Elsevier Editorial System(tm) for Science of the Total Environment
Manuscript Draft

Manuscript Number: STOTEN-D-18-10315R1

Title: Contribution of isotopic research techniques to characterize high-mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer.

Article Type: Research Paper

Keywords: Stable isotopes, Seasonal isotopic amplitude, Altitudinal line, Recharge, Mean transit time, Karst

Corresponding Author: Dr. Jorge Jódar, Ph.D.

Corresponding Author's Institution: Technical University of Catalonia

First Author: Ignasi Herms, M.Sc.

Order of Authors: Ignasi Herms, M.Sc.; Jorge Jódar, Ph.D.; Albert Soler, Ph.D.; Iñaki Vadillo, Ph.D.; Luis J Lambán, Ph.D.; Sergio Martos-Rosillo, Ph.D.; Joan A Núñez, M.Sc.; Georgina Arnó, Ph.D.; Joan Jorge, Ph.D.

Abstract: Water resources in high mountain karst aquifers are usually characterized by high rainfall, recharge and discharge that lead to the sustainability of the downstream ecosystems. Nevertheless, these hydrological systems are vulnerable to the global change impact. The mean transit time (MTT) is a key parameter to describe the behavior of these hydrologic systems and also to assess their vulnerability. This work is focused on estimating MTT by using environmental tracers in the framework of high-mountain karst systems with a very thick unsaturated zone (USZ). To this end, it is adapted to alpine zones a methodology that combines a semi-distributed rainfall-runoff model to estimate recharge time series, and a lumped-parameter model to obtain MTT. The methodology has been applied to the Port del Comte Massif (PCM) hydrological system (Southeastern Pyrenees, NE Spain), a karst aquifer system with an overlying1000 m thick USZ. Six catchment areas corresponding to most important springs of the system are considered. The obtained results show that hydrologically the behavior of the system can be described by an exponential flow model (EM), with MTT ranging between 1.9 and 2.9 years. These □□□□values are shorter than those obtained by considering a constant recharge rate along time, which is the easiest and most applied aquifer recharge hypothesis when estimating □□□□ through lumped-parameter models.

Response to Reviewers: COMMENTS FROM REVIEWERS: Reviewer #1

General comments

Thee paper by Herms et al. with title: "Contribution of isotopic research techniques to characterize high mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer." provides an interesting study regarding the contribution of isotopic research in karst aquifers. The concept is interest and the manuscript well written.

Thank you very much for your kind comments

However, I have a number of recommendations, which should be done before publication.

Abstract

Reviewer #1 - General comments #1: You have to include the innovative results of this study. Provide the innovation of this study:

Reply to general comment #1: Certainly, as the reviewer points, the innovative points of this study are not stated in the manuscript. In this regard, the study presents two innovations: (1) a global innovation and (2) the specific innovation with the case study.

(1) The study presents the adaptation of a procedural methodology to improve the estimation of the mean transit time (□) in high-mountain karst aquifers. The methodology is based on the previous approach presented by Vitvar et al., 1999 to estimate groundwater residence times in pre-alpine non-karstic aquifers (tertiary and quaternary deposits in a small basin with elevation ranges between 680 to 960 m a.s.l.) by means of developing a link between distributed rainfall-runoff models to estimate recharge series, and then a lumped-parameter model using environmental tracers to solve the convolution integral. In our case the method is adapted to estimate □□in high-mountain karst systems taking into account the existing vertical gradients of precipitation and air temperature along the slope of high mountains, the role played by the snow accumulation and ablation processes in the runoff generation, and considering the hydrological system to be modelled as the whole aquifer (i.e. the unsaturated zone and saturated zones).

(2) The adapted methodology is applied to the Port del Comte high mountain karst aquifer (NE, Spain) as a practical case study. Despite the strategic role played by this hydrogeological system as water resource provider to Barcelona, the hydrological behaviour of this system is completely unknown. This is the first hydrodynamic and transit time characterization of this hydrological system. Besides, the isotopic characterization of rainfall conducted in the Port del Comte has allowed to estimate the vertical gradient of the amplitude associated to the seasonal variation of the isotopic content (□18O and □2H) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in Table 4 of the manuscript) to correctly estimate the groundwater mean transit time when amplitude dumping method (Eq. 8 of the manuscript) is applied.

We have modified accordingly both the Abstract and the Introduction to highlight these points.

Reviewer #1 - General comment #2: Provide the future works to be implemented to generalize the results of this study.

Reply to general comment #2: Indeed. This study is the first stage in the full hydrogeological characterization of this aquifer system. The next step is to conduct the hydrogeochemical characterization of recharge and groundwater springs discharge to complement the results obtained in this work by focusing in relevant unsolved questions like (1) the role play by the epikarst zone in the total transit time of groundwater and how this role is reflected in the hydrogeochemical evolution of the springs discharge after important rainfall events and during low-flows and (2) the use of artificial tracers and environmental isotopes (34S, 15N, ..) to characterize not only the mean transit time (i.e. the first moment of the transit-time distribution) but also to profile the groundwater transit-time distribution in terms of fast, intermediate and slow groundwater flows. This investigation is crucial to evaluate the aquifer vulnerability. We have included this information in the last part of the discussion a section.

Reviewer #1 - General comment #3: Compare the results of this study with similar studies.

Reply to general comment #3: A comparation in terms the mean transit time associated to the hydrological karst systems of Port del Comte and Ordesa and Monte Perdido (Jódar et al. 2016b) was already included in the manuscript. Nevertheless, and following the reviewer suggestions, additional comparations with the results obtained by Einsiedl et al. (2012), Garvelmann et al. (2017), and Lauber and Goldscheider (2014) for alpine karst aquifer systems with an overlying unsaturated have been included in the manuscript.

Specific comments

Introduction

Reviewer #1 – Q1: L 76-81: Including all this reference is not useful. You have to discuss this works. I suggest retaining two or three and the rest to remove them in the discussion only if you have something important to provide. Also, I suggest including information from karst systems from other Mediterranean countries (e.g. From Italy, Greece etc. see suggested literature).

Answer to Reviewer #1 – Q1: Indeed. We have rephrased the paragraph while synthetizing the cited references. Additionally, and as the reviewer suggests, the references of Allocca et al., (2015) and Kazakis et al. (2018) have been added to this paragraph to include in the storyline a link to Mediterranean karst systems

Reviewer #1 – Q2: Provide the innovation of this study. It is not clear to me. (Characterization of the hydrological behaviour of karst aquifer is not enough for an international journal)

Answer to Reviewer #1 – Q2: As it’s commented in the eply to “general comment #1”, the study adapts procedural approach to estimate the mean transit time in mountain karst aquifers by using a semi-distributed conceptual rainfall-runoff model and a lumped parameter model combined in a row. The first model explicitly provides the aquifer recharge time series that is used by the second model for simulating the environmental tracer transport through the hydrological system, and hence obtaining the aquifer mean transit time. Besides, the methodology has been applied in the karst aquifer system of Port del Comte (NE Spain) characterizing for first time the hydrological behaviour of this important karst system. Moreover, this work provides an additional value of the vertical gradient of the amplitude associated to the seasonal variation of the water isotopic content (δ18O and δ2H) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in Table 4 of the manuscript) to correctly estimate the groundwater mean transit time when amplitude dumping method (Eq. 8 of the manuscript) is applied. We have modified accordingly both the Abstract and the Introduction to highlight these points.

Methodology

Reviewer #1 – Q3: Methodology: You can add photos of the karst spring and the cumulative precipitation gauges (maybe in supplementary materials)

Answer to Reviewer #1 – Q3: Following the reviewer suggestion photos from the main regional karst spring (S-1, S-2, S-3 and S-5) and also from the 8 cumulative precipitation gauges have been added as supplementary materials:

- Supplementary materials #1: Main regional karst springs of the Port del Comte massif (S-1, S-2, S-3 and S-5)
- Supplementary materials #2: The 8 cumulative precipitation gauges (pluviometers) used of the type CoCoRaHS RG202 Official-4

Results and discussion

Reviewer #1 – Q4: L 425-426: You plot the results in GMWL. What is the meaning of this? It provides altitude? Origin? You have to explain it. Discussion is actually missing. See also my previous comment.

Answer to Reviewer #1 – Q4: In the caption of the Figure 6 (Fig 5 in the new version) is explained the meaning of this acronym GMWL, which means the Global Meteoric Water Line. It is used to represent the isotopic variation of the rain globally. The position of the water samples isotopic composition respect to the GMWL indicates the origin of moisture generating rainfall and also indicates fractionation processes (e.g. evaporation, sublimation) affecting groundwater recharge. We have included the reference of Clarke and Fritz (1997) to help the reader if any question arise in this regard.

Conclusions

Reviewer #1 – Q5: Provide only the take home message. Avoid abbreviations in this section (e.g. The PCM.)

Answer to Reviewer #1 – Q5: Indeed. According to the reviewer suggestion we have modified the conclusions to summarize the important findings

COMMENTS FROM REVIEWERS: Reviewer #2

General comments

Reviewer #2 - General comment #1: This manuscript deals with the hydrological characterization of the karst aquifer system of the Port del Comte (NE of Spain) using stable isotopes. Specific objectives are to describe the isotopic seasonal variation of precipitation and springs to understand the groundwater flow time distribution by means of a semidistributed hydrological model and lumped parameter flow models. In my opinion, this work deserves to be published in Science of the Total Environment after a minor revision because the topic is highly relevant for the water resources management of the Barcelona city area.

The manuscript firstly presents a general introduction, describes in great detail the study area and the methodology, before showing and discussing results and finally giving a concluding section. I consider that the manuscript is well-written and presented but some sections (i.e., the methodology and study area) are extremely long and it might be a good idea to move some information to the Supplementary Material as well as some of the Figures and Tables. This might help to the better understanding of the manuscript.

Reply to general comment #1: Thank you very much for your comments. Following the reviewer suggestion, the sections ”Study area” and “Materials and methods” have been restructured to make them shorter, thus facilitating the reading.

Specific comments

Reviewer #2 – Q1: Graphical Abstract: The authors might consider including some numbers such as the average isotopic composition of the precipitation and groundwater considering the elevation and the transit time distribution.

Answer to Reviewer #2- Q1: Indeed. These numbers certainly improve the understanding of the graphical abstract. According to the reviewer suggestion, we have added the mean isotopic content values corresponding to pluviometers P-02 (Bassa Clot de la Vall Z= 1946 m a.s.l), P-03 (Refugi Bages Z= 1768, m a.s.l.) and P-04 (Casa X&A Bages Z= 1657, m a.s.l.), and also the mean isotopic content of the regional spring S-05 (Fonts del Cardener).

Highlights

Reviewer #2 – Q2: The acronym PCM needs to be described in the second highlight.

Answer to Reviewer #2- Q2: Indeed. We have rephrased the sentence.

Keywords

Reviewer #2 – Q3: I suggest the term "stable" instead of "environmental" isotopes

Answer to Reviewer #2- Q3: This word has been changed. Thank you for the observation.

Abstract and introduction

Reviewer #2 – Q4: The abstract properly summarizes the main findings of this research and the introduction content is appropriate. I do not have any major comment.

Answer to Reviewer #2– Q4: Thank you very much.

Reviewer #2 – Q5: L75: GW is not the first time that is mentioned, I think.

Answer to Reviewer #2– Q5: Thanks for catching this. We have defined the acronym the first time we mention Groundwater in the manuscript.

Reviewer #2 – Q6: Study area: Figure 1. a) The font size of the figure 1b is too small. b) Why the authors chose this geological cross section?

Answer to Reviewer #2– Q6: a) according to the reviewer suggestion, the image has been enlarged and the font size has been increased. b) The previous geological cross-section □□□ shows the structure of the sub-basin for one of the most important springs in the zone: the spring S-05. The idea was including this section to explain how the existing faults but also the geometry of the different layer materials condition both storage capacity and flow direction inside the aquifer. Nevertheless, and from a geological point of view, it is indeed better to add at least one more geological cross-section following a perpendicular direction to the previous one, to show the structure of the massif along a N-S direction. According to this, a new geological cross-section has been added. Therefore, the first previous cross-section is now identified as A-B, and the new second one as C-D.

Reviewer #2 – Q7: L123-124: a) Is there no dry season? B) Please, indicate the period of time used to evaluate the average precipitation per month in the meteorological station MS-01.

Answer to Reviewer #2– Q7:

According to the 'Iberian Climate Atlas: Air temperature and precipitation (1971-2000)' (Agencia Estatal de Meteorología de España (AEMET) and Instituto de Meteorologia – Portugal (IMA). 2011), the Köppen Climate Classification for the study area is 'Dfb type' (defined as 'cold without dry season and temperate summer'). The reference can be consulted in the following link:
https://www.aemet.es/documentos/es/conocermas/publicaciones/Atlas-climatologico/Atlas.pdf

This information has been included in the manuscript.

b) Indeed. The time period to evaluate the monthly average precipitation in MS-01 is comprised between September 2005 and April 2016. This information has been included in the figure caption.

Reviewer #2 – Q8: Table 1 might be supplementary material

Answer to Reviewer #2- Q8: The information contained in Table 1 is referenced in several places along the manuscript. To facilitate the reading of the manuscript we consider that it is better to maintain this table in its original position.

Reviewer #2 – Q9: Materials and methods: This section is extremely long and the authors might consider moving some parts of the text to the Appendix or Supplementary material.

Answer to Reviewer #2- Q9: According to the reviewer comments, we have moved some parts of the manuscript at a new Appendix A. In particular, the original 'Figure 4' and 'Table 2' have been moved to an Appendix.

Reviewer #2 – Q10: L215-216: Position of "only" in the sentence: "groundwater samples were only taken with uneven frequency when it was possible".

Answer to Reviewer #2- Q10: Thanks for catching this. It has been changed.

Reviewer #2 – Q11: L233-234: I would recommend moving these lines to the supplementary material.

Answer to Reviewer #2- Q11: We suppose there is a mistake in the line numbering of this comment. In our opinion, these two lines (233-234) are necessary to following up the paragraph.

Reviewer #2 – Q12: L255: Method

Answer to Reviewer #2- Q12: Indeed. The sentence has been rephrased.

Reviewer #2 – Q13: Fig 5: might be supplementary material.

Answer to Reviewer #2- Q13: The schematic representation of the groundwater system response to a hypothetical input tracer function is a corner stone concept of this research. The authors consider that maintaining this figure in the main body of the manuscript facilitates the comprehension and reading of the text.

Reviewer #2 – Q14: L367: Might it be Eq. 5?

Answer to Reviewer #2- Q14: Indeed. Thank you for the observation. We have modified that number.

Reviewer #2 – Q15: Results and discussion: The results are discussed and presented in a detailed manner. Table 5: Might it be Supplementary material?

Answer to Reviewer #2- Q15: This table provides unpublished important data regarding the amplitude associated to the seasonal variation of the water isotopic content ($\delta^{18}O$ and $\delta^{2}H$) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in this table) to correctly estimate the groundwater mean transit time when the amplitude dumping method (Eq. 8 of the manuscript) is applied. As stated in the abstract, this is one of the important findings of this work.

Reviewer #2 – Q16: L554-570: This equation and the associated text might be in the methodology.

Answer to Reviewer #2– Q16: Indeed. According to the reviewer suggestion, we have moved this part on the Methodology section inside a new sub-chapter named '3.5. Statistical analysis of the relationship between infiltration coefficient and recharge'.

Reviewer #2 – Q17: L635-658: In my opinion these lines break the flow of this section. The authors can consider include a new subsection explaining the implications of the estimation of dynamic volume stored in the aquifer for the springs in the management of water resources in Barcelona.

Answer to Reviewer #2– Q17: The authors fully agree with the reviewer's opinion. This part has been moved inside a new sub-section named "Evolution of results for groundwater management purposes".

COMMENTS FROM REVIEWERS: Reviewer #3

General Comment: The authors present the results of a groundwater modeling study of an aquifer in the Pyrenees. The topic is cogently introduced, the methodology is comprehensively explained, and the results are clearly presented and supported via high quality figures.

Overall, I think the work is well-developed and deserving of publication. I just have one major comment, and one minor comment, which I think should be addressed in revision.

Thank you very much for your kind comments

Reviewer #3 – Q1: First, a minor note: I generally disagree with the use of words like "proven" and "perfect" in research papers. In reality, these terms describe unattainable thresholds. Regardless of whether the authors might maintain they observed a "perfect mixing" in groundwater at their sites, the term rankles even the causal reader, and should be replaced.

Answer to Reviewer #3– Q1: The term 'perfect or complete mixing' is a term that can be easily found in the groundwater related bibliography when it is focussed on lumped parameter models. These models are commonly used to estimate mean transit time of hydrological systems. Despite of that, the authors fully agree with the reviewer point of view, and the terms "perfect mixing flow process" and "perfect mixing model" have been replaced by the terms "good mixing flow process" and "exponential flow model", respectively, throughout the manuscript

Reviewer #3 – Q2: As for my primary criticism, in its current form, the manuscript is a bit too close to a technical report, given the limited scope of the work and the authors' conclusions. It is obviously acceptable for a groundwater study to focus on a single aquifer. However, if the results of the work remain essentially descriptive, the work itself remains limited in applicability to a single site. Instead, I suggest the authors develop the discussion of their results to clearly note and illustrate what their work contributes to the broader discipline (other than the characterization of a single, previously uncharacterized aquifer), and how their results pertain to aquifers globally. Such discussion will increase the impact of the work and justify publication of the manuscript in an international journal.

Answer to Reviewer #3– Q2: Thank you for the sincere suggestion. Indeed, the former version of the manuscript did not focus on relevant aspects such as the applicability and usefulness of the applied methodology, which clearly improves what has been done so far when estimating groundwater transit times in high mountain kast systems with an overlaying thick unsaturated zone. In this sense, the manuscript has been modified, highlighting the key innovations, and discussing the obtained results. Additionally, a deep bibliographic revision has been conducted to find studies focused on characterizing the hydrological behaviour of high mountain karst systems with an overlying not saturated zone to compare with. Unfortunately, the search has not been very successful and only four publication were found. The scarce number of publications reflects the difficulties for characterizing such hydrological systems rather than the existence of only a small number of alpine hydrological karst systems with an overlying thick unsaturated zone. In this line, we have included in the manuscript a list of sites with similar hydrogeological settings (i.e. a high mountain karst aquifer with a thick unsaturated zone) than those of the Port del Comte Massif (PCM). The location of these sites is presented in a new figure that also shows the carbonate outcrops in Europe. Looking at the figure one realizes that the number of sites analogue to PCM might be much larger.

COMMENTS FROM REVIEWERS: Reviewer #4

General Comment: I think that this research has very interesting results, the methodology is well described and the study area description is of a good quality. The figures also are of a good quality. The conclusions are well sustained by data. There are some general concerns that I suggest to the authors in order to improve the manuscript, being the first one critical:

Thank you very much for your kind comments

Reviewer #4 – Q1: I feel that the results are too localized to the study site being investigated or some other areas that some of the authors have already published in Spain and a more general setting is needed, comparing the results and the methodological approach in other climates regimes. To declare what is the novelty of the work and why is so an important contribution to scientific knowledge.

Answer to Reviewer #4– Q1: The authors fully agree with the reviewer. The original work did not focus on the key aspects from a global perspective, including the applicability and usefulness of the applied methodology. In this sense, the introduction has been modified to highlight the novelty and importance of this work. Additionally, a deep bibliographic revision has been conducted to find studies focused on characterizing the hydrological behaviour of high mountain karst systems with an overlying not saturated zone to compare with. Unfortunately, the search has not been very successful and only five publication were found. Despite of that, the results of these studies are compared with the obtained in our manuscript. The scarce number of publications reflects the difficulties for characterizing such hydrological systems rather than the existence of only a small number of alpine hydrological karst systems with an overlying thick unsaturated zone. In this line, we have included in the manuscript a list of sites with similar hydrogeological settings (i.e. a high mountain karst aquifer with a thick unsaturated zone) than those of the Port del Comte Massif (PCM). The location of these sites is presented in a new figure that also shows the carbonate outcrops in Europe. Looking at the figure one realizes that the number of sites analogue to PCM might be much larger.

Reviewer #4 – Q2: The second issue is that more schematic geological profiles are needed to fully understand the aquifer geometry.

Answer to Reviewer #4– Q2: Indeed. A new geological cross-section has been included in Figure 1. The new section is orthogonal to the previous one and improves the understanding of the whole geometry of the Port del Comte Massif.

Reviewer #4 – Q3: The third and final issue is the abstract. Its need some rewriting will improve its quality, because some ideas are repeated, like the realization of the isotopic study.

Answer to Reviewer #4– Q3: Thanks for catching this. The abstract has been changed accordingly.

To whom concern:

The Port del Comte karst aquifer system discharges into the Cardener River, the most important tributary of the populated Llobregat River basin that provides drinking water to the city of Barcelona (NE Spain), where the population is larger than 2 million people, and where more than 70% of the water supply derives from surface waters. These waters also feed one of the major groundwater reservoirs for the Barcelona area, the aquifers of the Llobregat Delta (Otero et al., 2008). Surprisingly, the hydrological behavior of this important mountain karst system is still unknown.

In addition, high mountain environments are very sensitive to water driving vectors such the hydro-climatic forcing expected to be generated by climate change. Management and preservation of these water dependent systems requires a thorough understanding of the processes governing the hydrologic behavior of these systems. Furthermore, it is extremely important to characterize the hydrological behavior of the hydrological systems located in the mountain zones since they can be used as early warning system of water shortage events to minimize the impact of such events in the low valley zones.

Processes such as precipitation, evapotranspiration, aquifer recharge and runoff generation which force and describe the hydrological systems response also belong to the main knowledge areas considered by Science of the Total Environment, by including the atmosphere, hydrosphere, biosphere, lithosphere, and anthroposphere.

Barcelona, 20/09/2018

The authors: Ignasi Herms. Jorge Jódar, Albert Soler, Iñaki Vadillo, Luis Javier Lambán, Sergio Martos-Rosillo, Joan Agustí Núñez, Georgina Arnó, and Joan Jorge

Contribution of isotopic research techniques to characterize high-mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer.

Herms. I.[a], Jódar, J.[b,*], Soler, A.[c], Vadillo, I.[d], Lambán, L.J.[e], Martos-Rosillo, S.[e], Núñez, J.A.[a], Arnó, G.[a], Jorge, J.[f]

(a) Àrea de Recursos Geològics. Institut Cartogràfic i Geològic de Catalunya (ICGC), Barcelona, Spain

(b) Groundwater Hydrology Group. Dept. Civil Engineering and Environment, Technical University of Catalonia (UPC), Barcelona, Spain & Aquageo Proyectos S.L., Spain

(c) Grup de Mineralogia Aplicada i Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

(d) Centro de Hidrogeología, Universidad de Málaga (UMA), Málaga, Spain

(e) Instituto Geológico Minero de España (IGME), Spain

(f) Departament d'Enginyeria Minera, Industrial i TIC. Universitat Politècnica de Catalunya (UPC), Manresa, Spain

* Corresponding author: Jorge Jódar (jorge.jodar@hydromodelhost.com). Telf:(+34) 619712122

Dear Professor Damià Barcelo, Co-Editor in Chief of Science of the Total Environment

Manuscript. No.: STOTEN-D-18-10315

Title: "**Contribution of isotopic research techniques to characterize high-mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer**."

First of all we want to thank you and the reviewers for the effort of reviewing the manuscript.

We have corrected the manuscript by accounting the reviewer's sugestions.

Sincerely,

Ignasi Herms Canellas, M.Sc.
Jorge Jódar Bermúdez, Ph.D.
Albert Soler Gil, Ph.D.
Iñaki Vadillo Pérez, Ph.D.
Luis Javier Lambán Jiménez, Ph.D.
Sergio Martos Rosillo, Ph.D.
Joan Agustí Núñez, M.Sc.
Georgina Arnó Pons, B.Sc.
Joan Jorge Sánchez, Ph.D.

COMMENTS FROM REVIEWERS: Reviewer #1

General comments

Thee paper by Herms et al. with title: "Contribution of isotopic research techniques to characterize high mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer." provides an interesting study regarding the contribution of isotopic research in karst aquifers. The concept is interest and the manuscript well written.

Thank you very much for your kind comments

However, I have a number of recommendations, which should be done before publication.

Abstract

Reviewer #1 - General comments #1: You have to include the innovative results of this study. Provide the innovation of this study:

Reply to general comment #1: Certainly, as the reviewer points, the innovative points of this study are not stated in the manuscript. In this regard, the study presents two innovations: (1) a global innovation and (2) the specific innovation with the case study.

(1) The study presents the adaptation of a procedural methodology to improve the estimation of the mean transit time (τ) in high-mountain karst aquifers. The methodology is based on the previous approach presented by Vitvar et al., 1999 to estimate groundwater residence times in pre-alpine non-karstic aquifers (tertiary and quaternary deposits in a small basin with elevation ranges between 680 to 960 m a.s.l.) by means of developing a link between distributed rainfall-runoff models to estimate recharge series, and then a lumped-parameter model using environmental tracers to solve the convolution integral. In our case the method is adapted to estimate τ in high-mountain karst systems taking into account the existing vertical gradients of precipitation and air temperature along the slope of high mountains, the role played by the snow accumulation and ablation processes in the runoff generation, and considering the hydrological system to be modelled as the whole aquifer (i.e. the unsaturated zone and saturated zones).

(2) The adapted methodology is applied to the Port del Comte high mountain karst aquifer (NE, Spain) as a practical case study. Despite the strategic role played by this hydrogeological system as water resource provider to Barcelona, the hydrological behaviour of this system is completely unknown. This is the first hydrodynamic and transit time characterization of this hydrological system. Besides, the isotopic characterization of rainfall conducted in the Port del Comte has allowed to estimate the vertical gradient of the amplitude associated to the seasonal variation of the isotopic content ($\delta^{18}O$ and δ^2H) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in Table 4 of the manuscript) to correctly estimate the groundwater mean transit time when amplitude dumping method (Eq. 8 of the manuscript) is applied.

We have modified accordingly both the Abstract and the Introduction to highlight these points.

Reviewer #1 - General comment #2: Provide the future works to be implemented to generalize the results of this study.

Reply to general comment #2: Indeed. This study is the first stage in the full hydrogeological characterization of this aquifer system. The next step is to conduct the hydrogeochemical characterization of recharge and groundwater springs discharge to complement the results obtained in this work by focusing in relevant unsolved questions like (1) the role play by the epikarst zone in the total transit time of groundwater and how this role is reflected in the hydrogeochemical evolution of the springs discharge after important rainfall events and during low-flows and (2) the use of artificial tracers and environmental isotopes (^{34}S, ^{15}N, ..) to characterize not only the mean transit time (i.e. the first moment of the transit-time distribution) but also to profile the groundwater transit-time distribution in terms of fast, intermediate and slow groundwater flows. This investigation is crucial to evaluate the aquifer vulnerability. We have included this information in the last part of the discussion a section.

Reviewer #1 - General comment #3: Compare the results of this study with similar studies.

Reply to general comment #3: A comparation in terms the mean transit time associated to the hydrological karst systems of Port del Comte and Ordesa and Monte Perdido (Jódar et al. 2016b) was already included in the manuscript. Nevertheless, and following the reviewer suggestions, additional comparations with the results obtained by Einsiedl et al. (2012), Garvelmann et al. (2017), and Lauber and Goldscheider (2014) for alpine karst aquifer systems with an overlying unsaturated have been included in the manuscript.

<u>Specific comments</u>

Introduction

Reviewer #1 – Q1: L 76-81: Including all this reference is not useful. You have to discuss this works. I suggest retaining two or three and the rest to remove them in the discussion only if you have something important to provide. Also, I suggest including information from karst systems from other Mediterranean countries (e.g. From Italy, Greece etc. see suggested literature).

Answer to Reviewer #1 – Q1: Indeed. We have rephrased the paragraph while synthetizing the cited references. Additionally, and as the reviewer suggests, the references of Allocca et al., (2015) and Kazakis et al. (2018) have been added to this paragraph to include in the storyline a link to Mediterranean karst systems

Reviewer #1 – Q2: Provide the innovation of this study. It is not clear to me. (Characterization of the hydrological behaviour of karst aquifer is not enough for an international journal)

Answer to Reviewer #1 – Q2: As it's commented in the eply to "general comment #1", the study adapts procedural approach to estimate the mean transit time in mountain karst aquifers by using a semi-distributed conceptual rainfall-runoff model and a lumped parameter model combined in a row. The first model explicitly provides the aquifer recharge time series that is used by the second model for simulating the environmental tracer transport through the hydrological system, and hence obtaining the aquifer mean transit time. Besides, the methodology has been applied in the karst aquifer system of Port del Comte (NE Spain) characterizing for first time the hydrological behaviour of this important karst system. Moreover, this work provides an additional value of the vertical gradient of the amplitude associated to the seasonal variation of the water isotopic content (δ18O and δ2H) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in Table 4 of the manuscript) to correctly estimate the groundwater mean transit time when amplitude dumping method (Eq. 8 of the manuscript) is applied. We have modified accordingly both the Abstract and the Introduction to highlight these points.

Methodology

Reviewer #1 – Q3: Methodology: You can add photos of the karst spring and the cumulative precipitation gauges (maybe in supplementary materials)

Answer to Reviewer #1 – Q3: Following the reviewer suggestion photos from the main regional karst spring (S-1, S-2, S-3 and S-5) and also from the 8 cumulative precipitation gauges have been added as supplementary materials:

- Supplementary materials #1: Main regional karst springs of the Port del Comte massif (S-1, S-2, S-3 and S-5)
- Supplementary materials #2: The 8 cumulative precipitation gauges (pluviometers) used of the type CoCoRaHS RG202 Official-4

Results and discussion

Reviewer #1 – Q4: L 425-426: You plot the results in GMWL. What is the meaning of this? It provides altitude? Origin? You have to explain it. Discussion is actually missing. See also my previous comment.

Answer to Reviewer #1 – Q4: In the caption of the Figure 6 (Fig 5 in the new version) is explained the meaning of this acronym GMWL, which means the Global Meteoric Water Line. It is used to represent the isotopic variation of the rain globally. The position of the water samples isotopic composition respect to the GMWL indicates the origin of moisture generating rainfall and also indicates fractionation processes (e.g. evaporation, sublimation) affecting groundwater recharge. We have included the reference of Clarke and Fritz (1997) to help the reader if any question arise in this regard.

Conclusions

Reviewer #1 – Q5: Provide only the take home message. Avoid abbreviations in this section (e.g. The PCM.)

Answer to Reviewer #1 – Q5: Indeed. According to the reviewer suggestion we have modified the conclusions to summarize the important findings

COMMENTS FROM REVIEWERS: Reviewer #2

General comments

Reviewer #2 - General comment #1: This manuscript deals with the hydrological characterization of the karst aquifer system of the Port del Comte (NE of Spain) using stable isotopes. Specific objectives are to describe the isotopic seasonal variation of precipitation and springs to understand the groundwater flow time distribution by means of a semidistributed hydrological model and lumped parameter flow models. In my opinion, this work deserves to be published in Science of the Total Environment after a minor revision because the topic is highly relevant for the water resources management of the Barcelona city area.

The manuscript firstly presents a general introduction, describes in great detail the study area and the methodology, before showing and discussing results and finally giving a concluding section. I consider that the manuscript is well-written and presented but some sections (i.e., the methodology and study area) are extremely long and it might be a good idea to move some information to the Supplementary Material as well as some of the Figures and Tables. This might help to the better understanding of the manuscript.

Reply to general comment #1: Thank you very much for your comments. Following the reviewer suggestion, the sections ”Study area” and “Materials and methods” have been restructured to make them shorter, thus facilitating the reading.

Specific comments

Reviewer #2 – Q1: Graphical Abstract: The authors might consider including some numbers such as the average isotopic composition of the precipitation and groundwater considering the elevation and the transit time distribution.

Answer to Reviewer #2– Q1: Indeed. These numbers certainly improve the understanding of the graphical abstract. According to the reviewer suggestion, we have added the mean isotopic content values corresponding to pluviometers P-02 (Bassa Clot de la Vall Z= 1946 m a.s.l), P-03 (Refugi Bages Z= 1768, m a.s.l.) and P-04 (Casa X&A Bages Z= 1657, m a.s.l.), and also the mean isotopic content of the regional spring S-05 (Fonts del Cardener).

Highlights

Reviewer #2 – Q2: The acronym PCM needs to be described in the second highlight.

Answer to Reviewer #2– Q2: Indeed. We have rephrased the sentence.

Keywords

Reviewer #2 – Q3: I suggest the term "stable" instead of "environmental" isotopes

Answer to Reviewer #2– Q3: This word has been changed. Thank you for the observation.

Abstract and introduction

Reviewer #2 – Q4: The abstract properly summarizes the main findings of this research and the introduction content is appropriate. I do not have any major comment.

Answer to Reviewer #2– Q4: Thank you very much.

Reviewer #2 – Q5: L75: GW is not the first time that is mentioned, I think.

Answer to Reviewer #2– Q5: Thanks for catching this. We have defined the acronym the first time we mention Groundwater in the manuscript.

Reviewer #2 – Q6: Study area: Figure 1. a) The font size of the figure 1b is too small. b) Why the authors chose this geological cross section?

Answer to Reviewer #2– Q6: a) according to the reviewer suggestion, the image has been enlarged and the font size has been increased. b) The previous geological cross-section α–β shows the structure of the sub-basin for one of the most important springs in the zone: the spring S-05. The idea was including this section to explain how the existing faults but also the geometry of the different layer materials condition both storage capacity and flow direction inside the aquifer. Nevertheless, and from a geological point of view, it is indeed better to add at least one more geological cross-section following a perpendicular direction to the previous one, to show the structure of the massif along a N-S direction. According to this, a new geological cross-section has been added. Therefore, the first previous cross-section is now identified as A-B, and the new second one as C-D.

Reviewer #2 – Q7: L123-124: a) Is there no dry season? B) Please, indicate the period of time used to evaluate the average precipitation per month in the meteorological station MS-01.

Answer to Reviewer #2– Q7:

According to the 'Iberian Climate Atlas: Air temperature and precipitation (1971-2000)' (Agencia Estatal de Meteorología de España (AEMET) and Instituto de Meteorologia – Portugal (IMA). 2011), the Köppen Climate Classification for the study area is 'Dfb type' (defined as 'cold without dry season and temperate summer'). The reference can be consulted in the following link:
https://www.aemet.es/documentos/es/conocermas/publicaciones/Atlas-climatologico/Atlas.pdf

This information has been included in the manuscript.

b) Indeed. The time period to evaluate the monthly average precipitation in MS-01 is comprised between September 2005 and April 2016. This information has been included in the figure caption.

Reviewer #2 – Q8: Table 1 might be supplementary material

Answer to Reviewer #2– Q8: The information contained in Table 1 is referenced in several places along the manuscript. To facilitate the reading of the manuscript we consider that it is better to maintain this table in its original position.

Reviewer #2 – Q9: Materials and methods: This section is extremely long and the authors might consider moving some parts of the text to the Appendix or Supplementary material.

Answer to Reviewer #2– Q9: According to the reviewer comments, we have moved some parts of the manuscript at a new Appendix A. In particular, the original '**Figure 4'** and '**Table 2'** have been moved to an Appendix.

Reviewer #2 – Q10: L215-216: Position of "only" in the sentence: "groundwater samples were only taken with uneven frequency when it was possible".

Answer to Reviewer #2– Q10: Thanks for catching this. It has been changed.

Reviewer #2 – Q11: L233-234: I would recommend moving these lines to the supplementary material.

Answer to Reviewer #2– Q11: We suppose there is a mistake in the line numbering of this comment. In our opinion, these two lines (233-234) are necessary to following up the paragraph.

Reviewer #2 – Q12: L255: Method

Answer to Reviewer #2– Q12: Indeed. The sentence has been rephrased.

Reviewer #2 – Q13: Fig 5: might be supplementary material.

Answer to Reviewer #2– Q13: The schematic representation of the groundwater system response to a hypothetical input tracer function is a corner stone concept of this research. The authors consider that maintaining this figure in the main body of the manuscript facilitates the comprehension and reading of the text.

Reviewer #2 – Q14: L367: Might it be Eq. 5?

Answer to Reviewer #2– Q14: Indeed. Thank you for the observation. We have modified that number.

Reviewer #2 – Q15: Results and discussion: The results are discussed and presented in a detailed manner. Table 5: Might it be Supplementary material?

Answer to Reviewer #2– Q15: This table provides unpublished important data regarding the amplitude associated to the seasonal variation of the water isotopic content (δ18O and δ2H) in rainfall, an important but rarely reported parameter (only two additional references exist as reported in this table) to correctly estimate the groundwater mean transit time when the amplitude dumping method (Eq. 8 of the manuscript) is applied. As stated in the abstract, this is one of the important findings of this work.

Reviewer #2 – Q16: L554-570: This equation and the associated text might be in the methodology.

Answer to Reviewer #2– Q16: Indeed. According to the reviewer suggestion, we have moved this part on the Methodology section inside a new sub-chapter named '3.5. Statistical analysis of the relationship between infiltration coefficient and recharge'.

Reviewer #2 – Q17: L635-658: In my opinion these lines break the flow of this section. The authors can consider include a new subsection explaining the implications of the estimation of dynamic volume stored in the aquifer for the springs in the management of water resources in Barcelona.

Answer to Reviewer #2– Q17: The authors fully agree with the reviewer's opinion. This part has been moved inside a new sub-section named "Evolution of results for groundwater management purposes".

COMMENTS FROM REVIEWERS: Reviewer #3

General Comment: The authors present the results of a groundwater modeling study of an aquifer in the Pyrenees. The topic is cogently introduced, the methodology is comprehensively explained, and the results are clearly presented and supported via high quality figures.

Overall, I think the work is well-developed and deserving of publication. I just have one major comment, and one minor comment, which I think should be addressed in revision.

Thank you very much for your kind comments

Reviewer #3 – Q1: First, a minor note: I generally disagree with the use of words like "proven" and "perfect" in research papers. In reality, these terms describe unattainable thresholds. Regardless of whether the authors might maintain they observed a "perfect mixing" in groundwater at their sites, the term rankles even the causal reader, and should be replaced.

Answer to Reviewer #3– Q1: The term 'perfect or complete mixing' is a term that can be easily found in the groundwater related bibliography when it is focussed on lumped parameter models. These models are commonly used to estimate mean transit time of hydrological systems. Despite of that, the authors fully agree with the reviewer point of view, and the terms "perfect mixing flow process" and "perfect mixing model" have been replaced by the terms "good mixing flow process" and "exponential flow model", respectively, throughout the manuscript

Reviewer #3 – Q2: As for my primary criticism, in its current form, the manuscript is a bit too close to a technical report, given the limited scope of the work and the authors' conclusions. It is obviously acceptable for a groundwater study to focus on a single aquifer. However, if the results of the work remain essentially descriptive, the work itself remains limited in applicability to a single site. Instead, I suggest the authors develop the discussion of their results to clearly note and illustrate what their work contributes to the broader discipline (other than the characterization of a single, previously uncharacterized aquifer), and how their results pertain to aquifers globally. Such discussion will increase the impact of the work and justify publication of the manuscript in an international journal.

Answer to Reviewer #3– Q2: Thank you for the sincere suggestion. Indeed, the former version of the manuscript did not focus on relevant aspects such as the applicability and usefulness of the applied methodology, which clearly improves what has been done so far when estimating groundwater transit times in high mountain kast systems with an overlaying thick unsaturated zone. In this sense, the manuscript has been modified, highlighting the key innovations, and discussing the obtained results. Additionally, a deep bibliographic revision has been conducted to find studies focused on characterizing the hydrological behaviour of high mountain karst systems with an overlying not saturated zone to compare with. Unfortunately, the search has not been very successful and only four publication were found. The scarce number of publications reflects the difficulties for characterizing such hydrological systems rather than the existence of only a small number of alpine hydrological karst systems with an overlying thick unsaturated zone. In this line, we have included in the manuscript a list of sites with similar hydrogeological settings (i.e. a high mountain karst aquifer with a thick unsaturated zone) than those of the Port del Comte Massif (PCM). The location of these sites is presented in a new figure that also shows the carbonate outcrops in Europe. Looking at the figure one realizes that the number of sites analogue to PCM might be much larger.

COMMENTS FROM REVIEWERS: Reviewer #4

General Comment: I think that this research has very interesting results, the methodology is well described and the study area description is of a good quality. The figures also are of a good quality. The conclusions are well sustained by data. There are some general concerns that I suggest to the authors in order to improve the manuscript, being the first one critical:

Thank you very much for your kind comments

Reviewer #4 – Q1: I feel that the results are too localized to the study site being investigated or some other areas that some of the authors have already published in Spain and a more general setting is needed, comparing the results and the methodological approach in other climates regimes. To declare what is the novelty of the work and why is so an important contribution to scientific knowledge.

Answer to Reviewer #4– Q1: The authors fully agree with the reviewer. The original work did not focus on the key aspects from a global perspective, including the applicability and usefulness of the applied methodology. In this sense, the introduction has been modified to highlight the novelty and importance of this work. Additionally, a deep bibliographic revision has been conducted to find studies focused on characterizing the hydrological behaviour of high mountain karst systems with an overlying not saturated zone to compare with. Unfortunately, the search has not been very successful and only five publication were found. Despite of that, the results of these studies are compared with the obtained in our manuscript. The scarce number of publications reflects the difficulties for characterizing such hydrological systems rather than the existence of only a small number of alpine hydrological karst systems with an overlying thick unsaturated zone. In this line, we have included in the manuscript a list of sites with similar hydrogeological settings (i.e. a high mountain karst aquifer with a thick unsaturated zone) than those of the Port del Comte Massif (PCM). The location of these sites is presented in a new figure that also shows the carbonate outcrops in Europe. Looking at the figure one realizes that the number of sites analogue to PCM might be much larger.

Reviewer #4 – Q2: The second issue is that more schematic geological profiles are needed to fully understand the aquifer geometry.

Answer to Reviewer #4– Q2: Indeed. A new geological cross-section has been included in Figure 1. The new section is orthogonal to the previous one and improves the understanding of the whole geometry of the Port del Comte Massif.

Reviewer #4 – Q3: The third and final issue is the abstract. Its need some rewriting will improve its quality, because some ideas are repeated, like the realization of the isotopic study.

Answer to Reviewer #4– Q3: Thanks for catching this. The abstract has been changed accordingly.

Contribution of isotopic research techniques to characterize high-mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer.

Herms. I.[a], Jódar, J.[b,*], Soler, A.[c], Vadillo, I.[d], Lambán, L.J.[e], Martos-Rosillo, S.[e], Núñez, J.A.[a], Arnó, G.[a], Jorge, J.[f]

(a) Àrea de Recursos Geològics. Institut Cartogràfic i Geològic de Catalunya (ICGC), Barcelona, Spain

(b) Groundwater Hydrology Group. Dept. Civil Engineering and Environment, Technical University of Catalonia (UPC), Barcelona, Spain & Aquageo Proyectos S.L., Spain

(c) Grup de Mineralogia Aplicada i Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

(d) Centro de Hidrogeología, Universidad de Málaga (UMA), Málaga, Spain

(e) Instituto Geológico Minero de España (IGME), Spain

(f) Departament d'Enginyeria Minera, Industrial i TIC. Universitat Politècnica de Catalunya (UPC), Manresa, Spain

* Corresponding author: Jorge Jódar (jorge.jodar@hydromodelhost.com). Telf:(+34) 619712122

Abstract

Water resources in high mountain karst aquifers are usually characterized by high rainfall, recharge and discharge that lead to the sustainability of the downstream ecosystems. Nevertheless, these hydrological systems are vulnerable to the global change impact. The mean transit time (MTT) is a key parameter to describe the behavior of these hydrologic systems and also to assess their vulnerability. This work is focused on estimating MTT by using environmental tracers in the framework of high-mountain karst systems with a very thick unsaturated zone (USZ). To this end, it is adapted to alpine zones a methodology that combines a semi-distributed rainfall-runoff model to estimate recharge time series, and a lumped-parameter model to obtain MTT. The methodology has been applied to the Port del Comte Massif (PCM) hydrological system (Southeastern Pyrenees, NE Spain), a karst aquifer system with an overlying1000 m thick USZ. Six catchment areas corresponding to most important springs of the system are considered. The obtained results show that hydrologically the behavior of the system can be described by an exponential flow model (EM), with MTT ranging between 1.9 and 2.9 years. These MTT values are shorter than those obtained by considering a constant recharge rate along time, which is the easiest and most applied aquifer recharge hypothesis when estimating MTT through lumped-parameter models.

Comment [JJ1]: Answer to Reviewer #1 – General comment 1
Answer to Reviewer #1 – Q2
Answer to Reviewer #4– Q3

Keywords: Stable isotopes; Seasonal isotopic amplitude; Altitudinal line; Recharge; Mean transit time; Karst.

Comment [JJ2]: Answer to Reviewer #2 – Q3

1. Introduction

High mountain zones are known as "water towers" because they generate the main water resources feeding the most important rivers in the world (Viviroli et al., 2007). This phenomenon is especially important in the drought-prone Mediterranean area (Vicente-Serrano et al 2014), where water availability is scarce and greatly dependent on runoff from headwater basins (De Jong et al., 2009). Moreover, water discharge from mountain areas is critical to ensure water supply in the lowland and coastal fringe

(Viviroli and Weingartner, 2004; García-Ruiz et al 2011), where human activity (agriculture, industry, tourism) concentrates.

Future scenarios for climate change in the whole Mediterranean region forecast an increase in temperature and a decrease in precipitation at the end of the 21^{st} century (Giorgi and Lionello, 2008). These effects may well impact the Mediterranean high mountain zones (Nogués-Bravo et al., 2008; Lopez-Moreno et al., 2009; Ribalaygua et al., 2013), modifying the hydrological behavior of their headwater basins (Barnett et al., 2005; García-Ruiz et al. 2011, and references therein). Nevertheless, the first evidence of such changes has already been reported in the Pyrenees, the southernmost European range where glaciers can be found (Grunewald and Scheithauer, 2010). Pyrenean glaciers have undergone an intense retreat since the middle of the last century, causing most of them to face a certain close extinction (Chueca et al., 2007; René 2013; Marti et al., 2015; López-Moreno et al., 2016). In addition, during this period, both mean annual precipitation and number of rainy days have shown a clear decreasing trend in this zone (Lopez-Moreno et al., 2010), along with a lesser snowfall and snow accumulation (López-Moreno, 2005). These effects directly impact the water storage capacity of the associated headwater systems (Seibert et al., 2015), as well as their associated hydrological response in terms of both river discharge flowrates and timing of maximum discharges (López-Moreno and García-Ruiz, 2004; Gremaud et al., 2009). These changes will directly impact the downstream zones by complicating the current water stress situation in the Mediterranean zone (Milano et al., 2013; Hernández-Mora et al., 2014, Molina and Melgarejo, 2016). Because of the hydrological outlook that is not so promising, it is essential to understand the functioning of the mountain hydrological systems of the Mediterranean area, especially those scenarios in which groundwater (GW) plays a major role in the headwater discharge, because mountain aquifers maintain base flows to rivers during the recurrent Mediterranean dry periods (Hoerling et al 2012; Vicente-Serrano et al., 2014).

Comment [JJ3]: Answer to Reviewer #21 – Q5

Despite playing a strategic role, most high mountain hydrogeological systems are still insufficiently understood (Goldscheider, 2011). Conventional hydrogeological investigation techniques (Bakalowicz, 2005; Goldscheider and Drew, 2007) are often difficult to apply in alpine regions because of the difficult access and the harsh working conditions, along with the types of instruments needed for conducting research in high mountain zones (Lauber et al., 2014; Hood and Hayashi, 2010). However, a growing number of publications are focusing on the importance of groundwater in the functioning of high-mountain watershed rivers in different geological settings, including alluvial/rockfall/talus aquifers (Lauber and Goldscheider, 2014; Kurylyk and Hayashi, 2017), fractured aquifers (Jódar et al., 2017; Barberá et al., 2018a) and karst systems (Wetzel, 2004; Goldscheider, 2005; Gremaud et al., 2009; Mudarra et al., 2014; Allocca et al., 2015; Lambán et al., 2015; Chen, 2017; Barberá et al., 2018b; Kazakis et al., 2018). Determining the magnitude of groundwater recharge and aquifer Mean Transit Time (MTT) are key issues for understanding and managing alpine groundwater systems. Spring hydrograph analysis and environmental tracer methods allow for characterizing aquifer recharge and discharge processes, estimating recharge zone elevation and transit times, determining drainage structures, and assessing spring vulnerability, as well as calculating water resources in headwater aquifers (Wetzel, 2004; Rodgers et al., 2005; Einsiedl, 2005; Farlin and Maloszewski, 2013; Jódar et al., 2016b; Malard et al., 2016; Epting et al., 2018).

Comment [JJ4]: Answer to Reviewer #1 – Q1

In high-altitude alpine karst aquifers, groundwater recharge processes highly depend on temporal and spatial distribution of precipitation and snowmelt (Lauber and Goldscheider, 2014). The estimation of MTT in karst systems is conditioned by the existence of variable flow conditions. These systems normally show triple-porosity and different connected parts: the karstic conduits that allows rapid flow, and the fissured-porous matrix that shows intermediate to slow flow. Artificial tracer test normally injected in preferential flow paths (i.e. the channels) doesn't consider the fissured-porous matrix of the aquifer, which can be important as far as the total karst water volumes (Maloszewski et al., 2002). In this respect, the use of artificial tracers to characterize such hydrological systems is not enough since it doesn't allow characterizing all the components of the flow. Others important factors that govern the suitability of injection test for MTT estimations is the existence of a thick unsaturated zones (USZ): conducting tracer tests by injecting it at the surface of the thick USZ is likely a failing tracer test given the large uncertainties regarding the likelihood of hydraulic connection between the tracer injection point and the sampled system discharge point (Lauber and Goldscheider, 2014). Additionally, the adverse working conditions and the type of material of the instruments necessary to correctly perform the tracer test (Goldscheider et al., 2008) in high-mountain areas make it difficult to execute them.

As a result, the hydrogeological behavior of most of the mountain karst systems with an associated thick USZ remain uncharacterized, despite of being the exploration of these systems on the focus of speleogenetic research since the last decades (Ballesteros et al., 2015a, and references therein).

Lumped parameter models (LPMs) are useful to simulate the behavior of such complex mountain karst systems, even when they are poorly characterized. These models do not require a detailed hydrological knowledge of the physical system. Moreover, LPMs naturally integrate the USZ of the aquifer as a part of the whole hydrological system to be modeled (Turnadge and Smerdon, 2014). Additionally, the stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$) in rainfall have proved to be good environmental tracers for investigating the dynamics of such hydrological systems karst systems (Andreo et al., 2004). These tracers enter the system as recharge, migrate downgradient exploring the whole hydrological system, and leave the karst aquifer with spring discharge or by lateral mass transfer to other hydrogeologically connected aquifer units. In this line, this work is devoted to estimate MTT of a high-mountain karst aquifer with a thick unsaturated zone by using ^{8}O and ^{2}H as environmental tracers along with LPMs. To this end, it is considered the approach presented by Vitvar et al. (1999) to estimate MTT in a small Swiss pre-alpine aquifer. The original approach is adapted to high mountain zones by considering the existing vertical gradients of precipitation and air temperature along the slope of high mountains, but also the role played by the snow accumulation and ablation processes in the runoff generation. The resulting method combines in series two LPMs: (1) a semi-distributed rainfall-runoff HBV model (Bergström, 1976; Seibert, 2005) that simulates the observed hydrodynamical system response while taking into account the elevation dependences of the different hydrometeorological variables (i.e. Precipitation and temperature) and associated processes (e.g. snow accumulation and ablation), and (2) a FlowPC model (Małoszewski and Zuber, 1996) that estimates the mean transit time of the hydrological system while simulating the environmental tracer content evolution in the system discharge. This is done by numerically integrating a convolution integral (Maloszewski et al., 1983; Jódar et al., 2014). In our case, the

FlowPC model uses as input data: a) the recharge time series of the aquifer obtained with the HBV model, and b) the time series isotope content ($\delta^{18}O$ and $\delta^{2}H$) in recharge, which is obtained through a spatiotemporal characterization of the isotope contained of precipitation.

The methodology is applied to the hydrological system of Port del Comte Massif (PCM; NE Spain), a karst aquifer with a 1000 m thick USZ. The hydrological system mainly discharges though the Cardener springs into the homonym river, which is the main tributary of the Llobregat River, the first water resources provider to the city of Barcelona (NE Spain). Despite the strategic role of Cardener springs the hydrologic behavior of the karst system remains unknown. This study contributes to a better hydrological characterization of PCM hydrological system. Moreover, the proposed methodology can be applied to characterize other high mountain karst aquifers with an overlying thick USZ that are common in many alpine zones elsewhere the globe.

Comment [JJ5]: Answer to Reviewer #1 - Gegeneral comment 1
Answer to Reviewer #1 – Q2

2. Study area

The study area is located at the Port del Comte Massif (PCM), which is situated in the eastern part of the Pyrenees, NE Spain (Fig. 1). The elevation of the watershed ranges from approximately 900 m a.s.l., up to 2387 m a.s.l., at the ‘Pedró dels Quatre Batlles’ peak. With approximately 110 km^2, it contains one of the main mountain karst aquifers of the Catalan Pyrenees. The watershed of the massif divides the river basin of the Cardener River at the E and S and the river basin of the Segre River at the NW and SW. The massif constitutes an independent structural and hydrogeological unit.

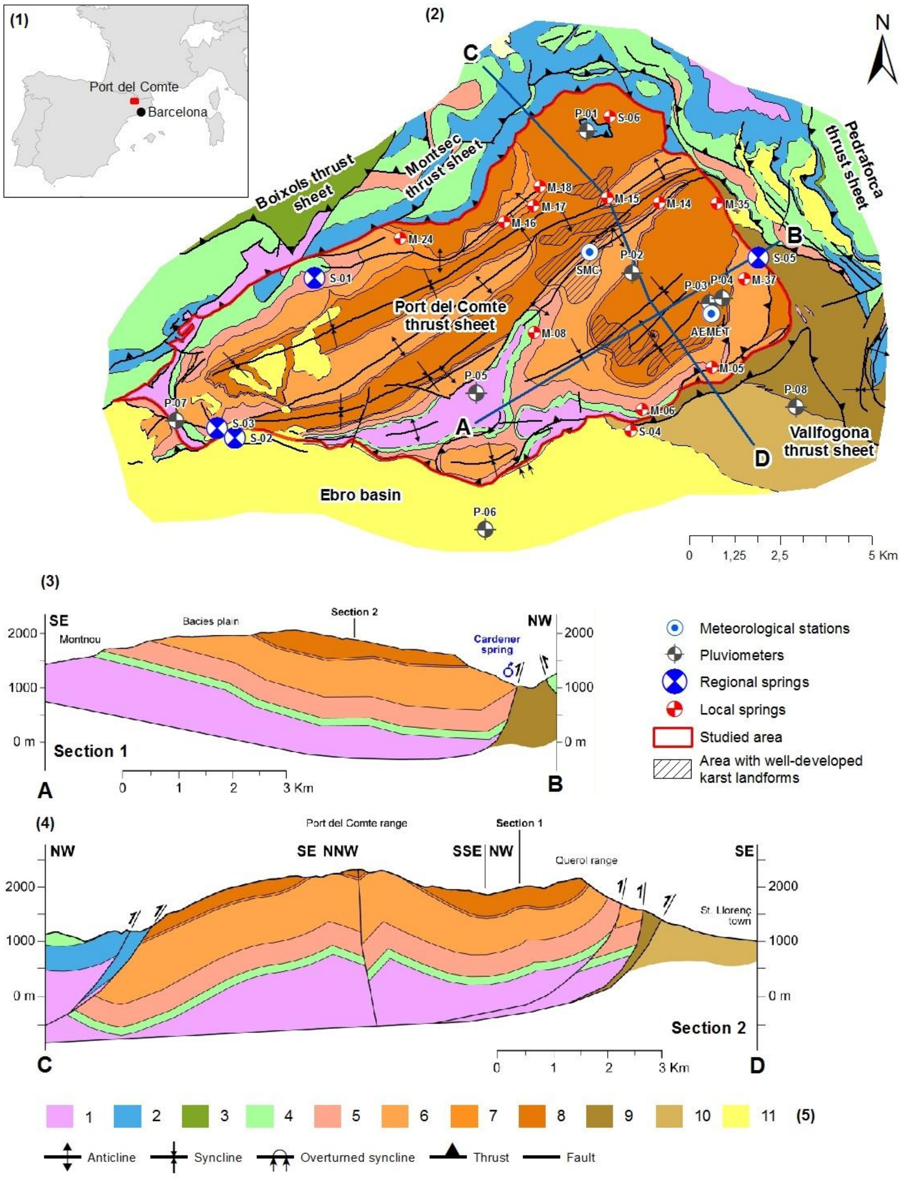


Fig. 1. (1) Location map of the study zone. (2) Geological map (geological map modified from ICGC, 2007). (3) Geological cross-section A-B. (4) Geological cross-section C-D. (5) Geological legend: [1] Triassic – shales, limestones, dolomites and evaporates; [2] Jurassic – marls, bioclastic limestones and dolomites; [3] Lower Cretaceous – mudstones, ammonite limestones and marl; [4] Upper Cretaceous – limestones, marls, calcarenites and terrigenous

Comment [JJ6]: Answer to Reviewer #2 – Q6
Answer to Reviewer #4– Q2

deposit; [5] Garumnian – red shales and limestones; [6] Lower Eocene – fissured and karstified alveoline limestones and dolomites; [7] Lower Eocene – marls, sandstones and limestone; [8] Lower Eocene – fissured and karstified micritic and bioclastic limestones; [9] Middle Eocene – sandstones, marls, conglomerates, limestones and evaporates; [10] Upper Eocene – continental alluvial systems: conglomerates and sandstones; [11] Oligocene – continental alluvial systems: conglomerates, breccias and sandstones.

2.1 Meteorological setting

From a climatic point of view, and according to the Köppen-Geiger classification (Peel et al., 2007), the study zone has a cold climate without dry season and temperate summer (defined as ‘Dfb’ type; accordingly to AEMET and IMA, 2011). At the meteorological station MS-01 (Fig. 1), which is located at 2315 m a.s.l., the average values of precipitation (P), temperature (T) and potential evapotranspiration (ETP) calculated with the Hargreaves and Samani (1982) equation are 1055 mm/yr, 3,24 °C and 525 mm/yr, respectively. These three variables show a seasonal variation (Fig. 2) and an elevation dependence. The measured vertical gradients (lapse rate) of precipitation (∇_zP), atmospheric temperature (∇_zT) and potential evapotranspiration (∇_zETP) are 8,9 mm/yr/100 m, −0,74 °C/100 m and −32,3 mm/yr/100 m, respectively. The snow cap is present in the upper zones of the basin in winter and spring, maintained annually for 3 to 4 months since 1800 m a.s.l., meaning that precipitation is partly produced as snow.

Despite the high average rainfall above 1000 mm/year, in most of the study area the surface runoff is almost nonexistent, and it is not observed until reaching lower altitudes.

Comment [JJ7]: Answer to Reviewer #2– Q7:

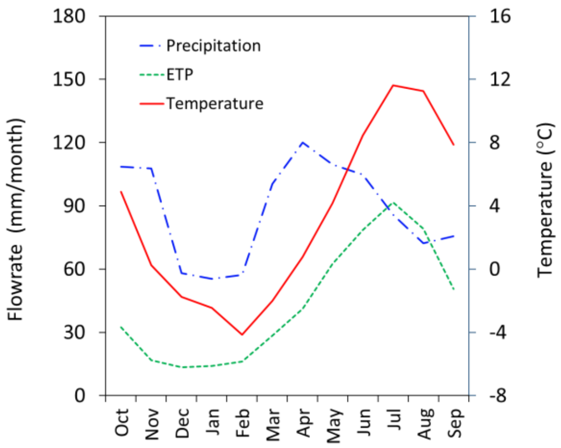


Fig. 2. Seasonal variation of precipitation, potential evapotranspiration and temperature measured at the meteorological station MS-01 (see Table 1) located at 2315 m a.s.l. for the period Sep 2005- Apr 2016.

Comment [JJ8]: Answer to Reviewer #2– Q7

2.2 General settings of the study zone

From a geological perspective, the massif belongs to the PCM thrust sheet that presents complex structural relationships in its contours (Fig. 1). On the E, the PCM mantle borders on the mantle of Cadí, coinciding with the point of origin for the Cardener River (spring S-05; Fig. 1). To the NE and NW, the PCM is limited by the tectonic plates of the mantles of Sierras Marginales, Montsec and Boixols. To the S, the PCM mantle overlaps with the conglomeratic materials of the Ebro Basin, the southern foreland basin of the Pyrenees. The internal structure of the PCM mantle is formed by a set of folds and thrusts detached above the Triassic. These folds have a constant direction NE-SW parallel to the NW limit of the mantle (Vergés, 1999). The stratigraphic series contains materials from the Triassic, Jurassic, Cretaceous and Paleogene with a total of approximately 1000 m thickness. The main karst aquifer inside PCM massif is in the Paleocene - Eocene carbonate rocks. The geologic structure and stratigraphy of the PCM thrust strongly influence the location of the existing karst springs, their groundwater geochemistry and their hydrologic behavior. The lower Upper Cretaceous/Paleocene (Garumnian facies) substrate materials underlying the Palaeocene aquifer are composed of sandstone, siltstone and shale. These materials constitute an impervious layer for the overlaying aquifer system.

From the geomorphological point of view, the PCM has a characteristic triangular geometry. The PCM has a smooth rounded landscape with a plain in the highest part without vegetation cover and with almost no soil, which corresponds to approximately 10% of the total area. The rest of the massif is covered by mountain meadows (29%) and forest (61%) with scarce soil depth up to medium developed soil cover. Different karstic forms progressively appear from 1950 m a.s.l. upwards, being well developed at 2050 m a.s.l., with sinkholes, dry caves, dolines and karren fields, generating a heterogeneous karstified hydrogeological system.

The hydrogeological conceptual model of the PCM aquifer system considers that recharge is produced by infiltration of precipitation as rainfall and snowmelt. The magnitude and distribution of infiltration is conditioned by the development of the karst landforms. The infiltration is produced (1) in a concentrated way through the local karstic elements such as dolines and (2) in a diffuse way by rain and snowmelt along the whole PCM area. The epikarst unsaturated zone (NSZ) presents a thickness close to 1000 m in the highest zones of the PCM. The infiltrated water flows vertically through the NSZ towards the saturated zone.

The hydrogeological system naturally discharges through the large number of existing springs. Approximately 100 springs have been found in the PCM showing large discrepancies in their mean discharge flow rate, ranging from values <<1 L/s up to values > 100 L/s. Most of these springs discharge a local subhorizontal interflow characteristic of a small entity (i.e., Local springs, Table 1). However, in terms of groundwater discharge, there are six important springs in the PCM (i.e., Regional springs, Table 1). These springs have been monitored regularly for this research, showing that all of them have a highly variable discharge flow rate (Fig. 3). Four of these regional springs (S-01, S-02, S-03 and S-05) are the principals discharging points of the whole hydrogeological system. The four springs are located at elevations between 944 and 1098 m a.s.l. (see Table 1). Through these main springs, the hydrogeological system discharges at two principal watersheds: the Cardener River watershed to the east and the Segre River watershed to the northwest. Groundwater flow direction is conditioned by the geological structure of PCM. Nevertheless, the exact position of the regional groundwater table is poorly known.

Table 1. Meteorological stations, pluviometers and springs in the study zone sampled during the period July 2013 – October 2015.

Code	Type	Name	Elevation (m a.s.l.)	Num. water samples (-)	Discharge rate (L/s)
MS-01	Met. Station	SMC-Z8	2315	-	-
MS-02	Met. Station	AEMET-0127O	1800	-	-
P-01	Pluviometer	Refugi de l'Arp	1936	7	-
P-02	Pluviometer	Bassa Clot de la Vall	1946	8	-
P-03	Pluviometer	Refugi Bages	1768	8	-
P-04	Pluviometer	Casa X&A	1657	8	-
P-05	Pluviometer	Casa Ramonet	1450	8	-
P-06	Pluviometer	Casa Cavallera	1216	7	-
P-07	Pluviometer	Camp. La Comella	1062	8	-

P-08	Pluviometer	Camp. Morunys	896	9	-
S-01	Regional Spring	Font Aiguaneix	1098	25	8 - 73
S-02	Regional Spring	Font Sant Quintí	944	25	70 – 575
S-03	Regional Spring	Font Can Sala	1062	25	0,25 – 148
S-04	Local Spring	Font Coll de Jou	1464	25	0,07 - 0,59
S-05	Regional Spring	Fonts del Cardener	1032	25	57 – 904
S-06	Local Spring	Font carretera Refugi Arp	1858	25	0,04 – 7
M-05	Local Spring	Font del Ginebró	1730	4	<0,001
M-06	Local Spring	Font de la Garganta	1657	4	0,02-0,49
M-08	Local Spring	Font Orris 02	1871	4	0,1 – 0,7
M-14	Local Spring	Font Estivella	2053	4	0,07 – 5
M-15	Local Spring	Font Arderic	2158	3	0,03 – 2,8
M-16	Local Spring	Font del Casalí	2077	1	<0,001
M-17	Local Spring	Font del Diumenge	1989	2	0,004 – 0,026
M-18	Local Spring	Font barraca Sangonella	1940	1	0,001 - 0,01
M-24	Local Spring	Font dels Acens	1550	4	0,06 – 0,23
M-35	Local Spring	Font Ca l'Arreplagant	1330	4	<0,001 – 0,02
M-37	Local Spring	Font La Part (esllav.)	1315	4	0,5 – 1

3. Materials and methods

3.1 Field work

To collect precipitation samples, a network of 8 cumulative precipitation gauges (pluviometers) of the type CoCoRaHS RG202 Official-4 was installed at elevations between 896 and 1935 m a.s.l. (P-01 a P-08; Fig. 1). The pluviometers consist of a polycarbonate cylindrical deposit with a diameter of 10,8 cm. The pluviometers include a top funnel that captures and guides precipitation into the storing deposit, where according to the technical procedure for the stations of the Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA), a 0,5 cm paraffin oil floating layer is added to avoid evaporation. The pluviometers were sampled seasonally (except the first winter with two campaigns), a total of 9 campaigns from Dec. 2013 to Dec. 2015. Additionally, one snow sampling survey was conducted in December 2003. The snow samples were obtained by drilling through the entire snow depth (Lambán et al., 2015) and were taken at different locations with elevations ranging from 1935 to 2150 m a.s.l.

Groundwater samples were collected under different hydrodynamic conditions between Oct. 2013 and Dec. 2015. In this period, the springs S-01 to S-06 were sampled approximately monthly, for a total of 25 sampling campaigns. Groundwater samples were taken before the snow arrival in autumn (Oct. 2013 and Oct. 2014), and after the snow-melting season (Apr. 2014 and Apr. 2015). In these springs, groundwater discharge was measured once every two weeks from Jul. 2013 to Oct. 2015 (Fig. 3). In springs S-01, S-02, S-03 and S-05 the discharge flow rate was measured by conducting slug-injection salt dilution tests (Cervi et al., 2014), whereas the volumetric method was used for the precision discharge measurement in springs S-04 and S-06. The M-## springs (Table 1) showed a tiny and intermittent discharge. Therefore, groundwater samples were only taken with uneven frequency when it was possible.

Comment [JJ9]: Answer to Reviewer #2– Q10

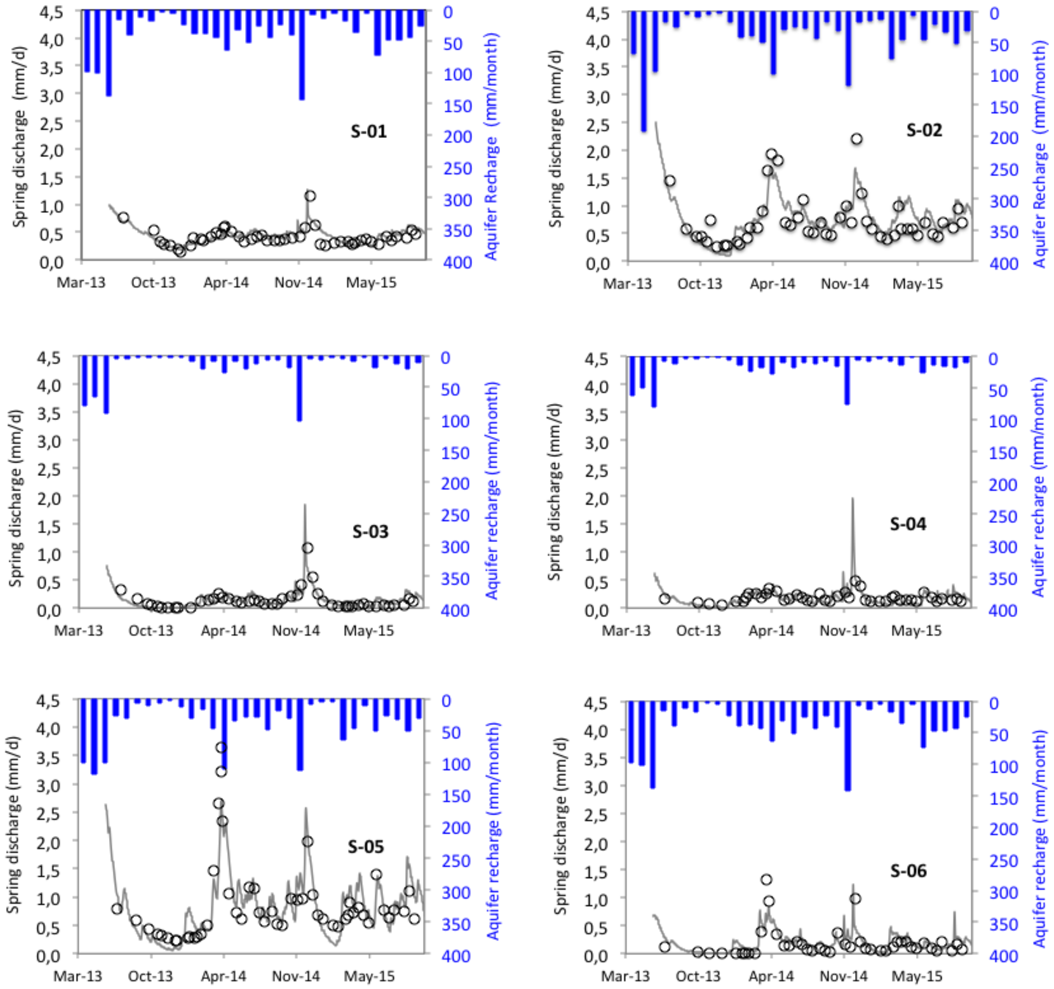


Fig. 3. Measured spring discharge (circles) in the six monitored springs (S-01 to S-06, Table 1) of the PCM hydrogeological system. Gray lines indicate the spring discharge numerically simulated with the HBV model (Seibert and Vis, 2012). For each spring, blue columns indicate the recharge values time series used as input data to the corresponding HBV model.

The isotopic composition (δ^2H and δ^{18}O) of all low salinity water samples was determined in the Center of Hydrogeology of the University of Málaga (CEHIUMA), where a Picarro® "L2130-I" isotopic water analyzer was used. The analytical uncertainties for $\delta^{18}O$ and $\delta^{2}H$ are ±0.2 ‰ and ±1.0 ‰, respectively. According to Coplen et al., (2011) several international and laboratory standards have been interspersed for normalization of analyses. The standards used (WICO-13, WICO-14, WICO-15) were calibrated in an interlaboratory comparison (Wassenaar et al., 2012). All results are given relative to the V-SMOW standard.

3.2 Approach for spring catchment delineation

A critical aspect to understand the behavior of karst hydrogeological flow systems is the delineation of the spring capture zones (i.e., recharge areas) and their boundaries (Goldscheider and Drew, 2007). Ideally, the delineation should be based on the proven information of connection between recharge areas and the discharge points. In high mountain zones, this connection may be confirmed by conducting tracer tests (Goldscheider et al., 2008; Mudarra et al., 2014; Barberá et al., 2018b). When this information is not available, the spring capture zone can be indirectly inferred by considering inputs from other classical information sources such as geophysics, structural geology and geomorphology data interpretation. However, 3D conceptual modeling techniques are currently being used to delineate the spring capture zones: Malard et al. (2015) analyze spring discharge hydrographs based on geological three-dimensional (3D) conceptual modeling (Butscher and Huggenberger, 2007, 2008; Martos-Rosillo et al., 2014; Ruiz-Costán et al., 2015; Malard et al., 2015; Ballesteros et al., 2015b; Epting et al., 2018).

In this work, a combined 3D conceptual methodology has been used to delineate the catchment areas associated with each spring. The delineating criteria are based on the information provided by three complementary methods: (1) the interpretation of the geological structure and the subsurface catchments relative to each spring location. To this end, a 3D geological model has been developed in the 3DMove software platform (Midland Valley Exploration Ltd.); (2) the analysis of the disposition and location of the karst landforms over the area, and (3) the analysis through GIS spatial analysis tools of the ground surface structure, including type of soils (CREAF, 2009) and vegetation (Appendix A) at the spring recharge elevation zones. In the case of the regional springs S-01, S-02, S-03 and S-05, the three listed methods have been applied to delineate their catchment zone, whereas in the case of the perched springs S-04 and S-06, only the previous methods (2) and (3) could be applied. Fig. A1 (Appendix A) shows the catchment zones (i.e., aquifer units) obtained for the selected springs.

Comment [JJ10]: Answer to Reviewer #2– Q12:

The delineated catchment zones associated with the regional springs divide PCM into two main blocks: (1) a southwestern block that includes only the catchment zone associated with S-05. This catchment zone is characterized by a syncline dipping NW structure (Fig. 1). From a functional point of view, this zone is hydrodynamically independent of the rest of PCM given the existence of an anticline and a main NE-SW fault that prevents lateral flows. (2) The northeastern block formed by the catchment zone associated with springs S-01, S-02 and S-03. The geological structure of this block regulates the regional groundwater flows, so as the Alinyà anticline controls the discharge of spring S-01, and the main syncline-anticline system dips SW along with the minor faults and synclines dipping south conditions the discharge of springs S-02 and S-03. Table A1 (Appendix A) provides the geographical details of the delineated groundwater catchment zones.

3.3 Characterizing the seasonal variation of environmental tracers

The evolution of some environmental variables is linked to the atmospheric temperature variation. As a result, these variables often show a similar seasonal pattern that can be characterized with a general sinusoidal function $\delta(t)$ (Jódar et al., 2014). This function consists of two additive terms, a sine-wave function [Eq. 1] plus a temporal linear trend for the mean [Eq. 2].

$$\delta(t) = A\sin(\omega(t - t_0) + \varphi) + \bar{\delta} \tag{1}$$

$$\bar{\delta} = \alpha(t - t_0) + \overline{\delta_0} \tag{2}$$

where A is the amplitude of the sinusoidal function, ω is the angular frequency, φ is the angular initial at time t_0, α is the slope of the linear trend, and $\overline{\delta_0}$ is the linear trend value at time t_0. The parameters A, α and $\overline{\delta_0}$ can be estimated by using the solution of any of the commonly available spreadsheet software's or manually. In this work, the root-mean-squared error (RMSE) is used as the selection criterion for the best fit to the measured isotope content time series.

In the case time series with a short amount of data (e.g., associated with the M-## springs in Table 1), it is not possible to obtain reliable estimates for, α, A, and $\overline{\delta_0}$ by using the method proposed above. In this case, no linear trend in the mean value is assumed (α = 0), and $\overline{\delta_0}$ and A are estimated as:

$$\overline{\delta_0} = \frac{1}{N}\sum_{i=1}^{N}\delta_i \tag{3}$$

$$A = \max\left(\mathrm{Abs}\left(\overline{\delta_0} - \delta_i\right)\right);\ \forall i = 1 \div N \tag{4}$$

where *N* is the number of the isotopic content value of the time series.

Hydrogeological systems transfer the isotopic input signal of recharge. The tracer input seasonal signal is buffered and delayed as it propagates through the aquifer towards the discharging point (Fig. 4). This tracer transport process through the hydrological system can be described by the convolution integral that relates the tracer input content in recharge δ_{in} to the tracer input content in the spring discharge δ_{out} as shown below.

$$\delta_{out}(t) = \int_{-\infty}^{t} \delta_{in}(t) g(t - t') dt' \quad (5)$$

where *t* is the time of tracer entry as recharge, *t'* is the integration variable and *g*(*t'*) is a weighting function describing the Transit Time Distribution (TTD) exit of tracer content that entered the aquifer at different times in the past. The differences between the input and the output tracer signals are related to the aquifer system MTT (τ) which is the first moment of the system TTD and is given by

$$\tau = \int_{0}^{\infty} t g(t) dt \quad (6)$$

where *V* is the volume of mobile water in the system (Małoszewski et al., 1983), and *Q* is the volumetric flow rate through the system. In the case of natural gradient hydrogeological systems, MTT corresponds to the mean amount of time for groundwater to travel from the recharge zone to the discharging spring. In this situation, MTT is related to the spring discharge flow rate *Q*, and the aquifer storage *V*as follows (Custodio and Llamas, 1976):

$$\tau = \frac{V}{Q} \quad (7)$$

Additionally, in natural gradient hydrogeological systems with a seasonal varying input tracer function, MTT can be estimated as (Małoszewski et al., 1983):

$$\tau = \frac{1}{\omega}\sqrt{\left(\frac{A_{\delta_{\mathrm{in}}}}{A_{\delta_{\mathrm{out}}}}\right)^2 - 1} \quad (8)$$

where $A_{\delta_{\mathrm{in}}}$ and $A_{\delta_{\mathrm{out}}}$ are the amplitudes of the seasonal variation of the isotopic content in the aquifer recharge and the spring discharge, respectively. As can be shown, the above equation compares $A_{\delta_{\mathrm{in}}}$ with respect to $A_{\delta_{\mathrm{out}}}$, so the larger the amplitude dampening is, the longer the transit time.

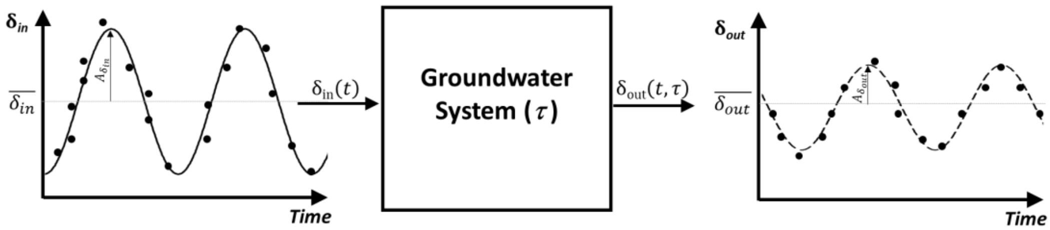


Fig. 4. Schematic representation of the groundwater system response $\delta_{\mathrm{out}}(t, \tau)$ to a hypothetical input tracer function $\delta_{\mathrm{in}}(t)$ (modified from Jódar et al., 2016b), where τ means MTT.

3.4 Numerical approach for simulating the aquifer behavior

To reproduce the observed spring discharge flow rates and the associated isotopic content, a two-step methodology has been used:

(1) Simulation of the hydrodynamic behavior of the hydrogeological system. To this end, the freely available version of the semi-distributed conceptual precipitation–runoff model HBV-Light (Seibert and Vis, 2012) is used. HBV is a conceptual rainfall-runoff model for catchment hydrology modeling that solves a general water balance equation. HBV has been used in different alpine mountain hydrologic research studies (Braun and Renner, 1992; Hottelet, et al., 1993; Uhlenbrook et al., 1999; Merz and Blöschl, 2004; Konz and Seibert, 2010; Staudinger et al., 2017; Epting, et al., 2018; Jódar et al., 2018). This model has become a standard tool for simulating high mountain snow-dominated hydrological systems. This code requires as input data some hydroclimatic catchment information such as the relative weight with respect to the total area of the different altitude and associated vegetation zones in the catchment, the vertical lapse rates ∇_zP and ∇_zT, as well as the time series of daily P, T, and ETP. The hydrological catchment can be separated into numerous elevation zones, depending on the elevation gap between the lowest and the highest points of the catchment. In this work, every zone has been divided into three elevation zones (Table A1 in Appendix A). Additionally, every elevation zone can be divided into different vegetation zones. Based on the Land Cover Map of Catalonia (CREAF, 2009), three vegetation zones are considered: (1) open areas corresponding to zones of both poor or no soils where karst landforms are very well-developed (karren fields, sinkholes, dolines, etc.), (2) areas with mountain meadows and soil moderately developed, and (3) alpine forest zones with moderate to well-developed soils. A two stacked linear reservoir is used to simulate the hydrological system dynamics. The upper reservoir is used to generate surface and subsurface runoff whereas the lower reservoir generates

groundwater runoff. The model considers vegetation zones parameters and catchment zone parametrer (Tables C1 and C2 of Appendix C, respectively). They are can be automatically calibrated by minimizing an efficiency objective function (R_{eff}; Table C3, Appendix C), which is already implemented in HBV. The model output includes the daily time series of aquifer recharge Q_R, which is used in the following step.

(2) Simulation of the transient isotopic content variation in the groundwater discharge. The temporal variation of the isotopic content in the spring discharge is simulated with FlowPC (Małoszewski and Zuber, 1996, 2002), a lumped parameter model typically used to estimate groundwater MTTs with the aid of observed environmental tracer data (Viville et al., 2006; Einsiedl et al., 2009; Katsuyama et al., 2010; Lauber and Goldscheider, 2014; Sánchez-Murillo et al., 2015; Mądrala et al., 2017). The program solves the convolution integral [Eq. 5] and transforms the isotopic input tracer signal $\delta_{in}(t)$ entering the hydrogeological system as recharge into the isotopic output tracer signal $\delta_{out}(t)$ leaving the system through the spring discharge. To this end, FlowPC includes among others two parametric TTDs which are especially well suited for simulating karst aquifer systems: (A) The exponential model (EM), also known as a "good mixing model", is typically applied in systems where the groundwater flow lines tend to converge towards the water sampling points (Zuber, 1986; Amin and Campana, 1996). (B) The Exponential-Piston model (EPM) or "real system model", which combines two parts in line, an unconfined upstream part where recharge enters the system and an exponential distribution of transit times is assumed, and a confined downstream part where the flow scheme is

Comment [JJ11]: Answer to Reviewer #2– Q14

Comment [JJ12]: Answer to Reviewer #3– Q1 approximated like the piston flow model (Zuber, 1986). The weighting function for EPM is described by the following equation.

$$g(t) = \begin{cases} 0 & t < \tau\left(1 - \frac{1}{\eta}\right) \equiv t_\tau \\ \frac{1}{\tau}\eta e^{-\frac{\eta}{\tau}+\eta-1} & t \geq t_\tau \end{cases} \quad (9)$$

where η is the ratio of total volume of the hydrogeological system to the volume of the system in which the exponential TDD exists, and τ is MTT. [Eq. 9] also describes the EM weighting functions when η =1, which is the lowest bound of this parameter. The model parameters (η and τ) are calibrated by minimizing the RMSE function.

FlowPC requires the time series of (1) monthly aquifer recharge $\widehat{Q_R}$ (hereinafter, a circumflex accent over a flow or an isotopic content variable indicates that the variable is cumulated monthly or averaged, respectively), which is obtained from the HBV model outputs for each simulation, and (2) the corresponding monthly averaged isotopic content of the recharge $\widehat{\delta_R}$. Given the karstic nature of the hydrogeological system, we assume that the isotopic content of local recharge and its seasonal characteristics (i.e., $\overline{\delta}_{in}, A_{\delta_{in}}$) are the same as the isotopic content and seasonal characteristics of local precipitation ($\overline{\delta}_P, A_{\delta_P}$). Since $\overline{\delta}_P$ and A_{δ_P} are known, then $\delta_P(t)$ is analytically obtained through [Eq.1]. As $\delta_P(t)$ is a daily time function, it is necessary to transform it into $\widehat{\delta_P}$. For the

j^{th} month, $\widehat{\delta_{\mathrm{P}}}_j$ is obtained by weighting the daily values of recharge isotopic content $\delta_{\mathrm{P}_{ij}}$ by the corresponding daily recharge rate $Q_{\mathrm{P}_{ij}}$ as

$$\widehat{\delta_{\mathrm{R}}}_j \sim \widehat{\delta_{\mathrm{P}}}_j = \frac{\sum_{i=1}^{N} \delta_{\mathrm{P}_{ij}} Q_{\mathrm{R}_{ij}}}{\sum_{i=1}^{N} Q_{\mathrm{R}_{ij}}} \quad (10)$$

where N is the number of days of the j^{th} month. The Appendix D includes all the technical details corresponding to the different FlowPC models used in this work

3.5 Statistical analysis of the relationship between the infiltration coefficient and recharge

To analyze the factors that controls the mean calculated infiltration coefficient (ξ) in the PCM, a linear regression model has been built, expressing the dependent variable ξ as a linear function of N explanatory variables Ψ_i as

$$\xi = \lambda_0 + \sum_{i=1}^{N} \lambda_i \Psi_i \quad (11)$$

where λ_0 is the intercept (constant) term, and λ_i ($i \geq 1 \div N$) are the regression coefficients associated with the predictors Ψ_i. In this study, the predictor variables of the linear regression model of the [Eq.11] are the elevation of the spring recharge zone Z_R (Table 3), the mean precipitation at the spring recharge zone P_{ZR} (Table 6), and the percentages of open areas, mountain meadows and forest in the spring catchment zones (VZ_1, VZ_2 and VZ_3, respectively; Table A1 in Appendix A). The coefficient of determination of the regression is one, so the model reproduces the whole variance of ξ. Table 7 shows the intercept value λ_0, the regression coefficients λ_i, and their corresponding standardized value β_i ($i \geq 1 \div N$). The standardized value β_i measures the expected change in ξ, in standard deviation units, for a one standard deviation change in Ψ_i, provided that other explanatory variables in the model (Ψ_j, $\forall i \neq j$) are fixed (Nimon and Oswald, 2013). The larger the absolute value of β_i, the more important the corresponding predictor Ψ_j is.

Comment [JJ13]: Answer to Reviewer #2– Q16

4. Results and discussion

4.1 Results from observed data

The isotopic content of the precipitation corresponding to the water samples taken is shown in Fig. 5A. The mean isotopic content of precipitation is lighter in winter and autumn than that in spring and summer, as one would expect given the dependence between the isotopic content in rainfall and temperature (Mook and De Vries, 2000). The obtained values are aligned between the Global Meteoric Water Line (GMWL) and the West Mediterranean Meteoric Water Line (WMMWL) (Fig. 5A). The local water meteoric water line (LMWL) that is obtained by linear regression (N= 76; R^2= 0,97) is defined as $\delta^2H = 8{,}05 \cdot \delta^{18}O + 12{,}74$. From a seasonal point of view, the isotopic content of precipitation in autumn and winter presents a larger variability than the isotopic content of precipitation in spring and summer, as shown in Fig. 5B by the error bars indicating the standard deviation associated with every seasonal value. The isotopic content in groundwater changes seasonally much less, than the isotopic content in precipitation (Fig. 5B), pointing out the existence of a good mixing flow process in the discharging points of the aquifer.

Comment [JJ14]: Answer to Reviewer #3– Q1

The geographical location of the study zone postulates the Mediterranean as the most important source of precipitation. This assumption is supported by the overall mean deuterium excess (dex= δ^2H - $8 \cdot \delta^{18}O$) value of 12,03 ± 3,37 ‰ obtained for all the precipitation samples analyzed (Celle-Jeanton et al., 2001; Jiménez-Martínez and Custodio, 2008). Nevertheless, the Atlantic fingerprint in rainfall can be observed in the above *dex* value through its variation interval, which provides a minimum *dex* value of 8,66 ‰ (Froehlich et al., 2001; Araguás-Araguás and Díaz-Teijeiro, 2005).

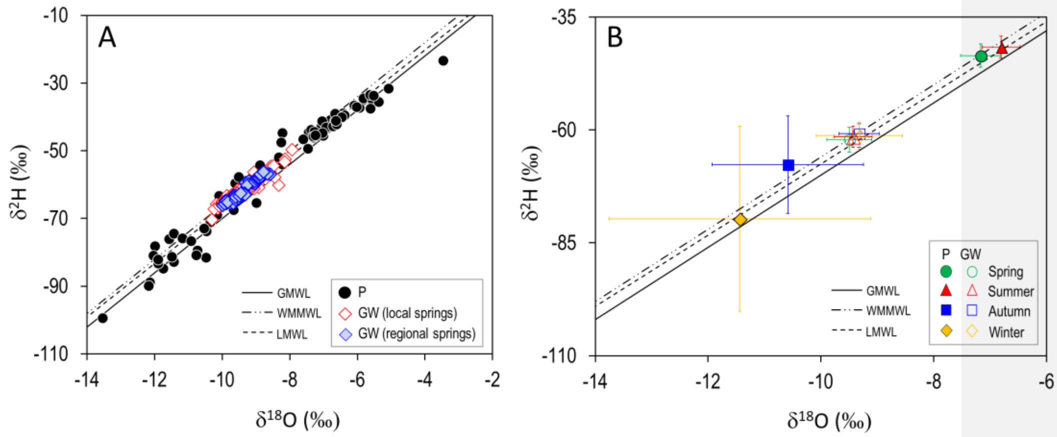


Fig. 5. (A) Values of $\delta^{18}O$ and δ^2H in precipitation (P; solid circles) and groundwater (GW) from local springs (empty red diamonds) and from regional springs (solid blue diamonds) for the period Oct. 2013 – Dec. 2015. (B) Seasonal overall averages of $\delta^{18}O$ and δ^2H for precipitation (P; solid symbols) and groundwater (GW; empty symbols). The spring, summer autumn and winter values are indicated by green circles, red triangles, blue squares and orange diamonds, respectively. GMWL (Clarke and Fritz, 1997) is the Global Meteoric Water Line (slope 8 and *dex*=10‰), WMMWL is the Western Mediterranean Meteoric Water Line (slope 8 and *dex*=14‰) and LMWL is the Local Meteoric water Line (slope 8,05 and *dex*=12,74‰).

Comment [JJ15]: Answer to Reviewer #1 – Q4

The isotopic composition of precipitation and spring discharge show a seasonal variation, which is not reflected in the deuterium excess. A seasonal variation in *dex* would indicate the existence of different moisture sources generating rainfall in the study zone by following a certain seasonal pattern (Schotterer et al 1993; Liu et al 2008; Froehlich et al 2008). The lack of such seasonal pattern supports the Mediterranean as the main rainfall source.

A sine-wave function [Eq.1] is used to characterize every one of the measured seasonal time series of isotopic content in water from the sampling points (Fig. B1 in Appendix B). Tables 2 and 3 show the calibrated mean isotopic content ($\bar{\delta}$) and amplitude (*A*) corresponding to the time series of isotopic content of precipitation and spring discharge, respectively.

Table 2. Mean value $\bar{\delta}_{in}$ and amplitude $A_{\delta_{in}}$ of the seasonal variation in the isotopic content of precipitation for the sampled pluviometers.

	$\bar{\delta}_{in}$ (‰)			$A_{\delta_{in}}$ (‰)	
Pluviometer	$\delta^{18}O$	$\delta^{2}H$	*dex*	$\delta^{18}O$	$\delta^{2}H$
P-01	-9.20	-59.91	14.56	3.34	26.89
P-02	-9.50	-62.29	13.88	2.87	23.23
P-03	-9.20	-60.25	12.94	3.29	27.92
P-04	-8.60	-56.11	12.87	3.02	26.05
P-05	-8.60	-55.65	12.37	3.05	23.31
P-06	-7.80	-51.10	9.53	2.76	23.96
P-07	-7.50	-49.06	10.24	2.59	20.92
P-08	-7.50	-50.22	9.40	2.55	19.53

Table 3. Mean value $\bar{\delta}_{out}$ and amplitude $A_{\delta_{out}}$ of the seasonal variation in the isotopic content of groundwater for the springs sampled. For every spring, the elevation of the corresponding recharge zone Z_R is included. For this elevation, the associated amplitude $A_{\delta_{ZR}}$ of the seasonal variation in isotopic content of precipitation is shown.

	$\bar{\delta}_{out}$ (‰)	$A_{\delta_{out}}$ (‰)	Z_R (m a.s.l)	$A_{\delta_{ZR}}$ (‰)

Spring	δ18O	δ2H	*dex*	δ18O	δ2H	δ18O	δ2H	dex	δ18O	δ2H
S-01	-9,31	-60,65	13,81	0,12	1,10	1892	1881	1852	3,16	26,23
S-02	-9,61	-62,82	14,06	0,25	1,93	2038	2046	1902	3,24	27,18
S-03	-9,18	-59,85	13,60	0,11	1,07	1830	1819	1702	3,12	25,88
S-04	-9,01	-58,11	13,95	0,10	0,67	1745	1686	1881	3,07	25,12
S-05	-9,73	-63,36	14,50	0,14	0,88	2099	2088	1994	3,28	27,41
S-06	-9,69	-64,03	14,80	0,15	0,90	2078	2140	1798	3,27	27,71
M-05	-9,01	-58,53	13,52	0,44	1,81	1744	1718	1793	3,07	25,31
M-06	-8,70	-54,75	14,88	0,54	2,51	1597	1428	2071	2,98	23,65
M-08	-9,49	-62,22	13,68	0,27	1,84	1979	2001	1826	3,21	26,92
M-14	-9,69	-64,01	13,53	1,08	8,01	2079	2138	1795	3,27	27,70
M-15	-9,73	-63,81	14,05	0,87	6,24	2099	2123	1901	3,28	27,61
M-16	-9,77	-64,13	14,05	0,65	4,00	2118	2147	1902	3,29	27,75
M-17	-9,76	-64,32	13,73	0,49	2,86	2110	2161	1836	3,29	27,83
M-18	-9,59	-63,12	13,64	0,62	4,12	2031	2070	1817	3,24	27,31
M-24	-9,41	-62,26	13,02	0,47	1,64	1941	2004	1690	3,19	26,93
M-35	-8,90	-57,02	14,14	0,94	7,54	1690	1602	1920	3,04	24,65
M-37	-8,44	-54,00	13,53	0,26	0,93	1469	1371	1795	2,90	23,33

The mean isotopic content in rainfall $\bar{\delta}_{in}$ shows a clear-cut linear relationship with elevation (Fig. 6) that allows defining Isotopic Altitudinal Lines (IAL) for δ^{18}O, δ^{2}H and *dex*, with slopes (i.e., vertical gradients $\nabla_z\delta^{18}\mathrm{O}$, $\nabla_z\delta^{2}\mathrm{H}$ and $\nabla_z dex$) of -1,9, -12,1 and 4,7 ‰/km, respectively. Vertical gradients ($\nabla_z\delta$) of mean isotopic content in precipitation are common in mountain zones (see Poage and Chamberlain, 2001, and references therein) and are related to the atmospheric decreasing thermal vertical profile existing along the slope of the mountains. $\nabla_z\delta$ values obtained for the study zone are like those obtained in other alpine areas, especially in the central Pyrenees and the Alps (Table 4).

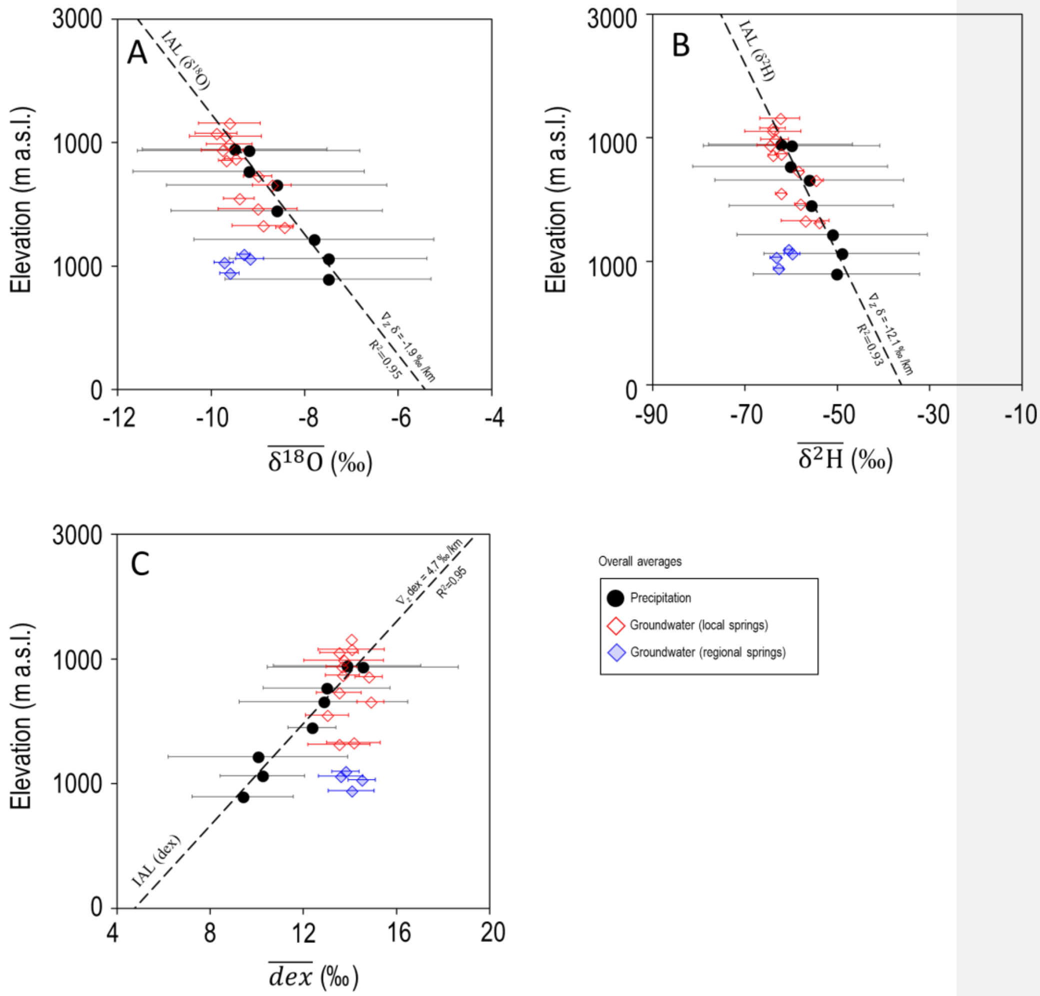


Fig. 6. Relationship between elevation and the mean isotopic content in precipitation and springs. (A) $\delta^{18}O$, (B) $\delta^{2}H$, and (C) *dex*. Error bars indicate the standard deviation. Dashed lines indicate the local Isotopic Altitudinal Line (IAL) of precipitation.

The vertical gradients of the mean isotopic content in precipitation depend linearly on the mean seasonal precipitation (Fig. 7). In the case of $\delta^{18}O$ and $\delta^{2}H$, the higher the seasonal precipitation is, the lower the seasonal gradient is. In the case of *dex*, the relationship is reversed, obtaining a higher $\nabla_z dex$ value as seasonal precipitation increases. In a seasonal framework, recycling moisture evaporated from the land surface to atmosphere may increase *dex* of local precipitation. Soil evaporation is maximum when atmospheric vapor pressure deficit (Δe = e-e_{sat}, e being the atmospheric water pressure and e_{sat} the saturating water pressure at the air parcel temperature) is maximum, if the soil contains water for evaporating. Therefore, to allow soil water to evaporate, it is necessary to have enough (1) soil water content, which is higher in spring and autumn since these are the rainiest seasons, and (2) atmospheric vapor pressure deficits (Δe). Satisfying these two conditions, $\nabla_z dex$ is maximum when the difference in *dex* (i.e., Δe) between the highest and the lowest points of the mountain slope is maximum. Given that e_{sat} is an increasing function of temperature (Gonfiantini et al., 2001), Δe will decrease as temperature declines. During the cold season, despite a thermal difference existing between the highest and lowest points of the mountain, the difference in Δe between these points is minimum. Additionally, the commented Δe difference is minimum as well when there is no thermal difference along the mountain slope, a situation that is favored by the cathabaltic winds in winter (Obleitner, 1994; Gladich et al., 2011) but is also favored by the vertical atmosphere air mixing during the typical summer local low pressure convective rainfall events.

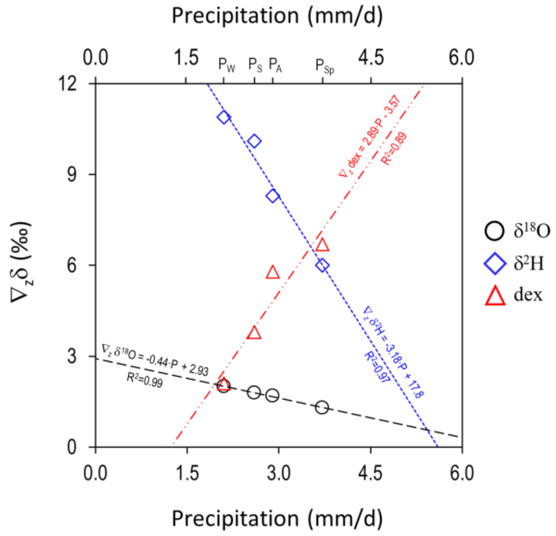


Fig. 7. Dependence of the vertical gradient of the mean isotopic content with respect to the mean seasonal precipitation. The subscripts Sp, S, A, and W stand for spring, summer, autumn and winter, respectively.

The amplitude of the seasonal variation in the isotopic content of precipitation $A_{\delta_{in}}$ relates linearly to elevation (Fig. 8) to allow defining Amplitude Altitudinal Lines (AAL) for $\delta^{18}O$ and $\delta^{2}H$ with slopes (i.e., vertical gradients $\nabla_z A_{\delta^{18}\mathrm{O}}$ and $\nabla_z A_{\delta^{2}\mathrm{H}}$) of 0,6 and 5,7 ‰/km, respectively. Similar vertical gradients have previously been reported in the central Pyrenees (Jódar el al., 2016b) and the Bernese Alps (Jódar el al., 2016a) (Table 4).

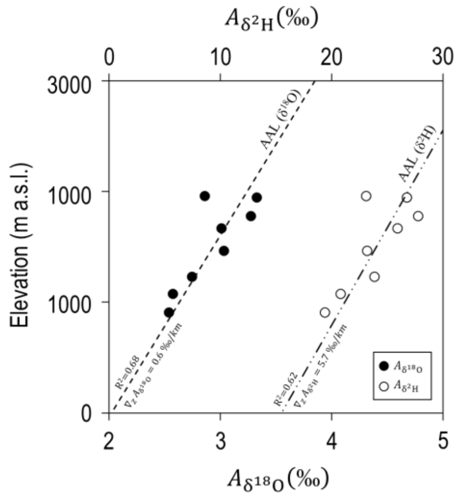


Fig. 8. Relationship between elevation and amplitude of the seasonal variation of the isotopic content (δ^{18}O, δ^{2}H) in precipitation. Dashed line and dashed-dotted line indicate the local Amplitude Altitudinal Lines (AALs) of precipitation for δ^{18}O and δ^{2}H, respectively.

Table 4. Vertical gradients of mean isotopic water content and amplitude of the seasonal variation of the isotopic water content in precipitation.

Zone	Z_{min} - Z_{max} (m a.s.l.)	$\nabla_z\delta^{18}$O (‰/km)	$\nabla_z\delta^{2}$H (‰/km)	$\nabla_z dex$ (‰/km)	$\nabla_z A_{\delta^{18}\mathrm{O}}$ (‰/km)	$\nabla_z A_{\delta^{2}\mathrm{H}}$ (‰/km)	Reference
Eastern Pyrenees (PCM[a])	896-1936	-1,9	-15,2	4,7	0,6	6,1	This study
Central Pyrenees (PNOMP[b])	772-2200	-2,2	-17,4	2,2	0,9	4,4	Jódar et al. (2016a)
Bernese Alps	874-2023	-3,0	-19,7	3,7	1,6	14,6	Jódar et al. (2016b)
Austrian Alps	580-2245	-1,9	-12,0	2,7	-	-	Froehlich et al. (2008)
Austrian Alps	469-1598	-1,3	-8,0	3,4	-	-	Froehlich et al. (2008)

Central Andes (western flank)	2380-4250	-4,7	-42,5	2,2	-	-	Aravena et al. (1989)
Central Andes (eastern flank)	2380-4250	-1,9	-14,3	1,1	-	-	Fiorella et al. (2015)
Central Andes (eastern flank)	200-4080	-1,7	-11,7	2,0	-	-	Gonfiantini et al. (2001)
Western Carpathians	104-2008	-2,1	-	-	-	-	Holko et al. (2012)
Mount Cameroon	10-4050	-1,16	-11,4	1,4	-	-	Gonfiantini et al. (2001)

(a): Port del Comte Massif; (b): Ordesa and Monte Perdido National Park

The mean isotopic content of groundwater corresponding to local (perched) springs shows a relationship with elevation dependence with a vertical gradient larger than that of precipitation (Fig. 6), indicating the existence of aquifer recharge along the mountain slope, a process also known as slope effect (Custodio and Jódar, 2016). Additionally, the evolution of the isotopic content in the spring discharge shows a seasonal dependence like precipitation but showing smaller amplitudes (Fig. B1 in Appendix B). Even being lumped, the seasonal pattern of recharge is observed in the spring discharge, indicating that MTT should not be longer than 5 or 6 years (DeWalle et al., 1997).

The isotopic altitudinal line (IAL, Fig. 6) allows estimation of the elevation of the recharge zone (Z_R) corresponding to every spring by projecting their mean isotopic content on IAL. Table 3 shows Z_R for all the springs, with their mean Z_R value ranging between 1420 m a.s.l. (M-37) and 2136 m a.s.l. (M-17). With a known value for Z_R, it is possible to calculate the amplitude of the variation in the isotopic content in precipitation at the recharge zone elevation ($A_{\delta_{ZR}}$) by projecting Z_R on the amplitude altitudinal line (AAL, Fig. 8). Table 2 shows $A_{\delta_{ZR}}$ for every spring. Finally, if both $A_{\delta_{ZR}}$ (i.e., $A_{\delta_{in}}$at the springs recharge zone) and $A_{\delta_{out}}$ are known, it is possible to obtain a first analytical estimate of MTT through [Eq. 8]. Table 5 provides the MTT values obtained for all the springs. As can be shown, the obtained MTT values range between 0,5 and 5 yr.

Table 5. MTT values estimated for the springs sampled

	$\delta^{18}O$			$\delta^{2}H$		
Spring	τ^a(yr)	τ^b(yr)	η(-)	τ^a(yr)	τ^b(yr)	η(-)
S-01	4,10	2,25	1,02	3,78	3,00	1,01
S-02	2,06	1,42	1,02	2,23	1,96	1,00
S-03	4,67	2,25	1,00	3,83	2,33	1,01
S-04	4,70	2,33	1,01	5,93	2,67	1,00
S-05	3,73	2,88	1,02	4,98	2,83	1,01
S-06	3,47	2,58	1,02	4,90	2,75	1,02
M-05	1,10	-	1,00	2,22	-	1,00
M-06	0,86	-	1,00	1,49	-	1,00
M-08	1,89	-	1,00	2,32	-	1,00
M-14	0,45	-	1,00	0,53	-	1,00
M-15	0,58	-	1,00	0,69	-	1,00
M-16	0,79	-	1,00	1,09	-	1,00
M-17	1,06	-	1,00	1,54	-	1,00
M-18	0,82	-	1,00	1,04	-	1,00
M-24	1,07	-	1,00	2,61	-	1,00
M-35	0,49	-	1,00	0,5	-	1,00
M-37	1,77	-	1,00	3,99	--	1,00

(a) Analytical MTT value obtained by [Eq. 8]. (b) Numerical MTT value obtained by FlowPC.

4.2 Aquifer recharge evaluation through HBV

The HBV semi-distributed conceptual rainfall–runoff model has been used to simulate the observed groundwater discharge in every spring. The spring discharges were measured every fortnight between July 2013 and October 2015. This period has been used for calibrating the HBV parameters, which are shown in Table C4 (Appendix C). The efficiency parameter R_{eff} that describes the goodness of the model fit ranges between 0,55 (S-01) and 0,77 (S-05) (Table C5, Appendix C). The computed discharges resemble the observed discharges by reproducing their temporal evolution in all the springs (Fig. 3).

The results from the HBV model indicated that recharge is especially concentrated in the open areas (VZ_1) and meadow areas (VZ_2). The yearly average effective recharge ranges from 210 mm/yr (S-04) to 637 mm/yr (S-06) (Table 6). The aquifer infiltration capacity ξ (i.e., the ratio between Q_{Re} – the effective recharge of the aquifer, and P_{ZR} - precipitation at the spring recharge zone) ranges as the yearly average ranges from 28,3% (S-03) to almost 62% (S-06) (Table 6).

Table 6. Mean annual precipitation P_{ZR}, mean aquifer recharge Q_R, seasonal distribution of recharge, infiltration capacity ξ.

Spring	P_{ZR} (mm/yr)	Q_R (mm/yr)	$\frac{Q_{R_{e\,Spring}}}{Q_R}$ (%)	$\frac{Q_{R_{e\,Summer}}}{Q_R}$ (%)	$\frac{Q_{R_{e\,Autumn}}}{Q_R}$ (%)	$\frac{Q_{R_{e\,Winter}}}{Q_R}$ (%)	ξ^a (%)
S-01	954	473	37,5%	15,0%	25,4%	22,1%	49,6%
S-02	1006	433	40,8%	12,3%	23,8%	23,1%	43,0%
S-03	793	227	38,1%	6,7%	27,2%	27,9%	28,6%

S-04	698	210	37,0%	10,2%	25,4%	27,4%	30,1%
S-05	1008	429	42,5%	14,3%	23,0%	20,2%	42,6%
S-06	1030	637	45,9%	8,9%	21,2%	24,0%	61,9%

(a) $\xi = Q_{R_e}/P_{ZR}$

Aquifer recharge follows a linear relationship similar to precipitation, as found by Martos-Rosillo et al. (2015) for the mountain carbonate aquifers in the Betic Cordillera (Southern Spain), where recharge is generally lower (Fig. 9A). In PCM, recharge is at a maximum in spring, accounting for 40,3% of the total recharge, and this outcome is explained by both rainfall and snow melt infiltration. Recharge is at a minimum (11,2%) in summer, coinciding with the period of minimum seasonal precipitation.

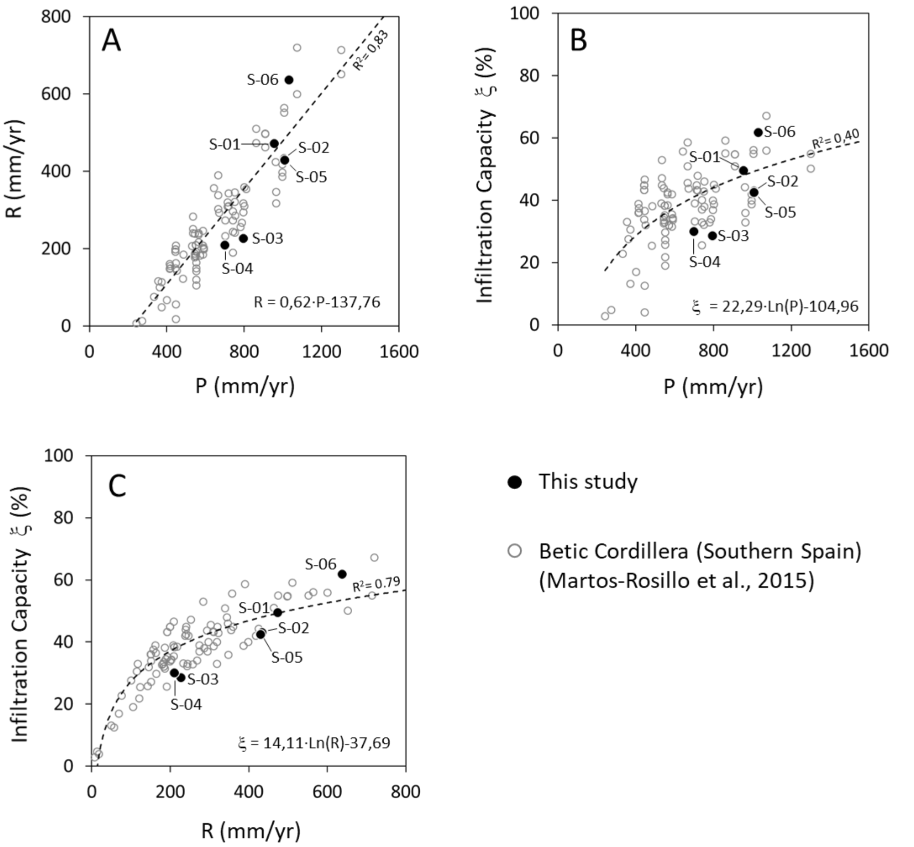


Fig. 9. (A) Mean annual rainfall versus mean annual recharge, (B) Mean infiltration coefficient versus mean annual rainfall, and (C) Mean infiltration coefficient versus mean annual recharge.

The relationship between ξ and P (Fig. 9B) is not as clear as the relationship between ξ and R (Fig. 9C), indicating that precipitation is a necessary condition for aquifer recharge, but it is not enough. In this respect, the results of the application of the linear regression model between the variables Z_{R}, P_{ZR}, and VZ_1, VZ_2 and VZ_3; shows that the Z_R and is the most important predictor controlling the aquifer infiltration capacity ξ. In addition, VZ_1 (karren fields and sinkholes at the highest parts of the massif) and VZ_3 (forest fields at the lowest of the massif) also play a role regarding ξ. These parameters reflect the differences in both the karstification degree and the vegetation covering the epikarst system in the PCM.

Table 7. No standardized (λ) and standardized (β) regression coefficients associated with the explanatory variables used in the multiple regression method.

Explanatory Variable	λ	β
Intercept (λ_0)	-39,562	--
Z_R	0,047	0,823
P_{ZR}	-0,007	-0,054
VZ_1	6,034	0,133
VZ_2	4,018	0,072
VZ_3	258,518	0,122

4.3 Determination of spring discharge mean transit time

To estimate the mean transit time of the spring discharge, the program FlowPC v3.2 (Małoszewski and Zuber, 1996) has been used. According to the hydrogeological setting, it is assumed that the EPM flow model can describe the behavior of the aquifers discharging through the springs of PCM. The lumped model parameters (η and τ) have been calibrated (Table 5) by fitting the isotopic contents observed in the spring discharge from December 2013 to December 2015 (Fig. 10). The goodness of fit is defined in terms of RMSE, ranging between 0,02‰ (S-05) and 0,04‰ (S-02) for $\delta^{18}O$ (Table D1, Appendix D), and between 0,17‰ (S-03) and 0,22‰ (S-04) for $\delta^{2}H$ (Table D2, Appendix D).

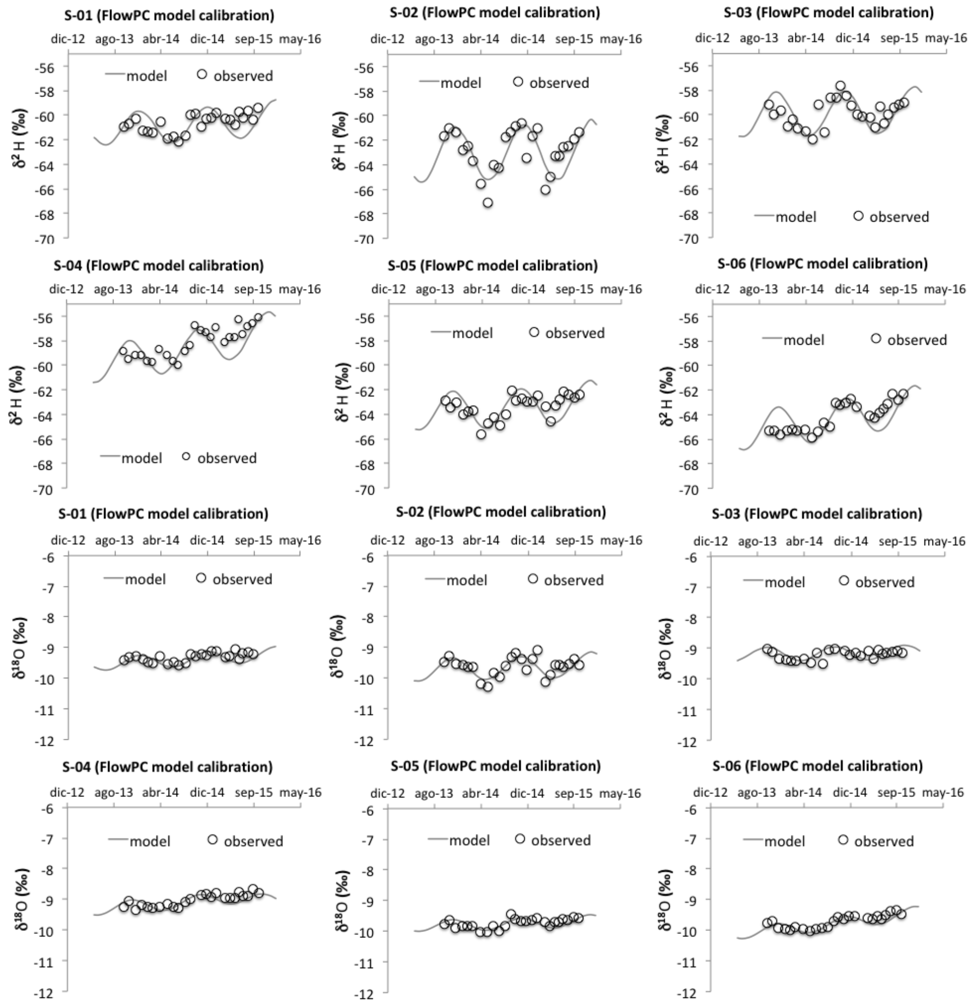


Fig. 10. Measured against simulated isotope content evolution with FlowPC and an EPM model. The gray line represents the best fit.

The estimated value of η is very close to 1 regardless of the spring, indicating that the corresponding aquifers behave as almost an exponential flow model in coherence with the behavior of a karst aquifer system discharging through a main spring. The estimated MTT with the applied methodology ranges between 1,69 yr (S-02) and 2,85 yr (S-05), while in the case of the analytical approach MTT ranges between 2,14 yr (S-02) and 5,31 yr (S-04).

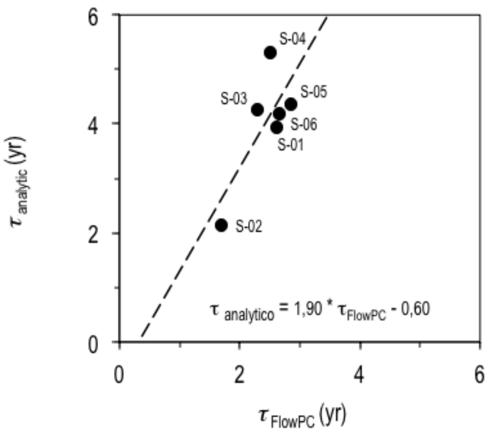


Fig. 11. Graph showing the MTT values estimated based on the lumped parameter model FlowPC (Maloszewski, 1996) versus the MTT values estimated based on the analytical model [Eq. 8] (Maloszewski et al., 1983)

The MTT values obtained by this numerical approach are 1,9 times shorter than the MTT values analytically obtained through [Eq. 8] that compares the amplitude of the seasonal isotopic content of recharge with the seasonal isotopic content in the spring discharge [Fig 11]. In the numerical case, the monthly isotopic content in recharge is weighted by the monthly volumetric recharge rate, whereas in the analytical case, the isotopic content weighting coefficients for the monthly recharge are all equal to 1 because recharge is assumed constant (i.e., steady state) for the whole period covered by the isotopic content time series. This assumption is worth keeping in mind when using [Eq. 8] for estimating groundwater mean transit times. In other words, if aquifer recharge shows a seasonal pattern, then the numerical approach should be used instead of the analytical approach to estimate MTT. The transit time discrepancies between both approaches may be critical when MTT is used as a vulnerability indicator for karst-fissure aquifers (Malík et al, 2016). The results obtained suggest that the numerical approach based explicitly on considering the recharge series in the LPM model provides a more accurate evaluation of hydraulic dynamics throughout the system. This allows better MTT estimations, similar of what concluded Vitvar et al. (1999) in pre-alpine non-karst aquifers. The MTT values obtained in this work are consistent with the conceptual model of the karst system. The aquifer presents specific zones with rapid recharge through surficial karstic elements (e.g. swallow holes) and slow recharge trough meadows and forest.

In terms of MTT, the results obtained in this study are similar to those obtained in other hydrological karst systems located in mountain zones: (1) In the case of the Ordesa and Monte Perdido karst aquifer system (Central Pyrenees, Spain), which is the highest calcareous massif in Western Europe, Lambán et al. (2015) and Jódar et al. (2016b) estimated MMT for several springs. For each spring the authors fitted a sinusoidal function [Eq. 1] to the measured tracer ($\delta^{18}O$ and $\delta^{2}H$) content time series corresponding to rainfall entering the system as recharge and the spring discharge, obtaining the amplitude of the seasonal variation of both the input and output system tracer function ($A_{\delta_{in}}$ and $A_{\delta_{out}}$, respectively; Fig. 4). Besides, the authors assumed a constant recharge rate along the year. This hypothesis allowed obtaining an analytical solution to the convolution integral [Eq. 5] (Jódar et al., 2014) but also applying [Eq. 8] to directly estimate MTT, that ranged between 1,12 and 4,48 yr.

(2) In the Wimbach high-alpine karst system (Berchtesgaden Alps) Einsiedl et al. (2009) estimated MTT with FlowPC. To this end, they used as tracer input function the

time series of ^{3}H content in rainfall measured in a meteorological station close to the study zone, and as system output the time series of ^{3}H content in groundwater discharge for different springs and also at the outlet of the hydrological catchment. They obtained MTT ranging between 4 and 5 yr for the considered springs, and 5 yr for the whole hydrologic catchment. For the same catchment, Maloszewski et al. (1992) evaluated the MTT by using monthly recharge time series instead of rainfall time series. The aquifer recharge time series was obtained by applying a seasonal infiltration coefficient to the observed monthly precipitation time series. With this approach they estimated a MTT of 4,15 yr. This value is close to that obtained by Einsiedl et al. (2009). Additionally, Garvelmann et al. (2017) expanded the previous studies in the Berchtesgaden Alps for a total of eight springs. For each spring they estimated MTT using two different methods; (A) by numerically solving the convolution integral [Eq. 5], and (B) though [Eq. 8] by previously conducting a sin-wave analysis [Eq. 1] to the input (i.e. rainfall) and output tracer functions. The MTT obtained by both methods did not show large discrepancies for the same spring. In terms of the obtained MTT the sampled springs were be classified in two groups: a first group with relatively short MTTs (0,7 to 1,9 yr) and a second group with longer MTTs (7,3 to 12,5 yr).

(3) In the Schneealpe massif Rank et al. (1992) used the environmental tracers to study the karstic-fissured-porous aquifer system of Schneealpe, The aquifer system that is drained by two principal springs is the main drinking water resource for Vienna (Austria). It is composed of a fissured-porous aquifer with a high storage capacity that partially feds a karst aquifer conformed by a high- conductivity drainage channel network. For each aquifer they estimated MTT by calibrating a LPM with a 8 years long time series of environmental tracer data, using ^{3}H and $\delta^{18}O$ for the fissured-porous and

the karst aquifer, respectively. In the former case MTTs ranged between 2,5 and 4,5 yr, whereas in the karst aquifer the estimated MTT was only 2 months. Maloszewski et al. (2002) recalibrated both LPMs by refining and extending up to 20 years the length of the observed time series of ^{3}H and $\delta^{18}O$ measurements. In the case of the fissured-porous aquifer the obtained MTTs ranged between 14 and 26 yr, being significantly larger than those obtained by Rank et al (1992). Nevertheless, in the case of the karst aquifer the obtained MTTs were similar ranging between1,2 and 1,5 months. The large discrepancy between the MTT associated to the Fissured-Porous and karst aquifer indicates that water enters the aquifer system at the surface and flows through it towards the conductive drainage channels until reaching the springs. Nevertheless, the short MTTs associated to the karst aquifer reveal a direct hydraulic connection between the sinkholes at the surface and the drainage channel network.

(4) In the Wetterstein Mountains karst aquifer system Lauber and Goldscheider (2014) used both artificial (uranine) and environmental tracers (^{18}O and ^{2}H) to investigate the hydrological behavior of the system. Despite the low recovery of artificial tracer during the tracer test, the fast tracer arrival observed in all the sampled springs, with peak times between 1,8 and 3,2 days, indicates as in the previous case, the existence of well-developed flow paths through thick (>1000 m) USZ. This result underlines the role that may play the USZ conditioning the hydrologic response of the karst system. The authors estimated the aquifer MTT with FlowPC by using as input tracer content that of precipitation, and assuming a constant (without any seasonality) aquifer recharge rate. The obtained MTT values ranged between 3 and 5 months, being significantly shorter than those MTT presented above for the other karst systems.

Comment [JJ16]: Answer to Reviewer #1– General Comment 3
Answer to Reviewer #3– Q2
Answer to Reviewer #4– Q1

The hydrological system MTT reflects the diversity of aquifer flow paths and groundwater mixing from the recharge zone to the discharge point. Considering that the different aquifers constituting the PCM show an exponential flow model (EM) behavior, and provided that MTT (τ; Table 5) and the aquifer mean recharge flow rate (Q_R; Table 6) are known, it is possible to estimate the aquifer storage (i.e., mixing) volume by using [Eq. 7]. In Table 8, the stored dynamic volume ('mobile water volume -V_m'; Małoszewski and Zuber (2002); where: $V_m = Q_R \cdot \tau$) is associated with the catchment areas (Fig. A1 of the Appendix A) discharging through the springs S-01 to S-06. S-05 and S-02 play a major role in terms of both groundwater discharge and aquifer storage. The springs S-05 and S-02 present a similar area and a similar discharge. Nevertheless, from a geometrical point of view, they are different: S-05 is rounded in shape whereas S-02 is elongated. Considering that aquifer recharge is produced mainly in the highest parts of PCM, it is clear that the distance between the recharge and discharge points is larger in the case of S-02. This difference is interesting if one considers that the mean transit time of S-02 is shorter than the mean transit time of S-05. The shorter transit time would indicate a higher development of the karst water conducting features in the catchment area of S-02. The springs S-04 and S-06 denote their perched character with the associated low discharge flow rates and groundwater reserve volumes.

Table 8. Estimation of dynamic volume V_m stored in the aquifer for the springs analyzed

Spring	V_m (hm^3)
S-01	2,44 + 0,49
S-02	11,54 + 2,61
S-03	1,72 + 0,04

S-04	0,03 + 0,01
S-05	19,39 + 0,20
S-06	0,09 + 0,01

The few available groundwater level depth data from old water wells in the PCM suggest the karst aquifer presents low regional hydraulic gradients in the phreatic zone ranging between 1 - 2%. Nevertheless, while considering the expected mean phreatic level above the horizontal plane from the spring levels (i.e., the groundwater that contributes to each spring discharge), the 3D geological model evaluates the total aquifer formation volume (V_{aq}) associated with the regional springs S-01, S-02, S-03 and S-05. Assuming V_{aq} as known, the mean aquifer interconnected porosity (ϕ) can therefore be estimated as the ratio V_{GW}/V_{aq}. In the PCM, the average ϕ obtained is 3,1%. This result agrees with the value obtained for other carbonate aquifers of the Betic Cordillera (Southern Iberian Peninsula) with an average value of 3% (Pulido-Bosch et al., 2004; Martos- Rosillo et al., 2014).

This work is aimed to characterize the hydrological behavior of a high mountain karst system with a overlaying thick UZS that plays a relevant role along with in the system response. The applied approach allows accounting the effects of the extreme alpine climate conditions on both the aquifer recharge rates and the isotopic composition of recharge. The used approach provides a more reliable assessment of the hydrological behavior of these alpine karst systems than the obtained applying the traditional approaches found in the scarce bibliography. The methodology used in this work for characterizing the hydrological behavior of PCM can be applied in many analogue high mountain karst systems whose hydrologic behavior still remains unknown. In this sense, Table 9 shows a brief summary of the available bibliography at the pan-European zone focused on high-mountain karst aquifers with a thick USZ in which this methodology could be tested (Fig. 12).

Table 9. Brief summary of published research studies of groundwater flow karst systems in mountain areas with thick USZ the pan-European zone.

Code	High mountain karst system	NSZ Thickness	Reference
1	Yunquera-Sierra de las Nieves	1000	Andreo et al. (2004); Pardo-Iguzquiza et al. (2015)
2	Alta Cadena	700	Mudarra and Andreo (2011)
3	Sierra Gorda	500	Mudarra and Andreo (2015)
4	Picos de Europa	1500	Ballesteros et al. (2015a); Ruiz and Poblete (2012)
5	Ordesa y Monte Perdido	1500	Lambán et al. (2015); Jódar et al. (2016b)
6	Port del Comte	1000	(This research)
7	Fontaine Vaucluse	800	Fleury et al. (2007)
8	Schlichenden Brünnen - Muotathal	1000	Jeannin (2001)
9	Wetterstein Mountains (Zugspitze)	1000	Lauber and Goldscheider (2014)
10	Wimbachtal catchment	1500	Maloszewski et al. (1992)
11	Totes Gebirge	1000	Laimer (2010)
12	Schneealpe Massif	900	Rank et al 1992; Maloszewski et al. (2002)
13	Cansiglio-Cavallo karst aquifer	800	Filippini et al. (2018)
14	Mount Kanin	2000	Zini et al. (2015); Turk et al. (2015)
15	Gacka	1000	Ozyurt et al. (2014)
16	Gran Sasso aquifer	1500	Falcone et al. (2008); Amuroso et al. (2013)
17	Arabika Massif	2500	Klimchouk (2009)
18	Aladaglar Mountains	2000	Ozyurt and Bayari (2008)

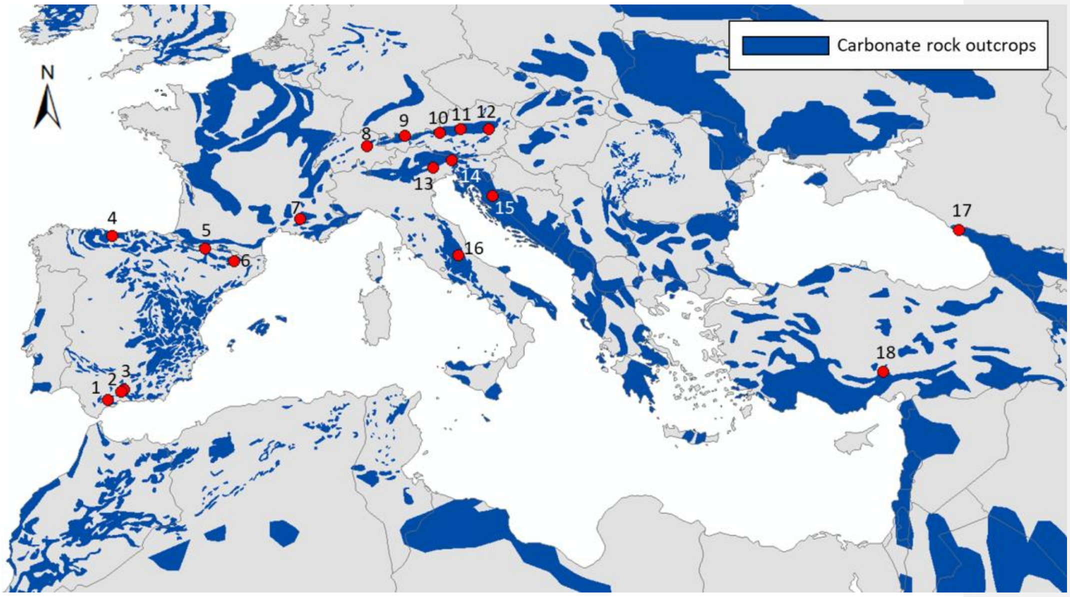


Fig. 12. Spatial distribution of carbonate rock outcrops at the pan-Mediterranean zone. Red points indicate the position of those high mountain karst aquifers zones with a thick (<500 m) NSZ referenced in the existing bibliography (map modified from the *World Map of Carbonate Rock Outcrops v.3.0*. Source: http://www.fos.auckland.ac.nz/our_research/karst). Numbers in bullets correspond to the codes shown in Table 9.

Comment [JJ17]: Answer to Reviewer #3– Q2
Answer to Reviewer #4– Q1

4.4 Evaluation of results for groundwater management purposes

MTT is a corner stone for groundwater management strategies, and many authors have used this variable as a proxy of vulnerability assessment in hydrogeological systems (Einsiedl et al., (2009) and Malik et al., (2016), among others). This work provides the first estimation of the MTT associated with most important springs discharging the PCM karst system. From the perspective of aquifer vulnerability, the intensive cattle grazing conducted in the PCM is the most threading activity to the groundwater resources stored in the underlying aquifer so far. The relatively large MTTs (2,25 yr) along with the exponential flow model describing the hydrologic behavior of PCM, points to groundwater mixing as a natural attenuation/dilution process inside the aquifer system. However, it must be taken in mind that the presence of unnoticed but likely well-developed flow paths through the USZ and also the existence of karst conductive features in the saturated zone of the PCM may favor fast contaminant migration from the recharge areas to the groundwater discharge points of this aquifer system, but this is investigation is out of the scope of this work.

From the perspective of water resources management the storage and dynamic volumes associated with the PCM aquifer system are also valuable information obtained in this study. In this line, it is worth to comment that the PCM aquifer system has an integrated groundwater storage capacity (V_{GW}) of 35,2 hm^3, and generates an overall mean annual groundwater discharge of 15,35 hm^3/yr, that represents 15% of the mean annual water consumption in the city of Barcelona (Barcelona City Council, 2018). Moreover, the average discharge of S-05, which is one of the main groundwater springs of the PCM represents 7% of the mean annual water consumption of Barcelona city. This discharge tributes to the Llobregat River Basin, which in turns provides critical water resources to the Barcelona metropolitan area. It is important keeping these numbers in mind to estimate the water resources availability given the increased frequency and severity of the Mediterranean droughts reported by the experts (Hoerling et al., 2012; Vicente-Serrano et al., 2014).

In the Pyrenean range, climate models forecast a precipitation decrease up to 14% with respect to the observed mean precipitation and a temperature increase between 2 and 4 °C that will reduce the amount of solid precipitation and the corresponding snowmelt runoff (López-Moreno et al., 2008, 2009). In addition, the duration of the snowpack will be shorter, shifting the timing of the snowmelt (Adam et al., 2009). The PCM is in the pre-Pyrenean zone to the South of the Pyrenean axial zone. Here, the elevation of the mountains is lower, and the climate conditions are not so severe, accelerating the impact of the forecast temperature increase on snow precipitation, snowmelt runoff generation and the dynamics of the hydrological systems located in this area. Therefore, the geographical and hydrogeological settings of the PCM, along with the groundwater transit times calculated, make the PCM aquifer system an exceptional observatory for anticipating and studying the climate change impact on southern Europe. In this line, it would be extremely important to maintain the observation research program to fully understand the hydrogeological behavior of this aquifer system.

Comment [JJ18]: Answer to Reviewer #23– Q17

4.5 Future works in PCM

This study is the first stage in the full hydrogeological characterization of this aquifer system. The next step is to conduct the hydrogeochemical characterization of recharge and groundwater springs discharge to complement the results obtained in this work by focusing in relevant unsolved questions like (1) the role play by the epikarst zone in the total transit time of groundwater and how this role is reflected in the hydrogeochemical evolution of the springs discharge after important rainfall events and during low-flows and (2) the use of artificial tracers and environmental isotopes (e.g. 34S, 15N) to characterize not only the mean transit time (i.e. the first moment of the transit-time distribution) but also to profile the groundwater transit-time distribution in terms of fast, intermediate and slow groundwater flows. This investigation is crucial to evaluate the aquifer vulnerability.

Comment [JJ19]: Answer to Reviewer #1– General Comment 2

5. Conclusions

A distributed rainfall-runoff model and a lumped-parameter model have been combined to estimate MTT in high-mountain karst systems with an overlying thick unsaturated zone by using the stable isotopes of precipitation as environmental tracers. The presented approach accounts for the effects of the alpine climate conditions on both the aquifer recharge rates and the isotopic composition of recharge. The used approach provides a more reliable assessment of mean transit time compared to traditional methods for such alpine karst systems.

The approach presented in this work has been used to characterize the hydrological behavior of the Port del Comte Massif, a high mountain karst aquifer with a 1000 m thick unsaturated zone located in the southeastern part of the Pyrenees. The percentage of precipitation that enters into the hydrogeological system as aquifer recharge reaches 61,9% (the highest studied spring in the area). This elevated infiltration capacity is controlled by the presence of karren fields and sinkholes at the highest parts of Port del Comte Massif, at elevations between 2050 and 2300 m a.s.l. The evolution of the isotopic content in the sampled springs shows a sinusoidal pattern that reflects the seasonal variation of the isotopic composition of recharge. This is consistent with the relatively short groundwater transit times (2,25 yr) obtained for the hydrological system, which is in agreement with its karstic nature of the aquifer system, and emphasizes the high vulnerability of the aquifer system to variations in recharge.

The mean annual groundwater discharge and the mean water storage of the Port del Comte Massif hydrogeological system represent 16 and 34% of the mean annual water consumption in the city of Barcelona, underlying the important role as a strategic water resource that the Port del Comte Massif may play for stakeholders and water resources managers when facing the drought episodes that the Mediterranean region iteratively suffers. Moreover, given the geographical position of the study zone, located to the south of the Pyrenean axial zone, and the hydrogeological settings of the associated karst aquifer system, the Port del Comte Massif is an exceptional watchtower for anticipating the impact of climate change in Southern Europe.

Comment [JJ20]: Answer to Reviewer #12– Q5

6. Acknowledgments

This research was supported by Agencia Estatal de Investigación (AEI) from the Spanish Government and the European Regional Development Fund (FEDER) from EU, REMEDIATION (CGL2014-57215-C4-1-R), and PACE-ISOTEC (CGL2017-87216-C4-1-R) projects, the PIRAGUA project (EFA210/16/ PIRAGUA) which is funded by the European Union through the Interreg-POCTEFA territorial cooperation program, the Catalan Government projects to support consolidated research groups MAG (Mineralogia Aplicada, Geoquimica i Geomicrobiologia, 2017SGR-1733) from Universitat de Barcelona (UB) and GREM (Grup de Recerca de Minería Sostenible) from the Universitat Politècnica de Catalunya (UPC), and the Junta de Andalucía research group RNM-308 (Hydrogeology Group). We also thank the Institut Cartogràfic i Geològic de Catalunya (Hydrogeology and Geothermics Team) and CCiT from the Universitat de Barcelona (UB) for their technical assistance, and especially Raul Carrey from the MAiMA group for the help in the laboratory analyses. The Meteorological Service of Catalonia (SMC) has kindly provided the meteorological data. The constructive comments and interesting suggestions from four anonymous reviewers are greatly appreciated since they have led to a substantial improvement of the final article

7. References

Adam, J.C., Hamlet, A.F., & Lettenmaier, D.P., 2009. Implications of global climate change for snowmelt hydrology in the twenty-first century. Hydrological Processes: An International Journal, 23(7), 962-972. https://doi.org/10.1002/hyp.7201

Agencia Estatal de Meteorología de España (AEMET) and Instituto de Meteorologia – Portugal (IMA). 2011. Iberian climate atlas. Air temperature and precipitation (1971-2000). https://www.aemet.es/documentos/es/conocermas/publicaciones/Atlas-climatologico/Atlas.pdf

Allocca, V., De Vita, P., Manna, F., Nimmo, J.R. 2015. Groundwater recharge assessment at local and episodic scale in a soil mantled perched karst aquifer in southern Italy. Journal of Hydrology, 529 (2015) 843–853. https://doi.org/10.1016/j.jhydrol.2015.08.032

Amin I.E., Campana, M.E. 1996. A general lumped parameter model for the interpretation of tracer data and transit time calculation in hydrologic systems. J Hydrol; 179 (1–4):1–21 https://doi.org/10.1016/0022-1694(95)02880-3

Andreo, B., Linan, C., Carrasco, F., De Cisneros, C. J., Caballero, F., Mudry, J. 2004. Influence of rainfall quantity on the isotopic composition (18O and 2H) of water in mountainous areas. Application for groundwater research in the Yunquera-Nieves karst aquifers (S Spain). Applied Geochemistry, 19(4), 561-574. https://doi.org/10.1016/j.apgeochem.2003.08.002

Araguás-Araguás, L.J., Díaz-Teijeiro, M.F. 2005. Isotope composition of precipitation and water vapour in the Iberian Peninsula. In “Isotopic Composition of

Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate" (pp. 173-190). IAEA-TECDOC-1453.

Aravena, R., Peña, H., Grilli, A., Suzuki, O., Mordeckai, M., 1989. Evolución isotópica de las lluvias y origen de las masas de aire en el altiplano chileno. Isotope hydrology investigations in Latín America. IAEA-TECDOC-502. IAEA, Vienna, pp. 129–142.

Bakalowicz, M. (2005). Karst groundwater: a challenge for new resources. Hydrogeology Journal, 13(1), 148-160. https://doi.org/10.1007/s10040-004-0402-9

Ballesteros, D., Jiménez-Sánchez, M., Giralt, S., García-Sansegundo, J., Meléndez-Asensio, M. 2015a. A multi-method approach for speleogenetic research on alpine karst caves. Torca La Texa shaft, Picos de Europa (Spain). Geomorphology, 247, 35-54.

Ballesteros, D., Arnauld Malard., A., Pierre-Yves Jeannin, P-Y., Jimenez-Sanchez M., García-Sansegundo, J., Meléndez-Asensio, M., Sendra, G. 2015b. KARSYS hydrogeological 3D modeling of alpine karst aquifers developed in geologically complex areas: Picos de Europa National Park (Spain). Environ Earth Sci. Volume 74, Issue 12, pp 7699–7714. https://doi.org/10.1007/s12665-015-4712-0

Barberá, J.A., Jódar, J., Custodio, E., González-Ramón, A., Jiménez-Gavilán, Vadillo, I., Pedrera, A., Martos-Rosillo, S., 2018a. Groundwater dynamics in a hydrologically-modified alpine watershed from an ancient managed recharge system (Sierra Nevada National Park, Southern Spain): insights from hydrogeochemical and isotopic information. Science of the Total Environment 640–641, 874–893, https://doi.org/10.1016/j.scitotenv.2018.05.305

Barberá, J. A., Mudarra, M., Andreo, B., De la Torre, B., 2018b. Regional-scale analysis of karst underground flow deduced from tracing experiments: examples from carbonate aquifers in Màlaga province, southern Spain. Hydrogeology Journal, 26(1), 23-40. https://dx.doi.org/10.1007/s10040-017-1638-5

Barcelona City Council, 2018. Evolution of water consumption in the city of Barcelona. http://www.bcn.cat/estadistica/angles/dades/economia/consum/evoconsum/coev04.htm (last access 08/07/2018).

Barnett, T.P., Adam, J.C., Lettenmaier, D.P., 2005. Potential impacts of a warming climate on water availability in snow-dominated regions. Nature, 438(7066), https://dx.doi.org/10.1038/nature04141

Bergström, S., 1976. Development and Application of a Conceptual Runoff Model For Scandinavian Catchments, SMHI, Report No. RHO 7 (134 pp Norrköping).

Braun, L.N., Renner, C.B., 1992. Application of a conceptual runoff model in different physiographic regions of Switzerland. Hydrological Sciences Journal, 37(3), 217-231. https://doi.org/10.1080/02626669209492583.

Butscher C, Huggenberger P., 2007. Implications for karst hydrology from 3D geological modeling using the aquifer base gradient approach. J Hydrol; 342 (1–2):184–98. https://doi.org/10.1016/j.jhydrol.2007.05.025

Celle-Jeanton,H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. Geophysical Research Letters, Vol. 28, no. 7, pages 1215-1218

Cervi, F., Marcaccio, M., Petronici, F., Borgatti, L., 2014. Hydrogeological characterization of peculiar Apenninic springs. Proceedings of the International Association of Hydrological Sciences, 364, 333-338.

Chen, Z., 2017. Modeling a geologically complex karst aquifer system, Hochifen-Gottesacker, Alps. PhD. Thesis. Karlsruher Instituts für Technologie, Germany. https://d-nb.info/1136660852/34

Chueca, J., Julián, A., López-Moreno, J.I., 2007. Recent evolution (1981–2005) of the Maladeta glaciers, Pyrenees, Spain: extent and volume losses and their relation with climatic and topographic factors. Journal of glaciology, 53(183), 547-557. https://doi.org/10.3189/002214307784409342

Clark, I.D., Fritz, P. 1997. Environmental isotopes in hydrogeology. Lewis Publishers, New York.

Coplen 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid Commun. Mass Spectrom. 2011, 25, 2538–2560.

CREAF, 2009. Land Cover Map of Catalonia (MCSC) 1:250,000. 4a edition (2009). http://www.creaf.uab.es/mcsc/usa/index.htm

Custodio, E., Llamas, M.R. (Eds.), 1976. Hidrología subterránea [Groundwater hydrology]. 2 Vols: 1–2350. Ediciones Omega, Barcelona.

Custodio, E., Jódar, J., 2016. Simple solutions for steady–state diffuse recharge evaluation in sloping homogeneous unconfined aquifers by means of atmospheric tracers. J. Hydrol. http://dx.doi.org/10.1016/j.jhydrol.2016.06.035

De Jong, C., Lawler, D., Essery, R., 2009. Mountain hydroclimatology and snow seasonality and hydrological change in mountain environments. Hydrological Processes 23, 955–961. https://doi.org/10.1002/hyp.7193

De Walle, D.R., Edwards, P.J., Swistock, B.R., Aravena, R., Drimmie, R.J., 1997. Seasonal isotope hydrology of three Appalachian forest catchments. Hydrological

Processes, 11(15), 1895-1906.b https://doi.org/10.1002/(SICI)1099-1085(199712)11:15<1895::AID-HYP538>3.0.CO;2-#

Einsiedl, F., 2005. Flow system dynamics and water storage of a fissured-porous karst aquifer characterized by artificial and environmental tracers. J Hydrol 312:312–321. https://doi.org/10.1016/j.jhydrol.2005.03.031

Einsiedl, F., Maloszewski, P., Stichler, W., 2009. Multiple isotope approach to the determination of the natural attenuation potential of a high-alpine karst system. Journal of Hydrology 365 (2009) 113–121. https://doi.org/10.1016/j.jhydrol.2008.11.042

Epting, J., M.Page, R., Auckenthaler, A., Huggenberger, P. 2018. Process-based monitoring and modeling of Karst springs – Linking intrinsic to specific vulnerability. Sci. Total Environ. 625, 403-415- https://doi.org/10.1016/j.scitotenv.2017.12.272

Falcone, R.A., Falgiani, A., Parisse, B., Petitta, M., Spizzico, M., Tallini, M. 2008. Chemical and isotopic (δ^{18}O‰, δ^{2}H‰, δ^{13}C‰, ^{222}Rn) multi-tracing for groundwater conceptual model of carbonate aquifer (Gran Sasso INFN underground laboratory–central Italy). Journal of hydrology, 357(3-4), 368-388.

Farlin, J., Maloszewski, P., 2013. On the use of spring baseflow recession for a more accurate parameterization of aquifer transit time distribution functions. Hydrology and Earth System Sciences, 17(5), 1825-1831. https://doi.org/10.5194/hess-17-1825-2013

Fiorella, R.P., Poulsen, C.J., Pillco Zolá, R.S., Barnes, J.B., Tabor, C.R., Ehlers, T.A., 2015. Spatiotemporal variability of modern precipitation δ^{18}O in the central Andes and implications for paleoclimate and paleoaltimetry estimates. Journal of

Geophysical Research: Atmospheres, 120(10), 4630-4656. https://dx.doi.org/10.1002/2014JD022893

Fleury, P., Plagnes, V., Bakalowicz, M. 2007. Modelling of the functioning of karst aquifers with a reservoir model: Application to Fontaine de Vaucluse (South of France). Journal of Hydrology 345, 38– 49. https://doi.org/10.1016/j.jhydrol.2007.07.014

Filippini,M., Squarzoni, G., De Waele, J., Fiorucci, A., Vigna, B., Grillo, B., Riva, A., Rossetti, S., Zini, L., Casagrande, G., Stumpp, C., Gargini, A. 2018. Differentiated spring behavior under changing hydrological conditions in an alpine karst aquifer. Journal of Hydrology, 556, 572-584. https://doi.org/10.1016/j.jhydrol.2017.11.040

Freixes, A., 2014. Els aqüífers càrstics dels Pirineus de Catalunya. Interès estratègic i sostenibilitat [The karstic aquifers of the Catalonian Pyrenees. Strategic interest and sustainability]. PhD. Thesis. Universitat de Barcelona. http://hdl.handle.net/2445/65187

Froehlich, K., Gibson, J.J., Aggarwal, P., 2001. Deuterium excess in precipitation and its climatological significance. In Study of environmental change using isotope techniques (Vol. 13, pp. 54-66). IAEA.

Froehlich, K., Kralik, M., Papesch, W., Rank, D., Scheifinger, H., Stichler, W., 2008. Deuterium excess in precipitation of Alpine regions–moisture recycling. Isotopes in Environmental and Health Studies, 44(1), 61-70. https://doi.org/10.1080/10256010801887208

García-Ruiz, J.M., López-Moreno, J.I., Vicente-Serrano, S.M., Lasanta–Martínez, T., Beguería, S., 2011. Mediterranean water resources in a global change scenario.

Earth-Science Reviews, 105(3-4), 121-139. https://doi.org/10.1016/j.earscirev.2011.01.006

Garvelmann, J., Warscher , M., Leonhardt, G., Franz, H., Lotz. A., Kunstman, H. 2017. Quantification and characterization of the dynamics of spring and stream water systems in the Berchtesgaden Alps with a long-term stable isotope dataset. Environ Earth Sci 76:766 https://doi.org/10.1007/s12665-017-7107-6

Giorgi, F., Lionello, P., 2008. Climate change projections for the Mediterranean region. Global and planetary change, 63(2-3), 90-104. https://doi.org/10.1016/j.gloplacha.2007.09.005

Gladich, I., Gallai, I., Giaiotti, D. B., & Stel, F. 2011. On the diurnal cycle of deep moist convection in the southern side of the Alps analysed through cloud-to-ground lightning activity. Atmospheric Research, 100(4), 371-376. https://doi.org/10.1016/j.atmosres.2010.08.026

Goldscheider, N., 2005. Fold structure and underground drainage pattern in the alpine karst system Hochifen-Gottesacker. Eclogae Geologicae Helvetiae, 98(1), 1-17. https://doi.org/10.1007/s00015-005-1143-z

Goldscheider N, Drew D (eds) (2007) Methods in Karst Hydrogeology. International Contributions to Hydrogeology 26, International Association of Hydrogeologists, Taylor & Francis, London, 264 pp. ISBN 978-0-415-42873-6

Goldscheider, N., Meiman, J., Pronk, M., Smart, C., 2008. Tracer tests in karst hydrogeology and speleology. International Journal of Speleology, 37(1), 3. http://dx.doi.org/10.5038/1827-806X.37.1.3

Goldscheider, N., 2011. Alpine Hydrogeologie [Alpine hydrogeology]. Grundwasser 16:1–1. https://doi.org/10.1007/s00767-010-0157-2

Gonfiantini, R., Roche, M.A., Olivry, J.C., Fontes, J.C., Zuppi, G.M., 2001. The altitude effect on the isotopic composition of tropical rains. Chemical Geology, 181(1-4), 147-167. https://doi.org/10.1016/S0009-2541(01)00279-0

Gremaud, V., Goldscheider, N., Savoy, L., Favre, G., Masson, H., 2009. Geological structure, recharge processes and underground drainage of a glacierised karst aquifer system, Tsanfleuron-Sanetsch, Swiss Alps. Hydrogeol. J. 17, 1833–1848. https://doi.org/10.1007/s10040-009-0485-4

Grunewald, K., Scheithauer, J., 2010. Europe's southernmost glaciers: response and adaptation to climate change. Journal of glaciology, 56(195), 129-142. https://doi.org/10.3189/002214310791190947

Hernández-Mora, N., del Moral Ituarte, L., La-Roca, F., La Calle, A., Schmidt, G., 2014. Interbasin water transfers in Spain: Interregional conflicts and governance responses. In Globalized Water (pp. 175-194). Springer, Dordrecht. ISBN 978-94-007-7322-6. https://doi.org/10.1007/978-94-007-7323-3_13

Hargreaves, G.H. and Samani, Z.A. 1982. Estimating potential evapotranspiration. Journal of Irrigation and Drainage Engineering, 108, 223-230

Hoerling, M., Eischeid, J., Perlwitz, J., Quan, X., Zhang, T., Pegion, P., 2012. On the increased frequency of Mediterranean drought. Journal of Climate, 25(6), 2146-2161. https://doi.org/10.1175/JCLI-D-11-00296.1

Holko, L., Dóša, M., Michalko, J., Šanda, M. 2012. Isotopes of oxygen-18 and deuterium in precipitation in Slovakia. Journal of Hydrology and Hydromechanics, 60(4), 265-276. https://doi.org/10.2478/v10098-012-0023-2

Hood, J.L., Hayashi, M., 2010. Assessing the application of a laser rangefinder for determining snow depth in inaccessible alpine terrain. Hydrology and Earth System Sciences, 14(6), 901. http://dx.doi.org/10.5194/hess-14-901-2010

Hottelet, Ch., Braun, L.N., Leibundgut, Ch., Rieg, A., 1993. Simulation of Snowpack and Discharge in an Alpine Karst Basin. IAHS Publication No. 218, pp. 249–260

ICGC, 2007. Mapa geològic comarcal de Catalunya 1:50 000. Full Alt Urgell (BDGC50M). http://www.icgc.cat/ca/Administracio-i-empresa/Descarregues/Cartografia-geologica-i-geotematica/Cartografia-geologica/Mapa-geologic-comarcal-de-Catalunya-1-50.000/Mapa-geologic-comarcal-de-Catalunya-1-50.000

Jeelani, G., Shah, R.A., Deshpande, R.D., Fryar, A.E., Perrin, J., Mukherjee, A., 2017. Distinguishing and estimating recharge to karst springs in snow and glacier dominated mountainous basins of the western Himalaya, India. Journal of hydrology, 550, 239-252. https://doi.org/10.1016/j.jhydrol.2017.05.001

Jeannin, P-Y. 2001. Modeling flow in phreatic and epiphreatic karst conduits in the Hölloch cave (Muotatal, Switzerland). Water Resources Research. Vol. 37, No. 2, pp 191-200. https://doi.org/10.1029/2000WR900257

Jiménez-Martínez, J. y Custodio, E., 2008. El exceso de deuterio en la lluvia y en la recarga a los acuíferos en el área circum-mediterránea y en la costa mediterránea española. Boletín Geológico y Minero, 119 (1): 21-32.

Jódar, J., Lambán, L.J., Medina, A., Custodio, E., 2014. Exact analytical solution of the convolution integral for classical hydrogeological lumped-parameter models and typical input tracer functions in natural gradient systems. J. Hydrol. 519, 3275–3289. http://dx.doi.org/10.1016/j.jhydrol.2014.10.027.

Jódar, J., Custodio, E., Liotta, M., Lambán, L.J., Herrera, C., Martos-Rosillo, S., Sapriza, G., Rigo, T., 2016a. Correlation of the seasonal isotopic amplitude of precipitation with annual evaporation and altitude in alpine regions. Sci. Total Environ., 550: 27-37. https://dx.doi.org/10.1016/j.scitotenv.2015.12.034

Jódar, J., Custodio, E., Lambán, L.J., Martos-Rosillo, S., Herrera-Lameli, C., Sapriza-Azuri, G., 2016b. Vertical variation in the amplitude of the seasonal isotopic content of rainfall as a tool to jointly estimate the groundwater recharge zone and transit times in the Ordesa and Monte Perdido National Park aquifer system, north-eastern Spain. Sci. Total Environ. 573, 505–517. https://dx.doi.org/10.1016/j.scitotenv.2016.08.117

Jódar, J., Cabrera, J.A., Martos-Rosillo, S., Ruiz-Constan, A., Gonzalez-Ramón, A., Lambán, L.J., Herrera, C., Custodio, E., 2017. Groundwater discharge in high-mountain watersheds: a valuable resource for downstream semi-arid zones. The case of the Bérchules River in Sierra Nevada (Southern Spain). Science of The Total Environment, https://doi.org/10.1016/j.scitotenv.2017.03.190

Jódar, J., Carpintero, E., Martos-Rosillo, S., Ruiz-Constán, A., Marín-Lechado, C., Cabrera-Arrabal, J.A., Navarrete-Mazariego, E., González-Ramón , A., Lambán, L.J., Herrera, C., González-Dugo, M.P. 2018. Combination of lumped hydrological and remote-sensing models to evaluate water resources in a semi-arid high altitude ungauged watershed of Sierra Nevada (Southern Spain). Sci. Total Environ., 625: 285-300. https://doi-org.recursos.biblioteca.upc.edu/10.1016/j.scitotenv.2017.12.300

Katsuyama, M., Tani, M., Nishimoto, S., 2010. Connection between streamwater mean residence time and bedrock groundwater recharge/discharge dynamics in weathered granite catchments. Hydrological Processes, 24(16), 2287-2299. https://doi.org/10.1002/hyp.7741

Kazakis, N., Chalikakis, K., Mazzilli, M., Ollivier, C., Manakos, A., Voudouris, K., 2018. Management and research strategies of karst aquifers in Greece: Literature overview and exemplification based on hydrodynamic modelling and vulnerability assessment of a strategic karst aquifer. Sci. Total Environ., 643: 592–609. https://doi.org/10.1016/j.scitotenv.2018.06.184

Klimchouk, A. Samokhin, G.V., Kasian, Y.M. 2009. The deepest cave in the world in the arabika massif (western caucasus) and its hydrogeological and paleogeographic significance. 2009 ICS Proceedings. 15th International Congress of Speleology

Konz, M., Seibert, J., 2010. On the value of glacier mass balances for hydrological model calibration. Journal of hydrology, 385(1-4), 238-246. https://doi.org/10.1016/j.jhydrol.2010.02.025

Kurylyk, B.L., Hayashi, M., 2017. Inferring hydraulic properties of alpine aquifers from the propagation of diurnal snowmelt signals. Water Resources Research. https://doi.org/10.1002/2016WR019651

Laimer, H.J. 2010. Neue Ergebnisse zur Karsthydrogeologie des westlichen Toten Gebirges (Österreich). (New karst hydrogeological research in the western Totes Gebirge, Austria). Grundwasser. Volume 15, Issue 2, pp 113–122

Lambán, L.J., Jódar, J., Custodio, E., Soler, A., Sapriza, G. and Soto, R., 2015. Isotopic and hydrogeochemical characterization of high-altitude karst aquifers in complex geological settings. The Ordesa and Monte Perdido National Park (Northern Spain) case study. Sci. Total Environ., 506–507: pp 466–479, https://doi.org/10.1016/j.scitotenv.2014.11.030

Lauber, U., Kotyla, P., Morche, D., Goldscheider, N., 2014. Hydrogeology of an Alpine rockfall aquifer system and its role in flood attenuation and maintaining baseflow. Hydrology and Earth System Sciences, 18(11), 4437. http://dx.doi.org/10.5194/hess-18-4437-2014

Lauber, U., Goldscheider, N., 2014. Use of artificial and natural tracers to assess groundwater transit-time distribution and flow systems in a high-alpine karst system (Wetterstein Mountains, Germany). Hydrogeology Journal, 22(8), 1807-1824. http://dx.doi.org/10.1007/s10040-014-1173-6

Liu, Z., Tian, L., Yao, T., & Yu, W. 2008. Seasonal deuterium excess in Nagqu precipitation: influence of moisture transport and recycling in the middle of Tibetan Plateau. Environmental Geology, 55(7), 1501-1506. http://dx.doi.org/10.1007/s00254-007-1100-4

López-Moreno, J.I., García-Ruiz, J.M., 2004. Influence of snow accumulation and snowmelt on streamflow in the central Spanish Pyrenees/Influence de l'accumulation et de la fonte de la neige sur les écoulements dans les Pyrénées centrales espagnoles. Hydrological Sciences Journal, 49(5). https://doi.org/10.1623/hysj.49.5.787.55135

López-Moreno, J. I., Goyette, S., Beniston, M., 2008. Climate change prediction over complex areas: spatial variability of uncertainties and predictions over the Pyrenees from a set of regional climate models. International Journal of Climatology, 28(11), 1535-1550. https://doi.org/10.1002/joc.1645

López-Moreno, J.I., Revuelto, J., Rico, I., Chueca-Cía, J., Julián, A., Serreta, A., Serrano, E., Vicente-Serrano, S.M., Azorin-Molina, C., Alonso-González, E., García-Ruiz, J.M., 2016. Thinning of the Monte Perdido Glacier in the Spanish Pyrenees since 1981. The Cryosphere, 10(2), 681-694. https://doi.org/10.5194/tc-10-681-2016

Mądrala, M., Wąsik, M., Małoszewski, P., 2017. Interpretation of environmental tracer data for conceptual understanding of groundwater flow: an application for fractured aquifer systems in the Kłodzko Basin, Sudetes, Poland. Isotopes in environmental and health studies, 53(5), 466-483. https://dx.doi.org/10.1080/10256016.2017.1330268

Malard, A., Jeannin, PY., Vouillamoz, J. et al 2015. An integrated approach for catchment delineation and conduit-network modeling in karst aquifers: application to a site in the Swiss tabular Jura. Hydrogeol J 23: 1 1341–1357. https://doi.org/10.1007/s10040-015-1287-5

Malard, A., Sinreich, M., Jeannin, P.Y., 2016. A novel approach for estimating karst groundwater recharge in mountainous regions and its application in Switzerland. Hydrological Processes, 30(13), 2153-2166. https://doi.org/10.1002/hyp.10765

Malík, P., Svasta, J., Michalko, J., Gregor, M., 2016. Indicative mean transit time estimation from δ18O values as groundwater vulnerability indicator in karst-fissure aquifers. Environmental Earth Sciences. 75. 10.1007/s12665-016-5791-2.

Małoszewski, P., Rauert, W., Stichler, W., Herrmann, A., 1983. Application of flow models in an alpine catchment area using tritium and deuterium data. Journal of Hydrology, 66: 319–330. http://dx.doi.org/10.1016/0022-1694(83)90193-2

Maloszewski, P., Rauert, W., trimborn, P., Herrmann, A., Rau, R. 1992. Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). Journal of Hydrology, 140: 343-360. https://doi.org/10.1016/0022-1694(92)90247-S

Małoszewski, P., Zuber, A., 1996. Lumped parameter models for the interpretation of environmental tracer data. Manual on mathematical models in isotope hydrology. IAEA-TECDOC 910. Vienna (Austria): IAEA; 1996

Małoszewski, P., Zuber, A., 2002. Manual on lumped parameter models used for the interpretation of environmental tracer data in groundwaters (IAEA-UIAGS/CD--02-00131). International Atomic Energy Agency (IAEA)

(https://inis.iaea.org/search/search.aspx?orig_q=RN:33037906, last access 12/04/2018)

Marti, R., Gascoin, S., Houet, T., Ribière, O., Laffly, D., Condom, T., Monnier, S., Schmutz, M., Camerlynck, C., Tihay, J.P., Soubeyroux, J.M., 2015. Evolution of Ossoue Glacier (French Pyrenees) since the end of the Little Ice Age. The Cryosphere, 9(5), 1773-1795. http://dx.doi.org/10.5194/tc-9-1773-2015.

Martos-Rosillo, S., Marín-Lechado, C., Pedrera, A., Vadillo, I., Motyka, J., Molina, J.L., Ortiz, P., Martín-Ramírez, J.M., 2014. Methodology to evaluate the renewal period of carbonate aquifers: a key tool for their management in arid and semiarid regions, with the example of Becerrero aquifer, Spain. Hydrogeology Journal, 22(3), 679-689. http://dx.doi.org/10.1007/s10040-013-1086-9

Martos-Rosillo, S., González-Ramón, A., Jiménez-Gavilán, P., Andreo, B., Durán, J.J., Mancera, E., 2015. Review on groundwater recharge in carbonate aquifers from SW Mediterranean (Betic Cordillera, S Spain). Environ Earth Sci. 74: 7571. https://doi.org/10.1007/s12665-015-4673-3

Merz, R., Blöschl, G., 2004. Regionalisation of catchment model parameters. Journal of hydrology, 287(1-4), 95-123. http://dx.doi.org/10.1016/j.jhydrol.2003.09.028

Milano, M., Ruelland, D., Fernandez, S., Dezetter, A., Fabre, J., Servat, E., Fritsch, J.M., Ardoin-Bardin, S., Thivet, G., 2013. Current state of Mediterranean water resources and future trends under climatic and anthropogenic changes. Hydrological Sciences Journal, 58(3), 498-518. http://dx.doi.org/10.1080/02626667.2013.774458

Molina, A., Melgarejo, J., 2016. Water policy in Spain: seeking a balance between transfers, desalination and wastewater reuse. International Journal of Water

Resources Development, 32(5), 781-798. http://dx.doi.org/10.1080/07900627.2015.1077103

Mook,W.G., De Vries, J.J., 2000. Volume I, Introduction: theory methods review. Environmental Isotopes in the Hydrological Cycle—Principles and Applications, International Hydrological Programme (IHP-V). Technical Documents in Hydrology (IAEA/UNESCO) No, 39 vol. 1 (http://www-naweb.iaea.org/napc/ih/IHS_publication.html, last access 12/04/2018).

Mudarra, M., Andreo, B. 2011. Relative importance of the saturated and the unsaturated zones in the hydrogeological functioning of karst aquifers: The case of Alta Cadena (Southern Spain). Journal of Hydrology 397, 263–280. https://doi.org/10.1016/j.jhydrol.2010.12.005

Mudarra, M., Andreo, B., Marín, A.I., Vadillo, I., Barberá, J.A., 2014. Combined use of natural and artificial tracers to determine the hydrogeological functioning of a karst aquifer: the Villanueva del Rosario system (Andalusia, southern Spain). Hydrogeology journal, 22(5), 1027-1039. http://dx.doi.org/10.1007/s10040-014-1117-1

Mudarra, M., Andreo, B., 2015. Role of the Soil-Epikarst-Unsaturated Zone in the Hydrogeological Functioning of Karst Aquifers. The Case of the Sierra Gorda de Villanueva del Trabuco Aquifer (Southern Spain). Hydrogeological and Environmental Investigations in Karst Systems. (ed. Andreo, B., Carrasco, F., Durán, J.J., Jiménez, P., LaMoreaux.) Series: Environmental Earth Sciences. Springer. 638 pp.

Nimon, K.F., Oswald, F.L., 2013. Understanding the results of multiple linear regression: Beyond standardized regression coefficients. Organizational Research Methods, 16(4), 650-674.

Nogués-Bravo, D., Araújo, M.B., Lasanta, T., López-Moreno, J.I., 2008. Climate change in Mediterranean mountains during the 21st century. AMBIO: A Journal of the Human Environment, 37(4), 280-285. https://doi.org/10.1579/0044-7447(2008)37[280:CCIMMD]2.0.CO;2

Obleitner, F., 1994. Climatological features of glacier and valley winds at the Hintereisferner (Ötztal Alps, Austria). Theoretical and Applied Climatology, 49(4), 225-239. https://doi.org/10.1007/BF00867462

Ozyurt, N.N., Bayari, C.S. 2008. Temporal variation of chemical and isotopic signals in major discharges of an alpine karst aquifer in Turkey: implications with respect to response of karst aquifers to recharge. Hydrogeology Journal 16: 297–309. http://dx.doi.org/10.1007/s10040-007-0217-6

Ozyurt, N.N., Lutz, H.O., Hunjak, T., Mance, D., Roller-Lutz, Z. 2014. Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times. Sci. Total Environ. 87 245–254. http://dx.doi.org/10.1016/j.scitotenv.2014.04.018

Pardo-Igúzquiza, E., Durán, J.J., Luque-Espinar, J.A., Robledo-Ardila, P.A., Martos-Rosillo, S., Guardiola-Albert, C., Pedrera, A. 2015. Karst massif susceptibility from rock matrix, fracture and conduit porosities: a case study of the Sierra de las Nieves (Málaga, Spain). Environ Earth Sci. 74:7583–7592. http://dx.doi.org/10.1007/s12665-015-4545-x

Peel, M.C., Finlayson, B.L., McMahon, T.A., 2007. Updated world map of the Köppen–Geiger climate classification. Hydrol. Earth Syst. Sci. 11, 1633–1644. http://dx.doi.org/10.5194/hess-11-1633-2007

Poage, M.A., Chamberlain, C.P., 2001. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. Am. J. Science 301 (1), 1–15. http://dx.doi.org/10.2475/ajs.301.1.1

René, P., 2013. Glaciers des Pyrénées: le réchauffement climatique en images. Éd. Cairn.

Ribalaygua, J., Pino, M.R., Pórtoles, J., Roldán, E., Gaitán, E., Chinarro, D., Torres, L., 2013. Climate change scenarios for temperature and precipitation in Aragón (Spain). Science of the Total Environment, 463, 1015-1030. https://doi.org/10.1016/j.scitotenv.2013.06.089

Rodgers, P., Soulsby, C., Waldron, S., 2005. Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment. Hydrol Process 19(11):2291–2307. http://dx.doi.org/10.1002/hyp.5677

Ruiz-Constán, A., Marín-Lechado, C., Martos-Rosillo, S., Fernández-Leyva, C., García-Lobón, J. L., Pedrera, A., López-Geta, J.A., Hernández-Bravo, J.A., Rodríguez-Hernández, L., 2015. Methodological Procedure for Evaluating Storage Reserves in Carbonate Aquifers Subjected to Groundwater Mining: The Solana Aquifer (Alicante, SE Spain). In Hydrogeological and Environmental Investigations in Karst Systems (pp. 255-262). Springer, Berlin, Heidelberg. http://dx.doi.org/10.1007/978-3-642-17435-3_28

Sánchez-Murillo, R., Brooks, E.S., Elliot, W.J., Boll, J., 2015. Isotope hydrology and baseflow geochemistry in natural and human-altered watersheds in the Inland Pacific Northwest, USA. Isotopes in environmental and health studies, 51(2), 231-254. http://dx.doi.org/10.1080/10256016.2015.1008468

Schotterer, U., Froehlich, K., Stichler, W., Trimborn, P., 1993. Temporal variation of 18O and deuterium excess in precipitation, river and spring waters in Alpine regions of Switzerland. In Isotope Techniques in the study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. Edited by IAEA. Proceedings series, ISSN 0074-1884, STI/PUB/908, ISBN 92-0-103293-5 (https://inis.iaea.org/search/search.aspx?orig_q=RN:25027909, last access 12/04/2018).

Seibert, J., 2005. HBV Light Version 2. User's Manual. Uppsala University, Dept. of Earth Science, Hydrology, Uppsala, Sweden.

Seibert, J., Vis, M.J.P, 2012. Teaching hydrological modelling with a user-friendly catchment-runoff-model software package, Hydrol. Earth Syst. Sci., 16(9), 3315–3325. http://dx.doi.org/10.5194/hess-16-3315-2012, 102012

Seibert, J., Jenicek, M., Huss, M., Ewen, T., 2015. Snow and ice in the hydrosphere. In Snow and Ice-Related Hazards, Risks and Disasters (pp. 99-137). ISBN: 978-0-12-394849-6. https://doi.org/10.1016/B978-0-12-394849-6.00004-4

Solder, J.E., Stolp, B.J., Heilweil, V.M., Susong, D.D., 2016. Characterization of mean transit time at large springs in the Upper Colorado River Basin, USA: a tool for assessing groundwater discharge vulnerability. Hydrogeology Journal, Volume 24, Issue 8, pp 2017–2033, https://doi.org/10.1007/s10040-016-1440-9

Staudinger, M., Stoelzle, M., Seeger, S., Seibert, J., Weiler, M., Stahl, K., 2017. Catchment water storage variation with elevation. Hydrological Processes, 31(11), 2000-2015. https://doi.org/10.1002/hyp.11158

Turnadge, C., Smerdon, B.D. 2014. A review of methods for modelling environmental tracers in groundwater: advantages of tracer concentration simulation. Journal of Hydrology, 519, 3674-3689. https://doi.org/10.1016/j.jhydrol.2014.10.056

Turk, J., Malard, A., Jeannin, P.-Y., Petric M., Gabrovšek, F., Ravbar, N., Vouillamoz, J., Slabe, T., Sordet, V., 2015. Hydrogeological characterization of groundwater storage and drainage in an alpine karst aquifer (the Kanin massif, Julian Alps). Hydrological Processes 29(8), 1986-1998. https://doi.org/10.1002/hyp.10313

Uhlenbrook, S., Seibert, J.A.N., Leibundgut, C., Rodhe, A., 1999. Prediction uncertainty of conceptual rainfall-runoff models caused by problems in identifying model parameters and structure. Hydrological Sciences Journal, 44(5), 779-797. https://doi.org/10.1080/02626669909492273

Vergés, J. 1999. Estudi geològic del vessant sud del Pirineu oriental i central. Evolució cinemàtica en 3D. PhD Thesis. University of Barcelona (UB), Faculty of Geology, 180 pp.

Vicente-Serrano, S.M., Lopez-Moreno, J.I., Beguería, S., Lorenzo-Lacruz, J., Sanchez-Lorenzo, A., García-Ruiz, J.M., Azorin-Molina, C., Morán-Tejeda, E., Revuelto, J., Trigo, R., Coelho, F., Espejo, F., 2014. Evidence of increasing drought severity caused by temperature rise in southern Europe. Environmental Research Letters, 9(4), 044001. https://doi.org/10.1088/1748-9326/9/4/044001

Vitvar, T., Gurtz, O., Lang, H. 1999. Application of GIS-based distributed hydrological modelling for estimation of water residence times in the small Swiss pre-alpine catchment Rietholzbach. Integrated Methods in Catchment Hydrology—Tracer. Remote Sensing and New Hydrometric Techniques (Proceedings of IUGG 99 Symposium HS4, Birmingham, July 1999). IAHS Publ. no. 258, 1999

Viville, D., Ladouche, B. and Bariac, T., 2006. Isotope hydrological study of mean transit time in the granitic Strengbach catchment (Vosges Massif, France). Application of the FlowPC model with modified input function. Hydrol. Process. 20, 1737–1751. https://doi.org/10.1002/hyp.5950

Viviroli, D., Weingartner, R., 2004. The hydrological significance of mountains: from regional to global scale. Hydrology and Earth System Sciences 8, 1016–1029. https://doi.org/10.5194/hess-8-1017-2004

Viviroli, D., Dürr, H.H., Messerli, B., Meybeck, M., Weingartner, R., 2007. Mountains of the world— water towers for humanity: typology, mapping and global significance. Water Resources Research 43 (7), W07447. https://doi.org/10.1029/2006WR005653

Wassenaar, L. I., Ahmad, M., Aggarwal, P., van Duren, M., Pöltenstein, L., Araguas, L., & Kurttas, T. 2012. Worldwide proficiency test for routine analysis of δ2H and δ18O in water by isotope-ratio mass spectrometry and laser absorption spectroscopy. Rapid Communications in Mass Spectrometry, 26(15), 1641-1648. https://doi.org/10.1002/rcm.6270

Wetzel, K., 2004. On the hydrogeology of the Partnach area in the Wetterstein Mountains (Bavarian Alps). Erdkunde 58:172–186. http://www.jstor.org/stable/25647659

Zini, L., Casagrande, G., Calligaris, C., Cucchi, F., Manca, P., Treu, F., Zavagno, E., Biolchi. S. 2015. The Karst Hydrostructure of the Mount Canin (Julian Alps, Italy and Slovenia). Hydrogeological and Environmental Investigations in Karst Systems. (ed. Andreo, B., Carrasco, F., Durán, J.J., Jiménez, P., LaMoreaux.) Series: Environmental Earth Sciences. Springer. 638 pp. https://doi.org/10.1007/978-3-642-17435-3

Appendix A: Groundwater catchment areas for the springs S-01 to S-06.

Comment [JJ21]: Answer to Reviewer #2– Q9

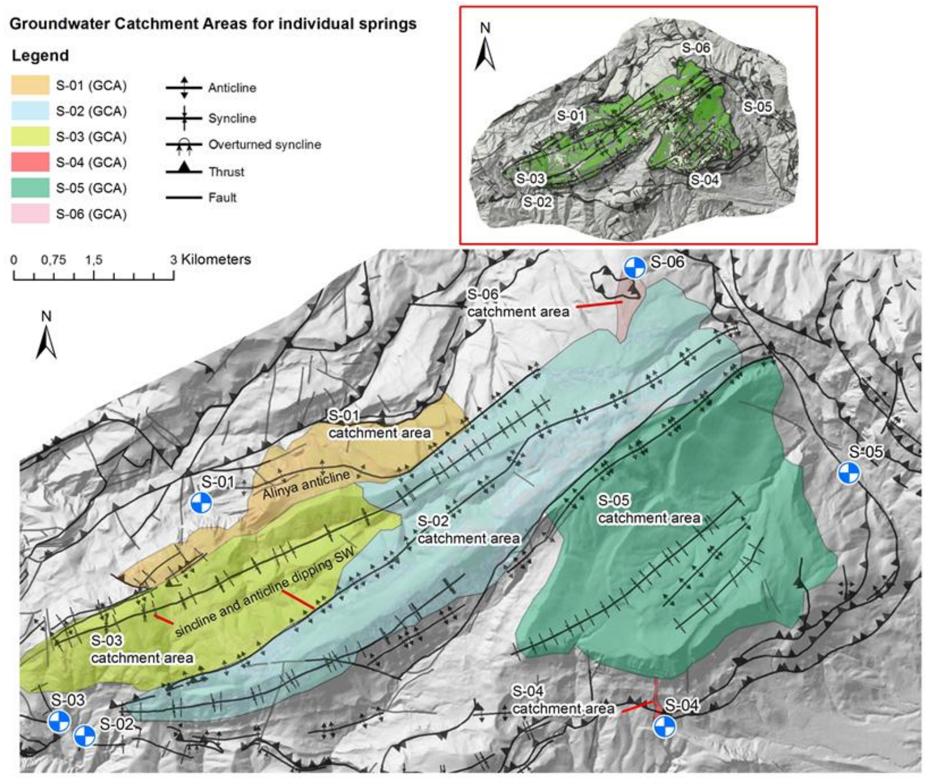


Fig. A1. Groundwater catchment areas for the springs S-01 to S-06.

Table A1. Distribution of geographical and elevation zones considered into the HBV semi-distributed rainfall-runoff model into the groundwater catchment zones. The areas of the different vegetation zones (VZs) are provided, considering the three different elevation zones into which every GWC is divided.

GWC		Elevation Zones			Vegetation Zone Areas			Percentage Areas		
Index	Associated Spring	Z_{min} (m a.s.l.)	Z_{max} (m a.s.l.)	EZ_{ij} [a] (ha)	VZ_1 [b] (ha)	VZ_2 [c] (ha)	VZ_3 [d] (ha)	VZ_1/EZ_{ij} (%)	VZ_2/EZ_{ij} (%)	VZ_3/EZ_{ij} (%)
1	S-01	1334	1600	204,0	41,8	56,8	105,5	20,5	27,8	51,7
		1601	1851	219,1	19,0	67,7	132,4	8,7	30,9	60,4
		1851	2141	122,8	4,8	6,8	111,1	3,9	5,5	90,5
2	S-02	1122	1543	106,9	8,2	26,0	72,7	7,7	24,3	68,0
		1544	1965	756,5	32,2	210,3	514,0	4,3	27,8	67,9

		1966	2385	1389,5	183,8	443,5	762,2	13,2	31,9	54,9
3	S-03	1201	1443	102,3	1,7	36,9	63,7	1,7	36,1	62,3
		1444	1686	561,2	19,5	178,9	362,8	3,5	31,9	64,6
		1687	1927	522,6	12,6	119,4	390,6	2,4	22,8	74,7
4	S-04	1468	1710	9,1	0,1	2,8	6,2	1,1	30,8	68,1
		1711	1847	0,9	0,1	0,5	0,3	11,1	55,6	33,3
		1848	1875	0,1	0,0	0,1	0,0	0,0	100,0	0,0
5	S-05	1421	1663	234,3	8,1	24,4	201,8	3,5	10,4	86,1
		1664	1973	635,5	45,4	126,0	464,1	7,1	19,8	73,0
		1974	2348	1278,4	215,5	495,0	568,0	16,9	38,7	44,4
6	S-06	1838	1926	11,9	0,7	0,7	10,5	5,9	5,9	88,2
		1927	2014	20,7	0,1	1,8	18,8	0,5	8,7	90,8
		2015	2101	13,4	0,0	2,3	11,2	0,0	17,2	83,6

(a) For a given elevation zone EZ_{ij} the subscripts "i" (from 1 to 6) and "j" refer to the corresponding groundwater catchment zone and elevation zone number, respectively; (b) VZ_1 corresponds to open areas; (c) VZ_2 corresponds to mountain meadows; (d) VZ_3 corresponds to forest zones

Appendix B: Sinusoidal functions fitting the measuring the isotopic content ($\delta^{18}O$ and δ^2H) variation in precipitation and spring discharges.

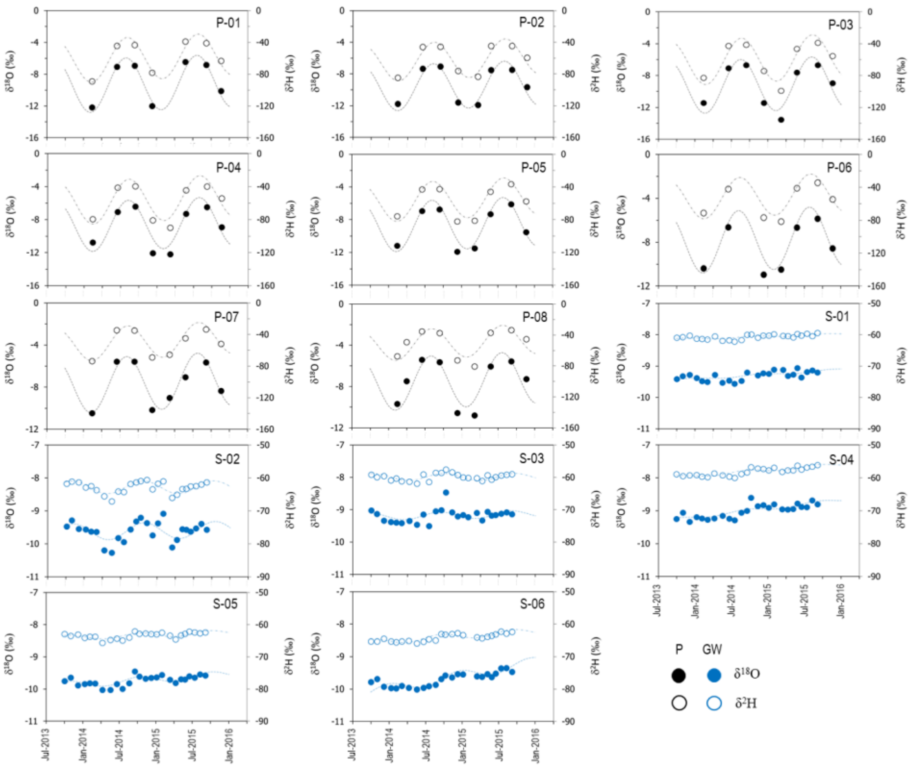


Fig. B1. Isotopic content of precipitation (P; black symbols) and spring discharge (GW; blue symbols). $\delta^{18}O$ and δ^2H are indicated by solid and empty symbols, respectively The dashed lines indicate the fitted sinusoidal function [Eq.1]. The identification codes correspond to those in Table 1.

Appendix C: HBV hydrological modeling

Table C1. List of abbreviations for the vegetation zone parameters of HBV (Seibert, 2005)

Parameter	Units	Valid range	Description
TT	°C	(-inf,inf)	Threshold temperature to produce accumulation of precipitation as snow. Melt of snow starts if temperatures are above TT calculated with a simple degree-day (degree-Δt in case of a non-daily time step) method
CFMAX	mm/Δt/°C	[0,inf)	Degree-Δt factor - CFMAX varies normally between 1.5 and 4 mm oC-1 day-1 (in Sweden), with lower values for forested areas. As approximation the values 2 and 3.5 can be used for CFMAX in forested and open landscape respectively.
SFCF	-	[0,inf)	Snowfall correction factor
CFR	-	[0,inf)	Refreezing coefficient
CWH	-	[0,inf)	Water holding capacity, according to: refreezing meltwater = CFR·CFMAX(TT-T)'
FC	mm	(0,inf)	Maximum soil moisture storage
LP	-	[0,1)	Soil moisture value above which AET reaches PET
BETA	-		Parameter that determines the relative contribution to runoff from rain or snowmelt

Table C2. List of abbreviations for the catchment parameters of HBV (Seibert, 2005)

Parameter	Units	Valid range	Description
PERC	mm/Δt	[0,inf)	Threshold parameter
UZL	mm	[0,inf)	Threshold parameter
K0	1/Δt	[0,1)	Storage (or recession) coefficient 0
K1	1/Δt	[0,1)	Storage (or recession) coefficient 1
K2	1/Δt	[0,1)	Storage (or recession) coefficient 2
MAXBAS	Δt	[1,100]	Length of triangular weighting function

Table C3. Objective functions for the calibration of the HBV hydrologic model, where Q_{obs_i} and Q_{sim_i} are the measured and computed of spring discharge values, respectively, $\overline{Q_{obs}}$ is the arithmetic mean of the observed spring discharge values, and $\overline{Q_{sim}}$ is the arithmetic mean of the computed spring discharge values.

Objective function	Observations
$R_{eff} = 1 - \frac{\sum_{i=1}^{N}(Q_{sim_i} - Q_{obs_i})^2}{\sum_{i=1}^{N}(Q_{obs_i} - \overline{Q_{obs}})^2}$	R_{eff} = 1 means perfect fit R_{eff} = 0, indicates that the model fits the observed data no better than a horizontal line through $\overline{Q_{obs}}$ R_{eff} < 0 means very poor fit
$R^2 = \frac{\left(\sum_{i=1}^{N}(Q_{obs_i} - \overline{Q_{obs}}) * (Q_{sim_i} - \overline{Q_{sim}})\right)^2}{\sum_{i=1}^{N}(Q_{obs_i} - \overline{Q_{obs}})^2 * \sum_{i=1}^{N}(Q_{sim_i} - \overline{Q_{sim}})^2}$	R^2 is the determination coefficient. The higher the R^2 value the better the model performance

Table C4. Calibrated values of the parameters in the HBV-light model

Catchment Parameters	Units	S-01	S-02	S-03	S-04	S-05	S-06
Snow Routine (VZ_1)							
TT	°C	-0,2	-4,52	-1,6	-1,1	-1	-1,1
CFMAX	mm/d/°C	1,9	2,4	2	1,7	2,8	1,2
SFCF	-	1	2,38	0,5	1	1,2	1,5
CFR	-	1	2,5	0,7	0,5	0,6	0,6
CWH	-	0,5	2	2	1	0,8	0,8
Snow Routine (VZ_2)							
TT	°C	-0,2	-4,39	-1,6	-0,5	-3	-0,46
CFMAX	mm/d/°C	1,9	1	2	1,6	1	2,1
SFCF	-	1	2,6	0,7	1	1,2	1,16
CFR	-	1	2,5	0,7	0,3	1	1
CWH	-	1	2	1	1	0,2	0,2
Snow Routine (VZ_3)							

TT	°C	4	6	6	0	5,5	6,5
CFMAX	mm/d/°C	1,5	1	1,5	1,5	1	4
SFCF	-	0,001	0,001	0,001	0,01	0,001	0,001
CFR	-	0,7	1	0,7	0,2	0,4	0,4
CWH	-	2	2	3	1	1	1
Soil Moisture Routine (VZ_1)							
FC	mm	95	75	80	75	50	80
LP	-	0,07	0,01	0,02	0,02	0,01	0,01
BETA	-	0,60	0,40	1,54	1,70	0,30	2,5
Soil Moisture Routine (VZ_2)							
FC	mm	180	120	150	125	139	150
LP	-	0,07	0,01	0,06	0,01	0,01	0,01
BETA	-	0,60	2,20	3,90	3,45	1,80	2,7
Soil Moisture Routine (VZ_3)							
FC	mm	750	550	490	750	660	700
LP	-	0,00	0,01	0,01	0,01	0,01	0,01
BETA	-	6,00	3,00	5,70	6,00	3,50	4,00
Response Routine							
PERC	mm/d	5	20,0	2,2	1,1	25,0	1,7
UZL	mm	100	80	100	110	100	100
K0	1/d	0,20	0,50	0,20	0,20	0,20	0,40
K1	1/d	0,07	0,11	0,13	0,17	0,20	0,20
K2	1/d	0,01	0,02	0,04	0,04	0,05	0,05
Routing Routine							
MAXBAS	d	1,7	6,2	2	2,45	4,3	4,22

Table C5. Goodness of the result of the HBV calibrations for each spring model

HBV model	R_{eff} (-)	R^2 (-)
S-01	0,55	0,55
S-02	0,66	0,67
S-03	0,73	0,78
S-04	0,57	0,73
S-05	0,77	0,80
S-06	0,62	0,66

Appendix D: FlowPC modeling

Table D1. Fitted parameters of the exponential-piston flow model (EPM) for the estimated mean transit times (τ) with FlowPC model and $\delta^{18}O$ data

Parameters	S-01	S-02	S-03	S-04	S-05	S-06
β (%)□	0	0	0	0	0	0
δ_β (‰)[b]	0	0	0	0	0	0
η (-)[c]	1,02	1,02	1,00	1,01	1,02	1,02
τ (yr)	2,25	1,42	2,25	2,33	2,88	2,58
RMSE (‰)	0,03	0,04	0,03	0,03	0,02	0,03

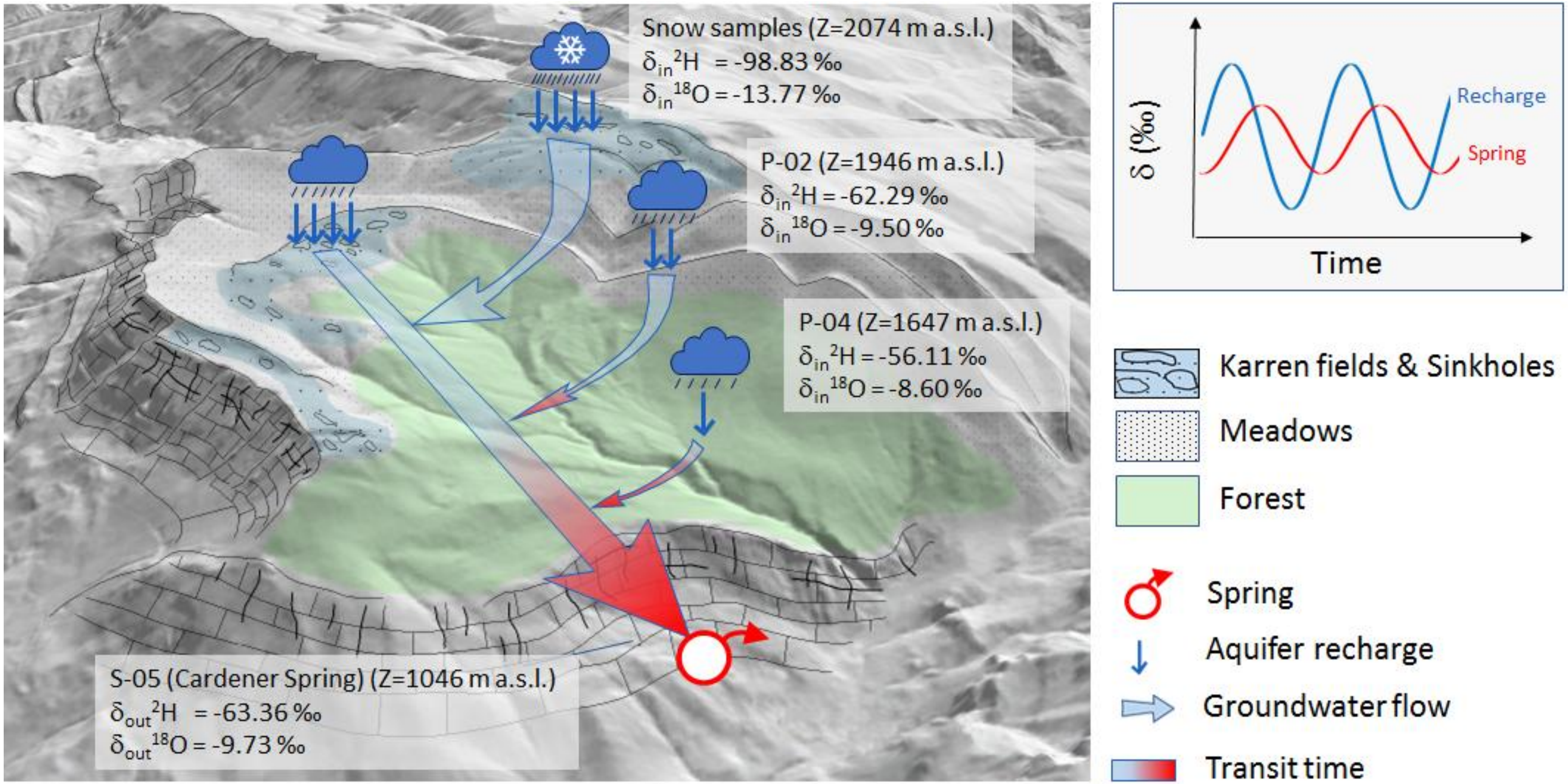
(a) A constant discharge component as a fraction (usually older) of the total spring volumetric discharge flow rate. (b) Constant isotopic content of β. (c) η is the ratio of the total volume to the volume with exponential distribution transit time (TTD). η = 1 means the Exponential model (EM) and η>1 for Exponential-piston flow model (EPM)

Table D2. Fitted parameters of the exponential-piston flow model (EPM) for the estimated mean transit times (τ) with FlowPC model and $\delta^{2}H$ data

Parameters	S-01	S-02	S-03	S-04	S-05	S-06
β (%)[a]	0	0	0	0	0	0
δ_β (‰)[b]	0	0	0	0	0	0
η (-)[c]	1,01	1,00	1,01	1,00	1,01	1,02
τ (yr)	3,00	1,92	2,33	2,67	2,83	2,75
RMSE (‰)	0,19	0,21	0,17	0,22	0,18	0,20

(a) A constant discharge component as a fraction (usually older) of the total spring volumetric discharge flow rate. (b) Constant isotopic content of β. (c) η is the ratio of the total volume to the volume with exponential distribution transit time (TTD). η = 1 means the Exponential model (EM) and η>1 for Exponential-piston flow model (EPM)

***Graphical Abstract**



***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Amplitude of seasonal isotopic composition of rainfall depends on elevation

Moisture generating rainfall in the study zone comes from the Mediterranean

The aquifer main recharge zones located at elevations between 2700 and 2100 m a.s.l

Considering transient recharge improves the estimations of mean transit times

Transit times in agreement with the karstic nature of the aquifer system

Contribution of isotopic research techniques to characterize high-mountain-Mediterranean karst aquifers: The Port del Comte (Eastern Pyrenees) aquifer.

Herms. I.[a], Jódar, J.[b,*], Soler, A.[c], Vadillo, I.[d], Lambán, L.J.[e], Martos-Rosillo, S.[e], Núñez, J.A.[a], Arnó, G.[a], Jorge, J.[f]

(a) Àrea de Recursos Geològics. Institut Cartogràfic i Geològic de Catalunya (ICGC), Barcelona, Spain

(b) Groundwater Hydrology Group. Dept. Civil Engineering and Environment, Technical University of Catalonia (UPC), Barcelona, Spain & Aquageo Proyectos S.L., Spain

(c) Grup de Mineralogia Aplicada i Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

(d) Centro de Hidrogeología, Universidad de Málaga (UMA), Málaga, Spain

(e) Instituto Geológico Minero de España (IGME), Spain

(f) Departament d'Enginyeria Minera, Industrial i TIC. Universitat Politècnica de Catalunya (UPC), Manresa, Spain

* Corresponding author: Jorge Jódar (jorge.jodar@hydromodelhost.com). Telf:(+34) 619712122

Abstract

Water resources in high mountain karst aquifers are usually characterized by high rainfall, recharge and discharge that lead to the sustainability of the downstream ecosystems. Nevertheless, these hydrological systems are vulnerable to the global change impact. The mean transit time (MTT) is a key parameter to describe the behavior of these hydrologic systems and also to assess their vulnerability. This work is focused on estimating MTT by using environmental tracers in the framework of high-mountain karst systems with a very thick unsaturated zone (USZ). To this end, it is adapted to alpine zones a methodology that combines a semi-distributed rainfall-runoff model to estimate recharge time series, and a lumped-parameter model to obtain MTT. The methodology has been applied to the Port del Comte Massif (PCM) hydrological system (Southeastern Pyrenees, NE Spain), a karst aquifer system with an overlying1000 m thick USZ. Six catchment areas corresponding to most important springs of the system are considered. The obtained results show that hydrologically the behavior of the system can be described by an exponential flow model (EM), with MTT ranging between 1.9 and 2.9 years. These MTT values are shorter than those obtained by considering a constant recharge rate along time, which is the easiest and most applied aquifer recharge hypothesis when estimating MTT through lumped-parameter models.

Keywords: Stable isotopes; Seasonal isotopic amplitude; Altitudinal line; Recharge; Mean transit time; Karst.

1. Introduction

High mountain zones are known as "water towers" because they generate the main water resources feeding the most important rivers in the world (Viviroli et al., 2007). This phenomenon is especially important in the drought-prone Mediterranean area (Vicente-Serrano et al 2014), where water availability is scarce and greatly dependent on runoff from headwater basins (De Jong et al., 2009). Moreover, water discharge from mountain areas is critical to ensure water supply in the lowland and coastal fringe

(Viviroli and Weingartner, 2004; García-Ruiz et al 2011), where human activity (agriculture, industry, tourism) concentrates.

Future scenarios for climate change in the whole Mediterranean region forecast an increase in temperature and a decrease in precipitation at the end of the 21st century (Giorgi and Lionello, 2008). These effects may well impact the Mediterranean high mountain zones (Nogués-Bravo et al., 2008; Lopez-Moreno et al., 2009; Ribalaygua et al., 2013), modifying the hydrological behavior of their headwater basins (Barnett et al., 2005; García-Ruiz et al. 2011, and references therein). Nevertheless, the first evidence of such changes has already been reported in the Pyrenees, the southernmost European range where glaciers can be found (Grunewald and Scheithauer, 2010). Pyrenean glaciers have undergone an intense retreat since the middle of the last century, causing most of them to face a certain close extinction (Chueca et al., 2007; René 2013; Marti et al., 2015; López-Moreno et al., 2016). In addition, during this period, both mean annual precipitation and number of rainy days have shown a clear decreasing trend in this zone (Lopez-Moreno et al., 2010), along with a lesser snowfall and snow accumulation (López-Moreno, 2005). These effects directly impact the water storage capacity of the associated headwater systems (Seibert et al., 2015), as well as their associated hydrological response in terms of both river discharge flowrates and timing of maximum discharges (López-Moreno and García-Ruiz, 2004; Gremaud et al., 2009). These changes will directly impact the downstream zones by complicating the current water stress situation in the Mediterranean zone (Milano et al., 2013; Hernández-Mora et al., 2014, Molina and Melgarejo, 2016). Because of the hydrological outlook that is not so promising, it is essential to understand the functioning of the mountain hydrological systems of the Mediterranean area, especially those scenarios in which groundwater (GW) plays a major role in the headwater discharge, because mountain aquifers maintain base flows to rivers during the recurrent Mediterranean dry periods (Hoerling et al 2012; Vicente-Serrano et al., 2014).

Despite playing a strategic role, most high mountain hydrogeological systems are still insufficiently understood (Goldscheider, 2011). Conventional hydrogeological investigation techniques (Bakalowicz, 2005; Goldscheider and Drew, 2007) are often difficult to apply in alpine regions because of the difficult access and the harsh working conditions, along with the types of instruments needed for conducting research in high mountain zones (Lauber et al., 2014; Hood and Hayashi, 2010). However, a growing number of publications are focusing on the importance of groundwater in the functioning of high-mountain watershed rivers in different geological settings, including alluvial/rockfall/talus aquifers (Lauber and Goldscheider, 2014; Kurylyk and Hayashi, 2017), fractured aquifers (Jódar et al., 2017; Barberá et al., 2018a) and karst systems (Wetzel, 2004; Goldscheider, 2005; Gremaud et al., 2009; Mudarra et al., 2014; Allocca et al., 2015; Lambán et al., 2015; Chen, 2017; Barberá et al., 2018b; Kazakis et al., 2018). Determining the magnitude of groundwater recharge and aquifer Mean Transit Time (MTT) are key issues for understanding and managing alpine groundwater systems. Spring hydrograph analysis and environmental tracer methods allow for characterizing aquifer recharge and discharge processes, estimating recharge zone elevation and transit times, determining drainage structures, and assessing spring vulnerability, as well as calculating water resources in headwater aquifers (Wetzel, 2004; Rodgers et al., 2005; Einsiedl, 2005; Farlin and Maloszewski, 2013; Jódar et al., 2016b; Malard et al., 2016; Epting et al., 2018).

In high-altitude alpine karst aquifers, groundwater recharge processes highly depend on temporal and spatial distribution of precipitation and snowmelt (Lauber and Goldscheider, 2014). The estimation of MTT in karst systems is conditioned by the existence of variable flow conditions. These systems normally show triple-porosity and different connected parts: the karstic conduits that allows rapid flow, and the fissured-porous matrix that shows intermediate to slow flow. Artificial tracer test normally injected in preferential flow paths (i.e. the channels) doesn't consider the fissured-porous matrix of the aquifer, which can be important as far as the total karst water volumes (Maloszewski et al., 2002). In this respect, the use of artificial tracers to characterize such hydrological systems is not enough since it doesn't allow characterizing all the components of the flow. Others important factors that govern the suitability of injection test for MTT estimations is the existence of a thick unsaturated zones (USZ): conducting tracer tests by injecting it at the surface of the thick USZ is likely a failing tracer test given the large uncertainties regarding the likelihood of hydraulic connection between the tracer injection point and the sampled system discharge point (Lauber and Goldscheider, 2014). Additionally, the adverse working conditions and the type of material of the instruments necessary to correctly perform the tracer test (Goldscheider et al., 2008) in high-mountain areas make it difficult to execute them.

As a result, the hydrogeological behavior of most of the mountain karst systems with an associated thick USZ remain uncharacterized, despite of being the exploration of these systems on the focus of speleogenetic research since the last decades (Ballesteros et al., 2015a, and references therein).

Lumped parameter models (LPMs) are useful to simulate the behavior of such complex mountain karst systems, even when they are poorly characterized. These models do not require a detailed hydrological knowledge of the physical system. Moreover, LPMs naturally integrate the USZ of the aquifer as a part of the whole hydrological system to be modeled (Turnadge and Smerdon, 2014). Additionally, the stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$) in rainfall have proved to be good environmental tracers for investigating the dynamics of such hydrological systems karst systems (Andreo et al., 2004). These tracers enter the system as recharge, migrate downgradient exploring the whole hydrological system, and leave the karst aquifer with spring discharge or by lateral mass transfer to other hydrogeologically connected aquifer units. In this line, this work is devoted to estimate MTT of a high-mountain karst aquifer with a thick unsaturated zone by using ^{8}O and ^{2}H as environmental tracers along with LPMs. To this end, it is considered the approach presented by Vitvar et al. (1999) to estimate MTT in a small Swiss pre-alpine aquifer. The original approach is adapted to high mountain zones by considering the existing vertical gradients of precipitation and air temperature along the slope of high mountains, but also the role played by the snow accumulation and ablation processes in the runoff generation. The resulting method combines in series two LPMs: (1) a semi-distributed rainfall-runoff HBV model (Bergström, 1976; Seibert, 2005) that simulates the observed hydrodynamical system response while taking into account the elevation dependences of the different hydrometeorological variables (i.e. Precipitation and temperature) and associated processes (e.g. snow accumulation and ablation), and (2) a FlowPC model (Małoszewski and Zuber, 1996) that estimates the mean transit time of the hydrological system while simulating the environmental tracer content evolution in the system discharge. This is done by numerically integrating a convolution integral (Maloszewski et al., 1983; Jódar et al., 2014). In our case, the

FlowPC model uses as input data: a) the recharge time series of the aquifer obtained with the HBV model, and b) the time series isotope content ($\delta^{18}O$ and $\delta^{2}H$) in recharge, which is obtained through a spatiotemporal characterization of the isotope contained of precipitation.

The methodology is applied to the hydrological system of Port del Comte Massif (PCM; NE Spain), a karst aquifer with a 1000 m thick USZ. The hydrological system mainly discharges though the Cardener springs into the homonym river, which is the main tributary of the Llobregat River, the first water resources provider to the city of Barcelona (NE Spain). Despite the strategic role of Cardener springs the hydrologic behavior of the karst system remains unknown. This study contributes to a better hydrological characterization of PCM hydrological system. Moreover, the proposed methodology can be applied to characterize other high mountain karst aquifers with an overlying thick USZ that are common in many alpine zones elsewhere the globe.

2. Study area

The study area is located at the Port del Comte Massif (PCM), which is situated in the eastern part of the Pyrenees, NE Spain (Fig. 1). The elevation of the watershed ranges from approximately 900 m a.s.l., up to 2387 m a.s.l., at the 'Pedró dels Quatre Batlles' peak. With approximately 110 km^2, it contains one of the main mountain karst aquifers of the Catalan Pyrenees. The watershed of the massif divides the river basin of the Cardener River at the E and S and the river basin of the Segre River at the NW and SW. The massif constitutes an independent structural and hydrogeological unit.

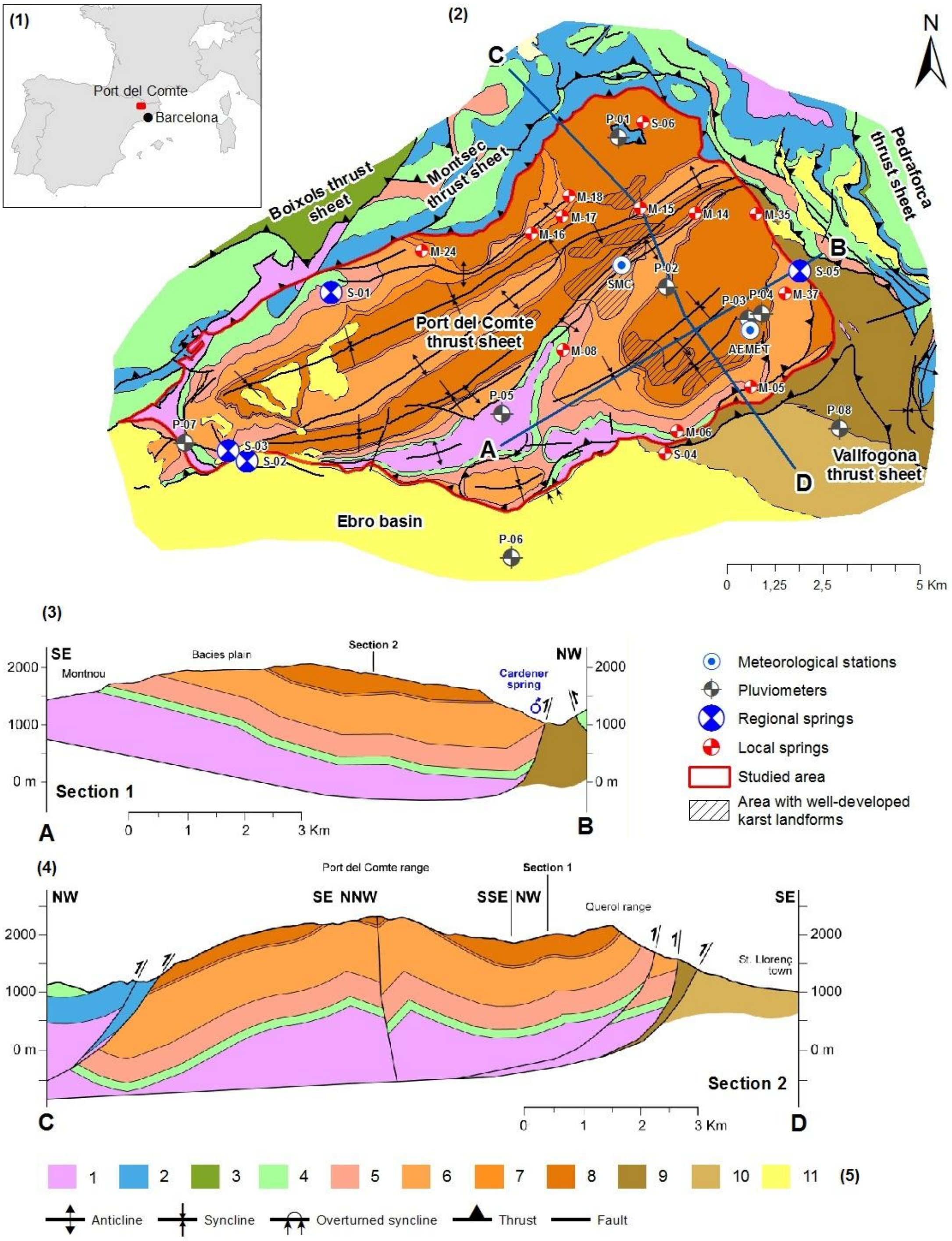


Fig. 1. (1) Location map of the study zone. (2) Geological map (geological map modified from ICGC, 2007). (3) Geological cross-section A-B. (4) Geological cross-section C-D. (5) Geological legend: [1] Triassic – shales, limestones, dolomites and evaporates; [2] Jurassic – marls, bioclastic limestones and dolomites; [3] Lower Cretaceous – mudstones, ammonite limestones and marl; [4] Upper Cretaceous – limestones, marls, calcarenites and terrigenous

deposit; [5] Garumnian – red shales and limestones; [6] Lower Eocene – fissured and karstified alveoline limestones and dolomites; [7] Lower Eocene – marls, sandstones and limestone; [8] Lower Eocene – fissured and karstified micritic and bioclastic limestones; [9] Middle Eocene – sandstones, marls, conglomerates, limestones and evaporates; [10] Upper Eocene – continental alluvial systems: conglomerates and sandstones; [11] Oligocene – continental alluvial systems: conglomerates, breccias and sandstones.

2.1 Meteorological setting

From a climatic point of view, and according to the Köppen-Geiger classification (Peel et al., 2007), the study zone has a cold climate without dry season and temperate summer (defined as 'Dfb' type; accordingly to AEMET and IMA, 2011). At the meteorological station MS-01 (Fig. 1), which is located at 2315 m a.s.l., the average values of precipitation (P), temperature (T) and potential evapotranspiration (ETP) calculated with the Hargreaves and Samani (1982) equation are 1055 mm/yr, 3,24 °C and 525 mm/yr, respectively. These three variables show a seasonal variation (Fig. 2) and an elevation dependence. The measured vertical gradients (lapse rate) of precipitation (∇_zP), atmospheric temperature (∇_zT) and potential evapotranspiration (∇_zETP) are 8,9 mm/yr/100 m, −0,74 °C/100 m and −32,3 mm/yr/100 m, respectively. The snow cap is present in the upper zones of the basin in winter and spring, maintained annually for 3 to 4 months since 1800 m a.s.l., meaning that precipitation is partly produced as snow.

Despite the high average rainfall above 1000 mm/year, in most of the study area the surface runoff is almost nonexistent, and it is not observed until reaching lower altitudes.

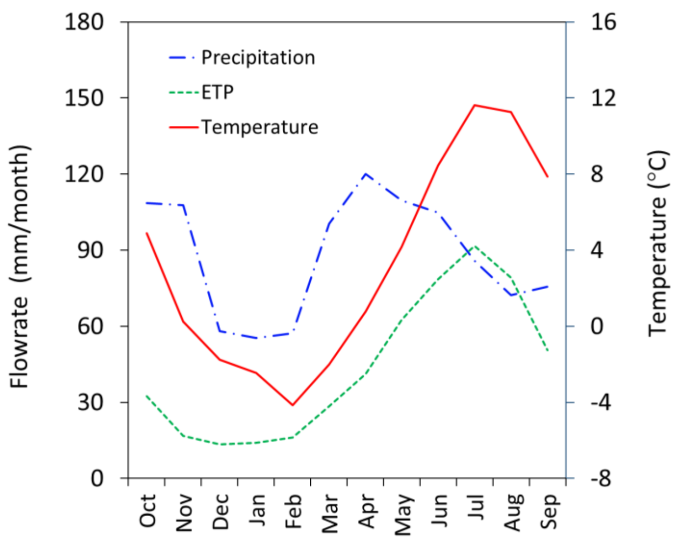


Fig. 2. Seasonal variation of precipitation, potential evapotranspiration and temperature measured at the meteorological station MS-01 (see Table 1) located at 2315 m a.s.l. for the period Sep 2005- Apr 2016.

2.2 General settings of the study zone

From a geological perspective, the massif belongs to the PCM thrust sheet that presents complex structural relationships in its contours (Fig. 1). On the E, the PCM mantle borders on the mantle of Cadí, coinciding with the point of origin for the Cardener River (spring S-05; Fig. 1). To the NE and NW, the PCM is limited by the tectonic plates of the mantles of Sierras Marginales, Montsec and Boixols. To the S, the PCM mantle overlaps with the conglomeratic materials of the Ebro Basin, the southern foreland basin of the Pyrenees. The internal structure of the PCM mantle is formed by a set of folds and thrusts detached above the Triassic. These folds have a constant direction NE-SW parallel to the NW limit of the mantle (Vergés, 1999). The stratigraphic series contains materials from the Triassic, Jurassic, Cretaceous and Paleogene with a total of approximately 1000 m thickness. The main karst aquifer inside PCM massif is in the Paleocene - Eocene carbonate rocks. The geologic structure and stratigraphy of the PCM thrust strongly influence the location of the existing karst springs, their groundwater geochemistry and their hydrologic behavior. The lower Upper Cretaceous/Paleocene (Garumnian facies) substrate materials underlying the Palaeocene aquifer are composed of sandstone, siltstone and shale. These materials constitute an impervious layer for the overlaying aquifer system.

From the geomorphological point of view, the PCM has a characteristic triangular geometry. The PCM has a smooth rounded landscape with a plain in the highest part without vegetation cover and with almost no soil, which corresponds to approximately 10% of the total area. The rest of the massif is covered by mountain meadows (29%) and forest (61%) with scarce soil depth up to medium developed soil cover. Different karstic forms progressively appear from 1950 m a.s.l. upwards, being well developed at 2050 m a.s.l., with sinkholes, dry caves, dolines and karren fields, generating a heterogeneous karstified hydrogeological system.

The hydrogeological conceptual model of the PCM aquifer system considers that recharge is produced by infiltration of precipitation as rainfall and snowmelt. The magnitude and distribution of infiltration is conditioned by the development of the karst landforms. The infiltration is produced (1) in a concentrated way through the local karstic elements such as dolines and (2) in a diffuse way by rain and snowmelt along the whole PCM area. The epikarst unsaturated zone (NSZ) presents a thickness close to 1000 m in the highest zones of the PCM. The infiltrated water flows vertically through the NSZ towards the saturated zone.

The hydrogeological system naturally discharges through the large number of existing springs. Approximately 100 springs have been found in the PCM showing large discrepancies in their mean discharge flow rate, ranging from values <<1 L/s up to values > 100 L/s. Most of these springs discharge a local subhorizontal interflow characteristic of a small entity (i.e., Local springs, Table 1). However, in terms of groundwater discharge, there are six important springs in the PCM (i.e., Regional springs, Table 1). These springs have been monitored regularly for this research, showing that all of them have a highly variable discharge flow rate (Fig. 3). Four of these regional springs (S-01, S-02, S-03 and S-05) are the principals discharging points of the whole hydrogeological system. The four springs are located at elevations between 944 and 1098 m a.s.l. (see Table 1). Through these main springs, the hydrogeological system discharges at two principal watersheds: the Cardener River watershed to the east and the Segre River watershed to the northwest. Groundwater flow direction is conditioned by the geological structure of PCM. Nevertheless, the exact position of the regional groundwater table is poorly known.

Table 1. Meteorological stations, pluviometers and springs in the study zone sampled during the period July 2013 – October 2015.

Code	Type	Name	Elevation (m a.s.l.)	Num. water samples (-)	Discharge rate (L/s)
MS-01	Met. Station	SMC-Z8	2315	-	-
MS-02	Met. Station	AEMET-0127O	1800	-	-
P-01	Pluviometer	Refugi de l'Arp	1936	7	-
P-02	Pluviometer	Bassa Clot de la Vall	1946	8	-
P-03	Pluviometer	Refugi Bages	1768	8	-
P-04	Pluviometer	Casa X&A	1657	8	-
P-05	Pluviometer	Casa Ramonet	1450	8	-
P-06	Pluviometer	Casa Cavallera	1216	7	-
P-07	Pluviometer	Camp. La Comella	1062	8	-

P-08	Pluviometer	Camp. Morunys	896	9	-
S-01	Regional Spring	Font Aiguaneix	1098	25	8 - 73
S-02	Regional Spring	Font Sant Quintí	944	25	70 – 575
S-03	Regional Spring	Font Can Sala	1062	25	0,25 – 148
S-04	Local Spring	Font Coll de Jou	1464	25	0,07 - 0,59
S-05	Regional Spring	Fonts del Cardener	1032	25	57 – 904
S-06	Local Spring	Font carretera Refugi Arp	1858	25	0,04 – 7
M-05	Local Spring	Font del Ginebró	1730	4	<0,001
M-06	Local Spring	Font de la Garganta	1657	4	0,02-0,49
M-08	Local Spring	Font Orris 02	1871	4	0,1 – 0,7
M-14	Local Spring	Font Estivella	2053	4	0,07 – 5
M-15	Local Spring	Font Arderic	2158	3	0,03 – 2,8
M-16	Local Spring	Font del Casalí	2077	1	<0,001
M-17	Local Spring	Font del Diumenge	1989	2	0,004 – 0,026
M-18	Local Spring	Font barraca Sangonella	1940	1	0,001 - 0,01
M-24	Local Spring	Font dels Acens	1550	4	0,06 – 0,23
M-35	Local Spring	Font Ca l'Arreplagant	1330	4	<0,001 – 0,02
M-37	Local Spring	Font La Part (esllav.)	1315	4	0,5 – 1

3. Materials and methods

3.1 Field work

To collect precipitation samples, a network of 8 cumulative precipitation gauges (pluviometers) of the type CoCoRaHS RG202 Official-4 was installed at elevations between 896 and 1935 m a.s.l. (P-01 a P-08; Fig. 1). The pluviometers consist of a polycarbonate cylindrical deposit with a diameter of 10,8 cm. The pluviometers include a top funnel that captures and guides precipitation into the storing deposit, where according to the technical procedure for the stations of the Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA), a 0,5 cm paraffin oil floating layer is added to avoid evaporation. The pluviometers were sampled seasonally (except the first winter with two campaigns), a total of 9 campaigns from Dec. 2013 to Dec. 2015. Additionally, one snow sampling survey was conducted in December 2003. The snow samples were obtained by drilling through the entire snow depth (Lambán et al., 2015) and were taken at different locations with elevations ranging from 1935 to 2150 m a.s.l.

Groundwater samples were collected under different hydrodynamic conditions between Oct. 2013 and Dec. 2015. In this period, the springs S-01 to S-06 were sampled approximately monthly, for a total of 25 sampling campaigns. Groundwater samples were taken before the snow arrival in autumn (Oct. 2013 and Oct. 2014), and after the snow-melting season (Apr. 2014 and Apr. 2015). In these springs, groundwater discharge was measured once every two weeks from Jul. 2013 to Oct. 2015 (Fig. 3). In springs S-01, S-02, S-03 and S-05 the discharge flow rate was measured by conducting slug-injection salt dilution tests (Cervi et al., 2014), whereas the volumetric method was used for the precision discharge measurement in springs S-04 and S-06. The M-## springs (Table 1) showed a tiny and intermittent discharge. Therefore, groundwater samples were only taken with uneven frequency when it was possible.

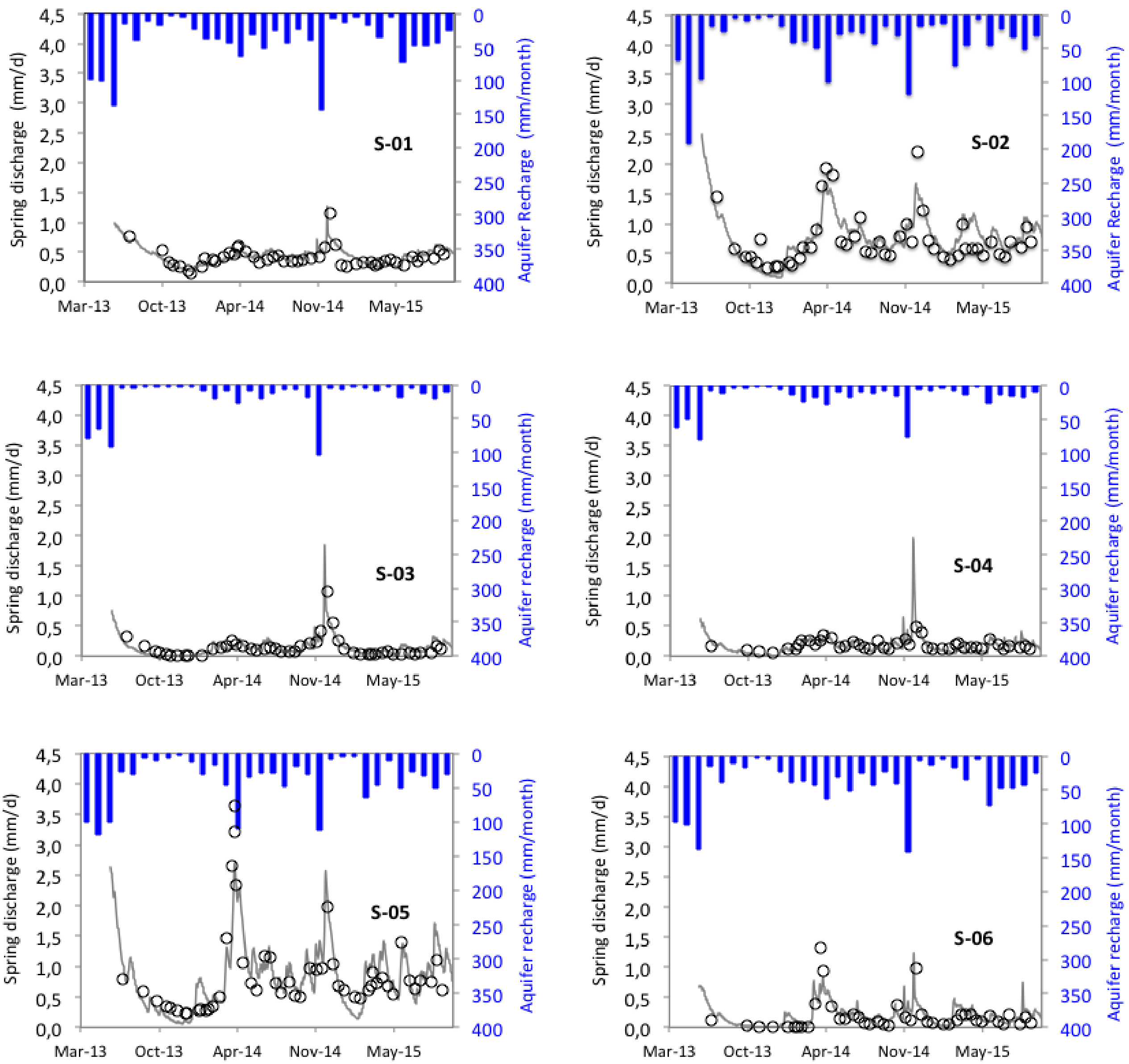


Fig. 3. Measured spring discharge (circles) in the six monitored springs (S-01 to S-06, Table 1) of the PCM hydrogeological system. Gray lines indicate the spring discharge numerically simulated with the HBV model (Seibert and Vis, 2012). For each spring, blue columns indicate the recharge values time series used as input data to the corresponding HBV model.

The isotopic composition (δ^2H and $\delta^{18}O$) of all low salinity water samples was determined in the Center of Hydrogeology of the University of Málaga (CEHIUMA), where a Picarro® "L2130-I" isotopic water analyzer was used. The analytical uncertainties for $\delta^{18}O$ and $\delta^{2}H$ are ±0.2 ‰ and ±1.0 ‰, respectively. According to Coplen et al., (2011) several international and laboratory standards have been interspersed for normalization of analyses. The standards used (WICO-13, WICO-14, WICO-15) were calibrated in an interlaboratory comparison (Wassenaar et al., 2012). All results are given relative to the V-SMOW standard.

3.2 Approach for spring catchment delineation

A critical aspect to understand the behavior of karst hydrogeological flow systems is the delineation of the spring capture zones (i.e., recharge areas) and their boundaries (Goldscheider and Drew, 2007). Ideally, the delineation should be based on the proven information of connection between recharge areas and the discharge points. In high mountain zones, this connection may be confirmed by conducting tracer tests (Goldscheider et al., 2008; Mudarra et al., 2014; Barberá et al., 2018b). When this information is not available, the spring capture zone can be indirectly inferred by considering inputs from other classical information sources such as geophysics, structural geology and geomorphology data interpretation. However, 3D conceptual modeling techniques are currently being used to delineate the spring capture zones: Malard et al. (2015) analyze spring discharge hydrographs based on geological three-dimensional (3D) conceptual modeling (Butscher and Huggenberger, 2007, 2008; Martos-Rosillo et al., 2014; Ruiz-Costán et al., 2015; Malard et al., 2015; Ballesteros et al., 2015b; Epting et al., 2018).

In this work, a combined 3D conceptual methodology has been used to delineate the catchment areas associated with each spring. The delineating criteria are based on the information provided by three complementary methods: (1) the interpretation of the geological structure and the subsurface catchments relative to each spring location. To this end, a 3D geological model has been developed in the 3DMove software platform (Midland Valley Exploration Ltd.); (2) the analysis of the disposition and location of the karst landforms over the area, and (3) the analysis through GIS spatial analysis tools of the ground surface structure, including type of soils (CREAF, 2009) and vegetation (Appendix A) at the spring recharge elevation zones. In the case of the regional springs S-01, S-02, S-03 and S-05, the three listed methods have been applied to delineate their catchment zone, whereas in the case of the perched springs S-04 and S-06, only the previous methods (2) and (3) could be applied. Fig. A1 (Appendix A) shows the catchment zones (i.e., aquifer units) obtained for the selected springs.

The delineated catchment zones associated with the regional springs divide PCM into two main blocks: (1) a southwestern block that includes only the catchment zone associated with S-05. This catchment zone is characterized by a syncline dipping NW structure (Fig. 1). From a functional point of view, this zone is hydrodynamically independent of the rest of PCM given the existence of an anticline and a main NE-SW fault that prevents lateral flows. (2) The northeastern block formed by the catchment zone associated with springs S-01, S-02 and S-03. The geological structure of this block regulates the regional groundwater flows, so as the Alinyà anticline controls the discharge of spring S-01, and the main syncline-anticline system dips SW along with the minor faults and synclines dipping south conditions the discharge of springs S-02 and S-03. Table A1 (Appendix A) provides the geographical details of the delineated groundwater catchment zones.

3.3 Characterizing the seasonal variation of environmental tracers

The evolution of some environmental variables is linked to the atmospheric temperature variation. As a result, these variables often show a similar seasonal pattern that can be characterized with a general sinusoidal function $\delta(t)$ (Jódar et al., 2014). This function consists of two additive terms, a sine-wave function [Eq. 1] plus a temporal linear trend for the mean [Eq. 2].

$$\delta(t) = A\sin(\omega(t - t_0) + \varphi) + \bar{\delta} \tag{1}$$

$$\bar{\delta} = \alpha(t - t_0) + \overline{\delta_0} \tag{2}$$

where A is the amplitude of the sinusoidal function, ω is the angular frequency, φ is the angular initial at time t_0, α is the slope of the linear trend, and $\overline{\delta_0}$ is the linear trend value at time t_0. The parameters A, α and $\overline{\delta_0}$ can be estimated by using the solution of any of the commonly available spreadsheet software's or manually. In this work, the root-mean-squared error (RMSE) is used as the selection criterion for the best fit to the measured isotope content time series.

In the case time series with a short amount of data (e.g., associated with the M-## springs in Table 1), it is not possible to obtain reliable estimates for, α, A, and $\overline{\delta_0}$ by using the method proposed above. In this case, no linear trend in the mean value is assumed (α = 0), and $\overline{\delta_0}$ and A are estimated as:

$$\overline{\delta_0} = \frac{1}{N}\sum_{i=1}^{N}\delta_i \tag{3}$$

$$A = \max\left(\mathrm{Abs}\left(\overline{\delta_0} - \delta_i\right)\right);\ \forall i = 1 \div N \tag{4}$$

where *N* is the number of the isotopic content value of the time series.

Hydrogeological systems transfer the isotopic input signal of recharge. The tracer input seasonal signal is buffered and delayed as it propagates through the aquifer towards the discharging point (Fig. 4). This tracer transport process through the hydrological system can be described by the convolution integral that relates the tracer input content in recharge δ_{in} to the tracer input content in the spring discharge δ_{out} as shown below.

$$\delta_{out}(t) = \int_{-\infty}^{t} \delta_{in}(t) g(t - t') dt' \qquad (5)$$

where *t* is the time of tracer entry as recharge, *t'* is the integration variable and *g*(*t'*) is a weighting function describing the Transit Time Distribution (TTD) exit of tracer content that entered the aquifer at different times in the past. The differences between the input and the output tracer signals are related to the aquifer system MTT (τ) which is the first moment of the system TTD and is given by

$$\tau = \int_{0}^{\infty} t g(t) dt \qquad (6)$$

where *V* is the volume of mobile water in the system (Małoszewski et al., 1983), and *Q* is the volumetric flow rate through the system. In the case of natural gradient hydrogeological systems, MTT corresponds to the mean amount of time for groundwater to travel from the recharge zone to the discharging spring. In this situation, MTT is related to the spring discharge flow rate *Q*, and the aquifer storage *V*as follows (Custodio and Llamas, 1976):

$$\tau = \frac{V}{Q} \tag{7}$$

Additionally, in natural gradient hydrogeological systems with a seasonal varying input tracer function, MTT can be estimated as (Małoszewski et al., 1983):

$$\tau = \frac{1}{\omega}\sqrt{\left(\frac{A_{\delta_{\mathrm{in}}}}{A_{\delta_{\mathrm{out}}}}\right)^2 - 1} \tag{8}$$

where $A_{\delta_{\mathrm{in}}}$ and $A_{\delta_{\mathrm{out}}}$ are the amplitudes of the seasonal variation of the isotopic content in the aquifer recharge and the spring discharge, respectively. As can be shown, the above equation compares $A_{\delta_{\mathrm{in}}}$ with respect to $A_{\delta_{\mathrm{out}}}$, so the larger the amplitude dampening is, the longer the transit time.

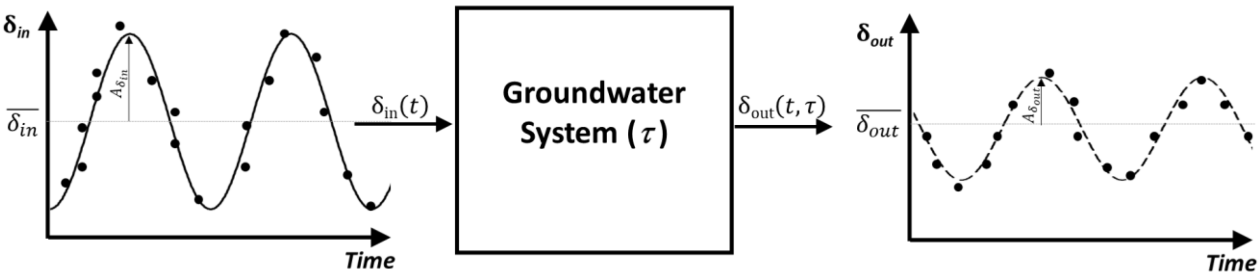


Fig. 4. Schematic representation of the groundwater system response $\delta_{\mathrm{out}}(t, \tau)$ to a hypothetical input tracer function $\delta_{\mathrm{in}}(t)$ (modified from Jódar et al., 2016b), where τ means MTT.

3.4 Numerical approach for simulating the aquifer behavior

To reproduce the observed spring discharge flow rates and the associated isotopic content, a two-step methodology has been used:

(1) Simulation of the hydrodynamic behavior of the hydrogeological system. To this end, the freely available version of the semi-distributed conceptual precipitation–runoff model HBV-Light (Seibert and Vis, 2012) is used. HBV is a conceptual rainfall-runoff model for catchment hydrology modeling that solves a general water balance equation. HBV has been used in different alpine mountain hydrologic research studies (Braun and Renner, 1992; Hottelet, et al., 1993; Uhlenbrook et al., 1999; Merz and Blöschl, 2004; Konz and Seibert, 2010; Staudinger et al., 2017; Epting, et al., 2018; Jódar et al., 2018). This model has become a standard tool for simulating high mountain snow-dominated hydrological systems. This code requires as input data some hydroclimatic catchment information such as the relative weight with respect to the total area of the different altitude and associated vegetation zones in the catchment, the vertical lapse rates ∇_zP and ∇_zT, as well as the time series of daily P, T, and ETP. The hydrological catchment can be separated into numerous elevation zones, depending on the elevation gap between the lowest and the highest points of the catchment. In this work, every zone has been divided into three elevation zones (Table A1 in Appendix A). Additionally, every elevation zone can be divided into different vegetation zones. Based on the Land Cover Map of Catalonia (CREAF, 2009), three vegetation zones are considered: (1) open areas corresponding to zones of both poor or no soils where karst landforms are very well-developed (karren fields, sinkholes, dolines, etc.), (2) areas with mountain meadows and soil moderately developed, and (3) alpine forest zones with moderate to well-developed soils. A two stacked linear reservoir is used to simulate the hydrological system dynamics. The upper reservoir is used to generate surface and subsurface runoff whereas the lower reservoir generates

groundwater runoff. The model considers vegetation zones parameters and catchment zone parametrer (Tables C1 and C2 of Appendix C, respectively). They are can be automatically calibrated by minimizing an efficiency objective function (R_{eff}; Table C3, Appendix C), which is already implemented in HBV. The model output includes the daily time series of aquifer recharge Q_R, which is used in the following step.

(2) Simulation of the transient isotopic content variation in the groundwater discharge. The temporal variation of the isotopic content in the spring discharge is simulated with FlowPC (Małoszewski and Zuber, 1996, 2002), a lumped parameter model typically used to estimate groundwater MTTs with the aid of observed environmental tracer data (Viville et al., 2006; Einsiedl et al., 2009; Katsuyama et al., 2010; Lauber and Goldscheider, 2014; Sánchez-Murillo et al., 2015; Mądrala et al., 2017). The program solves the convolution integral [Eq. 5] and transforms the isotopic input tracer signal $\delta_{in}(t)$ entering the hydrogeological system as recharge into the isotopic output tracer signal $\delta_{out}(t)$ leaving the system through the spring discharge. To this end, FlowPC includes among others two parametric TTDs which are especially well suited for simulating karst aquifer systems: (A) The exponential model (EM), also known as a “good mixing model”, is typically applied in systems where the groundwater flow lines tend to converge towards the water sampling points (Zuber, 1986; Amin and Campana, 1996). (B) The Exponential-Piston model (EPM) or “real system model”, which combines two parts in line, an unconfined upstream part where recharge enters the system and an exponential distribution of transit times is assumed, and a confined downstream part where the flow scheme is

approximated like the piston flow model (Zuber, 1986). The weighting function for EPM is described by the following equation.

$$g(t) = \begin{cases} 0 & t < \tau\left(1 - \frac{1}{\eta}\right) \equiv t_\tau \\ \frac{1}{\tau}\eta e^{-\frac{\eta}{\tau}+\eta-1} & t \geq t_\tau \end{cases} \quad (9)$$

where η is the ratio of total volume of the hydrogeological system to the volume of the system in which the exponential TDD exists, and τ is MTT. [Eq. 9] also describes the EM weighting functions when η =1, which is the lowest bound of this parameter. The model parameters (η and τ) are calibrated by minimizing the RMSE function.

FlowPC requires the time series of (1) monthly aquifer recharge $\widehat{Q_R}$ (hereinafter, a circumflex accent over a flow or an isotopic content variable indicates that the variable is cumulated monthly or averaged, respectively), which is obtained from the HBV model outputs for each simulation, and (2) the corresponding monthly averaged isotopic content of the recharge $\widehat{\delta_R}$. Given the karstic nature of the hydrogeological system, we assume that the isotopic content of local recharge and its seasonal characteristics (i.e., $\overline{\delta}_{in}, A_{\delta_{in}}$) are the same as the isotopic content and seasonal characteristics of local precipitation ($\overline{\delta}_P, A_{\delta_P}$). Since $\overline{\delta}_P$ and A_{δ_P} are known, then $\delta_P(t)$ is analytically obtained through [Eq.1]. As $\delta_P(t)$ is a daily time function, it is necessary to transform it into $\widehat{\delta_P}$. For the

j^{th} month, $\widehat{\delta_{P}}_j$ is obtained by weighting the daily values of recharge isotopic content $\delta_{P_{ij}}$ by the corresponding daily recharge rate $Q_{P_{ij}}$ as

$$\widehat{\delta_{R}}_j \sim \widehat{\delta_{P}}_j = \frac{\sum_{i=1}^{N} \delta_{P_{ij}} Q_{R_{ij}}}{\sum_{i=1}^{N} Q_{R_{ij}}} \tag{10}$$

where N is the number of days of the j^{th} month. The Appendix D includes all the technical details corresponding to the different FlowPC models used in this work

3.5 Statistical analysis of the relationship between the infiltration coefficient and recharge

To analyze the factors that controls the mean calculated infiltration coefficient (ξ) in the PCM, a linear regression model has been built, expressing the dependent variable ξ as a linear function of N explanatory variables Ψ_i as

$$\xi = \lambda_0 + \sum_{i=1}^{N} \lambda_i \Psi_i \tag{11}$$

where λ_0 is the intercept (constant) term, and λ_i ($i \geq 1 \div N$) are the regression coefficients associated with the predictors Ψ_i. In this study, the predictor variables of the linear regression model of the [Eq.11] are the elevation of the spring recharge zone Z_R (Table 3), the mean precipitation at the spring recharge zone P_{ZR} (Table 6), and the percentages of open areas, mountain meadows and forest in the spring catchment zones (VZ_1, VZ_2 and VZ_3, respectively; Table A1 in Appendix A). The coefficient of determination of the regression is one, so the model reproduces the whole variance of ξ. Table 7 shows the intercept value λ_0, the regression coefficients λ_i, and their corresponding standardized value β_i ($i \geq 1 \div N$). The standardized value β_i measures the expected change in ξ, in standard deviation units, for a one standard deviation change in Ψ_i, provided that other explanatory variables in the model (Ψ_j, $\forall i \neq j$) are fixed (Nimon and Oswald, 2013). The larger the absolute value of β_i, the more important the corresponding predictor Ψ_j is.

4. Results and discussion

4.1 Results from observed data

The isotopic content of the precipitation corresponding to the water samples taken is shown in Fig. 5A. The mean isotopic content of precipitation is lighter in winter and autumn than that in spring and summer, as one would expect given the dependence between the isotopic content in rainfall and temperature (Mook and De Vries, 2000). The obtained values are aligned between the Global Meteoric Water Line (GMWL) and the West Mediterranean Meteoric Water Line (WMMWL) (Fig. 5A). The local water meteoric water line (LMWL) that is obtained by linear regression (N= 76; R^2= 0,97) is defined as $\delta^2H = 8{,}05 \cdot \delta^{18}O + 12{,}74$. From a seasonal point of view, the isotopic content of precipitation in autumn and winter presents a larger variability than the isotopic content of precipitation in spring and summer, as shown in Fig. 5B by the error bars indicating the standard deviation associated with every seasonal value. The isotopic content in groundwater changes seasonally much less, than the isotopic content in precipitation (Fig. 5B), pointing out the existence of a good mixing flow process in the discharging points of the aquifer.

The geographical location of the study zone postulates the Mediterranean as the most important source of precipitation. This assumption is supported by the overall mean deuterium excess (*dex*= δ^2H - $8 \cdot \delta^{18}O$) value of 12,03 ± 3,37 ‰ obtained for all the precipitation samples analyzed (Celle-Jeanton et al., 2001; Jiménez-Martínez and Custodio, 2008). Nevertheless, the Atlantic fingerprint in rainfall can be observed in the above *dex* value through its variation interval, which provides a minimum *dex* value of 8,66 ‰ (Froehlich et al., 2001; Araguás-Araguás and Díaz-Teijeiro, 2005).

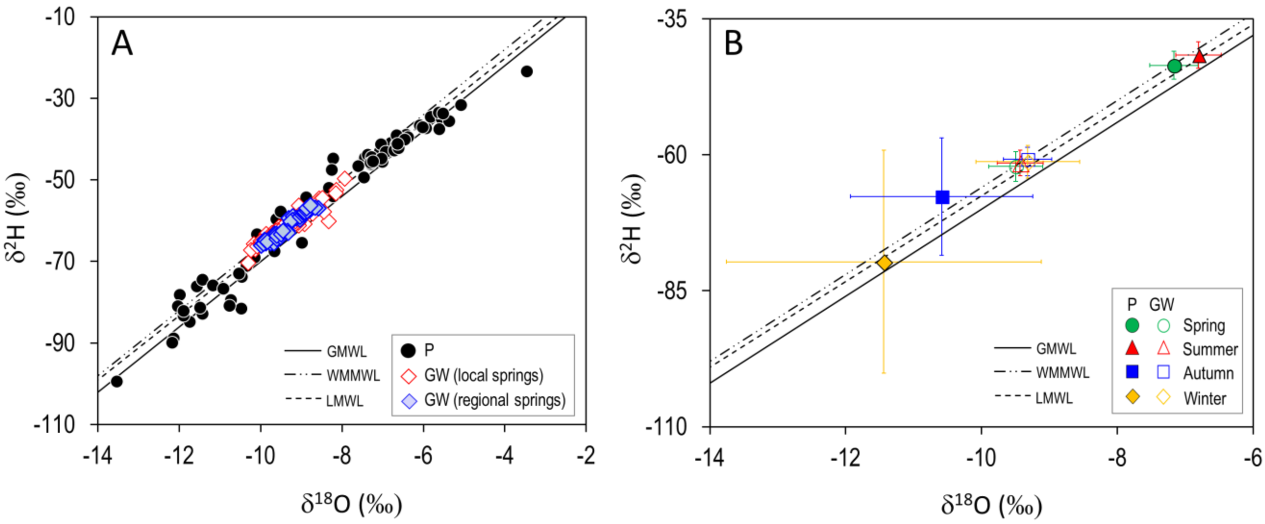


Fig. 5. (A) Values of $\delta^{18}O$ and δ^2H in precipitation (P; solid circles) and groundwater (GW) from local springs (empty red diamonds) and from regional springs (solid blue diamonds) for the period Oct. 2013 – Dec. 2015. (B) Seasonal overall averages of $\delta^{18}O$ and δ^2H for precipitation (P; solid symbols) and groundwater (GW; empty symbols). The spring, summer autumn and winter values are indicated by green circles, red triangles, blue squares and orange diamonds, respectively. GMWL (Clarke and Fritz, 1997) is the Global Meteoric Water Line (slope 8 and *dex*=10‰), WMMWL is the Western Mediterranean Meteoric Water Line (slope 8 and *dex*=14‰) and LMWL is the Local Meteoric water Line (slope 8,05 and *dex*=12,74‰).

The isotopic composition of precipitation and spring discharge show a seasonal variation, which is not reflected in the deuterium excess. A seasonal variation in *dex* would indicate the existence of different moisture sources generating rainfall in the study zone by following a certain seasonal pattern (Schotterer et al 1993; Liu et al 2008; Froehlich et al 2008). The lack of such seasonal pattern supports the Mediterranean as the main rainfall source.

A sine-wave function [Eq.1] is used to characterize every one of the measured seasonal time series of isotopic content in water from the sampling points (Fig. B1 in Appendix B). Tables 2 and 3 show the calibrated mean isotopic content ($\bar{\delta}$) and amplitude (*A*) corresponding to the time series of isotopic content of precipitation and spring discharge, respectively.

Table 2. Mean value $\bar{\delta}_{in}$ and amplitude $A_{\delta_{in}}$ of the seasonal variation in the isotopic content of precipitation for the sampled pluviometers.

	$\bar{\delta}_{in}$ (‰)			$A_{\delta_{in}}$ (‰)	
Pluviometer	$\delta^{18}O$	$\delta^{2}H$	*dex*	$\delta^{18}O$	$\delta^{2}H$
P-01	-9.20	-59.91	14.56	3.34	26.89
P-02	-9.50	-62.29	13.88	2.87	23.23
P-03	-9.20	-60.25	12.94	3.29	27.92
P-04	-8.60	-56.11	12.87	3.02	26.05
P-05	-8.60	-55.65	12.37	3.05	23.31
P-06	-7.80	-51.10	9.53	2.76	23.96
P-07	-7.50	-49.06	10.24	2.59	20.92
P-08	-7.50	-50.22	9.40	2.55	19.53

Table 3. Mean value $\bar{\delta}_{out}$ and amplitude $A_{\delta_{out}}$ of the seasonal variation in the isotopic content of groundwater for the springs sampled. For every spring, the elevation of the corresponding recharge zone Z_R is included. For this elevation, the associated amplitude $A_{\delta_{ZR}}$ of the seasonal variation in isotopic content of precipitation is shown.

	$\bar{\delta}_{out}$ (‰)	$A_{\delta_{out}}$ (‰)	Z_R (m a.s.l)	$A_{\delta_{ZR}}$ (‰)

Spring	$\delta^{18}O$	$\delta^{2}H$	*dex*	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	dex	$\delta^{18}O$	$\delta^{2}H$
S-01	-9,31	-60,65	13,81	0,12	1,10	1892	1881	1852	3,16	26,23
S-02	-9,61	-62,82	14,06	0,25	1,93	2038	2046	1902	3,24	27,18
S-03	-9,18	-59,85	13,60	0,11	1,07	1830	1819	1702	3,12	25,88
S-04	-9,01	-58,11	13,95	0,10	0,67	1745	1686	1881	3,07	25,12
S-05	-9,73	-63,36	14,50	0,14	0,88	2099	2088	1994	3,28	27,41
S-06	-9,69	-64,03	14,80	0,15	0,90	2078	2140	1798	3,27	27,71
M-05	-9,01	-58,53	13,52	0,44	1,81	1744	1718	1793	3,07	25,31
M-06	-8,70	-54,75	14,88	0,54	2,51	1597	1428	2071	2,98	23,65
M-08	-9,49	-62,22	13,68	0,27	1,84	1979	2001	1826	3,21	26,92
M-14	-9,69	-64,01	13,53	1,08	8,01	2079	2138	1795	3,27	27,70
M-15	-9,73	-63,81	14,05	0,87	6,24	2099	2123	1901	3,28	27,61
M-16	-9,77	-64,13	14,05	0,65	4,00	2118	2147	1902	3,29	27,75
M-17	-9,76	-64,32	13,73	0,49	2,86	2110	2161	1836	3,29	27,83
M-18	-9,59	-63,12	13,64	0,62	4,12	2031	2070	1817	3,24	27,31
M-24	-9,41	-62,26	13,02	0,47	1,64	1941	2004	1690	3,19	26,93
M-35	-8,90	-57,02	14,14	0,94	7,54	1690	1602	1920	3,04	24,65
M-37	-8,44	-54,00	13,53	0,26	0,93	1469	1371	1795	2,90	23,33

The mean isotopic content in rainfall $\bar{\delta}_{in}$ shows a clear-cut linear relationship with elevation (Fig. 6) that allows defining Isotopic Altitudinal Lines (IAL) for δ^{18}O, δ^{2}H and *dex*, with slopes (i.e., vertical gradients $\nabla_z\delta^{18}$O, $\nabla_z\delta^{2}$H and $\nabla_z dex$) of -1,9, -12,1 and 4,7 ‰/km, respectively. Vertical gradients ($\nabla_z\delta$) of mean isotopic content in precipitation are common in mountain zones (see Poage and Chamberlain, 2001, and references therein) and are related to the atmospheric decreasing thermal vertical profile existing along the slope of the mountains. $\nabla_z\delta$ values obtained for the study zone are like those obtained in other alpine areas, especially in the central Pyrenees and the Alps (Table 4).

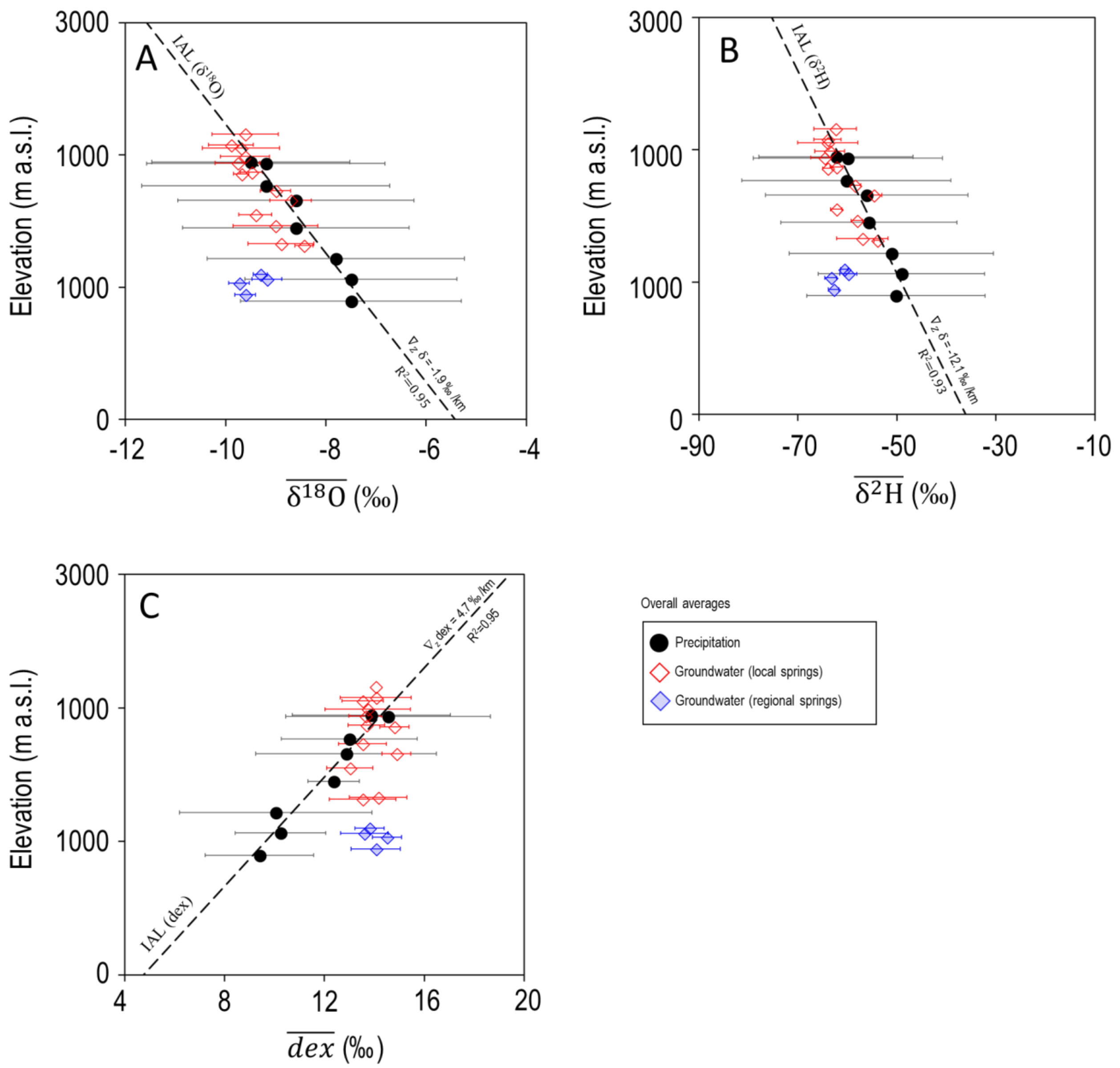


Fig. 6. Relationship between elevation and the mean isotopic content in precipitation and springs. (A) δ^{18}O, (B) δ^{2}H, and (C) *dex*. Error bars indicate the standard deviation. Dashed lines indicate the local Isotopic Altitudinal Line (IAL) of precipitation.

The vertical gradients of the mean isotopic content in precipitation depend linearly on the mean seasonal precipitation (Fig. 7). In the case of δ^{18}O and δ^{2}H, the higher the seasonal precipitation is, the lower the seasonal gradient is. In the case of *dex*, the relationship is reversed, obtaining a higher $\nabla_z dex$ value as seasonal precipitation increases. In a seasonal framework, recycling moisture evaporated from the land surface to atmosphere may increase *dex* of local precipitation. Soil evaporation is maximum when atmospheric vapor pressure deficit (Δe = e-e_{sat}, e being the atmospheric water pressure and e_{sat} the saturating water pressure at the air parcel temperature) is maximum, if the soil contains water for evaporating. Therefore, to allow soil water to evaporate, it is necessary to have enough (1) soil water content, which is higher in spring and autumn since these are the rainiest seasons, and (2) atmospheric vapor pressure deficits (Δe). Satisfying these two conditions, $\nabla_z dex$ is maximum when the difference in *dex* (i.e., Δe) between the highest and the lowest points of the mountain slope is maximum. Given that e_{sat} is an increasing function of temperature (Gonfiantini et al., 2001), Δe will decrease as temperature declines. During the cold season, despite a thermal difference existing between the highest and lowest points of the mountain, the difference in Δe between these points is minimum. Additionally, the commented Δe difference is minimum as well when there is no thermal difference along the mountain slope, a situation that is favored by the cathabaltic winds in winter (Obleitner, 1994; Gladich et al., 2011) but is also favored by the vertical atmosphere air mixing during the typical summer local low pressure convective rainfall events.

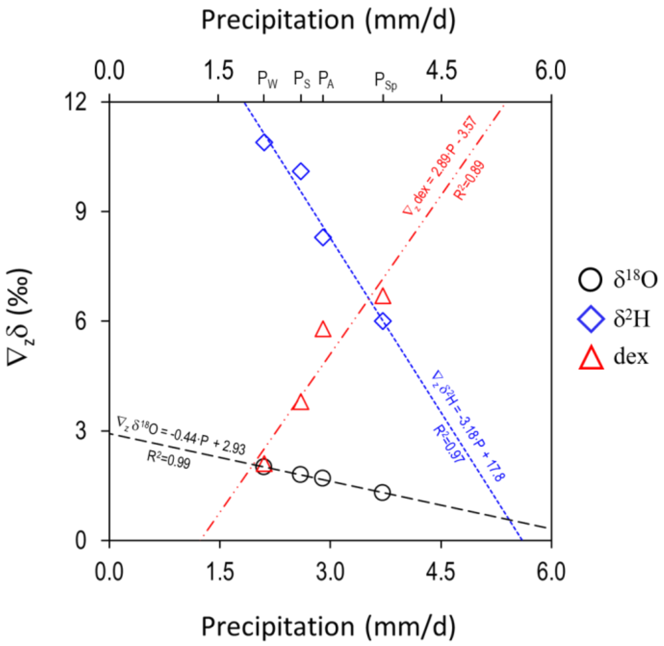


Fig. 7. Dependence of the vertical gradient of the mean isotopic content with respect to the mean seasonal precipitation. The subscripts Sp, S, A, and W stand for spring, summer, autumn and winter, respectively.

The amplitude of the seasonal variation in the isotopic content of precipitation $A_{\delta_{in}}$ relates linearly to elevation (Fig. 8) to allow defining Amplitude Altitudinal Lines (AAL) for δ^{18}O and δ^{2}H with slopes (i.e., vertical gradients $\nabla_z A_{\delta^{18}\mathrm{O}}$ and $\nabla_z A_{\delta^{2}\mathrm{H}}$) of 0,6 and 5,7 ‰/km, respectively. Similar vertical gradients have previously been reported in the central Pyrenees (Jódar el al., 2016b) and the Bernese Alps (Jódar el al., 2016a) (Table 4).

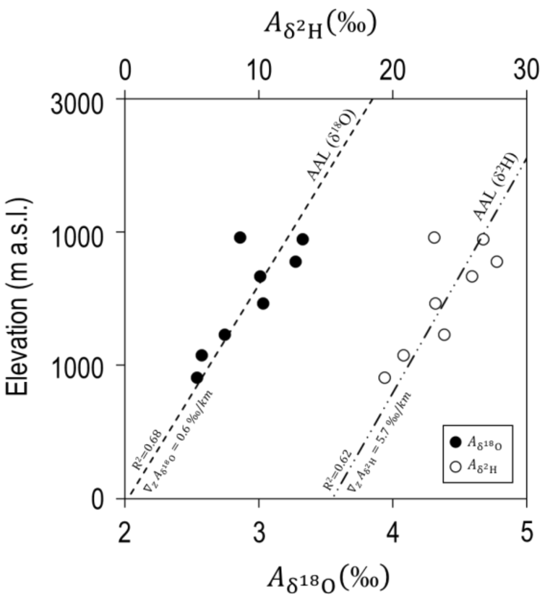


Fig. 8. Relationship between elevation and amplitude of the seasonal variation of the isotopic content ($\delta^{18}O$, δ^2H) in precipitation. Dashed line and dashed-dotted line indicate the local Amplitude Altitudinal Lines (AALs) of precipitation for $\delta^{18}O$ and δ^2H, respectively.

Table 4. Vertical gradients of mean isotopic water content and amplitude of the seasonal variation of the isotopic water content in precipitation.

Zone	Z_{min} - Z_{max} (m a.s.l.)	$\nabla_z\delta^{18}O$ (‰/km)	$\nabla_z\delta^2H$ (‰/km)	$\nabla_z dex$ (‰/km)	$\nabla_z A_{\delta^{18}O}$ (‰/km)	$\nabla_z A_{\delta^2H}$ (‰/km)	Reference
Eastern Pyrenees (PCM[a])	896-1936	-1,9	-15,2	4,7	0,6	6,1	This study
Central Pyrenees (PNOMP[b])	772-2200	-2,2	-17,4	2,2	0,9	4,4	Jódar et al. (2016a)
Bernese Alps	874-2023	-3,0	-19,7	3,7	1,6	14,6	Jódar et al. (2016b)
Austrian Alps	580-2245	-1,9	-12,0	2,7	-	-	Froehlich et al. (2008)
Austrian Alps	469-1598	-1,3	-8,0	3,4	-	-	Froehlich et al. (2008)

Central Andes (western flank)	2380-4250	-4,7	-42,5	2,2	-	-	Aravena et al. (1989)
Central Andes (eastern flank)	2380-4250	-1,9	-14,3	1,1	-	-	Fiorella et al. (2015)
Central Andes (eastern flank)	200-4080	-1,7	-11,7	2,0	-	-	Gonfiantini et al. (2001)
Western Carpathians	104-2008	-2,1	-	-	-	-	Holko et al. (2012)
Mount Cameroon	10-4050	-1,16	-11,4	1,4	-	-	Gonfiantini et al. (2001)

(a): Port del Comte Massif; (b): Ordesa and Monte Perdido National Park

The mean isotopic content of groundwater corresponding to local (perched) springs shows a relationship with elevation dependence with a vertical gradient larger than that of precipitation (Fig. 6), indicating the existence of aquifer recharge along the mountain slope, a process also known as slope effect (Custodio and Jódar, 2016). Additionally, the evolution of the isotopic content in the spring discharge shows a seasonal dependence like precipitation but showing smaller amplitudes (Fig. B1 in Appendix B). Even being lumped, the seasonal pattern of recharge is observed in the spring discharge, indicating that MTT should not be longer than 5 or 6 years (DeWalle et al., 1997).

The isotopic altitudinal line (IAL, Fig. 6) allows estimation of the elevation of the recharge zone (Z_R) corresponding to every spring by projecting their mean isotopic content on IAL. Table 3 shows Z_R for all the springs, with their mean Z_R value ranging between 1420 m a.s.l. (M-37) and 2136 m a.s.l. (M-17). With a known value for Z_R, it is possible to calculate the amplitude of the variation in the isotopic content in precipitation at the recharge zone elevation ($A_{\delta_{ZR}}$) by projecting Z_R on the amplitude altitudinal line (AAL, Fig. 8). Table 2 shows $A_{\delta_{ZR}}$ for every spring. Finally, if both $A_{\delta_{ZR}}$ (i.e., $A_{\delta_{in}}$ at the springs recharge zone) and $A_{\delta_{out}}$ are known, it is possible to obtain a first analytical estimate of MTT through [Eq. 8]. Table 5 provides the MTT values obtained for all the springs. As can be shown, the obtained MTT values range between 0,5 and 5 yr.

Table 5. MTT values estimated for the springs sampled

	$\delta^{18}O$			$\delta^{2}H$		
Spring	τ^a(yr)	τ^b(yr)	η(-)	τ^a(yr)	τ^b(yr)	η(-)
S-01	4,10	2,25	1,02	3,78	3,00	1,01
S-02	2,06	1,42	1,02	2,23	1,96	1,00
S-03	4,67	2,25	1,00	3,83	2,33	1,01
S-04	4,70	2,33	1,01	5,93	2,67	1,00
S-05	3,73	2,88	1,02	4,98	2,83	1,01
S-06	3,47	2,58	1,02	4,90	2,75	1,02
M-05	1,10	-	1,00	2,22	-	1,00
M-06	0,86	-	1,00	1,49	-	1,00
M-08	1,89	-	1,00	2,32	-	1,00
M-14	0,45	-	1,00	0,53	-	1,00
M-15	0,58	-	1,00	0,69	-	1,00
M-16	0,79	-	1,00	1,09	-	1,00
M-17	1,06	-	1,00	1,54	-	1,00
M-18	0,82	-	1,00	1,04	-	1,00
M-24	1,07	-	1,00	2,61	-	1,00
M-35	0,49	-	1,00	0,5	-	1,00
M-37	1,77	-	1,00	3,99	--	1,00

(a) Analytical MTT value obtained by [Eq. 8]. (b) Numerical MTT value obtained by FlowPC.

4.2 Aquifer recharge evaluation through HBV

The HBV semi-distributed conceptual rainfall–runoff model has been used to simulate the observed groundwater discharge in every spring. The spring discharges were measured every fortnight between July 2013 and October 2015. This period has been used for calibrating the HBV parameters, which are shown in Table C4 (Appendix C). The efficiency parameter R_{eff} that describes the goodness of the model fit ranges between 0,55 (S-01) and 0,77 (S-05) (Table C5, Appendix C). The computed discharges resemble the observed discharges by reproducing their temporal evolution in all the springs (Fig. 3).

The results from the HBV model indicated that recharge is especially concentrated in the open areas (VZ_1) and meadow areas (VZ_2). The yearly average effective recharge ranges from 210 mm/yr (S-04) to 637 mm/yr (S-06) (Table 6). The aquifer infiltration capacity ξ (i.e., the ratio between Q_{Re} – the effective recharge of the aquifer, and P_{ZR} - precipitation at the spring recharge zone) ranges as the yearly average ranges from 28,3% (S-03) to almost 62% (S-06) (Table 6).

Table 6. Mean annual precipitation P_{ZR}, mean aquifer recharge Q_R, seasonal distribution of recharge, infiltration capacity ξ.

Spring	P_{ZR} (mm/yr)	Q_R (mm/yr)	$\frac{Q_{R_{e\ Spring}}}{Q_R}$ (%)	$\frac{Q_{R_{e\ Summer}}}{Q_R}$ (%)	$\frac{Q_{R_{e\ Autumn}}}{Q_R}$ (%)	$\frac{Q_{R_{e\ Winter}}}{Q_R}$ (%)	ξ^a (%)
S-01	954	473	37,5%	15,0%	25,4%	22,1%	49,6%
S-02	1006	433	40,8%	12,3%	23,8%	23,1%	43,0%
S-03	793	227	38,1%	6,7%	27,2%	27,9%	28,6%

S-04	698	210	37,0%	10,2%	25,4%	27,4%	30,1%
S-05	1008	429	42,5%	14,3%	23,0%	20,2%	42,6%
S-06	1030	637	45,9%	8,9%	21,2%	24,0%	61,9%

(a) $\xi = Q_{R_e}/P_{ZR}$

Aquifer recharge follows a linear relationship similar to precipitation, as found by Martos-Rosillo et al. (2015) for the mountain carbonate aquifers in the Betic Cordillera (Southern Spain), where recharge is generally lower (Fig. 9A). In PCM, recharge is at a maximum in spring, accounting for 40,3% of the total recharge, and this outcome is explained by both rainfall and snow melt infiltration. Recharge is at a minimum (11,2%) in summer, coinciding with the period of minimum seasonal precipitation.

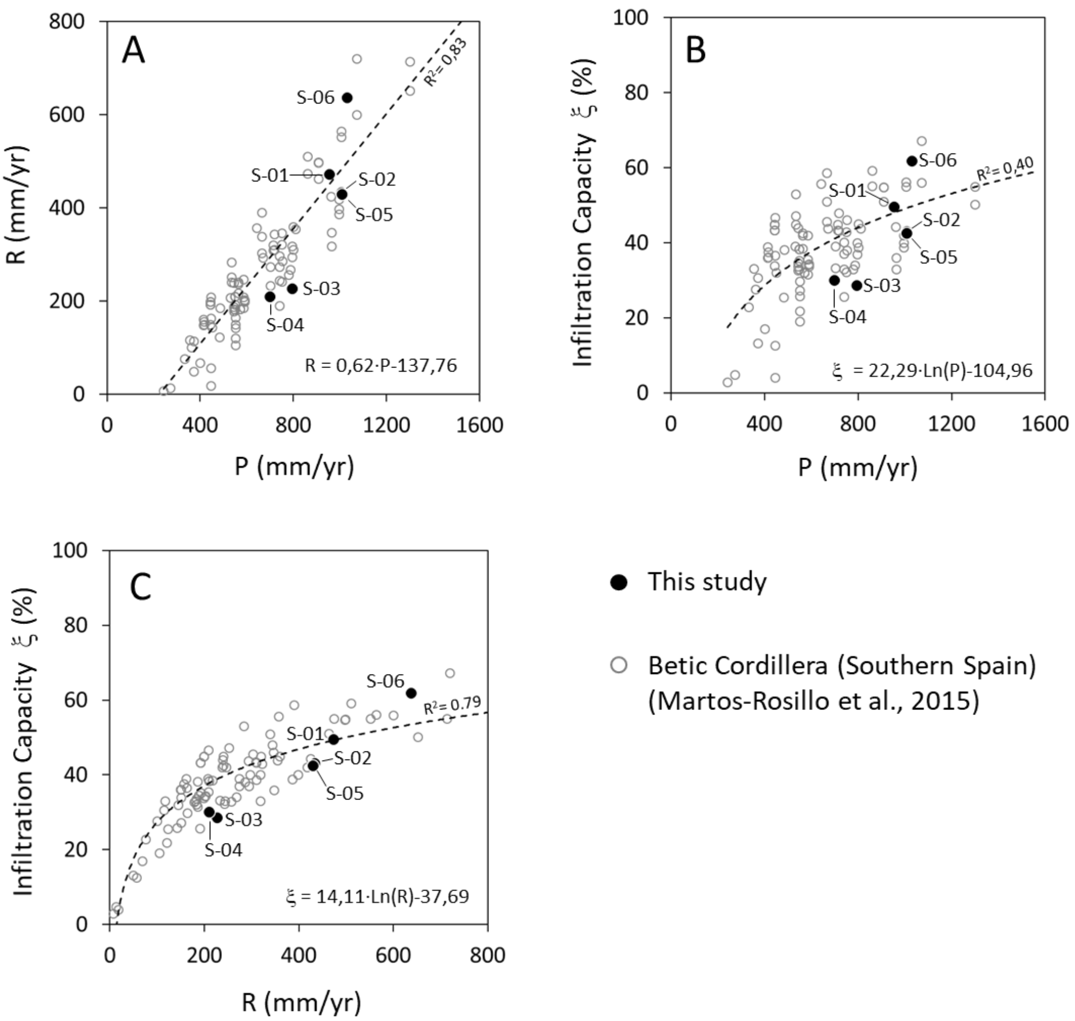


Fig. 9. (A) Mean annual rainfall versus mean annual recharge, (B) Mean infiltration coefficient versus mean annual rainfall, and (C) Mean infiltration coefficient versus mean annual recharge.

The relationship between ξ and P (Fig. 9B) is not as clear as the relationship between ξ and R (Fig. 9C), indicating that precipitation is a necessary condition for aquifer recharge, but it is not enough. In this respect, the results of the application of the linear regression model between the variables Z_R, P_{ZR}, and VZ_1, VZ_2 and VZ_3; shows that the Z_R and is the most important predictor controlling the aquifer infiltration capacity ξ. In addition, VZ_1 (karren fields and sinkholes at the highest parts of the massif) and VZ_3 (forest fields at the lowest of the massif) also play a role regarding ξ. These parameters reflect the differences in both the karstification degree and the vegetation covering the epikarst system in the PCM.

Table 7. No standardized (λ) and standardized (β) regression coefficients associated with the explanatory variables used in the multiple regression method.

Explanatory Variable	λ	β
Intercept (λ_0)	-39,562	--
Z_R	0,047	0,823
P_{ZR}	-0,007	-0,054
VZ_1	6,034	0,133
VZ_2	4,018	0,072
VZ_3	258,518	0,122

4.3 Determination of spring discharge mean transit time

To estimate the mean transit time of the spring discharge, the program FlowPC v3.2 (Małoszewski and Zuber, 1996) has been used. According to the hydrogeological setting, it is assumed that the EPM flow model can describe the behavior of the aquifers discharging through the springs of PCM. The lumped model parameters (η and τ) have been calibrated (Table 5) by fitting the isotopic contents observed in the spring discharge from December 2013 to December 2015 (Fig. 10). The goodness of fit is defined in terms of RMSE, ranging between 0,02‰ (S-05) and 0,04‰ (S-02) for $\delta^{18}O$ (Table D1, Appendix D), and between 0,17‰ (S-03) and 0,22‰ (S-04) for $\delta^{2}H$ (Table D2, Appendix D).

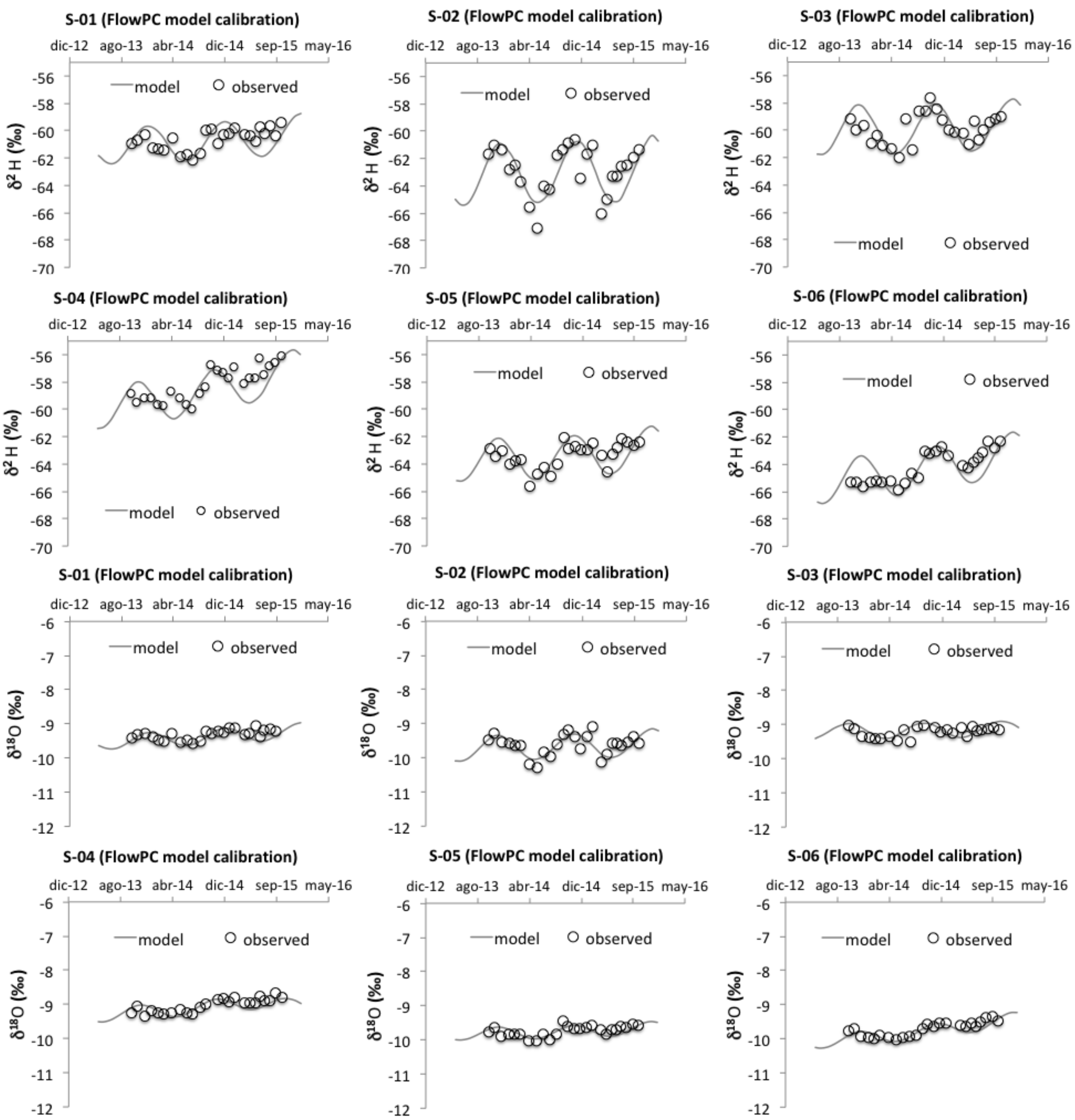


Fig. 10. Measured against simulated isotope content evolution with FlowPC and an EPM model. The gray line represents the best fit.

The estimated value of η is very close to 1 regardless of the spring, indicating that the corresponding aquifers behave as almost an exponential flow model in coherence with the behavior of a karst aquifer system discharging through a main spring. The estimated MTT with the applied methodology ranges between 1,69 yr (S-02) and 2,85 yr (S-05), while in the case of the analytical approach MTT ranges between 2,14 yr (S-02) and 5,31 yr (S-04).

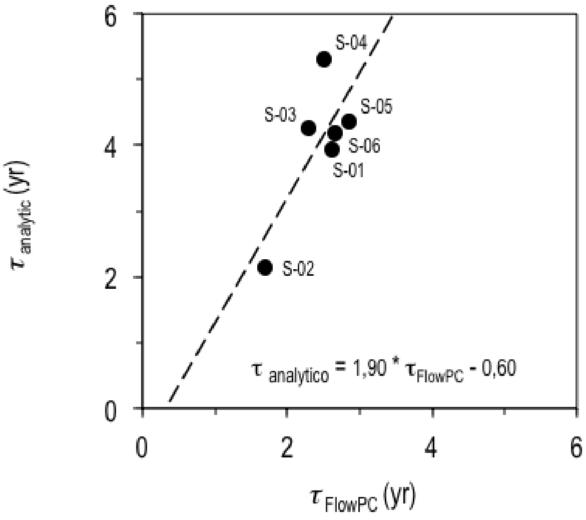


Fig. 11. Graph showing the MTT values estimated based on the lumped parameter model FlowPC (Maloszewski, 1996) versus the MTT values estimated based on the analytical model [Eq. 8] (Maloszewski et al., 1983)

The MTT values obtained by this numerical approach are 1,9 times shorter than the MTT values analytically obtained through [Eq. 8] that compares the amplitude of the seasonal isotopic content of recharge with the seasonal isotopic content in the spring discharge [Fig 11]. In the numerical case, the monthly isotopic content in recharge is weighted by the monthly volumetric recharge rate, whereas in the analytical case, the isotopic content weighting coefficients for the monthly recharge are all equal to 1 because recharge is assumed constant (i.e., steady state) for the whole period covered by the isotopic content time series. This assumption is worth keeping in mind when using [Eq. 8] for estimating groundwater mean transit times. In other words, if aquifer recharge shows a seasonal pattern, then the numerical approach should be used instead of the analytical approach to estimate MTT. The transit time discrepancies between both approaches may be critical when MTT is used as a vulnerability indicator for karst-fissure aquifers (Malík et al, 2016). The results obtained suggest that the numerical approach based explicitly on considering the recharge series in the LPM model provides a more accurate evaluation of hydraulic dynamics throughout the system. This allows better MTT estimations, similar of what concluded Vitvar et al. (1999) in pre-alpine non-karst aquifers. The MTT values obtained in this work are consistent with the conceptual model of the karst system. The aquifer presents specific zones with rapid recharge through surficial karstic elements (e.g. swallow holes) and slow recharge trough meadows and forest.

In terms of MTT, the results obtained in this study are similar to those obtained in other hydrological karst systems located in mountain zones: (1) In the case of the Ordesa and Monte Perdido karst aquifer system (Central Pyrenees, Spain), which is the highest calcareous massif in Western Europe, Lambán et al. (2015) and Jódar et al. (2016b) estimated MMT for several springs. For each spring the authors fitted a sinusoidal function [Eq. 1] to the measured tracer ($\delta^{18}O$ and $\delta^{2}H$) content time series corresponding to rainfall entering the system as recharge and the spring discharge, obtaining the amplitude of the seasonal variation of both the input and output system tracer function ($A_{\delta_{\mathrm{in}}}$and $A_{\delta_{\mathrm{out}}}$, respectively; Fig. 4). Besides, the authors assumed a constant recharge rate along the year. This hypothesis allowed obtaining an analytical solution to the convolution integral [Eq. 5] (Jódar et al., 2014) but also applying [Eq. 8] to directly estimate MTT, that ranged between 1,12 and 4,48 yr.

(2) In the Wimbach high-alpine karst system (Berchtesgaden Alps) Einsiedl et al. (2009) estimated MTT with FlowPC. To this end, they used as tracer input function the

time series of ^{3}H content in rainfall measured in a meteorological station close to the study zone, and as system output the time series of ^{3}H content in groundwater discharge for different springs and also at the outlet of the hydrological catchment. They obtained MTT ranging between 4 and 5 yr for the considered springs, and 5 yr for the whole hydrologic catchment. For the same catchment, Maloszewski et al. (1992) evaluated the MTT by using monthly recharge time series instead of rainfall time series. The aquifer recharge time series was obtained by applying a seasonal infiltration coefficient to the observed monthly precipitation time series. With this approach they estimated a MTT of 4,15 yr. This value is close to that obtained by Einsiedl et al. (2009). Additionally, Garvelmann et al. (2017) expanded the previous studies in the Berchtesgaden Alps for a total of eight springs. For each spring they estimated MTT using two different methods; (A) by numerically solving the convolution integral [Eq. 5], and (B) though [Eq. 8] by previously conducting a sin-wave analysis [Eq. 1] to the input (i.e. rainfall) and output tracer functions. The MTT obtained by both methods did not show large discrepancies for the same spring. In terms of the obtained MTT the sampled springs were be classified in two groups: a first group with relatively short MTTs (0,7 to 1,9 yr) and a second group with longer MTTs (7,3 to 12,5 yr).

(3) In the Schneealpe massif Rank et al. (1992) used the environmental tracers to study the karstic-fissured-porous aquifer system of Schneealpe, The aquifer system that is drained by two principal springs is the main drinking water resource for Vienna (Austria). It is composed of a fissured-porous aquifer with a high storage capacity that partially feds a karst aquifer conformed by a high- conductivity drainage channel network. For each aquifer they estimated MTT by calibrating a LPM with a 8 years long time series of environmental tracer data, using ^{3}H and $\delta^{18}O$ for the fissured-porous and

the karst aquifer, respectively. In the former case MTTs ranged between 2,5 and 4,5 yr, whereas in the karst aquifer the estimated MTT was only 2 months. Maloszewski et al. (2002) recalibrated both LPMs by refining and extending up to 20 years the length of the observed time series of ^{3}H and δ^{18}O measurements. In the case of the fissured-porous aquifer the obtained MTTs ranged between 14 and 26 yr, being significantly larger than those obtained by Rank et al (1992). Nevertheless, in the case of the karst aquifer the obtained MTTs were similar ranging between1,2 and 1,5 months. The large discrepancy between the MTT associated to the Fissured-Porous and karst aquifer indicates that water enters the aquifer system at the surface and flows through it towards the conductive drainage channels until reaching the springs. Nevertheless, the short MTTs associated to the karst aquifer reveal a direct hydraulic connection between the sinkholes at the surface and the drainage channel network.

(4) In the Wetterstein Mountains karst aquifer system Lauber and Goldscheider (2014) used both artificial (uranine) and environmental tracers (^{18}O and ^{2}H) to investigate the hydrological behavior of the system. Despite the low recovery of artificial tracer during the tracer test, the fast tracer arrival observed in all the sampled springs, with peak times between 1,8 and 3,2 days, indicates as in the previous case, the existence of well-developed flow paths through thick (>1000 m) USZ. This result underlines the role that may play the USZ conditioning the hydrologic response of the karst system. The authors estimated the aquifer MTT with FlowPC by using as input tracer content that of precipitation, and assuming a constant (without any seasonality) aquifer recharge rate. The obtained MTT values ranged between 3 and 5 months, being significantly shorter than those MTT presented above for the other karst systems.

The hydrological system MTT reflects the diversity of aquifer flow paths and groundwater mixing from the recharge zone to the discharge point. Considering that the different aquifers constituting the PCM show an exponential flow model (EM) behavior, and provided that MTT (τ; Table 5) and the aquifer mean recharge flow rate (Q_R; Table 6) are known, it is possible to estimate the aquifer storage (i.e., mixing) volume by using [Eq. 7]. In Table 8, the stored dynamic volume ('mobile water volume -V_m'; Małoszewski and Zuber (2002); where: $V_m = Q_R \cdot \tau$) is associated with the catchment areas (Fig. A1 of the Appendix A) discharging through the springs S-01 to S-06. S-05 and S-02 play a major role in terms of both groundwater discharge and aquifer storage. The springs S-05 and S-02 present a similar area and a similar discharge. Nevertheless, from a geometrical point of view, they are different: S-05 is rounded in shape whereas S-02 is elongated. Considering that aquifer recharge is produced mainly in the highest parts of PCM, it is clear that the distance between the recharge and discharge points is larger in the case of S-02. This difference is interesting if one considers that the mean transit time of S-02 is shorter than the mean transit time of S-05. The shorter transit time would indicate a higher development of the karst water conducting features in the catchment area of S-02. The springs S-04 and S-06 denote their perched character with the associated low discharge flow rates and groundwater reserve volumes.

Table 8. Estimation of dynamic volume V_m stored in the aquifer for the springs analyzed

Spring	V_m (hm^3)
S-01	2,44 + 0,49
S-02	11,54 + 2,61
S-03	1,72 + 0,04

S-04	0,03 + 0,01
S-05	19,39 + 0,20
S-06	0,09 + 0,01

The few available groundwater level depth data from old water wells in the PCM suggest the karst aquifer presents low regional hydraulic gradients in the phreatic zone ranging between 1 - 2%. Nevertheless, while considering the expected mean phreatic level above the horizontal plane from the spring levels (i.e., the groundwater that contributes to each spring discharge), the 3D geological model evaluates the total aquifer formation volume (V_{aq}) associated with the regional springs S-01, S-02, S-03 and S-05. Assuming V_{aq} as known, the mean aquifer interconnected porosity (ϕ) can therefore be estimated as the ratio V_{GW}/V_{aq}. In the PCM, the average ϕ obtained is 3,1%. This result agrees with the value obtained for other carbonate aquifers of the Betic Cordillera (Southern Iberian Peninsula) with an average value of 3% (Pulido-Bosch et al., 2004; Martos- Rosillo et al., 2014).

This work is aimed to characterize the hydrological behavior of a high mountain karst system with a overlaying thick UZS that plays a relevant role along with in the system response. The applied approach allows accounting the effects of the extreme alpine climate conditions on both the aquifer recharge rates and the isotopic composition of recharge. The used approach provides a more reliable assessment of the hydrological behavior of these alpine karst systems than the obtained applying the traditional approaches found in the scarce bibliography. The methodology used in this work for characterizing the hydrological behavior of PCM can be applied in many analogue high mountain karst systems whose hydrologic behavior still remains unknown. In this sense, Table 9 shows a brief summary of the available bibliography at the pan-European zone focused on high-mountain karst aquifers with a thick USZ in which this methodology could be tested (Fig. 12).

Table 9. Brief summary of published research studies of groundwater flow karst systems in mountain areas with thick USZ the pan-European zone.

Code	High mountain karst system	NSZ Thickness	Reference
1	Yunquera-Sierra de las Nieves	1000	Andreo et al. (2004); Pardo-Iguzquiza et al. (2015)
2	Alta Cadena	700	Mudarra and Andreo (2011)
3	Sierra Gorda	500	Mudarra and Andreo (2015)
4	Picos de Europa	1500	Ballesteros et al. (2015a); Ruiz and Poblete (2012)
5	Ordesa y Monte Perdido	1500	Lambán et al. (2015); Jódar et al. (2016b)
6	Port del Comte	1000	(This research)
7	Fontaine Vaucluse	800	Fleury et al. (2007)
8	Schlichenden Brünnen - Muotathal	1000	Jeannin (2001)
9	Wetterstein Mountains (Zugspitze)	1000	Lauber and Goldscheider (2014)
10	Wimbachtal catchment	1500	Maloszewski et al. (1992)
11	Totes Gebirge	1000	Laimer (2010)
12	Schneealpe Massif	900	Rank et al 1992; Maloszewski et al. (2002)
13	Cansiglio-Cavallo karst aquifer	800	Filippini et al. (2018)
14	Mount Kanin	2000	Zini et al. (2015); Turk et al. (2015)
15	Gacka	1000	Ozyurt et al. (2014)
16	Gran Sasso aquifer	1500	Falcone et al. (2008); Amuroso et al. (2013)
17	Arabika Massif	2500	Klimchouk (2009)
18	Aladaglar Mountains	2000	Ozyurt and Bayari (2008)

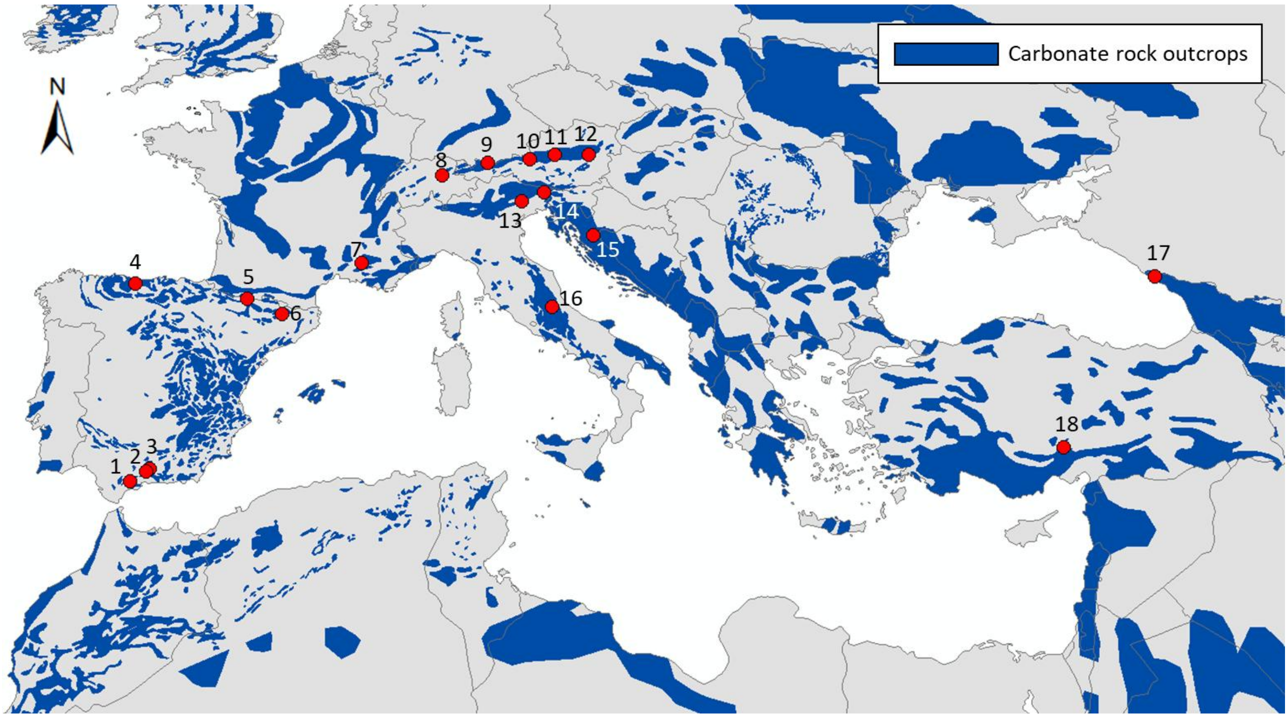


Fig. 12. Spatial distribution of carbonate rock outcrops at the pan-Mediterranean zone. Red points indicate the position of those high mountain karst aquifers zones with a thick (<500 m) NSZ referenced in the existing bibliography (map modified from the *World Map of Carbonate Rock Outcrops v.3.0*. Source: http://www.fos.auckland.ac.nz/our_research/karst). Numbers in bullets correspond to the codes shown in Table 9.

4.4 Evaluation of results for groundwater management purposes

MTT is a corner stone for groundwater management strategies, and many authors have used this variable as a proxy of vulnerability assessment in hydrogeological systems (Einsiedl et al., (2009) and Malik et al., (2016), among others). This work provides the first estimation of the MTT associated with most important springs discharging the PCM karst system. From the perspective of aquifer vulnerability, the intensive cattle grazing conducted in the PCM is the most threading activity to the groundwater resources stored in the underlying aquifer so far. The relatively large MTTs (2,25 yr) along with the exponential flow model describing the hydrologic behavior of PCM, points to groundwater mixing as a natural attenuation/dilution process inside the aquifer system. However, it must be taken in mind that the presence of unnoticed but likely well-developed flow paths through the USZ and also the existence of karst conductive features in the saturated zone of the PCM may favor fast contaminant migration from the recharge areas to the groundwater discharge points of this aquifer system, but this is investigation is out of the scope of this work.

From the perspective of water resources management the storage and dynamic volumes associated with the PCM aquifer system are also valuable information obtained in this study. In this line, it is worth to comment that the PCM aquifer system has an integrated groundwater storage capacity (V_{GW}) of 35,2 hm^3, and generates an overall mean annual groundwater discharge of 15,35 hm^3/yr, that represents 15% of the mean annual water consumption in the city of Barcelona (Barcelona City Council, 2018). Moreover, the average discharge of S-05, which is one of the main groundwater springs of the PCM represents 7% of the mean annual water consumption of Barcelona city. This discharge tributes to the Llobregat River Basin, which in turns provides critical water resources to the Barcelona metropolitan area. It is important keeping these numbers in mind to estimate the water resources availability given the increased frequency and severity of the Mediterranean droughts reported by the experts (Hoerling et al., 2012; Vicente-Serrano et al., 2014).

In the Pyrenean range, climate models forecast a precipitation decrease up to 14% with respect to the observed mean precipitation and a temperature increase between 2 and 4 °C that will reduce the amount of solid precipitation and the corresponding snowmelt runoff (López-Moreno et al., 2008, 2009). In addition, the duration of the snowpack will be shorter, shifting the timing of the snowmelt (Adam et al., 2009). The PCM is in the pre-Pyrenean zone to the South of the Pyrenean axial zone. Here, the elevation of the mountains is lower, and the climate conditions are not so severe, accelerating the impact of the forecast temperature increase on snow precipitation, snowmelt runoff generation and the dynamics of the hydrological systems located in this area. Therefore, the geographical and hydrogeological settings of the PCM, along with the groundwater transit times calculated, make the PCM aquifer system an exceptional observatory for anticipating and studying the climate change impact on southern Europe. In this line, it would be extremely important to maintain the observation research program to fully understand the hydrogeological behavior of this aquifer system.

4.5 Future works in PCM

This study is the first stage in the full hydrogeological characterization of this aquifer system. The next step is to conduct the hydrogeochemical characterization of recharge and groundwater springs discharge to complement the results obtained in this work by focusing in relevant unsolved questions like (1) the role play by the epikarst zone in the total transit time of groundwater and how this role is reflected in the hydrogeochemical evolution of the springs discharge after important rainfall events and during low-flows and (2) the use of artificial tracers and environmental isotopes (e.g. 34S, 15N) to characterize not only the mean transit time (i.e. the first moment of the transit-time distribution) but also to profile the groundwater transit-time distribution in terms of fast, intermediate and slow groundwater flows. This investigation is crucial to evaluate the aquifer vulnerability.

5. Conclusions

A distributed rainfall-runoff model and a lumped-parameter model have been combined to estimate MTT in high-mountain karst systems with an overlying thick unsaturated zone by using the stable isotopes of precipitation as environmental tracers. The presented approach accounts for the effects of the alpine climate conditions on both the aquifer recharge rates and the isotopic composition of recharge. The used approach provides a more reliable assessment of mean transit time compared to traditional methods for such alpine karst systems.

The approach presented in this work has been used to characterize the hydrological behavior of the Port del Comte Massif, a high mountain karst aquifer with a 1000 m thick unsaturated zone located in the southeastern part of the Pyrenees. The percentage of precipitation that enters into the hydrogeological system as aquifer recharge reaches 61,9% (the highest studied spring in the area). This elevated infiltration capacity is controlled by the presence of karren fields and sinkholes at the highest parts of Port del Comte Massif, at elevations between 2050 and 2300 m a.s.l. The evolution of the isotopic content in the sampled springs shows a sinusoidal pattern that reflects the seasonal variation of the isotopic composition of recharge. This is consistent with the relatively short groundwater transit times (2,25 yr) obtained for the hydrological system, which is in agreement with its karstic nature of the aquifer system, and emphasizes the high vulnerability of the aquifer system to variations in recharge.

The mean annual groundwater discharge and the mean water storage of the Port del Comte Massif hydrogeological system represent 16 and 34% of the mean annual water consumption in the city of Barcelona, underlying the important role as a strategic water resource that the Port del Comte Massif may play for stakeholders and water resources managers when facing the drought episodes that the Mediterranean region iteratively suffers. Moreover, given the geographical position of the study zone, located to the south of the Pyrenean axial zone, and the hydrogeological settings of the associated karst aquifer system, the Port del Comte Massif is an exceptional watchtower for anticipating the impact of climate change in Southern Europe.

6. Acknowledgments

This research was supported by Agencia Estatal de Investigación (AEI) from the Spanish Government and the European Regional Development Fund (FEDER) from EU, REMEDIATION (CGL2014-57215-C4-1-R), and PACE-ISOTEC (CGL2017-87216-C4-1-R) projects, the PIRAGUA project (EFA210/16/ PIRAGUA) which is funded by the European Union through the Interreg-POCTEFA territorial cooperation program, the Catalan Government projects to support consolidated research groups MAG (Mineralogia Aplicada, Geoquimica i Geomicrobiologia, 2017SGR-1733) from Universitat de Barcelona (UB) and GREM (Grup de Recerca de Minería Sostenible) from the Universitat Politècnica de Catalunya (UPC), and the Junta de Andalucía research group RNM-308 (Hydrogeology Group). We also thank the Institut Cartogràfic i Geològic de Catalunya (Hydrogeology and Geothermics Team) and CCiT from the Universitat de Barcelona (UB) for their technical assistance, and especially Raul Carrey from the MAiMA group for the help in the laboratory analyses. The Meteorological Service of Catalonia (SMC) has kindly provided the meteorological data. The constructive comments and interesting suggestions from four anonymous reviewers are greatly appreciated since they have led to a substantial improvement of the final article

7. References

Adam, J.C., Hamlet, A.F., & Lettenmaier, D.P., 2009. Implications of global climate change for snowmelt hydrology in the twenty-first century. Hydrological Processes: An International Journal, 23(7), 962-972. https://doi.org/10.1002/hyp.7201

Agencia Estatal de Meteorología de España (AEMET) and Instituto de Meteorologia – Portugal (IMA). 2011. Iberian climate atlas. Air temperature and precipitation (1971-2000). https://www.aemet.es/documentos/es/conocermas/publicaciones/Atlas-climatologico/Atlas.pdf

Allocca, V., De Vita, P., Manna, F., Nimmo, J.R. 2015. Groundwater recharge assessment at local and episodic scale in a soil mantled perched karst aquifer in southern Italy. Journal of Hydrology, 529 (2015) 843–853. https://doi.org/10.1016/j.jhydrol.2015.08.032

Amin I.E., Campana, M.E. 1996. A general lumped parameter model for the interpretation of tracer data and transit time calculation in hydrologic systems. J Hydrol; 179 (1–4):1–21 https://doi.org/10.1016/0022-1694(95)02880-3

Andreo, B., Linan, C., Carrasco, F., De Cisneros, C. J., Caballero, F., Mudry, J. 2004. Influence of rainfall quantity on the isotopic composition (18O and 2H) of water in mountainous areas. Application for groundwater research in the Yunquera-Nieves karst aquifers (S Spain). Applied Geochemistry, 19(4), 561-574. https://doi.org/10.1016/j.apgeochem.2003.08.002

Araguás-Araguás, L.J., Díaz-Teijeiro, M.F. 2005. Isotope composition of precipitation and water vapour in the Iberian Peninsula. In “Isotopic Composition of

Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate” (pp. 173-190). IAEA-TECDOC-1453.

Aravena, R., Peña, H., Grilli, A., Suzuki, O., Mordeckai, M., 1989. Evolución isotópica de las lluvias y origen de las masas de aire en el altiplano chileno. Isotope hydrology investigations in Latín America. IAEA-TECDOC-502. IAEA, Vienna, pp. 129–142.

Bakalowicz, M. (2005). Karst groundwater: a challenge for new resources. Hydrogeology Journal, 13(1), 148-160. https://doi.org/10.1007/s10040-004-0402-9

Ballesteros, D., Jiménez-Sánchez, M., Giralt, S., García-Sansegundo, J., Meléndez-Asensio, M. 2015a. A multi-method approach for speleogenetic research on alpine karst caves. Torca La Texa shaft, Picos de Europa (Spain). Geomorphology, 247, 35-54.

Ballesteros, D., Arnauld Malard., A., Pierre-Yves Jeannin, P-Y., Jimenez-Sanchez M., García-Sansegundo, J., Meléndez-Asensio, M., Sendra, G. 2015b. KARSYS hydrogeological 3D modeling of alpine karst aquifers developed in geologically complex areas: Picos de Europa National Park (Spain). Environ Earth Sci. Volume 74, Issue 12, pp 7699–7714. https://doi.org/10.1007/s12665-015-4712-0

Barberá, J.A., Jódar, J., Custodio, E., González-Ramón, A., Jiménez-Gavilán, Vadillo, I., Pedrera, A., Martos-Rosillo, S., 2018a. Groundwater dynamics in a hydrologically-modified alpine watershed from an ancient managed recharge system (Sierra Nevada National Park, Southern Spain): insights from hydrogeochemical and isotopic information. Science of the Total Environment 640–641, 874–893, https://doi.org/10.1016/j.scitotenv.2018.05.305

Barberá, J. A., Mudarra, M., Andreo, B., De la Torre, B., 2018b. Regional-scale analysis of karst underground flow deduced from tracing experiments: examples from carbonate aquifers in Màlaga province, southern Spain. Hydrogeology Journal, 26(1), 23-40. https://dx.doi.org/10.1007/s10040-017-1638-5

Barcelona City Council, 2018. Evolution of water consumption in the city of Barcelona. http://www.bcn.cat/estadistica/angles/dades/economia/consum/evoconsum/coev04.htm (last access 08/07/2018).

Barnett, T.P., Adam, J.C., Lettenmaier, D.P., 2005. Potential impacts of a warming climate on water availability in snow-dominated regions. Nature, 438(7066), https://dx.doi.org/10.1038/nature04141

Bergström, S., 1976. Development and Application of a Conceptual Runoff Model For Scandinavian Catchments, SMHI, Report No. RHO 7 (134 pp Norrköping).

Braun, L.N., Renner, C.B., 1992. Application of a conceptual runoff model in different physiographic regions of Switzerland. Hydrological Sciences Journal, 37(3), 217-231. https://doi.org/10.1080/02626669209492583.

Butscher C, Huggenberger P., 2007. Implications for karst hydrology from 3D geological modeling using the aquifer base gradient approach. J Hydrol; 342 (1–2):184–98. https://doi.org/10.1016/j.jhydrol.2007.05.025

Celle-Jeanton,H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. Geophysical Research Letters, Vol. 28, no. 7, pages 1215-1218

Cervi, F., Marcaccio, M., Petronici, F., Borgatti, L., 2014. Hydrogeological characterization of peculiar Apenninic springs. Proceedings of the International Association of Hydrological Sciences, 364, 333-338.

Chen, Z., 2017. Modeling a geologically complex karst aquifer system, Hochifen-Gottesacker, Alps. PhD. Thesis. Karlsruher Instituts für Technologie, Germany. https://d-nb.info/1136660852/34

Chueca, J., Julián, A., López-Moreno, J.I., 2007. Recent evolution (1981–2005) of the Maladeta glaciers, Pyrenees, Spain: extent and volume losses and their relation with climatic and topographic factors. Journal of glaciology, 53(183), 547-557. https://doi.org/10.3189/002214307784409342

Clark, I.D., Fritz, P. 1997. Environmental isotopes in hydrogeology. Lewis Publishers, New York.

Coplen 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid Commun. Mass Spectrom. 2011, 25, 2538–2560.

CREAF, 2009. Land Cover Map of Catalonia (MCSC) 1:250,000. 4a edition (2009). http://www.creaf.uab.es/mcsc/usa/index.htm

Custodio, E., Llamas, M.R. (Eds.), 1976. Hidrología subterránea [Groundwater hydrology]. 2 Vols: 1–2350. Ediciones Omega, Barcelona.

Custodio, E., Jódar, J., 2016. Simple solutions for steady–state diffuse recharge evaluation in sloping homogeneous unconfined aquifers by means of atmospheric tracers. J. Hydrol. http://dx.doi.org/10.1016/j.jhydrol.2016.06.035

De Jong, C., Lawler, D., Essery, R., 2009. Mountain hydroclimatology and snow seasonality and hydrological change in mountain environments. Hydrological Processes 23, 955–961. https://doi.org/10.1002/hyp.7193

De Walle, D.R., Edwards, P.J., Swistock, B.R., Aravena, R., Drimmie, R.J., 1997. Seasonal isotope hydrology of three Appalachian forest catchments. Hydrological

Processes, 11(15), 1895-1906.b https://doi.org/10.1002/(SICI)1099-1085(199712)11:15<1895::AID-HYP538>3.0.CO;2-#

Einsiedl, F., 2005. Flow system dynamics and water storage of a fissured-porous karst aquifer characterized by artificial and environmental tracers. J Hydrol 312:312–321. https://doi.org/10.1016/j.jhydrol.2005.03.031

Einsiedl, F., Maloszewski, P., Stichler, W., 2009. Multiple isotope approach to the determination of the natural attenuation potential of a high-alpine karst system. Journal of Hydrology 365 (2009) 113–121. https://doi.org/10.1016/j.jhydrol.2008.11.042

Epting, J., M.Page, R., Auckenthaler, A., Huggenberger, P. 2018. Process-based monitoring and modeling of Karst springs – Linking intrinsic to specific vulnerability. Sci. Total Environ. 625, 403-415- https://doi.org/10.1016/j.scitotenv.2017.12.272

Falcone, R.A., Falgiani, A., Parisse, B., Petitta, M., Spizzico, M., Tallini, M. 2008. Chemical and isotopic ($\delta^{18}O$‰, $\delta^{2}H$‰, $\delta^{13}C$‰, ^{222}Rn) multi-tracing for groundwater conceptual model of carbonate aquifer (Gran Sasso INFN underground laboratory–central Italy). Journal of hydrology, 357(3-4), 368-388.

Farlin, J., Maloszewski, P., 2013. On the use of spring baseflow recession for a more accurate parameterization of aquifer transit time distribution functions. Hydrology and Earth System Sciences, 17(5), 1825-1831. https://doi.org/10.5194/hess-17-1825-2013

Fiorella, R.P., Poulsen, C.J., Pillco Zolá, R.S., Barnes, J.B., Tabor, C.R., Ehlers, T.A., 2015. Spatiotemporal variability of modern precipitation $\delta^{18}O$ in the central Andes and implications for paleoclimate and paleoaltimetry estimates. Journal of

Geophysical Research: Atmospheres, 120(10), 4630-4656. https://dx.doi.org/10.1002/2014JD022893

Fleury, P., Plagnes, V., Bakalowicz, M. 2007. Modelling of the functioning of karst aquifers with a reservoir model: Application to Fontaine de Vaucluse (South of France). Journal of Hydrology 345, 38– 49. https://doi.org/10.1016/j.jhydrol.2007.07.014

Filippini,M., Squarzoni, G., De Waele, J., Fiorucci, A., Vigna, B., Grillo, B., Riva, A., Rossetti, S., Zini, L., Casagrande, G., Stumpp, C., Gargini, A. 2018. Differentiated spring behavior under changing hydrological conditions in an alpine karst aquifer. Journal of Hydrology, 556, 572-584. https://doi.org/10.1016/j.jhydrol.2017.11.040

Freixes, A., 2014. Els aqüífers càrstics dels Pirineus de Catalunya. Interès estratègic i sostenibilitat [The karstic aquifers of the Catalonian Pyrenees. Strategic interest and sustainability]. PhD. Thesis. Universitat de Barcelona. http://hdl.handle.net/2445/65187

Froehlich, K., Gibson, J.J., Aggarwal, P., 2001. Deuterium excess in precipitation and its climatological significance. In Study of environmental change using isotope techniques (Vol. 13, pp. 54-66). IAEA.

Froehlich, K., Kralik, M., Papesch, W., Rank, D., Scheifinger, H., Stichler, W., 2008. Deuterium excess in precipitation of Alpine regions–moisture recycling. Isotopes in Environmental and Health Studies, 44(1), 61-70. https://doi.org/10.1080/10256010801887208

García-Ruiz, J.M., López-Moreno, J.I., Vicente-Serrano, S.M., Lasanta–Martínez, T., Beguería, S., 2011. Mediterranean water resources in a global change scenario.

Earth-Science Reviews, 105(3-4), 121-139. https://doi.org/10.1016/j.earscirev.2011.01.006

Garvelmann, J., Warscher , M., Leonhardt, G., Franz, H., Lotz. A., Kunstman, H. 2017. Quantification and characterization of the dynamics of spring and stream water systems in the Berchtesgaden Alps with a long-term stable isotope dataset. Environ Earth Sci 76:766 https://doi.org/10.1007/s12665-017-7107-6

Giorgi, F., Lionello, P., 2008. Climate change projections for the Mediterranean region. Global and planetary change, 63(2-3), 90-104. https://doi.org/10.1016/j.gloplacha.2007.09.005

Gladich, I., Gallai, I., Giaiotti, D. B., & Stel, F. 2011. On the diurnal cycle of deep moist convection in the southern side of the Alps analysed through cloud-to-ground lightning activity. Atmospheric Research, 100(4), 371-376. https://doi.org/10.1016/j.atmosres.2010.08.026

Goldscheider, N., 2005. Fold structure and underground drainage pattern in the alpine karst system Hochifen-Gottesacker. Eclogae Geologicae Helvetiae, 98(1), 1-17. https://doi.org/10.1007/s00015-005-1143-z

Goldscheider N, Drew D (eds) (2007) Methods in Karst Hydrogeology. International Contributions to Hydrogeology 26, International Association of Hydrogeologists, Taylor & Francis, London, 264 pp. ISBN 978-0-415-42873-6

Goldscheider, N., Meiman, J., Pronk, M., Smart, C., 2008. Tracer tests in karst hydrogeology and speleology. International Journal of Speleology, 37(1), 3. http://dx.doi.org/10.5038/1827-806X.37.1.3

Goldscheider, N., 2011. Alpine Hydrogeologie [Alpine hydrogeology]. Grundwasser 16:1–1. https://doi.org/10.1007/s00767-010-0157-2

Gonfiantini, R., Roche, M.A., Olivry, J.C., Fontes, J.C., Zuppi, G.M., 2001. The altitude effect on the isotopic composition of tropical rains. Chemical Geology, 181(1-4), 147-167. https://doi.org/10.1016/S0009-2541(01)00279-0

Gremaud, V., Goldscheider, N., Savoy, L., Favre, G., Masson, H., 2009. Geological structure, recharge processes and underground drainage of a glacierised karst aquifer system, Tsanfleuron-Sanetsch, Swiss Alps. Hydrogeol. J. 17, 1833–1848. https://doi.org/10.1007/s10040-009-0485-4

Grunewald, K., Scheithauer, J., 2010. Europe's southernmost glaciers: response and adaptation to climate change. Journal of glaciology, 56(195), 129-142. https://doi.org/10.3189/002214310791190947

Hernández-Mora, N., del Moral Ituarte, L., La-Roca, F., La Calle, A., Schmidt, G., 2014. Interbasin water transfers in Spain: Interregional conflicts and governance responses. In Globalized Water (pp. 175-194). Springer, Dordrecht. ISBN 978-94-007-7322-6. https://doi.org/10.1007/978-94-007-7323-3_13

Hargreaves, G.H. and Samani, Z.A. 1982. Estimating potential evapotranspiration. Journal of Irrigation and Drainage Engineering, 108, 223-230

Hoerling, M., Eischeid, J., Perlwitz, J., Quan, X., Zhang, T., Pegion, P., 2012. On the increased frequency of Mediterranean drought. Journal of Climate, 25(6), 2146-2161. https://doi.org/10.1175/JCLI-D-11-00296.1

Holko, L., Dóša, M., Michalko, J., Šanda, M. 2012. Isotopes of oxygen-18 and deuterium in precipitation in Slovakia. Journal of Hydrology and Hydromechanics, 60(4), 265-276. https://doi.org/10.2478/v10098-012-0023-2

Hood, J.L., Hayashi, M., 2010. Assessing the application of a laser rangefinder for determining snow depth in inaccessible alpine terrain. Hydrology and Earth System Sciences, 14(6), 901. http://dx.doi.org/10.5194/hess-14-901-2010

Hottelet, Ch., Braun, L.N., Leibundgut, Ch., Rieg, A., 1993. Simulation of Snowpack and Discharge in an Alpine Karst Basin. IAHS Publication No. 218, pp. 249–260

ICGC, 2007. Mapa geològic comarcal de Catalunya 1:50 000. Full Alt Urgell (BDGC50M). http://www.icgc.cat/ca/Administracio-i-empresa/Descarregues/Cartografia-geologica-i-geotematica/Cartografia-geologica/Mapa-geologic-comarcal-de-Catalunya-1-50.000/Mapa-geologic-comarcal-de-Catalunya-1-50.000

Jeelani, G., Shah, R.A., Deshpande, R.D., Fryar, A.E., Perrin, J., Mukherjee, A., 2017. Distinguishing and estimating recharge to karst springs in snow and glacier dominated mountainous basins of the western Himalaya, India. Journal of hydrology, 550, 239-252. https://doi.org/10.1016/j.jhydrol.2017.05.001

Jeannin, P-Y. 2001. Modeling flow in phreatic and epiphreatic karst conduits in the Hölloch cave (Muotatal, Switzerland). Water Resources Research. Vol. 37, No. 2, pp 191-200. https://doi.org/10.1029/2000WR900257

Jiménez-Martínez, J. y Custodio, E., 2008. El exceso de deuterio en la lluvia y en la recarga a los acuíferos en el área circum-mediterránea y en la costa mediterránea española. Boletín Geológico y Minero, 119 (1): 21-32.

Jódar, J., Lambán, L.J., Medina, A., Custodio, E., 2014. Exact analytical solution of the convolution integral for classical hydrogeological lumped-parameter models and typical input tracer functions in natural gradient systems. J. Hydrol. 519, 3275–3289. http://dx.doi.org/10.1016/j.jhydrol.2014.10.027.

Jódar, J., Custodio, E., Liotta, M., Lambán, L.J., Herrera, C., Martos-Rosillo, S., Sapriza, G., Rigo, T., 2016a. Correlation of the seasonal isotopic amplitude of precipitation with annual evaporation and altitude in alpine regions. Sci. Total Environ., 550: 27-37. https://dx.doi.org/10.1016/j.scitotenv.2015.12.034

Jódar, J., Custodio, E., Lambán, L.J., Martos-Rosillo, S., Herrera-Lameli, C., Sapriza-Azuri, G., 2016b. Vertical variation in the amplitude of the seasonal isotopic content of rainfall as a tool to jointly estimate the groundwater recharge zone and transit times in the Ordesa and Monte Perdido National Park aquifer system, north-eastern Spain. Sci. Total Environ. 573, 505–517. https://dx.doi.org/10.1016/j.scitotenv.2016.08.117

Jódar, J., Cabrera, J.A., Martos-Rosillo, S., Ruiz-Constan, A., Gonzalez-Ramón, A., Lambán, L.J., Herrera, C., Custodio, E., 2017. Groundwater discharge in high-mountain watersheds: a valuable resource for downstream semi-arid zones. The case of the Bérchules River in Sierra Nevada (Southern Spain). Science of The Total Environment, https://doi.org/10.1016/j.scitotenv.2017.03.190

Jódar, J., Carpintero, E., Martos-Rosillo, S., Ruiz-Constán, A., Marín-Lechado, C., Cabrera-Arrabal, J.A., Navarrete-Mazariego, E., González-Ramón , A., Lambán, L.J., Herrera, C., González-Dugo, M.P. 2018. Combination of lumped hydrological and remote-sensing models to evaluate water resources in a semi-arid high altitude ungauged watershed of Sierra Nevada (Southern Spain). Sci. Total Environ., 625: 285-300. https://doi-org.recursos.biblioteca.upc.edu/10.1016/j.scitotenv.2017.12.300

Katsuyama, M., Tani, M., Nishimoto, S., 2010. Connection between streamwater mean residence time and bedrock groundwater recharge/discharge dynamics in weathered granite catchments. Hydrological Processes, 24(16), 2287-2299. https://doi.org/10.1002/hyp.7741

Kazakis, N., Chalikakis, K., Mazzilli, M., Ollivier, C., Manakos, A., Voudouris, K., 2018. Management and research strategies of karst aquifers in Greece: Literature overview and exemplification based on hydrodynamic modelling and vulnerability assessment of a strategic karst aquifer. Sci. Total Environ., 643: 592–609. https://doi.org/10.1016/j.scitotenv.2018.06.184

Klimchouk, A. Samokhin, G.V., Kasian, Y.M. 2009. The deepest cave in the world in the arabika massif (western caucasus) and its hydrogeological and paleogeographic significance. 2009 ICS Proceedings. 15th International Congress of Speleology

Konz, M., Seibert, J., 2010. On the value of glacier mass balances for hydrological model calibration. Journal of hydrology, 385(1-4), 238-246. https://doi.org/10.1016/j.jhydrol.2010.02.025

Kurylyk, B.L., Hayashi, M., 2017. Inferring hydraulic properties of alpine aquifers from the propagation of diurnal snowmelt signals. Water Resources Research. https://doi.org/10.1002/2016WR019651

Laimer, H.J. 2010. Neue Ergebnisse zur Karsthydrogeologie des westlichen Toten Gebirges (Österreich). (New karst hydrogeological research in the western Totes Gebirge, Austria). Grundwasser. Volume 15, Issue 2, pp 113–122

Lambán, L.J., Jódar, J., Custodio, E., Soler, A., Sapriza, G. and Soto, R., 2015. Isotopic and hydrogeochemical characterization of high-altitude karst aquifers in complex geological settings. The Ordesa and Monte Perdido National Park (Northern Spain) case study. Sci. Total Environ., 506–507: pp 466–479, https://doi.org/10.1016/j.scitotenv.2014.11.030

Lauber, U., Kotyla, P., Morche, D., Goldscheider, N., 2014. Hydrogeology of an Alpine rockfall aquifer system and its role in flood attenuation and maintaining baseflow. Hydrology and Earth System Sciences, 18(11), 4437. http://dx.doi.org/10.5194/hess-18-4437-2014

Lauber, U., Goldscheider, N., 2014. Use of artificial and natural tracers to assess groundwater transit-time distribution and flow systems in a high-alpine karst system (Wetterstein Mountains, Germany). Hydrogeology Journal, 22(8), 1807-1824. http://dx.doi.org/10.1007/s10040-014-1173-6

Liu, Z., Tian, L., Yao, T., & Yu, W. 2008. Seasonal deuterium excess in Nagqu precipitation: influence of moisture transport and recycling in the middle of Tibetan Plateau. Environmental Geology, 55(7), 1501-1506. http://dx.doi.org/10.1007/s00254-007-1100-4

López-Moreno, J.I., García-Ruiz, J.M., 2004. Influence of snow accumulation and snowmelt on streamflow in the central Spanish Pyrenees/Influence de l'accumulation et de la fonte de la neige sur les écoulements dans les Pyrénées centrales espagnoles. Hydrological Sciences Journal, 49(5). https://doi.org/10.1623/hysj.49.5.787.55135

López-Moreno, J. I., Goyette, S., Beniston, M., 2008. Climate change prediction over complex areas: spatial variability of uncertainties and predictions over the Pyrenees from a set of regional climate models. International Journal of Climatology, 28(11), 1535-1550. https://doi.org/10.1002/joc.1645

López-Moreno, J.I., Revuelto, J., Rico, I., Chueca-Cía, J., Julián, A., Serreta, A., Serrano, E., Vicente-Serrano, S.M., Azorin-Molina, C., Alonso-González, E., García-Ruiz, J.M., 2016. Thinning of the Monte Perdido Glacier in the Spanish Pyrenees since 1981. The Cryosphere, 10(2), 681-694. https://doi.org/10.5194/tc-10-681-2016

Mądrala, M., Wąsik, M., Małoszewski, P., 2017. Interpretation of environmental tracer data for conceptual understanding of groundwater flow: an application for fractured aquifer systems in the Kłodzko Basin, Sudetes, Poland. Isotopes in environmental and health studies, 53(5), 466-483. https://dx.doi.org/10.1080/10256016.2017.1330268

Malard, A., Jeannin, PY., Vouillamoz, J. et al 2015. An integrated approach for catchment delineation and conduit-network modeling in karst aquifers: application to a site in the Swiss tabular Jura. Hydrogeol J 23: 1 1341–1357. https://doi.org/10.1007/s10040-015-1287-5

Malard, A., Sinreich, M., Jeannin, P.Y., 2016. A novel approach for estimating karst groundwater recharge in mountainous regions and its application in Switzerland. Hydrological Processes, 30(13), 2153-2166. https://doi.org/10.1002/hyp.10765

Malík, P., Svasta, J., Michalko, J., Gregor, M., 2016. Indicative mean transit time estimation from δ18O values as groundwater vulnerability indicator in karst-fissure aquifers. Environmental Earth Sciences. 75. 10.1007/s12665-016-5791-2.

Małoszewski, P., Rauert, W., Stichler, W., Herrmann, A., 1983. Application of flow models in an alpine catchment area using tritium and deuterium data. Journal of Hydrology, 66: 319–330. http://dx.doi.org/10.1016/0022-1694(83)90193-2

Maloszewski, P., Rauert, W., trimborn, P., Herrmann, A., Rau, R. 1992. Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). Journal of Hydrology, 140: 343-360. https://doi.org/10.1016/0022-1694(92)90247-S

Małoszewski, P., Zuber, A., 1996. Lumped parameter models for the interpretation of environmental tracer data. Manual on mathematical models in isotope hydrology. IAEA-TECDOC 910. Vienna (Austria): IAEA; 1996

Małoszewski, P., Zuber, A., 2002. Manual on lumped parameter models used for the interpretation of environmental tracer data in groundwaters (IAEA-UIAGS/CD--02-00131). International Atomic Energy Agency (IAEA)

(https://inis.iaea.org/search/search.aspx?orig_q=RN:33037906, last access 12/04/2018)

Marti, R., Gascoin, S., Houet, T., Ribière, O., Laffly, D., Condom, T., Monnier, S., Schmutz, M., Camerlynck, C., Tihay, J.P., Soubeyroux, J.M., 2015. Evolution of Ossoue Glacier (French Pyrenees) since the end of the Little Ice Age. The Cryosphere, 9(5), 1773-1795. http://dx.doi.org/10.5194/tc-9-1773-2015.

Martos-Rosillo, S., Marín-Lechado, C., Pedrera, A., Vadillo, I., Motyka, J., Molina, J.L., Ortiz, P., Martín-Ramírez, J.M., 2014. Methodology to evaluate the renewal period of carbonate aquifers: a key tool for their management in arid and semiarid regions, with the example of Becerrero aquifer, Spain. Hydrogeology Journal, 22(3), 679-689. http://dx.doi.org/10.1007/s10040-013-1086-9

Martos-Rosillo, S., González-Ramón, A., Jiménez-Gavilán, P., Andreo, B., Durán, J.J., Mancera, E., 2015. Review on groundwater recharge in carbonate aquifers from SW Mediterranean (Betic Cordillera, S Spain). Environ Earth Sci. 74: 7571. https://doi.org/10.1007/s12665-015-4673-3

Merz, R., Blöschl, G., 2004. Regionalisation of catchment model parameters. Journal of hydrology, 287(1-4), 95-123. http://dx.doi.org/10.1016/j.jhydrol.2003.09.028

Milano, M., Ruelland, D., Fernandez, S., Dezetter, A., Fabre, J., Servat, E., Fritsch, J.M., Ardoin-Bardin, S., Thivet, G., 2013. Current state of Mediterranean water resources and future trends under climatic and anthropogenic changes. Hydrological Sciences Journal, 58(3), 498-518. http://dx.doi.org/10.1080/02626667.2013.774458

Molina, A., Melgarejo, J., 2016. Water policy in Spain: seeking a balance between transfers, desalination and wastewater reuse. International Journal of Water

Resources Development, 32(5), 781-798. http://dx.doi.org/10.1080/07900627.2015.1077103

Mook,W.G., De Vries, J.J., 2000. Volume I, Introduction: theory methods review. Environmental Isotopes in the Hydrological Cycle—Principles and Applications, International Hydrological Programme (IHP-V). Technical Documents in Hydrology (IAEA/UNESCO) No, 39 vol. 1 (http://www-naweb.iaea.org/napc/ih/IHS_publication.html, last access 12/04/2018).

Mudarra, M., Andreo, B. 2011. Relative importance of the saturated and the unsaturated zones in the hydrogeological functioning of karst aquifers: The case of Alta Cadena (Southern Spain). Journal of Hydrology 397, 263–280. https://doi.org/10.1016/j.jhydrol.2010.12.005

Mudarra, M., Andreo, B., Marín, A.I., Vadillo, I., Barberá, J.A., 2014. Combined use of natural and artificial tracers to determine the hydrogeological functioning of a karst aquifer: the Villanueva del Rosario system (Andalusia, southern Spain). Hydrogeology journal, 22(5), 1027-1039. http://dx.doi.org/10.1007/s10040-014-1117-1

Mudarra, M., Andreo, B., 2015. Role of the Soil-Epikarst-Unsaturated Zone in the Hydrogeological Functioning of Karst Aquifers. The Case of the Sierra Gorda de Villanueva del Trabuco Aquifer (Southern Spain). Hydrogeological and Environmental Investigations in Karst Systems. (ed. Andreo, B., Carrasco, F., Durán, J.J., Jiménez, P., LaMoreaux.) Series: Environmental Earth Sciences. Springer. 638 pp.

Nimon, K.F., Oswald, F.L., 2013. Understanding the results of multiple linear regression: Beyond standardized regression coefficients. Organizational Research Methods, 16(4), 650-674.

Nogués-Bravo, D., Araújo, M.B., Lasanta, T., López-Moreno, J.I., 2008. Climate change in Mediterranean mountains during the 21st century. AMBIO: A Journal of the Human Environment, 37(4), 280-285. https://doi.org/10.1579/0044-7447(2008)37[280:CCIMMD]2.0.CO;2

Obleitner, F., 1994. Climatological features of glacier and valley winds at the Hintereisferner (Ötztal Alps, Austria). Theoretical and Applied Climatology, 49(4), 225-239. https://doi.org/10.1007/BF00867462

Ozyurt, N.N., Bayari, C.S. 2008. Temporal variation of chemical and isotopic signals in major discharges of an alpine karst aquifer in Turkey: implications with respect to response of karst aquifers to recharge. Hydrogeology Journal 16: 297–309. http://dx.doi.org/10.1007/s10040-007-0217-6

Ozyurt, N.N., Lutz, H.O., Hunjak, T., Mance, D., Roller-Lutz, Z. 2014. Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times. Sci. Total Environ. 87 245–254. http://dx.doi.org/10.1016/j.scitotenv.2014.04.018

Pardo-Igúzquiza, E., Durán, J.J., Luque-Espinar, J.A., Robledo-Ardila, P.A., Martos-Rosillo, S., Guardiola-Albert, C., Pedrera, A. 2015. Karst massif susceptibility from rock matrix, fracture and conduit porosities: a case study of the Sierra de las Nieves (Málaga, Spain). Environ Earth Sci. 74:7583–7592. http://dx.doi.org/10.1007/s12665-015-4545-x

Peel, M.C., Finlayson, B.L., McMahon, T.A., 2007. Updated world map of the Köppen–Geiger climate classification. Hydrol. Earth Syst. Sci. 11, 1633–1644. http://dx.doi.org/10.5194/hess-11-1633-2007

Poage, M.A., Chamberlain, C.P., 2001. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. Am. J. Science 301 (1), 1–15. http://dx.doi.org/10.2475/ajs.301.1.1

René, P., 2013. Glaciers des Pyrénées: le réchauffement climatique en images. Éd. Cairn.

Ribalaygua, J., Pino, M.R., Pórtoles, J., Roldán, E., Gaitán, E., Chinarro, D., Torres, L., 2013. Climate change scenarios for temperature and precipitation in Aragón (Spain). Science of the Total Environment, 463, 1015-1030. https://doi.org/10.1016/j.scitotenv.2013.06.089

Rodgers, P., Soulsby, C., Waldron, S., 2005. Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment. Hydrol Process 19(11):2291–2307. http://dx.doi.org/10.1002/hyp.5677

Ruiz-Constán, A., Marín-Lechado, C., Martos-Rosillo, S., Fernández-Leyva, C., García-Lobón, J. L., Pedrera, A., López-Geta, J.A., Hernández-Bravo, J.A., Rodríguez-Hernández, L., 2015. Methodological Procedure for Evaluating Storage Reserves in Carbonate Aquifers Subjected to Groundwater Mining: The Solana Aquifer (Alicante, SE Spain). In Hydrogeological and Environmental Investigations in Karst Systems (pp. 255-262). Springer, Berlin, Heidelberg. http://dx.doi.org/10.1007/978-3-642-17435-3_28

Sánchez-Murillo, R., Brooks, E.S., Elliot, W.J., Boll, J., 2015. Isotope hydrology and baseflow geochemistry in natural and human-altered watersheds in the Inland Pacific Northwest, USA. Isotopes in environmental and health studies, 51(2), 231-254. http://dx.doi.org/10.1080/10256016.2015.1008468

Schotterer, U., Froehlich, K., Stichler, W., Trimborn, P., 1993. Temporal variation of 18O and deuterium excess in precipitation, river and spring waters in Alpine regions of Switzerland. In Isotope Techniques in the study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. Edited by IAEA. Proceedings series, ISSN 0074-1884, STI/PUB/908, ISBN 92-0-103293-5 (https://inis.iaea.org/search/search.aspx?orig_q=RN:25027909, last access 12/04/2018).

Seibert, J., 2005. HBV Light Version 2. User's Manual. Uppsala University, Dept. of Earth Science, Hydrology, Uppsala, Sweden.

Seibert, J., Vis, M.J.P, 2012. Teaching hydrological modelling with a user-friendly catchment-runoff-model software package, Hydrol. Earth Syst. Sci., 16(9), 3315–3325. http://dx.doi.org/10.5194/hess-16-3315-2012, 102012

Seibert, J., Jenicek, M., Huss, M., Ewen, T., 2015. Snow and ice in the hydrosphere. In Snow and Ice-Related Hazards, Risks and Disasters (pp. 99-137). ISBN: 978-0-12-394849-6. https://doi.org/10.1016/B978-0-12-394849-6.00004-4

Solder, J.E., Stolp, B.J., Heilweil, V.M., Susong, D.D., 2016. Characterization of mean transit time at large springs in the Upper Colorado River Basin, USA: a tool for assessing groundwater discharge vulnerability. Hydrogeology Journal, Volume 24, Issue 8, pp 2017–2033, https://doi.org/10.1007/s10040-016-1440-9

Staudinger, M., Stoelzle, M., Seeger, S., Seibert, J., Weiler, M., Stahl, K., 2017. Catchment water storage variation with elevation. Hydrological Processes, 31(11), 2000-2015. https://doi.org/10.1002/hyp.11158

Turnadge, C., Smerdon, B.D. 2014. A review of methods for modelling environmental tracers in groundwater: advantages of tracer concentration simulation. Journal of Hydrology, 519, 3674-3689. https://doi.org/10.1016/j.jhydrol.2014.10.056

Turk, J., Malard, A., Jeannin, P.-Y., Petric M., Gabrovšek, F., Ravbar, N., Vouillamoz, J., Slabe, T., Sordet, V., 2015. Hydrogeological characterization of groundwater storage and drainage in an alpine karst aquifer (the Kanin massif, Julian Alps). Hydrological Processes 29(8), 1986-1998. https://doi.org/10.1002/hyp.10313

Uhlenbrook, S., Seibert, J.A.N., Leibundgut, C., Rodhe, A., 1999. Prediction uncertainty of conceptual rainfall-runoff models caused by problems in identifying model parameters and structure. Hydrological Sciences Journal, 44(5), 779-797. https://doi.org/10.1080/02626669909492273

Vergés, J. 1999. Estudi geològic del vessant sud del Pirineu oriental i central. Evolució cinemàtica en 3D. PhD Thesis. University of Barcelona (UB), Faculty of Geology, 180 pp.

Vicente-Serrano, S.M., Lopez-Moreno, J.I., Beguería, S., Lorenzo-Lacruz, J., Sanchez-Lorenzo, A., García-Ruiz, J.M., Azorin-Molina, C., Morán-Tejeda, E., Revuelto, J., Trigo, R., Coelho, F., Espejo, F., 2014. Evidence of increasing drought severity caused by temperature rise in southern Europe. Environmental Research Letters, 9(4), 044001. https://doi.org/10.1088/1748-9326/9/4/044001

Vitvar, T., Gurtz, O., Lang, H. 1999. Application of GIS-based distributed hydrological modelling for estimation of water residence times in the small Swiss pre-alpine catchment Rietholzbach. Integrated Methods in Catchment Hydrology—Tracer. Remote Sensing and New Hydrometric Techniques (Proceedings of IUGG 99 Symposium HS4, Birmingham, July 1999). IAHS Publ. no. 258, 1999

Viville, D., Ladouche, B. and Bariac, T., 2006. Isotope hydrological study of mean transit time in the granitic Strengbach catchment (Vosges Massif, France). Application of the FlowPC model with modified input function. Hydrol. Process. 20, 1737–1751. https://doi.org/10.1002/hyp.5950

Viviroli, D., Weingartner, R., 2004. The hydrological significance of mountains: from regional to global scale. Hydrology and Earth System Sciences 8, 1016–1029. https://doi.org/10.5194/hess-8-1017-2004

Viviroli, D., Dürr, H.H., Messerli, B., Meybeck, M., Weingartner, R., 2007. Mountains of the world— water towers for humanity: typology, mapping and global significance. Water Resources Research 43 (7), W07447. https://doi.org/10.1029/2006WR005653

Wassenaar, L. I., Ahmad, M., Aggarwal, P., van Duren, M., Pöltenstein, L., Araguas, L., & Kurttas, T. 2012. Worldwide proficiency test for routine analysis of δ2H and δ18O in water by isotope-ratio mass spectrometry and laser absorption spectroscopy. Rapid Communications in Mass Spectrometry, 26(15), 1641-1648. https://doi.org/10.1002/rcm.6270

Wetzel, K., 2004. On the hydrogeology of the Partnach area in the Wetterstein Mountains (Bavarian Alps). Erdkunde 58:172–186. http://www.jstor.org/stable/25647659

Zini, L., Casagrande, G., Calligaris, C., Cucchi, F., Manca, P., Treu, F., Zavagno, E., Biolchi. S. 2015. The Karst Hydrostructure of the Mount Canin (Julian Alps, Italy and Slovenia). Hydrogeological and Environmental Investigations in Karst Systems. (ed. Andreo, B., Carrasco, F., Durán, J.J., Jiménez, P., LaMoreaux.) Series: Environmental Earth Sciences. Springer. 638 pp. https://doi.org/10.1007/978-3-642-17435-3

Appendix A: Groundwater catchment areas for the springs S-01 to S-06.

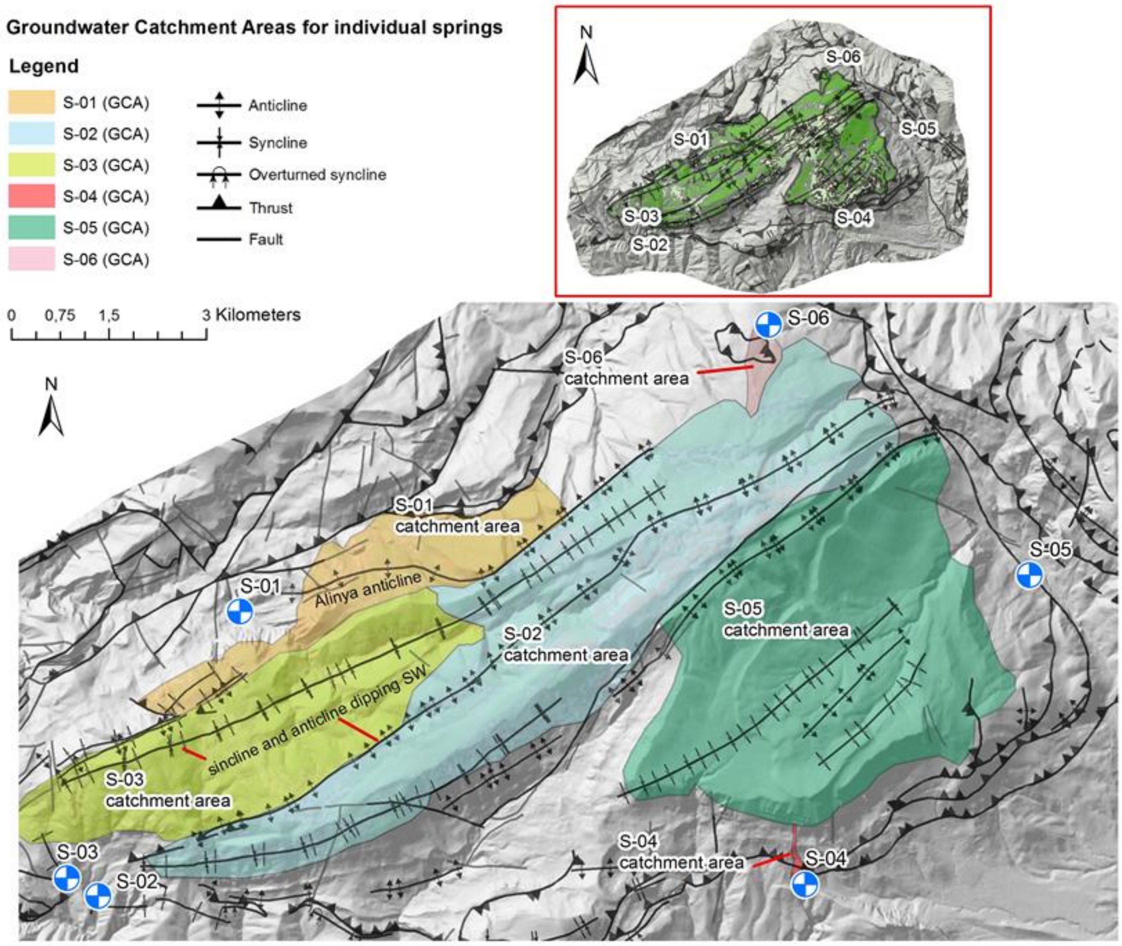


Fig. A1. Groundwater catchment areas for the springs S-01 to S-06.

Table A1. Distribution of geographical and elevation zones considered into the HBV semi-distributed rainfall-runoff model into the groundwater catchment zones. The areas of the different vegetation zones (VZs) are provided, considering the three different elevation zones into which every GWC is divided.

GWC		Elevation Zones			Vegetation Zone Areas			Percentage Areas		
Index	Associated Spring	Z_{min} (m a.s.l.)	Z_{max} (m a.s.l.)	EZ_{ij} [a] (ha)	VZ_1 [b] (ha)	VZ_2 [c] (ha)	VZ_3 [d] (ha)	VZ_1/EZ_{ij} (%)	VZ_2/EZ_{ij} (%)	VZ_3/EZ_{ij} (%)
1	S-01	1334	1600	204,0	41,8	56,8	105,5	20,5	27,8	51,7
		1601	1851	219,1	19,0	67,7	132,4	8,7	30,9	60,4
		1851	2141	122,8	4,8	6,8	111,1	3,9	5,5	90,5
2	S-02	1122	1543	106,9	8,2	26,0	72,7	7,7	24,3	68,0

		1544	1965	756,5	32,2	210,3	514,0	4,3	27,8	67,9
		1966	2385	1389,5	183,8	443,5	762,2	13,2	31,9	54,9
3	S-03	1201	1443	102,3	1,7	36,9	63,7	1,7	36,1	62,3
		1444	1686	561,2	19,5	178,9	362,8	3,5	31,9	64,6
		1687	1927	522,6	12,6	119,4	390,6	2,4	22,8	74,7
4	S-04	1468	1710	9,1	0,1	2,8	6,2	1,1	30,8	68,1
		1711	1847	0,9	0,1	0,5	0,3	11,1	55,6	33,3
		1848	1875	0,1	0,0	0,1	0,0	0,0	100,0	0,0
5	S-05	1421	1663	234,3	8,1	24,4	201,8	3,5	10,4	86,1
		1664	1973	635,5	45,4	126,0	464,1	7,1	19,8	73,0
		1974	2348	1278,4	215,5	495,0	568,0	16,9	38,7	44,4
6	S-06	1838	1926	11,9	0,7	0,7	10,5	5,9	5,9	88,2
		1927	2014	20,7	0,1	1,8	18,8	0,5	8,7	90,8
		2015	2101	13,4	0,0	2,3	11,2	0,0	17,2	83,6

(a) For a given elevation zone EZ_{ij} the subscripts "i" (from 1 to 6) and "j" refer to the corresponding groundwater catchment zone and elevation zone number, respectively; (b) VZ_1 corresponds to open areas; (c) VZ_2 corresponds to mountain meadows; (d) VZ_3 corresponds to forest zones

Appendix B: Sinusoidal functions fitting the measuring the isotopic content ($\delta^{18}O$ and δ^2H) variation in precipitation and spring discharges.

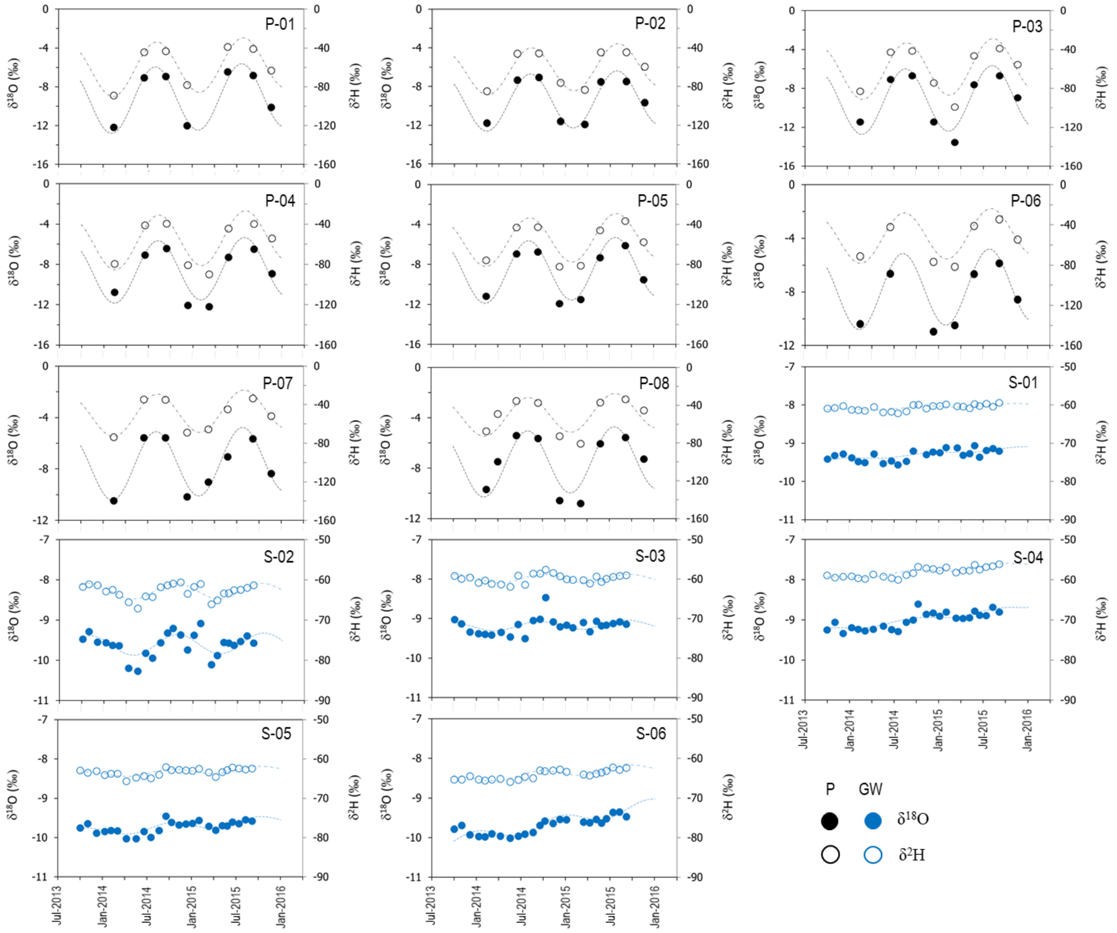


Fig. B1. Isotopic content of precipitation (P; black symbols) and spring discharge (GW; blue symbols). $\delta^{18}O$ and δ^2H are indicated by solid and empty symbols, respectively The dashed lines indicate the fitted sinusoidal function [Eq.1]. The identification codes correspond to those in Table 1.

Appendix C: HBV hydrological modeling

Table C1. List of abbreviations for the vegetation zone parameters of HBV (Seibert, 2005)

Parameter	Units	Valid range	Description
TT	°C	(-inf,inf)	Threshold temperature to produce accumulation of precipitation as snow. Melt of snow starts if temperatures are above TT calculated with a simple degree-day (degree-Δt in case of a non-daily time step) method
CFMAX	mm/Δt/°C	[0,inf)	Degree-Δt factor - CFMAX varies normally between 1.5 and 4 mm oC-1 day-1 (in Sweden), with lower values for forested areas. As approximation the values 2 and 3.5 can be used for CFMAX in forested and open landscape respectively.
SFCF	-	[0,inf)	Snowfall correction factor
CFR	-	[0,inf)	Refreezing coefficient
CWH	-	[0,inf)	Water holding capacity, according to: refreezing meltwater = CFR·CFMAX(TT-T)'
FC	mm	(0,inf)	Maximum soil moisture storage
LP	-	[0,1)	Soil moisture value above which AET reaches PET
BETA	-		Parameter that determines the relative contribution to runoff from rain or snowmelt

Table C2. List of abbreviations for the catchment parameters of HBV (Seibert, 2005)

Parameter	Units	Valid range	Description
PERC	mm/Δt	[0,inf)	Threshold parameter
UZL	mm	[0,inf)	Threshold parameter
K0	1/Δt	[0,1)	Storage (or recession) coefficient 0
K1	1/Δt	[0,1)	Storage (or recession) coefficient 1
K2	1/Δt	[0,1)	Storage (or recession) coefficient 2
MAXBAS	Δt	[1,100]	Length of triangular weighting function

Table C3. Objective functions for the calibration of the HBV hydrologic model, where Q_{obs_i} and Q_{sim_i} are the measured and computed of spring discharge values, respectively, $\overline{Q_{obs}}$ is the arithmetic mean of the observed spring discharge values, and $\overline{Q_{sim}}$ is the arithmetic mean of the computed spring discharge values.

Objective function	Observations
$R_{eff} = 1 - \frac{\sum_{i=1}^{N}\left(Q_{sim_i} - Q_{obs_i}\right)^2}{\sum_{i=1}^{N}\left(Q_{obs_i} - \overline{Q_{obs}}\right)^2}$	R_{eff} = 1 means perfect fit R_{eff} = 0, indicates that the model fits the observed data no better than a horizontal line through $\overline{Q_{obs}}$ R_{eff} < 0 means very poor fit
$R^2 = \frac{\left(\sum_{i=1}^{N}\left(Q_{obs_i} - \overline{Q_{obs}}\right) * \left(Q_{sim_i} - \overline{Q_{sim}}\right)\right)^2}{\sum_{i=1}^{N}\left(Q_{obs_i} - \overline{Q_{obs}}\right)^2 * \sum_{i=1}^{N}\left(Q_{sim_i} - \overline{Q_{sim}}\right)^2}$	R^2 is the determination coefficient. The higher the R^2 value the better the model performance

Table C4. Calibrated values of the parameters in the HBV-light model

Catchment Parameters	Units	S-01	S-02	S-03	S-04	S-05	S-06
Snow Routine (VZ_1)							
TT	°C	-0,2	-4,52	-1,6	-1,1	-1	-1,1
CFMAX	mm/d/°C	1,9	2,4	2	1,7	2,8	1,2
SFCF	-	1	2,38	0,5	1	1,2	1,5
CFR	-	1	2,5	0,7	0,5	0,6	0,6
CWH	-	0,5	2	2	1	0,8	0,8
Snow Routine (VZ_2)							
TT	°C	-0,2	-4,39	-1,6	-0,5	-3	-0,46
CFMAX	mm/d/°C	1,9	1	2	1,6	1	2,1
SFCF	-	1	2,6	0,7	1	1,2	1,16
CFR	-	1	2,5	0,7	0,3	1	1
CWH	-	1	2	1	1	0,2	0,2
Snow Routine (VZ_3)							

TT	°C	4	6	6	0	5,5	6,5
CFMAX	mm/d/°C	1,5	1	1,5	1,5	1	4
SFCF	-	0,001	0,001	0,001	0,01	0,001	0,001
CFR	-	0,7	1	0,7	0,2	0,4	0,4
CWH	-	2	2	3	1	1	1
Soil Moisture Routine (VZ_1)							
FC	mm	95	75	80	75	50	80
LP	-	0,07	0,01	0,02	0,02	0,01	0,01
BETA	-	0,60	0,40	1,54	1,70	0,30	2,5
Soil Moisture Routine (VZ_2)							
FC	mm	180	120	150	125	139	150
LP	-	0,07	0,01	0,06	0,01	0,01	0,01
BETA	-	0,60	2,20	3,90	3,45	1,80	2,7
Soil Moisture Routine (VZ_3)							
FC	mm	750	550	490	750	660	700
LP	-	0,00	0,01	0,01	0,01	0,01	0,01
BETA	-	6,00	3,00	5,70	6,00	3,50	4,00
Response Routine							
PERC	mm/d	5	20,0	2,2	1,1	25,0	1,7
UZL	mm	100	80	100	110	100	100
K0	1/d	0,20	0,50	0,20	0,20	0,20	0,40
K1	1/d	0,07	0,11	0,13	0,17	0,20	0,20
K2	1/d	0,01	0,02	0,04	0,04	0,05	0,05
Routing Routine							
MAXBAS	d	1,7	6,2	2	2,45	4,3	4,22

Table C5. Goodness of the result of the HBV calibrations for each spring model

HBV model	R_{eff} (-)	R^2 (-)
S-01	0,55	0,55
S-02	0,66	0,67
S-03	0,73	0,78
S-04	0,57	0,73
S-05	0,77	0,80
S-06	0,62	0,66

Appendix D: FlowPC modeling

Table D1. Fitted parameters of the exponential-piston flow model (EPM) for the estimated mean transit times (τ) with FlowPC model and $\delta^{18}O$ data

Parameters	S-01	S-02	S-03	S-04	S-05	S-06
β (%)□	0	0	0	0	0	0
δ_β (‰)[b]	0	0	0	0	0	0
η (-)[c]	1,02	1,02	1,00	1,01	1,02	1,02
τ (yr)	2,25	1,42	2,25	2,33	2,88	2,58
RMSE (‰)	0,03	0,04	0,03	0,03	0,02	0,03

(a) A constant discharge component as a fraction (usually older) of the total spring volumetric discharge flow rate. (b) Constant isotopic content of β. (c) η is the ratio of the total volume to the volume with exponential distribution transit time (TTD). η = 1 means the Exponential model (EM) and η>1 for Exponential-piston flow model (EPM)

Table D2. Fitted parameters of the exponential-piston flow model (EPM) for the estimated mean transit times (τ) with FlowPC model and $\delta^{2}H$ data

Parameters	S-01	S-02	S-03	S-04	S-05	S-06
β (%)[a]	0	0	0	0	0	0
δ_β (‰)[b]	0	0	0	0	0	0
η (-)[c]	1,01	1,00	1,01	1,00	1,01	1,02
τ (yr)	3,00	1,92	2,33	2,67	2,83	2,75
RMSE (‰)	0,19	0,21	0,17	0,22	0,18	0,20

(a) A constant discharge component as a fraction (usually older) of the total spring volumetric discharge flow rate. (b) Constant isotopic content of β. (c) η is the ratio of the total volume to the volume with exponential distribution transit time (TTD). η = 1 means the Exponential model (EM) and η>1 for Exponential-piston flow model (EPM)

Supplementary material for on-line publication only

Click here to download Supplementary material for on-line publication only: Supplementary materials.pdf