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Quality aspects of the Doñana groundwater resources (SW-Spain) before the intensification of agriculture

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ABSTRACT

This article presents the initial hydrochemical status of the Almonte-Marismas aquifer system in 1966 – before agricultural intensification. The investigated aquifer is of critical importance for the groundwater dependent Doñana wetland areas of the National and Natural park of Doñana (SW – Spain). The analytical database involves 158 samples collected in 1966 by the Food and Agriculture Organization (FAO) and the Geological Survey of Spain (IGME), including electrical conductivity, hardness, chloride, bicarbonate, sulphate, calcium, magnesium, sodium, and potassium in groundwater that generate information about the initial hydrochemical state before the intensification of agricultural activity. These historical data existed as hardcopy lab reports and were introduced into a MS Access database. The parameters EC, Cl, SO4 and K of the year 1966 show a variety of spatial patterns before intensification and suggest five different types of influence: (i) natural lagoon systems, (ii) creeks or rivers, (iii) irrigated areas, (iv) urban areas, and (v) marshes. The results suggest that anthropogenic activities such as fertilizer use, domestic activities and wastewater in surface streams downstream of urban areas are responsible for elevated parameter values in most of the observation points, although their specific contributions cannot be determined based on the available data of 1966. In the marshes (north) area, apart from fertilizer use elevated geogenic salinity may also contribute to high parameter concentrations for intensive irrigated crop cultivation and proximity to the Guadalquivir River.

Keywords: Doñana; groundwater, historical data, hydrochemistry, wetlands.

Aspectos de la calidad de los recursos hídricos subterráneos de Doñana (SW de España) antes de la intensificación de la agricultura

RESUMEN

Este articulo muestra el estado hidroquímico inicial del sistema acuífero Almonte-Marismas en 1966 antes de la intensificación agrícola. El acuífero investigado es de gran importancia para las zonas de humedales del Parque Nacional y Natural de Doñana (SO - España), que dependen de forma significativa del agua subterránea. La base de datos incluye 158 muestras recolectadas en 1966 por la Organización de las Naciones Unidas para la Agricultura y la Alimentación (FAO) y el Instituto Geológico y Minero de España (IGME). Los datos incluyen conductividad eléctrica, dureza, cloruro, sulfato, bicarbonato, calcio, magnesio, sodio y potasio en las aguas subterráneas y generan información sobre el estado hidroquímico antes de la intensificación de la actividad agrícola. Estos datos históricos existían como informes de laboratorio en papel y se introdujeron en una base de datos de MS Access. Los parámetros EC, Cl, SO4 y K del año 1966 muestran una variedad de patrones antes de la intensificación y sugieren cinco tipos diferentes de influencia: (i) sistemas de lagunas naturales, (ii) arroyos o ríos, (iii) áreas regadas, (iv) zonas urbanas, y (v) marismas. Los resultados sugieren que las actividades antropogénicas, como el uso de fertilizantes, las actividades domésticas y la presencia de aguas residuales en los cursos superficiales, aguas abajo de las áreas urbanas, son responsables de valores de parámetros elevados en la mayoría de los puntos de observación, aunque sus contribuciones específicas no pueden determinarse mediante los datos disponibles de 1966. En el área de las marismas (norte), también la elevada salinidad geogénica puede contribuir a altas concentraciones de parámetros, aparte del uso de fertilizantes para el cultivo intensivo de cultivos de regadío y la proximidad al río Guadalquivir.

Palabras clave: Doñana; groundwater, historical data, hydrochemistry, wetlands.

Introduction

The Almonte-Marismas aquifer system is located on the southwestern coast of Spain. It extends from Seville to Huelva and is limited by the Atlantic Ocean to the west and the Guadalquivir River to the east. The aquifer covers an area of about 3,400 km^2, of which 543 km^2 belong to the Doñana National Park, founded in 1969, and 682 km^2 to the Natural Park of Doñana, created in 1989 (Fig. 1). Both administrative sectors are together called the Doñana Natural Space (DNS) in this text.

The Doñana Natural Space can be divided into two main morphological and lithological environments, with fluvial (deltaic) and aeolian sand deposits in the northern and western sectors forming the Almonte-Marismas aquifer, and the wetlands in the eastern, southern and southeastern sectors. The Doñana national Park is considered as one of the most important wetland areas of Europe because of its strategic location close to Africa and its high ecological value. Owing to its considerable environmental interest, the Doñana National Park was declared a Biosphere Reserve by UNESCO's Man and the Biosphere Program (MAB Program) in 1980, and it was listed as a RAMSAR Convention site (international treaty for the conservation and sustainable use of wetlands) in 1982. The Doñana National Park was also declared as a World Heritage Site by UNESCO in 1994. The landscapes and the ecosystems of this large wetland area depend mainly on groundwater (Custodio et al., 2009).

The area has a Mediterranean climate with Atlantic influence, generally classified as sub-humid. Rainfall is variable, both seasonally and from year to year, with a 580 mm annual average, of which about 80 % falls between October and April. Summers are very dry and hot, while winters are short and mild (Serrano et al., 2006).

The Almonte-Marismas aquifer system is mainly formed by permeable sediments from Upper-Pliocene to the Quaternary. These sediments were mostly deposited in the Guadalquivir River Basin, overlying blue marine loams and sandy loams of Late Miocene and Early Pliocene age. These underlying sediments form an almost impermeable basement, which locally exceeds a thickness of 1,000 m in the southern part of the area (Rodríguez, 1998). Whilst the coastal part of the study area is mainly composed of permeable sandy deposits, southeastern Doñana is covered by the Guadalquivir River Marshes (Fig. 2).

The sediments are mainly formed by silicates, with smaller amounts of sodium and potassium feldspars, as well as some chlorite, illite and kaolinitizised feld-

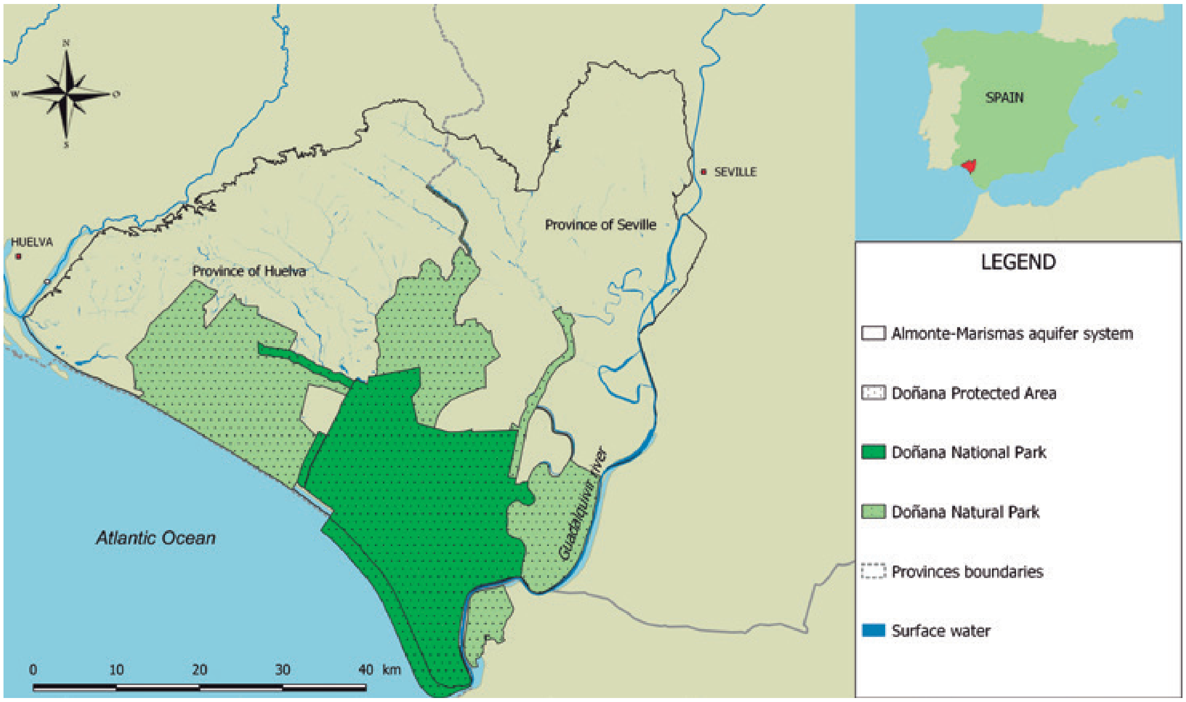

Figure 1. Location of the Almonte-Marismas aquifer system area (right) and map of Protected Areas (left). Data adapted from the Red de Información Ambiental de Andalucía (REDIAM) inventory (https://descargasrediam.cica.es/repo/s/RUR; 2017).

Figura 1. *Ubicación del área del sistema acuífero Almonte-Marismas (derecha) y mapa de Áreas Protegidas (izquierda). Datos adaptados del inventario de la Red de Información Ambiental de Andalucía (REDIAM) (https://descargasrediam.cica.es/repo/s/RUR; 2017).*

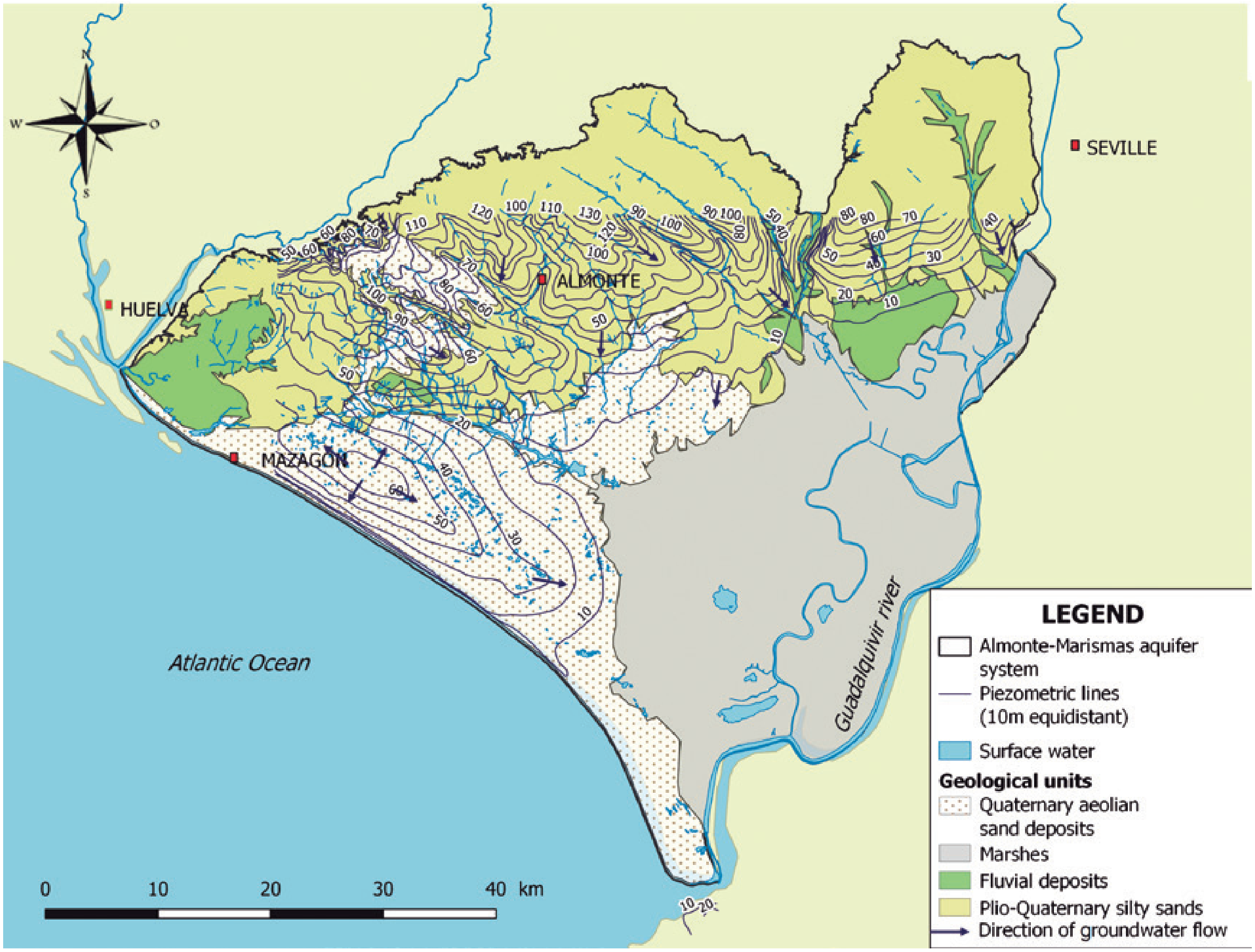

Figure 2. Hydrogeological context of the Almonte-Marismas aquifer (Adapted from GEODE – Geological digital continuous mapping, scale 1:50.000, IGME). Piezometric isolines are based on hydrogeological data from FAO and IGME (FAO, 1972).

Figura 2. *Contexto hidrogeológico del acuífero Almonte-Marismas (Adaptado de GEODE - Mapa continuo digital geológico, escala 1: 50,000, IGME). Las isolíneas piezométricas se basan en datos hidrogeológicos de la FAO y del IGME (FAO, 1972).*

spars (Pozo *et al.*, 2008; Ruiz *et al.*, 2004). The presence of carbonates is limited in the sandy wind-blown deposits; but increases close to Matalascañas and in the marshes.

The Almonte-Marismas aquifer shows unconfined conditions for the aeolian sand deposits unit with a shallow water table and several flow systems, changing into confined conditions when covered by silty-clay deposits below the marshes. The confined part of the aquifer contains saline water trapped during the deposition of Holocene sediments (Rodríguez, 1998). The aquifer thickness ranges from 15 to 100 m in the unconfined part and from 50 to over 200 m in the confined aquifer. The unconfined sector of the aquifer is mainly recharged by the infiltration of rainwater, whereas lateral inflows recharge the confined part of the aquifer. Piezometric isolines from 1968 (FAO, 1972) indicate a general groundwater flow from the recharge area of the aeolian sand deposits to the marshes and then to the sea. Furthermore, a water divide separates the south-western part of the aeolian sand deposit unit that discharges directly into the sea.

Due to the inhospitality of the wetlands, human historical activities in the Doñana Natural Space were mainly limited to hunting, forestry and animal husbandry (Manzano et al., 2013). The introduction of pine and eucalyptus forests for wood exploitation during the 20th century immobilized part of the sand dunes

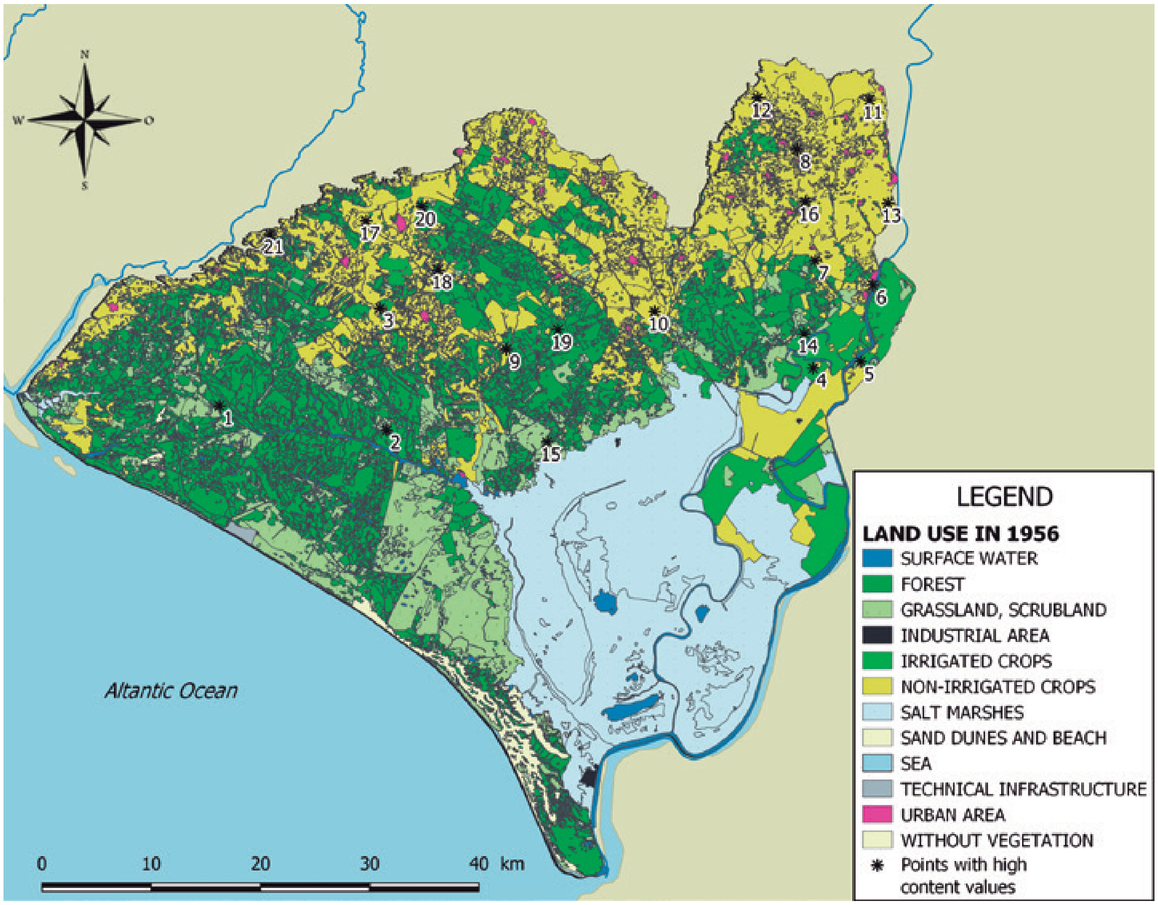

Figure 3. Map of land use in 1956. Geographical information adapted from REDIAM (http://www.juntadeandalucia.es/medioambiente/mapwms/REDIAM_MUCV25_56_escala_reconocimiento). Numbers refer to areas with elevated parameter values obtained by Kriging, listed in Table 2.

Figura 3. *Mapa del uso del suelo en 1956. Información geográfica adaptada de REDIAM (http://www.juntadeandalucia.es/medioambiente/mapwms/REDIAM_MUCV25_56_escala_reconocimiento). Los números se refieren a áreas con valores de parámetros elevados obtenidos por Kriging, enumerados en la Tabla 2.*

of the Park, and provoked a fall in the groundwater level as a consequence of increased evapotranspiration (Ojeda, 1992). In the 1960s, the southeastern area was mainly covered by marshland, forest and non-irrigated crops with some urban and industrial areas in the north and north-eastern sectors (Fig. 3). The western area was covered by pine forest, grassland, scrubland and sand dunes.

At the end of the 1970s, human activities started to intensify (Custodio et al., 2009). A hydrogeological investigation project of the Guadalquivir River Basin was initiated by the FAO and between 1969 and 1971 the Spanish government initiated a pilot project to explore the potential of local groundwater resources for agricultural purposes in the Guadalquivir River Basin (FAO, 1972). The results showed a high potential for agriculture and since then the groundwater has been intensively exploited. Tourism has also increased significantly since the end of the 1970s, affecting the quantity and quality of the Doñana water resources due to human activities (Manzano et al., 2005).

In recent years the hydrochemistry in Doñana has been widely studied (e.g. Poncela et al., 1992; Iglesias 1999; Lozano et al., 2002; Manzano et al., 2001, 2009; Lozano 2004 , amongst others). All of these studies are based on data obtained after the initiation of agriculture intensification and tourism. However, a large amount of available hydrochemical data obtained before the intensification of agriculture and tourism has been stored in internal hardcopy lab reports without being evaluated or published.

The purpose of this paper is to contribute to the existing knowledge about the anthropogenic footprint on groundwater quality by describing the initial hydrochemistry of the aquifer in 1966 before the agricultural exploitation started.

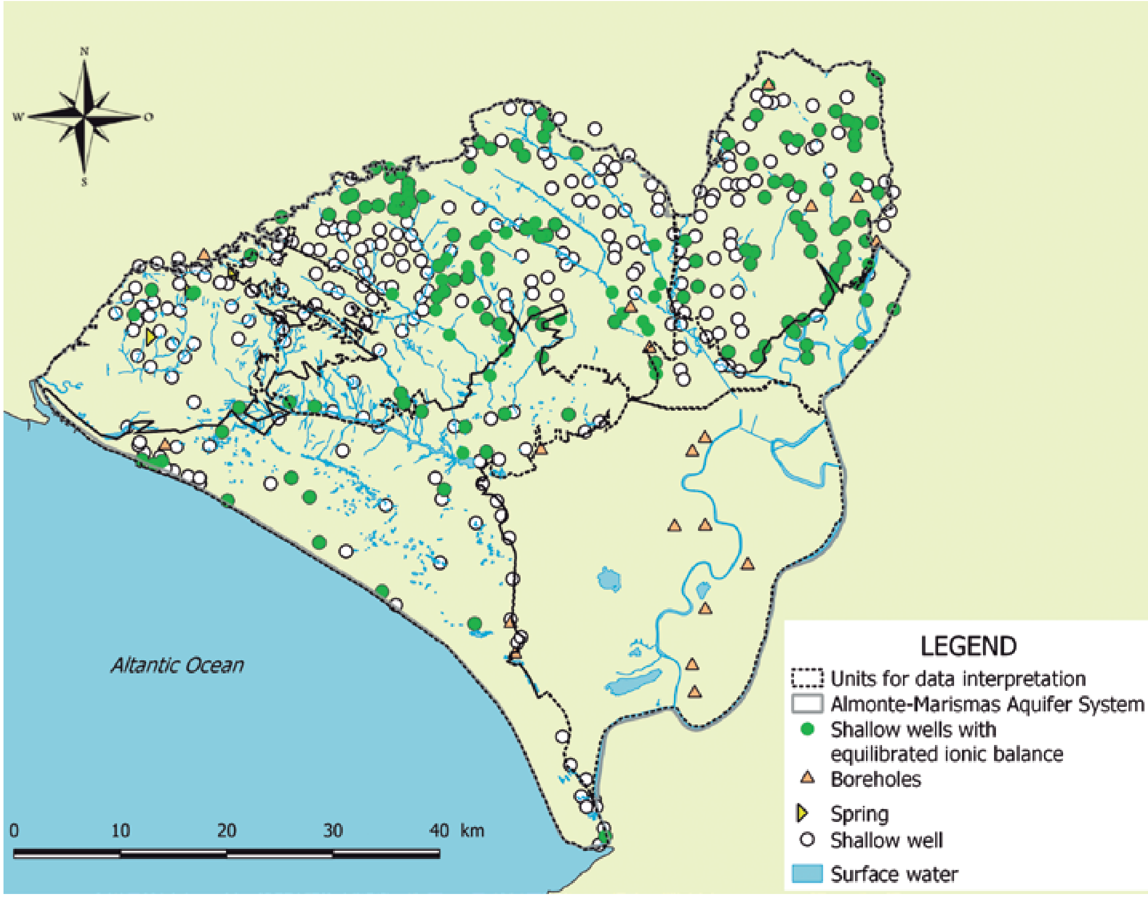

Figure 4. Sampling point network studied in 1966 by the FAO and IGME. Refer to Figure 2 for geological units.
Figura 4. *Red de puntos de muestreo estudiada en el año 1966 por FAO e IGME. Consulte la Figura 2 para las unidades geológicas.*

Methods

The article is based on hydrochemical data collected by the FAO in 1966 as part of surveys for the "Almonte-Marismas Agricultural Transformation Plan". The 1966 data used in this study were obtained as part of a survey by the FAO in collaboration with IGME to collect data about electrical conductivity, hardness, chloride, bicarbonate, sulphate, calcium, magnesium, sodium, and potassium in groundwater. These data were available as hardcopy lab reports and were introduced into a MS Access database. The distribution of sampling points studied is represented in Figure 4, showing a large number of sampling points dominated by shallow wells.

Taking into account the precision of pre-1980s analyses (Hiscock et al., 2005), only samples with ionic balance errors of less than 10 % were included, leading to 158 of the 417 samples being considered (Fig. 4).

Given the large number of measuring points, interpolation was considered a suitable method to illustrate the regional distribution of individual parameters. To avoid mixing up hydrogeological units, only data from shallow wells of less than 20 m depth were considered for studying the unconfined aquifer. Data from the confined aquifer with deeper boreholes of depths of between 31 m and 60 m (marsh areas) were interpolated separately. The geological units defined as aeolian sandy deposits, fluvial deposits and Plio-Quaternary silty sands are hydraulically interconnected and belong to the same aquifer system. Electric conductivity, sulphate, chloride and potassium were selected for the generation of distribution maps due to their relevance as indicators of anthropogenic activity and salinization. Since the electric conductivity (EC) does not depend on the ionic balance, all the 417 sampling points in the shallow aquifer (wells and springs) were considered for interpolation. An EC isoline of 1800 µS/

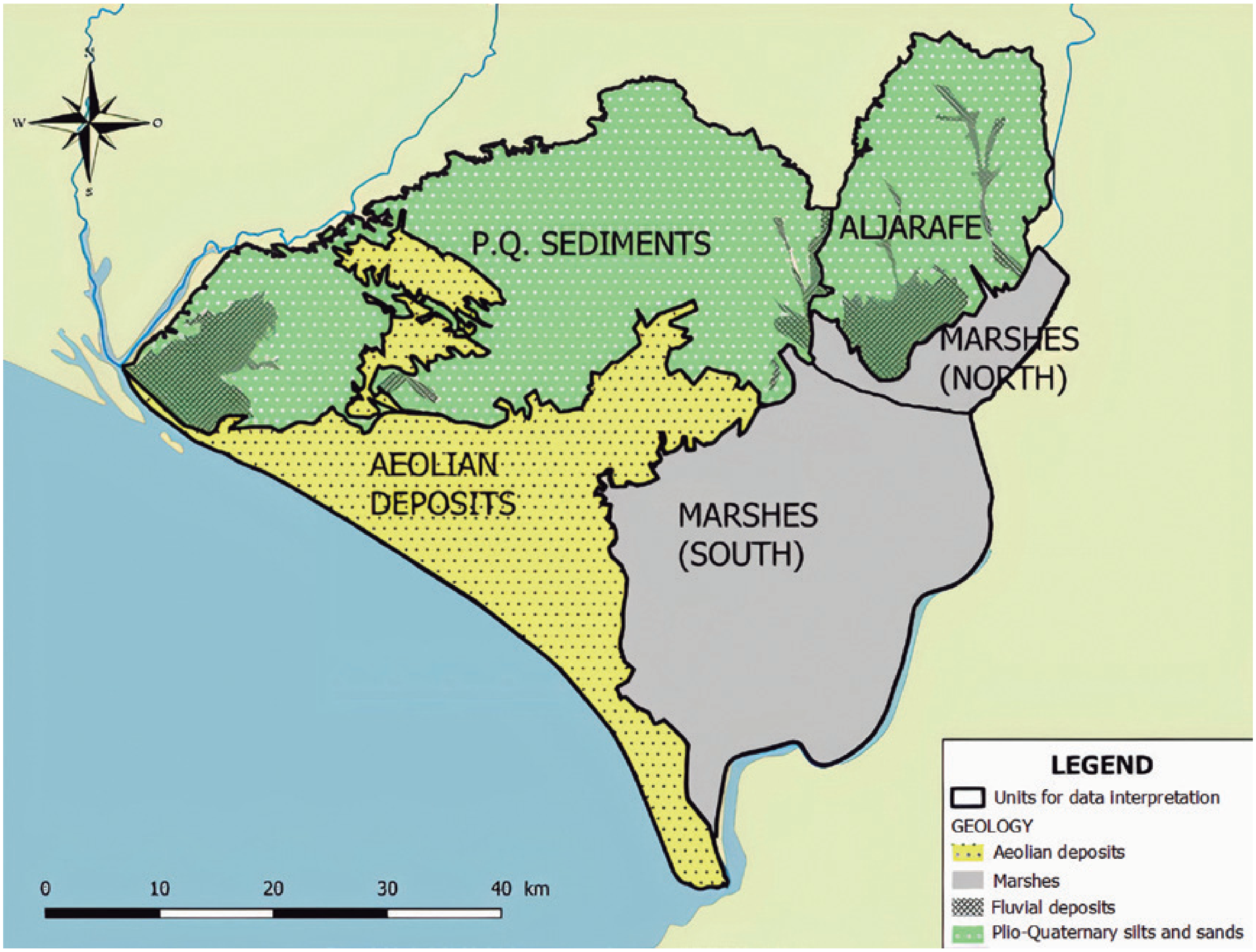

Figure 5. Definition of sectors within the Almonte-Marismas aquifer system.
Figura 5. *Definición de sectores dentro del sistema acuífero Almonte-Marismas.*

cm was marked to identify areas of limited suitability for crop production.

To take account for the geology, land use and well depth, the following sectors were defined to describe the hydrochemistry of the aquifer in 1966 (Fig. 5).

The Plio-Quaternary unit was sub-divided into P.Q. sediments and Aljarafe. The marshes in the northern part with shallow wells with less than 20 m depth (northern marshes) and the southern part with boreholes deeper than 20 m (southern marshes).

The generation of plots was performed with AQUACHEM 4.0 and parameter interpolation was done with SURFER Version 9.

Results and discussion

Electrical conductivity values

The comparison of the unconfined and confined aquifers (shallow and deep wells, respectively) shows significantly higher EC in the confined wells (Table 1). The spatial distribution of EC considering the shallow wells is shown in Figure 6.

The locations showing elevated solute concentrations obtained by Kriging based on measurements of nearby piezometers and their associated land use or hydrological situation are summarized in Table 2.

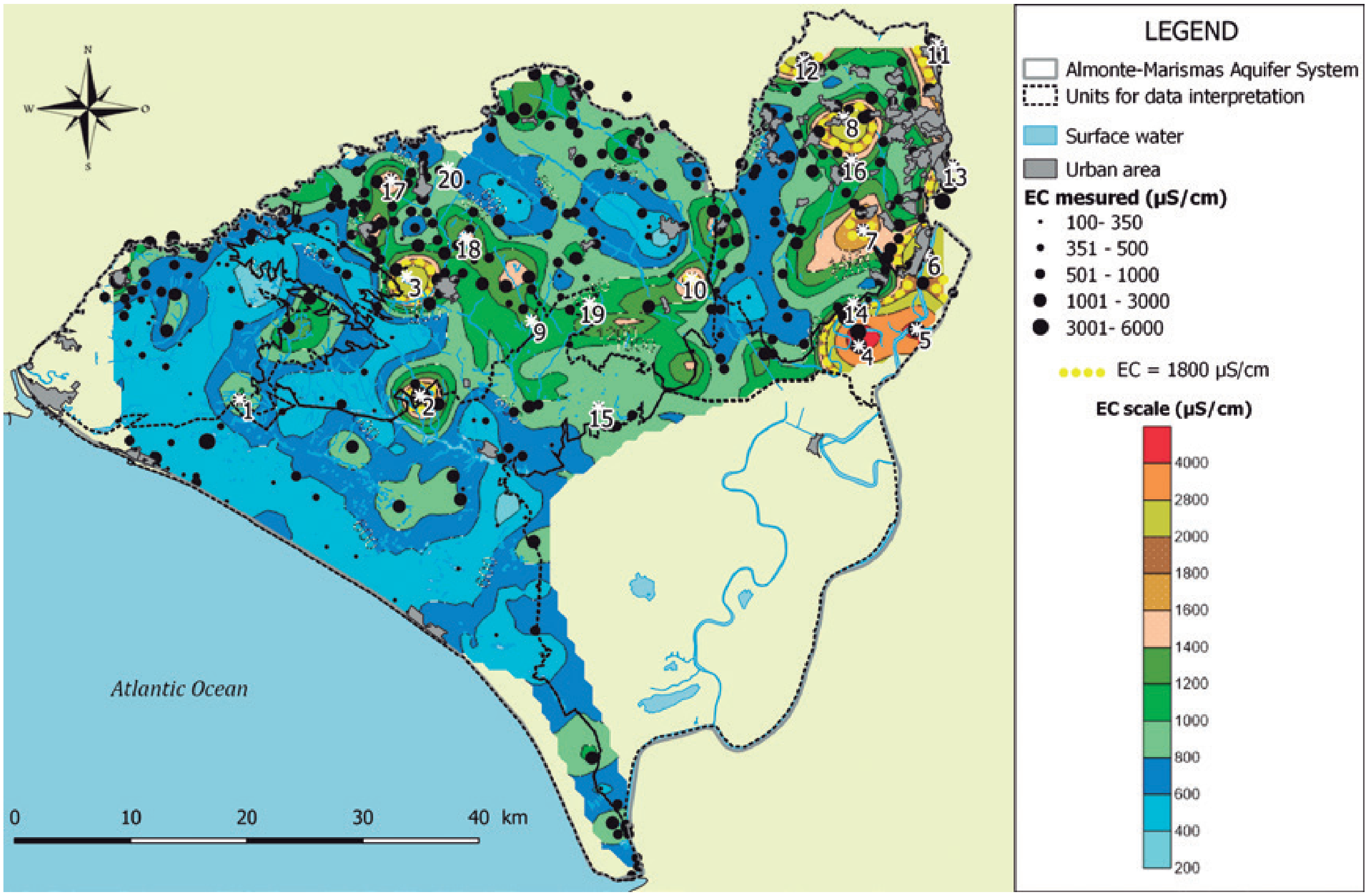

Figure 6. Contour map of EC in the first 20m of the shallow aquifer in year 1966. Refer to Figure 2 for geological details and legend. Numbers refer to areas with elevated parameter values obtained by Kriging as compiled in Table 2.

Figura 6. *Mapa de isolíneas de EC en los primeros 20 m del acuífero somero en el año 1966. Consulte la Fig. 2 para detalles geológicos y leyendas. Los números se refieren a áreas con valores de parámetros elevados obtenidos por kriging, listados en la Tabla 2.*

Piezometer	Shallow	Deep
Number of samples	417	13
Average (µS/cm)	981	3,716
Standard deviation (µS/cm)	951	4,144
Quartiles: 25% (µS/cm)	496	810
50% (µS/cm)	720	2,360
75% (µS/cm)	1,170	4,500
Min (µS/cm)	100	270
Max (µS/cm)	7,800	13,000
Variation range (µS/cm)	7,700	12,730

Table 1. EC data and basic statistics for the shallow aquifer (shallow wells) and the deep aquifer (boreholes).

Tabla 1. *Datos de CE y parámetros estadísticos básicos para el acuífero somero (sondeos someros) y para el acuífero profundo (sondeos profundos).*

More than 75 % of the unconfined aquifer is characterized by EC values below 1,170 µS/cm, indicating a moderately mineralised aquifer suitable for agricultural use. According to land use characteristics listed in Table 2, elevated EC at the various locations may be attributed to (i) fertilizers in irrigated and non-irrigated agricultural areas, (ii) wastewater and fertilizers transported by creeks downstream of urban and agricultural areas, (iii) proximity to the Guadalquivir river, and (iv) mixing with saline water trapped in the confined aquifer close to the marshes. Due to the map scale, points impacted by creeks listed in Table 2 are not always visible. A large number of locations are affected by more than one issue. Due to less anthropogenic activity, samples of the aeolian deposits unit show minor EC values. However, results suggest a general increase from southwest to northeast, showing the

Point	[Cl] > 1000 mg/L	[SO_4] > 250 mg/L	[K] >25 mg/L	EC > 1800 µS/cm	Land use/proximity
1			x		Creek
2		x	x	x	Forest, creek
3	x	x	x	x	Irrigated crops, creek
4	x		x	x	Marshes, river, crops*
5	x	x		x	Marshes, river, crops*
6		x		x	Marshes, urban, river, crops*
7		x		x	Non-irrigated crops
8				x	Non-irrigated crops
9		x			Non-irrigated crops, creek
10				x	Non-irrigated crops, creek
11		x		x	Creek
12				x	Creek
13		x	x	x	Non-irrigated crops, river
14		x		x	Irrigated crops, river
15			x		Lagoons
16		x			Urban, crops*
17		x			Crops*, urban
18		x			Crops*, creek,
19		x			Forest, creek
20		x			Crops*, creek

Table 2. Locations with elevated parameter values and associated land use. Crops* means non-irrigated and irrigated crops. River refers to the Guadalquivir River. Concentrations were obtained by Kriging based on measurements of nearby piezometers.

Tabla 2. *Ubicaciones con valores de parámetros elevados y uso de suelo asociado. Cultivos* significa cultivos no regados y regados. Río se refiere al río Guadalquivir. Las concentraciones se obtuvieron por kriging basado en mediciones de piezómetros cercanos.*

highest values in the northeastern part of the aquifer. This concurs with more recent studies, which reveal that groundwater mineralization increases along its flow path before discharging into the marshes as a result of geogenic processes (Manzano et al., 2007). EC values in the P.Q. sediments and Aljarafe units (Fig. 5) show higher EC values with peaks attributed to fertilizer use and wastewater in the proximity of surface streams.

The number of samples from deeper wells available for the confined aquifer in the southern marshes unit, ranging from 31 to 60 m depth, is only 13 and their spatial disposition is non-homogeneous. Therefore, no spatial interpolation was applied; nonetheless, the distribution of the sampling points and their EC values are represented in Figure 7.

The elevated EC values of the groundwater beneath the marshes in 1966 are attributed to ancient saline water and/or dissolution of evaporites within the confined aquifer below the marshes, which has already been confirmed by isotopic analyses in more recent sampling surveys (Plata et al., 1984) and other studies (Manzano and Custodio, 2005).

Major ion composition

The basic statistics for the composition of major ions are compiled in Table 3. Major ion concentrations are available only for the unconfined aquifer because the number of reliable data for the confined aquifer (Marshes-South) was too small.

To identify a potential influence of the geological background or land use on hydrochemistry, piper plots for the various geological units are shown in Figure 8 based on measured parameters listed in Table 3.

In the aeolian deposits unit, which corresponds to the principal recharge area, the water facies is heterogeneous. A large proportion of samples are of the Na-HCO_3 type, which may have evolved through the processes of freshening seawater in the aeolian deposits

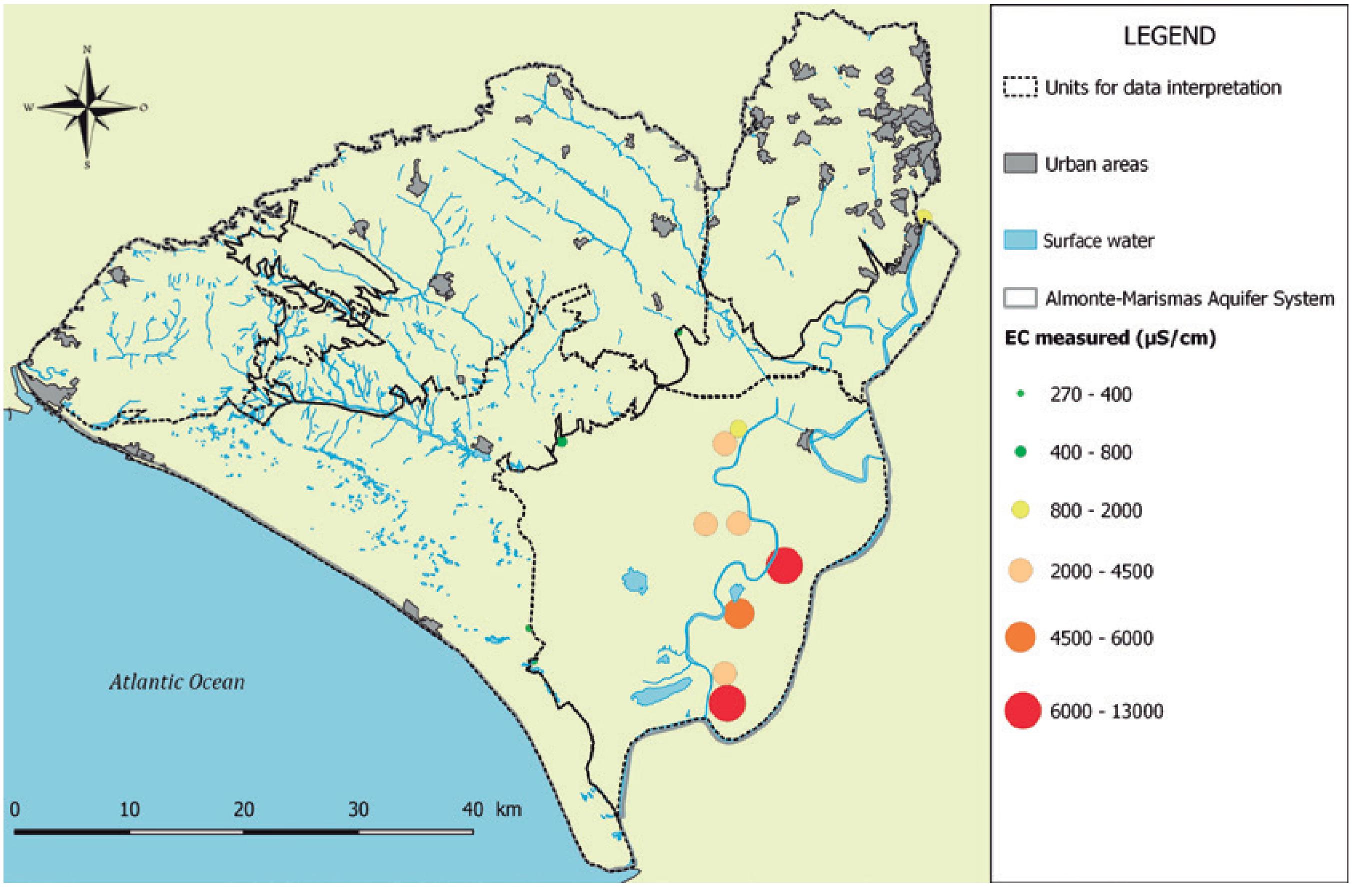

Figure 7. EC values of the confined aquifer. Refer to Figure 2 for geological details.
Figura 7. *Valores CE del acuífero confinado. Consulte la Fig. 2 para obtener detalles geológicos.*

Parameter	Samples	Min.	Max.	Arithmetic-Mean	Range	Standard-deviation	1rst quartile	2nd quartile	3rd quartile
CE	158	7	2639	187.2	2632	359.7	49.6	78.1	147.25
SO_4	156	0	1127	145.8	1127	203	31.25	62.5	110.5
K	158	0	226	11.33	226	22.4	1.5	3.75	11.5
Na	158	5	1610	136.6	1605	221.2	30.5	61.5	120
Ca	158	2	427	88.4	425	67.2	18	43.25	87.75
Mg	158	0	260	47.4	260	37.95	5.5	18	46
HCO_3	65	24	888	324.9	864	174	264	396	540
CO_3	128	0	522	152	522	120	0	3	168
Cl	123	7	2216	143	2109	254	49	81	128

Table 3. Basic statistic parameters of major ion concentrations for the unconfined aquifer in 1966 in mg/L.
Tabla 3. *Parámetros estadísticos básicos de las principales concentraciones de iones para el acuífero no confinado en el año 1966 en mg / L.*

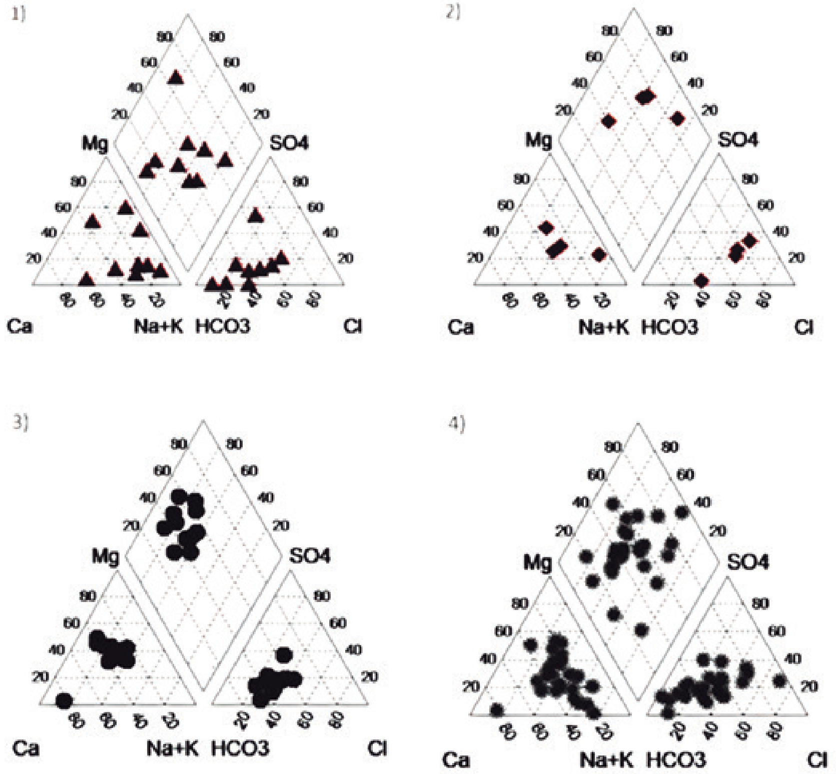

Figure 8. Hydrochemical facies in the various zones of the Almonte-Marismas aquifer in 1966. Aeolian deposits unit (1), northern marshes (2), Aljarafe (3) and P-Q, silty sands (4). Refer to Figure 5 for the spatial distribution of the various sectors.

***Figura 8.** Facies hidroquímicas en las diversas zonas del acuífero Almonte-Marismas en 1966. Unidad de depósitos eólicos (1), Marismas-Norte (2), Aljarafe (3) y P-Q. Arenas limosas (4). Consulte la Fig. 5 para la distribución espacial de los diversos sectores.*

unit. One hypothesis is that water of Na-Cl facies (typical for rainwater in this coastal area according to Manzano and Custodio, 2005) infiltrates and a Ca-HCO_3 water facies develops due to dissolution of calcite, present in the sand dunes. When this Ca-HCO_3 water replaces seawater, a new equilibrium is reached due to the sorption of calcium and desorption of sodium resulting in a Na-HCO_3 water type. However, this hypothesis claims that the aeolian deposits unit stored seawater in former times which has not been confirmed so far. Beside the Na-HCO_3 water facies, there are also samples with a Na-Cl facies and samples with elevated amounts of Ca and SO_4. The Na-Cl water type may result (i) from recharge of Na-Cl rainwater with short residence time in the aquifer, (ii) from dissolution of salt precipitates in the wetland areas or (iii) from seawater intrusion; the latter is the least likely process given the shallow sampling depths. Ca-SO_4 water may result from sulphide oxidation in the wetland areas during dry periods or to re-dissolution of salt efflorescence during rewetting after the dry periods. The general composition concurs with more recent hydrochemical studies by Manzano et al. (2013) who explored the significant processes involved in the complex evolution of different water types in the dune area, which in general are attributed mainly to geogenic processes.

The analyzed groundwater samples of the marshes also present hydrochemical variety, ranging from a large number of samples with Ca-HCO_3 facies through Na-Cl facies to Ca-SO_4 types. The Ca-HCO_3 facies indicates dominance of freshwater in equilibrium with calcite, whereas the Na-Cl facies points to seawater, and the Ca-SO_4 facies may be due to sulphide oxidation or evaporite dissolution.

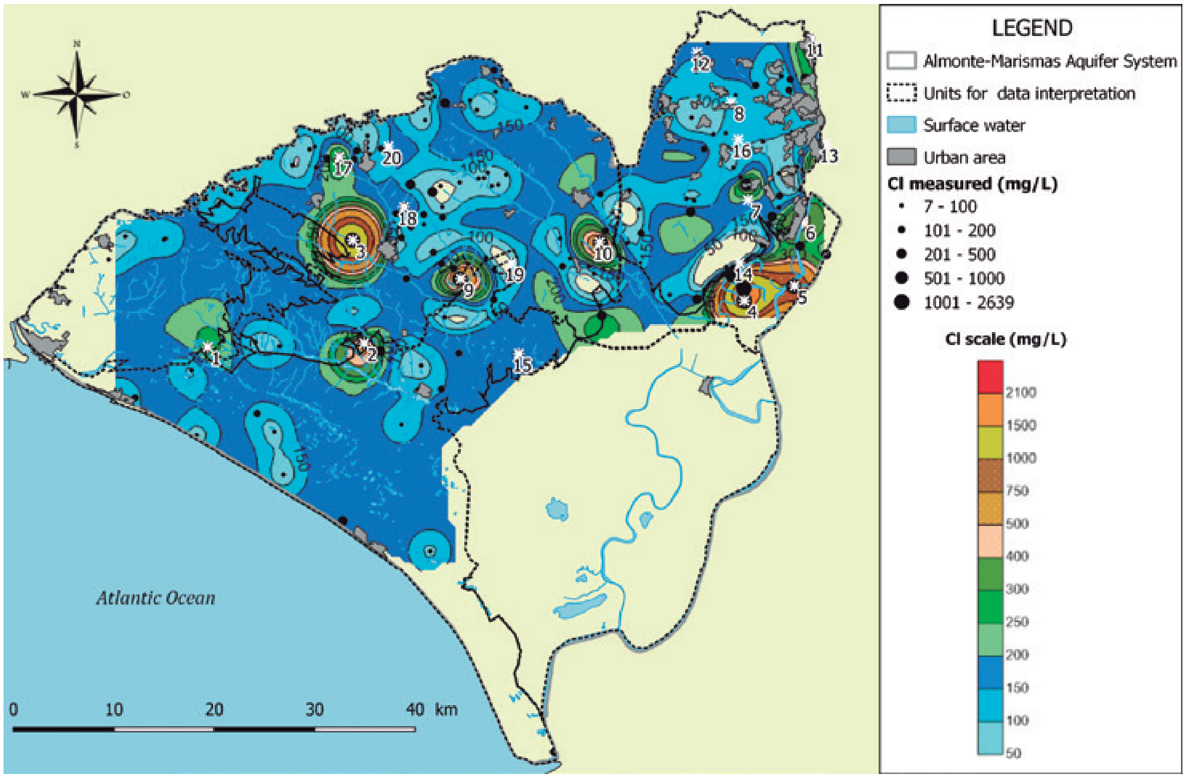

Figure 9. Contour map of chloride concentrations in the shallow part of the aquifer in year 1966. Refer to Figure 2 for geological units. Numbers refer to areas with elevated parameter values obtained by Kriging as compiled in Table 2.

Figura 9. *Mapa de isolíneas de las concentraciones de cloruro en la parte somera del acuífero en el año 1966. Consulte la Fig. 2 para las unidades geológicas. Los números se refieren a áreas con valores de parámetros elevados obtenidos por kriging como se muestra en la Tabla 2.*

The composition of samples from the Aljarafe and Plio-Quaternary units shows a wide spatial variety. This may be related to several of the processes mentioned above, but also to anthropogenic activities. In the vicinity of the marshes, mixing with fossil seawater could be a controlling factor for the elevated amounts of sulphate and chloride detected, whereas the impact of surface water, wastewater and agricultural discharges may be of importance especially close or downstream of urban areas.

Isoconcentration maps of chloride, sulphate and potassium were generated to illustrate the spatial distribution of key indicators for the influence of fertilizers, wastewater and salinization.

Chloride contents

The chloride isoconcentration map is similar to the EC map. The majority of the aquifer (75%) is characterized by chloride concentrations of less than 147 mg/L, while half the aquifer shows concentrations of less than 73.1 mg/L (Fig. 9).

In the aeolian deposits unit, the chloride concentration is quite homogeneous, generally between 100 mg/L and 200 mg/L, with some smaller areas with values below 100 mg/L. Just beyond the limit of the aeolian deposits unit, there are two areas characterized by higher concentrations (200 mg/L and up to 330 mg/L (*1) and a further area with a concentration of up to 880 mg/L (*2). Both points are located near creeks, not visible at map scale.

In contrast, in the northern marshes- zone, an area of high chloride concentration (between 1.000 and 2.632 mg/L) was identified at points *4 and *5, attributed to the impact of the Guadalquivir River (Fig. 9). Moreover, this land was cultivated with non-irrigated crops (Fig. 3) pointing also to the use of fertilizers.

North of this area and independently of the EC values, chloride decreases to concentrations between 0 and 200 mg/L, except for point *6, located in proximity of the marshes and the Guadalquivir River. Results suggest that the high EC values in this area are not due to high chloride concentrations, but maybe a consequence of anthropogenic inputs.

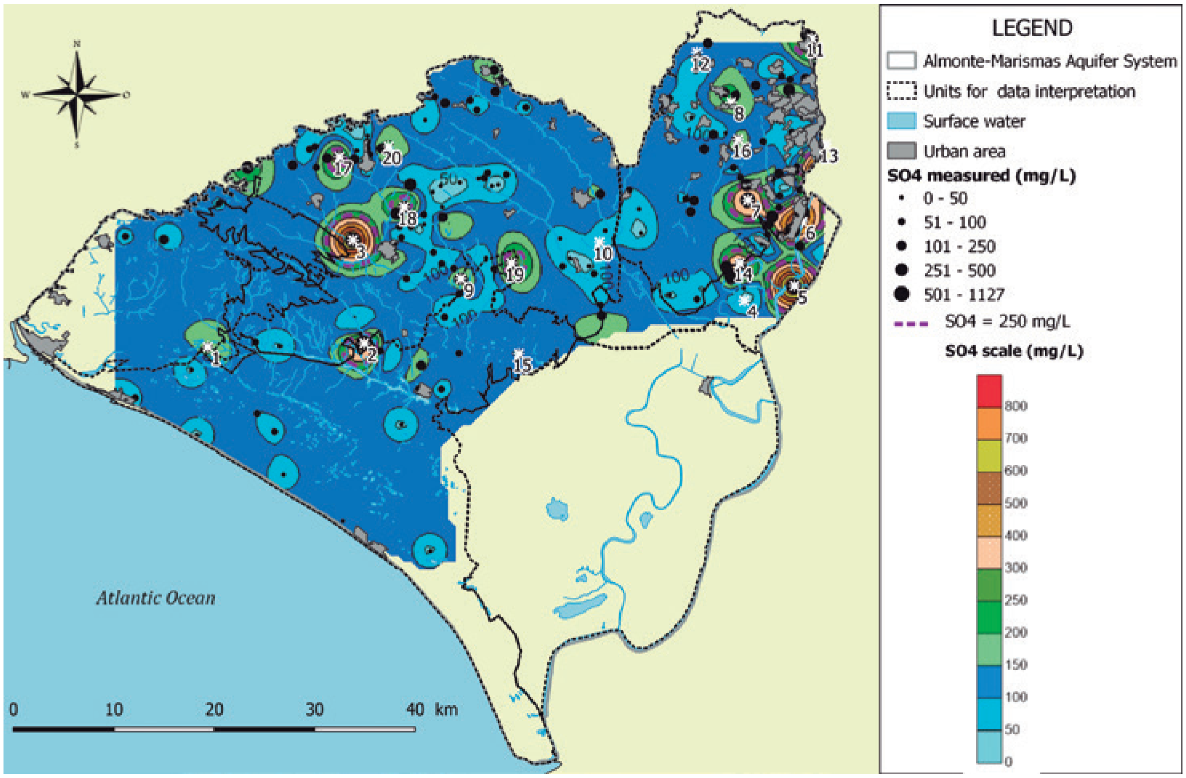

Figure 10. Contour map of sulphate concentrations in the shallow part of the aquifer in year 1966. Refer to Figure 2 for geological details and legend. Numbers refer to areas with elevated parameter values obtained by Kriging as compiled in Table 2.

Figura 10. *Mapa de isolineas de las concentraciones de sulfato en la parte somera del acuífero en el año 1966. Consulte la Fig. 2 para obtener detalles geológicos y leyendas. Los números se refieren a áreas con valores de parámetros elevados obtenidos por kriging como se muestra en la Tabla 2.*

The Plio-Quaternary silty sands sector of the aquifer is also characterized by chloride concentrations that vary from very low to 200 mg/L, except for point *3, which is probably impacted by its proximity to a surface stream and irrigated crops.

Sulphate contents

The presence of sulphate in groundwater can be a consequence of (i) atmospheric contribution, (ii) mixing with seawater, (iii) dissolution of sulphate salts present in the soil (as marine or continental evaporites), (iv) sulphide oxidation, or (v) anthropogenic contamination – for example, from fertilizers applied to crops.

Compared to the chloride isoconcentration maps, the number of points with elevated sulphate concentrations above the recommended threshold value for drinking water of 250 mg/L (BOE 2003, Real Decreto 140/2003) is more elevated (Fig 10). Concentrations are low and quite homogeneous in the aeolian deposits unit, which points to a major influence of rainwater infiltration with absence of sulphate sources in the sands. Location *2 on the border of the aeolian deposits unit concurs with a high chloride concentration and is close to a surface stream.

The northern marshes unit also shows low sulphate concentrations in large proportions, except for the eastern part which is characterized by generally higher values ranging from 400 mg/L up to 1,127 mg/L. Figure 11 shows correlations of analyzed chloride and sulphate concentrations measured in the proximity of the locations listed in Table 2. Samples close to locations *5 and *6 show elevated SO_4/Cl ratios and are probably controlled by the proximity to the Guadalquivir River or fertilizers applied to rice crops. In contrast, the EC measured close to location *4 is almost completely controlled by chloride pointing to a local source of mineralization.

Within the Aljarafe unit, in the area with a denser concentration of agricultural activities (non-irrigated olive grove), EC values correlate with sulphate but only to a minor degree with chloride concentrations, and they show elevated sulphate/chloride ratios (*7, *11, *14) (Figs. 11 and 12).

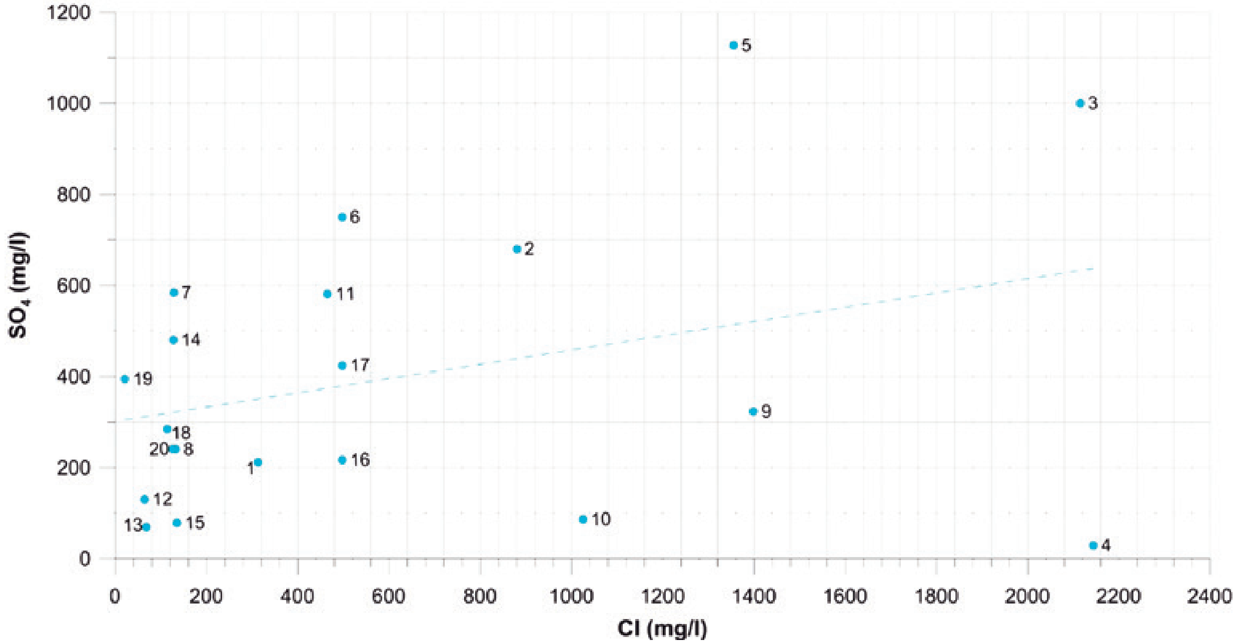

Figure 11. Correlation of measured sulphate and chloride concentrations. Point numbers indicate proximity to respective locations listed in Table 2.

***Figura 11.** Correlación de las concentraciones medidas de sulfato y cloruro. Los números de puntos indican la proximidad a las ubicaciones respectivas enumeradas en la Tabla 2.*

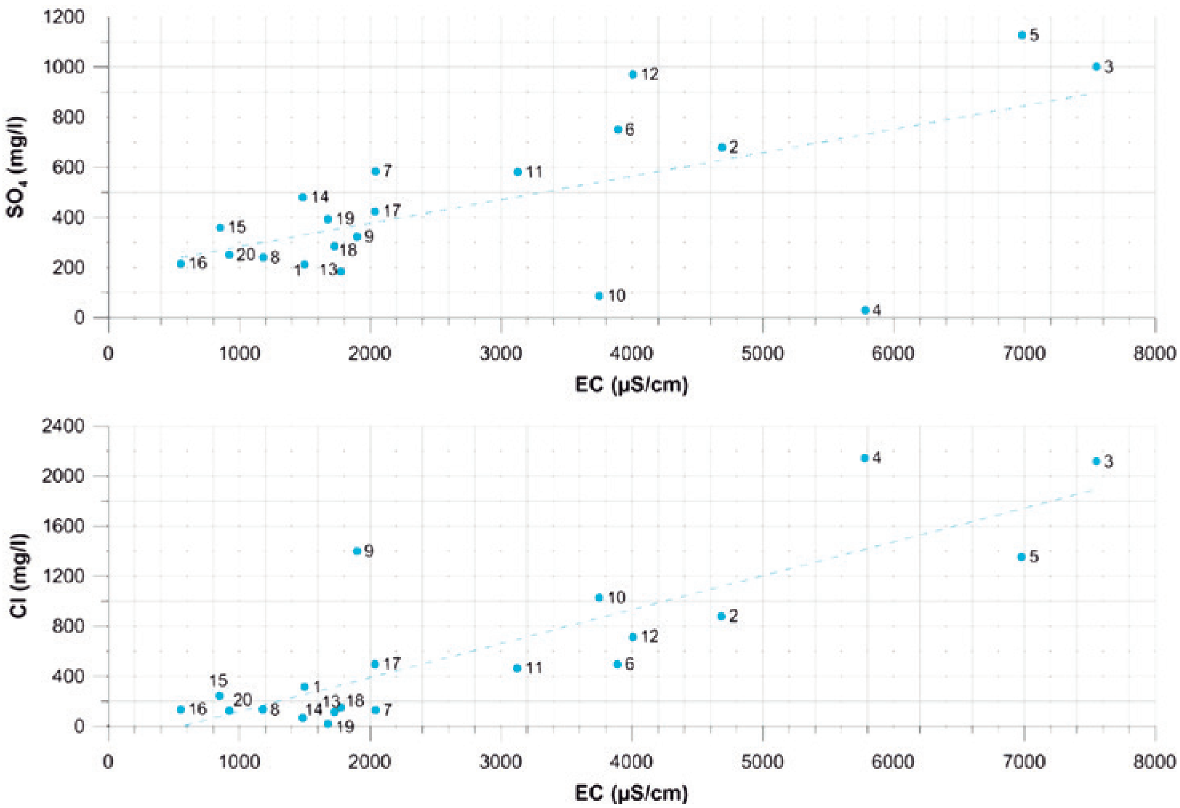

Figure 12. Correlation of measured chloride and sulphate concentrations versus EC. Point numbers indicate proximity to respective locations listed in Table 2.

***Figura 12.** Correlación de las concentraciones medidas de cloruro y sulfato versus CE. Los números de puntos indican la proximidad a las ubicaciones respectivas enumeradas en la Tabla 2.*

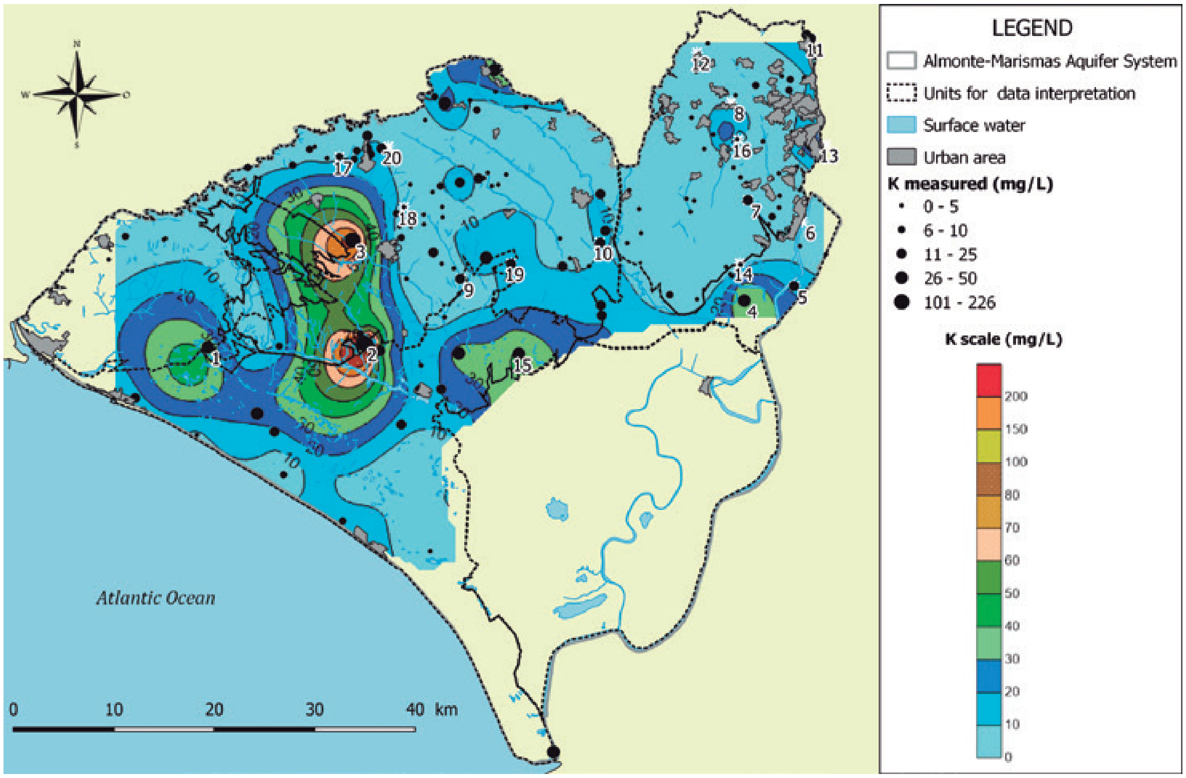

Figure 13. Contour map of the potassium concentrations in the shallow part of the aquifer in 1966. Numbers refer to areas with elevated parameter values obtained by Kriging as compiled in Table 2. Refer to Figure 2 for geological details and legend.

Figura 13. *Mapa de isolineas de las concentraciones de potasio en la parte somera del acuífero en el año 1966. Los números se refieren a áreas con valores de parámetros elevados obtenidos por kriging como se muestra en la Tabla 2. Consulte la Fig. 2 para detalles geológicos y leyenda.*

These sulphate concentrations are also attributed to anthropogenic activities such as fertilizer application. In the remaining part of the Aljarafe unit, concentrations are lower than in the eastern part of the northern marshes, showing values of between 100 mg/L and 400 mg/L. In the north-central area of the Aljarafe unit that is defined by EC values above 1000 µS/cm, the point with the highest chloride concentration (*3) corresponds to the point with the highest sulphate concentration, pointing to the influence of irrigated crops or wastewater in the proximity of streams (see Fig. 3 or URL of detailed land use). The three other points characterized by high sulphate content (*17 ,*18, *19, *20) are located in the sector P.Q. Sediments (Fig. 5) in proximity to streams, mainly non-irrigated crops or not far from urban areas (*17 and *20).

Potassium contents

The principal origins of potassium ions in groundwater are (i) the dissolution from rocks and soils such as feldspar dissolution, (ii) mixing with seawater, and (iii) anthropogenic inputs, such as industrial brines, wastewater or fertilizers. Potassium concentrations in groundwater in the study area are mainly below 11.5 mg/L (75%), with 50% below 3.1 mg /L (Fig. 13).

Points (*1) and (*2) of the aeolian deposits unit are characterized by elevated concentrations, showing 39 and 226 mg/L, respectively, which also concurs with elevated sulphate contents conditioned by proximity to streams (point *2) and small lagoons (point *1). The highest potassium content was measured at location *3, situated close to an urban area in the P.Q. sediment sector, showing also high EC, sulphate and chloride values. Points (*4) and (*5), sited in close proximity to the Guadalquivir River, also have elevated potassium values whereas higher concentrations at point (*15), located in scrubland and forest areas (Fig. 3), cannot be attributed directly to any anthropogenic influence and may be due to mixing with ancient saline groundwater. Point 16* represents a further point with high potassium content, probably due to its proximity to urban areas and creeks.

Conclusions

This study presents the initial hydrochemical status of the Doñana aquifer system in 1966 before intensive agricultural activities started. The parameters EC, Cl, SO4 and K of the year 1966 show a variety of spatial patterns before intensification and suggest five different types of influence: (i) natural lagoon systems, (ii) creeks or rivers, (iii) irrigated areas, (iv) urban areas, and (v) marshes. Our results suggest that anthropogenic activities such as fertilizer use, domestic activities and wastewater in surface streams downstream of urban areas are responsible for elevated parameter values in most of the observation points, although their specific contributions cannot be determined based on the available data of 1966. In the northern marshes area, elevated geogenic salinity may also contribute to high parameter concentrations besides fertilizer use for intensive irrigated crop cultivation and the proximity to the Guadalquivir River. Whereas EC, Cl and SO4 distributions are similar, K shows a distinct pattern with a clear maximum in the P.Q sediment unit attributed in a first approach to fertilizers and wastewater distributed by creeks. The fact that other areas with even higher population density and wastewater volumes, such as the eastern part of the Aljarafe unit do not show these elevated potassium concentrations points to the use of special fertilizers or specific local contaminations as principal cause. Although the overall mineralization is mainly controlled by chloride, concentrations of chloride and sulphate are generally correlated, showing an important variability of chloride sulphate ratios. Nonetheless, the available data do not indicate a specific link of chloride-sulphate ratios to land use or geological units.

Comparison with more recent data of the period from 1982 to 2007 was performed but the datasets did not allow us to form any sound conclusions due to the change of piezometer depths and locations and therefore these results have not been documented here.

References

BOE. 2003. Real Decreto 140/2003, de 7 de febrero, por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano.

Bustamante, J., Aragonés, D. and Afán, I. 2016. Effect of Protection Level in the Hydroperiod of Water Bodies on Doñana's Aeolian Sands. Remote Sensing, 8(10), 867.

Camprubí, L. 2016. La Naturaleza no existe: conservacionismos y relaciones internacionales en Doñana. Arbor. 192. 344pp

Custodio, E. and Palancar, M. 1995. Las aguas subterráneas en Doñana. Revista de Obras Públicas, Madrid 142 (3340), 31–535

Custodio, E. 2009. Las aguas subterráneas en Doñana: Aspectos ecológicos y sociales. Agencia Andaluza del Agua. 246pp

Davis, John C. 2002. Statistics and Data Analysis in Geology, Third edition. John Wiley & Sons, 428-437.

Day, B. and Nightingale, H (1984). Relationships between Groundwater Silica, Total dissolved solids and specific electric conductivity. Groundwater (22), 80–85.

De Stefano, L. and Llamas, M. R. 2012. Water, agriculture and the environment in Spain : can we square the circle? CRC Press. 338pp

Delgado, F., Lozano, E., Manzano, M. and Custodio, E. 2001. Interacción entre las lagunas freáticas de Doñana y el acuífero según los iones mayoritarios. In: Medina, A., Carrera, J. and Vives L. (eds.), Las Caras del Agua Subterránea, Serie Hidrogeología y Aguas Subterráneas 1-2001. IGME, 111-117.

Edmunds, W. M. and Sans, P (ed.). 2008. Natural groundwater quality. Blackwell Pub. 488pp

FAO. 1972. Proyecto piloto de utilización de las aguas subterráneas para el desarrollo agrícola de la cuenca del Guadalquivir. Anteproyecto de transformación de la zona de Almonte-Marismas (margen derecha): informe técnico. 1 Informe inédito. Food and Agricultural Organization. Naciones Unidas, Madrid, 1-534.

Fitts, C. R. 2002. Groundwater science. Academic Press. 692pp

Gascó, C., Antón, M. P., Pozuelo, M., Clemente, L., Rodríguez-Ramírez, A., Yañez, C., González, A. and Meral, J. 2006. Distribution and inventories of fallout radionuclides (239+240Pu, 137Cs) and 210Pb to study the filling velocity of salt marshes in Doñana National Park (Spain). Journal of Environmental Radioactivity, 89(2), 159–171.

Geboy, N. J., Schroeder, K.T. and Zupancic, J.W. 2006. Summary of Inorganic Compositional Data for Groundwater, Soil-Water, and Surface- Water Samples at the Headgate Draw Subsurface Drip Irrigation Site, Johnson County, Wyoming.

Goy, J.L., Rodríguez-Vidal, J., Bardají, T., Zazo, C., Borja, F. and Dabrio, C.J. 2014. Coastal Dunes and Marshes in Doñana National Park. In: Gutiérrez F, Gutiérrez M (eds) Landscapes and landforms of Spain. Springer, Dordrecht, pp 239–248.

Guardiola-Albert, C., García, N., Mediavilla, C. and Martín Machuca, M. 2009. Gestión de los recursos hídricos subterráneos en el entorno de Doñana con el apoyo del modelo matemático del acuífero Almonte-Marismas. Boletín Geológico y Minero. 120 (3): 361–37

Guardiola Albert, C. and Jackson, C. R. 2011. Potential impacts of climate change on groundwater supplies to the Doñana wetland, Spain. Wetlands, 31(5), 907–920.

Hiscock, K. M. 2005. Hydrogeology : principles and practice. Blackwell. 311pp.

Iglesias, M. 1999. Caracterización hidrogeoquímica del flujo del agua subterránea en El Abalario, Doñana, Huelva. Tesis Doctoral, ETSICCPB, Universidad Politécnica de Cataluña, Barcelona. 254pp.

Juárez, I., Custodio, E., Manzano, M. and Higueras, H. 2012. Relación aguas superficiales–aguas subterráneas y recarga del acuífero de Los Sotos, Doñana, España. Simposio del Agua en Andalucía., Cádiz. IGME, 1479–1489

Lozano, E., Coleto, C., Calabor, M. and Custodio, E. 2002. Saline Waters in the Coastal Area of the National Park of Doñana (SW of Spain) in Absence of Saline Water Intrusion. Hydrology & Ecology Section, Faculty of Civil Engineering and Geosciences, Delft University of Technology, 6–10.

Lozano, E. 2004. Las aguas subterráneas en los Cotos de Doñana y su relación con las lagunas. Tesis Doctoral, ET-SICCPB, Universidad Politécnica de Cataluña, Barcelona.

Lozano, E., Delgado, F., Manzano, M., Custodio, E. and Coleto, C. 2005. Hydrochemical characterisation of ground and surface water in 'the Cotos' área, Doñana National Park, southwestern Spain. In: Bocanegra, E.M, Hernandez, M.A. and Usunoff, E. (ed.)s Groundwater and Human Development. International Association of Hydrogeologist, Selected Papers on Hydrogeology, 6, Balkema, 217-231.

Manzano, M, Custodio, E., Loosli, H., Cabrera, M.C., Riera, X and Custodio, J. 2001. Paleowater in coastal aquifers of Spain. Palaeowaters in Europe: Evolution of Groundwater since the Pleistocene. Geological Society Special Publication, (189). London. 107–138.

Manzano, M., Custodio, E., and Colomines, M et al. 2005. El fondo hidroquímico natural del acuífero de Doñana. V Iberian Congress of Geochemistry/ IX Spanish congress of Geochemistry, Soria.

Manzano, M., Custodio, E., Iglesias, M. and Lozano, E. 2008. Groundwater baseline composition and geochemical controls in the Doñana aquifer system (SW Spain). Natural Groundwater Quality. W.M. Edmunds y P. Shand (Eds.). Blackwell.Publishing 216-232.

Manzano, M., Custodio, E., Higueras, H., Puig, R. and Soler A. 2009. Influencia de la gestión del acuífero sobre los humedales del manto eólico de Doñana Boletín Geológico y Minero, 120(3), 377–392.

Manzano, M., Custodio, E., Lozano, E. and Higueras, H. 2013. Relationships between wetlands and the Doñana coastal aquifer (SW Spain). In Groundwater and Ecosystems. Taylor & F, 169–182. London, UK.

Muñoz-Reinoso, J. C. and De Castro, F. J. 2005. Application of a statistical water-table model reveals connections between dunes and vegetation at Doñana. Journal of Arid Environments, 60(4), 663–679.

Ojeda, J.F. 1992. Políticas forestales y medioambiente en Doñana y su entorno. Agricultura y Sociedad (65), 303-357.

Olías, M., González, F., Cerón, J., Bolívar, J., González-Labajo, J. and García-López, S. 2008. Water quality and distribution of trace elements in the Doñana aquifer (SW Spain). Environmental Geology, 55(7), 1555–1568.

Oliver, M. A. and Webster, R. 1990. Kriging: a method of interpolation for geographical information systems. International Journal of Geographical Information Systems, 4(3), 313–332.

Oliver, M. A. and Webster, R. 1992. Sample adequately to estimate variograms of soil properties. Journal of Soil Science, 43(1), 177–192.

Plata, A., Boanza, E. and Silgado, A. 1984. Hidrología isotópica de las aguas subterráneas del Parque Nacional Doñana y zona de influencia. Cuadernos de Investigaciones, C7, CEDEX. Madrid: 1–139.

Poncela, R., Manzano, M. and Custodio, E. 1992. Medidas anómalas de tritio en el área de Doñana Hidrogeología y Recursos Hidráulicos (7), 351–365.

Pozo, M., Carretero, M.I., Ruiz, F, Rodríguez Vidal, J., Cáceres, L.M. and Abad, M. 2008. Caracterización mineralógica de facies sedimentarias de edad Pleistoceno superior-Holoceno en el Parque Nacional de Doñana (Huelva). Implicaciones paleoambientales. Geo-Temas 10, 953–956.

Rodríguez Ramírez, A. 1998. Geomorfología del Parque Nacional de Doñana y su entorno. Autonomous Organism National Parks. 146pp

Ruiz, F., Clemente, L., Yáñez, C. and Abad, M.. 2004. Late Holocene evolution of the southwestern Doñana National Park (Guadalquivir Estuary, SW Spain): A multivariate approach. Palaeogeography, Palaeoclimatology, Palaeoecology, 204(1–2), 47–64.

Ruiz, F., Rodríguez Ramírez, A, Caceres, L.M., Rodríguez Vidal, J., Carretero, M.I., Abad, M., Odias, M. and Pozo, M. 2005. Evidence of high-energy events in the geological record: Mid-Holocene evolution of the southwestern Doñana National Park (SW Spain). Palaeogeography, Palaeoclimatology, Palaeoecology, 229(3), 212–229.

Salvany, J. M. and Custodio, E. 1995. Características litoestratigráficas de los depósitos Plio-Cuaternarios del bajo Guadalquivir en el área de Doñana: implicaciones hidrogeológicas. Revista de la Sociedad Geológica de España, 8, 21–31.

Salvany, J. M., Larrasoaña, J., Mediavilla, C. and Rebollo, A. 2011. Chronology and tectono-sedimentary evolution of the Upper Pliocene to Quaternary deposits of the lower Guadalquivir foreland basin, SW Spain. Sedimentary Geology, 241(1), 22–39.

Serrano, L. and Serrano, L. 1996. Influence of Groundwater Exploitation for Urban Water Supply on Temporary Ponds from the Doñana National Park (SW Spain). Journal of Environmental Management, 46(3), 229–238.

Serrano, L., Reina, M., Martín, G., Reyes, I., Arechederra, A., León, D. and Toja, J. 2006. The aquatic systems of Doñana

(SW Spain): Watersheds and frontiers. Limnetica, 25(1–2), 11–32.

Suso, J. and Llamas, M. R. 1993. Influence of groundwater development on the Doñana National Park ecosystems (Spain). J. Hydrol, 141(14), 239–269.

Tortosa, G., Correa, D., Sánchez-Raya, J., Delgado, A., & Sánchez-Monedero, M. and Bedmar, E. 2011. Effects of nitrate contamination and seasonal variation on the denitrification and greenhouse gas production in La Rocina Stream (Doñana National Park, SW Spain). Ecological Engineering, 37(4), 539–548.

Trick, T. and Custodio, E. 2003. Hydrodynamic characteristics of the western Doñana Region (area of El Abalario), Huelva, Spain. Hydrogeology Journal, 12, 321-335.

Sacks, L.A., Herman, J.S., Konibow, L.F., and Vela, A.L. 1992. Seasonal dynamics of groundwater-lake interactions at Doñana National Park, Spain. Journal of Hydrology, 136, 123–154.

Yang, Q., Wang, L., Ma, H., Yu, K., Martín, J.D. 2016. Hydrochemical characterization and pollution sources identification of groundwater in Salawusu aquifer system of Ordos Basin, China. Environmental Pollution, 216, 340–349.

Zorrilla-Miras, P., Palomo, I., Gómez-Bagghetun, E., Martín-López, B., Lomas, P. and Montes, C. 2014. Effects of land-use change on wetland ecosystem services: A case study in the Doñana marshes (SW Spain). Landscape and Urban Planning, 122, 160–174.

Zunzunegui, M., Díaz Barradas, M.C., Ain-Lhout, F., Clavijo, A. and García Novo, F. 2005. To live or to survive in Doñana dunes: Adaptive responses of woody species under a Mediterranean climate. Plant and Soil, 273(1–2), 77–89.

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