Water-source contributions to barrier lakes and water-rock interactions in the Wudalianchi volcanic area, Northeast China

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ABSTRACT

Wudalianchi is a typical continental Cenozoic volcanic group rich in potassic volcanic rocks (Northeast China). Five hydrologically connected barrier lakes (Lakes 5 to 1) and upwelling cold mineral springs occur, forming a complex lake-groundwater system. Clarifying the water-source contributions and the role of water-rock interactions in the hydrological cycling for barrier lakes remains a challenge from scientific and engineering perspectives. In this study, seasonal variations of multiple isotopes were analyzed. δ18O and δD data indicate that the Wudalianchi lakes were mainly fed by mineral springs. The values, however, were greatly influenced by precipitation (rain and snow) and varying evaporation intensities. In contrast, 87Sr/86Sr ratios varied little between seasons (0.70701–0.7079), suggesting similar water-rock interactions through time. Nonetheless, Sr isotopic mixing models suggested that shallow mineral springs generally contributed >50% of the water to lower reaches. In contrast, the upstream wetland contributed >50% to Lake 5 and decreased down-valley (10.3–53.6%). Calculations based on the δ18O and δD Rayleigh fractionation equation suggest that evaporation in upper reaches was higher than the lower reaches. The evaporation in July was generally higher than in October. This study demonstrates the homogenous water-rock interactions and the associated water mixing effects on the terrestrial volcanic area.

Key words: barrier lake, hydrological processes, isotopes, water-source contributions, Wudalianchi

HIGHLIGHTS

• 87Sr/86Sr ratios varied little across seasons; δD and δ18O varied significantly.
• δD and δ18O values of lakes were impacted by evaporation and precipitation.
• Four endmember sources were identified by geochemical and isotopic data.
• Shallow mineral springs and wetland water contributed most to lake waters.
• Water-rock interaction and water mixing effect were highlighted in terrestrial volcanic area in eastern China.

INTRODUCTION

The Wudalianchi volcanic area is a typical terrestrial Cenozoic monogenetic volcanic group, which originated from partial melting of the mantle composed of a carbonate asthenosphere (in the mantle transition zone) (Tian et al. 2016; Lu et al. 2020). Volcanic material from different volcanoes is from the same magmatic source and deposited within the Quaternary strata, resulting in similar geological and sediment chemical characteristics (Xing et al. 2020). Wudalianchi volcanic rocks are the most typical Cenozoic potassic volcanic rocks in eastern China (Wang et al. 1988). The diversity of water-rock interactions is vital for understanding the geochemical characterizations of various hydrological compartments (e.g., rock weathering and bedrock fracturing) during water cycling (Négrel et al. 2018). With globalization, the contradiction of increasing water demand and the limited availability of water resources has restricted the sustainable development of the economy and society (Li et al. 2019). This is especially true in the Wudalianchi UNESCO Global Geopark, where the economy is closely linked to the mineral springs industry and tourism (Zhang et al. 2018a). Hydrologically, the barrier lakes in the Wudalianchi region are linked to upstream wetlands and the evolution of nearby cold mineral springs, forming a complex surface water–groundwater system (Mao et al. 2009; Gui et al. 2011). The region is
characterized by a long ice period in the winter (>6 months a year, surface water is thickly frozen in winter), an unbalanced amount of precipitation (~80% occurs during July to September), and seasonally variable forms of precipitation (rain and snow) (Gui et al. 2012; Figure 2), all of which may result in differences in water-source contributions to the lakes between seasons. Such hydrological variations need to be scientifically estimated to efficiently support environmental management strategies to maintain the sustainability of water resources in Wudalianchi (Gao et al. 2019).

In a catchment, atmospheric precipitation goes through the unsaturated zone and recharges the groundwater during rainy season (Zhao et al. 2018). The relatively small seasonal variations of δ18O and δD in the groundwater contrast markedly with the seasonal variations in precipitation, suggesting a relatively long residence time for groundwater (>1 year) (DeWalle et al. 1997). At global and regional scales, the δ18O and δD values of precipitation are influenced by temperature, latitude, and continental effects as well as the predominant moisture sources (Clark & Fritz 1997), which determines the isotopic distribution of river waters during rainy seasons (Li et al. 2015; Kikels et al. 2020). At the local scale, most studies on groundwater recharged have depended on local precipitation, while the cycling of surface water is influenced by local precipitation, temperature, wind speed, evaporation, water sources and their seasonal changes (Clark & Fritz 1997). Unlike river water, the basis for isotopic changes in lakes is equilibrium or kinetic fractionation that occurs at the water-vapor interface during evaporation processes (Qian et al. 2013). Such isotopic changes typically follow the Rayleigh fractionation equation and can be used to calculate evaporated portions from the water column (Huang & Pang 2012; Yang et al. 2018). However, the proposed method is still questionable (Qian et al. 2013; Zhong et al. 2019; Kalvâns et al. 2020), especially when assessing semi-arid and arid regions (Hao et al. 2019), because evaporation usually results in enriched values of δ18O and δD in surface waters with the recharge of groundwater (the isotopic value of groundwater obtained by measurement is relatively stable).

Sr isotopes (87Sr/86Sr) have been used effectively to fingerprint water sources and document water interconnections between surface and ground waters in time and space (Wang et al. 2007; Zieliński et al. 2016, 2017). A major advantage of using 87Sr/86Sr ratios as a tracer is that isotopic fractionation during evaporation and biogeochemical cycling is negligible. Hence, many case studies have highlighted the usefulness of the Sr isotope technique in hydrogeology to characterize the diversity of water-rock interactions and the mixing of water from different origins (Santoni et al. 2016; Négrel et al. 2018). The contributions of water from different sources often are determined by constructing binary mixing models of Sr (87Sr/86Sr) (Christensen et al. 2018; Xue et al. 2019) or by using multivariate mixing models based on mass balance equations of Sr concentration, 87Sr/86Sr ratios, δ18O, and other parameters (Phillips & Gregg 2001; Bu et al. 2016; Santoni et al. 2016).

The aims of the present study are to investigate the distinction of major hydrogeochemical processes and water-source contributions among seasons by characterizing the seasonal variations in 87Sr/86Sr and δ18O and δD values of Wudalianchi barrier lakes. We elucidated the major hydrogeochemical processes in the water cycling of the barrier lakes and estimated the contributions of major endmembers among seasons. Inherent in this study is a discussion of seasonal changes in lake water sources and the loss of water by evaporation based on δ18O and δD data. We identified the Sr characteristics of the water sources and the role of water-rock interactions in the terrestrial volcanic water system. Finally, we clarified the environmental significance of changing water-source contributions in the complex barrier lake-groundwater system of Wudalianchi.

MATERIALS AND METHODS

Site description

Wudalianchi is a UNESCO Global Geopark that encompasses 1,400 km² (518 km² in its core area); it is named after five hydrologically connected barrier lakes (Figure 1(a)) that were created by lava flows that blocked the river valley in 1710 AD in northern Heilongjiang Province (northeastern China). Lakes 1 to 5 are located along a valley from south to north; these five hydrologically connected barrier lakes, like a string of beads, cover a total area of 18.36 km², store 21.57 × 10⁶ m³ of water and are connected by a 5,250 m long river (Gui et al. 2011). The area of Lake 3 is the largest (8.2 km²), followed by Lake 5 (5.3 km²) and the smallest is Lake 1 (0.25 km²) (Gui et al. 2011, 2012). Lakes 2 and 3 are deeper with maximum depths of 10 m, and the maximum depth of Lake 5 can reach 6 m in summer and 4 m in winter (Zhang et al. 2018b). The river entering the lake is the Shilong River, which originates from a wetland in the northern part of the Geqiu volcano, and the Zhangtongshigou River (Figure 1(a)). Arable land and wetland surround the upper reaches of Lake 5, resulting in the input
of terrestrial materials (Gui et al. 2012). The swamps and swampy meadow wetlands in Wudalianchi are distributed all over the city. The area of 587 km² of swamp wetland accounts for 70.6% of the total wetland area in Wudalianchi, while the area of river wetland accounts for only 0.8% (Dong et al. 2008). From north to south, lakes eventually flow into the Nimoer River, which ultimately discharges to the Nen River. Fourteen Quaternary volcanoes with well-preserved cones and volcanic landscapes and edifices exist around the barrier lakes (Sun et al. 2019; Figure 1(a)). The major volcanic rock type is potassic Holocene and Pleistocene basalt (Mao et al. 2009).

There is a 68 km² Shilong lava on the west bank of the lakes ($\beta Q4_1$). The bottom lithology of Wudalianchi lakes is primary volcanic lava (Zhang et al. 2018b).

There are three major aquifers in the Yaoquan volcano area (YQVA). Water derived from a confined aquifer in the fissures and fractures of the Cambrian metamorphic rocks and Indosinian granodiorite of the Yaoquan volcano located west of Fanhua Spring (FhS) is the primary mineral spring (Mao et al. 2009). The upwelling primary mineral water mixes with the pore and fissure waters in the Cretaceous-Tertiary sandstone to form the secondary mineral water, which discharges as springs at the intersection of the major faults (Zhang et al. 2018a; Figure 1(b)). Phreatic water flows toward the southern and northern (SN) extensional faults and mixes with water from the deep confined aquifer, forming the south and north springs (SS and NS) (Figure 1(b)), which are two typical deep mineral springs (Zhang et al. 2018b). Shallow mineral springs include Quaternary phreatic water that is stored in a weakly confined shallow aquifer that receives meteoric waters and deep groundwater and is distributed on both sides of the five connected barrier lakes (Mao et al. 2009). In the YQVA, shallow mineral springs, such as Erlongyan Spring (ElyS) and FhS, emerge at the junction of the east-west (EW) and northeast (NE) trending fractures in the eastern section of the Yaoquan volcano (Zou et al. 2019). The water temperature of the mineral springs ranges between 2 and 6 °C, which contributes to rare hydrochemistry not only suitable for potable supply but also beneficial to therapeutic and medication purposes (Zhang et al. 2018a).

The Wudalianchi area is affected by the mid-temperate continental monsoon climate of China. Because of local topographic and elevational differences, the Wudalianchi area is characterized by a humid climate in the cold temperate zone of the Great Khingan Range and a semi-humid to semi-arid climate in the temperate zone of the Songnen Plain. The average annual rainfall and average annual evaporation is 548 mm and 1,257 mm, respectively (Figure 2; Gui et al. 2012). The annual average relative humidity is 69% (Figure 2). The minimum and maximum monthly temperature occurs in January (average: $-24^\circ$C) and July (average: $21.1^\circ$C), respectively. The average annual temperature is $-0.5^\circ$C (Zhang et al. 2018a). Except for the mineral water that flows all year around, surface water is frozen in the winter, which occurs from October to May. Ice thickness varies over the lake surface; shallow ice can be as thin as 90 cm, and thick ice can reach 3–4 m.
Sampling and analysis

For this study, we obtained lake water samples in July (high flow), October (low flow) and March (ice period) in the Wudalianchi lake region (Figure 1(a)). Lake 5, the most upstream lake, is located far from the road and is often covered with snow, making sample collection difficult. Thus, we collected only two samples in March. Although transportation to the other lakes (Lakes 4 to 1) was easier, temperatures were extremely low in March, resulting in the freezing of the water surface. The barrier lakes are relatively shallow (the maximum depth during high flow is 6–10 m; depths are even lower during the low flow period). Thus, during this study, we collected lake waters from the epilimnion (at a depth of 0.5 m or 0.5 m under ice).

A total of 37 lake samples were collected during three sampling campaigns for the determination of Sr contents, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^D$ and $\delta^{18}O$ values. We filtered the collected water samples through 0.45-μm cellulose acetate filter paper and preserved the samples in low-density polyethylene (LDPE) containers in a refrigerator at 4 °C for analysis (Zou et al. 2019). Before use, we soaked the LDPE containers in an acid solution for 24 hr and rinsed them with ultrapure water. Before sample collection, we rinsed the bottles two or three times with filtered lake water or groundwater. We analyzed the concentration of Sr using inductively coupled plasma mass spectrometry (ICP-MS). We determined the isotopic compositions of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) by a VG354 mass spectrometer. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NBS 987 Sr standard was $0.710249\pm 0.000031$ (2σ, $n = 20$). The calculated analytical uncertainty based on the standard was 0.00535%, and the standard deviation was 0.00025 (Yang et al. 2011). We determined the $\delta^D$ and $\delta^{18}O$ values using a Picarro IM-CRDS L2140-i (Santa Clara, CA, USA); precision of the H and O isotope analyses was within $<1.5\text{‰}$ and $<0.35\text{‰}$, respectively. The results were expressed in per mil (‰) deviations relative to Vienna Standard Mean Ocean Water (V-SMOW).

RESULTS AND DISCUSSION

Seasonal variations in $\delta^{18}O$ and $\delta^D$ values

In contrast to small seasonal variations in the $\delta^{18}O$, $\delta^D$ and deuterium excess values for shallow and deep mineral springs and well waters as indicated by Zhang et al. (2018b), the lake waters showed obvious seasonal variations (Figure 3, Table S1). The $\delta^D$ and $\delta^{18}O$ values exhibited the following decreasing order: July > October > March. In contrast, deuterium excess exhibited the following increasing pattern: July < October < March. These contrasting trends suggest the presence of different air mass sources and evaporation intensities across seasons. Although the lake waters collected in July and October plotted along a similar LEL with a slope between 4 and 6, the waters in July showed higher $\delta^{18}O$ and $\delta^D$ values and lower deuterium excess than in October, suggesting the great influence of rain and evaporation. In addition, the slope of the LEL for the mineral springs was 2.85, varying between 2 and 3, reflecting soil water infiltration or vadose zone soil water storage (Barnes & Allison 1988). The slope difference between lake water and mineral water further indicate that the lake water was affected by secondary evaporation.

It seems like the lake waters could just be evaporated rain water as they site along the LEL representative of evaporation, which seems like it would extend to align with the March lake values (Figure 3). However, in Wudalianchi catchment, the mineral spring samples usually plotted at the intersection of the LEL with LMWL, which
indicate that the isotopic values of mineral spring waters can be empirical approximation of the weighted mean isotopic composition of input waters to the catchment, while not precipitation (Qian et al. 2013). Nevertheless, differences in evaporation processes and water sources (rain and snow) appear to lead to big seasonal variations in the δ18O and δD values of the Wudalianchi lakes.

Seasonal variation of 87Sr/86Sr
Spatial variations in the geochemistry of relatively shallow springs with respect to Sr varied as a function of the level to which the deep mineral spring water was mixed with and diluted by other waters (e.g., rainwater, wetland water, and sewage; Vitòria et al. 2004) during its upward migration. The mixing of distinct water bodies created variations in 87Sr/86Sr ratios such that the values of deep (average 0.70686) and shallow (average 0.70677) mineral spring waters typically were higher than that of bedrock (0.70503–0.70589); however, they were lower than those of lake waters (0.70703–0.70816) and much lower than that of rainwater (~0.70970) in summer. This analysis differed from earlier studies that assumed the only source of Sr was the deep mineral spring waters (Zhang et al. 2018b) that originated from water-rock interactions (Qian 2007).

In this study, the seasonal variation of 87Sr/86Sr ratios for each lake collected in July (0.70714–0.70790), October (0.70701–0.70777), and March (0.70711–0.70779) was not as significant as those of δ18O and δD values. The measured values presumably reflected derivations in the Sr released during water-rock interactions that occurred in the subsurface of volcanic area, as low 87Sr/86Sr ratios were expected from the potassium volcanic rocks (0.70503 to 0.70589; Wang et al. 1988). The 87Sr/86Sr ratios found in Quaternary potassium volcanic rocks in Wudalianchi, however, were much lower than the carbonate (~0.71) and silicate (0.725) endmembers selected for the river system (Wang et al. 2007; Bu et al. 2016). Seasonally, the ratios were slightly lower in March and, to a lesser degree, in October, both of which were generally lower than in July, suggesting different mixing of endmembers across seasons (Figure 4(a)). In contrast, the δD and δ18O values of the groundwaters (e.g., from deep and shallow mineral springs, wells) were nearly identical. Thus, the processes responsible for the differences in the Sr isotopic composition of the lake waters differed from those responsible for the variations observed in δD and δ18O values (Figure 4(b)). This identifiable difference was likely caused primarily by variations in water-rock interactions and water-source contributions (Négrel et al. 2018). On the basis of the analysis of 87Sr/86Sr ratios and δD and δ18O values, the resulting isotopic data plot within the ‘space’ defined by four identified end members (Figure 4).

Determination of lake water sources
The water sources of Sr to the lakes included the following: (1) precipitation (rain or snow), (2) wetland waters in headwater areas, (3) deep mineral springs, (4) shallow fresh mineral springs, (5) a combination of surface runoff and shallow throughflow (soil water), and (6) inflow from rivers (Figure 5).

In this study, precipitation exhibited relatively high 87Sr/86Sr values (~0.71) and much higher Ca/Na mass ratios (>7) compared with lake water. The latter ratio probably resulted from the incorporation of airborne carbonate dust into the precipitation (Åberg 1995). In addition, the δ15N values of NO3 in the precipitation may have reflected

Figure 3 | Seasonal variations in δD and δ18O values of lakes and groundwaters in July, October, and March. GMWL: global meteoric water line, y = 8x + 10; LMWLQiqihar: the local meteoric water line from Qiqihar (the closest meteorological station contains the dataset from GNIP); LELJuly-Oct and LELMar: the local evaporation line for July-October (y = 4.37x – 33.94) and March (y = 2.91x – 53.23), respectively; MSWL: mineral spring water line, y = 2.85x – 52.39.
urban exhausts from the surrounding cities (Zhang et al. 2018b). Thus, carbonate minerals and urban exhausts appeared to have also influenced the chemistry of the rainwater. About 80% of the total precipitation concentrated during the high flow season (July to September) (Figure 2) and rainwater could be regarded as an isotopic endmember.

Wetlands are hydrologic features that result from the mixing of groundwater discharge at the surface of the Earth with rainfall. The wetlands studied herein are located in the headwaters (uppermost part) of the basin. Thus, wetland recharge represented groundwater that had not been significantly affected by evaporation or by inputs from mineral springs located down valley. As such, we used samples from the wetlands to characterize the wetland discharge from the headwater regions, which subsequently flowed laterally, ultimately feeding the lakes. In our study area, water from these headwater wetlands flowed directly into Lake 5 during both high and low flow and then flowed down valley along the channel to the lower reaches of the basin. Shallow mineral spring waters in the lower reaches of the basin were derived from phreatic water housed in Quaternary deposits that flowed upward to the surface. During upward migration, the fresh spring waters evolved from the mixing of the upwelling deep mineral spring waters and the downward infiltrating rainwater (Han et al. 2012; Zhang et al. 2018a). Thus, with respect to $^{87}$Sr/$^{86}$Sr ratios, shallow mineral spring waters were geochemically and isotopically equivalent to deeper groundwaters and served as an isotopic endmember (Figure 4). The discharge of spring waters along the bottom of the lake was likely responsible for the continuous supply of water to the lakes (Zhang et al. 2018b).

We used samples from groundwater wells to characterize water within the shallow groundwater system in different parts of the basin, particularly in areas dominated by anthropogenic inputs (e.g., agriculture; Zhang et al. 2018a). The shallow groundwater sampled from the well did not form an isotopic endmember. Rather, compositionally, this water plotted within the region defined by the other four endmembers (Figure 4). Thus, we felt the sampled well water reflected the infiltrating surface runoff and shallow throughflow that resulted from water-soil interactions. In addition, hydrologically, the Zhangtongshigou River (Site 11) flows directly into Lake 3, but its Sr ratios and water (H, O)

![Figure 4](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.177/901911/ws2021177.pdf)
isotopes do not form endmembers. Therefore, at the watershed scale, the inflow water of the catchment seems to consist of rainwater and waters that have undergone similar water-rock interactions to other water in subsurface. This reflects the multi-water system controlled by the typical geological genesis and similar isotopic properties caused by the homogeneous substances in Wudalianchi volcanic area.

### Calculation of mixing ratio and proportion of evaporation

Lake water variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were primarily caused by the mixing of waters from different sources that were characterized by different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents. The contributions from each source likely reflected the interaction of water from different aquifers (shallow and deep mineral springs) that had experienced different degrees of water-rock interactions (shallow fresh mineral springs, wetland water, and shallow groundwater observed in wells). An approximate quaternary mixing model was used to explain the chemical and isotopic composition of groundwater in terms of precipitation (rain and snow), shallow and deep mineral springs and wetland water (Figure 4(a)). Since Sr$^{2+}$ concentration is usually affected by more processes than $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, the interpretation of changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is less ambiguous than the simultaneous changes in solute concentrations (Santoni et al. 2016). In Wudalianchi, the strontium content of rainwater was similar to that of snow, and the distribution of lake water samples in different seasons was slightly overlapped; however, well binary mixing models were shown (Figure 4(a)).

To quantify the contributions of water from each lake water source, we used a three end-member mixing model to calculate the source contributions (mixing ratios) of Lakes 1 to 5 waters in July (Equation (1)). The model included the application of the following equations (Bu et al. 2016):

$$
\begin{align*}
&f_R \left( ^{87}\text{Sr} / ^{86}\text{Sr} \right)_R + f_S \left( ^{87}\text{Sr} / ^{86}\text{Sr} \right)_S + f_W \left( ^{87}\text{Sr} / ^{86}\text{Sr} \right)_W = \left( ^{87}\text{Sr} / ^{86}\text{Sr} \right)_L \\
&f_R + f_S + f_W = 1
\end{align*}
$$

The Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the lake waters satisfied a binary linear mixing relationship between wetland water and shallow fresh mineral spring waters in October and March (Equation (2)), as
shown in Figure 4(a). We calculated the contributions in this case using the following equation (Xue et al. 2019):

\[
\begin{align*}
\left\{ \begin{array}{l}
\frac{f_W^{87\text{Sr}}}{f_{S}} \times (\text{Sr}_W) + f_S^{87\text{Sr}} \times (\text{Sr}_S) = \left( \frac{87\text{Sr}}{86\text{Sr}} \right)_L
\end{array} \right.
\end{align*}
\]

\[f_W + f_S = 1\]

(2)

As discussed previously, we used the average values over the three seasons for each lake (Lakes 1 to 5). We used the lake water data at Site 7, which received wetland discharge, to characterize the composition of the wetland water (W) endmember (Table S2). Samples of shallow mineral spring waters (S) collected in March were used to characterize the shallow fresh mineral spring waters because the water cycling is relatively simple (low permeability and little precipitation in winter) and the strontium content was the lowest due to the influence of the ice-period season (0.70693; 0.07 mg/L). We used the average values of rain to characterize the endmembers of rain, respectively (Table S2).

The results showed that the contributions of rainwater to the lakes were relatively low, generally < 20% in July (17.2% ± 2.3%). Precipitation seems to be the only source of water independent of volcanic sources, and its limited contribution indicates that Sr in barrier lakes is dominated by water-rock interactions. The precipitation contributions calculated using Sr isotopes were close to the estimated values based on rainfall and lake storage, as shown in the Supplementary material (∼18.1%). It was much lower than contributions estimated for a forest-river system (74%, Bu et al. 2016), demonstrating the particularity of barrier lake-cold mineral spring system in Wudalianchi.

In October and March, the contribution of the shallow mineral spring waters to the lakes was generally higher than 50%, except that Lake 5 was dominantly fed by wetland water (62.5% and 75.7%, respectively) (Table 1). In contrast, the contribution of upstream wetland water was particularly high to Lake 5 (> 50%) and significantly decreased in lakes located along the lower reaches of the valley (as low as 10.3%) throughout the year.

We calculated the evaporated water for July and October only using the Rayleigh fractionation equation (Yang et al. 2018) (Table 2). In March, the lakes were covered by ice, and differences in the isotopic composition between the upstream and downstream lakes were small (Table S1). The δD and δ18O values between these two seasons varied because of seasonal differences in temperature and precipitation. As expected, the results showed that the proportions of evaporated water from each lake (Lakes 5 to 1) in July were generally higher than those in October (Table 2).

Environmental implications

The Wudalianchi area has the climatic characteristics of high evaporation but low precipitation, and the water isotopes of barrier lakes are easily affected by the seasonal differences of precipitation patterns (rain and snow) and proportion of evaporated water, showing great changes from season to season. According to the distribution of water isotopes of lake water samples in the meteoric water line, we can judge that the ultimate source of lake water is atmospheric precipitation, but it is of more practical significance to study the direct source of barrier lake water and its seasonal variation. In the Wudalianchi lakes, the \(\frac{87\text{Sr}}{86\text{Sr}}\) ratio and Sr\(^{2+}\) concentration accorded with binary mixing model of wetland water and shallow mineral spring in October and March; however, the rainwater contributed additionally to the barrier lake waters in July (Figure 4(a)). It can be indicated

<table>
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<th>Source contributions for lakes in July, October, and March</th>
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<tbody>
<tr>
<td>Season</td>
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<tr>
<td>Lake</td>
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<td>5</td>
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<td>1</td>
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Note: R%, S%, W%, and W% refer to the relative contributions of water from rain, shallow freshwater mineral spring, deep mineral spring, and wetland water, respectively.
from Figure 4(a) that the lake water samples deviated upward from the binary mixing line in July, reflecting the contribution of rainwater in the high-flow season, it is far less sensitive than water isotopes. While in October and March, the lake waters were more strictly distributed according to the linear mixing model. In March, the lake waters in upper reaches (Lakes 4 and 5) also seemed to be more affected by wetland water (53.6–75.7%; Table 1), even although the lake surface was covered with ice and snow during the frozen period. The water samples of the lakes were approximately linear in Figure 4(a). The distribution for each lake was successive from lakes 5 to 1, indicating the direct water supply from upstream lakes or rivers. The study also shows that during the hydrogeochemical cycle in Wudalianchi barrier lakes, temperature, proportion of evaporated water and precipitation have significant effects on the water isotope characteristics, which makes it difficult to calculate the mixing ratio by using the mixing model of $^{87}$Sr/$^{86}$Sr ratios and $\delta^{18}$O, although it can well indicate the mixing endmembers across seasons (Figure 4(b)). In addition, the water-source contributions to the Wudalianchi lakes in the terrestrial volcanic lava environment were stable, that is, it is directly recharged dominantly by shallow mineral spring and wetland water all the year round.

Previous research has documented that the water sources of the barrier lakes seem to be much related to different environmental problems (Zhang et al. 2018a). Lake 5 is prone to terrestrial material inputs (Gui et al. 2012), leading to strong eutrophication of lake waters (Wang et al. 2017). Shallow mineral springs act as sinks for nitrate with low ‘self-remediation’ (Zhang et al. 2018b). The contribution of precipitation is low, and its direct impact on the lakes is relatively minor, although evidence indicates that it is an important carrier of urban pollution nearby (Zhang et al. 2018b). The migration of fertilizers caused by rainfall-driven soil leaching during infiltration, however, may have caused enrichment of the subsurface environment in nutrients (Zhang et al. 2018a, 2018b). Finally, surface pollutants can cause environmental problems during lake–groundwater interactions, further complicating future carbon metabolism in both shallow mineral springs and sedimentary environments (Zou et al. 2019). In addition, affected by tourism and industry, the southeast of Yaoquan Lake showed the high content of nitrogen and phosphorus in sediment with high degree of eutrophication, which potentially threatens the sustainable development of the mineral water belt (Yang & Zeng 2012). Our findings demonstrated the processes by which lake-groundwater interactions and the associated environmental problems threaten the sustainable development of mineral water resources and the lake water environment.

CONCLUSION

This paper explores hydrological processes and quantifies the contribution of major water sources to barrier lakes across seasons in Wudalianchi. The results showed that the $\delta^{2}D$ and $\delta^{18}$O values of each lake exhibited large seasonal variations because of precipitation (rain and snow) and evaporation effects. Due to evaporation, the isotopic values of lake water in July and October were much higher than that of groundwater, whereas the isotopic values of lake water in March were generally lower than that of groundwater. The evaporation in the upper reaches of the basin was generally higher than the lower reaches in both July and October. Each lake possessed a higher evaporation in July than in October. In addition, the intersection of the LEL and LMWL indicated that the dominant water source came from a mineral spring rather than from atmospheric precipitation.

In contrast, $^{87}$Sr/$^{86}$Sr ratios varied little between seasons. The collected seasonal data reflected variations in the contributions of major water sources to the lakes, which was quantified using ternary mixing models. Fresh shallow mineral spring waters that originated from the Quaternary phreatic system provides a continuous water

<table>
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<th>Table 2</th>
<th>Evaporation from Lakes 1 to 5 in July and October</th>
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<tbody>
<tr>
<td></td>
<td>July</td>
</tr>
<tr>
<td>Lake</td>
<td>Remaining Evaporation</td>
</tr>
<tr>
<td>5</td>
<td>88.1% 11.9%</td>
</tr>
<tr>
<td>4</td>
<td>87.0% 13.0%</td>
</tr>
<tr>
<td>3</td>
<td>96.9% 5.1%</td>
</tr>
<tr>
<td>2</td>
<td>94.1% 9.6%</td>
</tr>
<tr>
<td>1</td>
<td>93.1% 9.6%</td>
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</tbody>
</table>

Note: The $\delta^{2}D$ and $\delta^{18}$O values measured in the most upstream waters from Lake 5 (Site 1, Figure 1) as the initial values from which to calculate proportion of evaporated water for the lakes downstream.
source to the shallow hydrological system and contributes most to the downstream lakes across seasons (generally >50%). In addition, wetland water contributed more than 50% of the recharge to the upstream lakes throughout the year. The contribution of rain in July, however, varied between 14.0 and 20.3%, which is similar to estimated values (~18.1%). The geochemical and isotopic compositions of the barrier lakes reflected the seasonally variable mixing associated with complex surface water–groundwater interactions as well as interactions between multiple sources of groundwater, which materially are based on the products of water-rock interactions. The interrelationship of this complex multi-source water body contributes to a greater risk of pollution through hydrological processes and thus needs further attention.

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DECLARATION OF COMPETING INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest

DATA AVAILABILITY STATEMENT

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

REFERENCES


Gui, Z., Xue, B., Yao, S., Zhang, F. & Yi, S. 2012 Catchment erosion and trophic status changes over the past century as recorded in sediments from Wudalianchi Lake, the northernmost volcanic lake in China. Quatern. Int. 282, 163–170.


