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Forest Canopy Can Efficiently Filter Trace Metals in Deposited Precipitation in a Subalpine Spruce Plantation

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Abstract: Trace metals can enter natural regions with low human disturbance through atmospheric circulation; however, little information is available regarding the filtering efficiency of trace metals by forest canopies. In this study, a representative subalpine spruce plantation was selected to investigate the net throughfall fluxes of eight trace metals (Fe, Mn, Cu, Zn, Al, Pb, Cd and Cr) under a closed canopy and gap-edge canopy from August 2015 to July 2016. Over the one-year observation, the annual fluxes of Al, Zn, Fe, Mn, Cu, Cd, Cr and Pb in the deposited precipitation were $7.29 \text{ kg}\cdot\text{ha}^{-1}$, $2.30 \text{ kg}\cdot\text{ha}^{-1}$, $7.02 \text{ kg}\cdot\text{ha}^{-1}$, $0.16 \text{ kg}\cdot\text{ha}^{-1}$, $0.19 \text{ kg}\cdot\text{ha}^{-1}$, $0.06 \text{ kg}\cdot\text{ha}^{-1}$, $0.56 \text{ kg}\cdot\text{ha}^{-1}$ and $0.24 \text{ kg}\cdot\text{ha}^{-1}$, respectively. The annual net throughfall fluxes of these trace metals were $-1.73 \text{ kg}\cdot\text{ha}^{-1}$, $-0.90 \text{ kg}\cdot\text{ha}^{-1}$, $-1.68 \text{ kg}\cdot\text{ha}^{-1}$, $0.03 \text{ kg}\cdot\text{ha}^{-1}$, $-0.03 \text{ kg}\cdot\text{ha}^{-1}$, $-0.02 \text{ kg}\cdot\text{ha}^{-1}$, $-0.09 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.08 \text{ kg}\cdot\text{ha}^{-1}$, respectively, under the gap-edge canopy and $1.59 \text{ kg}\cdot\text{ha}^{-1}$, $-1.13 \text{ kg}\cdot\text{ha}^{-1}$, $-1.65 \text{ kg}\cdot\text{ha}^{-1}$, $0.10 \text{ kg}\cdot\text{ha}^{-1}$, $-0.04 \text{ kg}\cdot\text{ha}^{-1}$, $-0.03 \text{ kg}\cdot\text{ha}^{-1}$, $-0.26 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.15 \text{ kg}\cdot\text{ha}^{-1}$, respectively, under the closed canopy. The closed canopy displayed a greater filtering effect of the trace metals from precipitation than the gap-edge canopy in this subalpine forest. In the rainy season, the net filtering ratio of trace metals ranged from -66.01% to 89.05% for the closed canopy and from -52.32% to 33.09% for the gap-edge canopy. In contrast, the net filtering ratio of all trace metals exceeded 50.00% for the closed canopy in the snowy season. The results suggest that most of the trace metals moving through the forest canopy are filtered by canopy in the subalpine forest.

Keywords: canopy filtering; closed canopy; forest hydrology; gap-edge canopy; throughfall; trace metal

1. Introduction

Trace metals in the environment originate mainly from metal refining, fossil fuel combustion, automotive exhaust emission and other human activities [1]. An increasing number of studies have demonstrated that trace metals mainly exist as particles in the atmosphere and can enter in natural regions with low human disturbance through atmospheric circulation [1,2]. The input of trace metals via atmospheric deposition is a large source of contamination for plants, soil and water, and continuous trace metal input has lasting negative impacts on biogeochemical cycling in ecosystems [3]. Forest ecosystems have often been considered as ecological filters that can efficiently decrease atmospheric pollutants and improve air quality [4,5], but the filtering efficiency of a forest ecosystem is often controlled by precipitation and canopy characteristics.

The term “trace element” is used loosely in the current literature to refer to elements that occur in small concentrations in natural biological systems [6]. Trace metals are introduced into terrestrial ecosystems via two pathways: dissolution in rain and snow (i.e., wet deposition) and direct particulate deposition (i.e., dry deposition) [7]. When precipitation passes through the forest canopy, the deposition precipitation is altered by the wash-off of some particles in the canopy that were deposited in dry periods or by ion exchange, i.e., uptake or leaching [8]. Some trace elements (e.g., Pb and Zn) [9,10] are taken up by the canopy. Lead, Cd and Cr are classified as nonessential trace elements; however, these elements can be highly toxic and can inhibit growth, even cause organismal death [11]. Iron, Mn, Cu, Zn and Al are essential trace elements that participate in plant physiological and biochemical processes, but excessive amounts of these elements can be toxic to plants [6].

In forest ecosystems, canopy gaps are created by dead and fallen trees and by intermediate cuttings, which are the primary modes of forest disturbance and regeneration [12,13]. A gap-edge canopy differs substantially from interior forest zones. Gap-edge and closed canopies represent two different forest canopy conditions, and the coverage of the gap-edge canopy area is less than that of the closed canopy area. The degree of precipitation interception will influence the accumulation of trace metals from precipitation. In addition, the structure of the canopy influences the ability of the canopy to capture suspended particles, and more trace metals may be intercepted by certain canopy structures. Due to the obstruction of the wind profile, which causes local advection and turbulent exchanges, an edge canopy can receive more atmospheric deposition than a closed canopy [9]. Several studies have focused on the effects of closed vs. open canopies on the canopy levels of trace metals received through atmospheric deposition [4,14]. However, no studies have addressed trace metal fluxes or filtration in gap-edge canopy layers [15]. Here, we hypothesized that the fluxes of trace metals are higher in a gap-edge canopy than in a closed canopy, and that the filtration of trace metals is lower in a gap-edge canopy than in a closed canopy.

As important freshwater conservation areas in the Yangtze River basin, subalpine forests in Southwest China play important roles in not only regulating the regional climate and biodiversity but also storing freshwater and conserving water and soil [16]. Since the 1950s, more than 400,000 hectares of pure dragon spruce (*Picea asperata* Mast.) plantations have replaced natural coniferous forests on the Eastern Tibetan Plateau. These plantations are harvested by large-scale industrial logging operations. The forest canopy of these plantations consists of a single canopy level rather than complex, multiple canopy levels as in natural forests. Therefore, these spruce plantations are likely ineffective in intercepting trace metals introduced via direct (dry) deposition.

The migration and transformation of trace metals in forest ecosystems occur through the two external inputs of wet and dry deposition. These processes affect trace metal pollution in various parts of the ecosystem. In spruce plantation ecosystems, certain trace metals play important biogeochemical roles, either as essential trace metals, such as Cu and Zn, or as nonessential trace metals (e.g., Pb, Cd and Cr) [9]. Therefore, quantification of these metals is important. Before precipitation reaches the soil surface, its chemical composition can be modified by contact with vegetation. Throughfall is commonly measured to quantify the load of atmospheric pollutants in forest ecosystems [17,18], where the contents of pollutants in throughfall differ from those in atmospheric precipitation [9]. In the present study, we measured the trace metals in throughfall in an area of an alpine spruce plantation to (1) observe patterns in annual trace metal concentrations and fluxes from the deposited precipitation and (2) compare the trace-metal filtering ability of a gap-edge canopy and a closed canopy in the subalpine spruce plantation. An understanding of these processes can increase our knowledge of the filtering effect of the forest canopy with respect to trace metals, and the main processes that control metal behavior after interaction with the forest canopy. The results of this study would provide insight into the filtration of trace metals deposited through precipitation in different canopy types and provide necessary information on water quality conservation in the upper reaches of the Yangtze River.

2. Materials and Methods

2.1. Site Description

The experimental site is located at the Long-term Research Station of Alpine Forest Ecosystems, Bipenggou Nature Reserve (102°53′–102°57′ E, 31°14′–31°19′ N; 2458–4619 m a.s.l.), Li County, Sichuan, Southwest China. The site is situated on the eastern edge of the Tibetan Plateau along the upper Yangtze River [19]. The mean annual air temperature is 2~4 °C, and the maximum and minimum temperatures are 23.7 °C and –18.1 °C, respectively. The mean annual precipitation ranges from 801 mm to 850 mm, with most rainfall occurring between May and August. Snowfall mainly occurs from October to April of the following year. The amount of snowfall is approximately 138.56 mm. The canopy forest vegetation is dominated by *Picea asperata* Mast with some understory shrubs (e.g., *Berberis diaphana* Maxin. and *Sorbus rufopilosa* Schneid) and grasses (e.g., *Deyeuxia scabrescens* (Griseb.) Munro ex Duthie). The expanded gap (the canopy gap plus the area that extends to the bases of the surrounding canopy trees) covers 23% of the experimental site [20].

2.2. Experimental Design

Three plots with similar topographical and environmental features were selected in a typical spruce forest gap (area: 100 m²) along a gradient from the gap-edge to the closed canopy (closed canopy area: 20 × 20 m) at 3000 m a.s.l. The mean tree age was approximately 60 a. The average diameter at breast height (DBH) and the average tree height in the experimental plots were 19.53 ± 1.99 cm and 7.63 ± 0.45 m, respectively. We selected an open area (20 × 20 m) approximately 50 m from the edge of the spruce plantation forest as the nonforested site to collect precipitation.

2.3. Precipitation Observations and Water Sampling

Precipitation: Rainfall was sampled in the nonforested site using 5 custom-made continuous rain gauges (each with a surface collection area of 0.64 m²).

Snowfall: Five cone-shaped collectors (top diameter of 100 cm, bottom diameter of approximately 20 cm) made of PVC and gridding cloth were used to observe and sample snowfall in the open site. Each collector was established 1 m above the ground surface. Each collector drained into a polyethylene (PE) bucket. As the snowfall fell directly into the polyethylene bucket, there was minimal exposure to external conditions and minimal snowfall evaporation.

Throughfall in the rainy season: Throughfall was recorded using 5 PVC rectangular gutters (each with a surface collection area of 400 × 16 cm) that were arranged beneath the closed canopy and gap-edge canopy in each plot. The gutters were established 1 m above the floor to avoid ground-splash effects and at a 5° horizontal angle to promote drainage. The lower end of each gutter was equipped with a plastic bucket.

Throughfall in the snowy season: Five cone-shaped collectors similar to the snowfall collectors were distributed beneath the closed canopy and the gap-edge canopy in each plot, and each collector drained into a PE bucket.

2.4. Chemical Analysis

Water samples were collected immediately after each rainfall event during the rainy season from August 2015 to July 2016. Due to the heavy snowfall and cruel natural conditions in winter, snow samples were collected once each month from November 2015 to April 2016. The samples were placed in clean polyethylene bottles. Upon collection, the water was poured from the polyethylene bucket into a graduated cylinder to measure the water volume. Then, the samples were rapidly transported to the laboratory where they were filtered using qualitative filter paper with a diameter of 12.5 cm. The filtered samples were adjusted to a pH of 1~2 with high-purity grade (GR) nitric acid. The concentrations of trace metals (i.e., Fe, Mn, Cu, Zn, Al, Pb, Cd and Cr) were determined using an inductively coupled plasma optical emission spectrometry system (Agilent 7900, US).

2.5. Calculations

The throughfall was calculated as follows (Formula (1)):

$$V_j = \frac{V'_i}{S} \times 10, \quad (1)$$

where V_j is the throughfall (mm), V'_i is the volume of water (mL), S is the surface area of collection, and 10 is the unit conversion factor.

The fluxes of trace metals in precipitation and throughfall were calculated using Formula (2) as follows [21]:

$$Flux_j = \frac{VWM_j \times V_j}{100}, \quad (2)$$

where $Flux_j$ (kg ha^{-1}) is the deposition flux of solute j in different forms of water, VWM_j is the weighted concentration (mg L^{-1}) of solute j in different forms of water, V_j is the water of different forms (mm), and 100 is the unit conversion factor.

The net throughfall fluxes (NTFs) and net throughfall ratios (NTRs) were calculated with Equations (3) and (4), respectively [22]:

$$\text{NTF} = \text{TF} - \text{BP}, \quad (3)$$

$$\text{NTR} = \text{NTF}/\text{BP}, \quad (4)$$

where BP and TF represent the bulk precipitation flux (kg ha^{-1}) and the throughfall flux (kg ha^{-1}), respectively. (Negative and positive N.TFs (NTRs) values represent filtered and leached amounts, respectively.)

2.6. Statistical Analysis

All statistical analyses were carried out using IBM SPSS version 20.0 statistics software (IBM SPSS Statistics Inc, Chicago, IL, USA), Univariate analysis was used to compare the concentrations, fluxes and net throughfall fluxes of trace metals among different canopy types and seasons. The statistical tests were considered significant at the $p < 0.05$ level.

3. Results

3.1. Annual Variations of Trace Metal Concentrations in Precipitation and Throughfall

After precipitation passed through the canopy, the concentrations of trace metals increased or decreased to different extents between the closed canopy and the gap-edge canopy. In the rainy season, the throughfall concentrations of the essential trace metals Fe, Mn and Cu were higher than those in the precipitation for both the closed canopy and the gap-edge canopy (Figure 1). The concentrations of Mn were 2.63-fold and 1.68-fold higher under the closed canopy and gap-edge canopy, respectively, than in the precipitation. In addition, the concentrations of Fe, Mn and Cu under the closed canopy were higher than those under the gap-edge canopy. Among the nonessential trace metals, only Cr showed a difference between throughfall and precipitation, with a higher gap-edge canopy value than that measured in precipitation (Figure 2). In the snowy season, the throughfall concentrations of all trace metals under the closed canopy and gap-edge canopy were lower than those in the precipitation. The concentrations of trace metals under the closed canopy were higher than those under the gap-edge canopy (except for Al and Pb). In addition, insignificant differences in trace metal concentrations were detected between the gap-edge canopy and the closed canopy, although there were significant seasonal effects on trace metal concentrations, as shown in Table 1 ($p < 0.05$).

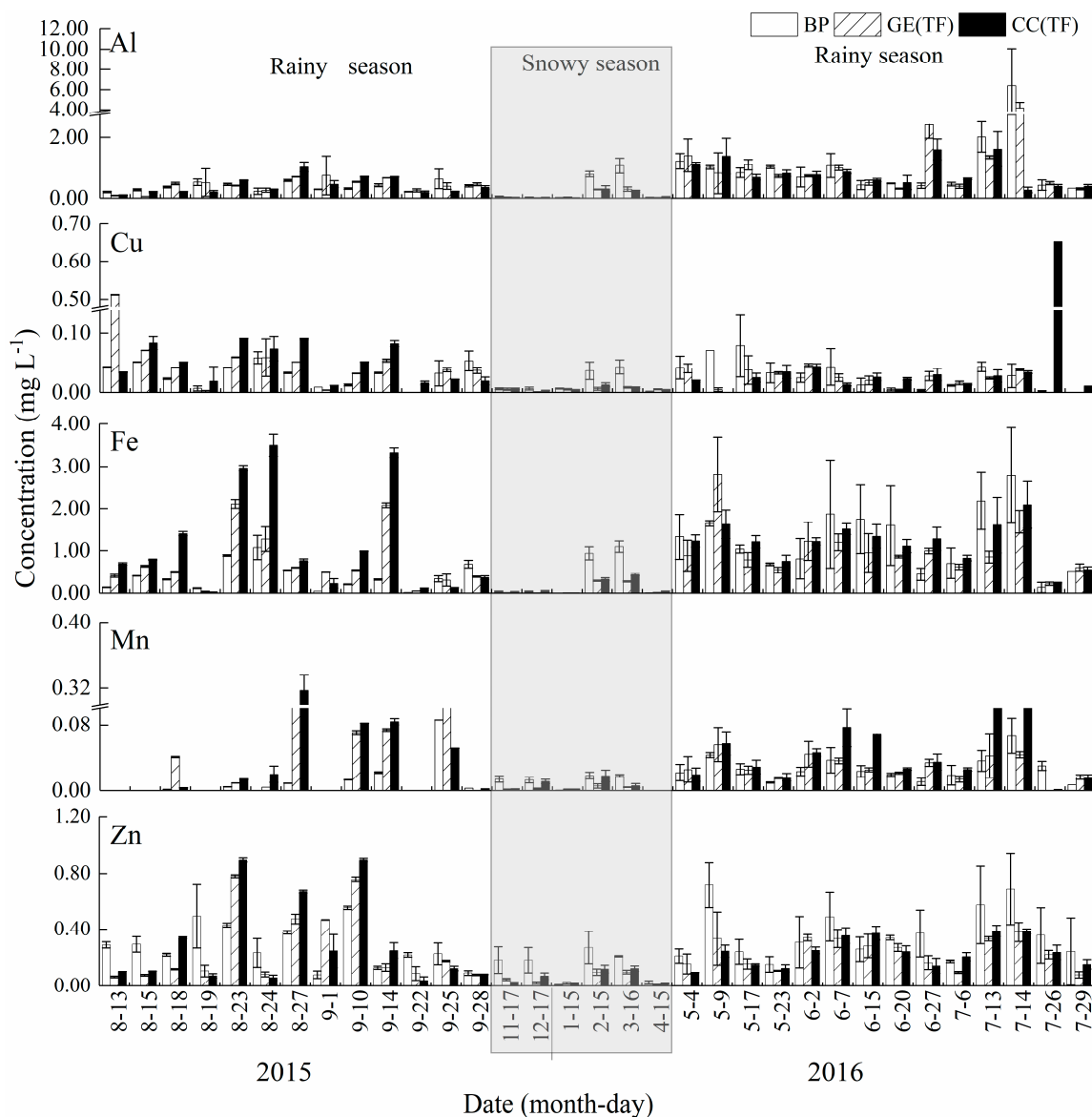


Figure 1. Concentrations of essential trace metals in bulk precipitation and throughfall. BP: bulk precipitation, GE: gap-edge canopy, CC: closed canopy. The bars and error bars are the means and 95% confidence intervals, respectively.

3.2. Annual Variations of Trace Metal Fluxes in Precipitation and Throughfall

The annual fluxes of Al, Zn, Fe, Mn, Cu, Cd, Cr and Pb were 7.29 kg·ha⁻¹, 2.30 kg·ha⁻¹, 7.02 kg·ha⁻¹, 0.16 kg·ha⁻¹, 0.19 kg·ha⁻¹, 0.06 kg·ha⁻¹, 0.56 kg·ha⁻¹ and 0.24 kg·ha⁻¹, respectively. The values in the rainy season were higher than those in the snowy season (Figures 3 and 4). The input of all trace metals from the precipitation, gap-edge canopy and closed canopy was 1.15 kg·ha⁻¹, 0.29 kg·ha⁻¹ and 0.30 kg·ha⁻¹, respectively, in the snowy season and 16.68 kg·ha⁻¹, 13.02 kg·ha⁻¹ and 15.96 kg·ha⁻¹, respectively, in the rainy season. Among the trace metal fluxes, the maximum values in the precipitation and under the closed canopy and gap-edge canopy were observed for Fe and Al in both seasons. In the snowy season, the throughfall fluxes of all trace metals under the closed canopy and gap-edge canopy were lower than those in the precipitation. Furthermore, there were no significant differences in trace metal fluxes between the gap-edge canopy and the closed canopy, but seasons had significant effects on the trace metal fluxes, as shown in Table 1 ($p < 0.05$).

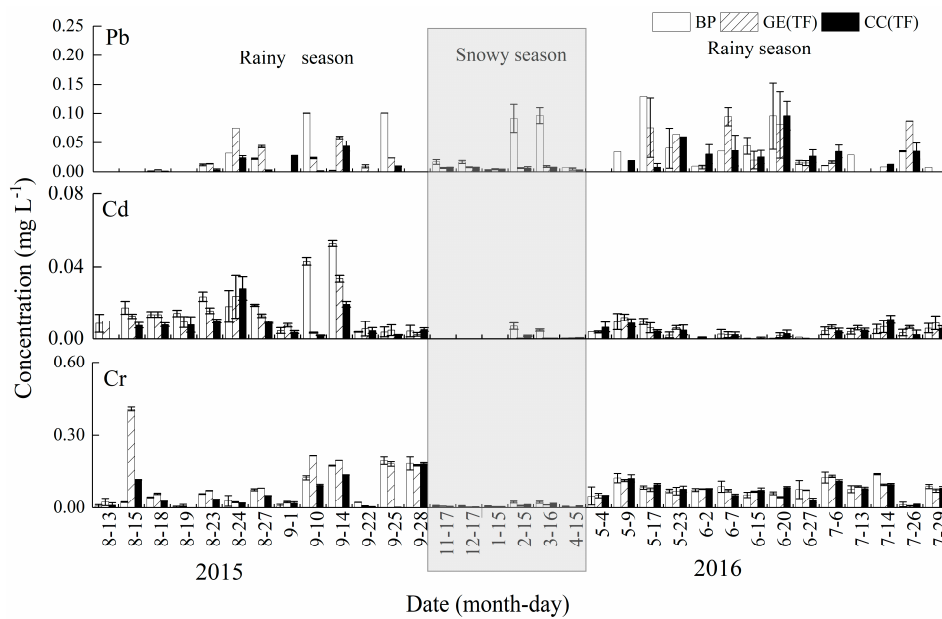


Figure 2. Concentrations of nonessential trace metals in bulk precipitation and throughfall. BP: bulk precipitation, GE: gap-edge canopy, CC: closed canopy. The bars and error bars are the means and 95% confidence intervals, respectively.

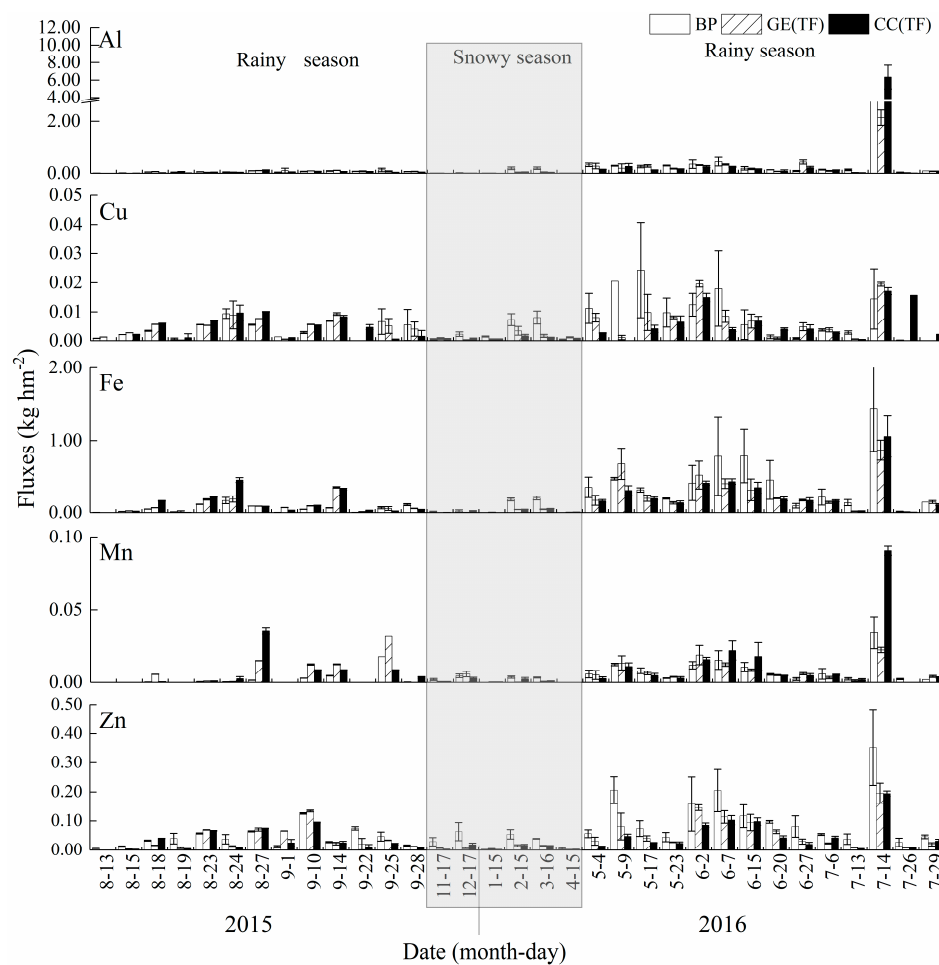


Figure 3. The fluxes of essential trace metals in bulk precipitation and throughfall. BP: bulk precipitation, GE: gap-edge canopy, CC: closed canopy. The bars and error bars are the means and 95% confidence intervals, respectively.

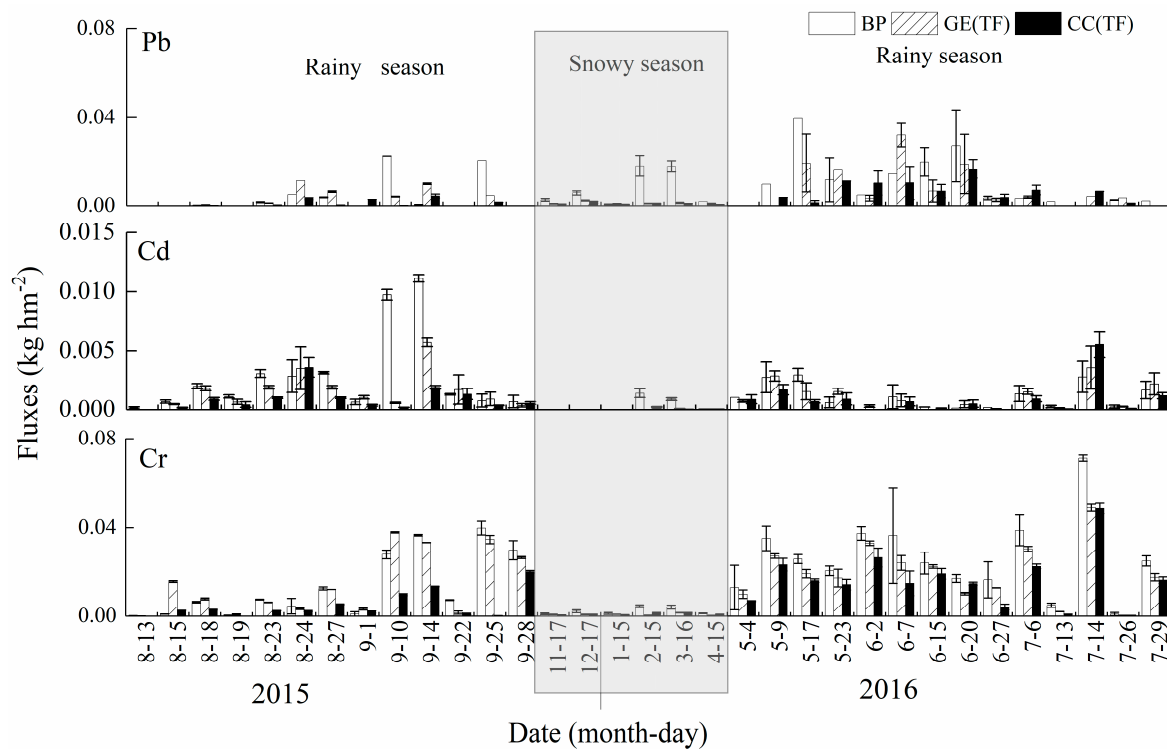


Figure 4. The fluxes of essential nonessential trace metals in bulk precipitation and throughfall. BP: bulk precipitation, GE: gap-edge canopy, CC: closed canopy. The bars and error bars are the means and 95% confidence intervals, respectively.

Table 1. Univariate analysis results (*F* values) regarding the effects of canopy and season on the concentrations and fluxes of trace metals in throughfall.

	Item	Al	Zn	Fe	Mn	Cu	Pb	Cd	Cr
Concentration	Canopy	0.22	0.22	1.64	1.25	0.13	0.88	0.72	1.43
	Season	7.70 **	31.83 **	44.60 **	12.24 **	6.89 **	11.18	37.28 **	39.94 **
Fluxes	Canopy	0.78	0.38	0.10	0.24	0.49	1.316	0.83	2.28
	Season	27.96 **	21.93 **	52.23 **	8.89 **	23.58 **	9.32 **	24.77 **	39.59 **
NTF	Canopy	0.60	1.02	0.005	5.06 *	0.57	5.57 *	1.32	10.59 **
	Season	0.54	0.32	0.004	0.48	0.24	0.57	0.26	4.74 *

*: $p < 0.05$; **: $p < 0.01$.

3.3. Variations of Net Throughfall Fluxes of Trace Metals Under the Closed Canopy and Gap-Edge Canopy

The net throughfall fluxes (NTFs) and net throughfall ratios (NTRs) of Al, Zn, Fe, Mn, Cu, Cd, Cr and Pb are shown in Table 2. The annual NTFs of these respective trace metals under the gap-edge canopy were $-1.41 \text{ kg}\cdot\text{ha}^{-1}$, $-0.76 \text{ kg}\cdot\text{ha}^{-1}$, $-1.35 \text{ kg}\cdot\text{ha}^{-1}$, $0.04 \text{ kg}\cdot\text{ha}^{-1}$, $-0.02 \text{ kg}\cdot\text{ha}^{-1}$, $-0.02 \text{ kg}\cdot\text{ha}^{-1}$, $-0.08 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.04 \text{ kg}\cdot\text{ha}^{-1}$ during the rainy season, and $-0.32 \text{ kg}\cdot\text{ha}^{-1}$, $-0.14 \text{ kg}\cdot\text{ha}^{-1}$, $-0.33 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$, $-0.00 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.04 \text{ kg}\cdot\text{ha}^{-1}$ during the snowy season. The NTFs of these respective trace metals under the closed canopy were $1.93 \text{ kg}\cdot\text{ha}^{-1}$, $-0.99 \text{ kg}\cdot\text{ha}^{-1}$, $-1.35 \text{ kg}\cdot\text{ha}^{-1}$, $0.11 \text{ kg}\cdot\text{ha}^{-1}$, $-0.03 \text{ kg}\cdot\text{ha}^{-1}$, $-0.03 \text{ kg}\cdot\text{ha}^{-1}$, $-0.25 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.10 \text{ kg}\cdot\text{ha}^{-1}$ during the rainy season, and $-0.26 \text{ kg}\cdot\text{ha}^{-1}$, $-0.14 \text{ kg}\cdot\text{ha}^{-1}$, $-0.30 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$, $-0.00 \text{ kg}\cdot\text{ha}^{-1}$, $-0.01 \text{ kg}\cdot\text{ha}^{-1}$ and $-0.04 \text{ kg}\cdot\text{ha}^{-1}$ during the snowy season. The NTRs of Mn was 33.09% and 89.05% in the rainy season under the two canopies, revealing greater leaching of this trace metal than that of the other trace metals.

Table 2. Net throughfall fluxes (NTFs) and net throughfall ratio (NTRs) values and standard deviation (in parentheses) of trace metals for the closed canopy and gap-edge canopy during the rainy and snowy seasons.

Canopy	Season	Throughfall (mm)	Item	Al	Zn	Fe	Mn	Cu	Cd	Cr	Pb	
Gap-edge canopy	Annual	645.47 (11.17)	NTF (kg·ha ⁻¹)	−1.73 (0.21)	−0.90 (0.04)	−1.68 (0.17)	0.03 (0.00)	−0.03 (0.01)	−0.02 (0.00)	−0.09 (0.01)	−0.08 (0.01)	
			NTR (%)	−23.75 (12.21)	−39.20 (21.33)	−23.93 (11.47)	19.75 (6.99)	−20.62 (13.45)	−32.85 (10.55)	−26.70 (7.95)	−35.95 (14.21)	
	Rainy season	530.33 (12.08)	NTF (kg·ha ⁻¹)	−1.41 (1.74)	−0.76 (0.41)	−1.35 (1.35)	0.04 (0.01)	−0.02 (0.05)	−0.02 (0.00)	−0.08 (0.05)	−0.04 (0.02)	
			NTR (%)	−36.09 (44.66)	−52.32 (28.08)	−32.06 (32.99)	33.09 (8.57)	−25.41 (50.88)	−39.32 (1.07)	−18.10 (11.21)	−27.33 (13.55)	
	Snowy season	115.14 (6.30)	NTF (kg·ha ⁻¹)	−0.32 (0.10)	−0.14 (0.05)	−0.33 (0.04)	−0.01 (0.00)	−0.01 (0.00)	−0.00 (0.00)	−0.01 (0.00)	−0.01 (0.00)	−0.04 (0.01)
			NTR (%)	−100.07 (32.11)	−101.06 (38.53)	−82.17 (4.07)	−49.55 (19.69)	−61.34 (16.09)	−95.33 (12.45)	−79.81 (22.41)	101.21 (17.67)	
Closed canopy	Annual	516.18 (10.29)	NTF (kg·ha ⁻¹)	1.59 (0.54)	−1.13 (0.04)	−1.65 (0.16)	0.10 (0.01)	−0.04 (0.01)	−0.03 (0.00)	−0.26 (0.01)	−0.15 (0.01)	
			NTR (%)	21.83 (13.41)	−49.23 (15.76)	−23.47 (10.91)	61.11 (23.41)	−24.22 (22.13)	−53.50 (27.99)	−46.81 (22.31)	−60.33 (20.34)	
	Rainy season	422.26 (11.16)	NTF (kg·ha ⁻¹)	1.93 (0.83)	−0.99 (0.50)	−1.35 (1.57)	0.11 (0.02)	−0.03 (0.06)	−0.03 (0.00)	−0.25 (0.05)	−0.10 (0.01)	
			NTR (%)	49.70 (21.51)	−68.45 (34.67)	−32.61 (37.10)	89.05 (16.87)	−31.88 (56.43)	−66.01 (11.33)	−53.55 (11.44)	−64.55 (5.41)	
	Snowy season	93.91 (5.55)	NTF (kg·ha ⁻¹)	−0.26 (0.22)	−0.14 (0.05)	−0.30 (0.04)	−0.01 (0.00)	−0.01 (0.00)	−0.00 (0.00)	−0.01 (0.00)	−0.01 (0.00)	−0.04 (0.01)
			NTR (%)	−82.04 (68.77)	−97.21 (37.51)	−75.45 (11.90)	−57.47 (12.21)	103.21 (32.04)	−91.41 (8.78)	−80.56 (18.97)	107.21 (17.69)	

4. Discussion

Before reaching the soil surface, the chemical composition of precipitation can be modified by contact with vegetation [22]. In a forest canopy, interactions between precipitation and the canopy lead to ion exchange and changes in element concentrations [23]. In the present study, the concentration differences between the snowy season and rainy season indicated seasonal variation (Figures 1 and 2). Freezing and thawing can damage the cell membranes of plant leaves, and the resulting change in the water content in plant tissues affects the exchange between cells and ions [24–26]. In the present study, seasons had significant effects on the trace metal measurements (Table 1). The extent of enrichment is affected by the solute characteristics [21]. Trace metals with higher concentrations of precipitation are mainly from terrigenous particles, such as Al and Fe, and the Sonja, which supports our findings [27]. Thus, in the present study, the higher concentrations of Al and Fe than of the other trace metals resulted in high fluxes in precipitation. The Al concentration was lower under both the gap-edge canopy and the closed canopy than in the nonforested site during both rainy and snowy seasons, whereas the Fe concentration was higher under both the gap-edge canopy and closed canopy than in the nonforested site in the rainy season. The Al and Fe concentrations accounted for 42.50% and 40.8%, respectively, of the nonforest input in the rainy season and 37.6% and 38.0%, respectively, of the nonforest input in the snowy season.

The brief interactions between vegetation and precipitation create high spatial variability of metal deposition from throughfall, which is very important for elemental cycling in forest ecosystems [28,29]. The concentrations of trace metals in precipitation were higher than those in throughfall in the winter. Snow evaporation and sublimation from the snow sampler during the winter may cause underestimation of total snowfall and overestimation of trace metal concentrations during winter. As such, the trace metal concentration values during winter should be treated with some caution. The annual trace metal fluxes should not be affected for the following two reasons: (1) total amount of trace metals in snow collector would not be affected by snow sublimation or evaporation. (2) concentrations of trace metals in precipitation and throughfall were much lower in snow than in rain, and total fluxes only account for less than 7% of total annual fluxes. Therefore, the fluxes did not differ between precipitation and throughfall in the winter. Consistent with our hypothesis, the results indicated that the annual fluxes of most trace metals (e.g., Zn, Cd, Cr, Cu and Pb) under the gap-edge canopy were higher than those under the closed canopy. Under the gap-edge canopy, the edge affects the wind speed and increases air turbulence, increasing the dry deposition velocities via inflow and advection processes. In addition, the surface of coniferous leaves has a strong capacity to trap dry-deposited particulates [30,31]. As a result, precipitation can wash off more metal particles from a gap-edge canopy than from a closed canopy. In the present study, the throughfall deposition of Zn, Cd, Cr, Cu and Pb under the gap-edge canopy was significantly enhanced relative to that under the closed canopy. The throughfall deposition of Zn, Cd, Cr, Cu and Pb under the gap-edge canopy was 1.20-, 0.14-, 1.57-, 1.05- and 2.68-fold higher, respectively, than that under the closed canopy. Canopy gaps have higher air temperatures and higher levels of solar radiation than do closed forest areas, and evaporation from leaves is another important factor contributing to increased metal concentrations in throughfall [32,33]. Accordingly, the concentrations of Cd, Cr and Pb under the gap-edge canopy were 1.31-, 1.43- and 1.43-fold higher, respectively, than those under the closed canopy.

The net throughfall input is the combined result of leaching and uptake by the canopy [10]. These processes are affected by vegetation type. For example, in pine-oak and oak forests, the elements Fe and Mn in throughfall were primarily derived from leaching. However, in our study, filtering was often the result of trace-metal leaching (except in the case of Mn). This result indicated that the trace metals were filtered (e.g., adsorbed or retained) by the canopy. The concentration of Mn under the closed canopy was 1.11- and 2.38-fold higher than that reported under a pine-oak forest and an oak forest, respectively [34]. In addition, Zn, Fe, Cu, Cd, Cr and Pb were filtered by the gap-edge canopy and the closed canopy, and the net filtering ratios of these metals were higher for the closed canopy than for the gap-edge canopy. In two evergreen oak stands in Spain, the net filtering ratio of Zn was

30.25% and 25.00% lower than that in our study [9]. In addition, the net filtering ratio of Al was 36.09% for the gap-edge canopy, and 49.70% of the Al was leached from the closed canopy during the rainy season. However, in the snowy season, the net filtering ratios of all trace metals exceeded 50%. There are two mechanisms by which foliar structures filter metals: (1) through the absorption and internalization through the cuticle and (2) through the penetration of metals through the stomatal pores [35]. Stomatal openings and cuticle expansion allow high levels of metal penetration from the atmosphere [36]. Canopy retention of Zn and Cd has been reported in previous studies [37,38], and some studies have reported canopy uptake of Zn, Cd, Cu and Pb [39]. Nonessential trace metals, such as Pb [40,41], Cd [42] and Cr [43], can also enter plant leaves via foliar transfer. These metals can penetrate cuticles and accumulate in leaf tissues. In a mid-subtropical forest, the filtration ratios of Pb and Cd by the canopy exceeded 80%, which is higher than that observed in the present study for the gap-edge canopy and closed canopy [44]. Among the essential trace metals, Mn presented the highest levels of leaching for both canopies in the rainy season, and this pattern, observed elsewhere, has been widely attributed to canopy leaching [10,37,45–49]. Additionally, the enrichment factor of Mn demonstrated high Mn enrichment in throughfall. A similar phenomenon was observed by Gandois [50], who attributed the results to internal cycling [37].

5. Conclusions

The forest canopy can be regarded as a self-regulating system that filters certain trace metals in deposited precipitation. The annual flux of trace metals in precipitation was $17.83 \text{ kg} \cdot \text{ha}^{-1}$, and the flux in the rainy season accounted for 93.55% of the total. The trace metals in precipitation were filtered by the closed canopy and gap-edge canopy, with filtration percentages of 4.30% and 21.94%, respectively. Snowfall in the snowy season accounted for 6.45% of the precipitation, and 73.95% and 75.11% of the trace metals in precipitation were filtered by the closed canopy and gap-edge canopy, respectively. Regarding essential trace metals, the closed canopy filtered 49.23%, 23.47%, 24.22%, 60.33%, 53.50% and 46.81% of the Zn, Fe, Cu, Pb, Cd and Cr, respectively, whereas the gap-edge canopy leached 19.75% of the Mn, and it filtered 23.75%, 39.20%, -23.93% , 20.62%, 35.95%, 32.58% and 26.70% of the Al, Zn, Fe, Cu, Pb, Cd and Cr, respectively. However, all of the trace metals demonstrated high net filtering ratios for both the gap-edge canopy and closed canopy in the snowy season. These results provide new insight into the filtration effects of subalpine forest on trace metals deposited via precipitation, and they can inform efforts to protect water quality in the upper reaches of the Yangtze River.

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