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Radium isotopes, radon and ^{210}Pb in karstic waters: Example of the Lez system (South of France)

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ABSTRACT

We present in this study the first data on Ra isotopes, ^{222}Rn, and ^{210}Pb in waters from the Lez karst system, one of the main ground-water resources in the South of France. The low Ra isotope activities of the Lez system waters (from 0.35 to 3.45 mBq/L of ^{226}Ra) were measured by gamma spectrometry using the method developed in our previous work. Our data reveal the coherent behavior of ^{226}Ra in Lez spring waters, well correlated to other major and trace elements, like Cl, Na, K, Mg, Li, Rb and Ba. The (^{228}Ra/^{226}Ra) ratios are distinct between the Lez spring (0.60 to 0.72) and two neighboring springs (0.52 to 0.65), showing the spatial variability in karst systems. In spite of their small variations in the Lez spring, it was possible to trace different water components and mixing processes from Lower-Cretaceous, Upper-Jurassic and Middle Jurassic end-members, in agreement with previous studies based on major and trace elements. Data obtained on waters derived from the Upper-Jurassic karst reveal that their (^{228}Ra/^{226}Ra) ratios are not related to the Th/U ratio of the Jurassic limestone, but are rather influenced by the soil and alterite cover of the recharge area.

^{222}Rn activities in the Lez spring are relatively low (0.5 to 3.7 Bq/L) compared to other karst regions. The highest ^{222}Rn activities are found in diluted waters following heavy rainfall episodes, suggesting a subsurface origin of Rn. Soil and alterite samples that have much higher ^{226}Ra activities (from 51 to 130 Bq/kg), compared to those from the main aquifer rocks (from 2.9 to 16 Bq/kg), are probably the main source of Rn, rather than the rocks of the karst itself. The study of several flood episodes reveals the correlation between Rn peak-values or total activity discharged at the spring with cumulative rainfall. Finally, ^{222}Rn dissolved in water decays to ^{210}Pb, and our data show that constraints on transfer times of underground waters can potentially be obtained from their coupled measurement.

1. Introduction

The use of radium isotopes (^{226}Ra, ^{228}Ra, ^{224}Ra and ^{223}Ra) and radon (^{222}Rn) in water as tracers of geochemical and hydrological processes is well known. Their behavior in aquatic systems and most applications have been reviewed in recent publications (Porcelli, 2011; Porcelli and Swarzenski, 2003). For example, the long-lived Ra isotopes, ^{226}Ra (^{238}U-series, $t_{1/2}$ = 1600 y) and ^{228}Ra (^{232}Th-series, $t_{1/2}$ = 5.75 y), can give useful information on the water origin, mixing proportions of water masses, and rock/sediment interactions. These processes have been studied in thermal waters (e.g. Sturchio et al., 1993), as well as in fresh groundwaters with contrasted ^{226}Ra activities or/and (^{228}Ra/^{226}Ra) isotopic ratios (e.g. Vinson et al., 2012). Meanwhile, the short-lived Ra isotopes, ^{224}Ra (Th-series, $t_{1/2}$ = 3.6 d) and ^{223}Ra (^{235}U–series, $t_{1/2}$ = 11.43 d), as well as ^{222}Rn (^{238}U–series, $t_{1/2}$ = 3.82 d), are more related to dynamic processes like water residence or transfer times, even though they are also largely applied in rock/sediment-water interaction studies. One of the main applications of Ra isotopes and Rn concerns their use as tracers of submarine groundwater discharge (SGD) and related processes in coastal environments (e.g. Rama and Moore, 1996; Rodellas et al., 2017). Additionally, the solubility and mobility of radon in water, and the contrasted activities between surface- and ground-waters, make radon a suitable tracer for studies related to groundwater flow paths and ground- and surface-water interactions (e.g. Hoehn and Von Gunten, 1989; Khadka et al., 2017).

However, the behavior of Ra isotopes in continental carbonate aquifers and in karst systems has been less studied (Guerrero et al., 2016). This is partly due to the much lower Ra activities compared to those of thermal waters, brines, and even other groundwaters

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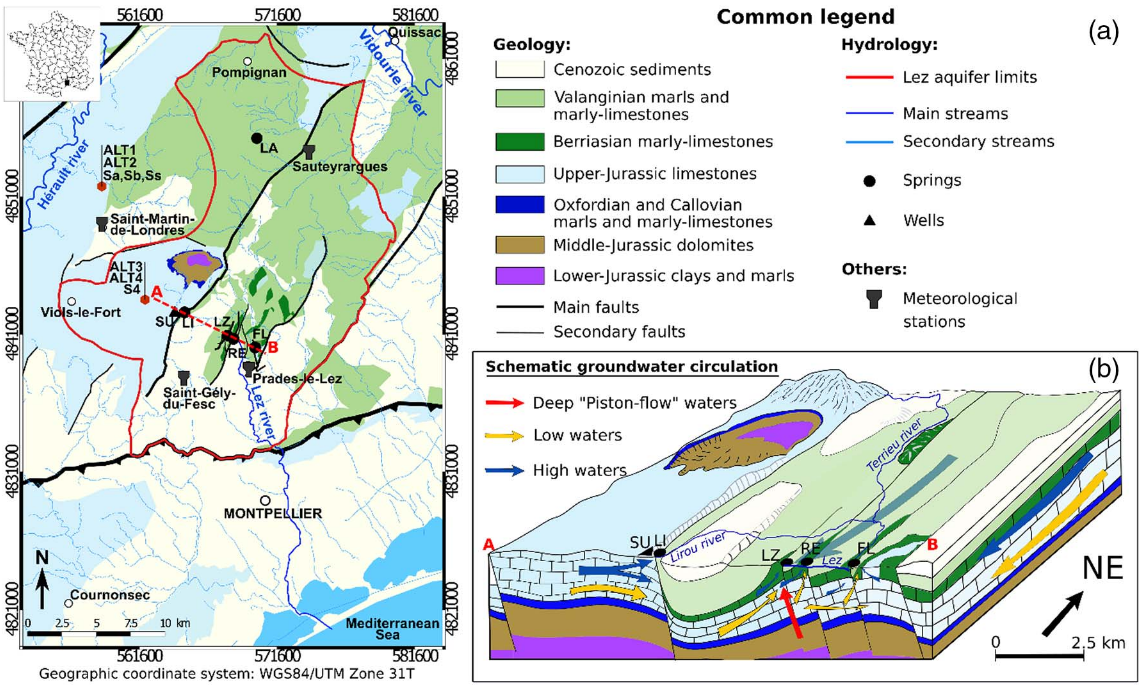

Fig. 1. (a) Simplified geological map and sampling point localities; (b) schematic groundwater circulation block diagram of the Lez aquifer. The front face of the block diagram in (b) corresponds to the AB-cross section in (a). Geological information taken from the BRGM digital geological maps of Montpellier and Saint Martin de Londres at 1/50000 scale (BRGM, 2017). Aquifer limits from Maréchal et al. (2013). Groundwater circulation block diagram modified from Paloc (1979).

interacting with rocks having higher U and Th contents than limestone (Vinson et al., 2012). There are also relatively few studies of Rn in karst systems, although its potential to infer the hydrodynamics in karst has been demonstrated by the pioneering works of Surbeck and Medici (1991), Monnin et al. (1994), Pane (1995), Eisenlohr and Surbeck (1995), and more recently by Savoy and Surbeck (2003); Savoy et al. (2011).

The aim of the present work was to test the possible use of Ra isotopes and Rn as geochemical and hydrodynamic tracers, applied in the well-known Lez karst system (South of France), that has been continuously monitored for several decades. We have also analyzed U-series in representative samples of rocks, karst-filling alterites and soils of the Lez watershed.

2. Geological and hydrogeological context

The Lez karst system or Lez aquifer (Fig. 1) is located 15 km north of the city of Montpellier (Hérault, France). With a watershed surface of 380 km^2 (Thiéry and Bérard, 1983), it consists of one main perennial outlet, the Lez spring, and several seasonal springs like Lirou, Restinclières, Fleurette and Lauret (Fig. 1a). This karstic system has developed in the 650 to 1100 m-thick massive limestones and marly-limestones of the Argovian and Kimmeridgian (Upper-Jurassic), and of the Berriasian (Lower-Cretaceous) (Marjolet and Salado, 1978). The lower boundary of this aquifer corresponds to the marls and marly-limestones of the Oxfordian and Callovian strata (base of the Upper-Jurassic), while the upper boundary is composed of the impermeable marls and marly-limestones of the Valanginian (Lower-Cretaceous), making this aquifer a partly confined system (Leonardi et al., 2013). At the surface, the impermeable layers of the Valanginian and Tertiary formations (Fig. 1a), cover about 280 km^2 of the watershed. The other 100 km^2 are composed of outcrops of Upper-Jurassic and Berriasian limestones and marly-limestones, respectively, corresponding to the main diffuse recharge zone (Maréchal et al., 2013). Additionally, some direct infiltration occurs through sinkholes, fractures and along the faults, giving a total recharge area of about 130 km^2 (Fleury et al., 2009).

The Lez spring and the other seasonal springs of this karstic system are located on normal faults striking NE-SW (Fig. 1a), where the karstified Berriasian limestones come in contact with the impermeable Valanginian marls acting as dams (Fig. 1b), thus forcing the water to rise up to the surface (Fleury et al., 2009). However, it seems that the Lez spring is also an overflow of a deeper regional system (Bonnet and Paloc, 1969), created during the Messinian salinity crisis (Audra et al., 2004; Clauzon, 1982).

The karstic spring of Lez is a Vauclusian-type spring that discharges at 65 m a.s.l., through a main conduit of 10 m^2 section. This perennial spring has an annual average groundwater discharge of 1.2 m^3/s (and up to 16 m^3/s during heavy rainfall events), making it one of the main karstic springs of the South of France and giving birth to the 28 km-long Lez River (Fig. 1). It is also the main source of water supply for human consumption of the city of Montpellier, and is under "active management" since 1982 (Avias, 1995), with average pumping rates of 1.0 ± 0.2 m^3/s during the last ten years. During dry periods, the pumping flow rates exceed the natural water discharge, causing the spring to go dry. Several previous studies have shown the complexity and heterogeneity of the Lez spring in terms of its structure, functioning and geochemistry (e.g. Fleury et al., 2009; Caetano Bicalho et al., 2012; Batiot-Guilhe et al., 2013). Most of these studies suggest three main types of groundwater circulation (Fig. 1b): i) water from the main aquifer compartments (Upper-Jurassic and Lower-Cretaceous), typical from dry "low-waters" seasons, where the piezometric level is lower than 60 m a.s.l., and characterized by a relative high and constant electrical conductivity ($750 < EC < 800$ µS/cm); ii) superficial waters that infiltrate into the aquifer, producing lower EC values (< 700 µS/cm); and iii) water from a deeper origin, characterized by a higher EC (> 840 µS/cm), mainly due to higher Na, Cl and Mg concentrations (Marjolet and Salado, 1978; Caetano Bicalho et al., 2012). This deep water component appears during high flood episodes, due to the increased pressure of the water table, an event described as a "piston effect" (Caetano Bicalho et al., 2012). Diluted and mineralized waters appear almost only during high flood events, when the piezometric level exceeds 65 m a.s.l., and discharge occurs at the natural spring.