Comparative study of cation composition in stream water flowing through the Paleogene layer in the southern Kyushu Mountains

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　　To further understand water chemistry composition of mountain streams in the basin that overlay the Paleogene layer, the experiments were conducted in the Takeo River in Saito City and the Tougaku River in Miyakonojyo City, Miyazaki Prefecture Japan. Samples were collected approximately 5 cm above the substrate from 10 riffles in each stream segment and the physicochemical parameters of water temperature, EC and pH of the water and the concentrations of cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured. Water sampling was performed randomly at all sampling points in winter (February 2017), spring (May 2017), summer (August 2017) and autumn (November 2017). In the Tougaku River, the ratio of Ca^{2+} and Na^+ was nearly 1:1, showed a significant positive correlation and was constant over the measurement period, suggesting that Ca^{2+} and Na^+ originate from the same mineral source, such as Ca-plagioclase feldspar and Na-plagioclase feldspar. In the Takeo River, Ca^{2+} concentration was positively correlated only with Mg^{2+} concentration and was negatively correlated with the other cation concentrations, indicating that Ca^{2+} and Mg^{2+} may be released from sources of which minerals are common but compositions are not the same and that Ca^{2+} sources consist mainly of carbonate rock containing calcite and dolomite. Because the stream environments of the Takeo River are suitable for leaf litter retention and subsequent mineral leaching, the main source of K^+ is considered to be biological, such as leaf litter. In the Tougaku River, since stream environments are less suited for leaf retention than are those in the Takeo River, the main sources of K^+ are K-contained minerals, such as K-feldspar, biotite and and/or illite.

　　Key words: stream water chemistry, cation, Paleogene layer, weathering, leaching from leaf litter

1. Introduction

　　The chemical composition of stream water is influenced by precipitation, groundwater and the soil (surface and subsurface water). Precipitation carries atmospheric gases and aerosols, and groundwater contains numerous ionic components derived from weathering of rocks, such as silicate, carbonate and sulfide rocks[5]. Soil can be defined as a complex matrix comprised of air, water, decomposed organic matter, living plants and animals and the residues of rock weathering[20]. Stream runoff transports nutrients derived from minerals, precipitation, and organic matter, directly downstream. Stream water composition is therefore largely influenced by the geochemistry of groundwater and soil water[7].

　　Field measurements in mountainous streams originating from the Paleogene layer in the southern Kyushu Mountains from 2012 to 2016 showed that ion concentrations and physicochemical parameters of the stream water were affected by sampling season, stream environment, or both, and that ion concentrations might be interdependent on each other, and affected by other physicochemical parameters. Na^+ originates from the weathering of plagioclase in sedimentary silicate rocks, and Mg^{2+} and Ca^{2+} originate almost entirely from the weathering of calcite and/or dolomite in sedimentary carbonate rocks in the study area. However, biomass input to stream water, i.e. through leachate from leaf litter, can lead to pronounced contributions of K^+.

　　The present study was conducted to further understand water chemistry composition of mountain streams in the basin that overlay the Miyazaki Formation, which was formed during the Cretaceous to middle Paleogene periods. In addition, the ionic composition of stream water determined in this study can be applied to other mountain streams which flow through basin overlays of the same geological conditions of these streams.

2. Site description

Experiments were conducted in the Takeo River in Saito City and the Tougaku River in Miyakonojyo City, Miyazaki Prefecture Japan. The Takeo River is a tributary of the Hitotsuse River originating in the southern Kyushu Mountains and flows over a range of elevation from 600 to 100 m. The Tougaku River is an upper-stream tributary of the Oyodo River originating in the southern Kyushu Mountains that flows from 500 to 200 m. These river basins overlay the Miyazaki Formation, which was formed during the Cretaceous to middle Paleogene periods. The formation consists of black slate, sandstone and shale. Consequently, the geologic structure of the basins is characterized by the prevalence of weak and extensively folded rock strata with numerous faults that are susceptible to weathering. These geologic conditions have formed steep and unstable basin slopes where several mid-sized landslides have occurred in the last 50 years[8,25]. To prevent landslides in the basin, seven 3 to 5 m high sabo dams have been constructed along the Takeo River since 1965[8]. The Tougaku River, however, is relatively more stable than the Takeo River, and fewer sabo dams (3 to date) have been constructed.

The study site consists of a section of river measuring approximately 1 km, between sabo dam No. 5 and a point approximately 50 m downstream of sabo dam No. 6 in the Takeo River, between sabo dams No. 1 and No. 2 in the Tougaku River (Fig. 1). The investigated rivers are first-order streams with a mean width of 10 m, mean depth (at modal flow) of 0.3 m, mean slope of 1/40, and mean current velocities ranging from 20 to 30 cm/sec. The stream bottom of each river is composed primarily of gravel, pebbles and cobble substrates, and the riparian vegetation consists of evergreen trees such as *Symplocos theophrastiifolia* Sieb. et Zucc., *Machilus japonica* Sieb. et Zucc., *Meliosma rigida* Sieb. et Zucc., and *Litsea acuminata Kurata*. Since the slope

of the stream basin is steep, tree leaves supplied to the forest floor of the slope tend to be deposited into the streambed.

3. Methods

3-1 Stream water sampling and estimation of water physicochemical parameters

There are different environments (streambed types) in the streams, such as riffles, pools, side-pools and springs[19]. Springs are the environments arising from cracks on the vertical cliffs of the bedrock slope running along the side of the stream, and side-pools are defined as stagnant areas of water along the stream margin. The findings of the previous study[19] also demonstrated that cation concentrations differed significantly among stream environments and seasons, likely due to the heterogeneous distribution of ions resulting from leachate from leaves. In this study, therefore, stream water samples were collected from riffles where the stream water is sufficiently turbulent to produce a uniform water composition from 30 to 50 cm.

Samples were collected approximately 5 cm above the substrate using a 250 ml polyethylene bottle from 10 riffles in each stream segment (refer to Fig.1). Since these sampling points were not distributed continuously, the water quality measurements at each sampling point were considered to be independent of each other

At the time of sampling, physicochemical parameters of water temperature, EC and pH of the water were measured with a water quality probe (WQC-20A, TOA Electronics Ltd., Japan). The collected water samples were transported to our laboratory and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured by ion chromatography (DX-120, Nippon Dionex K.K., Japan). (In the present study, anions were not analyzed or reported due to a malfunction of the experimental apparatus.)

Water sampling was performed randomly at all sampling points in winter (February 2017), spring (May 2017),
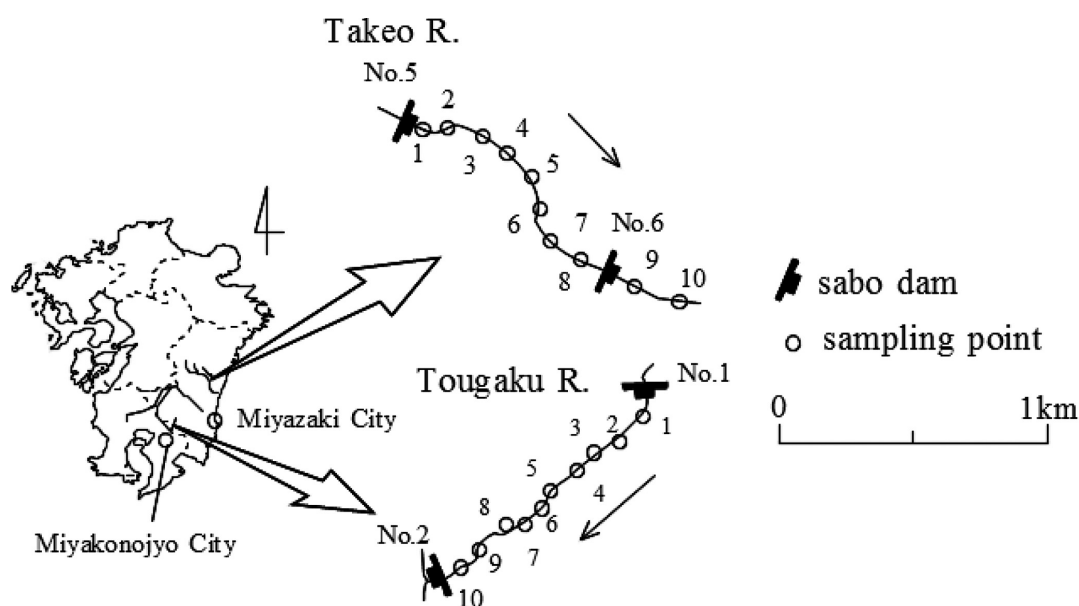

Fig. 1 Locations of the Takeo and Tougaku Rivers and sampling points

Table 1(a) Physicochemical values and cation concentrations at the Tougaku River sampling stations throughout 2017

| sampling date	month	season	No.	pH	EC	℃	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	total
20170202	Feb.	winter	1	9.1	58.4	8.6	8.869	0.586	0.790	1.621	11.350	23.215
20170202			2	8.9	58.3	8.9	9.048	0.546	0.896	1.610	11.567	23.668
20170202			3	9.5	113.8	9.8	9.022	0.349	0.867	1.609	11.710	23.557
20170202			4	9.5	115.1	10.5	9.546	0.320	1.435	1.670	11.633	24.603
20170202			5	9.6	116.0	12.0	7.700	0.450	1.000	1.400	8.500	19.050
20170202			6	8.4	58.8	8.9	8.140	1.072	0.551	0.892	9.403	20.058
20170202			7	9.8	68.4	8.1	13.183	0.606	1.085	1.239	10.489	26.602
20170202			8	10.0	112.5	9.8	12.443	0.385	0.770	1.479	10.698	25.776
20170202			9	9.5	100.3	10.7	9.691	0.583	0.850	1.614	11.610	24.348
20170202			10	9.3	97.3	13.0	7.400	0.440	0.900	1.300	8.400	18.440
20170523	May.	spring	1	9.4	99.5	18.8	3.329	0.293	0.368	0.649	4.388	9.027
20170523			2	9.2	100.4	19.4	3.532	0.234	0.464	0.669	4.549	9.448
20170523			3	9.5	104.1	20.4	3.527	0.267	0.470	0.674	4.674	9.613
20170523			4	9.2	102.6	20.7	3.594	0.256	0.462	0.695	4.940	9.946
20170523			5	9.5	103.0	17.0	5.200	0.300	0.700	0.850	5.500	12.550
20170523			6	8.9	98.6	19.7	3.239	0.269	0.424	0.663	3.862	8.457
20170523			7	9.2	105.3	18.8	4.024	0.289	0.470	0.726	4.662	10.170
20170523			8	9.2	101.2	19.5	3.862	0.312	0.463	0.741	4.801	10.180
20170523			9	8.9	101.1	21.7	3.674	0.275	0.504	0.749	4.901	10.103
20170523			10	9.0	100.3	18.0	5.100	0.300	0.700	0.880	5.000	11.980
20170828	Aug.	summer	1	8.9	102.8	20.0	4.817	0.272	0.639	0.860	6.199	12.787
20170828			2	8.9	102.2	21.0	4.789	0.246	0.590	0.871	6.261	12.756
20170828			3	8.6	98.9	20.8	7.026	0.386	0.917	1.486	9.812	19.625
20170828			4	8.7	97.5	20.0	4.200	0.250	0.700	0.660	4.200	10.010
20170828			5	8.5	96.3	21.0	4.000	0.210	0.750	0.650	4.100	9.710
20170828			6	8.4	99.8	22.0	7.175	0.512	1.355	1.422	8.062	18.526
20170828			7	8.6	100.4	19.0	4.875	0.409	1.010	1.000	5.999	13.294
20170828			8	8.6	103.4	19.0	4.684	0.247	1.052	0.918	5.000	11.899
20170828			9	8.6	106.3	21.0	7.495	0.259	1.685	1.684	10.544	21.668
20170828			10	8.7	105.3	22.0	4.000	0.210	0.400	0.600	4.000	9.210
20171109	Nov.	autumn	1	8.1	87.8	16.6	6.959	0.414	0.843	1.203	8.563	17.982
20171109			2	8.0	87.5	16.4	6.533	0.448	0.714	1.103	8.447	17.244
20171109			3	8.4	87.4	16.3	6.284	0.394	0.721	1.066	8.669	17.135
20171109			4	8.1	87.9	16.3	6.321	0.410	0.845	1.079	8.823	17.478
20171109			5	8.0	86.9	15.0	6.000	0.300	0.800	1.000	7.200	15.300
20171109			6	8.0	93.4	17.1	4.727	0.539	0.900	0.615	4.892	11.672
20171109			7	8.3	87.0	16.0	6.567	0.454	1.023	1.176	8.091	17.311
20171109			8	8.1	87.9	16.1	6.636	0.486	0.848	1.219	8.631	17.821
20171109			9	8.0	93.6	16.8	6.418	0.514	0.698	1.150	8.872	17.653
20171109			10	8.2	92.2	14.0	6.300	0.600	0.850	1.300	8.200	17.250

Table 1(b) Physicochemical values and cation concentrations at the Takeo River stations throughout 2017

| sampling date	month	season	No.	pH	EC	℃	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	total
20170203	Feb.	winter	1	7.3	76.9	6.5	2.393	0.071	0.767	2.240	9.291	14.761
20170203			2	7.7	80.3	6.8	2.668	0.162	0.667	2.471	8.740	14.709
20170203			3	7.9	83.8	8.6	3.015	0.083	0.594	2.669	8.368	14.729
20170203			4	7.6	79.3	5.5	3.108	0.018	0.580	2.510	7.322	13.537
20170203			5	7.5	78.7	7.5	2.995	0.245	0.643	2.580	7.514	13.977
20170203			6	7.3	77.4	5.6	2.287	0.020	0.512	2.228	8.939	13.986
20170203			7	7.5	80.8	6.1	2.575	0.049	0.520	2.357	8.373	13.874
20170203			8	7.9	83.8	7.7	2.957	0.088	0.559	2.572	8.014	14.190
20170203			9	7.6	79.7	6.2	3.035	0.090	0.638	2.509	7.385	13.656
20170203			10	7.5	78.9	6.6	3.253	0.025	0.601	2.626	7.658	14.163
20170524	May.	spring	1	7.2	95.3	13.3	2.337	0.026	0.707	3.135	8.948	15.154
20170524			2	7.1	85.7	15.5	2.868	0.014	0.672	2.668	7.529	13.752
20170524			3	7.6	69.1	18.4	3.243	0.047	0.644	2.261	6.303	12.498
20170524			4	7.4	83.8	21.4	3.831	0.044	0.734	2.725	8.564	15.897
20170524			5	7.5	79.8	20.0	3.575	0.000	0.704	2.452	7.621	14.352
20170524			6	7.2	95.7	13.1	2.262	0.028	0.710	3.138	8.988	15.126
20170524			7	7.4	83.4	15.7	2.728	0.056	0.635	2.612	7.332	13.362
20170524			8	7.4	69.6	17.4	3.198	0.000	0.628	2.110	5.693	11.629
20170524			9	7.6	82.7	21.4	4.299	0.195	1.016	2.706	8.548	16.765
20170524			10	7.1	38.3	21.4	5.808	0.879	1.646	1.041	1.660	11.034
20170829	Aug.	summer	1	7.9	86.9	24.9	2.320	0.051	0.609	1.840	7.122	11.942
20170829			2	7.5	87.7	21.3	2.406	0.000	0.641	2.096	8.608	13.751
20170829			3	7.7	85.3	20.0	2.607	0.000	0.687	2.507	10.167	15.968
20170829			4	6.6	93.4	20.7	2.887	0.138	0.631	3.740	12.510	19.907
20170829			5	6.8	89.8	23.9	2.694	0.069	0.659	3.575	12.055	19.052
20170829			6	7.8	60.0	24.8	2.220	0.077	0.566	1.840	7.049	11.752
20170829			7	7.7	60.0	21.6	2.542	0.259	0.853	2.264	9.319	15.237
20170829			8	7.6	60.0	19.2	2.419	0.553	0.894	1.615	6.363	11.845
20170829			9	6.6	93.1	20.6	2.784	0.081	0.634	3.795	12.877	20.171
20170829			10	6.8	92.4	23.0	2.631	0.071	0.608	3.307	10.910	17.527
20171110	Nov.	autumn	1	7.3	96.0	12.9	3.155	0.158	0.946	3.377	9.762	17.399
20171110			2	7.3	93.2	14.0	2.536	0.000	0.524	3.200	11.202	17.462
20171110			3	7.4	94.0	14.8	2.212	0.000	0.526	3.266	13.826	19.830
20171110			4	7.4	98.4	13.2	2.492	0.000	0.525	3.320	10.597	16.934
20171110			5	7.6	94.3	15.1	2.389	0.000	0.549	3.260	10.591	16.789
20171110			6	7.3	95.1	13.0	2.803	0.000	0.535	3.352	9.701	16.391
20171110			7	7.2	93.3	12.9	2.450	0.033	0.501	3.132	11.226	17.343
20171110			8	7.3	94.0	13.6	2.192	0.000	0.510	3.444	13.414	19.560
20171110			9	7.5	98.6	13.5	2.447	0.000	0.545	3.434	11.094	17.520
20171110			10	7.2	94.9	14.2	2.272	0.000	0.474	2.612	8.076	13.434

Table 2 Mean values and standard errors of physicochemical parameters and cation concentrations corresponding to the stream and sampling date

investigated stream	sampling date	month	season	pH	EC	°C	cation concentration (mg / l)					
							Na⁺	NH₄⁺	K⁺	Mg²⁺	Ca²⁺	total
Tougaku	20170202	Feb.	winter	9.4± 0.1	89.9± 8.2	10.0± 0.5	9.504± 0.602	0.534± 0.068	0.914± 0.073	1.444± 0.077	10.536± 0.415	22.932± 0.887
	20170523	May.	spring	9.2± 0.1	101.6± 0.7	19.4± 0.4	3.908± 0.219	0.279± 0.008	0.503± 0.035	0.730± 0.025	4.728± 0.136	10.147± 0.395
	20170828	Aug.	summer	8.7± 0.1	101.3± 1.0	20.6± 0.3	5.306± 0.434	0.300± 0.032	0.910± 0.122	1.015± 0.121	6.418± 0.743	13.949± 1.399
	20171109	Nov.	autumn	8.1± 0.0	89.2± 0.9	16.1± 0.3	6.275± 0.190	0.456± 0.027	0.824± 0.031	1.091± 0.060	8.039± 0.382	16.685± 0.604
Takeo	20170203	Feb.	winter	7.6± 0.1	79.9± 0.7	6.7± 0.3	2.828± 0.103	0.085± 0.022	0.608± 0.024	2.476± 0.049	8.160± 0.219	14.158± 0.140
	20170524	May.	spring	7.3± 0.1	78.3± 5.3	17.7± 1.0	3.415± 0.324	0.129± 0.085	0.810± 0.099	2.485± 0.191	7.119± 0.699	13.957± 0.588
	20170829	Aug.	summer	7.3± 0.2	80.9± 4.6	22.0± 0.6	2.551± 0.067	0.130± 0.053	0.678± 0.034	2.658± 0.272	9.698± 0.755	15.715± 1.059
	20171110	Nov.	autumn	7.3± 0.0	95.2± 0.6	13.7± 0.3	2.495± 0.092	0.019± 0.016	0.563± .043	3.240± 0.076	10.949± 0.537	17.266± 0.555
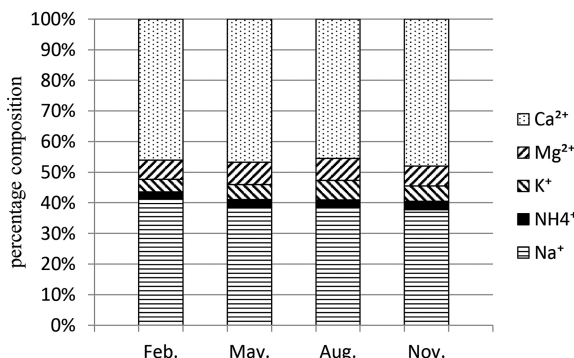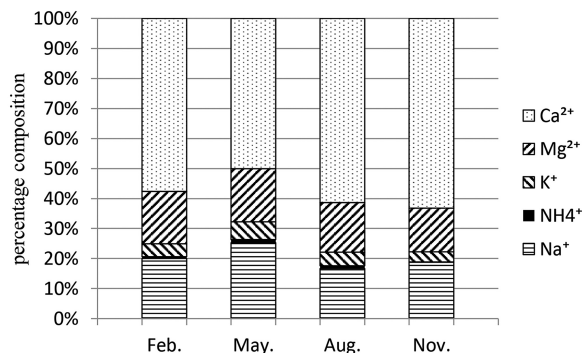
Fig. 2 Percentage of each cation concentration to total cation concentration for each sampling time (month) in a) the Tougaku River and b) the Takeo River
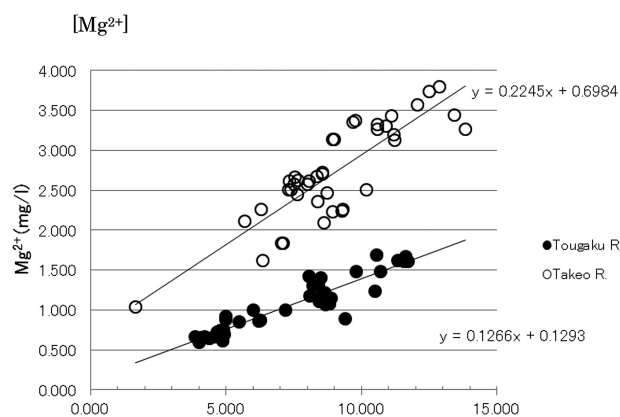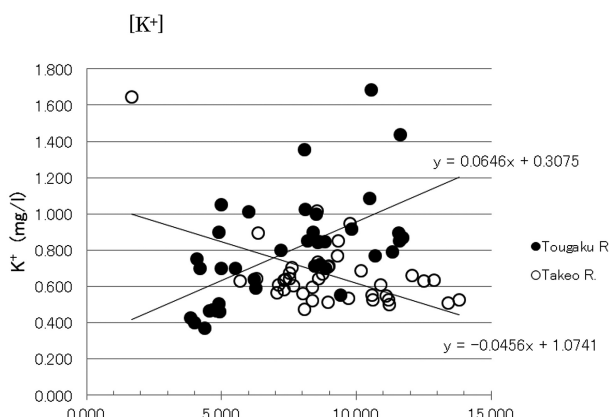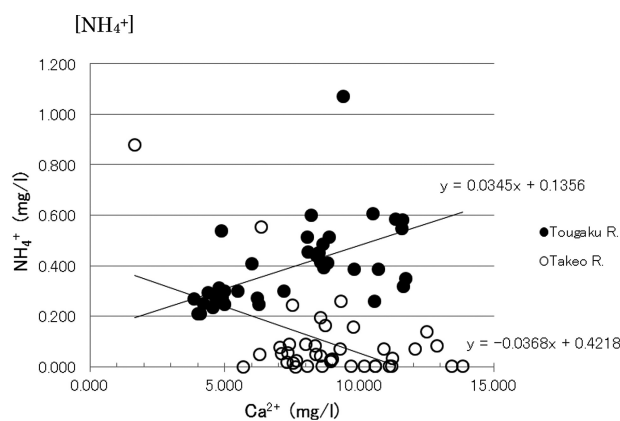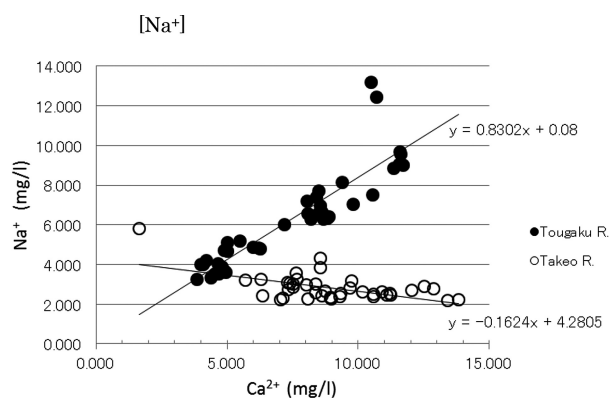
Fig. 3 Correlations between Ca²⁺ and each of Na⁺, NH₄⁺, K⁺ and Mg²⁺ in the Tougaku and Takeo Rivers

summer (August 2017) and autumn (November 2017) covering the rainy and floods season and the non-rainy and dry season.

3-2 Statistical analysis

To identify the relationships among physicochemical parameters and cation concentrations, correlation coefficients were calculated. The effect of sampling season (spring, summer, autumn and winter) and stream (Takeo River and Tougaku River) on water physicochemical parameters (temperature, EC and pH) and cation concentrations were analyzed by two-way analysis of variance (ANOVA). In the present study, sampling season and the stream were regarded as independent variables and each measurement value was regarded as a dependent variable.

4. Results

4-1 Stream water physicochemical parameters

Physicochemical parameters, including individual and total cation concentrations at each station at four sampling points throughout the year are shown in Table 1(a) for the Tougaku River and Table1(b) for the Takeo River. In this study, the sum of the concentrations of Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} was taken as the total cation concentration. The mean values and standard errors of each physicochemical parameter and cation concentration based on Table1(a) and Table1(b) corresponding to the sampling seasons are shown in Table 2.

4-1-1 pH and EC

The pH in the Tougaku River was higher than 8.0 at all sampling sites while the pH was lower than 7.9 at all sites in the Takeo River. EC values were higher in the Tougaku River than in the Takeo River, except for the sampling conducted in November 2017 (Table 2).

4-1-2 Cation concentrations

In the present study, no Li^+ was detected in any sample. The total cation concentrations in the Tougaku and Takeo rivers fluctuated in the range of 8.457 to 26.602 mg/l and 11.034 to 19.907 mg/l, respectively (Table 1(a) and 1(b)). The total cation concentrations in the Tougaku River were higher when water temperature was lower (November and February; Table 2).

The cation composition by percentage for each season (month) and river is shown in Fig.2. In the Tougaku River, Ca^{2+} accounted for 40% to 50% of the total, and Na^+ accounted for slightly less than 40%, except for in February when it was 41.2 %. Mg^{2+} and K^+ accounted for about 5% of the cation composition, and NH_4^+ was at most 2%. While the cation compositions in the Tougaku River were stable throughout the sampling period, those in the Takeo River were more variable. In the Takeo River, the most dominant cation was Ca^{2+}, which ranged from 50% to more than 60% and the second most dominant cation, Na^+, ranged from 15% to 25%. In the Takeo River, Ca^{2+} was at a maximum in November and a minimum in May, whereas Na^+ was at a maximum in May and a minimum in August. In both the rivers, the third most dominant cation was Mg^{2+}, and Mg^{2+} was two times higher in the Takeo River than in the Tougaku River.

The percentages of K^+ were consistent between the Tougaku and Takeo rivers, ranging from 4% to 6%. The NH_4^+ concentration percentages to total cation concentration were the smallest of all cations in both the rivers, and the percentages of NH_4^+ in the Tougaku River were twice those in the Takeo River.

The relationships between the concentration of Ca^{2+}, which is the most dominant cation in both the rivers, and Na^+, NH_4^+, K^+ and Mg^{2+} are shown in Fig.3. In the Tougaku River, there was a positive correlation between Ca^{2+} and the other cations. In the Takeo River, however, the correlations were negative between Ca^{2+} and the other cations, except for Mg^{2+}, which had a positive correlation.

4-1-3 Overall relationships between cation concentrations and water temperature

Fig.4 shows the relationship between cation concentrations and water temperature for each river. There was a negative correlation for all cations in the Tougaku River; however, there was no obvious correlation for all cations, except for K^+ in the Takeo River (Table 3).

4-2 Statistical analyses
4-2-1 Correlation analyses

The single-correlation coefficients among the measured physicochemical parameters and cation concentrations corresponding to each river are shown in Table 3. There were no significant correlations between cation concentrations and pH in the Tougaku River; however, significant correlations were observed between Mg^{2+}, Ca^{2+} and total cations in the Takeo River.

The relationship between cation concentrations and water temperature was negative and significant for all cations and total cations except for K^+ in the Tougaku River, while K^+ was the only cation to show a positive significant correlation with water temperature in the Takeo River. The relationships between Ca^{2+} concentration and all other cations were all significant in both the rivers. In the Tougaku River, there were significant correlations among all cations and the total cation concentration, and in the Takeo River, there were significant correlations between cations and the total cations, except for Na^+, NH_4^+ and K^+.

4-2-2 Two-way ANOVA

Table4 shows the results of the two-way ANOVA, which was used to compare sampling seasons (February, May, August and November as winter, spring, summer and autumn, respectively) and the streams (Tougaku River and Takeo River), which were regarded as independent variables, against each measurement parameter, which was

Table 3 One-way correlation coefficients between the physicochemical parameters in
a) the Tougaku River and b) the Takeo River.

a) Tougaku River

	pH	EC	℃	Na⁺	NH4⁺	K⁺	Mg²⁺	Ca²⁺	total
pH	1.000								
EC	*0.332	1.000							
℃	-0.296	*0.445	1.000						
Na⁺	0.276	-0.294	**-0.823	1.000					
NH4⁺	-0.192	**-0.668	**-0.652	**0.548	1.000				
K⁺	-0.112	0.032	-0.249	**0.552	0.175	1.000			
Mg²⁺	0.112	-0.126	**-0.621	**0.816	*0.376	**0.718	1.000		
Ca²⁺	0.082	*-0.316	**-0.759	**0.895	**0.552	**0.591	**0.935	1.000	
total	0.157	-0.306	**-0.796	**0.964	**0.567	**0.628	**0.918	**0.978	1.000

b) Takeo River

	pH	EC	℃	Na⁺	NH4⁺	K⁺	Mg²⁺	Ca²⁺	total
pH	1.000								
EC	-0.307	1.000							
℃	-0.200	-0.154	1.000						
Na⁺	-0.044	**-0.519	0.164	1.000					
NH4⁺	-0.026	**-0.715	0.199	**0.612	1.000				
K⁺	-0.082	**-0.621	*0.306	**0.776	**0.857	1.000			
Mg²⁺	**-0.537	**0.847	-0.061	*-0.347	**-0.521	*-0.460	1.000		
Ca²⁺	*-0.399	**0.752	0.018	**-0.564	**-0.523	**-0.53	**0.855	1.000	
total	**-0.534	**0.685	0.085	-0.245	-0.323	-0.267	**0.895	**0.932	1.000

" * " and " ** " indicate statistical significance at $P<0.05$ and $P<0.001$, respectively.

"total" indicates total cation concentration.

Table 4 Results of two-way analysis of variance.

physicochemical parameters	independent variables	n	mean square	F	P
pH	stream	1	41.328	482.195	＜0.0001
	season	3	2.104	24.55	＜0.0001
	interaction	3	1.234	14.403	＜0.0001
	residual error	72	0.086		
EC	stream	1	2833.390	19.098	＜0.0001
	season	3	205.070	1.382	n.s.
	interaction	3	878.408	5.921	＜0.001
	residual error	72	148.363		
temp.	stream	1	77.618	11.792	＜0.001
	season	3	250.900	38.117	＜0.0001
	interaction	3	369.870	56.191	＜0.0001
	residual error	72	6.582		
Na⁺	stream	1	234.736	243.91	＜0.0001
	season	3	25.432	26.426	＜0.0001
	interaction	3	32.894	34.18	＜0.0001
	residual error	72	0.962		
NH₄⁺	stream	1	1.819	84.615	＜0.0001
	season	3	0.045	2.084	n.s.
	interaction	3	0.133	6.2	＜0.001
	residual error	72	0.021		
K⁺	stream	1	0.302	6.74	＜0.05
	season	3	0.079	1.755	n.s.
	interaction	3	0.416	9.275	＜0.0001
	residual error	72	0.045		
Mg²⁺	stream	1	54.111	302.015	＜0.0001
	season	3	1.090	6.085	＜0.001
	interaction	3	1.068	5.959	＜0.001
	residual error	72	0.179		
Ca²⁺	stream	1	48.138	16.866	＜0.0001
	season	3	54.644	19.145	＜0.0001
	interaction	3	34.935	12.24	＜0.0001
	residual error	72	2.854		
total cation	stream	1	8.552	1.352	n.s.
	season	3	158.278	25.025	＜0.0001
	interaction	3	155.393	24.526	＜0.0001
	residual error	72	6.325		

n.s., not significant.

regarded as a dependent variable. Significant differences ($P<0.05$) were observed for stream, except for total cation concentration. Sampling season was a significant independent variable ($P<0.05$) for pH, temperature, Na^+, Mg^{2+}, Ca^{2+} and total cation concentration.
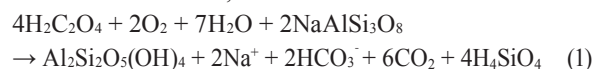
5. Discussion

5-1 Possible sources of Ca^{2+}, M^{2+} and Na^+

Minerals in stream water originate from various sources. For example, Mg^{2+} and Ca^{2+} in streams originate almost entirely from the weathering of sedimentary carbonate rocks, and approximately 90% of K^+ originates from the weathering of silicate materials, especially potassium feldspar and mica[1]. Pollution and atmospheric inputs are minor sources with atmospheric inputs being minimal and pollution contributing only slightly. Based on the results of a leaching experiment in previous studies[9,10,11], biomass contribution to stream water composition, i.e., through leachate from leaf litter, was also pronounced. Although there are numerous methods for determining the origins of the chemical constituents of stream water, differences in composition between stream water and groundwater are due only to the differences in the rate of rock weathering[10].

Based on the general composition of minerals in previous study results, possible sources of cations in the investigated streams were estimated as shown in Table5. In Table5, illite[25] was a secondary mineral formed by silicate mineral weathering and detected in groundwater sampled in the Tenjin River, which is near the Tougaku River.

In the Tougaku River, the ratio of Ca^{2+} and Na^+ was nearly 1:1, showed a significant positive correlation and was constant over the measurement period in the present study. These results suggest that Ca^{2+} and Na^+ originate from the same mineral source. Because kaolinite ($Al_2Si_2O_5(OH)_4$)), which is the secondary mineral formed by silicate mineral weathering, is detected in groundwater sampled in the Tenjin River[25] next to the Tougaku River, it is possible that the sources of Ca^{2+} and Na^+ are silicate minerals, such as Ca-plagioclase feldspar (anorthite) and Na-plagioclase feldspar (albite)[5] in the Tougaku River. Assuming that
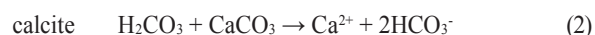
albite ($NaAlSi3O_8$) is attacked by organic acid ($H_2C_2O_4$) and kaolinite is formed, the reaction is as follows[6].

$$4H_2C_2O_4 + 2O_2 + 7H_2O + 2NaAlSi_3O_8$$
$$\rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 6CO_2 + 4H_4SiO_4 \quad (1)$$

Silicate minerals may also be the source of Mg^{2+} as well as the other Mg^{2+}-containing minerals in the Tougaku River.

In the Takeo River, on the other hand, Ca^{2+} concentration was positively correlated only with Mg^{2+} concentration and was negatively correlated with the other cation concentrations. This result indicates that Ca^{2+} and Mg^{2+} may be released from sources of which minerals are common but compositions are not the same.

Ca^{2+} sources consist mainly of carbonate rock containing calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) with small quantities of $CaSO_4$ minerals[5]. The weathering process is much simpler for carbonate minerals than silicate minerals. The overall reaction for calcite and dolomite are described as follows[5].

calcite $\quad H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad$ (2)
dolomite $\quad 2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad$ (3)

Mg-silicate minerals, chiefly amphiboles, pyroxenes, olivine, biotite, as well as dolomite, constitute the main sources of Mg^{2+}. Thus, it is possible that the release of Ca^{2+} from carbonate rock is accompanied by the release of Mg^{2+} in the Takeo River. This hypothesis is supported by the results of the multiple regression analysis in a previous study[19], which showed that the most significant independent variable affecting the Mg^{2+} concentration is the Ca^{2+} concentration in the Takeo River.

Although weathering of Na-containing rocks accounts for most of the Na^+ found in stream water, the constant supply of Na^+ through dissolution of trapped aerosols in rainwater input is thought to originate from ocean water in the Takeo basin, which significantly contributes to the ion supply along the coasts[11]. Thus, it is possible that an appreciable fraction of Na^+ in the stream water arises from silicate contained in the bedrock of the basin in which the study area is located and trapped aerosols in the Takeo River. Sodium in silicate rocks is present mainly as the albite component of plagioclase with $NaAlSi3O8$ formations, which contain no

Table 5 Possible origins of cations in the stream basins.

Mineral	Generalized composition	References
Calcite	$CaCO_3$	5)
Dolomite	$CaMg(CO_3)_2$	5)
Ca-plagioclase feldspar (anorthite)	$CaAlSi_3O_8$	5)
Na-plagioclase feldspar (albite)	$NaAlSi_3O_8$	5)
Olivin	$(Mg,Fe)_2SiO_4$	5)
Proxenes	$Ca(Mg,Fe)Si_2O_6$	5)
Amphiboles	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	5)
K-feldspar	$KAlSi_3O_8$	21)
	(orthoclase and microcline)	
Biotite	$(K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2)$	21)
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	25)
Dissolution of trapped aerosols		10), 11)
Leachate from leaf litter		10), 11), 18), 19)

Cl-, weathering slowly. Since plagioclase is a major source of Na^+ in groundwater, it is also likely to be a major source of Na^+ in stream water[5].

5-2 K^+ release by biological factors

Potassium in stream water comes predominantly (nearly 90%) from the weathering of silicate minerals, particularly potassium feldspar, as orthoclase and microcline ($KAlSi_3O_8$) and mica, and as biotite ($K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$)[21]. However, we showed that plant leaf litter inputs into stream water from the terrestrial ecosystem release K^+ due to leaching in the Takeo River[10,11,14,18], indicating that leaf litter is also one of the major sources of K^+ in stream water.

The results of correlation analysis showed that K^+ concentration in the stream water was significantly positively correlated with Na^+ and NH_4^+ concentrations, while Mg^{2+} and Ca^{2+} concentrations were negatively correlated with K^+ in the Takeo River. Previous studies showed that when leaves from evergreen trees entered the stream water in the Takeo River, stagnation of this biomass in side-pools resulted in a release of K^+ by leaching, the first stage of leaf decomposition[12,13], and a relatively high K^+ concentration was observed in the water. Na^+ originating from trapped aerosols may also be released from leaf litter.

In order for significant leaching to occur, leaves need to remain in one site for a sufficient period of time, which can be affected by factors such as channel morphology and riparian zone area[4]; the hydrological and substrate characteristics along the stream margin[24]; the seasonal patterns of litter fall and the discharge characteristics of the stream[26]; the amount of leaf litter entering a stream[22]; and biotic factors such as shredder density[15-17]. Consequently, leaching is more commonly encountered in side-pools because these sites satisfy the above-mentioned conditions for promoting litter retention.

The stream environments of the Takeo River are characterized by uniform substrates consisting of similarly-sized particles. Formation of side-pools along the stream margins was promoted by the uniform cross-sectional nature of the stream, low current velocity and shallow water depth. Substrates located along the stream margins are also more likely to trap leaves than are the same substrates when located in the main stream channel. The presence of sabo dams combined with interactions between hydrological and substrate characteristics along the stream margin further increase the potential for retention of litter[24]. Given that the increased retention times due to the sabo dams also contribute to creating an environment suitable for colonization by shredder fauna[23], litter decomposition in reaches with sabo dams is likely to be promoted.

The main source of K^+ in the Takeo River is therefore considered to be biological, such as leaf litter. Furthermore, evergreen tree species are dominant in the study area (e.g., *Quercus glauca*), and they constantly release carbon and nitrogen, as well as minerals, into the stream water[12,14]; therefore, NH_4^+ can be considered to be more heavily originated from biological sources such as leaf litter decomposition than mineral release into the Takeo River.

In the Tougaku River, however, stream environments are less well-suited for leaf retention and subsequent mineral release by leaching than are those in the Takeo River because of the non-uniform cross-sectional nature of the stream, relatively high current velocity, relatively deep water depth and less tortuous stream channel. Litter retention and subsequent decomposition in reaches with sabo dams are less promoted in the Tougaku River than in the Takeo River because there are fewer sabo dams in the Tougaku River than in the Takeo River. Furthermore, the K^+ concentration is significantly correlated with the other cation concentrations, except for NH_4^+. Therefore, it is likely that the main sources of K^+ are K-contained minerals, such as K-feldspar, biotite and and/or illite and not biological sources such as leaf litter. The relatively higher NH_4^+ concentrations in the Tougaku River than in the Takeo River were possibly due to biological activity in soils.

5-3 Disagreement with chemical equilibrium reactions of groundwater

In groundwater, rock weathering reactions that produce cations described in equations (1), (2), (3) are accelerated by soil acids that are biologically produced by soil microorganisms. These acids constitute the principal agents of rock weathering[2,3]. Acids supply hydrogen ions that replace cations on the mineral surfaces, thus promoting the breakdown and release of minerals. It is, therefore, mineral production and the subsequent release of cations by rock weathering reactions are seemingly affected by the pH of groundwater. Further, a previous study on stream water and Ca^{2+} concentration showed that Ca^{2+} release increased markedly at higher temperatures and low pH further increased Ca^{2+} release[11].

In the present study, however, no significant correlation between cation concentration and pH of the water was found, and water temperature and cation concentrations, except for K^+, showed a significantly negative correlation in the Tougaku River. The reasons for these many differences between the Tougaku River and the Takeo River include differences in mineral sources, kinetic rates of weathering reactions, microorganisms of the soil and stream water, and initial pH and temperature of background water. Furthermore, previous experiments also showed that Ca^{2+} was released from leaves and rocks at nearly the same rate 90 days after submergence[18], indicating that antecedent rainfall for a relatively long term prior to sampling of the water may affect cation release. Release of cations from bedrock and leaves is thus considered to be promoted through a combination of these factors. Further studies are needed to clarify these relationships.

6. Conclusion

It has been said that minerals in stream water originate from the weathering of bedrock in the basin. However,

the amount of allochthonous material that enters lotic ecosystems annually from terrestrial riparian forests is estimated to be considerable, and substances derived from the decomposition of leaf litter are thought to have an important impact on stream water quality. We have clarified the leaching characteristics of leaf litter of the evergreen species that are dominant in the riparian zone of the investigated stream and examined the influence of leachates on mountain stream water ionic composition by laboratory leaching experiments and field measurements since 2007 [9-19].

These results indicated that the primariy source of ions is rock weathering in the spring and simultaneous ion loading from multiple sources occurs in the riffle, pool and side-pool in the stream and that leaf litter is one of the primary sources of K^+, Mg^{2+} and Ca^{2+} in the stream water. Based on these results, it is also demonstrated that anion and cation concentrations throughout the stream reach are not always uniform due to heterogeneous distribution of ionic material caused by leachate from leaves, although stream water has been regarded as providing a uniform continuous body for the ionic materials, and changes in water composition due to the natural input and subsequent leaching from leaf litter were predicted.

These results also indicated that differences in composition between stream water and groundwater are due only to the ratios of rock weathering. It was revealed statistically that the ion concentrations and physicochemical parameters of the stream water were affected by sampling season or stream environment, or both, and that ion concentrations might be related to each other, affecting physicochemical parameters. Na^+ originates from the weathering of plagioclase in sedimentary silicate rocks and Mg^{2+} and Ca^{2+} originate almost entirely from the weathering of calcite and/or dolomite in sedimentary carbonate rocks in the study area. However, the contribution of biomass to stream water composition through leachate from leaf litter can be pronounced for K^+ concentrations. The findings of the previous studies also demonstrated that anion and cation concentrations in the study area differed significantly among stream environments and seasons, likely due to the heterogeneous distribution of ions resulting from leachate from leaves.

The present analysis conducted in another stream of which the basin overlays the same Paleogene layer in the southern Kyushu Mountains revealed that the cation concentrations and physicochemical parameters of stream water are affected by sampling season and that ion concentrations may be interrelated due to common effects of physicochemical and biological parameters, having similar mineral sources and kinetic rates of weathering reactions, as well as being exposed to similar microorganisms in the soil and stream water, initial pH and temperature of background water.

Minerals in the stream water of the Paleogene layer originate from a variety of sources. Based on the results of this study, it appears likely that Na^+ and Ca^{2+} originate from the weathering of plagioclase in sedimentary silicate rocks in the Tougaku River basin with Ca^{2+} originating almost entirely from the weathering of calcite and/or dolomite in sedimentary carbonate rocks and Na^+ being added from aerosol dust by rainfall as well as Na-plagioclase rock weathering in the Takeo River basin.

In the present study, anions were not analyzed or reported due to a malfunction of the experimental apparatus. In a previous study[19], SO_4^{2-} was detected every month in the Takeo River and sulfide rock weathering was considered to be the primary source of SO_4^{2-} [2-5]. Here, Na^+ and Ca^{2+} concentrations fluctuated in response to the SO_4^{2-} concentration in the Takeo River. While atmospheric gasses and aerosol dust may also contribute to SO_4^{2-} levels in stream water, multiple regression analysis showed that the significant independent parameter affecting SO_4^{2-} concentration was water temperature. Relatively lower pH values in the Takeo River than in the Tougaku River may be caused by SO_4^{2-}. Thus, the main sources of SO_4^{2-} in this study area remain to be identified.

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南九州第三紀層地域の山地渓流におけるカチオンの起源と水質組成に関する比較考察

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渓流水質組成を規定する第一の要因は、流域を構成する基岩の岩種や地質構造等の地質的要因であるといわれてきたが、南九州地域の第三紀層地帯を流れる竹尾川（一ツ瀬川水系;宮崎県）を対象とした5年にわたる追跡調査により、当該流域では、Na^+、Mg^{2+}、Ca^{2+} は基岩風化、特にMg^{2+}、Ca^{2+} はcalcite（$CaCO_3$）もしくは dolomite（$CaMg(CO_3)_2$）の機械的・化学的風化を起源とする可能性が高く、K^+ は河畔域から渓流に供給されるリターの初期分解過程である溶出段階において放出されるK^+ が渓流生態系における重要な供給であり、渓流水中のイオン組成を規定する重要な因子となりうることを明らかにしてきた。これらの既往研究結果を踏まえ、本研究は南九州地域の第三紀層地帯を流れる渓流水質組成への理解をさらに深めることを目的として、竹尾川近隣の東岳川（大淀川水系;宮崎県）を新たな対象渓流に加えて、渓流水におけるカチオンの組成と起源について比較考察を行った。

両渓流の対象区間（区間長約1.km）に設定した各10地点の瀬（riffle）で水質サンプルを採取し、水温、電気伝導度（EC）、pH、カチオン(Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+})濃度を測定した。採水および測定は、2017年2、5、8、11月に行った。

本研究では、水温、pH、およびHN_4^+、K^+を除くカチオン濃度において、渓流間、および採水時期で、有意な違いが認められ（$P<0.05$）、pHは東岳川で8～9、竹尾川で7～8であった。東岳川ではCa^{2+}とNa^+が総カチオン濃度の8割以上を占め、且つ、その割合はほぼ1:1であり、各カチオン濃度の占有率は観測期間中はほぼ一定であった。また、Ca^{2+}濃度と他のカチオン濃度との間には、有意な正の相関関係が認められた（$P<0.05$）。これに対して竹尾川ではCa^{2+}とNa^+が総カチオン濃度のそれぞれ50~60%、18~26%を占め、各カチオン濃度の占有率には季節変化が認められ、Ca^{2+}濃度と正の相関関係が認められたのはMg^{2+}のみで他のカチオンとは負の相関関係が認められた（$P<0.05$）。東岳川ではリター滞留が促進されない環境下にあるため、リター起源とするK^+が占める割合は少ないと推測された。さらに東岳川では、K^+を除くカチオン濃度が水温と有意な負の相関関係が認められた反面、竹尾川では水温と有意な相関関係が認められたのはK^+だけであった（$P<0.05$）。

これらの結果から、同じ第三紀層地帯を流れる近隣の渓流であっても,カチオンの起源並びにカチオン生成時のバックグラウンド水質や生物作用の違いにより、渓流水のカチオン組成が異なることが推測された。