Difference between rainfall and throughfall chemistry for different forest stands in the Qinling Mountains, China

Shengli Zhang, Jinxin Yu, Taichen Pan, Xiaoxiao Gao, Zhibin Qiu and Lin Hou

ABSTRACT

This study compared the effects of four forest canopies on throughfall chemistry in the Qinling Mountains, China. Rainfall and throughfall samples were collected in stands of *Quercus aliena* (Qa) var. *Acuteserrata*, *Pinus tabulaeformis* (Pt), *P. armandii* (Pa), and mixed broad-leaved (Mb) trees from 2009 to 2011. The results indicated that the pH of the rainfall, which was mildly acidic, increased as it passed through the forest canopy. The pH increased more within the broad-leaved forest canopy than the coniferous forest. Concentrations of SO_4^{2-} decreased as rainfall passed through the Qa canopy but increased after passing through the other species. The concentrations of NO_3^- and Zn, Cd and Pb decreased as rainfall passed through the four canopies. The coniferous forest canopy was more effective than the broad-leaved forest in reducing NO_3^- in rainwater. The decreases in Cd concentrations were similar among the four canopies. The Pb concentration decreased the most among the heavy metals, and the order of the decrease was Qa > Pt > Pa > Mb. The results may provide a basis for the selection of tree species for afforestation in water sources in the Qinling Mountains and similar areas.

Key words | forest, heavy metal, Qinling Mountains, rainfall, throughfall, water chemistry

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HIGHLIGHTS

- The broad-leaved forest canopies increased acidic rainfall pH more than the coniferous forest canopies.
- The coniferous forest canopies were more effective in reducing NO_3^- in the rainwater.
- The order of canopy decreasing Pb concentrations was *Quercus aliena* > *Pinus tabulaeformis* > *P. armandii* > mixed broad-leaved trees.
- The decreases in Cd concentrations were similar among the four canopies.

INTRODUCTION

Many countries and regions in the world use forests as industrial and domestic water supply sources. Even if these forests are protected, pollutants can be transported over long distances by the wind (Zhang *et al.* 2012). Rainfall captures some pollutants and brings them into the forest ecosystem. The forest canopy can absorb some of the pollutants, causing NH_4^+, NO_x, and some heavy metal element concentrations in throughfall water to decrease (Ferm 1993; Gordon *et al.* 2000; Klopatek *et al.* 2006; Marty *et al.* 2012; Zhang & Liang 2012). This is mainly because the

forest canopy is the first part of the forest that comes into contact with precipitation, it is highly dynamic in the growing season, and the tree leaves have a large surface area (leaf area index = 3–10 m^2 m^{-2}; Ulrich *et al.* 1995) that is conducive to absorption (Gandois *et al.* 2010). Therefore, the forest canopy is a key layer of forest ecosystems in improving water quality (Tan *et al.* 1999; Liu *et al.* 2000; Zhang & Li 2006; Zhang & Li 2007; Zhang 2008; Zhang & Liang 2012). So far, there have been many studies about the effects of forest canopies on water chemistry or about forest canopy interceptions of atmospheric depositions such as NH_4^+, NO_x, and SO_2 (Balestrini & Tagliaferri 2001; Klopatek *et al.* 2006; Kopáček *et al.* 2009; Zhang & Liang 2012; Kowalska *et al.* 2016). These studies were conducted mainly in Europe, the United States, Canada, East Asia, and West Asia. However, there has been less research focused on how heavy metal concentrations are affected by forests (Avila & Rodrigo 2004; Hou *et al.* 2005). The extent to which the canopy affects throughfall water chemistry depends on many factors, such as the vicinity of emission sources and natural conditions, including plot elevation, terrain orography, and plant type, age, and vigor (Balestrini & Tagliaferri 2001; Zimmermann *et al.* 2006). Tree stand types, especially tree species, are an important factor affecting the chemical composition of throughfall (Kowalska *et al.* 2016). Different tree species have unique functions in reducing the pollutants in throughfall (Eisalou *et al.* 2013; Kowalska *et al.* 2016). So far, tree species that have been studied mainly include spruce and beech in Europe (Oulehle & Hruška 2005; Gandois *et al.* 2010), pine and oak in Poland (Kowalska *et al.* 2016), Douglas-fir (*Pseudotsuga menziesii*) in the United States, *Cryptomeria japonica* (Japanese cedar) (Sase *et al.* 2008) and *Pinus pumila* (Uehara *et al.* 2015) in Japan, and *Quercus aliena* (Qa) var. *Acuteserrata* (Zhao *et al.* 2015) and *P. massoniana* (Liu *et al.* 2000) in China. There are studies on individual tree species affecting water chemistry, but there are few comparative studies on different tree species growing in the same area during the same period. Therefore, understanding the characteristics of different tree species in terms of water quality changes is difficult because most of the studies were conducted under varying external conditions, such as different meteorological conditions and different pollution sources. As a result, providing an accurate basis

for selecting the correct tree species for afforestation in water-supplying forests is difficult.

This study was undertaken to quantify changes in water chemistry as rainfall passed through four main types of forest stand canopies in the Huoditang natural forest region, which is located in the central part of the Qinling Mountains, China. The study was conducted in a concentrated area where the pollution sources were the same, the local level of atmospheric pollution was affected by both common air pollutants and heavy metals, and environmental conditions were similar throughout. Thus, the results of this study may provide an accurate basis for the selection of tree species for afforestation projects in watersheds in the Qinling Mountains and act as a reference for similar areas. The results may also provide an understanding about the effects of these four different tree stand canopies on water quality and may be used in the management of forests as water sources.

MATERIALS AND METHODS

The study area

The Qinling Mountains are an important water source for the middle segment of China's South-to-North Water Transfer Project, which is a national strategic project. The mountains are primarily located in northwest China's Shaanxi Province. The mountains have rich deposits of Pb and Zn. The production rate of these metals in the Qinling Mountains ranks seventh nationally.

Heavy metal pollution from mining and smelting has become a serious problem in some parts of the Qinling Mountains (Zhang 2009), and acid rain has also become common in recent years in the surrounding areas (Zhang *et al.* 2012). Acid rain impacts Chongqing municipality the most (Hong 2001; Wu *et al.* 2006; Zhang 2007), but it also occurs in parts of Henan, Shaanxi, and Hubei provinces (Zhao *et al.* 2006; Wang *et al.* 2007). Some of these areas are far from the Qinling Mountains; however, wind can transport atmospheric pollutants to these mountains from great distances (Zhang *et al.* 2012).

The Qinling Mountains' forests cover only about 40% of the area because of historic overharvesting. Almost all the

forests are state-owned, and most of the forests are natural second-growth stands (Liu et al. 1996; Zhang & Liang 2012).

The Huoditang forest (Figure 1) was chosen for this study because its vegetation, soil, and topography are representative of other forests of the Qinling Mountains (Zhang et al. 2006, 2012; Zhang 2008; Zhang & Liang 2012). The Huoditang forest is located at mid-elevations on south-facing slopes in the Qinling Mountains. Runoff from the forest flows into the Ziwu River, a tributary of the Han River. The Han River accounts for over 70% of the flow into the Danjiangkou Reservoir, which comprises the water supply for the middle segment of China's South-to-North Water Transfer Project. The Huoditang forest covers 28.5 km^2 in Ningshan County, Shaanxi Province, and lies between latitudes of 33°13′ and 33°28′N and longitudes of 108°21′ and 108°39′E. Elevations in the forest range from 1,420 to 2,470 m above sea level. Slopes in the area range between 30 and 35°. The dominant soil type is brown forest soil with an average thickness of about 50 cm. The soil is primarily formed from granite, gneiss, metasandstone, and schist.

The Huoditang forest region is located in a warm temperate zone and has a humid mountain climate. Mean annual temperatures range from 8 to 10 °C. The mean annual precipitation is 1,130 mm. The rainy season is between July and September and accounts for 53% of the annual precipitation. Snowfall occurs between late October and early April, and the precipitation in this period accounts for 13% of the annual precipitation. The climate is dry in spring and humid in autumn. The average annual relative humidity is 77%.

The forest was harvested during the 1960s and 1970s; much of the area is now covered by dense natural secondary growth. The dominant tree species are Qa var. *acuteserrata*, *Pinus tabulaeformis* (Pt), *P. armandii* (Pa), *Betula albosinensis*, *B. luminifera*, *Picea wilsonii*, *Abies fargesii*, and *Populus davidiana*. The forest cover is 92% (the rest is roads and Huoditang forest farm office areas), and the canopy closure is >0.7. There is no cultivated land in or around the Huoditang forest region.

Water sampling

We determined the effect of the forest canopies on rainfall water chemistry by comparing rainfall and throughfall concentrations. We were especially interested in the concentrations of the metals related to Pb–Zn mining and smelting. Four different forest stands were chosen for our study: Qa (4.5 ha), Pt (8.4 ha), Pa (6.3 ha), and mixed broad-leaved (Mb) forest (4.1 ha) (Figure 1). The selected characteristics of the four stands are shown in Table 1.

The concentrations in throughfall change considerably when rainfall amounts are relatively small because the effect of the washing of dry deposition that accumulates in the canopy is large for small events (Avila & Rodrigo 2004; Zhang & Li 2007). Therefore, in this study, rainfall and throughfall samples were only analyzed for rainfall events of >20 mm (Zhang & Li 2007; Zhang 2009; Zhang & Liang 2012). The rationale for this threshold is that the canopy interception loss rate during a 20-mm rainfall event is approximately equal to the average loss rate of rainfall events in Huoditang forest (Chen et al. 2013). The greater the amount of a rainfall event, the lower the canopy interception loss rate (Chen et al. 2013).

Rainfall and throughfall water samples were collected in 8.5 L plastic buckets (funnel diameter is 20 cm) fitted with multiperforated PVC film covers to permit rainfall or throughfall water but prevent insects or vegetative debris
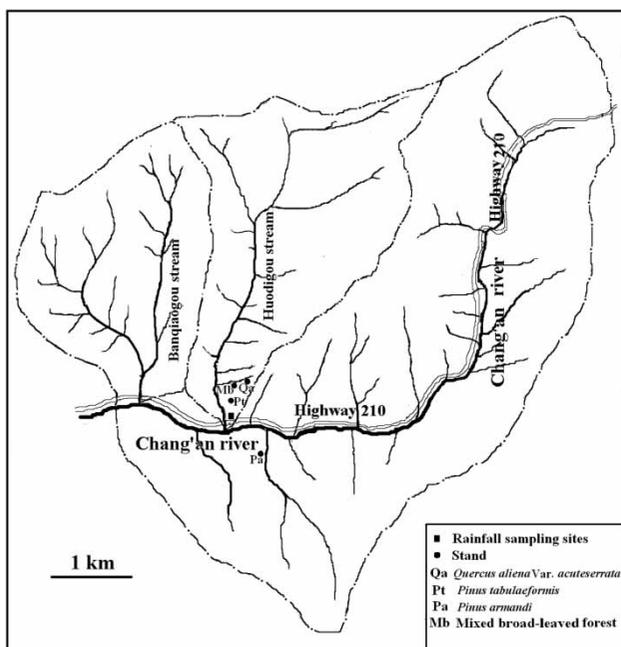
Figure 1 | Location of the stands in the Huoditang forest and a map of its drainage system.

Table 1 | Selected characteristics of the four forest stands in this study

Stand type	Elevation (m)	Aspect	Slope (°)	Stand density number (ha^{-2})	Stand age (years)	Canopy closure	Mean height of trees (m)	Mean DBH (cm)
Qa	1,680	SSW	37	2,900	62	0.7	13.5	15.2
Pt	1,600	SW	38	3,100	60	0.75	14	24.0
Pa	1,630	SSW	27	3,000	34	0.7	12	20.2
Mb	1,650	NNE	37	2,800	60	0.8	12.9	16.1

DBH, diameter at breast height.

from entering. The covers also minimized water loss due to evaporation. Rainfall collection sites were established at three unobstructed sites about 130 m to the left (east) of the Huodigou watershed outlet (Figure 1). The collection sites were approximately 1,200 m from a Qa stand, 800 m from a Pt stand, 500 m from a Pa stand, and 1,200 m from an Mb stand (Figure 1). Rainfall water was collected at the collection sites and mixed in the field within a day after a rainfall event. Part of the mixed water was taken as a rainfall sample. Throughfall was collected at three rectangular plots (5 m wide × 20 m long) within each stand. Three throughfall collection sites were assembled at the upper, middle, and lower portions of each plot, respectively. The plots were located in the upper, middle, and lower portions of each stand. The nine throughfall water samples collected in three plots of each stand were mixed. Part of the mixed water was taken as a stand sample. All the samples were volumetrically weighted.

The buckets were emptied and rinsed with clean stream water and then deionized water before each collection. Each collection represents one individual event.

All water samples were placed into 500 mL polyethylene bottles, taken to the laboratory within 24 h, and then stored below 0 °C until analysis.

The sampling periods were from May to October 2009, 2010, and 2011. The number of collections for each year varied depending on the number of rainfall events that were >20 mm. Six collections occurred in 2009, with seven in 2010 and eight in 2011.

Chemical analyses

The samples were melted and then filtered through 0.45 μm membrane filters before analysis. The pH of water samples was determined with a Delta 320 pH meter (Mettler-Toledo International Inc., Switzerland). The SO_4^{2-} concentrations in water samples were determined with a multiparameter spectrophotometer (NOV60, Analysis and Measurement Services Corporation, Italy). The NO_3^- and NH_4^+ concentrations were determined with an AA3 continuous flow analyzer (Bran + Luebbe Inc., Germany). The Ca^{2+}, Mg^{2+}, and K^+ concentrations were determined with an AA320 atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan). The Cu concentrations were determined with an AA-7000 graphite furnace atomic absorption spectrophotometer (GFAAS; Hitachi High-Technologies Corporation, Japan). The Pb, Cd, and Zn concentrations were determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES; Varian Inc., USA). For all samples, the reported concentrations are the mean of three measurements. Internal standards were used to check the accuracy of the GFAAS and ICP-AES analyses.

RESULTS AND DISCUSSION

Rainfall and throughfall pH

Rainfall pH in the Huoditang forest averaged 5.84 (Table 2) during the 3-year study period and ranged from a low of 3.93 on 9 June 2011 to a high of 7.82 on 6 September 2011. The pH generally increased as rainfall passed through the forest canopy (Table 2; Figure 2); the pH increased on average by 0.46, 0.45, 0.22, and 0.55 in the Qa, Pt, Pa, and Mb stands, respectively. These results indicate that when rainfall is weakly acidic (pH < 6.0), the Mb canopy increased the pH of the throughfall the most, followed by the Qa canopy, the Pt canopy, and then the Pa canopy.

Table 2 | Average pH and chemical concentrations

Chemical	Statistical parameter	Types of water				
		RF	Qa-TF	Pt-TF	Pa-TF	Mb-TF
pH	Mean	5.84	6.30	6.30	6.06	6.39
	Standard deviation	0.99	0.36	0.51	0.41	0.44
SO_4^{2-} (mg L^{-1})	Mean	30.7	29.67	37.37	34.14	31.07
	Standard deviation	28.11	17.48	45.58	28.84	28.13
NO_3^- (mg L^{-1})	Mean	0.21	0.17	0.15	0.10	0.15
	Standard deviation	0.25	0.29	0.15	0.16	0.19
NH_4^+ (mg L^{-1})	Mean	0.40	0.42	0.23	0.17	0.33
	Standard deviation	0.36	0.49	0.19	0.13	0.53
PO_4^{3-} (mg L^{-1})	Mean	0.09	0.23	0.13	0.13	0.15
	Standard deviation	0.04	0.29	0.05	0.08	0.09
Ca^{2+} (mg L^{-1})	Mean	1.94	2.86	2.25	2.44	2.95
	Standard deviation	1.60	1.84	1.04	1.05	1.33
Mg^{2+} (mg L^{-1})	Mean	0.26	0.83	0.47	0.73	0.75
	Standard deviation	0.25	0.75	0.31	0.47	0.46
K^+ (mg L^{-1})	Mean	2.59	4.56	2.85	4.01	3.97
	Standard deviation	3.95	3.09	3.06	3.29	2.55
Cd (µg L^{-1})	Mean	4.73	1.36	1.35	1.22	0.80
	Standard deviation	12.20	1.51	1.44	1.15	0.87
Pb (µg L^{-1})	Mean	18.19	5.58	6.64	6.66	10.80
	Standard deviation	30.94	5.79	6.75	6.78	26.88
Zn (µg L^{-1})	Mean	8.94	5.35	8.51	8.02	3.82
	Standard deviation	16.97	8.05	12.03	9.18	5.09
Cu (µg L^{-1})	Mean	3.41	3.14	4.02	3.07	3.87
	Standard deviation	3.20	2.42	2.90	2.44	2.35

RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand.
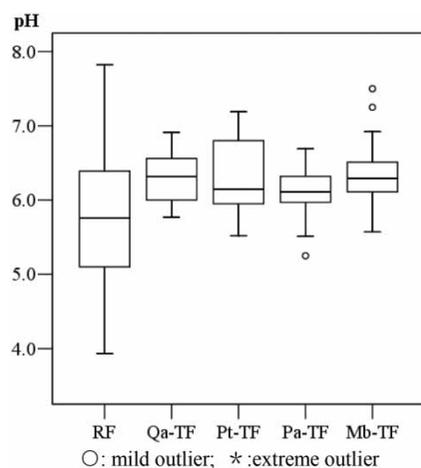
Figure 2 | The pH of rainfall and throughfall in four stands in the Huoditang forest. Abbreviations: RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand.

One explanation for the increase in pH as rainfall passed through the canopy is that base cations (e.g. Ca^{2+}, Mg^{2+}, and K^+) in leaf tissues can be exchanged for H^+ in the rainwater (Liu *et al.* 2000); this is dynamic especially during the growing season when the concentration of exchangeable base cations in leaves is relatively high (Li *et al.* 2007, 2010). A second explanation is that weakly basic anions leached from tree leaves neutralize the acidic cations in rainwater (Tao *et al.* 2007). As rainfall passed through the forest canopies, total base cation (Ca^{2+} + Mg^{2+} + K^+) concentrations increased by averages of 3.45, 0.77, 2.39, and 2.88 mg L^{-1} in the Qa, Pt, Pa, and Mb stands, respectively (see below for details). These changes are consistent with the increases in throughfall pH. The total base cation (Ca^{2+} + Mg^{2+} + K^+) concentrations of throughfall increased the most in the Qa and Mb canopies.

This indicates that base cations are more easily leached from broad-leaved canopies than from coniferous canopies ($P = 0.069$, less than the significance level of 0.10). This result agrees with a previous report where the canopy of a mixed coniferous and broad-leaved forest was more effective than the canopy of a pure *P. massoniana* forest at mitigating acidic rainfall (Li *et al.* 2010). Coniferous tree leaves secrete substantial quantities of viscous oils. These oils may repel water, thereby preventing the leaching of base cations from coniferous tree leaves. Another explanation for this result may be that the base cation content of the coniferous canopies was less than that of the broad-leaved canopy. Zhang *et al.* (1996) reported $(Ca + Mg + K)$ concentrations of 1.57% in Qa, 1.43% in Pt, and 1.12% in Pa leaves.

However, there were five instances during this study when the pH decreased in all stands, especially when the rainfall pH was relatively high. For example, rainfall pH was 7.62 on 26 August 2009. The pH of the throughfall was 6.16 in the Qa stand, 6.35 in the Pt stand, 6.21 in the Pa stand, and 6.01 in the Mb stand. This decrease in pH was likely caused by weak organic acid anions being involved in the neutralization of the acidity of the throughfall (Chiwa *et al.* 2004).

Sulfate, nitrate, ammonium, and phosphate concentrations

Rainfall SO_4^{2-} concentrations were high and variable during the study period (Figure 3). Rainfall SO_4^{2-} concentrations averaged $30.70 \, mg \, L^{-1}$ during the study period, ranging from 5.7 to $127 \, mg \, L^{-1}$ (Table 2; Figure 3). Rainfall SO_4^{2-} concentrations are affected by the amount of S pollution at its point of origin and the wind direction. For example, Chongqing city, which is located in the southwest of the Huoditang forest and is about 450 km away, was the largest source of SO_2 pollution in southwest China (Hong 2001; Wu *et al.* 2006). In July, the precipitation in the Qinling Mountains is mainly affected by the southwest monsoon; in September, it is mainly controlled by the southeast wind (Liu *et al.* 2003). This is the primary reason why the SO_4^{2-} concentrations varied so much.

The concentration of SO_4^{2-} changed greatly as rainfall passed through the forest canopies (Figure 3). Throughfall SO_4^{2-} concentrations ranged between 6.97 and $73 \, mg \, L^{-1}$,

5.31 and $200 \, mg \, L^{-1}$, 5.13 and $117 \, mg \, L^{-1}$, and 6.82 and $128 \, mg \, L^{-1}$ in the Qa, Pt, Pa, and Mb stands, respectively.

On average, SO_4^{2-} concentrations declined slightly as rainfall passed through the Qa canopy (Table 2). In contrast, average SO_4^{2-} concentrations increased slightly as rainfall passed through the other three canopies. The larger increases in SO_4^{2-} concentrations occurred as rainwater passed through the Pt canopy and the Pa canopy. One possible explanation for this result is that conifers, which have a greater leaf surface area index than broad-leaved trees (Robertson *et al.* 2000; Ren 2006), intercepted a higher level of dry SO_4^{2-} deposition (Robertson *et al.* 2000; Zeng *et al.* 2005). The other explanation is that coniferous tree leaves, which secrete more viscous oil than broad-leaved tree leaves, adsorbed more S pollutants. The Pt canopy increased the average SO_4^{2-} concentration of throughfall more than the Pa canopy. One explanation for this result might be that the greater stand density of the Pt stand (Table 1) intercepted more S pollutants than that of the Pa stand.

Rainfall NO_3^- concentrations averaged $0.21 \, mg \, L^{-1}$ during the study period (Table 2), ranging from 0.00 to $1.10 \, mg \, L^{-1}$ (Figure 3). As rainfall passed through the forest canopies, the average NO_3^- concentrations of rainfall declined by 20, 29, 53, and 27% in the Qa, Pt, Pa, and Mb stands, respectively. This indicates that all four forest canopies generally absorbed NO_3^- from rainfall. The decreases in average NO_3^- concentration were greater in the coniferous stands than in the broad-leaved stands. This implies that coniferous canopies were better than broad-leaved canopies at absorbing NO_3^- from rainfall. Furthermore, coniferous canopies were more effective than broad-leaved canopies in buffering rainfall NO_3^- pollution. This result is supported by the presence of fewer throughfall NO_3^- concentration extreme outliers for conifers than for broad-leaved trees in Figure 3.

Rainfall NH_4^+ concentrations averaged $0.40 \, mg \, L^{-1}$ during the study period, ranging from 0 to $1.48 \, mg \, L^{-1}$ (Table 2; Figure 3). The NH_4^+ concentrations increased by an average of only 5% as rainfall passed though the Qa canopy, but decreased by 42, 57, and 17% as rainfall passed through the Pt, Pa, and Mb canopies, respectively. All the canopies absorbed NH_4^+ from rainfall, with the exception of the Qa canopy. The possible explanation for
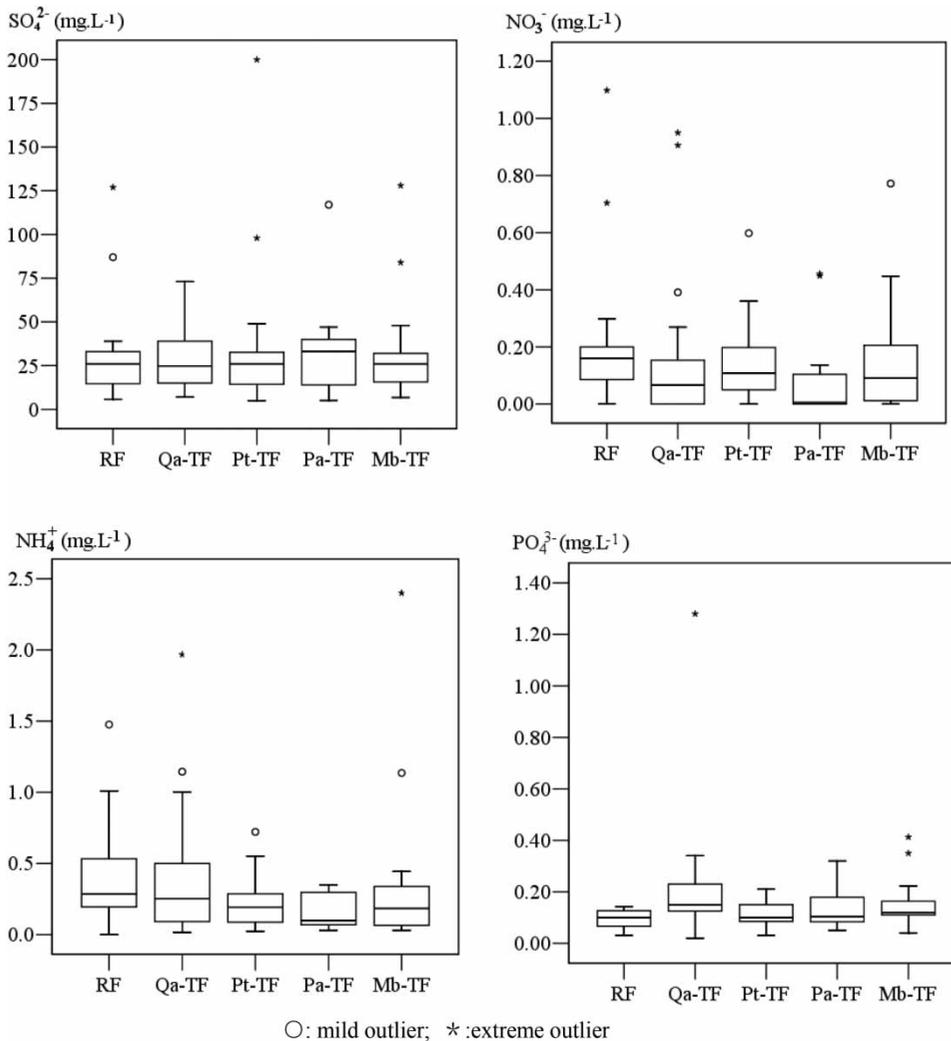
Figure 3 │ Concentrations of SO_4^{2-}, NO_3^-, NH_4^+, and PO_4^{3-} in rainfall and throughfall. Abbreviations: RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand.

this exception is that NH_4^+ in leaf tissues could be exchanged more easily for H^+ in rainwater as weakly acidic rainfall passed more easily through the Qa canopy than the other canopies. This dynamic is the same as base cations $(Ca^{2+} + Mg^{2+} + K^+)$, as previously mentioned.

Rainfall PO_4^{3-} concentrations averaged 0.09 mg L^{-1} during the study period, ranging from 0.03 to 0.14 mg L^{-1} (Table 2; Figure 3). The average PO_4^{3-} concentrations increased by 149, 36, 45, and 66% as water passed through the canopies of Qa, Pt, Pa, and Mb stands, respectively. This indicates that rainfall leached PO_4^{3-} from all four forest canopies. The amount of PO_4^{3-} leached from the canopies of broad-leaved trees was greater than that leached from

coniferous trees (Figure 3). Chen et al. (2004) reported that the P leached by rainfall mainly came from young leaves and meristems. A previous study reported P concentrations of 0.200% in Qa, 0.123% in Pt, and 0.120% in Pa leaves (Zhang et al. 1996). This result probably explains why more PO_4^{3-} was leached from the Qa canopy than from the Pt and Pa canopies. The relatively large amount of PO_4^{3-} that was leached from these forest canopies implies that the P supply is not limiting vegetative growth in the Huoditang forest. This is consistent with the generalization that N limits vegetative growth in temperate zones, whereas P limits vegetative growth in tropical zones (Herbert et al. 2003; Wang & Yu 2008).

Low N and P concentrations in throughfall can not only improve the quality of drinking water derived from it, but can also lower the risk of eutrophication within downstream water. From this viewpoint, coniferous canopies improve water quality more than broad-leaved canopies.
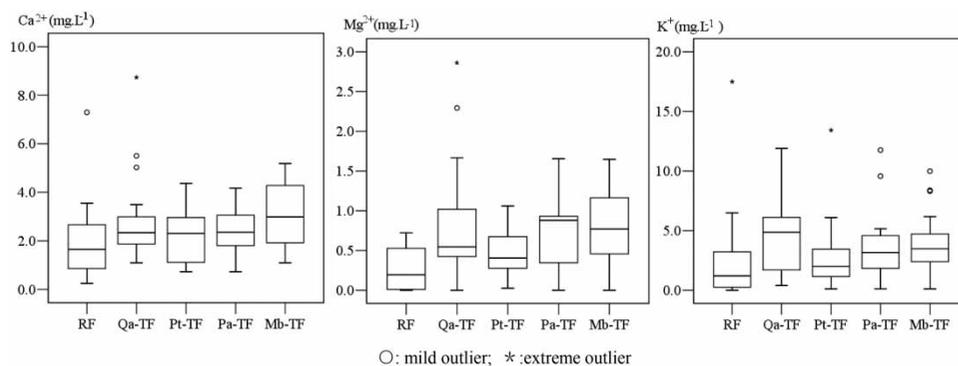
Base cation concentrations

The rainfall Ca^{2+} concentration averaged 1.94 mg L^{-1} in the Huoditang forest during the study period (Table 2). As rainfall passed through the forest canopies, the average rainfall Ca^{2+} concentrations increased by 47, 16, 26, and 52% in the Qa, Pt, Pa, and Mb stands, respectively. These increases demonstrate that rainfall leached Ca^{2+} from all four forest canopies. Furthermore, the largest Ca^{2+} losses were from the Mb trees, followed by the Qa (Table 2; Figure 4); this is perhaps because leaf Ca concentrations are higher in broad-leaved trees than in coniferous trees (Table 3). Alternatively, conifers secrete greater amounts of viscous oil than broad-leaved tree species. Leaf Ca concentrations of Pt are higher than those of Pa; however, the average throughfall Ca^{2+} concentration was lower in the Pt stand than in the Pa stand. One explanation is that Pt leaves may secrete a greater amount of viscous oil than Pa leaves (Chen *et al.* 2005).

Rainfall Mg^{2+} concentrations averaged 0.63 mg L^{-1} in the Huoditang forest during the study period (Table 2). As rainfall passed through the forest canopies, average rainfall Mg^{2+} concentrations increased by 215, 79, 178, and 187% in the Qa, Pt, Pa, and Mb stands, respectively. The changes

in Mg^{2+} concentration as rainfall passed through the forest canopy were similar to the changes in the Ca^{2+} concentration. The reason that more Mg^{2+} was leached from the broad-leaved canopies than from the coniferous canopies is probably the same as previously discussed for Ca^{2+}. The average throughfall Mg^{2+} concentration was lower in the Pt stand than in the Pa stand. The reason for this result is also the same as Ca^{2+}.

Rainfall K^+ concentrations averaged 2.59 mg L^{-1}, the highest of the base cation concentrations, during this study (Table 2). The relative changes in the K^+ concentration as rainfall passed through the forest canopies were similar to those observed for Ca^{2+} and Mg^{2+}, although there were more outliers (Figure 4). Specifically, as rainfall passed through the canopy, average rainfall K^+ concentrations increased by 76, 10, 55, and 54% in the Qa, Pt, Pa, and Mb stands, respectively. These results generally show that more K^+ was leached from broad-leaved canopies than from coniferous canopies (Table 2; Figure 4). The reason for this result was similar to our previous explanation for Ca^{2+}. Throughfall in the Pt stand had the lowest K^+ concentration in this study. One explanation for this result is the high concentrations of viscous oils in Pt (Chen *et al.* 2005).

There were more outliers for throughfall K^+ concentrations than for the other base cation concentrations (Figure 4), which implies that K^+ was more easily leached as rainfall passed through the stand canopies. The reason for this finding is probably that K is not as tightly bound to structural tissues or enzyme complexes as Mg and Ca (Balestrini & Tagliaferri 2001).

Figure 4 | Base cation concentrations in rainfall and throughfall. Abbreviations: RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand.

Table 3 │ Leaf nutrient concentrations of three tree species in this study[a]

Tree species	N%	P%	K%	Ca%	Mg%
Pa	1.298	0.12	0.524	0.474	0.121
Pt	1.184	0.123	0.695	0.614	0.118
Qa	2.172	0.2	0.607	0.732	0.23

[a]Data are derived from Zhang *et al.* (1996).

Cadmium and lead concentrations

In the Huoditang forest, the average rainfall Cd concentration was 4.73 $\mu g\,L^{-1}$ (Table 2). This amount was close to 5.0 $\mu g\,L^{-1}$, the maximum allowable concentration of Cd in drinking water stipulated in China's *Standards for Drinking Water Quality* (GB5749-2006). Rainfall Pb concentrations during the study period averaged 18.19 $\mu g\,L^{-1}$ (Table 2). The concentration was higher than the safe drinking water standard of 10.0 $\mu g\,L^{-1}$. As rainfall passed through the forest canopies, average Cd concentrations decreased dramatically; thus, the average throughfall Cd concentrations were much lower than China's safe water drinking standard. The average decreases were 71, 72, 74, and 83% in the Qa, Pt, Pa, and Mb stands, respectively. There were two extreme outliers for Cd concentrations in rainfall (Figure 5). These extreme outliers imply that air in the Huoditang forest was polluted with Cd. The average rainfall Pb concentration was the highest among the heavy metals tested in this study (Table 2). As rainfall passed through the forest canopies,

the average rainfall Pb concentrations decreased by 69, 64, 63, and 44% in the Qa, Pt, Pa, and Mb stands, respectively. The Qa canopy tended to reduce rainfall Pb concentrations the most in this study; however, the differences among the four canopy types were relatively small (Table 2; Figure 5).

The reason for the decline in Cd concentration as rainfall passed through the forest canopies is unclear.

There are three possible explanations for the large decreases in average Pb concentrations as rainfall moved through the forest canopies (Shang *et al.* 1991). First, about 50% of Pb absorbed from rainfall by leaves is deposited in the plant cuticle and cannot be moved. The second explanation is that Pb absorbed from rainfall reacts easily with surplus nonprotein sulfhydryl in plant cells to form insoluble compounds. Finally, some Pb absorbed from rainfall may form crystals that accumulate slowly on cell walls and are then deposited in the form of dense particles. The average rainfall Pb concentration was the highest among the heavy metals, and two outliers shown for the rainfall Pb concentration in Figure 5 indicate that air in the Huoditang forest was polluted with Pb as well.

Zinc and copper concentrations

Rainfall Zn concentrations averaged 8.39 $\mu g\,L^{-1}$ during the study period (Table 2), which is much lower than the maximum allowable Zn concentration (1,000.0 $\mu g\,L^{-1}$) in drinking water stipulated in China's *Standards for Drinking*

○: mild outlier; ＊:extreme outlier
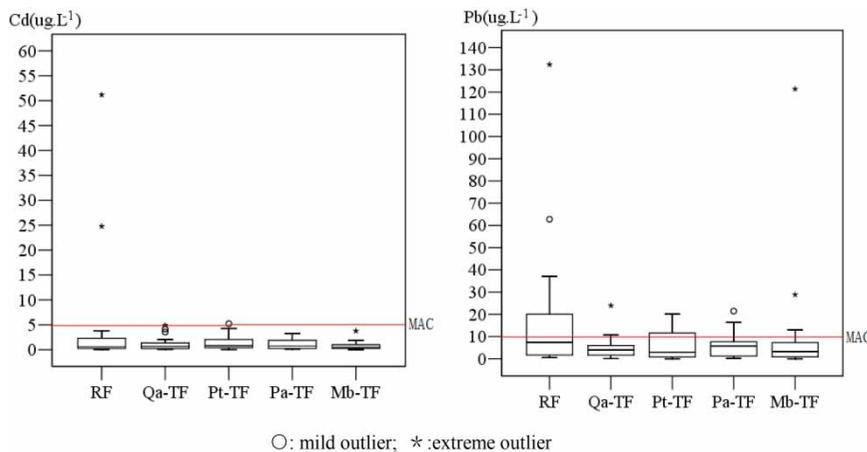
Figure 5 │ Cadmium and lead concentrations in rainfall and throughfall. Abbreviations: RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand; MAC, maximum allowable concentration in China's *Standards for Drinking Water Quality* (GB5749-2006).

Water Quality (GB5749-2006). The average Zn concentrations decreased as rainfall passed through all four canopies (Table 2). Specifically, the average Zn concentrations decreased by 40, 5, 10, and 57% in the Qa, Pt, Pa, and Mb stands, respectively. The larger decreases occurred as water passed through the broad-leaved canopies (Table 2; Figure 6). This implied that the broad-leaved canopies absorbed more Zn from rainfall than the coniferous canopies, perhaps because the broad-leaved trees required more Zn. This is supported by Avila & Rodrigo (2004), who reported that the canopy of a holm oak forest absorbed large amounts of Zn and Cd.

The Cu rainfall concentration during the study period averaged 3.41 μg L^{-1} (Table 2). This amount is still much lower than the maximum allowable Cu concentration (1,000.0 μg L^{-1}) in drinking water stipulated in China's *Standards for Drinking Water Quality* (GB5749-2006). As water passed through the forest canopy, average rainfall Cu concentrations decreased by 8% in the Qa stand and 10% in the Pa stand. In contrast, average Cu rainfall concentrations increased by 18% in the Pt stand and by 13% in the Mb stand. The average Cu concentration in rainfall was the lowest among the metals that were related to Pb–Zn mining and tested in this study (Table 2). The canopies of all four stands decreased throughfall Cu concentrations when the Cu rainfall concentrations were high. For example, Cu rainfall concentrations were 9.74 μg L^{-1} on 1 August 2011. Throughfall Cu concentrations were 4.40, 6.71, 0.91, and 5.15 μg L^{-1} in the Qa, Pt, Pa, and Mb stands, respectively.

In contrast, when rainfall Cu concentrations were low, Cu concentrations increased as rainfall passed through the forest canopies. For example, the rainfall Cu concentration was only 0.41 μg L^{-1} on 18 June 2011. Throughfall Cu concentrations were 8.00, 6.70, 1.77, and 3.77 μg L^{-1} in the Qa, Pt, Pa, and Mb stands, respectively. The results indicate that the canopies can mitigate Cu concentrations as water passes through them. The ability of a canopy to mitigate Cu concentrations can be measured by the standard deviation of the throughfall Cu concentrations. Based on this, we conclude that the Mb canopy was the most effective at mitigating throughfall Cu concentrations. Throughfall Cu concentrations and standard deviations were generally the highest in the Pt stand (Table 2). This implies that among the canopy types, the Pt canopy intercepted more dry-deposited Cu and was the least effective at mitigating throughfall Cu concentrations. This finding is also supported by the throughfall Cu concentration interquartile range being the largest for the Pt in Figure 6. An explanation for this result might be that the stand density and canopy closure were greater in the Pt stand than in the other stands (Table 1) and that Pt leaves secreted a greater amount of viscous oil (Chen *et al.* 2005).

CONCLUSIONS

(1) Rainfall pH, which was weakly acidic, increased as rainfall passed through the Qa, Pt, Pa, and Mb stands. The
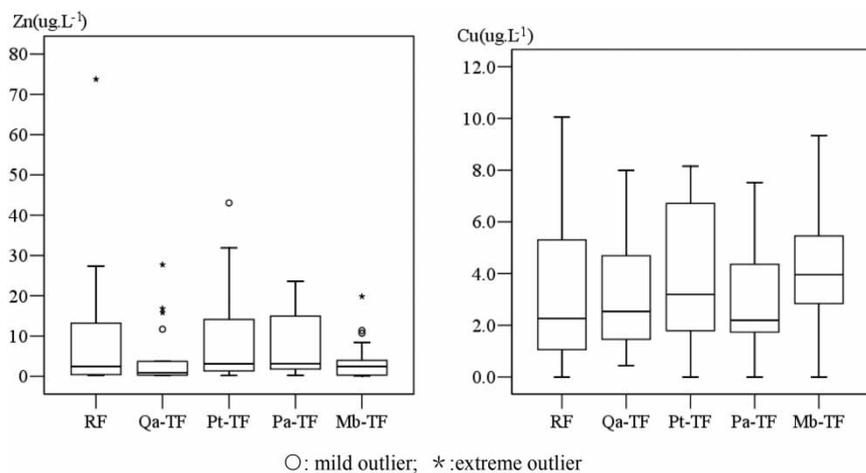
Figure 6 │ Zinc and copper concentrations in rainfall and throughfall. Abbreviations: RF, rainfall; Qa-TF, throughfall in the Qa stand; Pt-TF, throughfall in the Pt stand; Pa-TF, throughfall in the Pa stand; Mb-TF, throughfall in the Mb stand.

largest increase occurred as rainfall passed through the canopy of the Mb stand, followed by the Qa, Pt, and finally Pa stands.

(2) Concentrations of SO_4^{2-} decreased as rainfall passed through the Qa canopy, but increased as rainfall passed through the others. The SO_4^{2-} concentration had the highest increase as rainfall passed through the Pt canopy followed by the Pa. Concentrations of NO_3^- decreased as rainfall passed through all four forest canopies. The order of the decrease was Pa > Pt > Mb > Qa. Concentrations of NH_4^+ increased slightly as rainfall passed through the Qa canopy, but decreased as rainfall passed through the others. The Pa canopy caused the largest decrease in NH_4^+, followed by the Pt, and finally the Mb. The PO_4^{3-} concentration increased as rainfall passed through all four canopy types. The order of the increase was Qa > Mb > Pa > Pt.

(3) Base cation concentrations increased as weakly acidic rainfall passed through the forest canopies. The order of the increase was Qa > Mb > Pt > Pa.

(4) Concentrations of Zn, Cd, and Pb decreased as rainfall passed through the four forest canopies. The decrease in Pb concentration was greater than the decreases in Cd and Zn concentrations. Throughfall Zn concentrations were the lowest in the Mb stand, followed by the Qa, Pt, and finally Pa stands. The four canopy types had similar effects on rainfall Cd concentrations. As rainfall passed through the forest canopies, the rainfall Pb concentrations decreased by an average of 12.61, 11.55, 11.54, and 7.40 $\mu g\ L^{-1}$ in the Qa, Pt, Pa, and Mb stands, respectively. Rainfall Cu concentrations decreased as rainfall passed through the Qa and Pa canopies, but increased as rainfall passed through the Pt and Mb canopies.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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