A conceptual model for groundwater circulation using isotopes and geochemical tracers coupled with hydrodynamics: A case study of the Lez karst system, France

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Abstract

Geochemical and isotopic tracers ($\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$ and $\delta^{13}C_{TDIC}$) were used to constrain origins and chemical evolution of groundwater in a Mediterranean karst system. The Lez spring is the main perennial outlet of this karst system and supplies the metropolitan area of Montpellier (southern France) with drinking water. Groundwater samples were collected at the Lez spring and surrounding springs and wells under different hydrodynamic conditions during two hydrological years, from June 2008 until May 2010. The results show that multiple hydrological compartments interact through an important network of fractures and faults. They notably reveal connections between the main Jurassic limestone aquifer and the overlying Cretaceous (Valanginian) compartment, and between the surface and deep levels of the karst system. Isotopic tracers provided information about atmospheric recharge origins, lithological signatures and chemical evolution of waters.Long residence-time groundwaters, issued from deep layers have a Triassic hydrochemical fingerprinting, being enriched in $\delta^{13}C_{TDIC}$ and characterized by high concentrations in Cl^- as well as high Sr/Ca, Mg/Ca and $^{87}Sr/^{86}Sr$ ratios. Evidences suggest that these waters mix with waters from the lower layers of the main Jurassic aquifer constitute an intermediate storage compartment prone to rise through piston-flow mechanism. A two-end member hydrograph separation based on EC-TDS was used to determine the proportion of the deep compartment's contribution to the Lez spring outflow. On average over the study period, the main aquifer compartment and the deep aquifer compartment are estimated to contribute 92.6% and 7.4 % of groundwater flow at the Lez spring, respectively.

Key words: hydrogeology, karst, hydrochemistry, natural tracing, isotopes, hydrograph separation

1 - Introduction

Investigations on karst systems aim at establishing water origins (Bouchaou, Michelot, Qurtobi, Zine, Gaye, Aggarwal, Marah, Zerouali, Taleb and Vengosh, 2009; Desmarais and Rojstaczer, 2002; Wong, Mahler, Musgrove and Banner, 2012), evaluating quantitatively and qualitatively water resources and understanding karsts vulnerability to contamination (Charlier, Bertrand and Mudry, 2012; Massei, Mahler, Bakalowicz, Fournier and Dupont, 2007; Mendizabal and Stuyfzand, 2010). Geochemical and isotopic properties of groundwaters in karst systems reveal water-rock interactions and water mixing processes, occurring along flowpaths in the aquifer (Barbieri, Boschetti, Petitta and Tallini, 2005; Celle-Jeanton, Travi and Blavoux, 2001; Frondini, 2008; Millot, Petelet-Giraud, Guerrot and Négrel, 2010) and give information about transit time and origin of groundwater flow. The monitoring of physicochemical and chemical parameters provides insightful information about the reactivity and vulnerability of the aquifer to pollution and transfer processes. Temporal variations observed in groundwater chemistry are usually related to the physical characteristics and carbonate permeability of the aquifer, and help to identify hydrodynamic behaviour (Geyer, Birk, Liedl and Sauter, 2008; Kilroy and Coxon, 2005; Wittenberg, Kutiel, Greenbaum and Inbar, 2007). Coupling hydrodynamics and hydrochemistry by using mixing equations allows assessing solute transport for conservative compounds (Aquilina, Ladouche and Dörfliger, 2006; Batiot, 2002; Beven, 2001; Drever, 1982; Emblanch, Zuppi, Mudry, Blavoux and Batiot, 2003; Garry, 2007; Hartmann, Weiler, Wagener, Lange, Kralik, Humer, Mizyed, Rimmer, Barberá, Andreo, Butscher and Huggenberger, 2013; Katz, Catches, Bullen and Michel, 1998; Ladouche, Probst, Viville, Idir, Baqué, Loubet, Probst and Bariac, 2001; Long and Putnam, 2004; Petelet-Giraud and Negrel, 2007; Ribolzi, Moussa, Gaudu, Vallès and Voltz, 1997; Wang, Guo, Su and Ma, 2006). This approach is often used to assess the multiple end-members participation in water flow by using natural tracers. Mixing models based on mass conservation describe water contributions using isotopic or chemical tracers from rainwater, pre-event water and flow hydrograph.

The Lez Spring, one of the major karst springs in France, supplies water to the metropolitan area of Montpellier, France, since the 19^{th} century. Former studies have shown this karst system to be a complex and heterogeneous system in terms of structure and functioning (Fleury, Ladouche, Conroux, Jourde and Dörfliger, 2009; Joseph, Rodier, Soulte, Sinegre, Baylet and Deltour, 1988; Karam, 1989; Marjolet and Salado, 1976; Thierry and Bérard, 1983). Since 2008, the Lez Spring has been continuously monitored. Recent observations showed that the Lez spring flow can be described with different water types resulting from a mixing of various end-members: recently infiltrated waters; main aquifer compartment (mainly Jurassic limestone), and a deep aquifer compartment (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012). According to hydrological conditions, each compartment contributes in various proportions to the Lez spring flow. In particular, (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012) showed that waters with high TDS (Total Dissolved Solids) flow as a response to extreme hydrological conditions in relationship with intense rainfall over the watershed. This phenomenon has often been observed and reported by several works undertaken on karst terrains (Blavoux, Gilli and Rousset, 2004; Desmarais and Rojstaczer, 2002; Emblanch, Blavoux, Puig and Couren, 1998; Grobe and Machel, 2002; López-Chicano, Bouamama, Vallejos and Pulido-Bosch, 2001; Rosenthal, Zilberbrand and Livshitz, 2007). The deep karstification observed in some Mediterranean karst systems (e.g. the Lez and the Vaucluse karst systems) is generally put forth to explain the existence of long residence-time and relatively high TDS concentration waters flowing at the springs, especially after intense rainfalls. This specificity adds more complexity to karst systems situated in this context whereas other karst systems, that did not undergo a deep karstification process, are commonly crossed by waters in a rapid flow, i.e. with low residence times.

The present paper aims to i) understand the behaviour of the whole karst system together with the functioning of the various springs by using supplementary tracers, such as stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$), strontium isotopes ($^{87}Sr/^{86}Sr$) and Total Dissolved Inorganic Carbon isotopic composition ($\delta^{13}C_{TDIC}$), ii) assess both the origin and dynamics of groundwater within the different compartments of the system, iii) deepen the comprehension of groundwaters chemical evolution over the hydrological cycle, and iv) accomplish a preliminary hydrograph separation in order to estimate the proportions of deep water outflowing at the Lez spring.

2 - Study Area

2.1 - Geology

The Lez Spring (43.718°N, 3.844°E), located 15 km north of Montpellier and 28 km from the Mediterranean Sea, is the main perennial outlet of the Lez karst system, with maximum groundwater discharge around 15 m^3/s, and a mean annual discharge of 2.0 m^3/s (1963-2008, (Jourde, Batiot-Guilhe, Bailly-Comte, Bicalho, Blanc, Borrell, Bouvier, Boyer, Brunet, Cousteau, Dieulin, Gayrard, Guinot, Hernandez, Kong, Siou, Johannet, Leonardi, Mazzilli, Marchand, Patris, Pistre, Seidel, Taupin and Van-

Exter, 2011)). The Lez karst system also discharges at intermittent springs (Lirou, Restinclières, Fleurettes, and Gour Noir springs) (Fig. 1). Restinclières, Fleurettes and Gour Noir used to be perennial springs before 1962, when pumping within the Lez spring started to supply Montpellier and its metropolitan region with drinking water. The hydrogeological basin of the Lez spring is located between the Hérault and Vidourle river valleys and covers about 380 km^2 (Thierry and Bérard, 1983), while the recharge catchment through the Jurassic limestone outcrops located by the western and north-eastern limits of the basin is only about 188 km^2 (Leonardi, Jourde, Dausse, N.Dörfliger, Brunet and Maréchal, 2013). Indeed, most of the hydrogeological basin is confined by low-permeability aquitards (Marjolet and Salado, 1976). Local recharge also occurs through fractures and sinkholes within the basin, especially through the major fault of *Corconne-Les Matelles* (Fig. 1) located in the northern part of the basin (Dubois, 1964).

The lithology of the Lez karst system corresponds to massive limestone of the Upper Jurassic (Kimmeridgian) and Early Cretaceous (Beriasian) with a 650 to 1100 m thickness (Fig. 2). The marls and marly-limestones of the Middle Jurassic (Callovidian-Oxfordian) constitute the lower boundary of the aquifer. The marls and marly-limestones of the Early Cretaceous (Lower Valanginian) constitute the upper boundary of the aquifer, causing low permeability and a partly confined system. The major tectonic events that influenced the Lez aquifer were the Hercynian/Variscan orogeny, the Pyrenees formation, and the opening of the Lion Gulf (Bousquet, 1997).

A perched aquifer located within the Upper Valanginian layer (Fig. 2,) overlies the Lez aquifer (Pane-Escribe, 1995). The communication of this perched aquifer with the Jurassic layer is very limited due to the low permeability of the marls that compose it. However, point-source infiltration occurs from the Valanginian aquifer towards the Lez aquifer (Boinet, 2002). Indeed, groundwater outflowing from springs that drain the Valanginian aquifer (Lauret, Dolgue, and Lavabre springs) locally recharge the Lez karst system along the *Corconne-Les Matelles* fault (Boinet, 2002).

The Lez karst system was described by Avias (1992) as a Vaucluse-type system deeply developed below the present-day spring level. This results from an intense karstification (i.e. conduit enlargement caused by low-acidified water weathering over limestones) that reached several hundred meters during the Messinian Salinity Crisis- from 5.96 to 5.33 Ma (Celle-Jeanton, Travi and Blavoux, 2001; Cita and Ryan, 1978; Clauzon, 1982; Joseph, Rodier, Soulte, Sinegre, Baylet and Deltour, 1988; Ryan, 1976). The karstification network is mainly oriented along NS and EW directions in zones where tectonic deformation is weak and NE-SW near major tectonic changes (Leonardi, Jourde, Dausse, N.Dörfliger, Brunet and Maréchal, 2013). The Lez system is highly karstified, but the presence of impermeable Pliocene marine and continental sediments preserved it from seawater contamination (Bakalowicz, 2005; Fleury, 2005; Fleury, Bakalowicz and de Marsily, 2007).

2.2 - Rainfall

The precipitation data used in this study come from three Méteo France meteorological stations, (Valflaunès, Saint-Martin-de-Londres, and Prades) all at a distance lower than 12km from the Lez spring (Fig. 1). The hydrological year begins in September, after 2 to 3 months of relative dryness. The wet season (high stage) lasts from September to May and the dry season (low stage) from June to August. Over the last 40 years, the average annual rainfall calculated at the Valflaunes station was 942 mm with a minimum of 474 mm (year 1985) and a maximum value of 1,620 mm (year 1972). During the study period, the annual rainfalls were 849 mm for 2007-2008, 1,266 mm for 2008-2009 and 666 mm for 2009-2010. For the 1970-2010 period, the intra-annual rainfall distribution was: 37% in autumn, 27% in winter, 22% in spring, and 13% in summer.

3 - Materials and Methods

3.1 - Continuous monitoring and sampling

Samples were collected at the Lez spring for chemical and isotopic analysis twice a month, with daily sampling during high discharge events from June 2008 to May 2010. At Lirou, Restinclières, and Fleurettes springs, sampling was carried out during the wet season only, from September to May. An automatic sampler with 24 bottles (1l acid-cleaned polyethylene bottles) was used for water sampling at the Lez spring during high flows.

Additional samples were collected during low stage period from: 1) adjacent systems that are potentially connected to the Lez karst system, including Fontbonne and Sauve springs (Fig. 1), Valanginian springs and wells, including Boinet, Olivier, and Lavabre wells but also Lauret, Lavabre, and Dolgue springs, and 3) wells within the Lez spring hydrogeological basin (referred to as Lez KS wells): Fontanes, Laudou, Bois des Roziers, and Gour Noir (Fig. 1).

Temperature (T), pH, and Electrical Conductivity (EC T_{ref}=25°C) were measured in the field using a pH meter and conductivity meter (WTW 330 i) on each sample. Continuous data were obtained from automatic measurement. Temperature, turbidity, EC, and Groundwater Level (GW level) were measured at an hourly time step at the Lez Spring with an automatic data logger (CTD diver, SDEC) and hereafter referred to as Lez Well. Temperature, EC, and groundwater level measurements were performed at an hourly time step at the Lez Spring spillway and Lirou Spring (CTD diver, SDEC).

Rain waters were regularly sampled (monthly to bi-monthly) for water isotopes analysis from an underground tank connected to raingauges at Viols-le-Fort and Sauteyrargues stations (Fig. 1) between May 2009 and May 2010. To complete the lack of rainwater isotopic data at the beginning of the study period, the monthly average rainfall isotopic composition at the Montpellier raingauge, located 9 km downstream the Lez spring and sampled daily over the whole study period, was used as a reference for the input signal. The interpretation took into account the limitations related to the observed differences in the rainfall isotopic composition between Montpellier and the karst system recharge area.

49 samples were collected for $\delta^{13}C_{TDIC}$ measurement on dissolved carbonate at the following springs: 32 at the Lez spring, 8 at the Lirou spring, 6 at the Restinclières spring and 3 at Fleurettes spring. Water samples were collected in glass bottles and quickly sealed on the field with gas tight rubber/teflon plugs. Three $\delta^{13}C_{CO2}$ measurements from soil covers were carried out in April 2010 over the Lez spring catchment in order to characterize the main vegetal and pedogenic covers: (1) vineyards developed on Quaternary deposits (2) scrublands over Jurassic limestones and (3) olive grove developed on Tertiary deposits.

3.2- Analytical methods

Total alkalinity was measured at HydroSciences Montpellier (HSM) laboratory, by acid titration with HCl 0,01N. Major ions (Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and K^+) were analysed by ionic chromatography (DIONEX ICS 1000) on filtered samples (0.22µm) with an analytical accuracy of 5%, after an acidification with 1‰ suprapur HNO_3 for cations. Trace elements (Li, B, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Ba, Pb, and U) were analysed using Q-ICPMS X series II Thermo Fisher at the AETE (Analyse des Eléments en Trace dans l'Environnement) technical platform of University of Montpellier on filtered and acidified samples (0.22µm, 1‰ suprapur HNO_3), with a greater than 8% accuracy. Samples with ion balance error greater than 5% were excluded from the dataset. Samples for Total Organic Carbon (TOC) were collected in dark glass bottles previously combusted for 6 h at 550°C, acidified with 1‰ H_3PO_4 and analyzed with catalytically aided platinum 680 °C combustion technique (Shimadzu VCSH).

Isotopic compositions of water carbonate $\delta^{13}C_{TDIC}$ and soil $\delta^{13}C_{CO2}$ samples were analysed at *Université d'Avignon et des Pays de Vaucluse* (UAPV) Hydrogeology Laboratory on a Finnigan Mat Delta S mass spectrometer after acid digestion of the dry precipitate of carbonate. Isotopic carbonate values are reported relative to the V-PDB scale, with an overall uncertainty of ±0.05‰.

Water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) were analysed at the LAMA mass spectrometry laboratory of HSM on an Isoprime mass spectrometer. $\delta^{18}O$ was measured with the classical CO_2 equilibration method, with an overall uncertainty of ±0.1‰. δD was measured in continuous-flow mode with a Eurovector Pyr-OH analyser converting H_2O to H_2 on Cr at 1070°C, with an overall uncertainty of ±0.8‰. All isotopic water values are reported in this paper relative to the V-SMOW scale.

Strontium isotopic composition was measured on 16 samples collected across the whole system. $^{87}Sr/^{86}Sr$ ratios were measured at the Rennes University using the Faraday cups of a five-collector Finnigan MAT 262 mass spectrometer. Sr^{2+} was separated using a cation exchange column (Dowex AG50X8) with HCl_2N as eluent. All measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr$=0.1194. Initial $^{87}Sr/^{86}Sr$ ratios were calculated using $^{87}Rb/^{86}Sr$ ratios as determined by the isotope dilution method (Petelet, Luck, Ben Othman, Negrel and Aquilina, 1998). High-precision ^{84}Sr and ^{87}Rb spikes gave maximum errors of 2%.

4 - Results and Discussion

The Lez spring flow is composed of different water types resulting from a mixing of various hydrologic end-members. These water types were described by Caetano Bicalho et al. (2012) using a specific terminology that is applied in the present text and graphs: 1) "High waters" discharge during high water stages and are associated with high groundwater levels and EC oscillations; 2) "Low waters" discharge during low stage periods and are associated with low groundwater levels and high, stable EC; 3) "Dropping waters" discharge during the transition between the high and low stages and are associated with a decrease in groundwater level and an increase in EC. Extreme values of high or low EC were respectively referred to as

4)"Piston-flow waters" (EC>780 µS/cm) and 5)"Dilution waters" (EC< 600 µS/cm) (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012).

4.1 - Hydrochemistry and water isotopes

The complete dataset collected from the karst springs is presented in Table 1 and Table 2. Table 3 presents the average values and range of variations for the dataset.

EC indicates generally higher TDS in groundwater at the Lez spring than at other springs: the mean EC measured during both the fall and spring seasons was 711 $\mu S.cm^{-1}$ at Lez spring, 661 $\mu S.cm^{-1}$ at Restinclières spring, 655 $\mu S.cm^{-1}$ at Fleurettes spring and 581 $\mu S.cm^{-1}$ at Lirou spring. During the same period, Restinclières and Fleurettes springs generally presented higher values of temperature than the Lez spring (average temperatures of 17.0, 16.0 and 15.7°C, respectively) (Table 2). Restinclières and Fleurettes springs had a very similar geochemistry mostly associated with the presence of limestones (Chamayou and Auroux, 1992). Lirou waters had the lowest TDS (516 $mg.l^{-1}$ in average) and temperature (mean value of 14.3°C), which indicates a large participation of recent infiltration waters, suggesting rapid groundwater circulation. Hydrochemical facies of Lez (Table 1) and Lirou springs (Table 2) indicate different groundwater flowpaths for these springs, despite their geographical proximity. The Lirou spring drains a karst catchment characterized with fast infiltration and rapid groundwater transfers; it has a carbonated facies, i.e., concentrations are high in bicarbonates and low in Cl^-, SO_4^{2-}, Mg^{2+} and trace elements. Peaks of TOC concentration confirm rapid infiltration and a potential high vulnerability to superficial contamination.

The water isotopic input signal was calculated from three raingauges located at Sauteyrargues, Viols le Fort and Montpellier (Table 4). In the δ^2H vs. $\delta^{18}O$ diagram (Fig. 3), rainwater showed a wide range of composition, mostly distributed between the Global Meteoric World Line (GMWL) and the Mediterranean Meteoric World Line (MMWL). Likewise, most groundwater samples lied about these lines, indicating that they originated as meteoric recharge (Grobe and Machel, 2002; McIntosh and Walter, 2006).

The local meteoric water line was calculated from 22 rainwater samples collected during a hydrological year at the Lez basin raingauges (Sauteyrargues and Viols-le-Fort) by using linear least squares, and was $\delta D = 7.3 * \delta^{18}O + 7.8‰$. The relatively low slope (7.3) and y-intercept (+7.8‰) observed, suggest that partial evaporation of raindrops may have a measurable influence on the isotopic input signature over the area (Ladouche, Luc and Dörfliger, 2009)**.** In order to consider only the air masses origins and condensation processes that control the isotopic composition of meteoric water, and excluding fractionation linked with evaporation of water during the raindrops fall to the ground, nine evaporated rainwater samples (identified with low deuterium excess d<+8‰, with d = δ^2H - 8 × δ^{18}O) were removed from the previous dataset. This allowed the determination of a Local Meteoric Line (LML) of non-evaporated rainwaters: δD= 7.5*δ^{18}O+12.5‰. The y-intercept of this LML is +12.5‰, indicating that rainwaters in the Lez basin typically resulted from vapour transports temporally alternated from Mediterranean (d>12‰) and Atlantic origins (d=10‰) (Celle-Jeanton, Travi and Blavoux, 2001; Ladouche, Luc and Dörfliger, 2009).

The temporal variability of EC and δ^{18}O (Fig. 4) shows how ^{18}O isotopes varied during rainfall events on the monitored springs with respect to the rainfall water entry (infiltration) signal. The δ^{18}O weighted average of rainwater in the study period was about -6.2‰, while for the Lez waters the average was -5.7‰. In general, the groundwater samples showed a much reduced variability in δ^{18}O when compared to rainwater inputs (Fig. 4). The monthly rainwater means calculated for Montpellier station presented a relatively large δ^{18}O amplitude (-9.0‰ to +0.6‰ over the period); on the other hand, seasonal isotopic variations were strongly reduced at the springs, especially at the Lez and Restinclières springs, which showed a significant attenuation of the signal variability, typically about 1.5‰ in amplitude.

Despite the dampening of the signal and a low variability, δ^{18}O varied as much as +1‰ during the first high flows of autumn 2008 (zoomed δ^{18}O scale on Fig. 4). This variation is low but is still important enough to suggest that rapid infiltration waters participated to the Lez spring discharge, considering the isotopically enriched rainwaters during the same period (δ^{18}O = -3.78‰ for the corresponding 4-day long event at Montpellier station). Restinclières and Fleurette springs also presented dampening of the δ^{18}O signal which denotes a residence-time at least equal to the period of the input function, i.e. one year. This indicates the existence of an important storage component and an efficient mixing of infiltrated waters with stored waters, which suggests an important autogenic recharge through diffuse percolation of precipitation waters deposited directly onto the karst landscape. Consequently, the seasonal behaviours and recharges are difficult to identify solely from the springs characteristics (Barbieri, Boschetti, Petitta and Tallini, 2005; Long and Putnam, 2004; Négrel and Petelet-Giraud, 2005).

Unlike the other springs of the system, the Lirou spring showed a remarkable δ^{18}O variability, especially during the storms of October 2008 (Fig. 4) characterized by a relatively large rainfall amount (121 mm registered during the first day of a storm that lasted 3 days). This important rainfall input has triggered a large infiltration and an immediate hydrologic response of the Lirou spring, where a marked groundwater EC decrease was observed. This behaviour illustrates the great reactivity of Lirou spring compared to the other springs, indicating that it is effectively under a comparatively stronger influence of recent rainfalls, and presents short residence times through a shallow groundwater flow-path within the limestone bedrock.

4.2 - Carbon isotopes

The use of $\delta^{13}C_{TDIC}$ as a natural tracer in karst systems can help differentiating water originated from the unsaturated zone from water sourced from the saturated zone (Emblanch, Zuppi, Mudry, Blavoux and Batiot, 2003). In the unsaturated zone, the system behaves like an open system with regard to biogenic CO_2 from the soil (Clark and Fritz, 1997; Desmarais and Rojstaczer, 2002; Emblanch, Zuppi, Mudry, Blavoux and Batiot, 2003; Gillon, Barbecot, Gibert, Corcho Alvarado, Marlin and Massault, 2009; Gonfiantini and Zuppi, 2003; Yoshimura, Nakao, Noto, Inokura, Urata, Chen and Lin, 2001). Soil CO_2 was thus investigated under three different environments across the basin in April 2010. The mean results obtained for three different vegetal and pedogenic covers tested over the Lez system were as follow: (1) vineyards developed on Quaternary deposits: $\delta^{13}C_{CO2}$ = -22.28‰; (2) scrublands over Jurassic limestones: $\delta^{13}C_{CO2}$ = -21.69‰; and (3) olive grove developed on Tertiary deposits: $\delta^{13}C_{CO2}$ = -20.42 ‰. At each site, values presented little variability compared to the differences observed between different covers. Former studies over the Mediterranean karst basin of Vaucluse showed low seasonal variations on $\delta^{13}C_{CO2}$ in soil covers (Batiot, 2002) (Emblanch, Zuppi, Mudry, Blavoux and Batiot, 2003). Thus, the input $\delta^{13}C_{CO2}$ signal can be considered constant. The mean $\delta^{13}C_{CO2}$ value of -21.06 ‰ was used as the local biogenic soil CO_2 value.

The Lez spring displayed remarkable variations in $\delta^{13}C_{TDIC}$ values in the range -10.06‰ to -14.73‰ (Table 1). The most $\delta^{13}C_{TDIC}$-enriched waters, associated with high EC, corresponded to the fall periods of October 2008 and October 2009 (Fig. 5). A slow and progressive $\delta^{13}C_{TDIC}$ enrichment was observed during the dry season, extending from the 2008-2009 winter until the first recharge event in 2009 (autumn). Higher $\delta^{13}C_{TDIC}$ values indicate a comparatively larger contribution of groundwater marked with water-rock interaction ($\delta^{13}C_{rockcarbonate}$=0‰ to - 2 ‰) occurring in closed condition within the saturated zone. The most negative values were observed during the middle of the wet season, where $\delta^{13}C_{TDIC}$ as well as E.C. presented a sudden decrease (Fig. 5). These low $\delta^{13}C_{TDIC}$ values measured in groundwaters at the Lez spring suggests flushing of infiltration waters.

The variability of $\delta^{13}C_{TDIC}$ at the Lez spring supports the hypothesis that different compartments of the system contribute to the flow, with an enhanced participation of groundwater associated with higher water-rock interaction signature during the dry season, but also during the first flood events of the wet season. The contribution of freshly infiltrated waters to the Lez spring flow was observed to be more important during the entire humid season, especially after recharge events.

4.3 - Reactions controlling water chemistry

Isotopic ratios of C and Sr were coupled with water chemistry to characterize the chemical evolution of waters, comparing the behaviour of the various springs to one another and the chemical variations during dissimilar hydrological situations. The $\delta^{13}C_{TDIC}$ ratios in groundwater are affected by carbonate dissolution that is linked to the degree of openness to soil CO_2. The CO_2 gas/water isotopic exchange is a very quick process. Consequently, if the chemical equilibrium within the aquifer is attained under open conditions regarding the gaseous phase, the soil $\delta^{13}C_{CO2}$ determines the $\delta^{13}C$ of groundwater (Appelo and Postma, 2005). If the system is closed to soil CO_2, TDIC can be derived up to about equal proportions from the dissolution of CO_2 (g) and from the $CaCO_3$ weathering (Appelo and Postma, 2005).

Covariance of $\delta^{13}C_{TDIC}$ with Mg/Ca and with Sr/Ca (expressed as molar ratios in Fig. 6) indicates an evolution trend for the Lez system: the $\delta^{13}C_{TDIC}$ became more enriched as Mg/Ca and Sr/Ca increased (Fig. 6). $\delta^{13}C_{TDIC}$ was comparatively more enriched in the Lez system samples (except Lirou spring) than in the Valanginian ones, with the exception of Lauret and Boinet wells which were closer to typical Lez waters. Lirou generally showed $\delta^{13}C_{TDIC}$ values more depleted than other samples across the Lez system, which together with the high variability of $\delta^{18}O$, confirms the shorter water residence time, with a flowpath taking place in the shallow aquifer where the influence of soil CO_2 is comparatively more important than limestone dissolution. The coupling between $\delta^{13}C_{TDIC}$ and elemental ratios (Fig. 6) reflects different processes or origins for the groundwater outflowing at the Lez system springs on one hand and Valanginian springs on the other hand. The concomitant increases of $\delta^{13}C_{TDIC}$, Mg/Ca and Sr/Ca observed at the Lez spring (particularly well demonstrated during "Piston-Flow waters") suggest that groundwater possibly evolve via carbonate minerals dissolution under closed system conditions, i.e. with limited influence from surface waters. This reflects the relative isolation of the reservoir feeding Lez spring waters from shallow groundwater, and indicates longer residence times. On the other hand, the relatively higher Mg/Ca and higher Sr/Ca ratios observed in Valanginian waters are most likely due to the lithology of the drained compartments: the Cretaceous marls and marly-limestones are richer in Mg^{2+} than the Jurassic limestones, causing comparatively higher Mg/Ca and Sr/Ca ratios without coincident $\delta^{13}C_{TDIC}$ enrichment (Harrington, Herczeg and Le Gal La Salle, 2008; Moral, Cruz-Sanjulián and Olías, 2008; Stuart, Maurice, Heaton, Sapiano, Micallef Sultana, Gooddy and Chilton, 2010).

Among the various spring waters draining the Lez aquifer, the water described at the beginning of section 3 as “Piston-flow Water” (characterized by EC>780 µS/cm) at the Lez spring has the highest Sr^{2+} concentration. Strontium concentrations are highly correlated with [SO_4^{2-}], [B] and [Li] (R^2= 0.70, 0.80 and 0.76, respectively). It also shows a good correlation with [Cl^-], but only when peaks of [Cl^-] concentrations are observed, which indicates a common origin for both elements in this specific case. Several possible parameters can have a control on Sr^{2+} concentrations in waters, e.g. initial (atmospheric) inputs, mineralogy along flowpaths, mineral dissolution characteristics or residence time. Moreover, Sr^{2+} concentration could be influenced by multiple reactions, e.g. re-crystallization, incongruent dissolution or celestite precipitation (Bernasconi, 1999; Tellam, 1995). Two possible mechanisms can be proposed to describe the chemical reactions controlling Sr^{2+} concentration in Lez spring groundwater with high TDS. (i) The dissolution of dolomite promoting calcite precipitation led by evaporite salts dissolution, which enriches the fluids in both Sr^{2+} and Mg^{2+} with respect to Ca^{2+}. Indeed, during the calcite recrystallization, Sr/Ca increases in groundwater because the calcite lattice favours Ca^{2+} and Mg^{2+} over Sr^{2+} during the precipitation (Jacobson, Blum and Walter, 2002; McIntosh and Walter, 2006; Négrel and Petelet-Giraud, 2005; Nisi, Buccianti, Vaselli, Perini, Tassi, Minissale and Montegrossi, 2008; Stuart, Maurice, Heaton, Sapiano, Micallef Sultana, Gooddy and Chilton, 2010). In this case, high Sr/Ca ratios indicate that waters have been extensively altered by the incongruent dissolution of carbonate minerals and the dissolution of evaporites (Jacobson and Wasserburg, 2005; McIntosh and Walter, 2006; Samborska and Halas, 2010). (ii) The evaporite dissolution may enrich fluids in Sr^{2+} because they contain more Sr^{2+} than calcite and dolomite (Grobe and Machel, 2002; Jacobson and Wasserburg, 2005; McIntosh and Walter, 2006; Petelet, Luck, Ben Othman, Negrel and Aquilina, 1998; Wu, Xu, Yang, Yin and Tao, 2009). As Sr^{2+} concentrations increase, Mg/Ca ratios also increase, suggesting progressive water-rock interactions (McIntosh and Walter, 2006).

Sr isotopes were used to test these hypotheses, focusing on the highly mineralised waters of the Lez spring. The combined use of major elements, mineral saturation state, elemental ratios and $^{87}Sr/^{86}Sr$ help identifying the reactions that control the evolution of the waters chemistry, such as incongruent dissolution of dolomites and calcite precipitation (Jacobson and Wasserburg, 2005; Katz, Catches, Bullen and Michel, 1998; Kloppmann, Négrel, Casanova, Klinge, Schelkes and Guerrot, 2001; Nisi, Buccianti, Vaselli, Perini, Tassi, Minissale and Montegrossi, 2008; Oetting, Banner and Sharp, 1996; Wang, Guo, Su and Ma, 2006).

The upper panel of Figure 7 represents $^{87}Sr/^{86}Sr$ as a function of 1/[Sr]. The water samples from the Valanginian aquifer are clustered around a straight line pointing at an isotopic signature of $^{87}Sr/^{86}Sr$ between 0.7073 and 0.7075 for high [Sr] values, representative of Cretaceous and Jurassic formations. A few samples, notably the Lez water sample identified as "Piston-flow" (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012), and to a lower extent the Lirou and Lez Low Waters (Fig. 7), presented a relatively enriched $^{87}Sr/^{86}Sr$ ratio with high to median Sr concentrations. This behaviour indicates either possible extra sources of Strontium with different Sr isotope ratios along the flowpath, or chemical reactions involving Sr addition or removal (Grobe and Machel, 2002).

Meteoric waters generally have high $^{87}Sr/^{86}Sr$ ratios but low Sr concentrations, while carbonate rocks usually present low $^{87}Sr/^{86}Sr$ ratio (Négrel and Petelet-Giraud, 2005; Oetting, Banner and Sharp, 1996). However, according to the groundwaters' chemical properties and on the basis of Sr concentrations, the meteoric water influence can be ruled out. Sr^{2+} sources are therefore mostly related to the dissolution of Sr-rich minerals and/or the chemical evolution of waters, leading Sr^{2+} concentration to high values.

The Lez water samples corresponding to "Piston Flow" and to "Low Waters" also presented the highest Cl^- concentrations together with the highest $^{87}Sr/^{86}Sr$ ratios observed in the Lez system. The most radiogenic $^{87}Sr/^{86}Sr$ was observed at the Sauve spring, at the northern limit of the Lez catchment (Fig. 1), which is connected to an adjacent granitic system. This isotopic ratio in this case is probably associated to a granitic bedrock fingerprinting, this lithology being present on the upstream part of the Sauve catchment, unlike in the Lez basin. The lithology that could explain a common origin for high Cl^- and radiogenic $^{87}Sr/^{86}Sr$ at the Lez spring corresponds to the Triassic bedrock: the $^{87}Sr/^{86}Sr$ evolution curve peaked during Triassic (with a ratio $^{87}Sr/^{86}Sr$ ~ 0.708) and then continuously decreased from Late Triassic to Late Cretaceous rocks (Koepnick, Denison, Burke, Hetherington and Dahl, 1990). Oetting *et al.* (1996) also found higher $^{87}Sr/^{86}Sr$ ratios in waters from carbonate and evaporite aquifers, indicating a source of Sr^{2+} from underlying units.

These elements confirm the hypothesis presented by Caetano Bicalho et al. (2012) of a piston flow mechanism involving a deep water compartment, especially active at the onset of the humid season.

4.4 - Hydrograph separation at the Lez spring

Mass balance calculations were accomplished in an initial attempt to quantify mixing proportions at the Lez spring using a simple mixing model. The resolution of the end-member mixing, taking into account multiple hydrological reservoirs and water types is beyond the scope of the present paper. The intention of this mass balance calculation is to estimate the proportion of deep waters participating to the Lez outflow during the whole study period. Calculations were thus performed (Eq. 1 to 5) assuming a simple mixture of two end-members (deep and main aquifer compartments) that could be unambiguously identified by one parameter: EC. The choice of EC as tracer is justified by both the good representativeness of this parameter and the high frequency of the available data (continuous EC monitoring at the hourly time-step at the Lez spring).

The two end-members considered are defined as follows. (1) The main aquifer compartment, roughly corresponding to a water bearing the mean characteristics of the high stage season ("High Waters" and "Dilution waters" as defined by Caetano Bicalho et al. (2012)), with EC = 650µS/cm, corresponding to the baseline value of EC at the Lez spring during the wet season (Fig. 4). (2) The deep waters compartment, characterized by an EC value of 1,840 µS/cm corresponding to that of the Bajocian underlying aquifer which was measured (16-day average, corrected for temperature) in the 1200 m deep Antigone borehole (productive levels between 843 and 953 m) in the city of Montpellier (Chamayou and Auroux, 1992).

The contributions are calculated following Eq. 1 to 4:

$$Q_{spring} EC_{spring} = Q_{deep} EC_{deep} + Q_{main.aquifer} EC_{main.aquifer} \quad (1)$$

$$x_{deep} + x_{main.aquifer} = 1 \quad (2)$$

$$EC_{spring} = EC_{Main.aquifer} \times (1 - x_{deep}) + EC_{deep} \times x_{deep} \quad (3)$$

$$x_{deep} = \frac{EC_{spring} - EC_{main.aquifer}}{EC_{deep} - EC_{main.aquifer}} \quad (4)$$

Where:

Q_{spring}, $Q_{main.aquifer}$, Q_{deep} : water discharge at the spring, main compartment discharge, and deep compartment discharge at the spring;

EC_{spring}, $EC_{main.aquifer}$, EC_{deep} : electrical conductivity measured at the spring; main compartment and deep compartment electrical conductivities as defined above;

X_{main}, X_{deep} : end members contributions to the water discharge at the spring.

Figure 8 presents the two end-member separation achieved by the application of the equations 1 to 4, using the water discharge at the Lez spring and the EC measured, on a daily time-step, from the beginning of January 2008 until the end of May 2010. The mean contribution to the outflow at the Lez Spring is estimated to be 92.6% for the main aquifer compartment and 7.4% for the deep aquifer compartment. Winters are characterised by a lower participation of the deep compartment to the Lez outflow, about 5.3% compared to 10% during summer and about 6.2 % during autumn and spring. During the low stage, the average contribution of the deep compartment is remarkably stable. During the high stage this contribution is more variable and can reach peak values of 21.8%, immediately followed by a steep decrease. On average though, high-stage deep compartment contributions are proportionally lower (Fig. 8).

This hydrograph separation illustrates the temporal distribution of both end-members under a wide range of hydrological conditions, denoting their strong variability. The limitation of this calculation relies on the definition of the so-called deep compartment. The middle Jurassic layer taken as a reference point may result from a mixing between water circulating in Inf. Jurassic layers and a deeper flux which seems to rise through faults from deeper Triassic levels, carrying Cl-rich waters with higher TDS. This may constitute an intermediate storage compartment prone to react quickly through a piston-flow mechanism to a steep recharge.

4.5 - Conceptual model: Groundwater circulation within the Lez karst system

The results obtained in this work improve the argumentation presented by Caetano Bicalho *et al.* (2012) who suggested that the Lez spring water contains a small proportion of groundwater issued from deep layers. Apparently, a shallow buffering zone (Fig. 9) allows the storage of rising waters from deep origin. The water from this zone mainly participates to the outflow at Lez spring during high recharge events.

Water stable isotopes indicated that the Lez system springs (Lez, Lirou, Restinclières and Fleurettes) have a common recharge origin. The Lirou spring is the most sensitive to shallow infiltration waters among the springs. Groundwater flowpaths of Lirou spring are basically located on Jurassic limestones and outflow in the contact zone with the Valanginian layer. Thus it can be proposed that Lirou groundwaters do not flow bellow the Valanginian overlying unit in accord with the results obtained from chemical tracers (lower Mg/Ca and Sr/Ca ratios), water stable isotopes (high variability), $^{87}Sr/^{86}Sr$ ratio (lower values) and depleted $\delta^{13}C_{TDIC}$.

The hydrochemical characteristics of Restinclières and Fleurettes springs are very similar in terms of EC, elemental ratios and $\delta^{13}C_{TDIC}$, and can be mostly related to interaction with limestones and marly-limestones from Upper Jurassic and Early Cretaceous, indicating groundwater circulation bellow the Valanginian covering of the aquifer.

Lez, Restinclières and Fleurettes springs have rather similar properties during Lez spring high-flow periods, i.e., when all springs discharge simultaneously. The low-flow Lez waters tend to get progressively enriched in $\delta^{13}C_{TDIC}$. Indeed, at the beginning of high-flow periods, groundwater at the Lez spring are distinct from all the other springs, presenting higher chemical evolution, marked by longer water-rock interaction and possibly the presence of an evaporitic signature in a low percentage, i.e. a depleted $^{87}Sr/^{86}Sr$ Triassic signature. Finally, Lez spring waters corresponding to the "Piston Flow" waters (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012) have a specific hydrochemical fingerprint (high $\delta^{13}C_{TDIC}$, Mg/Ca and $^{87}Sr/^{86}Sr$ ratios), which clearly differentiate them from Restinclières and Fleurettes spring waters.

The results obtained from the hydrograph separation allowed to estimate the temperature of the deep end-member. Using a mean deep-water contribution of 7.4% (±1%) ; and considering the temperature of the high TDS waters at the Lez spring (17.4°C) and the annual air temperature average for the study area (16.1°C, at Montpellier Collège F.Rabelais meteorological station) (Hérault, 2009), by application of Eq. (4) and replacing EC with T, we obtain a temperature of the deep waters equivalent to 33.7°C (±2.1°C). Considering the average geothermic gradient of 1.8°C/100m for our study zone (Lucazeau, 1979), we obtain a characteristic depth of about 978 (±115) meters. This estimate is consistent with the hypothesis presented earlier of a storage compartment located within the mid-Jurassic calcareous formation, and acting as a buffer zone between the deep compartment and the main aquifer.

5 - Conclusion

In the present study, elemental geochemical tracers coupled with isotopic ratios ($\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$ and $\delta^{13}C_{TDIC}$) were used to understand groundwater origins and hydrochemical evolution in the Lez Karst system (southern France). Groundwater samples were collected from the Lez spring and surrounding springs and wells under various hydrological conditions during two years (from June 2008 until May 2010).

Water stable isotopes evidenced that the Lirou intermittent spring flow is more responsive to freshly infiltrated waters than the other springs of the system, denoting as a consequence shorter groundwater residence times. For the other springs, on the contrary, important signal attenuation is observed, indicating the existence of a mixing of infiltrated waters with longer residence time groundwater stored in the aquifer.

The similar fingerprinting of water stable isotopes measured at the various springs (Lez, Lirou, Restinclières and Fleurettes) indicates that their recharge has the same origin. However, the relative disparity of their water chemistry indicates that recharge waters flow along distinct flowpaths. The hydrochemical characteristics of Restinclières and Fleurettes springs are very similar to one another and can be mostly attributed to interaction with limestones and marly-limestones from Upper Jurassic and Early Cretaceous, indicating groundwater circulation bellow the Valanginian overlying unit. At the Lez spring, the high-TDS groundwaters ("Piston-Flow waters" with EC >780µS.cm^{-1}) issued from deep layers have probably been extensively modified by evaporite dissolution, calcite precipitation and incongruent dissolution of dolomite. This phenomenon was evidenced by: (i) high Mg/Ca and Sr/Ca ratios concomitant with an increase of $\delta^{13}C_{TDIC}$, possibly via calcite dissolution and incongruent dissolution of carbonate minerals under closed system conditions driven by evaporitic minerals dissolution; (ii) high Cl^- concentration positively correlated with [Sr^{2+}] and presumably of evaporitic origin; (iii) high $^{87}Sr/^{86}Sr$ ratio of the Cl-rich waters at the Lez spring, suggesting a Triassic signature, and (iv) high Sr/Ca ratio, which can be explained by calcite recrystallization involving a continuous addition of Sr^{2+} induced by Ca^{2+} depletion in water solution.

A simple 2-end member hydrograph separation was used to determine the relative proportions of the deep water compartment and the main aquifer to the Lez spring over the study period, using EC as tracer.

The deep compartment end-member was characterized by an EC value of 1,840 µS/cm, corresponding to that of the Bajocian underlying aquifer, measured in a 1200 m deep borehole in the city of Montpellier. The mean contribution to the Lez outflow was estimated to be 92.6% for the main aquifer compartment and 7.4% for the deep compartment. This analysis showed that the deep waters end-member as defined may result from a mixing between water circulating in Inf. Jurassic layer and a deep flux which seems to rise through faults from deeper Triassic levels, constituting an intermediate compartment prone to react through piston-flow mechanism to a strong recharge.

This approach combining hydrodynamics, hydrochemistry and isotope tracers on a continuous 2-year record appears to be a very efficient tool for characterizing groundwater flow on karst systems, and is potentially applicable to other complex karst systems with deep karstification. This work was efficient on shedding some light on the Lez system behaviour which is an intrinsically complex Vauclusian karst system. Differently from ordinary karst systems, long residence-times and deep water rising seem to be associated with this aquifer; such information being invaluable to the exploitation management of the Lez spring. The core of such a complexity is related to a multiplicity of compartments and lithologies that confer different chemical properties to the groundwaters.

Finally, the use of isotopes allowed refining the interpretation of the hydrochemical dataset, furnishing details about the chemical evolution of waters. This combination of methods seems to be efficient for characterizing groundwater flow on karst systems and is potentially applicable to other complex systems with deep karstification.

6 - Acknowledgments

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References

Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution. A.A. Balkema Publishers, Leiden,The Netherlands., 649p. pp.

Aquilina, L., Ladouche, B., Dörfliger, N., 2006. Water storage and transfer in the epikarst of karstic systems during high flow periods. Journal of Hydrology, 327(3-4): 472-485.

Bakalowicz, M., 2005. Karst groundwater: a challenge for new resources. Hydrogeol J 13: 148–160.

Barbieri, M., Boschetti, T., Petitta, M., Tallini, M., 2005. Stable isotope (2H, 18O and 87Sr/86Sr) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy). Applied Geochemistry, 20(11): 2063-2081.

Batiot, C., 2002. Etude experimentale du cycle du carbone en régions karstiques, Université d'Avignon et des Pays de Vaucluse, Avignon, 247 pp.

Bernasconi, S.M., 1999. Interstitial water chemistry in the western Mediterranean: results from leg 161. Proceedings of the Ocean Drilling Program, Scientific Results, 161: 426-432.

Beven, K.J., 2001. Rainfall-Runoff Modelling: the Primer. Chichester, Wiley.

Blavoux, B., Gilli, É., Rousset, C., 2004. Alimentation et origine de la salinité de la source sous-marine de Port-Miou (Marseille-Cassis). Principale émergence d'un réseau karstique hérité du Messinien. Comptes Rendus Geosciences, 336(6): 523-533.

Boinet, N., 2002. Inventaire spéléologique du causse de l'Hortus - Livre I, Club Loisir Plein Air, Montpellier.

Bouchaou, L., Michelot, J.L., Qurtobi, M., Zine, N., Gaye, C.B., Aggarwal, P.K., Marah, H., Zerouali, A., Taleb, H., Vengosh, A., 2009. Origin and residence time of groundwater in the Tadla basin (Morocco) using multiple isotopic and geochemical tools. Journal of Hydrology, 379(3-4): 323-338.

Bousquet, J.C., 1997. Géologie du Languedoc-Roussillon, Montpellier, France.

Caetano Bicalho, C., Batiot-Guilhe, C., Seidel, J.L., Van Exter, S., Jourde, H., 2012. Geochemical evidence of water source characterization and hydrodynamic responses in a karst aquifer. Journal of Hydrology, 450–451(0): 206-218.

Celle-Jeanton, H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean Region at three different time scales. Geophysical Research Letters, 28(7): 1215-1218.

Chamayou, J., Auroux, F., 1992. Les thermes du Lez - Port Marianne - Source Antigone. Gisement hydrominéral de la "source Antigone" dans son contexte hydrogéologique et structural. BRGM, Montpellier, pp. 25.

Charlier, J.-B., Bertrand, C., Mudry, J., 2012. Conceptual hydrogeological model of flow and transport of dissolved organic carbon in a small Jura karst system. Journal of Hydrology, 460–461(0): 52-64.

Cita, M.B., Ryan, W.B.F., 1978. Messinian erosional surfaces in the Mediterranean. Marine Geology, 27: 193-366.

Clark, I.D., Fritz, P., 1997. Environmental isotopes in hydrogeology, New York, p. 328 pp.

Clauzon, G., 1982. Le canyon messinien du Rhône: une preuve décisive du desiccated deep-basin model (Hsü, Cita and Ryan, 1973). Bulletin Society géol France, 24: 597–610.

Desmarais, K., Rojstaczer, S., 2002. Inferring source waters from measurements of carbonate spring response to storms. Journal of Hydrology, 260(1-4): 118-134.

Drever, J., 1982. Geochemistry of Natural Waters Prentice-Hall, Inc., Englewood Cliffs New Jersey, 388p pp.

Dubois, P., 1964. Les circulations souterraines dans les calcaires de la région de Montpellier. 2, BRGM, Montpellier.

Emblanch, C., Blavoux, B., Puig, J.-M., Couren, M., 1998. Le marquage de la zone non saturée du karst à l'aide du carbone 13The use of carbon 13 as a tracer of the karst unsaturated zone. Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science, 326(5): 327-332.

Emblanch, C., Zuppi, G.M., Mudry, J., Blavoux, B., Batiot, C., 2003. Carbon 13 of TDIC to quantify the role of the unsaturated zone: the example of the Vaucluse karst systems (Southeastern France). Journal of Hydrology, 279(1-4): 262-274.

Fleury, P., 2005. Sources sous-marines et aquifères côtiers méditerranéens. Fonctionnement et caractérisation, Université Paris VI - P. et M. Curie, Montpellier, 286 pp.

Fleury, P., Bakalowicz, M., de Marsily, G., 2007. Submarine springs and coastal karst aquifers: A review. Journal of Hydrology, 339(1-2): 79-92.

Fleury, P., Ladouche, B., Conroux, Y., Jourde, H., Dörfliger, N., 2009. Modelling the hydrologic functions of a karst aquifer under active water management - The Lez spring. Journal of Hydrology, 365(3-4): 235-243.

Frondini, F., 2008. Geochemistry of regional aquifer systems hosted by carbonate-evaporite formations in Umbria and southern Tuscany (central Italy). Applied Geochemistry, 23(8): 2091-2104.

Garry, B., 2007. Etude des processus d'écoulement de la zone non saturée pour la modélisation des acquières karstiques Université d'Avignon et des Pays de Vaucluse, Avignon, 204 pp.

Geyer, T., Birk, S., Liedl, R., Sauter, M., 2008. Quantification of temporal distribution of recharge in karst systems from spring hydrographs. Journal of Hydrology, 348(3-4): 452-463.

Gillon, M., Barbecot, F., Gibert, E., Corcho Alvarado, J.A., Marlin, C., Massault, M., 2009. Open to closed system transition traced through the TDIC isotopic signature at the aquifer recharge stage, implications for groundwater 14C dating. Geochimica et Cosmochimica Acta, 73(21): 6488-6501.

Gonfiantini, R., Zuppi, G.M., 2003. Carbon isotope exchange rate of DIC in karst groundwater. Chemical Geology, 197(1-4): 319-336.

Grobe, M., Machel, H.G., 2002. Saline groundwater in the Münsterland Cretaceous Basin, Germany: clues to its origin and evolution. Marine and Petroleum Geology, 19(3): 307-322.

Harrington, N.M., Herczeg, A.L., Le Gal La Salle, C., 2008. Hydrological and geochemical processes controlling variations in Na+-Mg2+-Cl--SO42- groundwater brines, south-eastern Australia. Chemical Geology, 251(1-4): 8-19.

Hartmann, A., Weiler, M., Wagener, T., Lange, J., Kralik, M., Humer, F., Mizyed, N., Rimmer, A., Barberá, J.A., Andreo, B., Butscher, C., Huggenberger, P., 2013. Process-based karst modelling to relate hydrodynamic and hydrochemical characteristics to system properties. Hydrol. Earth Syst. Sci., 17(8): 3305-3321.

Hérault, D., 2009. La station météorologique MONTPELLIER Collège F.RABELAIS. http://www.m2ing.com/meteo/montpellier/alco.htm.

Jacobson, A.D., Blum, J.D., Walter, L.M., 2002. Reconciling the elemental and Sr isotope composition of Himalayan weathering fluxes: insights from the carbonate geochemistry of stream waters. Geochimica et Cosmochimica Acta, 66(19): 3417-3429.

Jacobson, A.D., Wasserburg, G.J., 2005. Anhydrite and the Sr isotope evolution of groundwater in a carbonate aquifer. Chemical Geology, 214(3-4): 331-350.

Joseph, C., Rodier, C., Soulte, M., Sinegre, F., Baylet, R., Deltour, P., 1988. Approche des transferts de pollution bactérienne dans une crue karstique par l'étude des paramètres physico-chimiques. Revue des sciences de l'eau, 1-2: 73-106.

Jourde, H., Batiot-Guilhe, C., Bailly-Comte, V., Bicalho, C., Blanc, M., Borrell, V., Bouvier, C., Boyer, J.F., Brunet, P., Cousteau, M., Dieulin, C., Gayrard, E., Guinot, V., Hernandez, F., Kong, L., Siou, A., Johannet, A., Leonardi, V., Mazzilli, N., Marchand, P., Patris, N., Pistre, S., Seidel, J.L., Taupin, J.D., Van-Exter, S., 2011. The MEDYCYSS observatory, a Multi scalE observatory of flooD dYnamiCs and hYdrodynamicS in karSt (Mediterranean border

Southern France) Lambrakis, Nicolaos; Stournaras, George; Katsanou, Konstantina, pp. p551-560.
Karam, Y., 1989. Essais de modélisation des écoulements dans un aquifère karstique. Exemple de la source du Lez (Hérault, France). Université Sciences et Techniques du Languedoc, Montpellier, 286 pp.
Katz, B.G., Catches, J.S., Bullen, T.D., Michel, R.L., 1998. Changes in the isotopic and chemical composition of ground water resulting from a recharge pulse from a sinking stream. Journal of Hydrology, 211(1-4): 178-207.
Kilroy, G., Coxon, C., 2005. Temporal variability of phosphorus fractions in Irish karst springs. Environmental Geology, 47: 421–430.
Kloppmann, W., Négrel, P., Casanova, J., Klinge, H., Schelkes, K., Guerrot, C., 2001. Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes. Geochimica et Cosmochimica Acta, 65(22): 4087-4101.
Koepnick, R.B., Denison, R.E., Burke, W.H., Hetherington, E.A., Dahl, D.A., 1990. Construction of the Triassic and Jurassic portion of the Phanerozoic curve of seawater 87Sr/86Sr. Chemical Geology: Isotope Geoscience section, 80(4): 327-349.
Ladouche, B., Luc, A., Dörfliger, N., 2009. Chemical and isotopic investigation of rainwater in Southern France (1996-2002): Potential use as input signal for karst functioning investigation. Journal of Hydrology, 367(1-2): 150-164.
Ladouche, B., Probst, A., Viville, D., Idir, S., Baqué, D., Loubet, M., Probst, J.L., Bariac, T., 2001. Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France). Journal of Hydrology, 242(3-4): 255-274.
Leonardi, V., Jourde, H., Dausse, A., N.Dörfliger, Brunet, P., Maréchal, J.C., 2013. Apport de nouveaux traçages et forages à la connaissance hydrogéologique de l'aquifère karstique du Lez. Karstologia, 62: 7-14.
Long, A.J., Putnam, L.D., 2004. Linear model describing three components of flow in karst aquifers using 18O data. Journal of Hydrology, 296(1-4): 254-270.
López-Chicano, M., Bouamama, M., Vallejos, A., Pulido-Bosch, A., 2001. Factors which determine the hydrogeochemical behaviour of karstic springs. A case study from the Betic Cordilleras, Spain. Applied Geochemistry, 16(9-10): 1179-1192.
Lucazeau, F., 1979. Phénomènes de perturbations thermiques dues à des circulations karstiques dans la région de Montpellier. , U.S.T.L., Montpellier.
Marjolet, G., Salado, J., 1976. Contribution à l'étude de l'aquifère karstique de la source du Lez (Hérault). Etude du chimisme des eaux de la source du Lez et de son bassin Tome IX – FASC II. , Université des sciences et Techniques du Languedoc (Montpellier 2), Montpellier 101 pp.
Massei, N., Mahler, B.J., Bakalowicz, M., Fournier, M., Dupont, J.P., 2007. Quantitative Interpretation of Specif Conductance Frequency Distribution in karst. Ground Water, 45, (3): 288-293.
McIntosh, J.C., Walter, L.M., 2006. Paleowaters in Silurian-Devonian carbonate aquifers: Geochemical evolution of groundwater in the Great Lakes region since the Late Pleistocene. Geochimica et Cosmochimica Acta, 70(10): 2454-2479.
Mendizabal, I., Stuyfzand, P.J., 2010. Quantifying the vulnerability of well fields towards anthropogenic pollution: The Netherlands as an example. Journal of Hydrology, In Press, Accepted Manuscript.
Millot, R., Petelet-Giraud, E., Guerrot, C., Négrel, P., 2010. Multi-isotopic composition (δ7Li-δ11B-δD-δ18O) of rainwaters in France: Origin and spatio-temporal characterization. Applied Geochemistry, 25(10): 1510-1524.
Moral, F., Cruz-Sanjulián, J.J., Olías, M., 2008. Geochemical evolution of groundwater in the carbonate aquifers of Sierra de Segura (Betic Cordillera, southern Spain). Journal of Hydrology, 360(1-4): 281-296.

Négrel, P., Petelet-Giraud, E., 2005. Strontium isotopes as tracers of groundwater-induced floods: the Somme case study (France). Journal of Hydrology, 305(1-4): 99-119.

Nisi, B., Buccianti, A., Vaselli, O., Perini, G., Tassi, F., Minissale, A., Montegrossi, G., 2008. Hydrogeochemistry and strontium isotopes in the Arno River Basin (Tuscany, Italy): Constraints on natural controls by statistical modeling. Journal of Hydrology, 360(1-4): 166-183.

Oetting, G.C., Banner, J.L., Sharp, J.M., 1996. Regional controls on the geochemical evolution of saline groundwaters in the Edwards aquifer, central Texas. Journal of Hydrology, 181(1-4): 251-283.

Pane-Escribe, M., B. , 1995. Utilisation des éléments en trace comme traceurs des circulations souterraines en milieu karstique (site du lamalou, Hérault), Université de Montpellier II, 297p pp.

Petelet-Giraud, E., Negrel, P., 2007. Geochemical flood deconvolution in a Mediterranean catchment (Hérault, France) by Sr isotopes, major and trace elements. Journal of Hydrology, 337(1-2): 224-241.

Petelet, E., Luck, J.-M., Ben Othman, D., Negrel, P., Aquilina, L., 1998. Geochemistry and water dynamics of a medium-sized watershed: the Hérault, southern France: 1. Organisation of the different water reservoirs as constrained by Sr isotopes, major, and trace elements. Chemical Geology, 150(1-2): 63-83.

Ribolzi, O., Moussa, R., Gaudu, J.-C., Vallès, V., Voltz, M., 1997. Etude des crues de transition entre période sèche et période humide, par traçage naturel sur un bassin versant méditerranéen cultivé. Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science, 324(12): 985-992.

Rosenthal, E., Zilberbrand, M., Livshitz, Y., 2007. The hydrochemical evolution of brackish groundwater in central and northern Sinai (Egypt) and in the western Negev (Israel). Journal of Hydrology, 337(3-4): 294-314.

Ryan, W.B., 1976. Quantitative evaluation of the depth of the western Mediterranean before, during and after the Late Miocene salinity crisis. Sedimentology, 23(6): 791-813.

Samborska, K., Halas, S., 2010. 34S and 18O in dissolved sulfate as tracers of hydrogeochemical evolution of the Triassic carbonate aquifer exposed to intense groundwater exploitation (Olkusz-Zawiercie region, southern Poland). Applied Geochemistry, 25(9): 1397-1414.

Stuart, M.E., Maurice, L., Heaton, T.H.E., Sapiano, M., Micallef Sultana, M., Gooddy, D.C., Chilton, P.J., 2010. Groundwater residence time and movement in the Maltese islands - A geochemical approach. Applied Geochemistry, In Press, Corrected Proof.

Tellam, J.H., 1995. Hydrochemistry of the saline groundwaters of the lower Mersey Basin Permo-Triassic sandstone aquifer, UK. Journal of Hydrology, 165(1-4): 45-84.

Thierry, D., Bérard, P., 1983. Alimentation en eau de la ville de Montpellier – Captage de la source du Lez - études des relations entre la source et son réservoir aquifère, BRGM, Montpellier.

Wang, Y., Guo, Q., Su, C., Ma, T., 2006. Strontium isotope characterization and major ion geochemistry of karst water flow, Shentou, northern China. Journal of Hydrology, 328(3-4): 592-603.

Wittenberg, L., Kutiel, H., Greenbaum, N., Inbar, M., 2007. Short-term changes in the magnitude, frequency and temporal distribution of floods in the Eastern Mediterranean region during the last 45 years -- Nahal Oren, Mt. Carmel, Israel. Geomorphology, 84(3-4): 181-191.

Wong, C.I., Mahler, B.J., Musgrove, M., Banner, J.L., 2012. Changes in sources and storage in a karst aquifer during a transition from drought to wet conditions. Journal of Hydrology, 468–469(0): 159-172.

Wu, W., Xu, S., Yang, J., Yin, H., Tao, X., 2009. Sr fluxes and isotopic compositions in the headwaters of the Yangtze River, Tongtian River and Jinsha River originating from the Qinghai-Tibet Plateau. Chemical Geology, 260(1-2): 63-72.

Yoshimura, K., Nakao, S., Noto, M., Inokura, Y., Urata, K., Chen, M., Lin, P.W., 2001. Geochemical and stable isotope studies on natural water in the Taroko Gorge karst area, Taiwan--chemical weathering of carbonate rocks by deep source CO2 and sulfuric acid. Chemical Geology, 177(3-4): 415-430.

Fig. Captions

Fig. 1 – Hydrogeological map of the Lez karst system indicating sampled springs, wells, raingauges and cross-section locations (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012).
Fig. 2 – NW-SE Interpretative cross-section over the study area (Caetano Bicalho, Batiot-Guilhe, Seidel, Van Exter and Jourde, 2012).
Fig. 3 – Top: $\delta^{2}H$ (Deuterium) vs. $\delta^{18}O$ (‰) for the Lez system spring waters (Lez, Lirou, Fleurettes and Restinclières) and rainwater samples from the 3 raingauges (Saint Gély du Fesc, Viols le Fort and Sauteyrargues). Bottom: zoom showing spring water data in detail.
Fig. 4 – Rainfall (Montpellier, Viols le Fort and Sauteyrargues stations); E.C., $\delta^{18}O$ (‰); zoomed $\delta^{18}O$ (‰) and deuterium-excess for the Lez system springs (Lez, Lirou, Fleurettes and Restinclières).
Fig. 5 – Rainfall, E.C., water discharge and $\delta^{13}C_{TDIC}$ at the Lez spring (Sept.2008-March 2010).
Fig. 6 – Mg/Ca and Sr/Ca vs. $\delta^{13}C_{TDIC}$ for Lez karst system springs and wells, and for springs and wells belonging to the surrounding karst systems.
Fig. 7– $^{87}Sr/^{86}Sr$ ratio vs 1/[Sr] and $^{87}Sr/^{86}Sr$ ratio vs [Cl^-] for the Lez karst system springs and wells, and for springs and wells belonging to the surrounding karst systems. $^{87}Sr/^{86}Sr$ ratio typical ranges are indicated for Triassic, Jurassic and Late Cretaceous (Koepnick, Denison, Burke, Hetherington and Dahl, 1990) and granite and fresh waters (Kloppmann, Négrel, Casanova, Klinge, Schelkes and Guerrot, 2001).
Fig. 8 – Two end-member hydrograph separation from 2008 to 2010, using EC as tracer. The end-members are "Main aquifer compartment" with EC= 650µS/cm, and "Deep aquifer compartment", with EC= 1,840µS/cm.
Fig. 9 – Conceptual model for groundwater circulation through the Lez karst system.

Table Captions

Table 1– T, EC , pH, major and trace element concentrations and isotopic ratios for the Lez spring.

Table 2 – T, EC , pH, major and trace element concentrations and isotopic ratios for Lirou, Restinclières, and Fleurettes springs and other sampling points.

Table 3 – Average values and range of variations for T, EC, pH, major and trace element concentrations and isotopic ratios for the springs: Lez, Lirou, Restinclières and Fleurettes.

Table 4 – Water stable isotope range for the sampled springs and raingauges and water stable isotope weighted average for rainwater.

Table 1 – T, EC, pH. major and trace element concentrations and isotopic ratios for the Lez spring.

Sampling date	*Lez spring*	T°C (°C)	CE (µS.cm)	pH	HCO_3^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	toc (mg/l)	Li^+ (µg/l)	Br^- (µg/l)	B^{3+} (µg/l)	Sr^{2+} (µg/l)	Ba^{2+} (µg/l)	δ^2H (‰ V-SMOW)	$\delta^{18}O$ (‰ V-SMOW)	$\delta^{13}C$ TDIC (‰ V-PDB)	$^{87}Sr/^{86}Sr$
13/06/08	1		773		379.2	50.5	5.6	32.4	143.2	7.7	25.1	1.1	1.2	3.4		18.8	442.4	13.1	-30.4	-5.1		
15/06/08	2		763		375.5	48.3	6.5	30.9	140.1	7.4	24.2	1.1	3.9	3.2		17.7	419.9	12.6	-30.0	-5.7		
07/07/08	3	16.1	747	7.16	372.0	49.2	4.6	29.7	127.4	8.3	26.2	1.3	1.0						-31.7	-5.7		
21/07/08	4	16.4	746	7.05	354.3	50.7	4.7	28.1	132.8	8.2	28.4	1.4	1.1	4.0			426.5	16.9	-32.4	-5.6		
05/08/08	5	16.7	763	7.15	368.1	56.0	5.5	29.1	125.7	9.7	33.6	1.7	1.2	4.2			388.9	17.7	-32.7	-5.7		
26/08/08	6	16.9	756	7.19	361.3	56.3	4.8	27.8	123.9	10.1	34.2	1.7	0.4	4.1			373.9	18.5	-31.1	-5.2		
10/09/08	7	17.2	761	7.14	365.1	56.9	5.0	26.7	128.3	10.1	36.2	1.9	0.6	4.1			369.1	19.0	-34.3	-6.0	-12.7	
22/09/08	8	17.2	753	6.97	365.7	53.2	6.1	26.3	121.1	9.0	30.6	1.2	0.4	3.9			358.9	18.7	-34.4	-5.9	-12.4	
07/10/08	9	17.3	762	7.05	368.8	55.8	6.7	26.1	120.2	9.3	32.0	1.3	0.3	4.2		6.2	356.4	18.9	-34.0	-5.9		
13/10/08	10	17.3	763	7.14	365.1	63.3	6.6	26.7	116.5	9.2	33.3	1.3	0.6	4.1		5.9	352.6	18.3	-34.3	-5.9		
21/10/08 N°1	11	16.6	704	7.26	339.0	43.0	4.8	22.9	120.5	6.9	24.2	1.2	2.2	3.2	109.1	13.7	320.5	15.5	-31.5	-5.6		
21/10/08 N°2	12	16.7	643	7.24	283.0	37.3	5.5	20.9	105.9	5.9	21.3	1.0	3.6	3.1	107.2	12.8	326.4	13.9	-31.1	-5.6		
21/10/08 N°3	13	17	748	7.14	358.7	50.0	4.3	23.7	114.8	8.0	29.4	1.3	5.3	3.8	117.6	14.7	346.3	17.3	-34.1	-5.8		
21/10/08 N°4	14	17	748	7.11	339.2	49.8	3.5	23.8	115.3	8.1	29.4	1.2	4.4	3.8	121.4	14.5	347.3	17.5	-27.1	-3.2		
22/10/08 N°1	15	16.6	682	7.10	344.0	36.7	6.2	22.2	111.7	6.2	20.9	1.2	2.9	0.2	112.5	<LD	62.1	6.7	-31.6	-5.5		
22/10/08 N°2	16	16.7	681	6.89	348.9	35.7	6.8	21.1	113.4	6.4	20.6	1.2	2.7	3.0	109.2	17.3	324.5	16.3	-31.4	-5.6	-13.3	
23/10/08 N°1	17	16.9	855	6.94	336.7	80.0	5.3	37.3	112.2	11.0	49.7	2.2	2.2	6.5	136.9	19.1	543.6	22.1	-31.9	-5.5	-12.2	
23/10/08 N°2	18	16.9	859	7.08	339.2	80.1	5.0	37.2	112.9	11.0	50.2	2.2	2.0	6.3	134.2	18.7	540.9	22.4	-31.1	-5.5	-12.0	
24/10/2008 N°1	19	16.7	739	7.01	352.6	46.2	5.7	28.9	113.4	8.9	26.7	1.4	1.7	4.6	117.6	16.6	537.6	19.8	-31.1	-5.6	-13.1	
24/10/2008 N°2	20	16.5	707	6.93	348.9	36.6	6.1	26.5	115.8	8.1	20.3	1.2	1.6	4.1	112.3	15.1	519.2	18.7	-31.1	-5.5		
22/10/08	21		753		351.4	51.4	3.7	24.3	115.4	8.3	30.5	1.3	2.7	4.0		13.9	327.9	17.7	-33.5	-5.7		
23/10/08	22		847		336.7	78.4	5.3	36.1	110.6	10.9	48.6	2.1	1.3	6.2		18.6	541.1	21.7	-30.6	-5.2		
23/10/08	23		842		339.2	78.4	5.4	36.5	111.1	10.8	48.8	2.2	3.0	6.2	103.6	18.5	541.9	21.2	-31.5	-5.5		
24/10/08	24		741		348.9	47.9	5.8	29.4	114.6	9.0	28.0	1.5	1.6	4.5		17.4	487.7	20.4	-30.9	-5.5		
24/10/08	25		706		341.6	38.5	5.1	27.0	113.7	8.1	21.3	1.5	1.6	4.2		16.6	513.0	19.8	-31.2	-5.2		
24/10/08	26		692		339.2	36.2	6.4	26.3	114.9	7.9	19.4	2.6	2.4	3.9	109.7	17.7	467.6	19.3	-31.5	-5.4		
26/10/08	27	15.9	645	7.02	334.3	26.4	4.7	20.5	113.0	6.3	14.4	0.9	1.8		105.9				-30.6	-5.2		
27/10/08	28	17	656	7.46	341.6	27.2	5.5	21.5	112.8	6.5	15.1	0.9	2.1	2.9	106.1	12.1	430.3	16.6	-29.4	-5.2		
29/10/08	29	15.9	683	7.04	356.2	30.4	6.3	22.8	115.7	6.7	16.9	1.2	1.7	3.3	112.7	15.6	466.5	17.9	-29.5	-5.4		
31/10/08	30	15.9	705	7.00	356.2	34.5	6.8	23.5	118.0	6.6	19.1	1.4	1.6	3.5	113.9	17.1	480.2	17.8	-29.9	-5.4		
03/11/08	31	15.9	699	7.09	339.2	37.3	6.3	24.3	116.9	6.0	20.8	1.5	1.7	3.6	109.6	17.8	462.1	16.7	-28.8	-5.3		
05/11/08	32	15.7	650	7.13	341.6	24.3	6.8	21.1	117.3	5.0	13.3	1.0	2.8	2.8	101.0	14.8	394.4	15.7	-28.4	-5.1	-12.1	0.70762
07/11/08	33	15.4	644	6.95	351.4	21.3	7.2	20.5	119.9	4.9	11.4	0.9	3.0	2.6	103.0	13.8	394.2	15.1	-27.2	-5.2	-14.7	
12/11/08	34	15.5	705	7.07	373.3	35.6	7.0	23.6	122.0	5.8	19.0	1.1	5.6	3.5	107.8	15.1	431.8	15.4	-29.8	-5.3		
14/11/08	35	15.5	722	7.18	393.6	42.6	7.5	26.6	132.6	6.9	23.6	1.3	4.0	3.7	110.1	13.1	464.4	15.9	-29.7	-5.4		

Sampling date	*Lez spring*	T°C	CE	pH	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	toc	Li^+	Br^-	B^{3+}	Sr^{2+}	Ba^{2+}	δ^2H	$\delta^{18}O$	$\delta^{13}C$	$^{87}Sr/^{86}Sr$
		(°C)	(µS.cm)		(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(‰ V-SMOW)	(‰ V-SMOW)	TDIC (‰ V-PDB)	
18/11/08	36	15.5	721	7.10	362.5	40.0	6.6	26.0	129.0	7.2	22.7	1.2	4.6	3.7	106.9	14.0	460.3	15.3	-28.8	-5.3		
21/11/08	37	15.5	721	7.15	346.0	42.2	6.8	27.3	124.9	6.8	22.7	1.2	1.7	3.9	<LD	13.1	486.8	15.5	-29.8	-5.4		
05/12/08	38	15.8	741	7.35	355.1	45.0	5.0	27.3	127.5	8.0	26.2	1.3	1.2	3.9	115.8	19.4	482.1	16.4	-30.6	-5.6	-14.3	
16/12/08	39	15.1	661	7.23	372.2	28.2	6.3	27.9	124.9	7.2	15.8	1.1	1.1	3.4		19.9	528.0	15.8	-32.1	-5.4		
09/01/09	40	14.9	721	7.20	368.6	41.5	6.9	27.0	130.1	7.2	23.5	1.2	1.0	3.6	110.6	17.3	472.4	14.7	-35.1	-5.7		
28/01/09	41	14.8	689	7.28	361.2	28.9	5.4	27.5	124.6	6.8	16.4	0.9	1.4	3.3	73.1	16.6	502.3	15.3	-35.3	-5.7		
02/02/09	42	14.5	673	7.35	355.1	27.8	5.4	24.6	118.6	5.7	16.1	0.9	1.9	2.9	103.2	15.3	428.9	13.6	-37.6	-6.0		
09/02/09	43	14	599	7.39	361.2	34.2	5.2	23.8	123.3	6.1	19.5	1.0	1.3	3.1	99.6	14.8	420.4	13.5	-39.6	-6.3		
12/03/09	44	15.3	707	7.39	349.0	33.3	4.0	25.1	115.1	8.7	22.5	1.2	0.9	3.8	103.6	15.5	480.4	15.2	-37.7	-6.0		
27/03/09	45	15.5	723	7.11	271.5	43.2	4.1	31.5	130.6	8.6	26.8	1.1	2.2	4.9	112.1	11.5	510.5	15.8	-37.3	-6.0	-13.8	
09/04/09	46	15.4	661	7.24	347.8	32.3	4.6	29.1	113.6	3.8	17.6		1.5	4.3	133.1	10.3	530.7	15.8	-37.4	-5.9		
22/04/09	47	15	710	7.52	355.1	37.1	4.9	27.3	117.3	6.6	22.0	1.0	2.0	4.6	126.0	6.2	517.8	15.0	-38.7	-6.0	-13.9	
06/05/09	48	15.2	706	7.53	355.1	34.2	3.8	26.2	122.7	6.8	21.0	0.8	1.6	4.1		22.5	516.7	15.5	-38.1	-6.0		
13/05/09	49	15.4	708	7.22	355.2	36.6	3.1	25.0	118.0	7.5	25.0	0.8	1.2	3.9		18.5	509.9	16.3	-37.5	-6.1		
25/05/09	50	16	721	7.18	361.2	40.6	3.6	25.5	121.1	7.7	26.1	1.2	1.5	4.1		18.2	499.9	15.4	-37.6	-5.9		
27/05/09	51	15.8	723	7.17	361.2	40.8	3.6	25.4	123.8	7.7	25.0	1.1	0.9	4.1		18.6	489.7	17.9	-37.8	-5.9	-14.0	
03/06/09	52	16	727	7.18	361.4	41.2	3.6	24.3	119.8	7.8	25.1	1.1	0.8	3.9		17.6	446.3	16.4	-37.2	-5.9	-13.9	
04/06/09	53	16	728	7.29	383.8	41.5	3.7	24.2	119.7	7.7	25.3	1.1	0.6	4.0		17.7	454.2	16.4	-37.3	-6.1	-10.1	
09/06/09	54	15.9	725	6.99	366.1	43.7	3.5	24.3	121.4	7.8	26.3	1.6	0.6	3.9		17.6	439.5	16.3	-37.1	-5.9	-13.6	
11/06/09	55	16.1	732	7.15	363.7	45.4	3.7	25.1	121.5	8.0	28.7	1.6	1.5	4.2		18.4	439.4	16.8	-36.8	-5.9	-13.7	
23/06/09	56	16.2	729	7.10	356.8	16.3	5.5	21.9	124.5	9.9	8.9	0.6	0.9	3.7		20.2	414.9	17.3	-36.0	-5.8	-13.9	
16/07/09	57	16.7	761	7.08	378.3	50.0	3.8	23.0	127.2	8.5	31.3	1.7	2.0	4.5	118.0	21.6	382.9	18.0	-35.4	-5.7	-13.2	0.70786
03/08/09	58	17	771		374.6	53.2	4.0	26.0	123.7	9.9	35.0	1.8	0.4	4.3		22.3	396.9	18.9	-35.2	-6.3	-13.4	
25/08/09	59	17.2	787	7.29	369.8	58.0	3.9	25.8	128.4	10.4	37.3	1.9	0.8	3.7		25.4	416.3	20.5	-35.3	-6.1	-13.2	
02/09/09	60	17.2	771	7.34	373.4	57.3	4.2	25.7	123.0	9.0	34.8	1.7	2.2	4.3	170.0	21.3	385.6	19.5	-35.3	-6.1	-13.1	
17/09/09	61	17.2	765	7.04	400.3	52.2	4.1	23.0	127.5	9.9	32.9	1.7	0.5	4.0	<LD	20.5	363.9	19.0			-13.1	
07/10/09	62	17.3	776	6.98	278.2	57.0	3.5	23.7	118.6	9.1	33.7	1.4	1.4	4.1		21.4	403.0	19.3	-35.1	-6.1		
22/10/09	63	17.2	749	7.00	361.2	52.7	3.5	23.1	115.5	8.9	31.2	1.4	0.4	4.2	88.9	20.5	367.3	19.5	-35.7	-6.3	-13.6	
24/10/09	64	15	811	7.15	341.7	74.5	4.9	32.5	111.4	10.8	44.5	2.1	<LD	5.4		25.8	514.0	21.8	-34.9	-6.1		
25/10/09	65	15	844	7.13	342.9	84.7	4.7	36.0	109.8	11.5	49.7	2.3		5.9	118.0	25.5	555.7	22.4	-34.5	-6.1		
26/10/09	66	17	898	6.98	342.9	98.6	4.2	40.4	110.4	12.9	58.9	2.5	1.6	5.0	118.0	25.2	649.1	21.1	-34.7	-6.2	-12.1	0.70792
29/10/09	67	16.5	705	6.97	349.0	40.3	4.1	29.0	111.9	10.1	23.5	1.4		4.2		24.9	585.0	19.5	-35.5	-6.2	-13.2	
05/11/09	68	16.2	698	6.97	346.6	37.4	5.6	24.6	113.4	8.5	22.0	1.6	0.8	7.3		26.6	625.9	23.9	-34.6	-5.9	-13.6	
01/12/09	69	16.8	636	6.90	360.0	56.1	5.5	25.3	116.5	8.4	33.4	1.5							-34.5	-6.0	-13.6	
16/12/09	70	17	639	7.18	363.7	41.8	3.9	18.9	112.7	9.3	33.2	1.6	0.6						-34.9	-6.0	-13.5	
07/01/10	71	15.8	702	7.17	336.8	41.4	8.6	26.4	107.9	7.8	24.3	1.8	1.3	3.7	50.0	22.0	637.6	17.5	-35.1	-5.8	-13.7	
25/01/10	72	15	712	7.24	350.3	42.1	8.3	26.7	123.7	6.0	24.4	1.6	1.3	3.3		18.4	548.8	14.4	-36.1	-6.2	-14.3	

Sampling date	Lez spring	T°C	CE	pH	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	toc	Li^+	Br^-	B^{3+}	Sr^{2+}	Ba^{2+}	δ^2H	$\delta^{18}O$	$\delta^{13}C$	$^{87}Sr/^{86}Sr$
		(°C)	(µS.cm)		(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(‰ V-SMOW)	(‰ V-SMOW)	TDIC (‰ V-PDB)	
11/03/10	73	14.7	629	7.10	339.2	34.0	5.1	28.0	126.1	6.2	20.1	1.2	1.6	3.8		21.3	536.1	14.5	-37.2	-6.4	-14.0	
22/03/10	74	14.9	699	7.09	358.7	36.5	4.5	27.8	122.4	6.5	21.5	1.2	1.1	3.8		20.9	473.7	14.3	-36.7	-6.2		
07/04/10	75	14.9	631	7.20	370.9	33.5	4.6	27.4	126.7	6.9	20.2	1.1	1.4	3.6		20.0	518.6	14.0	-36.3	-6.2		
20/04/10	76	15.3	706	7.03	355.1	40.1	4.0	27.6	125.1	7.3	23.9	1.4	0.9	4.0		18.9	511.8	14.4	-35.8	-6.2		
03/05/10	77	15.4	717	7.01	353.8	39.4	4.9	29.6	127.8	6.7	24.8	1.5	1.3	4.1		25.3	491.7	15.6	-36.2	-5.9		
27/05/10	78	15.5	692	7.23	356.4	35.5	3.5	27.0	121.2	6.5	19.6	1.1	0.9	3.9		20.8	501.6	14.8			-14.0	

Table 2 – T, EC , pH, major and trace element concentrations and isotopic ratios for Lirou, Restinclières, and Fleurettes springs and other sampling points.

Sampling date	Spring	T°C	CE	pH	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	toc	Li^+	Br^-	B^{3+}	Sr^{2+}	Ba^{2+}	δ^2H	$\delta^{18}O$	$\delta^{13}C$	$^{87}Sr/^{86}Sr$
		(°C)	(µS.cm)		(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(‰ V-SMOW)	(‰ V-SMOW)	TDIC (‰ V-PDB)	
02/06/08	Lirou	14.3	630	7.07	371.1	12.4	1.4	10.1	129.2	1.2	4.8	0.1	1.2	0.3		10.7	74.6	6.1	-28.7	-4.8		
05/06/08	Lirou	14.1	646	7.65	401.5	13.8	1.4	8.7	132.7	0.9	4.8	<LD	1.7	0.3		8.8	64.7	6.6	-30.4	-5.3		
24/06/08	Lirou			7.10	376.9	11.7	2.8	8.4	127.4	1.7	4.8	0.1	1.5						-30.8	-5.3		
21/10/2008 N°1	Lirou	14.8	613	7.07	375.8	11.1	2.7	10.7	111.7	10.3	5.7	0.5	3.2	1.1			138.9	8.8	-34.1	-5.8		
21/10/2008 N°2	Lirou	14.9	624	7.14	370.9	11.4	2.2	12.1	110.7	12.6	6.4	0.6	2.0	1.2	97.0		157.2	9.2	-34.6	-5.9		
23/10/08 N°1	Lirou	14.5	517	7.04	300.1	7.7	2.0	6.0	107.4	0.7	4.3	0.4	2.7	0.2	92.2		64.3	6.2	-23.3	-4.3		
23/10/08 N°2	Lirou	14.4	522	7.00	314.8	8.0	2.4	6.0	107.7	0.7	4.3	0.4	3.9	0.2	88.9		69.1	6.2	-23.3	-4.3	-14.9	
22/10/08	Lirou	14.6	544	7.09	327.0	10.2	4.2	7.2	109.3	1.3	5.0	0.5	4.1	0.4	103.8		79.5	6.1	-26.1	-4.7	-15.0	
24/10/08	Lirou	14.4	543	7.20	339.2	8.4	2.2	6.2	112.8	0.8	4.6	0.4	2.2	0.3	88.1	9.2	66.5	6.8	-24.5	-4.2		
27/10/08	Lirou	14.4	561	7.11	344.0	8.5	2.8	6.4	116.5	0.8	4.5	0.4	6.4	0.3	95.3		68.1	6.9	-24.3	-4.5		
29/10/08	Lirou	14.3	565	7.08	351.4	8.6	3.0	6.4	117.8	0.9	4.5	0.3	3.0	0.3	<LD		71.7	6.6	-24.9	-4.6		
03/11/08	Lirou	14.3	552	7.30	339.2	9.0	1.8	6.5	116.1	0.7	4.5	0.3	1.5	0.2	96.7		69.6	6.4	-25.1	-4.4		
05/11/08	Lirou	14.3	590	7.15	363.6	10.7	1.7	7.5	124.7	0.9	5.0	0.2	2.8	0.2	94.0		73.8	6.2	-26.1	-4.7		
07/11/08	Lirou	14.1	618	7.04	378.2	11.4	1.5	7.5	131.0	0.8	5.3	0.2	12.0	3.1	99.5	17.1	364.2	17.1	-28.2	-4.9	-13.5	0.70786
12/11/08	Lirou	14.2	622	7.11	388.0	10.9	1.6	7.7	131.3	1.3	5.2	0.2	8.5	0.3	<LD		65.9	7.4	-29.5	-5.1		
14/11/08	Lirou	14	631	7.18	388.1	11.7	2.0	9.0	131.8	1.7	5.3	0.2	2.5		101.4				-29.7	-5.0		
18/11/08	Lirou	14.2	619	7.12	369.8	11.4	1.8	8.2	136.6	2.4	5.4	0.2	1.5		96.9				-29.3	-5.2		
21/11/08	Lirou	14.2	631	7.14	375.3	11.1	2.1	8.7	132.1	2.4	5.3	0.1	0.9						-29.8	-5.1	-16.2	
09/01/09	Lirou	14.1	617	7.15	392.4	10.8	2.2	9.3	135.2	3.2	5.4	0.3	0.5	0.4	99.7	7.0	65.8	7.0	-35.5	-5.9	-15.8	
16/01/09	Lirou		590	7.20	387.5	10.4	1.9	8.3	133.1	3.6	5.3	0.2	0.4	0.3	104.9	6.9	61.6	6.8	-35.3	-5.8		
28/01/09	Lirou	14	593	7.30	367.3	8.9	1.8	7.6	126.0	1.5	5.2	0.2	1.3	0.2	88.6	6.6	64.2	6.5	-34.7	-6.2		
02/02/09	Lirou	13.3	522	7.83	324.6	7.5	1.1	7.0	106.4	0.9	4.5	0.2	2.1	0.2	80.3	7.2	60.1	6.0	-40.3	-6.9		
09/02/09	Lirou	14	599	7.39	374.4	8.9	1.1	6.0	128.7	1.8	5.1	<LD	1.8	0.3	88.6	5.9	50.6	6.6	-38.1	-6.5		
09/04/09	Lirou	15	556	6.99	349.0	9.3	3.5	8.1	111.6	<LD	4.7	<LD	1.6	0.5	100.4	0.4	83.7	7.1			-15.8	
13/05/09	Lirou	14.3	593	7.11	373.4	8.7	1.3	8.2	121.7	3.8	5.1	<LD	1.0	0.4		9.7	79.1	7.1			-15.9	

Sampling date	Spring	T°C (°C)	CE (µS.cm)	pH	HCO_3^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	toc (mg/l)	Li^+ (µg/l)	Br^- (µg/l)	B^{3+} (µg/l)	Sr^{2+} (µg/l)	Ba^{2+} (µg/l)	δ^2H (‰ V-SMOW)	$\delta^{18}O$ (‰ V-SMOW)	$\delta^{13}C$ TDIC (‰ V-PDB)	$^{87}Sr/^{86}Sr$
05/03/10	Lirou	15	517	7.29	358.7	9.0	0.9	8.0	113.0	2.9	5.0	0.4	0.8	0.5		10.2	81.0	7.1	-37.4	-6.6		
07/04/10	Lirou	14.1	544	7.10	374.5	9.8	1.3	8.6	131.2	2.6	5.2	0.3	1.1	0.4		9.1	74.2	6.5	-37.9	-6.6		
03/05/10	Lirou	14.4	627	6.95	388.0	9.0	1.8	12.7	135.0	5.5	5.5	0.3	1.3	0.8		12.4	118.0	6.9	-35.5	-5.6		
27/05/10	Lirou	14.5	600	7.15	375.9	9.2	1.7	8.3	127.1	2.7	5.0	0.3	0.5	0.4		10.0	82.7	6.9			-15.9	
12/11/08	Restinclières	17.6	669	6.61	395.3	13.3	7.3	16.7	130.1	5.2	6.0	0.3	5.2	2.4		15.3	406.4	25.6	-29.8	-5.2	-14.6	
14/11/08	Restinclières	17.1	674	7.05	375.8	14.9	7.8	19.1	131.6	5.8	6.8	0.4	4.8	2.5	101.5	15.8	398.8	26.6	-31.4	-5.1		0.70756
18/11/08	Restinclières	17.2	669	7.06	382.6	16.6	8.4	21.6	139.7	6.6	7.9	0.5	5.9	2.5	109.9	16.1	400.0	27.7	-31.1	-5.2		
21/11/08	Restinclières	16.7	655	7.17	360.6	17.9	8.6	22.4	129.5	6.8	8.8	0.6	1.3	2.4	110.4	15.3	348.6	21.1	-30.3	-5.3		
05/12/08	Restinclières	16.6	634	7.17	362.5	16.5	6.9	19.9	121.8	6.5	8.3	0.5	2.3	2.2	114.4	14.0	306.4	19.0	-30.0	-5.2	-13.8	
16/12/08	Restinclières	17.6	719	7.20	430.2	27.7	9.4	27.7	133.9	8.5	14.7	1.0	1.2	3.2	<LD	21.4	429.2	24.7	-32.2	-5.1		
09/01/09	Restinclières	17.1	670	6.92	416.2	14.3	8.1	19.7	137.1	6.5	7.1	0.4	1.1	2.5	<LD	17.0	415.7	26.3	-33.2	-5.6		
16/01/09	Restinclières	16.5	673	7.09	393.0	15.4	8.1	21.8	139.5	6.6	7.6	0.4	0.9	2.4	<LD	16.1	386.8	25.2	-34.0	-5.9		
28/01/09	Restinclières	15.9	611	7.29	336.8	16.3	6.8	21.3	128.5	7.0	8.4	0.4		2.2	<LD	14.1	313.7	19.3	-33.5	-5.9		
02/02/09	Restinclières	16.8	675	7.07	397.9	12.5	6.8	17.7	132.3	5.4	6.5	0.3	1.7	2.1	<LD	13.4	357.2	23.1	-35.9	-6.1	-15.0	
09/02/09	Restinclières	16.2	673	7.22	397.9	12.4	5.1	18.3	132.7	4.9	6.5	0.2	1.7	2.0	106.2	13.1	355.0	26.4	-35.8	-6.1		
26/02/09	Restinclières	16.5	669	7.11	391.8	13.1	6.1	19.9	136.0	5.6	6.7	0.3	1.2	2.2	103.8	13.9	352.7	24.2	-38.2	-6.5		
12/03/09	Restinclières	16.5	649	7.38	361.2	15.8	8.5	22.9	125.3	6.6	8.3	0.4	1.2	2.4	<LD	14.8	317.3	23.1				
27/03/09	Restinclières	17	706	7.38	373.4	21.9	7.0	25.2	138.2	9.3	12.4	1.0	1.8	2.7	116.0	18.3	389.5	24.6	-35.8	-6.1		
09/04/09	Restinclières	17.5	706	7.07	373.4	29.0	5.8	25.9	133.2	5.5	9.2	1.1	1.6	4.7	116.1	13.8	517.8	27.5	-35.5	-6.2		
22/04/09	Restinclières	17.1	620	7.01	367.3	15.0	5.8	22.7	116.0	3.9	7.4	<LD	1.6	3.3	<LD	6.3	400.2	22.9	-36.1	-6.1		
06/05/09	Restinclières	16.7	658	7.42	373.4	14.0	5.8	22.5	122.7	5.9	7.2	0.3	2.1	3.2	360.5	2.4	413.6	25.1	-36.9	-6.2	-13.8	
13/05/09	Restinclières	16.5	614	7.54	355.1	14.9	4.3	19.8	118.0	6.2	7.4	0.2	2.0	2.5		18.9	343.4	20.2	-36.4	-6.2		
25/05/09	Restinclières	17.2	637	7.12	361.2	13.8	5.7	20.8	120.1	7.4	8.2	0.1	1.2	2.8		17.9	367.0	22.5	-36.5	-6.1		
27/05/09	Restinclières	17.5	702	7.14	379.5	26.8	5.3	24.5	123.2	8.6	15.7	0.8	0.9	3.8		18.7	471.4	25.3	-36.0	-5.8		
03/06/09	Restinclières	17.5	697	7.12	379.5	26.9	5.2	24.4	123.1	8.4	15.7	0.8	0.9	3.7		18.4	469.3	25.5	-36.2	-6.1		
09/06/09	Restinclières	18	704	7.16	378.2	27.8	5.3	25.5	124.5	9.0	16.2	0.8	0.9	3.9		18.2	479.4	27.5	-36.1	-6.2		
23/06/09	Restinclières	18.3	693	6.92	391.1	21.9	5.9	25.5	127.2	9.1	12.6	0.6	0.8	3.8		19.4	493.9	31.7	-36.3	-6.1	-13.7	
25/01/10	Restinclières	18.6	706	7.06	375.7	16.5	5.6	22.1	125.8	10.0	9.0	0.6	0.8	3.2		18.4	433.8	33.5	-35.0	-5.8	-13.3	
08/02/10	Restinclières	16.4	628	7.26	345.4	16.5	8.2	20.7	124.0	6.1	8.2	0.7	1.1	1.6		13.3	328.5	17.0	-35.8	-6.2		
22/02/10	Restinclières	16.9	681	6.91	390.5	13.3	7.3	19.8	142.4	5.6	7.4	0.5	1.4	1.9		14.9	454.7	21.4				
11/03/10	Restinclières	16.6	656	6.96	386.7								2.1	2.3		16.4	422.3	24.5	-38.0	-6.2		
22/03/10	Restinclières	16.4	594	6.98	367.3	15.2	5.7	23.3	131.3	5.9	7.8	0.6	1.1	2.7		18.8	374.2	23.8	-37.9	-6.2		
07/04/10	Restinclières	16.2	616		352.6	14.9	5.3	21.1	125.8	6.5	8.1	0.6	0.8	2.3		18.2	308.3	19.0	-37.2	-6.0		
20/04/10	Restinclières	16.2	580	7.18	361.1	15.4	5.7	23.7	127.5	6.5	8.2	0.6	1.1	2.5		18.4	360.3	21.0	-36.0	-5.9		
03/05/10	Restinclières	17	665	7.02	360.0	21.1	8.4	27.6	129.2	7.7	11.3	1.0	1.5	3.1		23.9	420.5	24.3	-35.6	-6.0		
20/05/10	Restinclières	17.1	683	6.91	374.5	22.9	6.3	27.8	131.8	8.2	13.2	0.8	1.4	3.7		22.5	464.6	23.8	-35.7	-5.8		
27/05/10	Restinclières	16.6	624	7.00	357.6	15.3	5.1	24.3	134.2	6.9	8.4	0.6	1.4	2.7		19.0	355.5	21.2				

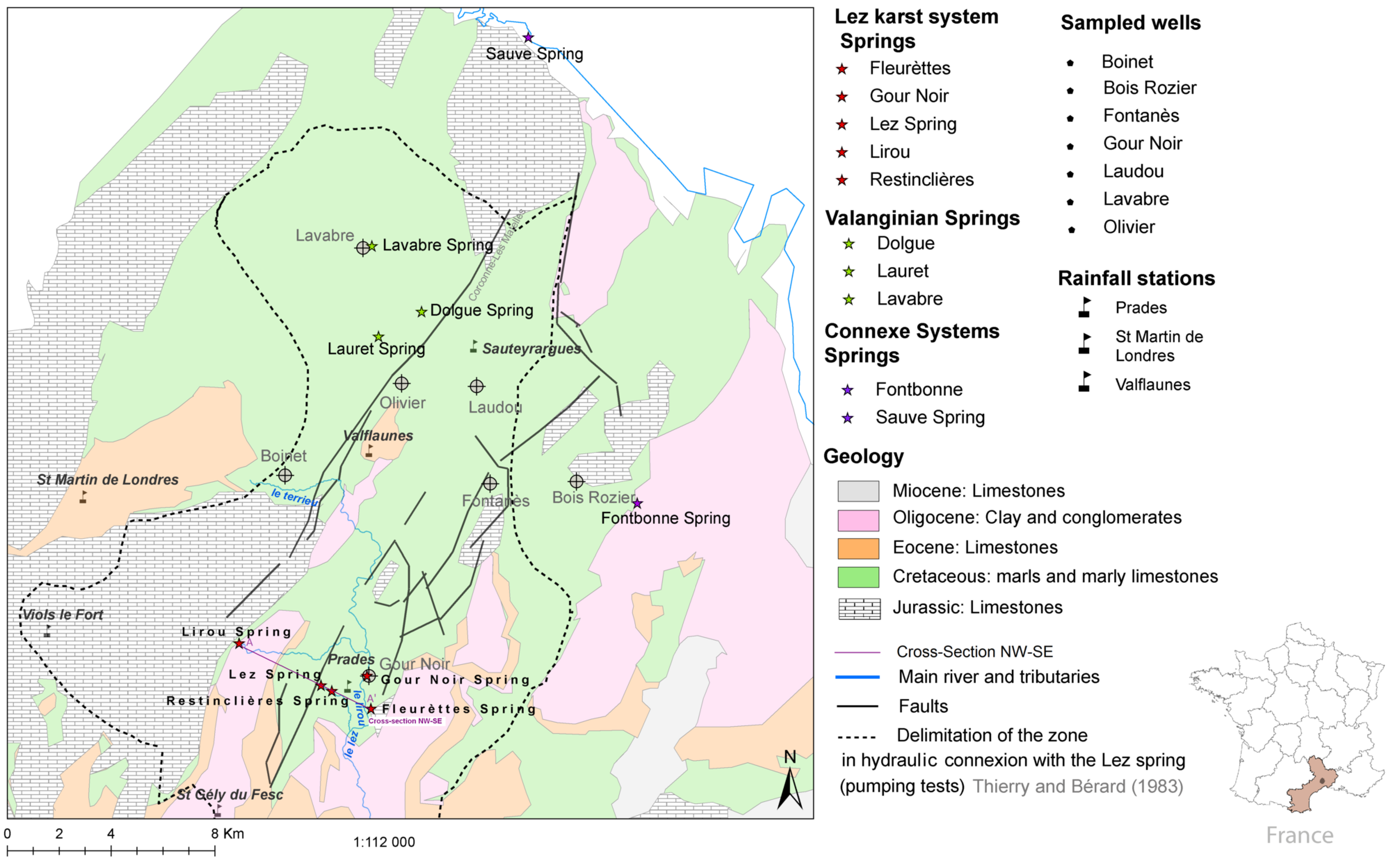
Sampling date	*Spring*	T°C (°C)	CE (µS.cm)	pH	HCO_3^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	toc (mg/l)	Li^+ (µg/l)	Br^- (µg/l)	B^{3+} (µg/l)	Sr^{2+} (µg/l)	Ba^{2+} (µg/l)	δ^2H (‰ V-SMOW)	$\delta^{18}O$ (‰ V-SMOW)	$\delta^{13}C$ TDIC (‰ V-PDB)	$^{87}Sr/^{86}Sr$
05/11/08	Fleurettes	15.5	649	6.98	385.5	11.5	3.4	21.0	132.2	2.3	5.1	0.2	3.3	1.5	89.0	12.7	231.6	10.2	-28.8	-5.0		
07/11/08	Fleurettes	14	677	6.98	405.0	12.4	5.1	20.1	138.1	3.3	5.7	0.3	2.3	1.9	102.4	13.5	302.4	15.7	-30.0	-5.1	-15.2	
09/11/08	Fleurettes	16.3	672	7.04	380.6	13.3	6.9	19.2	134.7	4.4	6.0	0.3	1.9	2.2	103.0	15.2	374.5	24.8	-31.7	-5.2		
12/11/08	Fleurettes	16.6	668	7.08	390.4	13.6	6.1	20.3	132.8	5.0	6.1	0.4	5.1	2.4	104.6	15.8	399.9	32.2	-32.0	-5.3		
14/11/08	Fleurettes	16.6	669	7.00	388.1	14.9	6.1	22.6	143.9	5.8	7.0	0.5	5.6	2.4	102.7	16.0	390.1	33.4	-31.9	-5.2		
18/11/08	Fleurettes	16.4	680	8.55	389.9	14.6	5.7	21.7	140.8	5.9	7.1	0.5	1.5	2.4	109.4	15.8	390.8	33.5	-31.6	-5.3	-14.5	
09/01/09	Fleurettes	16.4	662	7.06	356.4	14.6	6.0	22.5	140.5	5.9	7.2	0.4	1.1	2.4		16.0	397.9	31.4	-34.2	-6.0		
02/02/09	Fleurettes	15	568	7.22	336.8	7.8	2.5	16.8	114.4	1.7	4.9	0.4	2.1	1.1	84.3	12.0	185.1	9.9	-44.0	-7.4		
22/04/09	Fleurettes	16.1	668	7.17	385.7	13.2	4.7	23.3	129.0	5.4	6.7	0.4	1.8	3.0	102.2	1.6	418.9	31.1	-39.3	-6.5	-14.2	
09/02/09	Fleurettes	16	651	7.17	379.5	13.4	4.7	20.8	131.1	5.8	7.1	0.4	1.8	2.3	358.0	14.6	350.0	25.6	-37.0	-6.2		
08/02/10	Fleurettes	16.4	678	6.97	386.9	13.0	7.2	22.9	136.8	3.2	6.3	0.4	1.5	2.3		17.2	419.0	20.6	-36.1	-6.2		
22/02/10	Fleurettes	15.7	646	6.91	378.3								1.7	1.9		15.9	357.3	20.7	-38.4	-6.4		
11/03/10	Fleurettes	15.5	608	6.92	380.6	13.9	5.1	25.0	140.2	5.4	7.2	0.6	1.5	2.5		18.4	351.1	28.0	-37.7	-6.2		
07/04/10	Fleurettes	16.3	628	7.09	402.6	14.8	5.5	24.8	143.7	6.5	7.5	0.5	2.1	2.7		18.9	445.6	32.6	-37.1	-6.0		
03/05/10	Fleurettes	16.8	678	7.00	388.0	14.3	4.8	28.6	141.5	6.9	7.9	0.5	2.2	3.2		20.3	459.0	32.9	-35.7	-5.9		
20/05/10	Fleurettes	16	673	6.99	401.5	12.7	4.9	23.6	150.6	6.1	7.0	0.5	1.7	2.7		17.8	407.8	29.4				
16/07/09	Sauve spring	14.2	518	7.33	286.8	9.0	2.7	36.6	82.9	16.6	6.9	1.7	1.6	2.1	<LD	17.9	244.6	28.8	-34.8	-5.8	-13.9	0.70854
16/07/09	Fontbonne spring	18	629	7.43	366.6	11.3	5.4	16.6	129.4	5.0	5.2	0.2	1.0	1.9	<LD	13.0	277.2	9.1	-35.8	-5.7	-13.2	0.70764
21/07/09	Olivier well	18.6	677	7.84	341.8	17.2	25.9	28.7	107.2	20.3	8.8	1.3	1.3	9.3	154.9	56.5	1998.0	24.0	-35.9	-6.0	-10.9	0.70737
21/07/09	Boinet well	15.7	859	7.08	488.2	25.4	19.2	33.9	149.7	19.5	9.3	0.4	1.8	7.9	192.4	54.0	3266.0	16.0	-32.6	-6.3	-14.3	0.70733
21/07/09	Foux de Lauret	13.8	583	7.51	379.1	5.7	1.0	10.5	119.4	4.0	4.0	0.4	1.3	0.9	83.3	10.8	456.7	7.5	-38.5	-6.0	-15.0	0.70745
21/07/09	Dolgue spring	13.2	708	7.32	426.5	13.9	1.0	26.8	140.4	8.2	5.8	0.2	1.7	3.5	177.0	21.7	862.6	13.5	-35.6	-6.0	-16.0	0.70744
21/07/09	Lavabre spring	14	637	7.38	403.3	8.0		14.3	129.2	6.0	5.0	0.1	1.2	2.2	151.9	18.6	821.0	9.3	-36.8	-5.9	-16.4	0.70742
21/07/09	Lavabre well	18.5	640	7.16	424.0	10.8		19.0	126.1	6.5	6.0	0.7	1.0	2.5	140.0	15.6	666.5	9.4	-35.9	-6.0	-16.3	
31/08/09	Fontanes well	15.3	649	7.01	401.5	10.4	6.7	21.2	133.2	5.4	5.5	0.5	0.6	3.9	160.0	19.6	410.2	10.7	-34.1	-5.8	-13.5	0.70760
31/08/09	Laudou well	14.9	661	6.99	422.3	11.6		11.2	132.2	0.7	4.8	0.9	5.0	1.3	240.0	11.9	327.1	13.0	-36.2	-6.2	-15.8	0.70756
31/08/09	Bois Roziers well	15.8	605	7.07	375.9	10.4	3.5	16.0	128.2	3.1	6.5	0.6	1.0	1.6	150.0	13.8	329.4	9.2	-35.6	-6.0	-14.3	0.70761
02/09/09	Gour Noir well	17.4	664	7.23	407.6	13.0	3.4	14.8	137.5	3.4	7.5	0.8	1.8	2.2	<LD	16.2	296.8	15.3	-35.7	-5.9	-14.7	0.70764

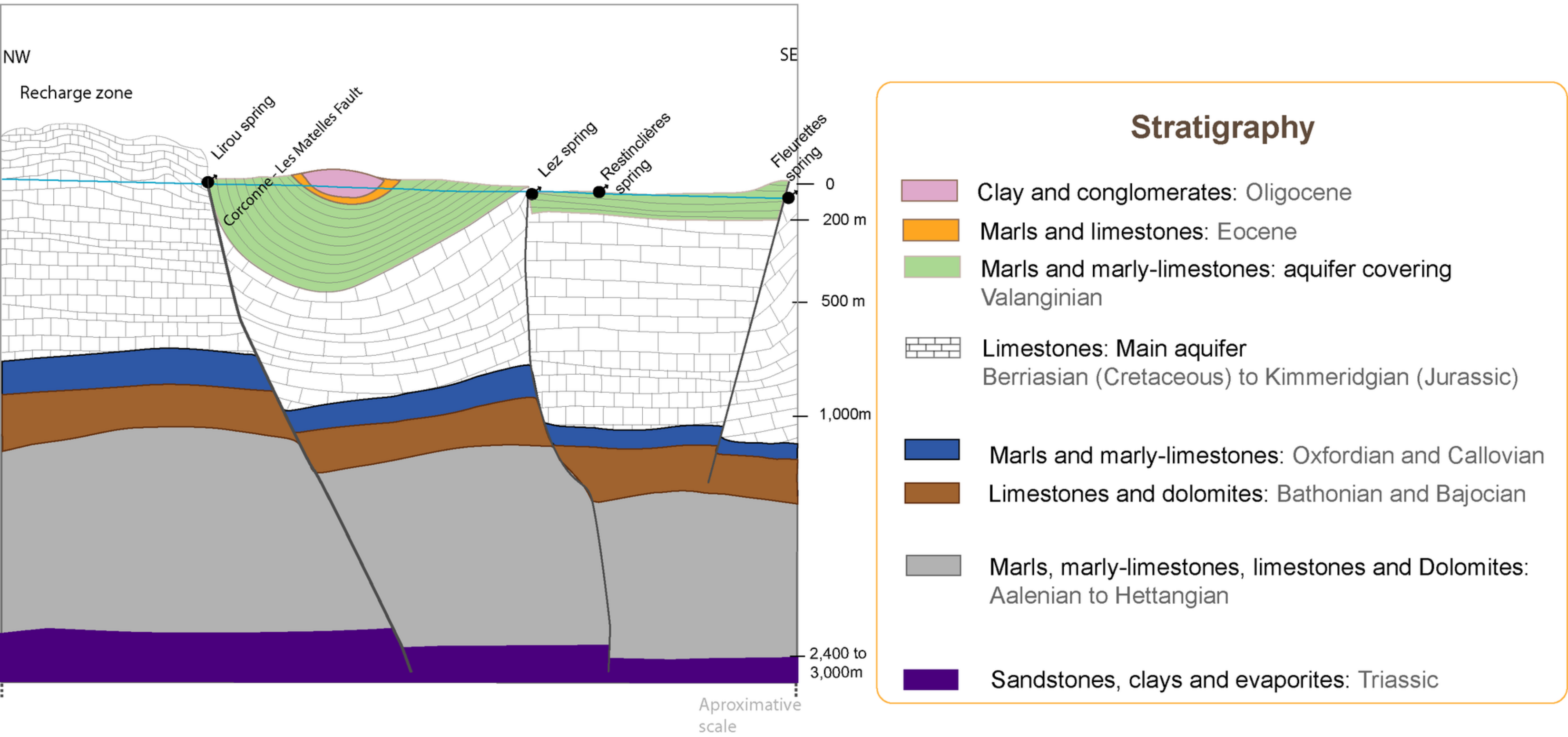
Table 3 – Average values and range of variations for T, EC, pH, major and trace element concentrations and isotopic ratios for the springs: Lez, Lirou, Restinclières and Fleurettes.

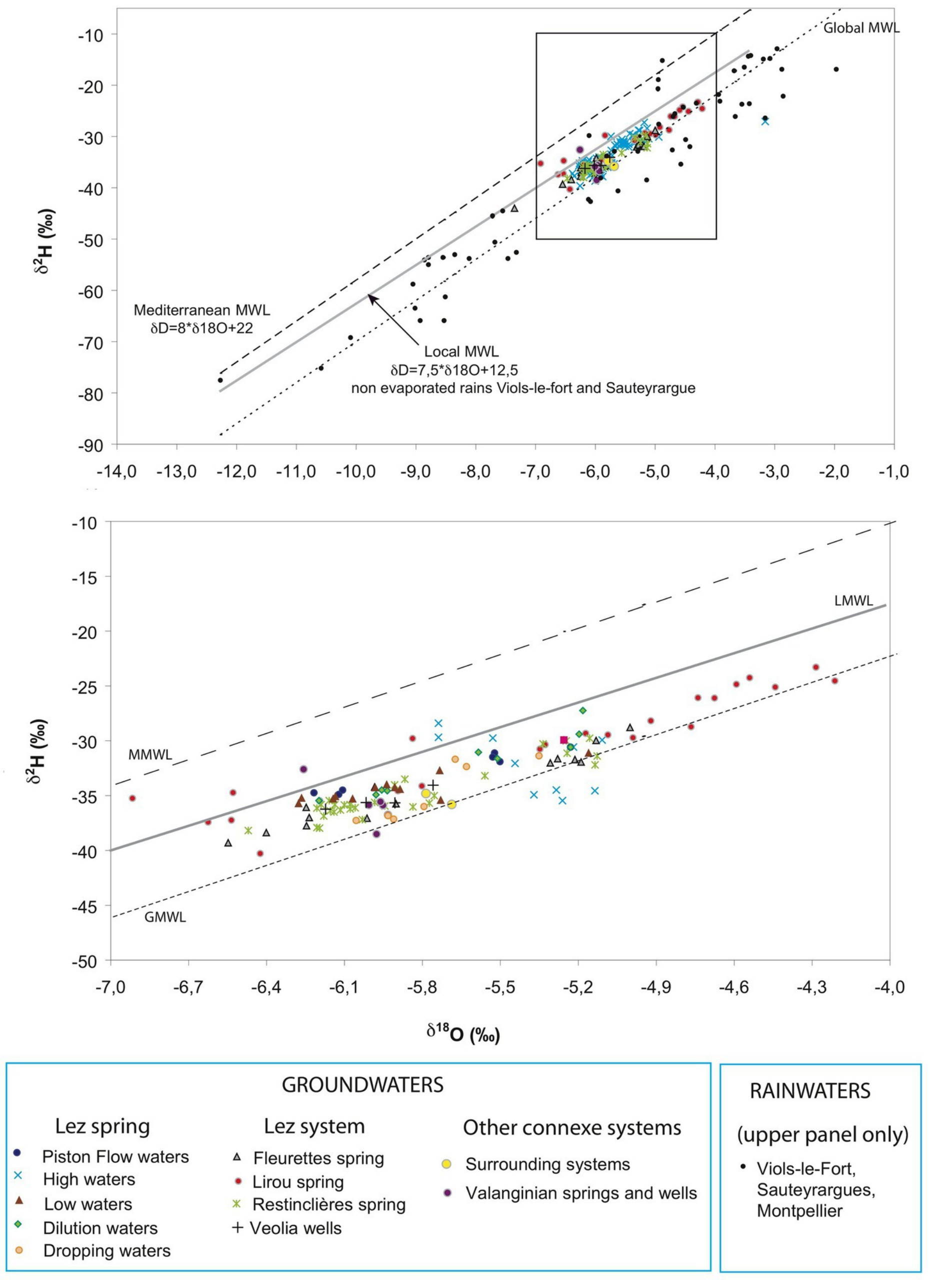
Spring	*Average and range*	T°C (°C)	CE (µS.cm)	pH	HCO_3^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	toc (mg/l)	Li^+ (µg/l)	Br^- (µg/l)	B^{3+} (µg/l)	Sr^{2+} (µg/l)	Ba^{2+} (µg/l)	δ^2H (‰ V-SMOW)	$\delta^{18}O$ (‰ V-SMOW)	$\delta^{13}C$ TDIC (‰ V-PDB)
Lez *(78 samples)*	Average	16.1	725	7.14	353.6	45.3	5.1	26.6	120.1	8.0	26.8	1.4	1.7	4.0	111.0	17.7	454.8	17.1	-33.6	-5.7	-13.3
	Minimum	14.0	599	6.89	271.5	16.3	3.1	18.9	105.9	3.8	8.9	0.6	0.3	0.2	50.0	5.9	62.1	6.7	-39.6	-6.4	-14.7
	Maximum	17.3	898	7.53	400.3	98.6	8.6	40.4	140.1	12.9	58.9	2.6	5.6	7.3	170.0	26.6	649.1	23.9	-27.1	-3.2	-10.1
Lirou *(29 samples)*	Average	14.3	585	7.17	363.5	10.0	2.0	8.1	122.6	2.5	5.0	0.3	2.6	0.5	95.1	8.7	90.0	7.2	-30.7	-5.3	-15.4
	Minimum	13.3	517	6.95	300.1	7.5	0.9	6.0	106.4	0.7	4.3	0.1	0.4	0.2	80.3	0.4	50.6	6.0	-40.3	-6.9	-16.2
	Maximum	15.0	646	7.83	401.5	13.8	4.2	12.7	136.6	12.6	6.4	0.6	12.0	3.1	104.9	17.1	364.2	17.1	-23.3	-4.2	-13.5
Restinclières *(33 samples)*	Average	17.0	661	7.1	375.9	17.8	6.6	22.4	129.3	6.8	9.3	0.6	1.7	2.8	137.6	16.2	395.6	24.1	-34.9	-5.9	-14.0
	Minimum	15.9	580	6.6	336.8	12.4	4.3	16.7	116.0	3.9	6.0	0.1	0.8	1.6	101.5	2.4	306.4	17.0	-38.2	-6.5	-15.0
	Maximum	18.6	719	7.5	430.2	29.0	9.4	27.8	142.4	10.0	16.2	1.1	5.9	4.7	360.5	23.9	517.8	33.5	-29.8	-5.1	-13.3
Fleurettes *(16 samples)*	Average	16.0	655	7.1	383.5	13.2	5.3	22.2	136.7	4.9	6.6	0.4	2.3	2.3	128.4	15.1	367.6	25.8	-35.0	-5.9	-14.7
	Minimum	14.0	568	6.9	336.8	7.8	2.5	16.8	114.4	1.7	4.9	0.2	1.1	1.1	84.3	1.6	185.1	9.9	-44.0	-7.4	-15.2
	Maximum	16.8	680	8.6	405.0	14.9	7.2	28.6	150.6	6.9	7.9	0.6	5.6	3.2	358.0	20.3	459.0	33.5	-28.8	-5.0	-14.2

Table 4 – Water stable isotope range for the sampled springs and raingauges and water stable isotope weighted average for rainwater.

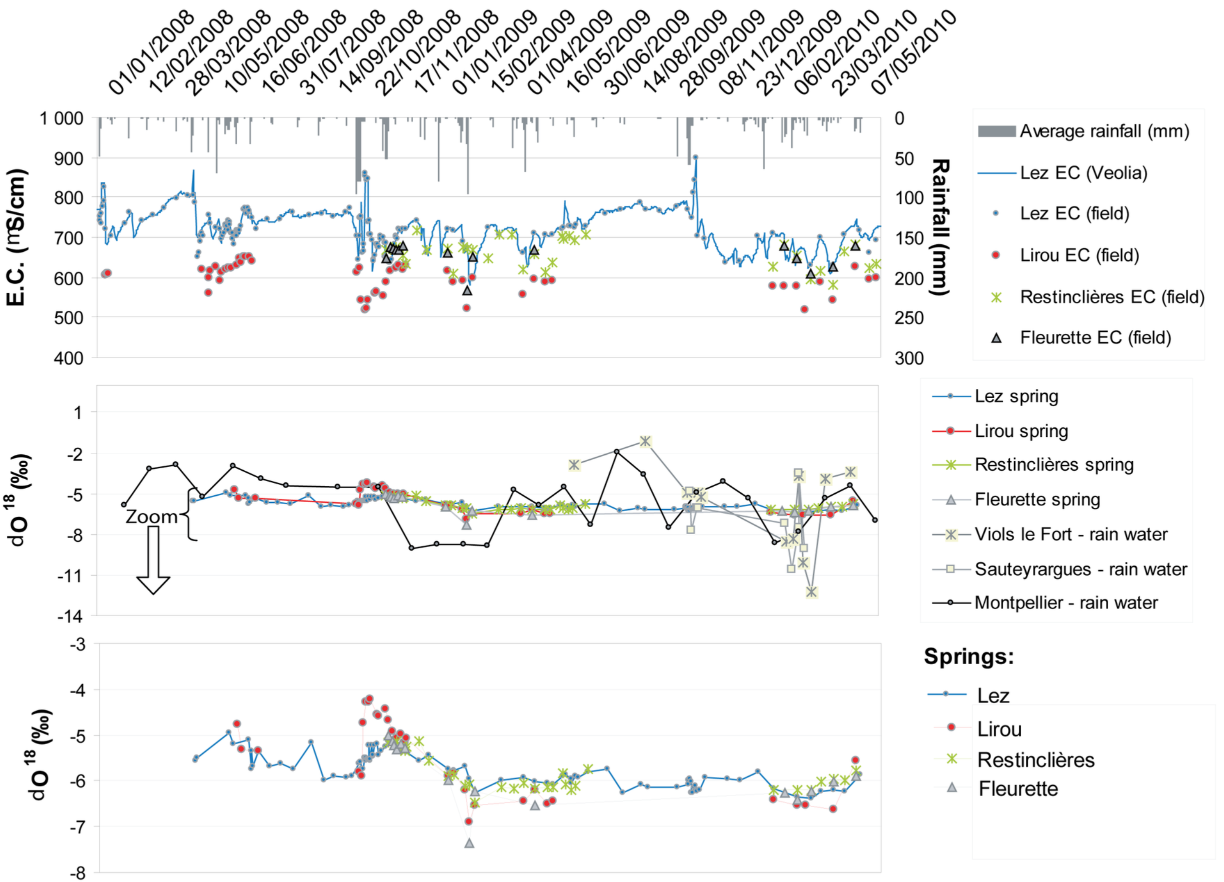
Springs / raingauges	$\delta^{18}O$ range (‰ VSMOW)	$\delta^{2}H$ range (‰ VSMOW)	$\delta^{18}O$ (‰ VSMOW) Rainwater weighted average	$\delta^{2}H$ (‰ VSMOW) Rainwater weighted average
Lez spring	-6.38 to -4.94	-39.6 to -30.1		
Lirou spring	-6.92 to -4.21	-40.3 to -23.3		
Restinclières spring	-6.47 to -5.13	-38.2 to -29.8		
Fleurettes spring	-7.35 to -5.00	-44.0 to -28.8		
Viols le Fort raingauge (06/09 to 05/10)	-12.27 to -2.88	-53.6 to -14.2	-4.93	-28.3
Sauteyrargues raingauge (10/09 to 05/10)	-10.59 to -3.44	-63.4 to -14.5	-7.55	-46.7
Montpellier raingauge (monthly means, 06/08 to 05/10)	-9.05 to +0.67	-58.8 to +5.6	-6.76	-41.4

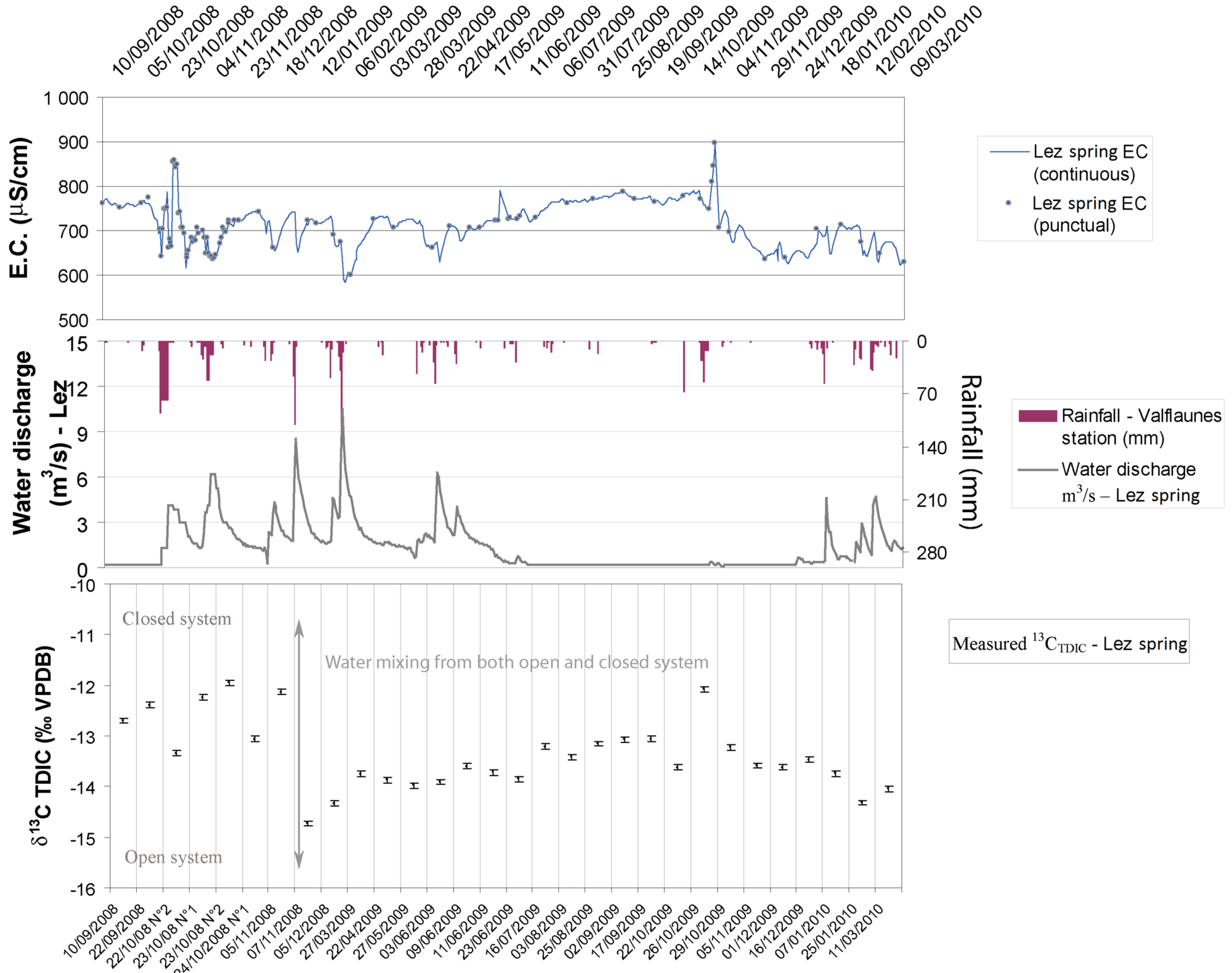

Lez karst system Springs
Fleurèttes
Gour Noir
Lez Spring
Lirou
Restinclières
Valanginian Springs
Dolgue
Lauret
Lavabre
Connexe Systems Springs
Fontbonne
Sauve Spring
Sampled wells
Boinet
Bois Rozier
Fontanès
Gour Noir
Laudou
Lavabre
Olivier
Rainfall stations
Prades
St Martin de Londres
Valflaunes
Geology
Miocene: Limestones
Oligocene: Clay and conglomerates
Eocene: Limestones
Cretaceous: marls and marly limestones
Jurassic: Limestones
Cross-Section NW-SE
Main river and tributaries
Faults
Delimitation of the zone in hydraulic connexion with the Lez spring (pumping tests) Thierry and Bérard (1983)
France
Sauve Spring
Lavabre
Lavabre Spring
Coronne-Les Matelles
Dolgue Spring
Lauret Spring
Sauteyrargues
Olivier
Laudou
Valflaunes
Boinet
St Martin de Londres
le terrieu
Fontanès
Bois Rozier
Fontbonne Spring
Viols le Fort
Lirou Spring
Prades
Gour Noir
Lez Spring
Gour Noir Spring
Restinclières Spring
Fleurèttes Spring
Cross-section NW-SE
le lirou
le lez
St Gély du Fesc
N
0
2
4
8 Km
1:112 000


NW
SE
Recharge zone
Lirou spring
Corconne - Les Matelles Fault
Lez spring
Restinclières spring
Fleurettes spring
0
200 m
500 m
1,000m
2,400 to 3,000m
Aproximative scale
Stratigraphy
Clay and conglomerates: Oligocene
Marls and limestones: Eocene
Marls and marly-limestones: aquifer covering Valanginian
Limestones: Main aquifer Berriasian (Cretaceous) to Kimmeridgian (Jurassic)
Marls and marly-limestones: Oxfordian and Callovian
Limestones and dolomites: Bathonian and Bajocian
Marls, marly-limestones, limestones and Dolomites: Aalenian to Hettangian
Sandstones, clays and evaporites: Triassic

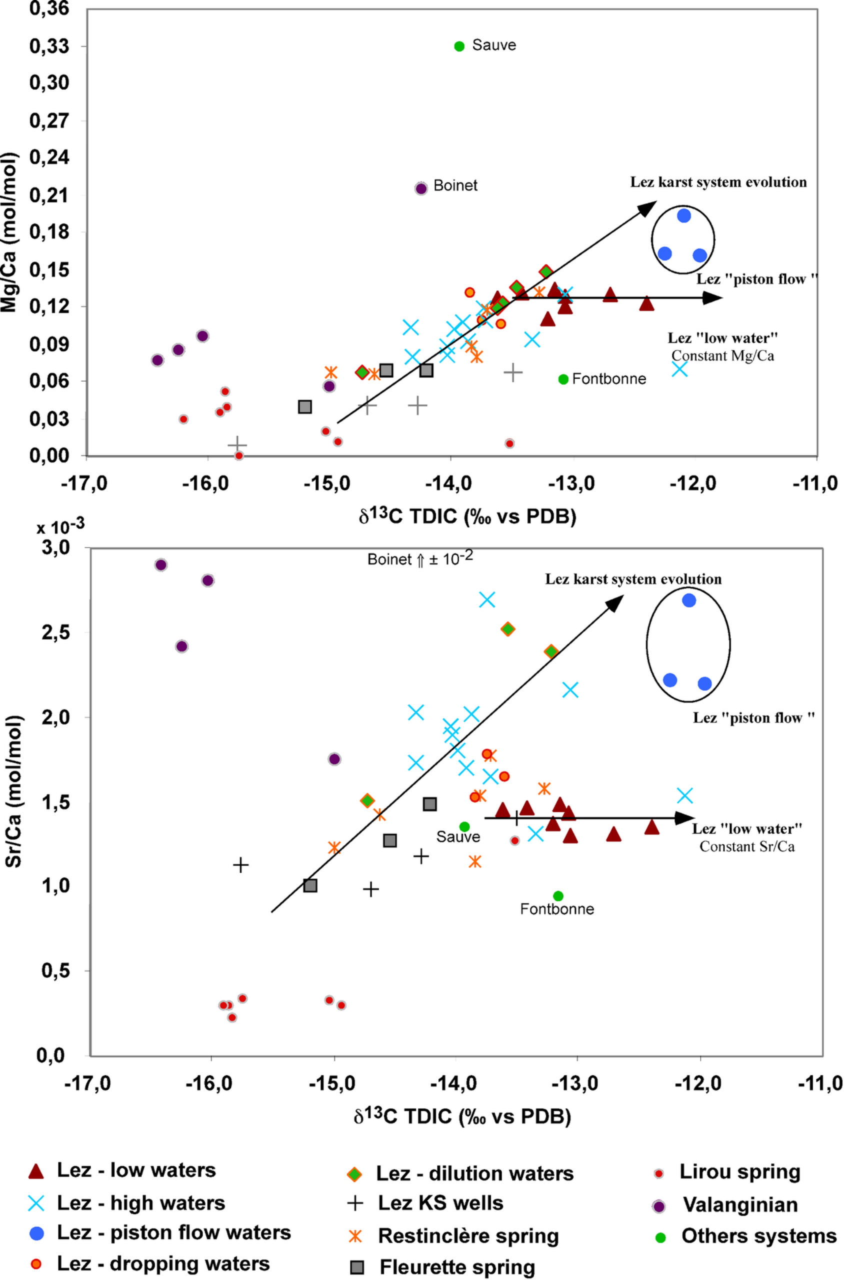


Global MWL
Mediterranean MWL
δD=8*δ18O+22
Local MWL
δD=7,5*δ18O+12,5
non evaporated rains Viols-le-fort and Sauteyrargue
δ²H (‰)
LMWL
MMWL
GMWL
δ¹⁸O (‰)
GROUNDWATERS
Lez spring
Piston Flow waters
High waters
Low waters
Dilution waters
Dropping waters
Lez system
Fleurettes spring
Lirou spring
Restinclières spring
Veolia wells
Other connexe systems
Surrounding systems
Valanginian springs and wells
RAINWATERS
(upper panel only)
Viols-le-Fort, Sauteyrargues, Montpellier

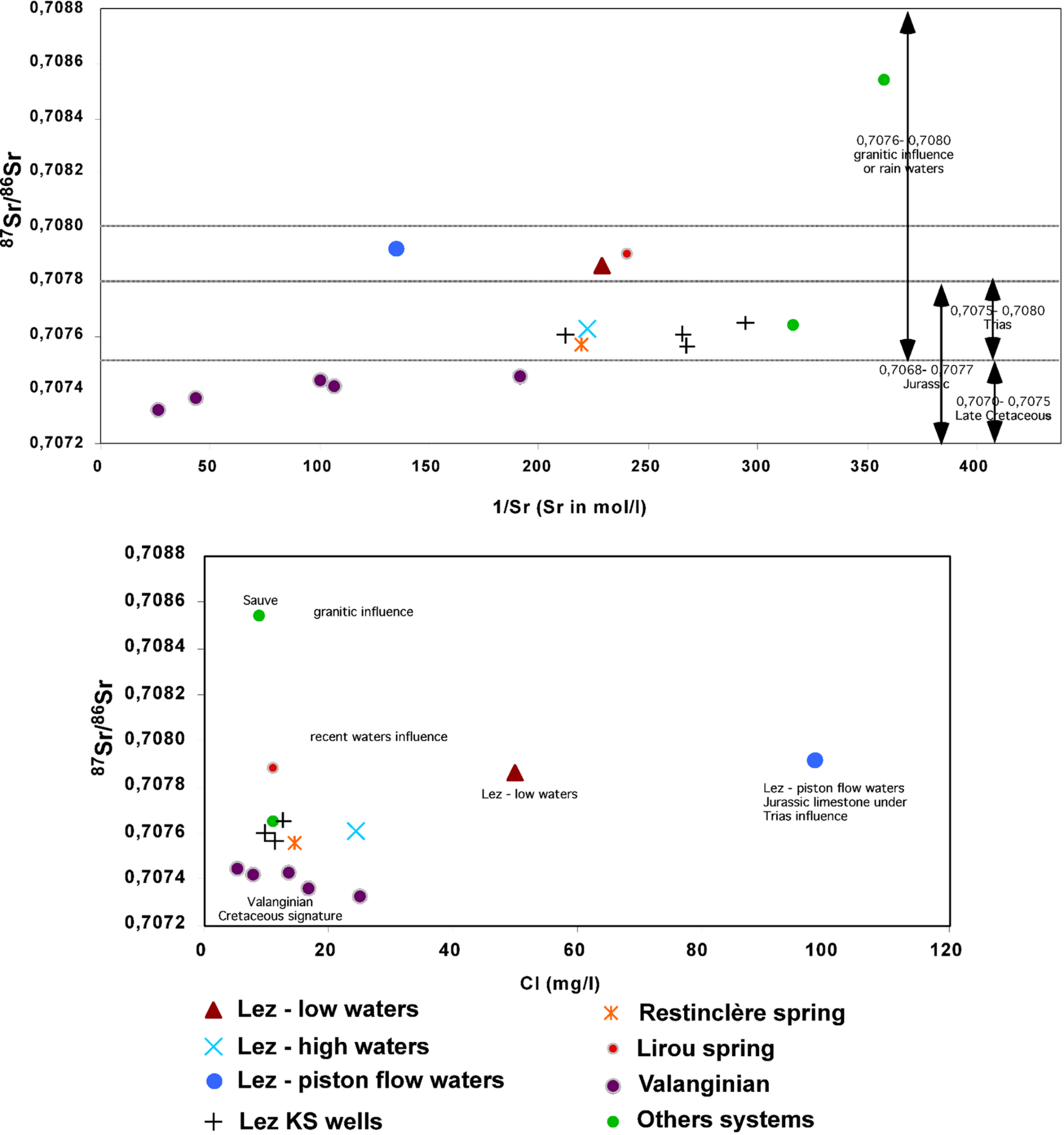

01/01/2008
12/02/2008
28/03/2008
10/05/2008
16/06/2008
31/07/2008
14/09/2008
22/10/2008
17/11/2008
01/01/2009
15/02/2009
01/04/2009
16/05/2009
30/06/2009
14/08/2009
28/09/2009
08/11/2009
23/12/2009
06/02/2010
23/03/2010
07/05/2010
E.C. (mS/cm)
Rainfall (mm)
Average rainfall (mm)
Lez EC (Veolia)
Lez EC (field)
Lirou EC (field)
Restinclières EC (field)
Fleurette EC (field)
dO 18 (‰)
Zoom
Lez spring
Lirou spring
Restinclières spring
Fleurette spring
Viols le Fort - rain water
Sauteyrargues - rain water
Montpellier - rain water
Springs:
Lez
Lirou
Restinclières
Fleurette



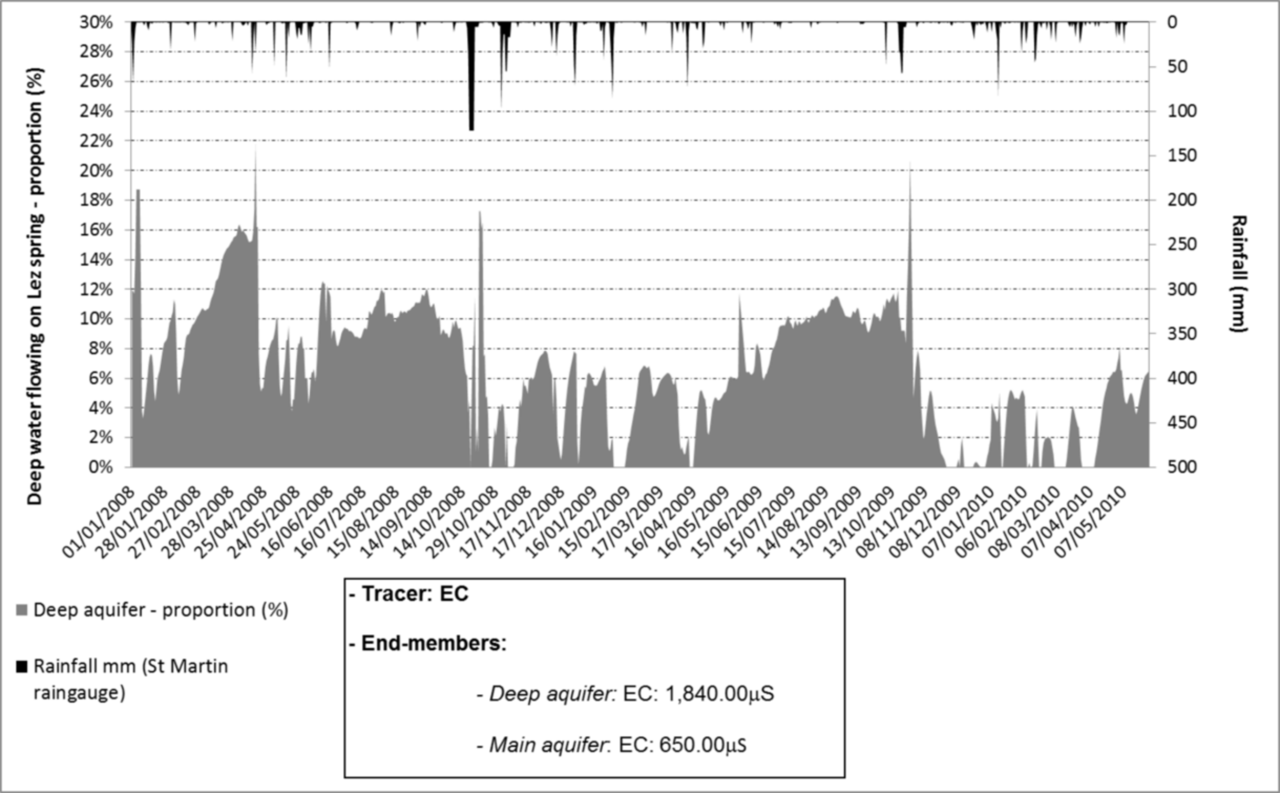
10/09/2008
05/10/2008
23/10/2008
04/11/2008
23/11/2008
18/12/2008
12/01/2009
06/02/2009
03/03/2009
28/03/2009
22/04/2009
17/05/2009
11/06/2009
06/07/2009
31/07/2009
25/08/2009
19/09/2009
14/10/2009
04/11/2009
29/11/2009
24/12/2009
18/01/2010
12/02/2010
09/03/2010
E.C. (µS/cm)
Lez spring EC (continuous)
Lez spring EC (punctual)
Water discharge (m³/s) - Lez
Rainfall (mm)
Rainfall - Valflaunes station (mm)
Water discharge m³/s – Lez spring
δ13C TDIC (‰ VPDB)
Closed system
Open system
Water mixing from both open and closed system
Measured 13C TDIC - Lez spring
10/09/2008
22/09/2008
22/10/08 N°2
23/10/08 N°1
23/10/08 N°2
24/10/2008 N°1
05/11/2008
07/11/2008
05/12/2008
27/03/2009
22/04/2009
27/05/2009
03/06/2009
09/06/2009
11/06/2009
23/06/2009
16/07/2009
03/08/2009
25/08/2009
02/09/2009
17/09/2009
22/10/2009
26/10/2009
29/10/2009
05/11/2009
01/12/2009
16/12/2009
07/01/2010
25/01/2010
11/03/2010

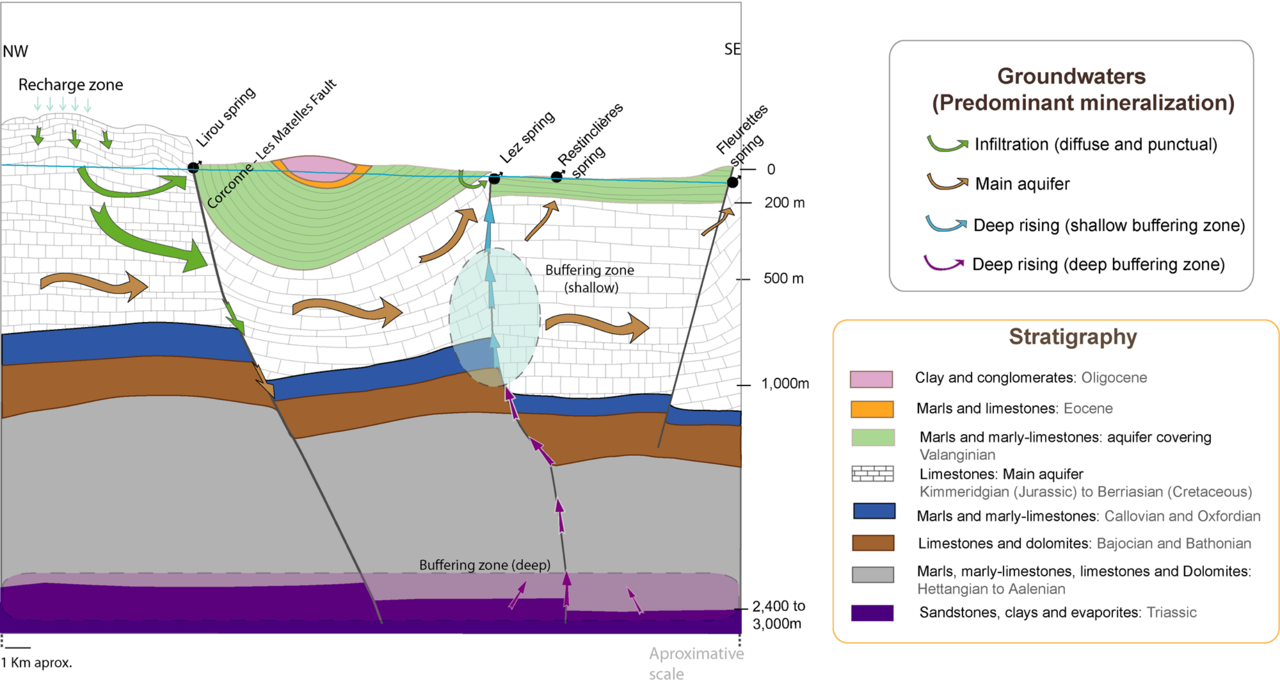


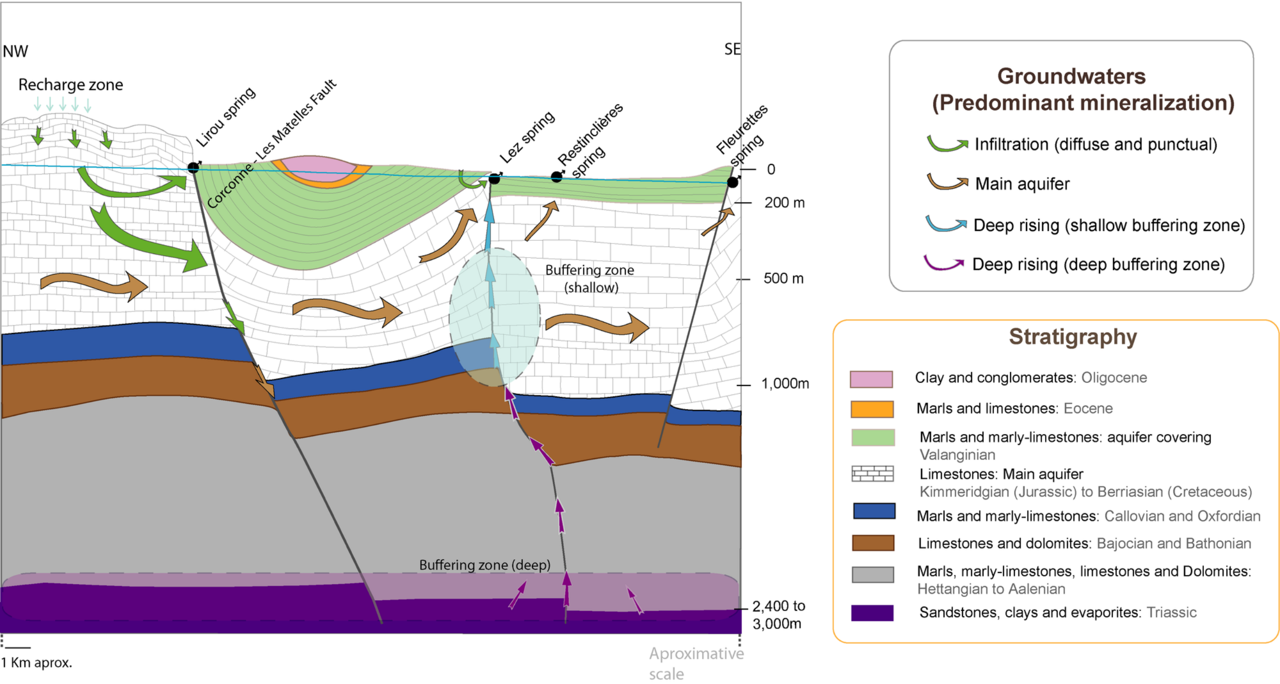
Mg/Ca (mol/mol)
0,36
0,33
0,30
0,27
0,24
0,21
0,18
0,15
0,12
0,09
0,06
0,03
0,00
Sauve
Boinet
Lez karst system evolution
Lez "piston flow "
Lez "low water"
Constant Mg/Ca
Fontbonne
-17,0
-16,0
-15,0
-14,0
-13,0
-12,0
-11,0
δ13C TDIC (‰ vs PDB)
x 10-3
Sr/Ca (mol/mol)
3,0
2,5
2,0
1,5
1,0
0,5
0,0
Boinet ⇑ ± 10-2
Lez karst system evolution
Lez "piston flow "
Lez "low water"
Constant Sr/Ca
Sauve
Fontbonne
-17,0
-16,0
-15,0
-14,0
-13,0
-12,0
-11,0
δ13C TDIC (‰ vs PDB)
Lez - low waters
Lez - high waters
Lez - piston flow waters
Lez - dropping waters
Lez - dilution waters
Lez KS wells
Restinclère spring
Fleurette spring
Lirou spring
Valanginian
Others systems



0,7088
0,7086
0,7084
0,7082
0,7080
0,7078
0,7076
0,7074
0,7072
$^{87}Sr/^{86}Sr$
0
50
100
150
200
250
300
350
400
1/Sr (Sr in mol/l)
0,7076- 0,7080
granitic influence
or rain waters
0,7075- 0,7080
Trias
0,7068- 0,7077
Jurassic
0,7070- 0,7075
Late Cretaceous
0,7088
0,7086
0,7084
0,7082
0,7080
0,7078
0,7076
0,7074
0,7072
$^{87}Sr/^{86}Sr$
Sauve
granitic influence
recent waters influence
Lez - low waters
Lez - piston flow waters
Jurassic limestone under
Trias influence
Valanginian
Cretaceous signature
0
20
40
60
80
100
120
Cl (mg/l)
Lez - low waters
Lez - high waters
Lez - piston flow waters
Lez KS wells
Restinclère spring
Lirou spring
Valanginian
Others systems


Deep water flowing on Lez spring - proportion (%)
Rainfall (mm)
0% 2% 4% 6% 8% 10% 12% 14% 16% 18% 20% 22% 24% 26% 28% 30%
0 50 100 150 200 250 300 350 400 450 500
01/01/2008 28/01/2008 27/02/2008 28/03/2008 25/04/2008 24/05/2008 16/06/2008 16/07/2008 15/08/2008 14/09/2008 14/10/2008 29/10/2008 17/11/2008 17/12/2008 16/01/2009 15/02/2009 17/03/2009 16/04/2009 16/05/2009 15/06/2009 15/07/2009 14/08/2009 13/09/2009 13/10/2009 08/11/2009 08/12/2009 07/01/2010 06/02/2010 08/03/2010 07/04/2010 07/05/2010
Deep aquifer - proportion (%)
Rainfall mm (St Martin raingauge)
- Tracer: EC
- End-members:
- Deep aquifer: EC: 1,840.00µS
- Main aquifer: EC: 650.00µS


NW
SE
Recharge zone
Lirou spring
Corconne - Les Matelles Fault
Lez spring
Restinclières spring
Fleurettes spring
0
200 m
500 m
1,000m
2,400 to 3,000m
Buffering zone (shallow)
Buffering zone (deep)
1 Km aprox.
Aproximative scale
Groundwaters (Predominant mineralization)
Infiltration (diffuse and punctual)
Main aquifer
Deep rising (shallow buffering zone)
Deep rising (deep buffering zone)
Stratigraphy
Clay and conglomerates: Oligocene
Marls and limestones: Eocene
Marls and marly-limestones: aquifer covering Valanginian
Limestones: Main aquifer Kimmeridgian (Jurassic) to Berriasian (Cretaceous)
Marls and marly-limestones: Callovian and Oxfordian
Limestones and dolomites: Bajocian and Bathonian
Marls, marly-limestones, limestones and Dolomites: Hettangian to Aalenian
Sandstones, clays and evaporites: Triassic



NW
SE
Recharge zone
Lirou spring
Corconne - Les Matelles Fault
Lez spring
Restinclières spring
Fleurettes spring
0
200 m
500 m
1,000m
2,400 to 3,000m
Buffering zone (shallow)
Buffering zone (deep)
1 Km aprox.
Aproximative scale
Groundwaters (Predominant mineralization)
Infiltration (diffuse and punctual)
Main aquifer
Deep rising (shallow buffering zone)
Deep rising (deep buffering zone)
Stratigraphy
Clay and conglomerates: Oligocene
Marls and limestones: Eocene
Marls and marly-limestones: aquifer covering Valanginian
Limestones: Main aquifer Kimmeridgian (Jurassic) to Berriasian (Cretaceous)
Marls and marly-limestones: Callovian and Oxfordian
Limestones and dolomites: Bajocian and Bathonian
Marls, marly-limestones, limestones and Dolomites: Hettangian to Aalenian
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