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THESIS

Cristina CAETANO BICALHO

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Thesis supervisors: **Dr. Hervé JOURDE** and **Dr. Christelle BATIOT-GUILHE**

Thesis co-supervisor: **Dr. Jean-Luc SEIDEL**

Thesis accomplished in the Laboratory: HydroSciences Montpellier (UMR 5569, CNRS-IRD-UM1-UM2)

THESIS

For obtaining the degree of
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Publicly presented and defended by:

Cristina CAETANO BICALHO

In December, 2nd 2010

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" Le difficile n'est pas d'apprendre ce qu'on ne sait pas,
c'est d'apprendre ce qu'on sait."

*"The difficulty does not lie in learning what we don't know, but in learning what we
already do know."*

Jacques Salomé

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Abstract

The Lez karst spring, located in the Mediterranean basin (southern France), supplies with water the metropolitan area of Montpellier (France) since the 19th century. Since 1981, an intense pumping is being performed directly in the main conduit with a maximum exploitation flow rate of about 1,700 l/s. To improve the understanding of groundwater origins and circulation dynamics in this karst system, as well as the impact of three decades of intense water exploitation, groundwater samples have been collected during various hydrologic conditions since March 2006. The springs and wells of the Lez karst system as well as surrounding springs and wells have been monitored for: physicochemical parameters, major and trace elements, Total Organic Carbon (TOC), faecal and total coliforms, ^{18}O , ^2H , $\delta^{13}\text{C}_{\text{TDIC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$.

During the first recharge events of autumn, high-mineralized waters have been observed at the Lez spring. This singular behaviour was monitored in a fine time-lag. A multivariate statistical analysis revealed the existence of different water-types discharging at the Lez spring. A coupled approach integrating geochemistry and isotopes were applied and provided insight into the different end-members, associated lithologies and the main reactions that control groundwater chemistry. Between the five distinguished water-types, the two more contrasting ones are emphasized: the first one correspond to more geochemically evolved, long residence-time waters, issued from deep layers where evaporite fingerprinting was identified. They are characterized by high mineralization and high concentrations in Cl, Na, Mg, Li, B and Br elements, high Sr/Ca, Mg/Ca and Cl/Br ratios and enriched $\delta^{13}\text{C}_{\text{TDIC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Between all the studied springs and wells, this chemical fingerprinting has been uniquely observed for the Lez spring groundwaters. The second water-type corresponds to low mineralized waters with high concentrations in NO_3 , bacteria and TOC, and represents the flux of rapid infiltration waters. They underline the vulnerability of the system to surface infiltration and anthropogenic contamination through the infiltration of waters by sinkholes and well-developed fracture networks. Hydrograph deconvolutions using multiple tracers were used to estimate the participation of two or three end-members in the various flood-events that occurred between 2008 and 2010. If we use chloride as tracer, the mean estimated participation of the different water types are, as follows: 12% for deep waters; 5% for recent waters and 83% for main aquifer waters.

The comparison between present and former studies carried out before the installation of the pumping plant (1973-1974 dataset), indicates historical changes in water hydrogeochemistry, evidencing a decrease of the deep compartment participation to the outflow of the Lez spring. This change in water hydrogeochemistry may be attributed to the intense pumping of the karst system and, in the absence of noticeable climatic changes, traduces the direct consequences of anthropogenic forcing on the overall functioning of the aquifer.

The multi-tracers approach combined to hydrodynamics appears as a very efficient tool for characterizing groundwater flows and their origins and seems to be potentially applicable to other similar complex Mediterranean karst systems that were subjected to deep karstification during the Messinian crisis. The features of this crisis seem to play a relevant role on the hydrogeological behaviour of the aquifer and chemical characteristics of waters by the participation of a deep compartment to the outflow of the karst system.

Key words: hydrogeology, karst, hydrochemistry, hydrodynamics, natural tracing, isotopes.

Résumé

La source karstique du Lez, localisée dans le bassin Méditerranéen (sud-est de la France), fournit de l'eau potable pour la ville de Montpellier et son agglomération depuis le XIX^e siècle. Depuis 1981, un pompage intensif est effectué directement dans le conduit principal au moyen d'une station souterraine de pompage, avec un débit maximal autorisé de 1,700 l/s. Afin de mieux caractériser la dynamique et l'origine des eaux souterraines, mais également d'évaluer l'impact de trois décennies d'un pompage intensif de l'aquifère, des prélèvements ont été réalisés dans différentes conditions hydrologiques depuis mars 2006. La source du Lez ainsi que d'autres sources et forages appartenant à ce système et aux systèmes karstiques voisins ont été régulièrement échantillonnées pour le suivi en continu des paramètres physico-chimiques, des éléments majeurs et en trace, du Carbone Organique Total (COT), des coliformes fécaux et totaux ainsi que des $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}_{\text{TDIC}}$ et $^{87}\text{Sr}/^{86}\text{Sr}$.

Au moment des crues de reprise qui surviennent après l'étiage, des eaux fortement minéralisées sont identifiées à la source du Lez. Ce comportement singulier a été étudié à un pas de temps fin. L'utilisation d'analyses statistiques multivariées a permis de caractériser les différents types d'eau s'écoulant à la source du Lez. Une approche couplée intégrant les données hydrochimiques et isotopiques a permis de définir les différents types d'eau et les lithologies associées, ainsi que les principales réactions qui contrôlent la chimie des eaux souterraines. Parmi les cinq types d'eau identifiés, deux correspondant à des pôles géochimiques très contrastés, et sont à mentionner : le premier pôle correspond à des eaux géochimiquement plus évoluées, caractérisées par une forte minéralisation, un enrichissement marqué en Cl, Na, Mg, Li, B et Br, des rapports Sr/Ca, Mg/Ca et Cl/Br élevés ainsi que des valeurs en $\delta^{13}\text{C}_{\text{TDIC}}$ et $^{87}\text{Sr}/^{86}\text{Sr}$ enrichies. Ces eaux, qui correspondent à une signature évaporitique, sont vraisemblablement issues d'un réservoir profond, et associées à un temps moyen de résidence important. Parmi toutes les sources et forages étudiés, cette signature chimique a été uniquement observée pour les eaux de la source du Lez.

Le second pôle correspond à des eaux faiblement minéralisées, contenant de fortes concentrations en NO_3 , bactéries et COT, représentant le flux d'infiltration rapide. Elles soulignent la vulnérabilité du système à l'infiltration rapide et à la contamination anthropique via des systèmes de pertes et de réseaux de fractures bien développé. Des déconvolutions d'hydrogramme à l'aide de multiples traceurs ont été réalisées pour estimer les proportions de participation des deux ou trois pôles d'eau précédemment définis dans les multiples événements de crue survenus entre 2008 et 2010. En considérant les chlorures comme traceur, la participation moyenne des différents types d'eau à l'écoulement à la source est la suivante : 12% pour les eaux profondes, 5% pour les eaux nouvellement infiltrées et 83% pour les eaux de l'aquifère principal.

La comparaison entre les données obtenues dans cette étude et les données obtenues avant l'installation de la station souterraine de pompage (données de 1973-1974) montre des changements notables dans la composition chimique des eaux de la source du Lez, en indiquant une diminution de la proportion de participation du réservoir profond aux écoulements à cette source. Cette modification de la composition chimique des eaux peut être attribuée au pompage intensif du système karstique et, en l'absence de changement climatique perceptible, traduit les conséquences directes de ce forçage anthropique sur le fonctionnement général de l'aquifère.

L'approche multi-traceurs combinée à l'hydrodynamique apparaît comme un outil très efficace pour caractériser les écoulements souterrains et leurs origines, et semble être potentiellement applicable à d'autres systèmes karstiques complexes similaires comprenant des compartiments profonds qui contribuent à l'écoulement de la source, notamment sur le pourtour méditerranéen où la crise messinienne a permis la mise en place d'une karstification profonde.

Mots clefs : hydrogéologie, karst, hydrochimie, hydrodynamique, traçage naturel, isotopes.

Résumé étendu en français

Introduction

Les aquifères karstiques peuvent renfermer d'importantes réserves d'eau et représentent donc une importance stratégique en termes de ressources. Ils fournissent l'eau potable à 25% de la population mondiale. En France, 30% de celle-ci provient des aquifères karstiques (Plagnes & Bakalowicz, 2002). Ainsi, la protection, la gestion et par conséquent, l'étude de ces aquifères sont nécessaires tant dans des pays industrialisés que dans des pays en développement (Cost Action 65, 1995).

La compréhension du comportement des aquifères karstiques (hydrodynamique et hydrochimie), ainsi que des processus de recharge, décharge et circulation, sont d'une importance cruciale pour le développement d'une gestion efficace de l'eau. Les études des systèmes karstiques visent à caractériser l'origine des flux souterrains, à évaluer quantitativement et qualitativement les ressources et enfin à estimer la vulnérabilité de ces aquifères aux contaminations anthropiques.

Le Lez est un fleuve côtier d'une longueur de 28 km, il apparaît au niveau de la source du Lez, qui constitue l'exutoire principal du système karstique étudié. La source du Lez alimente la ville de Montpellier en eau potable depuis le XIX^e siècle. Depuis 1981, un pompage à fort débit (1.300 l/s en moyenne) a été mis en place directement dans le conduit principal grâce à l'implantation d'une usine de pompage souterraine située à -48m sous le niveau de la source du Lez (65 m NGF). Un débit de restitution au cours d'eau de 160 l/s a été fixé afin de maintenir l'écoulement lorsque le débit pompé dépasse le débit naturel à l'exutoire. Des études antérieures ont montré qu'il s'agit d'un système karstique très complexe et hétérogène en termes de structure, d'organisation et de fonctionnement (Marjolet & Salado, 1976; Thierry & Bérard, 1983; Joseph *et al.*, 1988; Karam, 1989; Fleury *et al.*, 2009). Toutefois, l'origine des eaux souterraines et leurs cheminements doivent encore être précisés.

L'objectif principal de ce travail est d'étudier la dynamique des circulations souterraines et l'évolution hydrochimique des eaux au sein de cet aquifère karstique, conjointement à l'hydrodynamique. Dans ce but, différentes étapes ont été accomplies : (i) Tout d'abord, la caractérisation de la variabilité temporelle de la chimie des eaux de la source du Lez au cours du cycle hydrologique à partir de la caractérisation hydrogéochimique des types d'eau s'écoulant à l'exutoire en relation avec la réponse hydrodynamique de l'aquifère. Les interactions surface-souterrain ont également été étudiées afin d'estimer la vulnérabilité de l'aquifère. (ii) Ensuite, la détermination des origines de la minéralisation de l'eau, en déterminant les principales lithologies en interaction avec l'eau aussi que les principales réactions qui contrôlent les équilibres chimiques des eaux, afin de proposer un modèle conceptuel de circulations des eaux souterraines drainées vers la source du Lez. (iii) L'étude de la variabilité spatiale de la chimie des eaux et des circulations générales dans le système, afin de proposer un modèle conceptuel de circulations des eaux souterraines dans le système karstique du Lez. (iv) Enfin, la détermination de l'impact de l'exploitation intensive de la source du Lez depuis trois décennies sur l'évolution hydrochimique des eaux souterraines.

Il est envisagé que l'approche multi-traceur couplée à l'hydrodynamique, mise en œuvre dans cette étude, soit transposable à des études de fonctionnement hydrogéologique concernant d'autres systèmes karstiques Méditerranéens similaires.

Caractéristiques physiques du site étudié

L'aquifère karstique du Lez, localisé à environ 15 kilomètres au nord de la ville de Montpellier (Sud-est de la France), a une surface d'alimentation estimée à environ 380 km² (Thierry & Bérard, 1983). Son exutoire principal, la source du Lez est une source pérenne du type Vaclusien où l'eau s'écoule depuis une vasque située à une altitude de 65m NGF, au niveau de la faille de Corconne. Elle, donne naissance au fleuve côtier du Lez de 28 kilomètres de longueur, que se jette en Méditerranée à Palavas les Flots. Les eaux du système karstique du Lez sont également drainées par d'autres sources temporaires : Lirou, Restinclières, Fleurettes et Gour Noir. Les galeries qui aboutissent à la source sont de grande taille (environ 10m²) et permettent des pointes de crue de 15 à 20 m³/s.

D'un point de vue lithologique, ce système karstique est constitué par les calcaires massifs du Jurassique supérieur (Argovien à Kimméridgien) et de la base du Crétacé inférieur (Berriasien). La base de l'aquifère est constituée des marnes et marno-calcaires du Jurassique moyen (Oxfordien). La limite supérieure de l'aquifère correspond à la série marneuse et marno-calcaires du Crétacé inférieur (Valanginien). La source du Lez émerge à la faveur d'une faille normale mettant en contact les calcaires

Berriasien avec les marno-calcaires Valanginien, conférant ainsi au système karstique du Lez un fonctionnement de karst barré. Les formations calcaires de la région ont été affectées lors de la crise du Messinien par une karstification intense pouvant atteindre plusieurs centaines de mètres d'épaisseur, expliquant en partie la karstification profonde et complexe de cet aquifère (Ryan, 1976; Cita & Ryan, 1978; Clauzon, 1982).

Le climat de la zone étudiée est de type Méditerranéen, caractérisé par une pluviométrie annuelle moyenne d'environ 940mm (1970-2010). La répartition des pluies est très inégale à l'échelle annuelle et interannuelle. L'Automne est la période la plus pluvieuse, les événements pluvieux les plus importants étant généralement observés en Septembre ou Octobre, marquant ainsi le début du cycle hydrologique.

Stratégie d'étude et d'acquisition des données

De 2006 à 2010, des données ponctuelles ont été collectées par un échantillonnage régulier (bimensuel) et lors des crues (journalier et pluri-journalier) par le laboratoire HydroSciences Montpellier (HSM), au niveau de la source du Lez et des sources temporaires. Les paramètres physico-chimiques : température (T), pH et Conductivité Electrique (CE) ont été mesurés sur le terrain. Les éléments majeurs et en trace, les coliformes totaux et fécaux, le Carbone Organique Total (COT), ainsi que les isotopes stables de la molécule d'eau ($\delta^{18}\text{O}$, $\delta^2\text{H}$) ont été analysés à HSM. Le Carbone-13 du Carbone Inorganique Total Dissous ($\delta^{13}\text{C}_{\text{CTD}}$) et les isotopes de Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$), ont respectivement été analysés au Laboratoire d'Hydrogéologie d'Avignon et Géosciences Rennes. Au total, 234 échantillons ont été prélevés dans la source du Lez, 65 au Lirou, 16 dans à Fleurettes, et 33 à Restinclières.

De plus, afin de caractériser au mieux la signature hydrochimique des eaux de la source du Lez, des échantillons supplémentaires ont été prélevés une seule fois pendant l'étiage 2009, au niveau: (1) des forages appartenant au système karstique du Lez (Fontanes, Laudou, Bois Roziers, and Gour Noir); (2) des sources et forages du Valanginien (forages de Boinet, Olivier et Lavabre ; sources de Lauret, Lavabre et Dolgue); et (3) des systèmes voisins karstiques potentiellement connectés au système karstique du Lez (sources de Fontbonne et Sauve).

La T, la turbidité, la CE ($T_{\text{ref}} = 25^\circ\text{C}$) et le niveau piézométrique ont été mesurés à pas de temps horaire à partir de sondes (CTD diver, SDEC) installées à la source du Lez (au niveau de la station de pompage souterraine et à l'arrivée du débit restitué), aussi que à la source du Lirou. Les données pluviométriques ont été obtenues à partir de trois stations météorologiques de Météo France : Valflaunès, Saint-Martin-de-Londres, et de Prades. Des échantillons de pluie ont été prélevés dans les pluviomètres : Viol-le-Fort, Sauteyrargues et Saint Gély du Fesc.

Résultats et discussion

Variabilité temporelle de la chimie des eaux de la source du Lez au cours du cycle hydrologique

Une caractérisation des différents types d'eau s'écoulant à la source du Lez, basée sur une approche hydrochimique couplée à l'hydrodynamique, a tout d'abord été mise en œuvre en fonction des conditions hydrologiques. Cinq types d'eau ont été identifiés. Les eaux drainées à l'exutoire correspondent à un mélange en proportions variables d'eaux issues de différents compartiments de l'aquifère en fonction des conditions hydrologiques : un compartiment superficiel (sol et épikarst), un compartiment correspondant au système aquifère principal (calcaires du Jurassique principalement) et un compartiment profond (Marno-calcaires et dolomies des Jurassiques moyennes et autres lithologies contenant des évaporites).

La signature chimique de chaque type d'eau correspond aux circuits de circulation, à la lithologie des compartiments et aux proportions de mélange. Le premier pôle correspond aux eaux profondes, et se caractérise par des rapports élevés en Sr/Ca , Mg/Ca et Cl/Br , à des $\delta^{13}\text{C}_{\text{TDC}}$ enrichies, à des $^{87}\text{Sr}/^{86}\text{Sr}$ élevés, à des forts CE et Solides Total Dissous (TDS) et enfin avec des concentrations élevées en Cl, Na, Mg, Li, B et Br. Le deuxième pôle correspond à l'aquifère principal (Jurassique), marqué par des eaux très minéralisées, mais dont les concentrations restent inférieures au premier pôle. Le faciès chimique de ces eaux se caractérise par de fortes concentrations en Ca, HCO_3 et en Cl. Enfin, le troisième pôle correspond à des eaux d'infiltration rapide, marqués par une faible minéralisation et des fortes concentrations en COT, NO_3 et bactéries. Ce dernier pôle participe à l'écoulement à la source, en particulier, lors des événements de recharge. Elles s'infiltrant vers l'aquifère par le biais du réseau de fractures le long de l'épikarst et par les pertes temporaires localisées au niveau du contact Jurassique-Valanginien, en particulier le long de grandes failles tectoniques (réseau de failles Corconne-Les Matelles).

Origines de la minéralisation dans les eaux souterraines

L'interprétation des concentrations en éléments majeurs, en trace et des rapports molaires des éléments a mis en évidence que les eaux très minéralisées sont issues d'un compartiment profond, avec des temps de séjour plus longs. Ces eaux ont été largement modifiées par la dissolution de minéraux évaporitiques, la dissolution incongruente de dolomite et la précipitation de calcite. Les résultats en $\delta^{13}\text{C}_{\text{TDIC}}$, Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ soutiennent cette hypothèse et aident à définir les réactions chimiques qui semblent contrôler la chimie des eaux à la source du Lez.

La plupart des eaux très minéralisées en Na-Cl ont des rapports élevés en Sr/Ca et des fortes concentrations en Sr. Les rapports Sr/Ca augmentent en raison des précipitations de calcite et indiquent une importante évolution de la minéralisation des eaux où la dissolution incongruente semble contrôler la chimie des eaux profondes. Les concentrations élevées en Sr observées pour les eaux très minéralisées en Cl indiquent que la source commune de ces deux éléments contient plus de Sr que la calcite et la dolomie, ce qui indique la présence de la dissolution de minéraux évaporitiques (plus enrichies en Sr que la calcite et la dolomie, en étant également source de Cl).

Les variations significatives observées dans les rapports en $^{87}\text{Sr}/^{86}\text{Sr}$ du système du Lez suggèrent l'existence d'une source supplémentaire en Sr, causées par l'hétérogénéité de la constitution lithologique de la matrice rocheuse ainsi que par la complexité des réactions de dissolution eau-roche. L'absence de corrélation entre les rapports $^{87}\text{Sr}/^{86}\text{Sr}$ et $1/\text{Sr}$ pour les eaux très minéralisées de la source du Lez suggère que les réactions chimiques impliquent l'ajout ou le retrait de Sr dans les eaux. Le fait que, les eaux riches en Cl sont également plus radiogéniques, pourrait s'expliquer par la signature en $^{87}\text{Sr}/^{86}\text{Sr}$ du Trias. Toutefois, une signature enrichie en $^{87}\text{Sr}/^{86}\text{Sr}$ pourrait correspondre à des eaux du Jurassique inférieur, ou à des eaux d'infiltration récente ou encore à des eaux avec une signature granitique. Des investigations complémentaires doivent être mises en œuvre afin de caractériser définitivement cette origine.

Les proportions des pôles qui participent à l'écoulement de la source du Lez varient en accord avec l'hydrodynamique. La participation des eaux profondes semble être permanente à la source du Lez puisque même les eaux les plus diluées présentent une anomalie de minéralisation par rapport aux autres sources de la région. L'étude des proportions de mélange issues des différents pôles de l'aquifère pourrait être la clé pour comprendre cette composition complexe. Des déconvolutions d'hydrogramme à l'aide de multiples traceurs ont été utilisées pour estimer la participation de deux ou trois pôles dans des différents événements de crue survenus entre 2008 et 2010. En considérant les chlorures comme traceur, la participation moyenne des différents types d'eau dans l'écoulement à la source est la suivante : 12% pour les eaux profondes, 5% pour les eaux nouvellement infiltrées et 83% pour les eaux de l'aquifère principal.

Variabilité spatiale de la chimie des eaux et circulations générales dans le système

Des signatures semblables en isotopes stables de l'eau ont été observées pour les différentes sources qui correspondent aux exutoires du système karstique du Lez (Lez, Lirou, Restinclières et Fleurettes), indiquant une même zone de recharge. Cependant, la grande disparité observée dans leur hydrochimie indique des trajets de circulation de l'eau distincts au sein de l'aquifère. Cela montre que, bien qu'appartenant à l'aquifère, les eaux de sources se différencient par leur masses de soluté plutôt que par la signature isotopique de leurs eaux. Les caractéristiques hydrochimiques des sources de Restinclières et Fleurettes semblent être associées à des calcaires et marno-calcaires du Jurassique supérieur et du Crétacé inférieur, ou encore à des circulations moins profondes. En outre, ils ont une absence totale de signature évaporitique telle qu'observée à la source du Lez. Parmi ces sources, le Lirou est une exception car ses eaux présentent une minéralisation singulière, très faible vis-à-vis des autres sources, caractérisée par un temps de séjour plus court et une forte participation des eaux d'infiltration rapide. Le contenu isotopique de ces eaux met en évidence l'importante réactivité de cette source. Tout ceci indique que le Lirou est plus sous l'influence des pluies récentes que les autres sources.

Un lissage significatif du signal a été observé pour les isotopes stables de l'eau dans toutes les sources du système karstique, excepté pour la source du Lirou. Un tel lissage indique un temps de résidence au moins égal à la période d'un cycle hydrologique, soit un an. Elle illustre l'existence d'un important composant de stockage, favorisant un mélange efficace des eaux infiltrées avec les eaux stockées.

La minéralisation de l'eau observée dans les forages du système karstique du Lez (Fontanès, Laudou, Bois Roziers et Gour Noir) présente plus de similitudes avec les sources de Restinclières et Fleurettes qu'avec la source du Lez. Aucun des forages échantillonnés ne présente des eaux souterraines ayant des

caractéristiques chimiques comparables à celles de la source du Lez. L'hydrochimie des sources de Lauret, Dolgue et du forage de Lavabre sont plus semblables à l'hydrochimie des eaux des sources du système du Lez (Restinclières, Fleurettes et forages Lez) qu'aux forages d'Olivier et Boinet. Ces derniers présentent des propriétés chimiques proches de celle de la source de Sauve, située dans le contact entre les marnes du Crétacé et marno-calcaires et calcaires du Jurassique.

Impacts de l'exploitation intensive de la source du Lez sur l'hydrodynamique et la chimie des eaux

La comparaison entre les données obtenues dans cette étude et les données de la période 1973-1974 (Marjolet & Salado, 1976), montre des changements notables dans la composition chimique des eaux de la source du Lez depuis le début du pompage intensif en 1981. L'écoulement des eaux fortement minéralisées associé à l'occurrence des événements de recharge, décrit l'influence du niveau piézométrique sur l'écoulement des eaux très minéralisées d'origine profonde à la source du Lez. L'exploitation intense a entraîné une baisse générale des niveaux piézométriques dans l'aquifère. Les niveaux piézométriques atteints après un événement pluvieux sont beaucoup plus faibles aujourd'hui que ceux atteints avant la mise en œuvre de l'exploitation intensive de l'aquifère. Cela a des conséquences immédiates sur la géométrie des trajets de circulation au sein de l'aquifère karstique, et donc sur la contribution relative des eaux de différentes origines.

Actuellement, la circulation des eaux souterraines se fait préférentiellement dans des niveaux moins profonds et semble être caractérisée par des temps de séjour plus courts, ce qui pourrait avoir une influence directe sur la vulnérabilité de l'aquifère. Le pompage intensif a également diminué la proportion de participation du réservoir profond aux écoulements à la source du Lez. De plus, les valeurs actuelles en $p\text{CO}_2$ sont en environ 10% plus élevées et induisent une augmentation de la minéralisation en Ca-HCO_3 . Ces modifications pourraient, à long terme, entraîner une augmentation de l'épaisseur des conduits dans la matrice carbonatée et indiquent que les processus de karstification sont aujourd'hui plus forts qu'auparavant.

Les modifications de la composition chimique identifiées dans les eaux de la source du Lez, en l'absence de changement climatique perceptible, traduisent les conséquences directes de ce forçage anthropique sur le fonctionnement général de l'aquifère.

Conclusions et perspectives

Les principales contributions de ce travail à la connaissance du système Lez sont : (1) la caractérisation des multiples types d'eau et leurs origines; (2) l'identification des eaux d'origine profonde ainsi que leur caractérisation hydrochimique, dont l'identification de leur empreinte évaporitique ; (3) la caractérisation du système karstique du Lez dans l'ensemble, en incluant les principales sources de ce système et en proposant un modèle conceptuelle de circulation et (4) finalement, l'identification des impacts du pompage intensif dans les caractéristiques chimiques des eaux de la source du Lez.

L'approche multi-traceurs mise en œuvre combinée à l'hydrodynamique apparaît comme un outil très pertinent pour caractériser les écoulements souterrains et leurs origines. Il serait intéressant de l'appliquer à d'autres systèmes karstiques complexes comparables comprenant des compartiments profonds, notamment sur le pourtour méditerranéen où la crise messinienne a permis la mise en place d'une karstification profonde.

D'autres analyses multi-isotopiques permettront d'améliorer la connaissance des interactions eau-roche et de préciser l'origine du pôle profond, tels que $\delta^{11}\text{B}$, $\delta^{37}\text{Cl}$ et $\delta^7\text{Li}$. Les recherches futures devraient intégrer certains isotopes classiques pour la datation, comme le tritium (^3H), le ^{14}C , et d'autres traceurs comme les CFC (chlorofluorocarbones), qui ont récemment été utilisés dans des systèmes karstiques pour évaluer plus précisément l'âge des eaux souterraines et leurs temps de séjour.

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Introduction

Karst aquifers supply about a quarter of the world population with drinking water. They represent over 35% of the French territory and supply up to 30% of the total potable water (Plagnes & Bakalowicz, 2002). Fissured carbonate aquifers host huge resources of high-quality groundwater (GW) and optimizing the GW protection and management is a priority in both industrialized and developing countries (Cost Action 65, 1995).

Understanding karst aquifer behaviour (hydrodynamics and hydrochemistry) as well as recharge and discharge processes are of crucial importance for the development of an effective water management planning. Investigations on karst systems are motivated by a better assessment of water origins, a quantitative and qualitative evaluation of resources and the understanding of karst areas vulnerability to contamination. Geochemical and isotopic variations in groundwaters of karst systems are related to water-rock interactions and water mixing processes, occurring along flowpaths in the aquifer. The monitoring of physicochemical and chemical parameters provides insightful information about aquifer reactivity, its vulnerability to pollution and water transfer processes.

The Lez spring, the main outlet of the Karst System under study, supplies with water the metropolitan area of Montpellier (France) since the 19th century. Since 1981, an intense pumping (active management of the aquifer) is being performed directly in the main conduit, from an excavated pumping plant located 48 m below the Lez spring level, with a maximum pumping rate of 1,700 l/s. The pumping rate sometimes exceeds the natural water discharge but guarantees water supply all along the year. Former studies have shown this karst system to be a complex and heterogeneous system in terms of structure, organization, and functioning (Marjolet & Salado, 1976; Thierry & Bérard, 1983; Joseph *et al.*, 1988; Karam, 1989; Fleury *et al.*, 2009). However, after years of scientific investigations on the Lez karst system functioning, the dynamics and origin of groundwater remain relatively unknown.

At the Lez spring, high-mineralized waters flow as a response to extreme hydrological conditions provoked by intense rainfall. Some recent hydrogeological studies have reported similar behaviour in: Tennessee (Desmarais & Rojstaczer, 2002), Germany (Grobe & Machel, 2002) and in Mediterranean karst systems located in France, Egypt, Israel and Spain (Emblanch *et al.*, 1999; López-Chicano *et al.*, 2001;

Blavoux *et al.*, 2004; Rosenthal *et al.*, 2007). Mediterranean karst systems such as the Lez and the Vaucluse (South of France) ones, were subjected to intense karstification that reached several hundred of meters during the Messinian Salinity Crisis (Ryan, 1976; Cita & Ryan, 1978; Clauzon, 1982). Indeed, the closure of the straits connecting the Mediterranean to the Atlantic and the evaporation over the sea surface led to the decrease in the sea level exceeding 1,500 m over the entire duration of the crisis (Ryan, 1976; Clauzon, 1982). This phenomenon induced a deep and heterogeneous karst development and could help explaining the existence of high-mineralized waters flow observed after intense rainfall recharge at the Lez spring.

The Lez karst system offers many advantages that are greatly contributing to the advance of the karst hydrogeology science, like a large monitoring network belonging to the MEDYCYSS Observatory (“Multi scale observatory of flood dynamics and hydrodynamics in karts”), which is an experimental field laboratory that belongs to OSU OREME. The Lez spring has been regularly monitored for chemical and physicochemical parameters since 2006 by the HydroSciences-Montpellier Laboratory. The isotopic monitoring has been performed since 2008 as well as the monitoring of other springs of the Lez karst system. Moreover, an important historical dataset obtained before the beginning of the intense pumping, reported by Marjolet & Salado (1976), is available.

This thesis presents the studies carried out at the Lez karst system using hydrogeochemical and isotopical approaches, which are highly used to assess information about water-rock interactions, aquifer lithology, fluid mixing, water residence time and anthropogenic influence (Mudry, 1990; López-Chicano *et al.*, 2001; McIntosh & Walter, 2006; Moore *et al.*, 2009). The main objective of this work is to investigate the circulation dynamics and chemical evolution of GW over the different hydrological seasons along with the hydrodynamic responses of the Lez karst system, using the following data: (i) Physicochemical parameters: Temperature (T), Electrical Conductivity (E.C.) and Turbidity; (ii) hydrochemical and bacteriologic concentrations: major and trace elements and elemental ratios; Total and Faecal Coliforms; Total Organic Carbon (TOC) and (iii) isotopic data: water stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$), Carbon-13 of the Total Dissolved Inorganic Carbon ($\delta^{13}\text{C}_{\text{TDIC}}$) and Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$). This was achieved by investigating:

- The temporal variability of groundwater chemistry coupled with hydrodynamics, along the hydrological year, by the chemical characterization of water-types and their relation with the

aquifer hydrodynamic responses. This also includes the study of the relations between the aquifer and surface waters in order to understand the aquifer vulnerability;

- The origins of groundwater mineralization, by assessing the main lithologies and mineral-solution reactions associated with water chemistry;
- The spatial variability of groundwater chemistry and the general groundwater flow, by the comparative study of groundwater chemical properties concerning the Lez spring and the other springs of the karst system;
- The anthropogenic impacts on hydrodynamics and consequences for groundwater chemistry, by the study of the changes induced in the chemical composition of water because of intense water exploitation during 28 years, comparing recent data with data collected in 1973-1974.

Finally, it is expected that the multiple tracers approach combined with hydrodynamics used in this work will be applicable in other similar complex Mediterranean karst systems.

This document is structured as follows:

Chapter 1 is dedicated to a brief bibliographic review about karst hydrology, focusing on groundwater geochemical tracers, so as to place this work in the current state of the art.

Chapter 2 presents the physical characteristics of the study area, including geological, hydrogeological and climatic contexts. It also presents a description of the different monitoring and sampling methods and states the main techniques of data collection, laboratory analyses and data treatment. Finally, it presents the results of a hydrodynamic analysis for this karst system functioning.

Chapters 3 to 5 are devoted to the description and interpretation of the main results obtained in the present work. In **Chapter 3**, a preliminary hydrochemical characterisation of the Lez spring GW is presented through the use of statistical methods in order to identify water-types and their characteristics, as well as their relation with hydrodynamics. The natural vulnerability of the system was assessed using anthropogenic and recharge infiltration tracers. Finally, a conceptual model is proposed, describing the Lez spring functioning.

On Chapter 4, we pursue the investigation in order to better outline the geochemical evolution of the waters at the Lez karst system by isotopic study coupled with hydrogeochemistry. Further results are

presented using additional tracers such as water stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$), $\delta^{13}\text{C}_{\text{TDC}}$, and Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$). This chapter aims at understanding the correlations between the springs of the Lez system and the main reactions that control the geochemical evolution of the Lez spring waters and at, consequently, testing and refining the hypothesis presented in the precedent chapter. Hydrograph deconvolutions by geochemical tracers and mass-balance equations were used for estimating end-member participations during the Lez spring flooding. Finally, a conceptual model is proposed, describing the Lez karst system functioning.

On Chapter 5, the changes in the hydrochemical composition of waters induced by intense exploitation for 28 years have been analysed and discussed by comparing our dataset with data collected 37 years ago (Marjolet & Salado, 1976).

Chapter 1 - State of the art: Karst systems and groundwater geochemical tracers

Karst is an internationally used term for a relief composed mainly of carbonate rocks (limestone and dolomite) and which topography is essentially formed by the removal of rock by dissolution. Consequently a specific landscape and hydrologic functioning appear, characterized by unique topographic and subsurface features, including sinkholes, dolines, springs, caves, and underground streams (Mull *et al.*, 1988).

Karst systems are considered as aquifers because they normally contain groundwater, which can be used for water supply, and thus generate a certain economic interest. According to Ford and Williams (1989), carbonate rocks occupy about 12% of the planet dry, ice-free land. They estimate that 7–10% of the planet surface is covered by karsts. A large proportion of covered carbonate rocks were karstified during geological times. Consequently, karstic rocks may be one of the most important aquifer formations in the world, along with alluviums (Bakalowicz, 2005).

One of the most efficient approaches for studying karst systems is based on springs monitoring because they contain information about the functioning of the whole system and consequently the organization of conduits and storage. This approach is based on the analysis of springs hydrographs combined with natural tracing and mass balance obtained using rainfall data (Ford & Williams, 1989; Bakalowicz, 2005). Piezometric monitoring through observation wells is another approach for studying karst aquifer, although, due to their strong heterogeneity and anisotropy, wells in karst systems can hardly be connected to the main drainage axes of the system (Ford & Williams, 1989; Vaute *et al.*, 1997; Bonacci & Roje-Bonacci, 2000; Wang *et al.*, 2006); therefore the results obtained through this approach may well be inconclusive. Nevertheless, in spite of all the limitations associated to this method application, Karam (1989) considers that information obtained by piezometric network can be representative considering the specific case of the Lez karst system, because of the favourable conditions of this system, such as high fracturing and high karstification.

1.1 - Karst structure

Karst systems are highly discontinuous media, not only physically and geometrically, but also temporally. The spatial distribution of the various domains of permeability in such an heterogeneous and discontinuous medium is unpredictable, if not completely random (Labat *et al.*, 2002). Karst apparent heterogeneity is not a coincidence and originates from a distribution of voids around a main drainage axis that respects a certain hierarchy (Bakalowicz, 1977). The lithology, the faults distribution, the structure and the hydraulic potential are very important to generate and control groundwater flux (Ford & Williams, 1989; Milanovic, 2004).

Karsts are classified in three zones: (1) the upper zone or epikarst (<15 m thick), strongly permeable, facilitates rainwater infiltration; (2) the intermediate zone or unsaturated Zone (UZ), located below the epikarst, is characterized by a network of cracks of low-permeability fed by slow infiltration and/or rapid infiltration through preferential flows or sinkholes; and (3) the deeper zone: the saturated Zone (SZ) where the conduits transport fluxes from the infiltration zone and slow transfers from depth zone (Milanovic, 2004; Aquilina *et al.*, 2005; Aquilina *et al.*, 2006; Perrin *et al.*, 2007) (Figure 1).

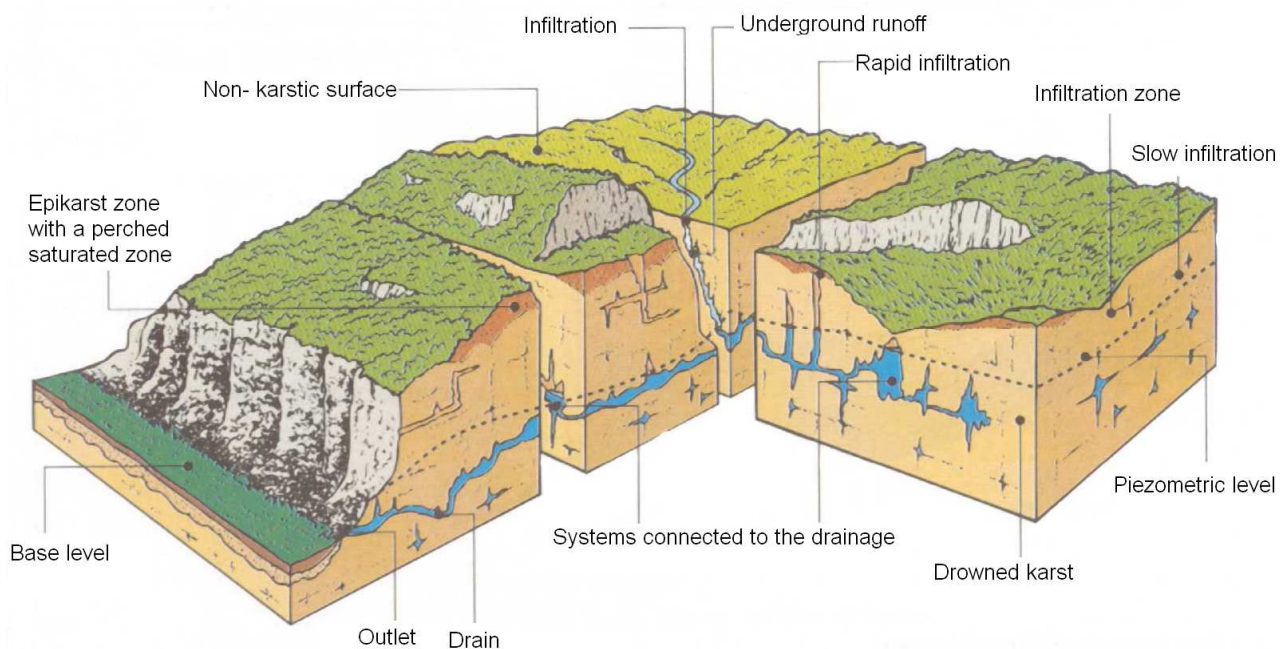


Fig. 1 – Karst physical structure scheme (Mangin, 1975).

The different roles played by the fissured matrix and the conduits are important to understand the karst hydrogeological behaviour. The recharge is concentrated in the conduits and diffuse in the zones of low permeability (Vaute et al., 1997). The storage capacity is strong in blocks and reduced in conduits. Furthermore, the flux is faster in the conduits and weaker in the low-permeability volumes (Perrin et al., 2007). As a consequence, karst spring hydrographs can be separated into a quick conduit flow and a slow diffuse flow with an intermediate regime mixing conduit and diffuse flows (Denic-Jukic & Jukic, 2003; Barfield *et al.*, 2004; Schilling & Helmers, 2008).

Karst features are environmentally significant because they are directly connected to the groundwater system, which makes the karst systems extremely vulnerable and highly susceptible to pollution (Jiang *et al.*, 2009). Pollutants can be rapidly drawn into the aquifer by means of enlarged cavities, especially during storm events (Drysedale et al., 2001). In this process, sinkholes are especially significant because they can funnel surface runoff to the groundwater system. Thus, pollutants carried by surface runoff through the karst have the potential, to reach rapidly the groundwater system (Mull et al., 1988). In karst springs with transport velocities of the order of 100 m/hr, recharge and conduit flow can result, at springs, in rapid responses to rainfall events (Kilroy & Coxon, 2005).

1.2 - Karstification process in carbonate aquifers

The specificity of karst systems is that the structure is formed by the flow itself due to carbonate rocks solubility. Those rocks are marked by low primary porosity (intergranular) and high secondary porosity (the presence of fissures and fractures), which improve their hydrodynamic properties. Moreover, groundwater circulation causes an increase of secondary porosity (fissures) by the progressive dissolution of carbonates. This process is called *Karstification*. In this way, slow percolation of water in fissures induces a deeper karst development, being limited to the hydraulic potential and its relation with vertical hydraulic conductivity (Bakalowicz, 1977; Ford & Williams, 1989; Milanovic, 2004).

The combined effect of the dissolution capacity of water and groundwater flow is the driving force of the karstification. Thus, dissolution of carbonated rocks by dissolved CO₂ is a key phenomenon in karstification. Rainwater becomes acid by dissolution of CO₂ through the atmosphere (global mean pCO₂:

0,038 %) (Ford & Williams, 1989) and of biogenic CO_2 after its infiltration in soil (its concentration is about one hundred time more important than the atmospheric one). Consequently, partial pressure of CO_2 ($p\text{CO}_2$) is normally controlled by soil horizons on the recharge zones (Drever, 1997).

At equilibrium, carbon dioxide concentration is proportional to $p\text{CO}_2$ in the gas phase. Once dissolved, carbon dioxide becomes carbonic acid (H_2CO_3), which forms ions H^+ , HCO_3^- (ion bicarbonate) and carbonate (CO_3^{2-}) when dissociated. The balance of this dissociation depends on the pH of the solution (Figure 2) (Drever, 1982). The molar fraction of each species also depends on the pH of the solution. On GW with a pH of about 7, H_2CO_3 and HCO_3^- are predominant and CO_3^{2-} are insignificant (Appelo & Postma, 2005).

Carbonate dissolution system can be used to show the relations between the three phases: gaseous-liquid-solid; when they are in contact long enough, the reversible reactions reach equilibrium. Nevertheless, equilibrium between water and carbonate rocks is a long process and can take months to be reached, depending on $p\text{CO}_2$ (which can be reached in a few minutes or a few hours), but also on the solid phase and on the type of prevailing water circulation (Bakalowicz, 1994; Gonfiantini & Zuppi, 2003).

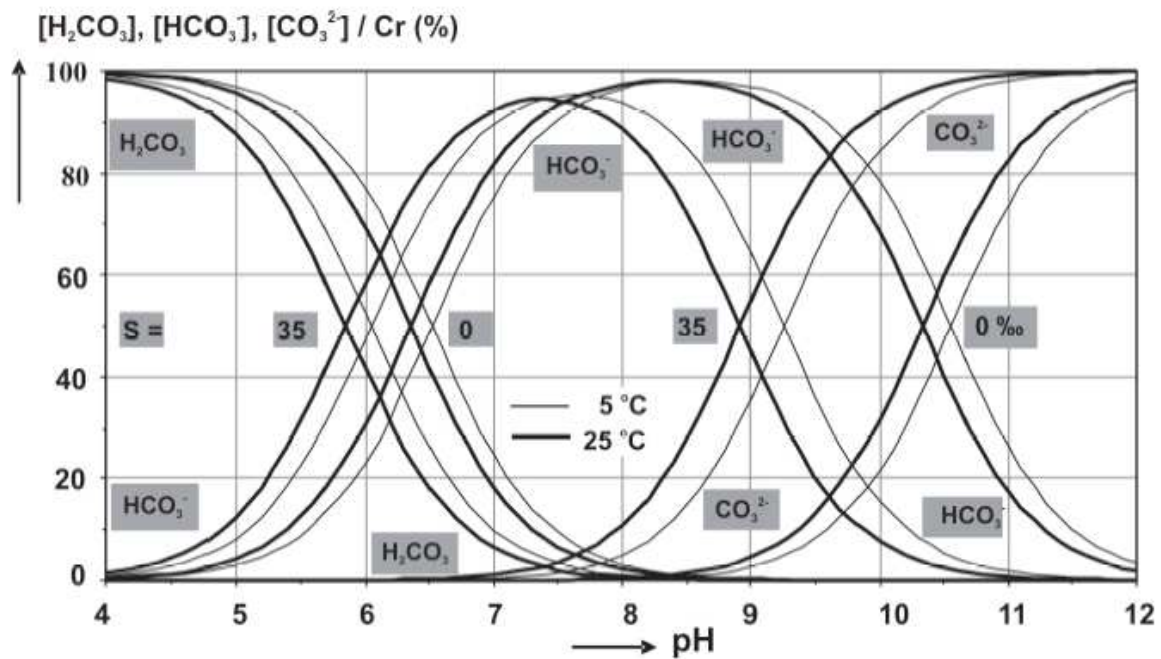


Fig. 2 – Distribution of carbonates species in pure water as a function of pH at 5°C and 25°C (Stumm & Morgan, 1995).

1.3 - Geochemical tracers of karstic transfers

Hydrochemical characteristics of groundwaters result from water-rock interactions determined by aquifer lithology and residence time within the system, water circulation conditions, anthropogenic influence and hydrological conditions. Many authors investigate relations between hydrogeochemical processes and karst physical characteristics (Bakalowicz, 1994; Vaute *et al.*, 1997; Petelet *et al.*, 1998; Perrin *et al.*, 2003a; Perrin *et al.*, 2003b; Barbieri *et al.*, 2005). Temporal variations observed in groundwater chemistry are usually related to the aquifer physical characteristics and carbonate permeability, and help to identify hydrodynamic behaviour. Physicochemical and hydrochemical parameters are increasingly used to obtain information about aquifer reactivity, vulnerability and water transfer processes, thus contributing to the development of hydrodynamic conceptual models.

Natural tracing approach can be extremely useful in the assessment of groundwater-surface water interactions, water dating, quantification of water-rock interactions and evaluation of water resource vulnerability (Emblanch *et al.*, 1998; Katz *et al.*, 1998; Nativ *et al.*, 1999; Batiot *et al.*, 2003b; Pulido-Leboeuf *et al.*, 2003; Négrel & Petelet-Giraud, 2005; Hébrard *et al.*, 2006; Adinolfi Falcone *et al.*, 2008; Bouchaou *et al.*, 2008; Silva-Filho *et al.*, 2009).

1.3.1 - Water-rock interaction tracers

The isotopic and hydrochemical compositions of groundwater reflect the mineralogical composition of the aquifer rock, giving information about the constitution of the rock matrix. The matrix determines and influences the chemical facies of the water, e.g. waters from dolomite and limestone aquifers are typically enriched in calcium, magnesium and bicarbonates.

Evaporitic minerals can be found in karst formations in Europe, associated with carbonates, and provide elements in groundwater solutes as Cl, Li, Br, B, Mg, SO₄, Ca, K and Sr (Mandia, 1991; Vengosh *et al.*, 2000; Sánchez-Martos *et al.*, 2002). The presence of chloride in groundwaters could be related to only one phenomenon or to the combination of several distinct processes such as sea water intrusion, deep brine rising, evaporite dissolution, geothermal water rise, anthropogenic origins and rainwater evaporation (Faillat & Puradimaja, 1995; Kloppmann *et al.*, 2001; Ghabayen *et al.*, 2006; Hébrard *et al.*, 2006).

Bromide is regularly used on investigations of chloride origins. Br concentration in waters can be related to the presence of evaporites and Br/Cl ratios are used to deduce the level of brines development and to constraint interpretation of Cl concentrations (Edmunds & Smedley, 2000). Br/Cl ratio is conservative and is not affected by water-rock interactions (Vengosh *et al.*, 1995; Bernasconi, 1999; Kloppmann *et al.*, 2001; Sánchez-Martos *et al.*, 2002; Cartwright *et al.*, 2006; Farber *et al.*, 2007; Harrington *et al.*, 2008).

Strontium is ubiquitous and connected with several lithologies like limestones, dolomites, marls, and evaporites. Since Sr is a divalent cation that shows similar behaviour to Ca, it often participates to diagenetic reactions and could be related to re-crystallization of bicarbonates (Bernasconi, 1999).

Magnesium is a good indicator of water residence time in carbonate rocks due to the slower solution kinetics of dolomite. Numerous studies have documented the usefulness of Mg/Ca ratios to trace water residence times (Plummer, 1977; Plummer *et al.*, 1978; Edmunds & Smedley, 2000; Fairchild *et al.*, 2000; López-Chicano *et al.*, 2001; Batiot *et al.*, 2003a; McMahon *et al.*, 2004; Moral *et al.*, 2008).

Br, Li, Mg, B and their molar ratio with Cl also provide information about evaporite mineralization. During seawater evaporation, residual brines are enriched with Br, Li, Mg and B; on the contrary, Cl disappears from the solution because of halite (NaCl) precipitation. In consequence, Br/Cl, Li/Cl, Mg/Cl and B/Cl ratios increase in the residual brines and the precipitate is characterized by lower ratio values (Casenave & Valentin, 1992; Bernasconi, 1999; Vengosh *et al.*, 2000; Cartwright *et al.*, 2006; Farber *et al.*, 2007; Harrington *et al.*, 2008).

1.3.2 - Anthropogenic and recharge infiltration water tracers

Aquifer vulnerability can be assessed through the use of contamination water tracers such as bacteria, organic matter, micro-pollutants such as pesticides, pharmaceutical residues, etc. (Einsiedl *et al.*, 2010), which provide information about the relation between the surface water and the karst system. Most anthropogenic pollutants reach groundwaters during rainfall events by rapid infiltration through sinkholes and open fractures (Mahler *et al.*, 2000).

1.3.2.1 - Total Organic Carbon (TOC)

Total Organic Carbon in groundwater originates from organic matter decomposition due to bacterial activity in the soil and is a very efficient tracer of seepage waters; its use for karst system investigation is only recent (Emblanch *et al.*, 1998; Batiot *et al.*, 2003a). Once dissolved, its concentration decreases due to biological degradation and for this reason, seepage waters present normally high TOC concentrations. Coupled with Mg concentration, TOC appears as an efficient tool to differentiate the origins of the waters taking part in the spring flow (Batiot *et al.*, 2003a; Batiot *et al.*, 2003b).

1.3.2.2 - Microbial tracers

The association of rapid chemical and bacteriological responses during floods seems to be a characteristic of karst aquifers (Personné *et al.*, 1998). Bacteriological tracers denote a rapid transport through the karst of waters issued from surface infiltration. The transport of microbial pathogens represents a serious threat to public health, mostly because of faecal bacteria that could be associated to pathogenic species (Joseph *et al.*, 1988; Personné *et al.*, 1998; Mahler & Lynch, 1999; Mahler *et al.*, 2000; Personné *et al.*, 2004; Stuart *et al.*, 2010).

The most relevant indicator of faecal contamination and possible presence of pathogens is the presence of *Escherichia coli*, the only member of thermo-tolerating coliforms that is exclusively associated to faecal matter (Dussart-Baptista *et al.*, 2003). The life duration of those bacteria is relatively short under the unfavourable conditions of aquatic environment (Livrozet, 1984). Low oxygen and organic carbon lead them towards an intense competition and their resulting disappearance (Dussart-Baptista 2003). The survival time of *E. coli* and *enterococci* in non-sterile waters is about 8-12 hours and cannot exceed one week for the former and few weeks for the latter (Personné *et al.*, 1998).

Generally, a bacterial contamination of faecal origin is always associated with strong turbidity (Dussart-Baptista *et al.*, 2003). Turbidity itself is not a danger for health (Dussart-Baptista 2003). However, by facilitating the transport of micro-organisms, turbidity is strongly associated with the appearance of water origin diseases (Mahler & Lynch, 1999; Dussart-Baptista 2003; Dussart-Baptista *et al.*, 2003). Moving sediments flushing through the aquifer can play a significant role in the concentration and transport of

contaminants (Mahler & Lynch, 1999). The nasty effects of contaminants associated to sediments are more potent during the first flood responses (Mahler & Lynch, 1999).

High bacteria concentrations during floods are often related to effluents of sewage treatment plants (Mahler et al., 2000). During dry season, faecal contamination in groundwaters can be caused by irrigation using residual waters (Mahler et al., 2000).

1.3.3 - Isotopes

1.3.3.1 - ^{18}O and ^2H

Stable water isotopes (18-Oxygen and Deuterium) are largely used for determining sources of water, flow patterns, mixing processes and for identifying potential evaporation processes. They are also often employed for evaluating the contribution of rainfall waters to a flood event by the use of a simple bi-component mixing model (Drever, 1982; Kattan, 1997; Cey *et al.*, 1998; Katz *et al.*, 1998; Beven, 2001; Ladouche *et al.*, 2001; Perrin *et al.*, 2003a; Perrin *et al.*, 2003b; Long & Putnam, 2004; Aquilina *et al.*, 2005; Bouchaou *et al.*, 2009; Ladouche *et al.*, 2009).

Oxygen and Hydrogen isotopic compositions vary mainly because of natural variations of the rainfall compositions and mixing processes with pre-existing waters. They are also influenced by evaporation and altitude effects (Drever, 1982; Ford & Williams, 1989; Kattan, 1997; Cey *et al.*, 1998; Nativ *et al.*, 1999; Beven, 2001; Vandenschrack *et al.*, 2002; Perrin *et al.*, 2003a; Long & Putnam, 2004; Barbieri *et al.*, 2005; Bouchaou *et al.*, 2009).

1.3.3.2 - Stable carbon isotope

The use of $\delta^{13}\text{C}_{\text{TDIC}}$ as a natural tracer in karst aquifers can help to differentiate water coming from the unsaturated zone from water coming from the saturated zone. In the unsaturated zone, the system behaves like an open system regards to the biogenic CO_2 of the soil. While the saturated zone is considered closed to the biogenic gas phase, where exchanges are not possible between the gas phase and the aquifer (Clark & Fritz, 1997; Emblanch *et al.*, 1998; Katz *et al.*, 1998; Yoshimura *et al.*, 2001; Batiot, 2002; Desmarais &

Rojstaczer, 2002; Emblanch *et al.*, 2003; Gonfiantini & Zuppi, 2003; Marfia *et al.*, 2004; Adinolfi Falcone *et al.*, 2008; Bouchaou *et al.*, 2009; Gillon *et al.*, 2009).

$\delta^{13}\text{C}_{\text{TDIC}}$ 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 exchanges are very quick; consequently, if the chemical equilibrium within the aquifer is attained under open conditions (regarding the gaseous phase), the soil $\delta^{13}\text{C}_{\text{CO}_2}$ determines the $\delta^{13}\text{C}$ of groundwater (Appelo & Postma, 2005). If the system is closed to soil CO_2 , TDIC is derived in about equal proportions from the dissolution of CO_2 (g) and from the CaCO_3 weathering (Appelo & Postma, 2005).

The carbon isotopic composition of groundwater ($\delta^{13}\text{C}_{\text{TDIC}}$) is composed of carbon from carbonate rocks and from soil CO_2 . $\delta^{13}\text{C}$ of carbonate rock is about $0 \pm 2\text{‰}$ (Clark & Fritz, 1997). The carbon isotopic composition of soil CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$), for the predominant vegetation type in a temperate climate (C3 vegetation type), ranges between -21 and -22‰ (Deines, 1980; Drever, 1982; Clark & Fritz, 1997).

1.3.3.3 - $^{87}\text{Sr}/^{86}\text{Sr}$

Strontium isotopes ($^{87}\text{S}/^{86}\text{Sr}$) are measured in hydrochemical studies to determine the various origins of Sr in waters and to assess end-member mixing processes. Isotopic abundance ($^{87}\text{S}/^{86}\text{Sr}$) in rocks changes because of the formation of radiogenic ^{87}Sr by radioactive decay of naturally occurring ^{87}Rb . In natural waters, $^{87}\text{S}/^{86}\text{Sr}$ is inherited from minerals and rock contributions and no isotope fractionation occurs. (Oetting *et al.*, 1996; Katz *et al.*, 1998; Petelet *et al.*, 1998; Kloppmann *et al.*, 2001; Barbieri *et al.*, 2005; Jacobson & Wasserburg, 2005; Négrel & Petelet-Giraud, 2005; Wang *et al.*, 2006; Petelet-Giraud & Négrel, 2007; Nisi *et al.*, 2008). Groundwater acquires dissolved Sr: (i) in its recharge area, through infiltration and percolation processes; (ii) along its flow path, through dissolution or ion exchange with minerals (Barbieri *et al.*, 2005; Wang *et al.*, 2006).

Solute chemistry and isotopic composition ratios in a groundwater system can be regarded as a chemical mixture from several sources, and the discrimination of the contribution from each geological formation is a difficult task. Strontium isotopes have been used for: understanding water circulation in reservoirs; quantifying water mixing from different origins; and examining geochemical interaction between

water and aquifer rocks (Oetting *et al.*, 1996; Katz *et al.*, 1998; Petelet *et al.*, 1998; Kloppmann *et al.*, 2001; Barbieri *et al.*, 2005; Jacobson & Wasserburg, 2005; Wang *et al.*, 2006; Petelet-Giraud & Negrel, 2007; Nisi *et al.*, 2008). Moreover, major element, mineral saturation state and Sr/Ca versus $^{87}\text{Sr}/^{86}\text{Sr}$ help identify the reactions that control the evolution of the waters geochemistry, like the presence of incongruent dissolution of dolomites and calcite precipitation (Oetting *et al.*, 1996; Dogramaci & Herczeg, 2002).

Sr isotopes represent a powerful tool to better constrain weathering reactions, weathering rates, flow pathways and mixing scenarios. Nevertheless, Sr isotopes are more useful when combined with other hydrogeochemical data to outline models of water-rock interaction and mixing as well as geochemical processes such as ion exchange (Shand *et al.*, 2009; Langman & Ellis, 2010).

Chapter 2 - Material and methods

2.1 - Geological and hydrogeological settings

The Lez spring is a Vaucluse-type spring, i.e. with a main conduit developed below the spring level, and is located on a major regional fault. This spring (65m a.s.l.) is the source of the Lez River that flows over 28 km to the Mediterranean Sea. This river has three main tributaries fed by temporary karst springs belonging to the Lez karst system.

The Lez spring is one of the main karst springs in France and is located 15 km north of Montpellier (France). It used to be a perennial spring; however, since 1982 water has been directly withdrawn from the main conduit to supply Montpellier and its metropolitan region with water. The pumping rate sometimes exceeds the natural water discharge in order to secure water supply throughout the year. Consequently, during low-water period, the spring dries up. Ecological water discharge at the Lez River is ensured during this period by a partial deviation of the pumped water to the river.

The Lez karst system discharges also at several seasonal outlets: Lirou, Restinclières, Fleurettes and Gour Noir (Figure 3). The Lez spring is the main perennial outlet of the system, with groundwater discharge that can reach about 15 m³/s during rainfall events, with an annual average discharge of 2,2 m³/s. Lirou is a temporary spring that flows only 4 months in a year. Fleurettes is the most ephemeral spring, flowing only a few weeks a year. Restinclières spring was perennial before the pumping, and according to recent field observations, it seems it remains a perennial spring despite the water exploitation.

The hydrogeological catchment of the Lez spring has an area of about 380 km² (Thierry & Bérard, 1983), and is located between the Hérault and Virdoule river valleys (Figure 3). As a large part of the hydrogeological catchment is relatively impermeable, due to the presence of marls and marly-limestones of the Valanginian, the Lez spring diffuse recharge area covers only 150 km² (Marjolet & Salado, 1976).

The diffuse recharge area over the catchment corresponds to the Jurassic limestone outcrops located by the western and northern limits of the basin (Figure 3). Localized infiltration occurs through fractures and sinkholes along the basin and through the major geologic fault of *Corconnes-Les Matelles* (located in the

proximity of Claret well), in the northern part of the basin. A certain number of fractures are also known to exist only just upstream from the Lez spring (Dubois, 1964).

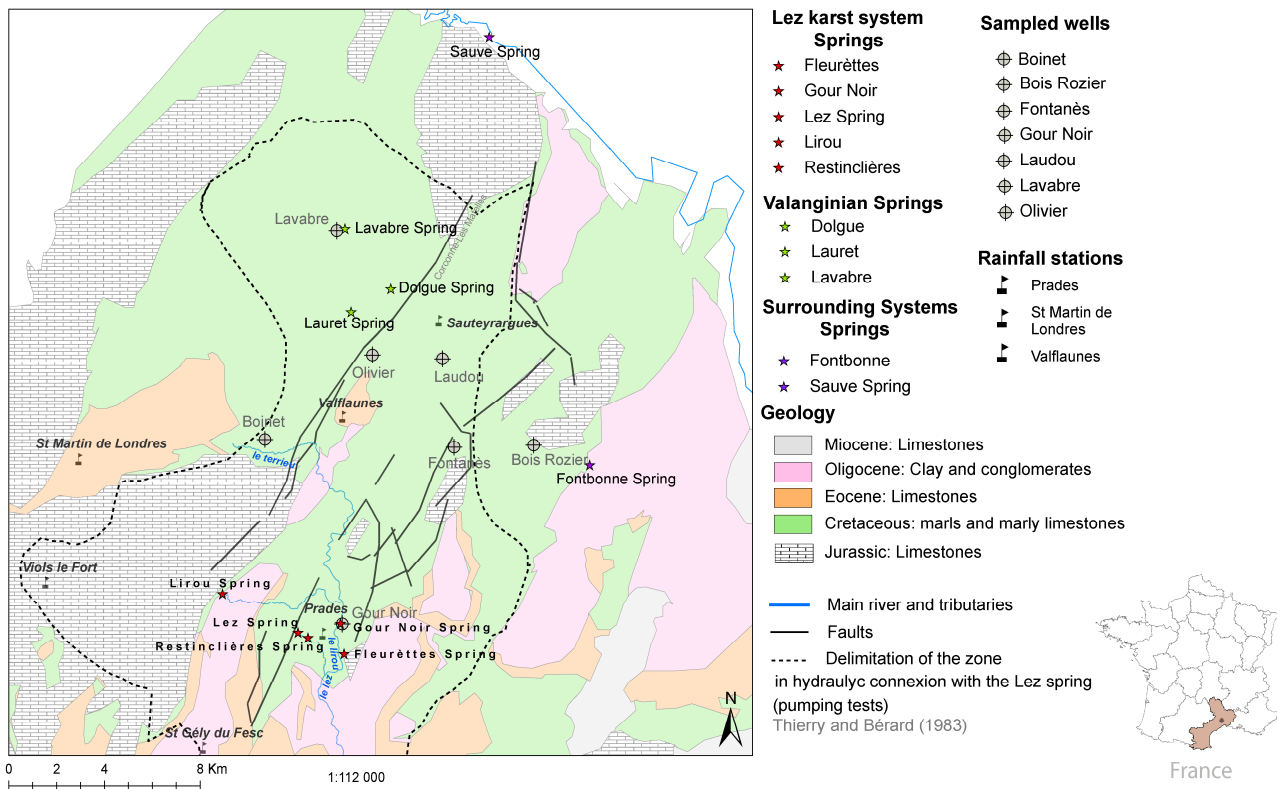


Fig. 3 – Hydrogeological map of the Lez karst system with sampled springs, wells and rain gauges location.

A perched aquifer is located within the upper Valanginian layer (marls and marly-limestones), superposing the Lez aquifer (Pane-Escribe, 1995), though, both aquifers are regarded as mostly hydrogeologically unconnected. The groundwater that outflow from some springs that drain the Valanginian aquifer, notably Lauret, Dolgue and Lavabre springs infiltrate into the Lez karst system through localized infiltration zones along the *Corconne-Les Matelles* fault (Boinet, 2002).

The cross section of the terminal conduit that reaches the Lez spring is greater than 10m². The conduits dimensions result from an intense karstification that reached several hundred of meters during the Messinian Salinity Crisis (Joseph et al., 1988) and affected the limestone formations during the Plio-Quaternary.

The lithology of the Lez karst system corresponds to massive limestone of the Upper Jurassic (Argovian to Kimmeridgian) and of the lower part of the Early Cretaceous (Berriasian), with 650 to 1100 m thickness (Figures 4 and 5). The marls and marly-limestone of the Middle Jurassic (Oxfordian) constitute the lower boundary of the aquifer. The marls and marly-limestone of the Early Cretaceous (respectively Lower

and Upper Valanginian) constitute the upper boundary of the aquifer. The major tectonic events that influenced the Lez aquifer were: the Hercynian/Variscan orogeny, the Pyrenees formation, and the opening of the Lion Golf (Bousquet, 1997). Accordingly, the Lez karst system is referred to as a partly confined system.

2.1.1.1 - Messinian salinity crisis

The Messinian Salinity Crisis resulted in the drying of the Mediterranean Sea caused by a disconnection from the Atlantic Ocean, between 5.96 and 5.33 million years ago. Because of the closure of the Gibraltar straight, the water flow from the Atlantic Ocean to the Mediterranean stopped and most seawater evaporated, which caused the lowering of the sea level and the accumulation of thick evaporite deposits in the Mediterranean basin (Ryan, 1976; Cita & Ryan, 1978; Clauzon, 1982).

Two features resulted from this event: 1) a sedimentary feature, corresponding to a thick evaporitic layer composed of carbonate, gypsum and halite; 2) a geomorphological feature with the incision of deep fluvial canyons and the occurrence of deep karstification in some karst systems. This crisis ended at the beginning of the Pliocene, with a rapid flooding of the Mediterranean basin (Mocochain *et al.*, 2006).

Fleury (2005) described two types of Mediterranean karsts which great depths can be explained by the Messinian hypothesis: (i) below sea level springs e.g.: Port-Miou (France), Morain-Toix (Spain), Chekka (Lebanon), etc.; and (ii) above sea level springs Thau (France), Vaucluse (France), Lez (France), etc. The second type of karst was partially filled with impermeable Pliocene marine and continental sediments, which clogged conduits and other geologic features that became partially or totally closed to sea intrusion (Fleury *et al.*, 2007). Those systems were highly karstified but they remained uncontaminated by seawater with the presence of impermeable fillings (Bakalowicz, 2005; Fleury, 2005; Fleury *et al.*, 2007). Such conditions favour rising karstic flowpaths that can mobilize important reserves in depth (Gilli & Audra, 2004). The reserves are large, with variable flow rates and water remaining fresh or slightly salty (Fleury *et al.*, 2007). The groundwater residence time may increased to several thousand years, while it is usually shorter than a year in well-developed karst aquifers (Bakalowicz, 2005).

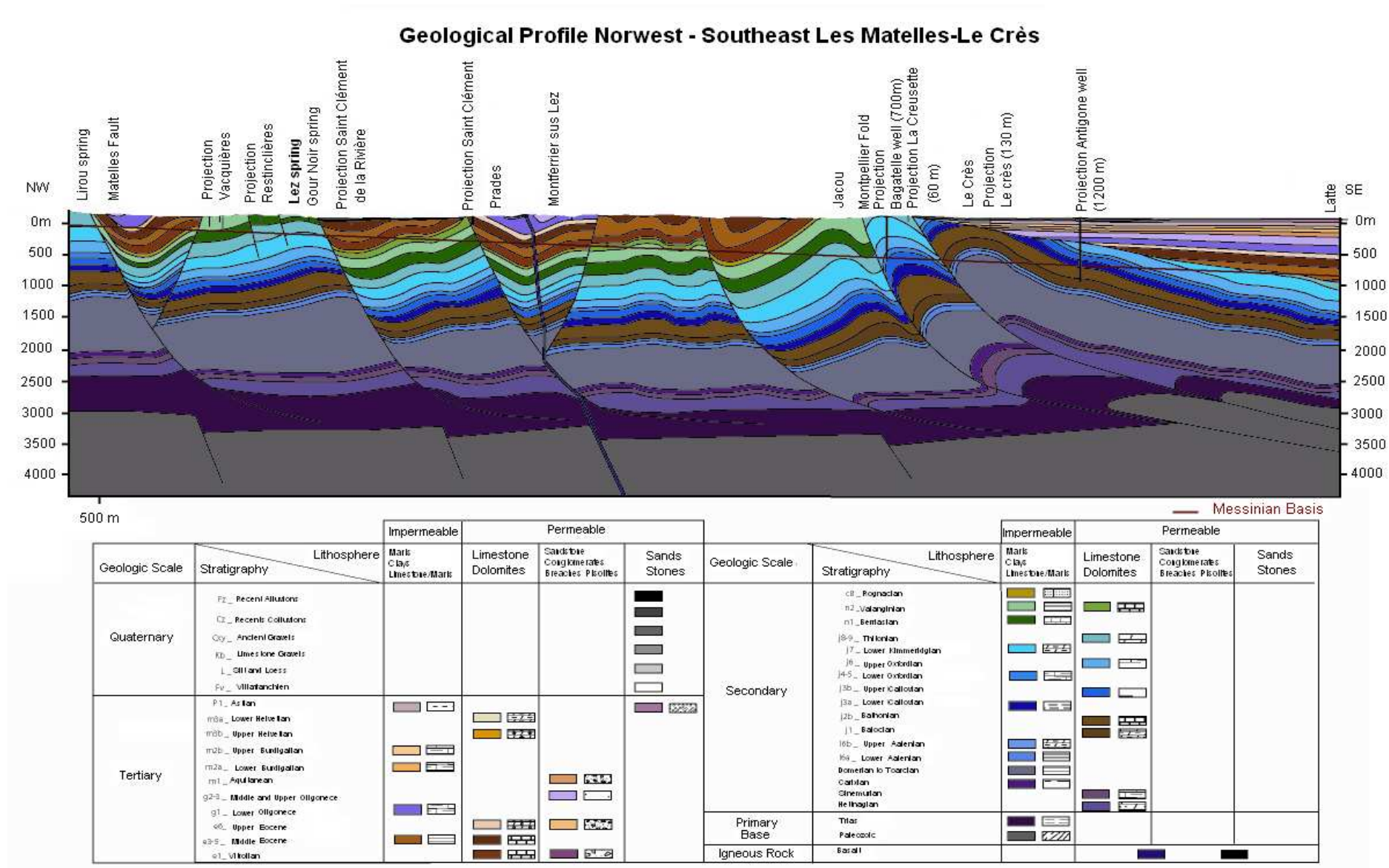


Fig. 4 – NW-SE geological cross-section: Les Matelles – Le Crès (Bossier, 2009).

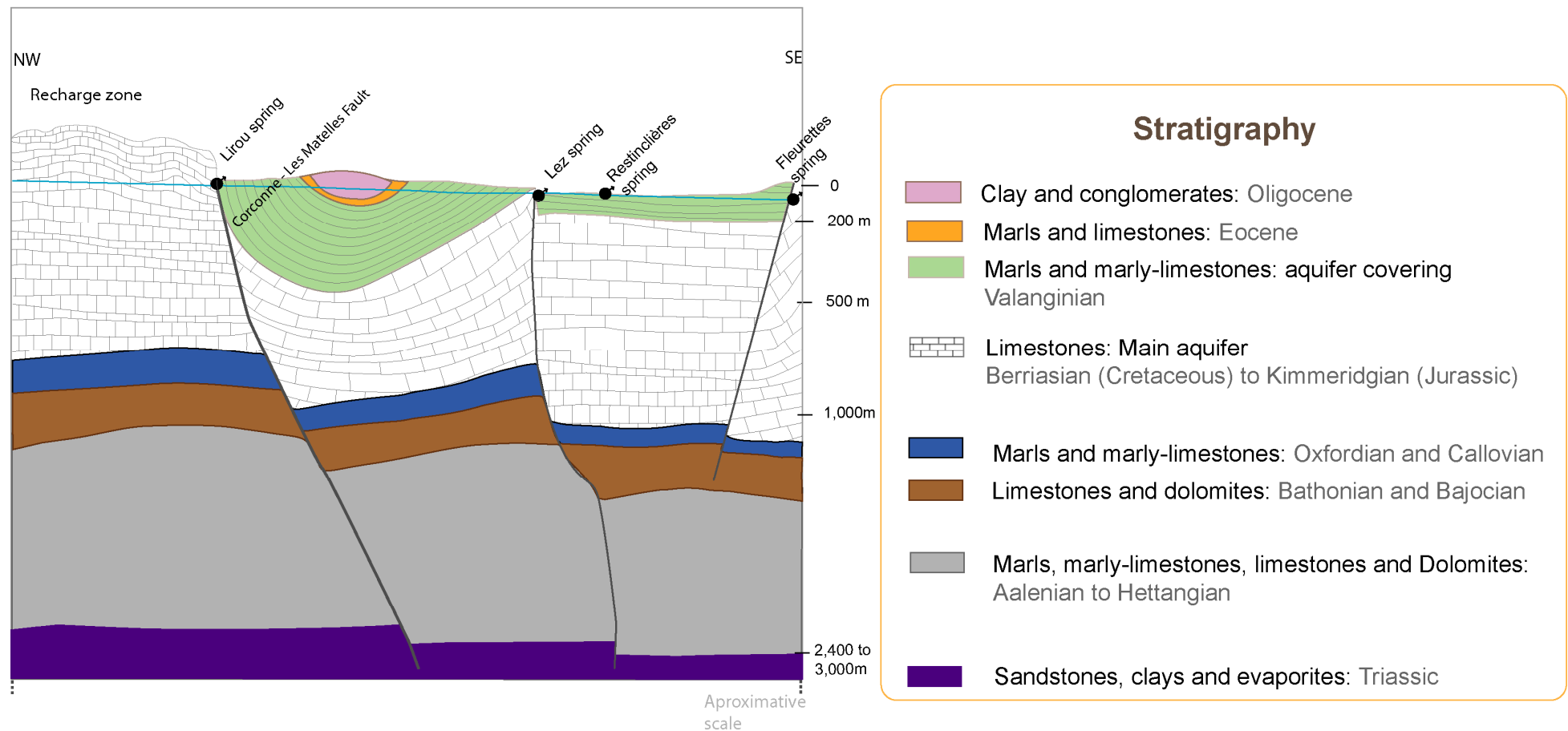


Fig. 5 – NW-SE simplified geological cross-section, Lez karst system.

2.2 - Water exploitation of the Lez spring

In 1965, the intense pumping of the water resource started at the Lez spring, where water was withdrawn directly from the main conduit. However, by 1982, exploited discharges became insufficient and the General Company of Water (Compagnie Générale des Eaux - CGE) determined that the pumping should be done from the underground. A deep pumping plant was dug (-48 m), located at about 400 m upstream the Lez spring (Figure 6). From this plant, four 1,800 mm diameter boreholes were dug, reaching the natural conduit leading to the spring. Three boreholes were equipped with immersed electric pumps, with a maximum pumping rate of 1,700 l/s. This pumping rate sometimes exceeds the natural water discharge but guarantees a water supply all through the year.

During low-water conditions, when pumping rates exceed the natural discharge of the karst spring, the water level in the conduit and in the spring-pool drops below the spring overflow level. Consequently, during low-water period, the spring dries up. Ecological water discharges at the Lez river in this period is maintained by a deviation of pumped water ($Q=160$ l/s) towards the river. During autumn and winter, the karst system is recharged and the water level in the conduit rises above the spring overflow level.

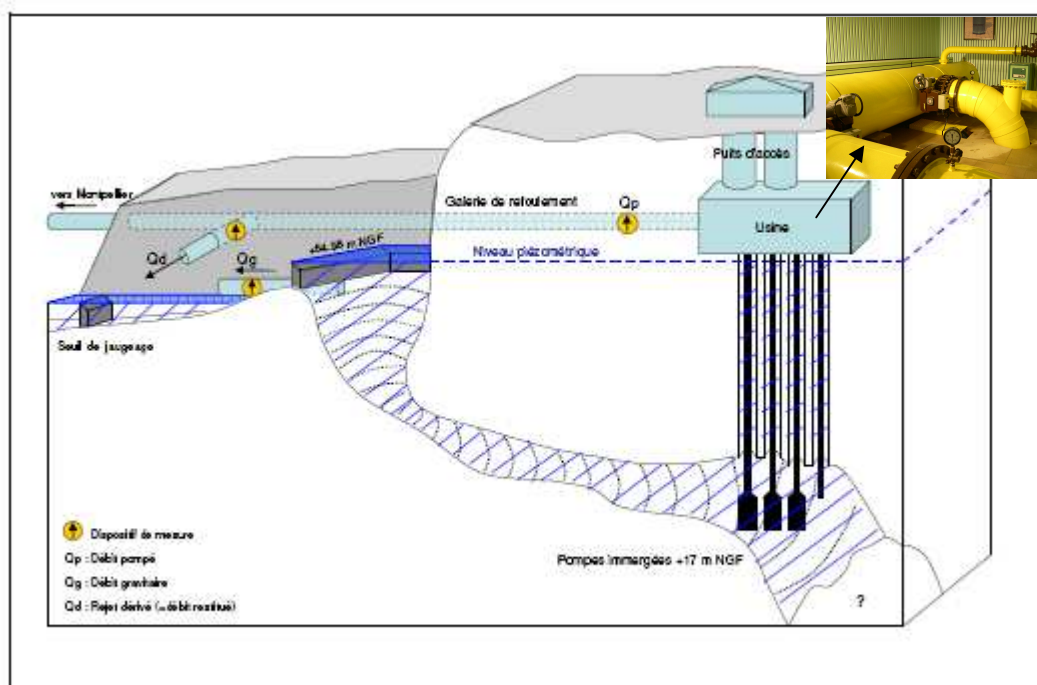


Fig. 6 – Scheme of the underground pumping plant at the Lez spring (Conroux, 2007).

2.3 - Hydrological settings: Mediterranean Climate

Mediterranean climate is characterized by dry and hot summers and wet autumns, winters and springs. Autumn precipitations are often convective, with heavy rainfalls. The hydrological regime is characterized by a strong temporal variability. The flood intensity and frequency vary considerably from one year to another according to the intensity and frequency of rainfalls but not all the strong events produce floods (Ribolzi *et al.*, 1997; Ferraris *et al.*, 2001; Martín *et al.*, 2006; Wittenberg *et al.*, 2007).

The Mediterranean basin response is usually delayed but sudden, and because of that, the hydrological behaviour of Mediterranean transitory streams is dominated by extreme events. The transitory flow depends exclusively on rainfalls and is clearly related to the characteristics of the basin. In karst zones, fractures and fissures facilitate infiltration, receiving the contribution of runoff infiltration coming from a non-karst watershed, but do not always contribute to the flow in the river (Latron & Gallart, 1998; Belmonte & Beltrán, 2001; Gaume *et al.*, 2004).

Fleury *et al.* (2009) estimated the volume of water needed to recharge the aquifer and could predict the height of rainfall that could cause flooding. The determined volumes represent approximately 100 mm of infiltration or 150 mm of rainfall at the end of the low stage. The precipitation impact on the Lez karst system depends on its level of saturation, which is related to how the pumping is withdrawing aquifer reserves and also to previous cumulative rainfall conditions (Jourde *et al.*, 2007; Dörfliger, 2008; Fleury *et al.*, 2009).

The average annual rainfall calculated over the last 40 years at Valflaunès raingauge (Météo France) was 942 mm (Figure 7). The total annual rainfall is highly variable from year to year: 1989 was the driest year during this period, with 474 mm, and 1972 was the wettest year, with 1,620 mm of rainfall. During the studied period, the annual rainfall was 810 mm for 2006-2007, 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% during autumn, 27% during winter, 22% during spring and 13% during summer (Figure 8). The first recharge events (rainfall events) of the hydrological cycle (or hydrological year: from September to September) start normally between September and October.

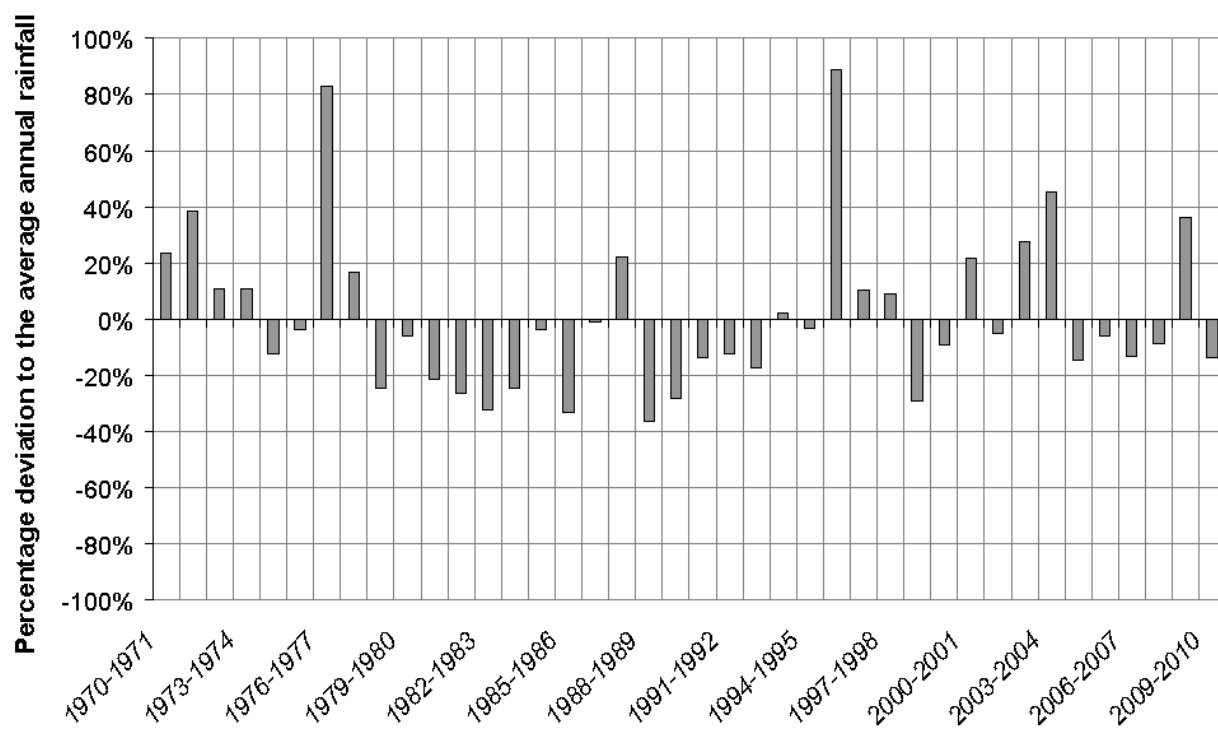


Fig. 7 – Percentage deviation to the average annual rainfall calculated from 1970 to 2010 (Valflaunès raingauge).

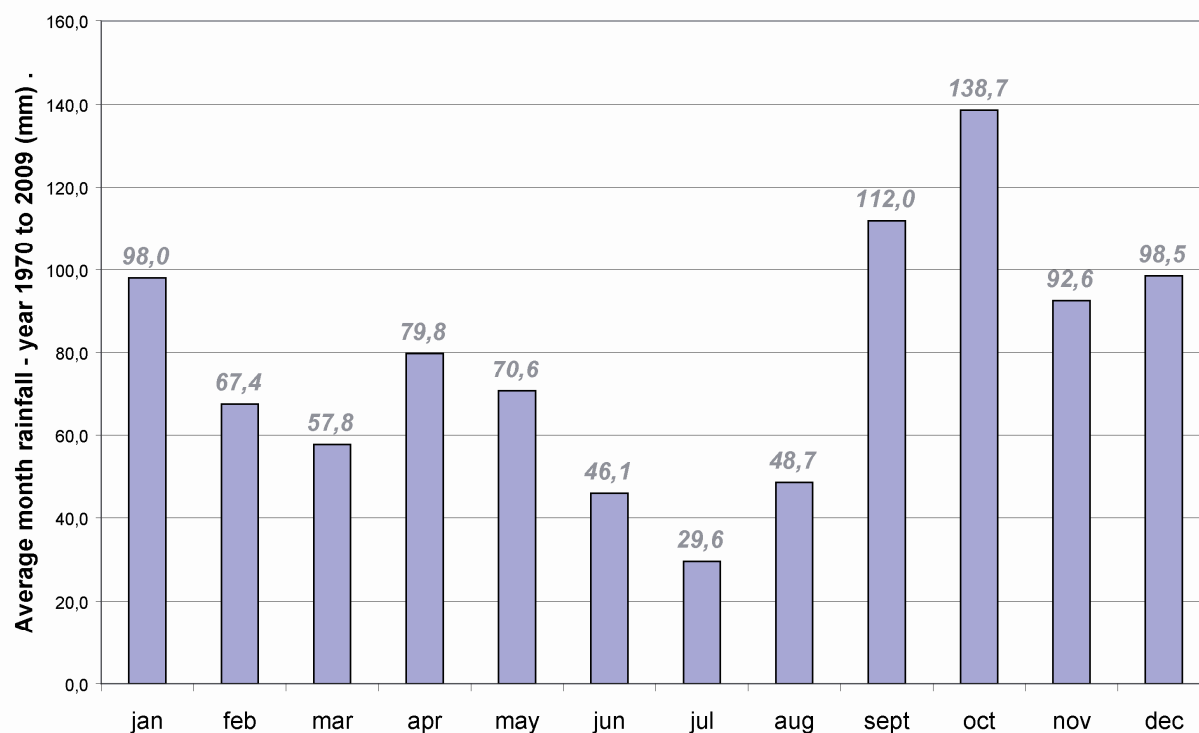


Fig. 8 – Average monthly rainfall calculated from 1970 to 2010 (Valflaunès raingauge).

2.4 - Strategy of study and data acquisition

2.4.1 - Continuous monitoring and sampling

Punctual data were obtained by regular samplings accomplished by HydroSciences Montpellier (HSM) from 2006 to 2010. Automatic measuring was accomplished by HSM and Veolia. Temperature (T), turbidity, Electrical Conductivity (EC $T_{ref}=25^{\circ}\text{C}$) and Groundwater Level (GW level) were measured using an hourly time-step at the Lez spring with an automatic datalogger (CTD diver, SDEC), at the observation well of Veolia pumping station (Lez well) that is located in the proximity of the Lez spring. HSM performed T, EC, and GW level measurements with an hourly time-step at the Lez spring spillway and at the Lirou spring (CTD diver, SDEC). Rainfall data were obtained from three meteorological stations of Météo France: Valflaunès, Saint-Martin-de-Londres, and Prades (Figure 3).

The piezometric network consists of 21 monitoring wells where water table measurements were performed by Veolia, at 14 monitoring wells equipped with automatic pressure sensors (hourly time-step), and 7 monitoring wells manually measured at a monthly time-step.

Samples were collected from the Lez spring twice a month, from March 2006 to May 2010, and daily during the floods that occurred within this period. Lirou, Restinclières and Fleurettes springs sampling started in October 2008 and lasted until May 2010, and were carried out during the wet season, when they were flowing. A total of 234 samples were collected from the Lez spring, 65 from the Lirou spring, 16 from Fleurettes, and 33 from Restinclières.

Additional samples were collected during the low stage period from: 1) surrounding systems that are potentially connected to the Lez karst system, including Fontbonne and Sauve springs; 2) Valanginian springs and wells, including Boinet, Olivier and Lavabre wells and Lauret, Lavabre and Dolgue springs; 3) Veolia wells belonging to the Lez karst system: Fontanes, Laudou, Bois Rozières, and Gour Noir.

Rainfall waters samples were regularly collected for water stable isotopes analysis from a buried reservoir connected to the rain gauges at Viols le Fort, Sauteyrargues and Saint Gély du Fesc. Three rainwater samples were collected for major elements analysis. Two samples of surficial runoff waters were collected from the infiltration zone close to the *Corconne-Les Matelles* fault (Brestalou) in February 2010.

Temperature, pH and EC were measured in the field using a pH meter and conductimeter (WTW 330 i). Total alkalinity was measured within a day, by acid titration with HCl 0,05N. Chemical and bacteriological analyses were performed at the laboratory. Major elements (Br^- , Cl^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were analyzed by ionic chromatography (DIONEX® ICS 1000) in filtered samples (0.22 μm) offering an analytical precision with a margin of error of less than 5%. Trace elements (Li, B, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Ba, Pb and U) were analyzed using Q-ICPMS X series II Thermo Fisher® at the AETE technical platform of University of Montpellier 2 in filtered samples (0.22 μm), offering an analytical precision with a margin of error of less than 8%. Total and faecal coliforms were analyzed with the Colilert-18 method (Niemela *et al.*, 2003) after sampling in sterile bottles. Samples were also taken for Total Organic Carbon (TOC), collected in dark glass bottles previously combusted for 6 h at 550°C and analysed with catalytically aided platinum 680°C combustion technique (Shimadzu VCSH).

$\delta^{13}\text{C}_{\text{TDC}}$ and soil $\delta^{13}\text{C}_{\text{CO}_2}$ samples were analyzed at Avignon Hydrogeology Laboratory (mass spectrometer Finnigan Mat Delta S type). Water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were analyzed at LAMA laboratory, which is part of HSM. $^{86}\text{Sr}/^{87}\text{Sr}$ samples were analyzed at the Geosciences Rennes.

An automatic sampler with 24 bottles (1l, acid-cleaned polyethylene bottles) was used for water sampling during floods. For these samples, analyses were performed on major and trace elements and on coliforms. The reliability of the sampler was checked for each measured parameter, since values obtained from automatic samplings were compared to values obtained from manual samplings. The results of this comparison (Figure 9) show that TOC concentrations increased by 44% with the automatic sampling probably due to contamination caused by algae proliferation on the inner walls of the sampling tube. Faecal Coliforms decreased by 20% with the automatic sampling which was probably due to the death of bacteria between the time of the sampling and the analysis itself. In the samples collected using the automatic sampler, the trace elements that were not considered are Al, As, Cd, Pb, Mn, Ni, Mo and U. Neither T nor calcium-bicarbonate equilibrium indexes were considered between the results obtained by automatic samplings. All the other major and trace elements were taken into consideration on the data interpretation because of the slight discrepancies observed.

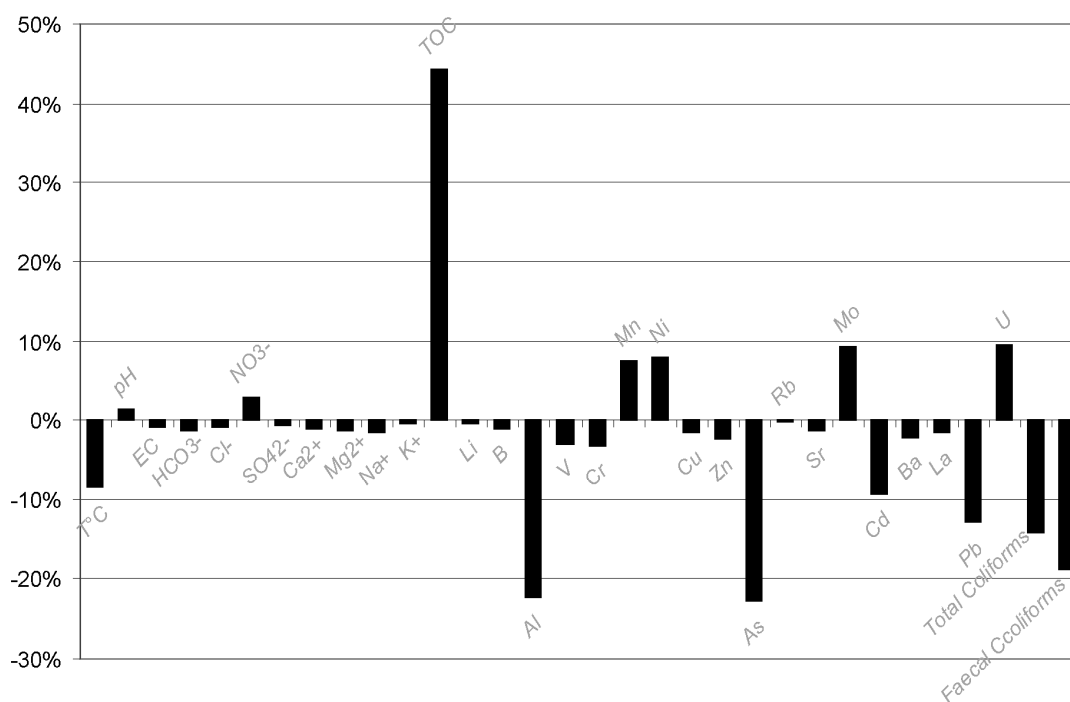


Fig. 9 – Percent error of measures and concentrations between manual and automatic sampling.

2.4.2 - Analytical methods

Aqueous speciation and fluid-mineral equilibrium were calculated with DIAGRAMS software, version 5.0 (Simler, 2009) .

EC Frequency Distribution (ECFD) was used to identify the sum of the populations of conductivities associated with the different GW types that flow through the GW system (Bakalowicz, 1977; Massei et al., 2007). EC Probability Density Function (ECPDF) and its normally distributed component populations were assessed with Peakfit v4.12 software (Seasolve, 2003) that automatically finds and fits peaks for a dataset. The assessment of different EC classes at a karst spring reveals the dynamics of chemically distinct GW types flowing through the karst, and the average EC of a GW type can be related to its origin and residence time (Massei *et al.*, 2007).

Discriminant Factorial Analyses (DFA) were used to interpret geochemical data sets and also as a decision method for defining multiple water-types based on geochemical data sets. The multivariate statistical technique identifies individual groups of samples and tests the membership of each sample to a defined group, as a function of the values for a number of considered variables. It minimizes intra-group variance and maximizes intergroup variance (Dagnelie, 1975; Saporta, 1990). The reduced dimension

achieved by such a statistical technique permitted reaching a simplified multi-criteria representation, highlighting the main trends for the datasets.

2.5 - Hydrodynamic behaviour of the Lez karst system

The experience shows that it is possible, in some cases, to classify wells by groups with similar hydrodynamic behaviour; this geographic assemblage permits the selection, for each group, of one well representative of the hydrodynamic behaviour of a given region monitored by many wells (Karam, 1989). In the case of the Lez karst system, previous hydrodynamic studies have already proposed to regroup wells that characterise hydrodynamic compartments (Karam, 1989; Conroux, 2007).

In the present work, the spatial and temporal hydrodynamics at the Lez karst system was assessed by analysing the piezometric levels on a daily basis, over a nine year period stretching from 2000 to 2009; each hydrological cycle (from September to September, Figure 10) has been analysed separately. The first objective of this analysis is to establish groups of wells that exhibit a common hydrodynamic behaviour in order to identify the hydraulic connectivity between the wells with each other and with the Lez well. The second objective is to identify the major hydrodynamic behaviour of the monitored wells as a function of the climatic context, assessing the wells connectivity based on the hydrodynamic response of this karst system to rainfall events. Moreover, this analysis intends to select some of the most representative wells for chemical sampling, in order to reduce the number of wells to be sampled, given the high number of available wells and the difficulty of this kind of sampling operation.

Different criteria were used to choose the hydrological cycles retained for the analysis of the hydrodynamic response to rainfall events. These years must be characterized by the most complete data series for all the monitored wells, and have contrasting total annual rainfall between each other. For this reason, 2003-2004 was chosen as a cycle of high pluviosity (annual rainfall of 1,353 mm) and 2004-2005 as a cycle of low pluviosity (annual rainfall of 796 mm).

The average piezometric surface (Figure 11) was calculated by IDW (Inverse Distance Weighted) interpolation method using a mean piezometric level calculated for the whole dataset (9 years of daily measures from the 14 monitored wells). Considering the climatic irregularity of the region and the heterogeneity of the karst system, it is important to highlight that this surface interpolation was not used for other purpose then to represent the major piezometric gradient and the consequent major GW flow direction in the system.

In the current work, four groups of wells were distinguished based on their hydrodynamic behaviour and mean piezometric level. The Group 1 (Bois Rozier, Bois des Avants, Gour Noir, Lez and St Gély) is constituted by wells that present a very similar hydrodynamic behaviour to the one of the Lez well, with a mean GW level of 60 m asl. This good hydraulic connectivity is attributed to the presence of the *Corconne-Les Matelles* tectonic fault, which plays a role of major drainage axis along the NE-SW direction (Thierry & Bérard, 1983; Conroux, 2007).

The Group 2 (Ste Croix de Quintillargues, Bois St Mathieu, Fontanés and Mas Martin) has a hydrodynamic behaviour quite similar to Group 1, but with slightly higher piezometric levels (mean piezometric level of 62 m). The general water table variations over time observed at the Lez well are simultaneously observed for the wells of this group, especially for Ste Croix de Quintillargues.

The Group 3 (Laudou and Les Matelles) corresponds to wells where the highest piezometric levels are observed (mean piezometric level of 85 m). The similar hydrodynamic behaviour of these wells may denote a good hydraulic connectivity, in spite of their distance to each other. However, they present a difference in their constant piezometric level of about 10 m. Les Matelles is located in a non-confined Jurassic limestone region, which allows the water table to rise without restraint in response to rainfall events, unlike wells located in confined areas, such as most of the monitored wells.

Group 4 (Claret and Coutach) also correspond to wells characterized by high piezometric level (mean piezometric level of 76m). The Coutach well is located on the supposed northeast limit of the Lez spring catchment area and is geographically close to the Claret well. Under important recharge events, both wells reach similar maximum piezometric levels, which are limited to 120 m (Conroux, 2007). The Claret well is close to the main drain (major fault of *Corconne-Les Matelles*), and for this reason, this well is much more subjected to water-head decreasing than Coutach is.

The analysis of the wells behaviour shows a better correlation between these wells during years of high rainfall than during years of low rainfall. For example, we observe a constant piezometric difference between Laudou and Les Matelles of about 14 m during years of high pluviosity such as 2003-2004, although it is more important (20 m) during years of low pluviosity like 2004-2005 (Figure 10). This illustrates a classical karst behaviour (Vaute et al., 1997) where the hydraulic connectivity between the aquifer compartments is better during recharge events.

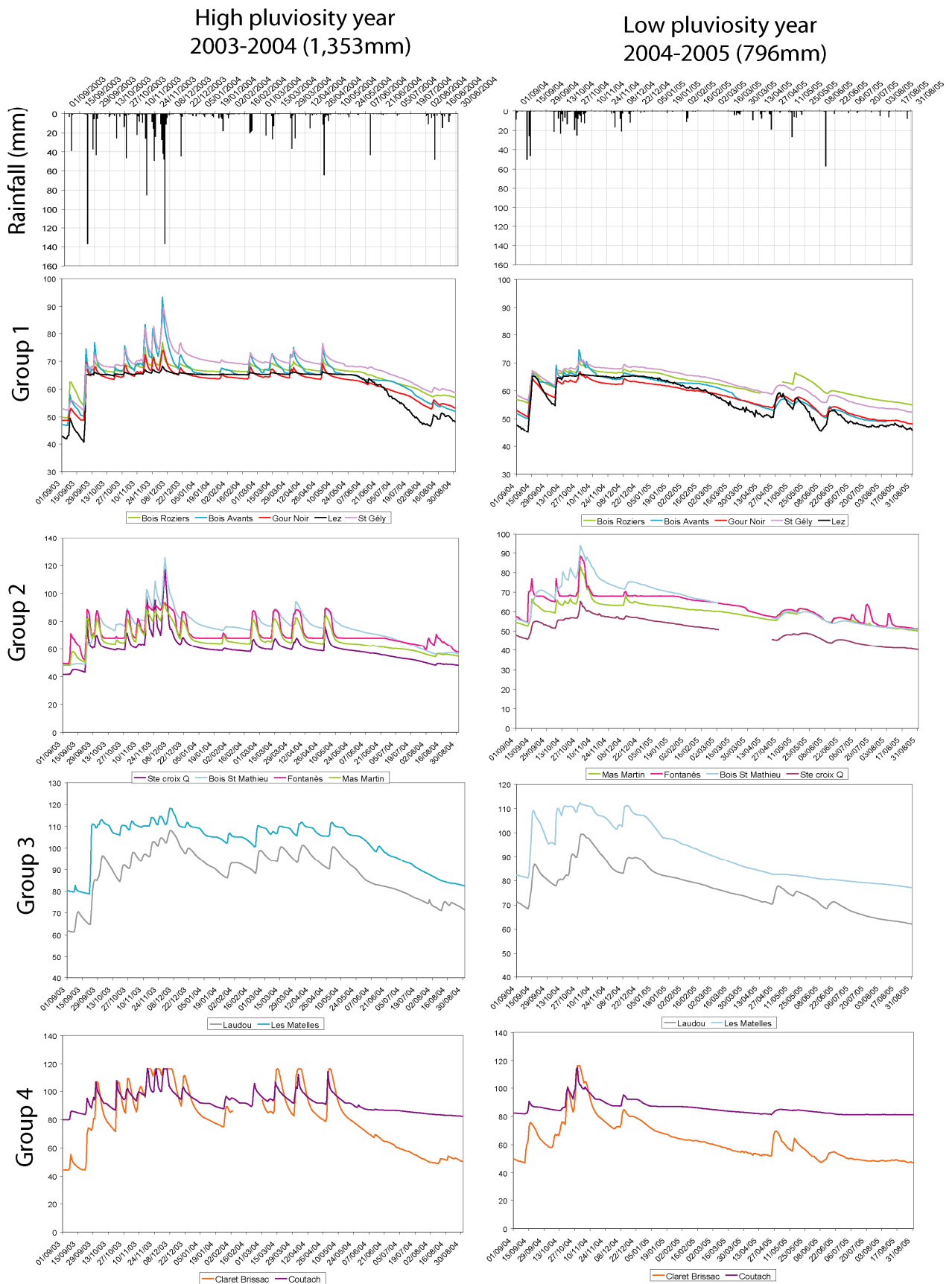


Fig. 10 – Piezometric variation during years of high pluviosity: 2000-2001 and 2008-2009 and years of low pluviosity: 2004-2005 and 2006-2007 for the Group 3 (Fontanès, Mas de martin, Bois St Mathieu and Sainte Croix de Quitillargues).

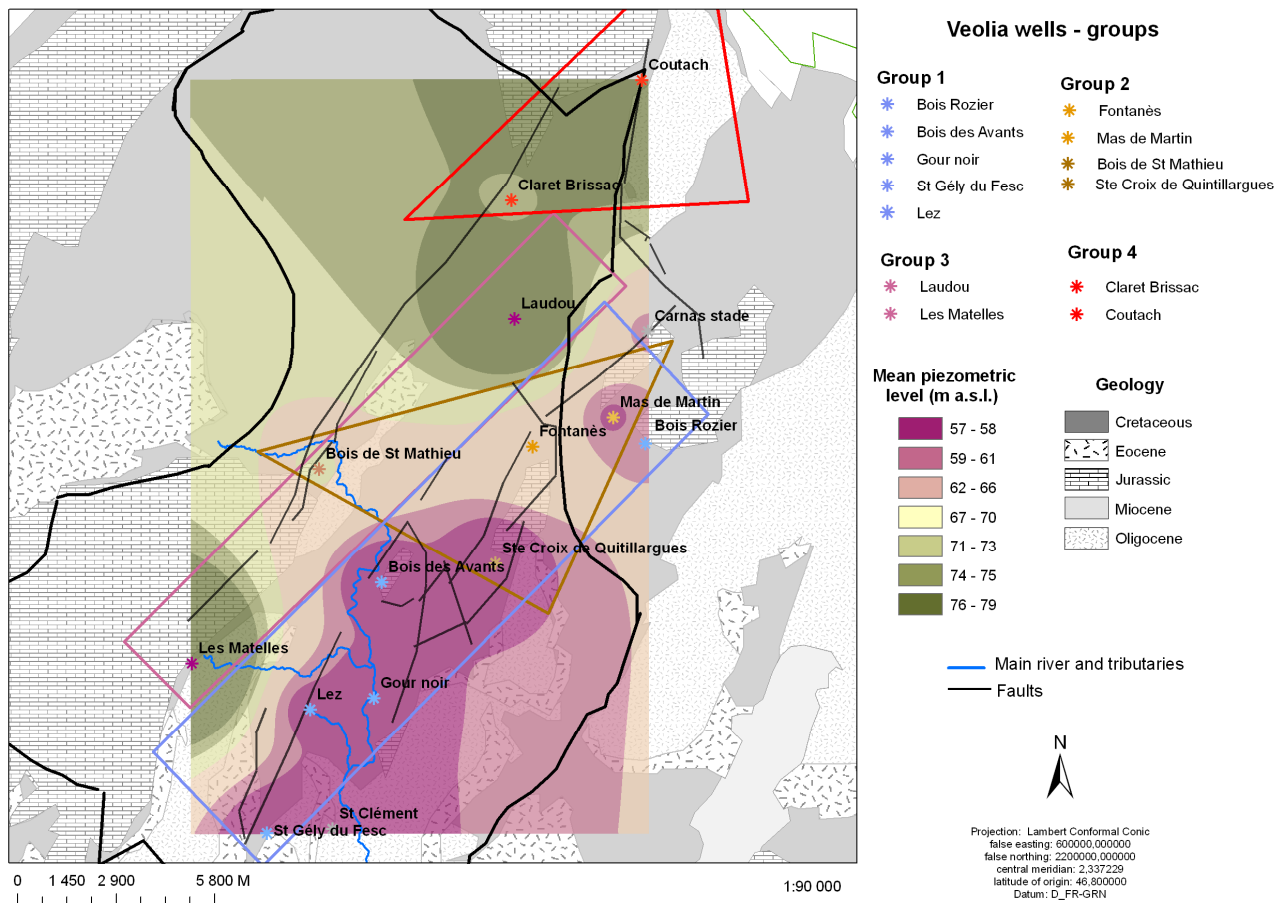


Fig. 11 – Piezometric IDW interpolation of average GW level by 15 wells over the Lez karst system; wells location and their group classification.

Once the groups were identified, it was possible to select four wells representative of the main hydraulic compartments for the water sampling: Laudou, Fontanès, Bois Roziers and Gour Noir. The described piezometric behaviour shows that hydrodynamics are associated to two major compartments. The first one, in the southwest, presents low piezometric levels and high piezometric variability (Groups 1 and 2). The second one, in the northeast, presents high piezometric levels and low piezometric variability (Groups 3 and 4). The mean difference between the piezometric levels of these two compartments explains the major piezometric gradient of the aquifer (Figure 11) and consequently, the predominant Northeast to Southwest axis of GW flow direction of this system.

Chapter 3 - Application of the hydrochemistry to understand the functioning of a karst system

Extracted from Article N°1

Article title:

“Geochemical evidence of water source characterisation and hydrodynamic responses in a karst system.”

Authors:

Bicalho C.C., Batiot-Guilhe C., Seidel J.L., Van Exter S., Jourde H.

Journal: Journal of Hydrology

Present Situation: Submitted

Abstract

The Lez karst spring, located in the Mediterranean basin (southern France), supplies with water the metropolitan region of Montpellier (France) since the 19th century. Since 1981, intense water exploitation is being performed directly in the main conduit with a maximum exploitation flow rate of about 1,700 l/s. To improve the understanding of groundwater origins and circulation dynamics in this karst system, groundwater samples have been collected during various hydrologic conditions from March 2006 to March 2010, for measuring and analysing: physicochemical parameters major and trace elements, Total Organic Carbon: TOC and faecal and total coliforms.

During the first recharge events of autumn, high-mineralized waters have been observed at the Lez spring. This singular behaviour was monitored in a fine time-lag. A multivariate statistical analysis revealed the existence of different water-types discharging at the Lez spring. During high stage periods, high-mineralized water initially discharges from the spring, followed by rapid infiltration water. This behaviour suggests that hydrodynamics affect groundwater circulation by soliciting different end-members, such as geochemically evolved, long residence-time water, and surficial recharge water. These characteristics were observed on a larger scale by monitoring three seasonal overflow springs connected to the Lez karst system.

A detailed analysis using major and trace elements and elemental ratios provide some insight into the different water origins, the associated lithologies and the mineral-solution reactions related to hydrodynamic responses. Between the five distinguished water-types, the two more contrasting ones are emphasized: the first one correspond to more geochemically evolved, long residence-time waters, issued from deep layers where evaporite fingerprinting have been identified. They are characterized by high mineralization and high concentrations in Cl, Na, Mg, Li, B and Br elements, high Sr/Ca, Mg/Ca and Cl/Br ratios. The second water-type corresponds to little mineralized waters with high concentrations in NO₃, bacteria and TOC, and represents the flux of rapid infiltration waters. They underline the vulnerability of the system to surface infiltration and anthropogenic contamination through the infiltration of waters by sinkholes and well-developed fracture networks.

Key words: karst, groundwater, natural tracing, hydrochemistry, water transit.

3.1 - Introduction

At the Lez spring, high-mineralized waters flow during extreme hydrological conditions provoked by intense rainfall. During the same recharge events, low mineralized groundwater with marked bacterial contamination and nitrate and TOC concentrations have been also observed. Anthropogenic tracers denote the rapid migration through the karst of waters issued from surface infiltration. The association of rapid chemical and bacteriological responses during floods seems also to be a characteristic of karst systems (Personné et al., 1998).

The flow of such different groundwater properties during a same flood event suggests that multiple end-members with contrasting characteristics are solicited. In order to identify the different water-types that constitute the Lez spring flow, a multivariate statistical method is used for the hydrochemical analysis of data collected from the Lez spring from March 2006 to May 2010. Multivariate statistical methods were used to identify the impact that natural and anthropogenic waters have on the groundwater quality of Nandong karst system (China) (Jiang et al., 2009); to evaluate how multiple origins of water and variations in aquifer flow paths affect the chemical characteristics of a spring draining a portion of northern Florida (Moore et al., 2009); to study the degree of karst development and the importance of the unsaturated zone (Spain) (Mudarra & Andreo, 2011) and to define genetic origin of chemical parameters in groundwaters (Algeria) (Belkhiri *et al.*, 2011).

This study addresses the Lez karst system circulation dynamics in order to better characterize GW transfers within the Lez karst system by analyzing water chemical and physicochemical variations during the different hydrological periods, together with the hydrodynamic response of the Lez system. The sub-objectives are:

- (i) defining the chemical GW characterization and its relation with aquifer hydrodynamic responses;
- (ii) assessing the main lithologies and mineral-solution reactions associated with water chemistry;
- (iii) identifying the relation between the aquifer and the surface waters, so as to understand aquifer vulnerability;
- (iv) contributing to the improvement of karst system conceptual modelling with a possible extended application towards other complex Mediterranean karst systems.

3.2 - Results

3.2.1 - *The Lez spring behaviour during flood events*

At the beginning of autumn 2008, the first rainfall events occurring after a long dry period generated over time high variations of the groundwater physicochemical parameters (Figure 12). Two major rainfall events participated to the flood that triggered the Lez spring on October 23, 2008. The first rainfall (95mm) triggered the Lez spring flow on October 20, 2008. The second one occurred on October 22, 2008 (80mm). Previous conditions were characterized by a low piezometric level, typical of the end of the low stage period, when waters have stable and elevated EC and T values.

Two days after the first rainfall, EC started to drop to 643 $\mu\text{S}/\text{cm}$; this phenomenon was concomitant with T decrease, calcite SI increase, Cl, SO_4 , Mg and Sr decrease, but also with a peak in total and faecal coliforms concentration.

Three days after the same rainfall event, a high EC peak (855 $\mu\text{S}/\text{cm}$) was observed, in relation with a T increase, still lower however than the T concentration observed during the low stage period. A decrease of calcite SI occurred simultaneously with peaks of Cl, Mg, SO_4 , Sr, and total coliforms concentration.

After the EC peak, a marked decrease of EC, with a minimal value of 616 $\mu\text{S}/\text{cm}$, could be observed 18 days after the first rainfall event. This second slope change was even more abrupt than the first one. As previously observed, a decrease of T as well as Cl, SO_4 , Mg, and Sr concentrations were observed. TOC and NO_3^- concentrations showed great variability after the event started, undertaking important peaks. Calcite SI slightly rose and total coliforms concentration increased to maximal values that remained high for one week after the flood started. Faecal coliforms, after attaining the first peak, did not experience a second increase of such importance.

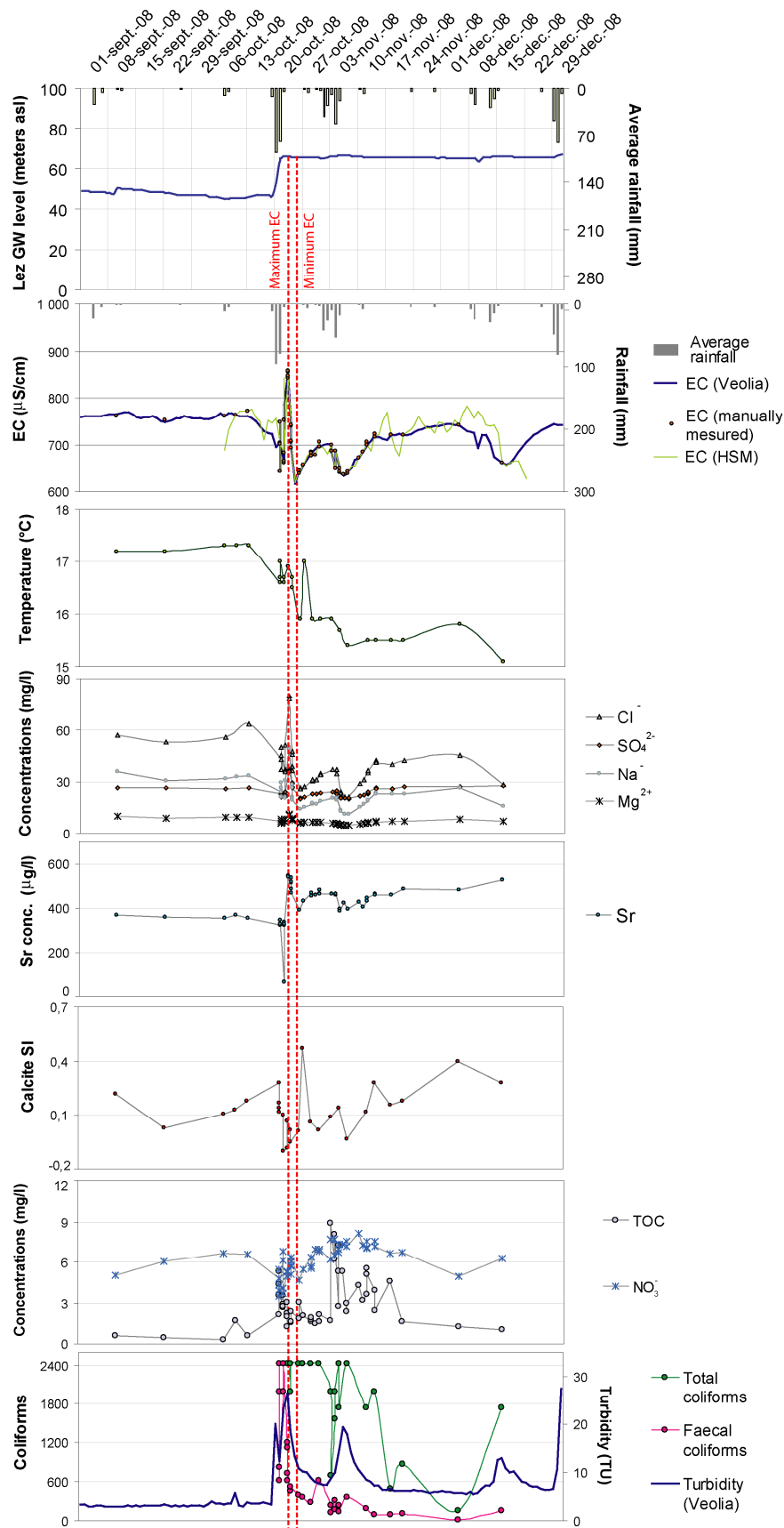


Fig. 12 – Daily rainfall average calculated for the rain gauges: Prades, St Martin and Valflaunès. Piezometric level at the pumping well of the Lez spring. T and EC monitored at the Lez spring by Veolia and EC measured on field by HSM. Time variations for: Cl, SO₄, Mg, Sr, TOC, NO₃, Calcite Saturation indexes, total /faecal coliforms (Colony Forming Units (CFU) per 100 ml) and Turbidity (TU). Red dashed lines indicate the maximum and minimum values of E.C.

3.2.2 - Characterization of the different groundwater types flowing at the Lez spring

After underlining the variability of Lez groundwater, the EC Frequency Distribution (ECDF) was used so as to identify the different GW types at the Lez spring over the entire hydrological cycle. Because of their contrasting annual rainfall, the results were presented for the hydrological cycles: 2006-2007 and 2007-2008 (Figure 13). Four classes were obtained for 2007-2008 and 2 classes for 2006-2007.

The hydrological cycle 2007-2008 was the wettest year throughout the whole survey period. On the contrary, 2006-2007 was a dry year in terms of annual rainfall. The number of classes seems related to annual pluviosity, as two classes of EC were not observed for the years with a low annual precipitation. This statistical analysis showed the existence of distinct GW types contributing to the groundwater flow at the Lez spring.

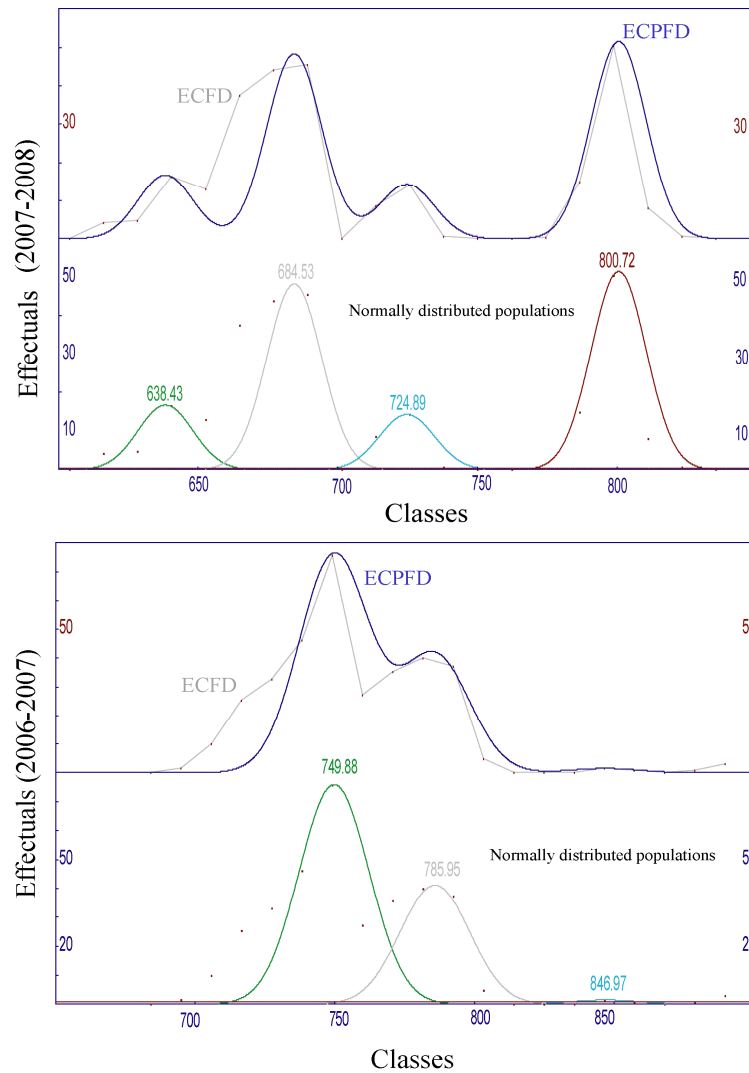


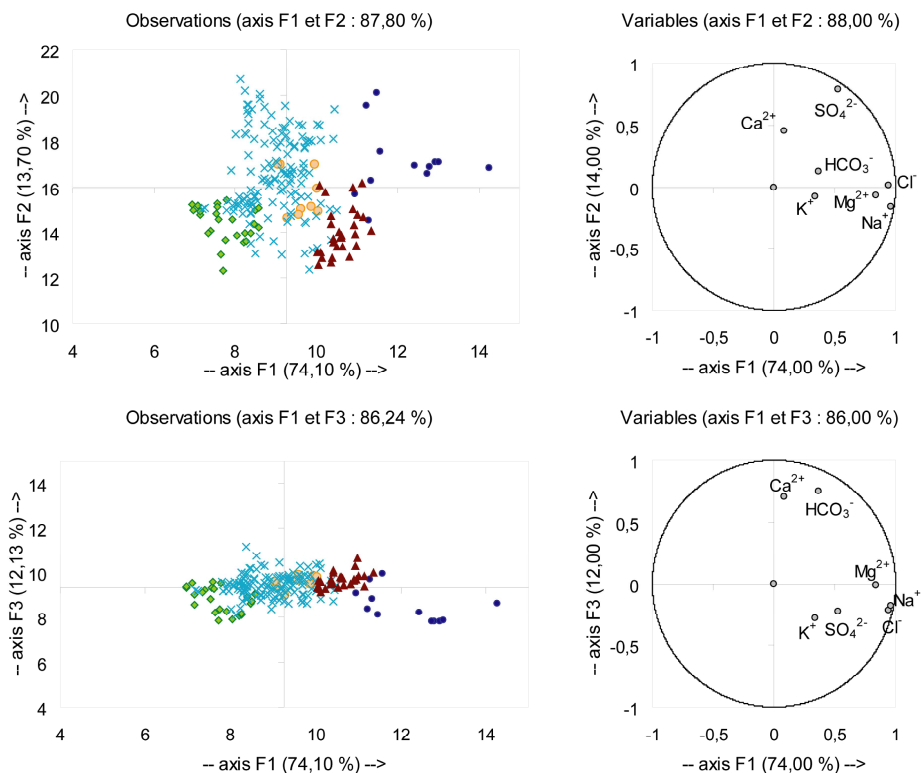
Fig. 13 – 2006/2007 and 2007/2008 hydrological cycles. Top: EC frequency distribution with the corresponding Probability Density Function. Bottom: normally distributed component populations.

Afterwards, once the existence of multiple water-types have been identified, Discriminant Factor Analyses (DFA) were used to the data set in order to identify the water types flowing at the Lez spring and for interpreting their chemical characteristics (Figure 14). The qualitative or dependent variable initially adopted on the foremost DFA application was determined by the analysis of temporal variations for chemical and physicochemical data, pluviosity and groundwater level (e.g. Figures 12 and 15). DFA being also a decision method, furnished suggestions regarding the qualitative variable; each suggestion of modification on the groups belonging furnished by the DFAs had its context carefully verified before being accepted or not. This procedure permitted to refine the groundwater types previously identified and also to interpret the groundwaters chemical characteristics.

The explicative or independent variables assumed were EC, major ions (Cl^- , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+}), trace elements (Li, B, Rb, Ba and Sr), pCO_2 and calcite SI. The qualitative or dependent variables were: 1) “*High waters*”, that discharge during high stage period and are associated to high groundwater level and EC oscillations; 2) “*Low waters*”, that discharge during low stage period and are associated to low groundwater level and stable and high EC; 3) “*Dropping waters*”, that discharge during the transition between high and low stage period and are associated to groundwater level decrease and EC increase. Extremely high or low EC values are referred to as: 4) “*Piston-flow waters*” ($\text{EC} > 780 \mu\text{S/cm}$) and 5) “*Dilution waters*” ($\text{EC} < 600 \mu\text{S/cm}$).

The F1-axis for the first DFA (major elements) represents the mineralization with Cl, Na and Mg. The F2-axis is defined positively by Ca and partially by SO_4 (Figure 14). “*Piston-flow waters*” and “*Low waters*” present a good discrimination. However, there is a considerable overlapping between “*High waters*” and “*Dilution waters*” in the negative part of the F1-axis and between “*High waters*” and “*Dropping waters*” in the positive part of the F1-axis. Mixing processes in the karst system could explain this overlapping. During transition periods, when two GW types succeed, mixing effects are even more pronounced. Accordingly, during those transition periods, some samples are representative of more than one GW type because of important mixing indexes.

Major elements



Major and trace elements

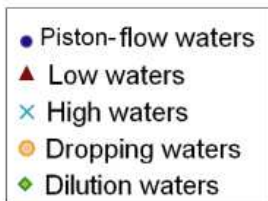
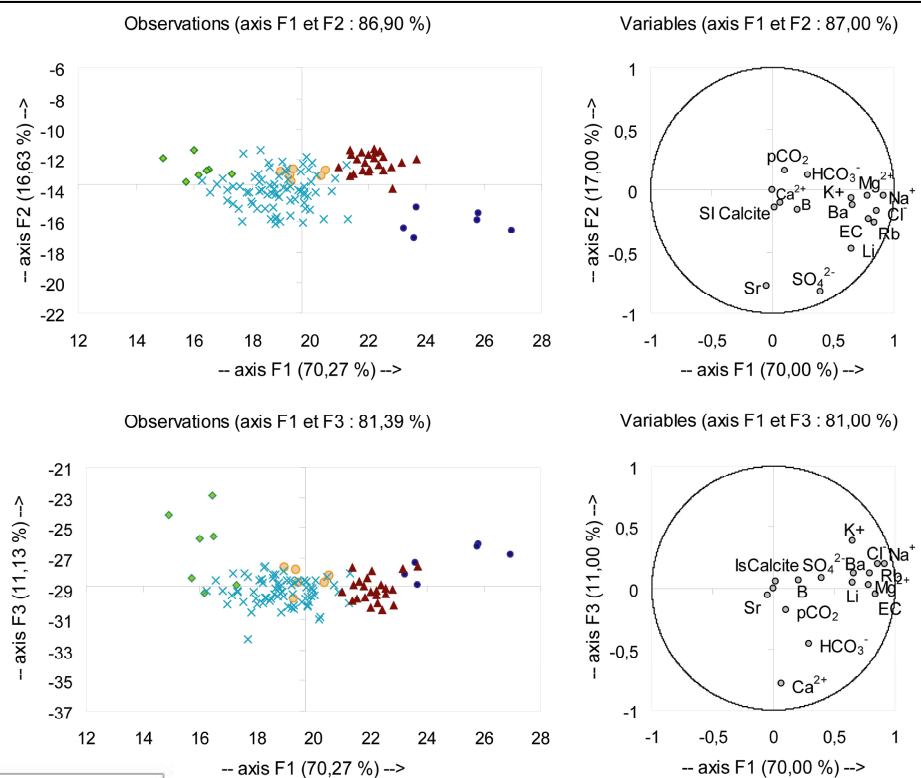


Fig. 14 – Top: DFA for the Lez spring data using major elements. Left: sample space; right: variable space. Bottom: DFA of the Lez spring data using major and trace elements. Left: sample space; right: variable space.

The second DFA (major and trace elements) shows a better discrimination between the five GW types. A remaining zone of overlapping between “*High waters*” and “*Dropping waters*” is still observed (Figure 14). The F1-axis is positively weighted by EC, Cl, Na, Mg, Ba, K, Rb and Li. The F2- axis is negatively weighted by Sr and SO₄. The trace elements help better characterize the “*Piston-flow waters*”, associated with a marked mineralization in Cl, Na, Li, Mg, Cr, Rb and Ba. The “*Low waters*” are the second high-mineralized waters compared to those elements, but SO₄ and Sr concentrations are lower than in “*Piston-flow waters*”. The “*Dilution waters*” remain the less mineralized waters.

Once identified, the water-types for the whole study period are displayed on Figure 15, where we can observe the variability of those “regime” periods throughout the years. Table 1 presents the average concentrations and the range of variation for the five GW types identified at the Lez (spill water from pumping), Lirou, Restinclières and Fleurettes springs, as well as specific data for other springs and wells sampled during the 2009 low stage period (Figure 15).

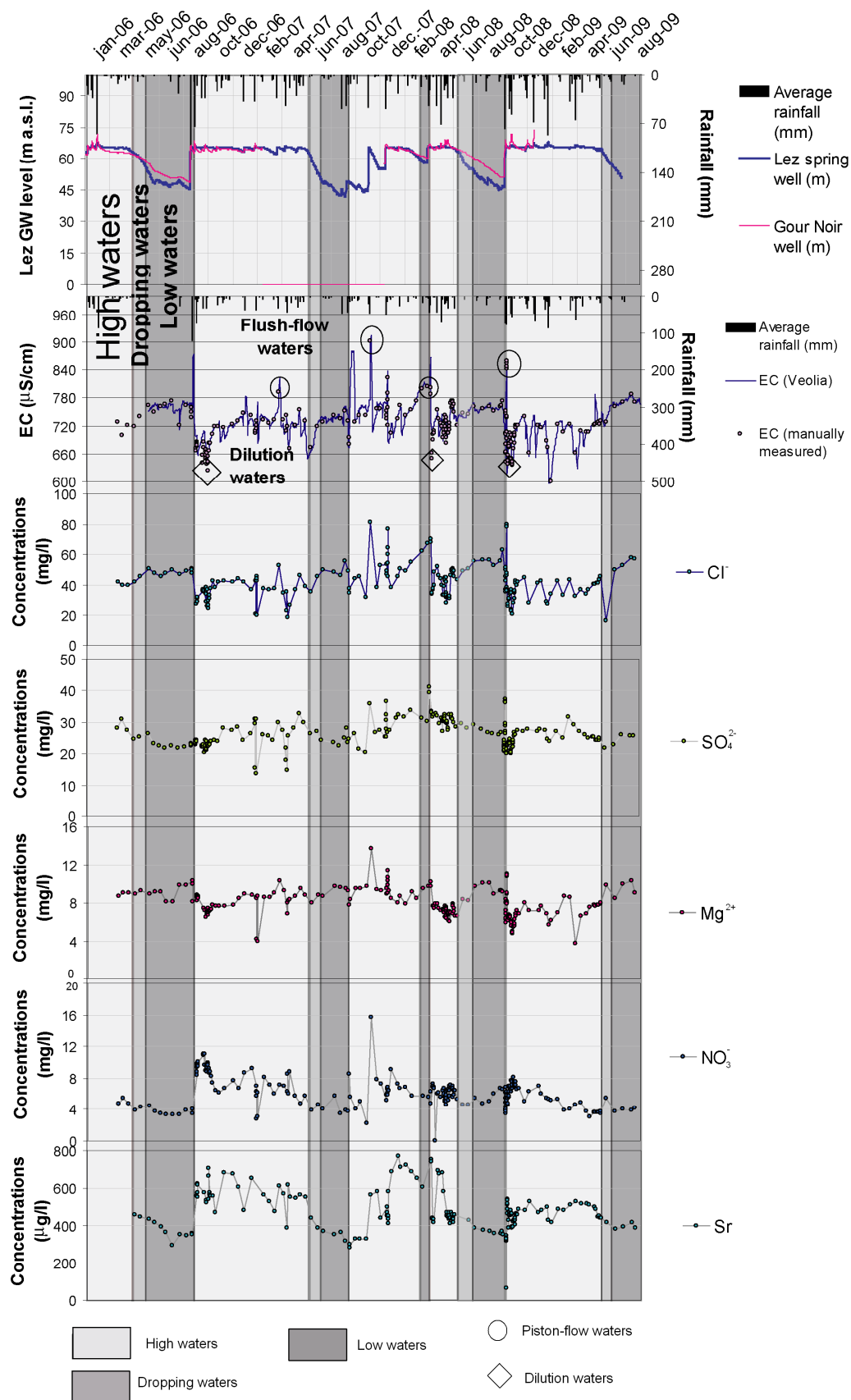


Fig. 15 – Daily precipitation calculated from Prades, St Martin and Valflaunès stations average, GW levels (m.a.s.l.) at “Lez spring” and “Gour Noir” wells; EC measured in the pumping well by Veolia, time variations for Cl, SO₄, NO₃, Sr and Mg concentrations.

Table 1: Mean concentrations and range of variations for each groundwater-type identified within the Lez karst system (March 2006-August 2009) and other regularly monitored Lez karst system springs. One sampling for other springs and wells belonging to Lez karst system, Valanginian and surrounding karst system (summer 2009).

	Average (range)										Single sampling									
	Dropping waters (9 samples)	Low waters (27 samples)	Dilution waters (23 samples)	High waters (133 samples)	Flush flow waters (11 samples)	Lirou (54 samples)	Fleurettes (10 samples)	Restinelières (23 samples)	Surrounding systems		Valanginian Systems						Lez System			
									Sauve spring	Fontbomme spring	Olivier well	Boinet well	Lauret spring	Dolgue spring	Lavabre spring	Lavabre well	Fontanes well	Laudou well	Bois Roziers well	Gour Noir well
T°C	16.2 (15.9 - 16.4)	17.1 (16.3 - 17.4)	16.2 (15.4 - 17)	15.5 (5 - 21)	15.5 (16.0 - 15.9)	14.3 (13.3 - 15.0)	15.9 (14.0 - 16.6)	17.1 (15.9 - 18.6)	14.2	18.0	18.6	15.7	13.8	13.2	14.0	18.5	15.3	14.9	15.8	17.4
pH	7.16 (6.99 - 7.3)	7.16 (7 - 7.3)	7.24 (7 - 7.3)	7.2 (6.9 - 7.6)	7.3 (6.9 - 7.6)	7.1 (6.9 - 7.8)	7.2 (7.0 - 8.6)	7.1 (6.6 - 7.5)	7.33	7.43	7.84	7.08	7.51	7.32	7.38	7.16	7.01	6.99	7.07	7.23
TDS	599.8 (544 - 619)	614.36 (571 - 659)	526.8 (481 - 556)	580.7 (508 - 645)	637.0 (612 - 664)	515.6 (410 - 570)	563.8 (485.0 - 580.0)	573.3 (530.0 - 605.0)	444.0	542.0	550.0	744.0	524.0	656.0	572.0	653.0	585.0	584.0	544.0	588.0
Si calcite	0.18 (0.03 - 0.36)	0.21 (0.14 - 0.43)	0.21 (0.03 - 0.47)	0.23 (0.13 - 1.03)	0.36 (0.08 - 0.82)	0.15 (0.00 - 0.75)	0.33 (0.08 - 1.69)	0.24 (0.04 - 0.58)	0.1	0.6	0.9	0.3	0.5	0.4	0.4	0.3	0.1	0.1	0.2	0.4
pCO ₂	0.023 (0.02 - 0.04)	0.025 (0.02 - 0.04)	0.02 (0.01 - 0.04)	0.02 (0.0 - 0.04)	0.02 (0.01 - 0.04)	0.03 (0.00 - 0.04)	0.03 (0.00 - 0.04)	0.03 (0.01 - 0.05)	0.01	0.01	0.00	0.04	0.01	0.02	0.01	0.03	0.04	0.04	0.03	0.02
EC	728.2 (673 - 747)	756.4 (719 - 799)	650.9 (623 - 686)	714.1 (699 - 773)	824.0 (777 - 902)	601.1 (517 - 701)	856.4 (568 - 880)	673.7 (614 - 706)	518.0	629.0	677.0	859.0	583.0	708.0	637.0	640.0	649.0	681.0	605.0	664.0
HCO ₃ ⁻	362.0 (330.7 - 383.8)	388.8 (337 - 421.5)	328.2 (283 - 351.4)	356.2 (271.54 - 405.9)	351.5 (336.7 - 403.0)	363.6 (265.1 - 406.9)	379.8 (336.8 - 405.0)	373.5 (355.1 - 391.1)	286.8	366.6	341.8	488.2	379.1	426.5	403.3	424.0	401.5	422.3	375.9	407.6
Cl ⁻	41.35 (16.39 - 63.3)	52.1 (45.9 - 63.3)	30.6 (20.9 - 39.6)	38.8 (19.1 - 55.1)	71.6 (52.9 - 81.9)	11.09 (7.55 - 14.97)	12.9 (7.7 - 14.9)	20.7 (13.8 - 29.0)	9.0	11.3	17.2	25.4	5.7	13.9	8.0	10.8	10.4	11.6	10.4	13.0
NO ₃ ⁻	4.3 (3.5 - 5.5)	4.4 (3.3 - 6.7)	8.3 (4.7 - 11.1)	6.29 (0 - 10.1)	6.7 (4.7 - 15.7)	3.0 (1.0 - 15)	5.1 (2.5 - 6.8)	5.5 (4.31 - 3.9)	2.66	5.44	25.88	19.16	1.01	1.02	0.00	0.00	6.74	0.00	3.55	3.36
SO ₄ ²⁻	25.9 (21.9 - 29.7)	24.9 (21.8 - 31.3)	22.6 (20.2 - 33.5)	26.7 (14.5 - 33.67)	35.3 (30.1 - 41.1)	8.3 (9.9 - 23.4)	20.8 (16.8 - 23.3)	23.4 (19.8 - 25.9)	36.6	16.6	28.7	33.9	10.5	26.8	14.3	19.0	21.2	11.2	16.0	14.8
Ca ²⁺	122.1 (113.4 - 132.8)	120.1 (111.9 - 128.4)	111.1 (82.0 - 121.7)	121.8 (109.5 - 146.0)	115.6 (110.6 - 126.1)	121.9 (105.6 - 138.4)	133.7 (114.4 - 143.9)	123.4 (115.9 - 133.2)	82.9	129.4	107.2	149.7	119.4	140.4	129.2	126.1	133.2	132.2	128.2	137.5
Mg ²⁺	8.3 (6.6 - 9.9)	9.4 (8.1 - 10.4)	6.6 (4.8 - 7.7)	7.6 (3.8 - 9.8)	10.8 (9.7 - 13.7)	2.16 (0.00 - 12.56)	4.55 (1.7 - 3.83)	7.4 (3.9 - 10.0)	16.6	5.0	20.3	19.5	4.0	8.2	6.0	6.5	5.4	0.7	3.1	3.4
Na ⁺	24.4 (19.9 - 29.1)	32.8 (29.4 - 37.3)	17.8 (11.2 - 25.6)	22.3 (12.9 - 32.7)	42.9 (34.9 - 56.4)	5.14 (4.28 - 6.38)	6.29 (4.90 - 7.24)	10.9 (7.2 - 16.2)	6.94	5.25	8.78	9.26	4.02	5.79	4.97	5.96	5.50	4.75	6.45	7.46
K ⁺	1.26 (0.99 - 1.59)	1.56 (0.96 - 2.01)	1.38 (0.85 - 2.47)	1.31 (0.00 - 7.29)	2.03 (1.55 - 2.52)	0.27 (0.00 - 0.66)	0.37 (0.24 - 0.47)	0.53 (0.0 - 1.10)	1.74	0.23	1.25	0.43	0.39	0.19	0.10	0.71	0.51	0.89	0.58	0.85
toc	0.89 (0.59 - 1.9)	0.69 (0.29 - 2.21)	3.70 (1.13 - 11.0)	2.51 (0.06 - 11.74)	2.49 (0.63 - 6.59)	2.88 (0.42 - 15.79)	2.64 (1.10 - 5.64)	1.27 (0.79 - 2.06)	1.60	0.99	1.28	1.75	1.32	1.68	1.24	1.02	0.80	4.98	1.03	1.80
Li	4.05 (3.71 - 4.45)	4.26 (3.41 - 5.6)	3.04 (0.2 - 4.62)	3.86 (2.58 - 5.49)	6.21 (5.30 - 6.52)	0.72 (0.05 - 14.40)	2.05 (1.13 - 2.39)	3.48 (2.51 - 4.75)	2.13	1.93	9.29	7.86	0.86	3.48	2.22	2.52	3.90	1.26	1.84	2.20
Br	-	96 (0 - 170)	106.9 (103 - 112.5)	103.4 (0.0 - 153.1)	124.9 (103.6 - 136.9)	59.5 (0.0 - 370.4)	128.4 (84.3 - 358.0)	158.9 (0 - 380.5)	0.00	0.00	154.90	192.40	83.30	177.00	151.90	140.00	160.00	240.00	150.00	0.00
B	19.3 (17.5 - 21.9)	20.82 (5.86 - 27.28)	17.7 (0 - 31.8)	19.2 (6.2 - 31.0)	23.64 (18.46 - 31.34)	10.0 (0.4 - 17.0)	14.6 (11.9 - 16.0)	15.2 (2.4 - 18.4)	17.9	13.0	56.5	54.0	10.8	21.7	18.6	15.6	19.6	11.9	13.8	16.2
Rb	1.23 (1.1 - 1.31)	1.43 (1.2 - 1.78)	0.93 (0.15 - 1.42)	1.11 (0.66 - 1.72)	1.68 (0.65 - 2.46)	0.22 (0.01 - 1.19)	0.43 (0.28 - 0.61)	0.74 (0.31 - 1.04)	1.25	0.49	1.23	0.69	0.16	0.38	0.22	1.77	0.50	0.89	0.41	0.88
Sr	439.8 (414.9 - 466.5)	378.2 (292 - 507)	438.9 (62.1 - 704.5)	466.6 (281.30 - 773.52)	558.3 (415.4 - 752.3)	83.7 (4.3 - 364.2)	335.8 (185.1 - 399.9)	439 (343.4 - 577.8)	244.8	277.2	1998.0	3286.0	456.7	862.6	821.0	686.5	410.2	327.1	329.4	296.8
Total colif.	82.3 (47.1 - 142.1)	55.1 (26.2 - 151.5)	2198 (1 583 - 2 420)	1 237.7 (26.2 - 2 420)	2 420 (2420 - 2 420)	766 (13.5 - 2 420)	834.1 (60.2 - 2 420)	316.2 (74.4 - 1 533.1)	648.80	0.00	3.10	6.20	2420.0	44.10	8.60	133.10	2.00	0.00	35.00	11.00
Fecal colif.	10.5 (6.3 - 18.7)	9.5 (3.1 - 13.2)	665.7 (148.3 - 2 420)	325.6 (1.0 - 2 420)	915.8 (613.1 - 1 203.3)	275.8 (7.8 - 1 117.8)	49.9 (7.8 - 117.8)	24.3 (2.0 - 81.3)	52.10	0.00	0.00	0.00	56.30	0.00	0.00	5.20	0.00	0.00	0.00	0.00

3.3 - Discussion

3.3.1 - Water-rock interactions: assessing deep waters end-member

Statistical analysis helped deciphering the multiple water types flowing at the Lez spring according to their chemical composition throughout the hydrological year. The water-types result from the mixing of variable proportions of different end-members. Data interpretation using major and trace elements and elemental ratios can provide some insight into different end-members associated with water origins and their lithologies.

Cl concentrations are notably higher at the Lez spring in comparison with other springs of the karst system and of surrounding systems, being particularly high for the “*Piston-flow*” groundwaters (Figure 16). Given the geological context of the Lez spring, two possible origins can explain Na-Cl mineralization; a shallow origin from the soil/epikarst compartment, where the flushed water had interacted or equilibrated within the soil zone, having possibly resided in small pores or fractures near the land surface (Marjolet & Salado, 1976; Joseph *et al.*, 1988); and a deep origin from a specific compartment within the saturated zone.

The high correlation between Cl and Na concentrations (Figure 16) suggests the existence of halite dissolution (Vengosh *et al.*, 1995; Bernasconi, 1999). The good correlations observed for elements such as Cl⁻, Mg²⁺, K⁺, SO₄²⁻, Na⁺, Ca²⁺, Li, B, Rb and Sr (Figure 14) provide indications of evaporitic mineral fingerprinting (Pulido-Leboeuf *et al.*, 2003).

Bromide is commonly used with chloride to identify the origin of salinity of groundwaters in sedimentary basins and is fundamentally used on investigations focusing on chloride origins related to evaporitic rock dissolution (Bernasconi, 1999; Kloppmann *et al.*, 2001; Sánchez-Martos *et al.*, 2002; Cartwright *et al.*, 2006). Cl/Br ratios (Figure 16) of the “piston-flow” waters (1300 <Cl/Br<1700) indicate an extra source of Br for those waters like halite dissolution which can provoke a Cl/Br ratio increase from 200 (rain waters) up to 1600 (Cartwright *et al.*, 2006). Cl/Br ratio data reinforce the hypothesis that Na and Cl are possibly originated from deep-seated formations containing evaporite minerals which rise through the fluid transport provided by means of the major tectonic accidents.

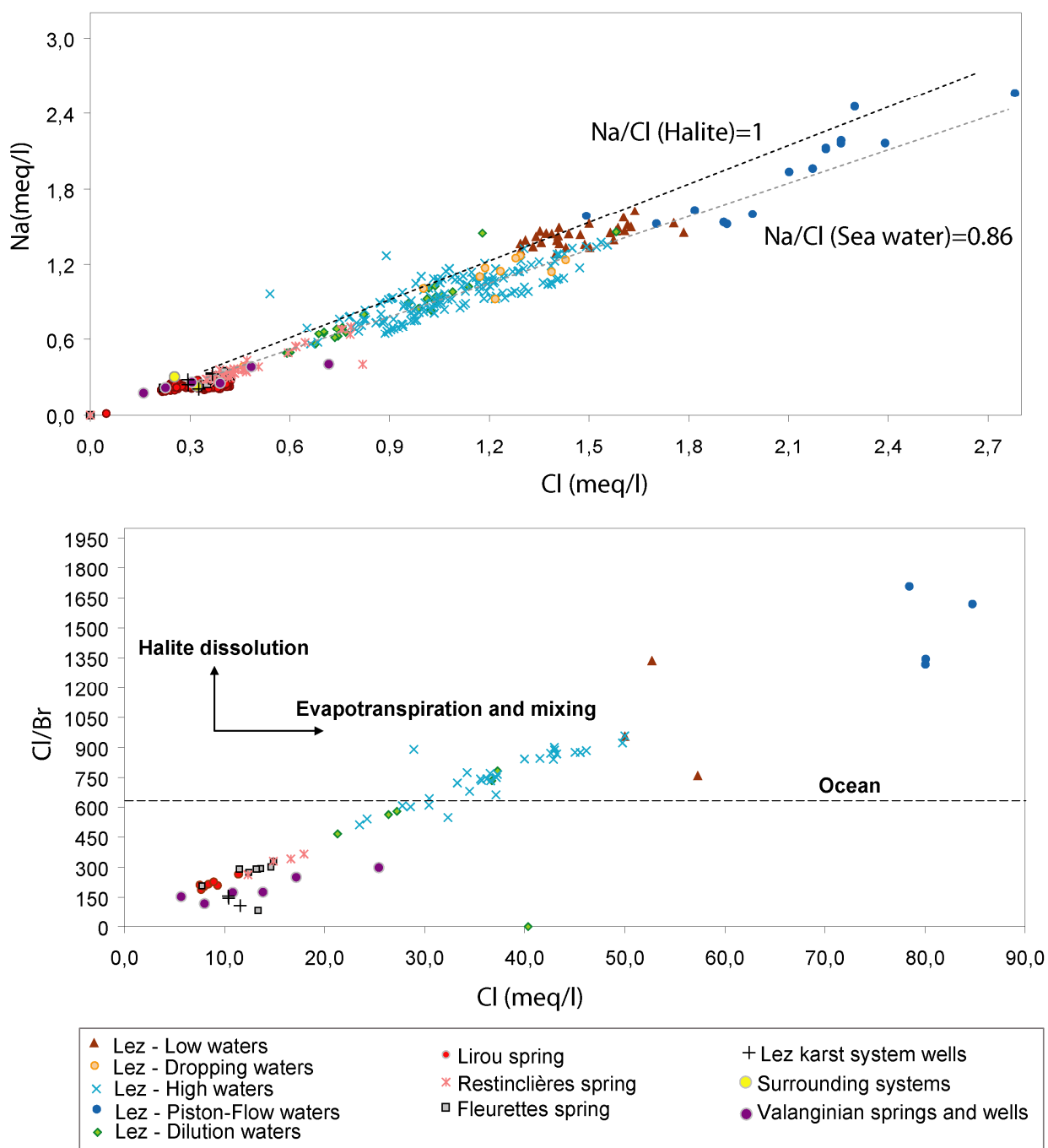


Fig. 16 – Na vs. Cl (meq/l); Cl/Br vs. Cl (mg/l) for all the Lez karst system springs and wells, and for springs/wells belonging to the surrounding karst system.

Figure 17 shows evidence for potentially different sources of Sr or Mg, which could be controlled by lithology and stratigraphy; e.g., different flowpaths can contribute with water of different initial Sr/Ca and Mg/Ca ratio, but differences can also be displayed within a single stratigraphic unit.

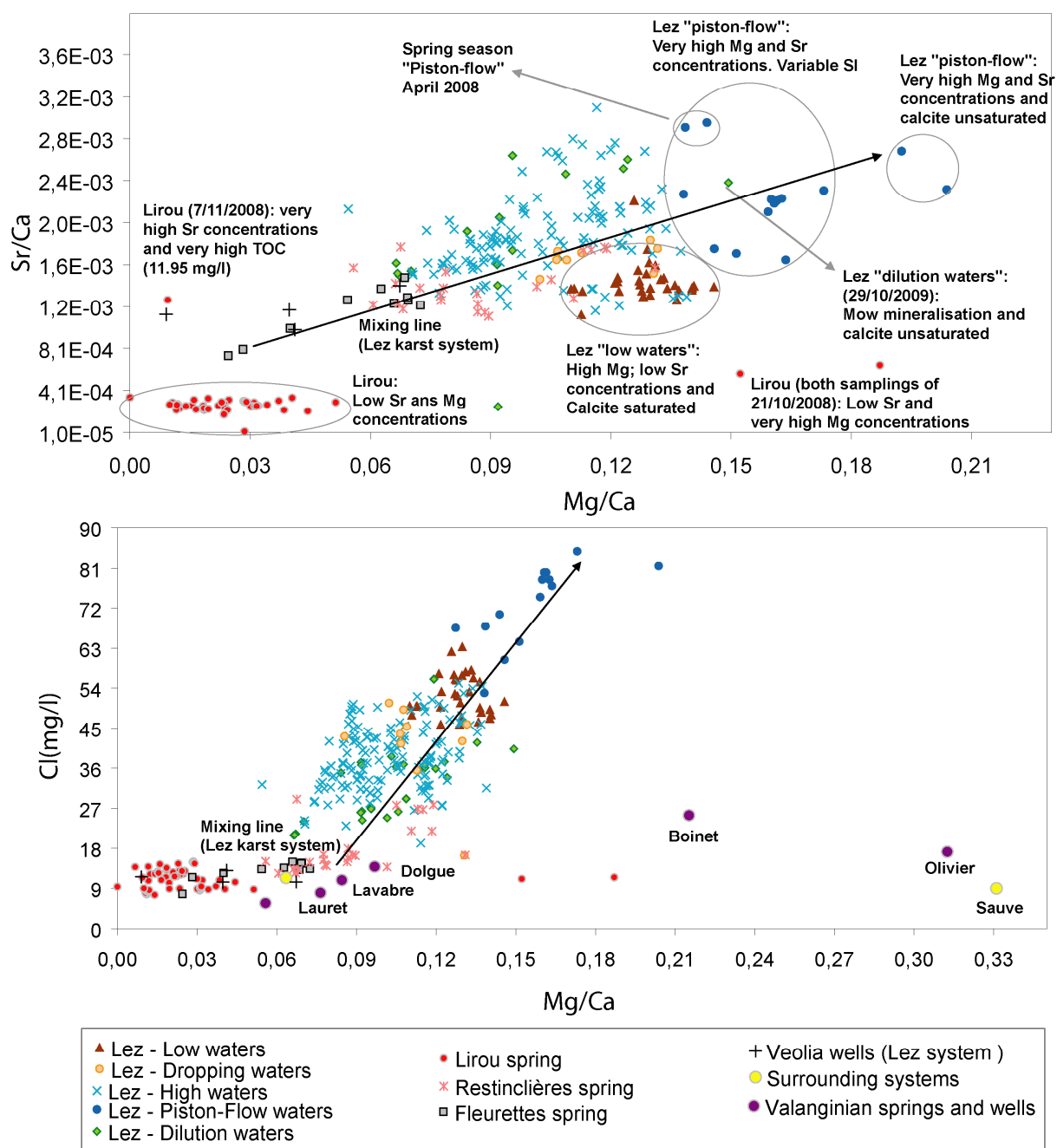


Fig. 17 –Sr/Ca vs. Mg/Ca and Cl vs. Mg/Ca for all the Lez karst system springs and wells, and for springs/wells belonging to the surrounding karst system.

Mg/Ca ratio depends on proportion of calcite and dolomite present in the aquifer rock (White, 1988). However, even very pure limestones can give rise to relatively high Mg/Ca ratios in waters with a long residence time in the aquifer. Numerous studies have documented the usefulness of Mg/Ca ratios to trace water residence times (Plummer, 1977; Plummer *et al.*, 1978; Edmunds & Smedley, 2000; Fairchild *et al.*, 2000; López-Chicano *et al.*, 2001; Batiot *et al.*, 2003a; McMahon *et al.*, 2004; Moral *et al.*, 2008). Therefore,

Mg/Ca ratios depend on the presence of dolomites and/or of chemical kinetics. For example, Mg/Ca ratios seem to be related to lithology at Sauve spring, Boinet and Olivier wells (Figure 17). In dolomite-rich bedrocks Mg concentrations can reach saturation even under quick flow conditions (Fairchild *et al.*, 2000). In contrast, Mg/Ca for the Lez waters seems to be related to long residence time and chemically evolved waters, with a potential deep Cl source that was not observed in the case of Boinet, Olivier and Sauve (Figure 17).

The Lez spring Mg/Ca ratios seem to be function of the distribution coefficient of Mg during progressive calcite recrystallization leading to an incongruent dissolution of dolomite. Incongruent dissolution is common in aquifers constituted of limestones and dolomites with the presence of gypsum, anhydride or halite dissolution (López-Chicano *et al.*, 2001; Marfia *et al.*, 2004; Barbieri *et al.*, 2005; Jacobson & Wasserburg, 2005; McIntosh & Walter, 2006; Rosenthal *et al.*, 2007; Frondini, 2008; Moral *et al.*, 2008). Excess of Ca in water solution induces calcite precipitation. As a consequence, HCO₃ concentrations decrease, producing calcite sub-saturation and additional dolomite dissolution and Mg concentration increase. Once calcite saturation is attained, only dolomite can dissolve. Mg/Ca rises significantly between calcite saturation and dolomite saturation (Fairchild *et al.*, 2000). A considerable increase in Sr concentrations is a side effect during incongruent dissolution because this element substitutes Ca, which explains also the Sr/Ca ratios increase (Fairchild *et al.*, 2000; Dogramaci & Herczeg, 2002; Samborska & Halas, 2010) (Figure 17).

3.3.2 - Surficial waters end-member and its implications on aquifer vulnerability

During the first recharge event, notably the event of October 2008, high bacteria (Total and Faecal coliforms), nitrate and TOC concentrations were observed. Bacteriological tracers denote the rapid transport through karst of waters issued from surface infiltration (Mahler & Lynch, 1999; Mahler *et al.*, 2000; Personné *et al.*, 2004).

The origin of faecal bacterial contamination in the basin is mostly related to the presence of sewerage treatment stations, of which residues are directly discharged in the basin (Joseph *et al.*, 1988; Cadier *et al.*, 2010). Over the basin area, there exist more than 20 sewage treatment-plants (Figure 18) that permanently release effluents on temporary rivers. These effluents stay on the bed of temporary rivers until been

remobilized by the first recharge events of autumn. They are directly injected with other pollutants through sinkholes or fractures potentially connected with the aquifer (Joseph et al., 1988).

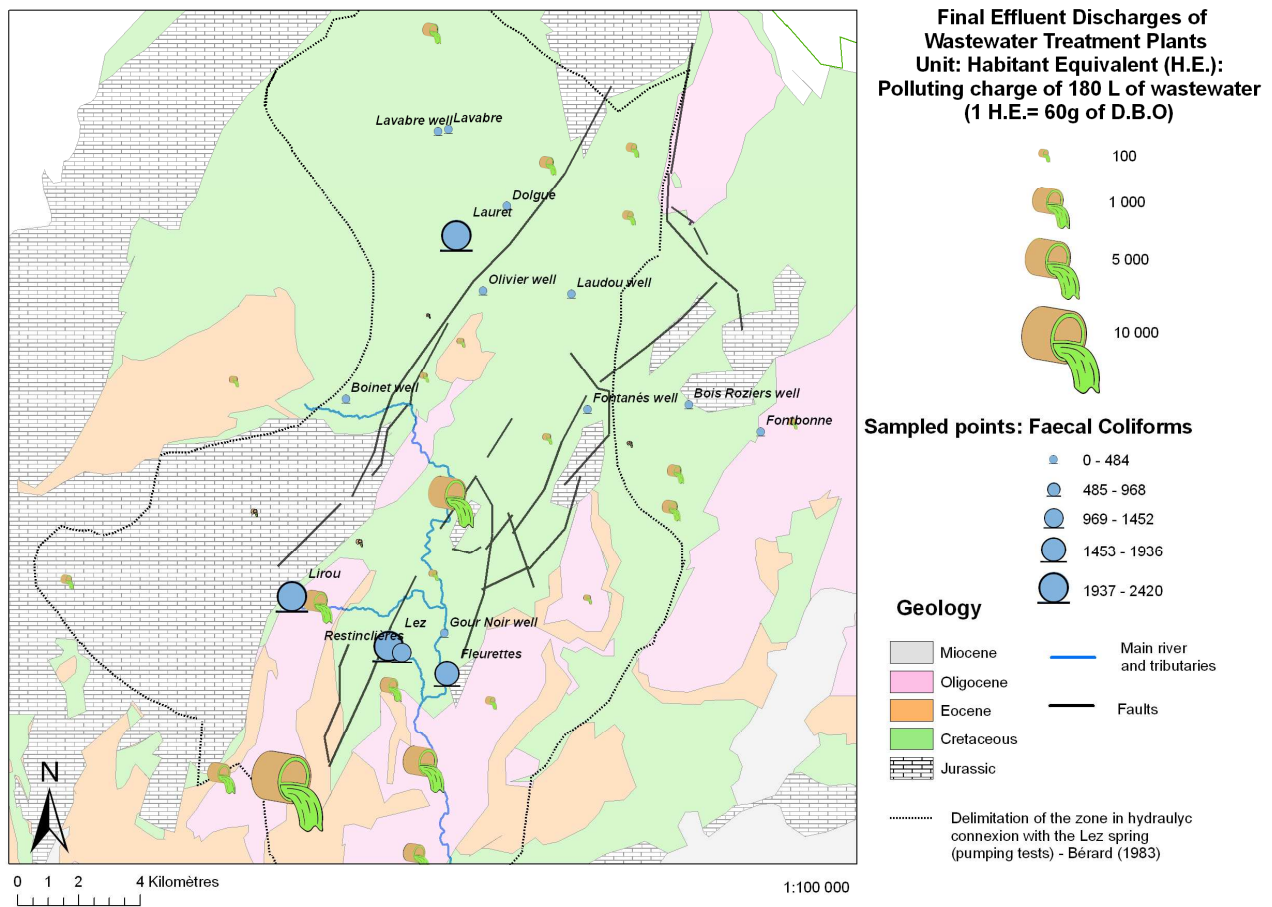


Fig. 18 – Spatial distribution of H.E. (Habitant Equivalent), referring about Final effluent Discharge of wastewater Treatment Plants and of Faecal Coliforms.

Participation of rapid surficial infiltrating waters to the spring flow is responsible for mineralized waters dilution (EC decrease) during recharge events. The “*Dilution-waters*” water-type is characterised by the most important participation of the surficial end-member.

Turbidity seems to be associated with bacterial contamination (Figure 19). The effect of contaminants combined with suspended solids are known to be more significant during the first flood responses (Mahler & Lynch, 1999). Generally, strong turbidity is always associated with bacterial contamination of faecal origin. However, the opposite is not always valid: low turbidity does not imply low bacterial concentration (Dussart-Baptista 2003).

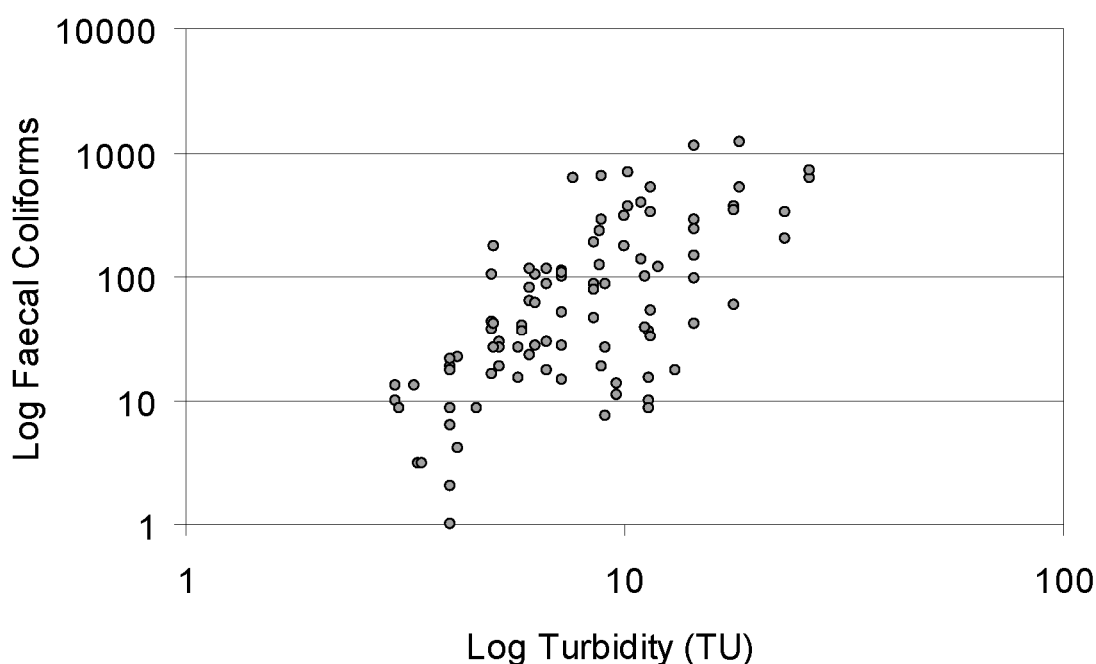


Fig. 19 – Log faecal coliforms vs. Log turbidity for the Lez spring.

3.4 - Conclusion

The Lez spring groundwaters flow results from a mixing of various groundwater types, issued from different compartments of the aquifer: a surficial compartment (surface and epikarst infiltration), shallow compartments (Berriasian and Valanginian), a deep compartment (middle and lower Jurassic and Triassic deposits: limestones, dolomites and evaporitic minerals) and a main aquifer compartment (upper Jurassic: limestones). Hydrological conditions influence the mixing proportions of water issued from those compartments that constitute the water that flow at the Lez spring (Figure 20).

At the beginning of the high stage, high mineralized waters with high concentrations in Cl, SO₄, Mg, Na, Br, Li, Sr, and high T flow at the Lez spring. Afterwards, rapid infiltration waters reach the spring and cause a dilution of mineralized waters and an increase of TOC, NO₃ and faecal bacteria.

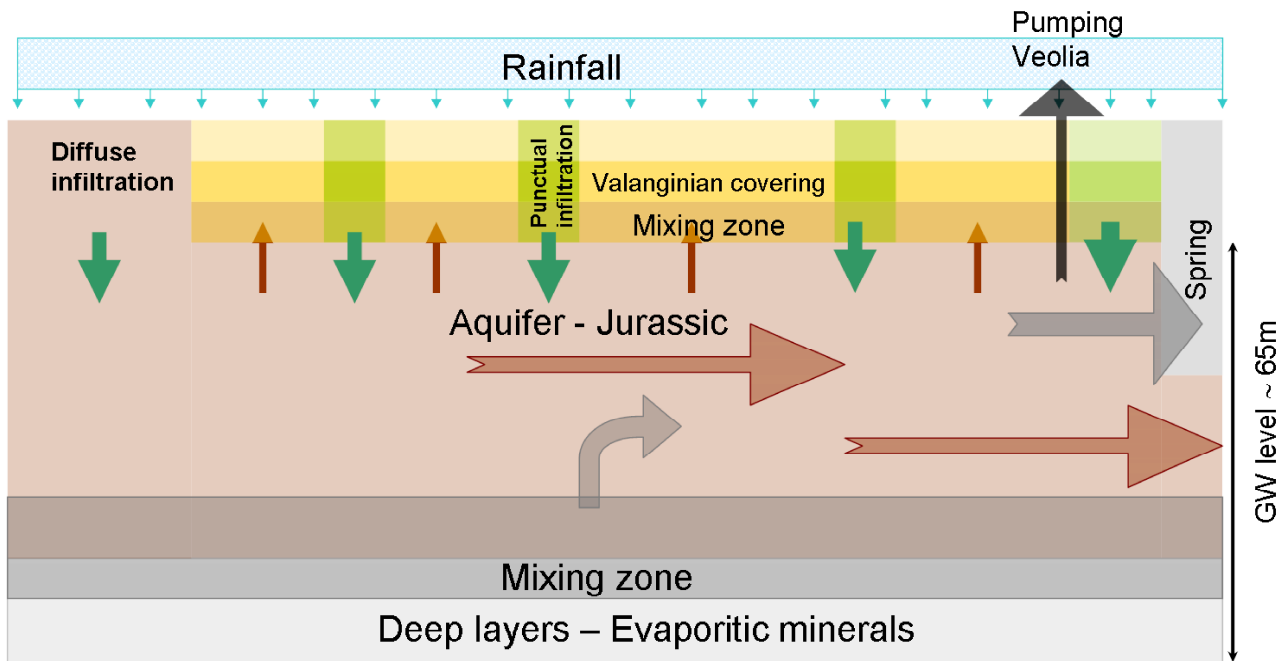


Fig. 20 – Conceptual model of Lez karst system functioning.

The high mineralization identified at the Lez spring is probably associated with groundwater issued from deep formations which rise by fractures and faults, where interactions with evaporitic minerals are hypothesized. The participation of this deep groundwater end-member has been regularly observed in the mixing that constitutes the outflow waters of the Lez spring. For the reason that even the most diluted groundwater exhibit a high mineralization ($600\mu\text{S.cm}$). Deep groundwater participation increases noticeably during the first autumn flood events, when the hydraulic head within the karst system is high enough to mobilize deep and long-residence-time waters towards the Lez spring.

Rapid infiltration waters reach the spring flow because of the existence of fractures, sinkholes and cavities, provoking dilution of the Lez mineralized groundwaters. Bacterial and organic contaminations suggest the participation of surficial waters to the Lez spring flow during rainfall events and point up the aquifer vulnerability.

Chapter 4 - Better constraining the chemical evolution of waters in a complex Mediterranean karst system by isotopical study combined with hydrogeochemistry

Extracted from Article N°2

Title:

“Isotopic ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) and geochemical monitoring of a Mediterranean karst system: chemical evolution and hydrodynamics of groundwaters.”

Authors:

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Journal: Chemical Geology

Present situation: under preparation for submission

Abstract

The Lez karst spring, located in the Mediterranean basin (southern France), supplies with water the metropolitan area of Montpellier (France) since the 19th century. Since 1981, an intense pumping is being performed directly in the main conduit with a maximum exploitation flow rate of about 1,700 l/s. In order to contribute to the advances already acquired by former studies on understanding the circulation dynamics at the Lez karst system, this study aims at continuing the studies about this system by enlarging the focus of analysis towards the other springs composing this system, and by searching for a better constraining of the chemical evolution of the Lez spring waters by the use of complementary tracers such as water stable isotopes (^{18}O and ^2H), Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) and Total Dissolved Inorganic Carbon isotopic composition ($\delta^{13}\text{C}_{\text{TDC}}$), in a foremost application on this karst system. Groundwater samples were collected from the Lez spring and surrounding springs and wells under a wide range of hydrologic conditions during three and half-year period.

A coupled approach integrating geochemistry and isotopes have been applied and provided insight into the different end-members, associated lithologies and the main reactions that control groundwater chemistry. long residence-time waters, issued from deep layers where evaporite fingerprinting have been identified. They are characterized by high mineralization and high concentrations in Cl, Na, Mg, Li, B and Br elements, high Sr/Ca, Mg/Ca and Cl/Br ratios and enriched $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Between all the studied springs and wells, this chemical fingerprinting has been uniquely observed for the Lez spring groundwaters.

This approach allowed to better characterize the relations of the Lez system springs with one another and with other system springs, as well as to unearth the main reactions that control the chemical evolution of Lez spring waters. The estimation of end-member discharge proportions at the Lez spring was obtained by hydrograph deconvolutions. Hydrograph deconvolutions using multiple tracers were used to estimate the participation of two or three end-members in the various flood-events that occurred between 2008 and 2010. If we use chloride as tracer, the mean estimated participation of the different water types are, as follows: 12% for deep waters; 5% for recent waters and 83% for main aquifer waters.

The multi-tracers approach combined to hydrodynamics appears as a very efficient tool for characterizing groundwater flows and their origins and seems to be potentially applicable to other similar complex Mediterranean karst systems that were subjected to deep karstification during the Messinian salinity crisis. The features of this crisis seem to play a relevant role on the hydrogeological behaviour of the aquifer and chemical characteristics of waters by the participation of a deep compartment to the outflow of the karst system.

Key words: karst, hydrogeology, natural tracing, Carbon isotopes, Strontium isotopes, water stable isotopes.

4.1 - Introduction

The Lez spring has the highest mineralization of all the system springs. Nevertheless Temperature (T) is lowest than Restinclières and Fleurettes temporary springs. This behaviour delineates a contradiction in the chemical evolution of those springs GW. Uncertainties could be clarified by a better understanding of the water transfers, the mixing proportions and the lithological context concerning these springs and their interrelation.

We extend the investigations to the Lez karst system functioning by implementing geochemical natural tracers, like stable water isotopes (^{18}O and ^2H), Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) and Total Dissolved Inorganic Carbon (TDIC) isotopic composition ($\delta^{13}\text{C}_{\text{TDIC}}$). The main objectives are: (i) a better characterization of the relations of the Lez system springs with one another and with other system springs (ii) the unearthing of the main reactions that control the chemical evolution of the Lez spring waters; (iii) an estimation of the end-member discharge proportions at the Lez spring by hydrograph deconvolutions and to (iv) propose a circulation model for this karst system.

The integrated monitoring technique adopted in this study offers clues for a more in-depth understanding of the regional hydrodynamics, based on the changes observed in monitored tracers over time and space.

4.2 - Results and discussion

4.2.1 - Springs correlation using major and trace elements

This study considered multiple sampling points (springs and wells) from the Lez system and from other systems. The complete collected dataset used on this study is presented on Table 2. A first analysis of the springs of the Lez system (Lez, Restinclières, Fleurettes and Lirou) is accomplished (Figures 21 and 22), so as to obtain a preliminary view of the main characteristics of the Lez systems in a regional context.

EC and T indicate contradictory information about waters mineralization at the Lez spring in comparison with the other springs of the system (Figure 21). EC indicates higher chemical evolution at the Lez spring, however, Restinclières and Fleurettes springs present higher T than the Lez spring. Those differences could be related to mixing proportions and/or mineralization origins, related to the associated lithologies. The understanding of the relation between those springs starts through a better description of their hydrochemical properties by using DFA. This method was applied in order to simplify the interpretation, due to the large number of samples and parameters to be analysed and interpreted (Table 2).

The considered qualitative variables (dependent) were the monitored springs of the Lez system. The assumed explicative (independent) variables were EC, major ions (Cl^- , NO_3^- , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+}) and trace elements (Li, B, Rb, Ba and Sr). F2 axis represents the mineralization in Cl^- , Mg^{2+} , K^+ , SO_4^{2-} , Li, B, Rb and Sr, characteristic of the Lez spring mineralization. Restinclières and Fleurettes springs are characterized by Ba concentrations and are more characterized by NO_3^- , HCO_3^- and Ca^{2+} than the Lez is, despite their low representativeness. The Lithological origin of Ba could be associated with Barite (BaSO_4), which could be present in dolomites of Cretaceous layer (Petelet et al., 1998). Ba quickly reaches saturation near to outcrop and therefore cannot be used as a residence time indicator (Edmunds & Smedley, 2000).

This analysis indicates similarities between Restinclières and Fleurettes springs mineralization, which is mostly attributed to limestones and dolomites from the Jurassic and Cretaceous. However, they do not present the evaporitic fingerprinting that is characteristic of the Lez spring (Bicalho *et al.*, submitted). Lirou spring has the less mineralized waters with a short residence time and important surficial waters participation. Despite their physical proximity, the Lez karst system springs seem to be related to distinct GW flowpaths.

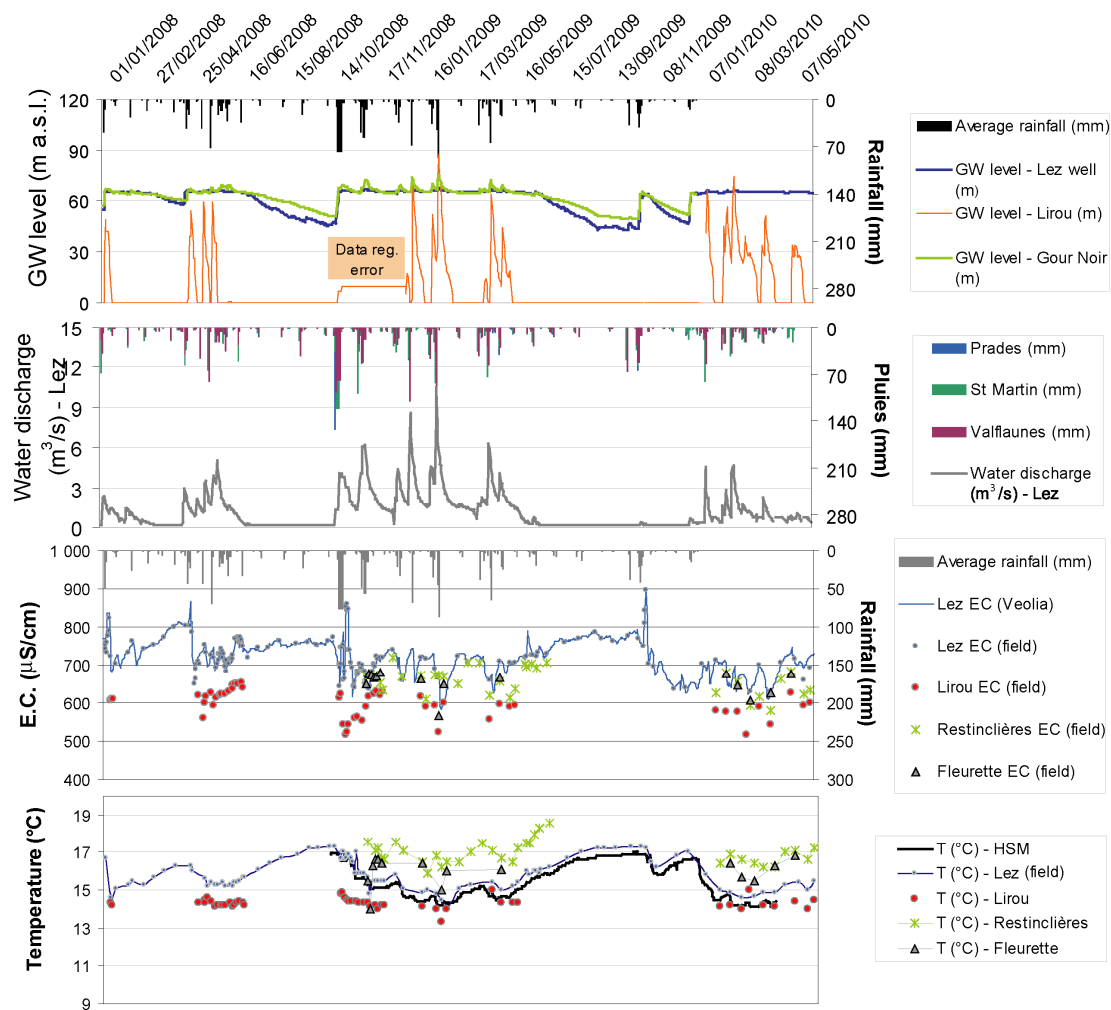


Fig. 21 - Arithmetic average daily rainfall calculated from rainfall data at Prades, St Martin and Valflaunès rain gauges, piezometric level at the Lez spring in the pumping well; at the Gour Noir and at the Lirou spring. T and EC monitored at the Lez spring by Veolia and EC and T measured on field by HSM at Lez, Lirou, Fleurettes and Restinclières springs.

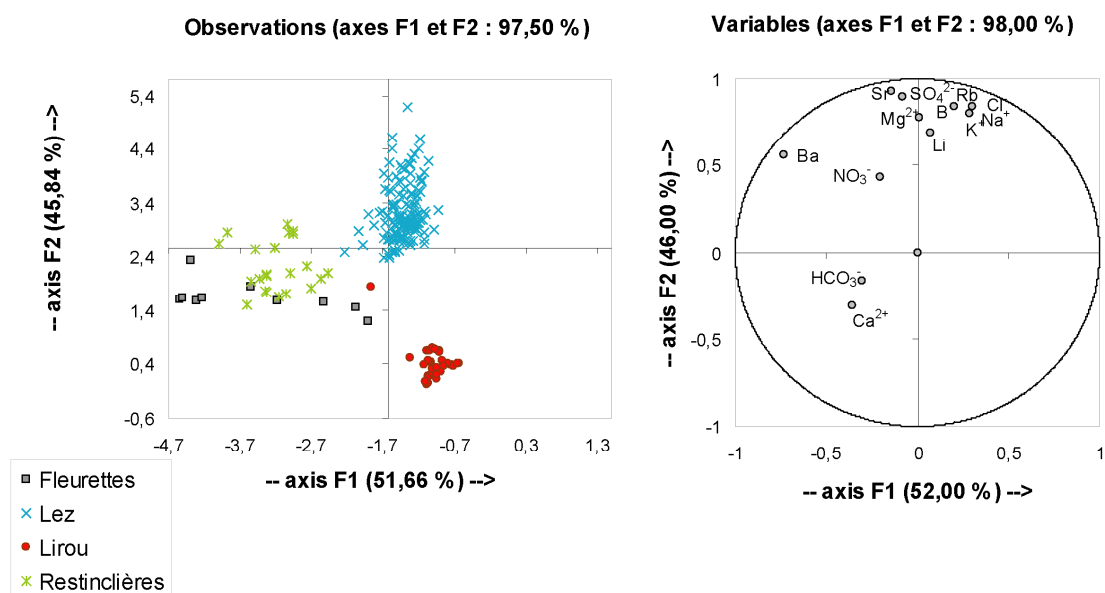


Fig. 22 – DFA of the Lez spring data using major and trace elements. Left: sample space; right: variable space. Lez (125 samples), Lirou (32 samples), Restinclières (21 samples) and Fleurettes (10 samples).

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

Lez spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
07/07/08	1	16.1	747	7.16	372.0	49.2	4.6	29.7	127.4	8.3	26.2	1.3	1.0						-31.70	-5.67		
21/07/08	2	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	-32.36	-5.63		
04/06/09	3	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	-37.27	-6.06	-10.06	
09/06/09	4	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	-37.15	-5.91	-13.60	
11/06/09	5	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	-36.83	-5.93	-13.72	
23/06/09	6	16.2	729	7.1	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	-36.00	-5.79	-13.85	
05/08/08	7	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	-32.71	-5.73		
26/08/08	8	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	-31.12	-5.16		
10/09/08	9	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	-34.27	-5.98	-12.70	
22/09/08	10	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	-34.42	-5.89	-12.39	
07/10/08	11	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	-33.99	-5.94		
16/07/09	12	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	-35.42	-5.73	-13.21	0.707859
03/08/09	13	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	-35.22	-6.27	-13.42	
25/08/09	14	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	-35.29	-6.07	-13.15	
02/09/09	15	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	-35.29	-6.14	-13.07	
17/09/09	16	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	0.0	20.5	363.9	19.0			-13.06	
07/10/09	17	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	-35.08	-6.14		
22/10/09	18	17.2	749	7	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	-35.71	-6.28	-13.62	
13/10/08	19	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	-34.26	-5.91		
21/10/08 N°2	20	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	-31.05	-5.58		
22/10/08 N°1	21	16.6	682	7.1	344.0	36.7	6.2	22.2	111.7	6.2	20.9	1.2	2.9	0.2	112.5	0.0	62.1	6.7	-31.62	-5.51		
26/10/08	22	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				-30.58	-5.23		
27/10/08	23	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	-29.39	-5.20		
07/11/08	24	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	-27.24	-5.18	-14.73	
29/10/09	25	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	-35.45	-6.20	-13.22	
05/11/09	26	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	-34.56	-5.94	-13.58	
01/12/09	27	16.8	636	6.9	360.0	56.1	5.5	25.3	116.5	8.4	33.4	1.5							-34.48	-5.96	-13.62	
16/12/09	28	17	639	7.18	363.7	41.8	3.9	18.9	112.7	9.3	33.2	1.6	0.6						-34.92	-5.98	-13.47	
21/10/08 N°1	29	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	-31.51	-5.63		
21/10/08 N°3	30	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	-34.08	-5.75		
21/10/08 N°4	31	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	-27.06	-3.16		
22/10/08 N°2	32	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	-31.40	-5.57	-13.34	
24/10/2008 N°1	33	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	-31.10	-5.55	-13.06	

Lez spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
24/10/2008 N°2	34	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	-31.11	-5.48		
29/10/08	35	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	-29.45	-5.43		
31/10/08	36	15.9	705	7	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	-29.93	-5.36		
03/11/08	37	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	-28.83	-5.26		
05/11/08	38	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	-28.41	-5.14	-12.13	0,707622
12/11/08	39	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	-29.82	-5.28		
14/11/08	40	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	-29.69	-5.37		
18/11/08	41	15.5	721	7.1	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	-28.76	-5.28		
21/11/08	42	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	0.0	13.1	486.8	15.5	-29.76	-5.38		
05/12/08	43	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	-30.57	-5.56	-14.33	
16/12/08	44	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	0.0	19.9	528.0	15.8	-32.06	-5.44		
09/01/09	45	14.9	721	7.2	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	-35.13	-5.73		
28/01/09	46	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	-35.34	-5.69		
02/02/09	47	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	-37.58	-5.95		
09/02/09	48	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	-39.62	-6.26		
12/03/09	49	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	-37.75	-5.98		
27/03/09	50	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	-37.28	-5.96	-13.75	
09/04/09	51	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	-37.44	-5.93		
22/04/09	52	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	-38.68	-6.01	-13.87	
06/05/09	53	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	-38.06	-6.05		
13/05/09	54	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	-37.52	-6.09		
25/05/09	55	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	-37.59	-5.91		
27/05/09	56	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	-37.80	-5.88	-13.98	
03/06/09	57	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	-37.20	-5.94	-13.91	
07/01/10	58	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	-35.08	-5.79	-13.74	
25/01/10	59	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	-36.10	-6.18	-14.32	
11/03/10	60	14.7	629	7.1	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	-37.18	-6.38	-14.04	
22/03/10	61	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	-36.67	-6.24		
07/04/10	62	14.9	631	7.2	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	-36.34	-6.20		
20/04/10	63	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	-35.81	-6.23		
03/05/10	64	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	-36.19	-5.87		
27/05/10	65	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			-14.03	
13/06/08	66		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	-30.40	-5.11		

Lez spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
24/10/08	69		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	-30.92	-5.53		
24/10/08	70		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	-31.22	-5.22		
24/10/08	71		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	-31.48	-5.44		
23/10/08	72		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	-30.58	-5.23		
23/10/08 N°1	73	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	-31.91	-5.50	-12.24	
23/10/08 N°2	74	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	-31.12	-5.52	-11.95	
23/10/08	75		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	-31.48	-5.53		
26/10/09	76	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	-34.74	-6.22	-12.08	0.707921
24/10/09	77	15	811	7.15	341.7	74.5	4.9	32.5	111.4	10.8	44.5	2.1	0.0	5.4		25.8	514.0	21.8	-34.90	-6.12		
25/10/09	78	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	-34.51	-6.11		
Lirou spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	toc	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
02/06/08	1	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	-28.73	-4.77		
05/06/08	2	14.1	646	7.65	401.5	13.8	1.4	8.7	132.7	0.9	4.8		1.7	0.3		8.8	64.7	6.6	-30.36	-5.33		
09/04/09	3	15	556	6.99	349.0	9.3	3.5	8.1	111.6	0.0	4.7		1.6	0.5	100.4	0.4	83.7	7.1			-15.75	
13/05/09	4	14.3	593	7.11	373.4	8.7	1.3	8.2	121.7	3.8	5.1		1.0	0.4		9.7	79.1	7.1			-15.86	
24/06/08	5			7.10	376.9	11.7	2.8	8.4	127.4	1.7	4.8	0.1	1.5						-30.76	-5.35		
21/10/2008 N°1	6	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	-34.14	-5.80		
21/10/2008 N°2	7	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	-34.56	-5.89		
22/10/08	8	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	-26.08	-4.74	-15.04	
23/10/08 N°1	9	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	-23.30	-4.28		
23/10/08 N°2	10	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	-23.30	-4.28	-14.94	
24/10/08	11	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	-24.55	-4.21		
27/10/08	12	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	-24.25	-4.54		
29/10/08	13	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	0.0		71.7	6.6	-24.86	-4.59		
03/11/08	14	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	-25.12	-4.44		
05/11/08	15	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	-26.11	-4.68		
07/11/08	16	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	-28.19	-4.92	-13.52	0.7079
12/11/08	17	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	0.0		65.9	7.4	-29.46	-5.09		
14/11/08	18	14	631	7.18	388.1	11.7	2.0	9.0	131.8	1.7	5.3	0.2	2.5		101.4				-29.72	-4.99		
18/11/08	19	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				-29.33	-5.17		
21/11/08	20	14.2	631	7.14	375.3	11.1	2.1	8.7	132.1	2.4	5.3	0.1	0.9		0.0				-29.80	-5.07	-16.20	

Lirou spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
09/01/09	21	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	-35.49	-5.91	-15.84	
16/01/09	22		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	-35.26	-5.84		
28/01/09	23	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	-34.73	-6.20		
02/02/09	24	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	-40.29	-6.92		
09/02/09	25	14	599	7.39	374.4	8.9	1.1	6.0	128.7	1.8	5.1		1.8	0.3	88.6	5.9	50.6	6.6	-38.05	-6.53		
25/01/10	26	14.1	579	7.08	360.0	10.5	3.5	7.5	124.3	1.0	5.0	0.4	0.9	0.2		8.2	65.0	5.9	-37.24	-6.42		
22/02/10	27	14	577	7.40	362.5								1.3	0.2		6.9	54.9	5.9	-37.97	-6.54		
05/03/10	28	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	-37.42	-6.55		
07/04/10	29	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	-37.86	-6.63		
03/05/10	30	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	-35.46	-5.57		
27/05/10	31	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			-15.90	

Fleurettes spring		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
05/11/08	1	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	-28.79	-5.00		
07/11/08	2	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	-29.97	-5.13	-15.20	
09/11/08	3	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	-31.72	-5.21		
12/11/08	4	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	-32.02	-5.31		
14/11/08	5	16.6	669	7	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	-31.93	-5.19		
18/11/08	6	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	-31.64	-5.28	-14.54	
09/01/09	7	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	-34.22	-5.98		
02/02/09	8	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	-43.99	-7.35		
22/04/09	9	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	-39.30	-6.55	-14.21	
09/02/09	10	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	-37.00	-6.24		
08/02/10	11	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	-36.08	-6.25		
22/02/10	12	15.7	646	6.91	378.3								1.7	1.9		15.9	357.3	20.7	-38.38	-6.40		
11/03/10	13	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	-37.74	-6.25		
07/04/10	14	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	-37.07	-6.01		
03/05/10	15	16.8	678	7	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	-35.74	-5.90		
20/05/10	16	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		17.9	244.6	28.8	-34.82	-5.79	-13.93	0.708537
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		13.0	277.2	9.1	-35.82	-5.69	-13.16	0.707640
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	-32.61	-6.26	-14.25	0.707333

		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
21/07/09	<i>Foux de Lauret</i>	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	-38.51	-5.98	-15.00	0.707451
21/07/09	<i>Dolgue spring</i>	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	-35.57	-5.96	-16.04	0.707440
21/07/09	<i>Lavabre spring</i>	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	-36.76	-5.93	-16.42	0.707422
21/07/09	<i>Lavabre well</i>	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	-35.87	-6.01	-16.25	
31/08/09	<i>Fontanes well</i>	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	-34.05	-5.76	-13.50	0.707602
31/08/09	<i>Laudou well</i>	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	-36.24	-6.17	-15.76	0.707564
31/08/09	<i>Bois Roziers well</i>	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	-35.63	-6.02	-14.28	0.707605
02/09/09	<i>Gour Noir well</i>	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		16.2	296.8	15.3	-35.66	-5.91	-14.69	0.707645
<i>Restinclières spring</i>		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	toc	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
12/11/08	1	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	-29.77	-5.16	-14.63	
14/11/08	2	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	-31.40	-5.13		0.707564
18/11/08	3	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	-31.14	-5.24		
21/11/08	4	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	-30.28	-5.34		
05/12/08	5	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	-30.02	-5.25	-13.84	
16/12/08	6	17.6	719	7.2	430.2	27.7	9.4	27.7	133.9	8.5	14.7	1.0	1.2	3.2		21.4	429.2	24.7	-32.20	-5.14		
09/01/09	7	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		17.0	415.7	26.3	-33.19	-5.56		
16/01/09	8	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		16.1	386.8	25.2	-34.03	-5.91		
28/01/09	9	15.9	611	7.29	336.8	16.3	6.8	21.3	128.5	7.0	8.4	0.4		2.2		14.1	313.7	19.3	-33.51	-5.87		
02/02/09	10	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		13.4	357.2	23.1	-35.85	-6.10	-14.99	
09/02/09	11	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	-35.83	-6.08		
26/02/09	12	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	-38.18	-6.47		
12/03/09	13	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		14.8	317.3	23.1				
27/03/09	14	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	-35.83	-6.14		
09/04/09	15	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	-35.46	-6.16		
22/04/09	16	17.1	620	7.01	367.3	15.0	5.8	22.7	116.0	3.9	7.4		1.6	3.3		6.3	400.2	22.9	-36.12	-6.06		
06/05/09	17	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	-36.86	-6.18	-13.80	
13/05/09	18	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	-36.38	-6.16		
25/05/09	19	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	-36.49	-6.14		
27/05/09	20	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	-36.03	-5.84		
03/06/09	21	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	-36.22	-6.08		

<i>Restinclières spring</i>		T°C	EC	pH	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TOC	Li	Br	B	Sr	Ba	δ ² H	δ ¹⁸ O	δ 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)	(‰)	(‰)	(‰)	
09/06/09	22	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	-36.14	-6.21		
23/06/09	23	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	-36.31	-6.12	-13.71	
25/01/10	24	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	-35.00	-5.75	-13.28	
08/02/10	25	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	-35.82	-6.19		
22/02/10	26	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	27	16.6	656	6.96	386.7								2.1	2.3		16.4	422.3	24.5	-37.97	-6.20		
22/03/10	28	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	-37.91	-6.21		
07/04/10	29	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	-37.19	-6.03		
20/04/10	30	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	-35.95	-5.94		
03/05/10	31	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	-35.63	-5.98		
20/05/10	32	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	-35.69	-5.77		
27/05/10	33	16.6	624	7	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				

4.2.2 - Study of seasonal recharge by using water stable isotopes

Oxygen and Hydrogen isotopes are largely used for determining sources of water, flow patterns, mixing processes and to identify eventual evaporation processes. They are also often used to determine the contribution of rainfall waters in a flood event using a simple mixing bi-component model (Drever, 1982; Ford & Williams, 1989; Kattan, 1997; Cey *et al.*, 1998; Katz *et al.*, 1998; Beven, 2001; Ladouche *et al.*, 2001; Perrin *et al.*, 2003a; Perrin *et al.*, 2003b; Long & Putnam, 2004).

Water stable isotope compositions change mainly because of natural variations in the rainfall compositions, mixing with pre-existing waters, and the influence of evaporation (Cey *et al.*, 1998; Beven, 2001; Perrin *et al.*, 2003a; Long & Putnam, 2004).

Isotopic input signal was studied from the three rain gauges distributed over the basin (Figure 3). To complete the lack of data at the beginning of the study period, the Montpellier rain gauge was used as a reference for the input signal, in spite of the differences in the rainfall isotopic composition between Montpellier and the karst system recharge area. Nonetheless, the interpretation considered the limitations of this consideration.

Groundwater samples show a small variability of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures when compared to rainwater inputs (Table 3). Information about storing characteristics can be obtained by comparing the isotopic input signal to the isotopic output signal at the spring. The rainwater samples present large $\delta^{18}\text{O}$ variations amplitudes; on the other hand, seasonal variations are strongly reduced at the springs, especially at the Lez spring, with a complete attenuation of the signal. Despite the dampening of the signal and a low variability, $\delta^{18}\text{O}$ varied by 1‰ during the first floods of autumn 2008 (Figure 23). This variation is subtle but is still high enough to suggest that rapid infiltration waters participate to the Lez spring flow, even if only in low proportions. Deconvolution results presented below describe better mixing phenomena between rain inputs and aquifer waters at the Lez spring during floods.

Table 3 – Water stable isotope range for the sampled springs and raingauges.

Spring / raingauges	N° of samples	$\delta^{18}\text{O}$ range (‰ vs. SMOW)	$\delta^2\text{H}$ range (‰ vs. SMOW)
Lez	235	-6.38 to -4.94	-39.62 to -30.08
Lirou	64	-6.92 to -4.21	-40.29 to -23.29
Restinclières	29	-6.47 to -5.13	-38.20 to -29.77
Fleurettes	16	-7.35 to -5.00	-43.98 to -28.79
Viols le Fort raingauge	12	-12.27 to -2.88	-53.6 to -14.2
Sauteyrargues	8	-10.59 to -3.44	-63.4 to -14.5
Montpellier	34	-9.05 to -1.97	-65.9 to -12.9

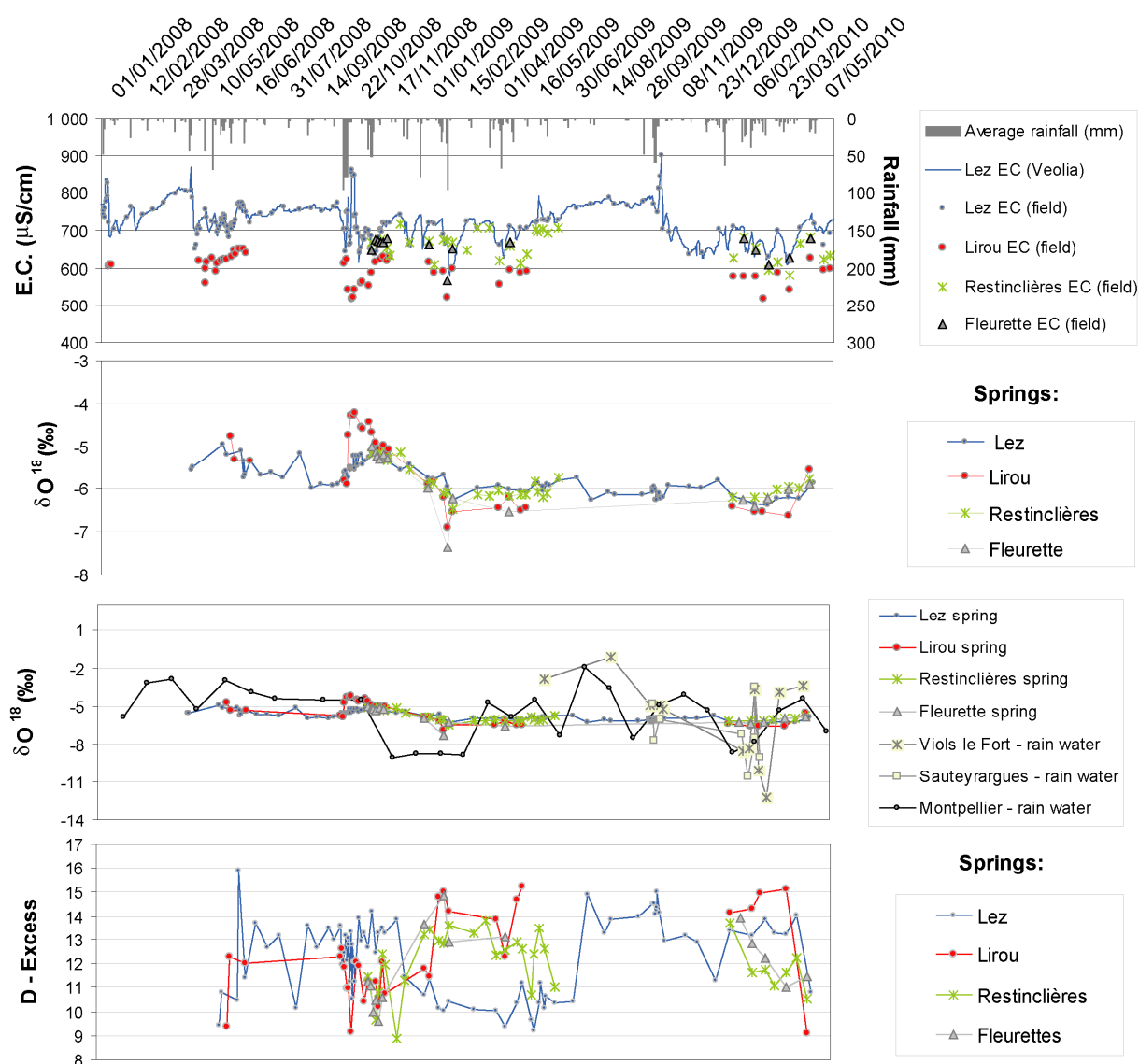


Fig. 23 – Rainfall (Montpellier, Viols le Fort and Sauteyrargues stations); E.C., $\delta^{18}\text{O}$ (‰); zoomed $\delta^{18}\text{O}$ (‰) and Deuterium-excess for the whole samples of the Lez system springs (Lez, Lirou, Fleurettes and Restinclières).

The other springs also present a manifest $\delta^{18}\text{O}$ signal dampening, with the exception of the Lirou spring. Such a dampening in the signal denotes a residence-time at least equal to the period of the input function, i.e. one year. It illustrates the existence of an important storage component favouring an efficient mixing of infiltrated waters with stocked water (Perrin *et al.*, 2003a; Négrel & Petelet-Giraud, 2005). Systems that have a predominantly autogenic recharge have normally well mixed waters flowing on the springs, and seasonal behaviours and recharges are difficult to identify (Ford & Williams, 1989; Long & Putnam, 2004; Barbieri *et al.*, 2005).

Unlike the other springs, the Lirou spring shows a remarkable variation of $\delta^{18}\text{O}$ - $\delta^2\text{H}$ signatures, observed during the storms of October 2008 (Figure 23). The same signature is observed in rainfall water at the Montpellier station in October 2008. This flood was caused by important storms that marked the rainfall of October 2008, where the “Saint Martin” rain gauge registered 121 mm the first day of storm. Such an important input should have provoked an immediate reaction from the Lirou spring. This behaviour shows the great reactivity of this one spring compared to the other springs, indicating that Lirou is effectively under a stronger influence of recent rainfalls than the other springs.

In the $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ diagram (Figure 24), rainwater shows a wide range of composition. Most of the samples are distributed between the Global Meteoric World Line (GMWL) and the Mediterranean Meteoric World Line (MMWL), indicating they originated as meteoric recharge (Grobe & Machel, 2002; McIntosh & Walter, 2006).

The first local meteoric water line calculated from rainwater samples was $\delta\text{D} = 7.28 * \delta^{18}\text{O} + 7.76\text{‰}$. The low Deuterium-excess ($d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$) observed ($d = +7.76\text{‰}$) suggests that partial evaporation of raindrops has a significant influence on the area (Ladouche *et al.*, 2009). Another Local Meteoric Line (LML) was calculated without evaporated waters samples: $\delta\text{D} = 7.5 * \delta^{18}\text{O} + 12.5\text{‰}$. The average Deuterium-excess of this precipitation line is $d = +12.5\text{‰}$, indicating that rainfall waters in the Lez basin resulted from a mixing of rainwaters which vapours had both Mediterranean ($d = 22\text{‰}$) (Ladouche *et al.*, 2009) and Atlantic origins ($d = 10\text{‰}$).

The Deuterium excess observed in rainwaters of Mediterranean origin is generally relatively high. This is caused by the strong kinetic isotopic effect occurring during the evaporation that takes place in the summer over the Mediterranean Sea, due to the low relative humidity of the atmosphere. Precipitations originating

from the Atlantic Ocean are more depleted in D than the ones originating from the Mediterranean Sea (Vandenschrick et al., 2002)

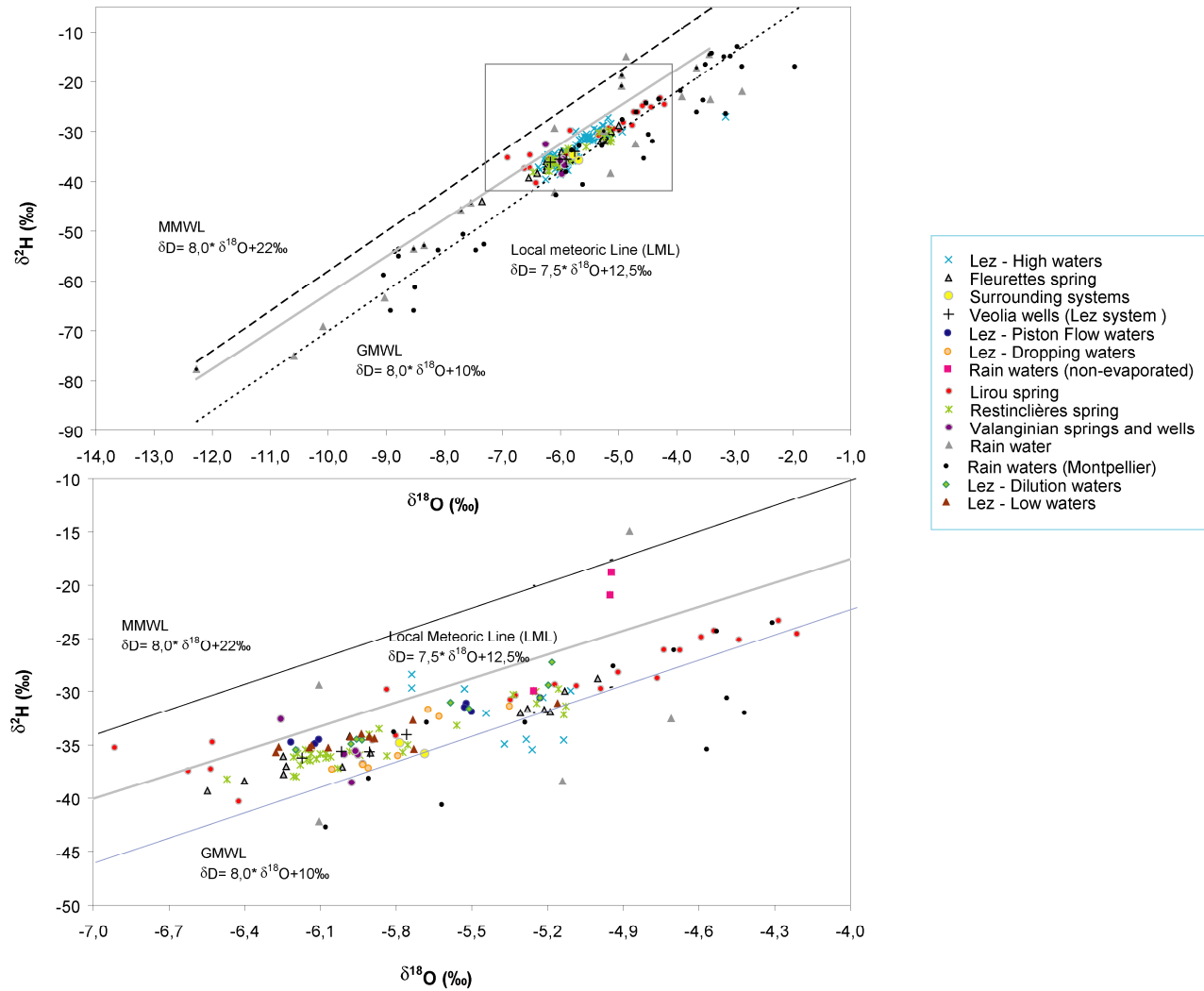


Fig. 24 – Top: $\delta^2\text{H}$ (Deuterium) vs. $\delta^{18}\text{O}$ (‰) for the whole samples of the Lez system springs (Lez, Lirou, Fleurettes and Restinclières) and the rainwater samples of the 3 raingauges (Saint Gély du Fesc, Viols le Fort and Sauteyrargues). Bottom: the same as top zoomed for showing springs results in detail.

The low correlation of $\delta^{18}\text{O}$ with altitude that can be observed on the studied basin shows that the orographic effect is not present in precipitation (Drever, 1982; Ford & Williams, 1989; Kattan, 1997; Nativ *et al.*, 1999; Vandenschrick *et al.*, 2002; Barbieri *et al.*, 2005; Bouchaou *et al.*, 2009). The total orographic variation in the study zone (in average about 200 m) is not high enough to induce a visible orographic effect.

4.2.3 - Reactions controlling water chemistry

$\delta^{13}\text{C}_{\text{TDIC}}$ of waters and soil $\delta^{13}\text{C}_{\text{CO}_2}$ were analysed so as to verify the levels of water-rock interaction. The use of $\delta^{13}\text{C}_{\text{TDIC}}$ as a natural tracer in karst systems can help to differentiate water coming from the unsaturated zone from water coming from the saturated zone (Emblanch *et al.*, 2003). In the unsaturated zone, the system behaves like an open system in regard to the biogenic CO_2 of the soil (Clark & Fritz, 1997; Emblanch *et al.*, 1998; Katz *et al.*, 1998; Yoshimura *et al.*, 2001; Batiot, 2002; Desmarais & Rojstaczer, 2002; Emblanch *et al.*, 2003; Gonfiantini & Zuppi, 2003; Adinolfi Falcone *et al.*, 2008; Gillon *et al.*, 2009).

Three measures of $\delta^{13}\text{C}_{\text{CO}_2}$ on soil covers were carried out in April 2010, over the Lez system catchment area, in order to characterize the main vegetal and pedogenic covers: (1) vineyards developed on Quaternary deposits -22.28‰; (2) garrigues over Jurassic limestones: -21.69‰ and (3) olive grove developed on Tertiary deposits: -20.42 ‰. The values present few variations from a site to another compared to the differences between the covers. Studies over the Mediterranean karst basin of Vaucluse showed low seasonal variations on $\delta^{13}\text{C}_{\text{CO}_2}$ in soil covers (Batiot, 2002; Emblanch *et al.*, 2003). Thus, the input $\delta^{13}\text{C}_{\text{CO}_2}$ signal can be considered constant and close to -22‰.; a mean $\delta^{13}\text{C}_{\text{CO}_2}$ value of about -21.06 ‰ was used as a local biogenic CO_2 value.

The Lez spring presents remarkable variations in $\delta^{13}\text{C}_{\text{TDIC}}$ values (Figure 25). The most $\delta^{13}\text{C}_{\text{TDIC}}$ -enriched waters correspond to the period of high EC in October 2008 and 2009. A slow $\delta^{13}\text{C}_{\text{TDIC}}$ enrichment is observed during the dry season, from the middle of the wet season until the first recharge event of 2009. The most negative values are observed during the middle of the wet season, where $\delta^{13}\text{C}_{\text{TDIC}}$ as well as E.C., go through a sudden decrease. The variability of the $\delta^{13}\text{C}_{\text{TDIC}}$ in the Lez spring indicates that compartments with different properties contribute to the flow, with the participation of waters with a high water-rock interaction during specific hydrological situations.

$\delta^{13}\text{C}_{\text{TDIC}}$ vs. Mg/Ca and vs. Sr/Ca (Figure 26) indicates two mixing lines: one for the Lez system and another for Valanginian samples. $\delta^{13}\text{C}_{\text{TDIC}}$ is more positive in the Lez system samples than in the Valanginian ones, with the exception of Lauret. The same behaviour is observed for Sr/Ca (Figure 26). Mg/Ca and Sr/Ca ratios for the Lez system and for the Valanginian springs are not associated with the same processes or origins:

- (i) The high levels of Mg/Ca and Sr/Ca and the concomitant increase with $\delta^{13}\text{C}_{\text{TDIC}}$ observed for the Lez spring show that waters possibly evolve via incongruent dissolution of carbonate minerals under closed system conditions (Dogramaci & Herczeg, 2002; Marfia *et al.*, 2004). This reflects the isolation of those waters from an active flow in shallow GW and longer residence times (Marfia *et al.*, 2004; McIntosh & Walter, 2006).
- (ii) The high Mg/Ca and Sr/Ca ratios observed for Valanginian samples are most likely due to their lithogy: the marls and marly-limestones of the Cretaceous layer are richer in Mg than the Jurassic limestones (Bicalho *et al.*, submitted).

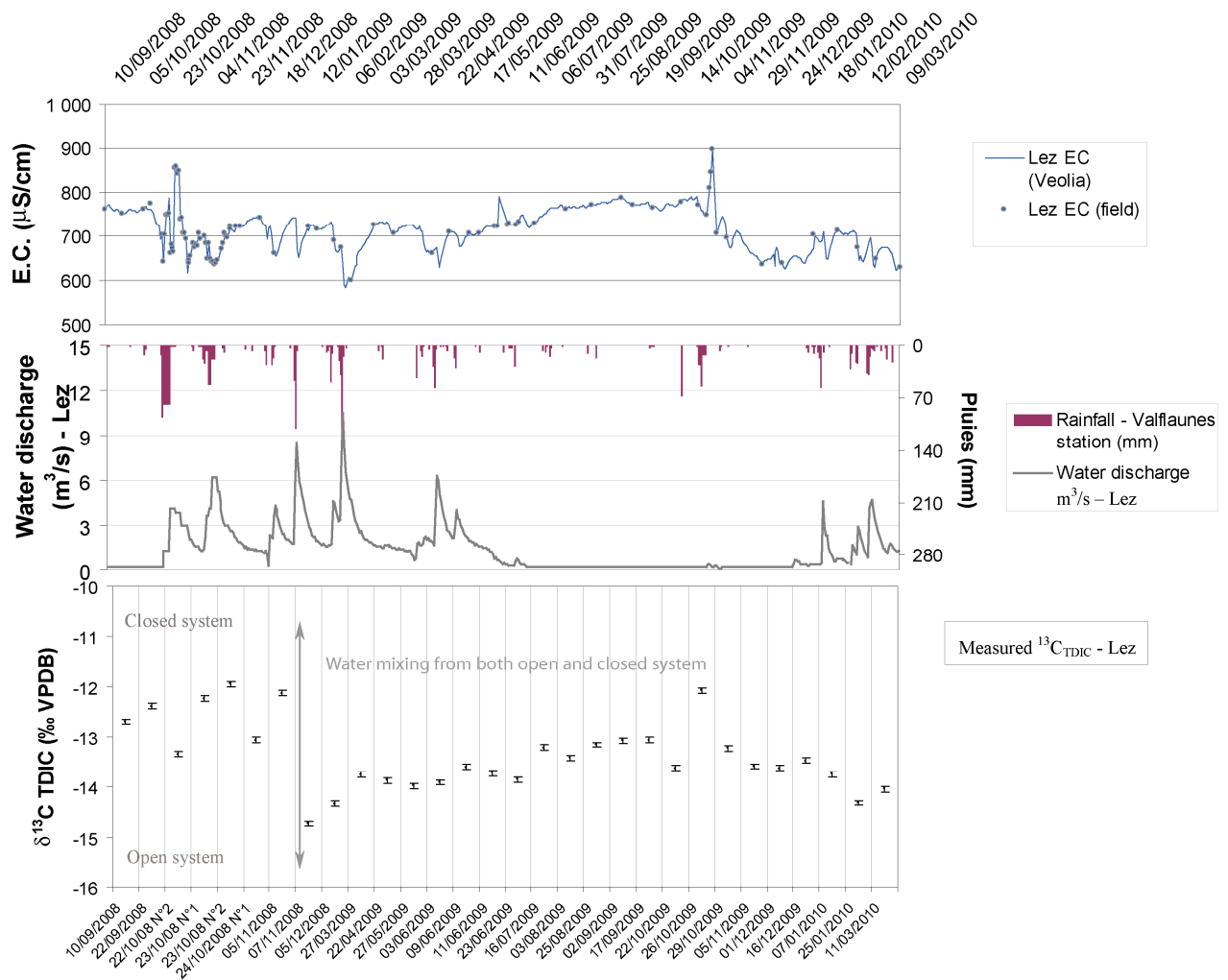


Fig. 25 – Rainfall, E.C., water discharge and $\delta^{13}\text{C}_{\text{TDIC}}$ at the Lez spring.

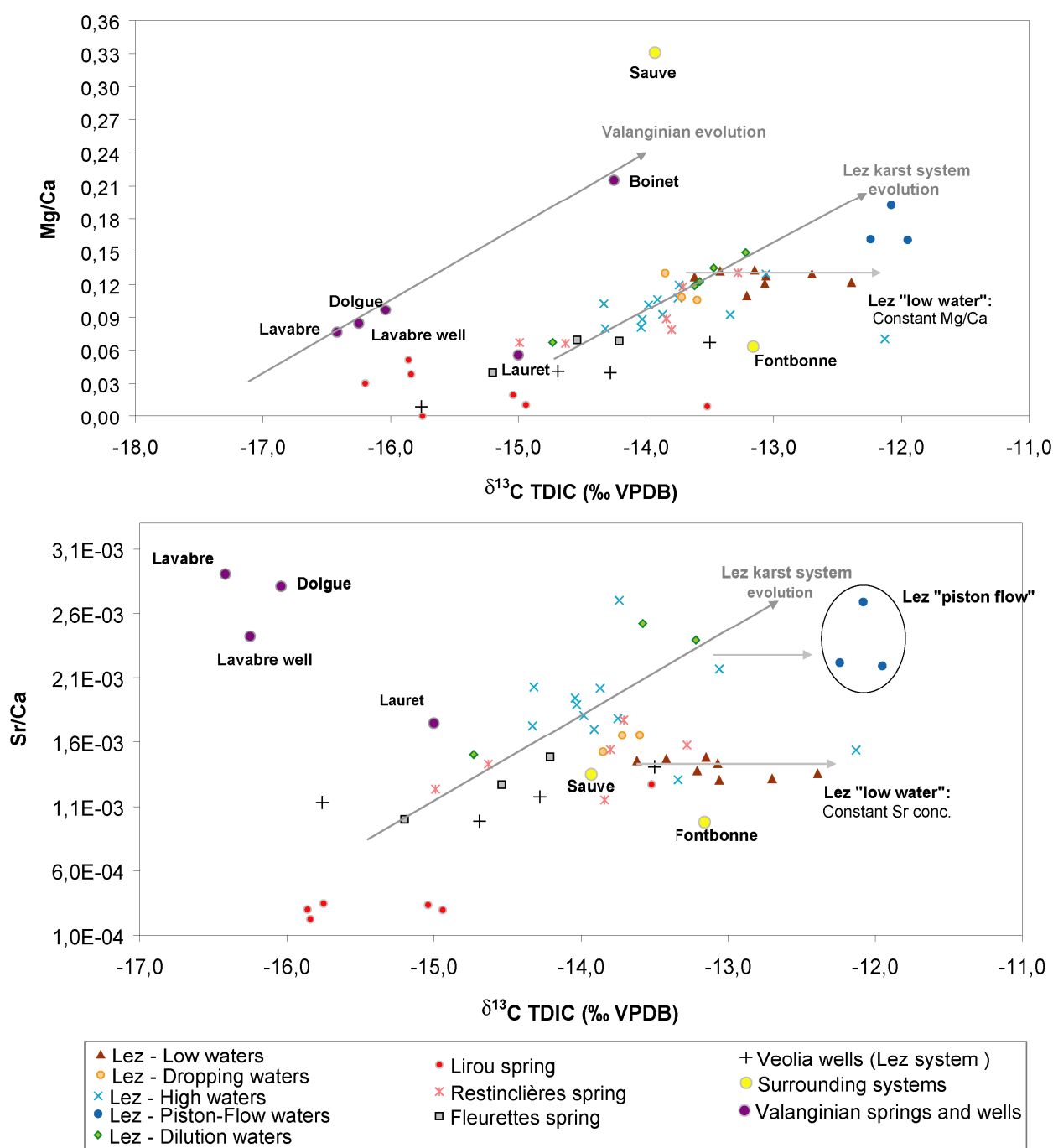


Fig. 26 - Mg and Sr/Ca vs. $\delta^{13}\text{C}_{\text{TDIC}}$ for all the Lez karst system springs and wells, and for springs/wells belonging to the surrounding karst systems.

Sr isotopes were used to confirm those hypotheses, leading to a better understanding of the reactions that control water chemistry at the Lez system, while focusing on the high-mineralized waters of the Lez spring. The Lez spring presents the higher Sr concentration of the Lez system. Sr has a good correlation with SO_4 , B and Li. A good correlation with Cl was only observed for the waters with the highest Cl concentrations, indicating a common origin for both elements in this specific case. Several possible end-

members can contribute to Sr concentration of the waters, which complicate the identification of Sr sources in groundwaters (Mcintosh & Walter, 2006; Nisi *et al.*, 2008; Wu *et al.*, 2009). Moreover, Sr concentration could be influenced by multiple reactions, e.g. re-crystallization reactions, incongruent dissolution or celestite precipitation (Tellam, 1995; Bernasconi, 1999).

The chemical reactions that seem to determine the chemistry of the high-mineralized waters of the Lez spring could influence Sr concentrations in two different ways:

(i) The incongruent dolomite dissolution and calcite precipitation led by evaporite salts dissolution enriches the fluids in both Sr and Mg. During the calcite recrystallization, the Sr/Ca increases because the calcite lattice favours Ca and Mg over Sr during the precipitation (Jacobson *et al.*, 2002; Négrel & Petelet-Giraud, 2005; McIntosh & Walter, 2006; Nisi *et al.*, 2008; Stuart *et al.*, 2010). Consequently, high Sr/Ca ratios indicate that waters have been extensively altered by the incongruent dissolution of carbonate minerals and the dissolution of evaporites (Jacobson & Wasserburg, 2005; McIntosh & Walter, 2006; Samborska & Halas, 2010).

(ii) The evaporite dissolution may enrich fluids in Sr because they contain more Sr than calcite and dolomite (Petelet *et al.*, 1998; Grobe & Machel, 2002; Jacobson & Wasserburg, 2005; McIntosh & Walter, 2006; Wu *et al.*, 2009). As Sr concentrations increase, Mg/Ca ratios increase also, suggesting progressive water-rock interactions (McIntosh & Walter, 2006).

Jacobson and Wasserburg (2005) findings suggest that future researches about the evolution of dissolved Sr in carbonate aquifers should consider the role that relatively common but few abundant minerals should exert under the overall chemistry of water-rock interactions. Their observations showed that anhydrite dissolution seemed to be the governing factor controlling the evolution of dissolved Sr in the aquifer. Thus, carbonate dissolution could possibly not be the main mechanism for Sr addition in aquifer groundwaters.

Solute chemistry and isotopic composition ratios in a groundwater system can be regarded as a chemical mixture from several sources, and the discrimination of the contribution from each geological formation is a difficult task. Strontium isotopes have been used for understanding water circulation in reservoirs, quantifying water mixing from different origins and examining geochemical interaction between water and aquifer rocks (Oetting *et al.*, 1996; Katz *et al.*, 1998; Petelet *et al.*, 1998; Kloppmann *et al.*, 2001; Barbieri *et al.*, 2005; Jacobson & Wasserburg, 2005; Wang *et al.*, 2006; Petelet-Giraud & Négrel, 2007; Nisi *et al.*, 2008). Moreover, major elements, mineral saturation state and Sr/Ca versus $^{87}\text{Sr}/^{86}\text{Sr}$ help identifying

the reactions that control the evolution of the waters chemistry, like the presence of incongruent dissolution of dolomites and calcite precipitation (Oetting *et al.*, 1996).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the Lez spring range from 0.707622 to 0.707921. For the whole Lez system (Lez, Restinclières, Fleurettes and Veolia wells) $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.70564 to 0.707921. The maximum variation for Sr isotope ratio for the Lez karst system is $5,84 \cdot 10^{-4}$ and is quite significant (Négrel & Petelet-Giraud, 2005). This range suggests the existence of extra-formational source(s) of Sr caused by the heterogeneity of the matrix as well as complex water-rock interactions and/or anthropogenic input (Oetting *et al.*, 1996; Négrel & Petelet-Giraud, 2005).

Carbonate rocks usually present low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and a high Sr concentration. Meteoric waters have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and low Sr concentration (Oetting *et al.*, 1996; Négrel & Petelet-Giraud, 2005). Most of the water samples presented on Figure 27 are clustered around a mixing line on the plot. The exceptions are the “*Piston-flow*” water samples at the Lez spring, which present relatively enriched $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with high Sr concentrations. When a sample is located above the mixing line, there should be other sources of Strontium with different Sr isotope ratio along the flow path. The lack of correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with $1/\text{Sr}$ suggests that chemical reactions involving Sr addition or removal occurred, i.e. the simple mixing from different Sr^{2+} origins cannot explain this behaviour (Grobe & Machel, 2002).

This same “*Piston-flow*” water sample has also a particular behaviour regarding $^{87}\text{Sr}/^{86}\text{Sr}$ versus Cl concentrations (Figure 27), presenting the highest Cl concentrations and the more enriched $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. For the Valanginian samples, an inverse situation is observed, with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Enriched $^{87}\text{Sr}/^{86}\text{Sr}$ observed at the Sauve spring is probably associated to granitic fingerprinting. The trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with increasing Cl suggests: (i) a mixing of saline ^{87}Sr -enriched water with a less saline and ^{87}Sr -enriched water component, or (ii) indicates that the Cl rich waters are also more $^{87}\text{Sr}/^{86}\text{Sr}$ radiogenic (Kloppmann *et al.*, 2001). The geologic context and the water chemistry attributes of the Lez spring indicate that this behaviour is related to the first hypothesis (i). Oetting *et al.* (1996) also found higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for waters from carbonate and evaporite aquifer, indicating a source of Sr from underlying units.

The Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio signature is more radiogenic than the Jurassic one. During the Jurassic, the $^{87}\text{Sr}/^{86}\text{Sr}$ varied from high values during the Late Triassic to low values during the Late Cretaceous (Koepnick *et al.*, 1990). However, an enriched $^{87}\text{Sr}/^{86}\text{Sr}$ signature could correspond to either lower Jurassic waters, or recent infiltration waters or again to granite fingerprinted water.

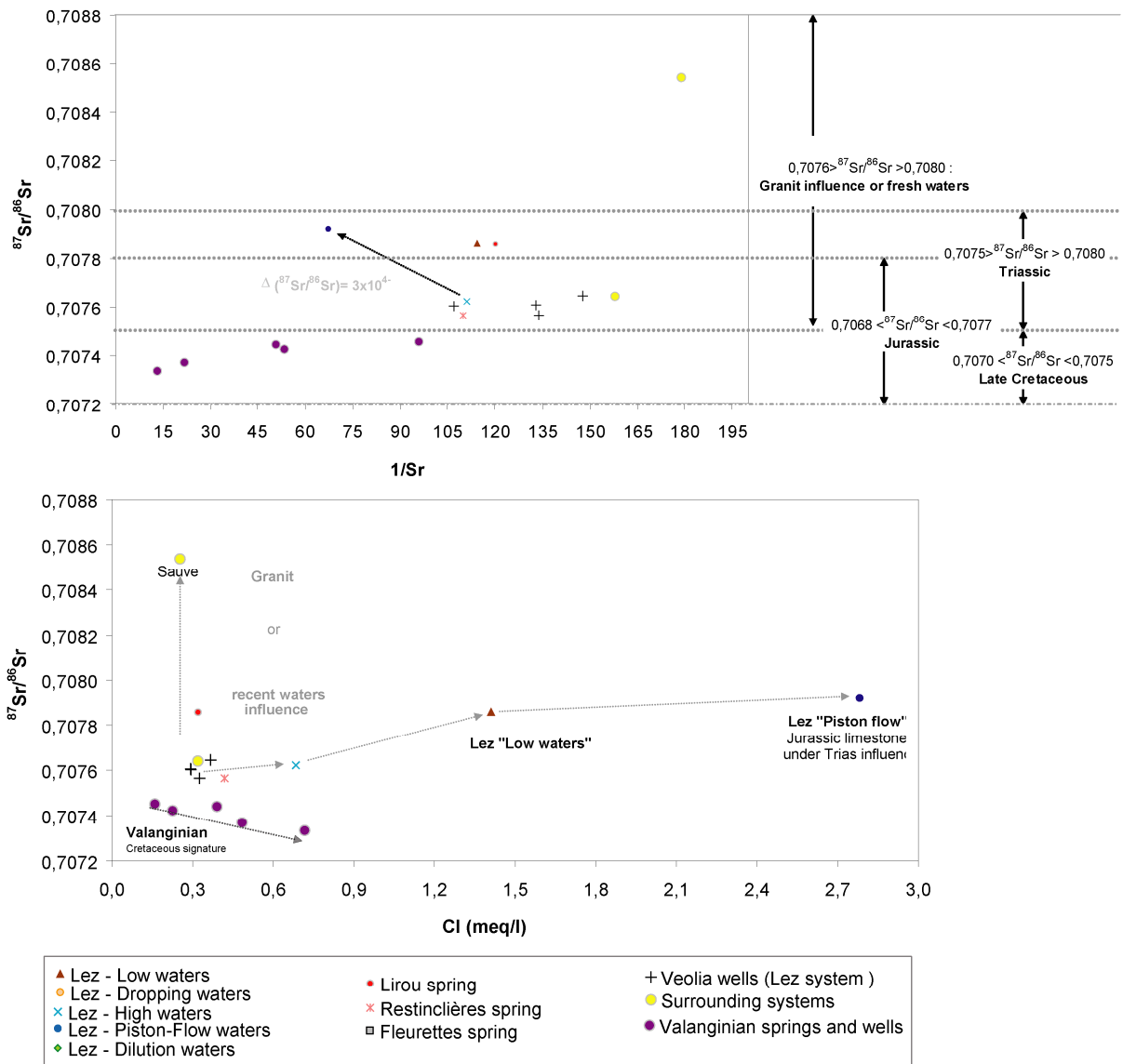


Fig. 27 – $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs $1/\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs Cl for all the Lez karst system springs and wells, and for springs/wells belonging to the surrounding karst system. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio typical range for Triassic, late Cretaceous and Jurassic (Koepnick et al., 1990) and granite and fresh waters (Kloppmann et al., 2001).

4.2.4 - Hydrograph deconvolution using various tracers

The hydrograph deconvolution approach is often used to represent the multiple end-members participation in floods at the outlets through the use of natural tracers. Mixing models based on mass conservation describe water quantities using isotopic or chemical tracers from rainfall water, pre-event water and flow hydrograph. Many authors used water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) on hydrograph deconvolutions for determining the multiple (2 or 3) components composing the mixing of the spring water (Drever, 1982; Beven, 2001; Ladouche *et al.*, 2001; Long & Putnam, 2004; Aquilina *et al.*, 2006). Other used Sr (Petelet-Giraud & Negrel, 2007) or Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) (Katz *et al.*, 1998; Wang *et al.*, 2006); $\delta^{13}\text{C}_{\text{TDIC}}$ (Batiot, 2002; Emblanch *et al.*, 2003); TOC (Garry, 2007) or EC (Ribolzi *et al.*, 1997), etc.

In the present work, mass balance calculations were attempted using the following tracers: T, EC, Cl and Mg concentrations and $\delta^{18}\text{O}$; and assuming a simple mixture of old and new water (Eq. 1 to 5).

$$Q_{\text{spring}} C_{\text{spring}} = Q_{\text{old}} C_{\text{old}} + Q_{\text{new}} C_{\text{new}} \quad (1)$$

$$Q_{\text{spring}} = Q_{\text{old}} * x_{\text{old}} + Q_{\text{new}} * x_{\text{new}} \quad (2)$$

$$x_{\text{old}} + x_{\text{new}} = 1 \quad (3)$$

$$Q_{\text{spring}} = Q_{\text{old}} * (1 - x_{\text{new}}) + Q_{\text{new}} * x_{\text{new}} \quad (4)$$

$$x_{\text{new}} = \frac{Q_{\text{spring}} - Q_{\text{old}}}{Q_{\text{new}} - Q_{\text{old}}} \quad (5)$$

The geochemical signatures of the main compartments of the system were used to define end-members signatures (Table 4). These ones should be well constrained for a more precise deconvolution attempt. In this work, the multiple end-members signatures were defined based on the hydrogeochemical characterization and on the end-members identification reported in Bicalho *et al.* (submitted). The considered end-members were: *main aquifer*, which was defined as the average of the low stage season; *Deep waters*, defined as the average of high-mineralized waters; and *recently infiltrated* or “*new*” *waters*, which could be considered as rainfall waters or surface waters, depending on the available data.

Three end-members deconvolutions were carried out for the tracers: EC, Cl, Mg and T, for which the input data were available through rainfall or runoff sampling. Deconvolutions using three end-members were achieved by two successive hydrograph separations. The first one distinguished rainfall or surficial waters

from aquifer waters. The second one decomposed aquifer waters into main aquifer and deep waters (Table 4).

The effectiveness of the various tracers in quantifying the mixing between the different sources of water is related to the difference between the end-members tracers and the reactions that may occur in the groundwaters. Oxygen and Hydrogen isotopes are highly efficient tracers because oxygen and hydrogen constitute conservatives tracers, which are efficient as waters origin tracers. However, tracers constituted of elements that are potentially subjected to reactions are more efficient as solute tracers, quantifying the interaction between surficial water and groundwater (Katz *et al.*, 1998; Emblanch *et al.*, 2003).

Deconvolution using water stable isotopes considered two end-members: rainfall waters and pre-event water. Due to the large temporal variability of the isotopical composition of rainfall water, the appropriate isotopic composition for hydrograph separation is obtained by the “cumulative incremental weighting”, based on the rainfall heights (Eq. 6), where it was obtained a $\delta^{18}\text{O}$ weighted input signal of -4.53‰, at Viols-le-Fort station. Those deconvolutions indicated the participation of 13% of rainfall water in the humid season of 2008-2009, being 38% in autumn and 13% in winter and 3.3% in 2009-2010 (Table 4).

$$\delta^{18}\text{O}_{\text{event-water}} = \frac{\sum_{i=1}^n \delta^{18}\text{O}_i}{\sum_{i=1}^n P_i} \quad (6)$$

Table 4 presents the results carried out for multiple flood events between 2008 and 2010. The mean participation of the three analysed water end-members is: 84% for the main aquifer; 6.2% for “new” waters (rainfall or surficial waters) and 9.8% for deep waters. The winters are characterised by the lowest participation of deep waters, about 5% against 10% for the springs and 16% for the autumns. During spring, we observe a “new” waters participation of 2.6%, when it is 5% during autumn and 5.7% during winters.

Table 4 – End-members definition and participation proportions in the flood events: Spring 2008, Autumn 2008, Winter 2008-2009, Spring 2009 and winter 2009-2010, at the Lez spring using the tracers: EC, Cl (mg/l), Mg (mg/l), T (°C), and $\delta^{18}\text{O}$. 3 and 2 mixing components considered.

Tracers	End-members		End-members definition	End-members proportions of participation on floods - Lez spring					
				Spring 2008	Autumn 2008	Winter 2008/2009	Spring 2009	Winter 2009/2010	Average
E.C. ($\mu\text{S.cm}$)	Deconv.1 (3 end-members)	Rainfall water	45	3.4%	8.2%	9.5%	8.5%	11.1%	8.1%
		Main aquifer	750	90.6%	86.2%	90.5%	91.3%	88.9%	89.5%
		Deep water	900	6.0%	5.7%	0.0%	0.2%	0.0%	2.4%
	Deconv.2 (3 end-members)	Surficial water	440	7.7%	18.5%	21.6%	19.4%	25.3%	18.5%
		Main aquifer	750	86.3%	75.8%	78.4%	80.4%	74.7%	79.1%
		Deep water	900	6.0%	5.7%	0.0%	0.2%	0.0%	2.4%
Cl (mg/l)	Deconv.1 (3 end-members)	Rainfall water	2.2	0.1%	6.6%	3.5%	0.0%	2.3%	2.5%
		Main aquifer	30	74.6%	76.7%	89.3%	91.5%	89.2%	84.3%
		Deep water	90	25.3%	16.7%	7.2%	8.5%	8.5%	13.2%
	Deconv.2 (3 end-members)	Surficial water	8.5	0.2%	8.6%	4.5%	0.0%	3.0%	3.3%
		Main aquifer	30	74.5%	74.7%	88.3%	91.5%	88.5%	83.5%
		Deep water	90	25.3%	16.7%	7.2%	8.5%	8.5%	13.2%
Mg (mg/l)	Deconv.1 (3 end-members)	Rainfall water	0.5	0.0%	5.1%	0.9%	0.0%	2.4%	1.7%
		Main aquifer	6	80.3%	82.6%	86.9%	77.6%	89.7%	83.4%
		Deep water	14	19.7%	12.3%	12.2%	22.4%	7.9%	14.9%
	Deconv.2 (3 end-members)	Surficial water	4.8	0.0%	5.2%	3.9%	0.0%	11.1%	4.0%
		Main aquifer	6	80.3%	82.5%	83.8%	77.6%	81.0%	81.0%
		Deep water	14	19.7%	12.3%	12.2%	22.4%	7.9%	14.9%
T (°C)	3 end-members	Surficial water	8	5.5%	0.0%	7.0%	3.5%	9.1%	5.0%
		Main aquifer	15	94.5%	68.1%	92.5%	92.9%	88.4%	87.3%
		Deep water	17	0.0%	31.9%	0.5%	3.6%	2.5%	7.7%
$\delta^{18}\text{O}$ (‰)	2 end-members	Rainfall water	-4.53 (2008) -4.93 (2009)	-	38.1%	13.2%	2.0%	3.3%	14.2%
		Deep water	-5.89 (2008) -5.98 (2009)	-	61.9%	86.8%	98.0%	96.7%	85.9%

Figure 28 presents the three end-member deconvolution achieved with Cl concentrations. At the Lez spring, Cl should be an efficient solute tracer, as the origin attributed to Cl at this spring is mainly lithologic. Deconvolution points out the larger deep waters participation to the flow at the beginning of the flood.

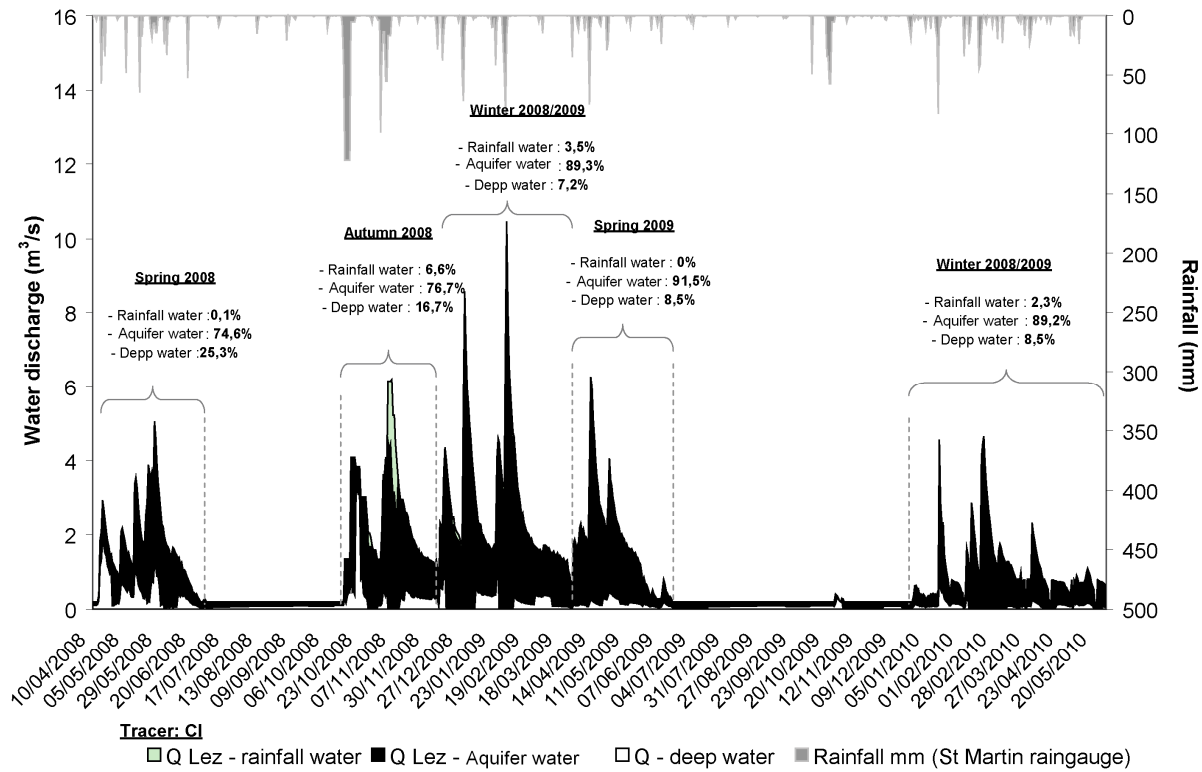


Fig. 28 – Hydrograph deconvolution of the floods from 2008 to 2010 using Cl, where: the end-member “rainfall waters” has Cl=2.2 mg/l and mixing proportion of 5%; end-member “aquifer waters” has Cl=30mg/l and mixing proportion of 83%; and end-member “deep waters” has Cl=90mg/l and mixing proportion of 12%.

The original T of the deep end-member can finally be calculated with a deep-water dilution factor estimated at about 8%. Considering the temperature of the high mineralized waters at the Lez spring (17.4°C) and the average air temperature of the study area (16.1°C) (Hérault, 2009), by application of Eq. 5, we obtain a T of deep waters equivalent to 34.7°C. Considering an average geothermic gradient of 1°C/33m, we obtain a depth of 613 meters. Therefore, it is important to highlight that the “deep” water end-member considered in this study was obtained in the spring flow, and, even though it is equivalent to the product of a mixing, it does not represent a “pure” deep end-member signature. Anyhow, this hydrograph deconvolution is useful to show the temporal distribution of end-members under a wide range of hydrological conditions.

4.3 - Conclusion: Conceptual model for groundwater circulation at the Lez karst system

The isotopical monitoring along multiple springs of the Lez karst system allowed a considerable advance on the comprehension of this system. Thus, a conceptual model of groundwater circulation was currently proposed (Figure 29), suggesting the possible groundwater origins and flowpaths for each of the main springs of this system.

The results obtained in this work complement the argumentation presented by Bicalho *et al* (submitted) suggesting that the Lez spring has a small proportion of groundwater that is issued from evaporitic layers. Apparently, a shallow buffering zone or reservoir (Figure 29) allows the accumulation of rising waters from deep origin. The water from this zone participates to the outflow on the Lez spring during high recharge events. This behaviour was evidenced by: (i) high levels of Mg/Ca and Sr/Ca and the concomitant increase with $\delta^{13}\text{C}_{\text{TDIC}}$, possibly evolved via incongruent dissolution of carbonate minerals under closed system conditions. This reflects the isolation of those waters from an active flow in shallow GW and longer residence times; (ii) the significant $^{87}\text{Sr}/^{86}\text{Sr}$ range observed for the Lez karst system, which suggests the existence of multiple sources of Sr, caused by matrix heterogeneity as well as complex water-rock interactions; (iii) the Cl rich waters have equally high Sr concentrations: an evaporitic origin could explain both concentrations; (iv) the Cl rich waters at the Lez spring are also more $^{87}\text{Sr}/^{86}\text{Sr}$ radiogenic: this can be explained by a Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ signature, which is more radiogenic the Jurassic one, and (v) the high Sr/Ca ratios, which can be explained by calcite recrystallization involving a continuous addition of Sr^{2+} induced by Ca^{2+} depletion in water solution.

In conclusion, waters issued from this deep compartment, have longer residence times and have been extensively modified by evaporite dissolution, incongruent dissolution of dolomite and calcite precipitation. However, this behaviour is exclusively observed at the Lez spring.

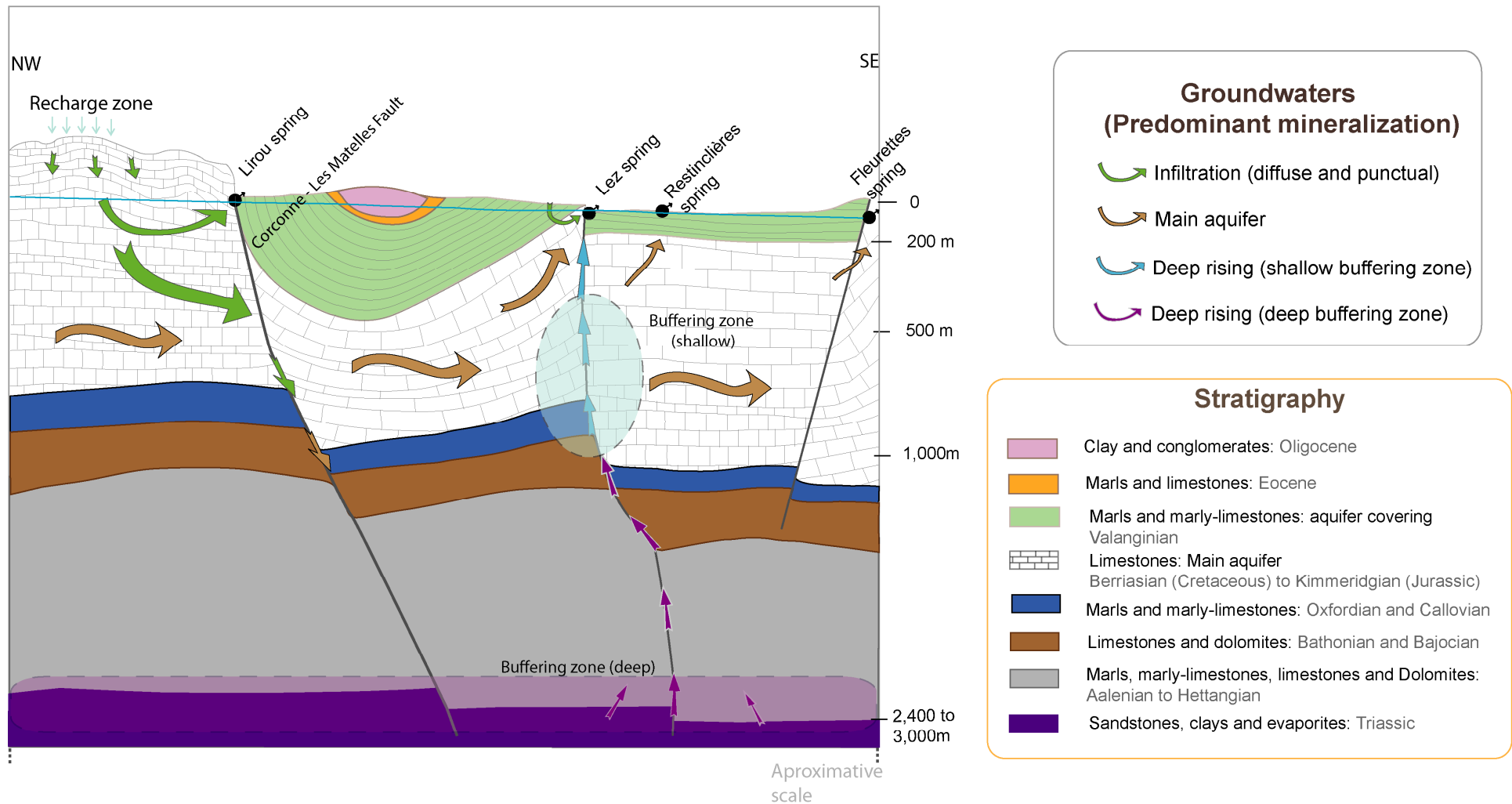


Fig. 29 – Conceptual model for groundwater circulation at the Lez karst system.

The end-member proportions that participate to the spring flow change along with the hydrodynamics. The participation of deep waters seems to be permanent at the Lez spring since even the most diluted waters are high-mineralized. The study of the mixing proportions issued from the multiple aquifer end-members could be the key to understand this complex composition. The end-member participation proportions during floods (cycles 2008-2009 and 2009-2010) were estimated by using hydrograph deconvolution based on chloride concentrations. The estimated participation for deep waters is as follow: 13%; recent waters: 3% and aquifer waters: 84%.

The higher reactivity observed at the Lirou spring evidenced by water stable isotopes denotes the low residence time of groundwater at Lirou spring. For the other springs, in the contrary, it is observed a global signal attenuation, indicating the existence of an important storage component favouring an efficient mixing of infiltrated waters with stocked water, and longer residence times.

The similar water stable isotopes fingerprinting observed for the Lez system springs (Lez, Lirou, Restinclières and Fleurettes) indicate that they have a common recharge area. However, the great disparity observed in their water chemistry indicates that recharge water percolates distinct flowpaths. The hydrochemical characteristics of Restinclières and Fleurettes springs seem to be mostly attributed to limestones and marly-limestones from Upper Jurassic and Early Cretaceous, due to groundwater circulation bellow the Valanginian covering of the aquifer. These waters are characterized by a more important lithological source of Mg than for the Lez spring, as evidenced by high Mg/Ca and low $\delta^{13}\text{C}_{\text{TDC}}$. The absence of evaporitic fingerprinting also contributes to distinguish the diverse springs between the Lez one.

Future investigations should consider other natural tracers like ^{14}C for better understanding groundwater residence time and $^{11}\text{B}/^{10}\text{B}$ ratio for definitively confirm the evaporite participation to the water mineralization.

Chapter 5 - Groundwater hydrochemistry changes induced at the Lez karst spring as a result of intense exploitation during 28 years

Extracted form Article N°3

Article title:

“Hydrodynamical changes and their consequences on groundwater hydrochemistry induced by three decades of intense exploitation in a Mediterranean Karst system.”

Authors:

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Journal: Environmental Earth Sciences

Present Situation: Submitted as guest author

The Lez karst spring, located in the Mediterranean basin (southern France), supplies with water the metropolitan area of Montpellier (France) since the 19th century. Since 1981, an intense pumping is being performed directly in the main conduit with a maximum exploitation flow rate of about 1,700 l/s. To improve the understanding of groundwater origins and circulation dynamics in this karst system, as well as the impact of three decades of intense water exploitation, groundwater samples have been collected during various hydrologic conditions since March 2006.

A previous hydrochemical study on the Lez karst system had been carried out before the installation of the pumping plant (1973-1974 dataset; Marjolet & Salado, 1976). This dataset was compared to the present one in order to identify possible changes on groundwater hydrochemistry. The results of this analysis indicate the existence of historical changes in water hydrogeochemistry and evidence a decrease of the deep compartment participation to the Lez spring outflow. This change in water hydrogeochemistry may be attributed to the intense pumping of the karst system and, in the absence of noticeable climatic changes, expresses the direct consequences of anthropogenic forcing on the overall functioning of the aquifer. This study aims to analyze the differences, to understand the water chemistry changes and to better foresee the aquifer evolution for the future.

Key words: karst, groundwater, natural tracing, hydrochemistry, water transit.

5.1 - Introduction

The present chapter analyses and discusses the changes induced in the chemical composition of water at the Lez spring as a result of intense exploitation since 1981, in comparison with the hydrochemical monitoring achieved in 1973-1974 (Marjolet & Salado, 1976), before the intense pumping starts.

The chemistry of karst springs is normally related to physical characteristics and helps distinguishing different types of hydrodynamical behaviour in the drained karst systems (López-Chicano *et al.*, 2001; Rosenthal *et al.*, 2007; Moral *et al.*, 2008; Belkhiri *et al.*, 2011; Mudarra & Andreo, 2011). Hydrodynamical characteristics such as recharge, thickness of infiltration zone, aquifer geometry and its fissured structure can deeply influence the groundwater transit time and water-rock interactions, as well as the hydrochemistry of waters draining a karst (López-Chicano *et al.*, 2001; Jiang *et al.*, 2009; Moore *et al.*, 2009; Stuart *et al.*, 2010).

The Lez aquifer combines many advantages that favour the advance of karst hydrogeology science, like a large monitoring network and an important historical dataset. Few works are reported in the literature relating the evolution of the aquifer behaviour before and after several years of intense exploitation (Rosenthal, 1988; Samborska & Halas, 2010). Rosenthal (1988) investigated the hydrochemical changes induced by two decades of intense exploitation of groundwater in a multiple layers aquifer system in Israel, provoking the ascension of brines and the salinization of waters.

The present comparison study was anticipated by Marjolet & Salado (1976), according to the following citation: “*The interest of this study is to provide a database. Effectively, the water capitation project foresee the possibility of 40 meters of withdrawing, it is possible that this intense exploitation will change circulation conditions in the aquifer, and consequently, the water chemistry*”.

5.2 - Results and interpretation

5.2.1 - *Lez typical autumn floods: 1973, 2008 and 2009*

The first comparing analysis between the current chemical characteristics of the Lez spring and the ones reported 35 years ago is focused on the autumn floods (Figure 30). These floods, occurring at the beginning of the rainy season, have been observed each year and showed only variations in intensity (EC values and element concentrations peaks). The cumulated rainfalls that triggered those floods were respectively: 86mm in 1973 and 200mm in 2008. In terms of annual rainfall, both 1973 and 2008 have rainfall surplus: about 10% for 1973 and about 35% for 2008. The maximum observed Cl concentrations were respectively: 112 mg/l in 1973 and 80 mg/l in 2008.

The rainfall recharge causes a transient pressure pulse to travel the system resulting in a discharge spike at the spring (Desmarais & Rojstaczer, 2002). Indeed, intense rainfall recharge causes the motion of more mineralized waters towards the spring, due to a piston flow effect. This phenomenon happens only during extreme hydrological situations and has been also observed in some karst systems (Emblanch *et al.*, 1999; López-Chicano *et al.*, 2001; Desmarais & Rojstaczer, 2002).

In Oct. 1973, the historic-highest Cl concentration ever measured (120mg/l) was observed at the Lez spring, during a rainfall event of 88mm. This flood event was triggered by the smallest rainfall event in terms of height between the three analysed floods. Nevertheless, considering that there was no intense pumping in 1973, the total water-head on the aquifer was considerably higher, in spite of the smaller height of the rainfall event. Therefore, the saturation state in the aquifer was more easily reached in 1973 than in 2008 or 2009. Nowadays, the first rainfall events recharge the karst aquifer not only after a long period of dryness but also of intense pumping. At present, the karst aquifer is more hydraulically depleted and needs greater heights of rainfall than it used to before the beginning of the intense exploitation, to reach the same piezometric levels.

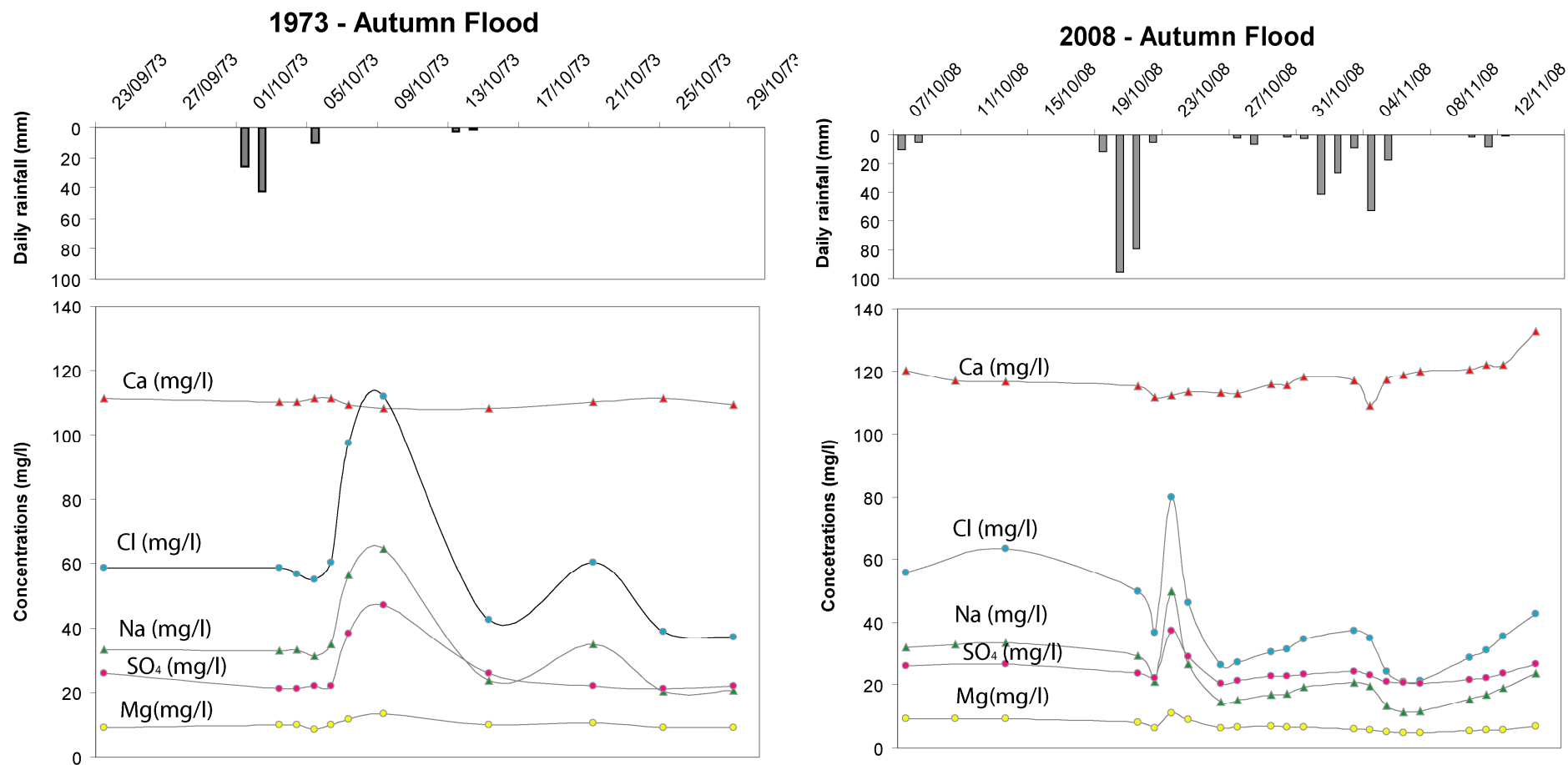


Fig. 30 – First autumn flood events of the years 1973, 2008 and 2009, considering variations for: Ca, Mg, Na, K, Cl and SO₄. Cl maxima were respectively: 112 mg/l in 1973, 80 mg/l in 2008 and 98 mg/l in 2009.

5.3 - Chemical changing description using Discriminant Factorial Analysis

In order to search for evidences of changes on water chemistry before and after intense pumping, the hydrological cycles of 1973-1974, 2006-2007, 2007-2008 and 2008-2009 were analysed using DFA. Two distinct DFA were carried out, both considering EC, pCO_2 and concentrations in Cl^- , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+} as independent variables. The dependant variable for the first DFA was the different hydrological cycles. Observation plots on axes F1 and F2, which represent 97.53% of the total variability, individualize the water year 1973-1974 from the other years (Figure 31).

The positive direction of F1 axis represents the mineralization with K, Na and Cl that characterizes the 1973-1974 waters. The negative direction of F1 axis represents mineralization with HCO_3^- and Ca which is the predominant mineralization for the 2006-2007, 2007-2008 and 2008-2009 waters. The positive direction of F1 axis represents the mineralization with K, Na and Cl that characterizes the 1973-1974 waters. F2 axis is characterized by an opposition between pCO_2 and Mg concentrations.

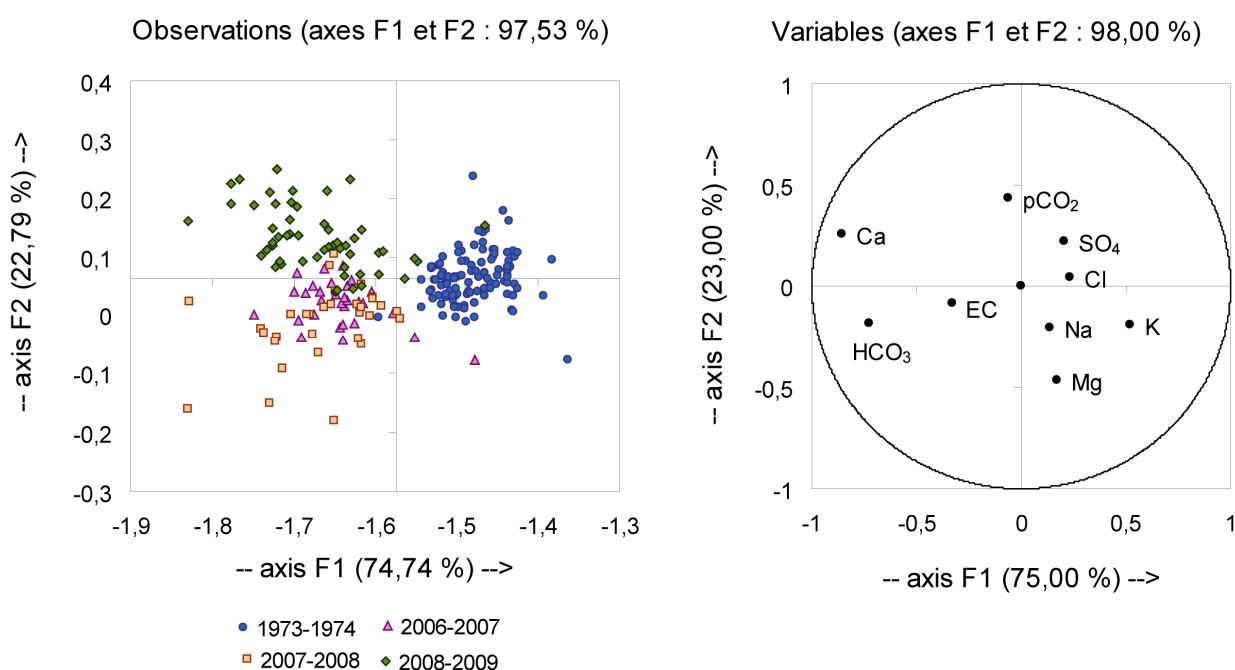


Fig. 31 – DFA for the Lez spring data for the years: 1973-1974, 2006-2007, 2007-2008 and 2008-2009. Left: sample space; right: variable space.

For the second DFA (Figure 32), the water-type identification used for the current Lez waters was applied to the samples of 1973-1974 (Bicalho *et al.*, 2009; Bicalho *et al.*, 2010). The “water-year-type” was

thus considered like the dependent variable for the calculation of the additional DFA. The global difference observed is that the whole system seems to have moved toward a new geochemical composition (Figure 32). The most mineralized waters, before and after intense pumping, are still the *Piston-flow waters*, which flow during the autumn floods. However, this water-type for “after pumping” conditions shows lower concentrations in Cl, Na, Mg, K and SO₄ and presents higher concentrations in Ca and HCO₃ than “before pumping” conditions

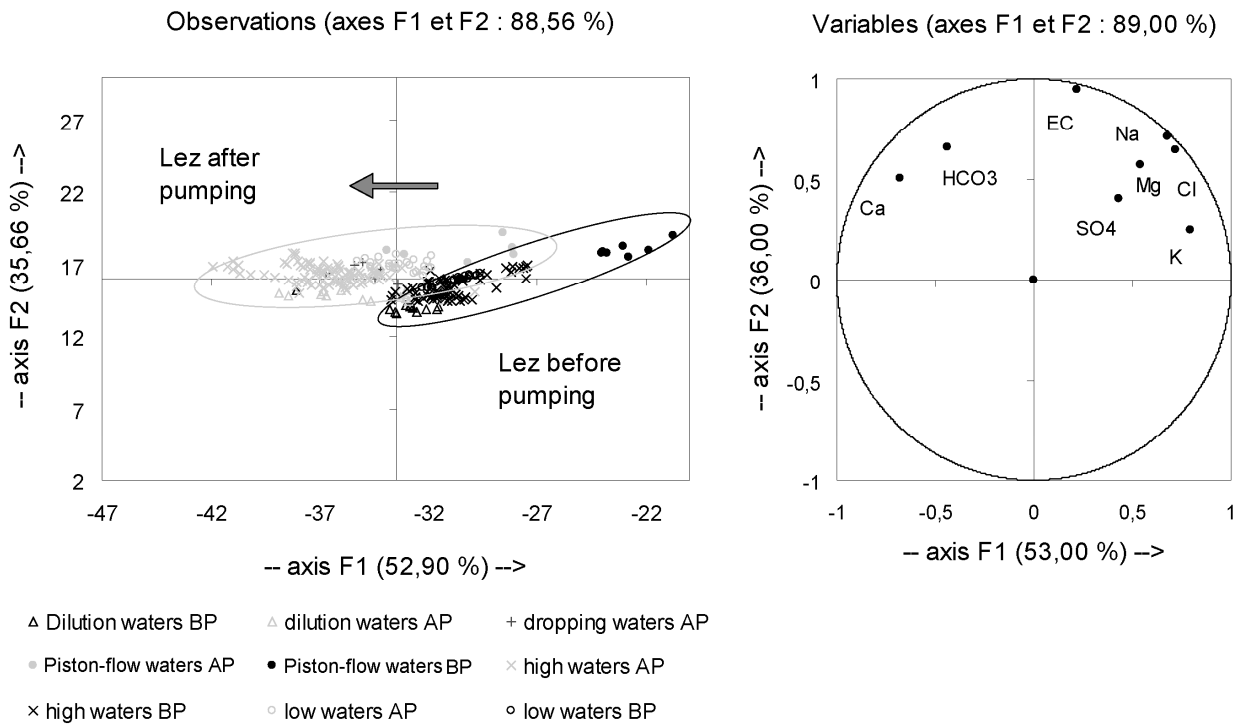


Fig. 32 – DFA for the Lez spring data: Low water Before Pumping (BP), piston-flow water BP, Dilution waters BP, High waters BP, Low waters (2008), Piston-flow waters, Dilution waters, Dropping waters and High waters. Left: sample space; right: variable space.

5.4 - Conceptual model of a possible hydrodynamical change before and after pumping

The hydrological conditions determine the different compartments participation to the mixing that composes the waters of the Lez spring outflow (Bicalho *et al.*, submitted). The intense exploitation causes a general decrease of the hydraulic head within the aquifer which does not reach any longer the hydraulic head that it used to, even for similar rainfall recharges. The participation of the waters from the deep compartment

to the Lez spring outflow is related to the occurrence of strong hydraulic head during the heavy autumn rainfall recharges (Bicalho *et al.*, 2010; Bicalho *et al.*, submitted). Indeed, intense pumping apparently led to the decrease of the deep compartment participation to the Lez spring water flow.

Figure 33 presents an adaptation of the conceptual model of Bicalho *et al.* (submitted) containing the hypothetical hydrodynamical differences that characterize the system for both years 1973 and 2009. The average concentration variations were calculated according to the average values of concentrations in Ca and Cl for low stage waters and high-mineralized waters (piston-flow waters) for both datasets (before and after pumping).

The origins of waters marked by a Ca-HCO₃ mineralization are associated to the main and shallow aquifers (Jurassic, Berriasian and Valanginian layers) (Marjolet & Salado, 1976; Bicalho *et al.*, submitted). While the origins of Cl, Na, Mg and SO₄ are mainly associated to deep layer with evaporitic fingerprinting (Bicalho *et al.*, submitted). The intense exploitation generated a new hydrodynamical equilibrium which induced a different water chemical composition, by changing the participations of the different compartments to the spring waters mixing, according to the hydrological conditions. Some of the most visible changes on water chemistry are: Na-Cl mineralization decrease and Ca-HCO₃ mineralization increase, after the intense pumping started.

The average chloride concentration decrease during autumn floods is about 33% between 1973 and 2009. During the low stage season, Cl concentration differences between both scenarios are less pronounced. However, higher concentrations for Ca and HCO₃ show that the participation of those waters increased after the intense exploitation has started. The increased participation of the shallow aquifer waters to the spring flow was already suspected by Marjolet and Salado (1976).

The waters from 2006 to 2009 presented a higher pCO₂ than in 1973-1974, potentially leading to a stronger karstification within the aquifer which could, in the long term, cause an augmentation of conduits diameter in the carbonate matrix. Under-saturated waters are observed when recharge is intense and when a very rapid draining of recently infiltrated waters takes place (López-Chicano *et al.*, 2001). This could indicate that water circulation “after-pumping” happens in compartments rather shallower than “before-pumping”, due to the decrease of the water residence time in the aquifer.

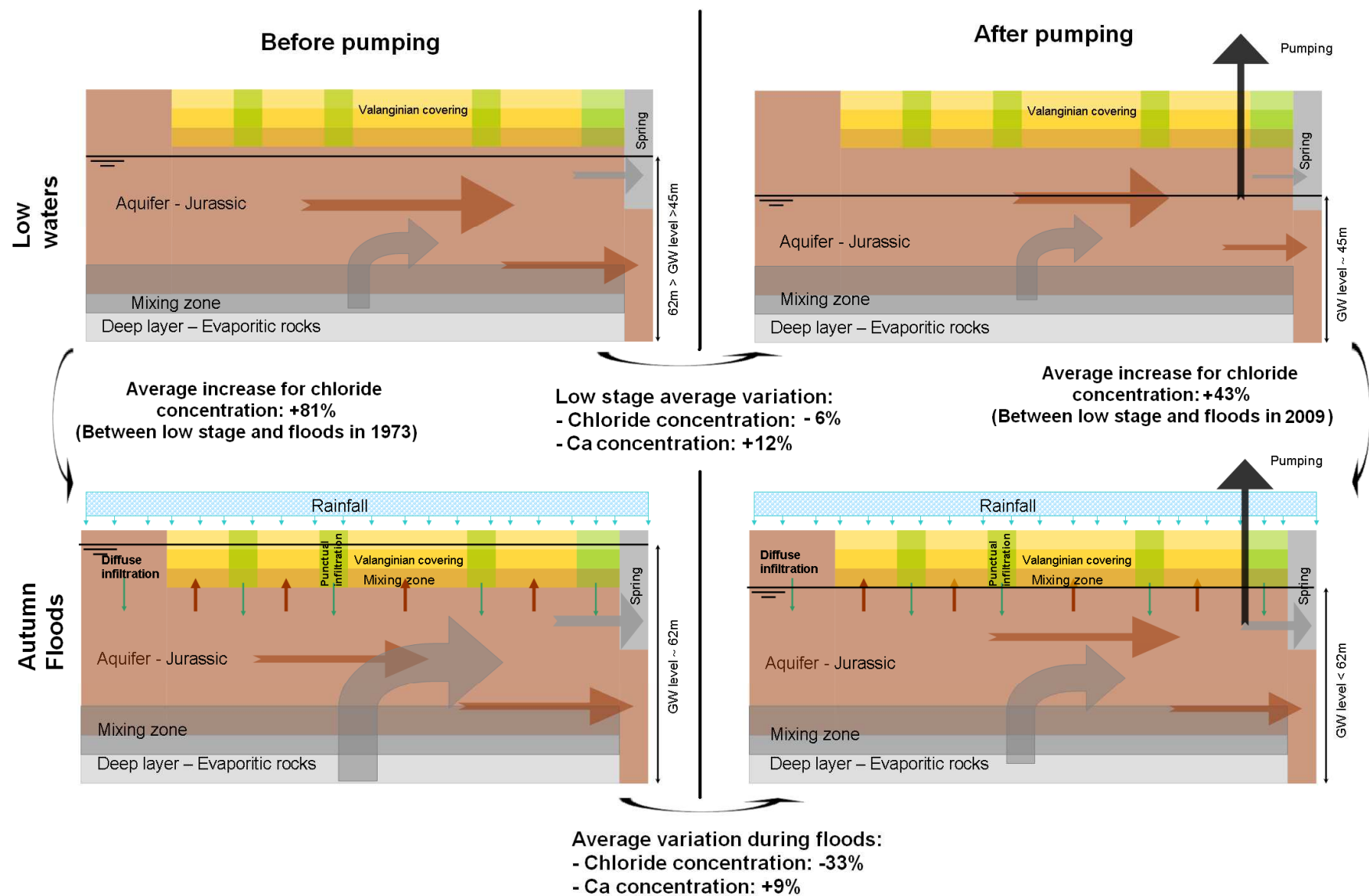


Fig. 33 – Left: Conceptual model of groundwater circulation within the Lez aquifer before pumping. Right: Conceptual model of groundwater circulation within the Lez aquifer after pumping.

5.5 - Conclusion

The distinct chemical characteristics, observed for each water type flowing at the Lez spring, suggest the probable occurrence of multiple origins and different lithologies influence on the groundwater mixing. High and low mineralized groundwaters seem to be respectively related to deep groundwater rising and to surficial infiltration waters. The hydrological conditions induce different proportions of the end-member participation on groundwater mixing of the Lez spring.

Despite differences between analytical methods, it is obvious that a significant chemical evolution of water appears after the beginning of the intense exploitation of the Lez spring. The global decrease of the total hydraulic head within the aquifer, especially in the proximity of the Lez spring, has modified the general groundwater circulation in the aquifer. This consequently changed the groundwater mixing induced by the participation of different compartments to the spring flow.

Apparently, the intense pumping mobilizes water from shallower levels in the aquifer, in flowpaths probably related to shorter residence times, which has a direct influence over the aquifer vulnerability. The current higher global $p\text{CO}_2$ levels observed in the spring waters induce a Ca-HCO_3 mineralization increase, which effectively happened. This could indicate that karstification processes is today more intense than it was before the intense aquifer exploitation has started. This could, in the long term, cause an augmentation of conduits diameter in the carbonate matrix.

The intense pumping has probably led to a decrease of the deep compartment participation to the Lez spring water flow; as a result, Cl concentration has decreased since the exploitation has started. Those results highlight the direct consequences of anthropogenic forcing on the overall functioning of the aquifer.

Conclusion

The Lez karst system has been widely studied over the past 40 years because of its great strategic importance in supplying the Montpellier metropolitan area with water. However, it still remains a little known karst system.

The main objective of this work was to investigate the circulation dynamics and to understand the water transfers in the Lez karst system, by analyzing water chemical and physicochemical variations during the different seasons of a hydrological cycle, along with hydrodynamic responses.

A large monitoring network over the study area combined with regular samplings for major and trace elements and foremost isotopic studies have allowed considerable advances in understanding the Lez karst system functioning.

Hydrodynamics and temporal variability of groundwater chemistry

The first step of this study was to identify the multiple water-types flowing at the Lez spring, defining their chemical composition throughout the hydrological cycle in order to identify their seasonal behaviours under a wide range of hydrological conditions. Observations suggest that the Lez spring flow is composed of different water-types issued from different compartments of the aquifer, e.g.: a surficial compartment (soil and epikarst), a compartment corresponding to the main aquifer (mainly Jurassic limestones) and a deep compartment (marly-limestones and dolomites from Middle Jurassic and possible underground lithologies containing evaporites). According to the hydrological conditions, each compartment contributes in different proportions to the outflow waters of the Lez spring.

The chemical fingerprinting of each water-type correspond to flowpaths, compartment lithologies and mixing proportions. The first end-member corresponds to deep waters, and is characterized by high Sr/Ca, Mg/Ca and Cl/Br ratios, enriched $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and high EC and TDS, with elevated concentrations in Cl, Na, Mg, Li, B and Br elements. The second end-member corresponds to the main aquifer (Jurassic), marked by high-mineralized waters, which concentrations remain inferior to the first end-member. Its mineralization facies is characterized by high calcium-bicarbonate and Cl concentrations. Finally, the third end-member corresponds to the surface infiltration waters, marked by low mineralization, high TOC, NO_3

and bacterial concentrations. The last one participates to the spring outflow especially during recharge events. They infiltrate into the aquifer through the fracture network along the epikarst and through temporary river losses (sinkholes) over marls and marly-limestone layer, in particular along major tectonic faults (*Corconne-Les Matelles* fault network).

Origins of groundwater mineralization

The interpretation of major and trace element concentrations and molar ratios provided evidences that high-mineralized waters are issued from a deep compartment, with longer residence times. These waters have been extensively modified by evaporite dissolution, incongruent dissolution of dolomite and calcite precipitation. Further evidences obtained by $\delta^{13}\text{C}_{\text{TDC}}$, Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ analysis sustain this assumption and help defining the chemical reactions that seem to control water chemistry at the Lez spring.

The most Na-Cl mineralized waters have high Sr/Ca ratios and Sr concentrations. The Sr/Ca ratios increase due to calcite precipitation and indicate an important evolution of water mineralization where incongruent dissolution seems to control deep waters chemistry. Furthermore, the high Sr concentrations observed for high Cl waters indicate that the source of both elements contains more Sr than calcite and dolomite do, which underlines the presence of evaporite dissolution (more enriched with Sr than with calcite and dolomite).

A significant variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios over the Lez system suggests the existence of extra-formational source(s) of Sr, caused by the heterogeneity of the lithologic constitution of the rock matrix as well as by complex water-rock dissolution reactions. The lack of correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ observed for the Lez spring high-mineralized waters suggests the existence of chemical reactions involving addition or removal of Sr from waters. The fact that Cl-rich waters are also more $^{87}\text{Sr}/^{86}\text{Sr}$ radiogenic could be explained by a Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ fingerprinting. However, an enriched $^{87}\text{Sr}/^{86}\text{Sr}$ signature could correspond to either lower Jurassic waters, or recent infiltration waters or again to granite fingerprinted water.

The end-member proportions that participate to the spring flow change along with hydrodynamics. The participation of deep waters seems to be permanent at the Lez spring since even the most diluted waters are highly mineralized. The study of the mixing proportions issued from the multiple aquifer end-members could be the key to understand this complex composition. Hydrograph deconvolutions using multiple tracers were

used to estimate the participation of two or three end-members in the various flood-events that occurred between 2008 and 2010. If we use chloride as tracer, the mean estimated participation of the different water types are, as follows: 12% for deep waters; 5% for recent waters and 83% for main aquifer waters.

Spatial variability of groundwater chemistry and general groundwater flow

A similar water stable isotopes fingerprinting was observed for the various springs that correspond to the outlets of the Lez aquifer catchment: Lez, Lirou, Restinclières and Fleurettes, indicating that they share the same recharge area. However, the great disparity observed in their hydrochemistry indicates that they have distinct water flowpaths within the aquifer. This shows that despite belonging to the same aquifer, those springs' waters are more distinguished by solute masses than by the water isotopic signature. The hydrochemical characteristics of Restinclières and Fleurettes springs seem to be mostly associated to limestones and marly-limestones from Upper Jurassic and Early Cretaceous, i.e. shallower circulations. Furthermore, they have a complete absence of the evaporites fingerprinting that was observed at the Lez spring. Among these springs, the Lirou is an exception since its waters present a singular and very low mineralization characterized by a short residence time and a high participation of rapid infiltration waters. The isotopic content of Lirou waters highlights the significant reactivity of this spring, indicating that Lirou is effectively under a stronger influence of recent rainfalls than the other springs.

A significant signal attenuation was observed for the water stable isotopes of all the karst system springs, excepted for the Lirou spring. Such a dampening in the signal denotes a residence-time at least equal to the period of the input function, i.e. one year. It illustrates the existence of an important storage component favouring an efficient mixing of infiltrated with stocked water.

The water mineralization observed in the Lez karst system wells (Fontanès, Laudou, Bois Roziers and Gour Noir) presents more similarities with Restinclières and Fleurettes springs than with the Lez spring. None of the sampled wells presents GW with chemical characteristics comparable to the Lez spring ones. The GW hydrochemistry of Lauret, Dolgue and Lavabre wells are less similar to Olivier and Boinet wells than to the Lez system (Restinclières, Fleurettes and Lez wells). Olivier and Boinet wells present chemical properties close to Sauve spring, situated in the contact between Cretaceous marls and marly-limestones and Jurassic limestones.

Anthropogenic impacts on hydrodynamics and consequences for groundwater chemistry

The comparison of our dataset with the data obtained during the hydrological cycle of 1974-1974 (Marjolet & Salado, 1976), before the intense exploitation, shows that significant changes in water chemistry occurred after the installation of the pumping plant at the Lez spring. The piston-flow effect associated to the occurrence of recharge events delineates the influence of the water-head increase which controls the flow of high-mineralized waters of deep origin at the Lez spring outflow. The intense exploitation has caused a general decrease of hydraulic heads within the aquifer. Consequently, after the dry season when the aquifer is depleted, the piezometric level reached for a given rainfall event is much lower now than it used to be before the intense exploitation of the aquifer. This has immediate consequences on the flowpaths geometry within the karst aquifer, and thus on the relative contribution of waters of different origins.

Apparently, water circulation nowadays concerns shallower levels in the aquifer and probably flowpaths related to shorter residence times, which could have a direct influence over the aquifer vulnerability. The current higher global $p\text{CO}_2$ levels observed in the spring waters induce a Ca-HCO_3 mineralization increase, and could indicate that karstification processes is today more intense than it was before the intense pumping of the aquifer started. This could, in the long term, cause an augmentation of conduits diameter in the carbonate matrix.

The intense pumping has probably led to a decrease of the deep compartment participation to the Lez spring water flow; as a result, the Cl concentration has decreased since the exploitation has started. Those results highlight the direct consequences of anthropogenic forcing on the overall functioning of the aquifer.

Mediterranean karst systems

The multi-tracers approach combined to hydrodynamics appears as a very efficient tool for characterizing groundwater flows and their origins and seems to be potentially applicable to other similar complex Mediterranean karst systems that were subjected to deep karstification during the Messinian salinity crisis. The features of this crisis seem to play a relevant role on the hydrogeological behaviour of the aquifer and chemical characteristics of waters by the participation of a deep compartment to the outflow of the karst system.

This study has also tested the efficiency of multiple water-rock interaction tracers for characterizing deep end-member water components, and highlights the use of Mg/Ca and Sr/Ca coupled with $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to assess deep end-member water components. The use of TOC and bacteria is relevant for tracing surficial waters and estimating the aquifer vulnerability.

Perspectives

This study presents evidences of water interactions with evaporite layers, which explain the mineralization facies of the Lez spring GW. However, it does not clarify the accurate origin of the deep high-mineralized water. The geological context of the study area allows referring this mineralization facies to Triassic layers or to evaporite “pockets” within limestones and/or dolomites from Early Jurassic layer.

Further multi-isotopic analyses will help building a better knowledge of the water-rock interactions and evaporite mineralization that characterize those waters, such as $\delta^{11}\text{B}$ (Kloppmann *et al.*, 2009; Langman & Ellis, 2010; Millot *et al.*, 2010), $\delta^{37}\text{Cl}$ (Desaulniers *et al.*, 1986; Annable *et al.*, 2007), $\delta^{15}\text{N}$, $\delta^7\text{L}$ and $\delta^{34}\text{S}$ (Einsiedl *et al.*, 2009; Samborska & Halas, 2010) hence providing a more conclusive evidence of chemical element origins (atmospheric, marine, evaporite or anthropogenic). Future investigations should consider some classical isotopic dating like Tritium (^3H) (Einsiedl, 2005; Einsiedl *et al.*, 2009; Long & Putnam, 2009), ^{14}C (Gonfiantini & Zuppi, 2003; Cartwright *et al.*, 2006; Gillon *et al.*, 2009), and other tracers like CFC (chlorofluorocarbons) (Long & Putnam, 2006; Long & Putnam, 2009), recently applied to karst systems for assessing more precisely the groundwater ages and residence times. For those future analyses, it is important that the samples will be mostly collected during the first recharge events of the hydrological cycle. The monitoring of E.C. and T monitoring at the Lez karst system wells should be performed continuously by equipping with CTD divers at least one well of each group identified in Chapter 2 (2.6).

Finally, to define even more precisely the recharge area of the Lez catchment area, it would be necessary to monitor the various wells and springs under multiples hydrological conditions, collecting samples for multiple isotopic analyses. Many of those measures will be carried out during the next months, thanks to the research project entitled: “Management of Mediterranean karst systems of multiple uses”. The Lez, its basin and the recharge area associated to the Lez karst system”. This multidisciplinary research and

management project will bring together several research teams like UMR HydroSciences Montpellier, UMR G-EAU, UMR TETIS, CERFACS, BIOTOPE, BRGM and partners such as Ville de Montpellier, Veolia, Conseil Régional du Languedoc Roussillon, AERM&C and Conseil Général de l'Hérault.

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Annexe 1 - Hydrological functioning of a complex Mediterranean karst system by multivariable tracing.


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37th IAH Congress
Hyderabad, India
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Hydrogeological functioning of a complex Mediterranean karst system by multivariable tracing

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HydroSciences
Montpellier



Introduction

The Lez Karst System (Lez KS) supplies the Montpellier metropolitan area with an average discharge of about 1.700 l/s.

This KS presents a complex structure and functioning, which infers with natural and human factors such as the Mediterranean climate and growing impact of human occupation.

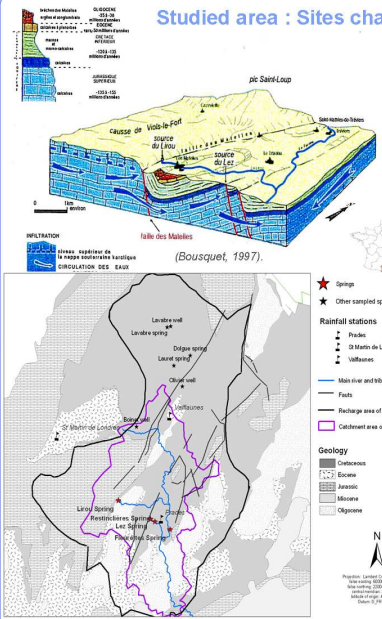
In this study, unlike previous studies on this KS, we used trace elements to characterize GW, which allowed a better understanding of its functioning.

Objectives and Methodology

Objective: Improve the comprehension of GW dynamics and KS vulnerability, as a function of hydrological and seasonal conditions.

Methodology: GW types identification according to hydrological conditions and GW chemical characteristics (major ions and trace elements) using multifactorial analysis.

Studied area : Sites characteristics and monitoring network



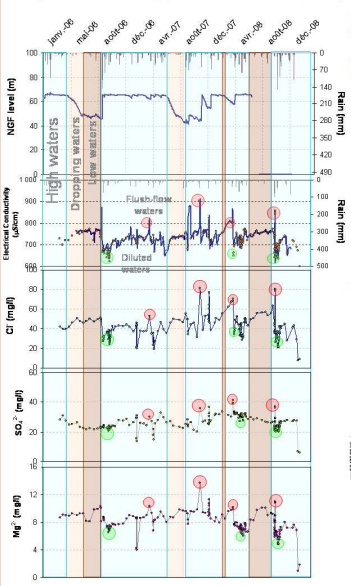
KS top: lower Cretaceous marl and marly limestones

KS: upper Jurassic and lower Cretaceous (Berriasian) massive limestone.

KS bottom: upper Jurassic (Oxfordian) marl and marly limestones.

- ❖ Main outlet of the Karst aquifer : the Lez spring (Vauclusean perennial spring)
- ❖ Hydrogeological catchment area associated to the Lez spring: around 380 km²
- ❖ Recharge area: around 200 km² (a large part of the hydrogeological catchment is impermeable).
- ❖ Seasonal outlets: Lirou, Restinclières and Fleurettes springs
- ❖ Average annual rainfall for the last 20 years: 990 mm
- ❖ Usual sampling period: T=15 days + flood events: Major ions, Traces elements and Total Organic Carbon (TOC)
- ❖ *In situ* monitored parameters : pH, Temperature (T), Electrical Conductivity (EC).

Identification of the different groundwater types at the Lez spring



Daily rainfalls, groundwater levels and (GW level) in the borehole "spring", EC measured in the pumping well by Véolia, time variations of Cl, SO₄ and Mg concentrations.

The samples collected at the Lez spring were previously characterized considering the variations of physical parameters including EC, GW level and rainfall, and chemical parameters including Cl, SO₄ and Mg concentrations.

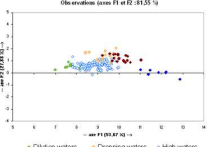
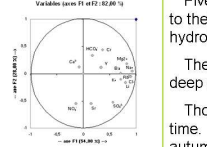
Results and discussion

Main types of GW:

- "high waters": discharging during wet season, associated to a high GW level and EC oscillations.
- "low waters": discharging during dry season, associated to low GW level, stable and high EC.
- "dropping waters": discharging during transition season between wet and dry season, associated to decreasing GW level and increasing EC.

Two other types were identified, discharging only at the beginning of the wet season, during the first autumn floods, which could be related to a piston flow effect, pushing out high-mineralized waters, followed by low-mineralized waters:

- "flush-flow waters": mineralized waters occurring during "high waters" at the beginning of hydrological year. EC > 720 µS/cm.
- "diluted waters": low mineralized waters occurring some days after "flush-flow waters". EC < 600 µS/cm.

Conclusion

Five different types of GW were identified, according to their physical and chemical characteristics, and the hydrological conditions.

These different types of GW are related to distinct deep and shallow karst compartments

Those compartments have distinct GW residence time. It varies from very long during the first flood of autumn to a very short for superficial percolating waters (high TOC and NO₃).

These results highlight the complexity of groundwater flow dynamics within a typical Mediterranean KS.

They also show a high vulnerability to anthropogenic contamination.

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Annexe 2 - Investigation of groundwater dynamics in a Mediterranean karst system by using multiple hydrogeochemical tracers.

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Investigation of Groundwater Dynamics in a Mediterranean Karst System by Using Multiple Hydrogeochemical Tracers

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Abstract The Lez karst aquifer, located in southern France, supplies the Montpellier metropolitan area with potable water and has a maximum exploitation capacity of about 1.700 l/s. The objective of this work is to improve the comprehension of groundwater dynamics in a particular Mediterranean karst system, using hydrogeochemical tracers. We identify the different types of groundwater with similar chemical characteristics (major and trace elements). During rainy season periods, this multitracer characterization shows that deep mineralized waters emerge at the springs just before rapid infiltration waters. This phenomenon shows that hydrodynamic conditions imply water circuits, with participation of specific compartments or creation of short cuts for superficial percolating waters. The data also highlight the vulnerability of the system to natural or anthropogenic contamination. **Key words:** karst, hydrochemistry, natural tracing, hydrodynamics.

1 Introduction

The Lez spring has supplied the metropolitan region of Montpellier (France) with water since the XIXth century. Since 1981, the active pumping has been performed directly from an excavated gallery intersecting the main conduit, 48 m below the Lez spring level, with a maximum pumping rate of 1.700 l/s. This discharge should guarantee water supply throughout the year by drawing upon the water reserves in the aquifer at a larger rate than the natural water discharge during dry seasons.

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This present work aims to better investigate the dynamics of the Lez KS groundwater by monitoring chemical and physical characteristics, and analyzing their variation over the hydrological cycle. The method is based on the analysis of physical parameters and geochemical data, such as major and trace elements, in order to assess the origin of the various water-types that contribute to the flow at the Lez spring.

Multivariate statistical techniques have several advantages such as reduction of data dimension quantities, consideration of different scales of chemical concentration with equal emphasis, and description of groups of variables with common chemical features. Jiang et al. [1] used Principal Component Analysis (PCA) to discriminate between natural and anthropogenic origins of the different factors that affect groundwater quality of the Nandong KS, China. Moore et al [2] also used PCA for evaluating how multiple sources of water and variations in aquifer flow paths affect a spring draining the Eocene portion of the Upper Floridan aquifer.

2 Geological and hydrogeological settings

The Lez spring is one of the main karst springs in France and is located 15 km north of Montpellier (France). The Lez KS discharges also at several seasonal outlets: Lirou, Restinclières, Fleurettes and Gour Noir. The Lez spring is the main perennial outlet of a hydrogeological catchment area of around 380 km², located between the Hérault and Vidourle rivers. As a large part of the hydrogeological catchment is impermeable (Figure 1), most of the recharge occurs where limestones outcrop, which correspond to a surface area of approximately 150km². Lez KS works as a dammed system. The aquifer, composed by Jurassic rocks, is barred by Lower Cretaceous marls and marly-limestones.

3 Monitoring and sampling

Temperature (T), Turbidity, Electrical Conductivity (EC) and groundwater (GW) level are recorded hourly in the observation well of Veolia pumping station. HydroSciences Montpellier (HSM) performs T, EC, and GW level measurements hourly at the Lirou spring and at the Lez spillway. Three raingauges of Météo France (Valflaunès, Saint-Martin-de-Londres, and Prades) were considered.

Samplings were carried out twice a month and daily during floods, since March 2006. Temperature, pH and EC were measured in the field. Total alkalinity was measured within a day, by acid titration with HCl. Chemical and bacteriological analyses were performed at HSM water chemistry laboratory. Major elements (Br⁻, Cl⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, and K⁺) were analyzed by ion chromatography.

Trace elements (Li, B, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Ba, La, Pb and U) were analyzed with Q-ICPMS at AETE technical platform of Montpellier 2 University.

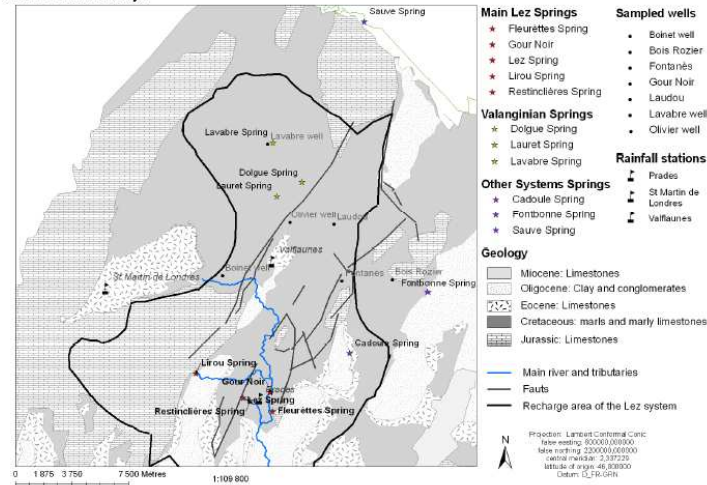


Fig. 1 Hydrogeological map of the Lez karst system, showing the monitoring and sampling network: sampled springs, wells and rainfall stations location.

4 Results and Interpretation

4.1 Characterization of the different types of groundwater at the Lez spring

For a preliminary verification of a multiple GW sources hypothesis, the frequency distribution of EC (CFD) of each water-year from 2005/2006 to 2007/2008 was achieved. CFD represents the sum of the populations of conductivities associated with water-types flowing through a system, assuming that a homogeneous water-type has EC normally distributed. Different modes of CFD in karst springs reflect the movement of chemically distinct water-types through the karst, and the average EC for an individual water-type depends of its origin and residence time [3].

Figure 2 presents the EC frequency distribution for 2007/2008 year with the corresponding Probability Density Function in the same plane, which was decomposed into its normally distributed component populations using a Peak-fitting

software. The observed water-types are in reality a mixture of different end-members that flow together in the aquifer and emerge on the spring.

It was observed that rainier years exhibit more water-types. Apparently, stronger rainfall events provoke the activation of water flow from specific compartments, soliciting the circulation of rare water-types. Consequently, a smaller number of populations were observed for relatively dry years, like the years 2005 to 2007, with three water-types. During the 2007/2008 water-year, which was a rainy year, four water-types were identified (Figure 2).

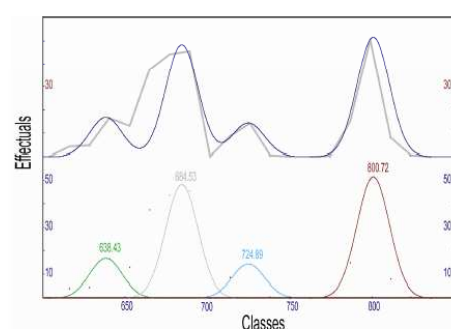


Fig. 2 2007/2008 water year. Top: EC frequency distribution with the corresponding Probability Density Function. Bottom: normally distributed component populations using Peak-fitting software.

4.2 Discriminant factorial analysis – Lez spring

Once CFD showed the existence of distinct water-types composing Lez spring flowing waters, Discriminant Factorial Analysis (DFA) was applied on centred-reduced variables in order to decipher the Lez water-types chemical characteristics, obtaining therefore informations about Lez KS water circulation.

DFA is a multivariate statistical technique that identifies individual groups of samples and tests the membership of each sample in a defined group, as a function of the values for a number of considered variables. It minimizes intra-group variance and maximizes intergroup variance.

The explicative variables used are EC, major ions (Cl^- , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+}), trace elements (Li, B, Rb, Ba and Sr), pCO_2 and calcite SI (Figure 3).

This statistical procedure identified five water-types defined as (1) “*High waters*”, discharging during the rainy season and associated with high GW level and large EC oscillations; (2) “*Low waters*”, discharging during dry seasons and associated with low GW level and stable, high values of EC; (3) “*Dropping waters*”, discharging during transitions between wet and dry seasons, associated with decreasing GW level and increasing EC. Waters with extremely high or low EC

values were discriminated as (4) “*Flush-flow waters*” ($EC > 780 \mu S/cm$) and (5) “*Dilution waters*” ($EC < 600 \mu S/cm$). Both these types discharge at the beginning of the wet season, during the first floods of autumn, when highly mineralized “*Flush-flow*” waters are followed by low-mineralized “*Dilution waters*”.

The DFA shows a good discrimination between the five water-types, despite a partial superposition between “*High waters*” and “*Dropping waters*”. Trace elements allow better characterisation of “*Flush-flow waters*”, whereas pCO_2 and HCO_3^- help to discriminate “*Low waters*”.

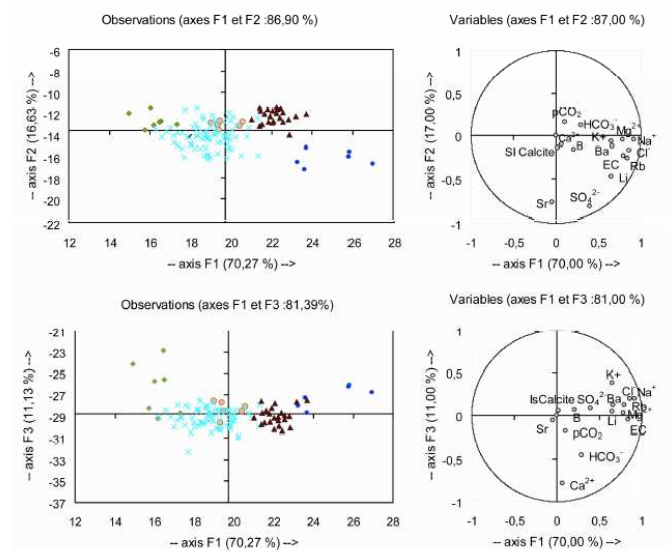


Fig. 3 DFA of the Lez spring data using major and trace elements. Left: sample space; right: variable space.

The F1 axis is positively defined by EC, Cl, Na, Mg, Ba, K, Rb and Li. The F2 axis is positively defined by pCO_2 and negatively by Sr and SO_4 . F1 and F2 together represent 87% of the total variance.

The water types can be chemically characterised as follows:

- “*Flush-flow waters*” are highly mineralized and enriched in Cl, Mg, SO_4 , Na, K, Li, Rb, Sr, Ba.
- “*Dilution waters*” are the less mineralized waters for all analysed elements.
- “*High waters*” are characterized by the typical presence of the same elements observed on “*Flush-flow waters*” but with smaller concentrations. The high data dispersion is agreed with the noticeable temporal variability observed for this water-type.

- “Low waters” are distinguished from “Flush-flow waters” by a less marked mineralization in “Cl-Na” and trace elements. They are characterized by stronger pCO₂.
- “Dropping waters” flow during the transition period between humid and dry season. Their mineralization properties are intermediate between “High waters” and “Low waters”, showing the evolution of the aquifer towards the dry season chemistry.

Conclusion and perspectives

The distinct chemical characteristics, observed for each water type, suggest the probable occurrence of multiple origins and different lithologies influence on the GW mixing. Highly mineralized GW and low mineralized GW seem to be respectively related to deep GW rising and to superficial infiltration waters. The hydrological conditions induce different proportions of the end-members participation on GW mixing that emerge from the Lez spring.

Further investigations would better define the Lez spring GW origins, in order to better constrain mixing phenomena related to the hydrodynamical functioning of the Lez karst system.

Acknowledgments This work was financed by CNPq, National Council of Technological and Scientific Development, of the Science and Technology Ministry of Brazil, HydroSciences Montpellier, IFR ILEE, Météo France, Montpellier city and Veolia.

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Annexe 3 - Groundwater hydrochemistry changes induced at the Lez karst spring as a result of intensive exploitation during 28 years.

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Groundwater hydrochemistry changes induced at the Lez karst spring as a result of intensive exploitation during 28 years

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Abstract The Lez karst aquifer, located in the Mediterranean basin (southern France), supplies the Montpellier metropolitan region with potable water and has a maximum authorized pumping discharge of about 1.700 L/s. The complexity of this system results from the heterogeneity of natural factors such as geological characteristics, spatial distribution of recharge processes, particularities of the Mediterranean climate, and the growing impact of human occupation. The particularity of this karst aquifer lies in the withdrawing of water directly from the main drain, which is located lower than the spring overflow level. The spring has been known to have a permanent water flow in the past; however, the recent increase in the water removal from the aquifer has caused the spring water flow to become only a seasonal phenomenon. Marjolet & Salado (1976) reported the results of studies of the Lez karst aquifer system and proposed a functioning model based on major elements data. In 1981, a pumping plant was installed for the aquifer exploitation. Comparison between the previous and the present data indicates historical changes in the water chemistry. We suggest that the changes for hydrogeochemical characteristics are a consequence of the active exploitation of the karst aquifer by modifying the water circulation dynamics. This study aims to analyse the differences, to understand the water chemistry changes, and to better foresee the aquifer evolution for the future.

Key words karstic aquifer; natural tracing; hydrochemistry; water transit

INTRODUCTION

The Lez karst aquifer, located in the Mediterranean basin (southern France), has supplied the Montpellier metropolitan region with potable water since 1982, with a maximum authorized pumping discharge of about 1.700 L/s. The particularity of this karst aquifer lies in the “active management” of the water resource, when pumping is performed in a well that intercepts the karstic conduit, saturated in water, below the spring level. Pumping is able to solicit water reserves that are not solicited on natural flow conditions, attaining water discharges that are higher than the natural discharge of the spring.

Marjolet & Salado (1976) reported the results obtained from a hydrochemical monitoring achieved in 1973 and 1974 at the Lez spring, before the active pumping starts, and proposed a functioning model.

Lez spring has been regularly monitored since 2006 by the Laboratory HydroSciences Montpellier, measuring chemical and physico-chemical parameters. From this survey, chemical data interpretations allowed a significant progress for the comprehension of water circulation in the Lez aquifer, and a new hydrodynamic conceptual model was proposed for this aquifer (Bicalho et al., submitted; Bicalho et al., 2009).

The present paper analyses and discusses the changes induced in the chemical composition of water as a result of intensive exploitation during 28 years, comparing with data of 37 years before. The chemistry of karst springs is normally related to physical characteristics and helps to distinguish different types of hydrodynamical behaviour of the drained karstic systems (López-Chicano *et al.*, 2001). Hydrodynamical characteristics like recharge, thickness of infiltration zone, aquifer geometry and its fissured structure can deeply infer on the groundwater transit time and water-rock interaction and influence hydrogeochemical behaviour of springs draining a karst (López-Chicano *et al.*, 2001).

The Lez aquifer unifies many advantages that favour the advance of karst hydrogeology science, like a large monitoring network and an important historical dataset. Few works are reported in the literature relating this comparison. Rosenthal (1988) investigated the hydrochemical changes induced by two decades of intense exploitation of groundwater in a multiple aquifer system in Israel, provoking the ascension of brines and the salinization of waters (Rosenthal, 1988).

MATERIALS AND METHODS

Geological and hydrogeological settings

The Lez spring is one of the main karst springs in France and is located 15 km north of Montpellier (France). The Lez KS discharges also at several seasonal outlets: Lirou, Restinclières, Fleurettes and Gour Noir. The Lez spring is the main perennial outlet of this KS. The aquifer, composed of Jurassic rocks, is barred by impermeable marls and marly-limestones of Lower Cretaceous. Accordingly, the Lez KS is referred to as a dammed system.

The hydrogeological catchment associated with the Lez spring has an area of about 380 km² (Thierry and Bérard, 1983), and is located between the Hérault and Vidourle river valleys. As a large part of the hydrogeological catchment is impermeable, the Lez spring recharge area is only around 150 km² (Marjolet and Salado, 1976) (Fig. 1).

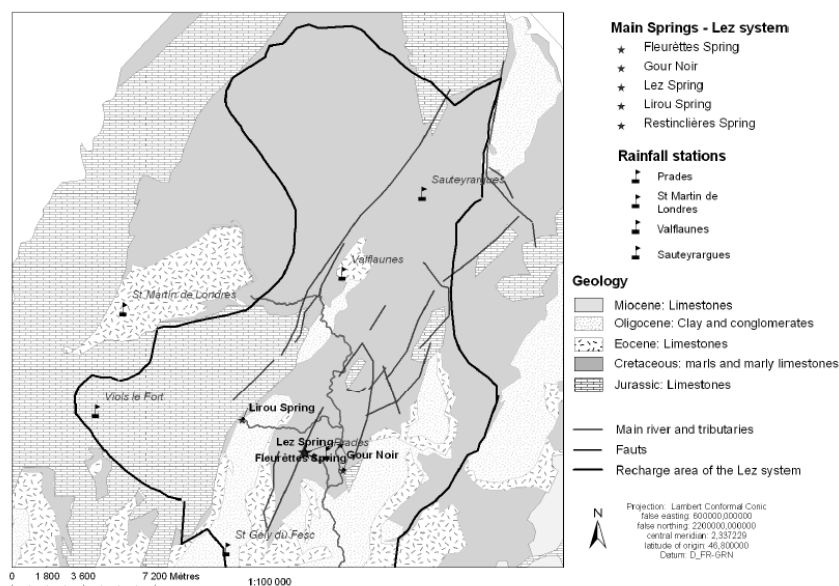


Fig. 1 Hydrogeological map of the Lez karst system, showing sampled springs, wells and rainfall stations location.

The regional geology is strongly related to the history of the Mediterranean Sea and the Pyrenees. The major tectonic events that influenced the Lez aquifer were: the Hercynian/Variscan orogeny, the Pyrenees formation, and the opening of the “Golfe du Lion” (Bousquet, 1997).

The average annual rainfall calculated over the last 40 years at Valflaunès raingauge was 942 mm. During this period, 1989 was the driest year with 474 mm, and 1972 was the most humid

with 1620 mm. Figure 2 presents the percentage of deviation to the average annual rainfall calculated from 1970 to 2008 at Valflaunès rain gauge. In 2008, the cumulated rainfall was 1244 mm, which indicates a humid year occurring after quite a long period of rain deficit that started in 2004. The average distribution of the precipitations over time is the following: 37% during autumn; 27% during winter, 22% during spring and 13% during summer. The first floods of the hydrological year normally start between September and October.

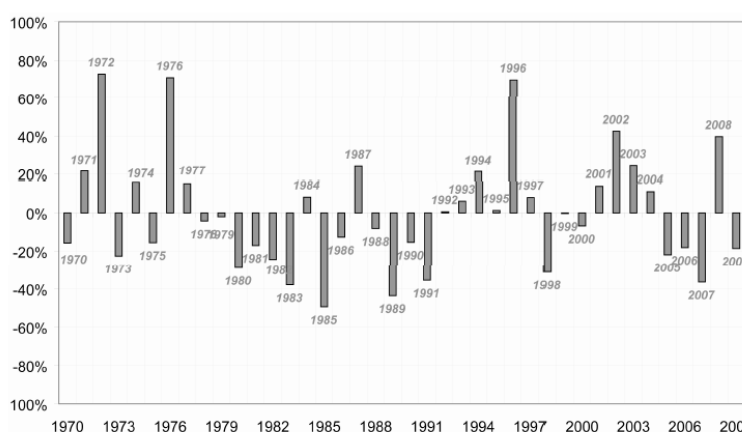


Fig. 2 Percentage deviation to mean annual rainfall calculated from 1970 to 2008 for Valflaunès rain gauge.

MONITORING AND SAMPLING

From March 2006 to November 2009, samplings were carried out twice a month and daily during floods. Temperature (T), Turbidity, Electrical Conductivity (EC $T_{ref} = 25^{\circ}\text{C}$) and GW level were measured with an hourly time step in the observation well of Veolia pumping station. HydroSciences Montpellier (HSM) performed T, EC, and GW level measurements with an hourly time step at the Lirou spring and at the Lez spring (spillway). Three rain gauges stations of Météo France (Valflaunès, Saint-Martin-de-Londres, and Prades) were considered (Fig. 1). T, pH and EC were measured in the field. Total alkalinity was measured within a day, by acid titration with HCL 0.05N. Major elements were analysed by ionic chromatography at HSM laboratory.

Marjolet & Salado (1976) achieved, from March 1973 to May 1974, samplings on the Lez spring with a 5–10 days interval during low stage and daily samplings during floods. T was measured in the field, pH and EC were measured in the laboratory. The chemical analyses were performed at the Service of Water Analysis of CERGA (*Centre d'Etudes et de Recherches sur la Géologie et ses Applications*). Ca^{2+} and Mg^{2+} were measured by complexometry with EDTA ($\pm 1\%$). Total alkalinity was measured by acid titration with H_2SO_4 , N/10, ($\pm 1\%$). Sulphates were measured by nephelometry after addition of BaCl_2 , (± 3 to 5%). Na^+ and K^+ were measured by flame photometry, (Na: ± 1 to 2%; K: 10%). Cl was measured by the Mohr method, by addition of AgNO_3 , (± 1 to 2%).

RESULTS AND INTERPRETATION

Lez typical autumn floods: 1973, 2008 and 2009

The first comparison of chemical characteristics on Lez spring after 37 years is focused on the autumn floods. Those floods, occurring at the beginning of the rainy season, were recurrently

observed each year, varying only in intensity (EC values and element concentrations peaks). The initial EC increase is due to rain input, loading the system with a concomitant compression of the aquifer. The rain loading causes a transient pressure pulse to travel the system resulting in the discharge spike on the spring (Desmarais and Rojstaczer, 2002). Indeed, intense rainfall recharge causes the motion of more mineralized waters, issued from deeper layers of the aquifer (saturated zone), towards the spring, due to piston flow effect. The occurrence of a diffuse flow on the aquifer is more reasonable for explaining piston flow, considering that water that flows to the spring is a mixing, with different proportions, of relatively old and renewed waters. This phenomenon is sporadic and happens only during extreme hydrological situations and has been observed in some karst systems (Desmarais and Rojstaczer, 2002; Emblanch, 1999; López-Chicano et al., 2001).

Figure 3 presents three autumn flood events that happened on the years 1973, 2008 and 2009. The cumulated rainfalls that triggered those floods were respectively: 86 mm in 1973, 200 mm in 2008 and 150 mm in 2009. Ca, Mg, Na, K, Cl and SO_4 concentrations for each flood are also presented. Cl maxima were respectively: 112 mg/L in 1973, 80 mg/L in 2008 and 98 mg/L in 2009.

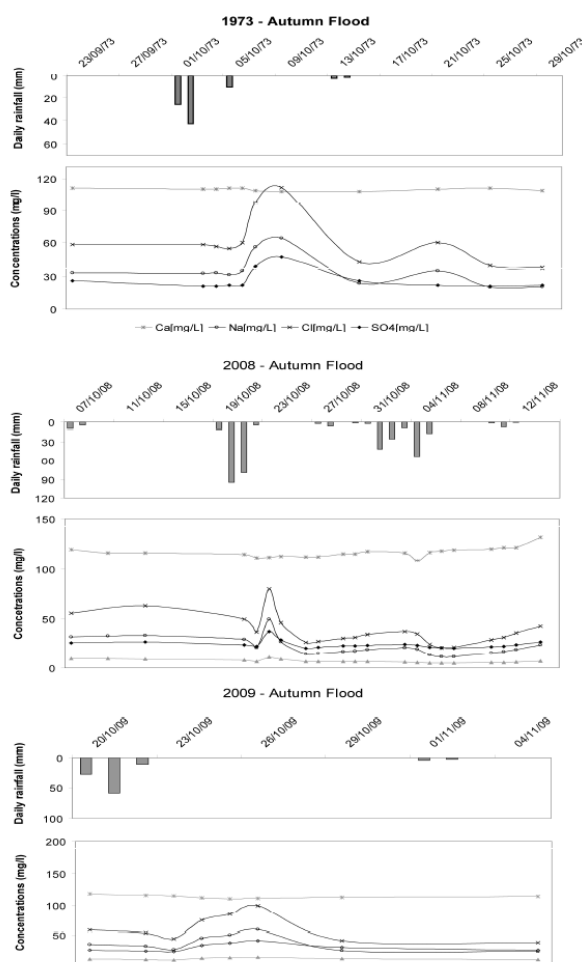


Fig. 3 Time variation of Ca, Mg, Na, K, Cl and SO_4 concentration during autumn flood events occurred in 1973, 2008 and 2009.

CHEMICAL CHANGING DESCRIPTION BY DISCRIMINANT FACTORIAL ANALYSIS

In order to search for variation evidence during other hydrological periods of the spring discharge, the time variations during floods were analysed for several parameters during the hydrological cycles of 1973–1974, 2006–2007, 2007–2008 and 2008–2009, from March to March. Those parameters were analysed by means of a Discriminant Factorial Analysis (DFA). Two distinct DFA were carried out, both of them considering EC, $p\text{CO}_2$ and concentrations in Cl^- , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+} as explicative variables. The dependant variable for the first DFA was the different hydrological cycles. DFA is a multivariate statistical technique that identifies individual groups of samples and tests the membership of each sample to a defined group, as a function of the values for a number of considered variables. It minimizes intra-group variance and maximizes intergroup variance (Dagnelie, 1975; Saporta, 1990). The reduced dimension achieved by such a statistical technique permitted attaining a simplified multi-criteria representation, highlighting the main trends for the datasets.

In Fig. 4, the observation plots on axes F1 and F2, which represent 97.53% of the total variability, individualizes the water year 1973–1974 from the other years.

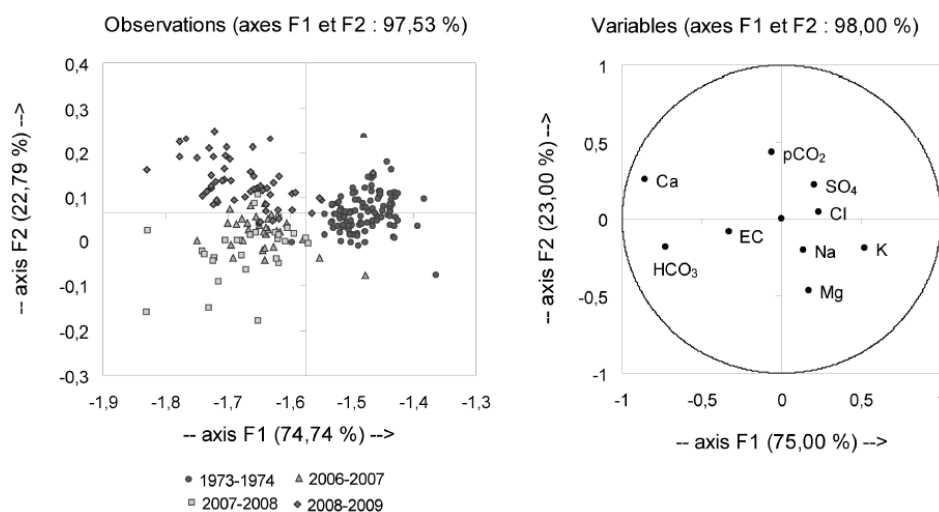


Fig. 4 DFA for the Lez spring data for the years: 1973–1974, 2006–2007, 2007–2008 and 2008–2009. Left: sample space; right: variable space.

The positive direction of F1 axis represents the mineralization with K, Na, Cl; that characterizes 1973–1974 waters. The negative direction of the F1 axis represents mineralization with HCO_3^- , Ca which is the predominant mineralization for waters of 2006–2007, 2007–2008 and 2008–2009. F2 axis is characterized by an opposition between $p\text{CO}_2$ and Mg concentrations.

The second DFA, presented in Fig. 5, additionally considers the water-types identification for current Lez waters reported in Bicalho *et al.*, (2009). The same procedure for water-type identification, based on hydrological conditions, water level and water chemical attributes, was applied to the Lez waters of 1973–1974. Consequently, the “water-year-type” was presently considered like the dependent variable for the calculation of the additional DFA. The global observed difference is that the whole system seems to have moved on the observations space toward a new geochemical condition, less influenced by Na-Cl signature and more influenced by a Ca- HCO_3^- signature. The most mineralized waters, before and after active pumping, are still *flush-*

flow waters, which flow during autumn floods. But, this water-type has lower contents in Cl, Na, Mg, K and SO₄ for “after pumping” conditions.

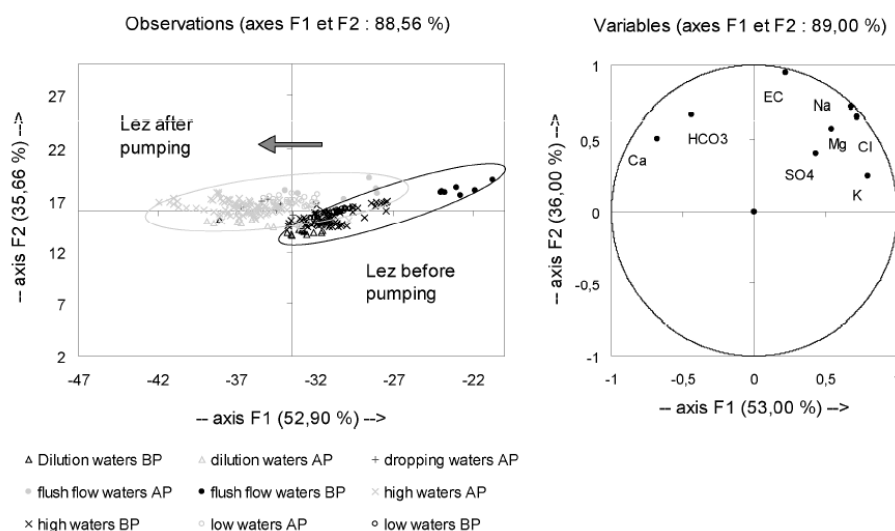


Fig. 5 DFA for the Lez spring data: Low water Before Pumping (BP), Flush flow water BP, Dilution waters BP, High waters BP, Low waters (2008), Flush flow waters, Dilution waters, Dropping waters and High waters. Left: sample space; right: variable space.

CONCEPTUAL MODEL OF POSSIBLE HYDRODYNAMICAL CHANGING BEFORE AND AFTER PUMPING

Based on the information already known about this aquifer, the objective is to identify possible evolutions on the aquifer hydrodynamics that should have occurred before and after active pumping, considering the main chemical changes occurred for the two situations. Bicalho *et al.* (submitted) presented a preliminary conceptual model for the description of the Lez aquifer behaviour during specific hydrological periods, like first floods of autumn, transition and dry season. Those behaviours are more or less representative of the spring flow depending on the mixing of various waters issued from different origins in the aquifer, e.g. surface, shallow compartments, deep layers and the main aquifer (Jurassic). The hydrological conditions will determine the different proportions of those compartments participation on the mixing that composes Lez spring waters.

In Fig. 6, this conceptual model is presented, containing the hypothetical hydrodynamical differences that characterized the system on both years: 1973 and 2009. Average perceptual variations were calculated between average values for Ca and Cl concentrations for low stage waters and high mineralized waters (flush flow waters) for both datasets, before and after pumping (1973 and 2009). Average perceptual variations were calculated between average values for Ca and Cl concentrations for low stage waters and high mineralized waters (flush flow waters) for both datasets, before and after pumping.

Intense exploitation generated a new hydrodynamical equilibrium which induced a new water chemical composition for the aquifer, by changing the proportions of those compartments participation on the spring waters mixing, depending on hydrological conditions. One of those observed changes is related to the Na-Cl mineralization that was higher before pumping begins.

Bicalho *et al.* (submitted) provided evidence that the Na-Cl mineralization identified at the Lez spring is probably associated with the participation of deep GW issued from the deeper part of

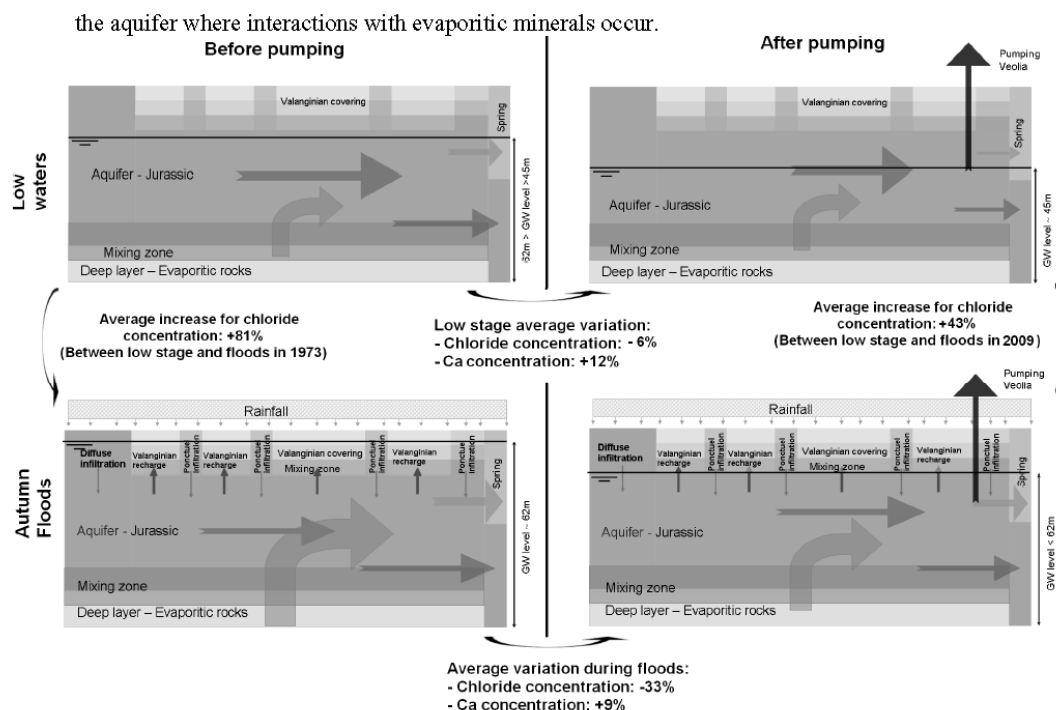


Fig. 6 Left: Conceptual model water circulation on Lez aquifer before pumping. Right: Conceptual model water circulation on Lez aquifer after pumping.

The participation of the waters from this deep compartment on the Lez spring flow seems to be related to the occurrence of strong hydraulic charges during heavy autumn rainfall inputs. The intense exploitation causes a general decrease on hydraulic charges within the aquifer. Consequently the aquifer no longer reaches the piezometric charge that it used to reach for comparable rainfall inputs. Indeed, pumping naturally led to the decrease of deep compartment participation on the Lez spring water flow.

The average chloride concentration decrease for this hydrological period is about 33% between 1973 and 2009. During the low stage season, Cl concentration differences between both scenarios were less pronounced. However, higher concentrations for Ca and HCO_3 showed that the participation of those waters increased after the exploitation has started. Ca- HCO_3 waters typically originated from the upper parts of the Jurassic aquifer and/or Berriasian and Valanginian layers (Bicalho et al., submitted; Marjolet and Salado, 1976). The increased participation of shallow aquifer waters on the spring flow was predicted by Marjolet & Salado (1976).

The waters from 2006 to 2009 presented higher pCO_2 than in 1973–1974. Under-saturated waters are observed when recharge is intense and a very rapid draining of recently infiltrated waters happens (López-Chicano *et al.*, 2001). This could indicate that water circulation at the Lez spring “after-pumping” occurs more preferentially in shallower compartments than “before-pumping”, involving the decrease of the water residence time in the aquifer.

CONCLUSION

Despite analytical methods differences, a significant water chemical evolution appears after the

installation of water exploitation of the Lez spring. The global decrease of the total load on the aquifer should have modified the Lez aquifer water circulation. This consequently changed the water proportion mixing induced by the participation of different compartments to the spring flow.

Apparently, water circulation nowadays attains shallower levels in the aquifer and probably in circuits of shorter residence times. The active pumping probably lead to a decrease of deep compartment participation on the Lez spring water flow and consequently the Cl concentration decreased since exploitation has started. The higher global pCO₂ levels presently reached in the aquifer induce a total mineralization increase, especially of Ca-HCO₃ type, and could indicate that karstification is today stronger than before pumping started. This could, in the long term, induce an augmentation of drains thickness in the carbonate matrix. Nevertheless, the active pumping did not provoke salinity increase in the Lez spring waters.

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Abstract

The Lez karst spring, located in the Mediterranean basin (southern France), supplies with water the metropolitan area of Montpellier (France) since the 19th century. Since 1981, an intense pumping is being performed directly in the main conduit with a maximum exploitation flow rate of about 1,700 l/s. To improve the understanding of groundwater origins and circulation dynamics in this karst system, as well as the impact of three decades of intense water exploitation, groundwater samples have been collected during various hydrologic conditions since March 2006. The springs and wells of the Lez karst system as well as surrounding springs and wells have been monitored for: physicochemical parameters, major and trace elements, Total Organic Carbon (TOC), faecal and total coliforms, ^{18}O , ^2H , $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$.

During the first recharge events of autumn, high-mineralized waters have been observed at the Lez spring. This singular behaviour was monitored in a fine time-lag. A multivariate statistical analysis revealed the existence of different water-types discharging at the Lez spring. A coupled approach integrating geochemistry and isotopes were applied and provided insight into the different end-members, associated lithologies and the main reactions that control groundwater chemistry. Between the five distinguished water-types, the two more contrasting ones are emphasized: the first one correspond to more geochemically evolved, long residence-time waters, issued from deep layers where evaporite fingerprinting was identified. They are characterized by high mineralization and high concentrations in Cl, Na, Mg, Li, B and Br elements, high Sr/Ca, Mg/Ca and Cl/Br ratios and enriched $\delta^{13}\text{C}_{\text{TDC}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Between all the studied springs and wells, this chemical fingerprinting has been uniquely observed for the Lez spring groundwaters. The second water-type corresponds to low mineralized waters with high concentrations in NO_3 , bacteria and TOC, and represents the flux of rapid infiltration waters. They underline the vulnerability of the system to surface infiltration and anthropogenic contamination through the infiltration of waters by sinkholes and well-developed fracture networks. Hydrograph deconvolutions using multiple tracers were used to estimate the participation of two or three end-members in the various flood-events that occurred between 2008 and 2010. If we use chloride as tracer, the mean estimated participation of the different water types are, as follows: 12% for deep waters; 5% for recent waters and 83% for main aquifer waters.

The comparison between present and former studies carried out before the installation of the pumping plant (1973-1974 dataset), indicates historical changes in water hydrogeochemistry, evidencing a decrease of the deep compartment participation to the outflow of the Lez spring. This change in water hydrogeochemistry may be attributed to the intense pumping of the karst system and, in the absence of noticeable climatic changes, traduces the direct consequences of anthropogenic forcing on the overall functioning of the aquifer.

The multi-tracers approach combined to hydrodynamics appears as a very efficient tool for characterizing groundwater flows and their origins and seems to be potentially applicable to other similar complex Mediterranean karst systems that were subjected to deep karstification during the Messinian crisis. The features of this crisis seem to play a relevant role on the hydrogeological behaviour of the aquifer and chemical characteristics of waters by the participation of a deep compartment to the outflow of the karst system.

Key words: hydrogeology, karst, hydrochemistry, hydrodynamics, natural tracing, isotopes.

Résumé

La source karstique du Lez, localisée dans le bassin Méditerranéen (sud-est de la France), fournit de l'eau potable pour la ville de Montpellier et son agglomération depuis le XIX^e siècle. Depuis 1981, un pompage intensif est effectué directement dans le conduit principal au moyen d'une station souterraine de pompage, avec un débit maximal autorisé de 1,700 l/s. Afin de mieux caractériser la dynamique et l'origine des eaux souterraines, mais également d'évaluer l'impact de trois décennies d'un pompage intensif de l'aquifère, des prélèvements ont été réalisés dans différentes conditions hydrologiques depuis mars 2006. La source du Lez ainsi que d'autres sources et forages appartenant à ce système et aux systèmes karstiques voisins ont été régulièrement échantillonnées pour le suivi en continu des paramètres physico-chimiques, des éléments majeurs et en trace, du Carbone Organique Total (COT), des coliformes fécaux et totaux ainsi que des $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}_{\text{TDC}}$ et $^{87}\text{Sr}/^{86}\text{Sr}$.

Au moment des crues de reprise qui surviennent après l'étiage, des eaux fortement minéralisées sont identifiées à la source du Lez. Ce comportement singulier a été étudié à un pas de temps fin. L'utilisation d'analyses statistiques multivariées a permis de caractériser les différents types d'eau s'écoulant à la source du Lez. Une approche couplée intégrant les données hydrochimiques et isotopiques a permis de définir les différents types d'eau et les lithologies associées, ainsi que les principales réactions qui contrôlent la chimie des eaux souterraines. Parmi les cinq types d'eau identifiés, deux correspondant à des pôles géochimiques très contrastés, et sont à mentionner : le premier pôle correspond à des eaux géochimiquement plus évoluées, caractérisées par une forte minéralisation, un enrichissement marqué en Cl, Na, Mg, Li, B et Br, des rapports Sr/Ca, Mg/Ca et Cl/Br élevés ainsi que des valeurs en $\delta^{13}\text{C}_{\text{TDC}}$ et $^{87}\text{Sr}/^{86}\text{Sr}$ enrichies. Ces eaux, qui correspondent à une signature évaporitique, sont vraisemblablement issues d'un réservoir profond, et associées à un temps moyen de résidence important. Parmi toutes les sources et forages étudiés, cette signature chimique a été uniquement observée pour les eaux de la source du Lez.

Le second pôle correspond à des eaux faiblement minéralisées, contenant de fortes concentrations en NO_3 , bactéries et COT, représentant le flux d'infiltration rapide. Elles soulignent la vulnérabilité du système à l'infiltration rapide et à la contamination anthropique via des systèmes de pertes et de réseaux de fractures bien développé. Des déconvolutions d'hydrogramme à l'aide de multiples traceurs ont été réalisées pour estimer les proportions de participation des deux ou trois pôles d'eau précédemment définis dans les multiples événements de crue survenus entre 2008 et 2010. En considérant les chlorures comme traceur, la participation moyenne des différents types d'eau à l'écoulement à la source est la suivante : 12% pour les eaux profondes, 5% pour les eaux nouvellement infiltrées et 83% pour les eaux de l'aquifère principal.

La comparaison entre les données obtenues dans cette étude et les données obtenues avant l'installation de la station souterraine de pompage (données de 1973-1974) montre des changements notables dans la composition chimique des eaux de la source du Lez, en indiquant une diminution de la proportion de participation du réservoir profond aux écoulements à cette source. Cette modification de la composition chimique des eaux peut être attribuée au pompage intensif du système karstique et, en l'absence de changement climatique perceptible, traduit les conséquences directes de ce forçage anthropique sur le fonctionnement général de l'aquifère.

L'approche multi-traceurs combinée à l'hydrodynamique apparaît comme un outil très efficace pour caractériser les écoulements souterrains et leurs origines, et semble être potentiellement applicable à d'autres systèmes karstiques complexes similaires comprenant des compartiments profonds qui contribuent à l'écoulement de la source, notamment sur le pourtour méditerranéen où la crise messinienne a permis la mise en place d'une karstification profonde.

Mots clefs : hydrogéologie, karst, hydrochimie, hydrodynamique, traçage naturel, isotopes.
