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Transfer of dissolved gases through a thick karstic vadose zone – implications for recharge characterisation and groundwater age dating in karstic aquifers

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Abstract:

This study analyses the impact of a thick vadose zone on gaseous transfers and Excess Air (EA) formation using dissolved noble and anthropogenic gas tracers (Ne, Ar, N₂, CFC, SF₆, O₂ and CO₂). Understanding gas transfers integrates the issues of equilibrium and water/air exchanges along the vadose zone. In this study, the noble and anthropogenic gases were analysed in air and water over vadose zone depths of 120 m and over two contrasted hydrodynamic periods therefore enabling a rare insight into the spatial and seasonal variations of equilibrium and water/air exchanges in a heterogeneous karst environment. The results highlight that both noble and anthropogenic gases of the caves are in equilibrium with the atmosphere up to at least depths of 120 m. In water, the Noble Gas Temperature (NGT) remains stable at 8°C whilst some EA is formed (up to 1.3 cm³ STP/kg at 120 m) during transfers in the vadose zone. The high EA value measured at the spring outlet cannot be explained by an increase during transfers via the vadose zone. This high EA value is due to rapid and high water level variations during recharge. The implications of these results are important to advance our understanding in the use of noble and anthropogenic gases in characterising recharge.
and quantifying groundwater ages. In particular, these results help to identify the parts
of the aquifer actively involved in dissolved gas transfers, highlight the futility of using
a time-lag factor for groundwater age dating in karstic systems, and improve our
understanding of the EA formation processes.

Keywords: dissolved gases, Excess Air (EA), karstic aquifers, thick vadose zone, transfers,
recharge, dating gaseous tracers

1 Introduction

In karts systems, the vadose zone, composed of soil, epikarst and the unsaturated
zone (Stephens, 1996), plays an important role in controlling the recharge processes of
groundwater. Several methods exist to investigate transfers of water along the vadose
zone and address the question of storage dynamics or travel time estimation of recharge
water. For example, many studies of cave drips have been carried out and provide
information on the capacitive role of the epikarst (Williams, 1983; Tooth and Fairchild,
2003; Musgrove and Banner, 2004; Fairchild et al., 2006; Garry et al., 2008; Arbel et
al., 2010; Kluge et al., 2010; Poulain et al., 2015). Another approach is numerical
modelling, which has the advantage of being applicable on a large scale and over long-
time frames. Models based on physical processes and using Richard’s equations are
applied to the porous vadose zone, that can be assimilated to homogeneous aquifers
(Vereecken et al., 2008). These physically-based approaches are interesting since they
can deal with the degree of saturation of the vadose zone. However, they cannot take
into account the heterogeneous properties of karst (Šimůnek et al., 2003), which is why
their application is scarce in karst aquifers.

Globally, karstic aquifers provide important groundwater resources (e.g.
Bakalowicz, 2005; Stevanović, 2018, 2019; Goldscheider et al., 2020). However, these
aquifers are renowned for their heterogeneous structures, including large voids
(conduits), associated with a porous matrix that induce spatially heterogeneous
hydrodynamic and hydrochemical properties (Bakalowicz, 2008). This heterogeneity
challenges the use of classical hydrogeological methods of investigation, including the basic piezometric map. To face these issues, development of additional innovative methods is essential to investigate and provide an understanding of karst aquifer functioning, especially within the vadose zone.

Hydrogeochemical methods integrate heterogeneities at the scale of the catchment with a large number of tracers that are commonly combined (Barnes and Allison, 1988; Plagnes, 1997; Pinault et al., 2001; Perrin et al., 2003; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; Aquilina et al., 2005; Carrasco et al., 2006; Fairchild et al., 2006; Kluge et al., 2010; Knierim et al., 2013; Kogovsek and Petric, 2014). Such methods are appropriate for investigating groundwater-rock interactions, origin and mixing of waters, and degrees of karstification (Sánchez et al., 2015). However, they fail to inform about physical processes such as air/water equilibrium, matrix/conduits exchange and recharge conditions that affect water transfers from the surface to the spring. In particular, little is known of the temperature and pressure conditions during recharge, even though such parameters can be critical in understanding hydrogeological processes.

Dissolved gases are sensitive to recharge conditions as their solubility in water depends on recharge temperature, salinity and pressure (Weiss, 1970, 1971). For noble gases, since their partial pressure in the atmosphere remains stable, their concentration in water only depends on the recharge conditions and especially temperature (Aeschbach-Hertig et al., 1999, 2000; Manning and Solomon, 2003; Ingram et al., 2007). With inverse models, noble gases have been used to determine the groundwater recharge temperature, known as Noble Gas Temperature NGT, (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999), which in turn can be used to infer information about the recharge period (Chatton et al., 2016).

Moreover, numerous studies have shown that the concentrations of dissolved noble gases in water can be higher than expected from the application of Henry’s law (Herzberg and Mazor, 1979; Heaton and Vogel, 1981; Stute et al., 1995). This phenomenon is known as Excess Air (EA). It is usually taken into account as a corrective term of dissolved gas concentrations in the application of dating methods using gases tracers such as CFCs, SF$_6$ or He. Two assumptions have been made for EA formation.
Firstly, Herzberg and Mazor (1979) and Mazor et al. (1983) suggested that during water transfers along the vadose zone the air is sucked into the water. In this case, the quantity of EA formed is linked to the vadose zone thickness. Secondly, Stute and Schlosser (2000) and Aeschbach-Hertig (2004) explained that EA formation is via the entrapment of air bubbles after a rapid increase in the water table, where the hydrostatic pressure increases during the water level change forces gas dissolution. In this case, concentrations of EA depend on water table fluctuations with higher values due to rapid and larger increases in the water table (Ingram et al., 2007; Massmann and Sültenfub, 2008).

In karst systems the vadose zones are often thick, for example, in the Mediterranean area the vadose zone can be up to 400m (Mudry and Puig, 1991; Fleury et al., 2007). Moreover, groundwater levels in karst aquifers can undergo rapid increases during recharge events (several tens of meters; e.g. Bailly-Comte et al., 2008). Finally, in karst systems the presence of an epikarst can often be associated with perched water tables (Klimchouk et al., 2000; Bakalowicz, 2004; Klimchouk, 2004). Such characteristics can significantly impact air/water equilibrium, gas transfers and EA formation. Despite this, the composition and evolution of the dissolved gases in the vadose zones of karstic systems are poorly documented.

Therefore, the use of dissolved gases in karst systems raises the following fundamental questions relating to the processes of air-water equilibrium (i) does the equilibrium occur at the surface of the epikarst or at the surface of the water table (base of the vadose zone); (ii) if the equilibrium is located at the surface of the epikarst, is the air in caves located at the bottom of a thick unsaturated zone still equilibrated with the atmospheric air; and (iii) is there re-equilibration during transfers along the thick vadose zone? Such questions are important for the application of noble gases as environmental tracers of recharge mechanisms in karst aquifers. In particular, the study of EA is required to improve our understanding of links with the aquifer structure and/or hydrodynamics, and the quantification of groundwater ages using gaseous dating tracers (e.g. CFCs and SF₆).

To address these questions, in this study the dissolved noble and anthropogenic gas tracers (neon (Ne), argon (Ar), nitrogen (N₂), chlorofluorocarbons (CFCs) and sulfur
hexafluoride (SF₆)) were measured in both air and water at different depths along a thick vadose zone (120 m deep) of a karst aquifer with a well-developed epikarst. This allowed us to identify the (i) air composition evolution along the vadose zone and its equilibrium with the atmosphere; (ii) gas evolution in air and in water to identify the equilibrium depth for dissolution of gases; and (iii) mechanisms of EA formation in a karstic system.

2 Study area

The area of investigation is located in a Jurassic carbonate plateau of the Causse du Larzac (south of France), and has an elevation between 700 and 900 m asl. This site is part of the Natural Regional Park of the Grand Causse (PNRGC). It is one of the study sites of the French National Observation Services H+ (http://hplus.ore.fr/), which is part of the Elter European Infrastructure (https://deims.org/83b01fa5-747f-47be-9185-408d73a90fb2), and has therefore been extensively studied (Plagnes, 1997; Bruxelles, 2001; Jacob, 2009; Tritz et al., 2011; Deville, 2013; Fores, 2016). Two main aquifer reservoirs are present: i) dolomites and limestone of the Early Jurassic and ii) the Middle to Upper Jurassic. These two carbonated series are separated by the Toarcian marls that outcrop at the Hospitalet’s fault, which constrains the emergence of the Durzon’s spring at the base of the carbonate series (fig 1-A).

The climate of the Causse du Larzac is Mediterranean, defined by wet winter and spring months, and a dry summer. Autumn is characterised by intense rainfall events caused by Cevenol episodes, with rainfall peaks that can reach up to 290 mm/day. This period constitutes an important recharge period for the aquifer. In this study, we refer to high and low flow periods to define two states observed during the hydrological cycle. The high flow period results from the autumn, winter and spring rainfall recharge, and is characterised by high spring flow and groundwater levels towards the beginning of the dry season. The low flow period is mainly during the dry season when the spring flow and groundwater levels are lower.

The mean potential evapotranspiration is 2.5 mm/day with a maximum value of 9 mm/day during summer. The air temperature is between -14°C and 35°C with an
average of 11°C. During recharge periods of spring and autumn the average monthly
air temperatures vary between 6°C and 16°C.

The Durzon’s spring, located at 533 m asl with a mean flow of 1.5 m³/s (Tritz
et al., 2011), drains a surface area between 98 and 117 km² (estimated by dye tracing;
Ricard and Bakalowicz, 1996; Fores, 2016) (Fig. 1-A). The aquifer is unconfined in the
two blocks located on each side of the Hospitalet fault. The saturated zone is developed
within the Middle Jurassic Dolomite in the southern region and both within the Middle
Jurassic dolomite and the Middle Jurassic limestone to the north of the Hospitalet fault.
The Durzon spring is the main spring that drains the catchment, and therefore represents
catchment-scale hydrodynamic and hydrogeochemical information. The Durzon system is
characterised by a thick vadose zone (up to 120 m deep, south of the Hospitalet’s
fault), and an epikarst developed in the dolomite (weathered to dolomitic sands)
especially in the southern part of the catchment. This lithology allows an important
storage of water in the near-surface. One manifestation of this storage is the formation
of temporary lakes, mainly located south of the catchment, that were last filled in 2014
(Fores, 2016). These changes in geology, vadose zone depths and epikarst thicknesses
results in heterogeneous hydraulic properties of the vadose zone between the southern
and the northern regions of the Durzon spring catchment.

Water storage in the vadose zone of the study area has previously been
investigated through the use of several geophysical methods that couple gravimetry and
seismology with hydrology. These studies confirmed the important role of the epikarst
for vadose zone water storage (Jacob, 2009; Deville, 2013). In addition, the fluxes from
the epikarst were modeled based on continuous gravimetric measurements (site of La
Jasse, the Larzac Observatory). The results showed that this flow corresponds to the
spring’s base flow (Fores et al., 2017).

Several accessible caves in the vadose zone are present in the southern area of
the Hospitalet’s fault. The Bise cave reaches a depth of 120m from the grounds surface,
and there is a stream that flows through the cave that is disconnected from the
saturated zone.
Fig 1. (A) Geological map of the Durzon karst system (modified from Fores, 2016). (B) Schematic cross-section at the Durzon spring highlighting with the location of sampling points with depth in the vadose zone, and hypothetical position of the water table.

Based on the analysis of the Durzon spring recession curves, the karst system shows a high dynamic volume (Mangin, 1975), which highlights the presence of large groundwater reserves at the site (Plagnes, 1997). Chemical variations are low during seasonal hydrological changes, except for a significant increase in the specific conductivity (SpC) and a decrease in the Mg\(^{2+}\) concentrations that result from the fast infiltration after recharge events (Plagnes, 1997). High values of Mg\(^{2+}\) concentrations
are correlated to the extension of the ruiniform dolomites from the Bathonian at the surface of the catchment (Plagnes, 1997).

Another catchment has been used, the Ironselle catchment located on the nearby Causse Méjean, 25 km north of the Durzon spring, and developed in the same geological and climatic context as the Durzon spring catchment. It presents a comparable structure of a carbonate plateau developed in dolomites and limestone from the Jurassic, but has a thicker vadose zone than the Durzon’s catchment allowing a deeper sampling at 395 m depth (the only site sampled on this catchment).

3 Methods

3.1 Dataset

Spring discharge (hourly time step since 1998), water temperature and specific conductivity (30 min time step since Dec-2011) are monitored by the Regional Natural Park of the Grands Causses (PNRGC). Dissolved gas samples for CFC-12, SF₆, Ne, Ar and N₂ analysis have been collected at the Durzon spring from 2009 to 2019 with a monthly time step between February 2010 and November 2011 (de Montety et al., 2012). These measurements of gases in the spring were compared with the data obtained in the vadose zone, at different stages of the hydrological cycle, to determine whether the vadose zone data can partly or fully explain the spring data.

The presence at different depths of the vadose zone of small streams or cavities containing water allows the sample of gases in air and in water along the vadose zone (Fig. 1-B). Four locations (shown in Fig. 1-A) with contrasted depths have been sampled to describe both the epikarstic and vadose zone: Canalettes and Reynelles at 5 and 9 m depth respectively for the epikarstic zone, a 45 m deep borehole in the unsaturated zone (Jasse), and an underground river at 120 m depth in the unsaturated zone (Bise).

In addition, air was sampled at the land’s surface (700 m a.s.l) and water was also sampled at the Durzon spring. Two sampling campaigns were undertaken during high and low flow conditions (March-2018 and Sept-2019 respectively) to evaluate the seasonal hydrological influence on the gas transfers.
Rainfall and potential evapotranspiration data used in this study are collected by Météo-France on Le Caylar station, located 14km south of the site, providing daily data since 2004. Air temperature is monitored by a flux tower located on the catchment.

The air temperature in the cave of la Bise is buffered to 10.8°C all year round (pers. comm.). The water level is also monitored in the vadose zone since 2013 in two boreholes of 20 and 51 m depth located on the La Jasse site (Fig. 1-A) and equipped with a SWS CTD Diver® since 2013.

To complement the Durzon spring data, samples were also collected during the low flow period in a similar karstic catchment, the Ironselle catchment. Air samples were collected at 395 m depths in the Cheminée cave at the Ironselle catchment.

### 3.2 Sampling and analysis

Air samples for noble gas analysis were collected by filling 130 mL glass bottles sealed with rubber caps using syringes. The air volume of the bottle was renewed 3 times before sampling with a slight overpressure to avoid later contamination from atmospheric air. Dissolved noble gases in water were collected in 500 mL glass bottles closed with rubber caps and sealed by a metal ring. A small submergable pump (Mini Twister 12 volts standard PVC – sdec-france) was used to sample the Ironselle spring and the cave waters. At the Canalettes (5 m depth), a peristaltic pump was required due to the very low flow rate. For the Jasse borehole (45 m depth) and the Durzon spring, a Grundfos MP1 pump was used. Samples were collected under water (directly in the groundwater or in a bucket) to avoid any air contamination, after having renewed the water 3 times. Two or three replicates were collected for each sampling point. CFC and SF6 water samples were collected without atmospheric contact in stainless-steel ampoules of 40 ml (CFC) and 300 ml (SF6) closed with two stainless-steel three-way valves. In addition, for each dissolved gas sample, physico-chemical parameters (T°C, pH, SpC and dissolved oxygen (DO)) were recorded using a portable multimeter HQ40D HACH. Only the groundwater temperature at the Jasse borehole was measured by the CTD Diver® located in the borehole, rather than at the land’s surface with the portable multimeter HQ40D HACH.
Both air and water samples were analysed at the CONDATE Eau analytical platform, University of Rennes, by gas chromatography analysis. For water sample analyses, Ne-Ar-N₂ were extracted by head space and measured by gas chromatography using a catharometer detector (µGC 3000 - SRA), with a precision of 8% for Ne and 5% for Ar and N₂. CFCs and SF₆ were extracted by the purge and trap method to concentrate the gases and quantified by gas chromatography with an electron capture detector (Labasque et al., 2014, 2006). The analyses are within a precision of 3% for CFC-12 and 5% for SF₆ in water. For air samples, excluding the extraction of gases from the liquid phase, the analytical process was the same as for water samples. The precision (repeatability) is about 10%, mainly due to the low pressure of air samples, and then possible contaminations. Air has been sampled at the surface of the catchment (March 2018 – high flow campaign) and in the analysis laboratory (September 2019 – low flow campaign) for the calibration. Every air sample was corrected from this calibration.

### 3.3 Calculation of recharge conditions (NGT and EA)

Ne, Ar and N₂ can be used to estimate Noble Gas Temperature (NGT) and Excess Air (EA) (e.g. Heaton and Vogel, 1981; Plummer et al., 2004, Chatton et al., 2016). N₂ is a major gas, which can be produced by biological reactions such as denitrification in anoxic systems (Blicher-Mathiesen et al., 1998; Mariotti, 1986; Smith et al., 1991). However, in karst systems anoxic conditions are rarely found, especially in an unconfined reservoir. For the Durzon system, the dissolved oxygen (DO) is always above 7.6 mg/l. For this reason, the N₂ dissolved concentration was assumed to remain stable during the hydrological cycle and was used to deduce NGT and EA.

Calculations were performed using the Unfraction Air (UA) conceptual model, following the methodology described by Aeschbach-Hertig and Solomon (2013). This simple model does not include degassing or gas partitioning. According to this model, the concentration of the dissolved gas \( i \) is given by:

\[
C_i(T,S,P,EA_{UA}) = C^*_i(T,S,P) + EA_{UA} \times z_i
\]

*Equation 1*
where $EA_{WA}$ is the concentration of dissolved dry air in water; $z_i$ the volume fraction of the gas $i$ in dry air (corresponding to $x_i$, the molar fraction) and $C^*$ is the moist air solubility equilibrium concentration at the given recharge temperature ($T^\circ$K), salinity ($S$‰) and pressure ($P$ atm) (Heaton and Vogel, 1981).

An inverse approach (Aeschbach-Hertig et al., 1999; Manning and Solomon, 2003) was also applied, where the model calculates the gas concentrations (mol/L) by applying Henry’s law for varying NGT and EA parameters. The best set of NGT and EA was obtained after minimization of the $\chi^2$ function using the following equations:

$$X^2 = \frac{\sum (C_{i \text{measured}} - C_{i \text{calculated}})^2}{\sigma^2}$$

**Equation 2**

with

$$C_{i \text{calculated}} = \left( \frac{\beta_i}{22.4} \times x_i(g) \times (P - p_{H2O}) \right) + \left( \frac{x_i}{V_M} \times \frac{EA}{1000} \right)$$

**Equation 3**

where $\beta_i$ is the Bunsen coefficient of dissolution (L/L atm), $x_i$ the molar fraction of the gas in dry air, $P$ the pressure (atm), $p_{H2O}$ the humidity pressure (atm), $V_M$ the molar volume of the gas (L/mol) and $EA$ the Excess Air (cm$^3$ STP/kg).

$$\ln \beta = a_1 + a_2 \left( \frac{100}{T} \right) + a_3 \ln \left( \frac{T}{100} \right)$$

$$+ S \left[ b_1 + b_2 \left( \frac{T}{100} \right) + b_3 \left( \frac{T}{100} \right)^2 \right]$$

**Equation 4**

where $a$ and $b$ are constants for the Bunsen calculation (Weiss, 1971, 1970), $T$ the NGT (recharge temperature in °K) and $S$ the salinity (‰). The salinity of groundwater from the Durzon and Ironselle aquifers is low (< 0.5 ‰), therefore the salinity correction can be neglected and fixed at 0 (Aeschbach-Hertig et al., 2000, 1999; Andrews and Lee, 1979).

And for recharge altitude less than 3000 m:
Where $H$ is the recharge altitude (m).

To take into account the analytical uncertainties, we used a Monte Carlo approach. 100 random concentrations are drawn for each gas based on a normal distribution centred on the measured value and within the range of the analytical error. Then, 100 sets of parameters are calculated. The uncertainty of NGT and EA was given by the standard deviation of these 100 simulations.

The gas result corresponds to the mean value of the replicate samples collected at each point. The final uncertainty corresponds to the largest magnitude of each uncertainty including the duplicate uncertainty.

We compared the results from our method of calculation using three gases to the results from the use of five noble gases using the work from Holocher et al. (2002). This comparison shows that the accuracy of the NGT and the EA is more dependent on the analytical uncertainties than the number of gases used for the calculation. The use of Ar and Ne is sufficient to determine NGT and EA as their dissolution highly depends on the variation of temperature and pressure respectively.

3.4 Calculation of CFC-12 and SF$_6$ atmospheric pressures

Determination of groundwater ages and flow models relies on the calculation of atmospheric mixing ratio (pptv) using Henry's law (International Atomic Energy Agency, 2006). The influence of the recharge elevation is small for elevations less than 1000 m (International Atomic Energy Agency, 2006) and has been fixed to 700 m asl in this study. In contrast, recharge temperature is an essential parameter to calculate the coefficient of solubility ($\beta_i$). The annual air temperature can be assumed to be close to the recharge temperature (Herzberg and Mazor, 1979). However, air temperature data representative of the recharge sites is not always available or known; therefore, another approach is to calculate the recharge temperature based on the water NGT. In this
study, we used the NGT, as we generally sampled noble gases and anthropogenic gases at the same time. However, we noticed some analytical problems for the dissolved noble gases sampled in September 2019 (low flow period), limiting their use for estimating the NGT for this campaign. Therefore, the mean NGT (9.1°C ± 2.2°C) calculated during low flow periods at the Durzon spring between 2009 and 2013 (6 values) was used. The same procedure was applied for EA computation, which is an essential corrective term especially for SF6 values.

4 Results

4.1 Evolution of gaseous tracers along the vadose zone – results in air samples

The gas composition of air samples in caves according to depth is reported in table 1 and Fig 2. During the high flow period (March), the proportion of O2, Ne, Ar and N2 remains stable with depth, with a concentration that is close to the atmospheric air reference (Fig. 2 and table 1). In contrast, the proportion of CO2 increases from the atmospheric value at the ground surface (430 ppm) to 2200 ppm at 120 m depth (Bise; Fig. 2). During the low flow period (September) a greater CO2 increase with depth was observed, with CO2 values almost doubled compared to high flow (from 2200 to 4200 ppm; Table 1) at the Bise in the Durzon spring catchment. In the Ironselle spring catchment, the CO2 values at 395 m depth during the low flow period reached up to 7400 ppm (Table 1).

The fractions of O2, Ne, Ar and N2 in air obtained at the different sampling points were similar to the atmospheric reference values. These results indicate that the air composition of the caves in the vadose zone is equilibrated with atmospheric air during both high and low flow periods.
Table 1: Proportions of O2, CO2, N2, Ne and Ar in cave air along the vadose zone profile in the Durzon catchment during high flow (March 2018) and low flow (September 2019), and in the deep Cheminée Cave located in the Ironselle catchment. Values are compared to the mole fraction in dry air (literature).

<table>
<thead>
<tr>
<th>Name</th>
<th>Sampling date</th>
<th>Depth (m)</th>
<th>O2 (%) ± 5%</th>
<th>CO2 (%) ± 5%</th>
<th>N2 (%) ± 5%</th>
<th>Ne (%) ± 8%</th>
<th>Ar (%) ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (surface)</td>
<td>March 2018</td>
<td>21</td>
<td>0.04</td>
<td>78</td>
<td>0.0018</td>
<td>0.934</td>
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<tr>
<td>Reference</td>
<td>(noaa.gov)</td>
<td></td>
<td>(Sano et al., 2013)</td>
<td>(Sano et al., 2013)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durzon</td>
<td>March 2018</td>
<td>0</td>
<td>21</td>
<td>0.043</td>
<td>78</td>
<td>0.0019</td>
<td>0.9</td>
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<tr>
<td>Canalettes</td>
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<td>21</td>
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<td>78</td>
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<td>0.9</td>
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<tr>
<td>Reynelle</td>
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<tr>
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<td>0.0019</td>
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<tr>
<td>Durzon</td>
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<td>20</td>
<td>0.041</td>
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<td>0.0018</td>
<td>1</td>
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<tr>
<td>Air (surface)</td>
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<td>1</td>
<td>± 1</td>
<td>± 2E-03</td>
<td>± 4</td>
<td>± 1.5E-04</td>
<td>± 5E-02</td>
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<td>0.42</td>
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<td>Cheminée</td>
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<td>78</td>
<td>0.0019</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>± 1</td>
<td>± 3.7E-02</td>
<td>± 4</td>
<td>± 1.5E-04</td>
<td>± 5E-02</td>
</tr>
</tbody>
</table>
Fig 2: Evolution of Ar-Ne-N$_2$-CO$_2$-O$_2$ proportions in air caves of the Durzon and Ironselle spring catchments during the transfer along the unsaturated zone – High flow period: sampling in March 2018; Low flow period: sampling in September 2019.

O$_2$, Ne, Ar and N$_2$ cannot inform about the potential time lag during transfers via the vadose zone, due to their constant atmospheric concentrations over time. Therefore, to investigate potential time lags during transfers the anthropogenic gases CFCs and SF$_6$ were used. The atmospheric concentrations of these gases have evolved since their industrial production in the 1950s and are well described (International Atomic Energy Agency, 2006).
Table 2: Fraction of CFCs and SF₆ (pptv) in air caves along the vadose zone profile on the Durzon catchment during high flow (March 2018) and low flow (October 2019).

<table>
<thead>
<tr>
<th>Name</th>
<th>Sampling date</th>
<th>Depth (m)</th>
<th>CFC-11 corrected (pptv)</th>
<th>CFC-12 corrected (pptv)</th>
<th>CFC-113 corrected (pptv)</th>
<th>SF₆ corrected (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USGS (air reference NH)</td>
<td>2018</td>
<td></td>
<td>219.30 ± 0.5</td>
<td>515.74 ± 1</td>
<td>70.34 ± 0.5</td>
<td>9.37 ± 0.05</td>
</tr>
<tr>
<td>Surface (air in study area)</td>
<td>March 2018</td>
<td>0</td>
<td>219 ± 21</td>
<td>516 ± 50</td>
<td>70 ± 15</td>
<td>9.4 ± 1.7</td>
</tr>
<tr>
<td>Canalettes</td>
<td>March 2018</td>
<td>-5</td>
<td>213 ± 20</td>
<td>508 ± 48</td>
<td>57 ± 6.3</td>
<td>9.2 ± 0.9</td>
</tr>
<tr>
<td>Reynelle</td>
<td>March 2018</td>
<td>-9</td>
<td>237 ± 21</td>
<td>549 ± 53</td>
<td>74 ± 16</td>
<td>9.9 ± 0.9</td>
</tr>
<tr>
<td>Bise</td>
<td>March 2018</td>
<td>-120</td>
<td>215 ± 32</td>
<td>504 ± 65</td>
<td>55 ± 13</td>
<td>9.2 ± 1.0</td>
</tr>
<tr>
<td>USGS (air reference NH)</td>
<td>2019</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air_labo (air in the analytic laboratory)</td>
<td>October 2019</td>
<td>0</td>
<td>217 ± 48</td>
<td>513 ± 116</td>
<td>70 ± 17</td>
<td>9.7 ± 1.4</td>
</tr>
<tr>
<td>Bise</td>
<td>September 2019</td>
<td>-120</td>
<td>161 ± 27</td>
<td>524 ± 70</td>
<td>71 ± 10</td>
<td>10 ± 1.3</td>
</tr>
</tbody>
</table>
The evolution of the gases (CFCs and SF$_6$) with depth; from the surface to -120m in the vadose zone, remains stable within the uncertainty (Fig. 3). These results show that the CFCs and SF$_6$ of air in caves is equilibrated with the atmosphere up to depths of 120m. These observations suggest a good aeration of caves and shows that the time lag had not affected the samples, even at 120 m depth.

4.2 Evolution of gaseous tracers along the vadose zone – results in water samples

NGT and EA were calculated from Ne-Ar-N$_2$ measured in water samples for low flow (Fig. 4 - red) and high flow (Fig. 4 - blue) periods (Table 3). The mean NGT obtained during the high flow period is $7.9 \pm 2 \degree C$ with $0.007 < \chi^2 < 0.6$, while in low flow period the NGT calculated ranges from $18.5\degree C$ to $26\degree C (\pm 3\degree C)$ with $2.2 < \chi^2 < 4.4$. The high NGT values during the low flow period are not consistent with the mean air temperature of the study area (around $11\degree C$). To focus on the evolution of the recharge temperature along the vadose zone, the NGT deviation from the sub-surface point
(Canalettes: -5m) was calculated. In figure 4, the evolution of the NGT deviation and water temperature evolution are compared.

Water temperature increases from 9°C close to the surface (-5 m) to 10.7°C at -120 m and 11.1°C at the spring. This increase does not correspond to the geothermal gradient, calculated from the mean annual temperature of 11°C. The vadose zone is therefore influenced by fast water circulation through conduits and fractures that causes thermal convection disturbing the geothermal gradient. The surrounding rock is colder than expected from the application of theoretical geothermal gradients which do not take in account water circulations (Lismonde, 2004).

While the water temperature increases with depth, the NGT remains stable during transfer along the vadose zone (Fig. 4).
Table 3: Summary of the noble gases, N2 concentrations and recharge conditions (NGT and EA using the UA model) during high flow and low flow at different depths along the vadose zone.

<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
<th>Hydrological context</th>
<th>Depth (m)</th>
<th>[Ar] (mol/L) ± 5%</th>
<th>[Ne] (mol/L) ± 8%</th>
<th>[N2] (mol/L) ± 5%</th>
<th>NGT (°C)</th>
<th>Mean NGT (°C)</th>
<th>EA (cm³STP/kg)</th>
<th>Mean EA (cm³STP/kg)</th>
<th>χ²</th>
<th>Delta NGT (°C)</th>
<th>Delta EA (cm³STP/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canalettes</td>
<td>-5</td>
<td></td>
<td>1.70E-05</td>
<td>8.51E-09</td>
<td>6.18E-04</td>
<td>7.5 ± 1.7</td>
<td>2.6 &lt; 6.0 &lt; 9.2</td>
<td>0 ± 0.6</td>
<td>0 &lt; 0.5 &lt; 1.8</td>
<td>0.9 ± 0.9</td>
<td>0.17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Canalettes</td>
<td>1.87E-05</td>
<td></td>
<td>9.68E-09</td>
<td>6.91E-04</td>
<td>4.5 ± 1.9</td>
<td>0.9 ± 0.9</td>
<td>0 &lt; 0.5 &lt; 1.8</td>
<td>0.44</td>
<td>2</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reynelles</td>
<td>-9</td>
<td></td>
<td>1.68E-05</td>
<td>8.36E-09</td>
<td>5.99E-04</td>
<td>8.5 ± 1.7</td>
<td>5.2 &lt; 8.0 &lt; 10.2</td>
<td>0 ± 0.4</td>
<td>0 &lt; 0.5 &lt; 1.8</td>
<td>0.6 ± 0.7</td>
<td>0.01</td>
<td>2.3</td>
<td>0.25</td>
</tr>
<tr>
<td>Reynelles</td>
<td>March</td>
<td></td>
<td>1.76E-05</td>
<td>9.50E-09</td>
<td>6.42E-04</td>
<td>7.5 ± 2.3</td>
<td>4.7 &lt; 8.3 &lt; 11.3</td>
<td>0.8 ± 0.8</td>
<td>0 &lt; 0.7 &lt; 1.6</td>
<td>1.3 ± 0.9</td>
<td>0.67</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>Jasse</td>
<td>2018</td>
<td>High Flow</td>
<td>-45</td>
<td>1.65E-05</td>
<td>8.85E-09</td>
<td>9 ± 2.3</td>
<td>4.7 &lt; 8.3 &lt; 11.3</td>
<td>0.6 ± 0.7</td>
<td>0 &lt; 0.7 &lt; 1.6</td>
<td>1.3 ± 0.9</td>
<td>0.67</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>Jasse</td>
<td>1.74E-05</td>
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<td>6.40E-04</td>
<td>7.5 ± 2.2</td>
<td>7.0 ± 2.2</td>
<td>1.3 ± 0.9</td>
<td>1.3 ± 0.9</td>
<td>0.8 ± 0.8</td>
<td>0 &lt; 0.7 &lt; 1.6</td>
<td>1.3 ± 0.9</td>
<td>0.67</td>
<td>1</td>
<td>0.9</td>
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<tr>
<td>Bise</td>
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<td>7.0 ± 2.2</td>
<td>7.0 ± 2.2</td>
<td>1.3 ± 0.9</td>
<td>1.3 ± 0.9</td>
<td>0.8 ± 0.8</td>
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<td>0.9</td>
</tr>
<tr>
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<td>-167</td>
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<td>1.04E-08</td>
<td>6.93E-04</td>
<td>8.0 ± 2.6</td>
<td>8.0 ± 2.6</td>
<td>2.3 ± 1.2</td>
<td>2.3 ± 1.2</td>
<td>2.3 ± 1.2</td>
<td>0.07</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>Canalettes</td>
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<td>1.22E-05</td>
<td>6.69E-09</td>
<td>4.00E-04</td>
<td>22.0 ± 2.8</td>
<td>22.0 ± 2.8</td>
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<td>-1.4 ± 0.8</td>
<td>2.2</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>Reynelles</td>
<td>-9</td>
<td></td>
<td>1.29E-05</td>
<td>7.12E-09</td>
<td>4.17E-04</td>
<td>20 ± 2.7</td>
<td>16.1 &lt; 19.3 &lt; 22.8</td>
<td>-1.3 ± 0.6</td>
<td>-2 &lt; -1.2 &lt; -2.8</td>
<td>-2.8</td>
<td>0.3</td>
<td>0.4</td>
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<tr>
<td>Reynelles</td>
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<td>7.41E-09</td>
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<td>18.5 ± 2.4</td>
<td>18.5 ± 2.4</td>
<td>-1 ± 0.6</td>
<td>-1 ± 0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Month</td>
<td>Low Flow</td>
<td>Jasse 2019</td>
<td>Jasse</td>
<td>Bise</td>
<td>Bise</td>
<td>Bise</td>
<td>Durzon</td>
<td>Durzon</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Sept</td>
<td>-45</td>
<td>1.19E-05</td>
<td>1.25E-05</td>
<td>1.14E-05</td>
<td>1.29E-05</td>
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<td>6.61E-09</td>
<td>6.79E-09</td>
<td>6.68E-09</td>
<td>7.54E-09</td>
<td>7.64E-09</td>
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<tr>
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<td>3.83E-04</td>
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<td>4.22E-04</td>
<td>4.33E-04</td>
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<td>6.15E-04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.5 ± 2.8</td>
<td>18.8 &lt; 22.3 &lt; 26.4</td>
<td>21 ± 2.3</td>
<td>26 ± 2.6</td>
<td>26 ± 2.7</td>
<td>20 ± 2.7</td>
<td>24 ± 3.4</td>
<td></td>
<td></td>
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<td></td>
<td>-1.5 ± 0.7</td>
<td>-1.5 ± 0.6</td>
<td>-1.3 ± 0.6</td>
<td>-0.8 ± 0.7</td>
<td>-0.7 ± 0.7</td>
<td>3.2 ± 1.0</td>
<td>4.4 ± 1.1</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2&lt;1.5&lt;2.2&lt;3.2</td>
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<td>-1.5±0.6</td>
<td>-0.8±0.7</td>
<td>-0.7±0.7</td>
<td>2.2&lt;3.8&lt;5.5</td>
<td>3.7&lt;5.2&lt;7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Summary of anthropogenic gases concentrations (pmol/L and pptv with recharge conditions used) during high flow and low flow at different depths along the vadose zone and physico-chemical parameters.

<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
<th>Hydrological context</th>
<th>Depth (m)</th>
<th>[CFC-12] (pmol/L) ± 3%</th>
<th>[SF₆] (pmol/L) ± 5%</th>
<th>Recharge Temperature (°C)</th>
<th>EA (cm³STP/kg) ± 5%</th>
<th>[CFC-12] (pptv) ± 5%</th>
<th>[SF₆] (pptv) ± 5%</th>
<th>SpC (µS/cm at 25°C)</th>
<th>Water Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canalettes</td>
<td>March 2018</td>
<td>High Flow</td>
<td>-5</td>
<td>2.5</td>
<td>0.0041</td>
<td>6</td>
<td>0.5</td>
<td>408</td>
<td>9.2</td>
<td>516</td>
<td>9.1</td>
</tr>
<tr>
<td>Canalettes</td>
<td>March 2018</td>
<td></td>
<td>-5</td>
<td>2.6</td>
<td>0.0041</td>
<td></td>
<td></td>
<td>422</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-9</td>
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<td>8</td>
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<td>419</td>
<td>8.5</td>
<td>471</td>
<td>9.0</td>
</tr>
<tr>
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<td>-9</td>
<td>2.3</td>
<td>0.0035</td>
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<td></td>
<td>419</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>March 2018</td>
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<td>2.1</td>
<td>0.0032</td>
<td>8.3</td>
<td>0.7</td>
<td>387</td>
<td>7.6</td>
<td>395</td>
<td>11.3</td>
</tr>
<tr>
<td>Jasse</td>
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</tr>
<tr>
<td>Bise</td>
<td>2018</td>
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<td>-120</td>
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<td>0.0027</td>
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<td>1.3</td>
<td>342</td>
<td>5.6</td>
<td>468</td>
<td>10.7</td>
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<tr>
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<td>338</td>
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<tr>
<td>Durzon</td>
<td>2019</td>
<td>Low Flow</td>
<td>-167</td>
<td>2.4</td>
<td>-</td>
<td>8</td>
<td>2.3</td>
<td>436</td>
<td>-</td>
<td>476</td>
<td>11.1</td>
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<tr>
<td>Durzon</td>
<td>2019</td>
<td>Low Flow</td>
<td>-167</td>
<td>2.3</td>
<td>-</td>
<td></td>
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<td>-</td>
<td></td>
<td></td>
</tr>
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<td>2.83</td>
<td>0.0019</td>
<td>9.1</td>
<td>5.5</td>
<td>519</td>
<td>3.0</td>
<td>395</td>
<td>10.3</td>
</tr>
<tr>
<td>Jasse</td>
<td>March 2018</td>
<td></td>
<td>-45</td>
<td>3.12</td>
<td>0.0031</td>
<td>9.1</td>
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<td>5.0</td>
<td>360</td>
<td>-</td>
</tr>
<tr>
<td>Bise</td>
<td>Sept 2018</td>
<td></td>
<td>-120</td>
<td>2.80</td>
<td>0.0014</td>
<td>9.1</td>
<td>5.5</td>
<td>427</td>
<td>2.2</td>
<td>461</td>
<td>11</td>
</tr>
<tr>
<td>Durzon</td>
<td>2019</td>
<td>Low Flow</td>
<td>-167</td>
<td>3.03</td>
<td>0.0010</td>
<td>9.1</td>
<td>5.5</td>
<td>317</td>
<td>1.7</td>
<td>428</td>
<td>12.1</td>
</tr>
</tbody>
</table>
For the evolution of the EA in the vadose zone, during the high flow period, the mean EA is 0.6 cm$^3$STP/kg in the unsaturated zone whilst at the spring the EA reaches up to 2.3 cm$^3$STP/kg (Fig. 4 – blue). Similar to the NGT, absolute EA values calculated during the low flow period were underestimated inducing negative values (Fig. 4). We thus used the EA deviation to follow the evolution along the vadose zone, where we observe a slight increase and formation of EA during transfer along the vadose zone.

The historical EA data of the Durzon spring (17 values from 2009 to 2013) shows very large variations during the hydrological cycle; ranging from 0.3 cm$^3$STP/kg during high flow periods to 11 cm$^3$STP/kg during low flow periods. Sampling campaigns of 2018 and 2019 agreed with this historical EA evolution, in spite of the underestimated low flow EA value. The highest values of EA measured at -120 m (Table 4) cannot explain the high EA value measured at the spring (up to 10.7 cm$^3$STP/kg in July 2011). Therefore, an additional process contributing to the EA values has to be involved during groundwater flow in the saturated zone.
The evolution of anthropic dissolved gases CFC-12 vs. SF₆ is represented in Fig 5. The samples from the high flow period are aligned according to depth and can be explained by a mixing line between actual water (2018) and an old end-member. SF₆ measured at the spring during the high flow period show concentrations higher than the peak atmospheric concentration in 2018, therefore the spring cannot be represented on the CFC-12 vs. SF₆ diagram. However, the CFC-12 values of the spring (between 408 and 412 pptv) are closer to the shallower vadose zone rather than the deeper vadose zone values.

Compared to the high flow samples, the low flow samples have lower SF₆ concentrations. There is no correlation between depth and SF₆ concentrations during the low flow period. In addition, the samples are better explained by a piston model, in particular Reynelles, or by a piston-exponential model where the exponential component varies between 10 and 50 % (Fig. 5).

![Figure 5: Evolution of SF₆ as a function of CFC₁₂](image_url)

*Figure 5: Evolution of SF₆ as a function of CFC₁₂ – Blue points: high flow sampling (March 2018); Red points: low flow sampling (September 2019) – Piston pathway model is represented in green*
5 Discussion

5.1 Influence of degassing processes on dissolved gases

The waters sampled during the low flow period in the vadose zone show low concentrations of noble gases. An underestimation of the dissolved noble gas concentrations results in an overestimation of the recharge temperatures and leads to negative EA values calculated using the Unfraction Air (UA) model. Two hypotheses can explain this underestimation of dissolved gas concentrations: (1) a problem occurred during the laboratory analysis or (2) a degassing phenomenon occurred during the transfer via the vadose zone of the karst. Degassing could explain why the UA model (Heaton and Vogel, 1981) that we used does not provide a good fit ($\chi^2$) between the observed data and the calculated values (Table 3 - Chi2).

The Partial Re-equilibration (PR) model (Stute et al., 1995) was used as a diagnostic to test the second hypothesis. As we used only three gases (Ne-Ar-N$_2$), the NGT was set at 11°C, which corresponds to the annual mean air temperature in the catchment, allowing us to add the fractionation coefficient (F) as a parameter to be set, with the EA. However, the PR model did not reproduce the observations nor the positive EA values along the vadose zone.

A model taking into account degassing does not therefore seem to better explain the values measured during the low flow period. This result is in good agreement with historical measured at the Durzon spring (since 2011); where no negative EA values were observed and for which the UA model well reproduced the EA and NGT values.

The analytical error is observed for all of the data for the same field campaign, therefore the absolute values are not possible to use, however the relative changes in the data (deviation) is valid and can be compared to relative changes from other field campaigns.
5.2 Impact of the epikarst and the unsaturated zone on air and water transfers

5.2.1 Gas transfer within the vadose zone

The measurement of matrix air within the epikarst and at different depths in the unsaturated zone constitutes a real scientific challenge due to the complexity of the underground environment within the karst systems, where accessibility and material input is not always possible. The results of this study show that the air in the cavities of the vadose zone of the Durzon catchment is in equilibrium with atmospheric air down to 120 m depth (Figs. 2 and 3). Only gaseous CO$_2$ increases with depth in the vadose zone and presents higher values in low flow period than in the high flow period. The evolution of gaseous CO$_2$ between high flow and low flow periods reflects the seasonal rhythm of the biomass with a higher production of CO$_2$ during summer (Paterson and Sweeting, 1986; Batiot-Guilhe et al., 2007). The flux of CO$_2$ moves down by diffusion and gravity from the top of the vadose zone (production area: epikarst) to the bottom, explaining the accumulation of CO$_2$ during transfer along the vadose zone.

For the Durzon karstic system, the dolomitic epikarst zone may include a perched aquifer (Plagnes, 1997, Fores et al., 2017). The results of this study suggest that the perched aquifer located in the surface horizons of the vadose zone of the karst does not cause a disconnection between the air mass of the vadose zone and the atmosphere. The gas results show that the epikarst must be seen as a very heterogeneous and discontinuous medium which allows both the storage of a volume of water (perched nappe) but also the transfer of air along the vadose zone via sub-vertical conduits, some of which can be penetrated by speleologists (up to 120 m deep).

Cavities in the vadose zone of the karst are well aerated, unlike porous media where a delay factor must be calculated to take into account gas diffusion (Busenberg and Plummer, 1992; Cook and Solomon, 1995; Oster et al., 1996; Zoellmann et al., 2000; Schwientek et al., 2009). In karst environments, despite the existence of a vadose zone of several tens or even hundreds of metres thick, it is not necessary to calculate a gas delay or diffusion coefficients to consider the transfer of air to the saturated zone. These results are nevertheless limited to the transmissive component of the karst,
i.e. the drains and cavities, and cannot be generalised to the capacitive component represented by the porous matrix of the rock, which was not analysed in this study.

5.2.2 Gas equilibrium

Using gaseous tracers in hydrosystems characterised by a perched aquifer (epikarst) located above a thick unsaturated zone raises important questions on gas equilibrium processes during transfers. For example, does the tracing start at the top of the vadose zone composed of a capacitive epikarst? Is there any equilibrium with the cave’s air above? Or does the tracing start at the top of the saturated zone? In this study, at 120m depth the air temperature is buffered at 10.8°C all year round at the Durzon site. High flow sampling was carried out at the time of a snow recharge episode, indicating a surface air temperature close to 0°C. Thus, large variations in air temperature between the surface and the bottom of the vadose zone are suspected. Despite this, no variations were observed in the NGT calculated from the dissolved gases (Fig. 4). This stability in the NGT results (around 8 ± 2°C) throughout the profile of the vadose zone indicates that there is no rebalancing of the dissolved gases in the water with the air in the cavities. The results are similar in low flow periods, confirming that noble gas equilibrium occurs in the near-surface horizon at the epikarst.

During high flow periods, according to the evolution of SF6 as a function of CFC-12, mixing is observed between the rapid infiltration of recent water from the surface and older water stored in the matrix porosity of the karst unsaturated zone (Fig. 5). With increasing depth in the vadose zone, the portion of recently infiltrated water decreases relative to the older pore matrix water. Therefore, the surface horizons have greater volumes of more recent waters compared with the deeper horizons of the vadose zone, which likely reflects transfer times within the vadose zone. This difference in mixing as a function of depth also highlights the fact that there is no resetting of the equilibrium between water and air in the cavities during transfer along the vadose zone, and similar to noble gas results, the gas equilibrium occurs in the sub-surface horizon. The mixing of groundwater of different flow pathways from the unsaturated zone and the saturated zone at the spring could explain the supposed non-alignment of CFC-12 concentrations of the spring with samples from the vadose zone with depth.
During low flow periods, similar to the high flow period, the water sampled at different depths of the vadose zone does not show a current atmospheric gas signature, which indicates there is no equilibrium with the air in the cavities during the low flow period. However, no correlation with the vadose zone depth is observed. Different processes are involved in water transfers that are not dependent on depth. The identification of these low flow processes requires further work.

5.3 EA formation

Two main hypothesis are proposed in previous studies to explain the EA formation: formation during the transfer along the vadose zone (Herzberg and Mazor, 1979) and/or acquisition of the EA due to water level variations (Aeschbach-Hertig, 2004). The evolution of EA suggests a slight increase of the signal during the transfer of water along the vadose zone (+ 0.8 cm$^3$ STP/kg during high flow period, Fig. 4). This enrichment in EA may be due to pressure variations within the vadose zone. Another hypothesis that could explain the enrichment of water in EA during its transfer along the vadose zone would be a flow that is sufficiently fast to cause air bubbles whose dissolution will be forced during a deep pressurisation (Herzberg and Mazor, 1979). However, the EA values observed during low flow and high flow periods at a depth of 120 m do not explain the maximum values measured at the spring. Further work in the Durzon catchment would be required to comment on the spatial representation of vadose zone results from this study relative to the whole catchment area. Nevertheless, the significantly greater EA values of the spring compared with the vadose zone (up to almost 5 times greater) suggests that the formation of EA does not solely depend on the transfer along the vadose zone.

Holocher (2002) experimentally investigated the formation of EA in near-saturated porous media using vertical sand columns. Simulating variations of the water level, he obtained a correlation between these variations and the measured EA between 0.14 and 1.62 cm$^3$ STP/kg for maximum variations of the piezometric level of one meter. The values observed in the literature are generally low (less than 2 cm$^3$ STP/kg), whilst EA values in the Durzon karstic system are high, up to 11 cm$^3$ STP/kg. These high EA
values seem to highlight the combination of factors favourable to EA formation in Mediterranean-type karstic systems such as:

- Intense recharge events known as Cevenol episodes (particular to the Mediterranean region);
- An aquifer structure that combines both a porous medium and conduits allowing strong and rapid elevations of the water table that results in the dissolution of trapped air bubbles;

With this configuration, the EA acts as a tracer of the magnitude of groundwater fluctuations, and therefore a tracer of recharge areas. Many points are still yet to be clarified, such as the influence of the lithological nature of the aquifer, which raises the question of whether the same answers would be found in a non-dolomitic karst. In addition, it is unknown whether there is a direct link between EA and rainfall recharge rates. Lastly, from the perspective of modelling the evolution of EA coupled with hydrodynamics, it is not yet clear whether we should expect a "zero" reset of EA after each hydrological cycle or on the contrary a long-term cumulative effect could be expected?

6 Conclusion

The use of dissolved gases as tracers in karstic aquifers, renowned for their air cavities in thick unsaturated zones and epikarsts, raises many questions relating to methods and applications. The composition and impact of air in the subsurface, where the dissolved gas equilibrium takes place along the vertical profile of the thick vadose zone, and the conditions of EA formation are still debated.

In this research, these questions were addressed by monitoring the evolution of noble and anthropogenic gases (Ne, Ar, N₂, CFC and SF⁶) in air and water along the vadose zone of the Durzon and the Ironselle catchments during two contrasted flow periods (low flow and high flow). The determination of the cave air composition and its comparison with the water concentrations show that at the Durzon site:

1. Air in caves was in equilibrium with the atmospheric air up to 120m deep;
2. The presence of a capacitive epikarst does not disconnect the unsaturated zone from the atmosphere;

3. The gas equilibrium appears to be achieved in a horizon close to the surface and then there is no gaseous re-equilibrium between air and water with depth in the vadose zone;

4. A small part of EA is formed during water transfer along the vadose zone but most of the EA observed at the spring is formed due to the water level variations of the saturated zone.

These observations indicate that there is no need to take into account a time-lag coefficient associated with the gas dispersion into the unsaturated zone of a karst system. This information is essential for the use of temporal gaseous tracers in karstic systems. Finally, the strong link between EA and discharge suggests the development of EA as a tracer of recharge in karst aquifers.

Therefore, for karstic aquifers where the hydrodynamics are complex, the EA provides a valuable tracer of variations in groundwater levels. Future work is required to integrate EA data into numerical models. This integration of the gas results with hydrodynamic models would be useful to bring a new constraint to numerical models. In karst systems, future research is required to study the reaction of gas tracers in other lithologies, such as limestone environments. As observed in this study, the formation of EA (and therefore the reaction of gases) is strongly linked to the karstic aquifer structures.

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8 Bibliography


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• We sampled air and water at different depths until 120 m along a thick vadose zone
• We investigated transfers of gas and groundwater through a thick vadose zone
• We investigated Excess Air formation in a karstic system with a thick vadose zone
• The air of the vadose zone is in equilibrium with the atmosphere until 120 m
• The main part of Excess Air is formed due to water table variations
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