Assessing Precipitation Redistribution and Hydro-Chemical Dynamics in a High-Elevation Evergreen Broad-Leaved Forest

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Abstract: Forest water dynamics and hydro-chemical characteristics are essential for understanding forest hydrology and ecological processes. Yet, such understanding is limited by a lack of long-term monitoring data and observations from specialized forest ecosystems such as those from high elevation. Here, we analyze the precipitation redistribution including interception, stemflow, and throughfall and hydro-chemical characteristics by using a 15 year (2005–2019) precipitation dataset in a high elevation, evergreen broad-leaved forest in Southwest China. The forest experienced an obvious seasonal variation in precipitation with a monthly average of 117.31 ± 91.21 mm. The precipitation redistribution was influenced by precipitation intensity and leaf area index and differed inter-annually and intra-annually, with a general pattern: throughfall > canopy interception > stemflow. Throughfall rate increased significantly from 2015 to 2019 after experiencing the January 2015 snowstorm. The majority of water within the study site was retained in the soil and apoplastic materials. The primary means of water output was evapotranspiration, with minimal surface runoff. Quality of surface water was affected by the weathering of rocks, resulting in a lower pH than that of atmospheric precipitation. During the rainy season, elemental Ca and Mg showed negative correlation with precipitation due to plant mediation. The other elements, pH, total dissolved solids, precipitation, air temperature, and water temperature showed different degrees of correlation with each other. Overall, while the water balance fluctuated over the past 15 years, the water-holding capacity remained relatively stable. Alkali cations such as Ca\(^{2+}\), Mg\(^{2+}\), and K\(^{+}\) in the water body showed a decreasing trend during 2005–2019, which is a potential threat to ecological stability.

Keywords: water budget; precipitation redistribution; hydro-chemical characteristics; ion concentration

1. Introduction

Forest ecosystems are one of the most important components of terrestrial ecosystems, covering about one third of the land surface, and provide a wide range of materials and resources for human society [1]. They regulate and redistribute precipitation [2], serving as the primary source of water and nutrients in the ecosystems [3,4]. Precipitation redistribution significantly alters the spatial distribution of rainfall [5] and occurs when precipitation passes through the plant canopy. Some of precipitation is intercepted by tree branches and leaves and can return to the atmosphere through evaporation. Retention of precipitation on canopy also affects hydrologic processes, including infiltration, erosion, soil moisture distribution, surface (subsurface) runoff, etc. [6,7]. Canopy retention can effectively weaken the kinetic energy of raindrops, reducing their erosive force. At the same time, it slows down the emergence of rainfall under the forest and the time of surface runoff, reduces the runoff volume of the surface of the forest floor, and realizes the basic function of
forests as a source of water [4]. On the other hand, some precipitation passing through the canopy forms stemflow along the tree trunk, penetrates through the inter-canopy gaps, or drips from the branches and leaves [8,9]. Stemflow and throughfall enter the surface layer of the forest ecosystem and form surface runoff or infiltrate into the soil layer and form soil water that participates in the hydrological cycle within the forest ecosystem [10]. In general, the three components of precipitation redistribution are mainly influenced by biological factors (i.e., plant size, canopy density, branch structure, leaf area index (LAI, the total surface area of leaves per unit of ground area), and bark morphology as well as climatic conditions (e.g., rainfall amount, intensity, and duration of rainfall) [11]. Forest canopies ultimately influence plant productivity by regulating soil water replenishment [12]. In turn, plant growth and development counteract patterns of precipitation redistribution. Canopy cover and LAI are found to be positively correlated with interception [13,14]. Furthermore, penetrating water and trunk stem flow are reported to be positively correlated with rainfall amount and intensity.

Nutrient input by precipitation is one of the main sources of nutrient substances in forest ecosystems and is the basis of nutrient cycling and nutrient balance in forest ecosystems [15,16]. Atmospheric precipitation has received increasing attention as an important source of nutrients in forest ecosystems and as a vital carrier for the movement, uptake, and utilization of various elements [17]. Compared with the nutrients produced by surface apoplastic and soil organic matter decomposition, nutrients input through precipitation have a more direct effect on promoting plant growth and nutrient cycling [3,18]. Water chemistry is an effective indicator for assessing changes in water quality. It reflects not only the effects of natural processes such as precipitation and rock weathering but also the effects of human activities. Time series of water chemistry play an important role in assessing the water quality [19–21]. However, researches on water chemistry in the past few decades have focused on rivers, oceans, and lakes [19,22,23], and relatively few studies have been conducted on the water chemistry of forest ecosystems. Through forest ecosystems, the composition and concentration of chemical elements in them change considerably as precipitation gets distributed [24–26]. In temperate forests, the concentration of metal elements varies with the entry of precipitation into forested areas [27]. In subtropical mixed evergreen deciduous forests, the ion concentrations of forest waters are relatively low from July to September and comparatively high from December to February [15]. Analyzing the chemical changes in the forest water environment is of great significance in understanding the mechanism of forest ecosystems in purifying water [28,29].

Currently, most studies mainly focus on changes in the amount of each precipitation redistribution component, the factors affecting it during forest precipitation [30–32], and changes in nutrient inputs to the forest floor during precipitation redistribution [8,33]. Previous comparisons of the hydrological characteristics of different forest types revealed that the amount of throughfall and canopy interception were greater in mixed forests than in pure forests, while the amount of stemflow was greater in pure forests than in mixed forests. The distribution of rainfall by the canopy of different vegetation types was characterized by the greatest amount of throughfall, followed by canopy interception, and the smallest amount of trunk stemflow [34,35]. However, there is a lack of long-term observations and data monitoring. In addition, studies on the chemical characteristics of water bodies have mainly focused on groundwater, lakes, and rivers [36–38].

Evergreen broad-leaved forests are the most typical broad-leaved forests in the warm and humid subtropical regions of China and are most widely distributed [39]. They have high primary productivity and play an important role in sequestering carbon and releasing oxygen, conserving soil and water, regulating the climate, and maintaining biodiversity. The forests in the Mourning Mountain Nature Reserve in Yunnan are among the largest and well-preserved subtropical evergreen broad-leaved forests in China [40,41]. The study of forest water balance and changes in hydro-chemical characteristics in different time scales can help to understand the hydrological situation of China’s subtropical forests and to
improve the hydrological and ecological functions of the forests, as well as the management of water resources.

Therefore, this study analyzes the characteristics of precipitation changes in different time scales in the study area based on monitoring data of the evergreen broad-leaved forest in the Mourning Mountains over the past 15 years. This includes (1) the characteristics of changes in water input, redistribution, storage, and output during precipitation in the evergreen broad-leaved forest in the Mourning Mountains, along with the factors influencing these changes and (2) the characteristics of precipitation and ion concentrations in surface water in the evergreen broad-leaved forest of the Mourning Mountains over the past 15 years. The results of this study serve as a reference for further research on large scale changes in water balance and hydro-chemical characteristics of forests, which can assist local government and forest managers in effective forest management.

2. Material and Methods

The research framework is shown in Figure 1. This study focused on an evergreen broad-leaved forest in Southwest China as the study area, with a primary emphasis on analyzing alterations in the water balance and water chemistry dynamics during 2005–2019.

**Figure 1. Technical route.**

**2.1. Description of the Study Area**

The study area is located in Xujiaba (24°32′ N, 102°01′ E), the core area of the Mourning Mountains National Nature Reserve in Jindong Yi Autonomous County, Pu’er City, Yunnan Province (Figure 2a), with an elevation of 2400–2600 m above sea level. Climate records in Xujiaba during the 2005–2019 period show a mean annual precipitation of 1407.66 mm, with 85% concentrated in May–October. The mean annual temperature is 11.3 °C, with a distinct rainy and dry season (Figure 2b). The soil is typically yellow-brown soil with loamy texture [42]. The study area experiences a transition from central subtropical to southern subtropical climate, preserving the largest area of primitive mesic wet evergreen broad-leaved forest in China.
The LAI was calculated as the average value from 3 time points to represent the LAI of the study area. Between 12:00 and 16:00, as well as during periods of relatively weak sunshine at 08:00. The LAI was measured at 2000 was used to measure the LAI every four months on days of high-intensity sunshine ranging from canopy tree at an average height of 20–30 m to shrub- and herb-layers. Lianas and woody plants are common, with abundant epiphytes, mosses, and ferns. The dominant tree species are Machilus bombycina, Populus rotundifolia, Schima noronhae Reinw, Castanopsis rufescens, Castanopsis delavayi, and other tall trees [43].

2.2. Monitoring of Data

Meteorological observations were carried out in the field (during 2005–2019), using a combination of manual observation and automatic recording instruments. Therefore, the data can be complemented and referenced to each other, improving the accuracy of data collection. The LAI-2000 Plant Canopy Analyzer (Li-Cor, Lincoln, NE, USA) was placed horizontally at 3.5 m from the ground to determine the LAI. Due to high crown cover (more than 90%) and the relatively weak understory light in the study area, the LAI-2000 was used to measure the LAI every four months on days of high-intensity sunshine between 12:00 and 16:00, as well as during periods of relatively weak sunshine at 08:00. The LAI was calculated as the average value from 3 time points to represent the LAI of the study area.

A 4 m × 25 m area with a slope of 10° was selected within the sample plot to set up an artificial surface runoff observation. Ten PVC water catchments (1.0 m × 0.2 m) and five rain gauges with a diameter of 20 cm were randomly installed to collect throughfall for long-term moisture observations in the study area. In order to minimize the influence of shrubs and herbaceous plants on the penetrating rain, catchment troughs and rain gauges were made at a height of no less than 50 cm above the ground and maintained at an inclination of about 0.5° to the ground. The lower end of the catchment troughs was connected to a 25 L polyethylene plastic bucket. In order to avoid the influence of withered branches and leaves on the measurement results, the water collection tank was cleaned of withered debris and other materials before rainy season. After rainfall, the volume of water in the rain gauge was measured with a 20 cm diameter measuring cup. For stemflow observation, we selected 16 trees representing 7 dominant species based on their diameter at breast height (DBH) and crown width (CWS). A 1.5 cm diameter polyethylene plastic pipe was cut along the center seam (the length depended on the trunk size), fixed to the opening of the trunk with a large head pin, and then spirally wrapped around the trunk from both sides. After securing with a tack, the seams were sealed tightly with glass glue and a 25 L polyethylene plastic bucket was connected to the lower end of the plastic tube for collecting stemflow from the trunk. All meteorological data were collected through regular monitoring carried out by the staff members of the Chinese Academy of Sciences (CAS), Mourning Mountain Subtropical Forest Ecosystem Research Station.

Figure 2. (a) Location map and high-level map of the study area; (b) The period 2005–2019 monthly mean temperature and precipitation map of the study area.
Canopy interception was calculated as the following formula:

\[ I = P - T - S \] (1)

where I is the canopy interception (mm), P is precipitation (mm), T is the penetrating rainfall (mm), and S is the stemflow (mm).

Precipitation data were collected in January, April, July, and October of each year from 2005 to 2018, with the sample size corresponding to the total number of months, and used to test hydro-chemical characteristics. Samples were taken from 3 small streams within the integrated observation site of the study area in January, April, July, and October of each year from 2005 to 2019. A sampling volume of about 2 L per point was collected, and 5 L of a composite mixture from the three points were taken for the analysis of hydro-chemical characteristics of surface flowing water. The collected samples were sent to the Biogeochemistry Laboratory of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences (CAS) for analysis. pH was measured using the glass electrode method (GB 6920-1986 [44]). Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\) concentration was detected by inductively coupled plasma emission spectrometry (HJ 776-2015 [45]). HCO\(_3\)\(^-\) ion concentration was detected by double indicator-neutralization titration method (LY/T 1275-1999 [46]). Cl\(^-\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\) concentration was detected by ion chromatography (HJ 84-2016 [47]). Total dissolved solids (TDSs, the total dissolved inorganic and organic matter concentration in aqueous solutions) were detected by conductivity method (LY/T 1275-1999 [46]). Air temperature data were obtained from the study area station data, and water temperatures were measured using thermocouples prior to each monitoring session, in January, April, July, and October of each year.

2.3. Data Processing and Statistical Analysis

Precipitation redistribution was obtained through direct measurements (i.e., through-fall and stemflow) and calculated according to formula 1 (canopy interception). The correlation analysis was performed using Pearson’s correlation fitting to each component, as well as rainfall intensity and LAI. Additionally, the relationships between ion concentration and precipitation, air temperature, water temperature were analyzed. Analysis of variance (ANOVA) and multiple comparisons with Duncan as a post-hoc test were used to verify differences between precipitation redistribution components at different time scales. Intra-annual and inter-annual variation in precipitation intensities and ion concentrations were also investigated in a similar way. Raw data were initially processed using Excel 2010 software (Microsoft Corporation, Redmond, WA, USA), statistical analyses were conducted in SPSS 26.0 (IBM Corporation, New Orchard Road, Armonk, NY, USA), while data visualizations were performed using Origin 2021 (OriginLab Corporation, Northampton, MA, USA).

3. Results

Based on our monitoring data, we conducted an analysis of the forest water balance and the alteration in water chemistry within a high-elevation evergreen broad-leaved forest in Southwest China from the following two aspects. The first aspect delves into the water balance, encompassing precipitation input, redistribution, storage (as moisture content), and output. In particular, we focus on the redistribution process, thoroughly examining its temporal variations and the factors influencing them. The second part mainly delves into the characteristics of atmospheric precipitation and surface water hydro-chemical changes at both inter-annual and intra-annual aspects, while briefly outlining the potential reasons for these changes.

3.1. Characterization of Water Dynamics in the Study Area

3.1.1. Characterization of Precipitation Inputs

During 2005–2019, the monthly average precipitation in the study area was 117.31 ± 91.21 mm, and the precipitation was primarily concentrated in the rainy season, which extended
from May to October, accounting for 86% of the total precipitation. Our observation recorded an extreme monthly precipitation event in January 2015 when snowfall reached 1129.2 mm (Figure 3a). We analyzed monthly precipitation and categorized the magnitude of precipitation into five classes. Our findings revealed that larger precipitation events and magnitudes predominantly occurred during the rainy season (Figure 3c). Precipitation magnitudes were dominated by the <5 mm class (34%) throughout the year followed by the 10–20 mm class (30%) and 5–10 mm class (20%) (Figure 3b). Precipitation intensity during dry season was characterized by <5 mm and 5–10 mm classes, whereas the rainy season was dominated by 10–20 mm and 20–40 mm classes.

Figure 3. (a) Histogram of annual precipitation in the study area; (b) frequency of occurrence of different precipitation classes; (c) percentage of different precipitation classes in each month. The same colors in (b,c) represent the same precipitation levels, blue is <5 mm, red is 5–10 mm, green is 10–20 mm, purple is 20–40 mm, and gray is >40 mm.

3.1.2. Characteristics of Precipitation Redistribution

A total precipitation of 2030.41 mm was recorded from 180 events in our data collection. This precipitation was redistributed through the forest canopy as follows: 69.11% through-fall, 0.42% stemflow, and 30.47% canopy interception. Our analysis of the inter-annual variation (Figure 4a–c) and intra-annual variation (Figure 4g–i) of each component of precipitation redistribution revealed specific variation across study periods. Typically, the intra-annual variability was larger than the inter-annual variability. In terms of inter-annual
variation, throughfall showed a not significant upward trend, while throughfall rate began to increase significantly in 2015 and later. Canopy interception and canopy interception rate showed a non-significant decreasing trend. Throughfall exhibited the smallest inter-annual variation and the largest intra-annual variation. Intra-annual variations of each component generally displayed single peaks during wet season, with non-significant peaks in stemflow. These variations were positively skewed, influenced by greater precipitation intensity. Statistical analysis revealed linearly positive correlations between precipitation intensity and throughfall, stemflow, and canopy interception (Figure 5a–c). Throughfall rate and canopy interception rate showed significant exponential relationship with precipitation, stabilizing when the precipitation level exceeded 5–10 mm (Figure 5g,i). LAI was linearly correlated with throughfall rate and canopy interception rate (Figure 5d,f). No significant relationship was found between precipitation and stemflow (Figure 5e).

Figure 4. (a) Inter-annual throughfall distribution; (b) inter-annual stemflow distribution; (c) inter-annual canopy interception distribution; (d) inter-annual throughfall rate distribution; (e) inter-annual stemflow rate distribution; (f) inter-annual canopy interception rate distribution; (g) intra-annual throughfall distribution; (h) intra-annual stemflow distribution; (i) intra-annual canopy interception distribution. Different letters indicate significant differences ($p < 0.05$) between years or months. Dashed line indicates the trend-mean across years or months.
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Figure 5. (a) Precipitation versus throughfall; (b) precipitation versus stemflow; (c) precipitation versus canopy interception; (d) LAI versus throughfall; (e) LAI versus stemflow rate; (f) LAI versus canopy interception rate; (g) precipitation versus throughfall; (h) precipitation versus stemflow rate; (i) precipitation versus canopy interception rate. The confidence intervals in the plots are 95%. (a–f) have linear regressions, and (g–i) have nonlinear regressions. Dots represent monthly observation with prediction trend (red) and 95% confident interval of the prediction (shade area).

3.1.3. Characterization of Precipitation Output

Surface runoff occurred occasionally before 2007 (Figure 6a) but exhibited a stable minimal runoff trend in the subsequent years. Instead, precipitation was predominantly retained within the forest and subsequently evaporated to the atmosphere. According to Lin et al. (2019) [48], during the rainy season (May–October) evapotranspiration was 458.27 mm, representing 35.61% of the precipitation. In contrast, during the dry season (November–April), evapotranspiration reached 309.42 mm, which was about 1.85 times of precipitation. The annual evapotranspiration was 767.69 mm, accounting for 52.80% of the annual rainfall in study area. A large amount of water was stored in the litterfall and soil. The average water content of the litterfall (160.41 ± 41.97 mm) was lower than that of the soil (573.19 ± 87.93 mm) across the years, with more pronounced intra-annual variations.

Figure 6. (a) Surface runoff volume, 2005–2019; (b) intra-annual water content of soil and litterfall; (c) inter-annual water content of soil and litterfall. Dots (a) represent monthly data with a nonlinear regression trend (green line). Standard errors and lines have been added to both (b,c).
3.2. Characterization of Water Quality in the Study Area

3.2.1. Characterization of Precipitation Water Quality

pH of rainfall varied from 4.38 to 9.69, but was averagely 7.01 across the period of 2005–2018. The pH values in 2011 and 2012 showed significant declines compared to other years (Figure 7a,d). TDS and its range fluctuated largely and significantly over the years, but the difference was not significant intra-annually (Figure 7b,e). \( \text{SO}_4^{2-} \) concentration was significantly decreased in July, relative to the other months. From 2005 to 2018, the concentration of \( \text{SO}_4^{2-} \) was generally increasing slowly (Figure 7c,f).

Figure 7. (a) Intra-annual variation in rainwater pH; (b) intra-annual variation in rainwater TDS; (c) intra-annual variation in rainwater \( \text{SO}_4^{2-} \) concentration; (d) inter-annual variation in rainwater pH; (e) inter-annual variation in rainwater TDS; (f) inter-annual variation in rainwater \( \text{SO}_4^{2-} \) concentration. Different letters indicate significant differences (\( p < 0.05 \)) between years or months. Dashed line is added to indicate changes in mean values between observation periods.

3.2.2. Characterization of Surface Water Quality

We sampled the flowing surface water to analyze the changes in surface water quality in the study area. We found that \( \text{Ca}^{2+} \) was the dominant cation, while \( \text{HCO}_3^- \) and \( \text{SO}_4^{2-} \) were the most common anions in surface runoff. Between 2005 and 2019, the concentrations of \( \text{Ca}^{2+}, \text{Mg}^{2+}, \) and \( \text{Na}^+ \) showed a decreasing trend and \( \text{NO}_3^- \) ions showed an increasing trend. No significant changes were observed in the concentrations of \( \text{Cl}^-, \text{K}^+, \text{HCO}_3^- \), and \( \text{SO}_4^{2-} \) overall (Figure 8). In addition, there was no obvious difference in the concentrations of other ions within the year, except for the significant variability in the concentrations of \( \text{Ca}^{2+} \) and \( \text{HCO}_3^- \) ions between dry and rainy seasons (Figure 9). pH showed a decreasing trend across years (Figure 8), with a lack of seasonal variation. Its range fluctuated between 3.04 and 7.9, with the average value in the rainy season (5.53) being slightly smaller in the dry season (5.93). Long-term average value was 5.73, which was weakly acidic. The inter-annual variation of TDS generally showed a decreasing trend (Figure 8), with the average value in the rainy season (36.83 mg/L) being smaller than that in the dry season (42.13 mg/L) and much lower than the freshwater criterion (1 g/L). The rainy season occurs during the hottest period of the year, as indicated by a significant relationship between precipitation and air temperature (\( p < 0.01 \)). High precipitation came with high \( \text{Ca}^{2+} \) and low \( \text{Cl}^- \) in surface water. Air and water temperatures exhibited a strong correlation.
throughout the observation period ($p < 0.01$). However, ions dissolved in surface water were clearly related more with water temperature than air temperature. Some major anions such as $\text{Cl}^-$, $\text{SO}_4^{2-}$, and $\text{NO}_3^-$, usually found increased with water temperature (Figure 10). The concentration of anions (i.e., $\text{SO}_4^{2-}$, and $\text{NO}_3^-$) exhibited a negative correlation with surface water pH ($p < 0.01$), while major cations (i.e., $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$) showed a positive correlation. Additionally, TDS demonstrated a similar trend to major cations (Figure 8) and exhibited a positive correlation with pH ($p < 0.01$) (Figure 10).

Figure 8. Inter-annual variation of pH, TDS, and elemental ion concentrations in surface water. The straight line in the figure is the regression line, the color area is the 95% confidence interval, blue indicates a downward trend, green indicates an insignificant trend of change, and orange indicates an upward trend.
Figure 9. (a) Intra-annual variation in surface water Ca\(^{2+}\) concentration; (b) intra-annual variation in surface water Mg\(^{2+}\) concentration; (c) intra-annual variation in surface water K\(^{+}\) concentration; (d) intra-annual variation in surface water Na\(^{+}\) concentration; (e) intra-annual variation in surface water Cl\(^{-}\) concentration; (f) intra-annual variation in surface water HCO\(_3\)\(^{-}\) concentration; (g) intra-annual variation in surface water SO\(_4^{2-}\) concentration; (h) intra-annual variation in surface water NO\(_3^{-}\) concentration; (i) intra-annual variation in surface water pH; (j) intra-annual variation in surface water TDS. Color indicates seasonal differences. Different letters indicate significant differences ($p < 0.05$) between months. Dashed line links mean values between observation periods.
The retention of precipitation by the vegetation canopy alters the distribution of precipitation [53]. The hydrological function of this retention is mainly reflected in the hydrological processes of throughfall, interception, and stemflow [34]. Our study showed that the components of precipitation redistribution in evergreen broad-leaved forests in the Mourning Mountains differed at different time scales (inter-annual and intra-annual), with the general characteristics of throughfall > canopy interception > stemflow. This was consistent with evergreen broad-leaved forest in Dagang mountain, Jiangxi [54]. Throughfall is influenced by rainfall, tree density, and canopy structure [55], which are similar to our results. Our study showed a positive relationship in all precipitation distribution components and precipitation. At the same time, contrast relationships were detected between throughfall and canopy interception to LAI. We observed no significant inter-annual variation in the total amount of throughfall. However, there was a notable difference in inter-annual throughfall rates, with a significant increase from 2015 to 2019 compared to other years. This increase was primarily attributed to the impact of the January 2015 snowstorm, which led to numerous treefalls and branch breakage, which significantly affected forest cover and LAI. A previous study also noted a decrease in LAI following a similar storm [56]. As canopy cover decreased, throughfall increased, leading to a decline in canopy interception, subsequently affecting evapotranspiration [57]. Intra-annual pattern revealed significant fluctuations in throughfall, particularly during the rainy season (Figure 4d). However, the percentage of throughfall tended to be stabilized when the rainfall magnitude exceeded...
5–10 mm, which was in line with the characteristics of precipitation redistribution in most of the forests [32,58].

Stemflow is influenced by a multitude of factors, including vegetation type, canopy structure, canopy area, diameter at breast height, bark smoothness, trunk branching angle, and leaf size, leaf smoothness, precipitation intensity, and seasonal duration of precipitation, canopy structure, canopy area, diameter at breast height (DBH), bark smoothness, trunk branching angle, and leaf size, leaf smoothness, precipitation amount, precipitation intensity and duration, and season [1,59–61]. Our results showed that stemflow accounts for a relatively small proportion of all precipitation components, constituting only 0.42% of the total, which aligns with observations in the Venezuelan Orinocoranos savanna semideciduous forest (0.4%–1.1%) [62]. However, it contrasts significantly with semi-arid evergreen spruce forests (Picea Crassifolia) in the Qilian Mountains, where stemflow can represent as much as 8.4% of the total precipitation [63]. This difference is likely attributed to the specific characteristics of forest type. The presence of an open and tall canopy with abundant epiphytes in our study area may contribute to higher stemflow, as rainwater runs off branches and accumulates in tree trunks. However, this increased stemflow is associated with some losses, such as evapotranspiration and epiphyte uptake.

Previous studies have shown that the amount of canopy interception is sensitive to changes in forest condition [64,65]. Canopy interception thresholds vary across different ecosystems, typically falling within the range of 0.2–4.7 mm [66]. Our results show that the interception rate tends to stabilize when the rainfall exceeds 5 mm (Figure 5g) and it forms a reciprocal relationship with penetration rate. The multi-year average interception rate in the canopy in the study area was 38.7%, higher than that of the majority of forests in the monsoon region of eastern China [67]. The higher interception rate in our study area could be attributed to factors such as anthropogenic disturbance, high forest depression, opened canopy, and complex canopy structure in the evergreen broad-leaved forests in the Mourning Mountains. This contributes to less precipitation penetrating the canopy directly to the surface. The higher retention rate reduces the direct scouring and erosion of rainwater on the ground surface. This, in turn, effectively decreases the risk of soil erosion in the study area. In addition, the increased retention rate elevates the humidity level within the forest, ensuring biodiversity, and contributes to ecosystem balance and stability.

Evapotranspiration represented the largest portion for water output, while the surface runoff accounted for a small proportion. The vegetation in the study area has been protected for many years. The dense forest cover and well-developed root system facilitate rapid absorption of precipitation and its subsequent transport to the leaves for transport, effectively returning water to the atmosphere. Canopy interception also accounted for the majority of precipitation redistribution. The water could be retained on canopy, in the soil, and on forest litter. Our results showed that the fluctuation in soil and withered material water content remained consistent over time. Increased evaporation led to a reduction in the water content of soil and withered material. However, it remained higher than that of another site in Southwest China during a similar period [27]. This indicates that the primary forests of the Mourning Mountains have a clear advantage in the capacity for water conservation.

4.2. Changes in Atmospheric Precipitation Water and Surface Water Quality in the Study Area

Water quality assessments are crucial for effective management [68]. Water quality is largely dependent on geographical conditions, and its pH results from a combination of ions [69]. Long-term mean pH of atmospheric precipitation in the study area was 7.01, while the mean pH of surface water was 5.73. It has been reported that the chemical composition of precipitation changed during its passage through the forest canopy [70]. The forest canopy has a buffering capacity and enriches acidic effect after precipitation passes through. A portion of the acid radical ions are retained in the canopy or interact with the weakly alkaline ions released from the leaf surface to achieve acid-base neutralization [71]. Therefore, there is a possibility that the source of acid radical ions in surface waters was not
coming from the atmosphere. We encourage future research to quantify both precipitation and surface runoff elemental ions for identifying their sources. HCO$_3^-$ are mainly derived from rock weathering [72], whereas, when the anions are more towards the HCO$_3^-$ end of the spectrum and the cations are more towards the Ca$^{2+}$ end of the spectrum, it indicates that the water body is more heavily affected by rock weathering [73]. Ca$^{2+}$ and HCO$_3^-$ were the main ions in the surface flowing water in the study area, indicating that the water body was heavily influenced by rock weathering. Meanwhile, the concentration of acid radical ions was much larger than that of precipitation (Figures 7 and 8), which is consistent with the lower pH in surface water. In addition, the increase in water temperature also had a direct effect on the pH of the water body [74]; this was partly due to the fact that an increase in water temperature leads to a decrease in dissolved oxygen content and an increase in CO$_2$ concentration, which reacts with water to produce carbonic acid, elevating the HCO$_3^-$ concentration of the water body. In addition, an increase in water temperature increased the ionic product constant of the water body, which indirectly decreased the pH of the water body. The SO$_4^{2-}$ concentration in atmospheric precipitation was generally increasing slowly from 2005 to 2018 (Figure 7c,f). This trend suggests that the source of acid in the precipitation process was increasing, possibly due to the rapid urbanization and industrialization development around the study area.

The concentrations of Ca$^{2+}$, Mg$^{2+}$, K$^+$, and other alkali cations generally showed a decreasing trend. These concentrations were higher in the dry season than in the rainy season (Figures 8 and 9a). It is evident from Figure 10 that there are negative correlations of varying degrees between the concentrations of Ca$^{2+}$, Mg$^{2+}$, and K$^+$ and precipitation. Precipitation is one of the key factors to ensure the growth and development of vegetation, while plant roots preferentially absorb elements such as Ca, Mg, and K in the process of obtaining nutrients [75]. In the rainy season, with the increase of precipitation, vegetation absorbs more Ca and Mg elements in the growing season than in the non-growing season, which ultimately leads to a lower concentration of Ca$^{2+}$, Mg$^{2+}$, and K$^+$ in surface waters in the rainy season than in the dry season. The overall decline in these elements leads to long-term changes in water chemistry, resulting in acidification and nutrient loss. Ultimately, these changes can have an impact on forest productivity and health [76]. The increase in the concentration of NO$_3^-$ was mainly concentrated after 2015. As a consequence of snowstorm disturbance, a large number of branches were broken and trees died. Decomposition of tree/branch debris provides NH$_4$ as byproduct, and through the process of nitrification, the concentration of nitrate in the water column increases [77]. At the same time, the formation of NO$_3^-$ from nitrification also increased the net production of terrestrial H$_3$O$^+$, which further reduced the pH of the water body [78].

As the primary and invaluable resource within terrestrial ecosystems, forest ecosystems play a significant role in the carbon and water cycle, material and energy exchange, and various interconnected circles [79]. Our study presents a comprehensive assessment of the water balance and water quality changes in the subtropical broad-leaved evergreen forest ecosystem of Southwest China over a decade. This serves as a functional platform for broader-scale temporal and spatial investigations. Our findings also demonstrate the valuable ecosystem services provided by the forest. For instance, the forest’s ability to reduce surface runoff can help mitigate the occurrence of flooding. Furthermore, the observed changes in water quality suggest the potential for enhanced purification capacity. Notably, the declining trend in cations might signify opportunities for improving water hardness. The results of our study offer insights into the current hydrological characteristics of the ecosystem, aiding relevant management organizations and personnel in identifying future management priorities and considerations.

5. Conclusions

Through the analysis of water balance and chemistry over the past 15 years in the evergreen broad-leaved forests of the Mourning Mountains, it became evident that the study area maintained constant precipitation levels despite a widespread decrease in
precipitation. This could be due to its unique geographic environment. The distribution of precipitation had three primary components: throughfall, canopy interception, and stemflow. These processes were influenced by precipitation intensity, LAI, and displayed varying trends over different time scales. The impact of the January 2015 snowstorm resulted in a significant increase in throughfall rate in 2015–2019. In the stage of water storage and export, the study area was similar to most other subtropical forests in that most of the water was stored in the soil and apoplastic material, and water was transported to the atmosphere through the evapotranspiration pathway. The dense forest canopy prevented acidic ions from the atmosphere from fully settling into surface water bodies, which have more acidic ions originating from rock weathering; this is the main reason why surface water pH is lower than atmospheric precipitation. Of course, this also implies the forest canopy has alkaline effect. In terms of inter-annual variability, there is a general trend of decreasing pH in surface water bodies, but this is recovered in 2019. The study area’s climatic characteristics, with simultaneous rainfall and high temperatures, mediated by plant influence, led to a negative correlation between the elements (i.e., Ca and Mg) and precipitation. The other elements, pH, TDS, PRCP, TEMP, and WT showed different degrees of correlation with each other. Overall, although the water balance fluctuated during the past 15 years, the water-holding capacity of the broad-leaved evergreen forests in the Ailao Mountains did not change significantly. As for water quality, there was a potential risk of alkali cation loss.

Author Contributions: Conceptualization, H.G. (Hede Gong); methodology, H.G. (Hede Gong); software, S.D.; validation, S.D., N.K., X.M. and H.G. (Hede Gong); formal analysis, S.D.; investigation, S.D., X.M. and H.G. (Hailong Ge); resources, H.G. (Hede Gong); writing—original draft, S.D.; writing—review & editing, N.K. and H.G. (Hede Gong); visualization, S.D.; supervision, H.G. (Hailong Ge); project administration, L.Z. All authors have read and agreed to the published version of the manuscript.

Funding: Ecological restoration mechanism of degraded slope farmland induced by soil erosion in the dry-hot valley region (912101/09910201G).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are available upon request from the corresponding author.

Acknowledgments: The authors acknowledge the data support provided by the National Forest Ecosystem Research Station at Ailaoshan. Special thanks are given to the editors and anonymous reviewers for their valuable comments and suggestions on this study.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Han, C.; Chen, N.; Sun, S.; Zhao, C.M. Progress of research on hydrological regulation function and mechanism of forest ecosystem. Chin. J. Ecol. 2019, 38, 2191–2199. [CrossRef]


15. Van Stan, J.T.; Gay, T.E.; Lewis, E.S. Use of multiple correspondence analysis (MCA) to identify interactive meteorological conditions affecting relative throughfall. *J. Hydrol.* **2016**, *533*, 452–460. [CrossRef]


39. Li, J.B. *Characterization of Four Subtropical Forest Apoplasts and Their Nutrient Dynamics*; Central South Forestry University of Science and Technology: Changsha, China, 2011.


41. Han, B.; Zou, X.M.; Kong, J.J.; Sha, L.Q.; Cao, T. Nitrogen fixation of epiphytic plants enwrapping trees in Ailao Mountain cloud forests, Yunnan, China. *Protoplasma* 2010, 247, 103–110. [CrossRef]


55. Ma, C.K.; Luo, Y.; Shao, M.G. Comparative modeling of the effect of thinning on canopy interception loss in a semiarid black locust (*Robinia pseudoacacia*) plantation in Northwest China. *J. Hydrol.* 2020, 590, 125234. [CrossRef]


66. Llorens, P.; Gallart, F. A simplified method for forest water storage capacity measurement. *J. Hydrol.* 2000, 240, 131–144. [CrossRef]


72. Xie, Y.C.; Huang, F.; Yang, H.; Yu, S. Role of anthropogenic sulfuric and nitric acids in carbonate weathering and associated carbon sink budget in a karst catchment (Guohua), southwestern China. *J. Hydrol.* 2021, 599, 126287. [CrossRef]


74. Pascual, G.; Sano, D.; Sakamaki, T.; Akiba, M.; Nishimura, O. The water temperature changes the effect of pH on copper toxicity to the green microalga *Raphidocelis subcapitata*. *Chemosphere* 2022, 291, 133110. [CrossRef]


76. Williamson, T.N.; Sena, K.L.; Shoda, M.E.; Barton, C.D. Four decades of regional wet deposition, local bulk deposition, and stream-water chemistry show the influence of nearby land use on forested streams in Central Appalachia. *J. Environ. Manag.* 2023, 332, 117392. [CrossRef]


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