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Seasonal δ^2H and δ^{18}O changes in river water from a high-altitude humid plain of the southern Alps (Cervières, France): tracking the transit time through a watershed

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Abstract. The Alps Mountains play a major role in the water cycle at a regional scale in Europe. This mountain range acts as the 'water tower' of Europe by storing large volumes of ice and snow, and by regulating the runoff of the rivers constituting freshwater reservoirs of paramount importance for the biodiversity and human activity. Located in the French Southern Alps, the Cerveyrette valley and a high-altitude (≈ 2000 m) swampy plain constitute a watershed of about 100 km^2. From August 2011 to July 2013, water samples were collected monthly from the Cerveyrette river upstream of the Cervières village (elevation = 1620 m) located in the Upper Durance catchment area. Apparent cyclicality in δ^2H and δ^{18}O of the river waters documented over these two years partly reflect seasonal variations in the isotopic compositions of precipitations that mainly occur as snow accumulating at altitudes ranging from ≈ 1700 m to 3300 m. The estimated time lag of three to four months between summer precipitations and their sampling in the Cerveyrette river at the discharge point of the watershed is interpreted to integrate both the mean transfer time of the water discharge and the rate of melting of the snow cover. Here, we show that the transfer time from mountain-accumulated snow toward the low-altitude cultivated areas (Provence) is a sensitive key variable responding to the current climate warming. Indeed, a lowering of the snow cover surface is expected to reduce the buffer effect of snow compared to rainfall, and to decrease the time period during which the discharge rate of the Durance river is large enough for constituting sizable water resources. Understanding and modeling water transit times in nival dominated watersheds are consequently critical to evaluate the impact of the ongoing climate warming on water circulation and resources in the Alps and downstream including the case of mitigation actions.

1 Introduction

We investigated through a new methodological approach the complex relationship between the atmospheric water circulation, the local precipitations, the buffer effect of snow, swamps and soils and the resulting main water outlet of a watershed located in an alpine context. We show the importance of the transfer time from mountain-accumulated snow to the lower cultivated areas as a sensitive key variable responding to the current climate change, with a lowering of the snow cover surface and a reduced buffer effect of snow compared to rainfall. This study explores a way to quantify the influence of climate change on this wide-area transfer time. Understanding and modeling water transit times will be useful to estimate the real impact of the ongoing climate changes on water circulation and water resources in the Alps and downstream including the case of mitigation actions.

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Mountains and highlands provide considerable quantities of water because air is forced to rise and subsequently to cool, thus releasing its moisture as condensates in the form of either rain or snow, a phenomenon called 'orographic precipitation'. The Alps mountain range, which are one of the major mountain ranges in Europe, plays a key role in the regional water cycle by acting as the 'water tower' for Europe, feeding the mains rivers that are the Danube, Pô, Rhine and Rhône. In addition, the storage at high altitude of snow and ice, which only melt in spring and summer, ensures a temporal delay in dispatching those winter precipitations as a water supply to the lowlands during the warm season when the agricultural demand for water is the highest of the year (Viviroli and Weingartner, 2004; Viviroli et al., 2011). Especially during spring and summer, the southernmost catchment areas of the Rhône inherit from the Alps runoff of which variation in magnitude is buffered by the progressive melting of the snow cover.

The word 'alpine' comes from the Alps, and refers to the zone above the natural tree-line, with persistent or permanent snowfields, rocky ridges, occasional wind- shaped trees and continuous to scattered tundra vegetation (Love, 1970). The tree-line, the lower boundary of the alpine life zone, is often fragmented over several hundred meters of altitude (Körner, 2003). Several factors define the alpine zone, including elevation, aspect and high relief, but climate is probably the best determinant of where the alpine zone begins to be defined (Price, 1981; Martin, 2001; Körner, 2003). Alpine climates are characterized by high winds, low temperatures, low effective moisture and short growing seasons for vegetation (Bénévent, 1926; Bezinge and Bonvin, 1974; Braun et al., 1980).

The stable isotopes of hydrogen and oxygen were early recognized as powerful natural tracers of the water cycle (Craig, 1961; Craig and Gordon, 1965; Dansgaard, 1964; Rozanski et al., 1993; Gat, 1996; Gat et al., 2001; Rozanski, 2005). δ^2H and δ^{18}O values of precipitation have been interpreted to locate the main sources of water evaporation (Merlivat and Jouzel, 1979; Uemura et al., 2008), trajectories of humid air masses (Masson-Delmotte et al., 2005; Vimeux et al., 2005; Guan et al., 2013), temperature effects under the mid- and high-latitudes (Dansgaard, 1964; Yurtsever, 1975; Rindsberger et al., 1983; Rozanski et al., 1993; Gat, 1996), amount effects under humid tropical and equatorial areas (Dansgaard, 1964; Rozanski et al., 1993), and the recycling of moisture released during the evaporation of soils, rivers, lakes and closed marine basins (Gat and Carmi, 1970; Froehlich et al., 2008; Wang and Yakir, 2000; Gibson and Edwards, 2002; Aemisegger et al., 2014; Langman, 2015; Wang et al., 2016; Juhlke et al., 2019).

δ^2H and δ^{18}O values of precipitations (rain, snow) follow an empirical linear relationship called the Global Meteoric Water Line (GMWL) and that was defined at the global scale (Craig, 1961; Dansgaard, 1964). Essentially, the hydrogen and oxygen isotope compositions of precipitation follow a Rayleigh's distillation law in both evolving reservoirs of vapour water and condensed water. As air temperature decreases in the residual clouds that migrate from warm low latitudes towards cold high latitudes, there is an increasing isotopic difference between precipitation and water vapour toward the Earth's poles. The generic formulation of the linear equation, given by Eq. (1) and describing the Global Meteoric Water Line (GMWL) is expressed as follows:

$$\delta\,^2H = S \times \delta^{18}O + b \qquad (1)$$

with 'S' being the slope and 'b' the intercept of the linear equation. For a slope S = 8, the intercept 'b' is called the "deuterium excess" (*d* or *d*-excess) defined for the first time by Dansgaard (1964). Indeed, during evaporation of a water mass, the water vapour is less depleted in deuterium than in ^{18}O as a consequence of the differential rates of diffusivity at the interface where the transition between the two states of water takes place. This parameter is especially sensitive to the physical conditions (temperature at the water-air interface, moisture content of the air and wind velocity) prevailing at the source of formation of humid air masses, which means during the evaporation of sea surface waters (Merlivat and Jouzel, 1979; Johnsen et al., 1989; Pfahl and Wernli, 2008). Under mid-latitudes, isotopic compositions of precipitations are strongly controlled by the dew point, itself reflecting accurately air temperatures above the ground (Lécuyer et al., 2020).

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Consequently, at a regional or local scale, the isotopic compositions of precipitations are well correlated to air temperatures at the seasonal scale (Rozanski et al., 1993). In the case of the Rhône river, some tributaries such as the Durance are fed by the water discharges that are controlled by the high-altitude nival regime of the Alps.

Our case study focuses on the seasonal variations in air temperature are recorded in the δ^2H and the δ^{18}O of waters from a mountain torrent such as the Cerveyrette, aggregating many streams upward at an altitude close to 2500 m, located close to Briançon where it feeds the Durance river. The coldest months of the year are characterized by the lowest δ^2H and δ^{18}O values of precipitations that are recorded with a time lag in the water samples of the Cerveyrette torrent collected in the downstream area located in the small town of Cervières (≈ 1600 m in altitude). This observed time lag enables us to estimate the transfer time of melted snow through the high-altitude watershed before being collected in one of the main Rhône tributaries, which is the Durance river that irrigates the Provence Region southward. Finally, changes in the deuterium excess of precipitation are discussed to identify the sources of air moisture, i.e. Atlantic versus Mediterranean marine water masses as well as possible superimposed local effects that introduce an additional level of complexity.

2 Geography and climatology of the studied area

Mountain Alps are exposed to the potential influence of the Atlantic Ocean and the Mediterranean Sea. If precipitation in northern Alps mainly derive from the condensation of moisture derived from the Atlantic Ocean, the southern Alps are also under the influence of the Mediterranean Sea. The Upper Durance catchment area is located in the French Southern Alps, 10 km east of the city of Briançon (Fig. 1A and B). This watershed, which is bordered by several mountain peaks (e.g. Col du Lautaret, Barre des Ecrins, Grand Pic de Rochebrune, Bric Bouchet), has an area close to 100 km^2, mainly comprising the Cerveyrette valley and its high-altitude swampy plain called “Plaine du Bourget” (Fig. 2A).

“Cerveyrette” is the name of both the river and the valley (from 3280 m to 1200 m above sea level) that is characterized by a marked topographic contrast between the dip slopes of the Lasseron Massif (2702 m a.s.l.) southward, forming high cliffs of massive dolomites and the dip slopes of the Chenaillet Massif (2650 m a.s.l.) northward, shaped by the ‘Schistes Lustrés’ and the serpentinized peridotites, gabbros, pillow lavas and radiolarites of the Jurassic ophiolite. At the end of the Last Glaciation Maximum (LGM ≈ 23 kyr to 18 kyr), the Cerveyrette glacier melted and vanished about 12 kyr ago (Cossart and Fort, 2008). The U-shape glacial valley, oriented NW-SE, is mostly occupied by the “Plaine du Bourget” (mean altitude of 1900 m), which is a high-altitude swamp with a mean longitudinal slope of 12% (Cossart and Fort, 2008). This valley collects during spring and summer all the waters resulting from the melting of the snow cover of the surrounding highs. Ultimately, they feed the Cerveyrette river having its source at 2506 m of altitude at the “Venton” location, west of the “Petit Rochebrune” peak (3078 m). This torrent, for which up to 15 tributaries have been documented, is a fourth-order stream 22.8 km long, becoming at Briançon (1187 m a.s.l.) a tributary of the Durance River, itself feeding the Rhône river that flows into the Mediterranean Sea.

Cervières area (Fig. 2B), located in the Queyras Massif, Central French Alps, is under the influence of a humid continental climate (Dfb) according to Köppen-Geiger classification (Peel et al., 2007). This climate mode is characterized by four distinct seasons, no dry season, the warmest month does not exceed 22°C in daily air temperatures. Summers are warm and humid while winters are cold. Precipitations occur throughout the entire year with a mean annual value of 700-800 mm; the minimal amount being recorded during July (≈ 40 mm) and the maximal value during October or November (≈ 75 mm). The mean air temperature (MAT) of the coldest month is lower than -3°C and may occur during December, January or February, which corresponds to the average temperature near the southern extent of winter. In addition, four months (June to September) have mean temperatures equal or higher than 10°C, which is the minimal temperature required for tree growth. The main wind direction is NNW to WNW from October to January, WSW to SSW during February and March, S during April and May and SSE from June to September (data from MeteoFrance™).

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At Montgenèvre (1860 m; N 44°55’54”, E6°43’19”), located 15 km north of Cervières, mean annual air temperatures (MAAT) ranged from 3°C to 5°C between years 2010 and 2014. The coldest month is either January or February with MAAT ranging from -5°C to 0°C while the warmest month (July or August) is characterized by MAAT comprised between 15°C and 20°C. In winter (December to March; November being sometimes included), snowfall precipitation ranges from 20 cm to 40 cm per week with sporadic events occurring in April or October. At Cervières, meteorological data monitored by MeteoFrance™ allowed monthly air temperatures to be calculated between years 2011 and 2013 for potential correlation with the δ^2H and δ^{18}O of the water samples that were collected from the Cerveyrette river.

3 Sampling strategy and analytical techniques

3.1 Sampling strategy

In August 2011, we collected 8 water samples of 1 L collected in several creeks (spots#4 and #2 shown for example in Figure 3) of the Cervières watershed, including the Cerveyrette, as well as in surrounding areas to test the degree of spatial isotopic inhomogeneity (Fig. 1B; Table 1). In addition, 1 L of water from the Cerveyrette river was collected each month over 2 years (from August 2011 until July 2013) just upstream the village of Cervières (Fig. 2B; Table 1).

3.2 Hydrogen and oxygen isotope measurements

For each water sample, the δ^2H (‰ VSMOW) corresponds to the average of five aliquots of 0.5 µL. These water aliquots were analyzed according to the protocol described by Morrison et al. (2001). The method is based on water reduction using a chromium-based reactor installed in a EuroEA3028-HT™ elemental analyser from Eurovector SpA (Milan-Italy). This elemental analyser has been upgraded with a EuroAS300 series liquid autosampler equipped with a 1µL 1BR-5 SGE syringe. The elemental analyser is connected online in continuous flow mode to an IsoPrime™ Isotopic Ratio Mass Spectrometer from IsoPrime UK Ltd (Cheadle-UK). The mass spectrometer is equipped with an electrostatic filter to prevent helium interferences on hydrogen mass 3 beams. The H_3^+ factor was calculated every day and was usually below 10 ppm/nA. The duration for each analytical run is approximately 300 s. Water samples collected from the vacuum line were pipetted into 13x32 mm vials with butyl/Teflon sealed caps. When the volume of water collected from the sublimation experiment was too small special inserts had to be placed inside the vials to accommodate the specifications of the liquid autosampler. Five injections were performed from each vial of water from which the standard deviations (2σ) reported in Table 2 were calculated. Hydrogen isotope ratios are reported relative to VSMOW in the ‰ δ unit, after scaling the raw data to the certified isotopic ratios of VSMOW2 and VSLAP2 (Werner and Brandt, 2001; Gröning et al., 2007) to which we also added aliquots of GISP former international standard (Gonfiantini, 1984; Hut, 1987; Araguas-Araguas and Rozanski, 1995; Koziet et al., 1995).

For the determination of δ^{18}O values, aliquots of 200 µL of water were automatically reacted at 313 K with CO_2 and analyzed using a MultiPrep™ system on line with an Elementar IsoPrime™ dual inlet IRMS. Standard deviations (2σ) are reported in Table 2. Oxygen isotope ratios are reported relative to VSMOW in the ‰ δ unit after scaling the raw data to the "true" isotopic ratios of SMOW, SLAP and GISP international standards.

4 Results

In a first step, eight spots (samples CERV1 to CERV8; Table 1), located within “Le Bourget” humid plain or in surrounding areas in the valley (Fig. 1B), were sampled for river water on August 18, 2011, including the Cerveyrette river and some of its tributaries. Water samples have δ^2H and δ^{18}O values ranging from -100.6‰ to -94.5‰, and from -14.55‰ to -13.46‰,

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respectively (Table 2; Fig. 4). Mean δ^2H of -97.5‰ and mean δ^{18}O of -14.01‰ are close to those sampled (sample CERV8-18-08-2011; Table 2) on the same date in the Cerveyrette at the northern entry of the small town of Cervières (Fig. 2B). The small standard deviations associated with both δ^2H (±2.4‰) and δ^{18}O (±0.35‰) values of the seven spots reflect the rather homogenous compositions of waters flowing through the watershed. River water δ^2H and δ^{18}O values align close to the Global Meteoric Water line (Craig, 1961; Dansgaard, 1964) in a δ^2H–δ^{18}O space (Fig. 4), thus suggesting that they preserved the original isotopic compositions of their meteoric water sources.

In a second step, at the spot #8 (Fig. 2B), a survey of the Cerveyrette river has been conducted over 2 years with a monthly-based water sampling. Hydrogen and oxygen isotope compositions of the river water range from -105.2‰ to -96.7‰ and from -14.87‰ to -13.75‰, respectively (Table 2). Variations through time of both isotopic compositions reveal a pseudo-cyclicity (Fig. 5). It is worthy to note that isotopic minima and maxima correspond respectively to the spring and autumn seasons.

The deuterium-excess varies through time from 11.1 to 15.9 with a mean value of 12.9 slightly higher than the intercept of the GMWL. Consequently, δ^2H and δ^{18}O values of the Cerveyrette river plot parallel to the GMWL but with a small offset, even if they belong to the global field of meteoric waters (Fig. 4). The lowest d-excess values of the Cerveyrette river are observed during summer 2011 and 2012 while the highest values are observed during the early spring 2012 and the late spring and early summer 2013 (Fig. 6).

5 Discussion

5.1 Relation between river water δ^2H and δ^{18}O and precipitation at the source

According to the dynamics of the surficial water cycle, the ultimate source of river water is rainfall and snow precipitation. Consequently, we can ask whether the δ^2H and δ^{18}O of river water represent faithfully or not those of precipitation at a local or regional scale depending on the size of the watershed. Isotopic compositions of river waters are potentially modified by evaporation processes, the importance of recharge zones (connected groundwaters), the distance to the moisture source and the amount of precipitation along the course of the river. Nan et al. (2019) have shown that many rivers worldwide have δ^2H and δ^{18}O drawing lines which slopes are lower than 8; a feature assigned to the progressive evaporation of running waters with an isotopic effect especially pronounced in warm and dry areas such as Africa.

By contrast, at high-latitudes, the deviation from the GMWL remains limited because of lower air temperatures relative to low latitudes. However, Yi et al. (2012) observed a negative correlation between the slope of the δ^2H–δ^{18}O correlation and the wetland area. For example, the Lena has a slope of 7.95 for a drainage area < 0.1x106 km^2 against a slope of 5.73 and a drainage area close to 0.9x106 km^2 for the McKenzie river (Yi et al., 2012). At high-latitudes, such isotopic patterns are in addition complicated by the extent of the permafrost coverage (Yi et al., 2012).

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It is therefore expected that small watersheds located in the Alpine mountains have their main outlet characterized by a δ^2H–δ^{18}O relationship close to the local meteoric water line (LMWL). Indeed, water samples from the Cerveyrette river define a linear trend (slope = 7.66 ± 0.80 using RMA regression; R^2 = 0.68; n = 31; Fig. 4) close to the GMWL (slope = 7.96 ± 0.02; Hoefs, 2018; Fig. 4). This observation suggests that the river water mostly preserved the original isotopic compositions of precipitations, which also means that the water did not suffer significant evaporation or mixing with other sources of water during its transit through the watershed. However, it must be noted that the linear trend defined by the Cerveyrette waters (Fig. 4) and waters from the Briançon area is shifted toward the left of the δ^2H–δ^{18}O bivariate plot indicating relatively large d-excess values comprised between 11.1 and 16.5 in these waters (Table 2).

5.2 Relation between air temperature and compositions of precipitation

The meteorological station of Ristolas with an altitude of 1600 m, is located ≈ 25 km southeast of Cervières, recorded Monthly Mean Air Temperatures (MAAT) that are reported in Table 3. Those temperature records range from ≈ -3°C in December up to ≈ 14°C in July. Expected monthly δ^{18}O values of precipitation were calculated using the T–δ^{18}O equation determined by Lécuyer (2013) for Europe IAEA/WMO stations (Table 3). Consequently, in the area of Cervières–Ristolas, the calculated oxygen isotope composition of meteoric waters varies from -20‰ in February to -5‰ in July with a mean value close of -12.3‰ instead of the observed mean δ^{18}O value of -14.3‰ recorded in the waters of the Cerveyrette river (Fig. 7). As the precipitations are equally distributed over the year (except at the end of summer; data from Montgenèvre station, Meteo France), the difference between these two isotopic values could mainly correspond to a difference in altitude between the location of Cerveyrette and the mean altitude range (2000 – 3000 m) of precipitation around the highs. As the vertical oxygen isotope gradient is close to -0.2‰ or -0.3‰ per 100 m (Tazioli et al., 2019), a mean altitude of precipitation in the range 2400 m to 2700 m may explain the mean δ^{18}O value of Cerveyrette waters close to -14.3‰ (Table 2; Fig. 7). Of course, this simple calculation stands only if we consider that post-precipitation processes such as snow sublimation, undercover snow melting and evaporation during the course of waters throughout the watershed play only a minute role in the final isotopic budget of the water collected at the entry of the Cervières village.

5.3 δ^2H and δ^{18}O variations recorded in the Cerveyrette and the nival regime of the watershed

Variations in air temperatures under our latitudes may be described by a sine wave in accordance with the existence of four seasons. Spring and autumn are characterized by intermediate air temperature close to the MAAT while the two other seasons are marked by the coldest and warmest temperatures. As air temperature is one of the main drivers controlling the stable isotope fractionation between humid air masses and the products of condensation, it has been recognized for decades that both δ^2H and δ^{18}O of precipitation mimic sine wave variations at the annual scale (Rozanski et al., 1993). This property can be used to estimate transit times of river water through a sine function fitting to the annual variations of the oxygen isotope record (Niinikoski et al., 2016). At Cervières, a pseudo-cyclicity of the measured δ^{18}O values is observed over two years as suggested by a best fit of data with a sine wave (Eq. (2)) using least-square approximation (Fig. 8):

$$\delta^{18}O = A \times \sin(P \times \{t + \phi\}) + k \quad (2)$$

with A the amplitude of the signal, P (= 2π/ω) the period, ϕ the phase shift and k the wave node. The least square approximation gives the following equation (3) that relates the cyclical variations in the δ^{18}O of Cerveyrette waters as a function of time reported in days:

$$\delta^{18}O = 0.37 \pm 0.05 \times \sin(2\pi/\{391.1 \pm 18.05\}) \times (t + 1.15 \pm 0.31) - 14.26 \pm 0.04 \quad (3)$$

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Even though only two oscillations are recorded in the isotopic signal, it is worthy to note that a full cycle of this sine wave signal corresponds to 391 ± 18 days, which is a period compatible with an annual frequency in air temperature variations. The lowest values should therefore correspond to the coldest months of the year while the highest values should match the warmest months. Thus, the minimal values for δ^2H (≈ -104‰) and $\delta^{18}O$ (≈ -14.8‰) of precipitation are expected to be observed during December/January/March according to meteorological data recorded in Ristolas (Table 3). However, these minimal values have been observed in the sampled Cerveyrette waters during March/April/May in 2011 and during April/May/June during 2012. Consequently, there is a time lag of about 3 to 4 months between the period of snow precipitation and accumulation on the highs and the period when the melted snow reaches the Cervières village as the main river outlet of the watershed.

As seen in Figure 8 the sine model is only an approximation, as expected for a simple explorative modeling: the residues are not evenly distributed along the curve. The complexification of the model by using, for example, the combination of two sine waves improves the residues distribution as expected when the number of parameters is increased. The results have to be taken only as roughly descriptive due to the limited number of cycles available and the annual fluctuations of the meteorological variables. However, this shed light on the complexity of the theoretical model that could be built and tested with a longer period of isotopic record.

Assuming that the parameters of the simplest sine model are sufficient for an acceptable estimation of the buffer effect of snow melting, therefore we only consider the dates of the minima and maxima of the modelled sine wave. Consequently, we consider that the stable isotope data of water rivers in a high-altitude plain can be used to estimate the time required to melt the snow cover during spring along with the time necessary to transfer the water through the watershed. The time lag we calculated is thus certainly much higher than the transfer time of water by diffusion and advection throughout the drainage basin.

5.4 Geographic sources of precipitation feeding the Cerveyrette watershed

Craig (1961) has shown that the GMWL has a slope S of 8 and a d-excess of 10‰, reflecting marine surface waters out of isotopic equilibrium with the atmosphere moisture. Similar slope and intercept values are observed for the European Meteoric Water Line (Skrzypek, 2011) for which the main source of moisture is carried by the westerlies forming in the Central Atlantic Ocean. This deuterium excess corresponds to a temperature close to 25°C and a mean relative humidity in the range 80-85% at the seawater-atmosphere interface of the source of evaporation (e.g. Merlivat and Jouzel, 1979; Clark and Fritz, 1997). In average, the d-excess value of precipitation over Europe is close to 10‰ as indicated by the intercept of the EMWL. However, seasonal variations in the d-excess of precipitation over Europe have been documented (Rozanski et al., 1993; Pfahl and Sodemann, 2014) and interpreted as reflecting seasonal variations in relative humidity and air temperature of the evaporating sea surface at tropical latitudes. For example, during the colder season, relative air humidity tends to be lower than during the warmer season (Rozanski et al., 1993). However, such effect on the kinetic isotopic fractionation that takes place during phase change could be partly offset by lower air temperatures during winter as revealed by the data reported in Bonne et al. (2019).

In the south of France, including the southern Alps, the wind pattern is more complex as westerlies compete with Mediterranean winds all over the year, which means that high d-excess values may be recorded in precipitation because of the evaporation of the warm Mediterranean Sea characterized by a moisture-poor overlying atmospheric layer (Gat and Carmi, 1970; Rindsberger et al., 1983; 1990; Delattre et al., 2015). If the d-excess for the Eastern Mediterranean Sea is known to be close to 22‰ according to Gat and Carmi (1970), the Western Mediterranean is characterized by a mean value close to 15‰ (Celle-Jeanton et al., 2001; Frot et al., 2002).

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Variations in the d-excess values have been documented in the Alps mountains and were interpreted as resulting from changing physical conditions (relative humidity and air temperature) at the Atlantic Ocean and Mediterranean sources (Froelich et al., 2008). They may also result from local effects including the high proportion of snow in the total amount of precipitation (Rozanski et al., 1993; Liebminger et al., 2006) and recycling of continental water vapour from stagnant water bodies and soils; both being responsible for an increase in d-excess (Froelich et al., 2008; Cui et al., 2009; Jódar et al., 2016; Wang et al., 2016).

At Cervières, calculated d-excess in the range 11‰ to 16‰ could result from a combination of synoptic effects with ultimate sources of moisture brought by prevailing winds either from the Atlantic Ocean (d-excess close to 10‰) or the Western Mediterranean Sea (d-excess close to 15‰). They could also be strongly influenced by local effects such as continental moisture recycling and out of isotopic equilibrium processes during snow formation. Indeed, an increase in d-excess may also occur during snow formation because the magnitude of isotopic disequilibrium during the phase change depends on the degree of the supersaturation ratio of the vapour over ice (Uemura et al., 2005). Sub-cloud evaporation such as partial evaporation of water droplets during their fall could be responsible for a lowering of the d-excess in the residual water, however, this process only concerns low altitude areas (< 2000 m) exposed to warm and dry conditions (Gat et al., 2001; Froehlich et al., 2008; Bershaw et al., 2020). Finally, sublimation of the top of the snow cover is another process that could also produce changes in d-excess (Sokratov and Golubev, 2009; Lechler and Niemi, 2012; Kopec et al., 2020) although the equation of state of water predicts that it should only play a negligible role at altitudes lower than 3000 m because of too high atmospheric pressure and ambient air temperature.

As already observed by Lambs et al. (2013) in the south of France, the measured d-excess variations record at Cervières do not follow a seasonal cyclicity over 2 years as revealed by the maximal d-excess values that occurred during spring in 2012 or summer in 2013 while the lowest values are recorded during summer in 2011 and 2012 (Fig. 6). Considering the 3 to 4 months delay between precipitation and flowing through the Cervières village, the lowest d-excess values of +10 are recorded during spring and summer (Fig. 6) when the main wind direction is S or SSE, a result in apparent contradiction with the d-excess value expected from Mediterranean moisture. The record of d-excess higher than 14‰ in winter is also a surprising result (Fig. 6). In such specific geographic context, it seems that the d-excess of the Cerveyrette river could neither track faithfully the source of air moisture nor be used to estimate the transfer time of water between the melting of snow cover and the downstream area of the watershed. However, such calculation can be performed by using the seasonal oxygen isotope record alone.

6 Conclusions

The stable isotope monitoring (δ^2H and $\delta^{18}O$) performed on a monthly basis over 2 years of a mountain river (Cerveyrette) that collected waters from a ≈ 100 km^2 nival watershed located in the South French Alps, close to Briançon, revealed a few interesting hydrological patterns:

- A small watershed such as the one defined by the Cerveyrette valley has its main outlet (Cerveyrette torrent) characterized by a δ^2H–$\delta^{18}O$ relationship close to the local meteoric water line (LMWL), thus suggesting that the river water mostly preserved the original isotopic compositions of precipitations. This observation means that the water did not suffer significant evaporation or mixing with other sources of water during its transit through the watershed. It is worthy to note that the linear trend defined by the Cerveyrette waters and waters from the Briançon area is shifted toward the left of the GMWL indicating relatively large d-excess values.
- Such d-excess values in the range 11‰ to 16‰ could result from a combination of synoptic effects with ultimate sources of moisture brought by prevailing winds either from the Atlantic Ocean (d-excess close to 10‰) or the Western Mediterranean Sea (d-excess close to 15‰). We consider that the d-excess of the Cerveyrette river could neither track

faithfully the source of air moisture, as it may be influenced by local evaporation, nor be used to estimate the transfer time of water between the melting of snow cover and the downstream area of the watershed.

- Despite the dampening effect of snow melting on the local seasonally-controlled rainfall δ^2H and δ^{18}O values, a residual annual cyclicity of 391 ± 18 days, is restored when fitting data to a sine wave.
- We deduce from the sine wave-like isotopic record a time lag of about 3 to 4 months between the period of snow precipitation and accumulation on the highs and the period when the melted snow reaches the Cervières village as the main river outlet of the watershed. This time transfer is interpreted to integrate both the mean transfer time of the water discharge and the rate of melting of the snow cover.

In the framework of this study, we show that the transfer time from mountain-accumulated snow toward the low-altitude cultivated areas (Provence) is a sensitive key variable responding to the current climate warming. Indeed, a lowering of the snow cover surface is expected to reduce the buffer effect of snow compared to rainfall, and to decrease the time period during which the discharge rate of the Durance river is large enough for constituting sizable water resources. Understanding and modeling water transit times in nival dominated watersheds are consequently critical to evaluate the impact of the ongoing climate warming on water circulation and resources in the Alps and downstream including the case of mitigation actions.

Code and data availability. Data are available as Excel files upon request to the first author.

Author contributions. The study was conceptualized by CL, JPF, GP and PD. FA and CL contributed to water sampling. FF performed the stable isotope measurements of water samples. CL wrote the manuscript and designed the illustrations.

Competing interests. The contact author has declared that neither they nor their co-authors have any competing interests.

Disclaimer.

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Review statement.

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Figure 1. Geographic location of Briançon in the French Alps along with the eight spots of river water sampling. Background maps were obtained from © GoogleEarth™. Our maps extracted from © GoogleEarth can be used in our publication as we have i) correctly attributed the property to © Google Earth ii) followed the general guidelines, especially with regard to fair use. (https://www.google.com/intl/en-GB_ALL/permissions/geoguidelines/)

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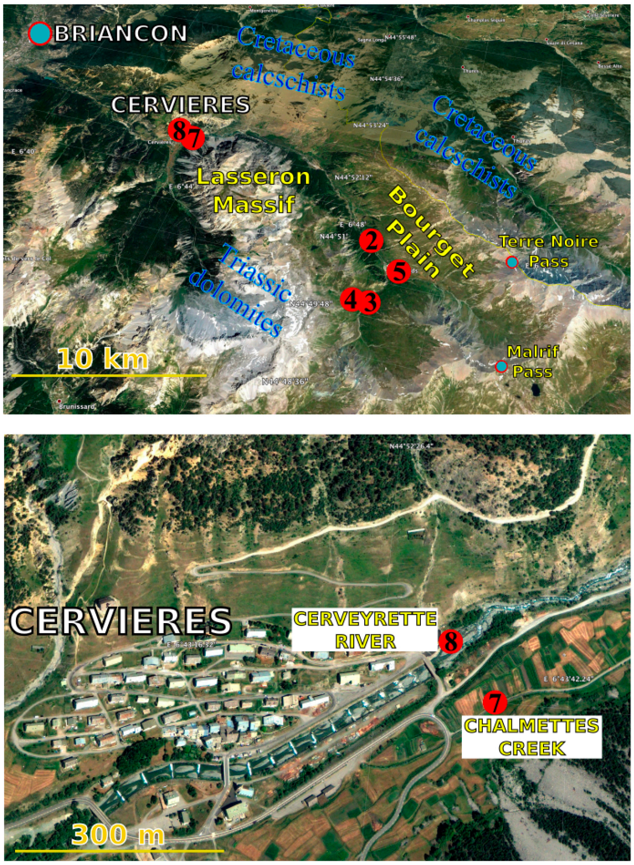

Figure 2. A) Location of Cervières and the Bourget Plain defining the watershed limited by several surrounding highs (≈ 2500 m) such as the Lasseron Massif (Triassic dolomites), the Terre Noire Pass (Cretaceous calcschists) and the Malrif Pass. B) Precise geographic location of the monthly water sampling from the Cerveyrette river (spot#8, close to the bridge east of the town) between August 2011 and July 2013. Background maps were obtained from © GoogleEarth™. Our maps extracted from © GoogleEarth can be used in our publication as we have i) correctly attributed the property to © Google Earth ii) followed the general guidelines, especially with regard to fair use. (https://www.google.com/intl/en-GB_ALL/permissions/geoguidelines/)

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Figure 3. Pictures of the Coutiers creek (spot#4; Table 1; Figure 2), tributary of the Cerveyrette near the place called "Les Fonts" (the springs) and of the Cerveyrette river downstream of Malrif Pass (spot#5; Table 1; Figure 2).

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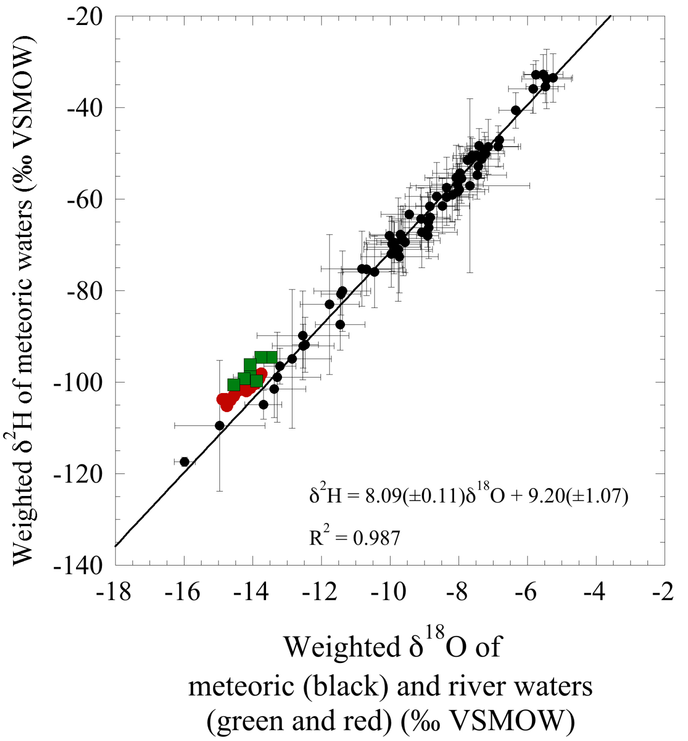

Figure 4. δ^2H– δ^{18}O binary plot of river waters from the Briançon area along with the Global Meteoric Water Line (GMWL). Green squares: river water samples in the Briançon area; red circles: Cerveyrette river sampled from August 2011 and July 2013 (Figures 1 and 2).

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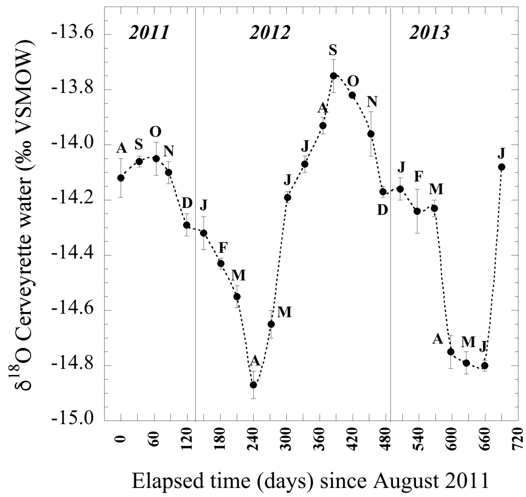
A)



B)

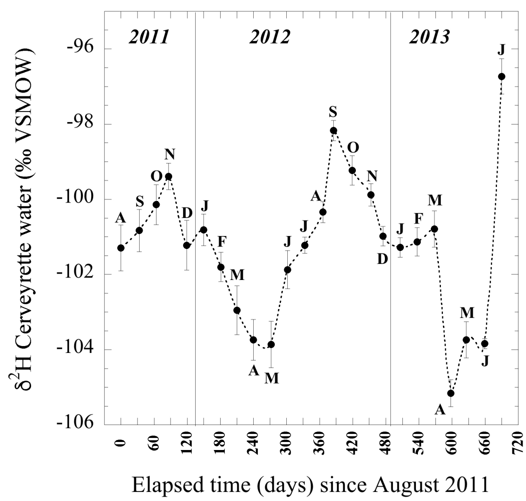


Figure 5. Monthly variation of $\delta^{18}O$ (A) and $\delta^{2}H$ (B) of the Cerveyrette river water from August 2011 to July 2013. Letters in bold indicate the month of the year. Elapsed time is counted in days from August 18th 2011 until July 16th 2013.

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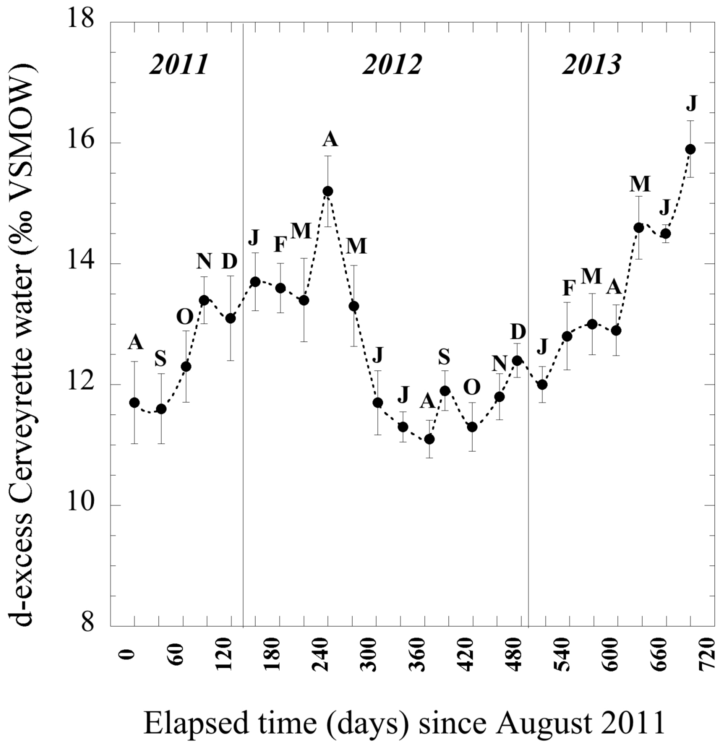

Figure 6. Monthly variation of the d-excess recorded in the Cerveyrette river water from August 2011 to July 2013. Letters in bold indicate the month of the year. Elapsed time is counted in days from August 18th 2011 until July 16th 2013.

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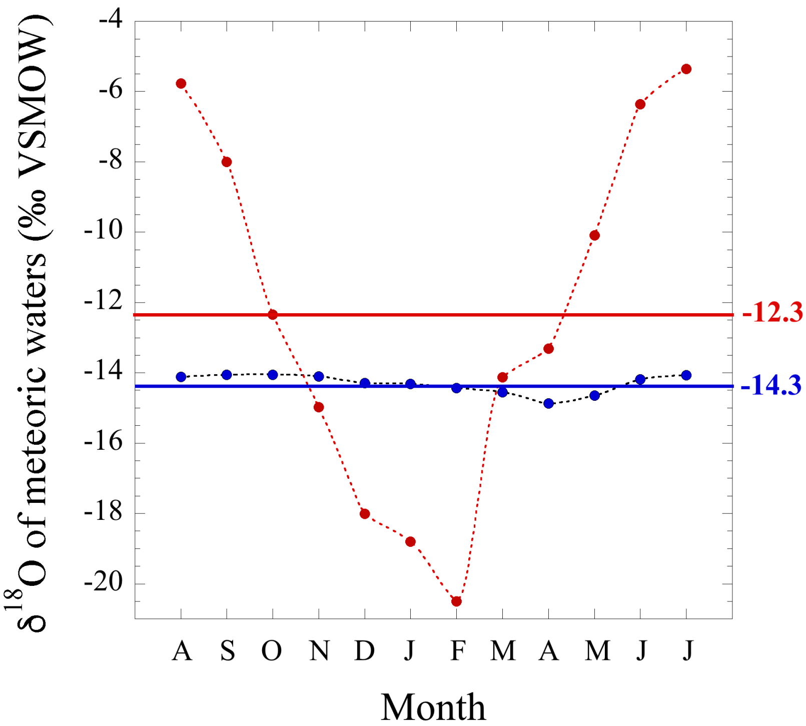

Figure 7. One-year variation (dotted red curve) and mean (horizontal red line) in the $\delta^{18}O$ of meteoric waters calculated from the monthly mean air temperature variations recorded at the meteorological station of Ristolas (25 km southeast of Cervières) by using the equation determined by Lécuyer (2013). These calculations are compared to the 2011-2012 Cerveyrette river water record (dotted blue curve) and its mean value (horizontal blue line). The 2‰ offset between the mean values is mostly assigned to the altitude difference between both towns (≈1600 m for Cervières and Ristolas) and the altitude range (2400 to 2700 m) of snow precipitation above the highs surrounding the Plaine du Bourget watershed (see section 5.2 for more explanations).

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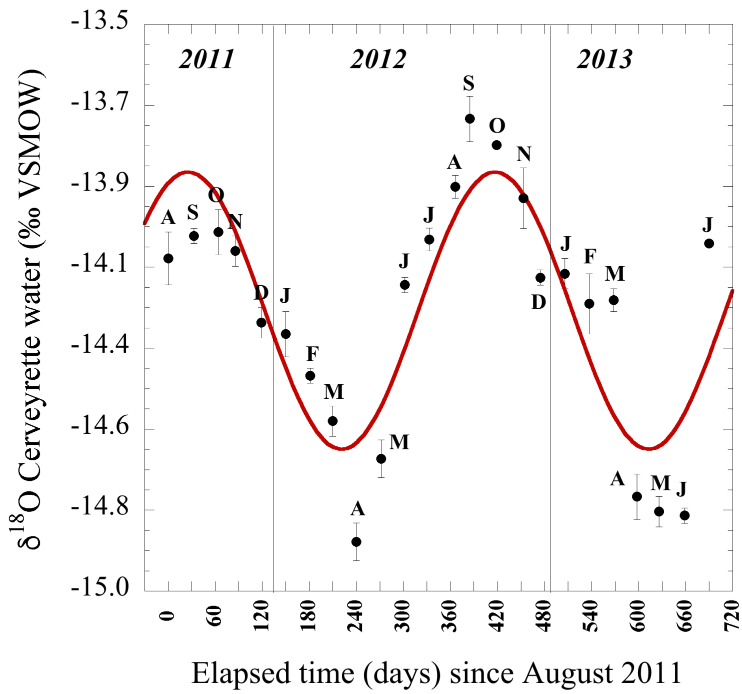

Figure 8. Same data as those reported in Figure 5A fitted by least square approximations with a sine wave function that suggests the preservation of the seasonal variations in the isotopic composition of meteoric waters themselves triggered by the seasonal changes in air temperature below the humid air mass. Fitted equation: $\delta^{18}O = (0.37\pm0.05)\sin(2\pi/(391.1\pm18.05)(t + 1.15\pm0.31)) -14.26\pm0.04$ ($R^2 = 0.73$).

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Table 1. Geographic coordinates and altitude of water sampling in the area of Briançon, France. See also Figures 1 and 2 for the geographic location of the sampling spots in the Plaine du Bourget watershed.

Sampling spot#	Geographic coordinates	Altitude (m)	Description
1	N 45°02'18.00" – E 6°14'38.31"	1270	Romanche torrent, downstream of road tunnel "Grand Clot"
2	N 44°51'00.16" – E 6°48'26.96"	2012	Haute Cerveyrette, downstream of "Fonts de Cervières"
3	N 44°49'56.84" – E 6°48'42.72"	2182	"Les Fonts", bridge over the Péas torrent
4	N 44°49'57.28" – E 6°48'37.47"	2203	"Les Fonts", small creek coming from "Les Coutiers"
5	N 44°50'34.85" – E 6°49'02.34"	2052	"Les Fonts", close to the bridge over the Col Malrif torrent
6	N 44°42'35.67" – E 6°50'55.77"	1765	"Aigue Blanche" torrent, Queyras Massif
7	N 44°52'12.26" – E 6°43'36.95"	1643	Cervières, Chalmettes spring coming out of the "Schistes Lustrés"
8	N 44°52'15.87" – E 6°43'33.24"	1632	Cerveyrette river, close to the bridge upstream Cervières

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Table 2. Hydrogen and oxygen isotope ratios of river waters sampled in the area of Briançon, France. The monthly water sampling of the Cerveyrette river at Cervières is indicated by the code CERV8 from August 18th 2011 until July 16th 2013. d-excess values are also reported according to the formula d-excess = $\delta^2H - 8\delta^{18}O$. SD = standard deviation (2σ).

Sample	Date	$\delta^{18}O$ H_2O ‰ VSMOW	SD	δ^2H H_2O ‰ VSMOW	SD	d-excess
CERV-01	18/08/2011	-13.46	0.15	-94.53	0.35	13.2
CERV-02	18/08/2011	-14.07	0.04	-97.63	0.61	15.0
CERV-03	18/08/2011	-13.76	0.04	-94.57	0.55	15.5
CERV-04	18/08/2011	-14.25	0.01	-99.26	0.59	14.8
CERV-05	18/08/2011	-13.89	0.15	-99.76	0.84	11.4
CERV-06	18/08/2011	-14.55	0.03	-100.56	0.55	15.9
CERV-07	18/08/2011	-14.08	0.05	-96.13	0.55	16.5
CERV8-18-08-2011	18/08/2011	-14.12	0.07	-101.29	0.61	11.7
CERV8-20-09-2011	20/09/2011	-14.06	0.02	-100.83	0.56	11.6
CERV8-21-10-2011	21/10/2011	-14.05	0.06	-100.14	0.53	12.3
CERV8-12-11-2011	12/11/2011	-14.10	0.04	-99.39	0.35	13.4
CERV8-15-12-2011	15/12/2011	-14.29	0.04	-101.22	0.66	13.1
CERV8-15-01-2012	15/01/2012	-14.32	0.06	-100.81	0.42	13.7
CERV8-15-02-2012	15/02/2012	-14.43	0.02	-101.80	0.39	13.6
CERV8-15-03-2012	15/03/2012	-14.55	0.04	-102.95	0.65	13.4
CERV8-14-04-2012	14/04/2012	-14.87	0.05	-103.74	0.54	15.2
CERV8-16-05-2012	16/05/2012	-14.65	0.05	-103.86	0.62	13.3
CERV8-15-06-2012	15/06/2012	-14.19	0.02	-101.87	0.51	11.7
CERV8-16-07-2012	16/07/2012	-14.07	0.03	-101.22	0.22	11.3
CERV8-28-08-2012	28/08/2012	-13.93	0.03	-100.34	0.28	11.1
CERV8-16-09-2012	16/09/2012	-13.75	0.06	-98.17	0.27	11.9
CERV8-20-10-2012	20/10/2012	-13.82	0.01	-99.23	0.39	11.3
CERV8-23-11-2012	23/11/2012	-13.96	0.08	-99.88	0.30	11.8
CERV8-15-12-2012	15/12/2012	-14.17	0.02	-100.98	0.26	12.4
CERV8-15-01-2013	15/01/2013	-14.16	0.04	-101.28	0.26	12.0
CERV8-15-02-2013	15/02/2013	-14.24	0.18	-101.13	0.38	12.8
CERV8-16-03-2013	16/03/2013	-14.23	0.03	-100.79	0.48	13.0
CERV8-15-04-2013	15/04/2013	-14.75	0.06	-105.16	0.36	12.9
CERV8-13-05-2013	13/05/2013	-14.79	0.04	-103.74	0.48	14.6
CERV8-15-06-2013	15/06/2013	-14.80	0.02	-103.84	0.13	14.5
CERV8-16-07-2013	16/07/2013	-14.08	0.00	-96.73	0.47	15.9

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Table 3. Mean, minimal and maximal values of air temperatures recorded in Ristolas, France during the last decade. δ^{18}Omw represents the oxygen isotope composition of meteoric waters calculated on the basis of the recorded mean air temperature by using the δ^2H–δ^{18}O linear relationship (European Meteoric Water Line from Skrzypek et al., 2011) obtained from the IAEA/WMO database available for the stations located in Europe.

Month	mean T air Ristolas	min T air Ristolas	max T air Ristolas	δ^{18}Omw calculated Ristolas
January	-4.5	-9.8	4.7	-18.5
February	-6.9	-17.5	3.5	-20.2
March	2.1	-4.5	6.8	-13.9
April	3.3	0.1	10.5	-13.0
May	7.8	1.8	13.3	-9.8
June	13.1	7.2	17.6	-6.1
July	14.5	9.6	17.5	-5.1
August	13.9	9.0	17.1	-5.5
September	10.7	4.4	13.8	-7.7
October	4.6	-1.2	10.0	-12.1
November	0.9	-3.3	5.8	-14.7
December	-3.4	-15.5	2.2	-17.7