



Multi-tracer groundwater dating for the characterization of a thermal flow system

Case of the Avène-thermal spring water

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Introduction

• Avène, a little village in the north of the Hérault



Introduction - A brief history on Avène Water

1736

Discovery of the curative properties of the Avène Thermal Spring Water

ATSW recommended by eminent dermatologists

1874

1871

The medical properties of ATSW are recognized by the French Academy of Medecine: Avène water is declared of public interest

ATSW exported to Chicago to treat the victims of the great fire



The Pierre Fabre Group takes over the hydrotherapy center at Avène and starts an extensive study program (scientific thermalism) on ATSW



A new hydrotherapy center dedicated to atopic dermatitis and psoriasis; birth of the brand Avène



A water laboratory, guarantor of the water quality



















Introduction - Hydrogeology

Two groundwater (GW) types

- <u>Avène thermal water</u>
 - naturally emerges at thermal springs
 - pumped from wells for thermal water production
 - calcic and magnesium bicarbonate water
 - ~25°C and low mineral content
- <u>"Cold" karst water</u>
 - ~11°C (= mean recharge temperature)
 - major ions composition is relatively close to Avene thermal water



Mixing/exchange of water ?

 \rightarrow Vulnerability to human pressure



Introduction - Context

- Avène Water lab.
 - Check physico-chemical stability of thermal water
 - Conduct hydrogeological studies on the recharge area (historical data from the 80's)
- New scientific questions
 - Residence Time Distribution (RTD) and Mean Residence Time (MRT)
 - Thermal flow <u>transfer</u> and <u>mixing</u> between thermal and "cold" karst end-members

Collaboration between PFDC and BRGM



Objectives and methods

- Multi-tracer GW dating to distinguish « cold » karst transfer from thermal flow system
 - Long and short time scale: ${}^{14}A/\delta {}^{13}C_{DIC}$ and CFCs, SF₆, ${}^{3}H$
 - Spatial...
 - Geochemical/age dating end-members
 - Lumped transfer model for the whole flow system
 - … and temporal approaches
 - Historical database (³H) to validate transfer model

• Validation with other natural tracers

- Stable isotopes of water
- Sr isotopes



Define a conceptual model of thermal flow system that focuses on GW exchanges and transfer



Results – Dissolved gases analyses



- Atmospheric evolution is known
- The value in water at a given time reflects
 - Piston transfer: signal is not modified (only a lag)
 - each signal is modified at each time step => Exponential Model (EM)
 - Binary mixing between 2 flow systems



Baseflow conditions after long recession



Neither a simple piston transfer nor a mixing between « old » and current water can explain the values for thermal water





- EM fit most data consistent for an unconfined aquifer
- Mean Residence Time (MRT) range from 4 to 200 years
- Wells associated to thermal springs (T1 and T2) show the same results
- T1?





- 2 main assumptions of binary mixing (dilution)
 - Thermal water of relatively low residence time (EM90) with 20% current water
 - Thermal water (EM200, T3 type) with 35% "cold" karst water (EM8, W1 type)



Use of ³H – Input function



congress

Use of 3H – Results

W1 : « Cold » karst end member

50 40 40 10 0 1980 1990 2000 2010 2020

T1 : 2 binary mixing scenarios 20 Measurements 16 80% EM90 / 20% current **Tritium unit** 12 65% EM200 / 35% EM8 8 4 0 1980 1990 2000 2010 2020

T3 : Thermal end member



- EM models are validated through time with ³H data
 - ─ Cold karst end-member ⇔ EM8
 - Thermal end-member \Leftrightarrow EM~200
- The two mixing assumptions are consistent with ³H data.



Comparison with other natural tracers

Objectives

- Can T1 water be explained by a binary mixing between thermal and « cold » karst water types?
- Does-it give the same relative contributions?

Methods

- Stable isotopes of water (²H vs. ¹⁸O)
- Sr isotopic ratios (⁸⁷Sr/⁸⁶Sr vs. 1/Sr)



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Strontium isotopes - Results



« Cold » karst end-member

Very high isotopic ratios not consistent with water/rocks interactions with Cambrian dolomites ⇒ radiogenic influence (allogenic recharge from siliclastic and metamorphism rocks)

- T1 water is a binary mixing between:
 - Thermal water in equilibrium with Cambrian dolomites (0.7090±0.0002)
 - «Cold» and radiogenic karst water (dilution)
- % dilution
 - Highly sensitive to the choice of the thermal end-member
 - Consistent with age dating results when using T2



Conclusion

- A large scale flow system
 - A local flow system through a shallow karst aquifer
 « Short » MRT (<10y) for the « cold » karst systems
 - A regional flow system with deep circulation
 Relatively old thermal water (~200-300 years of MRT with EM)
 Compartmentalization due to low permeable "varved" dolomites sequences
- Thermal flow transfers and GW exchanges
 - Thermal water from T2 and T3 show various degree of evolution along thermal flowpaths within Cambrian dolomites
 - T1 is a mixing of 30 to 40% of karst GW with thermal water
 - Water abstraction from wells (T2 or T3) prevent from diluting thermal water



Perspectives – Targeted new acquisition

- Can we monitor the karst contribution at T1 spring?
 - \Rightarrow New monitoring focusing on fast infiltration (if any):
 - High frequency monitoring to detect natural fluorescence of organic compounds
 - 3D fluorescence sampling after recharge events
 - Water-level and discharge to understand hydrodynamic interaction

Improve our knowledge to better protect the resource



Thank you for your attention

• Any questions?







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Results – C isotopes

• ¹⁴A in pCM (%)

Site	¹⁴ A (%) in 1993	¹⁴ A (%) in 2012	Change in conventional Radiocarbon Age (years)
T1	55.7	60.93 +/- 0.21	- 860
Т3	50.6	58.11 +/- 0.21	- 1270

- Uncorrected age shows a decrease of ~1000 years from 1993 to 2012.
- Calculated initial activities are lower than the measured values.
- \Rightarrow 'Atom Bomb' effect that increased pMC, but the input function is unknown...



Age dating is impossible with C isotopes A non negligible part of the thermal water is relatively recent



Strontium isotopes

- ⁸⁷Sr/⁸⁶Sr vs. 1/Sr gives a straight line for a binary mixing (Faure 1986)
- 2 end-members
 - 1. « Cold » karst end-member

Karst water from a well to lower seasonal effects and filter fast infiltration

→ W1

2. Thermal end-member

Thermal water in equilibrium with Cambrian dolomites without mixing with "cold" karst

→ T2 or T3





- > The best DM model is not better (Pe=1)
- > Mean Residence Time (MRT) are slightly higher for Cresson
- > FSO well and SSO spring are still unexplained



New sampling campaign (2014)

Medium flow conditions following the first flood event



T2, T3 and S1:

- Relatively more SF₆, but it is not significant without knowing EA
- A large scale EM model is still valid. Ages are lowered, especially for SFr.
- > <u>T1</u>:
 - The 2 main assumptions about mixing are still valid, with the same ratios



Stable isotopes of water





Results – Dissolved gases analyses

• Gas dissolution

- T°C: ~ mean temp. (vadose zone>10m) = 11°C
- Pressure
 - Excess air is unknown... but should be low (<3cc/mL) because of low groundwater level changes in response to recharge events (few meters)
 - Recharge altitude around 600 masl

• Graphical analysis

- The value in water at a given time reflects
 - air/water equilibrium at recharge date: Piston transfer
 - transfer of air/water equilibrium signal to the spring
 - Exponential Model (EM)
 - 1D Advective/Dispersive model (DM)
 - ...
 - Binary mixing between 2 flow systems



Specific conductivity @25°C at T1 450 440 Mean: 392µS/cm **Specific conductivity (hs/cm)** 420 420 410 400 390 380 320 320 Coefficient of variation (%): 0.62% 360 350 18/11/2010 0610712009 14/08/2013 01/04/2012 27/12/2014

