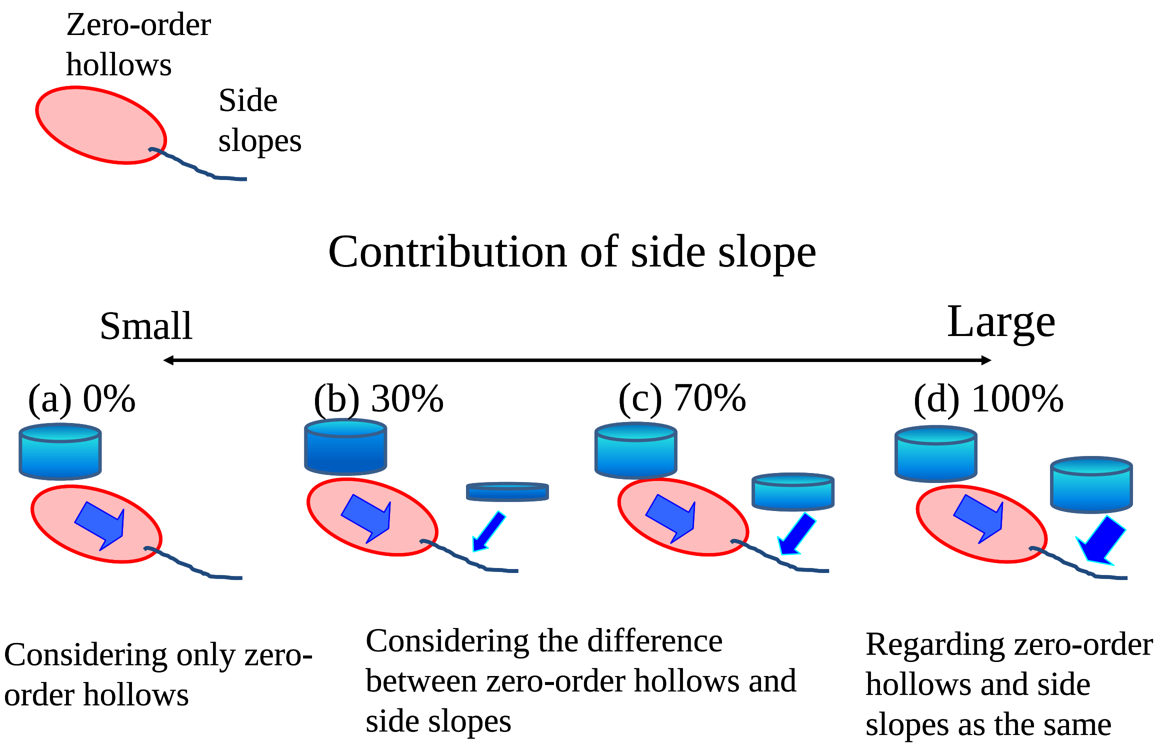


Figure 5.7 Schematic diagram of the contribution of side slopes. The size of the cylinder indicates the specific discharges of zero-order hollows and side slopes.

Concept 3

For Yozukugawa, I assumed that deep bedrock groundwater did not discharge at all. For Inokawa and Kusaki, I assumed that deep bedrock groundwater increased with catchment area. In these catchments, I determined the average discharge rate of deep bedrock groundwater discharge from observation (the change in a 10-value moving average). It increased linearly with catchment area (Fig. 5.8). I also expressed the average specific discharge of deep bedrock groundwater by the following equations.

Like the other two components, this value had its own variability. In the case of bedrock groundwater discharging, stream water discharge and chemistry are expressed as follows:

$$SD_{str} = SD_{soil} + SD_{bed} + SD_{deep}$$

$$C_{str} \times SD_{str} = C_{soil} \times SD_{soil} + C_{bed} \times SD_{bed} + C_{deep} \times SD_{deep} \quad ,$$

where SD_{deep} and C_{deep} are the specific discharge and concentrations of deep bedrock groundwater, respectively. At this time, I set C_{deep} equal to C_{bed}.

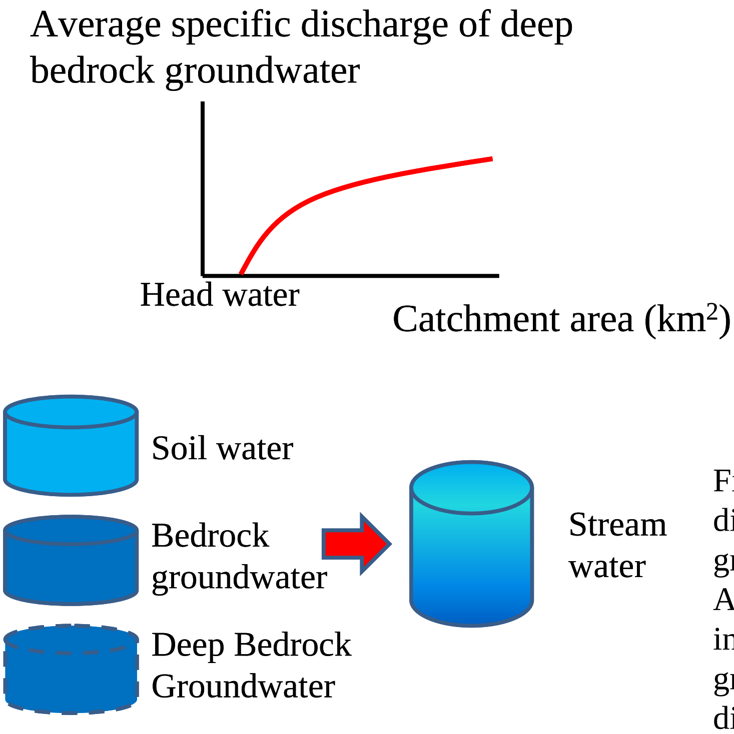


Figure 5.8 Schematic diagram of the deep groundwater discharge. As catchment area increased, deep bedrock groundwater began to discharge and increased in Inokawa and Kusaki.

5.3 Results

5.3.1 Topographic characteristics

The increase in the number of first-order streams with catchment area is shown in Figure 5.9.a. Overall, the number seemed to increase linearly as catchment area increased. The Inokawa catchment had the most first-order streams of the three catchments. The Yozukugawa and Kusaki catchments showed a very similar increase in first-order streams. I also illustrated the relationship between increasing ratio of first-order streams and catchment area (Fig 5.9.b). The points with the smallest *x*-values show the increasing ratio from zero-order hollows. In this figure, an increasing ratio close to 1 means that the relationship between catchment area increase and first-order stream increase is near 1:1. These values rarely exceeded 1, and they departed from 1 mostly in small catchments. In all the catchments, the values seemed to become constant above 0.1–0.3 km^2. The values for the Inokawa catchment became constant slightly faster than those for the other two catchments.

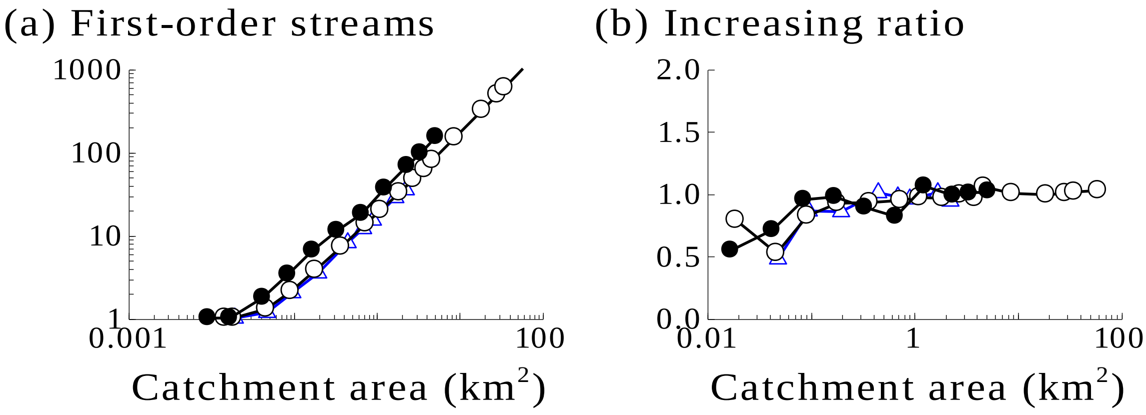


Figure 5.9 Relationships between the increase in first-order streams and catchment area. Solid circles represent Inokawa, open circles represent Yozukugawa, and triangles represent Kusaki.

Next, I determined the contributions of zero-order hollows and side slopes in relation to catchment area (Fig. 5.10). The contribution of zero-order hollows decreased gradually with catchment area and became nearly constant at about 30%. The contribution of side slopes showed an opposite tendency. It continued to increase with catchment area and became constant at about 70%. The catchment area at which values were regarded as constant was about 0.1–0.3 km^2 for all catchments. The side slope tendencies were almost the same as those of the increasing ratio of first-order streams.

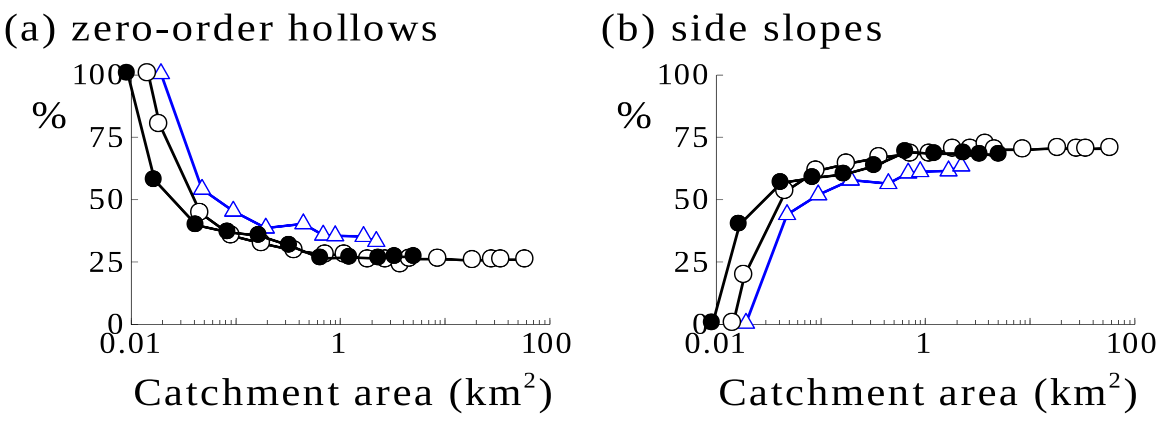


Figure 5.10 Relationships between microtopography and catchment area. Solid circles, open circles, and triangles represent Inokawa, Yozukugawa, and Kusaki, respectively.

Additionally, I examined the differences in slope and topographic index between zero-order hollows and side slopes (Table 5.1). This topographic index expresses the drainage capacity, and high values indicate high drainage capacity (Beven and Kirkby, 1979). For each catchment, the average values differed significantly by *t*-test ($P < 0.01$). The results showed that side slopes were steeper and had lower topographic indices than did zero-order hollows. Therefore, there was an overall (average) difference in slope and drainage capacity between zero-order hollows and side slopes in the entire catchment, which supports my assertion that the discharge rates of these as being different.

Table 5.1 Comparison of slope and topographic index between zero-order hollow and side slope. The numbers in the parentheses indicate standard deviations.

		Slope	**Topographic index**
Inokawa	zero-order hollow	30.8(11.3)	1.24(1.96)
	side slope	33.2(11.1)	0.96(1.85)
Yozukugawa	zero-order hollow	31.0(9.1)	1.51(2.01)
	side slope	32.4(8.7)	1.26(1.86)
Kusaki	zero-order hollow	27.3(8.9)	0.60(0.88)
	side slope	30.4(8.0)	0.49(0.87)

5.3.2 Modeling variations in discharge and chemistry

I changed the standard deviation of the log-normal distributions, which express the variability in soil water and bedrock groundwater, and examined the calculation results (Figs. 5.11–5.16). In these figures, I used Ca^{2+} in the Inokawa catchment as an example. The standard deviation of the distribution was changed in five steps, 0, 0.3, 0.5, 0.7, and 1.0, which are standard deviations of log values. These values as coefficients of variance were about 0, 31, 53, 80, and 131, respectively. I subsequently identified the standard deviation of the distributions of the two components as DD_{soil} and DD_{bed}.

The degree and profile of the distributions of specific discharge and Ca^{2+} were greatly changed with the given distribution (Figs. 5.11 and 5.12). When both DD_{soil} and DD_{bed} were less than 0.3, almost all specific discharges were within 0.5 mm/day. On the other hand, when both DD_{soil} and DD_{bed} were 1.0, specific discharge ranged widely and attained many large values. The response of Ca^{2+} was similar. When DD_{soil} and DD_{bed} were small, the distributions seemed normal. However, when DD_{soil} and DD_{bed} became larger, the shape of the distribution gradually became wide and trapezoidal.

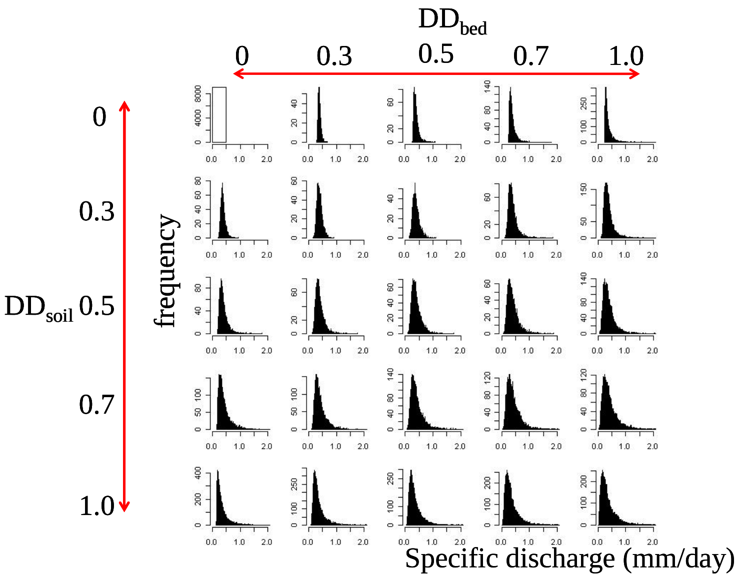


Figure 5.11 Response of the variability in specific discharge to the change in variability in each component. The *x*-axis shows specific discharge (mm/day), and the *y*-axis indicates frequency in generating 10 thousand random values.

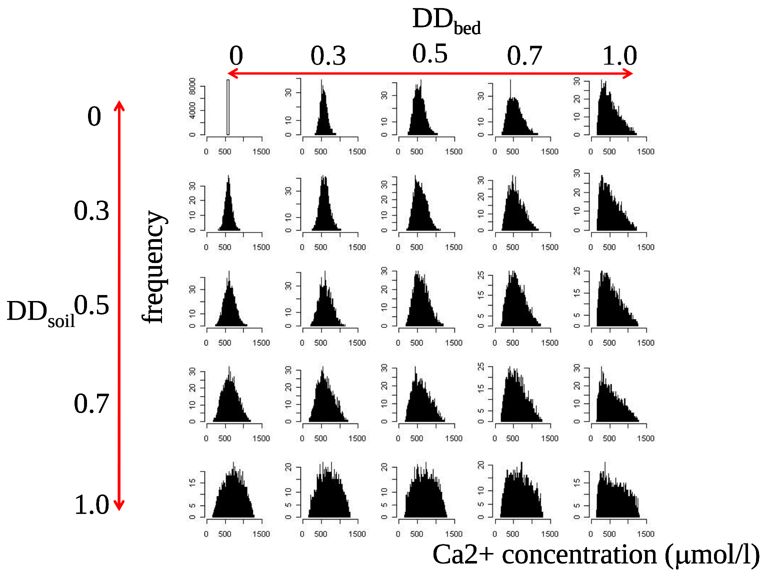
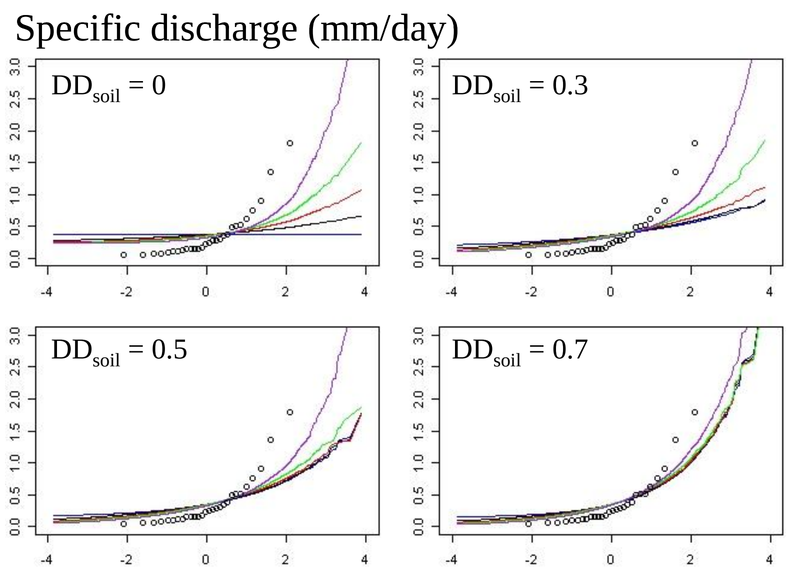


Figure 5.12 Response of the variability in Ca^{2+} concentration to the change in variability in each component. The *x*-axis shows Ca^{2+} concentration (μmol/l), and the *y*-axis indicates frequency in generating ten thousand random values.

Next, I compared the distribution profiles between observed values and calculations using a Q-Q plot (Figs. 5.13 and 5.14). In this figure, I used the observed values from catchments of less than 0.1 km^2. The *x*-axis was the theoretical quantile of a normal distribution. When both DD_{soil} and DD_{bed} were small, the calculation produced a distribution more gentle than the actual distribution profiles for specific discharge and Ca^{2+}. However, when either DD_{soil} or DD_{bed} was large (0.7 or 1.0), the calculation profiles drew close to the actual profiles. Especially, when DD_{soil} was 0.7 or 1.0, the profiles showed good suitability regardless of DD_{bed}. In this calculation, the average specific discharge of soil water was larger than that of bedrock groundwater (0.24 and 0.14 mm/day), so the results might well show a larger response to DD_{soil} than to DD_{bed}.



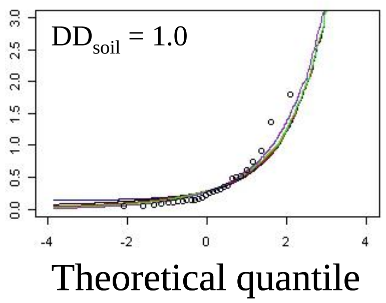
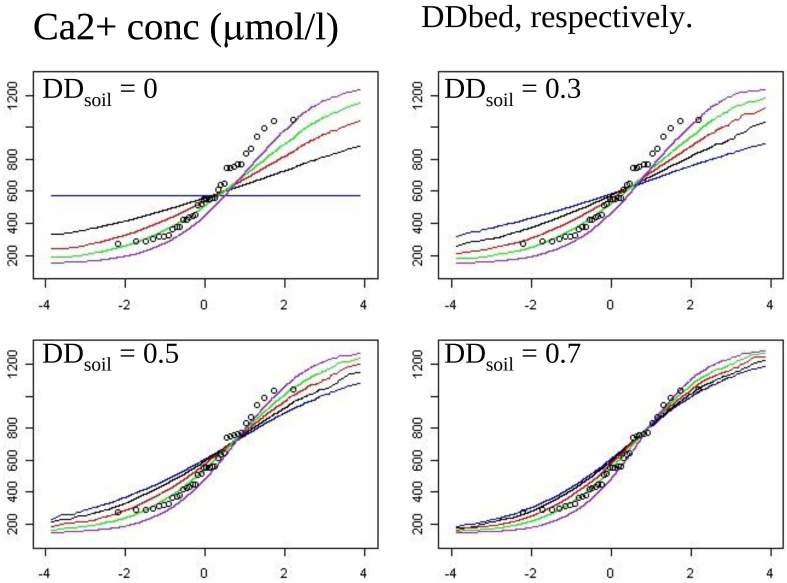


Figure 5.13 Response of the distribution profile of specific discharge to the change in variability in each component. The *x*-axis shows the theoretical quartile of the normal distribution, and the *y*-axis indicates specific discharge. The open circles are observed and the lines are calculated values. Each window indicates the difference in DDsoil, and each line indicates the difference in DDbed. The blue, black, red, and green lines indicate 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively.



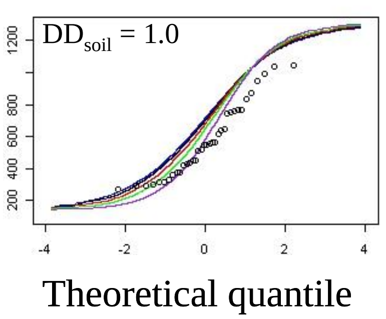


Figure 5.14 Response of the distribution profile of Ca^{2+} concentration to the change in variability in each component. The *x*-axis shows the theoretical quartile of a normal distribution, and the *y*-axis indicates the specific discharge. Open circles are observed and lines are calculated values. Each window indicates the difference in DDsoil, and each line indicates the difference in DDbed. The blue, black, red, and green lines indicate 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively.

Then, I determined the relationship between specific discharge and Ca^{2+} (Fig. 5.15). In the observations, these two showed no significant relationship. In the calculation, when DD_{soil} and DD_{bed} differed substantially, the relationship was sloped. For example, when DD_{soil} was 0 or 0.3 and DD_{bed} was 0.7 or 1.0, Ca^{2+} increased with specific discharge. When DD_{soil} was larger than DD_{bed}, the opposite tendency appeared,. and when DD_{soil} was the same as DD_{bed} or when DD_{soil} was slightly smaller than DD_{bed}, the results corresponded to reality.

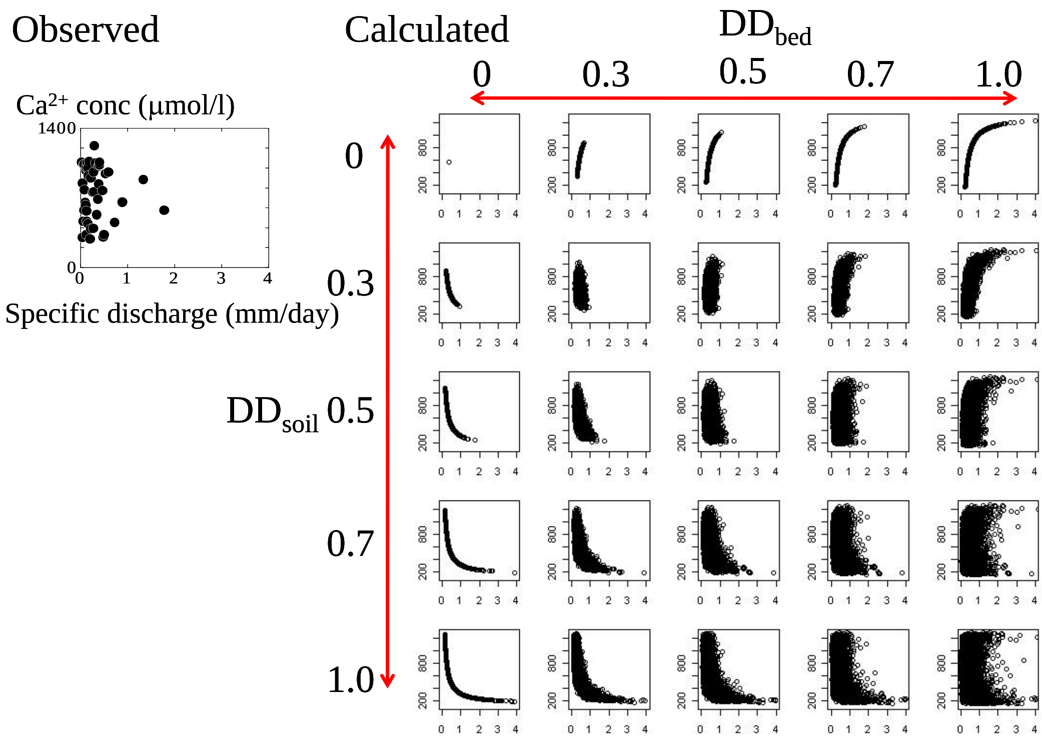


Figure 5.15 Response of the relationships between specific discharge and Ca^{2+} to the change in variability in each component. The upper left graph shows the observed values. The *x*-axis shows specific discharge (mm/day), and the *y*-axis indicates Ca^{2+} concentration (µmol/l).

Finally, I compared the observed CVs (coefficients of variation; CV_{max} from Chapter 4 and CV below 0.1 km^2) to the calculated CVs (Fig. 5.16). Neither of the observed CVs perfectly represented the degree of CV in real catchments. However, the ranges formed by these two indices were rough indications. For specific discharge, the calculated CVs did not reach 108 (CV below 0.1 km^2). However, when DD_{soil} was 1.0, the difference between the observed and calculated CV was small. For Ca^{2+}, in six cases (five when DD_{bed} was 1.0 and one when DD_{soil} was 1.0 and DD_{bed} was 0.7), the calculated CVs were within the range formed by the two observed values.

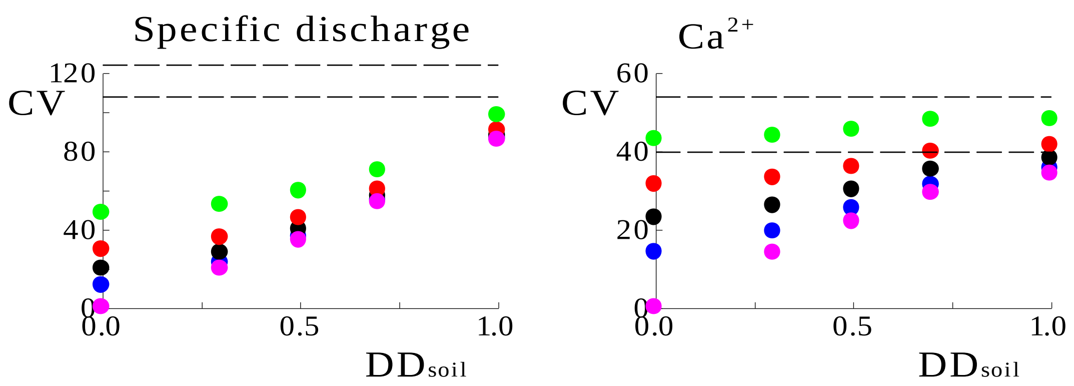


Figure 5.16 Comparison between calculated and observed CVs. The *x*-axis is the value of DDsoil, and the colors of the points represent values of DDbed. The purple, blue, black, red, and green points indicate 0, 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively. The two broken lines show CVmax and CV below 0.1 km^2.

From a comprehensive point of view, when I hypothesized that DD_{soil} and DD_{bed} were 1.0, the calculated variability expressed the actual variability well (with respect to the distribution profiles, the relationship between specific discharge and Ca^{2+}, and the degree of CVs). I also performed the same analyses in the other catchments and obtained almost the same results (shown in Appendix). Thus, I subsequently used the value of 1.0 for DD_{soil} and DD_{bed}.

I set the parameters (DD_{soil} and DD_{bed} to 1.0, average specific discharge of the two components to the average values of all dissolved matter species) and compared the calculated values to the observed CVs below 0.1 km^2 (Fig. 5.17). Almost all of the observed variables were on the line, which means that mixing of the two components could explain the variability not only in the specific discharge and Ca^{2+} in the Inokawa catchment but also in almost all the observed variables. Furthermore, this result suggested that the differences in CVs among the observed variables could be explained by mixing of the two components and also that the differences among the observed variables might be a result of the concentration of soil water and bedrock groundwater and of the difference between the two.

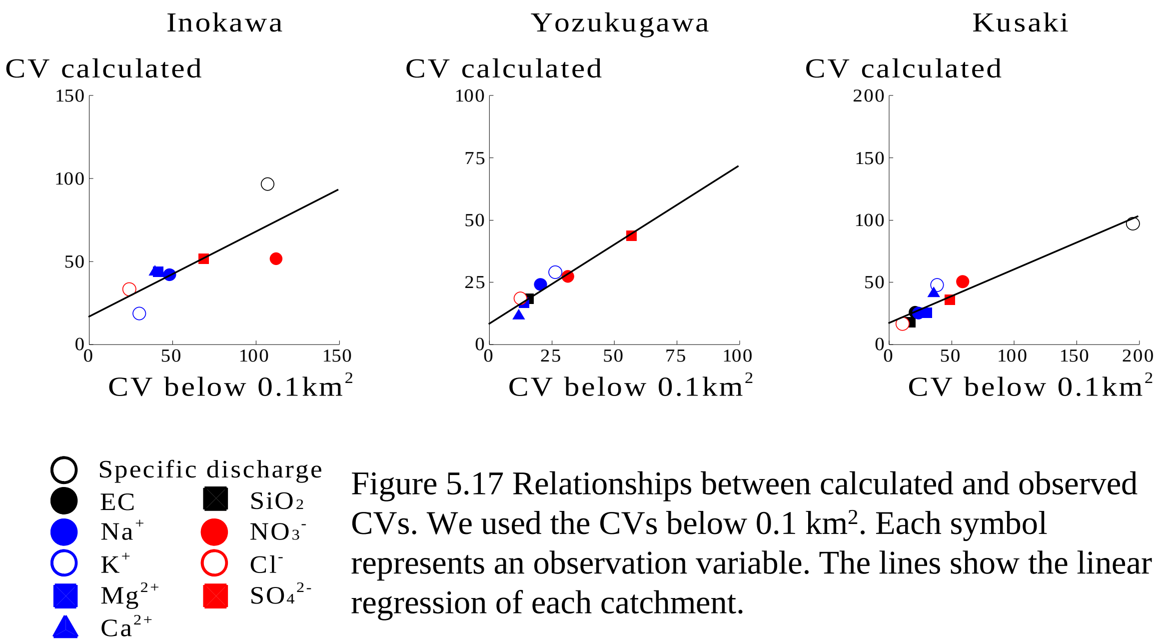


Figure 5.17 Relationships between calculated and observed CVs. We used the CVs below 0.1 km^2. Each symbol represents an observation variable. The lines show the linear regression of each catchment.

5.3.3 Modeling the convergence of stream discharge and chemistry

Response of model calculation depending on the side slope contribution

I determined calculation results with the observed values (moving CVs used in Chapter 4; Fig. 5.18). In these figures, I illustrate selected dissolved-matter species in the three catchments (Ca^{2+} in the Inokawa and SiO_2 in the other catchments) and specific discharge in two of the catchments (Inokawa and Kusaki). I considered deep bedrock groundwater discharge in the Inokawa and Kusaki catchments. In these figures, I limited *x*-values to within 0.3 km^2 because the change resulting from side slope contribution occurred only in small catchments. I show calculations for the entire catchments in the Appendix.

I describe the response of the model calculation to change in the side slope contribution. In the Yozukugawa calculation, the average concentrations were constant against catchment area and had no relationship to side slope contribution. However, in the Inokawa and Kusaki cases, average concentration increased with catchment area. Also, lower side slope contributions resulted in higher average concentrations. For average specific discharge, lower side slope contributions resulted in below average specific discharges.

The tendencies of standard deviation were different for specific discharge and concentration. Lower side slope contributions were linked to steeper decreases in specific discharge. However, the opposite tendency occurred for the standard deviation of concentration. For CVs, the tendencies of specific discharge and concentration were similar, and lower side slope contributions were linked to a more moderate decrease in the CVs.

The overall tendency was that only small catchments were influenced by change in the side slope contribution. Obvious differences were observed below 0.1 km^2; however, above 0.1 km^2, the tendencies of the four side slope contribution amounts became similar.

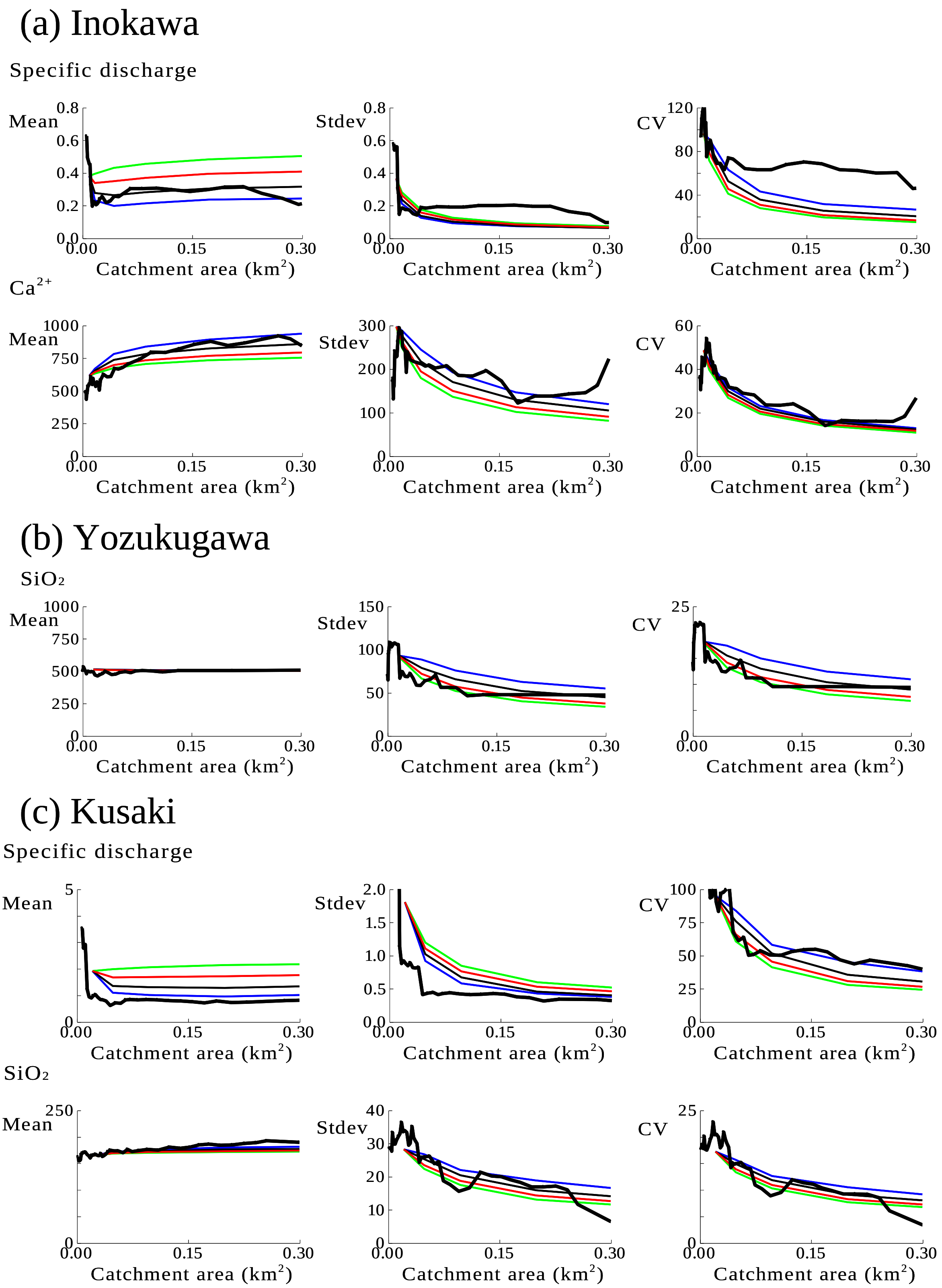


Figure 5.18 Change in mean and variation in specific discharge and dissolved matter with increasing catchment area. The black bold line indicates 10-value moving values of the observed values. The blue, black, red, and green lines show 0%, 30%, 70%, and 100% side slope contribution respectively.

Comparison between observed values and calculated values

I compared observed values to calculated values. I used 10-value moving averages, standard deviations, and CVs to express the observed values (Fig. 5.18). For average concentrations, all of the calculated values well expressed the constant average concentration in Yozukugawa and the increasing average values in Inokawa and Kusaki. For average specific discharge, when the side slope contribution was not equal to 100%, the decreasing tendency in small catchments of calculated values was similar to that of observed values. In Inokawa, the calculated values almost agreed with the observed values when the contribution was about 30%. In Kusaki, the decrease in the observed values in small catchments was steeper than calculated, and the calculated values were overestimated slightly.

For standard deviation of concentration, the observed values were almost within the range of calculated values formed by the four lines. In Inokawa and Kusaki, a side slope contribution of 30% was well suited, and in Yozukugawa, a 70~100% contribution was best. The standard deviations of specific discharge expressed the observed tendencies, decreasing rapidly in small catchments and then decreasing gradually. However, in both Inokawa and Kusaki, the calculated values departed from the observed values. In Inokawa, the calculated values were underestimates, but in Kusaki, the opposite tendency occurred.

The results for CVs were similar to those for standard deviations. In Yozukugawa, the result was almost the same because concentration was constant. In Inokawa, the calculated values of CVs of concentration were similar irrespective of side slope contribution, and they were almost consistent with the observed values. In Kusaki, the observed values of CVs were within the range established by the four lines and were similar to standard deviations. For CVs of specific discharge, calculated values underestimated observed values above 0.1 km^2 in Inokawa. For the Kusaki catchment, the calculated values almost expressed the observed values when the side slope contribution was 0~30%.

The calculated values were thought to express the actual confluence better when the side slope contribution was not equal to 100%. The calculated values well expressed the decrease in average specific discharge in small catchments and the decrease in variability. The side slope contribution was speculated to be 70~100% in Yozukugawa and about 30% in Inokawa and Kusaki.

5.4 Discussion

5.4.1 Determining factors of discharge and chemistry

The model calculations indicated that mixing of soil water and bedrock groundwater could explain the variability in small catchments and that soil water and bedrock groundwater have independent variability (if one of the two was small, the results did not express the actual very well; Figs. 5.11–5.16). These results suggest that the determining factors of soil water and bedrock groundwater were different and independent and that the specific discharge of soil water and bedrock groundwater must be determined in each headwater.

By my definition, the soil water flowed only through the soil layer and had a low concentration of mineral-derived dissolved matter. Thus, near-surface hydrological processes might determine the specific discharge of soil water. For example, in the distributed hydrological model, the variability in slope was one of the major factors determining variability in soil moisture and discharge rate, and steep slope was linked to fast drainage (Beven and Kirkby, 1979). Tsuboyama *et al*. (2000) showed from observations that thin soil depth caused fast drainage in two neighboring headwater catchments. The mean residence time of soil water becomes longer with depth from the soil surface (Asano *et al*., 2002). Therefore, a steep slope and thin soil layer might produce rapid drainage after rainfall and result in a lower soil water discharge rate in the low-flow condition. Also, the spatial variability in the topography and the soil layer determines the variability in specific discharge of soil water.

On the other hand, the spatial variability in bedrock groundwater discharge in headwater catchments may be derived from variability in the physical characteristics of the bedrock. Uchida *et al*. (2008) suggested that vertical expansion of hydrologically active bedrock may determine spatial variability in CV (temporal variation) of discharge and SiO_2 concentration of bedrock springs. Additionally, some researchers have revealed that the surface topography is not always the same as the bedrock topography (e.g. McDonnell *et al*., 1996), which might cause a dissimilarity between the catchment area of bedrock groundwater and that of soil water and might also influence the specific discharge of bedrock groundwater. For example, Oda *et al*. (2012) showed that intercatchment groundwater transfers occurred and greatly changed the water balance and runoff characteristics in headwater catchments during low flow. As a result, spatial variability in vertical and lateral bedrock characteristics might determine the variability in specific discharge of bedrock groundwater.

In previous studies, stream water discharge and chemistry showed no significant relationship to many topographic indices. One explanation for this observation might be that the variability in soil water and that in bedrock groundwater are generated independently. These results also illustrate the difficulty of exploring the determining factors of stream water discharge and chemistry from a simple comparison between discharge and chemistry and landscapes. In the future, I should explore methods for improving this situation. For example, a comparison between only the soil water component and topographic indices may be useful.

5.4.2 Difference in side slope contribution among catchments

When I treated zero-order hollows differently from side slopes, I was better able to explain the actual tendencies (Fig. 5.18). Also, the percentages of side slope differed among the catchments. Particularly, the percentage for Yozukugawa was lower than those for the other two areas.

The relationships between zero-order hollows and side slopes may change with time (Fig. 5.19). When specific discharges are large (during rainfall periods and just after a rainfall), specific discharges of both zero-order hollows and side slopes are large, and the difference between the two may be relatively small. Drainage of side slopes is faster than drainage of zero-order hollows (Troch *et al*., 2003; Fujimoto *et al*., 2008). Therefore, under the low-flow condition, the difference between the two may become relatively large and obvious, unless an extremely low-flow condition occurs.

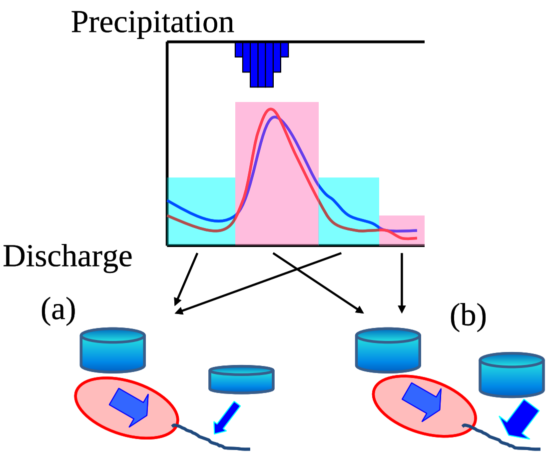


Figure 5.19 Conceptual diagrams of temporal variation in the relationships between zero-order hollows and side slopes. The blue curve line shows discharge of zero-order hollows, and the red curve line shows that of side slopes. (a) The difference between the two is large, and (b) the difference is small.

Observations showed that the specific discharge of stream water was larger in Yozukugawa than in Inokawa and Kusaki. So, I speculated that the influence of antecedent precipitation largely remained and affected observations in Yozukugawa and that this might result in larger percentages of side slope contribution compared with the other catchments. It is possible that these results may show only temporal variation. However, a difference among the catchments could possibly be indicated. It is known that differences in geology lead to differences in the discharge-duration curve (Mushiake *et al*., 1981) and, of course, that differences in precipitation (amount and seasonal trend) influence discharge rates. Although the seasonal trend of precipitation was similar in the three catchments, Yozukugawa had the largest annual precipitation of the three. Therefore, a difference in rainfall-runoff processes among the catchments may underlie the difference in temporal variation in the percentages of side slope. For example, if catchments have large precipitation or drain slowly, specific discharge becomes large, and the difference between zero-order hollows and side slopes might often become smaller. This circumstance may account for the differences among catchments in the model calculation.

Topographic analyses and model calculation showed that the influence of side slopes arose only in small catchments (mainly those less than 0.1 km^2). This result might reflect a change in catchment structure with increasing catchment area. As catchment area increased, the contribution of side slopes increased gradually. Also, the ratio of the contributions of side slopes and zero-order hollows became constant above a certain threshold area, reflecting the organization of streams. I propose the idea of considering the set of zero-order hollows and side slopes below the threshold area as an element of the catchment. The threshold area may differ among catchments because stream structures may reflect the characteristics of each catchment. In this study, the range of zero-order hollows was 0.0080~0.0186 km^2. Inokawa had the smallest catchment area of zero-order hollows, and the side slope contribution in Inokawa became constant at the smallest catchment area of the three catchments (Fig. 5.9). The catchment area of zero-order hollows has a similar index to drainage density, and drainage density is known to be influenced by climate (Chorley, 1957), bedrock geology (Tanaka, 1957), vegetation (Melton, 1958), and others. So, I should examine the catchment area of zero-order hollows of the catchment and should calculate the threshold area above which the contribution of side slopes is constant.

5.5 Conclusion

The model calculation revealed that the characteristics of spatial variability in stream water discharge and chemistry in headwater catchments could be explained by the mixing of soil water and bedrock groundwater. Additionally, by assuming that specific discharges of side slopes were smaller than those of zero-order hollows, I could better express the actual confluence.

These results advance our understandings of the formation and convergence of spatial variability in stream water discharge and chemistry and connect with the existing body of general knowledge. The conceptual model is applicable to every catchment with uniform geology, and it will be a useful tool for considering stream discharge and chemistry in mesoscale catchments.

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Chapter 6

Summary and Conclusion

6.1 Summary

In chapter 1, I put together current problems about the study of spatial variability of stream water discharge and chemistry. The existence of change with catchment area increase and the mechanism of generation and confluence of variability have not still been clear. We studied to elucidate these problems in subsequent chapters.

In chapter 2, I examined bedrock groundwater discharge with catchment area increase from the spatial variability of streamwater discharge and chemistry. The results showed that the relationship between bedrock groundwater discharge and catchment area was different among catchments with different geologies. Bedrock groundwater increased averagely with catchment area in Inokawa and in Kusaki. Especially in Inokawa, deeper bedrock groundwater sometimes began to discharge and increase as catchment area increased. However, bedrock groundwater did not increase with catchment area in Yozukugawa. It is because the variability in small catchments cover over the weak signal of bedrock groundwater increase in such catchments. The infiltration rate and homogeneity of the bedrock is thought to influence the bedrock groundwater discharge rate. Especially, sedimentary rocks, which include sand stone and tuff, have high infiltration rate and much heterogeneity, and have large bedrock groundwater discharge. Therefore, when we think about the relationships between catchment area and spatial variability of stream water discharge and chemistry, we should consider the difference of bedrock geology.

In chapter 3, I examined nitrate and phosphate uptake in streams using nutrient addition experimentNO_3^- uptake was rarely observed in the catchments examined in this study. PO_4^{3-} uptake was always observed in Aridagawa and rarely observed in Inokawa. When uptake occurred, uptake rates were within ranges reported previously. In the catchments examined here, the NO_3^- and PO_4^{3-} concentrations of stream water were high compared to biological demand in streams. Hence, the biological response to an increase of nutrient concentration would be very weak. It may be because of weak light intensity and large number of disturbance. Therefore, elucidation of biological uptake in streams may not be a valuable means of determining the spatial variability of NO_3^- and PO_4^{3-} in these catchments except for the seasons, which are suitable to algae growth like spring before leafing.

In chapter4, I verified the difference of convergence process among observed items and among catchments with using statistical methods. Results showed that specific discharge and dissolved matter content clearly differed, as the average specific discharge was larger in small sub-catchments than the whole catchment. These results suggested that the differences reported in previous studies might be derived from the differences in observed variables. From inter-site comparisons, I showed that the decrease in variability was moderate in small catchments and exceeded the influence of bedrock groundwater discharge as the catchment area increased. I proposed the hypothesis that the differences in hydrological processes derived from microtopography moderate the decrease in variability. Comparison of this chapter made it clear that there were differences in the observed variables among the catchments. This observation will improve our general knowledge of confluence processes.

In chapter5, I discussed the mechanisms of generation and confluence of the variability in small catchments using conceptual model. The model calculation revealed that the characteristics of spatial variability in stream water discharge and chemistry in headwater catchments could be explained by the mixing of soil water and bedrock groundwater. Additionally, by assuming that specific discharges of side slopes were smaller than those of zero-order hollows, I could better express the actual confluence. These results advance our understandings of the formation and convergence of spatial variability in stream water discharge and chemistry and connect with the existing body of general knowledge. The conceptual model is applicable to every catchment with uniform geology, and it will be a useful tool for considering stream discharge and chemistry in mesoscale catchments.

6.2 General conclusion

This study revealed the influence of several factors, which determine the relationships between spatial variability of stream discharge and chemistry and catchment area in low-flow condition (Fig. 6.1).

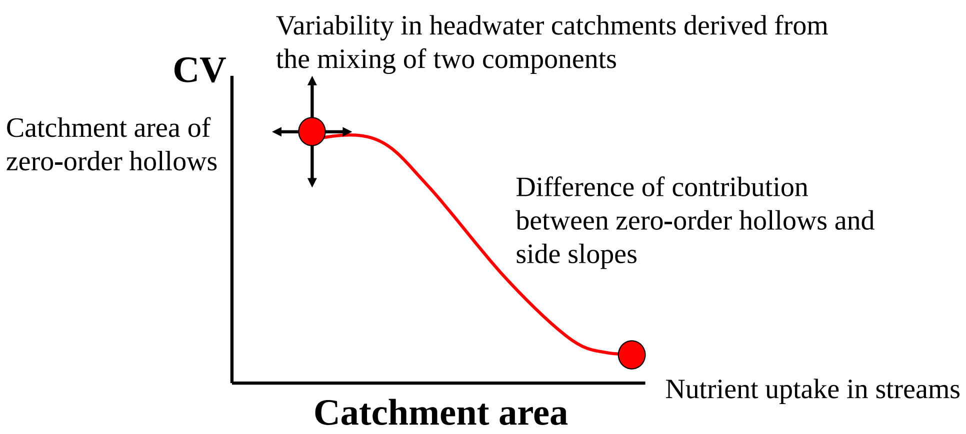
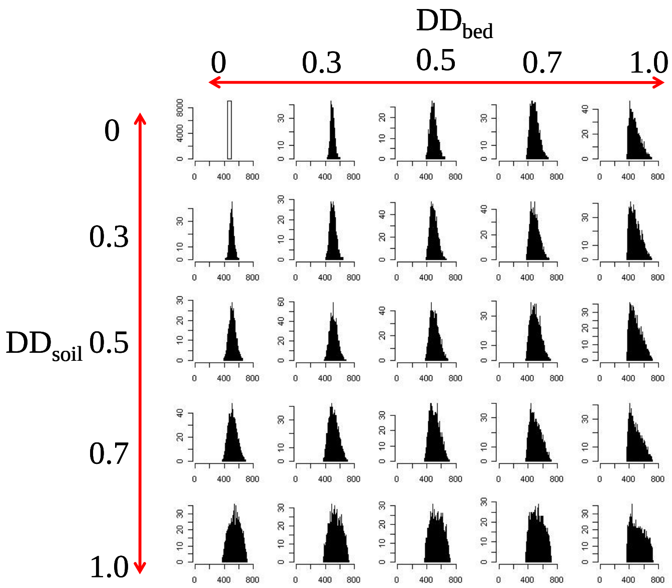


Figure 6.1 The conceptual diagrams of the factors, which influence the relationships between spatial variability of stream discharge and chemistry and catchment area in low-flow condition.

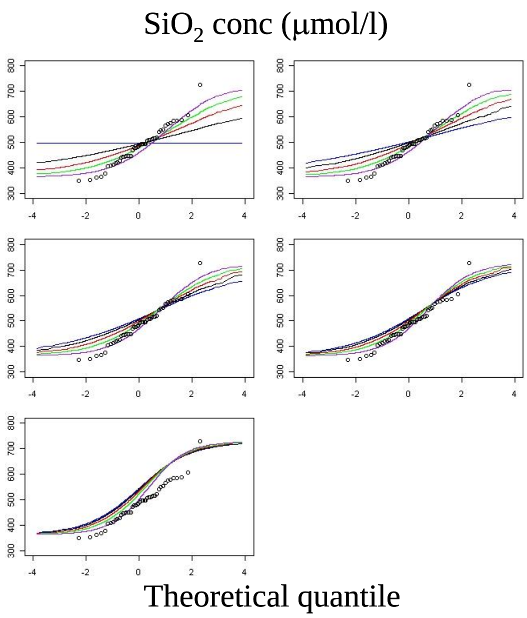
The method suggested from this study can be used as the framework for considering the influence of each factor, because it is able to consider each factor separately. The procedures are below. (1)To quantify deep bedrock groundwater discharge with catchment area from component separation of spatial variability stream water discharge and chemistry. (2) To quantify nutrient uptake in streams from nutrient addition experiment. (3) To examine the catchment area of zero-order hollow from observation. (4) To reproduce the characteristics of variability in headwater catchments from random mixing of several components, which have different flow path. And to know the degree of the components (5) To estimate percentage of side slope to zero-order hollow from model calculation of confluences with changing the percentages.

Through the method, we can obtain parameters about relationship between spatial variability of stream discharge and chemistry and catchment area. For future work, if we apply the same method in many catchments, we may detect the differences among catchments as the differences of parameters. Then we may elucidate how the differences of environmental factors (climate, geology, topography, soil, and so forth) influence on the spatial variability of stream discharge and chemistry from inter site comparison. And it will link to the prediction of spatial variability and the confluence of non-observed or poorly observed catchments.

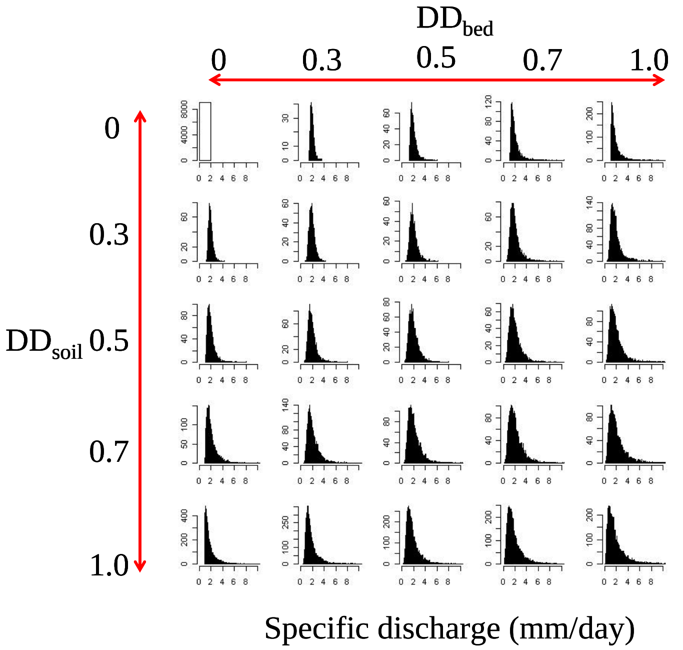
Appendix



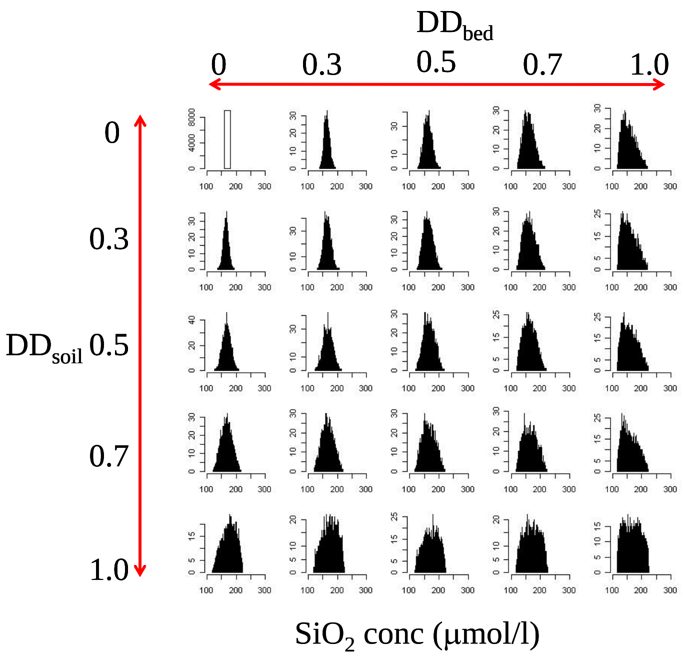
Appendix-1: Response of the variability in SiO_2 concentration to the change in variability in each component in Yozukugawa. The *x*-axis shows SiO_2 concentration (μmol/l), and the *y*-axis indicates frequency in generating ten thousand random values.



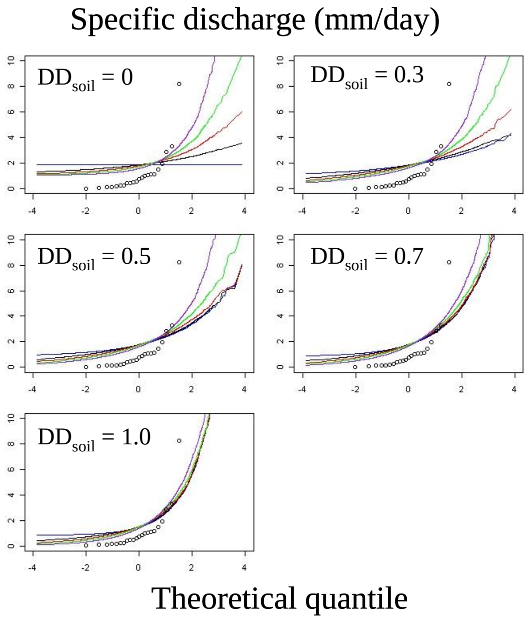
Appendix-2: Response of the distribution profile of SiO_2 concentration to the change in variability in each component in Yozukugawa. The *x*-axis shows the theoretical quartile of a normal distribution, and the *y*-axis indicates the specific discharge. Open circles are observed and lines are calculated values. Each window indicates the difference in DDsoil, and each line indicates the difference in DDbed. The blue, black, red, and green lines indicate 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively.



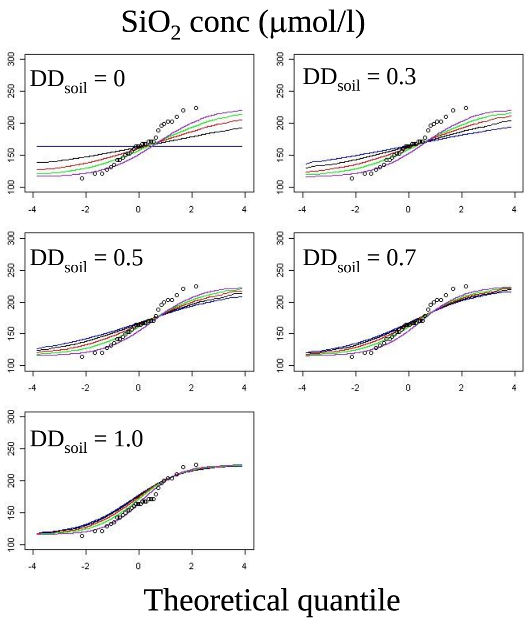
Appendix-3: Response of the variability in specific discharge to the change in variability in each component in Kusaki. The *x*-axis shows specific discharge (mm/day), and the *y*-axis indicates frequency in generating 10 thousand random values.



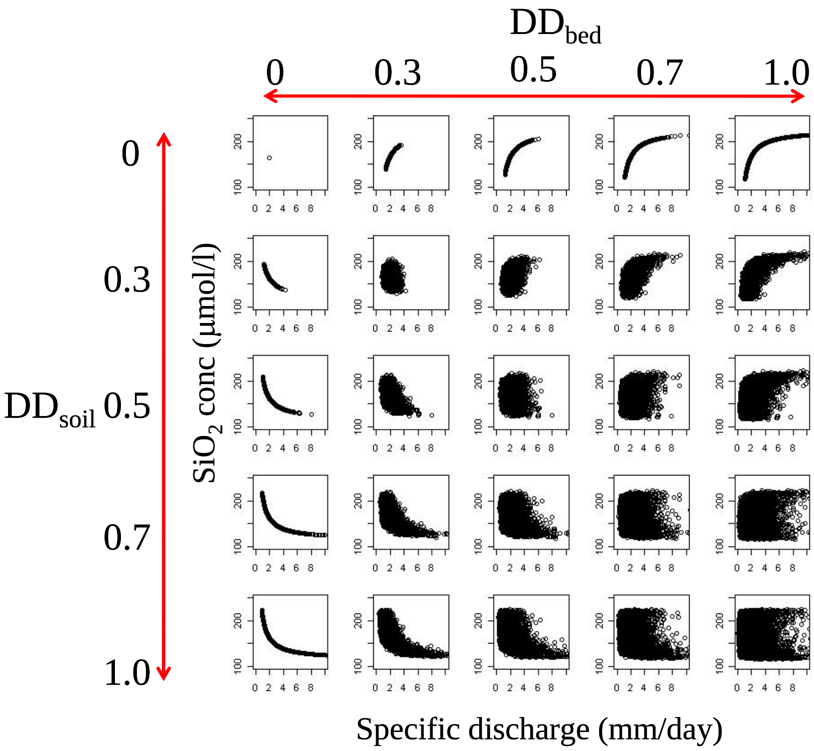
Appendix-4: Response of the variability in SiO_2 concentration to the change in variability in each component. The *x*-axis shows SiO_2 concentration (μmol/l), and the *y*-axis indicates frequency in generating ten thousand random values.



Appendix-5: Response of the distribution profile of specific discharge to the change in variability in each component in Kusaki. The *x*-axis shows the theoretical quartile of the normal distribution, and the *y*-axis indicates specific discharge. The open circles are observed and the lines are calculated values. Each window indicates the difference in DDsoil, and each line indicates the difference in DDbed. The blue, black, red, and green lines indicate 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively.



Appendix-6: Response of the distribution profile of SiO_2 concentration to the change in variability in each component in Kusaki. The *x*-axis shows the theoretical quartile of a normal distribution, and the *y*-axis indicates the specific discharge. Open circles are observed and lines are calculated values. Each window indicates the difference in DDsoil, and each line indicates the difference in DDbed. The blue, black, red, and green lines indicate 0.3, 0.5, 0.7, and 1.0 of DDbed, respectively.



Appendix-7: Response of the relationships between specific discharge and SiO_2 to the change in variability in each component in Kusaki. The *x*-axis shows specific discharge (mm/day), and the *y*-axis indicates SiO_2 concentration (µmol/l).