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Article

Using Water Temperature, Electrical Conductivity, and pH to Characterize Surface–Groundwater Relations in a Shallow Ponds System (Doñana National Park, SW Spain)

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Abstract: The physical limnology of a shallow pond system was characterized using field measurements of water temperature, pH, and electrical conductivity (EC). We determined the spatial variability in surface and groundwater temperature, pH, and EC along the pond's shore and along the several pond-shore transects, analyzed the water column temperature gradient and estimated the groundwater discharge rate using a heat transfer model. The fieldwork was conducted in Santa Olalla and Dulce ponds located in Doñana National Park in southwestern Spain during different stages from 2016 to 2018. The results of this study have improved the understanding of the thermal structure and the surface–subsurface heat exchange in the ponds and highlighted the importance of groundwater discharge in the pond water balance. It also showed the heterogeneous nature of groundwater discharge through the bottom sediments of the Santa Olalla pond. These results are consistent with previous studies and strengthen the existing hydrological and limnological knowledge of these ponds located in the protected area which is receiving a great deal of public attention.

Keywords: heat flow; surface water-groundwater interaction; hydrological monitoring; Doñana National Park

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1. Introduction

Doñana, in southwestern Spain, is an iconic World Heritage site within the Mediterranean region. The conservation of this ecosystem is particularly challenging, requiring coordinated actions across complex and sometimes very large watersheds. Although protected, Doñana is still affected by a range of threats. For example, water extraction and pollution have caused the degradation of a number of ponds within the wetland complex in spite of their protected status [1]. The Doñana area is located on the Atlantic Ocean coast, adjacent to the Guadalquivir River mouth (Figure 1a), and covers more than 3000 km^2. Inside the limits of the 543-km^2 Doñana National Park is the Doñana Biological Reserve (68 km^2), where numerous ponds form during rainy periods and interact with local groundwater flow systems. Different regional and/or local flow systems occur at different times of the year depending on the presence of surface ponds and the water table position relative to the ponds [2].

Santa Olalla is the largest pond (25 ha) in the area and the only pond that is permanently flooded. Its maximum depth is 2.2 m, and overflows and merges with Dulce pond, on its western shore (see Figure 1), and with a series of small ponds existing on its eastern shore in unusually wet years. The surface watershed has a size of 155 ha, and its lowest point is near the center of the pond at an altitude of 2.5 m above sea level. Only after intense drought periods has the pond been almost completely dry, so it is classified as a permanent water body. In such occasions, a number of submerged springs have been seen on its southern edge. Santa Olalla is a groundwater flow-through pond located above an unconfined aquifer consisting of fine aeolian sands [2,3]. The regional groundwater flow direction in the Doñana aquifer is from northeast to southwest towards the Atlantic Ocean. Local groundwater discharge from the aquifer to the lowest parts of the sand dunes is the main water input to Santa Olalla and other ponds. Since the early 1970s, the area has been subjected to different pressures, especially due to water demands from crop irrigation and from a coastal resort which is located only 3.8 km from Santa Olalla pond and less than 1 km from other dried-out ponds such as Charco del Toro (Figure 1b). In this type of ecosystem, groundwater discharge/recharge is the most difficult component of the water balance to quantify. Therefore, in hydrogeological studies of ponds in particular and, in any hydrogeological research in general, different methodologies are used to estimate the groundwater component and compare the values to improve the confidence in estimated fluxes. The theoretical base of using heat as a groundwater tracer was published in the 1960s, but recent work has significantly expanded the application to a variety of hydrogeological settings [4–7]. Temperature patterns started to be exploited to study subsurface flow systems. Early studies had several limitations, such as data-acquisition and computational techniques, although such limitations have been overcome throughout the years [8]. Heat transport by groundwater has proven to be useful as a tracer to identify surface water infiltration, flow through fractures and flow patterns in groundwater basins. Temperature measurements can be analyzed for recharge and discharge rates or to estimate interchange with surface water, hydraulic conductivity of streambed sediments, and even basin-scale permeability.

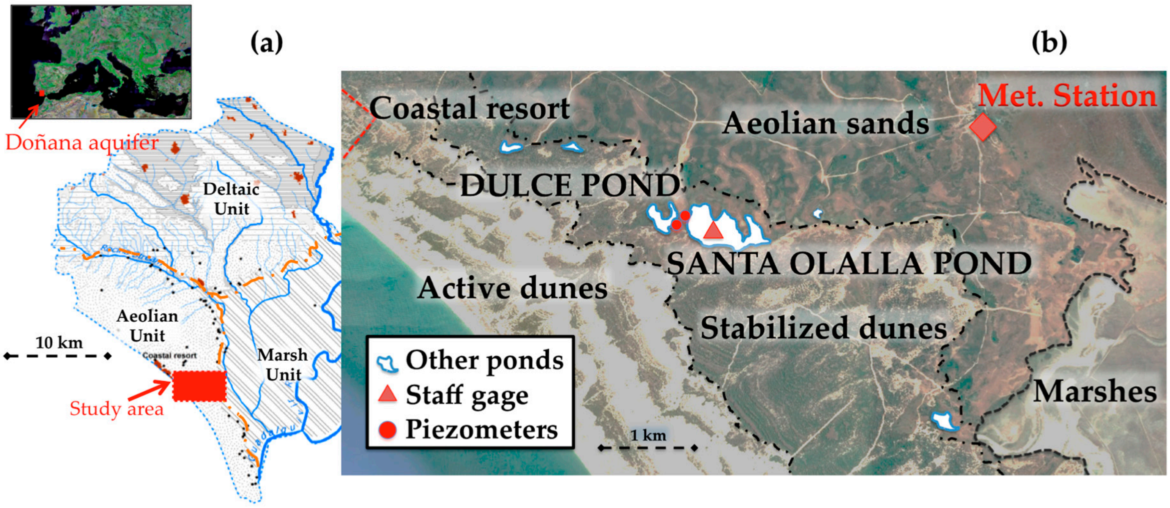

Figure 1. Study site: (**a**) Doñana aquifer in southwestern Spain showing main geological units, rivers and streams, as well as the study area; (**b**) Study area; meteorological station, staff gage in Santa Olalla pond. Dulce pond and other relevant ponds are highlighted, as well as the coastal resort. Active and stabilized dunes, aeolian sands and marshes are also marked.

In Santa Olalla, groundwater inputs have recently been estimated via water balances and the segmented Darcy method [9], while aquifer permeability and transmissivity were recently estimated using the methods based on the tidal influence on the short-term fluctuations of the piezometric level near the pond [10].

The objective of this study is to estimate the groundwater discharge from the sand aquifer to Santa Olalla pond in three different periods using different thermal approaches including field measurements, heat transfer modeling, and the analysis of thermal profiles. The results were compared to similar studies that were previously conducted in the pond.

2. Materials and Methods

Temperature was measured at three different periods: an intensive field campaign in July 2016 (1 in Figure 2), and two periods of hourly temperature data acquisition during a high water stage in spring 2017 (2 in Figure 2), and a low water stage from October 2017 to March 2018 (3 in Figure 2).

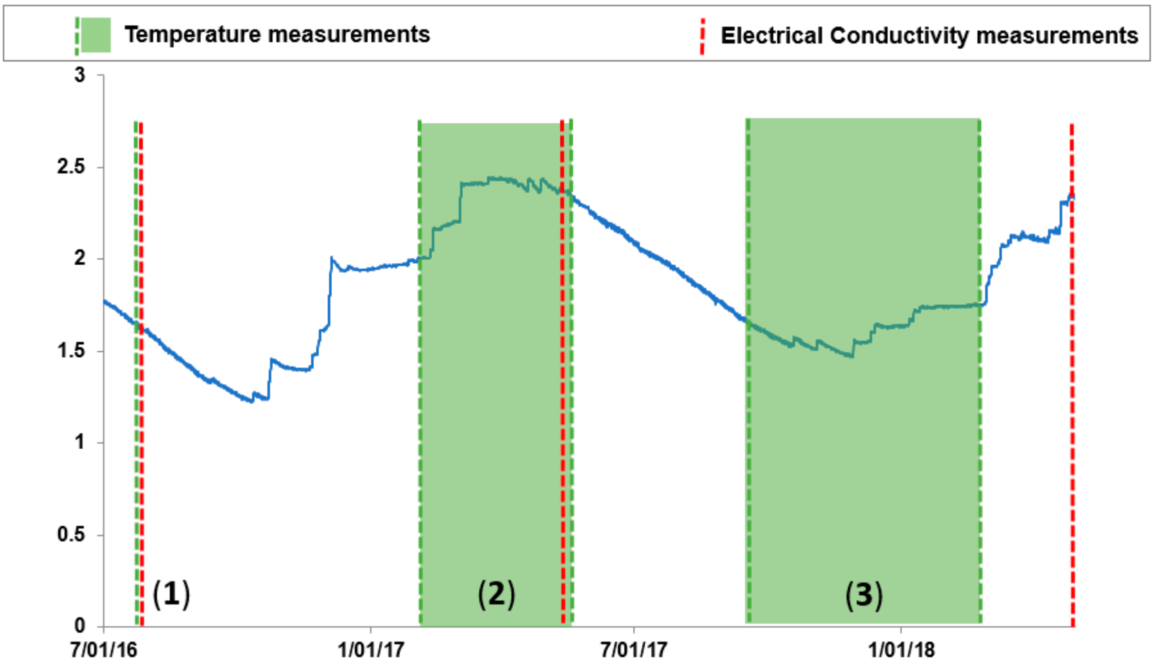

Figure 2. Water level in Santa Olalla pond from July 2016 to May 2018. (**1**) Measurement of surface and groundwater temperature (green) and electrical conductivity (red) in a two-day campaign along the pond's shoreline in July 2016. (**2**) Period for air, surface and groundwater temperature data acquisition at the staff gage (see Figure 3 for location) (high water stage). (**3**) Period for air, surface, and groundwater temperature data acquisition at the staff gage (low water depth). On 9 May 2018, after a rainy period, a surface water temperature, electrical conductivity (EC), and pH profile measured on the northwestern shore of the pond.

Surface and groundwater temperature and electrical conductivity (EC) were measured with a portable multi-meter (HACH-HQ40D) calibrated before each field trip and using a PVC mini-piezometer to insert the probe, in July 2016. The mini-piezometer was driven approximately 0.5 m deep into the pond sediments by hand at 12 points within 5–10 m of the shore (Figure 3). In addition, several profiles and transects of water EC, temperature, and pH were done on the northwestern shore of the ponds (see Appendixs A and B). As for the second and third stages of our study, a set of four auto logging temperature sensors (Maxim, iButtons DS1922L-F5) was installed inside a PVC tube attached to the Staff Gage of Santa Olalla pond. This tube was similarly driven 0.5 m deep into the pond sediments in the center of the pond. The deepest sensor was installed at a distance of 35 cm depth below the bottom of the pond. The iButtons were programmed to record temperature data at an hourly rate with a resolution of 0.0625 °C. Software 1D-Temp-Pro [11] was used for the analysis of one-dimensional vertical temperature profiles. This method numerically solves the flow and heat-transport equations and uses a graphical software package for simulating energy transport in variably saturated porous media (VS2DI). The program allows users to calibrate VS2DH models against measured data to estimate vertical groundwater/surface-water exchange. Temperature variations throughout the year at several depths have proven to be adequate to reproduce such water exchange with this transient state model. Parameters used in the modeling are shown in Table 1.

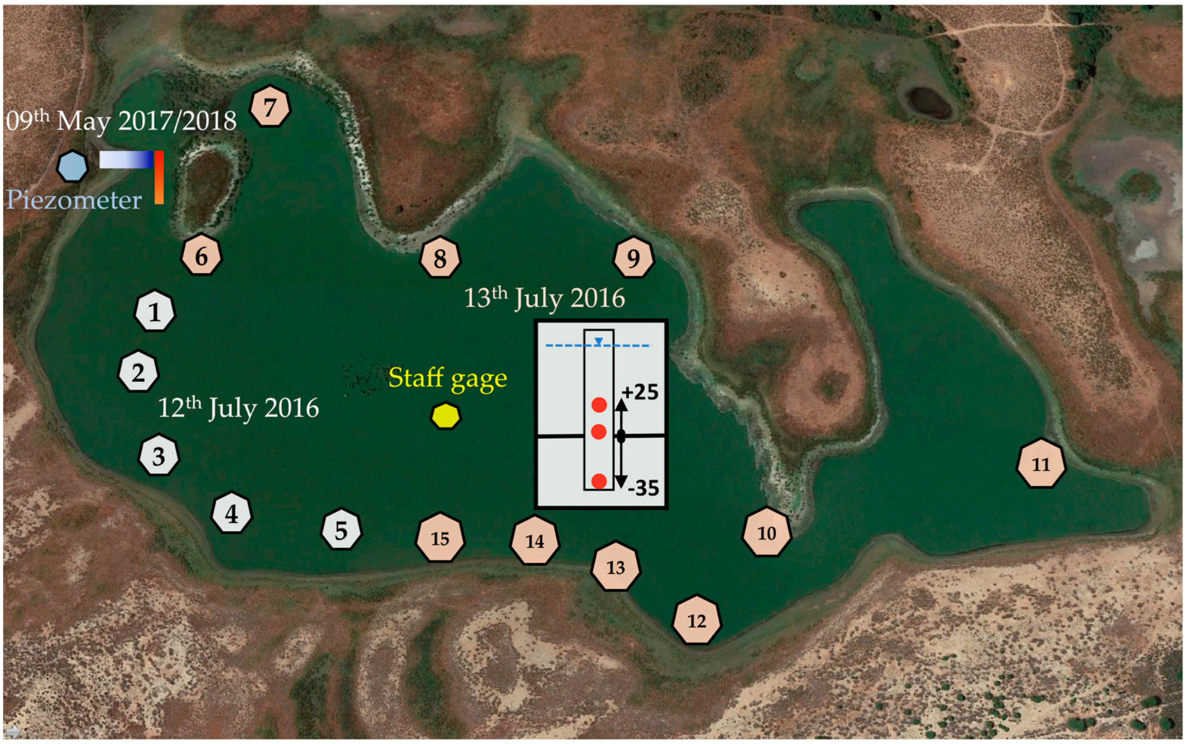

Figure 3. The locations of the measurement points along the pond's shoreline using a portable mini-piezometer (12th–13th July 2016); the piezometer (17 m depth), the surface water temperature—EC profile and the pond-shore temperature—EC transect (9th May 2017 and 9th May 2018). In the center of the figure, the staff gauge with the iButtons (red circles) used for the heat transfer modeling is shown (distance from the pond's floor is expressed in cm). Aerial Photo was taken on 26 July 2017 (Source: Google Earth).

3. Results

3.1. Field Campaigns in May–July (2016–2017–2018)

Figure 4 shows the water temperature and EC measured during the summer field campaign on 12th and 13th July 2016. Surface water EC was nearly constant in the perimeter of the pond with values ranging from 10.47 to 10.70 mS/cm at 25 °C. Surface water EC measured at sampling point 7 (13.3 mS/cm) is not representative for the pond and can be considered as an outlier, as this section of the pond was separated from the main water body, forming a small pool on the measurement date (13th July). Consequently, the water at point 7 experienced a greater evaporative concentration. Groundwater EC was lower than surface water EC in all the cases, ranging from 4.77 mS/cm to 10.7 mS/cm. Lower groundwater EC values were detected on the southwestern shore. No significant correlation between water EC and depth were observed (Figure 4).

Surface and groundwater temperatures varied a great deal. The maximum differences between surface water and groundwater temperatures were mostly observed in the afternoon, whereby groundwater was approximately 3 °C cooler than surface water. In the morning hours of the next sampling date, the reverse process occurs. Surface water was slightly cooler than groundwater, this behavior being smoother until midday. After midday, similar temperatures were measured in ground and surface water. As a rule of thumb, surface water temperatures were much more variable and greater than groundwater temperatures.

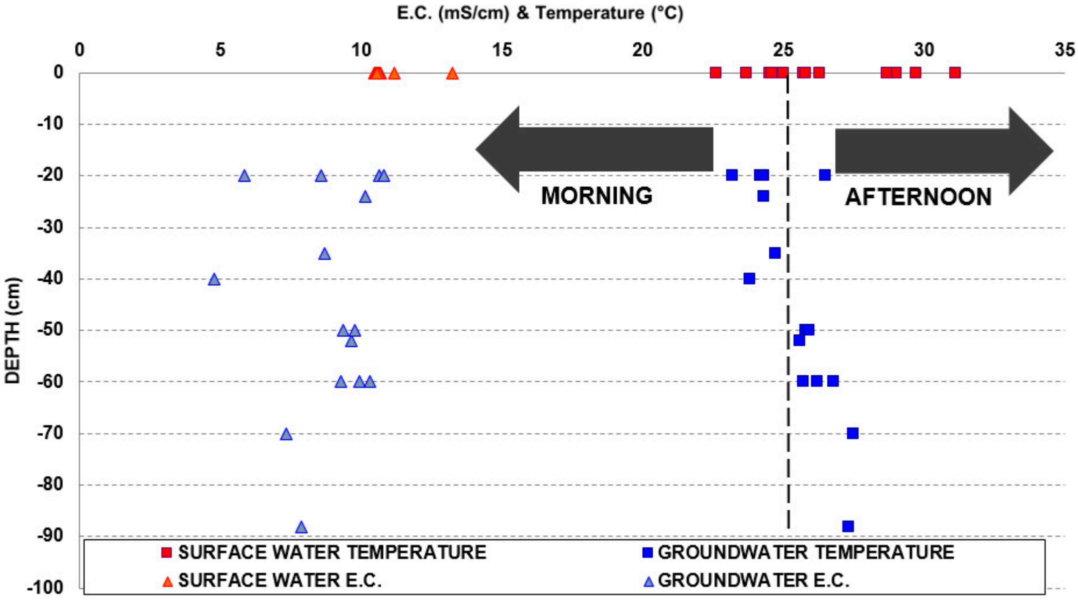

Figure 4. Water EC (left) a and temperature (right) vs. depth on 12–13 July 2016. Vertical dotted line distinguished between morning and afternoon water temperature measurements (see Appendix A for details).

On May 2017 and 2018, EC and temperature profiles were measured on the northwestern shore of Santa Olalla pond (Figures 5 and 6). On 9th May 2017, a profile from the water surface down to 5 cm into the bottom sediment was made (Figure 5). No significant variation was found in EC which ranged from 3.22 to 3.08 mS/cm. Nevertheless, the water column on the pond was thermally stratified, from nearly 29 °C near the surface to less than 20 °C below the bottom. Much of the variation occurred between the surface and the 5 cm below the surface indicating the surface heating by solar radiation. Groundwater temperature measured in the on-shore piezometer (Figure 7) was 22.6 °C and the EC was much lower (216 µS/cm) than pond water. The piezometric level was 53 cm above the ground, indicating the upward and pond-ward hydraulic gradient, meaning that groundwater discharged from the aquifer to the pond (Figure 8).

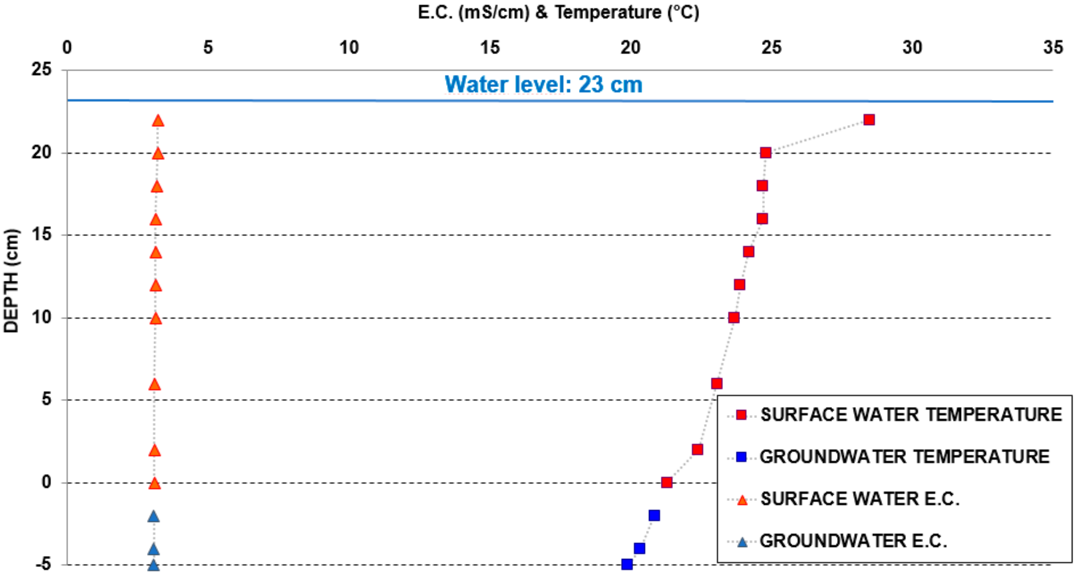

Figure 5. EC and water temperature vs. depth on the northwestern shore of the pond during the field campaign of May 2017.

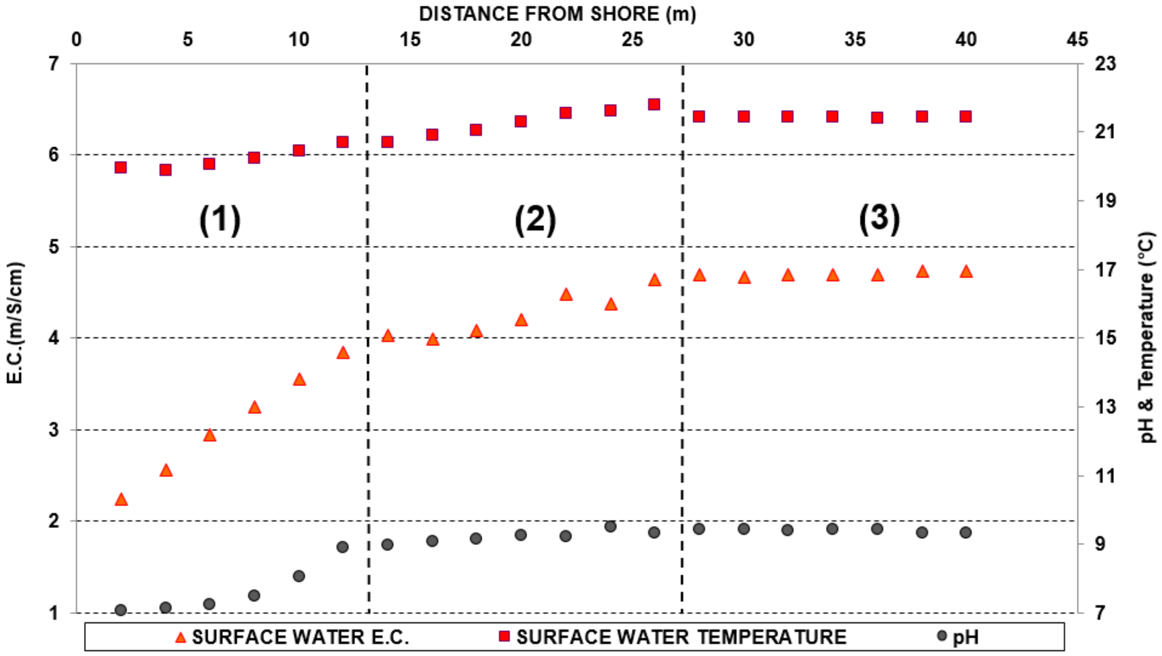

Figure 6. Water EC vs. distance from shore (left) and pH and water temperature vs. distance from shore (right) during the field campaign of 9 May 2018.

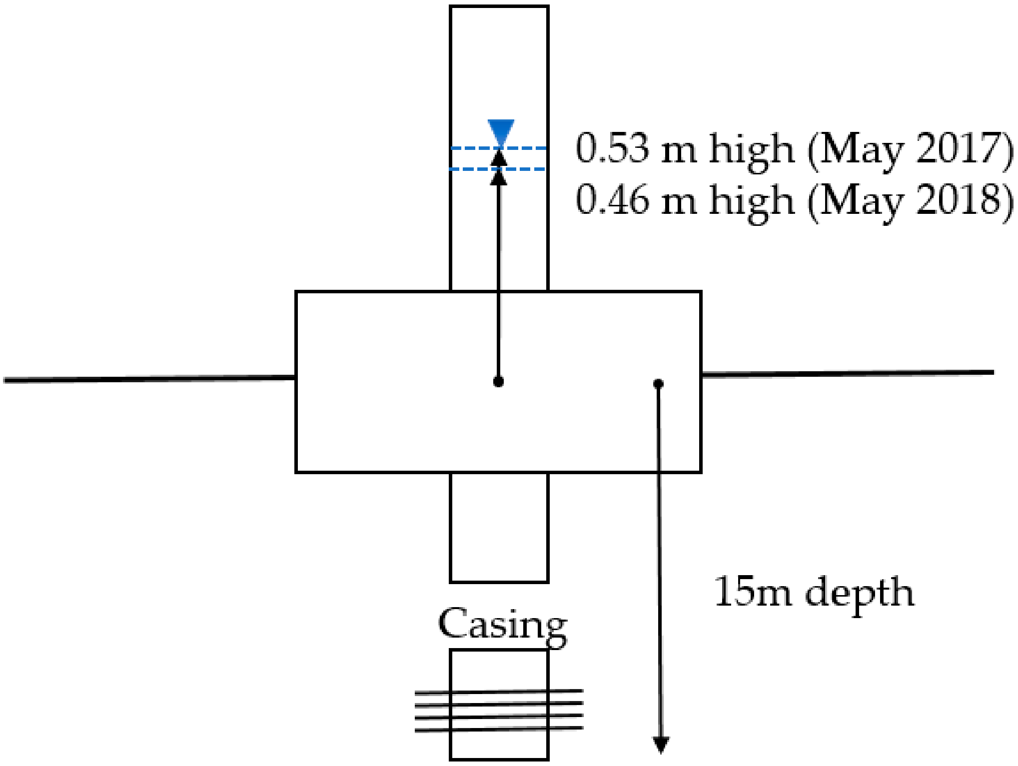

Figure 7. Sketch of the piezometer located near the northwestern shore of Santa Olalla pond. Groundwater level measured during the field campaign of May 2017 and May 2018. Dulce pond's piezometer has similar characteristics.

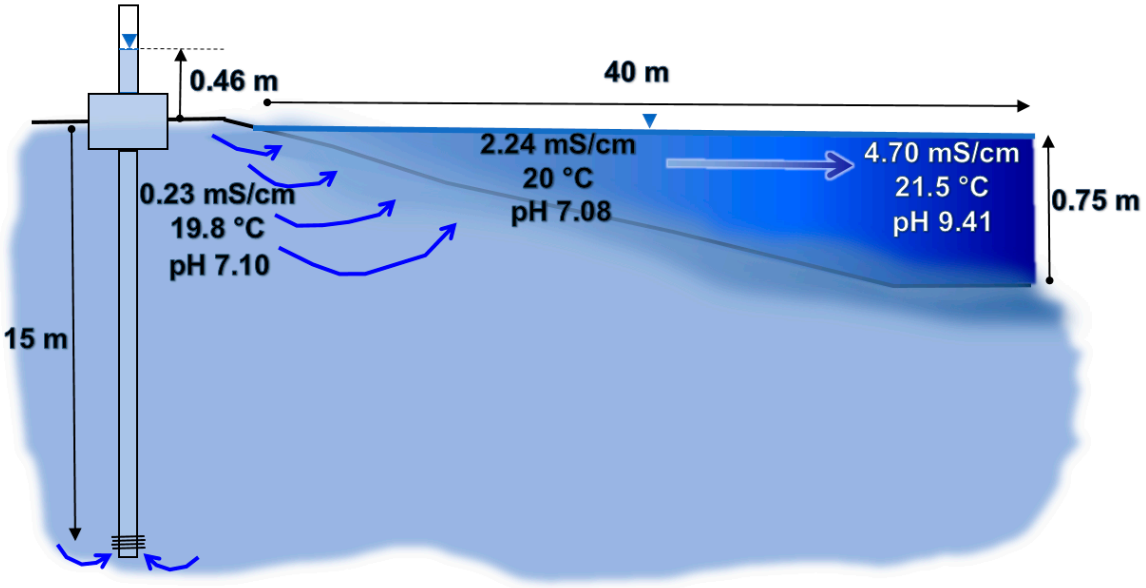

Figure 8. Sketch of the hydrological flows taking place at the northwestern shore of Santa Olalla pond in May 2018.

On 9th May 2018, after an intense rainfall period on the Atlantic coast of Spain and the Ebro Basin that lasted from March to the end of April, water EC, pH, temperature were measured along the same transect as in May 2017 (Figure 6). On this occasion, surface measurements were made from the shore to the center of the pond every two meters. Measurements ended when the values of every parameter were found to be stable, this was at a distance of about 40 m from the shore (Figure 6). The EC, increased from 2.24 to 4.70 mS/cm, while the groundwater EC in the piezometer was much lower at 0.234 mS/cm, very similar to the EC measured in the previous year. Groundwater temperature was 19.8 °C and pH was 7.10 (Figure 8). The shore-to-center change in the measured variables in this period (Figure 6) suggests that the groundwater input is a major component of the water balance in the pond, as sketched in Figure 8. On the other hand, it seems clear that three zones (depicted in Figure 6 as 1, 2 and 3) can be distinguished: 0–12 m, 12–26 m and 26–40 m. In the 0–12 m zone, all the measured properties are increasing, in the 12–26 m zone, temperature and EC are increasing, and in the 26–40 m zone all are uniform. There is even a clear difference in the slope of EC in each of the three zones as can be seen in Figure 6.

A similar transect measurement was made the same day in Dulce pond, where a piezometer similar to the one at Santa Olalla (Figure 7) was installed (see Figure 1b for location). No significant variation was found in the water EC in Dulce pond, although a hydraulic head at a depth of 15 m in the on-shore piezometer was 70 cm above the ground surface indicating the pond-ward flow of groundwater. The water EC was nearly constant, ranging from 1.1 to 1.2 mS/cm along the transect. On the other hand, pH ranged from 7.1 to 8.6 at a distance of 20 m from the shore. Temperature ranged from 20.0 to 21.8 °C in the same transect (see Appendix B for details). Groundwater in the piezometer had a temperature/EC/pH of 20.0 °C, 0.187 µS/cm, and 8.25, respectively.

3.2. Heat Transfer Modelling to Estimate Groundwater Discharge

Table 1 lists the parameters used in the thermal modeling. Boundary conditions (position of the temperature sensors) are shown in Figure 3. Thermal conductivity is a property related to the hydraulic conductivity (k) in heat-flow modeling, although k varies over a much broader range than the former. Parameters used in the thermal modeling (see Table 1) were based on bibliography References [12–15]. The modeling carried out with 1D temp pro V2 showed different results for each study period. Input parameters used for both periods were the same. Porosity was 0.3, thermal conductivity 1 W/m°C, sediment heat capacity 3.3×10^6 J(m^3/°C) and dispersivity 0.0005 m [13,14]. These inputs were chosen according to the values proposed by Fernández-Ayuso [9,10] for the porosity, Goto and Matsubayashi [12] for the thermal conductivity and the sediment heat capacity, and Jensen et al. [14] for the dispersivity. The model fitting was found to be very accurate to the measured values. The obtained discharge for the first study period (14 February 2017–16 May 2017) resulted on 0.36 hm^3/year. This value corresponds to a groundwater discharge through the perimeter of the pond, considering an average depth of 1.5 m. The hourly data series of the surface water, surface–groundwater interface, and groundwater temperature in the center of Santa Olalla pond, from February to May 2017 are shown in Figure 9. The water temperature recorded by the deepest sensor, IB-1, was fairly constant, increasing smoothly and at a constant rate from 17 to 18.5 °C during the study period. The temperatures in the pond's bed (IB-2) and above (IB-3) were not influenced by diurnal changes in air temperature, although such changes could be high, more than 15 °C between midday and night (Figure 9). It should be noted that IB-2 and IB-3 had a column of water of deeper than 2 m above them (Figure 2), buffering the changes in the water surface temperature.

Table 1. Parameters used in the thermal modeling (1D-Temp-Pro).

Modeling Conditions 1D Temp PRO V.2	
Porosity	0.3 (m^3/m^3) [1]
Thermal conductivity	1 (W/m°C) [2]
Sediment heat capacity	3.3×10^6 (J/m^3°C) [2]
Dispersivity	5×10^{-4} m [3]

[1] Fernández-Ayuso and Rodríguez-Rodríguez (2018); [2] Goto and Matsubayashi (2008); [3] Jensen et al. (1993).

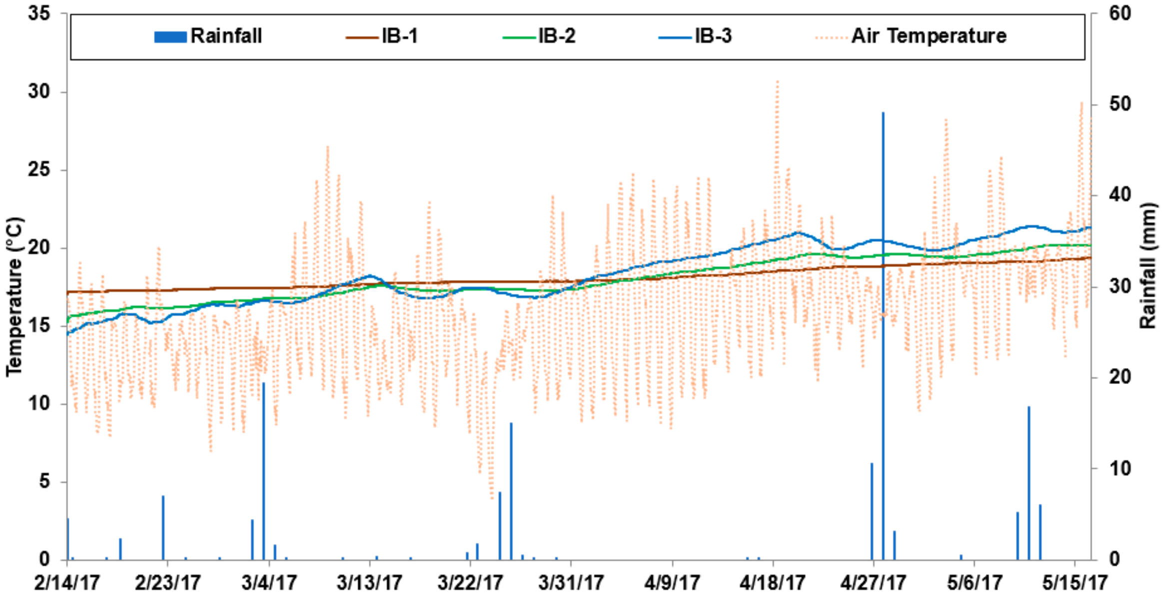

Figure 9. Hourly evolution of the surface, interface, and groundwater temperature in the center of Santa Olalla pond, from February to May 2017. **IB-3** corresponds to the iButton placed at a distance of 0.25 m from the pond's floor. **IB-2** corresponds to the iButton placed directly on the pond's floor, and **IB-1** corresponds to the sensor placed at a depth of −0.35 m below the pond's floor. Air temperature is also plotted, although air temperature was not used in the model setup. In the same sense, rainfall events are also shown.

On the other hand, longer-term declines of air temperature, as well as rainfall events, produces a temporal cooling of the surface waters of the pond that, due to mixing and processes of advection, reach the bottom of the pond, lowering the temperature of IB-2 and IB-3, but not IB-1. This is indicative of a process of groundwater discharge from the aquifer to the pond, as sensor IB-1, located beneath the sediment, is influenced by cooler groundwater temperature [13]. Otherwise, thermal changes in the surface water would affect the groundwater temperature.

3.3. Thermal Behavior and Heat Transfer Modelling to Estimate Groundwater during Low Water Depth

Groundwater discharge values during the second period (1 December 2017–10 February 2018) obtained from the heat transfer modeling were of an order of magnitude lower, that is, 0.05 hm^3/year. Figure 10 shows the temperature in such a period of low water stage in Santa Olalla pond. The vertical positions of IB-1, IB-2, and IB-3 were the same as Figure 9 except that the water stage was much lower (see Figure 2).

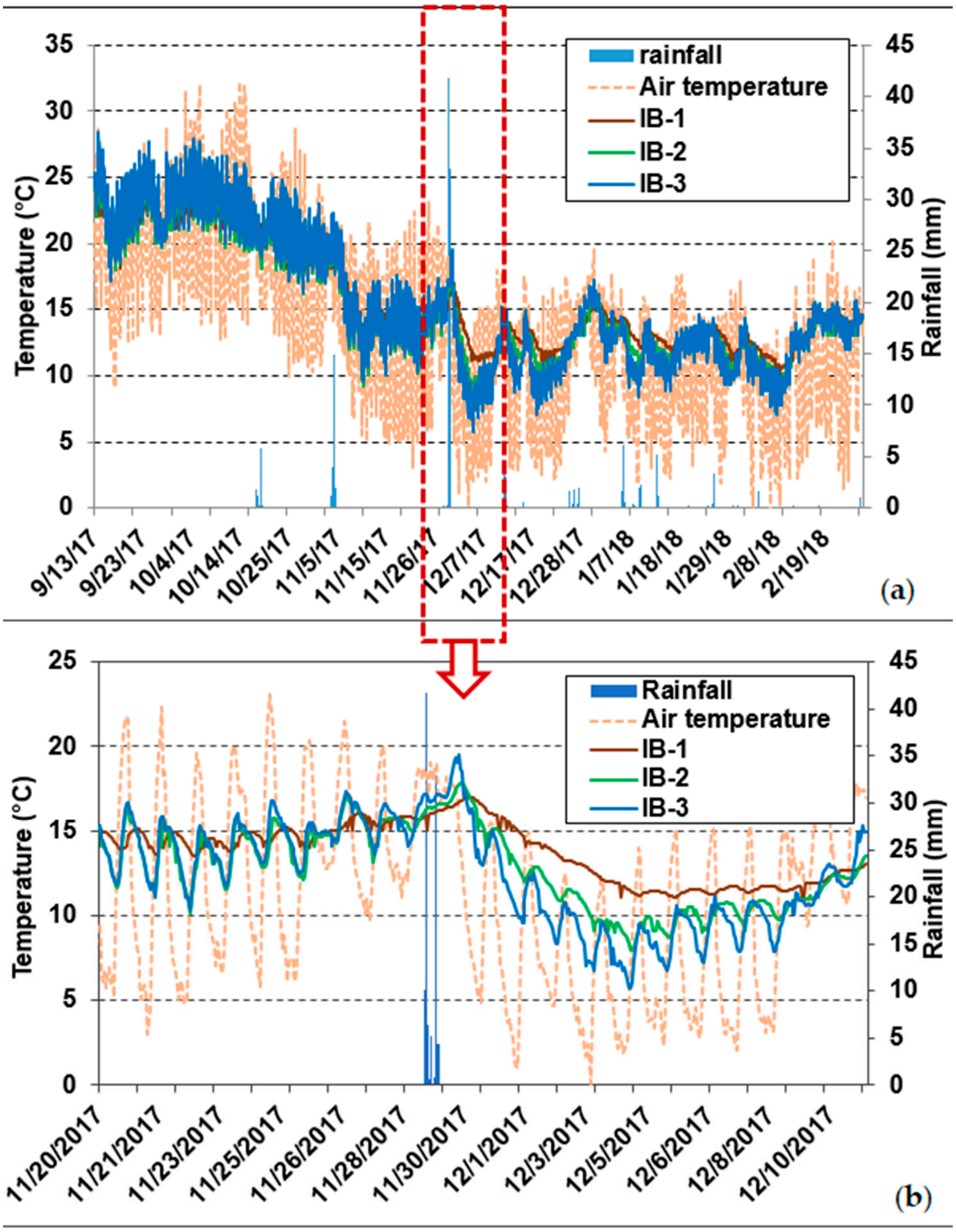

Figure 10. Hourly evolution of the surface, interface, and groundwater temperature in the center of Santa Olalla pond, from September 2017 to February 2018. Rainfall events are also shown.

From September 2017 to February 2018, the magnitude of temperature oscillations in IB-3 (Figure 10a) was higher than that during the period of higher water stage in February–March 2017 (Figure 9), indicating that the temperature oscillations from the water surface reached the bottom of the pond. In November 2017, pond water temperature (IB-3) oscillated between 12 and 16 °C following a diurnal pattern (Figure 10b). Groundwater temperature (IB-1) also oscillated daily, between 14 and 15 °C indicating the effects of heat conduction through the bottom sediment. This process of groundwater recharge during low water depth periods was taking place until a rainfall event. Such event totalized c. 80 mm of precipitation over the pond as well as an increment of c. 50 cm in the pond's water level, and took place from 29 to 30th November 2017. As it can be seen in Figure 10, surface water was lowered from 15 to 5 °C, oscillating in a daily pattern, whereas groundwater remains stabilized daily, but water temperature cooled from 16 to 12 °C during a five-day time interval (from 30 November 2017 to 4 December 2017), suggesting groundwater recharge from the center of the pond to the aquifer throughout all the third stage of this study.

4. Discussion

This study has shown that the groundwater inputs to Santa Olalla pond had high seasonal variability. In addition, the perimeter of the pond seems to be the preferential area of groundwater discharge (inflow) as stated by other authors [3]. The center of the pond, where the staff gage was placed, seems also to be a discharge (inflow) area especially during high water level stages, where hydraulic gradients are higher. Other authors did similar experiments in Dulce and Santa Olalla ponds in July and December 1985 [3]. They also applied a 2D model to quantify flows from and to the pond, as well as the transport of solutes. The results obtained by these authors indicate that Santa Olalla acts like a discharge pond during the wet phase of a hydrological cycle (December 1985), but they point to an inversion of the hydraulic gradient during the dry phase (July 1985), in which a water recharge toward the aquifer takes place, bringing salts via advection methods. The average EC in the groundwater oscillated between 0.2 mS/cm in deep (15-m) piezometers and 1.5 mS/cm in shallower (3.5-m) piezometers.

In a more recent work made in 2017 [8] the groundwater discharge rate estimated using a water balance method was 0.40 hm^3/year to Santa Olalla pond. Higher values for groundwater discharge (c. 1.30 hm^3/year) were obtained by the segmented Darcy method, also applied to the pond [9]. In this case, some of the discharge could not eventually go to the pond, but to the coast or to the Vera ecotone since the volumes of flow are higher than those estimated for the same period of time using the water balance method.

5. Conclusions

In this study, temperature, EC, and pH of pond water and groundwater were used as tracers to detect groundwater—surface water interactions and the hydrological functioning in a permanent pond, Santa Olalla, located above highly permeable dune sands. A semi-permanent Dulce pond adjacent to Santa Olalla was also investigated. The results showed a complex hydrological pattern likely reflecting the existence of several groundwater flow paths, ranging from local to regional, that affect the ponds in different periods and different water stages.

First, the field data collected at several periods during 2016–2018 suggest a net groundwater discharge throughout the shores, which contributes greatly to the water balance of the pond. Water EC measurements on the western shore after a two-month period of high rainfall revealed a remarkable gradient of more than +6 mS/100 m on a 40 m transect, indicating a local groundwater flow path discharging fresh groundwater onto the pond. At the same time, a similar transect made in nearby Dulce pond, did not show any change in water EC (gradient of 0 mS/100 m). On the other hand, a pH gradient was detected in both ponds, suggesting that this water characteristic is much more influenced by biological processes, such as the photosyntetic activity, taking up CO_2 dissolved in the water and, therefore, raising the pH from the shore to the center of the pond.

Second, temperature profiles made in the center of Santa Olalla pond during high and low water level periods suggests a net groundwater discharge during high water levels, but seepage of surface water to the aquifer (recharge) during low water stages. This leakage of pond's water to the aquifer could also explain why the water of Santa Olalla pond ranges from brackish in winter to saline in summer: Some of the salts have a way out of the system via recharge to the aquifer. Otherwise, the water salinity would have been much higher, of a brine type. In the same sense, and in an inter-annual behavior, during dry years, solutes in Santa Olalla may go from the pond to the aquifer, and during wet years this process is interrupted because the groundwater levels are above surface levels all around the shore. Of course, there could be other ways to lose salts from the pond (e.g., via Aeolian processes, when the wet surface of the pond shrinks in summer). Only during exceptionally rainy years, Santa Olalla and Dulce ponds connect with each other and form a continuous water body. Saline water from Santa Olalla then mixes with Dulce fresh water, and a brackish-water pond is created. This is another way out for Santa Olalla solutes.

Author Contributions: M.R.-R. and A.F.-A. conceived, designed and performed the experiments; A.F.-A. analyzed and executed the thermal model; F.M.-M. contributed to the analysis and conceptualization of the results; M.R.-R. and M.H. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Electrical conductivity (EC) and temperature of water in Santa Olalla pond measured in July 2016. At each location EC and temperature were measured at the surface of the pond bottom sediment and a certain depth below, ranging from 20 cm to 80 cm depending on the hardness of the sediment.

Location	Date	Time	EC (mS/cm)	Temperature (°C)	Depth (cm)
1	12 July 2016	17:49	10.50	29.7	0
1	12 July 2016		05.84	26.5	20
2	12 July 2016	18:07	10.47	29.0	0
2	12 July 2016		09.94	26.8	60
3	12 July 2016	18:31	10.49	29.0	0
3	12 July 2016		10.32	25.7	60
4	12 July 2016	18:50	10.50	28.7	0
4	12 July 2016		09.26	26.2	60
5	12 July 2016	19:49	10.55	28.7	0
5	12 July 2016		07.35	27.5	70
6	13 July 2016	10:20	10.63	22.6	0
6	13 July 2016		08.59	23.2	20
7	13 July 2016	10:40	13.25	23.7	0
7	13 July 2016		04.77	23.8	40
8	13 July 2016	10:58	10.68	24.5	0
8	13 July 2016		10.66	24.2	20
9	13 July 2016	11:24	10.60	25.0	0
9	13 July 2016		08.68	24.7	35
10	13 July 2016	11:51	10.61	24.6	0
10	13 July 2016		10.13	24.3	24
11	13 July 2016	12:08	11.18	24.6	0
11	13 July 2016		10.82	24.3	20
12	13 July 2016	12:48	10.70	25.7	0
12	13 July 2016		9.64	25.6	52
13	13 July 2016	13:05	10.62	25.8	0
13	13 July 2016		09.35	25.8	50
14	13 July 2016	13:27	10.65	26.3	0
14	13 July 2016		09.79	25.9	50
15	13 July 2016	14:12	10.56	31.1	0
15	13 July 2016		07.89	27.3	88

Appendix B

Table A2. Electrical conductivity (EC), pH, and temperature of water measured along the transects in Santa Olalla and Dulce ponds in 9 May 2018.

DISTANCE FROM SHORE (m)	EC (mS/cm)	pH	Temperature (°C)
SANTA OLALLA POND			
2	2.24	7.08	19.9
4	2.56	7.15	19.9
6	2.94	7.23	20.1
8	3.25	7.48	20.3
10	3.56	8.07	20.5
12	3.85	8.89	20.7
14	4.03	8.97	20.7
16	3.99	9.08	20.9
18	4.09	9.17	21.1
20	4.20	9.26	21.3
22	4.48	9.21	21.6
24	4.38	9.52	21.6
26	4.64	9.34	21.8
28	4.69	9.45	21.5
30	4.67	9.42	21.5
32	4.69	9.41	21.5
34	4.69	9.42	21.5
36	4.70	9.42	21.4
38	4.73	9.34	21.5
40	4.73	9.32	21.5
DULCE POND			
2	1.22	7.11	20.0
4	1.22	7.23	20.1
6	1.19	7.09	19.9
8	1.15	7.15	20.3
10	1.11	7.31	20.7
12	1.10	8.06	21.2
14	1.10	8.22	21.4
16	1.10	8.41	21.6
18	1.10	8.53	21.9
20	1.10	8.54	21.8
22	1.10	8.58	21.8

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