

The Floodscale experiment in the small catchment of Valescure, France: An overview of the isotopic and geochemical data base

Christophe Bouvier | Nicolas Patris | Rémi Freyrier | Christelle Guilhe-Batiot |
Jean-Luc Seidel | Jean-Denis Taupin | Pascal Brunet | Aurore Remes

HSM, Univ Montpellier, CNRS, IRD,
Montpellier, France

Correspondence

Christophe Bouvier, Université
Montpellier, CC 57, 163 rue Auguste
Broussonnet, 34090 Montpellier, France.
Email: bouvier@msem.univ-montp2.fr

Funding information

This work was funded by the Agence
Nationale de la Recherche (ANR)
FloodScale project under contract ANR-
2011-BS56-027, by French National
Observation Network "Réseau des Bassins
Versants" (RBV) and by French
HydroMeteorological Observatory
Cévennes-Vivarais (OHM-CV). The
Hymex/Mistrals program has also funded
a 6-month grant for Aurore Remes.

Abstract

A 3-year survey has been performed in the Cévennes mountain area, in the South of France, in order to separate surface, shallow sub-surface and groundwater contributions to the flash flood processes. Electrical conductivity, temperature, pH, major and trace elements, total organic carbon and stable isotopes of water were monitored during low flows and floods, in the small (3.9 km²) granitic catchment of Valescure (Gard, France). The data collected during the campaign are widely presented, in relation to the different hydrological compartments (rainfall, shallow soil water, groundwater, streamwater). This constitutes at present the most complete hydrogeochemical database in the Cévennes area, available within the Hymex data base [https://mistrals.sedoo.fr/HyMeX/\(Valescure chemistry and water isotopes\)](https://mistrals.sedoo.fr/HyMeX/(Valescure%20chemistry%20and%20water%20isotopes)), DOI of the referenced dataset: <https://doi.org/10.6096/MISTRALS-HyMeX.1406>.

KEYWORDS

flood generation, groundwater, hydrochemistry, rainwater, soil water, streamwater, water isotopes

1 | INTRODUCTION

A 3-year survey was conducted in the Cévennes mountain area, located in the South of France 50-100 km north of Montpellier, in order to separate surface, shallow sub-surface and groundwater contributions to the flash flood processes. The Cévennes mountain area is indeed prone to severe flash floods due to intense rainfalls (up to 500 mm in 24 hr) that can generate discharges exceeding 20 m³ s⁻¹ km⁻² in small catchments of a few square kilometres

(Delrieu et al., 2005). The flood processes still need to be better understood, in order to improve the hydrological models for flood prediction or climate change impact.

Geochemical studies are few in this region. Travi et al. (1994) monitored one flood event in the Rimbaud sub-catchment of the crystalline Real Collobrier in the Massif des Maures (South of France) and used $\delta^{18}\text{O}$ and Cl^- for a two-component hydrograph separation. Loye-Pilot and Jusserand (1990) also monitored one flood event in a small catchment in Corsica, using SiO_2 concentrations in a two-component separation method. They claimed that other chemical elements are not conservative, because of the throughfall effect possibly altering dissolved elemental ratios across the vegetation cover. Marc and Travi (1995) extended Travi et al. (1994) works. Comparing the same flood event on two sub-catchments of the Real Collobrier, they showed large differences in the contributions of event water and pre-event water,

Dataset

Identifier: DOI <https://doi.org/10.6096/MISTRALS-HyMeX.1406>.
Creator: HydroSciences Montpellier
Title: Valescure chemistry and water isotopes
Publisher: Hymex <https://www.hymex.org>
Publication year: 2016 Resource type: Dataset
Version: 1.0

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2018 The Authors. *Geoscience Data Journal* published by Royal Meteorological Society and John Wiley & Sons Ltd.

depending on the geology of the sub-catchment. In addition, Durand et al. (1992) and Marc et al. (2001) studied another small granitic catchment in Mont-Lozère (France), and suggested that shallow sub-surface water appeared to contribute significantly to the stream flow, as a major component of the pre-event water. However, these initial studies were based on a small number of events and catchments, and emphasized the need to perform additional observations to assess the regional variability, as shown by Marc and Travi (1995). Therefore, a geochemical survey has been implemented within the Floodscale Project dedicated to the observation and modelling of flash floods, in order to better understand the hydrological processes in the area, and to supply data contributing to produce proficient modelling for prediction and forecast of flash floods (Braud et al., 2014).

The objective of this paper was to present broadly the geochemical survey associated to both low and high flows in the small (3.9 km²) catchment of Valescure (Gard, France) developed within the Floodscale framework. Three campaigns were carried out during Hymex Special Operation Periods (SOP; see Ducrocq et al., 2014) in years 2012, 2013 and 2014, during the fall when flash floods are most likely to occur. The survey was completed by a periodic low-flow monitoring performed during the whole period October 2011 to December 2014.

After a brief description of the catchment, the paper details the collected data, including physico-chemical parameters, stable water isotopes, major and trace elements, total organic carbon (TOC). Then, isotopic and geochemical data are presented in relation to the different hydrological compartments, rainwater, soil water, groundwater and streamwater.

2 | THE VALESCURE CATCHMENT

The study area is a small headwater catchment of 3.9 km² located in the South of France, at the southern boundary of the Cévennes mountain area (Figure 1). This catchment is part of the Gardon watershed, where several flood-modelling studies have been undertaken (Bouvier et al., 2007; Moussa et al., 2007; Roux et al., 2011). The Valescure catchment is mainly forested, with an altitude ranging from 244 m to 815 m ASL. The hillslopes are steep with an average slope of 56%. The soil material is a Dystric Cambisol (FAO-WRB, 2014) less than 1 m deep (0.4 m on average) developed on variably weathered granite and gneiss fractured bedrock. Porosity ranges on average from 0.50 at the topsoil to 0.45 at the depth of 40 cm. Saturated hydraulic conductivity measured with a disk infiltrometer proved to exceed 200 mm/hr, from surface to 40 cm deep. Granulometry analysis was derived from the Hymex database as Particle size data Valescure¹, containing

40 samples at 30 cm of average depth, in the Valescure catchment: it resulted in 53.9% coarse fragment >2 mm (*SD* 10.4%), 9.4% coarse sand between 0.2 and 2 mm (*SD* 2.9%), 16.9% sand and silt (*SD* 10.2%), 4.4% clay <2 µm (*SD* 2.2%) and 15.4% organic matter (*SD* 7.9%). Below the soil, weathered structures and fractured bedrock are known to be highly permeable down to depths of several metres.

The Valescure basin has been instrumented and continuously monitored since 2003 for rainfall, soil water content and flow discharge at several points across the catchment. During the Floodscale monitoring, the annual precipitations were 1,266, 1,672 and 2,251 mm respectively for the years 2012, 2013 and 2014. Hydro-meteorological data of two rain gauges (Chateau and Downstream Valescure) and five stream gauges (Upstream Valescure, Cartau, Bastide, Abrits, Downstream Valescure) are available in the Hymex data base as ESPACE Valescure discharge² and Valescure weather station.³

Floods mostly occur in autumn, driven by very intense rain events that can exceed several hundred millimetres in 24 hr. The highest peak flow during the survey period was nearly 16 m³ s⁻¹ at the outlet of the catchment. During the 2012–2014 period, soil water content at depths between 20 and 40 cm was monitored continuously by 16 probes with a 15 min time step: the lowest water content (~0.10 cm³ cm⁻³) occurred at the end of the summer period, while the highest volumes reached the saturated water content (~0.40–0.50 cm³ cm⁻³) during floods. The field capacity was assessed at 0.15–0.20 cm³ cm⁻³. After a flood, the water content was found to drop back quickly (less than 3 days) to the baseline value. All the soil water content data are available in the Hymex data base (Bouvier and Brunet, 2016).

3 | SAMPLING STRATEGY OF WATER ISOTOPES AND CHEMISTRY

The sampling and measurements program was devised to characterize the geochemistry of all significant hydrological compartments (streamwater, rainwater, throughfall, soil water and groundwater) and assess their variability. Table 1 summarizes the complete sampling schedule and location.

3.1 | Rainwater and throughfall

Rainwater was collected for isotopic analysis bi-weekly to monthly during the whole study period at the Chateau site with a 400 cm² cross-section pluviograph connected to a

¹https://mistrals.sedoo.fr/?editDatsId=1175&datsId=1175&project_name=HyMeX&q=particle+size

²https://mistrals.sedoo.fr/?editDatsId=986&datsId=986&project_name=HyMeX&q=espace+Valescure+discharge and Valescure weather station

³https://mistrals.sedoo.fr/?editDatsId=892&datsId=892&project_name=HyMeX&q=Valescure+weather+station

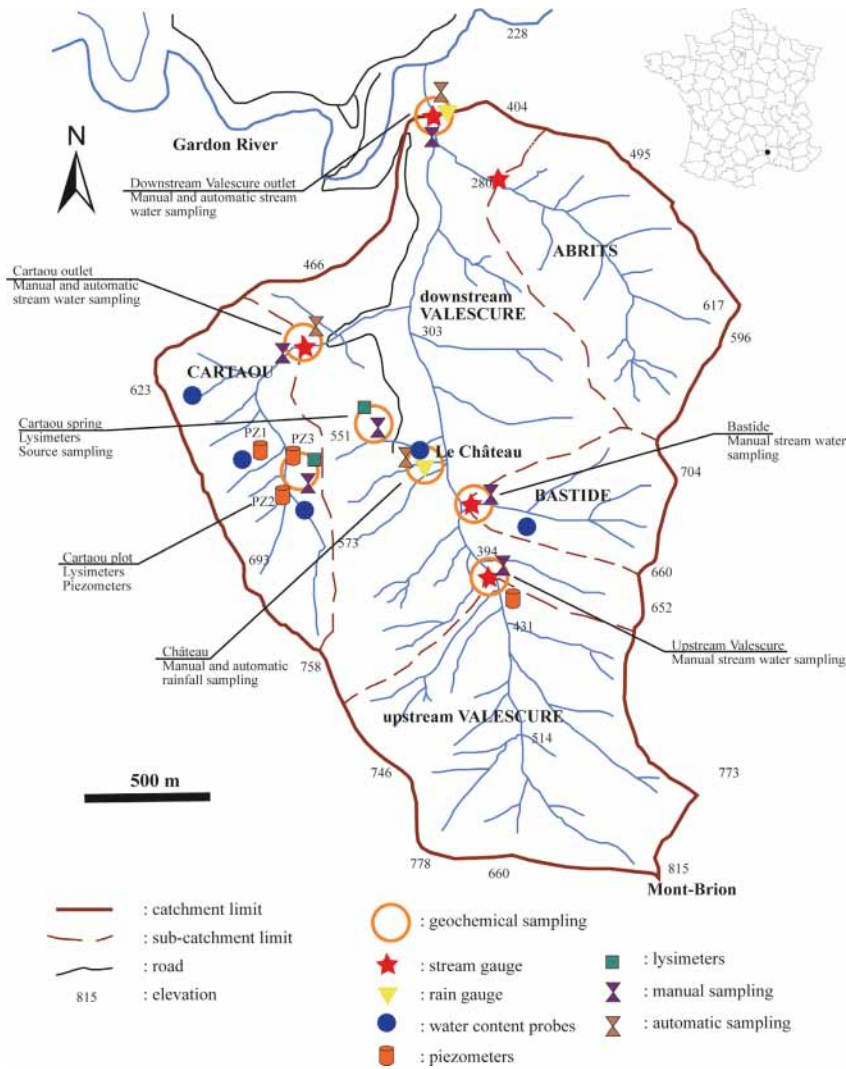


FIGURE 1 Valescure catchment and location of the hydrogeochemical set-up

TABLE 1 Sampling site description

Site	Coordinates	Area (km ²)	Elevation (m asl)	Device	Component	Sampling
Downstream Valescure	44.107°N 3.831°E	3.93	265	SIGMA9000 -	Streamwater Streamwater	Automatic Manual
Cartaou	44.099°N 3.826°E	0.52	390	SIGMA9000 -	Streamwater Streamwater	Automatic Manual
Bastide	44.093°N 3.834°E	0.27	415	-	Streamwater	Manual
Upstream Valescure	44.091°N 3.833°E	0.92	435	-	Streamwater	Manual
Château spring	44.097°N 3.829°E	unknown	420	SIGMA9000 Rain gauge Tensionic (10)	Rainwater Rainwater Soil water	Automatic Manual Manual
Cartaou plot	44.094°N 3.824°E	-	522	Piezometer (3) Tensionic (8) Throughfall (2)	Groundwater Soil water Rainwater	Manual Manual Manual

container protected from solar radiation to avoid evaporation. Eighty-five quasi bi-weekly cumulated rainfall collections were completed during the 39 months of the experiment, covering 376 rainy days. In addition to the

low-frequency cumulative sampling, rainfall was collected at the Chateau site at high frequency (1 to 4 hr time step) during selected rainfall events with a 24-position automatic rain sampler (SIGMA 9000, modified to collect rainfall)

equipped with a 280 cm² cross-section funnel and a flexible tubing dispatching rainwater into 1 L pre-cleaned plastic containers, and programmed to start at the onset of the event, the first container receiving any early rainfall between the installation and the activation of the collector.

Rainwater electrical conductivity and chemistry, including concentrations of total organic carbon, Ca, Al, Sr, Ba and Si were estimated from four samples obtained with the automatic sampler at Chateau.

In addition, two throughfall samples were collected in November and December 2014 for chemical analysis. Clean HDPE bottles were placed along leafless branches and trunks before the onset of the rain and received wet and dry deposit during approximately 1 week. Water stable isotopes were not expected to show sensitivity to the throughfall, and were thus not monitored.

3.2 | Soil water

Tensionic tension lysimeters (SDEC[®], France) were used to characterize the isotopic composition of the soil water after precipitation events corresponding essentially to the SOP 2013 and 2014. These lysimeters contain a porous ceramic chamber (approx. 10 ml, 22 mm in diameter) connected to a pair of plastic tubes that allow refilling while the instrument is kept in place in the ground. The ceramic cup at the bottom of the tension lysimeter is filled with deionized water, of which an aliquot is preserved for isotopic analysis. The volume of water in the ceramic captures the isotopic composition of soil pore water by isotopic diffusion. Dead volumes corresponding to the water contained in the tubes are not submitted to isotopic diffusion with the same velocity; therefore, a correction factor (using the filling water initial isotopic composition and considering 15% of the total lysimeter volume not being exchanged) was applied. The mean $\delta^{18}\text{O}$ correction was $\pm 0.17\text{‰}$, which is small compared to the total signal amplitude of 3.5‰.

Zhao et al. (2013) used a similar tension lysimeter system to collect the mobile portion of soil water by forced suction under high depression. Here, we used instead the ability of the system to allow diffusion through ceramic cups to retrieve the isotopic composition of the pore water. The suitability of Tensionic lysimeters for water isotopic measurements by diffusion was positively assessed during laboratory experiments. The diffusion of the isotopic signal was tested first with the ceramic cell plunged into a container filled with ~300 ml of water isotopically distinct from the cell filling water. Then, the set-up was tested using Valescure dried soil on which water with known isotopic composition, distinct from the filling water, was poured. Different humidity contents, from ~50% to saturation, and corresponding to the field conditions under which we planned to use the equipment, were tested. These

experiments showed that the isotopic composition of the water within the ceramic cell is largely controlled by that of the environment water after a few days of equilibration. In the case of humid soils, the calculated diffusion percentage plateaued about 85%–90% within 3 days. Results of isotopic diffusion were also verified during the whole 2014 campaign by extracting soil water when possible (humidity content $>0.30\text{ cm}^3\text{ cm}^{-3}$), applying a static depression in the cell after collection of the diffusion sample. Results agreed reasonably well between diffusion and extraction samples ($\delta^{18}\text{O}$ identical within $\pm 0.4\text{‰}$, except for two outliers).

Eighteen tension lysimeters were implemented on the catchment for soil pore water isotopic determination, at depths 20 to 40 cm. A first set of 10 lysimeters was deployed over a 10-m² area near Source Chateau during SOP 2013 and SOP 2014, and a second set of eight lysimeters was deployed over another 10-m² area in the Cartau sub-catchment, during SOP 2014. Eight measurement campaigns were achieved during the SOP 2013, and 24 during 2014, including 17 campaigns specifically during the September–December 2014 SOP. The frequency of rainfall events during fall generally allowed a few days in-between to collect the samples after the diffusion delay, and re-initialization of the lysimeters. The Tensionic probes brought valuable information concerning the stable isotopes of water, but were generally not able to supply enough water for chemical analysis. In addition, the ceramic cells generated contamination for several chemical elements (particularly Si and several trace elements).

Therefore, the chemical signature of the soil water was estimated in the laboratory by leaching experiments conducted on three different soil horizons representative of the Cartau catchment: Horizon A (0–7 cm), Horizon S (7–65 cm) and Horizon C (>65 cm). For the leaching experiment, soil samples were dried at 40°C and sieved at <2 mm. The water extraction procedure was adapted from Rodrigues et al. (2010) and Rocha et al. (2010). For each soil type, an aliquot of around 70 g of soil sample was added to 700 ml of ultrapure water (resistivity $>18.2\text{ M}\Omega$, Q-POP Element system, Millipore). HDPE bottles of 1 L were used for this experiment and shaken in a mechanical end-over-end shaker during 24 hr. For each soil type, seven samples of about 3 ml were collected and filtered using a syringe and a disposable 0.22 μm cellulose acetate filter after durations of 10 min, 30 min, 1, 2, 4, 10 and 24 hr.

3.3 | Groundwater

Three 10 m-deep piezometers (PZ1, PZ2 and PZ3) were implemented in November 2015 to collect nearly monthly samples of the groundwater compartment. PZ1 and PZ3 were drilled in the hillslope of the Cartau sub-catchment,

whereas PZ2 was located closer to the riverbed, where the consolidated rock is not as deep as under the hillslope. The water table depth was around 8–10 m for PZ1 and PZ3, whereas it was around 2 m for PZ2. All the piezometer data were integrated in this Valescure chemistry and water isotopes data base. Seventeen samplings were made in 2016 and 2017 in low-flow conditions, except for the 07/04/16 sampling which occurred during a flood recession. The samplings were performed nearly 50 cm below the water surface in the piezometers. For the first experiment, the piezometers were pumped and the sampling was performed after the water level came back to the initial level. As the results were identical before and after pumping, the next samplings were made without previous pumping.

3.4 | Streamwater

Five sites within the watershed were chosen for discrete year-round low-flow sampling of streamwater for chemistry and stable isotopes analysis. Three of them are representative of sub-catchment streamwaters: Upstream Valescure, Bastide, and Cartaou. Downstream Valescure is located on the major outlet, about 100 m upstream from the confluence with the Gardon River. Source Château is the major water spring of the basin, located on a forested hillslope near the geographic centre of the basin.

For low-flow streamwater sampling, 25 campaigns were performed between October 2011 and December 2014 (10/11-08/12: 3 campaigns; 01/13-09/13: 4; 01/14-08/14: 2; 09/14-12/14: 16). During SOP periods, the low-flow sampling was carried out at least 3 days after a rain event. For each sampling, streamwater electrical conductivity, pH and temperature were measured on-site.

Flood streamwater was sampled at the intra-event scale. Two 24-position automatic streamwater samplers (SIGMA

9000) equipped with 1 L pre-cleaned plastic bottles were installed at the Downstream Valescure and Cartaou sites, and programmed to start sampling according to information issued from the SOP control centre (Ducrocq et al., 2014). The selected events corresponded to a minimum of 50 mm cumulated rainfall within 24 hr and to hydrological discharge over $1.5 \text{ m}^3 \text{ s}^{-1}$ at the outlet of the basin (Figure 2). Eleven flood events were thus monitored (Table 2).

4 | ANALYTICAL METHODS

Temperature, pH and Electrical Conductivity ($T_{\text{ref}} = 25^\circ\text{C}$) were measured in the field together with all stream and spring water samplings, or in the laboratory for flood samplings, using a portable pH metre and conductivity metre (WTW 3210 i).

Streamwater samplings for major and trace element determination was filtered on-site with disposable PP syringe and Durapore membrane ($0.22 \mu\text{m}$) and stored in acid washed HDPE bottles. Aliquots for cations and trace elements were acidified with ultrapure HNO_3 (1‰ v/v). Water for total organic carbon analysis was sampled in pre-cleaned and combusted 30 ml amber glass bottles and acidified with H_3PO_4 (1‰ v/v). Samples for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses were collected in 15 ml amber glass vials capped with airtight lids. All samples were stored at 4°C before analysis.

Chemical analyses were performed at the HSM (HydroSciences Montpellier) water chemistry laboratory. Total alkalinity was measured by acid titration with HCl 0.01 N. Major ions (Cl^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were analysed by ion chromatography (ICS 1000 Dionex®). Precision error was $< \pm 5\%$. Trace elements (Li, B, Al, Si, Mn, Fe, As, Rb, Sr, Ba, REE and U) were analysed with Q-ICPMS (X Series II and iCAP Q, Thermo Scientific®) after acidification at 2% HNO_3

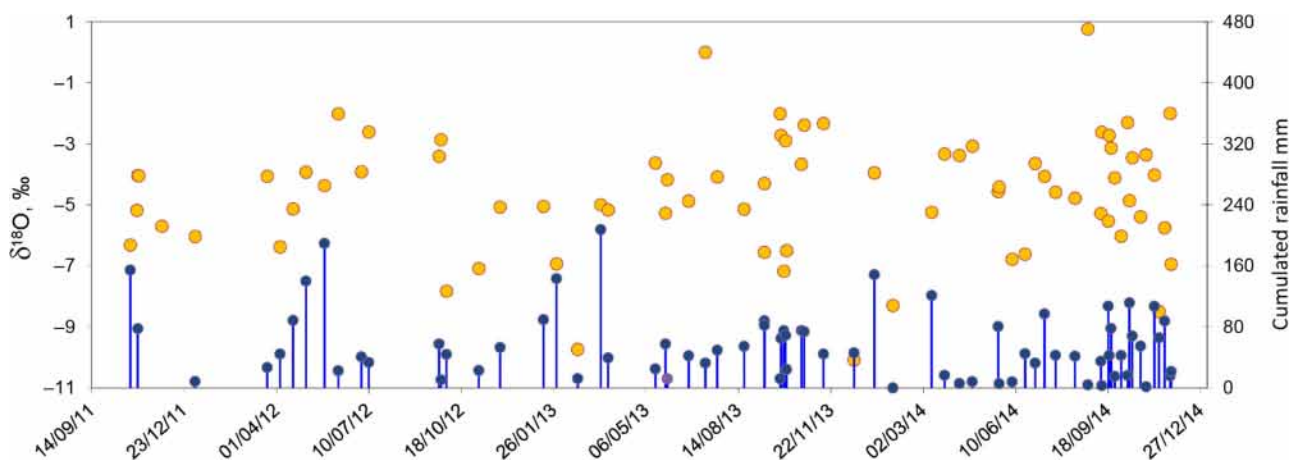
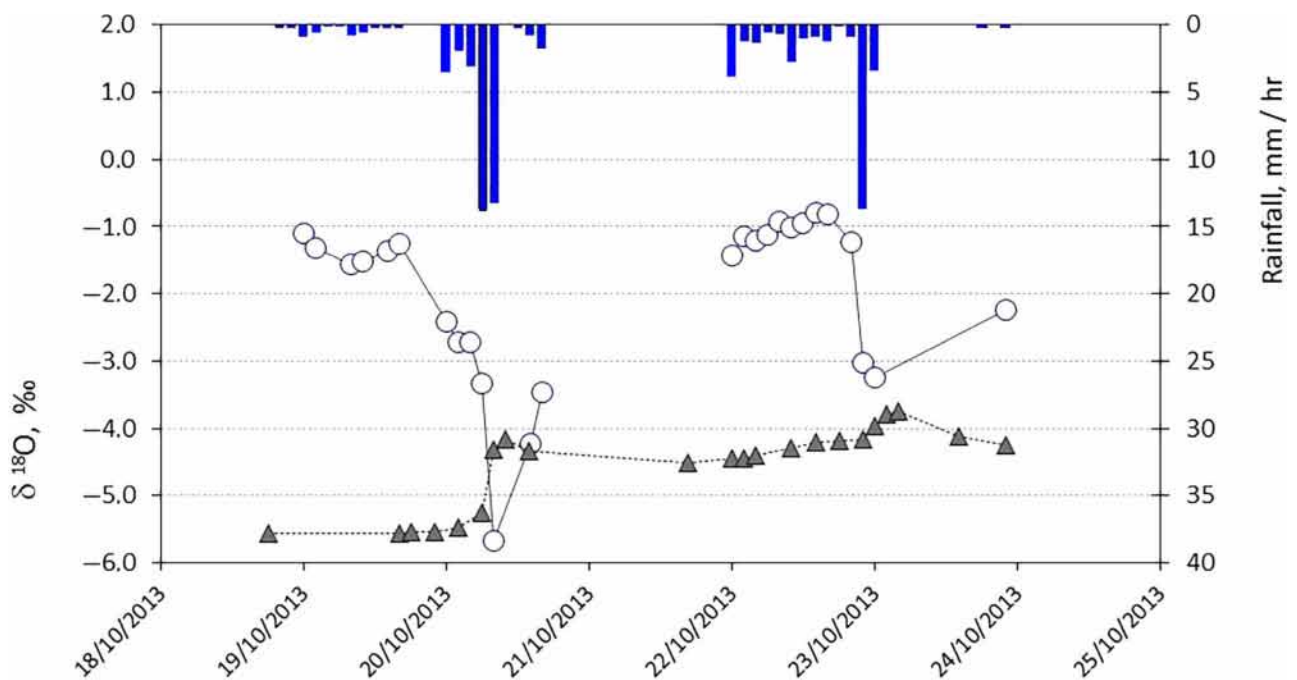


FIGURE 2 $\delta^{18}\text{O}$ isotopic compositions for cumulated rainwater samples during the October 2011–December 2014 period. $\delta^{18}\text{O}$ appears as yellow circles, whereas the blue bars represent the cumulated rainfall amounts at the date of each sampling

TABLE 2 Sampled flood events

Sampling stations	Begins	Ends	Time step (min)	Samples analysed	H(mm)	Qstart Down Val (m ³ /s)	Qmax Down Val (m ³ /s)
Valescure Aval	26/10/2012 06:45	27/10/2012 06:45	30-45	39	109	0.05	2.4
Valescure Aval	09/11/2012 16:00	10/11/2012 15:00	60	24	79.5	0.05	2.1
Valescure Aval, Cartaou	28/09/2013 10:45	29/09/2013 09:45	60	30	98	0.01	1.2
Valescure Aval, Cartaou	18/10/2013 18:00	23/10/2013 22:00	120	49	168.5	0.01	2.2
Cartaou	08/09/2014 19:00	09/09/2014 10:00	60	16			
Cartaou	17/09/2014 10:44	18/09/2014 08:44	60	21	206.1	0.04	15.4
Valescure Aval	19/09/2014 10:00	21/09/2014 08:00	120	16	78.7	0.65	3.7
Valescure Aval, Cartaou	09/10/2014 14:00	11/10/ 201410:00	120	19,16	123	0.14	7.5
Valescure Aval, Cartaou	11/10/ 201414:00	13/10/2014 12:00	120	4	60.5	0.68	2.0
Valescure Aval, Cartaou	14/11/2014 08:00	18/11/ 201404:00	240	11	161.4	0.29	8.2
Valescure Aval, Cartaou	28/11/2014 02:00	29/11/2014 10:00	120	17	134.8	0.62	2.3

**FIGURE 3** Variations of rainwater (open circles) and Valescure Aval streamwater (triangles) $\delta^{18}\text{O}$ during the 19–23 October 2013 rainfall events

v/v at the AETE-ISO (Analyse des Elements en Trace dans l'Environnement et Isotopes) technical platform of the OSU OREME, University of Montpellier. Precision error was

typically $\leq \pm 5\%$. A River water reference material for trace metals SLRS-5 (National Research Council, Canada) was analysed every 30 samples to check the analysis accuracy. Mean results

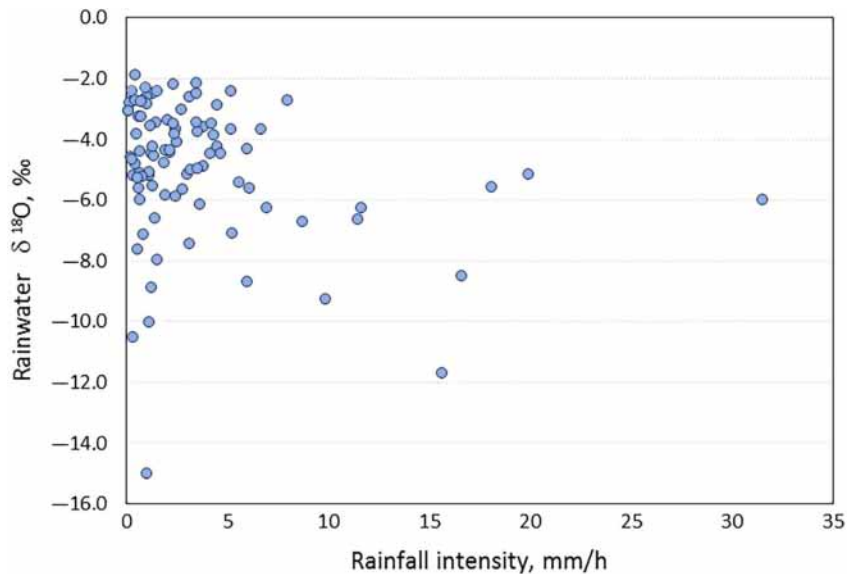


FIGURE 4 Variability of $\delta^{18}\text{O}$ in rainfall as a function of rain intensity at 1-4 hr time step during all events collected during SOP 2012–2014

TABLE 3 Physico-chemical parameters, major and trace elements in rainfall and throughfall

	Name	Sampling date	Conductivity ($\mu\text{S}/\text{cm}^2$)	TOC (mg/L)	Cl (mg/L)	Al ($\mu\text{g}/\text{L}$)	Si (mg/L)	Ca (mg/L)	Sr ($\mu\text{g}/\text{L}$)	Ba ($\mu\text{g}/\text{L}$)	Ca/Sr	Ba/Sr
Rainwaters	PI	26/10/12	5.0	—	—	2.35		0.380	1.11	2.35	342	2.11
	M	10/11/12	5.0	—	0.68	2.17	0.014	0.804	1.24	1.81	648	1.46
	P3	11/09/13	10.0	2.75	0.21	3.17		0.675	0.75	1.10	904	1.47
	P1	18/01/14	15.0	1.91	1.83	1.98	0.038	0.687	1.84	—	374	
		Mean value		8.8	2.35	0.91	2.42	0.026	0.636	1.23	1.75	516
	Standard deviation (1 σ)		4.8	0.63	0.84	0.52	0.017	0.181	0.45	0.63	263	0.37
Throughfalls	T1	28/11/2014	—	—	—	16.4	0.038	1.77	6.28	4.92	282	0.78
	T2	04/12/2014	—	—	—	37.2	0.169	5.06	13.4	10.8	377	0.80
		Mean value				26.8	0.104	3.42	9.86	7.86	329	0.79
		Standard deviation (1 σ)				14.8	0.092	2.33	5.06	4.17	67	0.02

are within the range of certified uncertainties. Total organic carbon (TOC) was measured on a carbon analyser SHIMADZU[®] TOC-VCSH (catalytic combustion method).

Water stable isotopes were measured on an Isoprime mass spectrometer at the LAMA laboratory of HSM, University of Montpellier. Oxygen isotopic composition was measured after equilibration of 200 μl of water with CO_2 by dual inlet technique, with an overall precision of $\pm 0.06\text{‰}$. Deuterium was measured by continuous-flow using a Eurovector Pyr-OH elemental analyser converting 0.5 μl injections of water to H_2 on Cr powder at 1070°C , with an overall precision of $\pm 0.6\text{‰}$. Water isotopic compositions are reported as $\delta^{18}\text{O}$ and $\delta^2\text{H}$ on the V-SMOW scale. Calibration of the isotopic compositions of unknown

samples to the scale was performed by repeated analyses of calibrated house standards in alternation with the samples. Deuterium excess ($d_{\text{exc}} = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$) was calculated and included in the database whenever both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ have been measured.

5 | DATA AND RESULTS

5.1 | Rainwater and throughfall

5.1.1 | Water isotopes

Cumulated rainfall $\delta^{18}\text{O}$ ranged within a large interval between 1‰ and -10‰ at a nearly decadal period

(Figure 2). The weighted average of the rainwater $\delta^{18}\text{O}$ was computed from the cumulated rain samples over the 2012–2014 period, and found to be $\delta^{18}\text{O} = -4.9\text{‰}$. There is a small seasonal trend as the 3-month weighted average for winter (December to February) is marked by a slight isotopic depletion of rainwater ($\delta^{18}\text{O} = -6.4\text{‰}$), compared to all other seasons (March to May, June to August and September to November with a mean $\delta^{18}\text{O}$ between -4.6‰ and -4.8‰). Moreover, all cumulative rainwater samples below -7‰ were collected between September and February.

At the event scale, rainfall isotopic composition was found to be relatively stable from one time step to another (time increments varying from 1 to 4 hr), but generally marked by clear depletions in heavy isotopes when rainfall intensified, in agreement with the amount effect. Rainfalls characterized by short-lived peaks of high intensity ($>10 \text{ mm hr}^{-1}$) came indeed with $\delta^{18}\text{O}$ depletions of a few ‰ units (Figure 3), although not systematically. When considering all the rainwater samples at the event scale, all extreme values ($\delta^{18}\text{O} > -3\text{‰}$ or $< -8\text{‰}$) corresponded to low or medium rainfall hourly amounts ($<15 \text{ mm hr}^{-1}$), whereas higher rainfall amounts exhibited reduced $\delta^{18}\text{O}$ variability, mainly between -5 and -9‰ (Figure 4). A similar behaviour is observed for deuterium excess d_{exc} , with values contained in the $+10\text{‰}$ to $+15\text{‰}$ range above

10 mm hr^{-1} , while the variability is wider for lower intensities, d_{exc} ranging between $+6.3\text{‰}$ and $+23.1\text{‰}$.

5.1.2 | Physico-chemical parameters, major and trace elements

All the chemical elements exhibited as expected low concentrations in comparison with those of the soil water, groundwater and streamwater. The mean concentrations were 0.64 mg/L for Ca, 0.03 mg/L for Si, $1.23 \text{ }\mu\text{g/L}$ for Sr, $2.42 \text{ }\mu\text{g/L}$ for Al etc..... (Table 3). EC ranged between 5 and $15 \text{ }\mu\text{S/cm}$. Throughfall showed however an increase of the chemical concentrations and a modification of the Ca/Sr and Ba/Sr ratios, in comparison with the rainwater directly collected in the gauges: the concentrations in the throughfall samples for Ca, Si, Sr, Al, Ba were five to 10 times higher than in the rainfall samples.

5.2 | Soil water

5.2.1 | Water isotopes

Figure 5 presents the time series of soil water $\delta^{18}\text{O}$ mean values for all the probes installed at 20 to 40 cm below the surface between September 2013 and December 2014. The soil water $\delta^{18}\text{O}$ mean values ranged between, -2 and -10

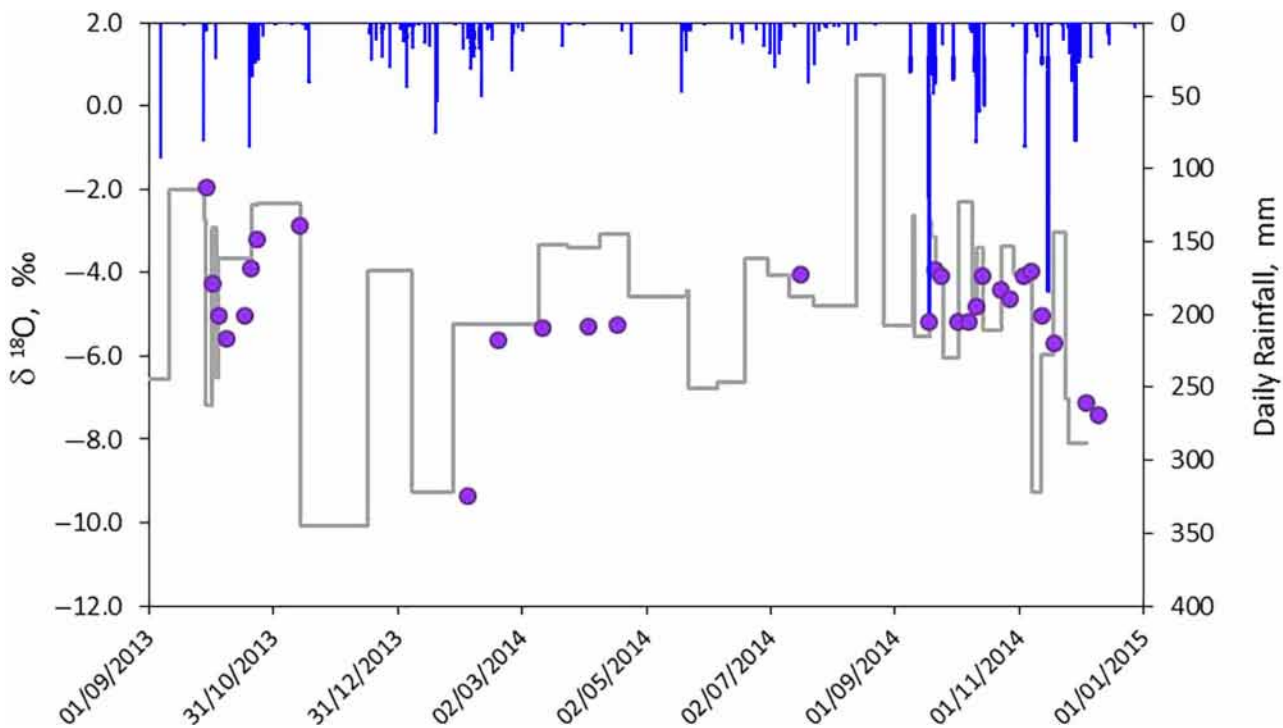


FIGURE 5 $\delta^{18}\text{O}$ temporal variability of soil water derived from Tensionic samples (Circles, mean $\delta^{18}\text{O}$ of the set of Tensionics). Grey line indicates $\delta^{18}\text{O}$ of the cumulated rainfall samples. Blue bars indicate daily rainfall amounts

TABLE 4 Results of soil leaching experiments

	Time (min)	Al ($\mu\text{g/L}$)	Si ($\mu\text{g/L}$)	Ca ($\mu\text{g/L}$)	Sr ($\mu\text{g/L}$)	Ba ($\mu\text{g/L}$)	Ca/Sr	Ba/Sr
Horizon A	7	323	290	1063	5.44	1.93	195	0.35
	25	388	430	1377	5.47	2.91	252	0.53
	63	422	390	4472	16.66	10.82	268	0.65
	126	537	450	1752	6.49	4.18	270	0.64
	242	591	400	1851	7.19	4.26	257	0.49
	429	653	350	5789	20.37	12.79	284	0.63
	1454	827	570	2632	10.24	5.01	257	0.49
Horizon S	7	152	10	317	2.34	1.10	135	0.47
	24	312	90	421	2.87	1.70	147	0.59
	65	419	160	363	2.59	1.42	140	0.55
	136	816	290	425	3.08	1.63	138	0.53
	263	688	240	422	2.91	1.79	145	0.61
	405	587	220	552	3.87	2.13	143	0.55
	1430	586	520	472	3.42	1.86	138	0.54
Horizon C	13	213	80	380	2.87	1.89	132	0.66
	43	219	100	358	2.75	2.05	130	0.75
	76	239	140	267	2.12	2.30	126	1.09
	110	248	120	304	2.34	2.42	130	1.03
	135	270	160	347	2.64	2.45	132	0.93
	252	241	160	296	2.26	2.38	131	1.06
	388	210	160	334	2.54	2.34	131	0.92
	1418	261	310	422	3.25	2.60	130	0.80

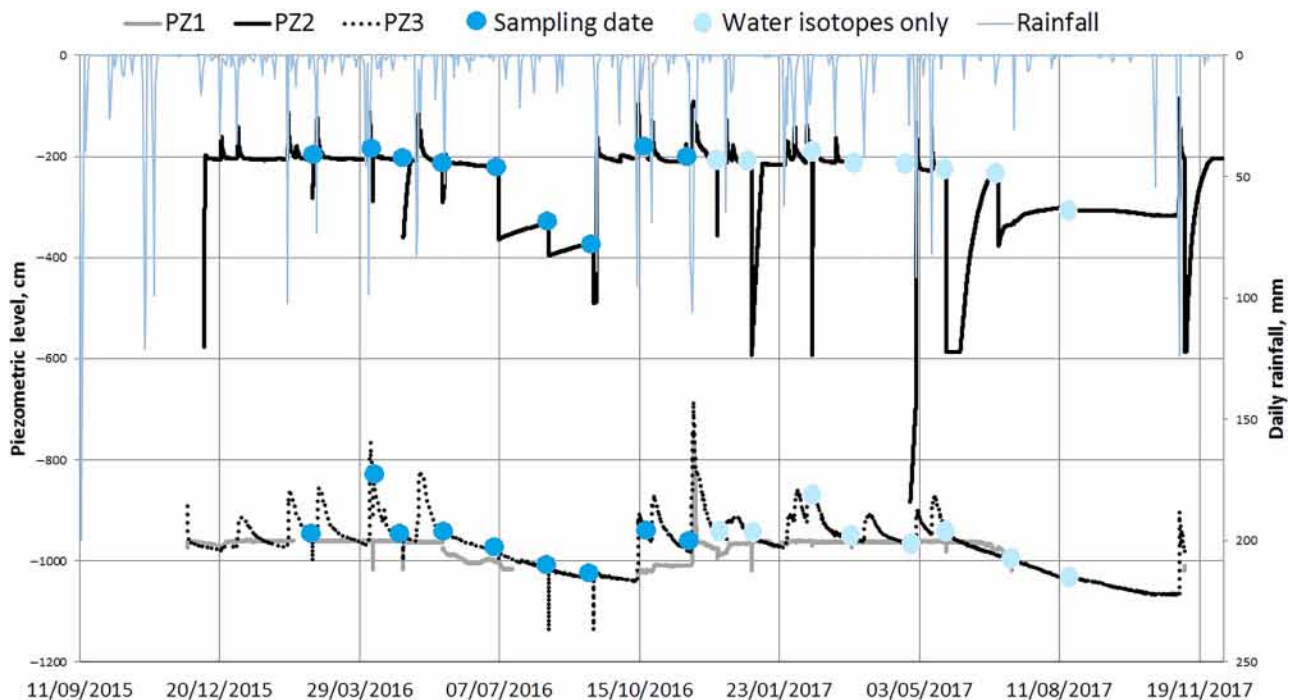
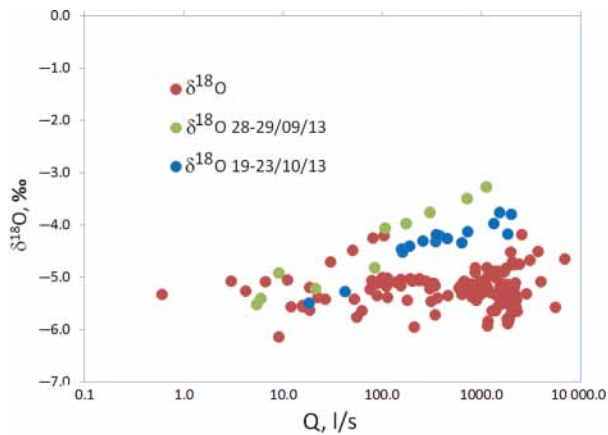


FIGURE 6 Variation of the piezometric levels in piezometers PZ1, PZ2 and PZ3 between November 2015 and November 2016. Blue circles highlight the sampling dates. Levels in PZ3 exhibit a slow recession, whereas levels in PZ2 show faster recession, 2–3 days after the rainfall. Transient level decreases correspond to pumping from the piezometers

TABLE 5 Physico-chemical parameters, major and trace elements in PZ3 piezometer

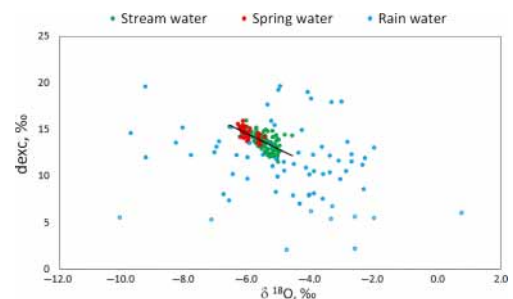
Name	Sampling date	Conductivity ($\mu\text{S}/\text{cm}^2$)	TOC (mg/L)	Cl (mg/L)	Al (Mg/L)	Si (mg/L)	Ca (mg/L)	Sr ($\mu\text{g}/\text{L}$)	Ba ($\mu\text{g}/\text{L}$)	Ca/Sr	Ba/Sr	$\delta^{18}\text{O}$ (%)
PZ3-1	24/02/2016	197	—	3.66	20.1	5.80	32.56	222	61.4	147	0.277	-5.62
PZ3-2	07/04/2016	88	0.76	4.60	2.10	5.09	8.07	35.2	13.2	229	0.376	-5.57
PZ3-3	29/04/2016	137	—	6.31	1.84	5.41	15.5	50.6	34.2	306	0.675	-5.58
PZ3-4	27/05/2016	138	3.63	7.26	19.5	5.61	17.0	59.9	313	284	0.572	-5.63
PZ3-5	06/07/2016	261	—	4.75	6.60	6.18	34.5	135	57.7	256	0.429	-5.62
PZ3-6	11/08/2016	230	3.12	3.82	4.71	6.18	30.8	108	58.5	285	0.542	-5.56
PZ3-7	12/09/2016	223	1.86	3.81	16.4	6.01	29.1	115	19.5	254	0.431	—
PZ3-8	20/10/2016	168	1.80	3.69	2.37	5.70	18.0	71.3	33.8	252	0.475	-5.51
PZ3-9	17/11/2016	187	0.630	4.03	10.0	6.29	23.1	70.8	41.3	326	0.583	-5.61
Mean value		181	1.97	4.66	9.32	5.81	23.2	96.3	42.7	260	0.484	-5.59
Standard deviation		54	1.21	1.29	7.60	0.40	9.1	57.2	15.7	52	0.122	0.04
												(1 σ)

**FIGURE 7** Relationship between streamwater $\delta^{18}\text{O}$ and streamwater discharge

‰ throughout the monitoring period. There is a strong general agreement between the soil water isotopic composition derived from the tension lysimeters and the isotopic signature of the previous rain events, suggesting that soil water may be largely controlled by rainwater on a short time scale, depending on the cumulated rain amount. Successive soil water samplings obtained during long relatively dry periods (especially during Spring 2014) showed that no significant modification in the isotopic soil water composition occurred, and that this compartment is therefore not measurably affected by evaporation.

5.2.2 | Physico-chemical parameters, major and trace elements

The dilution used for the leaching experiment (Table 4) implies that the absolute concentrations obtained are not representative of actual ones in the field. However, since a

**FIGURE 8** Relationship between deuterium excess (d_{exc}) and $\delta^{18}\text{O}$ for streamwaters (green dots), spring waters (red dots) and bi-monthly rainwaters (blue diamonds for $d_{\text{exc}} > +7\%$; grey diamonds for $d_{\text{exc}} < +7\%$). Black line is the linear regression line for streamwaters

standard operational method was used for all the samples, the ratios of the concentrations (between horizons as well as between elements) could be considered as realistic. Thus, it should be significant for example that (a) Ca and Sr concentrations are 3–6 times higher in horizon A than in horizons C and S, (b) Si and Ba concentrations are rather stable in the horizons A and C, and decrease in horizon S, and (c) Al concentrations are lower in horizon C compared to horizons A and S. In addition, the Ca/Sr ratios observed for leaching experiments were consistent with those measured in the field with the PTF cups, although the Ca/Sr of the PTF cups (167-216) are closer to those of horizon A (195-257) than those of horizon S (135-147), as expected.

5.3 | Groundwater

Piezometers PZ2 and PZ3 showed ephemeral rises during or after the rainfalls (Figure 6), whereas PZ1 was not

sensitive to the rainfalls and remained at the same water level, around 10 m deep. Both PZ1 and PZ2 exhibited anomalous chemical values, probably due to the addition of chemical products during the installation of the piezometers, which were not flushed away in PZ1 and PZ2. The very low renewal rate in PZ1 seems consistent with the observation that it does not respond hydraulically to the rainfalls, while for PZ2 the deepest part of the piezometer was dug in an unfractured rock. Chemical tracers (fluorescein and sulforhodamine B) were injected in the 3 piezometers after November 17, 2016 to study the groundwater transfer between the piezometers and the stream, and modified artificially the concentrations of most of the chemical elements; the subsequent results were thus not reported in the data base. However, the stable water

isotopes were not affected by the tracers during the period between December 09, 2016 and August 17, 2017 (eight samples). As a consequence, physico-chemical parameters (EC, TOC, major and trace element concentrations) are only presented for piezometer PZ3 until November 17, 2016 (Table 5).

5.3.1 | Water isotopes

Water isotopes exhibited very stable values throughout the year of observation in PZ3 ($\delta^{18}\text{O} = -5.59 \pm 0.04\text{‰}$) even for the 07/04/16 sample when other chemical elements revealed a mix of groundwater with rainfall and/or shallow soil water. PZ1 was found to be very stable as well, although somewhat more depleted ($\delta^{18}\text{O} = -5.93 \pm$

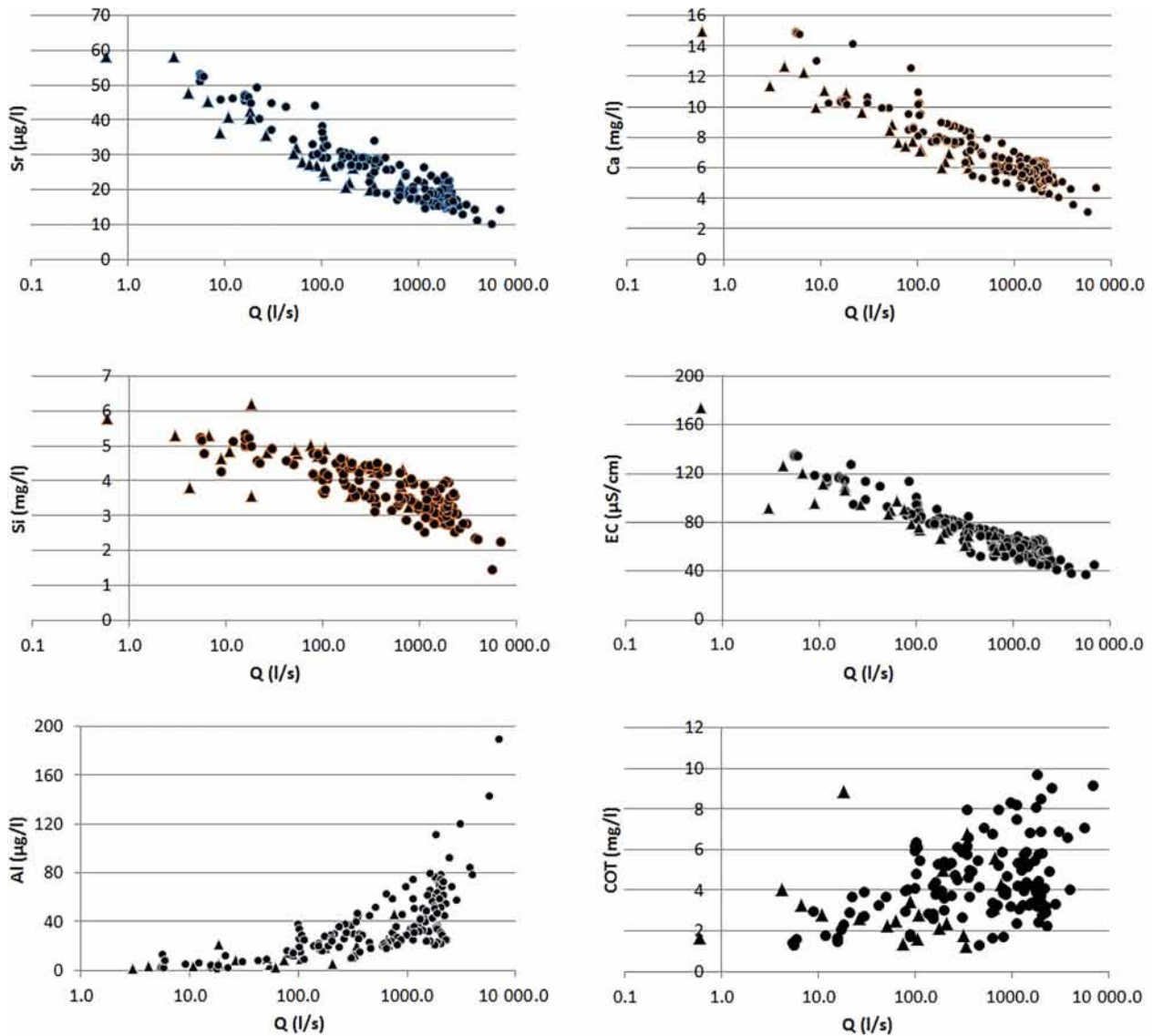


FIGURE 9 Relationship between concentration and streamwater discharge at Downstream Valescure station. Triangles denote low-flow manual sampling and circles flood automatic sampling

0.03‰), whereas PZ2 revealed more variability ($\delta^{18}\text{O} = -5.92 \pm 0.22\text{‰}$), possibly due to the proximity of the stream.

5.3.2 | Physico-chemical parameters, major and trace elements

Chemical elemental concentrations appeared to be linked to the piezometer level. Ca, Ba, Sr and EC were clearly diluted on the 07/04/16 (PZ3-1: Ca concentration decreased to 7 mg/L, Sr to 35 $\mu\text{g/L}$, Si to 5.1 mg/L and EC value to 88 $\mu\text{S/cm}$), which may indicate an active mixing of the groundwater with rainwater or soil water from the upper layers, a few days after the flood. At the opposite, the samples PZ3-5 to PZ3-7 associated to the lowest piezometric levels during the dry season (e.g. PZ3-6: Ca concentration increased to 31 mg/L, Sr to 108 $\mu\text{g/L}$, Si to 6.2 mg/L and EC value to 230 $\mu\text{S/cm}$) exhibited high mineralization. Al concentration was much lower at 8-10 m depth ($<20 \mu\text{g/L}$) than in 0-40 cm deep soil water ($>450 \mu\text{g/L}$), for any moisture conditions.

5.4 | Streamwater

5.4.1 | Water isotopes

The $\delta^{18}\text{O}$ throughout the basin varied within a limited range during low flows ($Q < 20 \text{ L/s}$), typically between -5.0 and -6.3‰ (Figure 7). During floods, $\delta^{18}\text{O}$ exhibited either low or high variability, depending on the $\delta^{18}\text{O}$ signature of the rainfall, the shallow soil water and the pre-event streamwater. Finally, only two floods, in 2013, exhibited a significant variation in $\delta^{18}\text{O}$ during the flood peak: September 28–29, 2013 and October 19–23, 2013. The isotopic variation of streamwater at Downstream Valescure during the latter event is presented in Figure 3.

Figure 8 presents the correlation between d_{exc} and $\delta^{18}\text{O}$ for bi-monthly rainwaters, streamwaters and springwaters during the 3 years of survey. The negative correlation for streamwaters, materialized by the black line (square regression line) is indicative of a seasonal limited but measurable evaporation effect, consistently with the reduced velocity of the low-flow transfers during the dry summer conditions.

5.4.2 | Physico-chemical parameters, major and trace elements

Figure 9 shows EC and elemental concentrations at the Downstream Valescure station as a function of discharge, during regular sampling as well as during floods. The concentrations are clearly correlated to the streamwater discharge. EC, Ca, Sr and Si concentrations decrease when

TABLE 6 Low-flow water compositions (mean value and standard deviation)

Station	EC ($\mu\text{S/cm}$)	TOC (mg/L)	Al ($\mu\text{g/L}$)	Si (mg/L)	Ca (mg/L)	Sr ($\mu\text{g/L}$)	Ba ($\mu\text{g/L}$)	Ca/Sr	Ba/Sr	$\delta^{18}\text{O}$ (‰)
Upstream Valescure	157.6 ± 20.8	3.4 ± 2.0	3.2 ± 2.3	5.4 ± 0.8	18.4 ± 2.4	55.0 ± 5.0	26.5 ± 3.0	335 ± 22	0.483 ± 0.042	-5.68 ± 0.22
Cartaou	104.3 ± 6.8	1.9 ± 0.4	2.1 ± 0.4	5.7 ± 1.0	10.1 ± 1.0	46.9 ± 3.3	9.1 ± 0.9	216 ± 15	0.193 ± 0.010	-5.88 ± 0.14
Source Chateau	83.7 ± 1.2	3.1 ± 2.3	2.7 ± 1.6	8.8 ± 1.0	6.9 ± 0.3	53.5 ± 2.1	4.5 ± 0.2	130 ± 3	0.083 ± 0.003	-6.19 ± 0.04
Downstream Valescure	122.7 ± 31.2	2.8 ± 1.2	3.8 ± 1.6	5.2 ± 0.9	12.2 ± 1.7	49.5 ± 8.3	14.6 ± 2.4	266 ± 10	0.294 ± 0.008	-5.26 ± 0.24
Bastide	109.2 ± 24.7	4.4	7.8 ± 1.7	6.2 ± 0.9	8.3 ± 0.8	37.9 ± 2.3	11.8 ± 0.7	220 ± 12	0.311 ± 0.009	-5.76 ± 0.33

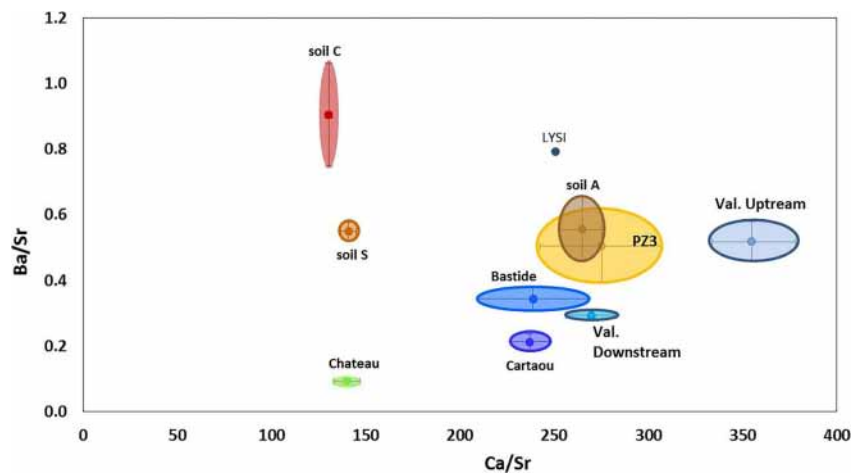


FIGURE 10 Ba/Sr vs Ca/Sr for streamwaters, soils A, C, S, PZ1 and PZ3 piezometers during low flow. The ellipse were drawn from the standard deviations of n measurements of the Ba/Sr and Ca/Sr ratios ($n = 5$ for Upstream and Downstream Valescure, Bastide, Cartau and Source Chateau, cf. Table 6; $n = 7$ for soil A and soil S, cf. Table 4; $n = 8$ for soil C; $n = 9$ for PZ1 and PZ3)

the discharge increases, because of dilution by the rainwater, whereas Al and TOC concentrations increase because of enrichment processes during water transfers at the interface between or within compartments.

5.4.3 | Spatial variability

Sampling at the outlet of different sub-catchments across the Valescure catchment and at the main spring gave an overview of the spatial variability of the physico-chemical parameters in smaller units. The physico-chemical properties of the lowest flows have been averaged over five sampling campaigns (October 2011, August 2012, July 2013 and two in September 2014) and reported in Table 6 for each station as low-flow water compositions (EC, TOC, Al, Si, Ca, Sr and Ba, elemental ratio signatures (Ca/Sr and Ba/Sr) and $\delta^{18}\text{O}$).

From a spatial point of view, streamwater isotopic composition was relatively uniform throughout the basin. The isotopic values of upstream and downstream Valescure stations were generally very close to one another ($\delta^{18}\text{O}$ within $\pm 0.2\text{‰}$), except at the end of the dry season, where a discrepancy of up to 0.7‰ was observed. Streamwater at the downstream station was then enriched with respect to the upstream station, and this was accompanied by a lower deuterium excess value ($\text{dex} = \delta\text{D} - 8 \cdot \delta^{18}\text{O}$) by 2 to 3‰ , indicating a notable evaporation effect. Indeed, during extreme low flows, ponds were forming in the river bed where the flow was much reduced, extending the time of the transfer towards the outlet of the catchment. Other stations generally had intermediate $\delta^{18}\text{O}$ values, whereas Source Chateau constantly exhibited more depleted values, consistently with values found in the piezometers.

For most of the chemical elements, the concentrations or elemental ratios at downstream Valescure seemed consistent with a mix of Cartau, Bastide and upstream

Valescure contributions in roughly equivalent proportions to the total discharge at downstream Valescure (about 20% each, whereas the contribution of source Chateau was negligible). An example is given for Ca/Sr and Ba/Sr ratios (Figure 10). This was also true for EC, TOC, Al, Ca, Ba, Sr, but not so for Si. In this latter case, the downstream part of the catchment (contributing the remaining 40% of the total discharge) could exhibit significantly lower values in Si concentrations than the other sub-catchments, possibly because of a different lithology—orthogneiss and schists—characterizing this part of the catchment. Note that the extreme (minimum and maximum) values were associated to Source Chateau and upstream Valescure respectively for EC, Ca, Si, Ba, Ca/Sr, Ba/Sr and to Cartau and Bastide for TOC and Al.

6 | CONCLUSION

The 3-year Floodscale geochemical campaigns at the Valescure catchment gave information about the temporal and spatial variability of a complete set of physico-chemical parameters, major and trace elements, total organic carbon and stable water isotopes in rainfall, soil and groundwater and streamwater. The campaigns included periodic low-flow samplings at five sites within the catchment all year round, as well as high-frequency flood samplings during the fall of years 2012, 2013 and 2014. This constitutes at present the most complete hydrogeochemical database in the Cévennes area, available from the Hymex data base as Valescure chemistry and water isotopes⁴. All these data are expected to help a lot in identifying surface, shallow sub-surface and groundwater contributions to flood hydrographs or performing hydrological rainfall-runoff models in a multi-objective framework.

⁴https://mistrals.sedoo.fr/?editDatsId=1406&datsId=1406&project_name=HyMeX&q=chemistry

ACKNOWLEDGEMENTS

This work was funded by the Agence Nationale de la Recherche (ANR) FloodScale project under contract ANR-2011-BSS6-027, by French National Observation Network “Réseau des Bassins Versants” (RBV) and by French HydroMeteorological Observatory Cévennes-Vivarais (OHM-CV). The Hymex/Mistrals program has also funded a 6-month grant for Aurore Remes. The authors greatly thank: Jean-François Didon-Lescot, Jean-Marc Domergue and Nadine Grard (UMR 7300 ESPACE) for their valuable help in collecting the samples, contributing to the field experiments, and supplying the hydrological data; Sandra Van-Exter for participating to the chemical analysis.

OPEN PRACTICES

This article has earned an Open Data badge for making publicly available the digitally-shareable data necessary to reproduce the reported results. The data is available at DOI 10.6096/MISTRALS-HyMeX.1406 57. Learn more about the Open Practices badges from the Center for Open Science: <https://osf.io/tvyxz/wiki>.

ORCID

Christophe Bouvier  <http://orcid.org/0000-0001-7098-1076>

Jean-Luc Seidel  <http://orcid.org/0000-0003-2940-8838>

Jean-Denis Taupin  <http://orcid.org/0000-0003-3429-7239>

REFERENCES

- Bouvier, C. and Brunet, P. (2016) Cévennes soil moisture measurements. *SEDOO OMP*, <https://doi.org/10.6096/mistrals-hymex.1423>.
- Bouvier, P.A., Ayrál, P., Brunet, A., Crespy, A. and Marchandise, C.M. (2007) Proceedings of the 1st International Workshop on Hydrological Extremes, FRIEND-AMHYCosenza; Italy, May 3–4, 2006, 229–238.
- Braud, I., Ayrál, P.A., Bouvier, C., Branger, F., Delrieu, G., Le Coz, J. *et al.* (2014) Multi-scale hydrometeorological observation and modelling for flash flood understanding. *Hydrology and Earth System Sciences*, *18*, 3733–3761. <https://doi.org/10.5194/hess-18-3733-2014>.
- Delrieu, G., Ducrocq, V., Gaume, E., Nicol, J., Payrastre, O., Yates, E. *et al.* (2005) The catastrophic flash-flood event of 8–9 September 2002 in the Gard region, France: a first case study for the Cévennes-Vivarais Mediterranean Hydro-meteorological Observatory. *Journal of Hydrometeorology*, *6*, 34–52.
- Ducrocq, V., Braud, I., Davolio, S., Ferretti, R., Flamant, C., Jansa, A. *et al.* (2014) HyMeX-SOP1: The field campaign dedicated to heavy precipitation and flash flooding in the northwestern Mediterranean. *Bulletin of the American Meteorological Society*, *95*, 1083–1100. <https://doi.org/10.1175/BAMS-D-12-00244.1>.

- Durand, P., Neal, C. and Lelong, F. (1992) Anthropogenic and natural contributions to the rainfall chemistry of a mountainous area in the Cévennes National Park (Mont-Lozere, southern France). *Journal of Hydrology*, *130*, 71–85. [https://doi.org/10.1016/0022-1694\(92\)90104-4](https://doi.org/10.1016/0022-1694(92)90104-4).
- FAO-WRB. (2014) World Reference Base for Soil Resources. World Soil Resources Reports 106, Food and Agriculture Organization of the United Nations, 143 p.
- Loÿe-Pilot, M.D. and Jusserand, C. (1990) Décomposition chimique et isotopique d'un hydrogramme de crue d'un torrent méditerranéen – réflexions méthodologiques. *Revue des Sciences de l'Eau*, *3*, 211–231.
- Marc, V., Didon-Lescot, J. F. and Michael, C. (2001) Investigation of the hydrological processes using chemical and isotopic tracers in a small Mediterranean forested catchment during autumn recharge. *Journal of Hydrology*, *247*, 215–229. [https://doi.org/10.1016/S0022-1694\(01\)00386-9](https://doi.org/10.1016/S0022-1694(01)00386-9)
- Marc, V., Travi, Y. and Lavabre, J. (1995) Etude du fonctionnement hydrologique de bassins versants méditerranéens par le traçage naturel chimique et isotopique. Tracer Technologies for Hydrological Systems (Proceedings of a Boulder Symposium, July 1995). IAHS Publ., no, 229, pp. 219–229.
- Moussa, R., Chahinian, N. and Bocquillon, C. (2007) Distributed hydrological modelling of a Mediterranean mountainous catchment - Model construction and multi-site validation. *Journal of Hydrology*, *337*, 35–51. <https://doi.org/10.1016/j.jhydrol.2007.01.028>.
- Rocha, L., Rodrigues, S.M., Lopes, I., Soares, A.M.V.M., Duarte, A.C. and Pereira, E. (2010) The water-soluble fraction of potentially toxic elements in contaminated soils: Relationships between ecotoxicity, solubility and geochemical reactivity. *Chemosphere*, *84*, 1495–1505.
- Rodrigues, S.M., Henriques, B., Coimbra, J., Ferreira da Silva, E., Pereira, M.E. and Duarte, A.C. (2010) Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. *Chemosphere*, *78*, 1301–1312. <https://doi.org/10.1016/j.chemosphere.2010.01.012>.
- Roux, H., Labat, L., Garambois, P.-A., Maubourguet, M.-M., Chorda, J. and Dartus, D. (2011) A physically-based parsimonious hydrological model for flash floods in Mediterranean catchments. *Natural Hazards & Earth System Sciences*, *11*, 2567–2582. <https://doi.org/10.5194/nhess-11-2567-2011>.
- Travi, Y., Lavabre, J., Blavoux, B. and Martin, C. (1994) Traçage chimique et isotopique (Cl, ¹⁸O) d'une crue d'automne sur un petit bassin versant méditerranéen incendié. *Hydrological Sciences Journal*, *39*, 605–619.
- Zhao, P., Tang, X., Zhao, P., Wang, C. and Tang, J. (2013) Identifying the water source for subsurface flow with deuterium and oxygen-18 isotopes of soil water collected from tension lysimeters. *Journal of Hydrology*, *503*, 1–10.

How to cite this article: Bouvier C, Patris N, Freydier R, et al. The Floodscale experiment in the small catchment of Valescure, France: An overview of the isotopic and geochemical data base. *Geosci. Data J.* 2018;5:14–27. <https://doi.org/10.1002/gdj3.57>