SALINE WATERS IN THE COASTAL AREA OF THE NATIONAL PARK OF DOÑANA (SW OF SPAIN) IN ABSENCE OF SALINE WATER INTRUSION.

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ABSTRACT

Wetlands in dune complexes in Doñana National Park are strongly influenced by groundwater. Hydrochemical studies have been performed to know the relationships between the small lakes existing at the inner side of the coastal dune belt and the aquifer, which is formed mainly by fine to medium silica sands. The aim of this work is to show the existence of brackish and saline waters in a coastal area with lakes in absence of marine water intrusion. These saline waters form in small lakes by evaporation, and affect the chemical and isotopic composition of the surrounding groundwaters. The mean electrical conductivity (EC) of unaffected groundwater (2 - 45 m depth) in the study area is around 0.25 mS/cm. It is of the Na-Cl type, and reflects mostly the local rain, including airborne marine salts incorporation into recharge water through dry deposition. The water of the small lakes present a wide range of EC, from 0.2 to 28 mS/cm, and are mainly of the Na-Cl type, but can be changed into Na-SO4 waters. In the surroundings of the lakes phreatic water (< 2 m depth) may acquire elevated EC values, from 0.1 to 7.5 mS/cm. The origin of this salinity increase is the mixing of groundwater and surface water affected by intense evaporation. The evolution of SO4 concentrations in lake water seems to be related with the chemical reactions taking place during dry and wet periods, mostly the reduction and precipitation of S compounds and their re-disolution afterwards. These processes modify the chemical and isotopic composition of the groundwater sampled near Dulce and Santa Olalla lakes, which show the mixing between surface and phreatic water. The observed salinity, chemical and isotopic composition distribution of the phreatic waters around these lakes suggests that fresh groundwater enters Santa Olalla lake along its N and W margins, while concentrated surface water infiltrates to the aquifer along its SE margin.

INTRODUCTION

The Doñana natural region and aquifer is located in the SW of Spain, partly occupying the ancient estuary of the Guadalquivir river (Figure 1 A). The National Park of Doñana extends over 50720 ha, including three morphogenetic systems: estuarine, littoral and eolian (Rodríguez-Ramírez et al., 1996). Two geomorphologic units have been identified in the eolian system: stabilized dunes and mobile dunes. Freshwater phreatic lakes, brackish lagoons and marshes, and saline tidal marshes form an extensive wetland area of paramount importance not only for migratory waterfowl, but also for a huge variety of resident fauna and vegetation.

The study area is located in the Doñana Biological Reserve (6794 ha) in the coastal area of the Doñana National Park (DNP). The studied small lakes and ponds (Ojillo, Navazo del Toro, Charco del Toro, Zahillo, Taraje, Dulce, Santa Olalla, Las Pajas, Sopetón and Manuela) are placed along the inland side of a set of partially unvegetated sand dune strings parallel to the coast (Figure 2). To the east of the lake system extends the seasonally inundated Guadalquivir river marshes (Figure 1 A and 2). Groundwater plays an important role in the water balance and in the chemical composition of small phreatic lakes (Winter, 1976, 1983, 1986; Winter and Llamas, 1993; Custodio, 2000). Similarly, chemical and physical processes occurring in the lakes may affect the chemical composition of groundwater downflow from them (LaBaugh, 1986; Vela et al., 1987; Sacks et al., 1992).
The studies on the hydrology of this phreatic lakes complex started early in the 1980's. Their salinity makes them very interesting from an ecological point of view (Montes et al., 1982; Pérez-Cabrera and Toja, 1989; López et al., 1991; López et al., 1994; Serrano, 1994; Serrano and Toja, 1995). Hydrogeological studies carried out in the 1990s established the conceptual model used as background for the present study (Vela, 1984; Sacks et al., 1992; Iglesias, 1999). Delgado et al. (2001a and b) and Lozano et al. (2001) developed a first approach to the physical and chemical processes that take place in the lakes and to their influence in the chemistry of groundwater in the surrounding unconfined aquifer. The nature of saline water was reviewed by Custodio (1992).

The aim of this work is to show the existence of saline waters in a coastal area with lakes in absence of marine water intrusion and to show the interaction between the lakes and the surrounding groundwater.

**MATERIALS AND METHODS**

Some tens of water samples from lakes, phreatic groundwater (1-2 m deep), and intermediate depth groundwater (down to 45 m) were collected to measure major ions and $^{18}$O and $^2$H isotopes at various times during the period 1998-2000. The groundwater samples were taken from short-screened boreholes of different depths, which belong to the Guadalquivir River Basin Authority (Confederación Hidrográfica del Guadalquivir, CHG) and from piezometers (< 3 m depth) controlled by the group of the Autonomous University of Madrid (Spain). The Geological Institute of Spain (IGME) has drilled a multilevel borehole recently. In May and November 2000, ca. 20 points of phreatic groundwater were sampled twice. These samples were taken in hand-drilled holes around Santa Olalla lake with the purpose of identify inflow and outflow areas using major ions, $\delta^{18}$O and $\delta^2$H.

Temperature, electrical conductivity (EC), pH and alkalinity were measured in the field. Major ions were analysed in the laboratories of the Geological Institute of Spain (IGME), and $\delta^{18}$O and $\delta^2$H were analysed at GGA (Institut für Geowissenschaftliche Gemeinschaftsaufgaben, Hannover, Deutschland) and at CEDEX (Madrid, Spain).
GEOLOGY AND HYDROGEOLOGY

On a local scale, groundwater flows eastward from the coastal dunes to the marshes (Figure 2). This regional flow pattern is locally disturbed by local flows discharging to the lakes and by evaporative discharge through vegetation. Groundwater shows local increases of salinity near some lakes that is due to water evaporation in the lakes. The hydrochemistry of the lakes changes seasonally and interannually, following the sequence of wet and dry years (Vela, 1984; Vela et al., 1987; Sacks et al., 1992, Delgado et al., 2001a and b; Lozano et al., 2001).

The figure 3 shows the evolution of the water depth of three lakes: Charco del Toro (temporal lake), Dulce and Santa Olalla (permanent lakes) (see the location of the lakes in figure 1 C). Charco del Toro Lake was dry almost the whole period of study, although it reached 1.25 m of water depth at the beginning (March 1998). The water level of Dulce and Santa Olalla ponds follows rainfall and the evaporation cycles. Santa Olalla water level was higher than Dulce since March 1998 to October 1999, and afterwards both levels were similar. During the study period Santa Olalla’s maximum water depth was 2.34 m (around 83 ha of surface area) in March 1998, after the rainy period, and the minimum water depth was only 0.15 m in August 2000. In Dulce Lake the maximum water depth was 1.77 m (around 17 ha of surface area) in March 1998, but in August 2000 it became completely dry.

HYDROCHEMISTRY

Local rainwater, incorporating dry fallout, is of the sodium chloride type due to airborne marine influence. The main process controlling the chemistry of groundwater is evapotranspiration. (Manzano et al., 1991; Iglesias, 1999). Groundwater keeps the meteoric water signature even thought there is some minor alteration of the scarce K-feldspar and Na-feldspar present in the sands. In the western unconfined area (El Abalario area), groundwater composition is very close to rainwater due to the low reactivity of the silica sands that form most of the aquifer. At a regional scale some calcite seems to be the only reactive mineral present in the ground, but only in the NE sector of the aquifer and in the deep layers, where groundwater evolves from the sodium chloride type and approaches the sodium-calcium-chloride-carbonate type (Manzano et al., 1991; Iglesias et al., 1996; Iglesias, 1999). To the S and SE groundwater becomes increasingly brackish under the marshes because of mixing with saline water trapped in the sediments of the SE sector (Custodio, 1992).
In the area of the studied lakes the hydrochemistry of surface water and groundwater is controlled by the existence of regional and local flows. In general groundwater EC (electrical conductivity) is low, with average values of 0.25 mS/cm, except for internal discharge zones and/or in areas locally influenced by the lakes (Vela, 1984; López et al., 1994).

Figure 3 Evolution of the water depth of Charco del Toro, Dulce and Santa Olalla lakes.

Hydrochemistry of lakes

During the period of study (1998-2001) surface waters of the lakes being considered showed an EC range between 0.2 and 28 mS/cm. The electrical conductivity tended to increase during this period due to the low rainfall causing a reduction of the swampy surface area in many lakes and the total drying up of some of them (Figures 3 and 4). As figure 3 shows Dulce and Santa Olalla lakes water were increasingly concentrated in the period from March 1998 to October 1999. Santa Olalla Lake has higher EC values, except in August and September 1999 when Dulce lake water reached 16.6 and 28 mS/cm respectively, compared with 7.7 and 11.6 mS/cm in Santa Olalla Lake.

Figure 4 Evolution of the electrical conductivity (EC) of Charco del Toro, Dulce and Santa Olalla lakes surface water.
The surface water of Dulce and Santa Olalla lakes (permanent lakes) is always of the Na-Cl type. The evolution of the chemical composition from March 1999 to May 2000 is shown in figure 5, A and B. In March 1999 lakes have freshwater (EC 0.9 mS/cm and 1.64 mS/cm respectively), while in August 1998 they reach one of the most concentrated compositions measured (16.6 mS/cm and 7.7 mS/cm respectively). Both lakes show a temporal rise of the ratio rSO₄/rCl (r = meq/L) in October 1999, simultaneously to the dilution of lake water due to the early autumn rainfall (Figure 4 and 5 A and B). Finally the chemical composition of both lakes returns to the initial composition in May 2000. This evolution shows how the concentration of the major ions is controlled by rainfall and groundwater contribution, and evaporation-dilution cycles, except the sulphate that is affected by other processes, as commented later on.

Evaporation can explain the temporal variation of the conservative solutes content in lake water. The low precipitation in the area during the period of study has caused the progressive concentration of water in the lakes during the dry season. There is only a dilution event during the wet season (Figure 4). Dilution includes direct rainfall contribution, increased groundwater contribution when the water table rises, and in some cases some shallow perched water inflow may be possible. This is under natural or close-to-natural circumstances, but the lakes close to Matalascañas (Charco del Toro) are affected by groundwater abstraction there, mostly in summer time, and then groundwater inflow to the lake is decreased or impossible.

Charco del Toro lake water increased its salinity during 1998 and had a maximum in autumn (from 0.76 mS/cm in March to 6.1 mS/cm in October, see figure 4). From March to August 1998 the water composition evolved to an increasingly concentrated Na-Cl water type (Figure 5 C). The lake was dry during 9 months of 1999 and the whole year 2000. The chemical composition of lake water varies from Na-Cl to Na-SO₄ type. This compositional change occurs between September and October 1998 (Figure 5 C), although the water EC keeps high (6.1 mS/cm) due to the lower dilution caused by the scarce rainfall during these months (Figure 4). In the flooding period of 1999 the water composition is the Na-SO₄ type. This evolution was also observed in Zahillo lake (SE of Charco del Toro), which is periodically dry (location in figure 2). The origin of this SO₄ enrichment in some lake waters could be explained by a combination of two processes, although they have not yet been completely checked and studies are being carried out:

- Oxidation of reduced S / SO₄ dissolution. R-X diffraction studies show that the organic matter-rich lake bottom sediments contains a significant concentration of non-mineral, reduced S, that will be oxidised and later on will be dissolved by the early autumn rainfall. Part of this S could be supplied...
by unaccounted dry fallout from Huelva industrial complex, located to the W (Iglesias et al., 1996), in which sulphide minerals from the nearby Iberian Pyrite Belt are treated.

- Gypsum precipitation in the swampy lakeshore during the drying up period and subsequent dissolution during the wet period. The existence of gypsum in these zones has been checked by R-X diffraction of some soil samples collected in Charco del Toro and Santa Olalla swampy shore. The origin of SO$_4$ is related with the former process.

This means that the lakes will act as a trap of S. While other ions (such as Cl and Na) could be exported during some periods by underground flow of brackish water, S is kept in the sediments (as organic S or gypsum) during such periods, and ready to be dissolved later on. In some periods lake water is depleted in SO$_4$ due to the generation of a reducing environment during which S is microbially reduced and deposited in the lake bottom. This reaction would be favoured by high summer temperatures, when lake water may reach 30ºC (Sacks et al., 1992), as occurs in August 1999 (Figure 5). This means that outflow to groundwater is also depleted in SO$_4$ during these periods.

**Groundwater hydrochemistry**

Due to the low reactivity of the siliceous sands that form the aquifer, the groundwater chemical composition, as commented above, is controlled by the recharge water, and locally by the mixing with lake waters. It is of the Na-Cl type (Figure 6) but with a great spatial and temporal variability.

Two different groups of groundwater were identified. Group 1 corresponds to waters down to 45 m depth, with an irregular spatial distribution. They are of the Na-Cl type with low mineralization (< 0.3 mS/cm). Their chemistry is controlled mainly by that of the local rain, including dry fallout dissolution, which consists mostly of marine airborne salts. Group 2 is quite heterogeneous and corresponds to waters down to 14 m depth and also to phreatic waters (< 2 m deep) sampled in the near-shore lake areas. It involves a wide range of chemical composition that varies between Na-Cl, Na-SO$_4$, Na-HCO$_3$, and Ca-HCO$_3$. This group presents higher electrical conductivity values, from 0.3 to 7 mS/cm and represents the mixing of surface lake waters of different salinity and composition, with phreatic water. As it has mentioned before, lake water chemical composition is modified by evaporation and also by oxidation-dissolution and/or precipitation-dissolution of the S chemical species.

Groundwater near Dulce and Santa Olalla lakes (see situation in figure 2) is of the Na-Cl type (Figure 6 A), with variable salinity depending on the influence of the lake water. Groundwater near Charco del Toro seasonal lake and Manuela pond is of the Na-SO$_4$ type, as lake water composition during the study period.

In order to check the previous model, 20 samples of phreatic water were collected in the boundaries of the Santa Olalla Lake in May 2000, and also in November 2000. The results were similar. Therefore only the data of May 2000 are presented. Phreatic water chemical composition in the surrounding area of Santa Olalla Lake (Figure 6 B) is of the Na-Cl type, with variable concentration and sulphate content. In some points (O_2, O_3, O_6) SO$_4$ contents is almost equal to the chloride concentration. This indicates a direct influence of lake processes. Since lake water was of the Na-Cl type during the study period the extra contribution of SO$_4$ to local groundwater is probably related to the processes that affect the S species in the swampy shore lake when water gets in.

The phreatic water in the Santa Olalla area present a wide range of EC (0.1 to 7.5 mS/cm) due to the different degree of mixing with the evaporated lake waters (Figure 6 B). This allows establishing the relationships between this lake and the aquifer. The observed salinity distribution around Santa Olalla suggests that low mineralised groundwater (EC < 0.3 mS/cm) enters Santa Olalla Lake along its N margin at the sampling time, while concentrated surface water (EC between 0.6 and 11.6 mS/cm) infiltrates to the aquifer along its SE margin (Figure 6 B). The W and S margin show seasonal changes: at the sampling time the W shore was a groundwater inflow boundary and the S margin combine inflow and outflow points.
ENVIRONMENTAL ISOTOPES

Figure 6 Hydrochemical diagrams: A. phreatic (0-2m) and deep (2-45m) groundwater, and B. phreatic water around Santa Olalla lake.

From previous work it is known that groundwater in the unconfined area has the isotopic signature of local rainfall: $\delta^{18}O = -4.7$ to $-5.0 \, \%e$; $\delta^2H = -28$ to $-30 \, \%e$ SMOW (Baonza et al., 1984; Vela et al., 1987; Manzano et al., 1991; Manzano et al., 2001; Iglesias, 1999).

Most of the groundwater data from the present study point to $\delta^2H = -30 \pm 3 \, \%e$ and $\delta^{18}O = -5 \pm 0.3 \, \%e$ SMOW (Figure 7) and correspond to rain recharge without previous evaporation, with a deuterium excess of $+10 \, \%e$. 
Samples from lake water follow an evaporation line (dotted line in Figure 7, slope 4.4). Some groundwater samples from boreholes also lie on this evaporation line, which means that they have been sampled in a flow path downflow from the lakes and represent the mixing of lake water and groundwater.

![Figure 7](image-url)  
*Figure 7* Plot of $\delta^{18}O$ versus $\delta^2H$ in groundwater (2-43 m), phreatic water and lake water in the study area.

The Cl-$\delta^{18}O$ relationship reveals that most groundwater and phreatic waters follow a trend of salinity increase without isotopic enrichment (indicated in the figure 8 A by the black arrow). It is due to the concentration by evapotranspiration of plants, since airborne salinity is already included in rainfall concentration since samples collect total deposition. At high salinities there is the effect of dissolving precipitated salts by unevaporated freshwater. All lake waters show the effect of fractionating evaporation in different degrees, resulting in a wide range of Cl and $\delta^{18}O$ contents. The dashed lines in the figure 8 A involve data points affected by direct evaporation.

![Figure 8](image-url)  
*Figure 8* A) Cl vs. $\delta^{18}O$ in lake water, phreatic water and deeper groundwater; B) SO$_4$ vs. $\delta^{18}O$ in lake water, phreatic water and deep groundwater.
The SO₄⁻²₁₈O relationship (Figure 8 B) shows the same trend of salinity increase for phreatic samples and deep groundwater. On the other hand, the heaviest lake waters and lowest SO₄ contents (30-50 mg/L) coincide with a low water levels period (dry season), while the lightest lake waters and a wide range of SO₄ contents (10-1000 mg/L) correspond to high water levels (wet season).

Figure 9 shows the evolution of rainfall, SO₄ content and δ¹⁸O of Dulce, Santa Olalla and Las Pajas lakes, and reveals how in the rainy periods (October 1999 and December 2000) the SO₄ content increases (dotted lines in the figure 9), with water dilution that makes water isotopic composition lighter (continuous line), while in the dry periods the isotopic composition is heavier and the SO₄ content stay low. So, the high SO₄ contents relative to rainwater are not explained by simple evaporation. This is in agreement with the hypothesis of oxidation of sulphur from the bottom sediments of the lakes, and dissolution at the beginning of the wet season of sulfate salts precipitated and formed in the swamplike shore lakes during the dry period. The remaining lake samples inside the dashed line (Figure 8 B) correspond to intermediate states of the evaporation process in the lakes, with SO₄ contents decreasing as δ¹⁸O increases by evaporation.

Vela et al. (1987) and Sacks et al. (1992) used the isotopic composition of phreatic water in the boundaries of Dulce, Santa Olalla and Las Pajas lakes, as well as measurements of head differences between the aquifer and the lakes to establish a first approach of the location of the inflow to and the outflow from the lakes. They proposed some inflow and outflow areas. But flows can be reversed depending on the hydraulic gradient between the lake and the phreatic level.

Looking at δ²H and δ¹⁸O values in May 2000 of the phreatic water in the boundaries of Santa Olalla, the N margin of the lake was a groundwater inflow area. Here the phreatic waters had very low EC values (0.15 mS/cm) and an isotopic composition close to that of rainwater (δ¹⁸O = -5‰ and δ²H = -30‰ SMOW). Lake water outflow to the aquifer occurred mostly in the E edge, where EC values in the phreatic waters were high (up to 4.5 mS/cm) and the isotopic composition was the heaviest of the area (δ¹⁸O = 0.7‰ and δ²H = -3.2‰ SMOW). The character of the W border varies seasonally. At the sampling time it was a recharge boundary. These results agree with the proposed model by the above-mentioned authors (Vela et al., 1987; Sacks et al., 1992).
CONCLUSIONS

In the coastal area of the Doñana National Park a group of small phreatic lakes along the inland side of a partially unvegetated sand dune string parallel to the coast exists. The chemical composition of lake water is controlled mainly by rainfall, airborne salts, the inflow and outflow of groundwater and evaporation. The evaporation-dilution cycles and some processes affecting S species produced either in the lake water or in the bottom sediments explain the salinity and the chemical composition changes. Lake water shows a wide EC range, from 0.2 mS/cm up to 28 mS/cm, due to concentration by direct evaporation. Direct evaporation controls the chemical composition of conservative solutes, except the sulfate that is subjected to others processes (related with reduced S oxidation-dissolution and with gypsum precipitation-dissolution in the swampy lake margins), and the isotopic composition of lake water.

The saline lake water affects the surrounding groundwater, especially the phreatic groundwater down 2 m depth and downflow the lakes. There is a wide range of EC values, 0.1 to 7.5 mS/cm, due to the different mixing degree with evaporated lake waters. The influence of saline lake water in the deep groundwater (down 45 m) is not so clear; only in some points groundwater sampled downflow the lakes show the evaporation signals (EC 1.5 mS/cm) and the sulfate modifications occurring in the lakes.

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