

**Hydrochemical Fluxes in Rainfall, Throughfall, and Stemflow in *Pinus sylvestris* var.  
*mongolica* Plantation, northeast China**

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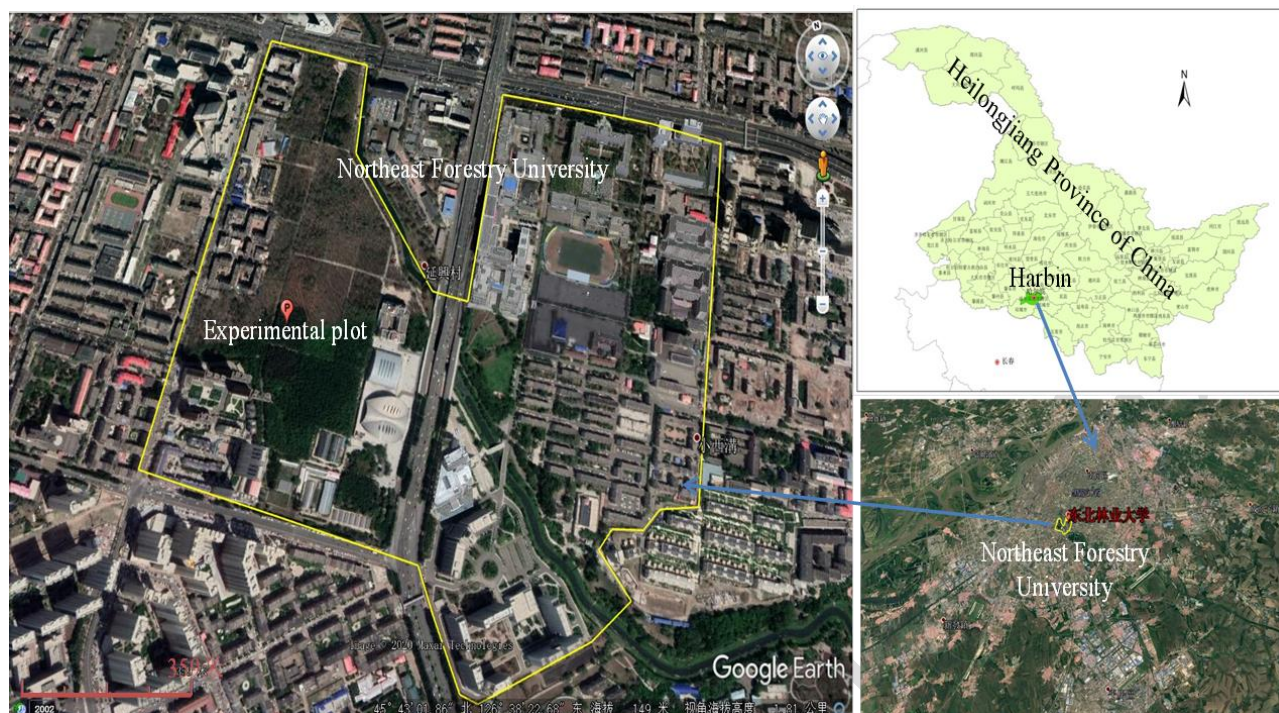
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## GRAPHICAL ABSTRACT



## ABSTRACT

Rainfall is one of the primary sources of chemical inputs in forest ecosystems, and the basis of forest nutrient cycling. To explore the variations of nutrient cycling and nutrient balance in rainfall redistribution process in urban forest ecosystem, we investigated the chemistry of rainfall, throughfall and stemflow in a plantation of *Pinus sylvestris* var. *mongolica* distributed in Harbin city of Northeastern China. Mean nutrient concentrations in stemflow were higher than in throughfall and rainfall. Over the growing season observation, the ions ( $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , K, Ca and Mg) fluxes in rainfall, throughfall and stemflow were  $64.021 \text{ kg}\cdot\text{ha}^{-1}$ ,  $44.928 \text{ kg}\cdot\text{ha}^{-1}$  and  $15.414 \text{ kg}\cdot\text{ha}^{-1}$  respectively. The net throughfall and stemflow deposit was  $-3.679 \text{ kg}\cdot\text{ha}^{-1}$ , in the growing season. The ion input in precipitation, throughfall and stemflow were mainly  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and Ca, and the canopy of *P. sylvestris* var. *mongolica* plantation can wash off  $\text{NO}_3^-$  and Mg in rainfall, but retain  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , K and Ca slightly. Our findings will facilitate a greater understanding of nutrient balance in canopy water fluxes in an urban area.

**Keywords:** urban forest, aqueous fluxes, canopy filtering, water chemistry, macronutrients input

## 1. Introduction

The rainfall interception and redistribution by forest canopy is very important to water cycles of forest ecosystem (Sheng and Cai, 2019). It not only changes the spatial distribution of rainfall inputting in the forest (Michopoulos *et al.*, 2018), but also alters the chemical characteristics of rainwater passing through forest canopy which accumulated nutrients by dry deposition (Lindberg *et al.*, 1986; Lovett *et al.*, 1993), and then affects the forest ecosystem biochemical cycles (Rodrigo *et al.*, 2003; Sheng *et al.*, 2015). With the intensity of global climate change, variation in rainfall patterns (amount and seasonality) will become more frequent and intense, and the changes can affect nutrient cycling in forest ecosystem (Su *et al.*, 2019). Therefore, a comprehensive understanding of the relationship between the rainfall and nutrient cycling in forest ecosystem is crucial to explore forest water conservation function, mechanism of forest purifying water quality and quantify the ecosystem service functions.

The rainfall is an important source of nutrients in forest ecosystems (Su *et al.*, 2019). In recent years, researches on forest hydrochemical characteristics have attracted more attention (Lu *et al.*, 2015; Lu *et al.*, 2017; Su *et al.*, 2019; Tan *et al.*, 2018; Tan *et al.*, 2019), and have become the hotspot in the field of forest hydrology. Over the past several decades, a large number of studies focus on rainfall redistribution by different natural forests in different regions (Wei *et al.*, 2005; Llorens *et al.*, 2007; Komatsu *et al.*, 2008; Magliano *et al.*, 2018; Nytch *et al.*, 2019). Although some studies have explored the rainfall distribution and hydrochemistry in different types of plantation ecosystems (Crockford *et al.*, 1996; Ma *et al.*, 2007; Li *et al.*, 2019), there are few studies and discussions on forest hydrochemistry in northeast China, especially on hydrochemical fluxes in an urban forest which under a complex and changeable environment.

The *Pinus sylvestris* var. *mongolica* is listed as an important tree species for the 3-Norths Shelter Forest Program in China due to its well-adapted characteristic and resistance to drought and barren and well-adapted. The community formed by *P. sylvestris* var. *mongolica* has significant effects on preventing wind, stabilizing soil, improving soil moisture and nutrient (Cao *et al.*, 2018), and plays

an important role in controlling desertification and protecting the farmland (Li *et al.*, 2015). *P. sylvestris* var. *mongolica* as the main tree species for carbon sequestration and desertification control, in addition to some research focuses on hydrological function of soil (Cao *et al.*, 2018) and litter layer (Wang *et al.*, 2015), there are few studies on the ecohydrologic process of the plantation ecosystems, especially in water chemistry of forest ecosystem hydrological processes (Wu *et al.*, 2019; Michopoulos *et al.*, 2020). So far, it has only been reported by Zhao *et al.* (2006) in the eastern mountains of Heilongjiang Province of China, but the hydrochemical fluxes along with rainfall redistribution process in *P. sylvestris* var. *mongolica* plantation ecosystem are not completely clear. Therefore, it is necessary to monitor the hydrochemical characteristics of each component in the rainfall redistribution process of *P. sylvestris* var. *mongolica* plantation.

Within this context, in this study, the rainfall, throughfall, and stemflow in the *P. sylvestris* var. *mongolica* plantation in Harbin city were monitored. Additionally, we measured the nutrient deposit of the *P. sylvestris* var. *mongolica* plantation to (1) analyze and evaluate the concentration of seven nutrients in rainfall, throughfall, and stemflow; and (2) to compare and evaluate nutrient deposit and nutrient exchange characteristics of the *P. sylvestris* var. *mongolica* plantation in an urban environment.

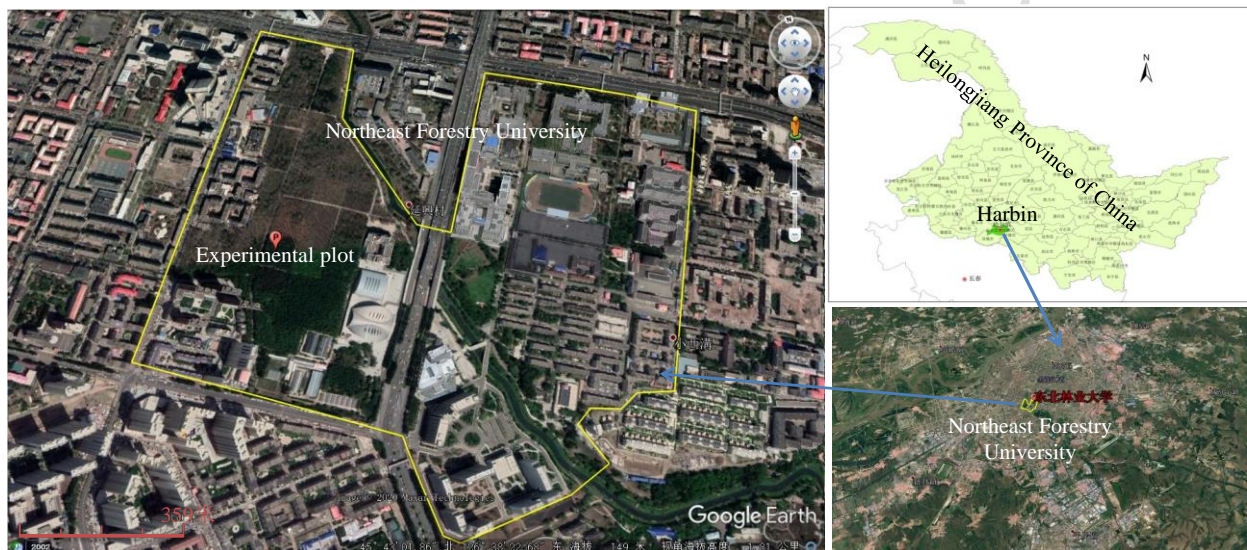
## **2. Materials and methods**

### *2.1. Site Descriptions*

This study was carried out during the growing season (May to October) of 2015 within a *P. sylvestris* var. *mongolica* plantation in Northeast China. The study area was located in the Urban Forest Demonstration Base of Northeast Forestry University, in Heilongjiang Province in Northeast China (126°37'15"E; 45°43'10"N). The Base is located in the urban area of Harbin, covering an area of 44 hm<sup>2</sup>, in which the *P. sylvestris* var. *mongolica* plantation area is about 0.5 hm<sup>2</sup> (figure 1). Harbin has a temperate continental monsoon climate, with an average annual temperature of 3.5°C. The average annual precipitation (1995-2010) is 500.1 mm, and the precipitation is mainly concentrated from June to August, accounting for 60~70% of the annual precipitation. The average

annual water surface evaporation is 726mm. The soil of the site was Haplic Phaeozem (FAO) and the pH value was about 6.48.

The *P. sylvestris* var. *mongolica* plantation was formed in 1957 with two-year seedling cavernous colonization. After more than 50 years of tending and management, the forest canopy density was 0.80, the tree heights were  $17.5 \pm 1.6$  m (mean  $\pm$  s.d.) with  $20.1 \pm 1.2$  cm diameter at breast height (DBH), and density was 1140 tree/ha. The understory species include *Lonicera maackii*, *Rhamnus ussuriensis*, *Ixeris polycephala*, and the sapling of *Fraxinus mandshurica*, *Phellodendron amurense* etc., and the ground coverages is 10%-50%.



**Figure 1.** Locations of the study area and observation plot

## 2.2. Sampling design

We collected samples from every rainfall events in the growing season of 2015. The precipitation ( $P$ ) was monitored using a tipping-bucket rain gauge (HOBO RG3-M, 0.2 mm/tip), which was installed on the roof platform (300m away from the sample site). There are also three collectors (cross sectional area is  $314.16\text{cm}^2/\text{collector}$ , the same below) located in an open area adjacent to the study plot to sample for chemical analysis.

To measure throughfall, we set up a  $20\text{m} \times 20\text{m}$  observation sample plot in the central area of the *P. sylvestris* var. *mongolica* plantation. The throughfall ( $T_f$ ) was collected and measured using 13 collectors across the plot. The collectors are crossed at the center of the plot, and the distance

between any adjacent collectors is 2 m in the same direction. Throughfall collectors were set up 50 cm above the forest floor to avoid understory effects and were evenly distributed at fixed positions throughout the growing period. At the end of each rainfall, the volume of rainwater in every gauge was immediately measured and the samples were collected for chemical analysis. Measurements unit was mm, equivalent of 1 liter of the water per square meter.

The stemflow ( $S_f$ ) was collected using a halved rubber collar, which spirally wrapped around each selected tree stem (Sheng *et al.*, 2019). The bottom part of the rubber collar was kept intact, and the collected stemflow was funneled into a plastic jug nearby the base of stem (Su *et al.*, 2019). Due to the similar diameter at breast height of trees in the plantation, 5 typical (non-dominant or pressed wood) *P. sylvestris* var. *mongolica* were selected as the monitored standard trees representing the mean growth of the plantation. After each rainfall, we immediately measured the volume of rainwater and collected samples for chemical analysis.

### 2.3. Chemical Analysis

The collected samples after each rainfall event were firstly placed in clean polyethylene bottles. Soon after, the samples were rapidly transported to the laboratory where they were filtered using qualitative filter paper and then were divided into two parts. One sample was directly used to measure the concentrations of anions (i.e.,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) by ion chromatograph (Metrohm 883), and the other sample was adjusted to a pH of 1~2 with high-purity grade (GR) nitric acid for measuring the concentrations of metal elements (i.e., K, Ca and Mg) by atomic absorption spectrometer (Thermo Scientific ICE-3500).

### 2.4. Data Analysis

The stand throughfall depth (mm) was calculated by the average value of the 13 throughfall collectors. The stand stemflow depth (mm) can be estimated according to the stemflow of standard trees, the tree number and the area of the studied plot (Equation (1)).

$$S_f = \frac{N \cdot S}{A \cdot 10^4} \quad (1)$$

where  $Sf$  is the stemflow volume (mm),  $N$  is the trees number in the plot,  $S$  is the average stemflow value (mL) of the 5 standard trees, and  $A$  is the area of the studied plot ( $m^2$ ).

The rainfall interception ( $I$ ) was estimated using the wet-canopy water balance equation as follows:

$$I = P - Tf - Sf \quad (2)$$

On a rainfall event basis, the volume-weighted mean E (VWME) of rainfall, throughfall and stemflow were calculated according to Equation (3). The input of a given nutrient was estimated according to Equation (4). See reference (Su *et al.*, 2019) for details.

$$VWM_E = \frac{\sum_{n=1}^i C_{i,E} \cdot V_{i,E}}{\sum_{n=1}^i V_{i,E}} \quad (3)$$

where  $VWM_E$  represents the mean concentration of a chemical element or compound ( $mg \cdot L^{-1}$ ),  $C_{i,E}$  represents the concentration at collector  $i$  for event  $E$  ( $mg \cdot L^{-1}$ ),  $V_{i,E}$  represents the rainfall, throughfall, and stemflow amount at collector  $i$  for event  $E$  (mm).

$$F = \frac{VWM_E \cdot V}{100} \quad (4)$$

where  $F$  represents the input of a certain element or compound ( $kg \cdot ha^{-1}$ ), and  $V$  represents the total volume of bulk precipitation, throughfall or stemflow (mm).

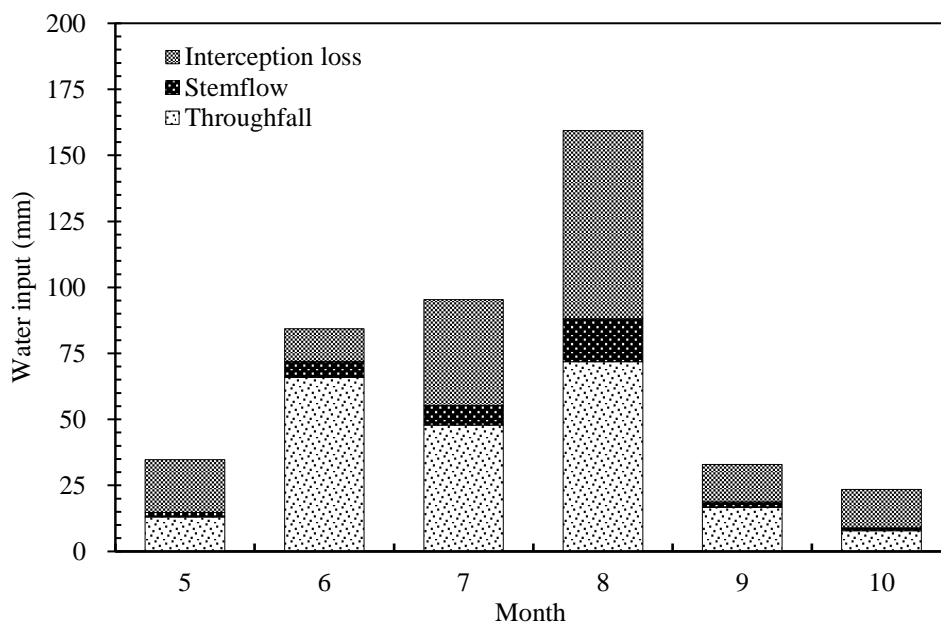
The total input is the sum of the solute in the throughfall and stemflow, and the difference value of the total input and rainfall input is regarded as the rainfall loading (Su *et al.*, 2019).

### 3. Results

#### 3.1. Hydrological Fluxes

From 1 May to 31 October, there were 31 discrete rainfall events occurred. The rainfall, throughfall, and stemflow of each month are shown in Fig. 2. The total rainfall during this period was 430.2 mm, and the maximum and minimum rainfall inputs were recorded in August (159.4 mm) and October (23.5 mm), respectively. The total throughfall was 223.1 mm, and the proportion occurring as throughfall ranged from 33.19% to 78.17% with a mean of 51.86%. The total stemflow amount was only 34.6 mm, accounting for 4.68% of rainfall in May, and 10.16% in August, which accounted for

a total of 8.04% of total rainfall across the study period. The total interception loss was 172.5 mm, representing 40.10% of total rainfall (Fig. 2).



**Figure 2.** Monthly input of water via throughfall, stemflow and interception loss

### 3.2. Chemistry of Canopy Water fluxes

The volume-weighted mean concentration of all solutes in the rainfall, throughfall, and stemflow are shown in Table 1. Most of the elements and compounds were more concentrated in throughfall and stemflow, except for  $\text{Cl}^-$  and Ca, whose concentration in rainfall were slightly larger than those in throughfall, and lower than those in stemflow.

Among the various nutrients in rainfall, the maximum and minimum values of concentration were  $4.508 \text{ mg}\cdot\text{L}^{-1}$  (Ca) and  $0.266 \text{ mg}\cdot\text{L}^{-1}$  (Mg), respectively, and the maximum is 16.95 times greater than the minimum. The concentrations of the solutes in rainfall showed a descending order as  $\text{Ca} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{K} > \text{Cl}^- > \text{Mg} > \text{PO}_4^{3-}$ .

Compared with the bulk precipitation, the ions concentrations in the throughfall has been increased to varying degrees just as  $\text{NO}_3^-$  increased by 127.52%,  $\text{PO}_4^{3-}$  3.72%,  $\text{SO}_4^{2-}$  41.21%, K 7.97% and Mg 76.36% respectively. The concentrations of all 7 solutes were also greater in stemflow than in throughfall. Compared to throughfall,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , K, Ca and Mg were enhanced in



stemflow by 63.20%, 39.98%, 26.30%, 101.40%, 236.37%, 249.12% and 354.47%, respectively (Table 1).

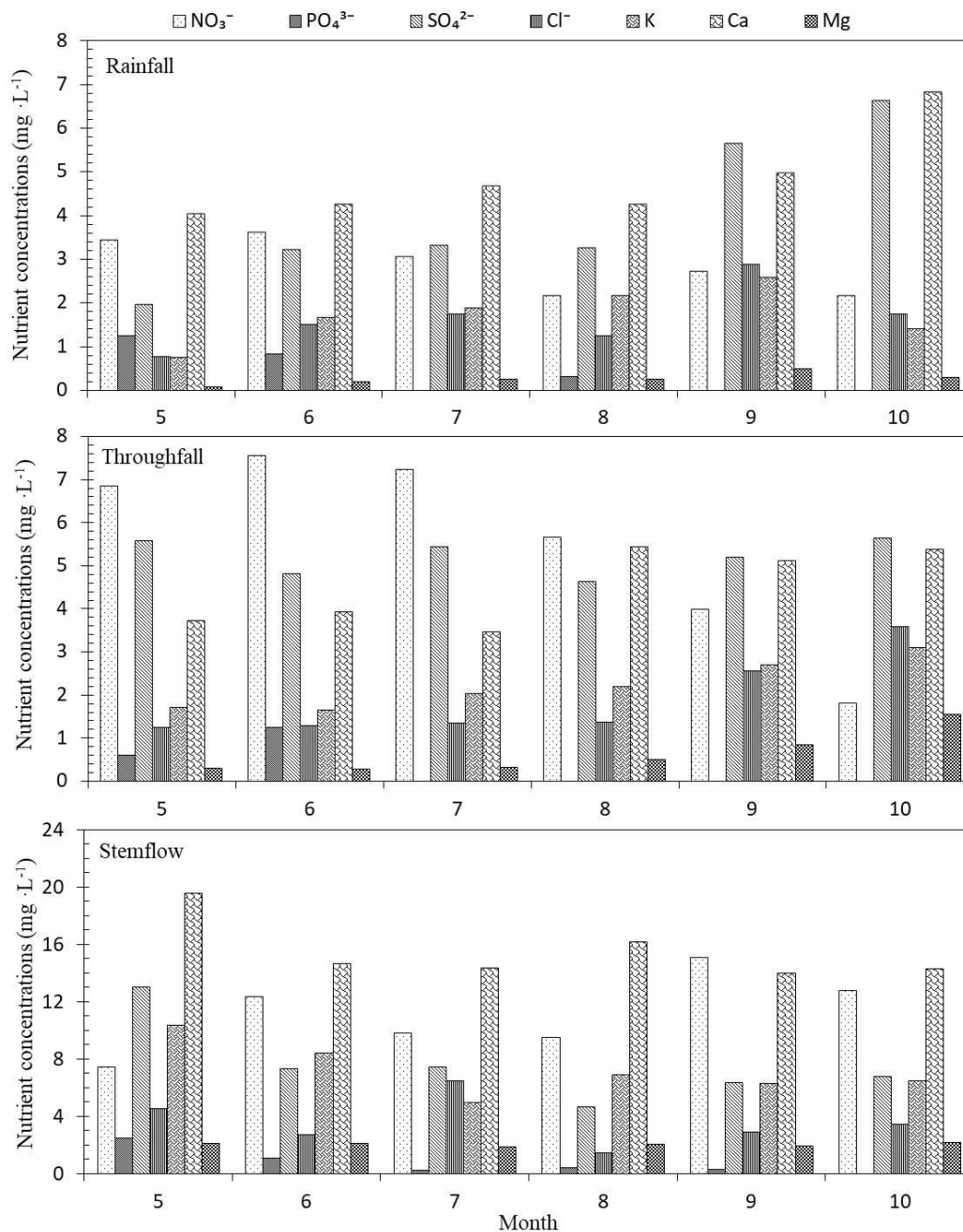
**Table 1.** Chemical characteristics of water in rainfall, throughfall and stemflow during the monitoring period. (Values represented means  $\pm$  standard error)

Chemical Variable	Concentrations (mg L <sup>-1</sup> )		
	Rainfall	Throughfall	Stemflow
NO <sub>3</sub> <sup>-</sup>	2.793 $\pm$ 0.622	6.355 $\pm$ 2.231	10.372 $\pm$ 2.750
PO <sub>4</sub> <sup>3-</sup>	0.384 $\pm$ 0.527	0.399 $\pm$ 0.513	0.558 $\pm$ 0.892
SO <sub>4</sub> <sup>2-</sup>	3.529 $\pm$ 1.753	4.983 $\pm$ 0.417	6.294 $\pm$ 2.841
Cl <sup>-</sup>	1.518 $\pm$ 0.701	1.495 $\pm$ 0.962	3.011 $\pm$ 1.747
K	1.885 $\pm$ 0.629	2.035 $\pm$ 0.567	6.846 $\pm$ 1.882
Ca	4.523 $\pm$ 1.031	4.430 $\pm$ 0.902	15.465 $\pm$ 2.140
Mg	0.412 $\pm$ 0.137	0.589 $\pm$ 0.494	1.340 $\pm$ 0.110

### 3.3. Temporal Dynamics of Water fluxes

The nutrient concentration responding to the rainfall, throughfall, and stemflow are shown as volumeweighted mean solute concentrations for each monthly period (Fig. 3). For rainfall, the highest concentration of the 7 solutes is 6.821 mg  $\cdot$  L<sup>-1</sup> (Ca), and the lowest value is 0 mg  $\cdot$  L<sup>-1</sup> (PO<sub>4</sub><sup>3-</sup>). Although the concentration of PO<sub>4</sub><sup>3-</sup> is low, but the changes are huge and special, especially the concentration of PO<sub>4</sub><sup>3-</sup> in July and September both are 0 mg  $\cdot$  L<sup>-1</sup>. Except PO<sub>4</sub><sup>3-</sup>, the highest concentration of the other 6 solutes in the rainfall, appeared for NO<sub>3</sub><sup>-</sup> in June, SO<sub>4</sub><sup>2-</sup> and Ca in October, and Cl<sup>-</sup>, K and Mg in September. In terms of the lowest value, Mg, Cl<sup>-</sup>, K, SO<sub>4</sub><sup>2-</sup> and Ca appeared in May, and NO<sub>3</sub><sup>-</sup> appeared in October. Among the concentration of other 6 solutes, NO<sub>3</sub><sup>-</sup> had the highest coefficient variation (CV, 73.8%) while Ca had the lowest CV (26.5%) (Table 2). The CVs of these 6 solutes ranked as follows: NO<sub>3</sub><sup>-</sup> > Mg > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > K > Ca.

In throughfall, NO<sub>3</sub><sup>-</sup> has the highest concentration (7.542 mg  $\cdot$  L<sup>-1</sup>), PO<sub>4</sub><sup>3-</sup> has the lowest concentration (0 mg  $\cdot$  L<sup>-1</sup>), and the concentration of PO<sub>4</sub><sup>3-</sup> in July, August and September are all 0 mg  $\cdot$  L<sup>-1</sup>. Among the 6 solutes (except PO<sub>4</sub><sup>3-</sup>), Mg had the highest CV (82.0%) while K had the lowest CV (41.9%) (Table 2). The CVs of these 6 solutes showed the following trend: Mg > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Ca > SO<sub>4</sub><sup>2-</sup> > K, which is quite different from that in rainfall.



**Figure 3.** Monthly concentrations of solutes in rainfall, throughfall and stemflow

For stemflow, the maximum and minimum values of concentration were 19.569 mg·L<sup>-1</sup> (Ca) and 0.106 mg·L<sup>-1</sup> (PO<sub>4</sub><sup>3-</sup>), respectively, and the maximum is 184.61 times greater than the minimum. The PO<sub>4</sub><sup>3-</sup> concentration each month was not negligible. Among 7 solutes, PO<sub>4</sub><sup>3-</sup> had the highest CV (109.2%) while Ca had the lowest CV (42.3%) in terms of concentration (Table 2). The CVs of these 7 solutes ranked as follows: PO<sub>4</sub><sup>3-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> > K > Mg > Ca.

**Table 2.** The CVs of the solutes in in rainfall, throughfall and stemflow

Parameter	CV (%)						
	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	K	Ca	Mg
Rainfall	73.8	-	57.9	60.9	53.7	26.5	68.3
Throughfall	52.7	-	42.1	54.2	41.9	46.3	82.0
Stemflow	63.0	109.2	64.2	61.5	47.8	42.3	42.6

### 3.4. Nutrient Input

We observed large variation in nutrient inputs within the *P. sylvestris* var. *mongolica* plantation. The inputted nutrient volume and rainfall loading are shown in Table 3. The highest inputted nutrient via throughfall was NO<sub>3</sub><sup>-</sup>, while Ca was the largest input for rainfall and stemflow. In rainfall, the input of 7 solutes during the study period is 64.021 kg·ha<sup>-1</sup>, of which the inputs of Ca, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were relatively large and accounted for the total rainfall input by 30.39%, 23.71% and 18.77%, respectively.

The total input of 7 solutes fluxes during the study period is 60.342 kg·ha<sup>-1</sup>, and the sequence of the 7 solute input fluxes was: NO<sub>3</sub><sup>-</sup> > Ca > SO<sub>4</sub><sup>2-</sup> > K > Cl<sup>-</sup> > Mg > PO<sub>4</sub><sup>3-</sup> (Table 3).. During the study period, the rainfall loading of 7 solutes fluxes is -3.679 kg·ha<sup>-1</sup>, and the amount of rainfall loading are sorted from largest to smallest as NO<sub>3</sub><sup>-</sup> > Mg > PO<sub>4</sub><sup>3-</sup> > K > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > Ca. During the interaction of rainfall and canopy layer, only NO<sub>3</sub><sup>-</sup> and Mg were leached from the canopy, in other words, these two nutrients in rainwater were increased after passing through canopies and stems. Meanwhile, the PO<sub>4</sub><sup>3-</sup>, K, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and Ca were retained by the canopy, and the retained quantities were 0.571, 1.199, 1.885, 2.154 and 4.222 kg ha<sup>-1</sup>, respectively.

**Table 3.** Macronutrients fluxes in different type of water comparison to total input, and rainfall loading during the growing season

Parameter	Nutrient Input (kg ha <sup>-1</sup> )						
	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	K	Ca	Mg
Rainfall	12.017	1.654	15.180	6.532	8.109	19.456	1.073
Throughfall	14.179	0.890	11.117	3.336	4.541	9.883	0.982
Stemflow	3.589	0.193	2.178	1.042	2.369	5.351	0.692
Total input	17.768	1.083	13.295	4.378	6.910	15.234	1.674
Rainfall loading	5.751	-0.571	-1.885	-2.154	-1.199	-4.222	0.601

## 4. Discussion

The interaction between rainfall and forest canopy can change the contents of compounds and elements (Tan *et al.*, 2018). Forest canopy can absorb atmospheric dry deposition, especially in an urban environment. While the rainfall was redistributed by forest canopy, the processes of absorption, adsorption, and leaching occurred between the rainwater and the forest canopy, which changed solute concentration in different hydrological components to varying degrees. In this study, the concentration of  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and Ca with a concentration sequence of stemflow > Rainfall > throughfall, at the same time,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , K and Mg with a sort order of stemflow > throughfall > rainfall. Those orders do not exactly agree with the results of stemflow > throughfall > rainfall in previous studies (Sheng *et al.*, 2015; Lu *et al.*, 2015; Lu *et al.*, 2017), but being consistent with the results of some recent studies. For example, in the hydrological process of evergreen and deciduous broad-leaved mixed forest, the concentration of  $\text{NO}_3^-$  followed a sort order of stemflow > rainfall > throughfall, for Ca and  $\text{Cl}^-$ , the orders became stemflow > throughfall > rainfall, while Mg and K concentrations are consistent with this study (Su *et al.*, 2019). In the secondary deciduous broad-leaved forest, the concentration rank of K in different hydrological component is consistent with this research, and Ca is: stemflow > throughfall > rainfall (Zhang *et al.*, 2019). However, in the *Pinus tabulaeformis* plantation, even the same solute in different hydrological component has different pattern at different stages of growth (Li *et al.*, 2019). Although stemflow has low quantities of water, it is important for plant growth, especially in arid and semi-arid areas (Carlyle-Moses *et al.*, 2018; Liu *et al.*, 2019; Li *et al.*, 2020). Previous studies have shown that the concentration characteristics of throughfall and stemflow depend on the interaction between atmospheric deposition and plants (Corti *et al.*, 2019), and are affected by rainfall characteristics (Zhang *et al.*, 2019), solute chemical activity and plant physiological characteristics (Tobón *et al.*, 2004; Van Stan II *et al.*, 2015). Normally, the compounds and elements concentrations in stemflow are higher than in throughfall (Su *et al.*, 2019). This is due to the sufficiently long residence times of the intercepted precipitation on the branch surfaces, which is conducive to solutes dissolution, and the higher leachability of bark for stemflow than throughfall (Tan *et al.*, 2018; Carlyle-Moses *et*

*al.*, 2018). However, in this study, due to the complex and changeable urban environment, and the variable influencing factors in the hydrological process of the *P. sylvestris* var. *mongolica* plantation, the concentrations of solutes in rainfall are not constant. Therefore, the concentration changes of the solutes in throughfall and stemflow also have more uncertainties.

The input of nutrients by rainfall is of great significance to the nutrient cycle of forest ecosystems (Liu *et al.*, 2019; Leandro Van Langenhove *et al.*, 2020). In this study, the input of 7 solutes in total rainfall and total throughfall were 64.021 kg·ha<sup>-1</sup> and 44.195 kg·ha<sup>-1</sup>, respectively, which were much larger than that in total stemflow (15.414 kg·ha<sup>-1</sup>). The rainfall loading of 7 solutes fluxes is -3.679 kg·ha<sup>-1</sup>, and the rainfall loading of each solute is different. Only the rainfall loading of NO<sub>3</sub><sup>-</sup> and Mg are positive, and the others are all negative. The result indicates that the *P. sylvestris* var. *mongolica* plantation in Harbin can retain SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, K, Cl<sup>-</sup> and Ca. Many previous studies have found that the rainfall loading of the same solute in hydrological process has different results according to different forest types in different regions. For example, in the evergreen and deciduous broad-leaved mixed forest (Shennongjia, Hubei province, China), the rainfall loading of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> are negative, and the rainfall loading of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, K, Ca and Mg are all positive (Su *et al.*, 2019). In the subtropical evergreen and deciduous broad-leaved mixed forest (The Mau Lancaster region, southwest China), the rainfall loading of Na and NH<sub>4</sub><sup>+</sup> are negative, the Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, K, Ca and Mg are all positive (Lu *et al.*, 2015), and except for NO<sub>3</sub><sup>-</sup>, it is consistent with the results of Su *et al.* (2019). In *Pinus densata* natural forest of southeast Tibet, the rainfall loading of N is negative, the P, S, K, Ca and Mg are all positive (Lu *et al.*, 2017). The rainfall loading of Ca in broad-leaved korean pine forest (Xiaoxing'an Mountains) is consistent with all above, but in the secondary deciduous broad-leaved forest (Changbai Mountains) (Zhang *et al.*, 2019) and in the secondary birch forest (Xiaoxing'an Mountains) are the opposite, negative (Sheng *et al.*, 2015). Generally, given the low content and slow-release rate, the dissolution degree of Ca is not as good as that of K, and the input of K by throughfall and stemflow should be greater than Ca (Su *et al.*, 2019). In this study, the ions retained by *P. sylvestris* var. *mongolica* canopy, probably results from the

particulate matter (PM) in the urban atmosphere, just as Berger et al. (2008) reported that the suspended pollen is a vital factor of influencing the flux of  $K^+$ . Urban forests have been proven to be efficient PM collectors and to improve air quality (Xu *et al.*, 2019). PM has strong adsorption and elements such as Ca, Mg and K are mainly found in the particles with large diameters. Therefore, the throughfall and stemflow contain a lot of particulate matter. When we filter the water for measuring the concentrations of ions, the large particles will be retained by the filter paper, thus reducing the ion concentration in the water. All those factors led to the input of 7 solutes by total rainfall, throughfall and stemflow in this study are all dominated by  $NO_3^-$ ,  $SO_4^{2-}$  and Ca, and the sum of total input by these three solutes accounts for more than 69% of the total inputs sum of 7 solutes.

This article has carried out observation and research on the hydrological process of *P. sylvestris* var. *mongolica* plantation in an urban area. However, due to the randomness of rainfall events, the complex environment of city, human activities and other factors have a greater impact on forest hydrochemical process. Therefore, long-term situ observations and more research are needed to verify the conclusions in this study using only one growing season data. In particular, the compounds such as  $SO_4^{2-}$ ,  $PO_4^{3-}$  and  $Cl^-$ , which have been less studied in the past, as well as hydrochemical fluxes in solid precipitation (eg. snow) needs to be further studied in detail.

## 5. Conclusion

This study of 7 nutrient solutes in open field rainfall and its interaction with forest cover provides new results on nutrient flux in *P. sylvestris* var. *mongolica* plantation ecosystems. Throughfall and stemflow composition is highly influenced by forest cover. Nutrient concentrations were greatest for stemflow, followed by throughfall and rainfall. Rainfall contributed significantly to nutrient input, some fluxes might not be modified or even decreased ( $PO_4^{3-}$ , K,  $SO_4^{2-}$ ,  $Cl^-$  and Ca), whereas some others might be considerably increased ( $NO_3^-$ , Mg). Although here data just collected and analyzed for one growing season, the study gives evidence toward rainfall being an important

nutrient source within the *P. sylvestris* var. *mongolica* plantation. Further studies are needed to explore the characteristic of more nutrient fluxes during rainfall redistribution process.

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