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Research article

Water stable isotopes and volumetric discharge rates to monitor the Rhône water's seasonal origin

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ABSTRACT

Along the 98 800 km² Rhône catchment area, 3 million people depend on the river resource and its sustainability. Flow rate monitoring of the French rivers showed the importance of the Swiss part of the Rhône (measured at station 1), the Isere (station 2) and the Durance rivers (station 3) contribution into the Rhône downstream (station 4) during summer when other recharges are decreasing. While their contribution is only of 10–30 % during most of the year, those rivers could contribute to more than 60 % of the Rhône flow rate during the driest period. The current study aims at confirming the key role of Alpine rivers contribution to the Rhône downstream flow by investigating an alternative monitoring tool of high-altitude water contribution. As a suitable tracer of latitude and altitude especially in a contrasted morphology, such as the Rhône watershed, water stable isotopes can be relevant to trace the origin of the recharge contributing to the waterflow. This study is based on a full hydrological cycle survey of the Rhône downstream water isotopes signature complemented by the current flow rate monitoring program of the Alpine rivers. With a linear regression model between both parameters data, the current study evidences the relevance of using water isotope signature to trace the seasonal change of water's origin and evaluate the high altitude waters contribution (RQ_{AR}) into the Rhône river downstream flow rate ($\delta^2H = 26.0 \times RQ_{AR} - 57.9$ with $R = 0.88$, $R^2 = 0.79$ and a p-value < 0.0001). It also confirms the key role of Alpine waters contribution to the Rhône River during summer with average value of $70 \pm 6\%$ and the importance to monitor the sustainability of their contribution in future drier period.

1. Introduction

Along the Rhône catchment area, 3 million people use the river resource for water supply. Hence, they depend on the hydraulic regime of its different sub-watersheds that contribute to recharge the Rhône River with: oceanic, continental and Mediterranean rainfalls as well as glaciers and snow water melt (Olivier et al., 2009).

Along the year, the relative contribution of each system to the Rhône River recharge evolves to a point that only a few of them sustain the flow rate in summer. Hence their contribution becomes essential. Indeed, monitoring of French rivers' flow rates has indicated the importance of the Alpine waters contribution during summer (Olivier et al., 2009; Ollivier et al., 2011). The Rhône, in Switzerland (measured at station 1), the Isere (station 2) or the Durance (station 3) rivers route those waters downstream and contribute to more than 50 % of the Rhône River flow rate measured at station 4 (Figure 1). Yet, climate change may impact on the Alpine resources availability through accelerated glaciers melt, altered precipitation regime and regular droughts (Beniston, 2012).

Thus, it is essential to confirm the heavy reliance of the Rhône low flow rate in summer on alpine waters, as it may become a key driver of vulnerability for future water resources management.

The current study aims at confirming the key role of Alpine rivers contribution to the Rhône downstream flow by investigating an alternative monitoring tracer of high-altitude recharge. Water stable isotope signature may provide useful hydrological information to do so. As a suitable conservative tracer, the water stable isotopes have been widely used to assess the contributions of water bodies that originates from different latitude and altitude (Jiaxin et al., 2015; Tetzlaff et al., 2017). Given the Rhône catchment area configuration and its diversity in terms of latitude and elevation, those tracers can be particularly relevant to:

- witness change of the origin of water;
- provide an alternative tool to trace Alpine waters specifically.

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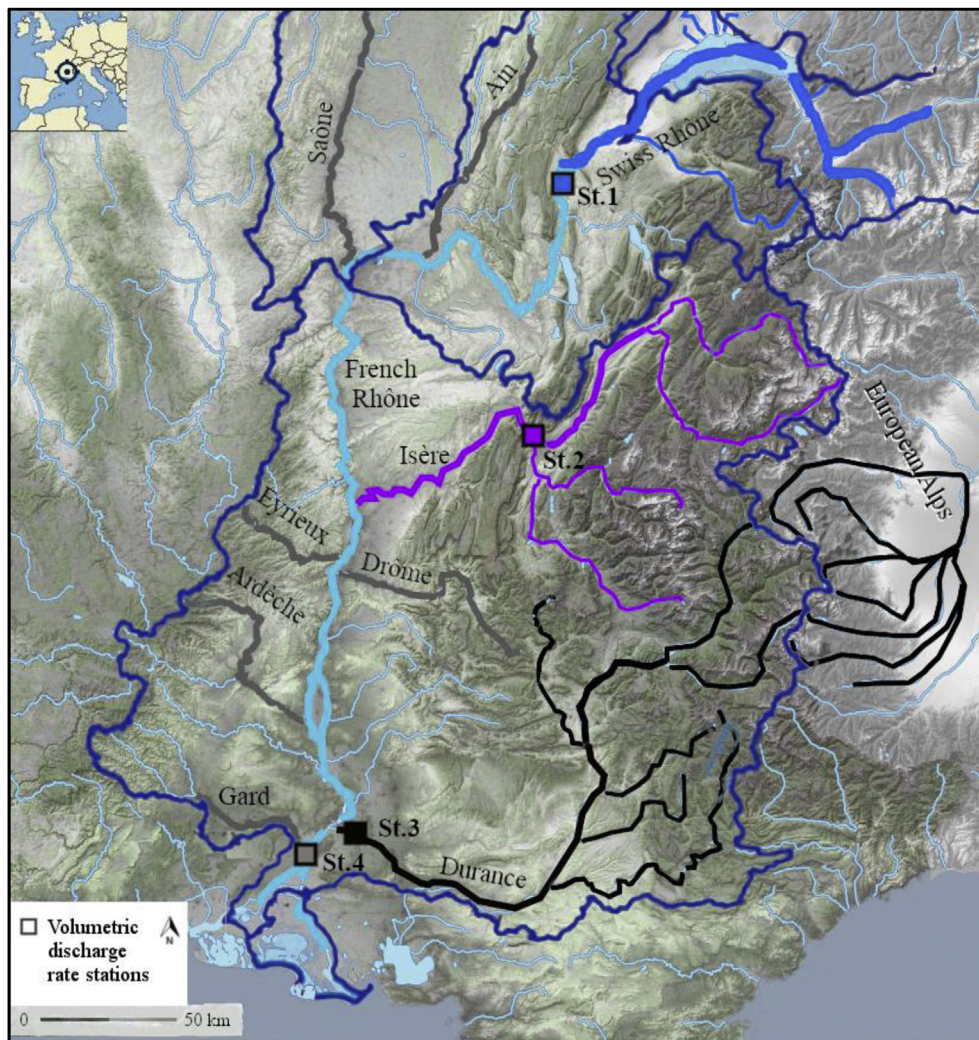


Figure 1. Rhône river watershed with the alpine tributaries identified and surface water monitoring station locations.

2. Site description

The Rhône River is one of the major European rivers with a drainage area of 98 800 km² (Figure 1). With its head in the Switzerland Alps, at 2 209 m, it flows through 300 km before reaching France after Lake Geneva. From there, the Rhône River flows along the western Alps towards the Camargue delta and ultimately the Mediterranean Sea after a 512 km long journey through France (Olivier et al., 2009).

The Rhône River's watershed comprises is comprised of four major mountainous catchment areas: The Alps, the Jura, the Cevennes, and the Vosges, with maximum heights of 4 807, 1 718, 1 699 and 1 424 m above sea level respectively. The Rhône's water recharge is ruled by precipitations of multiple origins: oceanic, continental and Mediterranean rainfall, as well as by glacier and snow melt (Olivier et al., 2009; Ollivier et al., 2011). The Rhône catchment area can be divided into three main hydrological sub watersheds (Figure 1). From the head to the Lake Geneva, the upper Swiss watershed is characterized by high mountains and 50 % of its recharge as snow. The mountainous regime of the Rhône in Switzerland is mainly characterized by low flow during winter (350 m³/s) and the highest flow in spring and summer due to glacier and snow melt (502 m³/s). After the confluence with the Ain River (44–174 m³/s), draining the Jura mountain, the Rhône River flows into its second main sub watershed from Lyon to Valence. This middle Rhône sub watershed is characterized by two main tributaries: The Saône and the Isere rivers. The Isere River is under an Alpine regime similar to that of the Swiss

Rivers, with low flow during winter (155 m³/s) and the highest flow in spring and summer (263 m³/s). The Soane River, which flows from the northern area, is the only typical lowland plain tributary. Unlike the upper catchment regime, its flow rates are ruled by an oceanic pluvial regime with higher rates in winter (700 m³/s) than in summer (160 m³/s). From Valence city to the Rhône's mouth, the third lower Rhône sub watershed is characterized by several tributaries which drain either the Alps (Drome, Durance) or the Cévennes (Eyrieux, Ardèche, Gard). Those last southern tributaries have a typical Mediterranean regime with highest discharge resulting from September to October floods. At the Rhône mouth, this diversity of upstream tributaries and their associated regime leads to highly seasonal flow rate variations from year to year (Ollivier et al., 2011). The Rhône River flow rate, monitored between 1920 and 2014, ranges from 2 000 m³/s in high flow periods to 1 080 m³/s in low flow periods during summer. The flow rate variation is tightly linked to the contrasting regime of the different watershed and thus to the origin of the recharge water over the year. This study focusses on the investigation of Alpine waters' contribution to low flow sustainability Table 1.

3. Materials and methods

The Alpine water contributes to the Rhône River though glacier runoff, snow melt, local groundwater and rainfall that enter to the Swiss (Alpine) part of the Rhône River, and its tributaries Isere and Durance.

Table 1. Hydrological characterization of the Rhône River basin (Olivier et al., 2009; Bravard and Clemens, 2008; Sandre Data base). Alpine tributaries (Isère, Durance) and Rhône in Switzerland are investigated.

	Rhône in Switzerland	Rhône in France	Ain	Saône	Isère	Eyrieux	Drôme	Ardèche	Durance	Gard
Catchment Area (km ²)	8 018	98 800	3 713	29 498	11 865	865	1 640	2 376	14 322	2 000
Mean catchment elevation (m)	1 655	700	669	373	1 463	725	900	620	1 137	137
Mean annual precipitation (mm)	1 624	1 031	1 011	952	1 306	1 150	845	1 600	1 079	730
Average volumetric discharge rate (m ³ /s)	183	1 700	957	475	335	16	25	63	26	33

The Alpine waters contribution to the Rhône River are compared to the others watershed contributions through volumetric discharge flow rates and water stable isotopes monitoring. These contributions are investigated 60 km ahead of the Mediterranean Sea (at Beaucaire) where all other the watershed's inputs have been collected. The monitoring spans from February 2017 to October 2018 allowing to consider two summer, as potential critical periods.

3.1. Discharges data

Daily volumetric flow rates (m³/s) are recorded on the French surface water monitoring database "HYDRO" (hydro.eaufrance.fr) and used to evaluate the volume of Alpine waters transferred to the Rhône River. For that purpose discharge rates were extracted, for the considered period, at four hydrometric stations (Figure 1): the first one close to the Rhône Alpine source at Surjoux (40 km downstream of the Lemman lake) which represent the Swiss part of the Rhône River; the second and the third stations on the Isère and Durance tributaries respectively, at the nearest point of their confluence with the Rhône River; and finally the Rhône River downstream, at Beaucaire (60 km ahead of the Mediterranean Sea). Their locations are shown on Figure 1, from station one to station four.

3.2. Water stable isotopes analysis

The stable isotope signature of water is defined by its geographic origins. Since waters with different origins feed the Rhône in proportions that is expected to vary over the year, the signature of the Rhône water downstream is expected to vary as well. Those variations are used to trace Alpine waters which show naturally depleted signatures.

Over the studied period, Rhône River water samples were collected at Beaucaire on a fortnightly basis for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis.

Raw waters were collected in tightly closed 10 mL glass bottles avoiding air bubbles.

The water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) compositions were determined by cavity ring down spectrometry using a Picarro L2130i according to the analytical scheme recommended by the IAEA (Penna et al.,

2010). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are reported in per mil (‰) relative to the V-SMOW2 (Vienna Standard Mean Ocean Water) reference material, and calibrated with the internal laboratory standards with maximum uncertainties of 0.2 and 0.5 ‰ respectively.

4. Results

Volumetric flow rates extracted from the data base are available in supplementary material.

Based on daily recorded data displayed in Figure 2, the Rhône River average volumetric flow rate, calculated at Beaucaire, over the period of investigation, is relatively low with respect to the long term average, showing an average of 1 380 m³/s, with a standard deviation of ± 850 m³/s. The daily flow rate values range widely from 9 660 m³/s in winter to 230 m³/s in summer.

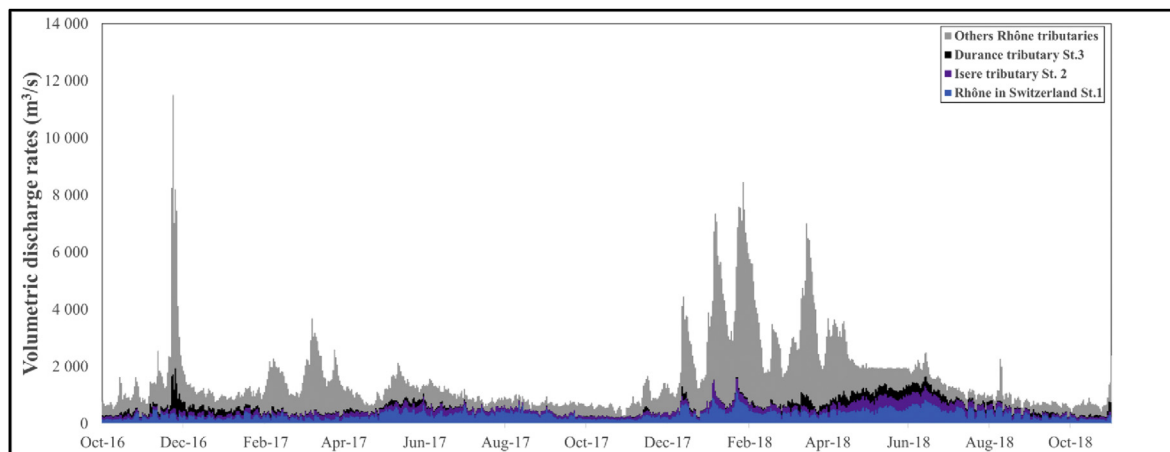
Over all, the high-flow period is observed in winter and spring from December to June, while the low-flow period is observed in summer and autumn, from June to December.

Yet, contrasted volumetric discharge rates are observed between both hydrological years. During the high flow period in 2017–2018, the volumetric discharge rates ($2\,880 \pm 790$ m³/s) are nearly twice as high as in 2016–2017 ($1\,580$ m³/s ± 480 m³/s).

Regarding the Alpine rivers, flow rate variations are coherent with a mountainous dominant regime. The lowest flow rates are recorded during winter, while the highest flow are recorded in spring and summer.

Regarding $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis, the Rhône River water at Beaucaire follows the Global Meteoric Water Line (GMWL: $\delta^2\text{H} = 8.13 \times \delta^{18}\text{O} + 10.8$) (Craig, 1961; Rozanski et al., 1992). The average values are -70 ± 6.0 ‰ and -10 ± 0.8 ‰ vs. V-SMOW2 for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ respectively. The isotope signatures exhibit significant seasonal variations over the studied period, from -11 to -8 ‰ for $\delta^{18}\text{O}$ and from -80 to -60 ‰ for $\delta^2\text{H}$ vs. V-SMOW2 (Figure 3).

As $\delta^{18}\text{O}$ and $\delta^2\text{H}$ follow similar trends and as $\delta^2\text{H}$ is the most discriminant parameter of both stable isotopes, $\delta^2\text{H}$ data is used hereafter for interpretation.

**Figure 2.** Monitoring of the Rhône volumetric discharge rates at Beaucaire from October 2016 to October 2018 sharing cumulative volumetric discharges rates of the main Alpine rivers (Swiss Rhône, Isère, Durance).

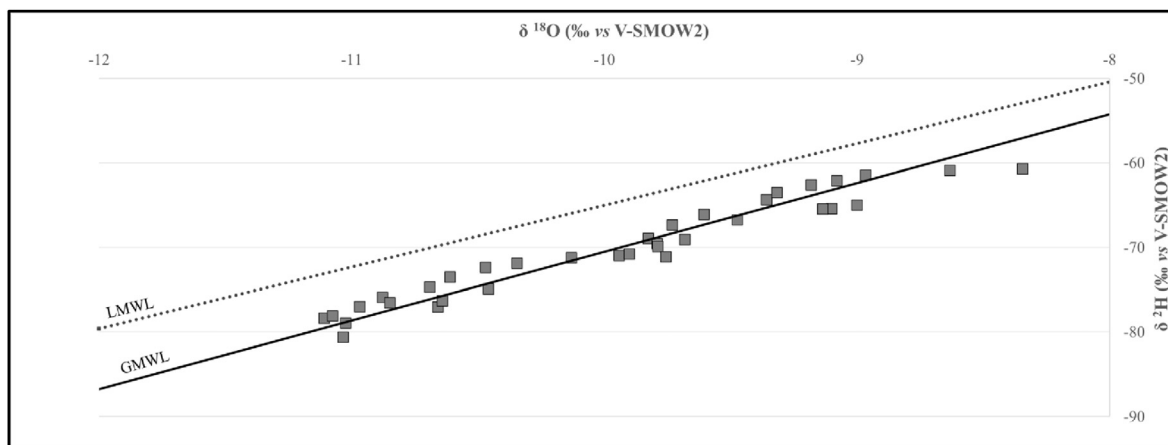


Figure 3. $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ (‰ vs. V-SMOW2) of the Rhône river water from February 2017 to October 2018. The Rhône water follows the GMWL shown for reference. Local Meteoric Water Line (LMWL) $\delta^2\text{H} = 7.3 \cdot \delta^{18}\text{O} + 7.3$ is displayed in dotted line as additional information (Ladouche et al., 2009).

To evaluate the high altitude Alpine rivers contribution, the $\delta^2\text{H}$ Rhône signature is plotted along with the daily cumulative relative contributions from Alpine rivers (RQ_{AR}) in Figure 4. This last parameter is calculated from the daily volumetric flow rates $Q_{(t)}$, taken from the data base, according to the following formula:

$$RQ_{AR}(\%) = \frac{Q_{(t)Swiss\ Rhône} + Q_{(t)Isere} + Q_{(t)Durance}}{Q_{(t)Rh\^one\ at\ Beaucaire}}$$

In average and over the studied period, the cumulative Alpine rivers relative contribution to the Rhône further downstream at Beaucaire is 47 %, showing a contrasted importance over the year (± 28 %). During the high flow period (December to June), the average contribution decreases to 27 % (± 10 %) while it becomes predominant during the low flow period as it reaches 65 % (± 10 %) (June to December). All data are available in supplementary material.

Regarding the water deuterium signature, Figure 4 reveals a fairly good synchronization between the cumulative relative Alpine contributions to the volumetric flow rate and the water stable isotope signal variations:

- During the low Alpine river contribution period, a significant water stable isotope signature enrichment is observed, from -81.5 to -63.1 ‰, along with a decreasing Alpine rivers contribution (a maximum of 79 % to a minimum of 12 %).

- During the high Alpine river's contribution period, the opposite behavior is observed: the water stable isotope signature decreases along with the increase in Alpine rivers contribution.

5. Discussions

As seen above, the size of the Rhône river watershed and the diversity of its recharges suggest that the water stable isotopes signature should fluctuate further downstream. Over 2017–2018, the observations confirm this hypothesis and show:

- a seasonal variations of water stables isotopes signature and Alpine waters contributions
- a relationship between the water stable isotope variations and the seasonal Alpine rivers cumulative relative contributions.

To confirm this relationship, a linear modeling approach is carried out between the $\delta^2\text{H}$ signature variations (dependent variable) and the cumulative Alpine rivers relative contribution, RQ_{AR} (explanatory variable).

Performed on XLSTAT software, the linear regression model produced is statistically significant and both parameters are well correlated as show by the test results.

$$\delta^2\text{H} = 26.0 \times RQ_{AR} - 57.9$$

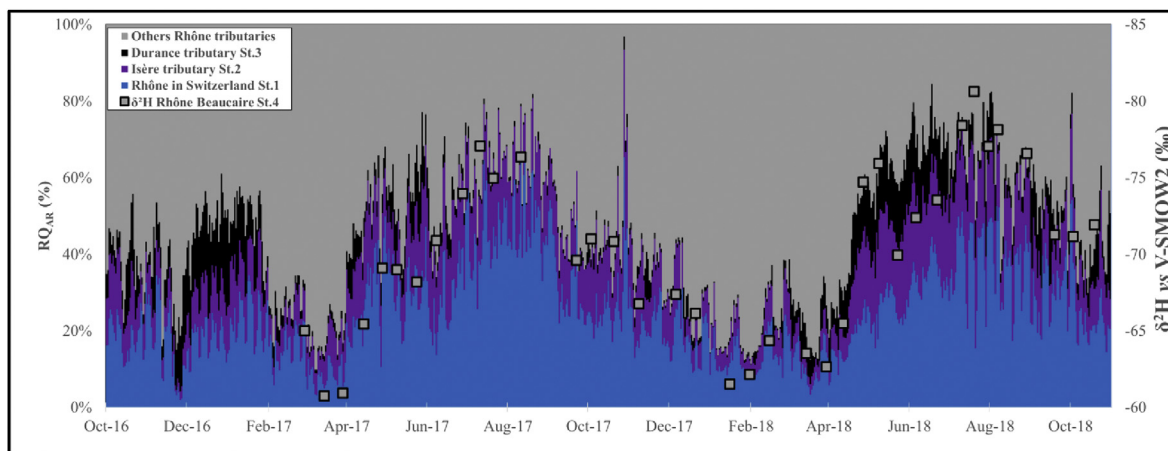


Figure 4. Time series of the cumulative relative Alpine rivers contribution to the Rhône volumetric flow rate (RQ_{AR}) along with the Rhône $\delta^2\text{H}$ signature, following similar seasonal trends. Note that the $\delta^2\text{H}$ scale is decreasing upward.

with $R = 0.88$, $R^2 = 0.79$ and a p -value < 0.0001 .

Consequently, the model confirms that the variations in water stable isotopes signature observed at the Rhône downstream can primarily be explained by the variations of the Alpine rivers contributions. The more depleted the isotope signatures is, the greater the contributions from Alpine rivers is.

According to this linear model, an average signature of the Alpine contributors of -83.9% is accounted for when the Alpine rivers relative contribution reaches 100%. Considering a 95% confidence interval on the mean, this value may vary between -86.5 to 81.2% .

To evaluate the model prediction reliability, this predicted signature is compared to the actual Rhône $\delta^2\text{H}$ signature monitored in Switzerland and reported in the IAEA Global Network of Isotopes in Rivers (GNIR) framework at Chancy (20 km upstream from the Swiss Alpine Rhône part flow rates monitoring station). From 2000 to 2016, the average $\delta^2\text{H}$ signature measured at Chancy is -85.9% (± 1.5) and can be considered as representative of a 100% Alpine rivers signature Figure 5.

This value falls within the 95% interval confidence of the predicted 100% Alpine rivers cumulative contribution signature (-83.9%). The relative differences can be accounted by measurement uncertainties (0.5‰), model dispersion, interannual variability and/or potential contrasted signatures between the Swiss and Italian Alpine waters.

Hence, the current study highlights:

- The ability of the stable isotopes of water to confirm and to trace the seasonal change of water origins in a diversified latitude and altitude watershed, which supports [Vrzel et al. \(2017\)](#) and [Halder et al. \(2015\)](#) conclusions on the interest of using $\delta^{18}\text{O}$ as a tracer of the seasonal watershed hydrological processes.
- The key role of Alpine water contribution during the summer (mid-July to early September) with an average supply of $70 \pm 6\%$ and a maximum rate at 79%.

Being able to monitor their contributions is essential as they may no longer be adapted to face water stress periods in the context of climate change. Indeed this current reliance could become a key driver of vulnerability.

[Beniston \(2012\)](#); [Uhlmann et al., 2013](#); [Kazi and Rahman, 2013](#) highlight the non-negligible influence of the melting of the alpine snowpack and glacier on the Alpine rivers flow rate. During the current generally hottest and driest period of summer (between mid-July and early September), significant quantities of water are provided to Alpine rivers and therefore to the Rhône at Beaucaire. According to [Huss \(2011\)](#), the specific average contribution of the glacier storage water melt was

estimated to 25% (1908–2008) of the total Rhône flow rate at Beaucaire, in August, when Alpine waters recharge reliance is the highest (Figure 4). In extreme dry years, such as during the 2003 drought, this contribution can increase to 40% ([Huss, 2011](#)).

However, according to the last climate predictions and European glaciers behavior models, 50% of existing mountain glaciers would disappear in 30 years and 90% of it by the end of the century, depending on the extent of future global warming ([Zekollari et al., 2019](#)). There will no longer be this water supply which, in the current climate, contributes to avoid severe low water levels downstream. In addition, with the future Alpine glacier's accelerated meltdown, those effects will be higher as altered precipitations regimes may combine with the accelerated glaciers melts. Under such conditions the population will be exposed to an increasing summer scarcity of the Rhône water resource ([Beniston, 2012](#)).

6. Conclusions

The Alps in general, and in Switzerland in particular have often, and rightly, been called Europe's water tower. Many of the rivers that supply Western and Central Europe originate from this area. More than 150 million people live in these different basins and depend on water originating in the central Alps. Their regime is thus essential to investigate as it may expose key drivers of vulnerability.

The current study evidences the relevance of using water stable isotope signature to trace the origin of water in a diversified latitude and altitude watershed and to monitor seasonal trend.

Applied to the Rhône River, the study confirms that:

- The seasonal isotopic composition of Rhône waters downstream responds to the variation of the Alpine waters routed by the Rhône, in Switzerland, the Isère or the Durance rivers (RQ_{AR}): $\delta^2\text{H} = 26.0 \times RQ_{AR} - 57.9$.
- The Alpine waters play currently a key role to supply the Rhône flow rate during the summer and low flow season (70% in average $\pm 6\%$) from mid-July to early September.

Among other Rhône recharges, Alpine water contribution is essential to investigate, especially in summer, as they sustain water low flow. A key role which in the context of climate change, may no longer be sustainable.

A survey of the Rhône River isotope signature would allow to monitor the contribution of Alpine water to the Rhône River and provide tools to assess the local effects of global warming on surface water runoff.

Declarations

Author contribution statement

Julien Jean-Baptiste: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Corinne Le Gal La Salle: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Patrick Verdoux: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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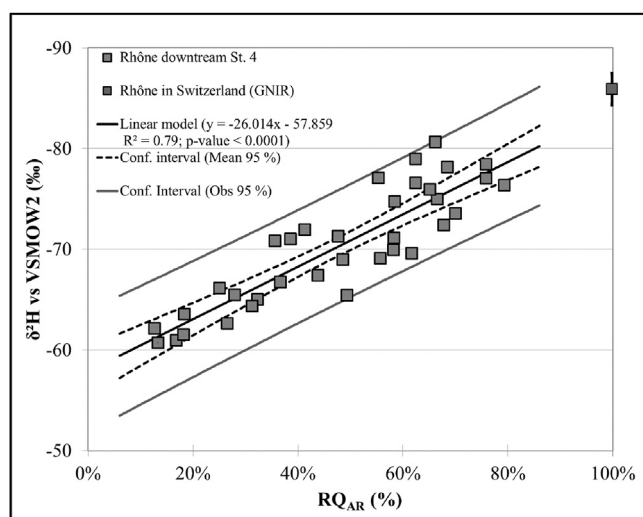


Figure 5. Evolution of the cumulative relative alpine rivers contribution vs $\delta^2\text{H}$ signature.

“Géochimie ISotopie environnementale” (Labo G.I.S) through the CHROME.research team.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2020.e04376>.

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