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Experimental study on leaching characteristics of cations from evergreen leaves submerged in water

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Approximately 30 fresh fallen leaves and 30 older fallen leaves of *Castanopsis* and *Quercus glauca* were collected from six riparian zone sample sites located approximately 10 km apart and spanning the full length of the river in May and November 2008 and in May 2009. The leaves were washed thoroughly with distilled water, and oven-dried at 80°C for 12 hours. Five fresh fallen leaves and five older fallen leaves of each species were selected at random and weighed. To clarify the influence of water temperature on the rate of cation leaching, each subsample was placed into a beaker filled with 1000 ml of distilled water and allowed to stand for 30 days in the laboratory at ambient temperature and constant temperatures of 10, 18 and 25°C. Furthemore subsamples were allowed to stand for 30 days at 10 and 25°C with regulating pH between 3 to 4 by the addition of 2 mol/l methanesulfonic acid for estimating the influence of lower pH of water on the rate of cation leaching. The electric conductivity (EC) and hydrogen ion concentration (pH) were measured at day 1 and every 5 days after submersion, and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, $Ca^{2+}$and Mg^{2+}) in the water were measured at 30 days after submersion.

The tough outer surfaces of evergreen leaves (e.g. cuticle) delays leaching and subsequent weight loss in leaves and lower pH and relatively high temperatures have a very marked effect on the breakdown of cutin, promoting leaching. K^+ was the most dominant cation under ambient conditions and rapidly leached from the leaves of both tree species under ambient conditions during the experiment independently of temperature and pH. The release rates of Ca^{2+} were accelerated markedly at higher temperatures without pH regulation and that a relatively lower pH increased Ca^{2+} release further.

Key words: leaching characteristics, cations, evergreen leaves, pH, calcium ion.

1. INTRODUCTION

Allochthonous material, such as leaves, twigs and other plant material, entering small streams represents the primary energy source available to the consumers in these systems. It has been demonstrated that this organic matter is retained within streams where it is decomposed by a variety of physical, chemical and biological processes[1]. The instream processing of this organic material induces the production of dissolved organic matter (DOM)[5, 23], nutrients[2, 24] and other substances. Given that the amount of allochthonous material that enters lotic ecosystems annually from terrestrial riparian forests is estimated to be considerable[6], substances derived from the decomposition of leaf litter are thought to have an important effect on stream water quality. Pioneering studies[12, 25, 27, 28] suggest that different tree species have markedly different effects on the chemical characteristics of streams through leaf litter leachates. While numerous subsequent studies have focused on the physical degradation of leaf litter[4, 11, 12, 19, 21] or on the chemical changes associated with leaf litter degradation in streams[5, 15, 17, 20, 25], few studies have examined the effects of materials leaching from leaf litter on stream water quality.

In some of these studies, a detailed understanding of the breakdown processes of forest leaves that enter streams has been obtained. However, except for phosphate and nitrogen, relatively little is known of the dynamics of leachates, particularly the ionic elements. The purpose of the present study is therefore to clarify the leaching characteristics of cations from the leaf litter of the evergreen species that are dominant in the riparian zone of a temperate stream in Japan.

2. SITE DESCRIPTION

The leaf litter of the evergreen species used in the experiments was collected in the Hitotsuse River in Saito City of Miyazaki Prefecture (Fig.1). The Hitotsuse River has its origins in the southern Kyusyu Mountains, and the river basin overlays the Miyazaki Formation, which consists of black slate, sandstone and shale and was formed in the Cretaceous to middle Paleogene periods.

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The geologic structure of the river basin is therefore characterized as being weak with a prevalence of extensively folded rock strata with numerous faults and is susceptible to weathering. The combination of these geological characteristics means that the slopes of the basin are steep and unstable and several mid-sized landslides have occurred in the last past fifty years[15].

The vegetation of the basin consists of evergreen tree species, such as *Quercus glauca*, *Castanopsis*, *Quercus myrsinaefolia* and *Cinnamomum japonicum*, broad leaved deciduous trees, such as *Meiosma tenuis*, *Aucuba japonica* Thunb. and *Actinidia polygama*, and evergreen conifers, such as *Cryptomeria japonica* and *Chamaecyparis obtusa* Sieb. et Zucc.

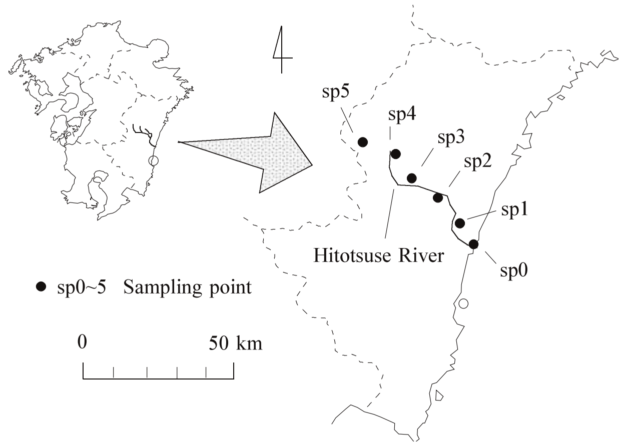

Fig. 1. Stream reach investigated and sampling sites.

3. METHODS

3-1. Materials

The leaves of *Quercus glauca* and *Castanopsis*, both of which are common in the riparian zone of the Hitotsuse River basin and make a substantial contribution toward annual litter fall, were used in the leaching tests. Leaves from each tree species were collected from six riparian zone sample sites located approximately 10 km apart and spanning the full length of the Hitotsuse River (refer to Fig.1), because the constant supply of Na^+ through rainwater input is thought to originate from sea water in the watershed and contributes significantly to the ion supply near the coasts[1], influencing the leaching characteristics of the leaves.

Approximately 30 fresh fallen leaves and 30 older fallen leaves of each tree species were collected from the stream bank at each sample site. Freshly fallen leaves retain their original shape and color without any skeletonization because of the relatively short time that has elapsed after falling. Similarly, older fallen leaves also retain their original shape without any skeletonization and appear brown in color. Leaves from these evergreen species were collected in May and November 2008 and in May 2009, with the laboratory experiments conducted shortly after the leaves were collected.

3-2. Laboratory leaching experiments

3-2-1. Experiments in 2008

In addition to nutrients taken up from soils, plant leaves also contain nutrients derived from aerosols that adhere to the trees as tree-trapped dust[7]. Since this matter remains on the leaves even after the leaves have fallen, the rate of leaching from leaves varies. In addition, the cation components that are leached from leaves appear to be attributed to the composition of this tree-trapped matter. To estimate the overall characteristics of cation leaching from the evergreen leaves under ambient temperatures, the leaves were washed thoroughly with distilled water to remove aerosol dust and atmospheric gases[7], air-dried for one week, and oven-dried at 80˚C for 12 hours. Five fresh fallen leaves and five older fallen leaves of each species were selected at random and weighed. Each subsample was placed into a beaker filled with 1000 ml of distilled water for the comparison of the experimentar values with the previous results[16, 18] and allowed to stand for 30 days in the laboratory at ambient temperature. The electric conductivity (EC) and hydrogen ion concentration (pH) were measured using a water quality probe (WQC-20A, TOA Electronics Ltd., Japan) at day 1 and every 5 days after submersion, and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) in the water were measured using ion chromatography (DX-120, Nippon Dionex K.K., Japan) at 30 days after submersion.

3-2-2. Experiments in 2009

1) Effect of temperature on cation leaching

To clarify the influence of water temperature on the rate of cation leaching, subsamples were prepared using the same methods for the leaching experiments conducted in 2008 described above. As before, each subsample was placed into a beaker filled with 1000 ml of distilled water, however, each beaker was then incubated at temperatures of 10, 18 and 25˚C in the chambers for 30 days. The EC and pH were measured at day 1 and every 5 days after leaf submersion, and the concentrations of cations in the water after 30 days were measured. The leaves in each subsample were then oven-dried at 80˚C for 12 hours and weighed. These experiments were conducted in May in 2009.

2) Effect of lower pH on cation leaching

To clarify the influence of lower pH of water on the rate of cation leaching, the following experiments were conducted. Leaf samples were prepared using the same methods described above. As before, subsamples were placed into a beaker filled with 1000 ml of distilled water and allowed to stand for 30 days at 10 and 25˚C. The pH of 3 to 4, which was the lowest value of precipitation of the basin measured in our preliminary survey, was obtained by the addition of 2 mol/l methanesulfonic acid, which does not interfere with the ion chromatography mass spectrometry used in the present study. The EC and pH were measured at day 1 and every 5 days after leaf submersion, and the concentrations of cations in the water after 30 days were measured. The leaves in each subsample were then oven-dried at 80˚C for 12 hours and weighed. These experiments were conducted in May in 2009.

4. RESULTS

4-1. Changes in EC and pH values at ambient temperatures

The water temperature during the experimental period fluctuated from 18 to 28˚C in May and from 8 to 18˚C in November. In 2008, the pH and EC of the distilled water

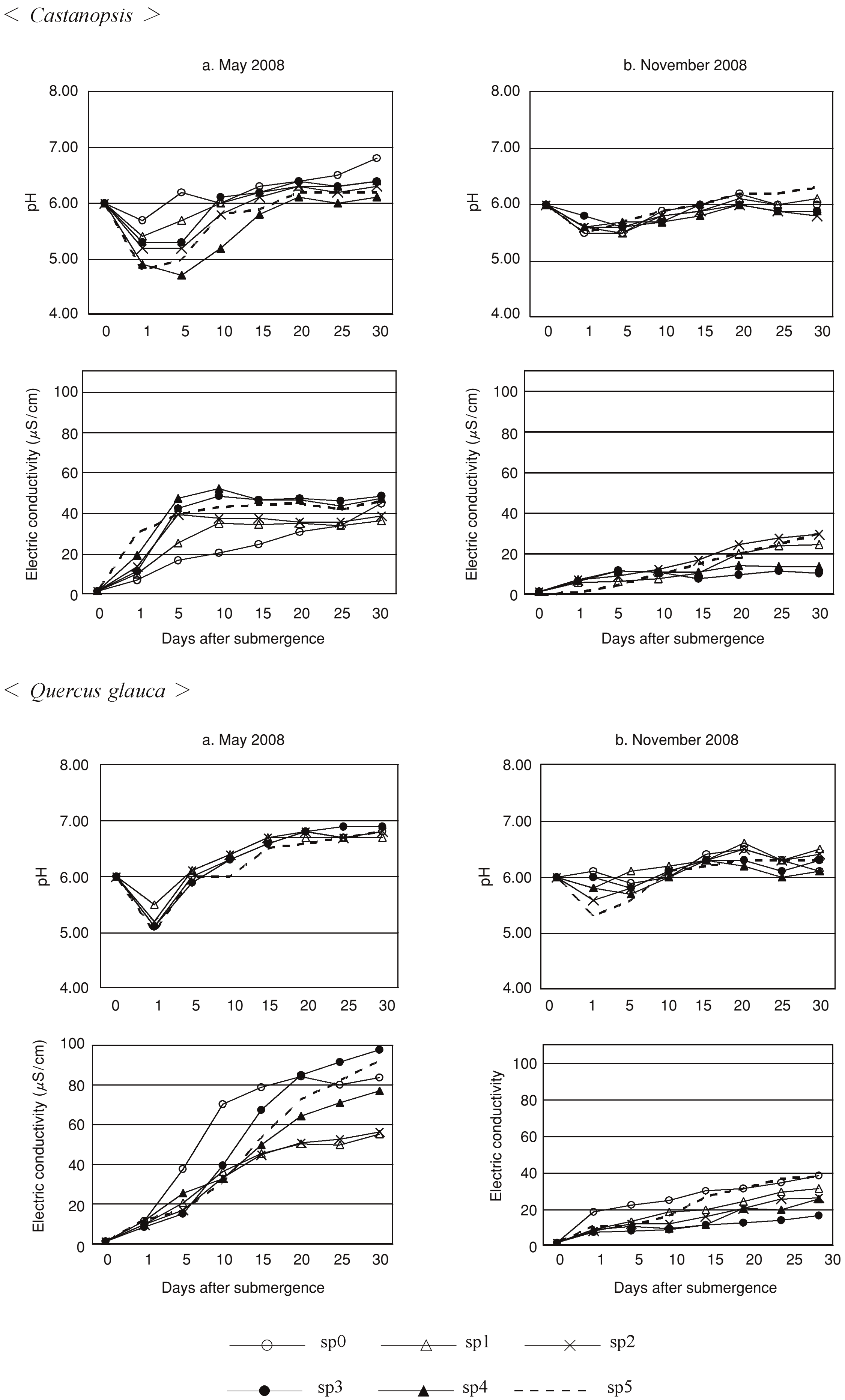

Fig. 2. Change in pH and EC of water containing submerged leaves in the measurement in 2008.

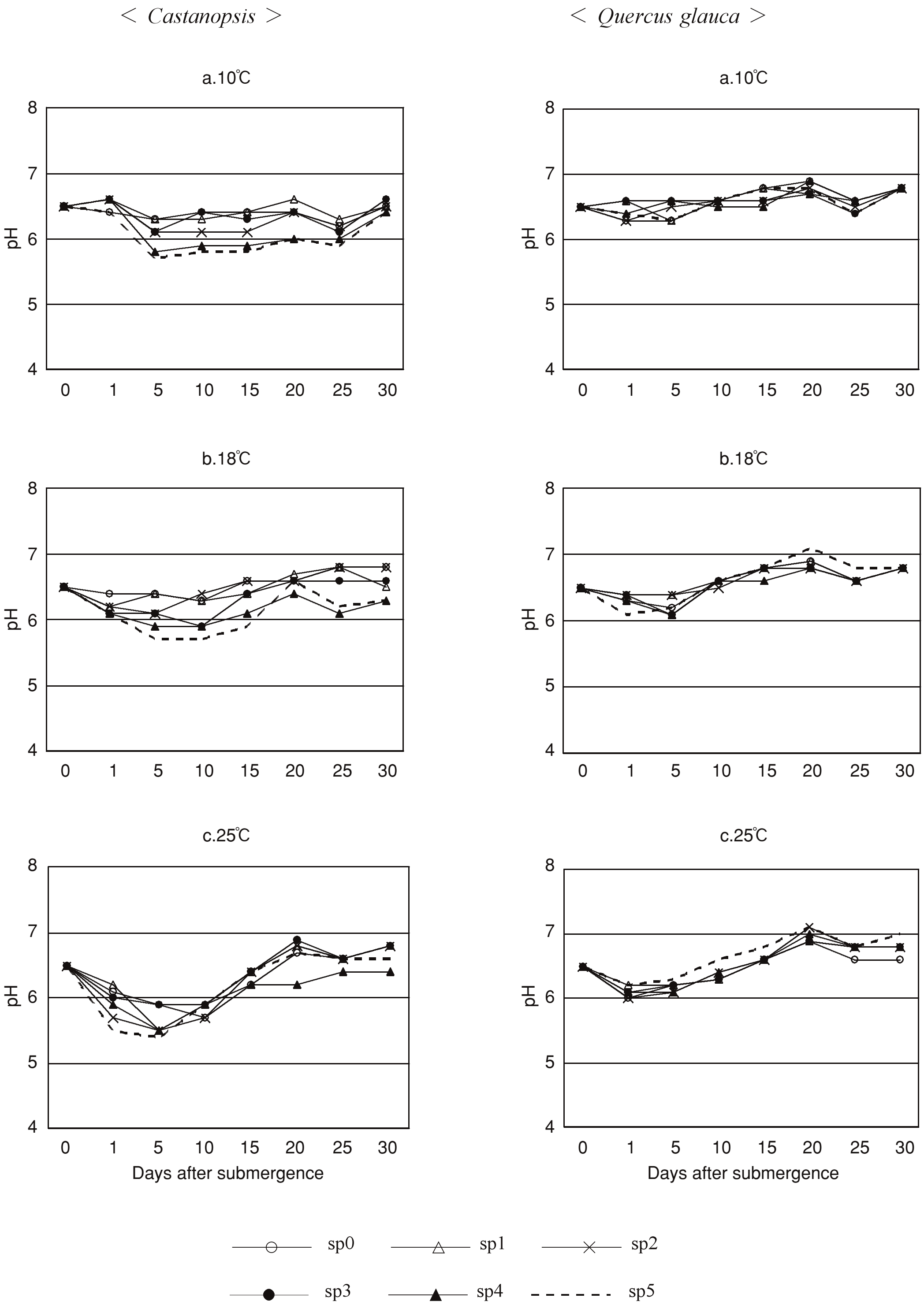

Fig. 3-1. Change in pH of water containing submerged leaves in the measurement in 2009.

in which the sub-samples were submerged varied with time as shown in Fig.2. The initial EC and pH of distilled water were 2.0 μS/cm and 6.0, respectively.

4-1-1. pH

A rapid decrease in the initial pH one day after submersion due to leaching was followed by a gradual increase in pH in all water samples for 15 days where after the pH remained roughly constant. The pH values ranged from 4.8 to 6.9 in May and from 5.4 to 6.8 in November. There were no marked differences in the pH fluctuation between water samples during the experiment period except for in *Castanopsis* in May. The mean pH values of *Castanopsis* and *Quercus glauca* after 30 days were 6.37 and 6.08 in May, and 6.8 and 6.28 in November, respectively, indicating that the mean pH values in May were slightly larger than those in November in both evergreen species.

4-1-2. EC

The EC increased with time in all water samples with

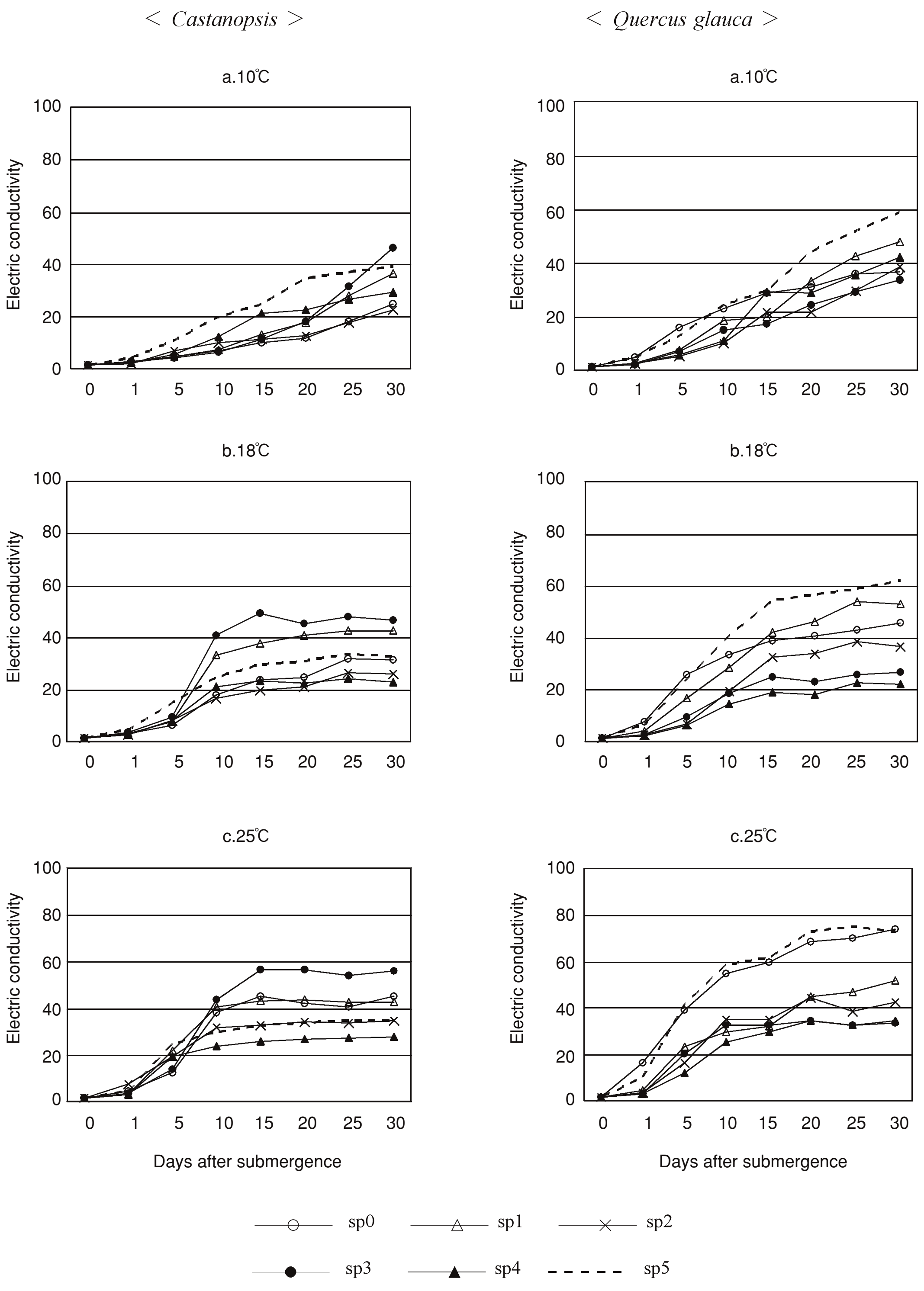

Fig. 3-2. Change in EC of water containing submerged leaves in the measurement in 2009.

obvious differences among the measurements observed after 5 days. In May, although EC increased in the water samples of both species within the first 10~15 days, it was generally constant in *Castanopsis* and higher in *Quercus glauca* after the 15th day. On the other hand, the EC increased slightly in both species during the measurement period in November. The differences between water samples were relatively more marked in May. The mean EC values after 30 days in *Castanopsis* and *Quercus glauca* were 41.84 and 11.89 μS/cm, and 51.76 and 24.37 μS/cm, in May and November, respectively. Based on these mean values, the increase in EC attributed to leaching from submerged leaves tended to be higher in *Quercus glauca* than in *Castanopsis*, and in May (warm period) than in November (cold period).

4-2. Changes in EC and pH values at constant temperatures

The pH and EC of distilled water at constant temperatures in 2009 varied over time as shown in Fig.3-1, 3-2.

Table 1. Overall comparison of cation concentrations leached from the leaves submerged in distilled water after 30days and experimental conditions on which the experiments were conducted

Experimental time		Experimental conditions		cations (mg/l)					Species
year	month	temperature (℃)	pH control	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
2008	May	ambient	-	1.137 ± 0.163	3.744 ± 2.195	3.042 ± 0.238	2.806 ± 0.357	2.982 ± 0.470	*Castanopsis*
	November	ambient	-	0.147 ± 0.031	0.444 ± 0.144	3.218 ± 0.654	0.046 ± 0.027	0.000 ± 0.000	
	May	ambient	-	0.595 ± 0.339	2.027 ± 0.735	2.262 ± 0.075	1.223 ± 0.312	0.575 ± 0.171	*Quercus glauca*
	November	ambient	-	0.137 ± 0.041	0.022 ± 0.009	1.350 ± 0.174	0.027 ± 0.018	0.000 ± 0.000	
2009	May	10	-	0.167 ± 0.043	0.235 ± 0.058	6.862 ± 0.993	0.238 ± 0.065	0.021 ± 0.015	*Castanopsis*
		18	-	0.502 ± 0.100	0.454 ± 0.075	6.587 ± 0.381	0.584 ± 0.056	0.144 ± 0.015	
		25	-	0.196 ± 0.059	0.452 ± 0.051	6.896 ± 0.656	0.659 ± 0.065	0.191 ± 0.023	
		10	3.0—4.0	0.411 ± 0.068	0.152 ± 0.061	8.715 ± 1.131	0.962 ± 0.208	0.490 ± 0.232	
		25	3.0—4.0	0.514 ± 0.090	0.247 ± 0.047	8.745 ± 0.626	2.129 ± 0.115	3.184 ± 0.316	
	May	10	-	0.104 ± 0.043	0.213 ± 0.062	5.212 ± 0.701	0.230 ± 0.026	0.032 ± 0.015	*Quercus glauca*
		18	-	0.236 ± 0.057	0.302 ± 0.047	4.889 ± 0.619	0.315 ± 0.035	0.100 ± 0.013	
		25	-	0.137 ± 0.050	0.208 ± 0.043	4.460 ± 0.557	0.498 ± 0.074	0.288 ± 0.055	
		10	3.0—4.0	0.250 ± 0.030	0.128 ± 0.067	9.456 ± 1.330	1.373 ± 0.205	0.707 ± 0.154	
		25	3.0—4.0	0.255 ± 0.037	0.176 ± 0.039	6.851 ± 0.660	1.381 ± 0.091	4.522 ± 0.858	

Concentrations are given per 1g of leaf. mean ± standard error

The initial EC and pH of distilled water were 1.5 μS/cm and 6.5 on 10.0℃, respectively. During each measurement period, the water temperatures were maintained exactly the same at 10, 18 and 25℃.

4-2-1. pH

After an initial rapid decrease one day after submersion, the pH gradually increased from 6.0 to 7.0 over time, returning to the initial pH during the experimental period at each constant temperature. Compared to the results in 2008, the initial decrease in pH was less notable. While no marked changes in pH were observed in water samples of *Quercus glauca* at different temperatures, the pH of water samples containing *Castanopsis* leaves ranged from 5.5 to 7.0 at 25℃. The mean pH values of *Castanopsis* water samples after 30 days were 6.48, 6.55 and 6.70 at 10, 18 and 25℃, respectively, and those in *Quercus glauca* were 6.80 at all temperatures, indicating that there were no marked differences in mean pH levels among measurement temperatures and tree species. Comparison of the experimental results with those obtained in 2008 indicated that the pH of the water was slightly higher at constant temperature than under ambient temperature.

4-2-2. EC

The EC increased considerably over the first 15 days, after which it increased slightly or remained constant at 18 and 25℃; gradual increases were observed throughout the experimental period in both tree species at 10℃. These fluctuations in EC during the experimental period are analogous to those obtained in May and November in 2008 when the mean temperatures during experimental period were approximately 25 and 10℃, respectively. The differences in EC observed in all water samples increased over time in all water samples. The mean water EC values after 30 days of leaf submergence in *Cas stanopsis* and *Quercus glauca* were 33.2, 33.9 and 40.3 μS/cm, and 43.2, 41.3 and 51.7 μS/cm under 10, 18 and 25℃, respectively, indicating that mean EC values tend to increase at higher temperature and are species-specific, being higher in *Quercus glauca* than in *Castanopsis*.

4-3. General description of the results at constant temperatures and controlled pH

Water pH values ranged between 3 and 4 in response to the addition of methanesulfonic acid after every measurement, resulting in continual increases of EC in water during the experiment. The mean EC values of water after 30 days submergence of leaves was 500 to 600 μS/cm in all water samples, independent of water temperature.

Taken together, these results indicate that in the absence of pH regulation, the pH fluctuates widely at higher temperatures during the experimental period; however, there is no marked difference in the mean pH values on the 30th day among the samples. The EC on the 30th day of after leaf submergence is relatively high at higher temperature in the same tree species.

4-4. Cation release

Table 1 shows the concentrations of cations leached from the submerged leaves in distilled water after 30 days under ambient temperature and at constant temperatures in May and November in 2008 and in May in 2009, respectively. In the table, concentrations are given per 1 g of leaf.

4-4-1. Cation concentrations under ambient temperatures

The ions detected in all samples during the experiment period were Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. The leached cation concentrations were higher in May than in November, and higher in *Castanopsis* compared to *Quercus glauca*. No Ca^{2+} was leached from the leaves of both tree species in November. The cations concentrations in leachate

Table 2. Overall comparison of weight loss rate of leaves corresponding to experimental conditions and tree species

Experimental conditions		Smple no.	*Castanopsis*				*Quercus glauca*			
			Weight of leaves (g)		Weight loss rate		Weight of leaves (g)		Weight loss rate	
temperature (℃)	pH controlling		before submergence a	30 days after submergence b	(a-b)/a	mean	before submergence a	30 days after submergence b	(a-b)/a	mean
10	-	1	1.42	1.15	0.19	0.21	1.62	1.34	0.17	0.14
		2	1.51	1.25	0.17		2.91	2.51	0.14	
		3	1.07	0.88	0.18		2.36	2.08	0.12	
		4	1.36	1.15	0.15		1.59	1.47	0.08	
		5	1.15	0.87	0.24		1.99	1.60	0.20	
		6	1.00	0.69	0.31		2.01	1.67	0.17	
18	-	1	1.21	0.94	0.22	0.31	1.53	1.21	0.21	0.18
		2	1.61	1.08	0.33		2.91	2.44	0.16	
		3	1.12	0.82	0.27		2.42	2.00	0.17	
		4	1.62	1.12	0.31		1.60	1.34	0.16	
		5	1.13	0.72	0.36		1.53	1.28	0.16	
		6	1.05	0.64	0.39		2.45	1.94	0.21	
25	-	1	1.55	1.05	0.32	0.36	2.50	1.97	0.21	0.22
		2	1.47	0.87	0.41		2.86	2.28	0.20	
		3	1.28	0.81	0.37		2.77	2.28	0.18	
		4	1.55	1.09	0.30		1.82	1.38	0.24	
		5	1.05	0.68	0.35		1.75	1.58	0.10	
		6	1.02	0.62	0.39		2.95	1.74	0.41	
10	3—4	1	1.48	1.24	0.16	0.20	1.45	1.22	0.16	0.19
		2	1.62	1.30	0.20		2.78	2.25	0.19	
		3	1.11	0.93	0.16		2.55	2.12	0.17	
		4	1.52	1.28	0.16		1.11	0.85	0.23	
		5	1.16	0.94	0.19		1.76	1.42	0.19	
		6	1.02	0.66	0.35		2.28	1.82	0.20	
25	3—4	1	1.34	0.91	0.32	0.31	1.77	1.31	0.26	0.22
		2	1.48	1.07	0.28		2.32	1.84	0.21	
		3	1.19	0.87	0.27		2.42	2.05	0.15	
		4	1.30	0.88	0.32		1.63	1.18	0.28	
		5	1.01	0.69	0.32		1.40	1.10	0.21	
		6	0.93	0.58	0.38		2.34	1.82	0.22	

after 30 days were $NH_4^+ > K^+ > Ca^{2+} > Mg^2 > Na^+$ and $K^+ > NH_4^+ > Mg^2 > Na^+ > Ca^{2+}$ in May 2008, and $K^+ > NH_4^+ > Na^+ > Mg^2 > Ca^{2+}$ and $K^+ > Na^+ > Mg^2 > NH_4^+ > Ca^{2+}$ in November 2008 in *Castanopsis* and *Quercus glauca*, respectively. K^+ was the most abundantly leached cation in the present study, which corroborated the findings of our studies[16, 18].

4-4-2. Cation concentrations at controlled temperatures

The ions detected in all samples during the experimental period were Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, with K^+ being the most abundantly leached cation as the measurements in 2008. With the exception of Ca^{2+} at 10 and 25˚C, the leached cation concentrations were higher in *Castanopsis* than in *Quercus glauca*. The concentrations of Mg^2 and Ca^{2+} increased with temperature, while those of NH_4^+ and Na^+ were highest at 18˚C in both tree species, and the concentration of K^+ in *Quercus glauca* was highest at 10˚C. The concentration of cations after 30 days was $K^+ > Mg^2 > NH_4^+ > Na^+ > Ca^{2+}$ at 10 and 25˚C in *Castanopsis* and at 10 and 18˚C in *Quercus glauca*.

4-4-3. Cation concentrations at pH controlled be-tween 3 and 4

Except for K^+ in *Quercus glauca*, the concentrations of cations in distilled water increased at 25˚C in both tree species. Particularly, Ca^{2+} and Mg^2 concentrations increased remarkably in both tree species. The rate of increase in cation concentration between at 10˚C and at 25˚C was highest in Ca^{2+}. The concentrations of leached cations after 30 days in both tree species were $K^+ > Mg^2 > Ca^{2+} > Na^+ > NH_4^+$ and $K^+ > Ca^{2+} > Mg^2 > Na^+ > NH_4^+$, at 10 and 25˚C, respectively, indicating that Mg^2 and Ca^{2+} release was higher at elevated temperatures.

4-4-4. Weight loss rate in leaves during experiment

Table 2 shows the weight loss rates of leaves submerged in distilled water in 2009. Weight loss was calculated by subtracting the weight of the leaves before submergence from the weight 30 days after submergence. No fragmentation of leaves occurred because microbe and invertebrate activity was removed in the tests.

A significant difference was observed in the mean weight loss rate for the three temperatures in both tree species (*Castanopsis*; $p<0.001$, *Quercus glauca*; $p<0.01$) incubated without controlling pH (Table 2). Comparison of mean weight loss rates for leaves incubated at set temperatures with and without pH-control in both tree species, however, revealed that the mean weight loss rates in the pH controlled samples were same or slightly lower than those without pH control, except for the *Quercus glauca* samples at 10˚C. Therefore, it is possible that lower pH may inhibit weight loss in leaves submerged underwater.

5. DISCUSSION

5-1. The initial stage of leaching of evergreen leaves

In the present study, physicochemical parameters, such as EC and pH, exhibited interesting fluctuations after immersion of the evergreen *Castanopsis* and *Quercus glauca* leaves in distilled water. The EC continued to increase in all samples for 15 to 30 days and pH values increased following the rapid decrease immediately after submergence. The rates of weight loss in leaves increased under higher incubation temperatures during experiments. These fluctuations in pH and EC, as well as weight loss, could be attributed to the leaching of some components from the leaves.

Generally, the new leaf litter that enters stream water undergoes leaching. Depending upon the species, leaves may release from 5 to 30% of its organic dry weight within 24 hours as dissolved organic matter[1, 23], particularly in the dissolved organic matter (DOM) from broad leaved deciduous leaves, such as maple, elm, yellow birch *Betula alleghaniensis* and beech *Fagus grandifolia*[13]. In the evergreen leaves used in the present study, the weight loss rates, however, ranged from 14 to 36% over 30 days. Based on the increase observed in EC[18], the weight losses of leaves are considered to occur over this period. It is possible that the tough outer surfaces of evergreen leaves (e.g. cuticle) delays leaching and subsequent weight loss in leaves because the outer layer of the epidermis, which consists of cutin, undergoes changes at high temperatures. This factor is of greater consequence in leaching of evergreen leaf litter than in that of deciduous leaf litter.

Since EC and cation concentrations increased more rapidly at relatively high temperatures, temperature is considered to have a marked effect on the breakdown of cutin. The rapid fluctuation observed in pH immediately after submergence may be due to the materials derived from cutin being degraded.

5-2. Cation release characteristics

Table 1 shows the change in cation concentrations associated with their release. The rough release rates of cations from the evergreen leaves under ambient temperature in the experiment conducted in 2008, except for NH_4^+, was $K^+ > Na^+ > Mg^{2+} > Ca^{2+}$, which corroborated the experimental results of previous studies[2, 10, 21]. Under the constant temperatures in 2009, however, the release rate of cations was $K^+ > Mg^{2+} > NH_4^+ > Na^+ > Ca^{2+}$. Furthermore, except for K^+, the amount of cations released in May in 2008 was considerably high except when pH was maintained at 3.0 ~ 4.0. It is possible that the differences in the release rate of cations between the measurements taken in 2008 and 2009 are due to the experimental conditions under which the experiments were conducted, such as ambient temperature and constant temperature, as well as phytochemical differences among leaves and between tree species, as described below.

The most dominant cation in all the water samples was K^+. K^+ rapidly leached from the leaves of both tree species during the experiment, accounting for more than 70% of all cations in most samples in which pH was not regulated. K^+ release was independent of temperature and water pH in the present experiments. In addition, K^+ is usually prevalent in most plant tissues and the results corroborate those of previous experiments[2, 10, 21]. However, the K^+ concentrations in natural stream water were considerably lower than the levels of the other major cations[18]. The lower K^+ concentrations may have been observed because K^+ utilization is increased during plant and animal growing seasons as it is indispensable to plant and animal growth. The lower concentration of K^+ in the stream water during the growing season may therefore suggest that there is a differential utilization of K^+ by the biota.

The concentrations of Na^+ were highest at 18°C in both species, with levels appearing to be independent of temperature. Although weathering of NaCl-containing rocks accounts for most of the Na^+ found in river water, the constant supply of Na^+ through rainwater input is thought to originate from the ocean water in the basin which contributes significantly to the ion supply along the coasts[1].

Rates of organic degradation and leaching are generally considered to be faster at warmer temperatures[11]. However, the concentrations of NH_4^+ and Na^+ in this study were highest at 18°C in both tree species, and the concentration of K^+ in *Quercus glauca* water samples was highest at 10°C, showing no clear relationship between temperature and cation release. Further experiments are therefore required to assess the effect of temperature on cation release from leaves submerged in water.

Ca^{2+} is known not to leach as readily as K^+[22]. The experimental results from 2009 indicated that the release rates of Ca^{2+} were accelerated markedly at higher temperatures without pH regulation and that a relatively lower pH increased Ca^{2+} release further. Ca^{2+} release from leaves is promoted through a combination of factors: Ca^{2+} increases in the leaves throughout the growing season and is retained in the leaf until major structural breakdown of the leaf occurs[21]. Also, because Ca^{2+} occurs as an exchangeable form which is highly mobile and is readily replaced by H^+, Ca^{2+} can readily be leached from the surface organic layers[29]. Further, release may be promoted by the relatively lower pH which would degrade the outer layer of leaves. When these factors are considered together, lower pH and relatively high temperatures have a very marked effect on the breakdown of cutin, promoting leaching. These release characteristics would also apply to Mg^{2+}.

Leaf breakdown is slower at low pHs in lakes, streams, and wetlands[29]. The reason for this would be because low pH inhibits the activities of microbial organisms and invertebrates, retarding subsequent leaf breakdown. While the release of cations was promoted at high temperatures in the same pH range, weight loss rate was inhibited at lower pH in the present study. Thus, many complex interactions exist between leaf breakdown and cation release. Although litter breakdown is also known to occur faster in hardwater streams compared with softwater streams[9], the extent to which the hardness of the water influences the rate of breakdown is unknown. For instance, the dry weight loss of plant detritus in streams with the highest Ca^{2+} concentration proceeded more than three times faster than in streams with the lowest Ca^{2+} concentration[8]. Therefore, the leaching of cations from leaves, in itself, may dominate the leaching characteristics of cations in streams.

However, the measurements in the present study were observed to vary slightly. This may be because the nutrient content of litter varies due to a natural variation in nutrient concentrations of plant tissue and changes in the type and timing of litter fall[20], and also because leaf chemical composition is not uniform between the leaves of the same species. The experimental results of the present study could therefore be influenced by phytochemical differences among leaves and variability of nutrient contents between sites and between different tree species.

6. CONCLUSIONS

The present study was conducted under abiotic conditions. The leaching in streams is complex, and microorganisms are critical mediators of these complex interactions. Animals and microbes, however, have little influence on leaching rates during the first week[1], although they likely influence subsequent weight losses due to leaching during later stages of decay in a natural stream.

Although attention has previously focused on the loss of soluble carbohydrates and polyphenols during leaching[26], the present study clarified that cations are also leached from leaves during submergence of the leaves. In the leaves of evergreen tree species, such as *Castanopsis* and *Quercus glauca*, the outer cutin layer would increase the period over which leaching occurred, extending the term to more than 15 days after submergence. Our results also showed that, in addition to temperature, pH is the primary environmental variable affecting the leaching of cations from leaves, with both of these variables having a very marked effect on the breakdown of cutin and subsequent release of Ca^{2+} and Mg^{2+}.

Minerals in stream water originate from a variety of 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]. Although pollution and atmospheric inputs can also act as sources of minerals, their contribution is considered to be minimal. However, the findings of this study also demonstrated the pronounced effect of biomass on stream water composition, and changes in water composition due to the natural input and subsequent leaching from leaf litter is considered likely. In addition, the possible alteration of K^+, Mg^{2+} and Ca^{2+} concentrations in stream water due to leachate from leaf litter during litter decomposition in the stream is supported by previous studies[3, 10, 14, 18]. Accurate knowledge for the leaching cations in natural streams is therefore required for understanding the ionic composition of stream water.

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常緑広葉樹リーフリターの陽イオン溶出特性に関する実験的考察

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要　約

河畔域から渓流に供給されるリターは膨大な量にのぼると推測され，リターからの溶出物は渓流水質の形成に重要な役割を果たすものと思われるが，溶存態イオンの常緑樹リターからの溶出特性については不明な点が多く残されている．そこで本研究は，おもに室内実験により，南九州地域の山地渓流河畔域に広く生育するシイ（*Castanopsis*）とアラカシ（*Quercus glauca*）の落葉からの陽イオン溶出特性の概要を明らかにし，それが渓流水質の形成に及ぼす影響を類推することを目的として行った．

宮崎県中央部を東流する一ツ瀬川河畔域を対象に河口から約10㎞間隔で6箇所の採取地点を設定し，そこに生育するシイとアラカシの落葉（落葉直後のものと落葉後数日を経たもの）を30枚ずつ採取し，十分な洗浄と乾燥の後，各5枚ずつ1000mlの蒸留水中に投入し，①自然状態，②水温を10，18，25℃に維持した状態，③水温を10，25℃に維持しメタンスルフォン酸の滴下によりｐＨを3～4に調整した状態，にそれぞれ30日間置いた．投入から1日後および5日間隔で30日後まで水中の電気伝導度（EC）とpHを測定した．さらに投入から30日後に陽イオン（Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}）濃度を測定した．実験は2008年5，11月，2009年5月に行った．

その結果，常緑樹ではクチン質表皮が分解に伴うイオン溶出と重量損失を遅らせ，相対的に高い水温と低いpHがクチン質の分解とその後の溶出促進に大きく影響していることが推測された．さらに陽イオンのなかでは，自然状態ではK^+が温度やpHへの依存性が低くもっとも溶出されやすいのに対し，水温を一定にした状態ではCa^{2+}が溶出されやすくその度合いは水温が高いほど促進され，さらに相対的に低いpHが温度以上にCa^{2+}の溶出を促進する因子であることが解った．Mg^{2+}もこれに準じた溶出特性を示した．

以上の結果から，常緑広葉樹が優占する山地渓流では，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陽イオン，とりわけK^+，Mg^{2+}，Ca^{2+} が主要供給源であり，渓流水中のイオン組成を規定する一因となり，それは水温のみならず渓流水のpHに強く影響されるうることが示唆された．