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Interdisciplinary Research for the Delimitation of Catchment Areas of Large Deep Karstic Aquifers: Origin of the Thermal Springs of Alhama de Aragón and Jaraba (Spain)

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Abstract: The integration of different sources of geological and hydrogeological information and the application of interdisciplinary methods have informed the origin of the thermal springs of Alhama de Aragón and Jaraba, as well as other associated semi thermal springs (1200 L/s of combined flow, 711 L/s at over 30 °C), which is the main objective of this article. These springs come mainly from the autogenous recharge that occurs in the Cretaceous calcareous outcrops that border the Almazán Basin to the north, both in the Ebro Basin (Jalón Valley) and in the Duero Basin. The aquifer, shaped by upper Cretaceous limestones under the Palaeogene and Neogene rocks of the Almazán Basin, has extensive depths of more than 4000 m in the NE sector. This hydrostratigraphic unit has been affected by a generalized pre-Paleogene karstification that provides the main porosity to the aquifer. The underground flow moves in a NW-SE direction, crossing the Duero-Ebro divide, favoured by the topographic difference in elevation between the two basins. The regional flow is coherent with the progressive increase in temperature, infiltrating recharge water age (about 20–25 years in the semi-thermal springs, and more than 60 years in the Alhama and Jaraba springs), mineralization, and flow of the springs through which the system discharges. This issue is key to being able to design any sustainable conservation strategy in terms of quantity and quality of resources within the recharge area of the most important thermal springs in Spain. The Jaraba and Alhama de Aragón hot springs share the same or similar temperature, chemical composition, and geological contact of the spring. Their tritium isotopic composition and its evolution over time are practically the same. Their isotopic composition in D and ¹⁸O is also very similar. Both springs share the same recharge zone of similar altitude and constitute the end of flow tubes of similar length and flow rate.

Keywords: karst aquifer; groundwater resources; thermal springs; delimitation of catchment area; tritium isotopes

1. Introduction and Objectives

The sustainable development of groundwater resources and their management largely depend on the knowledge of aquifer systems, spatial and temporal groundwater recharge and discharge rates, as well as groundwater storage. Demographic changes, population growth, and the rising demand for groundwater to meet drinking water needs, along with the impacts of climate change on groundwater conditions, are factors that must be studied to ensure sustainable groundwater management. In particular, thermal aquifers, such as the case studied, have special value, since they support the concentration of the most important and numerous spa establishments in Spain. But the springs' origin was still unknown. It is therefore of great interest to gain an understanding of the area of these springs in order to take a preventive conservation hydrogeological approach to maintaining them to avoid future problems of unsustainable exploitation or contamination.



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In karst aquifers, given the uniqueness and specificity of their hydrogeological functioning, the analytical methods used in non-karstified environments for the estimation and definition of spring catchment areas do not offer results that guarantee their functionality and effectiveness. This is due to a series of specific peculiarities that differentiate them from the rest of the aquifer typologies [1]. To this, we can add the complication of gaining knowledge of the origin of the thermal water associated with these calcareous rock complexes, since they usually come from deep areas that are difficult to investigate.

In the case studied, it was essential to learn the origin and recharge area before proposing a practical and concrete protection zone. That is why an interdisciplinary study has been carried out in which all existing data from different sources have been used to develop a conceptual model and then a numerical simulation [2]. All of this is particularly applicable to urban supplies, underground table water bottling plants, and spas. All these uses occur in the case studied, especially because it constitutes the largest concentration of spas in Spain.

The delimitation of catchment areas requires knowledge of a combination of topographical, geological factors, hydrogeological and hydrological considerations, etc. We will see in our karst system how the relationship between topography and the dividing lines between neighbouring hydrographic basins is not so simple, since the flow of groundwater from the thermal aquifer crosses below the Duero–Ebro dividing line.

Natural and artificial tracers can help delineate the spring catchment. Natural tracers include water temperature, which has been underutilized but may have great potential [3,4]. As will be seen, in our case the correspondence of the depths reached the flow lines of the system with the different temperatures of the springs associated with each of them being very clear. The chemical compositions of water, stable isotopes, and other parameters are also included as natural tracers (for example, for a low-temperature thermal system: [5]). The stable isotopes of the water molecule (¹⁸O and D) are often used to determine the average altitude of the recharge zone, which is especially useful in mountainous regions. Tritium (³H) can also inform us about the age of groundwater and, therefore, about the distances necessary to explain them, that is, the location of the charging area.

Regarding the background of the aquifer that is being studied, it refers to the preliminary work of [6], followed by [7,8]. However, despite these works, the origin of the springs and the conceptual hydrogeological model of the Alhama-Jaraba thermal system are still not clearly established. Initially it was thought that the main flow of thermal water came from the south (Sierra del Solorio), where there is a plateau with extensive outcrops of mainly Jurassic carbonate materials [6,8–10]. In other words, according to these authors, the water would be recharged in the Castilian branch of the Iberian Range and would come out through the aforementioned springs of different altitudes distributed along the Cretaceous alignment on the other edge of the Almazán Basin (Figure 1). Some of these authors leave open the possibility that part of the Alhama water may also come from the northwest of the Deza [6,9]. It is [7,11] who propose that the main recharge area of Alhama is distributed throughout the Cretaceous calcareous remnants and poljes of the entire northwestern Deza and explain this in a simplified 2D model. Finally, Ref. [12] propose that recharge occurs throughout the Palaeogene and Neogene rocks of the Almazán Basin, flowing into the Cretaceous limestones at the base of the basin and discharging into the Cretaceous outcrops at the margins.

It is understood that this uncertainty and disagreement was partly due to the lack of hydrogeological information available, in particular the lack of knowledge of the Cretaceous and its geometry at depths beneath the Palaeogene and Neogene deposits of the Almazán Basin. There was also a lack of data on piezometry and deep boreholes in the Cretaceous. This lack of information has been compounded by the fact that the area is sparsely populated and groundwater use is low. However, since the last general hydrogeological works by [8,11] 25 years ago, the authors of the present study have been able to generate and use new information, as well as to make use of existing information, all in an attempt to improve knowledge of the aquifers that give rise to these springs.

Thus, the geographical area of study is delimited by the hydrogeological areas that were considered a priori to be part of the thermal system of the Alhama and Jaraba springs, or that could interact with it. In this way, and from a geological point of view, the study area covers the entire Palaeogene, Neogene, and Cretaceous rocks of the Almazán Basin, between the hydrogeological divide between the Ebro and Duero basins, up to the peripheral Cretaceous edges of the Aragonese branch of the Iberian Range. It also includes the Jurassic-Cretaceous aquifers of the Castilian branch. This hydrogeological divide does not coincide with the Duero-Ebro hydrographic divide for the Cretaceous limestone hydrothermal aquifer, but goes far beyond it, entering the Duero Basin. It should be borne in mind that it is the same aquifer, and it is important to distinguish the separation of flows for both hydrogeological basins as shown by current knowledge. For this reason, we have also extended the scope of the study to part of the Rituerto and Morón basins (rivers belonging to the Duero Basin), which follow the Cretaceous in an apparent hydraulic connection beyond the hydrographic divide with the Duero. In addition to these areas, it also includes the Cretaceous and Jurassic aquifers on the edges, i.e., the Sierras de la Pica, Castejón, Miñana, and Cetina in the Aragonese branch, as well as the Sierra del Solorio, Sierra Ministra, Tierra de Medinaceli, and Altos de Radona in the Castilian branch. This represents a vast territory with a surface area of approximately 3500 km² in the centre–northeast of the Iberian Peninsula. This area includes the headwaters of the Jalón river (Ebro River Basin) and the dividing areas with the Duero river to the west and the Tajo river to the south (Figure 1).

The main objective of this study is to improve the knowledge of the origin of the Alhama hot springs and their hydrogeological functioning in order to define their catchment area. The integration of different sources of information, including conventional geological and hydrogeological methods, as well as environmental isotopes, aims to characterize the groundwater dynamics of this geothermal system. A conceptual model of hydrogeological functioning will be defined.

2. Geological and Hydrogeological Description of the Study Area

2.1. Geographical Location, Hydrography and Climate

The springs of Alhama de Aragón and Jaraba (Zaragoza), along with other upwellings associated with the same geological area, form the low-temperature hydrothermal system with the largest groundwater resources in the Iberian Peninsula and one of the largest in Europe (Figure 1) [11]. The total flow is around 1200 L/s (37.8 hm³/year), distributed between the springs of Jaraba (600 L/s, although 322 L/s is thermal flow, the rest is cold water, altitude 760 m), Alhama de Aragón (434 L/s, altitude 660 m), Deza (140 L/s, altitude 910 m), San Roquillo (10 L/s, altitude 900 m), and Embid de Ariza (30 L/s, altitude 800 m) [8,11]. The water temperature varies between 18 °C and 34 °C: in Deza the water rises between 18 °C and 20 °C, in Embid de Ariza 29 °C, in Alhama de Aragón between 27 °C and 34 °C, and in Jaraba between 18 °C and 32 °C. The flow above 30 °C is the largest and is estimated to be around 711 L/s, which represents 60% of the total flow in the system. This last flow represents 38% of all the thermal springs over 30 °C in the Iberian Peninsula, according to the data provided by [13]. There are also other springs in the Almazán Basin, which is part of the Duero Basin, with temperatures between 4 °C and 7 °C higher than the average temperature of the springs in the area, which is around 11 °C (Figure 1).

There are currently seven renowned spas and three natural mineral water bottling plants, making it one of the most important balneotherapy complexes in Spain. In Alhama de Aragón, these water settlements use about 300 L/s, the rest being discharged directly into the Jalón river, which flows through the vicinity. In Jaraba, there is a total flow of 600 L/s which arises through diffuse discharge and springs along a stretch of the river of 2 km from the Mesa river. From reports by [8], it can be deduced that this flow is distributed between 322 L/s with a temperature of 31–32 °C, and 277 L/s is cold water that comes out at 12 °C. The hot springs of Jaraba are used by spas and bottling plants.



Figure 1. Location map of the study area. (**B**) Areas of maximum accumulation of Palaeogene and Neogene sediments in the Duero Basin (according to [14]) and location of the Almazán Basin (CA), Aragonese Branch (RA), and Castellana Branch (RC) of the Cordillera Iberian. (**A**) Geological scheme of the Almazán Basin (Modified from [15,16]), and location of the main groups of springs: (1) thermal, more than 30 °C, (2) semithermal, between 20 and 30 °C and (3) those with temperatures above between 4 °C and 8 °C above the average temperature of the sources in the area, which is about 11 °C (4) Watershed between the Ebro Basin and the Duero and Tajo basins; (5) Iberian Massif; (6) Pyrenees; (7) Betic Cordillera; (8) Palaeogene and Neogene Basin; (9) Iberian Range and Catalan-Coastal Range.

The thermal and semi-thermal springs of this system are distributed along an alignment of Upper Cretaceous limestone in a NW–SE direction over a length of 57 km and with a maximum difference in height of 350 m between the highest and lowest source. This limestone band is on the edge of the Aragonese Branch of the Iberian Range in contact with the Palaeogene and Neogene rocks of the Almazán Basin. Sixteen kilometres further northwest of Deza there is another spring (Almazul, 10 L/s, 1000 m) which has a temperature of 16 °C and can also be considered as the first semi-thermal manifestation. To the SE, at the opposite end, are the springs of Alhama de Aragón (660 m) and Jaraba (750 m), the latter located at the end of the synclinorium, which structures the Cretaceous of the Almazán Basin, and which outcrops in an arc as a periclinal closure in the Ibdes-Jaraba area (Figures 1–3). The Almazán Basin has a synclinal shape with a depocenter, near the village of Almazán, in which the Palaeogene and Neogene sediments reach a thickness of 4500 m, thus representing one of the strongest non-marine Palaeogene and Neogene series in the Duero Basin and in the Iberian Peninsula (Figure 1).

The study site is a high area at an altitude of about 1000 m and forms the dividing line between the Duero and Ebro basins (upper basin of the Jalón river). To the north of the Almazán Basin, the mountain ranges are oriented in a NW–SE direction, forming the edge of the Aragonese branch of the Iberian Range (1313 m as the maximum relative altitude in the Sierra de Miñana). To the south, there is a high plateau that forms the Castilian branch of the Iberian mountain range.

From the hydrographic point of view, most of the study area belongs to the upper basin of the Jalón river, which divides the basin of the Duero to the west and the basin of the Tajo to the south. The dividing line between the basin of the Duero and the Ebro (Alto Jalón) is located in the high plateaux of the Almazán Basin at around 1100–1150 m and in the reliefs that protrude from it at an altitude slightly over 1300 m. The Jalón and its left margin are rivers with an enormous erosive capacity, in such a way that they have captured more than 3000 km² from the high plateau of the Duero Basin by the retreat of their headwaters during the Quaternary [17]. This is not the case with the tributaries on the right bank of the Jalón river (rivers Mesa 54 Km, 27 m³/s and Piedra, 76 Km, 24 m³/s for example), which are of lower energy and quite regulated by large karstic springs.

The average rainfall of the Jalón river basin for the period 1920–2002 was 437 mm/year, varying between 350 mm/year in the area closest to its mouth and 555 mm/year in the areas closest to the Sierra Ministra–Sierra del Solorio at its headwaters [18]. The average air temperature varies between 7 °C in the highest areas, and 10 °C in the sub-basins of the Mesa and Piedra rivers.

2.2. Geological Features

From a geological point of view, the study area covers the entire Palaeogene and Neogene deposits of the Almazán Basin between the hydrographic (and largely hydrogeological) divide of the Ebro with the Duero Basin up to the peripheral Cretaceous edges of the Aragonese branch of the Iberian Range, and the Jurassic–Cretaceous of the Castilian branch. The scope of the study has also extended to a part of the Rituerto Basin following the Cretaceous in an apparent hydraulic connection beyond the hydrographic divide with the Duero river. In addition to these areas, it includes the Cretaceous and Jurassic aquifers on the edges, i.e., the Sierras de la Pica, Castejón, Miñana, and Cetina in the Aragonese branch, as well as, the Sierra del Solorio, Sierra Ministra, Tierra de Medinaceli and Altos de Radona, in the Castilian branch.

In the study area, the Triassic materials outcrop in their three characteristic facies of the Iberian Range (Buntsandstein facies: conglomerates and sandstones, with a thickness greater than 300 m. Muschelkalk facies, dolomites, totaling a thickness of about 100 m. Keuper facies: 200 m of clays, silts, and gypsum). Subsequently, the marine carbonate Jurassic, the Upper Cretaceous, from the Utrillas sand facies to the marine and continental carbonate series and the Palaeogene and Neogene deposits that fill the Almazán Basin. For reasons of hydrogeological interest, we will focus on a more detailed description of those permeable formations most closely related a priori to the Jaraba and Alhama de Aragón thermal springs aquifer. That is to say, mainly the Jurassic and Cretaceous limestone.

The Jurassic is made up of carbonate formations of marine origin outcrop and extend in the Castilian branch to the south of the study area, at the headwaters of the Jalón river. These reach a total thickness of between 310 and 335 m.

The Jurassic is quite permeable and forms part of the recharge area of the Sierra del Solorio in the Aragonese branch of the Iberian Range, which is the area in which the Jaraba and Alhama springs were thought to be fed. It is anticipated, however, that within the study area the Jurassic is absent in most of the Aragonese branch of the Iberian Range and below the Palaeogene and Neogene successions of the Almazán Basin within the study area, so it will be left out of the hydrogeological game and its importance in this sense will lose interest.



Figure 2. Geological diagram of the study area with indication of the extension of the Jurassic below the Cenozoic, detail of the Paleogene stratigraphy and location of the karstification processes in the Cretaceous. 1. Precambrian and Paleozoic: quartzites and shales. 2. Lower and Middle Triassic: sandstones of the Buntsandstein facies and dolomites and marls of the Muchelcalk facies. 3. Upper Triassic: clays and gypsum of the Keuper facies. 4. Lower Jurassic: Dolomites. 5. Middle and Upper Jurassic: limestones and marls. 6. Cretaceous: Utrillas facies sands below. Upper limestones and marls. 7. Palaeogene of the Northern Zone (adapted from Huerta 2007). (7.1. Ocino Fm., 7.2. Almazul Fm., 7.3. Gomara Fm., 7.4. Gomara Fm., 7.5. Peroniel Fm., 7.6. Fm., 7.7. Bordalba Fm., 7.8. Deza Fm., 7.9. Valdehurtado Fm., 7.10. El Raido, 7.11. Alparrache Fm.). 8. Neogene: shales, siltstones, conglomerates. 9. Jurassic boundary below the Cenozoic. 10. Traces of pre-Palaeogene karstification due to the circulation of thermal and semi-thermal waters at the Cretaceous-Palaeogene and Neogene rocks contact (according to [6]). 12. Water divide between the Duero–Ebro. 13. Water divide between the Ebro-Tajo. 14. Overview of signs of karstification at the Cretaceous-Palaeogene and Neogene rocks contact.

Toward the north, these Jurassic carbonate formations gradually lose thickness, which is evident on the eastern edge, to such an extent that in Jaraba, the thickness is minimal and has practically disappeared in Alhama de Aragón. From this locality, and all along the edge of the Aragonese branch up to the periclinal closure of the Cardejón anticline, the Jurassic is not present either. It is from Jaray onwards that they appear again and outcrop along the Rituerto polje as far as the Sierra de la Pica. Below the Palaeogene and Neogene depositsof the Almazán Basin, and according to reflection seismic data and hydrocarbon exploration boreholes [20], such as the Gredal borehole, the Jurassic does not exist in nearly the entire Almazán Basin within the study area, except in the vicinity of the border with the Castilian branch. Between Arcos de Jalón and Jaraba, and according to the aforementioned reflection seismic, the Jurassic seems to have disappeared less than 5 km north of the contact between the Tertiary of the Almazán Basin and the Mesozoic of the Castilian branch. In hydrogeological exploration boreholes it has been detected about two kilometres south of Alconchel de Ariza and Cabolafuente (Zaragoza, [21]).

Figure 2 shows the approximate limit of the Jurassic rocks distribution below the Palaeogene and Neogene rocks in the region. In all this area where there is no Jurassic, the Cretaceous (Utrillas and Santa María de las Hoyas Facies) directly overlies the Triassic. This absence of Jurassic in most of the study area will be of great importance in the definition of the hydrogeological conceptual model

In discordance over all the aforementioned terrains are the sands and sandstones of the Utrillas facies, as well as the sands, clays and limestones of Santa María de las Hoyas. These formations have a combined thickness of about 200 m (6 in Figure 2).

The Cretaceous carbonate formations constitute the main thermal aquifer, and their thickness generally exceeds 300 m, although it varies from area to area. According to geological sheet data, and although the entire stratigraphic series does not always outcrop, the thickness varies between 545 m in the Soria area, 1178 m in the Sierra de La Pica and Sierra de Tajahuerce [16,22], 415 m in the Deza area, 390 m in Alhama de Aragón and 340 m in Jaraba. This carbonate Cretaceous is represented by 6 in Figure 2.

The boundary between Cretaceous and Palaeogene rocks differs from area to area. In most cases, it is an unconformity on which the Palaeogene rocks rest. In other cases, it is a paraconformity characterized by caliche cover and in other cases a surface with karstifications [19].

The stratigraphic scheme in Figure 2 shows the distribution of the Palaeogene and Miocene mega sequences of the north-eastern sector of the Palaeogene and Neogene deposits of the Almazán Basin [16], where their geometrical distribution and interrelation with other facies, the lateral changes, and which ones are directly supported by the Cretaceous aquifer can be appreciated.

2.3. Hydrogeological Features

In accordance with the stratigraphic succession of the area, the presence of two hydro stratigraphic formations is recognized to behave as important aquifers: one is formed by carbonate rocks from the Jurassic, and that constitutes the karstic system of the Sierra del Solorio within the Alto Jalón water body [18], and another is formed by carbonate rocks from the Upper Cretaceous, which form the hydrothermal aquifer. The Tertiary of the Almazán Basin forms a powerful series with little permeability, although some aquitard sections are locally differentiated within the Palaeogene (Figure 3).

Sierra del Solorio is a geographical region comprising the westernmost karstified Jurassic limestone and dolomite moors of the Alto Jalón, which act as a watershed between the Ebro, Tagus, and Duero basins, and the borders of the provinces of Guadalajara, Soria, and Zaragoza. It includes the headwaters of the Jalón river and its main tributary, the river Mesa. Before the confluence with this river, the Jalón is joined by the river Blanco and other less important streams, such as the Sagides, Chaorna, and Iruecha (Figure 3). Due to its relative proximity to the springs of Jaraba and Alhama, the Sierra del Solorio is the area where it was first thought that the water from these thermal springs could come from [6]. This is why we are going to describe the main hydrogeological characteristics of this unit, although there is still a lack of information. As the area is unpopulated, there is hardly any demand for water, and therefore there are few wells.

From the hydrogeological point of view, officially, the Sierra del Solorio forms part of a larger groundwater body (Páramos del Alto Jalón), which also includes the headwaters of the Piedra and Martin rivers [21,23–25]. This groundwater body contains a wide extension of Mesozoic carbonate outcrops, which are mainly included in the Castilian branch of the Iberian Range, and which in the Sierra del Solorio are almost exclusively from the Lower Jurassic.

The structure of the Sierra del Solorio karst is a gently folded tabular peneplain karst, the flow of which is conditioned by the impermeable base of the Keuper facies and the topography. Due to the manner and type of its water supply, it can be classified as an autochthonous karst whose pluvial and pluvio-nival supply is essentially carried out on the absorption surface of the limestone moorlands. The feeding area of this aquifer, up to the Mesa river, is about 576 km² [7,26]. The Jurassic soils, especially the dolomites and limestones of the Lías, form the main aquifers. The strength of these varies depending on whether other upper Jurassic levels are represented or not. Most frequently, they are about 200 m thick, although the thickness increases toward the Mesa river and decreases toward Medinaceli, where the impermeable Keuper already outcrops in the valleys, hydraulically separating some areas from others. The Cretaceous limestone, except for the 27 km² of outcrops south of Jaraba where the Mesa river crosses them and forms a canyon, is barely represented in the small islands on the northern edge of the Jurassic or emerging from the Palaeogene and Neogene deposits, with a surface area of barely 4 km², i.e., the Cretaceous calcareous outcrop on the edge of the Castilian branch of the Iberian Range is 5% of the total calcareous surface area, and the remaining 95% corresponds to the Jurassic.

The compartmentalization of this peneplain by the drainage network of the tributaries of the Jalón means that it does not behave as a large karst system, but rather as more or less isolated subsystems. Thus, and according to [7], this hydrogeological unit can be subdivided into two sectors: an eastern sector that forms the more continuous plateau of the Páramos of Maranchón, and that drains to the great spring of Mochales (more than 500 L/s [12]), and a western sector coinciding with the Medinaceli area, which is more fragmented in aquifers separated from each other. More than ten of these calcareous outcrops can be counted here, isolated from each other by the Keuper, which occupies the lower areas and valleys of the drainage network. Each of these small aquifers is associated with one or more springs, which represent its drainage.

According to [21], this sector of the body is bordered by closed contact (zero flow) with other groundwater bodies located to the west and south, which belong to the Tagus and Duero basins. To the north are the Palaeogene and Neogene sediments of the Almazán Basin, which according to [21] are not considered groundwater bodies.

Sierra del Solorio operates almost naturally, as there are hardly any areas of exploitation (less than 2 hm^3 /year in catchments for supplying small villages). Recharge is mainly through the infiltration of rainwater in the outcrops of the moorland, although there are also important permanent drains in the course of the Mesa river, where some 200 L/s seep after the Mochales springs and before reaching Jaraba. Jaraba's cold flow is largely due to these losses from the Mesa river, although there is also natural recharge from the 27 km² of Cretaceous limestone outcrops in the surrounding area. There are not enough wells in the area, so it is not possible to draw a general groundwater contour map, but the flow is directed in each sector toward various springs with sometimes quite significant flows. Referring to the flows of these springs in the low water year of 1988–1989 [7], for which data are available, we can cite in the eastern sector the Mochales spring on the Mesa river, located at an altitude of 980 m (696 L/s). In the area of Medinaceli, the sources of the Jalón and Fuencaliente streams in Ambrona (140 L/s in total), Urex (120 L/s), and Layna (60 L/s) on the Blanco river, mainly stand out. There are other less important ones which feed the streams of Chaorna (16 L/s), Iruecha (6 L/s), and Sagides (26–37 L/s).

For an average year, the resources of the Sierra del Solorio are estimated at some 63 hm³/year [21], of which 47 hm³/year correspond to the springs of the Mesa river and some 16 hm³/year to the area of Medinaceli [7].

The Cretaceous carbonate formations constitute the main thermal aquifer, and their thickness generally exceeds 300 m, although it varies from area to area. In this area of the Iberian Range around the Palaeogene and Neogene sediments of the basin of Almazán in the Duero Basin, they are one of the most important hydrostratigraphic formations and form very important karst aquifers that drain abundant springs, such as those of the Fuentona de Muriel [27] or the Grandes de Gormaz springs [28].

The karstification of these shallow peripheral systems has its origin in dissolution processes that occurred mainly during the Neogene and Quaternary [29]. However, it is necessary to learn if the thermal system studied here, which reaches a depth of 4500 m, has also been affected by these or other older dissolution processes, since the degree of

porosity that these calcareous formations may reach makes it a true aquifer. On the other hand, it is also essential to learn the geometry of the Upper Cretaceous at depth and its continuity and degree of hydraulic connection, as this can have an important influence on the subterranean flow within the same hydrostratigraphic formation.



Figure 3. Hydrogeological diagram of the study area. Geological features description: 1. Precambrian and Palaeozoic: quartzites and shales. 2. Lower and Middle Triassic: sandstones of the Buntsandstein facies and dolomites and marls of the Muchelcalk facies. 3. Upper Triassic: clays and gypsum of the Keuper facies. 4. Lower Jurassic: Carniolas (dolomites with small cavities) and dolomites. 5. Middle and Upper Jurassic: limestones and marls. 6. Cretaceous: Utrillas facies sands below. Upper limestones and marls. 7. Paleogene of the Northern Zone (adapted from [16]). 8. Neogene: shales, siltstones, conglomerate. 9. Jurassic boundary under the Cenozoic. Hydrographical and hydrogeological features description: 10. Water divide between the Duero-Ebro. 11. Water divide between the Ebro-Tajo. 12. Group of thermal springs (12.1. Jaraba. 12.2. Alhama de Aragón). 13. Group of semi-thermal springs (13.1. Embid de Ariza. 13.2. San Roquillo. 13.3. Deza. 13.4. Almazul). 14. Important cold springs in the Sierra del Solorio (14.1. Mochales. 14.2. Iruecha. 14.3. Chaorna. 14.4. Sagides. 14.5. Urex. 14.6. Layna. 14.7. Ambrona. 14.8. Esteras de Medinaceli or source of the river Jalón). 15. Poljes of the Rituerto river. 16. Flow lines in the Sierra del Solorio. 17. Sinkholes in the Mesa river. 18. Ground water contour and surface flow lines in the Tertiary of the Almazan Basin. Detail (A). Detailed location of springs in the Almazul area associated with the Palaeogene and Cretaceous (geological base taken from [16]). Detail (B). Detail of the location of the group of springs in the Cretaceous calcareous aquifer in Deza and San Roquillo, differentiating between deep flow (orange) and shallow flow (blue) (geological base taken from [16]). Detail (C). Detail of the situation of the group of thermal springs (red) and boreholes of the Cretaceous-calcareous and Palaeogene and Neogene aquifer (T) in Alhama de Aragón. Detail (D). Detail of the situation of the group of thermal springs (red), cold springs (blue), and boreholes of the Cretaceous-calcareous and Palaeogene and Neogene aquifer in Jaraba area.

Karstification of Cretaceous limestones at the Cretaceous-Palaeogene discontinuity is a source of porosity. In this area, apart from the karstification developed during the Neogene-Quaternary, as the most determining period for the current or sub-current morphology, traces of older karstification can also be observed in the Cretaceous limestones, as well as in the Cretaceous-Palaeogene sedimentary discontinuity, which holds special hydrogeological importance in this thermal aquifer.

The presence of signs of karstification along the Cretaceous-Palaeogene discontinuity at the border of the Almazán Basin with the Aragonese branch is a general feature identified by several authors [6,16,19]. In addition, all the thermal or semi-thermal springs are located in this contact of different permeability, so the relationship between both facts and the interest in characterizing this source of porosity are evident. In this karstification, we must distinguish the labyrinthine conduits in the limestones in contact with the Palaeogene generated by the circulation of groundwater in the thermal aquifer during the Neogene-Quaternary [6]. These can be considered to be a consequence of the circulation of the flow according to a scheme more or less similar to the present one (Figure 3). In addition, we must consider another much older one, prior to the configuration of the aquifer, which is represented by the paleokarsts developed in the Paleocene and Lower Eocene during the exposure to the exterior of the Upper Cretaceous limestones [16,19], and which probably constitute the main porosity at the depth of the thermal aquifer. It is not excluded that the more modern conduits in the upper part of the aquifer have taken advantage of this original karstification.

This karstification is recognized in at least seven points distributed between Deza (Soria) and Godojos (Zaragoza) in the Cretaceous limestones [19], but there are probably many more sites (Figure 2). The fact that these points are spread over a length of 30 km and are distributed at different altitudes according to a maximum difference in altitude of 350 m, indicates that karstification is quite widespread. Then, during the subsequent major sedimentation, this karstified discontinuity was buried and submerged by subsidence to a depth of more than 4500 m. This provided a widespread source of porosity at great depth, with geothermal gradients of around 100 °C, which may have allowed large flows of water to penetrate, heat up, and circulate along the basin floor. The degree and intensity of this karstification is unknown, but it is thought to be unimportant as the porosity values required in the aquifer modelling have not been significant (0.3%).

Referring to the karstification of the Cretaceous limestones during the Neogene-Quaternary, and according to [29], after the elaboration of the Intra-Miocene Erosion Surface, corrosion of the created planes occurs, causing the formation of small cavities and deposits of terra rossa during the middle-upper Miocene. Subsequently, the sedimentation of lacustrine carbonates occurs in more humid conditions, probably thanks to the greater intensity of the dissolution processes on the Mesozoic mountain edges. The upper Miocene-Ruscinian is characterized by a decrease in the base level due to the exorheic opening of the basin and the action of tensional tectonics. This entails a stage of the generation of poljes and corrosion surfaces, as would be the case of the poljes of Araviana [30], Cañada Hermosa [31], Rituerto, and Noviercas, in the upper Rituerto Basin to the north [32]. With the Ibero-Manchegan tectonic phases, during the Pliocene and favoured by the associated fracturing, the main stage of poljes formation takes place in the southern mountains, such as the Layna poljes [33].

Regarding the geometry and deep structure of the Almazán Basin, it must be said that on this northern edge of the Aragonese Branch, at the contact with the Almazán Basin, the structure has a general NW–SE orientation, unlike the edge with the Castilian branch, which is dominated by a W–E direction. At depth and on the basis of the ground water contour of the Palaeogene and Neogene base obtained from reflection seismic surveys, oil drilling, and the support of gravimetric studies, the geometry at depth of the Almazán Basin, and specifically of the Cretaceous calcareous aquifer, can be deduced [19]. The structure of the basin is characterized by folds with NW–SE to E–W directions, associated in some cases with north-vergence thrusts. Two sectors are considered to the west of the Almazán–Soria meridian, the fold axes are E–W, while to the east, as they approach the Aragonese branch, they acquire NW–SE directions typical of this unit of the Iberian Range. In the eastern sector of this basin, three areas with different structures can be distinguished

In the centre of the basin, east of Almazán, the main structure is the bottom of a syncline bordered by the Gómara monocline to the north, and the Almazán monocline to the south.

The Gómara monocline dips 20–30° to the south, gradually decreasing to the west. The folds are slightly asymmetric with north vergence and are associated in many cases with faults affecting the basement [19,34].

To the south is the Almazán monocline, which has very low northward dips in this eastern part, and further south, the Arcos monocline dips in the same direction. North of the Arcos monocline there is no more Jurassic, and this is observed in the seismic profiles from the Soria meridian to the end of the Almazán Basin at Jaraba, as well as in the Gredal-1 survey. On the southern flank of this monocline, the Cretaceous and especially the Jurassic rocks of the Castilian branch outcrop.

3. Methods

Intensive office and fieldwork was carried out in order to construct a conceptual model that formed the basis for the development of the numerical modelling [2]. In this model, the geometry of the Cretaceous carbonate hydrothermal aquifer has been graphically represented, considering the surface topography, geology, main hydrogeological units and their contacts, existing wells, and the extension of the sector to be modelled. By integrating different sources of information and applying interdisciplinary methods, sufficient knowledge of the thermal system has been obtained for its modelling. Specifically, the methodology followed is as follows:

3.1. Study on the Palaeogene Rocks Karstification of the Hydrothermal Aquifer

In this respect, previous studies in the area were analyzed, including the work of [16] and [1], in order to determine the shape, distribution and extent of the Palaeogene units and the origin of the karstification in the Cretaceous limestones, which directly influence the hydraulic conductivity of the hydrothermal aquifer.

3.2. Study on the Space Attributes of the Hydrothermal Aquifer and Application of the Bounded Plane Representation Technique

This knowledge will help to understand the geological structure and the existence of possible tectonic features that could break the continuity of the Cretaceous series that in principle is assumed, and that could modify the underground flow. Furthermore, in cases such as this one, and in accordance with the regional tectonic context, only a normal geothermal gradient is available, so that the identification of the heat source that gives rise to the geothermal system will be the areas of the aquifer that reach the greatest depth.

In order to understand the extent and limits of the Cretaceous water-bearing materials, the work of [19] was studied.

However, although reflection seismic and gravimetry provided the geometry of the deep parts of the basin, this map was too general for the edges of the basin, which is where the discharge zones of the Cretaceous calcareous aquifer are located, which are key in the process of simulating groundwater flow, for example. In addition, apart from the surface geology, data from other groundwater abstraction boreholes in the Palaeogene and Neogene rocks have been used, which have reached the Cretaceous and Jurassic [21], as well as geophysical studies in the Domain of Time, SEV, and gravimetry around Gómara and Almenar de Soria [35]. All this has been used to draw the structural contour lines of the Palaeogene and Neogene base by the method of boundary representation systems in the aforementioned edge zones, linking them with those of the deeper parts of the [19] map.

3.3. Study on Hydrothermal System Domain Boundaries

The results of several works and doctoral theses on the Cretaceous hydrogeology of the Almazán Basin rims in the Duero Basin [27,28,36] have been interpreted in order to locate the hydrogeological divide of the hydrothermal system that drains the springs located in the Ebro Basin of Alhama, Jaraba.

3.4. Carrying Out an Nventory of Water Points

From the information of the inventory of water points and pumping tests in wells, specific flow rates and ranges were determined for the permeability values of the different hydro-stratigraphic units, as starting values to support the mathematical model. The inventory in the Cretaceous-Palaeogene and Neogene aquifer is scarce and has not allowed groundwater contour maps to be drawn up, but it has been important for identifying different types of flow and discharge and recharge zones. In the Palaeogene and Neogene rocks, the inventory has served to confirm its low permeability and the identification of aquitards in the Palaeogene.

An inventory of 540 water points has thus been made, including permanent or ephemeral springs (70%), boreholes and wells (28%), galleries and effluent streams (2%). As the study area is very sparsely populated, with one of the lowest population densities in the European Economic Community, there are hardly any boreholes that could be used for a general isopieces map. Among the boreholes, there are 3 piezometers of the piezometric control network of the "Confederaciones Hidrográficas del Ebro" [21,37] "del Duero", which have been used to calibrate the groundwater flow simulation.

3.5. Isotopic Hydrochemical Studies

To improve the hydrogeological and hydrogeochemical conceptual model, a tritium isotopic monitoring of the thermal and semi-thermal springs has been carried out to improve the understanding of the groundwater dynamics in the system and to clarify the origin and age of the Alhama and Jaraba springs. All the above information has been compiled (taken from [1,8]), and several sampling campaigns have been carried out over the last two decades. Samples have also been taken in these springs for environmental isotope analyses (Deuterium and Oxygen 18) in an effort to determine the area of origin of the natural recharge.

4. Results and Discussion

4.1. Palaeogene and Neogene Hydrogeological Features

4.1.1. Aquitards Identifications

From the inventory of water points carried out, specific flow data from 60 boreholes and wells were available, as shown in Table 1. Although not all of them come from detailed pumping tests, most of them are considered to be quite reliable. Classified by lithological groups of similar hydrogeological behaviour, 17 correspond to the alluvial of the Jalón river and also of some tributaries, 23 to the Miocene (except the limestones of the Páramo), 1 to the Ocino Fm. of the Palaeogene, 1 to the Gómara Fm. of the Palaeogene, 9 to the limestones of the Upper Cretaceous, 8 to the Lías dolomites (Jurassic), and 1 to the Muchelkalck dolomites (Table 1). Transmissivity has been obtained according to the approximate formula of Calofre [38] and permeability considering the saturated thickness of the wells and transmissivity.

Lithological Group	Number of Pumping Tests	Specific Flow Rate q _e (L/s/m)	Transmissivity T (m ² /day) T = 100 q _e	Permeability K = T/b (m/day)
Aluvial deposits	17	1.47	147	30
Miocene period	23	0.082	8.2	0.1
Paleogene period (Fm.Gomara)	1	0.105	10.5	0.06
Paleogene period (Fm. Ocino)	1	0.2	20	0.5
Cretaceous	9	8.3	830	6-11.8
Jurassic (Lias)	8	0.56	54	1.14
Muchelkalk	1	0.012	1.2	0.024

Table 1. Specific flow, transmissivity, and permeability values of some of the hydro stratigraphic formations in the study area.

On the basis of these data, the detailed knowledge of the lithology, as well as the distribution and flow of springs and in this area, it can be concluded that both the Palaeogene and the Neogene of the study area are, overall, not very permeable.

The Palaeogene and Neogene rocks of the Almazán Basin of the Duero hydrographic Basin have been considered as an aquifer-aquitard of low permeability (officially called the "Tertiary" Aquifer of southeast Soria [39]. For the [21], this same Palaeogene and Neogene rocks has been considered impermeable and, in the Ebro Basin, (Upper Jalón) no type of aquifer has been defined.

4.1.2. Two Palaeogene and Neogene Flows: Shallow and Deep

Surface flow: Figure 3 presents a schematic Palaeogene and Neogene rock water table contour map based on 420 water points and rivers/streams flowing with water. The qualitative interpretation of this map indicates that: 1. The water table contour is quite adapted to the topography, with the water level of the boreholes close to the surface, which is typical for low-permeability soils. The impermeability of the geological formations of the basins of the Nágima, Santa Cristina, and Jalón rivers, for example, has been known for a long time and this has limited human supply by means of wells [40,41]. 2. Also, as a consequence of the above, the Duero–Jalón surface and underground divides coincide at surface level in most of the study area, except for the divide with the Rituerto river. 3. The rivers and streams of the Jalón Basin drain, but the discharge is not continuous and diffuse, and rather occurs through small, occasional springs, which are associated with more permeable levels within the Tertiary, either Neogene or Palaeogene. Some of these springs are located near the watershed. Most of the rivers do not discharge significant groundwater; this can be seen very well in the dry season when a large part of the riverbeds run dry, such as the Jalón and the Nágima during times of droughts.

On the other hand, as shown in Figure 3, we observe the large number of facies and lateral facies changes within the Palaeogene, which makes hydraulic continuity between the Palaeogene and Neogene aquitards and the Cretaceous difficult, since they are almost always surrounded by impermeable formations. This favours the disconnection and hydraulic isolation of the Palaeogene geological facies, and the subsurface flow is predominantly superficial and of limited spatial extent. Therefore, there is a relatively high number of small springs draining more permeable, weakly permeable layers interspersed between a mass of impermeable sediments (Figure 2; Detail 14).

• **Deep flow**: The Rituerto river and its tributary, the Arroyo de la Vega in the Duero Basin, have the behaviour of losing rivers, even though they flow through Palaeogene and Neogene sediments. Despite having a large catchment area (more than 600 km²), it is usual to see them dry most of the year (hence the historical name of Rituerto river, for example, which refers to a half-dry river). This is because the Palaeogene and Neogene sediments are not very thick here and the Cretaceous-calcareous aquifer

is close to the surface, sometimes outcropping, and this absorbs the recharge. All this has led to the formation of two large karstic depressions or poljes filled with Neogene and Quaternary sediments: the Rituerto polje and the Cañada Hermosa karstic depression [31]. This Cretaceous proximity to the surface has been geometrized in detail by means of different geophysical techniques in the work of [35].

Thus, it can therefore be concluded that two flows coexist in the Palaeogene and Neogene rocks of the area: a sub horizontal surface flow when the Tertiary is strong, and a deep flow when the underlying Cretaceous-calcareous aquifer is nearby. This flow, with a significant vertical component, feeds the thermal aquifer. In actual fact, what can be observed in Rituerto and Arroyo de la Vega is the surface manifestation of what is happening at depth: a zone of influence or absorption of Palaeogene and Neogene groundwater by the more permeable Cretaceous aquifer below (Figure 4).



Figure 4. Schematic hydrogeological cross-section along the bottom of the Almazán Basin showing the hydrogeological divide established in the mathematical model for the Cretaceous-Thermal aquifer. 1. Palaeogene and Neogene sediments of the Almazán Basin. 2. Edges of the Almazán Basin (mainly carbonate aquifer). 3. Topographic contour lines. 4. Depth of the top of the Cretaceous-thermal aquifer. 5. Water table. 6. Duero–Ebro surface divide. 7. Duero–Ebro hydrogeological divide, verified at the edges and assumed in the interior of the basin. 8. Duero–Ebro hydrogeological divide, maximum assumed position. 9. Springs. 10. Flow lines. 11. Hydrogeological cut (the power of the Cretaceous-thermal calcareous aquifer is exaggerated).

4.2. Hydrogeological Features of Thermal Aquifer

Figure 1B is a geological and topographical diagram showing the Palaeogene and Neogene of the Almazán Tertiary Basin as a whole, including the area belonging to the Duero Basin. In this basin, the topography ranges between 900 and 1000 m for the most part, while in the Ebro Basin (Jalón river), the altitudes range from 640 m in Alhama de Aragón to 1100 m at the boundary with the Duero. The highest peripheral areas correspond

to the Mesozoic calcareous rims, while the lower central areas are occupied by Palaeogene and Neogene terrigenous sediments. Also noted are those springs that have a temperature of 4 °C above the average of the rest of the springs in the region, which is around 11 °C, and which range between 15 °C and 18 °C in the Duero Basin (semi-thermal springs), and between almost 20 °C and 32 °C in the Ebro Basin (thermal springs).

In Figures 1–4, we can see how the semi-thermal and thermal springs in the Almazán Basin are always associated with the Cretaceous-calcareous and are found at the contact between this Cretaceous and the Palaeogene and Neogene. In the Jalón Basin, all the springs range between 18 °C and 32 °C and are located on the NE edge, except for Jaraba, which is nearby; in the rest of the southern peripheral edge, regardless of whether the Palaeogene and Neogene contact with the Cretaceous or Jurassic, there are no other manifestations. This Cretaceous-Palaeogene and Neogene contact has a drop of more than 400 m between the Duero–Ebro divide and Alhama de Aragón (Figure 4). In the Duero these semi-thermal manifestations are usually located in the lower altitude anticlinal domes that emerge from the Palaeogene and Neogene sediments, and represent the emergence of medium depth flows, since in the Soria plateau there are no significant topographic differences between the recharge and discharge areas [27,28,36].

On the other hand, there are certain tectonic accidents that break the hydraulic continuity of the thermal Cretaceous-calcareous aquifer at depth: As mentioned in Section 2.3, this work follows the interpretation of [19], on the deep geological structure of the Almazán Basin. This assumes that the Upper Cretaceous thermal aquifer has continuity and is hydraulically connected to each other under the Palaeogene and Neogene sediments. However, in certain sectors, different interpretations have to be considered, such as that of [42], where he admits that the Cretaceous lateral continuity is sometimes broken by reverse faults with important dips. This is also observed in the surface geology, such as the apparent interruption of the Cardejón mountains with the Castejón mountain range through the Soria fault, for example. The identification of tectonic fractures that locally interrupt the hydraulic continuity within the aquifer can be important for the modelling of the flow. In order to have the most realistic geometry possible, the previous information from the above-mentioned authors has been complemented by the dimensioning representation system. According to this analysis, we have been able to identify two features that have been considered in the modelling phase:

The first one refers to the sector between Embid de Ariza and Alhama. It is a series of several NW–SE isopach anticlines with westward vergence, involving the Palaeogene to the Triassic and faulted by sub-vertical reverse faults involving the Palaeozoic. These folds have verticalized western flanks and the eastern flank has lower dips. Toward the centre of the basin, there is a series of north-vergence folds, of which only the easternmost one is at the surface (east end of the Fuentelmonge Anticline), which has an ESE direction, oblique to the general structure of the Aragonese branch.

Deformation is progressively attenuated toward the basin centre and toward deposits of a more modern age. The most important implication from a hydrogeological point of view is that the fault jumps associated with some of these fault-folds displace the impermeable Triassic and Palaeozoic substrate in such a way that they act as a vertical barrier, interrupting the continuity of the Cretaceous south of Deza with the Embid area.

The second structure with hydrogeological implications is the Jaraba fault [43], a fault with a NE–SW direction and a large dip, dipping the NW block and confronting the impermeable Triassic and Mesozoic rocks with the Upper Cretaceous. The result is an impermeable barrier effect that isolates the area farthest from the periclinal closure of the SE Ibdes from the rest of the thermal aquifer. All these hydrogeological disconnections have been simulated in the numerical model, and as indicated, play a fundamental role in the calibration of this model [2].

4.3. Hydrochemical Features

4.3.1. Isotope Hydrochemical Features

Given the fractional discharge of the thermal system, through several springs that are distributed along the Cretaceous contact of the Aragonese Branch with the Palaeogene and Neogene sediments of the Almazán Basin, the tritium values of these springs have been used to estimate the age of the groundwater and its chronological distribution in space. The evolution in time of the tritium content of the waters of the springs of the aquifer has also been studied. For this purpose, all the data on tritium values of the springs over the last 40 years (from 1981 to 2021) have been compiled and are shown in Table 2.

Regarding the origin of the data and sampling, the following should be pointed out: 1. As can be seen in the above table, the values do not correspond to a continuous and systematic sampling, since they come from studies carried out by different organizations and years, but they do cover almost all the springs or groups of springs over time. Indeed, the 37 data in Table 2 come from our own investigations (year 1992, [11]) and year 2021 (for this work), as well as from reports of the [8] and other unpublished reports on tritium content obtained from the Pallarés Hot springs in 1982. 2. In the most important groups of springs of Jaraba and Alhama de Aragón, many discharges were initially analyzed; afterwards, sampling continued with those springs where there was certainty that they were of deep flows and not mixed. 3. Going down to the concrete, it has been observed that in Embid de Ariza (Table 2, year 1992) the most representative samples are those obtained from the catchment gallery and not from the washing place 500 m downstream and that the water arrives through a ditch where there is a contamination with modern sub-valve water. 4. In the springs of San Roquillo, the representative sampling of the regional flows should be performed during low water levels, since it has been observed that there is mixing by recent water infiltrated during rainy months.

• Groundwater age

For the various estimates of the age of the water in the springs, it is assumed that the Alhama aquifer approximately follows a piston flow model. As can be seen from the results of the conceptual model and the flow modelling, recharge is assumed to occur preferentially in the north-western sector of the Cretaceous-calcareous aquifer, where the groundwater moves without major mixing processes with the Palaeogene and Neogene rocks. The tritium content of the groundwater is therefore mainly controlled by the laws of radioactive decay.

The estimated age of the water of the Alhama and Embid springs (1993) for the years 1981/1982 and 1993 according to [8] is that they corresponded to recharge waters prior to 1952. In 1982 and on the basis of 12 monthly analyses throughout the year in the spring of the Pallarés Hot Springs gallery, the tritium content was practically nil; it can therefore be assured that the Alhama springs were not influenced by water from after 1952, nor by recharge from nearby outcrops.

Most of the Jaraba springs, at least the warmest ones, also correspond to recharges prior to 1952, although there are others with values that reflect mixing with more recent water. This mixture of waters is characteristic of Jaraba: springs with a temperature range between 18 °C and 32 °C, tritium isotopic variations, and greater dispersion in the composition of the waters.

This is logical, since the non-thermal Cretaceous limestone aquifer, which is here folded and sub-horizontal and expands to the southwest over an area of about 27 km² in the vicinity, drains cold water (between 12° and 14 °C) also at the lowest point of Jaraba. The Mesa river runs in a gorge parallel to the termination of the deep Cretaceous in contact with the Palaeogene and Neogene rocks for about 2 km, so the interaction of cold water from the river and discharges is important. This is not the case with the Jalón river in Alhama de Aragón, which cuts perpendicularly to the vertical layers of Cretaceous limestone in a minimum stretch of no more than 200 m, and there is no option for there to be much mixing of water. The ages obtained in the 1992 sampling for the Deza and San Roquillo

springs show that the waters possibly infiltrated in the 1980s [11]. For the 2000 sampling, the age of the waters of Deza and San Roquillo infiltrated about 12 years ago, and in Embid and Alhama, 36–40 years ago: values similar to those obtained by [11].

For the last sampling in the year 2021, as shown in Figure 5, where the tritium activity values have been represented, together with the values of tritium activity in precipitation in the station closest to the sampling points, Zaragoza, belonging to the Spanish Network of Isotope Monitoring in Precipitation (REVIP), managed by CEDEX and AEMET, and also the one in Madrid, used as a reference. In Madrid there are monthly measurements of tritium activity in precipitation from 1970 to 2020, with some information gaps, while in Zaragoza there are only annual weighted measurements from 2000 to 2019. In both cases the annual mean weighted with the amount of precipitation has been plotted. The values before 1970 and the gaps have been completed for the Madrid station with the model of tritium in precipitation in the northern hemisphere according to the criteria of [44–46].



Figure 5. Comparison of tritium values of groundwater samples with those of annual precipitation in Zaragoza and Madrid, belonging to the REVIP period 1953–2018 in semi-logarithmic scale. (A. Precipitation in Madrid. B. Precipitation in Zaragoza. C. Deza springs. D. San Roquillo springs. E. Springs of Alhama de Aragón. F. Jaraba spring).

The straight lines in Figure 5 link the tritium activity values of all recharge waters that could give rise to the measured value in each sample after radioactive decay. Any cut-off points of these decay lines with those linking the tritium activity values in the precipitation water have the same probability of corresponding to these recharge waters, depending on the flux model. In this case, and considering a piston flow model, both the waters of Embid and those of the Alhama de Aragón springs would correspond to waters recharged prior to the 1960s, i.e., more than 61 years old. Those of the San Roquillo and Deza springs would come from a recharge in the early 1990s or, at least, before the year 2000, i.e., some 20–25 years old.

These results from the 2021 campaign are somewhat older than the age values obtained from previous campaigns but remain in a similar range. In fact, it is thought that the ages of Alhama and Jaraba are close to a century old according to simple analytical calculations of the real velocity in relation to the length of the flow lines obtained from the groundwater contour map (Figure 6) of the mathematical model [2], the hydraulic conductivity and the porosity obtained from the modelling (0.3%). It is important to note how the simulated ground water contour could be assimilated to isochrones and fit very well to the progressively increasing age model Deza-San Roquillo-Embid de Ariza-Alhama/Jaraba, according to the regional flow.



Figure 6. Result of piezometric levels after the calibration of the numerical model [2].

Table 2. Tritium	isotope values	(in TU).
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Springs	1981 (1)	1982 (2)	1992 (3)	1993 (1)	2000 (4)	2021 (5)			
Deza springs									
Suso spring			7.2 + 0.13 8.1 + 1.0		4.12 + 0.12	1.57 + 0.29			
El Hocino spring			8.0 + 0.13 7.4 + 1						
San Roquillo									
San Roquillo spring			1.23 + 0.5		3.72 + 0.19	1.25 + 0.28			
Embid de Ariza									
Embid de Ariza gallery				0.74 + 1.37					
Lavadero	2.9 + 1.2		3.3 + 0.9 3.2 + 0.11		1.99 + 0.16	0.57 + 0.27			
		Alhama	springs						
El Chorrillo (termas san Roque)				5.8 + 1.6	1.28 + 0.15	0.63 + 0.28			
San Roque (B. Cantarero)				6.0 + 2.0					
Gallery (termas Pallares)	0.6 + 1 (1)			6.7 + 1.4					
Los Baños spring (B. Guajardo)				3.2 + 2.0					
Termal lack Baños del Rey	0.2 + 1			5.9 + 1.6 8.4 + 1.6					

Springs	1981 (1)	1982 (2)	1992 (3)	1993 (1)	2000 (4)	2021 (5)	
Jaraba springs							
Virgen de las Nieves spring				10.7 + 1.4			
San Vicente spring (B. Sicilia)		0.0 + 1.1		5.4 + 1.8			
San Luis spring (B. de Serón)		0.0 + 2.3		1.9 + 2.0			
San Antonio spring		0.0 + 1.1		3.3 + 1.4			
San Roque/Sta Dorotea (b. de seron)		0.0 + 1		3.8 + 2.0			
El Prado spring (B. de Serón)		0.0 + 2.4		10.0 + 1.4			
Sondeo "Cañar 2"				6.6 + 1.4			

Table 2. Cont.

Notes: (1) No tritium content was observed during the 12 months of 1981 (proc.: Pallarés Hot springs). (2) Taken from [8]. (3) Taken from [1]. (4) and (5) This work.

• Evolution of tritium content over time

On the other hand, the tritium content of some of the springs under study has been monitored over a long period of time and is shown in Figure 7. The following observations can be made:

- The shape of the tritium content curve of all the springs is a smoothing of the rainfall curve and shifted in time. In all cases, the upward curve is steeper than the downward curve, with a gentler slope, and is similar in shape to that of the rainfall. We can see how the decreasing trend is maintained with a similar slope in all cases, i.e., they are sub-parallel.
- Curves values are higher in the springs with more modern waters and progressively decrease in those with older waters (Deza/San Roquillo-Embid-Alhama/Jaraba) according to the underground flow, but in all cases, there is a certain mixture of post-1952 waters from 1982 onward. Indeed, it can be seen that in 1982, the thermal springs of Alhama and Jaraba were not influenced by water from after 1952, nor by the recharge of nearby outcrops, since their values are below 0.5 TU. It is from 1985 onward when the mixture of water infiltrated after 1952 begins to be noticed, but the values are still very low. In Embid, it would probably be a little earlier, around 1979, if a curve with the same function as that of Jaraba and Alhama were to be drawn. In Deza and San Roquillo, it would also be earlier, around 1975, if it were using the same procedure. There is a maximum tritium content in the Embid, Jaraba, and Alhama springs around 1992, displaced with respect to the maximum tritium content of the rains by 32–33 years. All this leads us to think that we are dealing with the same aquifer system whose recharge is far away, which has a large reservoir of old water, and that the recharge of young water has not been mixed to any great extent with the former because it is drained by the Deza and San Roquillo springs, purifying the system and causing long, deep, and old flows to reach Alhama.
- The thermal springs of Jaraba and Alhama de Aragón share the same or similar temperature, chemical composition, and geological contact of emergence. Their tritium isotopic composition and their evolution over time are practically the same, as shown in Figure 7. Its D and ¹⁸O isotopic composition is also very similar. All this shows that there is a hydrogeological parallelism and the same origin between both springs: As can be seen in the ground water contour map (Figure 6), both springs share the same recharge area of similar altitude and constitute the end of flow tubes of similar length and flow rate.



Figure 7. Evolution of the tritium content of precipitation in Madrid and in the springs of the Alhama de Aragón thermal aquifer (A. Precipitation in Madrid. B. Precipitation in Zaragoza. C. Deza springs. D. San Roquillo springs. E. Embid de Ariza. F. Springs of Alhama de Aragón. G. Jaraba spring (own data and from [8,11,47,48]).

4.3.2. Information Provided by Deuterium and Oxygen¹⁸

Table 3 presents the collected values of D and ¹⁸O and the new values for the year 2000 made for this work. We consider the data obtained to be valid since, for hydrothermal systems with low to medium temperatures, as is the case, the values of δD and $\delta^{18}O$ do not undergo substantial changes, which does not occur in those with high temperatures [49]. It can be seen that they do not differ substantially from the previous ones, which confirms that the recharge area is located in the same zone for all the springs. According to the rainfall data from a relatively close station in Madrid, which corresponds to recharge areas located between altitudes 1000–1300 m. Since both the Sierra del Solorio and the area of the Cretaceous outcrops in the Aragonese branch coincide with these altitudes, this isotope does not serve to discern which of the two areas is truly the recharge area. It is significant how the chloride content increases with flow, while ¹⁸O remains almost unchanged.

	1981 (1)		198	1982 (2)		2000
Springs	s180.0/ c2	c?11	δ ¹⁸ (δ ¹⁸ O ⁰ / ₀₀		s ¹⁸ 0 ⁰ /
	80 ·7 ₀₀	δ ⁻ Ο ⁻ / ₀₀ δ ⁻ Η -	Spring	Summer	Spring	o 0 %
M ^{al} de Alhama (Termas Pallarés)		-62	-8.71	-8.74		-8.68
M ^{al} de Alhama de A. (El Lago)		-60				
Embid de Ariza (galería)		-59	-8.74	-8.73	-8.46	-8.58
San Roquillo			-8.91	-9.03	-8.48	-8.73
M ^{al} de Suso (Deza)			-9.03	-9.02	-8.54	-8.86
M ^{al} de Ocino (Deza)			-8.94			

Table 3. Tritium isotope values (in TU).

Notes: (1) No tritium content was observed during the 12 months of 1981 (proc.: Pallarés Hot springs). (2) Taken from [8].

4.3.3. Hydrochemical Characteristic

A detailed analysis of the conventional groundwater chemistry is not the preferred objective of this work. Apart from the fact that no chemical analysis of its own has been carried out, only a first coherent approximation according to the proposed and simulated hydrogeological model is intended. Thus, and according to the extensive information on the analyses carried out (due to their large number they are not presented; see example: [8,11,47]), Figure 8 shows a Piper diagram that classifies the facies of the springs studied, differentiating in Alhama and Jaraba the thermal waters, which are in the majority, from the cold waters, which are in the minority. It can be observed that the springs of Jaraba and Alhama are similar, although those of Jaraba are of the Ca-Mg-HCO₃ type, while those of Alhama are more of the SO₄-Cl type. Embid is close to Alhama. Deza and San Roquillo are calcium bicarbonate and very similar to each other. All the springs in the system show an increasing gradation in the direction of flow, both in the mineralisation of their waters (Figure 9), in accordance with the increase in the temperature of the springs and the age of their waters. This is very consistent with the conceptual and simulated model.



Figure 8. Piper diagram of the chemical composition of the waters of the springs of the thermal system. (A. Alhama de Aragón springs. B. Jaraba springs. C. Embid de Ariza spring. D. San Roquillo springs. E. Deza springs F. Cold springs). (own data and from [8,11,47]).



Figure 9. (Left): Relationship between ¹⁸O values and their chloride content in the springs (in mg/L) of the Alhama de Aragón thermal aquifer. (**Right**): Increase in mineralisation of the springs (TDI) according to the regional flow.

Although the aquifer studied is dominated by carbonates, it has only a slight evaporative character reflected by the low abundance of gypsum/anhydrite in the rocks and by the imbalance of the water with respect to these phases. The possible origins of the SO⁴ and its slightly higher content in Alhama can be explained in terms of the lithology of the aquifers and aquitards present in the groundwater flow, without the need to resort in all cases to water mixtures. Thus, it has traditionally been proposed that the origin of the sulphates is attributed solely to the Keuper facies, and this is possible since it is present under the Cretaceous, although between the thermal calcareous aquifer and the Keuper there are layers that are not very permeable (marls and Utrillas facies). It is perhaps easier to explain it by the influence of the Palaeogene formations with gypsum intercalations in the contact of the thermal aquifer, which has been explained in the section on Hydrochemical characteristic geology. This contact with the Palaeogene seems to involve more the Alhama rim flow than the Jaraba flow, which goes more through the centre and southwest of the Almazán Basin. This Palaeogene even contains chloride salts, which explains why the water from the deep wells of Serón de Nágima is salty water, for example. On the other hand, in the Hydrochemical characteristic aquitards (and perhaps also in the Cretaceous limestones) supply wells in the Almaluez area, a high natural fluoride content has been observed [50].

4.3.4. Origin of the Springs

As mentioned in the Introduction, the hydrogeological conceptual model of the Alhama–Jaraba thermal system was not yet clearly established. Initially it was thought that the main flow of thermal waters came from the south (Sierra de Solorio) and not from the north and northwest. To the south there is a high plateau with extensive outcrops of carbonate materials, so the recharge water would flow through the Upper Cretaceous calcareous aquifer, which lies below the low-permeability Palaeogene and Neogene materials of the Almazán Basin, which would serve as aquitard, and then rise rapidly to the Deza, Embid, Alhama, and Jaraba springs from great depth along the Cretaceous alignment, taking advantage of the vertical arrangement of the limestone layers [10]. Analyzing the results of the present study can be concluded:

- Recharge in the Sierra del Solorio is overwhelmingly from Jurassic rather than Cretaceous carbonate outcrops, which is where all the thermal and semi-thermal springs are located. More than 95% of the recharge area of the Solorio mountain is formed by outcrops of Jurassic carbonate materials, and the rest by carbonates of the Upper Cretaceous aquifer and which are on the border with the Palaeogene and Neogene Tertiary rocks of the Almazán Basin.
- 2. The Jurassic carbonate aquifer is conserved almost in a natural regime and its hydraulic balance has been established quite clearly in previous works [7,26], so there is no surplus water to justify the large thermal flows of Alhama, Jaraba, and the rest of the springs, which add up to some 1200 L/s.
- 3. Even assuming large errors in the calculation of the balance of the Solorio mountain from these earlier studies, it must be admitted that the water recharged mainly in the Jurassic should somehow be transferred to the Upper Cretaceous limestones above. But as seen above, the Jurassic does not exist beneath most of the hydrothermal aquifer (Figure 3) except for a narrow strip of 5 km north of the border of the Castellana Branch with the Palaeogene and Neogene Tertiary, disappearing from Jaraba onward. This aquifer is therefore quite far from the springs of Alhama, Embid, San Roquillo, and Deza, making such a transfer practically impossible. And even if it could be achieved in the aforementioned strip, it would first have to cross some 200 m of poorly permeable lithology separating the two groups (sands and marls from the supposed hydraulic connection between the two aquifers, which could be provided by hypothetical fault jumps, and/or to the flow mostly concentrated through these faults [6,8]. In Hernández Pacheco's work, great importance is given to the circulation

through faults as the origin of the springs, such as the Alhama fault(s), but in the simulations carried out specifically in this mathematical model, the faults do not justify large circulation flows.

- 4. It is simpler and more logical for the water to be recharged in the Cretaceous aquifer itself, especially in the Rituerto Basin, where it was not known until now where the recharged water went, nor had any hydraulic balance been established. And that it then circulated through the deep zone or hot spot on the border of the Aragonese branch with the Almazán Basin and emerged without changing aquifer. Note that the thermal and semi-thermal springs are all on the border with the Aragonese branch, not in the Castilian branch, which is the deep, hot zone.
- 5. If the flow was from the Sierra del Solorio toward Jaraba and Alhama, it would be logical that the flow would be concentrated at the lowest point (Alhama) and not in five springs that are 30–40 km apart. Furthermore, there is no hydraulic gradient that would justify the water reaching areas so far away from Deza or San Roquillo (elevations of approximately 900 m), as the underground discharges in the Sierra del Solorio are also located at around 900 m.
- 6. The higher temperatures of the Jaraba and Alhama springs are not justified, as the flow does not pass through the deeper areas of the aquifer. It would be the other way round, as for the flow to reach Deza and the rest of the springs, the flow lines would have to pass through deeper areas. The deep wells that reach the Cretaceous on the edge of the Castilian branch are not thermal water wells, unlike some located in the Aragonese branch.
- 7. Nor are the values of groundwater age obtained from tritium for Alhama/Jaraba justified because the flow distances from the centre of gravity of the Sierra del Solorio to these springs (about 25 km) are not so large as to result in ages above 60 years, as occurs in our model with flow lines of 70 km. Neither does it explain the order of the increasing age of Deza-San Roquillo-Embid-Alhama/Jaraba; it would have to be the opposite, as the length of the flow lines increases toward Deza. Furthermore, if the flow first passed through Jaraba and ended in Alhama [8], the age of the latter spring would be greater, and yet its age and evolution is totally parallel to that of Jaraba. To validate these results, contaminant particles were monitored using the flow model to obtain ages of the same order of magnitude as those obtained using the tritium data. In this way, the hydrochemical aspects acquire all their value when connected to the results of flow modelling.

On the other hand, during the Quaternary, fluvial processes would take on a greater role, with a greater interlocking of the drainage network, and the progressive but very intense capture of this part of the Almazán Basin (Duro Basin) by the Jalón river (Ebro Basin). This produces a decrease in the base level that will be associated with an increase in the topographic and hydraulic gradient towards the Jalón. The lowering of the regional water table and the underground capture of the residual endorheic areas (poljes) of the Rituerto would also occur. Indeed, as we have seen, the thermal calcareous Cretaceous aquifer hydraulically connects the Ebro and Duero basins, jumping their divide. These captures between rivers can be seen to be preceded in this area by underground captures in the same aquifer, since the water depth of the Ebro Basin is greater. They are much more underground and slow captures, where in the wide plains of the Duero surface runoff with drainage toward the Duero can coexist, with the underground runoff directed toward the Ebro. Thus, there are the natural transfers from adjacent basins of the Araviana (Duero)-Quiles (Ebro), from this same Araviana to the Aranda de Moncayo (Ebro) [50]. And, as we have seen here, also from Rituerto to Henar and Jalón, through the springs of Deza, San Roquillo, Embid, Alhama, and Jaraba.

4.3.5. The Alhama-Jaraba Thermal System in the Context of Thermal Karst Aquifers

Deep carbonated rock aquifers, most of which are to some degree karstified, are probably the most important thermal water resources outside volcanic areas. In Europe, many spas are associated with such aquifers, such as the Buda thermal water system in Budapest, Hungary [51,52], as well as others important ones in Germany [53,54], Switzerland [55], France [56], and many other regions of the world [57]. In turn, geothermal installations in deep karst aquifers offer promising possibilities for CO₂ sequestration. Groundwater circulation at different scales can be understood within a conceptual framework of hierarchical flow systems, consisting of local, intermediate and regional flow systems [58–60]. Thermal water resources in continental carbonate rock aquifers outside volcanic zones are related to deep regional flow systems, characterized by a hydraulic continuity of a geological formation [61–63]. Springs draining these systems are often located close to the regional base level [64,65]. This is exactly what happens in our thermal system of Alhama and Jaraba, where water flows through Cretaceous limestones toward karst springs located at the base level. Water circulation in thermal karst systems, such as ours, is usually driven by gravity, caused by topographic gradients between high areas of meteoric recharge and low discharge zones [66]. Temperature-induced density gradients may be additional driving forces acting simultaneously and facilitating the upward flow of warm water towards springs, which is characteristic of other karst systems [63,67].

Regarding the sources of recharge and heat, Ref. [63] highlights the predominantly meteoric origin of waters in hypogenic aquifer–karst systems, but also mentions that sometimes congenital and magmatic waters are involved. The meteoric origin in this system has been confirmed with environmental isotopes. And from the hydrochemical point of view, it is evolved water since its initial composition has changed due to physical-chemical processes along the direction of the flow. We have seen how the main focus of this evolution is centred on understanding the context of the development of the flow through the deep Cretaceous limestones according to the structure of the karst system, together with the flow regime and the boundary conditions in a hydraulic and geochemical sense.

In the discharge areas of this karst system, in addition to positive thermal anomalies, travertine deposits can be observed (Deza, San Roquillo, Jaraba springs, etc.). As has been said, in the area of the Deza springs, for example, cold, warm, and hot springs coexist within the Cretaceous aquifer that discharge together but come from different flow systems. The flow, chemical composition and temperature of hot springs in regional flow systems are more stable compared to cold springs in local flow systems.

Regarding the origin of karstification, in deep calcareous aquifers such as this one, groundwater is a geological agent and also the main driver of porosity creation in deep carbonate rock aquifers. These processes can be summarized under the term hypogenic speleogenesis [63,68]. Numerous hydrogeochemical reactions are involved in this process, such as mixing corrosion, retrograde solubility of calcite, dissolution due to geogenic acids from deep sources and other processes. It is possible that the presence of Paleogene sulphates near the Cretaceous aquifer favours contact karstification in this sense, as well as the mixing of cold and hot waters. But, regardless of whether these processes may be present to a greater or lesser extent in our case, the process that is surely of greatest relevance is that caused by paleokarstification, where the now deep Creataceous rocks were exposed to epigenetic karstification in previous geological periods in a geomorphological environment different from the present one, as explained above. This paleokarst contributes to the porosity of this aquifer, as occurs in other cases [69] and is often reactivated by modern karstification [70].

5. Conclusions

Thermal aquifers, due to their often deep and confined location, could be considered naturally well-protected, renewable, and almost infinite resources [57]. This is the case of the Alhama–Jaraba aquifer, which has been protected and confined by the poorly permeable Palaeogene and Neogene Tertiary rocks. However, contamination of the spas that supply thermal and mineral water could occur because there are areas in the area where these springs are fed at risk of nitrate contamination, for example, given the extent of pig farming. The design of thermal spring protection zones using traditional analytical

methods for determining isochrons is insufficient in many cases, given the complexity of these aquifer systems and their deep flow. It is necessary to address this issue using other novel methodological techniques such as those applied here, which include, among others: In reference to the conceptual model: the detailed geometrization of the aquifers, and verification of the continuity and hydraulic connection between aquifers through stratigraphic and geological structural analysis with the application of the technique of bounded plans in layers and faults, and not only with geophysics. The application of paleogeography to understand the origin of porosity due to karstification and justify its widespread distribution and at all depths in the thermal aquifer. The location of recharge zones within the thermal aquifer with unknown hydraulic balances, in instances when it was not known where the water went, and which have been essential to take into account to correctly quantify natural recharge.

Ultimately, it is believed that this case of study is a good example of the functioning of a low-temperature thermal system in a natural regime associated with a calcareous aquifer that occupies the divide of two neighbouring basins allowing subway hydraulic communication between them, and which can be explained thanks to the water flow of the springs located in the basin at the lower altitude. The temperature of the waters is explained by the normal geothermal gradient due to the depths of up to 4500 m reached by the flows in the aquifer. These flows discharge progressively and partially through semi-thermal springs located on one of the edges of the aquifer at progressively lower altitudes (Deza, San Roquillo, Embid), where the temperature and age of the water also progressively increase. Finally, most of the flow follows a south-easterly direction, where the basement of the Almazán Basin and the "synclinorium" that structures this aquifer end. Here, the flow is discharged into the most distant springs of Alhama and Jaraba, some 70 km from the common recharge zone. These are the springs with the highest flow, the highest temperature, and the oldest water—probably more than 60 years.

These applied methods can be extrapolated to other similar cases in order to learn in a preliminary way the origin and hydrogeological functioning of thermal aquifers, which are exploited very little or not at all. This will serve to identify the recharge area and to propose early sustainable management of water resource conservation, such as the appropriate design of zones for the protection of singular thermal springs.

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