Applications of Hydro-Chemical and Isotopic Tools to Improve Definitions of Groundwater Catchment Zones in a Karstic Aquifer: A Case Study

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Abstract: Some researchers have proposed the groundwater protection zone (GPZ) method as a methodological framework for defining safeguard zones of groundwater bodies. Its goal is to protect the quality of water intended for human consumption and to facilitate a common implementation of this method in all European Union member states. One of the criteria used to establish GPZs is to define contributing catchment areas (CCAs). This methodology has been applied to the Sierra de Cañete, a region comprising a carbonate aquifer in the province of Malaga, Spain. The tools used to define CCAs are hydro-chemical and isotopic characterizations, namely water isotopes (i.e., ^{2}H, ^{18}O and tritium) and the isotopes of dissolved sulfates (i.e., ^{34}S and ^{18}O). Traditionally, the Sierra de Cañete aquifer has been divided into six sectors. Hydro-chemical and isotopic characterization differentiated between two large areas in the carbonate aquifer. The southern part presents younger water that is the result of faster recharge and that shows a high level of karstification, while the northern area has a slower flow, and recharge is produced over several years. In addition, the northern part is hydraulically connected to an alluvial aquifer (i.e., Llanos de Almargen) that borders the Sierra de Cañete to the north. This aquifer has high levels of pollution due to agricultural and livestock activities carried out in the Llanos de Almargen area. This pollution is transmitted to the carbonate aquifer when groundwater depletion occurs. Therefore, the Sierra de Cañete GPZ needs to be extended to include the Llanos de Almargen aquifer.

Keywords: groundwater; hydro-chemical; Isotopic; Catchment; Karstic

1. Introduction

Groundwater protection zones (GPZs method) were applied to catchments intended for human consumption in the Sierra de Cañete in the province of Malaga, Spain [1,2]. The objective was to use hydro-chemical and isotopic data to support other techniques applied to define zones of contribution to catchments. These tools can be used to define safeguard zones to protect groundwater for human consumption. The study focused on the demarcation of the contributing catchment areas (CCA) of the Sierra de Cañete. To achieve this goal, the research included the following:

- Hydro-chemical description of the aquifer;
- Analysis of water stable hydrogen and oxygen isotopes (i.e., 1H, 2H or deuterium, 16O and 18O), which allowed distinctions to be made between sectors within the aquifer depending on the amount of isotopes present—whether hydrogen or oxygen—since these bodies of water can be traced according to their origin;
- Tritium (3H) content analysis that revealed the age of the water;
- Sulfur isotope analysis (34S) to check for contamination in any sector of the aquifer.

In the Sierra de Cañete, the delimitation of the CCAs intended for human consumption has been determined by using structural, hydrodynamic (i.e., wells' piezometric levels and springs' flow regimes) and complementary methods [3]. The latter include hydro-chemical characterization and analyses of natural tracers based on water stable isotopes in the most representative catchments of the study area. The present research revised and supplemented these complementary methods, resulting in indirect methods that complement each other and help to delimitate CCAs more accurately.

2. Complementary Methods: Isotopic Tools

Water molecules have different properties according to the type of stable isotopes of hydrogen and oxygen that form them. Of these, ^{1}H, ^{2}H or deuterium, ^{16}O and ^{18}O are the most abundant. The content of the different stable isotopes varies throughout the water cycle because of their uneven behavior in phase changes and other reactions in water resulting from the isotopes' different mass. The consequence of this is an effect known as isotopic fractionation, which generates differences in the ratio of light and heavy isotopes between phases or compounds that interact and their reaction products. This allows researchers to distinguish between or "trace" waterbodies according to their origin [4–9].

This process is quite evident in rainfall because this water can undergo various processes that modify its isotopic composition from that of its source to that of any other phase of the local hydrological cycle. The isotopic differentiation of water throughout its evolution allows experts to trace the origin of water, as well as recharge zones or possible mixtures of water from different sources, which have gone through several hydrological processes. In groundwater, however, the superposition of different processes in space and time in aquifers can complicate the interpretation of isotopic data.

The contents of water stable isotopes (i.e., deuterium and oxygen) were determined in the CEDEX's Laboratory of Isotopic Applications (LAI), using an isotope-ratio mass spectrometer with a double introduction system to analyze light elements. The analytical results were expressed as isotopic deviations of the sample δ_m with respect to the Vienna Standard Mean Ocean Water (VSMOW)-Standard Light Antarctic Precipitation, which is expressed as:

$$\delta_m = \frac{R_m - R_{VSMOW}}{R_{VSMOW}} \times 10^3 \tag{1}$$

In this formula, R represents the ratio between the number of heavier molecules ($^{2}H_1H^{16}O$ or $^{1}H_2{}^{18}O$) and light ($^{1}H_2{}^{16}O$) elements existing in the sample. The uncertainty levels for analyses carried out in the LAI are $\pm 0.2‰$ for $\delta^{18}O$ and $\pm 1.5‰$ for δ^2H.

The samples of tritium (i.e., the unstable isotope of hydrogen) were also analyzed by the LAI. The tritium activity in the sample was measured in a liquid scintillation spectrometer after an electrolytic concentration process. The equipment used was a Quantulus 1220. The minimum detectable activity in this process falls in the range of 0.04–0.05 Bq/L. Tritium concentrations are expressed in tritium units.

Agricultural activities in the alluvial aquifers are usually one of the most important sources of pollution providing inorganic substances, such as sulfate, nitrate and metals, as well as organic elements, such as pesticides [10]. Although they increase the yields of farms, poorly-regulated implementation of pesticides results in surpluses stored in the soil, seeping into the unsaturated zone and, finally, into groundwater. The presence of pesticides in the soil and water is unequivocally the

evidence of the impact of agricultural activities on the environment. However, the same cannot be said for inorganic compounds (i.e., sulfate, nitrate and potassium) since many natural sources bring these solutes into the environment.

It is common practice to estimate the impact of these inorganic compounds in water resources using the hydro-chemical baseline of the relevant aquifer or groundwater body. This is the average concentration produced by hydrogeochemical processes as a result of the interaction of recharge water and rock and/or sediment. Therefore, low concentrations are often equated with no or low impacts and high concentrations with severe impacts.

In the case of dissolved sulfate, the latter assertion is incorrect because it is possible to find concentrations above the baseline that have originated from natural sources. These include, among others, (1) dissolution of evaporite rocks ($CaSO_4 = Ca^{2+} + SO_4^{2-}$), (2) oxidation of pyrite or other metal sulfide ($MeS + O_2 = Me + SO_4^{2-}$), (3) the mixture of fresh water with sea water or brine, (4) deposition of sulfur aerosols of volcanic origin and (5) wet or dry deposition of atmospheric sulfur (SO_x). The last source includes marine aerosols and secondary sulfates formed by oxidation. Therefore, high concentrations of dissolved sulfate can be found without being of anthropogenic origin.

In areas of human activity, the sources of sulfate are: (1) dry or wet deposition of sulfur emitted into the atmosphere by burning fossil fuels, (2) sulfate fertilizers (e.g., $(NH_4)_2SO_4$ and K_2SO_4) and/or (3) untreated sewage. Therefore, low concentrations of sulfate are not commonly found in areas under anthropogenic pressure, but this can also mean that human activities have been recently implanted. A more worrying alternative is that the compounds are held and/or stored in the unsaturated zone, and they have not been transferred yet to the saturated zone, so the problem could exist, but will not show up in tests.

In either of the previous cases, using just the concentration of dissolved sulfate would not reveal whether an impact exists or not because the final value can be caused by natural or artificial sources, or a mixture of these. In this case, the application of isotopic techniques is necessary to establish the origin and mixing ratio of each of the water sources.

The first isotopic studies of the sulfate molecule focused on $\delta^{34}S$ as a trace element of natural and anthropogenic sources. Some studies relate the sulfur to natural sources [11] but the dual use of the sulfate molecule (i.e., $\delta^{34}S$ and $\delta^{18}O_{SO4}$) allowed researchers to establish with a greater precision the origin of this ion [8].

The present study site has two main sulfate sources: (1) Triassic evaporates and (2) sulfate fertilizers applied on the olive trees in the area. In both cases, if the hydrogeochemical conditions include oxidation and isotopic fractionation does not occur through mycobacterial reactions, dissolved sulfate from gypsum or anhydrite and from sulfate fertilizers will retain the same isotopic value as the compound from which the sulfate comes. This is because the dissolution reaction is a process in which isotopic fractionation does not occur.

The purpose of the application of isotopes of sulfate is to demonstrate that, although the concentration of sulfate does not reveal the effects of farming because it is incipient to the area under study, the dual isotopic signal (i.e., $\delta^{18}O_{SO4}$ and $\delta^{34}S$) may indicate that the origin of the dissolved sulfate is agricultural. Therefore, this signal can be used as a tool to define any zones affected and/or contaminated by anthropogenic pressures and to establish protection areas in the aquifer.

The isotope ratios of $\delta^{34}S$ and $\delta^{18}O_{SO4}$ in the sulfate molecule were measured in the Central Services of the University of Barcelona, using an isotope ratio mass spectrometer. The standard deviation for $\delta^{34}S$ was 0.2‰ and 0.5‰ for $\delta^{18}O_{SO4}$.

3. Study Site

3.1. Site Description

The Sierra de Cañete is located in the western Mediterranean region, in southern Spain. These mountains cover a surface of approximately 55 km^2. It is the most eastern area of the groundwater bodies, Sierra de Cañete-Corbones, Sierra de Cañete-Sur and Setenil, belonging to three river basin districts, Guadalquivir, Andalusia Mediterranean Basins, and Guadalete and Barbate, respectively (Figure 1).
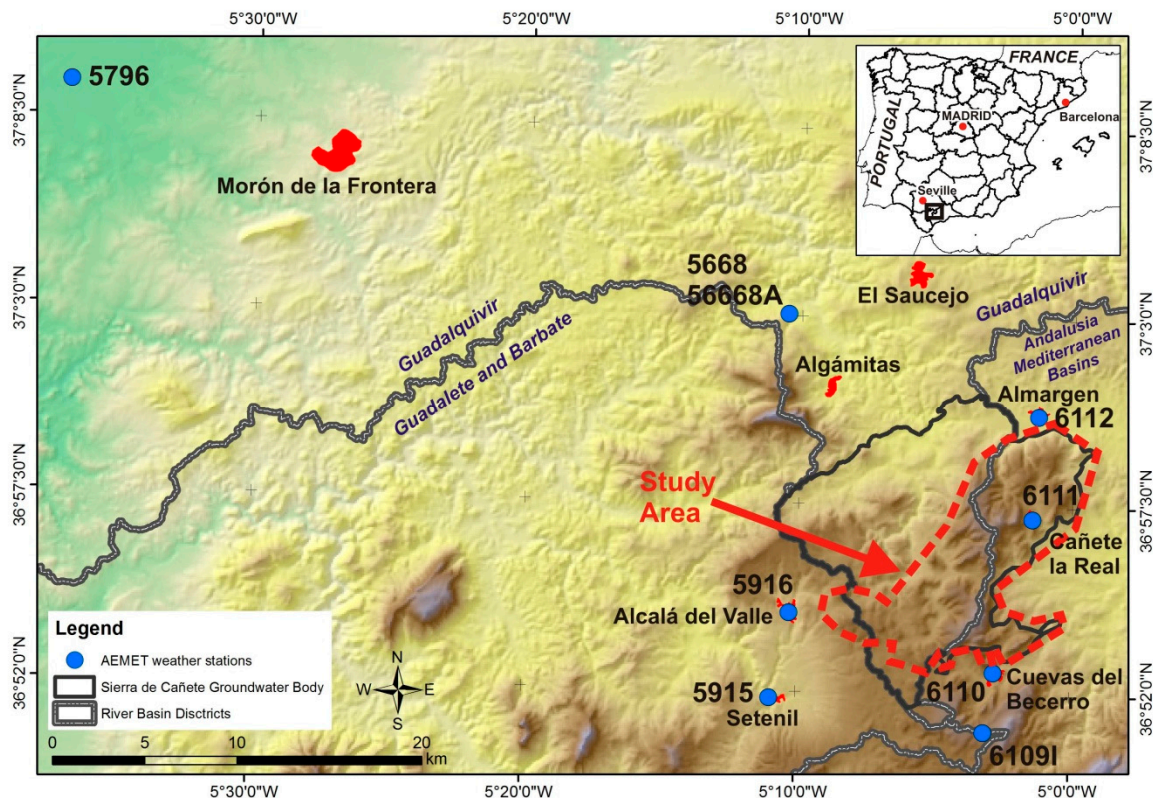

Figure 1. Geographical situation of the Sierra de Cañete aquifer.

Its annual precipitation is assessed in the range from 520 to 1280 mm, on the basis of partial data. The nearest weather stations of AEMET (Weather Agency of Spain) are placed surrounding the mountain zone (Figure 2a) and only have complete records for a few years. The reference weather station is 50 km away (Station 5796) and belongs the Spanish Network of Isotopes in Precipitation (REVIP, [9]. The rain records are complete from 1956, and the mean precipitation from 1956 to 2016 was about 560 mm/a. The analysis of the monthly variability, by means of the accumulated deviation with respect to the monthly mean, shows a high seasonality, a rough wet period from 1958 to 1979, a dry period from 1979 to nowadays and very strong changes in the precipitation tendencies inside those two periods (Figure 2b). Sampled were collected in one of these changes, when the 2004–2009 very dry period was followed by the 2009–2011 very wet period (Figure 2b).
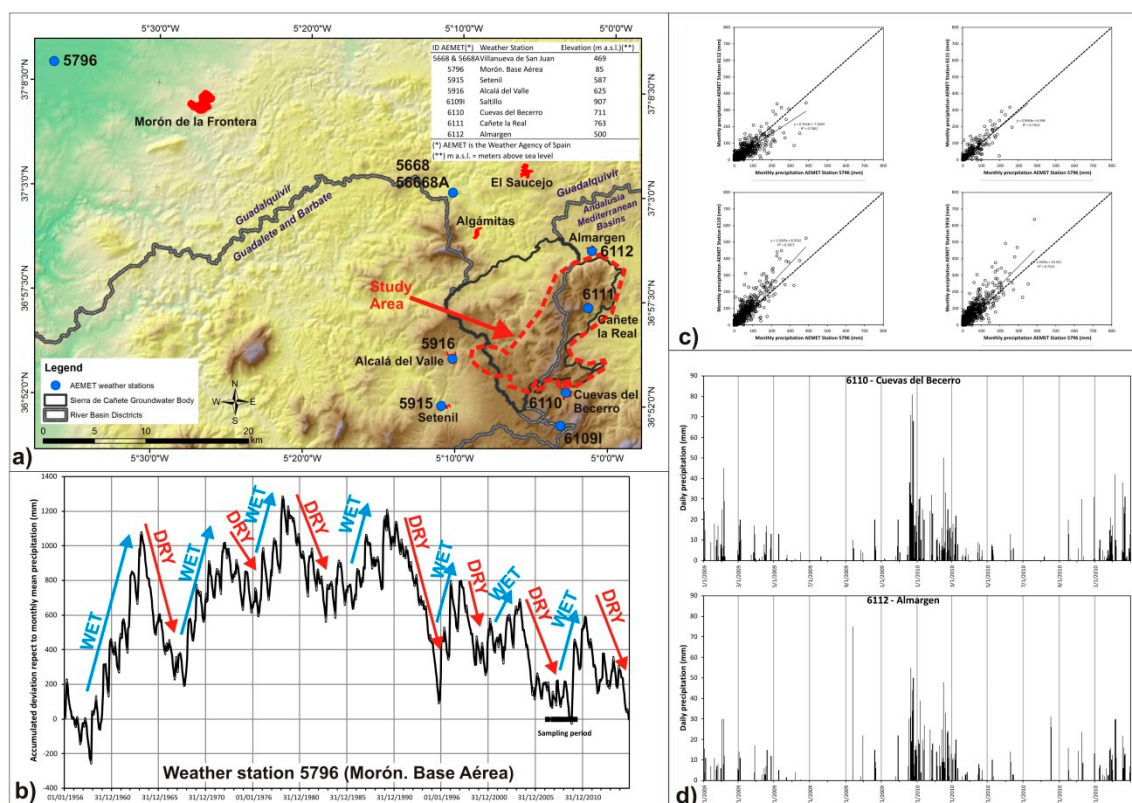
Figure 2. Characteristics of precipitation in the Sierra de Cañete aquifer. (**a**) Situation and elevation of some weather stations used in the analysis of precipitation. (**b**) Accumulated deviation with respect to the monthly mean of precipitation at Station 5796 and the period of hydro-chemical and isotopic sampling. (**c**) Comparison between monthly precipitation at Station 5796 with Stations 6112 (Almargen), 6111 (Cañete la Real), 6110 (Cuevas del Becerro) and 5916 (Alcalá del Valle). (**d**) Daily precipitation during 2009 and 2010 at Stations 6110 (Cuevas del Becerro) and 6112 (Almargen).

In general, the stations placed near the Sierra de Cañete show monthly precipitations greater than Station 5796, mainly for high values, but at the northern and eastern stations (6111 and 6112), the tendency shows similar or lower precipitation than in the reference station (Figure 2c).

The only weather stations situated in the Sierra de Cañete that have daily records for the years 2009 and 2010, when the isotopes were sampled, are 6110 (Cuevas del Becerro) and 6112 (Almargen). During the period December 2009–March 2010, the precipitation at Cuevas del Becerro was 1052 mm, while at Almargen, it was 899 mm. Then, it seems that precipitation reduces from south to north and from west to east.

The groundwater resources of the Sierra de Cañete are used by nine municipalities, of which six use wells for their supply (Alcalá del Valle, Almargen, El Saucejo, Olvera, Teba and Torre Alháquime and La Atalaya) Cañete la Real has a mixed system, as it is supplied both by springs and boreholes. The total of these population nuclei according to the last census realized by the National Institute of Statistics in 2009 is 36,250 inhabitants [12].

The predominant land uses in the Sierra de Cañete are the corresponding areas with plots dedicated to dryland cultivation (23.91%), areas occupied by Quercus sp. (22.81%) and scrub (21.11%). The main economic activity of all of the villages located in the study area is related to agriculture, and wheat crops and olive groves occupy a greater extent. Activities related to tourism are scarce. Even so, in recent years, there has been an increase in the sector related to rural tourism. The unemployment rates of all municipalities studied are around 6–8% of the total population [12].

The geological structure that presents the Mountain range of Cañete is an antiform that integrates two tectonic units separated by materials of the flysch of the Field of Gibraltar. There are numerous N-S direction fractures and fractures transverse to the structure (Figure 3).
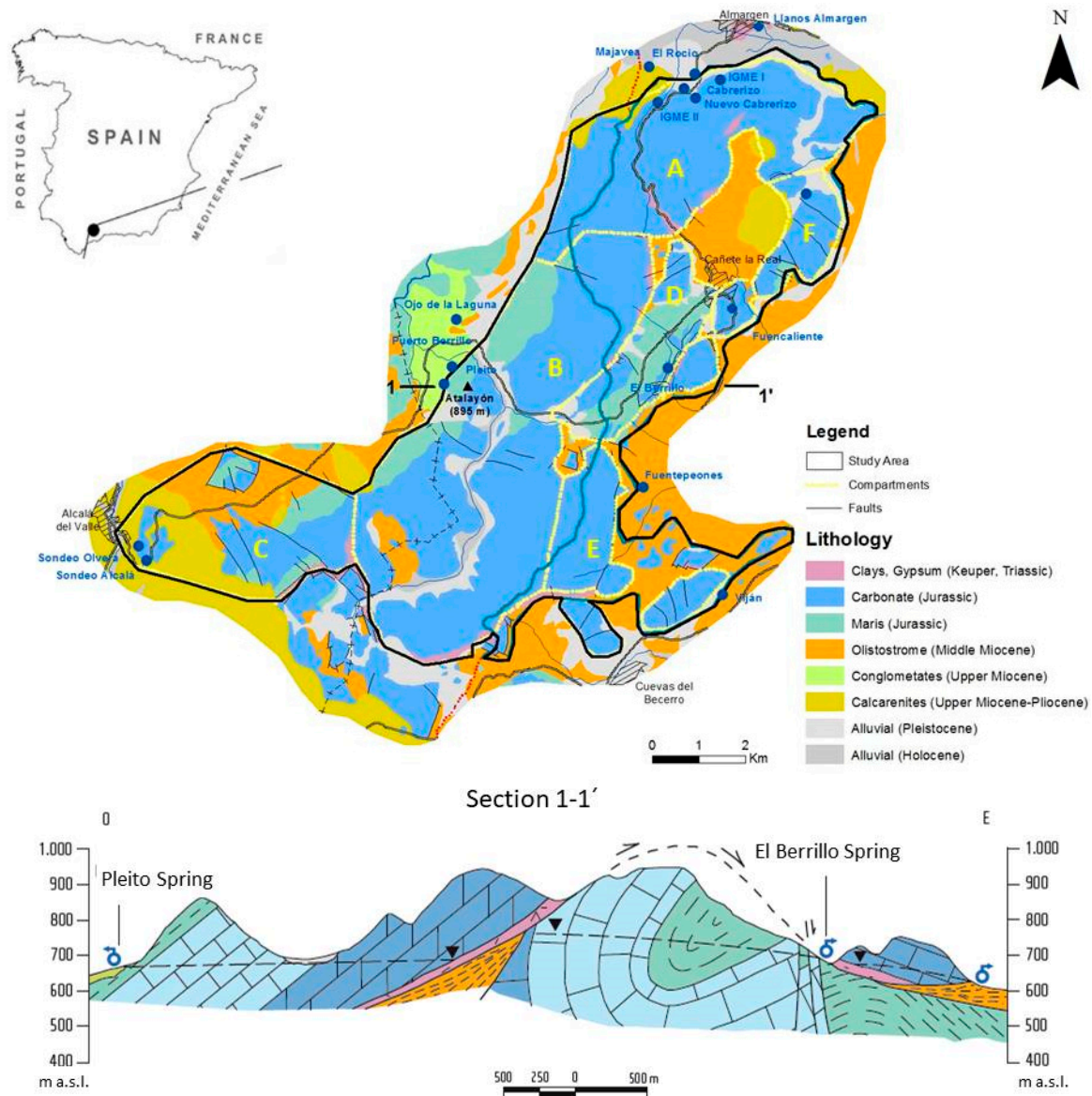

Figure 3. Hydrogeological setting of Sierra de Cañete.

Regarding geomorphology, the Sierra de Cañete presents a partially developed karst relief. As exokarstic forms emphasize the fields of limestone pavement in the zones near the town of Cañete la Real, and in addition, there are a dozen sinkholes, apparently inactive. It is also necessary to emphasize the existence of quarries of extraction of aggregates, mostly located to the north of the mountain range that function as artificial sinkholes with infiltration of the accumulated rainwater in them, which has been verified through field recognition [13].

Due to tectonic causes, the Sierra de Cañete is divided into several aquifers (i.e., compartments) (see Figure 3), which are recharged by rainwater infiltration. Groundwater flow occurs through fissures and conduits toward discharge springs that are located at different topographic heights according to aquifer divisions. These springs reveal moderate karstic processes [13].

The Almargen compartment (A in Figure 3) has 16 km^2 and discharges at the northern end of the mountain range through springs located at a height of 520–510 m a.s.l., including Majavea (30 L/s), which supplies Campillos town. This compartment is also exploited for supply to the populations of Almargen and El Saucejo. For this part, the carbonate aquifer of Sierra de Cañete is hydraulically connected to the alluvial aquifer of Llanos de Almargen on the northern edge of the mountain. The natural water flow normally goes from the alluvial aquifer to the carbonate one, but this flow is reversed in times of water shortage.

The compartment of La Atalaya (B in Figure 3) is the most extensive of the Sierra de Cañete (30 km^2), occupying most of the western slope of the mountain range, and is discharged at a height of 670–680 m a.s.l., by the most abundant springs of the area: Ojo de la Laguna (average flow of 35 L/s, with a significant summer decrease) and Pleito (average flow of 7 L/s with a decrease of the same in summer), among others. This compartment is currently in a natural state, as there are no significant extractions.

The Alcalá del Valle compartment (C in Figure 3; 11 km^2) occupies the southwestern end of the mountain range and is discharged to the height of 590–600 m a.s.l., through the springs of Alcalá del Valle, currently affected by the extractions that are carried out in its vicinity to supply the populations of Alcalá del Valle, Olvera and Torre Alháquime. The hydrogeological relation with the compartment of La Atalaya is not clear from the geometric point of view, and possibly, a transfer of resources from this last compartment to the one of Alcalá del Valle occurs.

In the eastern edge of the mountain range, other smaller compartments have been differentiated (none of them exceeds 4 km^2). These include La Nina (F in Figure 3; 3 km^2) and Fuentepeones (E in Figure 3; 4 km^2). The first one is used mainly for supply to the population of Teba, though probes have caused the disappearance of the spring by discharge to a height of 620 m a.s.l. The second is discharged by several springs located at a height between 675 and 700 m, the most significant of which is that of Fuentepeones with an average flow of 6 L/s, although it is exploited by means of a survey to supply the urban center of Cañete la Real, which affects its natural regime.

With respect to hydrometry, the springs usually have a minimum in summer and a maximum with the spring rains. Flow evolutions in the Majavea and Ojo de la Laguna springs reflect quite well the hydrogeological behavior of the Sierra de Cañete. The case of the spring Ojo de la Laguna stands out for presenting an irregular regime with typical responses of karst systems because it drains the part of the sierra where the karstic development is more evident. On the other hand, more common to the rest of the springs of this zone is the source of Majavea with a more regular hydrograph and with a more attenuated response to the pluviometric events.

3.2. Sample Collection and Analyses

A control network was established covering the entire study area, which consisted of 39 points. Of these, 15 were piezometers, 9 springs were used as flow control points and 15 functioned as specific quality control points. Nine sampling seasons were conducted in this network: 2 in 2007, 4 in 2008, 2 in 2009 and 1 in 2010. Water samples were collected in a single day for each field campaign [12].

Only the most representative sampling points were used in the present research (see Table 1 below and Figure 1 above), and the data were taken from Jimenez Madrid's [12].work. Hydro-chemical samples were collected from 2007–2010. Water isotopes (i.e., stable and tritium) samples were collected in the May 2009 and March 2010 field campaigns. The sulfur isotope samples were collected in the May 2009 field campaign, and the data were taken from unpublished research by Jiménez Madrid [12].

Notably, Sampling Point 13 corresponds to the alluvial aquifer of Llanos de Almargen, which was included in the control network because of the risk posed by intense livestock activity taking place on this aquifer. An analysis of these samples facilitated an assessment of the level of contamination in that groundwater body.

Table 1. Hydro-chemical and isotopic sampling points.

Point	Denomination	Elevation (m a.s.l.)
1	Sondeo Olvera (W)	655
2	Sondeo Alcalá (W)	645
3	Fuentepeones (S)	675
4	Viján (S)	685
5	El Rocío (W)	538
6	La Nina (W)	690
7	Majavea (S)	520
8	Ojo de la Laguna (S)	672
9	Pleito (S)	670
10	El Berrillo (S)	690
11	Cabrerizo (W)	528
12	Majorrego (W)	525
13	Llanos de Almargen (W)	488
14	IGME I (W)	534
15	Nuevo Cabrerizo (W)	617
16	Fuencaliente (S)	680
17	Cortijo Grande (S)	672
18	Puerto Berrillo (S)	688
19	IGME II (W)	586

Notes: m a.s.l. = meters above sea level; W = well; S = spring.

4. Results

4.1. Hydrochemistry

The materials forming the Sierra de Cañete aquifer and its surroundings are quite specific in nature. Most of the mountain is a carbonate aquifer overlapping Triassic evaporites. However, the Llanos de Almargen aquifer on the northern edge of the mountain is alluvial (see Figure 3 above). In addition, the Almargen compartment located in the northernmost area was found to be different from the carbonate aquifer. Due to potential groundwater flow between the carbonate and alluvial aquifers, these areas need to be differentiated in terms of the chemical composition of groundwater [12].

The groundwater in the Sierra de Cañete shows medium mineralization (Table 2 and Figure 4). Bicarbonate, calcium and magnesium are the major components, and no significant variations were found between summer and winter composition. The dominant hydro-chemical facies are calcium bicarbonate, but the magnesium values increase during the dry season mainly in the extremely tectonized areas, as in the tectonic window where the El Berrillo spring (i.e., Sample Point 10) is situated. The abundant content of magnesium may be due to a longer residence time of the groundwater, allowing a major dissolution of dolomite materials. The groundwater of the alluvial aquifer presents chlorinated-sodium facies [12].

Most of the points have electrical conductivity values of 500–700 μS/cm, except Majorrego (Sampling Point 12), Cabrerizo (11), and Llanos de Almargen (13). Conductivities of 2500 μS/cm were reached in the first and 800–1500 μS/cm in the second and third points. Therefore, these samples reveal generally low salinity water.

The Almargen compartment merits special attention because this is the area that borders the Llanos de Almargen aquifer. There, the electrical conductivity values reached 1200 μS/cm in 2009, which are values close to those found in the alluvial aquifer. This compartment's conductivity was previously around the average values of the area. A progressive increase was also observed in the iron concentration to around 500 mg/L [12] which is due to chemical and bacterial pollution related to livestock activity in Llanos de Almargen. In some wells, high values of chlorides were found because of the proximity of Triassic materials. These results indicate that certain sectors of the Almargen compartment are affected by mixing with groundwater with higher conductivity coming from Llanos de Almargen. This occurs during periods of low rainfall when groundwater withdrawal goes on for a long time.

Table 2. Maximum concentrations for selected physico-chemical parameters.

Sample	pH	C.E.	SO_4^{2-}	HCO_3^-	NO_3^-	NO_2^-	Cl^-	PO_4^{3-}	TOC	Fe^{2+}	Na^+	Ca^{2+}
Sondeo Alcalá	7.4	700	39	456	17.0	<0.05	36	<0.04	<0.5	<0.1	23	114
Sondeo Olvera	7.4	701	34	465	15.0	<0.05	37	<0.04	<0.5	<0.1	21	116
Majorrego	7.4	2,770	404	173	25.0	<0.05	662	<0.04	4.5	2.4	359	160
Majavea	7.7	625	38	331	17.0	<0.05	53	<0.04	<0.5	<0.1	29	75
Cabrerizo	7.6	1,449	34	332	14.0	<0.05	448	<0.04	<0.5	<0.1	219	87
Viján	7.6	507	22	341	20.0	<0.05	9	<0.04	<0.5	<0.1	6	77
Ojo de la Laguna	7.5	605	28	373	42.0	<0.05	13	<0.04	<0.5	0.3	7	96
El Berrillo	7.3	723	28	283	19.0	<0.05	119	<0.04	<0.5	<0.1	68	88
Fuentepeones	7.6	635	30	381	19.0	<0.05	56	<0.04	<0.5	<0.1	33	76
El Pleito	7.5	567	28	413	28.0	<0.05	12	<0.04	<0.5	<0.1	8	93
El Rocio	7.6	598	91	318	12.0	<0.05	100	<0.04	<0.5	<0.1	10	84
La Nina	7.7	665	128	332	12.0	<0.05	15	<0.04	<0.5	<0.1	10	105
IGME I	7.6	480	23	225	12.0	<0.05	14	<0.04	<0.5	<0.1	9	40
IGME II	7.3	835	104	242	12.0	<0.05	82	<0.04	<0.5	<0.1	66	72
Nuevo Cabrerizo	7.4	523	8	354	16.0	<0.05	18	<0.04	<0.5	<0.1	4	54
Llanos Almargen	7.4	1,356	79	241	80.0	<0.05	320	<0.04	1.22	0.3	92	132

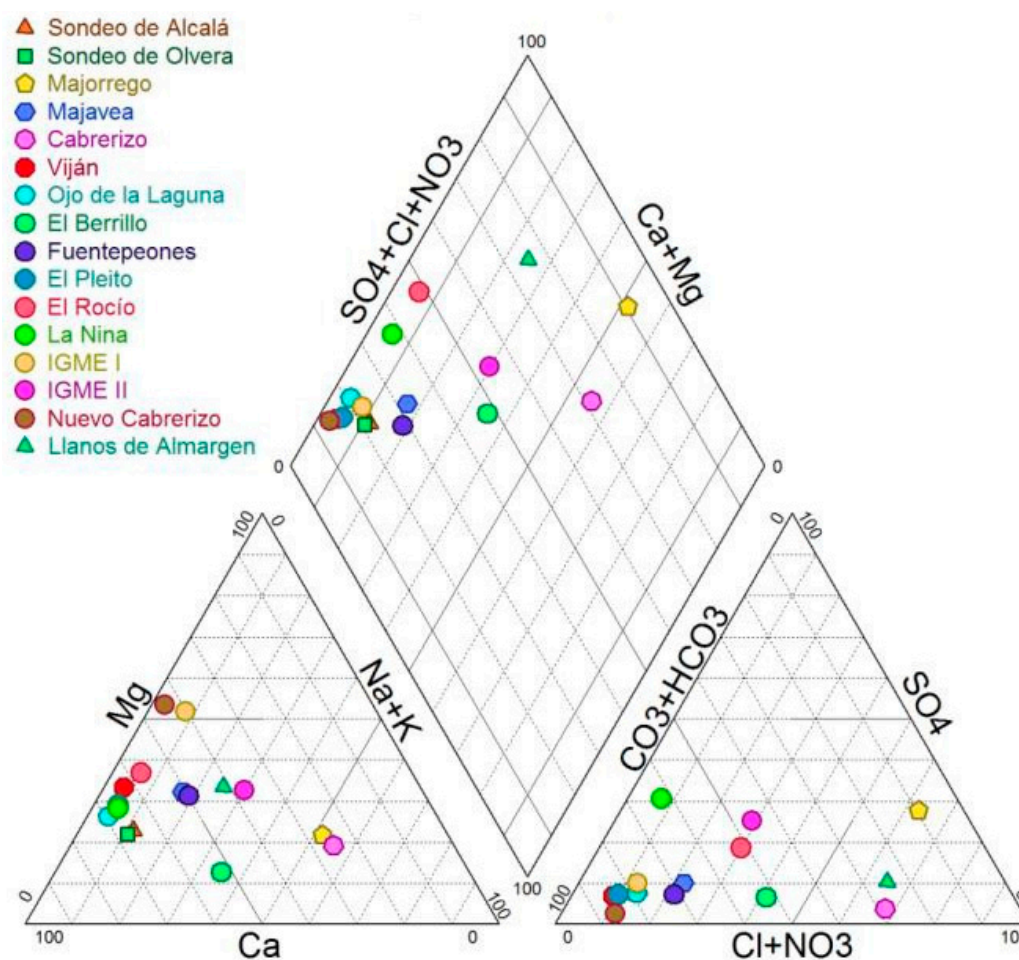Note: Data in mg/L, except C.E. in μS/cm.

Figure 4. Piper diagram with maximum concentrations.

In summary, the results show no evidence of chemical contamination in most of the sectors under study, except the northern part of the mountain and the Llanos de Almargen alluvial aquifer. High levels of certain ions (e.g., chloride, sodium and sulfate) appear in some of the northern wells. These could be associated with natural processes such as the dissolution of evaporites (i.e., gypsum and halite) from Triassic rocks. In the alluvial aquifer, contamination exists due to anthropogenic processes

(i.e., agriculture and livestock), and high levels of nitrates (i.e., close to 30 mg/L) have previously been detected [12]. These pressures could affect the northern part of this carbonate mountain and manifest as locally-induced contamination in some sectors of the aquifer.

4.2. Water Isotope Characterization

In the May 2009 and March 2010 field campaigns, samples were collected to determine water stable isotopes. Specific samples were taken to measure tritium activity in 2010. However, two composite samples were obtained in the laboratory by mixing several samples from 2009. The results are shown in Tables 3 and 4.

Table 3. Results of the analysis of stable isotopes in groundwater samples from the 2009 and 2010 field campaigns.

Point	2009 Campaign			2010 Campaign		
	$\delta^{18}O$ (‰)	δ^2H (‰)	d (‰)	$\delta^{18}O$ (‰)	δ^2H (‰)	d (‰)
(1) Sondeo Olvera	−6.23	−39.96	9.88	−5.72	−37.98	7.78
(2) Sondeo Alcalá	−6.06	−39.86	8.62	−5.70	−38.25	7.35
(3) Fuentepeones	−6.35	−41.13	9.67	−5.98	−40.13	7.71
(4) Viján	−6.40	−40.54	10.66	−6.23	−41.60	8.24
(5) El Rocío	−6.50	−41.67	10.33	−6.07	−40.39	8.17
(6) La Nina	−6.35	−40.30	10.50	−5.93	−39.33	8.11
(7) Majavea	−6.56	−41.59	10.89	−5.96	−39.79	7.89
(8) Ojo de la Laguna	−6.25	−39.89	10.11	−5.76	−38.23	7.85
(9) Pleito	−6.17	−39.37	9.99	−5.80	−38.61	7.79
(10) El Berrillo	−6.52	−40.63	11.53	−6.02	−39.51	8.65
(11) Cabrerizo	−6.47	−41.72	10.04	−5.91	−39.51	7.77
(12) Majorrego	−5.26	−33.35	8.73	–	–	–
(13) Llanos Almargen	−5.67	−37.06	8.30	−5.55	−38.07	6.33
(14) IGME I	−6.34	−39.92	10.80	–	–	–
(15) Nuevo Cabrerizo	–	–	–	−6.13	−40.52	8.52
(16) Fuencaliente	–	–	–	−6.08	−39.93	8.71
(17) Cortijo Grande	–	–	–	−5.85	−38.58	8.22
(18) Puerto Berrillo	–	–	–	−5.80	−37.59	8.81

Note: m a.s.l. = meters above sea level; source: Jimenez-Madrid, 2011.

Table 4. Results of the measurement of tritium activity in groundwater in the May 2009 (composite samples) and March 2010 field campaigns.

Campaign	Composite Sample	Tritium
2009	IGME I (14) + Cabrerizo (11) + Rocío (5)	1.96
	El Berrillo (10) + Viján (4) + Peones (3) + Laguna (8) + El Pleito (9)	3.65
2010	Majavea (7)	2.19
	Nuevo Cabrerizo (15)	3.52

Source: Jiménez-Madrid, 2011.

The analytical results for deuterium and $\delta^{18}O$ are presented in Table 2 above. This table also shows deuterium excess, defined by Dansgaard (1964) as:

$$d \ (‰) = \delta^2H - 8 \times \delta^{18}O \tag{2}$$

This indicates the possible origin of water vapor that causes rainfall and, therefore, aquifer recharge.

In 2009, samples located in carbonates showed a relatively small range of variation (see Figure 5), and they are grouped near the global meteoric water line (GMWL) [14]. They are lighter and more homogeneous than the weighted precipitation at the Morón-Base Aerea station, included in the REVIP

network [9], perhaps due to the elevation effect. Additionally, the amount or directional (continental) effects and mixing could be considered to explain these differences. Only alluvial samples show isotopic composition near that of the precipitation at the station.
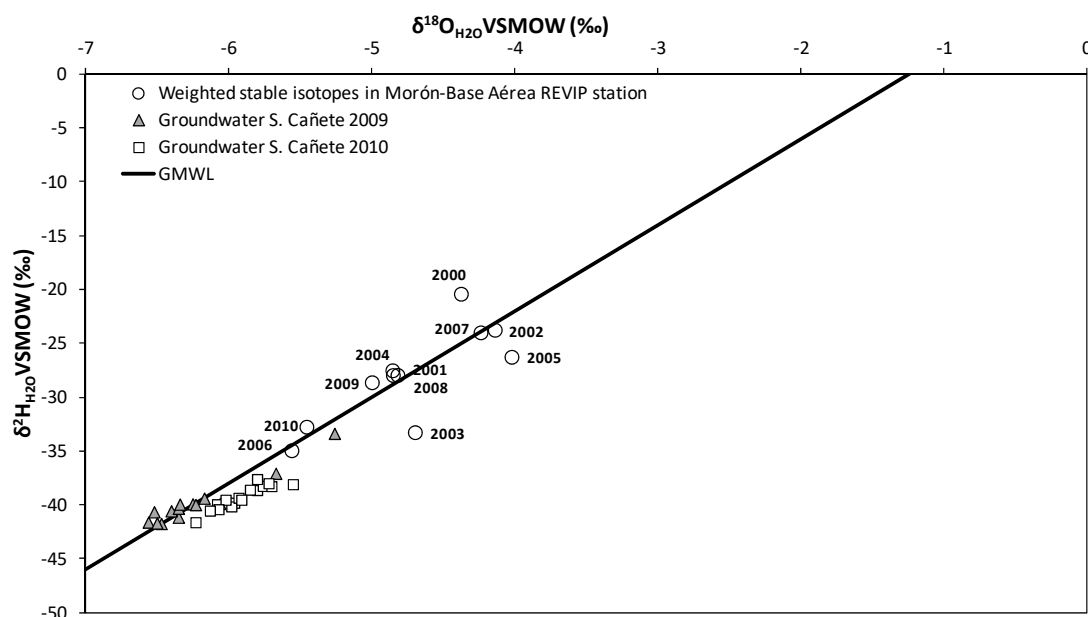

Figure 5. Comparison between weighted stable water isotope in the precipitation of the Morón-Base Aérea REVIP station and the groundwater samples of the Sierra de Cañete aquifer.

However, groundwater samples reveal some dispersion (Figure 6), manifested by the excess of deuterium, especially the sample from the supply to Alcalá del Valle (Sampling Point 2). As said, the two samples from catchments located in the alluvial materials (12 and 13) correspond to heavier water than the other samples. Samples 12 and 13 fall under the GMWL, which could indicate evaporation. The evaporation signal in the alluvial aquifer may be due to the irrigation system being based on the use of the alluvial and the Sierra de Cañete groundwater that is stored in pools exposed to the atmosphere. However, this process it not shown clearly in the δ^{18}O-δ^2H diagram.

Samples from the carbonate area showed greater variation in δ^{18}O and δ^2H in 2010. These results can be adjusted to fall on a line essentially parallel to the GMWL. This indicates a recharge with water with a different history from the samples in 2009, due to the various origins of precipitation and hydrogeological processes, as shown by the difference in the deuterium excess between the two sampling campaigns. Notably, 2009 was the last year of a dry period that began in 2004 (Figure 2), in which groundwater was more widely pumped. Autumn of 2009 and winter and spring of 2010 were extremely wet, with heavy and intense rainfall due to recurring depression systems that entered the Iberian Peninsula via the Gulf of Cadiz, which is located to the southwest of the Sierra de Cañete. This origin is further confirmed by the trend of isotopic values belonging to the samples from 2010 (Figure 6), with lighter δ^{18}O and δ^2H appearing from the southwest to the northeast and east. This is typical of fractionation in the direction of the rainfall phenomena and, therefore, recharge. In the 2009 values, this trend is not so clearly shown. Smaller excesses of deuterium can also be seen in the 2010 samples (i.e., an average of eight for carbonate samples) compared with 2009 (i.e., an average of 10.25), with less variability. This shows that the main source of groundwater comes from a more homogeneous zone of higher relative humidity, which belongs to a single period of recharge and to a water source also similar to rainfall. Increases in the value of δ18O could be interpreted as due to proximity to the area where the rains enter (i.e., Gulf of Cadiz), rather than evaporation.
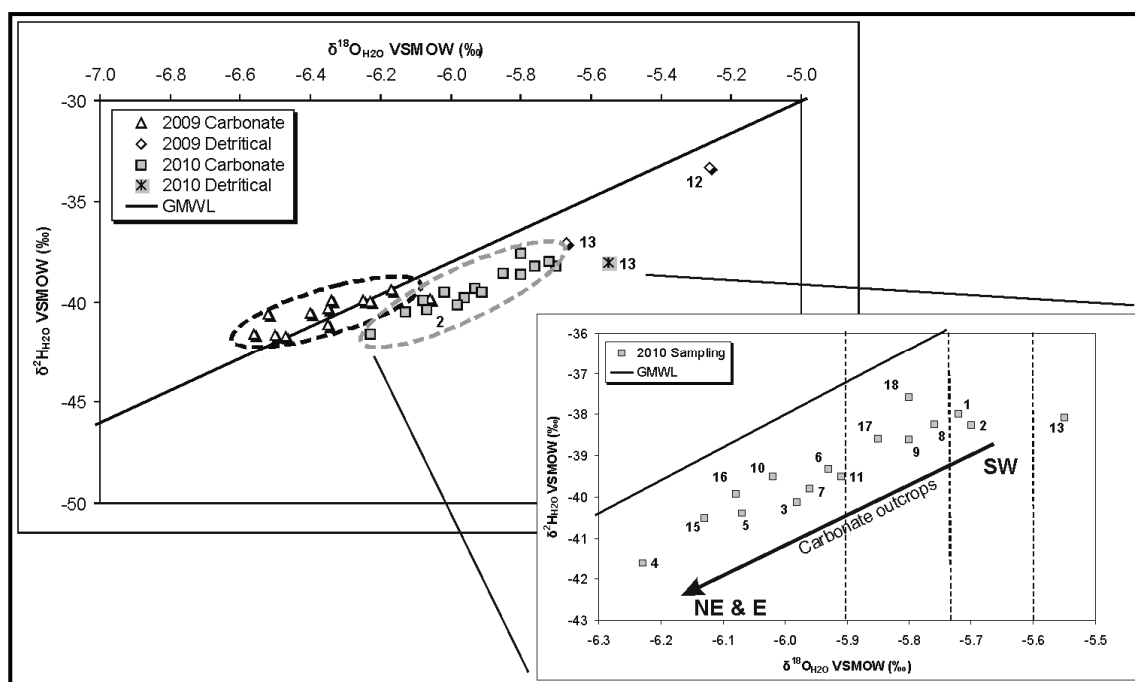
Figure 6. Isotopic results differentiated by field campaign and materials on which sampling points are located, with expansion in the 2010 sampling values (global meteoric water line (GMWL)).

In the 2009 samples, the deuterium excess variability suggests heterogeneity in the hydrogeological behavior of the entire water body, as compared to the recharge for periods in which dry years have prevailed and in which water input has occurred, almost certainly from various sources. The resulting water in different zones of the system and, therefore, in the samples corresponds to a mixture of rainfall water with a value close to the typical deuterium excess in meteoric water, although the δ^{18}O values are relatively high. In addition, water mixing due to groundwater pumping needs to be considered.

Water stable isotopes' deviation has also widely been used to estimate the elevation of recharge because isotopic fractionation in rainfall occurs when the temperature decreases with altitude [15]. In the Sierra de Cañete, the observation points are all at relatively low elevations, so the local gradient of isotopic fractionation cannot be established to estimate the zones of contribution in the bodies of water based solely on water stable isotopes. Therefore, a model of precipitation distribution was used as a reference point [16,17]. This model was developed using the annual averages of δ^{18}O weighted values supplied by the Spanish Network of Isotopes in Precipitation (REVIP), which is part of the Global Network of Isotopes in Precipitation [9].

The model of the values of δ^{18}O in precipitation in the Sierra de Cañete was compared to the analytical results in 2009, showing that the data do not fit the model. The sample values are almost always heavier than those in the model (see Figure 7). This would indicate that the system is recharged quickly due to its karstic nature, responding rapidly to rainfall events. These recharge events can be isotopically heavier than the values predicted by the model, which was built with average annual values during seven years (i.e., 2000–2006).
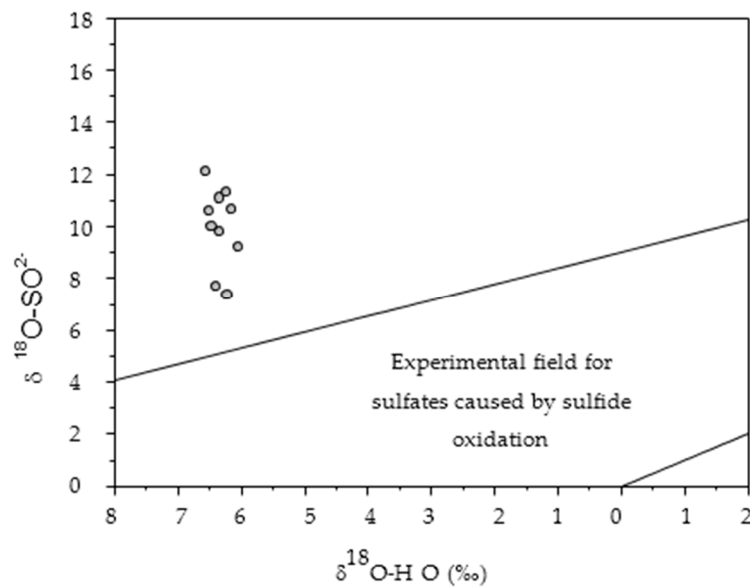
Figure 7. Representation of $\delta^{18}O$ of water versus $\delta^{18}O$ of sulfate to determine the origin of sulfide oxidation.

In addition, Figure 8 reveals the existence of at least three different groups of water. Group I covers the sampling points in the northern carbonate zone, at low altitudes and with values of $\delta^{18}O$ relatively close to the reference model. This sector could have represented, in 2009, a mixture of water with recharge components from several years, with deep, slow flows. Group II is formed of springs and wells at higher elevations and with an isotopic content quite different from the reference model. This sector corresponds to the rest of the carbonate aquifer, whose recharge shows evidence of karstification. The lowest points of this group are slightly heavier than the highest points, although the variation is relatively small (i.e., 0.6‰ in $\delta^{18}O$ and 50 m in elevation). Group III includes the sampling points located in the alluvial area, which have heavier water than the rest and which are quite far from the reference model. With respect to 2010, the three groups show an increase in $\delta^{18}O$, separating their values even further from the reference model. This increase is similar throughout the aquifer system.
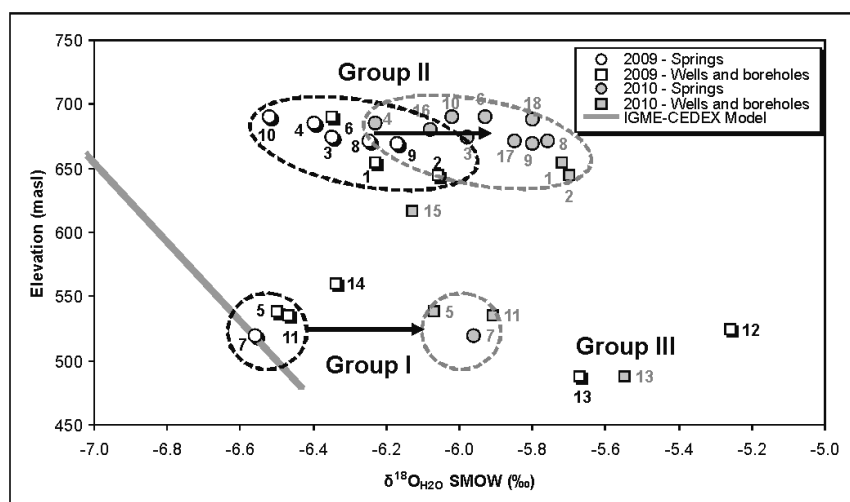

Figure 8. $\delta^{18}O$-elevation relationship. Note: the thick line is the model of $\delta^{18}O$ in precipitation in the Sierra de Cañete groundwater body.

Tritium also shows a different hydrogeological behavior within the system (Table 4). The northern sector appears to be a mixture of water with different ages (i.e., Group I: Sampling Points 5, 11 and 14), with lower activity than the rest of the carbonate area. Another sector (i.e., Group II: Points 3, 4, 8, 9 and 10) had a tritium activity in 2009 matching the average for 2000–2006 precipitation of 3.4 recorded by the nearest REVIP station, Morón de la Frontera [9].

The only tritium data available for 2010 come from the northern sector, but these are associated with two different groups. The most representative sample of Group I (sampling point 7) presents higher values of tritium than the mixture value does for 2009, which suggests the greater importance of recent water in this zone. The most typical sample of Group II (15) has a value just slightly below that of the mixture in 2009, indicating recent rainfall water. The decrease in this value appears to be related to increased rainfall of Atlantic origin because, in the Iberian Peninsula, the average tritium activity tends to increase from west to east [9].

Finally, comparisons between salinity and stable isotope composition have been frequently used to improve researchers' understanding of the evolution of water in aquifers, thereby differentiating between evaporation, dissolution or mixing processes. However, in Sierra de Cañete, a low variability in both ionic and water stable isotope content and considerable clustering of the samples can be observed. That is, little salinization or evaporation can be detected.

In 2010, a process of dilution and enrichment of $\delta^{18}O$ was found for the entire study area, with a tendency to homogenization between the different sectors of the Sierra de Cañete groundwater body.

Samples from The Llanos de Almargen alluvial aquifer indicate different hydrogeological and hydro-chemical behaviors.

4.3. Sulfur Isotope Characterization

The nitrate content of groundwater in the study site can be significant (Table 2) as a consequence of agricultural activity. On the other hand, the origin of sulfate may be related to agricultural activities. The dual use of sulfate isotopes (^{34}S; ^{18}O) also allows considering other factors for sulfates, such as the dissolution of evaporites.

To study the isotopes of sulfate, samples were collected from 10 points in May 2009. The results are shown in Table 5.

Table 5. Values of electrical conductivity, sulfate concentration, the deviation of isotopes of sulfate and water and the percentage of sulfate from fertilizers.

Reference	Electric Cond. (µS/cm)	Sulfate (mg/L)	Sulfate Isotopes δ^{34}S (‰)	$\delta^{18}O_{SO4}$ (‰)	Water Isotopes δ^2H (‰)	$\delta^{18}O_{H2O}$ (‰)	SO_4^{2-} from Fertilizer (%)	Max. NO_3^- (mg/L)
(1) Olvera	663	30	4.2	7.4	−39.96	−6.23	70	15
(2) Alcalá	662	26	5.6	9.2	−39.86	−6.06	60	17
(3) Peones	585	19	5.6	9.8	−41.13	−6.35	60	19
(4) Viján	483	15	5.2	7.7	−40.54	−6.4	60	20
(6) Nina	510	32	10	11.1	−40.3	−6.35	20	12
(7) Majavea	575	26	13.7	12.1	−41.59	−6.56	0	17
(8) Laguna	532	13	8.5	11.3	−39.89	−6.25	35	42
(9) Pleito	542	13	8.4	10.7	−39.37	−6.17	35	28
(10) Berrillo	668	19	3.6	10.6	−40.63	−6.52	70	19
(11) Cabrerizo	941	18	12	10	−41.72	−6.47	5	14

The isotopic values of sulfate (Table 5) vary between 3.6 and 13.7‰ for δ^{34}S and between 7.4‰ and 12.1‰ for δ^{18}O. The sulfate concentration does not exceed 32 mg/L, and the maximum electrical conductivity is 941 µS/cm for Cabrerizo.

The above results can be compared to Urresti et al.'s (2015) findings after the cited researchers established a control network of sampling in the Guadalhorce river basin with over 22 wells and springs. In addition to other analyses, the cited authors examined the concentration of sulfate and the sulfur isotopic signal. One of these points is located in the alluvial aquifer of Llanos de Almargen, an

area of interest in the present study because of its connection with the carbonate aquifer of the Sierra de Cañete. For [18] sample, the isotopic value for δ^{34}S is -1.0‰ and for $\delta18$O -1.2‰, and the sulfate concentration is 200 mg/L. These data indicate that the origin of sulfate at this point is caused by the oxidation of sulfides and the presence of fertilizer and manure.

In the present research, considering the results for the samples and the position of wells and springs in the study area, two sectors can be distinguished. The first is the northwestern sector represented by the Nina, Majavea, Ojo de la Laguna, Pleito and Cabrerizo well (6, 7, 8, 9 and 11), in which the values of δ^{34}S exceed 8‰. The second is the southeastern sector represented by the other supply points—Olvera, Alcalá, Fuentepeones, Viján and Berrillo (1, 2, 3, 4 and 10)—with values below 6‰.

Taking into account the values previously defined for the different origins of δ^{34}S, the high values of the northwestern sector show a predominant origin of sulfate from Triassic evaporites that compose the substrate. However, because the values of the southeastern sector are lower (3.6–5.6‰) and accompanied by $\delta^{18}O_{SO4}$ (7.4–10.6‰), the sulfate here could also be due to the oxidation of sulfides in limestone rock.

To verify this hypothesis, in Figure 7, the samples are represented by the field of values corresponding to the oxidation of sulfides. All samples are outside the defined rank for an origin of oxidation of sulfides. Therefore, the results do not support the hypothesis that the dissolved sulfate in the study area contributes to the sulfides in the carbonate aquifer.

Another hypothesis about the origin of dissolved sulfate was fertilizers. The values of isotopic signals are shown in Figure 9. These also match thresholds corresponding to sulfate derived from Triassic evaporites and from fertilizers.
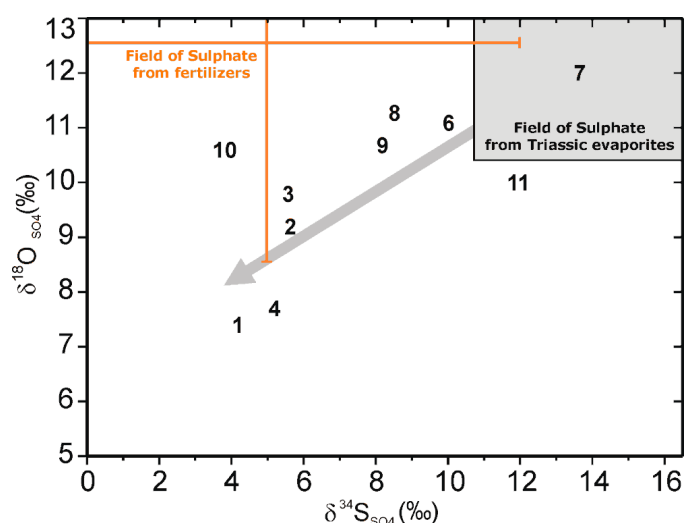

Figure 9. Distribution of values for δ^{34}S versus $\delta^{18}O_{SO4}$ for dissolved sulfate in the May 2009 field campaign sample. Source: Fields of occurrence of each source of sulfate (Triassic evaporites and fertilizers) adopted from [19].

Figure 9 confirms the presence of two sectors in the study area. The samples from Points 6, 8, 9 and 11 in the northwestern sector have the closest values to the field of sulfates originating from Triassic evaporites. Sample 7 has an undisputed origin in evaporites. Samples 1, 2, 3, 4 and 10 from the southeast sector tend to have lighter values belonging to the field of sulfates from fertilizers.

4.4. Natural and Anthropogenic Fingerprints in Sulfate Isotopes

The juxtaposition of the concentration values of sulfate in each sample with the value of the isotopic signal δ^{34}S also helps determine the origin of these sulfates. Figure 10 presents the data with corresponding thresholds for sulfates coming from evaporites (i.e., gypsum) and fertilizer and manure.
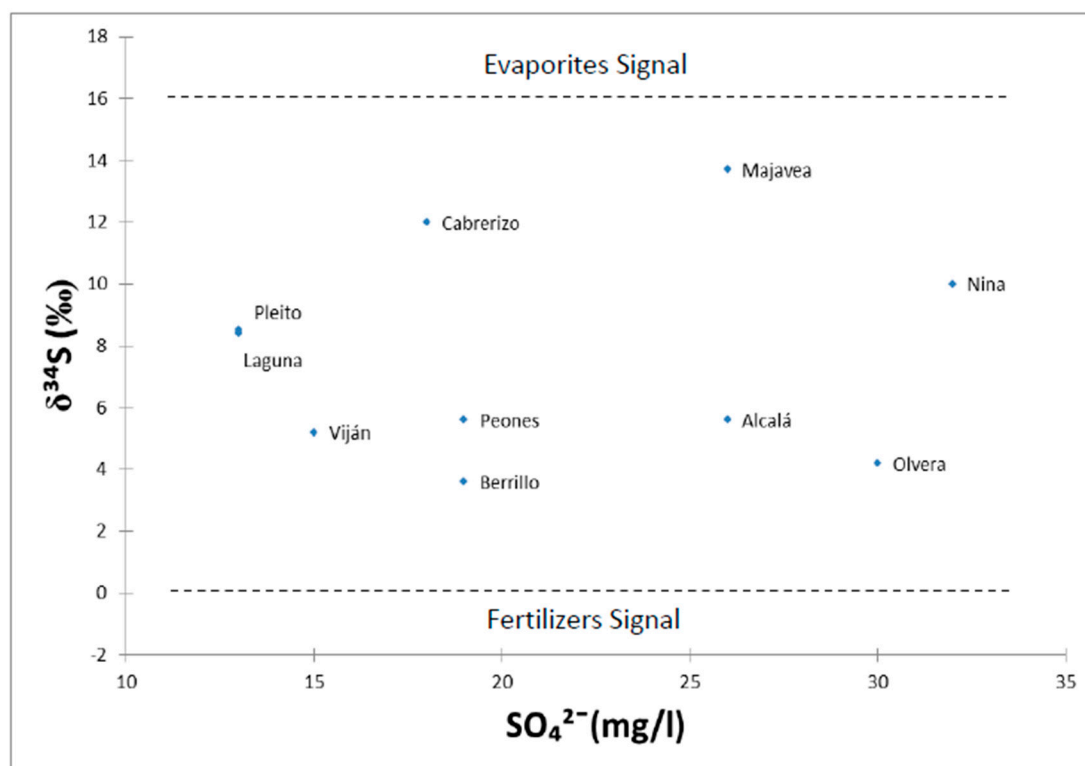

Figure 10. Representation of sulfate concentration (mg/L) versus δ^{34}S values. Source: Values of the isotopic signal corresponding to evaporites and fertilizer and manure adopted from [18].

All samples fall between the two thresholds, which indicates a mixed origin of sulfates. However, a marked difference appears between the northernmost supply points and those belonging to the southwestern area. The first group—Cabrerizo (11), Nina (6) and, especially, Majavea (7)—presents closer values to the signal for evaporites. The southern group—Viján (4), Peones (3), Berrillo (10), Alcalá (2) and Olvera (1)—has stronger signals for sulfates with anthropogenic origin.

As previously found, processes happening in the Llanos de Almargen alluvial aquifer need to be emphasized. When the data extracted from [18] corresponding to the wells located in Llanos de Almargen (i.e., SO_4^{2-} concentration: 200 m/l; δ^{34}S signal: -1.0‰), were placed on the graph, the point was shown to correspond to a signal of anthropogenic origin. This is an added argument for the conclusion drawn from the hydro-chemical analysis. The Llanos de Almargen aquifer has groundwater contamination of anthropogenic origin due to agricultural and livestock activities taking place there.

5. Discussion

5.1. Definition of CCAs

The hydro-chemical and isotopic analyses of water from the Sierra de Cañete corroborate the existence of compartments that hydrogeologically divide this mountain. Groundwater from the carbonate aquifer shows calcium bicarbonate hydro-chemical facies, low salinity and slight variation over time. This indicates a quite weak relationship between changes in the concentration of ions in rainwater, except for magnesium, which increases in times of drought. This may be due to a longer

residence in the aquifer, allowing greater dilution of dolomitic materials. The El Berrillo spring (10) is an exception, as it has calcium and magnesium bicarbonate facies.

To the north of the study site, the Llanos de Almargen alluvial aquifer presents chlorine and sodium hydro-chemical facies. This marks the hydrogeological difference in that area, which can be used to distinguish different compartments. However, the homogeneous nature of the hydro-chemical data, with the exceptions noted above, makes it difficult to characterize the different kinds of recharge water. Thus, only the existence of a northern boundary shared with Llanos de Almargen can be confirmed because the latter aquifer has different hydro-chemical features from the rest of the Sierra de Cañete.

The influence of this alluvial aquifer on the north side of the mountain is evident in some areas of the carbonate aquifer. In the Cabrerizo well (Sampling Point 11) sample for 2009, when the rains were scarce, a conductivity value of 1200 μS/cm was measured, a value close to that found in the Llanos de Almargen aquifer. The concentration values of iron also increase in times of little rain, as they did in 2009. These high concentrations are related to chemical processes of contamination leading to iron precipitation through oxidation processes and bacterial pollution originating from the corrosion of pipelines by the proliferation of ferruginous bacteria related to existing farming activity in the Llanos de Almargen area.

In the western part of the mountains, the Ojo de la Laguna (Sampling Point 8) and El Pleito (9) springs have high nitrate concentrations related to livestock activity near La Nava and El Atalayón. According to the stable isotopic characterization, compartments in the carbonate mountain areas can also be differentiated. However, the isotopic variability between samples is quite low, so clear interpretations of these data are likely limited in scope. The exception to this is samples that are from outside the carbonate area (i.e., Llanos de Almargen). They had heavier water in all field campaigns, indicating a different hydrogeological history.

However, the water isotope signals differentiate two large areas in the Sierra de Cañete. The area farther north that borders the Llanos de Almargen aquifer presents a slower flow and comes from refill during most years. The rest of the carbonate aquifer has younger water due to faster recharge by rain events, showing a more developed karstification.

The values for water stable isotopes are influenced by rainfall because, in the 2009 field campaign (i.e., during a dry period), the water was lighter than in 2010 (i.e., a wet year). Except for the area of Llanos de Almargen, the values fit basically along the GMWL, while the 2010 values fall along a parallel line to the GMWL. The geographical area of recharge also influences composition as the samples are lighter from the southwest to northeast and to the east.

Another differentiating factor is the elevation of wells or springs. This makes a difference between the northern sector of the carbonate aquifer, with a lower altitude, and the rest of the carbonate aquifer, with higher altitudes. The northern sector has adjusted samples closer to the reference distribution of $\delta^{18}O$ for the Sierra de Cañete groundwater body, according to [16] and data updated with the REVIP's 2000–2006 findings. The samples from the rest of the carbonate aquifer move away from the reference model.

The information provided by hydro-chemical and water isotope analyses can be added to the above data, including the presence of faults and fractures and the upwelling of impermeable materials that constitute the lines between the different zones of contribution. With all this information, six zones of contribution can be distinguished in the Sierra de Cañete (see Zones A–F in Figure 11).
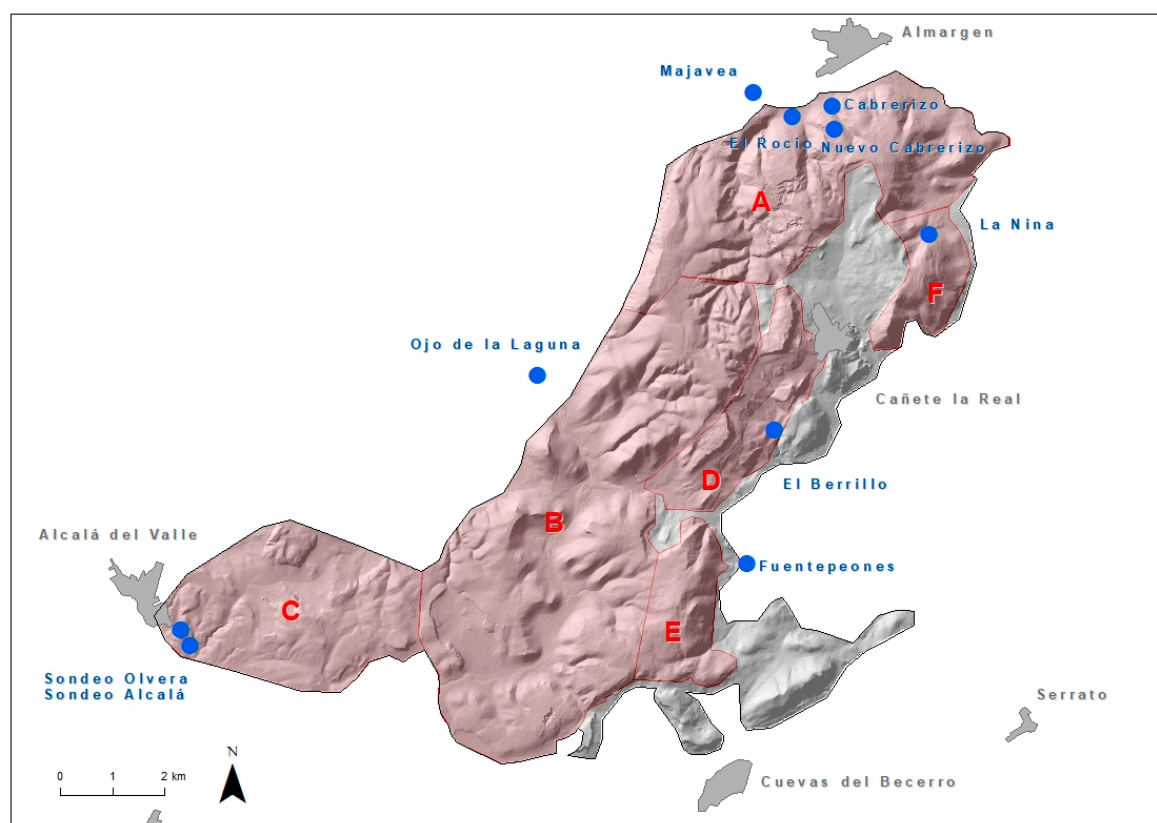
Figure 11. Contributing catchments areas in Sierra de Cañete.

5.2. Influence of Agricultural Pollution in CCAs

The threshold isotopic values set to differentiate the origin of sulfates are inaccurate, sometimes presenting a wider and other times a smaller range of values. Therefore, it is difficult to associate $\delta^{34}S$ values with different sectors of the Sierra de Cañete. However, the results do confirm the proposed definition.

As with water stable isotopes, an examination of the sulfur isotope signal facilitated differentiation between two big sectors in the Sierra de Cañete. The first is a northwestern sector in which the sulfate dissolved in groundwater comes from Triassic evaporites, that is a natural origin. The second is a southeast sector in which the sulfate dissolved in groundwater has an anthropogenic origin, coming from fertilizers used in the surrounding farmlands.

Thus, the CCAs of La Nina and Almargen present groundwater whose sulfates do not have a strong anthropogenic origin, but instead, come from the dissolution of Triassic evaporites. In contrast, wells located in the Berrillo, Fuentepeones and Alcalá del Valle CCAs have water with sulfates that have a more marked anthropogenic origin, coming from fertilizers used in the surrounding agricultural areas. In the La Atalaya CCA, the Laguna and Pleito springs have sulfates of an unknown origin because the data do not indicate a clear source.

Finally, the contamination present in the Llanos de Almargen alluvial aquifer needs to be mentioned. Both, the hydro-chemical and sulfate isotopic data indicate contamination due to human activity: high values in nitrate concentration, high conductivity and a sulfur isotopic signal corresponding to fertilizer and/or manure.

The problem with Llanos de Almargen is the hydraulic connection it has with the Almargen CCA, in the Sierra de Cañete. The latter area experiences mixing processes of groundwater from Llanos de Almargen and, therefore, receives any pollution that may exist in this water. This occurs, in particular, when groundwater pumping goes on for a long time in dry periods. This situation points

to the possible need to extend the area that feeds the Almargen CCA to include Llanos de Almargen, since, at certain times, the water flow is reversed, and the alluvial aquifer feeds the northern sector of the mountain. Anthropogenic pressures (i.e., livestock and agriculture) in the Llanos de Almargen area must be reduced to prevent these effects on the carbonate aquifer.

6. Conclusions

Hydro-chemical and isotopic characterizations (i.e., water and dissolved elements such as sulfate) of groundwater can be used as supporting tools to differentiate between sectors within aquifers. These sectors can be established according to how they correspond to surface areas that feed sectors from which water is collected for human consumption. After that, safeguard zones can be defined in which protection measures for groundwater need to be implemented.

The Sierra de Cañete is a carbonate aquifer. The northern edge of the mountain borders on the Llanos de Almargen alluvial aquifer. In the carbonate aquifer, the main factor influencing division into sectors is the lithology and possible faults or fractures. However, the hydro-chemical characterization and examination of various isotopes help to confirm potential compartments and identify possible hydraulic connections between sectors.

Due to the homogeneity of the samples, hydro-chemical analyses alone fail to differentiate between all of the sectors into which the carbonate aquifer can be divided, although these analyses lead to some important conclusions. The results reveal a clear difference between the carbonate and alluvial aquifers because the groundwater in the Sierra de Cañete shows medium mineralization and prevailing calcium bicarbonate facies, while the alluvial aquifer to the north of the mountain has water with sodium chloride hydro-chemical facies. Tritium activity also indicates different behaviors in sectors, although some samples are composite. This indicates that the residence time of northern water is longer than that of the rest of the carbonate aquifer.

As with the hydrochemistry of the samples, water isotope results show little variation between different samples and complicate interpretations, but some conclusions can still be draw:

- Regarding rainfall, the samples of the northernmost sector are in line with the general distribution models of isotopes in precipitation for each year, revealing that this sector is affected by annual transit times, which does not occur in the rest of the aquifer, while in other sectors, recharge is produced more quickly by rain events, probably because the carbonate aquifer is a more developed karst area.
- The influence of rainfall quantity on isotopic content is clear, since, in the 2009 field campaign (i.e., an extremely dry period), the samples were homogeneous in the entire aquifer, while, in 2010 (i.e., a year of abundant rainfall), samples were homogenized by sectors.
- The isotopic data clearly differentiate between two areas in the carbonate aquifer: the northern zone characterized by a slower flow from older recharges and the southeastern area with more intense karstification in which recharge varies according to rain events.

The present study used sulfur isotopes to identify the source of sulfate ions in the various sectors of the carbonate aquifer because the simple hydro-chemical study was not enough to distinguish between a natural or anthropogenic origin. As found previously, the northern part differs from the southeastern area. In the first, sulfates have an origin marked by dissolution of the evaporitic substrate. In the second area, sulfate ions have a mixed origin because the isotopic signal indicates a combination of natural and fertilizer origins.

In Llanos de Almargen, water from the alluvial aquifer contains sulfates that come from fertilizer and manure used in that area, in addition to a high concentration of nitrates detected in hydro-chemical analyses. This confirms the conclusion drawn from the hydro-chemical study that the water of this aquifer is contaminated by human activity.

The existing hydraulic connection between the alluvial aquifer and the northern part of the carbonate aquifer (i.e., the Almargen sector) threatens the quality of the mountain-derived water

intended for human consumption. This means the protection area of the Almargen sector needs to be extended to include Llanos de Almargen to establish stronger measures to control pollution in the alluvial aquifer. This sector cannot be categorized as a CCA because Llanos de Almargen does not contribute to the northern part of the mountain, but nonetheless, the sector is a zone of influence needing protection.

Given its importance to the quality of Sierra de Cañete water, a more comprehensive study of the Llanos de Almargen alluvial aquifer could be of significant value. The area's vulnerability to pollution needs to be understood better, and together with an inventory of anthropogenic pressures, the risk of contamination needs to be determined. In addition, an analysis of the hydrologic and hydrogeologic connections between the two aquifers would help to define more precisely the protection zones, or safeguard zones, of the Almargen sector of the Sierra de Cañete.

Groundwater protection zones studies are an important tool for the integrated management of groundwater and for designing protection measures. Therefore, protection areas must be delimited where an important groundwater contamination risk exists. Land uses and permitted activities inside them must be properly managed. Finally, the integration of these protection areas in land use planning policies will be completely necessary to ensure the effectiveness of the established measures.

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