

Water Resources Research

RESEARCH ARTICLE

10.1029/2018WR024302

Key Points:

- We studied how spatial variability of stream discharge and water chemistry decreased with increasing catchment area
- Variability of stream discharge and water chemistry differed from variation estimated by simple mixing of random variables
- Degree of similarity in parameters' values that were located close together in space related to the decrease of variability of parameters

Supporting Information:

- Supporting Information S1

Correspondence to:

T. Egusa,
egusa@fr.a.u-tokyo.ac.jp

Citation:

Egusa, T., Kumagai, T., Oda, T., Gomi, T., & Ohte, N. (2019). Contrasting patterns in the decrease of spatial variability with increasing catchment area between stream discharge and water chemistry. *Water Resources Research*, 55, 7419–7435. <https://doi.org/10.1029/2018WR024302>

Received 22 OCT 2018

Accepted 18 AUG 2019

Accepted article online 21 AUG 2019

Published online 30 AUG 2019

Contrasting Patterns in the Decrease of Spatial Variability With Increasing Catchment Area Between Stream Discharge and Water Chemistry

Tomohiro Egusa¹ , Tomo'omi Kumagai^{1,2} , Tomoki Oda¹ , Takashi Gomi³, and Nobuhito Ohte⁴

¹Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan, ²Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan, ³Department of International Environmental and Agricultural Science, Tokyo University of Agriculture and Technology, Tokyo, Japan, ⁴Department of Social Informatics, Graduate School of Informatics, Kyoto University, Kyoto, Japan

Abstract Understanding how spatial variability in stream discharge and water chemistry decrease with increasing catchment area is required to improve our ability to predict hydrological and biogeochemical processes in ungauged basins. We investigated differences in this decrease of variability with increasing catchment area among catchments and among specific discharge (Q_s) and water chemistry parameters. We defined the slope of the decrease in the variability with increasing catchment area as the rate of decrease in the standard deviation and coefficient of variation (δ_{SD} and δ_{CV} , respectively), both of which are -0.5 for the simple mixing of random variables (random mixing). All δ_{SD} and δ_{CV} values of Q_s were less than -0.5 , while those of most water chemistry values were greater than -0.5 , indicating that with increased catchment area the spatial variability of Q_s decreased more steeply than for random mixing, while for water chemistry they decreased less steeply. δ_{SD} and δ_{CV} had linear relationships with both the spatial dissimilarity index and relative changes in parameters' mean values with increasing catchment area. It suggested that differences in δ_{SD} or δ_{CV} for Q_s and water chemistry can be explained by the different spatial structures, where dissimilar values of Q_s and similar values of water chemistry, respectively, are located close together in space. Differences in δ_{SD} and δ_{CV} according to Q_s and water chemistry should significantly affect the determination of representative elementary area and therefore need to be considered when predicting representative elementary area from spatial variability of low-order streams.

1. Introduction

Predictions of stream water discharge and chemistry in poorly gauged or ungauged basins (PUBs) are among the main themes of catchment hydrology (Hrachowitz et al., 2013; Sivapalan, 2003a). Although there is usually a large spatial variability in hydrological and biogeochemical processes among catchments (McDonnell et al., 2007), we cannot observe all catchments due to labor and financial constraints. Therefore, it is necessary to develop methodologies to use data from gauged catchments to make predictions in ungauged catchments. The relationships between hydrological and biogeochemical processes and landscape parameters such as vegetation, topography, soil, and geology provide essential information on PUB (McDonnell et al., 2007; Wagener et al., 2007). However, such information remains insufficient to fully identify the sources of spatial variability in hydrological and biogeochemical processes, and therefore, other approaches are needed.

Many studies have examined the relationships between spatial variability in hydrological and biogeochemical processes and spatial scale to obtain information about the spatial representativeness and potential of extrapolation of these processes (Blöschl, 2001; Sivapalan, 2003b; Tetzlaff et al., 2010). Wood et al. (1988, 1990) used a rainfall-runoff model to demonstrate that spatial variability in stream discharge decreases with increasing catchment area; the minimum area where spatial variability became sufficiently small to be ignored was designated the representative elementary area (REA). The relationships between spatial variability and catchment area, and the resulting REA, are important information for PUB. The REA is considered a threshold area above which we can explain spatial variability in hydrological or biogeochemical processes using landscape characteristics (Capell et al., 2012; Ecrepont et al., 2019; Tiwari

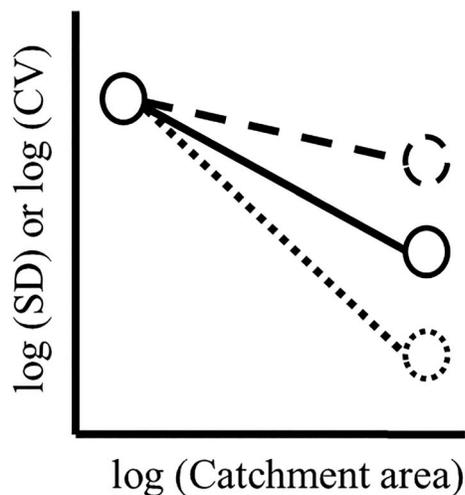


Figure 1. Conceptual diagram showing the difference in the decrease of spatial variability with increasing catchment area. The solid line shows the reference line (slope = -0.5) based on random mixing theory (Woods et al., 1995). The dotted and dashed lines indicate more and less steeply decreases in spatial variability with increasing catchment area than for the random mixing case, respectively. The slopes of these lines are referred to as the rate of decrease of the standard deviation (SD) and coefficient of variation, δ_{SD} and δ_{CV} , respectively (see section 2.3.1).

is, there is no organized pattern in the spatial arrangement of these parameters. For example, these parameters do not change with increasing catchment area due to groundwater discharge or in-stream processes, and similar values of specific parameters may not be located close together. In this case, the mixing of parameter values with increasing catchment area is essentially the same as random sampling from a population of parameter values. As a result, one reference line can be obtained for the decrease in variability with increasing catchment area (Figure 1). Woods et al. (1995) conducted multipoint observations of stream discharge within two catchments and found that the variability of stream discharge decreased more steeply than the reference line for both catchments, especially in small headwater catchments. However, Asano and Uchida (2010) reported that the variability of silica concentrations at approximately 60 locations within a catchment decreased less steeply than the reference line, especially in small headwater catchments. The limited number of parameters and catchments made it difficult to understand discrepancies in their results. Besides, the deviations from the reference line suggest the influence of spatial structure (Abbott et al., 2018). Barrios and Francés (2012) showed with a distributed hydrological model that REA became larger with increasing spatial correlation length of model parameters. In addition, locations of groundwater seeps to surface water could largely determine the formation of spatial variability of stream water chemistry (Zimmer et al., 2013). Therefore, we need to elucidate the linkages between the decrease in spatial variability of stream discharge and water chemistry with increasing catchment area and their spatial structure.

Geostatistical methods such as the semivariogram are useful for detecting spatial structure and have been widely used in hydrological and biogeochemical studies during the last two decades (reviewed by Isaak et al., 2014). Previous studies have quantified the spatial distance at which similarity is seen in observed values. Some studies have revealed spatial structures within the spatial variability of stream water chemistry (Dent & Grimm, 1999; Dong et al., 2017; Lessels et al., 2016; McGuire et al., 2014), and others have proposed methods to extrapolate stream discharge and water chemistry data to nearby locations (Archfield et al., 2013; Brennan et al., 2016; de Lavenne et al., 2016; Skøien & Blöschl, 2007; Ver Hoef et al., 2006). Such methods help to reveal the mechanisms in the decrease in spatial variability with increasing catchment area.

Our purpose was to obtain a better understanding of how the spatial variability of stream discharge and water chemistry decreases with increasing catchment area in small headwater catchments and how the size of REA is determined. For this purpose the following questions were addressed.

et al., 2017) and is useful as a unit area for distributed models (Sivapalan, 2018). Relationships between spatial variability and catchment area provide a basis for determining the locations and number of necessary observation points because small-scale catchments are generally easier to monitor and their processes easier to understand than for large-scale catchments (Frisbee et al., 2011; Uchida et al., 2005). Many studies have examined the relationships between spatial variability in stream discharge or water chemistry and catchment area, showing that the size of the REA differs greatly among catchments and parameters, ranging from a few to thousands of hectares (Asano et al., 2009; Didszun & Uhlenbrook, 2008; Egusa et al., 2013; Fischer et al., 2015; Likens & Buso, 2006; Lyon et al., 2012; Temnerud et al., 2007; Temnerud & Bishop, 2005; Woods et al., 1995; Zimmer et al., 2013).

Despite the large number of studies available, only a few have examined how spatial variability in stream discharge and water chemistry decreases with increasing catchment area and how the size of REA is determined. Woods et al. (1995) and Asano and Uchida (2010) were two exceptions and focused on the rate of decrease in spatial variability with increasing catchment area. To evaluate the rate of decrease in spatial variability and determine the underlying mechanism, a reference value is necessary. For this purpose, random mixing theory, which assumes a simple mixing of randomly distributed variables, was presented as the null hypothesis (Woods et al., 1995). This assumption means that there is no spatial structure with the variability of stream discharge or water chemistry; that

1. How does the rate of decrease in spatial variability with increasing catchment area differ among catchments and for stream discharge and water chemistry?
2. What type of spatial structure causes different rates of decrease in spatial variability with increasing catchment area?

2. Materials and Methods

2.1. Site Description

We studied three forest headwater catchments in the Kanto region of Japan (35.5°N, 139.5°E; Figure 2). All catchments are located in steep mountainous areas with slopes of more than 25°. The characteristics of the three catchments are given in Table 1. The climate of all three catchments is warm and humid, with a monthly average temperature of 0–5 °C in January and 20–25 °C in August (see Figure S1 for Inokawa and Oborasawa; see Koyanagi et al., 2003, for Kusaki). For all catchments rainfall is abundant from April to October, especially during the rainy season from June to July and during the typhoon season from September to October. Snowfall occurs occasionally from January to March; however, the amount is small and the effect of snowmelt on stream discharge is not clear (Figures 3a–3c).

Inokawa and Kusaki are underlain by sedimentary rock, and Oborasawa is underlain by igneous rock. In Inokawa, the bedrock is sandstone and mudstone of Neogene age (Nakajima et al., 1981). Although observations were conducted in the whole catchment, all points used for the analysis were in the mudstone area (Figure 2a). The bedrock of Kusaki is an accretionary complex of Jurassic age. Typical of accretionary complexes, a chert block is captured in *mélange* substrata; therefore, we studied both the chert and *mélange* areas (Figure 2b). The bedrock of Oborasawa is tuff and tuff breccia of Neogene age (Figure 2c).

The soils of Inokawa and Oborasawa are classified as Cambisols (Urakawa et al., 2016), and those of Kusaki are classified as Andosols, which is clearly influenced by volcanic sediments. In Inokawa and Oborasawa, soil depth was measured by a cone penetration test. In Inokawa, the average soil depths of two small catchments (~1 ha) were 2.87 and 2.22 m (Shiraki et al., 1999). In Oborasawa, the average soil depth was 1.64 m. At a small watershed (1.89 ha) named Oyasan, which is located 6 km west of the Kusaki catchments and has a similar geology to Kusaki, the average soil depth was 2.61 m (Shiraki et al., 2007).

2.2. Data

We sampled stream water under base flow conditions (Figure 3). The observation periods were as follows: 3–5 August 2009 in Inokawa, 27–29 August 2012 in Kusaki, and 25–26 June 2010 in Oborasawa. In each catchment, all points were observed only once. In total, there were 123, 90, and 48 observation points for Inokawa, Kusaki, and Oborasawa, respectively. For Inokawa, the observation points were the same as those used in Egusa et al. (2016).

There were rainfall events in all three catchments before the observations were made. In Inokawa, 117 and 1 mm of rain fell on 27–29 July and 2 August, respectively. The daily stream discharge values on 5 August decreased by 34–48% compared with those on 3 August in the three headwater catchments where we continuously monitored discharge (Figure 3d). In Kusaki, 26 mm of rain fell on 16–18 August and there was no rainfall during the week before our rain gauge observations in Oyasan. In Oborasawa, 97 and 24 mm of rain fell on 18–19 and 23 June, respectively. Daily stream discharges on 26 June decreased by 3–12% compared with those on 25 June at three points within Oborasawa (Figure 3e). In Oborasawa, 1 mm of rain fell between 14:00 and 18:00 on 26 June during our observations. However, there was no clear change in the stream discharge, and the influence on our observation results was negligible. We discuss the influence of these rainfall events before our observations campaigns on our observation results in section 2.4.

Here, specific discharge (Q_s) denotes the stream discharge per contributing catchment area. The stream discharge at an observation point was calculated by multiplying the cross-sectional area (S) by the water flow velocity (V). S was obtained by measuring water depths at an interval of 5–100 cm over the entire stream width. V was measured at the same interval of stream depth at 60% of the water depth from the water surface using an electromagnetic velocity meter (VE-20, Kenek, Tokyo, Japan). At points where discharge was low, the discharge was quantified using the bucket method, that is, measuring the water mass collected over a specific time interval.

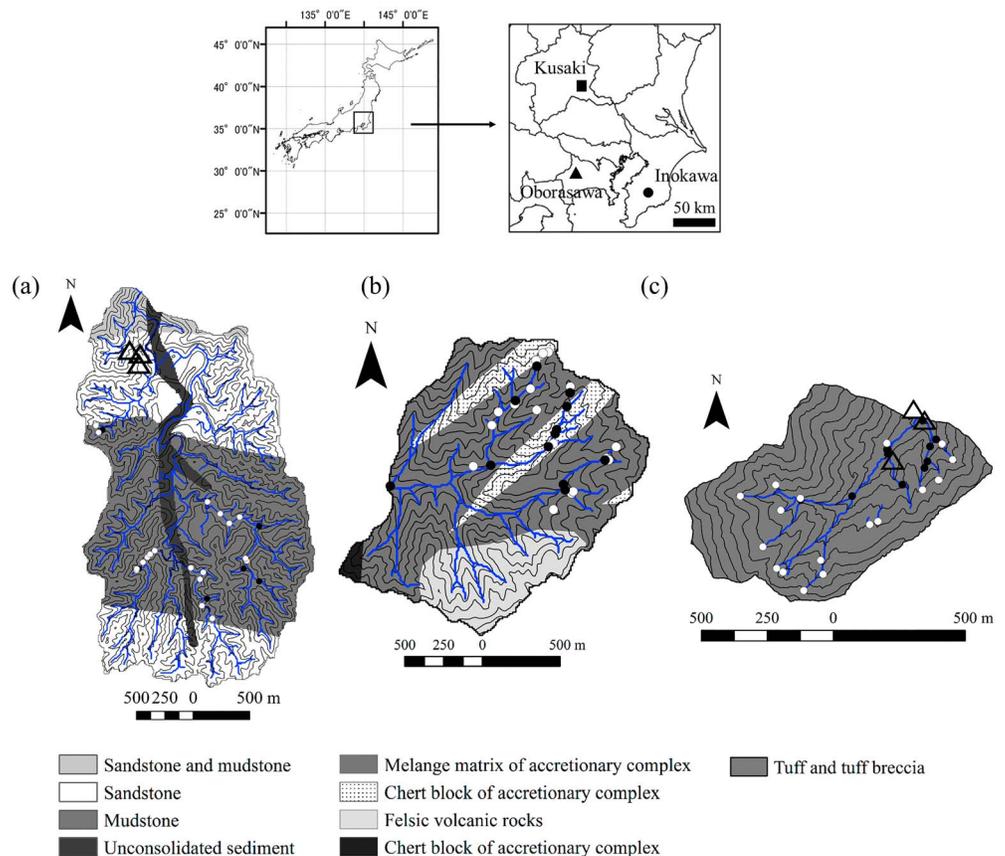


Figure 2. The locations of the three catchments in Japan and the locations of streams and observation points in (a) Inokawa, (b) Kusaki, and (c) Oborasawa. Blue and black lines show streams and contours, respectively. The interval of the contour line is 30 m. In Inokawa and Kusaki, open and solid circles denote first- and second-order streams, respectively. In Oborasawa, open and solid circles indicate the headwaters and first-order to third-order streams, respectively. For each catchment, we show only the points that were used for the analysis. The open triangles show the continuous monitoring points for stream discharge, Fukuroyamasawa A (1 ha), B (1 ha), and C (2 ha) in Inokawa No 1 (48 ha), No 3 (7 ha), and No 4 (5 ha) catchments in Oborasawa.

We measured the electrical conductivity (EC) in situ using an EC meter (D54, Horiba, Kyoto, Japan). The concentrations of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were analyzed in the laboratory using ion chromatography (LC10-A, Shimadzu, Kyoto, Japan). The Si concentration was analyzed for samples from Kusaki and Oborasawa using the molybdenum yellow method and a spectrophotometer (U-1800, Hitachi, Tokyo, Japan).

We obtained samples for analysis from all observation points. The criteria for excluding points were follows: (1) less than 80% of the catchment area contained the target geology (there were 77, 33, and 0 points for Inokawa, Kusaki, and Oborasawa, respectively); (2) either stream discharge or water chemistry was not observed (9, 16, and 11 points for Inokawa, Kusaki, and Oborasawa, respectively); (3) third-order or larger streams for Inokawa and Kusaki and fourth-order streams for Oborasawa (11, 10, and 0 points for Inokawa, Kusaki, and Oborasawa, respectively); and (4) there was another observation point nearby (1, 2, and 9 points for Inokawa, Kusaki, and Oborasawa, respectively). The last criterion was included because the analyses conducted in this study required independent data. When two observation points were adjacent to each other, if the difference in catchment area between them was less than 1 ha, or if they were on each side of a stream confluence, we excluded the downstream point. As a result, 25, 29, and 28 points were selected for Inokawa, Kusaki, and Oborasawa, respectively (Figure 2). The observation points were classified into first-order or second-order streams in Inokawa and Kusaki (cf. Figures 2a and 2b). For Oborasawa, we classified the observation points into headwater springs and first-order to third-order streams (cf. Figure 2c).

Table 1
Comparative Features of the Three Study Catchments

	Inokawa	Kusaki	Oborasawa
Location	35°11–13'N, 140°06–07'E	36°34–36'N, 139°22–26'E	35°28'N, 139°12'E
Catchment area	507 ha	227 ha	55 ha
Altitude	90–346 m	748–1,140 m	439–872 m
Slope	31.4° ± 12.0°	28.8° ± 8.7°	34.9° ± 9.0°
Mean annual rainfall	2,304 mm (1994–2010)	1,936 mm (1997–2002) ^a	2,950 mm (1982–2000) ^b
Mean air temperature	14.2 °C (1998–2000)	9.3 °C (1997–2002) ^a	12.1 °C (2009–2014) ^b
Bedrock	Sand stone and mudstone	Mélange and chert block	Tuff and volcanic breccia
Soil	Cambisol	Andosol	Cambisol

^aData from Koyanagi et al. (2003). ^bData from Uchiyama et al. (2014).

2.3. Data Analysis

We first quantified the rate of decrease in the spatial variability of the parameters (specific discharge, EC, and concentrations) with increasing catchment area (section 2.3.1). Then, we defined two indices to evaluate the spatial structure of the parameters. One was *relative difference*, which referred to the ratio (in percentage) of the parameters' mean values between low- and high-order streams. Positive and negative values of relative difference mean the increase and the decrease of the parameters' mean values, respectively. The other was D_{200} , which indicated the dissimilarity of parameter values within subcatchments (section 2.3.2).

2.3.1. The Decreasing Rate of Spatial Variability With Increasing Catchment Area

Random mixing theory assumes a simple mixing of randomly distributed variables. Therefore, the mixing of parameter values with increasing catchment area is equivalent to random sampling from the population of parameter values. As a result, the decrease in spatial variation of parameters with increasing catchment area (A) could be obtained from the law of large numbers:

$$\text{Var}(\bar{X}_A) = \sigma^2/A, \quad (1)$$

where \bar{X}_A is the samples' mean parameter value, with an average area of A , and σ^2 is the variance of the parameter values in the population. Equation (1) indicates that the sample variation should decrease at a rate of $1/A$ as the catchment area increases.

If the data characteristics follow the random mixing theory, the logarithmic relationship between the standard deviation (SD) or coefficient of variation (CV) and A should be linear, with a slope of -0.5 (Figure 1). If the slope is less than -0.5 , the decrease in the variation is referred to as being a greater decrease than for the random mixing case; if the slope is greater than -0.5 , the decrease in variation is less than the random mixing case. In this study, we referred to the slopes of the logarithmic functions of SD and CV with A as the rate of decrease of SD (δ_{SD}) and CV (δ_{CV}), respectively.

We compared δ_{SD} and δ_{CV} among the catchments and parameters via a t test with the Holm method and the Bartlett test using R software (version 3.4.2). For the comparison of δ_{SD} and δ_{CV} among catchments, all parameters were pooled within each catchment. When we compared δ_{SD} and δ_{CV} among parameters, we classified the water chemistry parameters into three groups based on their main source: (1) *atmospheric input*, where the concentration is comparable in soil water and groundwater (Cl^- in Inokawa and Cl^- and SO_4^{2-} in Kusaki and Oborasawa), (2) *biological activity*, where concentrations are higher in soil water than in groundwater (NO_3^- and K^+ in the three catchments), and (3) *mineral weathering*, where concentrations are lower in soil water than in groundwater (other water chemistry). This classification was based on soil water and groundwater data collected for Inokawa and Oborasawa (Egusa et al., 2016, for Inokawa; Figure S2 in the supporting information for Oborasawa). Because there was no information for Kusaki, we used the same classification as for Oborasawa.

2.3.2. Spatial Dissimilarity Index

An index of the spatial dissimilarity of two observation points i and j is given by

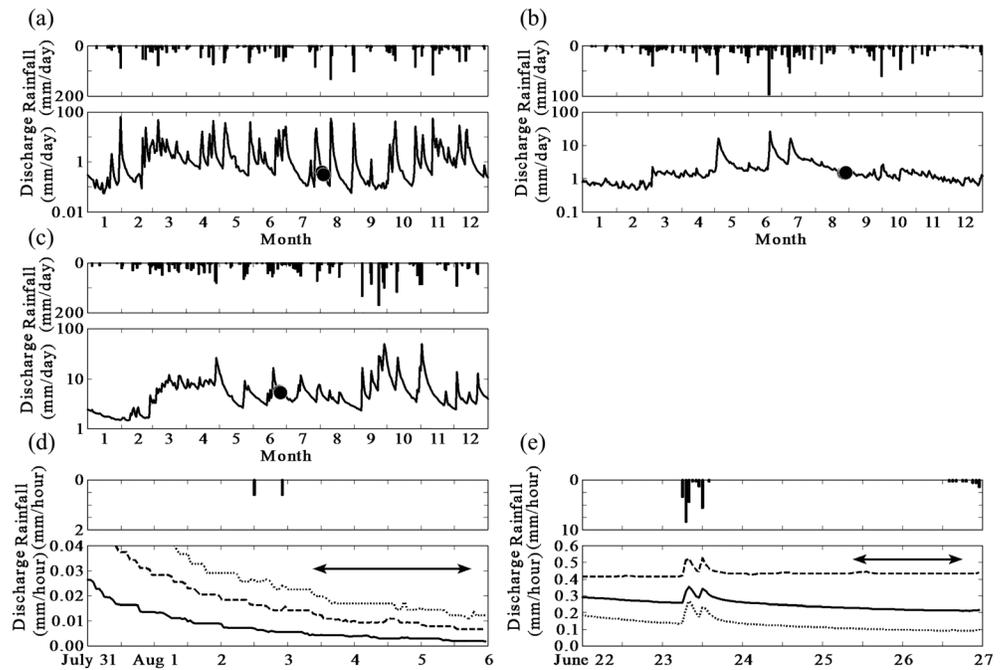


Figure 3. Daily rainfall and daily stream discharge for the year of our sampling campaign for (a) Inokawa, (b) Kusaki, and (c) Oborasawa. Points indicate the dates of our sampling campaigns. Daily stream discharge was measured at Fukuroyamasawa-C catchment for Inokawa and No 1 catchment for Oborasawa. For Kusaki, we used the daily rainfall and stream discharge data of Oyasan, which is 6 km west of Kusaki. Hourly rainfall and hourly stream discharge from 3 days before our sampling campaign for (d) Inokawa and (e) Oborasawa. The solid, dotted, and dashed lines show stream discharges at Fukuroyamasawa A, B, and C, respectively, for Inokawa and stream discharges at No 1, No 3, and No 4 catchments, respectively, for Oborasawa. Arrows indicate the duration of our sampling campaigns.

$$\gamma(h) = (Z_i - Z_j)^2 / 2, \quad (2)$$

where Z_i and Z_j are the observed values at points i and j , respectively, and h is the distance between points i and j (Wackernagel, 1998). A large value of $\gamma(h)$ indicates little similarity between the two points. Note that in order to use $\gamma(h)$, we should consider the pattern of connections among observation points (McGuire et al., 2014). For example, if we conduct sampling at two points in a river channel, the parameter values observed at these two points might be similar. Thus, we used only data from first-order streams and springs in this study (see Figure 2).

We defined the index of spatial dissimilarity within a small range, D_{200} (%), as

$$D_{200} = \frac{\overline{\gamma}_{(<200\text{ m})} - \overline{\gamma}_{(\text{all})}}{\overline{\gamma}_{(\text{all})}} \times 100, \quad (3)$$

where $\overline{\gamma}_{(<200\text{ m})}$ and $\overline{\gamma}_{(\text{all})}$ denote the averages of $\gamma(h)$ within a 200-m range and over whole the catchment, respectively. The 200-m range was used for this index because the catchment areas of the headwaters in this study were approximately 1 ha (100 m \times 100 m); therefore, 200 m was considered a reasonable distance to examine spatial similarities among first-order streams at their confluence. When D_{200} is zero, the spatial dissimilarity among observation points within the 200-m range is equal to that for whole the catchment. If D_{200} is a positive value, the degree of spatial dissimilarity is larger among points within the 200-m range than for the whole of the catchment. Conversely, if D_{200} is negative, the degree of spatial dissimilarity is smaller among points within the 200-m range than that for the whole of the catchment.

2.4. Influence of Antecedent Rainfall Events on Stream Discharge and Water Chemistry Data

In Inokawa and Oborasawa, rainfall events before the observation campaign caused a moderate change in stream discharge during our sampling period (Figures 3d and 3e), and therefore, we evaluated the

influence of Q_s on the δ_{SD} and δ_{CV} by using continuous stream discharge data for the three subcatchments (Figures 2a and 2c). For Inokawa, we used hourly stream discharges of continuous monitoring points at 12:00 on 4 August (Q_{ref}) and those at the time of our snapshot observations (Q_{obs}) and multiplied by Q_{ref}/Q_{obs} averaged over three points, with the observed Q_s . For Oborasawa, a similar verification was conducted using daily stream discharge data. The daily stream discharge on 25 June was 1.06 times larger than that on 26 June; therefore, we multiplied the observed Q_s on 26 June by 1.06.

When using this correlation factor, δ_{SD} and δ_{CV} values changed from -0.76 to -0.82 and -0.57 to -0.63 , respectively, in Inokawa and from -1.00 to -1.01 and -0.52 to -0.53 , respectively, in Oborasawa. Both the original and modified rates of decrease were smaller than -0.5 and thus were qualitatively similar. We used these modified values of Q_s in all our analyses.

Antecedent rainfall events might also impact water chemistry. However, in the two catchments, the fluctuations of water chemistry were usually small, even 1–2 days after rainfall events of 100 mm (Oda et al., 2011, for Inokawa; Figure S3 for Oborasawa) and at least 4 days passed between large rainfall events and our observations. The influence of rainfall events on the water chemistry results was thus assumed to be negligible, but this might still be a source of uncertainty.

Other observation campaigns were conducted in the two catchments under base flow conditions (Figures S4 and S5). It should be noted that not all the points of the two catchments used in the analysis were observed repeatedly. Most parameters recorded in the observations in this study were positively linear correlated with those of other observations. The tendency of the spatial variation in stream discharge and water chemistry was temporally stable under base flow conditions. This reinforced our assumption that the influence of antecedent rainfall events on our results was small.

3. Results

3.1. Relationships Between Q_s or Water Chemistry and Catchment Area

The catchment areas (average \pm standard error) of low- and high-order streams were 1.2 ± 0.2 ha ($n = 19$) and 4.6 ± 1.3 ha ($n = 6$), respectively, in Inokawa; 2.2 ± 0.5 ha ($n = 17$) and 11.8 ± 2.5 ha ($n = 12$), respectively, in Kusaki; and 0.89 ± 0.26 ha ($n = 18$) and 8.7 ± 3.3 ha ($n = 10$), respectively, in Oborasawa (Figure 4). Q_s decreased from low- to higher-order streams by 65% and 68% in Kusaki (Figure 4b) and Oborasawa (Figure 4c), respectively. The average values of EC and SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations in Inokawa (Figure 4a) and K^+ in Oborasawa (Figure 4c) increased from low- to higher-order streams by more than 10%. The average values of Q_s in Inokawa, Q_s and K^+ concentration in Kusaki (Figure 4b), and Q_s and EC, and Cl^- , NO_3^- , and SO_4^{2-} concentrations in Oborasawa (Figure 4c) decreased from low- to higher-order streams by more than 10%. The average values for the other 14 parameters remained relatively constant.

The SD and CV values of almost all parameters (except the CV of SO_4^{2-} in Kusaki) in Kusaki and Oborasawa decreased with increasing catchment area (Figures 4e, 4f, 4h, and 4i). The slopes of the decreases in these parameters varied substantially. In Inokawa, the SD of EC and the SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations increased with catchment area, and the CV of EC and the NO_3^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations increased with catchment area (Figures 4d and 4g).

3.2. Differences in the Rate of Decrease of All Parameters Among Catchments and for Q_s and Water Chemistry

Seven and six parameters had δ_{SD} and δ_{CV} values that were less than -0.5 (i.e., the reference slope for the random mixing case; see section 2.3.1 and Figures 1 and 5), respectively. The δ_{SD} and δ_{CV} values for all parameters ranged from -1.43 to 0.42 and from -0.78 to 0.26 , respectively. There were no significant differences in the δ_{SD} and δ_{CV} values pooled by catchment among all pairs of catchments when using all parameters for the statistical analysis ($p = 0.09$ – 0.74). However, in the analysis of water chemistry data alone, the δ_{SD} in Inokawa was significantly greater than for the other two catchments ($p < 0.01$), and the δ_{CV} for Inokawa was significantly greater than that for Kusaki ($p < 0.05$).

The δ_{SD} and δ_{CV} values for Q_s and the pooled water chemistry in each catchment are listed in Table 2. We found that the outliers, that is, the more negative values in Figure 5, were due to the rate of decrease of Q_s

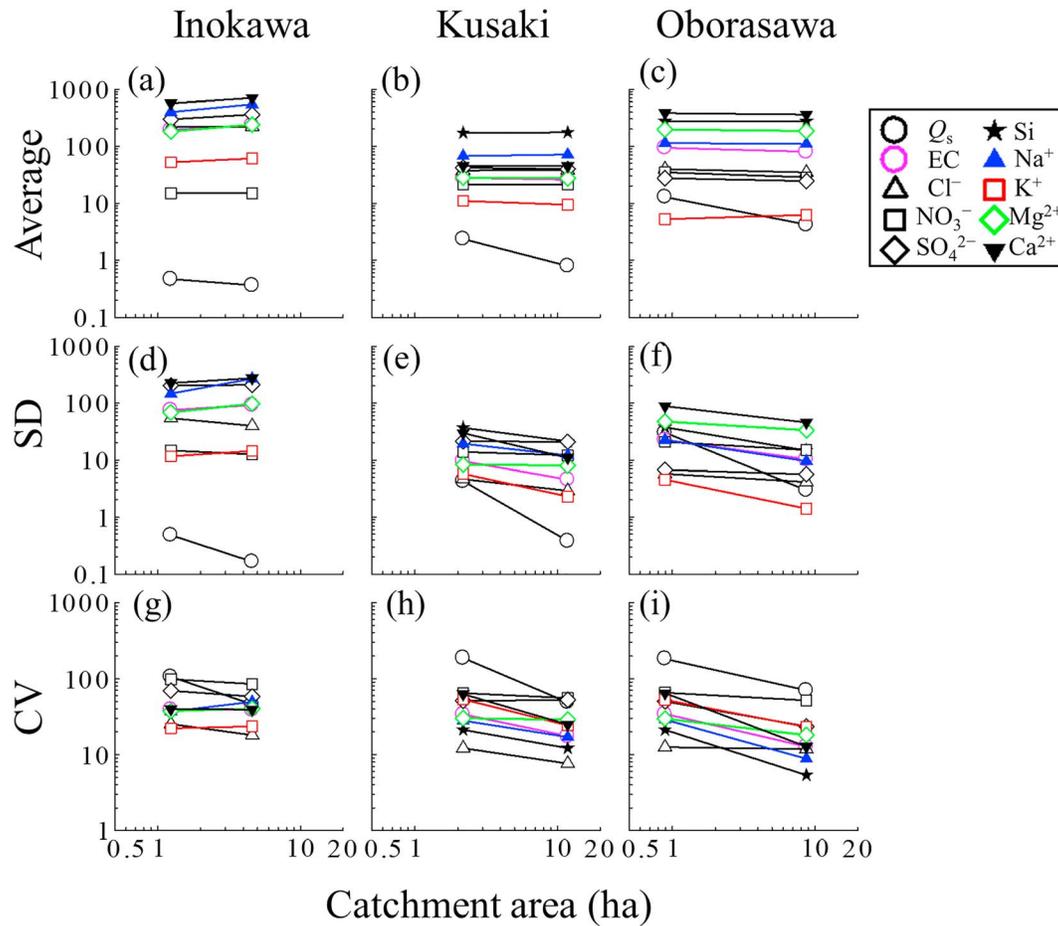


Figure 4. Relationships between catchment area and the average, SD, and coefficient of variation (CV) of Q_s and water chemistry parameters in Inokawa, Kusaki, and Oborasawa. A logarithmic axis is used for all variables. The units of the parameters are mm/day for Q_s , $\mu\text{S}/\text{cm}$ for EC, and $\mu\text{mol}/\text{L}$ for all concentrations.

with catchment area. The δ_{SD} of Q_s was less than the values for the other three water chemistry groups ($p < 0.01$; Figure 6a). For δ_{CV} , only the difference between Q_s and mineral weathering-derived solutes was significant ($p < 0.05$; Figure 6b).

3.3. Relationships Between the Relative Difference or D_{200} and the Rate of Decrease in Variation

The relative difference was positively linear correlated with δ_{SD} ($p < 0.001$; $R^2 = 0.65$; Figure 7a) and δ_{CV} ($p < 0.01$; $R^2 = 0.33$; Figure 7b). The Q_s in all three catchments and water chemistry in Inokawa differed markedly from the other groups of observations (Figures 7a and 7b). For example, the average Q_s values in the three catchments decreased significantly, and δ_{SD} and δ_{CV} values were considerably negative. Conversely, for the water chemistry in Inokawa average values increased with catchment size and δ_{SD} and δ_{CV} values were 0–0.5 (i.e., positive). Although the relative differences in the water chemistry in Kusaki and Oborasawa were small, the δ_{SD} and δ_{CV} values varied largely from -0.6 to 0 (Figures 7a and 7b).

It should be noted that the D_{200} values of most parameters were negative, and only the D_{200} of Q_s in Kusaki and Oborasawa, Cl^- in Kusaki, and Si in Oborasawa were positive (Figures 7c and 7d). The D_{200} was negatively linear correlated with δ_{SD} ($p < 0.001$; $R^2 = 0.41$; Figure 7c) and δ_{CV} ($p < 0.01$; $R^2 = 0.25$; Figure 7d). The D_{200} of Q_s in the three catchments and the water chemistry in Inokawa clustered differently from the other groups of parameters (Figures 7c and 7d). The D_{200} was higher for Q_s than the other parameters, and the δ_{SD} and δ_{CV} values were very negative (-0.5 to -1.5). The D_{200} values for water chemistry in Inokawa had particularly large negative values (-40% to -80%), and the δ_{SD} and δ_{CV} values were relatively high (-0.5 to 0.5).

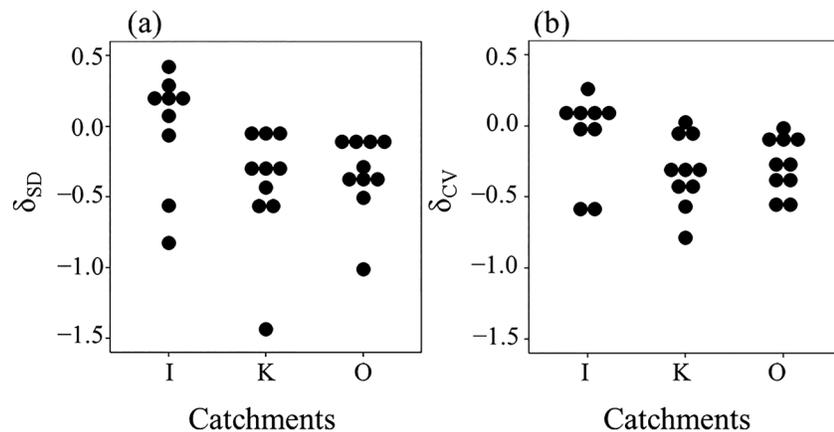


Figure 5. Comparisons of the (a) δ_{SD} and (b) δ_{CV} among the three catchments, Inokawa (I), Kusaki (K), and Oborasawa (O). The bin width of the values was set to 0.1. δ_{SD} and δ_{CV} are -0.5 for the random mixing case. Smaller and greater values than -0.5 indicate more and less steep decreases, respectively, than for the random mixing case (see Figure 1 and section 2.3.1).

4. Discussion

4.1. The Differences in the Rate of Decrease Between Q_s and Water Chemistry Were Caused by Different Spatial Structures of Q_s and Water Chemistry

Woods et al. (1995) demonstrated for two catchments that the SD of Q_s had a greater decrease with an increase in catchment area than for random mixing. However, Asano and Uchida (2010) reported that the SD of the Si concentration decreased less with increasing catchment area than for the random mixing case. It should be noted that the limited number of parameters and catchments resulted in difficulty in interpreting the results of these two studies. In this study, we used three catchments, which included many subcatchments, and multiple parameters (Q_s and the nine water chemistry parameters). The SD and CV of Q_s decreased more with increasing catchment area than for the random mixing case in all three catchments (Table 2) but decreased less with increasing catchment area than for the random mixing case for most water chemistry parameters (Table 2 and Figure 6). Thus, we demonstrated that the difference in Woods et al. (1995) and Asano and Uchida (2010) can probably be explained by the difference in their parameters (Q_s versus Si).

The average Q_s decreased with increasing catchment area (Figures 4 and 7). Based on previous studies conducted in steep forest headwater catchments similar as our sites, we speculate that groundwater infiltration from the stream to underground aquifers (e.g., Payn et al., 2009) and/or a difference in Q_s between a valley head and its side slopes (Fujimoto et al., 2008, 2011) caused the decreases in average Q_s (Figure 4). This would lead to larger and smaller values of Q_s tended to appear in the valley heads of first-order streams

and in downstream sites, respectively. Furthermore, according to the analyses of D_{200} of Q_s , the Q_s values in neighboring first-order catchments were dissimilar in Kusaki and Oborasawa. This meant a similar spatial structure as mentioned above, that is, larger and smaller Q_s values in two neighboring catchments. This situation may be due to groundwater exchange across the catchment boundary (Aishlin & McNamara, 2011; Genereux et al., 2005). Differences in vegetation and soil layer thickness are also potential influencing factors (Karlsen et al., 2016). As a result, the main catchment consists of groups of subcatchments with significantly differing Q_s values and the δ_{SD} and δ_{CV} of Q_s will decrease more than the random mixing case (Figure 8a).

Here, we have to keep in mind the possibility that the way we chose observation points could impact the Q_s results. We did not observe points without surface water although their catchment areas were sometimes larger

Table 2

The Rate of Decrease of the Standard Deviation (δ_{SD}) and Coefficient of Variation (δ_{CV}) for Specific Discharge (Q_s) and Water Chemistry Parameters in the Three Study Catchments

	δ_{SD}		δ_{CV}	
	Q_s	Water chemistry ^a	Q_s	Water chemistry
Inokawa	-0.82	0.09 ± 0.30	-0.63	0.01 ± 0.24
Kusaki	-1.43	-0.29 ± 0.21	-0.78	-0.27 ± 0.20
Oborasawa	-1.01	-0.27 ± 0.15	-0.53	-0.24 ± 0.19

Note. Values for water chemistry parameters are expressed as the average ± standard deviation.

^aAll water chemistry parameters are pooled.

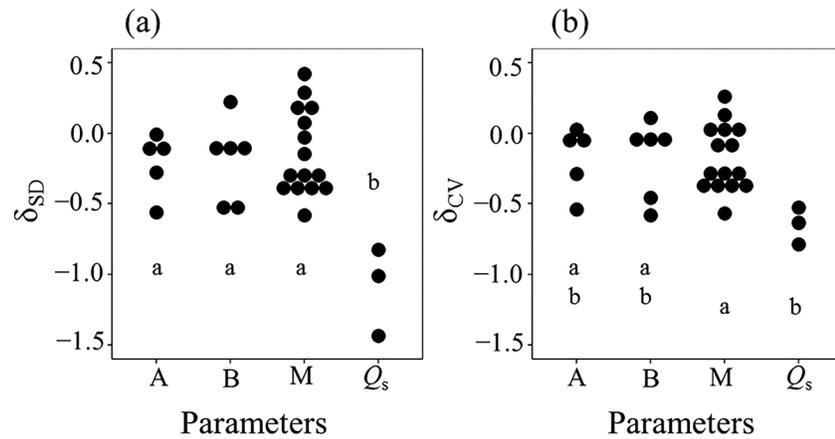


Figure 6. Comparisons of (a) δ_{SD} and (b) δ_{CV} values among parameters. A, B, and M indicate water chemistry derived from atmospheric inputs, biological activities, and mineral weathering, respectively, and Q_s denotes specific discharge. The bin width was set to 0.1. Different letters indicate significant differences among groups within each rate of decrease (t test with Holm's method; $p < 0.05$). δ_{SD} and δ_{CV} were -0.5 for the random mixing case. Smaller and greater values than -0.5 indicate more and less steep decreases, respectively, than for the random mixing case (see Figure 1 and section 2.3.1).

than the average area of first-order streams. Therefore, the average catchment area of observable first-order streams tended to become small and their average Q_s values may have become larger than when these dry first-order streams were included. That is, the Q_s trends shown in this study may depend on our observations. Conversely, other observation strategies may lead to different trends in Q_s , facilitating the identification of mechanisms forming the spatial variability of Q_s . Therefore, it will be worthwhile to try different observation strategies in the future, for example, dividing the main catchment into a number of subcatchments with a fixed catchment area and observing the water volume discharged from each subcatchment into streams, including zero values. This might provide new perspectives and interpretations of the spatial structure shown in this study.

In contrast to the case of Q_s , the average changes in water chemistry were small in Kusaki and Oborasawa and increased with catchment area in Inokawa (Figures 4 and 7), and the D_{200} values of the water chemistry parameters were negative in all catchments (except for the Cl^- in Kusaki and Si in Oborasawa; Figure 7). The D_{200} analysis indicated that the values of water chemistry in neighboring first-order catchments were similar. This characteristic would lead to the spatial structure of water chemistry that differs from that of Q_s (Figure 8b). As a result, the δ_{SD} and δ_{CV} values of water chemistry would decrease less than the random mixing case. The differences in δ_{SD} and δ_{CV} among the three water chemistry groups were not significant (Figure 6). All sites were fully covered with forests, and we targeted only the areas where the geology belonged to one group according to the geological map (Figure 2). The concentrations of water in first-order streams had a poor or no correlation with the average slope, elevation, and topographic wetness index (except for a positive correlation between SO_4^{2-} and the average slope and for a negative correlation between Mg^{2+} and the average elevation in Kusaki; data not shown). The D_{200} showed that similar values were located close together in space. We speculated that this might have occurred due to various factors. For example, due to the wind direction and/or spatial rainfall pattern, wet and dry deposition would be similar within neighboring catchments. In the case of NO_3^- , mineralization/nitrification processes are strongly dependent on temperature, and it is therefore possible that a similar temperature would cause similar NO_3^- concentrations within neighboring catchments. Although the geology of each site was categorized as being part of the same group, folding might make the characteristics of sedimentary rocks spatially heterogeneous. In future studies, it is necessary to collect detailed landscape information and clarify the factors leading to the spatial variability of water chemistry within each catchment.

In Inokawa, previous studies revealed that a large amount of groundwater infiltrates into the bedrock of a small headwater catchment (e.g., Oda et al., 2008), resulting in an increase in the concentrations of mineral derived solutes, and discharge of groundwater with high concentrations in downstream areas (Egusa et al., 2016). Water chemistry parameters with a positive relative difference in Inokawa were mineral-derived

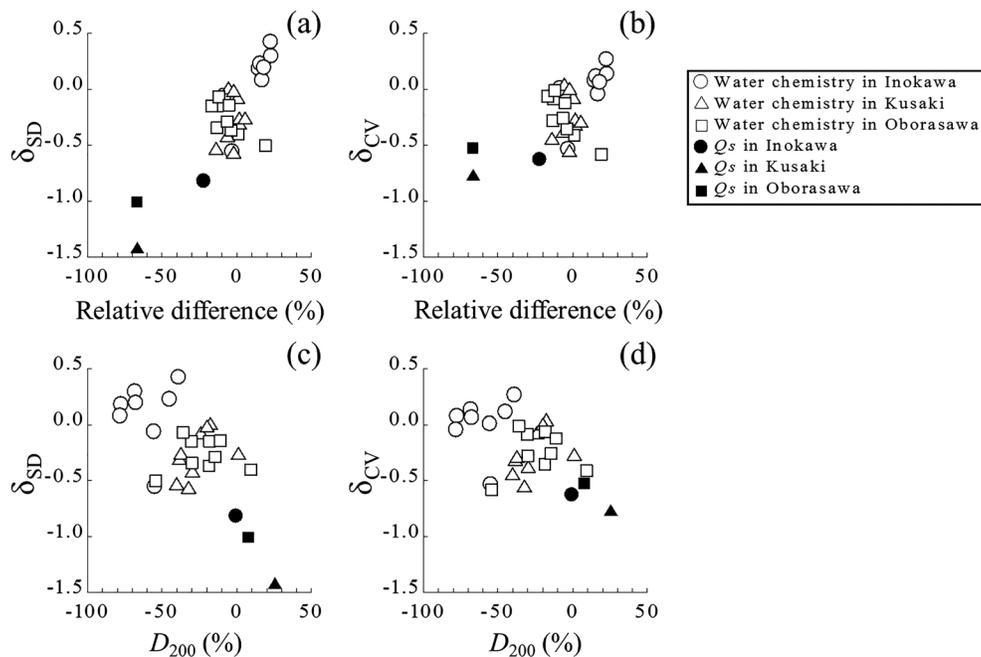


Figure 7. The (a, c) δ_{SD} and (b, d) δ_{CV} of Q_s and water chemistry as a function of (a, b) the relative difference and (c, d) the spatial dissimilarity index (D_{200}). Here, positive and negative values in D_{200} mean dissimilar and similar parameter values, respectively, are located close together in space. Positive and negative values in the relative difference indicate the average in parameter values increases and decreases with increasing catchment area, respectively (see section 2.3 and equation (3)). Solid and open symbols denote Q_s and water chemistry, respectively. The circle, triangle, and square denote the study catchments of Inokawa, Kusaki, and Oborasawa, respectively.

solutes (Figure 4a); therefore, it is reasonable to assume that groundwater discharge caused the increases in concentrations with catchment size. In areas where groundwater was discharged, the concentrations of mineral derived solutes would be high even in first-order streams and would increase with increasing catchment area. Thus, high concentrations of mineral derived solutes were located close together where groundwater was discharged. This would cause the positive values of relative difference (Figure 4) and highly negative values of D_{200} values (Figure 7), resulting in positive rates of decrease in δ_{SD} and δ_{CV} (Figure 5).

4.2. Temporal Stability of the Results

Our results were based on one-time sampling under base flow conditions. However, in Inokawa and Oborasawa, comparisons with other observation campaigns suggest that spatial patterns of Q_s and water chemistry during base flow conditions among the observation points were stable (see section 2.4). Previous studies also have shown that spatial patterns of water chemistry are temporally stable under base flow conditions (Abbott et al., 2018; Asano et al., 2009; Temnerud & Bishop, 2005; Zimmer et al., 2013), and even during stormflow periods (Abbott et al., 2018). For Q_s , although one study showed that spatial patterns were not temporally stable (Lyon et al., 2012), others have reported temporally stable spatial patterns (Asano et al., 2009; Bergstrom et al., 2016). Among these, Asano et al. (2009) targeted a temperate forested headwater catchment similar to those examined in this study. Therefore, at least under base flow conditions, the tendencies of our results are likely to be temporally stable.

However, it is unknown whether the tendency will continue during stormflow periods. Flow paths, which potentially cause a spatial variability of Q_s and water chemistry, change substantially with rainfall events (Blöschl & Sivapalan, 1995). For example, the influence of the flow paths through bedrock would become relatively smaller, while the influence of a shallow flow path would become larger. In addition, as the magnitude of rainfall increases, the effects of in-stream processes on stream water C, N, and P concentrations are expected to decrease (Raymond et al., 2016; Wollheim et al., 2018). These changes might increase the role of surface topography and lead to a different spatial structure and rate of decrease in Q_s and water chemistry from base flow conditions.

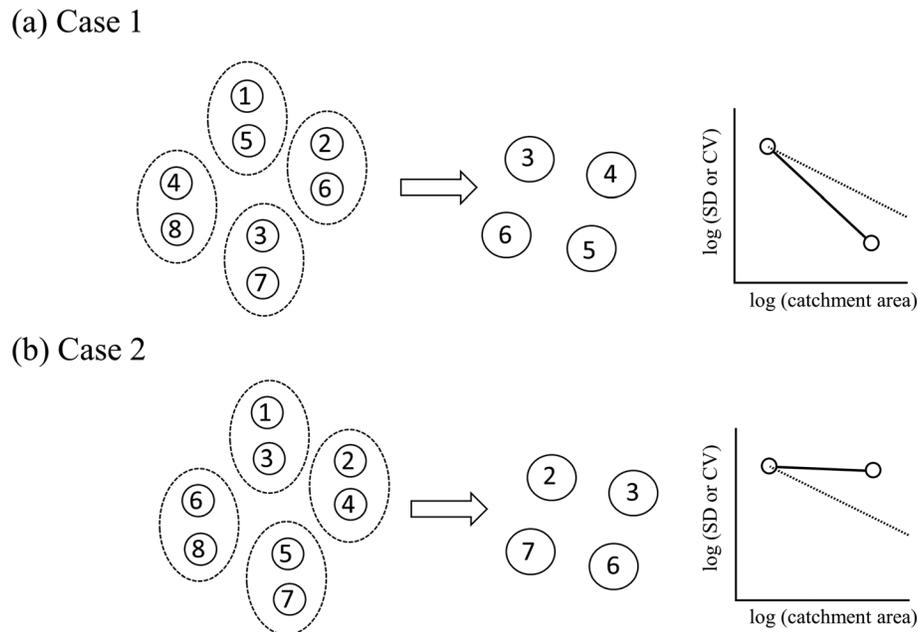


Figure 8. Conceptual diagram showing the influence of the spatial structure of parameters on the decrease of spatial variability with increasing catchment area. Each numeral denotes a parameter in a stream order catchment. Solid and dotted lines indicate the rate of decrease of cases 1 and 2, and the random mixing case, respectively. Note that variations in the parameters over the entire catchment are the same in cases 1 and 2. (a) In case 1, the differences between neighboring low-order stream catchments were relatively large, but the average values of neighboring low-order stream catchments differed relatively little. In this case, dissimilar values are located close together in space and the rate of decrease was steeper than for the random mixing case. (b) In case 2, the differences between neighboring low-order stream catchments were small, but the average values of neighboring low-order stream catchments differed greatly. In this case similar values are located close together in space and the rate of decrease was less steep than for the random mixing case.

Recently, the importance of direct runoff periods for quantifying annual chemical flux has been recognized (Oda et al., 2011; Raymond & Saiers, 2010; Zarnetske et al., 2018). The study of REA began with investigations of the spatial variability in rainfall-runoff responses using a hydrological model. However, most subsequent empirical studies have examined the spatial variability in stream discharge and water chemistry under base flow conditions, and only a few studies have examined the spatial variability or REA in direct runoff periods (Abbott et al., 2018; Didszun & Uhlenbrook, 2008; Karlsten et al., 2016; Zimmer et al., 2013). Therefore, in future studies, there is a need to determine how to link results obtained under base flow conditions with those in direct runoff periods.

4.3. Implications for REA Determination and Making Effective Observations

Our observation points were located mainly in first- and second-order streams, and their catchment areas varied from approximately 1 to 10 ha. The REA is generally defined for areas ranging from hundreds to thousands of hectares (e.g., Temnerud & Bishop, 2005; Woods et al., 1995). Thus, there may be a gap in scale between our study catchment area (<10 ha) and the REA (>100 ha). However, our findings are important for understanding REA formation and predicting its size. If we assume that random mixing was responsible for the decrease in CV values of Q_s from first-order streams, an observation area 1.7 times greater than the catchment area of our study is needed to obtain the CV values of the Q_s of second-order streams (Figure 9a). To obtain CV values for the water chemistry, the observation area would only need to be 0.3 times greater (Figure 9b). Therefore, if we do not consider the deviation from random mixing, there is likely to be a substantial error in the predicted size of the REA for first-order streams. The δ_{SD} and δ_{CV} values determined in this study could be reference values for predicting the REA in other temperate forest catchments.

The δ_{SD} and δ_{CV} values of Q_s were smaller than those of the water chemistry (Figure 6). However, this does not mean that there was a smaller REA for Q_s than for water chemistry. In first-order streams, the CVs of Q_s were 174 ± 64 ($n = 3$; average \pm SD) and were clearly larger than the CVs of water chemistry (39 ± 23 ; $n =$

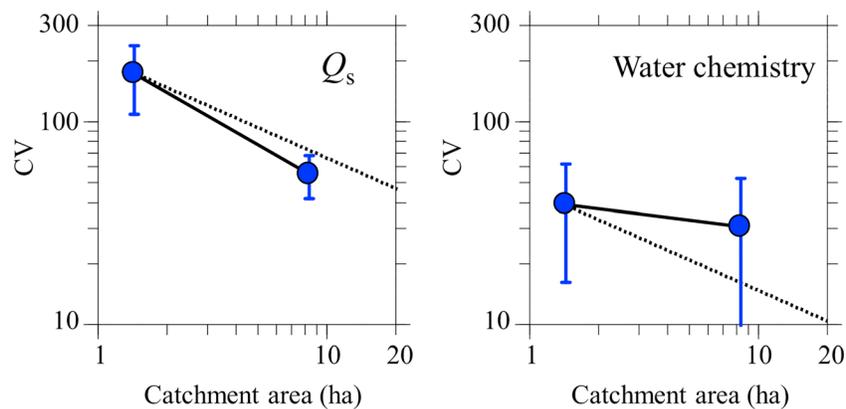


Figure 9. Comparison of decreases of the CV with increasing catchment area between Q_s and water chemistry parameters. A logarithmic axis is used for all variables. Points and error bars show the averages and SDs of the CV in each stream order, respectively. The catchment area for each stream order is the average value of three catchments. Solid and dotted lines show actual decreases in the CV with increasing catchment area and the cases when we assumed random mixing for first-order streams, respectively.

26). The CVs of Q_s and water chemistry were 55 ± 13 ($n = 3$) and 31 ± 22 ($n = 26$), respectively, in second-order streams. Therefore, the differences in δ_{SD} and δ_{CV} values between Q_s and water chemistry might cause the similar sizes of the REA of Q_s and water chemistry in our site.

Woods et al. (1995) and Asano and Uchida (2010) showed that the decrease in variability gradually followed random mixing theory as the catchment area increased. However, McGuire et al. (2014) demonstrated the existence of hierarchical spatial structures within stream water chemistry in a catchment of a few hundred hectares. Some studies have also shown that groundwater discharge increases with catchment area and strongly influences stream discharge and water chemistry (Egusa et al., 2016; Frisbee et al., 2011; Peralta-Tapia et al., 2015; Shaman et al., 2004; Wolock et al., 1997). Therefore, it will be an important future task to clarify tendencies in larger-scale catchments, preferably using spatially independent stream discharge and water chemistry data.

The relationships between the spatial variability in stream discharge and catchment area demonstrated in this study will be important information for designing future monitoring strategies. Most field observations of hillslope hydrology have been conducted at hillslope scales <1 ha (Uchida et al., 2005). In Japan, high rainfall and steep terrain cause large sediment fluxes (Hiraoka et al., 2015; Hotta et al., 2007), which make it a difficult to maintain weirs, even in an area of a few tens of hectares. Thus, often, we cannot observe points with a larger area than the REA. In such situations, averaging stream discharge from multiple small catchments and obtaining representative values for the surrounding catchments can perhaps be a realistic alternative. Our results show that the spatial variability of Q_s had a greater decrease than the random mixing from first- to second-order streams. Random mixing uses the same operation as random sampling for calculating the decrease in spatial variability, with an increasing number of samples. Therefore, it might be a more effective approach to observe stream discharge in second-order streams than in first-order streams.

4.4. Implications for Studies of Spatial Structure

Spatial structure provides major clues for underlying mechanism in various fields including hydrology, biogeochemistry, geomorphology, and ecology (e.g., Rietkerk et al., 2004; Rodríguez-Iturbe & Rinaldo, 1997) and is important for ecological management point of view. For example, it is essential to understand where and when stream nitrogen and phosphorous concentrations should be observed and/or how to manage catchments to reduce them, because high concentrations of nitrogen and phosphorous can increase harmful algae blooms (Heisler et al., 2008) and cause marine dead zones (Diaz & Rosenberg, 2008). McClain et al. (2003) highlighted the importance of recognizing hot spots and hot moments of biogeochemical and ecological processes for management purposes. Although the hot spot and hot moment concepts have been widely accepted in biogeochemical and ecological fields (reviewed by Vidon et al., 2010, and Bernhardt et al., 2017), it is insufficient at present to quantify temporal and spatial scale of hot spot and hot moment (Bernhardt et al., 2017). Abbott et al. (2018) attempted to determine the spatial structure and scale of hot

spots using points where there was a sudden decrease in the water chemical flux with increasing catchment area. Our analysis showed that decreases in spatial variability of stream discharge and water chemistry with increasing catchment area were related to their spatial similarity (Figure 7), suggesting that the rate of decrease in this study could be a promising indicator of the spatial structure and scale of hot spots. When the rate of decrease was positive, the clear hot spots in space were observed. When the rate of decrease was between 0 and -0.5 , although spatial variability decreased with increasing catchment area, similar parameter values were still located close together in space. Thus, the size of hot spots would be changed by the threshold values of parameters that define hot spots.

In this study, the observation points were classified by their stream order, and the spatial resolution was not very high. Previous studies reported new findings in hydrological and biogeochemical fields by increasing the temporal resolution (e.g., Kirchner & Neal, 2013). Therefore, increasing the spatial resolution of our methods might allow for detection of a more detailed spatial structure and contribute to the quantification of the scale of hot spots. Our study sites were in temperate forest catchments. Recently, it has been reported that a difference in biome might create different spatial structures (Pinay et al., 2018). In the future, similar observations should be made in the catchments of various biomes and the results compared.

5. Conclusions

This study demonstrated that the spatial variability of stream discharge and water chemistry decreased with increasing catchment area at a rate greater and less than those estimated by simple mixing of random variables, respectively, providing a unified view that explains different results of two previous studies (Asano & Uchida, 2010; Woods et al., 1995). The difference between stream discharge and water chemistry could be explained by their different spatial structures, with dissimilar values of stream discharge and similar values of water chemistry, respectively, located close together in space. Our results also suggest that the rates of variation decrease with catchment area in stream discharge and water chemistry significantly impacted the determination of the REA (Wood et al., 1988). Several hypotheses for the driving factors of the rates of variation decrease with catchment area among catchments and for the stream discharge and chemical parameters were proposed and must be verified in future studies. This verification will provide further information regarding the spatial structure of stream discharge and water chemistry within large-scale catchments, providing a powerful and promising tool for predicting the REA and contributing to efforts making inferences and generalizations about ungauged or poorly monitored catchments.

Acknowledgments

The authors thank the staff of Chiba Experimental Forest, The University of Tokyo, for supporting observations of rainfall and stream discharge in Inokawa, as well as Kanagawa Prefectural Government for financial and logistical support to maintain the observations in Oborasawa, and the Field Science Center, Tokyo University of Agricultural and Technology for kind permission to conduct observations in Kusaki. This paper was based on the PhD thesis of T. Egusa (Egusa, 2013). All data used in the analyses are available from a repository (Egusa, 2018; Data of Inokawa, Kusaki, Oborasawa. osf.io/rst4w).

References

- Abbott, B. W., Gruau, G., Zarnetske, J. P., Moatar, F., Barbe, L., Thomas, Z., et al. (2018). Unexpected spatial stability of water chemistry in headwater stream networks. *Ecology Letters*, *21*, 296–308. <https://doi.org/10.1111/ele.12897>
- Aishlin, P., & McNamara, J. P. (2011). Bedrock infiltration and mountain block recharge accounting using chloride mass balance. *Hydrological Processes*, *25*, 1934–1948. <https://doi.org/10.1002/hyp.7950>
- Archfield, S. A., Pugliese, A., Castellarin, A., Skoien, J. O., & Kiang, J. E. (2013). Topological and canonical kriging for design flood prediction in ungauged catchments: An improvement over a traditional regional regression approach? *Hydrology and Earth System Sciences*, *17*, 1575–1588. <https://doi.org/10.5194/hess-17-1575-2013>
- Asano, Y., & Uchida, T. (2010). Is representative elementary area defined by a simple mixing of variable small streams in headwater catchments? *Hydrological Processes*, *24*, 666–671. <https://doi.org/10.1002/hyp.7589>
- Asano, Y., Uchida, T., Mimasu, Y., & Ohte, N. (2009). Spatial patterns of stream solute concentrations in a steep mountainous catchment with a homogeneous landscape. *Water Resources Research*, *45*, W10432. <https://doi.org/10.1029/2008WR007466>
- Barrios, M., & Francés, F. (2012). Spatial scale effect on the upper soil effective parameters of a distributed hydrological model. *Hydrological Processes*, *26*, 1022–1033. <https://doi.org/10.1002/hyp.8193>
- Bergstrom, A., Jencso, K., & McGlynn, B. (2016). Spatiotemporal processes that contribute to hydrologic exchange between hillslopes, valley bottoms, and streams. *Water Resources Research*, *52*, 4628–4645. <https://doi.org/10.1002/2015WR017972>
- Bernhardt, E. S., Blaszcak, J. R., Ficken, C. D., Fork, M. L., Kaiser, K. E., & Seybold, E. C. (2017). Control points in ecosystems: Moving beyond the hot spot hot moment concept. *Ecosystems*, *20*, 665–682. <https://doi.org/10.1007/s10021-016-0103-y>
- Blöschl, G. (2001). Scaling in hydrology. *Hydrological Processes*, *15*(4), 709–711. <https://doi.org/10.1002/hyp.432>
- Blöschl, G., & Sivapalan, M. (1995). Scale issues in hydrological modelling: A review. *Hydrological Processes*, *19*(11), 4559–4579. <https://doi.org/10.5194/hess-19-4559-2015>
- Brennan, S. R., Torgersen, C. E., Hollenbeck, J. P., Fernandez, D. P., Jensen, C. K., & Schindler, D. E. (2016). Dendritic network models: Improving isoscapes and quantifying influence of landscape and in-stream processes on strontium isotopes in rivers. *Geophysical Research Letters*, *43*, 5043–5051. <https://doi.org/10.1002/2016GL068904>
- Capell, R., Tetzlaff, D., & Soulsby, C. (2012). Can time domain and source area tracers reduce uncertainty in rainfall-runoff models in larger heterogeneous catchments? *Water Resources Research*, *48*, W09544. <https://doi.org/10.1029/2011WR011543>

- de Lavenne, A., Skoien, J. O., Cudennec, C., Curie, F., & Moatar, F. (2016). Transferring measured discharge time series: Large-scale comparison of Top-kriging to geomorphology-based inverse modeling. *Water Resources Research*, *52*, 5555–5576. <https://doi.org/10.1002/2016WR018716>
- Dent, C. L., & Grimm, N. B. (1999). Spatial heterogeneity of stream water nutrient concentrations over successional time. *Ecology*, *80*(7), 2283–2298. <https://doi.org/10.2307/176910>
- Diaz, R. J., & Rosenberg, R. (2008). Spreading dead zones and consequences for marine ecosystems. *Science*, *321*, 926–929. <https://doi.org/10.1126/science.1156401>
- Didszun, J., & Uhlenbrook, S. (2008). Scaling of dominant runoff generation processes: Nested catchments approach using multiple tracers. *Water Resources Research*, *44*, W02410. <https://doi.org/10.1029/2006WR005242>
- Dong, X., Ruhí, A., & Grimm, N. B. (2017). Evidence for self-organization in determining spatial patterns of stream nutrients, despite primacy of the geomorphic template. *Proceedings of the National Academy of Sciences*, *114*(24), E4744–E4752. <https://doi.org/10.1073/pnas.1617571114>
- Ecrepont, S., Cudennec, C., Anctil, F., & Jaffrézic, A. (2019). PUB in Québec: A robust geomorphology-based deconvolution-reconvolution framework for the spatial transposition of hydrographs. *Journal of Hydrology*, *570*, 378–392. <https://doi.org/10.1016/j.jhydrol.2018.12.052>
- Egusa, T. (2013). Study on relationship between spatial variability in streamwater characteristics and catchment scale in forested headwaters. PhD thesis, The University of Tokyo, 116 pp.
- Egusa, T. (2018). Data of Inokawa, Kusaki, Oborasawa. Retrieved from osf.io/rst4w
- Egusa, T., Ohte, N., Oda, T., & Suzuki, M. (2013). Relationship between catchment scale and the spatial variability of stream discharge and chemistry in a catchment with multiple geologies. *Hydrological Research Letters*, *7*, 12–17. <https://doi.org/10.3178/HRL.7.12>
- Egusa, T., Ohte, N., Oda, T., & Suzuki, M. (2016). Quantifying aggregation and change in runoff source in accordance with catchment area increase in a forested headwater catchment. *Hydrological Processes*, *30*, 4125–4138. <https://doi.org/10.1002/hyp.10916>
- Fischer, B. M. C., Rinderer, M., Schneider, P., Ewen, T., & Seibert, J. (2015). Contributing sources to baseflow in pre-alpine headwaters using spatial snapshot sampling. *Hydrological Processes*, *29*, 5321–5336. <https://doi.org/10.1002/hyp.10529>
- Frisbee, M. D., Phillips, F. M., Campbell, A. R., Liu, F., & Sanchez, S. A. (2011). Streamflow generation in a large, alpine watershed in the southern Rocky Mountains of Colorado: Is streamflow generation simply the aggregation of hillslope runoff responses? *Water Resources Research*, *47*, W06512. <https://doi.org/10.1029/2010WR009391>
- Fujimoto, M., Ohte, N., & Tani, M. (2008). Effects of hillslope topography on hydrological responses in a weathered granite mountain, Japan: Comparison of the runoff response between the valley-head and the side slope. *Hydrological Processes*, *22*(14), 2581–2594. <https://doi.org/10.1002/hyp.6857>
- Fujimoto, M., Ohte, N., & Tani, M. (2011). Effects of hillslope topography on runoff response in a small catchment in the Fudoji Experimental Watershed, central Japan. *Hydrological Processes*, *25*(12), 1874–1886. <https://doi.org/10.1002/hyp.7943>
- Genereux, D. P., Jordan, M. T., & Carbonell, D. (2005). A paired-watershed budget study to quantify interbasin groundwater flow in a lowland rain forest, Costa Rica. *Water Resources Research*, *41*, W04011. <https://doi.org/10.1029/2004WR003635>
- Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison, W. C., et al. (2008). Eutrophication and harmful algal blooms: A scientific consensus. *Harmful Algae*, *8*(1), 3–13. <https://doi.org/10.1016/j.hal.2008.08.006>
- Hiraoka, M., Gomi, T., Oda, T., Egusa, T., & Uchiyama, Y. (2015). Responses of bed load yields from a forested headwater catchment in the eastern Tazawa Mountains, Japan. *Hydrological Research Letters*, *9*(3), 41–46. <https://doi.org/10.3178/hrl.9.41>
- Hotta, N., Kayama, T., & Suzuki, M. (2007). Analysis of suspended sediment yields after low impact forest harvesting. *Hydrological Processes*, *21*(26), 3565–3575. <https://doi.org/10.1002/hyp.6583>
- Hrachowitz, M., Savenije, H. H. G., Blöschl, G., McDonnell, J. J., Sivapalan, M., Pomeroy, J. W., et al. (2013). A decade of predictions in ungauged basins (PUB)—A review. *Hydrological Sciences Journal*, *58*(6), 1198–1255. <https://doi.org/10.1080/02626667.2013.803183>
- Isaak, D. J., Peterson, E. E., Ver Hoef, J. M., Wenger, S. J., Falke, J. A., Torgersen, C. E., et al. (2014). Applications of spatial statistical network models to stream data. *Wiley Interdisciplinary Reviews: Water*, *1*(3), 277–294. <https://doi.org/10.1002/wat2.1023>
- Karlsen, R. H., Grabs, T., Bishop, K., Buffam, I., Laudon, H., & Seibert, J. (2016). Landscape controls on spatiotemporal discharge variability in a boreal catchment. *Water Resources Research*, *52*, 6541–6556. <https://doi.org/10.1002/2016WR019186>
- Karlsen, R. H., Seibert, J., Grabs, T., Laudon, H., Blomkvist, P., & Bishop, K. (2016). The assumption of uniform specific discharge: Unsafe at any time? *Hydrological Processes*, *30*(21), 3978–3988. <https://doi.org/10.1002/hyp.10877>
- Kirchner, J. W., & Neal, C. (2013). Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. *Proceedings of the National Academy of Sciences*, *110*(30), 12,213–12,218. <https://doi.org/10.1073/pnas.1304328110>
- Koyanagi, N., Kuwabara, S., Kuwabara, M., Uchida, T., Kumakura, M., & Toda, H. (2003). Meteorological observations in university forests of TUAT in 1997–2002. *Field Science*, *3*, 37–47. (in Japanese)
- Lessels, J. S., Tetzlaff, D., Birkel, C., Dick, J., & Soulsby, C. (2016). Water sources and mixing in riparian wetlands revealed by tracers and geospatial analysis. *Water Resources Research*, *52*, 456–470. <https://doi.org/10.1002/2015WR017519>
- Likens, G. E., & Buso, D. C. (2006). Variation in streamwater chemistry throughout the Hubbard Brook Valley. *Biogeochemistry*, *78*(1), 1–30. <https://doi.org/10.1007/s10533-005-2024-2>
- Lyon, S. W., Nathanson, M., Spans, A., Grabs, T., Laudon, H., Temnerud, J., et al. (2012). Specific discharge variability in a boreal landscape. *Water Resources Research*, *48*, W08506. <https://doi.org/10.1029/2011WR011073>
- McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., et al. (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, *6*(4), 301–312. <https://doi.org/10.1007/s10021-003-0161-9>
- McDonnell, J. J., Sivapalan, M., Vaché, K., Dunn, S., Grant, G., Haggerty, R., et al. (2007). Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology. *Water Resources Research*, *43*, W07301. <https://doi.org/10.1029/2006WR005467>
- McGuire, K. J., Torgersen, C. E., Likens, G. E., Buso, D. C., Lowe, W. H., & Bailey, S. W. (2014). Network analysis reveals multiscale controls on streamwater chemistry. *Proceedings of the National Academy of Sciences*, *111*(19), 7030–7035. <https://doi.org/10.1073/pnas.1404820111>
- Nakajima, T., Makimoto, H., Hirayama, J., & Tokuhashi, S. (1981). *Geology of the Kamogawa district, Quadrangle Series, scale 1:50,000*, (pp. 101–107). Tokyo, Japan: Geological Survey of Japan.
- Oda, T., Asano, Y., & Suzuki, M. (2008). Estimating deep percolation in a small catchment in a Tertiary Formation using the Chloride Mass Balance Method. *Journal of Japan Society of Hydrology and Water Resources*, *21*(3), 195–204. (in Japanese with English summary). <https://doi.org/10.3178/jjshwr.21.195>

- Oda, T., Ohte, N., & Suzuki, M. (2011). Importance of frequent storm flow data for evaluating changes in stream water chemistry following clear-cutting in Japanese headwater catchments. *Forest Ecology and Management*, *262*(7), 1305–1317. <https://doi.org/10.1016/j.foreco.2011.06.032>
- Payn, R. A., Gooseff, M. N., McGlynn, B. L., Bencala, K. E., & Wondzell, S. M. (2009). Channel water balance and exchange with subsurface flow along a mountain headwater stream in Montana, United States. *Water Resources Research*, *45*, W11427. <https://doi.org/10.1029/2008WR007644>
- Peralta-Tapia, A., Sponseller, R. A., Ågren, A., Tetzlaff, D., Soulsby, C., & Laudon, H. (2015). Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. *Journal of Geophysical Research: Biogeosciences*, *120*, 847–858. <https://doi.org/10.1002/2014JG002878>
- Pinay, G., Bernal, S., Abbott, B. W., Lupon, A., Marti, E., Sabater, F., & Krause, S. (2018). Riparian corridors: A new conceptual framework for assessing nitrogen buffering across biomes. *Frontiers in Environmental Science*, *6*, 1–11. <https://doi.org/10.3389/fenvs.2018.00047>
- Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, *100*(1-3), 197–209. <https://doi.org/10.1007/s10533-010-9416-7>
- Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. *Ecology*, *97*(1), 5–16. <https://doi.org/10.1890/14-1684.1>
- Rietkerk, M., Dekker, S. C., de Ruiter, P. C., & van de Koppel, J. (2004). Self-organized patchiness and catastrophic shifts in ecosystems. *Science*, *305*(5692), 1926–1929. <https://doi.org/10.1126/science.1101867>
- Rodríguez-Iturbe, I., & Rinaldo, A. (1997). *Fractal river basins: Chance and self-organization*, (p. 547). Cambridge, UK: Cambridge University Press.
- Shaman, J., Stieglitz, M., & Burns, D. (2004). Are big basins just the sum of small catchments? *Hydrological Processes*, *18*(16), 3195–3206. <https://doi.org/10.1002/hyp.5739>
- Shiraki, K., Liu, R. G., Karakama, I., Shuin, Y., & Ohta, T. (1999). Water balances in the Fukuroyamasawa experimental watersheds in University Forest in Chiba, the University of Tokyo. *Bulletin of the Tokyo University Forests*, *102*, 71–86. (in Japanese with English summary)
- Shiraki, K., Shinomiya, Y., Urakawa, R., Toda, H., & Haibara, K. (2007). Numerical calculation of secondary discharge peak from a small watershed using a physically based watershed scale infiltration simulation. *Journal of Forest Research*, *12*(3), 201–208. <https://doi.org/10.1007/s10310-007-0008-x>
- Sivapalan, M. (2003a). Prediction in ungauged basins: A grand challenge for theoretical hydrology. *Hydrological Processes*, *17*(15), 3163–3170. <https://doi.org/10.1002/hyp.5155>
- Sivapalan, M. (2003b). Process complexity at hillslope scale, process simplicity at the watershed scale: Is there a connection? *Hydrological Processes*, *17*(5), 1037–1041. <https://doi.org/10.1002/hyp.5109>
- Sivapalan, M. (2018). From engineering hydrology to Earth system science: Milestones in the transformation of hydrologic science. *Hydrology and Earth System Sciences*, *22*(3), 1665–1693. <https://doi.org/10.5194/hess-22-1665-2018>
- Skoien, J. O., & Blöschl, G. (2007). Spatiotemporal topological kriging of runoff time series. *Water Resources Research*, *43*, W09419. <https://doi.org/10.1029/2006WR005760>
- Temnerud, J., & Bishop, K. (2005). Spatial variation of streamwater chemistry in two Swedish boreal catchments: Implications for environmental assessment. *Environmental Science and Technology*, *39*(6), 1463–1469. <https://doi.org/10.1021/es040045q>
- Temnerud, J., Seibert, J., Jansson, M., & Bishop, K. (2007). Spatial variation in discharge and concentrations of organic carbon in a catchment network of boreal streams in northern Sweden. *Journal of Hydrology*, *342*(1–2), 72–87. <https://doi.org/10.1016/j.jhydrol.2007.05.015>
- Tetzlaff, D., Carey, S. K., Laudon, H., & McGuire, K. (2010). Catchment processes and heterogeneity at multiple scales—benchmarking observations, conceptualization and prediction. *Hydrological Processes*, *24*(16), 2203–2208. <https://doi.org/10.1002/hyp.7784>
- Tiwari, T., Buffam, I., Sponseller, R. A., & Laudon, H. (2017). Inferring scale-dependent processes influencing stream water biogeochemistry from headwater to sea. *Limnology and Oceanography*, *62*(S1), S58–S70. <https://doi.org/10.1002/lno.10738>
- Uchida, T., Asano, Y., Onda, Y., & Miyata, S. (2005). Are headwaters just the sum of hillslopes? *Hydrological Processes*, *19*(16), 3251–3261. <https://doi.org/10.1002/hyp.6004>
- Uchiyama, Y., Nakajima, N., Yokoyama, T., & Yamanaka, Y. (2014). Report on hydrological observations by forest conservation project in Ohbora-sawa Watershed in the Tanzawa Mountains. *Results of Scientific Research on the Tanzawa Mountains*, *12*, 17–26. (in Japanese)
- Urakawa, R., Ohte, N., Shibata, H., Isobe, K., Tateno, R., Oda, T., et al. (2016). Factors contributing to soil nitrogen mineralization and nitrification rates of forest soils in the Japanese archipelago. *Forest Ecology and Management*, *361*, 382–396. <https://doi.org/10.1016/j.foreco.2015.11.033>
- Ver Hoef, J. M., Peterson, E., & Theobald, D. (2006). Spatial statistical models that use flow and stream distance. *Environmental and Ecological Statistics*, *13*(4), 449–464. <https://doi.org/10.1007/s10651-006-0022-8>
- Vidon, P., Allan, C., Burns, D., Duval, T. P., Gurwick, N., Inamdar, S., et al. (2010). Hot spots and hot moments in riparian zones: Potential for improved water quality management. *Journal of the American Water Resources Association*, *46*(2), 278–298. <https://doi.org/10.1111/j.1752-1688.2010.00420.x>
- Wackernagel, H. (1998). *Multivariate geostatistics: An introduction with applications*, (2nd ed. p. 43). Berlin Heidelberg, Germany: Springer-Verlag.
- Wagner, T., Sivapalan, M., Troch, P., & Woods, R. (2007). Catchment classification and hydrologic similarity. *Geography Compass*, *1*, 901–931. <https://doi.org/10.1111/j.1749-8198.2007.00039.x>
- Wollheim, W. M., Bernal, S., Burns, D. A., Czuba, J. A., Driscoll, C. T., Hansen, A. T., et al. (2018). River network saturation concept: Factors influencing the balance of biogeochemical supply and demand of river networks. *Biogeochemistry*, *141*, 503–521. <https://doi.org/10.1007/s10533-018-0488-0>
- Wolock, D. M., Fan, J., & Lawrence, G. B. (1997). Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River watershed, New York. *Hydrological Processes*, *11*(9), 1273–1286. [https://doi.org/10.1002/\(SICI\)1099-1085\(199707\)11:9<1273::AID-HYP557>3.3.CO;2-J](https://doi.org/10.1002/(SICI)1099-1085(199707)11:9<1273::AID-HYP557>3.3.CO;2-J)
- Wood, E. F., Sivapalan, M., & Beven, K. (1990). Similarity and scale in catchment storm response. *Reviews of Geophysics*, *28*(1), 1–18. <https://doi.org/10.1029/RG028i001p00001>
- Wood, E. F., Sivapalan, M., Beven, K., & Band, L. (1988). Effects of spatial variability and scale with implications to hydrologic modeling. *Journal of Hydrology*, *102*(1–4), 29–47. [https://doi.org/10.1016/0022-1694\(88\)90090-X](https://doi.org/10.1016/0022-1694(88)90090-X)
- Woods, R., Sivapalan, M., & Duncan, M. (1995). Investigating the representative elementary area concept: An approach based on field data. *Hydrological Processes*, *9*(3–4), 291–312. <https://doi.org/10.1002/hyp.3360090306>

- Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., & Raymond, P. A. (2018). Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. *Geophysical Research Letters*, *45*, 11,702–11,711. <https://doi.org/10.1029/2018GL080005>
- Zimmer, M. A., Bailey, S. W., McGuire, K. J., & Bullen, T. D. (2013). Fine scale variations of surface water chemistry in an ephemeral to perennial drainage network. *Hydrological Processes*, *27*, 3438–3451. <https://doi.org/10.1002/hyp.9449>