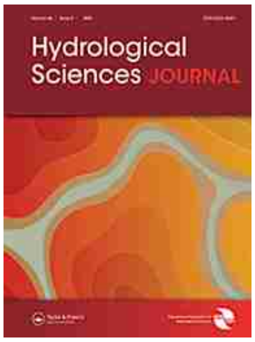

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Altitude isotope effects in Mediterranean high-relief terrains: a correction method to utilize stream water data

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ABSTRACT
Quantification of the isotope altitude effect from precipitation allows the identification of recharge altitudes in high-relief areas. However, steep terrains frequently limit the use of this precipitation-based approach. Perennial rivers often provide easy, year-round access for water sampling. However, in high-relief regions rivers may not adequately represent regional precipitation isotope patterns because they integrate isotope signals along their course. This prevents the calculation of an altitudinal isotope gradient from river water samples alone. We present a study that shows how a river-based sampling approach served to determine the altitude effect. Replacing the original sample site altitude with the mean upstream catchment elevation as calculated from a digital elevation model allowed us to establish a plausible altitude isotope effect from stream water. The correction approach was verified independently using precipitation isotope data. This approach can potentially be transferred to other regions where precipitation sampling at various elevations is difficult to determine.

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1 Introduction

Quantification of the isotope altitude effect in precipitation allows for the identification and prediction of groundwater recharge areas in mountainous watersheds. The identification of the mean catchment recharge altitude based on δ^{18}O and δ^{2}H measurements of water lead to a better understanding of spatial and temporal freshwater availability in the region of interest (Gat and Dansgaard 1972, Gonfiantini *et al.* 2001, Smerdon *et al.* 2009, Koeniger *et al.* 2016, Penna *et al.* 2017). Such knowledge contributes to the protection and sustainable use of valuable drinking water resources, in particular with respect to ongoing climate change (Reckerth *et al.* 2017, Marchina *et al.* 2020a). This is especially important in high mountain headwater catchments of the Mediterranean region in summer, during which increased demand from tourism overlaps with annual lows of precipitation. For instance, tourist numbers in the European Mediterranean region increased from 139 million in 2000 to 267 million in 2017 (UNWTO 2018). These numbers are expected to increase even more in the near future. The determination of recharge altitudes is therefore crucial to understand and quantify aquifer recharge in order to ensure future freshwater supply, particularly in Mediterranean islands and coastal areas (Viola *et al.* 2014, Santoni *et al.* 2018). For instance, in a study on the mountainous Mediterranean island of Corsica (France), Erostate *et al.* (2018) applied stable isotope measurements to identify two different potential recharge areas of a low-land coastal aquifer near the city of Bastia in northeastern Corsica. In another study from the Eastern Mediterranean, Koeniger *et al.* (2017) demonstrated the importance of the isotope altitude effect by outlining protection zones along the mean recharge altitudes of the major water resource for the city of Beirut (Lebanon).

River water and spring water are often assumed to be valid alternatives to precipitation collection because they carry an integrated isotope signal of upstream water compartments and precipitation. At first glance, these waters should therefore reflect the isotope shift in precipitation caused mainly by temperature changes along the steep relief, i.e. the isotope altitude effect. While the isotope altitude effect is usually determined directly from precipitation (D'Alessandro *et al.* 2004, Koeniger *et al.* 2017), springs (Bono *et al.* 2005) and stream waters (Kendall and Coplen 2001, Yao *et al.* 2009, Wen *et al.* 2012, van Geldern *et al.* 2014, Kuang *et al.* 2019) have also been used as precipitation proxies. Springs often offer meaningful estimates of regional precipitation. However, rivers in particular in high-relief regions may not adequately represent regional precipitation patterns because they integrate isotope signals from various subcatchments with variable elevation distributions along their course. The resulting local offset between river water and precipitation is referred to as the "catchment effect" (Dutton *et al.* 2005). On the one hand, placing precipitation collectors along steep profiles in high-relief catchments is often demanding in terms of field logistics

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Supplemental data for this article can be accessed here.

and due to the number of stations that need to be maintained. Perennial rivers, on the other hand, often provide easier, year-round access for water sampling. Thus, a crucial challenge is to correctly quantify the isotope altitude effect from river waters.

Altitude effects in the Mediterranean were subject to a variety of studies, and published values for $\delta^{18}O$ gradients range from −0.12 to −0.28‰ per 100 m increase in elevation (Celle-Jeanton *et al.* 2001, Poage and Chamberlain 2001, Longinelli and Selmo 2003, Bono *et al.* 2005, Ladouche *et al.* 2009, Liotta *et al.* 2013, van Geldern *et al.* 2014). Some of these studies use river or spring water instead of precipitation to determine the altitude effect. Because of the above limitations, the validity of this approach remains to be tested.

The main objective of this study is to test how rivers in such high-relief areas can be used as an alternative proxy to precipitation sampling. For this purpose, we will address the following questions:

- To what extent do river water isotope profiles change with respect to season and discharge events?
- How does the altitude isotope gradient change if sampling elevation is replaced by the mean subcatchment elevation?
- Can this correction approach for river water isotope data be verified directly by comparison to local precipitation data?

In this context, the island of Corsica (France) located in the Western Mediterranean appears well suited for a river-based approach to characterize altitude effects of precipitation in high-relief areas because of its exceptionally steep topographic gradients with altitudes up to >2500 m above sea level (m a.s.l.).

2 Methods

2.1 Study area

The Tavignanu catchment is located on the island of Corsica (France) in the Mediterranean Sea (Fig. 1). The island of Corsica covers an area of 8680 km^2. A north–south orientated mountain ridge, with the highest summit at 2706 m a.s.l., dominates its topography. The Tavignanu catchment is the second largest catchment of the island with an area of 806 km^2 (Fig. 1). The river has a total length of 87 km before it drains into the Mediterranean Sea. This short flow length and the high elevation of the upper reaches, above 1740 m a.s.l., results in a remarkably steep mean downhill gradient of about 20 m per km river length.

The Tavignanu River has two major headstreams of similar length (Fig. 2), namely the Tavignanu River and the Restonica River, that meet at the city of Corte (450 m a.s.l.). Both flow in a granitic basement and are fed by glacially formed source lakes, Lac de Nino (1743 m a.s.l.; site 1 in Fig. 1) and Lac de Melu (1710 m a.s.l.; site R1). Downstream of the city of Corte, the Tavignanu River flows in a schist formation before reaching a sedimentary plain for the last 15 km and finally reaching its river mouth.

2.2 Field sampling

Samples were collected every 3 months during five field campaigns, starting in February 2016. This sampling scheme covered all seasons. A total of 23 sampling points were visited regularly in the Tavignanu catchment (Fig. 1). Eleven sampling points were located along the Tavignanu River course (sites 1–11 in Fig. 1), whereas sampling point 3 was added later in the study, in October 2016, to search for anthropogenic impacts

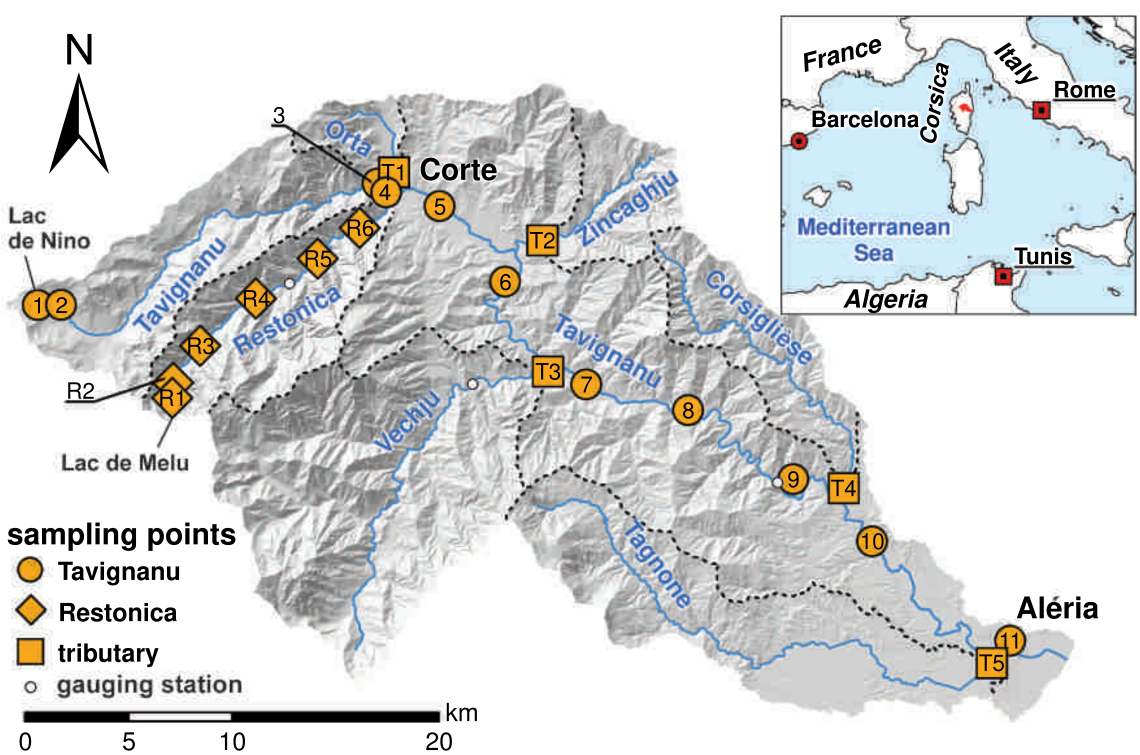

Figure 1. Inset: Location of Corsica in the Western Mediterranean. Map: Hillshade of the Tavignanu catchment. Sampling points are indicated for the Tavignanu (circles), the Restonica (diamonds), and tributaries (squares). Subcatchment boundaries are indicated with dashed lines.

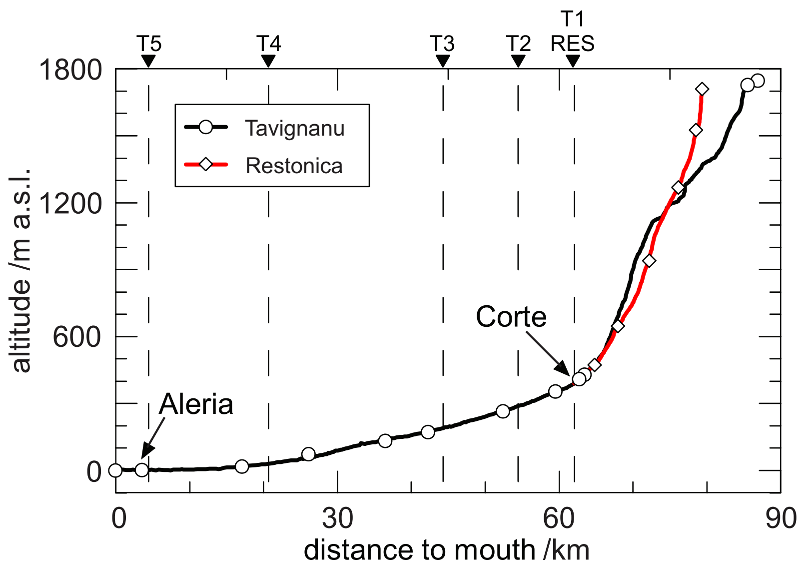

Figure 2. River profiles and sampling point locations of the Tavignanu (black) and Restonica (red) rivers. Downward-pointing triangles and dashed lines indicate tributary junctions. RES: confluence of Restonica and Tavignanu rivers at Corte.

on downstream sites located in the city of Corte. Additionally, water from six major tributaries was sampled at an additional 11 points (R1–R6 and T1–T5 in Fig. 1). A special focus was placed on the Restonica River (R1–R6), which is the first large water contributor to the Tavignanu River. In terms of accessibility, the remoteness of the upper Tavignanu River prohibited a regular sampling point distribution for this part because its valley is only accessible by foot.

The upstream sampling points of the Tavignanu (site no. 1) and the Restonica (R1) rivers were placed at the outlets of their corresponding source lakes. In addition, the tributaries T1–T5 were sampled shortly after their confluences to the main river. This offered a representative and integral sampling point for each subcatchment (Fig. 1). The sampling sites along the Tavignanu main course were set far enough downstream of the tributary inflows to ensure a sufficient mixture of the two water masses.

Samples for the oxygen and hydrogen isotope composition of the river water were collected from the middle of the stream and placed in 12-mL amber glass vials that were sealed with plastic caps and butyl rubber (BR)/polytetrafluoroethylene (PTFE) septa. The septa were placed with the BR side facing towards the sample to improve airtightness. In addition, sample containers were sealed with Parafilm® and stored at ~4°C and in the dark until analysis. Physico-chemical field parameters such as electric conductivity (EC) and temperature were measured with a WTW Multi 350i multiparameter instrument (WTW GmbH, Weilheim, Germany).

2.3 Local precipitation

Recently, a network for isotopes in precipitation has been established for several sites on the island of Corsica (Huneau *et al.* 2015). Monthly precipitation was collected at Aleria (17 m a.s.l.) and Corte (450 m a.s.l.) using oil-free Palmex® rain collectors (Palmex d.o.o., Zagreb, Croatia) that effectively prevent evaporative isotopic enrichment (Michelsen *et al.* 2018) and was analysed for oxygen and hydrogen isotope ratios. From these values, local meteoric water lines (LMWLs) were calculated using a precipitation amount weighted least squares regression (PWLSR) according to Hughes and Crawford (2012). This method was preferred over the conventional ordinary least squares regression (OLSR) to avoid a bias towards small amounts of summer precipitation. Additionally, precipitation-weighted LMWLs are favourable here, because they better reflect the average recharge and thus the overall contribution to the water budget. This is especially true for coastal, island, and Mediterranean locations (Crawford *et al.* 2014). Note that a discussion about the most appropriate regression method is still ongoing in the scientific literature (Krajcar Bronić *et al.* 2020, Marchina *et al.* 2020b).

2.4 Stable isotopes of oxygen and hydrogen

The oxygen (δ^{18}O) and hydrogen (δ^{2}H) stable isotope compositions were analysed with an isotope ratio infrared spectroscopy (IRIS) analyser, based on wavelength-scanned cavity ring-down spectroscopy (L 1102-i WS-CRDS, Picarro Inc., Santa Clara, CA, USA). All values are reported in the standard δ-notation in per mille (‰) vs. Vienna Standard Mean Ocean Water (VSMOW) according to

$$\delta = \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \qquad (1)$$

where R is the ratio of the numbers (n) of the heavy and light isotope of an element (e.g. $n(^{18}\text{O})/n(^{16}\text{O})$) in the sample and the reference (Coplen 2011). These results are multiplied by 1000 to express them in per mille (‰).

Four sequential injections of each sample were measured, and raw data were corrected for sample-to-sample memory effects. The reported value is the mean value. Data were corrected for instrumental drift during the run and normalized to the VSMOW/SLAP (Standard Light Antarctic Precipitation) scale by assigning a value of 0‰ and –55.5‰ (δ^{18}O)/0‰ and –427.5‰ (δ^{2}H) to VSMOW2 and SLAP2, respectively (Brand *et al.* 2014). For normalization, two laboratory-internal reference materials, which were calibrated directly against VSMOW2 and SLAP2, were measured in each run. External reproducibility based on repeated analyses of a control sample was 0.05‰ and 0.5‰ (±1 σ) for $\delta^{18}O$ and δ^2H. For a detailed description of the analytical procedure refer to van Geldern and Barth (2012).

2.5 Spatial analyses with geographic information system (GIS)

Spatial analyses were performed on a 10-m digital elevation model (DEM) that was processed with ArcMap 10.4.1 (Esri, Redlands, CA, USA). Streams were generated by calculating a flow-direction and flow-accumulation raster, after smoothing the DEM with the elevation void fill function. Subsequently, streams were defined by exceeding a flow-accumulation raster value threshold of 20 000. This procedure produced a river network that was almost identical to the official topographic map. After establishing a river network in this manner, subcatchments were delineated with the watershed tool using corresponding sampling point locations and river junctions as outlets. The "Locate-Features-along-Route-tool" was used to extract distance to mouth (dtm) values along the sampled streams. Subcatchment mean elevations were calculated as the mean value of the DEM with the "zonal statistics" tool.

3 Results and discussion

3.1 Seasonal and spatial and isotope patterns

As expected, oxygen ($\delta^{18}O$) and hydrogen (δ^2H) isotope values of river water showed a strong linear correlation (r^2 = 0.94). Therefore, only $\delta^{18}O$ values are described and discussed here; however, findings and conclusions apply analogously to δ^2H. All $\delta^{18}O$ and δ^2H analytical results are presented in Fig. 3 and the online supplementary material (Table S1).

The $\delta^{18}O$ values at the two source lake outlets of Lac de Nino (site 1) and Lac de Melu (site R1) ranged from between −9.3 and −9.2‰ in February to between −7.0 and −8.0‰ in July (Fig. 4, Table S1). Compared to values that were measured farther downstream along the Tavignanu River course (site 2), Lac de Nino values were relatively enriched in $\delta^{18}O$ and δ^2H. This enrichment of the lake water with respect the stream water was strongest in the warm season during July and October with $\delta^{18}O$ differences of 1.9 and 1.0‰, but less pronounced with changes of 0.2 and 0.3‰ in February and May during the cold season. In the Restonica headwaters downstream of Lac de Melu, this relative enrichment of the lake water was also clearly visible in July, during the warm season. Accordingly, lake waters show a clear evaporative signal as a result of water loss from the lake surface. The isotope signal of the source lakes was used to construct the local evaporation line (LEL) (Fig. 3).

Until the confluence between Restonica and Tavignanu, $\delta^{18}O$ values of the Restonica waters typically decreased along the river course (sites R2–R6) in May, July, and October. Corresponding differences between source lake waters (R1) and the last sampling site before the confluence with the Tavignanu (site R6) were −0.5, −0.5 and −0.7‰, respectively (Fig. 4). For the sampling campaign in February 2016, no such trend could be observed, and river water values remained stable along the Restonica River course.

Downstream of the confluence between the Tavignanu and the Restonica rivers at an elevation of 450 m a.s.l., $\delta^{18}O$ values gradually increased, with increments between +0.6 and +1.3‰ (sites 5–11). Note that the lowermost sampling point (site 11) before the Tavignanu enters the sea was affected by seawater during July and October due to baseflow conditions and tidal effects. The seawater contribution was indicated by elevated EC values. This influence caused isotope changes that were related not to altitude effects but

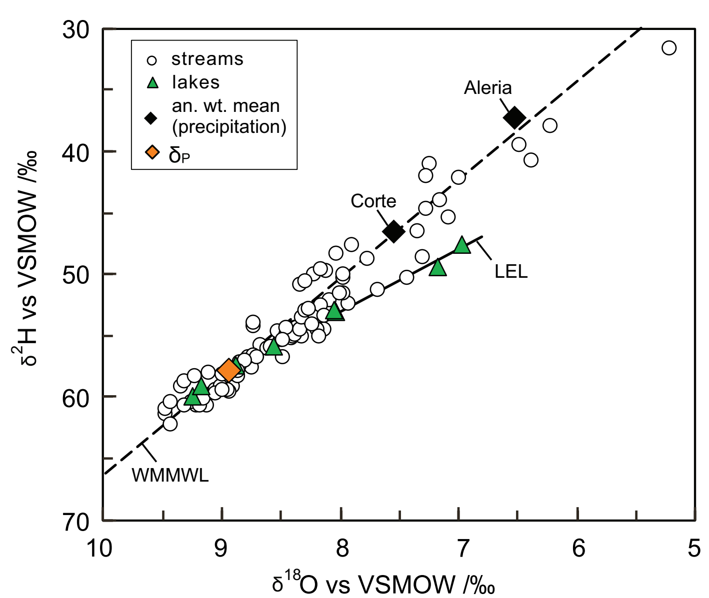

Figure 3. Dual isotope plot of river water and source lake samples (sites R1 and T1). For annual weighted (an. wt.) mean of precipitation from Corte and Aleria, refer to Table 2. The dashed line is the Western Mediterranean meteoric water line (WMMWL) of Celle-Jeanton *et al.* (2001). δ_P is the intersection of the local evaporation line (LEL) and the WMMWL. VSMOW–Vienna Standard Mean Ocean Water.

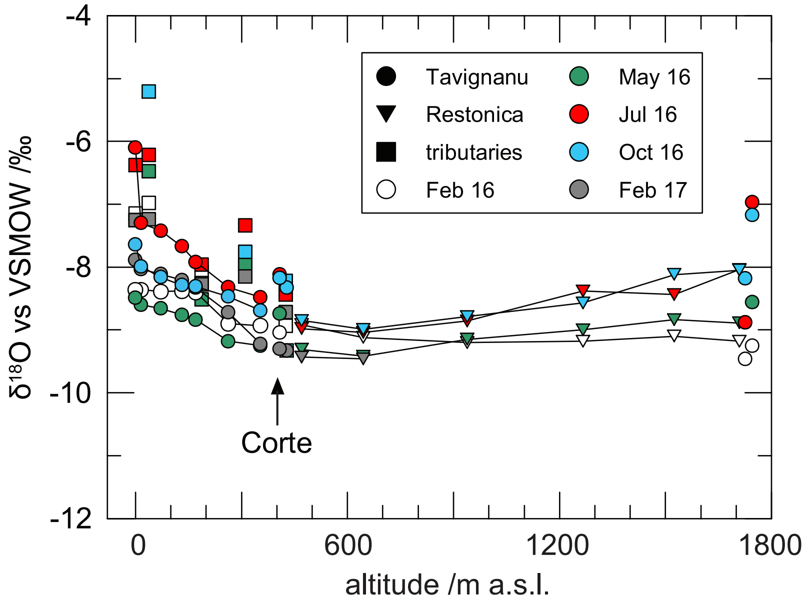

Figure 4. $\delta^{18}O$ values of river water samples versus sampling site altitude. Seasons are colour coded, whereas shapes identify tributaries and rivers. VSMOW–Vienna Standard Mean Ocean Water.

to seawater mixing, and therefore these two measurements are not further considered in this study (cf. Table S1).

Seasonal variability of isotope values in rivers can be further modulated by storm events or snow melt. Daily discharge values of the Tavignanu, Restonica and Vechju rivers were recorded at automated gauging stations (Fig. 5). Monthly discharge means (20-year average) for the Tavignanu River range between 11.2 and 16.2 $m^3\ s^{-1}$ from November to May and decrease to a summer low of 0.9–1.9 $m^3\ s^{-1}$ from July to September. July and October means have intermediate values of 5.2 and 4.8 $m^3\ s^{-1}$, representing a transitional phase between summer low and winter to spring high discharges.

Ten extreme discharge events above 150 $m^3\ s^{-1}$ were recorded for the period between July 1996 and June 2017. Four of these events fall in the sampling period between November 2016 and February 2017. Among these, the highest recorded discharge was 380 $m^3\ s^{-1}$ on 20 December 2016. Values for the other three events (within the 10 largest discharge events) are 228, 165, and 150 $m^3\ s^{-1}$.

Sampling campaigns in May, July and October 2016 were performed during discharge conditions that are representative of the long-term average discharge of the respective season. On the other hand, both February sampling campaigns in 2016 and 2017 were performed along the ring-downs of discharge event peaks. However, stable isotope patterns along river courses of both winter sampling campaigns did not reveal anomalous patterns. The overall shape closely follows the isotopic patterns of spring, summer, and autumn samplings (Fig. 4). In general, February and May isotope curves plot at lower values due to lower temperatures and potential snow

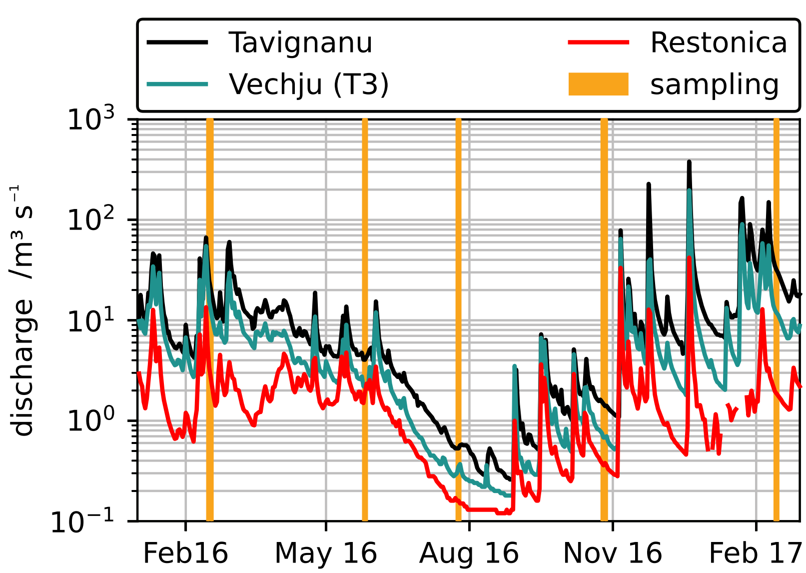

Figure 5. Discharge of rivers, with indications of seasonal sampling campaigns. See Fig. 1 for locations of gauging stations. Logarithmic scale is to cover flooding events.

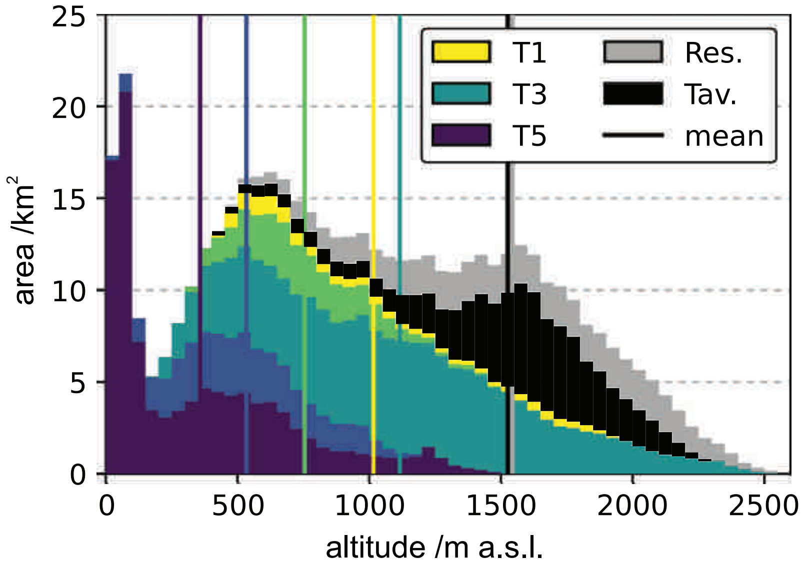

Figure 6. Elevation histogram for Restonica (Res.), Tavignanu (Tav.) and tributary subcatchments upstream from confluence.

melt influences in spring time. July and October curves are characterized by higher isotope values. Note that the overall shape of the rivers' isotope profiles is repeated in each season. In February 2017 the higher altitude sections were not accessible due to the road conditions, and these values are therefore absent from Fig. 4.

3.2 Apparent inverse altitude effect

Starting from sea level, the isotope values became progressively lower with increasing altitude along the river profile until the confluence of the Restonica and the Tavignanu at 450 m a.s.l. (Figs 2, 4). This negative correlation between river water isotope values and elevation corresponds to the expected altitude effect of precipitation (Siegenthaler and Oeschger 1980, Kern *et al.* 2014, Clark 2015).

However, upstream of this confluence, this trend was inverted during the May, July, and October campaigns, and we found increasing isotope values in the river water with increasing altitude (Fig. 4). This positive correlation between isotope values and elevation, an apparent inverse altitude effect, opposes the expected trend for input signals of precipitation that feeds the river water by surface runoff or by rapid flow through shallow subsurface flowpaths. During the February 2016 sampling campaign, we found stagnating stable isotope values in the river water upstream of 450 m a.s.l. These observations were also not in line with the expected decreasing values with increasing altitude.

It is well known that an "inverse" isotope effect in precipitation with positive elevation gradient can occur (Niewodnizański *et al.* 1981, Moran *et al.* 2007, Pang *et al.* 2011, Kong and Pang 2016, Jiao *et al.* 2019). The main reason for this inverse effect is mixing of moisture from different vapor sources at these higher altitudes. It occurs at higher elevations on the leeward side of a high mountain chain after the over peak air flow. Such inverse gradients often strongly depend on local weather conditions that control the local vapor cycle with respect to moisture recycling and subcloud evaporation, which thus can cause an inverse isotope effect (see Jiao *et al.* 2019). However, such an effect should be restricted to specific weather conditions during seasons with prevailing conditions for wind and moisture transport. This was not the case according to our observation, as the overall isotope profile along the river course did not change with the season. Moreover, river water will not only reflect the most recent precipitation event but will integrate the precipitation isotope signal in space and time (Kendall and Coplen 2001). Consequently, short-term weather conditions that might cause very special conditions, including an inverse isotope effect in precipitation events, should be damped or even removed in river water.

Another complexity results from the fact that both rivers, the Restonica and the Tavignanu, are fed by glacial source lakes. Prior to their respective outflows, both lakes are subject to evaporation effects that preferentially enrich the lake water in the heavy ^{18}O and ^{2}H isotopes. The amplitude of this evaporation effect depends on the season, with the strongest effect occurring during the warm season in July and August.

At first sight, one might conclude that reconstructing the altitude effect via river water samples may not be possible because of unknown secondary alterations of the pristine precipitation isotope value before it eventually enters the river. However, when considering the area distribution of different elevations (Fig. 6), a correction approach that allows for reconstructing the isotope altitude effect from river water data seems plausible. Most of the area in the headwaters of the Restonica and the Tavignanu rivers is located between 1200 and 2000 m a.s.l. (Fig. 6). This causes disproportionately larger contributions of precipitation to the river from this elevation span. As a result, isotope values of river water at a specific sampling site are lower than the corresponding precipitation isotope value at the same altitude ("catchment effect"). The reason is the integration of the isotope signal along the river course, which thus represents the elevation of the mean recharge area and not the sampling site elevation. This demands a deeper examination of the available regional and local precipitation isotope data.

3.3 Local precipitation and lake evaporation patterns

The regional Western Mediterranean meteoric water line (WMMWL) for our study region was established by Celle-Jeanton *et al.* (2001) as follows:

$$\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 13.7 \qquad (n = 146) \tag{2}$$

The slopes of the two LMWLs for Aleria (7.64 ± 0.44) and Corte (7.56 ± 0.50) calculated by PWLSR are in close agreement with the WMMWL. An advantage of the WMMWL is that it is based on a longer observation period than the currently available local data. Therefore, the WMMWL is assumed to sufficiently describe the isotope range of precipitation input on the catchment scale.

The regression through the isotope values of the seasonal samples taken from the two source lake outlets of the Tavignanu (1) and the Restonica (R1) produce a significantly lower slope when compared to the WMMWL (Celle-Jeanton *et al.* 2001). This regression describes the LEL according to the following equation:

$$\begin{aligned} \delta^2\text{H} = {} & (5.11 \pm 0.16) \times \delta^{18}\text{O} - (12.15 \pm 1.31) \\ r^2 = {} & 0.99\ (n = 8) \end{aligned} \tag{3}$$

The slope matches the generally accepted slopes for LELs, which typically range from 4 to 6 (Edwards *et al.* 2004, Gibson *et al.* 2008, 2016).

The intercept of the LEL and the WMMWL, denoted as δ_P, with values of −8.9‰ (δ^{18}O) and −58‰ (δ^2H), can serve as a proxy for the mean annual precipitation at the corresponding altitude of around 1700 m a.s.l. (Gibson *et al.* 1993). This is particularly useful because no precipitation data were available above 500 m a.s.l. Therefore, a δ_P value constructed in this manner yields an independent validation for testing the proposed correction method described below.

3.4 Correction of isotope values by mean catchment elevations

In an attempt to correct for the spatial distribution of elevation, all sampling points at the outflow of subcatchments, namely the tributary sampling points (T1–T5) and the sampling points of the Tavignanu (site 4) and Restonica (R6) located just upstream from Corte, were evaluated against the mean upstream catchment elevation (Table 1).

The upstream Restonica sampling sites R1 to R5 were not included because of the strong evaporation influence of the source lake water (Fig. 4). This evaporative signal is supposed to be lost with the addition of non-evaporated surface and groundwater water, which enters the stream through fissures and joints in the granitic rock, along the stream up to sampling point R6. Therefore, site R6 best represents the entire Restonica subcatchment. The same logic applies to sampling site 4, which best represents the upper Tavignanu subcatchment. In addition, samples of the Tavignanu River downstream of Corte were excluded from the correction procedure to avoid the multiple integration of upstream subcatchments.

The mean upstream catchment elevation replaces the original river sampling site altitude in Fig. 7. In other words, the measured δ-values at a specific site were shifted upwards until the elevation where the average river water originated from (Table 1).

After correcting for the altitude in this manner, the resulting slope of the regression that defines the altitude effect of river samples is described by (−0.19 ± 0.02)‰/100 m (r^2 = 0.68, n = 35). Uncertainty is reported as the standard error (SE).

Weighted annual precipitation means for Aleria, Corte and δ_P were added to Fig. 7 as independent validation values (Table 2). Note that these independent values were derived from monthly precipitation collection (Aleria, Corte) and the LEL/WMMWL intercept (δ_P) and should therefore directly represent the altitude effect in precipitation. These data points were not corrected in any manner and are used here to confirm our model-derived correction approach for river water. The direct comparison of precipitation isotope values and the OLSR of the corrected tributary isotope values shows that they overlap within (Aleria, δ_P) and along (Corte) the boundaries of the 95% confidence interval (CI) for the OLSR through the river water data (Fig. 7). A linear regression of these three independent data points yields a slightly lower slope of −0.14‰/100 m for the altitudinal gradient compared to the river water-derived slope. Note, however, that this value is within the 2-SE uncertainty. We therefore conclude that this validates the proposed correction method using mean catchment elevations.

A study from the Biguglia lagoon near Bastia in northeastern Corsica (Erostate *et al.* 2018) used stable isotope measurements of groundwater from a coastal aquifer to identify potential recharge areas. Based on a comparison with isotope precipitation data from Bastia and Corte, the authors identified two main sources for recharge: while the southern part of the aquifer is recharged by local precipitation, the northern part is characterized by significantly depleted stable isotope values that indicate a "higher-altitude water source." However, in their study it was not possible to further narrow down the recharge altitude within the catchment. The δ^{18}O values of groundwater at the Biguglia lagoon ranged between −8.0 and −9.1‰. By applying the altitudinal isotope gradient for Corsica from this study, these values translate into mean recharge altitudes of 1000 to 1500 m a.s.l. Compared to the values in the literature, the value of (−0.19 ± 0.02)‰ for δ^{18}O determined using the geographic information system (GIS) correction approach of this study falls within the interval of −0.12

Table 1. Upstream mean catchment elevation calculated for the two sampling sites, just upstream of their confluence at Corte along the Restonica (R6) and the Tavignanu (4), and all tributaries (T1 to T5). See Fig. 1 for locations.

ID	4	R6	T1	T2	T3	T4	T5
River	Tavignanu	Restonica	Orta	Zincaghju	Vechju	Corsiglièse	Tagnone
Site elevation (m a.s.l.)	409	471	427	312	188	38	2
Upstream mean catchment elevation (m a.s.l.)	1526	1544	1017	755	1116	534	358
Area (km^2)	81.8	62.6	13.5	32.1	162.2	45.5	104.1
Max. elevation (m a.s.l.)	2327	2582	1951	1575	2586	1231	1531
Min. elevation (m a.s.l.)	407	471	424	312	186	31	0

Table 2. Weighted average (wt. av.) isotope values of monthly precipitation samples at Corte and Aleria (see Fig. 1 for locations). VSMOW–Vienna Standard Mean Ocean Water.

Site	Altitude (m a.s.l.)	Sampling period	$\delta^{18}O_{wt.av.}$ /‰ VSMOW	$\delta^{2}H_{wt.av.}$ /‰ VSMOW
Aleria	17	March 2015 to March 2017	−6.52	−37.3
Corte	446	May 2015 to March 2017	−7.55	−46.5

to −0.28‰ per 100 m reported for the Mediterranean (see above). The European mean of −0.21‰ per 100 m, established by Poage and Chamberlain (2001), is also within ±1 SE of the calculated value for the Tavignanu Catchment. This also accounts for the value of (−0.17 ± 0.02) calculated for stream and spring waters in Corsica by van Geldern *et al.* (2014).

3.5 Limitations

In the high-relief area of this study, our approach was able to compensate for the accumulation of the stream signal by establishing a mean elevation of the upstream catchment area. However, this approach may also have its limitations. When applying this technique, one must keep in mind that isotope values of surface waters may not always adequately represent upstream precipitation, particularly if river water contributions depend on specific climatic, hydrological, and hydrogeological conditions.

Our correction approach assumes an equal spatial distribution of precipitation in the catchment. This is not always a valid assumption for high-relief terrains because of generally increased precipitation amounts at higher elevations. Nevertheless, our data show that elevation-corrected river isotope values agree well with measured precipitation isotope values. We presume that this relates to the small subcatchment size of our study site, that does not allow for a large spatial variability of precipitation amounts. This might limit the transferability of our approach to larger catchment sizes with less homogeneous precipitation distribution patterns.

One must also assume that secondary evaporation after precipitation is almost negligible. This should be valid for regions where geology and climate allow precipitation to infiltrate the ground quickly after rain events. Under such conditions, recharge of the rivers should occur via short-distance surface runoff or shallow subsurface flow. These conditions are met in our study area, and secondary evaporative enrichment in the high-altitude source lakes should not affect the sampling locations that were used in our correction approach (see above).

Finally, we must assume that groundwater-surface water interactions leave the isotope signal of the stream unchanged. Significant groundwater contributions from large underground water bodies, as for instance in karst areas, from paleowater aquifers or geothermal reservoirs with differing isotope compositions, might significantly shift the river water isotope composition with respect to regional precipitation.

4 Conclusions

The stable isotope analyses of water sampled from a perennial river in a high-relief region, over its entire course from its high-elevation source lakes down to sea level, coupled with isotope data from local rainfall allowed for the development, testing, and verification of a GIS-based elevation correction approach. This approach correctly determined the isotope altitude gradient that is important for identifying recharge areas and altitudes that feed low-land aquifers, which are vital drinking water resources. To our knowledge, the direct comparison of river water data with precipitation isotopes is new for a catchment with such a considerable altitudinal gradient.

When considering river water isotope ratios with associated sampling elevations in the Tavignanu Catchment, we were unable to construct a plausible altitude effect for the upstream catchment

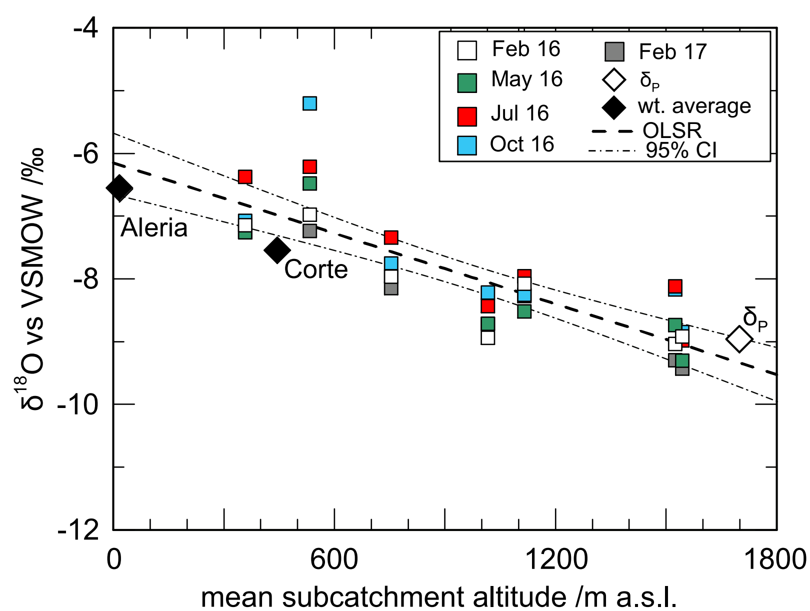

Figure 7. $\delta^{18}O$ values versus mean catchment elevation upstream from the respective sampling points for the Tavignanu, Restonica and tributaries. The dashed line is the ordinary least squares regression (OSLR) of the altitude-corrected river water isotope values with 95% confidence interval (CI). Weighted annual means of precipitation at Aleria and Corte (black diamonds) and the intercept (δ_P) of the WMMWL and the LEL (white diamond) were added as independent comparative values.

above 450 m a.s.l. An inverse isotope effect, as described in the literature for precipitation (e.g. Jiao *et al.* 2019), seemed unreasonable regarding the rather stable isotope pattern along the river course during all seasons. However, replacing the sampling site elevation with the calculated mean upstream catchment elevation yielded a valid linear altitude isotope effect from stream water with a good coefficient of determination. The calculated slope was verified from independent precipitation isotope measurements that were directly collected in the study area. In addition, it corresponds well with the literature values for the region. Nonetheless, precipitation data should always be favoured because they minimize environmental alterations.

One major advantage of the approach presented in this study is that collection of river water is logistically more feasible than regular precipitation sampling, which may become labour-intensive and more challenging in remote regions. Such correction of river water data may also offer a valuable opportunity in places where no stable isotope values from precipitation have been measured and data from the Global Network of Isotopes in Precipitation (GNIP) (IAEA/WMO 2021) are sparse. Further, a river-based approach delivers integrated data for the entire catchment area instead of isolated precipitation data points. This might prove more useful to quantify regional groundwater recharge, as it is not prone to statistical outliers (Kendall and Coplen 2001).

A sound knowledge of the isotope altitude gradient becomes increasingly crucial to protect areas where main recharge for drinking water purposes occurs. The approach presented in this study should be transferable to other high-relief regions to allow easier and meaningful determination of the precipitation altitude effect based on river water measurements. Further studies that involve sampling rainfall and river data at different altitudes could confirm our technique and would help to provide better validation.

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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