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Leaching characteristics of anions and cations from evergreen leaves supplied to the stream bed and influences on stream water composition in the Southern Kyusyu Mountains

Hirokazu Kitamura

Laboratory of Landscape Conservation, Minami-Kyushu University,
Takanabe, Miyazaki 884-0003, Japan

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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. The purpose of the present study is to clarify the leaching characteristics of leaf litter of the evergreen species that are dominant in the riparian zone of the investigated stream and to examine the influence of leachates on mountain stream water ionic composition by laboratory leaching experiments and field measurements.

Five fresh fallen leaves and fallen leaves of ten species of evergreen trees dominant in the riparian zone of the investigated reach were placed into a beaker filled with 500 cc of distilled water and allowed to stand for 30 days at ambient temperature between 25~30℃ after well washing with distilled water, air-dried for one week and oven-dried at 80℃ for 48 hours and the electric conductivity (EC), hydrogen ion concentration (pH) and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-} and SO_4^{2-}) were measured at 1 and 30 days after submersion. On the field measurements, stream water samples were collected from four different environments (springs, riffles, pools and side-pools) and were transported to our laboratory and EC, pH and the concentrations of the cations and anions were measured. The field measurements were conducted monthly from April 2006 to March 2007.

EC, pH, and cation and anion concentrations, continued to increase in all samples for 30 days following the immersion of evergreen tree leaves in distilled water for being attributed to the leaching of some components from the leaves. The EC values of water samples containing submerged green *Symplocos theophrastifolia* Sieb. et Zucc. leaves exceeded 150 S/cm, and pH values increased following the rapid decrease immediately after submergence, from 6.0 to 7.0. The most dominant cation in the water samples was K^+, accounting for more than 70% of all cations in most sample waters. On the 30th day after submergence, the order of average cation release rates from green leaves was $K^+ > Mg^{2+} > Ca^{2+} > Na^+$, which coincided to the experimental results in previous studies. The order of average anion release was $Cl^- > PO_4^{3-} > SO_4^{2-}$. In contrast to the high K^+ ratios in the water of the leaching experiments, the monthly K^+ concentrations in the stream water were relatively lower than those of the other cations and anions. The lower concentration of K^+ in the stream water during the growing season would suggest that there is a differential utilization of K^+ by the biota and stream sediment acts as an important agent for removal of leachate from water. Therefore, the clay component of the sediment may serve as a reservoir of chemically bound K^+ and biota may also provide a reservoir for K^+ if there is some net increase in biomass. The EC value is lower in the spring than in the other environments and that the K^+, Mg^{2+} and Ca^{2+} concentrations are considerably higher in the riffle, pool and side-pool, in which litter had been supplied, than in the spring where leaf litter is not deposited.

These results indicate that the primarily source of ions is rock weathering in the spring and simultaneous ion loading from multiple sources occurs in the riffle, pool and side-pool 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 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.

Key words: evergreen trees, leaf litter, leachate, cations and anions, stream environments.

1. INTRODUCTION

Allochthonous material, such as leaf litter, entering small streams represents the primary energy source available to the consumers in these systems. This organic matter has been shown to remain within streams where it is decomposed by a variety of physical, chemical and biological processes1). Arising from the instream processing of this organic material is the production of dissolved organic matter (DOM)6) 25), nutrients26) and physicochemical changes in water chemistry. The amount of allochthonous material that enters lotic ecosystems annually from terrestrial riparian forests is estimated to be considerable7), and substances derived from the decomposition of leaf litter are thought to have an important impact on stream water quality.

Pioneering studies that described the effect of leaf litter on the chemical quality of streams, including Schneller (1955)31) and Slack (1955)33), reported that the decay of leaves in pools generally induced greater water color and low dissolved-oxygen concentrations. Hynes (1960)12) indicated that the decomposition of spruce and red cedar needles released a substance toxic to fish, and Myers (1961)27) suggested that manganese was leached from oak trees in the watershed of the San Clemente Reservoir. These studies suggested that various tree species may make widely differing chemical contributions to streams through leaf litter leachates.

While many subsequent studies have focused on the physical degradation of leaf litter5) 11) 12) 22) 24) or on the chemical changes associated with degradation in streams6) 18) 20) 23) 27), few studies have examined the effects of materials leaching from leaf litter on stream water quality. The purpose of the present study, therefore, is to clarify the leaching characteristics of leaf litter of the evergreen species that are dominant in the riparian zone of the investigated stream and to examine the influence of leachates on mountain stream water ionic composition. The present study focuses on one of the most important stream water quality indices, anions and cations, as leachates from leaf litter in the stream water.

2. SITE DESCRIPTION

Experiments were conducted in the Takeo River in Saito City of Miyazaki Prefecture. The Takeo River, a tributary of the Hitotsuse River, ranges in elevation from 100m to 600m and originates in the Southern Kyusyu Mountains. The Takeo River Basin overlays the Miyazaki Formation, which was formed during the Cretaceous to middle Paleogene periods. The formation consists of black slate, sandstone and shale. The geologic structure of the basin, therefore, 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 fifty years. To prevent sediment disasters caused by landslides resulting from the weakness of this basin, seven 3 to 5m- high *sabo* dams have been constructed in the stream since 196518).

The study site consists of an approximately 1 km river reach between *sabo* dam No. 5 and approximately 50m downstream of *sabo* dam No. 6 (Fig. 1). The stream is a first-order stream with a mean width of 10 m, mean depth (at modal flow) of 0.3m, mean slope of 0.25, and mean current velocities ranging from 20−30cm/sec. The stream bottom is composed primarily of gravel, pebbles and cobble substrates and the riparian vegetation consists of evergreen deciduous trees, such as *Symplocos theophrastifolia* 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 removed to the stream bed.

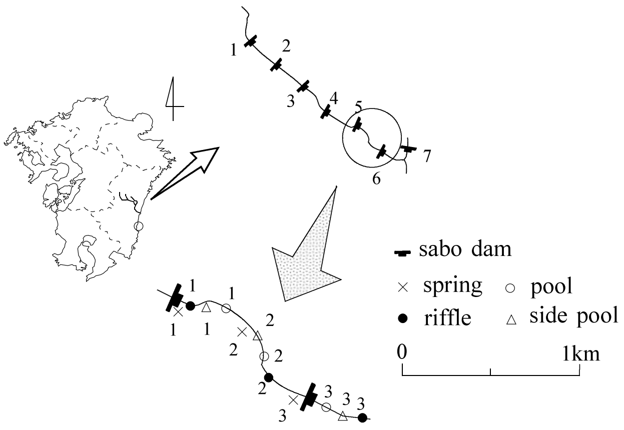


Fig. 1. Stream reach investigated and sampling sites.

3. METHODS

3-1. Materials and laboratory leaching experiments

Ten species of evergreen trees, shown in Table 1, are common in the riparian zone of the investigated reach and make a substantial contribution to annual litter fall. Approximately fifty pieces of fresh fallen leaves and fallen leaves of each tree species were collected from the stream bank of the reach. Fresh fallen leaves and fallen leaves are whole leaves categorized as follows. Fresh fallen leaves maintain the original shape without any skeletonization and still retain their original color because of the relatively short time elapsed after falling. Fallen leaves also hold the original shape without any skeletonization and appear to be brown. The leaves were collected on May 30, 2006 because in the investigated reach the evergreen species fall from May to July each year.

The collected leaves were well washed with distilled water to eliminate aerosol dust and atmospheric gases8), air-dried for one week and oven-dried at 80°C for 48 hours. Five fresh fallen leaves and fallen leaves of each species were selected at random and weighed. Then, each sample was placed into a beaker filled with 500cc of distilled water and allowed to stand for 30 days at ambient temperature between 25~30°C. The electric conductivity (EC) and hydrogen ion concentration (pH) were measured with a water quality probe (WQC-20A, TOA Electronics Ltd., Japan), and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-} and SO_4^{2-}) in the water were measured using ion chromatography (DX-120, NIPPON DIONEX K.K.) at 1 and 30 days after submersion, because maximum loss of soluble components

Table 1. Change in pH and EC (μS/cm) of water containing submerged leaves

Species	Categories	Days after submergence				$EC_{30/1}$	$EC_{g/b}$
		1		30			
		pH	EC	pH	EC		
Symplocos theophrastifolia sieb. et Zucc.	green leaves	6.3	33.6	6.1	152.6	4.54	1.21
	brown leaves	6.9	82.6	7.0	126.4	1.53	
Machilus japonica sieb. et Zucc.	green leaves	5.0	53.2	7.0	116.0	2.18	2.24
	brown leaves	6.0	23.8	6.8	51.8	2.18	
Meliosma rigida sieb. et Zucc.	green leaves	5.2	129.3	7.1	131.1	1.01	1.38
	brown leaves	5.0	89.7	6.9	94.7	1.06	
Litsea acuminata Kurata	green leaves	5.4	46.1	7.1	144.9	3.14	1.91
	brown leaves	5.4	39.6	7.0	76.0	1.92	
Quercus gilva Blume	green leaves	5.9	6.77	6.8	37.5	5.54	1.69
	brown leaves	5.8	10.03	6.6	22.2	2.21	
Castanopsis Spach	green leaves	5.3	19.40	6.3	24.3	1.25	0.91
	brown leaves	5.6	16.45	6.3	26.6	1.62	
Quercus glauca Thunb.	green leaves	5.6	14.41	6.7	64.9	4.50	1.36
	brown leaves	5.2	33.9	6.6	47.7	1.41	
Quercus myrsinaefolia Blume	green leaves	5.9	6.23	6.5	41.8	6.71	1.24
	brown leaves	5.8	7.46	6.6	33.7	4.52	
Pasania edulis Nakai	green leaves	6.1	7.65	7.0	76.4	9.99	1.54
	brown leaves	6.0	24.3	6.8	49.7	2.05	
Machilus thunbergii Sieb. et Zucc.	green leaves	5.8	34.1	6.8	133.4	3.91	5.21
	brown leaves	5.9	9.93	6.4	25.6	2.58	

$EC_{30/1}$: The ratios of mean EC value after 30 days to that after one day
$EC_{g/b}$: The ratios of mean EC value after 30 days of green leaves to that of brown leaves

through abiotic leaching occurs during the first 24 hours exposure of leaf litter to water and is completed within approximately four weeks[35].

3-2. Stream water sampling and estimation of sample ion content

Stream water samples were collected from four different environments (Fig.1): (a) springs from cracks on the vertical cliff of bedrock slope along the side of the stream approximately 150 cm above the stream margin; (b) riffles; (c) pools; and, (d) side-pools, which were considered to be stagnant areas of water along the stream margin. Since a series of sampling points (spring, riffle, pool and side-pool) are not continuously distributed, the water quality of a sampling point dose not affect that of each neighboring sampling point.

Samples were collected by hand in a 250 ml polyethylene bottle. Water from springs was collected from cracks in the bedrock and 10 cm below the water surface in riffles. In pools and side-pools, samples were collected approximately 5 cm above leaf litter pack on the substrate using a 250 ml polyethylene bottle. A water sampler was used to collect water in pools and side-pools that were deeper than 50 cm. At the time of sampling, water temperature, EC and pH of the water were measured. The collected water samples were transported to our laboratory and the concentrations of cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-} and SO_4^{2-}) were measured. The measurements were conducted using the same methods applied to the stream water described above.

These measurements were conducted monthly from April 2006 to March 2007.

4. RESULTS

4-1. Leaching characteristics of evergreen leaves

4-1-1. Changes in EC and pH values of water from submerged leaves

The pH and EC of the distilled water in which leaf samples were submerged varied with time as shown in Table 1. The initial EC and pH of distilled water was 1.36 μS/cm and 6.9, respectively. Marked increases in EC were observed one day after leaf submersion, indicating that some materials leached from submerged leaves immediately after submergence, resulting in rapid leaching during the initial 24 hours[10) 16) 38)]. The EC increased with time in all water samples with significant differences observed after 30 days, and the mean EC values of water after 30 days' submergence of green leaves of *Symplocos theophrastifolia* Sieb. et Zucc., *Machilus japonica* Sieb. et Zucc., *Meliosma rigida* Sieb. et Zucc., *Litsea acuminata* Kurata, and *Machilus thunbergi* Sieb. et Zucc. were 152.6, 116.0, 131.1, 144.9, and 133.4 μS/cm, respectively. The mean EC values on the 30th day were higher in green leaves than in brown leaves, with the exception of *Castanopsis* Spach. Based on these mean values, the increasing EC rates attributed to leaching from submerged leaves should tend to be lower in leaves with a relatively thicker outer layer of the epidermis, which consists of cutin.

The mean pH values of water decreased from the initial pH value one day after submersion, with the exception of brown *Symplocos theophrastifolia* Sieb. et Zucc. leaves, which was attributable to aerosol dust adhered to the leaves. The mean pH values increased with time in all water samples after 30 days' submergence, recovering

Table 2. Changes in cation (anion) concentration par 1g of leaves (mg/l). $R_{k/t}$ is the ratio of cation (anion) concentration to total cation (anion) concentration on the 30th day from submergence of leaves

(a) cation

Days after submergence		1						30						$R_{k/t}$				
Species	Category	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	total	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	total	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Symplocos theophrastifolia sieb. et Zucc.	green leaves	0.138	0.300	3.741	0.072	0.146	4.397	0.122	0.593	15.828	2.063	1.968	20.575	0.6	2.9	76.9	10.0	9.6
	brown leaves	0.308	0.183	3.555	0.674	0.898	5.618	0.179	0.665	10.785	2.586	2.379	16.593	1.1	4.0	65.0	15.6	14.3
Machilus japonica sieb. et Zucc.	green leaves	0.089	0.120	4.401	0.089	0.141	4.840	0.099	0.000	9.327	0.338	0.204	9.968	1.0	0.0	93.6	3.4	2.0
	brown leaves	0.412	0.198	4.533	0.132	0.187	5.463	0.238	0.000	5.128	1.112	2.117	8.594	2.8	0.0	59.7	12.9	24.6
Meliosma rigida sieb. et Zucc.	green leaves	0.685	0.079	11.827	0.659	0.544	13.795	0.248	0.355	12.558	0.725	0.828	14.714	1.7	2.4	85.3	4.9	5.6
	brown leaves	0.701	0.062	13.520	0.493	0.767	15.544	0.293	0.411	14.444	0.552	0.726	16.426	1.8	2.5	87.9	3.4	4.4
Litsea acuminata Kurata	green leaves	0.220	0.056	4.017	0.033	0.040	4.366	0.201	0.045	15.128	0.139	0.102	15.615	1.3	0.3	96.9	0.9	0.7
	brown leaves	0.798	0.134	6.013	0.123	0.194	7.263	0.408	0.434	15.504	0.504	0.290	17.141	2.4	2.5	90.5	2.9	1.7
Quercus gilva Blume	green leaves	0.279	0.000	1.695	0.018	0.057	2.050	0.095	0.967	8.684	0.326	0.229	10.300	0.9	9.4	84.3	3.2	2.2
	brown leaves	0.266	0.114	2.720	0.046	0.097	3.243	0.123	0.706	7.350	0.673	0.569	9.421	1.3	7.5	78.0	7.1	6.0
Castanopsis Spach	green leaves	2.653	0.000	6.219	0.964	0.456	10.292	0.435	0.624	8.327	1.866	1.139	12.392	3.5	5.0	67.2	15.1	9.2
	brown leaves	0.398	0.000	3.625	0.182	0.170	4.375	0.232	0.527	4.152	0.636	0.480	6.028	3.9	8.7	68.9	10.6	8.0
Quercus glauca Thunb.	green leaves	0.312	0.000	1.338	0.089	0.216	1.956	0.191	0.235	8.596	0.756	0.306	10.085	1.9	2.3	85.2	7.5	3.0
	brown leaves	0.145	0.000	1.172	0.098	0.107	1.522	0.051	0.000	1.166	0.189	0.134	1.541	3.3	0.0	75.7	12.3	8.7
Quercus myrsinaefolia Blume	green leaves	0.480	0.000	2.948	0.103	0.098	3.629	0.262	0.245	11.082	0.875	0.607	13.072	2.0	1.9	84.8	6.7	4.6
	brown leaves	0.069	0.000	0.484	0.008	0.019	0.580	0.053	0.030	1.982	0.162	0.136	2.364	2.3	1.3	83.8	6.9	5.7
Pasania edulis Nakai	green leaves	0.153	0.000	0.701	0.033	0.080	0.967	0.087	0.000	7.499	0.136	0.104	7.827	1.1	0.0	95.8	1.7	1.3
	brown leaves	0.528	0.000	2.279	0.039	0.061	2.907	0.303	0.020	6.677	0.228	0.246	7.473	4.0	0.3	89.4	3.1	3.3
Machilus thunbergii Sieb. et Zucc.	green leaves	0.227	0.000	3.980	0.051	0.088	4.347	0.232	0.000	16.850	0.317	0.221	17.620	1.3	0.0	95.6	1.8	1.3
	brown leaves	0.305	0.000	1.397	0.112	0.133	1.947	0.263	0.000	9.027	0.408	0.341	10.039	2.6	0.0	89.9	4.1	3.4
Average	green leaves	0.524	0.055	4.087	0.211	0.187	5.064	0.197	0.307	11.388	0.754	0.571	13.217	1.5	2.3	86.2	5.7	4.3
	brown leaves	0.393	0.069	3.930	0.191	0.263	4.846	0.214	0.279	7.621	0.705	0.742	9.562	2.2	2.9	79.7	7.4	7.8

(b) anion

Days after submergence		1						30						Rk/t				
Species	Category	F^-	Cl^-	NO^{3-}	PO_4^{3-}	SO_4^{2-}	total	F^-	Cl^-	NO^{3-}	PO_4^{3-}	SO_4^{2-}	total	F^-	Cl^-	NO^{3-}	PO_4^{3-}	SO_4^{2-}
Symplocos theophrastifolia sieb. et Zucc.	green leaves	0.078	1.232	0.371	0.000	0.323	2.004	0.114	1.630	0.650	0.000	1.770	4.164	2.7	39.1	15.6	0.0	42.5
	brown leaves	0.099	1.094	0.206	0.000	1.422	2.822	0.089	1.580	0.352	0.000	2.774	4.794	1.8	33.0	7.3	0.0	57.9
Machilus japonica sieb. et Zucc.	green leaves	0.676	0.177	0.000	0.406	0.142	1.402	0.000	0.352	0.083	0.454	0.130	1.019	0.0	34.5	8.2	44.6	12.7
	brown leaves	0.193	0.417	0.000	0.000	0.126	0.736	0.000	0.400	1.994	0.000	0.122	2.516	0.0	15.9	79.3	0.0	4.8
Meliosma rigida sieb. et Zucc.	green leaves	0.434	0.670	0.000	2.204	2.421	5.729	0.000	0.673	0.288	1.754	1.898	4.612	0.0	14.6	6.2	38.0	41.1
	brown leaves	0.456	0.660	0.000	1.101	2.417	4.634	0.000	0.741	0.218	0.675	1.918	3.552	0.0	20.9	6.1	19.0	54.0
Litsea acuminata Kurata	green leaves	0.031	0.576	0.000	0.085	0.329	1.021	0.044	0.579	0.053	0.808	0.270	1.754	2.5	33.0	3.0	46.0	15.4
	brown leaves	0.173	1.215	0.000	0.000	0.719	2.108	0.070	1.140	0.078	0.681	0.587	2.555	2.7	44.6	3.0	26.7	23.0
Quercus gilva Blume	green leaves	0.129	0.331	0.000	0.201	0.000	0.660	0.000	0.592	0.000	0.690	0.000	1.282	0.0	46.2	0.0	53.8	0.0
	brown leaves	0.255	0.464	0.000	0.000	0.000	0.718	0.000	0.708	0.000	0.000	0.000	0.708	0.0	100.0	0.0	0.0	0.0
Castanopsis Spach	green leaves	0.219	0.424	0.000	0.000	0.000	0.643	0.000	1.070	0.000	0.000	0.000	1.070	0.0	100.0	0.0	0.0	0.0
	brown leaves	0.204	0.440	0.000	0.000	0.000	0.644	0.000	0.651	0.000	0.000	0.000	0.651	0.0	100.0	0.0	0.0	0.0
Quercus glauca Thunb.	green leaves	0.067	0.479	0.000	0.000	0.194	0.740	0.000	0.856	0.000	0.491	0.430	1.776	0.0	48.2	0.0	27.6	24.2
	brown leaves	0.034	0.164	0.000	0.077	0.051	0.326	0.000	0.134	0.227	0.000	0.000	0.361	0.0	37.2	62.8	0.0	0.0
Quercus myrsinaefolia Blume	green leaves	0.226	0.626	0.000	0.000	0.106	0.958	0.000	0.772	0.567	0.000	0.152	1.490	0.0	51.8	38.1	0.0	10.2
	brown leaves	0.028	0.221	0.000	0.000	0.000	0.249	0.000	0.298	0.097	0.000	0.000	0.395	0.0	75.5	24.5	0.0	0.0
Pasania edulis Nakai	green leaves	0.036	0.169	0.000	0.000	0.064	0.270	0.000	0.244	0.277	0.844	0.078	1.443	0.0	16.9	19.2	58.5	5.4
	brown leaves	0.100	0.394	0.000	0.000	0.000	0.493	0.000	0.419	0.000	0.209	0.000	0.628	0.0	66.7	0.0	33.3	0.0
Machilus thunbergii Sieb. et Zucc.	green leaves	0.789	0.954	0.000	0.696	0.638	3.077	0.000	1.145	0.000	1.988	0.716	3.849	0.0	29.8	0.0	51.6	18.6
	brown leaves	0.086	0.472	0.000	0.000	0.160	0.717	0.000	0.886	0.000	0.474	0.430	1.790	0.0	49.5	0.0	26.5	24.0
Average	green leaves	0.268	0.564	0.037	0.359	0.422	1.650	0.016	0.791	0.192	0.703	0.544	2.246	0.7	35.2	8.5	31.3	24.2
	brown leaves	0.163	0.554	0.021	0.118	0.489	1.345	0.016	0.696	0.296	0.204	0.583	1.795	0.9	38.8	16.5	11.4	32.5

Table 3. Overall comparison of ranges and means of measured values

	Depth (cm)		Water temperature (℃)		pH		EC (μS/cm)	
	range	mean	range	mean	range	mean	range	mean
Spring	—	—	7.0–22.6	16.5	6.4–8.1	7.3	37.2–100.6	59.3
Riffle	5–40	16.3	8.2–22.7	15.3	6.6–8.0	7.4	66.0–99.2	86.4
Pool	80–130	99.7	8.2–22.7	15.3	6.6–8.0	7.4	69.4–97.0	85.2
Side-pool	5–30	21.4	6.7–22.7	15.4	6.5–7.8	7.2	52.3–100.3	82.0

Table 4. Overall comparison of ranges and means of ion concentrations in the stream water (mg/ l)

(a) anion

	F^-		Cl^-		NO^{3-}		SO_4^{2-}	
	range	mean	range	mean	range	mean	range	mean
Spring	0.001–0.137	0.055	2.240–6.144	4.691	0.168–3.105	1.576	1.834–6.954	4.420
Riffle	0.038–0.116	0.062	3.554–5.696	4.309	1.865–4.046	2.572	3.819–6.530	5.217
Pool	0.001–0.129	0.061	3.609–10.036	4.491	1.758–3.933	2.494	2.154–6.888	5.061
Side-pool	0.033–0.106	0.061	3.560–7.575	4.818	0.039–0.039	0.039	3.607–6.635	5.212

(b) cation

	Na^+		NH_4^+		K^+		Mg^{2+}		Ca^{2+}	
	range	mean	range	mean	range	mean	range	mean	range	mean
Spring	1.693–6.597	3.562	0.001–0.648	0.116	0.168–0.836	0.454	0.012–2.732	1.276	0.003–8.546	2.831
Riffle	2.181–3.894	2.796	0.001–0.317	0.055	0.473–1.359	0.653	1.840–3.740	2.828	6.042–13.839	9.368
Pool	2.156–5.808	2.819	0.001–0.879	0.095	0.455–1.646	0.652	1.041–3.853	2.715	1.660–13.559	8.856
Side-pool	2.189–4.874	3.071	0.002–0.296	0.070	0.470–2.872	0.943	1.170–3.692	2.658	4.242–13.765	8.486

to the initial pH value attributable to leaching. Unlike EC, there were no marked differences in pH after 30 days of being submerged among tree species and categories of leaves, although many complex interactions between pH and nutrient cycles were observed and their effect on accelerating the decomposition of leaves in aquatic ecosystems will be explained below[10) 11) 13) 38)].

4-1-2. Ion concentrations leached from submerged leaves

Table 2 shows the concentrations of cations and anions leached from leaves submerged in distilled water. In table 2, the concentrations per 1g leaves are indicated. The ions detected in all samples during the experiment period were Na^+, K^+, Mg^{2+}, Ca^{2+} and Cl^-. The cations and anions appeared to leach from the leaves immediately after submersion and the ion concentrations increased with time in all water samples. The mean total concentrations of K^+, Mg^{2+}, Ca^{2+}, Na^+ and Cl^- per 1g leaves on the 30th day were 11.39, 0.75, 0.57, 0.20 and 0.79 mg/l, respectively. The order of leaf type from highest to lowest total cation concentration after 30 days was *Symplocos theophrastifolia* Sieb. et Zucc. green leaves, *Machilus thunbergii* Sieb. et Zucc. green leaves, and *Litsea acuminata* Kurata brown leaves, with total cation concentrations of 20.58, 17.62 and 17.14mg/l, respectively. The water in which brown *Castanopsis* Spach, *Quercus glauca* Thunb., and *Pasania edulis* Nakai leaves were submerged had the lowest total cation concentrations of all the leaves examined, below 7.00 mg/l.

Among the cations, K^+ was leached most abundantly by all plant species in the present study. The ratios of K^+ concentration to total cation concentration on the 30th day exceeded 95% in water with submerged green *Litsea acuminata* Kurata, *Pasania edulis* Nakai, and *Machilus thunbergii* Sieb. et Zucc. leaves, and greater than 90% in water with submerged *Machilus japonica* Sieb. et Zucc. green leaves and *Litsea acuminata* Kurata brown leaves. Relatively low $R_{t/k}$ values less than 70% were observed in water with *Symplocos theophrastifolia* Sieb. et Zucc. brown leaves, *Machilus japonica* Sieb. et Zucc. brown leaves and *Castanopsis* Spach leaves.

The anion concentrations on the 30th day of after leaf submergence were in the same range as those of cations, with the exception of K^+. The difference in ion concentrations between categories depended on the leaf species and varieties of ion.

4-2. Stream water fluctuations

4-2-1. Overall comparisons of measured values in stream water

The ranges and means of stream depth and measured parameters, corresponding to the environments of the respective sampling sites during the experiment period, are shown in Table 3. The mean water temperature in the spring was 1℃ higher than the other stream environments sampled. The highest pH value was observed in the spring and the mean pH values were lowest in the side-pool. The range and mean of pH in the riffle was exactly the same as those in the pool, indicating the median value between spring and side-pool. The observed EC values were extremely low in the spring but higher at the other sample sites.

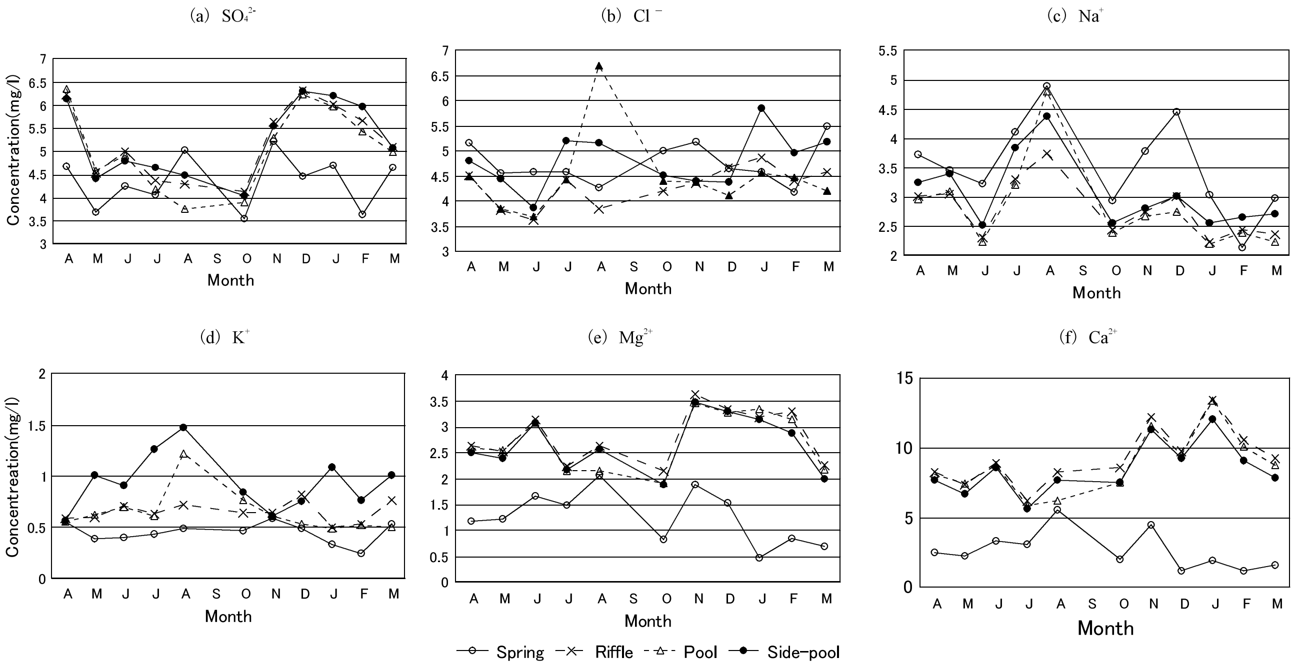


Fig. 2. Monthly fluctuations in major ion concentrations of the site.

The ranges and means of each ion concentration in the stream water, corresponding to the environments, are shown in Table 4. The measurements in September were disregarded due to an experimental apparatus malfunction. In the present study, Li^+ (cation) and NO^{2-}, Br^-, PO_4^{3-} and F^- (anions) were not detected in the stream water during the measurements. The mean ion concentrations were lowest in the spring and highest in the side-pool, with the exception of NO^{2-}, Na^+, and NH_4^+. Furthermore, the mean concentrations of K^+, Mg^{2+}, and Ca^{2+} were two to three times higher in the side-pool than in the spring. Other than the three springs that were sampled in the present study, no additional springs or tributaries flow into the reach and there are no artificial sources of ions. Consequently, the stream water was inferred to contain naturally ionic material in the reach investigated.

4-2-2. Monthly fluctuations in anion and cation concentrations

The monthly mean concentrations of the major ions corresponding to the environments of the respective sample sites during the experiment period are shown in Fig.2. Each ion concentration shows a unique monthly fluctuation. Na^+ and Cl^- indicated similar seasonal fluctuations in concentration for all stream bottom types. Na^+ is generally found in association with Cl^-, indicating their common origin. Although weathering of NaCl-containing rocks accounts for most of the Na^+ found in river water, the constant supply of Na^+ and Cl^- through rainwater input is thought to originate from sea water in the watershed and contributes significantly to the ion supply along the coasts[1].

Mg^{2+} and Ca^{2+} concentrations were lowest in the spring throughout the experiment period. The monthly mean concentrations of Mg^{2+} and Ca^{2+} in the side-pool equaled to those in the riffle and pool. The mean K^+ concentrations were highest in the side-pool except in November and lowest in the spring throughout the experiment period, as observed for Mg^{2+} and Ca^{2+}. The mean K^+ concentrations of the side-pool and pool were found to increase during the warm period from May to August. The concentrations in the spring slightly fluctuated from a minimum value of 0.27 mg/l in February.

The SO_4^{2-} concentrations in the riffle, pool, and side pool were observed to fluctuate similarly with a higher period from November to April and lower period from May to October. Those in the spring fluctuated each month within a range from a minimum value of 3.58 (mg/l) in October to a maximum value of 5.52 (mg/l) in November.

The results of multivariate analysis of monthly changes in mean concentrations of each ion (independent variable) for each sampling site (riffle, pool, and side-pool) and sampling season divided into four temporal groups (March to May, June to August, September to November, and December to February) (dependent variable) indicated significant relationships among the dependent variables ($P<0.005$). Furthermore, *Sheffe's* multiple range test indicated a significant difference in the monthly change in SO_4^{2-} concentrations between the spring and the side-pool and riffle ($P<0.005$), between the side-pool and the other sites for K^+ ($P<0.001$) and between the spring and the other sites for Mg^{2+} and Ca^{2+} ($P<0.0001$).

5. DISCUSSION

5-1. Differences in K^+ concentrations between laboratory experiments and field measurements

In the present study, physicochemical parameters, such as EC, pH, and cation and anion concentrations, continued to increase in all samples for 30 days following the immersion of evergreen tree leaves in distilled water. This is attributed to the leaching of some components from the leaves. The EC values of water samples containing submerged green *Symplocos theophrastifolia* Sieb. et Zucc. leaves exceeded 150 S/cm, and pH values increased following the rapid decrease immediately after submergence, from 6.0 to 7.0. The most dominant cation in the water samples was K^+, accounting for more than 70% of all cations in most sample waters. On the 30th day after submergence, the order of average cation release rates from green leaves was $K^+ > Mg^{2+} > Ca^{2+} > Na^+$, which coincided to the experimental results in previous studies4) 10) 24). The order of average anion release was $Cl^- > PO_4^{3-} > SO_4^{2-}$.

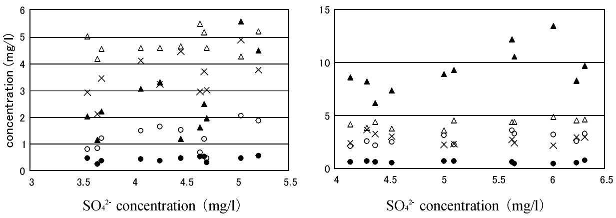
In contrast to the high K^+ ratios in the water of the leaching experiments, the monthly K^+ concentrations in the stream water were relatively lower than those of the other cations and anions, reflecting the lowest abundance and least variability of K^+ in river water among the major cations1). In a previous study20), the author found that the evergreen tree defoliation period in the riparian forests of the study reach is from May to July and the supply and deposition of newly fallen leaves are accelerated during this period, promoting subsequent litter decomposition in the investigated area. Furthermore, K^+ concentrations in stream water generally increased with increasing discharge21). In the study reach, stream discharge is higher from spring to summer and lower during autumn and winter. K^+ concentrations in the stream water, therefore, were predicted to increase during the period from May to July because of increased K^+ supply by leaching from fallen leaves and higher discharge. Contrary to this expectation, the K^+ concentrations in the stream water were considerably lower than the other major cations.

The lower K^+ concentrations may have been observed because K^+consumption is increased during plant and animal growing seasons as an indispensable mineral for plant and animal growth. In particular, plant growth during the warm period coincides with the high K^+concentration period and this seasonal change in biological demand corresponds to seasonal changes in flow conditions. The lower concentration of K^+ in the stream water during the growing season would suggest that there is a differential utilization of K^+ by the biota. K^+appears to be completely water soluble in plants but may combine with organic compounds24) and stream sediment acts as an important agent for removal of leachate from water22). Therefore, the clay component of the sediment may serve as a reservoir of chemically bound K^+. Biota may also provide a reservoir for K^+ if there is some net increase in biomass. These biological consumption may occur in PO_4^{3-} which was not detected in the stream water during the measurements.

5-1-2. Possibility of alteration of stream water composition from leaf leachate

Minerals in stream water originate from various sources. For example, it is said that 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 mica1). Although pollution and atmospheric inputs are small sources, atmospheric inputs are minimal, and pollution contributes only slightly. Based on the results of the leaching experiment in the present study, however, biomass contribution to stream water composition, i.e. through leachate from leaf litter, is also pronounced. Although there are numerous methods for detecting the origins of stream water composition, differences in composition between stream water and groundwater are due only to the ratios of rock weathering8).

(a) Spring (b) Riffle



(c) Pool (d) Side-pool

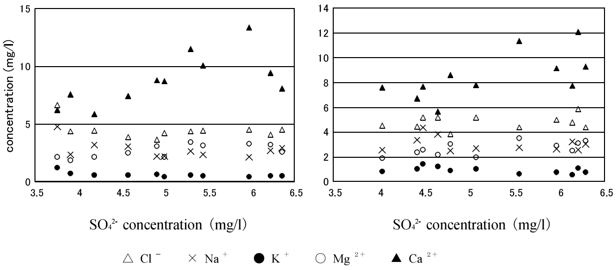


Fig. 3. Corrlation between SO_4^{2-} concentration and the major ion concentrations at four different environments.

SO_4^{2-} was detected every month at all sampling sites in the stream water but was not detected in the leachates from evergreen tree species in the leaching experiments; thus rock weathering can be identified as the primary SO_4^{2-} source, although atmospheric gasses and aerosol dust may contribute the certain part of the SO_4^{2-} source. Consequently, the concentrations of the major ions that came from other sources, such as Cl^-, K^+, Mg^{2+}, Ca^{2+} and Na^+, should vary independently of SO_4^{2-} concentration. Figure 3 shows the correlation of the monthly mean concentrations in the stream water between SO_4^{2-} and the other major ions. In the figure, relatively positive correlations are observed, the ion concentrations increase with increasing SO_4^{2-} concentration in the spring, with the exception of K^+ and Cl^- which is contributed through rainwater input from sea salts. Conversely, positive correlations between SO_4^{2-} and the other major ions are not observed in the other environments, with the exception of Ca^{2+}. These results indicate that the primarily source of ions is rock weathering in the spring and simultaneous ion loading from multiple sources occurs in the riffle, pool, and side-pool. Sulfide minerals occur in minor quantities in many different rock types, particularly in fine-grained black shale36), which is dominant in the study watershed. During certain months, the concentrations of SO_4^{2-} were higher in the riffle, pool, and side-pool than in the spring, which is thought to be attributed to leaching from the black shale substrates in the gravel, pebbles, and cobble of the stream bottom.

Based on these results, changes in water composition due to the natural input and subsequent leaching from leaf litter are predicted. This hypothesis is supported by the field measurements in the present study, i.e. that the EC value is lower in the spring than in the other environments and that the K^+, Mg^{2+}, and $Ca2^{2+}$ concentrations are considerably higher in the riffle, pool, and side-pool, in which litter had been supplied, than in the spring where leaf litter is not deposited.

The previous study20) clarified that leaves from riparian forests are input from May to July and tend to deposit in the side-pools of the reach for more than one month. Concentrations of the most abundant ionic leachate from leaves, K^+, are higher in the side-pool than in the other stream environments in the present study. These findings indicate that a natural ionic component is found in stream water with high plant litter content. The relatively high concentration of K^+ in the pool during the defoliation period of the evergreen trees, therefore, should also correspond with the litter leaching process. 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 the previous experimention 3) 10) 16).

Generally, new leaf litter readily leaches to stream water, and depending upon the species, may release from 5 to 30% of its organic dry weight within 24 hours as dissolved organic matter 1) 25). Previous experiments have also shown that anions and cations continue to leach from leaf litter for more than four weeks 19). In a natural stream, allochthonous material, such as leaves, supplied from terrestrial riparian forests into water is decomposed by a variety of physical, chemical, and biological processes. In particular, seasonal fluctuations occur in the densities of invertebrates in the investigated reaches (Kitamura *et al.* 2003, unpublished). These invertebrates, such as *Neoperla* Needham, *Goerodes japonicus* and *Anisocentropus immunis* McLachlan, shatter leaves into fragments by their feeding and nesting activities, accelerating litter decomposition. These seasonal biological factors may affect the leaching rates and the leaching rates of leaves in natural streams should be higher than those of the experimental results in the present study.

6. CONCLUSIONS

The present study 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.

For significant leaching to occur, leaves must reside at a site for a sufficient period of time. In addition, other factors are also important for the retention of leaves, including channel configuration and the area of the riparian zone 5); the hydrological and substrate characteristics along the stream margin 34); the seasonal patterns of litter fall and the discharge characteristics of the stream 39); the amount of leaf litter entering a stream 28); and, biological conditions such as shredder density 14) 17) 28) 30). Consequently, marked leaching in the side-pools should occur because these sampling points satisfy the above conditions for promoting litter retention.

However, not all of the litter supplied at a sample site in the present study was retained at the site, as most litter input from riparian forests into lotic systems is transported downstream. Accordingly, the litter characteristics at a site do not always reflect the water quality characteristics of that site. Litter decomposition and leaching of ionic materials from litter may be accelerated in natural streams because litter supplied into stream water is decomposed via multiple processes, including mechanical decomposition by invertebrates and chemical decomposition based on residence time in the various stream environments.

The stream environments reflect the geomorphological characteristics of the stream reach with *sabo* dams and show uniform substrates consisting of similar sized particles. Side-pools along the stream margins are promoted by the uniform cross-sectional distribution of low current velocity and shallow water depth. Substrates along the stream margins are more likely to trap leaves than the same substrates in the main stream channel. The presence of the *sabo* dams combined with the interactions between the hydrological and substrate characteristics along the stream margin further increase the potential for retention 34). Furthermore, given that the increased retention times attributed to the *sabo* dams also contribute to creating an environment suitable for colonization by shredder fauna 30), litter decomposition in reaches with *sabo* dams is likely to be promoted further. Thus, comparative studies of litter decomposition rates in reaches with and without *sabo* dams are needed in the future.

Further experiments are also required to determine whether substances other than anions and cations are leached from plants, including lignin, cellulose, hemicellulose 35), iron and manganese 15). The nature of the leached substances and the rates at which this occurs vary among plant species and the parts of the plant, as well as according to the stage of plant decomposition 9) 23) 29). Future studies should evaluate input of these substances to stream water composition.

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南九州地域の山地渓流河畔域に生育する常緑広葉樹 leaf litter の溶出特性と渓流水質に及ぼす影響について

北村泰一
南九州大学 環境造園学部 地域環境学科
緑地保全学研究室

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，渓流生態系は物質の一方向への移入が卓越する開放系であるため溶出成分はごく短期間に流出するであろうという先入観から，河畔域より渓流に供給されるリターの渓流水質への影響は注目されてはこなかった．そこで本研究は，室内溶出実験と現地調査により，南九州地域の山地渓流河畔域に広く生育する常緑広葉樹リターの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．

対象流域の河畔域に優占する常緑広葉樹（10種）の落葉（落葉直後のものと落葉後数日を経たもの）を採取し，十分な洗浄と乾燥の後，各5枚ずつ500ml の蒸留水中に投入し，投入から1日および30日後の水中の電気伝導度（ＥＣ），ｐＨ，陽イオン（Li^+, Na^+, $NH_4{}^+$, K^+, Ca^{2+} , Mg^{2+}）と陰イオン（F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, $PO_4{}^{3-}$, $SO_4{}^{2-}$）濃度を測定した．さらに，2006年4月～2007年3月の毎月1回，対象渓流のspring，riffle，pool，side-pool各3箇所から採水し同様の項目を測定した．

室内実験においては，リターからの溶出に起因して，ＥＣ，ｐＨ，陽イオン，陰イオン濃度は実験開始直後からすべてのサンプルで増加し，実験から30日後ではK^+，Mg^{2+}，Ca^{2+}，Na^+ が主要陽イオンを構成しこのうちK^+ が70％以上を占めた．これに対して現地渓流では生物体への吸収や底質粘土粒子への吸着などによる消失のため，K^+ は検出されたイオンのなかでは低い濃度を示した．さらに現地渓流では，リターが供給され滞留する傾向にあるpool，side-poolにおいてK^+，Mg^{2+}，Ca^{2+} 濃度がspringより高く，この傾向はK^+ で特に著しいものであった．

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K^+，Mg^{2+}，Ca^{2+}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が示唆された．