PRELIMINARY OUTLOOK OF SALTWATER INTRUSION CONDITIONS IN THE DOÑANA NATIONAL PARK (SOUTHERN SPAIN)

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ABSTRACT

The Doñana area is a natural region in southern Spain that comprises the largest wildlife reserve of Europe. Around the National Park, which includes the large marshes of the Guadalquivir delta and estuary, important agricultural developments and a large touristic resort draw large quantities of groundwater. The groundwater system has been altered and consequently some groundwater discharges important for wildlife has been reduced, groundwater levels lowered and the flow pattern changed. Saline surface and groundwater is found in some areas and as a remnant of evaporation in summer, when most of the marsh dries up. But also residual marine water is found in the sediments below the marsh. This paper tries to show the usefulness of chemical ratios to identify the origin of saline water and its movement in the ground. No simple rule for a preliminary outlook is found, in part due to the fact that the source of salinity, both for freshwater and saline water, is marine salts, directly or airborne over a short distance. The ratios $r_{Na}/r_{Cl}$, $r_{SO_4}/r_{Cl}$, $r_{Na}/r_K$, $r_{Mg}/r_{Cl}$, $r_{Mg}/r_{Ca}$ ($r=\text{meq}/l$) are considered since it is already known that the ratio $r_{Cl}/r_{Br}$ does not provide useful differences. High evaporation in ponds and drying wetlands produces a loss of $SO_4^{2-}$ and $K^+$, but no clear trend in $Na^+$, $Ca^{2+}$ and $Mg^{2+}$. Displacement of saline water of marine origin into fresher water sediments can be seen through a decrease of $Na^+$ and still more important of $K^+$, and an increase of $Ca^{2+}$ and some $Mg^{2+}$. Generally it is seen that the confined aquifer and the aquitard below the marsh are subjected to saline intrusion.

INTRODUCTION

The Doñana National and Natural Parks constitute the most important natural reserve of Europe. They are placed in Southern Spain, between Cadiz, Sevilla and Huelva (fig. 1), bordering the Atlantic Ocean. It is an area relatively well preserved due to the poor sandy soils and large temporary marshes, which in the past were a highly hostile environment for
Fig. 1.- Situation map of Doñana and depth to the clay basement (Menanteau, 1980).
human settlements except for hunting (it was one of the preferred areas of Europe), fishing and extensive cattle rising (the ancestors of the first American "cowboys" were from this area). The Doñana National Park is a RAMSAR and UNESCO-MAB site, an environmental priority for the European Community and theoretically protected by a series of local, national and international laws and agreements.

In the last decades large wetland areas have been converted into rice paddies, irrigated lands and orchards. A large irrigation project – the Almonte-Marismas Plan – now mostly bankrupt, was promoted and financed with public funds, and a large, although poorly conceived, touristic resort (Matalascanas) was installed along 4 km of the National Park shore, and is capable of holding up to 200,000 persons in the summer peak. The pressure for mass development continues since this is an easy expansion area for the Seville large human concentration and a source for short-term income for local inhabitants and benefits for developers and speculators. This pressure for land transformation clashes with the natural reserve preservation.

The Water Authority with competence in the area has been slow and biassed in its activities in the area. The degree of monitoring and study has been largely insufficient according to the importance of the area.

In relatively early works, Herteaux (1970) and Duque (1977) made early warnings on the conservation problems of Nature, with emphasis in those derived from the intensive use of groundwater for irrigated agriculture around the National Park periphery, and also for human supply of the fastly expanding urban centres. Later, an international group of experts made an evaluation of the situation (Hollis et al, 1989), and a very recent one has been just finished (Castells et al., 1992).

The existence of saline water in the aquifers was detected during the groundwater studies for the new large irrigation plans (FAO, 1970; 1975) and during the drilling of the wells, but only a general description of salinity was provided. The first detailed hydrogeological studies are those of IGME (1983), Llamas et al. (1987), Vela (1984) and Tenajas (1984), which provide chemical analysis of surface and groundwater, as well as the study of Baonza et al. (1982), which put the emphasis on environmental isotopes. The Doctoral Thesis of Rodriguez-Arévalo (1988) deal with the porewater salinity distribution and behaviour in two deep boreholes in the wetland area, although the detailed hydrochemical study has not been included. Later work (Custodio et al., 1992, Manzano et al., 1991) also contribute new data, although the emphasis was placed on the sand areas instead of the wetland areas; the area of the main touristic urban area of Matalascanas has been considered in more detail than in the other works, as a support to the drilling of point boreholes by the Geological Service of the MOPT.

The objective of this paper is a first discussion of salinity sources, salt water intrusion and risk of aquifer salinization by using data from other works. Simple study tools are used and discussed.
CHARACTERISTICS OF THE AREA

The area of what is now called Doñana region (Castells et al., 1992) is a coastal sedimentary basin infilled mostly by Pliocene sediments. They rest on mostly impervious Miocene materials which outcrop at the northern boundary and plunge towards the South, where they attain 150 to 200 m below sea level at the present coastline (fig. 1). The Pliocene sediments consist of a basal formation which includes old fluvial and beach terraces, and mostly sandy material with interlayerings grading from fine sand to clay; close to the coast, medium-size, almost pure silica, iron hydroxide-clad sands dominate, and they extend up to the coast. From Matalascañas to Mazagón (Huelva) they form a sea cliff. Quaternary sand dunes exist near the coast and a thin layer of loose sand covers most of the western area, concealing the weathered top Pliocene sands, which form a kind of fragipan (increase of iron particles and silt-sized material) and contain discontinuous lithoplinthite pans formed near old drainage valleys by outflowing, iron-transporting groundwater.

The eastern sector has been subjected to subsidence and then a bay was formed into which the Guadalquivir river discharged, contributing sediments to infill it. Up to 200 m of sands and silt-clays can be found (fig. 2). The area was closed by a sand spit leaving a half closed bay still existing at Roman times (Menanteau, 1980). During historical times the infilling process has transformed the area into a large flatland slightly above mean sea level, with only decimetric land elevation changes that correspond to a subtle but complex system of drainage features and tidal channels, currently modified by human intervention. This flat area, the Marisma (marsh), get inundated in normal winters by rainfall and mainly by the inflow of some tributaries (Guadiamar, Rocina stream system). Then there is a layer of 0.3 to 0.6 m of water. The marsh drains to the Guadalquivir and dries up by evaporation in summer, except for a few shallow depressions ("lucios") and the area affected by tides, now isolated by means of sluices. The marshy wetland is separated from the sea by the sand spit and a huge moving dune chain.

A few scattered, small groundwater outflows ("ojos") are found in the wetland, sometimes with quick-sand holes associated. They are used by the livestock and wild animals in dry periods. Along the wetland periphery the sand formations discharge groundwater, forming small creeks, seeps and phreatophyte plant belts. They are essential to maintain some vegetal species, the gallery forest and to provide drinking water and food to the non-migratory wildlife during the dry season. There is a major groundwater drainage of the sand areas through the Rocina valley, which runs almost parallel to the coast and feeds the wetlands with almost permanent water, and sustains a large and rich gallery forest. Other smaller streams with similar conditions have been destroyed to establish the Almonte-Marismas irrigated agricultural project. All of them are now badly affected by groundwater abstraction, as well as the other outflows and the Rocina itself (Suso, 1988; Suso and Llamas, 1991; Llamas, 1990; Sahuquillo et al., 1991; Rodríguez-Arévalo and Llamas, 1986; Custodio, 1992).

The hydrogeological characteristics of the sand areas allow for the water table to be close to the land surface in many areas and then a series of small, perennial and temporal lagoons exist, which are an essential part of the ecosystems as well, especially for waterfowl.
Fig. 2.- Representative cross section of the Doñana area after reinterpretation of well profiles from the Almonte-Marismas Plan (Salvany, 1991). 1.- Gravels; 2.- accumulation of marine bivalve shells; 3.- sand, sandstone, silt; 4.- sandy clay and sandy marl; 5.- clays and marls.
SALINE WATER IN DOÑANA

Groundwater salinity in Doñana is dominated by marine airborne salts, the dominantly siliceous nature of soil, the climatic conditions and the poorly developed soil. The result is low total dissolved solids, slightly acidic groundwater, dominantly of the sodium chloride type (Manzano et al., 1991), except when the wells attain the basal sediments or are in recent sand dunes, where carbonates are present and a calcium bicarbonate facies develop. Normal chloride contents is about 30 to 60 mg/l, and this characterizes inflows form other local continental sources as well. But there is saline water in some places and under some circumstances.

In the wetland there is surface saline water which is the result of freshwater evaporation and uptake of salts from previous dry periods, with possible inflow of sea water from the Guadalquivir river estuary in some areas and during high tide. The situation is aggravated when the drainage of agricultural lands is added. After evaporation concentrations may be greater than present seawater (Tenajas, 1984). A similar process can be seen in some lagoons (Sacks et al., 1992) in the sandy areas.

The small outflows (“ojos”) in the marshland have saline water as well (Baonza et al., 1982) although it is not clear if it is due only to evaporation of local groundwater, or to the mix of groundwater with highly evaporated surface water resulting from stagnation of flood water from the previous wet period, or to saline surface water recharged into the aquifer when the marsh get inundated.

The lower part of the marshland sediments constitute a semiconfined aquifer in continuity with the aquifer of the sand areas. The vertical permeability is small (Rodríguez et al., 1982) and then most of the possible groundwater transfer form the sandy areas is discharged along the periphery. Only a small fraction moves into the confined aquifer and discharges upwards into the marshland (Yagüe and Llamas, 1984). Its contribution was probably unnoticeable in the past, when the freshwater head potential was greater than land surface elevation. Currently, groundwater exploitation for irrigation has halted this process due to the general groundwater drawdown in this aquifer. This slow process has flushed out the possible connate saline water in a large part of the deep aquifer, but not in the SE part, where salinity of well water increases up to values about 1/3 of sea water. The salinity distribution is poorly known.

After some data and information from the farmers, the salinity fronts seem to be moving towards the North after intensive groundwater exploitation started (about 1980) and perhaps to the East as well, although information is poor. After data from the IGME (1983), groundwater head below most of the marshland was about 2 m above mean sea level, and then no fresh groundwater flow towards the possible offshore outcrops of the aquifer is possible was the aquifer depth is taken into account. The existence of saline water seem the result of unflushed marine water.
METHODOLOGY FOR A PRELIMINARY CHEMICAL SCREENING

It is well known that ion exchange processes between groundwater and the aquifer material produce characteristic signals useful to identify salinity evolution (Schoeller, 1962; Custodio and Llamas, 1976, sect. 10 and 13; Custodio and Bruggeman, 1987; Falkland and Custodio, 1991; Beekman, 1991). Also, the existence of organic matter in lacustrine, bay and estuarine deposits favors sulphate reduction. When carbonate material is present its dissolution (or precipitation) contribute to changes in calcium ion concentration, thus complicating the study (Bosch and Custodio, 1992). The different steps for a summary preliminary study of saline waters (more than 0.5 g/l Cl⁻) are described below. When a “r” precedes a chemical expression, it mean the value is given in meq/l.

All values of the ratio rCl/rBr are close to those of marine water, about 650. Considering the uncertainty in the ratio due to analytical inaccuracies, even for rainfall and freshwater, it is not usefull in this case to identify the origin on salinity. This agrees to some extent with the marine origin of salts, direct or airborne at close distance. Then this ratio will not be commented further.

The study of the ratio rNa/rCl is a first step to detect possible cation exchange processes. The normal value for seawater is 0.87 and for freshwater may vary in wide range, generally from 0.7 to 1.2, mostly reflecting soil weathering processes. When freshwater displaces saline water the ratio increases and conversely when saline water is invading the freshwater part of an aquifer. The process is more clear when water salinity is not too high, especially in the front part of the displacement zone. For more saline water the deviations are smaller, although the absolute ion mass exchanged may be large. Na⁺ is exchanged against Ca²⁺, mainly, but since Ca²⁺ is subjected to increase/decrease by calcite dissolution/precipitation, changes in the rCa/rCl ratio are more complex to study. More detailed chemical studies are needed that consider the difference between the actual water composition and the theoretical (closed system) mixing of two end-member waters.

The ratio rNa/rK is affected by cation exchange as well, although in a less straightforward way than the rNa/rCl. The normal value for sea water is about 47. For freshwater it may vary between 10 and 50. Generally K⁺ is hold stronger into the solid fase exchange sites than Na⁺ (Wayman, 1963; Matthes, 1982; Garrels and Christ, 1965). In a freshening process it is expected that the ratio will normally increase. It decreases when the process is towards salinization.

Since Mg²⁺ is hold looser than Ca²⁺ and is less affected by solution/precipitation when only calcite is involved, the ratio rMg/rCl may be useful to identify the trend towards sea water. The value for sea water is 0.19. In freshwater it is commonly much larger.

The ratio rMg/rCa may be useful to know the behaviour of Ca²⁺ if Mg²⁺ behaves as less reactive than Ca²⁺. The normal value for sea water is 5 and in freshwater commonly varies between 0.2 and 2. The exchange of Ca²⁺ against Na⁺ is reflected in some way in the ratio rMg/rCa, as well as precipitation/dissolution processes. In a freshening process, since Ca²⁺ is adsorbed preferently, the ratio should increase, and conversely in a hardening process.
The value of the ratio $r_{SO_4}/r_{Cl}$ for sea water is 0.10 and generally is higher for freshwater since some sulphate is added, of continental or artificial origin, to the airborne salts. Then, normal mixtures of fresh and sea water must have a value greater than 0.10, asymptotically attaining this value as salinity increases. But when sulphate is involved in reducing reactions the ratio falls to very small values.

The use of the $HCO_3^-$ anion has been avoided due to its complex behaviour and not being directly involved in ion exchange processes and salinization.

**CHARACTERISTICS OF SALINE WATER IN DOÑANA**

First, the general characteristics of surface water is considered, and then saline aquifer water and porewater in aquitards.

The lagoon system of Dulce-Santa-Olalla-Pajas is along an old valley tributing to the marshland at its western boundary (between the ecotones of La Vera and La Retuerta), now interrupted by eolian sands. They are at a decreasing elevation. This originally freshwater system is sustained by groundwater that evolves downstream to saline water (3.5 g/l Cl$^-$) (Sacks et al. 1992). The $r_{Na}/r_K$ ratio grows from 30 to 50 and the ratio $r_{SO_4}/r_{Cl}$ is sometimes very small (less than 0.01). The ratio $r_{Na}/r_{Cl}$ (0.85 to 0.95) is close to that of seawater, with a tilt towards a slight excess of Na$^+$. The value of $r_{Mg}/r_{Cl}$ is not essentially different from sea water although changes from slightly higher for freshwater to equal or lower for saline water, while the ratio $r_{Mg}/r_{Ca}$ increases first and then decreases, always inside the range 1.1 to 3.5, below the seawater value. The degree of evaporation may be very high as shown by the water isotope displacement (fig. 3). The slope is that of evaporation from surface water in a relatively humid environment (closeness to the sea).

As deduced from data collected by Tenajas (1984), surface water in the marshland shows a low $r_{Na}/r_K$ ratio (less than 20) only near freshwater inflows along the western boundary (ecotone of La Vera) of the wetland, that in part coincide with some deficiency in Na$^+$ and high $r_{Mg}/r_{Cl}$. High values or $r_{Na}/r_K$ (greater than 80, up to 110) are found close to the Palacio de Doñana (ecotone between La Vera and La Retuerta) and along the northern boundary. There is a tendency to coincide this high values with low $r_{SO_4}/r_{Cl}$ (less than 0.05), associated with areas rich in organic matter and with high salinity, but not necessarily very high salinity. This also coincides with a slight excess of Na$^+$ relative to seawater and a low $r_{Mg}/r_{Cl}$ ratio, but not necessarily a high $r_{Mg}/r_{Ca}$ ratio. Most waters have $r_{Mg}/r_{Cl}$ not far for 0.20. Since environmental isotope data is not available but for two "lucios" (fig. 3), it is not easy to differentiate chemically between salinity due to mixing with seawater and highly evaporated freshwater, but it seems probable that freshwater concentration by evaporation is generally the likely process; the $r_{Mg}/r_{Cl}$ ratio is perhaps the most indicative. It is worth noting that all data refer only to two surveys (April and June, 1984). More saline waters can be expected at more advanced stages of drying. It is known that shallow porewater in the marsh sediment can be more saline than seawater (Rodríguez-Avévalo, 1988; Rodríguez et al., 1992). The dissolution of salts from previous total drying stages plays a role.

Samples from the small groundwater outflows ("ojos") in the marshland were taken during
Fig. 3.- Oxygen-18/deuterium plot of waters from the Marisma (marsh) and surroundings, and evolution trends (after Baonza et al., 1982; Plata et al., 1983) and porewaters from the B1 (fig. 4) borehole in the Marisma (Rodríguez-Arévalo, 1988).
a dry summer (Baonza et al., 1982) and some of them show a clear and large water isotope deviation from the World Meteoric Line due to surface evaporation (fig. 3). Salinity ranges between 0.8 and 21 g/l Cl. The main chemical characteristics are:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Range (*)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>rNa/rCl</td>
<td>0.81 to 0.97</td>
<td>nil to slight Na⁺ excess</td>
</tr>
<tr>
<td>rSO₄/rCl</td>
<td>&lt;0.01 to 0.06</td>
<td>sulphate reduction</td>
</tr>
<tr>
<td>rNa/rK</td>
<td>25 to &gt;120</td>
<td>increasing with salinity</td>
</tr>
<tr>
<td>rMg/rCl</td>
<td>0.06 to 0.31</td>
<td>no clear trend. Low values for the most saline samples (0.06 to 0.13)</td>
</tr>
<tr>
<td>rMg/rCa</td>
<td>0.7 to 2.2</td>
<td>no clear trend</td>
</tr>
</tbody>
</table>

(*) Excluding the lowest and highest value. 9 samples

Isotopically these waters are the result of evaporation of normal local groundwater, with a slope of 6.4, typical of surface evaporation under a relatively wet environment, as for the lagoons. Any of the chemical ratios shows this fact clearly except the low rMg/rCl values for the most saline samples. The increase of rNa/rK with salinity and the sulphate reduction coincide with the organic activity in the ponded areas around these outflows.

Water isotopic data from deep wells in the marshland with some salinity (from 0.5 to 7 g/l Cl⁻) plot close to the same evaporation line, which coincides with the freshwater seawater mixing line. Thus a visual differentiation cannot be done but correcting for the possible seawater contribution possible evaporation effects fade out, which is not the case for the water from the "ojos". The most relevant chemical ratios are:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Range (*)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>rNa/rCl</td>
<td>0.5 to 0.8</td>
<td>systematic Na⁺ deficit, tending to be greater for the less saline samples</td>
</tr>
<tr>
<td>rSO₄/rCl</td>
<td>&lt;0.01 to 0.02</td>
<td>clear sulphate reduction</td>
</tr>
<tr>
<td>rNa/rK</td>
<td>30 to 450</td>
<td>low values for the less saline water; saline waters more than 40 without clear trend</td>
</tr>
<tr>
<td>rMg/rCl</td>
<td>0.14 to 0.24</td>
<td>no clear trend</td>
</tr>
<tr>
<td>rMg/rCa</td>
<td>0.05 to 1.3</td>
<td>no clear trend; relatively low values for the more saline samples</td>
</tr>
</tbody>
</table>

(*) Excluding the lowest and highest value. 12 saline water samples

The systematic Na⁺ deficit show a possible hardening process with agrees with the low rMg/rCa ratio for a rMg/rCl ratio close to or slightly higher than the seawater value. The high rNa/rK values of some samples agrees with the hardening process, although some biological processes may also be involved in the K⁺ decrease. Nothing is against the hypothesis of mixing of freshwater with seawater and the dominant process seem to be saline encroachment. Almost all the samples (10) are from 1981 and only 2 from 1989. In 1981 the intensive exploitation of the aquifer was starting, but most of the operating wells at that time were in the northern sector, not far from the saline part of the marshland deep confined aquifer. The fact that the
Fig. 4.- Situation of boreholes B1 and B2, and lithological profile of B1.
less saline water tend to present the greatest Na\textsuperscript{+} deficit agrees with what can be expected: that the advancing front is more affected by cation exchange.

Only a few samples presenting some salinity correspond to shallow wells at the marsh periphery or to the coastal sands. When compared, they seem chemically very different, as the groundwater environment is diverse as well. No further comments are worth.

Porewater from two boreholes B1 and B2 shown in figure 4 has been studied (Rodríguez-Arévalo, 1988). The study of the chemical analyses included in this work show the following chemical results (see figure 5):

<table>
<thead>
<tr>
<th>Ion or ratio</th>
<th>Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (g/l)</td>
<td>0.9 to 63</td>
<td>the highest salinity at shallow depth</td>
</tr>
<tr>
<td>rNa/rCl</td>
<td>0.5 to 1.0</td>
<td>slight downward decreasing trend in B1 and no trend in B2. Some Na\textsuperscript{+} deficit dominates</td>
</tr>
<tr>
<td>rSO\textsubscript{4}/rCl</td>
<td>0.02 to 0.13</td>
<td>about the seawater value, with sections of possible sulphate reduction, mainly in the upper part</td>
</tr>
<tr>
<td>rNa/rK</td>
<td>30 to 110</td>
<td>B1 presents high values in the upper third and then lower values. B2 is alike but less clear</td>
</tr>
<tr>
<td>rMg/rCl</td>
<td>0.04 to 0.32</td>
<td>lower values in the upper part. Values higher than in seawater in the lower half</td>
</tr>
<tr>
<td>rMg/rCa</td>
<td>0.2 to 3.0</td>
<td>slightly decreasing downwards</td>
</tr>
</tbody>
</table>

(*) Excluding the lowest and the highest value. 25 samples for borehole B1 and 15 samples for borehole B2

Both boreholes contain hypersaline water in the top. In B1 salinity is more than 3 times seawater concentration. Since there is not clear Na\textsuperscript{+} exchange in the top, the high rNa/rK ratio seem the result of surface or near surface evaporation of water and later penetration into the soil, in agreement with what Rodríguez et al. (1992) comment. In fact the water isotope data show this evaporation process in porewater at the upper part (fig. 3). The slope (4.2) seem lower than for lagoon evaporation and probably shows phreatic evaporation (after surface water disappears).

The SO\textsubscript{4}/rCl point to a marine origin of salinity in the lower half, but since there is sulphate reduction in some samples, it is not a reliable index.

The relatively high values of the rMg/rCl ratio and the low values of rMg/rCa seem the result of Ca\textsuperscript{2+} increase due to some Na\textsuperscript{+} deficit due to cation exchange, with some Mg\textsuperscript{2+} involved in the exchange as well. It can be seen (fig. 5) that changes in the ratios rMg/rCl, rMg/rCa, rNa/rCl and rNa/rK tend to coincide; a decrease which means a Na\textsuperscript{+} loss is accompanied by a higher K\textsuperscript{+} loss and an increase of Ca\textsuperscript{2+} and some Mg\textsuperscript{2+}. This support the exchange assumption. The slight Na\textsuperscript{+} deficit shows a hardening. This has three explanations. One is downward movement of the whole water column, with the upper saline water (highly evaporated surface water) invading the less saline part of the aquitard below. The second is
Fig. 5.- Salinity and ion ratio profiles of porewater from boreholes B1 and B2 after data from Rodríguez-Arévalo (1988).
the highly saline water being trapped in the sediments as they pile up after the bay became a closed basin. The third is the effect of dominantly horizontal flow through sandy layers created by groundwater abstraction at the boundaries and outside the marshland, that forces the replacement of less saline water by the more saline water existing in the opposite direction. The high values of \( r_{Na}/r_{K} \) and \( r_{Mg}/r_{Ca} \), and the low \( r_{Mg}/r_{Cl} \) ratio in the upper third of borehole B1 seem to favor the downward penetration of highly saline water, down to 30 m, which may agree with the first explanation, compounded with the second one. This means a non negligible vertical permeability. This is not only a question of decreasing head in the confined aquifer, but one of dense water in the top after the former bay was closed and filled up, thus allowing high evaporation rates (Konikow and Rodríguez-Arévalo, 1992; Rodríguez et al., 1992).

**CONDITIONS AT THE MATALASCAÑAS COASTAL SITE**

At the coastal resort of Matalascañas some point observation boreholes have been drilled to know the local hydrogeology. Three sites have been selected and 2 to 4 boreholes have been drilled per site, fitted with short screened sections and grouted for isolation. They penetrate a thick sequence of fine to medium size quartz sands with only a significant thin layer of clay about 80 m below sea level. The exploration depth is 150 m below sea level, up to a clay formation. This clay formation is probably not the bottom of the Pliocene deposits. The potentiometric head at the inner boundary of Matalascañas is about 10 m above mean sea level.

The evolution of the potentiometric head in the different tubes is shown in figure 6. The wells in Matalascañas have screens below 70 m and supply water the summer (July and August) flood of vacationers. The effect of this abstraction is noted by boreholes 2 and 3 in each site except at the coast line, and in an exaggerated form by boreholes 4, with the screen below the clay layer. This is due to the confined character of the deep sand layers, which are also affected by the wells screens; in summer time the deep layer head potentials are below sea level and much of the year below the elevation needed to compensate a column of seawater at the screen depth (about 5 m above mean sea level). This means that seawater encroachment through the deep layers is likely in the future under present exploitation pattern. The monitoring borehole called M, a long screened old well (fig. 6), show an intermediate head potential, the result of flow inside the well; this false high head lead to an erroneous feeling of protection against seawater encroachment. Figure 7 show this vertical flow inside the “M” well measured with a saline tracer (Custodio, 1992a).

The main chemical characteristics of borehole water in Matalascañas (MAT), in pure silica sand, as compared with data from boreholes in La Rocina (ROC), where deep sediments have some carbonates, is as follows:
Fig. 6.- Head evolution in the recently drilled boreholes in the three sites of Matalascañas. Sea level position is approximate since no accurate leveling is available. Data provided by the Geological Service of the MOPT.
Fig. 7.- Measurement of vertical flow between screens inside monitoring borehole M (ITGE 1042-8-131) by means of a saline solution. Data from the UPC Dep. of Ground Engineering group (in Custodio, 1992a).
CONCLUSIONS

A fast survey of saline water existence, its characteristics and the likely origin can be done combining some salinity data (Cl⁻, electrical conductivity or total dissolved solids) with selected ion ratios, although there are no straightforward rules. In the case of Doñana the ratio rCl/rBr does not add useful information since most of the salinity, both in fresh and in saline waters, is directly or indirectly marine (airborne salts transported a short distance).

The evaporation of surface continental water, sometimes up to a brine, produces an increase of the ratio rNa/rK and a decrease of rSO₄²⁻/rCl due to organic activity in the ponds and residual marshes. How the S and K are fixed or lately eliminated is uncertain. Other ratios do not show clear trends.

The mixing of freshwater with seawater changes the ratios rSO₄²⁻/rCl and rMg/rCl towards seawater values (0.10 and 0.18 respectively) but freshwater may present values close to those of sea water, and then the usefulness is lost.

The displacement of saline water by freshwater and conversely is easier to be noticed through the consequent cation exchanges. The trend towards salinization, the main phenomenon seen in the sediments and deep aquifer of the Doñana marsh area, is marked by hardening, the decrease of the ratios rNa/rCl, rMg/rCl, rMg/rCa and rNa/rK.

Since the ratios are sensible to chemical errors, good chemical analyses have to be used and some deviations have to be checked before giving there a meaning, in order to eliminate possible analytical errors.

To check some hypothesis, environmental isotope methods have to be included in a chemical
study as an independent method, further to the due consideration of hydrogeological and potentiometric data.

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