

RESEARCH ARTICLE

Effects of bedrock groundwater discharge on spatial variability of dissolved carbon, nitrogen, and phosphorous concentrations in stream water within a forest headwater catchment

Tomohiro Egusa¹  | Tomo'omi Kumagai^{1,2}  | Tomoki Oda¹  | Nobuhito Ohte³ 

¹Department of Forest Science, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan

²Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan

³Department of Social Informatics, Graduate School of Informatics, Kyoto University, Kyoto, Japan

Correspondence

Tomohiro Egusa, Department of Forest Science, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan.

Email: tomohiroegusa@gmail.com

Abstract

The quantitative evaluation of the effects of bedrock groundwater discharge on spatial variability of stream dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP) concentrations has still been insufficient. We examined the relationships between stream DOC, DIN and DIP concentrations and bedrock groundwater contribution to stream water in forest headwater catchments in warm-humid climate zones. We sampled stream water and bedrock springs at multiple points in September and December 2013 in a 5 km² forest headwater catchment in Japan and sampled groundwater in soil layer in small hillslopes. We assumed that stream water consisted of four end members, groundwater in soil layer and three types of bedrock groundwater, and calculated the contributions of each end member to stream water from mineral-derived solute concentrations. DOC, DIN and DIP concentrations in stream water were compared with the calculated bedrock groundwater contribution. The bedrock groundwater contribution had significant negative linear correlation with stream DOC concentration, no significant correlation with stream DIN concentration, and significant positive linear correlation with stream DIP concentration. These results highlighted the importance of bedrock groundwater discharge in establishing stream DOC and DIP concentrations. In addition, stream DOC and DIP concentrations were higher and lower, respectively, than those expected from end member mixing of groundwater in soil layer and bedrock springs. Spatial heterogeneity of DOC and DIP concentrations in groundwater and/or in-stream DOC production and DIP uptake were the probable reasons for these discrepancies. Our results indicate that the relationships between spatial variability of stream DOC, DIN and DIP concentrations and bedrock groundwater contribution are useful for comparing the processes that affect stream DOC, DIN and DIP concentrations among catchments beyond the spatial heterogeneity of hydrological and biogeochemical processes within a catchment.

KEYWORDS

bedrock groundwater, dissolved inorganic nitrogen, dissolved inorganic phosphorous, dissolved organic carbon, end member mixing analysis, forest headwaters, spatial variability, stream water

1 | INTRODUCTION

Carbon (C), Nitrogen (N), and Phosphorous (P) in stream water greatly affect aquatic ecosystems. Dissolved organic carbon (DOC) is especially important among the various forms of C in water because it can be a major energy source for organisms in streams (see review in Kaplan & Newbold, 1993) and transports metals such as mercury (Ravichandran, 2004) and iron (Sholkovitz & Copland, 1981). N and/or P or both can largely limit the primary production of aquatic ecosystems (Elser et al., 1990, 2007), while, excessive N and P cause harmful algal growth (Heisler et al., 2008), and dead zones in the sea area (Diaz & Rosenberg, 2008). Among various forms of N and P, dissolved inorganic N and P (DIN and DIP, respectively) can be easily used by plants and algae, and thus their importance has been especially emphasized by many previous studies. Therefore, it is necessary to fully elucidate the mechanism and predict the spatial variability of stream DOC, DIN and DIP concentrations.

In Japan, the forest area occupies 67% of the land (Japan Forestry Agency, 2012) and is in the mountainous headwaters (Sawano et al., 2005), which are major sources of water resources. Thus, it is important to obtain knowledge for DOC, DIN and DIP in forest headwater catchments (less than a few tens of km²). Previous research has revealed that a large variety of factors affected the spatial variability of stream DOC, DIN and DIP concentrations in forest headwater catchments. Generally, stream discharge and water chemistry in forest catchments are greatly affected by runoff sources and flow paths that compose the stream water, and therefore, it is vital to understand the compositions of the runoff sources and flow paths (McDonnell, 2003). Wetlands (e.g., Ågren et al., 2007; Buffam et al., 2007; Dillon & Molot, 1997) and riparian zones (McGlynn & McDonnell, 2003) could be the main sources of DOC, and thus the stream DOC concentration tends to increase with the portion of their area in the catchment. In addition to runoff sources and flow paths, many biogeochemical processes affected stream DOC, DIN and DIP concentrations. Deforestation would change biogeochemical processes in the soil and apparently increases stream DOC and DIN concentrations (e.g., Feller & Kimmins, 1984; Likens et al., 1970; Nieminen, 2004). Besides, a lot of studies have shown that the production and uptake of DOC, DIN and DIP in stream channels, that is, in-stream process, greatly affected stream DOC, DIN and DIP concentrations (reviewed by Cirno & McDonnell, 1997; Mineau et al., 2016; Ranalli & Macalady, 2010; Withers & Jarvie, 2008). It was reported that higher concentrations of DIN and DIP in stream water (Mulholland et al., 2008), higher primary production rates and ecosystem respiration rates in stream (Fellows et al., 2006; Hall & Tank, 2003), and larger volumes of the pool and the hyporheic zone in stream channels (Hall et al., 2002; Mulholland et al., 1997) facilitated DIN and DIP uptake in stream channels.

Among the various runoff sources and flow paths that compose the stream water, groundwater discharge through deep flow paths, including bedrock, is a significant potential process that affects the spatial variability of the stream DOC, DIN and DIP concentrations in forest headwater catchments. Since the 1980s, it has been empirically

shown that groundwater discharge through bedrock had a large influence on stream water discharge, chemistry, and residence time in many forest headwater catchments (e.g., Genereux et al., 2005; Hale & McDonnell, 2016; Iwasaki et al., 2015; Katsuyama et al., 2010; Kosugi et al., 2006; Pfister et al., 2017; Soulsby et al., 2007; Uchida et al., 2003). Moreover, in recent years, the framework of critical zone science, which explores complex interactions involving rock, soil, water, air, and living organisms, has been receiving attention globally (e.g., Giardino & Houser, 2015; Riebe et al., 2017). Despite the strong interests in bedrock groundwater dynamics, only a few studies have investigated the effects of groundwater discharge through bedrock on spatial variability of stream DOC, DIN and DIP concentrations to date. These previous studies have reported that bedrock groundwater discharge decreased stream DOC concentrations (Peralta-Tapia et al., 2015; Tiwari et al., 2017), and increased stream DIP concentrations (Pringle et al., 1993) and stream DIN concentrations in summer (Burns et al., 1998). Although these studies provide useful information, their target area covered only a limited range of geology and climate. Therefore, it is difficult to generalize these results. For example, the comparisons between spatial variability of stream DOC concentration and bedrock groundwater contribution to stream water using more than a few tens of points' observations have been conducted only in boreal catchments, which have remarkable seasonality of freezing and thawing from winter to spring and many lakes and mires as DOC sources.

Therefore, our objectives were to elucidate the effects of bedrock groundwater discharge on spatial variability of stream DOC, DIN and DIP concentrations in forest headwater catchments in warm-humid climate zones. To achieve this, we sampled stream water at multiple points and calculated the bedrock groundwater contribution to stream water from the concentrations of mineral-derived solutes. Then, we examined the relationships between stream DOC, DIN and DIP concentrations and bedrock groundwater contribution to stream water.

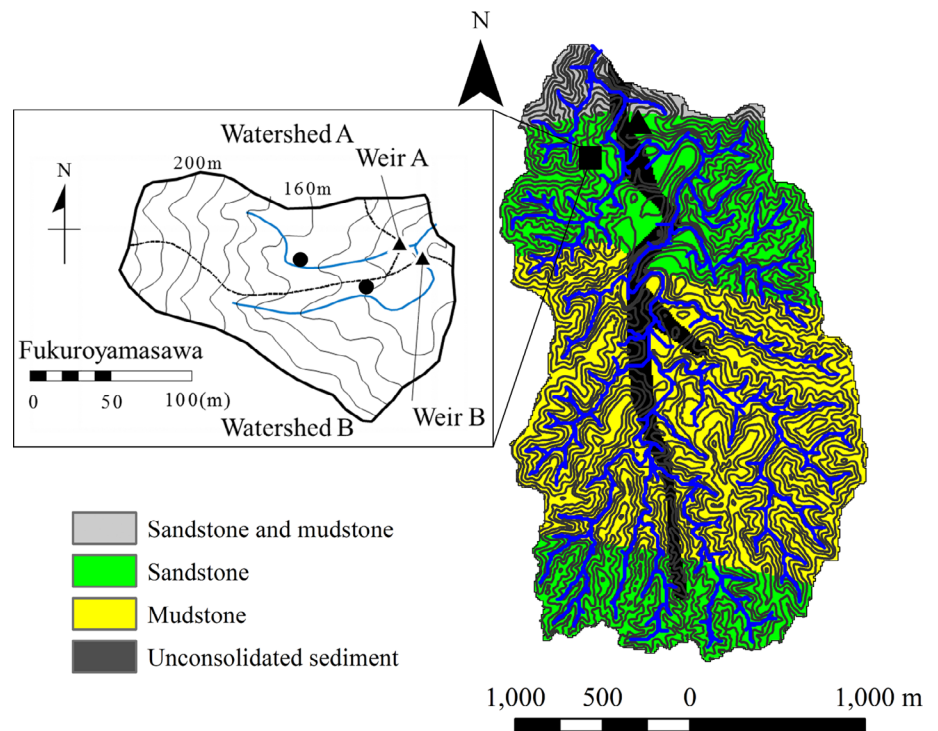
2 | MATERIALS AND METHODS

2.1 | Site description

This study was conducted in Inokawa catchment located in the Kiyosumi mountain, Boso Peninsula, Japan (35°12'N, 140°06'E; Figure 1). The catchment area of Inokawa is 5.07 km² and Fukuroyamasawa Experimental Watershed (FEW; 0.02 km²) is in the northwest within Inokawa catchment. The altitude ranges from 90 to 346 m a.s.l. and the average slope is 31°. The climate is warm and humid with the mean annual rainfall of 2304 mm (from 1994 to 2010) and with the annual mean temperature of 13.7°C (from 2006 to 2010). In usual years, Inokawa experiences abundant rainfall in rainy season (from June to July) and in typhoon season (from September to October). The minimum and maximum monthly mean temperature is 1.8°C in January and 24.8°C in August, respectively.

The bedrock of Inokawa is classified as Neogene age sedimentary rock and composed of sandstone and mudstone derived from

FIGURE 1 Topography and bedrock geology of Inokawa. The solid square show Fukuroyamasawa Experimental Watershed (FEW) and the solid triangle indicate a meteorological station. Blue and grey lines mean streams and contours of 20 m interval, respectively. Solid circles in FEW indicate the areas where groundwater in soil layer were sampled



subseafloor sediments (Nakajima et al., 1981). The proportion of sandstone and mudstone is not spatially uniform (Figure 1). We named the area of thicker turbidite sandstones as sandstone area and the area of massive bluish-grey mudstone that was likely deposited in a hemipelagic mud belt on the continental shelf as mudstone area. Most observation points in the present study were in the areas of these two geological groups. (Figure 2). There are no significant differences in the ranges of ion concentrations and in relative proportion of major ions between stream water of sandstone area and mudstone area (Egusa et al., 2016). Therefore, this study did not consider the geological heterogeneity within the catchment. The soil is mostly classified as Cambisol. Conifers and broad-leaf trees covered 46% and 54% of the catchment area, respectively.

Stream discharges have been continuously monitored at FEW. The altitude of FEW ranges from 126 to 230 m a.s.l. The FEW consists of two adjacent catchments. The north catchment is catchment A (FEW-A; 0.008 km²) and the south catchment is catchment B (FEW-B; 0.011 km²) (Figure 1). The average slopes are 34.2° in FEW-A and 33.4° in FEW-B. The mean soil depths were 2.87 m in FEW-A and 2.22 m in FEW-B. In 2013, FEW-A was covered by 80-year-old Japanese cedar (*Cryptomeria japonica*) and cypress (*Chamaecyparis obtusa*), and FEW-B was covered by 13-year-old of them. Thinning of 5% or less trees was carried out in FEW-B in March 2013. Then, 13% of remaining trees in FEW-B were brought down by heavy snow from January to March 2014.

In Inokawa, previous studies have revealed that a large amount of groundwater infiltrates into the bedrock in small catchments (Oda et al., 2008) and that groundwater with high concentrations of chemicals discharged in downstream areas (Egusa et al., 2016). Therefore, this site was assumed to be suitable for the objective of this

study (i.e., to examine the effect of groundwater discharge on spatial variability of stream DOC, DIN and DIP concentrations).

2.2 | Samplings and measurements

In this study, we compared the bedrock groundwater contributions with the stream DOC, DIN and DIP concentrations. The concentrations of the mineral-derived solutes of the stream water, groundwater in soil layer, and bedrock groundwater were necessary to calculate the bedrock groundwater contribution (Section 2.3.1). Therefore, we sampled the stream water and bedrock springs at multiple points in Inokawa (Section 2.2.1). The groundwater in soil layer was sampled at FEW (Section 2.2.2). We also measured the DOC, DIN and DIP concentrations of the groundwater in soil layer and the bedrock springs to compare with those of the stream water.

2.2.1 | Samplings of stream water and bedrock springs

We sampled stream water such that the gradient of the bedrock groundwater discharge in our catchments was sufficiently captured. Specifically, we comprehensively sampled stream water from small-scale catchments (<0.1 km²) to large-scale catchments (>1 km²), including many small-scale catchments. This was because small-scale catchments generally have large spatial variations of bedrock groundwater contribution to stream water (e.g., Egusa et al., 2016; Peralta-Tapia et al., 2015; Uchida & Asano, 2010) and because, in our catchments, bedrock groundwater discharge increased with an increase of

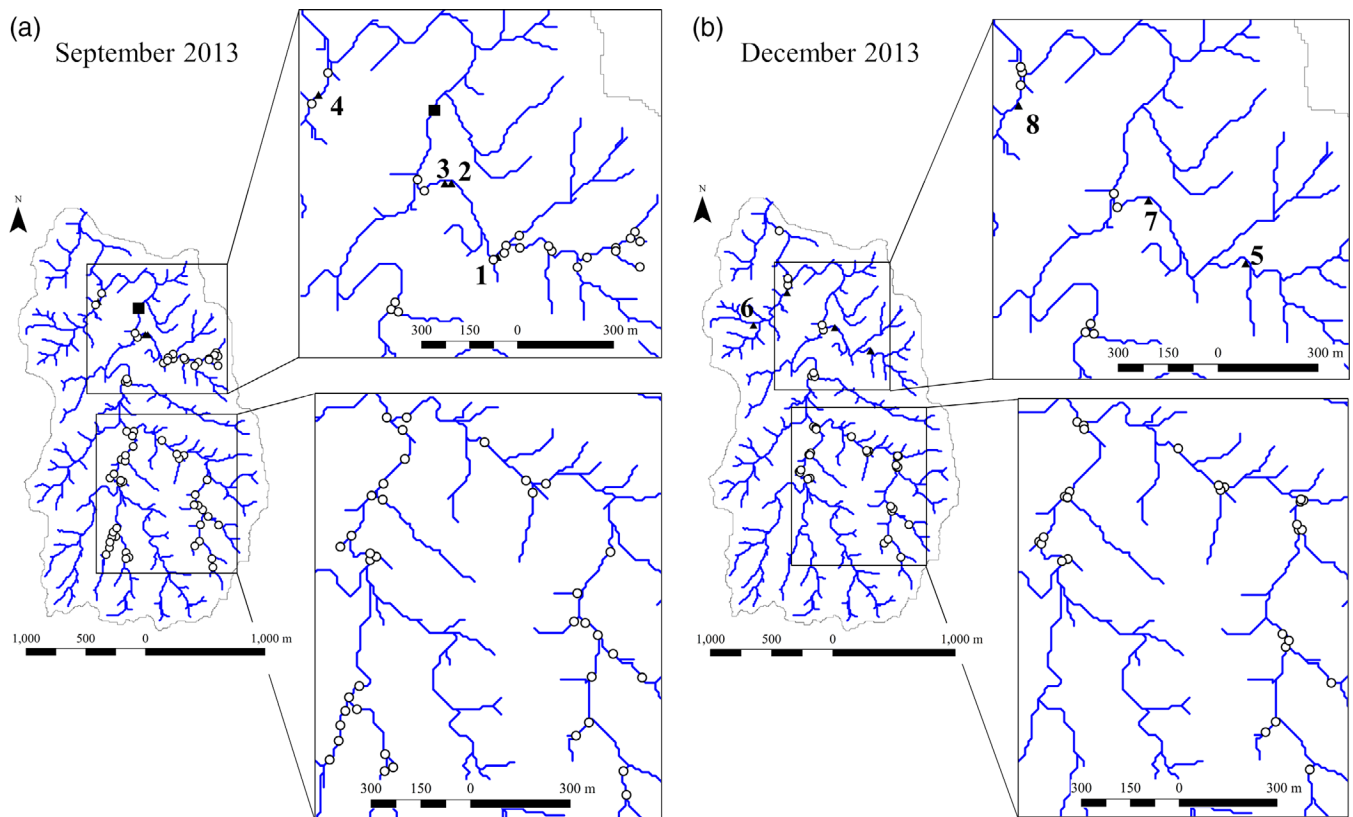


FIGURE 2 Sampling points of stream water and bedrock springs. The numbers in the figure are for each bedrock spring and correspond to the numbers in Table 1. We show only the points which were used for the analysis. Solid square means the location where stream water was taken for agricultural use in summer

catchment area (Egusa et al., 2016). We walked up along several streams and mainly sampled in the points where tributaries confluence. In addition, we sampled within a few days to minimize the effect of temporal variations on the results.

We sampled stream water at 64 points in 10–12 September 2013 and at 72 points in 18–19 December 2013 (Figure 2). 37 points of stream water were common to both periods. Bedrock springs were sampled at four points for each sampling campaign. The mean air temperatures were 21.8 and 4.2°C in September and December campaigns, respectively.

Although each sampling was conducted at base flow conditions (Figure 3a), a few amounts of rain fell in the sampling periods. There was only 3.7 mm of rainfall in 4 days just before our September sampling (Figure 3b). Then, 3.5 mm of rain fell from the evening of September 10 to the morning of September 11 and 3.5 mm of rain fell at the noon of September 11. Stream discharge of FEW-B slightly increased at the noon of September 11 due to the rainfall event. However, the impact of these rainfall events on our results would be negligible, because the rainfall rate was small and we sampled bedrock springs and main streams, which had high contribution of bedrock groundwater discharge, in the afternoon of September 11. There was no rainfall in the week before our December sampling (Figure 3a). Then, 14 mm of rain fell from the evening of December 18 to the morning of December 19 and it continued to rain until the end of our sampling campaign (Figure 3c). We compared the electrical

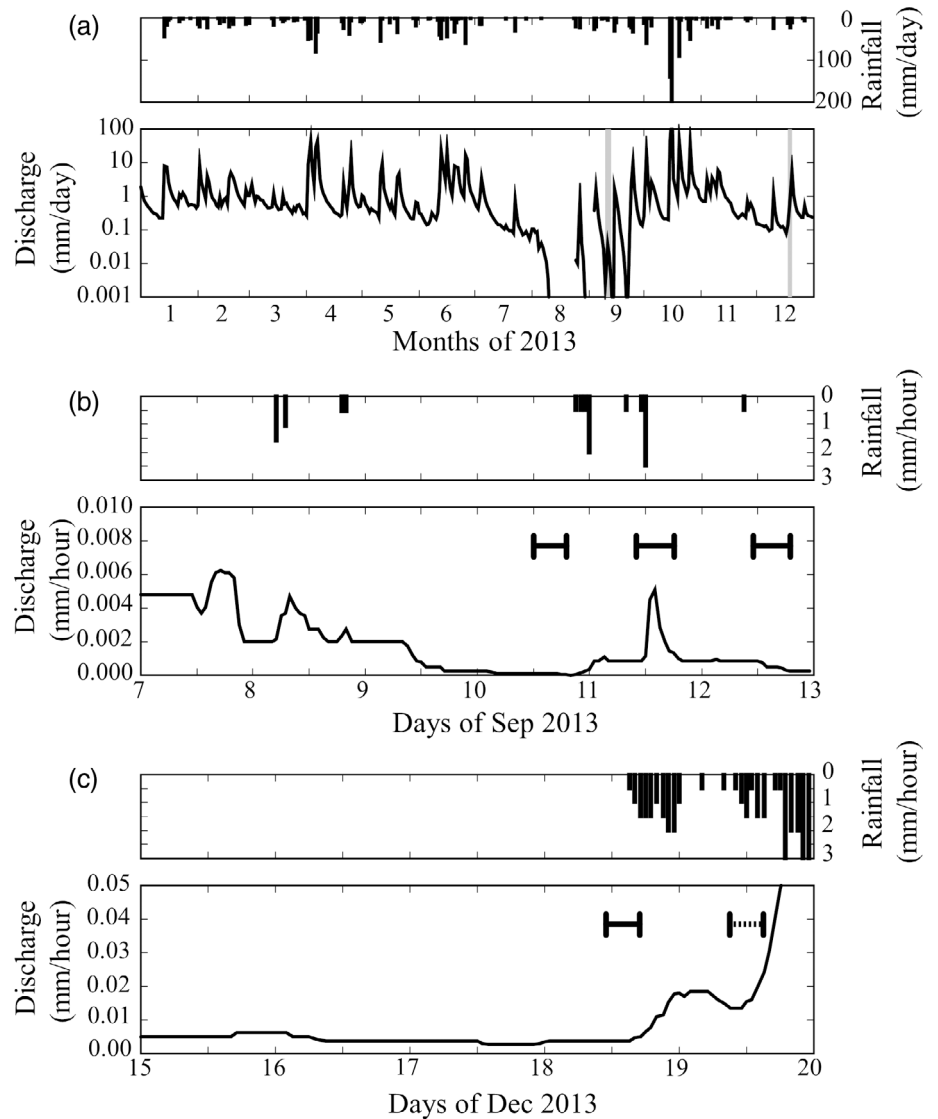
conductivity (EC) at the points sampled on December 18 and 19 with EC at the same points in September. The slopes of the linear regressions are 1.2 ($R^2 = 0.60$, $n = 31$) for December 18 and 0.75 ($R^2 = 0.45$, $n = 6$) for December 19, suggesting that the sampling on December 19 were largely affected by the rainfall event. Therefore, this study used stream water samples on December 18 and bedrock spring samples on December 19 for analysis.

We calculated the catchment area only for stream water samples on ArcGIS. We excluded the points where the location could not be identified on the map because their catchment area could not be calculated. Because stream water is taken for agricultural use at a point in summer season (Figure 2a), we did not use the stream water samples of downstream of the point in our September sampling. Consequently, 60 points of stream water and four points of bedrock springs and 37 points of stream water and four points of bedrock springs were used for analysis in September and December, respectively (Figure 2). Additionally, this study used the data of mineral-derived solutes concentrations of bedrock springs, which were observed from 2008 to 2009 ($n = 11$) for the analysis described in Section 2.3.1.

2.2.2 | Sampling of groundwater in soil layer

Groundwater in soil layer was collected in FEW using a PVC tube with a diameter of approximately 10 cm, which has small holes opened with an

FIGURE 3 (a) The daily rainfall and the daily discharge in Fukuroyamasawa Experimental Watershed B (FEW-B) in 2013. Shaded periods indicate the sampling dates. (b) The hourly rainfall and the hourly discharge in FEW-B in 7–12 September 2013. Bars indicate the sampling periods. (c) The hourly rainfall and the hourly discharge in FEW-B in 15–19 December 2013. Bars indicate the sampling periods. Note that stream water data in December 19 was not used in this study (See Section 2.2.1)



electric drill for collecting groundwater at the targeted depth. Two and three wells with a depth of 200–300 cm were installed in FEW-A and FEW-B, respectively. Although, our water sampling period was from 2011 to 2014, the period during which data was available differed for each solute. Mineral-derived solutes concentrations were measured in 2012 ($n = 28$). DOC, DIN and DIP concentrations were measured from 2012 to 2014 ($n = 35$), from 2011 to 2014 ($n = 71$), and from 2013 to 2014 ($n = 17$), respectively. DOC, DIN, and mineral-derived solutes concentrations were measured for samples of both FEW-A and FEW-B, while DIP concentration was measured only for samples of FEW-B.

2.2.3 | Water chemistry analysis

EC was measured using an EC meter (B173; Horiba, Kyoto, Japan). Samples were filtered using 0.45 μm pore size membrane filter, then samples for DIP analysis were frozen and those for other analyses were refrigerated until analysis. The concentrations of major ions (Na^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) were analyzed using ion

chromatography (LC10-A; Shimadzu, Kyoto, Japan). We defined the DIN concentration as the sum of NO_3^- and NH_4^+ concentrations. The detection limits of NO_3^- and NH_4^+ concentrations were both 0.1 $\mu\text{mol/L}$. The DOC concentration was analyzed by a wet oxidation method using a total organic carbon meter (TOC-V WP; Shimadzu, Kyoto, Japan). The detection limit of DOC concentration was 0.5 $\mu\text{g/L}$. The DIP concentration was analyzed by an ascorbic acid-molybdenum blue method using a spectrophotometer (V-550; Jasco, Tokyo, Japan). The detection limit of DIP concentration was 0.05 $\mu\text{mol/L}$.

2.3 | Data analysis

2.3.1 | Calculation of bedrock groundwater contribution of stream water using end member mixing analysis

We used End Member Mixing Analysis (EMMA; Hooper et al., 1990) to calculate bedrock groundwater contribution in stream water for

each observation point. In Inokawa, Egusa et al. (2016) already performed EMMA with the stream water and groundwater data that were obtained from 2008 to 2012. We conducted EMMA with our newly obtained stream water data in 2013 and groundwater data, including the observations from 2013. That is, no past analysis results from Egusa et al. (2016) were used in this study. This is because the locations of the sampling points were slightly different among the sampling campaigns, and because the DOC and DIP concentrations of the stream water samples were not measured in or before 2012.

At first, we made the following two assumptions: (1) Stream water is formed by mixing of groundwater through soil and bedrock, and thus the difference in the mixing ratio causes the spatial variability of the concentrations of mineral-derived solutes (Na^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-}). (2) The concentrations of mineral-derived solutes of groundwater through soil and bedrock are represented by the observed values of groundwater in soil layer in FEW and bedrock springs, respectively. Egusa et al. (2016) showed that concentrations of mineral-derived solutes in the groundwater in soil layer did not largely change below 100 cm of soil depth, that concentrations of mineral-derived solutes in bedrock springs were clearly higher than those of the groundwater in soil layer, and that concentrations of mineral-derived solutes in stream water were almost between those of the groundwater in soil layer and bedrock springs. These previous findings supported the above two assumptions. In addition, we sampled the surface soil at seven points in Inokawa and analyzed the samples to confirm the validity of our assumption that the mineral-derived solutes of the groundwater through soil in the whole catchment are represented by the observed values of the groundwater in the soil layer of FEW (Data S1).

Egusa et al. (2016) classified bedrock groundwater types in Inokawa according to the bedrock spring's chemistry. The first type had higher Ca^{2+} concentration ($\text{Ca}^{2+} > 800 \mu\text{mol/L}$) than the groundwater in soil layer. The second and the third types were characterized by their high Na^+ concentration ($\text{Na}^+ > 1500 \mu\text{mol/L}$) and high Na^+ and Cl^- concentrations ($\text{Na}^+ > 1500 \mu\text{mol/L}$ and $\text{Cl}^- > 500 \mu\text{mol/L}$), respectively. The discharge rates of these three types of bedrock groundwater were related to the altitude. The first, the second, and the third types discharged within the whole catchment, at

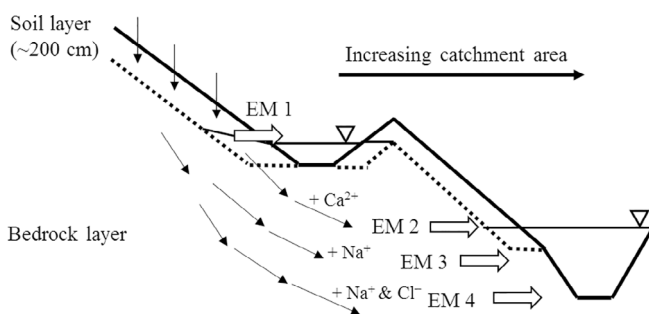


FIGURE 4 Conceptual diagram of flow paths in Inokawa. The thick solid line shows the ground surface, the dotted line indicates the boundary between the soil layer and the bedrock layer, and the thin solid line means the water table. Arrows show the flow pathway of soil water and groundwater. EM1–4 indicate four end members, respectively (See Section 2.3.1)

150–170 m, and below 150 m, respectively, indicating each type of bedrock groundwater was probably discharged from spatially independent groundwater aquifers.

Therefore, we decided to separate stream water into four end members, groundwater in soil layer and three types of bedrock groundwater as Egusa et al. (2016) did (Figure 4). This study referred to groundwater in soil layer as End Member 1 (hereinafter EM1). The first, the second, and the third types of bedrock groundwater were referred to as End Member 2 (EM2), End Member 3 (EM3), and End Member 4 (EM4), respectively. To separate into four end members, three different chemical concentrations or scores of principal component analysis (PCA) were needed. We calculated from first to third PCA scores with the concentrations of mineral-derived solutes of 97 points of stream water sampled in this study. In addition, for each end member, mineral-derived solutes concentrations were converted to PCA scores using principle component loadings.

Then, we used the PCA scores of the four end members and calculated the contribution ratio (R) of four end members to stream water for each sampling point as follow.

$$\sum_i EMscore_{ij} \cdot R_i = Strscore_j \quad (1)$$

$$\sum_i R_i = 1, \quad (2)$$

where, the subscript i and j represent four end members and three PCA scores, respectively. $EMscore$ and $Strscore$ indicate PCA scores of end members and stream water, respectively. We calculated R by analytically solving the resulting simultaneous linear equations. When the R dipped below zero, it was recalculated as zero. The four end member values used for EMMA were shown in the results section (Section 3.3).

2.3.2 | Uncertainty analysis

We evaluated the magnitude of the uncertainty generated by the spatiotemporal distributions of PCA scores for each end member. 100 000 sets of end members, which had different combinations of PCA scores, were generated randomly based on the observed mean values and SDs of them. For each observed stream water sample, we calculated bedrock groundwater contribution repeatedly using all sets of generated endmember values and examined the variation of bedrock groundwater contribution. We used normal distribution for random value generation.

3 | RESULTS

3.1 | DOC, DIN and DIP concentrations in stream water and bedrock springs

DOC concentration of stream water in less than 0.1 km² catchments varied widely in the range of 1–15 mgC/L for September and 1–5 mgC/L

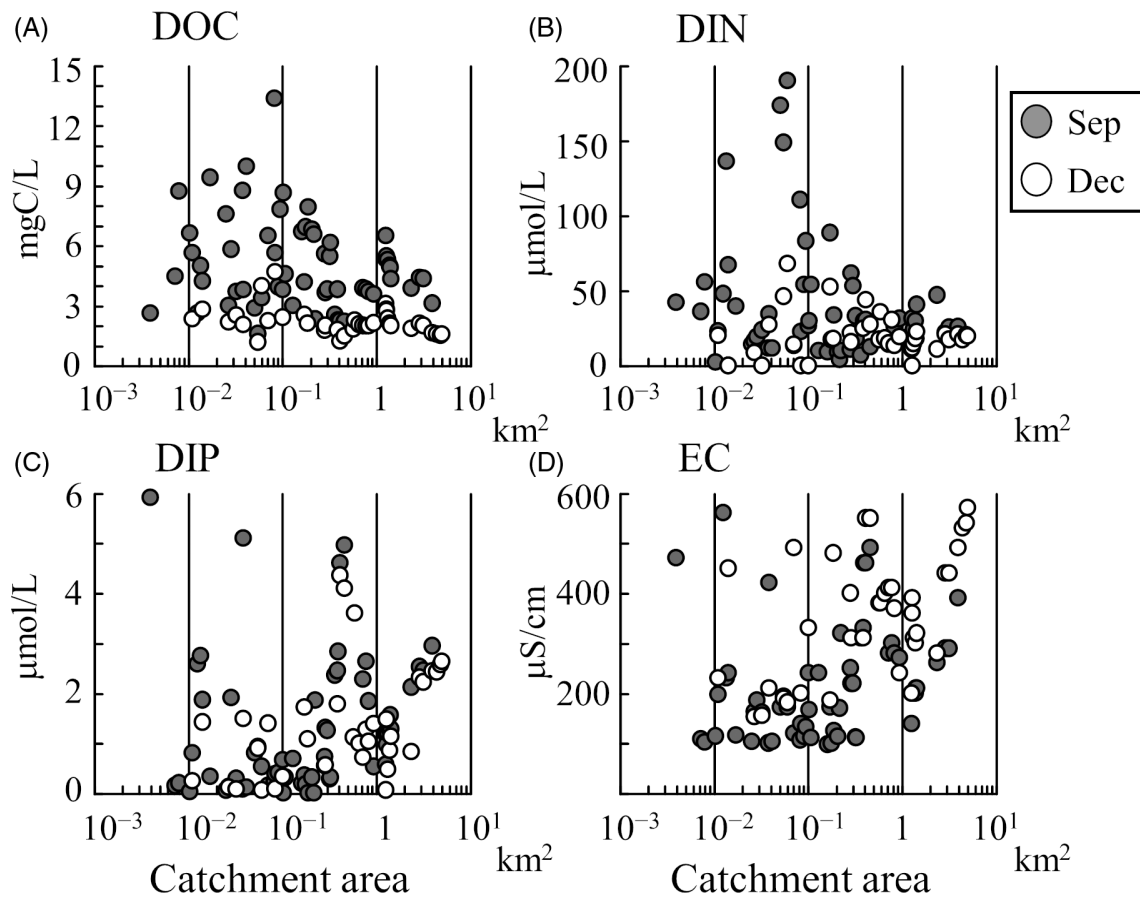


FIGURE 5 Relationships between catchment area and (a) DOC, (b) DIN, and (c) DIP concentrations, and (d) EC. A logarithmic axis is used for catchment area. The grey and white circles indicate observed values in September and in December 2013, respectively

for December (Figure 5a). Then, DOC concentration and the variation of it decreased with increasing catchment area. The DOC concentrations at the most downstream point (4.0 km² for September and 5.0 km² for December) were 3.1 and 1.6 mgC/L in September and December, respectively. The DOC concentrations in December were lower than those in September ($p < 0.001$, Mann-Whitney U test). In September samplings, NH₄⁺ concentration was detected at 18 points and the mean NH₄⁺ concentration at all points was 2.5 µmol/L, while NH₄⁺ concentration was below the detection limit in all points of December samplings. The variation of DIN concentration decreased with increasing catchment area and the concentration converged on approximately 20 µmol/L in catchments greater than 1 km² in area (Figure 5b). The DIN concentrations at the most downstream point were 25.9 and 19.5 µmol/L in September and December, respectively. The DIP concentration increased with increasing catchment area, especially above 0.1 km² (Figure 5c). The DIP concentrations at the most downstream point were 2.9 and 2.6 µmol/L in September and December, respectively. EC showed a similar tendency to DIP concentration, and the value increased with increasing catchment area (Figure 5d). EC values roughly correspond to the concentrations of mineral-derived solutes. The range of observed EC values was similar to that in Egusa et al. (2016) (100–600 µS/cm), which observed more than 150 points in Inokawa. That is, stream water samplings in this study could capture the whole ranges in

mineral-derived solutes concentrations and probably in the bedrock groundwater contribution of the targeted catchment.

Table 1 shows the spring water DOC, DIN and DIP concentrations. DOC and DIP concentrations in spring water did not differ between September and December. DIN concentration was higher in September than in December, and the composition of DIN was quite different between the two sampling periods. The spring waters in September had high NH₄⁺ and low NO₃⁻ concentrations, while those in December had high NO₃⁻ concentrations and lower NH₄⁺ concentrations than the detection limit. The DOC concentration of spring water ranged from 0.6 to 1.6 mgC/L, with many values near 1.0 mgC/L. In September, the DIN concentration of bedrock springs varied in the range of 53.4–126.5 µmol/L. While in December, DIN concentration of bedrock springs was at most 40.2 µmol/L and was below the detection limit at one of four springs. The DIP concentration of bedrock springs ranged from 2.8 to 9.6 µmol/L.

3.2 | DOC, DIN and DIP concentrations of groundwater in soil layer observed at FEW

Figure 6 shows the temporal changes in the DOC, DIN and DIP concentrations of the groundwater in soil layer observed at FEW.

TABLE 1 DOC, DIN and DIP concentrations of bedrock springs

Sampling date	Numbers on the map	DOC (mgC/L)	DIN ($\mu\text{mol/L}$)	NO_3^- ($\mu\text{mol/L}$)	NH_4^+ ($\mu\text{mol/L}$)	DIP ($\mu\text{mol/L}$)	End member type
11 September 2013	1	0.98	61.7	0.1	61.6	6.6	EM3
11 September 2013	2	0.89	53.4	BDL	53.4	6.7	EM4
11 September 2013	3	1.11	72.4	0.5	72.0	8.7	EM4
11 September 2013	4	1.53	126.5	5.8	120.7	9.2	EM4
19 December 2013	5	0.62	19.8	19.8	BDL	2.8	EM2
19 December 2013	6	1.05	34.6	34.6	BDL	7.3	EM3
19 December 2013	7	1.09	40.2	40.2	BDL	8.7	EM4
19 December 2013	8	1.58	BDL	BDL	BDL	9.6	EM4

Note: Numbers on the map correspond to the numbers on Figure 2. The classification criteria of each end member type is described in Section 2.3.1. BDL indicates below the detection limit (Section 2.2.3).

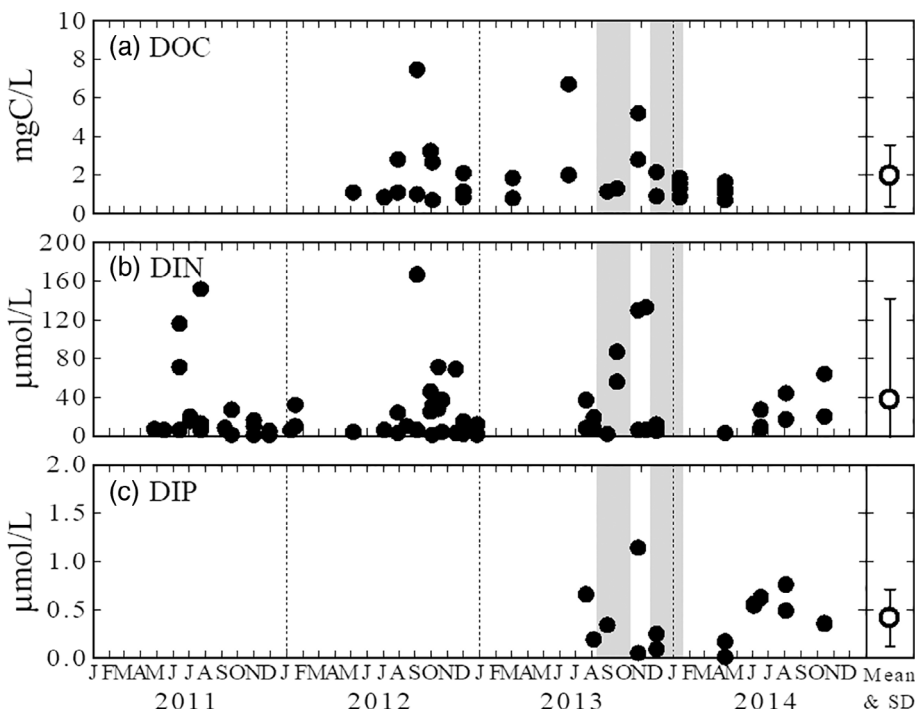


FIGURE 6 Temporal changes in (a) DOC, (b) DIN, and (c) DIP concentrations of groundwater in soil layer sampled at the Fukuroyamasawa Experimental Watershed (FEW) open circles and error bars indicate mean values and SDs over the entire period, respectively. Shaded periods show the periods of 1 month before and after our stream water sampling campaigns

The DOC, DIN and DIP concentrations varied widely in time and space. No clear seasonality was established for any solute. Although the observed values at FEW-B in 2013 and 2014 may have been affected by thinning and snow (Section 2.1), there was no clear difference in the observed values for different years. The variation in the DIN concentrations was substantial, and one sample contained a DIN concentration of more than 800 $\mu\text{mol/L}$ (8 September 2011), which was far from our plotted range. The mean ratios of NO_3^- to the sum of NO_3^- and NH_4^+

were approximately 80%, indicating that most of the DIN was NO_3^- .

The mean and SDs of the DOC, DIN and DIP concentrations over the entire period were 1.9 ± 1.6 mgC/L ($n = 35$), 37.1 ± 105.3 $\mu\text{mol/L}$ ($n = 71$), and 0.4 ± 0.3 $\mu\text{mol/L}$ ($n = 17$), respectively. The DOC, DIN and DIP concentrations observed within 1 month before and after our stream water sampling campaigns, which are shown with shaded areas in Figure 6, were nearly within the ranges indicated by the mean and SD for the entire period.

3.3 | Relationships between spatial variability of stream DOC, DIN and DIP concentrations and bedrock groundwater contribution

We converted the mineral-derived solutes concentrations (Na^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-}) of our stream water samples into the PCA scores (Figure 7). The cumulative contribution ratios from first to third principal components were 78.8%, 94.3% and 98.1%, respectively, meaning up to third PCA scores could sufficiently explain the variations in the concentrations of mineral-derived solutes in stream water. Although one point in December had extremely high first PCA score (First PCA Score = 8.1), other points were almost located within the range marked by four end members. That is, it is appropriate to perform EMMA using the four end members shown in this figure. We summarized the values of end members and their SDs in Table 2.

Figure 8 shows the relationships between bedrock groundwater contribution to stream water, which was the sum of contribution rates of each bedrock groundwater, and the stream DOC, DIN and DIP concentrations. The bedrock groundwater contribution had significant negative linear correlations with stream DOC concentration ($R^2 = 0.43$, $p < 0.001$ for Sep; $R^2 = 0.12$, $p < 0.05$ for Dec; Figure 8a,d), no significant correlation with stream DIN concentration ($p = 0.84$ for Sep; $p = 0.27$ for Dec; Figure 8b,e), and significant positive linear correlations with stream DIP concentration ($R^2 = 0.65$, $p < 0.001$ for Sep;

$R^2 = 0.15$, $p < 0.05$ for Dec; Figure 8c,f). The figures also show the DOC, DIN and DIP concentrations of groundwater in soil layer observed at FEW and bedrock springs. If DOC, DIN and DIP concentrations of stream water were formed by the end member mixing of groundwater in soil layer observed at FEW and bedrock springs, the concentrations in stream water would be plotted on the line connecting the concentrations of groundwater in soil layer and bedrock springs. DOC concentrations of stream water were plotted above the line connecting the concentrations of groundwater in soil layer and bedrock springs, particularly in September (Figure 8a,d). The DIN concentrations of stream water were mostly within the range in SDs of the concentrations of groundwater in soil layer and bedrock springs (Figure 8b,e). The DIP concentrations were plotted below the line connecting the concentrations of groundwater in soil layer and bedrock springs, particularly in December (Figure 8c,f).

4 | DISCUSSION AND CONCLUSIONS

4.1 | Interpretation of the results

In our site, stream DOC and DIP concentrations had significant correlations with bedrock groundwater contributions (Figure 8a,c,d,f). Correlation coefficients of these relationships were higher in

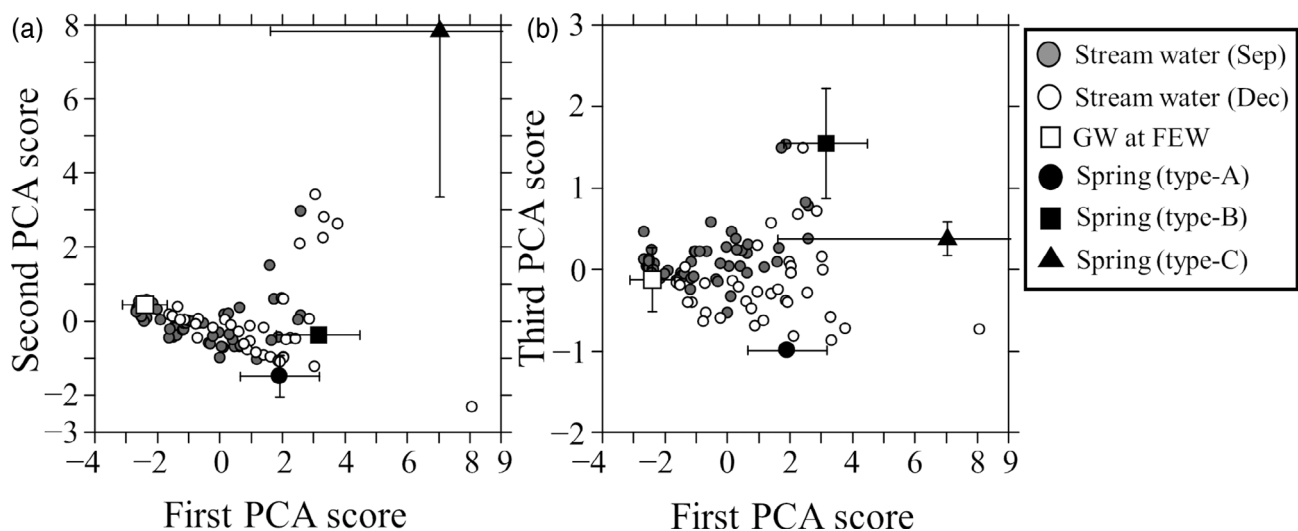


FIGURE 7 Principle component analysis (PCA) scores of stream water and end members. The grey and white circles indicate stream water in September and in December 2013, respectively. GW indicates groundwater in soil layer sampled at the Fukuroyamasawa Experimental Watershed (FEW). Spring means bedrock springs observed in Inokawa. The classification criteria of springs of type-A, B, and C were described in Section 2.3.1. The error bars represent the SD of the PCA scores of each end member

TABLE 2 PCA scores of end members

	First PCA score	Second PCA score	Third PCA score
End Member 1	-2.42 ± 0.70	0.43 ± 0.03	-0.12 ± 0.39
End Member 2	1.91 ± 1.26	-1.49 ± 0.56	-1.00 ± 0.05
End Member 3	3.14 ± 1.33	-0.37 ± 0.12	1.55 ± 0.67
End Member 4	7.03 ± 5.42	7.83 ± 4.48	0.38 ± 0.21

Note: Values are expressed as the average \pm SD.

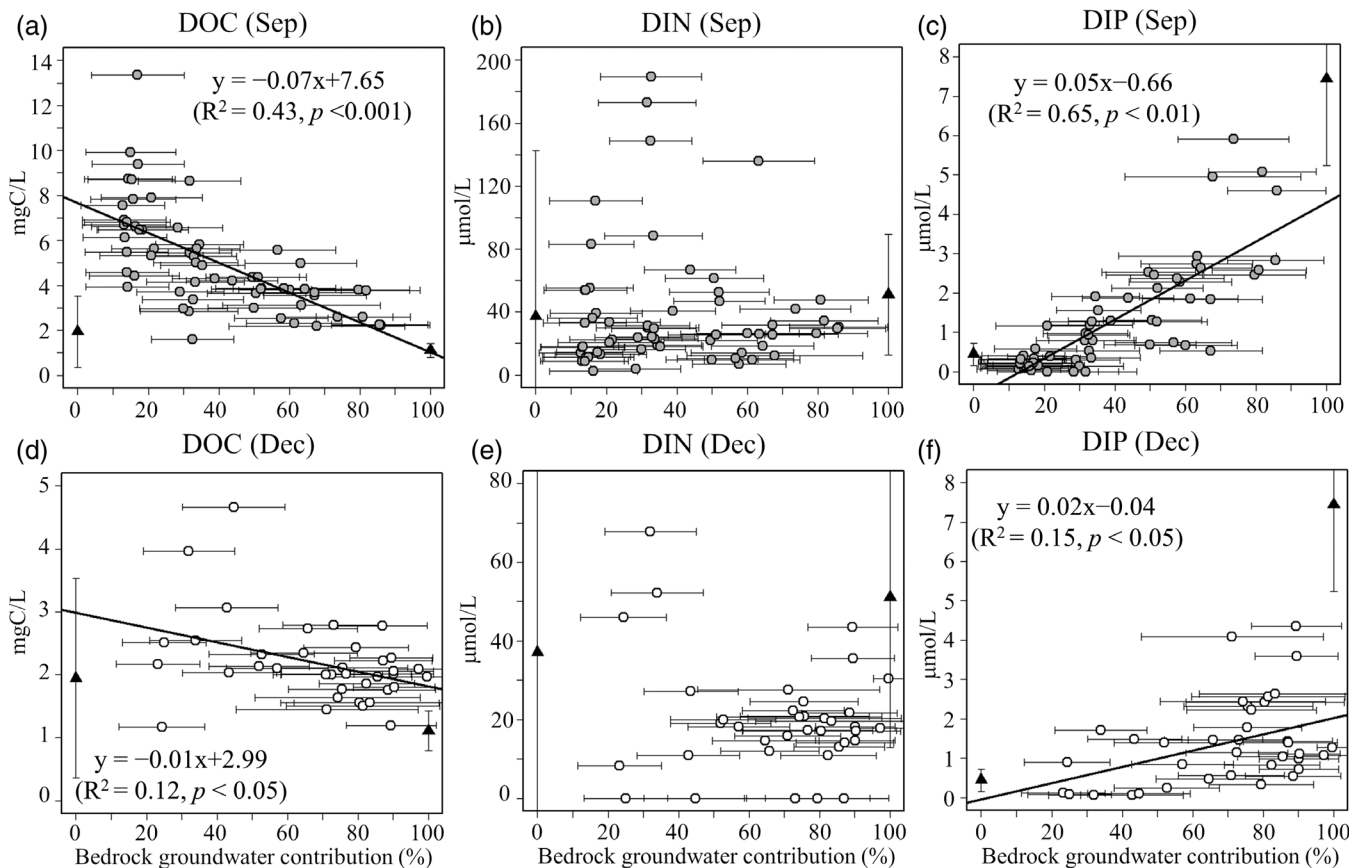


FIGURE 8 Relationships between the bedrock groundwater contribution in stream water and DOC, DIN and DIP concentrations. The bedrock contribution indicates the sum of the contribution ratios of EM2–4. The grey and white circles indicate stream water in September and in December 2013, respectively. The solid triangles show the average concentrations of groundwater in soil layer observed at the Fukuroyamasawa Experimental Watershed (FEW) and bedrock springs, and the vertical error bars with them mean the SD of them. The horizontal error bars represent the SD of bedrock groundwater contribution. Solid lines indicate regression lines for the results, which are shown only for significant relationships at a significant level of 5%

September than in December. We did not find any significant relationship between DIN concentrations and bedrock groundwater contributions.

4.1.1 | DOC

DOC concentrations of stream water had significant negative relationships with bedrock groundwater contributions. The results were similar to those reported for boreal forest catchments (Peralta-Tapia et al., 2015; Tiwari et al., 2017). This negative relationship corresponded to the observation result that DOC concentrations in bedrock springs were lower than those of groundwater in soil layer (Figure 8). DOC in forest catchments is generally produced mainly by the decomposition of litter and decreases in soil due to physical adsorption and/or decomposition (Kalbitz et al., 2000). Our observation results in a hillslope followed this general pattern (Figure S2 in Data S1). These mechanisms probably continue to decrease the DOC concentrations while groundwater infiltrates through the bedrock. It could result in low DOC concentrations of bedrock springs and the

negative relationships between DOC concentrations and bedrock groundwater contributions in this study.

DOC concentrations of stream water were higher than those expected from end member mixing of groundwater in soil layer and bedrock springs, especially in September (Figure 8a,d). DOC concentrations of groundwater in soil layer at FEW had no clear seasonality (Figure 6a). One possible explanation for the tendency in Figure 8 is the spatial heterogeneity of DOC concentrations of groundwater in soil layer in Inokawa. That is, the DOC concentrations of groundwater in soil layer observed in a 0.02 km² catchment, FEW may not have represented the whole 5 km² catchment and have been lower than those of the actual average values. The process by which DOC concentrations were established in forest catchments was spatially heterogeneous owing to many factors, such as tree species, water chemistry in soil water, ground temperature, soil water content, and depths of groundwater table (Cool et al., 2014; Grabs et al., 2012; Hinton et al., 1998; reviewed by Kalbitz et al., 2000), and could strongly regulate the stream DOC concentration (Aitkenhead et al., 1999). In addition, DOC might have been added to groundwater immediately before it flowed out to stream channel because

groundwater in soil layer need to pass through shallow soil, which had high DOC concentrations in water (Figure S2 in Data S1). These factors could explain the higher stream DOC concentrations than expected from end member mixing of groundwater in soil layer and bedrock springs. In addition, the DOC concentration in water passing through shallow flow paths might have a large temporal heterogeneity and the source area of DOC might temporally change reflecting the wetness conditions within a catchment (Richardson et al., 2020). It could result in the difference between the tendencies in September and December in our study.

Another possibility is in-stream DOC production. Mulholland and Hill (1997) demonstrated that only mixing of water through different flow paths could not fully explain the temporal variations of DOC concentrations in stream water and discussed that in-stream DOC production was important for forming the DOC concentration in stream water. Several other studies have also shown that the decomposition of terrestrial carbon source increased stream DOC concentrations in low-order streams (Johnson et al., 2006; Meyer et al., 1998). In-stream DOC production would be larger in streams with low stream discharge because lower stream discharge and shallower water depth would result in larger contact area per water volume between DOC sources such as root, leaves, and sediments, and stream water. In our site, the bedrock groundwater discharge increased with an increase of catchment area and increased stream discharge (Egusa et al., 2016; Figure 5d). Therefore, in-stream DOC production would be greater in places where catchment area size is small and bedrock groundwater contribution is low. It could result in the steep negative relationships between stream DOC concentrations and bedrock groundwater contributions. Furthermore, the difference between the results in September and December could be explained from the difference in decomposition rate caused by the difference in water temperature.

4.1.2 | DIN

Spatial variability in stream DIN concentration was poorly explained by bedrock groundwater contribution (Figure 8b,e). This was different result from a previous study, which showed that the DIN concentration in stream water increased in summer due to the discharge of DIN rich bedrock groundwater (Burns et al., 1998). The direct reasons of this were both groundwater in soil layer and bedrock had a wide range in DIN concentrations and their DIN concentrations were not different from each other (Figure 8). The processes that affect DIN concentration, for example, nitrification (Isobe et al., 2020) and denitrification (Duncan et al., 2013; Hill et al., 2000) are strongly affected by environmental factors like soil moisture and redox conditions, and highly heterogeneous on a scale of tens of meters. These spatial heterogeneity in processes could cause large variations in the DIN concentrations of groundwaters and would mask the small difference between DIN concentrations of groundwater in soil layer and bedrock groundwater.

The DIN concentrations of the bedrock springs in September were higher than those in December (Table 1). It would not be due to delayed discharge of thaw water (Burns et al., 1998) because snow

hardly accumulated at our site. The plausible reasons are the increase of leaching due to enhanced microbial activity in summer (Goodale et al., 2015) or DIN supply from bedrock weathering (Holloway et al., 1998; Holloway & Dahlgren, 2002). Besides, in September, most of DIN in bedrock springs was NH_4^+ and NO_3^- concentration was low, while the opposite tendency was observed in December (Table 1). It is presumed that in September the high temperature in near surface caused the increase of microbial respiration in aquifer (Riedel, 2019), resulting in an anaerobic environment. Then, nitrate ammonification (reviewed by Burgin & Hamilton, 2007) would be caused or nitrification would be limited. The sampling periods of our bedrock springs and groundwater in soil layer were different, and the number of measurements of bedrock springs was small. Therefore, more intensive samplings and using tools, for example, isotope ratios that can present the evidence of denitrification and/or supply from the bedrock are necessary for further elucidation of the mechanism.

4.1.3 | DIP

In our site, DIP concentrations of stream water positively correlated with bedrock groundwater contributions (Figure 8c,f). The results were similar to Pringle et al. (1993), which showed high phosphorus concentrations of stream water in catchments influenced by discharge of deep volcanic groundwater. The main sources of DIP in forest catchments were decomposition from organic matter and mineral weathering, and DIP concentration decreases with flow path length in soil due to biological uptake and physical adsorption (Soht et al., 2017). In our site, DIP concentrations of bedrock springs were obviously higher than those of groundwater in soil layer (Figure 8c,f). Therefore, DIP derived from decomposition of fresh organic matter would be retained in soil and plants, and stream DIP concentrations were mainly regulated by mineral weathering of bedrock.

The median value and the maximum value of DIP concentration in 1244 points of forested catchments in Japan was 0.20 and 3.75 $\mu\text{mol/L}$, respectively (Wakamatsu et al., 2006). These values were close to those of groundwater in soil layer and stream water influenced by bedrock groundwater discharge in our site. Therefore, our results showed the clear importance of bedrock groundwater discharge on stream DIP concentrations. Such high DIP concentrations of stream water and bedrock springs of our site would be due to bedrock geology. One of the major sources of phosphorous in rock is the deposited organic matter under the sea (Filippelli, 2011). The bedrock of our site is young in geological sense (~ 4 Ma) and deposited under the sea, and thus probably including a large amount of phosphorous derived from ancient organic matter.

DIP concentrations of stream water were lower than those would be expected from end member mixing of groundwater in soil layer and bedrock springs alone, especially in December. At FEW, DIP concentrations of groundwater in soil layer were low and had no clear seasonality (Figure 6c). Besides, DIP concentrations of bedrock groundwater did not have clear difference between in September and in December (Table 1). Therefore, the temporal variation of DIP

concentrations of groundwater could not explain the seasonally different tendencies in the relationships between DIP concentrations and bedrock groundwater distributions. Thus, in-stream DIP uptake is a probable reason. Previous many studies have reported that in-stream DIP uptake rate was significant based on nutrient addition experiments or mass balance approach (e.g., Davis & Minshall, 1999; Hall et al., 2002). We performed 10 times DIP addition experiments on 40–120 m stream channel of our site and confirmed the significant decrease of DIP concentration at three times of them (Egusa, 2013). In these experiments, NO_3^- addition was also performed at the same time and significant decrease of NO_3^- concentration was observed in only one time. Our site is a steep mountainous headwater catchment with a mean slope of 31° , and therefore the primary production in stream channels might be low due to the shading by trees and topography. Therefore, in our site, biological DIP uptake would be low and physical DIP adsorption may sometimes occur. Large amounts of rainfall and steep terrain cause large sediment discharges in Japan. In our site, annual sediment discharge was approximately 100–200 kilograms per hectare (Hotta et al., 2007). 342 mm of rain fell in 15–16 October 2013. It is plausible that this rainfall event replaced the sediments in stream channels with fresh ones, resulting in an increase of in-stream DIP adsorption. Future studies should elucidate the impact of sediment dynamics on in-stream DIP adsorption in our site.

4.2 | Implication of the study

The relationships between spatial variability of stream DOC, DIN and DIP concentrations and bedrock groundwater contributions shown in this study could be useful in comparing the factors that affect stream DOC, DIN and DIP concentrations among catchments because they enclose the effects of the various hydrological and biogeochemical processes within a catchment. Many previous studies have shown that large spatial heterogeneity of hydrological and biogeochemical processes exist, particularly in headwater catchments of size 1 km^2 or in smaller catchment area (e.g., Asano et al., 2009; Likens & Buso, 2006; Temnerud & Bishop, 2005). Previous detailed studies on DOC, DIN and DIP in forested catchments mainly targeted small catchments, probably because of labor and financial constraints (e.g., Osaka et al., 2010; Sebestyen et al., 2008). That is, when we compared the results of different catchments obtained from these detailed observations to elucidate the effects of catchment characteristics such as bedrock geology and climate on the factors that affect stream DOC, DIN and DIP concentrations, the spatial representativeness of the results might become an obstacle. The relationships between the spatial variability of stream DOC, DIN, DIP concentration and bedrock groundwater contributions using multi-point observations of stream water could overcome this obstacle, because the spatially representative information of stream DOC, DIN and DIP concentrations in the catchments could be obtained from these relationships. For example, the y-intercept in the relationship between the DOC concentration and bedrock groundwater contribution provides information on the sum of spatially averaged DOC concentration of groundwater in soil

layer and that of in-stream DOC production. Besides, the slope in this relationship indicates spatially averaged difference between the DOC concentration of groundwater in soil layer including in-stream DOC production and that of bedrock groundwater. In addition, the average DIP concentrations of observation points with high bedrock groundwater contribution would be regarded as the values indicating the influences of spatial heterogeneity in bedrock groundwater and in-stream uptake. Therefore, indexing from the relationships between the spatial variability of stream DOC, DIN and DIP concentrations and bedrock groundwater contributions could provide the representative values of the catchments and contribute to elucidate the relationships between the processes that affect stream DOC, DIN and DIP and the catchment characteristics.

Future studies should accumulate more case studies from a wide variety of catchments because the targeted area in this study was just one forested catchment with warm-humid climate. We showed clear relationships between stream DOC and DIP concentrations and bedrock groundwater contributions, and there was no significant relationship between stream DIN concentration and bedrock groundwater contribution (Figure 8). These relationships may not be the case in other catchments. For example, in our site, DOC concentration of bedrock springs was about 1 mgC/L (Table 1), while some previous studies have shown that groundwater in soil layer could have lower concentrations than 1 mgC/L (Osaka et al., 2010; Sebestyen et al., 2008). In addition, the stream DIP concentration is strongly affected by bedrock geology (Hensley et al., 2017; Wakamatsu et al., 2006). Therefore, the influence of bedrock groundwater discharge on the spatial distribution of stream DOC, DIN and DIP concentrations could vary greatly depending on the catchment characteristics, for example, bedrock geology and chemical properties of soil. Besides, previous studies have reported that in some catchments bedrock groundwater discharge increased with increasing catchment area (e.g., Egusa et al., 2016; Shaman et al., 2004), while in other catchments it did not increase with increasing catchment area (e.g., Uchida & Asano, 2010). Thus, it is still remained unclear how common the increase of bedrock groundwater discharge with increasing catchment area is. It is expected that such bedrock groundwater dynamics are also strongly dependent on the bedrock geology, especially the permeability of the bedrock (Hale et al., 2016; Hale & McDonnell, 2016; Pfister et al., 2017; Richardson et al., 2020) and should be elucidated in the future.

ACKNOWLEDGEMENTS

The authors thank the staff of Chiba Experimental Forest, The University of Tokyo for supporting observations of rainfall and stream discharge in Inokawa.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

ORCID

Tomohiro Egusa  <https://orcid.org/0000-0001-8993-1044>

Tomomi Kumagai  <https://orcid.org/0000-0001-8331-271X>

Tomoki Oda  <https://orcid.org/0000-0003-1677-4425>

Nobuhito Ohte  <https://orcid.org/0000-0003-0658-6834>

REFERENCES

- Ågren, A., Buffam, I., Jansson, M., & Laudon, H. (2007). Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *Journal of Geophysical Research: Biogeosciences*, 112(3), 1–11. <https://doi.org/10.1029/2006JG000381>.
- Aitkenhead, J. A., Hope, D., & Billett, M. F. (1999). The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrological Processes*, 13(8), 1289–1302. [https://doi.org/10.1002/\(SICI\)1099-1085\(19990615\)13:8<1289::AID-HYP766>3.0.CO;2-M](https://doi.org/10.1002/(SICI)1099-1085(19990615)13:8<1289::AID-HYP766>3.0.CO;2-M).
- 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(10), 1–9. <https://doi.org/10.1029/2008WR007466>.
- Buffam, I., Laudon, H., Temnerud, J., Mörth, C. M., & Bishop, K. (2007). Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. *Journal of Geophysical Research: Biogeosciences*, 112(1), 1–11. <https://doi.org/10.1029/2006JG000218>.
- Burgin, A. J., & Hamilton, S. K. (2007). Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment*, 5(2), 89–96. [https://doi.org/10.1890/1540-9295\(2007\)5\[89:HWOTRO\]2.0.CO;2](https://doi.org/10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2).
- Burns, D. A., Murdoch, P. S., Lawrence, G. B., & Michel, R. L. (1998). Effect of groundwater springs on NO_3^- concentrations during summer in Catskill Mountain streams. *Water Resources Research*, 34(8), 1987–1996. <https://doi.org/10.1029/98WR01282>.
- Cirmo, C. P., & McDonnell, J. J. (1997). Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: A review. *Journal of Hydrology*, 199(1–2), 88–120. [https://doi.org/10.1016/S0022-1694\(96\)03286-6](https://doi.org/10.1016/S0022-1694(96)03286-6).
- Cool, G., Lebel, A., Sadiq, R., & Rodriguez, M. J. (2014). Impact of catchment geophysical characteristics and climate on the regional variability of dissolved organic carbon (DOC) in surface water. *Science of the Total Environment*, 490, 947–956. <https://doi.org/10.1016/j.scitotenv.2014.05.091>.
- Davis, J. C., & Minshall, G. W. (1999). Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia*, 119(2), 247–255. <https://doi.org/10.1007/s004420050783>.
- Diaz, R. J., & Rosenberg, R. (2008). Spreading dead zones and consequences for marine ecosystems. *Science*, 321(5891), 926–929. <https://doi.org/10.1126/science.1156401>.
- Dillon, P. J., & Molot, L. A. (1997). Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resources Research*, 33(11), 2591–2600. <https://doi.org/10.1029/97WR01921>.
- Duncan, J. M., Groffman, P. M., & Band, L. E. (2013). Towards closing the watershed nitrogen budget: Spatial and temporal scaling of denitrification. *Journal of Geophysical Research: Biogeosciences*, 118(3), 1105–1119. <https://doi.org/10.1002/jgrg.20090>.
- Egusa, T. (2013). *Study on relationship between spatial variability in streamwater characteristics and catchment scale in forested headwaters* (Ph.D. thesis). The University of Tokyo.
- 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(22), 4125–4138. <https://doi.org/10.1002/hyp.10916>.
- Elser, J. J., Bracken, M. E. S., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., Ngai, J. T., Seabloom, E. W., Shurin, J. B., & Smith, J. E. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters*, 10(12), 1135–1142. <https://doi.org/10.1111/j.1461-0248.2007.01113.x>.
- Elser, J. J., Marzolf, E. R., & Goldman, C. R. (1990). Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: A review and critique of experimental enrichments. *Canadian Journal of Fisheries and Aquatic Sciences*, 47(7), 1468–1477. <https://doi.org/10.1139/f90-165>.
- Feller, M. C., & Kimmins, J. P. (1984). Effects of clearcutting and slash burning on streamwater chemistry and watershed nutrient budgets in southwestern British Columbia. *Water Resources Research*, 20(1), 29–40. <https://doi.org/10.1029/WR020i001p00029>.
- Fellows, C. S., Valett, H. M., Dahm, C. N., Mulholland, P. J., & Thomas, S. A. (2006). Coupling nutrient uptake and energy flow in headwater streams. *Ecosystems*, 9(5), 788–804. <https://doi.org/10.1007/s10021-006-0005-5>.
- Filippelli, G. M. (2011). Phosphate rock formation and marine phosphorus geochemistry: The deep time perspective. *Chemosphere*, 84(6), 759–766. <https://doi.org/10.1016/j.chemosphere.2011.02.019>.
- 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(4), 1–17. <https://doi.org/10.1029/2004WR003635>.
- Giardino, R., & Houser, C. A. (2015). Introduction to the critical zone. *Developments in Earth Surface Processes*, 19, 1–13. <https://doi.org/10.1016/B978-0-444-63369-9.00001-X>.
- Goodale, C. L., Fredriksen, G., Weiss, M. S., McCalley, C. K., Sparks, J. P., & Thomas, S. A. (2015). Soil processes drive seasonal variation in retention of ^{15}N tracers in a deciduous forest catchment. *Ecology*, 96(10), 2653–2668. <https://doi.org/10.1890/14-1852.1>.
- Grabs, T., Bishop, K., Laudon, H., Lyon, S. W., & Seibert, J. (2012). Riparian zone hydrology and soil water total organic carbon (TOC): Implications for spatial variability and upscaling of lateral riparian TOC exports. *Biogeosciences*, 9(10), 3901–3916. <https://doi.org/10.5194/bg-9-3901-2012>.
- Hale, V. C., & McDonnell, J. J. (2016). Effect of bedrock permeability on stream base flow mean transit time scaling relations: 1. A multiscale catchment intercomparison. *Water Resources Research*, 52(2), 1358–1374. <https://doi.org/10.1002/2014WR016124>.
- Hale, V. C., McDonnell, J. J., Stewart, M. K., Solomon, D. K., Doolittle, J., Ice, G. G., & Pack, R. T. (2016). Effect of bedrock permeability on stream base flow mean transit time scaling relationships: 2. Process study of storage and release. *Water Resources Research*, 52(2), 1375–1397. <https://doi.org/10.1002/2015WR017660>.
- Hall, R. J. O., Bernhardt, E. S., & Likens, G. E. (2002). Relating nutrient uptake with transient storage in forested mountain streams. *Limnology and Oceanography*, 47(1), 255–265. <https://doi.org/10.4319/lo.2002.47.1.0255>.
- Hall, R. J. O., & Tank, J. L. (2003). Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming. *Limnology and Oceanography*, 48(3), 1120–1128. <https://doi.org/10.4319/lo.2003.48.3.1120>.
- Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison, W. C., Dortch, Q., Gobler, C. J., Heil, C. A., Humphries, E., Lewitus, A., Magnien, R., Marshall, H. G., Sellner, K., Stockwell, D. A., Stoecker, D. K., & Suddleson, M. (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>.
- Hensley, R. T., McLaughlin, D. L., Cohen, M. J., & Decker, P. H. (2017). Stream phosphorus dynamics of minimally impacted coastal plain watersheds. *Hydrological Processes*, 31(8), 1636–1649. <https://doi.org/10.1002/hyp.11132>.
- Hill, A. R., Devito, K. J., Campagnolo, S., & Sanmugas, K. (2000). Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry*, 51(2), 193–223. <https://doi.org/10.1023/A:1006476514038>.

- Hinton, M. J., Schiff, S. L., & English, M. C. (1998). Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. *Biogeochemistry*, 41(2), 175–197. <https://doi.org/10.1023/A:1005903428956>.
- Holloway, J. M., & Dahlgren, R. A. (2002). Nitrogen in rock: Occurrences and biogeochemical implications. *Global Biogeochemical Cycles*, 16(4), 65–1–65–17. <https://doi.org/10.1029/2002GB001862>.
- Holloway, J. M., Dahlgren, R. A., Hansen, B., & Casey, W. H. (1998). Contribution of bedrock nitrogen to high nitrate concentrations in stream water. *Nature*, 395(6704), 785–788. <https://doi.org/10.1038/27410>.
- Hooper, R. P., Christophersen, N., & Peters, N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology*, 116(1–4), 321–343. [https://doi.org/10.1016/0022-1694\(90\)90131-G](https://doi.org/10.1016/0022-1694(90)90131-G).
- Hotta, N., Kayama, T., & Suzuki, M. (2007). Analysis of suspended sediment yields after low impact forest harvesting. *Hydrological Processes*, 21, 3565–3575. <https://doi.org/10.1002/hyp.6583>.
- Isobe, K., Ise, Y., Kato, H., Oda, T., Vincenot, C. E., Koba, K., Tateno, R., Senoo, K., & Ohte, N. (2020). Consequences of microbial diversity in forest nitrogen cycling: Diverse ammonifiers and specialized ammonia oxidizers. *The ISME Journal*, 14, 12–25. <https://doi.org/10.1038/s41396-019-0500-2>.
- Iwasaki, K., Katsuyama, M., & Tani, M. (2015). Contributions of bedrock groundwater to the upscaling of storm-runoff generation processes in weathered granitic headwater catchments. *Hydrological Processes*, 29(6), 1535–1548. <https://doi.org/10.1002/hyp.10279>.
- Japan Forestry Agency. (2012). *Forest resources of Japan 2012*. (in Japanese).
- Johnson, M. S., Lehmann, J., Selva, E. C., Abdo, M., Riha, S., & Couto, E. G. (2006). Organic carbon fluxes within and streamwater exports from headwater catchments in the southern Amazon. *Hydrological Processes*, 20(12), 2599–2614. <https://doi.org/10.1002/hyp.6218>.
- Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., & Matzner, E. (2000). Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Science*, 165(4), 277–304. <https://doi.org/10.1097/00010694-200004000-00001>.
- Kaplan, L. A., & Newbold, J. D. (1993). Biogeochemistry of dissolved organic carbon entering streams. In T. E. Ford (ed.), *Aquatic microbiology: An ecological approach*. Blackwell Scientific.
- Katsuyama, M., Tani, M., & Nishimoto, S. (2010). Connection between streamwater mean residence time and bedrock groundwater recharge/discharge dynamics in weathered granite catchments. *Hydrological Processes*, 24(16), 2287–2299. <https://doi.org/10.1002/hyp.7741>.
- Kosugi, K., Katsura, S., Katsuyama, M., & Mizuyama, T. (2006). Water flow processes in weathered granitic bedrock and their effects on runoff generation in a small headwater catchment. *Water Resources Research*, 42(2), 1–18. <https://doi.org/10.1029/2005WR004275>.
- Likens, G. E., Bormann, F. H., Johnson, N. M., Fisher, D. W., & Pierce, R. S. (1970). Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecological Monographs*, 40(1), 23–47. <https://doi.org/10.2307/1942440>.
- 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>.
- McDonnell, J. J. (2003). Where does water go when it rains? Moving beyond the variable source area concept of rainfall-runoff response. *Hydrological Processes*, 17, 1869–1875. <https://doi.org/10.1002/hyp.5132>.
- McGlynn, B. L., & McDonnell, J. J. (2003). Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research*, 39(4). <https://doi.org/10.1029/2002WR001525>.
- Meyer, J. L., Wallace, J. B., & Eggert, S. L. (1998). Leaf litter as a source of dissolved organic carbon in streams. *Ecosystems*, 1(3), 240–249. <https://doi.org/10.1007/s100219900019>.
- Mineau, M. M., Wollheim, W. M., Buffam, I., Findlay, S. E. G., Hall, R. O., Hotchkiss, E. R., Koenig, L. E., McDowell, W. H., & Parr, T. B. (2016). Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements. *Journal of Geophysical Research: Biogeosciences*, 121(8), 2019–2029. <https://doi.org/10.1002/2015JG003204>.
- Mulholland, P. J., Helton, A. M., Poole, G. C., Hall, R. O., Hamilton, S. K., Peterson, B. J., Tank, J. L., Ashkenas, L. R., Cooper, L. W., Dahm, C. N., Dodds, W. K., Findlay, S. E. G., Gregory, S. V., Grimm, N. B., Johnson, S. L., McDowell, W. H., Meyer, J. L., Valett, H. M., Webster, J. R., ... Thomas, S. M. (2008). Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature*, 452(7184), 202–205. <https://doi.org/10.1038/nature06686>.
- Mulholland, P. J., & Hill, W. R. (1997). Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. *Water Resources Research*, 33(6), 1297–1306. <https://doi.org/10.1029/97WR00490>.
- Mulholland, P. J., Marzolf, E. R., Webster, J. R., Hart, D. R., & Hendricks, S. P. (1997). Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams. *Limnology and Oceanography*, 42(3), 443–451. <https://doi.org/10.4319/lo.1997.42.3.0443>.
- Nakajima, T., Makimoto, H., Hirayama, J., & Tokuhashi, S. (1981). *Geology of the Kamogawa district*. In *Quadrangle series, scale 1:50,000* (pp. 101–107). Geological Survey of Japan.
- Nieminen, M. (2004). Export of dissolved organic carbon, nitrogen and phosphorus following clear-cutting of three Norway spruce forests growing on drained peatlands in southern Finland. *Silva Fennica*, 38(2), 123–132. <https://doi.org/10.14214/sf.422>.
- 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, 195–204. (in Japanese with English summary). <https://doi.org/10.3178/jjshwr.21.195>.
- Osaka, K., Ohte, N., Koba, K., Yoshimizu, C., Katsuyama, M., Tani, M., Tayasu, I., & Nagata, T. (2010). Hydrological influences on spatiotemporal variations of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in a forested headwater catchment in central Japan: Denitrification plays a critical role in groundwater. *Journal of Geophysical Research: Biogeosciences*, 115(G2). <https://doi.org/10.1029/2009JG000977>.
- 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(5), 847–858. <https://doi.org/10.1002/2014JG002878>.
- Pfister, L., Martínez-Carreras, N., Hissler, C., Klaus, J., Carrer, G. E., Stewart, M. K., & McDonnell, J. J. (2017). Bedrock geology controls on catchment storage, mixing, and release: A comparative analysis of 16 nested catchments. *Hydrological Processes*, 31(10), 1828–1845. <https://doi.org/10.1002/hyp.11134>.
- Pringle, C. M., Rowe, G. L., Triska, F. J., Fernandez, J. F., & West, J. (1993). Landscape linkages between geothermal activity and solute composition and ecological response in surface waters draining the Atlantic slope of Costa Rica. *Limnology and Oceanography*, 38(4), 753–774. <https://doi.org/10.4319/lo.1993.38.4.0753>.
- Ranalli, A. J., & Macalady, D. L. (2010). The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds - A review of the scientific literature. *Journal of Hydrology*, 389(3–4), 406–415. <https://doi.org/10.1016/j.jhydrol.2010.05.045>.

- Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter - A review. *Chemosphere*, 55(3), 319–331. <https://doi.org/10.1016/j.chemosphere.2003.11.011>.
- Richardson, C. M., Zimmer, M. A., Fackrell, J. K., & Paytan, A. (2020). Geologic controls on source water drive baseflow generation and carbon geochemistry: Evidence of nonstationary baseflow sources across multiple subwatersheds. *Water Resources Research*, 56, e2019WR026577. <https://doi.org/10.1029/2019WR026577>.
- Riebe, C. S., Hahm, W. J., & Brantley, S. L. (2017). Controls on deep critical zone architecture: A historical review and four testable hypotheses. *Earth Surface Processes and Landforms*, 42, 128–156. <https://doi.org/10.1002/esp.4052>.
- Riedel, T. (2019). Temperature-associated changes in groundwater quality. *Journal of Hydrology*, 572, 206–212. <https://doi.org/10.1016/j.jhydrol.2019.02.059>.
- Sawano, S., Komatsu, H., & Suzuki, M. (2005). Differences in annual precipitation amounts between forested area, agricultural area, and urban area in Japan. *Journal of Japan Society of Hydrology and Water Resources*, 18(4), 435–440. <https://doi.org/10.3178/jjshwr.18.435>.
- Sebestyen, S. D., Boyer, E. W., Shanley, J. B., Kendall, C., Doctor, D. H., Aiken, G. R., & Ohte, N. (2008). Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. *Water Resources Research*, 44(12), 1–14. <https://doi.org/10.1029/2008WR006983>.
- 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>.
- Sholkovitz, E. R., & Copland, D. (1981). The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochimica et Cosmochimica Acta*, 45(2), 181–189. [https://doi.org/10.1016/0016-7037\(81\)90161-7](https://doi.org/10.1016/0016-7037(81)90161-7).
- Sohrt, J., Lang, F., & Weiler, M. (2017). Quantifying components of the phosphorus cycle in temperate forests. *Wiley Interdisciplinary Reviews: Water*, 4(6), e1243. <https://doi.org/10.1002/wat2.1243>.
- Soulsby, C., Tetzlaff, D., van den Bedem, N., Malcolm, I. A., Bacon, P. J., & Youngson, A. F. (2007). Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. *Journal of Hydrology*, 333(2–4), 199–213. <https://doi.org/10.1016/j.jhydrol.2006.08.016>.
- 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>.
- 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, S58–S70. <https://doi.org/10.1002/lno.10738>.
- Uchida, T., & Asano, Y. (2010). Spatial variability in the flowpath of hill-slope runoff and streamflow in a meso-scale catchment. *Hydrological Processes*, 24(16), 2277–2286. <https://doi.org/10.1002/hyp.7767>.
- Uchida, T., Asano, Y., Ohte, N., & Mizuyama, T. (2003). Seepage area and rate of bedrock groundwater discharge at a granitic unchanneled hill-slope. *Water Resources Research*, 39(1), 1–12. <https://doi.org/10.1029/2002WR001298>.
- Wakamatsu, T., Konohira, E., Shindo, J., Yoshioka, T., Okamoto, K., Itaya, A., & Kim, M. S. (2006). Dissolved inorganic phosphate concentration in stream water in Japan and factors controlling the concentration. *Journal of Japan Society on Water Environment*, 29(11), 679–686. (in Japanese with English summary). <https://doi.org/10.2965/jswe.29.679>.
- Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of the Total Environment*, 400(1–3), 379–395. <https://doi.org/10.1016/j.scitotenv.2008.08.002>.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Egusa T, Kumagai T, Oda T, Ohte N. Effects of bedrock groundwater discharge on spatial variability of dissolved carbon, nitrogen, and phosphorous concentrations in stream water within a forest headwater catchment. *Hydrological Processes*. 2021;35:e13993. <https://doi.org/10.1002/hyp.13993>