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Integrating current and historical water chemistry data with long-term piezometric records to develop a regional-scale conceptual flow model: Las Salinas spring, Medina del Campo, Spain

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ABSTRACT

Study region: Old Las Salinas spring in Medina del Campo, Duero river basin, central Spain.
Study focus: Medina del Campo groundwater body (MCGWB) is a multilayer semiconfined aquifer subject to intensive pumping since the 1970's, where the current existence of spas where there used to be traditional baths could confirm the existence of deep groundwater flow paths. The old spring of Las Salinas (OSLS) is a saline anomaly in an aquifer with predominance of $CaCO_3H$ waters whose occurrence has not yet been formally explained. Long-term geological, geophysical, hydrogeological and hydrochemical records were integrated and complemented with field work to clarify its existence.
New hydrological insights for the region: Outcomes led to the conclusion that the hydrochemistry of the Olmedo and Palacio de las Salinas salt baths is associated with the existence of a major threshold in the impervious basement of the aquifer, which intercepted deep regional groundwater flow and caused upwelling to the surface under unperturbed conditions. These results allow for the development of a conceptual flow model at the regional scale that explains the changes in natural water chemistry that have been identified in recent decades.

1. Introduction

Saline springs are common in geological environments where rocks contribute soluble salts to groundwater. However, they are

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especially infrequent in non-saline geological environments such as the one presented in this paper. In these cases, saline groundwater is an exception, rather than the norm, and is sometimes attributed to long flowpaths and residence times. The hydrogeological literature classifies groundwater by its origin and contact time with the aquifer into different types: congenital waters, trapped at the time of sediment formation; fossil waters, trapped under ground for thousands of years; migrated waters, i.e., congenital waters that are displaced and accumulate in other materials where they can suffer a greater or lesser mixture with other waters; and mineral waters, with a varied chemical composition, characterized by the presence of solutes in notable or large concentrations that normal vadose waters do not have (Custodio and Llamas, 1983, 1033).

The work carried out in the framework of the European project NAIAD (2021) on the Medina del Campo groundwater body (MCGWB hereon), have led us to an interesting aspect: the proximity of two spas (separated by a distance of scarcely 25 km), both of sodium chloride waters (Armijo et al., 2018), in a region of predominantly, though not exclusively, calcium bicarbonate waters. While previous references refer to a horst and graven basement (TRAGSATEC, 1996; JCL, 2002) the available geological data was too limited to explain the effect of this arrangement on groundwater flow paths. Our observations have focused on the morphology of the river channels in the Medina-Olmedo axis (Fig. 1b), which seemed to be directly related to tectonic activity (IGME, 1998).

The original spring of Las Salinas (OSLS hereon), has been studied and documented since the 17th century. It was declared a mineral-medicinal water spring in 1892 (Ministerio de Fomento, 1892; Ministerio de la Gobernación, 1893; El Castellano, 1893 with more recent references in Castells and Ballespí, 1913; GOEBAME, 1927; SIEMCALSA, 2007). Its waters were described then as cold sodium-chloride iodine-brominated. The Olmedo spa was inaugurated much more recently, in 2005, and its waters present a thermal sodium chloride declaration (BOCYL, 2006). Therefore, both spas present in common the hydrochemical facies. Differences in thermal classification are however striking. In addition, the waters of the original Las Salinas spring are extremely saline, brine-type waters, similar to sea water.

Although previous works refer to a hypothetical threshold of the basement to explain the upwelling of OSLS (Baeza Rodríguez-Caro et al., 2001; Corral Lledó et al., 2010), the literature does not explain the reasons for these high salinity content, nor does it relate the occurrences of both spas. The aim of this research is to construct a comprehensive and rational conceptual model to explain the occurrence of saline waters in both springs.

The analysis of the factors that could be involved in the genesis of the upwelling of the OSLS led us to four areas of work with their specific objectives: (1) Lithological: exploring the presence of geological materials that could provide salts to the groundwaters; (2) geophysical: define the structure of the basement in the area; (3) hydrogeological: characterize the hydrodynamic conditions of the groundwater flow with particular emphasis on hydraulic transfers governed by vertical flows; and (4) characterize the hydrochemical conditions of groundwater. It was not an easy task, since the MCGWB was a little-known area of the territory, having been integrated in the central sector of the so-called Los Arenales aquifer (Fig. 1a), whose eastern sector has been densely studied in the previous literature as focus of recent and successful artificial recharge operations (current Los Arenales GWB) (Fig. 1c).

A common feature to detrital aquifers in large sedimentary basins is that the structure of the basement typically presents structural discontinuities. Structural factors play an important role in rock-water interaction, and give rise to complex flow patterns between the fractures of the basement and the sedimentary materials. These geological contexts typically give rise to geothermal processes, in which the mobilization of warmer fluids controls the dissolution of mineral species into groundwater (Webster and Nordstrom, 2003). The Duero sedimentary basin, central Spain, is not exempt from these. Giménez-Forcada et al. (2017) and Giménez and Smedley (2014) reported the existence of metalloids associated with inflows of oxidizing alkaline groundwaters near the Duero basin boundaries. This was attributed to the existence of major faults in the basement.

The Cenozoic sedimentary area of the Duero and Tagus rivers is associated with the Spanish Central System. Both basins present similar characteristics in the materials and structure of their aquifers, formed by permeable materials wrapped in a less permeable matrix. They differ in their dimensions, given that the Tagus basin is longer and deeper than the Duero basin. Investigations to characterize the groundwater flow geochemistry of the Tagus basin show the existence of saline waters in specific sectors where there are no lithological sources of salt (López Vera and Gómez Artola, 1984) as El Pradillo-I and Tres Cantos. The chloride concentration in these analyses (extracted from samples taken between 3000 and 3600 m deep), ranges between 117,000 and 123,000 mg / l.

The integration of these results has allowed us to establish a hypothetical conceptual flow model that explains the saline anomaly of the OSLS and the Olmedo thermal borehole (OTB in advance). Both spas owe their origin to a rise of the Paleozoic basement in the Medina-Olmedo area, where the southernmost fault is located. Geophysical work carried out in the field (electromagnetic soundings and vertical electrical soundings), together with the compilation, processing and analysis of previous geophysical data (gravimetry), have allowed us to define and locate the structural discontinuity. However, it will be necessary to use tools / methods of greater penetration to characterize the geometry of deep formations (such as the basal marine Cretaceous in the eastern half of the GWB), as well as to map the northern fault. The implications of the knowledge of the deep aquifer of the MCGWB are of interest in the fields of geothermal energy, health-associated tourism (spas), and groundwater management.

The MCGWB is a multilayer semiconfined detrital aquifer (IGME, 1982a,b, 1983; and) whose hydrogeological knowledge is still limited. It is known to exceed 2500 m in depth, and to be constituted by a superposition of subaquifers whose hydraulic heads vary with depth. Intensive exploitation of groundwater in this region since the 1970s has caused a progressive decrease in piezometric levels (Fig. 1e). This trend is especially evident in the deep boreholes (>200 m), which have traditionally been more exploited due to the greater piezometric head in the deeper parts of the aquifer (Giménez-Forcada et al., 2017, 214). Groundwater flow patterns have been altered as a result, which has had impacts both on the local and regional scales. This impact has affected the integrity of the groundwater resource, both in terms of quantity (extracting groundwater from a confined or semiconfined aquifer reduces hydrostatic pressure and induces a change in vertical gradients) (Gejl et al., 2019), and quality, showing clear symptoms of water insecurity. As shown in the following pages, this could lead to sustainability issues in the future.

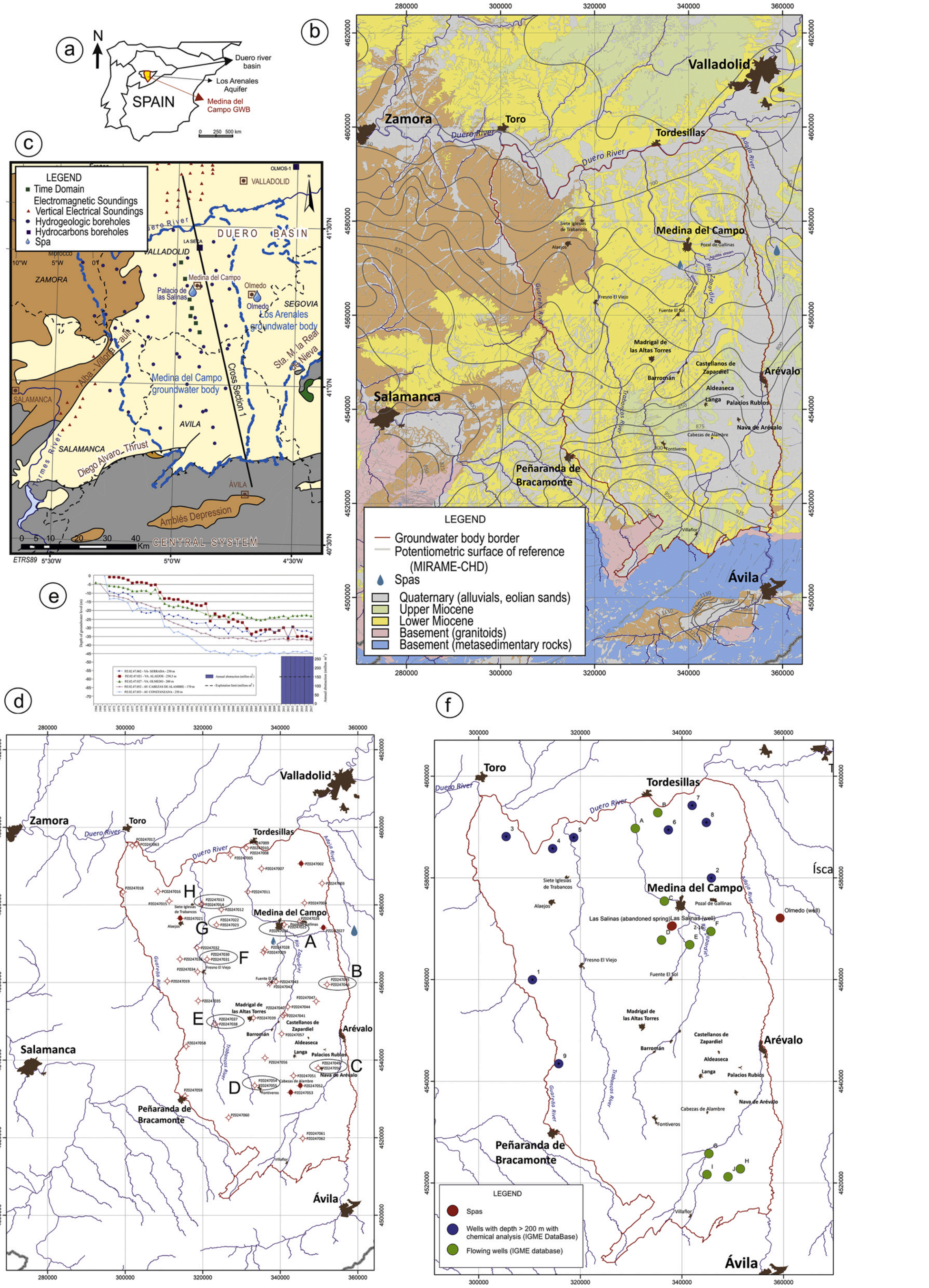

Fig. 1. (a) Geographical setting of the Medina del Campo groundwater body in the Duero Basin and in Los Arenales aquifer. (b) Simplified geological map of the Medina del Campo GWB and reference isopotentiometric surface (MIRAME-CHD) under perturbed conditions (1995). (c) Major tectonic structures in the study area and main data used for the geophysical study developed in section 4.2: Hydrogeological (blue dots),

hydrocarbons boreholes (green squares) and electromagnetic soundings (red squares) and Vertical electrical soundings (red triangles). (d) Location of the CHD piezometric network with indication of the nests used in this study (TS3); red dots are the representative piezometers of Fig. 1e. (e) Piezometric evolution of the five representative piezometers with the longest record in the MCGWB (data from MIRAME-CHD); (f) flowing wells (green dots) (TS1) (ii) Location of the IGME database (INFOIGME, 2021) (i) wells (depth > 200 m) with chemical analysis of groundwater (blue dots) (TS6); (Author's own).

2. Study region

The study area is located in the southern half of the Duero basin, central Spain (Fig. 1). The northern half of the study area corresponds to the south of the province of Valladolid and the southern half, to the north of the province of Ávila (La Moraña region).

Several tributaries to river Duero traverse the MCGWB from south to north. These are, from east to west, the Adaja (163 km long), the Zapardiel (93 km), the Trabancos (88 km) and the Guareña streams (61 km).

The area presents a cold steppe arid climate, classified as Bsk based on the Köppen-Geiger system. This is characterized by warm and dry summers and cold winters. Rainfall takes place mostly in autumn and early winter, as well as during the spring. Mean annual rainfall between 1981 and 2010 was 351 mm. The mean annual temperature was 12.9 °C, while potential evapotranspiration amounted to 730 mm (Nafría García et al., 2013).

The Medina del Campo weather station presents continuous rainfall records for the 1932–2000 period. An acceptable correlation exists between these and those of the Valladolid weather station, which presents the longest rainfall series in the vicinity of the study region (1851–2019) (Fig. 2).

2.1. Geology

The Duero catchment is an intraplate basin, generated during the Alpine orogeny as a result of the convergence of the Eurasian, Iberian and African plates, filled by Cenozoic sediments that exceed 2500 m in thickness towards the east and which wedge into the west and south of the basin (Casas-Sainz and de Vicente, 2009; Santisteban et al., 1996; Gómez-Ortiz et al., 2005). The western border of the Duero basin is tectonically characterized by highs and depressions in favor of NE-SW late-hercinic faults that were reactivated during the Paleogene and Miocene (De Vicente et al., 2007). In the southern basin border, Alpine compression caused the E–W thrusting of the Central System over the basin (Fig. 1b).

Its substratum is composed by Palaeozoic metamorphic and igneous rocks (outcropping at the western and southern border areas) and Mesozoic sedimentary rocks related with the rifting Alpine cycles (Sánchez-Moya and Sopeña, 2004). Triassic, Jurasic and Cretaceous-Paleocene rocks outcrop towards the eastern border, whereas only outcrops of the latter are found towards the western border.

In the area of interest (Fig. 3), outcropping Cenozoic sediments are composed by alternating cycles of gravels, sands and muds of arkosic, greywackic or sublithic composition derived from the igneous and metamorphic rocks of the Central System (Pineda et al.,

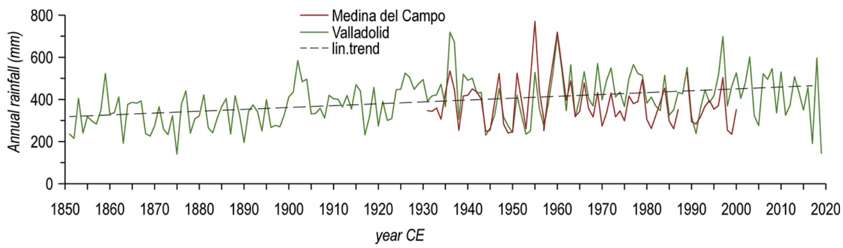

Fig. 2. Annual rainfall for the AEMET weather stations of Valladolid and Medina del Campo (source of data: Spanish Meteorological Agency – AEMET) (Author's own).

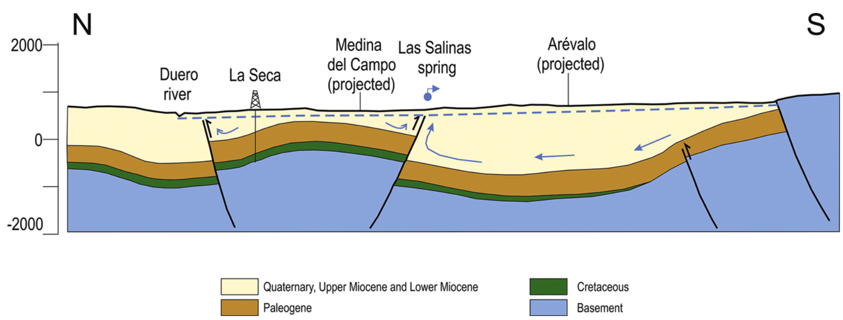

Fig. 3. Cross-section of MCGWB indicated in Fig.1c, and scheme of hydrogeological hypothesis for OSLS occurrence (Author's own).

2007). The gravel fraction is composed mainly of quartz and quartzite clasts, while sand and mud fractions are dominated by quartz, potassic feldspar and lithic fragments of igneous and metamorphic origin accompanied by clays (smectite, illite). Carbonate minerals (calcite and/or dolomite) can be present as cement or forming crusts. These sediments were deposited during Cenozoic in low sinuosity alluvial fan systems.

La Seca borehole (Fig. 1c), drilled in the northern part of the study area (Martínez Abad and Querol Muller, 1990) provides information about the stratigraphic series. From bottom to top, the borehole reached Paleozoic metamorphic rocks at a depth of 1188 m (Fig. 3). There is no record of Triassic or Jurassic rocks, whose nearest evidences are located 100 km eastwards and northwards and which are composed by a thin Triassic siliciclastic series (Muñoz et al., 1995). The Paleozoic metamorphic substratum is covered by 35 m of Upper Cretaceous white-yellowish arkosic sands, sometimes cemented by silica, and kaolinite or iron-rich levels. These sediments are overlain by 120 m of limestones and dolostones of Upper Cretaceous age and some marls at the bottom of the series. Equivalent rocks crop out around 50 km south-eastwards, in the vicinity of Santa María la Real de Nieva, where the lower part of this series is richer in gravel and the carbonated part is richer in dolostones and show frequent siliciclastic units (Martínez-Salanova et al., 1991).

The uppermost 1033 m of the La Seca borehole include siliciclastic Cenozoic sediments increasing in sandy beds to the top. The base is composed of Upper Cretaceous to Paleocene iron-rich and kaolinite-rich siliciclastics (gravels, sands and muds) characterized by the presence of silica cements and iron crusts (Blanco et al., 1982; Santisteban et al., 1996; Alonso Gavilán et al., 2004) and are overlaid by matrix-rich arkosic gravels and sands attributed to the Paleogene-Neogene. These rocks crop out along the southern border of the basin (Martínez-Salanova et al., 1991; Santisteban et al., 1991, 1996; Martín-Serrano et al., 1996; Alonso Gavilán et al., 2004). Muddy beds are thicker and more frequent in La Seca borehole than in the outcrops and that can be related to the more distal position of the borehole in relation to the southern border of the basin. In any case, there are no evaporite layers, as those typical of the basin centre, interbedded neither in the surface nor subsurface sediments.

2.2. Hydrogeology

From a hydrogeological standpoint, the region has been described by IGME (1970); PIAS (1977); IGME, 1980, 1982a,b, 1983, 1991, 2008, and further characterized more recently by IGME-DGA (2010a, b). The study area corresponds to the contact of MCGWB with Los Arenales groundwater body. Both are essentially the same aquifer, although some differences are observed: Los Arenales is formed by : (1) an upper unconfined aquifer (<130 m, including the first few tens of meters, corresponding to the Quaternary), (2) an intermediate and discontinuous silt-clay level (around 130–200 m) and (3) a deep semi-confined aquifer closely linked to the basement (which is affected by local and regional faults and by a weathering layer in the upper zones where comes in contact with Tertiary sediments) (>200 m). Meanwhile the Medina del Campo aquifer presents a wedging of the intermediate facies to the west that disappear in the half east of the MCGWB in such a way that the upper unconfined aquifer rest directly on the deep semi-confined aquifer (De la Hera-Portillo et al., 2020a).

The multilayer detrital aquifer behaves as a three-dimensional semiconfined system (IGME-DGA, 2010a, b), and is made up of permeable lenses of conglomerates and sands embedded in a semi-permeable sandy silt matrix (IGME, 2008). Permeable materials present limited spatial continuity and are randomly distributed in the vertical dimension showing a high anisotropy. The impervious basement is made up of the same igneous and metamorphic materials that conform the Gredos range.

The principal recharge to the aquifer is by meteoric infiltration, while additional inflow is received across surface and subsurface runoff. Under natural conditions, the main discharge is the river Duero, situated towards the north of the study zone, and this explains why the main direction of flow is from south to north. This general scheme is affected by the basement morphology, which is compartmentalized into horst and grabens and by significant abstractions of water. In this area the bicarbonate ion predominates, although sulphated and even chlorinated facies occur. Among the cations, calcium is usually dominant, although in some central and even northern areas, relevant concentrations of alkalines appear (CHD, 2015, 81). This has been recently justified by Giménez-Forcada et al., 2017 as the effect of cold-hydrothermal inflows associated with the water-rock interactions in the fissured aquifer media (igneous and metasedimentary bedrock) and in the sedimentary environment of the Duero basin.

Groundwater flows from the main recharge areas, located towards the south, to the areas in an around the Duero river (Fig. 1b), which behaves as the main discharge axis throughout the entire basin (López Geta and Ramírez-Ortega, 2015). Surface water courses act as outflow mechanisms for sub-superficial groundwater, as well as for surface runoff (Murillo, 2013). The majority of them have been mostly inactive for years, with the exception of the Arevalillo and Adaja streams. The latter is regulated by the Cogotas reservoir.

Previous works establish a difference between deep groundwater flow (beneath a depth of 130 m) and intermediate flow (above 200 m) (Tragsatec, 1996; JCL, 2002; Giménez Forcada et al., 2017). To avoid confusion, we will refer to deep groundwater flow as the flow travelling by the bottom of the aquifer. Isotopic dating in Los Arenales aquifer reveals that the age of deep groundwater is of more than 1000 years (Plata Bedmar et al., 1996).

From the late 1960s this area experienced a considerable growth of groundwater based agriculture and most groundwater extractions took place in the La Moraña area IGME, 1991; JCL, 2002. Groundwater extraction for the 2011–2018 period was estimated at 272 Mm^3/yr (CHD, 2017, 2018, 2019, 2020). In contrast, the aquifer's natural replenishment rate has been quantified at 149 Mm^3/yr (IGME-DGA, 2010a). However, current and historical extraction records are generally poor. This is a key aspect to plan groundwater exploitation in the short, middle and long term.

Six decades of groundwater pumping caused the water table to drop by an average of 28 m between 1972 and 2020 (Mayor et al., 2020) (Fig. 1d,e). The entire groundwater body is affected by overexploitation, except for a narrow band of municipalities located towards the border. The greater decreases are observed between the years 1970 and 2000. Since 2001, a change in the slope has been observed in the deepening of the levels, without ceasing to descend in a generic way throughout the groundwater body, but entering a

Table 1
Approximate water balance for the Medina del Campo groundwater body under natural and perturbed conditions (modified from De la Hera-Portillo et al., 2020b). Not all components are evaluated as the borders of the aquifer have been modified over time. Estimations are just available from the recognition of Medina del Campo as groundwater body (2000).

Inflow/Outflow	Component	Perturbed conditions Million m^3 (MIRAME-Duero)
Inflow	Precipitation	67
	Groundwater transfer from other GWBs	2
	Recharge from rivers, lakes and reservoirs	45
	Return from irrigation	38
Outflow	Groundwater transfer to other GWBs	−0
	Groundwater pumpings	273[1]
	Groundwater discharge to Duero river	?
	Discharges through springs and wetlands	
	Evapotranspiration from the water table	

[1] CHD (2015).

stabilization phase (MIRAME-CHD, 2020). The available groundwater resources is 149 million m^3/year (MIRAME-CHD, 2020). There is not available aquifer budget to contrast and compare the functioning of the system before and after intensive exploitation. An approach is provided in Table 1 for the current state.

2.3. Spas

The existence of two spas points to the presence of saline anomalies in the study area. Geological data suggests that there could be a basement threshold that causes deep upwelling. This is consistent with the morphology of certain surface streams. These are typically straight, except that there is a marked change of direction towards Medina del Campo (Simplón and Aguililla streams), which could be associated with the tectonic structure of the basement (PIAS, 1977). Evidence of old salt production facilities in the area, more specifically where Las Salinas spa currently is, reinforces the hypothesis of deep groundwater discharge in the area.

Historical data of the OSLS, collected before the inauguration of the spa, reveals that waters were extremely saline (>1 g/l). Data from 1892 points at a salinity in excess of 72 g/l (Ministerio de Fomento, 1892). This is probably attributable to a combination of factors. Take for instance hydrodynamic conditions (long flow paths and residence times), which cause groundwater to become saturated first in HCO_3^-, then in $SO_4^=$ and finally in Cl^-. Furthermore, evaporation can increase saline concentration substantially as spring waters reach the ground (Smedley and Kinniburgh, 2002). Las Salinas spa was inaugurated in 1891 (Bobo-Díez, 1912; IGME, 1913, 1947; Sánchez Ferre, 1992). Its name stems from the presence of saline deposits in ephemeral wetlands. The spa originally had four wells within a radius of 150 m, as well as 53 ponds for the elaboration of saline waters (Ministerio de Fomento, 1892; Ministerio de la Gobernación, 1893, 341). This process consisted in increasing the concentration of NaCl by exposing the water to evaporation.

The main well was located 45 m away from the spa (IGME, 2010). The well's original flow rate was 6000 L/h, and it yielded sulphurous sodium chlorinated water (I-Br variety) with an average temperature of 13 °C. Its waters were declared mineral-medicinal and of public utility in 1893 (El Castellano, 1893; IGME, 2001, 2010). Since then, the spa has operated intermittently due to different events (various ownership changes, Spanish Civil War). The other wells rendered 500–800 L/h of Na-Ca-Cl water of intermediate mineralization (dry residual: 1.164 mg/l), with an alkaline pH (8.51), high hardness (40.1 °F) and cold temperature (13.9 °C). Mineral indices indicate saturation in dolomite and goethite; stability in quartz, albite, calcite, aragonite and siderite; and undersaturation in gypsum, halite and fluorite (IGME, 2010, 139). Analyses dating back more than one century point to the upwelling of cold Cl-SO_4-Na water with presence of Br and Mg (Ministerio de Fomento, 1892). Some authors have identified cold-hydrothermal $NaHCO_3$ waters linked to the deep confined aquifer in the south part of the Duero Basin (Giménez-Forcada and Smedley, 2014; Giménez-Forcada et al., 2017). Nevertheless our hypothesis is that in Las Salinas location, there were cold-hydrothermal NaCl waters (at the priminegio spring), and currently they have been replacement to $NaHCO_3$ surface waters as consequence of the intensive exploitation.

The Olmedo spa is more recent. It was built in 2005 on the ruins of a 12th Century monastery. Its waters were declared mineral-medicinal in 2006 (BOE, 2006). Their composition is Cl-Na-F, with strong mineralization (dry residual: 5.898 mg/l), with an alkaline pH (7.98), moderate hardness (10.5 °F) and a temperature of 21.5 °C. Mineral indices show stability in regard to quartz, albite and fluorite, and undersaturation in calcite, aragonite, dolomite, gypsum, goethite and siderite (IGME, 2010, 141–142). The Olmedo spa captures groundwater by means of a 234 m borehole (Table 2). There is no surface evidence of upwelling in or immediately near the premises. The absence of saline lithology in the superficial part of the sedimentary log suggests that water salinity is associated with deep groundwater flow and long residence times.

3. Materials and methods

3.1. Time frame

The ensuing analyses focuses on three historical benchmarks: (1) before intensive aquifer use begun (early 1970s); (2) the moment of maximum perturbation due to overdraft (2001); and (3) the current situation (2019/20). Note that the choice of benchmark number (2) is debatable, as the highest yearly pumping on record is 2005 (CHD, personal communication). The year 2001 was picked instead

Table 2
Constructive characteristics and hydraulic parameters of the Olmedo Spa survey (data from López-Geta and Ramírez-Ortega, 2015). (1) Borehole depth in meters; (2) Description of the lithological column; (3) Tubing diameter in mm and material; (4) Tube thickness in mm; (5) Location filters; (6) Material located between pipeline and geological formation; (7) Piezometric level (13-10-2003); (8) Specific flow (L / s / m); (9) Transmissivity (m^2 / day); (10) Flow with which it was declared mineral-medicinal (l / s).

Unit	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
	0–11	Ocher slime								
	11–14	Ocher siliceous sand								
	27–30	Green clay siliceous sand								
Unit Pedraja de Portillo (Lower Middle Miocene)	30–71	Ocher silt with some sandy layer								
	71–81	Ocher silty-sandy clay								
	81–89	Gravel and siliceous sand								
	89–99	Ocher slime								
	99–104	Siliceous sand and ocher gravel								
	104–110	Clay and ocher silt								
	110–112	Ocher loamy sand and gravel				Cementation and bentonite				
	112–118	Ocher slime								
	118–132	Siliceous sand and gravel								
	132–136	Ocher clay	219 mm				59,77	0,65	40	15
	136–141	Sandy-clay gravel		4 mm						
Upper Toro Formation (Lower Miocene)	141–144	Ocher clay								
	144–148	Ocher Siliceous Gravel								
	148–163	Ocher clay								
	163–165	Ocher clay			155–160					
	165–169	Ocher clay								
	169–173	Ocher Siliceous Gravel				Siliceous gravel 3–5 mm				
	173–175	Clay and ocher silt								
	175–190	Siliceous gravel and blocks and ocher clay			183–189					
	190–201	Clayey gravel and ocher clay			192–201					
Lower Toro Formation (Paleogene)	201–234	Ocher clay			213–216					

because this is the year with the largest number hydrochemical analyses in the database of the Geological Survey of Spain.

Piezometric data stems from two major sources, namely, the Geological Survey of Spain (1970–2001), with 954 wells; and the Duero Basin Authority (2006–2018) with 58 boreholes. Water quality analyses were obtained from the database of the Geological Survey of Spain for the 1970–2001 period. Updated data for spa samples were collected during field campaigns in 2019 and 2020.

3.2. Lithological study

The lithological study consisted of the analysis of borehole logs of groundwater wells and oil boreholes, as well as geological maps (MAGNA, GEODE). This information was integrated into a GIS database with ArcGIS v10.6.1.

3.3. Geophysical study

A 3D model was built with Geomodeller software in order to establish the subsurface basin geometry of the basin (Lajaunie et al., 1997; Calgano et al., 2008; Guillen et al., 2008). The 3D model is built from geological and geophysical datasets obtained from previous databases (INFOIGME) and new geophysical surveys carried out for this study. The geological and geophysical data used were: geological maps from digital continuous geological map GEODE (INFOIGME); 51 hydrogeological and 2 hydrocarbons survey boreholes (Fig. 1c); 7 Time Domain Electromagnetic Soundings, carried out for this study, with 200–500 m loop-side lengths; vertical electrical soundings around de Alba-Villoria Fault (Díez-Balda et al., 1982). The preliminary 3D geological model was latterly improved (in geometry and density values) through the 3D inversion of the gravimetric anomaly obtained from gravimetric data of the National Geographical Institute database GRAVIMET (Mezcua et al., 1996; Ayala et al., 2016).

3.4. Vertical groundwater gradient

Piezometric data includes 81 long-term piezometric records (1971–2001) and 58 piezometric records from the 2006–2018 period.

The older piezometric records served the purpose of (a) identifying former flowing wells and when these stopped being so; and (b) analyzing pairs of wells with different depths located to less than 5 km in order to make an estimation of the variation of the vertical hydraulic gradient and its evolution over time. The same was applied to eight piezometric nests (16 piezometers) of the newer group. The others were discarded due to the well screens being located at different depths.

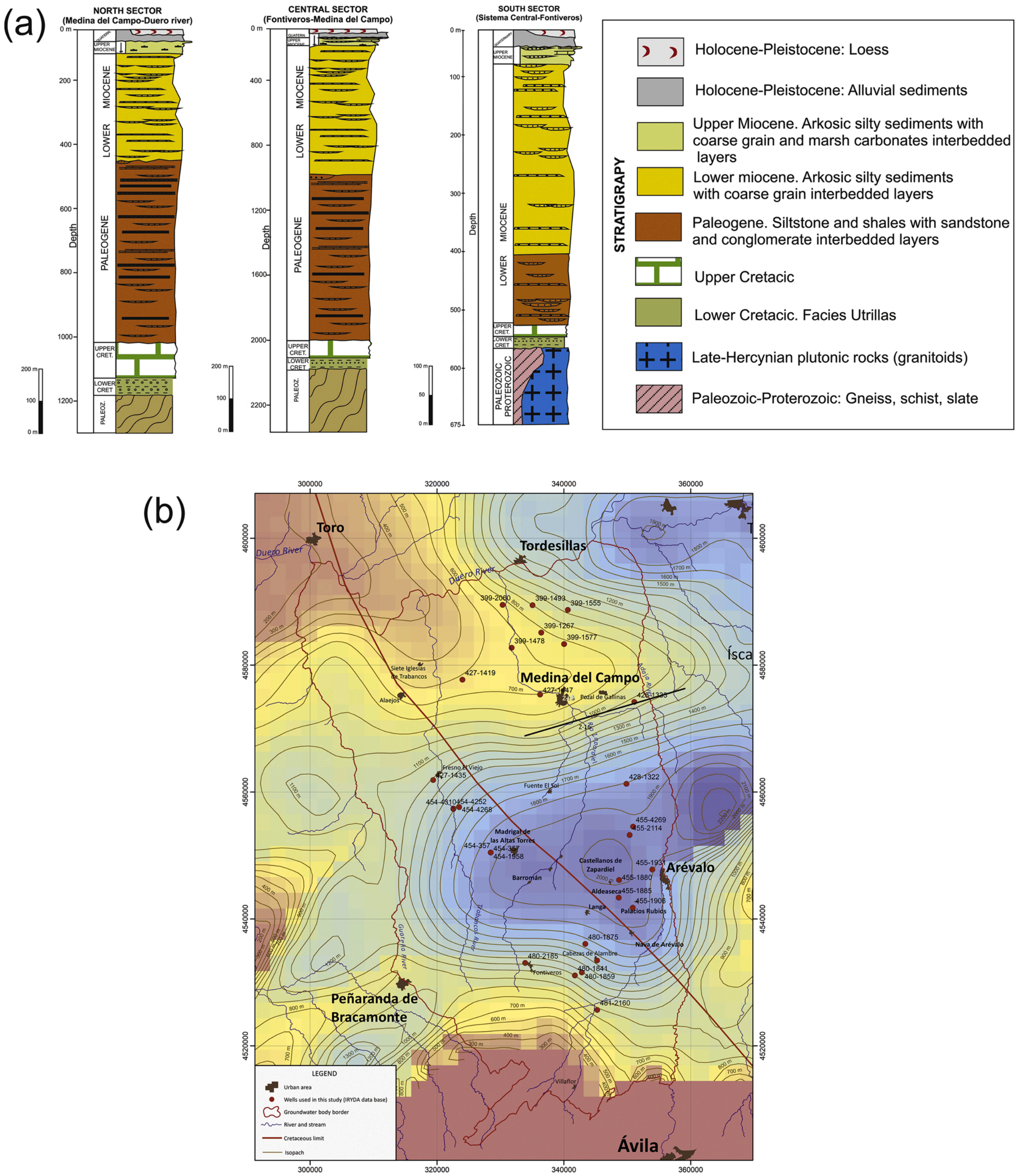

Fig. 4. (a) Isodepth map (from the topographic surface) of the Paleogene wall. The red dots are the soundings from the IGME IRYDA database with information from lithological columns from soundings carried out in the 60-70 years. (b) Typical columns for the three different sectors within the MCGWB. For its construction, the reports of the piezometers that make up the piezometry and quality control networks of the CHD have also been taken into account. The supposed fault that define the south discontinuity of the Palaeozoic threshold between Medina-Olmedo has been represented (Author's own).

3.5. Water quality data

Hydrochemical data includes analyses carried out for 115 wells between 1970 and 2001 obtained from the IGME database. These were all collected and analyzed by the Geological Survey of Spain, and present an ionic balance discrepancy of less than 5%. A further analyses for the wells use currently for the Palacio de las Salinas and Olmedo spas was carried out between 2019 and 2020. Water samples were collected in one liter bottles and analyzed in the Geological Survey of Spain's labs in Tres Cantos. Sixteen determinations were obtained (Cl, SO_4, HCO_3, CO_3, NO_3, Na, Mg, Ca, K, pH, CE, NO_2, NH_4, PO_4, SiO_2 and Mn oxidability). Graphical representation of the results was carried out by means of the INAQUAS software (Moreno and De la Losa, 2008).

This information is coupled with analyses compiled from various sources for the Las Salinas spa waters (years 1893, 1989, 1997 and 2005) and for the Olmedo spa waters (2007−2009, 2016–2019).

Three additional minero-medicinal springs existed in the study area, aside from the Palacio de las Salinas and Olmedo springs. Chucho 1 and Chucho 2 were both located approximately 3 km to the SW of the Las Salinas springs, and presented Ca-HCO_3 waters. In turn, Chucho 3 presented NaCl facies (IGME, 2001, 233). All three of them were located in the El Campillo municipality, and are poorly documented.

4. Results and discussion

4.1. Lithological records

Three sectors have been differentiated (Fig. 4a): The southern sector is characterized by the outcrop of the Paleozoic basement. It constitutes the contact zone of the Central System with the Cenozoic basin of the Duero. If present, Cretaceous materials underlying the Paleogene must be of reduced thickness. Paleogene materials present a lower thickness than Miocene materials, unlike in the central sector where the latter are the dominant formation. The basal Cretaceous it likely to exceed these in thickness, but data is insufficient to determine its depth. In the future, it will be necessary to address the characterization of this basal Cretaceous aquifer. The sedimentary fill reaches powers greater than 2100 m (not including the Cretaceous), consisting mainly of Miocene and Paleogene formations. The northern sector is characterized by a larger basal Cretaceous than in the previous sectors. The thickness of the Paleogene and Miocene formations averages 1000 m.

4.2. 3D geological model

The depth contour map of the Paleozoic basement (Fig. 4b) shows a structured basin with highs and depressions trending E-W to EN E-WSW. The maximum depths of the basement are located SE of Medina del Campo and south of Valladolid cities, where they reach to a depth of more than 2000 m. Near the Medina del Campo area, there is an E-W basement high distribution at about 1000 m depth. In the SW sector, the Miocene and Paleogene sediments located between the Alba-Villoria fault and the Diego Álvaro thrust reach a thickness of about 1000 m. East of Zamora, in the NW sector of the study area, the basement top is shallower, with only 200 m depth.

The 3D geological model exhibits differences in thickness of the Paleogene sediments and particularly in the Miocene ones (Fig. 5). While the thickness of Paleogene in the basin is relatively constant at 500 m, the thickness of Miocene is highly variable, reaching 1500 m. These variations are interpreted as a consequence of pop-up and pop-down tectonic structures associated to E-W to EN E-WSW reverse faults. On the other hand, the NE-SW faults, such as the Alba - Villoria Fault, must play an important role in the development of the basin, with important vertical displacement.

4.3. Piezometric logs

4.3.1. Flowing wells

Only 10 out of the 81 points of the older set were originally flowing wells (Fig. 1f, TS1). Most ceased to flow in between the 1970s and the early 1980s. The only exception is well 1516-2-0001, which lasted until 1992. This is the only one well in the set with a hydrochemical analysis for year 2001 (TS5), which resulted in Cl-Na waters.

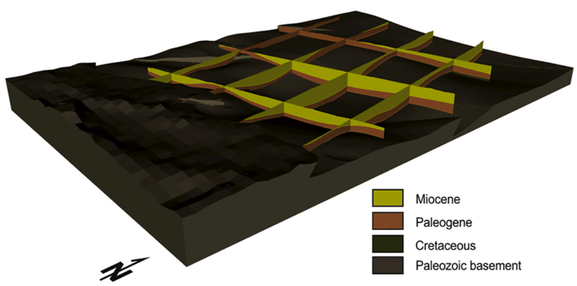

Fig. 5. (a) 3D Geological model of the Medina del Campo GWB created with the field and data bases integration of analysed results (Author's own).

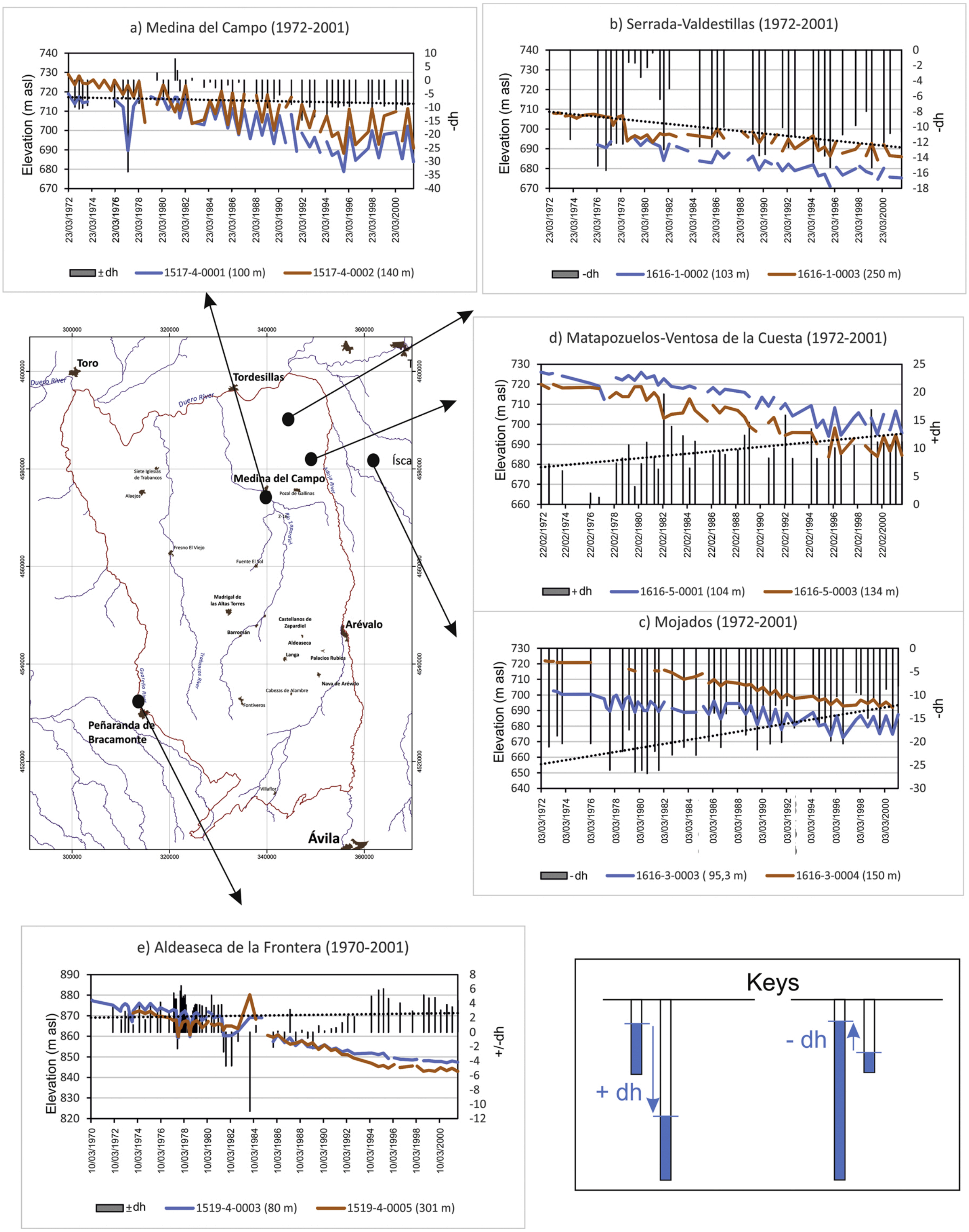

Fig. 6. Piezometric records of the 1970-2001 well pairs (TS2) (data from the Geological Survey of Spain database). The specific behavior of each area is expressed through the sign of dh in each legend. It is important to note that there is no information on the screens location in these wells. Therefore, the hydraulic potential of each well is the average of the subaquifers crossed (Author's own).

4.3.2. Long-term piezometric records

As explained earlier, the purpose of this analysis is to evaluate the evolution of the vertical groundwater gradient over time. This is done by comparing the long-term record of shallow wells with nearby deeper ones. In the case of the 1972–2001 period, five suitable well pairs were identified (Fig. 6), whereas a further eight piezometric nests (Fig. 1d) were used for the 2006–2018 interval (Figs. 7 and 8).

The 1972–2001 period shows that the groundwater head oscillates significantly with head and spatial location (Fig. 6). In certain years (1983−85), head in the deeper parts of the aquifer drop until they reach the level in the upper part. The eight nests show groundwater head differences for the 2009–2018 interval (Fig. 8). Flow direction is from the upper to the lower aquifer in most of the nests with different hydraulic gradient according to location.

Medina del Campo boreholes (Fig. 8a), separated by 3.5 km, present a higher hydraulic head in the deeper aquifer. The same behavior is observed in the Serrada-Valdestillas and Mojados well pairs (Fig. 8b and c), whereas the Matapozuelos-Ventosa de la Cuesta (Fig. 8d) and Aldeaseca de la Frontera (Fig. 8e) wells show a descending flow from the upper to the lower part of the aquifer.

In general terms, groundwater levels are observed to drop over the three decades. The deeper aquifer exhibits greater drawdowns, which is coherent with a semiconfined behavior. The area to the east of the Adaja stream presents the greater head differences, with an upward groundwater gradient. In the Aldeaseca area, towards the south, deep and shallow groundwater present a similar level. All this suggests that the northern part of the system was characterized by upward flow during the 1972–2001 period. This is consistent with Toth's classic conceptual model for large sedimentary basins (Toth, 1962, 1963, 1999). According to this, the southern area, close to the Gredos Range, is the main recharge area, while the main axis of the Duero valley makes up the deep discharge zone of the system.

Piezometric evolution over the 2006–2018 is assessed by means of piezometric nests, which were purposefully built to observe the vertical gradient as they present screens at different depths (Fig. 9). The Medina del Campo area presents a downward gradient (nest A, Figs. 1d and 8 a). This is the closest nest to the Palacio de las Salinas spa, and reveals a change in the groundwater head of the deepest part of the aquifer. A drop of several meters is observed, and is possibly associated with groundwater extractions during the irrigation season (April to November). This also explains why the area's springs and wetlands are no longer active.

Nest B, located on the left bank of the Adaja stream, presents a downward flow. This is consistent with this area being a recharge zone of the aquifer (Fig. 8b). The same is observed in nests C, E, F and H (Fig. 8c, e, f, h). In contrast, nests D and G present an upward gradient.

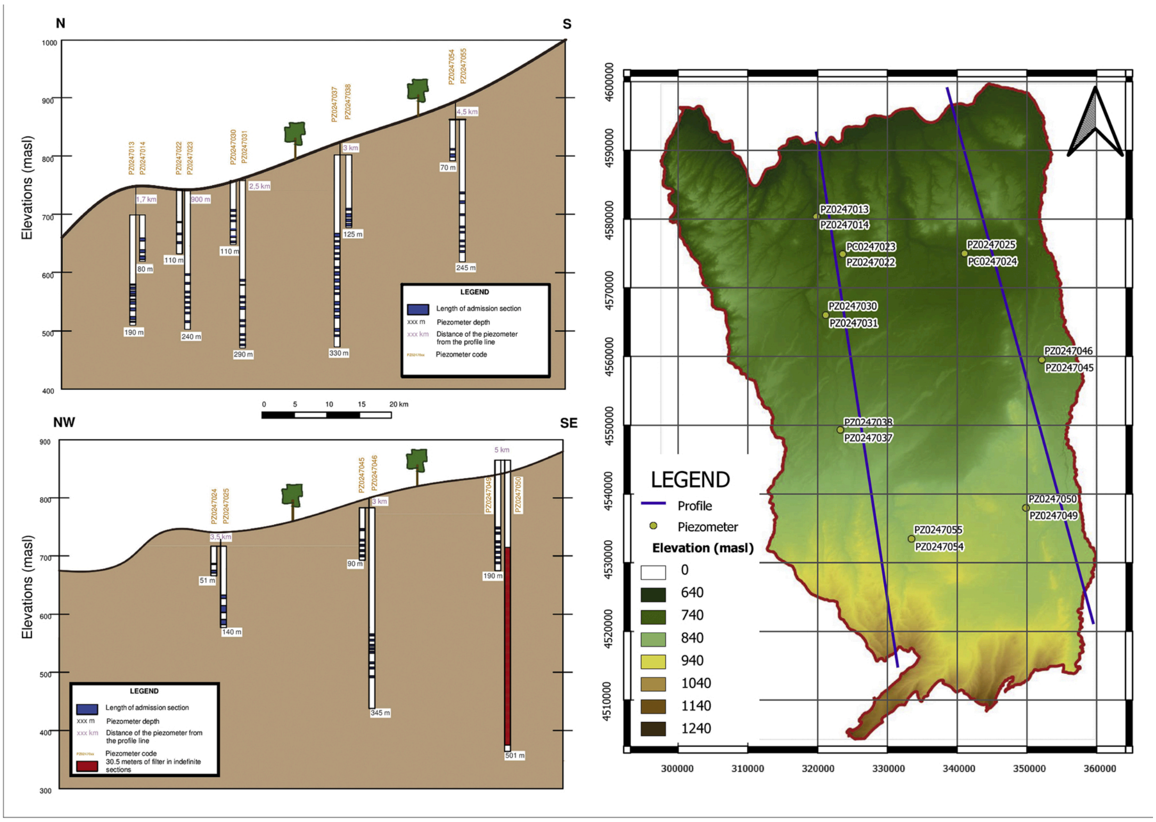

Fig. 7. Scheme of the piezometer nests controlled by the Duero Basin Authority, with indication of the screened sections (TS3),MCGWB. It is important to note that there is no overlap in the screened sections of seven of the 8 nests (exception is PZ0247049 and PZ0247050) (source: Author's own).

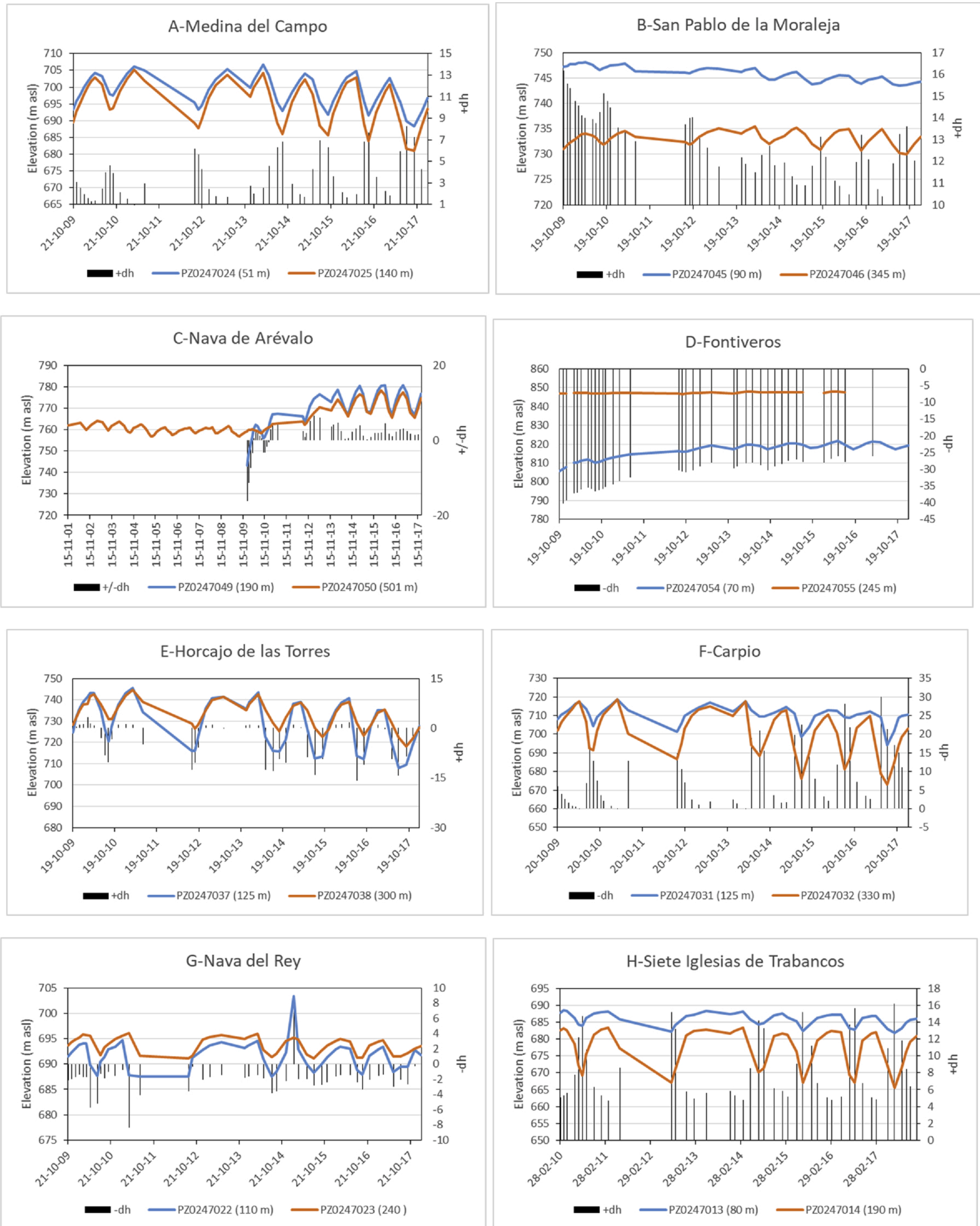

Fig. 8. Evolution of the eight piezometric nests located in the MCGWB (data from Duero Basin Authority, authors' own). Key of this figure is the same of Fig. 6: -dh implies upward flow and + dh downward flow (Data included in TS7).

The deep part of the aquifer presents greater hydraulic potential in the western part of the MC Figure 9 GWB, around the Zapardiel and Trabancos sub-basins, which results in upward groundwater flow. This however appears to be more related to the spatial configuration of permeability and internal hydraulic transferences than to the impervious basement.

The Fontiveros nest is the one that presents the greater head difference between the deep piezometer and the shallow one (32 m on average). This corresponds with an upward flow. The opposite case in the Carpio nest, where there is downward flow and an average head differential of 9 m. Interestingly, the Horcajo and Carpio nests, only 17 km apart, present a different hydraulic behavior.

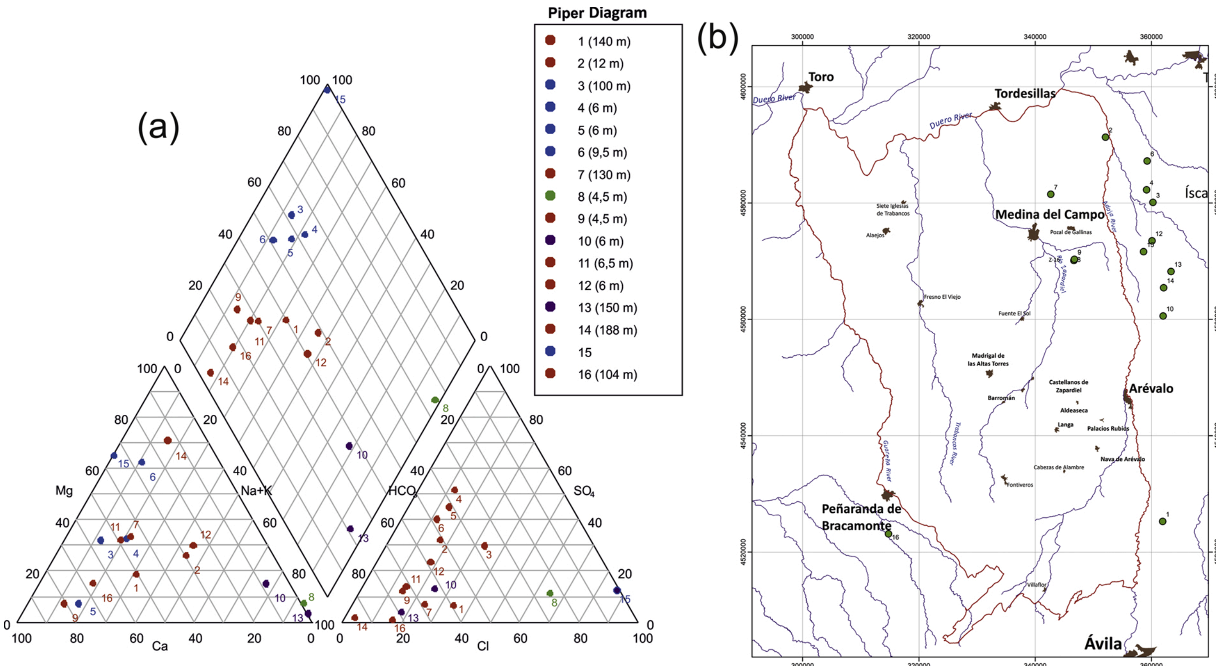

Fig. 9. (a) Piper diagram of the chemical analyses carried out in 1977 (TS4) (data from the IGME Water Points database). (b) Location of the points sampled in (a). ETRS89-Zone 30 (Author's own).

4.4. Groundwater quality

4.4.1. Medina del Campo GWB

Most of the 85 analyses for the 1970–2001 period resulted in Na-HCO_3 or Ca-HCO_3 waters, but with a predominant of the latter. This is consistent with the literature (IGME-DGA, 2010a; López Geta and Ramírez-Ortega, 2015). Piper diagrams are presented for years 1977 and 2001 (Figs. 9 and 10) . Na-Cl waters were however identified in the northern half of the aquifer, to the south of Medina del Campo and Olmedo towns. Also the analyzes of the years 1977 and 2001 reveal the presence of sodium bicarbonate waters in the northeast quadrant of the MCGWB (Fig. 9).

There were 16 water analytics for 1977, out of which 13 present an acceptable ionic balance discrepancy (<10 %). These are all of the HCO_3^- facies. There were also 20 analytics for year 2001, all of which present an acceptable ionic discrepancy. Wells presenting Na-Cl waters (1617-1-14 in 1977; and 1516-2-0001 and 1616-3-0003 in 2001) have, in contrast, very different depths: 4.5, 190 and 95.3 m, respectively.

For the deep confined aquifer, the representation of the chemical analysis for the 9 wells with chemical analysis (samples from 1982 to 2001), are shown in Fig. 11. These boreholes range from 505 m depth to 255 m depths (TS6). Without considering the recent spa analysis (samples 1–3) results show that a 50 % of the analysis are $CaHCO_3$ waters, a 30 % are $NaHCO_3$ waters, and a 20 % are ClNa (samples 4 and 5), which are representative of the deep groundwater flow. The presence of sodium bicarbonate waters is reported by some authors at the border of contact between the Cenozoic basin of the Duero and the Central System (Giménez-Forcada et al., 2017) attributed to cold-water thermal phenomena (cold-hydrothermal inflows) in the basement water-rock interaction. However, its presence in the northeastern half of the MCGWB had not been reported as such, but rather as a zone of "complex waters" at the Adaja-Duero confluence (IGME, 1980).

The sample from the Olmedo spa is very similar to sample 5, obtained near the confluence of the Trabancos River with the Duero, which we interpret as having responded (1987) to a deep underground discharge of the more saline flow of the aquifer.

The fact that wells 4 and 5 present chlorinated sodium waters reveals that the waters that circulate through the Paleogene reached heights of 350 m above sea level in the vicinity of the Duero channel in 2000. We do not have data that allow us to know whether today day there are springs that reach this salinity in this stretch of the Duero basin. It would be necessary to carry out a detailed study to discriminate regional discharge in the whole of the flow that the Duero receives in the section between Valladolid and Toro. However, given the current degree of exploitation of the aquifer, the groundwater discharge to the Duero likely occurs in the section between the Trabancos-Duero and Toro confluence, where the aquifer considerably reduces its thickness.

4.4.2. Spas

Old hydrochemical analyses for the Palacio de las Salinas spa refer to wells that have long-since disappeared (Table 3). Hydrochemical facies vary significantly from well to well, even though these are located in close proximity to each other. The oldest analysis dated from Ministerio de Fomento (1892) reports that anhydrous salts in 1 L-water sample contain: 0.0496 g of sodium sulfide; 0.0045

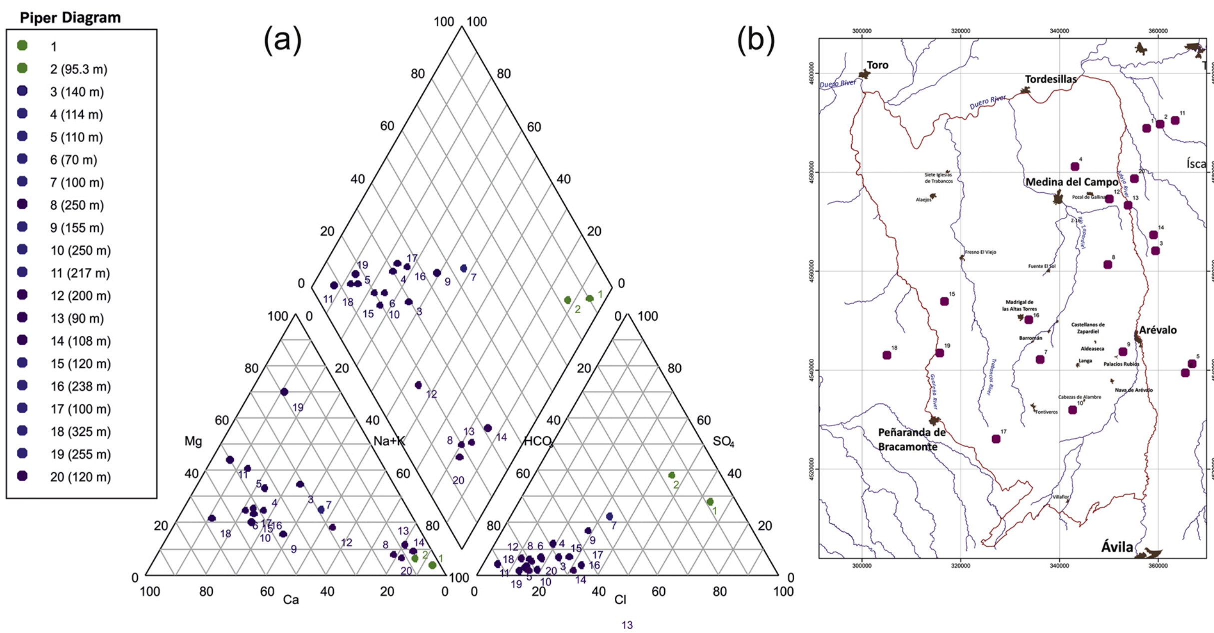

Fig. 10. (a) Piper diagram of the chemical analyses carried out in 2001 (TS5) (data from the IGME Water Points database). (b) Location of the points sampled in (a). ETRS89-Zone 30 (Author's own).

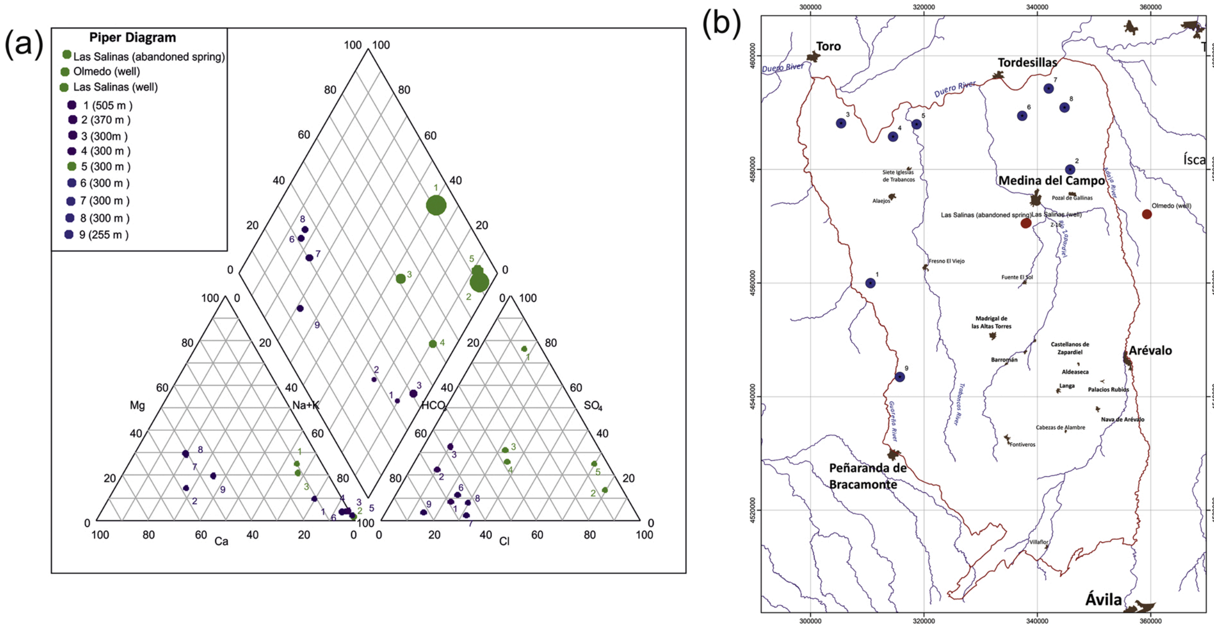

Fig. 11. (a) Piper diagram of the chemical analyzes carried out on different dates of the deepest existing boreholes (depth > 200 m) (TS6) in the MCGWB (data from the IGME Water Points database) compared with the current samples taken in the spas in 2019 and 2020. Dots coloured according to the hydrochemical facies. Symbols are scaled with respect to Electrical Conductivity (μS/cm); (b) Localization of the sampled points in (a). ETRS89-Zone 30 (Author's own).

g of sodium bromide; 55.9419 g of sodium chloride; 4.9789 g of magnesia chloride; 4.9020 g of soda sulfate; 2.5980 g of lime sulfate; 0.030 g of organic matter, which sum a total of 72.6541 g of anhydrous salts. A comparison with sea water (average salt concentration 38 g/l) shows that this sample doubles the salt concentration.

The ensuing analyses date from 1927, 1989, 1997 and 2005 (Table 3). Well #1 ("Tenacidad") rendered Cl-SO_4-Na waters, whereas well #2 ("Anita") was Cl-Na-Ca, and well #3 ("Manolito") HCO_3-Na-Mg. In the absence of further information, variations in hydrochemical composition could mean that each well captured a different aquifer layer. The fact that analyses were spaced several years

Table 3
Hydrochemical analyses of the Palacio de las Salinas spa. CE is expressed in µS/cm^{-1}, and temperature in Celsius degrees. Ionic charges have been omitted for simplicity.

	Manolito	Well #1 "Tenacidad"	Well #2 "Anita"	Well #3 "Manolito"
Date	1927	23–4-1989	1997	18–10-2005
Units	gr	mg/l	mg/l	mg/l
Cl	9.369720 g	2,411	1,060.9	266.2
SO_4	6.629722 g	1,150	283.2	139.5
HCO_3	0.571980 g	229.4	192.8	137.3
CO_3	–	0.0	0	–
NO_3	–	23.0	12.1	10.1
NO_2	–	0.09	0	–
NH_4	–	0.20	0	0.09
Na	7.087239 g	1.048	400	163.3
Mg	0,870717 g	211.6	83.6	26.8
Ca	0.628490 g	653.3	303	116.7
K		21.0	5.2	5.9
pH		7.60	7.7	8.51
CE		7,840	3,640	1425
Temperature		10.2	17	13.9
Hydrochemical facies		Cl-SO_4-Na	Cl-Na-Ca	HCO_3-Cl-Na-Mg
Source		Rodes (1989)	IGME (2001)	IGME (2005)

and that they were carried out in different laboratories could also explain discrepancies to some extent. The more recent analyses (Table 4) were from samples taken in the current well for spa uses and an abandoned spring for which there is no reference to relate with the OSLS, so we assume it is a different water point. Fig. 12 show the representation of these analyses in Piper diagram including a sample from the sea.

In contrast, Olmedo waters present a constant Cl-Na facies since the spa first became operational (2005) (Table 5). Electric conductivity shows a gradual decrease, while temperature increases slowly between 2010 and 2018, and sharply between 2018 and 2019. The reduction in saline content could be attributed to the wells tapping a greater share of shallow groundwater (HCO_3 facies). In fact, while Na and K concentration dropped between 2016 and 2019, Ca was observed to slowly increase. Nitrate concentration could be used as a proxy to evaluate the infiltration of shallow groundwater to the deeper parts of the aquifer (CGS, 2000), however, this is considered outside the scope of this paper.

The current waters of the Palacio de las Salinas spa should be mixed waters of deep saline waters and local waters of a calcium bicarbonate character or even somewhat deeper, with sulphated facies. No chemical data are available in the MCGWB at depths greater than 500 m. For this reason, as an approximation tool, we have made a "reasonable" comparison with a section of the Tagus basin lithologically similar to the sedimentary fill present in the central sector of Medina del Campo (2000 m depth of aquifer). Using the data from the Pradillo-1 survey extracted from López Vera and Gómez Artola (1984) we have calculated the concentration of the water mixture that would explain the saline concentration of the upwelling of the OSLSOSLS and the concentrations of the Olmedo spa. Based on the conservative nature of the chloride ion, the water obtained at any of these two points will present a C content that will be a mixture of two other C1 and C2 contents ($C1 < C < C2$) and there will be a fraction x of water 1 and 1- x of water 2, it must be fulfilled

Table 4
Hydrochemical analyses of the Palacio de las Salinas spa from samples taken in 2019. Concentrations are expressed in mg/L, CE in µS/cm-1, and temperature in Celsius degrees. Ionic charges have been omitted for simplicity.

	Current well	Abandoned spring	Current well	Abandoned spring	Sea water
Date	27-06-2019	27-06-2019	29–11-2019	29–11-2019	–
Units	mg/l	mg/l	mg/l	mg/l	gr/l
Cl	225	870	202	806	19.88
SO_4	299	5,269	331	4,459	2.74
HCO_3	426	498	322	430	0.12
CO_3	0	0	2,46	0	–
NO_3	5	115	7	94	–
NO_2	0,00	0,21	0,00	0,00	–
NH_4	0,00	0,19	0,00	0,00	–
Na	313	2151	199	1413	11.02
Mg	49	432	36	360	1.31
Ca	56	357	102	474	0.42
K	11	161	16	185	0.39
Br	–	–	–	–	0.07
pH	7,95	7,86	8,24	7,95	7.5-8.4
CE	1,680	11,320	1,600	10,980	50,000
Temperature					
Hydrochemical facies					
Source	Field campaign	Field campaign	Field campaign	Field campaign	http://dardel.info/IX/other_info/sea_water_ES.html

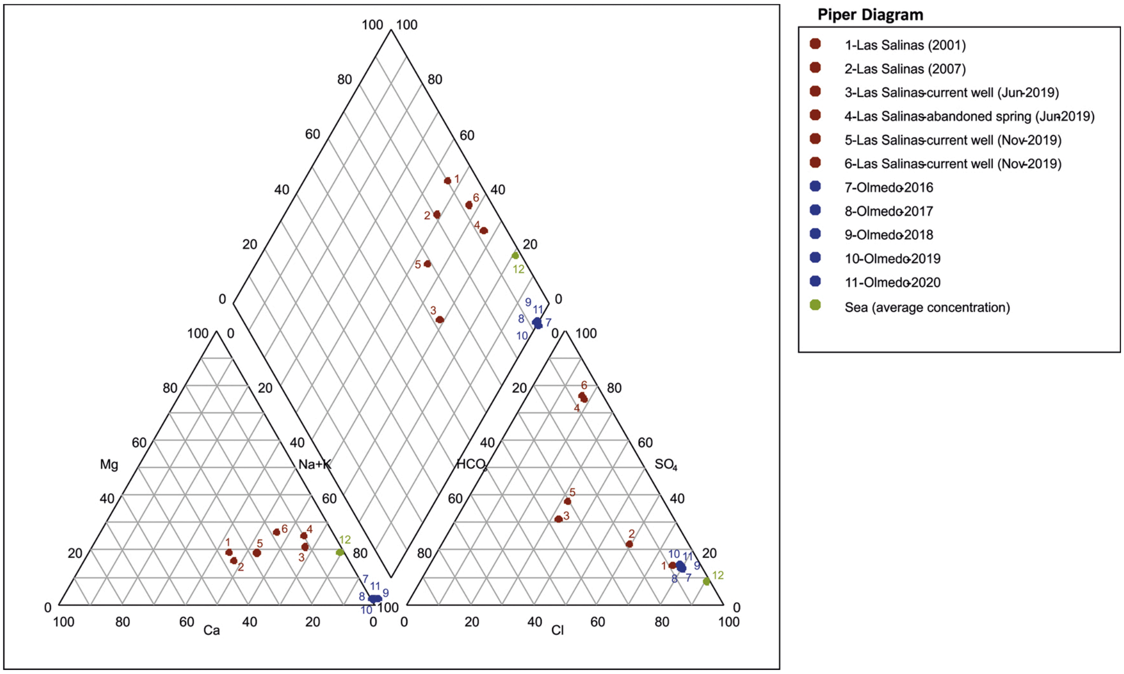

Fig. 12. Piper diagram for Las Salinas spa (former samples and 2019 samples), Olmedo spa (2016-2020) and sea water as reference (data from Tables 3 and 4). (Author's own).

Table 5
Hydrochemical analyses of the Olmedo spa. Concentrations are expressed in mg/L, CE in μS/cm^{-1}, and temperature in Celsius degrees. Ionic charges have been omitted for simplicity. Data represented in Fig. 12.

	Vademecum (2010)	2016	2017	2018	2019	2020
Date	2007–2009	08–08-2016	27–09-2017	11–10-2018	24–09-2019	26–08-2020
Cl	2,856.6	2,610.7	2,870.9	2,649.3	2,546.6	2,640
SO_4	742.3	630.9	677.0	615.7	621.1	692
HCO_3	341.6	313.9	328.2	331.4	325.1	332
CO_3	0.00	< 5.0	0.0	0.0	0.00	0
NO_3	0.00	18.6	4.9	4.9	8.5	0
NO_2	–	< 0.03	< 0.03	<.,03	< 0.05	0,00
NH_4	–	0.23	0.26	0.21	0.23	0,00
Na	2,304.9	2,052.5	2,056.0	1,907.5	1,779.0	2,219
Mg	9.3	< 8.0	< 8.0	5.2	< 8.0	9
Ca	24.6	22.7	25.0	25.4	26.6	1
K	2.8	5.0	4.0	3.4	3.0	7
pH	7.9	8.22	8.07	8.13	7.96	7.84
CE	9,780	8,430	8,260	8,090	8,020	8,390
Temperature	21.3	21.4	21.8	21.9	26.4	
Hydrochemical facies	Na-Cl	Na-Cl	Na-Cl	Na-Cl	Na-Cl	Na-Cl
Source	V-II (2010, 163–164)	Analizagua, S.L. (2016)	Analizagua, S.L. (2017)	Analizagua, S.L. (2018)	Analizagua, S.L. (2019)	Field campaign

that (Custodio and Llamas, 1983, I, 1036):

$C = C_1\ x + C_2\ (1\text{-}x)$

Where (Fig. 13):

C = mixing water (Las Salinas and Olmedo)

C_1 = saline water (Pradillo-1)

C_2 = Freshwater representative of the aquifer (CA0247041-Nava del Rey)

Sample 2 is considered representative of the non-saline waters of this aquifer, with calcium bicarbonate facies and electrical conductivity around 300 μS / cm. The waters of the original spring Las Salinas are representative of extremely saline waters with electrical conductivities of the order of those of sea water.

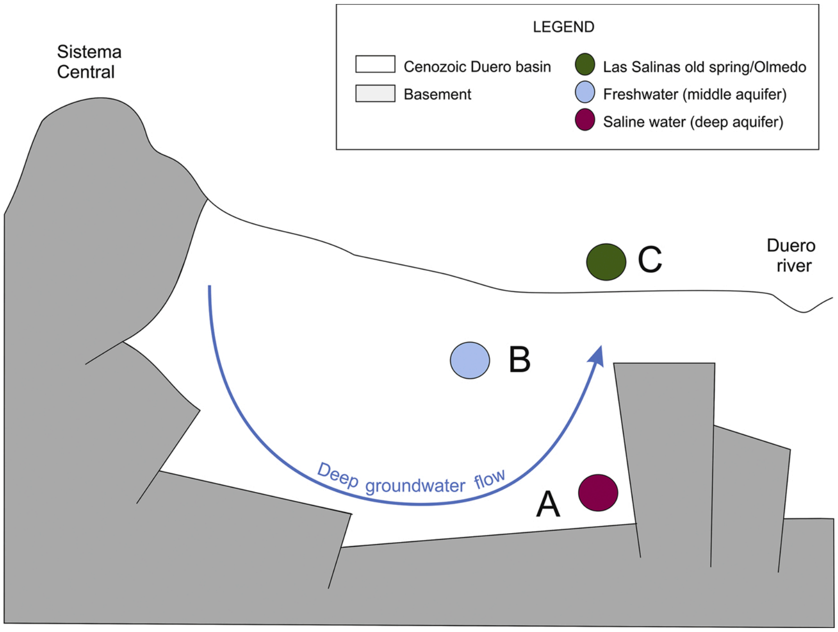

Fig. 13. Schematic overview of the saline mixing waters hypothesis for the spas of Palacio de Las Salinas and Olmedo (Author's own).

For the Pradillo-1 sample, the average of the three results obtained by López Vera and Gómez Artola (1984) has been calculated for the three samples taken between 3000 and 3300 m depth (EP-1-3112 m, EP-1-3197 m, sample taken at 3251 m). The concentrations and calculations are shown in Table 6. These are very different waters, which implies that, if the hypothesis is confirmed, the waters of the original Las Salinas spring are highly evolved waters, which respond to a long transit time within the aquifer. Most of the samples from the two spas present sodium as the dominant cation and chloride as the dominant anion, with the exception of the most recent samples taken in Las Salinas, which present either SO_4^{-2} or CO_3H^{-}as dominant.

Results indicate that the waters that currently feed the well of the Balneario de Las Salinas, receive very little inflow from the deep aquifer (6.3 %). This contribution is greater in the Olmedo spa but represents a scarce 2% of the total volume of water that receives the borehole. This all suggests that the hydraulic potential of the deep aquifer has undergone a downward evolution, which has resulted in the disappearance of the OSLS, and subsequently in changes in the water quality of the Las Salinas spa from 1927 to the present day. These have evolved from a predominantly sodium chlorinated composition, to calcium-sodium sulphated, and, recently, to sodium-calcium bicarbonate.

Basement uplift in the southern area of Medina del Campo makes it possible for the Olmedo borehole to capture the deepest waters of the known aquifer, located between the Lower Miocene-Paleogene (IGME, 2001). These waters are very saline, reaching electrical conductivities of the order of 8000 μS / cm according to a measurement made in situ on 08/26/2020, consistent with previous references (López Geta and Ramírez-Ortega, 2015; IGME, 1980). In fact, the chemical composition is very close to that of sea water (Avrahamov et al. 2010; BOE, 2011).

For the OSLS there are two relevant data associated with this observation: (i) the high salinity of the OSLS, higher than sea water; the use of the Br/Cl relation as isochemical tracers could provide some light on this (Custodio and Herrera, 2000); and (ii) the fact that OSLS was declared as variety iodine-brominated waters. Both facts are a clear indication of the marine origin. However, the available data does not allow to go ahead to define whether they are fossil, migrant or congenital waters. It would be needed to make an isotopical study to determine the age of the water pumped in Olmedo spa and in the abandoned spring of the Palacio de Las Salinas spa to shed further light on this matter.

Table 6
Estimation of the percentage of saline water in the sampled points of Palacio de las Salinas and Olmedo spas.

	C (mg/L)	C_1 (mg/L)	C_2 (mg/L)	X
Las Salinas-Manolito-Tenacidad-1924	9370	3185	23,1	295 %
Las Salinas-Anita-1989	1262	3185	23,1	39,1 %
Las Salinas-Tenacidad-2000	2411	3185	23,1	75,5 %
Las Salinas spa – Abandoned spring (06/2019)	870	3185	23,1	26,7 %
Las Salinas spa-current well (06/2019)	225	3185	23,1	6,3 %
Olmedo spa (2020)	2640	3185	23,1	82 %

5. Conclusions

- The original Las Salinas spring was a regional aquifer discharge point not identified as such in previous works.
- Analysis of the hydraulic potential in the pairs of wells and piezometers analyzed within the MCGWB reveals that the multilayer aquifer formations of the study area present a leaky behaviour.
- Saline concentrations found in the OSLS are similar to those of sea water, without any lithologies present in the subsoil to justify this. Saline anomalies - in an aquifer which mostly presents mostly calcium bicarbonate waters -, are possibly due to a structural discontinuity in the Palaeozoic basement. This threshold modifies groundwater flow patterns by acting as a hydraulic barrier. Thus, groundwater that would be expected to discharge in the Duero river, upwelled into the former Las Salinas spring.

Despite the fact that there is no continuous information on the evolution of this spring from the early records to the present day, the available data implies that:

a) The original saline spring disappeared decades ago.
b) A variation is observed in the chemical species of the groundwater in the Las Salinas area from sodium chloride facies to sulphated facies and bicarbonate facies.
c) The temporal evolution of the piezometric level of the aquifers subject to pumping shows that withdrawals affect both the surface and the confined aquifers. Piezometric evolutions are largely parallel, the greater drawdowns being observed in the irrigation season.
d) The relationship of the hydraulic potential between different aquifers levels reveals that vertical flows have changed over time. In the area near the OSLS (Medina del Campo) the vertical gradient was ascending and increasing until 2001. From 2006 to the present, however, it is observed that the flow is descending, so there may have been a reversal of flow. Also striking is the fact that in the municipality of Mojados, located 25 km east of Medina del Campo, although there is an upward flow, the vertical gradient shows a decreasing trend in the 2006–2019 period.
e) The hydrochemical data show an evolution of the groundwater in the Las Salinas area, from sodium chloride waters to sodium-calcium sulphated waters to warm sodium bicarbonate waters.

These facts may be interpreted as a consequence of intensive groundwater pumping, which has caused: (a) a drop in the water table in the unconfined perched aquifers; (b) a decrease in the piezometric level in the confined aquifers; (c) an increase in recharge as a result of the increase in vertical hydraulic gradient. All this means that the loss of the hydraulic potential of the confined aquifers translates into a lower inflow into the overlying ones.

These results show mixing processes in a complex groundwater flow system that is not yet completely understood. Unresolved aspects include the characterization of the deep groundwater aquifer, the dimensioning of the regional aquifer integrating the Cretaceous aquifer, and a clearer picture of the system's conceptual model in order to underpin sustainable groundwater management, a key issue to guarantee water security.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ejrh.2021.100781.

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